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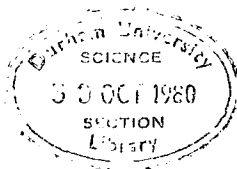
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AN INVESTIGATION OF ADSORBED SPECIES
AND RELATED MODEL COMPOUNDS BY
INELASTIC NEUTRON SCATTERING SPECTROSCOPY

By

KEITH ROBSON B.Sc., M.Sc.



A thesis submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy in the University of Durham.

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from it should be acknowledged.

June 1980

To Laura and my family
with thanks for their help and encouragement

"Scire est nescire, nisi id me scire alius scierit."

Lucilius

PREFACE

The work described in this thesis is original except where specifically stated to the contrary. It has not previously been submitted either wholly, or in part, for a degree at this or at any other university.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professor T.C. Waddington for supervising this research, and for his unfailing encouragement.

Of necessity, experimentation has been conducted at AERE Harwell and the ILL Grenoble, as well as in Durham. As a result, I have received assistance and advice from many people whose names are too numerous to mention individually below; to these I extend my deepest thanks.

I wish to record my particular appreciation of the work carried out in Durham by Mr.R. Coult, who has prepared many of the complexes studied in this work, and of the aid and constructive criticism given freely by Dr. J.Howard, Mr. K.P.Brierley and the rest of the neutron scattering group within the Chemistry Department of Durham University. My thanks go also to the whole University Support Group at AERE Harwell, but especially to Mr. D.H.C. Harris, Mr. G.Haines, Mr. S.Stevens and Mr. R.Hill, whilst the help of Dr. J. Tomkinson at Grenoble was appreciated.

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Finally, I must thank Mrs.C.Rowes and Mrs.A.Carrahar, who had the unenviable task of transcribing this work into a readable form, and Mrs.E.K.Jones, whose help and advice with the diagrams presented proved invaluable.

ABSTRACT

The theory of Inelastic Neutron Scattering (INS) Spectroscopy is outlined, and the spectrometers employed in the study of low frequency ($< 1500\text{cm}^{-1}$) vibrations of hydrogen-containing molecules described.

Square planar platinum-ethylene complexes of the general form $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$ and $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$ (where L is a Ligand) have been investigated by INS spectroscopy, and assignments made of their spectra below 850cm^{-1} . In all cases, a frequency was found representing the torsion of the ethylene group about an axis projected from the platinum atom through the centre of the C=C band, and the barrier to this rotation calculated.

INS active modes of $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ ($0-1450\text{cm}^{-1}$) have been tentatively identified, and a value for the barrier to the rotation of the acetylene molecule about an axis running through the mid-points of the Co-Co and C≡C bonds derived.

INS spectra of C_2H_4 and C_2D_4 adsorbed at two overpressures onto silver exchanged type A (Ag_{12}A) zeolite have been measured. On this basis of deuteration shifts and relative intensities, all three torsional modes and two of the three translational modes expected for the ethylene molecule relative to a silver ion have been assigned. In addition, several weak spectroscopic features appeared to indicate the presence of a second less populated adsorption site.

C_2H_2 and C_2D_2 adsorbed onto Ag_{12}A zeolite at one overpressure have been studied by INS spectroscopy. All six predicted acetylene-surface modes were observed, the presence of the torsional vibration of the acetylene molecule about an axis running parallel to the C≡C bond indicating the adsorbed molecule to be non-linear.

Finally, INS spectra of the complexes $\text{Cr}(\text{C}_6\text{H}_6)_2$, $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$, $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ and $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ have been recorded in the region $0\text{--}900\text{cm}^{-1}$. Assignments have been attempted and, wherever possible, the barrier to the rotation of the benzene ligand(s) about the six-fold axis calculated.

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CHAPTER I

INTRODUCTION

A. Neutrons

A neutron may interact with a target nucleus so that it is either absorbed or scattered. The exact nature and probability of the scattering interaction may be expressed by a single parameter known as the scattering length $(b)^1$, which is associated with the particular isotope encountered and its nuclear spin orientation. An alternative statement of the probability of interaction is with reference to the effective area presented to an incident neutron by a nucleus, that is, in terms of the total scattering cross-section, σ_T^2 :

$$\sigma_T = 4\pi b^2$$

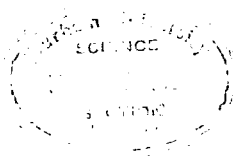
Considering an array of non-equivalent nuclei, neutron-nucleon interaction may take place according to the mean of the scattering length (coherent scattering), in which case interference effects are possible; or as a result of local deviations from the mean scattering potential (incoherent scattering), the randomness of which ensures the absence of interference. We may write¹:

$$\sigma_T = \sigma_{coh} + \sigma_{incoh}$$

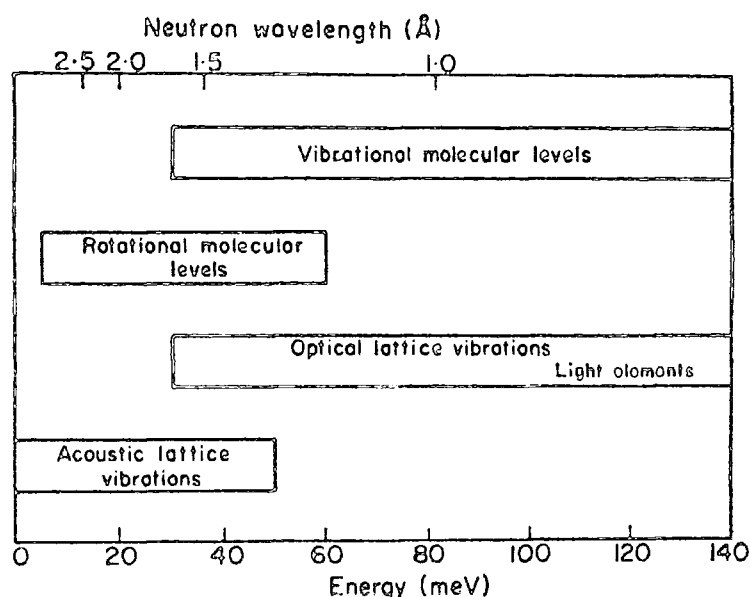
where σ_{coh} is the coherent scattering
cross-section

σ_{incoh} is the incoherent
scattering cross-section

Scattering by either coherent or incoherent means may take place inelastically or elastically, that is, with or without transfer of energy. It so happens that the energy distribution of thermal neutrons is of similar magnitude to that of molecular vibrations² (dia. 1(i)). Therefore, Inelastic Neutron Scattering (INS) is a complementary tool to those techniques normally employed in molecular spectroscopy, i.e. Raman and Infrared. It does not

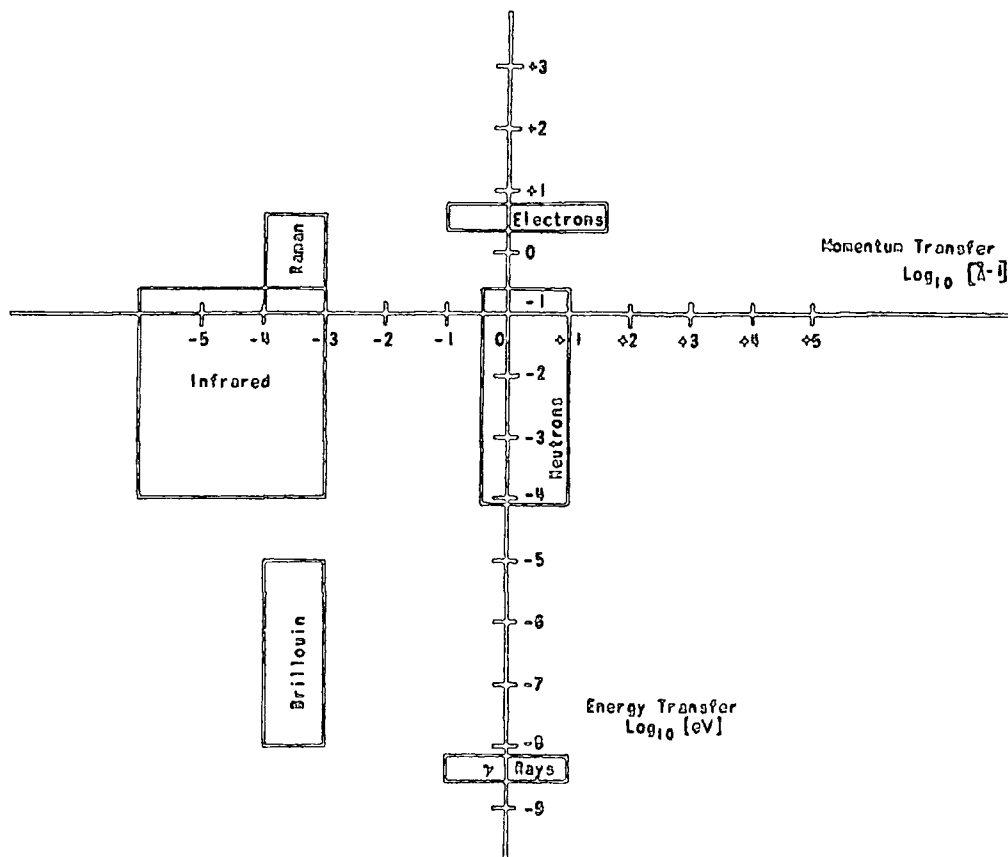


suffer, however, from the limitations of "conventional" spectroscopic methods as regards electromagnetic selection rules. That is not to say that there are no effective "selection rules", but that these are of a different form and relate to intensity considerations, because strictly speaking all vibrations are active (see later).



Diagram(i): The Possible Energy Ranges of Various Types of Excitation in Solids or Liquids (after Egelstaff³).

As well as transfer of energy, the similarity in the masses of neutrons and molecules means that transfer of momentum (in the approximate range 0.1 to $10\text{\AA}^{-1}$) is also possible (diagram(ii)). In consequence INS spectra, depending upon the angle at which they are recorded relative to the sample, may show intensity variations and, in the case of dispersive modes, frequency changes.



Dia.1(ii): Comparison of Momentum Transfer and Energy Transfer Space of Neutrons with Other Techniques (after Boutin and Yip⁴).

As a generalisation, it may be assumed that the incoherent cross-section of hydrogen is at least an order of magnitude⁴ larger than the incoherent cross-sections of other nuclei, and also larger than most coherent cross-sections⁵ (Table 2.1). Therefore, inelastic neutron scattering from a sample containing hydrogen (in reasonable concentration) will, to a first approximation, be almost totally incoherent, and dominated by vibrations involving the movement of hydrogen atoms. It is incoherent inelastic scattering from hydrogen-containing compounds which will be the main concern of this thesis.

Two instruments are principally employed in INS spectroscopy: the Beryllium Filter Detector (BFD) spectrometer⁶, and the Time-of-Flight (T-O-F) spectrometer⁷⁻⁹ (Chapter III). In the case of the BFD machine, a mono-

energetic incident neutron beam is incrementally varied in energy, and scattered neutrons (of a particular energy) detected at a fixed angle, so that a point by point spectrum is produced of neutron counts versus energy.

The T-O-F instrument employs a pulsed mono-energetic incident neutron beam which is scattered by the sample into an array of counters describing a solid angle. Separation of the scattered neutrons may be performed on the basis of the time required for travel between the sample and detector (time-of-flight). Thus after each pulse, the arrival times of neutrons at a counter are recorded within constant time intervals (e.g. 6 μ s wide) known as time-of-flight channels. From knowledge of the incident neutron velocity, time of arrival in channel numbers, and instrument geometry, the average reciprocal velocity of neutrons within a particular channel may be calculated. Data are therefore recorded at many angles simultaneously, and at each, a spectrum is recorded of neutron counts versus time-of-flight.

Important differences between the spectra obtained follow from the two techniques:

(i) BFD spectra are essentially independent of momentum transfer, whilst T-O-F spectra are very dependent upon momentum transfer. The latter machine may therefore be used to study this effect, via collection of data at various angles equivalent to several ranges of momentum transfer.

(ii) T-O-F spectra, as well as showing the inelastic region, also feature that part of the spectrum corresponding to zero energy transfer. A large distribution of elastically scattered neutrons is thus produced which is called the elastic peak. Diffusive processes may widen the narrow elastic peak expected, and measurement of the relative broadening (known as Quasi-elastic broadening)⁵ yields information to which computer models of diffusive motion may be fitted.

(iii) Whilst only one spectrum (detected neutron counts vs. energy) is obtained using a BFD spectrometer, several spectral representations (defined in Chapters II and III) may be plotted of T-O-F data. These include "corrected counts vs. T-O-F" (nine graphs 6H: thirteen graphs 4H5)⁹; "P(α , β) vs. cm⁻¹" (nine graphs 6H: thirteen graphs 4H5)¹⁰; $\rho(\omega)$ (one graph 6H and 4H5)¹⁰ and $2\beta \sinh(\beta/2) \frac{\rho(\alpha, \beta)}{\alpha}$ (one graph 6H and 4H5)¹⁰. Obviously it is not possible to reproduce all the data available in this thesis. Consequently, it must be remembered that those T-O-F spectra shown are chosen in an attempt either to demonstrate trends or illustrate certain specific features, and individually do not purport to tell the "whole story".

The observable in most neutron scattering experiments is the partial double differential cross-section, $\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)$:¹

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right) = \frac{\text{number of neutrons with energies between } E \text{ and } E+dE \text{ scattered into the solid angle } d\Omega \text{ per unit time}}{d\Omega \times dE \times \text{incident flux}}$$

For inelastic neutron spectroscopy, we may state from Chapter II:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)_{\text{single quantum incoherent}} = N \frac{k'}{k} \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \exp(-2W_{\ell}) \frac{A_{\lambda}}{1-A_{\lambda}} \frac{3Q^2 \hbar}{2M_{\alpha\lambda}} Z(\omega)$$

- where λ is neutron wavelength
- k is the wave vector of the incident neutron ($k = |\underline{k}| = \frac{2\pi}{\lambda}$)
- k' is the wave vector of the scattered neutron
- $\overline{|b_{\ell} - \bar{b}|^2}_N$ is the incoherent cross-section
- W_{ℓ} is the Debye-Waller factor
- A_{λ} equals $\exp\left(\frac{-\hbar\omega}{2K_B T}\right)$
- Q is the scattering vector, $Q = (\underline{k} - \underline{k}')$

$\hbar Q$	is momentum transfer $\hbar Q = \hbar(\underline{k} - \underline{k}')$
$\hbar$	is Plank's constant/ 2π
M	is the mass of the scattering atom
ω_λ	is the vibrational frequency (radians s^{-1})
$Z(\omega)$	is the density of states

As has been stated previously, strictly speaking all vibrations are active in the INS spectrum; however, from the form of the intensity relationship above, may be seen what effectively amount to the "selection rules" for neutron spectroscopy. That is to say that those factors which govern intensity are the incoherent cross-section, the Debye-Waller factor, the scattering vector, the mass of the scattering atom and the vibrational frequency. Greatest intensity therefore results when atoms with large incoherent cross-sections and small masses are present executing large amplitudes of vibration. Consideration of at least the first two of these criteria shows that hydrogen is the most favoured atom for inelastic neutron scattering, and it follows that, of vibrations involving hydrogen, internal torsions and whole body librations are likely to be amongst the most intense modes.

The expression for the partial double differential cross-section shows another interesting feature of INS spectroscopy, viz. that isotopic substitution causes not only a change in frequency, but also, via the incoherent cross-section, an intensity change.

In the case of the substitution of deuterium for hydrogen, a reduction of intensity of about 1/40 is expected from comparison of the relative incoherent cross-sections.

B. Background to the Employment of INS spectroscopy in the Study of Zeolite-adsorbate Interactions

The mechanism of metal-gas interactions at surfaces, and the bonding which

takes place, is of great scientific interest, and no little commercial importance. Zeolites¹¹ offer an excellent medium in which to investigate the problem at a slightly lower degree of complexity, for in the zeolite aluminosilicate lattice, metal atoms are held at fixed points in space, rather than forming the ill-defined surface of a bulk material. However, interest in zeolites is by no means limited only to their suitability as model systems: they are industrially important in their own right, particularly in the petrochemical industry (as catalysts).

Although infrared studies of zeolites and of zeolite-adsorption systems abound in the literature, a common feature runs through all of this work: the almost complete absence of data for the region below 300 cm^{-1} , where the vibrational frequencies resulting from cation-adsorbate interactions would be expected¹². The undoubted reason for this lack of information has been the difficulty experienced in getting zeolite material into a form such that an adequate amount of radiation could be transmitted, combined with the scarcity until comparatively recently of Fourier Transform Far-Infrared spectrometers.

To our knowledge, only four papers have been published reporting far-infrared spectra of zeolites¹²⁻¹⁵. Of these only one has described the employment of unsupported zeolite in disc form¹⁴, and again in only one instance has an attempt been made to investigate the adsorption of molecules other than water¹⁵.

In what was claimed to be the first paper devoted to the study of the far-infrared of zeolites, Brodskii et al.¹² investigated the following cation-exchanged forms of type X¹¹ zeolite:

- (a) NaX : $\text{Na}_{0.93}[(\text{AlO}_2)_{1.00}(\text{SiO}_2)_{1.43}]$
- (b) LiNaX : $\text{Li}_{0.54}\text{Na}_{0.33}[(\text{AlO}_2)_{1.00}(\text{SiO}_2)_{1.35}]$
- (c) KNaX : $\text{K}_{0.66}\text{Na}_{0.21}[(\text{AlO}_2)_{1.00}(\text{SiO}_2)_{1.33}]$
- (d) RbNaX : $\text{Rb}_{0.63}\text{Na}_{0.29}[(\text{AlO}_2)_{1.00}(\text{SiO}_2)_{1.31}]$
- (e) CsNaX : $\text{Cs}_{0.55}\text{Na}_{0.37}[(\text{AlO}_2)_{1.00}(\text{SiO}_2)_{1.35}]$

Samples ($3-4 \text{ mg cm}^{-2}$) were prepared as a result of an aqueous suspension of zeolite powder being applied to a substrate (transparent in the working spectral region), and allowed to dry in air. Several treatments involving differing degrees of heating and evacuation were then carried out:

- (i) evacuation to 2×10^{-1} Torr for 1 minute at 20°C
- (ii) evacuation to 2×10^{-2} Torr for 1 hour at 20°C
- (iii) evacuation to 2×10^{-4} Torr for 3 hours at 20°C
- (iv) evacuation to 5×10^{-5} Torr for 3 hours at 100°C
- (v) evacuation to 5×10^{-5} Torr for 3 hours at 400°C

spectra in each case being recorded in the region $30-470 \text{ cm}^{-1}$.

Two bands (at 500 cm^{-1} and 175 cm^{-1}) were identified as respectively librational and translational modes of adsorbed water, the absence of these vibrations after evacuation above 400°C being taken as evidence for the complete removal of water at this temperature. Further peaks were assigned, on the basis of their invariance with respect to dehydration, to motions of the aluminosilicate framework; whilst for each zeolite, at least one band was found which the authors considered to result from cationic vibration. An attempt was made to correlate the latter vibrations with the various cation locations possible within the type 13X zeolite framework (Chapter VI) and, as may be seen from Table 1.1, the vibrational frequencies of those cations believed to occupy the energetically equivalent and spectrally unresolved sites II' and II¹¹ were observed to be roughly proportional to $m^{-\frac{1}{2}}$ (where m is the mass of the particular cation present).

Table 1.1 The Spectroscopic Frequencies (cm^{-1}) and Assignments of Zeolites LiNaX, NaX, KNaX, RbNaX and CsNaX after Brodskii et al.¹²

Assignment	LiNaX	NaX	KNaX	RbNaX	CsNaX
Cation Site [/] I	150	64			
Cation sites [/] II' and II	400?	190	150	105	114
Framework Vibrations {	110	110	110		
	370	370			
	455	455			

[/] The nomenclature associated with cation locations within the framework of type 13X zeolite is discussed at length in Chapter VI and reference 11.

Later work by Brodskii et al.¹³, again using supported samples studied the absorption spectra of a number of cation substituted synthetic faujasite zeolites, as well as sodium type X and type Y¹¹ zeolites with differing silicon to aluminium ratios:

(a)	NaX	:	Na ₈₃	[	(AlO ₂) ₉₀ (SiO ₂) ₁₀₂	]	H ₇
(b)	NaX	:	Na ₇₆	[	(AlO ₂) ₈₈ (SiO ₂) ₁₀₄	]	H ₁₂
(c)	NaX	:	Na ₇₆	[	(AlO ₂) ₈₁ (SiO ₂) ₁₁₁	]	H ₅
(d)	NaY	:	Na ₆₆	[	(AlO ₂) ₇₂ (SiO ₂) ₁₂₀	]	H ₆
(e)	NaY	:	Na ₅₇	[	(AlO ₂) ₆₃ (SiO ₂) ₁₂₉	]	H ₆
(f)	NaY	:	Na ₅₁	[	(AlO ₂) ₅₄ (SiO ₂) ₁₃₈	]	H ₃
(g)	LiNaX	:	Li ₄₄ Na ₂₇	[	(AlO ₂) ₈₂ (SiO ₂) ₁₁₀	]	H ₁₁
(h)	KNaX	:	K ₅₄ Na ₁₇	[	(AlO ₂) ₈₂ (SiO ₂) ₁₁₀	]	H ₇
(j)	RbNaX	:	Rb ₅₂ Na ₂₄	[	(AlO ₂) ₈₃ (SiO ₂) ₁₀₉	]	H ₇
(k)	CsNaX	:	Cs ₄₅ Na ₃₀	[	(AlO ₂) ₇₉ (SiO ₂) ₁₁₃	]	H ₇
(l)	KY	}	Similar to sample (f) but with maximum replacement of Na ⁺ cations by K ⁺ (100%) and Cs ⁺ (70%) respectively.				
(m)	CsNaY						

In these experiments all samples were heated to 400°C and evacuated to 5×10^{-5} Torr for 4 hours, prior to spectra being measured in the region 20-470 cm⁻¹. As in the previous investigation, it proved possible to associate certain frequencies with vibrations of the framework. Similarly, bands corresponding to cation modes were identified and correlation made between these and given cation positions (Table 1.2). In this case both the cation frequencies associated with sites I' and II (unresolved in the spectra), and those resulting from site III, were shown to be inversely proportional to the square-root of the mass of the cation present.

Table 1.2 The Spectroscopic Frequencies (cm^{-1}) and Assignments
of Zeolites NaX, KNaX, RbNaX, CsNaX, NaY, KY and CsNaY
after Brodskii et al.¹³

Assignment	NaX(a)	NaX(c)	KNaX(h)	RbNaX(j)	CsNaX(k)	NaY(f)	KY(l)	CsNaY(m)
Cation sites [†] I' and II {	188	188	148	100?	55	} 160- 185	} 98- 135	57
Cation site [†] III	66	66	54	40	33			
Unexchanged sodium ions remaining at cation site [†] I'			188	182	185			170
Framework Vibrations {	88		87	83	82	90		
	110		110	110	120	110		116
						385	385	290 385

} denotes doublet

[†] The nomenclature used in this table to describe cation locations in type 13X zeolite is explained in Chapter VI and reference 11.

The sole attempt to investigate unsupported zeolite in disc form was reported in the study of a CaNaX zeolite (of composition $0.66\text{CaO}:0.31\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.56\text{SiO}_2$) by Drykheev et al.¹⁴. In this work, zeolite (without binder) was compressed into tablets $10 \times 8 \text{ mm}^2$ in size, and 12 mg cm^{-1} in thickness (employing a pressure of 50 kgf cm^{-2}), and spectra recorded between 60 and 400 cm^{-1} .

It was found that whilst evacuation to 300°C caused the appearance of new bands in the spectrum, continued heating to an ultimate temperature of 500°C caused no further significant change. From this, it was concluded that the dehydration process was essentially complete above 300°C . Assignment was made of several bands to framework vibrations, and peaks thought to derive from cation vibrations identified (Table 1.3).

Table 1.3 The Spectroscopic Frequencies (cm^{-1}) and Assignments
Reported for Zeolite CaNaX by Dyrkheev et al.¹⁴

Assignment	CaNaX
Cation site [/] I	65
"Interionic vibrations of Ca^{2+} ions relative to zeolite skeleton"	} 135 157
"Interionic vibrations or vibrations of elements of the zeolite skeleton affected by a change in fixation site of Ca^{2+} ions"	} 210 235 250 280
Framework vibrations	} 325 385

[/] Cation sites within type 13X zeolite are discussed
in Chapter VI and reference 11.

In the final account published, Butler et al.¹⁵ investigated Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} exchanged type Y zeolites as well as Na^+ , K^+ , Rb^+ , Cs^+ and Ca^{2+} exchanged type X zeolites. Spectra were measured using two different sample techniques:

- Zeolite (previously dehydrated) milled in petroleum jelly between low density polyethylene plates, and
 - Zeolite powder (0.2 mm thick) supported on a transparent substrate.
- Zeolites containing monovalent cations were activated by heat treatment at 400°C and evacuation to 10^{-4} Torr for 12 hours: those containing divalent cations were subjected to the higher temperature of 500°C .

As in previous work, vibrations of the aluminosilicate lattice and of cations located in various sites were assigned (Table 1.4). However, in this investigation there is also reported the only known far-infrared study of adsorbed species other than water, the molecules investigated being water (H_2O and D_2O), pyridine, dimethyl sulphoxide, tetrahydrofuran

Table 1.4 The Spectroscopic Frequencies (cm^{-1}) and Assignments of the Zeolites, NaX, KX, RbX, CsX, CaX, LiY, NaY, KY, CSY, AGY, MGY, CaY, SiY and BaY after Butler et al.¹⁵

Assignment	NaX	KX	RbX	CsX	CaX	LiY	NaY	KY	CSY	AGY	MGY	CaY	SiY	BaY
Cation Site I	160	156	108	86	287		167	107		50		256	189	137
Cation site II ^o	190	156	108	86	273	380	180	133	62	82		227	150	107
Cation site III	67	58	48	39					30					
					50							40	53	50
					65						64	65	67	60
	91	77	83	64 ^o	85						84	90	100	90
					100									
	109	106	118	126	132	100	122		109	122	132	131	122	
					152					150	157	162	165	157
Framework Vibrations					168	164 ^o		160	174 ^o	168		170	177	182
					204 ^o					190 ^o	190 ^o	202 ^o	204 ^o	200 ^o
					210	212			210	228		211	220	
					220						249		250	227
	218	230	259	254		296	273	270	280	270	275	267	266	270
	263	277	296	295										
	295	308												
	321	322			321	311		310	317	320		308	304	310
					359								330	343
					380	396	392	385	383	380	401	385	385	375
(Ring deformation)	382	373												

^o Bands resulting from residual sodium ions.

^f The nomenclature associated with cation locations within type 13X zeolite is described in Chapter VI and reference 11.

^o In the case of the monovalent cation-exchanged zeolites listed above, the band assigned to "site II" cations also encompasses those ions present at Site I' locations. For divalent cation-exchanged zeolites, the "site II" designation also includes ions present in both site I' and site II' positions. This is a statement of the near equivalence in potential energy of these sites, and the consequent difficulty encountered in achieving their spectral resolution.

and dichloromethane adsorbed to (0.05 Torr) on NaX, KX and KY zeolites.

In all the adsorbate-zeolite systems, the frequency of the site II cation vibration was found to shift to lower energy, and vibrations corresponding to the symmetric and antisymmetric stretches of the ligand relative to the cation could be identified (Table 1.5).

Table 1.5 Typical Data Relating to the Adsorption of 0.05 Torr H₂O/
Pyridine/Dimethyl Sulphoxide/Tetrahydrofuran or Dichloromethane¹⁵
Adsorbed on NaX/KX or KY Zeolites (after Butler et al.¹⁵).

Zeolite	Site [†] II vibrational frequency before adsorption	Typical Site [†] II vibrational frequency after adsorption	Typical Symmetric Stretching frequency	Typical Anti-symmetric Stretching frequency
NaX	190 cm ⁻¹	180 cm ⁻¹	155 cm ⁻¹	215 cm ⁻¹
KX	156 cm ⁻¹	ca. 140 cm ⁻¹	120 cm ⁻¹	165 cm ⁻¹
KY	133 cm ⁻¹	130 cm ⁻¹	115 cm ⁻¹	155 cm ⁻¹

[†] The location of cations within the type 13X zeolite framework is discussed in Chapter VI and reference 11.

In common with the far-infrared work, Raman spectroscopic measurements have suffered severe limitations, in this case imposed by the weakness of the Raman scattering produced¹⁶⁻¹⁸, and the often unacceptably high levels of fluorescence background encountered, especially when transition metal atoms are present¹⁶. It is therefore not surprising that many studies have been restricted to alkali or alkaline earth metal exchanged zeolites^{16,18-23}; although, for example, spectra of Tl⁺ and Ag⁺ exchanged type A zeolites²⁴, and Eu³⁺²⁵, Co²⁺, Cu²⁺ and Ce³⁺ exchanged type Y zeolites²⁶ have been published (Table 1.6). However, even with Group I and Group II metal-exchanged zeolites, a high temperature (typically 500°C) "burning out" treatment using oxygen has generally proved necessary to reduce fluorescence attributed to hydrocarbon impurities.

Table 1.6 summarises some of the most important papers which have been published of Raman investigations of zeolites and species adsorbed

TABLE 1.6 Summary of the Zeolite-adsorption Systems which have been
studied by Raman Spectroscopy

Adsorbed Species	Zeolite [†]	^a Reference
-	NaA, NaX, CaX, NaY et al.	16
-	TlA, AgA and LiA	24
-	EuY	25
-	NaY, LiY, KY, CoY, CuY, CeY and HY	26
Carbon dioxide	NaX and NaY	16
Acetonitrile	NaX and NaY	16
Propylene	NaA, NaX and NaY	16
Acrolein	NaY	16
Pyridine	LiX, NaX, KX, CsX, ZnX and HX	18
Pyridine	NaY, LiY, KY, CoY, CuY, CeY and HY	19,26
Acetylene	LiA, NaA, KA, MgA and CaA	20
Acetylene	LiX, NaX, KX, CsX, MgX, CaX and BaX	21,27
Dimethylacetylene	NaX and CsX	21
Pyrazine	LiX, NaX, KX, CsX, MgX, CaX and BaX	22
Cyclopropane	LiX, NaX, KX and CsX	23

[†] The structures of types A, X and Y zeolites are discussed at length in reference 11, whilst summaries of types A and X may be found in Chapter VI.

on zeolites. As far as is known, in no case, certainly in none of the reports listed above, have modes been observed which could be ascribed to cation-adsorbed species interaction. Conclusions regarding metal-adsorbate bonding have therefore, of necessity, been derived entirely from frequency shifts, which have taken place between the isolated and adsorbed molecule^{16,18-23, 26, 27}.

In contrast with the more conventional spectroscopic techniques, INS spectroscopy is well suited to zeolite studies, in that the aluminosilicate lattice of the zeolite is relatively transparent to neutrons, and thus, if an hydrogenous species is adsorbed, the predominant vibrational frequencies recorded will be those involving the adsorbed species and its interaction with the cation. That is not to suggest that the employment of INS spectroscopy is not without its own attendant disadvantages; chief amongst these are:

(i) that the resolution attainable in a neutron scattering experiment is always considerably poorer than that which is routinely achieved using an infrared or Raman spectrometer.

(ii) that experiments require several days, generally two days for a background and two days for the adsorbed species plus background, rather than the couple of hours necessary for the measuring of "conventional" spectra.

(iii) that unlike infrared or Raman instruments, which are always present, and around which may be designed experiments at the investigator's convenience, neutron beam facilities are severely rationed and allocated six months in advance. It is therefore a not inconsiderable logistic achievement to have an experiment ready for the beginning of the scheduled time and to have it completed within the prescribed period, especially in view of the probability of machine breakdowns, and the operating difficulties sometimes experienced even with the reactor.

C. The Systems Studied

The zeolite chosen for investigation was silver-exchanged type A¹¹, and the gases adsorbed were ethylene and acetylene. These systems followed naturally from previous INS studies which reported the adsorption of the same gases on the parallel system of silver-exchanged zeolite type 13X²⁸⁻³¹.

In order to aid understanding of the zeolite-adsorbed gas systems, INS spectra were obtained of simple organometallic complexes which contained metal-ethylene and metal-acetylene bonds, and which had already been well investigated by other techniques. These "model compounds" included cis- and trans- $\text{PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$ complexes (where L denotes a ligand group) and $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$.

Furthermore, as part of an ultimate intention to study the adsorption of benzene on silver-exchanged type 13X zeolite, the INS spectra of several benzene containing compounds have been measured.

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CHAPTER II

BACKGROUND THEORY

A. Neutron Scattering

There are several detailed sources¹⁻⁸ covering basic neutron scattering theory. In consequence, only the general principles behind the theory, and that theory specific to the experimental work undertaken, will be described here.

L The Application of Perturbation Theory to Neutrons

As a result of its wave-particle duality, the motion of a neutron through free space may be represented by a differential equation of the time-independent Schrödinger type:

$$\frac{-\hbar^2 \nabla^2}{2m} \psi_a = E \psi_a \quad 2(i)$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$\hbar$ is Planck's constant divided by 2π

m is the mass of a neutron

ψ_a is the wave-function of the neutron

(i.e. solutions of the equation)

E is the eigen value of the equation

A perturbation, resulting from neutron-system interaction, may be incorporated into equation 2(i) by the introduction of a potential term:

$$\frac{-\hbar^2 \nabla^2}{2m} \psi_s + V'(\underline{r}) \psi_s = E' \psi_s \quad 2(ii)$$

where ψ_s is the wave-function of equation 2(ii):

$$\psi_s = \psi_a + \psi_p$$

ψ_a is the wave-function representing the incident wave (equation 2(i))

ψ_p is the wave-function representing the scattered wave

$V'(\underline{r})$ is the potential function describing a part of the system through which the neutron is passing

$\underline{r}$ is the position vector of the neutron

Application of the Born approximation¹ which states that as $\underline{r} \rightarrow \infty$, $E' \sim E$ and $\psi_s \sim \psi_a$ simplifies 2.(ii) giving:

$$-\frac{\hbar^2 \nabla^2}{2m} \psi_p + V'(\underline{r}) \psi_a = E \psi_p \quad 2.(iii)$$

It should be stressed at this point that the extension of the Born approximation to neutron-nucleon interaction, which will be detailed later, and in fact, provides the foundation of all neutron scattering theory, is an extremely dubious practice. This is because it must be assumed that the short range nuclear forces apply only a small perturbation to the neutron and this completely disregards the great size of these forces. However, this contradiction has been considered¹ and the judgement is that, outside the range of nuclear forces, the Born approximation is valid and may be used as a basis for the discussion of neutron scattering theory.

Employment of the relations:

$$m\underline{v} = \frac{\hbar}{\lambda} \quad \text{and} \quad \underline{k} = \frac{1}{\lambda}$$

where $\underline{v}$ is the neutron velocity

λ is the De Broglie wavelength of the neutron with energy E

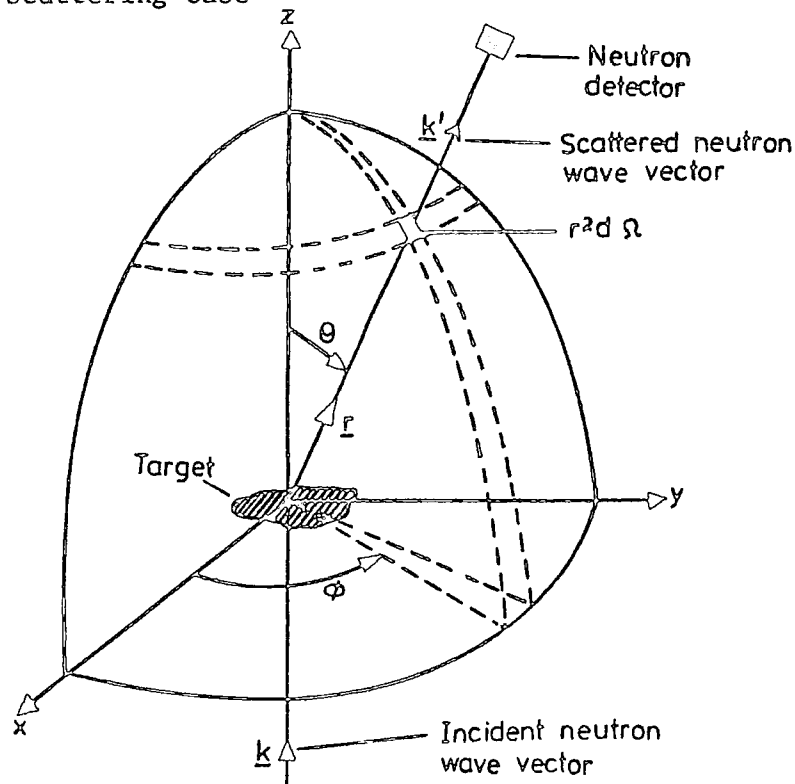
$\underline{k}$ is the neutron wave-vector (equivalent to its momentum)

in the substitution of equation 2.(iii) produces:

$$(\nabla^2 + \underline{k}^2) \psi_p = \frac{2m}{\hbar^2} V'(\underline{r}) \psi_a \quad 2.(iv)$$

2. The Scattering Cross-section of a Single Fixed Nucleus

a) Elastic Scattering Case



In order to investigate the scattering problem, consider an incident neutron described by a plane wave for which the following may be defined:

$\underline{k}$, the wave-vector whose magnitude $|\underline{k}| = 2\pi/\lambda = k$

$\psi_{\underline{k}}$, the wave-function = $\exp(i \underline{k} \cdot \underline{r})$

This incident neutron is scattered elastically by a fixed nucleus placed at the origin which has no possible internal excited states. As the nuclear forces which give rise to scattering are several orders of magnitude shorter in range than the wavelength of thermal neutrons (ca. 10^{-10} m), the neutron must be scattered spherically and isotropically. The following may therefore be defined for the scattered neutron:

$\underline{k}'$, the wave-vector

$\psi_{\underline{k}'}$, the wave-function = $\frac{F}{|\underline{r}|} \exp(i \underline{k}' \cdot \underline{r})$

where F is the scattering amplitude.

The function F , which relates the size of the perturbation to the resultant scattering is a power series in neutron energy:

$$F = -b + a_1 E + a_2 E^2 \text{ etc.}$$

where E is neutron energy

b, a_1 , a_2 are constants

For values of E less than about $8 \times 10^4 \text{ cm}^{-1}$ this reduces to

$$F = -b$$

where the constant b is known as the scattering length⁹, which may be complex or real, and in the latter case positive or negative. A complex value corresponds to neutron adsorption, whilst a positive or negative real value results from the relative phases of the incident and scattered waves. The magnitude of the scattering length varies not only for each element, but also for each isotope, and in addition, is dependent upon the relative orientation of the neutron and nuclear spins.

By definition:

N_i is the incident neutron flux (the number of neutrons (N_o) /unit area (L^2)/unit time (t)).

σ is the cross-section (the total number of neutrons scattered (N_s)/unit time (t)/ incident flux (N_i)).

$d\Omega$ is the solid angle ($\sin\theta \, d\theta \, d\phi$)

From the above it may be seen that σ has dimensions of area, N_s and N_o being dimensionless:

$$\sigma = \frac{1}{[t]} \cdot [L]^2 \cdot [t] = [L]^2$$

The solid angle $d\Omega$ is dimensionless and in consequence the differential cross-section $\frac{d\sigma}{d\Omega}$,

$$\text{where } \frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered into the solid angle,}}{\text{solid angle x time x incident flux}}$$

must also have dimensions of area.

For the scattering problem which has been outlined, the energy of the scattered neutron must remain that of the incident i.e. $\hbar^2 k^2 / 2m$. The transition probability from the k to the k' plane wave state under this condition is given by Fermi's Golden rule:¹⁰

$$\text{Prob}_{k \rightarrow k'} = \frac{2\pi}{\hbar} \left| \int d\underline{r} \psi_{k'}^* V(\underline{r}) \psi_k \right|^2 P_{k'} \quad 2(v)$$

where * denotes the complex conjugate

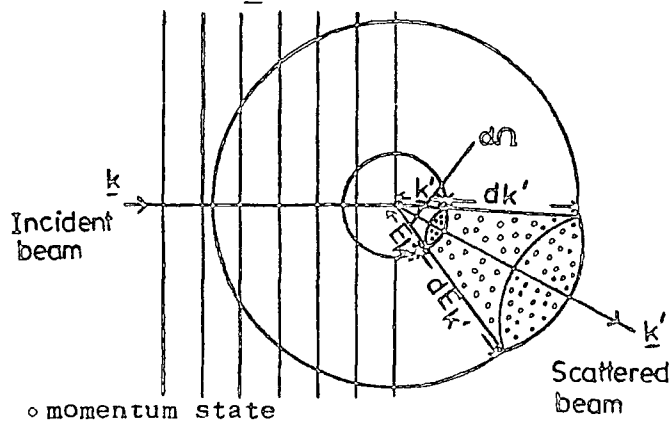
$V(\underline{r})$ is the interaction potential causing the transition
i.e. the interaction between the incident neutron and
target nucleus.

$P_{k'}$ is the density of the final scattering states per
unit energy range.

Evaluation of the term $P_{k'}$ requires that the wave-functions are normalised.¹⁰
In the case of a large box of volume L^3 , the initial and final states may be
written as:

$$\psi_k = L^{-3/2} \exp(i \underline{k} \cdot \underline{r}) \quad \text{and} \quad \psi_{k'} = L^{-3/2} \exp(i \underline{k}' \cdot \underline{r})$$

The density of final states can be found from the permitted values of
 $\underline{k}'$ in a box: $k'_x = 2\pi n_x / L$, etc., where the n 's may be positive or
negative integers or zero. There are therefore $(L/2\pi)^3 dk'_x dk'_y dk'_z$
states in the range $dk'_x dk'_y dk'_z$ of propagation vector. There are many
different final $\underline{k}'$ states with the same energy corresponding to different
directions of $\underline{k}'$ with a given magnitude, so that a small range of directions



must be considered at a time.

Taking the rate of transition into
an infinitesimal element of the
solid angle $d\Omega$, then $P_{k'} dE_{k'}$ is
equal to the number of states in the
volume range given by $d\Omega$ and the
magnitude element dk' (i.e. $k'^2 d\Omega dk'$),

where dk' corresponds to the energy element $dE_{k'}$ (see diagram above):

$$P_{k'} dE_{k'} = \left(\frac{L}{2\pi} \right)^3 k'^2 d\Omega dk'$$

Since $E_{k'} = \frac{\hbar^2 k'^2}{2m}$, $\frac{dE_{k'}}{dk'} = \frac{\hbar^2 k'}{m}$ and therefore

$$P_{k'} = \frac{L^3 m}{8\pi^3 \hbar^2} k' d\Omega \quad 2.(vi)$$

The above applies only to the case where there is one incident particle in the volume L^3 . To enable calculation of the cross-section the expression above must be divided by the incident neutron flux which is:

$$\frac{v}{L^3} = \frac{\hbar k'}{m} \cdot \frac{1}{L^3} \quad 2.(vii)$$

where v is the velocity of the incident neutrons.

In the case of elastic scattering where the velocities of incident and scattering neutrons are equal ($k = k'$), combining 2.(v), 2.(vi) and 2.(vii) gives:

$$d\sigma = \text{Prob}_{k \rightarrow k'} / \text{incident flux} = L^6 \left(\frac{m}{2\pi\hbar} \right)^2 \left| \int d\underline{r} \psi_{k'}^* V(\underline{r}) \psi_k \right|^2 d\Omega$$

$\int d\underline{r} \psi_{k'}^* V(\underline{r}) \psi_k$ may be expressed using Bra-Ket notation as $\langle \underline{k}' | V(\underline{r}) | \underline{k} \rangle$

and the normalisations may be cancelled yielding:

$$\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi\hbar} \right)^2 \left| \langle \underline{k}' | V(\underline{r}) | \underline{k} \rangle \right|^2 \quad 2.(viii)$$

But the scattering amplitude of the nucleus is defined as¹:

$$\frac{d\sigma}{d\Omega} = \left| f(\underline{k}, \underline{k}') \right|^2 = |b|^2 \quad 2.(ix)$$

$$\text{and therefore } f(\underline{k}, \underline{k}') = b = -\frac{m}{2\pi\hbar^2} \langle \underline{k}' | V(\underline{r}) | \underline{k} \rangle \quad 2.(x)$$

The scattering amplitude in the form shown above may therefore be seen to be an expression of the transition probability. (Note the phase of b is determined from a more rigorous derivation¹.)

From 2.(ix), the cross-section may be written:

$$\sigma = \int_{4\pi} \left(\frac{d\sigma}{d\Omega} \right) = 4\pi b^2 \quad 2.(xi)$$

b) Inelastic Scattering Case

When a neutron interacts inelastically with a nucleus, the energy of the scattered neutron is no longer equal to that of the incident, and the nucleus changes energy state.

If the initial state of the nucleus is denoted by λ , with energy E_λ , and the final state is λ' with energy $E_{\lambda'}$, then equation 2.(viii) becomes:

$$\left(\frac{\partial \sigma}{\partial \Omega} \right)_{\substack{\underline{k}', \lambda' \\ \underline{k}, \lambda}} = \frac{k'}{k} \left(\frac{m}{2\pi \hbar^2} \right)^2 \left| \langle \underline{k}' \lambda' | V(\underline{r}) | \underline{k} \lambda \rangle \right|^2 \quad 2.(xii)$$

assuming conservation of energy.

The latter condition may be brought into equation 2.(xii) and a double differential cross-section defined:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\substack{\underline{k}', \lambda' \\ \underline{k}, \lambda}} = \frac{k'}{k} \left(\frac{m}{2\pi \hbar^2} \right)^2 \left| \langle \underline{k}' \lambda' | V(\underline{r}) | \underline{k} \lambda \rangle \right|^2 \delta(\hbar\omega + E_\lambda - E_{\lambda'}) \quad 2.(xiii)$$

where ω is the change in radial frequency associated with

$$\text{the scattering event } \left(\hbar\omega = \frac{\hbar^2}{2m} (k^2 - k'^2) = E - E' \right)$$

The Dirac δ function in equation 2.(xiii) expresses the conservation of energy in the neutron-nuclei system.³ It may be defined thus:^{3,11}

$$\text{if } x \neq 0, \text{ then } \delta(x) = 0$$

$$\text{if } x = 0, \text{ then } \delta(x) = +\infty$$

$$\int_{-\infty}^{+\infty} \delta(x) dx = 1$$

It is necessary in equation 2.(xiii) to average over all the initial states of the nucleus (λ), which have probabilities P_λ , and sum over all the final states (λ'), in order to obtain the total partial differential cross-section. If the quantum numbers λ and λ' are taken to represent all those required to describe completely the initial and final states of the

target, and considerations of the spin states of the neutron are ignored, equation 2.(xiii) becomes:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right) = \frac{k'}{k} \left(\frac{m}{2\pi\hbar^2} \right)^2 \sum_{\lambda} P_{\lambda} \sum_{\lambda'} | \langle \underline{k}' \lambda' | V(\underline{r}) | \underline{k} \lambda \rangle |^2 \delta(\hbar\omega + E_{\lambda} - E_{\lambda'}) \quad 2.(xiv)$$

where $\sum_{\lambda} P_{\lambda} = 1$

The only form of interaction potential $V(\underline{r})$ which results in isotropic scattering, using the Born approximation, is a δ function^{1,2,3}. The Fermi pseudopotential^{1,3}:

$$V(\underline{r}) = \frac{2\pi\hbar^2}{m} b \delta(\underline{r}-\underline{R}) \quad 2.(xv)$$

where $\underline{R}$ is the position vector of the nucleus, is therefore introduced as a device to obtain the spherically symmetrical (s-wave) scattering required, the sign of the scattering length being defined such that b is positive for scattering by an impenetrable sphere of radius b^1 .

Substitution of equation 2.(xv) into equation 2.(x) yields for $\underline{R} = 0$:

$$f(k, k') = - \left(\frac{m}{2\pi\hbar^2} \right) \frac{2\pi\hbar^2}{m} b \int d\underline{r} \exp(-i\underline{k}' \cdot \underline{r}) \delta(\underline{r}) \exp(i\underline{k} \cdot \underline{r}) = -b \quad 2.(xvi)$$

In order to calculate the cross-section of a free nucleus, centre of mass co-ordinates are used. The nucleus is again fixed at the origin with an interaction potential $V(\underline{r})$, but the incident neutron now has reduced mass (μ):

$$\mu = \left(\frac{mM}{m+M} \right) = m \left(1 + \frac{m}{M} \right)^{-1}$$

where M is the mass of the nucleus

The differential cross-section from equation 2.(ix) is thus:⁸

$$\frac{\partial \sigma}{\partial \Omega} = |b|^2 \left(1 + \frac{m}{M} \right)^{-2} \quad 2.(xvii)$$

and therefore the bound atom cross-section (σ_b) may be related to that of the free (σ_f) by comparison of equations 2.(xi) and 2.(xvii):

$$\sigma_f = \sigma_b \left(1 + \frac{m}{M}\right)^{-2} \quad 2.(xviii)$$

For the example of hydrogen ($M=1$):

$$\sigma_f = \sigma_b (1 + 1)^{-2} = \sigma_b \cdot \frac{1}{4}$$

$$\text{i.e. } \sigma_f = \frac{4\pi|b|^2}{4} = \pi|b|^2$$

3. Scattering From an Array of Nuclei

In the case of a rigid array of N nuclei, where the position vector of the ℓ^{th} nucleus is represented by $\underline{R}_\ell$, and its scattering length by b_ℓ , the interaction potential becomes:

$$V(\underline{r}) = \frac{2\pi\hbar^2}{m} \sum_{\ell} b_{\ell} \delta(\underline{r} - \underline{R}_{\ell}) \quad 2.(xix)$$

$$\text{Hence } \langle \underline{k}' | V(\underline{r}) | \underline{k} \rangle = \frac{2\pi\hbar^2}{m} \sum_{\ell} b_{\ell} \int_{-\infty}^{+\infty} d\underline{r} \exp(-i\underline{k}' \cdot \underline{r}) \delta(\underline{r} - \underline{R}_{\ell}) \exp(i\underline{k} \cdot \underline{r})$$

$$= \frac{2\pi\hbar^2}{m} \sum_{\ell} b_{\ell} \exp(i\underline{Q} \cdot \underline{R}_{\ell}) \quad 2.(xx)$$

where $\underline{Q}$ is the scattering vector and the relation $\hbar\underline{Q} = \hbar(\underline{k} - \underline{k}')$ represents change in momentum.

From equations 2.(xiv) and 2.(xx) may be obtained the expression:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right) = \frac{k'}{k} \sum_{\lambda} P_{\lambda} \sum_{\lambda'} | \langle \lambda' | \sum_{\ell} b_{\ell} \exp(i\underline{Q} \cdot \underline{R}_{\ell}) | \lambda \rangle |^2 \delta(\hbar\omega + E_{\lambda} - E_{\lambda'}) \quad 2.(xxi)$$

In general:

(i) Any operator which represents a physical observable must be

Hermitian, i.e. it may be stated that:¹²

$$\langle m | \hat{A} | n \rangle = \langle n | \hat{A} | m \rangle^* \quad 2.(xxi)a$$

where $\hat{A}$ is an operator

$\hat{}$ indicates an operator in matrix form

(ii) The Hermitian adjoint A^+ of a matrix operator A is the matrix obtained by interchanging rows (r) and columns (c) and taking the complex conjugate of each element:^{10,12}

$$A_{rc}^+ = A_{cr}^*$$

and $A_{rc}^+ = \bar{A}_{rc}^*$

where $\bar{}$ denotes the transpose of the matrix

$$\text{i.e. } \bar{A}_{rc} = A_{cr}$$

But for a Hermitian matrix $A^+ = A$ ¹² and therefore:

$$\bar{A}_{cr} = A_{rc} = A_{rc}^+ = \bar{A}_{rc}^* = A_{cr}^* \quad 2.(xxi)b$$

(Note: in the above equations the $\hat{}$ nomenclature for a matrix operator has been left out to avoid confusion.)

(iii) From equations 2.(xxi)a and 2.(xxi)b may be written:

$$\langle m | A_{rc} | n \rangle = \langle n | A_{rc} | m \rangle^* = \langle n | \bar{A}_{rc} | m \rangle$$

(iv) The product of two matrix operators in Bra-Ket nomenclature may be represented:¹²

$$\langle m | \hat{B} | \lambda \rangle \langle \lambda | \hat{C} | n \rangle = \langle m | \hat{B}\hat{C} | n \rangle \quad 2.(xxi)c$$

Therefore returning to equation 2.(xxi):

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E} \right)_\alpha \dots \langle \lambda' | \sum_{\ell} b_{\ell} \exp(i\mathbf{Q} \cdot \mathbf{R}_{\ell}) | \lambda \rangle^2 \dots$$

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E} \right)_\alpha \dots \langle \lambda' | \sum_{\ell'} b_{\ell'} \exp(i\mathbf{Q} \cdot \mathbf{R}_{\ell'}) | \lambda \rangle \langle \lambda' | \sum_{\ell} b_{\ell} \exp(i\mathbf{Q} \cdot \mathbf{R}_{\ell}) | \lambda \rangle \dots$$

Using the Hermitian properties detailed previously, the first thermal average may be transformed into its complex conjugate, and the matrix operator may be transposed yielding:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right) \propto \dots \left| \langle \lambda \right| \sum_{\ell'} b_{\ell'}^* \exp(-i \underline{Q} \cdot \underline{R}_{\ell'}) \left| \lambda' \right\rangle \langle \lambda' \right| \sum_{\ell} b_{\ell} \exp(i \underline{Q} \cdot \underline{R}_{\ell}) \left| \lambda \right\rangle$$

after equations 2.(xxi)a and 2.(xxi)b.

Rewriting the above gives from equation 2.(xxi)c

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \propto \dots \left| \langle \lambda \right| \left(\sum_{\ell'} b_{\ell'}^* \exp(-i \underline{Q} \cdot \underline{R}_{\ell'}) \right) \left(\sum_{\ell} b_{\ell} \exp(i \underline{Q} \cdot \underline{R}_{\ell}) \right) \left| \lambda \right\rangle \dots$$

and using the relation

$$\left(\sum_p b_p \exp B_p \right) \left(\sum_T b_T \exp B_T \right) = \sum_{pT} b_p b_T \exp (B_p + B_T)$$

produces:

$$\begin{aligned} \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right) &\propto \dots \left| \langle \lambda \right| \sum_{\ell \ell'} b_{\ell'}^* b_{\ell} \exp(-i \underline{Q} \cdot \underline{R}_{\ell'} + i \underline{Q} \cdot \underline{R}_{\ell}) \left| \lambda \right\rangle \dots \\ &\propto \dots \sum_{\ell \ell'} b_{\ell'}^* b_{\ell} \left| \langle \lambda \right| \exp(-i \underline{Q} \cdot \underline{R}_{\ell'} + i \underline{Q} \cdot \underline{R}_{\ell}) \left| \lambda \right\rangle \dots \\ &\propto \dots \sum_{\ell \ell'} b_{\ell'}^* b_{\ell} \left| \langle \lambda \right| \exp(i \underline{Q} \cdot (\underline{R}_{\ell} - \underline{R}_{\ell'})) \left| \lambda \right\rangle \dots \end{aligned}$$

Therefore equation 2.(xxi) becomes:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right) = \frac{k'}{k} \sum_{\ell \ell'} b_{\ell'}^* b_{\ell} \sum_{\lambda \lambda'} P_{\lambda} \left| \langle \lambda \right| \exp(i \underline{Q} \cdot (\underline{R}_{\ell} - \underline{R}_{\ell'})) \left| \lambda \right\rangle \left| \delta(h_u + E_{\lambda} - E_{\lambda'}) \right| \quad 2.(xxii)$$

where $b_{\ell'}^*$ refers to the contribution to the scattering length resulting from the intrinsic spin of the ℓ^{th} nucleus (see later).

b_{ℓ} represents the fact that the scattering length is dependent upon which isotope constitutes the ℓ^{th} nucleus (see later.)

In the case of rigidly bound nuclei, the only disturbance caused by a neutron can be redistribution of nuclear spins and isotopes. Neither of these processes involves a change of energy state, and the scattering is therefore elastic, causing the energy dependence expressed by the delta function to disappear. The sum over λ may be performed because there is a closed set of final states and equation 2.(xxii) may be expressed:

$$\left(\frac{\partial \sigma}{\partial \Omega}\right) = \sum_{\ell, \ell'} [\exp(iQ \cdot (\underline{R}_\ell - \underline{R}_{\ell'}))] \overline{b_{\ell'}^* b_\ell} \quad 2.(xxiii)$$

where $\overline{b_{\ell'}^* b_\ell}$ denotes the value of $b_{\ell'}^*, b_\ell$ averaged over both random nuclear spin orientations and isotope distributions, i.e. $\overline{b_{\ell'}^* b_\ell} = \sum_{\lambda} P_{\lambda} \langle \lambda | b_{\ell'}^* b_\ell | \lambda \rangle$

As the value of b_ℓ depends both upon the isotope at $\underline{R}_\ell$ and its nuclear spin, if ℓ and ℓ' refer to different sites there can be no correlation between b_ℓ and $b_{\ell'}$, i.e.

$$\text{for } \ell \neq \ell' ; \overline{b_{\ell'}^* b_\ell} = \overline{b_{\ell'}^*} \overline{b_\ell} = |\bar{b}|^2$$

$$\text{for } \ell = \ell' ; \overline{b_{\ell'}^* b_\ell} = \overline{|b_\ell|^2} = \overline{|b|^2}$$

$$\text{and in general; } \overline{b_{\ell'}^* b_\ell} = |\bar{b}|^2 + \delta_{\ell\ell'} (\overline{|b|^2} - |\bar{b}|^2) \quad 2.(xxiv)$$

where $|\bar{b}|^2$ is the square of the mean

$$\text{i.e. it has the form } \left(\frac{3 + 4 + 5}{3}\right)^2$$

$\overline{|b|^2}$ is the mean of the squares i.e. it has the form $\frac{3^2 + 4^2 + 5^2}{3}$

$\delta_{\ell\ell'}$ is an expression of the fact that for $\ell = \ell'$, $\delta = 1$ and for $\ell \neq \ell'$, $\delta = 0$

It may be seen from comparison of equations 2.(xxiii) and 2.(xxiv) that

the differential cross-section may be represented by a sum:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{coh}} + \left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{incoh}}$$

where the coherent differential cross-section

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{coh}} = |\bar{b}|^2 \sum_{\ell\ell'} \exp(iQ \cdot (\underline{R}_{\ell} - \underline{R}_{\ell'})) = |\bar{b}|^2 \left| \sum_{\ell} \exp(iQ \cdot \underline{R}_{\ell}) \right|^2 \quad 2.(xxv)$$

and the incoherent differential cross-section

$$\begin{aligned} \left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{incoh}} &= \left(\overline{|b|^2} - |\bar{b}|^2 \right) \sum_{\substack{\ell\ell' \\ \ell=\ell'}} \exp(iQ \cdot (\underline{R}_{\ell} - \underline{R}_{\ell'})) \\ &= \left(\overline{|b|^2} - |\bar{b}|^2 \right) N = \overline{|b - \bar{b}|^2} N \quad 2.(xxvi) \end{aligned}$$

In physical terms, the coherent and incoherent scattering processes are radically different. In the former case, the cross-section is proportional to $|\bar{b}|^2$, and the neutron may be thought to see a mean scattering potential proportional to $\bar{b}$. In consequence strong interference effects are produced between waves scattered from each nucleus. These are such that, in the case of a crystal, coherent scattering may only take place if strict geometrical conditions are met.

For incoherent scattering the cross-section is proportional to the mean-square deviation $\overline{|b - \bar{b}|^2}$, and the process results from deviations from the mean scattering potential which are randomly distributed. As a result of this randomness, there can be no interference, and the cross-section is completely isotropic. An obvious corollary of the form of the incoherent scattering cross-section is that if a sample comprises only one isotope with no spin, then $\bar{b} = b$ and there can be no incoherent scattering.

4. Coherent and Incoherent Scattering Lengths

a) Scattering length independent of spin

When nucleic spins are ignored, the only variable which requires

consideration is the isotopic distribution. If an isotope M is taken which has a scattering length b_M , and a concentration c_M , then:

$$\bar{b} = \sum_M c_M b_M \quad 2.(xxvii)$$

$$\text{and } \overline{|b|^2} = \sum_M c_M |b_M|^2 \quad 2.(xxviii)$$

b) Scattering Length Independent of Isotope

In this case the interaction depends only upon the spins of the nucleus (i) and the neutron ($\frac{1}{2}$) which give rise to states of total spin ($i+\frac{1}{2}$) or ($i-\frac{1}{2}$), corresponding to scattering lengths b^+ and b^- . As there are $2i+1$ states of total angular momentum (i), there are $2(i+\frac{1}{2})+1$ states of spin ($i+\frac{1}{2}$) and $2(i-\frac{1}{2})+1$ states of spin ($i-\frac{1}{2}$). Thus

$$\text{The probability of interaction in the } (i+\frac{1}{2}) \text{ state} = \frac{(2i+2)}{(2i+2)+2i} = \frac{i+1}{2i+1}$$

$$\text{and the probability of interaction in the } (i-\frac{1}{2}) \text{ state} = \frac{2i}{(2i+2)+2i} = \frac{i}{2i+1}$$

$$\text{Hence } \bar{b} = \left(\frac{i+1}{2i+1} \right) b^+ + \left(\frac{i}{2i+1} \right) b^- \quad 2.(xxix)$$

$$\text{and } \overline{|b|^2} = \left(\frac{i+1}{2i+1} \right) |b^+|^2 + \left(\frac{i}{2i+1} \right) |b^-|^2 \quad 2.(xxx)$$

c) General Expression for Scattering length

Two general forms, one for coherent scattering length, and one for incoherent scattering length, may be obtained by combining the expressions for the spin independent and isotope independent cases discussed previously:

$$\bar{b} = \sum_M c_M \frac{1}{2i_M+1} \left((i_M+1)b_M^+ + i_M b_M^- \right) \quad 2.(xxxi)$$

from equations 2.(xxvii) and 2.(xxix)

$$\text{and } \overline{|b|^2} = \sum_M c_M \frac{1}{2i_M+1} \left((i_M+1)|b_M^+|^2 + i_M |b_M^-|^2 \right) \quad 2.(xxxii)$$

from equations 2.(xxviii) and 2.(xxx)

d) Consideration of the Cross-sections of Hydrogen

For hydrogen, $i = \frac{1}{2}$, $b^+ = 1.04 \times 10^{-14} \text{ m}$ and $b^- = -4.74 \times 10^{-14} \text{ m}$.

Hence from equation 2.(xxxi)

$$\bar{b} + \frac{3}{2} b^+ + \frac{1}{2} b^- = -0.375 \times 10^{-14} \text{ m}$$

and from equation 2.(xxxii)

$$\overline{|b|^2} = \frac{3}{2} |b^+|^2 + \frac{1}{2} |b^-|^2 = 6.49 \times 10^{-28} \text{ m}^2$$

TABLE 2.1 Cross-section Data for Various Isotopes (after Willis³⁾)

Atomic Number	Natural isotopic or elemental abundance in percent	$\sigma_{\text{coh}}^{\dagger}$ (barns)	$\sigma_{\text{incoh}}^{\dagger}$ (barns)
1	H(99.98) D(0.02)	1.8 5.6	79.7 2.0
4	Be	7.53	0.0
5	B	3.7	0.7
6	^{13}C C(1.1)	5.6 5.5	0.0 1.0
7	^{15}N N(0.4)	11.1 5.3	0.3
8	^{17}O ^{18}O (0.04) ^{18}O (0.2)	4.23 4.20 4.52	0.0
13	Al	1.50	0.0
14	Si	2.16	0.0
16	S	1.02	0.2
17	^{35}Cl ^{37}Cl (75.5) ^{37}Cl (24.5)	11.5 17.5 0.8	3.5
23	V	0.03	5.1
24	^{52}Cr Cr(83.8)	1.57 3.02	2.5
25	Mn	1.9	0.4
27	Co	0.79	5.2
29	Cu ^{63}Cu (69.1) ^{65}Cu (30.9)	7.3 5.6 15.5	1.2
35	Br	5.79	0.3
42	Mo	5.95	0.6
47	Ag ^{107}Ag (51.8) ^{109}Ag (48.2)	4.48 8.7 2.3	1.8 1.3 3.7
74	W ^{182}W (26.4) ^{183}W (14.4) ^{184}W (30.6) ^{186}W (28.4)	2.86 8.7 2.3 7.3 0.2	2.8
78	Pt	11.3	0.7

 $\dagger \quad 1 \text{ barn} = 10^{-24} \text{ m}^2$

But $\sigma_{\text{coh}} = 4\pi |\bar{b}|^2$ from the integration over 4π of equation 2.(xxv)

and $\sigma_{\text{incoh}} = 4\pi |\overline{b-\bar{b}}|^2$ from the integration over 4π of equation 2.(xxvi)

Therefore $\sigma_{\text{coh}} = 1.77 \times 10^{-28} \text{ m}^2$

and $\sigma_{\text{incoh}} = 79.83 \times 10^{-28} \text{ m}^2$

The value of the incoherent cross-section of hydrogen is larger than that of any other isotope by a factor of twenty (Table 2.1). It is therefore a good assumption in most hydrogenous systems (i.e. subject to concentration) that the total incoherent cross-section will be dominated by that of hydrogen.

5. Derivation of the Scattering Law

From equation 2.(xxi), the expression for the double differential cross-section in the case of scattering by an array of nuclei is:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E'} = \frac{k'}{k} \sum_{\lambda} P_{\lambda} \sum_{\lambda'} | \langle \lambda' | \sum_{\ell} b_{\ell} \exp(i \underline{Q} \cdot \underline{R}_{\ell}) | \lambda \rangle |^2 \delta(\hbar \omega + E_{\lambda} - E_{\lambda'})$$

Equations of the type shown above may be written in terms of the δ integral¹¹:

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp(-ixt) dt \quad 2.(xxxiii)$$

Therefore the δ function in 2.(xxi) may be expanded thus:

$$\delta(\hbar \omega + E_{\lambda} - E_{\lambda'}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt \exp\left(\frac{-it}{\hbar} (\hbar \omega + E_{\lambda} - E_{\lambda'})\right) \quad 2.(xxxiv)$$

Substituting 2.(xxxiv) in 2.(xxi) gives:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right) = \frac{k'}{k} \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt \exp\left(\frac{-it}{\hbar} (\hbar \omega + E_{\lambda} - E_{\lambda'})\right) \sum_{\lambda\lambda'} P_{\lambda} | \langle \lambda' | \sum_{\ell} b_{\ell} \exp(i \underline{Q} \cdot \underline{R}_{\ell}) | \lambda \rangle |^2$$

This may be expanded analogously to the previous example (equations 2.(xxi) et seq.) producing:

$$\left(\frac{\partial^2 \sigma}{\partial Q \partial E'}\right) = \frac{k'}{k} \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \sum_{\lambda\lambda'} P_{\lambda} < \lambda | \sum_{\ell} b_{\ell} \exp(iQ \cdot \underline{R}_{\ell}) | \lambda' >$$

$$x < \lambda' | \sum_{\ell'} b_{\ell'}^* \exp\left(\frac{i\hat{H}t}{\hbar}\right) \exp(-iQ \cdot \underline{R}_{\ell'}) \exp\left(\frac{-i\hat{H}t}{\hbar}\right) | \lambda >$$

2.(xxxv)

where $\hat{H}$ is the Hamiltonian operator of the target system

E_{λ} and $E_{\lambda'}$ are eigen values of the target system

The system above may be described in terms of time-dependent Heisenberg operators from the equation:

$$\frac{d\hat{R}_x(t)}{dt} = \hat{R}_x(t) \hat{H} - \hat{H} \hat{R}_x(t) \quad 2.(xxxvi)$$

$$= [\hat{R}_x(t), \hat{H}]$$

where $[,]$ denotes a commutative relationship
 $\hat{R}_x(t)$ is the time-dependent operator
 which is the solution to 2.(xxxvi)

Thus we define:

$$\exp(iQ \cdot \hat{R}_{\ell}(0)) = \exp\left(\frac{i\hat{H} \cdot 0}{\hbar}\right) \exp(iQ \cdot \underline{R}_{\ell}) \exp\left(\frac{-i\hat{H} \cdot 0}{\hbar}\right) \quad 2.(xxxvii)$$

$$\text{and } \exp(iQ \cdot \hat{R}_{\ell'}(t)) = \exp\left(\frac{i\hat{H}t}{\hbar}\right) \exp(iQ \cdot \underline{R}_{\ell'}) \exp\left(\frac{-i\hat{H}t}{\hbar}\right) \quad 2.(xxxviii)$$

The substitution of equations 2.(xxxvii) and 2.(xxxviii) into 2.(xxxv) and the summation over the final states which are a closed set yields:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E'} = \frac{k'}{k} \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \sum_{\ell\ell'} \overline{b_{\ell} b_{\ell'}^*} \langle\langle \exp(i\mathbf{Q} \cdot \hat{\mathbf{R}}_{\ell}(0)) \exp(-i\mathbf{Q} \cdot \hat{\mathbf{R}}_{\ell'}(t)) \rangle\rangle \quad 2.(xxxix)$$

where $\langle\langle \dots \rangle\rangle$ signifies the thermal average

$$\text{average} \sum_{\lambda} P_{\lambda} \langle \lambda | \dots | \lambda \rangle$$

Averaging over λ (probability P_{λ}) requires an average over the initial states of the nuclei which are present as a Boltzmann distribution:

$$P_{\lambda} = \frac{\exp\left(\frac{-E_{\lambda}}{K_B T}\right)}{Z}$$

where K_B is the Boltzmann constant

T is the temperature in K

Z is the partition function =

$$\text{Trace} \exp\left(\frac{-\hat{H}}{K_B T}\right) \quad \text{Where trace represents the sum of the diagonal elements of a matrix whose elements are of the form } \langle \lambda_i | \hat{H} | \lambda_j \rangle$$

The thermal average may therefore be stated as:

$$\langle\langle \dots \rangle\rangle = \sum_{\lambda} \left(\frac{\exp\left(\frac{-E_{\lambda}}{K_B T}\right)}{\text{Trace} \exp\left(\frac{-\hat{H}}{K_B T}\right)} \right) \langle \lambda | \dots | \lambda \rangle$$

If the value of b_{ℓ} is independent of ℓ , $\overline{b_{\ell} b_{\ell'}^*}$ may be taken outside the sum over ℓ and equation 2.(xxxix) may be formulated:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E'} = N \frac{k'}{k} \overline{b_{\ell} b_{\ell'}^*} S(\mathbf{Q}, \omega) \quad 2.(xi)$$

$$\text{where } S(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \sum_{\ell\ell'} \langle\langle \exp(i\mathbf{Q} \cdot \hat{\mathbf{R}}_{\ell}(0)) \exp(-i\mathbf{Q} \cdot \hat{\mathbf{R}}_{\ell'}(t)) \rangle\rangle \quad 2.(xli)$$

The above equation is suitable for all cases where there is only one chemical species present, or where the scattering of one species predominates

over all others. From previous discussion of the anomalously high incoherent cross-section of hydrogen, it may be seen that the latter condition may be applied to most hydrogenous systems.

The thermally averaged correlation function $S(\underline{Q}, \omega)$ defined above is known as the Scattering Law and allows description of dynamics of the scattering system in terms of the measurable parameters of momentum transfer ($\hbar \underline{Q}$) and energy transfer ($\hbar \omega$).

Analogously with equations 2.(xxv) and 2.(xxvi) may be written:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\text{coh}} = N \frac{k'}{k} |\bar{b}|^2 S_{\text{coh}}(\underline{Q}, \omega) \quad 2.(xlii)$$

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\text{incoh}} = N \frac{k'}{k} \overline{|b - \bar{b}|^2} S_{\text{incoh}}(\underline{Q}, \omega) \quad 2.(xliii)$$

$$\text{where } S_{\text{coh}}(\underline{Q}, \omega) = \frac{1}{2\pi \hbar N} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \sum_{\ell \ell'} \ll \exp(i\underline{Q} \cdot \hat{R}_{\ell}(0)) \exp(-i\underline{Q} \cdot \hat{R}_{\ell'}(t)) \gg \quad 2.(xliv)$$

$$S_{\text{incoh}}(\underline{Q}, \omega) = \frac{1}{2\pi \hbar N} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \sum_{\ell} \ll \exp(i\underline{Q} \cdot \hat{R}_{\ell}(0)) \exp(-i\underline{Q} \cdot \hat{R}_{\ell}(t)) \gg \quad 2.(xlv)$$

6. The Condition of Detailed Balance

A function $\tilde{S}(\underline{Q}, \omega)$ may be defined:¹

$$\tilde{S}(\underline{Q}, \omega) = \exp\left(\frac{\hbar \omega}{2K_B T}\right) S(\underline{Q}, \omega) \quad 2.(xlvii)$$

where $\hbar \omega$ is positive for neutron energy gain

so that the Scattering Law is made symmetrical. That is, in physical terms it is a representation of the fact that, whilst the probability of an up-scattering event (i.e. the neutron gaining energy $\hbar \omega$) is equal to that of a down-scattering event (i.e. the neutron losing energy $\hbar \omega$), the energy level populations capable of up-scattering are greater than those for down-scattering.

7. Correlation Functions

The physical dynamics of the scattering law may be more clearly visualised if $S(\underline{Q}, \omega)$ is thought of as the double Fourier Transform (over space and time) of the function $G(\underline{r}, t)^{1,3,8,11,13}$, the Pair Correlation Function:

$$S(\underline{Q}, \omega) = S_{\text{coh}}(\underline{Q}, \omega) = \frac{1}{2\pi\hbar N} \iint \exp(-i(\omega t - \underline{Q} \cdot \underline{r})) G(\underline{r}, t) d\underline{r} dt$$

$$\text{where } G(\underline{r}, t) = \left(\frac{1}{2\pi}\right)^3 \int d\underline{Q} \exp(i\underline{Q} \cdot \underline{r}) \frac{1}{N} \sum_{\ell\ell'} \ll \exp(i\underline{Q} \cdot \hat{R}_{\ell}(0)) \exp(-i\underline{Q} \cdot \hat{R}_{\ell'}(t)) \gg$$

2.(xlvii)

and a Fourier Transform may be generally defined:¹¹

$$\text{If } f(x_1, x_2, \dots, x_n) = \frac{1}{(2\pi)^n} \iint \dots \int F(y_1, y_2, \dots, y_n) \exp(+i(x_1 y_1 + x_2 y_2 + \dots + x_n y_n)) dy_1 \dots dy_n$$

$$\text{then } F(y_1, y_2, \dots, y_n) = \iint \dots \int f(x_1, x_2, \dots, x_n) \exp(-i(x_1 y_1 + x_2 y_2 + \dots + x_n y_n)) dx_1 \dots dx_n$$

Except when $t=0$, the two operators $\exp(i\underline{Q} \cdot \hat{R}_{\ell}(0))$ and $\exp(i\underline{Q} \cdot \hat{R}_{\ell'}(t))$ in equation 2.(xlvii) do not commute and their product may not be set equal to:

$$\exp(i\underline{Q} \cdot (\hat{R}_{\ell}(0) - \hat{R}_{\ell'}(t)))$$

However, since the term $\exp(i\underline{Q} \cdot \underline{r})$ commutes with the other operators, it may be included with the brackets representing the quantum mechanical averaging,^{2,13} yielding from equation 2.(xlvii):

$$G(\underline{r}, t) = \frac{1}{N} \sum_{\ell\ell'} \ll \left(\frac{1}{2\pi}\right)^3 \int d\underline{Q} \exp(i\underline{Q} \cdot \underline{r}) \exp(i\underline{Q} \cdot \hat{R}_{\ell}(0)) \exp(-i\underline{Q} \cdot \hat{R}_{\ell'}(t)) \gg \quad 2.(xlvii)a$$

Furthermore, it is a property of Fourier Transforms that the transform of a product may be written as a convolution of the transforms². Employing the three-dimensional δ function:

$$\delta(\underline{Q}' - \underline{Q}) = \left(\frac{1}{2\pi}\right)^3 \int d\underline{r}' \exp i(\underline{Q}' - \underline{Q}) \cdot \underline{r}'$$

as a Fourier integral produces from above²:

$$G(\underline{r}, t) = \frac{1}{N} \sum_{\ell\ell'} \ll \left(\frac{1}{2\pi}\right)^3 \int d\underline{Q} \int d\underline{Q}' \delta(\underline{Q}' - \underline{Q}) \exp(i\underline{Q} \cdot \underline{r}) \exp(i\underline{Q} \cdot \hat{R}_{\ell}(0)) \exp(-i\underline{Q}' \cdot \hat{R}_{\ell'}(t))$$

2.(xlvii)b

Expanding the Delta function and re-arranging then gives:

$$G(\underline{r}, t) = \frac{1}{N} \sum_{\ell \ell'} \ll \left(\frac{1}{2\pi} \right)^6 \int d\underline{Q} \int d\underline{Q}' \int d\underline{r}' \exp(i\underline{Q}(\underline{r}-\underline{r}')) \exp(i\underline{Q}' \underline{R}_{\ell}(o)) \exp(i\underline{Q}' \underline{r}') \exp(-i\underline{Q}' \hat{R}_{\ell'}(t)) \gg \quad 2.(xlvii)c$$

or^{1,8,13}

$$G(\underline{r}, t) = \frac{1}{N} \sum_{\ell \ell'} \int d\underline{r}' \ll \delta(\underline{r}-\underline{r}'+\hat{R}_{\ell}(o)) \delta(\underline{r}'-\hat{R}_{\ell'}(t)) \gg \quad 2.(xlviii)$$

Because the operators do not commute, the physical representation of the function is obscure and may only be readily seen when the classical limit is considered. In this case, all the nuclei are equivalent and the average may be discarded. Furthermore the δ functions may be combined and so equation 2.(xlviii) becomes^{1,8,13}:

$$G^{cl}(\underline{r}, t) = \langle \delta(\underline{r}-\underline{R}_{\ell}(t)+\underline{R}_{or}(o)) \rangle$$

where the subscript "or" refers to a nucleus ℓ placed at the origin

The Pair Correlation Function therefore represents the probability that if a nucleus is at the origin at time $t=0$, then some nucleus (including the possibility of the same one) will be a position $\underline{r}$ at time $t=t$.

Just as the Scattering Law may be divided into $S_{coh}(\underline{Q}, \omega)$ and $S_{incoh}(\underline{Q}, \omega)$ (equations 2.(xliv) and 2.(xlv)), so may the expression $G(\underline{r}, t)$. Therefore analogously to equation 2.(xlviii), the Self-Pair Correlation Function, $G_s(\underline{r}, t)$ may be defined:

$$G_s(\underline{r}, t) = \frac{1}{N} \sum_{\ell} \int d\underline{r}' \ll \delta(\underline{r}-\underline{r}'+\hat{R}_{\ell}(o)) \delta(\underline{r}'-\hat{R}_{\ell}(t)) \gg \quad 2.(xlix)$$

describing the case where $\ell=\ell'$, and which on Fourier Transformation yields

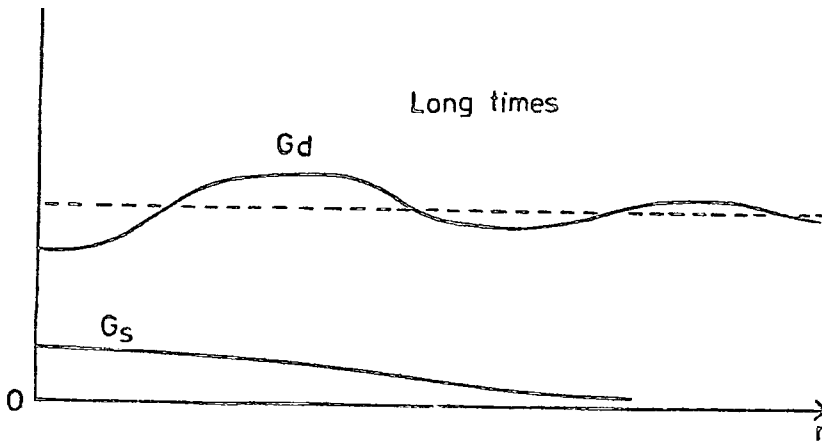
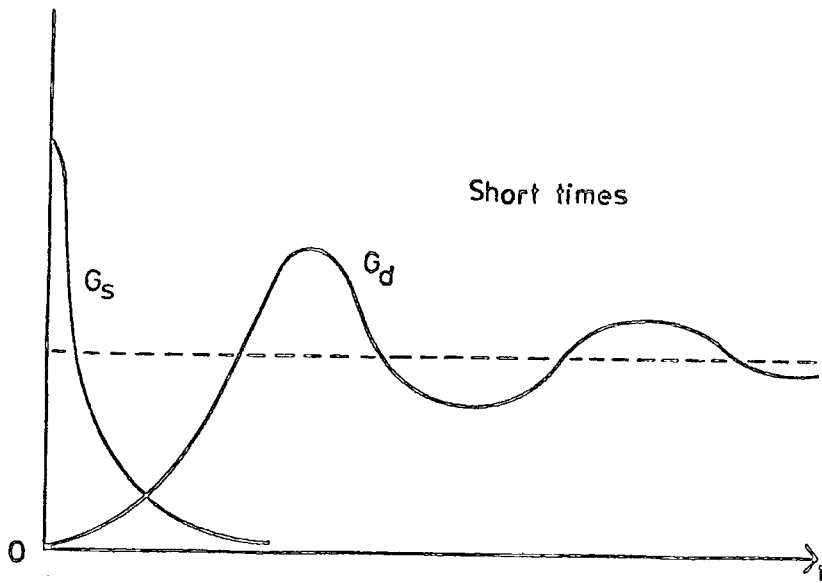
$$S_{incoh}(\underline{Q}, \omega).$$

Again considering the classical limit, the above expression becomes^{1,8,13}:

$$G_s^{cl}(\underline{r}, t) = \langle \delta(\underline{r}-\underline{R}_{or}(t)+\underline{R}_{or}(o)) \rangle$$

which is the probability that if a particular atom is at the origin at time

The Correlation Functions $G_d(\underline{r}, t)$ and $G_s(\underline{r}, t)$
Plotted in the Limiting Cases of Short and Long Times



$t=0$, then the same atom will be at a position $\underline{r}$ at time $t=t$.

In general, at time $t=0$, the operators in equation 2.(xlviii) commute and the equation simplifies to^{1,8}:

$$G(\underline{r}, 0) = \delta(\underline{r}) + \sum_{\ell' \neq \ell} \langle\langle \delta(\underline{r} - \hat{R}_{\ell'} + \hat{R}_{\ell}) \rangle\rangle \quad 2.(1)$$

where $\delta(\underline{r})$ arises from the specific case of $\ell = \ell'$

Similarly at time $t=0$, equation 2.(xlix) may be written^{1,8}:

$$G_s(\underline{r}, 0) = \delta(\underline{r}) \quad 2.(1i)$$

Comparing equations 2.(1) and 2.(li), it may be seen therefore that the Pair Correlation Function is a sum of the Self-Pair Correlation Function, and of another function which may be represented as $G_d(\underline{r}, t)$ and is called the Static (Distinct) Pair Correlation Function:

$$G_d^{cl}(\underline{r}, t) = \sum_{\ell \neq \text{or}} \langle \delta(\underline{r} - \underline{R}_\ell(t) + \underline{R}_{\text{or}}(0)) \rangle \quad 2.(lii)$$

Thus the Static Pair Correlation Function is a statement of the probability that if a particle is at the origin at time $t=0$, then a different particle will be at a position $\underline{r}$ at time $t=t$.

8. Scattering from Molecules

The expression for the Scattering Law (equation 2.(xli)):

$$S(\underline{Q}, \omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \sum_{\ell\ell'} \langle \exp(-i\underline{Q} \cdot \hat{\underline{R}}_\ell(0)) \exp(i\underline{Q} \cdot \hat{\underline{R}}_{\ell'}(t)) \rangle \quad 2.(liii)$$

is in the form of time-dependent Heisenberg operators, $\hat{\underline{R}}_\ell(t)$, which are functions of $\underline{R}_\ell$, the position vector of the ℓ^{th} scattering nucleus. When considering scattering from a molecule a more sophisticated position vector is required to take into account the orientation of $\underline{R}_\ell$ in space¹⁴. The vector $\underline{R}_\ell$, for a fixed nucleus, is therefore expanded as:

$$\underline{R}_\ell = \underline{c}_\ell + \underline{b}_\ell + \underline{u}_\ell \quad 2.(liv)$$

where $\underline{c}_\ell$ is the centre of mass position vector of the molecule containing the ℓ^{th} atom.

$\underline{b}_\ell$ is the equilibrium position vector of the scattering atom relative to the centre of mass.

$\underline{u}_\ell$ is the displacement vector of the atom from the mean.

In order to represent the free rotation of the molecule about the centre of mass, it is necessary further to expand both $\underline{b}_\ell$ and $\underline{u}_\ell$ as functions of Ω , the molecular orientation.

By Definition:⁸

$$\underline{b}_\ell = b_\ell \underline{I}_\ell(\Omega) - \text{dimensions of length} \quad 2.(lv)$$

where $b_\ell = |\underline{b}_\ell|$ is the mean distance from the centre of mass (Dimension = L)

$\underline{I}_\ell(\Omega)$ is a unit vector (Dimensionless - directional only)

Ω is the set of Euler angles fixing the orientation of the molecule

$$\underline{u}_\ell = \sum_\lambda \underline{a}_\ell^\lambda(\Omega) c_\ell^\lambda q_\lambda(t) - \text{dimension of length} \quad 2.(lvi)$$

where $\underline{a}_\ell^\lambda(\Omega)$ is a unit vector (Dimensionless - conveys sense of direction only)

c_ℓ^λ is an amplitude (Dimension = $M^{-\frac{1}{2}}$)

$q_\lambda(t)$ is a normal coordinate (Dimensions = $M^{\frac{1}{2}}L$) (From Cyvin¹⁵, it can be shown

that, for a harmonic oscillator,

$$\langle\langle q^2 \rangle\rangle = \frac{\hbar}{2\omega} \coth \frac{\hbar\omega}{2K_B T}$$

λ is an index denoting a normal mode ($\lambda = 1, 2, \dots, 3N - 6$ (or $3N - 5$ for a linear molecule), where N is the number of atoms comprising the molecule)

M is the mass of scattering atom

Each $\underline{c}_\ell$, $\underline{b}_\ell$ and $\underline{u}_\ell$ is time-dependent and may be written in Heisenberg representation in the thermal average similarly to $\underline{R}_\ell$ in equation 2(xli):

$$S(\underline{Q}, \omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \sum_{\ell\ell'} \sum_n P_n \langle \psi_n | \exp\{-i\underline{Q} \cdot (\hat{c}_\ell(o) + \hat{b}_\ell(o) + \hat{u}_\ell(o))\} \times$$

$$\times \exp\{-i\underline{Q} \cdot (\hat{c}_{\ell'}(t) + \hat{b}_{\ell'}(t) + \hat{u}_{\ell'}(t))\} | \psi_n \rangle \quad 2.(lvii)$$

Now from their definitions, it may be seen that $\underline{c}_\ell$ represents translational motion, $\underline{b}_\ell$ overall molecular rotations and vibrations, and $\underline{u}_\ell$ internal vibrations of the molecule.

If Heisenberg operators commute with each other, they may be considered independent. Considering equation 2.(lvii), the operator $\hat{c}_\ell(t)$ does commute with all the others and may be separately averaged as:

$$\langle\langle \exp(-i\underline{Q} \cdot \hat{c}_\ell(0)) \exp(i\underline{Q} \cdot \hat{c}_\ell(t)) \rangle\rangle$$

However, the operators $\hat{b}_\ell(t)$ and $\hat{u}_\ell(t)$ do not commute as a result of their mutual dependence on Ω . Therefore the operator averages of $\hat{b}_\ell(t)$ and $\hat{u}_\ell(t)$ may not strictly be separated, and this represents the fact that the displacement vectors $\underline{u}_\ell$ may rotate, as a result of molecular motion, during the finite time of the scattering event.

In order to circumvent this problem, it must be assumed, as a first approximation, that the operators $\hat{u}_\ell(t)$ and $\hat{b}_\ell(t)$ do commute and therefore can be separately averaged⁸. However the corollary of this approximation is that experimental studies of vibrational structure will always include rotational terms, assuming the molecule is able to undergo the latter process.

Therefore $S(\underline{Q}, \omega)$ may be written from equations 2.(xli) and 2.(lvii)

$$S(\underline{Q}, \omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \sum_{\ell, \ell'} \langle\langle \exp(-i\underline{Q} \cdot \hat{c}_\ell(0)) \exp(i\underline{Q} \cdot \hat{c}_{\ell'}(t)) \rangle\rangle$$

$$\langle\langle \exp(-i\underline{Q} \cdot \hat{b}_\ell(0)) \exp(i\underline{Q} \cdot \hat{b}_{\ell'}(t)) \rangle\rangle$$

$$\langle\langle \exp(-i\underline{Q} \cdot \hat{u}_\ell(0)) \exp(i\underline{Q} \cdot \hat{u}_{\ell'}(t)) \rangle\rangle \quad 2.(lviii)$$

The Fourier Transform of a product is a convolution¹¹ and therefore the above equation may be stated:

$$S(\underline{Q}, \omega) = \frac{1}{2\pi\hbar N} S_{\text{trans}}(\underline{Q}, \omega) \otimes S_{\text{rot}}(\underline{Q}, \omega) \otimes S_{\text{vib}}(\underline{Q}, \omega)$$

where $\otimes$ denotes a convolution which may be defined:¹¹

$$H(x) = f(x_1) \otimes g(x_1) = \int_{-\infty}^{+\infty} f(x_1) g(x-x_1) dx_1$$

$$\text{e.g. } S(\underline{Q}, \omega) = \int S_{\text{trans}}(\underline{Q}, \omega') S_{\text{rot}}(\underline{Q}, \omega - \omega') d\omega'$$

9. The Scattering Law for Vibrations

As the vibrational contribution to the total scattering can be separated

from those of rotation and translation to a good approximation (see previous discussion), the problem may be discussed in terms of the thermal average:

$$\langle\langle \chi_{\ell\ell'} \rangle\rangle = \langle\langle \exp(-i\mathbf{Q} \cdot \hat{\mathbf{u}}_{\ell}(0)) \exp(i\mathbf{Q} \cdot \hat{\mathbf{u}}_{\ell}(t)) \rangle\rangle \quad 2.(lix)$$

Following Zemach and Glauber¹⁶, the displacement vector of the ℓ^{th} nucleus ($\underline{u}_{\ell}$) from its equilibrium position ($\underline{b}_{\ell}$) may be defined (taking the molecular centre of mass as the origin) so that (cf. equation 2.(lvi)):

$$\underline{u}_{\ell}(t) = \sum_{\lambda} \underline{c}_{\ell}^{\lambda} q_{\lambda}(t) \quad 2.(lx)$$

where $\underline{c}_{\ell}^{\lambda}$ is the amplitude vector of the ℓ^{th}
atom in the λ^{th} normal mode
(Dimension of $M^{-\frac{1}{2}}$)

The normal modes are dynamically independent, therefore it is possible to separate their effects on the scattering. Furthermore, normal coordinates of different modes commute with one another, and thus the exponential functions of $\hat{\mathbf{u}}_{\ell}(t)$ may be written as products of exponentials, one for each mode:

$$\begin{aligned} \exp(i\mathbf{Q} \cdot \hat{\mathbf{u}}_{\ell}(t)) &= \exp(i\mathbf{Q} \cdot \sum_{\lambda} \underline{c}_{\ell}^{\lambda} q_{\lambda}(t)) \\ &= \exp\{i(\mathbf{Q} \cdot \underline{c}_{\ell}^{\lambda} q_{\lambda}(t) + \dots)\} \\ &= \prod_{\lambda} \exp(i\mathbf{Q} \cdot \underline{c}_{\ell}^{\lambda} q_{\lambda}(t)) \end{aligned} \quad 2.(lxi)$$

Expressing the thermal distribution for the whole molecule as a product of factors, one for each mode, results in:

$$\begin{aligned} \langle\langle \chi_{\ell\ell'} \rangle\rangle &= \prod_{\lambda} \langle\langle \chi_{\ell\ell'}^{\lambda} \rangle\rangle \\ &= \prod_{\lambda} \langle\langle \exp(i\mathbf{Q} \cdot \underline{c}_{\ell}^{\lambda} q_{\lambda}(t)) \exp(-i\mathbf{Q} \cdot \underline{c}_{\ell}^{\lambda} q_{\lambda}(0)) \rangle\rangle \end{aligned} \quad 2.(lxii)$$

As averages take the same form for each normal mode, the index λ will be dropped and the subsequent expressions will apply to one particular mode.

A normal coordinate $q(t)$ (equation 2.(lx)) may be defined as the coordinate of a one-dimensional harmonic oscillator with mass M (which will be taken as equal to unity) and angular frequency ω :

$$q(t) = i\left(\frac{2\omega}{\hbar}\right)^{-\frac{1}{2}} (\hat{a} \exp(-i\omega t) - \hat{a}^+ \exp(i\omega t)) \quad 2.(1xiii)$$

where $\hat{a}$ and $\hat{a}^+$ are the time-independent operators which cause the oscillator eigen functions to give the eigen functions of the next lowest/highest state. They have the following properties:

$$[a, a^+] = I \text{ and}$$

$$[a, a] = [a^+, a^+] = 0$$

Using the rule $\exp \hat{A} \exp \hat{B} = \exp(\hat{A} + \hat{B} + \frac{1}{2}[\hat{A}, \hat{B}])$,¹

each normal mode may be written as single exponential functions whose arguments are displaced oscillator coordinates:

$$\begin{aligned} \langle\langle \chi_{\ell\ell'} \rangle\rangle &= \langle\langle \exp(i\underline{Q}_{\ell} \cdot \underline{c}_{\ell} q(t)) \exp(-i\underline{Q}_{\ell'} \cdot \underline{c}_{\ell'} q(o)) \rangle\rangle \\ &= \langle\langle \exp\{i(\underline{Q}_{\ell} \cdot \underline{c}_{\ell} q(t) - \underline{Q}_{\ell'} \cdot \underline{c}_{\ell'} q(o))\} \exp\{\frac{1}{2}(\underline{Q}_{\ell} \cdot \underline{c}_{\ell})(\underline{Q}_{\ell'} \cdot \underline{c}_{\ell'})[q(t), q(o)]\} \rangle\rangle \end{aligned} \quad 2.(1xiv)$$

The average above may be evaluated by a modified form of Bloch's theorem,^{16,17} whereby if M is any multiple of an oscillator coordinate or a linear combination of them:

$$\langle\langle \exp M \rangle\rangle = \exp(\frac{1}{2} \langle\langle M^2 \rangle\rangle)$$

Equation 2.(1xiv) therefore becomes

$$\begin{aligned} \langle\langle \chi_{\ell\ell'} \rangle\rangle &= \exp\{-\frac{1}{2}(\underline{Q}_{\ell} \cdot \underline{c}_{\ell})^2 + (\underline{Q}_{\ell} \cdot \underline{c}_{\ell'})^2\} \langle\langle q^2(o) \rangle\rangle \\ &\quad + (\underline{Q}_{\ell} \cdot \underline{c}_{\ell})(\underline{Q}_{\ell'} \cdot \underline{c}_{\ell'}) \langle\langle q(t)q(o) \rangle\rangle \end{aligned} \quad 2.(1xv)$$

where the expectation values of $q^2(t)$ equal those of $q^2(0)$.

The term $\langle\langle q(t)q(o) \rangle\rangle$ may be expanded according to equation 2.(1xiii) and

the commutation rules applied to give:

$$\begin{aligned} \langle\langle q(t)q(0) \rangle\rangle &= \left(\frac{2\omega}{\hbar}\right)^{-1} (\langle\langle \hat{a}\hat{a}^+ \rangle\rangle \exp(-i\omega t) + \langle\langle \hat{a}^+\hat{a} \rangle\rangle \exp(i\omega t)) \\ &= \left(\frac{2\omega}{\hbar}\right)^{-1} ((\langle\langle n \rangle\rangle + 1)\exp(-i\omega t) + \langle\langle n \rangle\rangle \exp(i\omega t)) \quad 2.(lxvi) \end{aligned}$$

$$\text{where } \langle\langle n \rangle\rangle = \langle\langle \hat{a}^+\hat{a} \rangle\rangle$$

$$\langle\langle n \rangle\rangle + 1 = \langle\langle \hat{a}\hat{a}^+ \rangle\rangle$$

$\langle\langle n \rangle\rangle$ is thermally averaged excitation
quantum number of the oscillator

Now $\langle\langle n \rangle\rangle$ may be written in terms of a function representing the
occupancy number of the energy level under consideration:

$$\langle\langle n \rangle\rangle = (Z-1)^{-1}$$

$$\text{where } Z \text{ equals } \exp\left(\frac{\hbar\omega}{K_B T}\right)$$

Equation 2.(lxvi) therefore becomes:

$$\langle\langle q(t)q(0) \rangle\rangle = \left(\frac{2\omega(Z-1)}{\hbar}\right)^{-1} (Z \exp(-i\omega t) + \exp(i\omega t)) \quad 2.(lxvii)$$

$$\text{and similarly } \langle\langle q^2(0) \rangle\rangle = \langle\langle q(0)q(0) \rangle\rangle = \left(\frac{2\omega(Z-1)}{\hbar}\right)^{-1} (Z+1) \quad 2.(lxviii)$$

Substituting equations 2.(lxvii), 2.(lxviii) into equation 2.(lxv) yields:

$$\begin{aligned} \langle\langle \chi_{\ell\ell} \rangle\rangle &= \exp\left\{-\frac{1}{2}((Q.c_{\ell})^2 + (Q.c_{\ell}')^2)\right. \\ &\quad \times \frac{\hbar(Z+1)}{2\omega(Z-1)} \left. \exp\{(Q.c_{\ell})(Q.c_{\ell}')\} \right. \\ &\quad \times \left. \frac{\hbar Z^{\frac{1}{2}}(Z^{\frac{1}{2}} \exp(-i\omega t) + Z^{-\frac{1}{2}} \exp(i\omega t))}{2\omega(Z-1)} \right\} \quad 2.(lxix) \end{aligned}$$

Equation 2.(lxix) may be rewritten by substituting for the second
of the two exponential factors a modified Bessel function^{16,18} of the form:

$$\exp\left(\frac{x}{2}\left(y + \frac{1}{y}\right)\right) = \sum_{n=-\infty}^{\infty} y^n I_n(x)$$

where $I_n(x)$ is the n^{th} order modified Bessel
function of the first kind i.e.

$$I_n(x) = \sum_{a=0}^{\infty} \frac{(-1)^a (x/2)^{b+2a}}{a!(b+a)!}$$

If in the Bessel function:

$$y = \exp(i\omega t) Z^{-\frac{1}{2}}$$

$$\frac{x}{2} = \exp\left(\frac{(Q \cdot c_{\ell})^2 Z^{\frac{1}{2}}}{2\omega(Z-1)}\right)$$

and the relations:

$$\frac{(Z+1)}{(Z-1)} = \frac{\exp(\hbar\omega/K_B T)}{\exp(\hbar\omega/K_B T)} = \tanh\left(\frac{\hbar\omega}{2K_B T}\right)^{-1} = \coth\left(\frac{\hbar\omega}{2K_B T}\right)$$

$$\frac{1}{(Z-1)} = \frac{\exp(-\hbar\omega/2K_B T)}{\exp(\hbar\omega/2K_B T) - \exp(-\hbar\omega/2K_B T)} = \frac{\exp(-\hbar\omega/2K_B T)}{2 \sinh(\hbar\omega/2K_B T)}$$

are employed then equation 2(lxix) may be stated:

$$\langle\langle x_{\ell\ell'} \rangle\rangle = \exp\left\{-\frac{((Q \cdot c_{\ell})^2 + (Q \cdot c_{\ell'})^2)\hbar}{4\omega} \coth\left(\frac{\hbar\omega}{2K_B T}\right)\right\}$$

$$\times \sum_{n=-\infty}^{\infty} \exp(in\omega t) \exp\left(\frac{-n\hbar\omega}{K_B T}\right) I_n\left(\frac{(Q \cdot c_{\ell})(Q \cdot c_{\ell'})\hbar}{2\omega \sinh(\hbar\omega/2K_B T)}\right) \quad 2(lxx)$$

The general form for all normal modes, substituting the above into equation 2(xxxix) and using the δ function relation discussed previously (equation 2(xxxiii)), may therefore be expressed:

$$\frac{\delta^2 \sigma}{\delta Q \delta E'} = \frac{k'}{k} \sum_{\ell\ell'} \overline{b_{\ell}^* b_{\ell'}} \exp(-iQ \cdot (b_{\ell} - b_{\ell'}))$$

$$\times \prod_{\lambda} \left[\exp\left\{-\frac{((Q \cdot c_{\ell}^{\lambda})^2 + (Q \cdot c_{\ell'}^{\lambda})^2)\hbar}{4\omega_{\lambda}} \coth\left(\frac{\hbar\omega_{\lambda}}{2K_B T}\right)\right\}\right]$$

$$\times \exp\left(\frac{-n_{\lambda} \hbar\omega_{\lambda}}{2K_B T}\right) I_{n_{\lambda}}\left(\frac{(Q \cdot c_{\ell}^{\lambda})(Q \cdot c_{\ell'}^{\lambda})\hbar}{2\omega_{\lambda} \sinh(\hbar\omega_{\lambda}/2K_B T)}\right) \delta(\hbar\omega - \hbar \sum_{\lambda} n_{\lambda} \omega_{\lambda}) \quad 2(lxxi)$$

where n_{λ} is the number of quanta of energy transferred for the λ th normal mode

From the above it will be seen that each normal mode gives rise to an energy delta function at its characteristic frequency.

Experimentally, the argument of the Bessel function is found to be small, and as a result the function may be approximated by the first term in its power series expansion:

$$I_n(x) \sim \left(\frac{x}{2}\right)^{|n|} (|n|!)^{-1}$$

Thus equation 2.(lxxi) may be written, for the case of incoherent inelastic scattering ($\ell = \ell'$):

$$\begin{aligned} \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\text{incoh}} &= \frac{k'}{k} \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \\ &\times \sqrt[n_{\lambda}]{} \left[\exp\left(\frac{-(Q \cdot c_{\ell}^{\lambda})^2 \hbar}{2\omega_{\lambda}} \coth\left(\frac{\hbar\omega_{\lambda}}{2K_B T} \right) \right) (|n_{\lambda}|!)^{-1} \right. \\ &\times \exp\left(\frac{-n_{\lambda} \hbar\omega_{\lambda}}{2K_B T} \right) \left(\frac{(Q \cdot c_{\ell}^{\lambda})^2 \hbar}{4\omega_{\lambda} \sinh(\hbar\omega_{\lambda}/2K_B T)} \right) |n_{\lambda}| \\ &\left. \times \delta(\hbar\omega - \hbar \sum_{\lambda} n_{\lambda} \omega_{\lambda}) \right] \end{aligned} \quad 2.(lxxii)$$

and for the case of incoherent elastic scattering ($n_{\lambda} = 0$):

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\substack{\text{incoh} \\ \text{elastic}}} = \frac{k'}{k} \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \exp(-2W_{\ell})$$

where W_{ℓ} is called the Debye-Waller factor:

$$W_{\ell} = \frac{1}{2} \sum_{\lambda} \frac{(Q \cdot c_{\ell}^{\lambda})^2 \hbar}{\omega_{\lambda}} \coth\left(\frac{\hbar\omega_{\lambda}}{2K_B T} \right) \quad 2.(lxxiii)$$

a) Elastic Scattering

Equation 2.(lxxiii) shows that the intensity of incoherent elastic scattering from a simple harmonic oscillator is proportional to the incoherent cross-section attenuated by the Debye-Waller factor which arises from interference effects between atoms on different sites being smoothed out by thermal vibrations^{3,8}. As would be expected therefore, the influence of temperature is such that intensity will decrease (and the band broaden), as temperature increases.

The other factors to which the Debye-Waller factor is proportional, i.e. ' Q ' and ' c_{ℓ}^{λ} ', may best be considered with reference to the expression stated previously (Cyvin¹⁵ and from Zemach and Glauber¹⁶) that:

$$\langle\langle q_{\lambda}^2 \rangle\rangle = \frac{\hbar}{2\omega_{\lambda}} \coth\left(\frac{\hbar\omega_{\lambda}}{2K_B T} \right) \quad 2.(lxxiv)$$

Comparing this with equation 2.(lxxiii), it may be seen that

$$-2W_{\ell} = (\underline{Q} \cdot \underline{c}_{\ell}^{\lambda})^2 \ll q_{\lambda}^2 \gg$$

and terms $\underline{c}_{\ell}^{\lambda}$ and q_{λ} may be multiplied together to give an expression similar to equation 2.(lx):

$$(\underline{Q} \cdot \underline{c}_{\ell}^{\lambda})^2 \ll q_{\lambda}^2 \gg = \ll (\underline{Q} \cdot \underline{u}_{\ell}^{\lambda})^2 \gg \quad 2.(lxxv)$$

For a monatomic cubic crystal in particular, and as a good approximation in general,^{1,3} it can be said that:

$$\sum_{\lambda} (\underline{Q} \cdot \underline{u}_{\ell}^{\lambda})^2 = \frac{Q^2 \langle u^2 \rangle}{3} \quad 2.(lxxvi)$$

where $\langle u^2 \rangle$ is the mean-square amplitude of

vibration of the scattering atom.

and therefore substitution of this expression into equation 2.(lxxiii) yields:

$$W_{\ell} = \frac{Q^2 \langle u^2 \rangle}{6} \quad 2.(lxxvii)$$

Thus for a given frequency and temperature, the Debye-Waller factor is proportional to the product of the Scattering Vector squared and the mean-square amplitude of vibration.

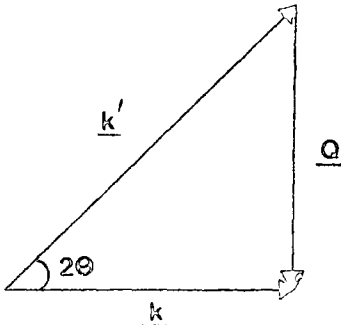
The influence of ' $\underline{Q}$ ' may be more readily seen from the relation between the incident ($\underline{k}$) and scattered ($\underline{k}'$) wave vectors which is shown below. The magnitude of $\underline{Q}$ will be given by:

$$Q^2 = k^2 + k'^2 - 2kk' \cos(2\theta)$$

For elastic scattering $\underline{k}' = \underline{k}$ and therefore

$$Q^2 = 2k^2 (1 - \cos(2\theta))$$

$$Q = 2k \sin \theta$$



Obviously as θ increases, the value of Q will increase and therefore intensity will decrease.

Considering the $\langle u^2 \rangle$ factor, it may be seen that scattering intensity will decrease as the mean-square amplitude of vibration increases.

b) Inelastic Scattering

For incoherent inelastic scattering (equation 2.(lxxii)) additional factors may be seen to affect intensity, i.e.:

$$\exp\left(\frac{-n_\lambda \hbar \omega_\lambda}{2K_B T}\right) \left(\frac{(Q \cdot c_\ell^\lambda)^2 \hbar}{4\omega_\lambda \sinh(\hbar \omega / 2K_B T)} \right) |n_\lambda|$$

The term written to the power $|n_\lambda|$ is usually small, and in consequence single quantum scattering ($n_\lambda = \pm 1$) is found to have a very much greater intensity than multiple quantum events. (It should be noted, however, that in the case of instruments capable of large ' Q ' transfers, e.g. BFD spectrometers, the magnitude of the term may be increased sufficiently to enable overtones to be seen quite clearly.) Similarly, the simultaneous transfer of single quanta to n normal modes (i.e. combination bands) will again raise the second term to the n th power as a result of the product term, $\prod_\lambda$ (see equation 2.(lxxiii)).

The double differential cross-section, when written in terms of single quantum events, thus becomes⁸:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\text{single quantum incoh}} = \frac{k'}{k} \sum_\ell \overline{|b_\ell - \bar{b}|^2} \exp(-2W_\ell) \frac{A_\lambda}{(1-A_\lambda)} \frac{(Q \cdot c_\ell^\lambda)^2 \hbar}{2\omega_\lambda} \delta(\hbar \omega - \hbar \omega_\lambda) \quad 2(\text{lxxviii})$$

$$\text{where } A_\lambda = \exp\left(\frac{-\hbar \omega_\lambda}{2K_B T}\right)$$

Employing the relation (equation 2.(lxxiv))

$$\langle\langle q_\lambda^2 \rangle\rangle = \frac{\hbar}{2\omega_\lambda} \coth\left(\frac{\hbar \omega_\lambda}{2K_B T}\right)$$

to substitute for that part of equation 2.(lxxviii) which reads:

$$\frac{(Q.c_{\ell}^{\lambda})^2 \hbar}{2\omega_{\lambda}}$$

produces:

$$\frac{(Q.c_{\ell}^{\lambda})^2 \ll q_{\lambda}^2 \gg}{\coth(\hbar\omega_{\lambda}/2K_B T)}$$

Using the argument developed previously (equation 2.(lxxv) et seq.), this may be restated as:

$$\frac{Q^2 \langle u^2 \rangle}{3 \coth(\hbar\omega_{\lambda}/2K_B T)}$$

Hence substitution of this expression back into equation 2.(lxxviii) yields:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\text{single quantum incoherent}} = \frac{k'}{k} \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \exp(-2W_{\ell}) \frac{A_{\lambda}}{(1-A_{\lambda})} \frac{Q^2 \langle u^2 \rangle}{3 \coth(\hbar\omega_{\lambda}/2K_B T)} \delta(\hbar\omega - \hbar\omega_{\lambda}) \quad 2.(lxxix)$$

It may be assumed to a good approximation that $\coth\left(\frac{\hbar\omega_{\lambda}}{2K_B T}\right)$ is equal to unity for the example of Beryllium Filter Detector Spectroscopy, where typically $\omega_{\lambda \min}$ is 70cm^{-1} and T is ca. 15K. Hence the above reduces to:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\text{single quantum incoherent}} = \frac{k'}{k} \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \exp(-2W_{\ell}) \frac{A_{\lambda}}{1-A_{\lambda}} \frac{Q^2 \langle u^2 \rangle}{3} \delta(\hbar\omega - \hbar\omega_{\lambda}) \quad 2.(lxxx)$$

However, when considering Time-of-Flight instruments, where $\omega_{\lambda \min}$ may be as low as 10cm^{-1} and T can be anything between 90 and 300K (Chapter III), the 'coth term' can be most significant and must be stated explicitly.

Thus for incoherent inelastic scattering, intensity is directly proportional to the Scattering Vector squared and the mean-square amplitude of vibration, as well as being controlled by the incoherent cross-section and Debye-Waller.

10. The Density of States

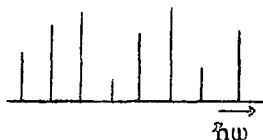
The normalised density of states $Z(\omega)$ may be defined^{1,3}:

$$Z(\omega) = \frac{1}{3N} \sum_{\lambda} \delta(\omega - \omega_{\lambda})$$

where $3N$ refers to the total number of
vibrations

$$\int_{-\infty}^{+\infty} Z(\omega) d\omega = 1$$

This function ($Z(\omega)$) may be pictured as a series of delta-like functions, each of which corresponds to a given normal mode, and whose height represents the degeneracy of the mode, e.g.



If the expression for the density of states is substituted into equation 2(lxxix), the expression becomes:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\text{single quantum incoherent}} = N \frac{k'}{k} \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \exp(-2W_{\ell}) \frac{A_{\lambda}}{1-A_{\lambda}} \frac{Q^2 \langle u^2 \rangle}{\coth(\hbar\omega_{\lambda}/2K_B T)} Z(\omega) \quad 2(lxxxi)$$

11. The Influence of Momentum Transfer Upon INS Spectra

For a dispersive mode, $d\omega/dk$ (hence $d\omega/dQ$) is not equal to a constant. In consequence, it would be anticipated that in T-O-F inelastic neutron spectroscopy, where there is a wide range of momentum transfer ($\hbar Q$), there will be variation of intensity and peak position. As ' Q ' varies with angle of observation (see previously), the spectra obtained for each angle will be expected to differ.

In addition, Kittel¹⁹ has shown that for one dimension:

$$Z(\omega) d\omega = \frac{\omega(Q)}{d\omega/dQ} d\omega \quad \text{i.e. } Z(\omega) \propto (d\omega/dQ)^{-1} \text{ at constant } Q$$

$$\text{but } \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right) \propto Z(\omega) \quad \text{from equation 2(lxxxi)}$$

and therefore it may be seen that intensity will vary across each spectrum according to the gradient of the dispersion curve ($d\omega/dQ$) at each point along the energy axis.

Dispersive modes are those with small force constants, and in general, they correspond to intermolecular vibrations. Hence momentum transfer dependence of the above type is often an indication of lattice modes.

12. Theoretical Considerations Applied to Time-of-Flight Spectrometry

a) Functions used in the analysis of data

The corrected counts from Time-of-Flight experiments are written by the Circa programme (Chapter III) into the form of:

(i) The Symmetric Scattering Law $S(\alpha, \beta)$:^{20,21,22}

$$S(\alpha, \beta) = \frac{K_B T}{\exp(-\beta/2)} S(Q, \omega) = K_B T \tilde{S}(Q, \omega)$$

$$\text{where } \alpha = \frac{\hbar^2 Q^2}{2MK_B T}$$

$$\beta = \frac{\hbar \omega}{K_B T} \quad - \quad \text{is positive for neutrons which gain energy}$$

From comparison of equations 2.(xliii) and 2.(lxxxi)

$$S(Q, \omega) = \exp(-2W_\ell) \exp(-\beta/2) \frac{Q^2 \langle u^2 \rangle}{2 \sinh(\beta/2) \coth(\beta/2)} Z(\omega)$$

By definition (and from above):

$$\begin{aligned} \tilde{S}(Q, \omega) &= \frac{1}{\exp(-\beta/2)} \exp(-2W_\ell) \exp(-\beta/2) \frac{Q^2 \langle u^2 \rangle}{2 \sinh(\beta/2) \coth(\beta/2)} Z(\omega) \\ &= \exp(-2W_\ell) \frac{Q^2 \langle u^2 \rangle}{2 \sinh(\beta/2) \coth(\beta/2)} Z(\omega) \end{aligned} \quad 2.(lxxxii)$$

and so:

$$\begin{aligned} S(\alpha, \beta) &= K_B T \tilde{S}(Q, \omega) \\ &= K_B T \exp(-2W_\ell) \frac{Q^2 \langle u^2 \rangle}{2 \sinh(\beta/2) \coth(\beta/2)} Z(\omega) \end{aligned} \quad 2.(lxxxiii)$$

This function has the advantages of making the scatterer isotropic whatever its orientation to the incident neutron beam (i.e. it concerns only the magnitude, not the direction of the scattering vector $\underline{Q}$), and furthermore of writing the variables in dimensionless forms. The term $\exp(-\beta/2)$ preserves the condition of detailed balance, and putting it explicitly into the expression for the cross-section ensures that there will not be violation of the limiting form (i.e. Maxwellian distribution) of the neutron spectrum

$$(ii) \quad P(\underline{Q}, \beta)^{20,23}$$

$$\begin{aligned} \text{where } P(\underline{Q}, \beta) &= 2 \beta \sinh(\beta/2) \frac{S(\underline{Q}, \beta)}{\underline{Q}} \\ &= 2 \left(\frac{\hbar \omega}{K_B T} \right) \sinh(\beta/2) K_B T \exp(-2W_\ell) \frac{Q^2 \langle u^2 \rangle}{2 \sinh(\beta/2) \coth(\beta/2)} \frac{2MK_B T}{\hbar^2 Q^2} Z(\omega) \\ &= \frac{2M\omega}{\hbar} K_B T \exp(-2W_\ell) \frac{\langle u^2 \rangle}{\coth(\beta/2)} Z(\omega) \end{aligned} \quad 2.(1xxxiv)$$

The above function therefore removes both the momentum transfer dependence from the spectrum for each angle, and also the factor $(\sinh(\beta/2))$ from the expression for the Scattering Law which has the effect of dampening intensity across the spectrum as ω increases in wavenumber.

$P(\underline{Q}, \beta)$ allows direct comparison between the spectrum obtained for each angle and that obtained by extrapolation to zero ' $\underline{Q}$ ' i.e. $\rho(\beta)$ (see next section) by using the same form of intensity function in each case.

$$(iii) \quad \text{The Density of States}^{4,20,22}$$

A Time-of-Flight spectrum measures intensity in terms of $\underline{Q}$ and ω , and in consequence cannot be directly compared with an optical spectrum which is obtained at zero $\underline{Q}$. It is therefore necessary to remove the momentum transfer dependence from the intensity expression, and the analogous functions $\rho(\beta)$ and $\rho(\omega)$ carry this out.

They combine data from all angles into their extrapolation to zero momentum transfer for each value of ω considered. However, their effectiveness suffers from the limited $\underline{Q}$ range available on most Time-of-

Flight Spectrometers: small values of momentum transfer are rarely attainable. Consequently, the extrapolation is subject to error in the low ' Q ' region, all the more so in view of the fact that $S(\alpha, \beta)/\alpha$ vs α and $\tilde{S}(Q, \omega)/Q^2$ vs Q are not linear over the full range of momentum transfer.

$$\rho(\beta) = 2\beta \sinh(\beta/2) \left(\frac{S(\alpha, \beta)}{\alpha} \right)_{\alpha \rightarrow 0}$$

which from above equals $\frac{2M\omega}{\hbar} K_B T \exp(-2W_\ell) \frac{\langle u^2 \rangle}{\coth(\beta/2)} Z(\omega)$

$$\begin{aligned} \text{and } \rho(\omega) &= \frac{4M\omega}{\hbar} \sinh(\beta/2) \left(\frac{\tilde{S}(Q, \omega)}{Q^2} \right)_{Q^2 \rightarrow 0} \\ &= \frac{4M\omega}{\hbar} \sinh(\beta/2) \exp(-2W_\ell) \frac{Q^2 \langle u^2 \rangle}{2 \sinh(\beta/2) \coth(\beta/2) Q^2} Z(\omega) \\ &= \frac{2M\omega}{\hbar} \exp(-2W_\ell) \frac{\langle u^2 \rangle}{\coth(\beta/2)} Z(\omega) \end{aligned} \quad 2.(1xxxv)$$

Comparison of equations 2.(1xxxiv) and 2.(1xxxv) shows that:

$$\rho(\beta) = K_B T \rho(\omega)$$

The physical significance of the two expressions above is that they are both directly proportional to the amplitude weighted density of states.

b) Intensity Relations from the Scattering Law

Marshall and Lovesey¹ have shown that the general equation for inelastic neutron scattering from a one-dimensional harmonic oscillator (in terms of $S(Q, \omega)$) may be written:

$$S_n(Q, \omega) = \exp\left(\frac{-\hbar Q^2}{2M\omega_0} \coth\left(\frac{\hbar\omega_0}{2K_B T}\right)\right) \exp\left(\frac{\hbar\omega}{2K_B T}\right) \sum_{n=-\infty}^{\infty} \delta(\hbar\omega - n\hbar\omega_0) I_n(y) \quad 2.(1xxxvi)$$

where ω_0 is the frequency of the fundamental

$$y = \frac{\hbar Q^2}{2M\omega_0} \operatorname{cosech}\left(\frac{\hbar\omega_0}{2K_B T}\right)$$

$$I_{\pm n}(y) = \frac{(y/2)^n}{n!}$$

$S_n(\underline{Q}, \omega)$ refers to the contribution to the Scattering Law from the transfer of n quanta to a particular normal mode, where n is the integral measure of the number of units of energy ($\hbar\omega_0$) lost ($n > 0$) or gained ($n < 0$) by the neutron.

For energy gain Time-of-Flight Spectrometry the above becomes^{25,26}:

$$S_n(\underline{Q}, \omega) = \frac{1}{n!} \exp\left(\frac{-\hbar Q^2}{2M\omega_0} \coth\left(\frac{\hbar\omega_0}{2K_B T}\right)\right) \left(\frac{\hbar Q^2}{2M\omega_0}\right)^n \left(\exp\left(\frac{\hbar\omega_0}{K_B T}\right) - 1\right)^{-n} \quad 2.(lxxxvii)$$

^{25,26}, Howard et al. have investigated the limiting cases of this equation.

(i) Momentum Transfer Dependence

When ω_0 and T are constants, equation 2.(lxxxvii) may be reduced to:

$$S_n(\underline{Q}, \omega) \propto (Q^2)^n \exp(-DQ^2)$$

$$\text{where } D = \frac{\hbar}{2M\omega_0} \coth\left(\frac{\hbar\omega_0}{2K_B T}\right)$$

and $(-DQ^2)$ is the Debye-Waller factor

From the above it may be seen that a plot of

$$\log\left(\frac{S_n(\underline{Q}, \omega)}{\exp(-DQ^2)}\right) \text{ vs } \log(Q^2) \quad 2.(lxxxviii)$$

will give a straight line with a gradient n .

(ii) Temperature Dependence

For the case where ω_0 and $\underline{Q}$ are constants, equation 2.(lxxxvii) shows that:

$$S_n(\underline{Q}, \omega) \propto T^n \exp\left(\frac{\hbar Q^2}{2M\omega_0} \coth\left(\frac{\hbar\omega_0}{2K_B T}\right)\right)$$

In general, it is found that the exponential term varies only slightly with temperature, providing M is large, and so to a first approximation:

$$S_n(\underline{Q}, \omega) \propto T^n$$

That is a plot of

$$\log S_n(Q, \omega) \text{ vs } T^n \quad 2.(lxxxix)$$

will give a straight line with a gradient n .

An alternative way of illustrating the temperature dependence is via the function $P(\alpha, \beta)$, where

$$P(\alpha, \beta) = \frac{4M\omega_o K_B T}{\hbar Q^2} \exp(\beta/2) \sinh(\beta/2) S(Q, \omega)$$

Substituting $n = -1$ in equation 2.(lxxxvii) produces:

$$P_1(\alpha, \beta) = H T \exp\left(\frac{-\hbar Q^2}{2M\omega_o} \coth\left(\frac{\hbar\omega_o}{2K_B T}\right)\right)$$

$$P_1(\alpha, \beta) = H T \exp(-DQ^2) \quad 2.(xc)$$

where H is a constant

and for $n = -2$

$$P_2(\alpha, \beta) = H' T \exp\left(\frac{-\hbar Q^2}{2M\omega_o} \coth\left(\frac{\hbar\omega_o}{2K_B T}\right)\right) \frac{\hbar Q^2}{2M\omega_o} \coth\left(\frac{\hbar\omega_o}{2K_B T}\right)$$

where H' is a constant

For ratios of $\omega_o : T$ between about 0.25 and 0.286, the approximation may be made that $\coth\left(\frac{\hbar\omega_o}{2K_B T}\right)$ is equal to $\frac{2K_B T}{\hbar\omega_o}$ and thus:

$$P_2(\alpha, \beta) = H' T \frac{\hbar Q^2}{2M\omega_o} \exp\left(\frac{-\hbar Q^2}{2M\omega_o} \coth\left(\frac{\hbar\omega_o}{2K_B T}\right)\right) \frac{2K_B T}{\hbar\omega_o}$$

Therefore considering the temperature dependence only:

$$P_2(\alpha, \beta) = H'' T^2 \exp(-DQ^2) \quad 2.(xci)$$

From the above relations a plot of

$$\log\left(\frac{P(\alpha, \beta)}{\exp(-DQ^2)}\right) \text{ vs } T \quad 2.(xcii)$$

will be a straight line with a gradient of one for $P_1(\alpha, \beta)$ and of gradient two for $P_2(\alpha, \beta)$.

13. Theoretical Considerations Applied to Beryllium Filter Detector Spectrometry

a) Relation of the Scattering Law to Raw Data

Detection of neutrons by the BFD may be normalised to a constant number of monitor counts for each value of incident energy selected (see Chapter III). The efficiency of the monitor is, however, proportional to the reciprocal of the incident velocity. Using the relation

$$\frac{mv^2}{2} = \frac{\hbar^2 k^2}{2m}$$

it may be seen that $v^{-1} \propto k^{-1}$, and thus the counts detected by the BFD may be related to the differential cross-section²⁷:

$$\text{Detected Counts} \propto \frac{\partial^2 \sigma}{\partial \Omega \partial E'} \times k \quad 2.(xciii)$$

If equation 2.(lxxx) is written in terms of the density of states,

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{\text{single quantum incoherent}} = \frac{k'}{k} \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \exp(-2W_{\ell}) \frac{A_{\lambda}}{1-A_{\lambda}} Q^2 < u^2 > Z(\omega) \quad 2.(xciv)$$

is obtained.

But by comparison of equations 2.(lxxviii) and 2.(lxxx):

$$\frac{(Q \cdot c_{\ell}^{\lambda})^2 \hbar}{2\omega_{\lambda}} \equiv \frac{Q^2 < u^2 >}{3}$$

and from equation 2.(lx):

$$c_{\ell}^{\lambda} \propto M^{-\frac{1}{2}}$$

and hence

$$\frac{Q^2 \hbar}{2M\omega_{\lambda}} \propto \frac{Q^2 < u^2 >}{3}$$

Substituting this in the expression for the double differential cross-section above (equation 2.(xciv)) gives:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)_{\text{single quantum incoherent}} \propto \frac{k'}{k} \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \exp(-2W_{\ell}) \frac{A_{\lambda}}{1-A_{\lambda}} \frac{3Q^2 \hbar}{2M\omega_{\lambda}} Z(\omega) \quad 2.(xcv)$$

By definition $\underline{Q} = \underline{k} - \underline{k}'$, but for a BFD spectrometer $|\underline{k}'| \approx 0$, and therefore $\underline{Q} \approx \underline{k}$.

Using the relation

$$\hbar\omega_{\lambda} = \frac{\hbar^2 k^2}{2m}$$

it can be seen that k^2 is proportional to ω_{λ} , and hence substitution in 2.(xcv) using the fact that $Q^2 \approx k^2 \propto \omega_{\lambda}$ yields:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)_{\text{single quantum incoherent}} \propto \sum_{\ell} \overline{|b_{\ell} - \bar{b}|^2} \exp(-2W_{\ell}) \frac{Z(\omega)}{M} \quad 2.(xcvi)$$

Thus for a BFD investigation of inelastic features, the detected counts are directly proportional to the reciprocal mass-weighted density of states. The additional factors governing intensity, the scattering length and the Debye-Waller factor, are those also present in the case of elastic scattering.

b) Intensity Relations from the Scattering Law

Again using the equation 2.(lxxxvi) derived by Marshall and Lovesey¹, but this time under the experimental conditions of BFD spectrometry (i.e. small T , large ω_0 and neutron energy loss), Howard²⁵ has shown that

$$S_n(\underline{Q}, \omega) \propto \frac{n}{n!} \left(\frac{m}{M}\right)^n \exp\left(-\frac{m}{M}\right)^n \quad 2.(xcvii)$$

That is overtones may be seen quite readily using a BFD spectrometer, provided that ω_0 is intense and the vibration involves ligands of light mass.

B. Rotational Barriers

The potential barrier to rotation may be described by means of a Fourier series in θ , the angle through which one group is rotating relative to the other:

$$V(\theta) = \sum_m (V_m \cos m\theta + V'_m \sin m\theta) \quad 2.(xcviii)$$

where V_m and V'_m are coefficients

Consideration of the symmetry of the molecule concerned may enable simplification of the above equation. For example, if the barrier is encountered n times on rotation through 2π , then the $\sin \theta$ terms disappear and the potential function may be written:

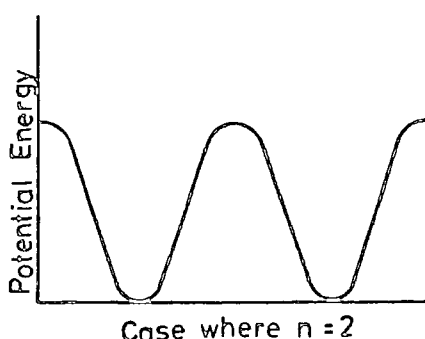
$$V(\theta) = \sum_m \frac{V_{mn}}{2} (1 - \cos mn\theta) \quad 2.(xcix)$$

where V_{mn} are parameters describing the barrier

In general, a good enough approximation is afforded by consideration of the first few terms in the expansion, in the simplest case:

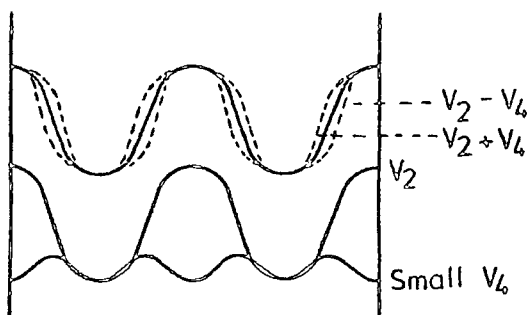
$$V(\theta) = \frac{V_n}{2} (1 - \cos n\theta) \quad 2.(c)$$

where V_n is the height of the barrier

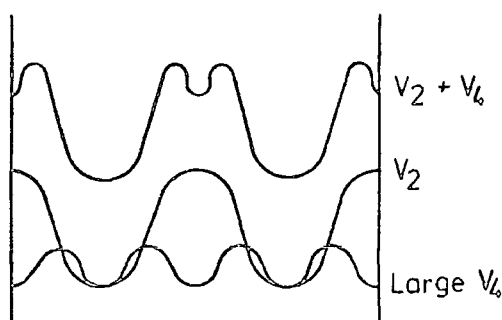


Several assessments have been made of the relative effect of the second term in the expansion, $\frac{V_{2n}}{2} (1 - \cos 2n\theta)$.²⁸⁻³² These have shown that for symmetrical cases the term V_{2n} is very small. (For example, in

the case of methyl group rotations, V_{2n} is about 3% of V_n^{31} .) When V_n is very large compared to V_{2n} , the influence of the second term is solely to alter the shape of the potential energy well³⁴:



However, where V_{2n} is larger than in the above case, but still smaller than V_n , more profound changes take place with a meta-stable well being produced³³ and the barrier height being raised:



1. Equations of Motion

Having chosen the correct representation of the potential function, the expression must be substituted into the Schrödinger equation. If the expression in equation 2.(c) is used, we may write³⁴:

$$\frac{1}{I_R} \frac{d^2 \psi(\theta)}{d\theta^2} + \frac{8\pi^2}{h^2} \left[E - \frac{V_n}{2} (1 - \cos n\theta) \right] \psi(\theta) = 0 \quad 2.(ci)$$

where I_R is the reduced moment of inertia

$$I_R = I_A \left(1 - I_A \sum_g \frac{\lambda_g^2}{I_g} \right) \quad 34, 35$$

where I_A is the moment of inertia of the rotor about its own axis

λ_g is the cosine of the angle between the axis of the rotor and the g^{th} principle axis of the whole molecule.

I_g is the g^{th} principle moment of inertia.

Equation 2.(ci) is in the same form as the Mathieu equation:

$$\frac{d^2 y}{dx^2} + (b - s \cos^2 x)y = 0$$

$$\text{if } b = \frac{4E_{v\sigma}}{n^2 F} \quad \text{and } s = \frac{4V_n}{n^2 F}$$

$$\text{where } F = \frac{h^2}{8\pi^2 I_R}$$

$$E_{v\sigma} = \left(E - \frac{V_n}{2} \right)_{v\sigma}$$

v is the principal torsional quantum number.

σ is the sublevel designation.

Mathieu's equation has different solutions for different angular periods and consequently its evaluation is very time consuming. However, tables of solutions are available, for example those of Herschbach,³⁶ which allow simplification of the process of determining s and b for periodicities which are multiples of three. Thus, if the value of $\Delta E_{v\sigma}$ is known for the transition from $V=0$ to $V=1$, and I_R is known, then $\Delta b_{v\sigma}$ may be found. $\Delta b_{v\sigma}$ may then be correlated with a value of s from the appropriate tables and hence V_n calculated.

There are, however, two limiting cases of equation 2.(ci) which allow simpler solution and these will be detailed in the next two sections.

2. The Low Barrier Approximation

When V_n tends to zero, $b_{v\sigma}$ is very much larger than s , and consequently it may be stated that:

$$\frac{d^2 y}{dx^2} + b_{v\sigma} y = 0$$

The solutions to the above are $y = \exp(\pm ipx)$, where $p=0,1,2,3,\dots$ etc. However, the condition $\psi(\theta) = \psi(\theta + \frac{2\pi}{n})$ necessitates $p=0,2,4,6,\dots$ etc., and therefore substituting back into the equation produces the result that $b_{v\sigma} = p^2$. Hence:

$$E_p - \frac{V_n}{2} = \frac{n^2 h^2 p^2}{32\pi^2 I_R}$$

which is very similar to the expression for a free uniaxial rotor.

3. The High Barrier Approximation

When the barrier is high (greater than 10kJ mol^{-1} ³⁷) the rotor may oscillate only within small variations of θ at the bottom of the potential energy well. As a result of this, terms above the second in the expansion:

$$\cos n\theta = 1 - \frac{n^2 \theta^2}{2!} + \frac{n^4 \theta^4}{4!} - \frac{n^6 \theta^6}{6!} \dots$$

may be ignored.

The Schrödinger equation may therefore be written³⁴:

$$\frac{d^2 \psi(\theta)}{d\theta^2} + \frac{8\pi^2 I_R}{h^2} \left[E_s - \frac{V_n n^2 \theta^2}{4} \right] \psi(\theta) = 0$$

which is the form of a simple harmonic oscillator with eigen values:

$$E_s = (t + \frac{1}{2}) \left[\frac{n^2 h^2 V_n}{8\pi^2 I_R} \right]^{\frac{1}{2}}$$

where t is a quantum number ($0,1,2,3,\dots$ etc)

For the transition $0 \rightarrow 1$ therefore:

$$\bar{V}_n = \frac{8\pi^2 c I_R \bar{\nu}^2}{n^2 h}$$

where $\bar{V}_n$ is the barrier height in cm^{-1}

$\bar{\nu}$ is the vibrational frequency in cm^{-1}

c is the velocity of light

4. The Das Approximation

For high and intermediate barriers an approximate solution to the Mathieu equation has been developed by Das³⁸. This is of most use when Herschbach's tables are not of the correct periodicity or do not cover the range of values required.

The Mathieu equation eigen function has been expanded as a converging series:

$$E_a = \frac{V_n}{G} \left[G(2a+1) - \frac{1}{4}(a^2 + (a+1)^2) - \frac{G^{-1}}{16} (a^3 + (a+1)^3) \right. \\ \left. - \frac{G^{-2}}{128} (5a^4 + 5(a+1)^4 + a^2 + (a+1)^2) \dots \right]$$

$$\text{where } G = \left(\frac{32\pi^2 I_R V_n}{n^2 h^2} \right)^{\frac{1}{2}}$$

p is the torsional quantum number

Similarly, the corresponding eigenvalues may also be represented by a series. Considering the transition $0 \rightarrow 1$, the expression for the barrier may be written in successive terms:

$$\begin{aligned} \text{(i)} \quad \bar{V}_n &= \bar{\nu}^2 H^{-1} \\ \text{(ii)} \quad \bar{V}_n &= \left(\bar{\nu} + \frac{H}{4} \right)^2 H^{-1} \\ \text{(iii)} \quad \bar{V}_n^2 &= \left(\bar{\nu}^2 + \frac{3H^2}{16} - \frac{\bar{\nu}H}{2} \right) \bar{V}_n H^{-1} + \left(\frac{H}{16} \right)^2 \end{aligned}$$

$$\text{where } H = \left(\frac{n^2 h^2}{8\pi^2 c I_R} \right)$$

from which it will be seen that the first expression is the same as that obtained previously using the High Barrier Approximation.

In general, it is found that three terms of the Das approximation are sufficient to give good agreement with the values obtained from Herschbach's tables.

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CHAPTER III

INSTRUMENTATION, DATA ANALYSIS AND EXPERIMENTAL TECHNIQUES

A. Inelastic Neutron Scattering (INS) Spectrometers

Time-of-Flight (T-O-F) spectrometers 4H5 and 6H at AERE Harwell, and IN4 at the Institut Laue-Langevin (ILL) Grenoble were used in the investigation of the long wavelength spectral region ($0-450\text{cm}^{-1}$). Higher energy studies ($70-1250\text{cm}^{-1}$) were carried out with the Beryllium Filter Detector (BFD) spectrometers on the Pluto and Dido reactors at AERE Harwell.

Several authors^{1,2,3} have discussed the principles of design and operation of INS spectrometers; however, because they remain relatively uncommon, those mentioned above will be described more extensively.

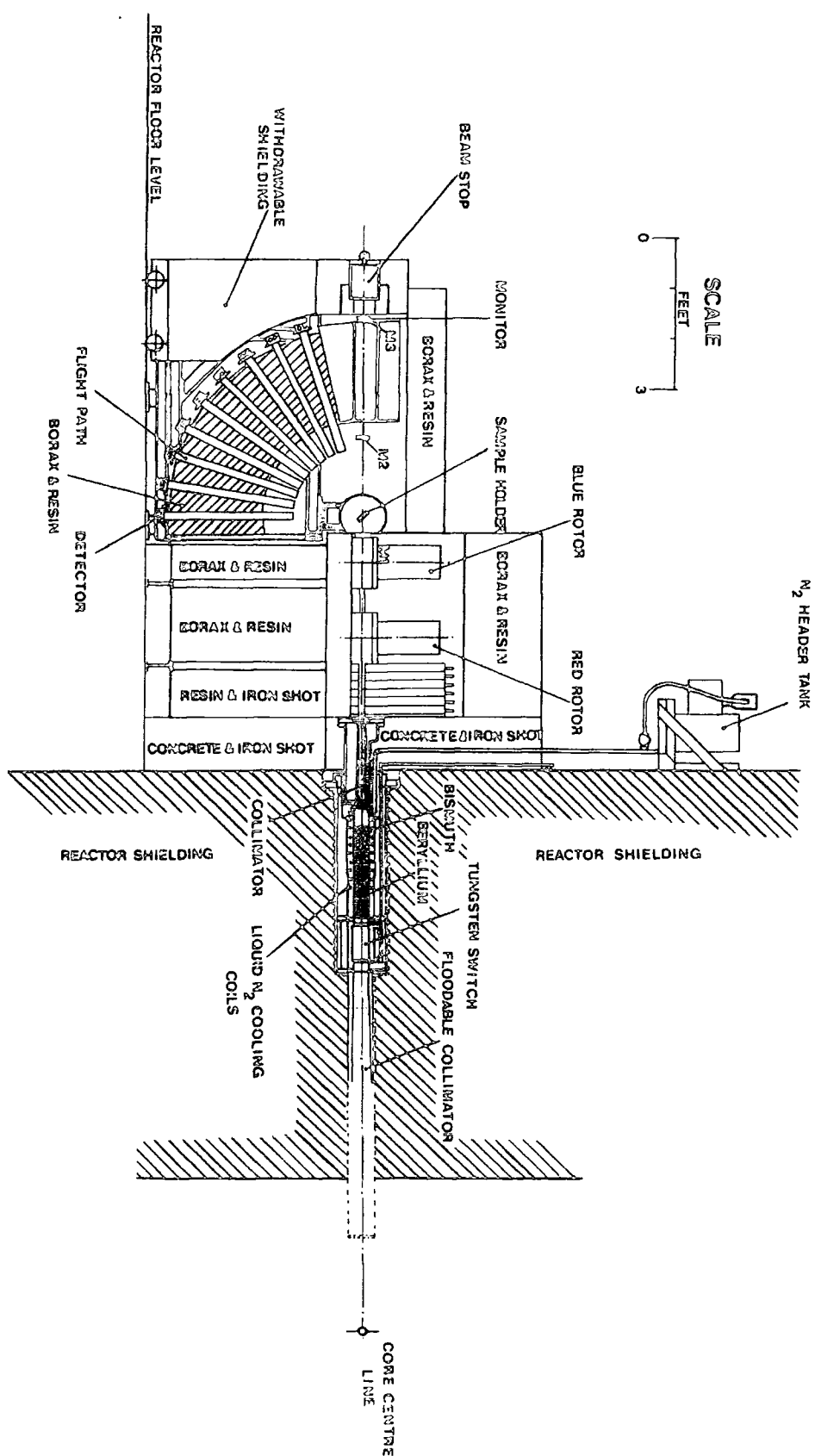
1. The Dido 6H Time-of-Flight Spectrometer⁴ (dia.3(i))

a) Collimation of the Neutron Beam

Neutrons entering the 6H beam tube travel through a beryllium polycrystal, and then a bismuth single crystal, both of which are cooled to liquid nitrogen temperature. The beryllium polycrystal Bragg scatters those neutrons with wavelengths less than the Bragg cut off ($3.96\text{ \AA}$, 42 cm^{-1}) i.e. fast neutrons; whilst the bismuth crystal, besides providing further attenuation of fast neutrons, reduces gamma ray intensity to workable levels. Liquid nitrogen cooling of the beryllium crystal ensures greater transmission of thermal neutrons by reducing the Debye-Waller contribution to the scattering.

b) Monochromation

The beam leaving the collimator is "chopped" by two elliptically shaped rotors which are made of cadmium-magnesium alloy (opaque to neutrons) and have "banana" shaped slots⁵ cut through them. The rotors are spun about a vertical axis in an evacuated steel tank,^{6,7} and by variation of speed, and the relative phasing, a monoenergetic neutron beam of the



dia. 3(ii) The 6H Time-of-Flight Spectrometer,

AERE Harwell.

requisite wavelength is produced 5 cm wide and 2.5 cm high.

c) Sample Positioning

Samples under investigation are held in a "sample changer" which allows cyclic alternation of three sample positions. One position contains a plate of standard cross-section made of vanadium, which is chosen because of its important properties of scattering isotropically and almost totally incoherently. The former property permits correction for individual detector efficiencies at all angles in space, whilst the latter enables calculation of absolute incoherent cross-sections. The remaining positions are occupied by the sample and its "background" or empty sample container. This procedure enables subtraction from the sample spectrum of time-dependent background scattering attributable to the container. The employment of continuous cycling overcomes variations in neutron flux and in instrument characteristics. The length of time required in each position may be set by the user via the Cassandra system,^{8,9} which then automatically controls cycling and the recording of counts for each position.

The sample changer may be evacuated to reduce loss of resolution resulting from the effect of air scattering on the monochromatic beam (ideally the resolution would be further enhanced by evacuation or helium filling of the flight path between sample changer and detectors) and is operational over a wide temperature range, 90-500K.

d) Neutron Detection

Neutrons scattered from the sample are detected using 2.5cm diameter 2 atmosphere $^{10}\text{BF}_3$ proportional counters arranged to cover an arc of scattering angles between 18° and 90° in 9° increments. For scattering angles 18° , 27° and 36° , two pairs of counters 15 cm long are employed, whilst the remaining angles have three pairs of length 31 cm: all of the detectors are positioned a uniform 1.2 m from the sample.

