

VIBRATIONAL SPECTROSCOPY AT HIGH PRESSURES

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TO

KATE

UNITS

We all deplore, or at least it is to be hoped we do, the use of non S.I. units. Whilst we are all aware of the existence of such a precise system, familiarity with other related units often leads us to use these in preference. For this reason all non S.I. units used in this thesis are given below with their S.I. equivalent.

1 kbar	=	10^8 Pa	
1 megabar	=	10^{12} Pa	
1 p.s.i.	=	$6.98 \times 10^3 \text{ N m}^{-2}$	
θ_c	=	$T - 273.15 \text{ K}$	(T = temperature K, θ_c = temperature celsius)
1 Å	=	10^{-10} m	
1 in.	=	$2.54 \times 10^{-2} \text{ m}$	

CONTENTS

Page

CHAPTER 1	An Introduction to the Vibrational Spectroscopy of Solids at High Pressures	1.
CHAPTER 2	A Discussion of the Operation of a Diamond Anvil Cell and the Development of Ancillary Equipment	27.
CHAPTER 3	Use of Ruby R Lines in the Estimation of Pressure at Ambient and at Low Temperature	72.
CHAPTER 4	The Diamond Anvil Cell : History, Analysis and Design	98.
CHAPTER 5	A Study of the HgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) Systems Under High Pressure and Various Temperatures	162.
CHAPTER 6	The Vibrational Spectroscopy of Three Solid Phases of Benzene	242.
CHAPTER 7	A Study of the X-ray Diffraction, Far-i.r., and Raman Spectra of CsNiCl_3 at Various Temperatures and High Pressure	270.

CHAPTER 1

AN INTRODUCTION TO THE VIBRATIONAL
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1.1 Introduction

The use of high pressures by chemists and physicists is now well established although the field is still expanding. In the area of vibrational spectroscopy better cell designs and good coupling to sensitive spectrometers have produced an increased interest in this type of work. This chapter is intended as an introduction to the various types of high pressure devices available for studying the vibrational spectra of solids at high pressures. A fairly complete set of references to both equipment and spectroscopic data is given. The literature up to May, 1975, is covered by four excellent reviews (Ferraro 1971, Adams and Payne 1972, Ferraro and Basile 1974, and Payne 1975). There is also an excellent catalogue of high pressure work from 1900 to 1977 covering author and subject indices; this is edited by L. Merrill and can be obtained from "The High Pressure Data Centre, Brigham Young University, Provo, Utah". References in this chapter will be concerned mainly with work in the period May 1975 to May 1977. They have been compiled by following Chemical Abstracts. This review of the literature is mainly concerned with high pressure vibrational spectroscopy but several references to X-ray work are also given because very often, when interpreting vibrational

spectra of solids, the first thing that is done is to obtain some information about the structure. Therefore X-rays and vibrational spectroscopy are really two techniques that should be used together in interpreting high pressure work.

1.2 Equipment

Broadly speaking there are three classes of high pressure cell suitable for vibrational spectroscopy; hydrostatic cells, diamond anvil cells and Drickamer cells.

Hydrostatic Cells

In this type of cell the sample is simply immersed in a gas or liquid and the pressure applied by compression of this medium. Maximum pressures reported are ca. 8 to 15 kbar using sapphire windows. These restrict the wavelengths to above 2000 cm^{-1} in the i.r. and are compatible with Raman use at room temperature. Fondere, Obriat, Marteau and Vu (1975) reported that sapphire windows in fact transmit at low temperatures (4.2 K) in the far-i.r. ($10\text{--}350\text{ cm}^{-1}$). Therefore this particular type of cell lends itself to high pressure low temperature far-i.r. (Johnson and Sievers 1974) or Raman (Wilkinson and Bodenheimer 1975) spectroscopy using a helium pressure transmitting medium. Lowndes (1976) used thick quartz and thick silicon windows in his cell of this type to do room temperature and high pressure (0-7 kbar) far-i.r. spectroscopy. Reports of this type of cell being used in the X-ray experiment, constructed entirely out of beryllium, using kerosine as a pressure transmitting medium, with

4.

temperature variation between 80 and 300 K have been found (Morrison and Schriber 1969, 1972 and 1974). The pressure was limited to less than 4 kbar.

Whilst the hydrostatic type of cell is restricted to moderately low pressures, it is capable of producing results under very hydrostatic conditions and versatile enough to be used in different instruments.

1.3 Diamond Anvil Cell (DAC)

This design allows work up to 250 kbar routinely (Block and Piermarini 1975, Bassett 1967) although pressures of greater than 1 megabar have been claimed (Mao and Bell 1976, Yakovlev 1976). The maximum pressure obtainable at a sample is not necessarily the best indication of the reliability of any one design; what really matters is the force generated, as simply decreasing the area over which any force is applied will increase the pressure at the sample ($P = \frac{F}{A}$). The two opposed anvil faces are between ca. 0.5 mm diameter and 1.2 mm diameter depending on the pressure range desired. They must always be aligned accurately parallel and remain so throughout each pressure cycle. Several variants of the original design of Wier, Lippincott, Van Valkenberg and Bunting (1959) have appeared but many still follow the original. Four ways of applying the force to the cell to provide pressure are known; (i) use of a hydraulic system (Adams, Payne and Martin 1973); (ii) a screw with either a calibrated spring or with spring washers (Piermarini and Bock 1975); (iii) using gas pressure

(Webb, Gubse and Towle 1976); and (iv) using a compact system of levers fitting around the outside of a central insert containing the diamonds (Syassen and Holzapfel 1975); each method offering advantages in particular applications. Diamond anvil cells have also been reported to have been used at temperatures as low as 0.03 K (Webb, Gubse and Towle 1976) with the use of a He dilution refrigerator; and as high as 2,500^oC (Mao and Bell 1976) using laser heating, a quite phenomenal range. The other most important point is the versatility of the DAC; that is, spectra of the same sample under elevated pressure can be recorded on several instruments. Thus we have obtained far-i.r., Raman and mid-i.r. of a sample of benzene at various temperatures and pressures (Adams and Appleby 1977).

Interest in the DAC has increased largely due to the fact that it can be used under conditions in which the sample experiences pressures that are hydrostatic or nearly so. This pressure can be determined accurately by use of the R fluorescence lines of a chip of ruby included with the sample in a metal gasket (with a suitable pressure transmitting medium) (Piermarini 1975, Adams, Appleby and Sharma 1976). A good summary of DAC work was presented by Block and Piermarini (1976) in an article called "The diamond cell stimulates high pressure research".

Raman work with the DAC using a metal gasket and hence a sample under hydrostatic conditions, has become moderately straightforward due to research into efficient coupling to a good spectro-

meter (Adams, Payne and Martin 1973). More recently the use of an ellipsoidal mirror for collecting radiation has made it possible to obtain the Raman spectrum of any material which gives a spectrum in a glass capillary at room pressure (Adams, Sharma and Appleby 1977). Fluorescence of diamond anvils while under laser excitation has been reported (Payne 1975) and a further paper adds still more data to enable the choice of a good diamond anvil for use in Raman spectroscopy (Adams and Sharma 1977a). Reports of variable temperature work with the DAC in a Raman spectrometer are very few, the lowest temperatures being ca. 100 K achieved by circulating liquid nitrogen, and the highest ca. 400 K (Adams and Appleby 1977a). It seems likely however that cooling and heating techniques used in other experiments with the DAC will soon spread to Raman spectroscopy giving a temperature range from close to 0 K up to several thousand degrees.

Mid-i.r. work is still limited to a trickle of reports. With the DAC gasketed in this region the transmission is very low (< 2%) making experiments difficult. A beam condenser with two ellipsoid mirrors and several other elements has been used (Ferraro et al 1966). This is known to be difficult to align. A further solution to the problem was found by Adams and Sharma (1977b) by using a KBr refracting beam condenser incorporating 3 lenses. In this report a detailed study of the optics of a DAC were given. Using conventional spectrophotometers, wide slit programmes and slow scans are necessary for this work and it seems most likely

that the major breakthrough in this work will occur with the use of fourier i.r. machines which have a multiplex advantage over dispersive instruments. Some improvement will also be gained with on-line computing facilities. To date, there are no reports of low temperature work in this region but wire-wound heaters have enabled work at a few hundred degrees centigrade (Adams and Sharma 1976b).

Far-i.r. experiments with a DAC used non-hydrostatically without a gasket in an interferometer have been reported (Ferraro, Mitra and Postumus 1966 and Payne 1975) but no reports of work using a gasketed DAC in an interferometer have been found.

Recently a gasketed DAC was used in a far-i.r. fourier spectrometer at temperatures between 180 K and 450 K and it is hoped to improve this temperature range (Adams and Appleby 1977b). One report of emission studies using the sample as a source in a heated DAC with an FS 720 and gasketed liquid samples has appeared in the literature (Peterkin and Lauer 1975).

High pressure X-ray use of the DAC seems to be increasing very rapidly. The first report came from the "National Bureau of Standards" U.S.A. (Wier and Piermarini 1962). Pressure of 60 kbar, on ungasketed powder samples were achieved. The pressure range was soon extended by Bassett, Takahashi and Stook (1967) to 300 kbar again on ungasketed powder samples. Miniature 'diamond anvil bombs' consisting of two opposed anvils backed by

two stainless steel platens forced together by screws to generate the pressure were known earlier than this (Lawson and Tang 1950, and Jameson 1956). They were able to reach pressures up to 10 kbar on ungasketed powder samples. These were small and easy to use. Merrill and Bassett (1976) also produced a similar device this time using beryllium platens and a gasket to give hydrostatic pressure. This device was used on standard X-ray equipment up to pressures of 40 kbar. Data on single crystals under hydrostatic pressure have been collected by Bassett (1976) using his 'diamond anvil bomb'. Other workers have obtained data by constructing all of the DAC (Mauer, Hubbard, Piermarini and Block 1975) or part of it (Renäud et al 1971) from beryllium or boron carbide, both being transparent to X-rays.

Temperature variation from liquid helium (Endo and Mitsui 1976) up to 1000°C (Sung 1976) using DACs has been reported. A DAC has also been used in a novel application for measuring strain and strength of materials by firing an X-ray beam normal to the

loading axis and examining the diffraction cones up to pressures of 300 kbar: of course, no gaskets are used (Kinsland and Bassett 1976).

1.4 Drickamer Cells

This type of cell was developed by Drickamer (1957) and is nominally a hydrostatic cell but with one difference; the pressure transmitting medium is solid NaCl. This is compressed

by tungsten carbide rams and extrudes throughout the cell giving pseudo-hydrostatic conditions. This cell has been up to 200 kbar, and temperatures of 500°C (Sherman 1966); also liquid helium temperatures have been reached (Lewis and Sherman 1974). Since NaCl is the pressure medium, i.r. spectroscopy is limited to the region above 400 cm⁻¹ but the cell has been used successfully in Raman spectroscopy (Nicol, Ebisuzaki, Ellenson and Karim 1972); visual and electronic measurements (Drickamer 1961, 1973); luminescence measurements (Drickamer and Wilson 1975); and also other types of spectroscopy.

Development of equipment in the various fields examined above has progressed quickly, but few papers appear to explain the theories behind the various observations. Lattice dynamics of structural phase transitions were examined by Cochran (1972) and the applications of the functional approach to bond variations under pressure was discussed by Gutmann and Mayer (1976). The frequency shift of vibrational modes with temperature and pressure of ionic crystals were linked to anharmonicity (Lowndes and Rastogi 1976). Wong (1975) also performed similar calculations on a molecular crystal.

Phase transitions induced by pressure have been studied since the work of Bridgman (1968) and the subject has been reviewed exhaustively by Pistorius (1976) who gives over 1000 references.

This work will provide a valuable source of information for anyone interested in high pressure work, particularly phase transitions.

1.5 Studies of Vibrational Spectra and X-ray Diffraction at High Pressures

There are a number of reasons for interest in high pressure X-ray and vibrational spectroscopy. The first and foremost is to study phases not stable under ambient conditions. Interest by geochemists is growing in this area as they try to simulate conditions within the earth (Mao and Bell 1976). A second reason is that, studying the behaviour of vibrational frequencies of a solid under pressure can help to give a better understanding of the ambient spectrum as vibrations of different symmetries often shift at different rates with applied pressure. A third reason is to try and provide answers to the questions; why do phase transitions occur under pressure and why is one structure preferred to another?

Reports of work appearing in the literature of interest in this area are summarised below. Four sections are considered; organic molecular systems, inorganic molecular systems, complex inorganic systems, and lattice compounds.

Organic Molecular Systems

The phase transitions occurring in organic polymers such as polyethylene were first observed visually using a DAC (Van

Valkenberg and Powers 1963). More recently, Bassett, Block and Piermarini (1974) examined the high pressure phase using X-rays and reported the unit cell dimensions. Wu (1974) also reported the pressure and temperature dependence of the vibrational frequencies of crystalline polymethylenes.

Polymorphism in aromatic systems has been studied. Raman, i.r., and far-i.r. spectra of three phases of benzene (Appleby and Adams 1977) plus a high pressure single crystal study on Phase II by Block, Wier and Piermarini (1970) have been reported. They also reported similar studies on high pressure phases of naphthalene and anthracene. Nicol (1975) also studied the effect of pressure on defect fluorescence in these systems up to 40 kbar from 30 to 450 K. The derivatives of benzene have received attention, hexamethylbenzene being investigated by Raman spectroscopy to 8 kbars and between 100 K and 400 K and a new high pressure phase being characterised (Bodenheimer and Wilkinson 1975). A similar Raman investigation into the different phases of *p*-dichlorobenzene under pressure has also been published (Figuiere and Swarc 1974). A qualitative investigation into the phase diagrams of 8 other benzene derivatives using i.r. spectroscopy was reported by Hamman (1976a). Wier, Piermarini and Block (1969) reported single crystal high pressure data for CS₂, Br₂, CCl₄ giving the space group of three high pressure phases of CCl₄. Adams and Sharma (1976a) thoroughly investigated the

polymorphs of CCl_4 and CBr_4 by Raman spectroscopy also producing spectra of their photo decomposition products under pressure.

The influence of pressure on the infrared spectra of hydrogen bonded solids has been reported up to 40 kbars by Hamman (1976, 1977b). Organic molecular H bonded solids and inorganic hydrogen bonded ions such as FHF^- in the solid salt NaHF_2 have been studied. Phase transitions were discovered and explanations advanced for the various shifts.

Inorganic Molecular Systems

Hydrogen has been solidified at low temperature and studied up to high pressures. Raman spectra have been reported up to 9 kbar at 4 K (Thiery and Fabre 1974, Deirana and McTague 1973) and it was also shown that a phase transition to a superconducting form occurred above 1 megabar at 4 K. (Yakovlev 1976). Another gas frozen at 85 K and studied under pressure this time with X-rays is Xe. The gas was frozen into a small hole in the flat of one of the diamonds of a DAC and a gasket placed over it. As pressure was applied the gasket flowed into the hole compressing the solid. Pressures up to 110 kbar are reported; (Holzapfel and Syassen 1975) and the possibility of a transition to a metallic state was discussed. The mercuric halides have been examined by far-i.r. and Raman spectroscopy. All the phases of HgCl_2 (Adams

and Appleby 1977c) and HgBr_2 (Adams and Appleby 1977d) up to 40 kbar were characterised vibrationally, the highest pressure phase of HgCl_2 adopting the CO_2 structure but the highest pressure phase of HgBr_2 , the CdI_2 structure, or some polytype of it. The yellow phase of HgI_2 found at RT and above 13 kbar which had previously been reported as continuous was found to be two different phases (Adams and Appleby 1977e). A phase stable above 75 kbar was shown by X-ray (Mickler 1972) to have a structure belonging to one of the polytype of CdI_2 .

Peercy, Samara and Morrison (1975) reported the pressure and temperature dependencies of the dielectric constant, Raman spectrum and lattice constants of SnI_4 from 0-300 K and 0-4 kbar. Their results were analysed and anharmonicity discussed. A similar analysis and set of results was reported by Wong (1975) on dichloro-bis(pyridine) zinc II.

Water, or more correctly, ice has been studied under high pressure and slowly the vibrational spectra of this complicated system are being characterised. Raman studies have identified phases VI, VII and VIII (Adams, Sharma and Appleby 1977, Whalley 1975, Wong and Whalley 1976, and Holzappel 1974).

Finally in this section attention is drawn to a large amount of work taking place on semiconductors at high pressure, one such study being the Raman spectra of Si and GaP using a DAC reported by Weinstein and Piermarini (1975).

Complex Ionic Systems

Hexahalogen compounds have been studied under high pressure and recent reports include MTeX_6 , MSeX_6 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) up to 30 kbar by far-i.r. spectroscopy (Adams, Findlay, Coles and Payne 1976), and studies of the phase diagram of KAsF_6 and KSbF_6 by Heynes and Pistorius (1975, 1976), several high pressure phases being reported. The Raman spectrum of PbTiO_3 up to 80 kbar was reported by Cerdeira, Holzapfel and Baverle (1975) and showed a ferroelectric to paraelectric transition.

Crystallographic data at high pressures has also been collected for CsClO_4 , CsBF_4 , (Whalley and Pistorius 1976), $(\text{MeNH}_3)_2\text{CdCl}_4$ (Clapius, Hind and Arend 1976), KMnF_3 SrTiO_3 (Okai and Juchiro 1975), CsZF_3 ($\text{Z} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Mg}$) (Longo and Kafkas 1969, 1970), and $\text{K}_4[\text{Fe}(\text{CN})_6]_3$ (Hara and Minamura 1974). Phase transitions were reported for all but the latter.

CsNiCl_3 was also examined by far-i.r., Raman and X-ray techniques under hydrostatic pressure and temperatures down to 12 K (Chapter 7). The data are discussed in terms of anharmonicity.

Lattice Compounds

High pressure X-ray work on simple lattice compounds, halides and oxides is summarised by Drickamer, Lynch, Clenden, and Albuerne (1966), 28 materials being reported in all. Lowndes (1976) reported vibrational and X-ray data up to ca. 15 kbar on

the alkali and heavy metal halides, giving Grüneisen parameters and a full analysis of the vibrational shifts with T and P. Mamola and Wu (1976) reported the effect of pressure on F centres in RbCl and Nicol (1976) the dependence of impurity induced Raman spectra of KI under pressure up to 30 kbar and temperatures down to 80 K. AgI has been studied extensively, five phases being identified by Raman spectroscopy (Hanson, Fjeldy and Hocheimer 1975). X-ray diffraction and optical methods were also used (Bassett and Takahishi 1965) up to a pressure of 100 kbar and temperature of 200°C. Hocheimer et al (1976) were also responsible for reporting the Raman spectra of the high pressure phases of the copper halides.

The phase diagrams of ZnBr_2 , Tl_2CO_3 , have been investigated up to 80 kbar by X-ray methods and the structure of the high pressure phase determined. (Meisalo and Kalliomaki 1975, 1976) A single crystal of calcite II was formed in a DAC then X-ray diffraction carried out and the crystal structure solved (Merrill and Bassett 1975). Raman i.r. and Brillouin scattering (Peercy and Fritz 1974, 1975) were reported for TeO_2 a second order phase transition being observed. The X-ray diffraction pattern up to 90 kbar has also been reported (Skelton 1975).

Single crystal X-ray data collected on azides (Pb, Ba, K, Na, Tl) gave their anisotropic compressibilities and also proved the DAC to be a useful means of obtaining data on small and/or explosive crystals (Wier, Block, Piermarini 1970). The

Raman study of TiN_3 showed that the transition which occurred at pressure was triggered by the coupling of two vibrational modes of the same symmetry (Cristoe and Igbal 1974). In a similar study on CsN_3 new phases were reported by Cristol and Igbal (1975).

A series of papers by Adams and Sharma (1975, 1976) confirm the i.r. of all the phases of the KNO_3 , NaNO_3 , NH_4NO_3 , KNO_2 , NaNO_2 below 40 kbar and Sherman and Wilkinson (1976) report a Raman study of KNO_3 from 0-10 kbar and 77-600 K. The high pressure phases of the ammonium halides have also been well characterised by Raman spectroscopy. Shand and Hocheimer (1976) studied the chloride and iodide, whilst the bromide has been studied by Geisel and Hocheimer (1976), and Ebisuzaki (1975, 1976).

Summary

There are many reports in the literature on the different aspects of high pressure work; that is, study of phase diagrams and attempting to solve the different structures and the study of the effect of pressure on the vibrational spectrum as such. Only a few of these use i.r., Raman and X-ray data which history has shown are the only sure ways to be certain about the vibrational spectrum.

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CHAPTER 2

A DISCUSSION OF THE OPERATION OF A DIAMOND ANVIL CELL AND THE DEVELOPMENT OF ANCILLARY EQUIPMENT

CHAPTER 2

A DISCUSSION OF THE OPERATION OF A DIAMOND ANVIL CELL AND THE DEVELOPMENT OF ANCILLARY EQUIPMENT

2.1 Introduction

The ability to obtain spectra of solids at elevated pressures is now becoming a standard technique and the subject has been reviewed recently (Ferraro 1971, Adams and Payne 1972). In this chapter the technique of loading and using the 'Diamond Anvil Cell', (DAC) (Figure 2:1) and also the coupling of it with various spectrometers are discussed. When working with sample volumes of less than 20 ml and a cell with transmission of less than 10% (Adams and Sharma 1977), the success of the cell is determined by correct operation of it and good coupling to the spectrometer being used. Other development work carried out on pieces of equipment used to obtain the results in this thesis is also summarised.

2.2 Operation of the DAC

After manufacturing a DAC the first problem is to select diamond anvils, which will be suitable for high pressure vibrational spectroscopy, to use in this cell. This problem is discussed more fully by Adams and Payne (1974) and Adams and Sharma (1976). Briefly, the criteria are that the anvil should be mechanically sound (discussed further in Chapter 3), and should be of Type II a or b. For vibrational spectroscopy these are most useful as

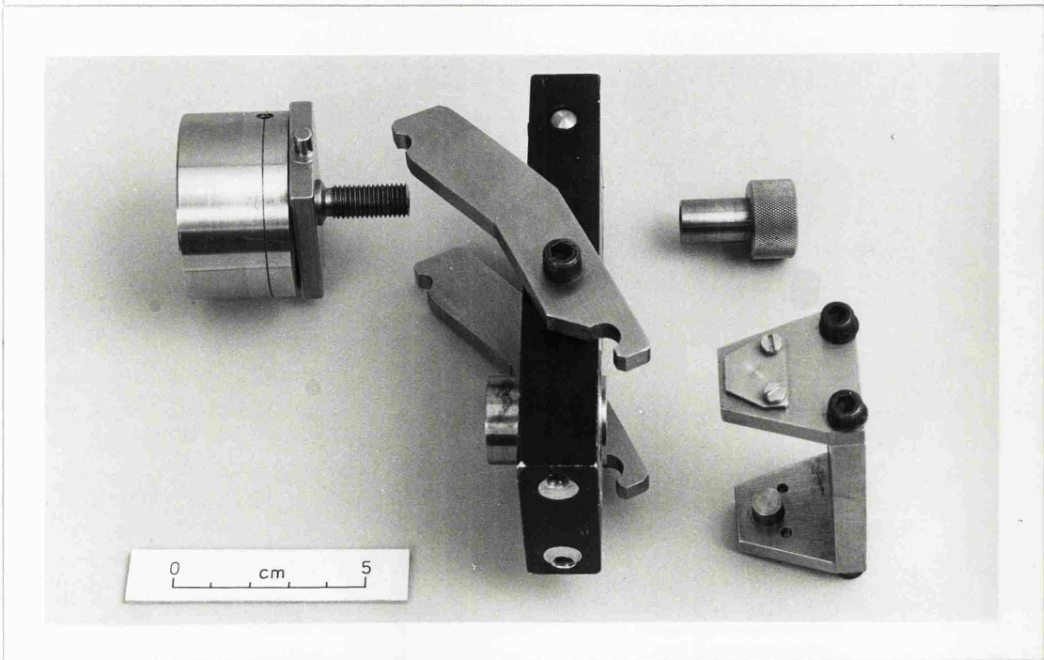
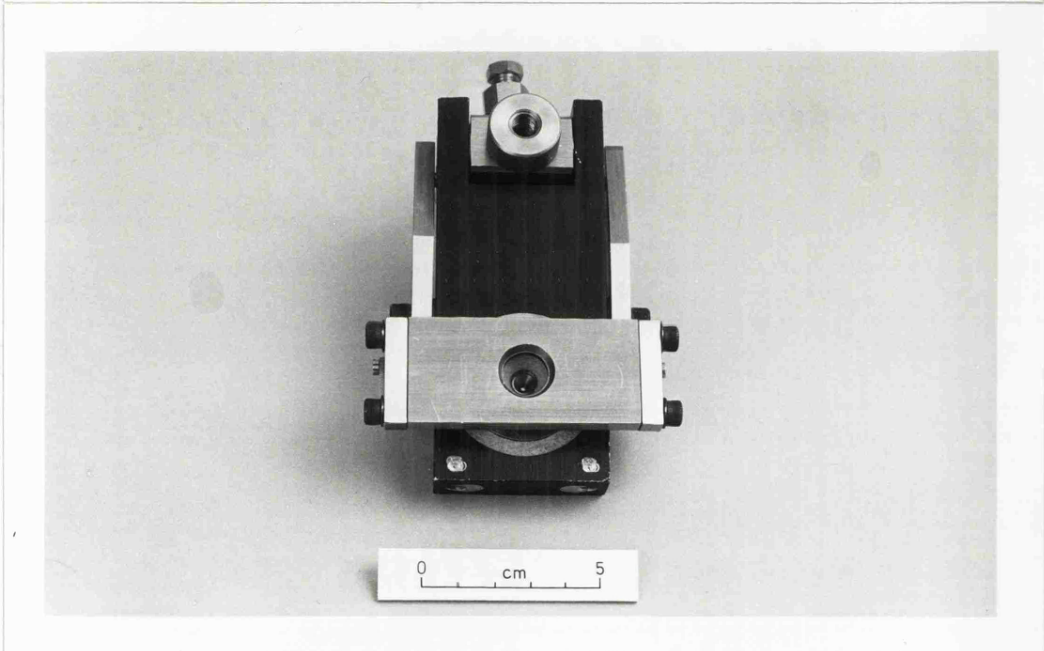
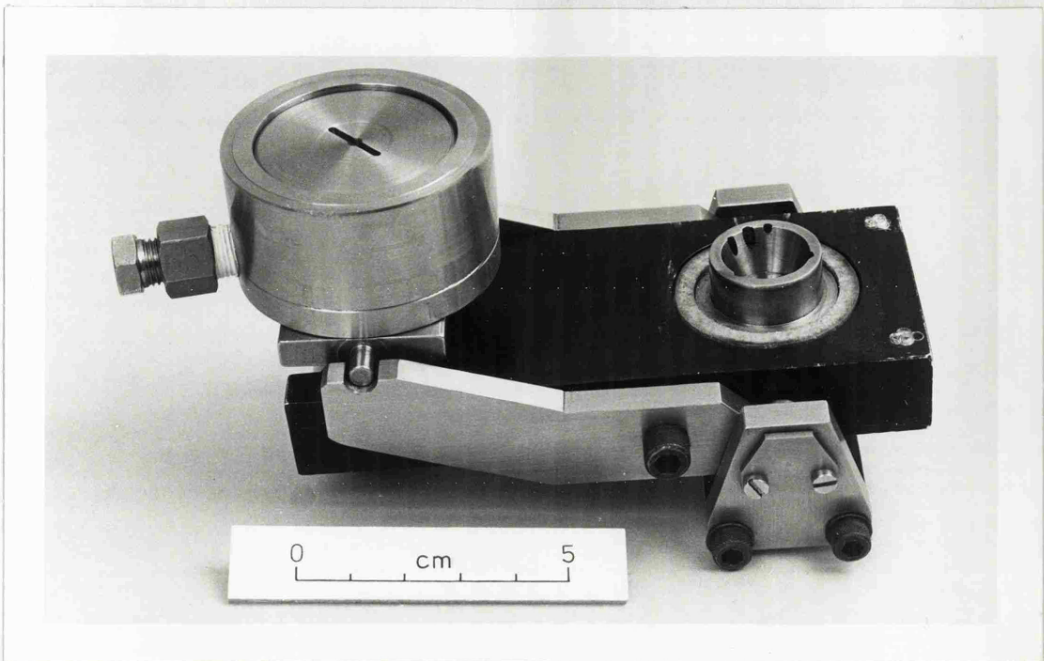
FIGURE 2:1

Pictures of the diamond anvil cell,
showing

(Top) Assembled cell side view

(Middle) Assembled cell front view

(Bottom) Exploded view of cell



type IIb has low fluorescence (of particular importance in the Raman experiment) but absorbs strongly in the mid-i.r. above 1800 cm^{-1} whilst type IIa is more transparent in the mid-i.r. but shows more fluorescence under the conditions used in Raman spectroscopy.

Having selected two suitable anvils they must be mounted in the DAC. All diamond anvils are mounted onto an optically flat surface of an anvil holder, figure 2:2, usually made of (EN58) stainless steel. This is done using a microscope. Of particular value was a non-inverting binocular microscope produced by Vickers; M69 (Supplied by James Swift and Son Ltd., Basingstoke). With this microscope a locating ring is mounted onto the anvil holder using araldite (slow setting). After this has set, the diamond is placed inside the locating ring and carefully bonded to it with the same adhesive. Care must be taken to avoid getting araldite under the diamond anvil. The accurate alignment of the anvil over the hole in the anvil holder is completed using a microscope, with 90° incident viewing. This mounting sequence is shown pictorially in figure 2:2. Two diamonds are mounted in this fashion being particularly careful that the centres of the faces which make contact are coincident. One should now be able to observe Newton's fringes where the two diamonds are touching. On adjustment of the cell to obtain parallel diamond faces one should be able to make the fringes pass around the circumferences of the two diamond faces in contact,

FIGURE 2:2

(Top left)

A diamond anvil holder without a diamond showing the optically flat groove onto which the diamond is mounted.

(Top right)

A diamond anvil holder with the locating ring in position ready for adhesive to secure it to the anvil.

(Middle left)

A diamond anvil holder with a mounted diamond ready for use.

(Middle right)

(i) A gasket.

(ii) A beryllium insert.

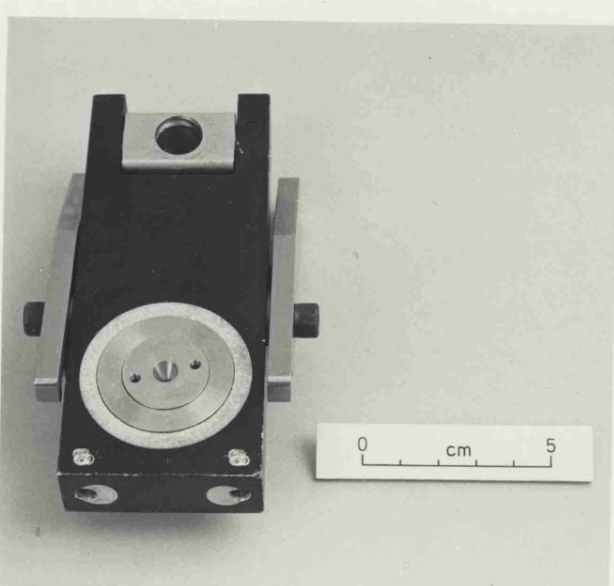
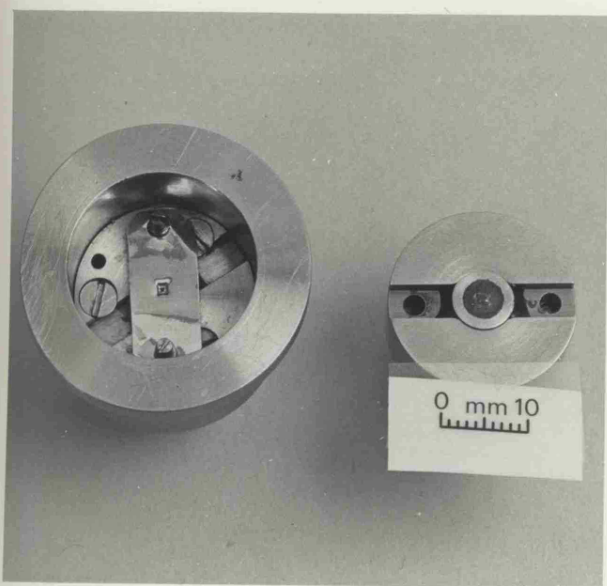
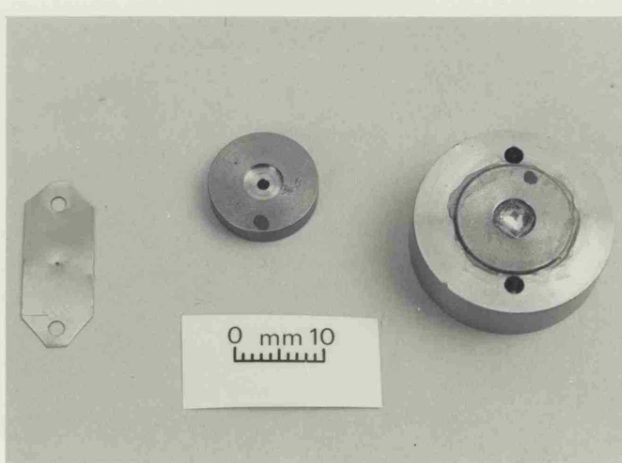
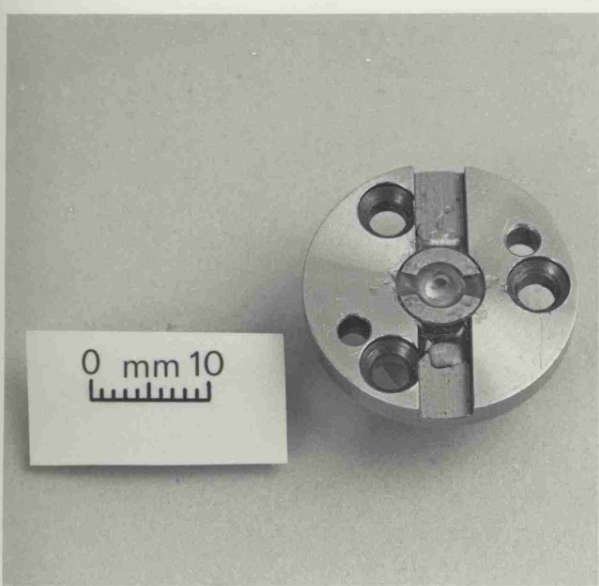
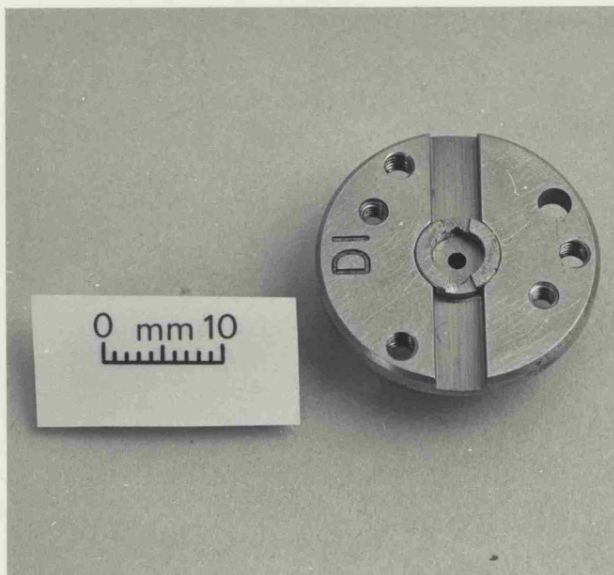
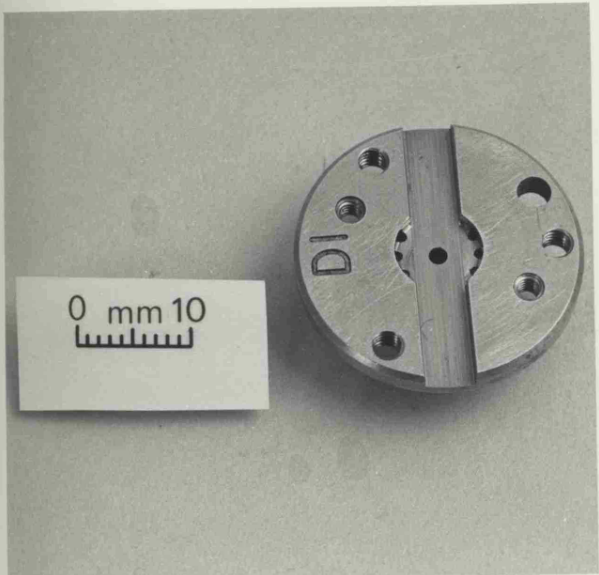
(iii) A beryllium insert mounted in a modified moving anvil holder.

(Bottom left)

A gasket in position over the fixed anvil ready for the moving anvil holder to be inserted.

(Bottom right)

Central insert in cell body ready for final assembly; see figure 2:1.



with equal intensity on all sides, by applying hard pressure on the moving anvil holder. A photomicrograph of Newton's fringes observed in our DAC is shown in figure 2:3. Having achieved this state of parallelism we must test the assembled cell under pressure. The most satisfactory method is considered to be observation of a low pressure phase transition under the microscope. If the transition occurs in the centre of the diamond anvil faces (figure 2:3b) we are sure that they are aligned and will remain so under pressure. If the transition does not take place in the centre of the diamond anvil face (Figure 2:3c) the cell must be realigned. This test was usually performed by placing finely ground HgI_2 between the diamond anvils and observing the red to yellow transition (figure 2:3) at ca. 13 kbar. Alignment of the diamond anvils was checked after each high pressure experiment by microscopic observation of the fringes. The cell is now ready for use in a mode described as "ungasketed". This simply means the material under observation is placed directly onto the diamond as described in testing the cell. The obvious problem of using the cell without a gasket is that the pressure across the diamond anvil face will be non-hydrostatic. (Duecker and Lippincott 1966). This is particularly tiresome in vibrational spectroscopy because as seen in figure 2:4, spectra of high pressure samples often show peaks due to the sample at zero pressure and probably a distribution of other pressures. This can cause immense problems during interpretation. This pressure gradient can be removed by using a thin metal sheet of molybdenum or inconel between the diamonds (0.05-0.2 mm thick) with a central hole of 0.4 mm.

FIGURE 2:3

Various photomicrographs taken using a "Wild" microscope M21 with "Wild" photographic accessories. Colour film (Kodak Photomicraph Film PCF 135) and black and white film (Kodak Paratomic X) was used.

(Top) Newton fringes

(Middle) Transition of red HgI_2 to yellow HgI_2 at 13 kbar taking place in the centre.

(Bottom) Transition of TlBr at ca. 7 kbar taking place off centre in a cell which is out of alignment.

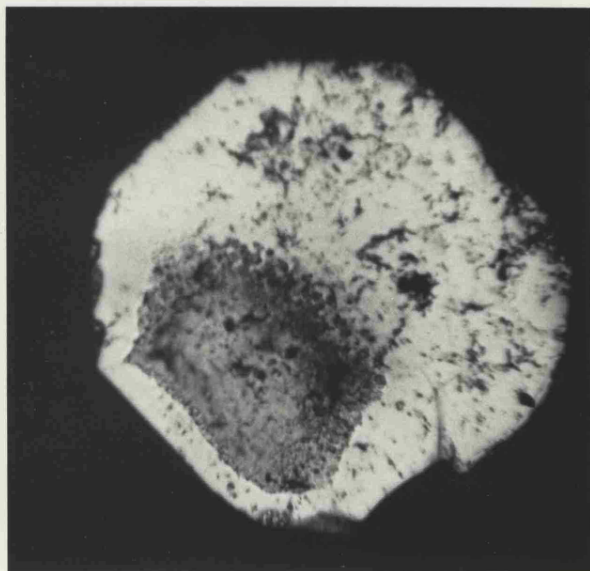
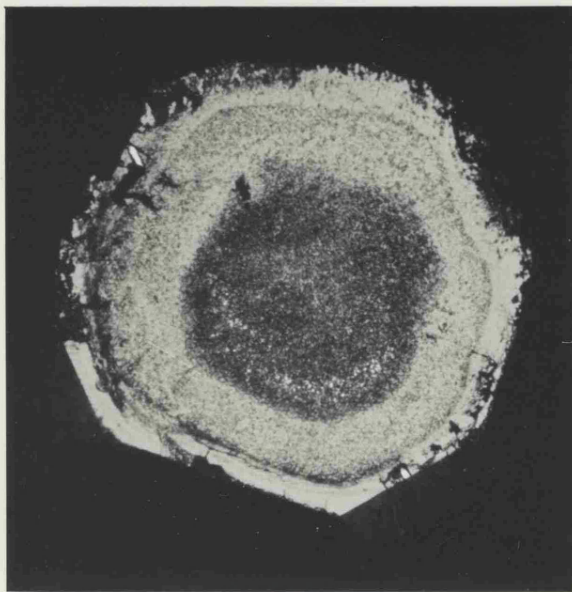
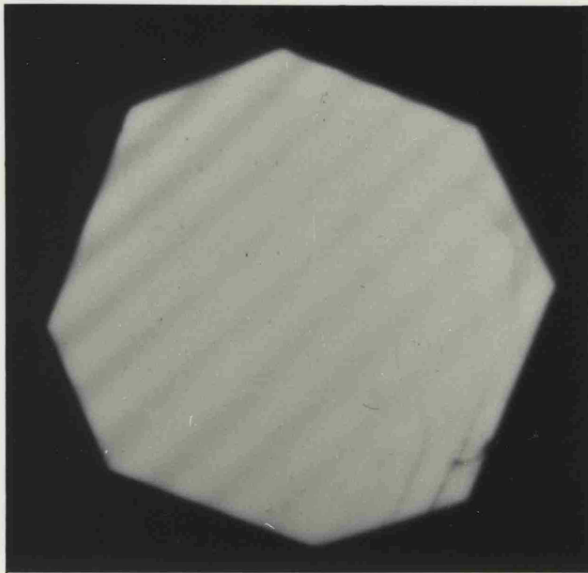
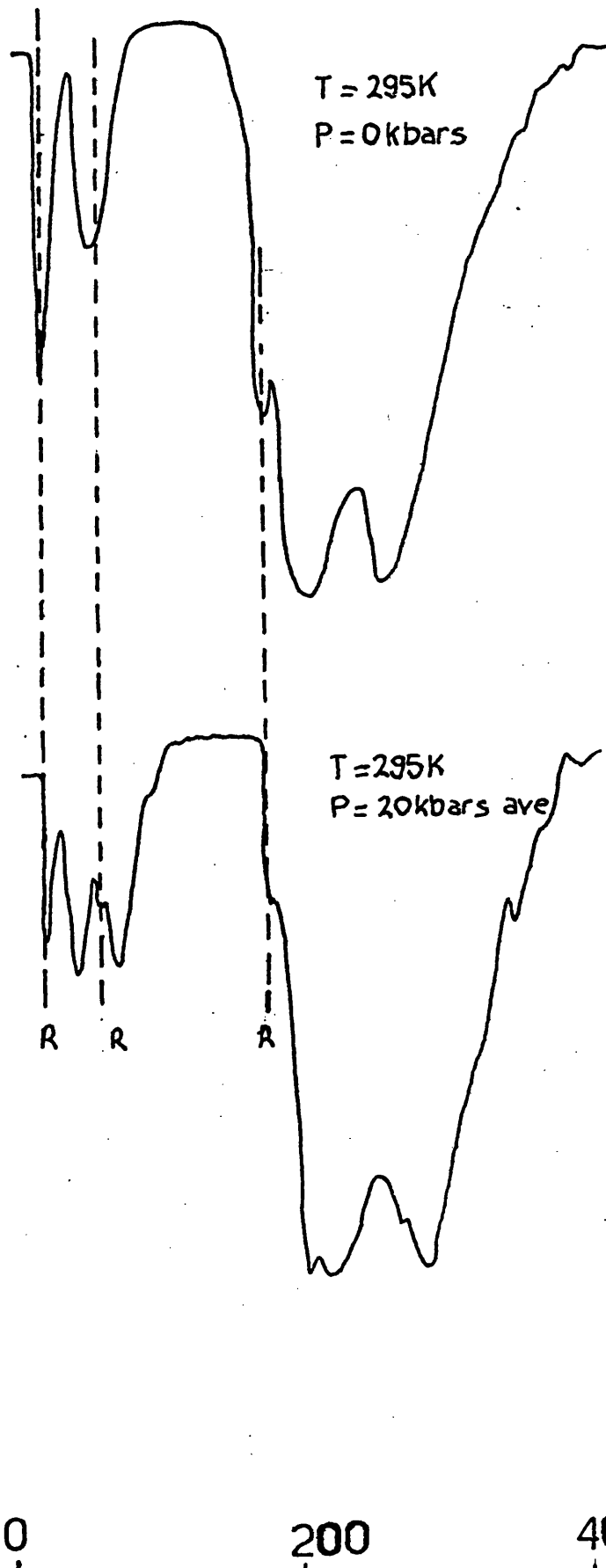


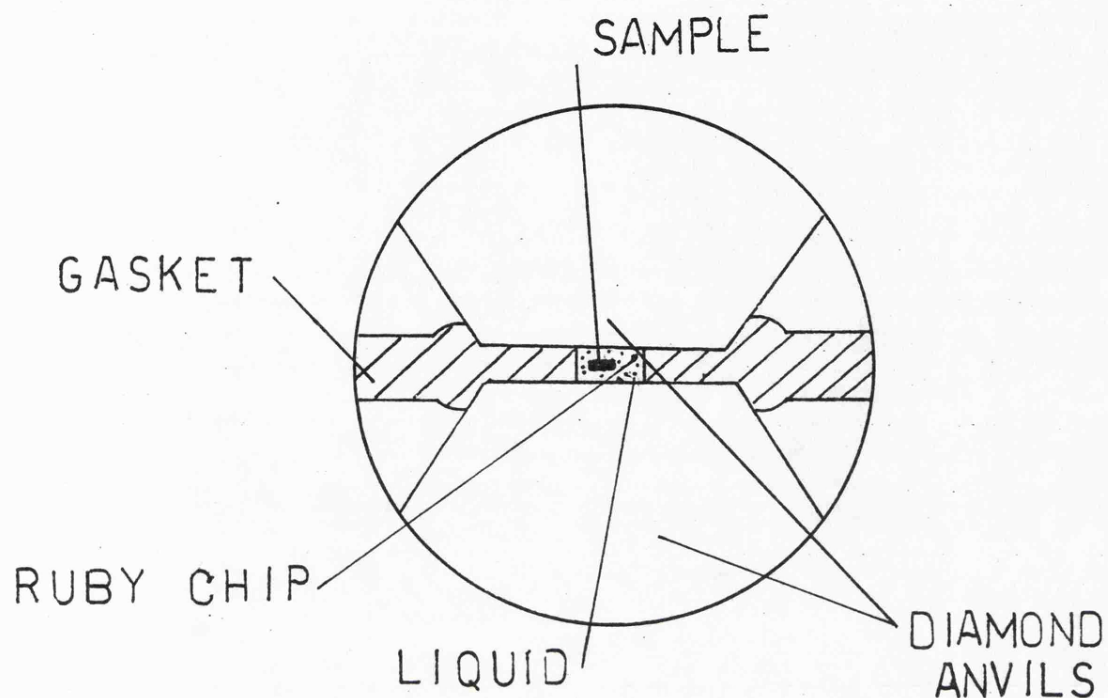
FIGURE 2:4

Far-i.r. spectrum of CsNiCl_3 .

In the high pressure spectrum bands labelled R can be seen. These are due to non-pressurised material and correspond directly to the room pressure spectrum.

CsNiCl_3 Far I.R.

This is a gasket. The hole in the gasket and the two opposed diamond anvil faces form a cylinder which could be described as the sample compartment. Gaskets are prepared by first manufacturing a small piece of metal with holes to match the locating pins in the cell. Two locating pins are used to preserve alignment of the gasket if it is removed and replaced for any reason. A gasket is shown in figure 2:2. This gasket is then placed over the fixed anvil, the moving anvil holder placed over it and the cell assembled (figure 2:2) and approximately 100 p.s.i. applied to the hydraulic system, indenting the gasket. The indented gasket is then removed, and the indentation is centre punched, observing it through a small magnifying eye piece. Finally a 0.4 mm hole is drilled using a small hand drill and jig and all the burs removed. In practice, 20 or more gaskets were prepared at a time. The cylindrical sample compartment created by use of a gasket is loaded under the binocular microscope as follows: the gasket is placed over the fixed anvil and a drop of liquid, (typically 4:1 ethanol:methanol) placed in the hole. Then, using a needle, some of the finely ground sample under investigation is placed in the liquid, and finally, a chip of ruby is put in the hole. The ruby acts as a pressure sensor (see Chapter 4 where this is discussed more fully). The cylindrical sample compartment is then sealed with the fixed anvil. This is shown diagrammatically below. A small amount of pressure is applied to keep the sample in position, ca. 60 p.s.i.



The DAC is now ready for use. Having loaded the DAC an outline of the methods used to obtain mid-i.r., far-i.r., Raman spectra, X-ray information and u.v. spectra are described below. It is important to note that in every experiment the DAC could be moved without loss of pressure from any spectrometer to another and the spectrum recorded. This is particularly important because during any experiment the DAC could be removed to the Raman spectrometer and the pressure determined accurately (± 0.5 kbar) from the shift of the R lines of Ruby.

2.3 The mid-i.r. region

Recently work on a refracting beam condenser for infrared spectroscopy with a DAC has been reported, (Adams and Sharma 1977).

In this paper, the optics of the DAC are discussed in terms of numerical aperture and a beam condenser using KBr or KRS-5 lenses described. Using a beam condenser of this type, mid-i.r. spectra of ungasketed samples in a DAC have been obtained routinely on a Perkin Elmer 225 spectrophotometer and several bench top instruments. It was also possible to record the spectra of ungasketed and gasketed samples directly on a Perkin Elmer 580 spectrophotometer, although an improvement in transmission of some 50% was found when using a suitable beam condenser. Spectra of gasketed samples in the DAC used with the beam condenser could only be obtained with some difficulty in the Perkin Elmer 225 spectrophotometer. The major difference between the two spectrophotometers (PE225 and PE580) is that the PE580 has a 'live zero' and a smaller focus giving the advantage indicated when using the DAC. This simply means that instead of subtracting the signal beam and reference beam and amplifying the difference as is done in the PE225 the signal beam and reference beam are amplified electronically and then the difference taken. In all the spectrophotometers used, slow scanning speeds and wide slit programs were a feature of this very difficult work.

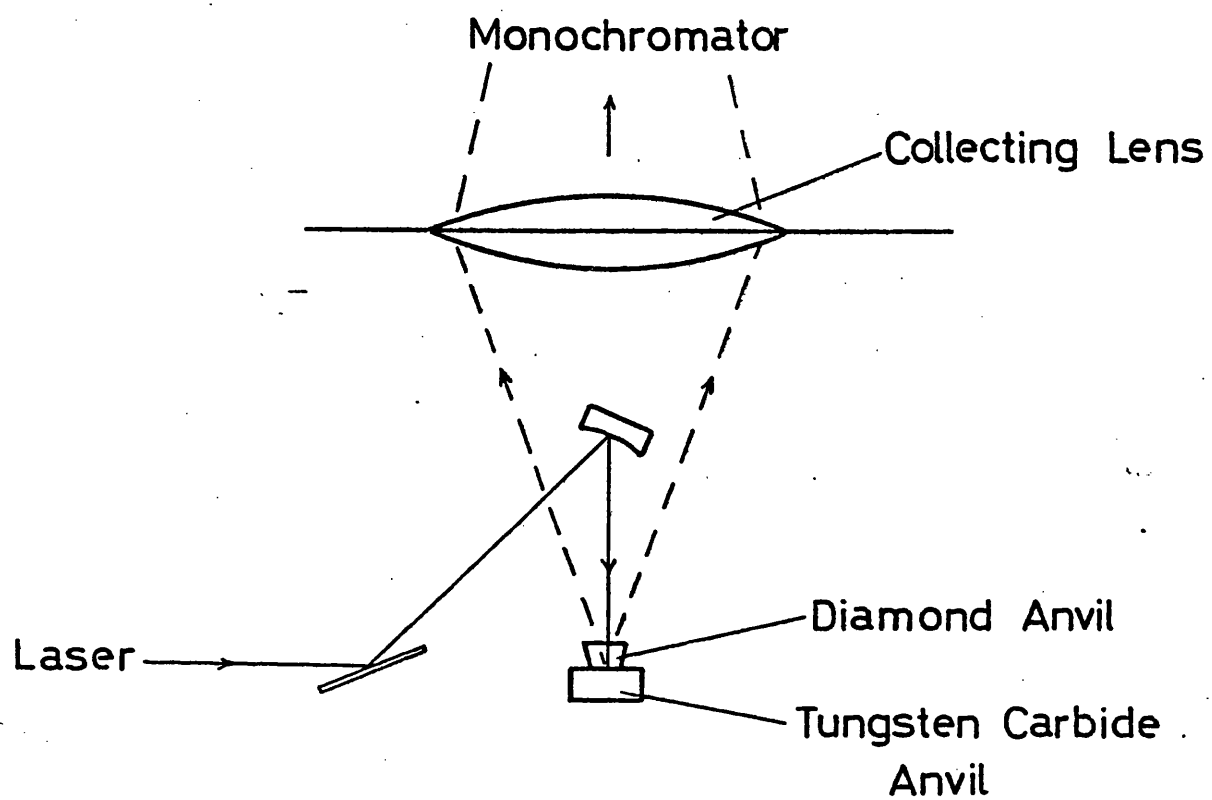
I would like to thank Dr. Shiv K. Sharma for instruction in using the beam condenser and help in obtaining spectra in this area.

2.4 Raman Spectroscopy

The first laser Raman spectra of samples contained at high pressures in a DAC were reported by Brasch et al (1968) and Postumus et al (1968) who studied HgI_2 . They used 0° scattering geometry in which the laser is fired straight through the cell towards the entrance slit of the spectrometer. Mitra (1971) was of the opinion that the DAC is not generally suitable for Raman spectroscopy because he believed forward scattering geometry to limit the experimenter to transparent non-ionic solids with no polariton effect and high Raman scattering efficiency. However it has been shown (Adams, Payne and Martin 1973, Hawke et al 1974, and Weinstein et al 1975) that this approach can be used successfully and is illustrated in figure 2:5. We have reported an improved method of coupling the DAC optically to a Coderg T800 Raman spectrometer (Adams, Sharma and Appleby 1977). The need for efficiency in this respect arises largely because of the very small sample sizes involved and the fact that we are using 0° or 180° geometry. With this technique we have studied Raman spectra at high pressures using both a DC detection system and an EMI 9558A photomultiplier run at 0°C and more recently a Brockdeal Ortec 5C1 photon counter with an RCA C31034-02 photomultiplier run at -35°C . Installation of this photon counting system is summarised later.

FIGURE 2:5

The arrangement of DAC and mirrors for 0° scattering.



(Not to Scale)

Optics of the DAC

Consider the arrangements of figure 2:6. A laser beam is focused such that after allowing for the effect of the high refractive index of diamond, η_D (2.4195 at 5893 Å; Wood 1964), the focus is at the sample contained within the gasket of a cell loaded as above. Since the sample is small we treat it as a point source in considering the collection of scattered radiation.

The Raman scatter, from a sample in a 4:1 methanol:ethanol mixture, in a cone of apex semi-angle 49° will be collected and transmitted by the diamond anvil (Adams, Sharma and Appleby 1977). It is evident that the most critical part of the system is the geometry of the anvil support material which limits the cone angle of collection. Here, the mechanical requirement that as much as possible of the diamond be supported if very high pressures are to be reached safely, conflicts with the optical requirements. In practice we reach a reasonable compromise by considering the numerical aperture of the transmitted beam, NA_t , for our DAC and computing the half angle $\emptyset$, of the emergent beam.

$$NA_t = \eta_D \sin \theta_D = \eta_{air} \sin \emptyset$$

θ_D is the angle of the ray to the normal in diamond.

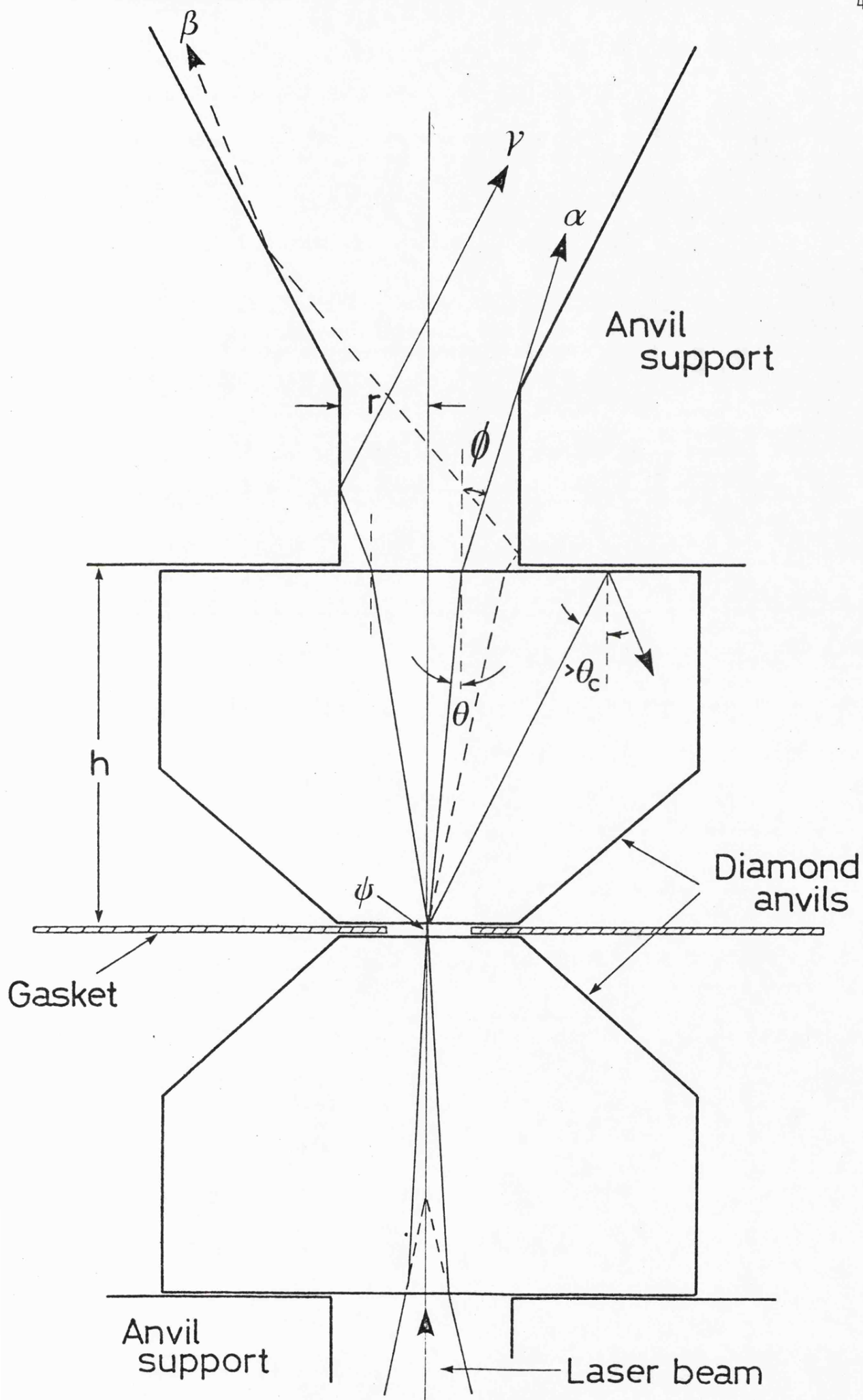
$$\theta_D = \tan^{-1} (r/h)$$

For $r = 0.45$ mm, $h = 2$ mm,

$$\theta_D = 12.7^\circ, \emptyset = 32.1^\circ, \text{ and } NA_t = 0.53.$$

FIGURE 2:6

Ray paths in a DAC used for Raman Spectroscopy.



Only rays $\theta < 5.8^\circ$ will pass directly out of the cell (e.g. ray α) but others with $5.8^\circ < \theta < 12.7^\circ$ will be collected after reflection from the walls of the anvil support (e.g. rays β , γ). See figure 2:6 for the diagram and definitions of the symbols.