The unscattered beam passes through three fission chambers or monitors. The first of these is situated immediately after the rotors and provides a measurement of incident neutron intensity, the second and third are placed at distances of 0.5 m and 1.2 m behind the sample and indicate the neutron transmission by the sample. By use of the monitors a value can be calculated for incident neutron velocity (see later: "Clodop and Prescat").

e) Method of Operation

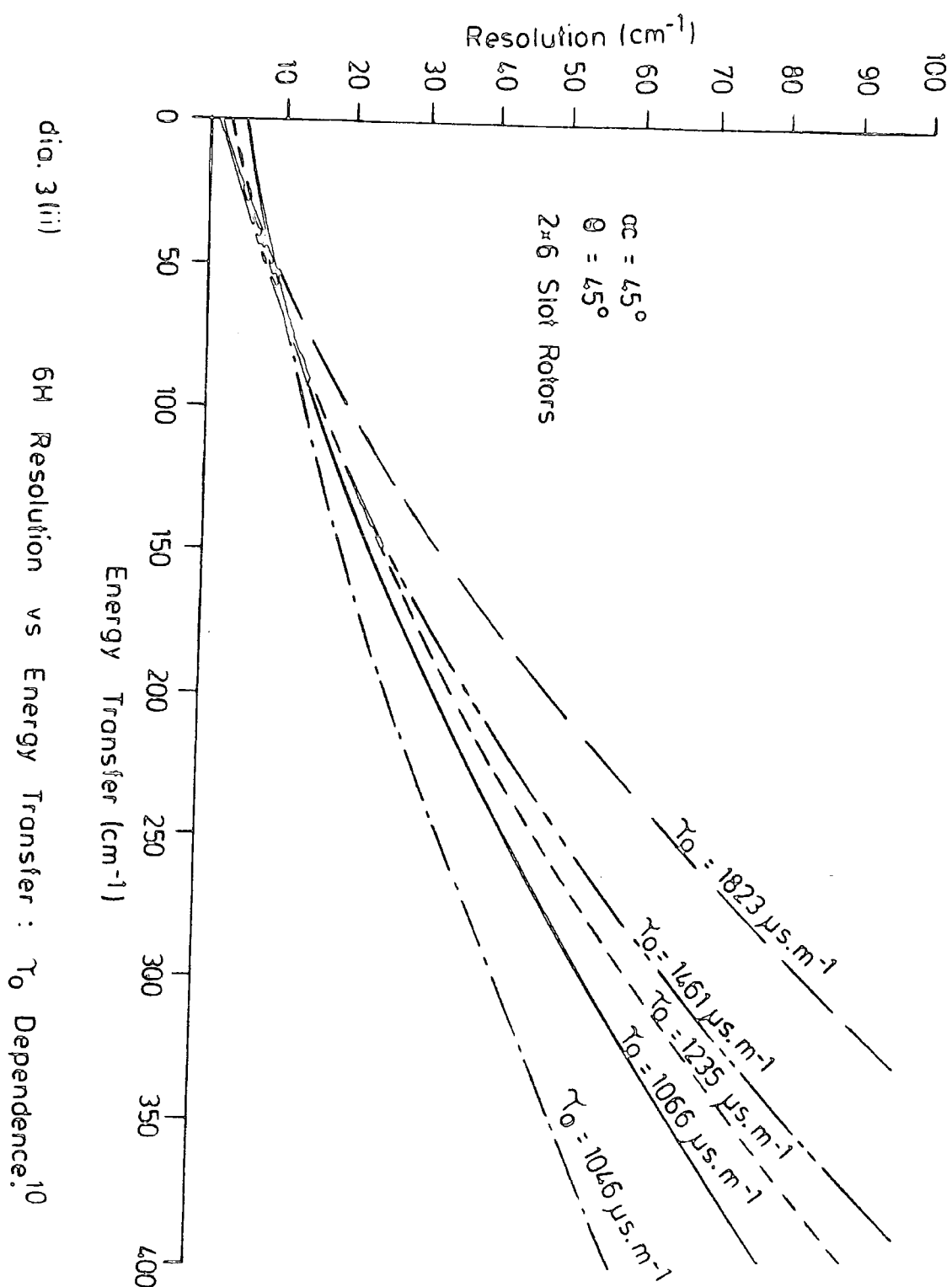
Incident neutrons interacting inelastically with the sample absorb quanta of energy corresponding to the various vibrational^a transitions present in the sample. As a result, they are upscattered (i.e. they gain energy) and their resulting time-of-flight is less than for neutrons which are not scattered.

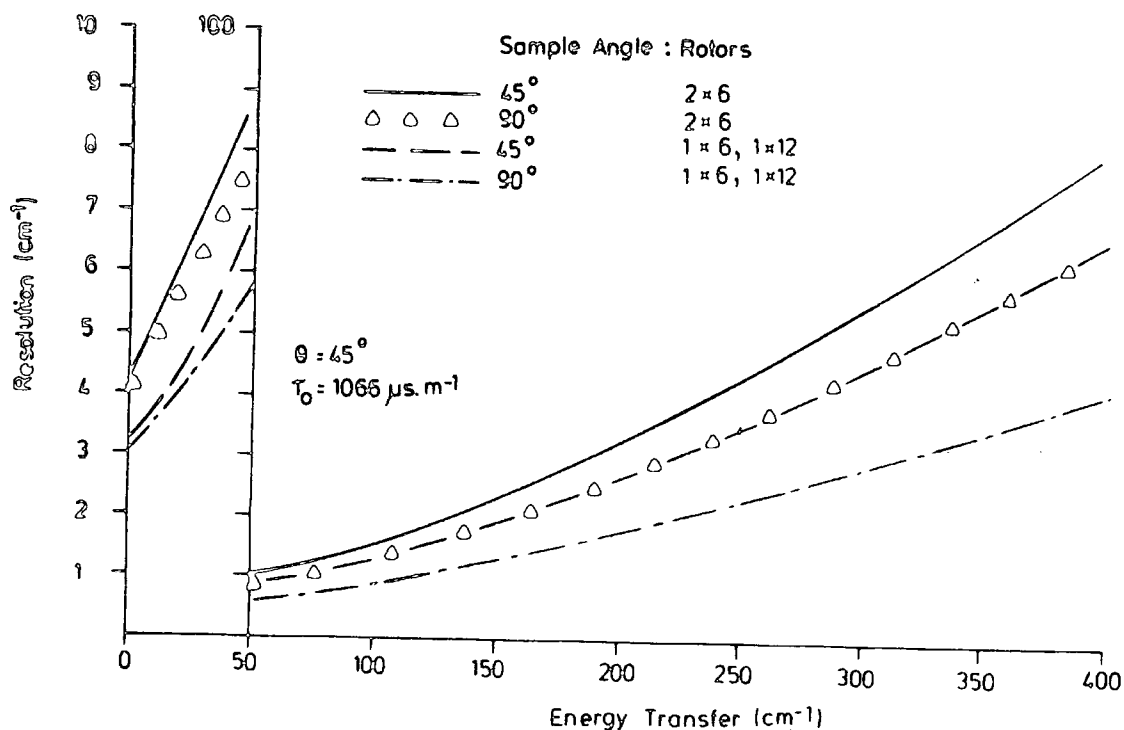
f) Data Collection

A pulse from the rotor drive system triggers a crystal controlled digital clock, which then times in "channels" the arrival of a particular neutron at a particular counter angle. Each channel is 6 μ second wide and there are 512 channels per pulse; the time period covered is thus 3072 μ second from the start pulse. The resulting scattered neutron distribution spread over the 512 time-of-flight channels is recorded by the Cassandra time-of-flight analyser⁸ for each sample position and angle and may be viewed on a closed-circuit television display.

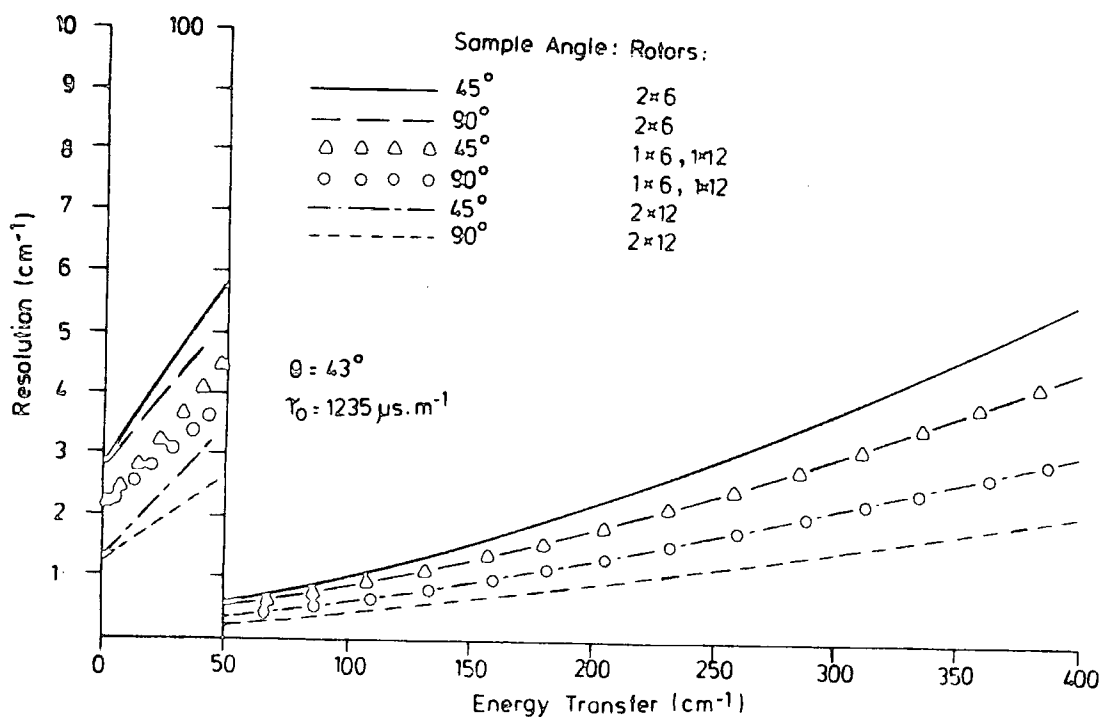
g) Resolution Considerations

Harryman and Hayter¹⁰ consider that the important resolution variables for a given instrument are the incident wavelength, the number of rotor slots and the sample orientation, and have published tables of resolution versus energy transfer for each angle of the 6H and 4H5 spectrometers. (Gate width and finite detector size have been shown to be negligible considerations.)





dia. 3(iii)a

6H Resolution vs Energy Transfer : Rotor Dependence.¹⁰

dia. 3(iii)b

4H5 Resolution vs Energy Transfer : Rotor Dependence.¹⁰

TABLE 3.1 Typical Values of Resolution for 4H5 and 6H T-O-F Spectrometers (after Harryman and Hayter¹⁰)

4 H 5										6 H									
A) 2 x 6 slot rotors, peak flux and 45° sample altitude										A) 2 x 6 slot rotors, peak flux and 45° sample altitude									
Centre of Peak		Time of Flight		Detector Angle		Resolution cm ⁻¹				Centre of Peak		Time of Flight		Detector Angle		Resolution cm ⁻¹			
cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	66°	74°	82°	90°			cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	63°	72°	81°	90°		
1235	0.0			3.2	3.3	3.4	3.5			1066	0.0			4.3	4.4	4.5	4.6		
1100	7.2			3.7	3.8	4.0	4.1			1000	5.1			4.7	4.8	5.0	5.1		
1000	14.5			4.2	4.5	4.7	4.8			900	14.9			5.6	5.8	5.9	6.1		
850	30.7			5.7	6.1	6.5	6.7			800	28.8			7.0	7.2	7.5	7.7		
700	58.4			8.8	9.5	10.2	10.5			650	62.7			11.1	11.5	12.0	12.5		
500	141.0			21.1	22.8	24.3	25.0			500	131.5			21.7	22.6	23.5	24.3		
400	235.9			39.2	42.3	45.0	46.0			400	226.4			40.1	41.6	43.0	44.4		
B) 2 x 12 slot rotors, peak flux and 45° sample altitude										B) 1 x 6+1 x 12 slot rotors, peak flux and 45° sample altitude									
Centre of Peak		Time of Flight		Detector Angle		Resolution cm ⁻¹				Centre of Peak		Time of Flight		Detector Angle		Resolution cm ⁻¹			
cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	66°	74°	82°	90°			cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	63°	72°	81°	90°		
1235	0.0			1.7	1.9	2.1	2.2			1074	0.0			3.3	3.4	3.5	3.7		
1100	7.2			2.2	2.5	2.7	2.9			1000	5.6			3.7	3.8	4.0	4.2		
1000	14.5			2.8	3.1	3.5	3.7			900	15.5			4.4	4.7	4.9	5.2		
850	30.7			4.2	4.7	5.3	5.6			800	29.3			5.7	6.0	6.4	6.8		
700	58.4			7.0	7.9	8.8	9.3			650	63.2			9.4	10.1	10.7	11.3		
500	141.0			18.0	20.1	21.9	22.8			500	132.1			18.9	20.2	21.5	22.6		
400	235.9			34.0	37.6	40.7	42.1			400	227.0			35.2	37.3	39.3	41.2		

Ideally the smallest value of incident reciprocal velocity would be preferred (dia.3(ii)). However, there is a considerable fall-off in flux to the short wavelength side of peak flux, and as counting statistics are proportional $\sqrt{\text{flux}}$, it may be seen that an attempt to collect high resolution data under short wavelength conditions could result in large variations in counts.

Employment of 1 x 12 slot rotor coupled with 1 x 6 slot rotor, or even 2 x 12 slot rotors would give increased resolution (dia.3(iii) and Table 3.1). Again, compared with 2 x 6 slot rotors the disadvantage is the reduction in neutron flux, which would be in the order of a factor of 3 for 1 x 12 + 1 x 6 slot rotors, and a factor of 12 for 2 x 12 slot rotors.

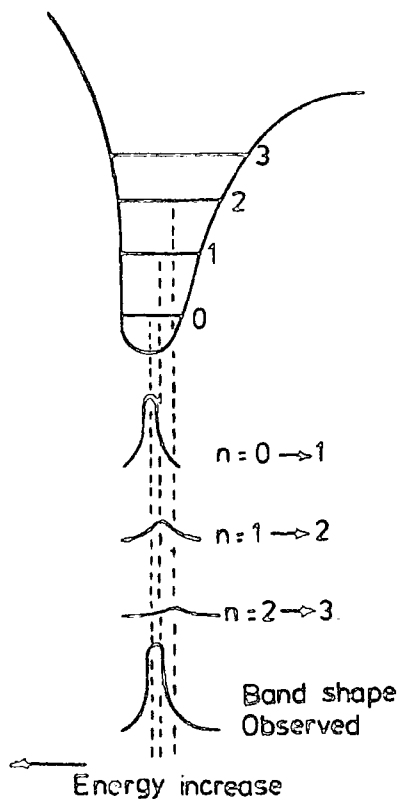
A third possibility for improvement of resolution would be to position the sample at 90° to the beam, compared with the 45° attitude normally used. This would avoid variation in the path length of scattered neutrons, but has the drawback of rendering unusable the high angle counters, which in general contain most scattered neutron counts and often consequently the most useful data. As an alternative to this, it has been shown¹⁰ that cutting down the vertical height of the beam to 1.25 cm results in the equivalent increased resolution of the 90° sample position for the mid- and far inelastic regions; however this causes the flux to be halved.

In view of the conflicting requirements of flux and resolution, a configuration of 45° sample position, 2 x 6 slot rotors and peak flux ($4.2\text{\AA}$, 37.5cm^{-1}) has been employed throughout this work yielding the typical values for resolution shown in Table 3.1.

Samples have been run at reduced temperatures with the intention of sharpening the definition of transition bands. Considering an anharmonic potential energy well which has unequal energy gradations between the levels, then the fundamental seen will result from the transitions $n \rightarrow n-1$,

TABLE 3.2 Comparison of Energy Level Populations at Room and liquid Nitrogen Temperatures

Transition Frequency	50cm ⁻¹		100cm ⁻¹		150cm ⁻¹		200cm ⁻¹	
Temperature	298K	77K	298K	77K	298K	77K	298K	77K
Population of Energy level n = 0	100	100	100	100	100	100	100	100
Population of Energy level n = 1, $\frac{N_1}{N_0} = \exp (-E/k_B T)$	78.6	39.3	61.7	15.4	48.5	6.07	38.1	2.38
Population of Energy level n = 2, $\frac{N_2}{N_0} = \exp (-2E/k_B T)$	61.8	15.4	38.1	2.38	23.5	0.368	14.5	0.0569
Population of Energy level n = 3, $\frac{N_3}{N_0} = \exp (-3E/k_B T)$	48.5	6.07	23.5	0.368	11.4	0.0224	5.53	0.00136



where $n = 1, 2, 3$ etc. Although as n increases, the intensity of the transition will decrease because of the Boltzmann distribution (Table 3.2), the effect of the superimposition of the higher transitions will be to introduce asymmetry and broadening into the shape of the more intense $1 \rightarrow 0$ transition. It is therefore useful to reduce the populations of the levels greater than $n = 1$ by cooling, whilst ensuring that the $n = 1$ level is not so depopulated that, in the case of an upscattering spectrometer, excessive counting times are required.

A further advantage of the employment of low temperature is the decreased effect of Collisional Broadening upon transition bands. From Grant et al.¹¹ the Full Width at Half Maximum (FWHM) attributable to this may be expressed as equal to:

$$4 \left(\frac{(\ln 2) K_B T \hbar^2 Q^2}{2M_v} \right)^{\frac{1}{2}} = 11.398 \left(\frac{TQ^2}{M_v} \right)^{\frac{1}{2}} \text{ cm}^{-1}$$

where K_B is the Boltzmann constant, T is temperature (K), $\hbar$ is Planck's constant divided by 2π , Q is momentum transfer ($\text{\AA}^{-1}$) and M_v is the Sachs-Teller¹² effective mass (AMU):

$$M_v^{-1} = M^{-1} + \frac{1}{3} \left(\frac{Y_v^2 + Z_v^2}{I_x} + \frac{Z_v^2 + X_v^2}{I_y} + \frac{X_v^2 + Y_v^2}{I_z} \right)$$

where M is the total molecular mass, I_x , I_y and I_z are moments of inertia about the principal axes, and X_v , Y_v and Z_v are the equilibrium co-ordinates of the scattering atom v in these axes.

TABLE 3.3 Collision Broadening as a Function of Momentum Transfer (Q)

6H Counter Angle	63°			72°			81°			90°		
	Q	Collision * Broadening	Potential Resolution [†]	Q	Collision * Broadening	Potential Resolution [†]	Q	Collision * Broadening	Potential Resolution [†]	Q	Collision * Broadening	Potential Resolution [†]
50cm ⁻¹	2.1Å ⁻²	20.5cm ⁻¹	9.2cm ⁻¹	2.3Å ⁻²	22.5cm ⁻¹	10.1cm ⁻¹	2.5Å ⁻²	24.5cm ⁻¹	10.2cm ⁻¹	2.7Å ⁻²	26.4cm ⁻¹	10.6cm ⁻¹
100cm ⁻¹	2.6Å ⁻²	25.4cm ⁻¹	16.5cm ⁻¹	2.8Å ⁻²	27.4cm ⁻¹	17.4cm ⁻¹	3.0Å ⁻²	29.3cm ⁻¹	17.7cm ⁻¹	3.2Å ⁻²	31.3cm ⁻¹	17.4cm ⁻¹
150cm ⁻¹	3.0Å ⁻²	29.3cm ⁻¹	25.2cm ⁻¹	3.2Å ⁻²	31.3cm ⁻¹	26.0cm ⁻¹	3.4Å ⁻²	33.3cm ⁻¹	27.1cm ⁻¹	3.7Å ⁻²	36.2cm ⁻¹	27.3cm ⁻¹
200cm ⁻¹	3.4Å ⁻²	33.3cm ⁻¹	34.4cm ⁻¹	3.6Å ⁻²	35.2cm ⁻¹	35.8cm ⁻¹	3.8Å ⁻²	37.2cm ⁻¹	36.8cm ⁻¹	4.0Å ⁻²	39.1cm ⁻¹	38.4cm ⁻¹

* Calculated using the empirically derived Sachs-Teller effective mass for solid propane (M_v=405±25) and a temperature of 298K

† Data for 2 x 6 slot rotors and peak flux¹⁰

Although the expression for Collisional Broadening is a general one, the effective mass relation stated above is only applicable to the gas phase, where the atom v is not hindered in its recoil by intermolecular interactions.

When considering the liquid and solid states, it is noticeable that there is a decrease in the width of inelastic peaks, and this implies that the effective value of M_v must increase. As yet theory has not progressed to the point where effective masses for liquids and solids can be determined other than empirically, but obviously it is these values which have most relevance to resolution considerations for the systems and compounds studied in this thesis.

In an attempt to estimate the relative size of the Collisional Broadening effect, the empirical value of $M_v = 405^{+25}_{-11}$, which is the average for the torsional modes of solid propane, has been substituted into the expression of Grant et al.. Then Collisional Broadening for a temperature of 298K has been calculated using values of Q typical of the stated energy Transfers at the given 6H counter angles (Table 3.3). Comparison with the resolution data of Harryman and Hayter¹⁰ given alongside shows Collisional Broadening can have a noticeable effect on resolution. It is therefore beneficial to use reduced temperatures, and as a result of the $T^{1/2}$ dependence, broadening will be diminished by, for example, a factor of a half if a spectrum is measured at 77K rather than 298K.

2. The Dido 4H5 Time-of-Flight Spectrometer¹³

The design of this instrument and mode of operation are essentially similar to 6H; some important differences between the machines are:-

(i) 4H5 has a cold source placed before a collimator of the same design as 6H. The cold source, which is a liquid Hydrogen cooled bulb (20K) about 8 cm in diameter, thermalises fast neutrons causing an increase in the "useful" flux incident upon the bismuth polycrystal (dia.3(iv)).

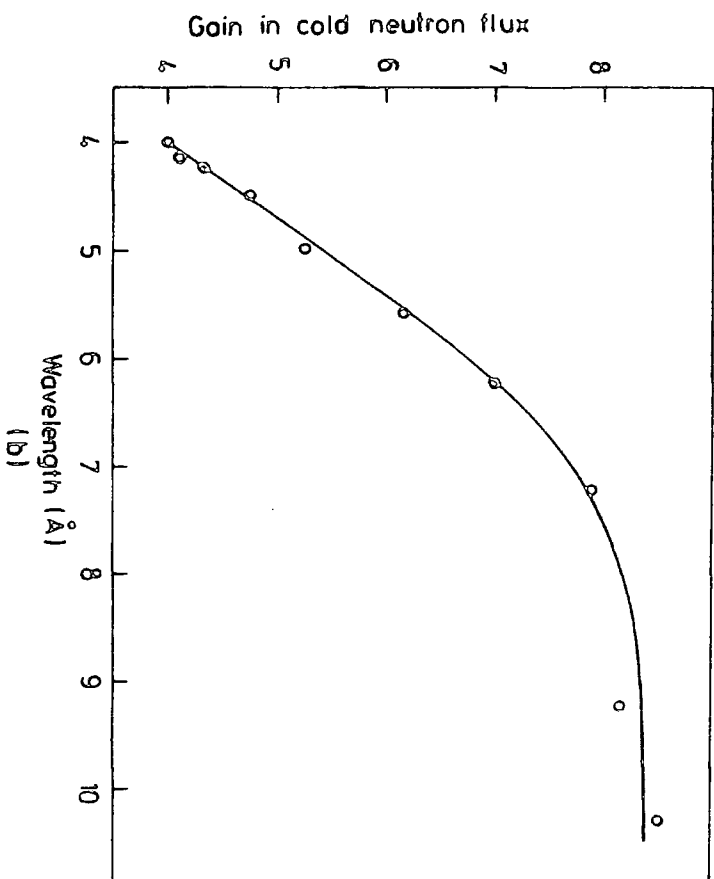
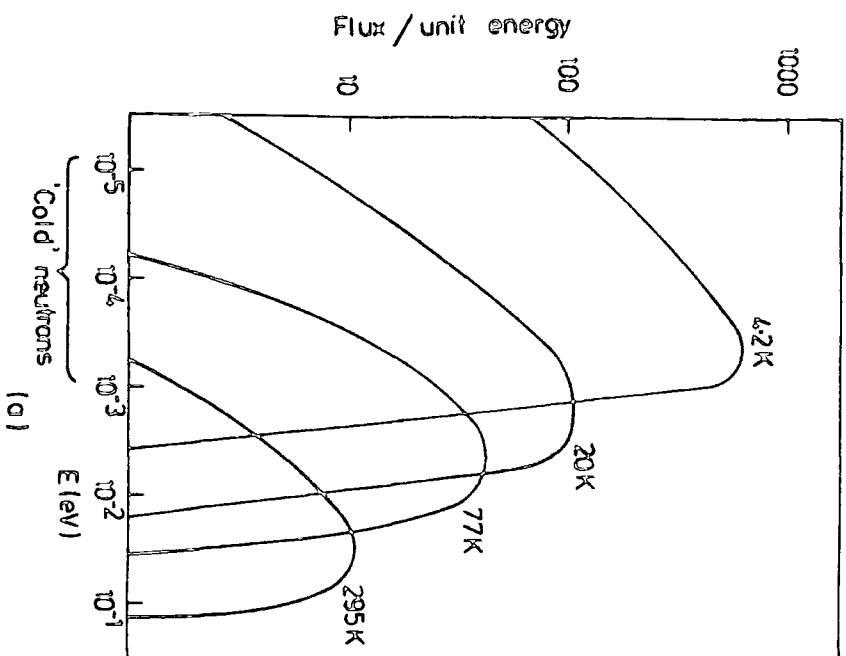
(ii) As a corollary of the above, peak flux using 4H5 is at lower wavelength ($5.3 \text{ \AA} / 23.5 \text{ cm}^{-1}$) than 6H ($4.2 \text{ \AA} / 37.5 \text{ cm}^{-1}$) and the value of the flux at this wavelength is twice that of 6H (Table 3.4).

(iii) 4H5 does not have the constant flight path between sample and detector present on 6H, the lengths being 1.9 m for the first 7 counters, 1.7 m for counter 8, 1.5 m for counter 9, 1.4 m for counter 10, 1.35 m for counter 11 and 1.3 m for counters 12 and 13.

(iv) The detectors on 4H5 are positioned at the following angles, 13° , 18° , 23° , 28° , 33° , 38° , 43° , 50° , 58° , 66° , 74° , 82° and 90° . The number of counter pairs and the active length of the counters for each of these angles varies thus: 6 x 15 cm, 6 x 15 cm, 8 x 15 cm, 2 x 15 cm + 6 x 25 cm, 4 x 31 cm, 4 x 31 cm, 4 x 31 cm, 4 x 31 cm, 4 x 31 cm, 4 x 31 cm, 4 x 31 cm, 4 x 31 cm and 4 x 31 cm. It may be seen that the counter area is much larger on 4H5 than 6H (Table 3.4).

(v) The detectors on 4H5 are being progressively changed from 2 atmosphere $^{10}\text{BF}_3$ proportional counters to the higher efficiency ^3He type. (This process was started in early 1978 and is still continuing.)

(vi) Resolution data for 4H5 in the 2 x 6 slot rotors configuration used in this work are shown in Table 3.1 along with those for 2 x 12 slot rotors. Comparison between the values for 6H and 4H5 shows the latter to be capable of the greater resolution. From consideration of the previous discussion of resolution, this should not be so because all variables are either similar to 6H, or less favourable as in the case of peak



dia. 3 (iv) The effect of liquid hydrogen moderation on the cold neutron flux. (c) Neutron flux per unit energy range for various moderator temperatures. (d) Gain in cold neutron flux obtained by using liquid hydrogen moderation relative to the flux of thermal neutrons at the same wavelengths. (After Allen and Higgins.²⁶)

TABLE 3.4

Comparison of Instrument Specifications for the T-O-F Spectrometers 6H, 4H5 and 1N4

Instrument	(I) Neutron Flux at sample	(II) Sample Area	(III) $\frac{\text{Detector Area}}{(\text{Sample to Detector Distance})^2}$	A (I) x (II)	B (I) x (II) x (III)	$\frac{B}{B_{1N4}}$
6H	$5 \times 10^4 \text{ n cm}^{-2} \text{ s}^{-1}$ (Peak flux 37.5 cm^{-1})	$5 \times 2.5 \text{ cm}^2$	$\frac{3 \times 4(15 \times 2.5) + 6 \times 6(31 \times 2.5) \text{ cm}^2}{120^2 \text{ cm}^2}$ $= \frac{3240}{14400} = 0.23$	$0.63 \times 10^6 \text{ ns}^{-1}$	$1.44 \times 10^5 \text{ ns}^{-1}$	2.6
4H5	$10^5 \text{ n cm}^{-2} \text{ s}^{-1}$ (Peak flux 23.5 cm^{-1})	$5 \times 2.5 \text{ cm}^2$	$\frac{44(15 \times 2.5) + 12(25 \times 2.5) + 24(31 \times 2.5) \text{ cm}^2}{190^2 \text{ cm}^2}$ $\frac{+8(31 \times 2.5) \text{ cm}^2 + 8(31 \times 2.5) \text{ cm}^2 + 8(31 \times 2.5) \text{ cm}^2}{170^2 \text{ cm}^2}$ $\frac{+8(31 \times 2.5) \text{ cm}^2 + 16(31 \times 2.5) \text{ cm}^2}{135^2 \text{ cm}^2}$ $= \frac{4260}{36100} + \frac{620}{28900} + \frac{620}{22500} + \frac{620}{19600} + \frac{1240}{16225} + \frac{1240}{16900}$ $= 0.31$	$1.25 \times 10^6 \text{ ns}^{-1}$	$3.88 \times 10^5 \text{ ns}^{-1}$	6.9
1N4	$3 \times 10^4 \text{ n cm}^{-2} \text{ s}^{-1}$ (Peak flux 101 cm^{-1} ; Graphite first order reflection)	$9 \times 4 \text{ cm}^2$	$\frac{37 \times 6(15 \times 2.5) \text{ cm}^2}{400^2 \text{ cm}^2}$ $= \frac{8325}{160000} = 0.052$	$1.08 \times 10^6 \text{ ns}^{-1}$	$0.56 \times 10^5 \text{ ns}^{-1}$	1.00

flux. The explanation lies not in a variable, but in the inherent design of 4H5: the longer flight paths between sample and detectors compared with 6H, allow the distribution of times-of-flight of the scattered neutrons to "spread out", thereby occupying more time channels.

3. IN4 Time-of-Flight Spectrometer (dia.3(v))

The principle of operation is, with the exceptions to be detailed, analogous to 6H and 4H5:-

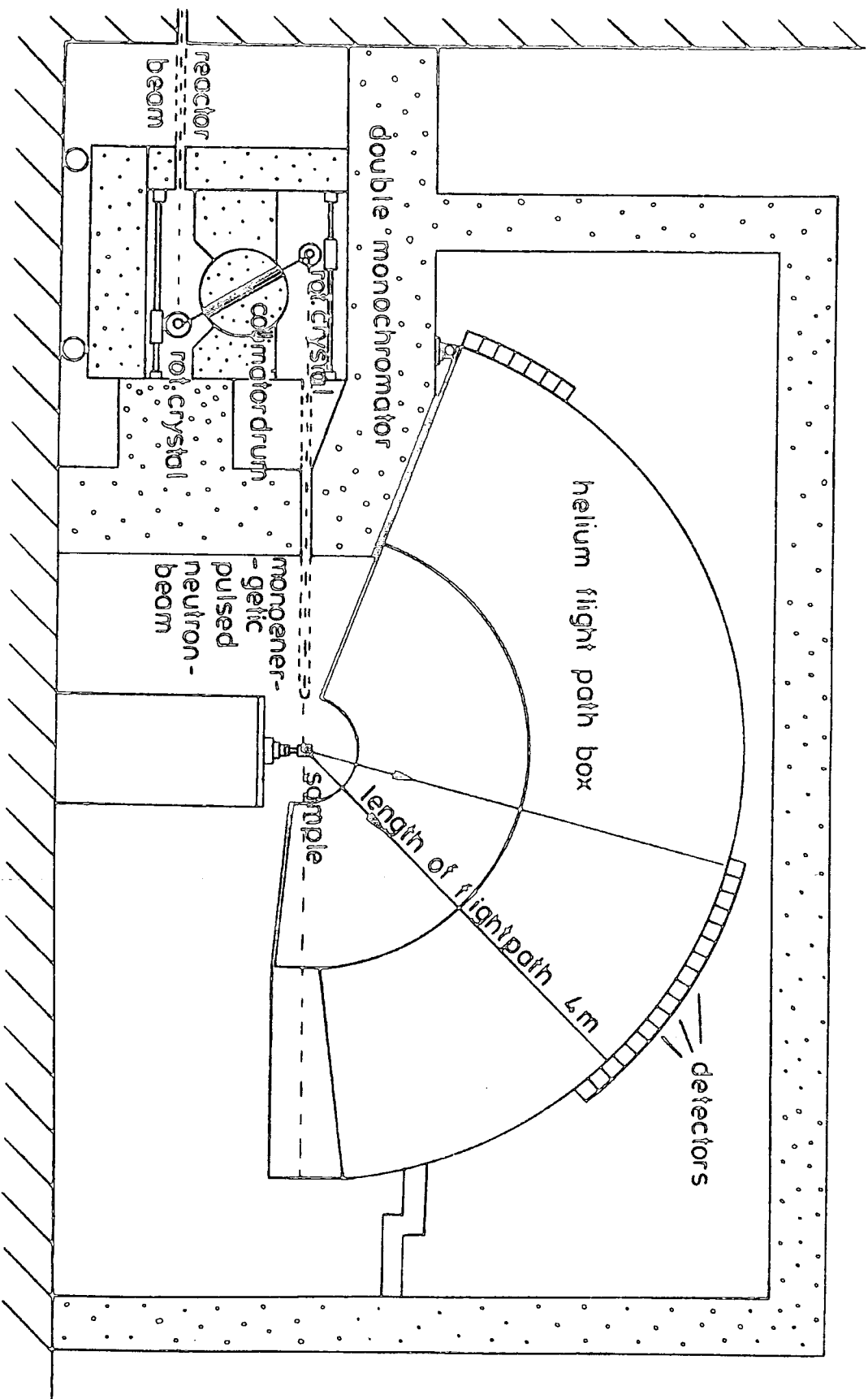
(i) The spectrometer is situated on a thermal beam tube of the High Flux Reactor at the ILL Grenoble, where typically the reactor power is in the order of 56MW (26MW at Harwell). Table 3.4 nevertheless shows that the flux per cm^2 is less than for the Harwell instruments, although to some extent this is mitigated by the larger beam area ($9 \times 4 \text{cm}^2$). The large reduction in flux compared with the initial value may be explained by the long distance between the neutron source and sample (11m), and the higher efficiency of single crystal monochromation.

(ii) Monochromation is achieved by Bragg scattering using two single crystals, one or both of which are rotated, and not by a chopper system such as that employed at Harwell. The incident neutron energy may be selected by choice of crystals and by variation of their relative displacements; spinning the crystal produces a pulsed monochromatic beam.

Double monochromation of the beam is found to afford greatly reduced number of epithermal neutrons and higher order containments (i.e. $\lambda/2$, $\lambda/3$ etc from $\lambda = 2d \sin \theta$; where λ is the wavelength of the monochromated beam, d is the lattice spacing of a given crystal, and θ is the incident angle of the thermal neutron beam relative to that plane).

(iii) Collimators, if required, may be fitted after the rotating crystals, but in general their use is unnecessary as sufficient collimation is provided by the second single crystal.

(iv) There are 37 detector boxes, each containing six 4 atmosphere



dia. 3 (w)

The IN4 Time-of-Flight Spectrometer, ILL Grenoble¹⁵

³He counters (2.5 cm diameter x 15 cm active length), which may be placed in any of 67 positions on the periphery of an aluminium enclosed arc 4m in radius. The highest scattering angle provided is 158.4° and the lowest 8° , whilst 22.5° is the lower limit for angular resolution.

Where full angular resolution is required, it is not possible to use all of the 222 counters simultaneously because the time-of-flight analyser has only 128 inputs. However, when this is not required, up to 6 detectors may be connected in parallel. In the latter case, the detector area is larger than for any of the Harwell instruments, but because of the increased flight path, the number of detected counts is still less.

(v) Data is collected by a Telefunken TR86 system, and may be displayed for each angle as a time-of-flight distribution convoluted with the resolution function of the instrument.

(vi) IN4 is used to best advantage in the down scattering mode (i.e. where neutrons lose energy to the sample), and in this configuration is capable of much greater resolution than 4H5 or 6H. In order to obtain the optimum resolution in this configuration the concept of an "energy window" is introduced. This arises as a result of the finite number of channels available, each corresponding to an equal time-of-flight increment. The relation between energy and time-of-flight is not linear, however, and as time-of-flight increases, the energy spread within each channel becomes wider and resolution consequently poorer. It is advantageous, therefore, to keep increases in the time-of-flight small, so that features of interest occur in the region of the instrument's best resolution, and this may be achieved by having the incident energy only slightly larger than the transition(s) to be investigated. Naturally to operate IN4 in this way requires that the position of the energy transfer(s) must be known approximately in advance, so that a suitable incident wavelength may be selected.

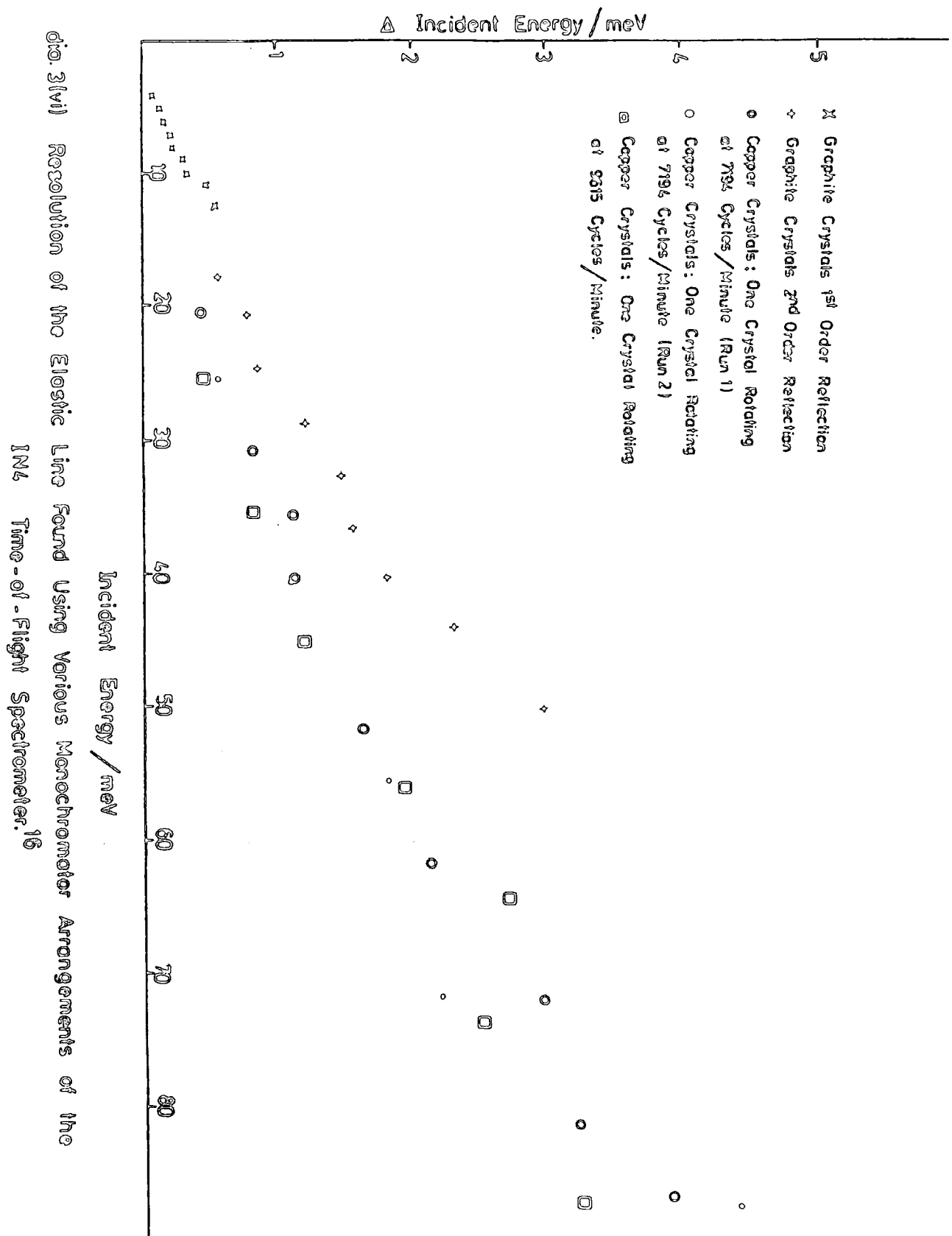


Fig. 3(vii) Resolution of the Elastic Line Found Using Various Monochromator Arrangements of the IN4 Time-of-Flight Spectrometer.¹⁶

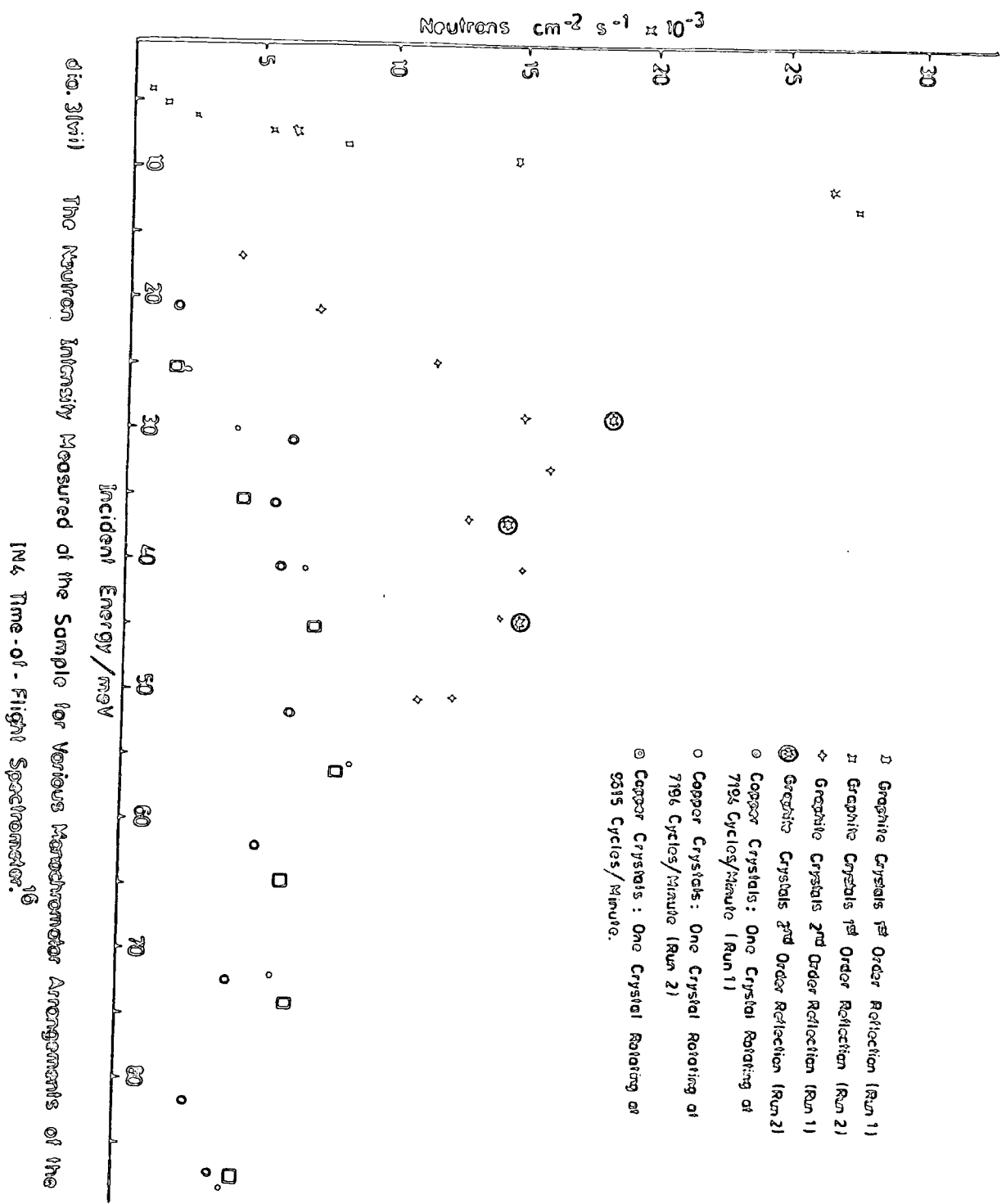


Fig. 3 (iii) The Neutron Intensity Measured at the Sample for Various Monochromator Arrangements of the IN4 Time-of-Flight Spectrometer.¹⁶

(vii) As IN4 is a downscattering instrument, it is possible to use liquid Helium temperature without the depopulation effect giving rise to increased running times.

(viii) Suck¹⁶ has compared resolution and intensity for the various crystal configurations available (dias 3(vi) and 3(vii)). However, it should be noted that because the resolution was measured of the vanadium elastic peak, the instrument was not being used in its highest resolution mode, and consequently the measurements very much correspond to the worst values attainable. Nonetheless, comparison with 4H5 and 6H, is still very favourable (Table 3.4).

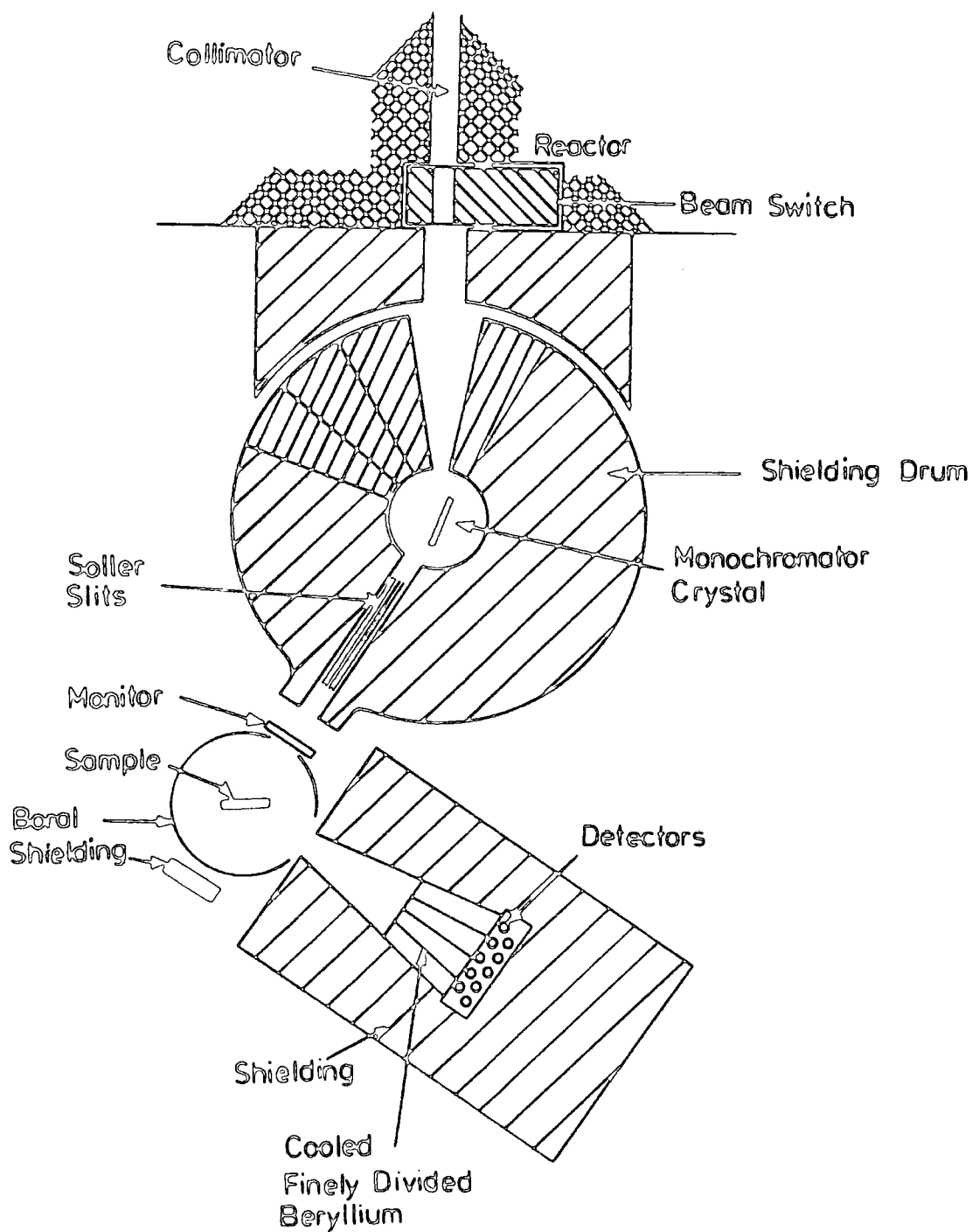
In summary, it was found that with two rotating graphite monochromators in first order reflection, a range of incident energies from 5 to 12.6 meV may be provided: the greatest intensity of any configuration is at the latter value, and the best possible resolution of the instrument at 4meV. With the two rotating graphite crystals in second order reflection, an energy range is covered between 14 and 50.4 meV; whilst with copper crystals (normally one rotating and one in reflection) the region 20 to 87 meV is spanned. Over their comparable energy regions, the intensities for the copper crystals are smaller by a factor of 2 to 2.5 than the graphite crystals, which is attributable to the smaller mosaic spread and lower reflectivity of the former. However, in compensation, the copper crystals give a resolution 1.5 times greater than that of graphite. (Rotating both copper crystals results in an additional intensity loss by a factor of between 2 and 3.)

In the work carried out on IN4 graphite crystals have been exclusively employed, both in first and second order reflections.

4. The Pluto Beryllium Filter Detector (BFD) Spectrometer¹⁷ (dia.3 (viii))

a) Monochromation

The neutron beam passing through the Pluto 7H2L hole is monochromated by Bragg scattering from an aluminium single crystal:



dia 3 (viii) The Pluto Beryllium Filter Detector Spectrometer,
AERE Harwell.

$$\lambda = 2d \sin \theta$$

where λ is the wavelength of the monochromated neutron beam, d is the lattice spacing for a given plane of the aluminium crystal, and θ is the incident angle of the beam relative to the plane.

It may be seen that the required incident energy of the neutrons upon the sample may be obtained by selection of d and θ .

b) Collimation

The incident beam is collimated between the crystal and sample by 2 x 15 cm long soller slits of 0.6° in 2θ angular divergence.

c) Sample Positioning

A sample ($5 \times 5 \text{ cm}^2$) is suspended from a centre loading liquid nitrogen cooled cryostat so that the face of the sample is at $40^\circ \pm 10^\circ$ to the incident beam. Reduced temperature is employed to diminish the effect of multiple quantum scattering (proportional to the square of the temperature from Chapter II).

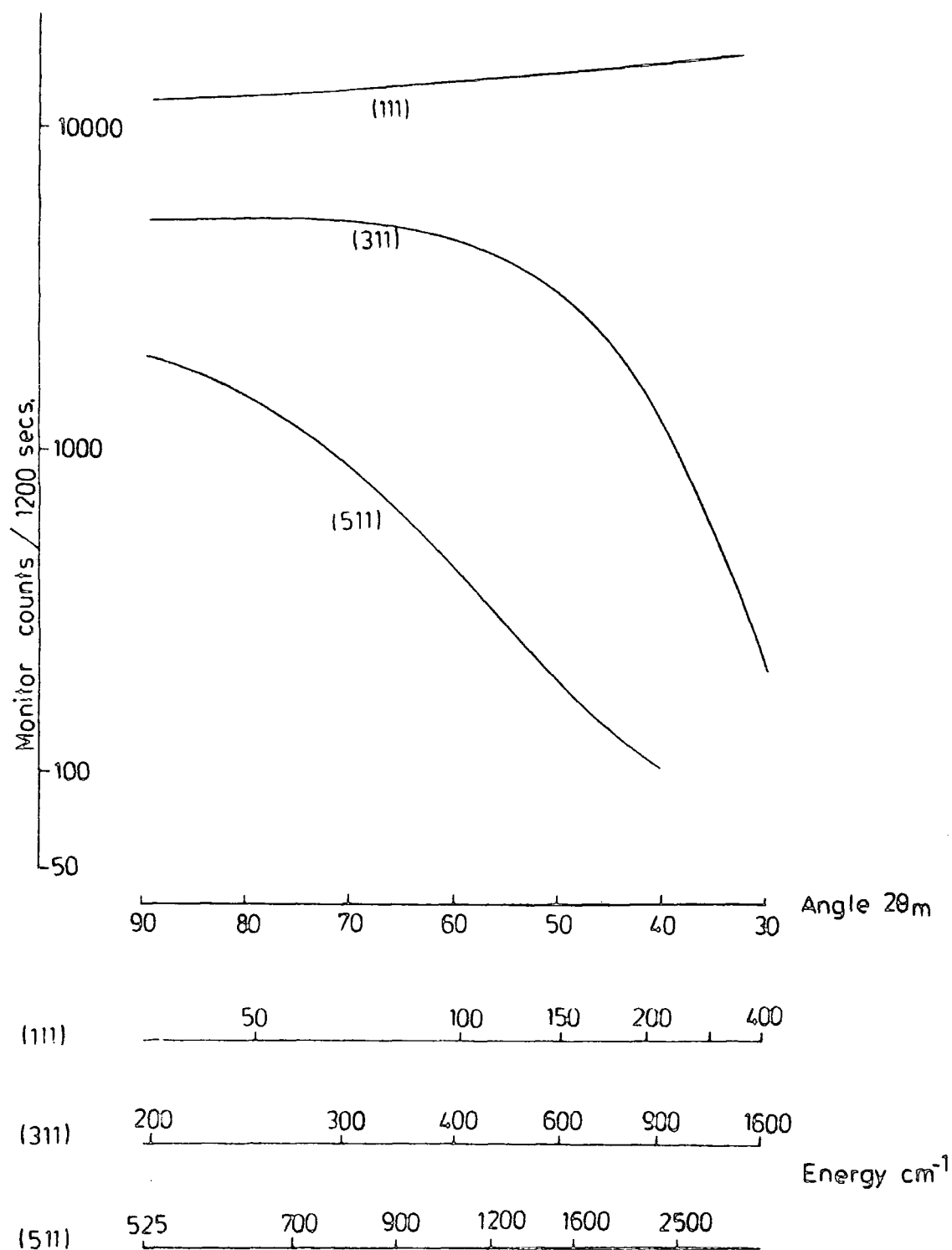
d) Neutron Detection

A fission chamber type monitor placed immediately before the sample gives a measure of the incident neutron flux upon the sample.

Scattered neutrons are detected by nine (5 cm diameter) 2 atmosphere $^{10}\text{BF}_3$ counters positioned horizontally, so that a filter is between their cross-section and the sample. This filter consists of a 4 x 4 matrix of beryllium blocks cooled to liquid nitrogen temperature to increase neutron transmission.

e) Mode of Operation

Having selected the energy range to be studied, and the plane(s) to be used, a PDP8 mini computer calculates the required incident angles for the crystal relative to the beam. The crystal is then turned automatically to each angle in turn, whilst keeping the sample table and beryllium filter in the same orientation at each "take-off" angle.



dia.3(ix) The Relation of Neutron Flux and Monochromator Plane
for the Pluto Beryllium Filter Detector Spectrometer
(AERE Harwell).¹⁷

(The beryllium filter detector is not sensitive to momentum transfer (Chapter II) and as a result is placed at 90° to the incident beam to diminish background.)

Once the machine has positioned at the relevant energy, counting of scattered neutrons takes place, on the basis of either time or monitor counts. The latter option is more generally employed because the numbers of incident neutrons vary according to plane, angle, and also the flux of the incident thermal beam (dia.3(ix)).

Only those neutrons which lose sufficient energy to the sample may be detected (i.e. the BFD is an energy loss instrument), otherwise they cannot pass through the beryllium filter, which has a Bragg cut off at $4.96 \text{ \AA}$ (42 cm^{-1}). Thus peaks in detected scattered neutron counts correspond to transitions in the sample where energy is being absorbed.

f) Plane Selection

The definition of peak heights relative to the background (i.e. signal to noise) is less with a BFD spectrometer than with a T-O-F spectrometer, and the use of 20% scatterers is recommended^{17,18} compared with 10% for the latter.

As the incident energy upon a sample is increased using only one plane, so must the value of the incident angle (θ) be decreased. Towards the high energy end of a plane, values of θ become closer and closer together for linear increments in energy (dia.3(ix)). It is therefore best to use the low energy sections of a plane if resolution is to be optimised. In general, the lower order planes are found to have less resolution but greater flux than higher order planes (see later), and a compromise solution is therefore employed to keep statistical considerations in balance with the needs of resolution:

70 - 250 cm^{-1}	1.1.1. Plane
200 - 750 cm^{-1}	3.1.1. Plane
700 - 1250 cm^{-1}	5.1.1. Plane

g) Response Function

Diagram 3(x) shows variation of intensity plotted as a function of incident energy as the BFD passes through the transition region of a sample. The curve illustrates the combined effects of the transmission of the beryllium block, the variation of counter efficiency with incident energy, and the magnitude of the wave vector of the scattered neutron not being equal to zero (Chapter II). Considering the first factor, it was stated previously that neutrons with energies greater than 42cm^{-1} were not detected. In fact, a plot of beryllium transmittance against energy (dia. 3(x)c) shows that above the "cut off" at 42cm^{-1} , 3.5% of the neutrons are transmitted and that it is not until a second cut-off at 52cm^{-1} , that the beryllium truly becomes opaque.

It is also worth noting at this point, that the transition energy does not correspond to the peak maximum as in "conventional" spectroscopy, but to the "tail" of the BFD band shape. A useful exercise is therefore to calculate a correction factor, relating the peak maximum found, to the actual transition energy represented.

h) Correction Factor

The incident neutron beam of the instrument is not completely mono-energetic as a result of mosaic spread in the aluminium crystal and finite soller slit widths. It is possible to incorporate the effect of this factor, together with the response function mentioned above, into a true correction factor.

Following Gamlen et al¹⁷, the incident energy distribution is assumed to be Gaussian:

$$f(E_i) = (2\pi\sigma^2)^{1/2} \exp(-E_i^2/2\sigma^2)$$

where E_i is incident energy and σ is $\sqrt{\text{variance}}$.

E_i may be related to the incident angle of the neutron beam upon the crystal (θ) by the relations $\lambda = 2d \sin \theta$ and $k_i = \frac{2\pi}{\lambda}$, where k_i is

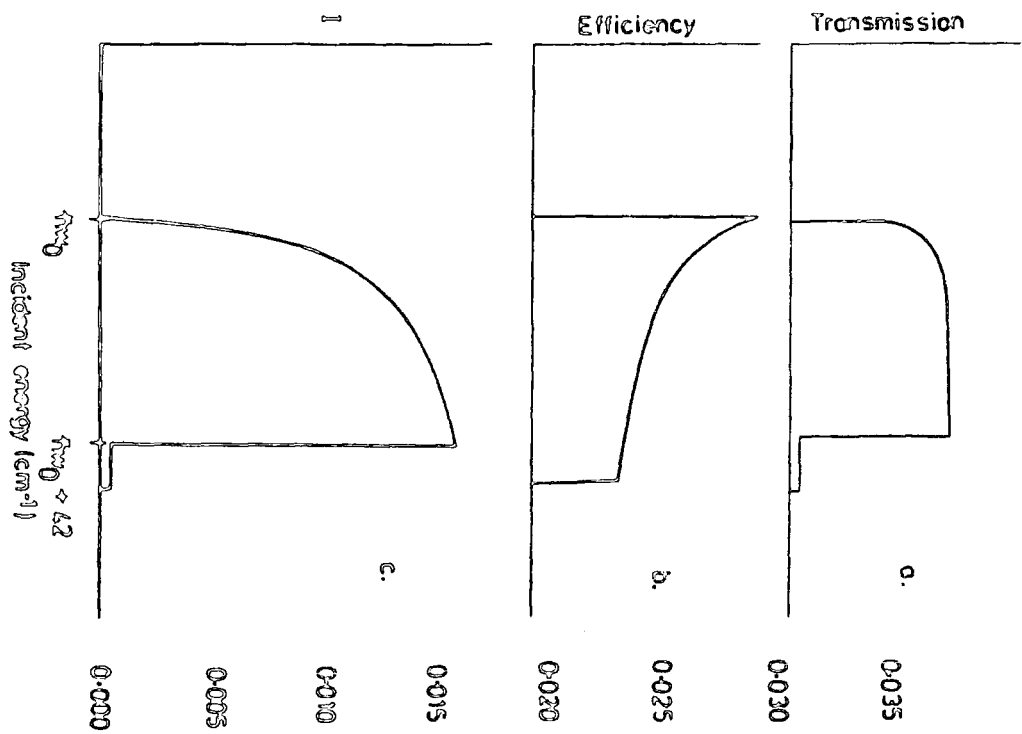


Fig. 3.1 (a) Transmission, (b) Efficiency and (c) Incident Energy vs Incident Energy through a Region of Specular Confining a Transition?

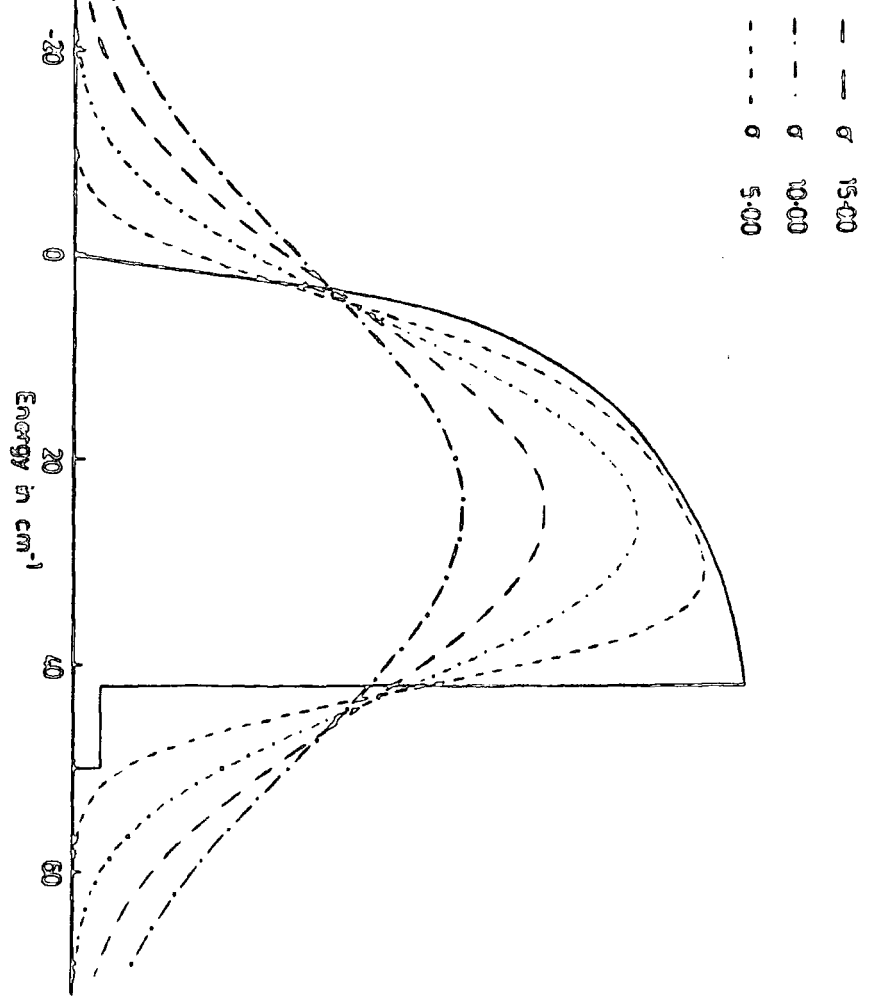
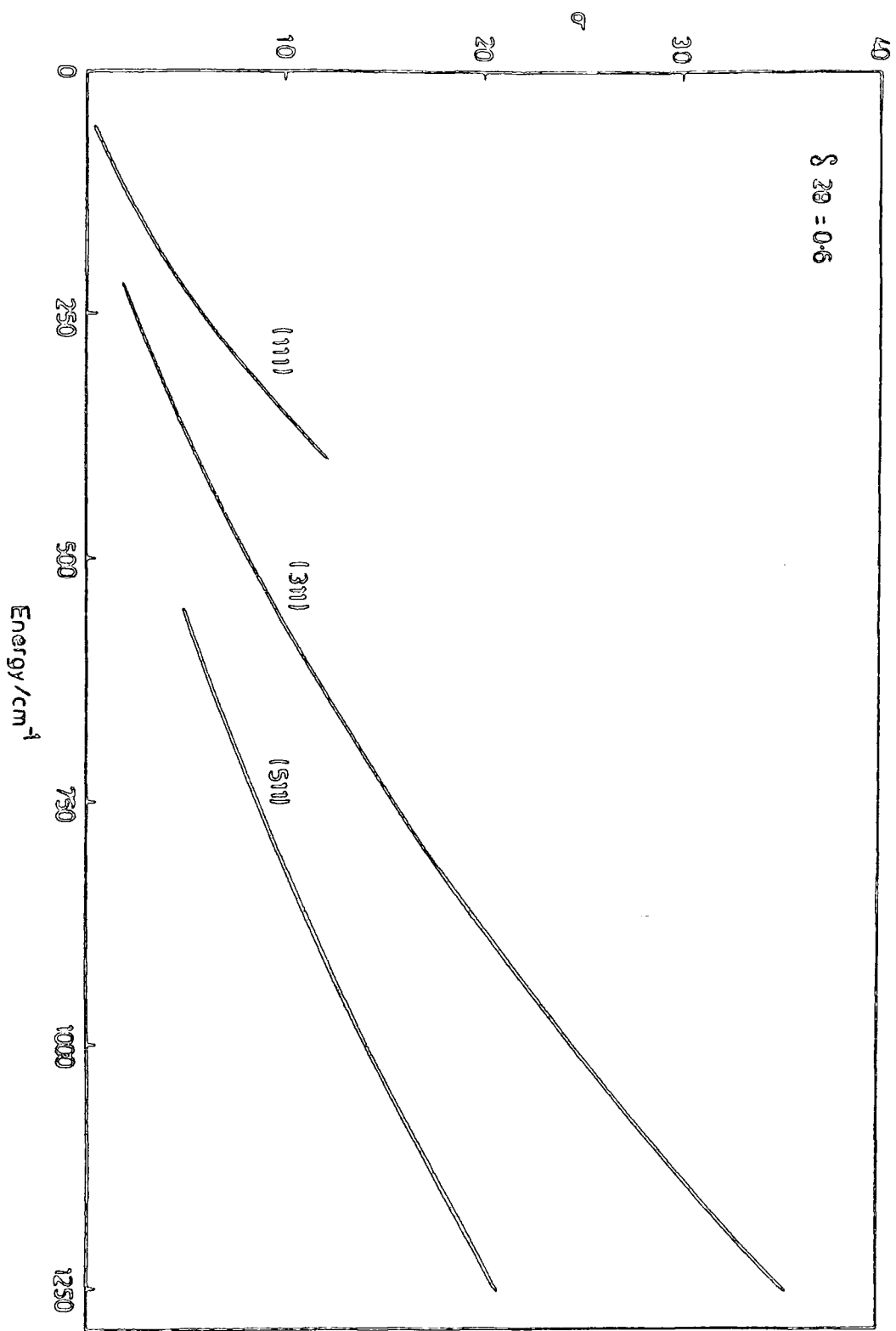


Fig. 3.2 (a) The Boronitium Filler Theoretical Band Shape?



die.33m) Relation of σ (variance) and Energy for the Aluminum 111, 311 and 511 Planes of the Pluto Beryllium Filter Detector Spectrometer.¹⁷

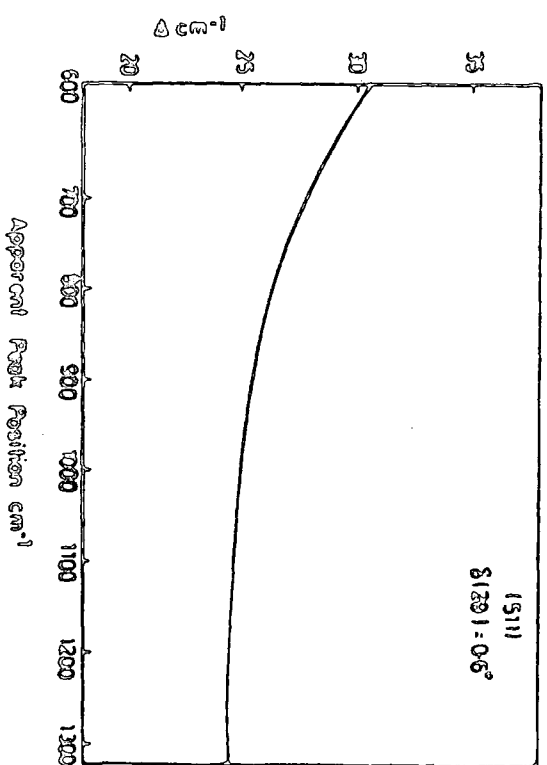
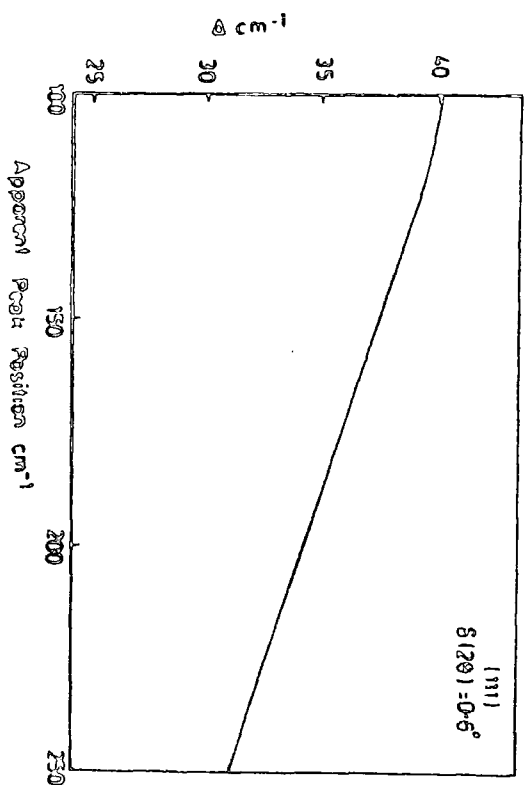
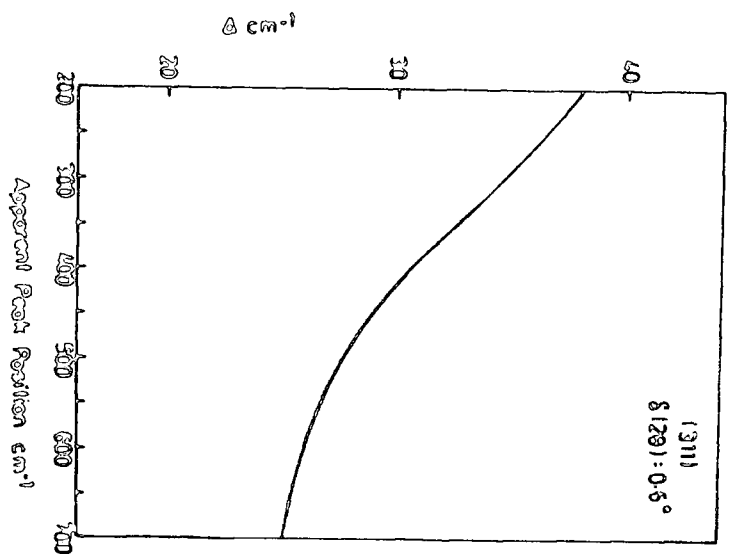


Figure 3.11(iii) Comparison Figures for the Aluminium 111, 311 and 511 Reflections of the Powder Diffraction Filter Detector Spectrometer.

the wave vector of the incident neutron.

$$\text{Thus } E_i = \frac{\hbar^2 k_i^2}{2m} = \frac{\hbar^2 \pi^2}{2m} \cdot \frac{1}{d^2 \sin^2 \theta}$$

where $\hbar$ is Planck's constant divided by 2π , and m is the mass of a neutron.

The major source of error in θ arises from the finite soller slit width

($d\theta$), so that the error in E_i may be stated in terms of the error in θ

using Bragg's law:

$$dE_i = 2E_i \cot \theta d\theta$$

Knowing E_i , $\cot \theta$ and $d\theta$, dE_i maybe calculated, and a value of σ obtained

by making dE_i the value of the Full Width at Half Maximum of the Gaussion mentioned previously.

$$\text{i.e. } dE_i = 2\sigma \sqrt{2} \log_e 2 = 2.35\sigma$$

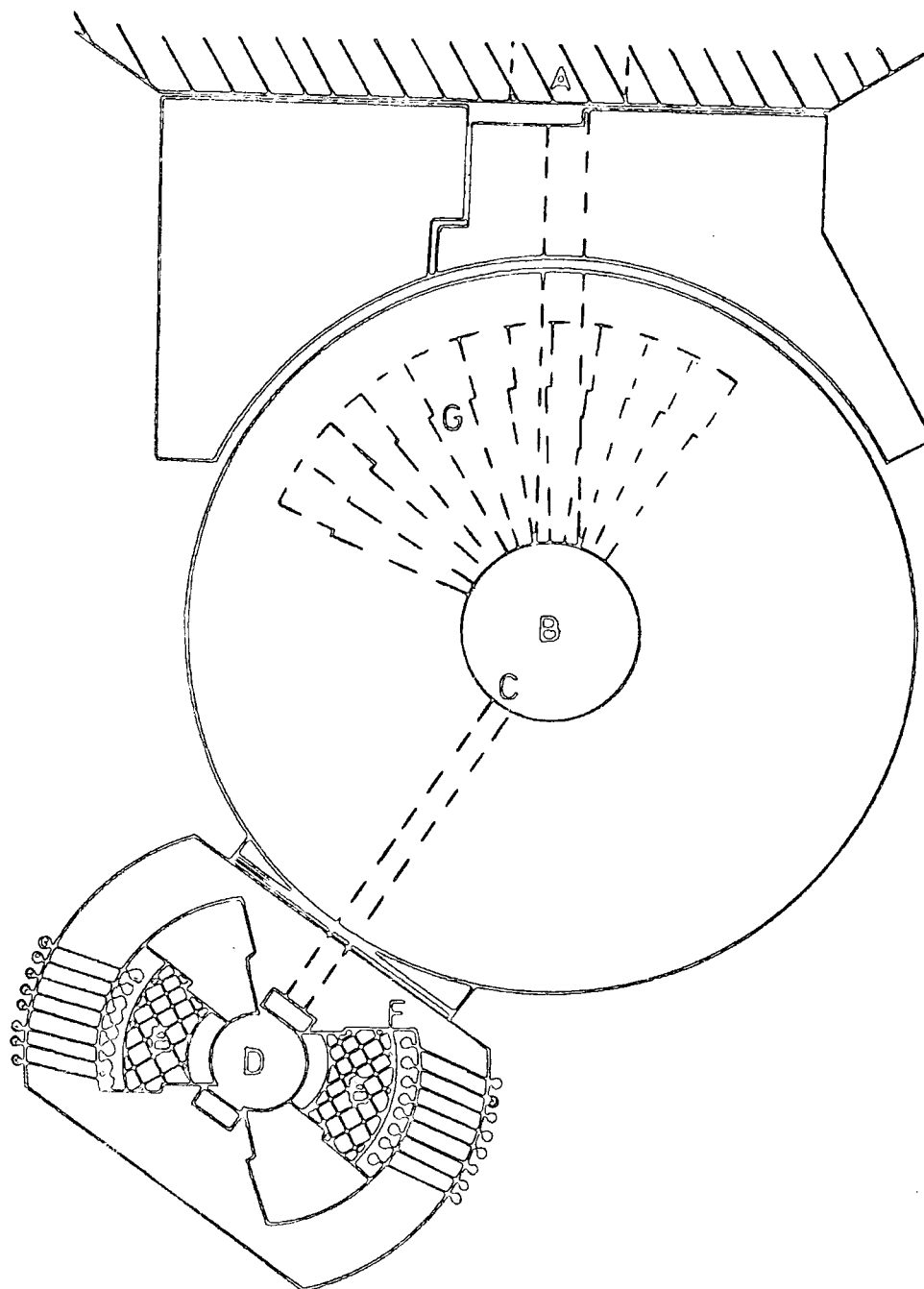
$$\text{and hence } \sigma = \frac{2E_i \cot \theta d\theta}{2.35}$$

From the above equation it may be seen that σ increases as one steps in increasing energy across a plane, by virtue of $\cot \theta$'s reciprocal relation to the decreasing value of θ . Dia.3(xi) illustrates the above case, the convoluted spectrum becoming increasingly symmetrical and the displacement (Δ) of the peak maximum from the actual transition energy decreasing from the Response Function value of 40 cm^{-1} to a minimum value at 24.5 cm^{-1} . The corollary of this process is that the peak becomes broader and resolution poorer. Thus taking the example of the Aluminium 3.1.1. plane (dia.3(xii)), the resolution at 250 cm^{-1} is 42 cm^{-1} ($\sigma=2.5$), whilst at 850 cm^{-1} it has become 55 cm^{-1} ($\sigma=20$).

Dia.3(xiii) shows the correction factors obtained by the above procedure, i.e. the displacement (Δ) of the peak maximum above the true transition energy plotted as a function of incident energy.

5. The Dido Beryllium Filter Detector (BFD) Spectrometer (dia.3(iv))

The Dido instrument operates in a similar manner to the Pluto BFD,



A In-pile collimators

B Monochromator

C Beam shutter

D Sample position

E Be filter blocks (cooled)

F BF_3 detector arrays

G Shielding segments

dia. 3biv) The Dido Beryllium Filter Detector Spectrometer,
AERE Harwell.

TABLE 3.5

Comparison of Instrument Specifications for the Pluto and Dido BFD Spectrometers

Instrument	(i) Neutron flux at sample	(ii) Sample Area	(iii) $\frac{\text{Detector Area}}{\text{(Sample to Detector Distance)}^2}$	A (ii) x (iii)	B (i) x (ii) x (iii)	A/A_{Pluto}	B/B_{Pluto}
Pluto BFD	$9.3 \times 10^6 \text{ n cm}^{-2} \text{ s}^{-1}$ (Peak flux with Aluminum 1.1.1. plane monochromatization and 0.6° collimation)	$5 \times 5 \text{ cm}^2$	$\frac{9 \times [(5/2)^2 \pi] \text{ cm}^2}{36 \text{ cm}^2} = \frac{177}{1296} = 0.14$ (* There are 9 x 10^3 BF ₃ counters mounted "end on")	3.5 cm^2	$3.26 \times 10^7 \text{ n s}^{-1}$	1.0	1.0
Dido BFD	$2 \times 10^6 \text{ n cm}^{-2} \text{ s}^{-1}$ (Estimate based upon the Dido Triple Axis Spectrometer which shares the same (10H) beam hole and also has Aluminum monochromatization. The value given is for peak flux with Aluminum 1.1.1. plane monochromatization and 0.47° collimation)	$6 \times 7 \text{ cm}^2$	$\frac{2 \times [8 \times (41 \times 5)] \text{ cm}^2}{31.5 \text{ cm}^2} = \frac{3280}{2652} = 1.24$ (* There are 16 x 10^3 BF ₃ counters mounted vertically in two banks, each containing eight counters)	52.1 cm^2	$10.42 \times 10^7 \text{ n s}^{-1}$	14.9	3.27

there are, however, some major differences between the two machines:

(i) No figures of flux have been measured for this instrument and the value shown in Table 3.5 is purely an estimate based upon the neighbouring spectrometer.

(ii) Collimation is provided by 11 soller slits each 50 cm long and 0.4 mm thick giving an angular divergence of 0.47° in 2θ . The incident beam produced upon the sample is $6 \times 7 \text{ cm}^2$ and this is about 1.5 times larger than for the Pluto machine.

(iii) The sample is positioned at 55° to an incident beam in a centre loading liquid helium cryostat, which rests in the well formed by two surrounding counter banks. In consequence, movement of the sample table results in the movement of the cryostat and detector banks as an integral unit.

(iv) Each detector bank houses eight (5cm diameter x 41cm active length) 2 atmosphere $^{10}\text{BF}_3$ counters mounted vertically. Only one of the counter banks has been operational during the course of this work, but even in this uncompleted state the detector area is approximately ten times that of the Pluto BFD (Table 3.5).

(v) The values of incident angle of the neutron beam upon the monochromator crystal (θ), and "take-off" angle (ω), to which the sample table moves to receive the incident beam, are calculated on the Harwell computing system and the values obtained as punched tape. The machine is then operated by feeding these energy points defined by θ and ω sequentially into a microprocessing unit via the punched tape.

(vi) The planes used for given energy regions are somewhat different using the Dido instrument compared with those of Pluto as a result of machine limits, i.e. lower energies are obtainable on each plane with the Pluto BFD, and hence the resolution is better on the latter instrument.

The planes used for each energy region are:

96	-	416 cm ⁻¹	1.1.1.Plane
336	-	896 cm ⁻¹	3.1.1.Plane
824	-	1624 cm ⁻¹	5.1.1.Plane

(v) A program based upon the σ curve corrections derived by Gamlen et al.¹⁷ has been produced by Howard¹⁹ for the Dido BFD. This calculates the displacement in energy of the observed peak above the value of the actual transition for a given value of incident energy.

(vi) Spectra measured using the Pluto BFD normalised on monitor counts are in a similar form to optical spectra (Chapter II). This is not the case for the Dido instrument, where a large inherent time-variable background is found to be superimposed upon the true spectrum. The presence of this background may be established from the large variations seen, when comparing the times taken for identical energy points of spectra run, using nominally the same value of monitor counts (often in the order of 10-20 seconds using the Aluminium 3.1.1. plane with 3500×10^3 monitor counts). As the times taken should be approximately the same at constant flux, it becomes necessary to "time normalise", when a "sample" spectrum has subtracted from it that of the "empty container".

If the total number of scattered counts yielded by the "sample" at an energy E, for a given number of monitor counts Z, requiring time t_1 , is S_1 ; then we may write

$$\frac{S_1}{t_1} = \frac{S_S}{t_1} + \frac{S_{EC}}{t_1} + \frac{S_B}{t_1} + \frac{S_{TVB_1}}{t_1}$$

where S_S = counts attributable to the sample
 S_{EC} = counts attributable to the empty container
 S_B = counts attributable to time-dependent machine background
 S_{TVB} = counts attributable to time-variable background

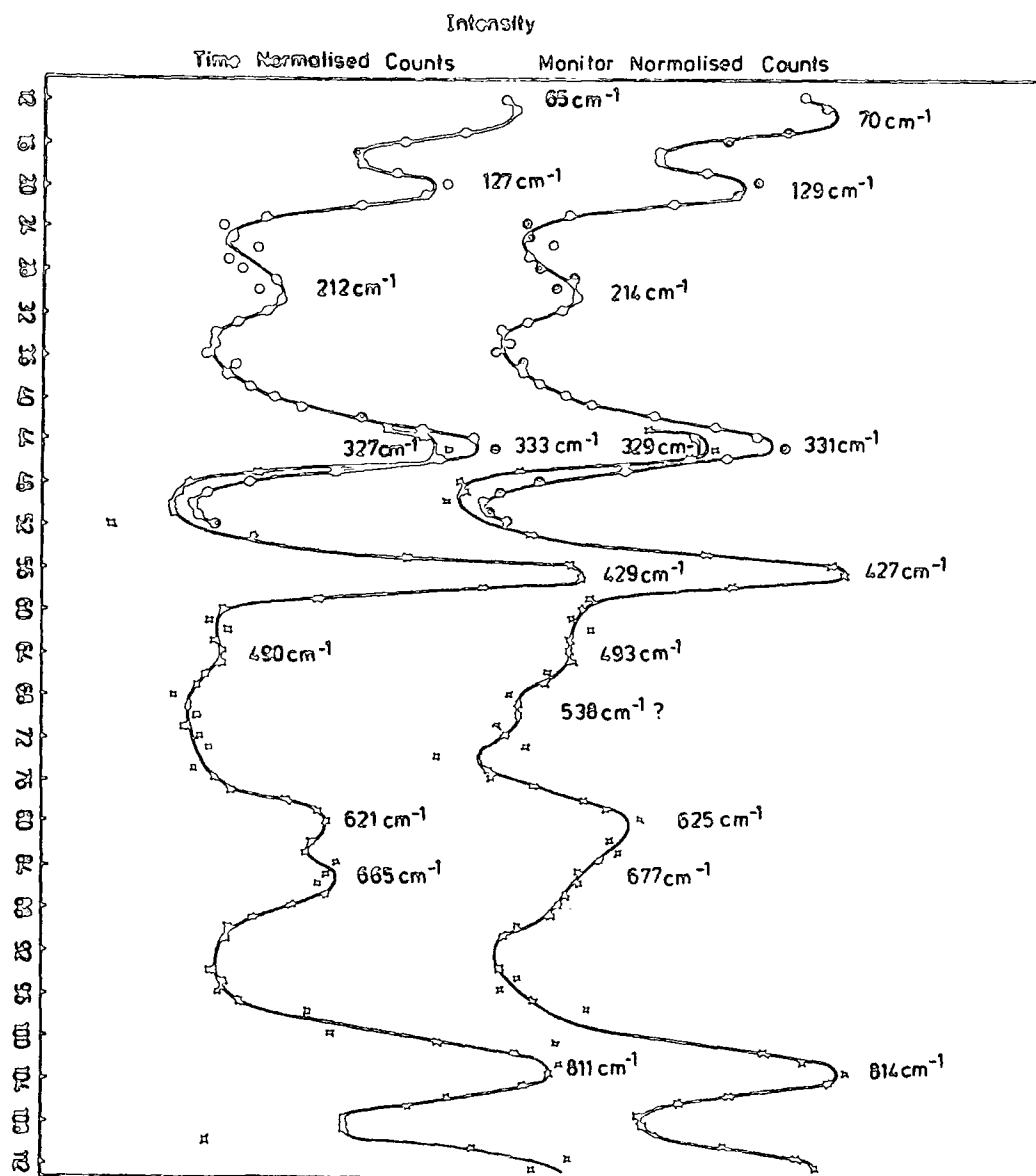
Similarly the total number of scattered counts S_2 , yielded by the "empty" container at energy E, for Z monitor counts requiring time t_2 will be



$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ IR (Silica background subtracted)

0.10 BFD Spectrometer

Incident Neutron Energy / meV



$$\frac{S_2}{t_2} = \frac{S_{EC}}{t_2} + \frac{S_B}{t_2} + \frac{S_{TVB_2}}{t_2}$$

Considering the Pluto instrument $t_1 = t_2$ i.e. $S_{TVB_1} = S_{TVB_2} = 0$ and hence

$$S_S = S_1 - S_2$$

In the case of the Dido machine $t_1 \neq t_2$, therefore we introduce an "average time" $(t_1 + t_2)/2$ into the subtraction

$$\text{i.e.} \quad \left(\frac{S_1}{t_1} - \frac{S_2}{t_2} \right) \left(\frac{t_1 + t_2}{2} \right) = \left[\frac{S_S}{t_1} + \left(\frac{S_{TVB_1}}{t_1} - \frac{S_{TVB_2}}{t_2} \right) \right] \left(\frac{t_1 + t_2}{2} \right)$$

If the assumption is now made that at an "average time" the time-variable backgrounds are not too dissimilar, the above becomes

$$S_S = \frac{S_S}{t_1} \left(\frac{t_1 + t_2}{2} \right)$$

Obviously the subtracted spectrum obtained will be subject to large errors if the values of the two time-variable backgrounds are radically different at average time. However, experience has shown this rarely the case, and in general, the time normalised subtracted spectrum is found to be a "smoothed" version of the uncorrected one (dia.3(xv)).

B. Data Analysis

Unlike BFD spectra, which can be obtained in a form immediately comparable with optical spectra by plotting "detected neutron counts per 1000n monitor counts" versus energy, "raw" T-O-F data require several corrections to be made and then formulation in terms of various useful functions (e.g. $\rho(\omega)$) before comparison. To carry out these corrections/formulations, several programs have been developed at AERE Harwell.

1. Clodop and Prescat²⁰

The data stored by Cassandra^{8,9} is recorded onto DEC tape when a run has been completed, and is then processed on the AERE 370/165 computer.

"Clodop" produces a line-printer output of counts against channel number for each angle of each sample position and also for the monitors.

"Prescat" uses the Clodop data to calculate the parameters required in the next stage of data analysis, i.e.

- (i) the incident reciprocal velocity
- (ii) the infinite energy channel (i.e. the time channel which would receive neutrons taking zero time to travel from the sample to the detector)
- (iii) the total time each position was in the neutron beam
- (iv) the total counts in each monitor
- (v) the total counts in the vanadium elastic peak for each angle
- (vi) the centre of gravity (in channels) for each vanadium elastic peak

2. Circa^{20,21}

Circa initially corrects the counts produced by prescat according to the equation:

$$\text{Corrected counts (y)} = \left(\frac{a_1 C_1}{V_1} - \frac{a_2 C_2}{V_2} \right) \frac{N\sigma_v}{N\sigma_s} \frac{1}{\delta\tau} \frac{1}{a_3}$$

where

$$a_1 = \frac{\text{total counts in monitor 1 in the vanadium position}}{\text{total counts in monitor 1 in the sample position}}$$

$$a_2 = \frac{\text{total counts in monitor 1 in the vanadium position}}{\text{total counts in monitor 1 in the background position}}$$

$$C_1 = \text{Sample counts per channel}$$

$$C_2 = \text{Background counts per channel}$$

$$V_1 = \text{Total counts in the vanadium elastic peak for the sample run}$$

$$V_2 = \text{Total counts in the vanadium elastic peak for the background run}$$

$$(V_1 = V_2 \text{ if sample and background run at the same time})$$

$$N\sigma_v = \text{Vanadium cross-section x number of vanadium atoms cm}^{-2}$$

$$N\sigma_s = \text{Sample cross-section x number of sample atoms cm}^{-2}$$

$$\delta\tau = \text{Channel width in } \mu \text{ second m}^{-1}$$

$$a_3 = \text{corrected counts factor (} \propto \text{ sample orientation, incident reciprocal velocity and angle)}$$

The counts y are then corrected for the energy dependence of the counter efficiency:

$$y_c = \frac{y e_{\tau_0}}{e_{\tau}}$$

where e_{τ_0} = counter efficiency at incident reciprocal velocity (τ_0),
and e_{τ} = counter efficiency at reciprocal velocity (τ)

Finally a line printer output is produced of sample counts (C_1), background counts (C_2), corrected counts (y), efficiency corrected counts (y_c) and time-of-flight for each channel number. In addition, for each channel there is produced a value of:-

(i) ALPHA from

$$\alpha = \frac{\hbar^2 Q^2}{2MK_B T}$$

where $\hbar$ = Planck's constant / 2π

Q = scattering vector

M = mass of the sample element

K_B = Boltzmann's constant

T = sample temperature in K

As $Q^2 = k_0^2 + k^2 - 2k_0 k \cos \theta$, where k_0 and k are the neutron wave vectors before and after scattering then:

$$\alpha = \frac{\hbar^2}{2AK_B T} \cdot 1.5079 \times 10^{46} \left(\frac{1}{\tau^2} + \frac{1}{\tau_0^2} - \frac{2 \cos \theta}{\tau \tau_0} \right)$$

where τ_0 and τ are the reciprocal velocities before and after scattering, and A is the atomic weight of the sample element in AMU.

(ii) BETA from

$$\beta = \frac{\hbar \omega}{K_B T} \quad \text{and} \quad \hbar \omega = \hbar^2 \left(\frac{k^2 - k_0^2}{2m} \right) = \Delta E, \text{ so that}$$

$$\beta = \frac{2.54 \times 10^{22} \hbar^2}{2mK_B T} \left(\frac{1}{\tau^2} - \frac{1}{\tau_0^2} \right)$$

where m = neutron mass (1.6748×10^{-24} g)

ω = change in radial frequency resulting from the scattering event.

ΔE = energy gained by the scattered neutrons

(iii) Q (measured in $\text{\AA}^{-1}$)

$$Q = 1589 \sqrt{\frac{1}{\tau^2} + \frac{1}{\tau_o^2} - \frac{2 \cos \theta}{\tau \tau_o}}$$

(iv) Q^2

(v) ENERGY in meV

$$E = 5.2271 \times 10^6 \left(\frac{1}{\tau^2} - \frac{1}{\tau_o^2} \right)$$

(vi) ENERGY in optical wave number

$$\text{cm}^{-1} = 8.066E$$

(vii) $S(\alpha, \beta)$

$$S(\alpha, \beta) = \frac{K_B \times 10^{-16} \tau^4 e^{\beta/2} T y_c}{m C_2}$$

(viii) $P(\alpha, \beta)$

$$P(\alpha, \beta) = 2\beta \sinh \beta/2 \frac{S(\alpha, \beta)}{\alpha}$$

3. The Roundabout Programs²²

(i) Dougal

A "smoothed" spectrum is produced by the method of cubic splines²³.

A listing is then generated of the positions of peaks and shoulders versus time-of-flight.

(ii) Dylan

The areas and half widths of the quasi-elastic peaks are found from $s(\alpha, \beta)$ (calculated in circa) for various values of β , having previously subtracted a suitable background.

(iii) Florence

The program evaluates $\lim_{\alpha \rightarrow 0} \left(\log_e \frac{S(\alpha, \beta)}{\alpha} \right)$

and then the frequency distribution function

$$\rho(\beta) = 2\beta \sinh \beta/2 \left(\lim_{\alpha \rightarrow 0} \frac{S(\alpha, \beta)}{\alpha} \right)$$

The evaluation of this function allows for the comparison of T-O-F data with that for optical spectroscopy, the 'Q' dependence having been removed (see Chapter II).

(iv) Zebedy

This is a program for plotting pairs of variables from the various data forms listed on the circa hard copy output. The most usual combination plotted is $P(\alpha, \beta)$ versus Energy (cm^{-1}).

C. Experimental Techniques

1. Model Compound Containment

A container is required which scatters almost totally elastically, possesses a fairly featureless inelastic region, and does not absorb neutrons. Of the materials which fulfil these criteria, the most commonly used are aluminium and silica, of which the former has the smaller cross-section and least structured inelastic spectrum. Consequently aluminium is used whenever possible.

When dealing with solids which were stable both with respect to air and vacuum, sachets were employed made from 0.05mm thick aluminium foil.

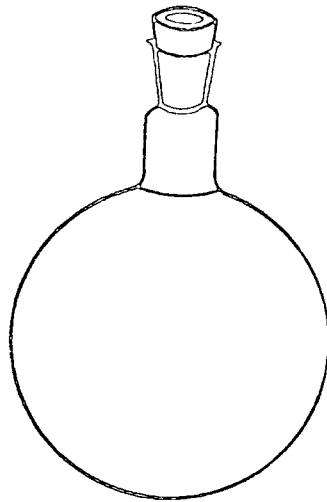
For solid compounds which were air/water sensitive, but unaffected by pumping, air-tight sample holders (dia.3(xvi)a) were made from two thin walled silica plates (0.5 mm thick x 5 cm diameter). These were equipped with a B10 socket into which a brass stopper could be sealed with picene. Within the stopper was a screw and dowty seal, which upon release allowed for evacuation and pressure equalisation within a Time-of-Flight sample changer.

A second type of air-tight silica cell was required for unstable solids, and for liquids (dia.3(xvi)b). This was produced from two thick wall silica plates (1mm thick x 5 cm diamter), and possessed four "dimples" which acted as spacers between the front and back plates. Once filled via a B10 cone, a cell of this type was sealed under nitrogen, and was then capable of withstanding being mounted in an evacuated sample changer.

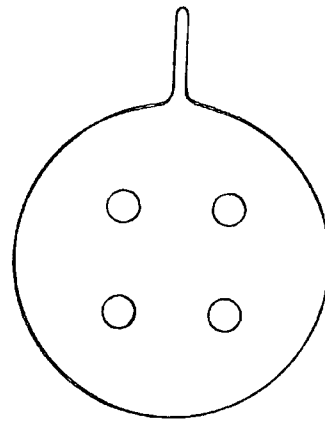
TABLE 3.6

The Applicability of Surface Sample Containers to Instrument and Experiment

Type of Container	Experiment to which Applicable	Instrument to which Applicable
Circular Flat Type (dia.3 (xvii))	Zeolite + Hydrogenous gas	4H5, 6H and Pluto BFD
Rectangular Flat Type (dia.3(xviii))	Zeolite + Hydrogenous gas	4H5, Pluto and Dido BFDs and IN4
Cylindrical Type with Cu/Al Weld I (dia.3 (xix))	Zeolite + Deuterated gas	6H
Cylindrical Type with Cu/Al Weld II (dia.3 (xx))	Zeolite + Deuterated gas (Metal Powders)	Pluto and Dido BFDs, and IN4
Cylindrical Type: Aluminium Weld (dia.3 (xxi))	Zeolite + Deuterated gas (Metal Powders)	4H5, Pluto and Dido BFDs



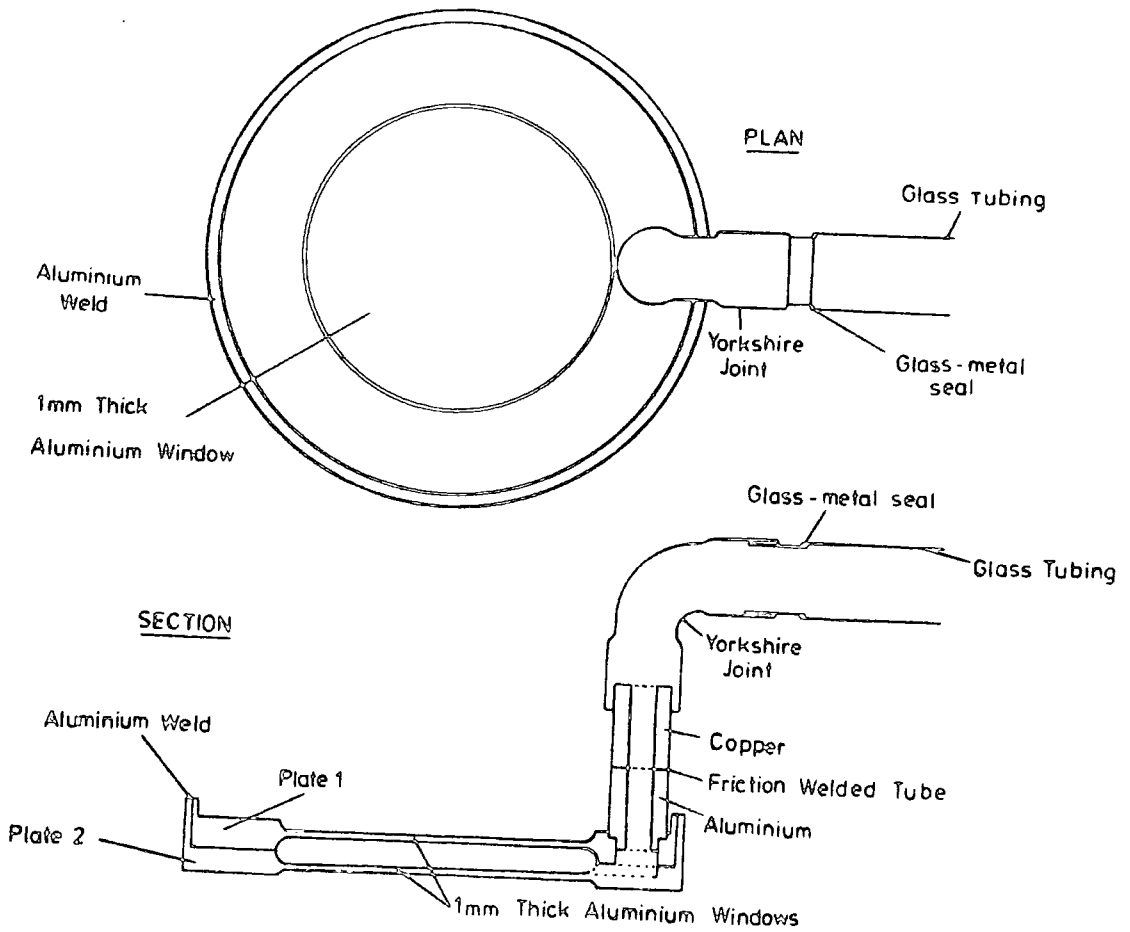
(a) Thin Wall (Powder) Type



(b) Thick Wall (Liquid) Type

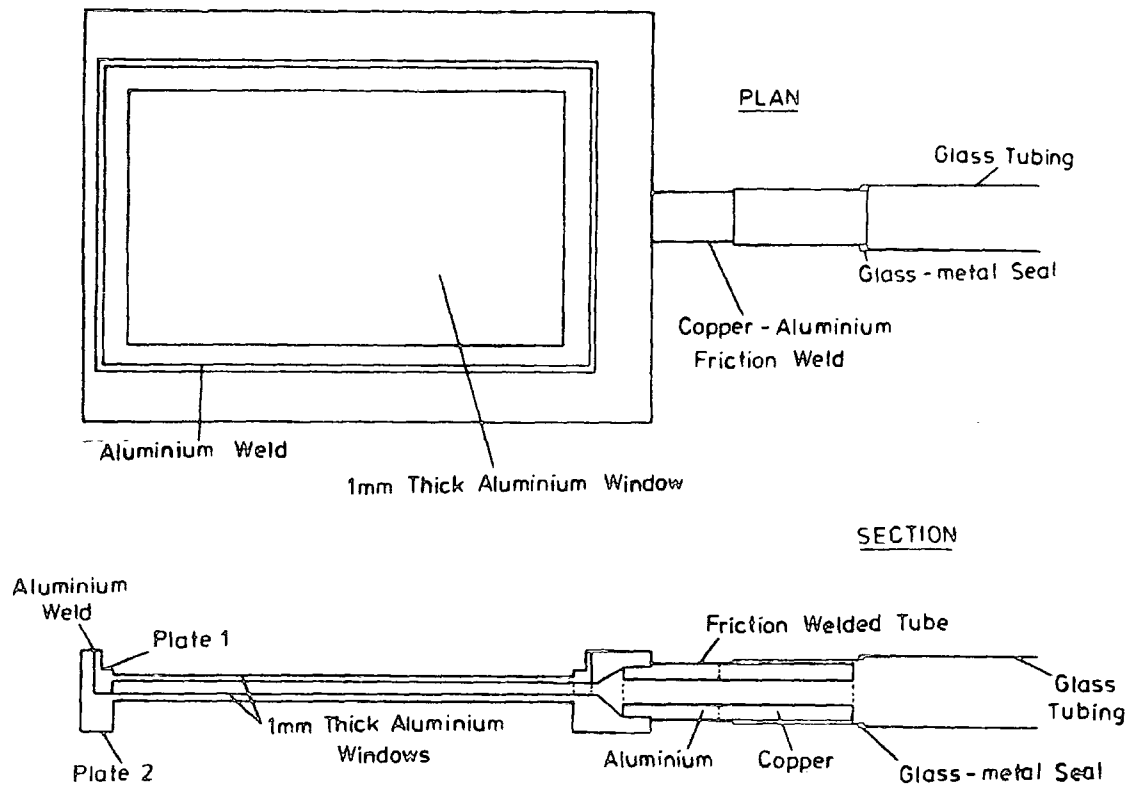
dia. 3(xvi)

Silica Sample Cells Used for Model Compound Containment

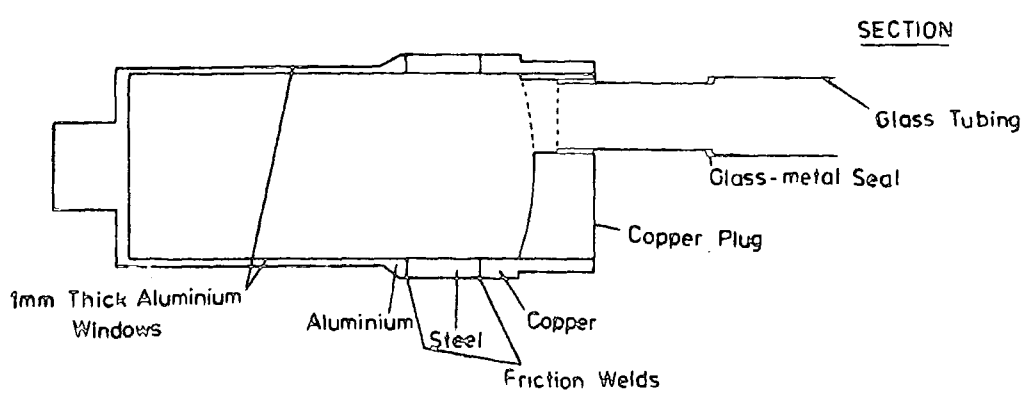


dia. 3(xvii)

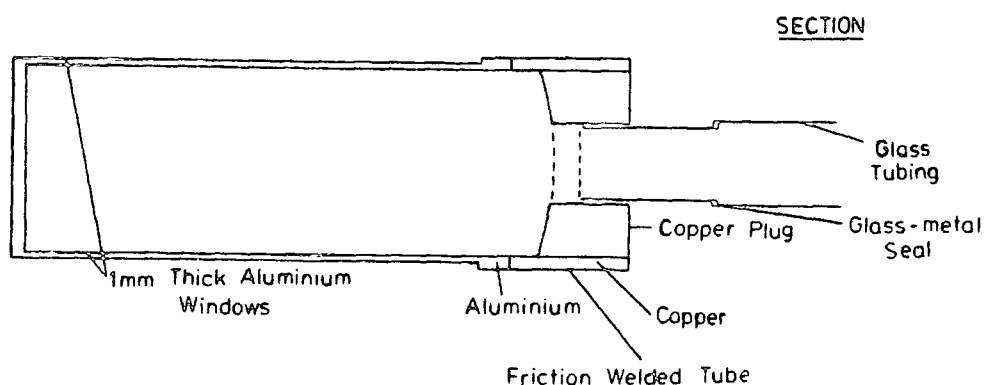
Sample Cell for Zeolite Containment: Circular Flat Type



dia.3(xviii) Sample Cell for Zeolite Containment: Rectangular Flat Type



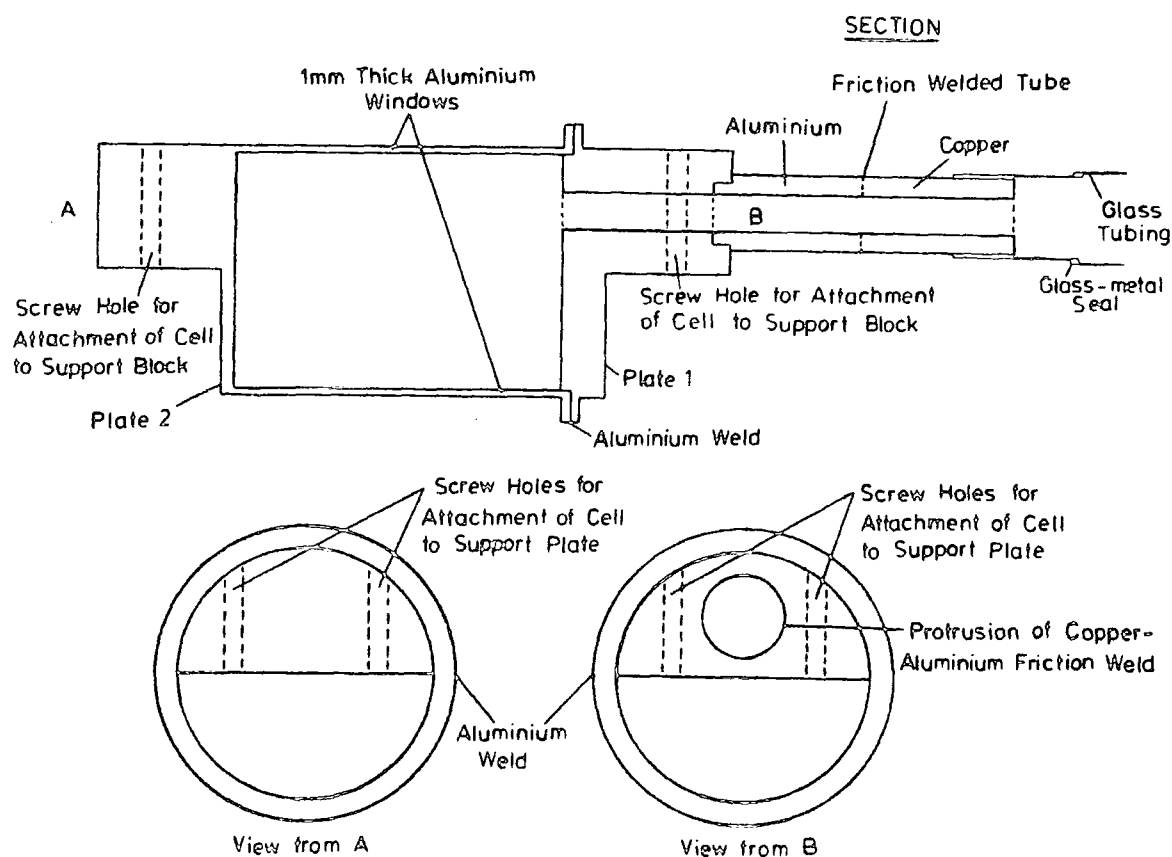
dia.3(xlx) Sample Cell for Zeolite Containment: Cylindrical Type
with Copper - Steel - Aluminium Friction Weld I



dia.3(xx)

Sample Cell for Zeolite Containment:

Cylindrical Type with Copper - Aluminium Friction Weld II



dia.3(xxi)

Sample Cell for Zeolite Containment:

Cylindrical Type with Aluminium Weld

2. Surface Sample Containment

In the case of surface samples, the least featured inelastic region possible is necessary, because they are in general, low scatterers. As a result of this requirement, all surface experiments were carried out using aluminium containers.

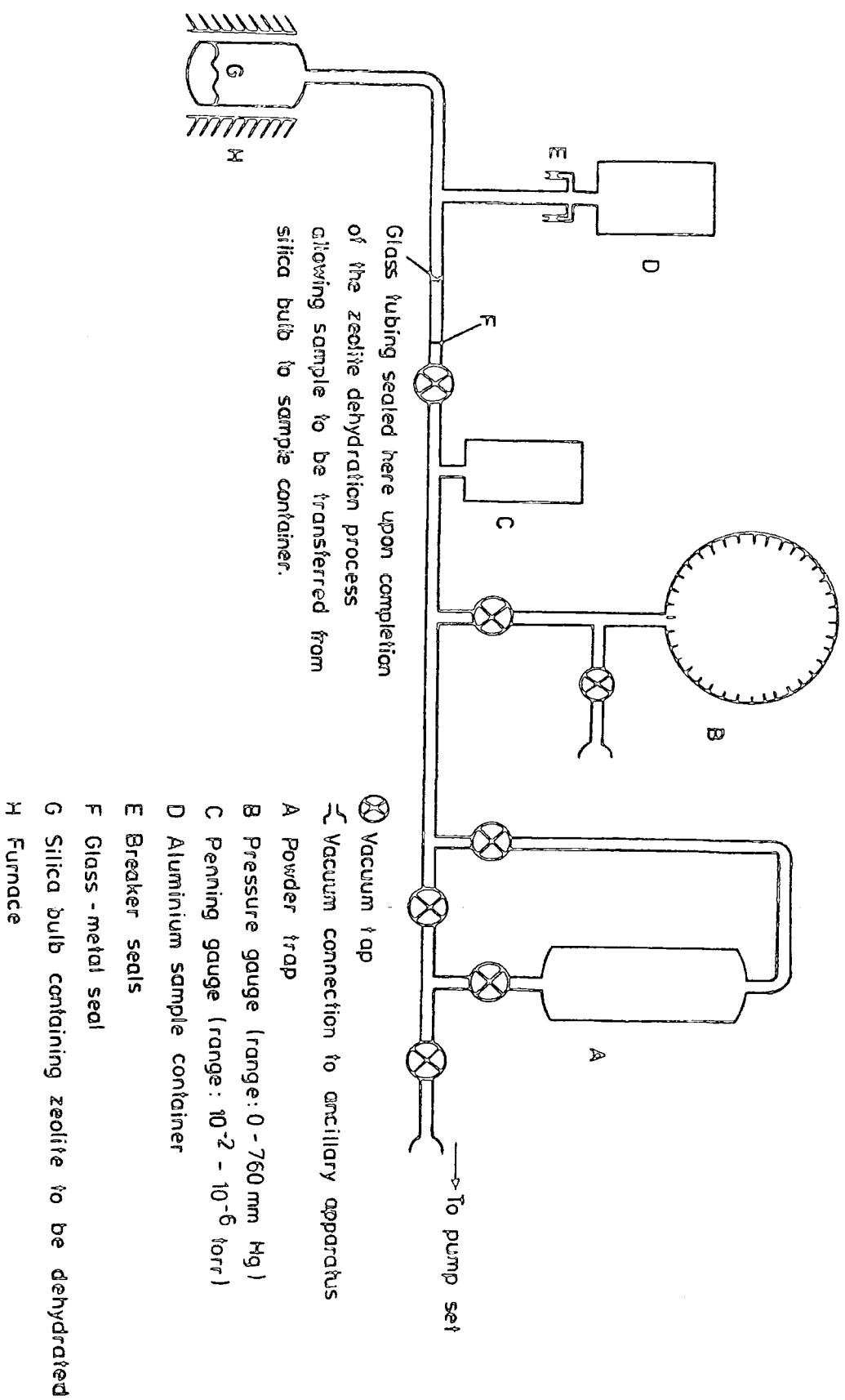
A second demand of surface experimentation was the need to maintain the cell in an evacuated state. In order to produce a leak-tight cell which could be pumped out, one of two methods of construction was employed:-

- (i) The cell was produced in two halves which were welded together, and then a copper/aluminium friction weld (bored out as a tube) was welded onto the integral sample can.
- or (ii) the container was made by boring out a large diameter copper/aluminium friction weld.

The employment of the friction weld facilitated the attachment of a glass to metal seal, by which the whole assembly could be joined to a vacuum line. Non-uniform design of sample changers and cryostats, and the different scattering properties of the systems under investigation, made it necessary to design several different types of sample cell (Table 3.6).

3. Preparation of Surface Samples

Zeolite samples were initially evacuated at room temperature, in a large diameter (7cm) silica bulb, by means of an oil diffusion pump set. (The experimental set up is shown in dia.3(xxii)). When the pressure, measured by a penning gauge at the pump head, was below 10^{-5} Torr slow heating was applied by means of a cylindrical furnace. Care was taken to ensure that the pressure in the system never exceeded 10^{-3} Torr, as the temperature was raised incrementally to 723K. At this temperature, heating was continued for several hours until an ultimate



dia3 (xiii)

The Vacuum Line Used in the Dehydration of Zeolite Samples

vacuum better than 10^{-5} Torr was attained. Heating was then terminated and the bulb allowed to regain ambient temperature.

Next, both bulb and sample container were sealed off from the main body of the vacuum line, and the zeolite powder (still under vacuum) was transferred by shaking into the sample cell. The latter was then sealed off from the bulb and its spectrum measured.

In order to introduce a gas to the zeolite, it was necessary to attach the sample container to a gas-handling system by means of a glass breaker-seal. The gas-handling system was then evacuated prior to being filled with the requisite gas. Upon breaking the seal, by the manipulation of ball bearings using a magnet, gas was admitted to the cell. After adsorption had been accomplished, the container was re-sealed below the breaker-seal and its spectrum re-measured on the spectrometer.

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CHAPTER IV

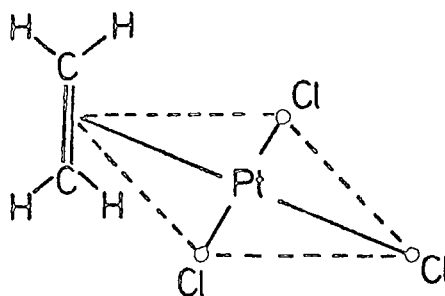
SQUARE PLANAR PLATINIUM COMPLEXES CONTAINING

π -BONDED ETHYLENE

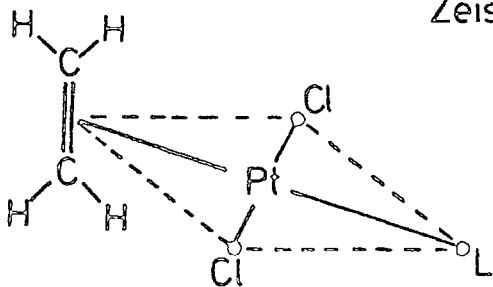
A. Introduction

In order to facilitate later INS spectroscopic studies of ethylene adsorbed on zeolite surfaces, it is advantageous to investigate metal-olefin interactions in systems which have previously been well characterised. In this context, compounds of the type $\text{cis- and trans- PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$ (where L is a ligand) provide excellent models.

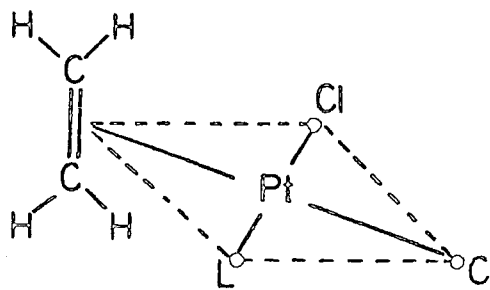
The structures of the complexes may be thought of as being derived from Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$, which is square-planar:



Zeise's salt



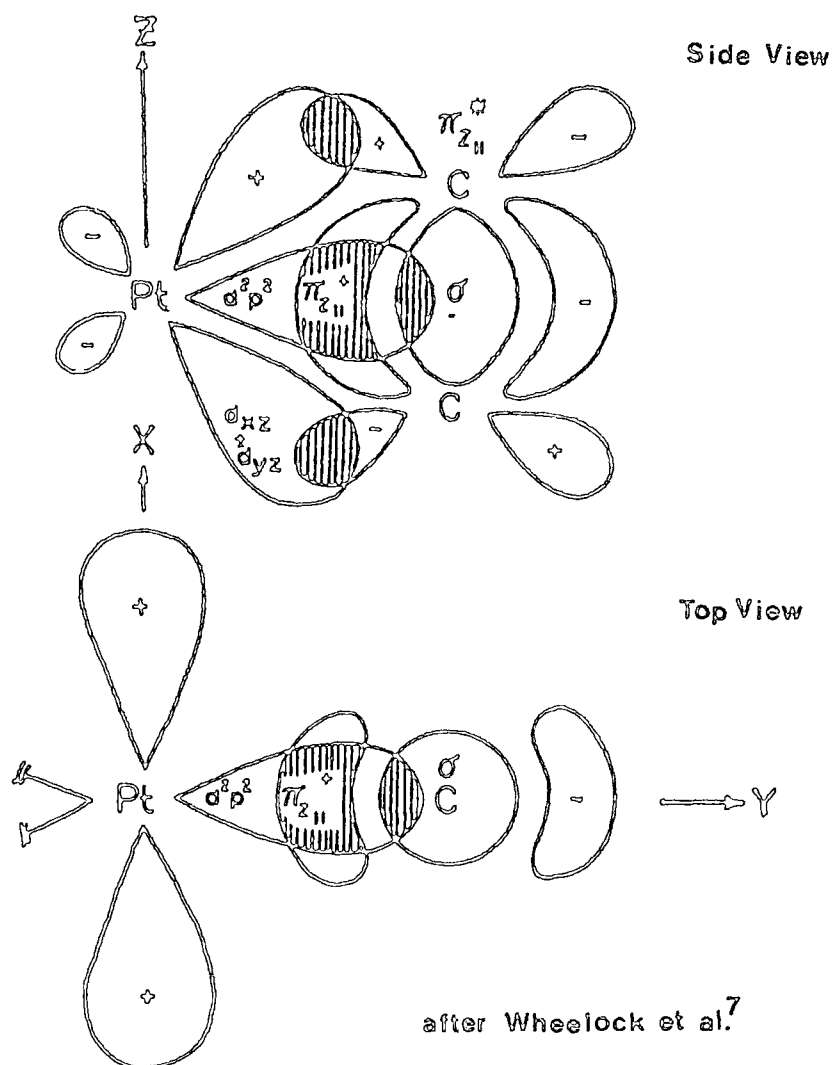
Trans complex



Cis complex

X-ray diffraction studies of Zeise's salt¹⁻⁴ have shown that the olefin group is oriented perpendicularly to the plane, the bonding between the platinum and the olefin being described in terms of the Dewar-Chatt-Duncanson model^{5,6} as refined by Wheelock et al.⁷ This postulates that for divalent platinum complexes, a σ bond, formed by overlap of a $5d^{26p^2}$ hybrid orbital (formed from the d_{xy} , $d_{x^2-y^2}$, p_x and p_y orbitals of the metal) with the π orbital of ethylene, is supplemented by a π back-bond, resulting from

overlap of a filled metal d orbital and the ethylene antibonding π^* orbital. Both the in-plane d_{xy} and out-of-plane d_{xz} orbitals of platinum are filled, and are therefore available for back-bonding. However, in the latter case there is the further possibility of hybridisation between the metal's filled d_{xz} and empty p_z orbitals to produce a filled hybrid with lobes in the direction of the olefin ligand, and an empty hybrid directed away from the ethylene molecule. Such hybridisation ($5d6p$) is considered to allow greater d_{π} overlap with the olefin π^* orbital than that possible with d_{xy} or d_{xz} orbitals alone^{6,7}, calculations⁸ having indicated that only a small amount of p_z character is required for this effect to become appreciable. Confirmatory evidence that back-bonding similar to that outlined above does take place has been afforded by neutron diffraction studies of Zeise's salt^{9,10}. These have shown the ethylene molecule to have lost planarity, with the hydrogen atoms bending symmetrically away from the central platinum atom, as a result of the assumption of some sp^3 character by the carbon atoms.



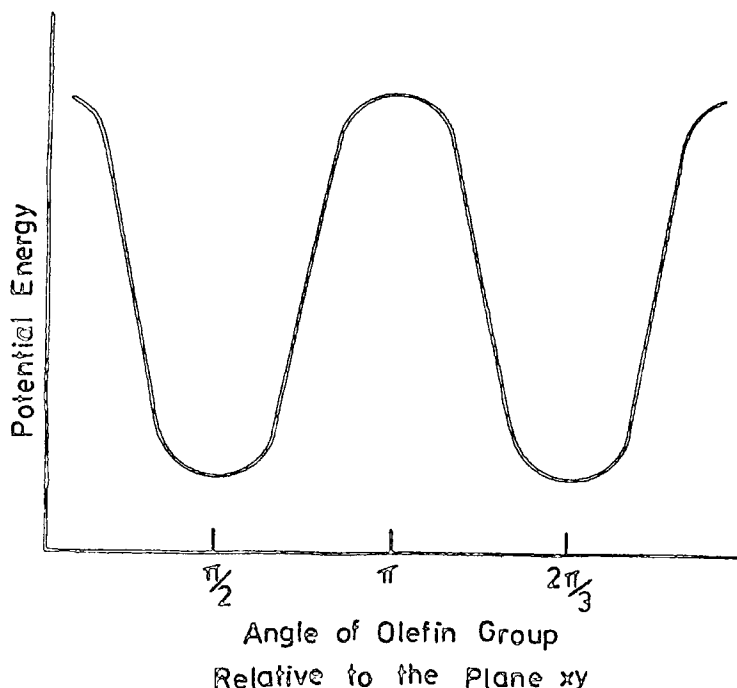
Rotation of the olefin occurs at room temperature¹¹ and has been proved, by variable temperature ¹H and ¹³C NMR¹², to take place about an axis perpendicular to the carbon-carbon bond. A model suggested by Cramer¹³ may be invoked to explain the presence of a potential barrier to this motion; whereby, on rotation, whilst the σ bond is relatively unaffected, the metal-olefin π back-bond is perturbed as the olefin moves from being perpendicular to being parallel to the plane. A potential barrier thus arises as a result of the differences in π electron density in these two alternative environments. If the bond energy is taken as being proportional to the overlap integral (S) between the appropriate orbitals of the metal and olefin squared, and inversely proportional to the energy separation (ΔE) between the π^* orbital of the olefin and the d orbitals of platinum, then¹⁴:

$$\text{Potential barrier} \propto \frac{S_1^2}{\Delta E_1} - \frac{S_2^2}{\Delta E_2}$$

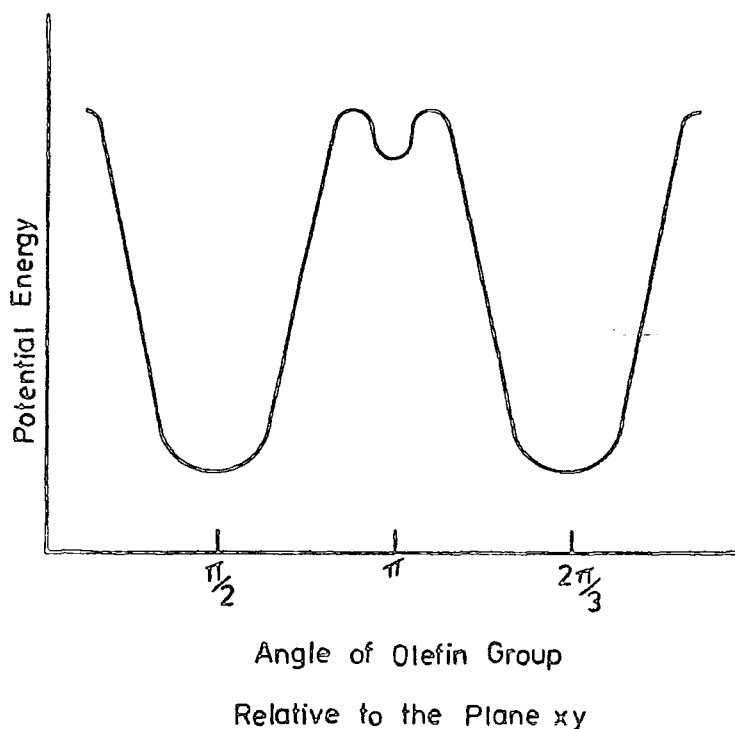
where S_1 and ΔE_1 refer to the "parallel" orientation

S_2 and ΔE_2 refer to the "vertical" orientation

A pictorial representation of the barrier is therefore:



Molecular Orbital calculations carried out by Wheelock et al.⁷ have shown the above picture to be an over-simplification in the case of divalent trans-ethylene-platinum complexes. Using trans-PtCl₂(C₂H₄).NH₃ as a model, the presence of a second minimum in potential energy was established corresponding to a metastable well when ethylene was parallel to the plane.



Both kinetic (NMR) and spectroscopic (INS) techniques may be employed to investigate potential barriers, and particularly using the former, much study has been directed towards platinum-olefin complexes, especially those containing ethylene¹⁴⁻¹⁷. Each method yields different information about the barrier problem. Kinetic measurements (as a function of temperature) enable calculation of the energy of activation, while spectroscopic studies (at a single temperature) give information concerning the energy of one (or more) transitions within the potential energy well. From the latter, together with a suitable model for the shape of the barrier, may be calculated both a barrier height, and also the Zero Point Energy by solution of the Mathieu equation (Chapter II). The two measurements may be related thus:

$$\text{Energy of Activation} + \text{Zero Point Energy} = \text{Barrier Height}$$

It proved difficult, however, to find examples of complexes from those which had been studied by NMR, where few enough hydrogen atoms were present to allow relatively easy interpretation of INS spectra. Ghosh et al.¹⁸ therefore measured the INS spectra of $K[PtCl_3(C_2H_4)] \cdot H_2O$, $[PtCl_2(C_2H_4)]_2$, $Cs[PtCl_3(C_2H_4)]$ and $[PdCl_2(C_2H_4)]_2$ and compared their data with that for $Pt(acac)Cl(C_2H_4)$ (where $acac = MeCO \cdot CH \cdot COMe^-$).

The torsional (rotational) mode about the bond between the metal and the centre of the carbon-carbon bond of the olefin was found in all cases to correspond with the most intense low energy vibration. Comparison of the barrier to rotation calculated from this frequency with that obtained from NMR showed that the potential function was best represented by the form:

$$V(\theta) = \frac{V_0}{2} (1 - \cos \theta) + \frac{V_4}{2} (1 - \cos 4\theta)$$

Further studies of the torsional frequencies in ethylene-containing complexes have been carried out by Howard et al. INS spectra of the compounds $\pi-C_5H_5Rh(C_2H_4)_2$, $[Rh(C_2H_4)_2Cl]_2$, and $\pi-C_5H_5Rh(C_2H_4)SO_2$ ¹⁹; $Ir(C_2H_4)_4Cl$ and $[Ir(C_2H_4)_2Cl]_2$ ²⁰; $[Rh(C_2H_4)_3(CD_3CN)_2]BF_4$ ²¹; and $2AgNO_3 \cdot C_2H_4$ ²² were measured. For those complexes where the ethylene groups were in a cis configuration (first, second and fifth listed), the torsion was observed to split into an in-phase and out-of-phase contribution. This phenomenon was also reported for those compounds with three equatorial ethylene ligands (fourth and sixth listed), and in the case of $Ir(C_2H_4)_4Cl$, an additional frequency corresponding to the torsioning of an axial ethylene group could be assigned. Where possible, the barrier heights calculated were compared with those obtained from NMR data.

B. Experimental

The trans-ethylene complexes, $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$, $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{CD}_3\text{CN}$, $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{DCON}(\text{CD}_3)_2$ and $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{D}_5\text{ND}_2$, were formed from Zeise's dimer, $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$, by addition of one equivalent of the appropriate ligand in ethanol, using the same procedure as that described by Meester et al. for the analogous compounds with hydrogen ligands²³. The cis-ethylene complex, $\text{PtCl}_2(\text{C}_2\text{H}_4).(\text{CD}_3)_2\text{SO}$ was prepared similarly to the method described in the literature by Boucher and Bosnich for $\text{PtCl}_2(\text{C}_2\text{H}_4).(\text{CH}_3)_2\text{SO}$ ²⁴. In all cases, deuterated ligands were employed to simplify analysis of INS spectra by decreasing the intensity of those hydrogenous modes which were not of interest.

INS spectra were measured using polycrystalline powders contained in thin-walled silica cells. Time-of-Flight data were obtained in the case of the trans-ethylene complexes at 243K using the 6H Spectrometer (reduction of temperature being necessary to counteract thermal instability), and in the case of the cis-ethylene complex at 293K using the 4H5 Spectrometer. BFD spectra were recorded employing the Pluto Spectrometer (liquid nitrogen temperature) for the samples $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$, $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{DCON}(\text{CD}_3)_2$ and $\text{PtCl}_2(\text{C}_2\text{H}_4).(\text{CD}_3)_2\text{SO}$, and the Dido instrument (at temperatures of 16K and 77K respectively) for compounds $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{CD}_3\text{CN}$ and $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{D}_5\text{ND}_2$.

Far-infrared measurements ($50\text{--}400\text{cm}^{-1}$) were made at ambient and liquid nitrogen temperatures using a Beckman-RIIC FS720 Fourier Transform Spectrophotometer, whilst the near-and mid-regions ($200\text{--}850\text{cm}^{-1}$) were scanned at room temperature using a Perkin-Elmer 577 Spectrometer. With the former instrument, samples were run as nujol mulls supported on polyethylene disc, with the latter, as nujol mulls between caesium iodide plates.

Raman spectra were measured between 0 and 850cm^{-1} as solids, and between 0 and 100cm^{-1} as solutions in ethanol, with a Cary 82 Raman Spectrometer employing a Spectra-Physics Model 125 He/Ne laser at $15,802\text{cm}^{-1}$ (14mW power).

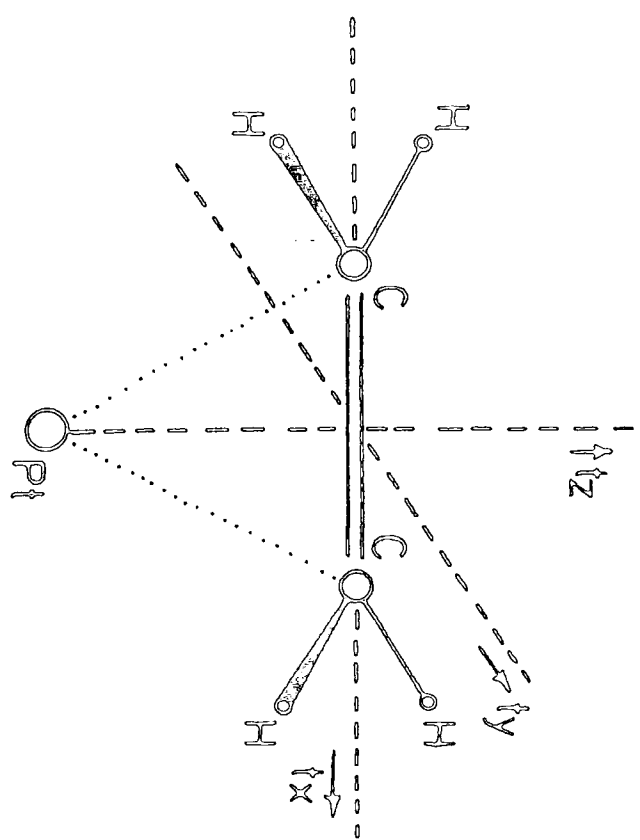
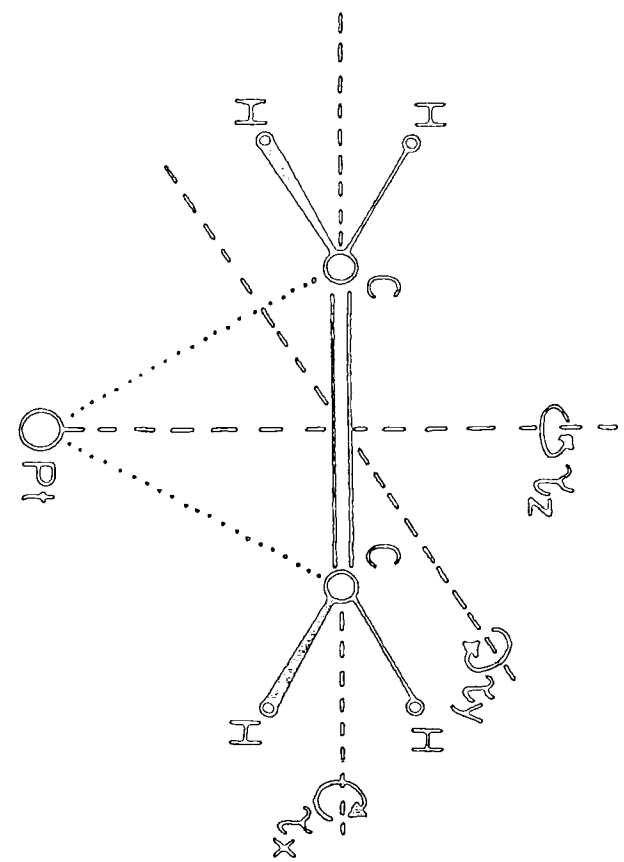
C. Discussion of Results

1. The Trans-ethylene Complexes: $\text{PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$

Previous INS studies of ethylene containing complexes similar to those under present investigation (Zeise's salt and dimer)^{18,22} have shown that motions of the ethylene group dominate the spectra as a result of the very large incoherent scattering cross-section of the protons contained therein. Furthermore, there is evidence for little mixing occurring between platinum-chlorine bending modes (found in the region $90\text{--}210\text{cm}^{-1}$ in Zeise's salt) and hydrogen displacements²⁶. It may therefore be assumed that in T-O-F spectra ($0\text{--}250\text{cm}^{-1}$), and in general as a good first approximation, that INS intensity will derive solely from vibrations involving ethylene.

Addition of ethylene to the square plane causes the appearance of six new modes (dia.4(i)): three of these may be considered as hindered rotations (τ_x , τ_y or antisymmetric stretch and τ_z), the remaining three corresponding to hindered translations (t_x or wag, t_y or rock and t_z or symmetric stretch). The vibrations τ_z , t_x and t_y have all been found previously in T-O-F data¹⁸ (i.e. below 250cm^{-1}), the most intense of these, and indeed the most intense band below about 700cm^{-1} , being τ_z . Of the remaining three modes, τ_x observed with optical spectroscopy at 1180cm^{-1} ²⁸, has not been located in INS spectra of Zeise's salt and dimer,²² whilst τ_y and t_z have been observed in the BFD region (Table 4.1).

The relative intensities expected of the various translations and rotations may be compared employing the approximation (Chapter II) that intensity is proportional to $Q^2 \langle u^2 \rangle$, where Q is the scattering vector



dia. 4 (i) The three hindered rotations, ν_x , ν_y (antisymmetric stretch) and ν_z , and the three hindered translations, τ_x (wag), τ_y (rock) and τ_z (symmetric stretch), of ethylene relative to platinum.

Table 4.1 The Spectroscopic Frequencies (cm^{-1}) and Assignments of
Zoloto's salt ($\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$) and Dimer ($[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$)

$[\text{PtCl}_3(\text{C}_2\text{H}_4)]$		$[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$		Assignment ^{22,29}
Infrared ²⁶⁻³⁰ and Raman	INS ^{18,22}	Infrared ²⁶⁻²⁹ and Raman	INS ^{18,22}	
121			110	PtC_2 wag (τ_x)
	165		170	C_2 torsion (τ_z)
219		201	190	Pt-C_2 rock (τ_y)
405	400	405 } 412 }	400	Pt-C_2 symmetric stretch (τ_z)
493	490	481 } 492 }	487	Pt-C_2 anti- symmetric stretch (τ_y)
720	720	721 } 725 }	718	CH_2 rock
841	840	814 } 818 } 828 }	820	CH_2 rock
975		972 } 977 } 982 }	985	CH_2 wag
1010	1020	1021 } 1026 } 1036 }	1030	CH_2 wag
1180		1176		CH_2 twist
1243	1230	1237 } 1245 }	1230	C=C stretch
1426	1440	1424	1400	CH_2 scissor

and $\langle u^2 \rangle$ is the mean-square amplitude of vibration of the scattering atom. In the case of a translational mode this relation may be restated as²⁵:

$$\text{Intensity} \propto Q^2 (M \omega_\lambda)^{-1}$$

where M is the mass of the molecule considered

and ω_λ is the radial frequency of the vibration

Whilst for a rotational mode, the appropriate form is²⁵:

$$\text{Intensity} \propto Q^2 r^2 (I_R \omega_\lambda)^{-1}$$

where r is the perpendicular distance between the scattering atom and the axis of rotation

and I_R is the reduced moment of inertia of the molecule concerned

Considering initially BFD spectra, where to a first approximation Q^2 and ω_λ^{-1} cancel (Chapter II), then for an ethylene translation:

$$\text{Intensity} \propto M^{-1} \propto (28)^{-1}$$

where 28 is the mass of ethylene in AMU

and for an ethylene rotation (or torsion):

$$\text{Intensity} \propto r^2 (I_R)^{-1}$$

Using the values of I_R about each principal axis appropriate for a "Zeise's salt" structure of the ethylene molecule¹⁰ (Appendix), the ratio of the predicted BFD intensities is:

$$\begin{array}{cccccc} t_x & : & t_y & : & t_z & : & \tau_x & : & \tau_y & : & \tau_z \\ 1.000 & : & 1.000 & : & 1.000 & : & 6.742 & : & 2.648 & : & 3.038 \end{array}$$

This ratio may then be corrected to give a guide to the intensities expected for neutron energy gain spectra by employment of the frequencies assigned each mode in the INS spectrum of Zeise's salt²² (Table 4.1), and

the values of Q^2 associated with each frequency. Since however, Q varies not only with respect to frequency, but also with respect to scattering angle and the particular T-O-F instrument used, it is perhaps informative to compare the intensity ratios calculated for the 4H5 and 6H Spectrometers at the one angle they have in common, 90° .

Mode	t_x	t_y	t_z	τ_x^*	τ_y	τ_z
Frequency	110cm^{-1}	190cm^{-1}	400cm^{-1}	-	487cm^{-1}	170cm^{-1}
Intensity ratio for the 90° angle of 4H5	1.338	1.147	1.000	-	2.603	3.559
Intensity ratio for the 90° angle of 6H	1.408	1.169	1.000	-	2.563	3.676

* τ_x was not observed in the INS spectra of Zeise's salt or dimer.

From predicted intensities, it will be seen that in the higher frequency spectrum, that is above about 250cm^{-1} , but below those energies where internal ethylene modes are located ($\text{ca. } 700\text{cm}^{-1}$), only two bands of appreciable intensity should be seen, i.e. those corresponding to the symmetric and antisymmetric stretches.²²

In forthcoming discussions of experimentally derived T-O-F intensities, measurements have been carried out by fitting peaks (using a Du Pont Curve Resolver) to selected $P(\alpha, \beta)$ spectra. In the first instance, Gaussians have been placed at observed T-O-F transition frequencies but, where necessary, they have also been positioned at energies indicated from the form of the total T-O-F bandshape. The areas of the peaks thus generated have been varied so as to achieve "best fit" with the overall band profile and the resultant intensity ratio measured. This ratio has then been compared with that predicted from consideration of suggested assignments (suitably corrected for frequency and " Q^2 ").

a) $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$

The INS spectra of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$ are shown in dias.4(ii)-iv), and are summarised in Table 4.2., together with infrared and Raman data.

From the previous discussion of expected intensities, and bearing in mind the inherent lack of resolution of the BFD spectrometer at low frequency (Chapter II), it would be expected that three intense bands would be visible in the BFD spectrum below 650cm^{-1} ²², namely, those corresponding to the symmetric stretch (τ_z), anti-symmetric stretch (τ_y) and C_2 torsion (τ_z) of the ethylene molecule (Table 4.1). Infrared and Raman data²³ for the equivalent NH_3 compound have placed the symmetric stretch at 386cm^{-1} and the anti-symmetric stretch at 475cm^{-1} . Consequently, the vibration at 388cm^{-1} in the BFD spectrum of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$ may be assigned to the symmetric stretch and that at 474cm^{-1} to the anti-symmetric stretch.

Intensity (Monitor Counts)

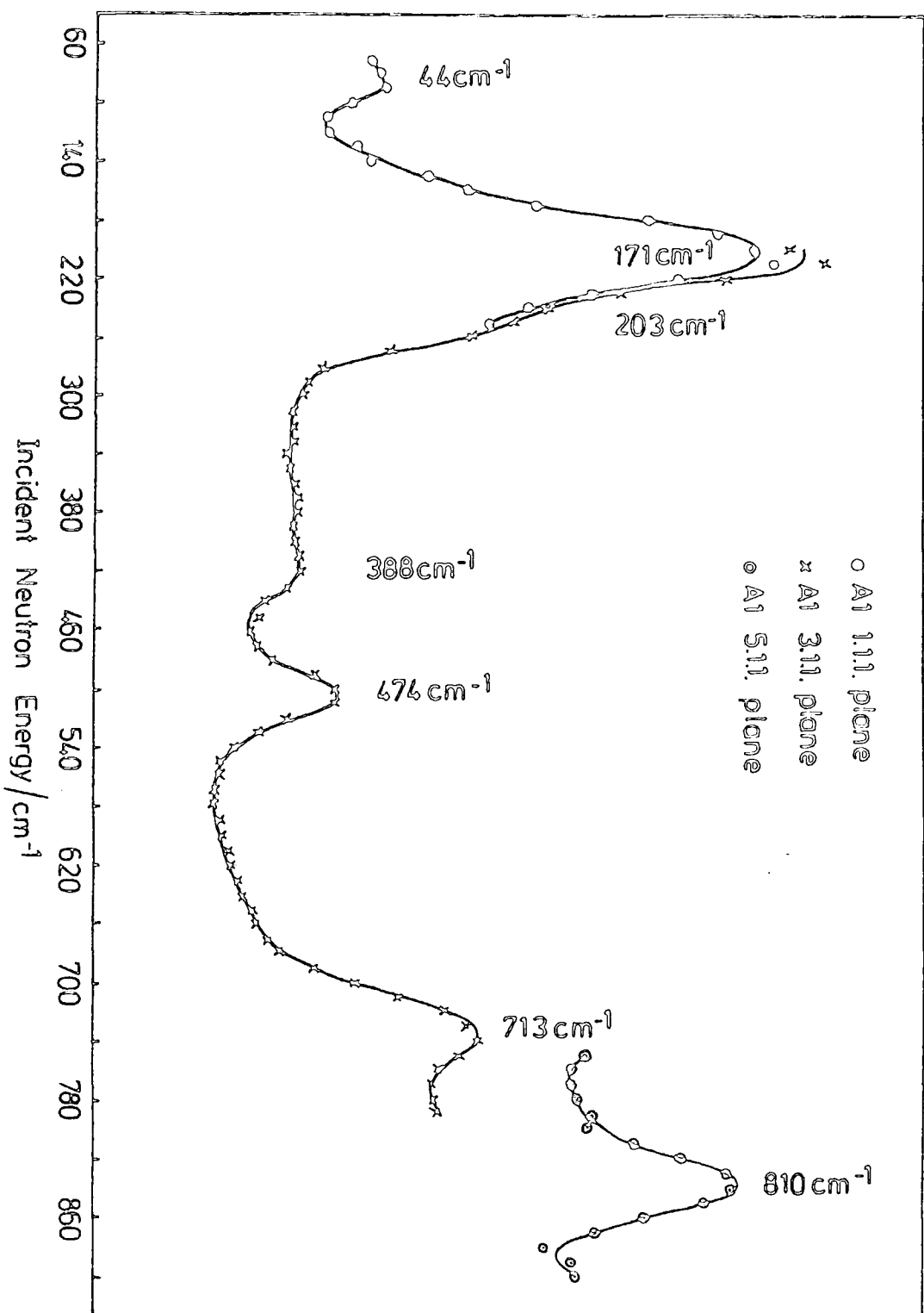
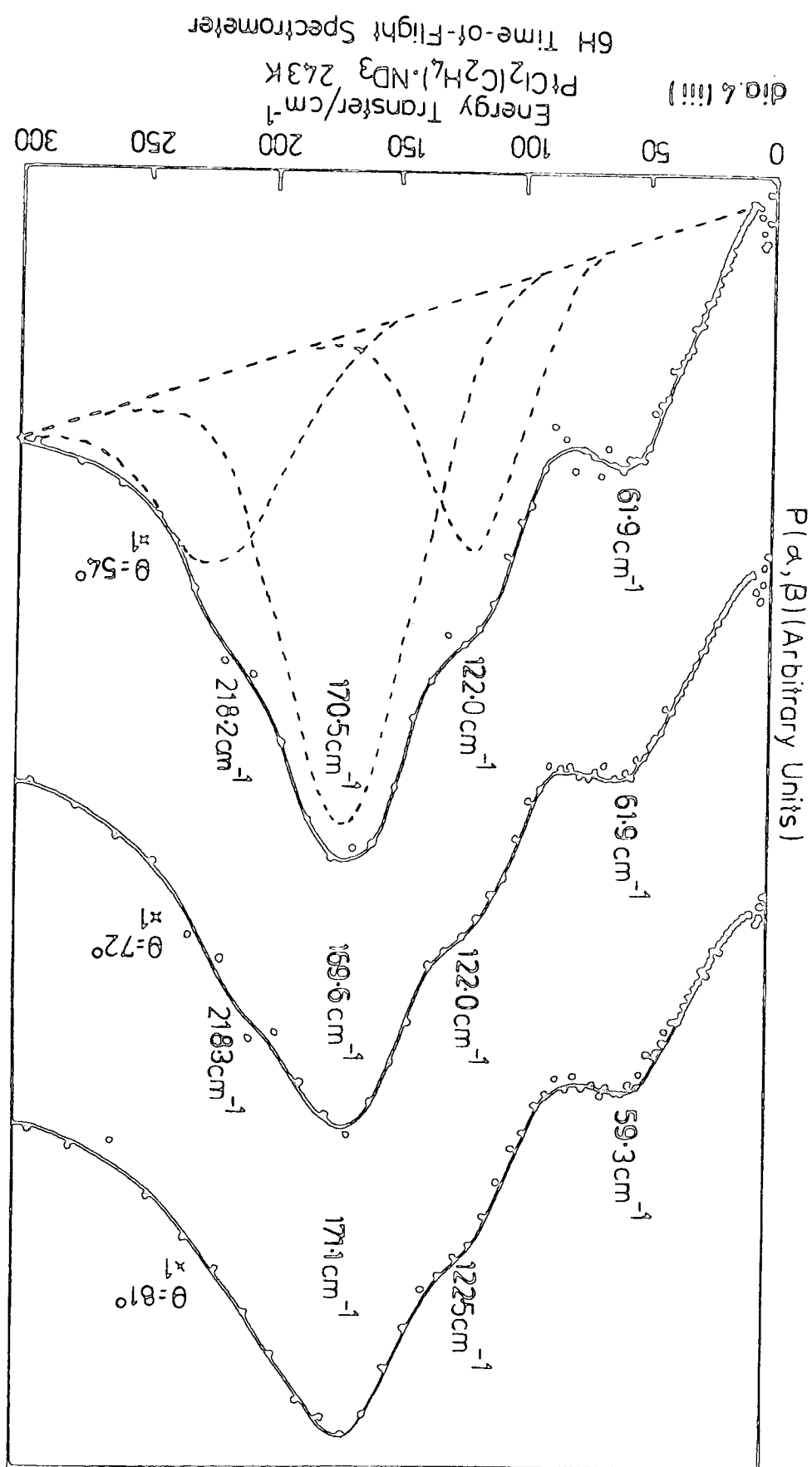


fig. 4 (iii)

PtCl₂C₂H₄ND₃ (Silica background not subtracted)

Pluto BFD Spectrometer : Liquid Nitrogen temperature



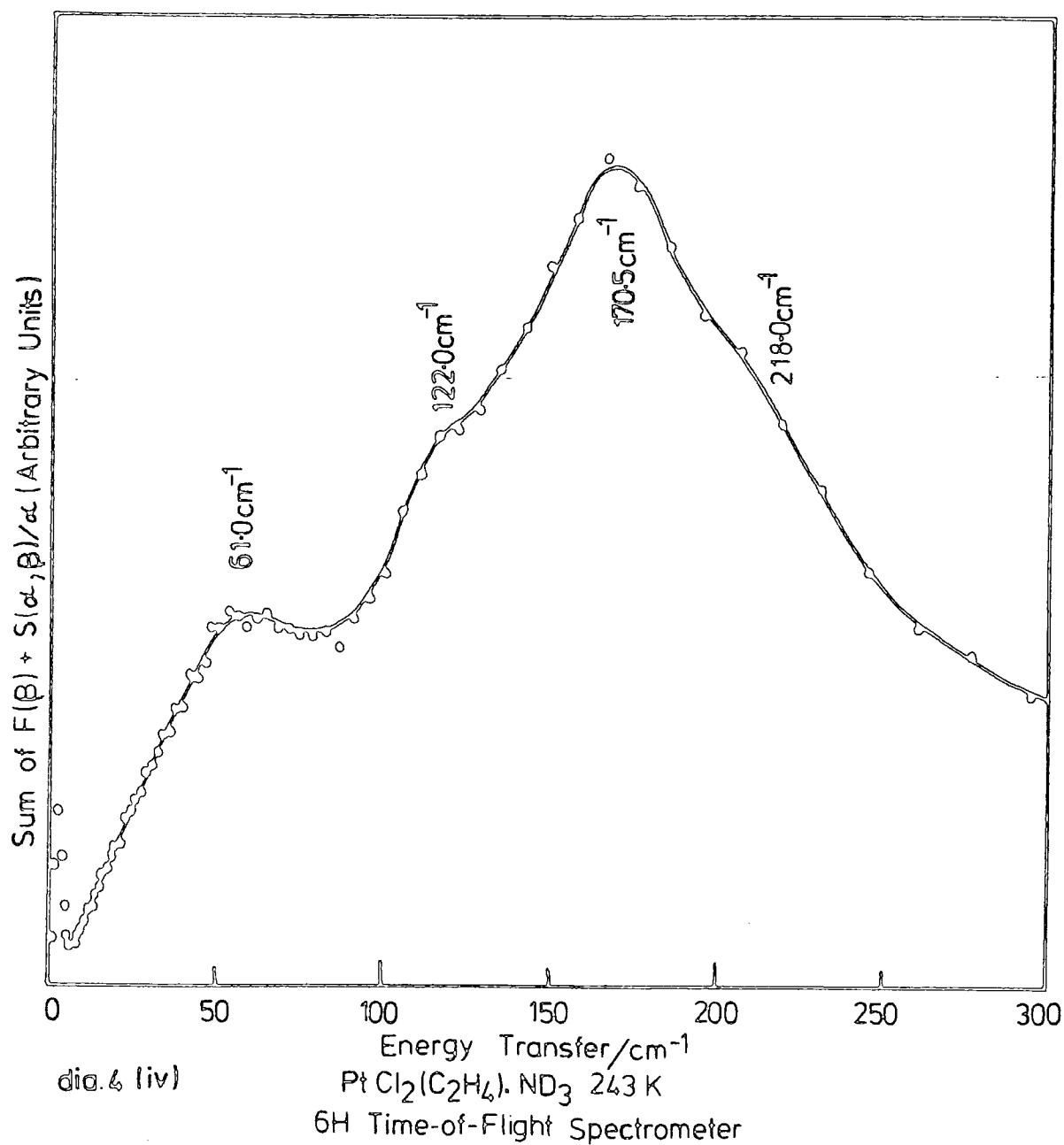


TABLE 4.2 The Spectroscopic Frequencies (cm⁻¹) and Assignments of trans-PtCl₂(C₂H₄)₂.ND₃ Compared with its NH₃ Analogue

trans-PtCl ₂ (C ₂ H ₄).NH ₃ 23			trans-PtCl ₂ (C ₂ H ₄).ND ₃				
Infrared	Raman	Assignment	Infrared	Raman	INS		Assignment
					BFD	T-O-F	
				480	44±10	61.0±3.5	Lattice Vibration Pt-C ₂ wag(τ _x)
166m	155s	*			171±10	170.5±10.0	C ₂ torsion (τ _z) *
185s	207v	°	186s	205m			°
225m		°	220s		203±10	218.0±13.0	Pt-C ₂ rock (τ _y)
332sh 338vs	330sh 336vs(338p) 348m	ν(Pt-Cl) ν _s (Pt-Cl) ν _{as}	330sh 337s 346sh	330s 344sh			ν(Pt-Cl) ν _s (Pt-Cl) ν _{as}
378s	381c(386p) 392m	ν _s (Pt-C ₂)	378v	377v	388±10		ν _s (Pt-C ₂) (τ _z)
				415vv			
4750	4750h(480) 483vs	ν _{as} (Pt-C ₂) and ν(Pt-L)	467v	436sh 462sh 481v	474±10		ν(Pt-N)? ν _{as} (Pt-C ₂) (τ _y)
			720m 735sh }		713±10 810±10		CH ₂ rock CH ₂ rock CH ₂ rock

° Disordered within the unit cell
 v = very strong; s = strong; sh = shoulder; () denote solution data; p = polarized
 m = medium band; v = weak; vv = very weak; sh = shoulder; () denote solution data; p = polarized
 ν_o = symmetric stretch; ν_{as} = asymmetric stretch.

The most intense feature in the entire spectrum which occurs at 171 cm^{-1} (170.5 cm^{-1} T-O-F data) must therefore correspond to the C_2 torsion, and this is in agreement on frequency and intensity grounds with earlier INS investigations.^{18,22}

The peak designated the C_2 torsional mode shows two distinct shoulders in the $P(\alpha, \beta)$ spectra, one to high frequency, and the other to long wavelength. The former, seen at 218 cm^{-1} (203 cm^{-1} BFD spectrum) appears to be the Pt-C_2 rock (t_y) located in infrared^{28,29}, Raman²⁹ and INS^{18,22} investigations of Zeise's dimer in the region $190\text{--}201\text{ cm}^{-1}$, and in optical studies only of Zeise's salt between 210 and 219 cm^{-1} ^{26,29} (Table 4.1). The second shoulder, observed at 122 cm^{-1} in the neutron energy gain spectra, but not found in the BFD spectrum, may also be correlated with a platinum-ethylene translational mode, in this case the Pt-C_2 wag (t_x). This is again in accordance with infrared measurements of Zeise's salt (121 cm^{-1})²⁶, and the INS spectra of Zeise's dimer (110 cm^{-1})²². The experimental ratio of intensities, $t_x : t_y : \tau_z$, thus evaluated from the $P(\alpha, \beta)$ spectrum (angle 54°) on the basis of these assignments is 1.00: 1.00: 2.55, which compares reasonably with predicted values of 1.06: 1.00: 3.04.

Of the remaining unidentified INS vibrations, those at 713 cm^{-1} and 810 cm^{-1} must correspond to CH_2 rocking modes, the former of which is found at about 720 cm^{-1} for both $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ and $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$ ^{22,29}, and the latter at 840 cm^{-1} for Zeise's salt and $814\text{--}28\text{ cm}^{-1}$ for the dimer.^{22,29}

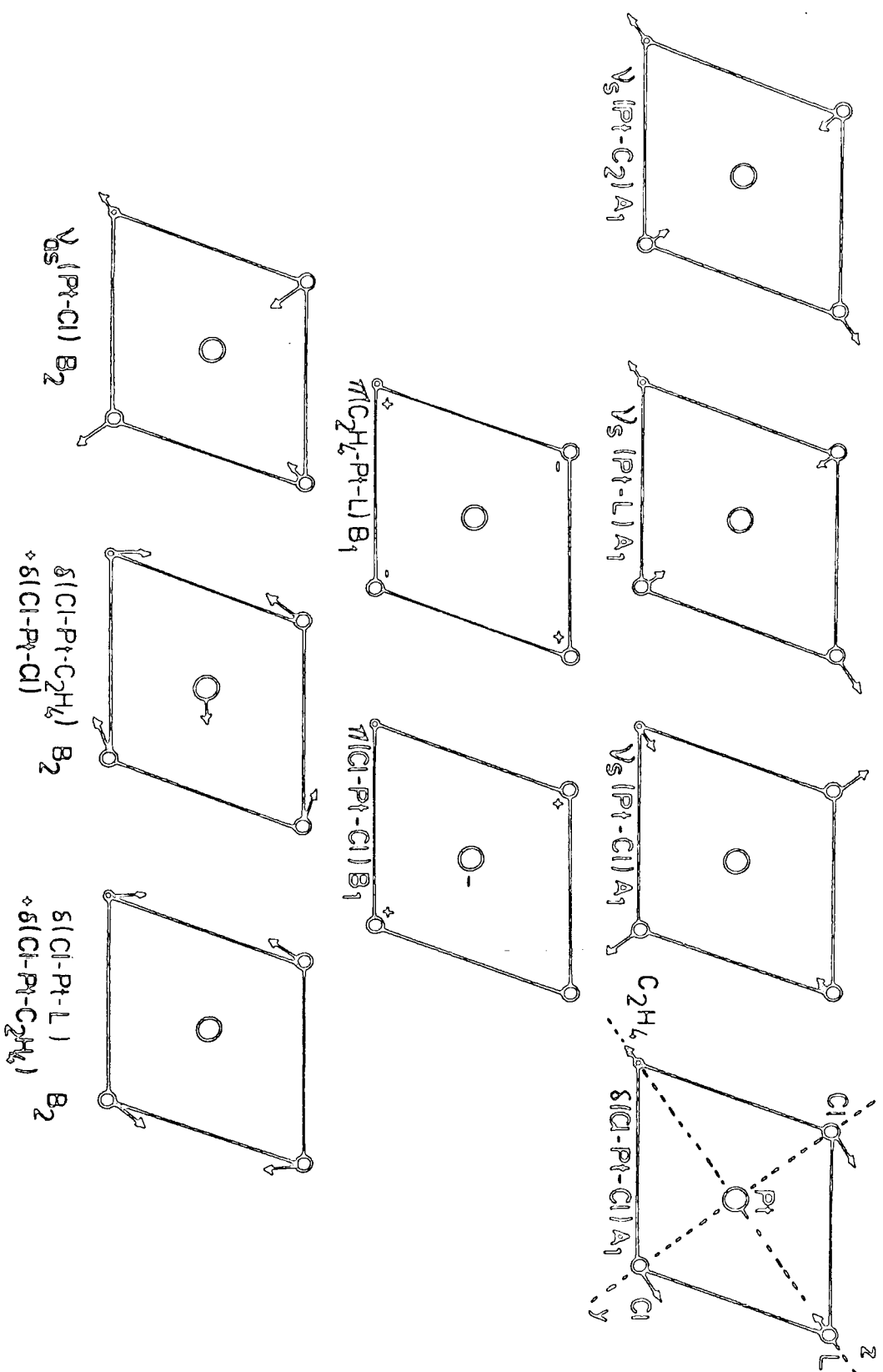
Finally, the peak found at 44 cm^{-1} in the BFD spectrum may, on account of this instrument's poor frequency resolution at low energies, be assumed to be the equivalent of that located at 61 cm^{-1} in T-O-F data. Although no infrared measurements could be made in this region, a transition was

observed in the Raman spectrum at 48 cm^{-1} using $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{ND}_3$ powder. Further Raman spectra were recorded of the complex in ethanolic solution, and of a "background" which consisted of the silica sample tube filled with ethanol. It was not possible in the solution work to find at 48 cm^{-1} a band of an intensity such that it could not be attributed to the background, and hence it would seem reasonable to presume that the vibration found in this region represents a lattice mode. Some support for this conclusion may be derived from the work of Fritz and Sellmann³¹, where an infrared active peak at 48 cm^{-1} in the spectrum of $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{NH}_3$ has been assigned to a lattice vibration. Unfortunately, the presence of this frequency was not reported in the infrared measurements also carried out on $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{NH}_3$.

Compared with the region of the $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{NH}_3$ spectrum investigated by Meester et al.²³, the infrared and Raman spectra of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{ND}_3$ are essentially in agreement (Table 4.2). We may thus further assign the symmetric and antisymmetric chlorine stretches (guided by the hydrogenous ligand complex where both vibrations occur at 338 cm^{-1} ²³) to the frequencies 330 cm^{-1} (Raman) and 337 cm^{-1} (infrared) respectively.

Bands in the spectra to longer wavelength are, however, more difficult to identify as they result from various bending modes of the square planar skeleton, the activities and possible splitting of which are problematical in the absence of accurate structural data. Discussion and assignment of this part of the spectrum must therefore of necessity be extremely tentative.

Vibrations at 161 cm^{-1} and 183 cm^{-1} in the infrared spectrum of $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ have been designated $\delta(\text{Cl-Pt-Cl}_{\text{trans}}) + (\text{Cl-Pt-C}_2\text{H}_4)$ and $\delta(\text{Cl-Pt-Cl})$ respectively (Table 4.3 and dia.4(v)).²⁶ However, for $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$, effectively the reverse assignments have been made³²⁻⁴ with a band at 181 cm^{-1} in the INS spectrum being identified with $\delta(\text{N-Pt-Cl})$, and a peak at 156 cm^{-1}



dio. 4 (v) The normal modes of the square planar molecule WX_2YZ analysed in C_{2v} symmetry.

TABLE 4.3 The Infrared Spectroscopic Frequencies and Assignments of Zeise's Salt below 410cm^{-1} (after Grogan and Nakamoto²⁶)

Frequency (cm^{-1})	Assignment	Symmetry
407	$\nu_s(\text{Pt-C}_2\text{H}_4)$	A_1
339	$\nu_{as}(\text{Pt-Cl})$	B_2
331	$\nu_s(\text{Pt-Cl})$	A_1
310	$\nu(\text{Pt-Cl}_t)$	A_1
210	$\delta(\text{Cl-Pt-C}_2\text{H}_4)$ $+\delta(\text{Cl-Pt-Cl})$	B_2
183	$\delta(\text{Cl-Pt-Cl})$	A_1
161	$\delta(\text{Cl-Pt-Cl}_t)$ $+(\text{Cl-Pt-C}_2\text{H}_4)$	B_2
121	$\pi(\text{C}_2\text{H}_4\text{-Pt-Cl}_t)$	B_1
92	$\pi(\text{Cl-Pt-Cl})$	B_1

ν = stretch; δ = bend in zy plane; π = bend out of zy plane;
s = symmetric; as = antisymmetric; t identifies that chloride ion trans to the olefin.

TABLE 4.4 The Spectroscopic Frequencies and Assignments of $\text{trans-Pt}(\text{NH}_3)_3\text{Cl}_2$ - (after Howard and Waddington³²)

Infrared and Raman ³³ (cm^{-1})	INS (cm^{-1})	Assignment
248		$\delta(\text{N-Pt-N})$
235	239	$\pi(\text{Pt-N})$
207	213	
	181 ³⁴	$\delta(\text{N-Pt-Cl})$
	162	Torsion
156		$\delta(\text{Cl-P-Cl})$
136	140	$\pi(\text{Pt-Cl})$
	95	
	50	

δ = in-plane bend; π = out-of-plane bend.

labelled $\delta(\text{Cl-Pt-Cl})$ (Table 4.4). Comparison of the spectra obtained by Meester et al.²³ for $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{NH}_3$ with those recorded in the present work for the ND_3 complex indicates that the 185cm^{-1} infrared vibration of the former appears insensitive to deuteration, whilst the 166cm^{-1} frequency has no obvious analogue in the infrared spectrum of the deuterated compound. It would seem reasonable on both intensity and frequency grounds that assignments of the two bands should be made following the general conclusions for $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ and $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$, that is to bending modes involving predominantly chlorine. However, on the basis of the present evidence, it is impossible to conclude which of the two assignment schemes pertains.

The frequencies of 207cm^{-1} and 225cm^{-1} in the Raman and infrared spectra respectively of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{NH}_3$ are virtually unshifted on deuteration, but are capable of several conflicting assignments. One possible correlation of the 225cm^{-1} vibration is with the Pt-C_2 rock (t_y), both on the grounds of the reported intensity of this mode in Zeise's salt and dimer,^{26,27,29} and also the frequency at which it has been observed in Zeise's salt^{26,29} and the other trans complexes to be discussed in succeeding sections. On this assignment scheme, the lower energy vibration would, as a consequence of its invariance with deuteration, implicitly represent a bending mode involving mainly chlorine and/or ethylene. However, because of previous assignments, this criterion could only be fulfilled if the transition resulted from splitting of the bands at 185cm^{-1} or 225cm^{-1} . Conversely, the 225cm^{-1} infrared frequency of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{NH}_3$ is not far removed from energies at which Pt-N bends have been located (for example, 235cm^{-1} and 248cm^{-1} in $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$ ³³). Furthermore, the deuteration shift expected for a mode equivalent to an NH_3 translation is extremely small (0.960°). Indeed,

✓ This deuteration shift has been evaluated making the approximation that the bend could be likened to that of a linear triatomic molecule of the form, $\text{X-Y-Z: C}_2\text{H}_4\text{-PtCl}_2\text{-NH}_3$. The appropriate formula of Herzberg³⁵ for a bending mode of a molecule of this type has then been employed, assuming:
(i) that the bond lengths are those contained in Appendix 2, and
(ii) that the bending constant remains unchanged on deuteration.

In order to check the validity of this approach, the deuteration shifts expected for the bending modes (t_x and t_y) of the ethylene group in Zeise's salt were calculated, and checked against those indicated using an approach similar to the above. The results were $t_x: 121\text{cm}^{-1}(\text{C}_2\text{H}_4) \rightarrow 117\text{cm}^{-1}(\text{C}_2\text{D}_4)$ ²⁶ = 0.967 and $t_y: 210\text{cm}^{-1}(\text{C}_2\text{H}_4) \rightarrow 198\text{cm}^{-1}(\text{C}_2\text{D}_4)$ ²⁶ = 0.943, compared with predicted shifts of 0.968.

the deuteration shift, if such it is, between the 225cm^{-1} infrared band of the NH_3 ligand complex, and the 220cm^{-1} infrared peak of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$ is 0.978. If this identification is made, and the 225cm^{-1} frequency is taken as representing a Pt-N bend, then the rocking mode (t_y) of the ethylene group could be assigned to the 207cm^{-1} Raman band of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{NH}_3$. Unfortunately, the INS spectral data offer little additional guidance, because the error in the frequency determination of the ethylene rock (t_y) encompasses both optically derived bands. It is therefore partly from the evidence of the optical spectra of Zeise's salt^{26,29} and partly because the $P(\alpha, \beta)$ spectra display greater resolution of the feature assigned in the INS spectra as the ethylene rock (t_y), that this mode has been tentatively identified with the higher frequency vibration (225cm^{-1}).

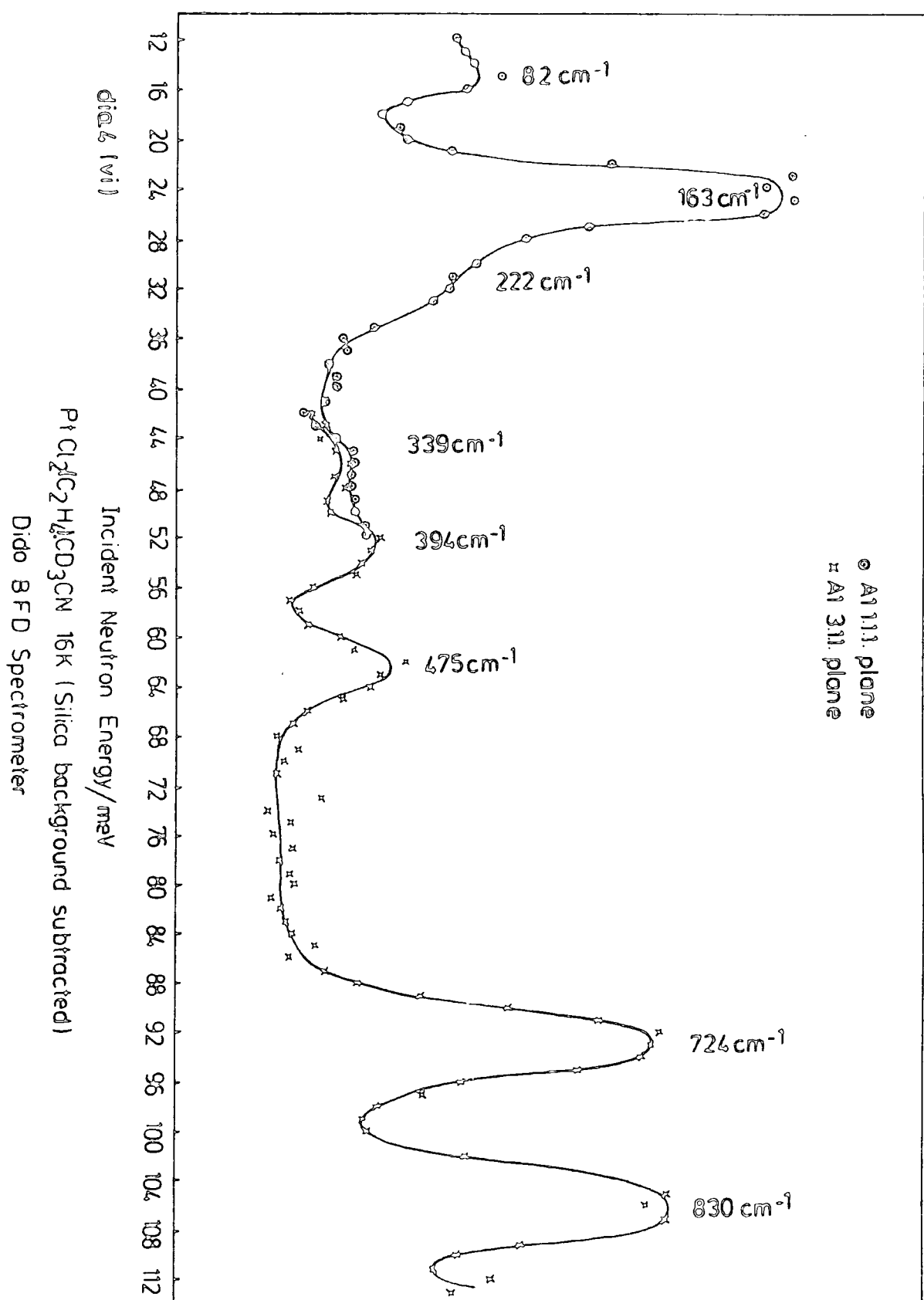
Considering now the higher frequency Raman and infrared spectra, Meester et al.²³ designated an infrared vibration of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{NH}_3$ located at 475cm^{-1} a platinum-ligand mode. Although the spectra of the complexes with deuterated and hydrogenous ligands are very similar in this region, a shoulder seems to have appeared at 436cm^{-1} in the Raman of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$. If this is correlated with the 475cm^{-1} vibration, a deuteration shift of 0.918 is found, which is in good agreement with that calculated for the Pt-N stretch using the reduced masses of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)-\text{NH}_3$ and $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)-\text{ND}_3$ (0.926).

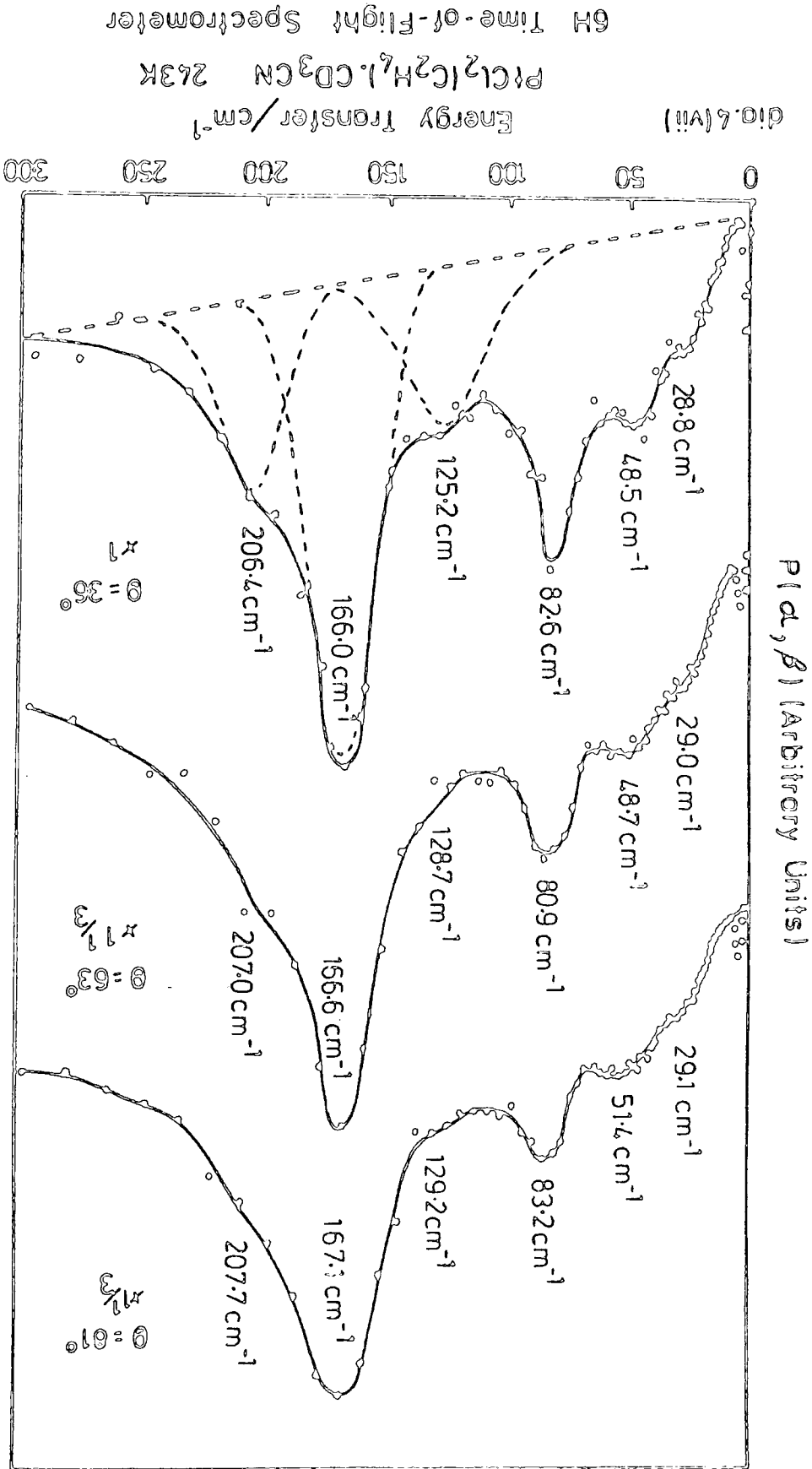
At still higher frequency in the infrared of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$, a peak occurs at 720cm^{-1} with a shoulder at 735cm^{-1} . From the INS data, and the assignments of Miraishi²⁹ for Zeise's salt and dimer, this undoubtedly corresponds to a CH_2 rocking mode.

b) $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{CD}_3\text{CN}$

The INS spectra of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{CD}_3\text{CN}$ are shown in dias.4(vi)-(viii), and are summarised, together with infrared and Raman data, in Table 4.5.

Intensity (Time Normalised Counts)





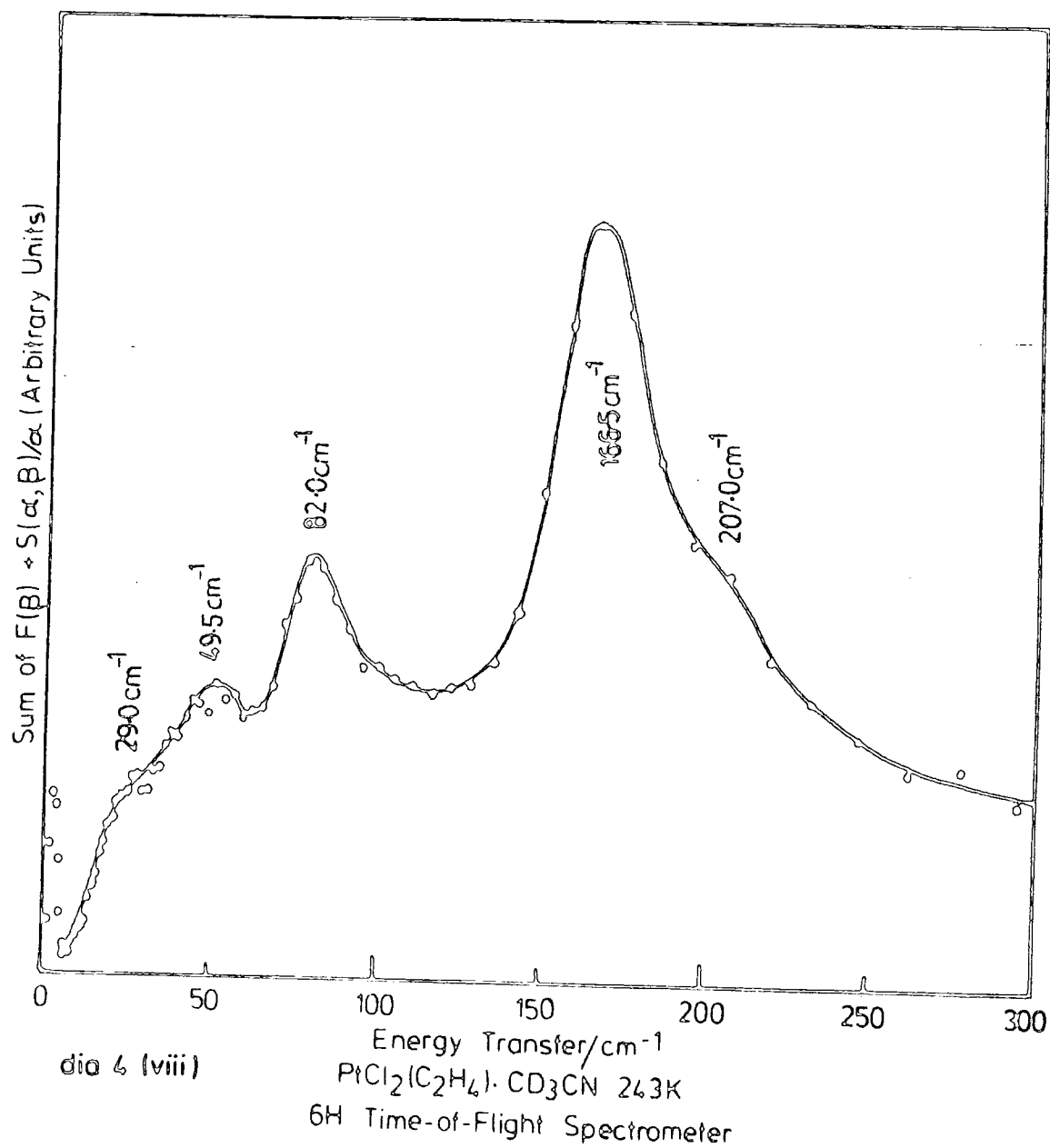


TABLE 4.8 The Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)_2\text{CD}_3\text{CN}$ Compared with its CH_3CN Analogue

$\text{trans-PtCl}_2(\text{C}_2\text{H}_4)_2\text{CH}_3\text{CN}^{23}$			$\text{trans-PtCl}_2(\text{C}_2\text{H}_4)_2\text{CD}_3\text{CN}$				
Infrared	Raman	Assignment	Infrared	Raman	INS		Assignment
					BFD	T-O-F	
				28s		29.0 $\pm$ 2.0	Lattice Vibrations
				40w		49.5 $\pm$ 3.0	
			56w	53s	82 $\pm$ 8	82.0 $\pm$ 4.5	
			107s	109s		127.5 $\pm$ 7.0	Pt-C ₂ wag (τ_x)
126s		*	124s	141w			
163s	150s	*	162s	168vs	163 $\pm$ 8	166.5 $\pm$ 9.5	C ₂ torsion (τ_z)
191sh		*	181s				
200s	200s	*	199s	205s	222 $\pm$ 8	207.0 $\pm$ 12.0	Pt-C ₂ rock (τ_y)
243s		$\nu(\text{Pt-L})$	229s				$\nu(\text{Pt-N})$
			287s	284vs			
				322s			
348vs	337sh 344vs(342P)	$\nu_{\text{as}}(\text{Pt-Cl})$ $\nu_{\text{o}}(\text{Pt-Cl})$	338sh 346vs	344s	339 $\pm$ 8		$\nu_{\text{as}}(\text{Pt-Cl})$ $\nu_{\text{o}}(\text{Pt-Cl})$
				361s			
				368s			
386s	384s(384P)	$\nu_{\text{o}}(\text{Pt-C}_2)$	394s	392sh 406m	394 $\pm$ 8		$\nu_{\text{o}}(\text{Pt-C}_2)(\tau_z)$
482s	479s	$\nu_{\text{as}}(\text{Pt-C}_2)$	478s	488w	475 $\pm$ 8		$\nu_{\text{as}}(\text{Pt-C}_2)(\tau_y)$
			721s 735sh	714w	724 $\pm$ 8		CH ₂ rock
			840s 865w		830 $\pm$ 8		CH ₂ rock

* This sample gave poor Raman spectra.
 * Discussed within the text

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder; () denote solution data;
 P = polarized Raman band; ν_{o} = symmetric stretch; ν_{as} = antisymmetric stretch.

As for the previous complex, the three most intense bands in the BFD spectrum below 700cm^{-1} , those at 163cm^{-1} (166.5cm^{-1} T-O-F data), 394cm^{-1} and 475cm^{-1} , may be assigned to the C_2 torsional mode (τ_z), the symmetric stretch (t_z) and the antisymmetric stretch (τ_y) respectively of ethylene. Again this is in accordance with the study of Meester et al.,²³ who found, for $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{CH}_3\text{CN}$, the latter two frequencies at 394cm^{-1} and 482cm^{-1} .

The C_2 torsional mode displays a shoulder to high frequency (observed in the neutron energy gain spectra at 207cm^{-1} , and in the BFD spectrum at 222cm^{-1}) which presumably represents the Pt-C_2 rock (t_y). However, for this complex the evidence for a band to the long wavelength side of the τ_z peak, which would correspond to the Pt-C_2 wag (t_x), is slightly more speculative. Nevertheless, there does appear to be a shoulder present in the $\text{P}(\alpha, \beta)$ spectra at about 127.5cm^{-1} , which becomes more clearly discernible at low angle. Furthermore, the ratio of the intensities $t_x : t_y : \tau_z$, found from the $\text{P}(\alpha, \beta)$ spectrum (angle 36°) on the basis of these assignments, 1.00: 1.00 : 2.55, is not too dissimilar from the calculated values of 1.00: 1.06: 3.11.

In order to study more fully the bands identified at 29cm^{-1} , 49.5cm^{-1} and 82cm^{-1} , supplementary Raman spectra were measured of the complex as a solid and in ethanolic solution. Only the equivalents of the two lower frequency peaks were observed in the solid phase Raman spectra, and in common with the findings for $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$, no corresponding vibrations of the correct intensities could be located in the solution work. Similarly, therefore, it must be presumed that the 29cm^{-1} and 49.5cm^{-1} frequencies are lattice modes, and the degree of dispersion evident in the 6H spectra between various angles appears to provide further corroboration.

Assignment of the 82cm^{-1} transition, however, provides more difficulty by virtue of its non-location in the optical spectra. Nonetheless, the

intensity of this peak appears from the evidence of the $P(\alpha, \beta)$ spectra, to be dramatically angularly dependent. Hence the frequency, analogously with the 29cm^{-1} and 49.5cm^{-1} bands, has been ascribed to a lattice vibration.

Of the remaining INS peaks, those at highest energy (724cm^{-1} and 830cm^{-1}) may be assigned to the CH_2 rocking modes found at similar energies in both Zeise's salt and dimer^{22,29}. This leaves one band unaccounted for in the BFD spectrum; that situated at 339cm^{-1} . This is in the region of the spectrum where Meester et al.²³ have identified the Pt-Cl symmetric and antisymmetric stretches (342cm^{-1} and 345cm^{-1} respectively) for the complex $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{CH}_3\text{CN}$.

It is unreasonable to assume that the motion of the chlorine atoms themselves would be seen in the INS spectrum because they have an incoherent cross-section of 3.5 barns compared with the 79.7 barns of hydrogen and furthermore, only number two. However, in square planar complexes, the symmetric stretch of the chlorine atoms ($\nu_s(\text{Pt-Cl})_{\text{dia.4(v)}}$) gives rise to a sympathetic symmetric stretch in the $\text{C}_2\text{H}_4\text{-Pt-Ligand}$ part of the system. It is therefore probable that the $\nu_s(\text{Pt-Cl})$ mode is being observed in the INS spectrum as a result of "mirroring" by the ethylene group, which of course contains four protons. If the effect is considered simplistically in terms of four springs connecting the four ligands of the square planar complex to the central platinum atom, it may be seen that the intensity of the "mirrored" Cl-Pt-Cl stretch will depend upon the ligand opposite the ethylene group. If a ligand lighter than ethylene is present, the relative moments of inertia of the two groups will decree that the lighter group moves through a very much greater amplitude of vibration than ethylene. As a result, $\nu_s(\text{Pt-Cl})$ will display only weak or negligible intensity, which is presumably the case for the complex $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{ND}_3$. Conversely, where the ethylene group is the lighter of the two diametrically opposed ligands, the amplitude of vibration of ethylene will be correspondingly

greater, and the platinum-chlorine symmetric stretch will show up with increased intensity.

Considering now the optical spectra of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{CD}_3\text{CN}$, the additional assignment of the Pt-Cl antisymmetric stretch may be made to the infrared band at 346cm^{-1} , whilst the location of the Pt-Cl symmetric mode may be confirmed from the Raman peak at 344cm^{-1} .

As with $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{ND}_3$, the identification of bands to the low frequency side of the chlorine stretching region is somewhat difficult and hence exceedingly tentative. However, the assignments of Grogan and Nakamoto²⁶ for $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ (Table 4.3) may be used as guidance. In this case, it appears that the 163cm^{-1} infrared frequency of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{CH}_3\text{CN}$ remains unchanged on deuteration, whilst that at 191cm^{-1} is shifted approximately 10cm^{-1} . The intensity of the former vibration appears too great for identification with the formally infrared inactive C_2 torsion and, furthermore, does not seem inversely sensitive to temperature in the manner which has been reported for such modes.³⁶ It may therefore seem that the assignments for Zeise's salt should be reversed (or that an analogous pattern to that suggested for $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ ^{33,34} should be followed), with the unshifted band (163cm^{-1}) being correlated with $\delta(\text{Cl-Pt-Cl})$, and the 191cm^{-1} shoulder with $\delta(\text{Cl-Pt-N})$. However, when it is considered that scarcely any deuteration shift is expected of the $\delta(\text{Cl-Pt-N})$ vibration (0.989°), and that the experimentally determined shift is 0.948 , it would appear that the justification for so doing is slight.

Of the vibrations remaining, that at 124cm^{-1} in the far-infrared of the CD_3CN complex is almost unchanged in frequency from the hydrogenous compound, whilst that at 107cm^{-1} has no reported analogue in the spectrum

✓ This shift has been calculated making the approximation that the bend could be compared with that of a linear triatomic molecule of the form, X-Y-Z : $\text{C}_2\text{H}_4\text{-PtCl}_2\text{-CH}_3\text{CN}$. The appropriate formula of Herzberg³⁵ for a bending mode of this type has then been employed assuming:

- (i) that the bond lengths are those contained in Appendix 3, and
- (ii) that the bending constant remains unchanged on deuteration

of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{CH}_3\text{CN}$. On grounds of both frequency and invariance to deuteration, the former must be designated the Pt-C_2 wag (t_x). It would thus appear that the 107cm^{-1} peak represents the out-of-plane chlorine bend, $\pi(\text{Cl-Pt-Cl})$, reported at the slightly lower frequency of 92cm^{-1} in Zeise's salt²⁶ (Table 4.3). In fairness, though, it should be pointed out that this mode might possibly be assigned to the 82cm^{-1} peak located in the INS spectra. However, the apparently dispersive nature of the 82cm^{-1} frequency in the INS spectra, coupled with its non-location in the optical spectra (this mode is considered to be of moderate intensity in Zeise's salt^{27,29}) would seem to invalidate this assignment.

The remaining low frequency peak, that at 200cm^{-1} in the infrared spectrum of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{CH}_3\text{CN}$, is unshifted on deuteration, and of the bending modes predominantly involving chlorine and/or ethylene, as yet unassigned, only the Pt-C_2 rock has not been identified. For this reason it has been correlated with the $207/222\text{cm}^{-1}$ INS vibration.

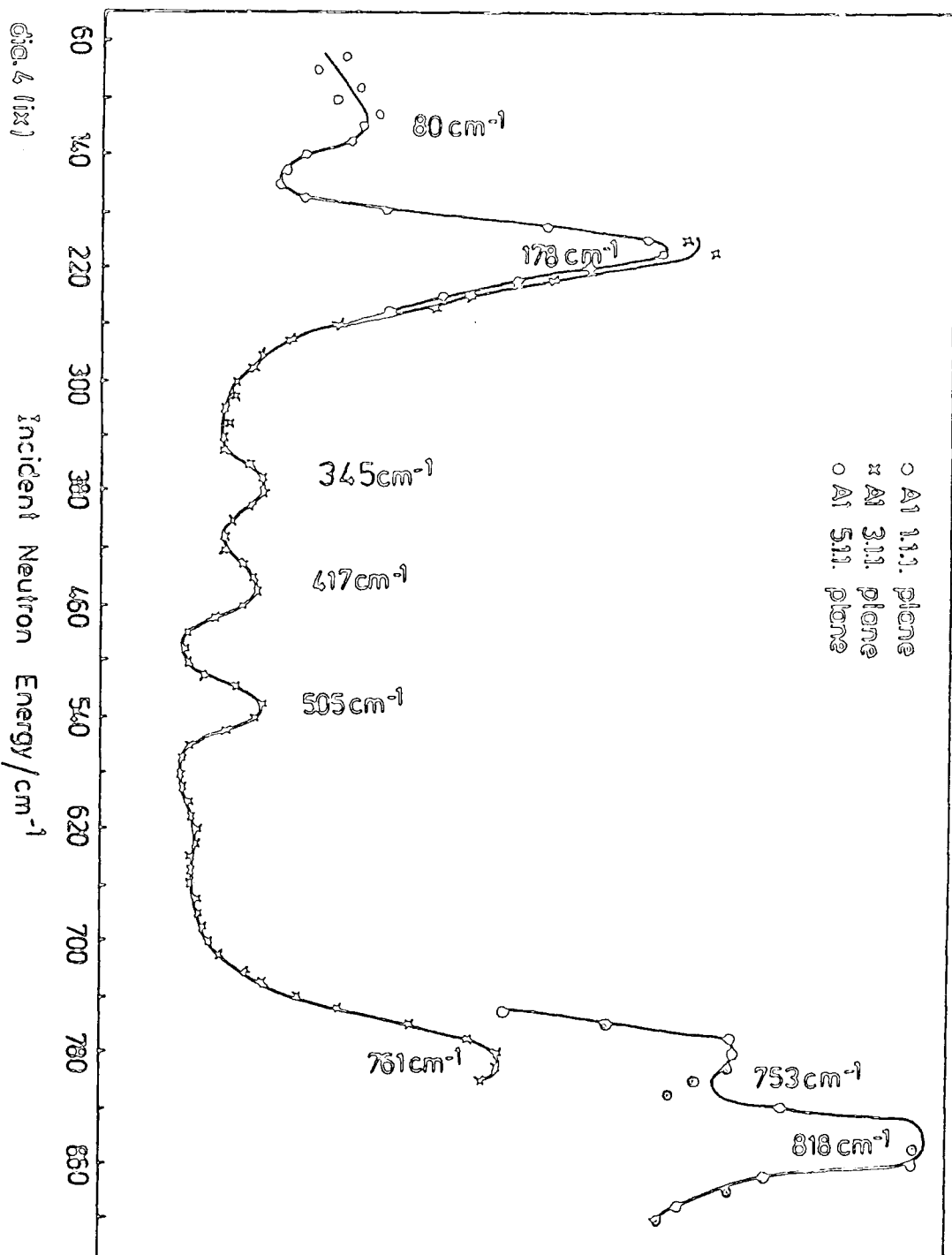
The infrared band at 243cm^{-1} in the compound containing the hydrogenous ligand has apparently moved on deuteration to 229cm^{-1} . This represents a deuteration shift of 0.977, whilst that calculated using the reduced masses of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{CH}_3\text{CN}$ and $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{CD}_3\text{CN}$ is 0.970. There would therefore seem to be support for the assignment of the 243cm^{-1} frequency by Meester et al.²³ to $\nu(\text{Pt-N})$.

Considering finally the higher energy bands, sufficient data are available only for the positive assignment of the $721/735\text{cm}^{-1}$, and the $840/865\text{cm}^{-1}$ infrared vibrations to the two CH_2 rocking modes of ethylene; although the Raman frequencies of 361cm^{-1} and 368cm^{-1} are not dissimilar to those observed in the infrared spectrum of the liquid CD_3CN used in the preparation of the complex under investigation (356cm^{-1} and 374cm^{-1}).

c) $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{DCON}(\text{CD}_3)_2$

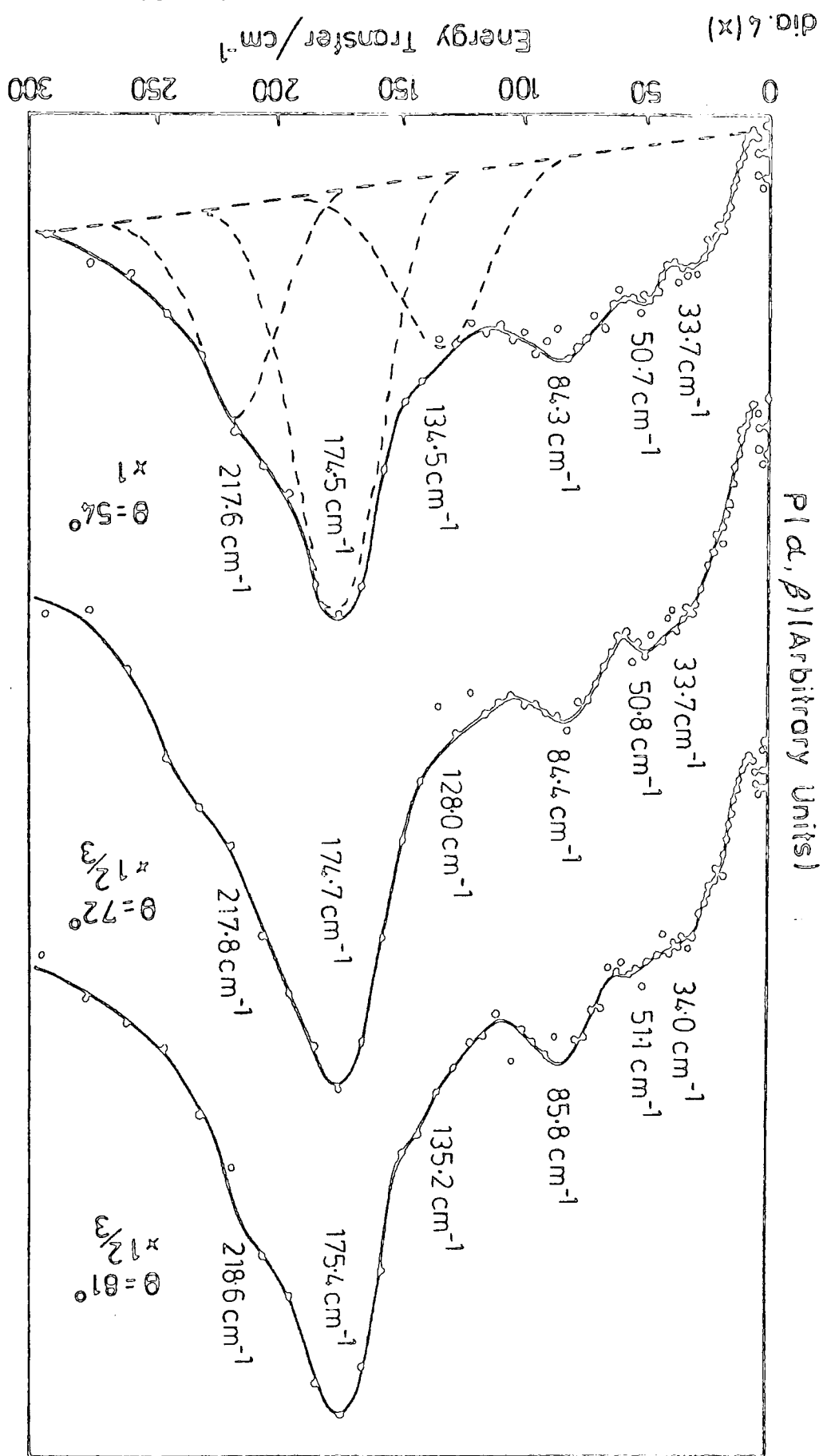
The INS spectra of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{DCON}(\text{CO}_3)_2$ are shown in dias.4(ix) -

Intensity (Monitor Counts)



$\text{PtCl}_2(\text{C}_2\text{H}_4)\text{D CON (CD}_3)_2$ (Silica background not subtracted)

Puho BFD Spectrometer : Liquid Nitrogen temperature.



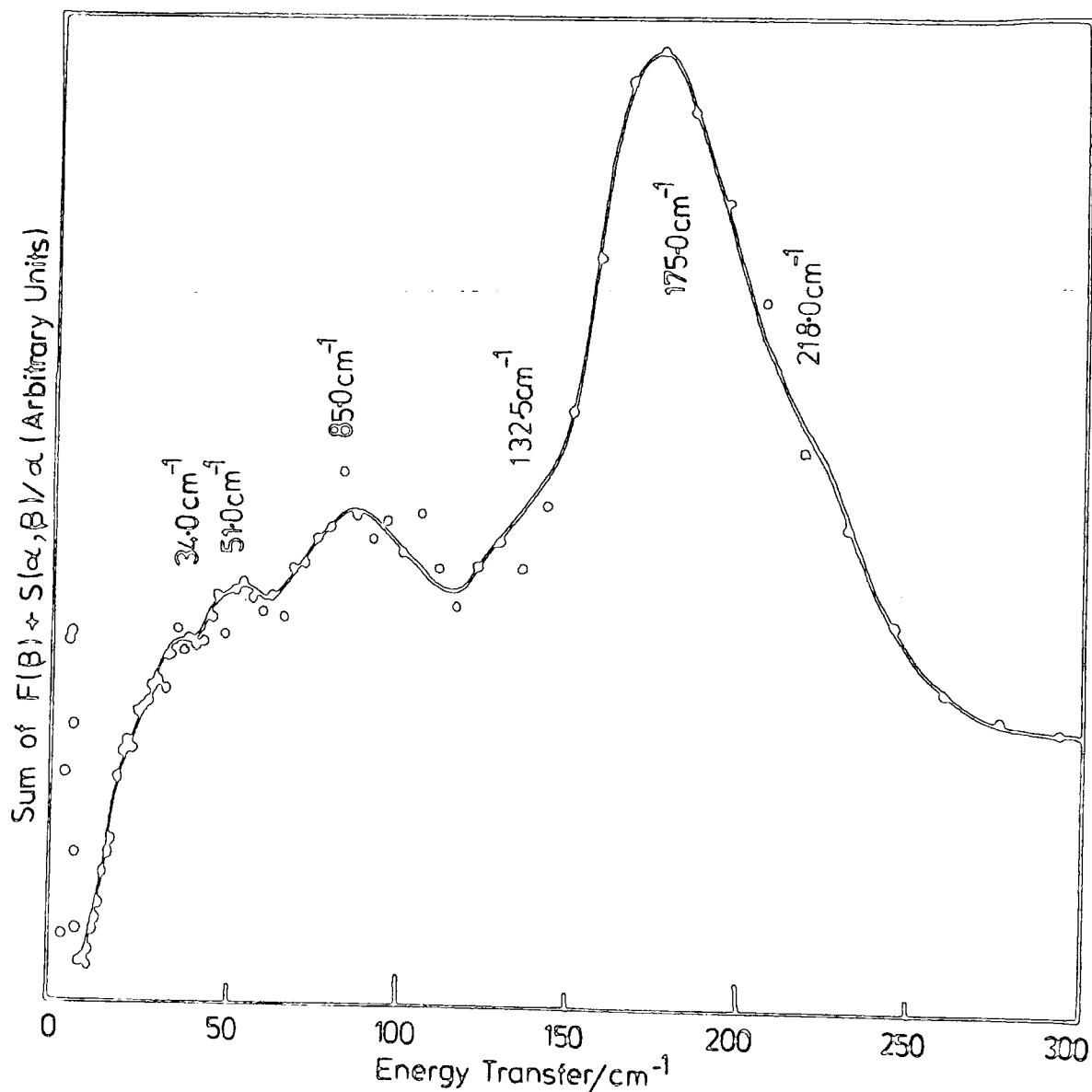


fig. 4 (xi)

 $\text{PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{DCON}(\text{CD}_3)_2$ 243 K

6H Time-of-Flight Spectrometer

TABLE 4.0 The Spectroscopic Determination (cm^{-1}) and Assignments of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)_2\text{DCCN}(\text{CD}_3)_2$ Compared with its $\text{DCCN}(\text{CH}_3)_2$ Analogue

$\text{trans-PtCl}_2(\text{C}_2\text{H}_4)_2\text{DCCN}(\text{CD}_3)_2$			$\text{trans-PtCl}_2(\text{C}_2\text{H}_4)_2\text{DCCN}(\text{CD}_3)_2$				
Infrared	Raman	Assignment	Infrared	Raman	INS		Assignment
					BFD	T-O-F	
				30sh 44s		34.0 $\pm$ 2.0	} Lattice Vibrations
			53s	59sh		51.0 $\pm$ 3.0	
53s			65s	82s	80 $\pm$ 10	85.0 $\pm$ 4.5	
129s		°	117sh 132s	135vs 144vs		132.5 $\pm$ 7.5	Pt-C ₂ wag (t_x)
170s		°	159sh 167s	169vs			°
			180s	176vs	178 $\pm$ 10	175.0 $\pm$ 10.0	C ₂ Torsion (τ_2)
			193s				°
		°					
205sh 218s		°	213s	206vs 220vs		218.0 $\pm$ 13.0	Pt-C ₂ rock (t_y)
			278sh				°
			290sh				°
			303sh				°
			318vs				°
				331s 340s	345 $\pm$ 10		ν_g (Pt-Cl)
341vs	(340)	ν_g (Pt-Cl)	338vs 360sh				ν_{as} (Pt-Cl)
		ν_{as} (Pt-Cl)					
397s	(403)	ν_g (Pt-C ₂)	396s	407s	417 $\pm$ 10		ν_g (Pt-C ₂)
			423s	430s			
			470vs	472vs 490vs			
404s		ν_{as} (Pt-C ₂)	503s	507vs 587vs	505 $\pm$ 10		ν_{as} (Pt-C ₂)
			616s	604vs			
			670s				
			749sh 767s } 822vs		753 $\pm$ 10/ 761 $\pm$ 10 818 $\pm$ 10		CH ₂ rock CH ₂ rock

* This sample gave poor Raman spectra
° Discussed within the text

vs = very strong; s = strong; m = medium; w = weak; vs = very weak; sh = shoulder; () denote solution data;
P = polarized Raman band; ν_g = symmetric stretch; and ν_{as} = antisymmetric stretch.

(xi) and are summarised, together with infrared and Raman data in Table 4.6.

Use of the intensity relations developed previously enables straightforward identification in the INS spectra of the C_2 torsional mode (τ_z), symmetric stretch (t_z) and antisymmetric stretch (τ_y) of the ethylene group at the frequencies, $175/178\text{cm}^{-1}$, 417cm^{-1} and 505cm^{-1} respectively. The two latter compare with published frequencies of 406cm^{-1} and 484cm^{-1} for the corresponding symmetric and antisymmetric stretches of ethylene in the complex $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{HCON}(\text{CH}_3)_2$.²³

Once more the C_2 torsional peak may be seen in the $P(\alpha, \beta)$ spectra to display a distinct shoulder to high frequency, and a less well resolved shoulder to long wavelength, which becomes increasingly distinct with decreasing angle. Following precedent, the high frequency shoulder (218cm^{-1}) may be designated the Pt- C_2 rocking mode (t_y), whilst the second shoulder (132.5cm^{-1}) appears to correlate with the Pt- C_2 wag (t_x). Using the above assignments, the intensities $t_x:t_y:\tau_z$ have been measured in the $P(\alpha, \beta)$ spectrum (angle 54°). The resultant ratio; 1.00: 1.04: 2.30, will be seen to be not markedly different to those obtained for the complexes $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{ND}_3$ and $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{CD}_3\text{CN}$, and compares with anticipated values of 1.04: 1.00: 3.08.

Of the lowest frequency T-O-F vibrations, those at 34.0cm^{-1} , 51.0cm^{-1} and 85.0cm^{-1} all appear dispersive from the T-O-F data and furthermore, although represented in solid phase Raman spectra, could not be located when ethanol solution spectra were measured. Consequently, they would appear to be lattice modes.

Returning to the BFD spectrum, by analogy with the complexes discussed before, the two intense bands at $753/761\text{cm}^{-1}$ and 818cm^{-1} must correspond to the two CH_2 rocking modes. However, it is interesting to note that the former peak is to higher energy in this compound than the comparable bands observed for the compounds $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{ND}_3$ and $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{CD}_3\text{CN}$.

The vibration of moderate intensity observed at 345cm^{-1} is very close to the Cl-Pt-Cl symmetric stretching frequency (340cm^{-1}) identified for the $\text{HCON}(\text{CH}_3)_2$ compound²³. The presence of this vibration in the BFD spectrum may again be explained using the reasoning applied for $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{CD}_3\text{CN}$, the seemingly greater intensity of the chlorine mode relative to the ethylene symmetric stretch in the $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{DCON}(\text{CD}_3)_2$ complex being explicable as a consequence of the greater mass of the $\text{DCON}(\text{CD}_3)_2$ ligand.

Turning now to the infrared and Raman spectra of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{DCON}(\text{CD}_3)_2$, the additional assignment of the platinum-chlorine antisymmetric stretch may be made to the frequency of 338cm^{-1} which compares with a literature value for the analogous $\text{HCON}(\text{CH}_3)_2$ complex of 341cm^{-1} ²³.

In the region of the infrared spectrum immediately below these frequencies ($278\text{--}318\text{cm}^{-1}$), there are a number of vibrations which have no analogue in the reported spectra of the $\text{HCON}(\text{CH}_3)_2$ compound. Certainly, the shoulders at 278cm^{-1} and 290cm^{-1} are also represented in the infrared spectrum of $\text{DCON}(\text{CD}_3)_2$ (280cm^{-1} and 290cm^{-1}), but the others must be assumed to result from platinum-ligand modes. Unfortunately, Meester et al.²³ failed to identify any such vibrations in their study of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{HCON}(\text{CH}_3)_2$ and hence there are particular difficulties in their positive assignment. However, it is possible that the 318cm^{-1} infrared band, found for the deuterated compound, but apparently absent from the spectrum of the hydrogenous complex, corresponds to the $\nu(\text{Pt-O})$ mode. It would then be expected to correlate on the basis of the deuteration shift calculated from the reduced masses of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\text{--HCON}(\text{CH}_3)_2$ and $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\text{--DCON}(\text{CD}_3)_2$ (0.964) with a frequency at approximately 330cm^{-1} in the $\text{HCON}(\text{CH}_3)_2$ ligand complex spectrum. The only reasonable explanation for the non-identification of such a vibration would thus be if it, in fact, coincided with the very intense band at 341cm^{-1} designated $\nu_{\text{as}}(\text{Pt-Cl})$ by Meester et al.²³, in which case the actual deuteration shift would be 0.933.

Support for the identification of the 318cm^{-1} infrared band of the $\text{DCON}(\text{CD}_3)_2$ complex with $\nu(\text{Pt-O})$ may perhaps be gained from the broad agreement between this frequency and that suggested for the complex $\text{trans-PtCl}_2(\text{C}_2\text{H}_4) \cdot (4\text{CH}_3\text{-Py-NO})$ by Shupack and Orchin (323cm^{-1})³⁷. Conversely, there has been a counter assignment of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4) \cdot (4\text{CH}_3\text{-Py-NO})$ by Meester et al.²³ which has placed the $\nu(\text{Pt-O})$ vibration at 296cm^{-1} ; whilst in the same study, the analogous mode for $\text{trans-PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{Urea}$ was considered to occur at 299cm^{-1} .

In the region of the $\text{trans-PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{DCON}(\text{CD}_3)_2$ optical spectrum to still lower energy, the infrared peak at 180cm^{-1} appears to become more intense on cooling from room to liquid nitrogen temperature. Similar effects have been reported previously for torsional modes³⁶, and hence this vibration has been correlated with the INS frequency of 175cm^{-1} designated the ethylene C_2 torsion (τ_z). Also following the evidence of the INS data, the infrared bands at 218cm^{-1} and 129cm^{-1} in the spectrum of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{HCON}(\text{CH}_3)_2$ may be assigned to the Pt-C_2 rock (t_y) and wag (t_x) respectively.

Two additional peaks in the low frequency infrared spectrum of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{DCON}(\text{CD}_3)_2$, remain unconsidered, those at 167cm^{-1} and 193cm^{-1} . The former appears to be equivalent to a vibration in the infrared spectrum of the $\text{HCON}(\text{CH}_3)_2$ ligand compound at 170cm^{-1} , whilst the 193cm^{-1} frequency seems to have no analogue. Following the assignments for Zeise's salt²⁶, the 167cm^{-1} and the 193cm^{-1} peaks may be identified as $\delta(\text{Cl-Pt-O}) + (\text{Cl-Pt-C}_2\text{H}_4)$ and $\delta(\text{Cl-Pt-Cl})$ respectively. Conversely, it may be argued that the higher frequency, because no analogous peak has been located in the spectrum of the hydrogenous ligand complex might represent a bending mode of the $\text{DCON}(\text{CD}_3)_2$ ligand relative to platinum which has been shifted on deuteration. However, if this were true, then the minimum deuteration shift (from the 205cm^{-1} band of $\text{trans-Pt-Cl}_2(\text{C}_2\text{H}_4) \cdot \text{HCON}(\text{CH}_3)_2$) would be 0.941, which would not be in very close

agreement with a predicted value of $0.991^{\wedge}$.

In the case of this complex, the evidence for the mode $\pi(\text{Cl-Pt-Cl})$ is scant; however, it is possibly represented by the 98cm^{-1} frequency located in the infrared spectrum of the $\text{HCON}(\text{CH}_3)_2$ ligand compound, and has proved too weak to be observed for $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{DCON}(\text{CD}_3)_2$.

Turning finally to frequencies higher than the platinum-chlorine stretching region, the optical spectra of the $\text{DCON}(\text{CD}_3)_2$ ligand complex follow the assignments from the INS data, with the exceptions of two moderately intense infrared bands at 616cm^{-1} and 670cm^{-1} , the former of which is also observed in the infrared spectrum of $\text{DCON}(\text{CD}_3)_2$.

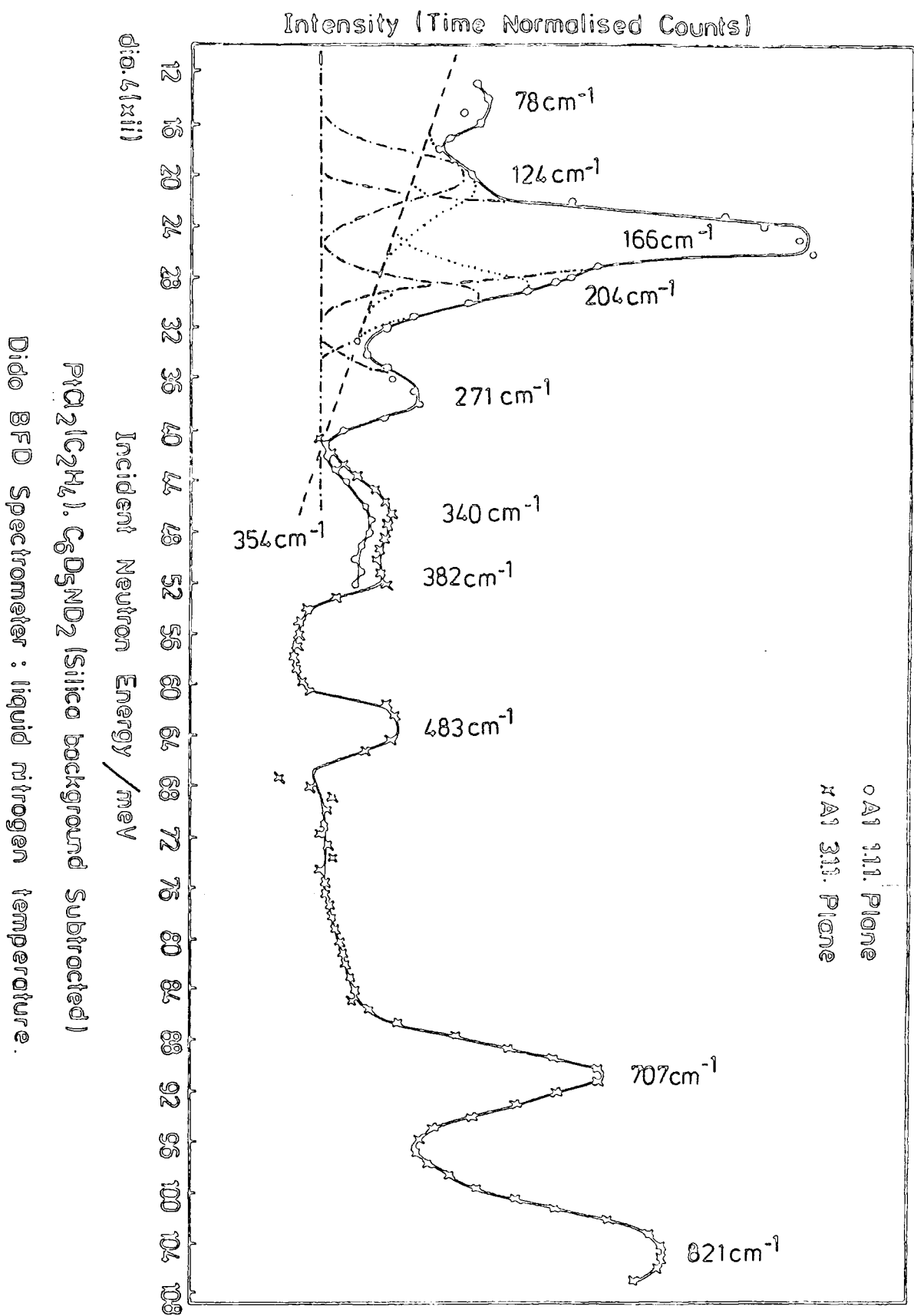
d) $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{D}_5\text{ND}_2$

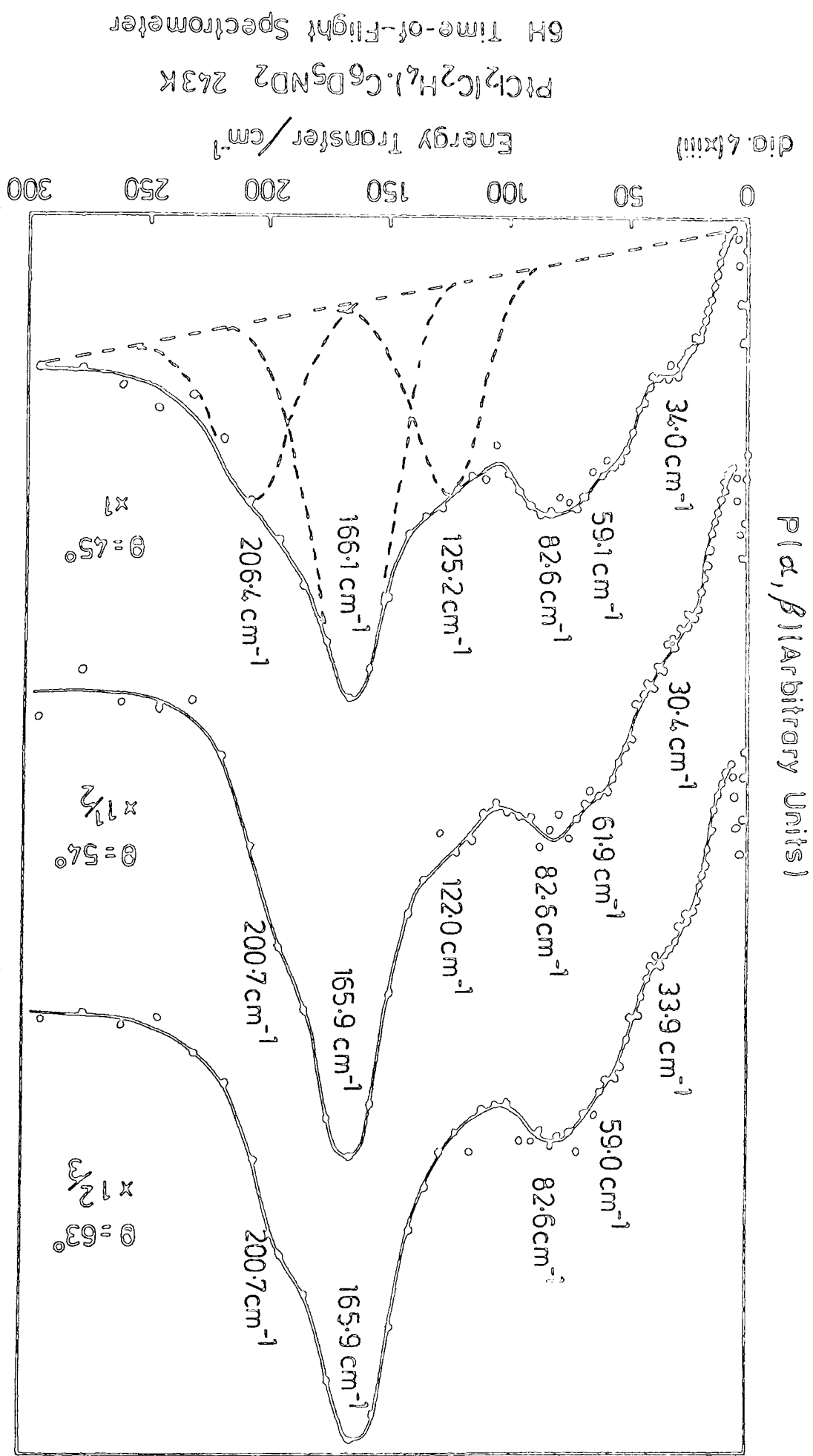
The INS spectra of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{D}_5\text{ND}_2$ are shown in dias.4(xii) - (xiv) and are summarised, together with infrared and Raman data in Table 4.7.

By comparison with the trans complexes described earlier, the C_2 torsion (τ_z), symmetric stretch (t_z) and antisymmetric stretch (τ_y) of the ethylene molecule relative to the platinum atom may be assigned to bands located in the BFD spectrum at 166cm^{-1} , 382cm^{-1} and 483cm^{-1} . Once more the latter two values are in agreement with these determined optically for the symmetric and antisymmetric stretches of ethylene in the complex $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{H}_5\text{NH}_2^{23}$ (385cm^{-1} and 474cm^{-1} respectively).

The C_2 torsional peak displays two shoulders, one to high frequency and one to long wavelength, which are more distinctly resolved in the $\text{P}(\alpha, \beta)$ spectra. The former, situated at 202.5cm^{-1} (204cm^{-1} BFD), may be identified as the Pt-C_2 rocking mode (t_y), whilst the latter, located at 123.5cm^{-1} (124cm^{-1} BFD) may be correlated with the Pt-C_2 wag (t_x).

$\wedge$ This shift has been calculated making the approximation that the bend could be compared with that of a linear triatomic molecule of the form, $\text{X-Y-Z}:\text{C}_2\text{H}_4\text{-PtCl}_2\text{-HCON}(\text{CH}_3)_2$. The appropriate formula of Herzberg³⁵ for a bending mode of this type has then been employed assuming:
(i) that the bond lengths are those contained in Appendix 4, and
(ii) that the bending constant remains unchanged on deuteration.





P1C₂H₄.C₆D₅ND₂ 263K
6H Time-of-Flight Spectrometer

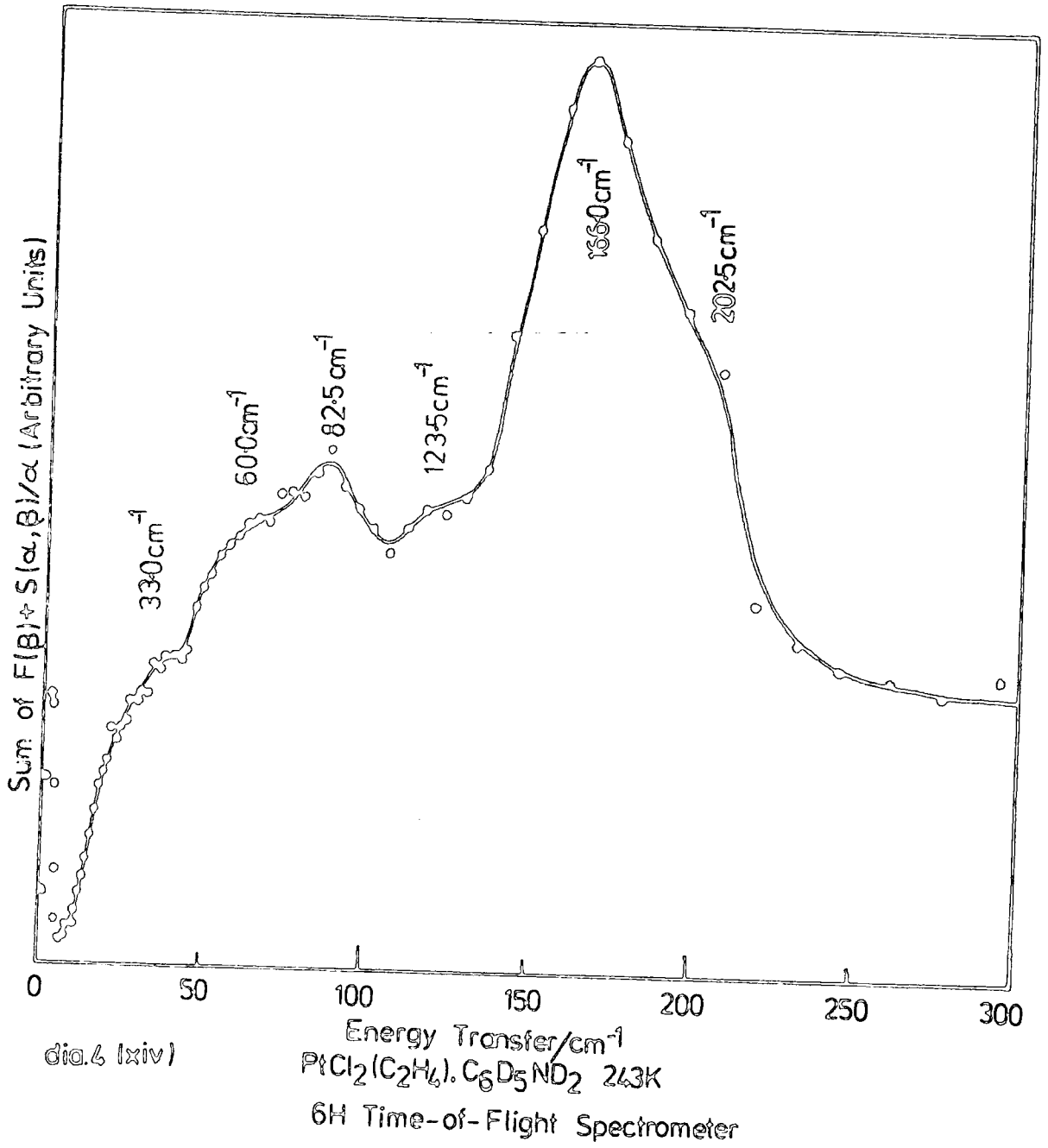


TABLE 4.7 The Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_5)_2$ Compared With Its $\text{C}_6\text{H}_5\text{NH}_2$ Analogue

$\text{trans-PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_5)_2$ 23		$\text{trans-PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_5)_2$			
Infrared	Raman	Assignment	Infrared	Raman	INS
					BFD T-O-F
123s				20s	33.0-2.0
159sh			87s	38s	Lattice Vibrations
166s			108sh	51sh	60.0-3.5
			119s	59sh	82.5-4.5
			140s	82m	
				115sh	123.5-7.0
159sh					Pt-C ₂ diag(τ_z)
166s					
	150s		164sh	160s	C ₂ Torsion(τ_z)
			170s		
208s			200s	200s	202.5-12.0
216sh				213sh	Pt-C ₂ rock(τ_z)
330sh	333s(337P)	ν (Pt-Cl)	330sh	338s	ν (Pt-Cl)
338s	330sh(347P)	ν_a (Pt-Cl)	339s		ν_s (Pt-Cl)
348s	351s	ν_g (Pt-L)			
362s	365s(365P)	ν_o (Pt-C ₂)	362vs	360s	ν_s (Pt-C ₂)(τ_z)
			407s	403s	ν (Pt-L)?
433s	435s(436P)	ν (Pt-L)			
474s	472s	ν_{ad} (Pt-C ₂)	475sh	480s	ν_{ad} (Pt-C ₂)(τ_z)
			903s	905s	Ring deformation in-phase
			962s	965s	CH ₂ rock
			720s		
			747s		
			830s		
			840vs		CH ₂ rock

* Discovered within 80%

vs = very strong; s = strong; sh = shoulder; v = weak; vs = very weak; sh = shoulder; () denotes solution data; P = polarized Raman band; ν_o = asymmetric stretch; ν_{ad} = antisymmetric stretch.

As a result of a mechanical fault, the 1700 spectrometer, during the measurement of this spectrum, failed to position at the value of 20 (Figure III), which has been corrected. It has therefore proved necessary to correct the energy scale so that it corresponds to the 20 values normally used, and consequently, larger than normal error bars have had to be added for the transition energies listed above.

The intensity relation ($t_x : t_y : t_z$) thus evaluated for these assignments from the $P(\alpha, \beta)$ spectrum (angle 45°), 1.09: 1.00: 2.26, compares with calculated values of 1.02: 1.00: 3.07.

The other peaks situated in the $P(\alpha, \beta)$ spectra at 33cm^{-1} , 60cm^{-1} and 82.5cm^{-1} , all show dispersion. Furthermore, whilst analogues of these bands are seen in solid phase Raman studies, these are absent from Raman spectra obtained for the complex in ethanolic solution. Hence the vibrations appear to represent lattice modes.

Returning to the middle-frequency region of the BFD spectrum, $\nu_s(\text{Pt-Cl})$ may be observed at $340\text{cm}^{-1}/354\text{cm}^{-1}$, in close proximity to the frequency reported for this mode in the equivalent $\text{C}_6\text{H}_5\text{NH}_2$ ligand complex.²³ (337cm^{-1}) Bearing in mind the arguments previously advanced for the presence of this vibration in the INS spectrum, it will be noted that the ligand opposite the ethylene group is now sufficiently massive that the intensity of $\nu_s(\text{Pt-Cl})$ is comparable with that of $\nu_s(\text{Pt-C}_2)$.

The remaining unassigned peak in this frequency range, that placed at 271cm^{-1} , has no obvious counterpart in any of the complexes described hitherto, nor is a transition reported within 35cm^{-1} of this value in either Raman or infrared of Zeise's salt^{26,29} or the complex $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{H}_5\text{NH}_2$ ²³ and its deuterated ligand analogue. Consequently discussion of this vibration is best deferred until all the available INS, infrared and Raman data have been considered.

Of the BFD bands as yet unassigned, only those at highest energy (707cm^{-1} and 821cm^{-1}) remain. By comparison with the INS spectra of the preceding $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{L}$ complexes and also of Zeise's salt and dimer²², these may be identified with the two anticipated CH_2 rocking modes.

Turning now to the infrared and Raman spectra of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{D}_5\text{ND}_2$, the additional assignment of the Pt-Cl antisymmetric stretch may be made to the frequency of 339cm^{-1} , which is not far removed from that published for

trans-PtCl₂(C₂H₄).C₆H₅NH₂(338cm⁻¹).

To lower energies, identification of bands becomes increasingly difficult and hence tentative. However, it is perhaps possible to associate the ethylene C₂ torsional mode (τ_z) located from INS spectra at 166cm⁻¹ with the 164cm⁻¹ frequency which is only observed in the infrared of the C₆D₅ND₂ ligand complex on cooling to liquid nitrogen temperature. Also, by analogy with the INS spectra, the bands located at 123cm⁻¹ and 206cm⁻¹ in the infrared spectrum of trans-PtCl₂(C₂H₄).C₆H₅NH₂ may be correlated with the Pt-C₂ wag (t_x) and Pt-C₂ rock (t_y) respectively.

This leaves unaccounted for the infrared peaks at 140cm⁻¹ and 170cm⁻¹ in the spectrum of the complex trans-PtCl₂(C₂H₄).C₆D₅ND₂. In view of the absence of a deuteration shift associated with the latter frequency, it must be assumed to represent a chlorine bending mode, most probably $\delta(\text{Cl-Pt-Cl})$ after the band located in Zeise's salt at 183cm⁻¹²⁶. The 140cm⁻¹ vibration, however, presents more difficulty in assignment in that it appears to have no analogue in the infrared spectrum of the hydrogenous ligand complex. Furthermore, the minimum deuteration shift it might have undergone (from the 159cm⁻¹ infrared band of trans-PtCl₂(C₂H₄).C₆H₅NH₂) would be 0.881, whilst the maximum shift expected of any Pt-C₆H₅NH₂ bending or stretching mode is 0.973. This therefore appears an unlikely correlation, and consequently the peak must represent a bending mode predominantly involving chlorine atoms, and may perhaps be designated either $\delta(\text{Cl-Pt-N}) + \delta(\text{Cl-Pt-C}_2\text{H}_4)$ after Zeise's salt (161cm⁻¹)²⁶ or $\pi(\text{Pt-Cl})$ after trans-Pt(NH₃)₂Cl₂ (136cm⁻¹)³³ (Table 4.3).

Of the higher energy vibrations, both of those in the infrared spectrum of trans-PtCl₂(C₂H₄).C₆H₅NH₂ which have been associated with $\nu(\text{Pt-L})$, at 346cm⁻¹ and at 433cm⁻¹,²³ are absent from the infrared spectrum of the deuterated ligand complex. The latter band appears to have moved to a frequency of 407cm⁻¹ in the infrared spectrum of trans-PtCl₂(C₂H₄).C₆D₅ND₂,

which represents an isotopic shift of 0.940, compared with that calculated by comparison of the reduced masses of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\text{-C}_6\text{H}_5\text{NH}_2$ and $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\text{-C}_6\text{D}_5\text{ND}_2$ (0.973). The 346cm^{-1} peak is not apparently present at all in the infrared spectrum of the $\text{C}_6\text{D}_5\text{ND}_2$ ligand complex unless it has moved beneath the intense band at $330\text{-}9\text{cm}^{-1}$. If this were the case, an approximate deuteration shift of between 0.954 and 0.980 would be indicated. Although the latter shift is nearer the magnitude predicted, the $433\text{-}407\text{cm}^{-1}$ frequencies would seem to be the better correlation on intensity grounds.

At still higher energy in the spectrum of $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\text{-C}_6\text{D}_5\text{ND}_2$, the infrared band at 562cm^{-1} may be assigned to an in-phase ring deformation following work reported for aniline_{d7} vapour³⁸; whilst the infrared vibrations at $720\text{-}47\text{cm}^{-1}$ and $820\text{-}40\text{cm}^{-1}$ may be identified, by comparison with the INS data detailed previously, as the two CH_2 rocking modes of ethylene.

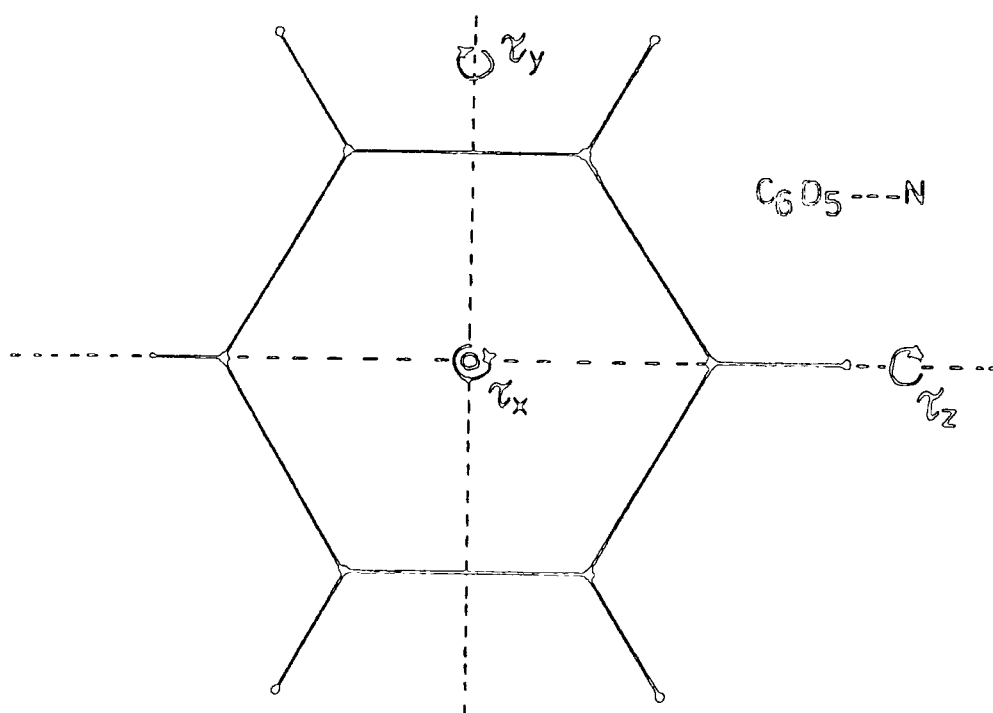
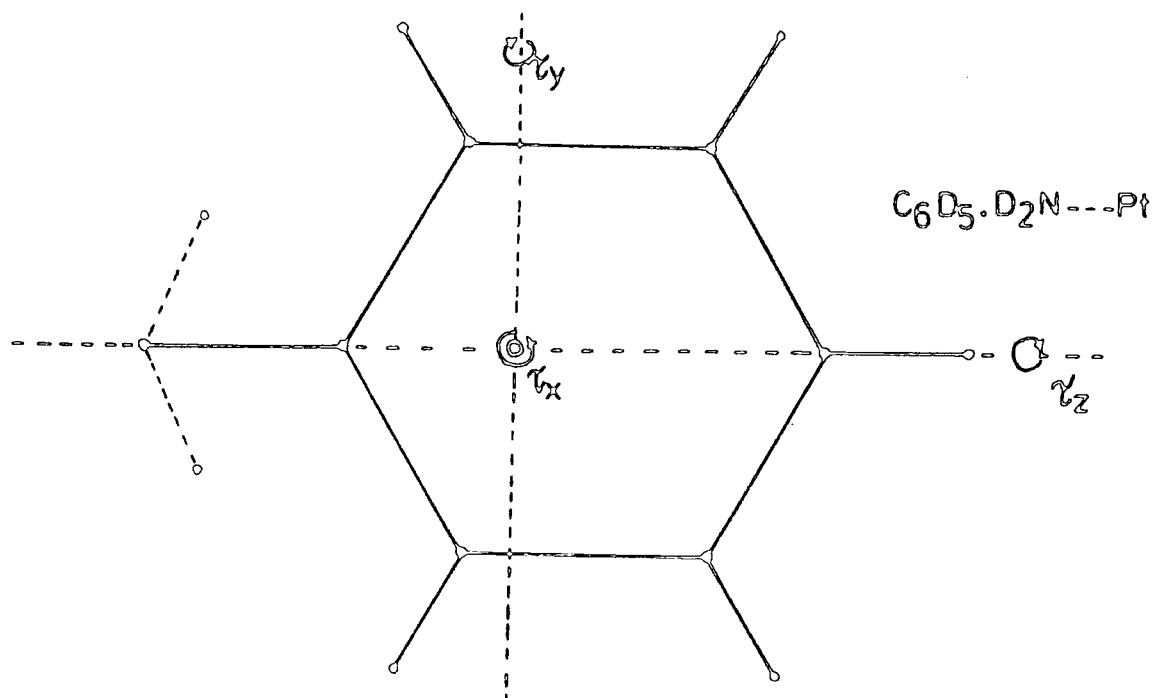
Returning finally to the BFD frequency of 271cm^{-1} , it would appear from the assignments previously detailed that all the low frequency modes expected to involve ethylene directly or indirectly have been located. It therefore seems that the peak must represent one of the following:

- (i) an internal aniline mode
- (ii) a torsional/translational mode of aniline relative to platinum
- (iii) an overtone/combination band.

In order to differentiate between the options listed above, it is necessary to consider the intensity of the 271cm^{-1} band. Measurements indicate that the intensity of this peak relative to that of the ethylene C_2 torsion (τ_z) is between 1:5.85 and 1:5.75 (depending upon whether the background is taken as line---- or -.-.-). It must be stressed, however, that this is, of necessity, only a rough guide, because the position of the background is subject to such wide error.

As an additional aid to intensity analysis, the purity of the $\text{C}_6\text{D}_5\text{ND}_2$ in

dia.4(xv) Definitions of the torsional modes in Aniline.



the complex was checked by ^1H NMR. This showed that, as a result of manipulation during the preparation of the $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{C}_6\text{D}_5\text{ND}_2$, the deuterium present in the $\text{C}_6\text{D}_5\text{ND}_2$ had been reduced to 96.4% from the 98% originally specified, and that the protons which had exchanged had done so at the nitrogen atom. The composition of the " $\text{C}_6\text{D}_5\text{ND}_2$ " may therefore be stated to be 87.5% $\text{C}_6\text{D}_5\text{ND}_2$: 12.5% $\text{C}_6\text{D}_5\text{NH}_2$.

Even taking into account the above findings, it would appear unlikely that an internal ring mode (such as that reported at 209cm^{-1} for aniline vapour³⁸), involving mainly deuterons describing relatively small amplitudes of vibration, could account for the intensity of the 271cm^{-1} frequency. Calculations were therefore made to determine the predicted intensities of the three hindered rotations and three hindered translations of the $\text{C}_6\text{D}_5\text{ND}_2$ group relative to platinum (dia.4(xv)). (It was considered that torsional/translational modes of the whole of the $\text{C}_6\text{D}_5\text{ND}_2$ molecule were more likely candidates for consideration than those involving only the C_6D_5 section, because of the presence in the former case of two protons situated on the nitrogen atom of 1/8th of the aniline molecules.)

Table 4.8 Intensity Data for $\text{C}_6\text{D}_5\text{ND}_2$, $\text{C}_6\text{D}_5\text{NH}_2$ and C_2H_4 -

Mode	Intensity			
	100% $\text{C}_6\text{D}_5\text{ND}_2$	100% $\text{C}_6\text{D}_5\text{NH}_2$	87.5% $\text{C}_6\text{D}_5\text{ND}_2$ +12.5% $\text{C}_6\text{D}_5\text{NH}_2$	C_2H_4
τ_x	0.023	0.231	0.049	6.742
τ_y	0.019	0.299	0.054	2.648
τ_z	0.032	0.132	0.044	3.038
t	0.012	0.152	0.030	1.000

where τ is a torsion about the axis indicated (dias.4(i) and 4(xv))
and t is a translation about any axis.

Whilst the intensity of vibrations involving ethylene and $C_6D_5ND_2$ are not strictly comparable (because their respective Debye-Waller factors may be expected to be somewhat different (Chapter II)), it may be seen from Table 4.8 that, even with the amount of hydrogen present in the " $C_6D_5ND_2$ " group which has been indicated, it is unreasonable that any of the modes τ_x , τ_y , τ_z or t of $C_6D_5ND_2$ (dia.4(x)) will be observed in the INS spectrum. Indeed, the most intense predicted mode, τ_y , is only about 5.4% of the intensity of the least intense ethylene mode, the translation. This evidence therefore appears to support the intuitive belief that the torsional modes of $C_6D_5ND_2$ would be located at much lower frequency.

A further possibility may be considered of a mode the equivalent of an ND_2 translation, in which ND_2 alone bends between the relatively massive C_6D_5 and $PtCl_2(C_2H_4)$ groups. This may be compared simplistically with a linear triatomic molecule X-Y-Z of the form: $C_6D_5-ND_2-PtCl_2(C_2H_4)$. The intensity of such a mass mode involving, to a first approximation, only ND_2 motion has been calculated allowing for the 12.5% NH_2 actually thought to be present. However, the prediction is that a vibration of this type will only give rise to a band 1/8th of the intensity of that anticipated for an ethylene translational mode, or to restate if slightly differently, $\sim 1/24$ th of the intensity expected for the ethylene C_2 torsion (τ_z). This is clearly not in accord with the experimentally derived data, and the suggestion of an ND_2 bend must thus be deemed untenable.

Finally, the possibility remains of an overtone/combination band. From the form of the intensity relation for Inelastic Neutron Scattering (Chapter II), it will be seen that a band of this type will only be observed if it derives from an extremely intense fundamental. This clearly rules out the possibility of an overtone of the vibration location in the BFD spectrum at $124 \pm 8 \text{ cm}^{-1}$. However, a combination band between the $124 \pm 8 \text{ cm}^{-1}$ and $166 \pm 8 \text{ cm}^{-1}$ frequencies deserves more attention. Theoretically, an

intensity ratio of the 271cm^{-1} peak relative to that of the ethylene C_2 torsion (τ_z) of between 1:8.49 and 1:4.92 would be expected depending upon whether the background denoted ---- or that labelled - - - - - (dia.4(xii)) is assumed. This compares with the actual experimentally derived ratios of between 1:5.85 and 1:5.75 for backgrounds ---- and - - - - - respectively. It must therefore be concluded that the assignment of the 271cm^{-1} frequency to a combination band is reasonable on intensity grounds. However, additional support for this identification may perhaps be obtained if the INS spectrum of the complex $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{D}_5\text{NH}_2$ is measured. The appearance of the 271cm^{-1} frequency, with the same relative intensity compared with the ethylene C_2 torsion (τ_z) as has been found for $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{D}_5\text{ND}_2$, would confirm the indications from the intensity discussions above that a counter assignment to an ND_2/NH_2 stretch or bend, or to an internal aniline mode, would be invalid.

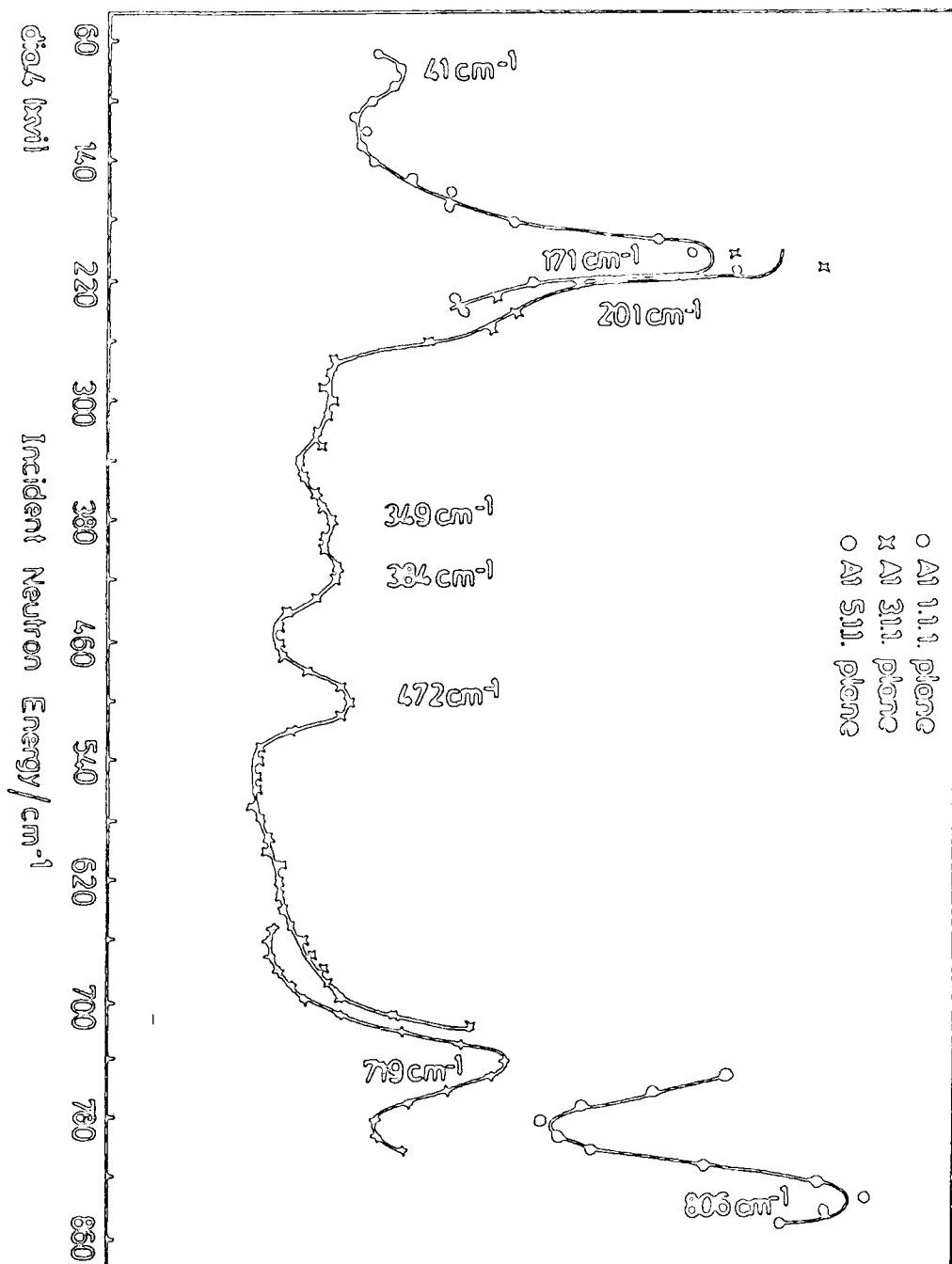
2. The cis-Ethylene Complex: $\text{PtCl}_2(\text{C}_2\text{H}_4).(\text{CD}_3)_2\text{SO}$

The INS spectra of $\text{cis-PtCl}_2(\text{C}_2\text{H}_4).(\text{CD}_3)_2\text{SO}$ are shown in dias. 4(xvi) - (xviii) and are summarised together with infrared and Raman data, in Table 4.9.

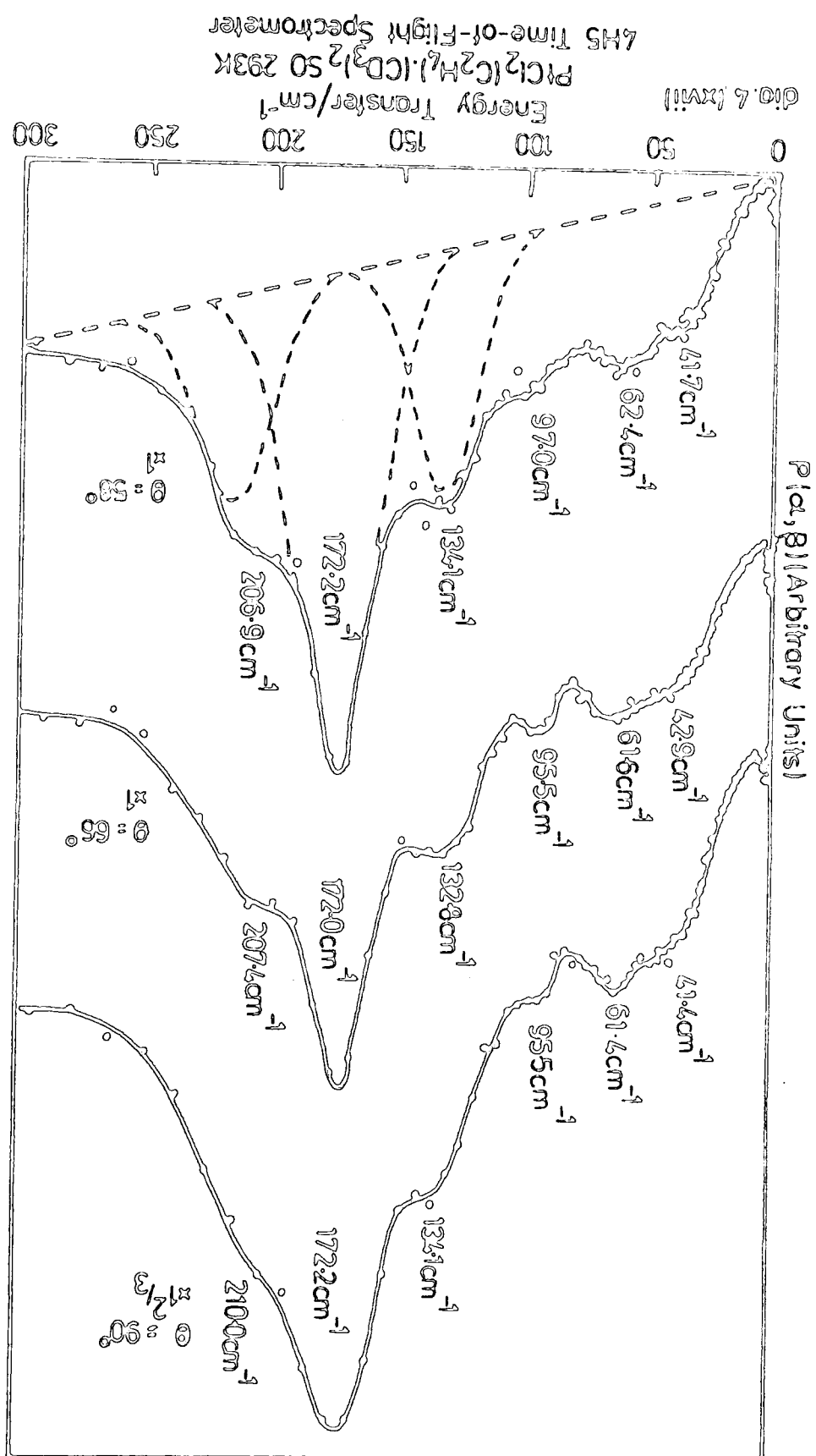
The INS spectra may be seen to be similar to those obtained for the trans complexes. Thus, following previous assignments, the C_2 torsion, symmetric stretch and antisymmetric stretch of ethylene may be correlated with the bands at $171/172\text{cm}^{-1}$, 384cm^{-1} and 472cm^{-1} respectively. Similarly, the two highest energy BFD vibrations, at 719cm^{-1} and 806cm^{-1} , may be identified as the two CH_2 rocking modes expected in this area of the spectrum.^{22,29}

The ethylene C_2 torsional peak clearly displays shoulders to both high and low frequency in BFD and $\text{P}(\alpha,\beta)$ spectra. The former shoulder, found at 208cm^{-1} in $\text{P}(\alpha,\beta)$ spectra and at 201cm^{-1} in the BFD spectrum, may be assigned to the Pt-C_2 rocking mode (t_y)^{22,26,29}; whilst the latter, located at 133.5cm^{-1} in $\text{P}(\alpha,\beta)$ spectra, almost certainly represents the Pt-C_2 wag (t_x)^{22,26}.

Intensity (Monitor Counts)



PI(C₂H₅CD₃)₂SO (Silica background not subtracted)
 Pluto BFD Spectrometer : Liquid Nitrogen temperature



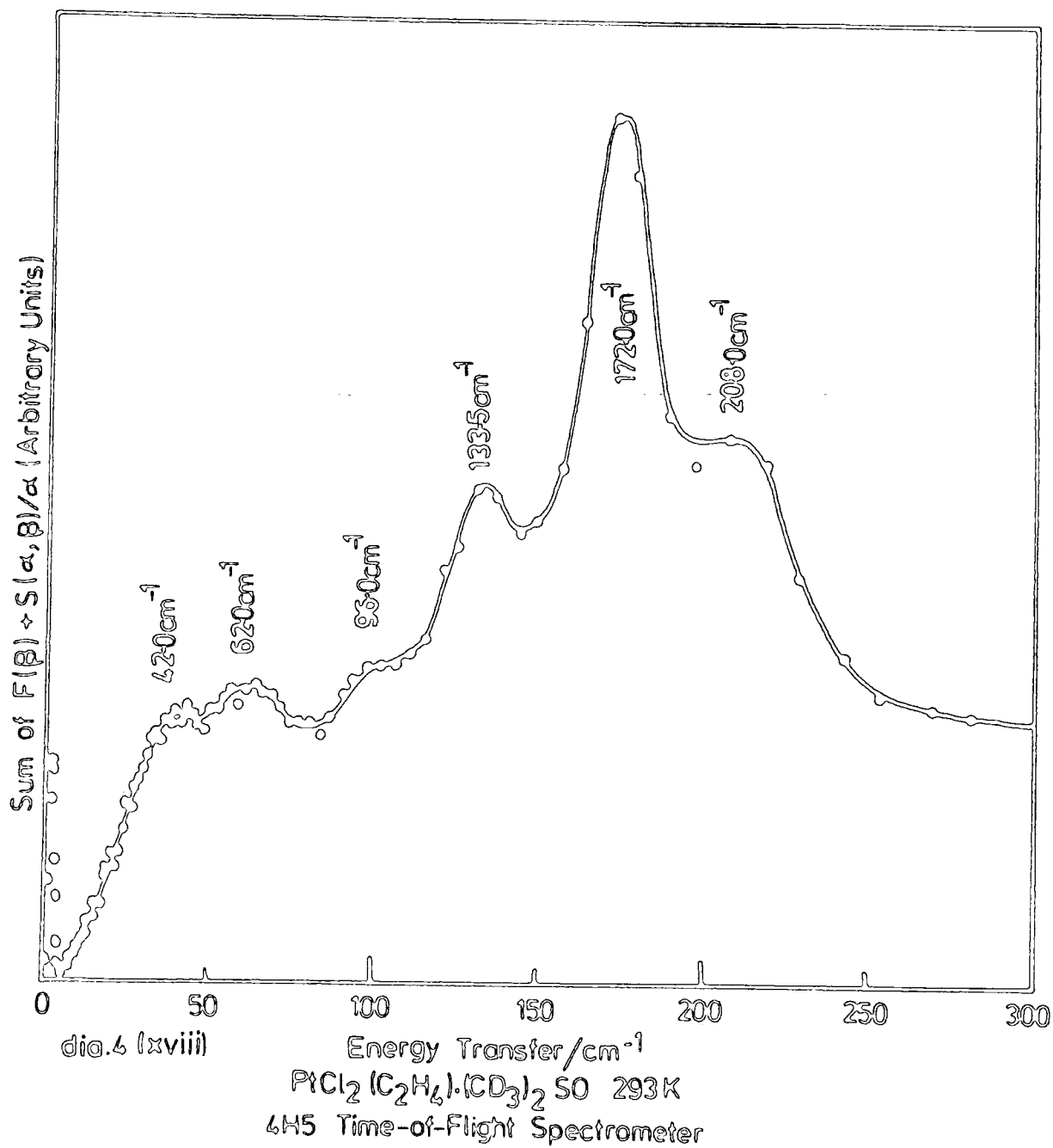


TABLE 4.9 The Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{cis-PtCl}_2(\text{C}_2\text{H}_5)_2(\text{CD}_3)_2\text{SO}$

Infrared	Raman	INS		Assignment	Infrared	Raman	INS		Assignment
		BFD	T-O-F				BFD	T-O-F	
57w	18vs 44s 60s 77w	41 $\pm$ 10	42.0 $\pm$ 2.0 62.0 $\pm$ 2.5	Lattice Vibrations	258s 280m 318s 338s 349sh	262m 321m 339vs	349 $\pm$ 10		* * $\nu(\text{Pt-Cl})$ $\nu(\text{Pt-Cl})$
107w	106w		96.0 $\pm$ 4.0						
130w			133.5 $\pm$ 6.5	Pt-C ₂ wag (τ_x)	380w 408m	384m 411m	384 $\pm$ 10		$\nu(\text{Pt-C}_2)(\tau_x)$ $\nu_s(\text{Pt-S})?$
141m	144w			*	468w	472w	472 $\pm$ 10		$\nu_{as}(\text{Pt-C}_2)(\tau_y)$
152w				*	628sh 635w	640m 650sh			$\nu_s(\text{C-S})$ $\nu_{as}(\text{C-S})$
168sh 179m	168s	171 $\pm$ 10	172.0 $\pm$ 9.0	C ₂ torsion (τ_z)	713w	716w	719 $\pm$ 10		CH ₂ rock
200sh 207m 217m	201m 221m	201 $\pm$ 10	208.0 $\pm$ 11.5	Pt-C ₂ rock (τ_y) *	773s 785sh 809sh 828s		806 $\pm$ 10		CD ₃ rock? CH ₂ rock

* Discussed within the text

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder;
 ν_s = symmetric stretch; ν_{as} = antisymmetric stretch.

The intensity ratio $t_x : t_y : t_z$ thus evaluated from the $P(\alpha, \beta)$ spectrum (angle 58°) employing these assignments, 1.05: 1.00: 2.50, accords fairly well with calculated values of 1.02: 1.00: 3.02.

Of the remaining unassigned bands in the INS spectrum, that at 349cm^{-1} seems, by analogy with the trans complexes, capable of assignment to the $\nu(\text{DMSO-Pt-Cl})$ square planar mode, the presence of which in the INS data may again be rationalised as resulting from sympathetic motion of the ethylene group.

This leaves the three as yet undiscussed vibrations in the $P(\alpha, \beta)$ spectrum below 100cm^{-1} , all of which appear to display dispersion. In order to aid identification of these modes, solution Raman data were obtained in this region and compared with the solid phase studies. Bands analogous to the 42cm^{-1} and 62cm^{-1} INS peaks were located in solid phase studies but not in the solution work, and hence these would appear to be lattice vibrations. The evidence for the highest energy mode, 96cm^{-1} , is unfortunately less positive, in that it was not located at all by the optical techniques. However, of the three bands, it perhaps displays the greatest dispersion, and consequently has been grouped amongst the lattice modes.

In the infrared and Raman, the spectra of $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CD}_3)_2\text{SO}$ have been compared with those reported for $(\text{CD}_3)_2\text{SO}^{39}$, $\text{cis-PtCl}_2((\text{CH}_3)_2\text{SO})_2^{40}$ and $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CH}_3)_2\text{SO}^{40,41}$ (Table 4.10). By reference to the assignments made for the latter compounds, several bands in the spectrum of the $(\text{CD}_3)_2\text{SO}$ ligand complex have been identified. For example, vibrations at 318cm^{-1} and 338cm^{-1} in the infrared spectrum of $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CD}_3)_2\text{SO}$ presumably correspond to those found about $309\text{--}11\text{cm}^{-1}$, and between 333 and 338cm^{-1} in the complexes $\text{cis-PtCl}_2((\text{CH}_3)_2\text{SO})_2^{40}$ and $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CH}_3)_2\text{SO}^{40,41}$, and which have been designated Pt-Cl stretches.

The peak at 408cm^{-1} in the infrared spectrum of the $(\text{CD}_3)_2\text{SO}$ ligand complex may perhaps be tentatively assigned to the Pt-S stretch which has been lowered following the substitution of deuterons for protons. The

TABLE 4.10 Reference Spectroscopic Frequencies (cm^{-1}) and Assignments of DMSO and DMSO-Containing Compounds

(CH ₃) ₂ SO ³⁹		(CD ₃) ₂ SO ³⁹		cis-PtCl ₂ (CH ₃) ₂ SO ⁴⁰		cis-PtCl ₂ (C ₂ H ₅) ₂ (CH ₃) ₂ SO ^{40, 41}		
Infrared		Assignment		Infrared		Assignment		
Solution	Vapour	Solution	Vapour	Solution	Vapour	Solution	Vapour	
661m 690s	672m 689m	ν (C-S) ν_s (C-S) $_{as}$	611 619	ν (C-S) ν_s (C-S) $_{as}$	309s 333s 428s 448sh	ν (Pt-Cl) ν (Pt-Cl) ν (Pt-S) ν (Pt-S)	311s 338s 443 468	ν (Pt-Cl) ν (Pt-Cl) ν (Pt-S) ν (Pt-S)
887w 921m 946s 1012s	898w 915m 828w 1008m 1016m	CH_3 rock	748m	CD_3 rock				
			750m 756sh 803m, sh 815m 824m, sh					
			811m				812w	

s = strong; m = medium; w = weak; sh = shoulder; ν_s = symmetric stretch; ν_{as} = antisymmetric stretch.

expected shift, using the reduced masses of $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CH}_3)_2\text{SO}$ and $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CD}_3)_2\text{SO}$ is 0.971. Kukushkin et al.^{40,41} report two frequencies designated $\nu(\text{Pt-S})$ for $\text{cis-PtCl}_2((\text{CH}_3)_2\text{SO})_2$, but only one for $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CH}_3)_2\text{SO}$. The deuteration shift resulting from use of the lower frequency of the former complex is 0.953. Unfortunately, this corresponds to the vibration which was not found for $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CH}_3)_2\text{SO}$, and hence a deuteration shift of 0.921 would seem to be indicated, which is in poor agreement with experiment.

Those bands at 628cm^{-1} and 635cm^{-1} in the infrared spectrum of $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CD}_3)_2\text{SO}$ almost certainly represent the symmetric and antisymmetric stretches respectively of C-S, these frequencies being reasonably adjacent to those identified for $(\text{CD}_3)_2\text{SO}$ vapour (611 and 619cm^{-1}).³⁹

Of the remaining infrared vibrations to high energy, those at 773 and 785cm^{-1} may probably be correlated with CD_3 rocking modes³⁹, whilst those situated at 713 and 809cm^{-1} seem, from comparison with the INS data, to correspond to CH_2 rocking vibrations of ethylene.

The assignment of the lower frequency optical spectra is again difficult, especially so in the absence of data for the $(\text{CH}_3)_2\text{SO}$ ligand complex. However, on frequency grounds it would appear that the $\text{Pt-C}_2\text{wag} (t_x)$ may be correlated with the 130cm^{-1} infrared band, and the $\text{Pt-C}_2\text{rock} (t_y)$ with the 207cm^{-1} peak.

The intensity of the 152 and 179cm^{-1} bands in the infrared shows sensitivity to temperature, and hence should perhaps be taken to represent torsional modes, of which the latter is probably the τ_z vibration of ethylene. The 107cm^{-1} infrared peak may probably be associated with a deformation mode of the square plane involving predominantly chlorine atoms and may therefore be related to the out-of-plane-bending mode $\pi(\text{Cl-Pt-Cl})$, located at 92cm^{-1} in Zeise's salt²⁶ (Table 4.3). Of the unassigned vibrations, at 141cm^{-1} , 168cm^{-1} and 200cm^{-1} , certainly the two former transitions, by

analogy with the trans complexes discussed previously, must represent the two bending modes $\delta(\text{Cl-Pt-Cl}_t) + \delta(\text{O-Pt-C}_2\text{H}_4)$ and $\delta(\text{Cl-Pt-O})$ (although which is which may not be established), whilst the 200cm^{-1} frequency is also probably a bending mode involving chlorine atoms and/or the $(\text{CD}_3)_2\text{SO}$ molecule.

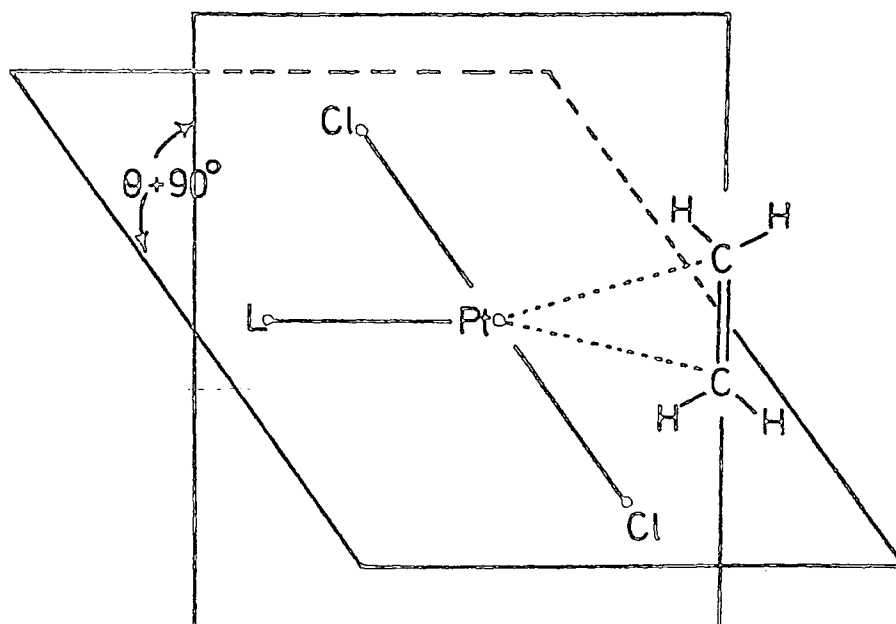
Finally, the remaining bending vibrations involving $(\text{CD}_3)_2\text{SO}$, and also the symmetric and antisymmetric stretches of this group relative to platinum, possibly correspond to the frequencies of 217cm^{-1} , 258cm^{-1} and 280cm^{-1} , the absence of data for the hydrogenous ligand compound, perforce making definite assignments virtually impossible.

Conclusion

Table 4.11 summarises the INS assignments for the trans- and cis- $\text{PtCl}_2(\text{C}_2\text{H}_4)_2\text{L}$ complexes.

Table 4.11 The INS Frequencies (cm⁻¹) Found for the Platinum-ethylene Complexes Studied Compared with those Reported for Zeiss's Salt and Dimer, 18,27

$K[PtCl_3(C_2H_4)]$ 18,27	$[PtCl_2(C_2H_4)]_2$ 18,27	trans- $PtCl_2(C_2H_4) \cdot ND_3$	trans- $PtCl_2(C_2H_4) \cdot CD_3CN$	trans- $PtCl_2(C_2H_4) \cdot DCON(CD_3)_2$	trans- $PtCl_2(C_2H_4) \cdot C_6D_5ND_2$	cis- $PtCl_2(C_2H_4) \cdot (CD_3)_2SO$	Assignment
-	110	61.0±3.5	29.0±2.0	34.0±2.0	33.0±2.0	42.0±2.0	Lattice Vibrations
185	170	122.0±6.5 170.5±10.0	49.5±3.0	51.0±3.0	60.0±3.5 82.5±4.5	62.0±2.5	
-	150	218.0±13.0	82.0±4.5	85.0±4.5	82.5±4.5	96.0±4.0	
-	-	-	127.3±7.0 166.5±9.5	132.5±7.5 175.0±10.0	123.5±7.0 166.0±9.5	133.5±6.5 172.0±9.0	Pt-C ₂ wag (τ _x) C ₂ rotation (τ _z)
-	150	207.0±12.0	207.0±12.0	210.0±13.0	202.5±12.0	208.0±11.5	Pt-C ₂ rock (τ _y)
-	-	-	339±8	343±10	340±16/ 354±8	349±10	$\nu_s(Cl-Pt-Cl)$ or $\nu(L-Pt-Cl)$
400	400	389±10	394±8	417±10	382±16	384±10	$\nu(Pt-C_2)$ (τ _x)
450	487	474±10	473±8	505±10	483±16	472±10	$\nu_s(Pt-C_2)$ (τ _z)
720	718	713±10	724±8	753±10/ 761±10	707±16	719±10	$\nu_{os}(Pt-C_2)$ (τ _y)
830	820	810±10	830±8	819±10	821±16	805±10	CH ₂ rock

D. Barrier Calculations1. $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$ ComplexesDia. 4.(xix) Definition of the Dihedral Angle for $\text{PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$ Complexes

From consideration of the symmetry of the ethylene molecule, the barrier must be encountered twice upon rotation through 2π , hence (Chapter II) the potential function may be written in terms of a Fourier cosine series:

$$V(\theta) = \frac{V_0}{2} + \sum_{n=1}^{\infty} \frac{V_n}{2} \cos n\theta$$

If the ligand is considered as a point mass, then the molecule as a whole has a C_2 axis running through the C=C bond, the platinum atom and the ligand, so that $V(\theta) = V(\pi - \theta)$. In consequence, odd terms in n will cancel with each other, and so the cosine series may be rewritten:

$$V(\theta) = \frac{V_0}{2} + \sum_{n=1}^{\infty} \frac{V_{2n}}{2} \cos 2n\theta$$

A good approximation to the barrier equation has often been afforded by using only the first term in the cosine expression⁴², i.e:

$$V(\theta) = \frac{V_0}{2} (1 - \cos 2\theta)$$

The above expression has a minimum at $\theta=0$ and a maximum, V^* , at $\theta = 90^\circ$

$$\frac{dV(\theta)}{d\theta} = \frac{V_0}{2} (2 \sin 2\theta) = 0$$

$$\frac{d^2V(\theta)}{d\theta^2} = \frac{V_0}{2} (4 \cos 2\theta) = 2V_0 \cos 2\theta$$

By definition the force constant is the second derivative of the potential energy, i.e. $\frac{d^2V(\theta)}{d\theta^2} = k$, where k is the force constant,

and from the harmonic oscillator approximation:

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{I_R}}, \quad \text{where } I_R \text{ is the reduced mass}$$

and so:

$$\omega = \frac{1}{2\pi} \sqrt{\frac{2V_0}{I_R}} = \frac{1}{\pi} \sqrt{\frac{V_0}{2I_R}}$$

However, the above potential function has no metastable well such as that proposed in the model for $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{NH}_3$ ⁷. In order to allow for this factor, and to make compatible data from NMR and INS measurements, Ghosh et al.¹⁸ proposed a two parameter model incorporating the second term in the cosine series expansion:

$$V(\theta) = \frac{V_0}{2} (1 - \cos 2\theta) + \frac{V_4}{2} (1 - \cos 4\theta)$$

$$\frac{dV(\theta)}{d\theta} = \frac{V_0}{2} (2 \sin 2\theta) + \frac{V_4}{2} (4 \sin 4\theta) = 0$$

$$= \frac{V_0}{2} (2 \sin 2\theta) + \frac{V_4}{2} (8 \sin 2\theta \cos 2\theta) = 0$$

$$= \left(\frac{V_o}{2} + \frac{V_4}{2} \cdot 4 \cos 2\theta \right) 2 \sin 2\theta = 0$$

This expression for the potential function has a minimum at $\theta = 0^\circ$ and, providing V_4 is positive and greater than $V_o/4$, it also has a metastable minimum at $\theta = 90^\circ$ with a well depth of V_m^* : the maximum, V^* , is placed at

$$\theta = 0.5 \cos^{-1}(-V_o/4V_4)$$

In order to relate the above model to experimental measurements, the two parameter model must be rewritten in terms of one constant by making the assumption that $V_o = V_4$:

$$V(\theta) = \frac{V_o}{2} [(1 - \cos 2\theta) + (1 - \cos 4\theta)]$$

This formulation gives rise to a ground state minimum at $\theta = 0^\circ$, and a metastable minimum at $\theta = 90^\circ$ of potential energy V_o . The maximum is now defined at $\theta = 0.5 \cos^{-1}(-1/4) = 52.25^\circ$, with a potential energy, V^* , of $25V_o/16$, and this compares reasonably with the theoretical computation of Wheelock et al.⁷ which placed $\theta_{\max}$ at $67.5^\circ \pm 11.25^\circ$.

Taking the second derivative of the potential energy produces:

$$\frac{d^2V(\theta)}{d\theta^2} = \frac{V_o}{2} [(4 \cos 2\theta) + (16 \cos 4\theta)] = k$$

and hence again applying the harmonic oscillator approximation:

$$\omega = \frac{1}{2\pi} \sqrt{\frac{20V_o}{I_R}} = \frac{1}{\pi} \sqrt{\frac{5V_o}{I_R}}$$

As all the trans-PtCl₂(C₂H₄).L complexes are of the form for which Wheelock et al.⁷ derived their model, it seems appropriate to use the potential form derived by Ghosh et al.¹⁸ for calculation of barrier heights.

Table 4.12 shows the values calculated for the barriers of each trans complex using the High Barrier Approximation. The validity of application

Table 4.12 Barrier Data for the trans-PtCl₂(C₂H₄).L Complexes

Complex	$\bar{\nu}$ cm ⁻¹	I_R^f (Å ² AMU)	5V _o kJ mol ⁻¹	V _o kJ mol ⁻¹	V [*] (=25V _o /16) kJ mol ⁻¹	V _m [*] (=9V _o /16) kJ mol ⁻¹
trans-PtCl ₂ (C ₂ H ₄).ND ₃	170.5±10.0	19.05	98±12	19.6	30.6	11.0
trans-PtCl ₂ (C ₂ H ₄).CD ₃ CN	166.5±9.5	19.05	94±11	18.8	29.4	10.6
trans-PtCl ₂ (C ₂ H ₄).DCON(CD ₃) ₂	175.0±10.0	19.20	104±13	20.8	32.5	11.7
trans-PtCl ₂ (C ₂ H ₄).C ₆ D ₅ ND ₂	166.0±9.5	19.27	94±12	18.8	29.4	10.6

^f For data used in calculation of Reduced Masses (I_R) see Appendix.

Table 4.13 Barrier Data of Ghosh et al.¹⁸

Complex	$\bar{\nu}$ cm ⁻¹	5V _o kJ mol ⁻¹	V _o kJ mol ⁻¹	V [*] (=25V _o /16) kJ mol ⁻¹	V _m [*] (=9V _o /16) kJ mol ⁻¹
Pt(acac(C ₂ H ₄)complexes ^f (average)	—	—	—	—	—
[PtCl ₂ (C ₂ H ₄)] ₂	170±5	106	25.4	39.7	14.3
K[PtCl ₃ (C ₂ H ₄)]·H ₂ O	185±5	118	23.6	36.9	13.3
Cs[PtCl ₃ (C ₂ H ₄)]	190±5	125	25.0	39.0	14.1
[PtCl ₂ (C ₂ H ₄)] ₂	155±5	87.8	17.6	27.4	9.9

of this approximation may be seen with reference to the values obtained for trans-PtCl₂(C₂H₄).ND₃ using successive terms of the Das Approximation⁴³:

- (a) First Das approximation: 98.237 kJ mol⁻¹
 (Equivalent to High Barrier Approximation:
 Chapter II)
- (b) Second Das approximation: 99.260 kJ mol⁻¹
- (c) Third Das approximation: 99.265 kJ mol⁻¹

The free energy of activation to rotation is known from NMR studies of several neutral platinum complexes including Pt(acac)Cl(C₂H₄)¹⁵ and Pt(acac)Br(C₂H₄)¹⁶. Ghosh et al.¹⁸ suggested that, as substitution of simple ligands cis- and trans- to the ethylene group leads to no noticeable change in barrier height, it was reasonable to obtain an average value for the NMR barrier (52.2±1.3 kJ mol⁻¹) from compounds such as the above and apply it to the complexes they were studying. Similarly, they took an average value for the entropies of activation from the only complexes for which these were known Pt(acac)Br(trans but-2-ene), Pt(acac)Cl(trans but-2-ene) and Pt(acac)Cl(tetramethylethylene)¹⁶ (-55.2±12.5 J mol⁻¹ K⁻¹). Using these two averages, an activation energy was calculated of 38.9±3.3 kJ mol⁻¹ which, on addition of the zero point energy (0.8 kJ mol⁻¹), yielded a value for V^{*} of 39.7±3.3 kJ mol⁻¹.

Table 4.13 shows the values of V₀, V_m^{*} and V^{*} obtained by Ghosh et al.¹⁸ for the complexes investigated in their work, together with the reference value calculated from the NMR data. It will be seen that the V₀ values for the trans-PtCl₂(C₂H₄).L complexes compare well with those reported by Ghosh et al., particularly good agreement being found with the value for [PtCl₂(C₂H₄)]₂. Generally, there seems to be an indication that the C₂ torsional mode (τ_z) occurs at higher energies in K[PtCl₃(C₂H₄)]·H₂O and Cs[PtCl₃(C₂H₄)] than in the simple complexes. (A similar trend is apparent in the case of the respective V₀ values.) Possibly, this might be explained as the result of crystal field interactions having a greater

effect upon the torsional frequencies of the salts.

The values of V^* and V_m^* may also be compared with those reported in the theoretical work on $\text{PtCl}_2(\text{C}_2\text{H}_4).\text{NH}_3$ ⁷. In the present data, V^* lies in the range $29.4\text{--}32.5\text{ kJ mol}^{-1}$ and V_m^* between 10.6 and 11.7 kJ mol^{-1} , as opposed to the theoretical predictions of $116\pm 8.4\text{ kJ mol}^{-1}$ for the former, and $9.6\pm 8.4\text{ kJ mol}^{-1}$ for the latter.

2. $\text{cis-PtCl}_2(\text{C}_2\text{H}_4).(\text{CD}_3)_2\text{SO}$

Consideration of symmetry again allows the discarding of the $\sin \theta$ term in the potential function. Although there is no C_2 axis in this molecule, the orbitals of the platinum atom with which the ethylene group is interacting remain the same. Furthermore, any steric considerations must be small because NMR work has shown that substitution of small ligands cis- and trans- to ethylene causes little difference in barrier height.¹⁶

The barrier data have therefore been calculated using the model of Ghosh et al.¹⁸ and are shown below:

Complex	$\bar{\nu}\text{ cm}^{-1}$	$I_R(\text{\AA}^2\text{ AMU})$	$5V_o$ kJ mol^{-1}	V_o kJ mol^{-1}	$V^*(=25V_o/16)$ kJ mol^{-1}	$V_m^*(=9V_o/16)$ kJ mol^{-1}
$\text{cis-PtCl}_2(\text{C}_2\text{H}_4).(\text{CD}_3)_2\text{SO}$	172 ± 9.0	19.54	103 ± 11	20.6	32.2	11.6

The values above correspond very closely to those found for the $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{L}$ compounds, and are again similar to those reported by Ghosh et al.¹⁸

Appendix: Structural Data Used in the Calculation of the Reduced Moments of Inertia (I_R) of cis- and trans- $\text{PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$ Complexes

No crystal structures have, to our knowledge, been determined of the trans- or cis- $\text{PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{L}$ compounds studied. Consequently, values of bond angles and bond lengths have been taken from those known for the respective constituents of the compound, and in each case a Pt-L bond length has been assumed.

1. Ethylene

The coordinates below are derived from the bond lengths and bond angles reported by Love et al.¹⁰ for C_2H_4 in the complex $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$:

Hx+1.249	Hx+1.249
y-0.785	y+0.785
z-0.429	z-0.429

Cx+0.688
y 0.000
z+0.072

Cx-0.688
y 0.000
z+0.072

Hx-1.249	Hx-1.249
y-0.785	y+0.785
z-0.429	z-0.429

2. $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{ND}_3(\text{dia.4(xx)})$

$\text{PtCl}_2(\text{C}_2\text{H}_4)$: values from the neutron diffraction study of $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$
by Love et al.¹⁰

ND_3 : gas phase values from the work Helminger et al.⁴⁴

Pt-N : band length by comparison with that obtained by Alderman
et al.⁴⁵ for $\text{PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{NH}(\text{Me})_2$.

The coordinates resulting from the above assumptions are listed below:

Hx+1.249	Hx+1.249
y-0.785	y+0.785
z-2.472	z-2.472

Cx+0.688
y 0.000
z-1.971

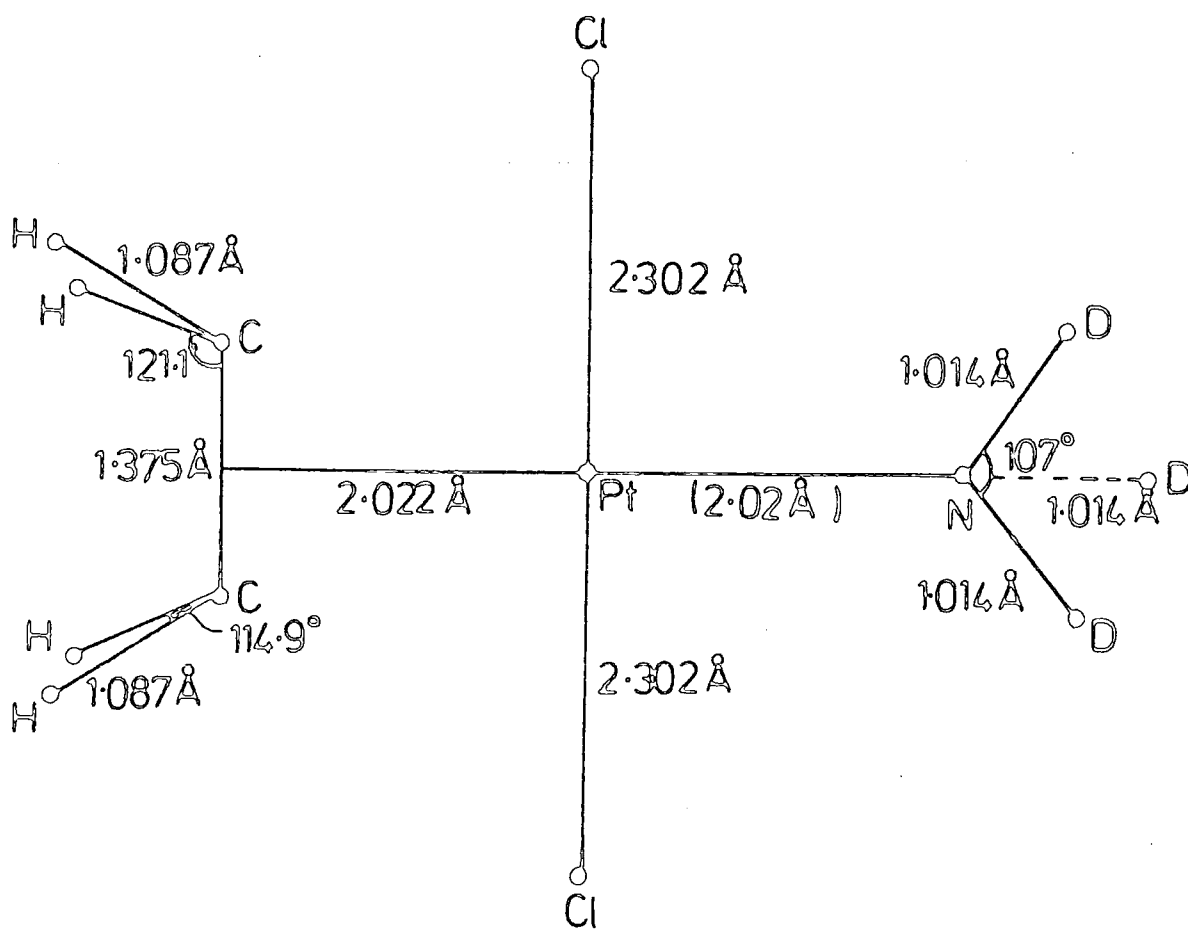
Cx-0.688
y 0.000
z-1.971

Hx-1.249	Hx-1.249
y-0.785	y+0.785
z-2.472	z-2.472

Clx 0.000	Ptx 0.000	Clx 0.000
y-2.302	y 0.000	y+2.302
z+0.051	z+0.051	z+0.051

	Nx 0.000	
	y 0.000	
Dx-0.469	z+2.071	Dx-0.469
y-0.813		y+0.813
z+2.454	Dx+0.939	z+2.454
	y 0.000	
	z+2.454	

dia. 4(xx) trans - $\text{PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{ND}_3$



Ethylene group shown rotated through 180 degrees.

3. $\text{trans-PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{CD}_3\text{CN}$ (dia.4(xxi))

$\text{PtCl}_2(\text{C}_2\text{H}_4)$: values from Zeise's salt.¹⁰

CD_3CN : liquid phase values from the study Thomas et al.⁴⁶

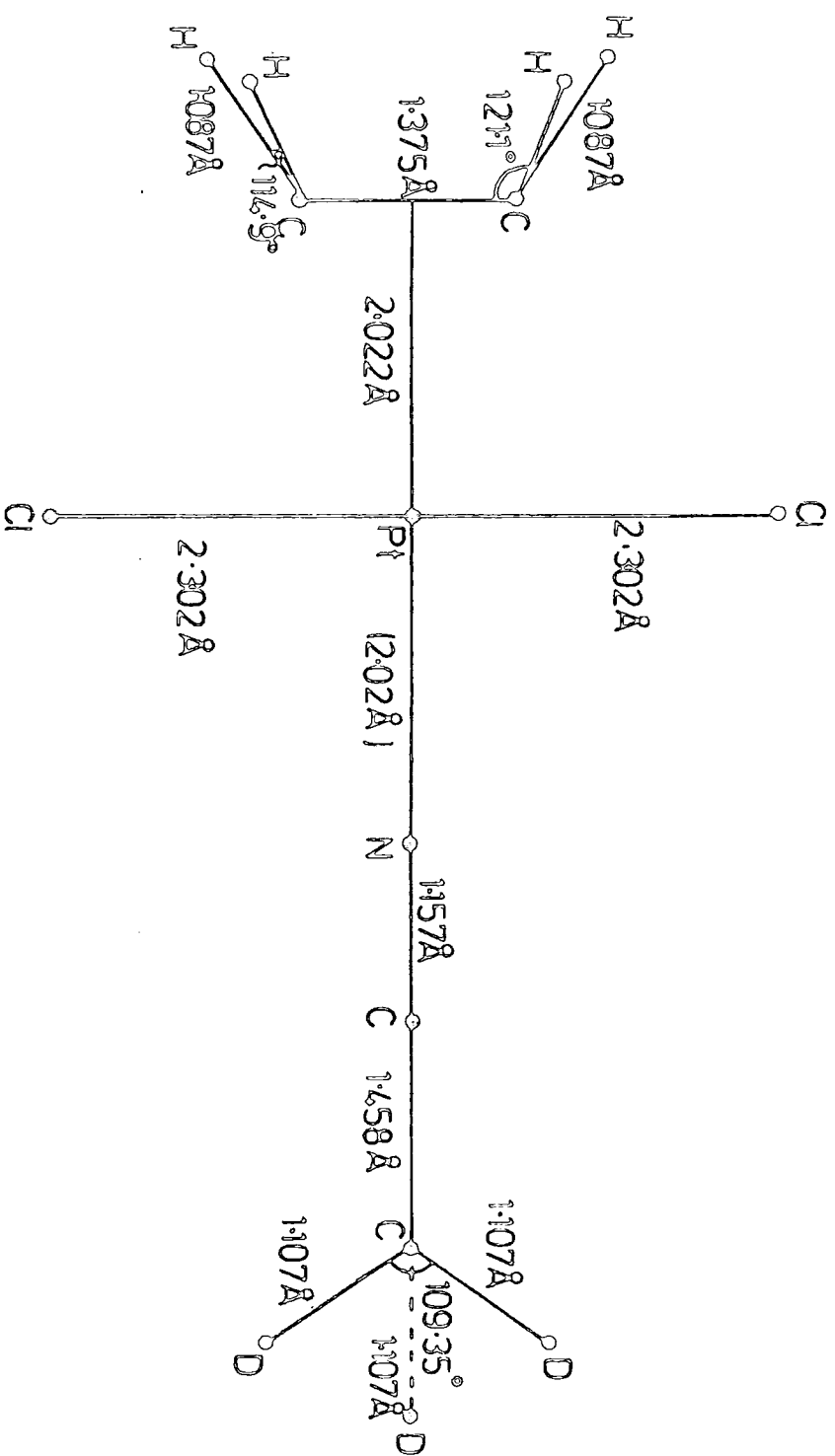
Coordination of acetonitrile by the nitrogen lone pair is assumed after Meester et al.²³, and hence,

Pt-N: value used for $\text{PtCl}_2(\text{C}_2\text{H}_4) \cdot \text{ND}_3$.⁴⁵

The coordinates resulting from the above assumptions are listed below:

Hx+1.249	Hx+1.249	
y-0.785	y+0.785	
z-2.800	z-2.800	
Cx+0.688		
y 0.000		
z-2.298		
Cx-0.688		
y 0.000		
z-2.298		
Hx-1.249	Hx-1.249	
y-0.785	y+0.785	
z-2.800	z-2.800	
Clx 0.000	Ptx 0.000	Clx 0.000
y-2.302	y 0.000	y+2.302
z-0.276	z-0.276	z-0.276
Nx 0.000		
y 0.000		
z+1.744		
Cx 0.000		
y 0.000		
z+2.901		
Cx 0.000		
y 0.000		
Dx-0.522	z+4.359	Dx-0.522
y-0.903		y+0.903
z+4.730	Dx+1.043	z+4.730
	y 0.000	
	z+4.730	

dia. 6 (xxi) trans-PtCl₂(C₂H₄).CD₃CN



Ethylene group shown rotated through 180 degrees.