Collection of radiation

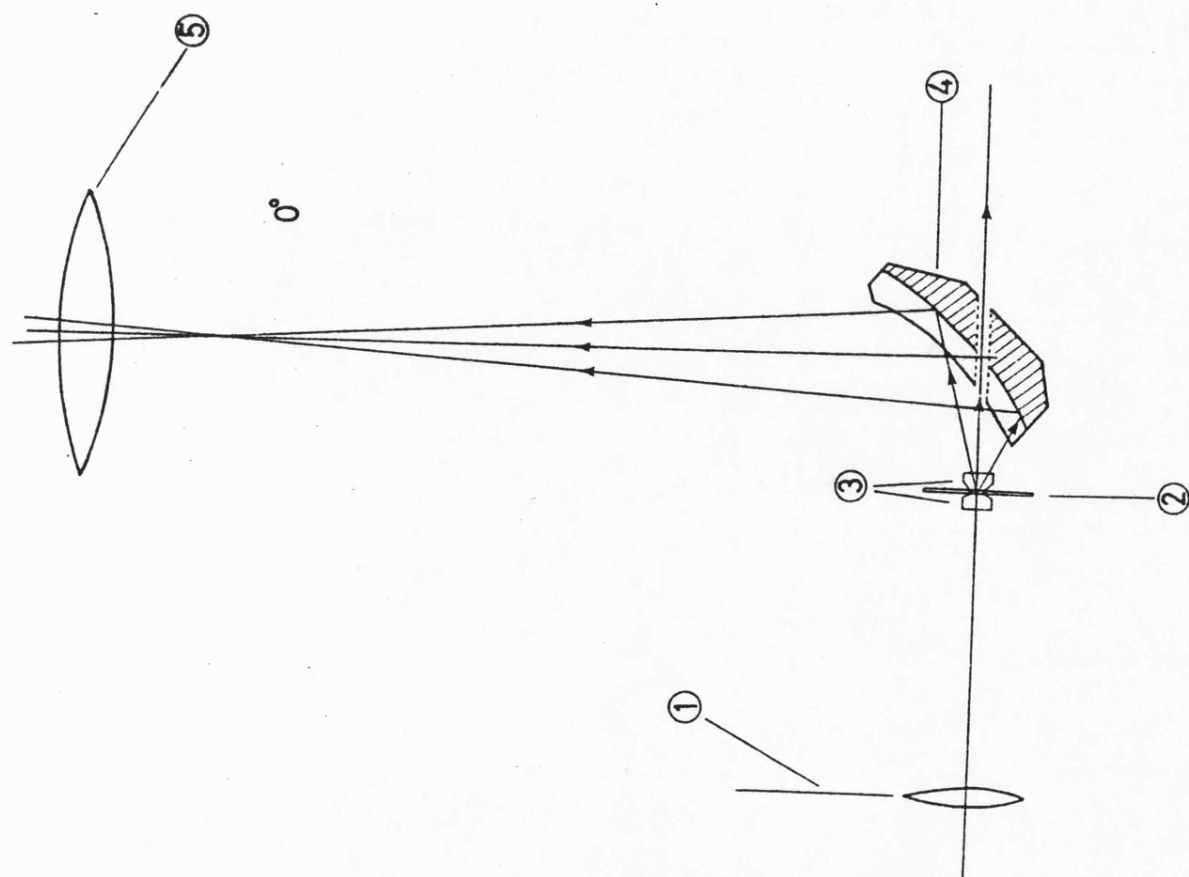
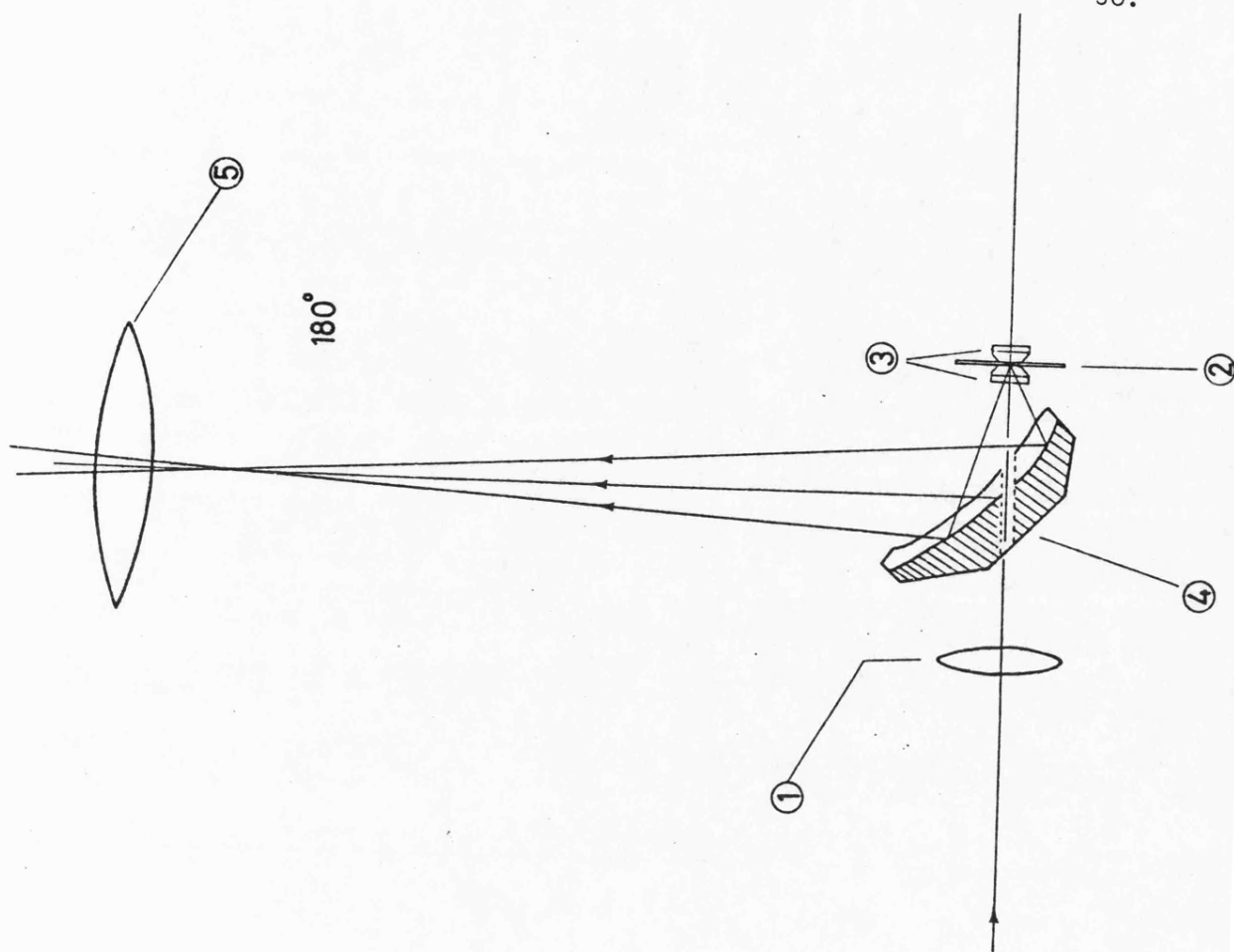
To collect the Raman radiation from the DAC we use a Perkin Elmer 90° off-axis ellipsoid with a numerical aperture of 0.7 (figure 2:7). This is the same mirror as is used in the 6:1 beam condenser commonly used for i.r. spectroscopy with DAC's. A 4 mm diameter hole has been drilled through our mirror to allow the laser beam to pass through it in either 0° or 180° scattering. Because the laser beam does not pass to the monochromator, relatively high laser powers may be used without degrading the performance at low Raman shifts. The difference in this respect between an ellipsoidal mirror with or without a hole is especially marked on a double monochromator instrument. The loss of Raman signal due to the hole in the mirror is ca. 10%. The ellipsoidal mirror has a magnification of x6. Accordingly the collected beam of numerical aperture 0.53 is reduced to one of ca. 0.1 which is well matched to standard collecting optics.

The advantages of using a 90° off-axis ellipsoid mirror are that the beam is turned through 90° in 0° or 180° scattering matching most standard spectrometers, and only 1 reflecting surface is used whereas two are necessary for 0° and 180° modes. In

FIGURE 2:7

The use of the 90° off-axis ellipsoid in the 0° and 180° Raman experiment with the DAC.

- (1) Laser focusing lens
- (2) Gasket
- (3) Diamond anvils
- (4) Ellipsoid mirror
- (5) Collecting lens



practice we have found that it is possible to obtain spectra of any sample in the DAC at high pressure from which a normal Raman spectrum can be obtained in a capillary tube at room pressure.

Installation of the ^{51}Cr Photon Counter into a Coderg T800 Raman Spectrometer

This operation should have been a simple one taking a matter of days but in fact from the beginning to the end the process took some four months. Therefore a brief summary of the modifications and installation problems is given. The existing Coderg photomultiplier housing complete with Peltier cooling was useless for photon counting with the RCA C31034-02 photomultiplier because it only reached a temperature of 0°C and not the one of -35°C required to reduce the dark counts to an acceptable level ca. 5 c/s. It had inefficient electrical screening and poor electrical connectors of the BNC type. This was rectified by stripping the old housing, removing the Peltier system, and rebuilding the housing as follows. Wrapping a $\frac{1}{4}$ " i.d. copper pipe around a metal cylinder made the tube housing the evaporator of a conventional refrigeration unit (in fact a Frigidaire Model 25). Connection to the unit was made by non-conducting flexible pipes to avoid R.F. pick-up. TNC connectors replaced the BNC ones, and all connections and electrical socket mountings were kept scrupulously clean to maintain perfect electrical contact. If the slightest form of bad contact existed, the photon counting system was able to pick up spurious counts due to electrical switching within a vicinity of 20 ft and this was not

conducted along the mains. A metal shield connected to the earth of the signal lead was wrapped around the photomultiplier, and the housing filled with expanded polyurethane foam insulation. Finally all mechanical seals were given a thin coat of varnish to ensure that the assembly was water-tight and a small heater was added on the tube base to prevent icing.

The screened leads which were used to connect the 5C1 to the photomultiplier did not have sufficient screening and had to be encased in copper pipe. The only other modification was to the 5C1. The time constants for the analogue output and the set measurement cycle times were found to be impractical in use and therefore a set of switchable external time constants and a device to vary the measurements cycle time were manufactured within the Department. The system as finally installed was free from electrical interference with a dark count of ca. 5 c/s and very high sensitivity.

2.5 Far-i.r. Spectroscopy

Use of the ungasketed DAC with far-i.r. fourier spectrometers has been reported (Adams and Payne 1974). No reports of any work using DACs with gaskets and obtaining reasonable results have been found. Payne (1975) achieved excellent results using an ungasketed DAC in a Beckman RIIC FS-720, the optical path of the machine being shown in figure 2:8, but he could not obtain spectra of samples held in gasketed DACs using this machine. It was decided to try to develop a system which could be used with the gasketed DAC; all efforts were concentrated on a run-down Beckman RIIC FS-620 as

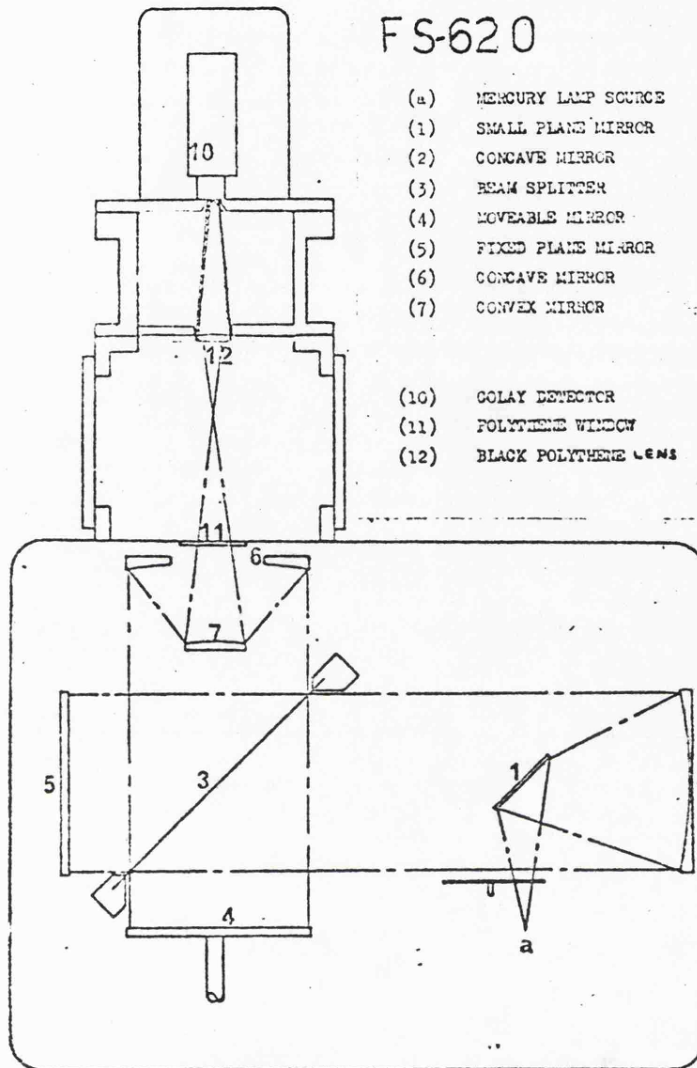
this was basically similar to the FS-720 and available for extensive modification. Modifications began with conversion of the optics from on-axis, figure 2:8a, to off-axis operation, figure 2:8b, which provided greater throughput as mirrors 1 and 7 do not block the centre of the beam in the off-axis mode. The original electronics, (mainly a valve system), were replaced by a more modern version (FS 300 supplied by Beckman RIIC) with solid state circuits and a solid state Golay detector was added (Pye Unicam Ir-50).

Without realising it, we had already made a system which was suited for DAC work. It had a transmission when the DAC was in position of approximately twice that of the FS-720. The reason for this was discovered to be the difference in the collecting optics of the FS-620 and FS-720. A scale drawing of the two sets of optics is given in figure 2:9. It can be seen that the black field lens of the FS-720 system is much thicker than that of the FS-620, therefore restricting transmission. The reason for the thicker field lens in the FS-720 is so that the background of this machine will be considerably improved at lower frequency. The backgrounds of both the FS-620 and FS-720 are given in figure 2:10 which clearly indicates the difference. We have therefore traded a decrease in energy in the lower frequency region less than 100 cm^{-1} for greater overall transmission of the system when using the DAC. The performance at low frequency could be improved by using a thicker 50 # beam splitter ($20\text{-}200\text{ cm}^{-1}$).

FIGURE 2:8

FS-720 optical pathway. Showing the use of off-axis optics and FS-620 optical pathway; showing the use of on-axis optics.

FS-620



FS-720

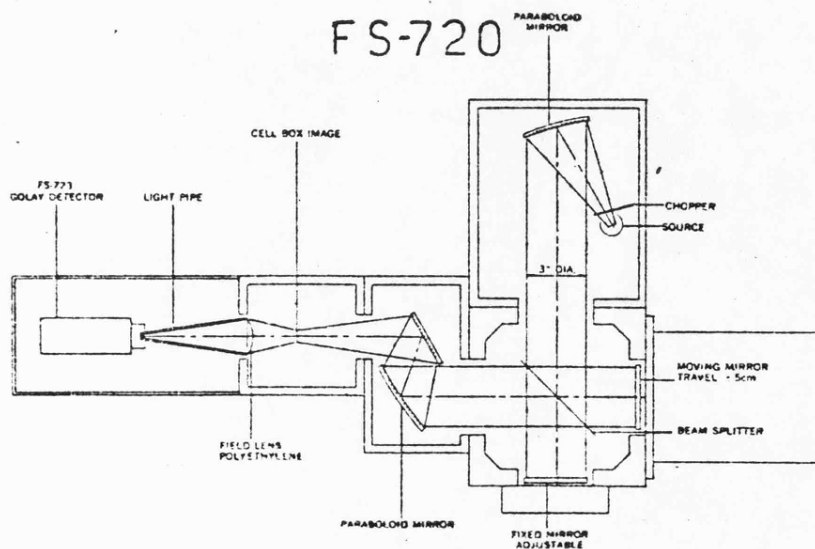


FIGURE 2:9

Collecting optics of FS-720 and FS-620.

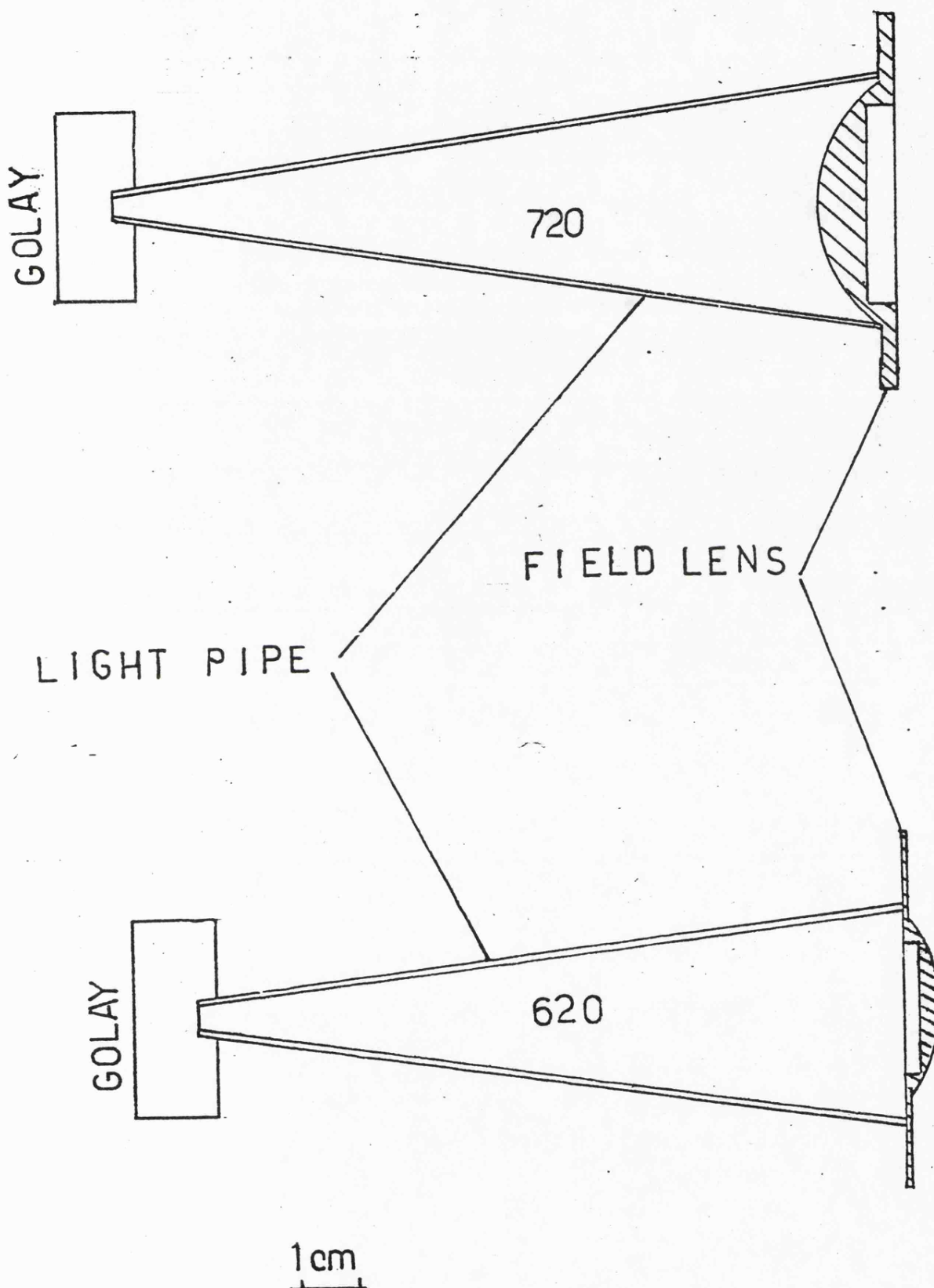
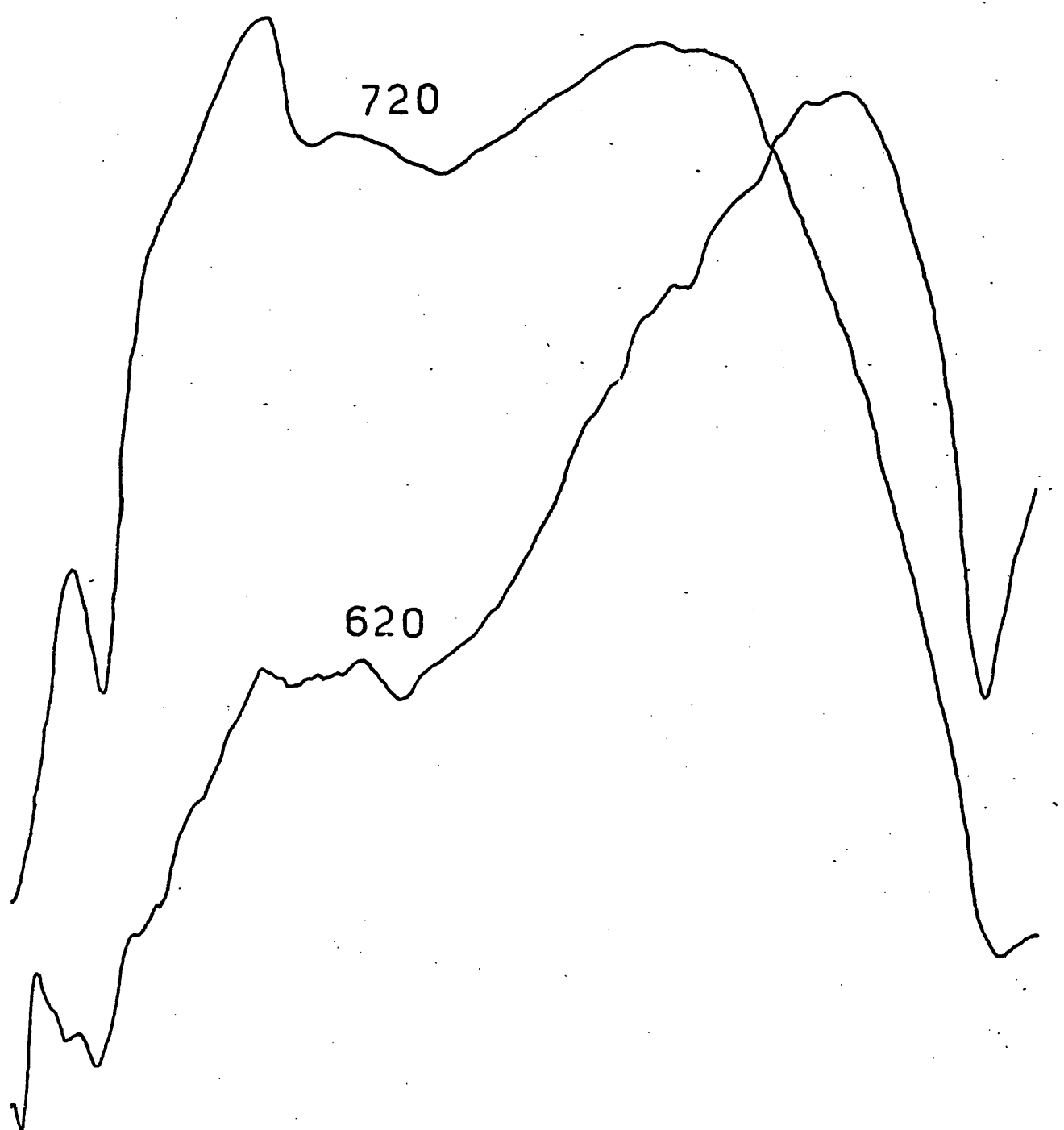


FIGURE 2:10

The background of the FS-720 and the background of the FS-620 using a 25# beam splitter, a sample interval of 8μ path difference and a symmetric interferogram.



50

200

400 cm^{-1}

More recent modifications include the addition of a multiple scan control unit to take advantage of the $\sqrt{N}$ increase in signal to noise for N scans of the same spectrum, and a new sample module to facilitate low temperature high pressure spectroscopy. A vacuum of $<10^{-5}$ torr can be obtained in this module giving greater transmission. An attachment to the extended fixed anvil holder of a DAC through which liquid nitrogen is circulated by a reciprocating suction pump is also provided. This device is shown in figure 2:11. The same device is also used in low temperature high pressure Raman spectroscopy. Other advantages include enclosure of the Golay detector inside the vacuum enclosure and easy mounting of the DAC. This module was designed by the author and manufactured by Allbon and Saunders Ltd., Abingdon. Having assembled all this equipment the technique of obtaining far-i.r. spectra of samples in a gasketed DAC has become relatively routine within our laboratory. In the far-i.r. choice of the pressure transmitting fluid is important and useful liquids are:

Liquid	Region of Transparency	Useful Pressure Range
Nujol ⁺	0-4000 cm^{-1}	0-40 kbar
EtOH/MeOH	Opaque	0-200 kbar
Octene ⁺	0-400 cm^{-1}	0-40 kbar
*Silicone oil ⁺	0-200 cm^{-1}	0-40 kbar

⁺ These liquids freeze or form glasses at pressures above 15 kbar but the status of the R lines of ruby show that the sample is still under moderately hydrostatic pressure.

* Silicone oil is a good high frequency filter.

FIGURE 2:11

Low temperature device for cooling DAC.

Shown in place on the extended fixed anvil holder.

The liquid nitrogen is circulated through the pipes connected by the stainless steel bellows to the copper annulus.



Of course we must not overlook the fact that data are output from our fourier spectrometers on paper tape and this digital information must be processed by a computer before it is in a form which we can describe as a spectrum. The program used in this work to perform the inverse fourier cosine transform of the interferograms obtained from the FS-620 was written by Dr. D.W. Waddington but implemented on the Cyber 72 (the University's central computer) and developed by the author. Programs for plotting spectra at the digital plotter, band analysis, interferogram investigation and data sorting were also used by the author. The fourier program and plotting program are fully documented and presented in Appendix I.

2.6 X-ray

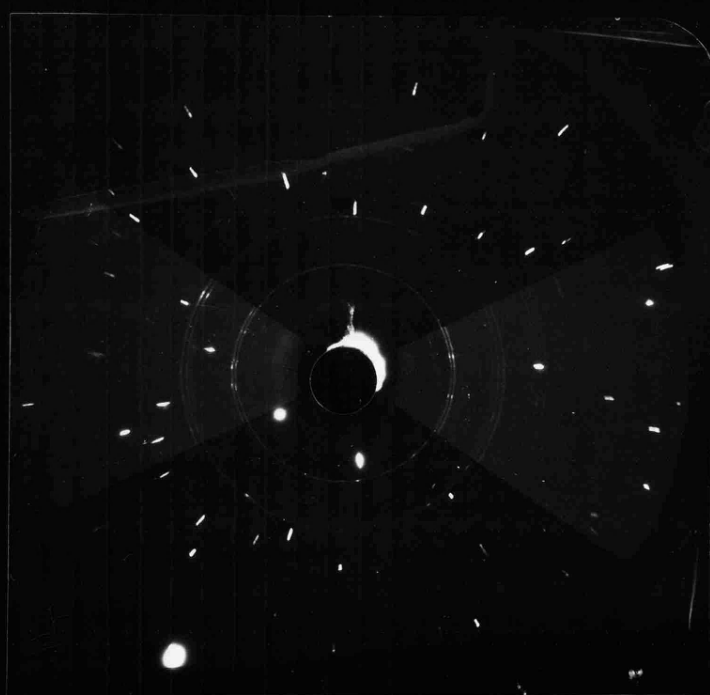
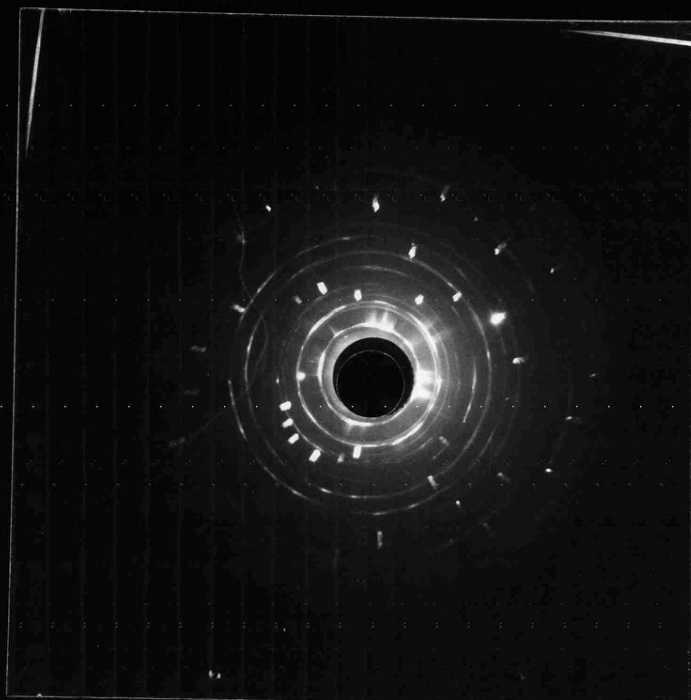
Reports of DAC's used in X-ray diffraction methods have been relatively common especially within the last year. They include single crystals studied in the gasketed mode (Mauer et al 1976, Merrill et al 1974, and Andre et al 1971), and powder diffraction methods (Bassett et al 1967). One of our DAC's was converted for use with X-rays by obtaining from W.A. Bassett (University of Rochester, New York), two discs of beryllium (figure 2:2) 12.7 mm dia. by 3.2 mm thick with a small axial hole 3.3 mm recessed 0.76 mm to position the diamond, and a hole of 1.0 mm dia. through the centre. This material is transparent to X-rays and therefore by simply incorporating one disc into the diamond anvil holder as shown in figure 2:2 we were able to construct a cell transparent to X-rays at least up

FIGURE 2:12

X-ray diffraction patterns of powdered NaCl held in a gasket.

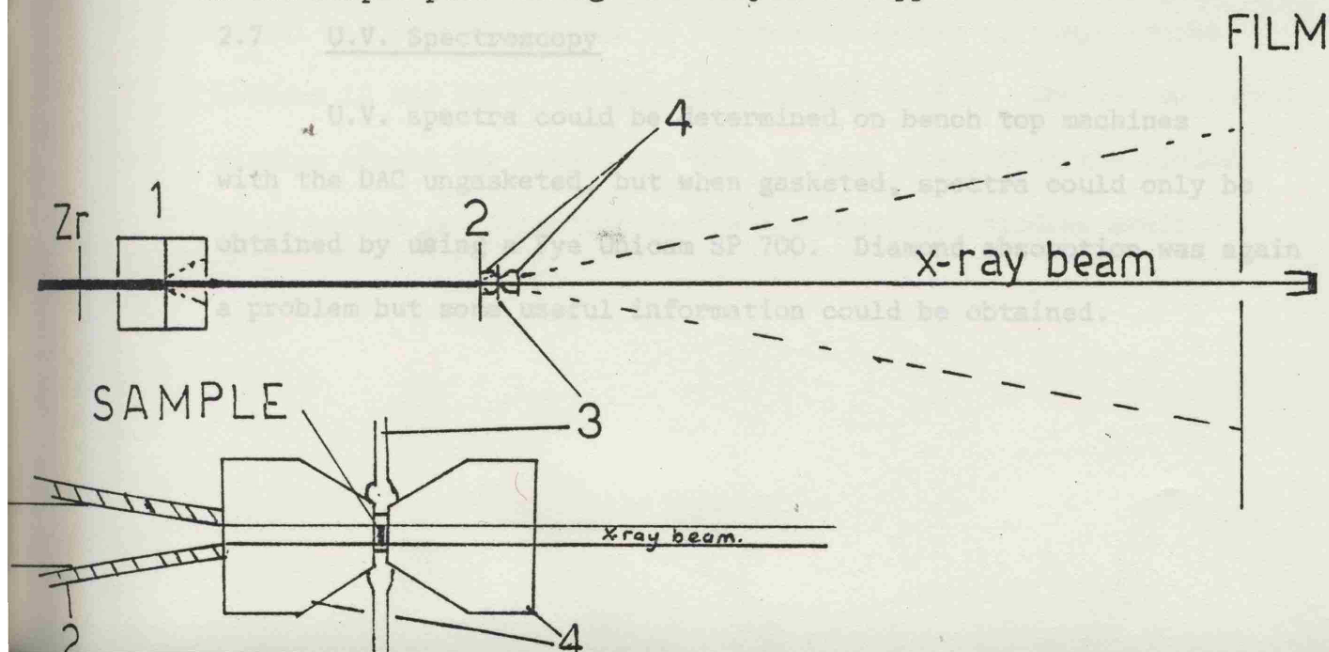
(Top) First picture taken, this can be shown to consist mainly of lines due to diffraction from the edges of the gasket hole.

(Lower) A picture using the small brass collimator discussed in the text. A high pressure exposure was taken with a shield over the film then with the shield removed an ambient pressure exposure taken over the whole film.



to 60° cone angle on each side of the cell.

The cell was mounted onto a standard Phillips camera bracket using a mounting designed by the author and manufactured in the Chemistry Department at Leicester. The apparatus was completed by using a 0.5 mm collimator and a flat plate film cassette from a Phillips Laue camera PW 1030. A PW 1009 generator ran at 48 KV and 16 mA with a fine focus molybdenum tube and a zirconium filter was used. The first picture of NaCl recorded is shown in figure 2:12. It can be shown that most of the lines are due to X-ray diffraction from the edge of the gasket hole. This problem was solved by manufacturing three tiny collimators made of brass with pinholes of 0.1, 0.2, and 0.5 mm. These were arranged as shown below so that the X-ray beam passed from the X-ray tube through a zirconium filter, a 0.5 three-pinhole standard collimator (1), then into our small 0.1 one pinhole collimator (2), passing through one diamond (4), the hole in the gasket (3), the sample and finally emerging through the other diamond (4) and passing into a lead backstop. The diffraction lines of the single pinhole collimator are blocked by the opaque gasket and the diffraction lines of the sample pass through the beryllium support on to the film.



This system could be used in front $2\theta < 30^\circ$ or back $2\theta > 150^\circ$ reflection. The cell was loaded as described earlier and the small collimator support attached to the extended nose piece of the DAC. The DAC was then held over a 100 watt table lamp so that the light transmitted through the tiny gasket hole could be seen and the small single pinhole collimator placed in position and adjusted to give maximum intensity of transmitted light. Lasers were also used (of course not using direct visual observation) but the above method proved most successful. It was impossible to use a microscope for this alignment as the single pinhole collimator restricted transmission. The cell was finally aligned on the camera bracket by removing the lead backstop, placing a geiger counter in the main beam and adjusting the DAC for maximum transmission.

A typical exposure of 24 h was found to be necessary using Kodirex X-ray film. An ambient pressure diffraction pattern was usually recorded on the same film for calibration purposes, a sample to film distance of 60 mm was typical. A successful exposure is shown in figure 2:12. No diffraction lines due to collimator or gasket can be seen.

2.7 U.V. Spectroscopy

U.V. spectra could be determined on bench top machines with the DAC ungasketed, but when gasketed, spectra could only be obtained by using a Pye Unicam SP 700. Diamond absorption was again a problem but some useful information could be obtained.

2.8 Useful Development Work Carried out on a Closed Circuit Helium Cryostat

All the low temperature ambient pressure spectra reported in this thesis were carried out using a closed circuit C.T.I. model 21 helium cryostat covering the temperature range from 12 to 300 K. Considerable effort was dissipated into getting spectra at a genuine 12 K, as in its commercial state, the C.T.I. model 21 provided with its vacuum turret is incapable of giving temperatures of below 120 K with any reasonable sample size. The reason for this was found to be radiation loss to the outer vacuum shroud only some 50 mm away at room temperature. This was solved by adding a radiation shield, with suitable ports for spectroscopic use, which came between the sample and the outer walls. The shield was kept at a nominal 80 K by use of a secondary cold station available within the cryostat. A chromel, iron, gold thermocouple attached to the sample and taken directly out through an epoxy seal in one of the windows was attached to the sample and used to monitor the temperature in the test work and also in the results shown in this thesis.

With this modification the cryostat proved to be a most useful and versatile piece of equipment capable of temperatures between 12 and 300 K controlled to within ± 0.5 K. The vacuum turret fitting around the sample was made in such a way that the windows could be changed depending on the application. Windows available

include Rigidex for far-i.r., KBr for mid-i.r., quartz for Raman spectroscopy and supported 5 thou beryllium windows for low temperature Laue or powder back or front reflection X-ray methods.

2.9 Summary

In this chapter an outline of the operation of a DAC including loading and use in various spectrometers is given. Also the development of the spectrometers and other pieces of equipment used to produce the work in this thesis is summarised.

It can be said from experience that development work is very long and tedious, the work presented in this Chapter probably taking about 18 months. But the improvements in all systems used are justified in that reasonable results with a gasketed DAC under pressure can be obtained on the same sample and the pressure determined accurately.

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CHAPTER 3

USE OF RUBY R LINES IN THE ESTIMATION OF PRESSURE

AT AMBIENT AND AT LOW TEMPERATURE

CHAPTER 3

USE OF RUBY R LINES IN THE ESTIMATION OF PRESSURE AT AMBIENT AND AT LOW TEMPERATURES

3.1 Introduction

When using the DAC with a gasket in an attempt to maintain hydrostatic pressure, it became more difficult to estimate the pressure at the sample. The relationship between applied load and the pressure at the sample, used to estimate pressure in a DAC without a gasket, is not valid for a DAC with a gasket. This is because the gasket itself absorbs an unknown fraction of the applied load in each experiment. It was therefore necessary to find a reliable pressure sensor which could be incorporated within the gasket.

It was recently recognised that the R_1 and R_2 fluorescence lines of ruby are pressure-dependent and provide a simple and versatile means of determining the pressure on a sample in devices such as the DAC.

Since its introduction by Forman et al (1972) various aspects of the pressure and temperature dependencies of R_1 and R_2 have received attention (Barnett et al 1973, Piermarini et al 1973, Hawke et al 1974), and there are several earlier reports of their thermal dependence (Gibson 1916, Deutschbein 1932, Schawlow 1961, McCumber and Sturge 1963). We reported the first detailed study

of R_1 and R_2 at low temperatures and under a combination of low temperature and high pressure (Adams, Appleby and Sharma 1976). The following Chapter is concerned mainly with this work.

3.2 Experimental

The temperature dependence of the R_1 and R_2 lines was studied using a single crystal of ruby, containing 0.05% Cr, mounted in a CTI-21 closed-circuit cryostat. A copper-constantan thermocouple referenced to liquid nitrogen was attached to the crystal by silver paste (metallising preparation, Johnson and Matthey) and the crystal itself was mounted in the same paste directly onto the cold head of the cryostat. Attention is drawn to the mounting of the crystal, as initially it was mounted in Araldite (Rapid) (Ciba Geigy) which became a very good thermal insulator at low temperatures and the crystal could not be cooled effectively. The sample temperature was controlled to ± 0.5 K. Spectra were excited with an Ar ion laser using 50 mW 514.5 nm radiation to ensure that there was no local heating of the sample. The emission was studied using a Coderg T800 triple monochromator Raman spectrometer calibrated using Ar and Ne lines.

The DAC used was a modified Mark II cell cooled using the apparatus described in Chapter 2.

For a typical high pressure run, one chip of ruby containing 0.5% Cr was placed in a 4:1 methanol:ethanol mixture contained in a molybdenum gasket with a hole of ca 0.4 mm diameter and of thickness 0.05 mm. In some cases where it was impractical to use

methanol:ethanol, silicone oil was substituted. Unfortunately this froze under ca 10 kbar pressure, although it is still a convenient medium. The temperature of a sample loaded in the DAC was monitored by attaching a copper-constantan thermocouple referenced to liquid nitrogen, to one diamond with silver paste.

3.3 Results and Discussion

Fixed Points

In the initial report of the pressure-dependence of R_1 and R_2 the scale was established (at 25°C) by reference to the liquid-to-solid transition points of CCl_4 , H_2O , $n\text{-C}_7\text{H}_{16}$, and $\text{C}_2\text{H}_5\text{Br}$; and the ice VI/VII transition, (Forman et al 1972). In attempting to repeat and extend this work it became clear that basic difficulties are involved which limit the accuracy attainable. The use of liquid-to-solid transition points introduces errors in that non-hydrostatic forces are created at the freezing pressure as the formation of a solid phase impinges upon grains of entrapped ruby. Further, the exact transition point may not be sharp, or its detection by visual means imprecise. With solid-to-solid transitions sluggish behaviour is the principal problem.

Whilst this work was in progress calibration of the R_1 shifts was extended first to 195 kbar (Piermarini et al 1975) and then to 291 kbar (Piermarini and Block 1975) by reference to the X-ray-determined lattice constants of NaCl under pressure, combined with the Decker equation of state. This method supercedes in accuracy anything based upon fixed points, although we find that

within experimental error our fixed-points lie on the line determined by reference to NaCl and from which R_1 is known to shift by $-0.76 \pm 0.006 \text{ cm}^{-1} \text{ kbar}^{-1}$ ($0.365 \text{ \AA kbar}^{-1}$), (Piermarini and Block 1975). Thus, at the ice VI/VII transition we observed shifts of $R_1 = 16.5$ and $R_2 = 17.6 \text{ cm}^{-1}$: using the literature values for this transition we obtain

	Bridgman, 21.84 kbar	Kennedy & La Mori, 21.42 kbar
R_1	0.756	0.770
R_2	0.805	$0.818 \text{ cm}^{-1} \text{ kbar}^{-1}$

showing that Bridgman's value is marginally closer to the 21.71 kbar calculated from an R_1 shift of $0.76 \text{ cm}^{-1} \text{ kbar}^{-1}$. The yellow-to-red transition in HgI_2 was observed at an R_1 shift of 9.2 cm^{-1} and an R_2 shift of 9.6 cm^{-1} (using silicone oil as the pressure transmitting fluid): the quoted transition pressure (Drickamer 1963, Brasch et al 1968) gives shifts ($\text{cm}^{-1} \text{ kbar}^{-1}$) of 0.71 and 0.74 based upon R_1 and R_2 respectively; a more accurate value is suggested in retrospect using $0.76 \text{ cm}^{-1} \text{ kbar}^{-1}$ from the NaCl work (Piermarini and Block 1975), viz., 12.0 kbar. Finally, the KNO_3 II/IV transition (2.86 kbar) (Rapoport and Kennedy 1965), although too sluggish to be trustworthy, gave $\Delta R_1 / \Delta P \approx 0.70 \text{ cm}^{-1} \text{ kbar}^{-1}$. With the appearance of the NaCl-based calibration, we have adopted the value for R_1 of $0.76 \text{ cm}^{-1} \text{ kbar}^{-1}$ at ambient temperature as the basis of further work, here reported, on the comparative behaviour

of R_1 and R_2 , and on the low temperature/high pressure calibration.

Origin of the R_1 and R_2 shifts

In order to understand the behaviour of the R_1 and R_2 lines it is helpful to consider their origin. An isolated Cr^{3+} ion in a cubic field would show a single band due to the spin-forbidden transition ${}^2E \leftarrow {}^4A_2$. In ruby Cr^{3+} occupies one of the Al^{3+} sites ($\underline{D}_{3d}$) but is displaced along the c -axis due to its slightly different size, thereby assuming $\underline{C}_{3v}$ site symmetry. Static fields of $\underline{D}_{3d}$ and $\underline{C}_{3v}$ symmetry cannot split the 2E level, but the degeneracy is removed by spin-orbit coupling (which is symmetry-forbidden in the cubic situation) resulting in a pair of levels $E_{3/2}$, $E_{1/2}$ separated by $\Delta R \approx 29 \text{ cm}^{-1}$. Accordingly there are two lines in the R (= red) region of the spectrum, R_1 and R_2 , with $\nu(R_1) < \nu(R_2)$, (Chang 1969). Each line is actually a doublet with a splitting of 0.38 cm^{-1} arising from the splitting of the ground state into Kramers doublets: this is only observed at very low temperatures and in an unstrained sample, (Schawlow 1961), conditions not met in our work.

With increase of pressure the whole electron-level manifold of Cr^{3+} will be reduced in span (Drickamer and Frank 1973), leading to a lowering of the transition energies of R_1 and R_2 (as is found). To this must be added a further increase or reduction due to any non-parallelism of the 4A_2 and $E_{3/2}$, $E_{1/2}$ levels when plotted versus crystal field strength: this term is likely to be small for Cr^{3+} as the 4A_2 and 2E levels are nearly parallel in the cubic case.

Some modification of this picture may result from the anisotropy of the thermal and stress parameters. It is known that the coefficients of linear compression along and perpendicular to the c-axis of ruby are the same (Bridgman 1949): the effect of increase of pressure, at a given temperature, should then be as outlined above. On the other hand, the thermal expansion coefficients are markedly anisotropic (Sharma 1951, Watchman et al 1962). Thus:

$$\alpha_{\parallel} = (0.6582 \times 10^{-5}) + (0.4995 \times 10^{-8})T + (0.2578 \times 10^{-11})T^2$$

$$\alpha_{\perp} = (0.5425 \times 10^{-5}) + (0.5534 \times 10^{-8})T + (0.2876 \times 10^{-11})T^2$$

where T is the temperature in °C.

Hence, upon heating ruby from a very low temperature, expansion will be greatest along the c-axis, increasing the structural departure from cubic. This will not affect the symmetry of the site on which Cr^{3+} is located but the spin-orbit coupling will be slightly more allowed, accounting for the slight increase found in ΔR , from 29.3 ± 0.2 (150 K) to 29.7 ± 0.2 (293 K) cm^{-1} . This decrease in $\nu(R_1)$ and $\nu(R_2)$ from very low temperature is barely 20 cm^{-1} up to 300 K, whereas a shift of 20 cm^{-1} in $\nu(R_1)$ is produced at room temperature by only 26.3 kbar pressure. The decrease in $\nu(R_1)$, $\nu(R_2)$ upon heating is attributed principally to the lowering of the $E_{3/2}$ and $E_{1/2}$ levels relative to the 4A_2 ground state as the crystal field energy decreases due to expansion of the lattice. Since increases of temperature and pressure both cause $\nu(R_1)$ and $\nu(R_2)$ to fall, there is a danger that pressure may be over-estimated if

there is significant local heating (e.g. by a laser beam) because the high phonon conductivity of diamond will act as a sink such that the temperature as measured by a thermocouple attached to a diamond anvil will not reflect the extent of local heating.

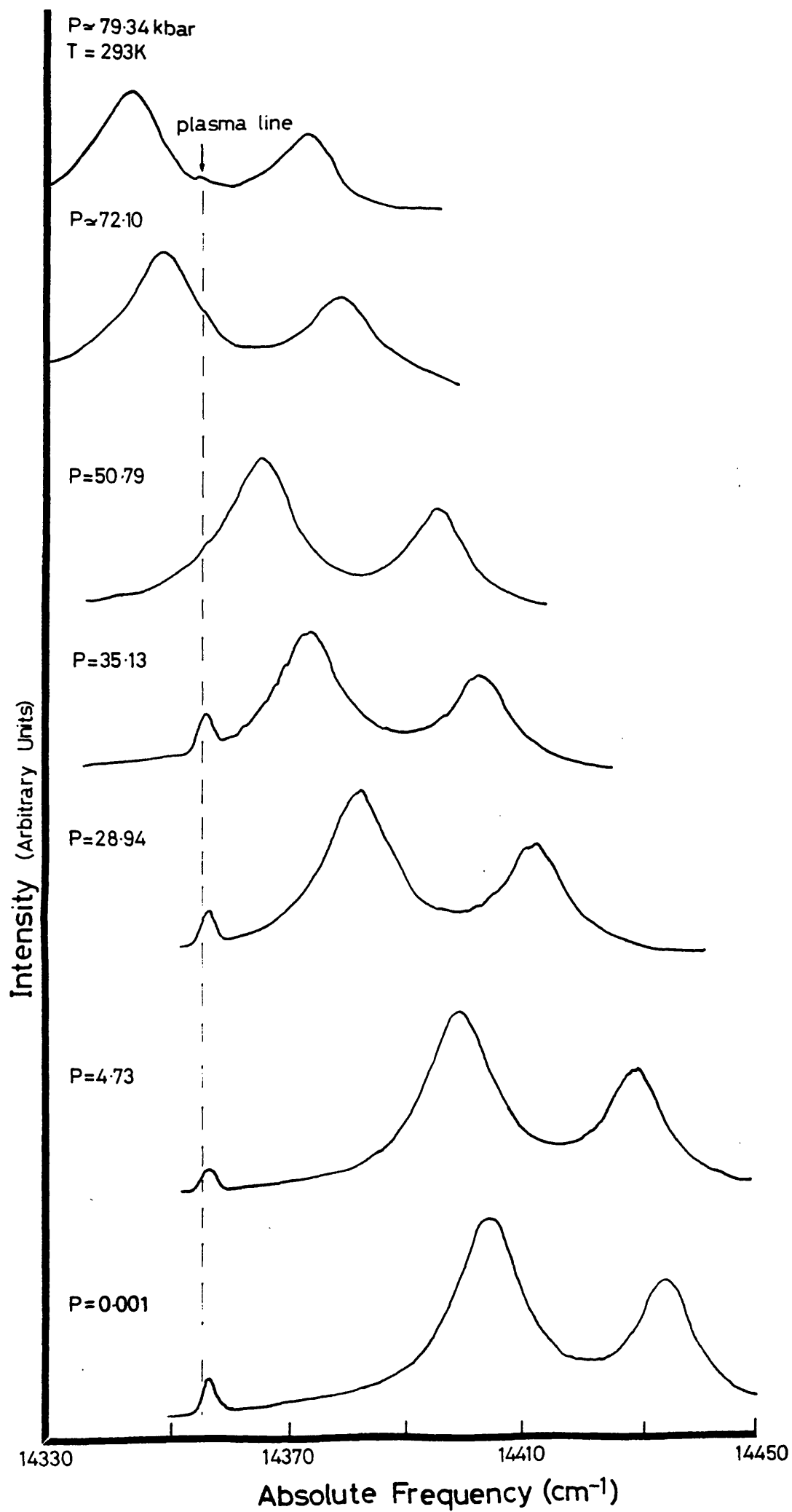
Behaviour of the R₁ and R₂ lines under hydrostatic pressure

We confirm an earlier report that under hydrostatic conditions the R₁ and R₂ lines shift by the same amounts, Figure 3:1, and thus retain the spacing $\Delta R = 29.7 \pm 0.2 \text{ cm}^{-1}$ at room temperature (Barnett et al 1973): we find that conditions start to become non-hydrostatic above ca. 50 kbar, as indicated by a change in ΔR and an increase in half-bandwidth, $\Delta\nu_{1/2}$. This contrasts with a claim (Piermarini et al 1973) that, using an identical technique, conditions remain hydrostatic up to 100 kbar in ethanol: methanol.

Since either line may apparently be used in a pressure calibration others in the field appear to have settled for the use of R₁ alone, taking gradient values of -0.77 ± 0.03 , (Piermarini et al 1975), -0.754 , (Hawke et al 1974), and $-0.76 \pm 0.006 \text{ cm}^{-1} \text{ kbar}^{-1}$ (Piermarini and Block 1975) respectively. In contrast, we emphasise the importance of keeping both lines under observation: this point is developed below.

Figure 3:1

Variation of the ruby R_1 and R_2 fluorescence
lines with pressure (kbar) at ambient temperature.



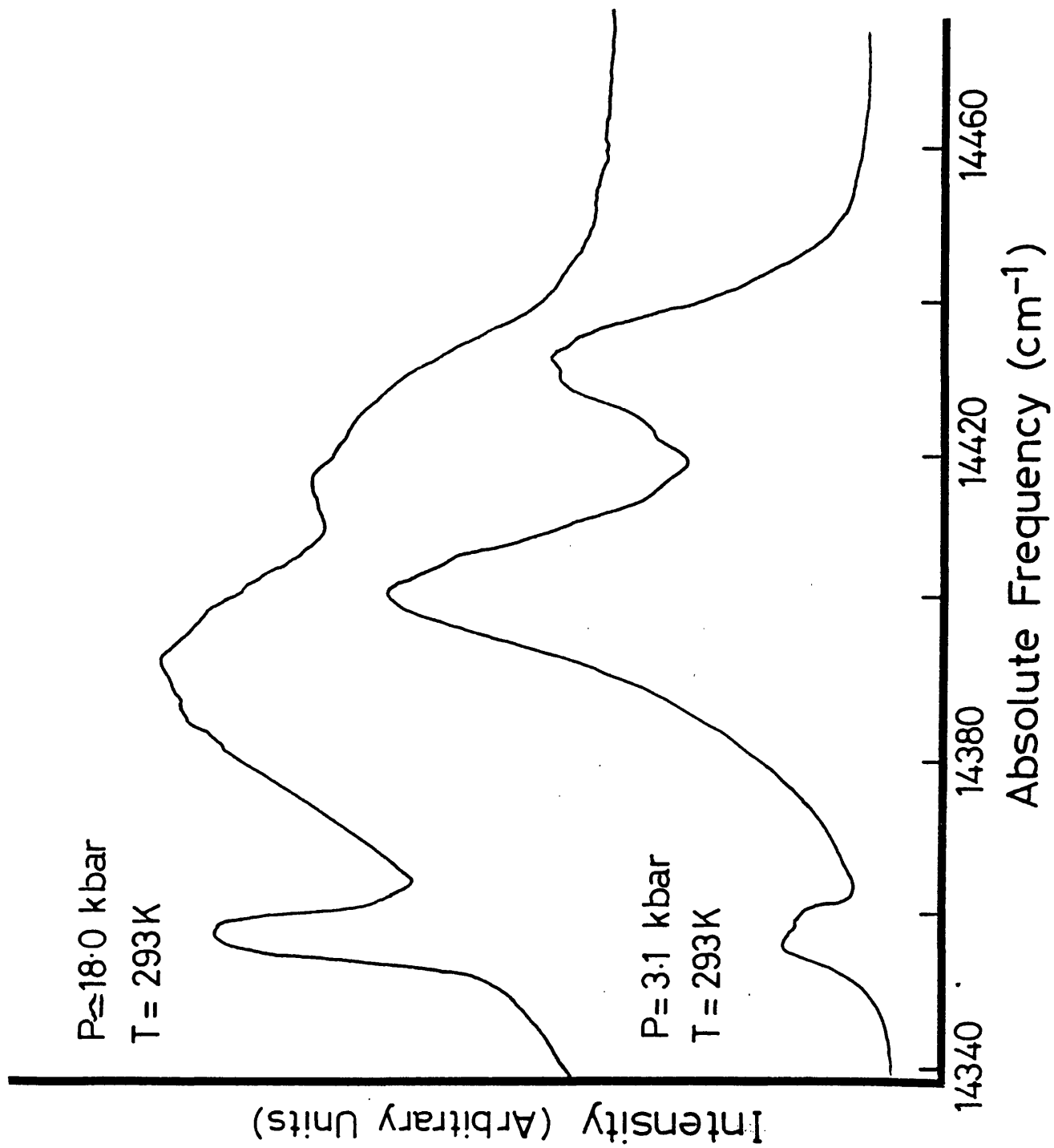
Strain and its effect on $\Delta\nu_{1/2}$

It is known that strains affect the widths of the R_1 and R_2 lines, (Schawlow 1961). For a strain-free sample at 77 K $\Delta\nu_{1/2} \approx 0.3 \text{ cm}^{-1}$. In our work we found values of 0.8 and 0.5 cm^{-1} for R_1 and R_2 respectively for the crystal used for the low-temperature calibration at ambient pressure. These values are not unusual: the ruby rod used by Collins et al in their first experiments on the optical maser contained sufficient strains that $\Delta\nu_{1/2}$ was ca. 1 cm^{-1} at 77 K, (Schawlow 1961).

The behaviour of $\Delta\nu_{1/2}$ under the conditions encountered in high pressure work is complex and subject to many variables, including the history of the sample. With the finely-powdered ruby used for pressure calibration $\Delta\nu_{1/2}$ remains approximately constant or shows a very slight decrease (Piermarini et al 1973 and this work) whilst the pressure remains hydrostatic (ΔR constant): it is increased, often substantially, if the pressure becomes non-hydrostatic (ΔR changes), and may be further increased by rapid (adiabatic) increase or decrease in pressure. Thus, application of ca. 40 kbar pressure followed by rapid release caused $\Delta\nu_{1/2}$ for R_1 and R_2 to increase by 0.8 and 1.6 cm^{-1} respectively, and ΔR to increase by 0.2 cm^{-1} . An extreme case of the effect of non-hydrostatic pressure on $\Delta\nu_{1/2}$ is shown in Figure 3:2 for which far from hydrostatic conditions were created by packing the entire gasket hole with ruby powder. Even in the normal experimental situation, with ruby immersed in a pressure-transmitting

Figure 3:2

The ruby R_1 and R_2 lines from a sample under non-hydrostatic conditions at ambient temperature.



fluid, the use of changes in $\Delta\nu_{1/2}$ to estimate pressure gradients is extremely hazardous, as shown below. We emphasise that, in our opinion, more consistent results are obtained using ΔR as the indicator of the magnitude of a shear component.

Behaviour of the R_1 and R_2 lines under non-hydrostatic pressure

When the pressure becomes non-hydrostatic R_1 and R_2 move at different rates but sometimes ΔR increases and sometimes it decreases. When R_2 moves more rapidly than R_1 gradients of -0.80 and $-0.75 \text{ cm}^{-1} \text{ kbar}^{-1}$ respectively are typical, i.e. ΔR decreases; when R_1 moves faster than R_2 , with typical values of -0.83 and $-0.75 \text{ cm}^{-1} \text{ kbar}^{-1}$, ΔR increases. The important feature to note is that the smaller shift in each case is about the same and, even in quite substantially non-hydrostatic conditions, differs by no more than $\pm 0.02 \text{ cm}^{-1} \text{ kbar}^{-1}$ from the hydrostatic value of $-0.76 \text{ cm}^{-1} \text{ kbar}^{-1}$.

These results indicate that the monitoring of R_1 alone, which now seems to be becoming accepted practice, may lead to substantial errors in estimation of pressure under slightly non-hydrostatic conditions. On a purely pragmatic basis it is now our practice to observe both lines: if a change in ΔR indicates the development of a non-hydrostatic component we use the lesser of the two gradients to estimate the average pressure on the sample. We find that this procedure leads to values of phase transitions close to those obtained by independent means, and suggests that it is essentially meaningful. For example, the HgBr_2 II/III

transition is known to be at 22.07 kbar at room temperature, although it is a little sluggish, (Bridgman 1937 c). The Raman spectra were obtained using a DAC with a molybdenum gasket 0.05 mm thick and a hole of initial diameter 0.30 mm. Because HgBr_2 is soluble in methanol:ethanol, silicone oil was used as the pressure transmitting fluid although it freezes at ca. 10 kbar: it is obvious, therefore, that the pressure on each particle of ruby will not be completely hydrostatic. The phase transition was readily detected spectroscopically, and will be discussed elsewhere. In a typical experiment the shifts of R_1 and R_2 at the transition point were 22.5 and 18.5 cm^{-1} respectively, corresponding to pressures of 29.60 and 24.34 kbar if the gradient $-0.76 \text{ cm}^{-1} \text{ kbar}^{-1}$ is applied. The lower value, derived from the R_2 shift, is much closer to the reported transition pressure, 22.07 kbar, especially when allowance is made for the rather sluggish nature of the change.

The increase or decrease of ΔR under non-hydrostatic conditions is readily understood on the basis of some uniaxial stress results on ruby due to Schawlow, (Schawlow 1961). He showed that a stress applied parallel to the c-axis caused ΔR to decrease, whereas a stress normal to c caused ΔR to increase. In a high pressure experiment there is commonly only one grain of ruby present; it is therefore reasonable that when it experiences a non-hydrostatic pressure there will be differently-sized components along and perpendicular to c with the result that, overall, there

is a change in ΔR . In the case that many grains of ruby are present it may happen that the shear stress contours will cause some partial alignment of them: more probably, for some ΔR will increase and for others it will decrease, so that the net result will be a considerable broadening of each band and a change in ΔR in a sense corresponding to the forces acting along the preferred alignment direction.

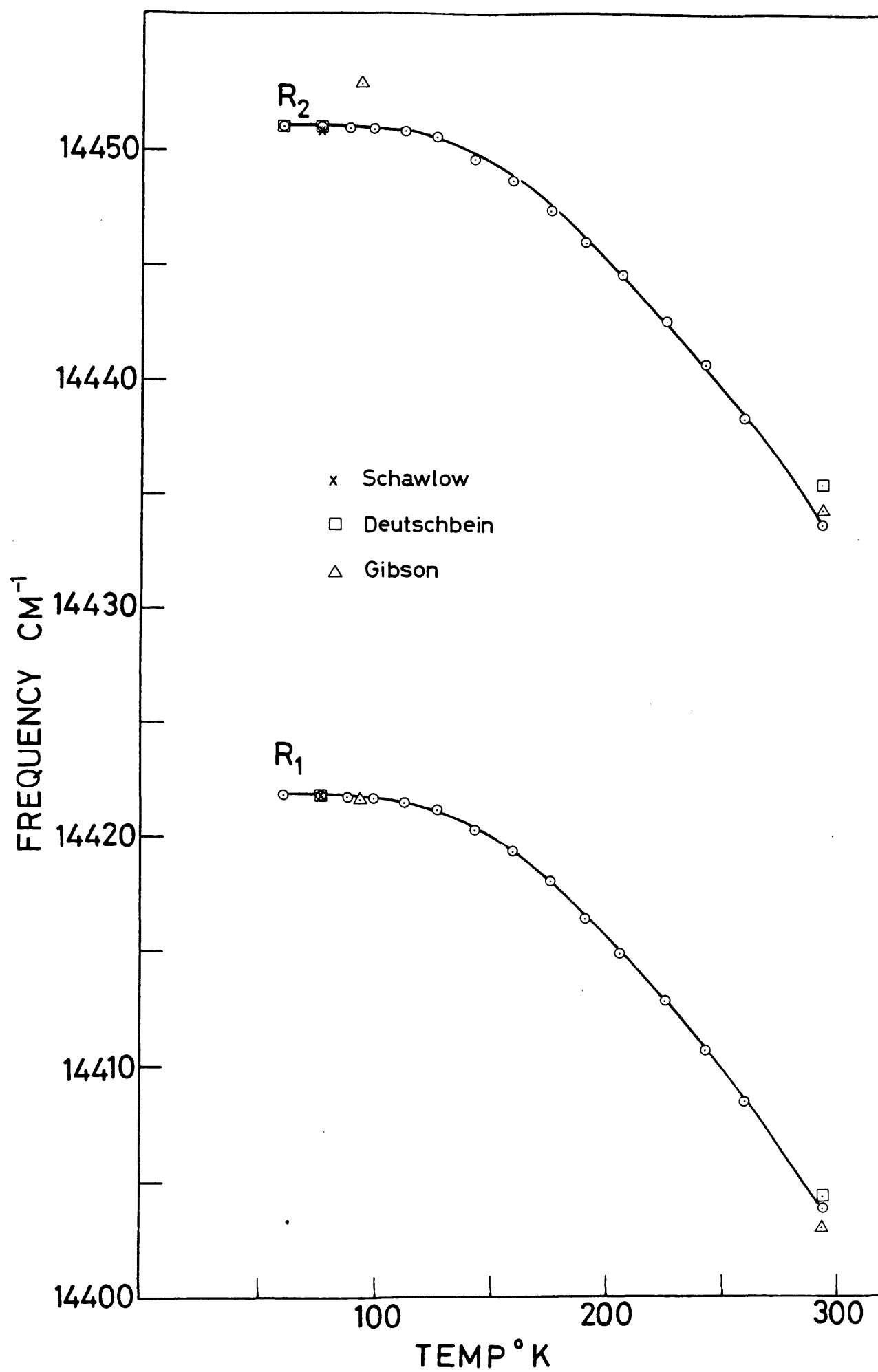
Behaviour of R_1 and R_2 at low temperatures and high pressures

The thermal dependence of R_1 and R_2 is illustrated in Figure 3:3. The frequencies are in generally good agreement with earlier values, (Gibson 1916, Deutschbein 1932, Schawlow 1961). The separation, ΔR , increases from $29.3 \pm 0.2 \text{ cm}^{-1}$ at 150 K to $29.7 \pm 0.02 \text{ cm}^{-1}$ at 293 K. Other studies have been made of the effect of temperature upon $\Delta \nu_{1/2}$, (Schawlow 1961, McCumber and Sturge 1963). Initially the effect upon $\nu(R_1)$ and $\nu(R_2)$ of increasing temperature is extremely small but above ca. 150 K, where the terms in T and T^2 in the thermal expansion equations begin to assume importance, both transition frequencies decrease exponentially, having a coefficient of $-0.134 \text{ cm}^{-1} \text{ K}^{-1}$ at room temperature.