4. $\text{trans-PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{DCON}(\text{CD}_3)_2$ (dia 4. (xxii))

$\text{PtCl}_2(\text{C}_2\text{H}_4)$: values from Zeise's salt.¹⁰
 $\text{DCON}(\text{CD}_3)_2$: values from the electron diffraction study of
 $\text{HCON}(\text{CH}_3)_2$ by Vilkov et al.⁴⁷ but with r_{CD}
 assumed to be $1.107\text{\AA}$ as in CD_3CN .⁴⁶

Ligand coordination is assumed to take place via oxygen in agreement with the work of Meester et al.²³ and hence,

Pt-O : bond length by comparison with that obtained
 by X-ray diffraction for the compound
 $[\{\text{p}(\text{o-CH}_3\text{C}_6\text{H}_4)(^t\text{Bu})_2\} \text{Pt} \{\text{P}(\text{C}_6\text{H}_4)(^t\text{Bu})_2\} - (\text{NO}_3)]$.⁴⁸

The coordinates resulting from the above assumptions are listed below:

Hx-1.249	Hx-1.249
y-0.190	y+1.331
z-3.328	z-2.943

Cx-0.688
 y+0.448
 z-2.650

Cx+0.688
 y+0.448
 z-2.650

Hx+1.249	Hx+1.249
y-0.190	y+1.331
z-3.328	z-2.943

Clx 0.000	Ptx 0.000	Clx 0.000
y-2.280	y-0.049	y+2.183
z-1.255	z-0.690	z-0.124

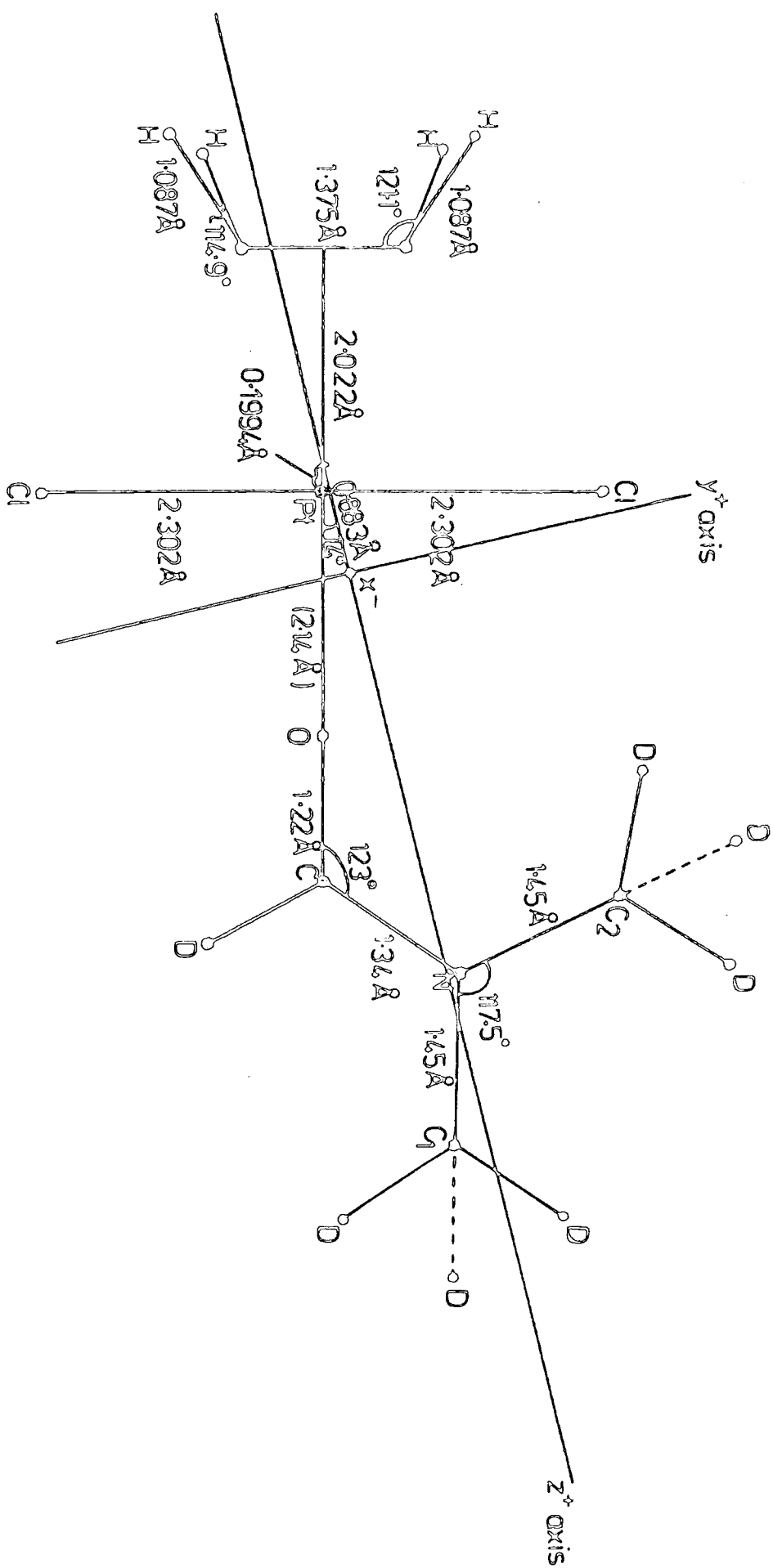
Ox 0.000
 y-0.575
 z+1.385

Cx 0.000
 y-0.874
 z+2.567

Dx 0.000	Nx 0.000
y-1.911	y+0.036
z+2.831	z+3.551

CD_3 x 0.000	CD_3 x 0.000
y-0.433	y+1.704
z+5.188	z+3.211

dia. 46xii) trans - $\text{P}^+\text{Cl}_2(\text{C}_2\text{H}_4)_2 \cdot \text{D CON} (\text{CD}_3)_2$



5. $\text{trans-PtCl}_2(\text{C}_2\text{H}_4).\text{C}_6\text{D}_5\text{ND}_2$ (dia.4(xxiii))

$\text{PtCl}_2(\text{C}_2\text{H}_4)$: values from Zeise's salt.¹⁰

$\text{C}_6\text{D}_5\text{ND}_2$: values from liquid phase study of Lister et al.⁴⁹

Pt-N: value by comparison with that obtained for
 $\text{PtCl}_2((\text{CH}_3)_3\text{C}-\text{C}=\text{C}-\text{C}(\text{CH}_3)_3).\text{p-MeC}_6\text{H}_5\text{NH}_2$ by Davies
 et al.⁵⁰

The coordinates resulting from the above assumptions are listed below:

Hx+1.235	Hx+1.235
y-0.916	y+0.916
z-3.358	z-3.358

Cx+0.856
 y 0.000
 z-2.913

Cx-0.253
 y 0.000
 z-3.095

Hx-0.470	Hx-0.470
y-0.916	y+0.916
z-3.638	z-3.638

Clx-0.032	Ptx-0.032	Clx-0.032
y-2.302	y 0.000	y+2.302
z-0.971	z-0.971	z-0.971

Nx-0.373
 y 0.000
 z+1.106

Dx-0.627	Dx-0.627
y-0.828	y+0.828
z+1.581	z+1.581

Cx-0.143
 y 0.000
 z+2.489

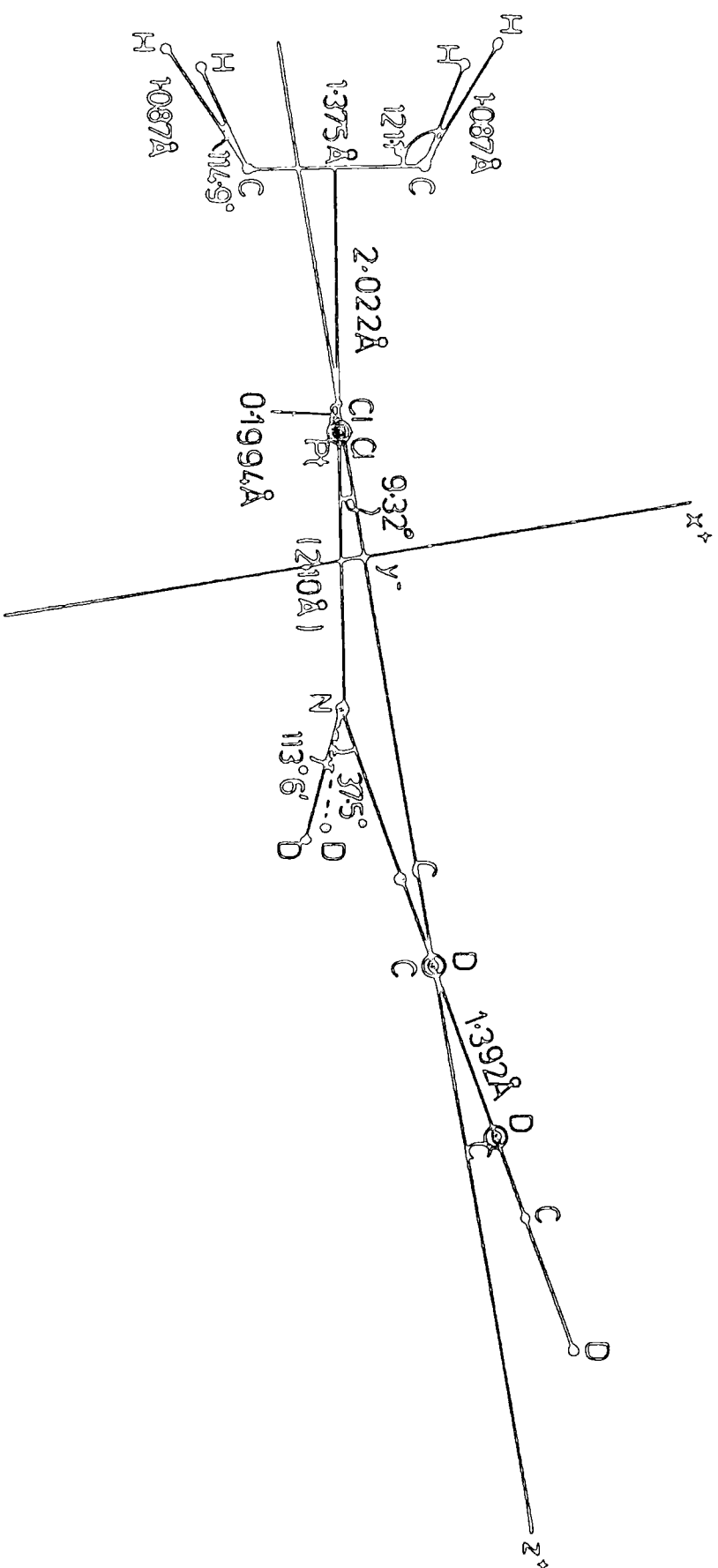
Dx-0.114	Cx-0.029	Cx-0.029	Dx-0.114
y-2.136	y-1.206	y+1.206	y+2.136
z+2.645	z+3.175	z+3.175	z+2.645

Dx+0.284	Cx+0.199	Cx+0.199	Dx+0.284
y-2.136	y-1.206	y+1.206	y+2.136
z+5.079	z+4.549	z+4.549	z+5.079

Cx+0.313
 y 0.000
 z+5.235

Dx+0.489
 y 0.000
 z+6.295

dia. 4 (xxiii) trans - $\text{PtCl}_2(\text{C}_2\text{H}_4)_2 \cdot \text{C}_6\text{D}_5\text{ND}_2$



6. $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)(\text{CD}_3)_2\text{SO}$ (dia. 4(xxiv))

$\text{PtCl}_2(\text{C}_2\text{H}_4)$: values from Zeise's Salt.¹⁰

$(\text{CD}_3)_2\text{SO}$: values from liquid $(\text{CH}_3)_2\text{SO}$ ⁵¹ but with r_{CD} assumed to be $1.07\text{\AA}$.

Coordination of dimethyl sulphoxide is assumed to take place via the sulphur atom after the work of Boucher and Bosnich²⁴, and hence,

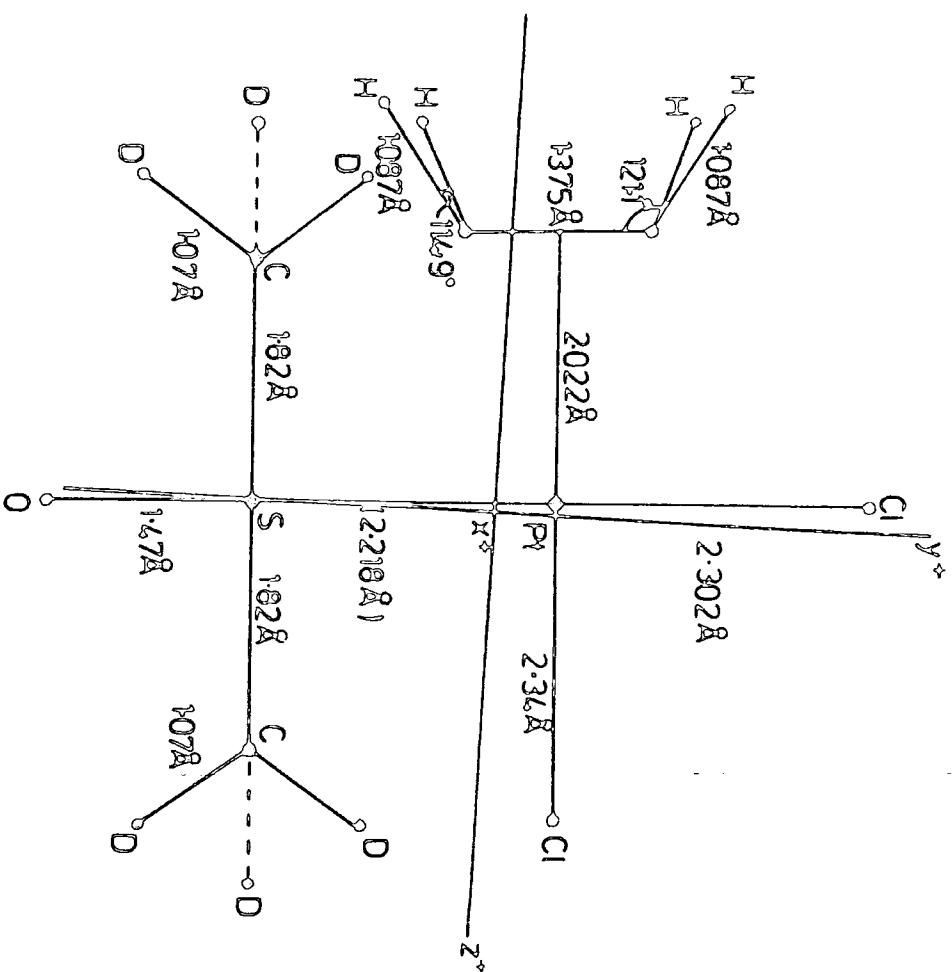
Pt-S: value by comparison with that found for

$[(\text{Et}_2\text{S})\text{PtBr}_2]_2$ by Sales et al.⁵²

The coordinates resulting from the above assumptions are listed below:

Hx+1.249	Hx+1.249		
y-0.412	y+1.158	Clx 0.000	
z-2.523	z-2.523	y+2.675	
		z 0.000	
Cx+0.688			
y-0.373			
z-2.022	Ptx 0.000	Clx 0.000	
	y+0.373	y+0.373	
Cx-0.688	z 0.000	z+2.340	
y+0.373			
z-2.022			
Hx-1.249	Hx-1.249		
y-0.412	y+1.158		
z-2.523	z-2.523		
		Sx 0.000	
		y-1.847	
		z 0.000	
	CD ₃ x-0.745	Ox+1.460	CD ₃ x-0.745
	y-2.685	y-2.019	y-2.685
	z-1.583	z 0.000	z+1.583

dia. 6 (xiv) cis - $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{CD}_3)_2\text{SO}$



Ethylene group shown rotated through 180 degrees.

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CHAPTER V

STUDIES OF CO-ORDINATED ACETYLENE : THE COMPLEX $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$

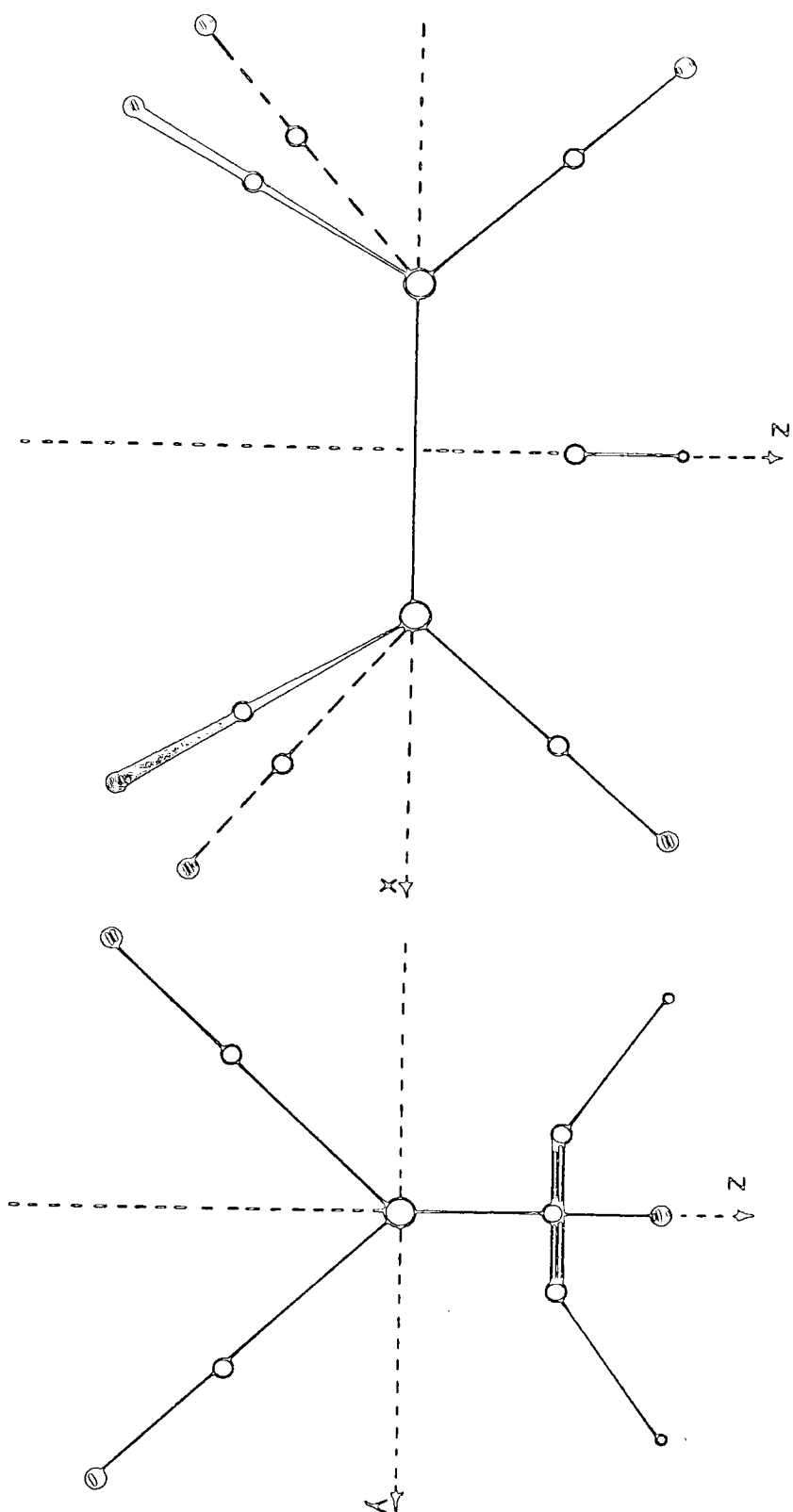
A. Introduction

$\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$ is a rare example of a simple complex which contains π -bonded acetylene and exists out of solution. It is therefore ideally suited to be a model upon which studies of acetylene adsorbed on zeolite surfaces may be based.

Although the structure of $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$ has not been determined, that of $\text{Co}_2(\text{CO})_6\text{PhC}_2\text{Ph}$ is known¹. In the latter, diphenylacetylene has been shown to coordinate above, and perpendicularly to, the cobalt-cobalt bond, assuming a non-linear configuration in which both phenyl groups are bent away from the $\text{Co}_2\text{-C}_2$ bond. An approximate description² of the environment of the cobalt atom would be, therefore, that it was contained within a distorted trigonal bipyramid; whilst the ethynyl carbons may be seen to have roughly tetrahedral symmetry. The presumed structure of $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$ based upon the findings for the diphenylacetylene complex is shown in dia.5(i).

The first infrared spectra of the $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$ complex were measured by Sternberg et al.^{3,4}, but only tentative assignments were possible. Subsequently, studies were carried out by Iwashita et al.⁵ employing infrared and NMR techniques in which the complexes $\text{Co}_2(\text{CO})_6\text{CHCD}$, $\text{Co}_2(\text{CO})_6\text{C}_2\text{D}_2$, $\text{Co}_2(\text{CO})_6^{13}\text{CHCH}$, and $\text{Co}_2(\text{CO})_5\text{C}_2\text{H}_2\text{P}(\text{C}_6\text{H}_5)_3$, as well as $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$ were investigated. From the data, assignments of the vibrational frequencies were made and information relating to the structure deduced.

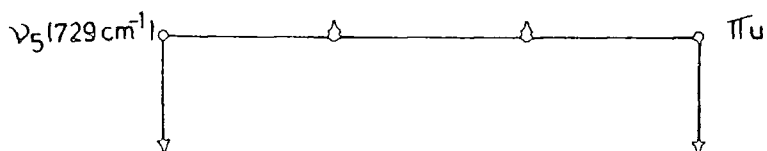
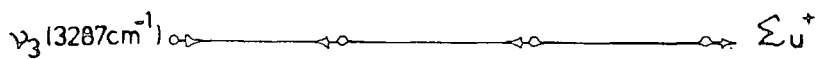
Dia.5(ii) shows the normal modes of linear acetylene, whilst the proposed models for the co-ordinated alkyne are illustrated in dia.5(iii). The corresponding symmetry species and spectroscopic activities expected for each configuration are listed in Table 5.1. On the basis of this information,



dia. 511) The presumed structure of $\text{Co}_2(\text{CO})_8 \cdot \text{C}_2\text{H}_2$

Key: Hydrogen $\circ$; Carbon $\bigcirc$; Oxygen $\odot$; Cobalt $\bigcirc$.

dia.5(ii) The Normal Modes of Linear Acetylene.⁶



dia.5(iii) The Possible Models of the Coordinated Acetylene Molecule.⁵

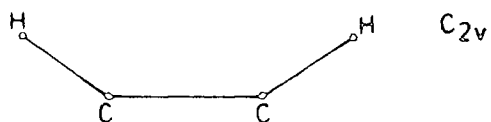
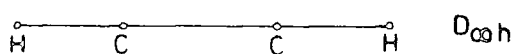


TABLE 5.1 Correlation of Symmetry with Infrared/Raman Activity

Acetylene Model	Vibrational Species	Number of Vibrations	Activity
$D_{\infty h}$	Σ_g^+	2	Raman
	Σ_u^+	1	Infrared
	π_g	1	Raman
	π_u	1	Infrared
C_{2v}	A_1	3	Infrared, Raman
	A_2	1	Raman
	B_1	0	Infrared, Raman
	B_2	2	Infrared, Raman
C_{2h}	A_g	3	Raman
	A_u	0	Infrared
	B_g	1	Raman
	B_u	2	Infrared
C_2	A	4	Infrared, Raman
	B	2	Infrared, Raman

it was possible for Iwashita et al.⁵ to conclude that the presence of two C-H stretching modes (Σ_g^+ and Σ_u^+), as well as the $\nu(C=C)$ vibration (Σ_g^+) in the infrared spectrum implied a loss of $D_{\infty h}$ symmetry by the acetylene molecule in the complexed state. Asymmetry was ruled out by the fact that the acetylene protons only yielded one signal ($\delta=4.0\text{ppm}$) in the NMR spectrum. Comparison of $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ with the triphenylphosphine substituted complex showed that whilst the infrared spectra were similar, the NMR spectra differed, the substituted compound producing a doublet at $\delta=5.25\text{ppm}$ ascribed as the result of phosphorus-hydrogen spin-spin coupling through the cobalt atoms. Consequently, it was concluded that both protons were equivalent in $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2\cdot\text{P}(\text{C}_6\text{H}_5)_3$, and hence that a C_2 structure was also unlikely in the case of $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$. The presence of five strong

infrared active bands was thus taken as affording additional confirmation for the likely symmetry of the co-ordinated acetylene as C_{2v} .

It was noted that the vibrational frequencies derived from acetylene in the $Co_2(CO)_6.C_2H_2$ complex were very similar to those of the first electronically excited state. However, Ingold and King⁷, and Innes⁸ had shown that in this state the alkyne adopted a trans bent configuration as a result of a change of hybridisation from sp to sp^2 . It was therefore necessary to reconcile the C_{2v} symmetry indicated from the activities of the infrared bands with the C_{2h} symmetry of the trans configuration suggested by the frequencies. Consequently Iwashita et al.⁵ proposed that the trans form of excited acetylene becomes amended to the cis form on complexation. As support for this hypothesis the authors pointed out that both the trans and cis structures were almost equivalent energetically, and also that the latter configuration avoided the possibility of steric repulsion between an acetylene proton and the cobalt carbonyl moiety. Further evidence for a change in acetylene hybridisation was obtained from NMR investigations of the compound $Co_2(CO)_6.^{13}CHCH$ where the value of the ^{13}CH coupling constant was determined by spin-perturbation to be between that of acetylene and ethylene⁹.

It was therefore possible to put forward a bonding model⁵ whereby the co-ordinated alkyne assumes an ethylene like shape, two cis sites being occupied by hydrogen atoms, and the remaining two empty cis sites (with non-bonding orbitals) forming σ bonds, one to each cobalt atom. Back donation by the metal atoms may then take place from the filled d orbitals of the metal atoms (dsp^3 hybridised) into the antibonding π^* orbitals of acetylene. Indeed, this back bonding has been suggested as contributing more to the stabilisation of the alkyne-metal bond than the forward process¹⁰. The net effect is thus the transference of a ligand electron from the highest bonding (π) orbital to the lowest antibonding (π^*) orbital.¹¹

In a later paper, Iwashita¹² made a normal co-ordinate analysis of the $\text{Co}_2\text{C}_2\text{H}_2$ part of the complex, and determined the force constants of the complexed acetylene which were compared with those of the alkyne in the excited state. The spectral region examined was extended into the far-infrared and tentative identification was made of additional vibrations found.

Recently a Raman investigation of a series of compounds $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{R}_2$ (where $\text{R}=\text{H}$, CF_3 , CH_3 , COOCH_3 and C_6H_5) and $\text{Fe}_2(\text{CO})_6\text{S}_2$ has been carried out by Kettle and Stanghellini¹³ which has led to several frequencies of the $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ molecule being re-assigned.

B. Experimental

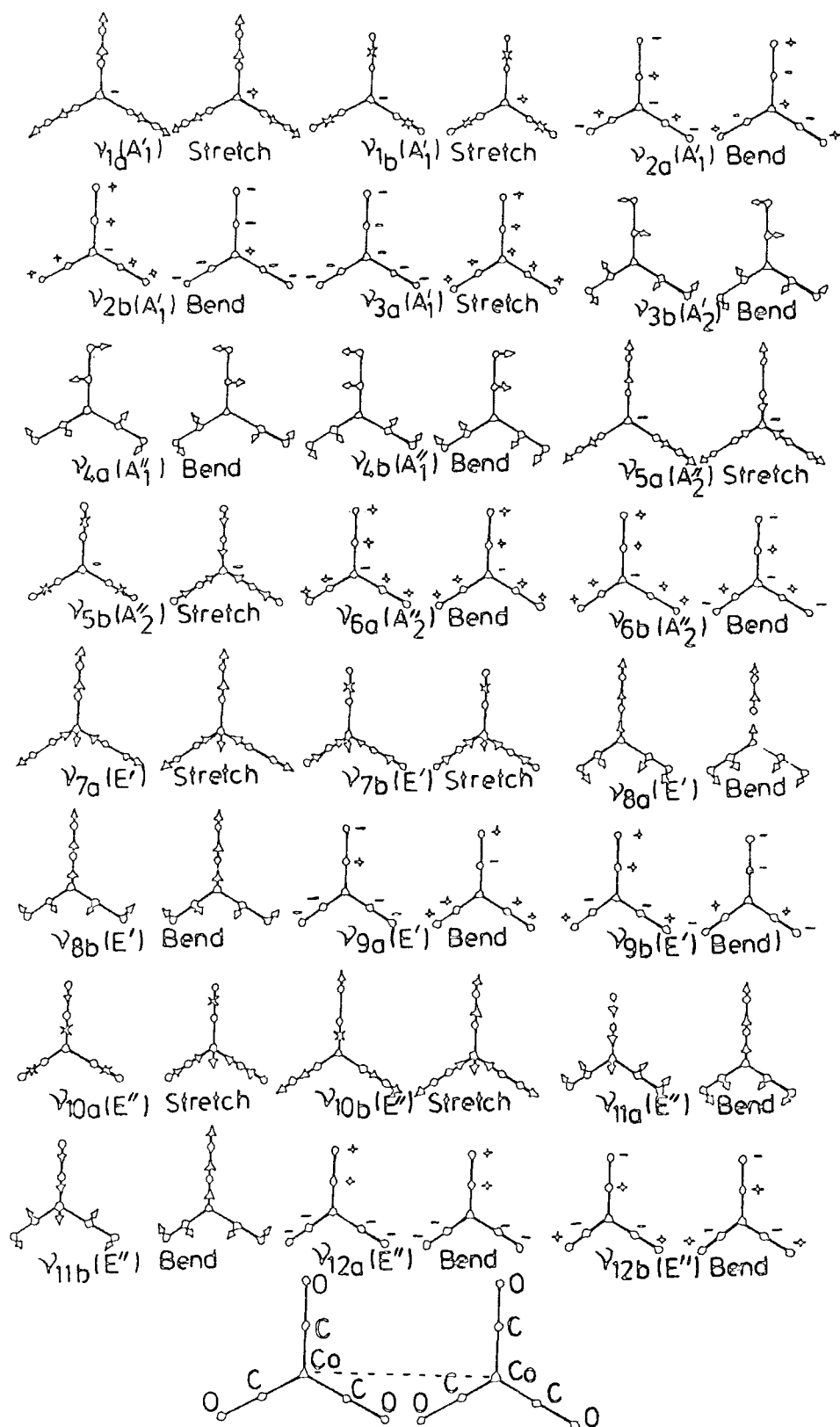
$\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ was prepared by the method described in the paper of Iwashita et al.⁵

Time-of-Flight spectra were obtained of the complex at temperatures of 88 and 233K using the 4H5 Cold Neutron Spectrometer. Higher frequency studies were carried out at 23K with the Dido BFD Spectrometer, and at liquid nitrogen temperature with the Pluto BFD Spectrometer. In all cases the sample was contained in a thick-wall silica liquid cell.

C. Discussion of Results

Before assignment of the vibrational frequencies, it is perhaps worthwhile considering in greater detail the symmetry of the $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ molecule and the vibrational modes expected.

The $\text{Co}_2(\text{CO})_6$ fragment of the complex has been analysed in D_{3h} symmetry, the principal axis being taken as that labelled 'x' in dia.5(i). The 36 species resulting from this analysis, $5A_1' + 2A_1'' + A_2' + 4A_2'' + 6E' + 6E''$, are illustrated in dia. 5(iv). By means of the correlation table below (Table 5.2), these may be seen to correspond in C_{2v} symmetry to $11A_1 + 8A_2 + 10B_1 + 7B_2$, providing the axes used are those represented in dia.5(i), that is the x axis parallel to the cobalt-cobalt bond, the y axis parallel to the



dia. 5liv) The Normal Vibrations of the $\text{Co}_2(\text{CO})_6$ Moiety :

D_{3h} symmetry.

acetylene carbon-carbon bond, and the z axis coinciding with the C_2 axis of the whole molecule.

Table 5.2 Correlation of C_{2v} , D_{3h} and T_d Symmetries

D_{3h}	C_{2v}	T_d	C_{2v}
A'_1	A_1	A_1	A_1
A'_2	B_2	A_2	A_2
A''_1	A_2	E	$A_1 + A_2$
A''_2	B_1	F_1	$A_2 + B_1 + B_2$
E'	$A_1 + B_2$	F_2	$A_1 + B_1 + B_2$
E''	$A_2 + B_1$		

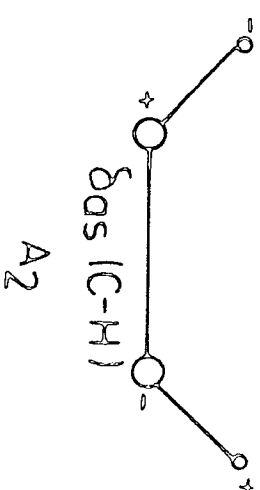
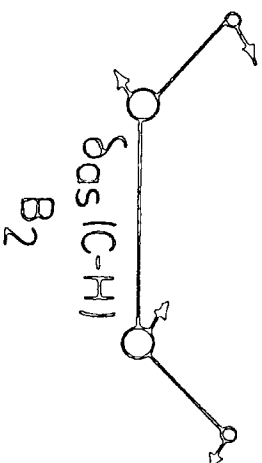
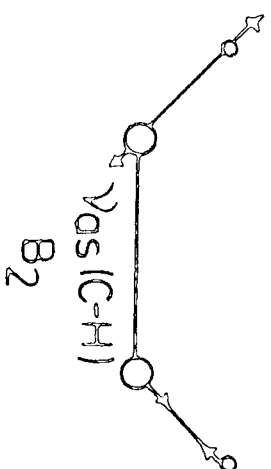
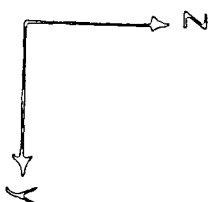
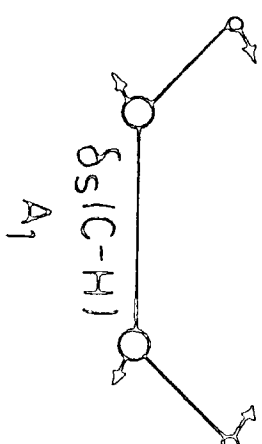
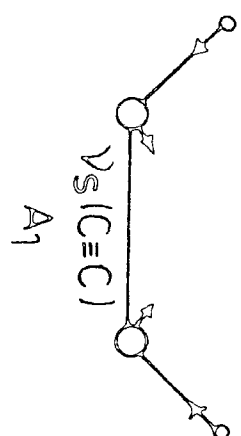
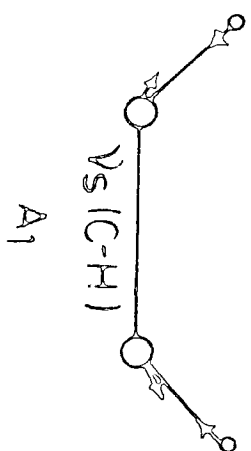
The acetylene molecule has also been analysed using the C_{2v} point group and the axes defined in dia.5(i). The vibrational symmetries thus indicated, $3A_1 + A_2 + 2B_2$, are shown in dia.5(v). By subtracting the species of the two fragments from those predicted for the whole molecule, the symmetries may be found of the 6 additional vibrations expected when

$$Co_2(CO)_6 \quad (3(14) - 6 = 36) \quad \text{and} \quad C_2H_2 \quad (3(4) - 6 = 6)$$

are combined to form $Co_2(CO)_6 \cdot C_2H_2$ ($3(18) - 6 = 48$) (Table 5.3)

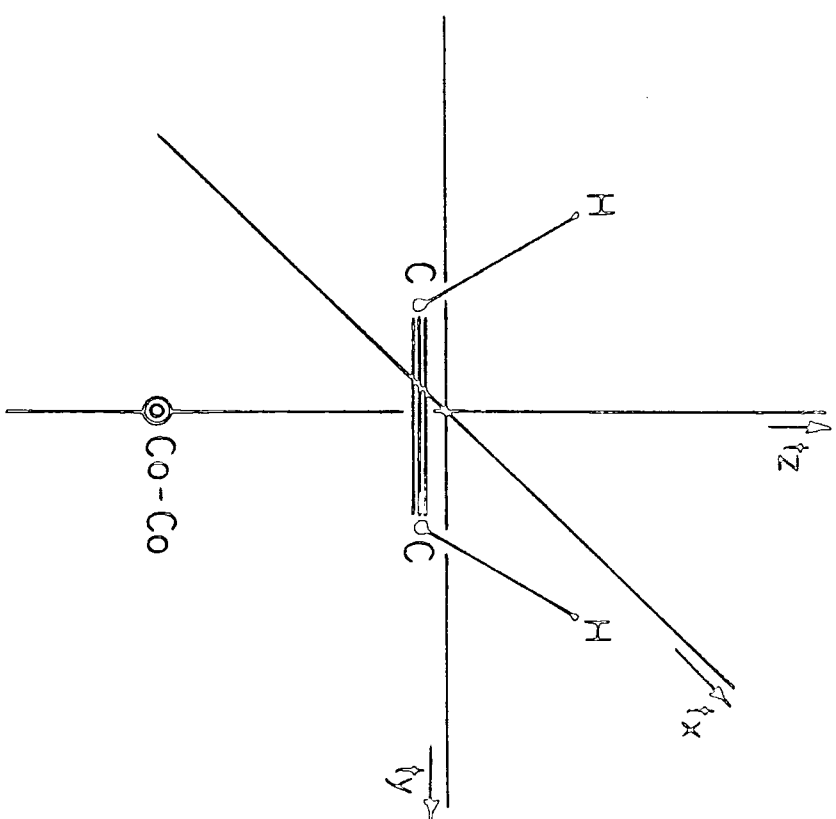
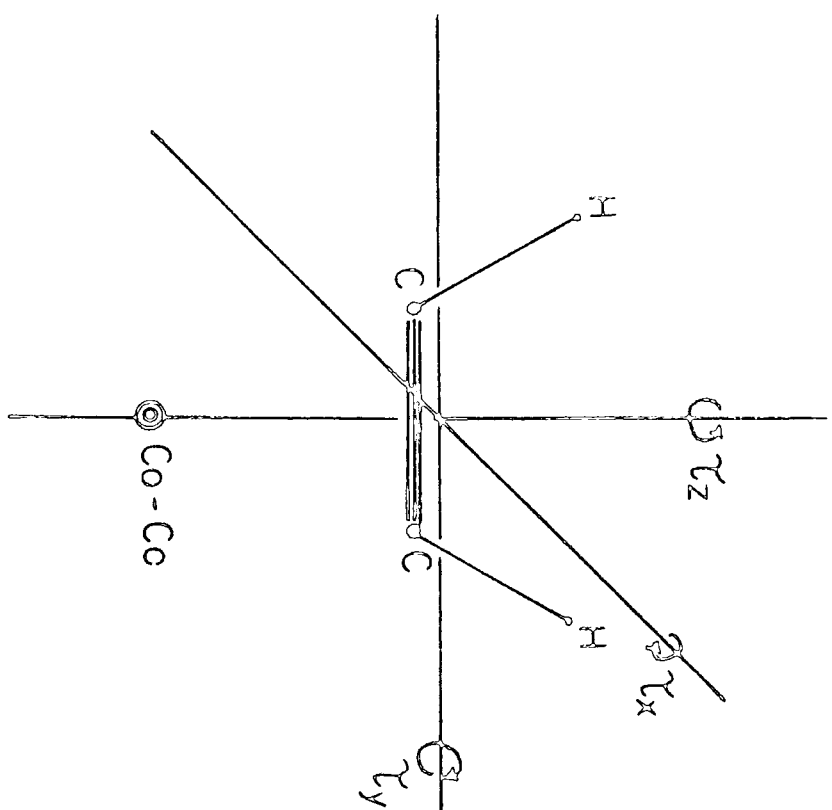
Table 5.3 The Vibrational Species of the $Co_2(CO)_6 \cdot C_2H_2$ Complex

Species	Stretching Vibrations	Bending Vibrations	Total Vibrations
$Co_2(CO)_6 \cdot C_2H_2$	$8A_1 + 2A_2 + 4B_1 + 3B_2$	$7A_1 + 8A_2 + 8B_1 + 8B_2$	$15A_1 + 10A_2 + 12B_1 + 11B_2$
$Co_2(CO)_6$	$5A_1 + 2A_2 + 4B_1 + 2B_2$	$6A_1 + 6A_2 + 6B_1 + 5B_2$	$11A_1 + 8A_2 + 10B_1 + 7B_2$
C_2H_2	$2A_1 + 0A_2 + 0B_1 + 1B_2$	$1A_1 + 1A_2 + 0B_1 + 1B_2$	$3A_1 + 1A_2 + 0B_1 + 2B_2$
Transla- tional and Torsional Modes	$1A_1 + 0A_2 + 0B_1 + 0B_2$	$0A_1 + 1A_2 + 2B_1 + 2B_2$	$1A_1 + 1A_2 + 2B_1 + 2B_2$



dia.5(v) The normal modes of the non-linear

C_2H_2 molecule : C_{2v} symmetry



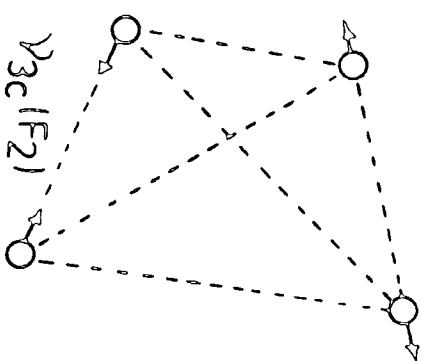
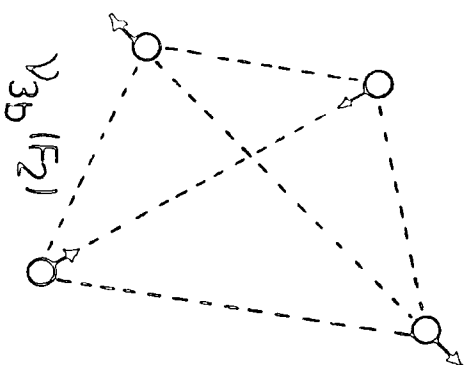
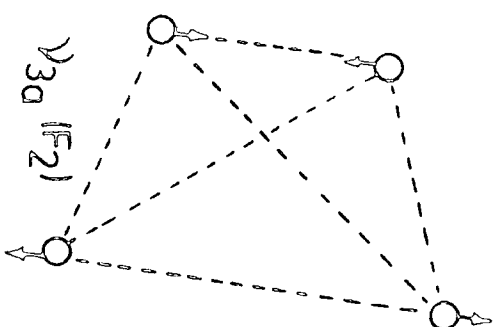
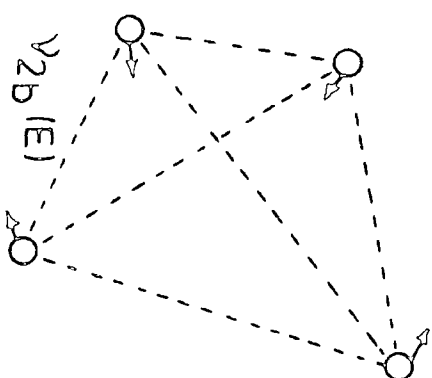
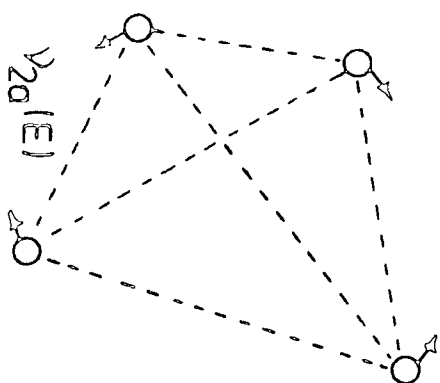
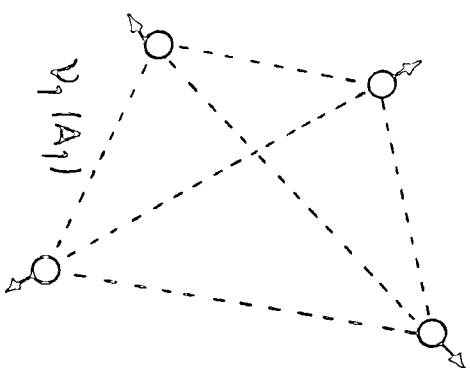
dia. 5 (vi) The three hindered rotations, τ_x (antisymmetric stretch), τ_y and τ_z , and the three hindered translations, t_x , t_y and t_z (symmetric stretch) of acetylene relative to the cobalt - cobalt bond.

The modes thus obtained for the three hindered translations and three hindered torsions of acetylene relative to the $\text{Co}_2(\text{CO})_6$ moiety (dia. 5(vi)) are $A_1 + B_1 + B_2$ and $A_2 + B_1 + B_2$ respectively. This is not in agreement with the analysis of Iwashita¹², which suggested that there should be the following species, $2A_1 + A_2 + 2B_1 + B_2$. It must be presumed that the discrepancy between the two descriptions results from the differing approximations made, the method detailed above assuming weak interaction between acetylene and the $\text{Co}_2(\text{CO})_6$ moiety, and that of Iwashita considering $\text{Co}_2\text{C}_2\text{H}_2$ as a separable unit which may be discussed in terms of C_{2v} symmetry. For two reasons, it is our considered opinion that the approximation derived in this work is the better description of the system. Firstly, Iwashita does not take into consideration the carbonyl modes which may be expected to have great influence upon the symmetry of the cobalt-cobalt bond, especially as the disagreement is fundamentally between an A_1 mode predicted in his analysis and a B_2 mode indicated in our description. Secondly, it is perhaps more physically reasonable to assume that the bonding of acetylene to $\text{Co}_2(\text{CO})_6$ will be relatively weak.

As an additional aid to analysis, dia. 5(vii) illustrates the normal modes of a tetrahedron to which Co_2C_2 may be compared. The modes predicted from T_d symmetry, $A_1 + E + F_2$, may be correlated with the C_{2v} point group after Table 5.2:

T_d		C_{2v}
A_1	$\longrightarrow$	A_1
E	$\longrightarrow$	$A_1 + A_2$
F_2	$\longrightarrow$	$A_1 + B_1 + B_2$

In previous studies of ethylene complexes¹⁴, and of ethylene^{15,16} and acetylene^{16,17} adsorbed on Ag13X zeolite, vibrations identified as translations t_x, t_y and t_z , and torsions, τ_z and τ_y (equivalent to τ_x in this work), have been located below 500 cm^{-1} . It will be seen from Table 5.4 that these



dia.5(vii) The normal modes of a tetrahedral

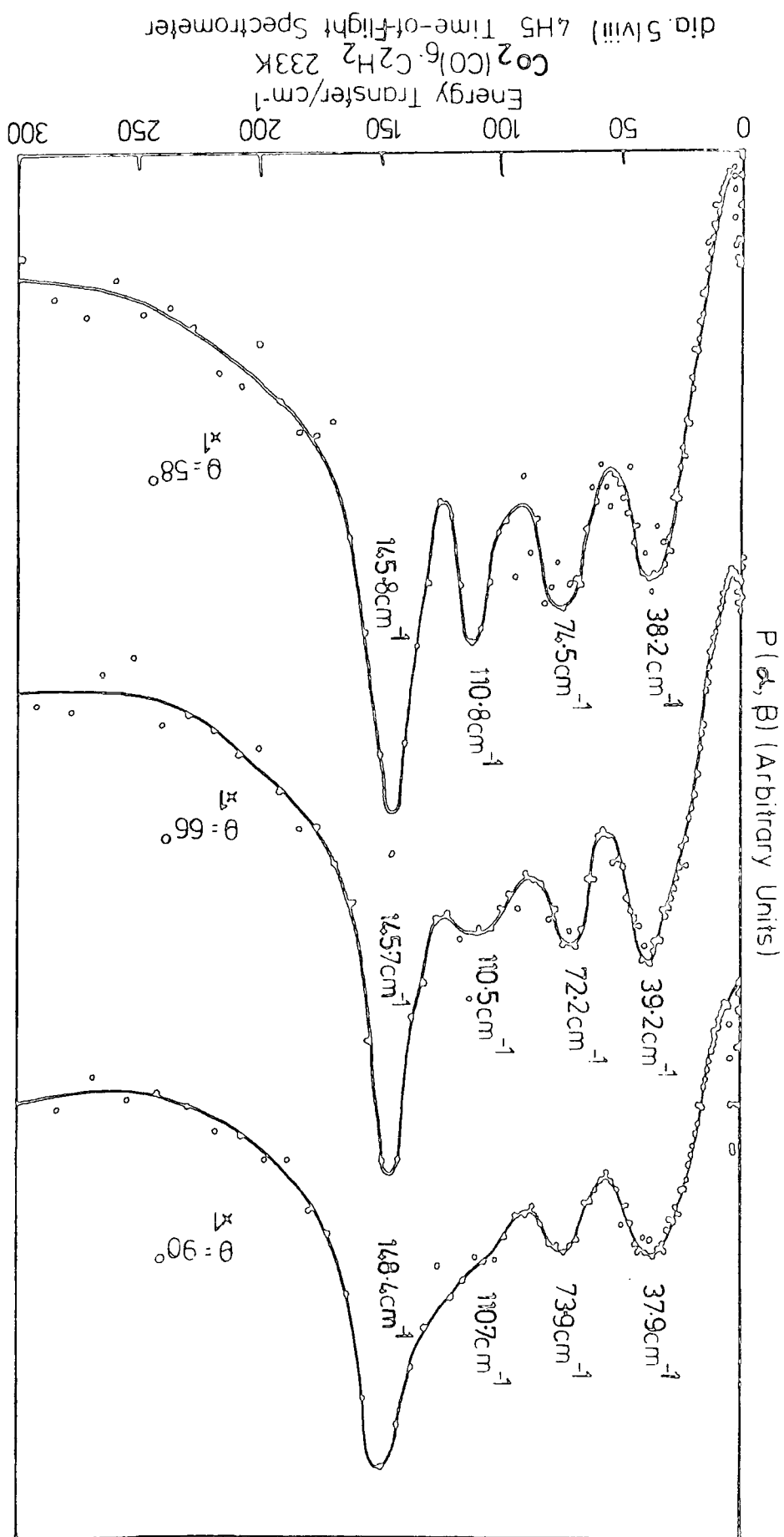
X_4 molecule : T_d symmetry

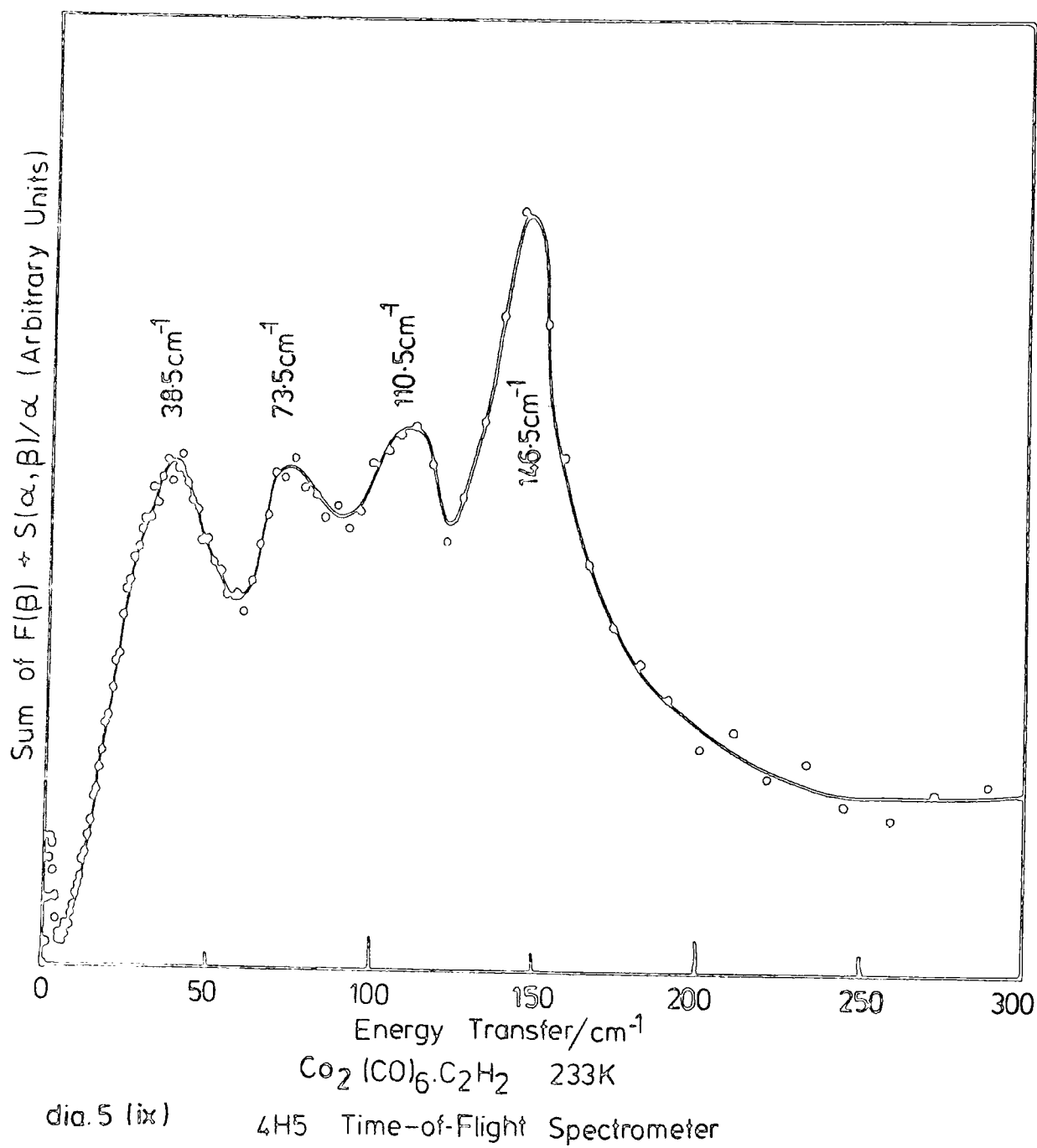
various modes include representatives of all the symmetry species of the C_{2v} point group. Similarly, reference to Table 5.3 and dia.5(iv) shows that all the species of C_{2v} symmetry are again found in the numerous Co-CO stretches and Co-C-O bends. As these vibrations have been assigned to frequencies below 515cm^{-1} in the study of Iwashita et al.⁵, and below 580cm^{-1} in the work of Kettle and Stanghellini¹³, it would not be altogether surprising if mixing between the various Co-C-O and Co-CO modes and those involving the translations and torsions (of the acetylene moiety) was to take place on a somewhat extensive scale. It might therefore be anticipated that bands found in the INS spectra of $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$ could be broadened, and perhaps have intensities at variance with predictions which do not take into account the possibility of mixing.

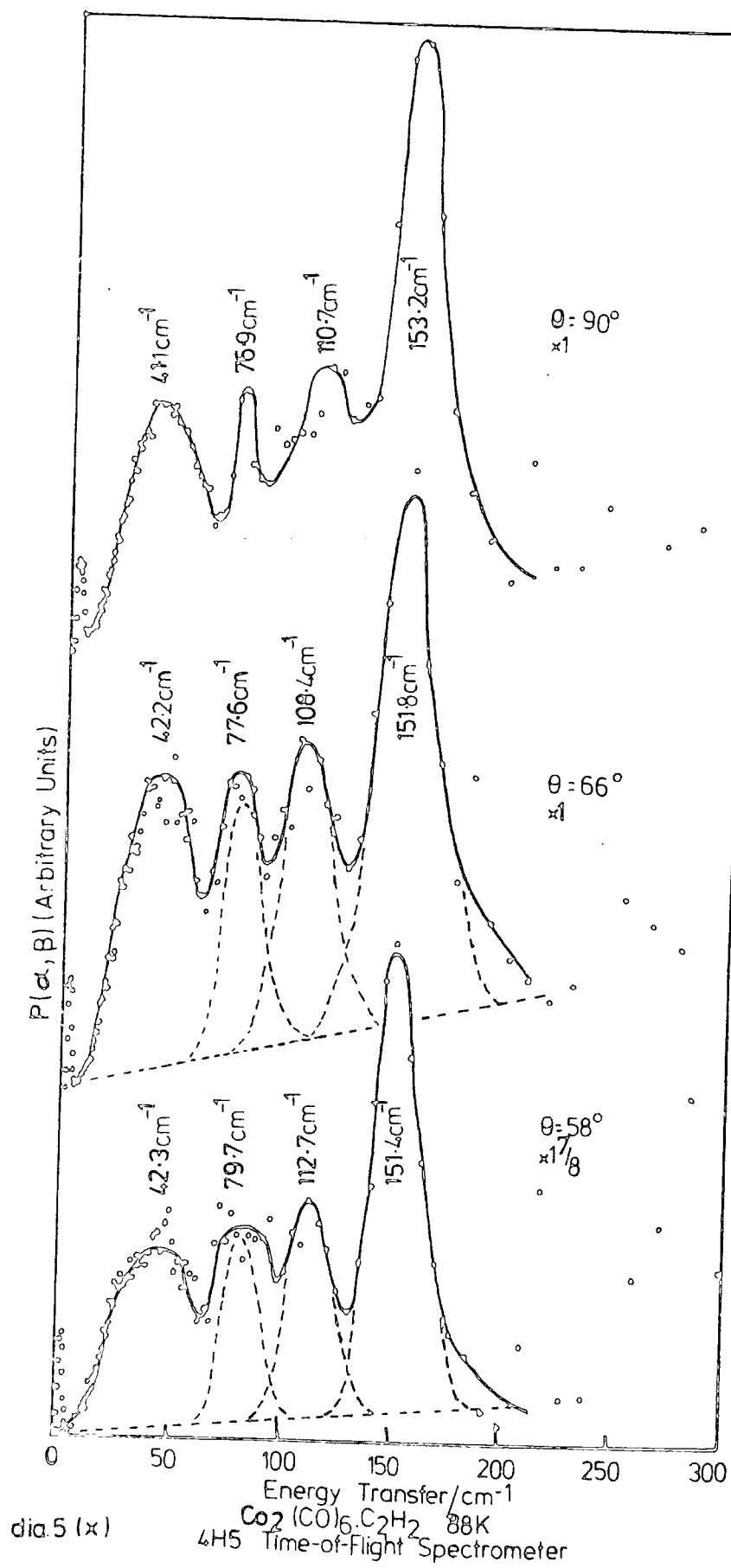
TABLE 5.4 The Symmetries of the Vibrations Expected to be "Active" in the INS Spectrum Assuming the Absence of Mixing

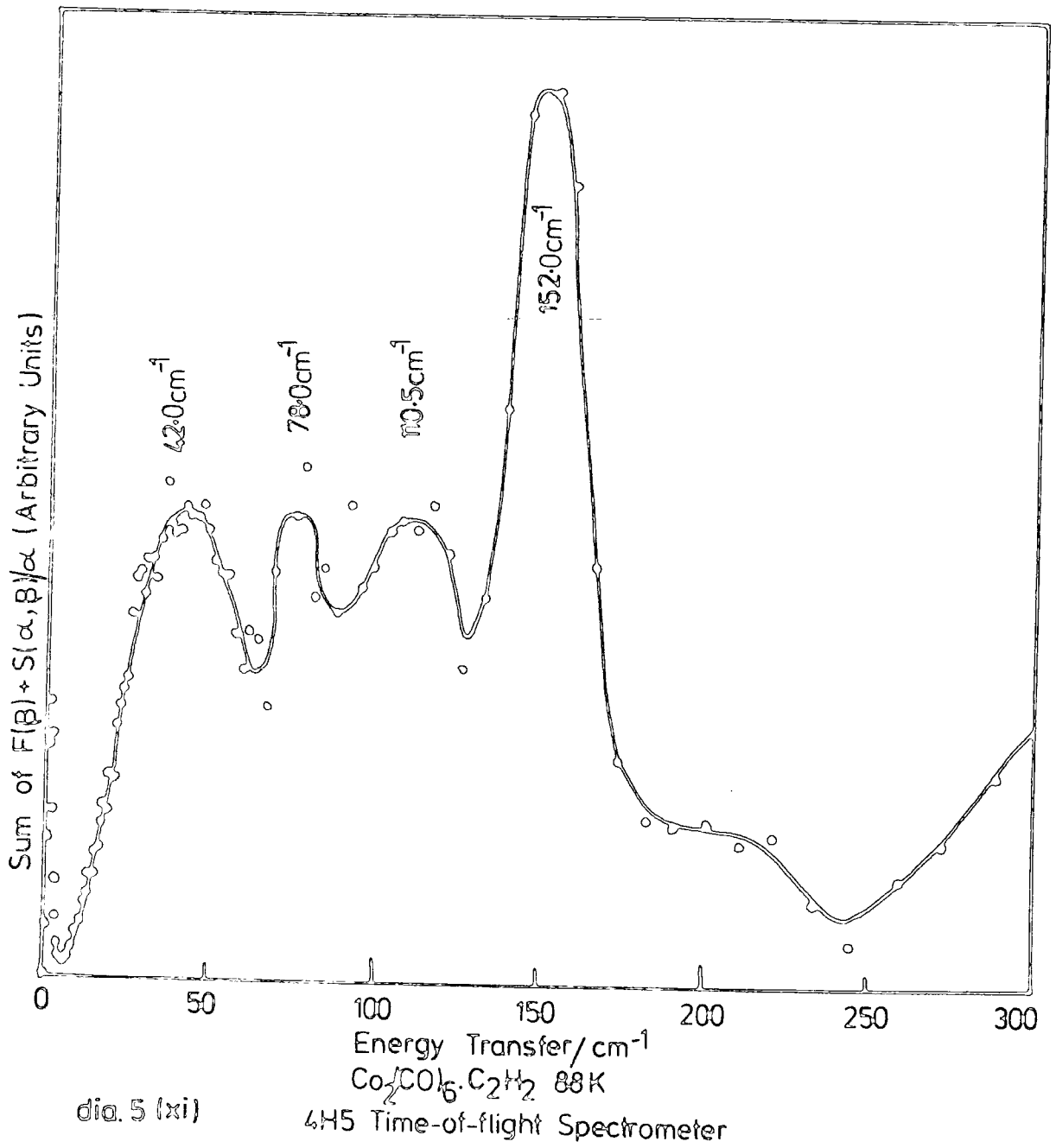
Description of Vibration	Symmetry Species
$\nu_s(\text{C-H})$	A_1
$\nu_s(\text{C=C})$	A_1
$\delta_s(\text{C-H})$	A_1
$\nu_s(\text{Co}_2\text{-C}_2)$ or t_z	A_1
$\delta_{as}(\text{C-H})$	A_2
Torsion τ_z	A_2
Torsion τ_y	B_1
Translation t_x	B_1
$\nu_{as}(\text{C-H})$	B_2
$\delta_{as}(\text{C-H})$	B_2
$\nu_{as}(\text{Co}_2\text{-C}_2)$ or τ_x	B_2
Translation t_y	B_2

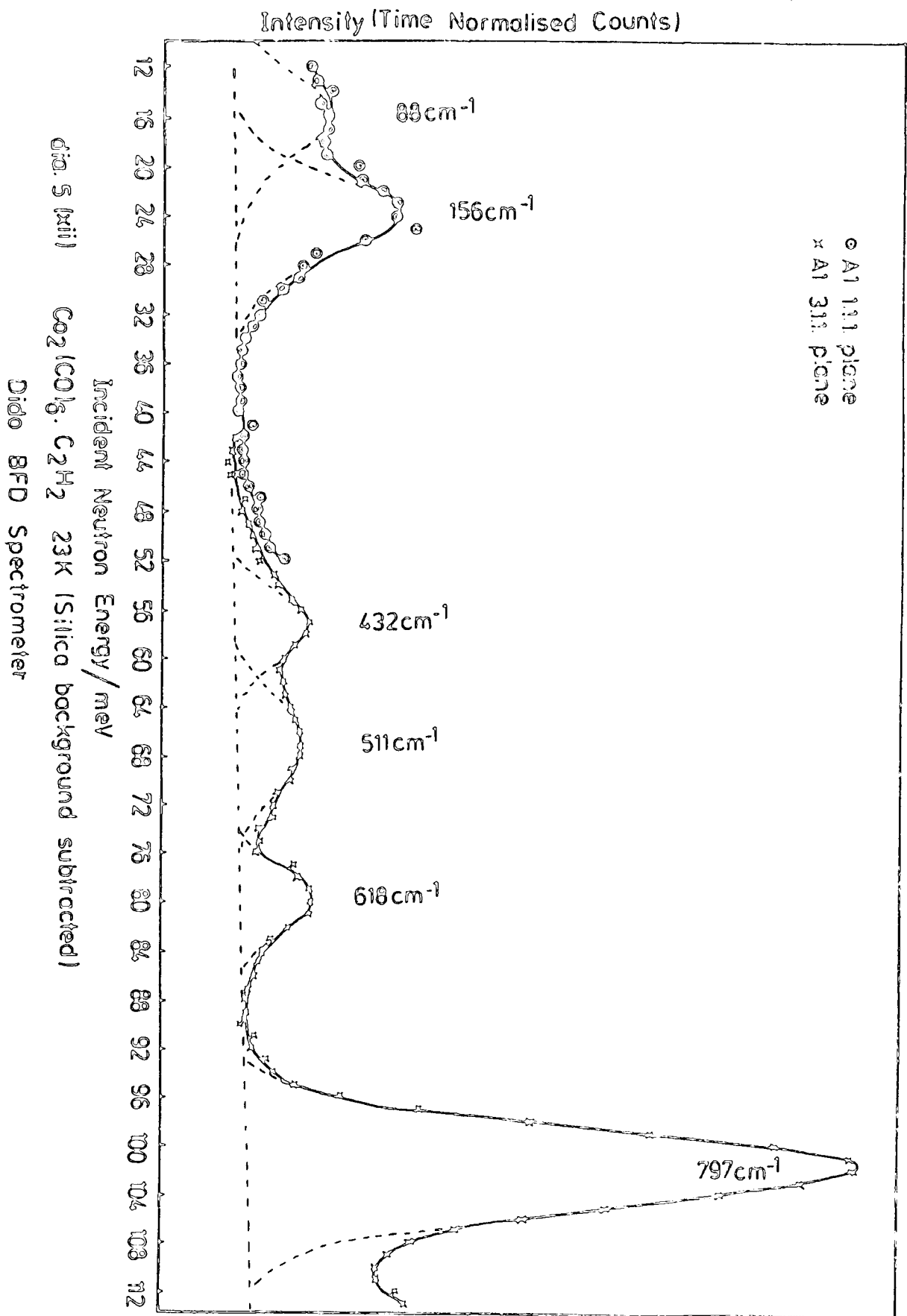
Note: The axes chosen in this analysis follow those of Iwashita¹² and are not those adopted in Chapter IV, or in the various studies of torsional modes carried out by Howard et al.¹⁵⁻¹⁷ As a result, translations and torsions denoted x or y in the table above correspond with those labelled y or x in Chapter IV and in the work of Howard et al.



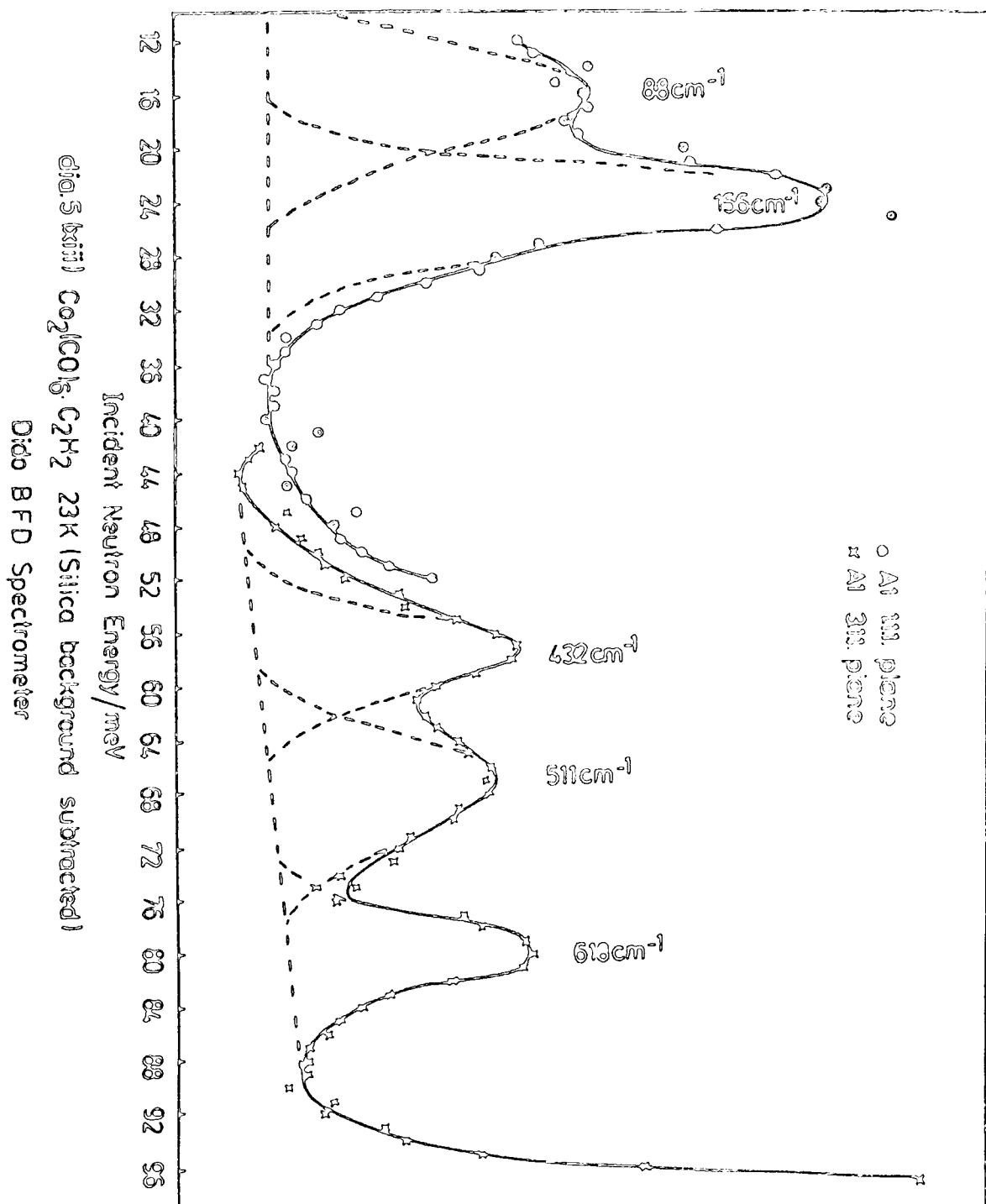








Intensity (Time Normalised Counts)



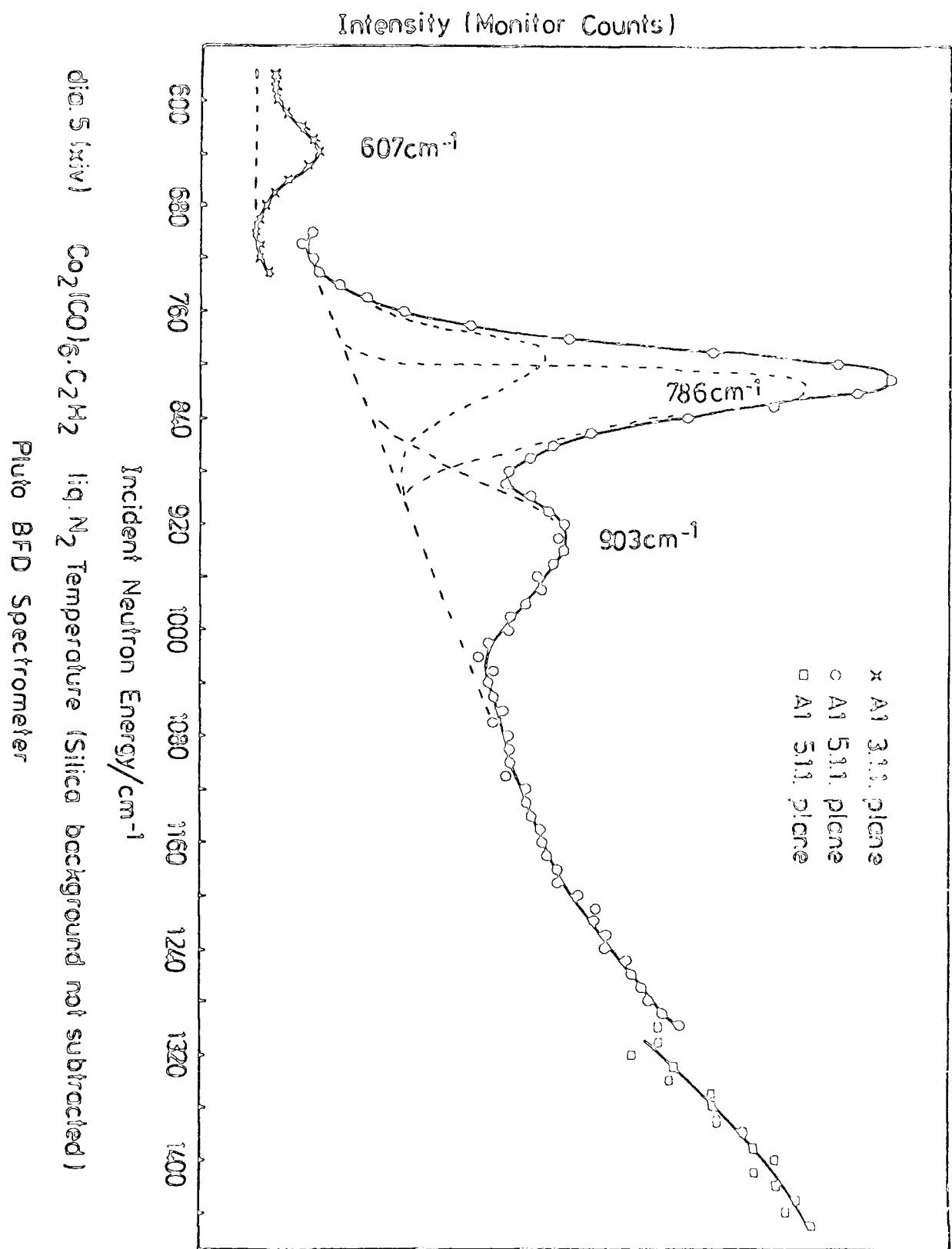


TABLE 5.5 Comparison of the Spectroscopic Frequencies (cm^{-1}) of the Di-Cobalt Hexacarbonyl Acetylene Complex obtained by Different Techniques

$\text{Co}_2(\text{CO})_8\text{C}_2\text{H}_2$ Infrared cm^{-1}	$\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$ Infrared cm^{-1}	Infrared 5.12×10^{-1} cm^{-1}	Assignment 5.12×10^{-1}	Infrared 13×10^{-1} cm^{-1}	$\text{Co}_2(\text{CO})_8\text{C}_2\text{H}_2$ Raman 13×10^{-1} cm^{-1}	Assignment 13×10^{-1}	Infrared 13×10^{-1} cm^{-1}	T-O-Fa	T-O-Fa	BFD	Assignment	Symmetry
		110a	} $\delta(\text{OC})-\text{Co}-(\text{CO})$					38.5 $\pm$ 2.0	42.0 $\pm$ 2.0		Lattice Vibration	B_2 or B_1 B_1 or D_2
		130a						73.5 $\pm$ 3.0	78.0 $\pm$ 3.5	88 $\pm$ 8	t_y or t_x	
								110.5 $\pm$ 5.0	110.5 $\pm$ 5.0		t_x or t_y	
		207a	$\nu(\text{Co}-\text{Co})$		210vs, p 310m, p	$\nu(\text{Co}-\text{Co})$ impurity?		146.5 $\pm$ 7.0	152.0 $\pm$ 7.5	156 $\pm$ 8	C_2 torsion (τ_z)	A_2
421.5a		359a	} $\nu(\text{Co}-\text{CO})$ $+ \delta(\text{Co}-\text{C}-\text{O})$	360a								A_1
450.8a		385a		380a								
491.8a		392a		392a	395a, p	$\nu_s(\text{Co}_2-\text{C}_2)$				432 $\pm$ 8	$\nu_s(\text{Co}_2-\text{C}_2)(t_z)$	
		420a		427a	435m, p							
520.0a		450a	} $\nu_{as}(\text{Co}_2-\text{C}_2)$	452a								B_2
		492a		~485a, sh 495a	490a	$\nu_{as}(\text{Co}_2-\text{C}_2)$ $+ \delta(\text{Co}-\text{C}-\text{O})$				511 $\pm$ 8	$\nu_{as}(\text{Co}_2-\text{C}_2)(t_x)$	
		515a		~512a, sh								
561.0a		551a	$\nu_{as}(\text{Co}_2-\text{C}_2)$	522a	~520a							A_2 B_1 A_1 A_1 or B_2
586.7a		605a	$\nu_s(\text{Co}_2-\text{C}_2)$	554a	556a, p	$\delta_{as}(\text{C}-\text{H})$				618 $\pm$ 8 607 $\pm$ 10	$\delta_{as}(\text{C}-\text{H})$	
602.0a	657.2a	768a	$\delta_a(\text{C}-\text{H})$	580a						797 $\pm$ 8 786 $\pm$ 10	CH twist (τ_y) $+ \delta_a(\text{C}-\text{H})?$	
751.4a	861.5a	894a	$\delta_{as}(\text{C}-\text{H})$	605a	-610a					903 $\pm$ 10	$\delta_{as}(\text{C}-\text{H})$ or $\delta_{as}(\text{C}-\text{H})$	

vs = very strong; s = strong; a = antinegative; m = medium; sh = shoulder; p = polarized Raman band; ν_s = symmetric stretch (t_z); ν_{as} = antisymmetric stretch (t_x)

a Data recorded at 233K / Data recorded at 88K

The INS spectra of $\text{Co}_2(\text{Co})_6\text{C}_2\text{H}_2$ are shown in dia.5 (viii) - (xiv), and the observed frequencies tabulated against those found by Iwashita et al.^{5,12} and by Kettle and Stanghellini¹³ in Table 5.5. In the latter study, polarised Raman bands were located at 210, 310, 395, 435 and 556 cm^{-1} . Only one of these frequencies has an analogue in the INS spectrum, that at 435 cm^{-1} (432 cm^{-1} INS). By virtue of its A_1 symmetry, and presence in the BFD spectrum, this mode must correspond to the symmetric stretch (t_z) of the acetylene group relative to the cobalt atoms, rather than the previous assignments of 605 cm^{-1} ^{5,12} and 395 cm^{-1} ¹³. The infrared frequency equivalent to that found in the INS spectrum for the symmetric stretch is reported by Iwashita et al.⁵ as 424 cm^{-1} . The deuterated acetylene spectrum, also measured, shows a band at 421.5 cm^{-1} (Table 5.5). If these both correspond to the symmetric stretch, and they are of weak intensity, then the deuteration shift would be 0.994. This compares favourably with the value predicted on the basis of a crude model of acetylene bound to an infinitely large mass (0.964).

The intensities of other INS bands have been calculated relative to that assigned above as t_z (Table 5.6). These must be regarded as approximate because the $\text{Co}_2(\text{Co})_6\text{C}_2\text{H}_2$ spectrum has been measured in three sections (one T-O-F and two BFD). Consequently, each part has had to be normalised with respect to the others on the basis of the intensities of common frequencies.

However, comparing these ratios with those predicted¹⁴ for the translational and the torsional modes of acetylene relative to the cobalt-cobalt bond, it may be seen that prediction and experiment are in close agreement for the assignment of the lowest frequency BFD vibration (156 cm^{-1}) to $\tau_z(A_2)$, which is the torsional mode of acetylene about an axis projected through both the centres of the cobalt-cobalt and carbon-carbon bonds (dia.5(i)). Additional support for this assignment may be found from the similar location of the analogous torsion in INS studies of various π -bonded ethylene complexes¹⁴⁻¹⁶.

TABLE 5.6
Comparison of Predicted and Observed Intensities and Deuteration Shifts for the
Hindered Translational and Torsional Modes of Co-ordinated Acetylene

Mode	Frequency	Intensity Ratio Predicted *	Intensity Ratio Found	Deuteration Shift Predicted*	Deuteration Shift Found
$\nu_{as}(Co_2-C_2) : \tau_x(B_2)$	$511 \pm 8 \text{ cm}^{-1}$	3.636	1.441	0.889	0.875
CH Twist : $\tau_y(B_1)$	$797 \pm 8 \text{ cm}^{-1}$	12.000	9.987	0.741	0.784
C_2 Torsion : $\tau_z(A_2)$	$156 \pm 8 \text{ cm}^{-1}$	2.711	2.915	0.911	—
translation: $t_x(B_1)/t_y(B_2)$	$78 \pm 3.5 \text{ cm}^{-1}$	1.000	0.812-0.750 ^f	0.964	—
translation: $t_y(B_2)/t_x(B_1)$	$110.5 \pm 5 \text{ cm}^{-1}$	1.000	1.162-1.093 ^f	0.964	—
$\nu_s(Co_2-C_2) : t_z(A_2)$	$432 \pm 8 \text{ cm}^{-1}$	1.000	1.000	0.964	0.894

* Calculated using the model for the structure of complexed acetylene of Iwashita¹² bound to a very large mass.
^f Intensities (corrected for frequency and Q^2) derived from P(α , β) spectra (angles 58° and 66°) recorded at 86K and stated arbitrarily relative to $\tau_z = 2.915$.

Turning now to the T-O-F spectra, as well as that band identified with τ_z , three other peaks are visible, at $38.5\text{--}42\text{ cm}^{-1}$, $73.5\text{--}78\text{ cm}^{-1}$ and 110.5 cm^{-1} . The former of these almost certainly comprises a number of vibrational frequencies which are ill-resolved. However, these appear dispersive and the lowest frequency band(s) must as a result be regarded as a lattice vibration(s).

The vibration at 110.5 cm^{-1} has been identified in the far-infrared work of Iwashita as an (OC)-Co-(CO) bending mode¹². Whilst mixing might be invoked to explain its presence in the INS spectra, it appears from intensity considerations (Table 5.6) to be more properly designated a translational mode of acetylene, either $t_x(B_1)$ or $t_y(B_2)$. Again, a measure of corroboration for this assignment is afforded by the identification of similar translational vibrations in the spectra of ethylene-containing "model compounds" including Zeise's salt^{14,18-20} in the region $\text{ca.}100\text{--}220\text{ cm}^{-1}$.

The final T-O-F band may also on intensity grounds be correlated with the remaining translational model, either t_y or t_x . In this case the intensity found experimentally is slightly smaller than that predicted. This might possibly be explained by mixing taking place, whereby the $73.5\text{--}78\text{ cm}^{-1}$ frequency loses intensity to a Co-CO stretch or Co-C-O bend of the same symmetry species (B_2 or B_1) which is present at similar frequency.

Returning to the higher energy spectra, an infrared frequency approximately equivalent to the BFD band at $786/797\text{ cm}^{-1}$ (768 cm^{-1} ^{5,12,13}) has been generally assigned as the totally symmetric C-H bend (A_1). However, the INS intensity measurements (Table 5.6) indicate strongly that a correlation with $\tau_y(B_1)$, the torsion of acetylene about an axis parallel to the $\text{C}\equiv\text{C}$ bond, is more justified. In studies of the ethylene containing π -complex, Zeise's salt, infrared measurements²⁰ have located this mode at about 1180 cm^{-1} .

A substantial lowering in the frequency of this vibration has been observed, however, in INS studies of ethylene adsorbed on Ag13X Zeolite^{15,16}, where it has been reported at 418 cm^{-1} . Similar results have been found for acetylene adsorbed on the same zeolite, with a frequency of 523 cm^{-1} indicated^{16,17}. It is therefore not unreasonable to suppose that the more ellipsoidally symmetrical charge distribution of acetylene compared with ethylene will allow a lowering in energy of this mode in $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ relative to Zeise's salt. Correlation of this frequency with those observed in the infrared for the hydrogenous and deuterated acetylene compounds (768 cm^{-1} and 602 cm^{-1} respectively)⁵ leads to a deuteration shift of 0.784, which is in reasonable accord with the predicted value of 0.741. This assignment therefore seems strongly favoured and provides support for the structural deductions of Iwashita et al.⁵ because, of course, the mode τ_y would only be observed in the INS spectrum if the acetylene molecule had become non-linear on complexation.

An alternative explanation of the $797/786\text{ cm}^{-1}$ BFD band would, however, reconcile the conflicting assignments of τ_y and $\delta_s(\text{C-H})$. It is possible to fit a Gaussian (using a Du Pont Curve Resolver) beneath the 786 cm^{-1} INS frequency at about the energy indicated by infrared studies (769 cm^{-1}). This would split the intensity of the band into two components in the ratio of 1 (769 cm^{-1}) to 1.466 (795 cm^{-1}). An assignment of the lower frequency peak generated to $\delta_s(\text{C-H})$ would then provide agreement with the work of Iwashita et al.⁵, whereas the higher energy band would still be a reasonable choice for the τ_y vibration, because it would remain, in accordance with prediction, the most intense frequency below 1180 cm^{-1} (6.424 times as intense as t_z).

The INS frequencies of 511 and 618 cm^{-1} in the $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ complex have been variously assigned by previous authors. Iwashita et al.⁵ designated the former vibration (515 cm^{-1}) as a cobalt-carbonyl group stretch or bend and a frequency at 605 cm^{-1} as a cobalt-acetylene stretch.

In this study, a band at 551 cm^{-1} was also correlated with a cobalt-acetylene stretch, and it was on the basis of normal coordinate analysis¹² and deuteration shift that the lower frequency vibration was assigned as the antisymmetric mode.

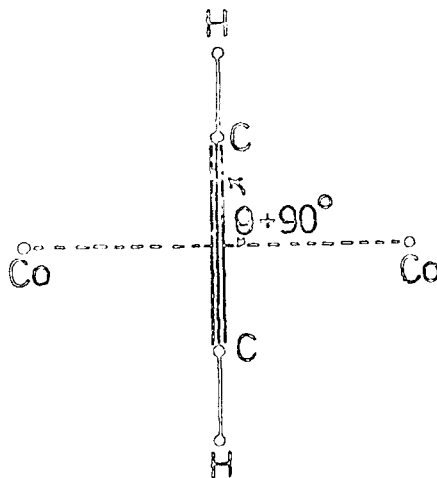
Kettle and Stangellini¹³ also considered infrared bands at 512 and 522 cm^{-1} as cobalt-carbonyl stretches or bends, but in this case polarisation data showed that the vibration at ca. 556 cm^{-1} could not be the antisymmetric cobalt-acetylene stretch. They further re-assigned the 605 cm^{-1} band as an antisymmetric C-H bend in accordance with their polarisation data, believing that the isotopic shift found by Iwashita et al.⁵ was an underestimation based upon misassignment of the deuterated spectrum.

The re-assignment of the 605 cm^{-1} peak by Kettle and Stangellini¹³ appears reasonable in view of the INS data which indicates an intensity approximately equal to that of t_z , and the absence of any remaining translational mode with which this might be correlated. This leaves the 511 cm^{-1} BFD frequency to be considered. It would be unusual from previous INS studies of ethylene-containing organometallic complexes^{15,16}, and of acetylene bound to silver in silver-exchanged zeolite 13X¹⁷, for the antisymmetric M-C₂ stretch to be displaced more than approximately 100 cm^{-1} to the high frequency side of the symmetric stretch. This suggests, perhaps, that the INS band may probably be assigned to the Co₂-C₂ antisymmetric stretch (B₂). However, if the observed intensities are consulted (Table 5.6) it will be seen that the value for the 511 cm^{-1} frequency, while larger than that expected for a translational mode, is substantially less than that predicted for τ_x . In view of the alternative assignments which have already been made for the INS frequencies below 797 cm^{-1} , it must be concluded that the only reasonable remaining correlation for the 511 cm^{-1} band is with the antisymmetric stretch. However, mixing needs to be invoked to explain the lack of agreement between calculated and observed

intensity values, as well as the fact that the BFD peak observed is broader than the resolution of the instrument ($34\text{-}40\text{ cm}^{-1}$). It is, though, interesting to note that similar non-agreement with prediction is also present in the BFD spectra of Zeise's salt and dimer^{15,16}, where the symmetric and antisymmetric stretches of ethylene relative to platinum have almost equal intensities, rather than the anticipated ratio of approximately 1:2.648.

This leaves the INS peak at 903 cm^{-1} unassigned. It would be anticipated that non-linear acetylene would give rise to three bending vibrations (dia.5(v)), the symmetric (A_1), the in-plane antisymmetric (B_2) and the out-of-plane antisymmetric (A_2). Of these, one antisymmetric bend has been definitely located in agreement with the work of Kettle and Stanghellini¹³. This probably corresponds to the out-of-plane mode, which might be expected to be of lowest frequency, analogously with ethylene and *cis*-1,2-dichloroethylene⁶. It is likely, therefore, that the remaining INS frequency represents one of the other bending modes, although it is not clear which one. However, if the "alternative explanation" of the $797/786\text{ cm}^{-1}$ BFD peak is correct, and the vibration identified by Iwashita et al.⁵ as the symmetric bend is indeed present as a component of this band, then their further assignment of a frequency at 894 cm^{-1} to an antisymmetric in-plane bend might be supported.

Of necessity, the assignments made have had to be tentative; however, a further INS study of $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{D}_2$ might enable more positive identifications to be made on the basis of deuteration shifts, especially valuable in this case where mixing probably causes discrepancies between predicted and observed intensities.

D. Barrier Calculation

dia.5(xv) Plane view of the $C_2H_2 - Co_2$ system showing the definition of the angle of rotation θ .

To the best of our knowledge, no NMR measurements have been made of the height of the barrier to rotation of C_2H_2 in the complex $Co_2(CO)_6 \cdot C_2H_2$, nor is there a model of the potential function ($V(\theta)$) as in the case of the platinum-ethylene square planar complexes²¹. Consequently, the simplest model for $V(\theta)$ will be used in the calculation of barrier height.

The symmetry of the acetylene molecule requires that the barrier be encountered twice upon rotation through 2π . Therefore, from Chapter II, the potential function may be expressed as a Fourier cosine series:

$$V(\theta) = \frac{V_0}{2} + \sum_{n=1}^{\infty} \frac{V_n}{2} \cos n\theta$$

The $Co_2(CO)_6$ species itself has a C_2 symmetry axis running through the centre of the Cobalt-Cobalt bond (and thence through the centre of the $C \equiv C$ bond of the acetylene molecule). Thus $V(\theta) = V(\pi - \theta)$, and so odd terms in $n\theta$ must cancel, the equation becoming:

$$V(\theta) = \frac{V_0}{2} + \sum_{n=1}^{\infty} \frac{V_{2n}}{2} \cos 2n\theta$$

Generally, it is believed to be a good approximation to ignore second terms in the cosine expansion²², and hence may be obtained the form:

$$V(\theta) = \frac{V_0}{2} (1 - \cos 2\theta)$$

This potential function has no metastable well, but has a minimum at $\theta=0^\circ$, and a maximum when the $C\equiv C$ axis lies parallel to the Co-Co axis.

The second derivative with respect to θ of the above equation is equal to the force constant, k . Therefore substitution for k in the Harmonic Oscillator Approximation yields:

$$\omega = \frac{1}{\pi} \left(\frac{V_0}{2I_R} \right)^{\frac{1}{2}}$$

Table 5.7 shows the values obtained for the potential barrier to rotation of C_2H_2 in the complex $Co_2(CO)_6 \cdot C_2H_2$ calculated using the High Barrier Approximation. The validity of this treatment may be seen with respect to barriers calculated (from T-O-F data measured at 88K) employing successive terms of the Das approximation²³:

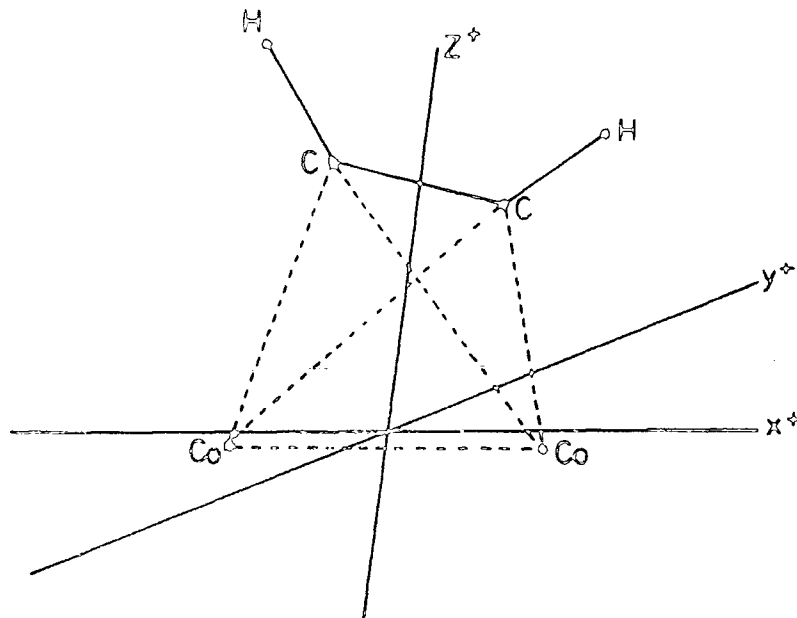
First Approximation : 59.305 kJ mol⁻¹ (Equivalent to the High Barrier Approximation: Chapter II)
 Second Approximation : 60.217 kJ mol⁻¹
 Third Approximation : 60.224 kJ mol⁻¹

Table 5.7 The Barrier to the Rotation of Acetylene in the Complex $Co_2(CO)_6 \cdot C_2H_2$

$Co_2(CO)_6 \cdot C_2H_2$	$\bar{\nu} \text{ cm}^{-1}$	$I_R \text{ } ^0\text{A}^2\text{AMU}$	$V_0 \text{ kJ mol}^{-1}$
88K	152.0 ± 7.5	} 14.47	59 ± 6
233K	146.5 ± 7.0		55 ± 5

APPENDIX: Structural Data used in the Calculation of Reduced Moment of Inertia

The crystal structure of $\text{Co}_2(\text{CO})_6 \cdot \text{C}_2\text{H}_2$ has not been determined. The reduced moment of inertia of the complex (I_R) has therefore been calculated on the basis of the X-ray diffraction study of $\text{Co}_2(\text{CO})_6 \cdot \text{PhC}_2\text{Ph}^1$, but with the additional assumptions that $r_{\text{CH}} = 1.08 \text{ \AA}$ and $\angle \text{CCH} = 120^\circ$ (after Iwashita¹²).



The co-ordinates of C_2H_2 and $\text{Co}_2(\text{CO})_6 \cdot \text{C}_2\text{H}_2$ resulting from the above model are listed below:

C_2H_2 :

Hx 0.000	Hx 0.000
y -1.234	y +1.234
z -0.863	z -0.863
Cx 0.000	Cx 0.000
y -0.694	y +0.694
z +0.072	z +0.072

$\text{Co}_2(\text{CO})_6 \cdot \text{C}_2\text{H}_2$:

Hx 0.000		Hx 0.000	
y -1.234		y +1.234	
z +2.143		z +2.143	
Cx 0.000	Cx 0.000		
y -0.694	y +0.694		
z +1.208	z +1.208		
Cox -1.235	Cox +1.235		
y 0.000	y 0.000		
z -0.116	z -0.116		
Cx -2.538	Cx -2.030	Cx +2.030	Ox +2.588
y +2.299	y +1.350	y +1.350	y +2.299
z -1.444	z -0.896	z -0.896	z -1.444
Ox -2.588	Cx -2.030	Cx +2.030	Ox +2.588
y 0.000	y 0.000	y 0.000	y 0.000
z +2.539	z +1.443	z +1.443	z +2.539
Ox -2.588	Cx -2.030	Cx +2.030	Ox +2.588
y -2.299	y -1.350	y -1.350	y -2.299
z -1.444	z -0.896	z -0.896	z -1.444

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CHAPTER VI

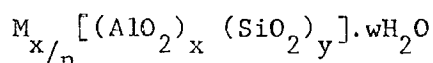
THE SILVER-EXCHANGED TYPE A ZEOLITE-ETHYLENE ADSORPTION SYSTEM

A. Background

1. Introduction

Zeolites^{1,2}, as they naturally occur, or as synthesised, are hydrated aluminosilicates of elements of groups one and two. Their structure is based upon an assemblage of AlO_4 and SiO_4 tetrahedra linked together by the sharing of all oxygens so as to form an infinite three-dimensional framework. This framework is an "open structure", in that it contains channels and interconnected voids, which may be occupied by water molecules and by the cations necessary for electrical neutrality when an aluminium atom is substituted for a silicon atom. Both water molecules and cations have considerable freedom of movement. Hence the latter generally may be exchanged to varying degrees by other cations. Similarly, in many zeolites intra-crystalline water may be removed continuously and reversibly, although in others, dehydration causes structural damage to the framework. It is only to the former, that is those which remain structurally intact upon complete dehydration, that the title "Molecular Sieves" should be applied.

The chemical formula of a zeolite, in terms of one crystallographic unit cell is¹:



where M is a cation of valence n

w is the number of water molecules

[] denotes the framework composition

The ratio y/x usually has a value between 1 and 5 dependent upon the actual structure of the zeolite, whilst the sum $x+y$ is the total number of tetrahedra in the unit cell¹.

All told, there are 34 naturally occurring zeolite minerals and approximately 100 synthetic types¹: that chosen for investigation in this

work was type A. Its structure will be described below with reference to the fundamental "building block" of which it is composed, the sodalite unit, and the structure of type 13X zeolite which has been the subject of previous INS studies involving adsorbed species³⁻⁶.

2. General Structural Considerations

a) Sodalite

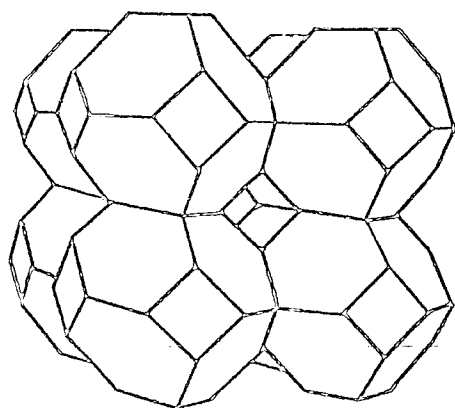
The Sodalite unit⁷⁻⁹ is a truncated octahedron or "14-hedron" (8 hexagonal faces and 6 square faces) formed of 24 (Al,Si) atoms, present as vertices, interconnected by 36 oxygen atoms.

It should be noted that the mineral sodalite (dia.6(i)), where the truncated octahedra share both square and hexagonal faces, is not itself a zeolite.

b) Linde Type 4A Zeolite

Linde type 4A zeolite (Na_{12}A)⁷⁻¹⁴ possesses a pseudo unit cell of composition, $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]\cdot 27\text{H}_2\text{O}$, which displays cubic symmetry (unit cell dimension = $12.32\text{\AA}$ ¹⁴). The description "pseudo unit cell" derives from the idealised high symmetry structure ($\text{Pm}\bar{3}\text{m}$) which results if framework silicon and aluminium atoms are not differentiated¹. In fact, the "real structure" contains an ordered arrangement of strictly alternating SiO_4 and AlO_4 tetrahedra, which causes the cubic cell constant to be doubled and the maximum possible symmetry to be lowered ($\text{Fm}\bar{3}\text{c}$). It follows, therefore, that the "real" unit cell of type A zeolite contains eight formula units of composition, $\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]\cdot 27\text{H}_2\text{O}$. However, in common with most authors, the description of type A zeolite structures within this work will be based upon the concept of the pseudo cell.

In Na_{12}A zeolite (dia.6(i)), the sodalite units are linked together by four bridging oxygen atoms across square faces of the truncated octahedra. An almost spherical internal cavity $11.4\text{\AA}$ in diameter is thereby formed known as an "α" cage (or 26-hedron of Type I¹⁵). This may be entered



Sodalite

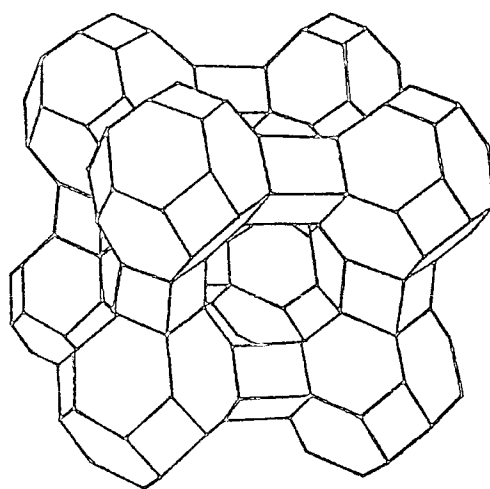
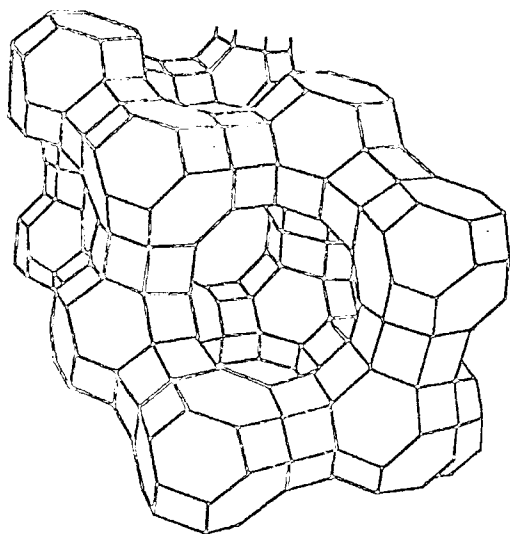
Zeolite
Type AZeolite
Type 13X

TABLE 6.1 Cation Locations Within Type A Zeolite

Position	Designation	Number
In an 8-ring	S1	} 3 per pseudo unit cell
Adjacent to an 8-ring, but displaced into a 26-hedron [/] (α cage)	S1*	
In a 6-ring	S2	} 8 per pseudo unit cell
Adjacent to a 6-ring, but displaced into a 26-hedron (α cage)	S2*	
Adjacent to a 6-ring, but displaced into a sodalite (β) cage	S2'	
Against a 4-ring ^{//} forming one of the ribs of a 26- hedron (α cage)	S3	12 per pseudo unit cell
In the centre of a Sodalite (β) cage	SU	1 per pseudo unit cell
In the centre of a 26-hedron (α cage)	S4	1 per pseudo unit cell

[/] A 26-hedron of Type I¹⁵ (or α cage), such as is present in Type A zeolite, consists of eight 6-rings, six 8-rings and twelve 4-rings.

^{//} In type A zeolite, a "4-ring" site corresponds to one of the four faces each of the cuboids linking adjacent sodalite units possesses opening into a 26-hedron (α cage).

through six approximately circular windows $4.2\text{\AA}$ in diameter, the circumferences of which contain eight oxygen atoms and are hence known as "8-rings". A second set of voids (β cages: $6.6\text{\AA}$ in diameter) is contained within the sodalite units themselves. These interconnect with the α cages through distorted "6-rings" of oxygen atoms $2.2\text{\AA}$ in diameter. There may, therefore, be considered to be two interconnecting pore systems, one of diameter $11.4\text{\AA}$ with $4.2\text{\AA}$ constrictions, and the other of alternate $11.4\text{\AA}$ and $6.6\text{\AA}$ cavities separated by $2.2\text{\AA}$ constrictions.

The possible cation positions within type A zeolites (derived from the classification system of Barrer¹⁵) are shown in Table 6.1. The nomenclature defined therein will be that adopted in the remainder of this text.

The actual position and distribution of cations within the zeolite lattice is obviously dependent upon a number of factors, e.g.

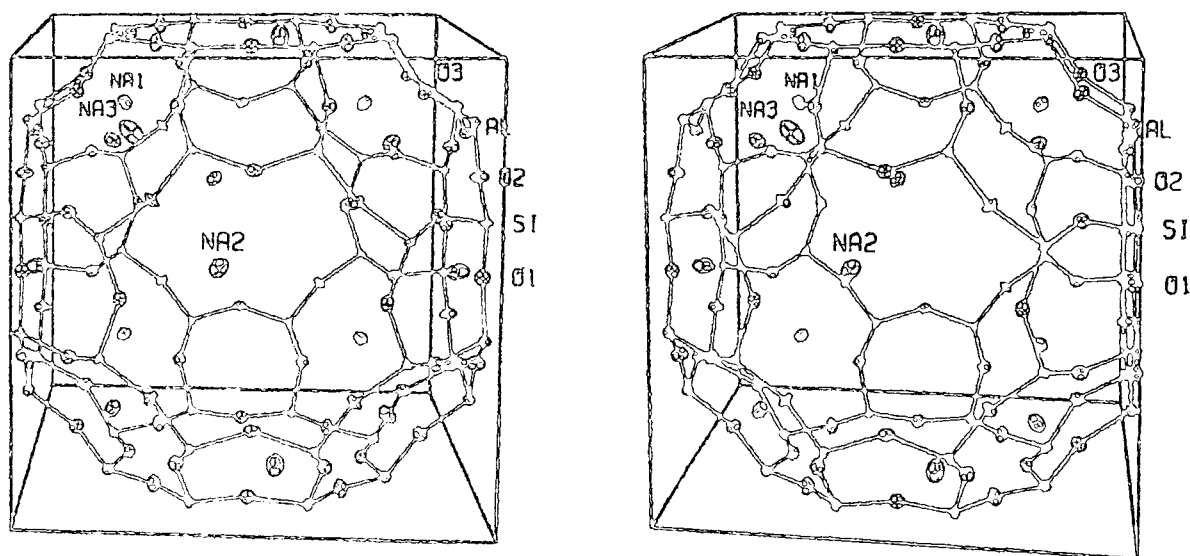
- a) the Al/Si ratio
- b) the ionic radius of the cation
- c) the charge on the cation
- d) the state of hydration/complexation of the cation

It is reasonable, therefore, that those positions most favourable to the cation under consideration will fill first, and subsequently any remaining cations will occupy sites in order of increasing unsuitability.

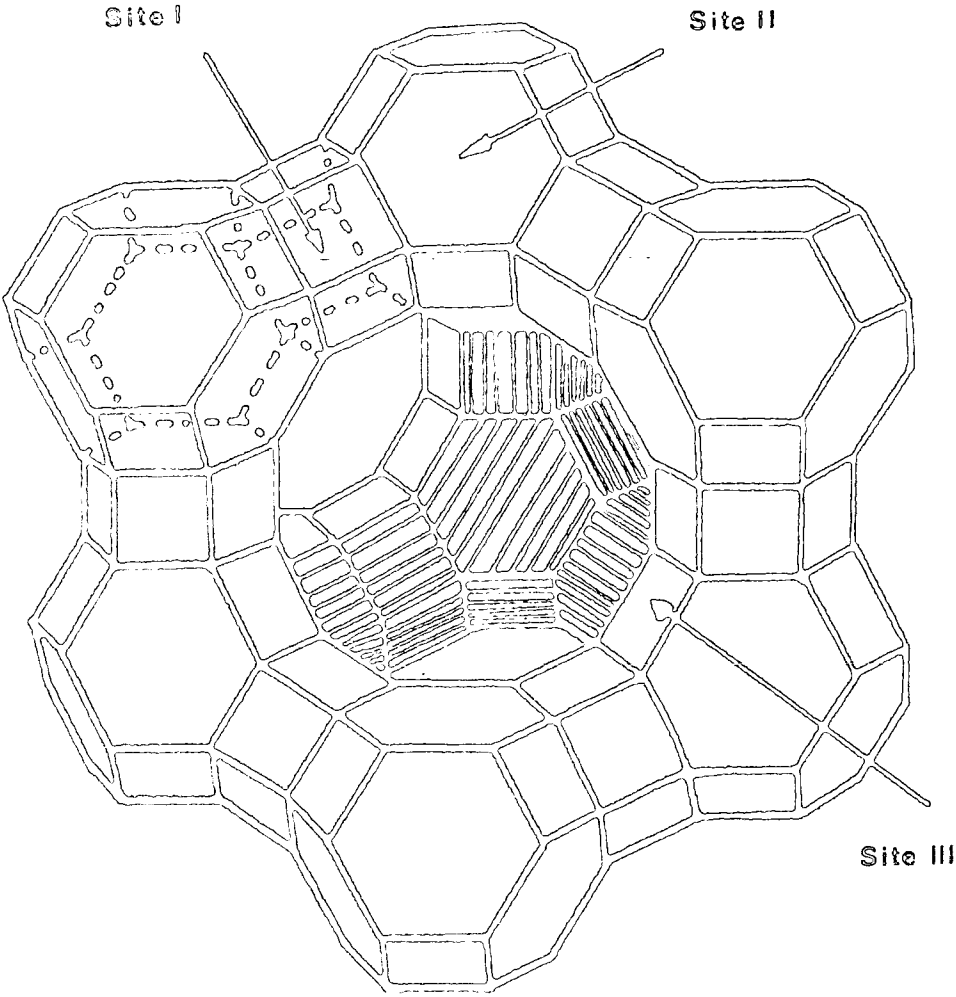
Several X-ray structural determinations based upon powder data have been published of hydrated $\text{Na}_{12}\text{Azeolite}$ ^{14,16-18}, whilst single crystal work has been carried out by Gramlich and Meier¹⁹.

In the single crystal study, it was found that eight sodium ions occupied positions on three-fold axes near the centre of 6-rings ($S2^*$). Each was tetrahedrally co-ordinated by four nearest neighbours: three oxygen atoms of the 6-ring and one water molecule. The remaining four sodium ions could not be located with certainty. However, three of these were thought to be adjacent to 8-rings ($S1^*$), with the twelfth, probably entirely hydrated, near the centre of the large cavity ($S4$).

Single crystal analyses of dehydrated Na_{12}A zeolite have been published by Smith and Dowell²⁰, Yanagida et al.²¹ and Subramanian and Seff²². The latter two determinations again located eight sodium ions on three-fold axes near the centre of 6-rings (S2^*), although the displacement of the sodium ions into the α cage was not found to be as large as in the hydrated case. A further three sodium ions occupied positions in the plane of 8-rings (S1), but off centre, making closest approach to only three oxygen atoms. (As a result of the longer and less symmetrical approaches made to the framework by the S1 cations, these sites are energetically less favourable than the 6-ring (S2^*) locations.) The final sodium ion, found on a two-fold axis normal to a 4-ring within the α cage (S3), is statistically distributed over twelve equivalent sites. Compared with the occupants of the other cation positions, the S3 ion not only makes a closer approach to surrounding sodium ions, but is also situated further from framework oxygen atoms. The S3 site is therefore the least favoured cation location. (A stereoscopic representation of the structure of dehydrated Na_{12}A zeolite after Subramanian and Seff²² is featured in dia.6(ii).)



Dia.6(ii) Stereoview of Dehydrated Na_{12}A Zeolite (after Subramanian and Seff²²)
The cation positions Na1 , Na2 and Na3 correspond to those denoted S2^* , S1 and S3 in the text.



Dia.6(iii) Cation Positions in Faujasites

TABLE 6.2

Cation Locations in Type 13X Zeolite

Position	Designation	Number
In the centre of a hexagonal prism linking adjacent sodalite (β) cages	I	16 per unit cell
In a 14-hedron (β) cage adjacent to a hexagonal prism	I'	32 per unit cell
In the centre of a sodalite (β) cage	U	8 per unit cell
In a 6-ring linking a sodalite (β) cage and a 26-hedron [†] (supercage)	II	32 per unit cell
Near a 6-ring of site II, but displaced into the sodalite (β) cage	II'	
Near a 6-ring of site II, but displaced into the 26-hedron (supercage)	II*	
Against a 4-ring ^{††} forming one of the "ribs" of a 26-hedron (supercage)	III	48 per unit cell
In the centre of a 26-hedron (supercage)	IV	8 per unit cell
In a 12-ring of a 26-hedron (supercage)	V	16 per unit cell

[†] A 26-hedron of Type II¹⁵ (or supercage), such as is present in type 13X zeolite, consists of eight 6-rings, six 12-rings and twelve of the approximately square faces of the hexagonal prisms which link adjacent sodalite units.

^{††} A '4-ring' site in type 13X zeolite corresponds to one of the square faces of a sodalite unit (14-hedron).

In various structural investigations²¹⁻³, the effect of dehydration upon the Na_{12}A zeolite has been shown to cause a decrease in the unit cell dimension: the most recent estimate²² of the dehydrated value is $12.292\text{\AA}$.

c) Linde Type 13X Zeolite

Type 13X zeolite^{7,9-12} has a unit cell composition of

$\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}]\cdot 264\text{H}_2\text{O}$ and like type A zeolite displays cubic symmetry. In this case, though, the sodalite units (β cages) are linked by 6 bridging oxygen atoms across hexagonal faces, so that a tetrahedral (diamond-like) arrangement is produced (dia.6(i)). The resultant structure²⁴⁻⁷ is very open with huge ($12\text{\AA}$ diameter) almost spherical cavities (supercages or 26-hedra of Type II¹⁵), each of which is surrounded tetrahedrally by four similar cavities separated one from another by constrictions $8-9\text{\AA}$ in diameter, formed by distorted "12-rings" of oxygen atoms. Indeed, type 13X zeolite has the largest void space of any known zeolite, amounting to about 51% on dehydration.

The possible cation positions within type 13X zeolite (derived from the classification system of Barrer¹⁵) are listed in Table 6.2 and illustrated in dia.6(iii). The nomenclature defined therein will be that adopted in the remainder of the text.

The distribution of cation sites found for sodium type 13X (Na13X) zeolite of unit cell composition $\text{Na}_{80}[(\text{AlO}_2)_{80}(\text{SiO}_2)_{112}]^1$, and dehydrated potassium type 13X (K13X) zeolite of unit cell composition $\text{K}_{86.5}[(\text{AlO}_2)_{86.5}(\text{SiO}_2)_{105.5}]^{27}$ is displayed in Table 6.3.

Table 6.3 Cation Distributions in Na13X and K13X Zeolites

Site	Number Available	Occupancy	
		Na13X*	K13X
I	16	4	9.2
I'	32	32	13.6
II	32	32	25.6
III	48	4	38.2

* Not all of the cations were located

It has been found²⁷, and may be seen from Table 6.3, that large cations (e.g. K^+) tend to fill more type III sites, and fewer type I' sites, than do sodium ions. The volumetric and gravimetric findings of Yates²⁸ for ethylene adsorbed on Ag13X may be taken to illustrate this trend, with two adsorption sites being located in approximately equal numbers which must correspond to positions II and III (as sites I and I' are inaccessible to most organic molecules).

3. Silver Ion Exchange with Linde Type 4A Zeolite

Almost total replacement of the sodium ions in Linde type 4A ($Na_{12}A$) zeolite by silver ions may be accomplished by repeated ion-exchange employing a 0.2M solution of $AgNO_3$ (containing the exact equivalence of the sodium ions to be exchanged) and a temperature of 25°C.¹⁴

On the basis of investigations which had shown silver ions to take up the same positions in hydrated silver-exchanged type A ($Ag_{12}A$) zeolite as those occupied by sodium ions in $Na_{12}A$ zeolite²⁹, X-ray intensity measurements were used to follow the exchange process of silver ions for sodium ions³⁰⁻³². These indicated that the first sodium ion replaced was that adjacent to the 4-ring of oxygen atoms (exchange=1/12), followed by the eight sodium ions near the centre of the 6-rings (exchange = 1/12 $\rightarrow$ 9/12), and ultimately the three sodium ions at or near the centre of the 8-rings (exchange=9/12 $\rightarrow$ 12/12). Confirmation of the above order was inferred from adsorption measurements carried out at the same time using ethane on variously exchanged samples of $(Ag, Na)_{12}A$ zeolite activated at 250°C and 10^{-3} mm pressure. These demonstrated that replacement of sodium by silver ions caused no reduction in ethane adsorption up to about 80% exchange, but that exchange above this value caused the amount adsorbed to decrease until, at complete exchange, the diminution was to about one-half. The factor controlling adsorption may be regarded as the constriction at the 8-ring of oxygen atoms through which molecules must pass in order to be

adsorbed on the internal surface of the zeolite. Consequently, ions occupying the 8-ring sites will reduce the effective pore size if they possess an ionic radius greater than that of sodium, and hence adsorption will progressively decrease on exchange.

4. Crystalline and Thermal Properties of Type A Zeolite

Thomas et al.³³, by water adsorption capacity measurements and X-ray diffraction studies, showed the thermal transformation of Na_{12}A zeolite to begin at 550°C , so that above 670°C the zeolite ceased to be a single phase.

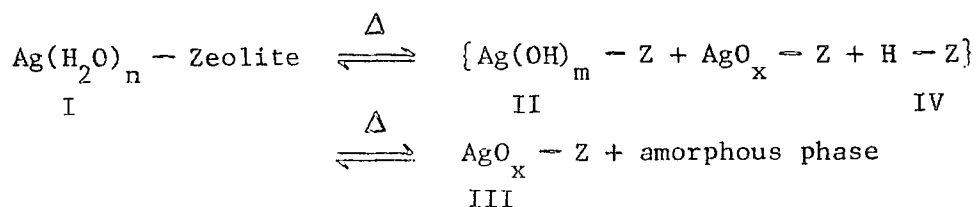
The crystallinity of variously silver-exchanged type A zeolites has also been studied³⁴⁻⁶, the former two investigations in the light of previous reports of the comparative stability of Ag_{12}A zeolite^{14,37}. It was found^{34,35} that the intensities of selected X-ray powder reflections (hydrated state) decreased with increasing silver exchange. However, this was ascribed to interference resulting from the high scattering power for X-rays displayed by silver, rather than a breakdown of crystallinity with exchange. Support for this conclusion was obtained by re-exchanging a sample of Ag_{12}A zeolite using NaNO_3 solution and finding peak intensities similar to the original Na_{12}A .

Considering now the thermal properties of type A zeolite, Evolved Gas Analysis (EGA) and Differential Scanning Calorimetry (DSC)^{38,39} studies of Na_{12}A zeolite have indicated the presence of three processes, occurring at temperatures of $370\text{--}400^{\circ}\text{C}$, $420\text{--}420^{\circ}\text{C}$ and $540\text{--}600^{\circ}\text{C}$. These have been explained as the respective "removal of water in solvating polylayer with counterions", water bound to oxygen of the aluminosilicate framework in α cages, and water hydrogen bonded in β cages.

Pertaining more to the work of this thesis, Differential Thermal Analysis (DTA) measurements have been performed on $(\text{Na},\text{Ag})_{12}\text{A}$ zeolite at various degrees of exchange^{34,35}. An endothermal effect was seen between 130°C and 230°C (corresponding to dehydration), and two higher temperature

exothermal features observed in the 600°C to 910°C region. The lower temperature exothermal effect shifted from 780°C to 560°C on exchange from Na₁₂A to Ag₁₂A zeolite, and was considered to result from loss of structure. (A conclusion which may also be reached from a Thermal Gravimetric Analysis (TGA) study carried out by Banerjee on fully silver-exchanged type A zeolite⁴⁰.) Additional X-ray measurements^{34,35} confirmed these findings, proving Ag₁₂A zeolite to be structurally stable up to the temperature of the lower exothermal effect (~ 600°C), but transformed into an amorphous phase at about 700°C. The higher temperature exothermal effect was consequently taken to represent the reported recrystallisation of Ag₁₂A zeolite into a β cristobalite structure¹⁴.

Determination of the specific surface area of (Ag,Na)₁₂A zeolite^{34,35}, by adsorption of oxygen on samples subjected to various temperatures, showed that some degradation of the zeolite structure did, in fact, occur below 600°C, the amount being dependent upon the degree of exchange of silver for sodium. However, as this was not evident from the DTA curves, the effect was felt to be small, confirming the findings of Giordano⁴¹ (also from DTA measurements), that there was negligible structural damage caused to Ag₁₂A zeolite by calcination at 400°C, and reduction with hydrogen at 250°C. As a result of their investigations, it was concluded by Matsumoto et al.³⁵ that Ag₁₂A zeolite was structurally less stable with respect to temperature than Na₁₂A zeolite, and the following scheme was suggested to explain the observed effects:



In the above process, the combined effect of the polarising power of the silver ion and the application of heat is to cause dissociation of water molecules complexed to the silver ion (I). The co-ordinated hydroxyl groups thus formed (II) may, in turn, be cleaved leading to the formation

of silver oxide (III). Meanwhile, the protons which have been released by these two processes bond to oxygen atoms of the zeolite framework forming structural hydroxyl groups (IV). Subsequent dehydration of the latter at higher temperature then causes breakdown of the zeolite lattice producing the first exothermic effect. On the basis of this scheme, the lower temperature stability of silver-exchanged A zeolite may be explained as resulting from the greater polarising power of the silver ion compared with the sodium ion.

Dehydration under vacuum causes Ag_{12}A zeolite to change colour dramatically from pale grey to deep orange. This is a reversible process: Ag_{12}A becomes bright yellow if allowed to cool in air, and ultimately returns to its initial pale grey state on more prolonged exposure to air at room temperature. These colour changes are thought to originate from alteration of the ligands surrounding silver ions³⁵. Considering the three complexes postulated in the dehydration scheme (I, II and III), it is suggested³⁵ that according to the spectrochemical series, the absorption spectrum of Ag^+ in II should shift to a longer wavelength compared with I, that is, from the ultraviolet to the visible spectrum. Similar shifts are expected for complex III, and hence the colour changes observed on dehydration.

5. X-ray Investigations of Type A Zeolites and of Adsorbed Species

As well as those studies detailed previously^{14,16-22, 42}, crystal structures of the following exchanged type A zeolites have been published: K_{12}A ^{43,44}, Tl_{12}A ^{45,46,60}, Rb_{11}NaA ^{47,48}, $\text{Cs}_7\text{Na}_5\text{A}$ ⁴⁹, $\text{Cs}_7\text{K}_5\text{A}$ ⁴⁴, $\text{Ag}_{6.5}\text{Tl}_{5.5}\text{A}$ ⁵⁰, Ca_6A ^{51,60}, Sr_6A ⁵¹, $\text{Cd}_{9.5}\text{Cl}_4(\text{OH})_3\text{A}$ ⁵², $\text{Eu}_{5.75}\text{Na}_{0.5}\text{A}$ ⁵³, $\text{Zn}_5\text{Na}_2\text{A}$ ^{54,55}, $\text{Mn}_{4.5}\text{Na}_3\text{A}$ ⁵⁵⁻⁷, $\text{Co}_4\text{Na}_4\text{A}$ ^{55,58,59,65} and $\text{Ni}_{2.5}\text{Na}_7\text{A}$ ⁵⁵. Pertaining more to this thesis is a series of determinations which have dealt with the effect of various dehydration and thermal treatments of Ag_{12}A zeolite⁶⁰⁻⁶⁴.

X-ray diffraction studies of adsorption systems have included: O_2 on $\text{Eu}_{4.5}\text{Na}_3\text{A}$ ⁶⁵; CO on $\text{Co}_4\text{Na}_4\text{A}$ ⁶⁶; S_8 on Na_{12}A ⁶⁷; Cl_2 on Ag_{12}A ⁶⁸, $\text{Eu}_{5.5}\text{NaA}$ ⁶⁹ and $\text{Co}_4\text{Na}_4\text{A}$ ⁷⁰; Br_2 on Na_{12}A ⁷¹ and Ag_{12}A ⁷²; I_2 on $\text{Co}_4\text{Na}_4\text{A}$ ⁷³; NH_3 on Na_{12}A ^{74,75}

and $\text{Ag}_{12}\text{A}^{76}$ and cyclopropane on $\text{Co}_4\text{Na}_4\text{A}^{77}$ and $\text{Mn}_4\text{Na}_4\text{A}^{78}$. Again directly relevant to the work carried out here, have been the investigations of C_2H_2 adsorbed on $\text{Na}_{12}\text{A}^{78,79}$, $\text{Mn}_{4.5}\text{Na}_3\text{A}^{80,81}$ and $\text{Co}_4\text{Na}_4\text{A}^{81}$; and of C_2H_4 adsorbed on $\text{Ag}_{12}\text{A}^{82}$ and $\text{Co}_4\text{Na}_4\text{A}^{83}$.

a) The Structure of Ag_{12}A Zeolite

Single crystal measurements of fully hydrated Ag_{12}A zeolite^{60,61} (unit cell dimension = $12.288\text{\AA}$) have shown the cations to be distributed over three positions within the framework (Table 6.4). Eight silver ions were located on three-fold axes near 6-rings; of these, five were recessed into the large (α) cavity (S2^*) and in co-ordination with at least one water molecule, and the three remaining displaced into the sodalite (β) cage ($\text{S2}'$) with three water molecules bridging between them. A further three silver ions were associated with 8-rings, but off-centre (making closest approach to only three oxygen atoms) and displaced into the α cage (S1^*). The final cation was found placed within the large cavity opposite a 4-ring (S3). As a result of the low overall symmetry of the silver ions in the α cavity many water positions exist with low occupancies, and hence no definite positions or occupancies could be determined.

Table 6.4 The Distribution of Cations in Fully Hydrated and Partially Dehydrated Ag_{12}A zeolite

Cation Site	Occupation in Fully Hydrated Ag_{12}A Zeolite	Occupation in Partially Dehydrated Ag_{12}A Zeolite
S1		1
S1*	3	2
$\text{S2}', \text{S2}^*$		3
S2'	3	2
S2*	5	3
S3	1	1

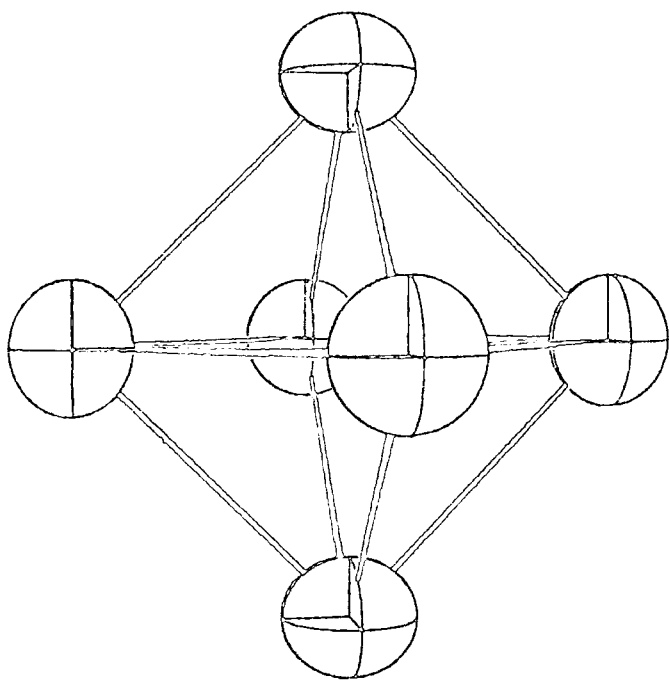
[/] Position defined within the section of the text relating to the structure of partially hydrated Ag_{12}A zeolite.

A partially hydrated crystal of Ag_{12}A zeolite⁶¹ (unit cell dimension = $12.206\text{\AA}$) was produced by heating at 200°C in a stream of O_2 for 12 hours, and then evacuating at 350°C and 10^{-5} Torr for 48 hours. Once again eight silver ions were distributed over three-fold axes associated with 6-rings. In this case, three extended into the α cage (S2^*), two were situated within the sodalite unit (β cage) $0.44\text{\AA}$ from the plane ($\text{S2}'$), and three within the sodalite unit $1.19\text{\AA}$ from the plane (a location which will be denoted $\text{S2}''$). In the first two positions mentioned, the silver ion is trigonally co-ordinated to three of the 6-ring oxygen atoms; in the latter, the three silver ions lie relatively far inside the sodalite cavity arranged triangularly to maximise intercationic distances and bridged by three water molecules. The distribution within the sodalite unit may alternatively be considered as three silver ions ($\text{S2}''$) occupying sites near three of four tetrahedrally placed 6-rings, with two silver ions ($\text{S2}'$) located in positions on opposite sides of an origin.

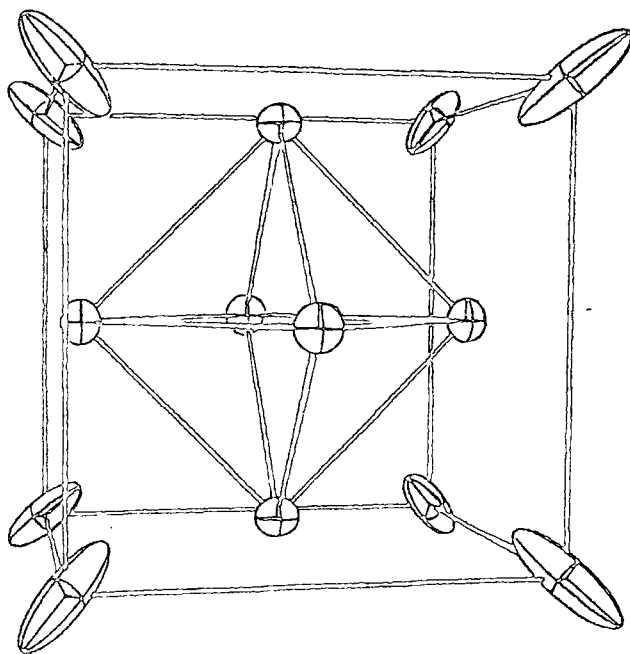
An additional three silver ions were found adjacent to 8-rings, but displaced off-centre (as in the case of hydrated Ag_{12}A zeolite); two of these occupied positions where the cation was recessed into the α cage (S1^*), the third lay within the 8-ring plane (S1). The twelfth silver ion was statistically divided among twelve equivalent positions corresponding to a two-fold axis opposite a 4-ring (S3).

The structural evidence was considered consistent with the reported results of Beyer⁶¹ (who found for similarly prepared Ag_{12}A zeolite that only 70% of the silver ions could be reduced by H_2 at 150°C), if it was assumed that the three irreducible cations were those hydrated silver ions situated furthest within the sodalite cage ($\text{S2}''$). The corollary of this is that even vacuum dehydration at 350°C is insufficient to remove the water molecules within the β cavity (possibly because each water molecule is co-ordinated to two silver ions), and that the partially hydrated Ag_{12}A zeolite investigated corresponded to Ag_{12}A trihydrate.

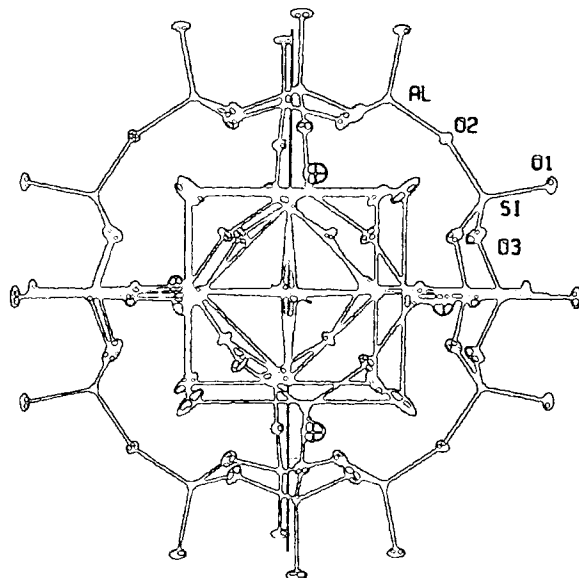
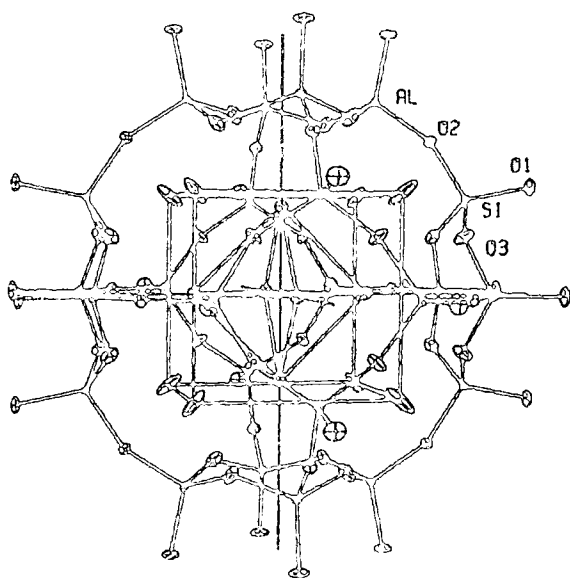
Several additional studies^{62,63} have been carried out on single crystals subjected to more severe dehydration processes. From these it appears that the eight 6-ring silver ions ($S2^*$ and $S2'$ positions of the fully hydrated zeolite) occupy a relatively stable environment, the effect of heat being only to bring the ions closer to the centre of the 6-rings; whilst the less energetically favoured 8-ring ($S1^*$) and 4-ring silver ions ($S3$) are progressively reduced. The reduction of silver ions therefore proceeds to a maximum of four, which migrate into the sodalite (β) cavities to form a suggested octahedral Ag_6 molecule^{62,63} at position SU (dia.6(iv)). A complex of the formula $(Ag^+)_8(Ag_6)$ may therefore be proposed in which the Ag_6 molecule is enclosed by a "cube", the corners of which correspond to the stable silver ions within the centre of 6-rings ($S2^*$) (dias. 6(v)-(vii)).



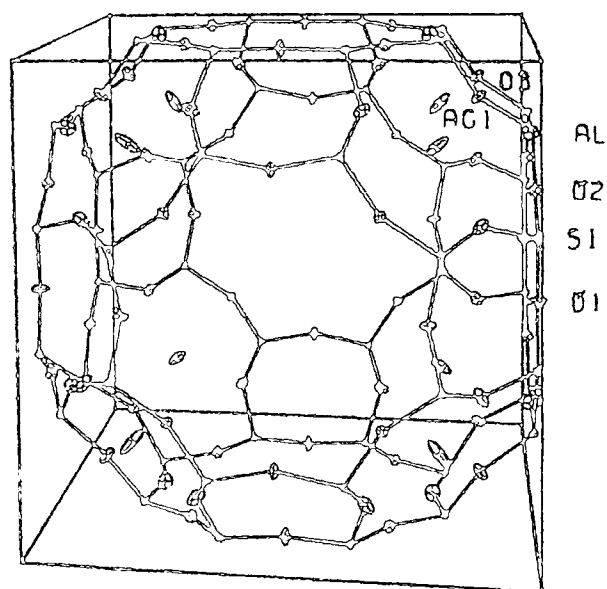
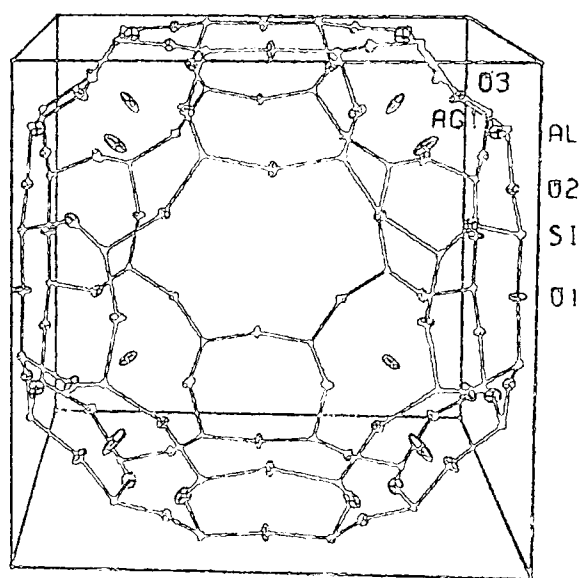
dia.6(iv) The Octahedral Ag_6 Molecule
(after Kim and Seff⁶³)



dia.6(v) The Octahedral Ag_6 Molecule.
Stabilised by Co-ordination to
Eight 6-ring Silver Ions ($S2^*$)
(after Kim and Seff⁶³)



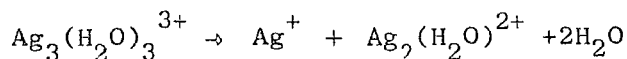
dia.6(vi) Stereoview of an Octahedral Ag_6 Molecule Stabilised Within a Cubic Arrangement of Eight Silver Ions (S2^*) (after Kim and Seff^{62,63})



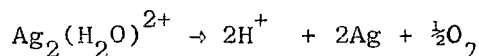
dia.6(vii) Stereoview of the Large (α) Cavity of an Idealised Structure of $\text{Ag}_8^+\text{Ag}_4\text{OH}^+\text{Si}_{12}\text{Al}_{12}\text{O}_{47}$ (after Kim and Seff⁶³). (Position Ag1 corresponds to that denoted S2^* within the text.)

Interaction must be assumed to occur between the atoms of the Ag_6 clusters and four equivalent framework oxide ions, with the silver atoms behaving as weak lewis acids with respect to the framework, accepting electron density and delocalising it through co-ordination interaction onto the silver ions at the 6-rings. Without this stabilisation afforded the Ag_6 molecule by the silver and oxide ions, the retention of metal atoms within the zeolite structure would be impossible.

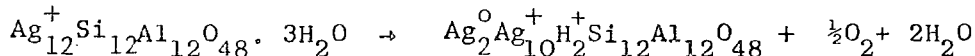
The following scheme has been suggested for silver ion reduction⁶³ involving initially the residual water molecules found in the sodalite (β) cages of partially hydrated Ag_{12}A zeolite at about 350°C ⁶¹:



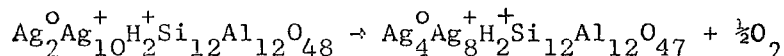
followed by:



which would be equivalent to the overall cell reaction:



After depletion of the supply of water molecules, additional silver ions must be reduced by framework oxide ions, causing the diffraction pattern to deteriorate. Evacuation to 10^{-5} Torr at 425°C for about ten days, therefore, leads to all four silver atoms in unfavourable sites being reduced:



It is obvious that the formation of Ag_6 molecules stabilised by eight silver ions requires more silver atoms than are present in the unit cell. There is thus an occupancy of 2/3 of the sodalite units by Ag_6 molecules with the remaining β cavities empty of all reduced silver ions.

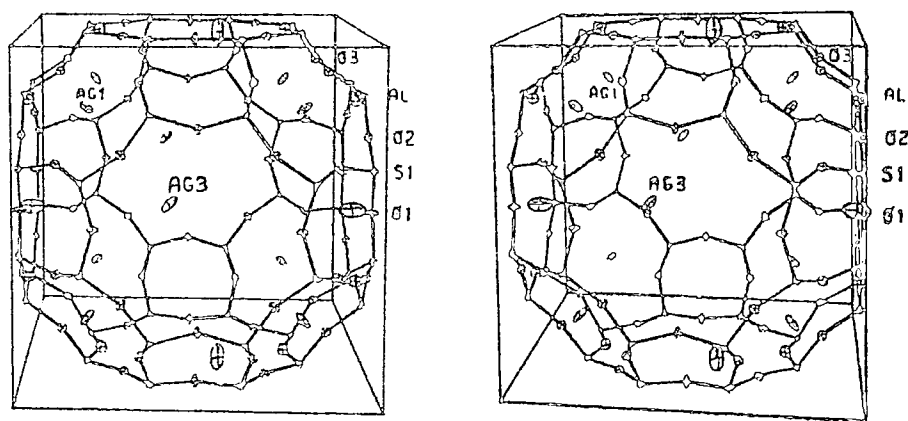
More severe conditions still (heating above 450°C) are found to give rise to the appearance of crystallites of silver⁸⁴, which result from reduction proceeding to include 6-ring silver ions, thereby causing the destabilisation of the $(\text{Ag}^+)_8(\text{Ag}_6)$ system in some sodalite units. Ultimately, the reaction goes towards completion (475° and 10^{-5} Torr pressure for 7 days),

the diffraction pattern indicating silver powder and moderately large silver crystals to be present, and the framework to have broken down (with the cell constant decreasing from $12.295\text{\AA}$ to $11.42\text{\AA}$). Under these circumstances only two silver ions and two silver atoms are thought to remain per unit cell, that is, ten out of twelve silver ions have been reduced.

Interesting evidence of the almost total reversibility of the dehydration scheme outlined above has been afforded by studies of an Ag_{12}A single crystal subjected to the following treatment⁶⁴:

- (a) Dehydration at 250°C and 8×10^{-6} Torr for 16 hours
- (b) Oxygenation by 100 Torr O_2 at 400°C for 0.3 hour
- (c) Dehydration at 400°C and 10^{-5} Torr for 1 hour
- (d) Hydrogenation by 12 Torr H_2 at 330°C for 0.5 hour
- (e) Re-oxygenation by 100 Torr O_2 at 330°C for 1 hour

The combination of dehydration (see above) and the hydrogenation treatment caused complete loss of the zeolite crystalline diffraction pattern and the appearance of lines indicative of silver metal. Oxygen treatment restored the zeolite lattice diffraction pattern and the silver was re-oxidised to a limit of eleven silver ions per unit cell. The final structure determined showed eight equivalent silver ions on three-fold axes near the centres of 6-rings (S2^*), and three equivalent cations in the 8-ring planes



dia.6(viii) Stereoview of Ag_{12}A Zeolite Following Subjection to Various Treatments (after Kim and Seff⁶⁴). (Sites Ag1 and Ag3 in the diagram correspond to those denoted S2^* and S1 within the text.)