The establishment of a pressure calibration at low temperature is a matter of some difficulty as there are few fixed-point transitions known under these conditions. Moreover, displacive and reconstructive phase transitions become very sluggish at low temperature and are unlikely to be determinable within acceptable

Figure 3:3

Variation of the ruby R_1 and R_2 lines with temperatures
(X Schawlow, $\square$ Deutschbein, Δ Gibson, O Adams, Appleby,
Sharma).

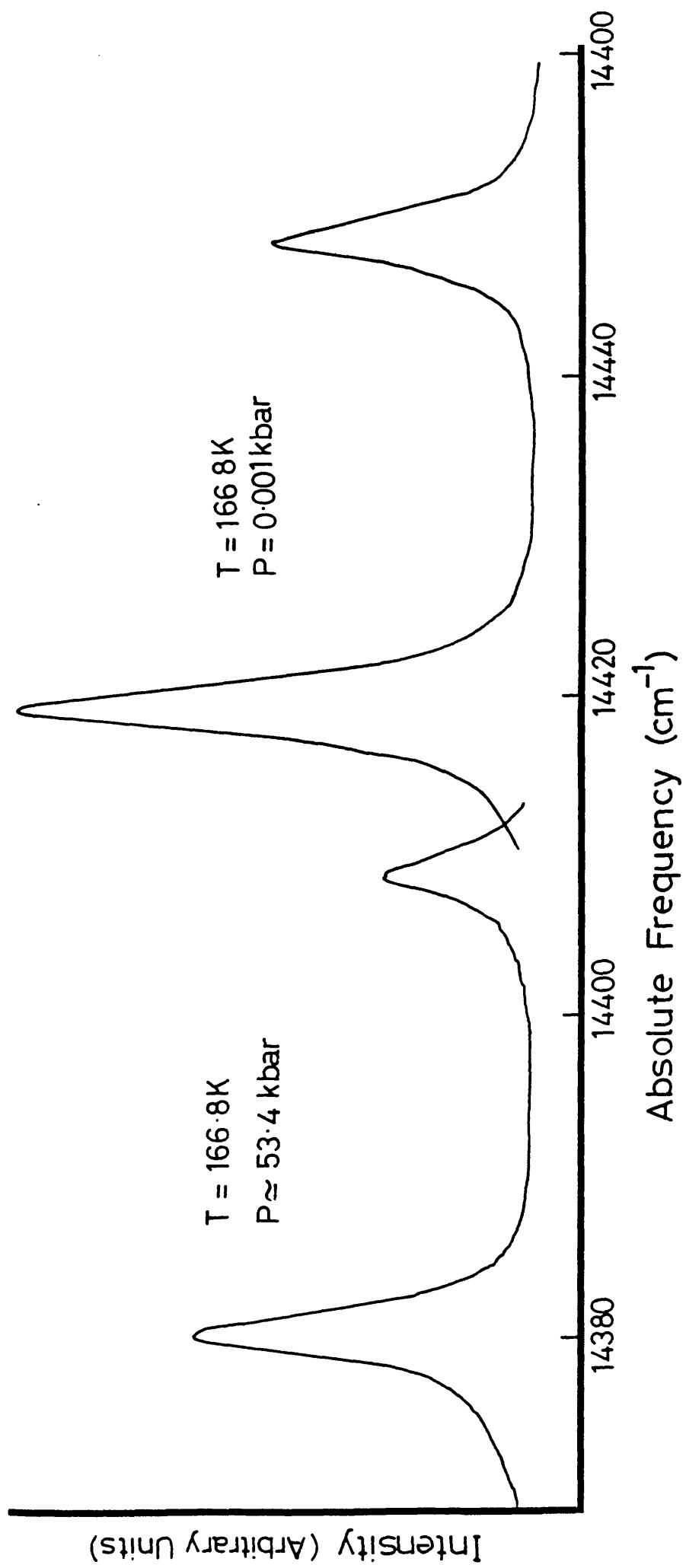


accuracy. Although we have studied several high-pressure phase transitions at temperatures down to ca. 160 K we consider that more reliable results are obtained if the transition is first induced at a suitably elevated temperature (e.g. ambient), followed by cooling. Clearly, this approach is not applicable if the phases desired are not stable above some low temperature.

Figure 3:4 shows the effect of cooling and pressure upon the R_1 and R_2 ruby lines. Cooling caused significant sharpening of both lines and an associated intensity increase. In our equipment there was a drop in applied pressure upon cooling: it was found that if a pressure of 4.5 kbar was applied at room temperature and the cell cooled to 166.8 K the $\nu(R_1)$ and $\nu(R_2)$ values were exactly those found at 166.8 K and at ambient pressure. A series of runs were performed in which pressure was applied at room temperature (and determined from R_1 and R_2 positions) followed by cooling to 166.8 K. The pressure at low temperature was taken to be that applied at room temperature less 4.5 kbar. In this way it was found that both R_1 and R_2 shifted by $0.73 \pm 0.02 \text{ cm}^{-1} \text{ kbar}^{-1}$ at 166.8 K. Up to 41 kbar the pressure experienced by ruby in methanol:ethanol remained hydrostatic but, above that, a non-hydrostatic component developed progressively. In a typical experiment R_2 shifted more than R_1 by 0.8 cm^{-1} at 53.4 kbar, indicating a non-hydrostatic component of ca. 1 kbar. We expect that the limit of hydrostatic pressure will be further depressed at lower temperatures in the methanol:ethanol (4:1) mixture. A very recent report by Fabre et al (Fabre et al 1975) shows that

Figure 3:4

Variation of the ruby R_1 and R_2 lines with pressure
at a temperature of 166.8 K.



the shift of R_1 has dropped to $0.6 \text{ cm}^{-1} \text{ kbar}^{-1}$ at 4.2 K in the range up to 9 kbar.

The sensitivity of $\Delta\nu_{1/2}$ to change of temperature in the region from ambient to ca. 150 K further emphasises the danger of using changes in this parameter as an indicator of the development of a non-hydrostatic component: we recommend the monitoring of ΔR as a more reliable procedure. In one experiment at 166.8 K we found that ΔR increased by 0.5 cm^{-1} , indicating a non-hydrostatic component, but $\Delta\nu_{1/2}$ actually decreased by 0.4 cm^{-1} , possibly due to local cooling.

$\Delta\nu_{1/2}$ and the estimation of pressure gradients

The widths of the R_1 and R_2 lines are subject to many variables of which temperature is one of the more important. If local heating occurs due to a laser beam or an i.r. source, for example, the increases in $\Delta\nu_{1/2}$ may be confused with those due to development of a shear stress. There is no doubt that $\Delta\nu_{1/2}$ is a sensitive indicator of the local strain experienced by a grain of ruby and, as such, will increase with increase of a non-hydrostatic component. However, the relationship between such increases is not simple, and cannot be used reliably to estimate the magnitude of local pressure gradients. Here we differ from others (Piermarini et al 1973) who, although admittedly aware of the dangers, have used $\Delta\nu_{1/2}$ increases in a semi-quantitative way, dividing the increase in $\Delta\nu_{1/2}$ consequent upon a pressure increase by $0.76 \text{ cm}^{-1} \text{ kbar}^{-1}$: we are not convinced that this procedure is valid; it

certainly leads to demonstrably false results. Thus, using this method to estimate pressure gradients in an ungasketed sample of NaCl in a DAC, a value of $6000 \text{ kbar cm}^{-1}$ was deduced. Pressure gradients of the order of 40 kbar cm^{-1} are commonly experienced, (Towle and Riecker 1966), but not values a hundred times this. Moreover the shear strength of NaCl at 50 kbar is only ca. 3 kbar, (Bridgman 1937b), a fact which underlies the Drickamer type of high pressure cell in which NaCl is used as a quasi-fluid. It is also relevant to recall that in an ungasketed sample there is a pressure multiplication effect and that this is dependent upon sample thickness, (Towle and Riecker 1966). This does not necessarily imply the existence of a large pressure gradient over the central region of the sample; the pressure multiplication effect may arise because the annular region does not support its share of the applied load. In view of these problems associated with $\Delta v_{1/2}$, we maintain that it is safer to use the shifts of the R_1 and R_2 lines for estimating both average pressure and pressure gradients under non-hydrostatic conditions.

3.4 Summary

The effect of pressure at low temperatures upon the R_1 and R_2 lines of ruby has been investigated for the first time to establish a calibration for use in high pressure/low temperature work. Also the R_1 and R_2 lines of ruby were re-investigated at ambient temperatures up to ca. 70 kbar and the half-band widths and separation of R_1 and R_2 were discussed, with respect to hydrostatic and non-hydrostatic pressures.

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CHAPTER 4

THE DIAMOND ANVIL CELL: HISTORY ANALYSIS AND DESIGN

CHAPTER 4

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4.1. History

The DAC design first appeared in the literature some eighteen years ago (Wier, Lippincott, Van Valkenberg, Bunting, 1959). An outline of the cell, and a section of the central portion are given in Figure 4:1. The central portion consisted essentially of two opposed diamond anvils; one held in a stationary holder (R) and the other in a movable holder (S). Pressure was generated by a screw (T) compressing a "calibrated" spring (U), and was transmitted to the moving anvil holder (S) via a lever arm (W) and presser plate (X); the sample was compressed between the two opposed diamond anvils.

So good was this initial design, that to date, the majority of DAC's around the world still follow it; that is, they maintain as a means of applying pressure on the central portion, the idea of a cell body, lever arms and a presser plate.

One exception to this is a new cell proposed by Holzapfel (1976) who moves away from the conventional design. A cross-section of the cell is shown in Figure 4:2. Here the pressure is applied on the cylindrical central insert by a compact system of levers. Development of the central portion has taken place along several different lines. While a complete survey of the development of the DAC is not attempted, areas of interest are covered below.

Figure 4:1 The Wier Cell

Parts Labelled	R Stationary diamond holder
	S Movable diamond holder
	T Pressure generating screw
	U Spring
	W Lever arm
	X Presser plate

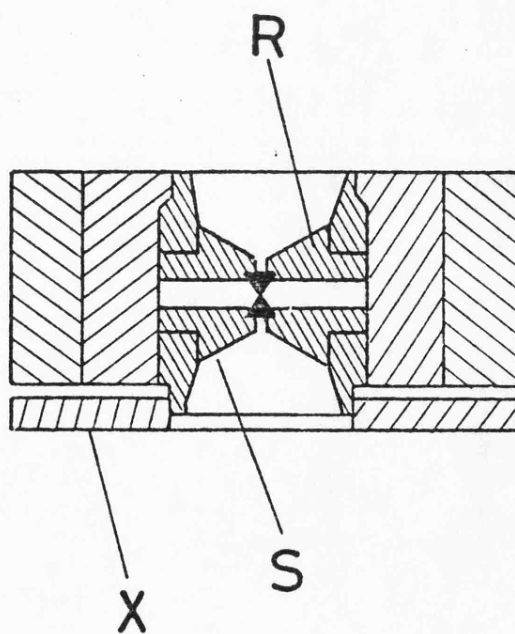
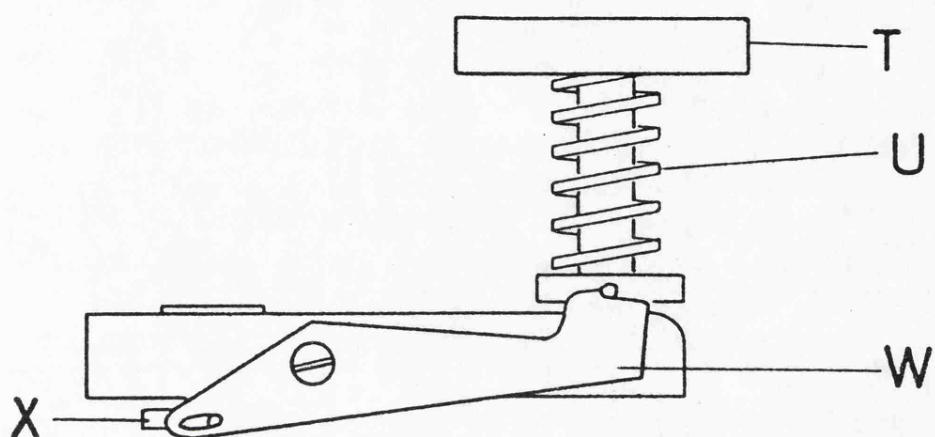
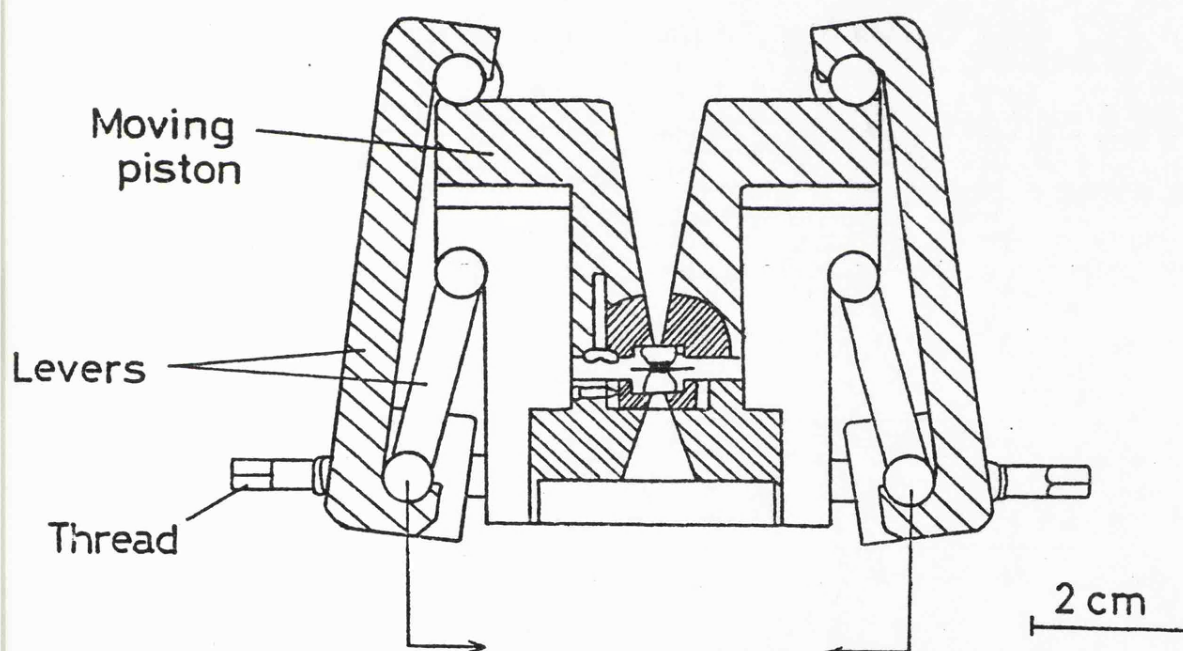


Figure 4:2

The Holzapfel Cell showing a new approach
to DAC work.



At the National Bureau of Standards, U.S.A., the Wier cell was redesigned and developed by Piermarini et al (1973) who produced the "Waspaloy" cell, Figure 4:3. This cell has pushed back the barriers of high pressure work and has had excursions to 600 kbar. It differs principally from Wier's cell in the following ways:

- i) It is larger and more robust.
- ii) The moving anvil is mounted on a hemisphere to facilitate alignment of the diamonds: the anvil holder has also been lengthened.
- iii) The fixed anvil holder is provided with translatory adjustment.
- iv) The spring (U) is replaced by Belleville spring washers.

Bassett, also in U.S.A., came up with ideas producing a small compact diamond anvil device, Figure 4:4a (Bassett 1974) capable of reaching 25 kbar. He was also the first to produce a DAC with two half cylinders or rockers immediately behind the diamond anvils, Figure 4:4b (Bassett 1967). These are to provide for initial alignment of the diamonds and also to provide some translational freedom.

In our own group, research with the DAC began with the arrival of a version of the Wier cell from the U.S.A. From this, our Mark I cell was developed in collaboration with Beckman R.I.I.C. Ltd. (Adams, Payne, and Martin 1975) and is shown in Figure 4:5.

Figure 4:3

The Waspaloy Cell

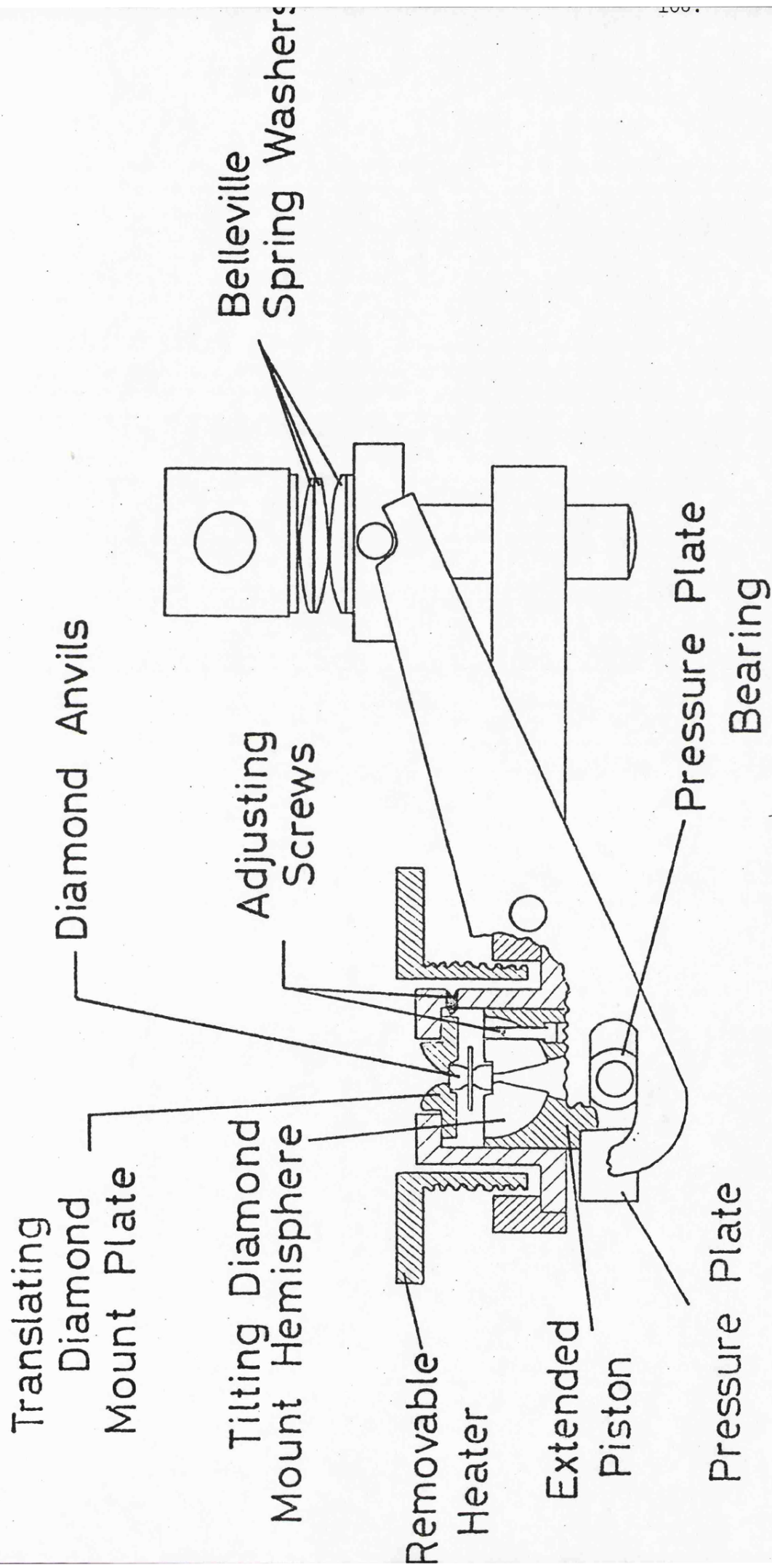


Figure 4:4

The Bassett cells (a) A simple diamond anvil device

(b) A more conventional cell showing
the first use of half cylinders
as anvil supports

Parts shown (a) (1) Stainless steel platens

(2) Beryllium discs

(3) Inconel gasket

(4) Diamond anvils

Parts shown (b) (A) Diamond anvils

(B) Stationary piston

(C) Sliding piston

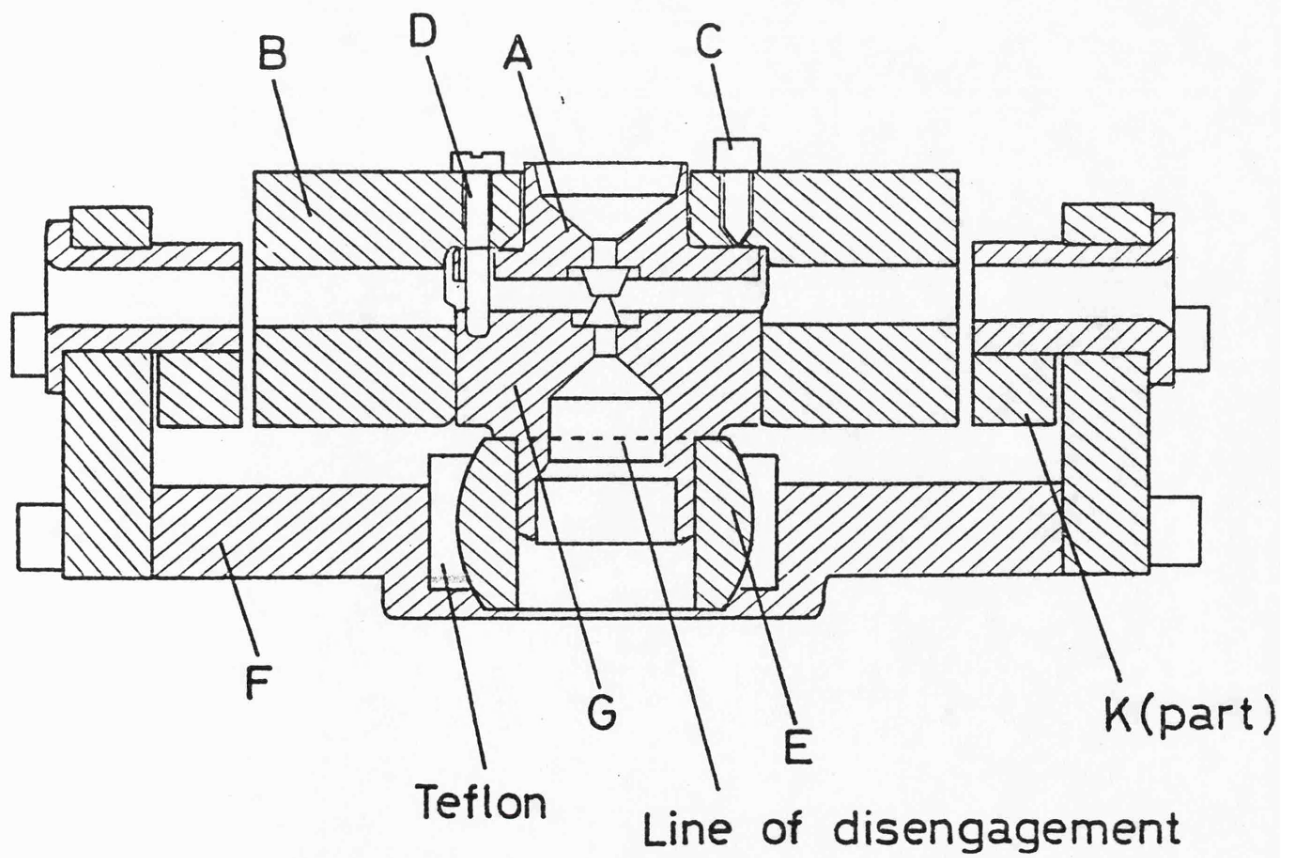
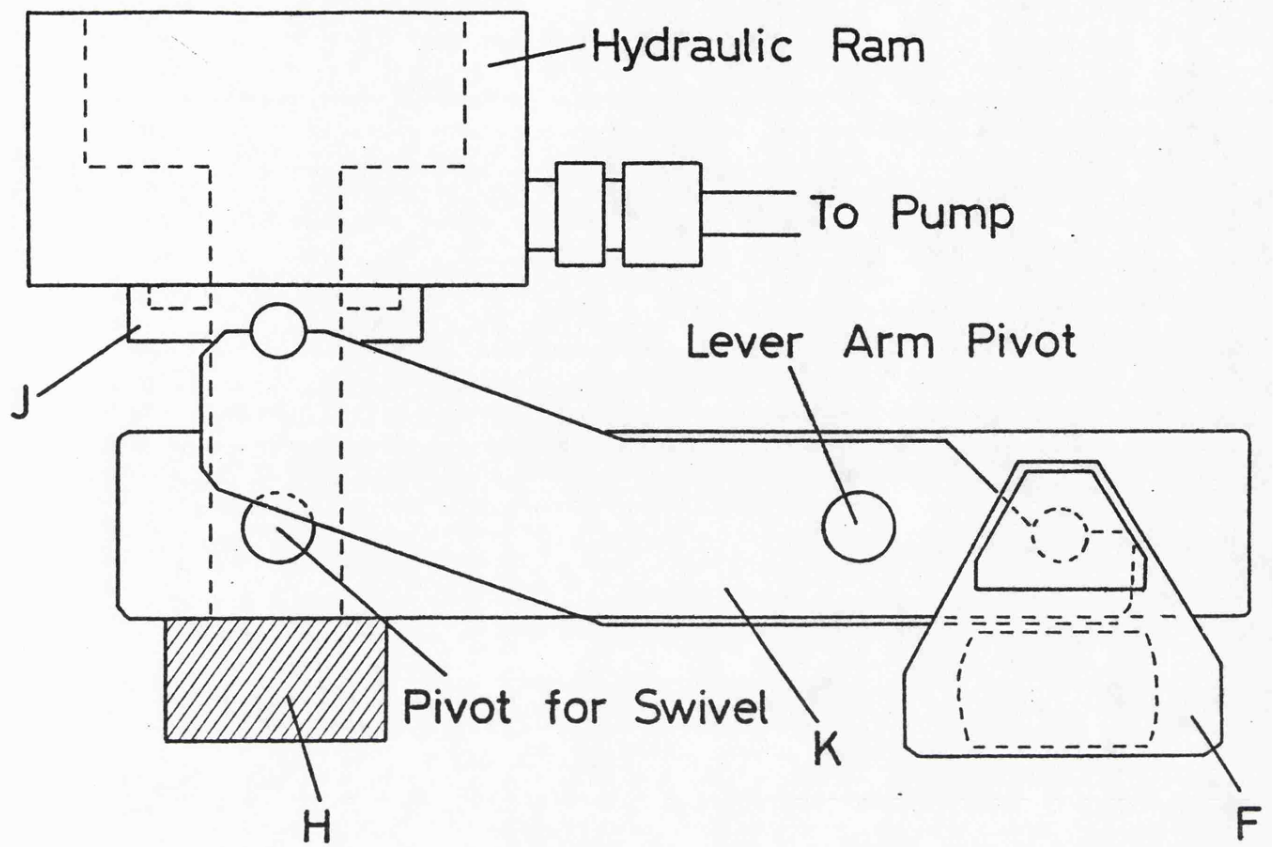
(D) Driver screw

Figure 4:5

Mark I cell outline and section of the central portion.

Parts labelled are:

- | | |
|---|----------------------------------|
| A | Fixed anvil |
| B | Main body of cell |
| C | Adjusting screw |
| D | Radial locating pin |
| E | PTFE lined hemispherical bearing |
| F | Presser plate |
| G | Moving anvil |
| K | End part of lever arm |



The body of the cell was made from aluminium alloy and all other parts were made from KE 896 steel. It differs from Wier's cell principally in the following ways.

- i) The pressure was applied by a hydraulic ram of particular use when the cell was used in vacuo.
- ii) The pressure was transmitted from the presser plate (F) to the moving anvil (G) by means of a hemispherical bearing (E). This was to prevent the presser plate (F) from forcing the diamonds to misalign. It is now known that hemispherical bearings can be very inefficient if misalignment occurs at large applied loads.

Having obtained results with the Mark I cell and used it for some time, it was felt that it could be considerably improved and modified to give a cell which could be used at high pressures and temperatures from 150 to 500 K. A Mark II cell was therefore designed (Payne 1975) and is shown in Figure 4:6. It differed from the Mark I cell principally again in the central portion, but retains the idea of a cell body, lever arms and presser plate. The central portion was now insulated by the paxolin parts 1a and 5a. Part 1b (the central insert) had an extended nose piece onto which a heating or cooling coil could be placed. The hemispherical bearing (Part 2) was abandoned as it had proved inefficient. The anvil supports behind the diamonds were also shaped to give effective conical light pipes for use in the far i.r.

Figure 4:6

The Mark II cell outline and section of the central portion.

Parts labelled are:

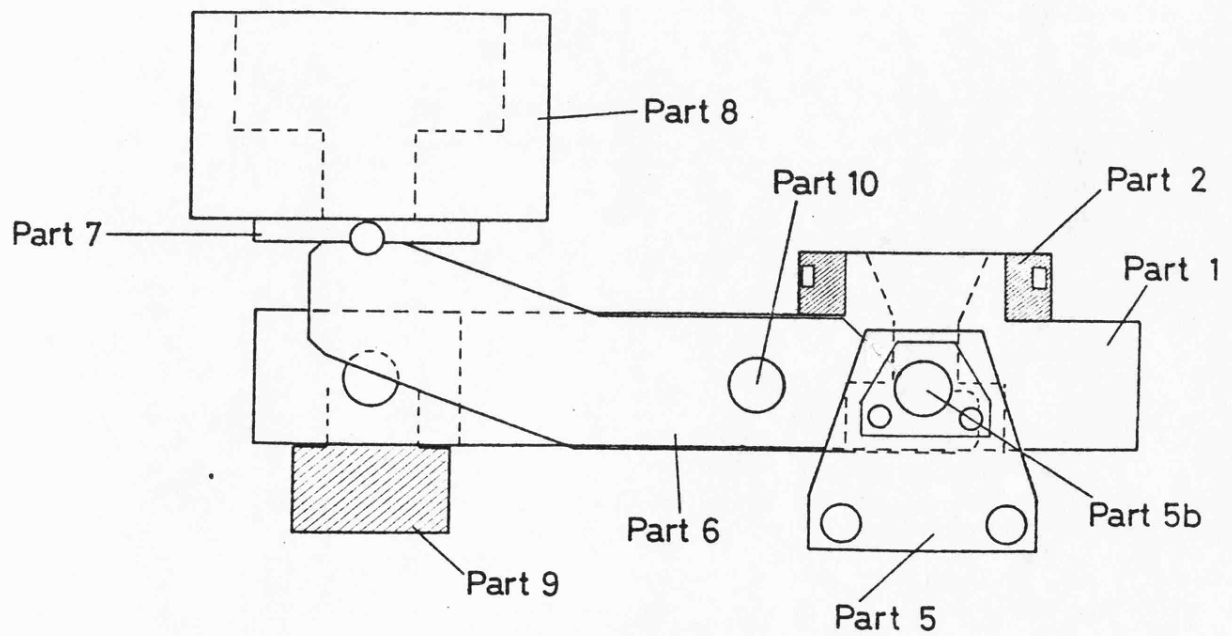
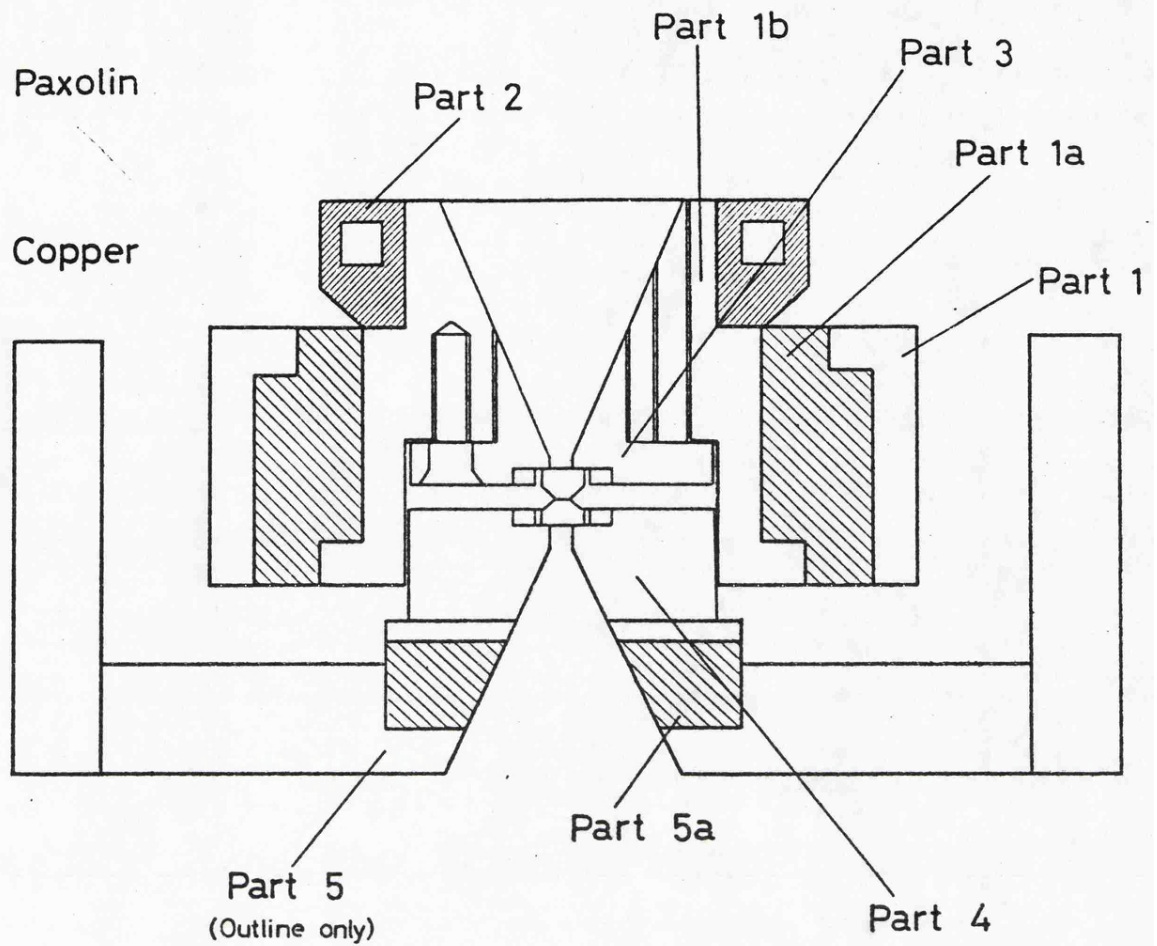
Part	1	Cell body
	1b	Central insert
	2	Copper annulus
	3	Fixed anvil holder
	4	Moving anvil holder
	5	Presser plate
	5a	Paxolin washer
	5b	Presser plate pivot
	6	Lever arms
	7	Piston plate
	8	Hydraulic piston
	9	Knurled backing screw
	10	Central pivot



Paxolin



Copper



The Mark II cell was modified by the author; the length of contact of the moving piston with the barrel was lengthened to give more stability, causing the force to act normally to the diamonds, thereby preventing misalignment. A second locating pin was added so that a gasket with two holes in it could be positioned accurately over the diamonds. More recently a central insert of the Waspaloy type was designed and used by the author; Figure 4:7. This is known as the Mark IIa cell. The Mark II cell could be criticised on the following points. Firstly, pressures are limited to less than 100 kbar because the diamonds misalign above this pressure, due to bad design of the central insert and cell body. (They were never really designed for pressures in excess of 50 kbar). Secondly, the central insert is made of stainless steel which is a very bad thermal conductor; therefore temperature variation experiments were limited. Advantages of the Mark II cell are that it offers some temperature variation and is easy to load, and is versatile in the sense that it can be used for spectroscopy in i.r., far-i.r., u.v., and Raman spectrometers.

One other cell which deserves note was reported by Mao and Bell (1975). It achieved the enormous pressure of 1 megabar, albeit on a small sample. The centre and an outline of this cell are shown in Figure 4:8. The points to note are that the moving anvil piston was very long, the diamond anvil supports were made of tungsten or boron carbide and the cell body was stepped to prevent any unnecessary translatory force being passed to the

Figure 4:7

Mark IIa DAC - section of central insert

The cell body is the same as that for the Mark II cell.

Parts labelled:

- | | |
|----|------------------------|
| 1 | Cell body |
| 1b | Central insert |
| 2 | Copper cooling annulus |
| 3 | Fixed anvil holder |
| 4 | Moving anvil holder |
| 5 | Presser plate |
| 5a | Paxolin insert |
| 5b | Presser plate pivot |
| 6 | Lever arms |
| 7 | Piston plate |
| 8 | Hydraulic ram |
| 9 | Knurled backing screw |
| 10 | Central pivot |

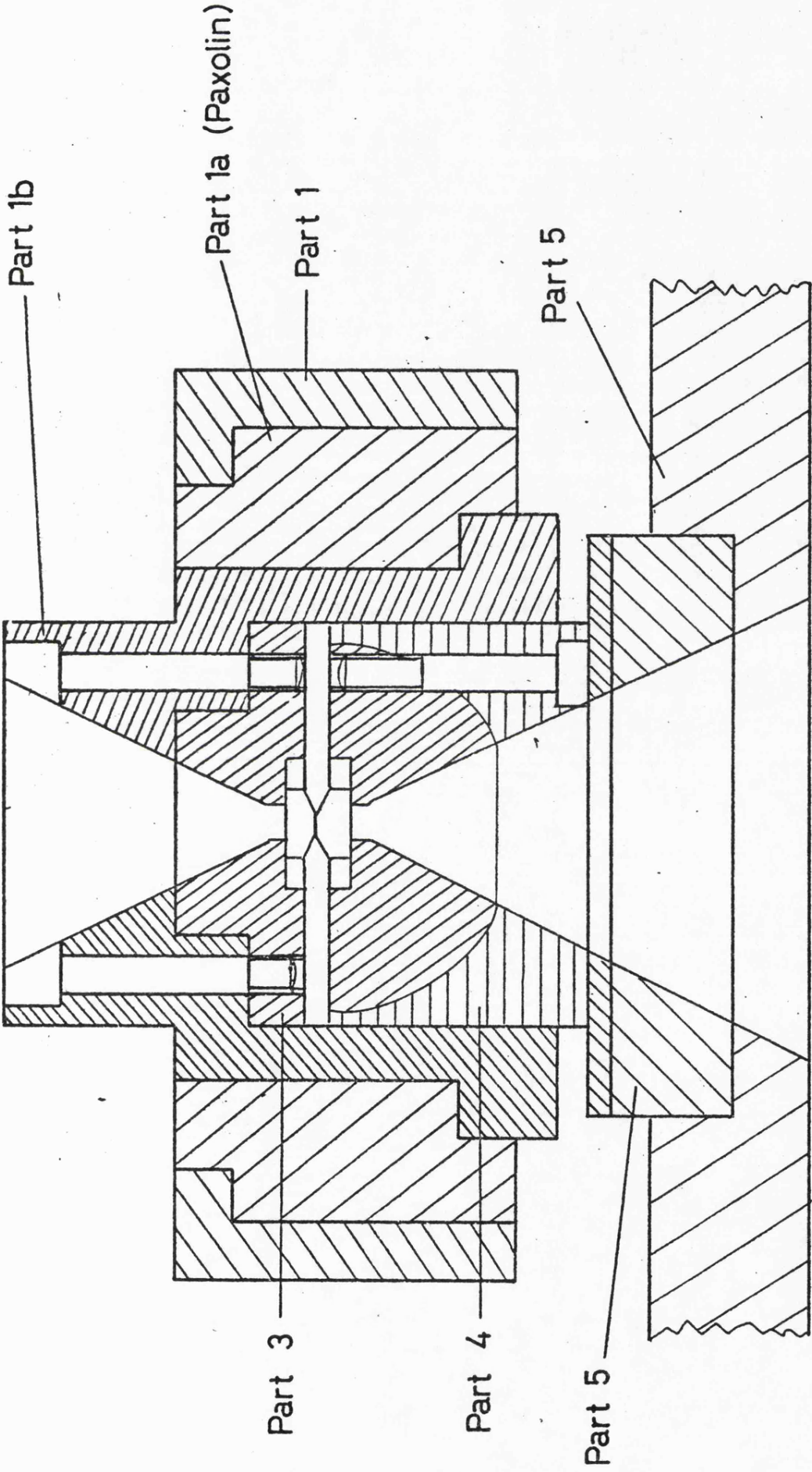
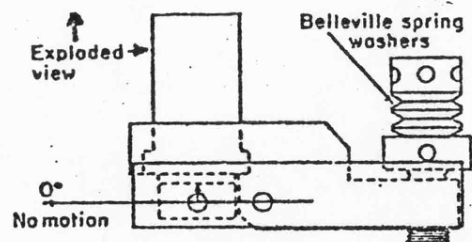
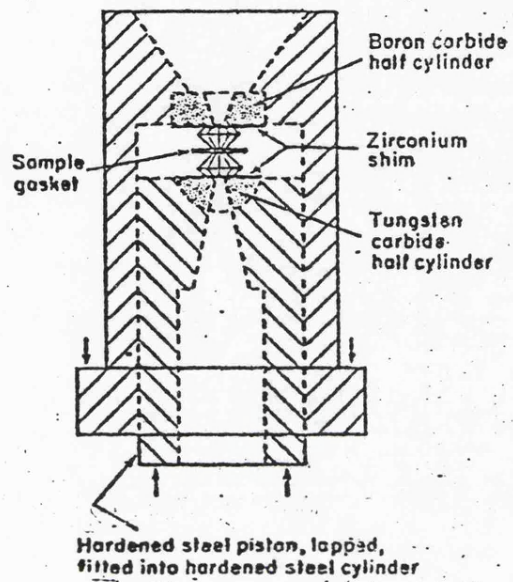


Figure 4:8

The Mao and Bell cell showing a long moving anvil holder and a stepped cell body.



moving anvil holder by the lever arms.

The brief summary given illustrates development of the DAC in our own laboratory and elsewhere, the point being that as we have become more and more demanding in our experimental results, and as we have needed hydrostatic pressures up to 100 kbar or more and temperature variation from 4 K (Webb et al 1976) to 2000 K (Mao and Bell 1975) DAC designs have altered and progressed to what they are today. While the basic layout is settled, development still goes on in trying to reach ultra-high pressures.

At this stage it was decided to look at the Mark IIa DAC analytically and design a Mark III cell which would solve some of the problems which had developed in the former. For this reason a full structural analysis of the Mark IIa DAC was undertaken and is presented below. From this analysis it was proposed to design a cell capable of excursions to 1 megabar (10⁸ Pa) and which would still be capable of giving spectroscopic information.

4.2. Structural Analysis of the DAC

An analysis of this type clearly goes into the realms of engineering and a good introduction to the subject can be found in Roark (1954). I would like to acknowledge the help of Mr. C.M. Morrison, Leicester University Engineering Department, who checked the final calculations and provided helpful discussion.

Definitions of basic words used in conjunction with this subject are given below.

Bending moment (refers to a beam) : the bending moment at any section of the beam, is the moment of all forces that act on the beam to the left of that section, taken about the horizontal axis of the section, for a horizontal beam loaded vertically.

Strain : Any forced change in the dimension of a body, e.g. a stretch is a "tensile strain".

Stress : The internal force exerted by either of two adjacent parts of a body upon the other across an imagined plane of separation, is defined as "stress". When the forces are parallel to the plane of section, the stress is called "shear stress".

A mathematical analysis of the type to be undertaken assumes that the material is elastic, isotropic, homogeneous, infinitely divisible without change in properties, and that Hooke's law is obeyed. Whilst none of these assumptions are strictly true, a stress or strain derived mathematically is found nearly always to be within experimental error of the real stress or strain; that is the approximations are realistic.

In any structural analysis the weakest possible part of the structure is always considered, that is the analysis must always consider the minimum section of the part being studied. The reason for this is that if the minimum section of the part considered will support the maximum load expected for the design, we are sure this part will not fail.

Each part of the Mark IIa DAC shown in Figure 4:7 will be considered in turn, working outwards from the diamond anvils. If we consider a certain maximum pressure required, for instance 1 megabar (10^{11} Pa) at the diamond, we can calculate the force required to achieve this.

$$F = PA$$

$$F = \text{Force N}$$

$$P = \text{Pressure Pa}$$

$$A = \text{Area M}^2$$

The rapid increase in applied force as the area increases is evident, see Table I. For this analysis we will consider a diamond with surface area 10^{-6} M² bearing 10^{11} Pa with a base of 10^{-5} M². The corresponding force through the centre of the diamond anvil is 10^5 N.

The shape of the diamond anvil itself is obviously of paramount importance. The only criterion is that it should obey the principle of "massive support". Whilst this is a statement of common sense diamond anvils have failed in use when they have been too thin or too narrow. Two exaggerated drawings of diamond anvils which do not obey this principle are shown in Figure 4:9a,b; the anvils currently used by the author (c), Piermarini (d), Holzapfel (e), and Mao and Bell (f), are also shown. One other point of note is that the face of the diamond anvil, the one which bears the load, should be the main cleavage plane 1,1,1 as it is impossible for the diamond to cleave along this plane if the force is normal to it. It is in fact impossible to polish diamonds along

Table I

The relationship between applied force and surface area of the diamond anvil when we generate 10^{11} Pa.

$$P = 10^{11} \text{ Pa}$$

	A (M ²)	F (N)
1	$1.5^2 \times 10^{-6}$	2.25×10^5
2	$1.0 \times 10^{-6} \text{ }^\dagger$	$1 \times 10^5 \text{ }^\dagger$
3	$(0.75)^2 \times 10^{-6}$	5.6×10^4
4	$(0.5)^2 \times 10^{-6}$	2.5×10^4
5	$(0.25)^2 \times 10^{-6}$	6.25×10^3

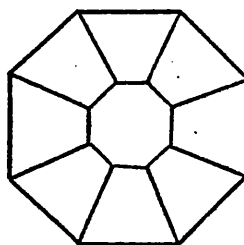
[†] Values used in the hypothetical analysis of the Mark IIa cell.

Figure 4:9

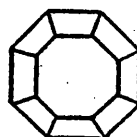
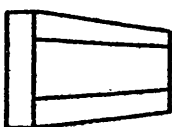
Various diamond anvils

- a) and b) A diamond not obeying the principal
 of massive support
- c) Diamond used by author
- d) Diamond used by Piermarini (1973)
- e) Diamond used by Holzapfel (1976)
- f) Diamond used by Mao and Bell (1975)

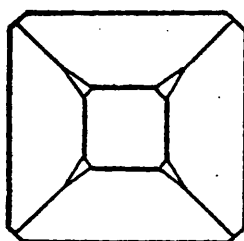
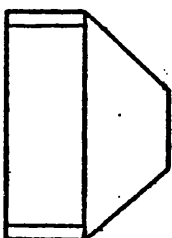
a



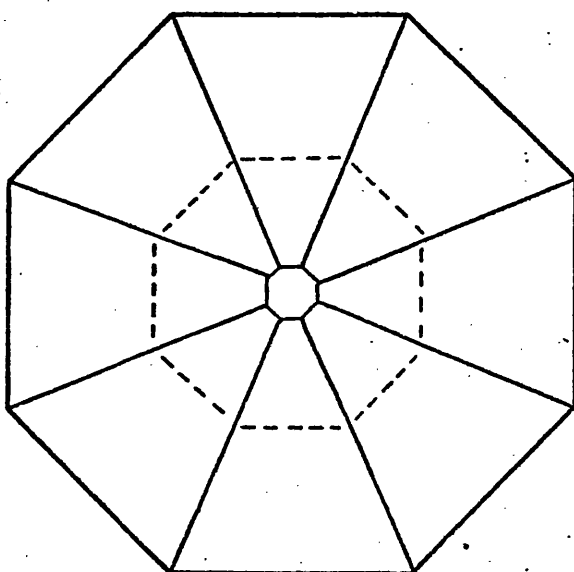
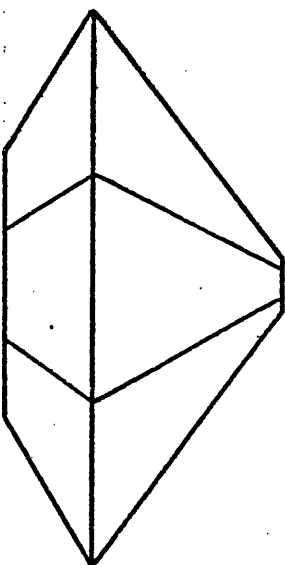
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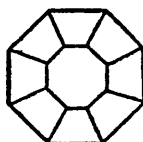
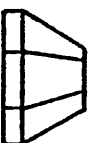
c



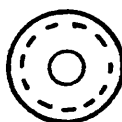
d



e



f



1mm

this plane and an offset of approximately 5° to it was finally settled upon. All the diamonds used in this work were produced by L.M. Van Moppes Ltd., Basingstoke. Other types of anvil have been tried and some success has been achieved at low pressure using sapphires and tungsten carbide.

If the force through the centre of the diamond is 10^5 N and the base of the diamond anvil is 10^{-5} m² the material immediately behind the diamond will need a compressive strength equal to S_c where

$$\left(\frac{F}{A}\right) = S_c = \frac{10^5}{10^{-5}} = 10^{10} \text{ NM}^{-2}$$

We must now consider the stress experienced by parts immediately behind the diamond anvil supports in the Mark IIa cell. All parts are clearly labelled with part numbers; Figures 4:6, 4:7. The central insert Part 1b, can be divided up as shown in Figure 4:10 into two circular flanges 1bi, 1biii and a hollow cylinder 1bii for the purpose of analysis.

Central Insert, Part 1bi Circular Flange

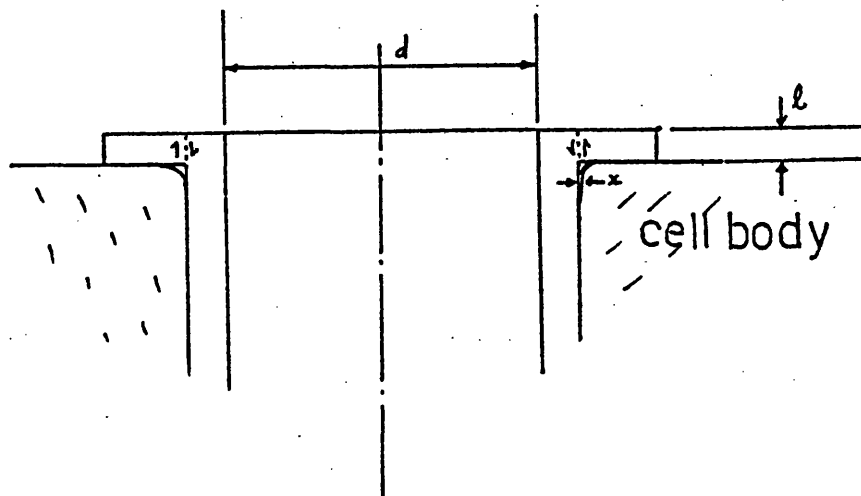
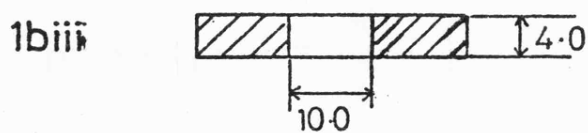
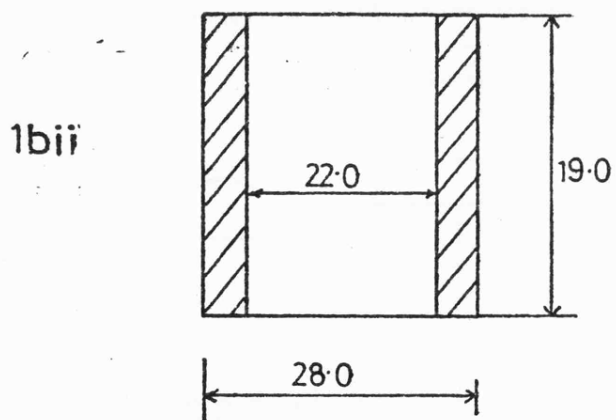
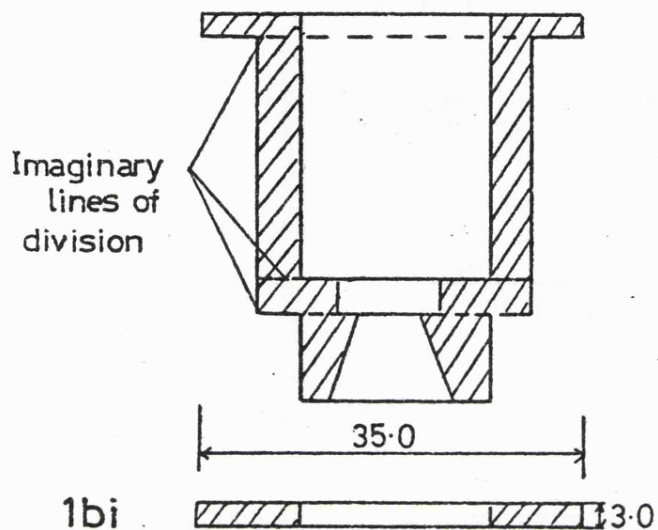


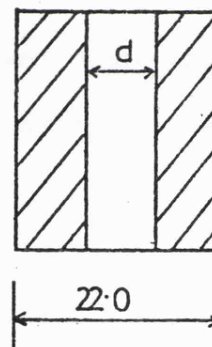
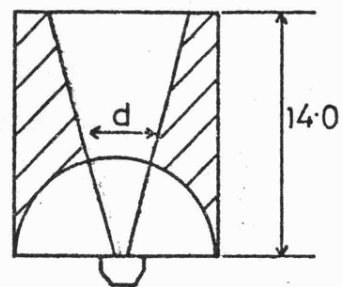
Figure 4:10

The central insert of the Mark IIa cell showing
lines of hypothetical divisions considered in
analysis.

Part 1b



Part 4



$$d = 7.0 \times 10^{-3} \text{ m}$$

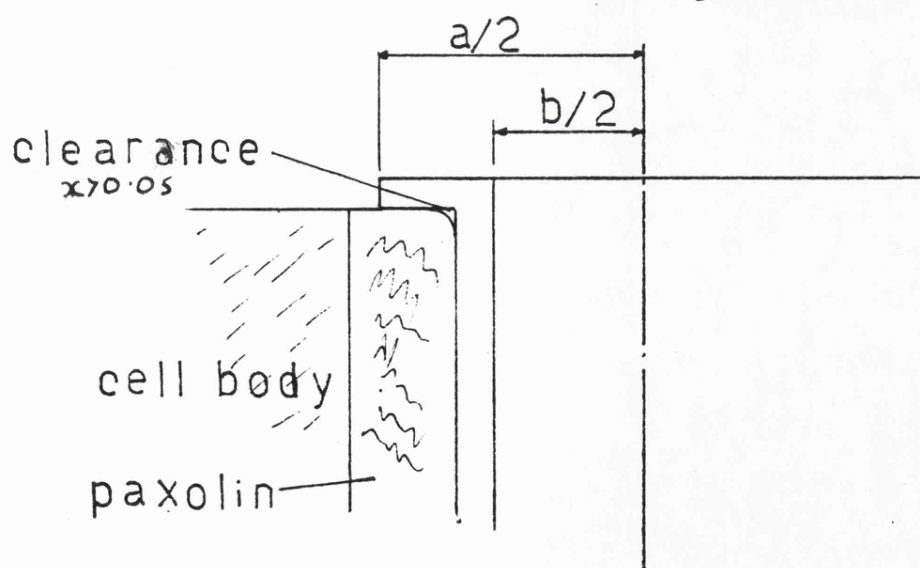
If the clearance between the support and the barrel (x) is small (< 0.05 mm), there will be no bending of the flange.

Therefore we can consider the shear stress indicated in the diagram.

$$\begin{aligned}\tau &= F/A & \tau &= \text{shear stress} \\ &= \frac{10^5}{d \cdot \pi \cdot l} & d &= \text{diameter in M} \\ & & l &= \text{length in M} \\ &= \frac{10^5}{\pi \cdot 28 \cdot 3 \cdot 10^{-6}}\end{aligned}$$

$$\therefore \text{Shear stress } \tau = 3.8 \times 10^8 \text{ N M}^{-2}$$

Consider now the same case with bending allowed, that is, as in our Mark IIa cell where we have a paxolin or asbestos insert.



This is a typical example of a circular flat plate loaded on its inner edge and supported uniformly. This corresponds directly to case number 16 part 1 Roark (1954).

$$A = 346 \times 10^{-6} \text{ M}^2$$

$$\omega = \frac{F}{A} = \frac{10^5}{346 \times 10^{-6}} \quad \omega = \text{unit applied load}$$

$$\underline{\text{unit applied load} = 2.9 \times 10^8 \text{ NM}^{-2}}$$

$$\sigma_{\max} = WZ \quad \sigma_{\max} = \text{maximum stress}$$

where

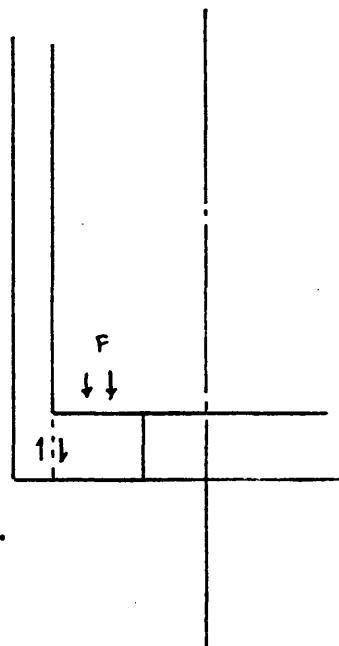
$$W = \frac{3 \omega}{4mt^2(a^2 - b^2)} \quad \begin{array}{l} t = \text{thickness in M} \\ m = \text{Poissons number (3)} \\ a \text{ and } b \text{ defined in diagram above} \end{array}$$

$$Z = 3a^4(m+1)\log\frac{a}{b} + 4a^2b^2 + b^4(m-1) - a^4(m+3)$$

$$\therefore \sigma_{\max} = 3.1 \times 10^{16} \times 5.3 \times 10^{-7}$$

$$\underline{\text{Maximum stress} = 1.7 \times 10^{10} \text{ NM}^{-2}}$$

Part lbiii Circular Flange - This can be considered in pure shear stress as there will be little bending.



indicates line
of shear stress

$$\tau = \frac{F}{A} = \frac{10^5}{d\pi l} = \frac{10^5}{22 \cdot \pi \cdot 4 \cdot 0.10^{-6}}$$

$$\text{Maximum shear stress} = 3.6 \times 10^8 \text{ NM}^{-2}$$

Part lbii Hollow cylinder - This can be analysed as follows.

$$\sigma_{\max} = \frac{F}{A} = \frac{10^5}{\pi(14^2 - 11^2) \times 10^{-6}}$$

$$\text{Maximum stress} = 4.2 \times 10^8 \text{ NM}^{-2}$$

The deformation can be calculated

$$\epsilon = \frac{\sigma_{\max}}{E}$$

E = Modules of elasticity see Table

ϵ = unit longitudinal strain

ϵ' = unit transverse strain

V = Poissons number

$$= 2.2 \times 10^{-3}$$

$$\therefore \text{The longitudinal deformation} = \underline{\ell \epsilon = 4.2 \times 10^{-5} \text{ M}} \text{ (stretch)}$$

$$\epsilon' = V\epsilon$$

$$= 0.3 \times 2.2 \times 10^{-3}$$

$$= 6.6 \times 10^{-4}$$

$$\text{Lateral deformation} = \underline{d\epsilon' = 1.8 \times 10^{-5} \text{ M}} \text{ (decrease in diameter)}$$

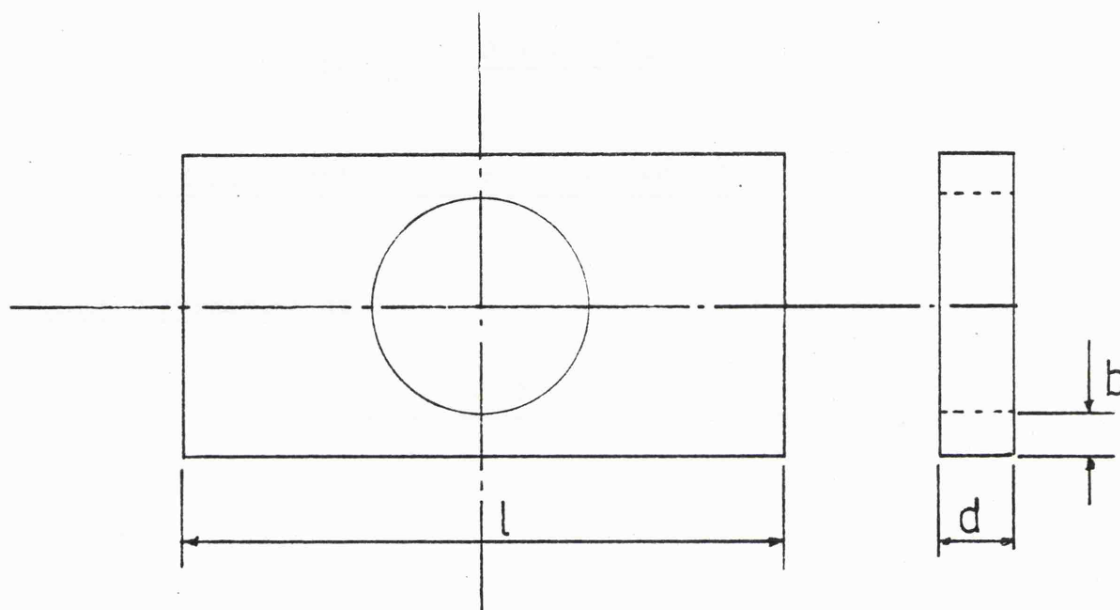
Part 4 The Moving Piston (hollow cylinder) - This can be analysed in the same manner if it is considered as a cylinder with a hole of radius equal to the radius of the cone at half height, as shown in the figure.

$$\sigma_{\max} = 4.4 \times 10^8 \text{ NM}^{-2}$$

$$\text{Compression of piston along axis} = \underline{3.2 \times 10^{-5} \text{ M}}$$

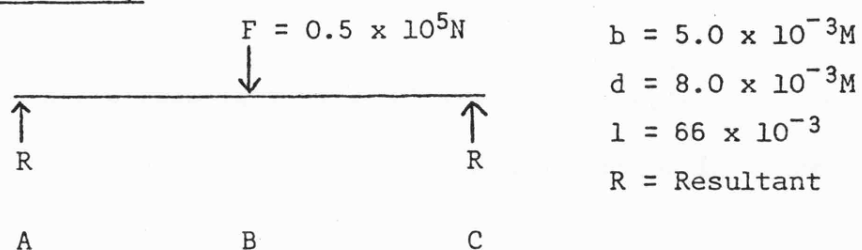
$$\text{Lateral expansion of piston} = \underline{1.6 \times 10^{-5} \text{ M}}$$

Part 5 The Presser Plate



Considering the plate in minimum section as indicated above it can be regarded as two beams interconnected by a web. Analytically, the problem is considered in terms of one beam dimension b by d , length l carrying half the force.