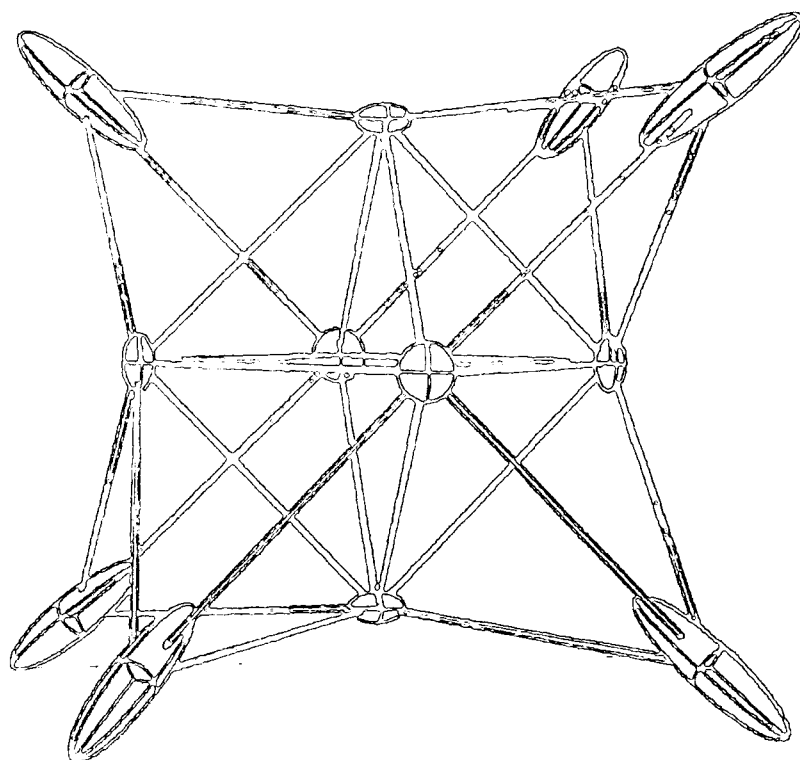
but not at their centres (S1). 0.56 silver atoms were located at the neutral silver atom position (SU) where Ag_6 clusters would be expected to have formed (i.e. 9% of the sodalite units held Ag_6 molecules), whilst the remaining 0.44 atoms were found to have left the crystal, presumably as the oxide. Confirmation of the relative stabilities of the cation position may therefore be seen with the 6-ring and 8-ring sites refilling sequentially, but with the most unfavourable position, the 4-ring, remaining vacant (dia.6(viii)).

b) Structural Investigations of Ethylene Adsorbed on Type A Zeolites

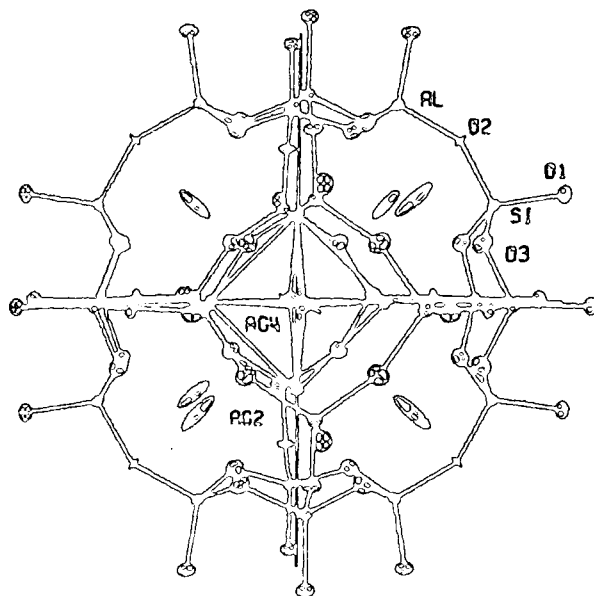
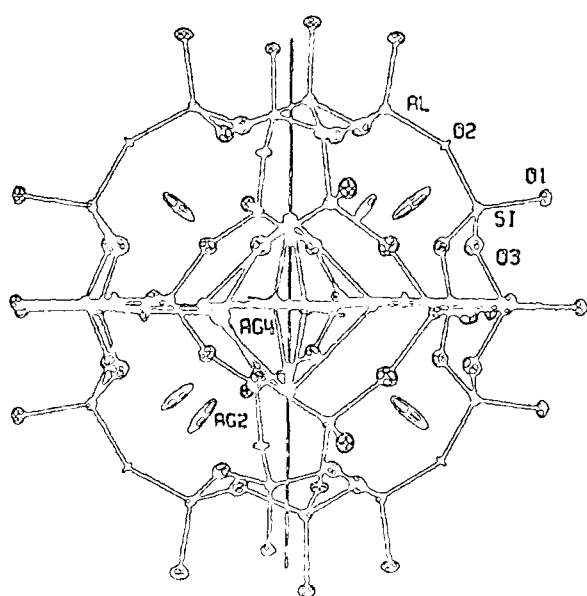
A structural report has been published of ethylene adsorbed or partially decomposed Ag_{12}A zeolite⁸². The single crystal used was dehydrated at 400°C and 5×10^{-6} Torr for 4 days and then exposed to 120 Torr of C_2H_4 gas at 23°C .

The temperature treatment of the crystal caused the formation of approximately 2.76 silver atoms per unit cell, which were believed, by analogy with previous studies⁶²⁻⁴, to result from the reduction of the 4-ring silver ion, and 1.76 of the three 8-ring cations. On the assumption that these had formed neutral Ag_6 molecules, it was calculated that 46% of the unit cells in the crystal must contain Ag_6 molecules in sodalite (β) cavities (at site SU).

Considering initially this 46% of unit cells, sorption of ethylene proved to have little effect on the Ag_6 clusters with their numbers remaining constant, and their co-ordinates scarcely changing. There was, however, a change in the number of co-ordinated 6-ring (S2^*) silver ions, from the anticipated value of eight (for the complex $(\text{Ag}^+)_8(\text{Ag}_6)$) with the formation of the new complex $(\text{Ag}^+)_6(\text{Ag}_6)$ (dias.6(ix) and 6(x)). The removal of two silver ions from co-ordination with Ag_6 thus indicated caused the silver-silver bond length (the edge of the Ag_6 octahedron) to decrease, consistent with the diminished ability of six silver ions to withdraw electron density



dia.6(ix) The Octahedral Ag_6 Molecule (SU) Stabilised by Six Surrounding Silver Ions at S2^* positions (after Kim and Seff⁸²)

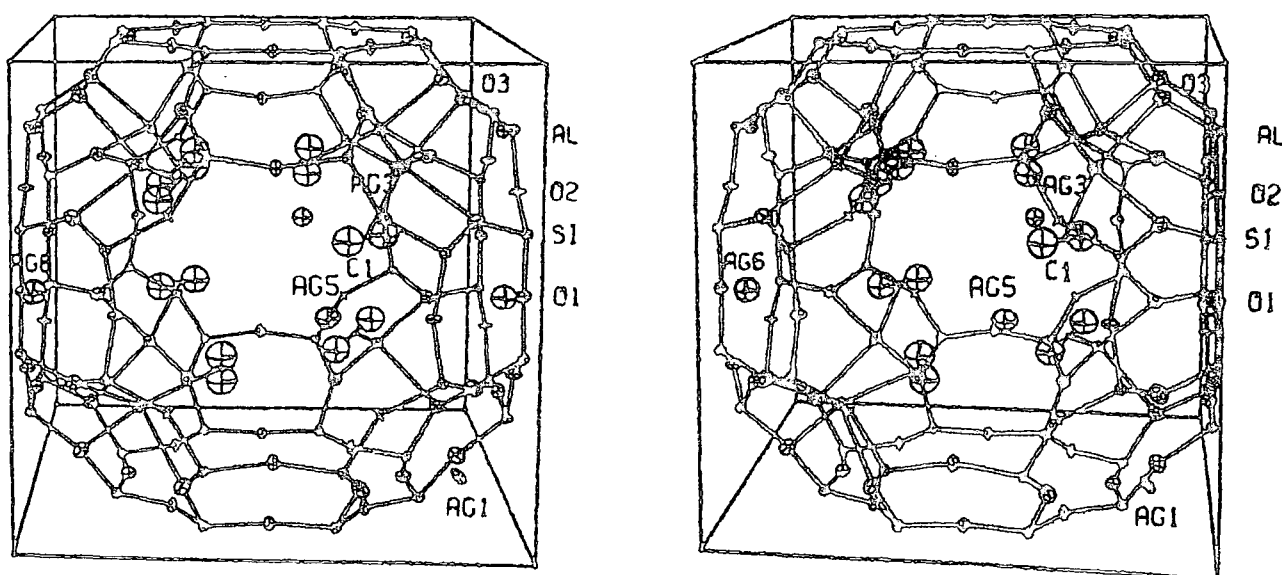


dia.6(x) Stereoview of the Octahedral Ag_6 Molecule Stabilised at the Centre of a Sodalite Unit by Six Surrounding Silver Ions (after Kim and Seff⁸²) (Positions AG2 and AG4 correspond with those denoted in the text S2^* and SU respectively.)

from the Ag_6 cluster. Additionally, the $\text{Ag}-\text{Ag}^+$ distance was seen to shorten as a result of stronger interaction.

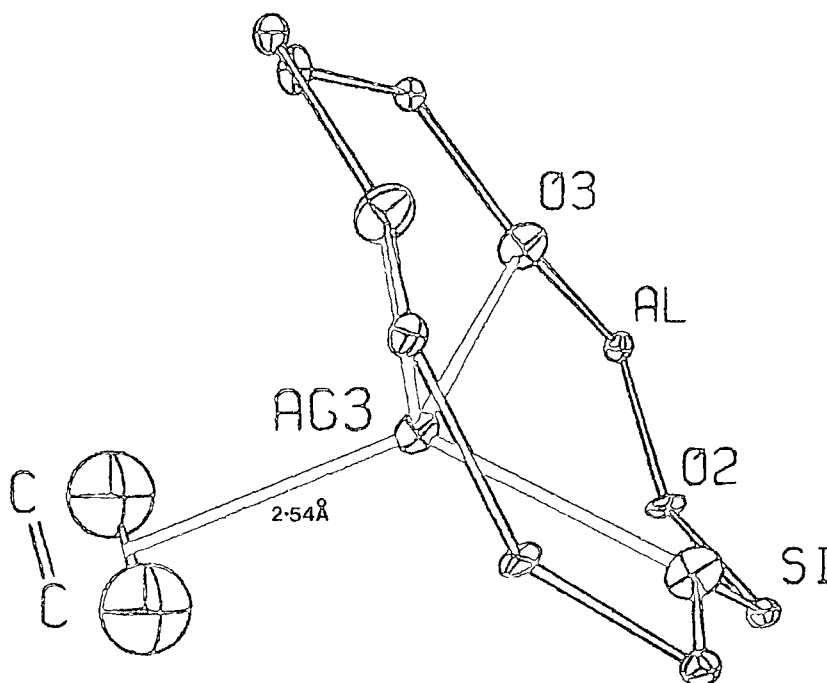
The remaining silver ions located within this unit cell (two) were associated with 8-rings (S1); these were found not to complex with ethylene, in common with the other cations.

In the remaining 54% of unit cells whose sodalite (β) cavities did not contain Ag_6 molecules, one out of eight 6-ring silver ions was observed, upon ethylene adsorption, to recede about $1\text{\AA}$ into the sodalite unit, thereby taking up an $\text{S2}'$ position. No ethylene molecule could be located in co-ordination with this ion, although it was suggested that this might possibly be the result of poor experimental resolution. Conversely, each of the remaining seven 6-ring cations, now protruding $1.2\text{\AA}$ into the α cage (S2^*), was found to form a lateral π complex with one ethylene molecule, thus assuming a tetrahedral configuration (dia.6(xi)).



dia. 6(xi) Stereoview of the Ag_{12} -A-Ethylene Sorption Complex in the Large (α) Cavity (after Kim and Seff⁸²). (Position AG3 corresponds with that denoted S2^* in the text, whilst sites AG5 and AG6 both refer to those denoted S1.)

Both carbon atoms of the complexed ethylene molecule were established as being equivalent (dia.6(xii)), each $2.54\text{\AA}$ from a silver ion and, whilst not accurately determined, the C=C bond length appeared not to be significantly different from that reported for ethylene gas ($1.334\text{\AA}$ ⁸⁵). No significant approach was made by the olefin to the zeolite framework: the smallest C-O distance ($3.76\text{\AA}$) being such that the hydrogen atoms were considered too far (greater than $3.0\text{\AA}$) from the nearest oxide ions to interact (even if C-H ...O were linear).



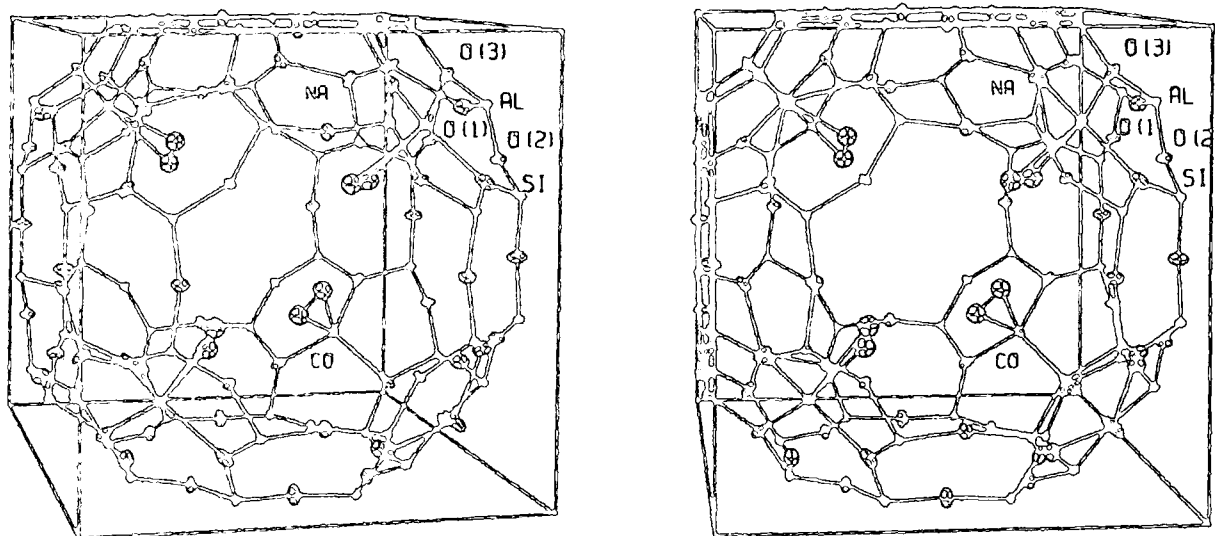
dia.6(xii) The $\text{Ag}(\text{C}_2\text{H}_4)^+$ Complex in the Large (α) Cavity (after Kim and Seff⁸²). (Position AG3 corresponds to that denoted S2^* in the text)

Again, as with the 46% of unit cells whose sodalite cavities contained Ag_6 molecules, an additional two silver ions were located per unit cell positioned within 8-rings (S1). Similarly, these appeared not to be co-ordinated to ethylene.

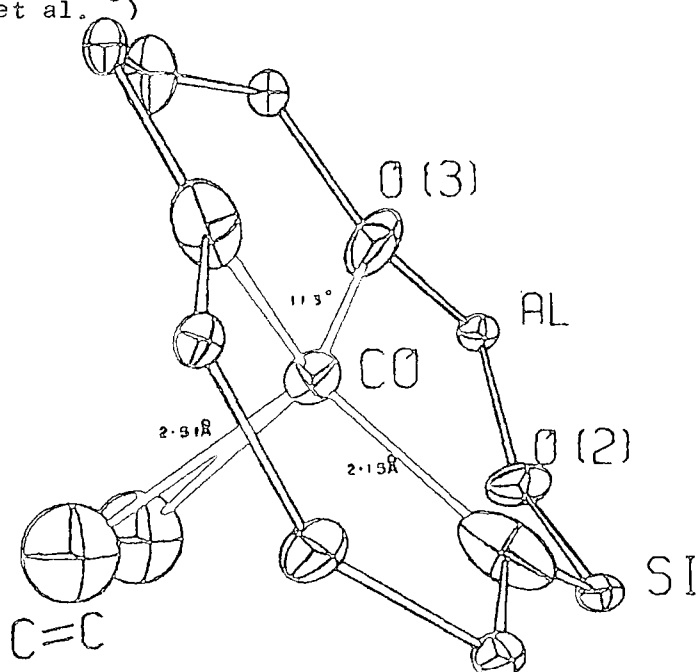
The result, that ethylene does not displace Ag_6 as a ligand to six Ag^+ ions is in contrast to work involving the adsorption of NH_3 on similarly treated Ag_{12}A zeolite in which N_3H_3 and N_3H_5 were formed⁷⁶. According to Kim and Seff⁸² this indicates that for the co-ordination numbers and geometries

involved, the ligand strength of Ag_6 is between those of ethylene and the triazines with respect to Ag^+ .

The crystal structure of the ethylene sorption complex, $\text{Co}_4\text{Na}_4\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 4\text{C}_2\text{H}_4$ ⁸³, has shown one ethylene molecule to bond laterally and symmetrically to each of the four cobalt ions (which occupy 6-ring $\text{S}2^*$ sites), thereby causing these ions to adopt tetrahedral co-ordination (dias.6(xiii) and (xiv)). The cobalt-carbon distance, $2.51\text{\AA}$ (compared with a value of $2.54\text{\AA}$ for C_2H_4 adsorbed on Ag_{12}A zeolite⁸²), was indicative of weak bonding, as was the $\text{C}=\text{C}$ bond length which differed little from that of the gas. Negligible framework-ethylene interaction could be inferred from the distance of the nearest $\text{C}-\text{H} \cdots \text{O}$ approach, $3.4\text{\AA}$.



dia.6(xiii) Stereoview of the $\text{Co}_4\text{Na}_4\text{A}$ -ethylene Sorption Complex (after Riley et al.⁸³)



dia.6(xiv) The $\text{Co}(\text{C}_2\text{H}_4)^{2+}$ Complex in the Large (α) Cavity (after Riley et al.⁸³)

In order to distribute cationic charge more evenly, the sodium ions, positioned at the remaining four 6-ring sites, were found to recess into the β cages (S2'); there was no evidence of co-ordination between these ions and ethylene molecules.

6. Spectroscopic Investigations of Zeolite-Ethylene Systems

No infrared or Raman spectroscopic studies have been undertaken, to our knowledge, of type A zeolite-adsorbed ethylene systems. However, investigations^{28,86,87} which have taken place employing type 13X zeolite, and especially the silver exchanged form, may be expected to afford some insight into the system which is the subject of this work.

Carter et al.⁸⁶ have reported infrared spectra in the region $1300-3300\text{cm}^{-1}$ for ethylene adsorbed on Li^+ , Na^+ , K^+ , Ag^+ , Ca^{2+} , Ba^{2+} and Cd^{2+} exchanged type 13X zeolites. These were activated, prior to adsorption, by evacuation to 5×10^{-6} Torr at 450°C . Spectra were then measured with an over-pressure of 9-11 cm ethylene, and again upon re-evacuation.

In all spectra, the infrared forbidden vibrations, denoted ν_2 (C=C stretch) and ν_3 (CH_2 symmetric deformation) after Herzberg⁸⁸, featured quite strongly, indicating both that olefin interaction with the surface had taken place⁸⁹, and that dissociation was absent. Bonding was shown to be weak by the complete removal of adsorbed gas, upon evacuation at room temperature, from all but the silver and cadmium exchanged forms. For the two latter zeolites stronger interaction was indicated, with the employment of temperatures in excess of 200°C (as well as evacuation) being necessary for the displacement of ethylene from Cd13X zeolite, and by the requirement of still more stringent conditions in the case of Ag13X zeolite.

Calorimetric data from both this work⁸⁶ and previous studies⁹⁰, also displayed this trend with the heat of adsorption for ethylene on Ag13X proving to have the largest value. Furthermore, correlation was found between this data and the shift of ν_2 (C=C stretch)⁸⁸ in the various adsorption

systems to lower frequency as compared with gaseous ethylene (Table 6.5). This was taken to infer that the ethylene-cation interaction took place via the π electrons of the ethylene C=C bond.

Table 6.5 Frequency Shift ($\Delta\nu_2$) and Calorimetric Data for Ethylene Adsorbed on Several Cation Exchanged Type 13X Zeolites^{86,87}

Zeolite	Average Heat of Adsorption kcal mol ⁻¹	$\Delta\nu_2$ [*] cm ⁻¹	Desorption Data (from Infrared Spectra)
NaX	8.6 ^{**}	-10 [*]	Removed by evacuation at room temperature
CdX	14.9	-29 [*]	Removed by evacuation at 200°C
AgX	18.1	-45 [*]	Not removed by evacuation at 200°C

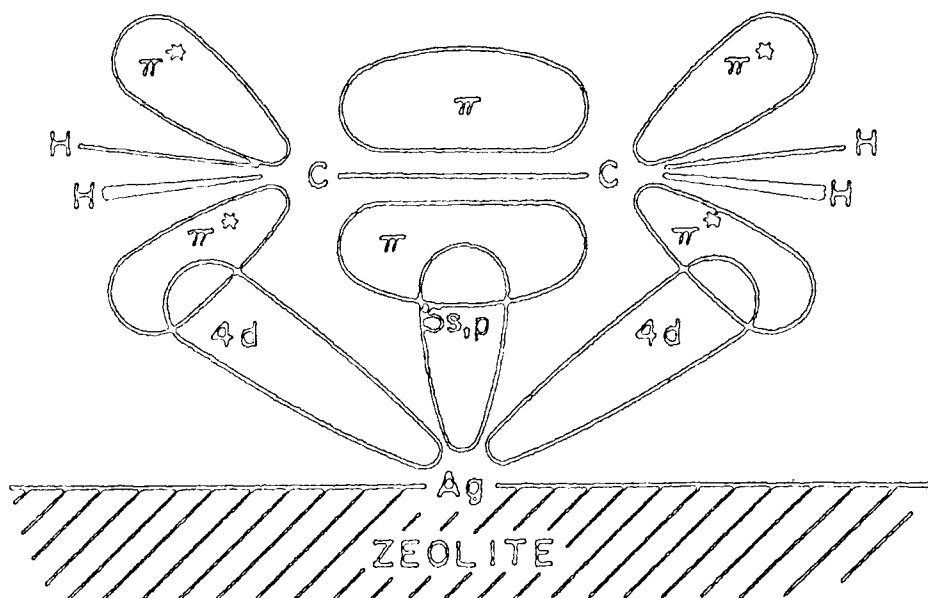
^{*} Shift in ν_2 relative to frequency for gaseous ethylene (1623cm⁻¹)⁸⁸

^{*} Data for zeolites in contact with gaseous ethylene

^{**} In order to shed insight upon the system which is the concern of this chapter, reference values for ethylene adsorbed on sodium and calcium exchanged type A zeolites have been reported as 10 kcal mol⁻¹ ⁹¹ and 8.0-9.7 kcal mol⁻¹ ⁹² respectively.

The relative orientation of the dipole moment change with respect to the surface appeared to influence the band shape of ethylene vibrations in those zeolites exchanged with cations other than silver. Vibrations with changes perpendicular to the surface (ν_2 , ν_3) were found to be narrow, whilst that involving a dipole moment change parallel to the surface (antisymmetric CH₂ deformation: ν_{12} ⁸⁸) proved to be broad. This latter fact was explained by the suggestion that rotation of the ethylene molecule took place (about an axis projected from the cation and passing through the centre of the C=C band) causing modulation and hence band widening. Conversely, in the case of the silver exchanged zeolite, the ν_{12} vibration broadened very little. It was therefore proposed that in this system the stronger bonding, implied from the spectroscopic and calorimetric data, prevented free rotation, and instead gave rise to a torsional mode.

A bonding scheme^{86,87} may therefore be put forward for silver-ethylene interaction in which there is overlap of the olefin π orbitals with either a 5s orbital or a 5sp hybrid orbital of the cation to form a σ -band. (The use of a hybridised orbital appears the more likely possibility as this would continue to allow interaction of the cation with the framework oxygen atoms without the introduction of new spatial and angular restrictions.) Although a similar mechanism is probable in the other adsorption systems, this scheme may be taken a stage further in the case of silver, so that back-donation of electron density takes place from filled silver 4d orbitals into the vacant π^* orbitals of ethylene according to the Chatt-Dewar-Duncanson model.^{93,94} As the silver ion's interaction with the framework is partly covalent, a necessary consequence is that its d orbitals are fixed in space (dia.6(xv)).



dia.6(xv) The Spatial Arrangements of Orbitals Involved in the Bonding Between Silver and Ethylene (after Yates et al.^{86,87}).

It may thus be seen that attempted olefin rotation involves bond breaking.

In the Ag13X-ethylene system alone, a shoulder was found to the low frequency side of the vibration at 1320cm^{-1} assigned to ν_3 (the CH_2 symmetric deformation⁸⁸). Whilst evacuation at room temperature improved resolution and made apparent two discrete bands at 1318cm^{-1} and 1310cm^{-1} , further pumping at 100°C caused the 1318cm^{-1} frequency to disappear. It was thus proposed that these observations might be indicative of two adsorbed ethylene species, and in order to test this conclusion volumetric and gravimetric investigations²⁸ were undertaken. These showed the presence of two adsorption sites within the zeolite (dia.6(iii)). The first position (type III), to which the less easily removed ethylene bonded, was demonstrated to be a cation situated inside a 4-ring of a sodalite octahedron which formed the wall of a supercage; there were 4.4 of these sites occupied by ethylene per supercage. The second position (type II), to which the more weakly bonded ethylene attached, corresponded to a silver ion located within a 6-ring of a sodalite unit: the occupancy of these sites numbered 3.6 ethylene molecules per supercage. The differing bond strengths of the two positions may therefore be rationalised by the fact that the 6-ring cations do not protrude into the α cage as much as do cations in the 4-rings, and hence do not allow as close an approach by ethylene. (It should be noted that structural reports²⁴⁻⁷ indicate yet another cation location within the hexagonal prisms (I); however, this is not suitable for bonding to adsorbed species.)

^1H NMR studies^{95,96} have been carried out of ethylene interactions with Li^+ , K^+ , Ag^+ , Cd^{2+} and Ba^{2+} exchanged type 13X zeolites using both chemical shift and wideline techniques.

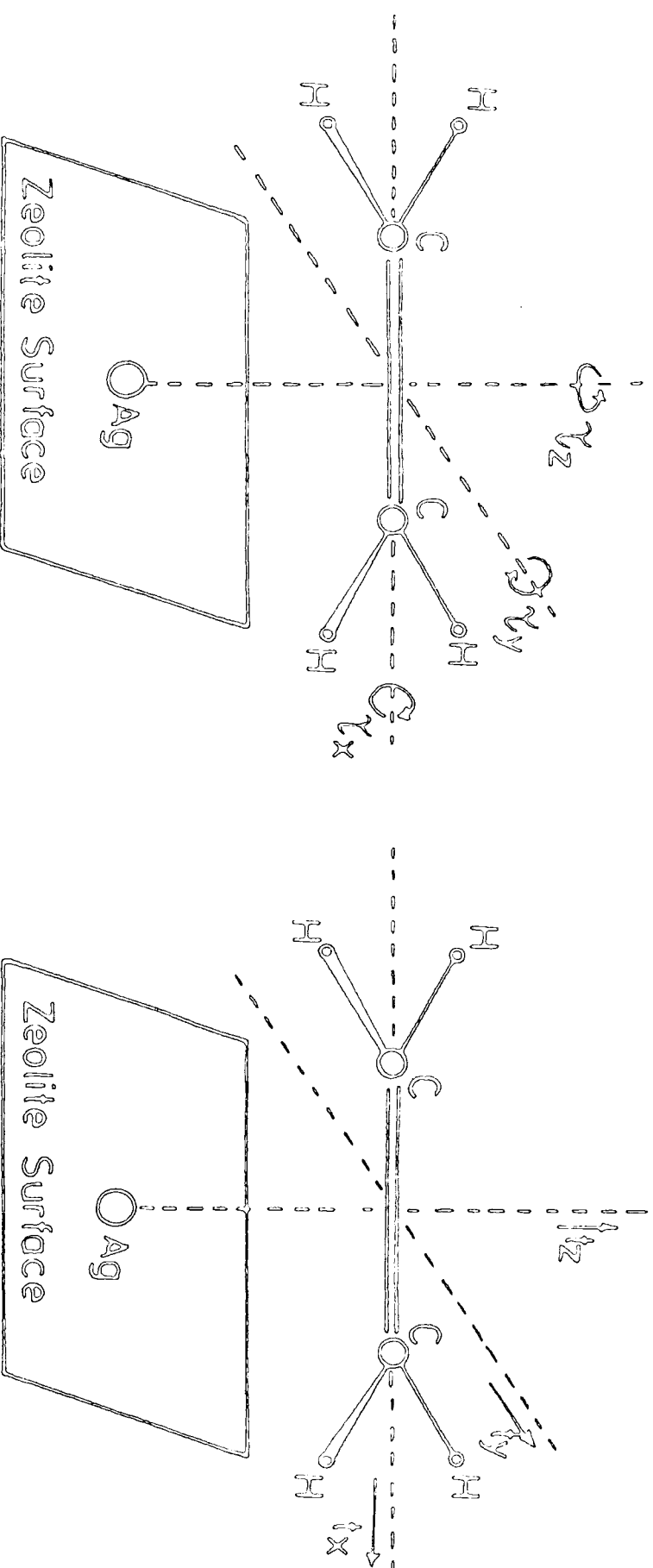
In all cases an overpressure of 10cm of the olefin was employed corresponding to the high coverage case of Yates et al.^{28,86,87} For zeolites other than the silver-exchanged form, a simple line-width broadening relation was observed as temperature was lowered from room temperature to 77K, interpreted as showing ethylene rotation slowing down.

However, with Ag13X zeolite, broadening took place to 178K, at which temperature ethylene re-orientation was quenched. Obviously there is apparent discrepancy here between NMR and infrared data concerning the rotation/non rotation of ethylene adsorbed on Ag13X zeolite above 178K. However, this may be explained by the fact that the time scale of the NMR measurements (ca. 3×10^{-7} s) is between five and six orders of magnitude longer than the period of the infrared radiation involved. Hence events occurring on an infrared time scale appear static when viewed by NMR^{89,95}

Mossbauer spectroscopy^{97,98} has been used to investigate ethylene adsorption on a ferrous exchanged type A zeolite ($\text{Fe}_{2.66} \text{Na}_{6.68} \text{Al}_2 \text{O}_2^+$). As in the studies of the alkali metal exchanged forms of type 13X zeolite described above, free rotation of the olefin was observed, in this case about both the sodium and the ferrous ions (the latter of which were located in the 6-rings of the α cage (S2^*)). Bonding was weak, enabling desorption upon evacuation for 5 minutes, and a heat of adsorption of $8.4\text{--}10 \text{ kcal mol}^{-1}$, was estimated for the ferrous ion-ethylene interaction.

Of immediate relevance to the work of this thesis are the previous INS investigations which have been carried out on the Ag13X-ethylene system³⁻⁵. Zeolite samples, prepared by evacuation to 5×10^{-6} Torr at 450°C , had ethylene (C_2H_4 and C_2D_4) adsorbed on them to a pressure of 500 Torr. Spectra were then measured at this over-pressure, considered equivalent to the high coverage case of Yates^{28,87}, where 8 ethylene molecules were located per supercage occupying sites II and III (dia.6(iii)). Subsequently, the samples were re-evacuated for 30 minutes at room temperature, and spectra were observed corresponding to the low coverage case (where 4.4 ethylene molecules had been found per supercage situated at type III sites). An additional experiment employing trans- $\text{C}_2\text{H}_2\text{D}_2$ was also carried out, but in this case only the low coverage state was investigated.

† " 0.9NaAlO_2 " in the formula of the ferrous-exchanged type A zeolite refers to NaAlO_2 occluded within the sodalite units.



dia. 6 (xvi). The three hindered rotations, γ_x , γ_y (antisymmetric stretch) and γ_z , and the three hindered translations, τ_x , τ_y and τ_z (symmetric stretch), of ethylene relative to the zeolite surface.

TABLE 6.6 Reported INS Vibrational Frequencies (cm^{-1}) for C_2H_4 , $\text{C}_2\text{H}_2\text{D}_2$ and C_2D_2 Adsorbed on Ag13X Zeolite at Low and High Coverages³⁻⁵

	C_2H_4	C_2D_4			$\text{C}_2\text{H}_2\text{D}_2$				Assignment
	Observed	Predicted ^a	Predicted ^b	Observed	Predicted ^a	Predicted ^{b*}	Predicted ^{b*}	Observed	
Low Coverage (T-O-F)	39.5 $\pm$ 1.8 ~80	32.5 $\pm$ 1.5 ~75	32.8 $\pm$ 1.5 ~75	35 $\pm$ 1.8 75 $\pm$ 5	Data not available				τ_z t_z
High Coverage (T-O-F)	22 56 ~80sh	Data not available			Data not available				τ_z τ_x t_z
High and Low Coverages ^f (BFD)	258 $\pm$ 21 418 $\pm$ 28	220.8 $\pm$ 18 295.5 $\pm$ 20	221.8 $\pm$ 18 298.8 $\pm$ 20	199 $\pm$ 20 276 $\pm$ 20	235 $\pm$ 19 353.6 $\pm$ 23.7	235 $\pm$ 19 352.9 $\pm$ 23.6	235 $\pm$ 19 349.9 $\pm$ 23.4	270 $\pm$ 14 338 $\pm$ 14 380 $\pm$ 14	τ_y τ_x

^a Calculated using gas geometry.⁹⁹
^b Calculated using Zeise's salt structure.¹⁰⁰
^c There are two configurations in this case because the C-D bonds are not all equivalent in Zeise's salt.⁵
^d In the case of $\text{C}_2\text{H}_2\text{D}_2$, Low coverage data only was obtained.

From measurements of the Full Width at Half Maximum (FWHM) of the elastic peak, it was established, in accordance with the work of Yates et al.^{86,87}, that the ethylene molecule was not freely rotating. Analysis of the inelastic part of the spectrum was then carried out applying the intensity relations and deuteration shifts predicted from two models of the adsorbed ethylene molecule: (i) a planar (gaseous) configuration⁹⁹, and (ii) a non-planar (Zeise's salt) structure¹⁰⁰ in which the hydrogen atoms were bent out of the plane and away from the cation. As a result, three frequencies were assigned corresponding to the torsional modes τ_x , τ_y and τ_z of the ethylene relative to the silver cation, and a fourth identified as a hindered translation (dia.6(xvi) and Table 6.6). In the high coverage case only τ_z , the torsional mode of the ethylene molecule about an axis projected from the cation through the centre of the C=C bond, was considered as being split into contributions corresponding to the in-phase and out-of-phase movements of ethylene molecules on neighbouring sites II and III. Using the observed frequencies of τ_z at both coverages, barriers to rotation were calculated.

Additional studies were reported of ethylene (C_2H_4) adsorbed to 400 Torr on Na13X zeolite, which had been prepared analogously to the silver exchanged samples. These results were inconclusive because of the poor resolution attained, although quasi-elastic broadening did indicate that ethylene diffusive motion was occurring in this instance, again in agreement with the findings of Yates et al.^{86,87}

B. Experimental

$Ag_{12}A$ zeolite was prepared from $Na_{12}A$ (BDH Chemicals Ltd.) by repeated ion-exchange employing a 0.2M solution of $AgNO_3$ (containing the exact equivalence of the sodium ions to be exchanged) and a temperature of 25°C¹⁴. The sample was washed thoroughly to remove excess silver ions, and was then degassed to a pressure below 10^{-5} Torr at 450°C.

Upon dehydration, the zeolite powder was transferred, under vacuum, into an aluminium sample cell (Chapter III), and the INS spectrum of the cell plus zeolite measured for use as a background. Ethylene gas, either cylinder C_2H_4 (> 99.9% purity) or C_2D_4 supplied by Merck, Sharp and Dohme Ltd. (99 atom % D), was then admitted into the sample cell (at room temperature) via a glass breaker seal, and adsorbed at an overpressure of approximately 450 Torr. Upon adsorption being completed, the cell and zeolite were evacuated to 100 Torr and sealed off from the vacuum line. After the High Overpressure INS spectrum had been recorded, the cell was re-attached to the vacuum line by means of a second glass breaker seal, and the sample re-evacuated for about 30 minutes at room temperature. The Low Overpressure INS spectrum was then measured.

The experimental details relating to the recording of the INS spectra of the $Ag_{12}A$ -ethylene adsorption system are summarised in Table 6.7.

Table 6.7 INS Spectra Measured of the $Ag_{12}A$ Zeolite - ethylene Adsorption System

Gas	Residual Overpressure of Gas	Instrument	Temperature
C_2H_4	100 Torr	6H	116K
C_2H_4	100 Torr	IN4 [*]	5K
C_2H_4	0.01 Torr	6H	153K
C_2H_4	0.01 Torr	IN4 [*]	5K
C_2H_4	100 Torr	Dido BFD	liq. N_2
C_2H_4	0.003 Torr	Dido BFD	liq. N_2
C_2D_4	100 Torr	4H5/6H	118K/138K
C_2D_4	70 Torr	IN4 [∗]	5K
C_2D_4	0.003 Torr	4H5	118K
C_2D_4	0.01 Torr	IN4 [∗]	5K
C_2D_4	100 Torr	Pluto BFD	liq. N_2
C_2D_4	0.003 Torr	Pluto BFD	liq. N_2

* Incident energies of 12.5 and 22.9 meV employed

∗ Incident energies of 12.6 and 22.7 meV employed

Except where stated to the contrary, all spectra included in this chapter have had a background corresponding to the sample cell plus dehydrated Ag_{12}A zeolite subtracted.

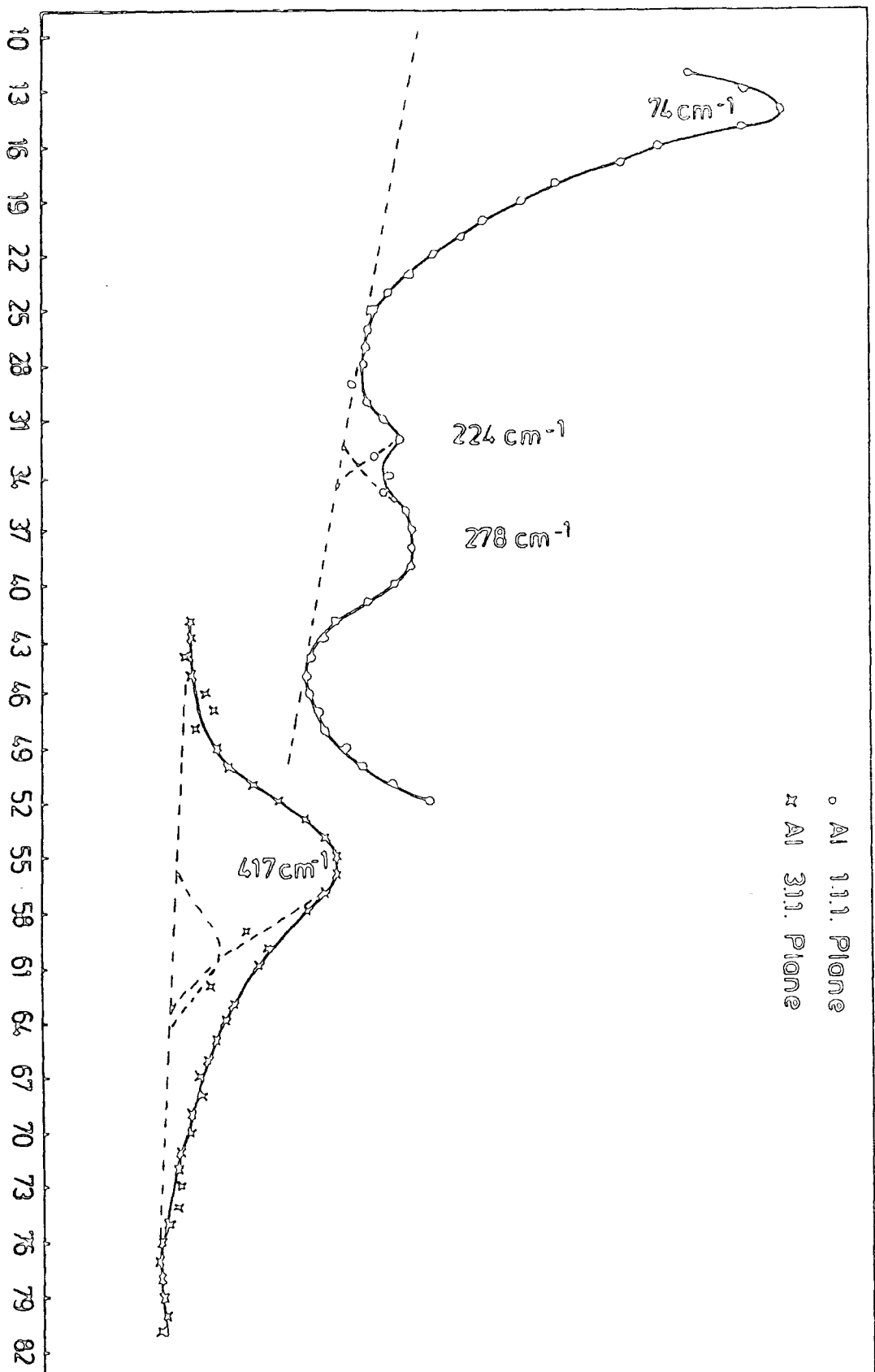
Peak resolution and the measurement of INS intensities have been carried out using a Du Pont Curve Resolver. Assuming the backgrounds indicated ----- on the spectra, Gaussians have been placed, in the first instance at observed transitions, but where necessary at energies indicated from the form of the total bandshape. The peak areas thus generated have been varied to achieve a "best fit" with the overall band profile, and the resultant intensity ratio measured. This has then been compared (directly in the case of ratios obtained from BFD spectra, but after suitable correction for " Q^2 " and frequency in the case of values derived from T-O-F data (Chapter II)) with the intensity ratio predicted on the basis of the suggested assignments.

C. Discussion of Results

The BFD spectra obtained for the Ag_{12}A zeolite-ethylene adsorption system are shown in dias.6(xvii) and 6(xix) (High Overpressure) and dias.6(xxi) and 6(xxii) (Low Overpressure), whilst the analogous T-O-F data are displayed in dias.6(xxiii)-6(xxii) and dias.6(xxxiii)-6(xxxix) respectively. The spectroscopic frequencies thus derived are summarised in Tables 6.8 and 6.10.

INS spectra of Zeise's salt and dimer^{4,5} show the two lowest frequency internal ethylene vibrations (the CH_2 rocking modes) to occur at $718\text{-}20\text{cm}^{-1}$ (ν_{17}^{102}) and $820\text{-}40\text{cm}^{-1}$ (ν_{23}^{102}). It is to be expected that in weaker complexation with silver rather than platinum, these will shift to higher frequency. Indeed, for gaseous ethylene, the equivalent rocking vibrations are located at 810cm^{-1} (ν_{10}) and 1236cm^{-1} (ν_6)¹⁰³. It may thus be anticipated with some certainty that the lowest frequency intramolecular mode of C_2H_4 complexed within Ag_{12}A zeolite will be found at $\text{ca.}800\text{cm}^{-1}$,

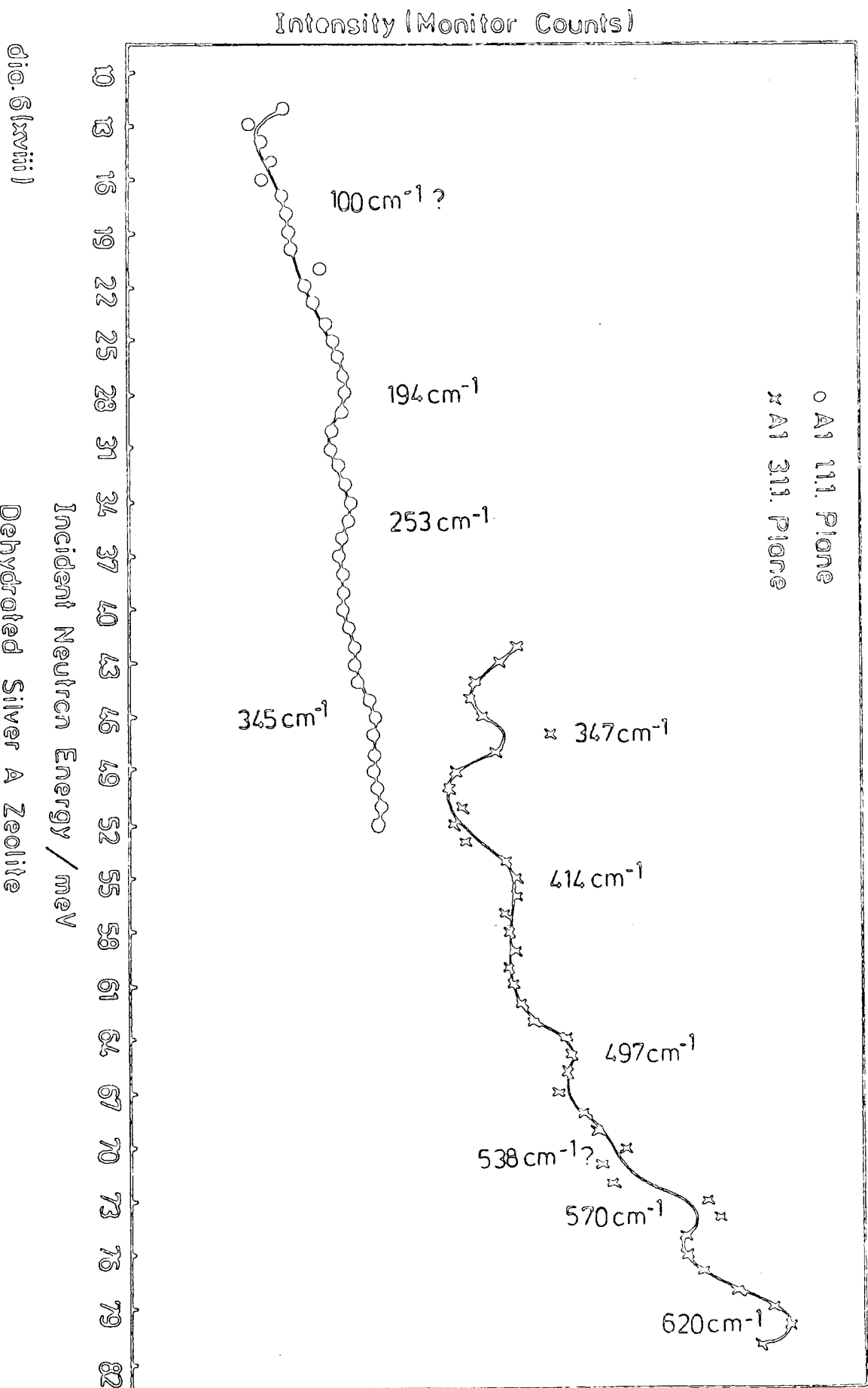
Intensity (Time Normalised Counts)



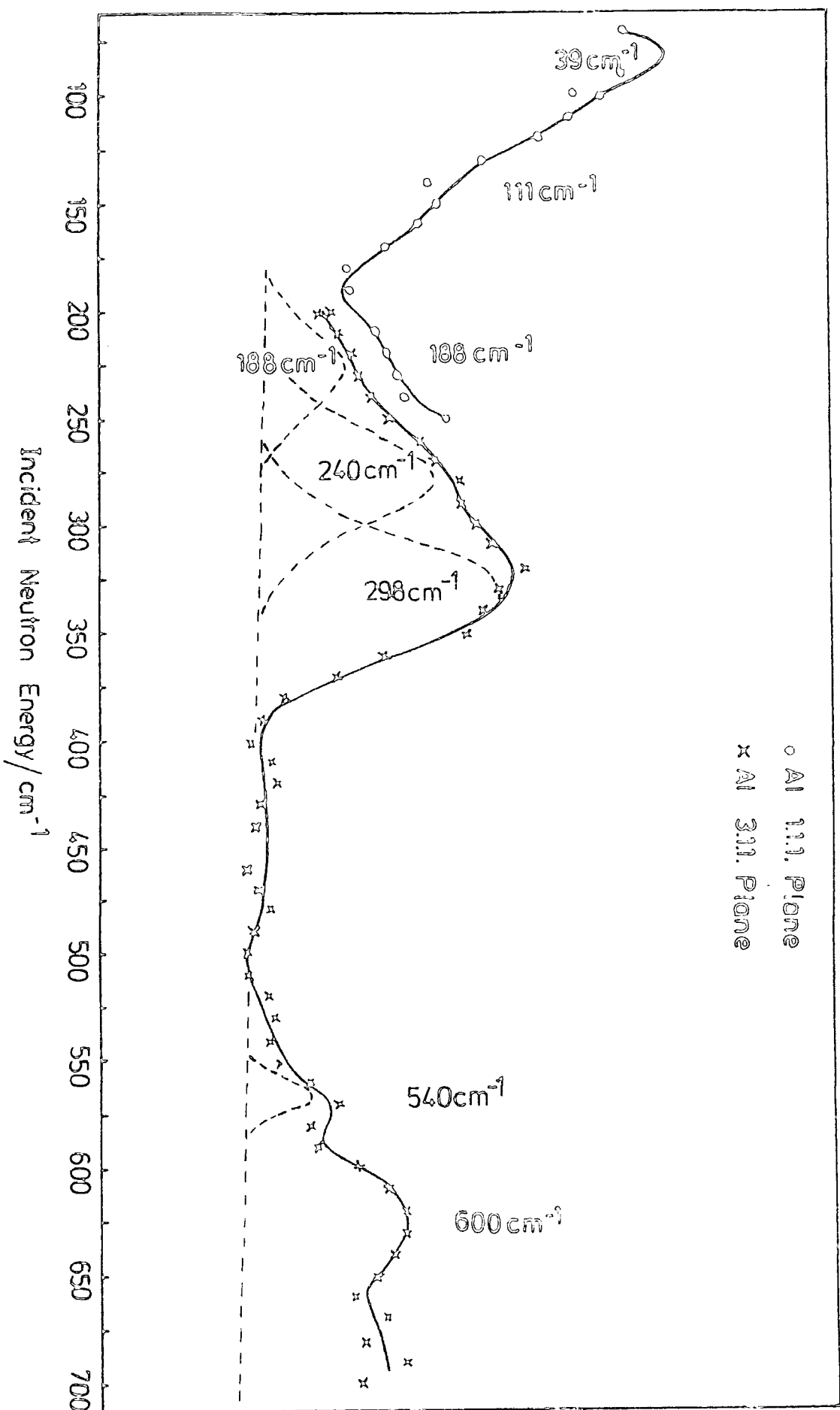
doi.61xvii)

Ethylene adsorbed on Silver A Zeolite at a pressure of 100 Torr

Dido BFD Spectrometer : Liquid Nitrogen Temperature.



Intensity (Monitor Counts)



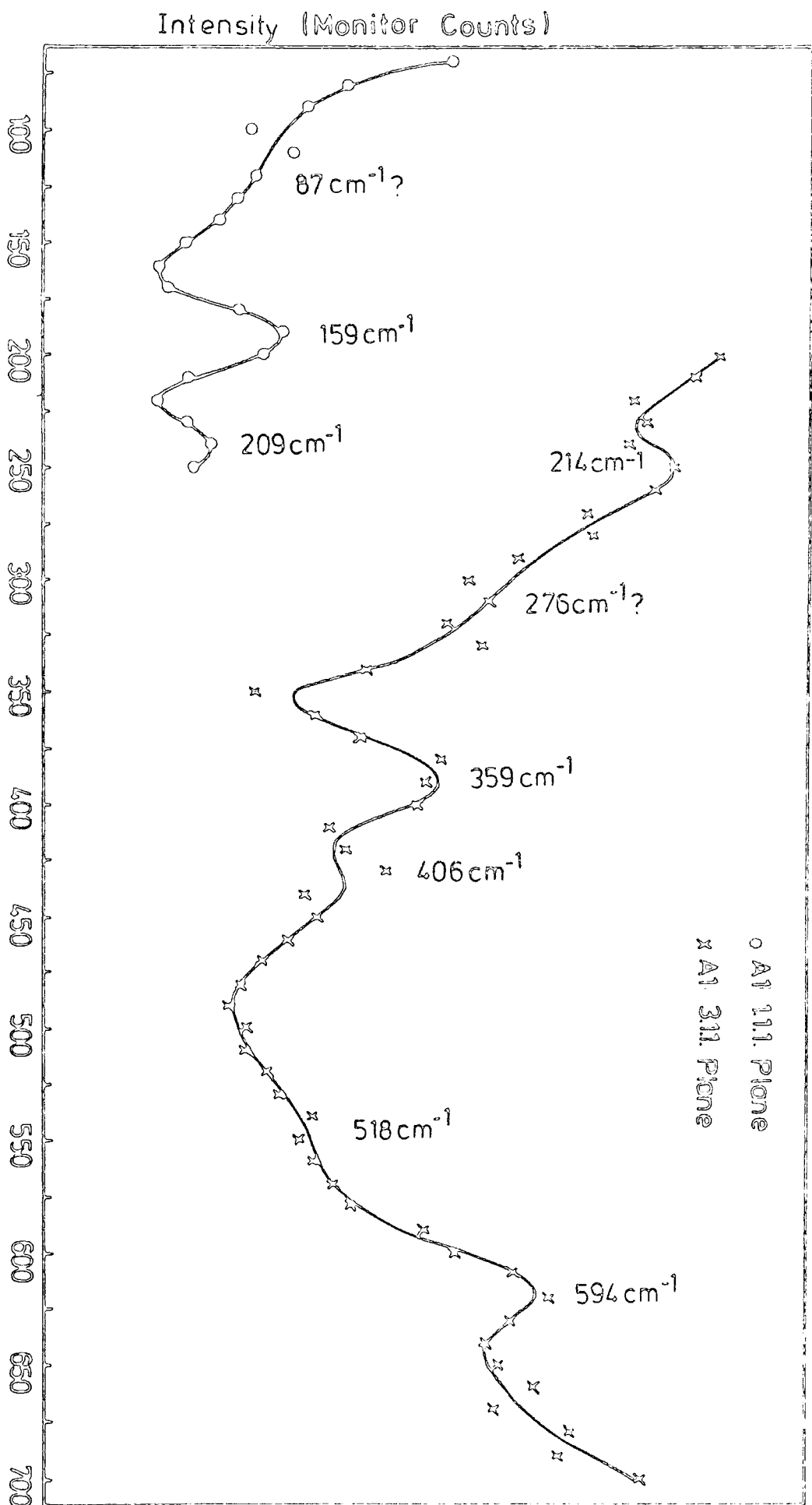
dia (xix) Perdeutero - ethylene adsorbed on Silver A Zeolite at a pressure of 100 Torr
Puho BFD Spectrometer : Liquid Nitrogen temperature

Pluto BFD Spectrometer : Liquid Nitrogen Temperature

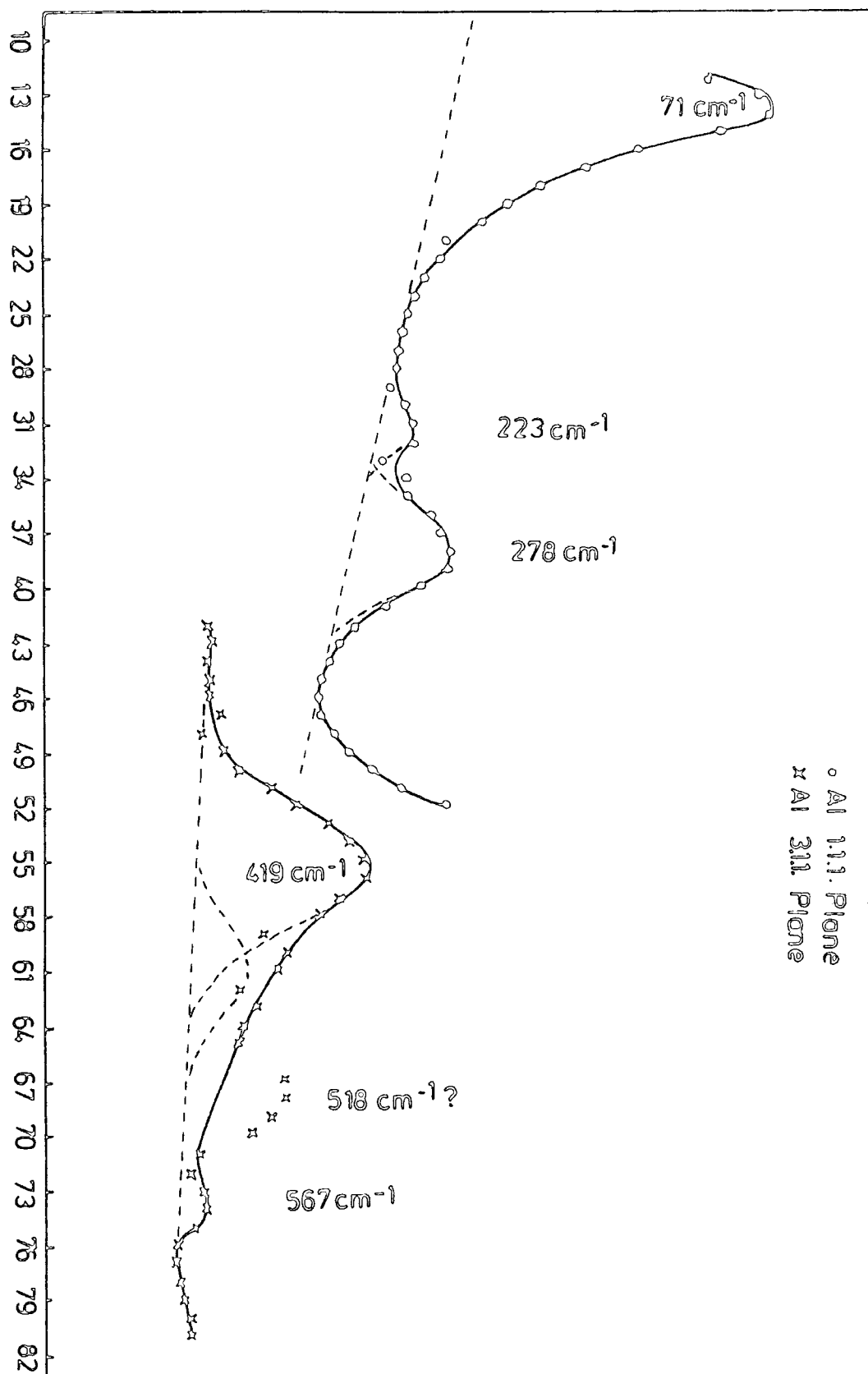
Dehydrated Silver A Zeolite

Incident Neutron Energy / cm^{-1}

dia. 6 (xx)



Intensity (Time Normalised Counts)

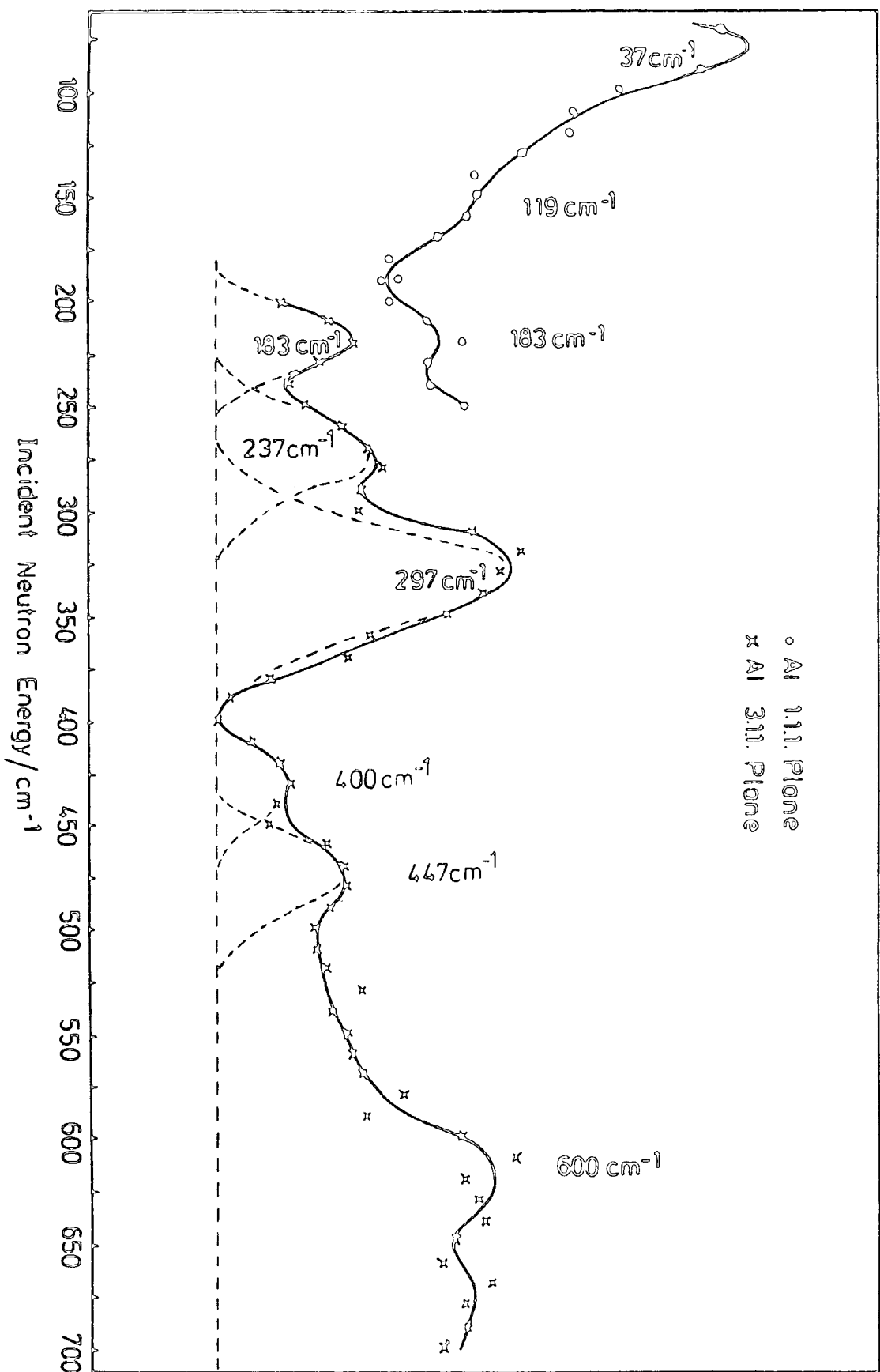


dia. 6(xxi)

Ethylene adsorbed on Silver A Zeolite at a pressure of 3×10^{-3} Torr

Dido BFD Spectrometer : Liquid Nitrogen temperature

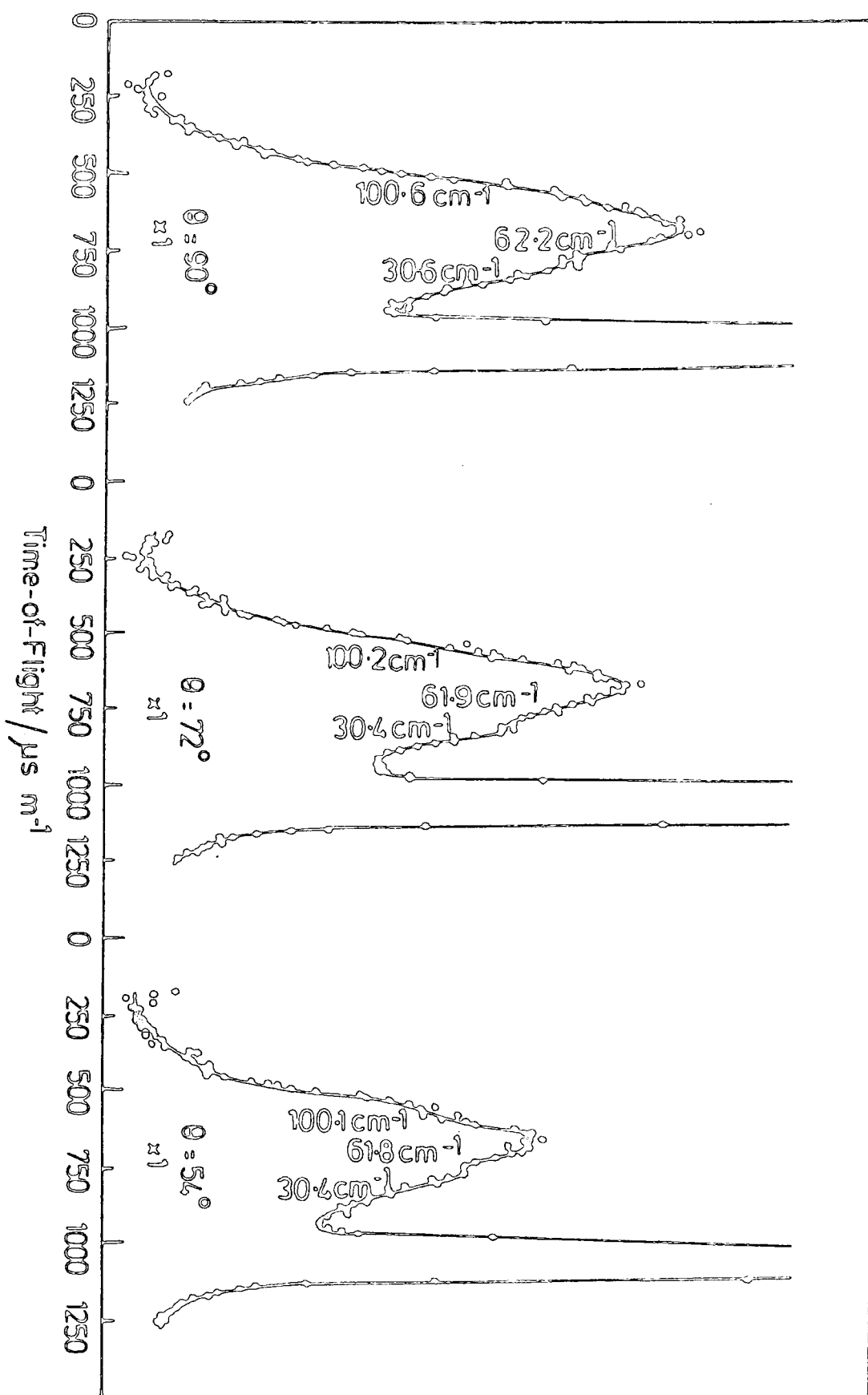
Intensity (Monitor Counts)



dia. 61x11) Perdeutero - ethylene adsorbed on Silver A Zeolite at a pressure of 3×10^{-3} Torr.

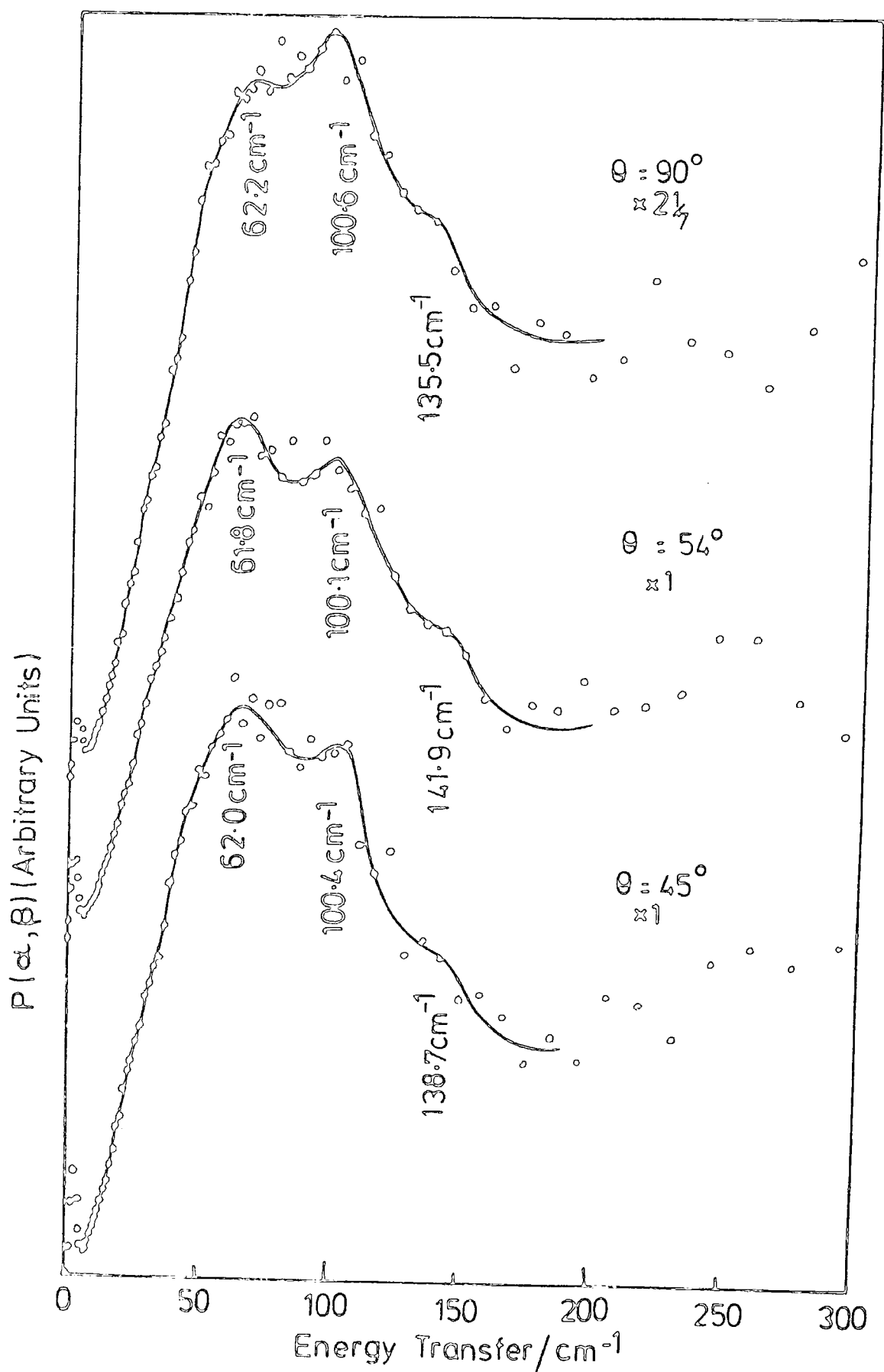
Puio BFD Spectrometer : Liquid Nitrogen temperature

Intensity (Arbitrary Units)



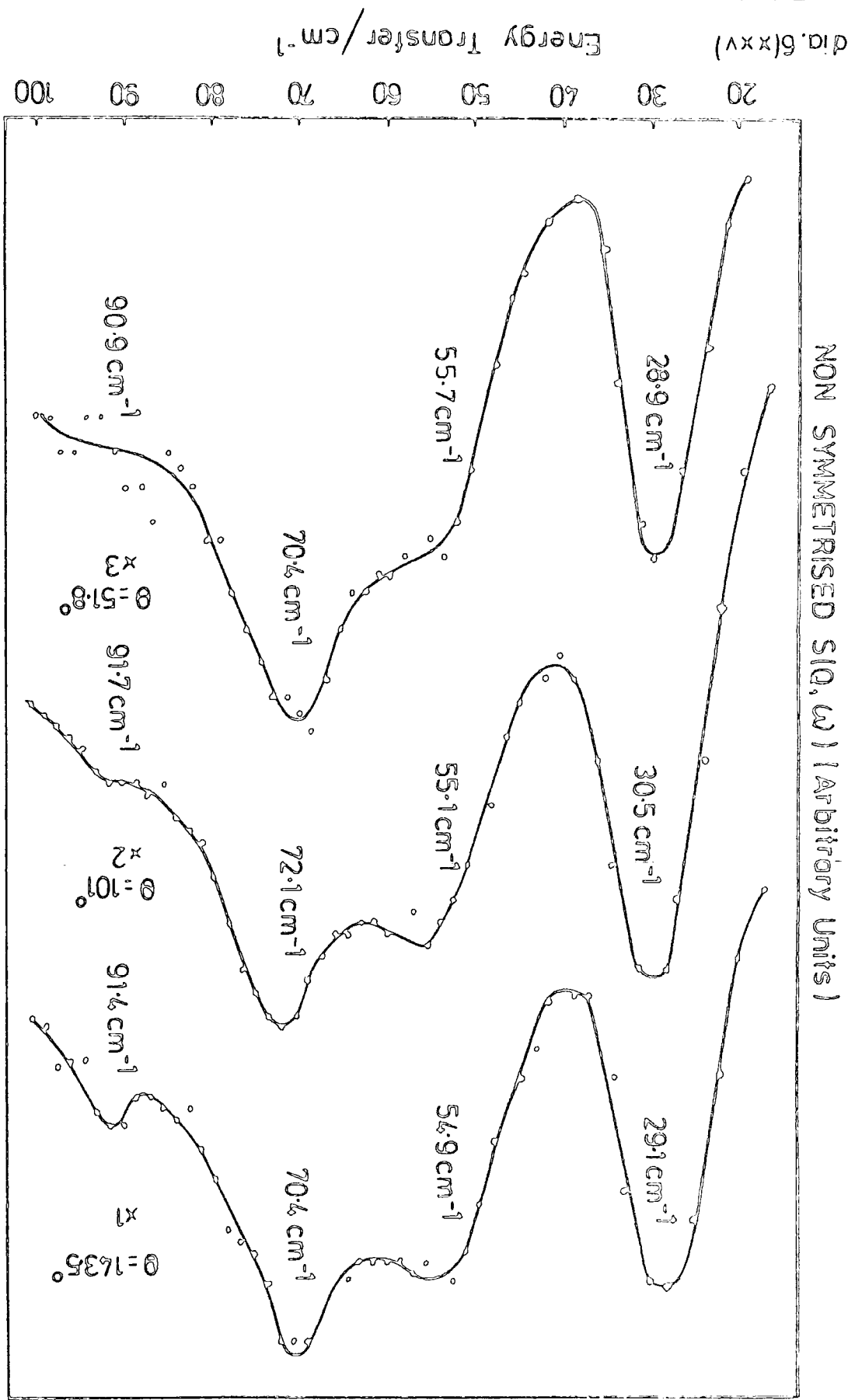
dia. 61xxiii) Ethylene adsorbed on Silver A Zeolite at a pressure of 100 Torr (116 K)

6H Time-of-Flight Spectrometer.



dia. 6(xxiv) Ethylene adsorbed on Silver A Zeolite at a pressure of 100 Torr (116 K)

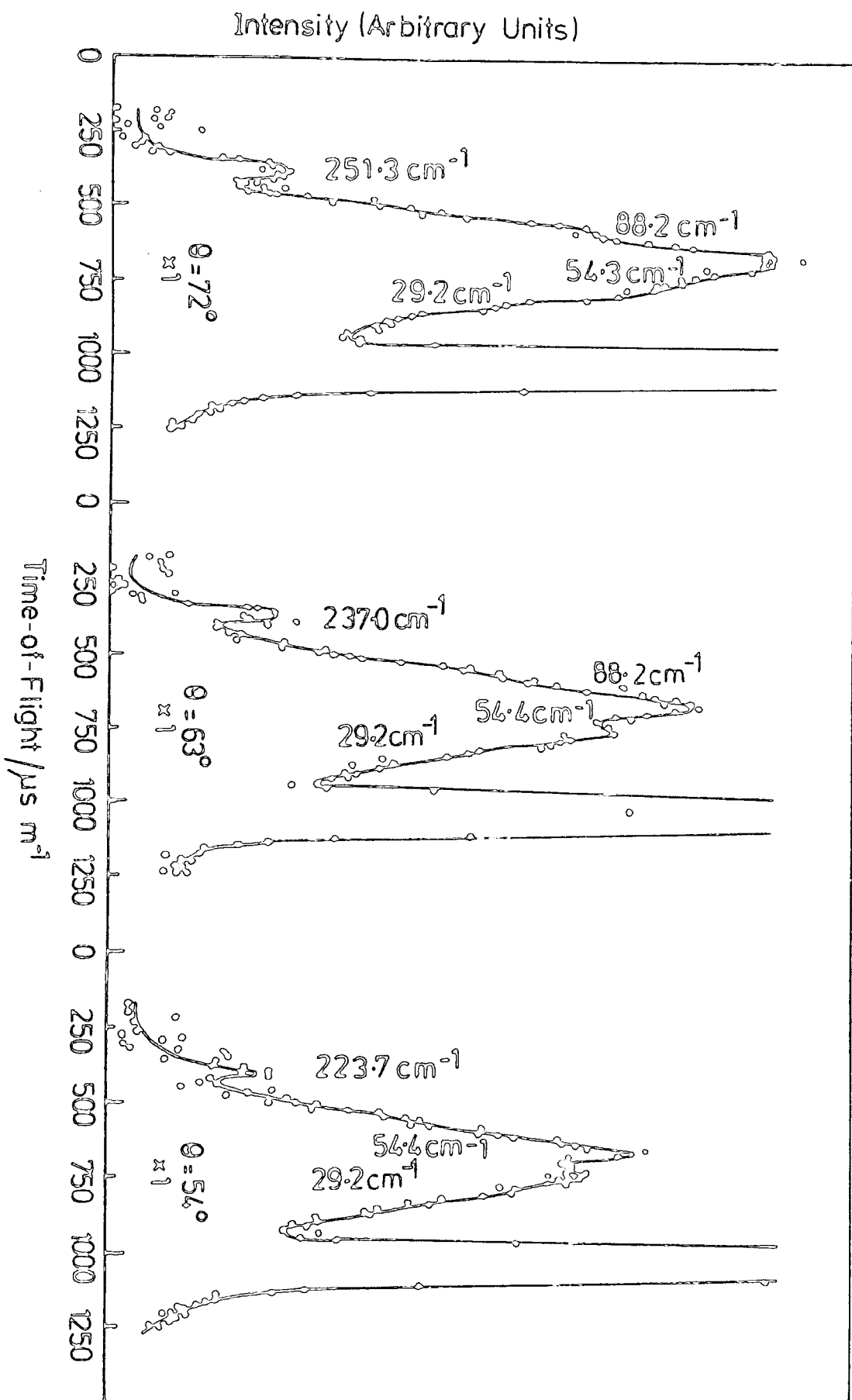
6H Time-of-Flight Spectrometer

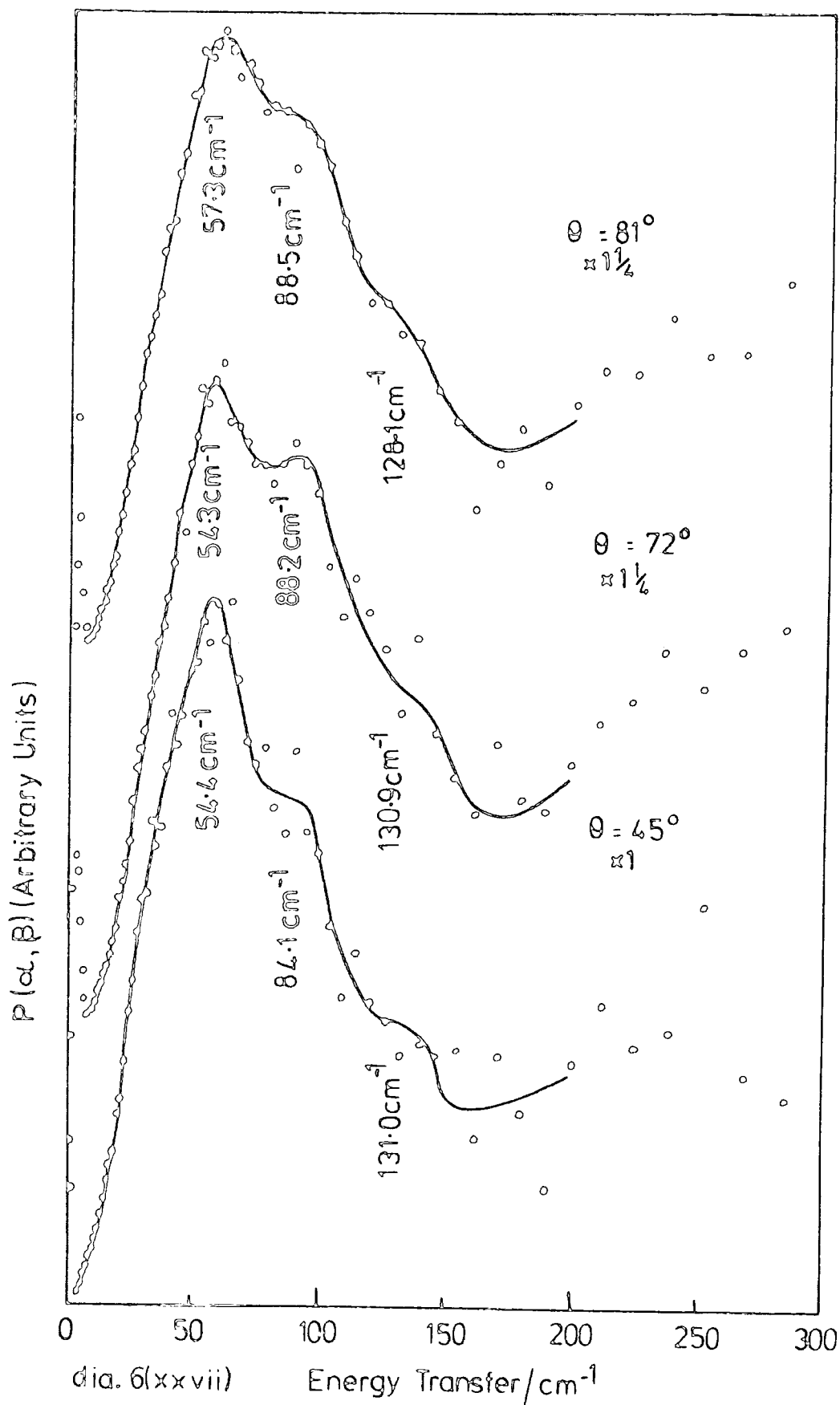


Ethylene adsorbed on Silver A Zeolite at a pressure of 100 Torr (15K)

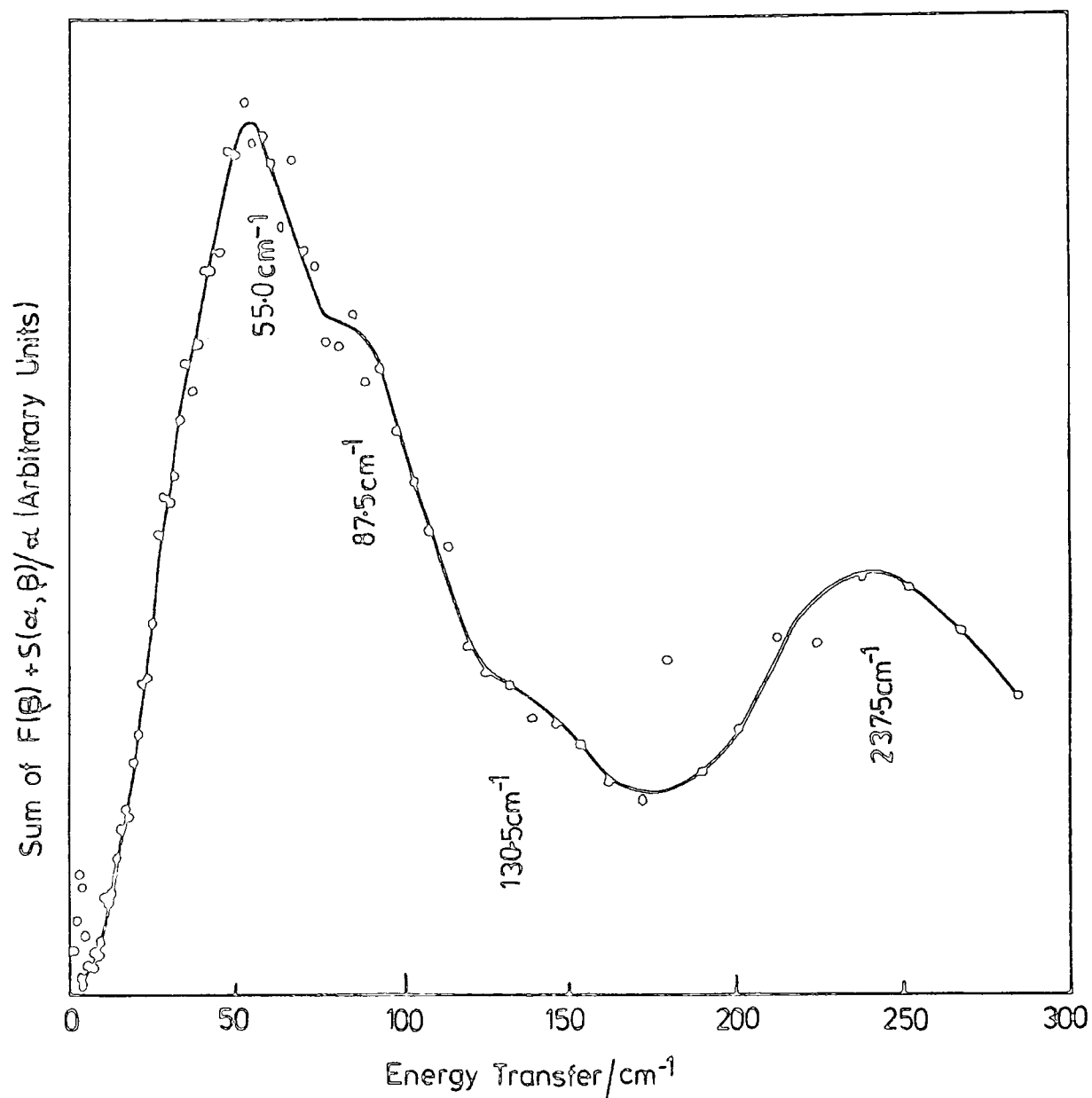
IN4 Time-of-Flight Spectrometer (22.9 meV incident energy)

dia. 6(xvii) Perdeutero-ethylene adsorbed on Silver A Zeolite at a pressure of 100 Torr (138 K)
6H Time-of-Flight Spectrometer.





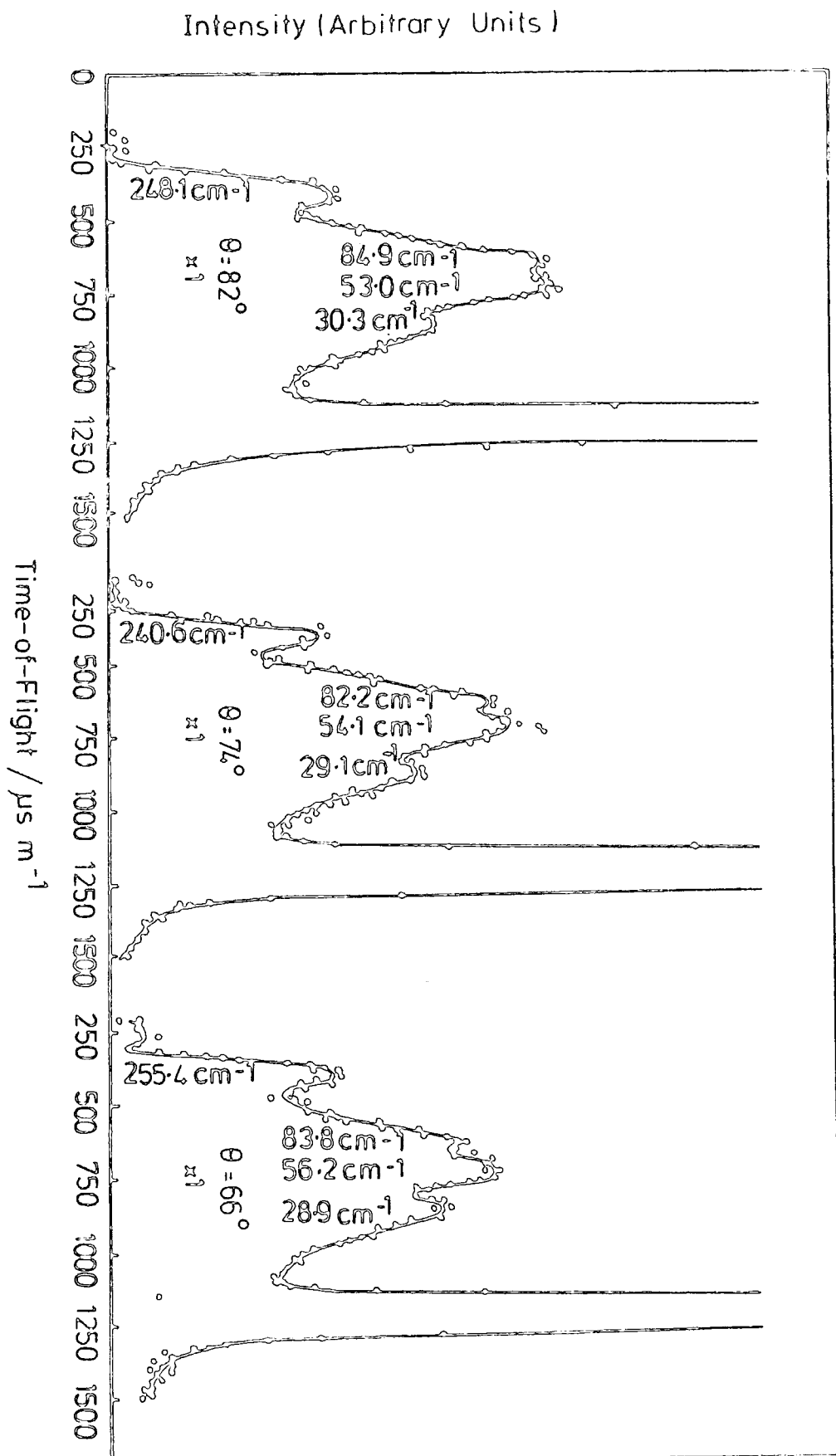
Perdeutero-ethylene adsorbed on Silver A Zeolite
 at a pressure of 100 Torr (138 K)
 6H Time-of-Flight Spectrometer.

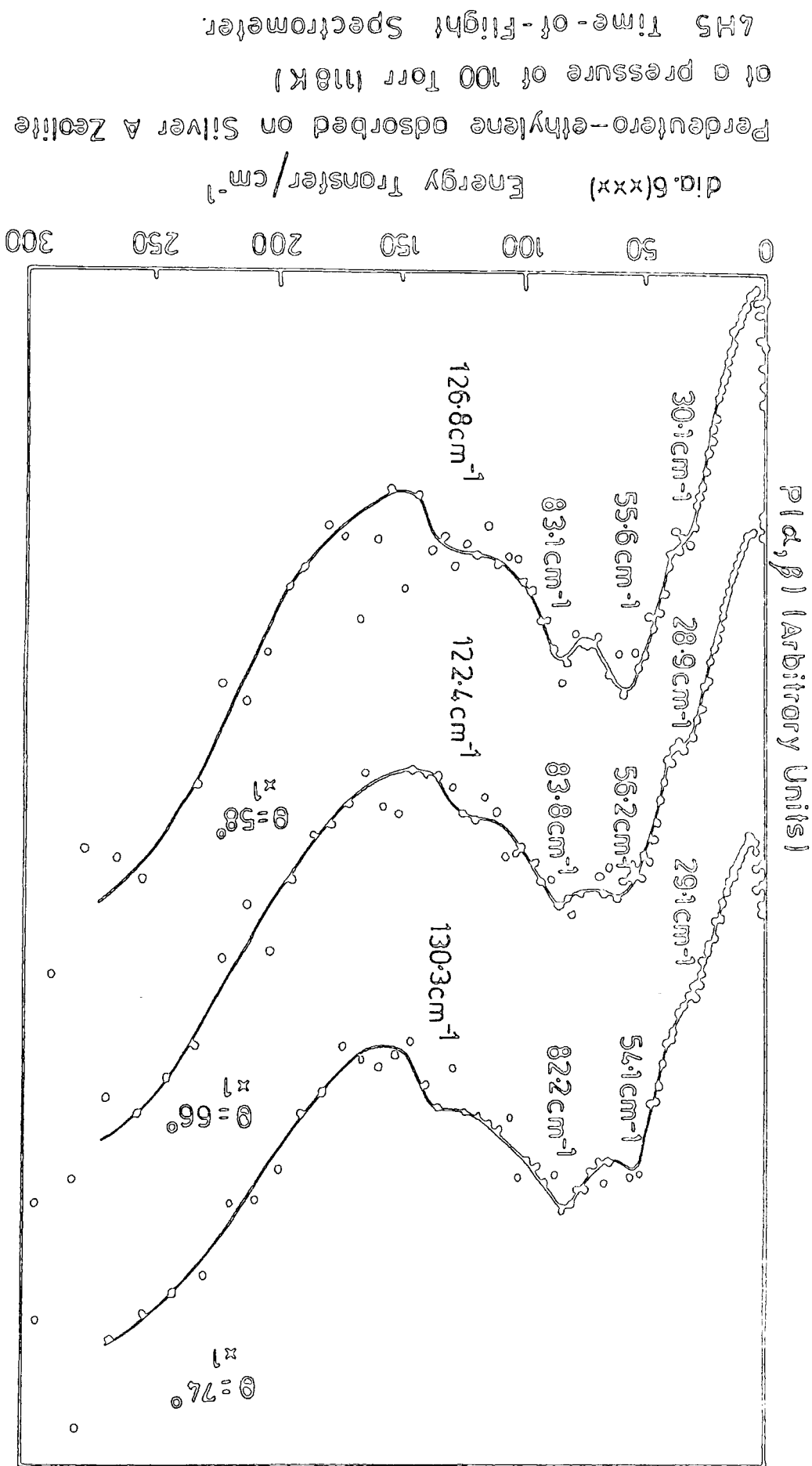


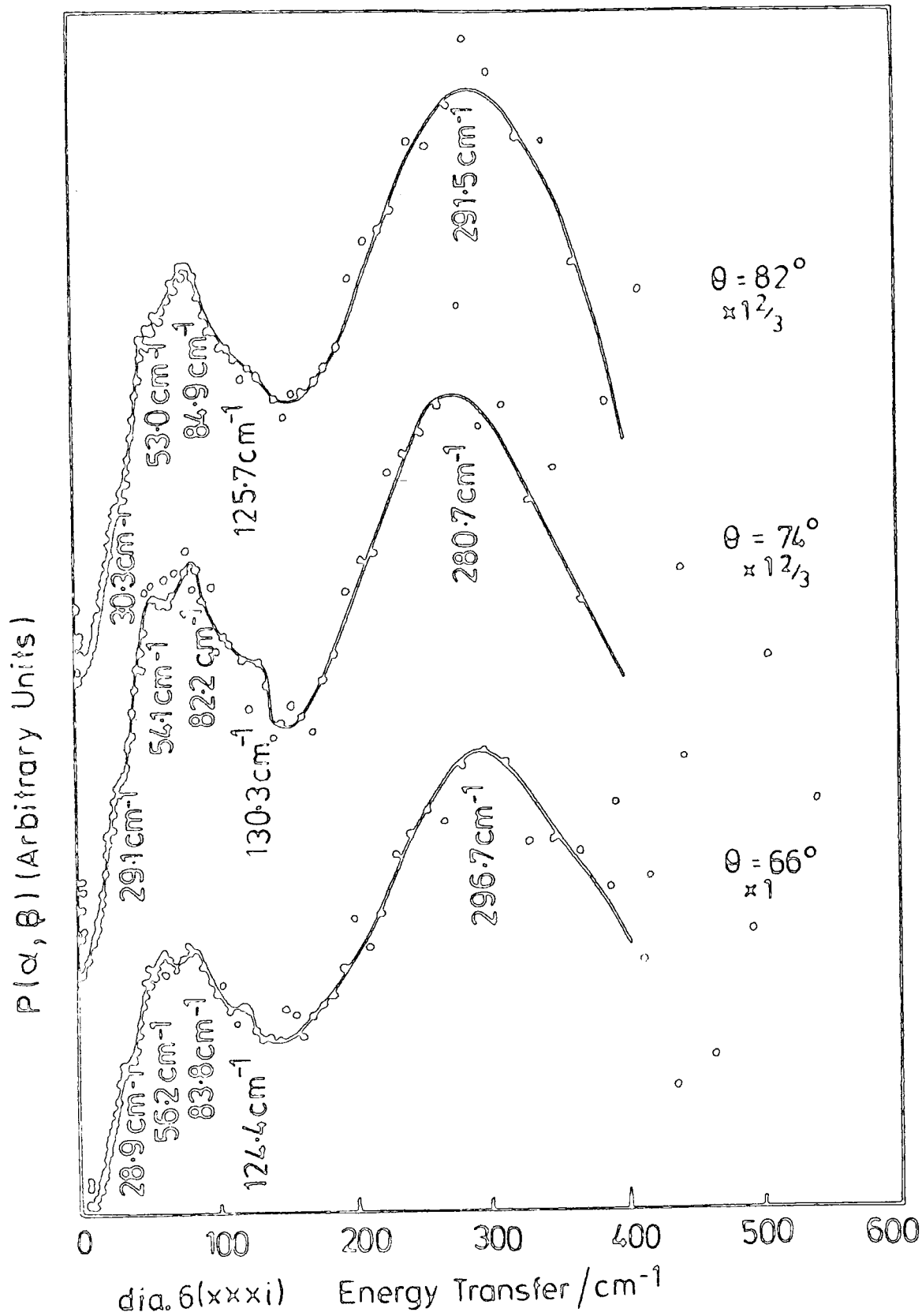
dia. 6(xxviii) Perdeutero-ethylene adsorbed on Silver A Zeolite at a pressure of 100 Torr (138 K)
6H Time-of-Flight Spectrometer.

dia. 61xix) Perdeutero-ethylene adsorbed on Silver A Zeolite at a pressure of 100 Torr (118 K)

4H5 Time-of-Flight Spectrometer.

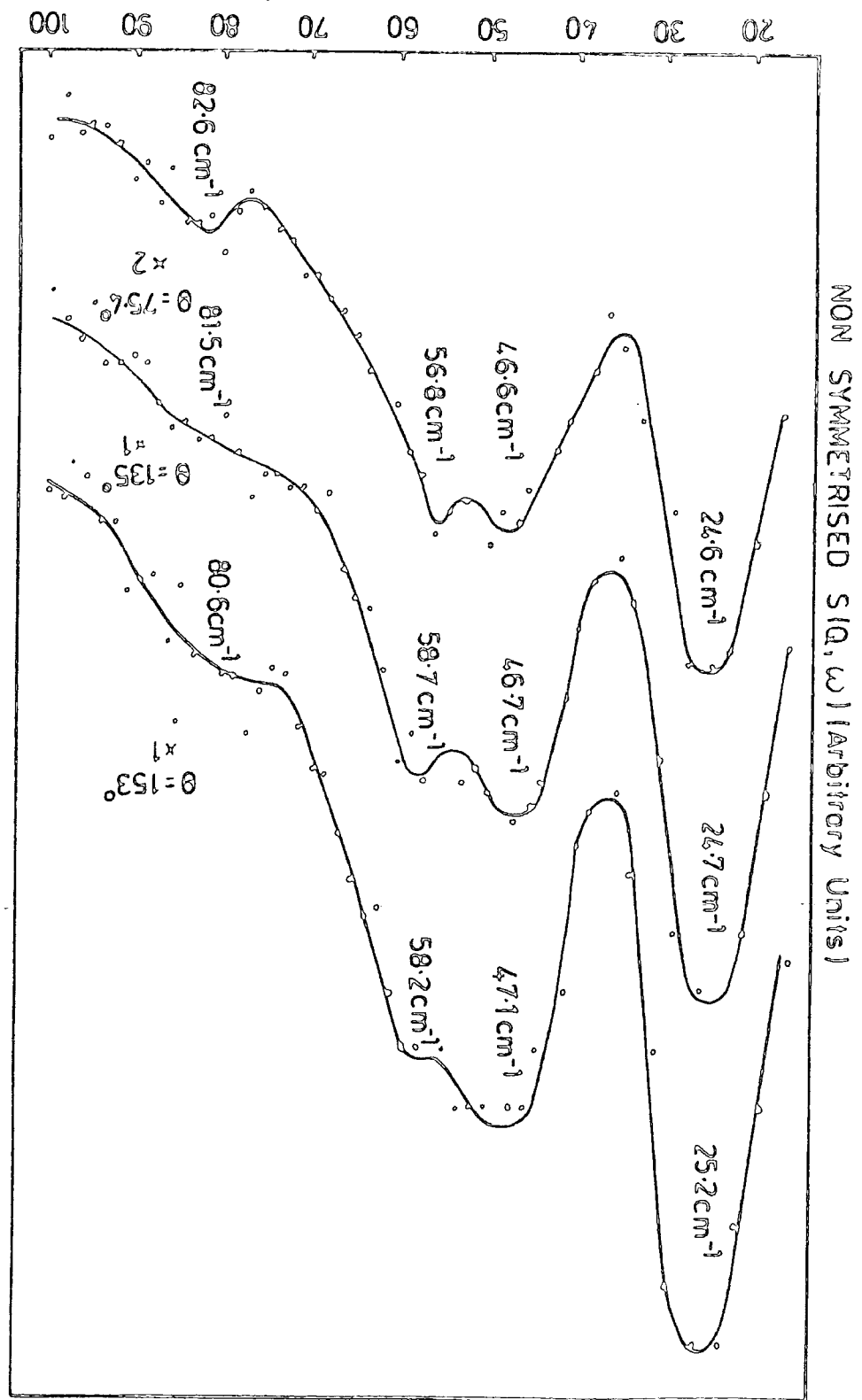


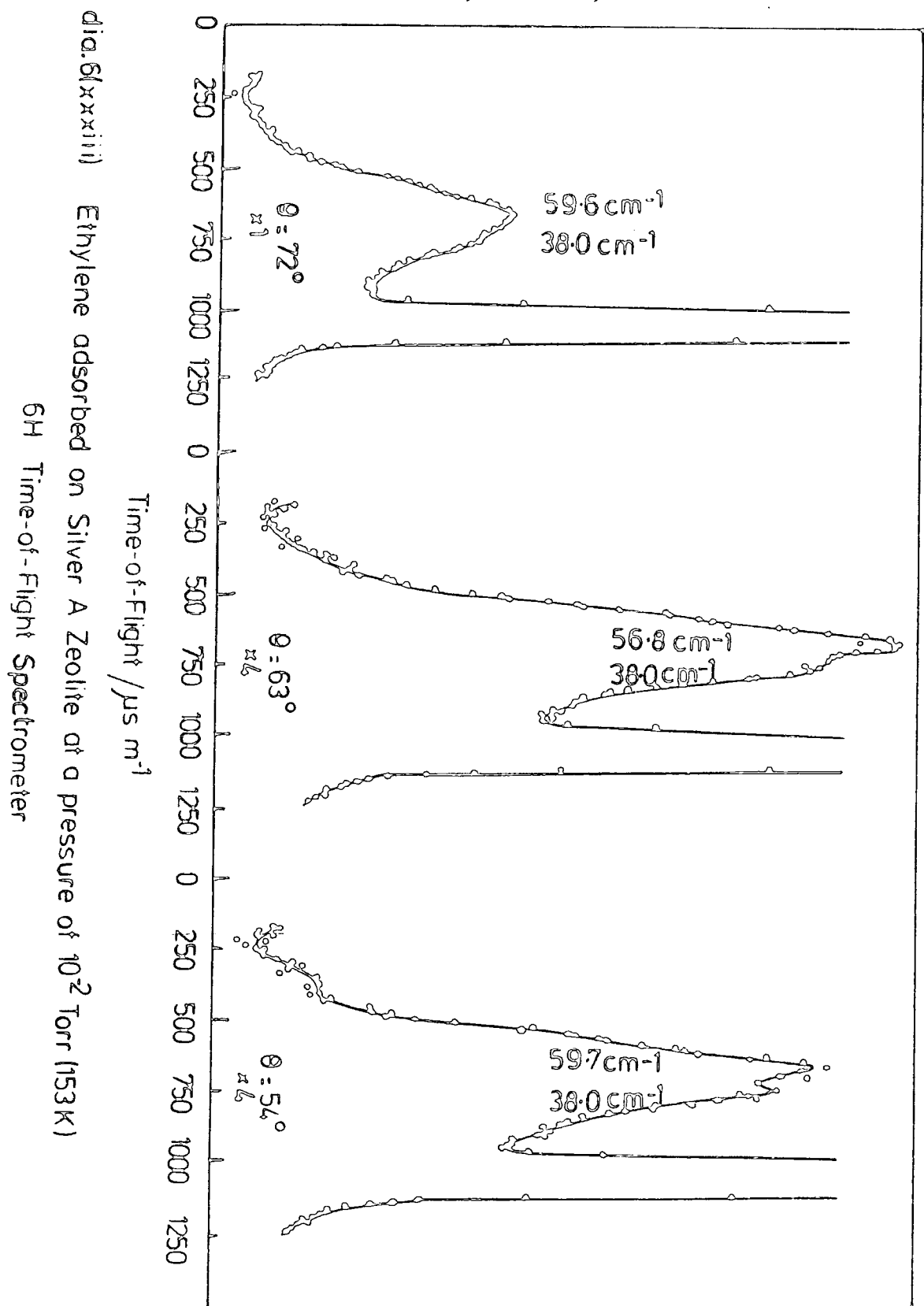


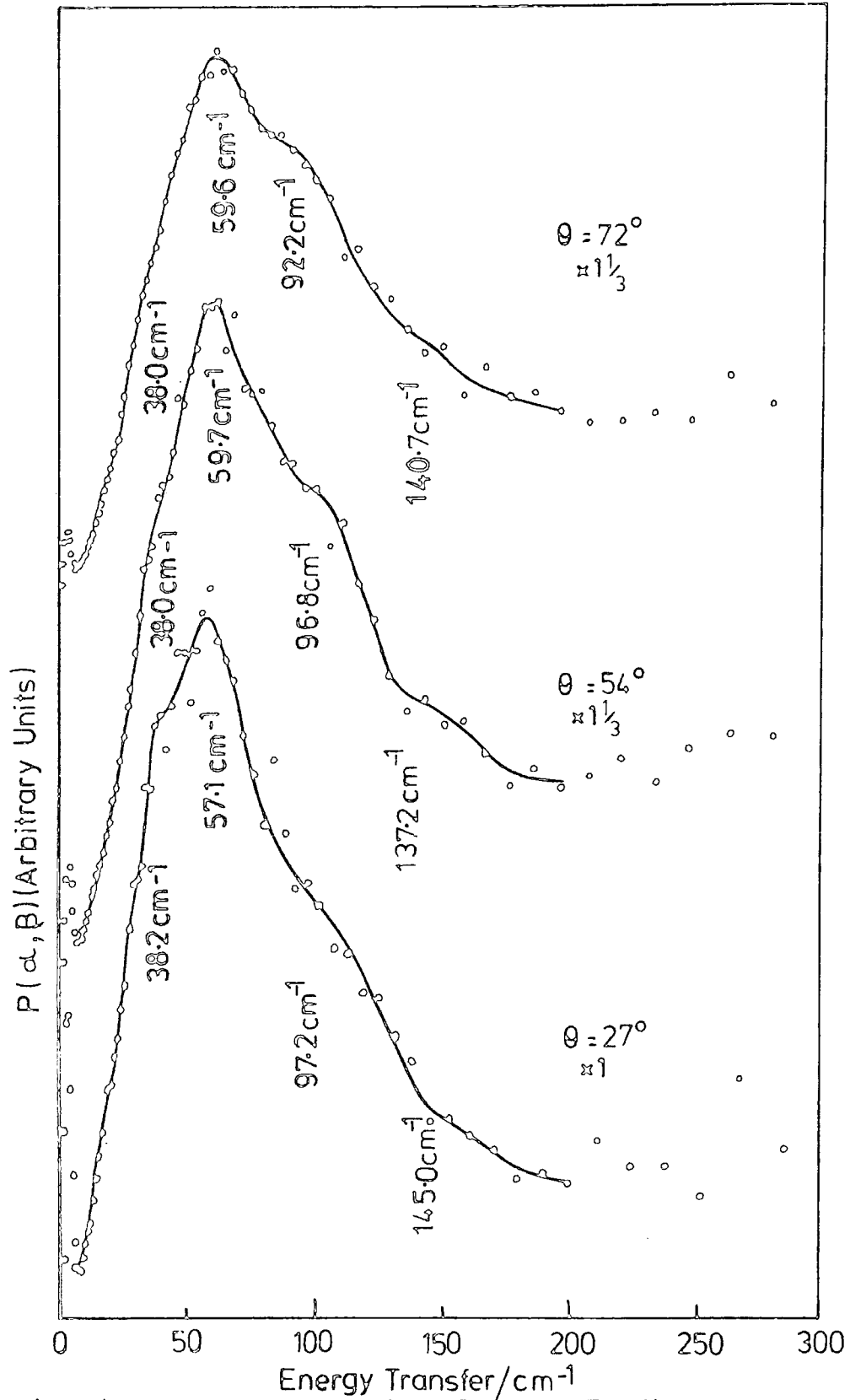


Perdeutero - ethylene adsorbed on Silver A
Zeolite at a pressure of 100 Torr (118 K)
4H5 Time-of-Flight Spectrometer

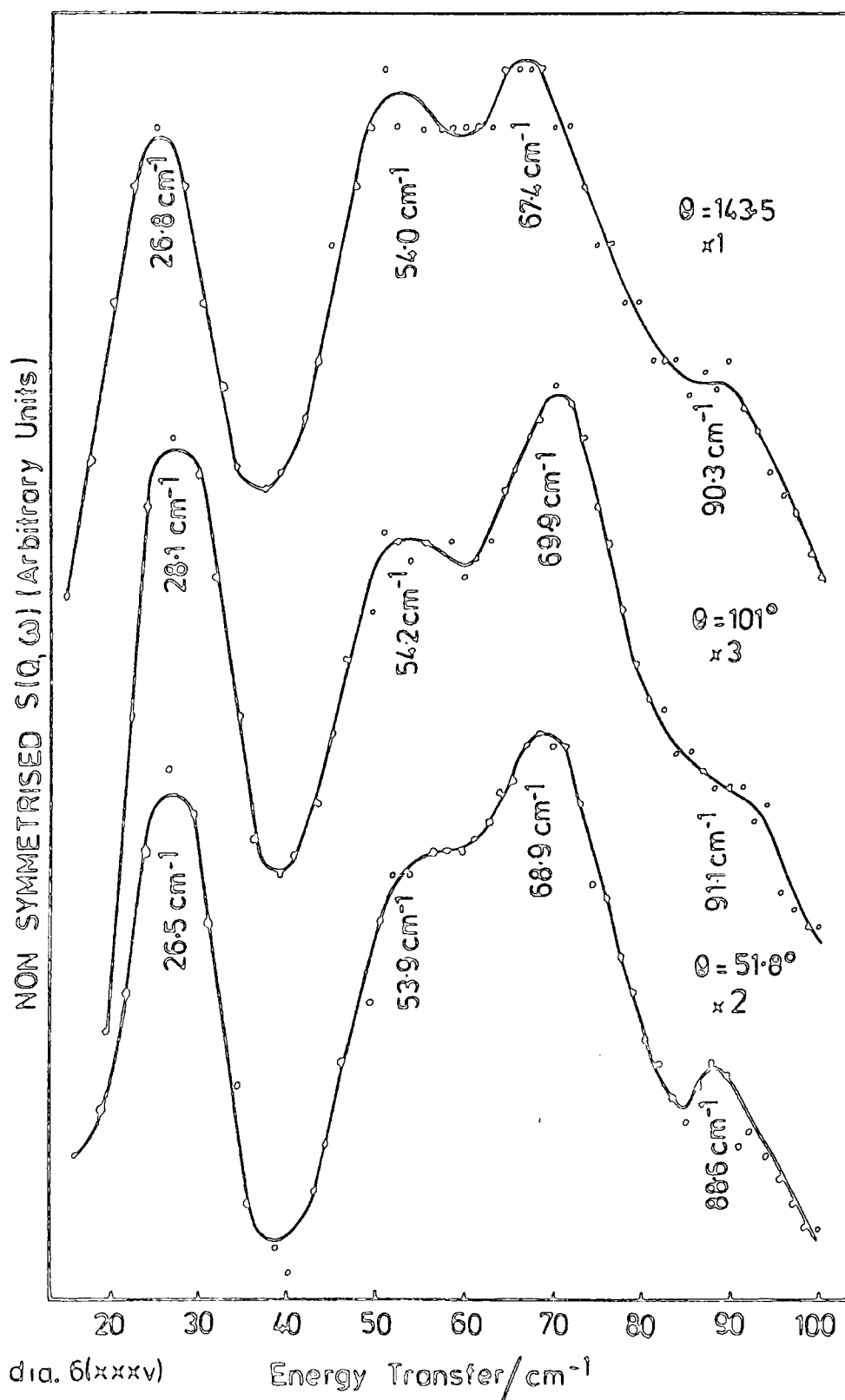
dia.6(xxxii)
 Perdeutero-ethylene adsorbed on Silver A Zeolite
 at a pressure of 70 Torr (5K)
 INK Time-of-Flight Spectrometer (22.7 meV incident energy)



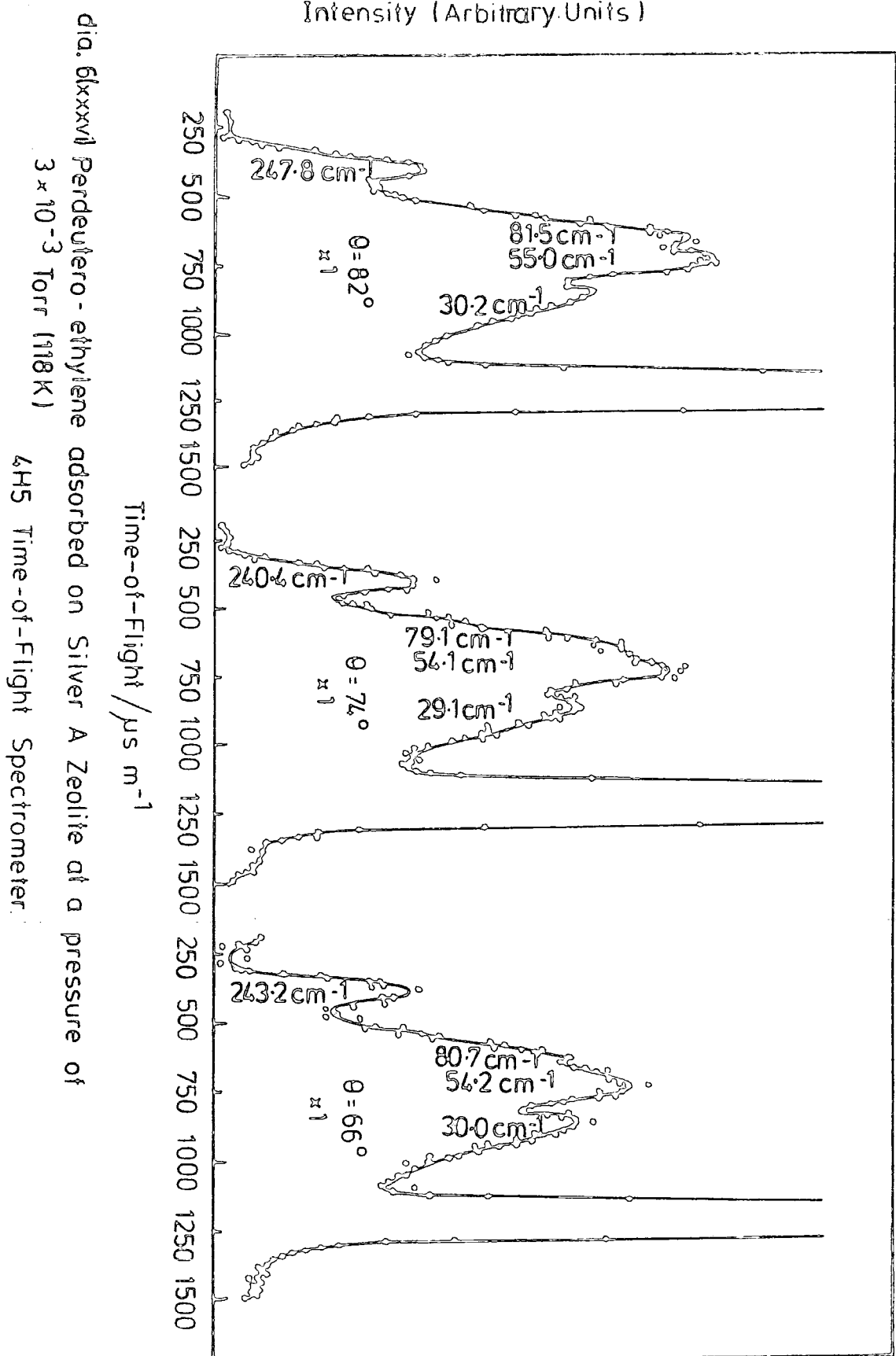




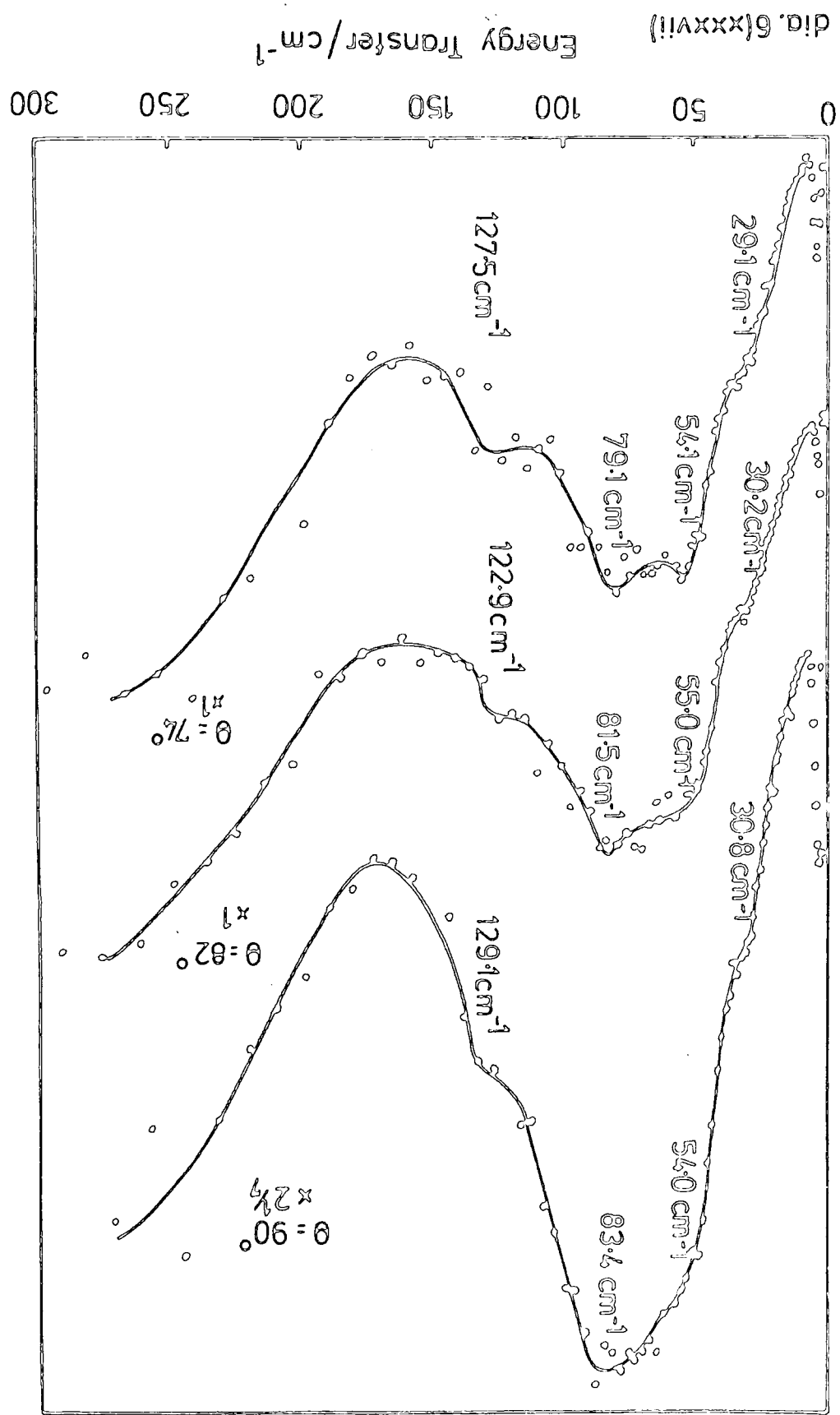
dia. 6(xxxiv) Ethylene adsorbed on Silver A Zeolite
at a pressure of 10^{-2} Torr (153 K)
6H Time-of-Flight Spectrometer.



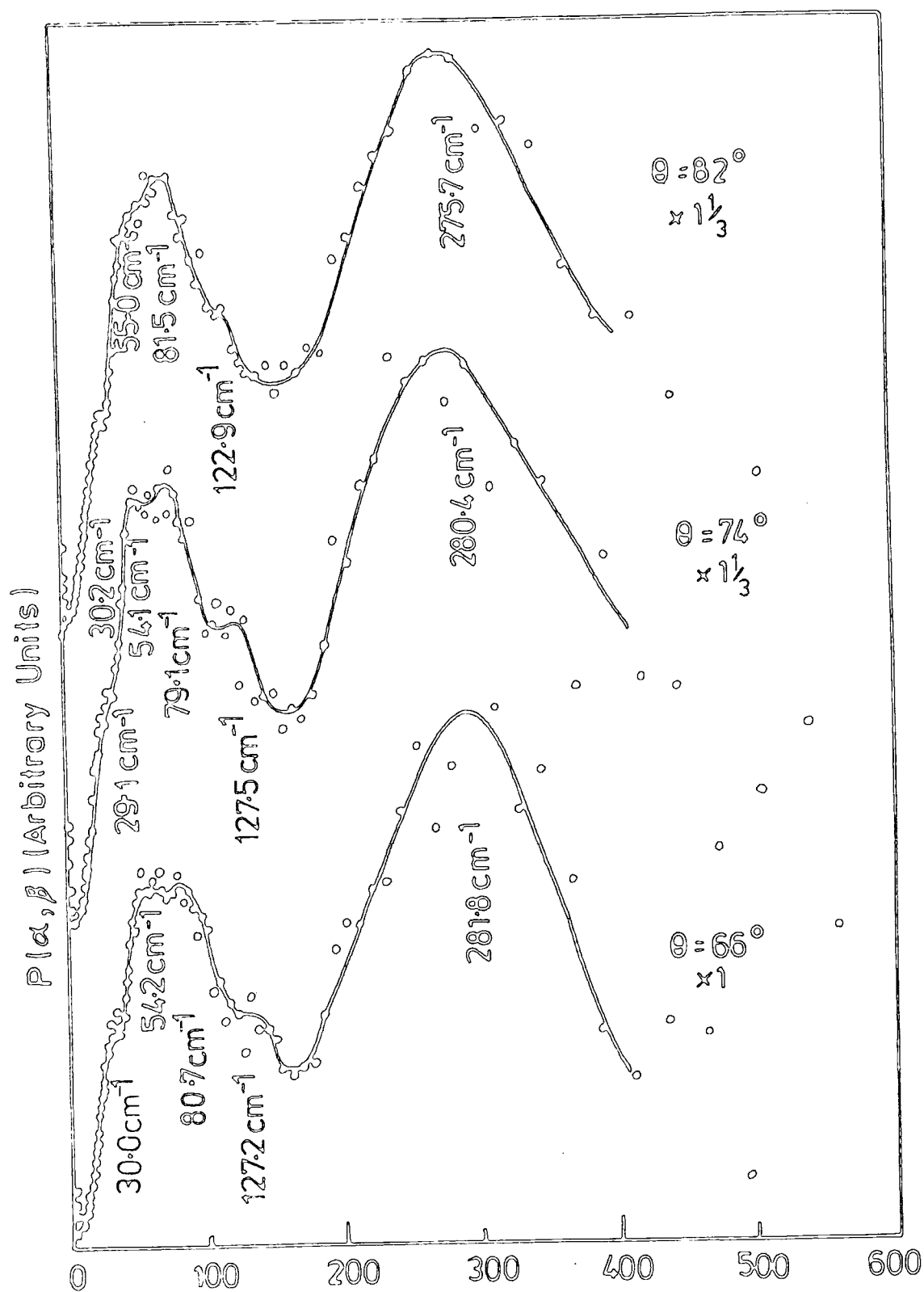
Ethylene adsorbed on Silver A Zeolite at a pressure of 10^{-2} Torr (5K)
 IN4 Time-of-Flight Spectrometer (22.9 meV incident energy)



$P(\alpha, \beta)$ (Arbitrary Units)



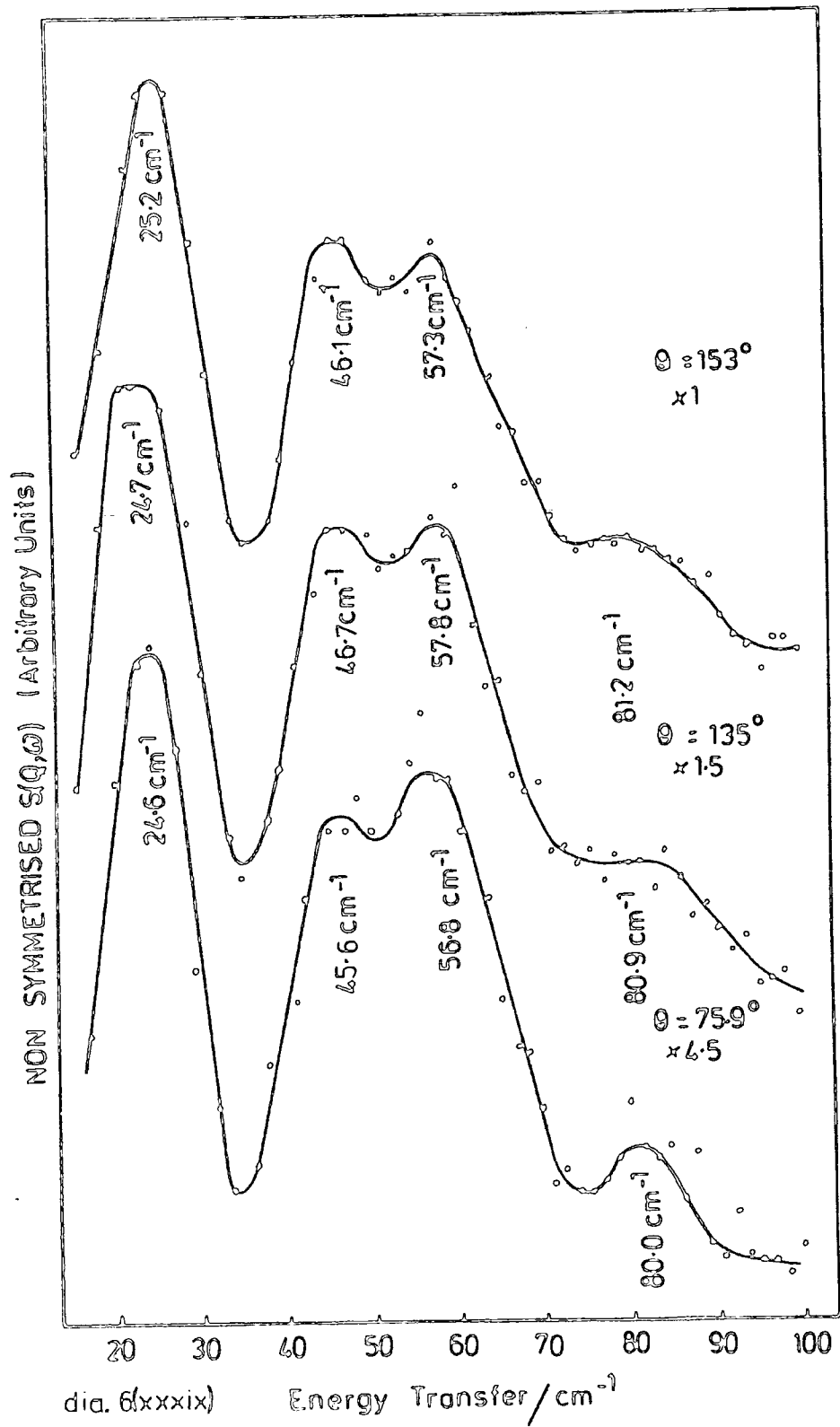
dia. 6 (xxxxvii)
 Perdeutero-ethylene adsorbed on Silver A Zeolite
 at a pressure of 3×10^{-3} Torr (118 K)
 4H5 Time-of-Flight Spectrometer.



dia.6(xxxviii)

Perdeutero - ethylene adsorbed on Silver A Zeolite
 at a pressure of 3×10^{-3} Torr (118K)

LH5 Time-of-Flight Spectrometer



Perdeutero-ethylene adsorbed on Silver A Zeolite
 at a pressure of 10^{-2} Torr (15K)

IN6 Time-of-Flight Spectrometer (22.7 meV incident energy)

TABLE 6.8 The Spectroscopic Frequencies (cm^{-1}) Determined for C_2H_{2-4} and C_2D_{2-4} Adsorbed on Ag_{12}A Zeolite at High and Low Coverages

	Spectroscopic Frequencies (cm^{-1}) of C_2H_{2-4} Adsorbed on Ag_{12}A Zeolite				Spectroscopic Frequencies (cm^{-1}) of C_2D_{2-4} Adsorbed on Ag_{12}A Zeolite			
	Dido BFD	6H	1N4		Pluto BFD	4H5	6H	1N4
High Overpressure	417 $\pm$ 8				600 $\pm$ 10	289.5 $\pm$ 17.0		
	278 $\pm$ 8				298 $\pm$ 10	248.0 $\pm$ 13.5	237.5 $\pm$ 15.5	
	224 $\pm$ 8	139.5 $\pm$ 7.5 100.5 $\pm$ 5.0	91.5 $\pm$ 1.5 71.0 $\pm$ 1.5		188 $\pm$ 10	126.5 $\pm$ 6.0 83.5 $\pm$ 3.5	130.5 $\pm$ 7.0 87.5 $\pm$ 4.5	81.5 $\pm$ 1.5 58.0 $\pm$ 2.0
	74 $\pm$ 8	62.0 $\pm$ 3.5	55.0 $\pm$ 2.0 29.5 $\pm$ 2.5		111 $\pm$ 10	54.5 $\pm$ 2.5	55.0 $\pm$ 3.0	47.0 $\pm$ 2.0 25.0 $\pm$ 2.5
Low Overpressure	567 $\pm$ 8				600 $\pm$ 10			
	518 $\pm$ 8?				447 $\pm$ 10			
	419 $\pm$ 8				400 $\pm$ 10	279.5 $\pm$ 15.5		
	278 $\pm$ 8				297 $\pm$ 10	244.0 $\pm$ 13.5		
Overpressure	223 $\pm$ 8	141.0 $\pm$ 8.0 95.5 $\pm$ 5.0	90.0 $\pm$ 1.5		183 $\pm$ 10	126.5 $\pm$ 6.0 81.0 $\pm$ 3.5		80.5 $\pm$ 1.5
	71 $\pm$ 8	58.5 $\pm$ 3.0	68.5 $\pm$ 1.5		119 $\pm$ 10	54.5 $\pm$ 2.5		57.5 $\pm$ 2.0
		38.0 $\pm$ 2.5	54.0 $\pm$ 2.0		37 $\pm$ 10	30.0 $\pm$ 1.5		46.0 $\pm$ 2.0
			27.0 $\pm$ 2.5					25.0 $\pm$ 2.5

and that for co-ordinated C_2D_4 this band will be situated at approximately $586cm^{-1}$. (The latter value is that predicted by Arnett and Crawford for the ν_{10} vibration in C_2D_4 ¹⁰³).

In order to analyse spectral features occurring at frequencies lower than those predicted for internal C_2H_4 and C_2D_4 modes, that is in the region of the spectrum where vibrations expected to result from surface-ethylene interactions should be located, use will be made of predicted intensity ratios[†] and deuteration shifts (Table 6.9) calculated on the basis of two models for the structure of complexed ethylene:

- (i) a planar gas phase like geometry¹⁰¹
- (ii) a Zeise's salt configuration¹⁰⁰, in which the four hydrogen atoms bend out of the "gas phase plane" and away from the cation with which interaction is occurring.

(In both cases the C-D bond length has been assumed to be $0.01\text{\AA}$ ⁰ shorter than that of C-H)

The intensity ratios in Table 6.9 show that the three ethylene-surface vibrations predicted to have greatest intensity are τ_x , τ_y and τ_z (dia.6(xvi)). The two latter torsions have been located in INS spectra^{4,5}, and the former in infrared spectra¹⁰², of Zeise's salt and dimer:

	τ_z cm^{-1}	τ_y cm^{-1}	τ_x cm^{-1}
Zeise's salt	185	490	1180
Zeise's dimer	170	487	1176

Investigations of the compound $AgNO_3 \cdot \frac{1}{2}C_2H_4$ ^{4,5} (in the T-O-F region only) have shown the mode τ_z to occur at lower frequency ($140cm^{-1}$) than for the platinum complexes detailed above, reflecting the weaker bonding in this salt between ethylene and the silver cation. Similarly, in INS studies of

[†] Calculated using the relations stated in Chapter IV that the intensity of a translation is proportional to M^{-1} , and the intensity of a rotation is proportional to $r^2(I_R)^{-1}$. In the case of ethylene adsorbed on $Ag_{12}A$ zeolite, M is the mass of ethylene, r is the perpendicular distance between the scattering atom and the axis of rotation and I_R is the moment of inertia of ethylene evaluated using the appropriate model.

Table 6.9

The Intensity Ratios and Deuteration Shifts Predicted for Zeolite-ethylene Vibrations on the Basis of Two Models for the Complexed Ethylene Molecule

Mode*	Gas Phase Geometry ¹⁰¹			Zeise's Salt Geometry ¹⁰⁰		
	Intensity Ratio ^f For C ₂ H ₄ Adsorption	Intensity Ratio ^f For C ₂ D ₄ Adsorption	Deuteration Shift	Intensity Ratio ^f For C ₂ H ₄ Adsorption	Intensity Ratio ^f For C ₂ D ₄ Adsorption	Deuteration Shift
τ_x	6.999	4.000	0.713	6.737	3.766	0.726
τ_y	2.526	2.113	0.859	2.645	2.139	0.856
τ_z	3.285	2.545	0.828	3.037	2.410	0.838
t_x	1.000	1.000	0.935	1.000	1.000	0.935
t_y	1.000	1.000	0.935	1.000	1.000	0.935
t_z	1.000	1.000	0.935	1.000	1.000	0.935

* The three hindered rotations and three hindered translations of ethylene relative to the zeolite surface are defined in dia.6(xvi).

^f Calculated using the relations stated in Chapter IV that the intensity of a translation is proportional to M^{-1} , and the intensity of a rotation is proportional to $r^2(I_R)^{-1}$. In the case of ethylene adsorbed on Ag12A zeolite, M is the mass of ethylene, r is the perpendicular distance between the scattering atom and the axis of rotation and I_R is the moment of inertia of ethylene evaluated using the appropriate model.

TABLE 6.10 The Spectroscopic Frequencies (cm^{-1}) and Assignments for Ethylene Adsorbed on Ag_{12}A zeolite

	Frequencies		Observed Deuteration Shift	Predicted Deuteration Shift ^a	Predicted Deuteration Shift ^b	Assignment
	C_2H_4 BFD T-O-F	C_2D_4 BFD T-O-F				
High Overpressure	417 $\pm$ 8	600 $\pm$ 10	0.715 $\pm$ 0.038	0.713	0.726	Internal C_2D_4 vibration probably ν_{10}^+
	278 $\pm$ 8	540 $\pm$ 10	0.863 $\pm$ 0.063	0.859	0.856	
	224 $\pm$ 8	298 $\pm$ 10	0.839 $\pm$ 0.078	0.859	0.856	
	139.5 $\pm$ 7.5	240 $\pm$ 10	0.935 $\pm$ 0.107	0.935	0.935	
	91.5 $\pm$ 1.5	188 $\pm$ 10	0.891 $\pm$ 0.031	0.935	0.935	
	71.0 $\pm$ 1.5	111 $\pm$ 10	0.817 $\pm$ 0.046	0.828	0.838	
	55.0 $\pm$ 2.0	39 $\pm$ 10	0.855 $\pm$ 0.070	0.828	0.838	
	29.5 $\pm$ 2.5	25.0 $\pm$ 2.5	0.847 $\pm$ 0.172	0.935	0.935	
Low Overpressure	567 $\pm$ 8	600 $\pm$ 10				Internal C_2D_4 vibration probably ν_{10}^+
	518 $\pm$ 87	447 $\pm$ 10				
	419 $\pm$ 8	400 $\pm$ 10	0.709 $\pm$ 0.038	0.713	0.726	
	278 $\pm$ 8	297 $\pm$ 10	0.853 $\pm$ 0.062	0.859	0.856	
	223 $\pm$ 8	237 $\pm$ 10	0.821 $\pm$ 0.077	0.859	0.856	
	141.0 $\pm$ 8.0	183 $\pm$ 10	0.897 $\pm$ 0.099	0.935	0.935	
	90.0 $\pm$ 1.5	119 $\pm$ 10	0.884 $\pm$ 0.033	0.935	0.935	
	68.5 $\pm$ 1.5	126.5 $\pm$ 6.0	0.839 $\pm$ 0.049	0.828	0.838	
	54.0 $\pm$ 2.0	80.5 $\pm$ 1.5	0.852 $\pm$ 0.071	0.828	0.838	
	27.0 $\pm$ 2.5	57.5 $\pm$ 2.0	0.926 $\pm$ 0.196	0.935	0.935	
	71 $\pm$ 8	37 $\pm$ 10				
		46.0 $\pm$ 2.0				
		25.0 $\pm$ 2.5				

^a Calculated using Gas phase geometry.¹⁰¹

^b Calculated using Zeise's salt configuration.¹⁰⁰

^c Vibrational numbering follows Arnett and Crawford.¹⁰³

ethylene adsorbed onto Ag13X zeolite³⁻⁵, the same order of relative frequencies of the torsional modes, τ_x , τ_y and τ_z , has been established (Table 6.6) as for Zeise's salt and dimer^{4,5}, but in common with the findings for $\text{AgNO}_3 \cdot \frac{1}{2} \text{C}_2\text{H}_4$ ^{4,5}, a shift was observed of all three vibrations to lower energy (τ_z , 39.5cm^{-1} , $\tau_y = 258\text{cm}^{-1}$ and $\tau_x = 418\text{cm}^{-1}$).

1. The BFD Spectra of Ethylene Adsorbed onto Ag_{12}A Zeolite at High Overpressure

The BFD spectrum of C_2H_4 adsorbed at High Overpressure onto Ag_{12}A zeolite (dia.6(xvii)) displays three intense peaks at 74cm^{-1} , 278cm^{-1} and 417cm^{-1} . Matching bands of equivalent intensity allows correlation of these with transitions in the analogous C_2D_4 spectrum (dia.6(xix)) at 39cm^{-1} , 240cm^{-1} and 298cm^{-1} , the two latter frequencies resulting from resolution of the feature situated between incident energies of 200cm^{-1} and 390cm^{-1} (using as guidance the BFD spectrum of C_2D_4 adsorbed at Low Overpressure (dia.6(xxii)) which displays greater resolution).

From preceding discussion, it would appear likely that the highest energy surface-ethylene vibration of appreciable intensity should correspond to the mode τ_x . It is, therefore, perhaps unsurprising that the observed deuteration shift ($417\text{cm}^{-1} \rightarrow 298\text{cm}^{-1}$) of 0.715 is in good agreement with prediction for τ_x ($0.713^*/0.726^\dagger$), and that the frequency of 417cm^{-1} is almost identical to that reported for the τ_x vibration in studies of C_2H_4 adsorbed onto Ag13X zeolite (418cm^{-1})^{4,5}.

Similarly, the least intense of the three major peaks which occur in the BFD spectrum of C_2H_4 adsorbed at High Overpressure, that at 278cm^{-1} , is in close proximity to the region of the spectrum where the torsion τ_y was located in the Ag13X zeolite- C_2H_4 system (258cm^{-1})^{4,5}. Identification with τ_y , following the latter system, seems further indicated by the observed

[†] The suffixes * and / will be used to denote those deuteration shifts (or intensity ratios) predicted using respectively a gas phase geometry¹⁰¹ and a Zeise's salt configuration¹⁰⁰ for the adsorbed ethylene molecule.

deuteration shift ($278\text{cm}^{-1} \rightarrow 240\text{cm}^{-1}$) of 0.863, which is comparable with values anticipated of this mode ($0.859^*/0.856^\dagger$).

Testing the assignments suggested above for the BFD spectrum of C_2H_4 adsorbed at High Overpressure, it is found that the intensity of the $\tau_{x_H}^\dagger$ mode relative to τ_{y_H} ($2.771:1.00^*/2.547:1.000^\dagger$) agrees well with that derived experimentally, 2.478:1.000. This is despite the inaccuracy of the measurement which necessitated the assumption of a background and the determination of the areas of two peaks occurring on different planes by square counting. Likewise, for the analogous C_2D_4 BFD spectrum, the observed intensity ratio $\tau_{x_D} : \tau_{y_D}$ measured by curve resolution, 1.867:1.000, compares most favourably with anticipated values of $1.893:1.000^*/1.761:1.000^\dagger$.

The remaining band of large intensity in the BFD spectra of ethylene adsorbed at High Overpressure on Ag_{12}A zeolite ($74\text{cm}^{-1} \text{C}_2\text{H}_4/39\text{cm}^{-1} \text{C}_2\text{D}_4$) should, by analogy with the Ag_{13}X -ethylene adsorption system³⁻⁵, Zeise's salt and dimer^{4,5} and the complex $\text{AgNO}_3 \cdot \frac{1}{2}\text{C}_2\text{H}_4$ ^{4,5}, represent the as yet unassigned torsion of the ethylene group, τ_z . However, consideration of this region of the INS spectrum is perhaps best deferred until the T-O-F data are reviewed.

In addition to the frequencies discussed above, there is a less intense band in the BFD spectrum of C_2H_4 adsorbed at High Overpressure situated at 224cm^{-1} , which appears to correlate with a shoulder displayed at 188cm^{-1} in the equivalent C_2D_4 spectrum. The implied deuteration shift is therefore 0.839, which is adjacent to those expected for torsions τ_y and τ_z (Table 6.9). Clearly, on intensity grounds, it cannot be assigned to τ_{z_H} , and yet it is equally improbable to suppose that the antisymmetric stretch (τ_{y_H}) would be split, to the extent of 54cm^{-1} , as a result of interaction between olefin molecules bonded at neighbouring sites. An alternative explanation is thus

[†] Surface-ethylene modes involving hydrogenous and deuterated species will be denoted by the respective subscript "H" or "D", e.g. τ_x will be the vibration τ_x of C_2H_4 . H

required, and that which seems most likely is that the 224cm^{-1} transition represents a torsional mode of an ethylene molecule complexed at a second adsorption site. Were this to be the case, however, it would still be necessary to decide which of the vibrations τ_{z_H} or τ_{y_H} was represented.

It is perhaps unlikely that an ethylene C_2 torsion (τ_z) would occur at a higher frequency than those found for Zeise's salt and dimer (185cm^{-1} and 170cm^{-1} respectively)^{4,5} and $\text{AgNO}_3 \cdot \frac{1}{2}C_2H_4$ (140cm^{-1})^{4,5}, in view of the weaker interaction expected between ethylene and Ag_{12}A zeolite. Furthermore, consideration of the pattern of assignments for Zeise's salt and dimer^{4,5} and for ethylene adsorbed on Ag_{13}X zeolite³⁻⁵ shows that if the 224cm^{-1} peak were to represent τ_{z_H} , then τ_{y_H} should be situated to higher energy. In fact, the only likely situation for such a band would be within the high frequency "tail" of the vibration at 417cm^{-1} previously designated τ_{x_H} (at approximately 456cm^{-1}). This should then correlate, on the deuteration shift expected of τ_y , to a frequency between $390\text{cm}^{-1} \neq$ and $392\text{cm}^{-1} *$ ($420\text{cm}^{-1} \neq - 422\text{cm}^{-1} *$ uncorrected incident neutron energy) in the BFD spectrum of C_2D_4 adsorbed at High Overpressure. There is no evidence for a peak of sufficient intensity in this region and, consequently, a deuteration shift of the approximate magnitude of that anticipated for the vibration τ_{x_H} is suggested (taking the 456cm^{-1} band in the spectrum of C_2H_4 adsorbed at High Overpressure beneath the broad peak situated at 298cm^{-1} in the equivalent C_2D_4 spectrum). It thus appears likely that the 456cm^{-1} feature represents τ_{x_H} of a second site[†], and the 224cm^{-1} transition $\tau_{y_H}^2$. This would then place the $\tau_{z_H}^2$ mode expected of the second site (by analogy with the INS scheme of assignments for Zeise's salt and dimer^{4,5}) below the peak situated at 74cm^{-1} in the BFD spectrum of C_2H_4 adsorbed at High Overpressure, in possible agreement with experiment.

[†] In future discussion, the torsions and translations of site I will be given the suffix 1, e.g. τ_{x_1} , τ_{y_1} , τ_{z_1} and t_1 , and those of the second site the suffix 2, e.g. τ_{x_2} , τ_{y_2} , τ_{z_2} and t_2 .

If the analysis above is correct, then the ratio of the intensity of the peaks $\tau_x^1 : \tau_x^2$ and $\tau_y^1 : \tau_y^2$ should give an approximate value of the respective numbers of each site. The former ratio has been calculated from the BFD spectrum of C_2H_4 adsorbed on $Ag_{12}A$ zeolite at High Overpressure (5.667:1.000); however, following the argument advanced previously, it is not possible to measure this ratio ($\tau_{x_D}^1 : \tau_{x_D}^2$) in the equivalent C_2D_4 spectrum (dia.6(xix)), because the bands resulting from the two sites are not resolved. It is possible, though, to compare the ratio $\tau_y^1 : \tau_y^2$ obtained from the hydrogenous spectrum (4.385:1.000) with that derived from the deuterated data (2.143:1.000). It is found that, whilst the ratios $\tau_{x_H}^1 : \tau_{x_H}^2$ and $\tau_{y_H}^1 : \tau_{y_H}^2$ are not significantly different (bearing in mind that one is comparing weak features in a subtracted spectrum), the ratios $\tau_{y_H}^1 : \tau_{y_H}^2$ and $\tau_{y_D}^1 : \tau_{y_D}^2$ are profoundly different. The large discrepancy in the two latter ratios can only be reasonably explained as the result of errors in the curve resolution of the $188cm^{-1}$ peak ($\tau_{y_D}^2$), as it has already been established that the ratio $\tau_{x_D}^1 : \tau_{y_D}^1$ is close to prediction.