Diagrammatically



This case is again presented in Roark (1954), 109, case 11.

Resolving Vertically

$$2R = 0.5 \times 10^5$$

$$\underline{R = 2.5 \times 10^4 \text{ N}}$$

Maximum Bending Moment at B

$$BM_{\max} = \frac{0.5 \times 10^5 \text{ l}}{4}$$

$$\underline{\text{Maximum Bending Moment at B} = 8.4 \times 10^2 \text{ N M}^{-2}}$$

Maximum deformation at B

$$y_{\max} = \frac{1}{48} \times \frac{0.5 \times 10^5 \text{ l}^3}{EI} \quad I = \text{moment of inertia}$$

$$I = \frac{bd^3}{12}$$

$$\text{Maximum deformation at B, } \underline{y_{\max} = 7.4 \times 10^{-3} \text{ M}}$$

Maximum fibre stress at B

$$\sigma_{F\max} = \frac{6 BM_{\max}}{bd^2} = 7.72 \times 10^9 \text{ N M}^{-2}$$

The maximum stress is $7.72 \times 10^9 \text{ N M}^{-2}$ at B, being compression in the fibres at the top of the beam and tension in fibres at the bottom of the beam.

Part 5b The Presser plate pivot. We can consider this again in pure shear as there will be little bending.

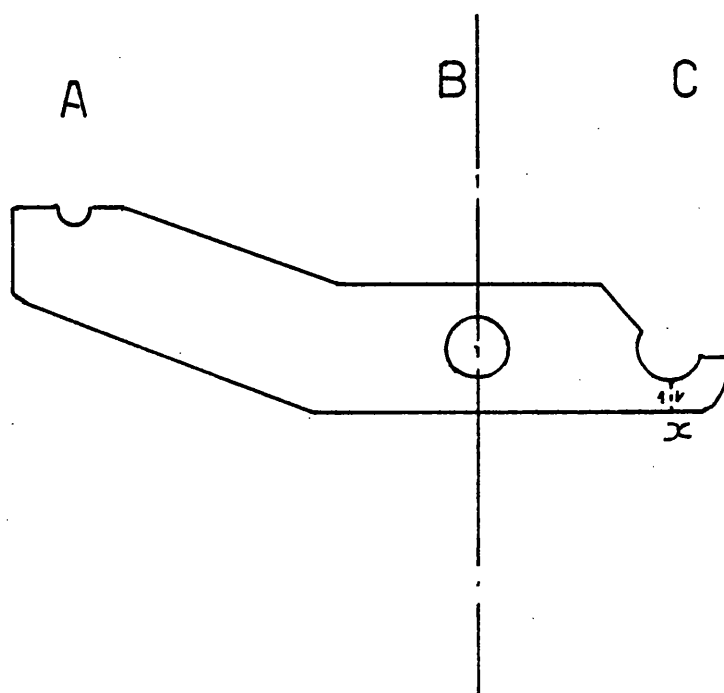
$$A = \pi(3.5)^2 \times 10^{-6}$$

$$\tau = \frac{5.0 \times 10^4}{A} = 1.3 \times 10^9$$

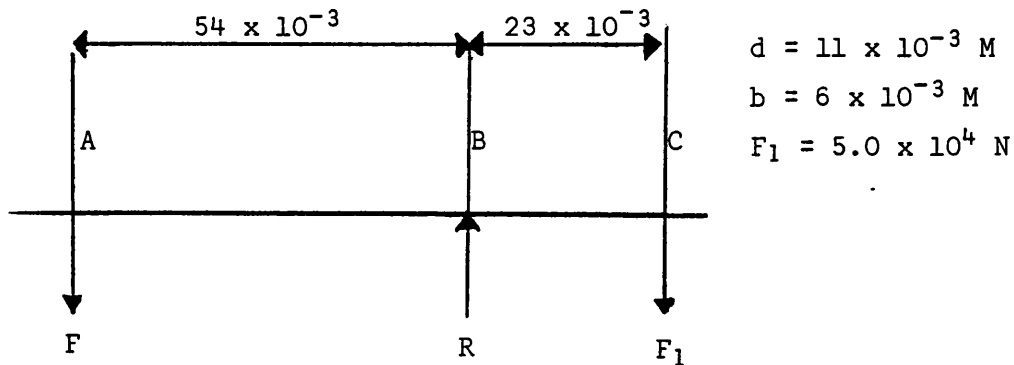
Maximum shear stress is $1.3 \times 10^9 \text{ N M}^{-2}$

Part 6 The lever arms.

The lever arms can be considered as straight beams as the radius of curvature is greater than ten times the depth (Roark 1954). Again we must consider minimum section, which is taken as the width of the lever arm minus the diameter of the hole for the central pivot. The reason for not considering the section x indicated in the diagram, is that the main fibre strain will be over the central pivot at B. But the force at the presser plate end is calculated and the section (x) is considered in pure shear.



Diagrammatically



Taking Moments about B

$$54 \times 10^{-3} \times F = 23 \times 10^{-3} \times F_1$$

$$\therefore \underline{F = 2.0 \times 10^4 \text{ N}}$$

Resolving Vertically

$$R = F + F_1 = \underline{7.0 \times 10^4 \text{ N}}$$

Considering possible shear at C

$$\tau = \frac{F}{A} = \frac{5.0 \times 10^4}{5.5 \times 6 \times 10^{-6}}$$

Maximum shear stress at C, $\tau = \underline{1.5 \times 10^9 \text{ N M}^{-2}}$

Maximum Bending Moment at B (using same method as for Part 5)

$$M_{B \text{ max}} = \frac{7.0 \times 10^4 \times 54 \times 23 \times 10^{-6}}{77 \times 10^{-3}} = 1.13 \times 10^3 \text{ NM}$$

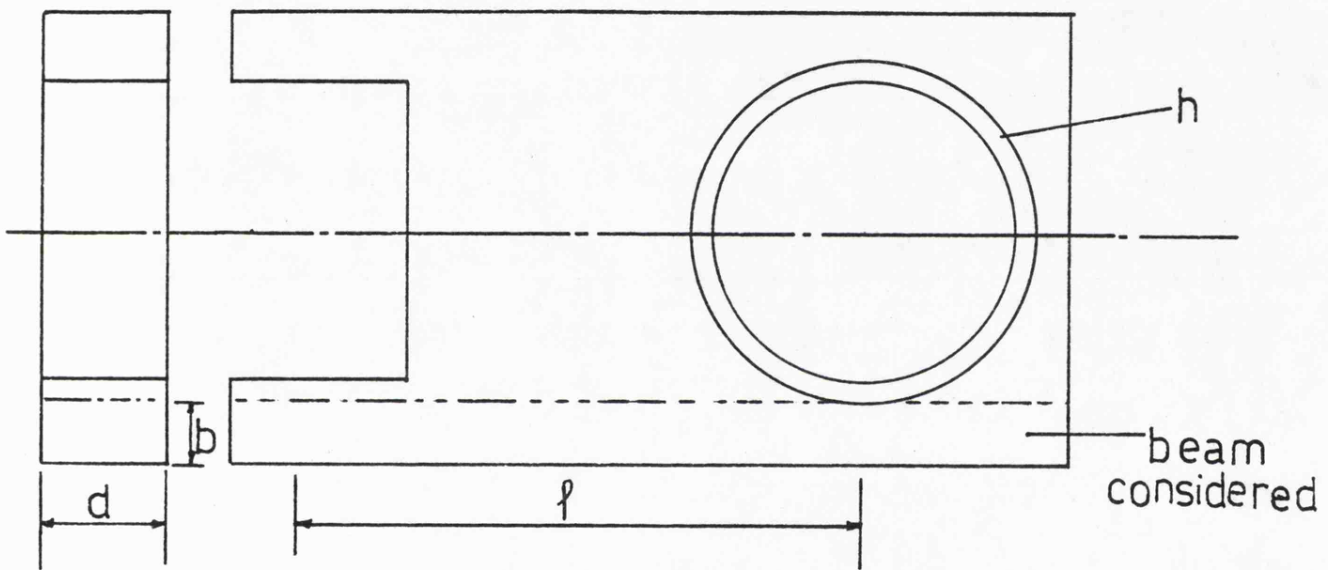
Maximum fibre stress = $\underline{9.3 \times 10^9 \text{ N M}^{-2}}$ being compression at the

bottom of the beam and tension at the top of the beam, at B.

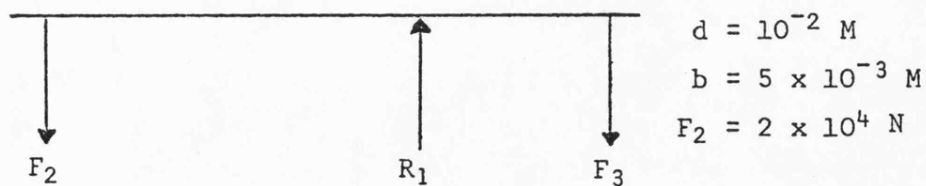
Similarly maximum deformation = $5.4 \times 10^{-4} \text{ M}$

Part 1 Cell Body

This again can be analysed as a thin beam, as indicated in the diagram, taking the minimum section indicated.



Diagrammatically



$$d = 10^{-2} \text{ M}$$

$$b = 5 \times 10^{-3} \text{ M}$$

$$F_2 = 2 \times 10^4 \text{ N}$$

As for the lever arms

$$F_2 = 2.0 \times 10^4 \text{ N}$$

$$F_3 = 5.0 \times 10^4 \text{ N}$$

$$R = 7.0 \times 10^4 \text{ N}$$

$$BM_{\max} = 1.13 \times 10^3 \text{ NM}$$

$$\sigma_{F\max} = 1.1 \times 10^{10} \text{ NM}^{-2}$$

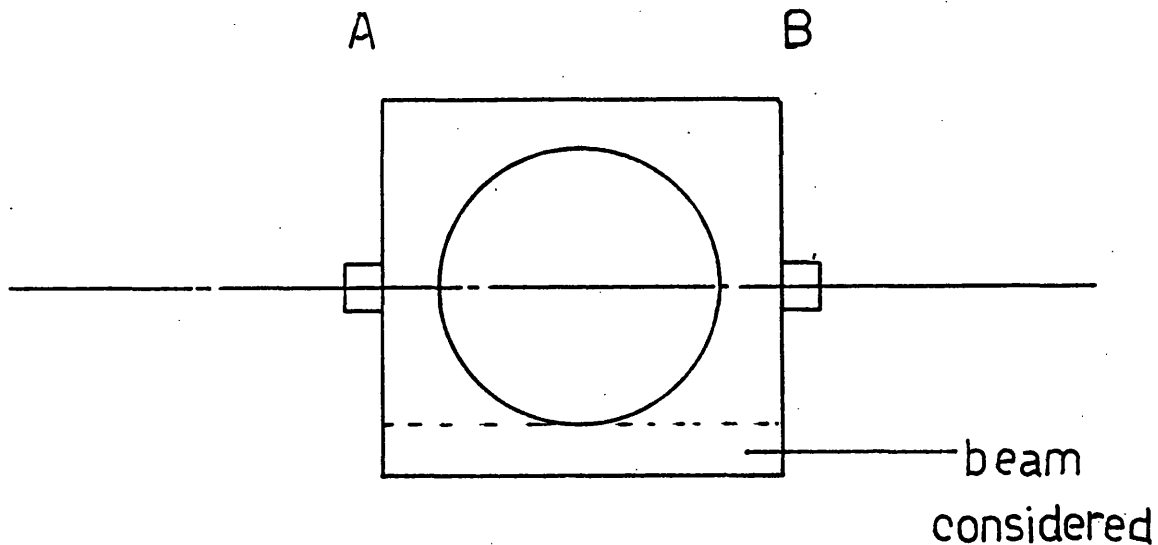
$$\text{Maximum deformation} = 2.3 \times 10^{-3} \text{ M}$$

The cell body also has a circular flange.h which can be analysed in pure shear.

$$\tau_{\max} = \frac{1.0 \times 10^5}{3 \times 44 \times 10^{-6} \times \pi}$$

$$\text{Maximum shear stress} = \underline{2.4 \times 10^8 \text{ N M}^{-2}}$$

Part 7 The Piston plate. This can be analysed as two thin beams as was the cell body.



$$BM_{\max} = 2.5 \times 10^2 \text{ N M}$$

$$\sigma_{F\max} = 1.17 \times 10^{10} \text{ N M}^{-2}$$

$$\text{Maximum deformation} = 6.3 \times 10^{-3} \text{ M}$$

The pins can be analysed in pure shear to give a maximum shear stress of $1.6 \times 10^9 \text{ N M}^{-2}$.

Part 8 The hydraulic ram

The hydraulic ram would have to generate a force of 4×10^4 N as it has a surface area of 1.0×10^3 M². This would require a pressure of 4×10^7 N M⁻² (5730 psi). Considering the hydraulic ram o-ring seal supports, it can be shown that in pure shear, they would need to be able to withstand a stress of 4×10^8 N M⁻², presuming they did not bend but failed by shearing. The threaded portion of the hydraulic ram will have to survive a stress of 5.3×10^8 N M⁻² and the knurled backing screw 7.4×10^8 N M⁻².

4.3. Design of the Mark III DAC

The analysis for a 10^{-6} M² diamond bearing 10^{11} Pa in our existing Mark IIa cell is summarised in Table II. The stress or deformation for any part with any size of diamond at any pressure can simply be estimated from this table. The dimensions of the part in question must remain constant. Relevant data for a design of this type are given in Table III (mechanical properties and physical properties of useful materials) and Table IV (the upper limits of other high pressure cells with their equivalent diamond sizes). What is immediately obvious from Table II and Table III is that if we tried to generate 10^{11} Pa in our existing Mark IIa DAC with diamonds having 10^{-6} M² working faces, we would exceed the strength of many of the parts, particularly the ones which bend during use; that is the cell body, the lever arms, the presser plate

Table II Summary of results obtained when analysing the Mark IIaDAC producing 10^8 Pa on a 10^{-6} m² diamond anvil.

Part No.	Description	Maximum Stress NM ⁻²	Maximum Deformation M	Material
3&4	Diamond Anvil Support	10^{10}		A.I.S.I. 310
1b	Circular flange top	3.8×10^8 ^P		A.I.S.I. 310
		1.7×10^{10}		A.I.S.I. 310
1b	Circular flange bottom	3.6×10^8 ^P		A.I.S.I. 310
1b	Barrel	4.2×10^8	4.2×10^{-5} e	A.I.S.I. 310
4	Piston moving	4.4×10^8	3.2×10^{-5} c	A.I.S.I. 310
5	Presser plate	7.7×10^9	7.4×10^{-3} b	A.I.S.I. 310
5b	Presser plate pivot	1.3×10^9 P		A.I.S.I. 310
6	Lever arms	9.3×10^9	5.4×10^{-4} b	A.I.S.I. 310
1	Cell body	1.1×10^{10}	2.3×10^{-3} b	Alloy
7	Piston plate	1.1×10^{10}	6.3×10^{-3} b	A.I.S.I. 310
8	Hydraulic ram			
	i o-ring support	4.0×10^8 P		A.I.S.I. 310
		3.6×10^{14}		A.I.S.I. 310
	ii threaded section	5.3×10^8		A.I.S.I. 310
9	Knurled backing screw	7.4×10^8		A.I.S.I. 310
10	Central pivot	2.0×10^9		A.I.S.I. 310

P = analysed in pure shear stress; e = longitudinal deformation;

c = compressive deformation; b = bending deformation.

Table III Mechanical and physical properties of materials useful in DAC design taken from Smithells (1967).

Material	Youngs Modulus NM ⁻²	Ultimate Tensile Strength NM ⁻²	Ultimate Compressive Strength NM ⁻²	0.2% Proof Strength NM ⁻²	Thermal Conductivity
A.I.S.I. 310	1.9×10^{11}	7.0×10^8		3.9×10^8	0.03
Nimonic 90A	2.2×10^{11}	1.2×10^9		8.1×10^8	0.03
Waspaloy*		1.3×10^9		9.0×10^8	
Alloy NP8	6.98×10^{11}	3.1×10^8		1.5×10^8	0.3
Pyropholite			1.7×10^8		
Tungsten Carbide			2.96×10^9		
Inconec X750		9.45×10^8			0.038
Monel		9.9×10^8			0.06
Copper		2.16×10^8			0.94
Beryllium copper (fully tested)		1.48×10^9		1.3×10^9	0.5
Socket Head Shoulder Cap Screw		6.9×10^9		1.1×10^9	

* Waspaloy is an alloy developed in U.S.A. for use in turbines as it maintains its strength at high temperatures.

and the piston plate. Even parts which do not bend but only support pure shear stress would be very close to their yield point.

This is not an unexpected result as other workers use much smaller applied forces between 1.5 and 3×10^4 N to generate their maximum pressures (see Table IV) and not one of 1×10^5 N used in this analysis. The reason for this is that there are no materials available to support the loads which a force of this magnitude acting on a diamond of reasonable size would produce. I note that reduction of the applied force to one third of the value used in the analysis brings all parts which do not bend within their ultimate strengths. The parts which bend could obviously be redesigned to surmount these problems.

In considering the design of a DAC for use in vibrational spectroscopy we must first decide on the limiting conditions within which we would like the cell to perform.

- (i) Pressure range
- (ii) Diamond size hence optical throughput
- (iii) Temperature range
- (iv) The DAC must be versatile and capable of taking over from all previous designs; that is, it must fit in all existing DAC mounts and this limits certain dimensions.
- (v) The DAC must be as simple as possible and hence easy to manufacture and therefore economic.

The diamond size is obviously the most important consideration as this can limit the pressure scale. For vibrational spectroscopy the limit on diamond anvil size is set by the limiting conditions of transmission through the cell (Adams and Sharma 1976).

Table IV The relationship between highest pressure obtained,
diamond size and maximum applied force. Taken from the literature.

Diamond Size $M \times 10^3$	Area M^2	Highest Pressure Pa	Applied Force N	Reference
0.8 (oct)	7.5×10^{-7}	4.0×10^{10}	3.0×10^4	Holzapfel 1976
0.6 (oct)	5.0×10^{-7}	5.0×10^{10}	2.5×10^4	Piermarini 1973
0.4 (dia)	1.5×10^{-7}	1.0×10^{11}	1.5×10^4	Mao & Bell 1975

oct distance across flats of a regular octahedron.

Success within the group at Leicester has been obtained by the use of a gasket between the diamonds with a central hole of 0.4×10^{-3} M diameter and a pair of diamonds with a face of 7.6×10^{-4} M square. The optical throughput could be improved by increasing the gasket hole to 0.6×10^{-3} diameter and increasing the size of the diamond face to 1.14×10^{-3} M maintaining the same proportional area of contact between gasket and diamond. An increase in thickness is also necessary to maintain massive support. This would increase the optical throughput considerably, making the i.r. experiment routine and the far-i.r. experiment very easy. The temperature range required is ideally 77 K to 600 K. 600 K is chosen as the maximum as very little useful vibrational spectroscopy could be done above this temperature. The maximum pressure required is obviously as high as possible given the size of diamond selected by the optical criteria. Consulting Table II we see that the material supporting the diamond anvil is the one which requires the most compressive strength and normally this would limit the pressure range. After recent consultation with DeBeer's of Johannesburg they will be able to supply us with a special form of sintered diamond in the form of a disc which will stand the otherwise fatal load. Therefore the restriction on pressure range will, in this design, be decided by the dimensions of parts such as the presser plate, lever arms and cell body.

The versatility of the DAC will be maintained if we observe the same overall dimensions and the same ideas of mounting.

Simplicity and economy will be observed at all times in the design. The greatest priority here is to safe-guard the diamond anvils currently costing ca. £450.00 each.

The design for simplicity can be divided into two parts, the design of the central insert and the design of the apparatus to apply a force on the central insert. The central insert must be able to support two diamonds in perfect alignment up to the highest pressure. It should provide for an easy means of heating and cooling and be reasonably cheap to make; that is, the number of high tolerance parts should be kept to a minimum. Whilst the rig or cell body which will apply force on the central insert must be able to apply a force at 90° to the diamond anvil faces without distortion of any form which could lead to damage of a diamond anvil, it is probably better if it has a built-in safety allowance; that is if the diamond anvil is in danger of failure due to indentation into its seat the rig would fail in some harmless way, probably due to shearing of a pivot and protect the diamond anvil.

We must now consider each in turn in more detail. Dimensions will only be discussed where necessary and a scaled assembly drawing is presented in Figure 4:11. Before we can do this however we must calculate the maximum force through the centre of the diamond which the rig will be capable of applying. If we accept that the stress in the levers and plates could be brought into the correct

range by increasing their dimensions and choosing the correct material, the weaknesses in the cell design are the central pivots Parts 10. Table V shows the relationship between the diameter of the central pivot (given a maximum ultimate strength of $1.4 \times 10^9 \text{ N M}^{-2}$ and a maximum shear stress of $1.0 \times 10^9 \text{ N M}^{-2}$ [Unbrako Ltd., Coventry]) and the ultimate pressure available at the diamond face ($1.14 \times 10^{-3} \text{ M sq.}$) plus the projected dimensions of the lever arms (Part 6). From this data a pivot of $8 \times 10^{-3} \text{ M}$ was chosen with lever arms of $b = 10^{-2} \text{ M}$, $d = 20 \times 10^{-3} \text{ M}$. This limits the pressure on a $1.14 \times 10^{-3} \text{ M sq.}$ diamond anvil to $2.7 \times 10^{10} \text{ Pa}$ with a force of $3.5 \times 10^4 \text{ N}$. While a higher pressure is desirable, the restriction of the design has imposed a reasonable compromise.

The Central Insert (Part 1b in the Mark IIa)

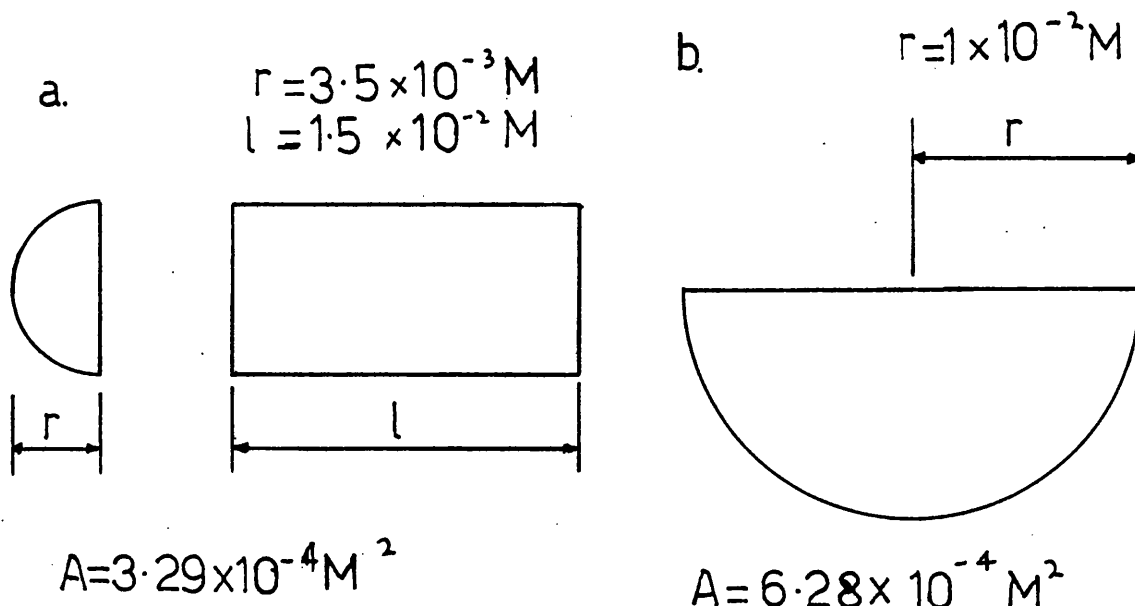
We again adopt the tactic of working outwards from the diamond anvils and our first concern is for the anvil support. In the U.S.A. two types of diamond anvil supports are used. One is the half cylinder (Mao and Bell 1975, Bassett 1967) and the other is the hemisphere developed in the waspaloy cell (Piermarini 1973). There are two reasons for the use of these shapes. The first is the need to be able to manipulate the diamonds when they are mounted initially to achieve parallelism and incidence and the second is that a shape of this type has a large surface area to give maximum transfer of load to the next part and provide maximum support for the anvil holder itself. The two choices are illustrated below.

Table V The relationship between the diameter of the central pivot and the maximum pressure on a 1.14×10^{-3} M sq. diamond.

M x 10 ³	N x 10 ⁻⁴	N x 10 ⁻⁴	Pa x 10 ⁻¹⁰	M x 10 ³	
Diameter of pivot	Max Force Acting	Force at Diamond	Pressure Developed	Min. Depth of Lever Arms to Support Force Acting	
				b = 6	b = 10
7.0	3.8	2.7	2.07	15	10
8.0	5.0	3.5	2.7	25	20
9.5	7.0	5.4	4.0	35	25

b = breadth of lever arm at minimum section

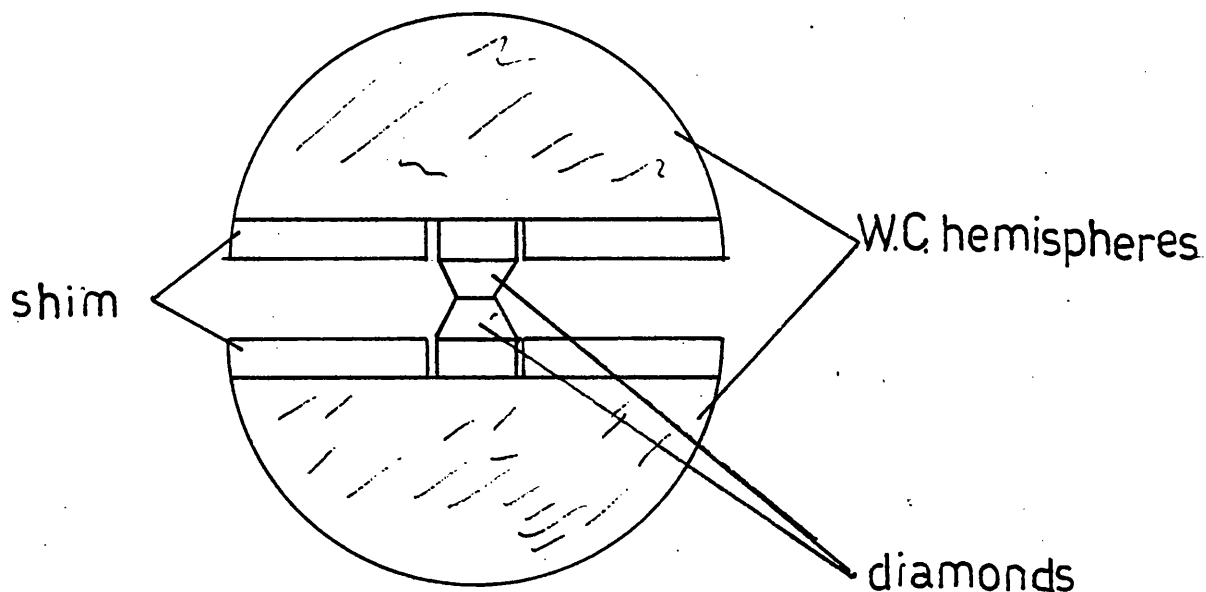
If we keep the Mark IIa restriction of dimension and compute the areas of each we see that;



The hemisphere has the largest surface area. The choice of material here must be tungsten carbide (boron carbide could easily be substituted when transparency to X-rays is required as it has a similar compressive strength) as it has such a large compressive strength, see Table III, but it must be noted that this strength would be halved at $500^{\circ}C$ (Smithells, 924, 1967). Even at half of the room temperature value the tungsten carbide would probably be better than anything else at the same elevated temperatures.

I also propose that each diamond should be backed by tungsten carbide but for the case of the hemisphere only one of the anvil supports need be movable. As the surface on which the diamond sits must be optically flat, a locating shim for mounting the diamond initially is proposed which could easily be removed to facilitate easy repolishing. This shim could simply be araldited or held by small screws and if the sintered diamond from DeBeers

arrives it could take the place of this shim. The development so far is summarised below.



We must also make an optical path through the system and a cone angle of $26-30^\circ$ is chosen as this was found practically and theoretically (Adams and Sharma 1977) to be the most successful. The hole immediately behind the diamond is very important optically (Adams and Sharma 1977) and it should be as large as possible without presenting any risk to the diamond. A hole of 1.2×10^{-3} M with a diamond anvil base of 9.1×10^{-6} M² is used in this design giving a ratio of supported diamond to unsupported diamond of 5.5:1. We also have to add locating pins to locate one diamond anvil over the other and a gasket between these.

At this stage we will consider the problems of heating and cooling a DAC. The principal problem in the Mark IIa DAC was that the central insert, being made of A.I.S.I. 310, gave very poor thermal conductance through to the diamonds (see Table III),

therefore whether heating or cooling, there was always a huge temperature gradient (ca. 100° when cooling to 77 K) between the heater or cooler itself and the diamonds. There are several ways around this problem. For heating, one could pass a large current through the gasket itself. Unfortunately this is precluded because the resistance of material typically used for gaskets, molybdenum or inconel is very low ca. $0.01 \rightarrow 0.04 \Omega$. Other ways would be to increase the thermal conductivity of the central insert by either choosing a different material, say beryllium copper (see Table III) or adding copper which, having a large thermal conductivity, would, if inserted correctly, provide a useful path for the heat or cold. In an experiment on the Mark II cell, addition of copper locating pins passing through the central insert enabled the temperature to fall from 160 K to 100 K on cooling.* The thermal contact between the heater or cooling annulus could be improved by changing the shape to a slightly tapered version so that the extended nose piece and the cooling annulus or heating coil were in intimate contact. The design so far is summarised below. Copper locating pins are shown but alternatively one could make the central insert of beryllium copper, retaining the tungsten carbide inserts immediately behind the diamond.

Initial alignment of the diamonds to give parallelism also concerns us a great deal. We must consider that to make holes in our proposed tungsten carbide hemisphere, for screws or

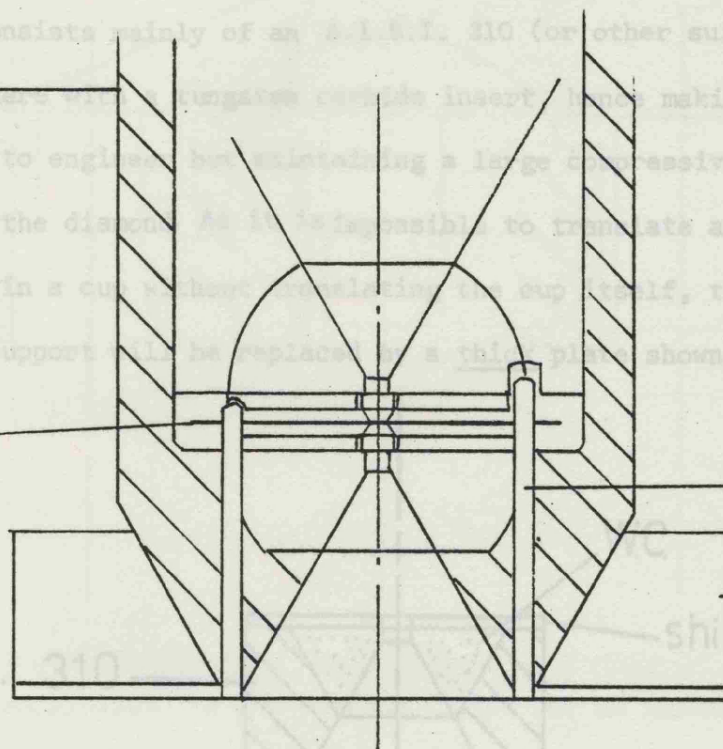
* with liquid nitrogen.

central insert

gasket

Cu locating pin

Cu block



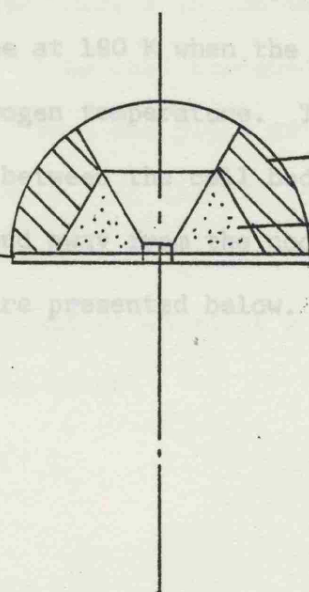
other reasons, is difficult and expensive. Provision for translating one diamond with respect to the other was made in the Mark IIa cell and this was found to be extremely useful when mounting diamonds. Considering all of these points one way to solve them is to design an anvil support as follows.

As already stated the central insert of the Mark II cell experienced temperature gradients on heating or cooling such that the top flange of the insert could be at 190°K when the extended nose piece was cooled to liquid nitrogen temperature. Therefore if we have thermal contact between the body and the central insert

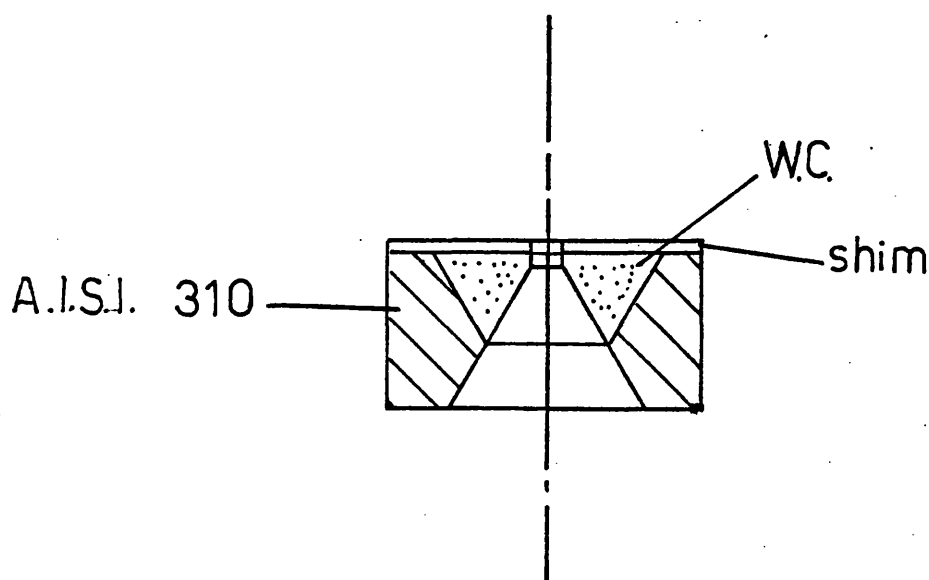
shim

A.I.S.I. 310

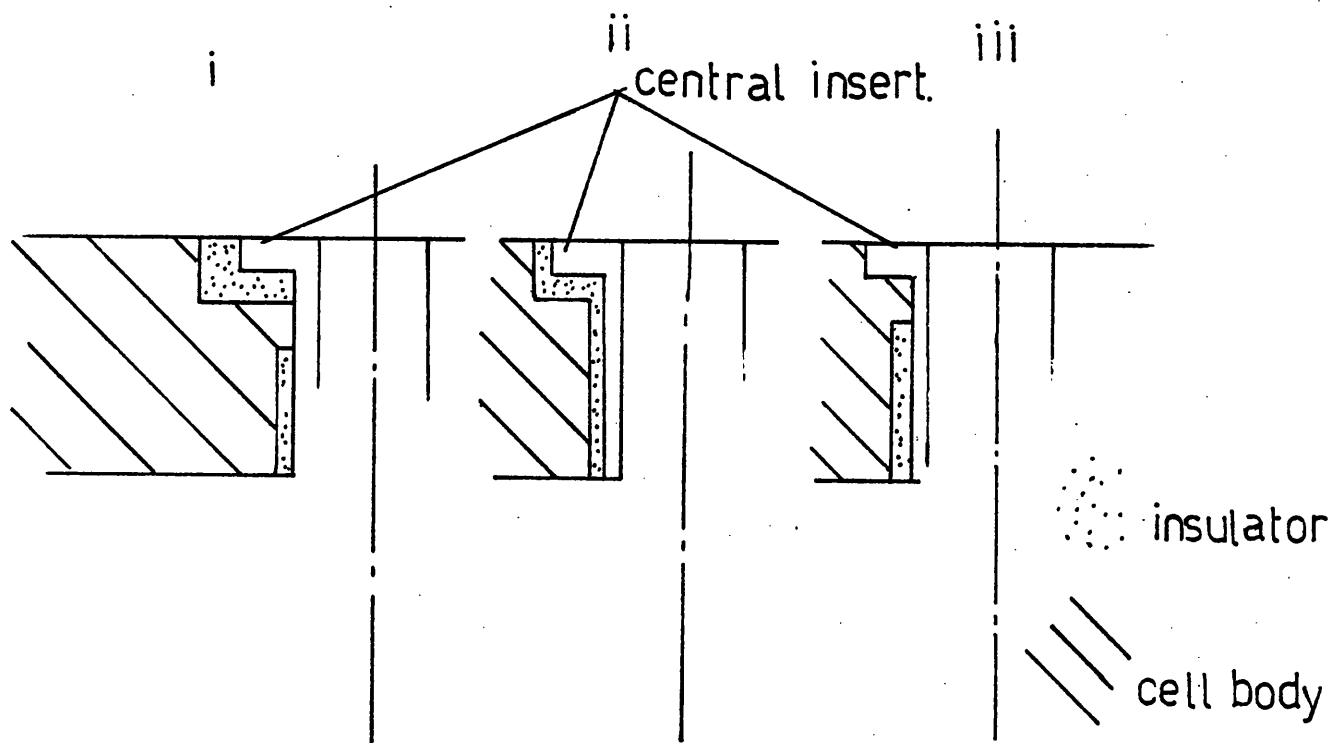
WC insert



This consists mainly of an A.I.S.I. 310 (or other suitable material) hemisphere with a tungsten carbide insert, hence making it much easier to engineer but maintaining a large compressive strength behind the diamond. As it is impossible to translate a hemisphere in a cup without translating the cup itself, the fixed anvil support will be replaced by a thick plate shown below.



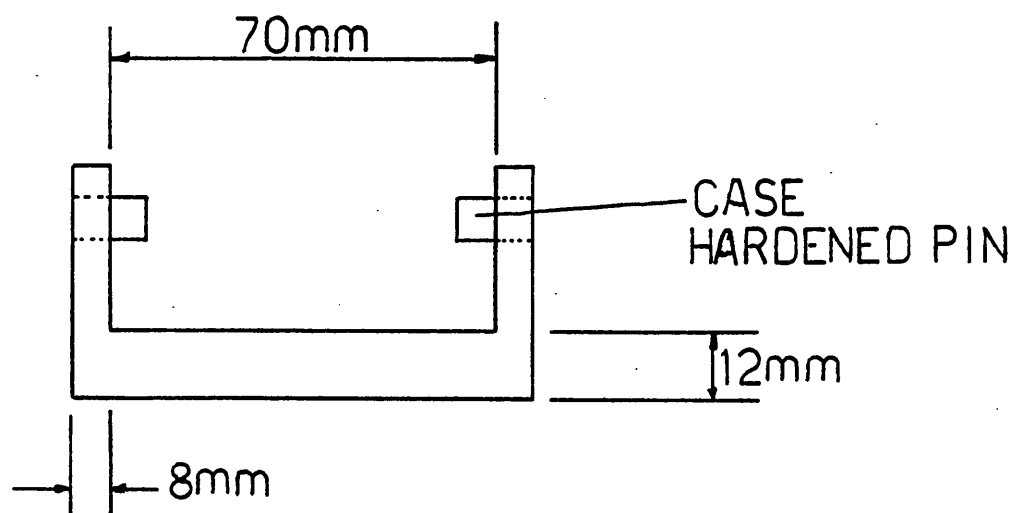
The top flange of the central insert is increased in thickness to support the required load. We complete our design of the central insert by considering possible insulation. As already stated the central insert of the Mark II cell experienced temperature gradients on heating or cooling such that the top flange of the insert could be at 180 K when the extended nose piece was cooled to liquid nitrogen temperature. Therefore if we must have thermal contact between the cell body and the central insert it should be at the end away from the cooling or heating block. Three possibilities are presented below.



Pyropholite is the obvious choice for an insulator as it has a high compressive strength. The problem is that it tends to distort in manufacture and as we require a perfect fit of the support under the top flange of the central insert if we are to avoid failure of this top flange and hence damage to the diamonds, iii as above is the choice, where the only insulation is not load supporting.

The Cell Body or Rig

The presser plate (Part 5 in the Mark IIa) could be considerably improved by using case hardened pins as pivots and making the whole thing from one piece of material, probably a nimonic alloy or waspaloy. No thermal insulation is proposed as the nimonic alloys have such a low thermal conduction although a pyropholite washer could be added at a later date. The proposed plate is shown below.



$$b_{\text{min sect}} = 10\text{mm}$$

This can be analysed as before if the force through the centre of the plate is $3.5 \times 10^4 \text{ N}$, giving

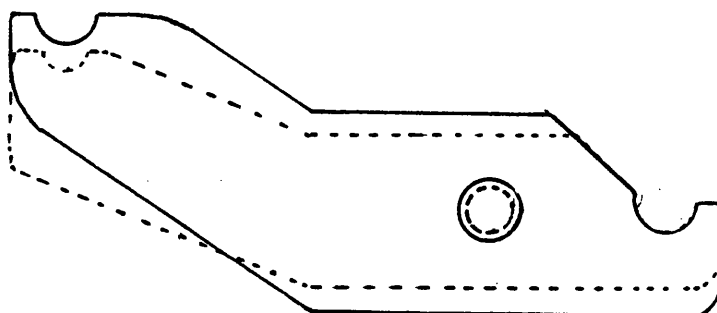
$$\text{Maximum bending moment} = 2.5 \times 10^2 \text{ N M}$$

$$\text{Maximum deformation} = 3.6 \times 10^{-4} \text{ M}$$

$$\text{Maximum stress} = 1.16 \times 10^9 \text{ N M}^{-2}$$

The Lever Arms (Part 6 in the Mark IIa DAC)

The design of this part was discussed earlier and the result expressed in Table V. A diagram is given below showing how the Mark IIa lever arms are developed.



— MARK III
 ---- MARK IIa

$b = 10\text{mm}$

The Cell Body (Part 1 in the Mark IIa cell)

By a similar argument to that of the lever arms (as they both bear the same load) the cell body needs to be of similar dimension of minimum section and made of a nimonic alloy or waspaloy. This choice of material will also help in insulating the central insert, as it has such a low thermal conductivity. The central flange of the cell body labelled as h in the Mark IIa is increased in thickness to 5.0×10^{-3} M and the hole for the central insert re-dimensioned appropriately. A central pivot of diameter 8.0×10^{-3} M is chosen, a shoulder headed cap screw locked in place by "Locktite" being ideal. The lever arms will fit flush up to the cell body which will have a Teflon coating approximately 0.2×10^{-3} M thick. All pins and plates will have flush fits to avoid bending of the pins and hence failure. A diagram of the cell body is not given but reference to the assembly drawing given, Figure 4:11, illustrates all points.

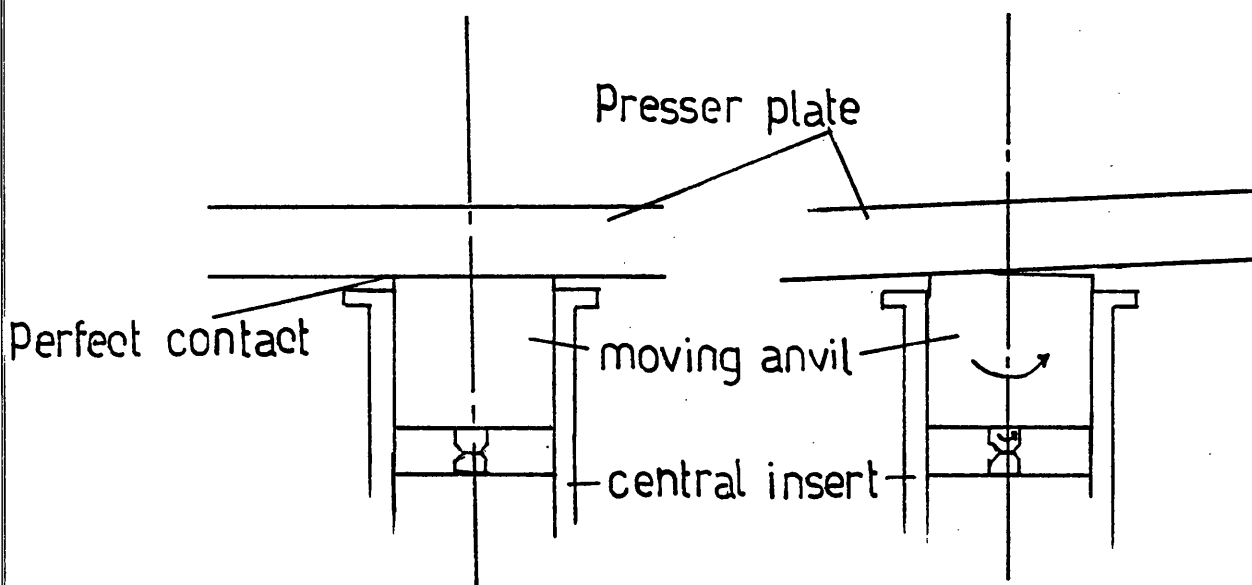
We now consider the low pressure end of the cell body or rig, the hydraulic ram, Part 8, the piston plate, Part 7, and the knurled screw, Part 9. This assembly must be capable of generating 1.2×10^4 N.

The piston plate has to be increased in dimension, its thickness being doubled and the pivots being increased to 8 mm giving a maximum stress of 10^9 N M⁻² with a maximum deformation

of 5.0×10^{-4} M, assuming a nimonic alloy or waspaloy is chosen as the material.

The knurled backing screw and piston are also redesigned, the piston being equipped with anti-extrusion backing rings which are necessary at high pressure (above 1.3×10^7 N M²). The plastic pipe feeding oil to the piston is replaced by a copper one, which will be required to take the estimated oil pressure of 2000 psi or 1.3×10^7 N M⁻². This can be generated easily by our existing Tangyi hand pumps (Tangyi Ltd., Birmingham).

The final part of the design is to consider the possibility of the rig twisting and forcing the presser plate not to make perfect contact with the moving anvil and hence forcing the diamond anvils to misalign. This is illustrated below.



This type of twisting was often seen in the Mark IIa cell and gave rise to a great deal of concern. This could have been one of the

major factors contributing to indentation of the diamond anvils. This twisting can be accommodated if we allow the piston plate to rotate relative to the cell body as the presser plate will always remain parallel to the piston plate. This could be achieved in two ways, one involving a hemispherical bearing and the other a V block and groove assembly. Both are shown in Figure 4:12. The V block and groove assembly is preferred as hemispherical bearings are not very reliable. If they do not align properly at low loads they tend not to align at all. A case hardened carbon steel would be used for the V block and groove assembly.

4.4. Summary

A brief history of the development of the DAC has been given, followed by development of the DAC here at Leicester. Finally the DAC used for the work in this thesis has been fully analysed and a Mark III DAC developed from this analysis. Manufacture of this is taking place at the time of writing.

A computer aided design of a DAC proposed by Leicester University Engineering Department could also be a very profitable idea. This would make it possible to analyse the DAC as a whole, without having to artificially divide it up as I have done. Unfortunately this is a long term project and was not undertaken by me.

Figure 4:11

Assembly drawing of Mark III DAC

Part 1	Cell body
1b	Central insert
3	Fixed anvil holder
4	Moving anvil holder
5	Presser plate
6	Lever arms
7	Piston plate
8	Hydraulic piston
9	Knurled backing screw
10	Central pivot
11	Insulator
12	V block assembly

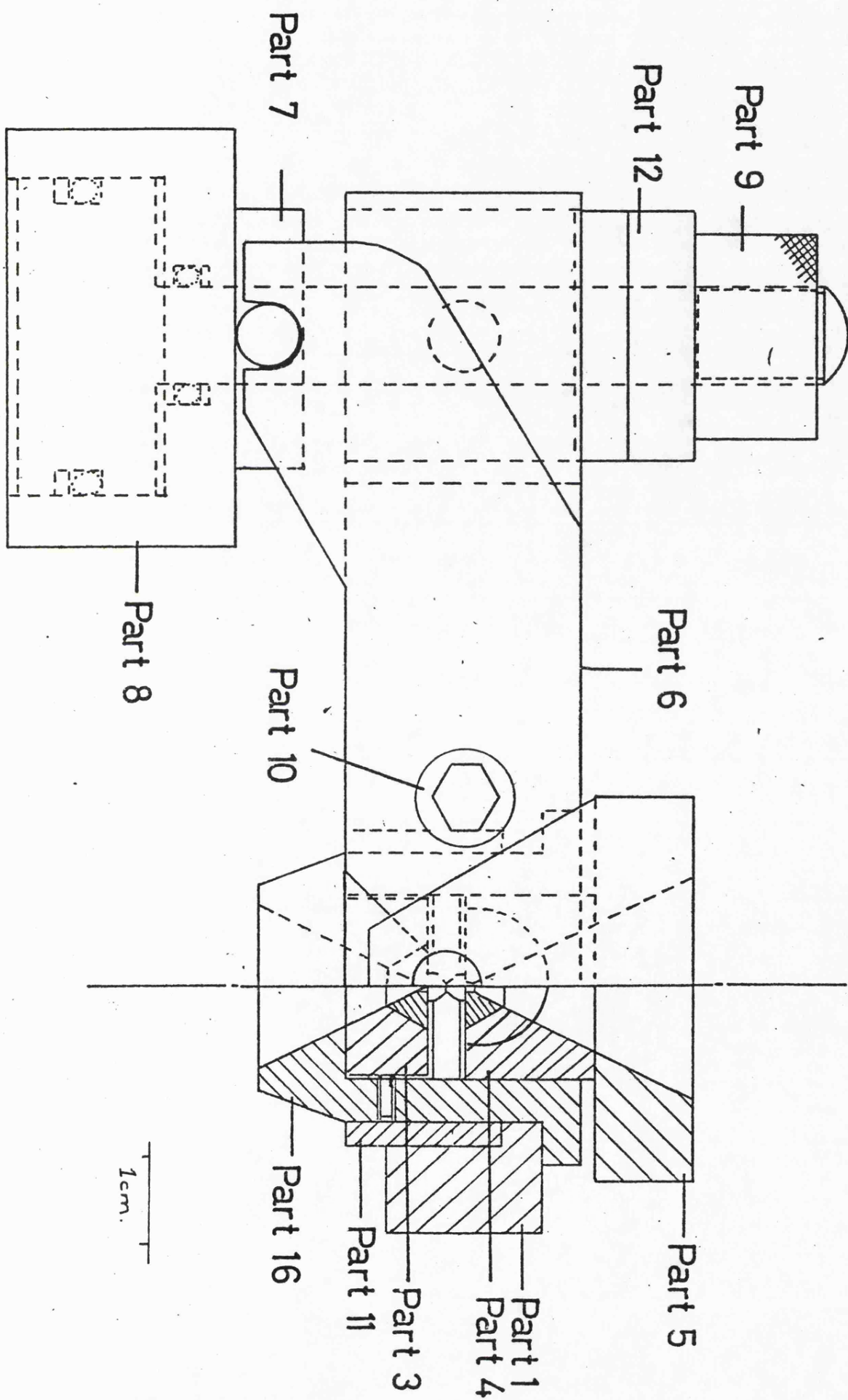
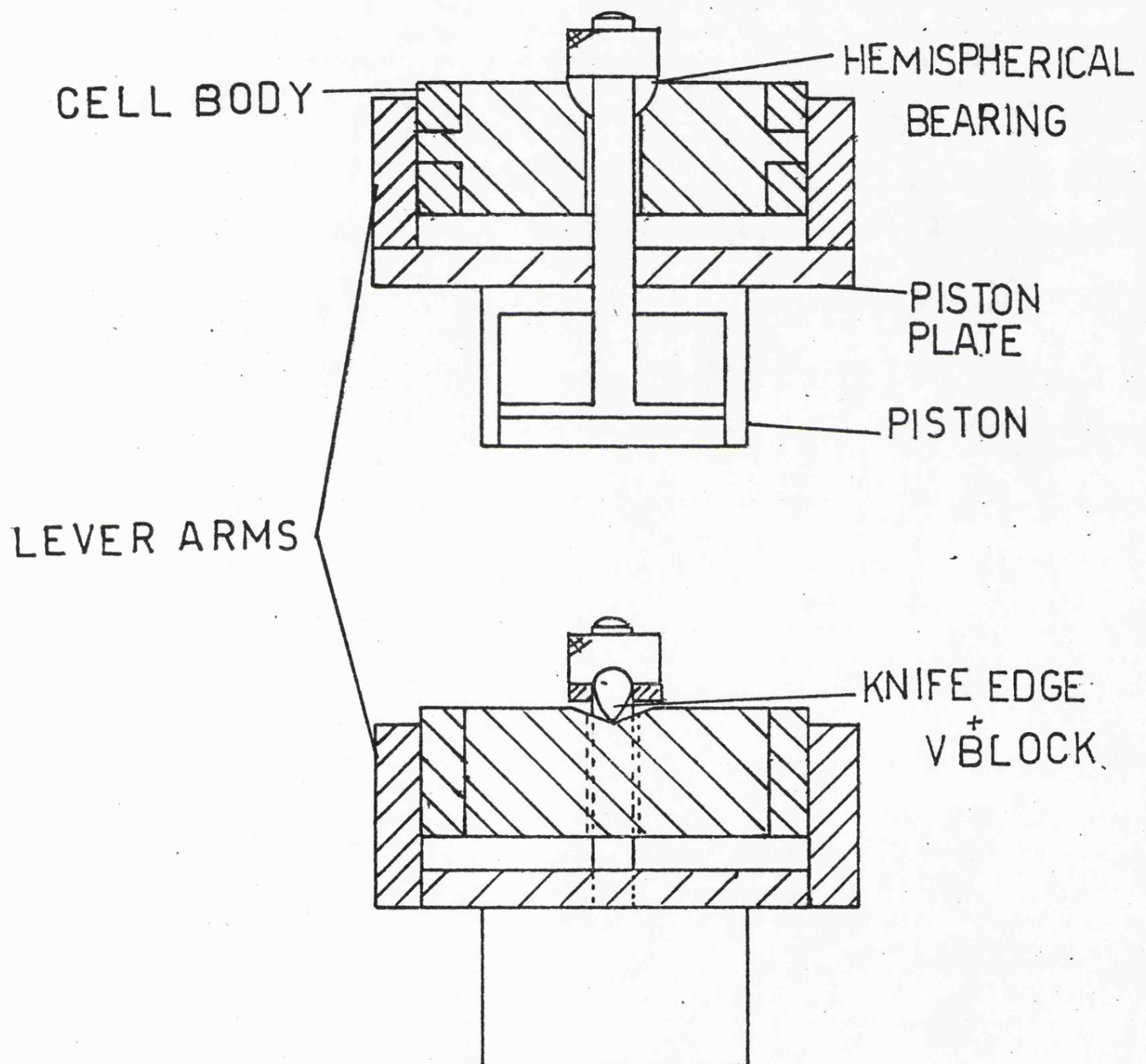


Figure 4:12

Two possible solutions to the problem of twisting in DACs. Sections of the hydraulic ram area are shown.

- a) Hemispherical bearing
- b) V block assembly



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CHAPTER 5A STUDY OF THE HgX_2 (X = Cl, Br, I) SYSTEMS UNDER HIGH
PRESSURES AND VARIOUS TEMPERATURES

CHAPTER 5

A STUDY OF THE HgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) SYSTEMS UNDER HIGH PRESSURES AND VARIOUS TEMPERATURES

5.1 Introduction

This work was undertaken with the idea of investigating the effect of pressure on a series of linear triatomic systems. It was hoped that the variation in the structure of the materials going from the chloride to the iodide would prove interesting when subjected to a pressure study. The preliminary results were communicated by us (Adams and Appleby 1976) and the final results are in the press (Adams and Appleby 1977 a,b, and Adams, Appleby and Barlow 1977). This chapter is based on the work presented in these papers. Each material will be discussed in turn and a comparison of the results given at the end of the chapter.

5.2 Experimental

The Mark II cell was loaded using a molybdenum gasket. All the techniques and instruments used were as discussed in Chapter 2. The mercury salts attacked inconel, therefore it could not be used as gasket material.

5.3 Mercuric Chloride

From compression measurements, | Bridgman (1937) found that HgCl_2 showed only one phase transition up to 45 kbar at ambient

temperatures. A recent n.q.r. study has revealed a second-order transition below this (Balashov and Ikhenov 1975) as indicated in figure 5:1. We have investigated all three phases by both i.r. and Raman spectroscopy under conditions of, or near, hydrostatic compression up to ca. 30 kbar. This is the first study of combined i.r. and Raman spectroscopy under such conditions. The phase diagram of figure 5:1 is based upon that given by Pistorius (1976) with the addition of the data of Balashov and Ikhenov (1975) and of our own investigations of the transition lines.

Assignment for HgCl₂(I)

The results are illustrated in figures 5:2, 5:3, and 5:4, and Tables 1 and 2. Surprisingly, there is no satisfactory literature assignment of the entire vibrational spectrum of the ambient pressure phase, HgCl₂(I), despite many partial studies. This phase has the symmetry $P\overline{m}nb$ (D_{2h}^{16}) with $z = 4$ (Wyckoff 1964). All atoms are on sites $4c$ and are arranged in planar sheets stacked along a . A factor group analysis (f.g.a.) for HgCl₂(I) is given in Table 3. The two Hg-Cl bonds are not required, crystallographically, to be equal (they have lengths 2.23 and 2.27 Å), neither is the molecule required to be linear. The actual distortions from strict linear centrosymmetric geometry are sufficiently slight that $D_{\infty h}$ forms a good basis for understanding the spectra.

$\nu_1, \nu(Hg-Cl)_{\underline{S}}$, is present in the Raman spectra as an intense band at 315 cm^{-1} with asymmetry on the high frequency side: these are the expected $A_g + B_{2g}$ components, Table 3B. The i.r. counter-

FIGURE 5:1

The Phase Diagram of HgCl_2

(Pistorius 1975, Balashov and Ikhenov 1975,
and this work).

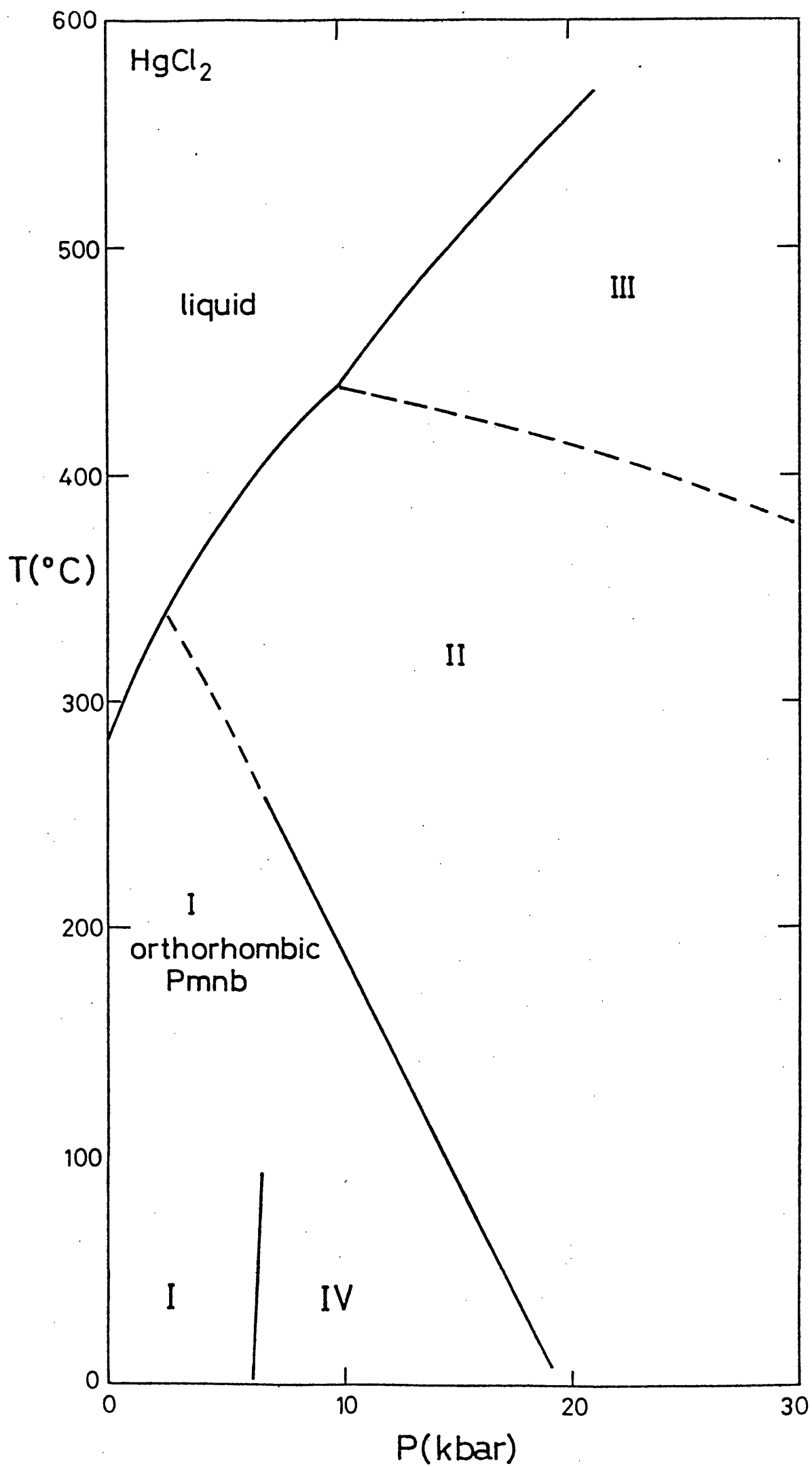
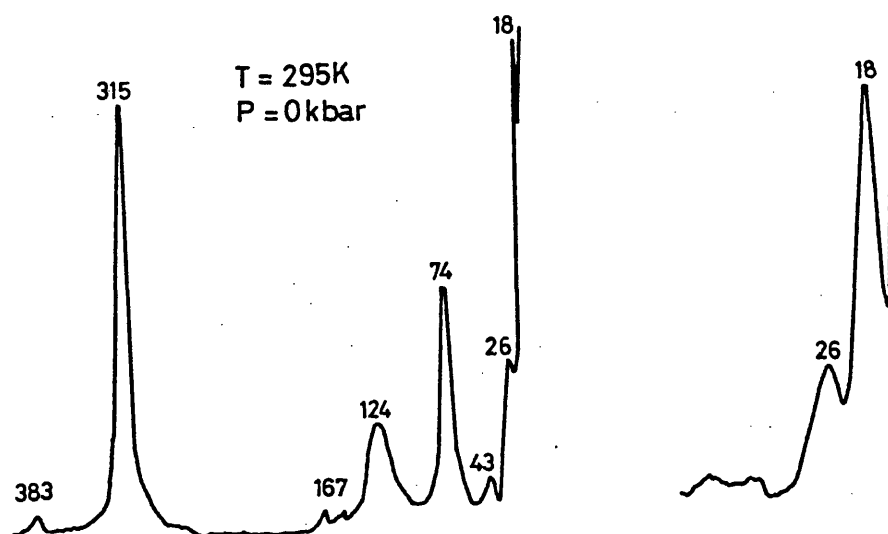


FIGURE 5:2

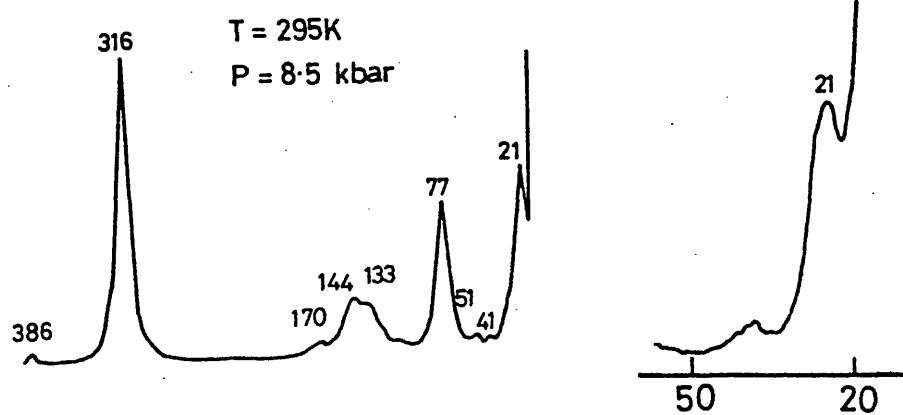
Raman Spectra of HgCl_2 at 295 K and Various Pressures.
Spectral Slit Width 1.5 cm^{-1} , 60 mW 514.5 nm radiation
at the sample.



I



IV



II

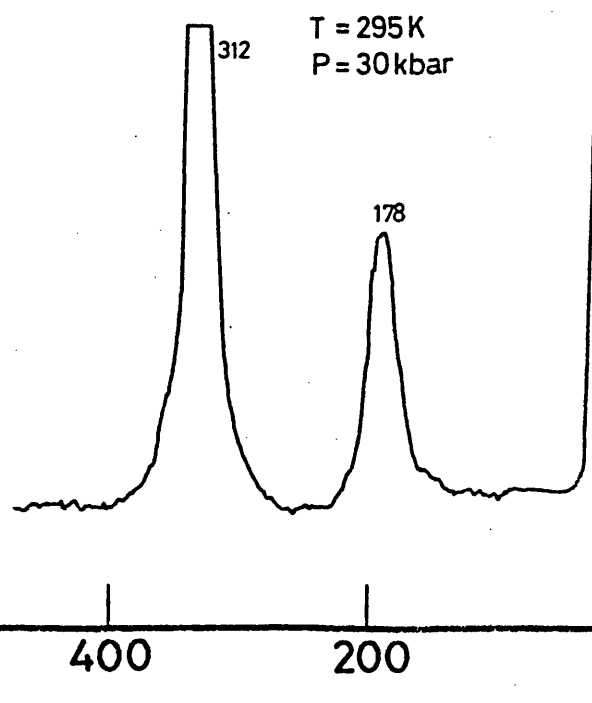


FIGURE 5:3

Raman Spectra of HgCl_2 at 150 K and Various Pressures
(kbar). Conditions as for Figure 5:2.

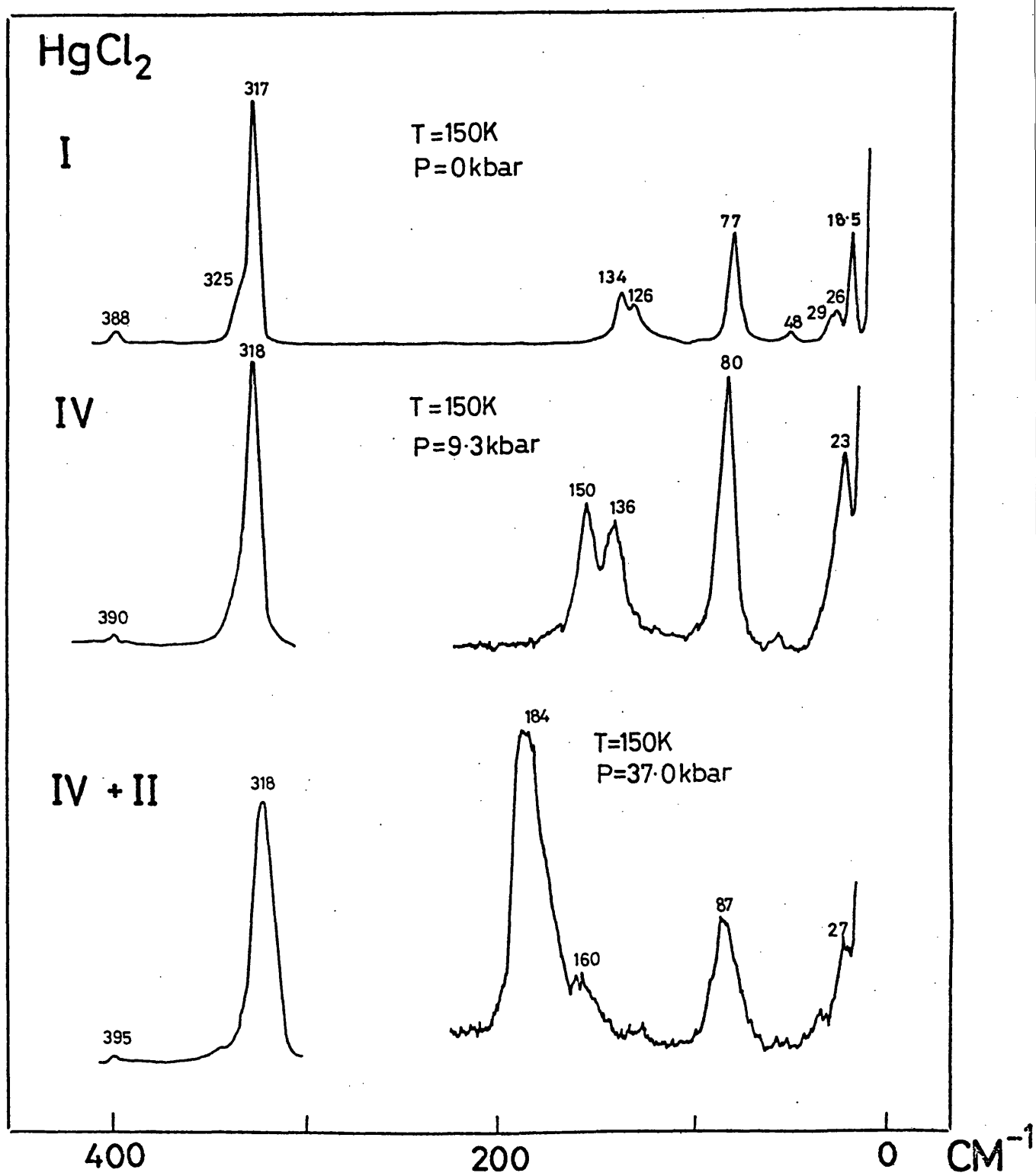


FIGURE 5:4

Far-i.r. Spectra at Ambient Temperatures of HgCl_2
at Various Pressures.

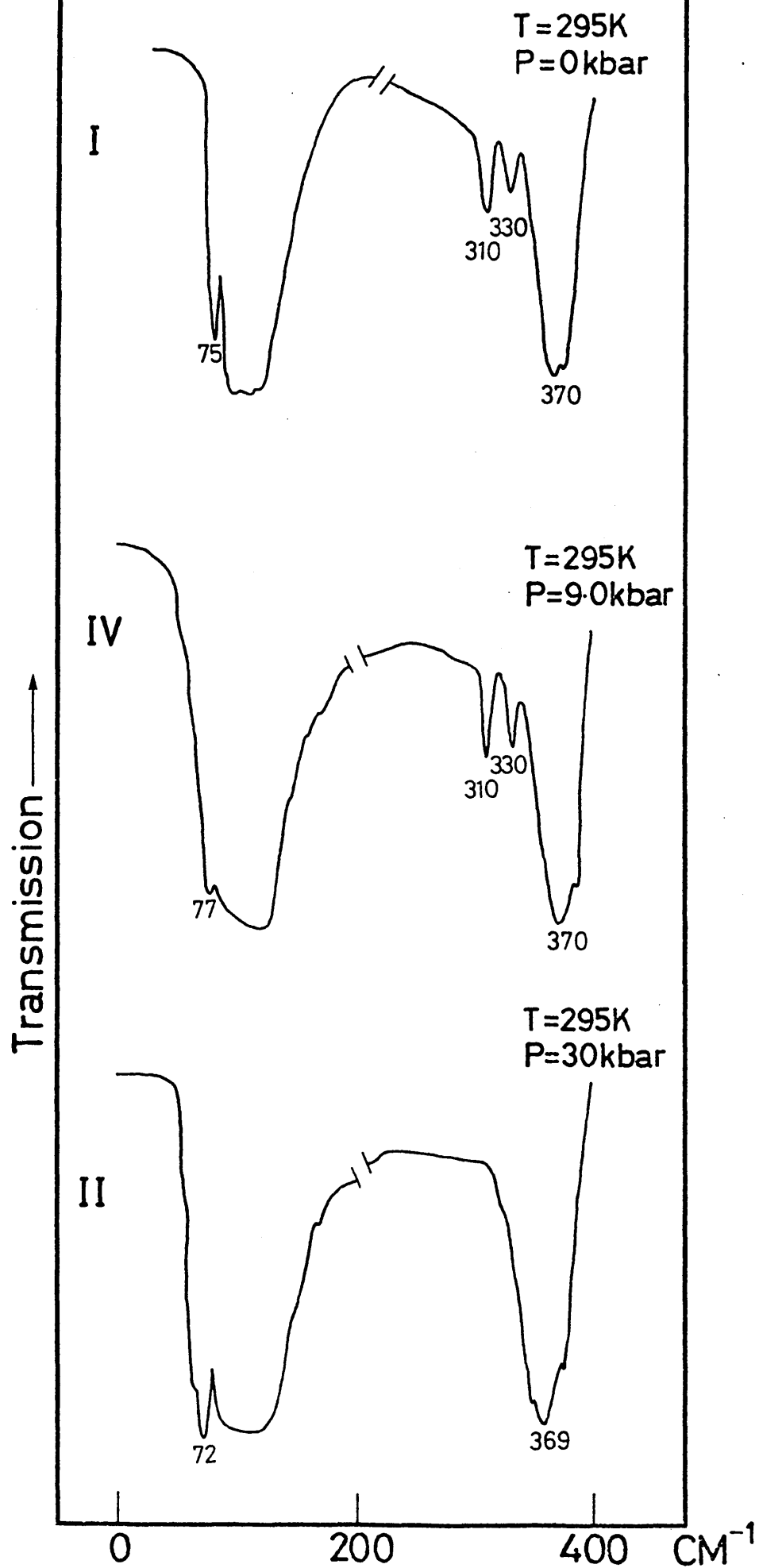


TABLE 1 Raman frequencies/cm⁻¹ for HgCl₂ at various pressures

A : 295 K

Pressure/kbar	ν_L , translatory			ν_L , rotatory			ν_3	Phase
	18	26	43	74	124	168		
0.001	18	26	43	74	124	168	315	I
2.0	18.5	26	41.5	49	128	167	315	I
4.6	20	26	42.5	51.5	129	168.5	315	IV
8.6	21.5		41	51	133	170	316	IV
13.8	22		41	53	139	152	316	IV
18.4	22		42	79		161	314	II
23.0						171	312	II
29.8						178	312	II

B : 150 K

0.001	18.5	26,29	48	77	126	134	315	388	I
0.8	18.5	29	49	78	126	135	317,325sh	388	I
9.3	22		54,58	80	136	150	318	390	IV
21.0	24			83	146.5	163.5	318	393	IV
37.3	27			87	160	184	318	395	IV + II
38.1	27			88		184	318	396	IV + II

TABLE 2 I.r. frequencies/cm⁻¹ for HgCl₂ at various hydrostatic pressures.

Pressure/kbar	0.001	10	30
ν_3 , $\nu(\text{Hg-Cl})_{\underline{\text{as}}}$	370	370	359
ν_1 , $\nu(\text{Hg-Cl})_{\underline{\text{s}}}$	$\left\{ \begin{array}{l} 330 \\ 310 \end{array} \right.$	330	-
		310	-
ν_2 , $\delta(\text{ClHgCl})$	106 ^a	108 ^a	109 ^a
ν_{L}	75	77	72
Phase	I	IV	II

^a Band centre recorded.

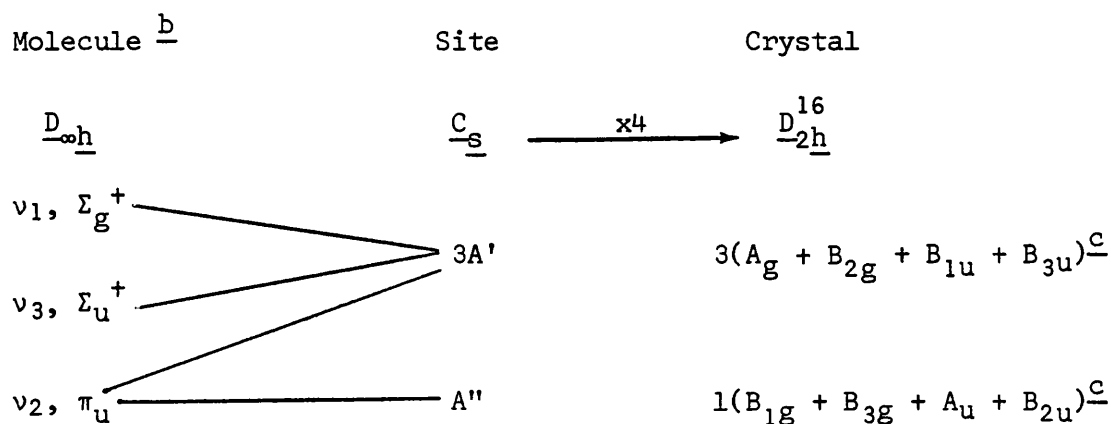
TABLE 3 Factor group analysis and mode correlation scheme for $\text{HgCl}_2(\text{I})$.

A. Fga

D_{2h}^{16}	N_T^a	T_A	T	R(x,y)	v_i	Activities
A_g	6		2	1	3	Raman
B_{1g}	3		1	1	1	
B_{2g}	6		2	1	3	
B_{3g}	3		1	1	1	
A_u	3		1	1	1	Inactive
B_{1u}	6	1	1	1	3	I.r.
B_{2u}	3	1	0	1	1	
B_{3u}	6	1	1	1	3	

^a N_T total number of modes in unit cell, T_A acoustic branch modes, T optic branch translatory lattice modes, R(x,y) rotatory lattice modes, v_i molecular internal modes.

B. Correlation scheme



^b Approximate geometry, see text.

^c These sum to give column v_i of A.

parts of this correlation quadruplet, $B_{1u} + B_{3u}$, appear as a pair of sharp, medium intensity, bands at 310, 330 cm^{-1} . In contrast ν_3 , $\nu(\text{Hg-Cl})_{\text{as}}$, is intense in i.r. spectra but very weak ($A_g + B_g$ components coincident) in Raman spectra.

Under $D_{\infty h}$ symmetry ν_2 , $\delta(\text{HgCl}_2)$, is i.r.-active only. Although it may attain Raman-activity in the crystal by virtue of both site and correlation fields, it is expected to be intense in the crystal i.r. spectra but weak in Raman spectra. Accordingly we associate it with the region of intense i.r. absorption ca. 100 cm^{-1} which has no Raman counterpart: this i.r. band shows three unresolved components in exact agreement with theory which requires $B_{1u} + B_{2u} + B_{3u}$. By an analogous argument the molecular rotatory modes, which originate as π_g (Raman-active only) in $D_{\infty h}$, are expected to be weak in i.r. spectra of the solid but intense in Raman spectra. These considerations indicate that Raman bands in the interval 120-180 cm^{-1} are of rotatory type. Finally, bands below 85 cm^{-1} in both Raman and i.r. spectra are attributed to translatory modes of which five of the theoretical six were found at room temperature in the Raman spectra, and both of the predicted ($B_{1u} + B_{3u}$) i.r. bands (40, 75 cm^{-1} in the mull spectrum). This assignment differs from others (Poulet and Mathieu 1963, Randi and Gesmundo 1964, Mikawa, Jacobsen and Brasch 1966, Ross 1972) chiefly in the ν_2 /rotatory mode description. If bands from 75-135 cm^{-1} are all ascribed to ν_2 components an unreasonably large factor group splitting is implied.

In the absence of a single-crystal assignment (at present underway at our laboratory) we cannot be sure of the symmetry labels of the Raman translatory modes. Nevertheless it is helpful for interpretation of the high pressure data to have at least an outline understanding of them. The crystal translatory modes originate from molecular motions classified in $\underline{D_{\infty h}}$ as Σ_u^+ (along the molecular axis) and π_u (degenerate; normal to the axis). The π_u is both site and correlation field split, yielding a crystal vector $A_g + B_{1g} + B_{2g} + B_{3g}$ for the Raman-active components. It is not unreasonable that these should be in mutual proximity as the correlation field, in particular, is unlikely to be large in a molecular crystal such as this. Accordingly we assign the bands at 26 cm^{-1} (split at 150 K) and 18 cm^{-1} (rather broad both at 295 and 150 K) to translatory modes of π_u origin, implying a site splitting of π_u of ca. 10 cm^{-1} . This leaves an $A_g + B_{2g}$ pair which originates from Σ_u^+ : due to its intensity the 74 cm^{-1} band is assigned as A_g ; that at 43 cm^{-1} is, by elimination, B_{2g} .

The high pressure results: $\text{HgCl}_2(\text{II})$

Bridgman (1937) located a single phase transition in HgCl_2 , at ca. 18 kbar at room temperature, which became increasingly sluggish at lower temperatures. Our Raman spectra, obtained on successively increasing the pressure at ambient temperature, show clearly that at 19.3 kbar a new phase has appeared and exists in equilibrium with $\text{HgCl}_2(\text{IV})$. The spectrum at 30 kbar shows only features due to $\text{HgCl}_2(\text{II})$: this spectrum is much simpler than those

of either phases I or IV (discussed below); the ν_3 component is no longer present ca. 386 cm^{-1} , ν_1 is greatly increased in intensity, and the translatory lattice mode region is clear.

These experiments were repeated, having first cooled the sample to 150 K, Figure 5:3. In the 21 kbar spectrum there is still no sign of phase II and even at 37 kbar, although $\text{HgCl}_2(\text{II})$ is now clearly present as judged by a strong band at 184 cm^{-1} , it is in equilibrium with phase I. This behaviour is typical of a sluggish phase transition: nevertheless $\text{HgCl}_2(\text{II})$ is unambiguously characterised by these experiments as having a much simpler spectrum than $\text{HgCl}_2(\text{I})$.

In the i.r. spectra (room temperature only) the IV/II transition is most clearly characterised by the prompt disappearance of the two sharp ν_1 factor group components at 310, 330 cm^{-1} , and by a decrease in the frequency of ν_3 , a most unusual result of increasing pressure. Concurrently the 75 cm^{-1} lattice mode gains intensity substantially and the region of intense absorption ca. 100 cm^{-1} associated with ν_2 shifts to higher energy. There is no significant i.r. absorption by $\text{HgCl}_2(\text{II})$ in the interval $120\text{--}340\text{ cm}^{-1}$, and certainly none corresponding to the strong Raman band at 180 cm^{-1} (at 30 kbar).

The high pressure results: $\text{HgCl}_2(\text{IV})$

Careful examination of the 295 K Raman spectra obtained at pressures in the interval up to 10 kbar shows a number of small but

significant and repeatable changes in the region below 180 cm^{-1} . No such changes were found in the i.r. spectra, although the extreme experimental difficulties encountered in the $20\text{--}200\text{ cm}^{-1}$ region with a gasketed DAC limits the detail that can be reliably observed. Bridgman did not find a phase transition in HgCl_2 until ca. 18 kbar at ambient temperature, viz., the so-called I/II transition. However, a very recent report (Balashov and Ikhenov 1975) of some n.q.r. measurements shows clearly that there is a second-order transition at 6.9 kbar at 312 K.

In the 295 K Raman spectra for the 0-10 kbar range the changes effected by increase of pressure are: (i) a positive shift of the 18 and 74 cm^{-1} bands, assigned to translatory modes; this is normal and does not necessarily indicate a phase change. (ii) A rapid loss of intensity of the 26 cm^{-1} band which either disappears or breaks into two or three weak components which merge into the edge of the 18 cm^{-1} band, now shifted to ca. 23 cm^{-1} . (iii) Rapid upward shift by ca. 10 cm^{-1} of the higher frequency component of the weak, unresolved doublet at 43 cm^{-1} . Having reached 56 cm^{-1} this band is unaffected by a subsequent pressure increase of 6.5 kbar. (iv) A similar differential shift of the components of the unresolved band at 124 cm^{-1} resulting in its resolution. Apart from progressive frequency shifts with pressure the spectra obtained above 10 kbar remain remarkably constant in appearance until development of phase II ensues. This Raman data therefore provides independent evidence for the existence of a

new phase which we label $\text{HgCl}_2(\text{IV})$. In contrast with the IV/II change, it is evident from the spectral changes, that the structural differences between phases I and IV are subtle.

Balashov and Ikhenov (1975) showed that the I/IV transition pressure decreases linearly with temperature by $3.6 \text{ kbar deg}^{-1}$ in the range 256.5–365.0 K and remarked that if the linear dependence were maintained to 0°K the transition pressure would be 5.45 kbar. Even allowing for pronounced deviation from linearity this strongly suggests that $\text{HgCl}_2(\text{IV})$ cannot be prepared at ambient pressure at any temperature. Accordingly our 150 K ambient pressure Raman spectrum must be that of $\text{HgCl}_2(\text{I})$. Comparison with the 295 K spectrum shows that the 28 and 128 cm^{-1} bands have been resolved into doublets: this also happened with increase of pressure. In contrast, the 48 cm^{-1} band remains single at 150 K until pressures ca. 9 kbar are applied: this is the only real Raman evidence at 150 K for the existence of a new phase.

The Structure of $\text{HgCl}_2(\text{II})$

The strict i.r.-Raman exclusions plainly indicate that this phase has a centrosymmetric unit cell. Further, the great simplification of the Raman spectrum in the lattice mode (translatory and rotatory) region, and the disappearance of the ν_1 factor group components from the i.r. spectrum strongly imply a structure of higher symmetry than that of $\text{HgCl}_2(\text{I})$. It is, however, significant that $\text{HgCl}_2(\text{II})$ appears to be composed of the same kind

of molecular unit as the other phases in that the ν_1 and ν_3 molecular internal modes remain in similar regions throughout. These three phases therefore represent three different solutions to the problem of packing the same linear molecules. In the higher pressure phases it must be presumed that the intermolecular interactions are increased. An indication of this is given by the decrease in ν_3 which accompanies the IV/II transition.

Other known solutions to the problem of packing linear AB_2 molecules are represented by the structures of $HgBr_2$, CO_2 (Wyckoff 1964), CS_2 (Baenziger and Duax 1968), XeF_2 (Lohr and Lipscomb 1963), and KrF_2 (Burbank, Falconer and Sunder 1975), and our high pressure polymorphs might well adopt one of them. $HgCl_2(II),(IV)$ plainly do not adopt the $HgBr_2$ structure as it has the space group $\underline{C}_{2v}^{12}$ and from observation of models it is so different a structure from $HgCl_2(I)$ that a transition to it would require a reconstructive process of catastrophic proportions. Factor group analyses for the other structures are shown in Table 4. The XeF_2 structure may be rejected immediately: it requires only one ν_1 component as opposed to the two observed, and only one i.r. absorption below 150 cm^{-1} .

The CO_2 , CS_2 , and KrF_2 structures predict almost identical far-i.r. spectra. Each requires four or five bands below 150 cm^{-1} and the observed spectrum of $HgCl_2(II)$ is compatible with either. Similarly, all three structures are compatible with the absence of translatory modes from the Raman spectrum of phase II. The only

TABLE 4 Factor group analysis for the crystals of some linear triatomic molecules.

D_{4h}	$KrF_2(D_{4h}^{14}, Z' = 2) \overset{a}{\text{--}}$						$XeF_2(D_{4h}^{17}, Z' = 1)$					
	$N_T \overset{b}{\text{--}}$	T_A	T	R	ν_i	$\nu(\text{Hg-Cl})$	N_T	T_A	T	R	ν_i	$\nu(\text{Hg-Cl})$
A_{1g}	1				1	1	1				1	1
A_{2g}												
B_{1g}												
B_{2g}	1				1	1						
E_g	2			2			1			1		
A_{1u}												
A_{2u}	2	1			1	1	2	1			1	1
B_{1u}	2		1		1	1						
B_{2u}												
E_u	4	1	1		2		2	1			1	

D_{2h}	$CS_2(D_{2h}^{18}, Z' = 2)$						$CO_2(T_h^6, Z' = 4)$					
	N_T	T_A	T	R	ν_i	$\nu(\text{Hg-Cl})$	N_T	T_A	T	R	ν_i	$\nu(\text{Hg-Cl})$
A_g	2			1	1	1	A_g	1			1	1
B_{1g}	1			1			E_g	1		1		
B_{2g}	1			1			T_g	3		2	1	1
B_{3g}	2			1	1	1	A_u	2	1		1	1
A_u	2		1		1		E_u	2	1		1	
B_{1u}	4	1	1		2	1	T_u	6	1	2	3	1
B_{2u}	4	1	1		2	1						
B_{3u}	2	1			1							

$\overset{a}{\text{--}}$ Z' = number of molecules in primitive cell

$\overset{b}{\text{--}}$ N_T total number of modes in primitive cell

T_A acoustic modes, T optic branch translatory modes

R rotatory modes, ν_i internal modes of molecules

$\nu(\text{Hg-Cl})$ subset of ν_i due to ν_1 and ν_3 molecular modes.

basis for a decision is therefore in the relative predictions for the Raman-active rotatory and ν_1 mode regions.

The CS_2 structure requires four rotatory modes spread among four non-degenerate symmetry species and the spectrum does not seem to be compatible with this, although the possibility cannot be altogether excluded. A decision between the KrF_2 and CO_2 structures is delicate but the latter is considered to be more probable chiefly because it more naturally accounts for the increased intensities associated with the ν_1 and rotatory mode regions. In the CO_2 structure the cell remains tetramolecular: the four ν_1 modes couple via S_6 site symmetry to yield the components $A_g + T_g$ in T_h^6 , both of which are Raman-active. The very high observed intensity of ν_1 in $\text{HgCl}_2(\text{II})$ is correlated with the T_g species, and the unresolved shoulder with A_g . In contrast, the KrF_2 structure requires only the components $A_g + B_{2g}$ (in D_{4h}), and the cell is halved.

Since the CO_2 structure forms an acceptable basis in accounting for the spectra of $\text{HgCl}_2(\text{II})$ we do not at this stage search for new, hypothetical, structures. Whatever the new structure is, the change to it appears to involve the modes which are assigned as molecular rotatory.

The Structure of $\text{HgCl}_2(\text{IV})$ and the Mechanism of the Phase Transitions

The similarity of the spectra of phases I and IV implies a subtle structural difference. $\text{HgCl}_2(\text{I})$ has the symmetry of space

group D_{2h}^{16} and all of the atoms lie in mirror planes. Accordingly, there is no crystallographic requirement that the Hg-Cl bond lengths be equal or the molecule linear; the bond lengths are different and the molecule is not quite linear. We propose that the second-order transition to $\text{HgCl}_2(\text{IV})$ consists of a rearrangement of the molecules relative to each other within each mirror plane with retention of space group. Expressed crystallographically, this takes advantage of the fact that the sets of Wyckoff sites $4c$ have no geometrical restrictions upon them other than that they remain in the mirror plane. Such a rearrangement would require a combination of translatory motions, and rotary motion about axes normal to the plane. Credence is lent to this view by knowledge that the small spectral changes accompanying the I/IV transition are all in the region of the translatory and rotatory lattice modes.

Since the structures of phases I and IV are almost identical the mechanism of the IV/II transition is considered in terms of a hypothetical I/II transition since the structure of phase I is fully characterised. The spectroscopic results are consistent with the view that $\text{HgCl}_2(\text{II})$ has the CO_2 structure (cubic, T_h^6). To move from the orthorhombic phase I to a phase with the CO_2 structure the following changes are necessary.

- (i) Translate the layers of $\text{HgCl}_2(\text{I})$ relative to each other by $c/4$.
- (ii) Alter the relative lengths of the three axes such that they become equal (c is halved due to the change in symmetry).
- (iii) Rotate each molecule out of the ac plane.

In practice these changes must occur in one concerted movement. Examination of a model of $\text{HgCl}_2(\text{I})$ indicates that the first result of compression is likely to be the translatory and rotatory motions specified above as leading to phase IV. Further compression would then increase the repulsive energy rapidly but this could be relieved by allowing adjacent molecules to "dive" under one another by means of rotation about axes parallel to $\underline{c}$ passing through the mercury atoms, accompanied by translations, to give the cubic CO_2 structure. These movements are indicated in Figure 5:5. In principle this mechanism could be tested by explicit calculation of lattice energies but this is frustrated at present by the lack of suitable potential functions. It would be simple to calculate the energetics based upon an electrostatic model with fractional atomic charges but, even should that support the proposed mechanism, agreement would be regarded as fortuitous because dispersive forces must be dominant in a crystal of this type.

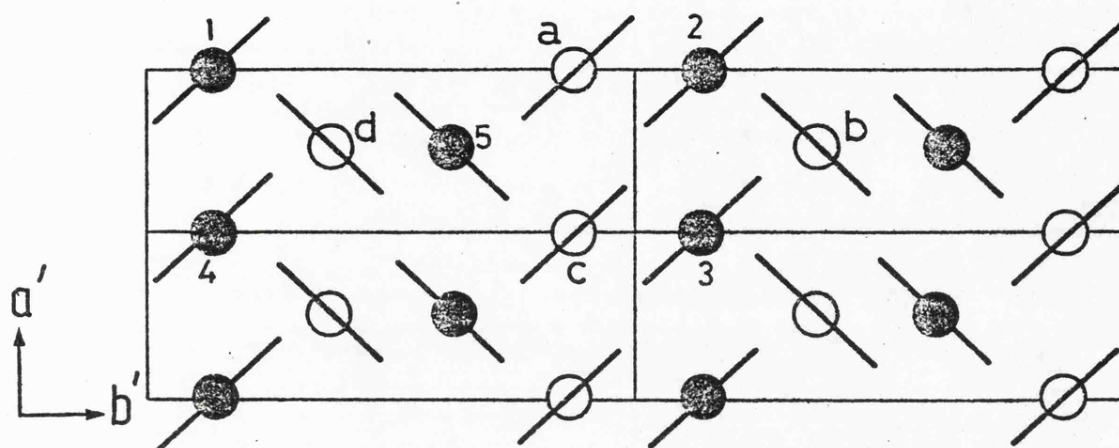
Summary of HgCl_2 work

Raman and far-i.r. spectra of phases I, II and IV under hydrostatic pressures are given. Assignments of the spectra of each phase are discussed and a mechanism for interconversion of the proposed phases given. The high pressure phase II is believed to adopt the CO_2 structure.

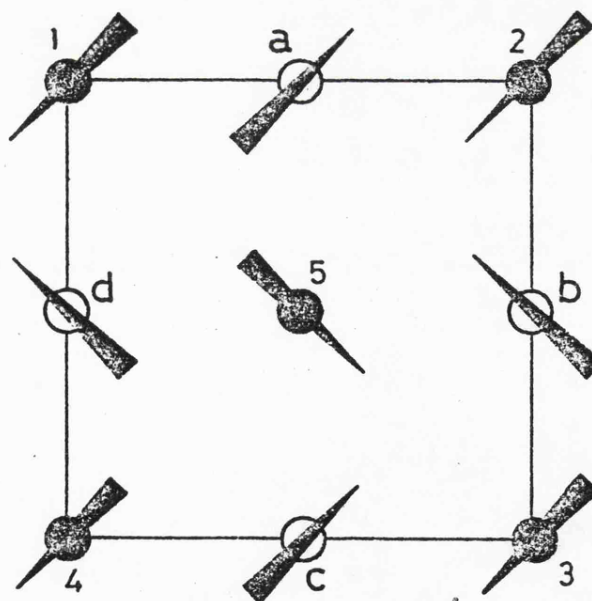
FIGURE 5:5

The relationship between $\text{HgCl}_2(\text{I})$ and $\text{HgCl}_2(\text{II})$ adopting the CO_2 Structure. Letters and numbers indicate molecules which correspond in the two drawings. Open circles and full circles indicate molecules half a unit cell apart.

I



II



5.4 Mercuric Bromide

Mercuric bromide exists in four polymorphic modifications (Bridgman 1937, Pistorius 1976). The phase diagram is shown in Figure 5:6. The structure of the ambient phase $\text{HgBr}_2(\text{I})$ is known (Wyckoff 1964) but no information is available on the other three. A study of the Raman and i.r. of all four phases was undertaken with the objective of characterising each phase, and identifying its structure within the limits of vibrational spectroscopy. This work has been published (Adams and Appleby 1977b). Commercial HgBr_2 was recrystallised twice from ether before use. The spectra are given in figures 5:7 to 5:9 and the frequencies listed in Tables 5 and 6.

$\text{HgBr}_2(\text{I})$

Although many reports (Mikawa, Jacobsen, and Brasch 1966, Decamps and Hadni 1968, Decamps, Marqueton, Durand and Abba 1973) have been made of its i.r. and Raman spectra no satisfactory assignment exists for $\text{HgBr}_2(\text{I})$, chiefly because no single-crystal study has been made of it. A study is in progress at this time within our group. It has a layer structure (Wyckoff 1964) which is related to that of the cadmium dihalides but differs from it in that two colinear Hg-Br bonds are much shorter than the other four which complete a tetragonally distorted octahedron. The two Hg-Br bond lengths are very different (2.49 and 3.25 Å) and the

FIGURE 5:6

Phase Diagram of HgBr_2

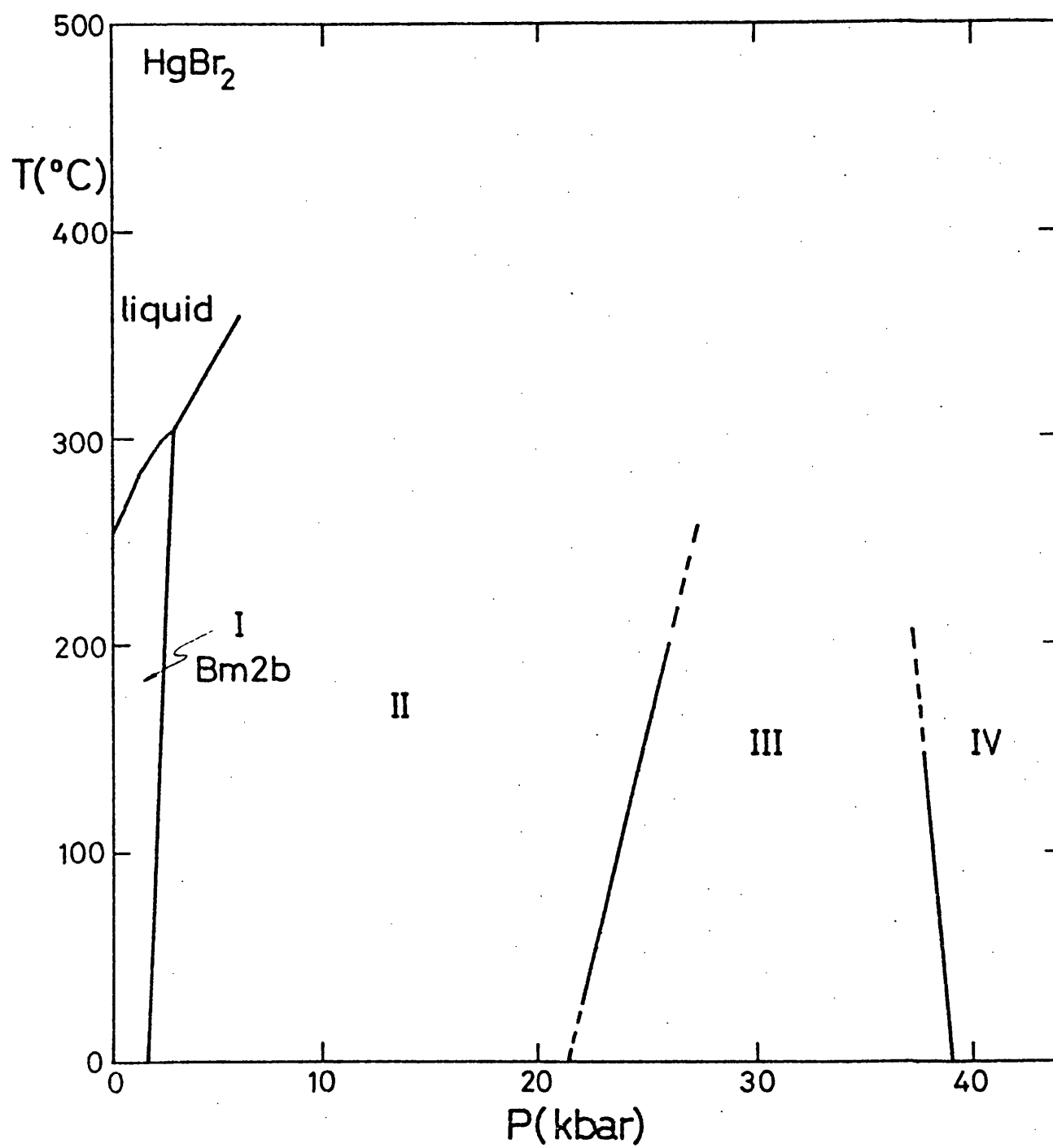


FIGURE 5:7

Raman Spectra of Polymorphs of HgBr_2 at 295 K.
Spectral Slit Width 1.5 cm^{-1} , 60 mW 514.5 nm
radiation at the Sample.

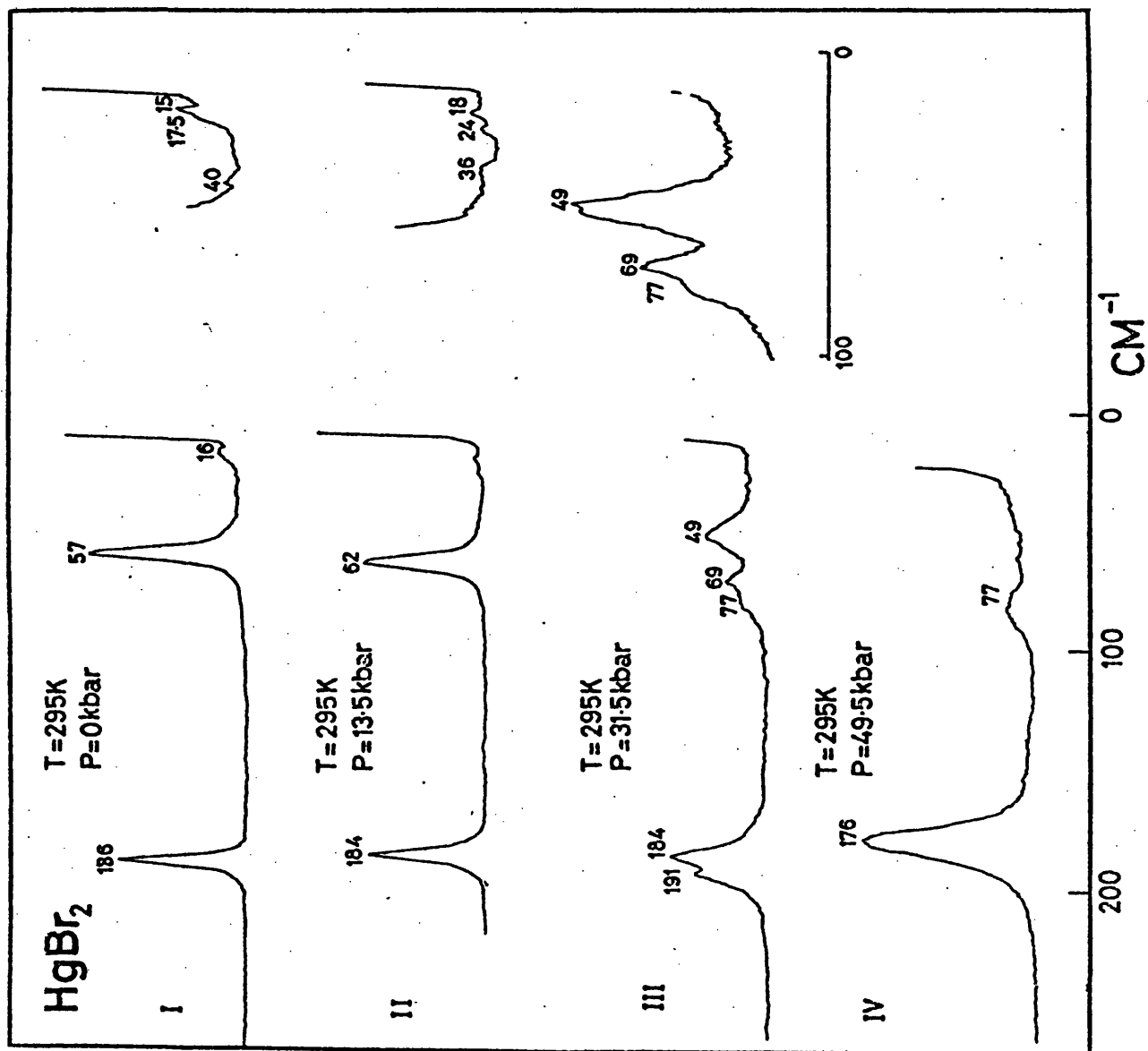


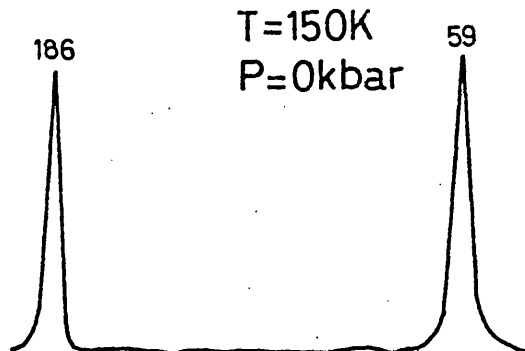
FIGURE 5:8

Raman Spectra of Polymorphs of HgBr_2 at 150 K.

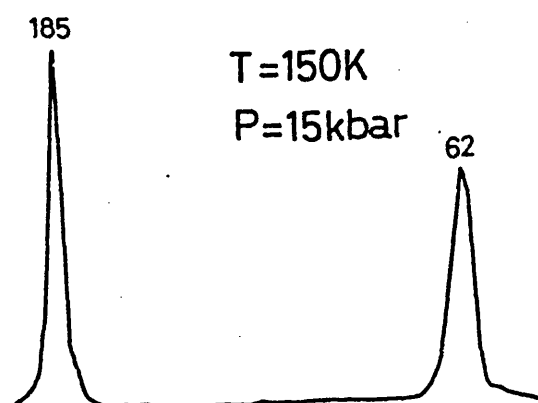
Conditions as for Figure 5:7.



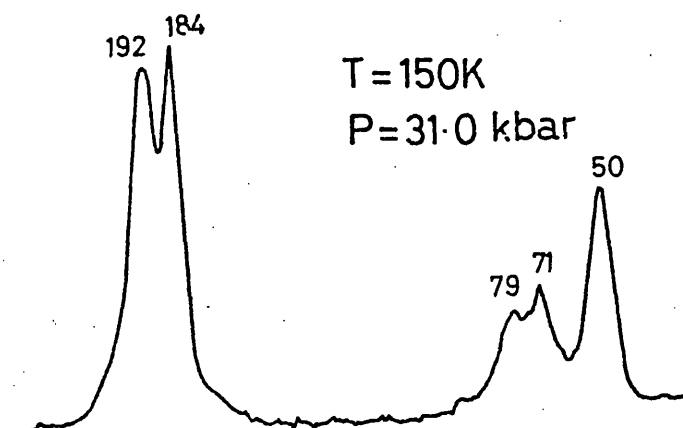
I



II



III



IV

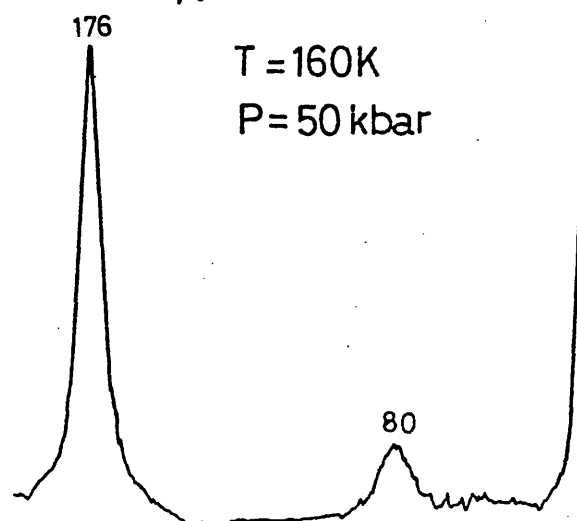
200 100 0 cm^{-1}

FIGURE 5:9

I.r. Transmission Spectra of Polymorphs of HgBr_2
at Ambient Temperatures.

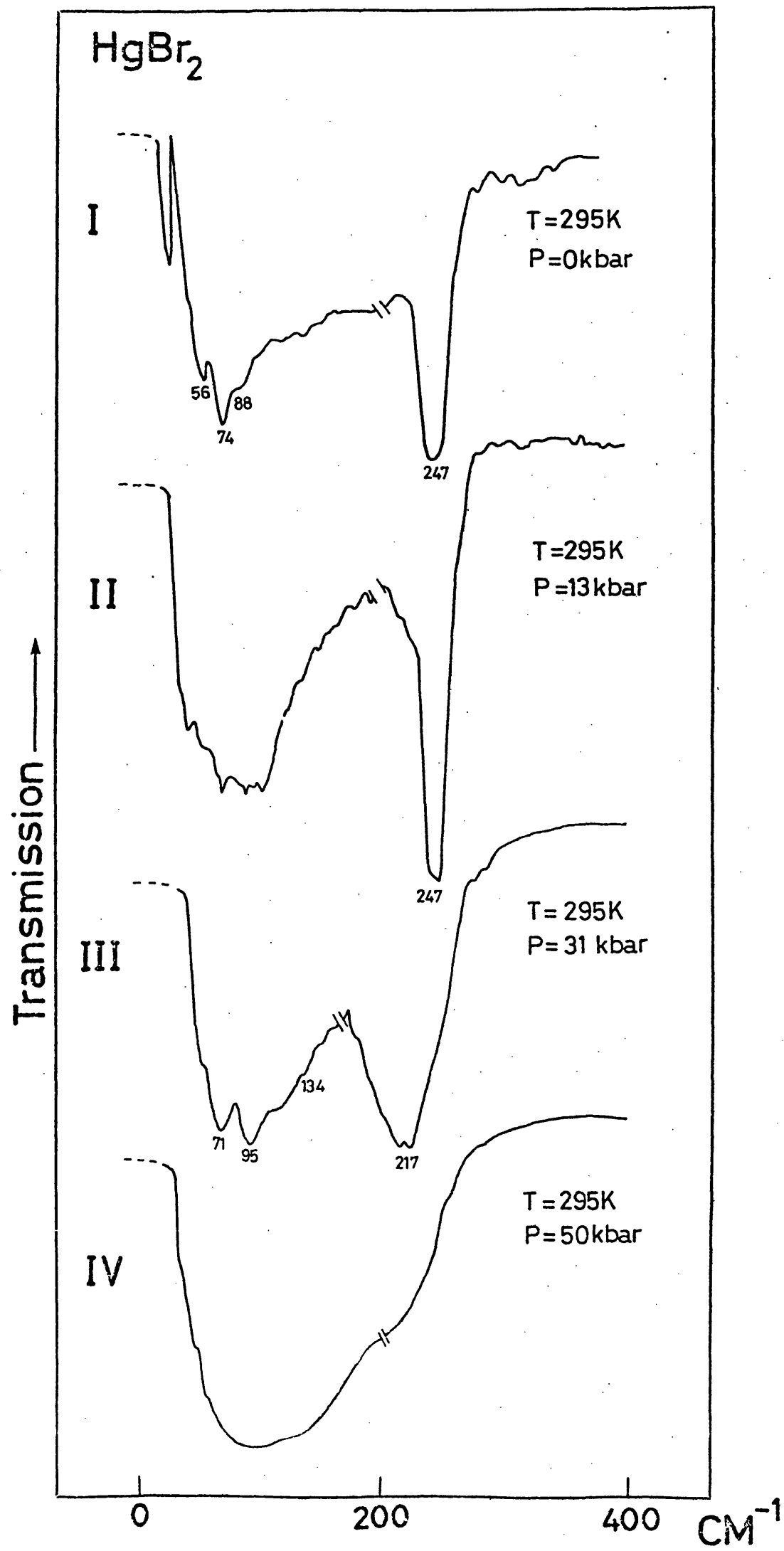


TABLE 5 Raman wavenumbers/cm⁻¹ for HgBr₂ at various pressures at ambient temperature.

Pressure/kbar	0	6.3	18.8	23.3	31.6	35.8	49.5
Phase	I	II	II	III	III	IV	IV
				191	191		
	186	185	184	184	184	179	176
				74	77	78.5	77
	57	61	60	60	69		
				50	49		
	40	38					
	17.5	22	24				
	15	17	18				

TABLE 6 I.r. wavenumbers/cm⁻¹ for HgBr₂ at various pressures at ambient temperature.

Pressure/kbar	0	10	20	30	40
Phase	I	II	II	III	IV
	247.5	247	238	<u>ca.</u> 217 br ^a	<u>ca.</u> 210 sh ^b
				134 sh	
	88 sh			95	
	74	<u>ca.</u> 86 br	82 br	71	<u>ca.</u> 100 ^b
	56			56 sh	
	31				

^a unresolved components on low-frequency side .

^b see Figure 4

structure is profoundly different from that of $\text{HgCl}_2(\text{I})$.

The $\text{HgBr}_2(\text{I})$ structure is orthorhombic, $\underline{\text{C}}_{2v}^{12} = \text{Bm}\bar{2}\text{b}$ with a bimolecular primitive cell (Wyckoff 1964). The factor group analysis (f.g.a.) is shown in Table 7. This clearly predicts that all the i.r. modes will also be Raman active but, in practice, the molecular symmetry, $\underline{\text{D}}_{\infty\text{h}}$, exerts the major influence in determining the relative intensities in the two effects.

In the ν_1 , $\nu(\text{HgBr}_2)_{\underline{\text{s}}}$ region the Raman spectrum shows a single band (186 cm^{-1} at 295 K) which can be resolved into a doublet at low temperature, in accord with f.g.a. predictions which require two components, $A_1 + B_2$. However, these bands do not show through in the i.r. spectra under the conditions we have used in this work, although it is possible that they might be seen under forcing conditions. Similarly, the intense i.r.-active ν_3 , $\nu(\text{HgBr}_2)_{\underline{\text{a}}}$, (247 cm^{-1} at 295 K), was not seen in the Raman spectra.

Below 100 cm^{-1} both i.r. and Raman spectra show several bands: these may originate from factor group components of ν_2 , $\delta(\text{HgBr}_2)$, and from rotatory and translatory lattice modes. There is no a priori means of identifying individual contributions, and it is probable that they will, in any case, be significantly mixed. However, on the basis of the behaviour found for ν_1 and ν_3 we consider that ν_2 will be intense in the i.r. spectra (it should yield three bands, $A_1 + B_1 + B_2$) but either weak or absent from Raman spectra. An analogous argument suggests that the rotatory modes ($A_1 + A_2 + B_1 + B_2$) will

TABLE 7 Factor group analysis and correlation scheme for HgBr_2 .A : F.g.a.

							Activities
$\underline{C}_{2v}^{12}$	N_T^a	T_A	T	R(x,y)	v_i	i.r.	Raman
A_1	6	1	1	1	3	<u>z</u>	<u>x^2</u> , <u>y^2</u> , <u>z^2</u>
A_2	3		1	1	1		<u>xy</u>
B_1	3	1		1	1	<u>x</u>	<u>zx</u>
B_2	6	1	1	1	3	<u>y</u>	<u>yz</u>

B : Correlation

Molecule ^b	Site	Crystal
$\underline{D}_{\infty h}$	$\underline{C}_s(\underline{yz}) \xrightarrow{x^2} \underline{C}_{2v}^{12}$	
v_1, Σ_g^+		$3(A_1 + B_2)^c$
v_3, Σ_u^+		
v_2, π_u		
	A''	$A_2 + B_1^c$

^a N_T total number of unit cell modes, T_A acoustic branch modes,
 T optic branch translatory lattice modes, R(x,y) rotatory
 lattice modes (2 axes only), v_i molecular internal modes.

^b Approximate geometry, see text.

^c These sum to give column v_i of A.

be present in Raman but not in i.r. spectra, as is the case for $\text{HgCl}_2(\text{I})$.

At room temperature the Raman spectrum is dominated by an intense band at 57 cm^{-1} which we accordingly attribute to rotatory motion of the molecules. The i.r. spectrum is more complex in this region exhibiting three intense bands which could well be the expected ν_2 components (56 , 74 , and 88 cm^{-1}), together with weak features $< 50\text{ cm}^{-1}$ which correspond to some weak, sharp bands in the Raman spectra which are probably due to translatory modes.

$\text{HgBr}_2(\text{II})$

According to | Bridgman (1937) the I/II transition takes place at room temperature at ca. 3 kbar, after which phase II is stable up to ca. 23 kbar. The transition is known to be sluggish at this temperature: therefore $\text{HgBr}_2(\text{II})$ was prepared by heating (I) to 348 K before applying pressure, as well as by direct application of pressure at 295 and 150 K. Spectra obtained at these three temperatures were consistent with each other and differed from those of $\text{HgBr}_2(\text{I})$ only in rather minor respects.

The most significant spectroscopic change associated with the transition was that ν_1 decreased in frequency slightly with increase of pressure, whereas the 57 cm^{-1} band (probably due to rotatory motion) showed a normal increase and lost intensity

slightly in comparison with ν_1 . In the i.r. spectra the complex region $< 100 \text{ cm}^{-1}$ became broadened to the extent that most of the components could not be seen clearly. The weak Raman bands $< 50 \text{ cm}^{-1}$ also suffered positive shifts with increase of pressure.

Because the pressure range in which $\text{HgBr}_2(\text{II})$ is stable is considerable there can be no doubt that this phase was obtained and characterised by i.r. and Raman spectroscopy. Nevertheless, it is doubtful whether the above differences would have been associated with a phase change in the absence of a knowledge of the phase diagram. In contrast the major spectral changes accompanying the transformations to phases III and IV are self-evident.

$\text{HgBr}_2(\text{III})$ and (IV)

Further increase of pressure upon phase II eventually resulted in development of new features which first showed in the Raman spectra as the development of wings on either side of the band ca. 60 cm^{-1} , and as broadening of the ν_1 region. These rapidly developed with pressure yielding the spectrum of pure $\text{HgBr}_2(\text{III})$ shown in Figure 5:7. Equally marked changes occurred in the i.r. spectra, Figure 5:9. Above ca. 40 kbar the rather complex Raman spectrum of phase III was dramatically simplified leaving a spectrum (phase IV) consisting of two rather broad bands at 80 and 176 cm^{-1} ; cooling to 150 K produced some sharpening but did not reveal any new features. The i.r. spectrum also showed major changes. These observations independently confirm Bridgman's reports of these transitions.

Structures of HgBr_2 (II), (III) and (IV)

As there are no structural data for these phases we are restricted to making such deductions as are possible on the basis of the spectra.

The most striking feature of our results is the trend of the $\nu(\text{Hg-Br})$ frequencies to lower values as pressure is increased. This is contrary to normal behaviour, since a symmetric mode might reasonably be expected to shift to higher frequency by at least $0.5 \text{ cm}^{-1} \text{ kbar}^{-1}$. The only exception to this unusual trend is seen in the Raman spectrum of phase III in which it appears that correlation coupling has raised one component. The basic structural reason for this frequency decrease is considered to be a trend to higher coordination number at mercury.

On the present evidence a transition from this general understanding to the particular structures of phases II, III and IV is almost impossible. The results characterise these phases by means of their vibrational spectra but raise intriguing problems which must eventually be settled by single-crystal X-ray crystallography at equivalent pressures. Undoubtedly the most puzzling result is that the spectra of phases I and II are almost identical. No bands were lost or gained in the transition, with the reservation that the breadth of the i.r. absorption below 100 cm^{-1} may obscure some more significant difference. By 18.8 kbar the two Raman bands have moved together by only 5 cm^{-1} . A similar situation was found for HgCl_2 in that the ambient phase I and the first high-pressure

phase IV showed only the most minor spectral differences, although these were more pronounced than those shown by the HgBr_2 I, II comparison. What is more significant is that the I/IV transition in HgCl_2 is second order and was not detected by Bridgman (1937) who used a compression curve method, whereas the HgBr_2 I/II transition is first order and was detected by him; it has an accompanying volume change comparable with those for the II/III and III/IV transitions. We suggested that the HgCl_2 I/II transition involves reorientation of the HgCl_2 molecules within the mirror planes upon which they lie, thereby retaining the space group of phase I. It may be that such an explanation should be attached to the HgBr_2 I/II transition as well as to, or instead of, the HgCl_2 I/IV transition.

The spectra of $\text{HgBr}_2(\text{IV})$ are strongly reminiscent of those yielded by materials with the CdI_2 structure (Lockwood 1973). A high-symmetry environment is implied by the profound simplification of the Raman spectra upon leaving phase III, whilst the i.r. spectra similarly show pronounced differences, Figure 5:9. Significantly, there is a further decrease in $\nu(\text{Hg-Br})$ in the Raman spectra, reaching 176 cm^{-1} at 49.5 kbar, making a shift of -10 cm^{-1} from ambient pressure. The difficulty is that there is no basis for deciding whether this decrease is large enough to imply a change from a structure in which some of the Hg-Br bonds differ in length from others, to one in which they are all equal (as they must be in a CdI_2 -type layer). We therefore content ourselves with noting that

both i.r. and Raman spectra are consistent with selection rules for both CdCl_2 and CdI_2 structures, thus:

$$A_{1g} + E_g + A_{2u} + E_u$$

where the g-modes are Raman-active and the u-modes i.r.-active.