This leaves unassigned the vibrations located at $111cm^{-1}$, $540cm^{-1}$ and $600cm^{-1}$ in the BFD spectrum of C_2D_4 adsorbed at High Overpressure. The shoulder at $111cm^{-1}$ has no obvious analogue in the equivalent C_2H_4 spectrum, although the $74cm^{-1}$ peak of the latter is asymmetric. (It may, however, be observed in the T-O-F spectra of the hydrogenous species which will be considered later.) It seems probable, on intensity grounds, that this represents a translational mode and, consequently, may correspond to the ethylene symmetric stretch (t_z), which is the highest frequency of such modes in Zeise's salt and dimer ($400cm^{-1}$ in both cases)^{4,5,102}, and has been located at $ca.80cm^{-1}$ in the $Ag_{13X}-C_2H_4$ system^{4,5}.

Taking into account previous discussion, the $600cm^{-1}$ peak may be correlated with the lowest energy intramolecular ethylene mode (ν_{10}) which

has been predicted, for gaseous C_2D_4 , to occur at $586cm^{-1} \times 10^3$.

Finally, the $540cm^{-1}$ shoulder remains to be considered. In view of the situation of this band above the highest frequency zeolite-ethylene mode ($\tau_{x_D}^1$), and yet below the lowest energy C_2D_4 internal vibration (ν_{10}) identified above, assignment is difficult. However, it will be noted that the sum of the frequencies of the two intense peaks $\tau_{y_D}^1$ ($240 \pm 10cm^{-1}$) and $\tau_{x_D}^1$ ($298 \pm 10cm^{-1}$) is approximately equal to that of this feature. It is therefore suggested that the $540cm^{-1}$ peak might correspond to a combination band. Calculation (using the relations derived in Chapter II) indicate that the intensity of such a band should be approximately 19.5% of $\tau_{x_D}^1$, this compares with the value of ca. 8.8% of $\tau_{x_D}^1$ obtained by fitting a gaussian below the $540cm^{-1}$ shoulder using the Du Pont Curve Resolver (dia. 6(xix)). The assignment of a combination band cannot, therefore, be ruled out on intensity grounds and, indeed, it appears possible that the curve fitting has produced an underestimation of the intensity of the $540cm^{-1}$ band as a consequence of the ill-definition of the $600cm^{-1}$ frequency.

2. The BFD Spectra of Ethylene Adsorbed onto $Ag_{12}A$ Zeolite at Low Overpressure

It will be seen that the BFD spectrum of C_2H_4 adsorbed at Low Overpressure onto $Ag_{12}A$ zeolite (dia. 6(xxi)) is almost superimposable on that described previously for High Overpressure (dia. 6(xvii)). However, three features are noticeable:

- 1) that the "tail" of the $419cm^{-1}$ transition (previously assigned to $\tau_{x_H}^1$) is more evident.
- 2) that a band of small intensity has become apparent at $567cm^{-1}$.
- 3) that a peak is observable at $518cm^{-1}$.

Comparison with the spectrum of dehydrated zeolite (dia. 6(xviii)) shows that the $567cm^{-1}$ frequency probably corresponds to a zeolite lattice mode

located at 570cm^{-1} , which has been amplified by C_2H_4 adsorption. Unfortunately, the 518cm^{-1} feature is more difficult to explain. A peak of comparable intensity is not found in the spectrum of C_2H_4 adsorbed at High Overpressure; indeed, there is no evidence at all for such a band. It seems strange that the spectra for the two overpressures should be identical in all respects except one. However, it is noticeable that the four points which comprise the peak almost fit a straight line, and this perhaps indicates displacement of these from the other points in this region of the spectrum. In fact, between the first point of the feature, and the point immediately preceding, the reactor had "tripped". Consultation with the reactor log showed that upon the "trip" occurring, the reactor loading had been changed, with the removal of neutron absorbing cobalt isotope rigs. These had not been replaced until approximately the final point of the four displaced. The BFD spectrum of C_2H_4 adsorbed at Low Overpressure has been Time Normalised, but this assumes constant flux (Chapter III). This condition was manifestly not met because the time per point while the cobalt rigs were raised was dramatically shorter than when they were in position: that is to say, that with the rigs removed the flux was greater than when they were in position. Hence Time Normalisation has given rise to an artifact.

Similarly, to the findings for the hydrogenous species, the BFD spectrum of C_2D_4 adsorbed at Low Overpressure on Ag_{12}A zeolite (dia.6(xxii)) is fundamentally the same as that measured at High Overpressure (dia.6(xix)). However, the removal of the some perdeuteroethylene has produced greater resolution of the three bands at 183cm^{-1} , 237cm^{-1} and 297cm^{-1} . It would seem that the intensity of the peak at intermediate frequency has been reduced on evacuation, the intensity ratio, $\tau_{x_D}^1(297\text{cm}^{-1}) : \tau_{y_D}^1(237\text{cm}^{-1})$ having changed from 1.867:1.000 to 2.269:1.000, so that the excellent agreement between observation and prediction ($1.893:1.000^*/1.761:1.000^*$) found for the BFD spectrum of C_2D_4 adsorbed at High Overpressure has been completely

overturned. This is in stark contrast with the $\tau_{x_H}^1 : \tau_{y_H}^1$ ratio from the equivalent C_2H_4 spectrum, where the values (2.531:1.000), again determined by square counting compare favourably with prediction (2.771:1.000^{*}/2.547:1.000^{*}). Of the reasons which might be put forward to explain this discrepancy, that which seems most reasonable is that, for some reason, the background assumed for the BFD spectrum of C_2D_4 adsorbed at Low Overpressure (dia.6(xxii)) is incorrect.

Two additional bands are observed distinctly in the spectrum of C_2D_4 adsorbed at Low Overpressure, those at $400 \pm 10 \text{ cm}^{-1}$ and $447 \pm 10 \text{ cm}^{-1}$. (It is arguable that these may also be discerned in the analogous High Overpressure spectrum (dia.6(xix)) at uncorrected incident neutron energies of approximately 415 cm^{-1} and 480 cm^{-1} respectively.) As with the 540 cm^{-1} band of High Overpressure C_2D_4 , these peaks lie in the region of the spectrum between the surface modes expected of the ethylene molecule and its internal vibrations. Although the lower frequency may perhaps be explained by association with the lattice mode shown in the BFD spectrum of Dehydrated $Ag_{12}A$ zeolite at 406 cm^{-1} (dia.6(xx)), an alternative suggestion may perhaps describe both transitions. It is noticeable that the two frequencies are just about within the error bars of the values for the two τ_x modes located in the BFD spectra of adsorbed C_2H_4 , at $417 \pm 8 \text{ cm}^{-1}$ and $456 \pm 8 \text{ cm}^{-1}$ (High Overpressure), and $419 \pm 8 \text{ cm}^{-1}$ and $464 \pm 8 \text{ cm}^{-1}$ (Low Overpressure). It is therefore necessary to calculate the intensity (if any) expected of an hydrogenous mode with particular relevance to the claimed purity of the C_2D_4 employed (99 atom % Deuterium).

The intensity of a given mode may be stated as

$$\propto \% \times \sigma_{inc}$$

where % refers to the percentage of scattering atoms present

and σ_{inc} is the incoherent cross-section of those scattering atoms.

Thus:

Hydrogen Mode	Deuterium Mode
Intensity $\propto \% \times \sigma_{inc_H}$	Intensity $\propto \% \times \sigma_{inc_D}$
$\propto 1 \times 80$	$\propto 99 \times 2$
$\propto 80$	$\propto 198$

The intensity of a specific mode involving hydrogen (present as 1% in 99% deuterium) is therefore 40.4% of that anticipated for the same deuterium mode.

Returning to the BFD spectrum of C_2D_4 adsorbed at Low Overpressure, it may be seen that, taking the worst possible case in which a flat background is assumed (-----dia.6(xxii)), and hence the intensities of the $400cm^{-1}$ and $447cm^{-1}$ bands are maximised, the intensity of the hydrogenous mode $(\tau_{x_H}^1 + \tau_{x_H}^2)$ is 49.25% of that of the deuterated mode $\tau_{x_D}^{1+2}$ ($297cm^{-1}$). Whilst the intensity observed for the $400cm^{-1}$ and $447cm^{-1}$ frequencies therefore appears too large for this assignment, it must be pointed out that the background in this region of the spectrum is radically different to that of the BFD spectrum of C_2D_4 adsorbed at High Overpressure. Indeed, it is perhaps indicative of a background sloping right to left which would, of course, reduce the intensities of the peaks at $400cm^{-1}$ and $447cm^{-1}$ relative to that at $297cm^{-1}$, and more importantly reduce the intensity of the $447cm^{-1}$ transition relative to that at $400cm^{-1}$. This would then cause the intensity of the $447cm^{-1}$ band to resemble more closely that expected of $\tau_{x_H}^2$. Some support for this conclusion with regard to the background may be gathered from the poor $\tau_{x_D}^1 : \tau_{y_D}^1$ ratio for this spectrum which has been discussed previously. Furthermore, an indication that at least some of the intensity of the $400cm^{-1}$ and $447cm^{-1}$ peaks derives from the hydrogenous τ_x modes may, perhaps, be seen from INS studies of ethylene adsorbed on Ag13X

zeolite^{4,5}. Here an unexplained feature in the "Low Coverage" C_2D_4 spectrum was found at $413cm^{-1}$, whilst the τ_{x_D} mode of the C_2D_4 molecule was reported at $276cm^{-1}$, and the equivalent C_2H_4 vibration identified at $418cm^{-1}$.

It is worthwhile considering at this juncture the relative intensities of peaks assigned in the BFD spectra of C_2H_4 and C_2D_4 adsorbed at Low Overpressure, and the comparison between these, and those found for the analogous High Overpressure spectra. In the case of the BFD spectrum of C_2H_4 adsorbed at Low Overpressure, the ratio $\tau_{x_H}^1 : \tau_{x_H}^2$ is 4.556:1.000, in contrast with that obtained for the equivalent High Overpressure spectrum (5.667:1.000). The intensity ratios for $\tau_y^1 : \tau_y^2$ evaluated from the spectra of C_2H_4 and C_2D_4 adsorbed at Low Overpressure are 4.833:1.000 and 1.733:1.000 respectively, as opposed to values from the High Overpressure spectra of 4.385:1.000 and 2.143:1.000. Although there are obviously great discrepancies between the data for adsorbed C_2H_4 and C_2D_4 , it seems reasonable to point out that they are internally consistent with a ratio of Site 1: Site 2, indicated from the C_2H_4 data of between 4.385:1.000 and 5.667:1.000 (average approximately 5:1), and from the C_2D_4 data of between 1.733:1.000 and 2.143:1.000 (average ca.2:1). Perhaps the reason for the internal consistency, therefore, arises from the facts:

- (i) that the hydrogenous and deuterated spectra have been obtained on different spectrometers
- (ii) that as a corollary of (i), the backgrounds assumed in each case differ
- and (iii) that the site ratios may be predetermined by slight differences in the dehydration treatments to which the $Ag_{12}A$ zeolite samples were subjected prior to adsorption of C_2H_4 or C_2D_4 .

3. T-O-F Spectra of Ethylene Adsorbed onto Ag_{12}A Zeolite at High Overpressure

Considering the low energy data, the $p(\alpha, \beta)$ spectrum of C_2H_4 adsorbed at High Overpressure onto Ag_{12}A zeolite (dia.(xxiv)) displays three peaks at frequencies of $100.5 \pm 5.0 \text{ cm}^{-1}$, $62.0 \pm 3.5 \text{ cm}^{-1}$ and $139.5 \pm 7.5 \text{ cm}^{-1}$, whilst an additional band ($30.5 \pm 2.0 \text{ cm}^{-1}$) is evident in the analogous T-O-F spectrum (dia.6(xxiii)). Of these, the first and last vibrations must be correlated with the peaks observed in the equivalent IN4 spectrum (dia.6(xxv)) at $91.5 \pm 1.5 \text{ cm}^{-1}$ and $29.5 \pm 2.5 \text{ cm}^{-1}$ respectively. However, the higher resolution of the IN4 spectrometer shows that the 62.0 cm^{-1} transition derived from the 6H data is, in fact, comprised of two bands at $71.0 \pm 1.5 \text{ cm}^{-1}$ and $55.0 \pm 2.0 \text{ cm}^{-1}$ (Table 6.8).

A similar pattern is followed for C_2D_4 adsorbed at High Overpressure (dias.6(xxvi) - (xxxii)), with the lowest and second highest frequencies of the transitions found using 4H5/6H ($126.5 \pm 6.0 / 130.5 \pm 7.0 \text{ cm}^{-1}$, $83.5 \pm 3.5 / 87.5 \pm 4.5 \text{ cm}^{-1}$, $54.5 \pm 2.5 / 55.0 \pm 3.0 \text{ cm}^{-1}$ and $29.5 \pm 1.5 / 29.0 \pm 2.0 \text{ cm}^{-1}$) corresponding to IN4 peaks situated at $25.0 \pm 2.5 \text{ cm}^{-1}$ and $81.5 \pm 1.5 \text{ cm}^{-1}$ respectively (dia.6(xxxii)). In this case, the $54.5 \pm 2.5 / 55.0 \pm 3.0 \text{ cm}^{-1}$ band displayed in the spectra obtained at Harwell is resolved in the IN4 results into two vibrations occurring at $58.0 \pm 2.0 \text{ cm}^{-1}$ and $47.0 \pm 2.0 \text{ cm}^{-1}$.

Straightforward correlation of the five frequencies thus located gives rise to the deuteration shifts shown in Table 6.10. From these it appears that the shifts observed for the transitions, $139.5 \text{ cm}^{-1} \rightarrow 130.5 \text{ cm}^{-1}$, $91.5 \text{ cm}^{-1} \rightarrow 81.5 \text{ cm}^{-1}$ and $29.5 \text{ cm}^{-1} \rightarrow 25.0 \text{ cm}^{-1}$, of 0.935 ± 0.107 , 0.891 ± 0.031 and 0.847 ± 0.172 respectively, are indicative of those anticipated for translational modes (0.935). Confirmation therefore seems to be given to the assignment of the shoulder occurring at $111 \pm 10 \text{ cm}^{-1} / 119 \pm 10 \text{ cm}^{-1}$ in the BFD spectrum of C_2D_4 adsorbed at High/Low Overpressure to the vibration expected to be the highest frequency of such modes^{4,5}, the symmetric stretch (t_z) of ethylene relative to the surface. The deuteration shifts of the remaining bands,

$71.0\text{cm}^{-1} \rightarrow 58.0\text{cm}^{-1}$ and $55.0\text{cm}^{-1} \rightarrow 47.0\text{cm}^{-1}$ (0.817 ± 0.046 and 0.855 ± 0.070 respectively) appear to suggest an identification with the τ_z vibration of ethylene ($0.828^*/0.838^{\dagger}$).

In order to check the assignments indicated above, intensity measurements have been made on the IN4 spectra, and the following ratios obtained:

C_2H_4 Adsorbed at	$\nu \text{ cm}^{-1}$	:	28.9	:	55.7	:	70.4	:	90.9
High Overpressure	Corrected								
(Angle 51.8°)	Intensity Ratio :		1.000	:	3.771	:	19.132	:	7.506
					1.000		5.073	:	1.990
							2.549	:	1.000
C_2D_4 Adsorbed at	$\nu \text{ cm}^{-1}$	:	24.6	:	46.6	:	56.8	:	82.6
High Overpressure	Corrected								
(Angle 75.4°)	Intensity Ratio :		1.000	:	1.076	:	3.851	:	1.959
					1.000	:	3.580	:	1.821
							1.966	:	1.000

It will be seen that the intensity ratio of the 70.4cm^{-1} peak relative to that located at 90.9cm^{-1} in the IN4 spectrum of C_2H_4 adsorbed at High Overpressure is slightly smaller than the ratio predicted for the torsion $\tau_{z_H}^1$ with respect to a translational mode ($3.285:1.000^*/3.037:1.000^{\dagger}$). This trend is also displayed by the ratio derived from the equivalent transitions in the IN4 spectrum of C_2D_4 adsorbed at High Overpressure, $1.966:1.000$, compared with anticipated values of $2.545:1.000^*/2.410:1.000^{\dagger}$. However, this will be discussed in greater detail later. More importantly, the corrected intensities show the two lowest frequency modes to be of almost negligible intensity compared with the two bands at higher energy. This, of course, reinforces the observations from the 4H5 and 6H P(α, β) spectra where the two peaks are insignificant features. Whilst this may be explained in the case of the $55.7\text{cm}^{-1}/46.6\text{cm}^{-1}$ band of $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ adsorbed at High Overpressure on the basis of an assignment to τ_z^2 (i.e. to the ethylene C_2 rotation of the second site), the lack of intensity of the lowest frequency is more worrying. In order to substantiate a correlation with a translation,

the intensity of the $28.9\text{cm}^{-1}/24.6\text{cm}^{-1}$ peak of $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ adsorbed at High Overpressure should be approximately one third of that designated τ_z^1 . (It is scarcely conceivable that a translational mode of the second site should be located, and the remaining translation of Site 1 prove impossible to find.) However, two factors are evident with respect to the lowest frequency vibration, firstly that the error bars of the points derived from the C_2H_4 and C_2D_4 spectra overlap, possibly indicating that there is in fact no deuteration shift and, secondly, that the intensity of this frequency with respect to the other transitions perhaps depends on scattering angle as witnessed by the greater than expected differences seen between the intensity ratio (measured at different angles) of the spectra of C_2H_4 and C_2D_4 adsorbed at High Overpressure. It is therefore possible that this band represents an amplified lattice mode.

Considering the relative intensities of $\tau_z^1 : \tau_z^2$, values of 5.073:1.000 (C_2H_4 data) and 3.580:1.000 (C_2D_4 data) have been obtained. The ratio thus found for the hydrogenous species is in close agreement with values previously measured for the Site 1:Site 2 ratio from BFD spectra of C_2H_4 adsorbed at High and Low Overpressures. In contrast, the ratio derived from the IN4 spectrum of C_2D_4 adsorbed at High Overpressure is larger than those reported previously. (It is, in fact, intermediate between the values found from BFD spectra of C_2D_4 adsorbed at High and Low Overpressures and those suggested for adsorbed C_2H_4 from all sources.)

The translation situated at $100.5\text{cm}^{-1}/83.5\text{--}87.5\text{cm}^{-1}$ in the $P(\alpha, \beta)$ spectra of $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ adsorbed at High Overpressure appears to be "Q" dependent. The bands with which this transition has been correlated in the IN4 spectra ($91.5\text{cm}^{-1}\text{C}_2\text{H}_4/81.5\text{C}_2\text{D}_4$) has, as mentioned previously, slightly greater intensity relative to the τ_z^1 vibration than is expected. These observations may perhaps be explained in two ways: either as the result of a combination band between the lowest and next to highest frequency

peaks derived from the IN4 data, or as an overtone of the transition assigned

to τ_z^2 :

System	Frequency of the Transition 6H or 4H5/IN4	Frequencies of the Transition(s) Suggested to Give Rise to Combination Band/Overtone	Frequency Predicted for Combination Band/Overtone
C ₂ H ₄ Adsorbed at High Overpressure (6H spectrum)	100.5±5.0cm ⁻¹ / 91.5±1.5cm ⁻¹	(71.0±1.5cm ⁻¹ 29.5±2.5cm ⁻¹) 2(55.0±2.0cm ⁻¹)	=100.5±4.0cm ⁻¹ =110.0±4.0cm ⁻¹
C ₂ D ₄ Adsorbed at High Overpressure (6H spectrum)	87.5±4.5cm ⁻¹ / 81.5±1.5cm ⁻¹	(58.0±2.0cm ⁻¹ 25.0±2.5cm ⁻¹) 2(47.0±2.0cm ⁻¹)	=83.0±4.5cm ⁻¹ =94.0±4.0cm ⁻¹
C ₂ D ₄ Adsorbed at High Overpressure (4H5 spectrum)	83.5±3.5cm ⁻¹ / 81.5±1.5cm ⁻¹	(58.0±2.0cm ⁻¹ 25.0±2.5cm ⁻¹) 2(47.0±2.0cm ⁻¹)	=83.0±4.5cm ⁻¹ =94.0±4.0cm ⁻¹

Of the two suggested explanations, the combination band appears more favoured from consideration of the frequencies involved.

4. T-O-F Spectra of Ethylene Adsorbed onto Ag₁₂A Zeolite at Low Overpressure

Turning now to the T-O-F data for ethylene adsorbed at Low Overpressure onto Ag₁₂A zeolite (dias.6(xxxiii)-6(xxxix)), it will be seen that the frequencies located and assignments derived follow closely those for the High Overpressure spectra. These are shown, together with the deuteration shifts observed, in Table 6.10.

Once more considering the intensities of the bands found from the IN4 data leads to the following ratios:

C_2H_4 Adsorbed at	$\nu \text{ cm}^{-1}$	:	26.5	:	53.9	:	68.9	:	88.6
Low Overpressure	Corrected								
(Angle 51.8°)	Intensity Ratio :		1.000	:	2.087	:	9.260	:	2.816
					1.000	:	4.436	:	1.349
							3.289	:	1.000
C_2D_4 Adsorbed at	$\nu \text{ cm}^{-1}$	:	24.6	:	45.6	:	56.8	:	80.0
Low Overpressure	Corrected								
(Angle 75.4°)	Intensity Ratio :		1.000	:	1.678	:	6.130	:	2.484
					1.000	:	3.652	:	1.480
							2.468	:	1.000

The intensity ratio of the band at 68.9 cm^{-1} relative to that situated at 88.6 cm^{-1} in the IN4 spectrum of C_2H_4 adsorbed at Low Overpressure (3.289:1.000) is now almost identical with that predicted for the torsion τ_{zH}^1 relative to a translational mode ($3.285:1.000^*/3.037:1.000^*$). Similarly, for C_2D_4 adsorbed at Low Overpressure, the intensity ratio derived from the IN4 spectrum for the 56.8 cm^{-1} peak with respect to that at 80.0 cm^{-1} (2.468:1.000) compares very favourably with that anticipated for τ_{zD}^1 relative to a translation ($2.545:1.000^*/2.410:1.000^*$).

As was found for the High Overpressure work, the lowest frequency vibration is again of negligible intensity with respect to the Site I modes. However, the Site 1:Site 2 ratio, as calculated from the intensities of τ_z^1 relative to τ_z^2 are in much closer agreement to each other: 4.436:1.000 for C_2H_4 adsorbed at Low Overpressure, and 3.652:1.000 for the equivalent C_2D_4 spectrum. The value of the ratio is, in the case of C_2D_4 adsorbed at Low Overpressure, close to that obtained from the High Overpressure data (3.580:1.000) whilst for C_2H_4 adsorbed at Low Overpressure, it is similar to the values obtained from the analogous High Overpressure spectrum and BFD work.

The angular dependency of the $95.5 \text{ cm}^{-1}/81.0 \text{ cm}^{-1}$ band seen in the $P(\alpha, \beta)$ spectra of C_2H_4/C_2D_4 adsorbed at Low Overpressure is less striking than in the High Overpressure spectra. Moreover, the intensity of the highest frequency IN4 derived transition is no longer greater than prediction.

It is, however, interesting to check from the frequencies whether a combination band or overtone could exist as suggested in the High Overpressure case:

System	Frequency of the Transition 6H/IN4	Frequencies of the Transitions Suggested to Give Rise to Combination Band/ Overtone	Frequency Predicted for Combination Band/Overtone
C ₂ H ₄ Adsorbed at Low Overpressure (6H spectrum)	95.5±5.0cm ⁻¹	(68.5±1.5cm ⁻¹ + 27.0±2.5cm ⁻¹) 2(54.0±2.0cm ⁻¹)	=95.5±4.0cm ⁻¹ =108.0±4.0cm ⁻¹
C ₂ D ₄ Adsorbed at Low Overpressure (4H5 spectrum)	81.0±3.5cm ⁻¹	(57.5±2.0cm ⁻¹ + 25.0±2.5cm ⁻¹) 2(46.0±2.0cm ⁻¹)	=82.5±4.5cm ⁻¹ =92.0±4.0cm ⁻¹

Again, the evidence from the frequencies is that any "Q" dependency found in this region of the spectrum would be likely to result from the presence of a combination band.

5. Conclusions

It appears from the data presented that at least two sites for ethylene adsorption are present on Ag₁₂A zeolite after employment of the dehydration treatment described in the experimental section. This is in contrast to the work of Kim and Seff⁸², who, for the ethylene sorption complex of partially decomposed Ag₁₂A zeolite, found evidence of only one such site situated in the 6-rings (S2*). Estimates of the relative numbers of the two sites from intensity measurements have, as expected of comparisons between weak features, proved extremely variable with values ranging from 1.733:1.000 to 5.667:1.000. In fairness, however, it must be pointed out that discrepancies in the above ratio seem to vary as a function of the individual zeolite sample chosen, rather than as a function of overpressure. This perhaps is

indicative that the number of respective adsorption sites have been predetermined as a result of the dehydration treatment carried out on each zeolite sample prior to adsorption, in common with the observations reported by Kim and Seff⁶²⁻⁴.

It further seems that the occupancies of the respective adsorption sites by ethylene have not been noticeably affected by the evacuation procedure employed. This is, of course, the converse of the findings of Yates et al.^{28,86,87} and of Howard et al.³⁻⁵ for the $\text{Ag13X-C}_2\text{H}_4$ adsorption system, but must be assumed to reflect stronger interaction between ethylene and Ag_{12}A zeolite.

It is probable that the dehydration conditions used have not been severe enough to cause reduction of 8-ring silver ions (S1), but may well have caused the 4-ring ions (S3) to be reduced and consequently to migrate. For acetylene adsorbed on Na_{12}A zeolite^{78,79} (Chapter VII), in which no migration occurs, six acetylene molecules are found per α cage. These bond preferentially to the 8-ring (S1) cations, so that all such sites are occupied; the remaining acetylene molecules then complex with three of the eight cations present in less favoured 6-ring (S2^*) sites. It appears reasonable to suppose that in the case of the Ag_{12}A zeolite, samples studied in this work, the two adsorption sites occupied will have been those indicated from the Na_{12}A -acetylene adsorption system, i.e. sites S1 and S2^* . Below are shown ratios $\text{S2}^*:\text{S1}$ anticipated of various occupancies of the respective sites up to the maximum of eight decreed for the former site and three for the latter site:

		S2^*							
		1	2	3	4	5	6	7	8
S1	1	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000
	2	0.500	1.000	1.500	2.000	2.500	3.000	3.500	4.000
	3	0.334	0.667	1.000	1.334	1.667	2.000	2.334	2.667

All values are stated relative to $\text{S1} = 1.000$.

It may therefore be seen that the experimentally determined ratios seem

to indicate occupancies of sites $S2^*:S1$ of between 5:3 and 5.5:1. The mode value (of approximately 4:1), however, corresponds to an $S2^*:S1$ ratio of 8:2 which would suggest the reduction of one 8-ring ($S1$) cation (as well as the 4-ring ($S3$) cation), and occupation of all other available sites.

D. Barrier Calculation

Work carried out on Zeise's salt¹⁰⁴ has shown the potential functions describing the C_2 torsion of ethylene (τ_z) to be of the form (Chapter IV):

$$V(\theta) = \frac{V_0}{2} (1 - \cos 2\theta) + \frac{V_4}{2} (1 - \cos 4\theta)$$

This may be approximated by a one parameter function for $V(\theta)$ if the assumption is made that $V_4 = V_0$:

$$V(\theta) = \frac{V_0}{2} [(1 - \cos 2\theta) + (1 - \cos 4\theta)]$$

This function has a ground state minimum at $\theta=0$, a metastable minimum at $\theta=\pi/2$, and a maximum at $\theta_{\max} = 0.5 \cos^{-1}(0.25)$.

The second derivative with respect to θ of the equation above is equal to the force constant, k . Therefore substitution for k in the Harmonic Oscillator Approximation yields:

$$\omega = \frac{1}{\pi} \left(\frac{5V_0}{2I_R} \right)^{\frac{1}{2}}$$

where I_R is the reduced moment of inertia of the ethylene molecule

Employing the assigned frequencies for τ_z^1 and τ_z^2 of 71.0cm^{-1} and 55.0cm^{-1} (C_2H_4 adsorbed at High Overpressure), and 68.5cm^{-1} and 54.0cm^{-1} (C_2H_4 adsorbed at Low Overpressure), values for V_0^1 of $3.59 \pm 0.15\text{kJ mol}^{-1}$ and V_0^2 of $2.15 \pm 0.16\text{kJ mol}^{-1}$ may be determined from the former data, and values for V_0^1 of $3.34 \pm 0.15\text{kJ mol}^{-1}$ and V_0^2 of $2.08 \pm 0.16\text{kJ mol}^{-1}$ from the latter data. These compare with barrier heights of 23.6kJ mol^{-1} and 14.32kJ mol^{-1} calculated respectively for Zeise's salt¹⁰⁴ and the complex $\text{AgNO}_3 \cdot \frac{1}{2}C_2H_4$ ^{4,5}, and 1.14kJ mol^{-1} evaluated for ethylene adsorbed at Low Coverage on Ag13X zeolite^{4,5}.

Appendix: Structural Data Used in the Calculation of Moments of Inertia

Moments of inertia of ethylene about the three principal axes have been calculated from the co-ordinates listed below for the two models of the complexed molecule:

(i) Planar gas phase geometry after Dowling and Stoicheff¹⁰¹:

Hx+1.233	Hx+1.233	Dx+1.288	Dx+1.228
y-0.928	y+0.928	y-0.920	y+0.920
z 0.000	z 0.000	z 0.000	z 0.000
Cx+0.670		Cx+0.670	
y 0.000		y 0.000	
z 0.000		z 0.000	
Cx-0.670		Cx-0.670	
y 0.000		y 0.000	
z 0.000		z 0.000	
Hx-1.233	Hx-1.233	Dx-1.228	Dx-1.228
y-0.928	y+0.928	y-0.920	y+0.920
z 0.000	z 0.000	z 0.000	z 0.000

(ii) Zeise's salt configuration after Love et al.¹⁰⁰:

Hx+1.249	Hx+1.249	Dx+1.244	Dx+1.244
y-0.785	y+0.785	y-0.777	y+0.777
z-0.429	z-0.429	z-0.372	z-0.372
Cx+0.688		Cx+0.688	
y 0.000		y 0.000	
z+0.072		z+0.124	
Cx-0.688		Cx+0.688	
y 0.000		y 0.000	
z+0.072		z+0.124	
Hx-1.249	Hx-1.249	Dx-1.244	Dx-1.244
y-0.785	y+0.785	y-0.777	y+0.777
z-0.429	z-0.429	z-0.372	z-0.372

For both models, the C-D band length has been assumed to be $0.01\text{\AA}$ shorter than that of C-H.

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CHAPTER VII

THE SILVER EXCHANGED TYPE A ZEOLITE-ACETYLENE ADSORPTION SYSTEM

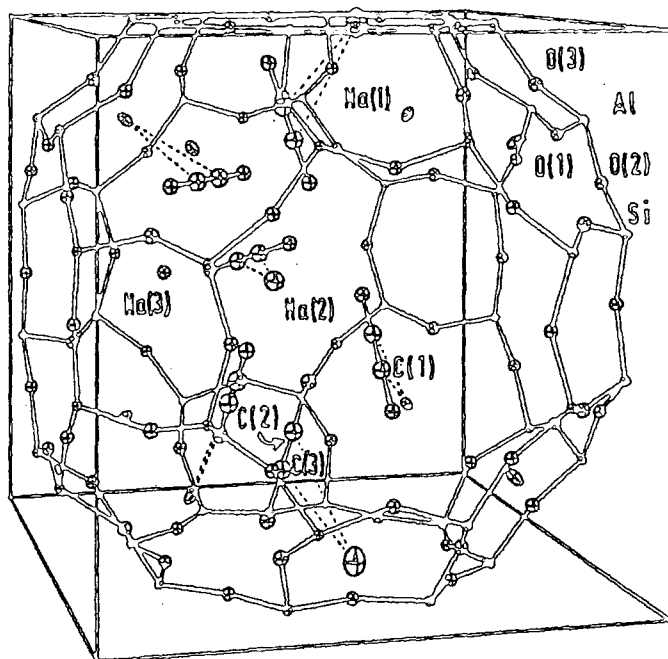
A. Background

1. Structural Investigations of Acetylene Adsorbed on Type A Zeolites

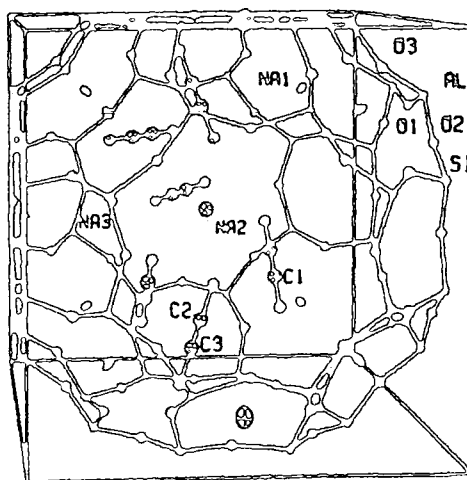
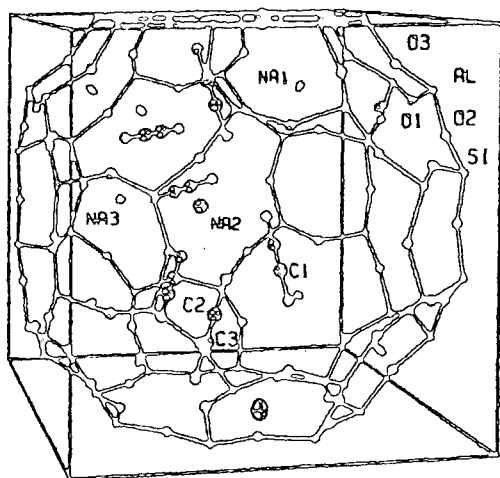
Although structural data specifically relating to an Ag_{12}A -acetylene sorption complex are absent from the literature, single crystal determinations have been published of acetylene adsorbed on sodium^{1,2} and on manganese^{3,4} and cobalt⁴-exchanged type A zeolites.

In the investigation involving Na_{12}A (the only one of the above-mentioned studies which has employed a "wholly exchanged" form of type A zeolite), the sample was dehydrated, prior to adsorption of acetylene at a pressure of 650 Torr, by means of evacuation at 3×10^{-6} Torr and 350°C for 48 hours.

The positions of the cations in dehydrated, uncomplexed, sodium type A zeolite^{5,6} have been described more fully elsewhere (Chapter VI), but in outline they are: eight occupying 6-rings (S2^*), three located in 8-rings (S1), and a twelfth distributed statistically over twelve 4-ring (S3) sites. Upon the introduction of acetylene, three gas molecules were found to coordinate laterally and symmetrically with three of the 6-ring sodium ions at a distance of $2.8 \text{ \AA}$, thereby causing these cations to migrate further into the α cage (S2^*). It proved more difficult, however, in view of the constraint of experimental resolution, to define conclusively the distribution of a further three acetylene molecules which were adsorbed. Accordingly several models were put forward. Of these, the one most consistent with crystallographic data suggested that the three gas molecules were equivalent, each interacting asymmetrically ($\text{Na}^+-\text{C} = 3.0 \text{ \AA}$ and $2.6 \text{ \AA}$) with an 8-ring sodium ion (S1) (dias. 7(i) and 7(ii)). It was thought, however, that the 4-ring cation (S3), which would be expected to be the most suitable for complexation, had "disrupted the structure to some extent",



Dia.7(i). The Na₁₂A-acetylene Sorption Complex (after Amaro and Seff^{1,2}). In this diagram the cation sites Na(1), Na(2) and Na(3) correspond to those denoted S2*, S1 and S3 respectively in the text.



Dia.7(ii). Stereoview of the Na₁₂A-acetylene Sorption Complex (after Amaro and Seff²). In this diagram, cation sites Na1, Na2 and Na3 correspond with those denoted S2*, S1 and S3 respectively in the text.

and that one (or possibly two) of the three acetylene molecules associated with the 8-ring sites also made a symmetrical approach to this lone ion ($\text{Na}^+-\text{C} = 2.6 \text{ \AA}$). In support of this belief it was pointed out that the 4-ring sodium ion had moved approximately $0.9 \text{ \AA}$ from its position in

dehydrated Na_{12}A , presumably as the result of participation in some kind of bonding.

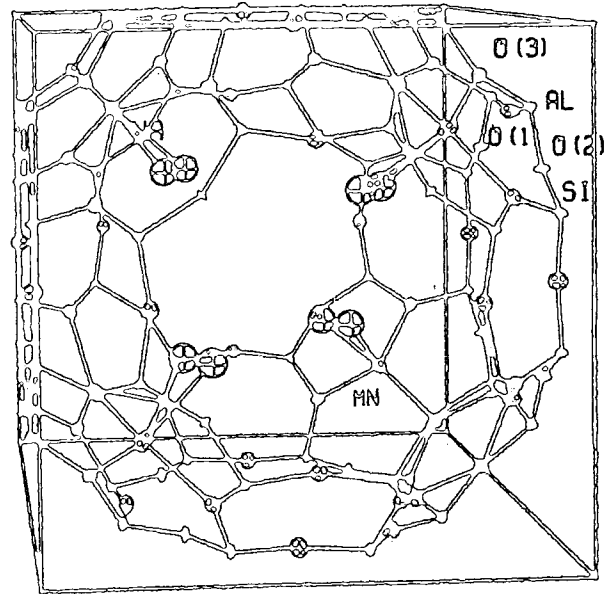
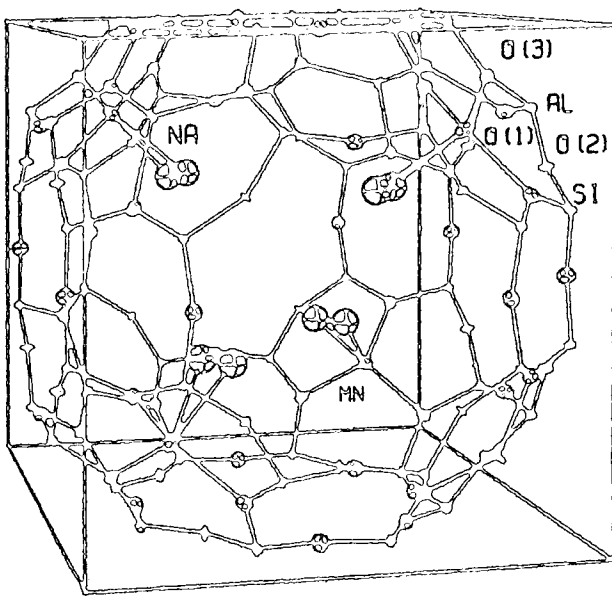
Another model, considered perhaps the more reasonable, proposed that one acetylene molecule was associated both symmetrically with the 4-ring cation ($\text{Na}^+-\text{C} = 2.6 \text{ \AA}$), and simultaneously asymmetrically with a sodium ion in an 8-ring site ($\text{Na}^+-\text{C} = 2.6$ and $3.0 \text{ \AA}$), whilst the two other acetylene molecules bonded symmetrically to the remaining 8-ring cations ($\text{Na}^+-\text{C} = 2.6 \text{ \AA}$). In all the models, acetylene-sodium ion interaction was suggested to take place by lateral π bonding.

Two further important facts emerge from the structural investigation:

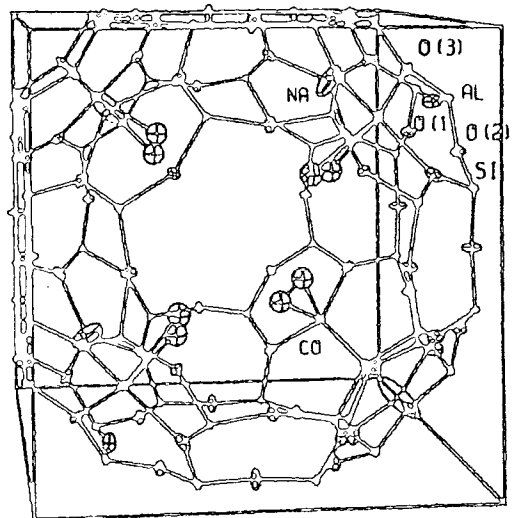
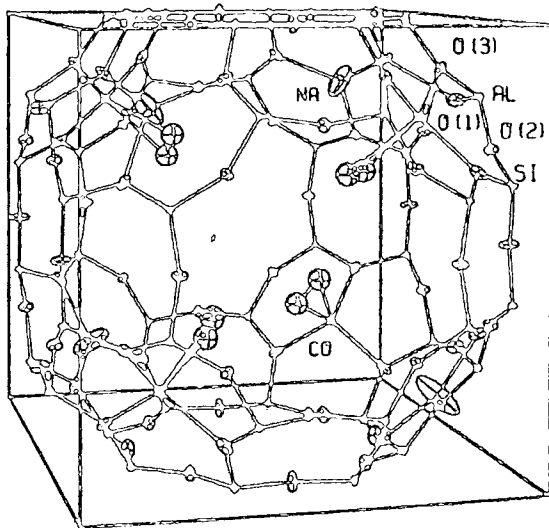
- (i) that all three 8-ring cations complex, whilst only three out of eight 6-ring ions bond (indicating that co-ordination with the former sites is more energetically favourable than with the latter).
- (ii) that, accuracy in determination aside, the $\text{C}\equiv\text{C}$ bond lengths of approximately $1.0 \text{ \AA}$ are not much shorter than for the gas ($1.2 \text{ \AA}$ ⁷).

The two additional crystal structure studies, which have been carried out on zeolite-acetylene adsorption systems have employed $\text{Mn}_{4.5}\text{Na}_3\text{A}$ ^{3,4} and $\text{Co}_4\text{Na}_4\text{A}$.⁴ Although in both zeolites all cations occupy 6-ring positions, it was found in the sorption complexes that only the transition metal ions bonded to acetylene (dias. 7(iii) and 7(iv)). This interaction was symmetrical, causing the complexing ions to move through the plane of the 6-ring into the α cage (S2^*), and adopt tetrahedral co-ordination. Coincidental with this movement (in order to ensure that the optimum distribution of cationic charge was maintained), the sodium ions retreated into the sodalite cavities ($\text{S2}'$), and in so doing presumably prevented the approach of acetylene molecules.

In both sorption complexes, lateral π interaction between the cation and acetylene was seen to take place, with the $\text{C}\equiv\text{C}$ bond length similar to



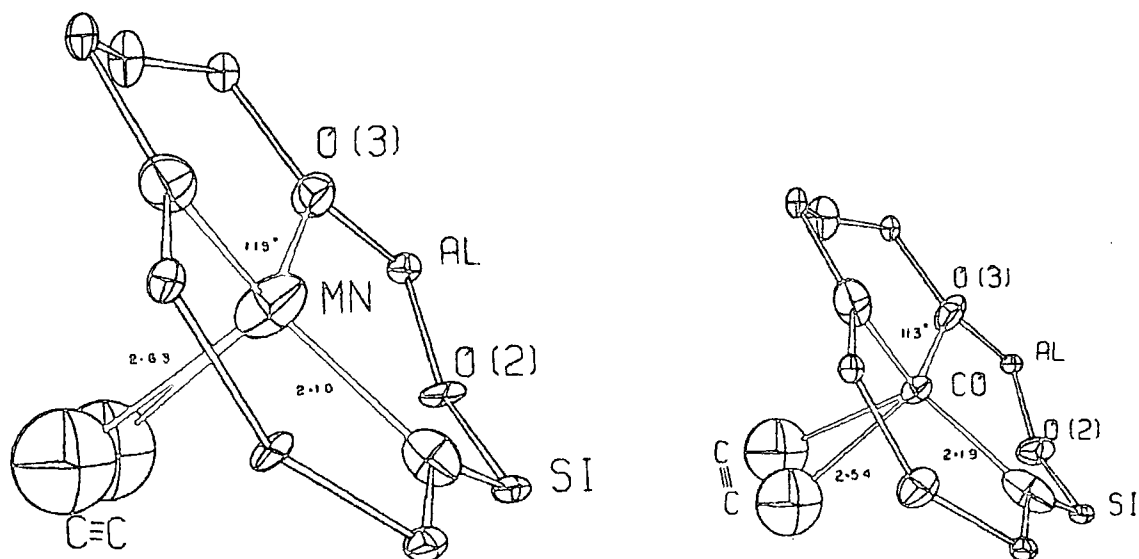
Dia.7(iii). Stereoview of the $\text{Mn}_{4.5}\text{Na}_3\text{A}$ -acetylene Sorption Complex
(after Riley and Seff⁴).



Dia.7(iv). Stereoview of the $\text{Co}_4\text{Na}_4\text{A}$ -acetylene Sorption Complex
(after Riley and Seff⁴).

the gaseous value. Comparable with the findings for the Na_{12}A -acetylene system, the acetylenic carbon atoms were located at distances from the

transition metal ions in the manganese and cobalt complexes of 2.63 Å and 2.54 Å respectively (dia.7(v)). Also closely following the study of the sorption complex of sodium type A zeolite,¹ the nearest C-H---O approach was determined to be at least 3.0 Å, and hence the possibility of bonding between acetylene and the framework was considered unlikely.



Dia.7(v). Co-ordination Environments of Mn(II) and Co(II) in the $\text{Mn}_{4.5}\text{Na}_3\text{A}$ and $\text{Co}_4\text{Na}_4\text{A}$ -acetylene Sorption Complexes (after Riley and Seff⁴).

2. Spectroscopic Investigations of Zeolite-Acetylene Adsorption Systems

Whilst spectroscopic studies have not been carried out of acetylene adsorbed on silver exchanged type A zeolite, infrared and Raman data are available for the Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} exchanged type A zeolite-acetylene systems,⁸ and for the Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} and Ba^{2+} exchanged type 13X zeolite-acetylene systems.⁹

In both the investigations above, samples were heated to an ultimate temperature of 500°C in 300 mmHg of oxygen (in order to "burn out fluorescence"), before evacuation at room temperature to 10^{-6} Torr. After adsorption of acetylene to 650 mmHg, all spectra were recorded at ambient temperature,

except for Raman measurements of the lithium exchanged zeolites (where liquid nitrogen temperature was necessary in order to prevent laser-induced desorption of acetylene).

Considering firstly the study involving type A zeolites,⁸ it was found that complete desorption of acetylene from the Ca^{2+} and Mg^{2+} exchanged forms could be achieved by evacuation for five minutes at room temperature. In the case of Na_{12}A , the length of time required had to be increased to one hour, whilst for $\text{K}_{7.67}\text{Na}_{4.23}\text{A}$, heat treatment at 200°C was necessitated for "several hours".

In no spectrum were bands located which could be attributed to cation-acetylene interaction. The study of the interaction process was therefore restricted to consideration of changes which were seen to have taken place between the vibrational spectra of the adsorbed and gaseous acetylene molecules (Table 7.1).

On zeolites exchanged with sodium and calcium, the mutual exclusion principle was found no longer to apply to the acetylene molecule, with all five fundamental frequencies observable in both infrared and Raman spectra. The lowering of the $\text{D}_{\infty\text{h}}$ symmetry of the molecule thus implied, and the change in frequency of ν_2 in the spectra of the adsorption complexes (compared with acetylene gas), were taken to indicate that bonding to the surface had taken place. However, the shift in ν_2 was not considered sufficiently large as to suggest that the acetylene molecule had ceased to be linear.

Two modes of interaction are conceivable for acetylene adsorbed on zeolites: "end on" via hydrogen bonding between the acidic protons of the acetylene molecule and framework oxygen atom, and "side on" resulting from overlap of acetylene's π system with a cation. Studies of acetylene on alumina have shown both schemes to exist,¹⁵ "end on" interaction giving rise to an increase in the frequency of the $\text{C}\equiv\text{C}$ stretching mode relative to gaseous

TABLE 7.1 The Frequencies (cm^{-1}) of Acetylene in Various Phases Compared with those Reported for Various Cation Exchanged Type A Zeolite-acetylene Complexes (after Tam et al.⁸).

Mode ¹⁰	Vibration	Activity	Acetylene			Zeolite				
			Gas ¹⁰	Liquid ¹¹	Crystal ¹²⁻¹⁴	Li _{9.65} Na _{2.35} A	Na ₁₂ A	K _{7.67} Na _{4.33} A	Mg _{3.1} Na _{5.8} A	Ca _{4.15} Na _{3.7} A
ν_1	$\nu(\text{C-H})$	R	3374	3341	3324	-	3321	3310	-	3327
ν_2	$\nu(\text{C}\equiv\text{C})$	R	1974	1961	1956	1957	1953	1951	1956	1957
ν_3	$\nu(\text{C-H})$	IR	3287	-	3226	-	3205	-	-	3214
ν_4, ν_4'	$\delta(\text{H-C}\equiv\text{C})$	R	612	630	626	-	642	-	-	640
ν_5, ν_5'	$\delta(\text{H-C}\equiv\text{C})$	IR	729	-	760	-	760	-	-	750

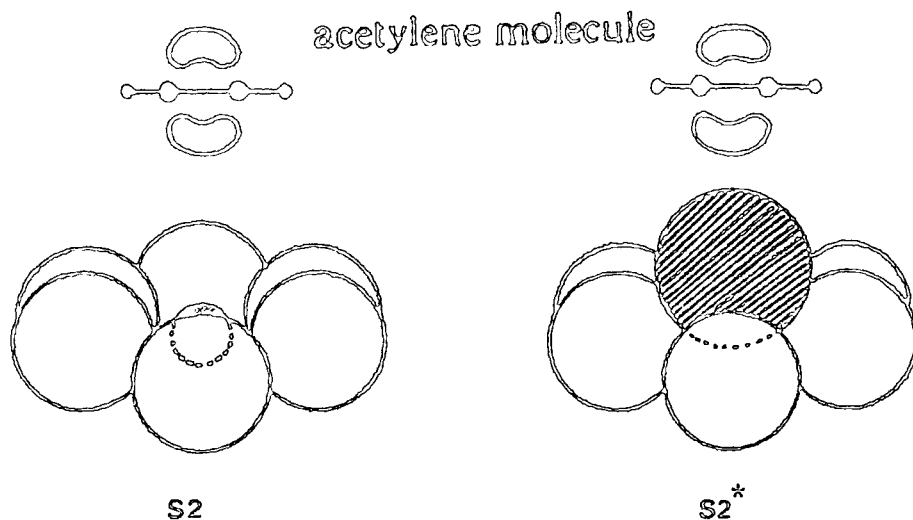
acetylene, and "side on" causing a reduction in frequency. In the type A zeolite-acetylene systems studied by Tam et al.,⁸ there was a universal lowering in frequency of the ν_2 mode indicating "side on" interaction. This is of course in accord with the X-ray structural data of Amaro and Seff^{1,2} described earlier for acetylene adsorbed on Na_{12}A zeolite, but in contradiction with the work of Tsitsishvili et al.¹⁶ These authors, in their infrared investigation of C_2H_2 and C_2D_2 adsorbed on Co^{2+} , Ni^{2+} , Mn^{2+} , Na^+ , Ca^{2+} and H^+ exchanged type A and Co^{2+} , Ni^{2+} and Mn^{2+} exchanged type X zeolites, found no ν_2 vibration, and this, together with the frequencies they recorded for ν_3 , caused them to postulate "end on" interaction.

From the relative lowering in frequency of ν_2 between the gaseous state and adsorption complex ($\Delta\nu_2$), the strength of the cation-acetylene interaction may be seen. This is a function of at least three variables:⁸

- (i) the extent of the shielding of the cation by the framework.
- (ii) the repulsion between the acetylene π system and the negatively charged framework.
- (iii) the electrostatic attraction between the π orbitals of acetylene and the cation.

The increase in $\Delta\nu_2$ on going from Li^+ to Na^+ and to K^+ exchanged forms of zeolite A (Table 7.1) was therefore reasoned to result from cations of larger ionic radius being increasingly less well screened (either within the same site (dia.7(vi)) or by occupation of alternative sites of lower shielding), as the trend was plainly contrary to the order of polarisation power.

For the Na_{12}A adsorption system,⁸ ν_2 appeared distinctly asymmetric in the Raman spectrum, enabling the band contour to be resolved into peaks at 1954 cm^{-1} and 1949 cm^{-1} , that at 1954 cm^{-1} being the more intense. This result was again believed to be in agreement with the X-ray work of Amaro and Seff,^{1,2} in which two or possibly three different adsorption sites were located, and it was suggested that the less intense



Dia.7(vi). Diagrammatic Representation of the Limiting Cases for the Interaction of Acetylene with the Cation Site S2 of a Type A Zeolite (after Tam et al.⁸).

band probably resulted from interaction of acetylene with the energetically more favourable site S1 cations, whilst the higher frequency peak represented interaction involving site S2* cations.

A normal coordinate analysis⁸ was attempted on the Na_{12}A and $\text{Ca}_{4.15}\text{Na}_{3.7}\text{A}$ systems assuming a 1:1 interaction between cation and adsorbed species. The force constants between the cation and acetylene were chosen arbitrarily in each case, and their influence tested on the in-plane stretching modes which were considered to be the most sensitive. From these calculations, frequencies of 46 cm^{-1} (Na_{12}A) and 41 cm^{-1} ($\text{Ca}_{4.15}\text{Na}_{3.7}\text{A}$) were obtained for acetylene-cation vibrational interactions. However, these must necessarily be of doubtful accuracy as they have been derived from observed frequencies which were very much larger.

Similar results were reported for parallel studies of acetylene adsorbed on exchanged type 13X zeolites,⁹ although all Raman spectra of these systems proved to be of much lower intensity than their type A equivalents, allowing only ν_2 to be observed. Once more, the activity of ν_2 in the infrared spectrum showed interaction to have taken place, and as before bond strength

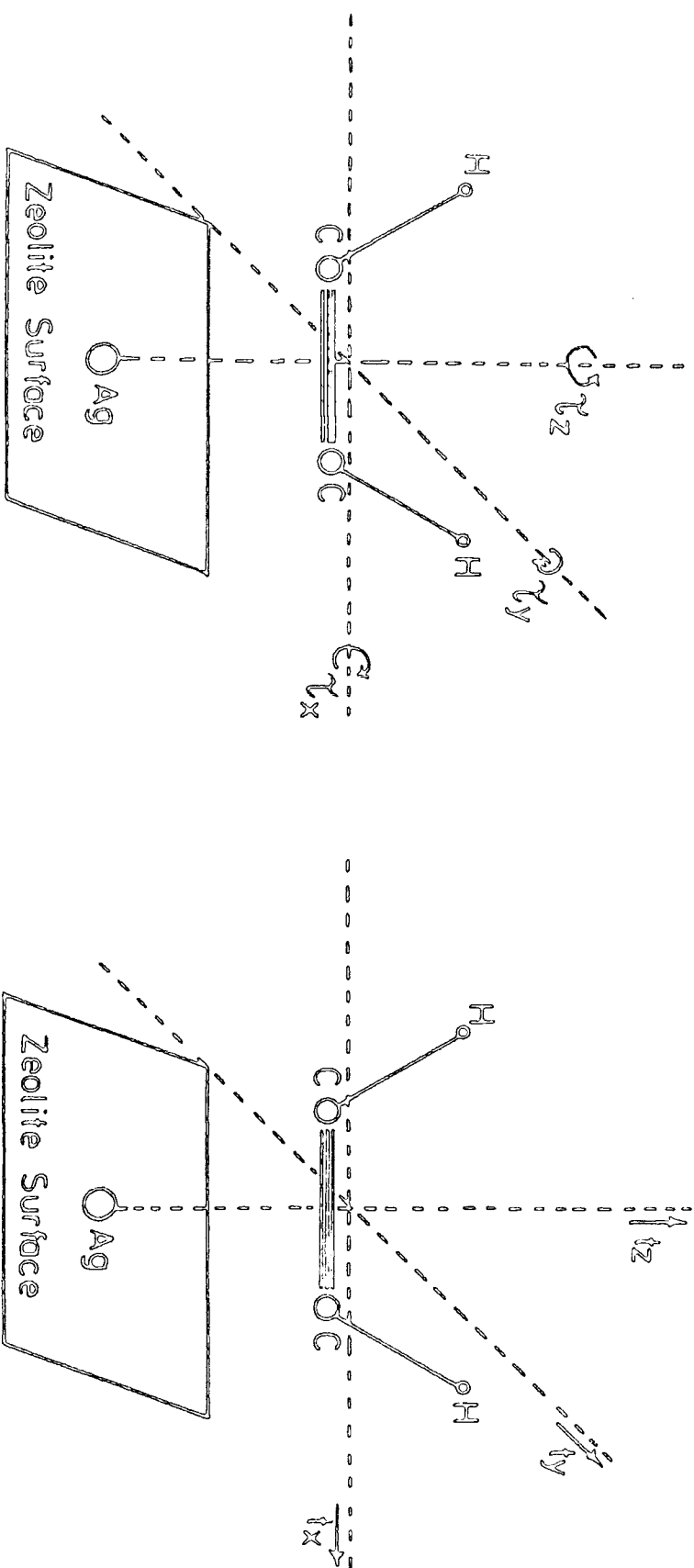
could be correlated both with the shift of ν_2 to lower frequency, and presumed cation screening effects (Table 7.2). It was thus concluded that the increased shifts ($\Delta\nu_2$) observed for the alkali metal-exchanged type 13X zeolite systems (in the order $\text{Na}^+ \rightarrow \text{K}^+ \rightarrow \text{Cs}^+$) were indicative of the increased placement of cations (of successively greater ionic radius) within poorly screened site II* and III positions; whilst the values for the alkaline earth metal and lithium-exchanged zeolites were representative of the situation of well shielded cations within site II' locations. (There is a discussion of cation locations in type 13X zeolites, and the nomenclature associated with them, in Chapter VI.)

Table 7.2 Correlation of Ionic Radius with the Frequency (cm^{-1}) of the ν_2 Mode for a Series of Cation Exchanged Type 13X Zeolite-acetylene Systems.⁹

Cationic Form of the Type 13X Zeolite	% ion exchange	Cationic radius ⁷ (Å)	ν_2 (cm^{-1})
Li^+	60	0.60	1958
Na^+	-	0.95	1954
K^+	90	1.33	1952
Cs^+	70	1.69	1951
Mg^{2+}	54	0.65	1956
Ca^{2+}	87	0.99	1958
Ba^{2+}	87	1.35	1956

As seen in the investigation involving Na_{12}A ,⁸ ν_2 in the spectrum of the Na 13X-acetylene complex⁹ was found to display asymmetry to lower wavenumber. This was again ascribed to acetylene interaction taking place on two sites, in this case the lower frequency band being assigned to site III interaction.

A complementary INS study to that undertaken of the Ag13X-ethylene system¹⁷⁻¹⁹ has been made of acetylene adsorbed on Ag13X zeolite.^{19,20}



dia. 7 (vii). The three hindered rotations, τ_x , τ_y (antisymmetric stretch) and τ_z , and the three hindered translations, t_x , t_y and t_z (symmetric stretch) of acetylene relative to the zeolite surface.

TABLE 7.3 Reported INS Vibrational Frequencies (cm^{-1}) for C_2H_2 and C_2D_2 Adsorbed on Silver 13X Zeolite^{19,20}

Observed C_2H_2 Frequencies	C_2D_2 Frequencies		Assignments	Ratio of Observed Frequencies	Predicted Ratio of Frequencies	
	Predicted	Observed			Non-linear	Linear
T-O-F BFD 27 $\pm$ 1.5 53.5 $\pm$ 2.5	23 $\pm$ 1.2 45.5 $\pm$ 2	T-O-F BFD 24 $\pm$ 1.5 46 $\pm$ 2.5	τ_z	0.89 $\pm$ 0.11	0.850	0.849
			τ_z	0.86 $\pm$ 0.08	0.850	0.849
			τ_z ?		0.964	0.964
			τ_y	0.75 $\pm$ 0.15	0.850	0.849
86 $\pm$ 14 150 $\pm$ 14	83 $\pm$ 13 127.5 $\pm$ 12	102 $\pm$ 6 113 $\pm$ 14 (300?)				
523 $\pm$ 14 673 $\pm$ 14 794 $\pm$ 14	384 $\pm$ 10	380 $\pm$ 14 584 $\pm$ 14	τ_x	0.73 $\pm$ 0.05	0.734	Indeterminate
			Intramolecular modes ν_4 and ν_5			

Zeolite samples were prepared analogously to those of the ethylene study and spectra measured at one overpressure (40 Torr) of acetylene (C_2H_2 and C_2D_2).

In view of the small amount of spectroscopic data available for simple complexes containing acetylene, and the complete absence of any INS studies, known INS data for ethylene-containing complexes^{18,19,21-23} and the Ag13X-ethylene¹⁷⁻¹⁹ system were used as guidance in assignment. Vibrational analysis was also assisted by predicted intensity relationships and deuteration shifts calculated on the basis of two models²⁰ for the adsorbed acetylene molecule; (i) linear and (ii) with an $\hat{HCC}$ bond angle of 170° .

Frequencies were identified corresponding to the three torsional vibrations, τ_x , τ_y and τ_z , of acetylene relative to the surface, and to the hindered translation t_z (dia.7(vii) and Table 7.3). Similarly to the high coverage ethylene-Ag13X complex,^{18,19} splitting (through interaction between neighbouring sites) was observed of the torsional mode, τ_z , of acetylene about an axis drawn between the cation and the centre of the $C\equiv C$ bond. Proof of the non-linearity of the acetylene molecule in the complexed form was furnished by the appearance of τ_x in the INS spectrum.

Investigation was also attempted of the Na13X-acetylene system^{19,20} but (as had been previously found with INS studies of the Na13X-ethylene system^{18,19}) resolution proved poor and no conclusions could be drawn, save that acetylene was probably linear in this complex, and that the diffusive motion of acetylene adsorbed on the surface of sodium 13X zeolite was not as marked as for ethylene.

B. Experimental

Ag₁₂A zeolite was prepared and degassed as described in Chapter VI. Upon dehydration, the zeolite powder was transferred, under vacuum, into an aluminium sample cell (Chapter III), and the INS spectrum of the cell plus zeolite measured for use as a "background". Acetylene gas, either

cylinder C_2H_2 (> 99.9% purity) or C_2D_2 supplied by Merck, Sharp and Dohme Ltd. (99 atom % D), was then admitted into the sample cell (at room temperature) via a glass breaker seal, and adsorbed at an over-pressure of approximately 450 Torr. After adsorption was complete, the cell and zeolite were evacuated to "backing-pump pressure" (typically for a couple of minutes) and the spectrum re-measured.

The experimental details relating to the recording of the INS spectra of the $Ag_{12}A$ -acetylene adsorption system are summarised below:

Gas	"Backing-Pump Pressure"/ Residual Over-pressure of Gas	Instrument	Temperature
C_2H_2	0.01 Torr	6H	153 K
C_2H_2	0.10 Torr	Dido BFD	18 K
C_2D_2	0.15 Torr	4H5	118 K
C_2D_2	0.10 Torr	Pluto BFD	liq. N_2

Except where stated specifically to the contrary, all spectra shown in this chapter have had a background corresponding to the sample cell plus dehydrated $Ag_{12}A$ zeolite subtracted.

Peak resolution and the measurement of INS intensities have been carried out using a Du Pont Curve Resolver. Assuming the backgrounds indicated ---- on the spectra, Gaussians have been placed, in the first instance at observed transitions, but where necessary at energies indicated from the form of the total bandshape. The peak areas thus generated have been varied to achieve a "best fit" with the overall band profile, and the resultant intensity ratio measured. This has then been compared (directly in the case of ratios obtained from BFD spectra, but after suitable correction for " Q^2 " and frequency in the case of values derived from T-O-F data (Chapter II)) with the intensity ratios predicted on the basis of the suggested assignments.

C. Discussion of Results

The two lowest frequency internal vibrations of solid phase C_2H_2 have been located at respectively $747.5-768.8\text{ cm}^{-1}$ (ν_5 , infrared)¹² and ca. 626 cm^{-1} (ν_4 , Raman).¹⁴ Similarly, for solid C_2D_2 , infrared spectra have shown the ν_5 band to be present in the region $552.4-567.5\text{ cm}^{-1}$, and $2\nu_4$ to occur at 1057.5 cm^{-1} .¹² To lower frequencies, measurements carried out on polycrystalline acetylene have indicated that the highest energy lattice vibrations active in the infrared spectrum are situated at 122 cm^{-1} (C_2H_2) and 118 cm^{-1} (C_2D_2),²⁴ whilst Raman data (for crystalline C_2H_2 only) have established the existence of an additional lattice mode at 171.7 cm^{-1} .¹⁴ From the preceding, it appears reasonable to assume that vibrations observed in the INS spectra of the Ag_{12}^A -acetylene adsorption system above ca. 200 cm^{-1} , but below approximately 550 cm^{-1} for studies involving C_2H_2 (or below approximately 450 cm^{-1} in the case of investigations employing C_2D_2), must correspond to modes of the acetylene molecule relative to the surface. In order to aid identification of such vibrations, use will be made of predicted intensity ratios and deuteration shifts calculated primarily on the basis of three models for the adsorbed acetylene molecule:

- (i) a linear form (structural data from the crystalline state)²⁵
- (ii) the structure postulated by Iwashita for the C_2H_2 moiety in the complex $Co_2(CO)_6 \cdot C_2H_2$.²⁶
- (iii) the geometry assumed by Howard and Waddington for C_2H_2 adsorbed on $Ag13X$ zeolite.^{19,20}

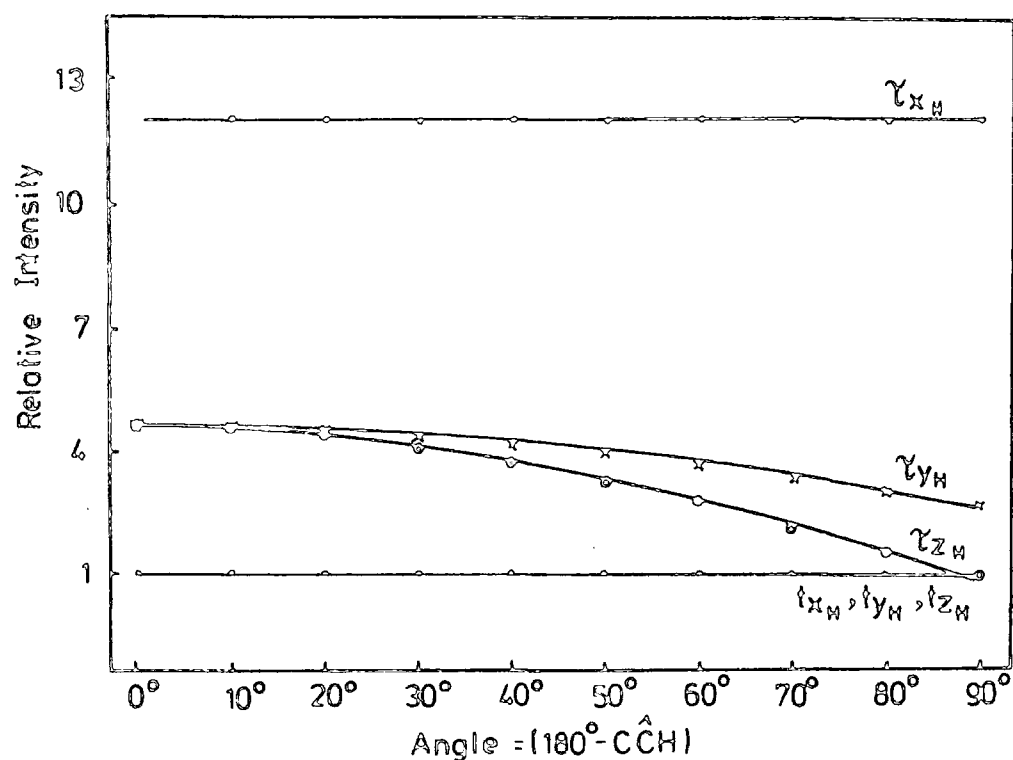
Furthermore, in view of the lack of definite information concerning the configuration actually adopted by the acetylene molecule adsorbed on Ag_{12}^A zeolite, additional data relating to deuteration shifts and intensity ratios have been calculated from the latter two models employing the bond length parameters originally assumed, but with various values substituted for the $\hat{CCH}$ bond angle. This information is given in Tables 7.4 and 7.5 and is represented graphically in dias.7(viii)-(xi).

TABLE 7.4 The Deuteration Shifts and Intensity Ratios Predicted for Acetylene Adsorbed on Ag₁₂ A Zeolite

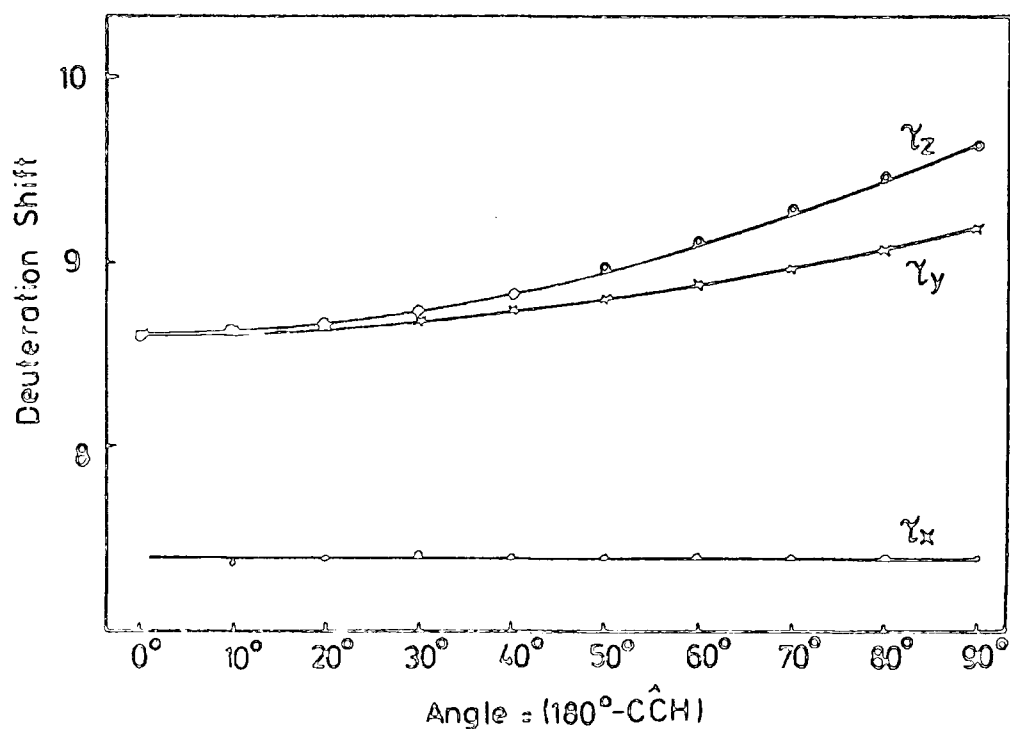
Based Upon the "Iwashita Model"*

Angle = 180°-C [^] CH	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Deuteration Shift	T _x	-	0.737	0.740	0.742	0.740	0.741	0.741	0.741	0.741
	T _y	0.862	0.863	0.866	0.869	0.874	0.884	0.881	0.889	0.897
	T _z	0.862	0.864	0.868	0.874	0.884	0.896	0.911	0.928	0.946
Intensity Ratio C ₂ H ₂	t	0.964	0.964	0.964	0.964	0.964	0.964	0.964	0.964	0.964
	T _x	-	12.046	12.045	11.989	12.017	11.987	11.998	12.002	11.996
	T _y	4.583	4.557	4.473	4.336	4.148	3.913	3.635	3.321	2.979
Intensity Ratio C ₂ D ₂	T _z	4.583	4.530	4.364	4.091	3.716	3.250	2.711	2.126	1.542
	t	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Intensity Ratio C ₂ D ₂	T _x	-	5.948	6.015	6.013	6.005	6.003	6.004	5.996	5.994
	T _y	3.629	3.609	3.547	3.448	3.308	3.130	2.918	2.677	2.411
	T _z	3.629	3.600	3.498	3.334	3.096	2.785	2.403	1.960	1.479
	t	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

* The Iwashita Model²⁶ assumes the bond length of C≡C to be 1.388 Å and that of C-H to be equal to 1.08 Å. In the above table these parameters have been retained, but various values for the bond angle C[^]CH have been substituted in place of the 120° originally postulated. In addition the bond length C-D has been taken to be 0.01 Å shorter than C-H.



dia.7(viii) The Variation of Intensity Ratio with Bond Angle $\hat{CCH}$ Found for C_2H_2 Using the Model for the Adsorbed Acetylene Molecule based upon that of Iwashita.²⁶

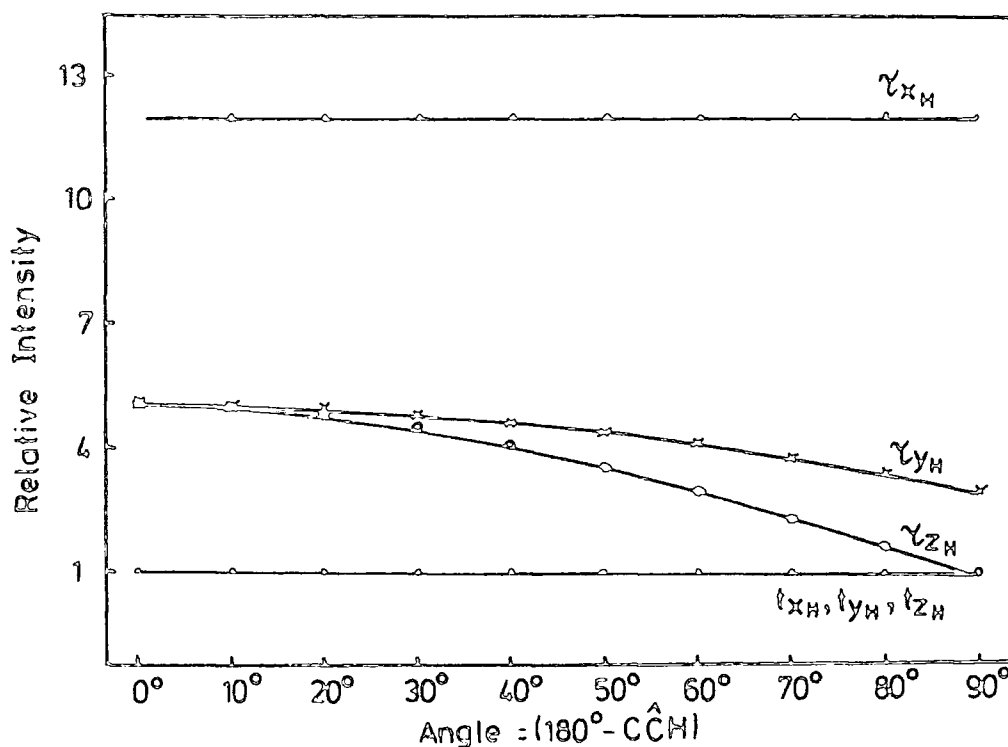


dia.7(ix) The Variation of Deuteration Shift with Bond Angle $\hat{CCH}$ Found Using the Model for the Adsorbed Acetylene Molecule based upon that of Iwashita.²⁶

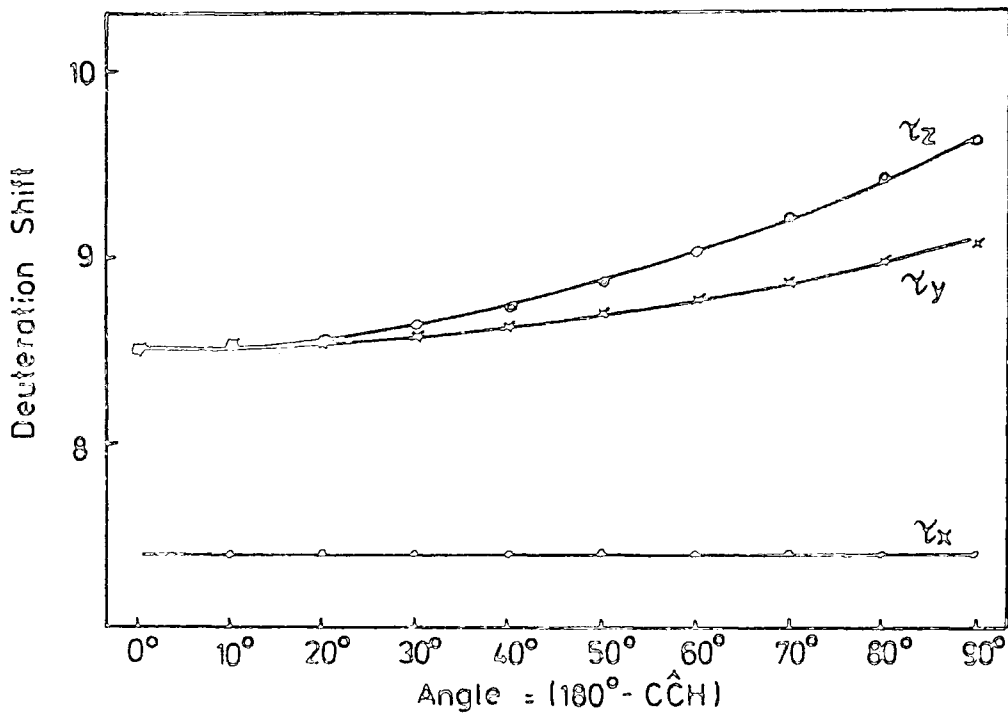
TABLE 7.5 The Deuteration Shifts and Intensity Ratios Predicted for Acetylene Adsorbed on Ag₁₂ A Zeolite
Based Upon the Model of Howard and Waddington*

Angle = 180°-CCH	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Deuteration Shift	τ_x	-	0.740	0.742	0.741	0.741	0.740	0.741	0.741	0.741
	τ_y	0.851	0.852	0.854	0.858	0.863	0.870	0.878	0.887	0.908
	τ_z	0.851	0.853	0.857	0.864	0.874	0.887	0.904	0.923	0.964
	ϵ	0.964	0.964	0.964	0.964	0.964	0.964	0.964	0.964	0.964
Intensity Ratio C ₂ H ₂	τ_x	-	12.022	12.008	11.979	12.017	12.017	11.988	11.993	12.009
	τ_y	5.063	5.034	4.947	4.803	4.607	4.360	4.067	3.740	3.379
	τ_z	5.063	5.003	4.822	4.522	4.105	3.579	2.966	2.297	1.619
	ϵ	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Intensity Ratio C ₂ D ₂	τ_x	-	5.977	6.009	6.000	6.009	5.998	5.998	6.000	5.996
	τ_y	3.903	3.882	3.820	3.714	3.571	3.388	3.171	2.924	2.651
	τ_z	3.903	3.870	3.768	3.592	3.340	3.006	2.586	2.090	1.545
	ϵ	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

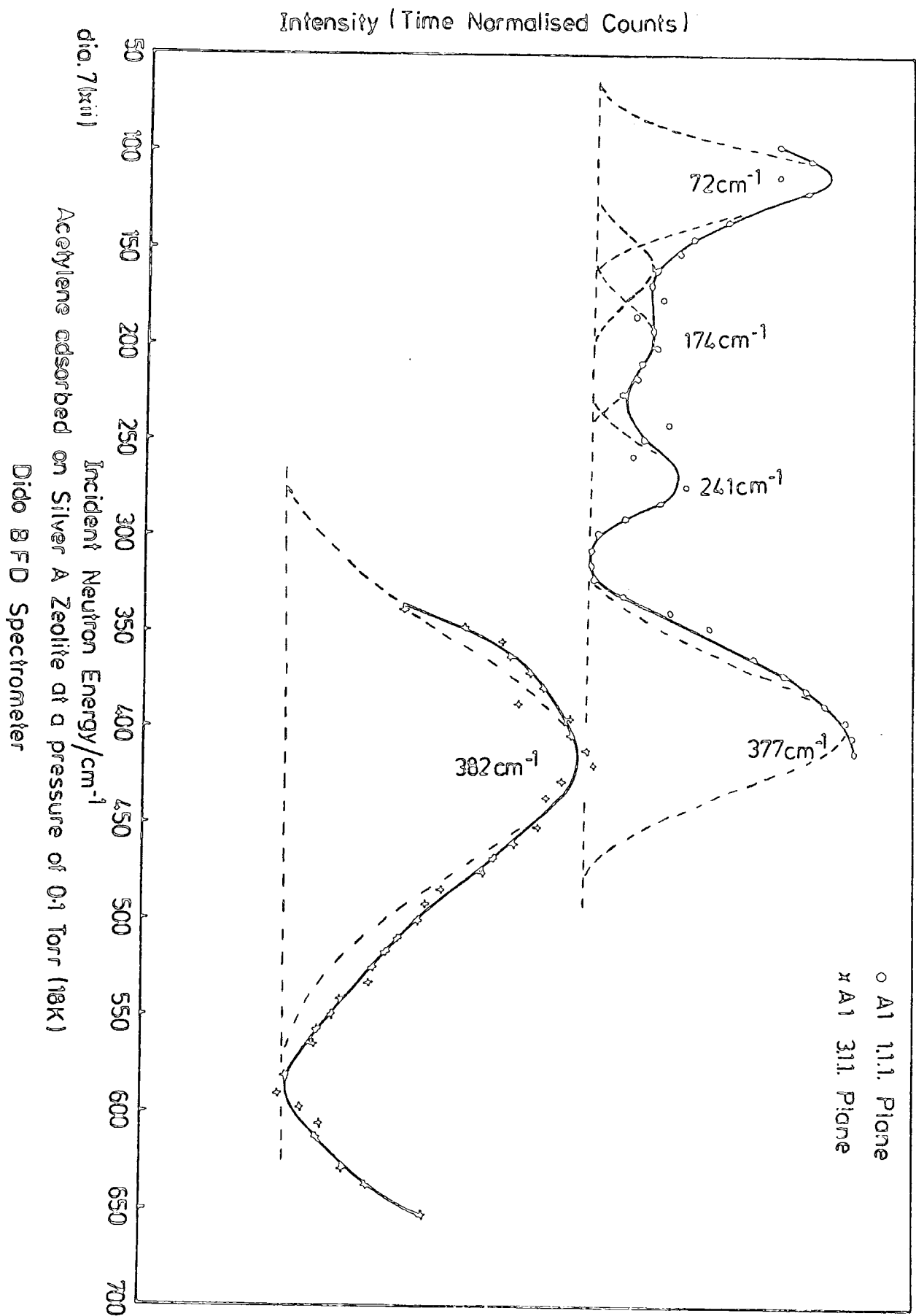
* The model of Howard and Waddington^{19,20} assumes the bond length of C≡C to be 1.20 Å, and that of C-H to be equal to 1.06 Å. In the above table these parameters have been employed, but various values for the bond angle CCH have been substituted in place of the 170° originally postulated. In addition, the bond length C-D has been taken to be 0.01 Å shorter than C-H.



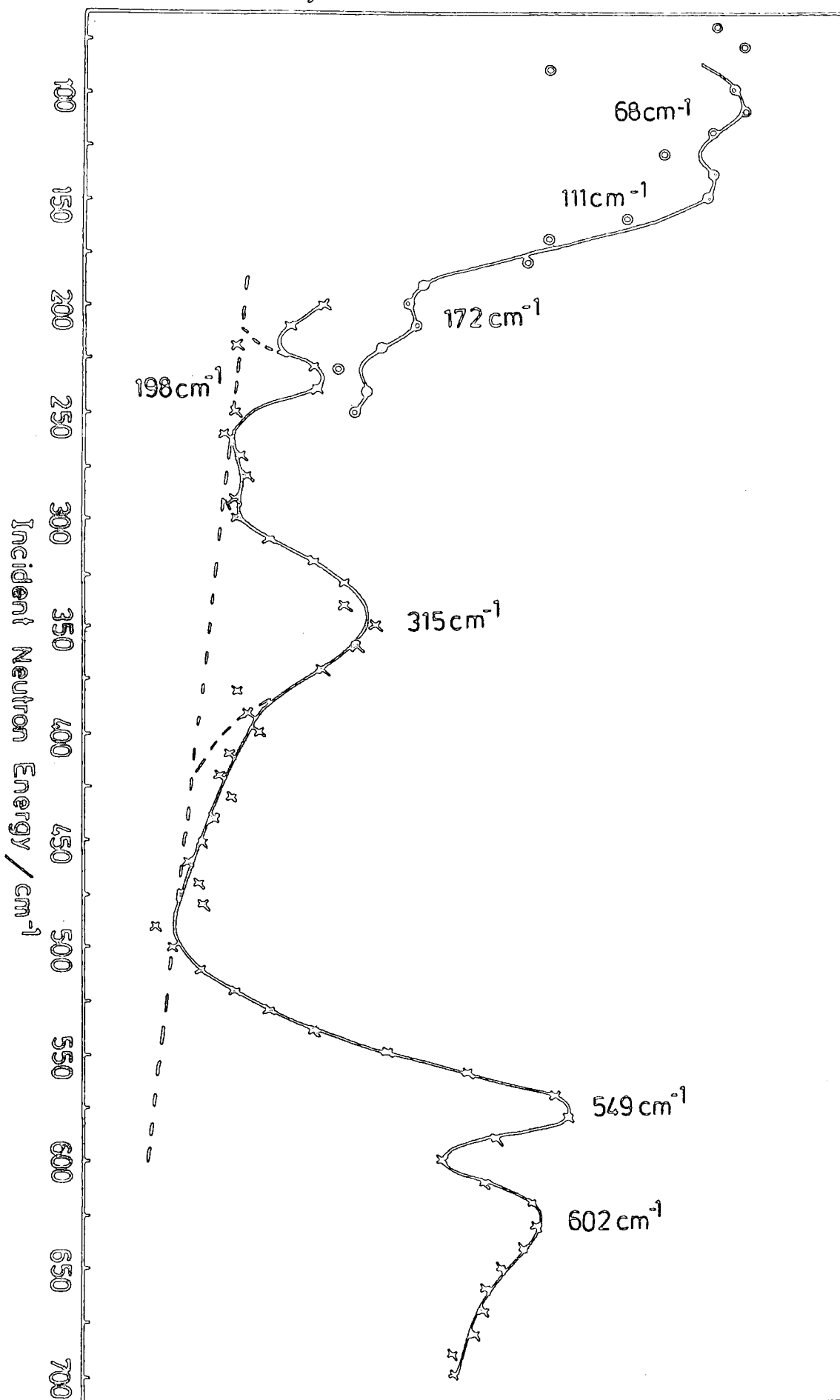
dia.7(x) The Variation of Intensity Ratio with Bond Angle $\hat{CCH}$ Found for C_2H_2 Using the Model for the Adsorbed Acetylene Molecule based upon that of Howard and Waddington.^{19,20}



dia.7(xi) The Variation of Deuteration Shift with Bond Angle $\hat{CCH}$ Found Using the Model for the Adsorbed Acetylene Molecule based upon that of Howard and Waddington.^{19,20}

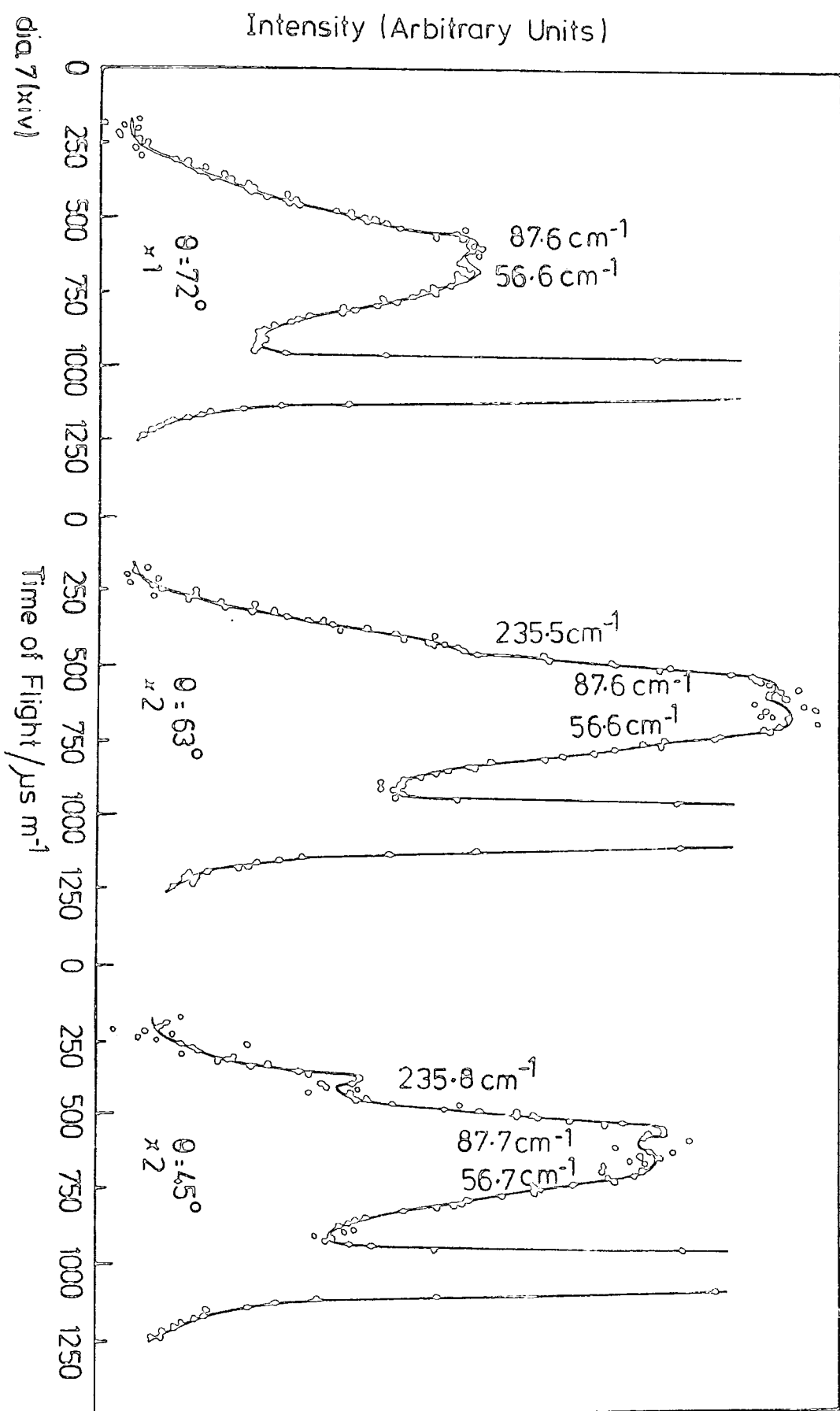


Intensity (Monitor Counts)

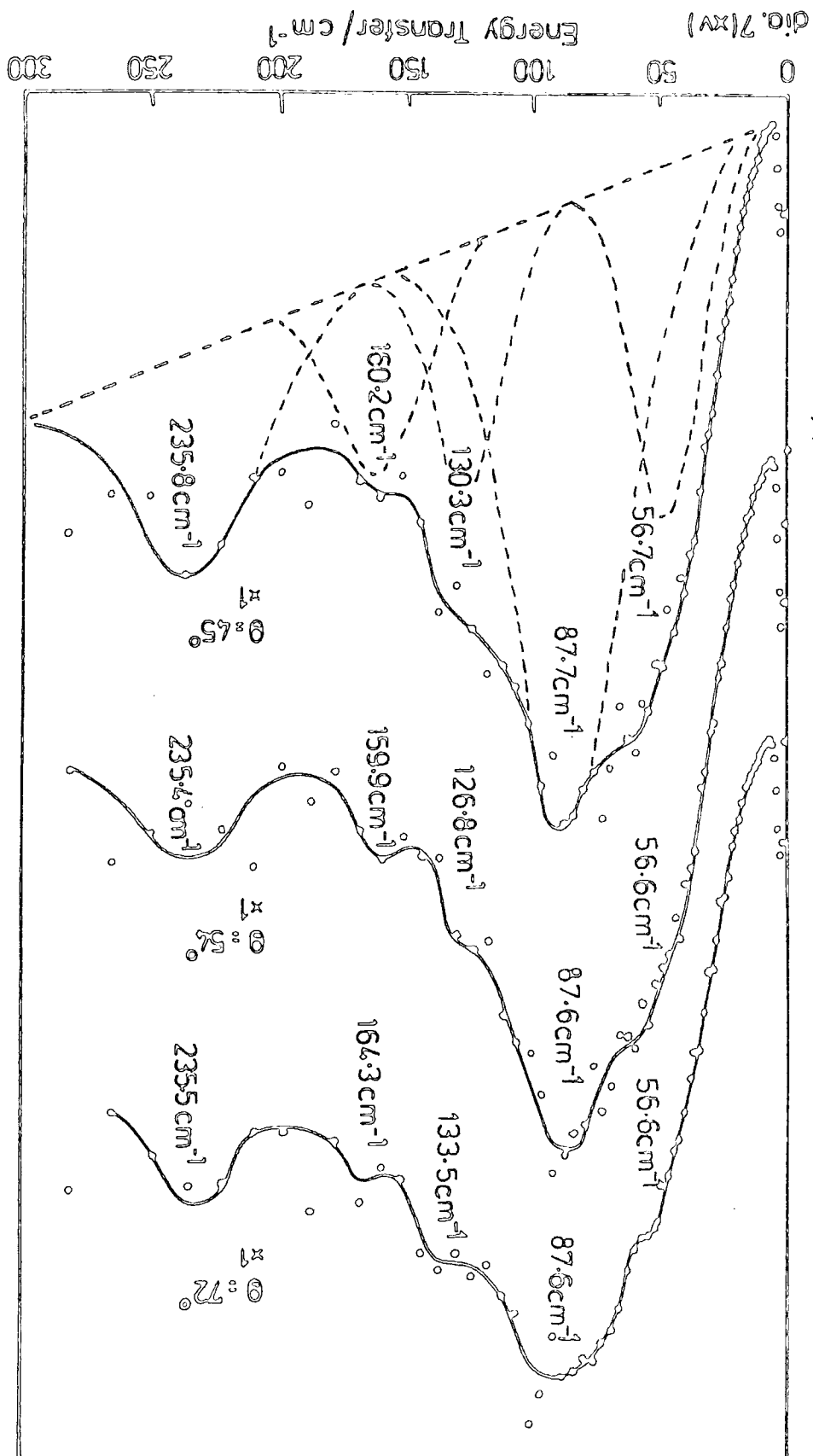


dia 7 (xiii) Perdeuterio - acetylene adsorbed on Silver A Zeolite at a pressure of 0.1 Torr
Pluto BFD Spectrometer: liquid nitrogen temperature

Acetylene adsorbed on Silver A Zeolite at a pressure of 10^{-2} Torr (153K)
 6H Time-of-Flight Spectrometer.



$P(\alpha, \beta)$ (Arbitrary Units)



Acetylene adsorbed on Silver A Zeolite
at a pressure of 10^{-2} Torr (153 K)
64 Time-of-Flight Spectrometer.

Perdeutero-octylene adsorbed on Silver A Zeolite at a pressure of 0.15 Torr (118K)
 4H5 Time-of-Flight Spectrometer

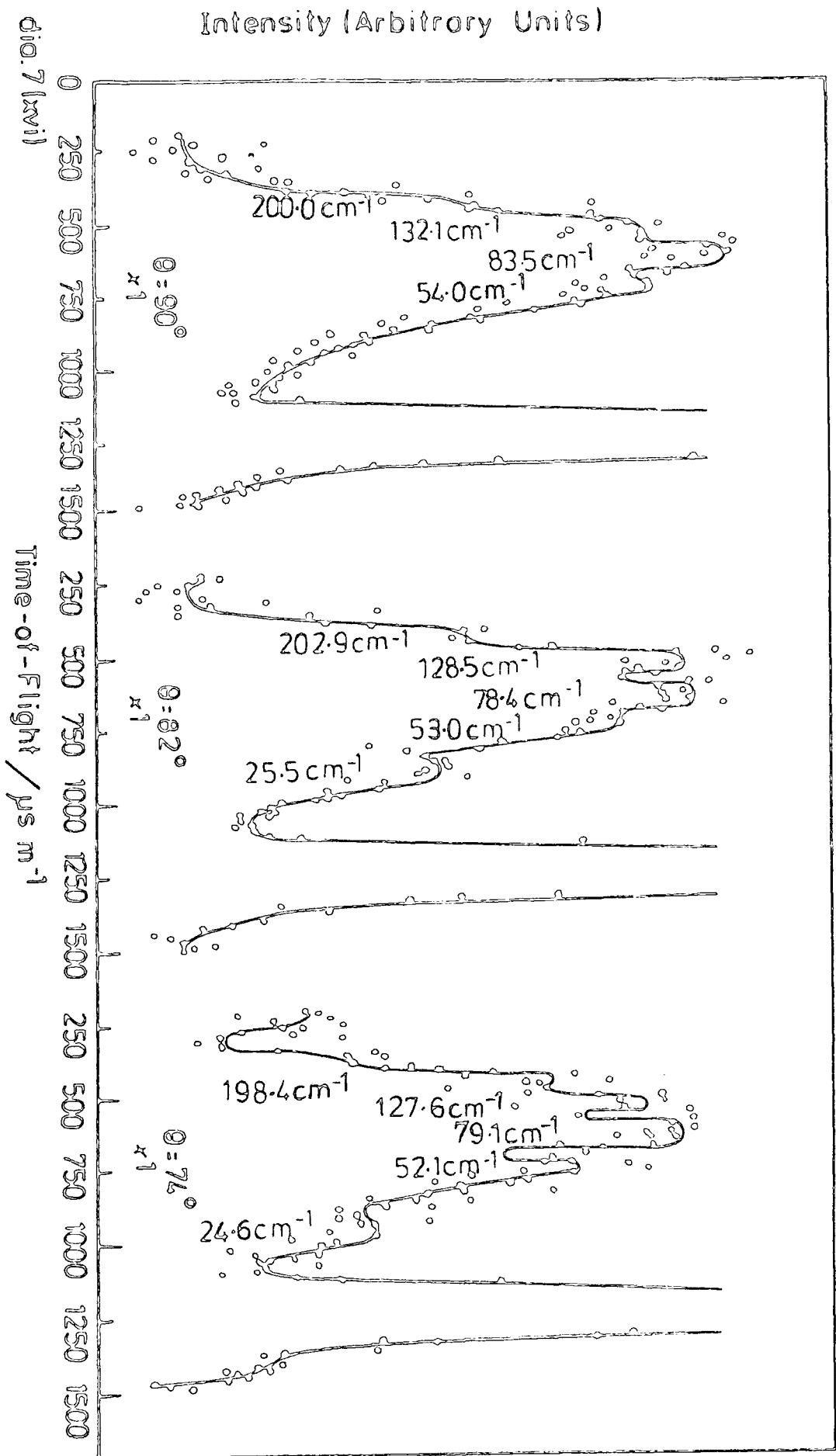


TABLE 7.6 The Spectroscopic Frequencies (cm^{-1}) and Assignments For Acetylene Adsorbed on Ag_{12} Zeolite

Frequencies		Observed Deuteration Shift	Predicted Deuteration Shift*	Predicted Deuteration Shift†	Predicted Deuteration Shift‡	Assignment
C_2H_2 BFD	C_2D_2 BFD T-O-F					
382/377 $\pm$ 8	602 $\pm$ 10	0.825 $\pm$ 0.044/ 0.836 $\pm$ 0.045 0.822 $\pm$ 0.071/ 0.851 $\pm$ 0.104	Indeterminate	0.741	0.740	} Internal acetylene vibrations } ν_5 ν_4
	549 $\pm$ 10					
	315 $\pm$ 10					
	198 $\pm$ 10					
241 $\pm$ 8	235.5 $\pm$ 14.5	0.822 $\pm$ 0.071/ 0.851 $\pm$ 0.104	0.852	0.889	0.852	τ_y
174 $\pm$ 8	161.0 $\pm$ 9.5	0.989 $\pm$ 0.121	0.964	0.964	0.964	τ_z
72 $\pm$ 8	130.0 $\pm$ 7.5	0.996 $\pm$ 0.110	0.964	0.964	0.964	τ
	87.5 $\pm$ 4.5	0.920 $\pm$ 0.092	0.852	0.911	0.853	τ_z
	56.5 $\pm$ 3.0	0.938 $\pm$ 0.099	0.964	0.964	0.964	τ
	68 $\pm$ 10					lattice vibration?
	25.0 $\pm$ 1.5					

* Deuteration shift predicted for linear acetylene: the structural parameters used are those for C_2H_2 in the crystalline state,²⁵ but with the additional assumption that the bond length C-D is 0.01 Å shorter than C-H.

† Deuteration shift predicted from the "Iwashita Model" for C_2H_2 complexed in $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ ($\text{C}\equiv\text{C} = 1.388$ Å, $\text{C}-\text{H} = 1.08$ Å and $\angle\text{CCH} = 120^\circ$).²⁶ The additional assumption has been made that the bond length C^*D is 1.07 Å.

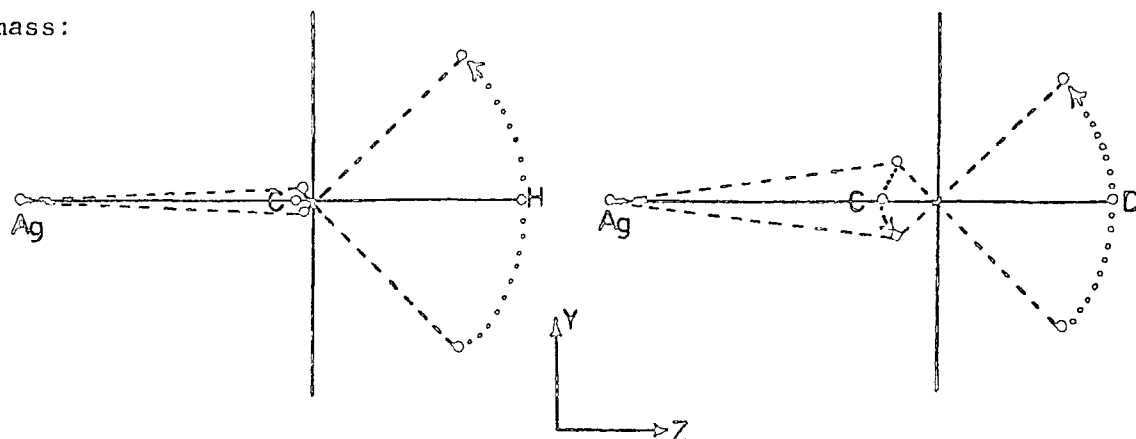
‡ Deuteration shift predicted from the model of Howard and Waddington for acetylene adsorbed on Ag_{13}X zeolite ($\text{C}\equiv\text{C} = 1.20$ Å, $\text{C}-\text{H} = 1.06$ Å, $\text{C}-\text{D} = 1.05$ Å and $\angle\text{CCD} = 170^\circ$).^{19,20}

The INS spectra obtained for the silver A zeolite-acetylene adsorption system are shown in dias.7(xii)-(xvi), and the spectroscopic frequencies derived from these are summarised in Table 7.6.

Considering initially the BFD data (dis.7(xii) and (xiii)), the two highest energy peaks in the spectrum of C_2D_2 adsorbed onto $Ag_{12}A$ zeolite (549 cm^{-1} and 602 cm^{-1}) may be assigned, bearing in mind preceding discussion, to the lowest frequency internal acetylene modes ν_4 and ν_5 respectively. As previously stated, these occur at ca. 529 cm^{-1} and $552.4\text{--}567.5\text{ cm}^{-1}$ ¹² in the infrared spectrum of solid C_2D_2 and thus the movement to higher frequency observed for the bands in the adsorbed species as opposed to the solid phase is in the region of 20 cm^{-1} for ν_4 , and $\sim 50\text{ cm}^{-1}$ for ν_5 . The former shift is approximately of the order reported for C_2H_2 adsorbed on alkali metal and alkaline earth metal-exchanged type A zeolites ⁸ (Table 7.1), whilst the latter increase in frequency is very much greater, and is comparable in magnitude with the shifts of the ν_4 and ν_5 bands found for the $Ag_{13X}\text{-}C_2H_2$ adsorption complex ^{19,20} (Table 7.3).

To lower energy, a transition at 315 cm^{-1} in the BFD spectrum of the $Ag_{12}A$ zeolite- C_2D_2 adsorption system must, in view of the spectral region in which it is located, represent a vibration of acetylene relative to the zeolite surface. Consideration of the work carried out on the complex $Co_2(CO)_6\cdot C_2H_2$ (Chapter V) implies that the highest frequency (and most intense) adsorbate-surface mode would be expected to be τ_x , the torsional mode about an axis running parallel to the $C\equiv C$ bond (dia.7(vii)). Indeed, a similar trend has been noted in INS studies of ethylene and acetylene adsorbed onto Ag_{13X} zeolite, ¹⁸⁻²⁰ and of ethylene adsorbed onto $Ag_{12}A$ zeolite (Chapter VI). Correlation of the 315 cm^{-1} band with that of highest energy, and by far the greatest intensity, in the BFD spectrum of C_2H_4 adsorbed onto $Ag_{12}A$ zeolite ($382/377\text{ cm}^{-1}$), however, gives rise to a deuteration shift of $0.825 \pm 0.044/0.836 \pm 0.045$. This compares unfavourably with the shifts predicted for the τ_x vibration by all models which assume complexed

acetylene to be non-linear (ca. 0.741). Furthermore, the frequency of the $382/377\text{ cm}^{-1}$ peak is considerably less than that assigned to $\tau_{x_H}^\dagger$ in the study of C_2H_2 adsorbed onto Ag13X zeolite (523 cm^{-1}).^{19,20} Conversely, the position of the band is in the region of the spectrum in which the τ_{x_H} mode has been located in INS investigations of C_2H_4 adsorbed onto Ag13X zeolite^{18,19} and Ag_{12}^A zeolite (Chapter VI) (418 cm^{-1} and $417/419\text{ cm}^{-1}$ respectively); whilst evidence from the BFD spectrum of $Co_2(CO)_6 \cdot C_2H_2$ possibly indicates that the τ_x vibration is to be found to lower frequency (797 cm^{-1} , Chapter V) in acetylene complexes than in those containing ethylene, for example Zeise's salt (1180 cm^{-1}) and Zeise's dimer (1176 cm^{-1}).²⁷ Taking into account partly the latter factors, but more especially the great intensity of the $382/377\text{ cm}^{-1}$ peak, it appears that an identification with τ_x is unavoidable (the corollary of this being that the acetylene molecule must be non-linear in the adsorbed state). However, in order to explain the smaller than expected deuteration shift of this mode it must be suggested that there is a larger contribution from carbon motion than would be expected from the simple description of a torsion. Perhaps, this may best be rationalised as the result of rotation of the complexed C_2H_2 and C_2D_2 molecules taking place about different axes as a consequence of their differing centres of mass:



Stylised "Side-on" View of the Acetylene Molecule Co-ordinated Within Ag_{12}^A Zeolite

[†] Surface-acetylene modes involving hydrogenous and deuterated species will be denoted by the respective subscript "H" or "D", e.g. τ_{x_H} will be the vibration τ_x of C_2H_2 .

A peak observed at 241 cm^{-1} in the BFD spectrum of C_2H_2 adsorbed on Ag_{12}A zeolite appears to correlate with a feature situated at 198 cm^{-1} in the spectrum of the deuterated species. The deuteration shift implied is therefore 0.822 ± 0.071 . These bands are also represented in T-O-F data (dias.7(xiv)-(xvi)), at 235.5 cm^{-1} (C_2H_2) and 200.5 cm^{-1} (C_2D_2), the deuteration ratio indicated in this case being 0.851 ± 0.104 . Both deuteration shifts are close to that anticipated of the mode τ_y ($0.852^*/0.889^{\dagger}/0.852^{\dagger\dagger}$).[†] However, the frequency implied for the τ_{y_H} vibration, whilst comparable with those reported for the analogous modes of C_2H_4 adsorbed onto Ag13X zeolite^{18,19} (258 cm^{-1}) and Ag_{12}A zeolite (278 cm^{-1} : Chapter VI), is considerably higher than that identified for C_2H_2 adsorbed onto Ag13X zeolite^{19,20} (150 cm^{-1}). Nevertheless the position of this band in the spectrum is again in broad agreement with INS work carried out on acetylene (Chapter V) and ethylene-containing complexes,^{18,19} in which the τ_y vibration was suggested to be the second highest frequency of the six acetylene/ethylene translational and torsional modes after τ_x .

The intensity ratios of the bands τ_{x_H} (377 cm^{-1}) to τ_{y_H} (241 cm^{-1}) and τ_{x_D} (315 cm^{-1}) to τ_{y_D} (198 cm^{-1}) calculated assuming the backgrounds indicated (----) are 6.750:1.000 and 5.667:1.000, whilst the predicted values for the hydrogenous and deuterated species are $3.300:1.000^{\dagger}/2.388:1.000^{\dagger\dagger}$ and $2.058:1.000^{\dagger}/1.540:1.000^{\dagger\dagger}$ respectively. It may therefore be seen that the observed intensity of the τ_y vibration is considerably less than that anticipated. However, this finding is very much in accordance with the experimental intensities derived from the BFD spectrum of the complex $\text{Co}_2(\text{CO})_6.\text{C}_2\text{H}_2$ (Chapter V), where the τ_y mode was found to be so much weaker than prediction that its intensity was not only the least (rather than the intermediate) of the three torsions, τ_x , τ_y and τ_z , but was also only slightly

[†] In forthcoming discussion, the superscripts *, $\dagger$ and $\dagger\dagger$ will refer to the deuteration shifts or intensity ratios predicted on the basis of the three models for the co-ordinated acetylene molecule, that is (i) a Linear Geometry,²⁵ (ii) the configuration of Iwashita²⁶ and (iii) the structure of Howard and Waddington.^{19,20}

greater than those of the translational modes, t_x , t_y and t_z .

Similarly, with ethylene-containing complexes, for example Zeise's salt and dimer,^{18,19} the antisymmetric stretch of the ethylene molecule relative to the platinum atom (τ_y) has been seen to display intensity comparable with that of the symmetric stretch (t_z), rather than the greater intensity predicted (Chapter V).

The remaining bands in the BFD spectra of C_2H_2 and C_2D_2 adsorbed onto $Ag_{12}A$ zeolite are perhaps best considered in conjunction with the T-O-F data (dias.7(xiv)-(xvi)) in which they are better resolved. Unfortunately, the failure to obtain a reasonable $P(\alpha, \beta)$ spectrum for adsorbed C_2D_2 tends to preclude a discussion of the relative intensities of the transitions observed for this species in the long wavelength region. Indeed, it is necessary to treat all frequencies derived for adsorbed C_2D_2 from neutron energy gain spectra as being somewhat less accurate than those stated for C_2H_2 , as a result of the difficulty experienced when reading peak positions from a Time-of-Flight scale.

The T-O-F results permit resolution of the second most intense feature in the BFD spectrum of the $Ag_{12}A$ zeolite- C_2H_2 adsorption system (72 cm^{-1}) into three bands, namely those situated at $56.5 \pm 3.0\text{ cm}^{-1}$, $87.5 \pm 4.5\text{ cm}^{-1}$ and $130.0 \pm 7.5\text{ cm}^{-1}$. Likewise, in the case of C_2D_2 adsorbed onto $Ag_{12}A$ zeolite, the BFD peak at 68 cm^{-1} may be seen to result from frequencies of $25.0 \pm 1.5\text{ cm}^{-1}$, $53.0 \pm 2.5\text{ cm}^{-1}$ and $80.5 \pm 3.5\text{ cm}^{-1}$, whilst a band equivalent to that observed at 111 cm^{-1} in the BFD spectrum may be distinguished at $129.5 \pm 6.0\text{ cm}^{-1}$. It seems reasonable to correlate the three peaks derived from the T-O-F spectrum of the hydrogenous species with the three highest energy modes observed in the comparable C_2D_2 spectrum. The deuteration shifts thus indicated are 0.938 ± 0.099 ($56.5 \rightarrow 53.0\text{ cm}^{-1}$), 0.920 ± 0.092 ($87.5 \rightarrow 80.5\text{ cm}^{-1}$) and 0.996 ± 0.110 ($130 \rightarrow 129.5\text{ cm}^{-1}$). Both the former and latter shifts are of a magnitude similar to those anticipated for translational modes of the

acetylene molecule relative to the surface (0.964). However, the $87.5 \rightarrow 80.5$ cm^{-1} frequency, by virtue of the intensity it displays in $P(\alpha, \beta)$ spectra of the Ag_{12}A zeolite- C_2H_2 adsorption system, must represent the remaining unidentified torsional mode, τ_z (dia.7(vii)), the implied deuteration shift corresponding with predictions for this mode of $0.852^*/0.911^{\dagger}/0.853^{\dagger\dagger}$.

It is noteworthy that the frequency of τ_z in the spectrum of C_2H_2 adsorbed on Ag_{12}A zeolite is substantially higher than the corresponding vibrations identified from the $\text{Ag}_{13}\text{X}-\text{C}_2\text{H}_2$ (27 cm^{-1} and 53.5 cm^{-1})^{19,20} and $\text{Ag}_{13}\text{X}-\text{C}_2\text{H}_4$ (22 cm^{-1} and 56 cm^{-1} High Coverage: 39.5 cm^{-1} Low Coverage)¹⁷⁻¹⁹ adsorption systems, but not too dissimilar from that found for τ_z^1 in the case of C_2H_4 adsorbed on Ag_{12}A zeolite ($68.5-71.0 \text{ cm}^{-1}$: Chapter VI). Additionally, in contrast with the Ag_{13}X systems studied by INS spectroscopy,¹⁷⁻²⁰ but in common with the $\text{Ag}_{12}\text{A}-\text{C}_2\text{H}_4$ adsorption system, there appears to be no evidence for the τ_z mode being split as a result of interaction between adsorbed molecules present on neighbouring sites.

It is not, unfortunately, strictly possible to compare the intensities of τ_z and τ_x vibrations in the BFD spectrum of C_2H_2 adsorbed onto Ag_{12}A zeolite because the former band encompasses the lowest frequency acetylene translational mode, suggested from the T-O-F data to occur at 56.5 cm^{-1} . However, if the contribution of the latter peak is ignored, the ratio $\tau_x : \tau_z$ obtained is 2.00:1.00, which compares with calculated ratios of $4.426 \pm 1.000^{\dagger}$ and $2.403:1.000^{\dagger\dagger}$. The intensity ratio of the frequencies 56.5 cm^{-1} (t): 87.5 cm^{-1} (τ_z): 130.0 cm^{-1} (t) may also be determined employing the $P(\alpha, \beta)$ spectrum (angle 45°) for C_2H_2 adsorbed onto Ag_{12}A zeolite. The values resulting, 1.218:4.090:1.000, correspond with those predicted of $1.000:5.026:1.000^*$, $1.000:2.711:1.000^{\dagger}$ and $1.000:5.003:1.000^{\dagger\dagger}$.

Of the remaining features which are as yet undiscussed, that located at 174 cm^{-1} (BFD)/ $161.0 \pm 9.5 \text{ cm}^{-1}$ ($P(\alpha, \beta)$) in the INS spectrum of C_2H_2 adsorbed onto Ag_{12}A zeolite may be associated with the shoulder situated

at 172 cm^{-1} in the BFD spectrum of the deuterated species. The deuteration shift thus derived (from the BFD spectra) is 0.989 ± 0.121 , which compares favourably with that expected for a translational mode of acetylene relative to the surface (0.964). Following the INS findings for $\text{Co}_2(\text{CO})_6 \cdot \text{C}_2\text{H}_2$ (Chapter V) and for Zeise's salt and dimer,^{18,19} this, the highest frequency translational vibration, may be assumed to represent the acetylene-silver symmetric stretch, t_z . However, once more, the frequency designated t_z appears more related to that found from INS studies carried out on the $\text{Ag}_{12}\text{A-C}_2\text{H}_4$ system ($139.5\text{--}141.0\text{ cm}^{-1}$, Chapter VI), than that located in the analogous $\text{Ag}_{13}\text{X-C}_2\text{H}_2$ system^{19,20} (86 cm^{-1}). On the basis of the above assignments, the intensity ratio of t_z relative to τ_z , measured from the $\text{P}(\alpha, \beta)$ spectrum (angle 45°) of C_2H_2 adsorbed onto Ag_{12}A zeolite, is $1.000:3.864$, which compares reasonably with predictions of $1.000:5.026^*$, $1.000:2.711^+$ and $1.000:5.003^{++}$.

The final feature unassigned, located at $25.0 \pm 1.5\text{ cm}^{-1}$ in the T-O-F spectrum of C_2D_2 adsorbed onto Ag_{12}A zeolite, has no obvious analogue in either the T-O-F or $\text{P}(\alpha, \beta)$ spectra involving the hydrogenous species. In view of the limited data available for this band, it must be assumed to represent a lattice mode.

In conclusion, it appears that the acetylene molecule adsorbed onto Ag_{12}A zeolite adopts a non-linear geometry, evidence for this coming from the appearance of the τ_x mode in the INS spectrum. In contrast with the results obtained for the analogous system using ethylene (Chapter VI), there is no apparent evidence for the existence of a second adsorption site. However, this statement should perhaps be qualified with respect to the quality of the data obtained for this system, and the admission that the very broad band designated τ_{x_H} possesses a long "tail" similar to that seen for the equivalent mode in the Ag_{12}A -ethylene adsorption system (and which has been suggested to indicate the presence of a second adsorption site (τ_x^2)).

to higher frequency (Chapter VI)). This lack of an additional adsorption site is very much at variance with the findings of single crystal work carried out on the Na_{12}A -acetylene adsorption system by Amaro and Seff,^{1,2} and Raman and infrared spectroscopic studies of acetylene adsorbed on several alkali metal and alkaline earth metal type A zeolites by Tam et al.⁸ Both of these investigations have indicated the presence of at least two adsorption sites within the zeolite framework corresponding to locations S1 and S2^* .

D. Barrier Calculation

In the absence of information concerning the potential function ($V(\theta)$) describing the rotation of C_2H_2 about the silver ion in the Ag_{12}A adsorption complex, the simplest model for $V(\theta)$ will be used in the calculation of barrier height. Thus following Chapter V, in which the barrier to the rotation of C_2H_2 in the complex $\text{Co}_2(\text{CO})_6 \cdot \text{C}_2\text{H}_2$ was determined, the form

$$V(\theta) = \frac{V_0}{2} (1 - \cos 2\theta)$$

will be employed. This potential function has no metastable well, but possesses a minimum at $\theta = 0^\circ$, and a maximum at $\theta = 90^\circ$.

The second derivative with respect to θ of the above equation is equal to force constant, k . Therefore substitution for k in the Harmonic Oscillator Approximation yields:

$$\omega = \frac{1}{\pi} \left(\frac{V_0}{2I_R} \right)^{\frac{1}{2}}$$

where I_R is the reduced moment of inertia of the acetylene group.

Employing the assignment $\tau_z = 87.5 \text{ cm}^{-1}$, a value for V_0 of $19.08 \pm 2.01 \text{ kJ mol}^{-1}$ is obtained using the structure suggested for the adsorbed acetylene molecule by Howard and Waddington,^{19,20} whilst that calculated on the basis of the Iwashita configuration²⁶ for the adsorbed species is $19.84 \pm 2.09 \text{ kJ mol}^{-1}$. These compare with values of $55\text{-}59 \text{ kJ mol}^{-1}$ determined for the rotational barrier for acetylene in the complex $\text{Co}_2(\text{CO})_6 \cdot \text{C}_2\text{H}_2$ (Chapter V), and 1.14 kJ mol^{-1} and $3.34\text{-}3.59 \text{ kJ mol}^{-1}$ (τ_z^1)/ $2.08\text{-}2.15 \text{ kJ mol}^{-1}$ (τ_z^2) derived for the barriers to the rotation of ethylene

adsorbed on respectively Ag13X (Low Coverage)^{18,19} and Ag₁₂A (Chapter VI) zeolites.[†] In the latter two cases, however, a more complex model has been used for the potential function which has yielded values of $5V_0$ rather than V_0 as outlined above (Chapter VI).

[†] In contrast with the studies carried out on the Ag13X-C₂H₄ adsorption system,¹⁷⁻¹⁹ no measurements have been made of C₂H₂ adsorbed onto Ag13X zeolite at "Low Coverage". No data therefore exist concerning the barrier to rotation of acetylene in the absence of interaction between molecules adsorbed onto neighbouring sites, and hence it is not possible to make straightforward comparison with the barrier height derived for the Ag₁₂A-C₂H₂ adsorption system.

APPENDIX: Structural Data Used in the Calculation of Moments of Inertia

Moments of inertia of acetylene about the three principal axes have been calculated from the co-ordinates listed below for the three models of the complexed molecule:

(i) Linear Form (structural data from that of Sugawara and Kanda for the crystalline state²⁵):

Hx+1.650	Dx+1.640
y 0.000	y 0.000
z 0.000	z 0.000
Cx+0.600	Cx+0.600
y 0.000	y 0.000
z 0.000	z 0.000
Cx-0.600	Cx-0.600
y 0.000	y 0.000
z 0.000	z 0.000
Hx-1.650	Dx-1.640
y 0.000	y 0.000
z 0.000	z 0.000

(ii) Structure postulated by Iwashita for the acetylene moiety in the complex $\text{Co}_2(\text{CO})_6\cdot\text{C}_2\text{H}_2$ ²⁶:

Hx+1.644	Dx+1.634	
y 0.000	y 0.000	
z-0.170	z-0.156	
Cx+0.600		Cx+0.600
y 0.000		y 0.000
z+0.014		z+0.026
Cx-0.600		Cx-0.600
y 0.000		y 0.000
z+0.014		z+0.026
Hx-1.644	Dx-1.634	
y 0.000	y 0.000	
z-0.170	z-0.156	

(iii) Geometry assumed by Howard and Waddington for acetylene adsorbed on Ag 13X zeolite^{19,20}:

Hx+1.234
y 0.000
z-0.863

Dx+1.229
y 0.000
z-0.794

Cx+0.694
y 0.000
z+0.072

Cx+0.694
y 0.000
z+0.132

Cx-0.694
y 0.000
z+0.072

Cx-0.694
y 0.000
z+0.132

Hx-1.234
y 0.000
z-0.863

Dx-1.229
y 0.000
z-0.794

For all three models, the C-D bond length has been assumed to be 0.01 Å shorter than that of C-H.

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CHAPTER VIII

ORGANOMETALLIC COMPLEXES CONTAINING BENZENE

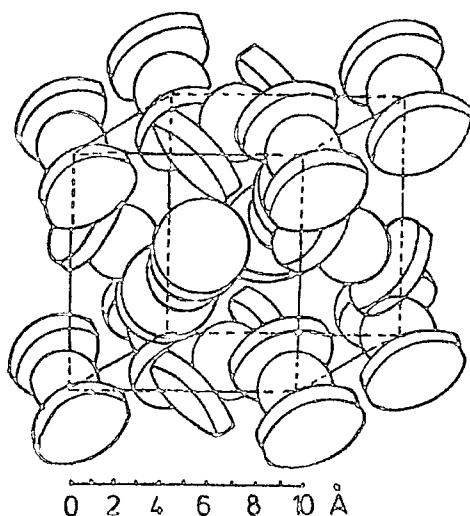
As a precursor to later INS investigation of benzene adsorbed on zeolite and metal surfaces, it was considered advisable to study metal-benzene interactions in several simple systems whose structures were well defined, and whose "conventional" spectroscopic properties were well known. Bearing in mind these criteria, the compounds chosen for study were $\text{Cr}(\text{C}_6\text{H}_6)_2$ and $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ and $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ and $\text{C}_6\text{H}_6\text{Mn}(\text{Co})_3\text{Br}$.

A. $\text{Cr}(\text{C}_6\text{H}_6)_2$ and $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$

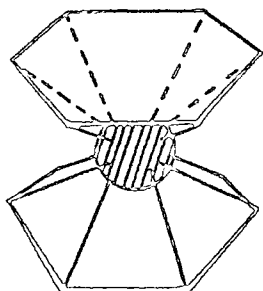
1. Introduction : $\text{Cr}(\text{C}_6\text{H}_6)_2$

a) The Structure of $\text{Cr}(\text{C}_6\text{H}_6)_2$

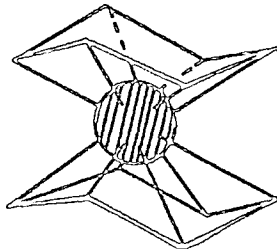
The first crystal structure determination of $\text{Cr}(\text{C}_6\text{H}_6)_2$, carried out by Weiss and Fischer in 1956¹, established that the unit cell was cubic (unit cell edge = $9.67 \pm 0.03 \text{ \AA}$) and contained four molecules (dia.8(i)).



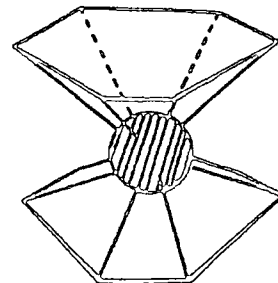
The space group indicated, $Pa3-T_h^6$, suggested a centrosymmetric sandwich structure for the individual molecules[†] and, on the assumption that these possessed D_{6h} symmetry (dia. 8(ii)a), bond lengths were derived for C-C and Cr-C of $1.38 \pm 0.05 \text{ \AA}$ and $2.19 \pm 0.10 \text{ \AA}$ respectively (Table 8.1)



(a)



(b)



(c)

dia.8(ii.)

Three Models which have been Proposed for the Structure of $Cr(C_6H_6)_2$ (after Fritz et al.²)

- In model (a) both the benzene ligands, and the molecule as a whole, possess D_{6h} symmetry.
- (b) both the benzene ligands, and the molecule as a whole, possess D_{3d} symmetry.
- (c) each benzene ligand is of D_{3h} symmetry, whilst the symmetry of the complex is D_{3d} .

Subsequently, an infrared investigation of $Cr(C_6H_6)_2$ by Fritz and Lüttke (1959)³ concluded that six-fold symmetry was not, in fact, present and proposed that the molecular symmetry be amended to D_{3d} (dias 8(ii)b and 8(ii)c). However, the same investigators soon afterwards changed their interpretation of the spectrum as a result of an infrared and Raman study concerned mainly with $Cr(C_6H_6)_2I$, postulating D_{6h} symmetry for both $Cr(C_6H_6)_2$ and $Cr(C_6H_6)_2^{+4}$. Similarly, Snyder (1959)⁵, in his assignment of the infrared spectrum of solid $Cr(C_6H_6)_2$, assumed the molecular symmetry to be D_{6h} .

A short while later (1960), the controversy was re-opened by the publication of a refined X-ray crystal structure (Reliability index, $R=0.063$) by Jellinek⁶ (Table 8.1). Although this confirmed the gross features of

[†] Each molecule at site symmetry S_6

TABLE 8.1(a) Interatomic Distances and Angles in $\text{Cr}(\text{C}_6\text{H}_5)_2$ as Reported by Various Authors

	Weiss and Fischer ¹ (1956)	Jellinek ⁶ (1960)	Cotton et al. ⁷ # (1963)	Jellinek ⁸ ** (1963)
Method of Investigation Reliability Index (R)	X-ray Diffraction -	X-ray Diffraction 0.063	X-ray Diffraction 0.061	X-ray Diffraction 0.063
Bond Length C-C	1.38 $\pm$ 0.05 Å	1.353 $\pm$ 0.014 Å 1.439 $\pm$ 0.014 Å	1.386 $\pm$ 0.017 Å 1.407 $\pm$ 0.017 Å 1.387 $\pm$ 0.017 Å	1.357 $\pm$ 0.014 Å 1.438 $\pm$ 0.014 Å
Bond Length Cr-C	2.18 $\pm$ 0.10 Å	2.132 $\pm$ 0.010 Å 2.135 $\pm$ 0.010 Å	2.132 $\pm$ 0.012 Å 2.138 $\pm$ 0.012 Å	2.132 $\pm$ 0.010 Å 2.134 $\pm$ 0.010 Å
Distance of Mean Carbon Plane from Chromium	-	1.613 $\pm$ 0.007 Å	1.616 $\pm$ 0.010 Å	1.612 $\pm$ 0.007 Å
Bond Length C-H	-	-	-	1.03 Å 1.06 Å 1.10 Å 1.12 Å
Bond Angle C-C	-	118.9 $\pm$ 1.0° 121.0 $\pm$ 1.0°	-	118.5 $\pm$ 1.0° 121.4 $\pm$ 1.0° 119.0 $\pm$ 0.8° 120.9 $\pm$ 0.8°
Unit Cell Edge (a)	9.67 $\pm$ 0.03 Å	9.667 Å	-	-
Molecular Symmetry	D _{3h}	D _{3d}	D _{3d} D _{3h}	D _{3d}

* The left-hand column displays the results of a least-squares refinement carried out ignoring the contribution of hydrogen atoms; the right-hand column shows the findings of a least-squares refinement taking the hydrogen atoms into account.

** The left-hand column displays those data derived from an isotropic refinement by difference syntheses; the right-hand column shows the values obtained from an anisotropic refinement by least-squares.

TABLE 8.1(b) Interatomic Distances and Angles in Cr(C₆H₅)₂ as Reported by Various Authors

Method of Investigation Reliability Index (R)	Ibers ¹⁰ † (1964) X-ray Diffraction 0.047	Haaland ¹¹ ‡ (1965) Electron Diffraction -	Keulen and Jellinek ¹² (1966) †† X-ray Diffraction 0.031	Förster et al. ^{15,16} (1968 and 1969) Neutron Diffraction 0.030
Bond Length C-C	1.381±0.008Å 1.412±0.008Å	1.392Å 1.423±0.002Å	1.416±0.003Å 1.417±0.003Å	1.406±0.050Å 1.424±0.055Å
Bond Length Cr-C	2.126±0.006Å 2.127±0.006Å	2.150±0.002Å	2.140±0.002Å 2.143±0.002Å	2.137±0.032Å 2.095±0.032Å
Distance of Mean Carbon Plane from Chromium	1.604±0.004Å	1.613±0.0025Å	1.606±0.001Å	1.575±0.025Å
Bond Length C-H	1.07±0.070Å 1.04±0.070Å	1.06Å 1.090±0.005Å	0.92±0.030Å 0.95±0.030Å	1.015±0.100Å 1.081±0.050Å
Bond Angle C-C-C	-	-	-	-
Unit Cell Edge (a)	-	-	9.553Å	-
Molecular Symmetry	D _{3d} D _{6h}	D _{6h}	D _{6h}	D _{3d}

† The left-hand column displays the results of a least-squares refinement constrained to D_{3d} symmetry; the right-hand column shows the findings of a least-squares refinement constrained to D_{6h} symmetry.

‡ Gas phase study.

†† Single crystal data measured at 100K.

the structure as reported by Weiss and Fischer¹ (e.g. unit cell edge = $9.667\text{\AA}$), the molecular symmetry was found to differ distinctly from D_{6h} , with the benzene ligands, whilst planar, possessing alternate C-C bond lengths of $1.353 \pm 0.014\text{\AA}$ and $1.439 \pm 0.014\text{\AA}$. These distances, it was argued, were very similar to those expected for respectively double and single bonds between carbon atoms with sp^2 hybridisation, and hence D_{3d} symmetry appeared to be proven (dia.8(ii)c). However, Jellinek's findings were in turn rebutted in 1963 by Cotton et al.⁷ (Table 8.1) who, from a study of alternative data ($R=0.061$), reported that the lengths of alternate C-C bonds within the benzene ligands differed by less than $0.02\text{\AA}$, and tended to a mean value of approximately $1.4\text{\AA}$. Indeed, when an alternative refinement was carried out taking into consideration the position of hydrogen atoms, both C-C bond lengths became $1.387 \pm 0.017\text{\AA}$.

In the same year, Jellinek⁸ published a re-analysis of his data (incorporating a least-squares refinement with anisotropic temperature factors, $R=0.053$), which substantially reaffirmed his previous results. (Table 8.1). Consequently, in order to explain the lack of correspondence between his findings and those of Cotton et al.⁷, he suggested that in the latter's work orientational disorder of the molecules had given rise to an apparent additional two-fold rotation axis (through the metal atom, and perpendicular to the planes of the benzene ligands), which had caused enhancement of the molecular symmetry from D_{3d} to D_{6h} . In support of this theory, he cited the example of ferrocene, where a similar effect had been shown to occur.

Conflicting views were again expressed in 1964, with Fritz⁹, in a review of benzene complexes, stating his belief that the benzene ligands of $\text{Cr}(\text{C}_6\text{H}_6)_2$ were trigonally distorted in the manner described by Jellinek^{6,8}; whilst Ibers¹⁰ reported the outcome of a re-analysis and refinement ($R=0.047$) of the data of Cotton et al.⁷ (Table 8.1) which, he concluded, displayed

no evidence for a significant deviation from D_{6h} symmetry. An identical conclusion was reached by Haaland (1965)¹¹ from a somewhat inconclusive electron diffraction study of the gaseous molecule (Table 8.1), which showed that if any difference in the C-C bond lengths of the ligand molecule existed, then the discrepancies could not exceed $0.02\text{\AA}$. Similarly, in 1966, Keulen and Jellinek¹² published the results of a single crystal study ($R=0.031$), carried out at 100K, which indicated the C-C bond lengths to be equal. These data were not considered to be sufficiently good, however, totally to disprove the hypothesis⁸ that orientational disorder in the crystal was the cause of the (apparent) D_{6h} symmetry.

In contrast, the far-infrared spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2$ was analysed by Fritz and Fischer in 1967 employing D_{3d} symmetry¹³. Although a tentative assignment of all the strong bands in the solution spectrum had been shown to be feasible assuming six-fold symmetry¹⁴, it was argued that the lower symmetry solid-state spectrum arose from distortion of the benzene ligands in $\text{Cr}(\text{C}_6\text{H}_6)_2$ caused by intramolecular, rather than crystal forces. This conclusion was reached by analogy with results obtained for $\text{V}(\text{C}_6\text{H}_6)_2$ in two crystalline forms (cubic and monoclinic), which had indicated that crystal factor and site group had negligible influence on the spectrum of the ligands of that molecule. However, the reasoning was somewhat at variance with the earlier report of Snyder⁵, who had commented that changes in the solid state of $\text{Cr}(\text{C}_6\text{H}_6)_2$ were reflected in the spectra measured.

Shortly afterwards (1968/69), two neutron diffraction works were published ($R=0.030$) which claimed to prove D_{3d} symmetry^{15,16} (Table 8.1). Lowering of D_{6h} symmetry was suggested to occur not only as a result of the benzene ligands having unequal alternate C-C bond lengths, but also as a consequence of distortion of the ligand rings from planarity, with the adoption of D_{3d} symmetry in the manner illustrated in dia.8(ii)b.

Opposing views were voiced by Andrews et al. (1969)¹⁷, who performed heat capacity measurements (5-350K) and vapour pressure measurements (323-363K) on $\text{Cr}(\text{C}_6\text{H}_6)_2$. It was found that the entropy calculated employing the third law of Thermodynamics (350K) agreed with the spectroscopic (statistical) entropy calculated for the gas-phase using reported assignments^{2,5†}, the structural data of Haaland¹¹ and the assumption of six-fold symmetry. As no evidence for a phase transition was apparent from the heat capacity measurements, it was concluded that the phase existing at 350K remained stable to 5K. The data were, however, capable of interpretation in two ways: either (i) the molecule possessed D_{6h} symmetry, or (ii) the molecule was distorted to D_{3d} symmetry, and a disordered phase of the type suggested by Jellinek⁸ persisted to at least 5K. Of the two possibilities, the latter was thought the less likely, because the small difference between molecular orientations postulated (60° rotation about the main symmetry axis) was considered to be a small perturbation which was unlikely to be "frozen in".

Positive proof for the symmetry of $\text{Cr}(\text{C}_6\text{H}_6)_2$ was first afforded by the gas-phase infrared spectrum measured by Ngai et al. (1969)¹⁹: all modes expected to be active under D_{6h} symmetry in the spectral region studied ($400\text{--}4000\text{cm}^{-1}$) were located with one exception, whereas insufficient frequencies were observed to substantiate the alternative assignment of D_{3d} symmetry (see later). Mean C-C amplitudes of vibration were subsequently calculated²⁰ from these and Raman²¹ frequencies. It was found that the mean C-C amplitude of vibration in $\text{Cr}(\text{C}_6\text{H}_6)_2$ was larger than in C_6H_6 , whilst the electron diffraction study¹¹ had concluded that the converse should hold if two different types of C-C bond (i.e. three-fold symmetry) were present. Hence further support was yielded for the

† The frequencies of those vibrations not assigned by Fritz et al.² or Snyder⁵ were estimated by comparison with the data of Calloman et al. for benzene¹⁸

hexagonal structure.

Recently, Azokpota (1977)²², in a study primarily concerned with chromocene, has reported heat capacity measurements carried out on $\text{Cr}(\text{C}_6\text{H}_6)_2$ in the temperature range 110-300K. This work, similarly to that of Andrews et al.¹⁷, indicated that there was no evidence for any order-disorder phase transition, and an ordered structure was concluded to exist at room temperature with D_{6h} molecular symmetry.

b) The Barrier to the Rotation of the Benzene Ligands in $\text{Cr}(\text{C}_6\text{H}_6)_2$

The contribution of non-bonded interactions to the total potential describing reorientation of the benzene groups in $\text{Cr}(\text{C}_6\text{H}_6)_2$ about their hexad axis has been calculated by Campbell et al.²³ The potential energy of interaction between any two non-bonded atoms in the crystal lattice was assumed to be a function dependent only on the nature of the two atoms and their separation. Hence, in the cases of C-C, C-H and H-H interactions, a potential described as an "exponential -6 function" was applied:

$$V = Ar^{-6} + B\exp(-Cr)$$

where V is the potential energy of interaction
between the non-bonded atoms.

r is the distance between the non-bonded
atoms.

and A, B and C are empirically determined parameters
dependent on the pairs of interacting
atoms.

However, for M-M, M-C and M-H interactions, insufficient data existed to enable the parameters A, B and C to be calculated, and a "Lennard-Jones 6-12 potential" needed to be used:

$$V = 4\epsilon \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6$$

where σ is the finite distance at which the potential energy equals zero.

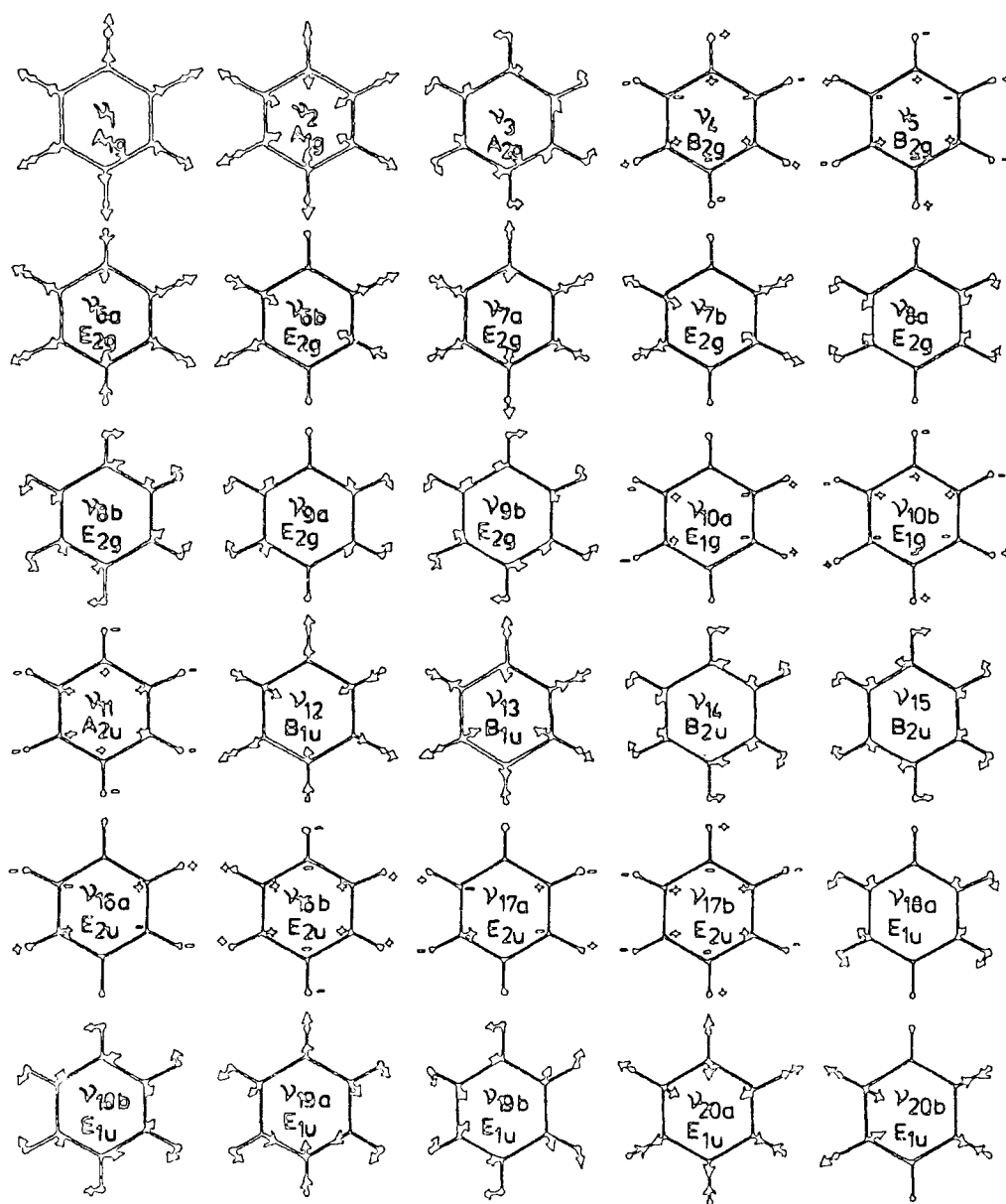
and ϵ is the absolute value of the depth of the potential energy well

(Both σ and ϵ differ for interactions between different atoms.)

Calculation of potential energy as a function of angle for the in-plane rotation of benzene about its six-fold axis (employing a model in which only one ligand group rotated whilst all other atoms remained fixed) showed that no contribution was made to the potential by non-bonded interactions between the two rings of a single molecule, and that the observed barrier could be explained as the consequence of crystal packing forces, and bonding forces within the molecule. The potential resulting from the latter (intramolecular) forces was independent of angle, but that arising from the former (intermolecular) forces displayed minima at $60n^\circ$ (where $n = 0, 1, 2, 3, 4, 5$),[†] and maxima at $30n^\circ$ (where $n = 1, 3, 5, 7, 9, 11$).[†] Reasonable agreement was noted between the measured $\Delta H_{\text{sublimation}}$ and the calculated value for the potential energy at 0° rotation and also between a value for the activation energy for benzene group rotation derived experimentally from Pulse-NMR measurements ($4.56 \text{ kcal mol}^{-1}$) and that obtained by calculation.