However, comparison of the structural models of $\text{HgBr}_2(\text{I})$, CdCl_2 and CdI_2 implies that a transition to the CdI_2 type would be less disruptive.

Phase III appears still to be composed of molecules in that the $\nu(\text{Hg-Br})$ frequencies are close to or higher than those of phase I. The presence of a $\nu(\text{Hg-Br})$ doublet clearly implies a cell that is at least bi- and, probably, tetra-molecular. Increased complexity below 150 cm^{-1} in both i.r. and Raman spectra implies a low-symmetry structure, and is compatible with one of monoclinic symmetry. The spectra also imply retention of the inversion centre since there appear to be i.r.-Raman exclusions, although this evidence is possibly equivocal in view of the analysis of $\text{HgBr}_2(\text{I})$ above. Structurally, it appears that the layers of $\text{HgBr}_2(\text{I})$ must have been buckled because removal of the mirror planes present in it present the only major change possible. A transition to a monoclinic cell with factor group $\underline{C}_{2h}$ would accommodate our observations. We are not aware of any linear AB_2 molecule that crystallises in a monoclinic structure. A transition to the monoclinic CuCl_2 structure, though feasible, is ruled out by the selection rules, and the positions of $\nu(\text{Hg-Br})$.

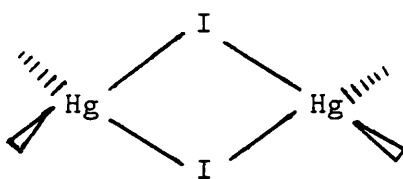
Summary of HgBr₂ work

Raman and far-i.r. spectra of phases I, II, III, and IV under hydrostatic pressures are given. The spectra of each phase are assigned as far as possible and probable structures discussed. The highest pressure phase IV has most probably the structure of CdI₂ or a polytype of it.

5.5 Mercuric Iodide

The curious polymorphism of mercuric iodide poses a number of unsolved problems. The object of this work was to obtain spectroscopic evidence which might be of value in this context. The results have been reported (Adams, Appleby and Barlow 1977).

At ambient temperature and pressure, HgI₂ adopts a red layer structure in which mercury is tetrahedrally coordinated to iodine and each iodine forms half of a normal halogen bridge.



Above ca. 127^oC (slightly different values are quoted) the red form changes to a yellow one which is isostructural with the ambient pressure phase I of HgBr₂. A detailed single crystal X-ray study of the two forms has confirmed the essential features of earlier

powder data (Jeffrey and Vlasse 1967). Expansion of the red HgI_2 lattice by heating, thus yields a yellow polymorph: strangely, however, compression of the red form (at ambient temperature) above ca. 13 kbar yields a phase which |Bridgman (1915) found to be continuous with the high temperature yellow form, figure 5:10, and which has subsequently been confirmed as being yellow, by several workers (Brasch, Melveger and Lippincott 1968). In Chapter 2, figure 2:3b photomicrographs of this transition confirm these reports. His discovery struck |Bridgman as "so unnatural" that he investigated the phenomena with exceptional thoroughness but reached no firm conclusions. The Raman spectra of the two yellow preparations are said to be identical (Brasch, Melveger and Lippincott 1968). The only X-ray study of the high pressure yellow form yielded powder data that were indexed on the basis of the same space group as the high temperature yellow form (C_{mc2_1} , $z = 4$): there was apparently a slight decrease in one of the cell parameters.

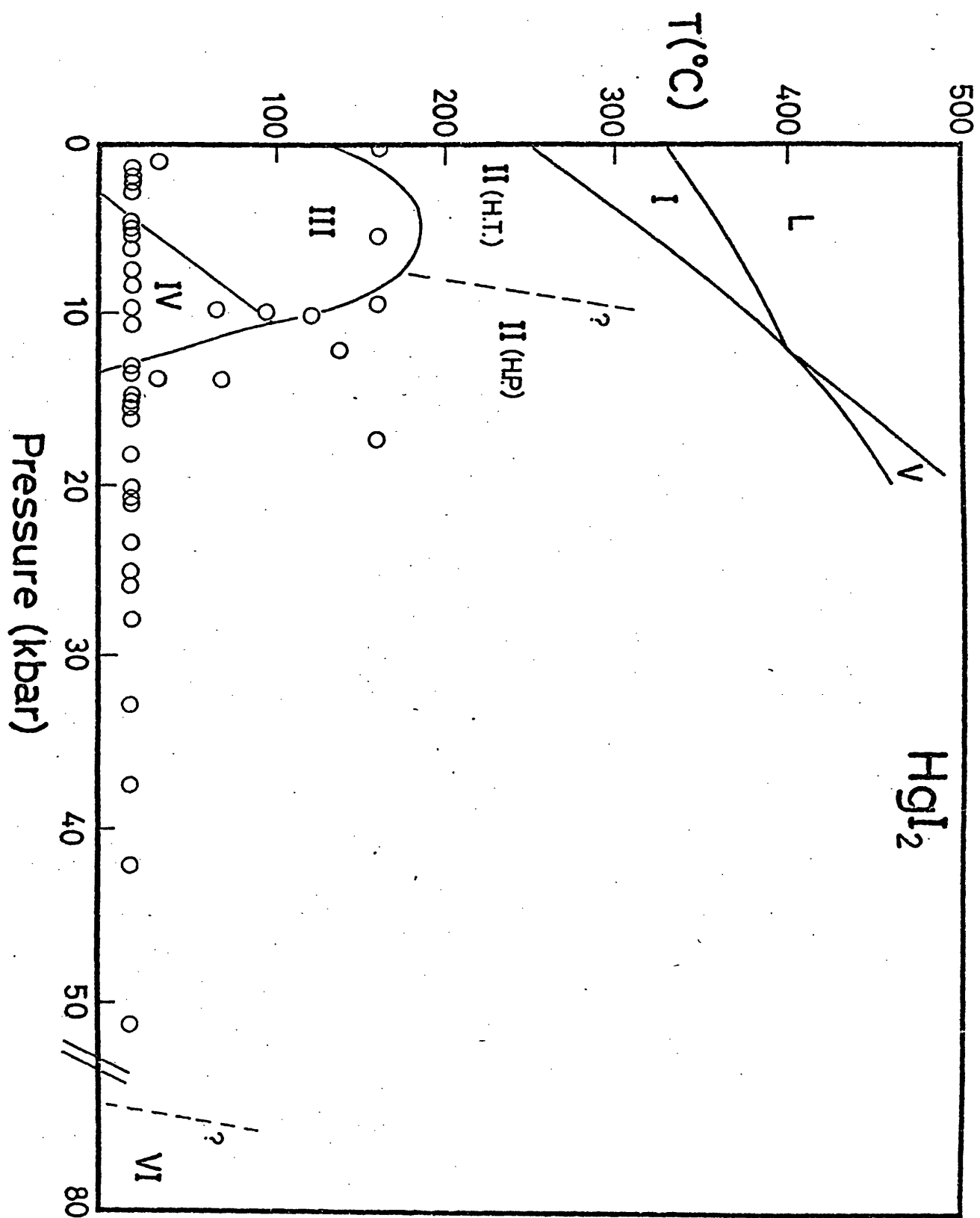
<u>a</u>	<u>b</u>	<u>c</u>	<u>Ref</u>
High temp. 4.702	7.432	13.872	Jeffrey and Vlasse (1967)
High press. 4.70	7.43	13.63	Mikler (1972)

Mikler discovered a further polymorph of HgI_2 stable above ca. 75 kbar, which did not have the common $4H\text{-CdI}_2$ structure but could be

FIGURE 5:10

Phase Diagram of HgI_2 (Pistorius 1976).

The open circles indicate the positions (P and T)
of experiments carried out.



indexed on the basis of the hexagonal group $P\bar{3}1D_3^4$. If a drawing of this structure is composed with the atom positions given, it can clearly be seen that it is physically unrealistic. Pistorius (1976) believed this phase to be the 8H polytype of CdI_2 . $P\bar{3}1$ is not a known polytype of CdI_2 (Montero and Kiefer 1973).

An orange form of HgI_2 was claimed by Kohlscuuter (1927) and has been disputed ever since. Reported colours, lifetimes, and properties differ wildly and according to the most recent X-ray investigation of a single crystal, (Schwarzenbach 1969) this phase is a complex superstructure of red HgI_2 , containing a tetrahedron of HgI_2 tetrahedra (Hg_4I_{10}). The space group is $I4_2/amd$ with $z = 16$. Jeffrey and Vlasse found $z = 128$ and the location of this form on the phase diagram is unknown. This form is said to be found as single crystals amongst crystals of the yellow form when they are grown from solution. The yellow crystals revert rapidly to the red form and are only metastable at room temperature. It seems likely that the orange form exists as some mixture of the red and yellow which has become stable and moderately organised.

Finally a claim based upon a d.t.a. study (Tonkov and Tikhomirova, 1970) shows that $HgI_2(IV)$ exists in the region indicated in figure 5:10. It is not known whether this is to be identified with the orange form.

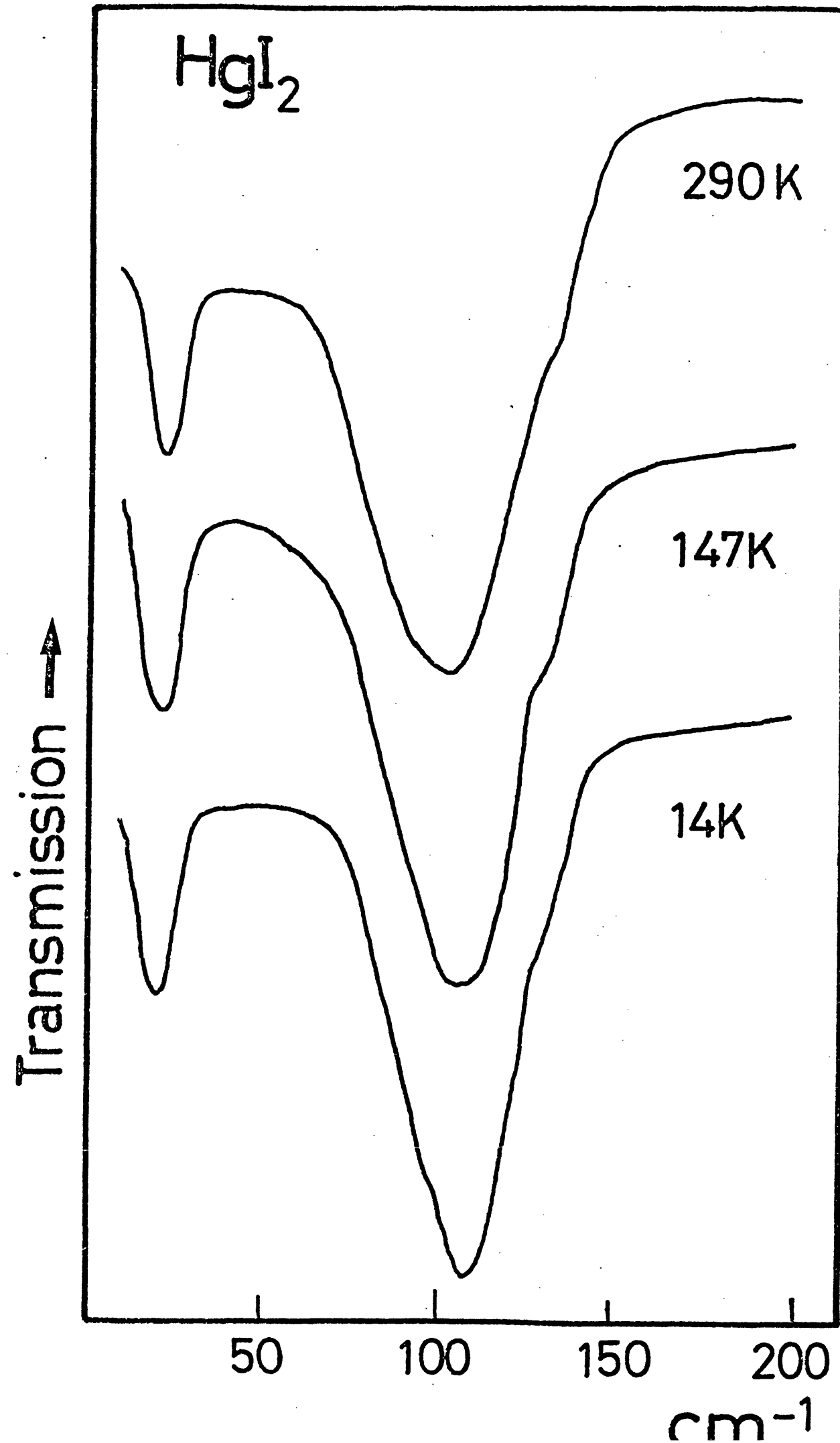
Results and Discussion

Red HgI₂ : the I.R. Spectrum

There have been many vibrational spectroscopic studies of red HgI₂. It should show three i.r.-active modes, $A_{2u} + 2E_u$ in D_{4h}^{15} . Assignment of the two E_u modes has been unequivocally established by single crystal reflectance (Ogawa, Harada, Matsuura and Shimanouchi 1976) as being at 25 and 105 cm^{-1} but the evidence for the A_{2u} mode position is still only circumstantial. It is evidently weak and no significant far-i.r. reflectance spectrum can be obtained from a crystal in light polarised parallel to the crystal c-axis (Ogawa, Harada, Matsuura and Shimanouchi 1976, and Adams, Appleby and Barlow 1977). Shoulders on the broad 105 cm^{-1} band have been reported at 60 (Mon 1966); 92 and 132 (Mikawa, Jacobsen and Brasch 1966); 62 vw , 132 (Marqueton, Abba, Decamps, and Nusonivici 1971), 88, 139, 200 (Krauzman, Krauzman and Poulet 1971) and 62.5 cm^{-1} (Decamps and Hadni 1968). There is no a priori means of deciding which of these features is to be associated with the A_{2u} mode. The spectra of HgI₂ nujol mulls, figure 5:11 show a shoulder at ca. 132 cm^{-1} seen most clearly at 150 K, but no band at 62 cm^{-1} . The most compelling evidence for assignment of the 132 cm^{-1} band to the A_{2u} mode ~~remains~~ its proximity to the 144 cm^{-1} Raman band. These two form a Davydov doublet created by vibrational interaction of the two types of layer in the unit cell, although it should be noted that this assignment yields a larger Davydov splitting than that associated with the other modes.

FIGURE 5:11

Far-i.r. Spectra of HgI_2 (Nujol Mulls) at
Various Temperatures and Ambient Pressure.



Variable temperature reflectance and transmission work was undertaken to search for evidence of the III to IV phase transitions. The published line is shown in figure 5:10. If this is extrapolated at 1 bar the transition should take place at -44°C (229 K). Plots of frequency versus temperature for all modes are given in figure 5:12 and wavenumbers versus temperature in Table 8. No breaks in these plots were found, indicating that the transition was not observed although it is possible that it was so sluggish (as is the red to yellow transition) that the transition occurred over a large temperature range and may not have been complete even at very low temperatures.

Red HgI_2 : The Raman Spectrum

The assignment of symmetry species has been well established by four concordant single crystal studies (Ogawa, Harada, Matsuura and Shimanouchi 1976, Adams and Hooper 1971, Rogstad 1973 and Nakashima, Mishima and Mitsuishi 1973). A study of the Raman spectrum of the powder down to 20 K showed no sign of the III to IV transition, figure 5:12 and Table 8, but the 144 cm^{-1} band is abnormally temperature sensitive. It is the only Raman active mode in which mercury atoms move in directions normal to the sheets but the X-ray parameters (Jeffrey and Vlasse 1967) do not indicate any abnormal motion of mercury parallel to $\underline{c}$. A low temperature crystal structure determination would however prove interesting.

TABLE 8 Vibrational wavenumbers (cm^{-1}) for Red HgI_2 at ambient pressure and various temperatures.

T/K	Raman				I.r.	
	<u>416^a 293 12</u>				<u>290 14</u>	
	<u>II III</u>					
	(hT)					130 sh
	145		142 sh	142	102	109
	41	112	113.5	114.3	24	24
	37	29.0	29.0	30.5		
	11.5	17.0	17.5	19.0		

^a Mixture of yellow and red forms.

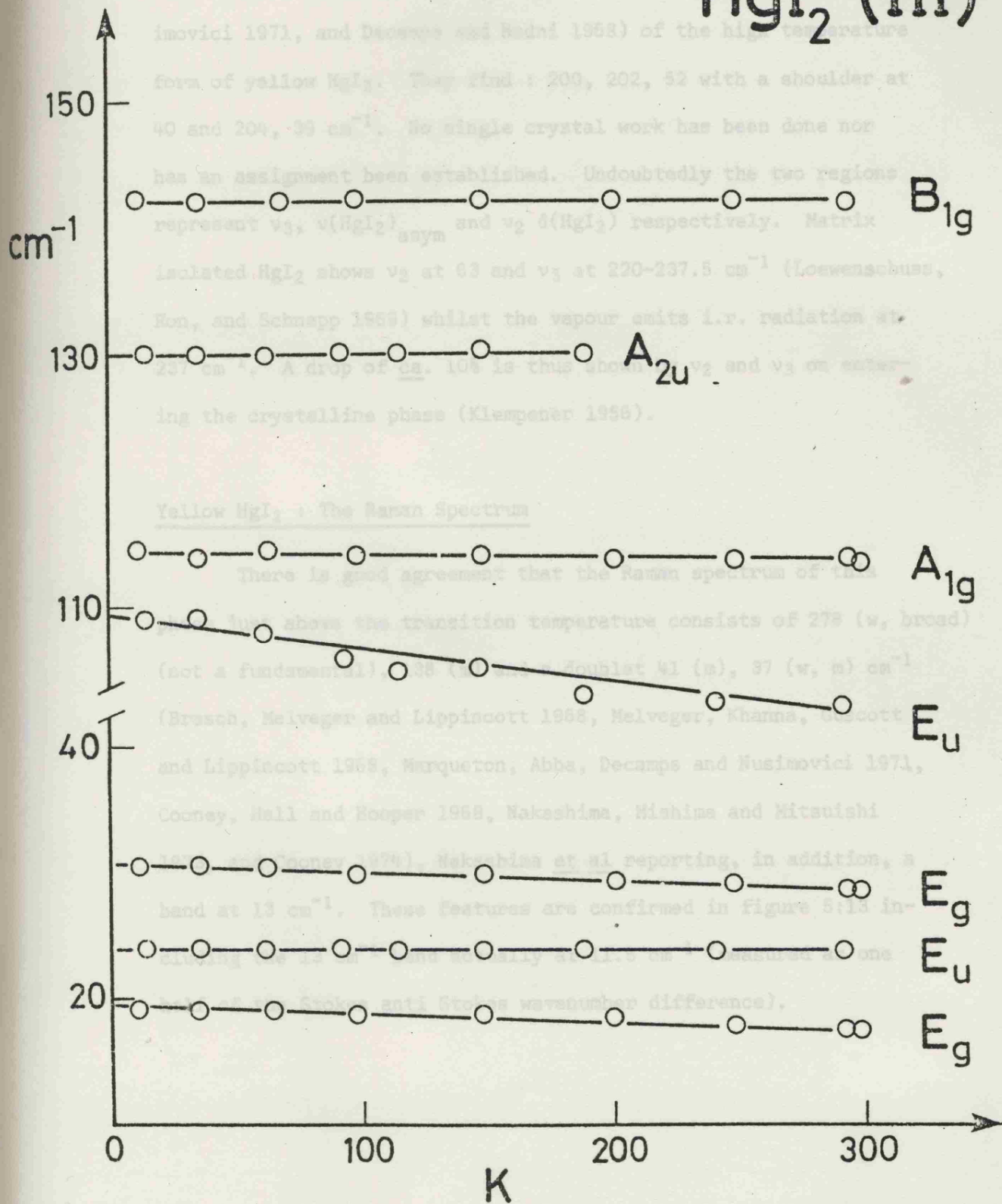
FIGURE 5:12

Plots of Frequency (cm^{-1}) Versus Temperature
for All the Vibrational Modes of Red HgI_2 .

Yellow HgI_2 : The Infrared Spectrum

There have been three concordant studies (Melveger, Khanna, Guscott, and Lippincott 1968, Marqueton, Abba, and Nusimovici 1971, and Decamps and Nedel 1968) of the high temperature form of yellow HgI_2 . They find : 209, 202, 52 with a shoulder at 40 and 204, 39 cm^{-1} . No single crystal work has been done nor has an assignment been established. Undoubtedly the two regions represent ν_3 , $\nu(\text{HgI}_2)_{\text{asym}}$ and ν_2 , $\delta(\text{HgI}_2)$ respectively. Matrix isolated HgI_2 shows ν_2 at 63 and ν_3 at 220-237.5 cm^{-1} (Loswanschuss, Ron, and Schnapp 1969) whilst the vapour emits i.r. radiation at 237 cm^{-1} . A drop of ca. 10% is thus shown ν_2 and ν_3 on entering the crystalline phase (Klemperer 1956).

HgI_2 (III)



Yellow HgI_2 : The Raman Spectrum

There is good agreement that the Raman spectrum of this form shows the transition temperature consists of 278 (w, broad) (not a fundamental), 136 (m, doublet 41 (m), 37 (w, m) cm^{-1} (Brasch, Melveger and Lippincott 1968, Melveger, Khanna, Guscott and Lippincott 1968, Marqueton, Abba, Decamps and Nusimovici 1971, Cooney, Hall and Hooper 1968, Nakashima, Hishima and Mitsubishi 1971, and Cooney 1971). Nakashima et al reporting, in addition, a band at 13 cm^{-1} . These features are confirmed in figure 5:13 in- (showing the 13 cm^{-1} band clearly at low temperatures and one at 13 cm^{-1} and Stokes anti Stokes wavenumber difference).

Yellow HgI₂ : The Infrared Spectrum

There have been three concordant studies (Melveger, Khanna, Guscott, and Lippincott 1968, Marqueton, Abba, Decamps, and Nusimovici 1971, and Decamps and Hadni 1968) of the high temperature form of yellow HgI₂. They find : 200, 202, 52 with a shoulder at 40 and 204, 39 cm⁻¹. No single crystal work has been done nor has an assignment been established. Undoubtedly the two regions represent ν_3 , $\nu(\text{HgI}_2)_{\text{asym}}$ and ν_2 $\delta(\text{HgI}_2)$ respectively. Matrix isolated HgI₂ shows ν_2 at 63 and ν_3 at 220-237.5 cm⁻¹ (Loewenschuss, Ron, and Schnepf 1969) whilst the vapour emits i.r. radiation at 237 cm⁻¹. A drop of ca. 10% is thus shown by ν_2 and ν_3 on entering the crystalline phase (Klempner 1956).

Yellow HgI₂ : The Raman Spectrum

There is good agreement that the Raman spectrum of this phase just above the transition temperature consists of 278 (w, broad) (not a fundamental), 138 (m) and a doublet 41 (m), 37 (w, m) cm⁻¹ (Brasch, Melveger and Lippincott 1968, Melveger, Khanna, Guscott and Lippincott 1968, Marqueton, Abba, Decamps and Nusimovici 1971, Cooney, Hall and Hooper 1968, Nakashima, Mishima and Mitsuishi 1973, and Cooney 1974), Nakashima et al reporting, in addition, a band at 13 cm⁻¹. These features are confirmed in figure 5:13 including the 13 cm⁻¹ band actually at 11.5 cm⁻¹ (measured as one half of the Stokes anti Stokes wavenumber difference).

FIGURE 5:13

Raman Spectra of HgI_2 at Various Temperatures.

Conditions: 60 mW of 647.1 nm radiation (Kr^+)
at the sample and a spectral slit width 0.5 cm^{-1}
were used.

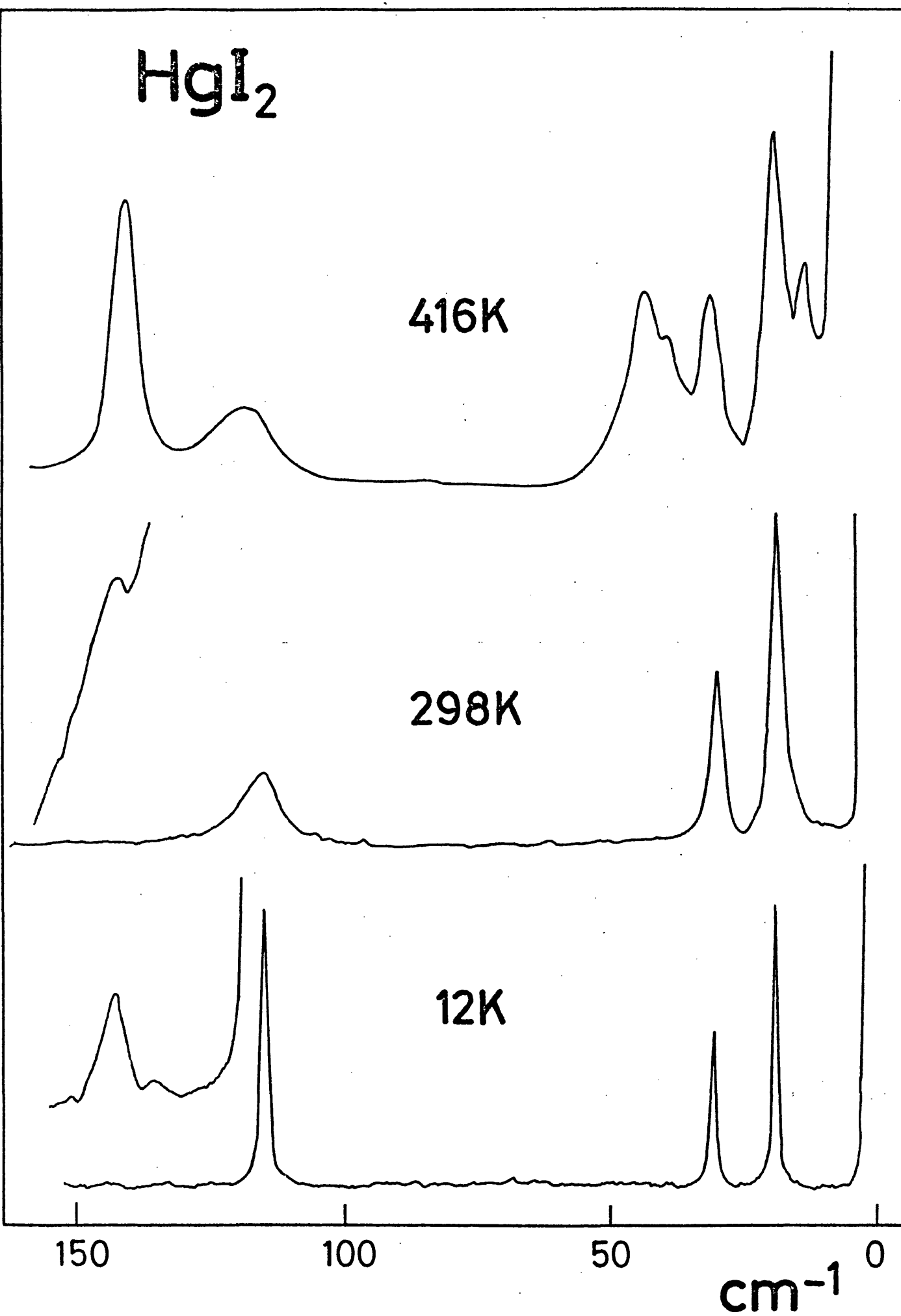
HgI₂**416K****298K****12K**

150

100

50

0

cm⁻¹

The High Pressure Results

With increase of pressure on red HgI_2 at ambient temperature, all the Raman bands shifted to higher frequency as shown in figures 5:14, 5:15 and Table 4 until 10.3 kbar, where the characteristic features of yellow HgI_2 appeared. By 13.2 kbar pure yellow HgI_2 was obtained. This region of mixed-phase behaviour is similar to Bridgman's "region of indifference" (Bridgman 1915). There is a break in the slopes of frequency versus pressure lines at 6.0 kbar. This is the only evidence that has been found in support of the III to IV transition located by d.t.a. measurements and is in agreement with it. The i.r. measurements, figure 5:16 and Table 4, showed the bands to rise with pressure but the band centred at 104 cm^{-1} was broad and difficult to measure accurately.

At ambient temperatures the Raman spectrum of yellow HgI_2 at 13.2 kbar shows pronounced differences from that of the yellow HgI_2 formed by heating the red phase at ambient pressure, see figures 5:13, 5:15. (i) There is no 11.5 cm^{-1} band; (ii) The doublet below 100 cm^{-1} has shifted upwards by ca. 10 cm^{-1} and the components have reversed intensities relative to those of the high temperature yellow form; (iii) ν_1 (ca. 145 cm^{-1}) has developed a clear shoulder on the low frequency side. These differences are supported by even more pronounced changes in the far-i.r. spectrum of the same sample (the cell, under pressure, was transferred repeatedly between the two instruments). Whereas high temperature yellow HgI_2 has a simple two band far-i.r. spectrum, the high pressure

TABLE 9 Vibrational wavenumbers (cm^{-1}) for HgI_2 at ambient temperature and various pressures.

(a) Raman

Phase	III		II (hP)	
Pressure/kbar	0.001	8.0	13.5	21.0 [†]
	17.5	20.0		
	29.0	34.2		
			47.0	47.5
			≈ 51.0 sh	≈ 54 sh
	113.5	119.0		
			140.5	141.5
			≈ 135 sh	≈ 135 sh

(b) I.r.

Phase	III		II (LP)		
Pressure/kbar	0.001	8.0	13.0	31.0	45.0
	24	24	41	40	40
				48	48
				56	56
	*102	106		76	82.5
				93 sh	102 sh
				186	182.5

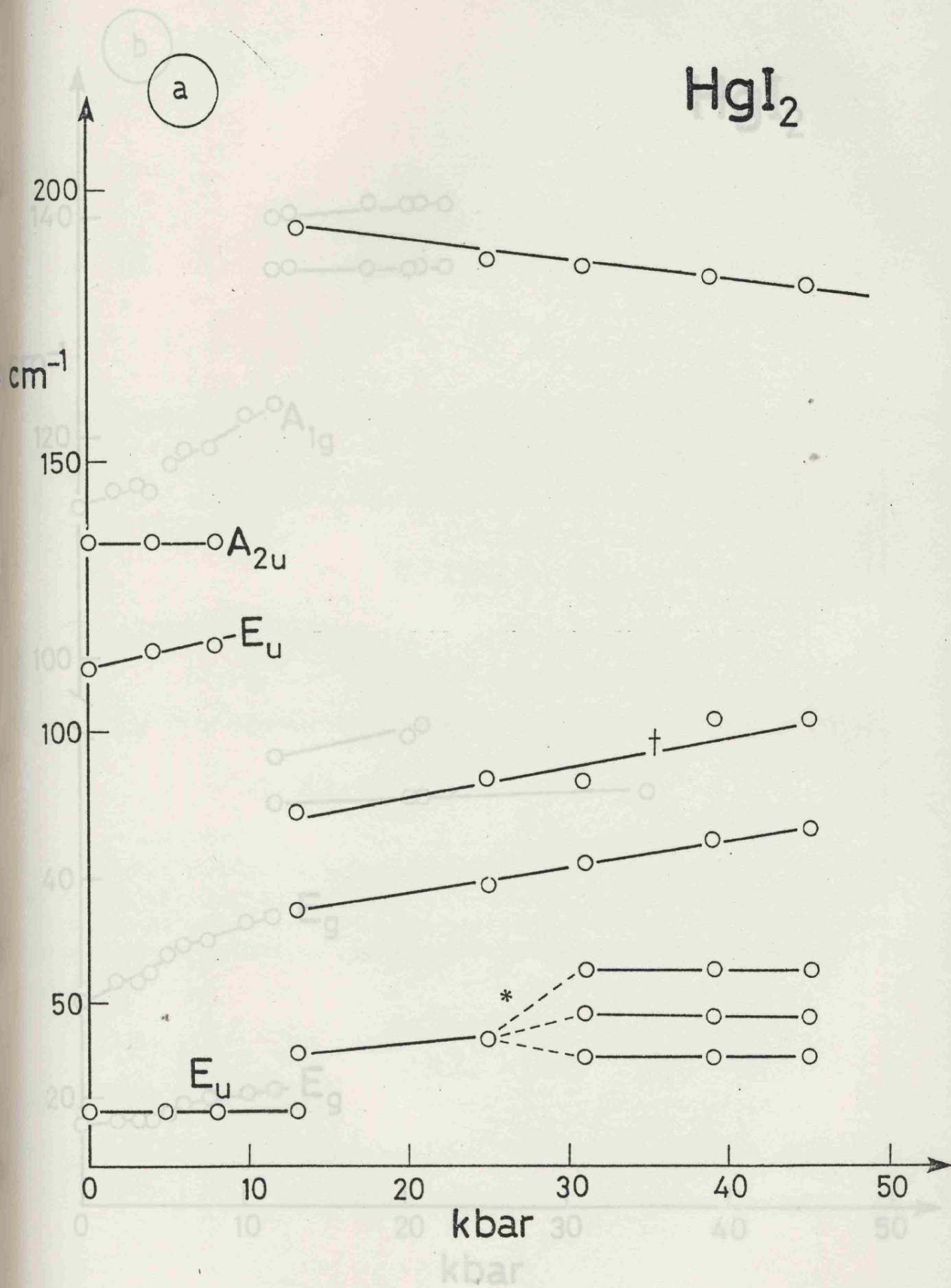
[†] Raman experiments are progressively more difficult at higher pressures as the sample darkens, see text.

* Broad band centre near $\frac{1}{2}$ peak height is recorded.

FIGURE 5:14

Plot of Frequency (cm^{-1}) Versus Pressure (kbar)
for HgI_2

- a i.r. active modes.
- † this band is a shoulder and difficult to measure.
- * this band is resolved into three components
with increasing pressure.
- b Raman active modes.



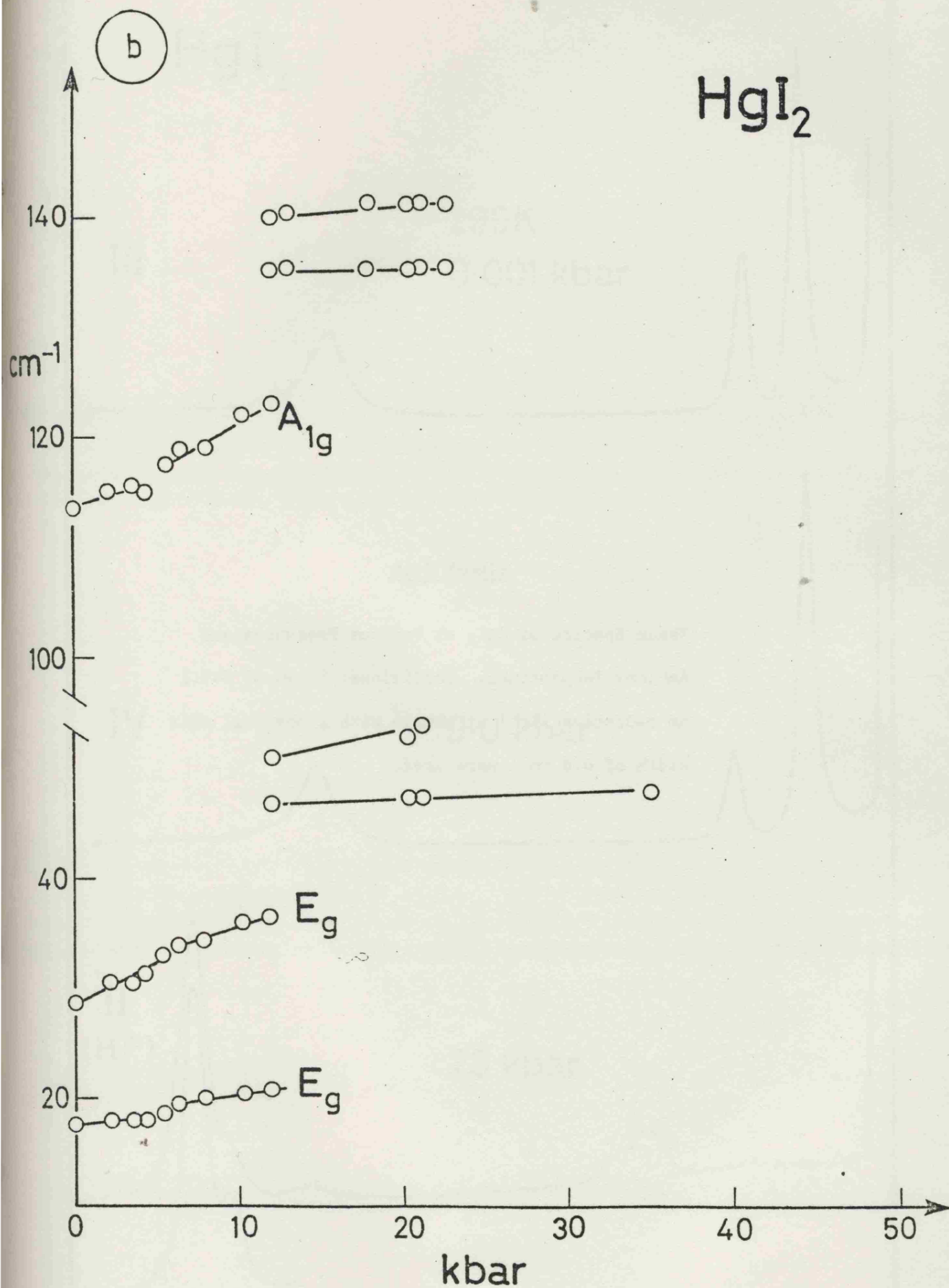


FIGURE 5:15

Raman Spectra of HgI_2 at Various Pressures and Ambient Temperature. Conditions: 60 mW of 647.1 nm radiation (Kr^+) at sample with a spectral slit width of 0.6 cm^{-1} were used.

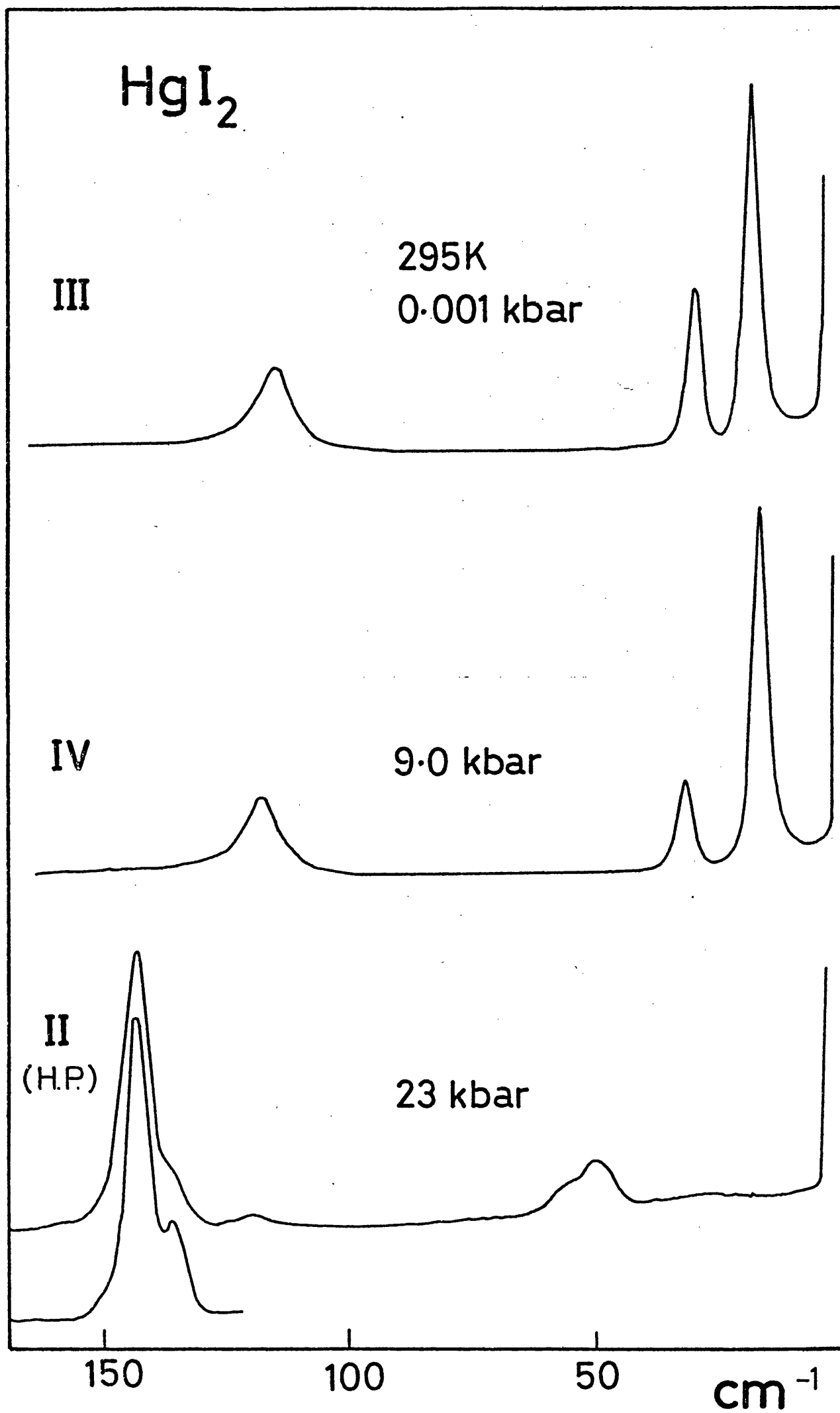
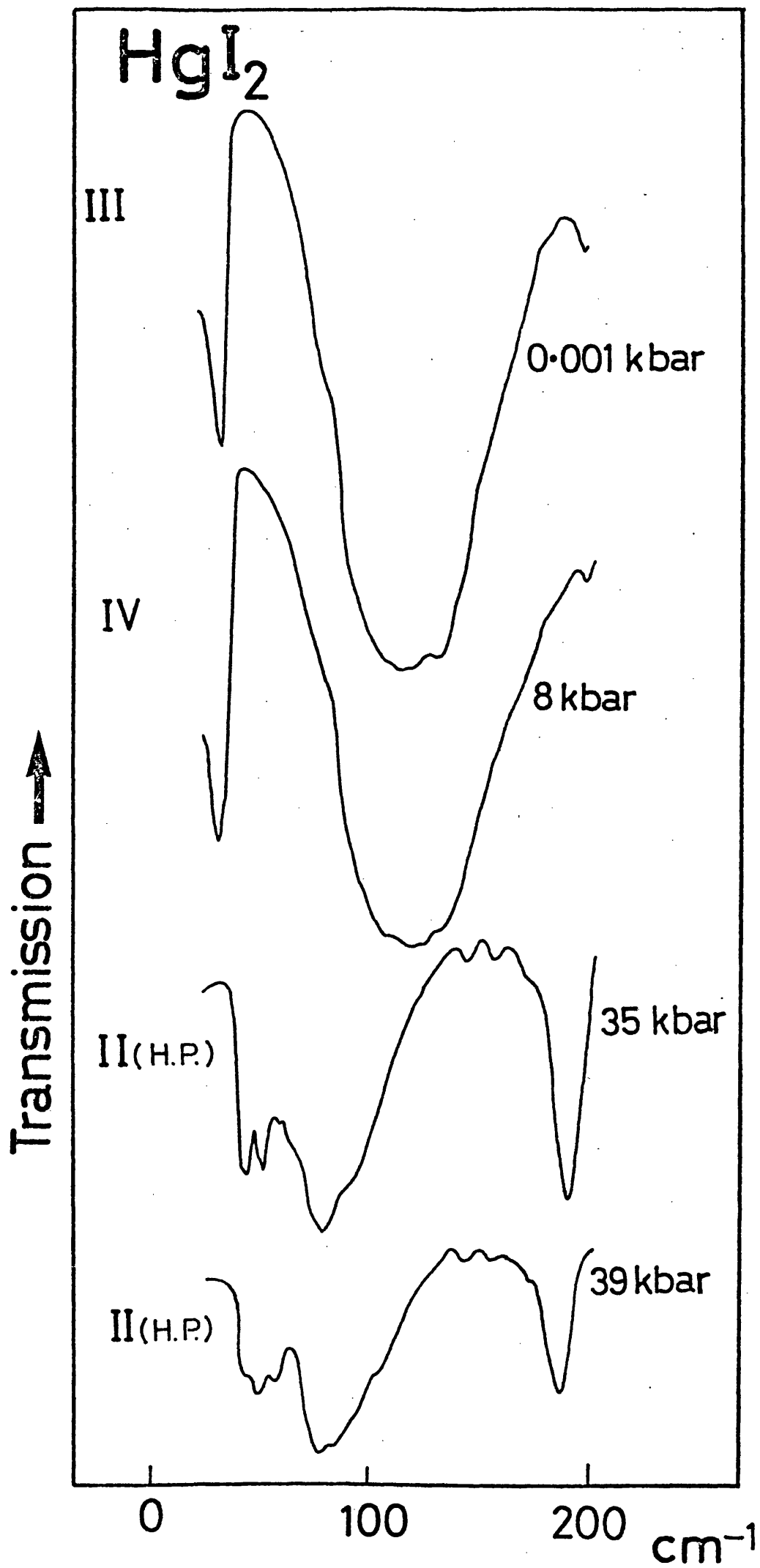


FIGURE 5:16

Far-i.r. of HgI_2 at Various Pressures and
Ambient Temperature.



form shows a much more complex absorption and in particular, has an intense region of absorption, ca. 70 cm^{-1} which has no counterpart in the high temperature form, figure 5:16.

Further Raman experiments were conducted beginning at ambient pressure and 142 and 162°C respectively. In each case the spectra of yellow HgI_2 obtained were identical with that shown by Melveger and co-workers (1968), obtained under similar conditions, in showing a structureless ν_1 band, and a doublet ca. 45 cm^{-1} in which the lower frequency band has the lower intensity. Their "yellow" HgI_2 was contaminated with traces of red HgI_2 , as was the high pressure yellow HgI_2 of Brasch et al (1968). After passing through the red phase, in each case (i.e. at 142 and 162°C) spectra that were similar to those of the high pressure yellow HgI_2 obtained at room temperature and less than 15 kbar, were obtained. A far-i.r. spectrum obtained at 86°C and 21.0 kbar was likewise similar to that of the ambient temperature high pressure yellow form.

From these data we concluded (Adams, Appleby and Barlow 1977) that the high temperature and high pressure forms of yellow HgI_2 differ in structure. The phase boundary between them must intersect the Bridgman red-yellow boundary (between phases II and III) below 8 kbar. A key experiment, which was not undertaken due to technical difficulties, is to obtain high pressure spectra above 182°C entirely within the yellow phases, in order to observe the transition between the two yellow forms. With the recognition of the exist-

ence of this new phase boundary, and the knowledge that there is a further transition ca. 75 kbar to a phase with a structure related to that of CdI_2 , the phase diagram of HgI_2 is seen to bear a close relationship to that of HgBr_2 (see section 5:5, figure 5:6). The phase diagrams are considered to correspond as follows:

HgBr_2	HgI_2
I	High temperature yellow form
II	
III	High pressure yellow form
IV	Phase stable >75 kbar

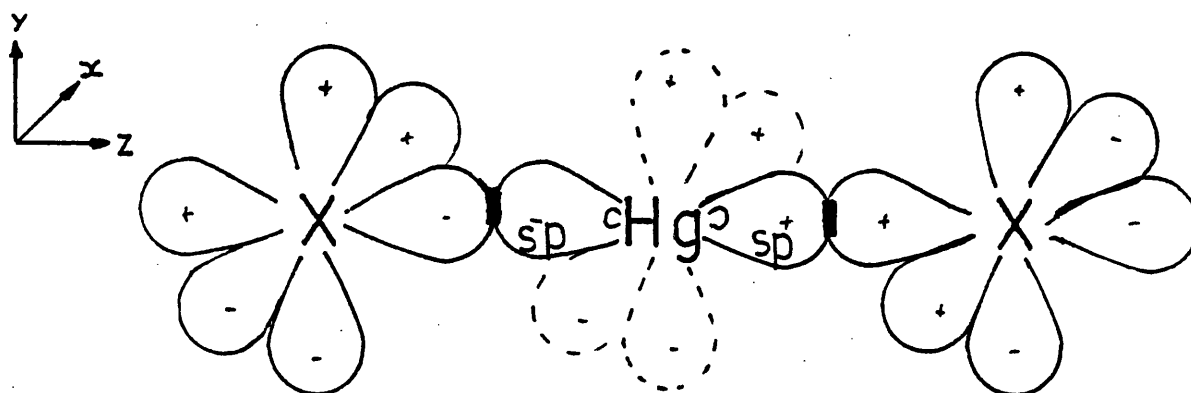
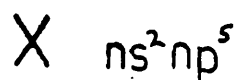
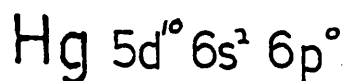
The structural relationship between phases I and II of HgBr_2 is a subtle one; in the absence of detailed X-ray evidence it cannot be said which phase should be regarded as the analogue of high temperature yellow HgI_2 . Our structural identification of $\text{HgBr}_2(\text{III})$ with high pressure yellow HgI_2 depends principally upon comparison of their Raman spectra, although it is supported by the far-i.r. evidence. The quality of the far-i.r. spectra of $\text{HgBr}_2(\text{III})$ was not outstanding but the general features were in accord with the data for HgI_2 . Moreover, ν_3 (i.r. active) mode of high pressure HgI_2 is the only one, in both i.r. and Raman spectra of this phase, to decrease in frequency with increase of pressure. HgBr_2 showed a similar decrease of ν_3 with increase of pressure. The same explanation is advanced for HgI_2 ; that is, a trend to more covalent intermolecular bonding which eventually results in a transition to a CdI_2 type structure.

With increases of pressure on yellow HgI_2 the colour darkened progressively to black and it became increasingly more difficult to obtain Raman spectra : this shift of the absorption edge of HgI_2 has been studied directly by Drikamer (1963) whose measurements also ceased at ca. 50 kbar. For this reason it is unlikely that Raman spectra of HgI_2 will be obtainable near and above the 75 kbar phase transition.

5.6 Discussion of the Structures of the Various Polymorphs of the HgX_2 Systems

Having used the tools of far-i.r. and Raman spectroscopy to probe the structures of the various polymorphs of the mercuric halides, we are in a position to try to rationalise why they adopt certain structures in the solid state. They are all linear molecules in the gas phase (Gregg et al 1937). Mercury is presumably sp-hybridised although it could equally well be described as dsp and in fact the truth is probably $d^a sp^b$ where a and b are constants between 0 and 1, (6s, 6p and 6d being the orbitals used.) Mercury is however bonding to either a p orbital or an sp hybrid on the halide. There will, of course, be two vacant 6p orbitals at 90° on mercury and two filled non-bonding p-orbitals on the halogen.

If we now focus our attention on the solid we must consider the coordination sphere of mercury as obviously other molecules will be close enough to interact. It is difficult to define such a



sphere for mercury within which anything may be considered as bonded.

This subject was examined by Grednic (1965) who proposed a Van der Waals radius for mercury of r where $1.5 < r < 1.73 \text{ \AA}$. This came from consideration of the crystal structure of metallic mercury which is 12-coordinate and has two typical Hg-Hg distances of $3.00 \text{ \AA}$ and $3.466 \text{ \AA}$. The halide radii are better known and are taken from Alcock (1972); Cl 1.75 , Br 1.85 , I $1.98 \text{ \AA}$. All radii so far referred to are the so-called non-bonded radii or Van der Waals radii. It must be stressed that these radii are only being used as guide-lines. If we look at the crystal structure of the ambient temperature and pressure mercury halides several conclusions can be drawn.

	Solid			Vapour
	2 at	2 at	2 at	
HgCl ₂	2.25	3.34	3.63	2.34
HgBr ₂	2.48	3.23	3.23	2.44
HgI ₂ (yellow)	2.62	3.46	3.46	2.61
HgI ₂ (red)	4 at 2.78			

Table compiled from data of Gregg et al (1937), Braekken and Schalter (1934), and Verwel and Bijvoet (1931).

Considering the chloride, the sum of the Van der Waals radii, taking $\text{Hg max} = 1.73 \text{ \AA}$, is $1.73 + 1.75 = 3.48 \text{ \AA}$. There are clearly two very strong bonds at $2.25 \text{ \AA}$ considerably shorter than the vapour, plus the possibility of a weak interaction with others close to the limit of the coordination sphere of mercury. The space group of this crystal, Pmnb, is adopted by some twenty other molecular crystals (Adams 1974) and HgCl₂ clearly obeys Kitaigorodskii's theory of packing. The ambient phase of HgCl₂ is therefore well described as molecular, with very little, if any, intermolecular bonding between chlorine and a mercury of different molecules.

The sum of the Van der Waals radii for the bromide, again taking Hg max , is $1.73 + 1.85 = 3.58 \text{ \AA}$. All the nearest neighbours (Br) are well within this distance and it should also be noted that the shortest bond length in the solid is longer than that of the

vapour, a reverse situation to that of the chloride. As bromine is less electronegative than chlorine (2.8 to 3.0, Grednic (1965)), that is, its p-orbitals have a principal quantum number of one greater than the chloride, it can take part in partial intermolecular bonding to a Hg of another molecule. A similar situation occurs in the Cl_2 , Br_2 and I_2 crystals where bonding from filled p-orbitals between molecules becomes more important as we progress down the group at the expense of intramolecular bonding (Adams 1974). If partial bonding by filled p-orbitals on Br to vacant orbitals on the Hg of another molecule is the case then this explains why the bond length in the solid is not smaller than the vapour and why HgBr_2 adopts a space group $\text{Bm}2\text{b}$ which allows four equivalent long bonds.

The iodine atom is again less electronegative than the chlorine or bromine (2.5) and the sum of the Van der Waals radii is $1.73 + 1.98 = 3.71 \text{ \AA}$. All four iodine atoms are closer than this and the distance is longer than that in the vapour. The red HgI_2 structure is unique, that is, it is not adopted by any other known solid. If the iodide followed the trend set by the bromide we would expect it to have six iodines at almost equivalent positions, that is we expect the four long bonds to be shorter in the iodide. But the mercury has become 4-coordinate probably sp^3 hybridised. There is no obvious reason for this but it is obviously thermodynamically more stable. Ogawa et al (1975) calculated the partial charges on mercury and iodine in red HgI_2 as mercury 0.75 e and iodine -0.37 e. Whilst this interaction obviously contributes to the bonding it is still largely covalent.

Summarising: the chloride adopts a structure which is clearly molecular. The bromide adopts a structure which allows four extra long bonds to be formed due to a decrease in electronegativity of the halide and the iodide at ambient conditions does not fit into a general trend adopting a unique structure consisting of tetrahedra. This is not entirely surprising as the structural chemistry of mercury II is known to be complex and variable (Grednic 1962).

If we now consider the results of the high pressure and variable temperature work it comes as no shock that the high pressure phase II of mercuric chloride adopts the CO_2 structure which is more efficient in its use of space than the ambient phase of HgCl_2 . Conversely adoption of the CO_2 structure by HgCl_2 is a good indication that the ambient phase is truly molecular. Also the fact that HgBr_2 finally adopts the CdX_2 ($\text{X} = \text{Cl}, \text{I}$) structure under pressure points towards the importance of bonding by p-orbitals between the mercury and bromine of different molecules for this material. In the CdX_2 structure Cd is octahedrally coordinated to six equivalent halogen atoms. If HgBr_2 adopts this structure Hg would presumably bond using all of its p-orbitals. Red HgI_2 on heating adopts the $\text{HgBr}_2(\text{I})$ ambient structure; this is what we would have expected for the ambient phase of HgI_2 but as to why the red tetrahedral phase is more stable with respect to the HgBr_2 structure remains a mystery. Finally, compression of HgI_2 yields

the CdX_2 structure giving marked similarities between the phase diagram of HgI_2 and HgBr_2 . It is worth noting that in the silver halides the fluoride, chloride and bromide all adopt the sodium chloride structure whilst the iodide adopts the wurtzite structure. This again is presumably due to the fall in electronegativity of the halogen in progressing down the group. The interesting thing is on application of pressure to AgI it adopts the sodium chloride structure. This is similar to the mercuric halides and indicates that bromine and iodine whilst both halogens, can cause different structures in the solid phase with the same metal. We can therefore rationalise the known structures adopted by most of the polymorphs studied.

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CHAPTER 6

THE VIBRATIONAL SPECTROSCOPY OF THREE SOLID PHASES
OF BENZENE

CHAPTER 6

THE VIBRATIONAL SPECTROSCOPY OF THREE SOLID PHASES OF BENZENE

6.1 Introduction

Solidification of liquid benzene, either by cooling or by application of pressure, yields benzene I which has been shown by X-ray (Cox, Cruickshank and Smith 1958) and neutron diffraction (Bacon, Curry and Wilson 1964) to have the symmetry of the orthorhombic group $Pbca \equiv D_{2h}^{15}$ with $z = 4$. Many detailed studies of the i.r. and Raman spectra of this phase which, together with FG-matrix (Harada and Shiminouchi 1966) and inter-molecular potential function calculations (Taddei, Bonadeo, Marzocchi and Califano 1971) have resulted in a complete understanding of it.

Much less is known about benzene II which is only stable under pressure above ca. 11 kbar (Bridgman 1914, Bridgman 1938 and Klein, Nourbakhsh and Adler 1968). Its structure has been determined by single-crystal X-ray diffraction (Piermarini, Mighell, Wier and Block 1969) at 25 kbar and 294 K and shown to be $P 2_1/c = C_{2h}^5$ $z = 2$. Ellenson and Nicol (1974) have recently characterised C_6H_6 II by Raman spectroscopy in both the internal and lattice mode regions, and have computed all the lattice mode frequencies (Raman and i.r. active using an atom-atom inter-molecular potential function). Their spectra were obtained using a high pressure cell of the Drickamertype (see Chapter 1).

The work presented in this chapter had three objectives. The first was to obtain i.r. and far-i.r. spectra of C_6H_6 II under conditions comparable to those used by Ellenson and Nicol for their Raman work, and hence to complete the spectroscopic characterisation of this phase. The second was to repeat some of the Raman work using our DAC to make comparison with Ellenson and Nicol's results and hence to assess the relative capabilities of the two types of high pressure device. The third reason was to search for evidence of benzene III, a second high pressure polymorph, the existence of which is not well established. These results have been submitted for publication (Adams and Appleby 1977).

6.2 Experimental

Analar benzene was used and the equipment and cell were as discussed in Chapter 2. Photon counting was used for the Raman experiment. 0.2 mm thick inconel gaskets were used which were reduced in thickness to 0.08 mm by the end of the experiment. A polycrystalline sample of benzene was prepared in each experiment and no attempt was made to obtain a single crystal.

As the transition to phase II is known to be sluggish (Bridgeman 1914, 1938 and Ellenson and Nicol 1974) it was prepared as suggested by Ellenson and Nicol; that is, it was heated to $100^{\circ}C$ overnight with a pressure of >20 kbar. By doing this, and monitoring the Raman lattice modes, pure benzene II was prepared.

The cell was repeatedly transferred with the sample under constant pressure between the instruments used to obtain the spectra.

6.3 Results and Discussion

The data are summarised in Tables 1 and 2 and Figures 6:1 to 6:4.

Raman and I.r.-Active Lattice Modes

The Raman spectrum of benzene I in the region of its lattice modes is shown in Figure 6:1 : no direct comparison with the benzene I spectrum of Ellenson and Nicol is possible as theirs was obtained at 77 K and 11 kbar at which temperature the spectrum is much sharper and some of the bands are also better separated due to their different pressure sensitivities. Nevertheless it is clear that the major features of our spectra correspond. Figure 6:1(b) shows the Raman spectrum after compression to 20.3 kbar and leaving overnight at 100°C : it corresponds closely with the spectrum shown by Ellenson and Nicol for a sample of benzene II at 23 kbar and 77 K, apart from some sharpening and band shifts due to differences in conditions.

The DAC was then transferred to the far-i.r. instrument and the spectra of Figure 6:2(b), and then of 6:2(o), obtained. This is plainly different from the spectrum of phase I, Figure 6:2(a), and shows three bands ($2A_u + B_u$ in $\underline{C_{2h}^5}$) as predicted by theory. Their frequencies, Table 1, are very close to the values calculated

Table I Lattice mode wavenumbers/cm⁻¹ for the solid
phases of benzene.

Phase	Pressure (kbar)	T, °K	Lattice Modes			
<u>Infrared</u>						
I	0.001	295	72	88	100	^a
II	{	20.4	295	108	121	157
		20.4	188	109	121	155
[II	19	295	107.7	121.1	143.9]	^b
III	{	34.4	295	<u>c</u>	193	205
		34.4	188	<u>c</u>	194	205
<u>Raman</u>						
I	6.0	295	63	86.5	104.5	144
II	{	20.4	295	99.5	157.5	182.5
		32.8	295	110.5	174.5	203.5
		32.8	136	115.5	182.5	210
		40.0	295	121.5	183.5	214
III	{	33.3	295	118	187	215
		33.3	136	123.5	196	215
		34.4	295	128.3	207.9	235.5

^a This phase is known to show further bands under some preparative conditions at ambient pressure, see Haranda and Shiminouchi (1971).

^b Calculated values of Ellenson and Nicol (1974).

^c Unresolved shoulder, see Figure 6:2.

Table 2 I.r. wavenumbers/cm⁻¹ for the solid phases of benzene at ambient temperature.

C ₆ H ₆ I 1.6 kbar	C ₆ H ₆ II 20.3 kbar	C ₆ H ₆ III 34.4 kbar	Assignment ^a
1830			$\nu_{10} + \nu_{17}$
1755			$\nu_6 + \nu_{15}$
1715			$\nu_4 + \nu_{12}$
1680	1680	1690	$\nu_4 + \nu_{17}, \nu_1 + \nu_{11}$
1620	1620	1628	$\nu_6 + \nu_{12}$
1547	1550	1567	$\nu_{10} + \nu_{11}$
1478	1480	1486	ν_{19}
1402	1411	1442	$\nu_5 + \nu_{16}$
1310	1325	1340	ν_{14}
1260	1255 ^b	1276	$\nu_{10} + \nu_{16}$
1210			
1180			
1149			
1144	1170	1186	ν_{15}
1035	1045	$\left\{ \begin{array}{l} 1065 \\ 1047 \end{array} \right.$	ν_{18}
1011	1016	1019	ν_{12}
$\left. \begin{array}{l} 981 \\ 975 \end{array} \right\}$	$\left\{ \begin{array}{l} 991 \\ 985 \\ 972 \\ 967 \end{array} \right.$	$\left\{ \begin{array}{l} 1002 \\ 998 \\ 977 \\ 970 \end{array} \right.$	ν_{17}
770	<u>c</u>		$\nu_{11} + \nu_L$
680	≈ 685	695	ν_{11}

^a Mair and Hornig (1949)

^b Further unresolved components to high frequency

^c Broad region of absorption - see text

FIGURE 6:1

Raman spectra of solid phases of benzene in the lattice mode region.

- (a) Benzene I at 295 K and 5.3 kbar. Spectral slit width 1.7 cm^{-1} , 50 mW 514.5 nm radiation at the sample.
- (b) Benzene II at 295 K and 20.3 kbar. Spectral slit width 2.4 cm^{-1} , 250 mW at the sample.
- (c) Benzene II at 136 K and 32.8 kbar. Spectral slit width 1.9 cm^{-1} , 400 mW 514.5 nm at the sample.
- (d) Benzene III at 295 K and 34.4 kbar. Spectral slit width 2.4 cm^{-1} , 250 mW 514.5 nm at the sample.

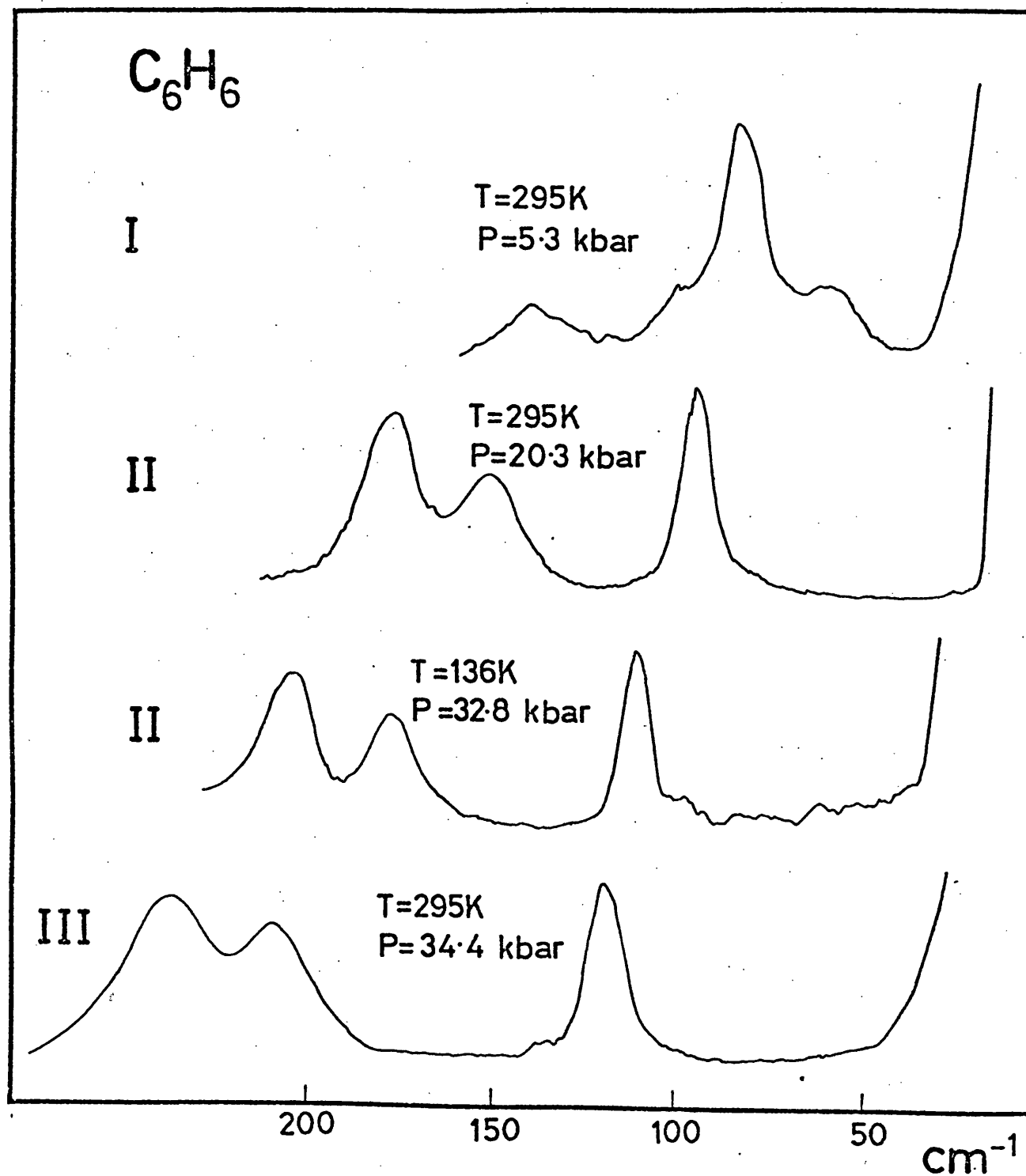


FIGURE 6:2

Far-i.r. spectra of solid phases of benzene.

- (a) Benzene I at 295 K and 4.1 kbar.
- (b) Benzene II at 295 K and 20.3 kbar.
- (c) The sample of (b) at 188 K.
- (d) Benzene III at 295 K and 34.4 kbar.
- (e) The sample of (d) at 188 K.

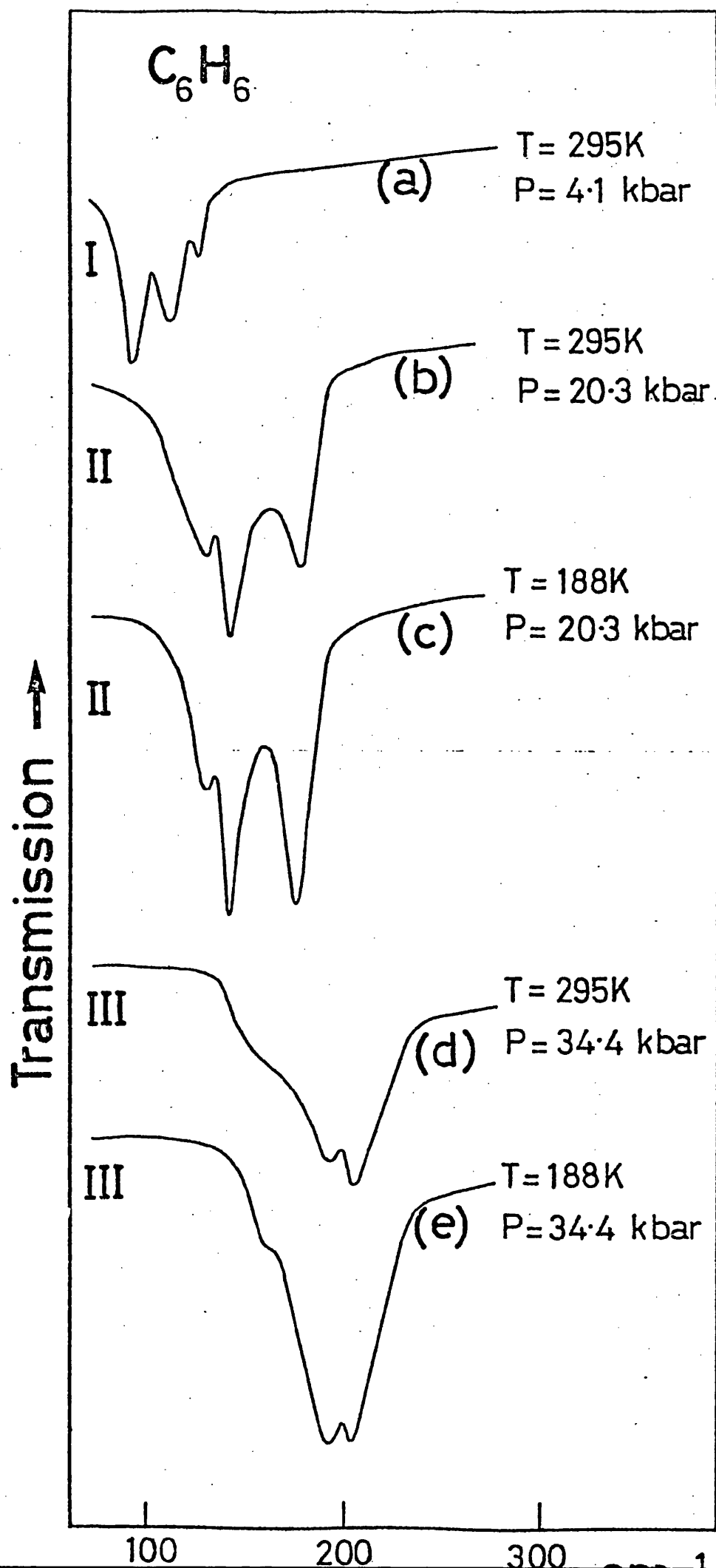


FIGURE 6:3

Mid-i.r. spectra at ambient temperature of

(a) benzene I, 1.6 kbar;

(b) benzene II, 20.3 kbar; and

(c) benzene III, 34.4 kbar.

Spectral slit width 3.7 cm^{-1} throughout.

Spectra (b) and (c) were obtained using the same samples as were used for the Raman spectra of Figure 1 (b), (d) and the far-i.r. spectra of Figure 2 (b), (d). The rising background at the high-frequency end is due to two-phonon absorption in the diamond anvils.

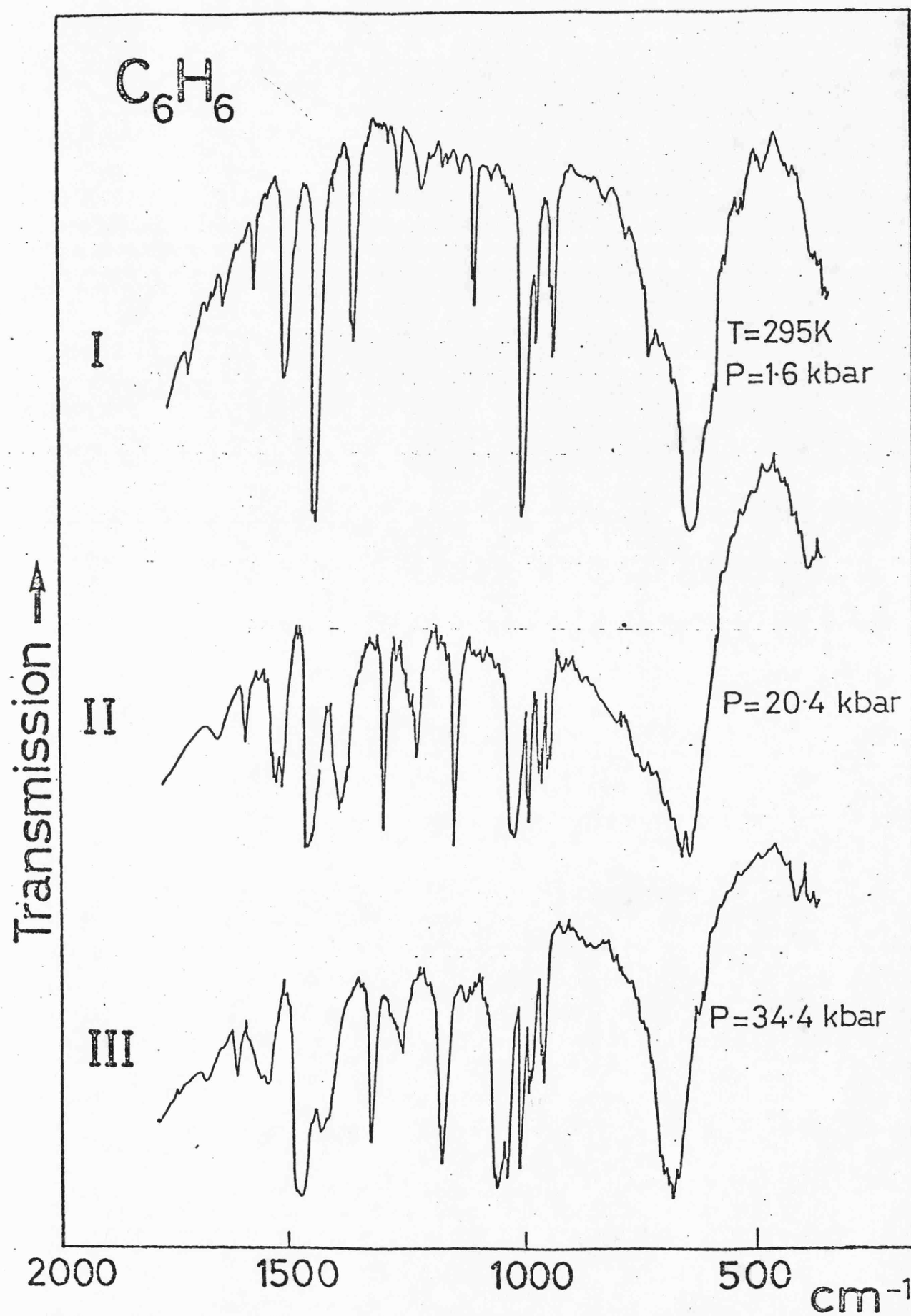
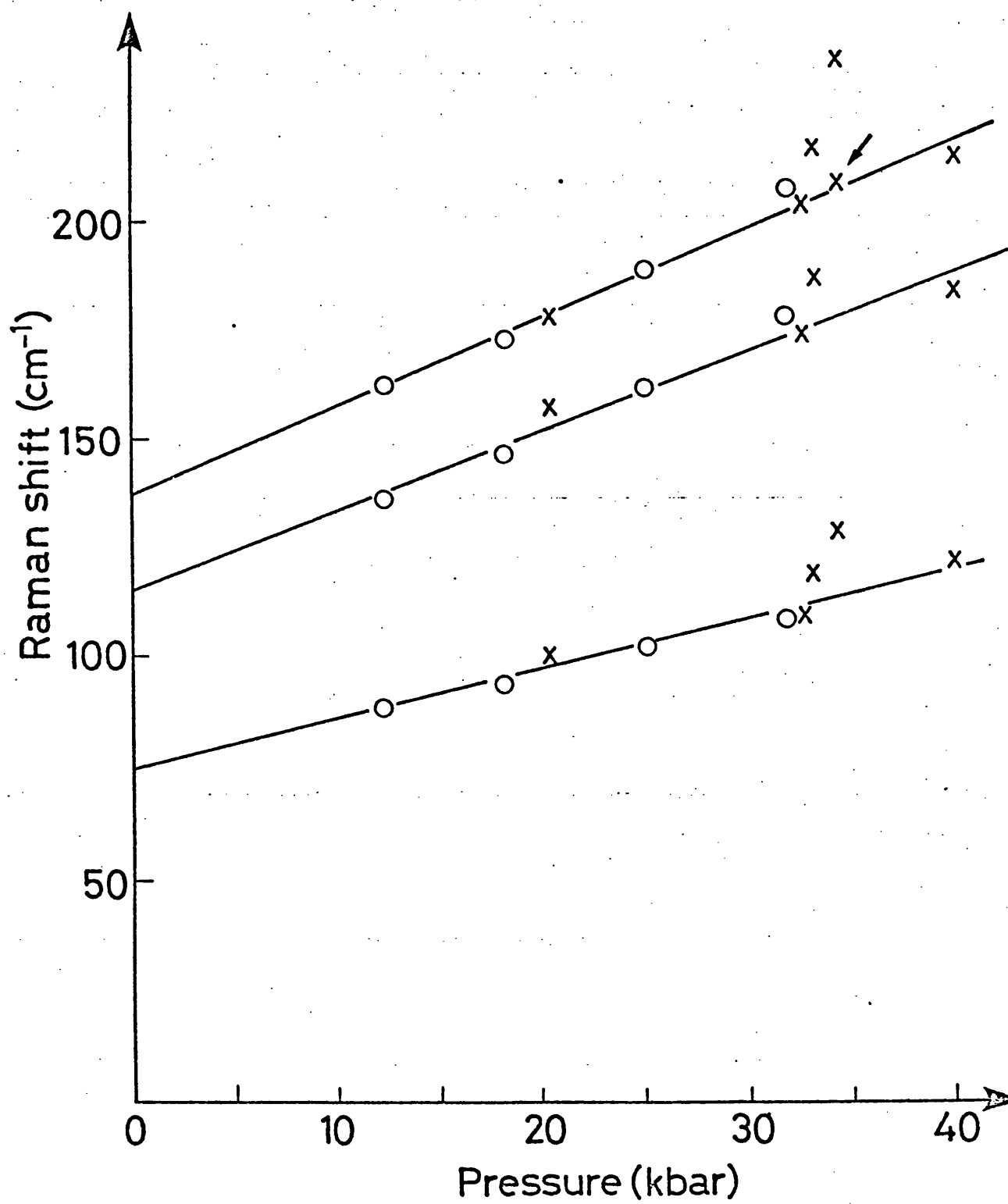


FIGURE 6:4

Raman-active lattice mode pressure dependencies
for benzene II and III. The point indicated by
an arrow belongs to the middle data set,

O = Ellenson and Nicol's data.

X = this work.



by Ellenson and Nicol for a sample at 295 K and 19 kbar.

Benzene III

There have been two claims that a further high pressure form of benzene (phase III) exists. Block, Weir, and Piermarini (1970) reported visual observations which indicate a transition from benzene II to another phase at still higher pressures and 270°C , estimating the transition pressure as 40 kbar but possibly subject to a large error. The triple point liquid -II-III was estimated to be at $590 \pm 15^{\circ}\text{C}$ and 40 kbar. They also found an inflection on the melting curve at a pressure of ca. 30 kbar at 310°C . Akella and Kennedy (1971) also found a slight but definite break in the slope of the melting curve of benzene, using differential thermal analysis, and proposed a triple point between the liquid and phases II and III at $335 \pm 5^{\circ}\text{C}$ and 22.5 ± 0.5 kbar, suggesting that the high pressure transition seen by Block et al at an estimated 40 ± 20 kbar was that between phases II and III. However, Akella and Kennedy were unable to obtain supporting evidence for this transition during excursions across the supposed II/III boundary at lower temperatures. This suggests that the transition, if real, is very sluggish.

At pressures of up to 40 kbar at ambient temperature no evidence for the II/III transition was found; the frequencies of the three Raman bands in the lattice mode region of phase II fitted onto a linear plot, Figure 6:4, which correlates well with

the data of Ellenson and Nicol for this phase. However, leaving a sample of benzene II overnight at 100°C and 40 kbar, followed by cooling to room temperature, resulted in insignificant changes in the appearance of the Raman spectrum but in very large frequency shifts, Table 1. Concurrently the pressure was found to have dropped to 34.4 kbar: this drop was not due to any leak in the apparatus, and the cell subsequently maintained 34.4 kbar for a week without any adjustment. If the pressure drop was due to a mechanical relaxation of the cell, the observed frequencies should have been on the phase II lines of Figure 6:4. The large shifts and the drop in pressure are consistent with a phase transition to a form of lower volume. This sample was then examined by both far-i.r., Figure 6:2(d,e), and mid-i.r. spectroscopy, Figure 6:3(c), completing the spectroscopic characterisation of the material at this pressure. As in the Raman experiments, the far-i.r. spectra showed little difference in appearance but very large frequency shifts, Table 1. Further experiments showed that the new phase (benzene III) could be prepared as described above by initial compression to 36.0 kbar but not at 32.8 kbar. This suggests either that the II/III phase boundary is strongly curved towards higher pressures as temperature is reduced or, more probably, that the transition simply becomes more sluggish and does not take place at all without an excess pressure of > ca. 10 kbar.

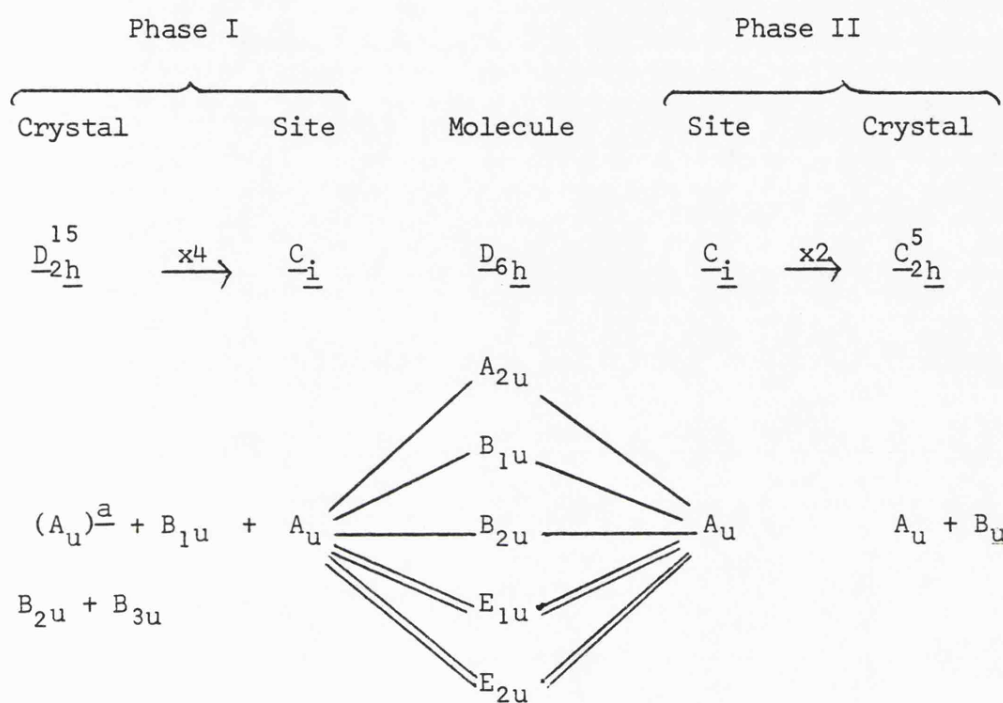
These results support those of Block et al and Akella and Kennedy in showing that some, as yet unspecified, change takes place in solid benzene ca. 30 kbar. Several inconsistencies remain

and must be resolved by further experiments by both compression and spectroscopic methods. Thus, the failure to observe any change in the number of Raman or i.r.-active lattice modes on entering phase III suggests that the transition may proceed without change of space group or of cell content. The nearest precedent for this is found in octafluoronaphthalene which undergoes a transition with retention of space group ($P2/m$), but the cell is doubled along the a -axis, (Mackenzie, Arthur and Pawley 1977). The results also indicate that a volume change accompanies the transition with $\Delta V/V \approx 0.15$, implying that it is first order.

Assignment of the internal mode i.r. spectra

In both phases I and II D_{6h} molecules of benzene are on C_i sites: hence all u -modes are i.r.-active and have the same symmetry, A_u . In C_6H_6 I correlation coupling leads to an i.r.-active triplet (B_{1u} , B_{2u} , B_{3u}) from each site group mode, but in C_6H_6 II there is only a doublet ($A_u + B_u$) because the cell is halved with respect to that of phase I, see Table 3. For phase I almost all of the symmetry-allowed splittings have been observed for the fundamentals and accounted for by calculations based upon semi-empirical atom-atom potential functions (Taddei, Bonadeo, Marzocchi and Califano 1971). We are not aware of any new assignments of the i.r.-active combinations subsequent to the work of Mair and Hornig (1949). The vibrational representation of benzene with point group D_{6h} can be shown to be

Table 3 Correlation scheme for the i.r.-active modes
of solid benzene.



$\underline{a}$ Inactive species

$$\Gamma = 2A_{1g} + A_{2g} + 2B_{2g} + 4E_{2g} + E_{1g} + A_{2u} + 2B_{1u} \\ + 2B_{2u} + 2E_{2u} + 3E_{1u} \quad (3N-6 = 30)$$

All the fundamentals have been assigned and are listed in Table 4.

If we are to discover which modes could give i.r. combinations we must consider that in D_{6h} only ungerade or u-modes are i.r.-active and that combinations must be of the form $u \times g = u$ and $g \times u = u$ and not $g \times g = g$ and $u \times u = g$ where g is gerade.

There will be no combinations of the type $g \times g$ or $u \times u$ in the i.r. spectrum. All possible i.r. combinations are listed in Table 5 and the frequencies which are in the region of our experiment assigned in Table 2.

Because of the very low light levels the i.r. spectra were run at a spectral slit width of 3.7 cm^{-1} . Hence, most of the Davydov splittings known to be present in benzene I, and those predicted on symmetry arguments for benzene II, were not resolved. Our spectrum of benzene I at 1.6 kbar is closely similar to that of the same phase at -65°C shown by Mair and Hornig.

The signal/noise ratios in the region of ν_{11} , A_{2u} (ca. 680 cm^{-1}) are too low to enable useful conclusions to be drawn, but the E_{1u} fundamentals ν_{18} and ν_{19} show pronounced broadening on entering phase II. Clearly, we must ask whether this broadening is due to the development of shear stress in the sample: this appears not to be the case, for two reasons. Firstly, the ruby R-lines of the internal calibrant show no significant distortion

Table 4 Wavenumbers/cm⁻¹ for benzene fundamentals.

Γ	Frequency	Label
$2A_{1g}$	3060, 990	ν_2, ν_1
A_{2g}	1340	ν_3
$2B_{2g}$	995, 703	ν_5, ν_4
$4E_{2g}$	3040, 1596, 1174, 606	$\nu_9, \nu_8, \nu_7, \nu_6$
E_{1g}	859	ν_{10}
A_{2u}	687	ν_{11}
$2B_{1u}$	3069, 1010	ν_{13}, ν_{12}
$2B_{2u}$	1312, 1147	ν_{15}, ν_{14}
$2E_{2u}$	980, 410	ν_{17}, ν_{16}
$3E_{1u}$	3063, 1478, 1036	$\nu_{20}, \nu_{19}, \nu_{18}$

Table 5 The Possible I.r.-Active Combination Modes
 Resulting from the I.r.-Active (u) and Raman
 Active (g) Modes in D_{6h} .

	A_{1g}	A_{2g}	B_{2g}	E_{2g}	E_{1g}
A_{2u}	A_{2u}	A_{1u}	B_{1u}	E_{2u}	E_{1u}
B_{1u}	B_{1u}	B_{2u}	A_{2u}	E_{1u}	E_{2u}
B_{2u}	B_{2u}	B_{1u}	A_{1u}	E_{1u}	E_{2u}
E_{2u}	E_{2u}	E_{2u}	E_{1u}	$A_{1u}+A_{2u}+E_{2u}$	$B_{1u}+B_{2u}+E_{1u}$
E_{1u}	E_{1u}	E_{1u}	E_{2u}	$B_{1u}+B_{2u}+E_{1u}$	$A_{1u}+A_{2u}+E_{2u}$

of the kind attributable to shear stress: this is not a wholly satisfactory answer because all that this tells us is that the immediate neighbourhood of the ruby particle is hydrostatic to a good approximation. The second, and more substantive, point is that at both 20.3 and 34.4 kbar the spectra contain both broad and sharp bands, including examples of both sorts which shift significantly with pressure. The widths of ν_{18} and ν_{19} at high pressure are indicative of increased Davydov splitting. As in the i.r. and Raman lattice mode regions, the internal mode spectra show no major changes following the II/III transition, except for several substantial band shifts and some relatively minor intensity changes.

ν_{18} and ν_{19} should both be quartets ($2A_u + 2B_u$) in benzene II; ν_{18} is the most sensitive to increase of pressure and at 34.4 kbar (phase III, structure unknown) was resolved into a sharp component at 1047 cm^{-1} and a broad multiplet centred at 1065 cm^{-1} .

Next we consider u-species fundamentals inactive in D_{6h} but allowed in the solid phase by virtue of the site field. In benzene I these are:

ν_{17}, E_{2u}	975 m-s	ν_{15}, B_{2u}	1144 m-s
	981 sh		1146 m-s
ν_{12}, B_{1u}	1011 m	ν_{14}, B_{2u}	1310 w-m

On entering phase II the most obvious change is that ν_{17} splits

into the two doublets predicted by theory ($2A_u + 2B_u$). The other three bands or groups of bands all rise substantially in frequency with increase of pressure: each should yield a doublet in phase II but none were resolved although ν_{15} 1186 cm^{-1} is definitely broader than the others at 34.4 kbar (phase III) and could reasonably be the envelope of a nearly resolved pair.

All other bands in phases I and II (and probably also in III) are due to g-u combinations (since first overtones are i.r. forbidden in a centro-symmetric group): the discussion is based on Mair and Hornig's assignments which we support (for the range 800 to 1850 cm^{-1}) with one exception. Thus, the band at 1680 cm^{-1} in our benzene I spectrum is assigned to $\nu_4 + \nu_{17} = E_{1u}$ in Mair and Hornig's scheme; we consider that the label $\nu_1 + \nu_{11} = A_{2u}$ should be attached in addition.

With the exception of $\nu_6 + \nu_{12} = 1620\text{ cm}^{-1}$, which remains rather sharp up to 34.4 kbar, the chief effect of high pressure is to broaden these bands and to shift them to higher frequencies. Since each of these combinations is the product of an E-species with either another doubly-degenerate or a non-degenerate species, each product can accommodate at least four i.r.-active Davydov components: since these are mostly unresolved the resultant bands are broad. The $\nu_{10} + \nu_{16} = 1260\text{ cm}^{-1}$ combination, which is $E_{1g} \times E_{2u} = B_{1u} + B_{2u} + E_{1u}$ and can therefore yield 8 Davydov components ($4A_u + 4B_u$), develops pronounced asymmetry on its high-frequency

side with increase of pressure and is consistent with the presence of many components.

Finally the behaviour of the region ca. 700-900 cm^{-1} is discussed. The absorption centred ca. 770 cm^{-1} in phase I was assigned by Mair and Hornig to unspecified combinations of $\nu_{11}(\text{A}_{2\text{u}})$ with "torsional lattice modes": these results support this origin. The 770 cm^{-1} band is seen in benzene I to be the only peak in a broad region tailing off to high frequency from ν_{11} at 680 cm^{-1} . The number of possible $\nu_{11} + \text{g-type}$ lattice mode combinations is very considerable. Taking all possible i.r.-active products of the Raman-active lattice modes with the Davydov components of ν_{11} (i.e. $\text{A}_{\text{u}} + \text{B}_{1\text{u}} + \text{B}_{2\text{u}} + \text{B}_{3\text{u}}$ in $\text{D}_{2\text{h}}^{15}$) yields $12(\text{B}_{1\text{u}} + \text{B}_{2\text{u}} + \text{B}_{3\text{u}})$, i.e. 36 bands. The Raman-active lattice modes range from 57 to 128 cm^{-1} (at 138 K) and the components of ν_{11} from 681 to 707 cm^{-1} ; their combinations may therefore span the region 738 to 835 cm^{-1} , which correlates well with the region of absorption shown by benzene I.

In phase II only three Raman-active lattice modes are found which will combine with the components of ν_{11} , $\text{A}_{\text{u}} + \text{B}_{\text{u}}$ in $\text{C}_{2\text{h}}^5$. Thus there are $3(\text{A}_{\text{u}} + \text{B}_{\text{u}}) = 6$ bands allowed. This is a severe reduction from the plethora of combinations allowed in benzene I. The Raman lattice modes are also highly sensitive to pressure: this allows the above combinations to shift rapidly away from ν_{11} , whilst the restrictive selection rules reduce their number. The result is the greatly reduced i.r. absorption

seen on the high-frequency side of ν_{11} in the spectra of phases II and III.

Comparison of the DAC and the Drickamer Cell Types

The DAC design type is capable of use to much higher pressures (> 1 megabar has been claimed) than the Drickamer cell type and is therefore a natural choice for work significantly above 100 kbar. Because the Drickamer cell type is filled with NaCl, it cannot be used at i.r. wavenumbers (cm^{-1}) lower than ca. 600. In contrast, the same DAC can be used at nearly all i.r. frequencies and for Raman work, a most powerful (and, so far, unique) combination of techniques for the study of materials at high pressure. However the DAC uses minute sample volumes, 25 nanolitres in our experiments, whereas the Drickamer design used by Ellenson and Nicol and Ebisuzaki (1972) accommodates ca. 200 x this volume, and this seems to confer a slight advantage on the latter. Our Raman spectra in the lattice mode region compare with Ellenson and Nicol's, but we were unable to match their signal/noise ratios in the internal mode region, although we could see the same bands. However, small changes in DAC technique could well alter this situation.

6.4 Summary

The vibrational spectra of benzene II have been characterised by Raman, mid-i.r. and far-i.r. spectroscopy using the same sample and thereby emphasising the remarkable versatility of the DAC.

The three far-i.r. active lattice modes were recorded for the first time and are in good agreement with the calculated values.

The possibility of the existence of benzene III was examined and a quantitative comparison of the DAC and Drickamer type cell put forward.

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CHAPTER 7

A STUDY OF THE X-RAY DIFFRACTION, FAR-I.R., AND
RAMAN SPECTRA OF CsNiCl_3 AT VARIOUS TEMPERATURES
AND HIGH PRESSURES

CHAPTER 7A STUDY OF THE X-RAY DIFFRACTION, FAR-I.R., AND RAMAN SPECTRA OF
CsNiCl₃ AT VARIOUS TEMPERATURES AND HIGH PRESSURES7.1 Introduction

The interatomic forces in a crystal are usually strongly dependent on the interatomic spacing. Consequently, the lattice potential energy (U) for a crystal can be written as a power series in the displacements (r) of the atoms from their equilibrium positions.

$$U = U_0 + a_1 r^2 + a_2 r^3 + a_3 r^4 \quad \text{where } a_i \text{ are different constants}$$

If such a series is truncated after the quadratic term this is known as the "harmonic approximation". More simply, the displacement of an atom from its equilibrium position then obeys the mathematical description of an ideal spring. If this was the case, which it clearly is not, the lattice mode frequencies would be independent of temperature as would the volume of the crystal. If we are to understand solids this power series must be expanded past the quadratic (harmonic) term to include cubic and quartic terms. These are known as the anharmonic terms. Inclusion of these terms allows the phenomena of thermal expansion and allows normal modes to interact, and hence the presence of overtones and combinations.

Thermal expansion creates a temperature dependent frequency shift from that of the harmonic normal modes (temperature independent) and a further temperature dependent shift which is due to the coupling of normal modes and can be distinguished from the effects of thermal strain (Lowndes 1976). Thermal strain is the strain which occurs when the temperature is raised from 0 K and the volume V_0 changes to V_T , the volume at some temperature T. The theoretical temperature dependence of the optic phonons of alkali halides was described by Lowndes (1971, 1976). Whilst a complete study of this work is not undertaken, the following outline is given.

The temperature dependence of each phonon frequency in the Brillouin zone stems from anharmonicity in the two ways suggested above. This can be formulated as follows if the harmonic frequency is written as $\omega^h(q,j)$ (where q is the wavevector and j some vibrational frequency) and is shifted by a term due to thermal expansion of the crystal on raising the temperature above 0 K. We can write:

$$\omega_T^E(q,j) = \omega^h(q,j) + \Delta\omega_T^E(q,j) \quad \dots\dots (1)$$

The quasiharmonic frequency ($\omega^E(q,j)$) is that which would result if the anharmonicity was removed and it would only depend on the volume of the crystal. As has been stated already anharmonic terms also permit coupling of normal modes which change the phonon energies and give them finite lifetimes. At a temperature T and frequency Ω each of the quasiharmonic frequencies suffers a frequency dependent

complex shift of

$$\Delta\omega_T^A(q,j,\Omega) + i\Gamma_T(q,j,\Omega) \quad (\text{Lowndes 1971})$$

the real part of which shifts the frequency from $\omega_T^E(q,j)$ to the quasinormal frequency $\omega_T(q,j)$ which is the solution for Ω given by

$$\Omega^2 = \omega_T^E(q,j)^2 + 2\omega_T^E(q,j)\Delta\omega_T^A(q,j,\Omega) = \omega_T(q,j)^2$$

Therefore the frequency of any mode at a temperature T can be written as follows:

$$[\omega_T(q,j)]^2 = [\omega^h(q,j)]^2 + 2\omega^h(q,j)[\Delta\omega_T^A(q,j,\Omega) + \Delta\omega^E(q,j)] \quad \dots (2)$$

where $P = 0$ (Lowndes 1976).

This can be rewritten for the $q = 0$ wave vector (considering the zone centre phonons only) and a pressure P which is applied to reduce the volume and shape of the crystal to that at absolute zero.

$$[\omega_{TP}(0,j)]^2 = [\omega^h(0,j)]^2 + 2\omega^h(0,j)\Delta\omega_T^A(0,j,\Omega) \quad \dots (3)$$

The $\Delta\omega^E(0,j)$ term will be zero if the volume and shape are the same as that at 0 K. We can also write both at 0 K and 0 pressure.

$$[\omega_{00}(0,j)]^2 = [\omega^h(0,j)]^2 + 2\omega^h\Delta\omega_0^A(0,j,\Omega^1) \quad \dots (4)$$

where $\Omega \approx \Omega^1$ and by substituting for $\omega^h(0,j)$ from (4) to (3)

we have:

$$\begin{aligned}\Delta\omega_T^A(0,j,\Omega) - \Delta\omega_0^A(0,j,\Omega) &= \{[\omega_{T,P}(0,j)]^2 - [\omega_{0,0}(0,j)]^2\}/2\omega^h(0,j) \\ &\approx \{[\omega_{T,P}(0,j)]^2 - [\omega_{0,0}(0,j)]^2\}/2\omega_{0,0}(0,j) \equiv f(T) \quad \dots (5) \\ &(\text{as all } \omega_{0,0} \text{ terms are constant})\end{aligned}$$

Equation (5) therefore allows an experimental determination of the change in the anharmonic self-energy between temperature T and 0 K via suitable studies of the temperature and pressure dependence of $\omega(0,j)$. It can also be shown that above the Debye temperature $f(T)$ is linear therefore it can be extrapolated to absolute zero to enable the evaluation of $\Delta\omega_0^A(0,j,\Omega)$ and therefore $\Delta\omega_T^A(0,j,\Omega)$. Maradudin and Fein (1962) and Cowley (1963) showed that $\Delta\omega_T^A$ is made up of cubic and quartic terms in anharmonicity where the cubic term is always negative and the quartic term may be positive or negative. Lowndes (1976) gives a very full account of this and the use of many body thermodynamic Green's functions as a quantitative theory for the handling of anharmonicity. The theory he used gave values which were in good agreement with experimental results for ionic crystals thus proving the above approach to be a sound one.

Having proved that the anharmonic self energy between T and 0 K can be determined by a study of $\omega(0,j)$ with T and P (equation 5), how are these variables related? This can be shown if we consider (writing ω_i for $\omega(0,j)$).

$$\omega_i = f_1(T, P) \quad (f_i \text{ are different functions})$$

$$\text{or } \ln \omega_i = f_2(T, P) \quad \dots \quad (6)$$

($\ln \omega_i$ is considered as this is directly related to an experimental property which will be derived later).

We can write, if our system is infinitely divisible small and isotropic

$$d(\ln \omega_i) = \left(\frac{\delta(\ln \omega_i)}{\delta T} \right)_P dT + \left(\frac{\delta(\ln \omega_i)}{\delta P} \right)_T dP \quad \dots \quad (7)$$

(This approximation is one made in the application of all classical calculus and is not further discussed).

$$\text{Also } \ln V = f_3(P, T) \quad \dots \quad (8)$$

$$\therefore d(\ln V) = \left(\frac{\delta(\ln V)}{\delta P} \right)_T dP + \left(\frac{\delta(\ln V)}{\delta T} \right)_P dT \quad \dots \quad (9)$$

If (8) and (6) are true we can express $\ln \omega_i$ as a function of T and V.

$$\ln \omega_i = f_4(V, T) \quad \dots \quad (10)$$

$$d(\ln \omega_i) = \left(\frac{\delta(\ln \omega_i)}{\delta V} \right)_T dV + \left(\frac{\delta(\ln \omega_i)}{\delta T} \right)_V dT \quad \dots \quad (11)$$

Substituting $d(\ln V)$ from equation (9) into equation (11) gives:

$$d(\ln \omega_i) = \left(\frac{\delta(\ln \omega_i)}{\delta T} \right)_V dT + \left(\frac{\delta(\ln \omega_i)}{\delta(\ln V)} \right)_T \left[\left(\frac{\delta(\ln V)}{\delta P} \right)_T dP + \left(\frac{\delta(\ln V)}{\delta T} \right)_P dT \right] \quad \dots \quad (12)$$

Comparing coefficients for (12) and (7) we obtain:

For dT

$$\left(\frac{\delta(\ln\omega_i)}{\delta T}\right)_P = \left(\frac{\delta(\ln\omega_i)}{\delta T}\right)_V + \left(\frac{\delta(\ln\omega_i)}{\delta(\ln V)}\right)_T \left(\frac{\delta(\ln V)}{\delta T}\right)_P \quad \dots\dots (13)$$

For dP

$$\left(\frac{\delta(\ln\omega_i)}{\delta P}\right)_T = \left(\frac{\delta(\ln\omega_i)}{\delta(\ln V)}\right)_T \left(\frac{\delta(\ln V)}{\delta P}\right)_T \quad \dots\dots (14)$$

Rearranging equation (14) and substituting into (13) we obtain:

$$\overbrace{\left(\frac{\delta(\ln\omega_i)}{\delta T}\right)_P}^{(i)} = \overbrace{\left(\frac{\delta(\ln\omega_i)}{\delta T}\right)_V}^{(ii)} + \overbrace{\left(\frac{\delta(\ln\omega_i)}{\delta P}\right)_T \left(\frac{\delta(\ln V)}{\delta T}\right)_P \left(\frac{\delta P}{\delta(\ln V)}\right)_T}^{(iii)} \quad \dots\dots (15)$$

Equation (15) states that the rate of change of frequency with temperature T and at constant pressure P , is equal to the sum of two terms (ii) and (iii). (ii) is the rate of change of frequency with temperature at constant volume V and (iii) can be understood as the change in frequency if the volume of the crystal at T K is returned to that at 0 K and zero pressure by application of a pressure P (Lowndes 1971). This equation can be written in macroscopic terms as

$$\overbrace{\Delta_T \omega_i|_P}^{(i)} = \overbrace{\Delta_T \omega_i|_V}^{(ii)} + \overbrace{\Delta \omega_i|_T}^{(iii)} \quad \dots\dots (16)$$

Both forms (15) and (16) have been reported in the literature (Wong 1975, Lowndes 1971, 1976, and Peercy, Samara and Morosin 1975).

Hence we have divided the frequency shift with temperature into a term due to thermal expansion (iii) which will be a measure of $\Delta\omega^E(0,j)$ and a term at constant volume (ii) which will be a measure of $(\Delta\omega_T^A(0,j) - \Delta\omega_0^A(0,j))$ as the quasiharmonic frequency remains constant under constant volume (see equations (2) and (3)).

$$\Delta\omega^E(0,j) = \Delta\omega_i|_T$$

$$\Delta_T\omega_i|_V = \Delta\omega_T^A(0,j) - \Delta\omega_0^A(0,j) \quad (\text{Lowndes 1971})$$

More important, and the aim of the exercise, all terms in equation (16) can be measured experimentally, (i) by direct spectroscopic observation of the separate frequencies at various temperatures and constant pressure and (iii) by measuring the relationship between the volume and temperature at constant pressure, the volume and pressure at constant temperature, and the frequency and pressure at constant temperature. Term (iii) can also be written as $-\alpha \gamma_i$ where α is the thermal expansion (volume) coefficient and γ_i the Gruneisen parameter definitions as follows.

$$\alpha = \left(\frac{\delta(\ln V)}{\delta T} \right)_P, \gamma_i = \frac{1}{\kappa} \left(\frac{\delta(\ln \omega_i)}{\delta P} \right)_T$$

$$\kappa = - \left(\frac{\delta(\ln V)}{\delta P} \right)_T \quad (\text{compressibility})$$

If terms (i) and (iii) are known (ii) can be calculated directly and hence the anharmonic self energy calculated. The techniques used in this work to unravel term (iii) in (15) are now summarised.

For the volume and temperature at constant pressure a single crystal was examined by X-ray diffraction at various temperatures. For the volume variation with pressure at constant temperature a DAC loaded with a gasket and a powder sample was used in the X-ray diffraction experiment. The frequency variation with pressure at constant temperature was studied with a DAC loaded similarly, used with a Raman or far-i.r. spectrometer. Lowndes (1976) was of the opinion that DAC's are very difficult to use in the far-i.r., and pressure gradients and the lack of hydrostatic pressure are major problems. He referenced several papers in which ungasketed DAC's were used. Of course the pressure gradients were large and the pressure non-hydrostatic. But as explained in Chapter 2 and Chapter 3, the far-i.r. experiment can be conducted under hydrostatic pressure and the pressure determined to within ± 0.2 kbar by use of a metal gasket and the R fluorescence lines of ruby.

Having steered a course through a general application of the theory we must now consider the use of this theory for a particular material. CsNiCl_3 was studied and a recent report of its "normal coordinate analysis" had been produced by our group (Adams, Christopher and Stevens, 1977) and the spectra are fully characterised and understood. CsNiCl_3 crystallises in the space group $P6_3/mmc$ (D_{6h}^{44}) with $z = 2$. (Tischenko 1955). This is a hexagonal group and is not isotropic. We must therefore look at the theory developed above to see how this anisotropy affects it. Equation (3) can only be written if the volume at 0 K has the same shape

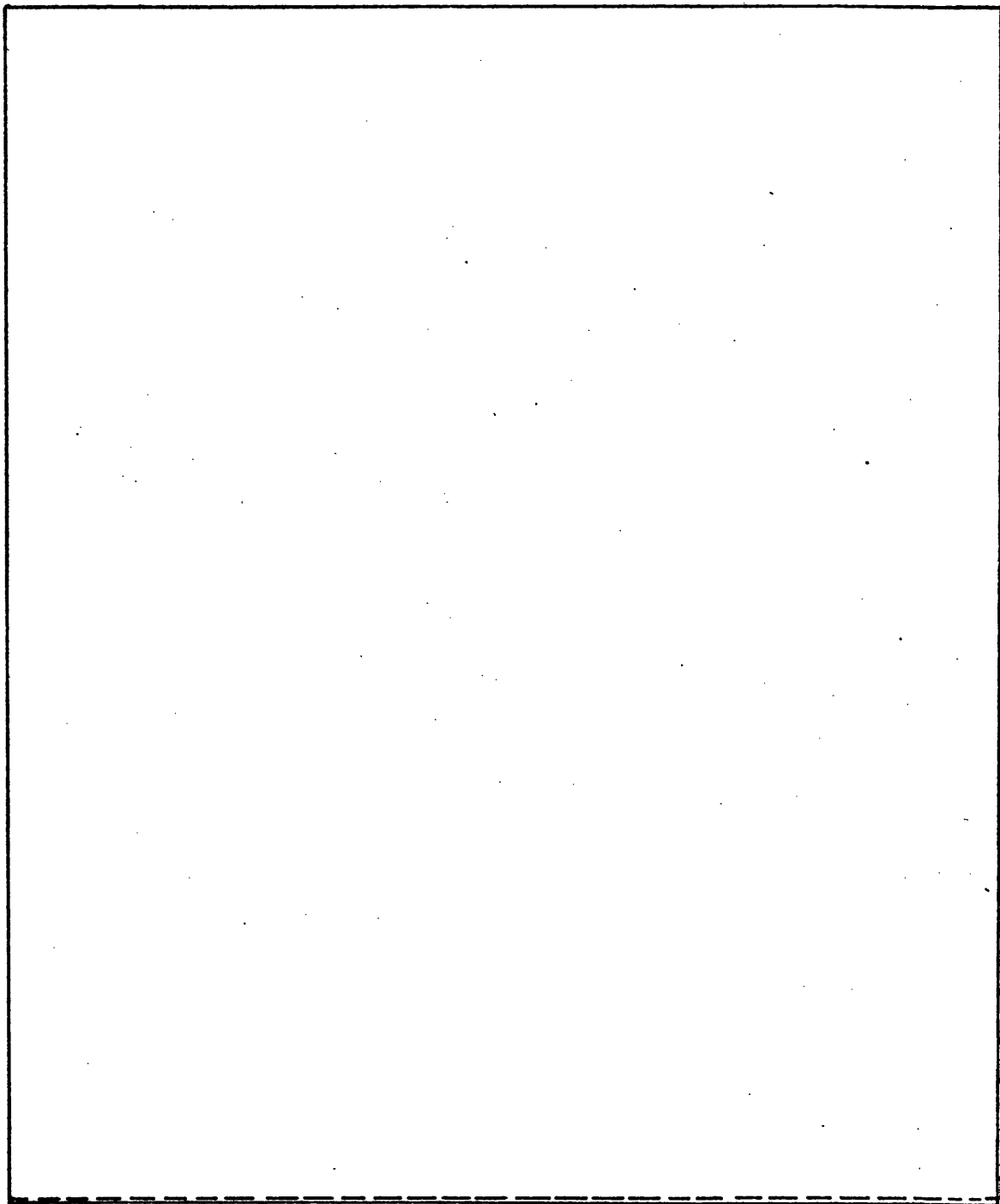
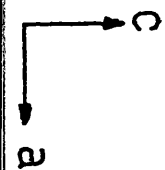
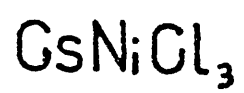
as the volume produced by application of pressure at some temperature T for the anisotropic case. That is, we can only use volume if we are careful to maintain constant shape. A more general form of the frequency dependence could be obtained if we write as for equation (10).

$$\ln \omega_i = f_5(a,b,c,T) \quad (\text{where } a,b,c \text{ are orthogonal axes})$$

This complicates the issue considerably. A detailed discussion of the thermodynamics of anisotropic solids is given by Thurston (1964) and a typical example presented by Peercy, Fritz and Samara (1975) for the tetragonal form of TeO_2 . It is sufficient to say that we will have 6 Gruneisen parameters and 6 thermal expansion parameters which will be related by their elastic constants for a general anisotropic case. But nature has been very kind and for this crystal the volume and shape at 0 K can be produced within the limits of our experiment by application of pressure to the crystal at room temperature T . This is illustrated in figure 7:1. The differences in the a and c directions are 0.4% and 0.3% respectively and hence the difference in volume is 1.5%. The error in determining lattice parameters from high pressure X-ray experiments is of the order of 1% ($\pm 0.5\%$). Therefore this difference in volume is within the limits of experimental error. The theory given above can be directly applied to CsNiCl_3 as if it were isotropic.

FIGURE 7:1

The (a,c) face of the unit cell of CsNiCl_3 at 0 K (solid line) is compared to a unit cell generated with the same volume at room temperature and high pressure (dashed line).



1 Å

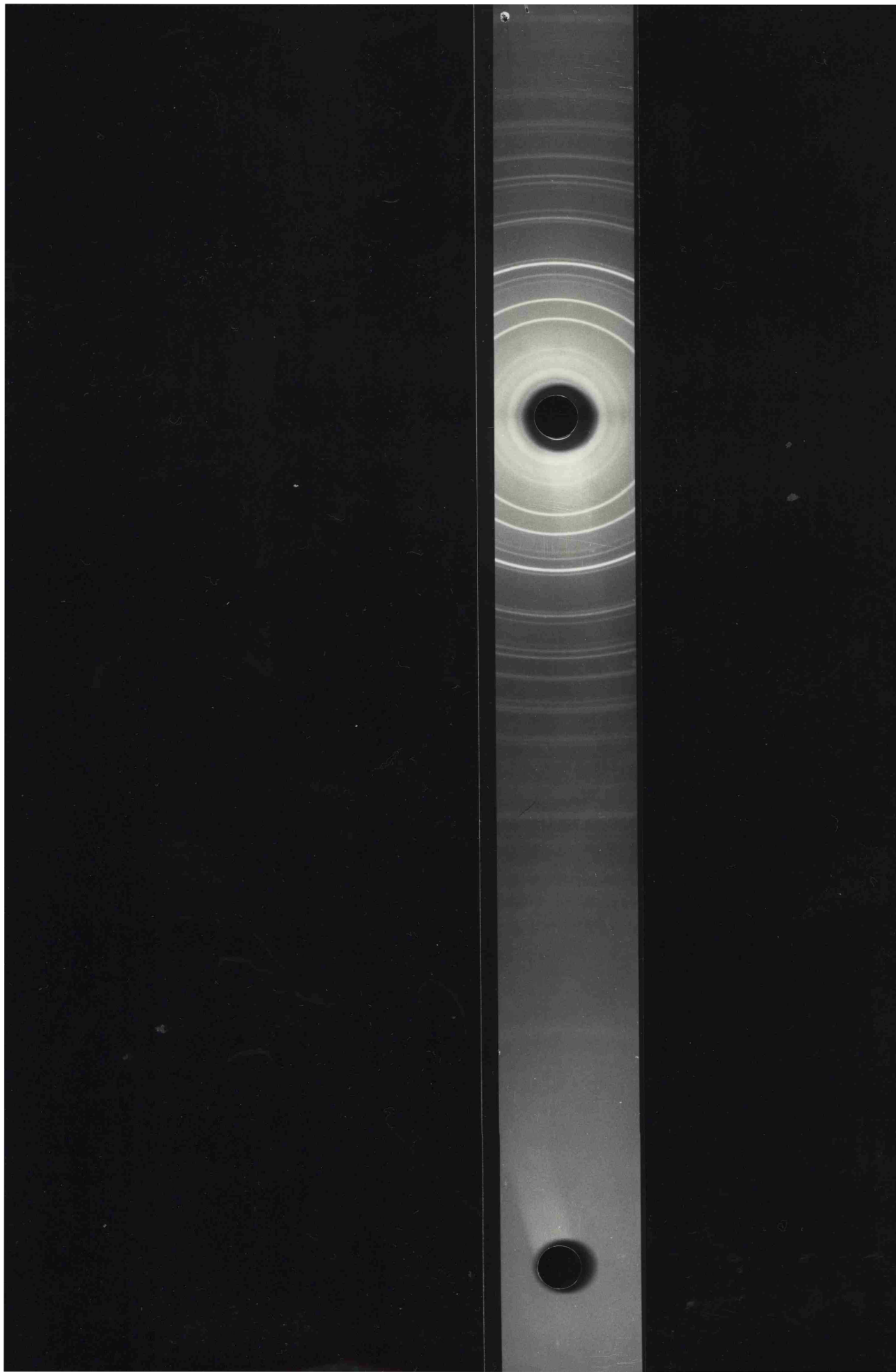
7.2 Experimental

CsNiCl_3 was recrystallised from aqueous HCl and the same sample used in all experiments. The DAC and CTI model-21 were used as discussed in Chapter 2 to determine the pressure dependence of volume and frequency, and temperature dependence of frequency. The temperature dependence of volume was determined using a small single crystal (ca. $0.1 \times 0.1 \times 1$ mm) mounted on a Stoe Weisenberg camera with a Stoe liquid nitrogen cryostat and CuK_α radiation. The temperature could only be maintained at ± 5 K. Only high values of 2θ ($2\theta > 130^\circ$) were used and exposures at several temperatures were made on one piece of film to avoid errors due to shrinkage. A single crystal was used as a powder sample failed to give lines at high values of 2θ as shown in figure 7:2. It would have been preferable to use a powder sample with the CTI which has a large range of accurately-controllable temperatures ($0 \rightarrow 300$ K ± 0.5 K) (see Chapter 2). In all X-ray experiments least square fits were performed to give the lattice constants. The error in the pressure experiment in lattice parameters was considered to be ca. ± 0.5 (max) Å, and in the temperature experiment ca. ± 0.005 Å. The high error in the pressure experiment was because values of $2\theta < 30^\circ$ are available for a powder sample in the DAC. $2\theta > 160^\circ$ could not be studied as the powder sample gave no lines at ambient temperature, figure 7:2, (see Chapter 2). The frequency versus pressure data was fitted to a straight line by a least squares method.

A computer programme was constructed to perform the analysis of the temperature dependence of frequency and is given in

FIGURE 7:2

X-ray powder diffraction pattern of CsNiCl_3 using
a 0.2 mm Linderman glass capillary CuK_α radiation
and a Debye Scherrer camera.



Appendix 2. It is fully documented and therefore not discussed further.

7.3 Results and Discussion

The far-i.r. and Raman spectra at various temperatures and pressures are given in figures 7:3, 7:4, 7:5, and 7:6 and the wave-numbers and Gruneisen parameters summarised in tables 1 and 2.

The X-ray diffraction data are given in table 3 and the plots of lattice constant versus temperature and pressure in figure 7:7.

Plots of volume versus temperature and pressure, compressibility versus pressure and thermal expansion (volume) versus temperature, are given in figure 7:8 and the compressibilities and thermal expansion data are given in table 4. The results of the analysis, that is, $\Delta_T \omega_i|_V$, $\Delta \omega_i|_T$, and $\Delta_T \omega_i|_P$ are given in figure 7:9 which also shows the way that $\Delta_T \omega_i|_V$ has been extrapolated to 0 K (discussed further in the text). Values of $\Delta \omega_T^E(q,j)$, $\Delta \omega_T^A(q,j)$ and $\Delta \omega_0^A(q,j)$ calculated from the data of figure 7:9 are given in table 5 at various temperatures. Finally the Debye temperature was calculated by the method of Plendl (1969) from the reflectivity data of Chadwick, Dunsmuir, Forrest, Lane and Fernando (1971) and found to be ca. 105 K.

The Far-i.r. and Raman Spectra

The spectra behaved normally with both increase in pressure and decrease in temperature, all modes shifting to higher frequency. The only point to note is that the intensity of the Raman active lattice mode (E_{2g} at 58 cm^{-1}) decreases both with pressure and temperature, an as yet unexplained result.

Table 1 The wavenumbers/cm⁻¹ of CsNiCl₃ at various temperatures
and ambient pressure

Far-i.r.

T (K)	A _{2u}	E _{1u}	E _{1u}	A _{2u}	E _{1u}
292	54	78	178	205	258
244	54	78	178	205	260
194	54	78	178	206	262
150	54	81	178	208	262
99	55	82	178	209	265
18	55	82	178	209	266

Raman

	E _{2g}	E _{1g} /E _{2g}	E _{2g}	A _{1g}
292	58	141.5	196	267
264	58	142.5	196	268
209	59	143.5	198	269.5
165	59.5	144.0	198.5	271.0
110	60.0	145.0	199.5	272.0
12	60.0	145.0	199.5	272.0

Table 2 The wavenumbers/cm⁻¹ of CsNiCl₃ at various pressures (kbar).

$(\frac{\delta\omega}{\delta P})_T$ at ambient temperature and the Gruneisen parameter

γ_i are also given.

<u>P(kbar)</u>	<u>0.001</u>	<u>12.5</u>	<u>16.0</u>	<u>18.5</u>	<u>21.5</u>	<u>29.5</u>	<u>31.0</u>	<u>39.5</u>	<u>$(\frac{\delta\omega}{\delta P})_T^*$</u>
A _{2u}	54	64		72		85			1.14
$\gamma_{A_{2u}}$	4.7	3.5							
E _{2g}	58	61.5		64		69.0		74	0.39
$\gamma_{E_{2g}}$	1.5	1.3							
E _{1u}	78	90		95		100			0.78
$\gamma_{E_{1u}}$	2.2	1.9							
E _{1g} /E _{2g}	143	150		153	155	157		163	0.48
$\gamma_{E_{1g}/E_{2g}}$	0.75	0.6							
E _{1u}	178		188				190		0.44
$\gamma_{E_{1u}}$	0.4	0.5							
E _{2g}	196	204		206	210	213		221	0.63
$\gamma_{E_{2g}}$	0.7	0.7							
A _{2u}	205		218				232		0.83
$\gamma_{A_{2u}}$	0.9	0.8							
E _{1u}	258		270				277		0.56
$\gamma_{E_{1u}}$	0.5	0.4							
A _{1g}	267			280	282	286		295	0.70
$\gamma_{A_{1g}}$	0.6	0.5							

* Calculated by least squares fit to all experimental data.

FIGURE 7:3

Raman spectra of CsNiCl_3 at various temperatures.
Conditions 50 mW of 647.1 nm radiation was used
with a spectral slit width of 2.1 cm^{-1} and photon
counting as described in Chapter 2.