The authors were able to conclude, as a result of their investigation, that an approximate value of the activation energy for ring re-orientation in the solid state could be obtained by consideration solely of non-bonded (intermolecular) interactions, that is to say that crystal packing forces

[†] Displacements stated relative to an assumed original eclipsed configuration of the two benzene ligands of $\text{Cr}(\text{C}_6\text{H}_6)_2$.



dia. 8 (iii) The Normal Modes of Vibration of Benzene under D_{6h} Symmetry
after Pitzer and Scott²⁵ and Bailey et al.³¹

TABLE 8.2 Vibrational Analysis of Benzene Employing D_{6h} Symmetry

Description of Vibration	Symmetry Species											
	A _{1g}	A _{2g}	B _{1g}	B _{2g}	E _{1g}	E _{2g}	A _{1u}	A _{2u}	B _{1u}	B _{2u}	E _{1u}	E _{2u}
ν(C-C)	1 ⁽¹⁾	0	0	0	0	1 ⁽⁸⁾	0	0	0	1 ⁽¹⁴⁾	1 ⁽¹⁹⁾	0
ν(C-H)	1 ⁽²⁾	0	0	0	0	1 ⁽⁷⁾	0	0	1 ⁽¹³⁾	0	1 ⁽²⁰⁾	0
δ _{1pb} (C-C-C)	0	0	0	0	0	1 ⁽⁶⁾	0	0	1 ⁽¹²⁾	0	0	0
δ _{opb} (C-C-C)	0	0	0	1 ⁽⁴⁾	0	0	0	0	0	0	0	1 ⁽¹⁶⁾
δ _{1pb} (C-H)	0	1 ⁽³⁾	0	0	0	1 ⁽⁹⁾	0	0	0	1 ⁽¹⁵⁾	1 ⁽¹⁸⁾	0
δ _{opb} (C-H)	0	0	0	1 ⁽⁵⁾	1 ⁽¹⁰⁾	0	0	1 ⁽¹¹⁾	0	0	0	1 ⁽¹⁷⁾
Total Number of Stretches of Each Species	2	0	0	0	0	2	0	0	1	1	2	0
Total Number of Bends of Each Species	0	1	0	2	1	2	0	1	1	1	1	2
Total Number of Vibrations of Each Species	2	1	0	2	1	4	0	1	2	2	3	2
Activity	R	I.a	I.a	I.a	R	R	I.a	IR	I.a	I.a	IR	I.a

ν = stretch; δ_{1pb} = in-plane bend; δ_{opb} = out-of-plane bend; R = Raman active;
 IR = infrared active; I.a. = inactive; () = number of vibration after Wilson

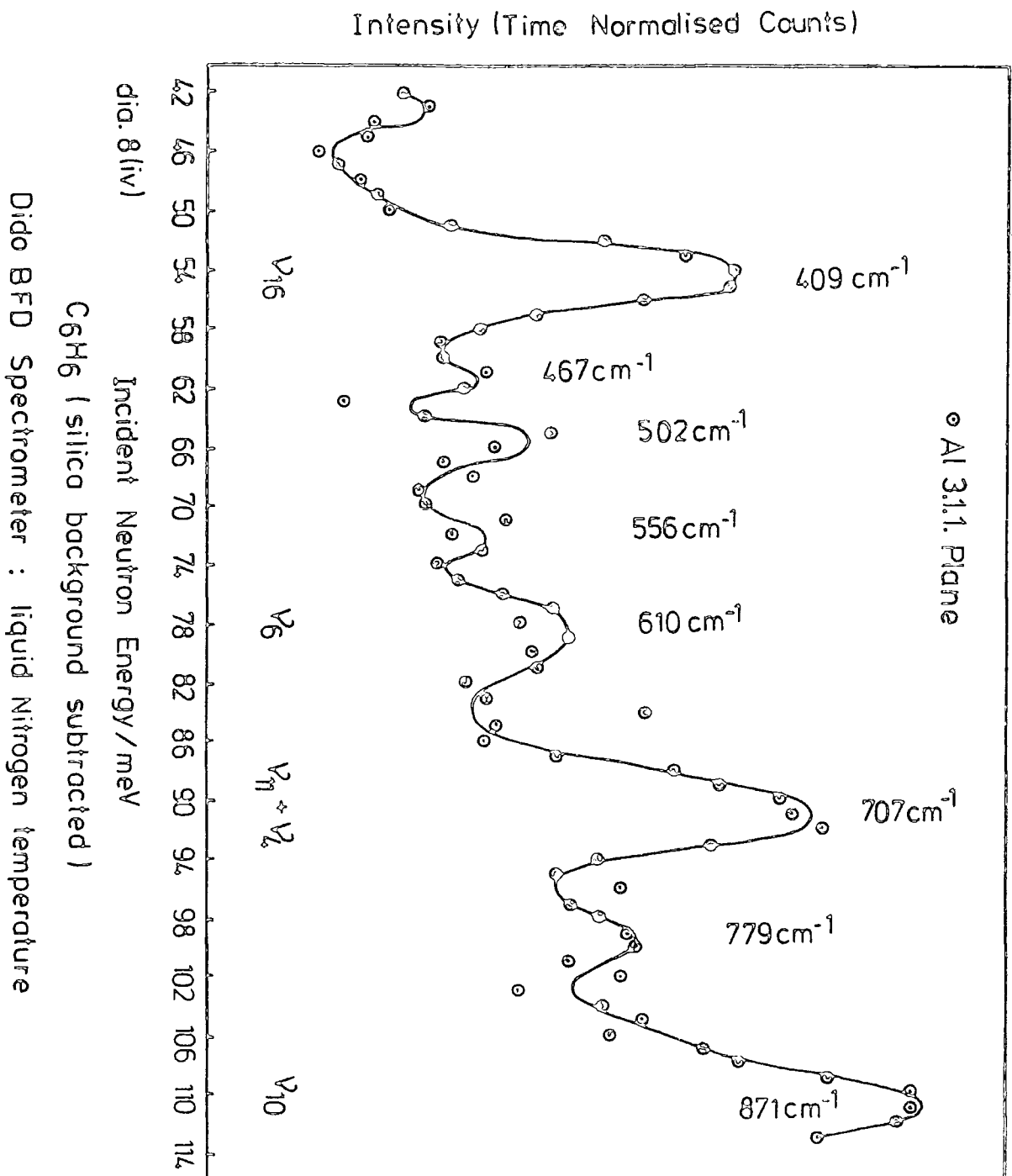


TABLE 8.3 The Spectroscopic Frequencies (cm⁻¹) and Assignments of Benzene in the Liquid and Solid Phases as Reported by Various Authors

Number of 24 Vibrations	Symmetry Species and Activity (D _{6h} Point Group Assumed)	Ingold et al. (Liquid)	Pitzer and Scott (Liquid)	Mair and Hornig (Liquid)	Bornstein et al. (Solid)	Graham (Solid)
ν_1	A_{1g} (R)	991.6	992	992 ^{oo}	990.9	
ν_2	A_{1g} (R)	3061.9	3062	3062 ^{oo}	3063.3	
ν_3	A_{2g} (i.o.)	1326	1298	(1340)		
ν_4	B_{2g} (i.o.)	703	685	703 ^{oo}	704.9	707 ^{ff}
ν_5	B_{2g} (i.o.)	985	(1016)	(995)	1004.9	
ν_6	E_{2g} (R)	605.6	606	606 ^{oo}	{ 606.3 609.6 }	610
ν_7	E_{2g} (R)	3046.8	3047 ^{oo}	3047 ^{oo}	{ 3042.0 3047.5 }	
ν_8	E_{2g} (R)	1596	1596	1596 ^{oo}	1584.2	
ν_9	E_{2g} (R)	1178.0	1178	1178 ^{oo}	{ 1174.3 1174.8 }	
ν_{10}	E_{1g} (R)	848.9	849	849 ^{oo}	{ 862.5 869.3 }	871
ν_{11}	A_{2u} (IR)	671	671	675	696.9 [697]	707 ^{ff}
ν_{12}	B_{1u} (i.o.)	(1010)	(1010) ^{oo}	(1010)	1011.4 [1011]	
ν_{13}	B_{1u} (i.o.)	(3060)	(3060) ^{oo}	3071 ^{oo}		
ν_{14}	B_{2u} (i.o.)	(1648)	1693	1310	1312.6 [1313]	
ν_{15}	B_{2u} (i.o.)	(1110)	1170	1150	1146.4 [1147]	
ν_{16}	E_{2u} (i.o.)	405	400	(405)	{ 404.8 [404] 413.0 [413] }	409
ν_{17}	E_{2u} (i.o.)	(970)	985	975	{ 978.3 [978] 983.9 [983] }	
ν_{18}	E_{1u} (IR)	1033	1033	1036	{ 1034.8 [1034] 1038.6 [1038] }	
ν_{19}	E_{1u} (IR)	1480	1480	1478		
ν_{20}	E_{1u} (IR)	{ 3073 ^{oo} (3080)	(3080) ^{oo}	3083 ^{oo}	3063 ^{oo}	

() Frequency inferred from overtone, combination band or calculation.
 [] Frequency inferred from UV spectrum.
 oo Assigned from the work of Lohmeyer³² (3073cm⁻¹ value is for benzene vapour).
 ff From the work of Sitar³⁵ and Epstein and Stolar³³.
 ff It did not prove possible to resolve the ν_{14} and ν_{11} in the RPD spectrum of solid benzene.
 n Raman active.
 IR Infrared active.
 i.o. Inactive

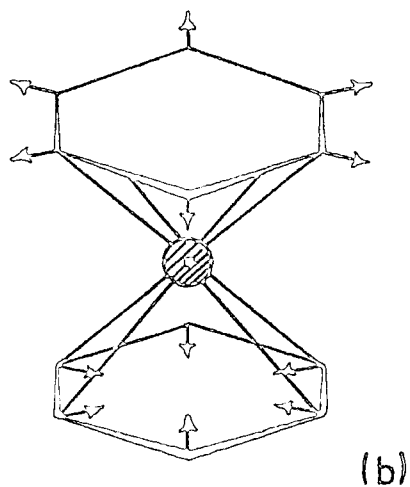
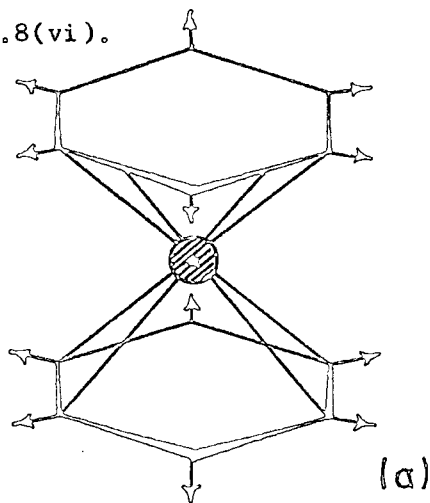
were found to be the dominant factors in the determination of molecular conformation in the solid state. It was, however, pointed out that in solution, conformation would be determined entirely by intramolecular forces.

c) Previous Spectroscopic Studies of $\text{Cr}(\text{C}_6\text{H}_6)_2$

In order to obtain a clearer understanding of the various spectroscopic investigations which have been carried out on $\text{Cr}(\text{C}_6\text{H}_6)_2$, it is first necessary to consider the symmetry of the molecule, and the activities of the vibrational species anticipated.

The benzene molecule itself possesses D_{6h} symmetry. From this description may be obtained the vibrations (ν_1 to ν_{20}) which are listed in Table 8.2 (following the numbering convention of Wilson²⁴) and illustrated in dia.8(iii). In addition, as reference data for forthcoming discussion, the spectroscopic frequencies assigned to these modes in optical studies (of both the solid and liquid states) are displayed in Table 8.3, together with those fundamentals observed in the INS spectrum (42-113 meV) of solid benzene (dia.8(iv)).

The $\text{Cr}(\text{C}_6\text{H}_6)_2$ molecule contains 69 (i.e. $3(25)-6$) normal vibrations. Of these, 60 ($2[3(12)-6]$) are derived from the two mechanically coupled benzene ligands, each of whose 30 normal modes may now be either in-phase (ip) or out-of-phase (op) with the identical vibrations of the second benzene molecule (dia.8(v)). The remaining nine modes (ν_{21} to ν_{26}) result from motion of the benzene groups relative to the chromium atom and are shown in dia.8(vi).



dia.8(v) An Example of the In-phase (a) and Out-of-phase (b) Species Generated in $\text{Cr}(\text{C}_6\text{H}_6)_2$ from One Mode of an Individual Benzene Molecule (in this case $\nu_1(A_{1g})$).

TABLE 8.4 Vibrational Analysis of Cr(C₆H₅)₆ Employing D_{6h} Symmetry

Description of Vibration	Symmetry Species											
	A _{1g}	A _{2g}	B _{1g}	B _{2g}	E _{1g}	E _{2g}	A _{1u}	A _{2u}	B _{1u}	B _{2u}	E _{1u}	E _{2u}
ν(C-C)	(1 _{1p}) 1	0	(14 _{op}) 1	0	(19 _{op}) 1	(8 _{1p}) 1	0	(1 _{op}) 1	0	(14 _{1p}) 1	(19 _{1p}) 1	(8 _{op}) 1
ν(C-H)	(2 _{1p}) 1	0	0	(13 _{op}) 1	(20 _{op}) 1	(7 _{1p}) 1	0	(2 _{op}) 1	(13 _{1p}) 1	0	(20 _{1p}) 1	(7 _{op}) 1
δ _{1pb} (C-C-C)	0	0	0	(12 _{op}) 1	0	(6 _{1p}) 1	0	0	(12 _{1p}) 1	0	0	(6 _{op}) 1
δ _{opb} (C-C-C)	0	0	0	(4 _{1p}) 1	0	(16 _{op}) 1	0	0	(4 _{op}) 1	0	0	(16 _{1p}) 1
δ _{1pb} (C-H)	0	(3 _{1p}) 1	(15 _{op}) 1	0	(18 _{op}) 1	(9 _{1p}) 1	(3 _{op}) 1	0	0	(15 _{1p}) 1	(18 _{1p}) 1	(9 _{op}) 1
δ _{opb} (C-H)	(11 _{op}) 1	0	0	(5 _{1p}) 1	(10 _{1p}) 1	(17 _{op}) 1	0	(11 _{1p}) 1	(5 _{op}) 1	0	(10 _{op}) 1	(17 _{1p}) 1
ν(δ-Cr-δ)	(21) 1	0	0	0	0	0	0	(23) 1	0	0	0	0
torsion (δ-Cr-δ)	0	0	0	0	0	0	(22) 1	0	0	0	0	0
Ring tilt	0	0	0	0	(24) 1	0	0	0	0	0	(25) 1	0
δ(δ-Cr-δ)	0	0	0	0	0	0	0	0	0	0	(26) 1	0
Total Number of Stretches of Each Species	3	0	1	1	2	2	0	3	1	1	2	2
Total Number of Bends of Each Species	1	1	1	3	3	4	2	1	3	1	4	4
Total Number of Vibrations of Each Species	4	1	2	4	5	6	2	4	4	2	6	6
Activity	R	I.A.	I.A.	I.A.	R	R	I.A.	IR	I.A.	I.C.	IR	I.C.

ν = stretch; δ_{1pb} = in-plane bend; δ_{opb} = out-of-plane bend; 1p = ligand rings in-phase; op = ligand rings out-of-phase;
 R = Raman active; IR = infrared active; I.A. = inactive; (24) = number of vibration (numbers assigned to internal codes
 of the benzene ligands (ν₁ - ν₂₀) follow those of Wilson, those assigned to the remaining modes follow
 Fritz et al. 2,4

TABLE 6.3 Description of the Normal Modes of Vibration of $\text{Cr}(\text{C}_6\text{H}_6)_2$

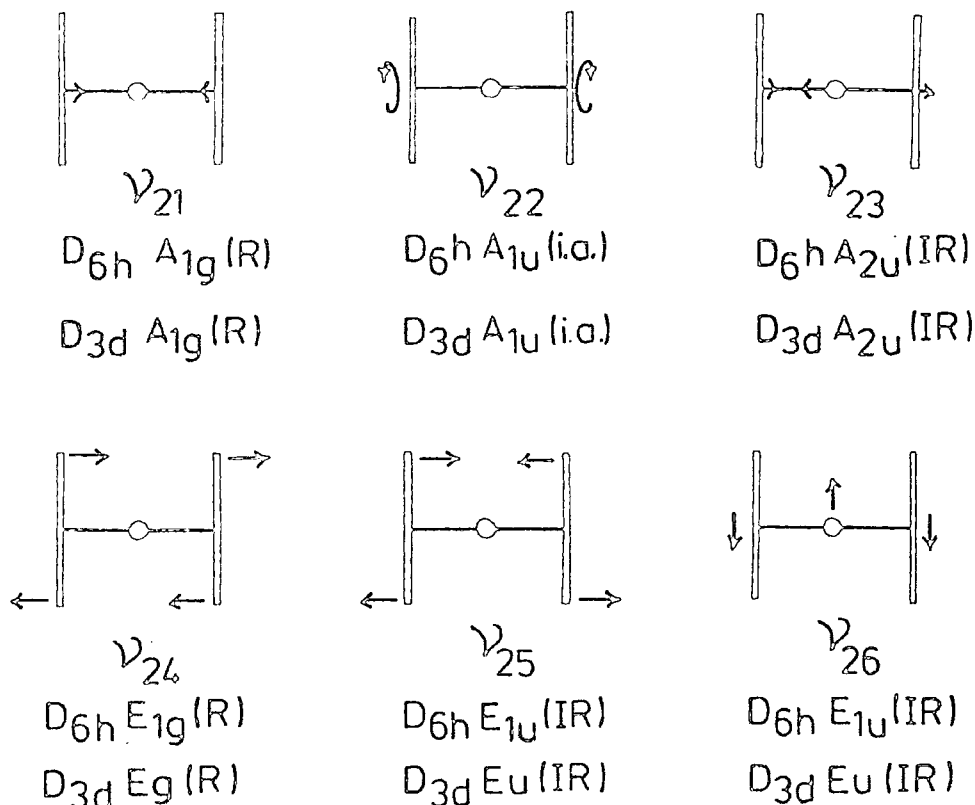
Number of Vibration ν_n	Description	Symmetry Species and Activity (D_{6h})		Symmetry Species and Activity (D_{3d})	
		In-phase ($\nu_{n,p}$)	Out-of-phase ($\nu_{n,op}$)	In-phase ($\nu_{n,p}$)	Out-of-phase ($\nu_{n,op}$)
ν_1	$\nu(\text{C-C})$	$A_{1g}(\text{R})$	$A_{2u}(\text{IR})$	$A_{1g}(\text{R})$	$A_{2u}(\text{IR})$
ν_2	$\nu(\text{C-H})$	$A_{1g}(\text{R})$	$A_{2u}(\text{IR})$	$A_{1g}(\text{R})$	$A_{2u}(\text{IR})$
ν_3	$\delta_{ipb}(\text{C-H})$	$A_{2g}(\text{i.a.})$	$A_{1u}(\text{i.a.})$	$A_{2g}(\text{i.a.})$	$A_{1u}(\text{i.a.})$
ν_4	$\delta_{opb}(\text{C-C-C})$	$B_{2g}(\text{i.a.})$	$B_{1u}(\text{i.a.})$	$A_{1g}(\text{R})$	$A_{2u}(\text{IR})$
ν_5	$\delta_{opb}(\text{C-H})$	$B_{2g}(\text{i.a.})$	$B_{1u}(\text{i.a.})$	$A_{1g}(\text{R})$	$A_{2u}(\text{IR})$
ν_6	$\delta_{ipb}(\text{C-C-C})$	$E_{2g}(\text{R})$	$E_{2u}(\text{i.a.})$	$E_g(\text{R})$	$E_u(\text{IR})$
ν_7	$\nu(\text{C-H})$	$E_{2g}(\text{R})$	$E_{2u}(\text{i.a.})$	$E_g(\text{R})$	$E_u(\text{IR})$
ν_8	$\nu(\text{C-C})$	$E_{2g}(\text{R})$	$E_{2u}(\text{i.a.})$	$E_g(\text{R})$	$E_u(\text{IR})$
ν_9	$\delta_{ipb}(\text{C-H})$	$E_{2g}(\text{R})$	$E_{2u}(\text{i.a.})$	$E_g(\text{R})$	$E_u(\text{IR})$
ν_{10}	$\delta_{opb}(\text{C-H})$	$E_{1g}(\text{R})$	$E_{1u}(\text{IR})$	$E_g(\text{R})$	$E_u(\text{IR})$
ν_{11}	$\delta_{opb}(\text{C-H})$	$A_{2u}(\text{IR})$	$A_{1g}(\text{R})$	$A_{2u}(\text{IR})$	$A_{1g}(\text{R})$
ν_{12}	$\delta_{ipb}(\text{C-C-C})$	$B_{1u}(\text{i.a.})$	$B_{2g}(\text{i.a.})$	$A_{2u}(\text{IR})$	$A_{1g}(\text{R})$
ν_{13}	$\nu(\text{C-H})$	$B_{1u}(\text{i.a.})$	$B_{2g}(\text{i.a.})$	$A_{2u}(\text{IR})$	$A_{1g}(\text{R})$
ν_{14}	$\nu(\text{C-C})$	$B_{2u}(\text{i.a.})$	$B_{1g}(\text{i.a.})$	$A_{1u}(\text{i.a.})$	$A_{2g}(\text{i.a.})$
ν_{15}	$\delta_{ipb}(\text{C-H})$	$B_{2u}(\text{i.a.})$	$B_{1g}(\text{i.a.})$	$A_{1u}(\text{i.a.})$	$A_{2g}(\text{i.a.})$
ν_{16}	$\delta_{opb}(\text{C-C-C})$	$E_{2u}(\text{i.a.})$	$E_{2g}(\text{R})$	$E_u(\text{IR})$	$E_g(\text{R})$
ν_{17}	$\delta_{opb}(\text{C-H})$	$E_{2u}(\text{i.a.})$	$E_{2g}(\text{R})$	$E_u(\text{IR})$	$E_g(\text{R})$
ν_{18}	$\delta_{ipb}(\text{C-H})$	$E_{1u}(\text{IR})$	$E_{1g}(\text{R})$	$E_u(\text{IR})$	$E_g(\text{R})$
ν_{19}	$\nu(\text{C-C})$	$E_{1u}(\text{IR})$	$E_{1g}(\text{R})$	$E_u(\text{IR})$	$E_g(\text{R})$
ν_{20}	$\nu(\text{C-H})$	$E_{1u}(\text{IR})$	$E_{1g}(\text{R})$	$E_u(\text{IR})$	$E_g(\text{R})$
ν_{21}	$\nu_s(\theta\text{-Cr-}\theta)$	$A_{1g}(\text{R})$		$A_{1g}(\text{R})$	
ν_{22}	Torsion ($\theta\text{-Cr-}\theta$)	$A_{1u}(\text{i.a.})$		$A_{1u}(\text{i.a.})$	
ν_{23}	$\nu_{as}(\theta\text{-Cr-}\theta)$	$A_{2u}(\text{IR})$		$A_{2u}(\text{IR})$	
ν_{24}	Symmetric Ring Tilt	$E_{1g}(\text{R})$		$E_g(\text{R})$	
ν_{25}	Antisymmetric Ring Tilt	$E_{1u}(\text{IR})$		$E_u(\text{IR})$	
ν_{26}	Deformation $\delta(\theta\text{-Cr-}\theta)$	$E_{1u}(\text{IR})$		$E_u(\text{IR})$	

ν = stretch; δ_{ipb} = in-plane bend; δ_{opb} = out-of-plane bend; s = symmetric;

as = antisymmetric; θ = C_6H_6 ; R = Raman active; IR = infrared active;

i.a. = inactive.

° Numbering of those normal modes which result from internal vibrations of the benzene ligands (ν_1 to ν_{20}) follows the convention of Wilson²⁴; numbering of the remaining modes follows Fritz et al.^{2,4}



dia.8(vi) The Normal Modes of $Cr(C_6H_6)_2$ Which Involve Motion of the Benzene Ligands Relative to the Chromium Atom (after Fritz et al.²)

Obviously the structure of $Cr(C_6H_6)_2$ is of fundamental importance in determining the activities of its normal vibrations. However, as has been detailed previously, this has proved somewhat controversial. Therefore, the normal modes anticipated for the $Cr(C_6H_6)_2$ molecule are described in Table 8.5 in terms of both the symmetry groups which have been suggested, D_{6h} and D_{3d} . Conversely, the full vibrational analysis of the complex has, in order to avoid excessive duplication, been carried out assuming D_{6h} symmetry only (Table 8.4). Correlation between the two symmetry classes may, however, be effected by means of Table 8.6, whilst a summary of the activities of the vibrations under each symmetry is made in Table 8.7.

Although initial analysis of the infrared spectrum of $Cr(C_6H_6)_2$ by Fritz and Luttkie³ suggested D_{3d} molecular symmetry, almost immediately afterwards the authors changed their interpretation of the spectrum, and adopted D_{6h} symmetry for $Cr(C_6H_6)_2$ in common with $Cr(C_6H_6)_2I$ ⁴ (see later). The results of the latter investigation, carried out on the solid (KBr disc), the vapour and in solution (CS_2 and C_2Cl_4), are summarised in Table 8.8

TABLE 8.6 Correlation of D_{6h} and D_{3d} Symmetries

D_{6h}		D_{3d}
A_{1g}	→	A_{1g}
A_{2g}	→	A_{2g}
E_{1g}	→	A_{2g}
B_{2g}	→	A_{1g}
E_{1g}	→	E_g
E_{2g}	→	E_g
A_{1u}	→	A_{1u}
A_{2u}	→	A_{2u}
B_{1u}	→	A_{2u}
B_{2u}	→	A_{1u}
E_{1u}	→	E_u
E_{2u}	→	E_u

TABLE 8.7 The Activities of the Normal Vibrations of $Cr(C_6H_5)_2$ Under D_{6h} and D_{3d} Symmetries

Symmetry	Infrared Active Vibrations	Raman Active Vibrations	Inactive Vibrations
D_{6h}	10	15	21
D_{3d}	20	19	7

TABLE 8.8(a) The Infrared and Raman Spectroscopic Frequencies (cm⁻¹) and Assignments of Cr(C₆H₅)₆ in the Region Below 900cm⁻¹

Fritz et al. ¹ (1959)		Snyder ⁵ (1959)		Fritz et al. ² (1961)		Fritz and Fischer ¹³ (1967)	
Infrared Frequency	Vibration: Symmetry and Description	Infrared Frequency	Vibration: Symmetry and Description	Infrared Frequency	Vibration: Symmetry and Description	Far-Infrared Frequency	Vibration: Symmetry and Description
633	10 _{op} (E _{1u}) i.m.b.	868 860 851 836		866	16 _{1p} + 24		
794	11 _{1p} (A _{2u}) i.m.b.	796	11 _{1p} (A _{2u}) i.m.b.	832 794 769 726 702	10 _{op} (E _{1u}) ⁷ i.m.b. 11 _{1p} (A _{2u}) i.m.b. 21 + 25 21 + 23		
		737		673			
				626	22 + 24		
490	25(E _{1u}) Ring tilt(cg)	492	25(E _{1u}) Ring tilt(cs)	512	10 _{op} - 24		
459	23(A _{2u}) ν _{as} (θ-Cr-θ)	456	23(A _{2u}) ν _{as} (θ-Cr-θ)	490 459 425 418	25(E _{1u}) Ring tilt(as) 23(A _{2u}) ν _{as} (θ-Cr-θ) 21 + 26	490 459	23(A _{2u}) ν _{as} (θ-Cr-θ) 25(E _{1u}) Ring tilt(cg)
(320)	24(E _{1g}) Ring tilt(s)			332°	24(E _{1g}) Ring tilt(s)		
(305)	22(A _{1u}) Torsion			(305)	22(A _{1u}) Torsion		
(260)	21(A _{1g}) ν _g (θ-Cr-θ)			270°	21(A _{1g}) ν _g (θ-Cr-θ)		
(140)	26(E _{1u}) Deformation			(140)	26(E _{1u}) Deformation	171/159°	26(E _{1u}) Deformation
						152	22(A _{1u}) Torsion

ν = stretch; σ = symmetric; as = anti-symmetric; 1p = in-phase; op = out-of-phase; i.m.b. = internal mode of the benzene ligands.
 7 The numbering of the vibrations has been changed to follow the convention of Fritz et al.^{2,4}
 8 Assignment of symmetry was discussed in this paper, description of the normal modes is given in the above table in terms of D_{6h} symmetry. It should be noted that the assignments are given in the normal modes of the benzene ligands rather than "g" and "u" which are commonly used in the literature.
 9 The frequency assigned from Raman spectroscopy data.
 10 The frequency assigned from Raman spectroscopy data.

Note: In order to avoid possible confusion, the designations "1p" and "op" (in-phase and out-of-phase respectively) have been adopted to describe the internal modes of the benzene ligands rather than "g" and "u" which are commonly used in the literature.

TABLE 8.8 (b) The Infrared and Raman Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{Cr}(\text{C}_6\text{H}_5)_2$ in the Region below 900cm^{-1} (D_{6h} symmetry has been assumed)

Ngai et al. 19 [†] (1969)		Nakamoto et al. 39 (1970)		Schäfer et al. 21 (1971)	
Infrared Frequency	Vibration: Symmetry and Description	Infrared Frequency	Vibration: Symmetry and Description	Raman Frequency	Vibration: Symmetry and Description
860	$10(E_{1u})$ i.m.b.				
830	$2 \times 24^2 + 26^1 13$ or $2 \times 24^2 + 22^1 13$			811	$10(E_{1g})$ i.m.b.
780	$11(A_{2u})$ i.m.b.			791	$11(A_{1g})$ i.m.b.
				733	
680	{ Free Benzene			683	{ Free Benzene
675				651	
650				604	$6_{1p}(E_{2g})$ i.m.b.
480	$25(E_{1u})$ Ring tilt(as)	489-91	$25(E_{1u})$ Ring tilt(as)	490	
450	$23(A_{2u}) \nu_{as}(\theta-Cr-\theta)$	453-75	$23(A_{2u}) \nu_{as}(\theta-Cr-\theta)$		
				400	$16_{op}(E_{2g})?$ i.m.b.
				335	$24(E_{1g})$ Ring tilt (s)
				277	$21(A_{1g}) \nu_s(\theta-Cr-\theta)$
				178	

ν = stretch; θ = symmetric; ω = antisymmetric; $1p$ = in-phase; op = out-of-phase; i.m.b. = internal mode of the benzene ligands. $\dagger$ The numbering of the vibrations has been changed to follow the convention of Fritz et al.^{2,4}

$\ddagger$ Although D_{3d} symmetry was assumed in this paper, description of the normal modes is given in the above table in terms of D_{6h} symmetry to enable straightforward comparison with other work.

() Frequency inferred from combination band.

o Raman band.

oo Frequency compared from C_6D_6 solution data.

$\dagger$ See above data.

Note In order to avoid possible confusion, the designations "ip" and "op" (in-phase and out-of-phase respectively) have been adopted to describe the internal modes of the benzene ligands rather than "u" and "g" which are commonly used in the literature.

for the spectral region below 900cm^{-1} , in which the six modes of the benzene ligands relative to the metal atom (dia.8(vi)), as well as the lowest frequency internal benzene modes, were assigned.

In the same year (1959), Snyder⁵, in a paper which primarily sought to compare the spectra of $\text{Cr}(\text{C}_6\text{H}_6)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)_2$, reported the spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2$ samples which had been sublimed onto a cooled infrared-transparent window (Table 8.8). With the exception of the vibration $\nu_{10\text{op}}(\text{E}_{1\text{u}})$, which was placed at 1014cm^{-1} rather than 833cm^{-1} ⁴ (because it was considered that as an out-of-plane C-H bend it should occur at a frequency in $\text{Cr}(\text{C}_6\text{H}_6)_2$ higher than that suggested for C_6H_6 (854cm^{-1} ³⁴), the bands located and assignments derived followed from the earlier work of Fritz et al.⁴

A crude partial Normal Co-ordinate Analysis (NCA) was carried out for the internal ligand modes of $\text{A}_{2\text{u}}$ and $\text{E}_{1\text{u}}$ symmetry, assuming (i) that the benzene rings were uncoupled from the rest of the $\text{Cr}(\text{C}_6\text{H}_6)_2$ molecule, and (ii) that their geometry was the same as that of free benzene. Employing the fundamental frequencies of $\text{Cr}(\text{C}_6\text{H}_6)_2$, force constants were calculated, which were shown to be decreased in value (relative to C_6H_6) in the case of those resulting from the C-C stretches, $\nu_{10\text{p}}(\text{A}_{2\text{u}})^\dagger$ and $\nu_{19\text{ip}}(\text{E}_{1\text{u}})^\dagger$, but increased substantially in value in the case of that derived from the out-of-plane hydrogen bend, $\nu_{11\text{ip}}(\text{A}_{2\text{u}})^\dagger$ (dia.8(iii)).

A more comprehensive spectroscopic investigation of $\text{Cr}(\text{C}_6\text{H}_6)_2$ was published in 1961 by Fritz et al.², which as well as detailing the solid (KBr disc and Nujol mull), vapour and solution (CS_2 and C_2Cl_4) infrared

[†] The labelling of these modes has been changed from that used originally so that the convention of Fritz et al. is now followed.^{2,4}

spectra, also described the first solution (C_6H_6) Raman spectrum (Table 8.8). However, measurement of the latter spectrum, because of the dark colour and low solubility of the complex, and also the similarity of solvent absorptions, only permitted confirmation of the frequencies previously designated ν_{21} (ν_s ($\text{O}-\text{Cr}-\text{O}$), A_{1g}) and ν_{24} (symmetric ring tilt, E_{1g}) from analysis of combination bands. In contrast, the infrared spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2$ could be further assigned in the region containing internal ligand vibrations, and several additional transitions resulting from combination bands were identified.

The spectroscopic study of $\text{Cr}(\text{C}_6\text{H}_6)_2$ was extended into the far-infrared ($33\text{--}600\text{cm}^{-1}$) by Fritz and Fischer (1967)¹³, who measured both solid phase (nujol mull) and solution (CS_2) spectra (Table 8.8). Two previously unobserved low frequency transitions were located at 152cm^{-1} and 171cm^{-1} (159cm^{-1} CS_2 solution), which were correlated with ν_{22} (torsional mode, A_{1u}) and ν_{26} (deformation mode, E_{1u}) respectively, in both cases, re-assignment being necessitated from the frequencies first indicated from combination band analysis, 305cm^{-1} (ν_{22}) and 140cm^{-1} (ν_{26})^{2,4}. To higher energy, the assignments of the bands at 459cm^{-1} and 490cm^{-1} were reversed, with the former being designated ν_{25} (antisymmetric ring tilt, E_{1u}) and the latter being identified as ν_{23} (ν_{as} ($\text{O}-\text{Cr}-\text{O}$), A_{2u}).

In a lengthy discussion of the symmetry of $\text{Cr}(\text{C}_6\text{H}_6)_2$ as deduced from spectroscopic investigations, it was pointed out by Fritz and Fischer that work carried out on $\text{V}(\text{C}_6\text{H}_6)_2$ in two crystalline forms (monoclinic and cubic) had shown the infrared spectrum of the benzene ligands of that complex to be little influenced by either crystal factor or site group. It was therefore argued by analogy that the number of frequencies recorded in the infrared spectrum of solid phase $\text{Cr}(\text{C}_6\text{H}_6)_2$ should be ascribed to the presence of D_{3d} molecular symmetry, rather than the effect of factor group splitting on the spectrum of a molecule of D_{6h} symmetry. Hence

D_{3d} symmetry was assumed in this study.

In an attempt to establish conclusively the symmetry of the $\text{Cr}(\text{C}_6\text{H}_6)_2$ molecule, a detailed investigation ($400\text{--}4000\text{cm}^{-1}$) of the vapour phase infrared spectrum was carried out by Ngai et al. (1969)¹⁹ (Table 8.8). Eight infrared active frequencies were located in the region under study, as opposed to the nine infrared active frequencies expected under D_{6h} symmetry, or the nineteen indicated under D_{3d} symmetry (Table 8.7)[†]. It was therefore concluded that D_{6h} molecular symmetry prevailed (at least in the vapour state), with $\nu_{18\text{ip}}$ being the unobserved mode.

Additionally, the uncertainty which was thought to exist regarding the assignment of the mode $\nu_{10\text{op}}(E_{1u})$ was considered. It was suggested that the vibration, as an out-of-plane bending mode, should occur at a higher frequency in $\text{Cr}(\text{C}_6\text{H}_6)_2$ than that established for benzene (854cm^{-1} ³⁴). This view led to the re-assignment of $\nu_{10\text{op}}$ from 833cm^{-1} ^{2,4} to 860cm^{-1} and to the parallel conclusion that the 833cm^{-1} transition must originate from a combination band. Amongst other assignments made, the scheme of Fritz et al.^{2,4} was followed regarding ν_{23} ($\nu_{\text{as}}(\text{O--Cr--O}), A_{2u}$) and ν_{25} (antisymmetric ring tilt, E_{1u}), with these modes being correlated with frequencies of 450cm^{-1} and 480cm^{-1} respectively, rather than vice versa as suggested in the later paper of Fritz and Fischer¹³.

Support for the original assignment scheme of Fritz et al.^{2,4} relating to ν_{23} and ν_{25} was, indeed, furnished by infrared measurements made by Nakamoto et al.³⁹ on pure $\text{Cr}(\text{C}_6\text{H}_6)_2$ samples subjected to high and low pressure (Table 8.8). It was considered that as ν_{23} ($\nu_{\text{as}}(\text{O--Cr--O}), A_{2u}$) involved a volume change larger than that of the mode ν_{25} (antisymmetric ring tilt, E_{1u}), the infrared band representing the former vibration should

[†] Although D_{6h} molecular symmetry indicates a total of 10 infrared active vibrations for $\text{Cr}(\text{C}_6\text{H}_6)_2$, and D_{3d} molecular symmetry suggests 20 infrared active vibrations (Table 8.7), evidence from previous work led Ngai et al.¹⁹ to expect the deformation mode, $\nu_{26}(E_{1u})$, to lie outside the frequency range investigated (at 171cm^{-1} ¹³).

be the more sensitive to pressure variation. This belief was apparently confirmed by experiment with the frequency of 489cm^{-1} moving to 491cm^{-1} , and that at 453cm^{-1} moving to 475cm^{-1} , on the application of pressure. Hence

ν_{23} ($\nu_{\text{as}}(\text{O-Cr-O}), A_{2u}$) was identified with the $453\text{-}75\text{cm}^{-1}$ transition, and ν_{25} (antisymmetric ring tilt, E_{1u}) with the $489\text{-}91\text{cm}^{-1}$ peak.

The final spectroscopic investigation of $\text{Cr}(\text{C}_6\text{H}_6)_2$ was a solid phase Raman study (KBr disc and pure pellet) carried out in 1971 by Schäfer et al.²¹ (Table 8.8). In the region of the spectrum which is of most concern to the present work (below 900cm^{-1}), it was possible to make the further correlation of the modes $\nu_{16\text{op}}(E_{2g})$, $\nu_{6\text{ip}}(E_{2g})$, $\nu_{11\text{op}}(A_{1g})$ and $\nu_{10\text{ip}}(E_{1g})$ with the frequencies 400cm^{-1} , 604cm^{-1} , 791cm^{-1} and 811cm^{-1} respectively. On the basis of these and past assignments,^{2,5} a preliminary partial Normal Co-ordinate Analysis (Table 8.9) was attempted of those internal modes of the benzene groups within $\text{Cr}(\text{C}_6\text{H}_6)_2$ derived from optically active vibrations of free benzene (initial force constants for $\text{Cr}(\text{C}_6\text{H}_6)_2$ being taken from the latter molecule and subsequently refined to reproduce observed frequencies). This showed that for $\text{Cr}(\text{C}_6\text{H}_6)_2$, and several other complexes with which it was compared ($\text{Mo}(\text{C}_6\text{H}_6)_2$, $\text{W}(\text{C}_6\text{H}_6)_2$, $\text{V}(\text{C}_6\text{H}_6)_2$, $\text{Cr}(\text{C}_6\text{H}_6)_2^+$, $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, $\text{C}_6\text{H}_6\text{Mo}(\text{CO})_3$, $\text{C}_6\text{H}_6\text{CrC}_5\text{H}_5$ and $\text{C}_6\text{H}_6\text{MnC}_5\text{H}_5$), frequency shifts in the internal benzene modes between the free and complexed states resulted from changes in the off-diagonal force constants, rather than the on-diagonal elements which changed little.

In later work, the Raman data from this study, and the infrared results of Ngai et al.¹⁹, were used to calculate mean C-C amplitudes of vibration within the benzene ligands of $\text{Cr}(\text{C}_6\text{H}_6)_2$ ²⁰, thereby yielding the first conclusive proof for the possession of D_{6h} molecular symmetry by $\text{Cr}(\text{C}_6\text{H}_6)_2$ in the vapour phase (see previously).

As well as the above mentioned partial Normal Co-ordinate Analysis, a series of refined Normal Co-ordinate Analyses of $\text{Cr}(\text{C}_6\text{H}_6)_2$ as a 25 atom molecule have been published by Brunvoll, Cyvin and Schäfer⁴⁰⁻⁴².

TABLE 8.9

The Spectroscopic Frequencies (cm^{-1}) and Assignments Suggested by a Series of Normal Co-ordinate Analyses of $\text{Cr}(\text{C}_6\text{H}_5)_2$ for the Region Below 900cm^{-1} (D_{6h} Symmetry has been assumed).

Observed Frequency	Schäfer et al. ²¹ (1971)		Brunvoll et al. ⁴⁰ (1971)		Schäfer et al. ⁴¹ (1972)		Cyvin et al. ⁴² (1971)	
	Calculated Frequency	Assignment	Calculated Frequency	Assignment	Calculated Frequency	Assignment	Calculated Frequency	Assignment
860	860	$10_{op}(E_{1u})$ i.m.b.	860	$10_{op}(E_{1u})$ i.m.b.	885	$10_{op}(E_{1u})$ i.m.b.	860	$10_{op}(E_{1u})$ i.m.b.
-			860	$10_{1p}(E_{1g})$ i.m.b.	864	$10_{1p}(E_{1g})$ i.m.b.	860	$10_{1p}(E_{1g})$ i.m.b.
794	794	$11_{1p}(A_{2u})$ i.m.b.	916	$11_{1p}(A_{2u})$ i.m.b.	916	$11_{1p}(A_{2u})$ i.m.b.	794	$11_{1p}(A_{2u})$ i.m.b.
791			880	$11_{op}(A_{1g})$ i.m.b.	880	$11_{op}(A_{1g})$ i.m.b.	791	$11_{op}(A_{1g})$ i.m.b.
-			709	$4_{1p}(B_{2g})$ i.m.b.	709	$4_{1p}(B_{2g})$ i.m.b.	709	$4_{1p}(B_{2g})$ i.m.b.
-			709	$4_{op}(B_{1u})$ i.m.b.	709	$4_{op}(B_{1u})$ i.m.b.	709	$4_{op}(B_{1u})$ i.m.b.
604	603.6	$6_{1p}(E_{2g})$ i.m.b.	604	$6_{1p}(E_{2g})$ i.m.b.	606	$6_{1p}(E_{2g})$ i.m.b.	604	$6_{1p}(E_{2g})$ i.m.b.
-			604	$6_{op}(E_{2u})$ i.m.b.	606	$6_{op}(E_{2u})$ i.m.b.	604	$6_{op}(E_{2u})$ i.m.b.
490			439	$23(A_{2u})\nu_{as}(\text{O-Cr-O})$	439	$23(A_{2u})\nu_{as}(\text{O-Cr-O})$	490	$23(A_{2u})\nu_{as}(\text{O-Cr-O})$
459			459	$25(E_{1u})\text{Ring tilt}(as)$	459	$25(E_{1u})\text{Ring tilt}(as)$	459	$25(E_{1u})\text{Ring tilt}(as)$
-			409	$16_{1p}(E_{2u})$ i.m.b.	399	$16_{1p}(E_{2u})$ i.m.b.	409	$16_{1p}(E_{2u})$ i.m.b.
409			409	$16_{op}(E_{2g})$ i.m.b.	399	$16_{op}(E_{2g})$ i.m.b.	409	$16_{op}(E_{2g})$ i.m.b.
335			335	$24(E_{1g})\text{Ring tilt}(s)$	334	$24(E_{1g})\text{Ring tilt}(s)$	335	$24(E_{1g})\text{Ring tilt}(s)$
277			254	$21(A_{1g})\nu_s(\text{O-Cr-O})$	254	$21(A_{1g})\nu_s(\text{O-Cr-O})$	277	$21(A_{1g})\nu_s(\text{O-Cr-O})$
171			171	$26(E_{1u})\text{Deformation}$	170	$26(E_{1u})\text{Deformation}$	171	$26(E_{1u})\text{Deformation}$
152			152	$22(A_{1u})\text{Torsion}$	152	$22(A_{1u})\text{Torsion}$	152	$22(A_{1u})\text{Torsion}$

ν = stretch; s = symmetric; as = antisymmetric; $1p$ = in-phase; op = out-of-phase; i.m.b. = internal mode of the benzene ligands

In all cases, a model was adopted in which the benzene ligands were planar, the molecular symmetry was D_{6h} and the molecular structure was that determined for the gas phase by Haaland¹¹.

In the papers of Brunvoll et al.⁴⁰ and Schäfer et al.⁴¹, an approximate force field was created which assumed (i) that there was no interaction between modes of different symmetries, and (ii) that the force constants of the internal ligand vibrations could be approximated by those previously calculated for free benzene from the assignments of Brodersen and Langseth⁴³. A final harmonic force field was then produced by refinement so that consistency was achieved between the frequencies generated by calculation and those measured experimentally^{2,4,5,13,19,21}. Employing this final force field, mean C-C amplitudes of vibration were calculated for the benzene ligands which compared favourably with those reported in the electron diffraction study of Haaland.¹¹

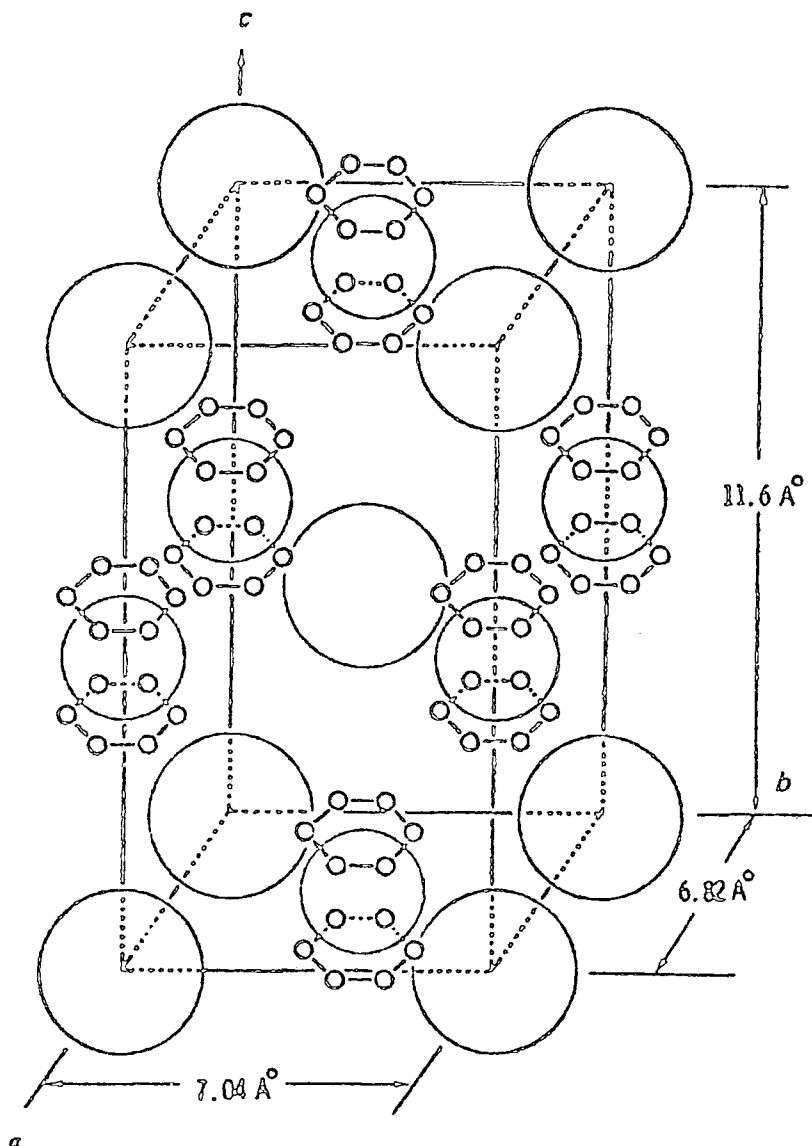
An alternative set of symmetry co-ordinates (internal co-ordinates) was employed in the Normal Co-ordinate Analysis carried out by Cyvin et al.⁴². Again the force field created was refined to fit exactly reported vibrational frequencies^{2,13,21}; however, in this case mean amplitudes of vibration were calculated for all types of interatomic distances in $Cr(C_6H_6)_2$ not just the C-C bonds. These showed that not only were the interatomic distances within one ligand very similar to those of benzene, but that once more excellent agreement existed between the value of the C-C mean amplitude of vibration obtained by calculation and that determined by electron diffraction.¹¹ In contrast, perpendicular amplitude correction co-efficients^{42,44} which were also evaluated, did not show such similarity with those of benzene, and this was ascribed to the presence of a large central atom and second benzene ligand in $Cr(C_6H_6)_2$ (which were suggested to cause steric hindrance to modes involving excessive deformation out of the ring plane).

Finally, the results of partial Normal Co-ordinate Analyses^{5,20,21}, which considered ligands and framework separately (and which failed to show the presence of kinematic coupling), were contrasted⁴⁵ with the results of the total molecule Normal Co-ordinate Analyses⁴⁰⁻⁴² (which revealed kinematic coupling). The examples chosen were the modes $\nu_{11op}(\delta_{opb}(C-H), A_{1g})$, and $\nu_{11ip}(\delta_{opb}(C-H), A_{2u})$, located respectively at 791cm^{-1} in the Raman spectrum²¹ and 794cm^{-1} in the infrared spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2^{2,4,5}$, and which derive from the ν_{11} vibration ($\delta_{opb}(C-H), A_{2u}$) of benzene situated at 687cm^{-1} ³⁴. In the Normal Co-ordinate Analyses which treated the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$ as isolated molecules with D_{6h} symmetry^{5,20,21}, it was necessary to increase the value of the force constant by ca. 40% compared with that of free benzene in order to explain the frequency change. However, the "whole molecule" Normal Co-ordinate Analyses⁴⁰⁻⁴² enabled reproduction of the observed ν_{11ip} and ν_{11op} frequencies employing a force constant exactly the same as that of free benzene, the frequency increase between free and complexed benzene being shown to result from strong coupling between respectively $\nu_{11op}(A_{1g})$ and $\nu_{21}(\nu_s(\text{O-Cr-O}), A_{1g})$ in the Raman spectrum, and $\nu_{11ip}(A_{2u})$ and $\nu_{23}(\nu_{as}(\text{O-Cr-O}), A_{2u})$ in the infrared spectrum.

2. Introduction: $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$

a) The Structure of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$

In contrast with the uncharged species, $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ has always been assumed from spectral evidence to possess D_{6h} symmetry^{2,4}. However, the conflicting evidence of a preliminary room temperature space group and unit cell determination, which suggested a structure for $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ in which $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ ions were oriented along the c axis (with probably disordered benzene rings)⁴⁶, and a proton resonance study which had been interpreted as showing these ions oriented along the a axis⁴⁷, led Morosin to investigate the X-ray crystal structure of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ in greater detail.⁴⁸



dia.8(vii) The Crystal Structure of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ at 173K (after Morosin⁴⁸)

A room temperature determination ($R=0.055$) showed the benzene rings to be either completely disordered or rotating (the former suggestion was considered the more probable), with the rotation axis of the $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ ion along the c axis of a body-centred tetragonal cell possessing dimensions $a = b = 7.031 \pm 0.003 \text{ \AA}$ and $c = 11.754 \pm 0.005 \text{ \AA}$. Although the data were consistent with 4/mmm symmetry, space group $\text{I}\bar{4}\text{m}2(\text{D}_{2d}^9)$ was selected because a simple disordered model could be proposed which would involve the minimum of changes to ensure compatibility with low temperature data.

These indicated that, upon cooling (173K), the benzene rings became ordered, with an orthorhombic structure being adopted (cell dimensions: $a = 6.82\text{\AA}$, $b = 7.04\text{\AA}$ and $c = 11.64\text{\AA}$), belonging to space group Immm (D_{2h}^{25}) (dia.8(vii)).

Table 8.10 Structural Data for $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ at Room Temperature⁴⁸

Bond Length C-C	$1.40\text{\AA}^{\neq}$
Bond Length Cr-C	$2.13 \pm 0.04\text{\AA}$
Distance of Mean Carbon Plane from Chromium	$1.59\text{\AA}$
Closest C-I Separation	$3.90 \pm 0.04\text{\AA}$
Closest Intermolecular C-C separation	$3.43 \pm 0.04\text{\AA}$

[≠] C-C bond distance was fixed at this value in the least-squares refinement.

b) The Barrier to the Rotation of the Benzene Ligands in $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$

To our knowledge, no investigation has been made of the barrier to the rotation of the benzene groups in $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$. Consequently, the work of Campbell et al.²³ pertaining to $\text{Cr}(\text{C}_6\text{H}_6)_2$ will be used as guidance in this study.

c) Previous Spectroscopic Studies of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$

As has been stated previously, the species $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ has been shown to possess six-fold symmetry^{2,4}. The normal vibrations expected will therefore be identical to those described for $\text{Cr}(\text{C}_6\text{H}_6)_2$ (Table 8.5 and dias.8(iii) and (vi)), but, of course, with the proviso that the descriptions employing D_{6h} symmetry will apply.

The first major investigation of the spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ was reported by Fritz et al. in 1959⁴, in a paper which also presented the infrared spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2$. From infrared and Raman measurements, carried out respectively on the solid (KBr disc) and of the complex in

TABLE 8.11 The Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{Cr}(\text{C}_6\text{H}_5)_2$ Suggested from Experiment and Normal Co-ordinate Analysis (D_{6h} symmetry is assumed)

Fritz et al. ⁴ (1959)	Fritz et al. ² (1961)	Saito et al. ⁴⁹ (1967)	Schäfer et al. ²¹ (1971)	Cyvin et al. ⁴⁵ (1970)
Frequency	Vibration: Symmetry and Description	Infrared Frequency	Vibration: Symmetry and Description	Calculated Frequency
837 ^f 803 ^o 795 ^f 790 ^o	10 _{op} (E _{1u}) i.m.b. 10 _{1p} (E _{1g}) i.m.b. 11 _{1p} (A _{2u}) i.m.b. 11 _{op} (A _{1g}) i.m.b.	858 795	10 _{1p} (E _{1g}) i.m.b. 11 _{1p} (A _{2u}) i.m.b.	837 795 794
(630) 616 ^o (543)	6 _{op} (E _{2u}) i.m.b. 6 _{1p} (E _{2g}) i.m.b. 16 _{1p} (E _{2u}) i.m.b.			615.9 6 _{1p} (E _{2g}) i.m.b.
400 ^f 420 ^o 415 ^f 390 ^o (320) 270 ^o (144)	23(E _{1u}) Ring tilt (m) 16 _{op} (E _{2g}) i.m.b. 23(A _{2u}) ν _{as} (β-Cr-θ) 24(E _{1g}) Ring tilt (o) 22(A _{1u}) torsion 21(A _{1g}) ν _o (β-Cr-θ) 26(E _{1u}) Deformation	467 418	25(E _{1u}) Ring tilt (as) 23(A _{2u}) ν _{as} (β-Cr-θ)	490 459 25(E _{1u}) Ring tilt (m)

ν = stretching; o = out-of-phase; m = calculated; 1p = in-phase; op = out-of-phase; i.m.b. = internal mode of the benzene ligand.
 f = infrared band.
 o = Raman band.

solution (CH_3OH), were derived the frequencies and assignments displayed in Table 8.11 for the region of the spectrum of interest in this work (below 900cm^{-1}). Nine normal modes were located in the infrared spectrum as opposed to ten predicted under the assumption of D_{6h} molecular symmetry.[†] Furthermore, the facility with which the Raman spectrum of the cationic species could be measured in comparison with $\text{Cr}(\text{C}_6\text{H}_6)_2$, allowed identification of all fifteen normal vibrations expected to be Raman active under that symmetry (Table 8.7). Consequently, D_{6h} symmetry could be confirmed under the double criteria^{††} of the number of normal vibrations observed, and the number of these seen only in the Raman spectrum.

Subsequently, a still more comprehensive spectroscopic study of $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ was published by Fritz et al.², which supplemented the spectra reported previously with the infrared spectra of the complex in nujol mull and in solution (H_2O and CH_3OH), and with the Raman spectrum of the complex in aqueous solution (Table 8.11). As well as re-affirming the frequencies and assignments of the earlier paper, several additional transitions were identified as combination bands.

A re-investigation of the solid-phase infrared spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ (KBr disc) was undertaken in 1967 by Saito et al.⁴⁹, as part of a study which attempted to calculate the C-H out-of-plane force constants of the ligand molecules (Table 8.11). Whilst the assignment scheme of Fritz et al.^{2,4} was generally followed, the 858cm^{-1} frequency was, in this work, assigned to $\nu_{10ip}(\text{E}_{1g})$. However, no reason was given for the

[†] The infrared active mode not located, the deformation mode $\nu_{26}(\delta(\text{O}-\text{Cr}-\text{O}), \text{E}_{1u})$ would be expected to occur in the far-infrared which was not investigated in this work.

^{††} As the $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ species has a centre of inversion, the rule of mutual exclusion must apply to the normal vibrations. However, since vibrations of the benzene ligands should have only weak coupling between in-phase and out-of-phase modes, frequency splittings might be expected to occur. These can be small and so "pseudo-coincidences" may occur. The experimental criteria for distinguishing molecular symmetry (e.g. D_{6h} from D_{3d}) are thus (i) the number of observed normal modes, (ii) the number of pseudo-coincidences and (iii) the number of normal modes appearing only in the Raman spectrum.⁹

correlation of this band with $\nu_{10_{ip}}(E_{lg})$ rather than with $\nu_{10_{op}}(E_{lu})$ as suggested by Fritz et al.^{2,4}. In view of the fact that the E_{lg} species would be expected to be Raman active, and the E_{lu} species infrared active, this identification must be considered dubious.

Two incomplete and approximate Normal Co-ordinate Analyses have been published of $Cr(C_6H_6)_2I$ ^{21,45} as part of studies carried out by Cyvin et al. concerned primarily with $Cr(C_6H_6)_2$. In the first work²¹, a partial Normal Co-ordinate Analysis was made of some benzene ligand modes of $Cr(C_6H_6)_2I$, using force constants initially taken from benzene. Refinement was then achieved by allowing the calculated frequencies to tend to those observed², and the modified force constants thus derived were compared with those calculated for similar ligand vibrations of other benzene-containing complexes ($Cr(C_6H_6)_2$, $Mo(C_6H_6)_2$, $W(C_6H_6)_2$, $V(C_6H_6)_2$, $C_6H_6Cr(CO)_3$, $C_6H_6Mo(CO)_3$, $C_6H_6CrC_5H_5$ and $C_6H_6MnC_5H_5$).

In the second paper⁴⁵, the partial Normal Co-ordinate Analysis approach was dropped in favour of a "25 atom" model which employed both the same structural parameters and the same force field as had been generated previously for $Cr(C_6H_6)_2$. Calculated frequencies were obtained not only for $Cr(C_6H_6)_2I$, but also for the complexes $(C_6H_6)_2M$ and $(C_6H_6)_2M^+$ (where $M=Cr, V, Mo$ and W , and $M^+ = Mo^+, W^+, Tc^+$ and Re^+), comparison being made only between those observed frequencies where assignments had been established for all of the complexes (ν_{23} , ν_{25} and $\nu_{11_{ip}}^+$). As in the case of $Cr(C_6H_6)_2$, kinematic coupling was shown to be the cause of the frequency change found between $\nu_{11_{ip}}(A_{2u})$ of the complexes (located in the range $742-798cm^{-1}$) and $\nu_{11}(A_{2u})$ of free benzene ($687cm^{-1}$ ³⁴) (see previously). In addition, it was found, contrary to expectation, that the

† The assignments stated in this work for the vibrations ν_{23} and ν_{25} of $Cr(C_6H_6)_2I$ are the reverse of those reported by Fritz et al.^{2,4} and Saito et al.⁴⁹ It must therefore be presumed that a re-assignment has been made following the far-infrared study of $Cr(C_6H_6)_2$ by Fritz and Fischer¹³, which placed ν_{23} at a higher frequency ($490cm^{-1}$) than ν_{25} ($459cm^{-1}$).

frequencies of ν_{23} and ν_{25} were influenced less by electronic configuration than by the mass of the central atom.

3. Experimental

$\text{Cr}(\text{C}_6\text{H}_6)_2$ was purchased from Strem Chemicals Inc., and $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ prepared from the neutral species following a standard literature preparation.⁵⁰

INS spectra of both complexes were measured with the samples (polycrystalline powders) contained in thick wall (1mm) silica cells. Time-of-Flight data were obtained at 233K using the 4H5 spectrometer, whilst BFD spectra were recorded employing the Dido Instrument at 18K ($\text{Cr}(\text{C}_6\text{H}_6)_2$) and 12K ($\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$) respectively.

Far-infrared measurements ($40\text{--}250\text{cm}^{-1}$) were made at liquid nitrogen temperature using a Beckman-RIIC FS720 Fourier Transform Spectrophotometer, whilst the near- and mid-infrared regions were scanned at room temperature employing a Perkin-Elmer 577 Spectrometer. With the former instrument, samples were run as nujol mulls supported on polyethylene disc, with the latter, either as CsI discs or as nujol mulls between CsI plates.

Raman spectra ($\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ only) were measured in the range $0\text{--}900\text{cm}^{-1}$ with a Cary 82 Raman Spectrometer employing a Spectra Physics Model 125 He/Ne laser at $15,802\text{cm}^{-1}$ (6mW power).

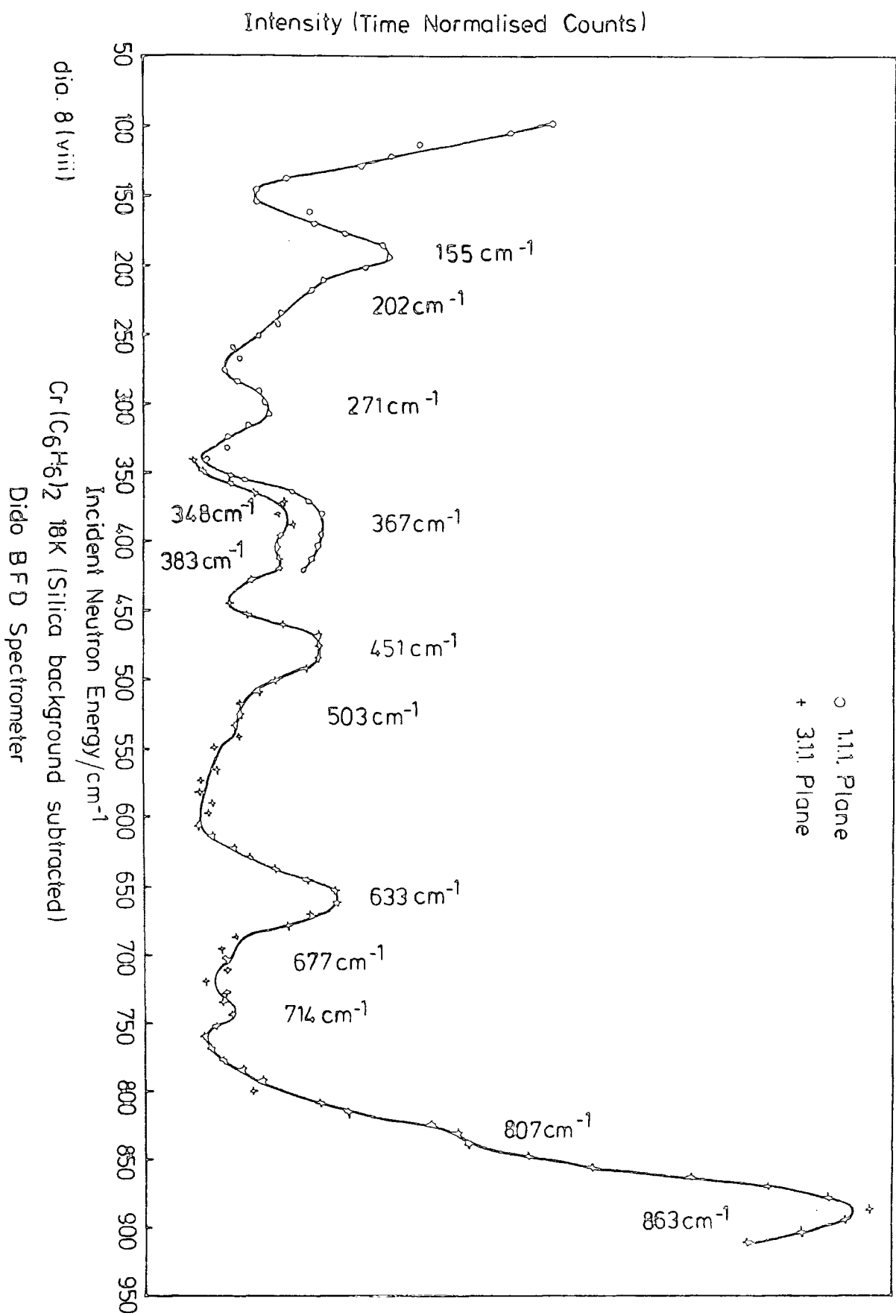
4. Discussion of Results

a) $\text{Cr}(\text{C}_6\text{H}_6)_2$

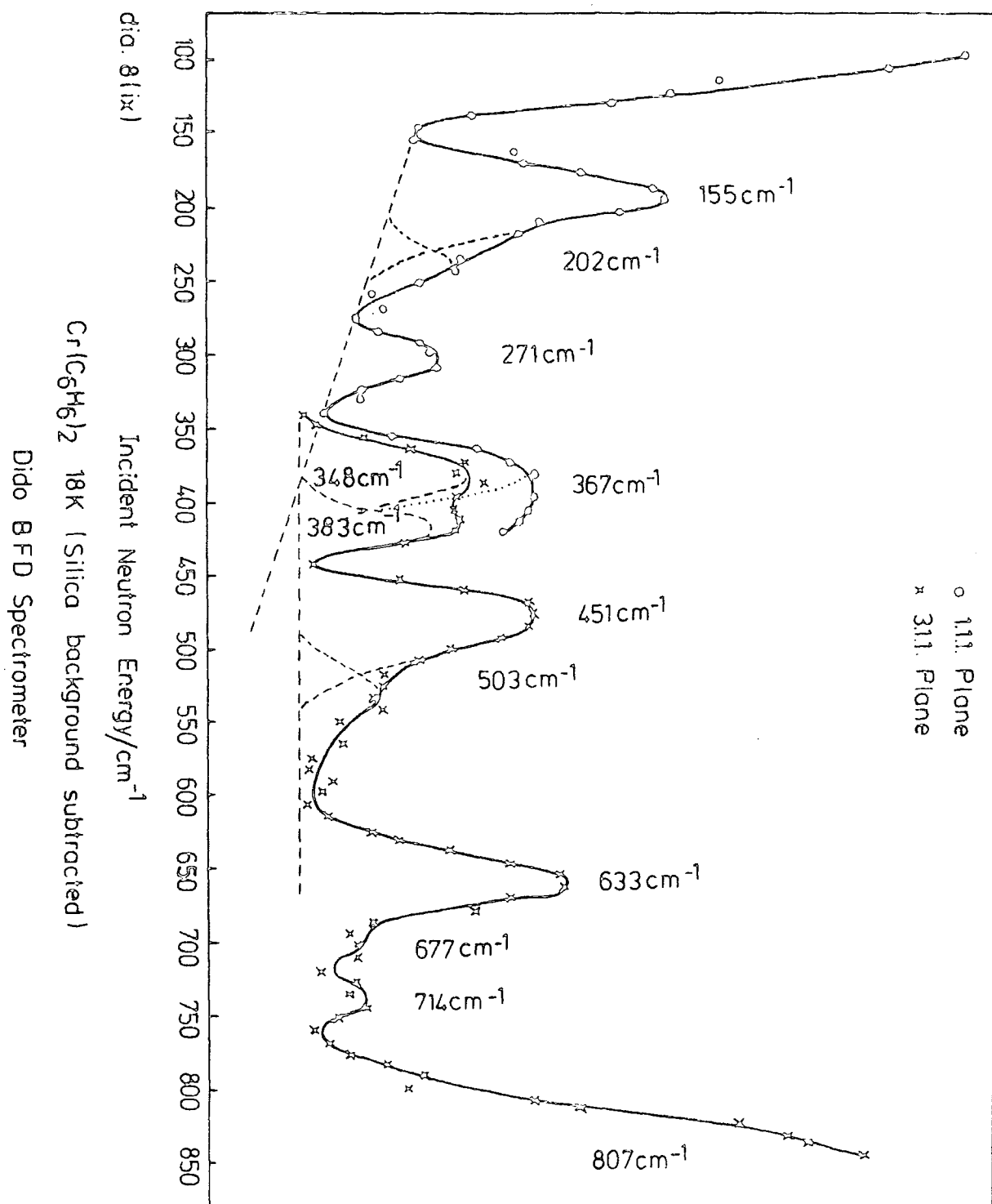
The INS spectra of $\text{Cr}(\text{C}_6\text{H}_6)_2$ are shown in dias.8(viii)-(xi), and are summarised in Table 8.12.

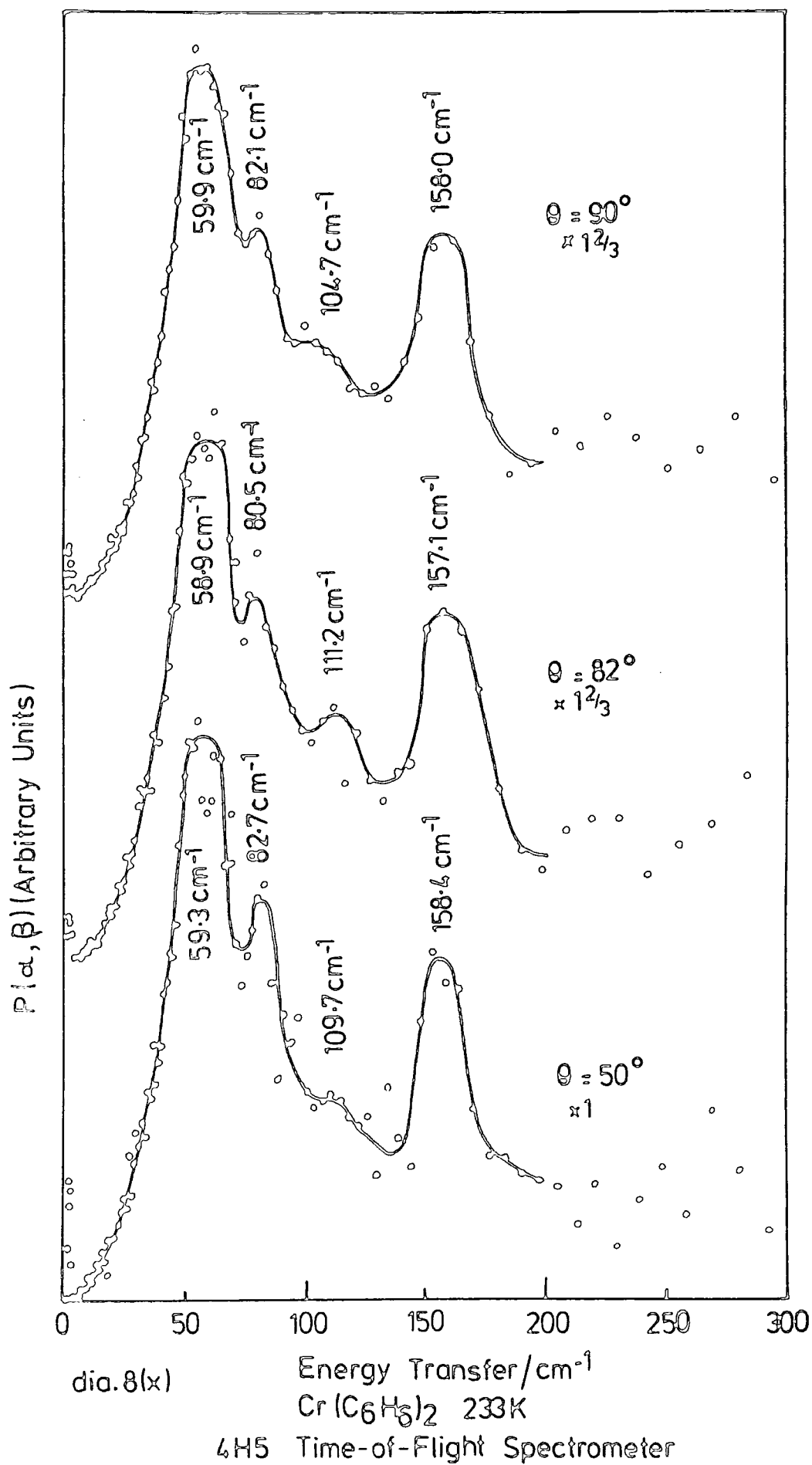
Employment of Tables 8.8 and 8.9, which contain respectively details of previous assignment schemes and the results of various Normal Co-ordinate Analyses carried out on $\text{Cr}(\text{C}_6\text{H}_6)_2$, allows reasonably easy identification of the internal modes of the benzene ligands[†]. Hence the 863cm^{-1} BFD

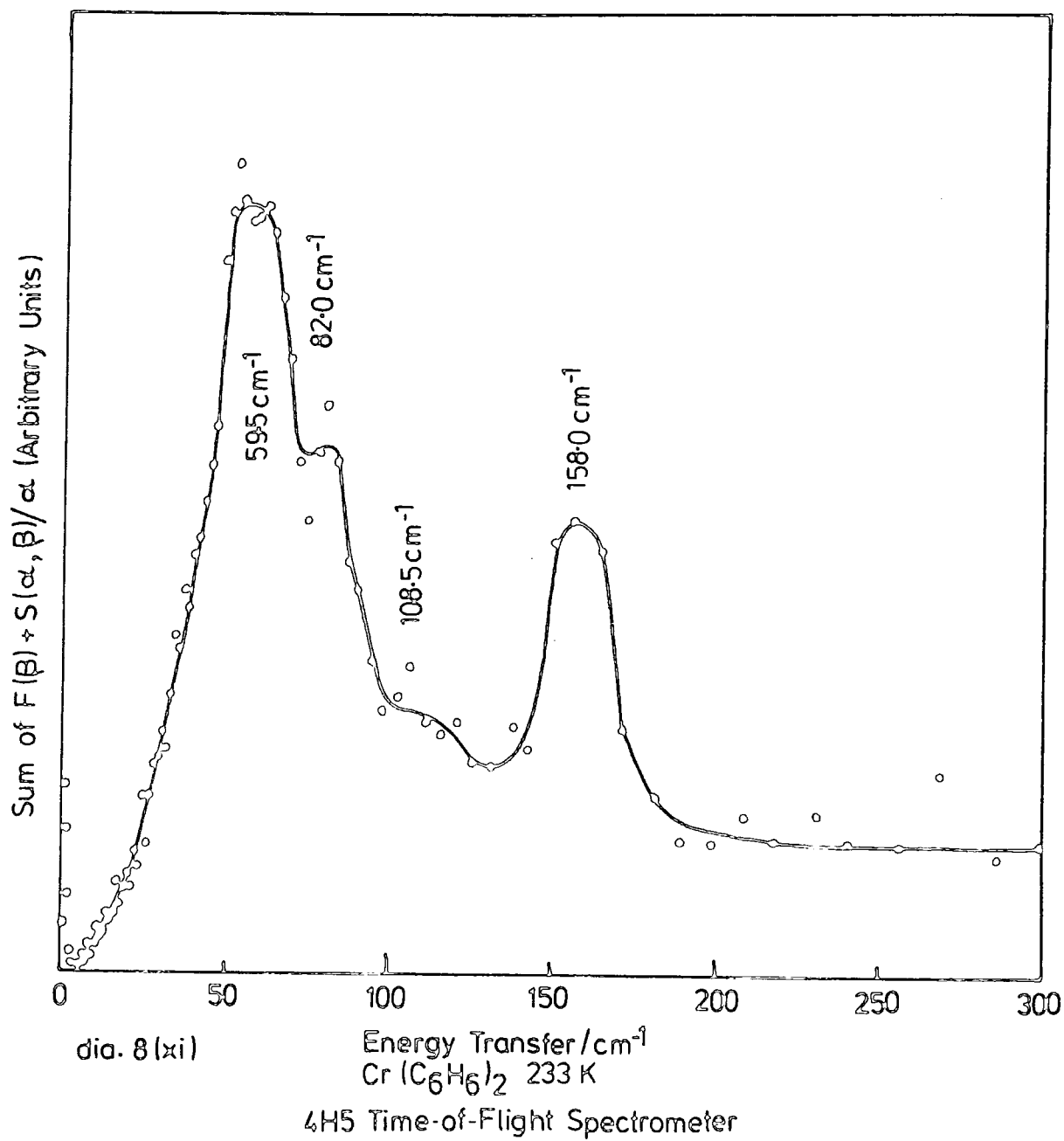
[†] It will be assumed in forthcoming discussion that D_{6h} symmetry is possessed by $\text{Cr}(\text{C}_6\text{H}_6)_2$.



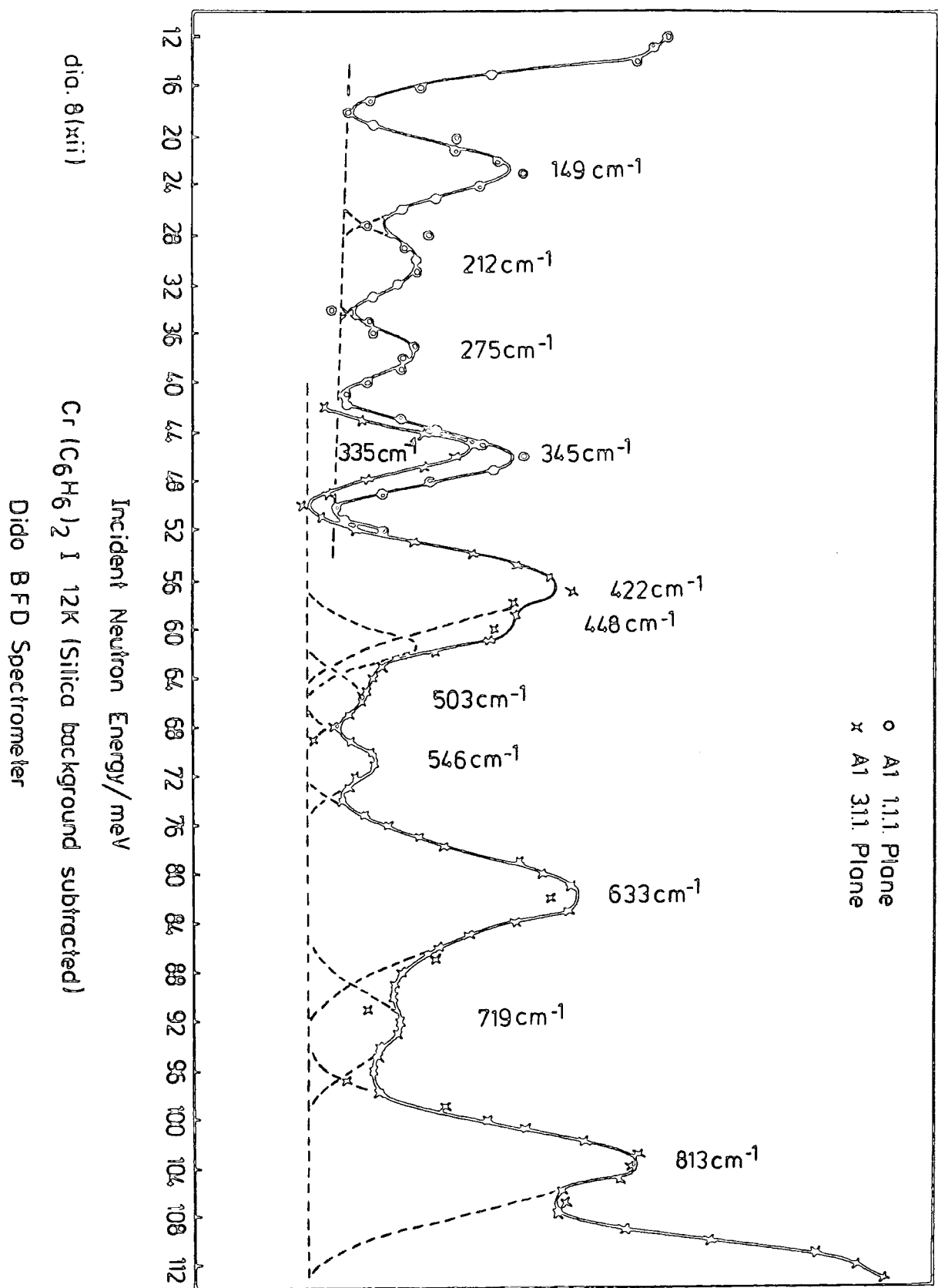
Intensity (Time Normalised Counts)

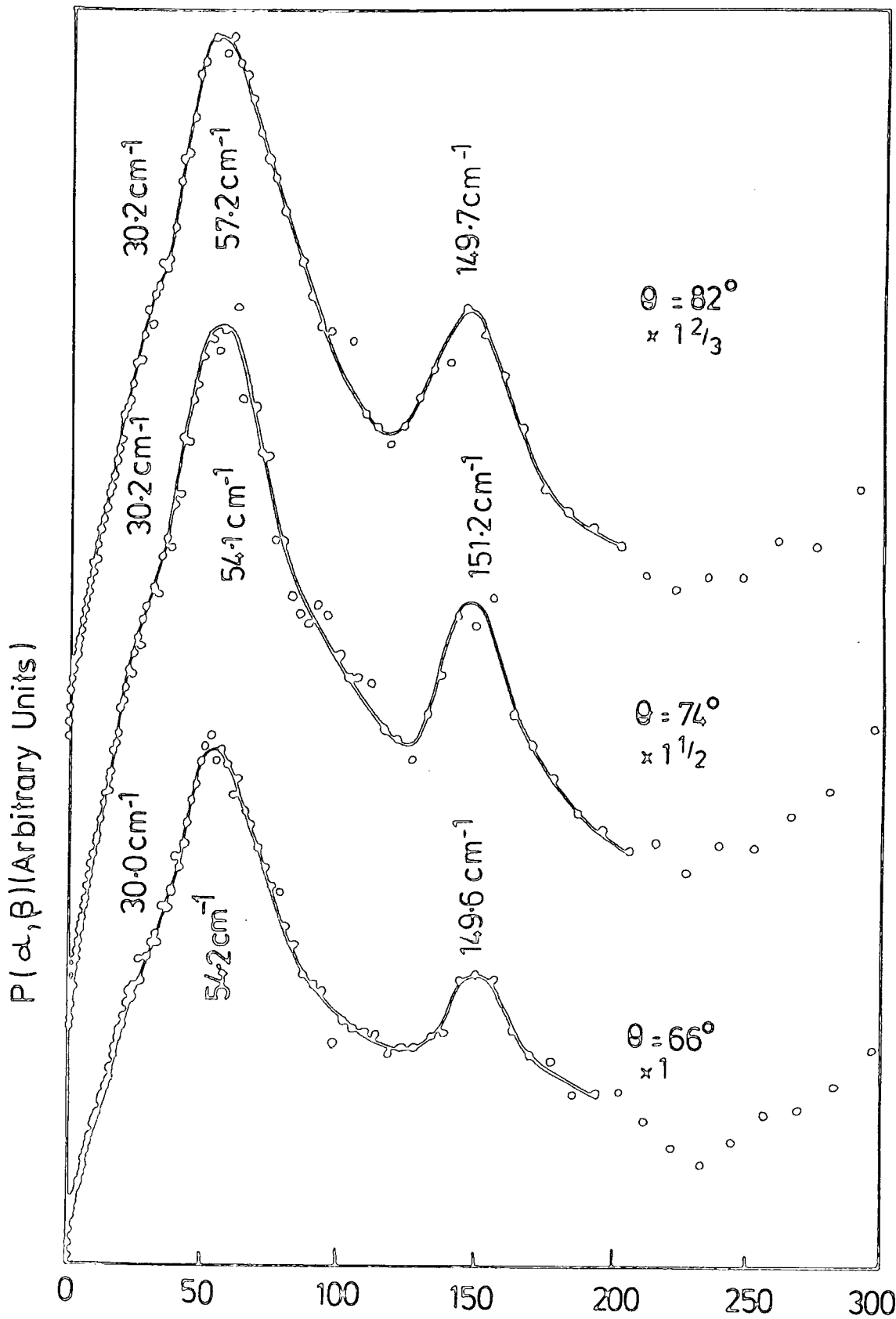






Intensity (Time Normalised Counts)





dia. 8 (xiii)

Energy Transfer / cm^{-1}

$\text{Cr}(\text{C}_6\text{H}_6)_2$ I 233 K

4H5 Time-of-Flight Spectrometer

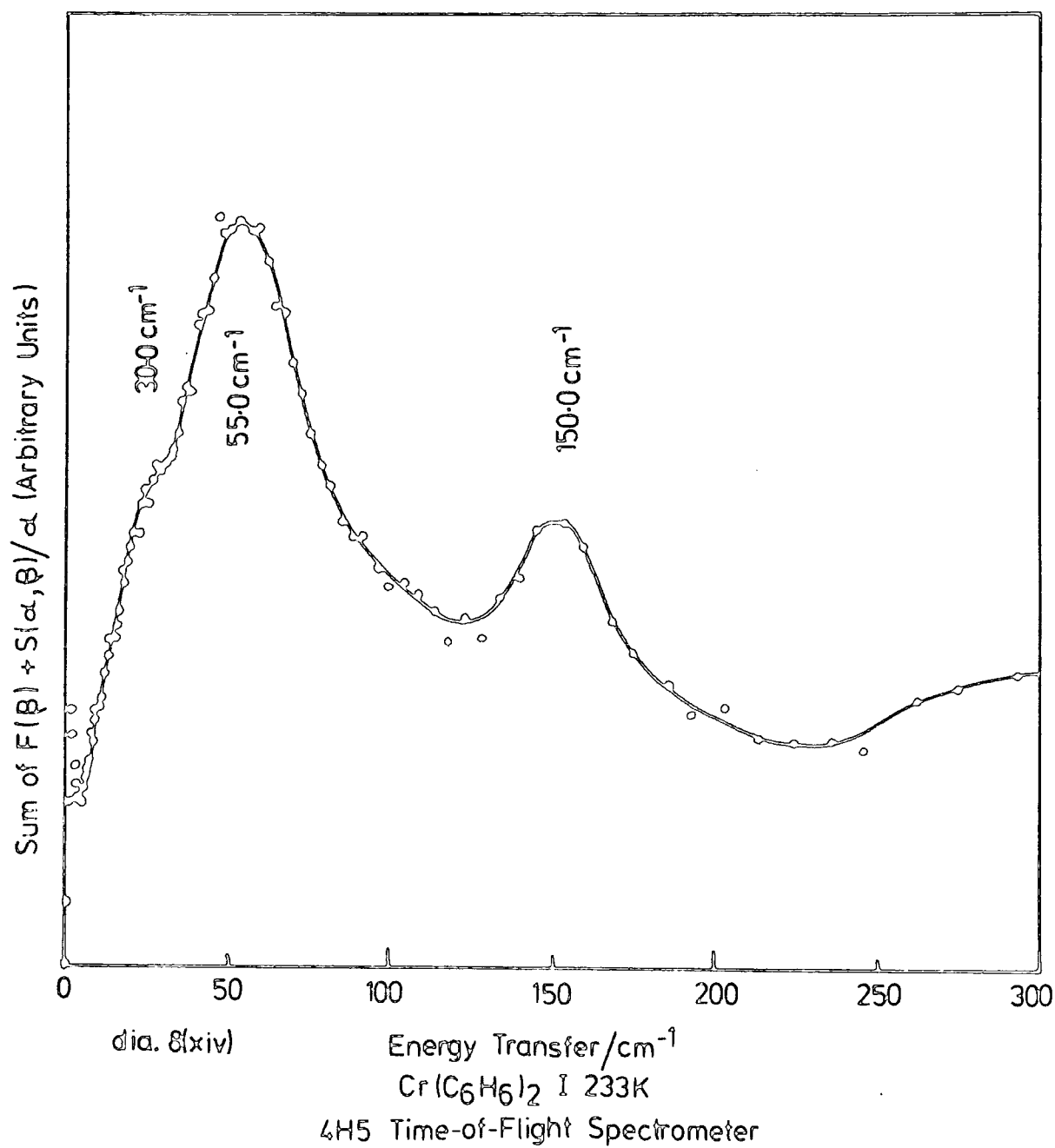


TABLE 8.12

The INS Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{Cr}(\text{C}_6\text{H}_5)_2$ and $\text{Cr}(\text{C}_6\text{H}_5)_2\text{I}$ (D_{6h} symmetry has been assumed for both complexes)

$\text{Cr}(\text{C}_6\text{H}_5)_2$			$\text{Cr}(\text{C}_6\text{H}_5)_2\text{I}$		
INS Frequency		Assignment	INS Frequency		Assignment
T-O-F	BFD		T-O-F	BFD	
59.5 $\pm$ 2.5		Lattice Mode(s)?	30.0 $\pm$ 1.5		Lattice mode?
82.0 $\pm$ 3.5			55.0 $\pm$ 2.5		Composite band perhaps containing 22(A _{1u}) Torsion?
108.5 $\pm$ 5.0		22(A _{1u}) Torsion?			
		Lattice Mode?			
158.0 $\pm$ 8.0	155 $\pm$ 8	26(E _{1u}) Deformation?			
			142 } 149 }	149 + 8	26(E _{1u}) Deformation?
	202 $\pm$ 8	Combination Band ^a	150.0 $\pm$ 7.5		Combination Band ^a
	271 $\pm$ 8	21(A _{1g}) ν _s (θ -Cr- θ)		212 $\pm$ 8	21(A _{1g}) ν _s (θ -Cr- θ)
	348 $\pm$ 8	24(E _{1g}) Ring tilt (s)		275 $\pm$ 8	24(E _{1g}) Ring tilt (s)
	367 $\pm$ 8	16 _{1p} (E _{2u}) + 16 _{op} (E _{2g}) i.m.b.		345 $\pm$ 8/335 $\pm$ 8	16 _{op} (E _{2g}) i.m.b.
				422 $\pm$ 8	25(E _{1u}) Ring tilt (as)
	451 $\pm$ 8	25(E _{1u}) Ring tilt (as)		448 $\pm$ 8	23(A _{2u}) ν _{as} (θ -Cr- θ)
	503 $\pm$ 8	23(A _{2u}) ν _{as} (θ -Cr- θ)		503 $\pm$ 8	Combination Band ^a
	633 $\pm$ 8	6 _{1p} (E _{2g}) + 6 _{op} (E _{2u}) i.m.b.		546 $\pm$ 8	16 _{1p} (E _{2u}) i.m.b.
	677 $\pm$ 8 ?	4 _{1p} (B _{2g}) + 4 _{op} (B _{1u}) i.m.b.		633 $\pm$ 8	6 _{1p} (E _{2g}) + 6 _{op} (E _{2u}) i.m.b.
	714 $\pm$ 8	11 _{1p} (A _{2u}) + 11 _{op} (A _{1g}) i.m.b.		719 $\pm$ 8	4 _{1p} (B _{2g}) + 4 _{op} (B _{1u}) i.m.b.
	807 $\pm$ 8			813 $\pm$ 8	11 _{1p} (A _{2u}) + 11 _{op} (A _{1g}) i.m.b.
	863 $\pm$ 8	10 _{1p} (E _{1g}) + 10 _{op} (E _{1u}) i.m.b.			

^a Discussed in text

ν = stretch; s = symmetric; as = antisymmetric; 1p = in-phase; op = out-of-phase; i.m.b. = internal mode of the benzene ligand.

frequency may be designated $\nu_{10_{op}}(E_{1u}) + \nu_{10_{ip}}(E_{1g})$, after $\nu_{10_{op}}$ observed in the infrared spectrum (gas-phase) at 860cm^{-1} ¹⁹, and $\nu_{10_{ip}}$ suggested from Normal Co-ordinate Analysis to lie at $860/864\text{cm}^{-1}$ ⁴⁰⁻⁴².

Similarly, the band situated in the INS spectrum at 807cm^{-1} is undoubtedly derived from $\nu_{11_{ip}}(A_{2u})$, found in the infrared spectrum at 794cm^{-1} ^{2,4,5} and $\nu_{11_{op}}(A_{1g})$, located at 791cm^{-1} in the Raman spectrum²¹. It may be inferred that the infrared and Raman inactive modes $\nu_{4_{ip}}(B_{2g})$ and $\nu_{4_{op}}(B_{1u})$ are represented by the 714cm^{-1} BFD transition, support being yielded both by the frequencies indicated for these modes by calculation (709cm^{-1})⁴⁰⁻⁴², and by the frequency attributed to the equivalent mode in solid benzene ($\nu_4(B_{2g})$, 703cm^{-1})³⁴. In addition, the vibrations $\nu_{6_{ip}}(E_{2g})$ and $\nu_{6_{op}}(E_{2u})$ only appear capable of assignment to the 633cm^{-1} INS peak, although this band is not particularly close either to the frequency at which the former mode was observed in the Raman spectrum (604cm^{-1})²¹, or that indicated for the latter mode by Normal Co-ordinate Analysis (604 or 606cm^{-1})⁴⁰⁻⁴².

Finally, the 383cm^{-1} BFD vibration may be identified as $\nu_{16_{ip}}(E_{2u}) + \nu_{16_{op}}(E_{2g})$ in agreement with the evidence of Raman spectroscopy which located $\nu_{16_{op}}$ at 400cm^{-1} ²¹, and of Normal Co-ordinate Analysis, which suggested the two vibrations to be of equal frequency, and to occur at $399/409\text{cm}^{-1}$ ⁴⁰⁻⁴².

It should be noted, though, that the assignment of $\nu_{16_{ip}}$ to a frequency equivalent to that of $\nu_{16_{op}}$ runs counter to the findings of Fritz et al. for $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}^{2,4}$, where $\nu_{16_{op}}$ was observed in the Raman spectrum at 420cm^{-1} , but $\nu_{16_{ip}}$ was placed, from combination band analysis, at 543cm^{-1} (a splitting between the two modes of 123cm^{-1}). However, in the case of $\text{Cr}(\text{C}_6\text{H}_6)_2$, the apparent absence of a transition in the BFD spectrum in the region of 543cm^{-1} would seem to deny this possibility. It may thus be seen with respect to the internal benzene ligand modes located in this study of $\text{Cr}(\text{C}_6\text{H}_6)_2$, that the frequency splittings between $\nu_{n_{ip}}$ and $\nu_{n_{op}}$ are (as expected) much smaller than the resolution of the BFD spectrometer.

Turning now to the modes of $\text{Cr}(\text{C}_6\text{H}_6)_2$ which involve motion of the ligands relative to the chromium atoms (ν_{21} - ν_{26} inclusive, dia.8(vi) and Table 8.5), correlation of the INS bands at 271cm^{-1} and 348cm^{-1} may be made with $\nu_{21}(\nu_s(\emptyset\text{-Cr-}\emptyset), A_{1g})$ and ν_{24} (symmetric ring tilt, E_{1g}), the frequencies obtained in this work comparing reasonably with those reported for the vibrations from Raman spectra ($270/277\text{cm}^{-1}$ and $332/335\text{cm}^{-1}$ respectively)^{2,21}. Additionally, it is evident that the two INS peaks at 451cm^{-1} and 503cm^{-1} correspond to those found from infrared measurements of the solid at 459cm^{-1} and 490cm^{-1} ^{2,4,5,13,39}. Assignment of these frequencies has, however, proved controversial, with some authors identifying the former as ν_{25} (antisymmetric ring tilt, E_{1u}) and the latter as $\nu_{23}(\nu_{as}(\emptyset\text{-Cr-}\emptyset), A_{2u})$ ¹³, and others opting for the reverse designation^{2,4,5,19,39}. From the standpoint of the BFD spectrum, it would seem reasonable to suppose that the intensities of the two ring tilts (ν_{24} and ν_{25}) will be approximately equal, and likewise the intensities of the two stretches ν_{21} and ν_{23} (both pairs of vibrations merely representing the in-phase and out-of-phase components of the same mode). Thus given that the assignments of $\nu_{21}(\nu_s(\emptyset\text{-Cr-}\emptyset), A_{1g})$ and ν_{24} (symmetric ring tilt, E_{1g}) appear well established, it should be possible to use the intensity ratio observed between these modes on the 1.1.1. plane of the BFD spectrum (Table 8.13(a)) to identify the equivalent antisymmetric (out-of-phase) vibrations ν_{23} and ν_{25} present on the 3.1.1. plane (Table 8.13(b)). Employment of this rule of thumb leads to correlation of the 451cm^{-1} band with ν_{25} (antisymmetric ring tilt, E_{1u}), and the 503cm^{-1} peak with $\nu_{23}(\nu_{as}(\emptyset\text{-Cr-}\emptyset), A_{2u})$, in agreement with the scheme of Fritz and Fischer.¹³ Furthermore, additional support for these assignments may be derived from the facts that the ring tilting modes ν_{24} and ν_{25} represent hindered rotations (each doubly degenerate), whilst the stretches ν_{21} and ν_{23} correspond to

TABLE 8.13(a) The Intensities Displayed of Peaks Located on the 1.1.1.Plane of the BFD Spectrum of Cr(C₆H₅)₂-

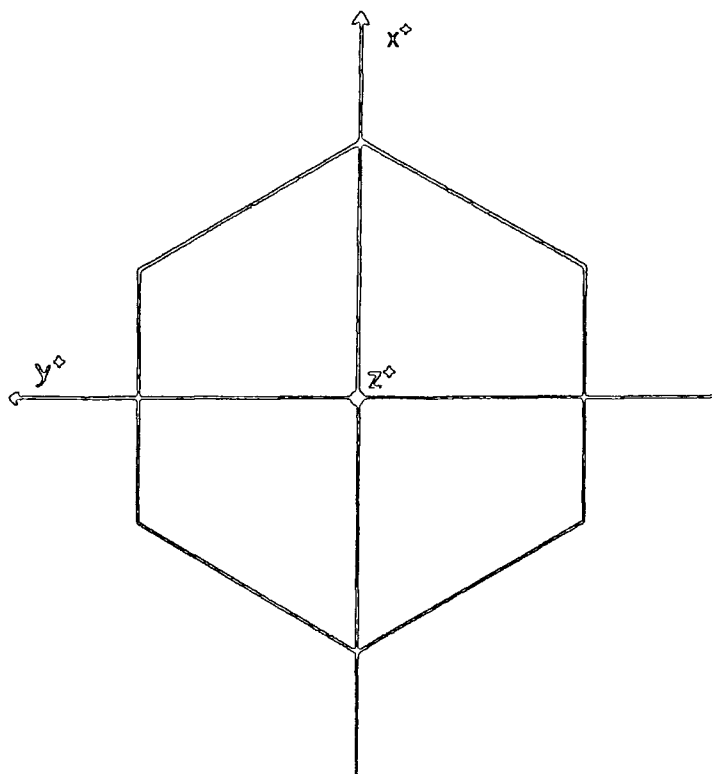
Frequency	Assignment	Description	Intensity	Intensity Ratio
155cm ⁻¹	-	-	43%	3.583
202cm ⁻¹ *	-	-	10%	0.833
271cm ⁻¹	$\nu_{21}(\nu_s(\text{D-Cr-D}), A_{1g})$	Translation	12%	1.000
348cm ⁻¹ *	$\nu_{24}(\text{symmetric ring tilt}, E_{1g})$	Rotation	35%	2.917

TABLE 8.13(b) The Intensities Displayed of Some Peaks Located on the 3.1.1 Plane of the BFD Spectrum of Cr(C₆H₅)₂-

Frequency	Assignment	Description	Intensity	Intensity Ratio
348cm ⁻¹ *	$\nu_{24}(\text{symmetric ring tilt}, E_{1g})$	Rotation	28%	2.917
383cm ⁻¹ *	$\nu_{16}^{1p}(E_{2u}) + \nu_{16}^{op}(E_{2g})$	l.o.b.	16%	1.667
451cm ⁻¹	$\nu_{25}(\text{antisymmetric ring tilt}, E_{1u})$	Rotation	44%	4.584
503cm ⁻¹ *	$\nu_{23}(\nu_{as}(\text{D-Cr-D}), A_{2u})$	Translation	12%	1.250

ν = stretch; s = symmetric; as = antisymmetric; 1p = in-phase; op = out-of-phase; l.o.b. = Informal mode of the benzene ligand.

* Calculated listed at approximate frequencies.



dia.8(xv) Definition of Axes Within the Benzene Molecule

TABLE 8.14 Intensities Predicted in the BFD Spectrum for Hindered Translational and Rotational Modes of the Benzene Ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$.

Mode [†]	"Free" C_6H_6 Model [*]	"Complexed" C_6H_6 Model ^{**}
t_x } The deformation mode $\nu_{26}(\text{E}_{1u})$ represents	1.000	1.000
t_y } both these translations	1.000	1.000
t_z , represented both by $\nu_{21}(\text{A}_{1g})$ and $\nu_{23}(\text{A}_{2u})$	1.000	1.000
r_x } Each ring tilt ($\nu_{24}(\text{E}_{1g})$ or $\nu_{25}(\text{E}_{1u})$ represents	2.706	2.809
r_y } both of these rotations	2.706	2.809
τ_B , represented by the torsion $\nu_{22}(\text{A}_{1u})$	2.706	2.809

t = hindered translation mode; τ = hindered rotational (torsional) mode.

[†] The axes x , y and z referred to are those illustrated in dia.8(xv).

^{*} Structural data taken from that of Stoicheff for liquid benzene⁵¹ (Appendix 1).

^{**} Structural data taken from that of Förster et al.^{15,16} for the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$ (Appendix 2).

$\dagger$ Calculated using the relation for a translation: Intensity $\propto M^{-1}$ (see Chapter IV), where M is the mass of benzene.

$\dagger\dagger$ Calculated using the relation for a rotation: Intensity $\propto r^2(I)^{-1}$ (see Chapter IV), where r is the perpendicular distance between the scattering atom and the axis of rotation, and I is the moment of inertia of benzene about that axis.

hindered translations (each singly degenerate). Calculation of the relative intensity theoretically predicted for a rotation compared with a translation shows that the former should be ca. 2.7-2.8 times as intense as the latter (Table 8.14). However, although at first sight this appears borne out in practice by the experimental intensities of ν_{24} and ν_{25} on the one hand relative to ν_{21} and ν_{23} on the other hand (Table 8.13(a) and (b)), when the degeneracies of the species are taken into account, it is seen that the intensity ratio displayed by the rotations relative to the translations is in fact only approximately half that anticipated. Nevertheless, at least in qualitative agreement with prediction, the bands suggested to represent the translations ν_{21} and ν_{23} ($\nu_s(\text{O-Cr-O}), A_{1g}$, and $\nu_{as}(\text{O-Cr-O}), A_{2u}$, respectively) are less intense than those believed to result from the rotations ν_{24} and ν_{25} (symmetric (E_{1g}) and antisymmetric (E_{1u}) ring tilts respectively).

This leaves the vibrations ν_{26} (deformation, E_{1u}) and ν_{22} (torsion, A_{1u}) unassigned. However, before trying to identify these in the INS spectra, it is worthwhile reflecting in slightly greater detail upon the nature of ν_{22} , and the relation of this mode to the whole-body libration of the $\text{Cr}(\text{C}_6\text{H}_6)_2$ molecule about its hexad axis. In the solid phase, the rotational barrier associated with the vibration ν_{22} (which may be regarded as a mode involving out-of-phase rotation of the benzene ligands about the six-fold axis of $\text{Cr}(\text{C}_6\text{H}_6)_2$ dia. 8(vi)) derives from both intramolecular and intermolecular forces. In contrast, the rotational barrier to the whole-body libration (which may be regarded as a mode involving in-phase rotation of the benzene ligands of $\text{Cr}(\text{C}_6\text{H}_6)_2$) results from intermolecular forces only. It has been shown by Ratcliffe⁵³ that for "ethane type" coaxial two top systems, the frequencies (ω) of the in-phase (ip) and out-of-phase (op) rotations may be related thus:

$$\omega_{op}^2 - \omega_{ip}^2 = \omega_{free}^2$$

intramolecular + intermolecular forces intermolecular forces intramolecular forces

Where ω_{free} is the frequency of the mode ν_{22} in the absence of intermolecular forces i.e. in the gas phase or in solution

and that the moment of inertia to be used in the calculation of the barriers associated with the "in-phase" and "out-of-phase" rotations is that of one top. Considering the first finding, it will be remembered that Campbell et al.²³ found the rotational barrier within $\text{Cr}(\text{C}_6\text{H}_6)_2$ arising from the ν_{22} mode to be governed predominantly by intermolecular forces (intramolecular forces proving negligible). Hence it would be expected that the vibration ν_{22} and the whole-body libration should be close together in frequency, possibly even degenerate. The second finding, relating to the moment of inertia, will be applied in future discussion of the suitability of certain assignments for ν_{22} in the INS spectrum.

Comparison of the frequencies attributed to ν_{26} (deformation, E_{1u}) and ν_{22} (torsion, A_{1u}) in the far-infrared, $171(159\text{cm}^{-1}\text{CS}_2 \text{ solution})$ and 152cm^{-1} respectively, with those derived from the INS study apparently reveals that the 171cm^{-1} band was not located. However, it should be remembered that in this region of the spectrum, the resolution of both the BFD and 4H5 Spectrometers is poor ($\text{ca. } 42\text{cm}^{-1}\text{BFD, } > 19\text{cm}^{-1}\text{4H5}^\dagger$), being in the former case very much greater than, and in the latter case comparable with, the reported separation of the vibrations in the infrared spectrum. It is therefore something of an open question as to whether both modes could

[†] A discussion of the resolution of the various spectrometers used in this work is included in Chapter III.

exist under the single peak (155cm^{-1} BFD, 158.0cm^{-1} T-O-F) and if not, whether the transition represents ν_{22} (torsion, A_{1u}) as originally suggested,¹³ or whether it should be re-assigned to ν_{26} (deformation, E_{1u}).

In order to assess the likelihood of the first possibility, it is necessary once more to consider intensity relations in the BFD spectrum. However, since theoretically predicted intensities have previously been shown to be inaccurate in the case of this molecule, discussion will be restricted to the qualitative rather than the quantitative. Therefore the intensity expected for ν_{22} (torsion, A_{1u}) will be inferred from the intensities displayed by the two rotational(torsional) modes already assigned, the ring tilts $\nu_{24}(E_{1g})$ and $\nu_{25}(E_{1u})$, whilst taking into account the double degeneracies present in respect to the latter vibrations. Likewise, an indication of the intensity predicted for the translational mode ν_{26} (deformation, E_{1u}) may be obtained by reference to the translations which have been identified previously, $\nu_{21}(\nu_s(\text{O-Cr-O}), A_{1g})$ and $\nu_{23}(\nu_{as}(\text{O-Cr-O}), A_{2u})$, bearing in mind that the degeneracy of ν_{26} is twice that of either ν_{21} or ν_{23} .

The results of intensity measurements, carried out on the 1.1.1.Plane of the BFD spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2$ (employing a Du Pont Curve Resolver), are displayed in Table 8.13(a). From these, it seems reasonable to conclude that the intensity beneath the 155cm^{-1} peak is sufficient to allow the presence of both the deformation mode $\nu_{26}(E_{1u})$ and the torsional mode $\nu_{22}(A_{1u})$ (but not the additional presence of the whole-body libration of the $\text{Cr}(\text{C}_6\text{H}_6)_2$ molecule about its six-fold axis, if this vibration were degenerate in energy with ν_{22}). No positive evidence exists, however, to substantiate the co-existence of ν_{22} and ν_{26} : the 155cm^{-1} band in the neutron energy loss spectrum is not noticeably asymmetrical (except to the higher energy side, where there is a shoulder situated at 202cm^{-1}), and, more importantly, none of the $P(\alpha, \beta)$ spectra display any suggestion

of a second transition within the 158.0cm^{-1} peak.

The 202cm^{-1} shoulder would seem to be precluded from identification with the infrared active mode ν_{26} (deformation, E_{1u}), both on the grounds of the reported absence of a similar frequency in the far-infrared¹³, and also by the great disparity between the frequency of 202cm^{-1} and that assigned to ν_{26} by Fritz and Fischer (171cm^{-1})¹³. Likewise, the designation ν_{22} (torsion, A_{1u}) appears to be unlikely in view of a resultant barrier to ligand rotation of $145.21 \pm 11.73^* / 142.71 \pm 11.53^{**} \text{kJ mol}^{-1}$ (Table 8.15), which would compare poorly with the very approximate guide to the barrier height provided by the activation enthalpy (E_a), suggested in the NMR study of Campbell et al.²³ to equal $4.56 \text{kcal mol}^{-1}$ (19.03kJ mol^{-1}). In addition, any attempt to assign either ν_{22} or ν_{26} to the 202cm^{-1} BFD peak would have to explain the lack of intensity which this band would possess in comparison with that anticipated (qualitatively) for either mode. Hence, in the absence of any remaining normal vibrations of the $\text{Cr}(\text{C}_6\text{H}_6)_2$ molecule with which the 202cm^{-1} transition may be identified, it must be ascribed to a combination band, probably, on intensity grounds, that resulting from the peaks

$$\left. \begin{array}{l} 155 \pm 8 \text{ cm}^{-1} \\ 158.0 \pm 8.0 \text{ cm}^{-1} \end{array} \right\} + 59.5 \pm 2.5 \text{ cm}^{-1} = \left\{ \begin{array}{l} 214.5 \pm 10.5 \text{ cm}^{-1} \\ 217.5 \pm 10.5 \text{ cm}^{-1} \end{array} \right.$$

(although that arising from the transitions

$$108.5 \pm 5.0 \text{ cm}^{-1} + 82.0 \pm 3.5 \text{ cm}^{-1} = 190.5 \pm 8.5 \text{ cm}^{-1}$$

is also possible).

* Henceforth, this symbol will denote calculation based upon the amended structural data of Förster et al. for $\text{Cr}(\text{C}_6\text{H}_6)_2$ ^{15,16} (Appendix 3), which lead to a moment of inertia (I) for the mode ν_{22} (torsion, A_{1u}) of $180.555 \text{Å}^2 \text{AMU}$ (see text).

** Henceforth, this symbol will denote calculation based upon the structural data of Stoiceff for liquid benzene⁵¹ (Appendix 1), which lead to a moment of inertia (I) for the mode ν_{22} (torsion, A_{1u}) of $177.444 \text{Å}^2 \text{AMU}$ (see text).

Irrespective of the set of structural parameters employed, calculation of barrier heights to the rotation of the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$ has been made (following the study of Campbell et al.²³ and the discussion of Laane⁵²) assuming a six-fold barrier.

TABLE 8.15 The Barrier to the Rotation of the Benzene Ligands in
 $\text{Cr}(\text{C}_6\text{H}_6)_2$ Suggested by Several Possible Torsional Frequencies

Frequeney (cm^{-1})	Barrier [*] Calculated Using the Model of "Complexed" C_6H_6^+ (kJ mol ⁻¹)	Barrier [*] Calculated Using the Model of "Free" $\text{C}_6\text{H}_6^{**}$ (kJ mol ⁻¹)
59.5 $\pm$ 2.5	12.60 $\pm$ 1.08	12.38 $\pm$ 1.06
82.0 $\pm$ 3.5	23.93 $\pm$ 2.09	23.52 $\pm$ 2.05
108.5 $\pm$ 5.0	41.90 $\pm$ 3.95	41.17 $\pm$ 3.88
$\begin{cases} 155 \pm 8 \\ 158.0 \pm 8.0 \end{cases}$	$\begin{cases} 85.50 \pm 9.05 \\ 88.84 \pm 9.23 \end{cases}$	$\begin{cases} 84.03 \pm 8.90 \\ 87.31 \pm 9.07 \end{cases}$
202 $\pm$ 8	145.21 $\pm$ 11.73	142.71 $\pm$ 11.53

* Following the study of Campbell et al.,²³ and the discussion by Laane⁵², a six-fold barrier to the rotation of the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$ has been assumed.

° Calculation based upon the structural data of Förster et al. for $\text{Cr}(\text{C}_6\text{H}_6)_2$ ^{15,16}. However, in view of evidence pointing to D_{6h} molecular symmetry being the correct description of the complex, the parameters have been somewhat amended, with the benzene ligands being assumed to be planar, and an average C-C and C-H bond length being obtained from the two lengths measured of each (Appendix 3).

** Calculation based upon the structural data of Stoiceff for liquid benzene⁵¹ (Appendix 1).

As a consequence of the inconclusive evidence (of intensity and bandshape) relating to a joint assignment of the $155/158.0\text{cm}^{-1}$ INS peak to ν_{22} (Torsion, A_{1u}) and ν_{26} (deformation, E_{1u}), it remains, finally, to consider the barrier to the rotation of the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$ which would arise from this frequency. Calculation shows that this would be of the order of $85.50\text{--}88.84^*/84.03\text{--}87.31^{**}\text{kJ mol}^{-1}$ (Table 8.15), which would be a great deal larger than the very crude estimate of the barrier yielded by the activation enthalpy (19.06 kJ mol^{-1})²³. All that can be said regarding the $155/158.0\text{cm}^{-1}$ band is that, whilst the presence of ν_{22} (torsion, A_{1u}) cannot be ruled out, the consequent barrier height tends to indicate that it is unlikely. Certainly, it would appear unjustifiable to assign the transition to ν_{22} alone: from consideration of both the far-infrared data of Fritz and Fischer¹³ and, to a lesser extent, qualitative predicted intensities, ν_{26} (deformation, E_{1u}) must be contained within the $155/158.0\text{cm}^{-1}$ band. Furthermore, since ν_{26} would be indicated from the latter intensity considerations to be more intense than ν_{22} , and as the band profile of the $155/158.0\text{cm}^{-1}$ peak is symmetrical, it seems reasonable to assume that the frequency of the ν_{26} mode is near enough represented by $155/158.0\text{cm}^{-1}$. As a corollary, it must follow that the 159cm^{-1} infrared band obtained of $\text{Cr}(\text{C}_6\text{H}_6)_2$ in CS_2 solution¹³ has been miscorrelated with the 171cm^{-1} frequency of the solid and should, in fact, be related with the 152cm^{-1} transition (Table 8.8).

If, as seems probable, ν_{22} (torsion, A_{1u}) is not contained within the $155/158.0\text{cm}^{-1}$ INS peak, then the problem of its identification amongst the low frequency T-O-F peaks must be faced. Consideration of relative intensity is of very little use in the $P(\alpha, \beta)$ spectra because there is no band within the energy range covered whose assignment is secure, and whose bandshape is clearly discernible. It is, therefore, in the absence of

solution data for the lowest frequency far-infrared and Raman spectra of $\text{Cr}(\text{C}_6\text{H}_6)_2$, impossible to make a conclusive judgement as to which of the T-O-F vibrations might represent the torsion, ν_{22} . However, considering these more closely, it may be seen that the 82.0cm^{-1} peak in the $P(\alpha, \beta)$ spectra gives rise to a barrier to benzene ligand rotation $(23.93 \pm 2.09^* / 23.52 \pm 2.05^{**} \text{ kJ mol}^{-1})$ (Table 8.15) which is in good agreement with that suggested by the crude yardstick of the activation enthalpy $(19.06 \text{ kJ mol}^{-1})^{23}$. On this basis, therefore, it would appear a reasonable assignment to ν_{22} (torsion, A_{1u}). In fairness, though, it should be admitted that this correlation runs counter to that suggested for $\text{V}(\text{C}_6\text{H}_6)$, where the frequency of the torsional mode equivalent to ν_{22} has been cited as 118cm^{-1} ⁵².

The 59.5cm^{-1} band seems to be comprised of several transitions which become better resolved in the lower angle data (e.g. 50°). The work of Campbell et al.²³, however, indicates that the frequency of the whole-body libration of $\text{Cr}(\text{C}_6\text{H}_6)_2$ about its six-fold axis should be, if not degenerate with, at least close to that of ν_{22} (torsion, A_{1u}). It is possible, therefore, that some of the intensity of the 59.5cm^{-1} peak results from this vibration, the remainder presumably arising from other lattice modes. Calculation of the barrier height to benzene ligand rotation, assuming that the frequency of the whole-body libration is approximately equal to 59.5cm^{-1} , produces a value of $12.60 \pm 1.08^* / 12.38 \pm 1.06^{**} \text{ kJ mol}^{-1}$ (Table 8.15). This would imply an intramolecular component of the benzene rotational barrier of $11.33 \pm 3.17^* / 11.14 \pm 3.11^{**} \text{ kJ mol}^{-1}$ and (using the relation $\omega_{\text{op}}^2 - \omega_{\text{ip}}^2 = \omega_{\text{free}}^2$ ⁵³ stated previously) a frequency for ν_{22} (torsion, A_{1u}) in solution or the gas phase of $56.5 \pm 8.5\text{cm}^{-1}$.

Finally, the 108.5cm^{-1} shoulder must, in view of its dispersive nature, be assigned either to a lattice mode, or to an overtone or combination band resulting from a lattice mode.

(b) $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$

The INS spectra of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ are shown in dias.8(xii)-(xiv), and are summarised in Table 8.12.

Taking into account the discussion detailed previously for $\text{Cr}(\text{C}_6\text{H}_6)_2$, and the assignments suggested for $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ from optical spectroscopy^{2,4,49} and Normal Co-ordinate Analysis^{21,45} (Table 8.11), the higher frequency ($> 250\text{cm}^{-1}$) INS spectrum of the cationic species may be readily analysed. Hence, considering initially the internal modes of the benzene ligands, the 813cm^{-1} BFD peak may be designated $\nu_{11\text{ip}}(\text{A}_{2\text{u}}) + \nu_{11\text{op}}(\text{A}_{1\text{g}})$, of which the former has been found at 795cm^{-1} in the infrared spectrum^{2,4,49} and the latter at 790cm^{-1} in the Raman spectrum^{2,4}. Similarly, it may be inferred that the 719cm^{-1} INS frequency, by analogy with the findings for the 714cm^{-1} peak of $\text{Cr}(\text{C}_6\text{H}_6)_2$, represents the infrared and Raman inactive modes $\nu_{41\text{p}}(\text{B}_{2\text{g}})$ and $\nu_{4\text{op}}(\text{B}_{1\text{u}})$. Further, the vibrations $\nu_{61\text{p}}(\text{E}_{2\text{g}})$ and $\nu_{6\text{op}}(\text{E}_{2\text{u}})$, located respectively in the Raman spectrum at 616cm^{-1} ^{2,4}, and in the infrared spectrum (from combination band analysis) at 630cm^{-1} ^{2,4}, would appear to give rise to the 633cm^{-1} BFD transition.

This leaves the assignments of the modes $\nu_{16\text{op}}(\text{E}_{2\text{g}})$ and $\nu_{161\text{p}}(\text{E}_{2\text{u}})$ to be discussed. Previous work has placed the former at 420cm^{-1} in the Raman Spectrum, whilst the latter has been considered from combination band analysis of the infrared spectrum to lie at 543cm^{-1} ^{2,4}. Certainly, the INS peak at 422cm^{-1} may be partly attributed to the $\nu_{16\text{op}}$ mode, in accordance, not only with the aforementioned optical work carried out on $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$, but also with observed (400cm^{-1})²¹ and calculated ($399/409\text{cm}^{-1}$)⁴⁰⁻⁴² frequencies of the vibration in $\text{Cr}(\text{C}_6\text{H}_6)_2$. The correlation of $\nu_{161\text{p}}$ with the BFD band at 546cm^{-1} , however, appears more conjectural in view of the exceedingly large frequency splitting which would exist between the in-phase and out-of-phase motions in the cationic species, compared with the uncharged species (where both modes are believed from Normal Co-ordinate

Analysis to be of equal frequency⁴⁰⁻⁴²). Conversely, the 546cm^{-1} transition is most definitely present in the INS spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$, whilst being absent from that of $\text{Cr}(\text{C}_6\text{H}_6)_2$. Unfortunately, INS intensity data cannot really be used either to confirm or deny the suggested^{2,4} large splitting of the ν_{16} vibration because the band profile of the 422cm^{-1} frequency, which is more definitely established, contains an additional ill-resolved band (see later). Consequently, the optical assignments of the $\nu_{16\text{ip}}$ and $\nu_{16\text{op}}$ modes will be followed in this work, but an alternative identification of the 546cm^{-1} peak, perhaps as a combination band ($\nu_{10\text{op}}$ (857cm^{-1} , infrared) - ν_{24} ($345\pm 8/335\pm 8\text{cm}^{-1}$, INS) = $512\pm 8/522\pm 8\text{cm}^{-1}$)^{2,4}, must be borne in mind.

A further interesting point to note about the ν_{16} vibrations is that they, alone of the modes derived from internal ligand motions which have been reviewed above ($\nu_{11\text{ip}}/\nu_{11\text{op}}$, $\nu_{4\text{ip}}/\nu_{4\text{op}}$ and $\nu_{6\text{ip}}/\nu_{6\text{op}}$), have moved to higher frequency ($\nu_{16\text{op}} + 39\text{cm}^{-1}$, $\nu_{16\text{ip}} + 163\text{cm}^{-1}$) in the spectrum of the charged as opposed to the uncharged species (Table 8.12). This is perhaps surprising, given that the $\nu_{4\text{ip}}$ and $\nu_{4\text{op}}$ vibrations, which in common with $\nu_{16\text{ip}}$ and $\nu_{16\text{op}}$ are out-of-plane C-C-C bends (dia.8(iii)), remain fixed in frequency.

Turning now to those vibrations of the $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ molecule which involve motion of the benzene ligands relative to the chromium atom (dia.8(vi)), identification of the modes ν_{21} ($\nu_s(\emptyset\text{-Cr-}\emptyset)$, A_{1g}) and ν_{24} (symmetric ring tilt, E_{1g}) may be made straightforwardly with the 275cm^{-1} and $345/335\text{cm}^{-1}$ BFD peaks, in both cases, the frequencies obtained from experiment corresponding excellently with those reported from the Raman spectrum (279cm^{-1} , ν_{21} and 333cm^{-1} , ν_{24})^{2,4}. Assignment of the antisymmetric (or out-of-phase) equivalents of the two above modes, ν_{23} ($\nu_{as}(\emptyset\text{-Cr-}\emptyset)$, A_{2u}) and ν_{25} (antisymmetric ring tilt, E_{1u}), has been disputed, though, with infrared work suggesting the former to occur at 415cm^{-1} and the latter at 466cm^{-1} ^{2,4,49}, and partial Normal

TABLE 8.16 Intensities Predicted in the BFD Spectrum for Hindered Translational and Rotational Modes of the Benzene Ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$

Mode [†]	"Free" C_6H_6 Model [*]	"Complexed" C_6H_6 Model ^{**}
t_x } The deformation mode $\nu_{26}(\text{E}_{1u})$ represents t_y } both these translations	1.000	1.000
t_z , represented both by $\nu_{21}(\text{A}_{1g})$ and $\nu_{23}(\text{A}_{2u})$	1.000	1.000
τ_x } Each ring tilt (ν_{24} τ_y } (E_{1g}) or $\nu_{25}(\text{E}_{1u})$) τ_z } represents both of these rotations	2.706	2.641
τ_z , represented by the torsion $\nu_{22}(\text{A}_{1u})$	2.706	2.641

t = hindered translational mode; τ = hindered rotational (torsional) mode.

[†] The axes x , y and z referred to are those illustrated in dia. 8(xv).

^{*} Structural data taken from that of Stoicheff for liquid benzene ⁵¹ (Appendix 1).

^{**} Structural data taken from that of Morosin for the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}^{48}$ and that of Fürster et al. for the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$ ^{15,16} (Appendix 4).

$\nearrow$ Calculated using the relation for a translation:

Intensity $\propto M^{-1}$ (see Chapter IV), where M is the mass of benzene.

$\nearrow\nearrow$ Calculated using the relation for a rotation:

Intensity $\propto r^2(I)^{-1}$ (see Chapter IV), where r is the perpendicular distance between the scattering atom and the axis of rotation, and I is moment of inertia of benzene about that axis.

TABLE 8.17(a) The Intensities Displayed of Peaks Located on the 1.1.1.
Plane of the BFD Spectrum of $\text{Cr}(\text{C}_6\text{H}_5)_2\text{I}$

Frequency	Assignment	Description	Intensity	Intensity Ratio
149cm^{-1}	-	-	35%	2.917
212cm^{-1}	-	-	15%	1.250
275cm^{-1}	$\nu_{21}(\nu_s(\text{O}-\text{Cr}-\text{O}), A_{1g})$	Translation	12%	1.000
345cm^{-1}	$\nu_{24}(\text{symmetric ring tilt}, E_{1g})$	Rotation	38%	3.167

TABLE 8.17(b) The Intensities Displayed of Some Peaks Located on the 3.1.1.
Plane of the BFD Spectrum of $\text{Cr}(\text{C}_6\text{H}_5)_2\text{I}$

Frequency	Assignment	Description	Intensity	Intensity Ratio
335cm^{-1}	$\nu_{24}(\text{symmetric ring tilt}, E_{1g})$	Rotation	22%	3.167
422cm^{-1}	$\left\{ \begin{array}{l} \nu_{16_{\text{op}}}(E_{2g}) \\ \nu_{25}(\text{antisymmetric ring tilt}, E_{1u}) \end{array} \right.$	$\left\{ \begin{array}{l} \text{i.m.b.} \\ \text{Rotation} \end{array} \right.$	$\left. \begin{array}{l} \\ \end{array} \right\} 58\%$	8.349
448cm^{-1}	$\nu_{23}(\nu_{as}(\text{O}-\text{Cr}-\text{O}), A_{2u})$	Translation	13%	1.871
503cm^{-1}	-	-	7%	1.008

ν = stretch; s = symmetric; as = antisymmetric; ip = in-phase;

op = out-of-phase; i.m.b. = internal mode of the benzene ligands.

* Gaussians fitted at approximate frequencies.

Co-ordinate Analysis indicating the reverse⁴⁵. In order to decide the correct correlation, it is necessary to consider the intensities expected of the respective modes (Table 8.16). However, taking into account findings for $\text{Cr}(\text{C}_6\text{H}_6)_2$, this will be confined to a qualitative discussion.

It was demonstrated with respect to $\text{Cr}(\text{C}_6\text{H}_6)_2$ (Table 8.13(a)) that the intensity of ν_{24} (symmetric ring tilt, E_{1g} , 348cm^{-1}) in the BFD spectrum was approximately three times greater than that displayed by ν_{21} ($\nu_s(\emptyset\text{-Cr-}\emptyset)$, A_{1g} , 271cm^{-1}) situated on the same plane (1.1.1.), a similar state of affairs being found to hold for ν_{25} (antisymmetric ring tilt, E_{1u} , 451cm^{-1}) relative to ν_{23} ($\nu_{as}(\emptyset\text{-Cr-}\emptyset)$, A_{2u} , 503cm^{-1}), this time for the 3.1.1. plane (Table 8.13(b)). Employing a Du Pont Curve Resolver to measure intensities in the BFD spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$, the 422cm^{-1} band was found to be over four times as intense as the 448cm^{-1} shoulder, and the 345cm^{-1} band about three times the intensity of the 275cm^{-1} peak (Table 8.17). In view of the earlier assignments made for the 275cm^{-1} and 345cm^{-1} bands to ν_{21} ($\nu_s(\emptyset\text{-Cr-}\emptyset)$, A_{1g}) and ν_{24} (symmetric ring tilt, E_{1g}) respectively, it would appear that similar results are afforded for $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ as for $\text{Cr}(\text{C}_6\text{H}_6)_2$ regarding the intensity of a ring tilt mode relative to a stretching mode. Hence the 422cm^{-1} BFD frequency may be designated ν_{25} (antisymmetric ring tilt, E_{1u}), and the 448cm^{-1} band ν_{23} ($\nu_{as}(\emptyset\text{-Cr-}\emptyset)$, A_{2u}), in accordance with the evidence of Normal Co-ordinate Analysis⁴⁵. In addition, the greater than (qualitatively) predicted intensity displayed by the 422cm^{-1} peak relative to that at 448cm^{-1} may, perhaps, be taken as proof for the existence of the mode $\nu_{16\text{op}}(E_{2g})$ beneath the former peak. Indeed, the "excess" intensity of the 448cm^{-1} frequency is of the order of that present for the 546cm^{-1} band, perhaps offering support for the designation of the latter $\nu_{16\text{ip}}(E_{2u})$.

Thus, all the expected low frequency internal ligand modes have been located, as have all those modes of the ligands relative to the chromium atom which have been assigned above 250cm^{-1} ^{2,4,49}. However,

one transition remains undiscussed in this region of the spectrum, a shoulder located at 503cm^{-1} , which it is interesting to note is also present in the BFD spectrum of $\text{Cr}(\text{C}_6\text{H}_6)_2$. In the latter compound, this was correlated with $\nu_{23}(\nu_{\text{as}}(\text{O}-\text{Cr}-\text{O}), \text{A}_{2\text{u}})$, an option denied in the case of $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$, both by the preceding identification of ν_{23} at 448cm^{-1} in the INS spectrum and, moreover, by the lack of an infrared peak at similar frequency.^{2,4,49} Consequently, it must be assumed to represent a combination band e.g. $149\pm 8\text{cm}^{-1} + 345\pm 8/335\pm 8\text{cm}^{-1} = 494\pm 16/484\pm 16\text{cm}^{-1}$.

Finally, assignment must be attempted of the low frequency vibrations $\nu_{22}(\text{torsion}, \text{A}_{1\text{u}})$ and $\nu_{26}(\text{deformation}, \text{E}_{1\text{u}})$, a task which proved difficult in the case of $\text{Cr}(\text{C}_6\text{H}_6)_2$. No previous far-infrared study has been carried out on $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ and thus the frequency indicated for $\nu_{26}(144\text{cm}^{-1})^{2,4}$ has been derived from combination band analysis. In like manner, ν_{22} has been suggested to occur at 303cm^{-1} . However, the latter identification is clearly in error, not only because the enormous barrier to ligand rotation which would result ($320.42^\dagger/321.10^{**}\text{kJ mol}^{-1\dagger}$) would be very much larger than that indicated for $\text{Cr}(\text{C}_6\text{H}_6)_2^{23}$ (see previously), but, more importantly, because of the absence of a BFD peak at this frequency. It therefore appears necessary to search the lower frequency INS spectrum not only for $\nu_{26}(\text{deformation}, \text{E}_{1\text{u}})$, but also for $\nu_{22}(\text{torsion}, \text{A}_{1\text{u}})$, and this will be carried out assuming the qualitative intensity relations suggested for the equivalent modes ν_{22} and ν_{26} of $\text{Cr}(\text{C}_6\text{H}_6)_2$; that is that the former, as a singly degenerate rotational mode, should be about half the intensity of a ring tilt (ν_{24} or ν_{25}), and the latter, as a doubly degenerate translational mode, should be approximately twice the intensity of a stretch (ν_{21} or ν_{23}).

[†]Henceforth, this symbol will denote calculation based upon the supplemented structural data of Morosin for $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}^{48}$, which leads to a moment of inertia. (I) for the mode $\nu_{22}(\text{torsion}, \text{A}_{1\text{u}})$ of 177.072amu^2 (Appendix 5).

^{††}Calculated assuming a six-fold barrier to benzene ligand rotation within $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$.

Considering firstly the $149/150.0\text{cm}^{-1}$ peak, it may be seen from Table 8.17 that the intensity possessed is sufficient to allow the presence of both the deformation mode $\nu_{26}(E_{1u})$ and the torsional mode $\nu_{22}(A_{1u})$ (but not the additional presence of the whole-body libration of $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ about its six-fold axis, if this vibration were degenerate in energy with ν_{22}). This scheme was also thought possible for $\text{Cr}(\text{C}_6\text{H}_6)_2$ (see previously); however, as in the case of the uncharged species, no evidence is displayed either in BFD or P (α, β) spectra for any asymmetry which might demonstrate positively the existence of both transitions. In contrast, the far-infrared spectrum of the solid obtained in this work points to the existence of two peaks situated at 140cm^{-1} and 149cm^{-1} . It seems unreasonable though, in view of the strong and equal intensities displayed by the two bands, that one vibration should be attributed to the formally infrared inactive torsional mode ν_{22} , and the other to the infrared active deformation ν_{26} . It is perhaps more likely that both peaks represent the vibration ν_{26} (deformation, E_{1u}), which has had its degeneracy lifted by crystal field effects. If this assignment is correct, and the frequencies indicated are close to those reported for ν_{26} in $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ (from combination band analysis, 144cm^{-1} ^{2,4}), and in $\text{Cr}(\text{C}_6\text{H}_6)_2$ (from INS spectra, $155/158.0\text{cm}^{-1}$), the further correlation of the $149/150.0\text{cm}^{-1}$ INS transition with ν_{26} appears justified. Unfortunately, no similar definite conclusion may be reached regarding ν_{22} (torsion, A_{1u}), except that it could be present below the latter peak. However, from comparison of the barrier ($77.48\text{-}78.53^\circ/77.65\text{-}78.69^{\text{**}}\text{kJ mol}^{-1}$) suggested by this frequency (Table 8.18) with the crude approximation to the barrier to benzene rotation in $\text{Cr}(\text{C}_6\text{H}_6)_2$ yielded by the activation enthalpy (19.06kJ mol^{-1}) ²³, it would seem that the torsional mode should possibly occur to lower energy. Assuming that this is correct, then before examination of the lowest frequency T-O-F vibrations, the remaining unassigned BFD transition (212cm^{-1}) may be ascribed, following

TABLE 3.13 The Barrier to the Rotation of the Benzene Ligands in $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$
Suggested by Several Possible Torsional Frequencies

Frequency (cm^{-1})	Barrier ^{††} Calculated Using the Model of "Complexed" C_6H_6 [†] (kJ mol ⁻¹)	Barrier ^{††} Calculated Using the Model of "Free" C_6H_6 ^{**} (kJ mol ⁻¹)
30.0±1.5	3.14±0.32	3.15±0.32
55.0±2.5	10.56±0.98	10.58±0.98
149±8	77.48±8.54	77.65±8.56
150.0±7.5	78.53±8.05	78.69±8.07
212±8	156.86±12.06	157.19±12.09

^{††} Following the study of Campbell et al.²³, and the discussion by Laane⁵², of the barrier to the rotation of the benzene molecules in $\text{Cr}(\text{C}_6\text{H}_6)_2$, a six-fold barrier has been assumed.

[†] Calculation based upon the structural data of Morosin for $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ ⁴⁸. However, as the C-H bond lengths within the ligand benzene molecules were not quoted in this work, an average value has been taken of the two C-H bond lengths reported within the benzene ligands of $\text{Cr}(\text{C}_6\text{H}_6)_2$ by Förster et al.^{15,16} (Appendix 5).

^{**} Calculation based upon the structural data of Steichoff for liquid benzene⁵¹ (Appendix 1).

$\text{Cr}(\text{C}_6\text{H}_6)_2$, to a combination band e.g. $149\pm 8/150.0\pm 7.5\text{cm}^{-1} + 55.0\pm 2.5\text{cm}^{-1} = 204\pm 10.5/205\pm 10.0\text{cm}^{-1}$.

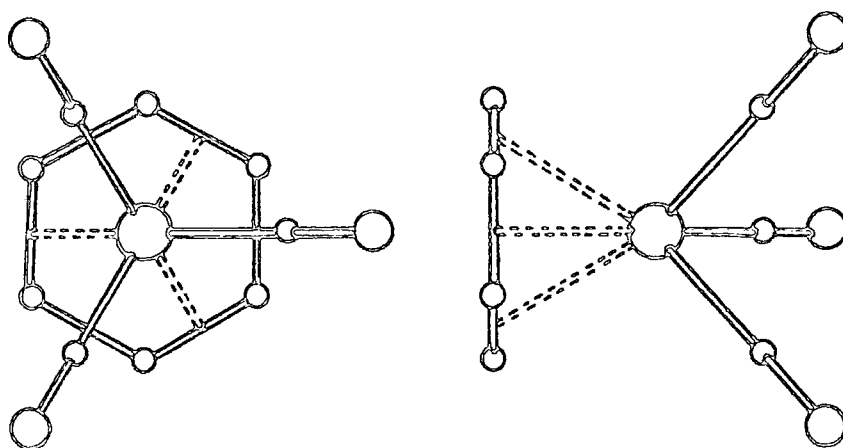
Unlike the $P(\alpha, \beta)$ spectra of $\text{Cr}(\text{C}_6\text{H}_6)_2$, those of the cationic species show only two bands lower in frequency than that assigned to ν_{26} (deformation, E_{1u}), that is at 30.0cm^{-1} and at 55.0cm^{-1} . Of these, the former would give rise to a barrier to benzene ligand rotation within $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ of $3.14\pm 0.32^\dagger/3.15\pm 0.32^{**}\text{kJ mol}^{-1}$, and the latter a barrier of $10.56\pm 0.98^\dagger/10.58\pm 0.98^{**}\text{kJ mol}^{-1}$. The $3.14^\dagger/3.15^{**}\text{kJ mol}^{-1}$ value suggested by the 30.0cm^{-1} frequency is in poor agreement with that reported for the analogous barrier in $\text{Cr}(\text{C}_6\text{H}_6)_2$ (19.06kJ mol^{-1} ²³), and the transition would therefore appear reasonably assigned to a lattice mode. The 55.0cm^{-1} peak, on the evidence displayed by its Full Width at Half Maximum (FWHM), seems to be a composite of several unresolved bands (two of which may be observed in optical spectra (Table 8.12)). In the absence of better resolved $P(\alpha, \beta)$ spectra, no conclusive judgement can be made as to whether the mode ν_{22} (torsion, A_{1u}) or the whole-body libration of the $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ group about its six-fold axis are contained within the 55.0cm^{-1} T-O-F band. However, in view of the asymmetry displayed to the high energy side of this peak, it is probable that both ν_{22} and the whole-body libration occupy positions in the spectrum similar to those thought likely for $\text{Cr}(\text{C}_6\text{H}_6)_2$ (i.e. at 82.0cm^{-1} and ca. 59.5cm^{-1} respectively).

B. $\frac{\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3}{3}$ and $\frac{\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}}{3}$

1. Introduction : $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$

a) The Structure of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$

The structure of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, as determined by single crystal X-ray diffraction at room temperature, was reported in outline by Corradini and Allegra in 1959,^{54,55} and in greater detail by Allegra in 1961⁵⁶ (Table 8.19). Crystals of the compound were shown to contain two molecules in a monoclinic unit cell ($a=6.09\text{\AA}$, $b=10.99\text{\AA}$, $c=6.58\text{\AA}$ and $\beta=101.5^\circ$) belonging to space group $\text{P2}_1/\text{m}$ (C_{2h}^2)[†]. Within each $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ molecule (dia.8(xvi)), the six carbon atoms of the benzene group were located at an equal distance from the central chromium atom $2.19\pm0.03\text{\AA}$, whilst the three carbonyl groups were collinear with the metal atom, leading to a pyramidal structure for the $\text{Cr}(\text{CO})_3$ moiety (angle $\text{OC-Cr-CO} \sim 90^\circ$). It was noted that the plane containing the six benzene ring carbon atoms was parallel to that containing the three oxygen atoms of the carbonyl ligands, and that the bonds of the carbonyl groups displayed a "staggered configuration" relative to the carbon-carbon bonds of the benzene ring, i.e.



dia.8(xvi)a Model of the $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ Molecule after Allegra⁵⁶

[†] Each molecule at site symmetry C_s

TABLE 8.19 Interatomic Distances and Angles in $C_6H_6Cr(CO)_3$ as Reported by Various Authors

Structural Parameters	Corradini and Allegre (1959) ^{54,55} and Allegre (1961) ⁵⁶	Bailey and Dahl (1965) ⁵⁷	Rees and Coppens (1972/3) ^{58,59}	Chiu et al. (1975) ⁶⁰	
Method of Investigation	X-ray Diffraction	X-ray Diffraction	X-ray Diffraction Neutron Diffraction	Electron Diffraction	
Reliability Index (R)	0.185	0.042	0.035	0.053	
Bond lengths within the Benzene Group	C-H 1.4 $\pm$ 0.04 Å (π 6) C-C	1.371 $\pm$ 0.011 Å 1.402 $\pm$ 0.008 Å 1.404 $\pm$ 0.008 Å 1.421 $\pm$ 0.011 Å	0.90 $\pm$ 0.02 Å 0.98 $\pm$ 0.02 Å 0.86 $\pm$ 0.02 Å 1.401 $\pm$ 0.002 Å 1.421 $\pm$ 0.002 Å 1.402 $\pm$ 0.002 Å 1.418 $\pm$ 0.002 Å	1.085 $\pm$ 0.003 Å 1.039 $\pm$ 0.003 Å 1.036 $\pm$ 0.003 Å 1.404 $\pm$ 0.003 Å 1.421 $\pm$ 0.002 Å 1.403 $\pm$ 0.002 Å 1.419 $\pm$ 0.003 Å	1.101 $\pm$ 0.04 Å 1.417 $\pm$ 0.003 Å
Displacement of the Hydrogen Atoms of Benzene out of the Ring Plane Towards Chromium	2.19 $\pm$ 0.03 Å (π 3)	2.230 $\pm$ 0.009 Å 2.218 $\pm$ 0.008 Å 2.216 $\pm$ 0.008 Å	2.240 $\pm$ 0.002 Å 2.229 $\pm$ 0.002 Å 2.217 $\pm$ 0.002 Å	2.240 $\pm$ 0.003 Å 2.230 $\pm$ 0.003 Å 2.220 $\pm$ 0.003 Å	2.208 $\pm$ 0.003 Å
Bond Lengths Between Chromium and Benzene	Cr-C 1.7 Å	1.724 Å	1.726 Å	0.03 Å	
Bond Lengths Within the $Cr(CO)_3$ Group	Cr-C 1.81 Å (π 2) 1.88 Å (π 1) C-O 1.15 $\pm$ 0.03 Å (π 3) 3.05 $\pm$ 0.06 Å (π 2) 3.03 $\pm$ 0.04 Å (π 1)	1.842 $\pm$ 0.008 Å (π 2) 1.841 $\pm$ 0.010 Å (π 1) 1.150 $\pm$ 0.008 Å (π 2) 1.135 $\pm$ 0.008 Å (π 1) 2.992 $\pm$ 0.009 Å (π 2) 2.976 $\pm$ 0.011 Å (π 1)	1.841 $\pm$ 0.001 Å (π 2) 1.842 $\pm$ 0.002 Å (π 1) 1.159 $\pm$ 0.002 Å (π 2) 1.157 $\pm$ 0.002 Å (π 1) 3.000 $\pm$ 0.003 Å (π 2) 2.995 $\pm$ 0.004 Å (π 1)	1.843 $\pm$ 0.003 Å (π 2) 1.843 $\pm$ 0.004 Å (π 1) 1.153 $\pm$ 0.002 Å (π 2) 1.156 $\pm$ 0.003 Å (π 1) 2.997 $\pm$ 0.005 Å (π 2) 2.998 $\pm$ 0.007 Å (π 1)	1.863 $\pm$ 0.003 Å 1.153 $\pm$ 0.003 Å 3.016
Bond Angle within $Cr(CO)_3$ Group	~90° (π 3)	89.4° (π 2) 86.7° (π 1)	89.13° (π 2) 86.54° (π 1)	89.14° (π 2) 86.37° (π 1)	89.6 $\pm$ 1.1°
Bond Angle within $Cr(CO)_3$ Group	OC-Cr-CO				
Unit Cell Dimensions	$\begin{Bmatrix} a \\ b \\ c \\ \beta \end{Bmatrix}$ 8.09 $\pm$ 0.03 Å 10.98 $\pm$ 0.03 Å 6.58 $\pm$ 0.03 Å 101.5 $\pm$ 1.0°	$\begin{Bmatrix} a \\ b \\ c \\ \beta \end{Bmatrix}$ 6.17 $\pm$ 0.02 Å 11.07 $\pm$ 0.04 Å 6.57 $\pm$ 0.02 Å 101.5 $\pm$ 0.1°			

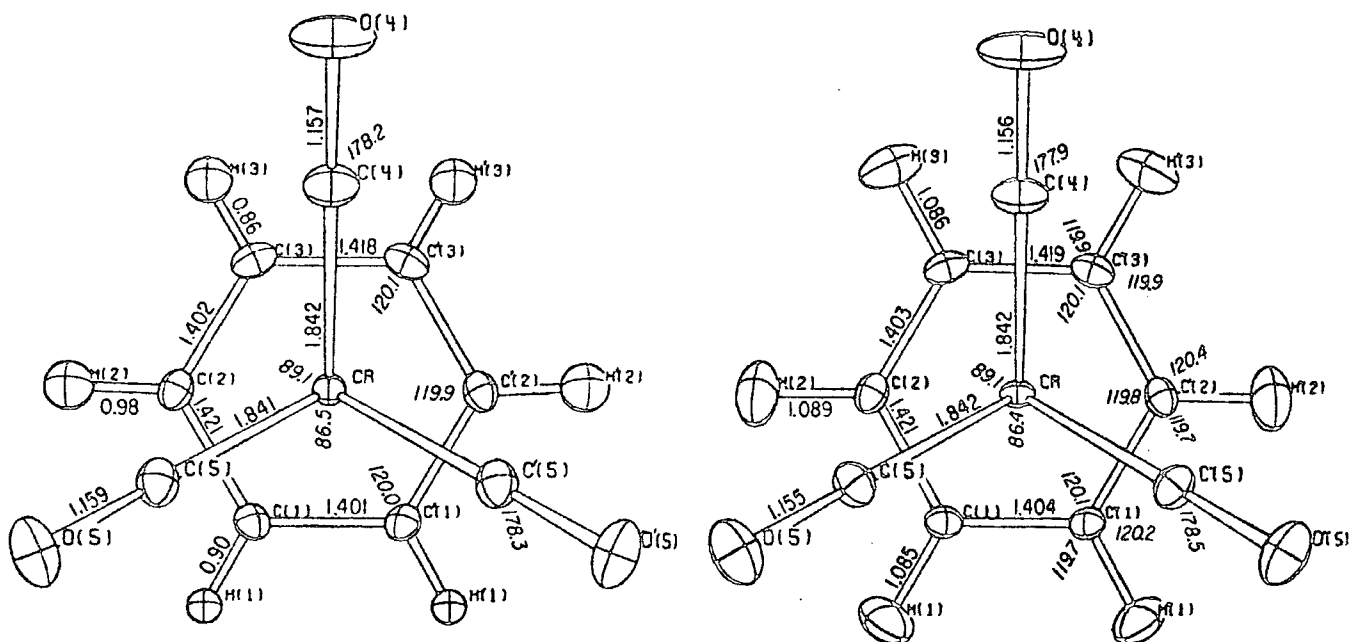
dimensional X-ray structural study of a $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ single crystal (Table 8.19). As well as reaffirming the unit cell dimensions derived from the earlier two-dimensional investigation of Corradini and Allegra⁵⁴⁻⁶, several refinements of the internal molecular parameters were carried out in order to discover whether the benzene group was trigonally distorted in the manner which had been proposed for the benzene ligands of $\text{Cr}(\text{C}_6\text{H}_6)_2$ (see previously).

Initially, an isotropic least-squares treatment of the experimental data determined the carbon-carbon bond lengths within the benzene ring to be $1.412\text{\AA}$, while difference synthesis located the six hydrogen atoms in positions believed to be characteristic of those occupied in free benzene. Further isotropic least-squares refinement applied to all atoms other than hydrogen (each of which was fixed $1.08\text{\AA}$ from the ring carbon atom to which it was bonded), led to alternate carbon-carbon distances of $1.393\text{\AA}$ and $1.395\text{\AA}$ (average $1.394\text{\AA}$). A rigid body isotropic least-squares refinement was then attempted, with the benzene molecule constrained to D_{6h} symmetry (carbon-carbon bond lengths = $1.392\text{\AA}$ and carbon-hydrogen bond lengths = $1.08\text{\AA}$). Poor agreement was, however, found with experiment, which was attributed to anisotropic thermal motion. Consequently, an anisotropic refinement (Reliability index, $R = 0.042$) was made of the positions of all atoms other than hydrogen (which were constrained as in the isotropic refinements detailed above). Four independent carbon-carbon distances resulted, from which two average bond lengths of $1.393\text{\AA}$ and $1.408\text{\AA}$ could be obtained, representing alternate carbon-carbon bonds. Both values, though, were the same within experimental error ($1.401\text{\AA}$), and it was thus concluded that the deviation of the benzene ring from D_{6h} symmetry was negligible.

Comparison of the carbon-carbon bond length finally derived ($1.401\text{\AA}$) with that reported within the benzene ligands of $\text{Cr}(\text{C}_6\text{H}_6)_2$ ($1.387\text{\AA}$ ⁷/ $1.392\text{\AA}$ ¹⁰) showed good agreement. In contrast, the average chromium-ring carbon bond

length ($2.221\text{\AA}$), and the distance of the benzene ring plane from the chromium atom ($1.724\text{\AA}$) in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ were both longer than those measured for $\text{Cr}(\text{C}_6\text{H}_6)_2$ ($2.125\text{\AA}$ and $1.605\text{\AA}$ respectively¹⁰), reflecting the weaker bonding considered to be present in the carbonyl-containing complex.

Disagreement with the above conclusion regarding D_{6h} symmetry was voiced by Rees and Coppens (1972/73)^{58,59} following further single crystal work (78K), this time employing both X-ray and neutron diffraction (Table 8.19 and dia.8(xvii)). Assuming $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ to be a rigid body (with the exception of the hydrogen atoms), two alternate carbon-carbon bond distances were determined. The first labelled "cis" were those bonds intersected by the projections of the Cr-C-O bonds onto the benzene plane, and were $1.423\text{\AA}$ in length (that is to say, $0.024\text{\AA}$ longer than the carbon-carbon bond distances determined for uncomplexed benzene, and equivalent to those reported within the benzene ligands of $\text{Cr}(\text{C}_6\text{H}_6)_2$ ^{11,12}). The second carbon-carbon bond, denoted "trans" were those bonds not intersected by the projection



dia.8(xvii) Structures Determined for $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ by X-ray (left) and Neutron (right) Diffraction (after Rees and Coppens^{58,59}).

of the Cr-C-O bonds onto the benzene plane and were $1.406\text{\AA}$ in length (that is to say $0.007\text{\AA}$ longer than the carbon-carbon bond distances present in free benzene). In addition, neutron diffraction showed the hydrogen atoms of the benzene ring to be displaced an average distance of $0.03\text{\AA}$ from the ring plane towards the chromium atom. This phenomenon was explained by the suggestion that, on complexation, the P_{π} orbitals of the benzene ring carbon atoms bent towards the chromium atom. Hence the trigonal hybrids which form σ bonding orbitals with hydrogen, and which lie in the nodal plane of the carbon P_{π} orbitals, no longer exactly coincided with the benzene ring plane.

The vapour phase structure of $C_6H_6Cr(CO)_3$ has recently (1975) been investigated by Chiu et al. (Table 8.19)⁶⁰. Electron diffraction measurements were made at 413K and, on the basis of these data, auxiliary vibrational calculations were carried out. Valence force constants of the compound (described by cartesian co-ordinates) were chosen by analogy with complexed benzene²¹ and $Cr(CO)_6$ ⁶¹ in such a way as to reproduce approximately mean amplitudes of vibration previously determined from a vibrational analysis based on symmetry co-ordinates⁶². The approximate force field was then used to calculate mean amplitudes of vibration for several proposed conformers[†] of $C_6H_6Cr(CO)_3$. From these, and structural parameters derived from the electron diffraction data, theoretical radial distribution curves were generated which were compared with those obtained experimentally by electron diffraction measurements. It was shown to be impossible for an individual conformer with three-fold symmetry to reproduce theoretically the experimental data, best fits necessitating models employing mixtures of

[†] The term conformer is used to denote forms of $C_6H_6Cr(CO)_3$ which differ only with respect to the rotational arrangement of the benzene ring relative to the carbonyl groups.

conformers. Consequently, it was concluded that $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ existed as a mixture of several conformations in the gaseous state. Furthermore, whilst neither differences of enthalpy between the various conformations, nor the barrier to the rotation of the benzene group could be calculated, there was considered to be sufficient evidence to indicate that the benzene ligand within $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ was essentially an unhindered rotor in the vapour phase.

b) The Barrier to the Rotation of the Benzene Ligand in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$

To our knowledge, the only information available regarding the rotational barrier of the benzene group within $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ is contained within the previously discussed electron diffraction study of Chiu et al.⁶⁰ This showed that, at least in the gaseous phase (413K), the benzene ligand was almost an unhindered rotor, with $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ existing as a mixture of several conformers.

c) Previous Spectroscopic Studies of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$

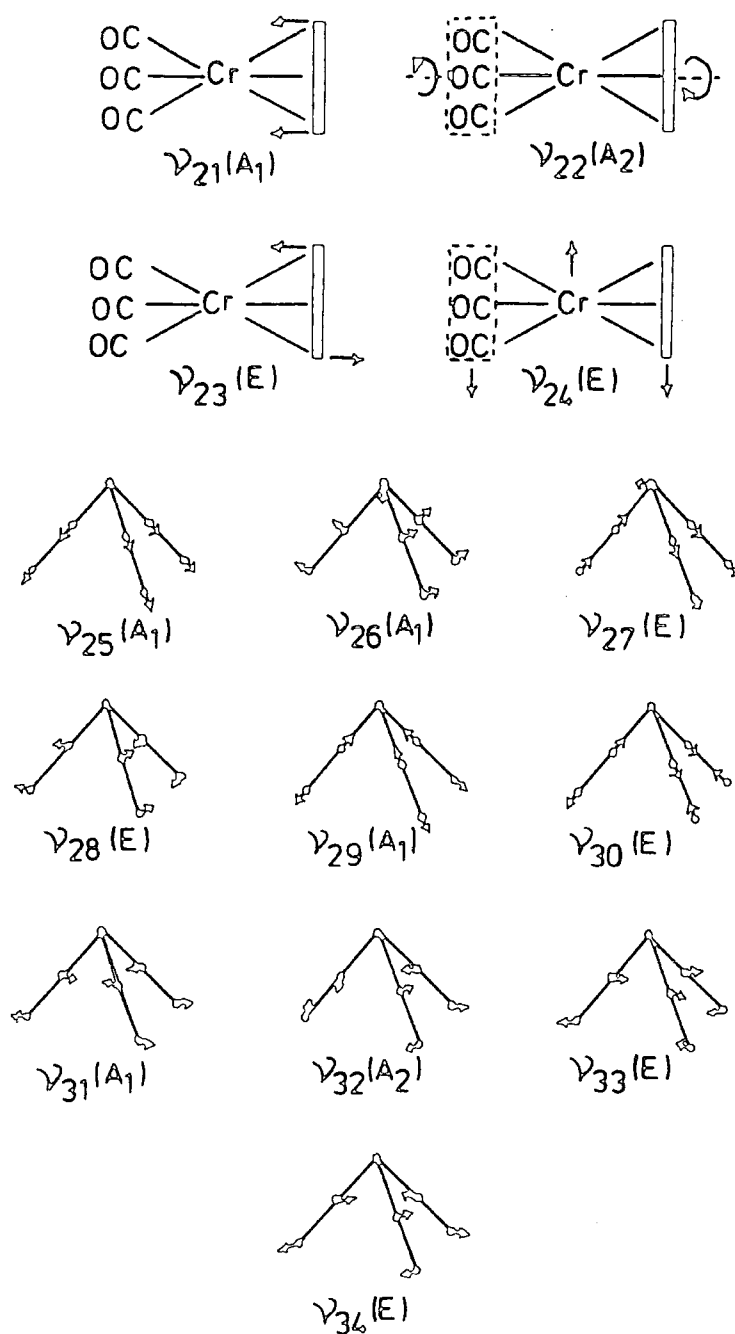
Before reviewing the spectroscopic work carried out on $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, it is worthwhile considering the symmetries and activities of the 51 (3(19)-6) normal vibrations predicted. Thirty of these are derived from internal modes of the benzene ligand, which are equivalent to those illustrated in dia.8(iii) and listed in Table 8.2 for free benzene. (Reference frequencies for the vibrations within the latter molecule (liquid and solid phases) are displayed in Table 8.3.) In contrast to benzene, however, $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ possesses C_{3v} rather than D_{6h} molecular symmetry. Hence correlation between these two symmetry classes employing Table 8.20, leads to the description of the internal modes of the benzene ligand given in Tables 8.21 and 8.22 (where the numbering system, ν_1 to ν_{20} , as for the free molecule, follows that of Wilson²⁴). Of the remaining normal vibrations of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, 15 (ν_{25} to ν_{34}) result from internal modes of the $\text{Cr}(\text{CO})_3$ moiety (dia.8(xviii) and Tables

8.21 and 8.22), whilst $6(\nu_{21} \text{ to } \nu_{24})$ represent motions of the benzene group relative to the $\text{Cr}(\text{CO})_3$ fragment (dia.8(xviii) and Tables 8.21 and 8.22).

Table 8.20 Correlation of D_{6h} and C_{3v} Molecular Symmetries

D_{6h}		C_{3v}
A_{1g}	$\longrightarrow$	A_1
A_{2g}	$\longrightarrow$	A_2
B_{1g}	$\longrightarrow$	A_1
B_{2g}	$\longrightarrow$	A_2
E_{1g}	$\longrightarrow$	E
E_{2g}	$\longrightarrow$	E
A_{1u}	$\longrightarrow$	A_2
A_{2u}	$\longrightarrow$	A_1
B_{1u}	$\longrightarrow$	A_2
B_{2u}	$\longrightarrow$	A_1
E_{1u}	$\longrightarrow$	E
E_{2u}	$\longrightarrow$	E

The infrared spectrum of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (above $\text{ca. } 250\text{cm}^{-1}$) was first reported by Fritz and Manchot in 1962⁶³. Study of samples containing both hydrogenous and deuterated benzene in the solid state (KBr and KI disc, as well as nujolmull), vapour state and in solution (CS_2 and CCl_4) enabled a comprehensive assignment scheme to be drawn up (part of which is reproduced in Table 8.23(a) for the region of the spectrum of interest in this work, below 1000cm^{-1}). On the basis of the results obtained, the symmetry of the molecule as a whole was confirmed as C_{3v} . In addition,



dia. 8(viii) The Normal Modes of Vibration (ν_{21} to ν_{34}) of $C_6H_6Cr(CO)_3$
 (Vibrations ν_1 to ν_{20} are identical to those of Benzene :
 see dia. 8 (iii).)

TABLE 8.21 Vibrational Analysis of $C_6H_5Cr(CO)_3$ Employing C_{3v} Symmetry

Description of Vibration	Symmetry		
	A_1	A_2	E
$\nu(C-C)$	$2^{(1),(14)}$	0	$2^{(8),(19)}$
$\nu(C-H)$	$1^{(2)}$	$1^{(13)}$	$2^{(7),(20)}$
$\delta_{ipb}(C-C-C)$	0	$1^{(12)}$	$1^{(6)}$
$\delta_{opb}(C-C-C)$	0	$1^{(4)}$	$1^{(16)}$
$\delta_{ipb}(C-H)$	$1^{(15)}$	$1^{(3)}$	$2^{(9),(18)}$
$\delta_{opb}(C-H)$	$1^{(11)}$	$1^{(5)}$	$2^{(10),(17)}$
$\nu(C-O)$	$1^{(29)}$	0	$1^{(30)}$
$\nu(Cr-CO)$	$1^{(25)}$	0	$1^{(27)}$
$\delta(Cr-C-O)$	$1^{(31)}$	$1^{(32)}$	$2^{(33),(34)}$
$\delta(OC-Cr-OC)$	$1^{(26)}$	0	$1^{(28)}$
$\nu(Cr-\emptyset)$	$1^{(21)}$	0	0
Ring Tilt	0	0	$1^{(23)}$
Torsion($(CO)_3-Cr-\emptyset$)	0	$1^{(22)}$	0
$\delta((CO)_3-Cr-\emptyset)$	0	0	$1^{(24)}$
Total Number of Stretches of Each Species	6	1	6
Total Number of Bends of Each Species	4	6	11
Total Number of Vibrations of Each Species	10	7	17
Activity	IR and R	i.a.	IR and R

ν = stretch; δ_{ipb} = in-plane bend; δ_{opb} = out-of-plane bend;
 R = Raman active; IR = infrared active; i.a. = inactive; () = number
 of vibration (numbers assigned to internal modes of the benzene ligand
 (ν_1 - ν_{20}) follow those of Wilson²⁴; those assigned to the remaining modes
 follow Fritz and Manchot⁶³).

TABLE 6.22 Description of the Normal Modes of Vibration of $C_6H_5Cr(CO)_3$ Assuming C_{3v} Symmetry

Number of Vibration*	Description	Symmetry Species and Activity (C_{3v})
ν_1	$\nu(C-C)$	A_1 (IR and R)
ν_2	$\nu(C-H)$	A_1 (IR and R)
ν_3	$\delta_{ipb}(C-H)$	A_2 (i.a.)
ν_4	$\delta_{opb}(C-C-C)$	A_2 (i.a.)
ν_5	$\delta_{opb}(C-H)$	A_2 (i.a.)
ν_6	$\delta_{ipb}(C-C-C)$	E (IR and R)
ν_7	$\nu(C-H)$	E (IR and R)
ν_8	$\nu(C-C)$	E (IR and R)
ν_9	$\delta_{ipb}(C-H)$	E (IR and R)
ν_{10}	$\delta_{opb}(C-H)$	E (IR and R)
ν_{11}	$\delta_{opb}(C-H)$	A_1 (IR and R)
ν_{12}	$\delta_{ipb}(C-C-C)$	A_2 (i.a.)
ν_{13}	$\nu(C-H)$	A_2 (i.a.)
ν_{14}	$\nu(C-C)$	A_1 (IR and R)
ν_{15}	$\delta_{ipb}(C-H)$	A_1 (IR and R)
ν_{16}	$\delta_{opb}(C-C-C)$	E (IR and R)
ν_{17}	$\delta_{opb}(C-H)$	E (IR and R)
ν_{18}	$\delta_{ipb}(C-H)$	E (IR and R)
ν_{19}	$\nu(C-C)$	E (IR and R)
ν_{20}	$\nu(C-H)$	E (IR and R)
ν_{21}	$\nu_s(Cr-\emptyset)$	A_1 (IR and R)
ν_{22}	Torsion ($\emptyset-Cr-(CO)_3$)	A_2 (i.a.)
ν_{23}	Ring Tilt	E (IR and R)
ν_{24}	$\delta(\emptyset-Cr-(CO)_3)$	E (IR and R)
ν_{25}	$\nu_s(Cr-CO)$	A_1 (IR and R)
ν_{26}	$\delta(OC-Cr-CO)$	A_1 (IR and R)
ν_{27}	$\nu_{as}(Cr-CO)$	E (IR and R)
ν_{28}	$\delta(OC-Cr-CO)$	E (IR and R)
ν_{29}	$\nu_s(C-O)$	A_1 (IR and R)
ν_{30}	$\nu_{as}(C-O)$	E (IR and R)
ν_{31}	$\delta(Cr-C-O)$	A_1 (IR and R)
ν_{32}	$\delta(Cr-C-O)$	A_2 (i.a.)
ν_{33}	$\delta(Cr-C-O)$	E (IR and R)
ν_{34}	$\delta(Cr-C-O)$	E (IR and R)

ν = stretch; δ_{ipb} = in-plane bend; δ_{opb} = out-of-plane bend;

s = symmetric; as = antisymmetric; $\emptyset = C_6H_5$; R = Raman active;

IR = infrared active; i.a. = inactive.

* The numbering of those normal modes which result from internal vibrations of the benzene ligand (ν_1 to ν_{20}) follows that of Wilson²⁴, the numbering of the remaining modes follows Fritz and Manchot.⁶³

TABLE 0.23(c) The Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ Reported by Various Authors for the Region below 1000cm^{-1}

Prite and Monohot (1962) ⁶³		Adams (1964) ⁶⁴		Brown and Carroll (1965) ⁶⁵		Cataliotti et al. (1970) ⁶⁶	
Infrared Frequency	Vibration: Symmetry and Description	Infrared Frequency	Vibration: Symmetry and Description	Infrared Frequency	Vibration: Symmetry and Description	Infrared Frequency	Vibration: Symmetry and Description
078	1(A_1) i.o.b.						
008	10(E) i.o.b.						
009	17(E) i.o.b.						
003	23 + 25						
038	31 + 25						
011	23 + 25						
704	11(A_1) i.o.b.						
710							
004	31(A_1) i.o.b.	000	31(A_1) i.o.e.			687,669	33(E) i.o.e.
						659	31(A_1) i.o.e.
033	33(E) i.o.e.	034	33(E) i.o.e.	640	33(E) i.o.e.	634	34(E) i.o.e.
012 (563) ^a	6(E) i.o.b.					615	6(E) i.o.b.
535	35(A_1) i.o.e.	535	34(E) i.o.e.	540	34(E) i.o.e.	537	25(A_1) i.o.e.
080	17-10					492	} 27(E) i.o.e.
403 (448) ^b	30(A_1) i.o.e.	403	25(A_1) i.o.e.	407	25(A_1) i.o.e.	487	
422	10(E) i.o.b.					424	16(E) i.o.b.
330	23(E) Ring tilt					333	} 23(E) Ring tilt
320						330	
310							
303	27(E) i.o.e.	303	27(E) i.o.e.				
203	21(A_1) $\nu_{\text{C}}(\text{Cr}-\text{O})$			200	21(A_1) $\nu_{\text{C}}(\text{Cr}-\text{O})$	298	21(A_1) $\nu_{\text{C}}(\text{Cr}-\text{O})$
						132 ^{oo}	
						110 ^{oo} (93) ^{oo}	26(A_1)

ν = stretch; σ = symmetric; $\sigma\sigma$ = antisymmetric; i.o.b. = internal mode of benzene ligand; i.o.e. = internal mode of the $\text{Cr}(\text{CO})_3$ moiety.

() Solution data: ^a in CS_2 ; ^b in CCl_4 ; ^c in CH_2Cl_2 ; ^d in $\text{CHCl}_2\text{CCl}_3$; P = polarized Raman band; dP = depolarized Raman band.

⁶³ The vibrations have been (or) numbered as so to follow the convention of Prite and Monohot.

⁶⁴ Ring group symmetry (C_2) has been considered in addition to molecular symmetry (C_{3v}) (See Table 0.24).

⁶⁵ Infrared data of Prite and Monohot.

⁶⁶ Raman data of Davidson and Riley (1971).

TABLE 8.23(b) The Infrared and Raman Frequencies (cm^{-1}) and Assignments of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$.
Reported by Various Authors for the Region Below 1000cm^{-1}

Adams and Squire (1970) ⁶⁹			Schäfer et al. (1972) ⁷⁰	
Raman Frequency	Infrared Frequency	Vibration ν : Symmetry ν and Description	Raman Frequency	Vibration: Symmetry and Description
900 (900,P) ^a	978 979	1(A _g) i.m.b.	980	1(A _g) i.m.b.
908	966 970	17(E) i.m.b.	971	17(E) i.m.b.
909	901 909	10(E) i.m.b.	902	10(E) i.m.b.
898	887			
828	837	24 + 34	842	
789	784 785	11(A _g) i.m.b.	800(793,P) ^a	11(A _g) i.m.b.
664 (657,P) ^c	667 670	31' (A _g)/31'' (B _u) i.m.c.	664(657,P) ^a	31(A _g) i.m.c.
658	654 658	32' (B _g)/32'' (A _u) i.m.c.		
640	635 638	33a' (A _g), 33b' (B _g)/33a'' (B _u) 33b'' (A _u) i.m.c.	644	33(E) i.m.c.
617	612 613	6(E) i.m.b.	614	6(E) i.m.b.
543		34a' (A _g) i.m.c.	543	34(E) i.m.c.
537(536,dP) ^d	533 536	34b' (B _g)/34a'' (B _u), 34b'' (A _u) i.m.c.	535 (532,P) ^a	25(A _g) i.m.c.
490	488 492	27a' (A _g), 27b' (B _g)/ 27a'' (B _u), 27b'' (A _u) i.m.c.		
486 (483,P) ^c	483 486	25' (A _g)/25'' (B _u) i.m.c.	486(480,P) ^a	26(A _g) i.m.c.
427	421 424	16(E) i.m.b.	426	16(E) i.m.b.
333(332,dP) ^c		23a' (A _g) Ring tilt	332(332,dP) ^a	23(E) Ring tilt
328	328 330	23b' (B _g)/23a'' (B _u), 23b'' (A _u) Ring tilt		
296(301,P) ^c	298 301	21' (A _g)/21'' (B _u) $\nu_s(\text{Cr}-\text{O})$	306 ^a 298(301,P) ^a	27(E) i.m.c. 21(A _g) $\nu_s(\text{Cr}-\text{O})$
131	146 153	28(E) i.m.c.	132	24(E) $\delta(\text{O}-\text{Cr}-(\text{CO})_3)$
103	119 121	26(A _g) i.m.c.	110	28(E) i.m.c.
	60 87	Lattice Modes and 24(E) $\delta(\text{O}-\text{Cr}-(\text{CO})_3)$		
	43 49			

ν = stretch; s = symmetric; as = antisymmetric; i.m.b. = internal mode of the benzene ligand; i.m.c. = internal mode of the $\text{Cr}(\text{CO})_3$ moiety.

() Solution data: ^a in CS_2 ; ^b in CCl_4 ; ^c in CH_2Cl_2 ; ^d in $\text{CHCl}_2\text{CCl}_2$;

^o in C_6H_6 ; P = polarised Raman band; dP = depolarised Raman band.

ν Two vibrations have been (re-)numbered so as to follow the convention of Fritz and Manchoz⁶³

ν Site group symmetry (C_3) has been considered in addition to molecular symmetry (C_{3v}) (see Table 8.24).

^o Infrared data of Fritz and Manchoz.⁶³

^{oo} The left hand side column contains data for ambient temperatures, the right hand side column that for liquid nitrogen temperature.

TABLE 2.23(c) The Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$ Reported by Various Authors for the Region Below 1000cm^{-1}

Myron and Lippincott (1972) ⁷¹			Buttery et al. (1974) ⁷²		
Raman Frequency	Infrared Frequency	Vibration [†] : Symmetry ^{°°} and Description	Raman Frequency		Vibration [†] : Symmetry ^{°°} and Description
981	981	1(A ₁) i.m.b.			
972	972	5(A ₂) i.m.b.			
	959	2 + 28			
903	911	} 17(E) i.m.b.			
	905				
	889				
839	839	21 + 34			
800	786	10(E) i.m.b.			
	755				
666	670	31(A ₁) i.m.c.	668, 663	665°, 664°	31(A _g)/31"(B _u) i.m.e.
	659	32(A ₂) i.m.c.		658°	32"(A _u) i.m.c.
650		11(A ₁) i.m.b.			
641	638	} 33(E) i.m.c.		640°	33a'(B _u), 33b"(A _u) i.m.e.
	628				
616	611	6(E ₂) i.m.b.			
	576	25 + 28			
545		} 34(E) i.m.c.	545	543°	34a'(A _g)/34b"(B _u) i.m.c.
534	534		535	537°	34b'(B _g)/34b"(A _u) i.m.c.
489	490	27(E) i.m.c.	491	490°	{ 27a'(A _g), 27b'(B _g)/27b"(B _u) 27b"(A _u) i.m.e.
485	484	25(A ₁) i.m.c.	487	486°	25'(A _g)/25"(B _u) i.m.c.
	457	23 + 26			
	440	21 + 26			
427	424	} 16(E ₂) i.m.b.			
	418				
	412		21 + 28		
362					
334	330	23(E) Ring tilt			
320	328				
	322				
293	300	21(A ₁) $\nu_s(\text{Cr}-\text{O})$			
248		2 + 28			
146			148		{ 26'(A _g)/26"(B _u) i.m.c. 28a'(A _g), 28b'(B _g)/ 28b"(B _u), 28b"(A _u) i.m.c.
134	146	26(A ₁) i.m.c.	135	131°	
			114		
110	121	28(E) i.m.c.	111	103°	
68		24(E) $\delta(\text{O}-\text{Cr}-(\text{CO})_3)$			
47	44	} Lattice Modes			
	39				

ν = stretch; s = symmetric; as = antisymmetric; i.m.b. = internal mode of the benzene ligand; i.m.c. = internal mode of the $\text{Cr}(\text{CO})_3$ moiety.

() Solution data: ^a in CS_2 ; ^b in CCl_4 ; ^c in CH_2Cl_2 ; ^d in $\text{CHCl}_2\text{CCl}_2$; P = polarised Raman band; dP = depolarised Raman band.

[†] Two vibrations have been (re)numbered so as to follow the convention of Fritz & Manchoz.⁶⁹

^{††} Site group symmetry (C_0) has been considered in addition to molecular symmetry (C_{3v}) (See Table 2.24).

[°] Infrared data of Fritz and Manchoz.⁷³

^{°°} Ligand benzene has been assumed to possess C_{6v} molecular symmetry.

it was suggested that the benzene group within $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ also possessed three-fold symmetry in a similar manner to that which had been proposed for the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$ (i.e. as a result of the benzene ring being composed of alternate short and long carbon-carbon bonds).

Subsequently (1964) Adams⁶⁴, in an infrared investigation (nujol mull) concerned with the modes $\nu(\text{Cr-CO})$ and $\delta(\text{Cr-C-O})$ of a series of 52 inorganic complex carbonyls[†], concluded that the vibration $\nu_{26}(\delta(\text{OC-Cr-CO}), \text{A}_1)$ had been mis-assigned by Fritz and Manchot⁶³, contrasting the frequency of the band identified as ν_{26} in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (483cm^{-1}), with that established for the analogous mode in $\text{Cr}(\text{CO})_6$ ($\text{ca. } 100\text{cm}^{-1}$). In consequence, he re-labelled the vibration at 483cm^{-1} $\nu_{25}(\nu_s(\text{Cr-CO}), \text{A}_1)$, and ascribed the frequency formerly suggested for ν_{25} (535cm^{-1}) to $\nu_{34}(\delta(\text{Cr-C-O}), \text{E})$, a pattern of assignments endorsed by Brown and Carroll (1965)⁶⁵ following further infrared work (KBr disc and nujol mull) in the same spectral region (Table 8.23(a)).

Another limited study of the infrared spectrum of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ($250\text{--}700\text{cm}^{-1}$) was undertaken by Cataliotti et al.⁶⁶ in 1970 using KBr disc and CCl_4 solution (Table 8.23(a)). In contrast with previous reports, three vibrations (excluding that attributable to the benzene ligand mode, $\nu_6(\text{E})$, at 615cm^{-1}) were located between 600cm^{-1} and 700cm^{-1} . These were considered to represent the three predicted infrared active Cr-C-O bends, $\nu_{31}(\text{A}_1, 659\text{cm}^{-1})$, $\nu_{33}(\text{E}, 667 \text{ and } 669\text{cm}^{-1})$ and $\nu_{34}(\text{E}, 634\text{cm}^{-1})$. Furthermore, employing the argument that the observed lowering in frequency of the stretches $\nu(\text{C-O})$ ($\nu_{29}(\text{A}_1)$ and $\nu_{30}(\text{E})$) in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ relative to $\text{Cr}(\text{CO})_6$ should be reflected by an equivalent increase in the frequency of the stretches $\nu(\text{Cr-C})$ ($\nu_{25}(\text{A}_1)$ and $\nu_{27}(\text{E})$) in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, again relative to the parent carbonyl, the bands at 537cm^{-1} and $492/487\text{cm}^{-1}$ were designated ν_{25}

[†] The frequency range investigated in the study was restricted to $468\text{--}682\text{cm}^{-1}$.

and ν_{27} respectively. Support for the above re-assignments was claimed from a partial Normal Co-ordinate Analysis in which the benzene group was assumed to be a point mass (hence possessing no internal vibrations) and the modes ν_{22} (torsion ($\emptyset$ -Cr-(CO)₃), A₂) and ν_{23} (Ring tilt, E) were ignored. Having initially inferred frequencies for ν_{26} (δ (OC-Cr-CO), A₁) and ν_{28} (δ (OC-Cr-CO), E) from Cr(CO)₆ (94cm^{-1} (ν_{26}) and 72cm^{-1} (ν_{28})), calculation led to values for the two deformations of 93cm^{-1} and 74cm^{-1} respectively. In addition, the position of the unobserved vibration ν_{24} (δ ($\emptyset$ -Cr-(CO)₃), E) was determined as 140cm^{-1} (Table 8.25).

Spectroscopic evidence for the assignment of ν_{26} (δ (OC-Cr-CO), A₁) was subsequently yielded by the low frequency Raman spectrum of C₆H₆Cr(CO)₃ measured by Davidson and Riley⁶⁷, in which a band at 110cm^{-1} (solid phase)/ 93cm^{-1} (CH₂Cl₂ solution) was, by analogy with the spectrum of C₆H₅CH₃Cr(CO)₃ (the principle concern of the work), correlated with ν_{26} (A₁) (Table 8.23(a)).

Following work by Buttery et al.⁶⁸ which had shown that analysis of the region of the spectrum containing ν (C-O) ($\text{ca. } 1800\text{--}2000\text{cm}^{-1}$) required consideration of full factor group symmetry, a thorough reinvestigation of the Raman (solid phase and CH₂Cl₂ solution) and infrared (solid phase at both ambient and liquid nitrogen temperatures) spectra of C₆H₆Cr(CO)₃ was carried out by Adams and Squire in 1970⁶⁹ (Table 8.23(b)). The findings for the " ν (C-O) region" of the spectrum were shown to hold equally for the section to lower energy in which ν (Cr-CO) and δ (Cr-C-O) were situated ($\text{ca. } 480\text{--}680\text{cm}^{-1}$), viz: non-coincidence between Raman and infrared bands, and also a larger number of vibrations than that predicted by C_{3v} molecular symmetry. On the other hand, near coincidences in the infrared and Raman spectra between transitions representing internal modes of the benzene ligand were considered to confirm the reduction in molecular symmetry of the benzene ring (from D_{6h} to C_{3v}) proposed by Fritz and Manchot⁶³. (No internal benzene vibrations of A₂ symmetry were, however, observed.)

Table 8.24 Correlation Between Molecular Point Group and
Crystal Factor Group

Point Group (C_{3v})	Site Group (C_s)	Factor Group (C_{2h})
A_1	A'	$A_g(R) + B_u(IR)$
A_2	A''	$B_g(R) + A_u(IR)$
E	$A' + A''$	$\begin{cases} A_g(R) + B_u(IR) \\ B_g(R) + A_u(IR) \end{cases}$

R = Raman active; IR = infrared active.

Considering the spectroscopic assignments of Adams and Squire in somewhat greater detail, it may be seen that, amongst the internal modes of the complexed benzene group below 1000cm^{-1} , the designations of the frequencies previously attributed to $\nu_{10}(E)$ and $\nu_{17}(E)$ by Fritz and Manchot⁶³ (965cm^{-1} and 902cm^{-1} respectively) were interchanged. This was justified on the grounds of both the relative positions of the bands in the spectrum of free benzene ($\nu_{10} = 854\text{cm}^{-1}$ and $\nu_{17} = 975\text{cm}^{-1}$ ³⁴), and force constant calculations performed on $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ which had placed $\nu_{10_{ip}} / \nu_{10_{op}}$ at 858cm^{-1} and $\nu_{17_{ip}} / \nu_{17_{op}}$ at 936cm^{-1} .⁴⁹

Within the region of the spectrum containing $\nu(\text{Cr-CO})$ and $\delta(\text{Cr-C-O})$, the band at 483cm^{-1} , on account of its polarisation, was re-assigned to $\nu_{25}(\nu_s(\text{Cr-CO}), A_1)$, thereby returning the vibration to the frequency at which it had been identified by Adams⁶⁴ and by Brown and Carroll⁶⁵.

The 490cm^{-1} transition was found to be split in the Raman spectrum, whilst its infrared equivalent became a doublet on cooling. Consequently, the E mode suggested was correlated with the antisymmetric equivalent of ν_{25} i.e.

$\nu_{27}(\nu_{as}(\text{Cr-CO}), E)$, after the scheme of Cataliotti et al.⁶⁶. ν_{34} was restored to 540cm^{-1} following Adams⁶⁴ and Brown and Carroll⁶⁵, whilst the 664cm^{-1} band (as a result of polarisation measurements) was designated $\nu_{31}(\delta(\text{Cr-C-O}), A_1)$ in agreement with the assignments of Fritz and Manchot⁶³ and Adams⁶⁴, but once

more counter to that of Cataliotti et al.⁶⁶ The remaining $\delta(\text{Cr-C-O})\text{E}$ mode, ν_{33} was ascribed to the transition at 640cm^{-1} in the Raman spectrum as a consequence of the infrared peak analogous to that present in the Raman displaying evidence of being split upon cooling. Again this effectively returned the mode to the spectral position pertaining before the work of Cataliotti et al.⁶⁶ Finally, the as yet unidentified vibration in the $\delta(\text{Cr-C-O})$ region at 658cm^{-1} was proposed by elimination to represent the formally inactive mode $\nu_{32}(\delta(\text{Cr-C-O}), A_2)$, which had become active as a result of the influence of site symmetry.

To lower frequency, the positions of the two well established vibrations $\nu_{21}(\nu_s(\text{Cr-}\emptyset), A_1)$ and $\nu_{23}(\text{Ring tilt}, E)$ were further confirmed by Raman depolarisation measurements (296cm^{-1} and 333cm^{-1} respectively). Amongst the lowest energy modes, it was considered that the transition whose frequency changed from 60cm^{-1} to 87cm^{-1} on cooling represented a lattice vibration. A similar designation was contemplated for the Raman bands at 131cm^{-1} and 108cm^{-1} , which could not be located in solution spectra. However, it was concluded that alternative assignments of the 131cm^{-1} Raman (146cm^{-1} , infrared) transition to $\nu_{28}(\delta(\text{OC-Cr-CO}), E)$ and the 108cm^{-1} Raman (119cm^{-1} , infrared) frequency to $\nu_{26}(\delta(\text{OC-Cr-CO}), A_1)$ could be justified, the latter correlation, of course, being in agreement with the aforementioned Raman work of Davison and Riley⁶⁷ in which ν_{26} was located at 110cm^{-1} in the solid phase. Identification of the two remaining modes predicted at long wavelength, $\nu_{22}(\text{torsion } (\emptyset\text{-Cr-(CO)}_3), A_2)$ and $\nu_{24}(\delta(\emptyset\text{-Cr-(CO)}_3), E)$ did not, however, prove possible.

Further Raman studies of $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ (solid phase and CS_2 and C_6H_6 solutions) were published by Schäfer et al.⁷⁰ (1972), as a preliminary step towards the presentation of a total vibrational analysis of the molecule (Table 8.23(b)). In this work, the frequencies of 658cm^{-1} and 490cm^{-1} recorded by Adams and Squire⁶⁹ could not be located. Whilst, in

the former case, the absence of the band is, perhaps, explicable in view of its assignment to $\nu_{32}(\delta(\text{Cr-C-O}), A_2)$, the inability to find the latter transition (believed by Adams and Squire⁶⁹ and by Cataliotti et al.⁶⁶ to represent $\nu_{27}(\nu_{\text{as}}(\text{Cr-CO}), E)$) made it necessary to carry out several re-assignments. Hence, ν_{27} was restored to the frequency suggested for the mode in some of the earliest spectroscopic investigations of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (306cm^{-1})^{63,64}. In addition, $\nu_{25}(\nu_{\text{s}}(\text{Cr-CO}), A_1)$ was put back to 535cm^{-1} (in agreement with previous findings of Fritz and Manchot⁶³ and Cataliotti et al.⁶⁶) following measurements which showed the band to be polarised rather than depolarised as reported by Adams and Squire⁶⁹. The remaining polarised Raman frequency (486cm^{-1}) freed by the latter re-assignment, was then ascribed to $\nu_{26}(\delta(\text{OC-Cr-CO}), A_1)$, again reverting to the assignment scheme of Fritz and Manchot⁶³.

To low frequency, the transition at 132cm^{-1} was attributed to $\nu_{24}(\delta(\text{O-Cr-(CO)}_3), E)$, rather than $\nu_{28}(\delta(\text{OC-Cr-CO}), E)$, as suggested by Adams and Squire⁶⁹. In turn, the latter mode was re-assigned to a frequency of 110cm^{-1} , thereby revising previous identification as $\nu_{26}(\delta(\text{OC-Cr-CO}), A_1)$.^{67,69}

In the same year (1972), the Raman (solid phase and C_6H_6 , CS_2 and CHCl_3 solutions) and infrared (nujol and Kel-F mulls at liquid nitrogen temperature and CCl_4 , CS_2 and C_2Cl_4 solutions at ambient temperature) spectra of $\text{C}_6\text{D}_6\text{Cr}(\text{CO})_3$ and its hydrogenous analogue were re-investigated by Hyams and Lippincott⁷¹ (Table 8.23(c)). Almost total agreement was recorded between the assignments put forward for the $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ compound and those suggested by Adams and Squire⁶⁹ as far as the carbonyl modes, $\nu(\text{Cr-CO})$ ($\nu_{25}(A_1)$ and $\nu_{27}(E)$) and $\delta(\text{Cr-C-O})$ ($\nu_{31}(A_1)$, $\nu_{32}(A_2)$, $\nu_{33}(E)$ and $\nu_{34}(E)$), and the benzene-chromium vibrations, the ring tilt ($\nu_{23}(E)$) and symmetric stretch ($\nu_{21}(A_1)$). However, disagreement was registered with respect to the vibrations $\nu_{26}(\delta(\text{OC-Cr-CO}), A_1)$ and $\nu_{28}(\delta(\text{OC-Cr-CO}), E)$, the frequencies designated being the reverse of those suggested by Adams and Squire (108cm^{-1} and 131cm^{-1} respectively).⁶⁹

In addition, $\nu_{24}(\delta(\text{O-Cr-(CO)}_3), \text{E})$ was correlated with a Raman transition at 68cm^{-1} , rather than the 132cm^{-1} band ascribed by Schäfer et al.⁷⁰

Similar lack of agreement with the assignments of earlier investigators was also displayed concerning several low energy internal benzene ligand modes as a consequence of the attribution of $\nu_{11}(\text{A}_1)$ to a frequency of 654cm^{-1} , as opposed to $\text{ca.}800\text{cm}^{-1}$ suggested by previous authors^{63,69,70}. This led to the next two successively higher energy internal benzene vibrations being "displaced" relative to the prior assignment schemes; hence, the band at 800cm^{-1} was identified as $\nu_{10}(\text{E})$ instead of $\nu_{11}(\text{A}_1)$ ^{63,69,70} and that at 905cm^{-1} as $\nu_{17}(\text{E})$ instead of $\nu_{10}(\text{E})$ ^{69,70}. Furthermore, as a result of the placement of ν_{17} at lower frequency, it was necessary to re-assign the 972cm^{-1} transition to $\nu_5(\text{A}_2)^+$.

Single crystal Raman work carried out on $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ was reported in 1974 by Buttery et al.⁷² (Table 8.23(c)). Although primarily interested in the 2000cm^{-1} region of the spectrum, the investigation also encompassed modes occurring to lower frequency. Substantial confirmation was given to the assignment scheme of Adams and Squire⁶⁹ relating to vibrations of the Cr(CO)_3 moiety, with identification of $\nu(\text{Cr-CO})$ (ν_{25} and ν_{27}) and $\delta(\text{Cr-C-O})$ (ν_{31} , ν_{32} , ν_{33} and ν_{34}), following the latter authors. Indeed, the only dispute between the two studies centred upon the modes $\nu_{26}(\delta(\text{OC-Cr-CO}), \text{A}_1)$ and $\nu_{28}(\delta(\text{OC-Cr-CO}), \text{E})$, the frequencies of which (following Hyams and Lippincott⁷¹) were assigned in the reverse order to that suggested by Adams and Squire (108cm^{-1} and 131cm^{-1} respectively).⁶⁹ No discussion was attempted either of the internal vibrations of the benzene ligand, or of those arising from motion of the benzene group relative to the Cr(CO)_3 fragment.

Also in 1974, an attempt was made to reconcile the dispute which had

⁺ An alternative assignment of the 972cm^{-1} vibration to $\nu_1(\text{A}_1)$ could be ruled out because the band with which ν_1 had been correlated by previous authors ($978\text{--}80\text{cm}^{-1}$)^{63,69,70} corresponded to the only one in this section of the spectrum which was polarised.

arisen between Hyams and Lippincott⁷¹ and earlier authors regarding the assignment of several of the low frequency internal modes of the complexed benzene group. Adams and Squire⁷⁴, from Raman study of $C_6H_5XCr(CO)_3$ complexes (where $X = -NH_2, -OCH_3$ and $-COOCH_3$), proposed that the $654cm^{-1}$ transition attributed by Hyams and Lippincott⁷¹ to $\nu_{11}(A_1)$ (and by other investigators⁶⁹ to $\nu_{32}(\delta(Cr-C-O), A_2)$) should in fact represent $\nu_4(A_2)$, which, although formally infrared and Raman inactive under C_{3v} molecular symmetry, becomes active under the influence of factor group symmetry ($B_g(Raman) + A_u(infrared)$). Adoption of this assignment then allowed restoration of the internal vibrations of the benzene group, $\nu_{11}(A_1)$, $\nu_{10}(E)$ and $\nu_{17}(E)$ to the frequencies ascribed prior to the study of Hyams and Lippincott⁷¹ (respectively $800cm^{-1}$, $902cm^{-1}$ and $971cm^{-1}$ ^{69,70}).

In addition to the partial Normal Co-ordinate Analysis of $C_6H_6Cr(CO)_3$ performed by Cataliotti et al.⁶⁶ in 1970 (see previously and Table 8.25), a partial Normal Co-ordinate Analysis concerned with the benzene ligand within $C_6H_6Cr(CO)_3$ has been reported by Schäfer et al(1971)²¹. Employing an initial force field based upon that of free benzene, refinement was carried out to achieve best fit with the observed frequencies[†] of those internal modes of the benzene ligand predicted to be infrared or Raman active under D_{6h} symmetry (Table 8.2). Comparison was then made between the resultant force constants and those calculated for the analogous modes within C_6H_6 and within the benzene ligands of the compounds $Cr(C_6H_6)_2$, $Cr(C_6H_6)_2^+$, $Mo(C_6H_6)_2$, $W(C_6H_6)_2$, $V(C_6H_6)_2$, $C_6H_6Mo(CO)_3$, $C_6H_6CrC_5H_5$ and $C_6H_6MnC_5H_5$. As a result, frequency shifts between internal vibrations of free and complexed benzene were shown to arise from changes in the "off-diagonal"(interaction) force constants, rather than the "on-diagonal" force constants (which remained in all cases similar to those of free benzene).

[†] The assignment scheme employed was that of Fritz and Manchot⁶³ modified only with respect to $\nu_{10}(E)$ which was placed at $902cm^{-1}$ rather than $965cm^{-1}$ as originally suggested.

TABLE 8.25 The Spectroscopic Frequencies (cm^{-1}) and Assignments Suggested by a Series of Normal Co-ordinate Analyses of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ for the Region Below 1000 cm^{-1} (C_{3v} molecular symmetry has been assumed)

Cataliotti et al. (1970) 66			Schäfer et al. (1971) 21			Cyvin et al. (1972) 75, 76			Adamo et al. (1975) 77		
Infrared Frequency	Calculated Frequency	Vibration: Symmetry and Description	Infrared Frequency	Calculated Frequency	Vibration: Symmetry and Description	Infrared Frequency	Calculated Frequency	Vibration: Symmetry and Description	Infrared Frequency	Calculated Frequency	Vibration: Symmetry and Description
			975	974.5	$1(A_1)$	980	990	$5(A_2)$	979	1002	$5(A_2)$
			902	902	$10(E)$	965	965	$1(A_1)$	965	1029	$1(A_1)$
			784	784	$11(A_1)$	800	800	$17(E)$	904	1042	$18(E)$
								$10(E)$	865	973	$10(E)$
								$11(A_1)$	790	890	$11(A_1)$
										749	$4(A_2)$
668	667	$33(E)$				664	707	$4(A_2)$	666	665	$31(A_1)$
659	659	$31(E)$					664	$31(A_1)$			$31(A_1)$
634	633	$34(E)$	612	611.4	$6(E)$	644	644	$33(E)$	637	626	$33(E)$
						614	614	$6(E)$	614	658	$6(E)$
						543	543	$34(E)$	543	546	$34(E)$
537	538	$25(A_1)$				535	535	$25(A_1)$			
										503	$32(A_2)$
									490	465	$16(E)$
488	488	$27(E)$				486	486	$26(A_1)$	484	497	$25(A_1)+21(A_1)$
						465	465	$32(A_2)$			
						426	426	$16(E)$	424	437	$27(E)+23(E)$
						332	332	$23(E)$	330	321	$23(E)+27(E)$
						306	306	$27(E)$			
298	298	$21(A_1)$				298	298	$21(A_1)$	298	317	$21(A_1)+25(A_1)$
	140	$24(E)$				132	132	$24(E)$	131	136	$28(E)$
						110	110	$28(E)$	121	123	$26(A_1)$
	93	$26(A_1)$						$22(A_2)$			
	74	$28(E)$							86	86	$24(E)$
									47	47	$22(A_2)$

* Values from the normal coordinate calculations for the benzene ligands fixed at those of free benzene.
 † Values from the normal coordinate calculations for the benzene ligands fixed at those of free benzene.

Full Normal Co-ordinate Analyses of $C_6H_6Cr(CO)_3$ have been published by Cyvin et al. in 1972^{75,76} and by Adams et al.⁷⁷ in 1975 (Table 8.25). In the studies of Cyvin et al. (a continuation of a series of investigations concerned with π -arene-transition metal compounds), the employment of two different sets of symmetry co-ordinates, denoted "conventional" and "physical", in the vibrational analysis of $C_6H_6Cr(CO)_3$ were discussed. The former of these sets attempted to represent the modes of $C_6H_6Cr(CO)_3$ in terms of symmetry species describing the molecule as a whole. (i.e. $10A_1 + 7A_2 + 17E$) The latter, in contrast, represented the molecular vibrations in terms of the symmetry species of the component groups, C_6H_6 (six-fold local symmetry) and $Cr(CO)_3$ (C_{3v} symmetry), which were then correlated with an overall C_{3v} molecular symmetry, i.e.

(a) C_6H_6 : thirty co-ordinates taken from free benzene,

$$2A_{1g} + A_{2g} + 2B_{2g} + 4E_{2g} + E_{1g} + A_{2u} + 2B_{1u} + 2B_{2u} + 3E_{1u} + 2E_{2u}$$

(b) $Cr(CO)_3$: fifteen co-ordinates constructed identically to those of a pyramidal $X(YZ)_3$ molecule with linear XYZ chains,

$$4A_1 + A_2 + 5E$$

and (c) $C_6H_6 - Cr(CO)_3$: six co-ordinates involving the motions of the C_6H_6 and $Cr(CO)_3$ groups relative to each other,

$$A_1 + A_2 + 2E$$

Direct employment of the "conventional" set of symmetry co-ordinates, however, proved difficult and, hence, the force field constructed initially was based upon the physical set of symmetry co-ordinates with the assumption that:

- (i) the structural parameters of the $C_6H_6Cr(CO)_3$ molecule were those determined by Bailey and Dahl⁵⁷.
- (ii) the frequencies of the vibrations were those reported in the

infrared study of Fritz and Manchot⁶³ and the Raman investigation of Schäfer et al.⁷⁰ (Values from the latter work were used wherever possible.)

- (iii) the force constants of benzene were those previously derived for free benzene⁴⁰.
- (iv) the force constants of the $\text{Cr}(\text{CO})_3$ fragment could be obtained by comparison with $\text{Cr}(\text{CO})_6$ ⁶¹
- (v) the force constants of the modes representing motions of the benzene ligand relative to the $\text{Cr}(\text{CO})_3$ fragment could be chosen in an approximate order of magnitude by comparison with those suggested for $\text{Cr}(\text{C}_6\text{H}_6)_2$ ⁴⁰ and $\text{Fe}(\text{C}_5\text{H}_5)_2$.⁷⁸

Initially, an approximate force field was created in which all interaction terms between co-ordinates belonging to two different types were considered to vanish. From this, a final force field was generated which reproduced exactly the experimentally observed frequencies of the species of A_1 and E symmetry, and in which the force constants of $\nu_{22}(\text{torsion}(\emptyset\text{-Cr-(CO)}_3), A_2)$ and $\nu_{32}(\delta(\text{Cr-C-O}), A_2)$ were arbitrarily fixed (in the case of ν_{22} so that a frequency of 100cm^{-1} was produced).

The final force field was then transformed to "conventional" co-ordinates in order to study the influence of kinematic coupling. Whilst no coupling was found between internal vibrations of the C_6H_6 and $\text{Cr}(\text{CO})_3$ fragments, coupling was observed between internal vibrations of both moieties and those representing motions of the benzene ligand relative to $\text{Cr}(\text{CO})_3$.

Mean amplitudes of vibration were derived for the $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ molecule at temperatures of OK and 298K, the influence of the frequency of the lowest energy A_2 mode, $\nu_{22}(\text{torsion}(\emptyset\text{-Cr-(CO)}_3))$, being tested by executing runs with the force constants adjusted to make ν_{22} equal to 50cm^{-1} and 200cm^{-1} , as

well as 100cm^{-1} . The sole effect noted was the change registered in the mean amplitudes pertaining to $\text{C}_6\text{H}_6\text{-Cr(CO)}_3$ distances, specifically those distances which depend on the angle of rotation of the benzene and Cr(CO)_3 moieties relative to each other around the three-fold axis. Comparison was made between calculated mean amplitudes of vibration for $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ and those of C_6H_6 , Cr(CO)_6 and $\text{Cr(C}_6\text{H}_6)_2$. It was discovered that the values of the mean amplitudes of vibration for the benzene ligand within $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ were, in common with the findings for the ligands of $\text{Cr(C}_6\text{H}_6)_2$, similar to the corresponding ones of free benzene. Likewise, the mean amplitudes of vibration derived for the Cr(CO)_3 fragment, and for the benzene group relative to the Cr(CO)_3 moiety, closely followed the analogous ones reported for Cr(CO)_6 and for $\text{Cr(C}_6\text{H}_6)_2$ respectively.

Finally, perpendicular amplitude correction factors were calculated for $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ which showed, in accordance with results for $\text{Cr(C}_6\text{H}_6)_2$, that substantial shifts had taken place between the free and complexed benzene molecules. However, although the shifts recorded in the case of $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ were in the same direction as those reported for $\text{Cr(C}_6\text{H}_6)_2$, significant quantitative differences existed between the values determined for the two molecules.

Recently, a Normal Co-ordinate Analysis of $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ and its deuterated analogue was published by Adams et al.⁷⁷ (Table 8.25). The force field was set up in internal co-ordinates assuming that:

- (i) the benzene ligand possessed D_{6h} local symmetry
- (ii) the overall molecular symmetry was C_{3v}
- (iii) the structural parameters were those determined in the X-ray study of Bailey and Dahl⁵⁷
- (iv) the fundamental frequencies of the symmetry species of $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ were those reported by Adams and Squire⁶⁹ (with the exception of the modes $\nu(\text{C-O})$ ($\nu_{29}(A_1)$ and $\nu_{30}(E)$)

which were taken from the hexane solution data of Fritz and Manchot⁶³)

- (v) the fundamental frequencies of the symmetry species of $C_6D_6Cr(CO)_3$ were those derived by Fritz and Mancot⁶³ (modified after Hyams and Lippincott⁷¹ and Adams and Squire^{69,74})

Two refinements were carried out on the force field: in the first (Refinement I), the force constants of the benzene ligand were fixed at values taken from free benzene (so that an estimate of the effects of kinematic coupling could be made), in the second (Refinement II), the most general refined force field possible was generated.

Considering initially the former refinement, the values of the force constants to which the complexed benzene group were constrained were those obtained from a force field which had been set up for free benzene employing frequencies for C_6H_6 , C_6D_6 and $C_6H_3D_3$. Estimates of the skeletal force constants, on the other hand, were taken by analogy with $Cr(CO)_6$ ⁶¹. Refinement was then carried out to achieve best fit with the frequency assignments of the hydrogenous and deuterated ligand-containing complexes by variance of some of the skeletal force constants. (These did not, however, include the lowest energy skeletal deformation modes $\nu_{24}(\delta(\emptyset-Cr-(CO)_3), E)$,

$\nu_{26}(\delta(OC-Cr-CO), A_1)$ and $\nu_{28}(\delta(OC-Cr-CO), E)$ whose identifications were believed to be uncertain, and whose corresponding force constants were kept constant at an arbitrary value[†] which produced calculated deformation frequencies in the range $80-140cm^{-1}$). The final mean absolute error achieved over all assigned frequencies was $30cm^{-1}$, whilst the mean error for the skeletal modes alone was $14cm^{-1}$ (Table 8.25). From the results

[†] It was noted that the use of different values for these force constants had no marked effect on the values of the refined skeletal force constants, and very little influence on calculated frequencies for internal benzene ligand modes.

of this refinement, it was concluded by the authors that kinematic coupling, although a factor, did not account for most of the observed frequency shifts between free and complexed benzene. In contrast with Cyvin et al.^{75,76}, therefore, these were ascribed to force constant changes.

In the case of Refinement II, all force constants other than those associated with $\nu_{24}(\delta(\emptyset\text{-Cr-(CO)}_3), E)$, $\nu_{26}(\delta(\text{OC-Cr-CO}), A_1)$ and $\nu_{28}(\delta(\text{OC-Cr-CO}), E)$ were allowed to vary, the final fit having a mean absolute error of 17cm^{-1} (with the largest error in any frequency being 69cm^{-1} for $\nu_{23}(\text{Ring tilt}, E)$ of $\text{C}_6\text{D}_6\text{Cr(CO)}_3$). Calculated mode descriptions for $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ were found to be in general agreement with the assignment scheme of Adams and Squire^{69,74}. However, the band previously labelled $\nu_{17}(E)$ (963cm^{-1})^{69,70} was re-identified as $\nu_{18}(E)$, and the descriptions of several modes in the region $320\text{-}490\text{cm}^{-1}$ were amended, with the following observed frequencies being attributed thus:[†]

$$490\text{cm}^{-1}, \nu_{16}(E); \quad 484\text{cm}^{-1}, \nu_{25}(A_1) + \nu_{21}(A_1); \quad 424\text{cm}^{-1}, \nu_{27}(E) + \nu_{23}(E); \\ 330\text{cm}^{-1}, \nu_{23}(E) + \nu_{27}(E) \text{ and } 298\text{cm}^{-1}, \nu_{21}(A_1) + \nu_{25}(A_1).$$

As may be seen, mixing was found to be extensive amongst the " $\nu(\text{Cr-CO})$ " and " $\nu(\text{Cr-}\emptyset)$ " modes of A_1 and E symmetry, so much so that it was concluded that descriptions such as $\nu(\text{Cr-CO})$ and $\nu(\text{Cr-}\emptyset)$ were rendered almost meaningless.

With respect to the lower energy vibrations, it was pointed out that the frequencies derived for the modes $\nu_{22}(\text{torsion}(\emptyset\text{-Cr-(CO)}_3), A_2)$ (47cm^{-1}) $\nu_{24}(\delta(\emptyset\text{-Cr-(CO)}_3), E)$ (86cm^{-1}), $\nu_{26}(\delta(\text{OC-Cr-CO}), A_1)$ (123cm^{-1}) and $\nu_{28}(\delta(\text{OC-Cr-CO}), E)$ (136cm^{-1}) were likely to be highly inaccurate in view of the approximations made in the force field.

[†] In the section of the spectrum below $\text{ca. } 500\text{cm}^{-1}$, uncertainty in assignment was considered to be large in view of the great disparity recorded between observed and calculated frequencies of the mode $\nu_{23}(\text{Ring tilt}, E)$ of $\text{C}_6\text{D}_6\text{Cr(CO)}_3$.

2. Introduction : $C_6H_6Mn(CO)_3Br$

Neither the structure of $C_6H_6Mn(CO)_3Br$, nor the barrier to the rotation of the benzene ligand within $C_6H_6Mn(CO)_3Br$, have been investigated. It is necessary therefore to assume both a structure and a rotational barrier related to that previously described for $C_6H_6Cr(CO)_3$. Similarly, although the infrared spectrum of $C_6H_6Mn(CO)_3Br$ has been reported above $600cm^{-1}$ (Table 8.26)⁷⁹, no attempt was made to identify any modes. Consequently, analysis of the optical and INS spectra of $C_6H_6Mn(CO)_3^+$ will be carried out following the guidance offered by the predicted vibrations (dias.8(iii) and 8(xviii) and Tables 8.21 and 8.22) and assignments (see earlier) of the analogous species $C_6H_6Cr(CO)_3$.

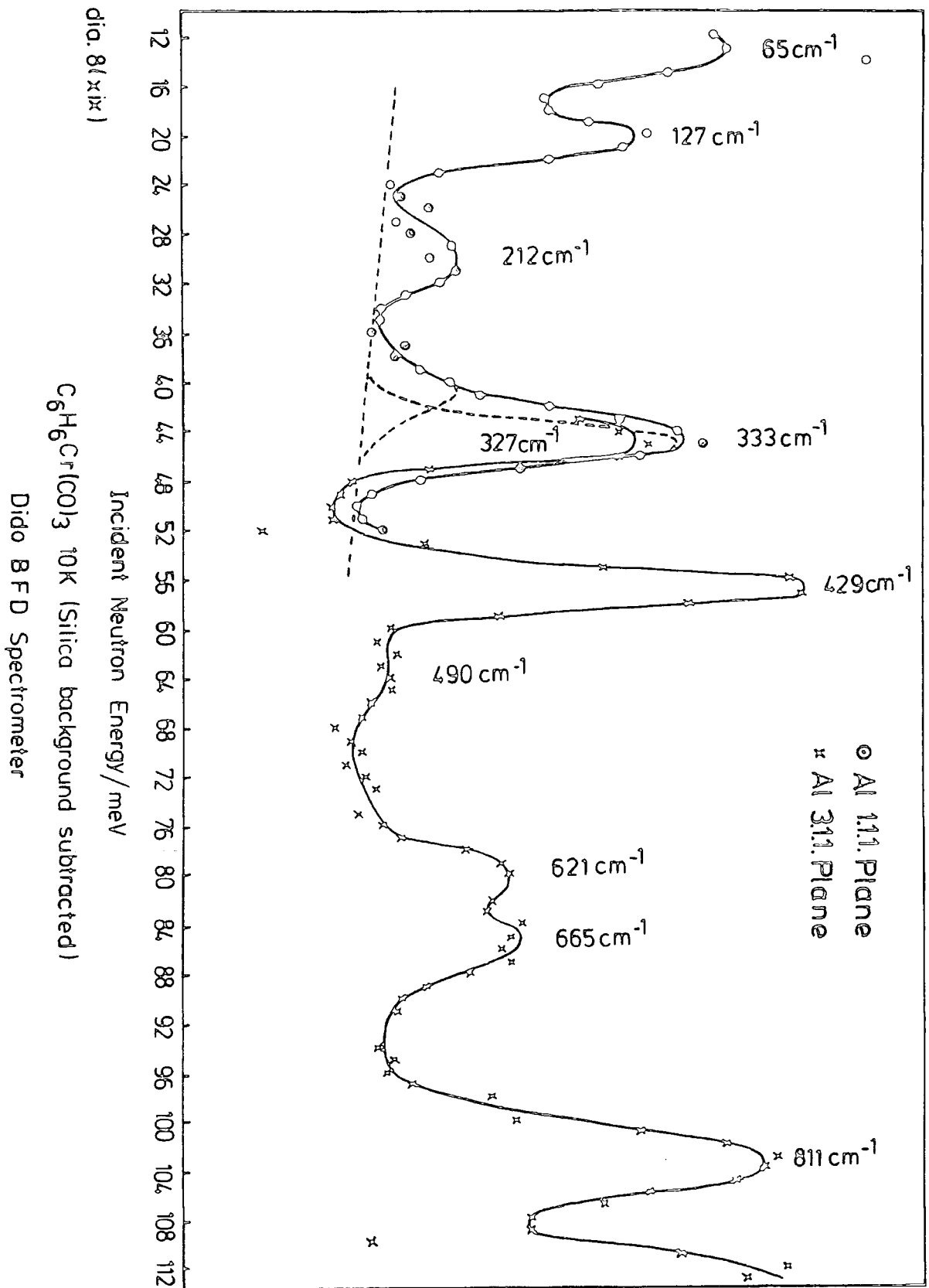
3. Experimental

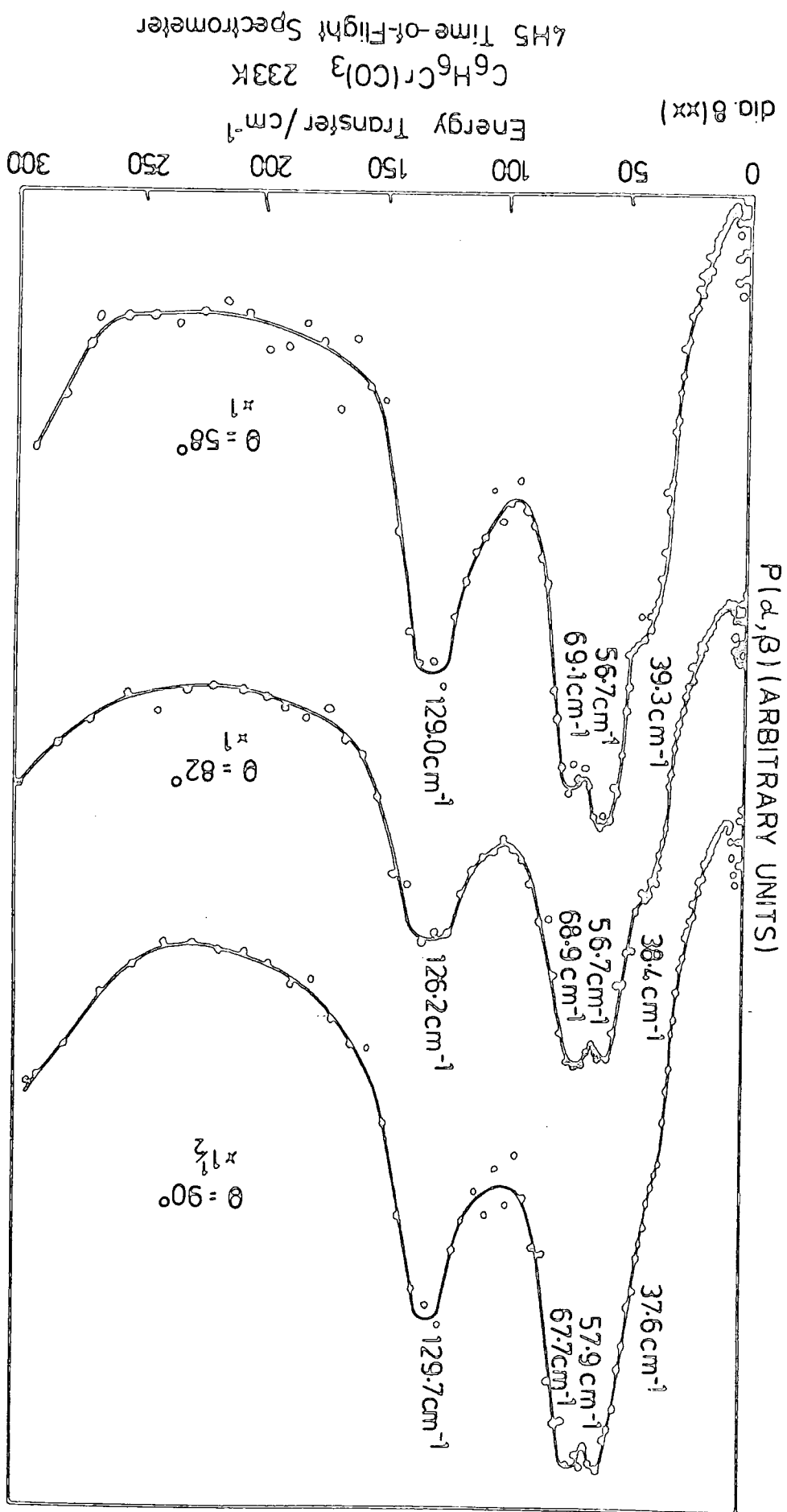
$C_6H_6Cr(CO)_3$ was purchased from Strem Chemicals Inc., whilst $C_6H_6Mn(CO)_3Br$ was prepared following a literature method.⁷⁹

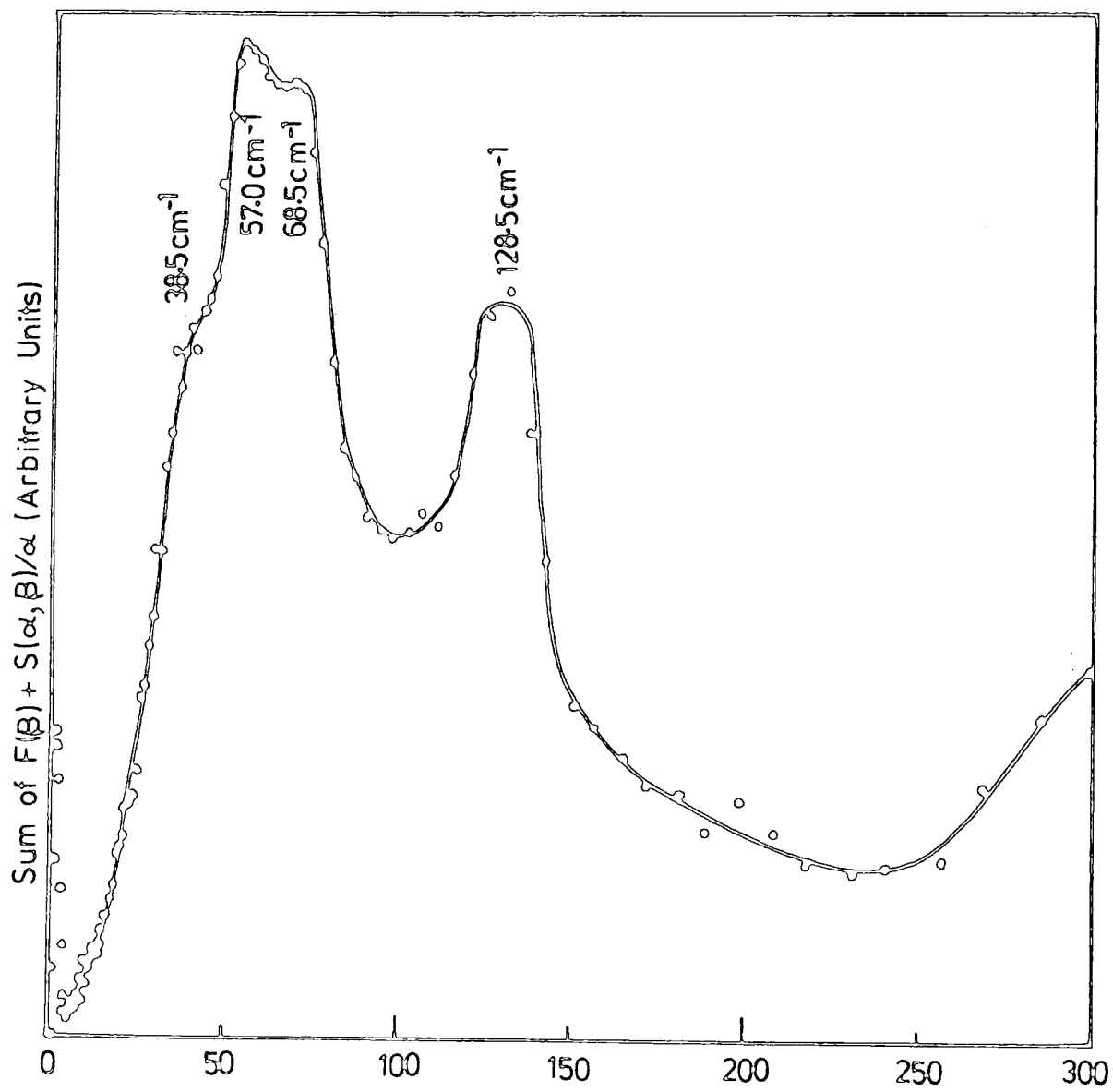
INS spectra of both compounds were measured with the samples (polycrystalline powders) contained in silica, a thin wall (0.5mm) cell being used for $C_6H_6Cr(CO)_3$ and a thick wall (1mm) cell for $C_6H_6Mn(CO)_3Br$. Time-of-flight data were obtained, in the case of the chromium complex at 233K, and in the case of the manganese complex at both 88K and 233K, using the 4H5 Spectrometer, whilst BFD spectra were recorded employing the Dido Instrument at 10K ($C_6H_6Cr(CO)_3$) and 18K ($C_6H_6Mn(CO)_3Br$) respectively.

Far-infrared measurements ($40-250cm^{-1}$, $C_6H_6Cr(CO)_3$; $60-400cm^{-1}$, $C_6H_6Mn(CO)_3Br$) were made at liquid nitrogen temperature using a Beckmann-RIIC FS720 Fourier Transform Spectrometer, whilst the near- and mid-infrared regions of $C_6H_6Mn(CO)_3Br$ only were scanned at room temperature employing a Perkin-Elmer 577 Spectrometer. With the former instrument, samples were run as nujol mulls supported on polyethylene disc, with the latter, either as CsI

Intensity (Time Normalised Counts)

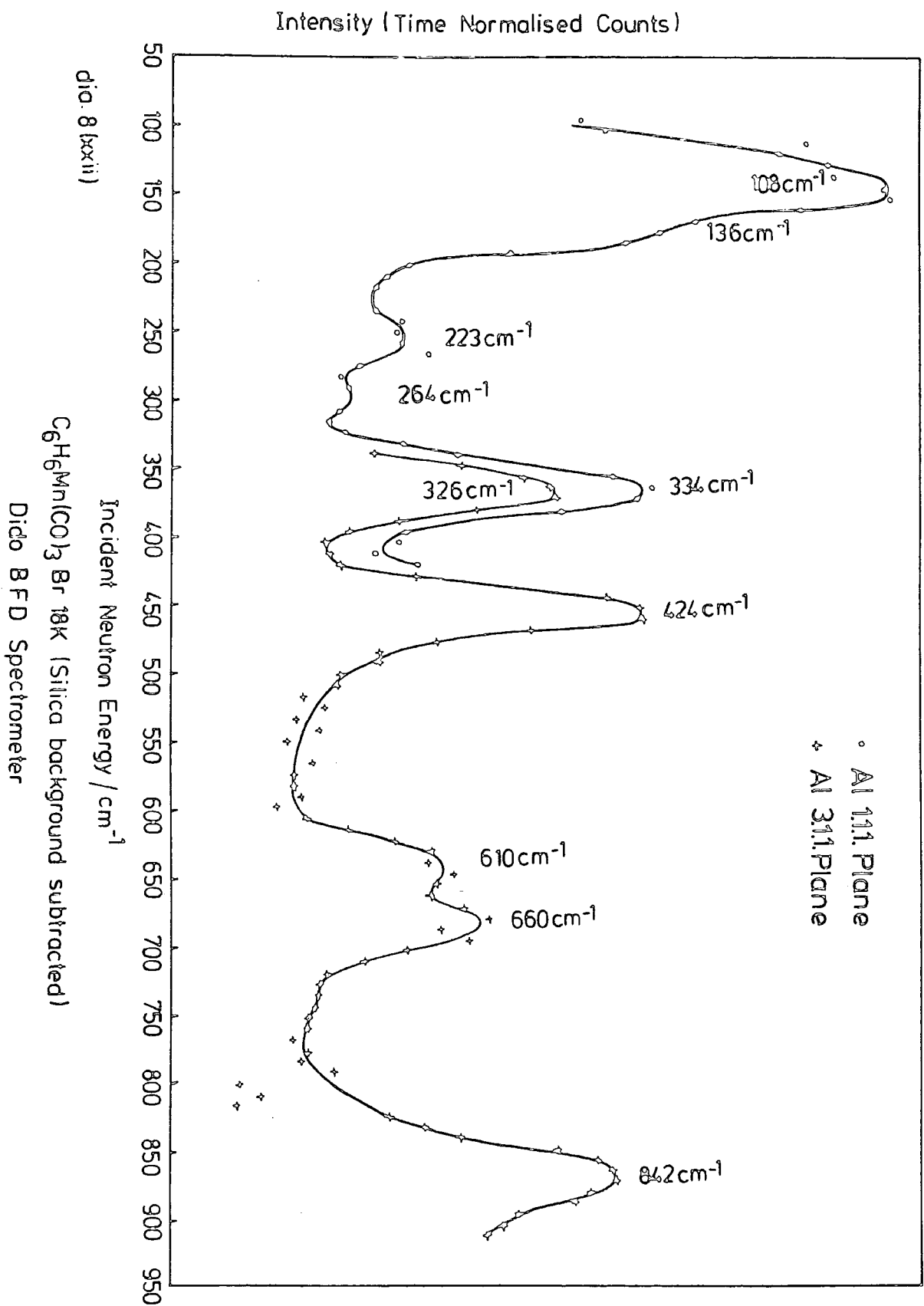




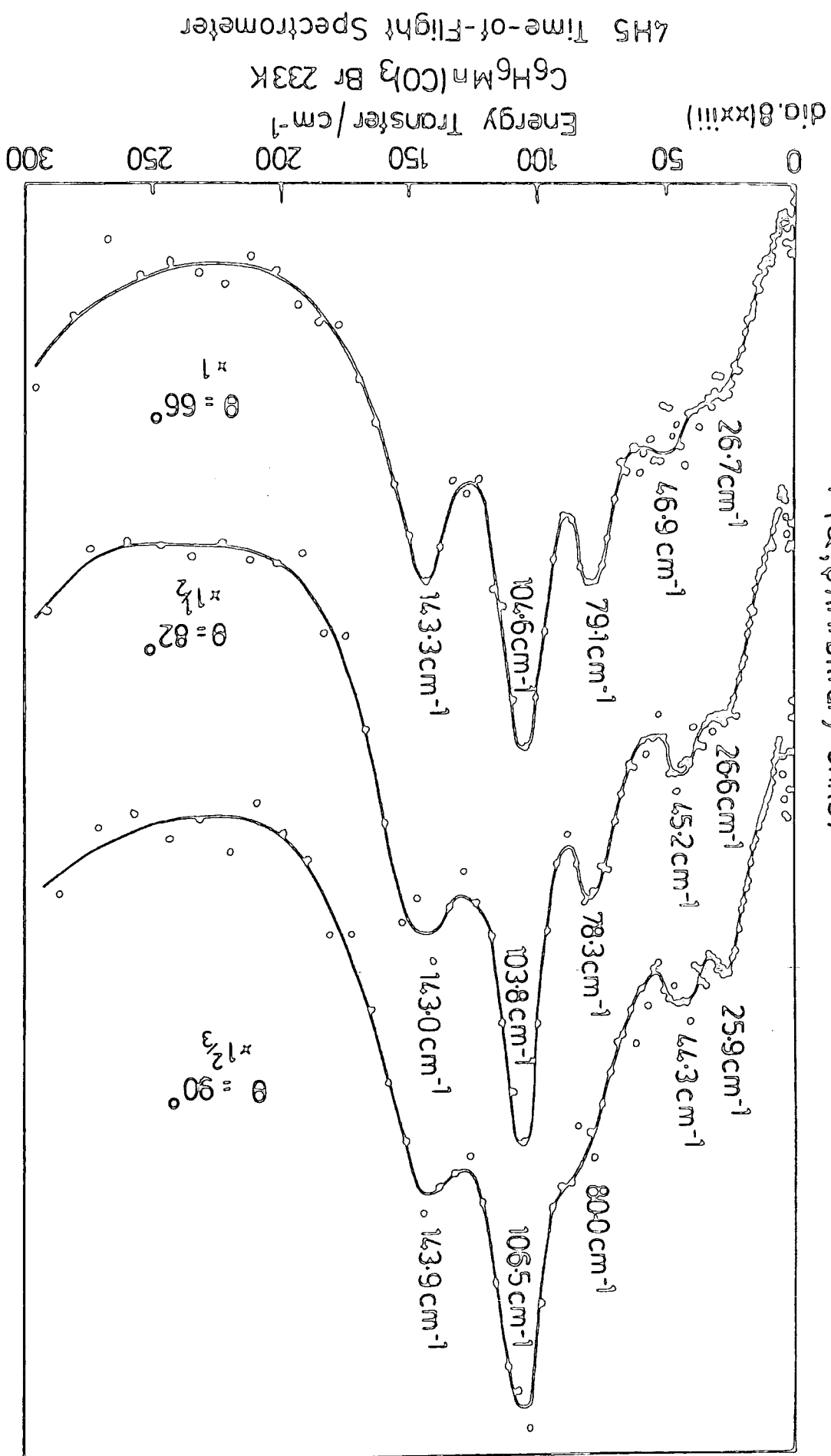


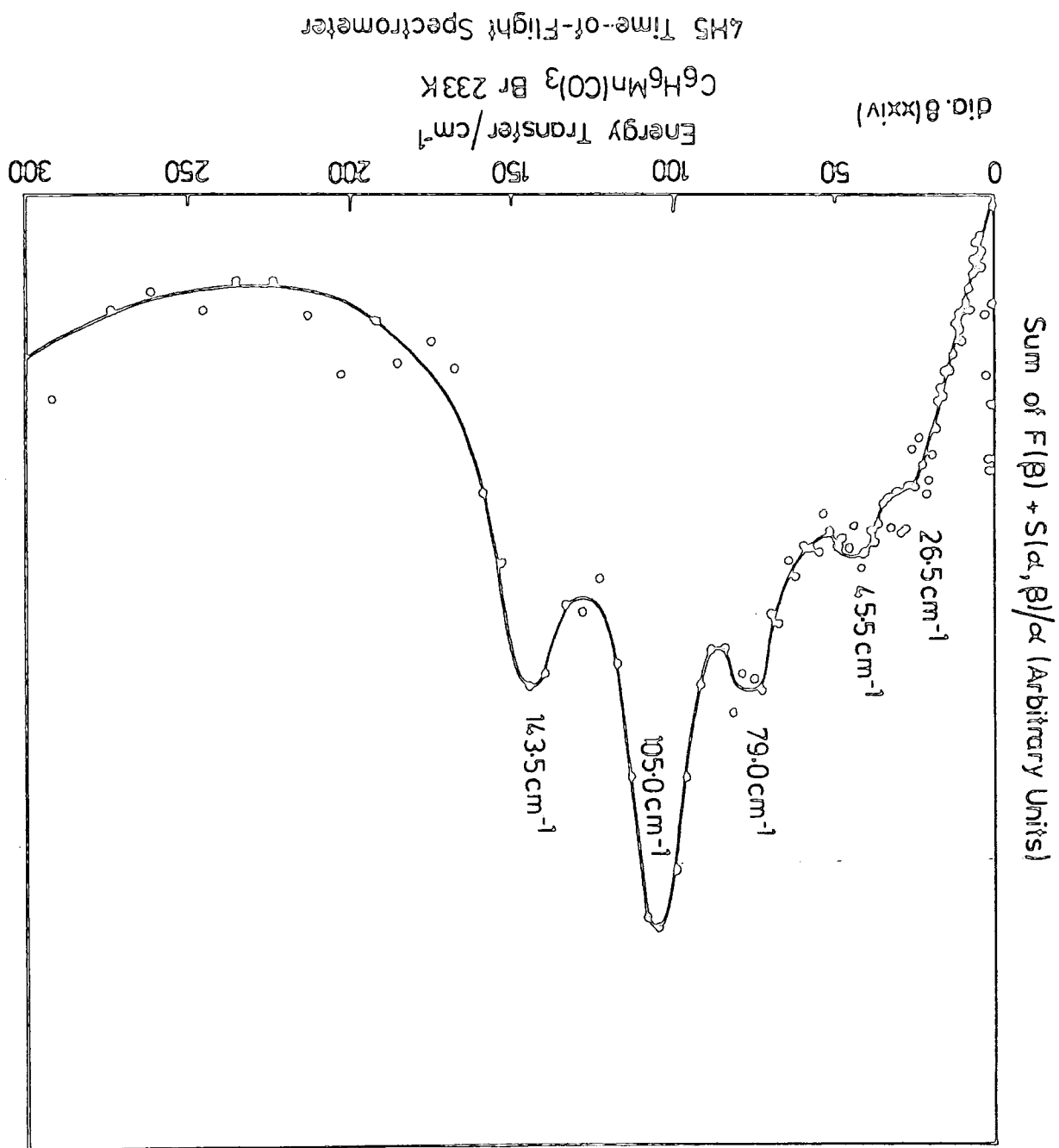
dia 8(xxi)

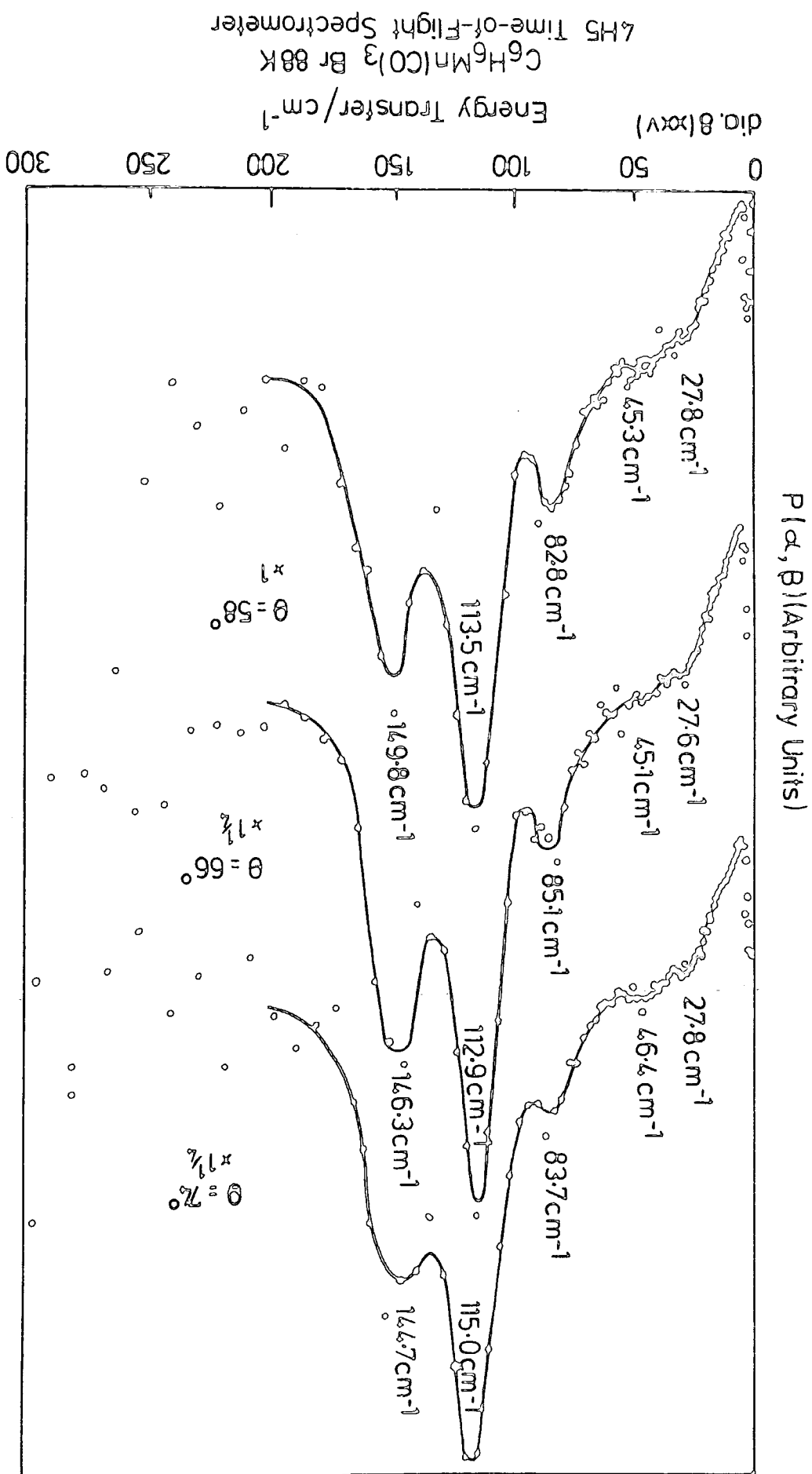
$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ 233K
4H5 Time-of-Flight Spectrometer



$P(\alpha, \beta)$ (Arbitrary Units)







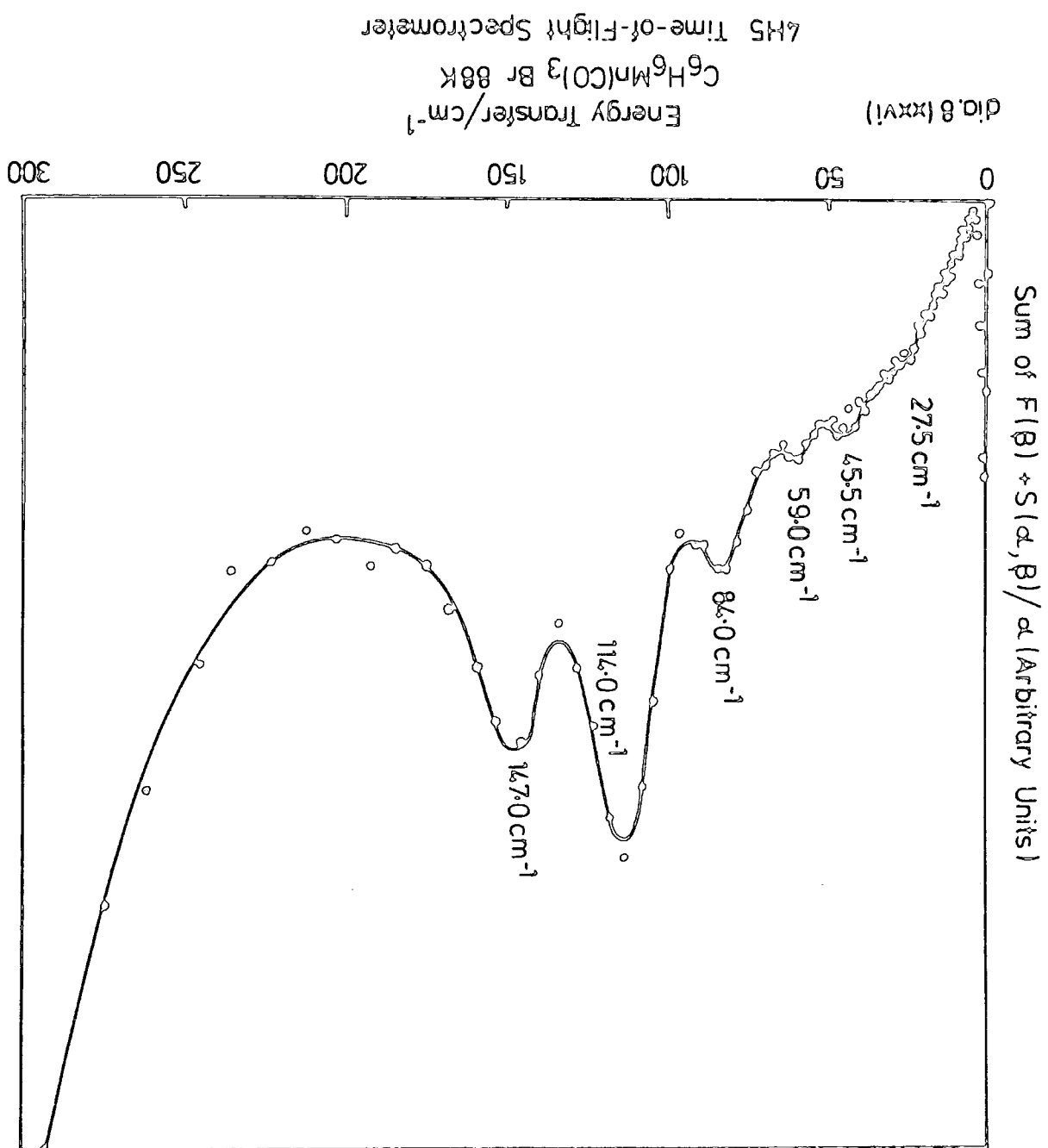


Table 8.26 The Spectroscopic Frequencies (cm^{-1}) and Assignments of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ and $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$

(C_{3v} molecular symmetry has been assumed)

$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$					$\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$				
Infrared	Raman	INS Frequency		Assignment	Infrared [†]	Raman ^{††}	INS Frequency		Assignment
		T-O-F	BFD				T-O-F ^{††}	T-O-F ^{††}	
	30m	38.5 $\pm$ 2.0		} Lattice Modes 22(A ₂) Torsion? Lattice Mode?		47m	26.5 $\pm$ 1.5	27.5 $\pm$ 1.5	} Lattice Modes
48m 86s	50m 65m	57.0 $\pm$ 2.5 68.5 $\pm$ 3.0	65 $\pm$ 8		82sh ^{oo}	61m 78m	45.5 $\pm$ 2.0 59.0 $\pm$ 3.0 79.0 $\pm$ 3.5 84.0 $\pm$ 3.5 105.0 $\pm$ 5.0 114.0 $\pm$ 5.0	45.5 $\pm$ 2.0 59.0 $\pm$ 3.0 84.0 $\pm$ 3.5 105.0 $\pm$ 5.0 114.0 $\pm$ 5.0	
121s 151m	111vs 132vs	128.5 $\pm$ 6.0 127 $\pm$ 8		28(E) i.m.c. 24(E) $\delta(\text{O}-\text{Cr}-(\text{CO})_3)$	118s 154sh 162vw 203s	124m 163vs	143.5 $\pm$ 7.0 147.0 $\pm$ 6.5	136 $\pm$ 8	28(E) i.m.c. 24(E) $\delta(\text{O}-\text{Mn}-(\text{CO})_3)$
	298vs		212 $\pm$ 8	Combination Band ^a		270w		223 $\pm$ 8 264 $\pm$ 8	} Combination Bands or Overtones ^a 21(A ₁) _s (Mn-O)
	333w		327 $\pm$ 8 / 333 $\pm$ 8	21(A ₁) _s (Cr-O) 23(E) Ring tilt	285sh 295m 310w	317w		326 $\pm$ 8 / 334 $\pm$ 8	
			429 $\pm$ 8 490 $\pm$ 8	16(E) i.m.b. 27(E) i.m.c.	372w 418vw 456w 519vs 595vs 613sh 638vs	461w		424 $\pm$ 8	16(E) i.m.b. 27(E)+25(A ₁) i.m.c. 34(E) i.m.c. 33(E) i.m.c. 6(E) i.m.b. 31(A ₁) i.m.c. 4(A ₂) i.m.b.
			621 $\pm$ 8 665 $\pm$ 8 811 $\pm$ 8	6(E) i.m.b. 4(A ₂) i.m.b. 11(A ₁) i.m.b.	819w 845vw 981vw			660 $\pm$ 8	
						984w		842 $\pm$ 8	11(A ₁) i.m.b. 1(A ₁) i.m.b.

^a ν = O-Cr-O; δ = symmetric; as = antisymmetric; i.m.b. = internal mode of the benzene ligand; i.m.c. = internal mode of the Cr(CO)₃ moiety; vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

^o Discussed in text.

^{oo} Shoulder on polythene peak.

[†] The infrared work carried out on $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3$ by Winkhaus et al.⁷⁹ located only two bands below 1000 cm^{-1} , at 827 cm^{-1} (w) and at 643 cm^{-1} (o).

^{††} This compound gave poor Raman spectra.

[‡] Data recorded at 233K.

^{‡‡} Data recorded at 80K.

discs or as nujol mulls between CsI plates.

Raman spectra were measured in the range $0-900\text{cm}^{-1}$ with a Cary 82 Raman Spectrometer employing in the case of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ a Spectra Physics Model 164 Ar laser at 19436.3cm^{-1} (200mW power), and in the case of $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ a Spectra Physics Model 125 He/Ne laser at $15,802\text{cm}^{-1}$ (6mW power).

4. Discussion of Results

(a) $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$

The INS spectra of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ are shown in dias.8(xix)-(xxi), and are summarised in Table 8.26.

Guided by the various assignment schemes previously discussed, identification of the internal modes of the benzene ligand may be carried out straightforwardly. Hence the 811cm^{-1} BFD band may be assigned to $\nu_{11}(\text{A}_1)$ in accordance with the frequencies suggested for the mode by infrared and Raman spectroscopy ($784-800\text{cm}^{-1}$)^{63,69,70} and Normal Co-ordinate Analyses ($784-800\text{cm}^{-1}$)^{21,76}. The 665cm^{-1} peak may be ascribed to $\nu_4(\text{A}_2)$ in agreement with Adams and Squire⁷⁴, who opted for this designation of the optically observed transition at 654cm^{-1} in preference to prior assignments of $\nu_{32}(\delta(\text{Cr-C-O}), \text{A}_2)$ ⁶⁹ and $\nu_{11}(\text{A}_1)$ ⁷¹. Infrared and Raman data ($611-617\text{cm}^{-1}$)^{63,66,69-71} and Normal Co-ordinate Analysis ($611.4-621\text{cm}^{-1}$)^{21,76,77} point to the 621cm^{-1} BFD frequency representing $\nu_6(\text{E})$. Finally, the 429cm^{-1} INS band may be attributed to $\nu_{16}(\text{E})$, following optical spectroscopy ($418-427\text{cm}^{-1}$)^{63,66,69-71} and Normal Co-ordinate Analysis (426cm^{-1})⁷⁶.

This leaves only one unexplained feature in the section of the BFD spectrum between approximately 400cm^{-1} and 850cm^{-1} : the shoulder situated at 490cm^{-1} . It may be noted, however, that the mode $\nu_{27}(\nu_{\text{as}}(\text{Cr-CO}), \text{E})$ has been assigned at $487-92\text{cm}^{-1}$ in various spectroscopic investigations^{66,69,71,72} and at 488cm^{-1} in Normal Co-ordinate Analysis⁶⁶. Whilst it would not normally be expected that a carbonyl mode would be of sufficient intensity to be observed in the INS spectrum, it is not improbable that this vibration

might become visible as a result of mixing with a mode of identical symmetry[†] which involves a large amount of proton motion and is of similar frequency. In fact, in the specific instance of ν_{27} ($\nu_{as}(\text{Cr-CO}), E$), a ready candidate with which mixing might take place is supplied by the adjacent intense internal benzene ligand mode $\nu_{16}(E)$ situated at 429cm^{-1} in the BFD spectrum.

Considering the possibility of mixing in a slightly wider context, it may be seen that morerecent papers^{66,69,71,72} have placed the carbonyl modes

$\nu_{25}(\nu_s(\text{Cr-CO}), A_1)$, $\nu_{27}(\nu_{as}(\text{Cr-CO}), E)$, $\nu_{31}(\delta(\text{Cr-C-O}), A_1)$, $\nu_{32}(\delta(\text{Cr-C-O}), A_2)$, $\nu_{33}(\delta(\text{Cr-C-O}), E)$ and $\nu_{34}(\delta(\text{Cr-C-O}), E)$ in the region of the spectrum between $\text{ca. } 480\text{cm}^{-1}$ and 670cm^{-1} (Table 8.23). Furthermore, intense internal benzene ligand vibrations have been located in the INS spectrum at 429cm^{-1} ($\nu_{16}(E)$), 621cm^{-1} ($\nu_6(E)$) and 665cm^{-1} ($\nu_4(A_2)$). Comparing the descriptions of these internal benzene vibrations and carbonyl modes (under C_{3v} molecular symmetry), it is evident that mixing may well be widespread in this area of the spectrum. Moreover, when the findings of Adams and Squire⁶⁹ are taken into account (i.e. that the benzene vibrations ν_{16} , ν_6 and ν_{11} are themselves split by site group symmetry, in an analogous manner to that reported for the carbonyl modes ($\nu_{25} - \nu_{34}$), and the vibrations of the C_6H_6 group relative to the $\text{Cr}(\text{CO})_3$ moiety ($\nu_{21} - \nu_{24}$)) it might be expected that mixing could be very extensive indeed.

To lower frequency, $\nu_{21}(\nu_s(\text{Cr-}\emptyset), A_1)$ and $\nu_{23}(\text{ring tilt}, E)$ have been generally assigned to the frequencies $296\text{--}301\text{cm}^{-1}$ ^{63,65,66,69-71} and $328\text{--}338\text{cm}^{-1}$ ^{63,66,69-71} respectively. Whilst the latter may be correlated, following past work^{63,66,69-71}, with the very strong BFD peak at $327/333\text{cm}^{-1}$,

ν_{21} , in contrast, is not apparently observed. Consideration of the relative intensities expected for the two vibrations (Table 8.27) shows that ν_{23} , as

[†] Such mixing in this area of the spectrum has been commented upon by Adams et al.⁷⁷ in their Normal Co-ordinate Analysis of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$.

Table 8.27 Intensities Predicted in the BFD Spectrum for Hindered Translational and Rotational Modes of the Benzene Ligand within $C_6H_6Cr(CO)_3$.

Mode [†]	"Complexed" $C_6H_6^*$
$t_x^{\nearrow}$ } The deformation mode $t_y^{\nearrow}$ } $\nu_{24}(E)$ represents $t_z^{\nearrow}$ } <u>both</u> these translations , represented by the symmetric stretch $\nu_{21}(A_1)$	1.000 1.000 1.000
$\tau_x^{\nearrow\nearrow}$ } The ring tilt ($\nu_{23}(E)$) $\tau_y^{\nearrow\nearrow}$ } represents <u>both</u> of these $\tau_z^{\nearrow\nearrow}$ } rotations , represented by the torsion $\nu_{22}(A_2)$	2.690 2.692 2.691

t = hindered translational mode; τ = hindered rotational (torsional) mode.

[†] The axes x, y and z referred to are those illustrated in dia.8(xv).

* Structural data taken from that of Rees and Coppens^{58,59} for the benzene ligand of $C_6H_6Cr(CO)_3$ (Appendix 6).

$\nearrow$ Calculated using the relation for a translation: Intensity $\propto M^{-1}$ (see Chapter IV), where M is the mass of benzene.

$\nearrow\nearrow$ Calculated using the relation for a rotation:

Intensity $\propto r^2 (I_R)^{-1}$ (see Chapter IV), where r is the perpendicular distance between the scattering atom and the axis of rotation, and I_R is the reduced moment of inertia of benzene about that axis.

a doubly degenerate rotational mode, would be expected to be about 5.5 times as intense as ν_{21} , a singly degenerate translational mode. It thus seems reasonable to suppose that the asymmetry displayed by the band profile of the ν_{23} transition to low frequency is caused by the unresolved presence of ν_{21} , an explanation given further credibility by the inherent resolution of the BFD spectrometer (ca. 42cm^{-1})[†].

In an attempt to find support for this proposition, gaussians were fitted (using a Du Pont Curve Resolver) to frequencies of 298cm^{-1} and 333cm^{-1} representing $\nu_{21}(\nu_s(\text{Cr}-\phi), A_1)$ and $\nu_{23}(\text{ring tilt}, E)$ respectively, and the bandshape of the 333cm^{-1} BFD peak matched. The results showed the high frequency band to be 4.263 times as intense as that to lower frequency, in fair agreement with prediction (given the accuracy of the intensity measurement). Hence, it appears that ν_{21} is present as an unresolved component of the $327/333\text{cm}^{-1}$ peak.

The 212cm^{-1} transition in the BFD spectrum of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (which is scarcely visible in the $P(\alpha, \beta)$ spectra) has not been observed by either infrared or Raman spectroscopy,^{67,69-71} nor is it predicted by Normal Co-ordinate Analysis^{66,76,77}. The only inactive (A_2) mode of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ which has not been firmly assigned is $\nu_{22}(\text{torsion } (\phi-\text{Cr}-(\text{CO})_3))$. However, calculation of the barrier to benzene ligand rotation resulting from the 212cm^{-1} frequency yields a value of $425.14 \pm 32.69 \text{ kJ mol}^{-1}$ (Table 8.28), whereas Chiu et al.⁶⁰ found the benzene group within gas phase $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ to be almost freely rotating. Whilst, in the solid, intermolecular forces would be expected to give rise to a barrier to rotation (as was found to be the case for $\text{Cr}(\text{C}_6\text{H}_6)_2$), it is perhaps unreasonable that it should be as large as $425.12 \pm 32.69 \text{ kJ mol}^{-1}$. Furthermore, the intensity displayed by the

[†] The resolutions of the various spectrometers used in this work are discussed in Chapter III.

212cm^{-1} peak is considerably less than that which would be predicted qualitatively.[†] Hence, it appears necessary to attribute the 212cm^{-1} frequency to a combination band:

$$68.5 \pm 3.0\text{cm}^{-1} + \begin{cases} 128.5 \pm 6.0\text{cm}^{-1} \\ 127 \pm 8\text{cm}^{-1} \end{cases} = \begin{cases} 197.0 \pm 9.0\text{cm}^{-1} \\ 195.5 \pm 11\text{cm}^{-1} \end{cases}$$

This leaves the low energy assignments which are particularly difficult for this compound because the modes $\nu_{26}(\delta(\text{OC-Cr-CO}), A_1)$ and $\nu_{28}(\delta(\text{OC-Cr-CO}), E)$ as well as the $\text{C}_6\text{H}_6\text{-Cr}(\text{CO})_3$ vibrations $\nu_{22}(\text{torsion}(\phi\text{-Cr-(CO)}_3), A_2)$ and $\nu_{24}(\delta(\phi\text{-Cr-(CO)}_3), E)$ are predicted to be situated in this region of the spectrum^{67,69-72}. Furthermore, the intensities of the two former modes need not be inconsiderable, in the case of ν_{26} because the vibration causes motion of the Cr atom (and hence the protons of the benzene group riding on it), and in the case of ν_{28} because its symmetry is identical to that of ν_{24} (thus allowing the possibility of mixing). Indeed, if the influence of site group symmetry is taken into account, it is possible for mixing to occur between components of $\nu_{26}(\nu_{26}'(A_g)$ and $\nu_{26}''(B_u))$ and components of $\nu_{24}(\nu_{24a}'(A_g)$ and $\nu_{24a}''(B_u))$ (Table 8.24).

Unfortunately, it is not strictly possible to decide assignments on intensity grounds in this part of the spectrum; firstly, because there is no band in the $P(\alpha, \beta)$ spectra whose assignment is secure and whose bandshape is well resolved, and secondly, because mixing might be expected to alter predicted intensity ratios to some extent. Nevertheless, it will be borne in mind that $\nu_{22}(\text{torsion}(\phi\text{-Cr-(CO)}_3), A_2)$ represents a singly degenerate rotational mode and should consequently be approximately half the intensity of $\nu_{23}(\text{ring tilt}, E)$, whilst $\nu_{24}(\delta(\phi\text{-Cr-(CO)}_3), E)$ represents a doubly degenerate translational mode and should thus be about twice the intensity suggested for $\nu_{21}(\nu_s(\text{Cr-}\phi), A_1)$

[†] ν_{22} , as a singly degenerate rotational mode, should be approximately half the intensity of the doubly degenerate rotational mode $\nu_{23}(\text{ring tilt}, E)$.

by curve resolution. Taking into account the intensity ratio obtained previously for $\nu_{23} : \nu_{21}$ (4.263:1.000), it must thus be expected that the vibrations ν_{22} and ν_{24} would be of roughly equal intensity.

An optically derived frequency, $146\text{--}153\text{cm}^{-1}$ (infrared)^{69,71}/ $131\text{--}148\text{cm}^{-1}$ (Raman)⁶⁸⁻⁷², has been variously designated $\nu_{28}(\text{E})$ ⁶⁹, $\nu_{24}(\text{E})$ ⁷⁰ and $\nu_{26}(\text{A}_1)$ ^{71,72} (Table 8.23), whilst to longer wavelength a band at $119\text{--}121\text{cm}^{-1}$ (infrared)^{69,71}/ $108\text{--}114\text{cm}^{-1}$ (Raman)^{67,69-72} has, with similar uncertainty, been correlated with $\nu_{26}(\text{A}_1)$ ^{67,69} and $\nu_{28}(\text{E})$ ⁷⁰⁻². Although the latter is not apparently present in the INS spectra of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, a peak equivalent to the former transition is found at $128.5 \pm 6.0\text{cm}^{-1}$ ($\text{P}(\alpha, \beta)$)/ $127 \pm 8\text{cm}^{-1}$ (BFD). However, the intensity displayed by this vibration is such that it may only reasonably be assigned to either $\nu_{22}(\text{torsion}(\emptyset\text{-Cr}-(\text{CO})_3), \text{A}_2)$ or $\nu_{24}(\delta(\emptyset\text{-Cr}-(\text{CO})_3), \text{E})$. Calculation of the barrier to benzene ligand rotation based upon the $128.5/127\text{cm}^{-1}$ frequency yields a value of $156.19 \pm 14.93\text{kJ mol}^{-1}$ / $152.57 \pm 19.83\text{kJ mol}^{-1}$ (Table 8.28). This perhaps seems large when the findings of Chiu et al.⁶⁰ relating to the rotation of the benzene group within $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ in the gas phase are taken into account. Consequently, assignment to

$\nu_{24}(\delta(\emptyset\text{-Cr}-(\text{CO})_3), \text{E})$ appears more justified. Furthermore, this correlation offers a possible explanation for the asymmetry (to long wavelength) evident in the 128.5cm^{-1} $\text{P}(\alpha, \beta)$ peak at low angle. In more recent spectroscopic studies of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, the $119\text{--}121\text{cm}^{-1}$ (infrared)/ $108\text{--}114\text{cm}^{-1}$ (Raman) frequency has been designated $\nu_{28}(\delta(\text{OC-Cr-CO}), \text{E})$ ⁷⁰⁻⁷². This vibration, of course, possesses the same symmetry as that now suggested to give rise to the $128.5/127\text{cm}^{-1}$ INS peak ($\nu_{24}(\delta(\emptyset\text{-Cr}-(\text{CO})_3), \text{E})$) and therefore mixing between the two modes may occur.[†]

Turning now to three lowest energy $\text{P}(\alpha, \beta)$ transitions ($38.5 \pm 2.0\text{cm}^{-1}$, $57.0 \pm 2.5\text{cm}^{-1}$ and $68.5 \pm 3.0\text{cm}^{-1}$), it seems reasonable, on intensity grounds, to correlate $\nu_{26}(\text{torsion}(\emptyset\text{-Cr}-(\text{CO})_3), \text{A}_2)$ with one of the latter two peaks;

[†] It will be noted that thus far assignment of the low frequency modes of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ follows the optical study of Schäfer et al.⁷⁰ and the Normal Co-ordinate Analysis of Cyvin et al.⁷⁶

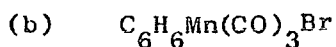
Table 8.28 The Barrier to the Rotation of the Benzene Ligand within
 $C_6H_6Cr(CO)_3$ Suggested by Several Possible Torsional Frequencies

Frequency (cm^{-1})	Calculated Barrier [/] ($kJ\ mol^{-1}$)
38.5 $\pm$ 2.0	14.02 $\pm$ 1.50
57.0 $\pm$ 2.5	30.73 $\pm$ 2.76
68.5 $\pm$ 3.0	44.39 $\pm$ 3.97
{ 127 $\pm$ 8	{ 152.57 $\pm$ 19.83
{ 128.5 $\pm$ 6.0	{ 156.19 $\pm$ 14.93
212 $\pm$ 8	425.14 $\pm$ 32.69

[/] Calculation of the barrier to the rotation of the benzene ligand within $C_6H_6Cr(CO)_3$ has been carried out employing the structural data of Rees and Coppens^{58,59} (Appendix 6) and assuming a three-fold barrier.

whilst the former feature (a weak shoulder), in agreement with past spectroscopic work⁷¹ (Table 23(c)), appears reasonably assigned to a lattice vibration.

Unfortunately, the poor resolution of the 57.0 cm^{-1} and 68.5 cm^{-1} bands, possibly (in view of the dispersion evident) a result of mixing with lattice modes, prevents conclusive identification of the ν_{22} mode. However, the 68.5 cm^{-1} $P(\alpha, \beta)$ frequency (233K) is presumably represented in the infrared spectrum by the band observed at 60 cm^{-1} (ambient temperature) / 87 cm^{-1} (liquid nitrogen temperature), which has been designated a lattice vibration by Adams and Squire⁶⁹. Assuming this correlation to be correct, there would be strong grounds for the 57.0 cm^{-1} peak corresponding to ν_{22} (torsion ($\emptyset$ -Cr-(CO)₃)_{A₂}), a result in fair agreement with the frequency derived for ν_{22} from the Normal Co-ordinate Analysis of Adams et al. (47 cm^{-1})⁷⁷. In any event, Table 8.28 shows the barrier to rotation of the benzene ligand within $C_6H_6Cr(CO)_3$ arising from both frequencies, 30.73 $\pm$ 2.76 $kJ\ mol^{-1}$ (57.0 $\pm$ 2.5 cm^{-1}) and 44.39 $\pm$ 3.97 $kJ\ mol^{-1}$ (68.5 $\pm$ 3.0 cm^{-1}).



The INS spectra of $C_6H_6Mn(CO)_3Br$ are shown in dias 8(xxii)-(xxvi), and are summarised in Table 8.26.

Following the spectroscopic assignments of $C_6H_6Cr(CO)_3$, the internal benzene ligand modes of $C_6H_6Mn(CO)_3Br$ may be identified within the BFD spectrum. Thus $\nu_{11}(A_1)$ may be recognised at $842cm^{-1}$, the mode occurring at a higher frequency in $C_6H_6Mn(CO)_3Br$ than that recorded for the equivalent vibration in $C_6H_6Cr(CO)_3$ ($811cm^{-1}$). This finding may possibly arise from the fact that ν_{11} represents an out-of-plane C-H bending vibration (dia.8(iii)). Its frequency, therefore, will be particularly sensitive to the strength of the interaction (and hence the bond length) between the benzene group and the metal atom. Thus, it may be suggested that in $C_6H_6Mn(CO)_3^+$ this interaction is stronger (and the metal-benzene group bond length shorter) than in $C_6H_6Cr(CO)_3$ causing ν_{11} to move to higher energy.

In contrast with ν_{11} , both $\nu_4(A_2)$ and $\nu_6(E)$ appear at similar frequencies in $C_6H_6Mn(CO)_3Br$ ($660cm^{-1}$ and $610cm^{-1}$ respectively) to those established for the chromium complex ($665cm^{-1}$ and $621cm^{-1}$ respectively.). Likewise, the position of $\nu_{16}(E)$ within the spectrum of $C_6H_6Mn(CO)_3Br$ ($424cm^{-1}$) is little changed in comparison with that of the analogous mode in $C_6H_6Cr(CO)_3$ ($429cm^{-1}$). A further similarity between the ν_{16} peaks of $C_6H_6Mn(CO)_3Br$ and $C_6H_6Cr(CO)_3$ is the asymmetry displayed by their band profiles to higher energy. This presumably results in the case of the cationic species from the same cause as that suggested for $C_6H_6Cr(CO)_3$; viz. mixing between $\nu_{16}(E)$ and carbonyl modes (particularly $\nu_{27}(E)^\dagger$) lying in this region of the spectrum (see later).

To longer wavelenth, the ring tilt mode (ν_{23}, E) may be assigned to the very intense BFD band at $326/334cm^{-1}$, the frequency being in close agreement with that measured for ν_{23} in $C_6H_6Cr(CO)_3$ ($327/333cm^{-1}$). Furthermore in common with the findings for $C_6H_6Cr(CO)_3$, optical spectroscopic evidence (see later) points to the placement of the vibration $\nu_{21}(\nu_s(Mn-\phi), A_1)$

† ν_{27} has been identified in optical spectra of $C_6H_6Cr(CO)_3$ at 487-492 cm^{-1} , 66, 69, 71, 72

within the bandshape of ν_{23} (ring tilt, E), which is predicted to be considerably more intense (Table 8.27)[†]. However, it is noteworthy that for $C_6H_6Mn(CO)_3Br$, the band profile of ν_{23} is not obviously asymmetrical as was found for $C_6H_6Cr(CO)_3$, and consequently, any accurate determination of the relative intensities of the two vibrations employing curve resolution is precluded.

Of the weak features located to lower energy at $223cm^{-1}$ and $264cm^{-1}$ in the BFD spectrum of $C_6H_6Mn(CO)_3Br$, the former is not observed in either infrared or Raman spectra (see later), whilst the latter is apparently represented by the weak Raman band situated at $270cm^{-1}$. Considering the $223cm^{-1}$ frequency first, it may be seen that no optically active fundamental vibration of $C_6H_6Cr(CO)_3$ has been identified between $ca. 160cm^{-1}$ and $290cm^{-1}$ (Table 8.23), whilst the only A_2 (infrared/Raman inactive) normal mode expected anywhere in the region of the spectrum below approximately $450cm^{-1}$ is ν_{22} (torsion($\emptyset$ -Mn-(CO) $_3$), A_2). Whilst the barrier to benzene ligand rotation within $C_6H_6Cr(CO)_3$ (and presumably also within $C_6H_6Mn(CO)_3Br$) appears to be determined by intermolecular forces, which one would expect to be considerably greater in $C_6H_6Mn(CO)_3Br$ (an ionic crystal held together by electrostatic (coulombic) forces) than in $C_6H_6Cr(CO)_3$ (a molecular crystal held together by Van der Waals forces), it is possibly unreasonable to suppose that the barrier height which would result from the $223cm^{-1}$ frequency of $C_6H_6Mn(CO)_3Br$ ($470.40 \pm 34.46 \text{ kJ mol}^{-1}$; Table 8.29) and the barrier height indicated for $C_6H_6Cr(CO)_3$ ($30.73 \pm 2.76 \text{ kJ mol}^{-1}$ ($57.0 \pm 2.5cm^{-1}$) or $44.39 \pm 3.97 \text{ kJ mol}^{-1}$ ($68.5 \pm 3.0cm^{-1}$); Table 8.28) should be so disparate.

[†] The intensities of the translational and rotational modes of $C_6H_6Mn(CO)_3Br$ must be assumed (in the absence of structural data for the complex) to be analogous to those determined for $C_6H_6Cr(CO)_3$.

TABLE 8.29

The Barrier to the Rotation of the Benzene Ligand within
 $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ Suggested by Several Possible Torsional Frequencies

Frequency (cm^{-1})	Calculated Barrier* (kJ mol^{-1})
$\left\{ \begin{array}{l} 26.5+1.5^{\text{f}} \\ 27.5+1.5^{\text{ff}} \end{array} \right.$	$\left\{ \begin{array}{l} 6.64+0.77 \\ 7.15+0.80 \end{array} \right.$
$\left\{ \begin{array}{l} 45.5+2.0^{\text{f}} \\ 45.5+2.0^{\text{ff}} \end{array} \right.$	$\left\{ \begin{array}{l} 19.58+1.76 \\ 19.58+1.76 \end{array} \right.$
$\left\{ \begin{array}{l} 79.0+3.5^{\text{f}} \\ 84.0+3.5^{\text{ff}} \end{array} \right.$	$\left\{ \begin{array}{l} 59.04+5.35 \\ 66.74+5.68 \end{array} \right.$
$\left\{ \begin{array}{l} 105.0+5.0^{\text{f}} \\ 108+8 \\ 114.0+5.0^{\text{ff}} \end{array} \right.$	$\left\{ \begin{array}{l} 104.29+10.17 \\ 110.33+16.95 \\ 122.93+11.02 \end{array} \right.$
$\left\{ \begin{array}{l} 136+8 \\ 143.5+7.0^{\text{f}} \\ 147.0+6.5^{\text{ff}} \end{array} \right.$	$\left\{ \begin{array}{l} 174.96+21.19 \\ 194.79+19.47 \\ 204.41+18.48 \end{array} \right.$
223+8	470.40+34.36
264+8	659.27+40.56

^f T-O-F data recorded at 233K

^{ff} T-O-F data recorded at 88K

- Calculation of the barrier to the rotation of the benzene ligand within $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ has been carried out employing the structural data of Rees and Coppens relating to $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ^{58,59} (Appendix 7) and assuming a three-fold barrier.

However, this argument is somewhat conjectural; perhaps more conclusively, the intensity displayed by the 223cm^{-1} band is very much less than that anticipated on the basis of qualitative predictions for ν_{22} in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3^+$. Consequently, it seems that assignment of the 223cm^{-1} frequency to a combination band^{††}

$$\begin{aligned} 84.0 \pm 3.5\text{cm}^{-1} + 114.0 \pm 5.0\text{cm}^{-1} &= 198.0 \pm 8.5\text{cm}^{-1} \quad \neq \\ 79.0 \pm 3.5\text{cm}^{-1} + 105.0 \pm 5.0\text{cm}^{-1} &= 184.0 \pm 8.5\text{cm}^{-1} \quad \neq \end{aligned}$$

or an overtone

$$\begin{aligned} 2 [114.0 \pm 5.0\text{cm}^{-1}] &= 228.0 \pm 10.0\text{cm}^{-1} \quad \neq \\ 2 [105.0 \pm 5.0\text{cm}^{-1}] &= 210.0 \pm 10.0\text{cm}^{-1} \quad \neq \end{aligned}$$

is necessary. Likewise, the still less intense vibration at 264cm^{-1} is situated in an area of the spectrum ($160\text{--}290\text{cm}^{-1}$) in which only an overtone ($2 \times 134\text{cm}^{-1} = 268\text{cm}^{-1}$) has been reported for $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3^{71}$. It would seem that the arguments advanced refuting correlation of ν_{22} with the 223cm^{-1} peak militate even more strongly against correlation of ν_{22} with the 264cm^{-1} transition. Hence the latter frequency must also correspond to either a combination band

$$\begin{aligned} 105.0 \pm 5.0\text{cm}^{-1} + 143.5 \pm 7.0\text{cm}^{-1} &= 248.5 \pm 12.0\text{cm}^{-1} \quad \neq \\ 114.0 \pm 5.0\text{cm}^{-1} + 147.0 \pm 6.5\text{cm}^{-1} &= 261.0 \pm 11.5\text{cm}^{-1} \quad \neq \\ 108 \pm 8\text{cm}^{-1} + 136 \pm 8\text{cm}^{-1} &= 244 \pm 16\text{cm}^{-1} \end{aligned}$$

or an overtone

$$\begin{aligned} 2[143.5 \pm 7.0\text{cm}^{-1}] &= 287.0 \pm 14.0\text{cm}^{-1} \quad \neq \\ 2[147.0 \pm 6.5\text{cm}^{-1}] &= 294.0 \pm 13.0\text{cm}^{-1} \quad \neq \\ 2[136 \pm 8\text{cm}^{-1}] &= 272 \pm 16\text{cm}^{-1} \end{aligned}$$

Finally, the $P(\alpha, \beta)$ spectra must be considered: however, no guidance regarding the relative intensities of the modes $\nu_{22}(\text{torsion } (\text{O-Mn}-(\text{CO})_3), A_2)$ and $\nu_{24}(\delta(\text{O-Mn}-(\text{CO})_3), E)$ is available, on account of the inability to resolve $\nu_{21}(\nu_s(\text{Mn-O}), A_1)$ from $\nu_{23}(\text{ring tilt}, E)$ in the BFD spectrum. It

[†] ν_{22} , as a singly degenerate rotational mode, should be approximately half the intensity of the doubly degenerate rotational mode $\nu_{23}(\text{ring tilt}, E)$.

^{††} Henceforth the suffix $\neq$ will be used to denote T-O-F data measured at 233K, and the suffix $\neq$ will be used to denote T-O-F data measured at 88K.

must therefore be assumed that in common with the findings for $C_6H_6Cr(CO)_3$, ν_{22} and ν_{24} are of similar intensity, with the former being possibly slightly the more intense.

Guided by the INS assignment scheme of $C_6H_6Cr(CO)_3$, and in agreement with the preceding discussion, $\nu_{24}(\delta(\emptyset-Mn-(CO)_3), E)$ may be associated with the second most intense (and highest frequency) $P(\alpha, \beta)$ peak, the frequency indicated for $C_6H_6Mn(CO)_3Br$ ($143.5 \pm 7.0^\dagger / 147.0 \pm 6.5 \text{ cm}^{-1} \dagger\dagger$ T-O-F, $136 \pm 8 \text{ cm}^{-1}$ BFD) comparing with that of $128.5 \pm 6.0 \text{ cm}^{-1}$ (T-O-F) / $127 \pm 8 \text{ cm}^{-1}$ (BFD) recorded for the equivalent vibration of the chromium complex. In similar agreement with predicted intensities, the $105.0 \pm 5.0^\dagger / 114.0 \pm 5.0 \text{ cm}^{-1} \dagger\dagger$ band of $C_6H_6Mn(CO)_3Br$ (the most intense vibration in the $P(\bar{\theta}, \beta)$ spectrum) would appear only reasonably assigned to the remaining unidentified fundamental expected in this region of the spectrum, $\nu_{22}(\text{torsion}(\emptyset-Mn-(CO)_3), A_2)$. It will be noted that the frequency attributed ν_{22} in $C_6H_6Mn(CO)_3Br$ represents a considerably larger barrier to benzene ligand rotation within the molecule than that suggested for $C_6H_6Cr(CO)_3$ ($30.73 \pm 2.76 \text{ kJ mol}^{-1}$ ($57.0 \pm 2.5 \text{ cm}^{-1}$) / $44.39 \pm 3.97 \text{ kJ mol}^{-1}$ ($68.5 \pm 3.0 \text{ cm}^{-1}$). This undoubtedly reflects in the main the increased intermolecular forces expected in an ionic as opposed to a molecular crystal; however, it is interesting to speculate as to whether a contributory factor may be increased intramolecular forces within the cationic species.[†]

Considering the lowest energy T-O-F bands, those observed at $26.5 \pm 1.5^\dagger / 27.5 \pm 1.5 \text{ cm}^{-1} \dagger\dagger$ and at $45.5 \pm 2.0^\dagger / 45.5 \pm 2.0 \text{ cm}^{-1} \dagger\dagger$, as well as that visible only in the "sum of $F(\beta) + S(\alpha, \beta)/\alpha$ " spectrum at $59.0 \pm 3.0 \text{ cm}^{-1} \dagger\dagger$ (dia.8(xxvi)), are undoubtedly lattice modes as evidenced by the degree of dispersion they display. The more intense $79.0 \pm 3.5^\dagger / 84.0 \pm 3.5 \text{ cm}^{-1} \dagger\dagger$ vibration,

[†] These are, perhaps, indicated by the elevation in frequency of ν_{11} observed on going from $C_6H_6Cr(CO)_3$ to $C_6H_6Mn(CO)_3Br$ (see previously).

in contrast, displays little dispersion and is more difficult to identify conclusively. It may represent a lattice mode in common with the bands observed to lower energy, but assignment to either $\nu_{26}(\delta(\text{OC-Mn-CO}), A_1)$ or $\nu_{28}(\delta(\text{OC-Mn-CO}), E)$ cannot be ruled out on intensity grounds[†]. As will be seen in the succeeding discussion of the optical spectra of $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$, however, if assignment to a mode $\delta(\text{OC-Mn-CO})$ is necessitated, then attribution to the A_1 vibration (ν_{26}) is the more likely.

Turning to the optical spectra of $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$, the infrared bands at 845cm^{-1} , 613cm^{-1} and 418cm^{-1} may be straightforwardly assigned to the internal benzene ligand modes $\nu_{11}(A_1)$, $\nu_6(E)$ and $\nu_{16}(E)$, the frequencies derived comparing well with those measured by INS spectroscopy (842cm^{-1} , 610cm^{-1} and 424cm^{-1} respectively). Similarly, the ring tilt, $\nu_{23}(E)$, located at $326/334\text{cm}^{-1}$ in the BFD spectrum, may be identified at 334cm^{-1} in both infrared and Raman spectra, whilst $\nu_{21}(\nu_s(\text{Mn-}\emptyset), A_1)$, guided by the frequency assigned the equivalent mode in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ($296\text{-}301\text{cm}^{-1}$) ^{63,65,66,69-71} may be attributed to the infrared band of moderate intensity situated at 295cm^{-1} . (It will therefore be noted that similarly to $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, both the ν_{21} and ν_{23} vibrations are, in the BFD spectrum, encompassed by the band profile of the more intense ν_{23} mode.)

To lower energy, the 154cm^{-1} and 162cm^{-1} infrared frequencies and the 163cm^{-1} Raman frequency appear to correlate with $\nu_{24}(\delta(\emptyset\text{-Mn-(CO)}_3), E)$ located at $143.5^\circ/147.0^\circ/136\text{cm}^{-1}$ in INS spectra. In the same region of the spectrum the 118cm^{-1} (infrared)/ 124cm^{-1} (Raman) band would seem by analogy with assignments for $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (121cm^{-1} infrared/ $108\text{-}114\text{cm}^{-1}$ (Raman)) ⁶⁹⁻⁷² to represent $\nu_{28}(\delta(\text{OC-Mn-CO}), E)$, ⁷⁰⁻² whereas the 82cm^{-1} (infrared)/ 78cm^{-1} (Raman) vibration corresponds either to a lattice mode or, perhaps more likely, to

[†] The intensity displayed by the modes ν_{26} and ν_{28} need not be negligible, in the case of the former vibration because motion of the manganese atom would be expected to give rise to sympathetic movement of the protons of the benzene group "riding" on it, and in the case of the latter vibration, because mixing is possible with the intense mode $\nu_{24}(\delta(\emptyset\text{-Mn-(CO)}_3), E)$ which possesses identical symmetry.

the other $\delta(\text{OC-Mn-CO})$ mode $\nu_{26}(\text{A}_1)$. The remaining low frequency bands (47cm^{-1} and 61cm^{-1} ; Raman) may, following the INS assignments for the vibrations situated at $45.5^{\pm}/45.5^{\pm\pm}\text{cm}^{-1}$ and $59.0^{\pm\pm}\text{cm}^{-1}$, be identified as lattice modes.

Considering now the frequency range 500cm^{-1} to 700cm^{-1} , it may be seen that three very intense vibrations are observed in the infrared spectrum of $\text{C}_6\text{H}_6(\text{Mn}(\text{CO})_3\text{Br})$, at 638cm^{-1} , 595cm^{-1} and 519cm^{-1} respectively. Likewise for $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, three very intense infrared bands have been reported in this same spectral region, which have been identified as $\nu_{31}(\text{ca. } 667\text{cm}^{-1})^{63,64,69-72}$, $\nu_{33}(\text{ca. } 635\text{cm}^{-1})^{63-5,69-72}$ and $\nu_{34}(\text{ca. } 533\text{cm}^{-1})^{64,65,69-72}$. It seems reasonable to assign the $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ frequencies following the guidance afforded by the chromium complex, and thus the 638cm^{-1} , 595cm^{-1} and 519cm^{-1} bands have been correlated with $\nu_{31}(\delta(\text{Mn-C-O}), \text{A}_1)$, $\nu_{33}(\delta(\text{Mn-C-O}), \text{E})$ and $\nu_{34}(\delta(\text{Mn-C-O}), \text{E})$ respectively.

At slightly longer wavelength, the 456cm^{-1} (infrared)/ 461cm^{-1} (Raman) peak of $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ may be taken to represent the remaining unassigned modes of the $\text{Mn}(\text{CO})_3$ moiety expected, by analogy with $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, in this general region of the spectrum, $\nu_{25}(\nu_s(\text{Mn-CO}), \text{A}_1)$ and $\nu_{27}(\nu_{as}(\text{Mn-CO}), \text{E})$. In common with the $\delta(\text{Mn-C-O})$ modes ν_{31} , ν_{33} and ν_{34} discussed above, it is noticeable that these vibrations occur at slightly lower frequency in $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ than those assigned to the equivalent vibrations of the chromium complex ($483-87\text{cm}^{-1}$, $\nu_{25}^{64,65,69,71,72}$ and $488-92\text{cm}^{-1}$, $\nu_{27}^{66,69,71,72}$).

Finally, the 981cm^{-1} (infrared)/ 984cm^{-1} (Raman) band of $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ may be attributed to the internal benzene ligand mode $\nu_1(\text{A}_1)$ identified at $978-981\text{cm}^{-1}$ in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3^{63,69-71}$, whilst the remaining weak features in the infrared (372cm^{-1} , 310cm^{-1} , 285cm^{-1} and 203cm^{-1}) and Raman (317cm^{-1} and 270cm^{-1}) spectra of $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$, analogues of which have either not been reported or not assigned in optical spectra of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, may perhaps be assumed to represent various combination bands and overtones.

Appendix: Structural Data Used in the Calculation of Moments of Inertia

1. "Free" Benzene

The co-ordinates below have been derived from the bond lengths and bond angles reported by Stoicheff⁵¹ for liquid benzene.

Hx+2.4810
y 0.0000
z 0.0000

Cx+1.3970
y 0.0000
z 0.0000

Hx+1.2405	Cx+0.6985	Cx+0.6985	Hx+1.2405
y+2.1486	y+1.2098	y-1.2098	y-2.1486
z 0.0000	z 0.0000	z 0.0000	z 0.0000

Hx-1.2405	Cx-0.6985	Cx-0.6985	Hx-1.2405
y+2.1486	y+1.2098	y-1.2098	y-2.1486
z 0.0000	z 0.0000	z 0.0000	z 0.0000

Cx-1.3970
y 0.0000
z 0.0000

Hx-2.4810
y 0.0000
z 0.0000

2. "Complexed Benzene Model" for $\text{Cr}(\text{C}_6\text{H}_6)_2$

Structural data for "complexed benzene" have been taken from the neutron diffraction results of Förster et al.^{15,16} for the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2$. However, following evidence for the latter molecule in fact possessing D_{6h} symmetry²⁰ (rather than the D_{3d} symmetry suggested in the neutron diffraction study), the "complexed benzene" molecule has been assumed to be planar (with all internal C-C-C bond angles equal to 120°), and averages have been employed of the two lengths reported for both the C-C and C-H bonds ($1.424\text{\AA}$ and $1.406\text{\AA}$, and $1.081\text{\AA}$ and $1.015\text{\AA}$ respectively).

Hx+2.4630
y 0.0000
z 0.0000

Cx+1.4150
y 0.0000
z 0.0000

Hx+1.2315	Cx+0.7075	Cx+0.7075	Hx+1.2315
y+2.1330	y+1.2254	y-1.2254	y-2.1330
z 0.0000	z 0.0000	z 0.0000	z 0.0000

Hx-1.2315	Cx-0.7075	Cx-0.7075	Hx-1.2315
y+2.1330	y+1.2254	y-1.2254	y-2.1330
z 0.0000	z 0.0000	z 0.0000	z 0.0000

Cx-1.4150
y 0.0000
z 0.0000

Hx-2.4630
y 0.0000
z 0.0000

3. $\text{Cr}(\text{C}_6\text{H}_6)_2$

The amended structural data of Förster et al.^{15,16} (described in Appendix 2) have been employed together with the chromium-benzene ring plane distance (i.e. z co-ordinate) suggested in the same study ($1.575\text{\AA}$).

4. "Complexed Benzene Model" for $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$

The structural parameters for "complexed benzene" have been based upon the findings for the benzene ligands within $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$ reported by Morosin⁴⁸. However, as the C-H bond lengths and C-C-C bond angles within the ligand benzene molecules were not quoted in this work, an average has been taken of the two C-H bond lengths determined within $\text{Cr}(\text{C}_6\text{H}_6)_2$ by Förster et al.^{15,16} (see Appendix 2), and the internal C-C-C bond angles have all been assumed to equal to 120° .

Hx+2.4480

y 0.0000

z 0.0000

Cx+1.4000

y 0.0000

z 0.0000

Hx+1.2240 Cx+0.7000

y+2.1200 y+1.2124

z 0.0000 z 0.0000

Cx+0.7000 Hx+1.2240

y-1.2124 y-2.1200

z 0.0000 z 0.0000

Hx-1.2240 Cx-0.7000

y+2.1200 y+1.2124

z 0.0000 z 0.0000

Cx-0.7000 Hx-1.2240

y-1.2124 y-2.1200

z 0.0000 z 0.0000

Cx-1.4000

y 0.0000

z 0.0000

Hx-2.4480

y 0.0000

z 0.0000

7. $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$

The structure of $\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3\text{Br}$ has not been reported. Moments of inertia, therefore, have had to be calculated employing the structural parameters of Rees and Coppens for $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ^{58,59}, but with the mass of a manganese atom substituted for that of the chromium atom. (This approximation, causes negligible change in the co-ordinates given previously for the atoms within the $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ molecule (Appendix 6)).

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APPENDIX

The Board of Studies in Chemistry requires that each postgraduate research thesis contain an appendix listing

- (a) all research colloquia, research seminars and lectures (by external speakers) arranged by the Department of Chemistry since 1 October 1976;
- and (b) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out.

1. Research Colloquia, Seminars and Lectures

1.1 1976-77

a) University of Durham Chemistry Colloquia

Wednesday, 20th October

Professor J.B. Hyne (University of Calgary), "New Research on an Old Element - Sulphur".

Wednesday, 10th November

Dr. J.S. Ogden (Southampton University), "The Characterization of High Temperature Species by Matrix Isolation".

Wednesday, 17th November

Dr. B.E.F. Fender (University of Oxford), "Familiar but Remarkable Inorganic Solids".

Wednesday, 24th November

Dr. M.I. Page (Huddersfield Polytechnic), "Large and Small Rate Enhancements of Intramolecular Catalysed Reactions".

Wednesday, 8th December

Professor A.J. Leadbetter (University of Exeter), "Liquid Crystals".

Wednesday, 26th January

Dr. A. Davis (ERDR), "The Weathering of Polymeric Materials".

Wednesday, 2nd February

Dr. M. Falk, (NRC Canada), "Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases".

Wednesday, 9th February

Professor R.O.C. Norman (U. of York), "Radical Cations; Intermediates in Organic Reactions".

Wednesday, 23rd February

Dr. G. Harris (U. of St. Andrews), "Halogen Adducts of Phosphines and Arsines".

Friday, 25th February

Professor H.T. Dieck (Frankfurt U.), "Diazadienes - New Powerful Low-Valent Metal Ligands".

Wednesday, 2nd March

Dr. F. Hibbert (Birkbeck College, London), "Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids".

Friday, 4th March

Dr. G. Brink (Rhodes U., R.S.A.), "Dielectric Studies of Hydrogen Bonding in Alcohols".

Wednesday, 9th March

Dr. I.O. Sutherland (Sheffield U.), "The Stevens' Rearrangement: Orbital Symmetry and Radical Pairs".

Friday, 18th March

Professor Hans Bock (Frankfurt U.), "Photoelectron Spectra and Molecular Properties: A Vademecum for the Chemist".

Wednesday, 30th March

Dr. J.R. MacCallum (U. of St. Andrews), "Photooxidation of Polymers".

Wednesday 20th April

Dr. D.M.J. Lilley (G.D. Searle, Research Div.), "Tails of Chromatin Structure - Progress towards a Working Model".

Wednesday, 27th April

Dr. M.P. Stevens (Univ. of Hartford), "Photocycloaddition Polymerisation".

Wednesday, 4th May

Dr. G.C. Tabisz (Univ. of Manitoba), "Collision Induced Light Scattering by Compressed Molecular Gases".

Wednesday, 11th May

Dr. R.E. Banks (UMIST), "The Reaction of Hexafluoropropene with Heterocyclic N-Oxides".

Wednesday, 18th May

Dr. J. Atwood (Univ. of Alabama), "Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates".

Wednesday, 25th May

Professor M.M. Kreevoy (Univ. of Minnesota), "The Dynamics of Proton Transfer in Solution".

Wednesday, 1st June

Dr. J. McCleverty (Univ. of Sheffield), "Consequences of Deprivation and Overcrowding on the Chemistry of Molybdenum and Tungsten".

Wednesday, 6th July

Professor J. Passmore (Univ. of Brunswick), "Adducts Between Group V Pentahalides and a Postscript on S_7I^+ ".

b) Durham University Chemical Society

Tuesday, 19th October

Dr. J.A. Salthouse (Univ. of Manchester), "Chemistry and Energy".

Tuesday, 26th October

Dr. R.E. Richards (Univ. of Oxford), "NMR Measurements on Intact Biological Tissue".

Tuesday, 2nd November

Dr. B. Sutcliffe (Univ. of York), "The Chemical Bond as a Figment of the Imagination".

Tuesday, 16th November

Mr. R. Ficken (Rohm & Haas), "The Graduate in Industry".

Tuesday, 30th November

Dr. R.J. Donovan (Univ. of Edinburgh), "The Chemistry of the Atmosphere".

Tuesday, 16th January

Professor I. Fells (Univ. of Newcastle), "Energy Storage: the Chemists' Contribution to the Problem".

Tuesday, 8th February

Dr. M.J. Cleare (Johnson Matthey Research Centre), "Platinum Group Metal Compounds as Anti-Cancer Agents".

Tuesday, 1st March

Professor J.A.S. Smith (Q.E. College, London), "Double Resonance".

Tuesday, 8th March

Professor C. Eaborn (Univ. of Sussex), "Structure and Reactivity".

1.2 1977-78

a) University of Durham Chemistry Colloquia

Tuesday, 27th September

Dr. T.J. Broxton (La Trobe Univ. Australia), "Interaction of Aryldiazonium Salts and Arylazoalkyl Ethers in Basic Alcoholic Solvents".

Wednesday, 19th October

Dr. B. Heyn (Univ. of Jena, D.D.R.), " σ -Organo-Molybdenum Complexes as Alkene Polymerisation Catalysts".

Thursday, 27th October

Professor R.A. Filler (Illinois Inst. of Technology, U.S.A.), "Reactions of Organic Compounds with Xenon Fluorides".

Wednesday, 2nd November

Dr. N. Boden (Univ. of Leeds), "NMR Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin- $\frac{1}{2}$ Pairs".

Wednesday, 9th November

Dr. A.R. Butler (Univ. of St. Andrews), "Why I lost Faith in Linear Free Energy Relationships".

Wednesday, 7th December

Dr. P.A. Madden (Univ. of Cambridge), "Raman Studies of Molecular Motions in Liquids".

Wednesday, 14th December

Dr. R.O. Gould (Univ. of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry".

Wednesday, 25th January

Dr. G. Richards, (Univ. of Oxford), "Quantum Pharmacology".

Wednesday 1st February, 2.30 p.m.

Professor K.J. Ivin (Queens University, Belfast), "The olefin metathesis reaction: mechanism of ring-opening polymerisation of cycloalkenes".

Friday 3rd February

Dr A. Hartog (Free University, Amsterdam, Holland), "Surprising recent Studies in Organo-magnesium Chemistry".

Wednesday 22 February

Professor J.D. Birchall (Mond Division, I.C.I. Ltd.), "Silicon in the Biosphere".

Wednesday 1st March

Dr A. Williams (University of Kent), "Acyl Group Transfer Reactions".

Friday 3rd March

Dr G. van Koten (University of Amsterdam, Holland), "Structure and Reactivity of Arylkopper Cluster Compounds".

Wednesday 15 March

Professor G. Scott (University of Aston), "Fashioning Plastics to match the Environment".

Wednesday 22 March

Professor H. Vahrenkamp (University of Freiburg, Germany), "Metal-Metal Bonds in Organometallic Complexes".

Wednesday 19 April

Dr M. Barber (UMIST), "Secondary Ion Mass Spectra of Surfaces and Adsorbed Species".

Tuesday 16th May

Dr P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Adsorbed Species on Metals".

Thursday 18th May

Professor M. Gordon (University of Essex), "Three Critical Points in Polymer Science".

Monday 22nd May

Professor D. Tuck (University of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds".

Wednesday - Thursday 24th, 25th May

Professor P. von R. Schleyer (University of Erlangen, Nürnberg),

I. "Planar Tetra-co-ordinate Methanes, Perpendicular Ethylenes, and Planar Allenes".

II. "Aromaticity in Three Dimensions".

III. "Non-classical Carbocations".

Wednesday 21st June

Dr S.K. Tyrlik (Academy of Science, Warsaw), "Dimethylglyoxime-cobalt Complexes - Catalytic Black Boxes".

Friday 23rd June

Professor W.B. Pearson (University of Florida), "Diode Laser Spectroscopy at 16 μm ".

Friday 30th June

Professor G. Mateescu (Cape Western Reserve University),

"A Concerted Spectroscopy Approach to the Characterization of Ions and Ion Pairs : Facts, Plans, and Dreams".

(b) Durham University Chemical Society

Thursday 13th October

Dr J. C. Young, Mr A.J.S. Williams (University of Aberystwyth),

"Experiments and Considerations Touching Colour".

Thursday 20th October

Dr R.L. Williams (Metropolitan Police Forensic Science Dept.),

"Science and Crime".

Thursday 3rd November

Dr G.W. Gray (University of Hull), "Liquid Crystals - Their Origins and Applications".

Thursday 24th November

Mr G. Russell (Alcan), "Designing for Social Acceptability".

Thursday 1st December

Dr B.F.G. Johnson (University of Cambridge), "Chemistry of Binary Metal Carbonyls".

Thursday 2nd February

Professor R.A. Raphael (University of Cambridge), "Bizarre Reactions of Acetylenic Compounds".

Thursday 16th February

Professor G.W.A. Fowles (University of Reading), "Home Winemaking".

Thursday 2nd March

Professor M.W. Roberts (University of Bradford), "The Discovery of Molecular Events at Solid Surfaces".

Thursday 9th March

Professor H. Suschitzky (University of Salford), "Fruitful Fissions of Benzofuroxans".

Thursday 4th May

Professor J. Chatt (University of Sussex), "Reactions of Co-ordinated Dinitrogen".

Tuesday 9th May

Professor G.A. Olah (Case Western Reserve University, Cleveland, Ohio), "Electrophilic Reactions of Hydrocarbons".