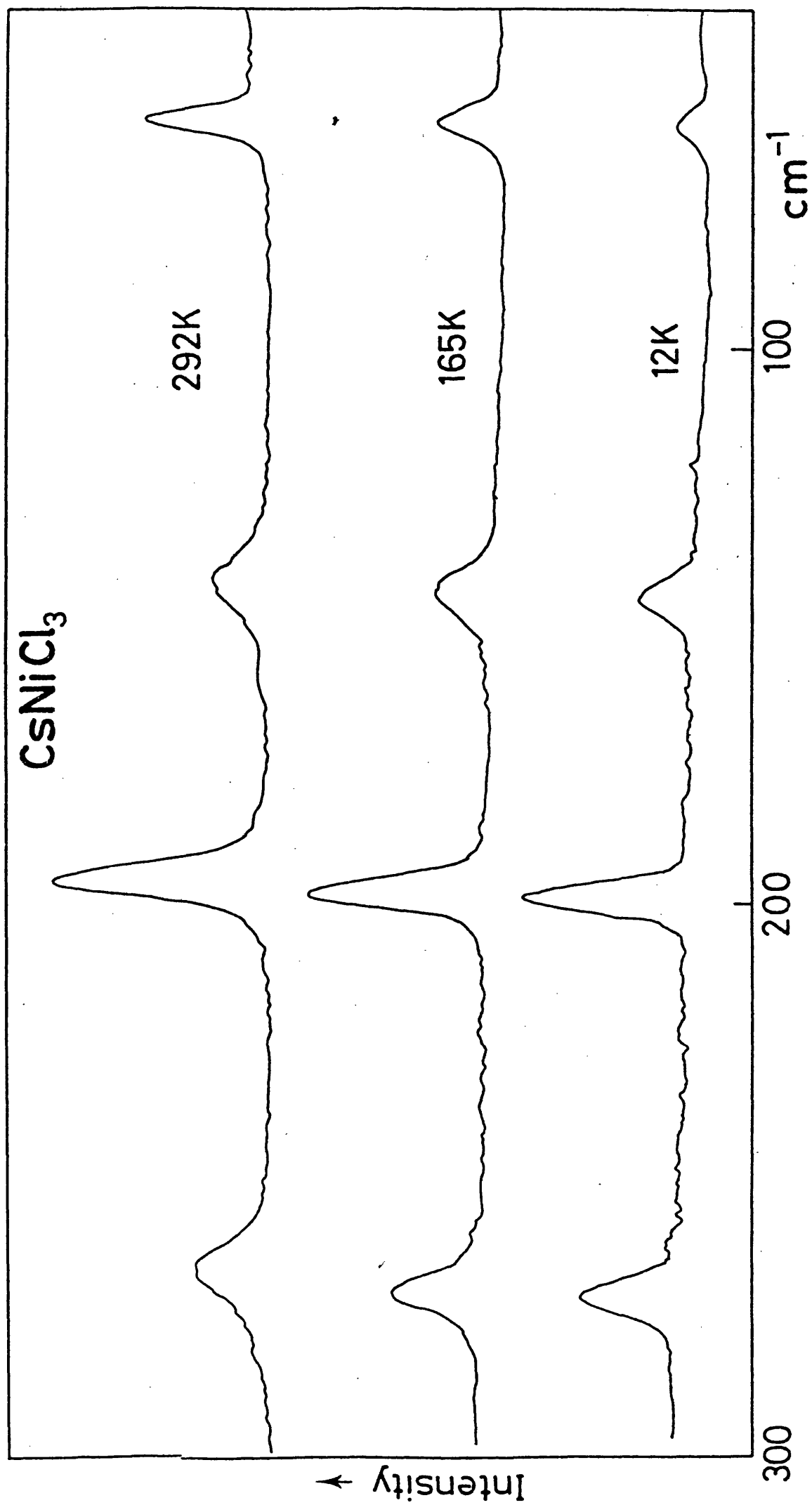
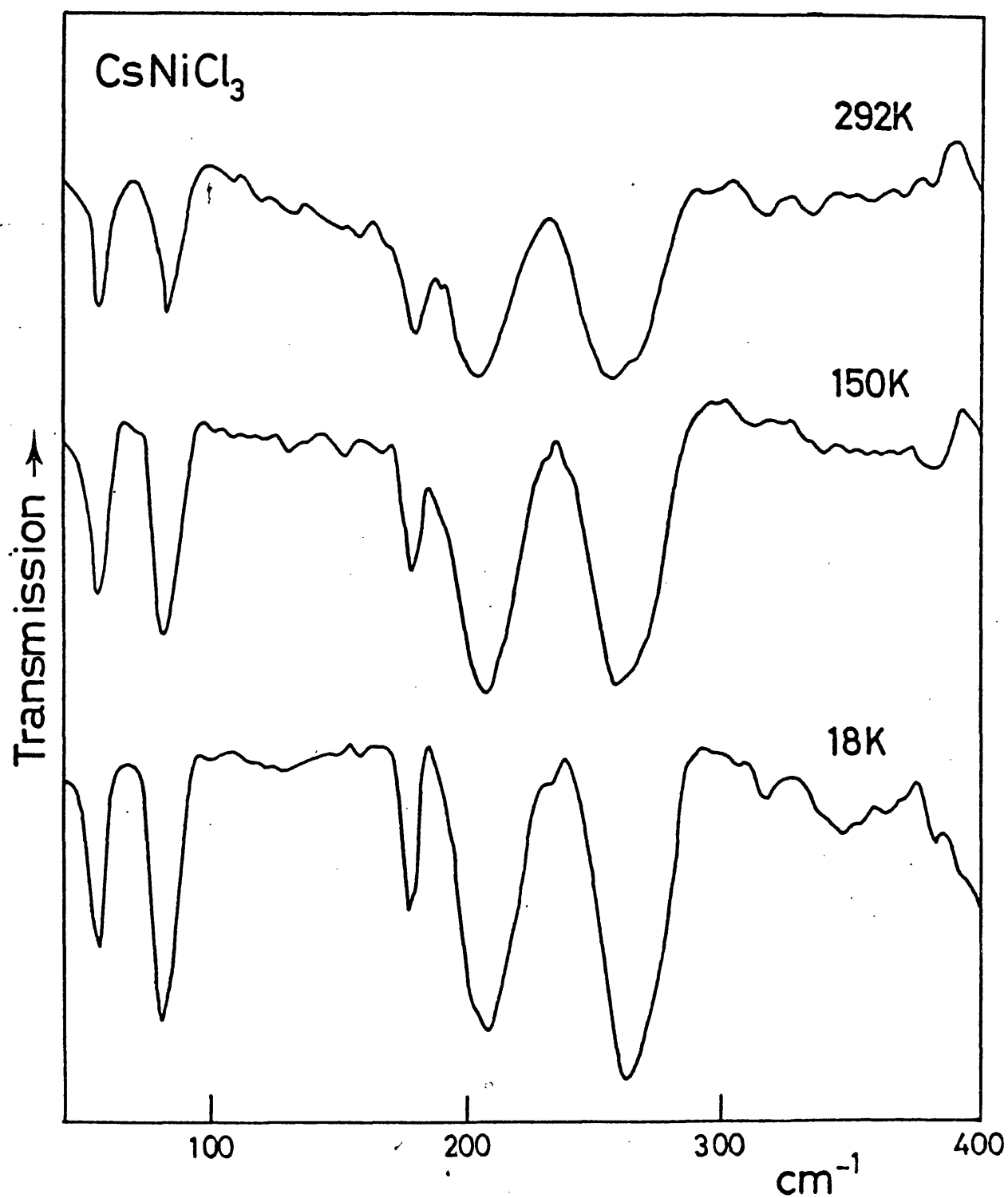


FIGURE 7:4

Far-i.r. spectra of CsNiCl_3 at various temperatures.



↑
 cm^{-1}



300

250

200

150

100

50

 A_{1g} E_{1u} A_{2u} E_{2g} E_{1u} E_{2g}/E_{1g} E_{1u} A_{2u} E_{2g}

300

200

100

0

← K

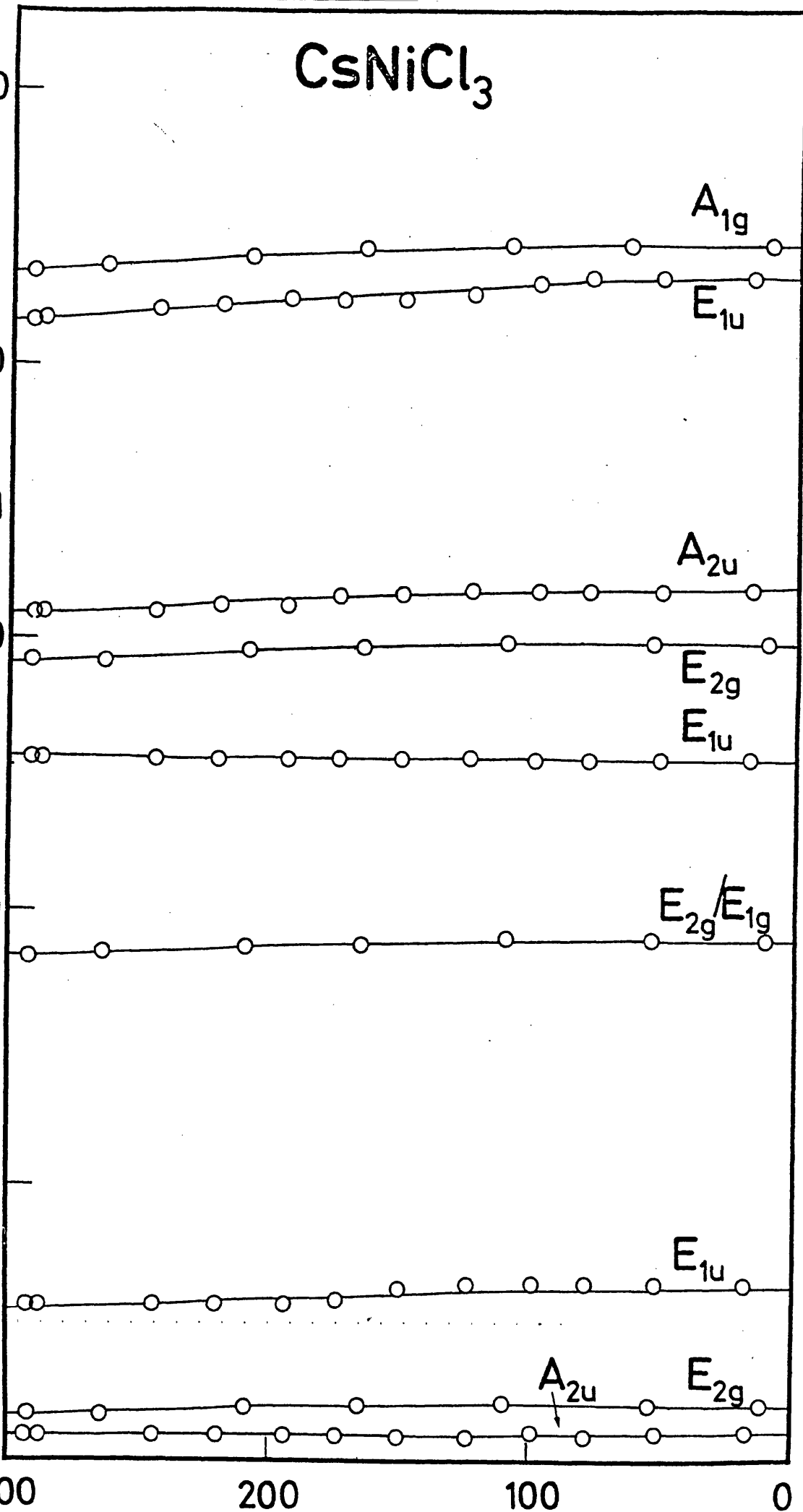


FIGURE 7:5

Far-i.r. spectra of CsNiCl_3 at various pressures (kbar).

Transmission $\rightarrow$ 295K
0 kbar

16 kbar

18.5 kbar

30 kbar

36 kbar

100

200

300

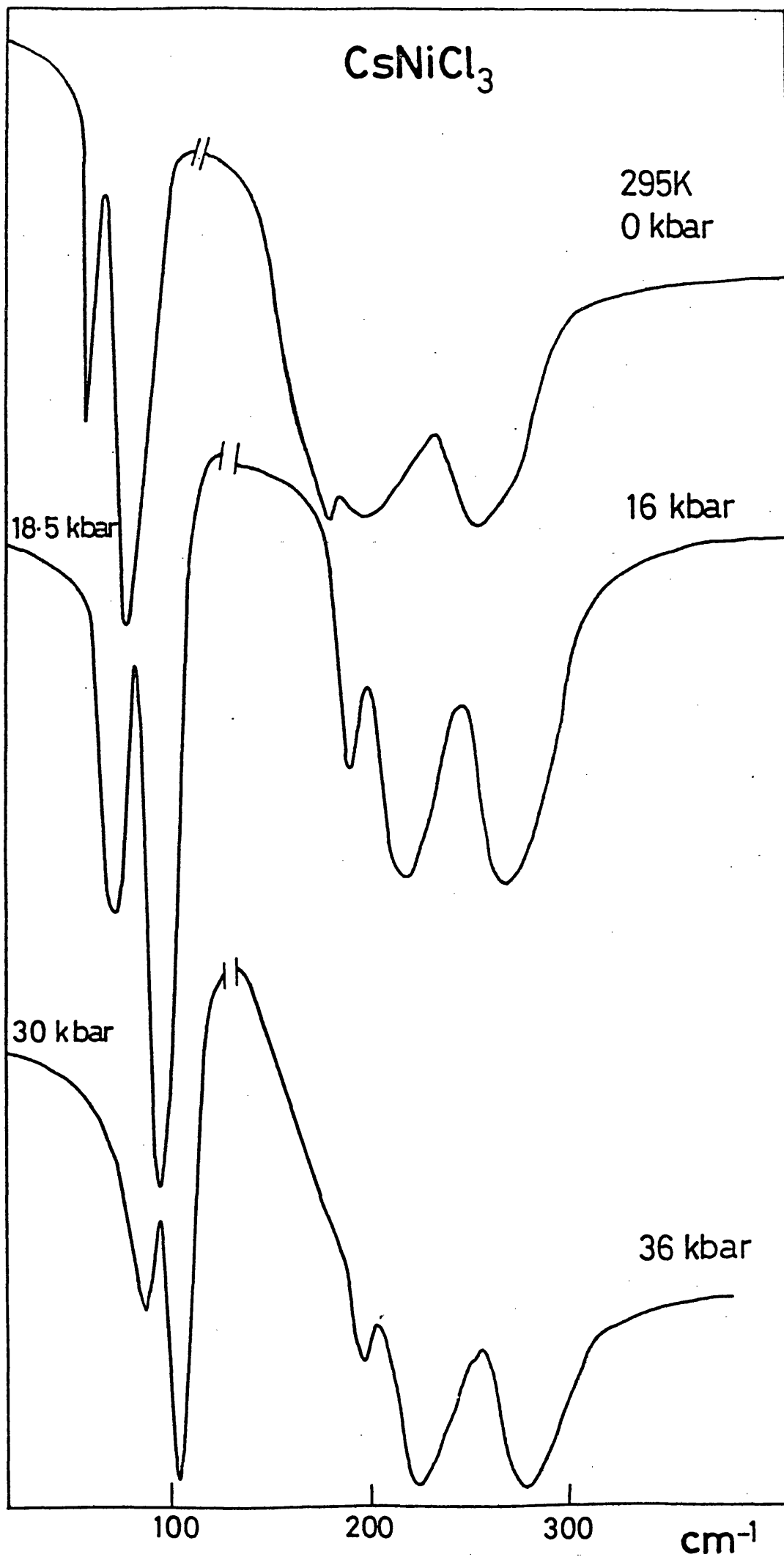
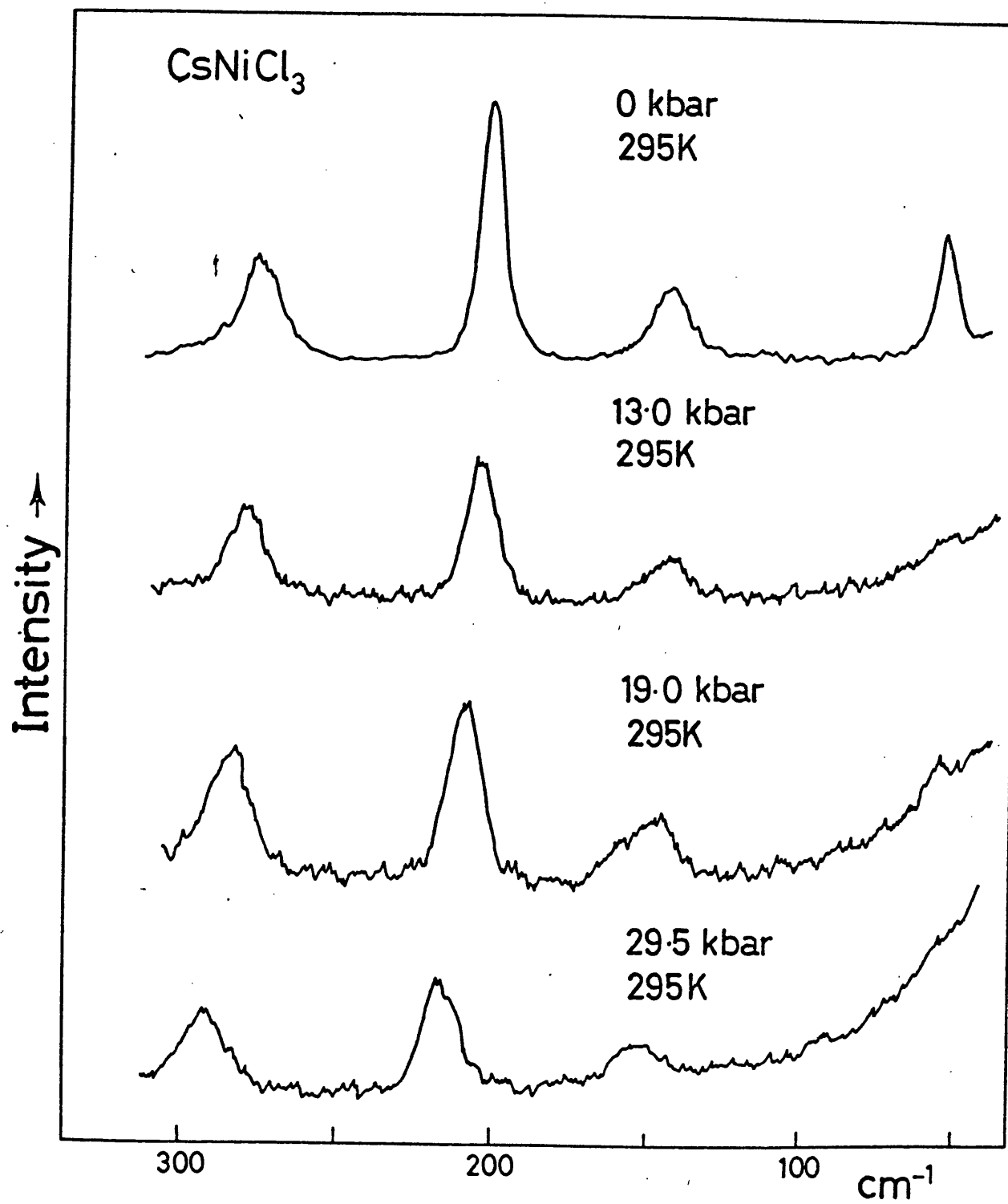
 cm^{-1} 

FIGURE 7:6

Raman spectra of CsNiCl_3 at various pressures (kbar).

Conditions: 600 mW of 647.1 nm radiation was used with a spectral slit width of 2.1 cm^{-1} and a DC detection system described in Chapter 2.



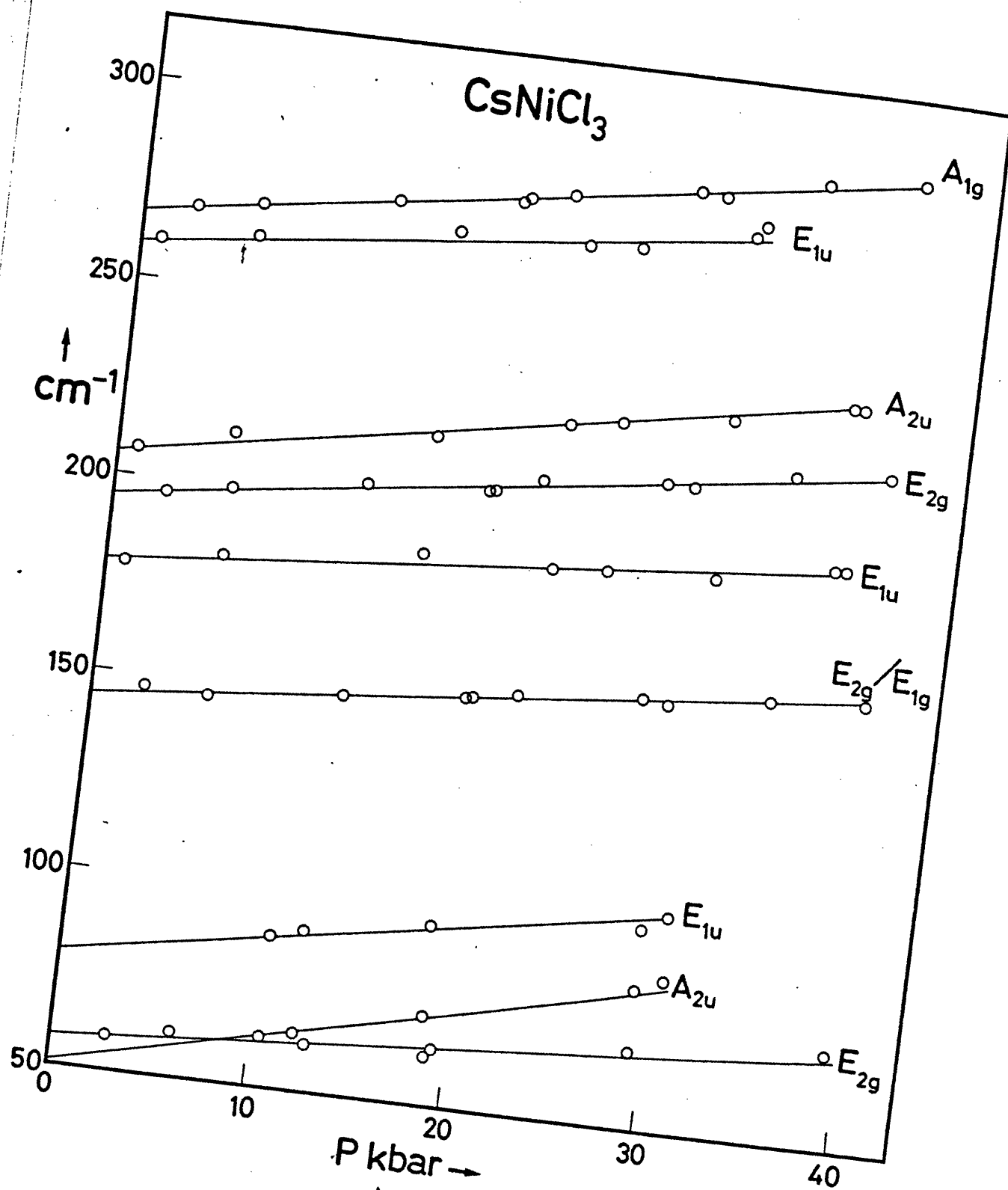


Table 3 The lattice constants/ $\text{\AA}$ of CsNiCl_3 at (i) various pressures (kbar) and (ii) various temperatures.

(i)

Pressure (kbar)	a*	c *
0.01	7.16	5.94
13.3	6.97	5.93
17.3	6.94	5.86
25.3	6.92	5.78
26.0	6.88	5.79
36.0	6.76	5.69

(ii)

T (K)	a †	c †
300 (± 2)	7.16	5.94
243 (± 5)	7.15	5.93
198 (± 5)	7.14	5.93
180 (± 5)	7.13	5.92
167 (± 5)	7.11	5.92
132 (± 5)	7.11	5.90

* Approximate error 1%

† Approximate error 0.05%

} Taken from Azareff and Buerger (1958)
by observation of the quality of the
photographs produced.

Table 4 (a) Compressibility/kbar⁻¹ at several pressures
 (b) Thermal expansion (vol)/K⁻¹ versus temperature

(a)	Compressibility (kbar ⁻¹ x 10 ³)	Pressure (kbar)
	4.40	0.001
	4.48	4.0
	4.56	8.0
	4.64	12.0
(b)	Thermal expansion (x 10 ⁶) (K ⁻¹)	Temperature (K)
	103.7	50
	149.6	100
	161.3	150
	163.2	200
	165.9	250
	166.3	300

FIGURE 7:7

Plots of lattice parameters versus temperature and pressure. The dotted line indicates extrapolation to 0 K.

CsNiCl_3

$\leftarrow K$

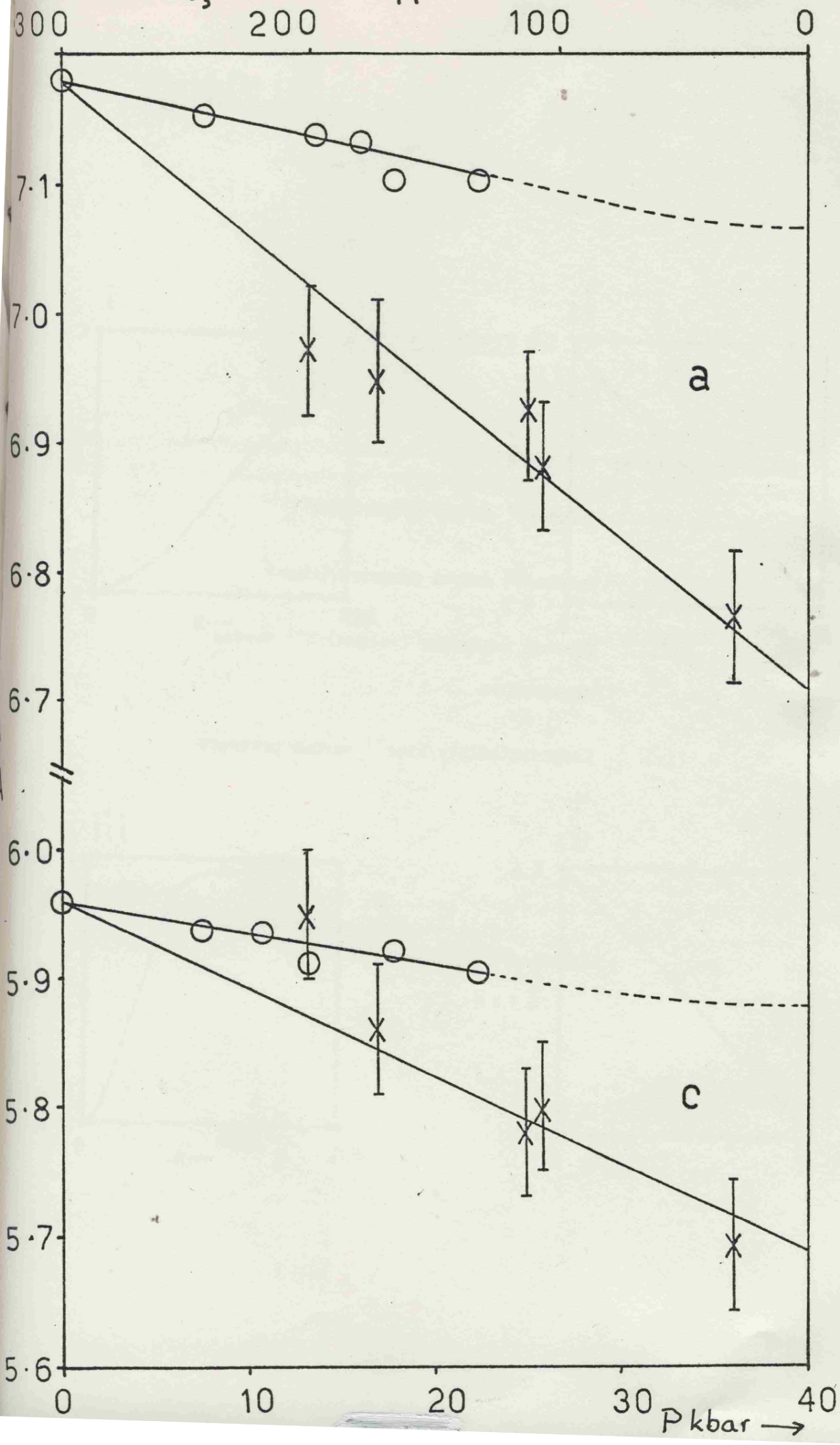
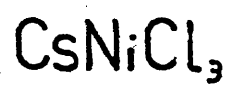


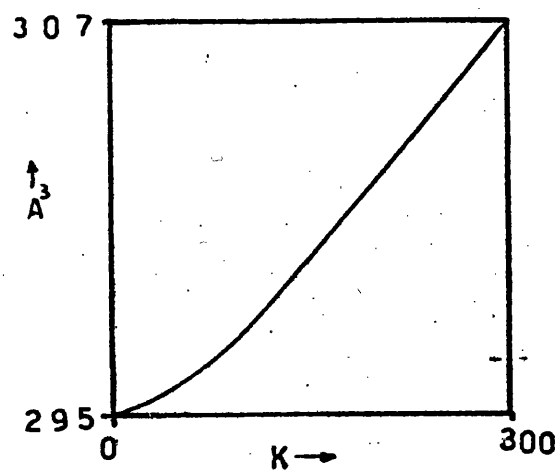
FIGURE 7:8

Plots of

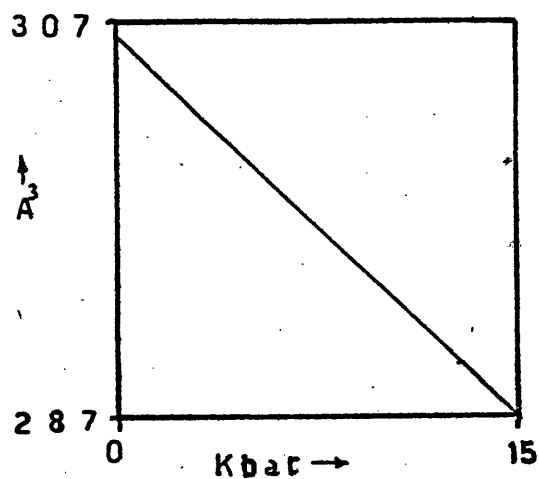
- (i) Volume/ $\text{\AA}^3$ versus temperature
- (ii) Volume/ $\text{\AA}^3$ versus pressure/(kbar)
- (iii) Thermal expansion (volume)/ K^{-1} versus temperature
- (iv) Compressibility/ kbar^{-1} versus pressure



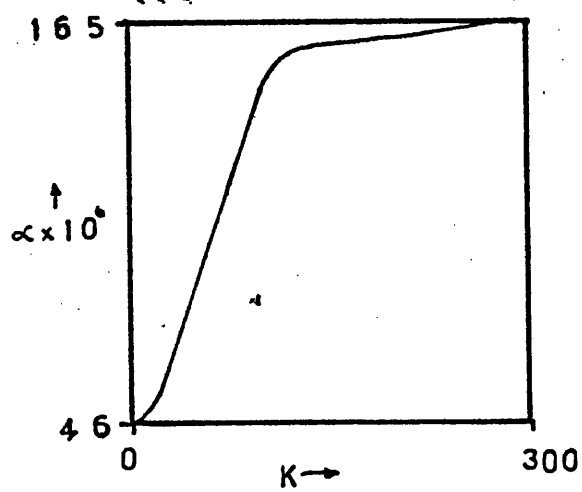
i



ii



iii



iv

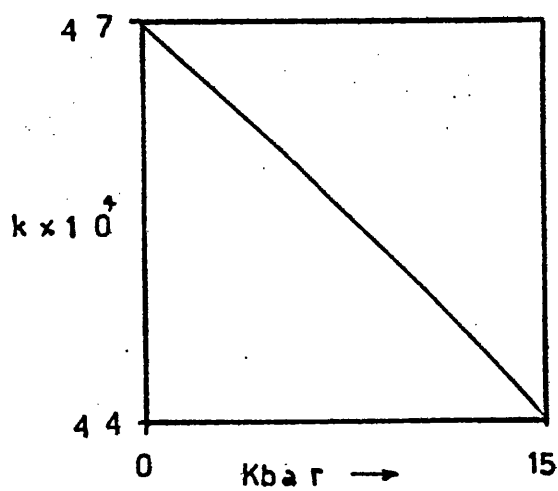


Table 5 The contributions of the various terms to the temperature shifts of the vibrational frequencies of CsNiCl_3 (cm^{-1}).

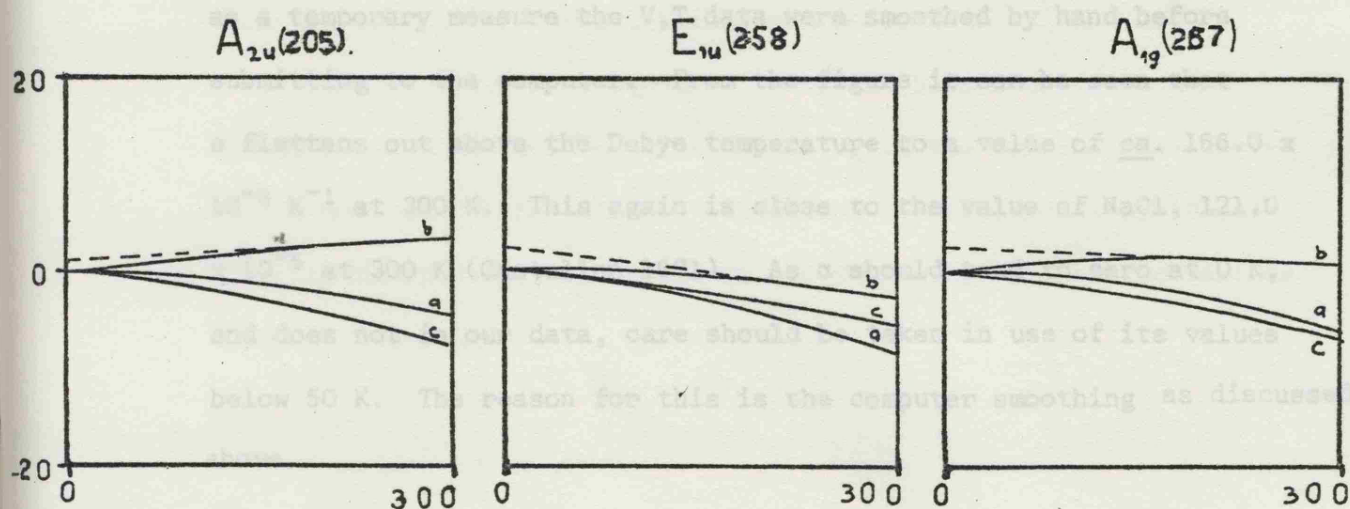
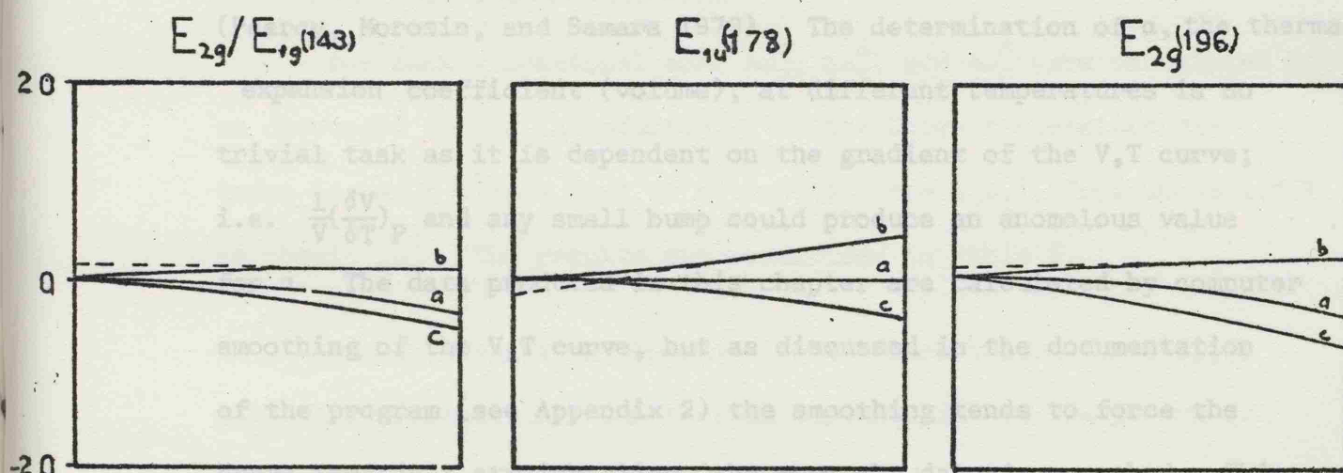
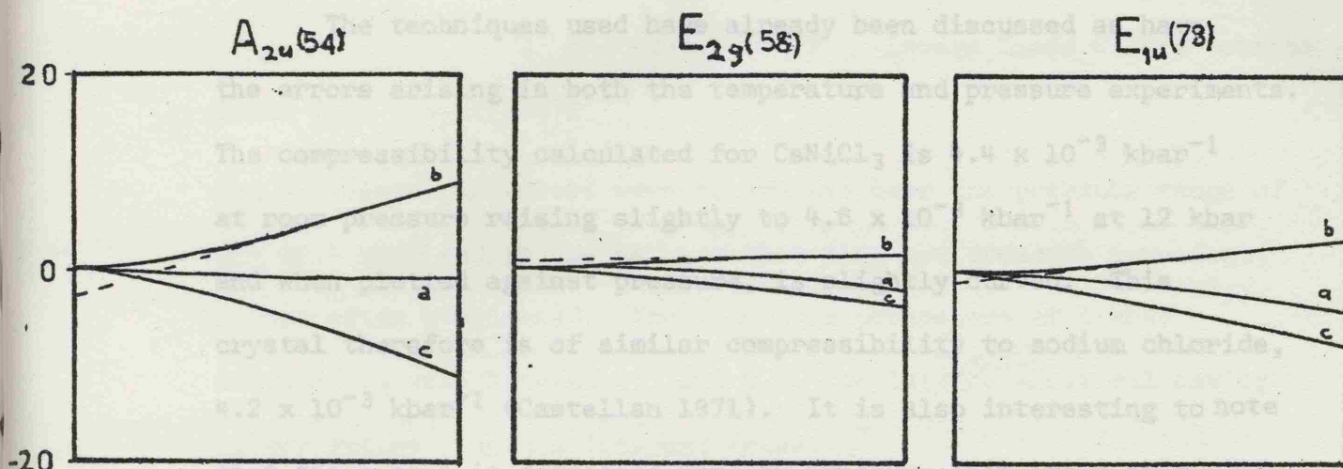
	$\Delta\omega_0^A$	$\bar{\Delta}_0$	$\Delta\omega_T^A$				$\Delta\omega_T^E$			
			60 K	100 K	200 K	300 K	60 K	100 K	200 K	300 K
$A_{2u}(54)$	-3.2	0.058	-2.7	-1.7	2.0	6.1	-1.0	-2.3	-6.4	-10.6
$E_{2g}(58)$	0.8	0.013	1.0	1.3	2.0	2.3	-0.3	-0.8	-2.2	-3.7
$E_{1u}(78)$	-1.2	0.015	-1.1	-0.9	0.4	1.6	-0.7	-1.5	-4.3	-7.3
$E_{1g}/E_{2g}(143)$	1.0	0.007	1.2	1.5	1.8	1.9	-0.4	-1.0	-2.7	-4.5
$E_{1u}(178)$	-1.3	0.007	-0.9	-0.4	1.2	2.8	-0.2	-0.6	-2.1	-3.9
$E_{2g}(196)$	2.0	0.010	2.5	3.0	3.9	3.9	-0.6	-1.3	-3.5	-5.9
$A_{2u}(205)$	1.5	0.007	2.2	2.8	4.2	4.8	-0.8	-1.7	-4.7	-7.8
$E_{1u}(258)$	3.0	0.011	2.7	2.6	1.6	-0.2	-0.5	-1.1	-3.1	-5.2
$A_{1g}(267)$	3.0	0.011	3.6	4.2	4.6	4.0	-0.6	-1.4	-3.9	-6.6

FIGURE 7:9

Plots for all vibrational frequencies of CsNiCl_3 of (a) $\Delta_T \omega_i|_P$, (b) $\Delta_T \omega_i|_V$, (c) $\Delta \omega_i|_T$ (see equation (16)) against temperature. The extrapolation of (b) to 0 K is also shown, dashed line (see text).

CsNiCl₃

The X-Ray Data



cm^{-1}
K

The X-Ray Data

The techniques used have already been discussed as have the errors arising in both the temperature and pressure experiments. The compressibility calculated for CsNiCl_3 is $4.4 \times 10^{-3} \text{ kbar}^{-1}$ at room pressure raising slightly to $4.6 \times 10^{-3} \text{ kbar}^{-1}$ at 12 kbar and when plotted against pressure, is slightly curved. This crystal therefore is of similar compressibility to sodium chloride, $4.2 \times 10^{-3} \text{ kbar}^{-1}$ (Castellan 1971). It is also interesting to note that the a axis is decreased more by pressure than the c axis. This result was also observed for $(\text{CH}_3)_4\text{NMnCl}_3$ a similar compound (Peercy, Morosin, and Samara 1973). The determination of α , the thermal expansion coefficient (volume), at different temperatures is no trivial task as it is dependent on the gradient of the V,T curve; i.e. $\frac{1}{V}(\frac{\delta V}{\delta T})_P$ and any small bump could produce an anomolous value for α . The data produced in this chapter are calculated by computer smoothing of the V,T curve, but as discussed in the documentation of the program (see Appendix 2) the smoothing tends to force the curve towards a straight line, the more the data is smoothed. This can be cured by using an exponential curve fitting routine but as a temporary measure the V,T data were smoothed by hand before submitting to the computer. From the figure it can be seen that α flattens out above the Debye temperature to a value of ca. $166.0 \times 10^{-6} \text{ K}^{-1}$ at 300 K. This again is close to the value of NaCl, 121.0×10^{-6} at 300 K (Castallen 1971). As α should tend to zero at 0 K, and does not in our data, care should be taken in use of its values below 50 K. The reason for this is the computer smoothing as discussed above.

α is of the general form

$$\alpha = \left(\frac{C}{T}\right)^2 e^{-C^1/T} \quad (\text{where } C \text{ and } C^1 \text{ are constants})$$

Taken from Levy (1968).

The Gruneisen parameters were determined over the pressure range of 0 → 12.5 kbar and it can be seen that they are pressure dependent, a fact often overlooked. The Gruneisen parameters at 1 kbar for CsNiCl_3 vary between 4.7 and 0.4, the lattice modes all having larger values than the internal modes.

Results of the computer analysis

For each vibrational mode $\Delta\omega_T^E$, $\Delta\omega_T^A$, and $\Delta\omega_0^A$ were calculated as discussed in the introduction. As the Debye temperature was known it was a simple task to extrapolate the $\Delta\omega_i|_V$ from above 110 K to obtain $\Delta\omega_0^A$. The results are summarised in table 5.

Peercy, Samara and Morosin (1975) demonstrated for SnI_4 , a molecular crystal, that the thermal dependencies of the phonon frequencies of the external modes are dominated by the pure volume ($\Delta\omega_T^E$) term. For these modes $\Delta\omega_T^E$ is an order of magnitude bigger than the $\Delta\omega_T^A$ shifts. For the internal modes both $\Delta\omega_T^E$ and $\Delta\omega_T^A$ were found to contribute equally. Wong (1975) calculated a term $\bar{\Delta}_0$ which was given by $\frac{\Delta\omega_0^A}{\nu_0} = \bar{\Delta}_0$ where ν_0 is the original frequency of the mode at 0 K for all the vibrations in dichlorobis(pyridine) zinc(II) to find that $\bar{\Delta}_0$ varied in the following way for the various types of vibration.

(ν = stretching, δ = bending)

$$\nu_{\text{lattice}} \approx \delta_{\text{lattice}} > \nu_{\text{Zn-N}} > \nu_{\text{Zn-Cl}} > \delta_{\text{N-Zn-N}}$$

Gervais, Piriou and Cabannes (1973) state that for Be_2SiO_4 the cubic anharmonicity is prominent in the internal modes whilst both cubic and quartic terms contribute to the external modes. Their assignment may be unreliable as they treated the material as Be cations in an SiO_4 lattice whilst in fact, the Be oxygen bond is comparable in strength with the Si oxygen bond (Adams 1974). CsNiCl_3 is a typical complex ionic crystal and it can be seen from the n.c.a. that the A_{2u} (54) is an almost pure lattice mode (98% Cs-Cl out of plane vibration) and the A_{2u} (205) is an almost pure internal Ni-Cl vibration (98%), whilst all other modes are considerably mixed. The data of table 5 indicate that at 300 K, the thermal dependence of the phonon frequencies of both external and internal modes are dominated by $\Delta\omega_T^E$ and no distinction can be made between them. This is in contrast to Peercy et al (1975) and seems to suggest that a range of $\Delta\omega_T^E$ and $\Delta\omega_T^A$ contributions can be found. With the appearance of more data on different systems this idea could be examined in more detail.

If the parameter calculated by Wong $\bar{\Delta}_0$ is calculated for CsNiCl_3 (see table 5) the modes can be organised into the following order

$$A_{2u}(54) > E_g(58) = E_{1u}(78) = E_{1u}(258) = A_{1g}(267) > A_{2u}(205) = E_{1u}(178) \\ \approx E_{1g}/E_{2g}(143)$$

This agrees well with Wong's observation that $\bar{\Delta}_0$ is larger for a lattice mode $A_{2u}(54)$ than for an internal mode $A_{2u}(205)$ but little more can be said due to the mixing of different contributions in the other modes of CsNiCl_3 .

We come now to discuss the anharmonic self energy shift $\Delta\omega_T^A$, and the contribution to it by the first and second order cubic and quartic terms necessary to expand the power series describing the potential energy of a solid past the quadratic term to give a more precise, although still approximate, understanding. Before embarking on this task the possible sources of error are examined in determining the $\Delta\omega_T^A$ values. The extrapolation of $\Delta\omega_i|_V$ to 0 K to give $\Delta\omega_0^A$ is obviously one source of error although for CsNiCl_3 the portions of the curves above 150 K can be seen, in figure 7:9, to be virtually linear. Looking at equation (16) $\Delta\omega_i|_P$ is known to better than 0.5 cm^{-1} but $\Delta\omega_i|_T$ term (iii) involves perhaps the biggest approximation; that is the relationships between volume (shape), and temperature, and frequency and pressure at 300 K is considered to be approximately that at temperatures between 0 and 300 K, or more simply, γ_i the Gruneisen parameter is assumed to be the same at 0 and 300 K. Fortunately Lowndes (1971, 1976) was able to show this to be "an adequate approximation" by determination of γ_i at low temperature for the alkali halides. This was not technically possible for CsNiCl_3 as the compressibility could not be determined by X-rays at low temperature although the pressure dependence of frequency could. In the light of Lowndes' work the error is taken to be better than $\pm 5\%$ with the hope that technical

development will allow determination of γ_i at low temperature and hence the facility to check this approximation.

Lowndes (1976) was able to show by reference to earlier work, (Maraududin and Fien (1962) and Cowley (1963)), that theoretically $\Delta\omega_T^A$ is composed of frequency independent and frequency dependent parts, i.e. for the zone centre phonons

$$\Delta\omega_T^A(0,j,j^1,\Omega) = \Delta\omega_T^A(0,j,j^1) + \bar{\Delta}\omega_T^A(0,j,j^1,\Omega)$$

where $\Delta\omega_T^A(0,j,j^1)$ for the alkali halides is dominated by a first order quartic term with about 10% of a second order quartic term, whilst $\bar{\Delta}\omega_T^A(0,j,j^1,\Omega)$ is dominated by a second order cubic term with up to 30% of the second order quartic term. That is,

$$\Delta^A(0,j,j^1) = \Delta^4(0,j,j^1) + \Delta^8(0,j,j^1)$$

$$\Delta^A(0,j,j^1,\Omega) = \Delta^6(0,j,j^1,\Omega) + \Delta^8(0,j,j^1,\Omega)$$

where Δ^4 = first order quartic, Δ^8 = second order quartic and Δ^6 = second order cubic terms. Each of these terms is derived from an equation involving occupation numbers and anharmonic force constants. Dividing $\Delta\omega_T^A$ in this way, Lowndes (1976) was able to show (knowing the harmonic frequency and the "Fourier transformed anharmonic force constants" throughout the Brillouin zone for the alkali halides) that the above division of $\Delta\omega_T^A$ is genuine and the theoretical values reasonably fit those of experiment.

It is however impossible to divide $\Delta\omega_T^A$ up in this way for CsNiCl_3 as all the data are not known but it can be seen that $\Delta\omega_T^A$ is, in general, dependent on first and second order quartic terms

and a second order cubic term. Cubic terms are negative and quartic terms may be either positive or negative (as already stated). The data of table 5 reveal that nearly all the modes at 300 K are dominated by quartic terms, that is, $\Delta\omega_T^A$ is positive with the exception of $\Delta\omega_T^A$ for the $E_{1u}(258)$ which becomes negative at approximately 300 K. This is indicative of either a change of sign of the quartic terms or dominance of the cubic terms for the $E_{1u}(258)$. There are two other trends; the first is those modes which begin with a negative $\Delta\omega_T^A$, which changes sign at around 150 K ($A_{2u}(54)$, $E_{1u}(78)$ and $E_{1u}(178)$) indicating low temperature dominance of either negative cubic or quartic terms, and the second is those modes which begin positive and stay positive, dominated by quartic terms ($E_{2g}(58)$, $E_{1g}/E_{2g}(143)$, $E_{2g}(196)$, $A_{2u}(205)$ and $A_{1g}(267)$). It is interesting to note that Lowndes (1976) found for CsBr and CsCl that $\Delta\omega_T^A$ (for the i.r. active lattice mode) in fact began negative at 0 K and then became positive. This is in good agreement with the results for the $A_{2u}(54)$, $E_{1u}(78)$ and $E_{1u}(178)$ for CsNiCl_3 which are by and large the i.r. lattice modes and the ones which give rise to the Debye characteristic temperature, see Plendl (1969). These results indicate that both cubic and quartic terms can be found in the thermal dependence of the internal and external vibrational modes; this is in strong disagreement with the work of Gervais and co-workers.

7.4 Summary

An introduction to a theory for treating anharmonicity is

given and the particular application to CsNiCl_3 studied. The results show that a greater understanding of solids is possible by extending the power series past the quadratic harmonic term to include first and second order cubic and quartic anharmonic terms. The possibility of errors is also discussed and a better calculation could be made by knowledge of the temperature dependence of frequency if we extended the study of γ_i , the Gruneisen parameter from room temperature to lower temperatures.

References;

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APPENDICES

COMPUTER PROGRAMS

APPENDIX 1

(i) The inverse fourier transform program used to compute all the far-i.r. spectra given in this thesis. The program is called MIRROR.

PROGRAM MIRROR(INPUT,OUTPJT,TAPE8,TAPE6,TAPE3,TAPE7=INPUT,TAPE2=OUTPUT,TAPE1=INPUT)

SUMMARY OF FUNCTION OF PROGRAM

THIS PROGRAMME READS IN DIGITISED INTERFEROGRAMS AND PERFORMS THE INVERSE FOURIER TRANSFORMS
THERE ARE FACILITIES FOR AVERAGING AND RATIOING
COMPUTING DATA FROM SOLIDS AND LIQUIDS.
THE FINAL SPECTRA ARE AUTOMATICALLY RATIOED
THE MAIN CONTROL DATA BEING SUPPLIED BY THE USER

HISTORY

INITIAL VERSION D.W.WADDINGTON. LEICESTER UNIVERSITY OCTOBER 1974
UPDATED AND MODIFIED CONTINUOUSLY UPTO APRIL 1977. R.APPLEBY.

MODIFICATIONS

A ROUTINE TO COMPUTE ALPHA FROM SOLUTION SPECTRA.
SUBROUTINE LIQUID.
A SPIKE EDITING ROUTINE WAS ADDED
SUBROUTINE SPKED
A GAIN RATIO FUDGING ROUTINE WAS ADDED.
SUBROUTINE FUDGE.
A ROUTINE TO PLOT AT THE PLOTTER THE UNRATIOED SPECTRA WAS ADDED
SUBROUTINE PLOTTA.
SEVERAL ROUTINES WERE DEVELOPED AND MODIFIED.

DIMENSION W(300),RR(300),RS(300),RB(300),TR1(1024),TI1(1024),
TR2(1024),TI2(1024),Z(2500),CS(260)
REAL IW,L,INTEGR,PUNCH,P
INTEGER S,Q,H,Y,FS,GRAPH,CARDS,T,R,TAPE,COUNT,N1,N2,X,AVE,PKS

FILES USED

TAPE7=INPUT CARD READER
TAPE2=OUTPUT LINEPRINTER
TAPE8 DATA IS INPUT ON THIS FILE FROM THE PAPER TAPE READER
TAPE3 DATA IS OUTPUT ON THIS FILE FOR PLOTTING.
TAPE5 WORKFILE

CALLS

THIS PROGRAM CALLS THE FOLLOWING ROUTINES.

APODISE
DOUT
FFT
FUDGE
INTAPE
LINPR
LIQUID
PLOTTA
PRCARD
TITLE
SCALE
SET
SPKED

SUMMARY OF INPUT DATA

H=EXPERIMENT NUMBER (I)
Q=RUN NUMBER (I)
2N=NUMBER OF POINTS TO BE TRANSFORMED (I)
IW=INITIAL WAVENUMBER REQUIRED (R)
FW=FINAL WAVENUMBER REQUIRED (R)
P=OUT-OFF WAVENUMBER (I)
GB=BACKGROUND GAIN (VOLTAGE RATIO)
GS=SAMPLE GAIN(VOLTAGE RATIO)
Y=NUMBER OF BACKGROUND TAPES
X=NUMBER OF SAMPLE TAPES(I)
NSTART: THE GRAND MAXM MUST LIE IN THE FIRST NSTART+1 POINTS
IF GRAPH=0 NO MODULUS PRINTOUT IS GIVEN
IF CARDS NON ZERO FINAL SPECTRUM IS PUNCHED
AVE=1 SPECTRA NOT AVERAGED.AVE=1 THEN FINAL SPECTRA AVERAGED
SY=SAMPLE INTERVAL
ILIQ CONTROL PARAMETER IF 1 PROGRAM GIVES OUTPUT IN TERMS OF ALPHA
IUNRAT IS A CONTROL PARAMETER IF 1 OUTPUT UNRATIOED SPECTRA ON
THE PLOTTER.
PKS IF 1 SPIKE EDITING SUBROUTINE CALLED.


```

C      IC IF 1 GAIN RATIO FUDGING CALLED OR IF 2 ALPHA SCALED FOR LIQID.
C      DIGITISED INTERFEROGRAMS MUST BE INPUT IN THE ORDER BACKGROUNDS
C      (1 TO Y)
C      FIRST SAMPLE(1TOX) SECOND
C
C      READ(7,7)H,Q,GB,GS,X,Y,ILIQ,N,IW,FW,P,NSTART,GRAPH,CARDS,AVE,SY,
C      1IUNRAT,PKS,IC
C      7  FORMAT(I4,2X,I4,2X,F6.0,2X,F6.0,2X,I2,2X,I2,2X,I2/I4,2X,F4.0,2X,F5
C      1.0,2X,F4.0,2X,I4,2X,I1,2X,I1,2X,I1,2X,F3.0,2X,I1,2X,I1,2X,I1)
C      PUNCH,RANGE,INS,FS,ALL USED BY THE PROGRAMME AS REQUIRED CONSTANTS
C      J=X+Y
C      SI=SY/10
C      PUNCH=SI/P
C      RANGE=2*N*PUNCH
C      INS=INT(IW*RANGE)
C      FS=INT(FW*RANGE)
C      M=NUMBER OF OUTPUT POINTS
C      M=FS-INS+1
C      G=GS/GB
C      G IS THE GAIN RATIO
C      CALL TITLE(H,Q,N,P,M)
C      RS ARRAY CONTAINING SAMPLE DATA FOR AVERAGING
C      RB ARRAY CONTAINING BACKGROUNO DATA
C      THIS LOOP CLEARS RS(S) AND RB(S)
C      DO 1 S=1,M
C      RS(S)=J.0
C      RB(S)=J.0
C      1  WS(S)=(INS+S-1)/RANGE
C      WS(S) IS REQUIRED BY SUBROUTINE LINPR FOR THE RANGE AND INCREMENT
C      TAPE=J
C      TAPE IS USED TO KEEP TRACK OF EACH RUN AND INCREMENTED BY 1
C      FOR EACH TAPE COMPLETED
C      2  TAPE=TAPE+1
C      IF (TAPE.GT.(X+Y)) GOTO 33
C      IF (TAPE.LE.Y) GOTO 3
C      T IS ALSO A CONTROL PAREMETER T=4 FOR BG T=3 FOR SAMPLE T=5 FOR
C      RATIONG SPECTRA
C      T=3
C      GOTO 4
C      3  T=4
C      4  N1=2*NSTART
C      N2=2*N
C      THE FOLLOWING SUBROUTINES PLOT THE UNRATIOED SPECTRA
C      CALL INTAPE(N1,Z,F)
C      CALL SET(NSTART,N,TR1,Z,N2,N1,MAX)
C      IF (PKS) 52,50,52
C      52 READ(7,51)PKS
C      51 FORMAT(I1)
C      CALL SPKED(SY,MAX,3.0,TR1,N)
C      53 CALL APOOIZE(TR1,N2,N)
C      CALL FFT(N2,TR1,II1,TR2,II2,CS,RR,INS,M)
C      IF (GRAPH) 5,6,5
C      5  CALL DOUT(T,TAPE,G,AVE)
C      CALL SCALE(RR,M,FACTOR,YMIN)
C      IF (IUNRAT.EQ.0) GOTO 60
C      IF (AVE.EQ.1) GOTO 63
C      K1=J+X
C      CALL PLOTTA(W,RR,FACTOR,FW,IW,M,K1,YMIN)
C      GOTO 60
C      63 K1=J+1
C      CALL PLOTTA(W,RR,FACTOR,FW,IW,M,K1,YMIN)
C      60 CALL LINPR(W,RR,M,YMIN,FACTOR,1)
C      5  CONTINUE
C      IF (T.EQ.3) GOTO 13
C      IF (T.EQ.4) GOTO 20
C      GOTO 2
C      13 IF(AVE.EQ.1) GOTO 35
C      DO 11 S=1,M
C      11 RS(S)=RS(S)+RR(S)
C      GOTO 2
C      20 DO 22 S=1,M
C      22 RB(S)=RB(S)+RR(S)
C      GOTO 2
C      35 WRITE(6,101)(RR(S),S=1,M)
C      101 FORMAT(6F10.6)
C      GOTO 2
C      33 IF (AVE.EQ.1) J=Y+1
C      T=5
C      K1=Y+1

```

SUBROUTINE STINSTOP (N, I, J, I1, I2, NMAX)
THIS SUBROUTINE FINDS THE MAX AND TAKES N POINTS EACH SIDE
OF THE AVERAGE POINT (SUM) AND SUBTRACTS THIS FROM ALL THE
OTHERS

WRITTEN BY B. SCHWARTZ FOR DOCUMENTED AND DEVELOPED BY
R. APPELOV. CALIFORNIA UNIVERSITY 7/22/75

PARAMETERS

STOP MAX MUST BE IN THE FIRST NSTOP+1 POINTS

MAX NUMBER OF POINTS TO BE TRANSFORMED

ARRAY INTO WHICH FINAL DATA IS PUT

ARRAY CONTAINING DATA

1 DIMENSION OF 1

2 DIMENSION OF 2

MAX POINTS MAX POINT

1 DIMENSION 1111, 1121

1111 PRECISION SUM

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SUBROUTINE LIQUID(RS,M,W)

THIS SUBROUTINE ENABLES THE USER TO PROCESS DATA COLLECTED ON
SOLUTION SPECTRA AND OUTPUTS THE RATIOED SPECTRUM IN A
IN TERMS OF ALPHA

R.APPLEBY. 26/11/76.

INPUT

RS(I) ARRAY CONTAINING DATA.

M NO OF OUTPUT POINTS

G GAIN RATIO

FROM CARDS

C CONCENTRATION IN MOLES/LT

AL PATH LENGTH IN CMS.

DIMENSION RS(M),W(M)

FINT=0.0

READ(7,100) C,AL

F=1/(C*AL)

DO 10 I=1,M

RS(I)=RS(I)*F*0.01

FINT=FINT+RS(I)

WRITE(2,101)AL,C,FINT

FORMAT(2F10.0)

101 FORMAT(54H ABSORPTION COEFFICIENT CALCULATED FROM $-1/(C*L).GS/GB$ /M

115H CELL LENGTH = ,F8.5,4H CMS/16H CONCENTRATION = ,F6.4,3H M./25H

2 INTEGRATED ABSORPTION = ,E12.5/)

RETURN

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SUBROUTINE SPKED(SI,XMAX,AVE,DAT,N)

SPIKE EDITING SUBROUTINE
WRITTEN BY R. APPLEBY. 20/6/76.

DIMENSION DAT(N)

INTEGER X,XMAX,P,P1

THIS SUBROUTINE IS DESIGNED TO REMOVE 3 POINTS AT A DISTANCE
OF X FROM XMAX. X IS CALCULATED FROM THE SAMPLE INTERVAL
AND THE FREQUENCY OF THE INTERFERENCE FRINGE ETC,
PARAMETERS.

SI = SAMPLE INTERVAL.

XMAX = MAX VALUE OF THE INTERFEROGRAM.

AVE = THE AVERAGE VALUE OF A POINT.

DAT ARRAY CONTAINING THE DATA.

N = DIMENSION OF DAT.

FREQ = FREQUENCY SEPERATION OF FRINGES.

READ(7,100)FREQ

X=1.024/(FREQ*SI)

X IS THE NUMBER OF POINTS FROM XMAX OF SPIKE..
LOOP TO REMOVE SPIKE.

DO 10 I=1,3

P=XMAX-X-1+I

DAT(P)=AVE

P1=XMAX+X-1+I

DAT(P1)=AVE

CONTINUE

WRITE(2,200) X,XMAX,AVE,DAT

FORMAT(F8.2)

FORMAT(I5,I5,F12.6/6F12.6)

RETURN

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MIR 1000

SUBROUTINE RATIO(RS,RB,IX,IY,G,M,AVE)
THIS SUBROUTINE RATIOS THE SPECTRA HELD IN RS AND RB
PUTTING THE RESULT INTO RS
PARAMETERS

RS=ARRAY CONTAINING SAMPLE SPECTRUM
RB=ARRAY CONTAINING BACKGROUND SPECTRUM
IX=NUMBER OF SAMPLE TAPES
IY=NUMBER OF BACKGROUND TAPES
G=RELATIVE GAIN SAMPLE TO BACKGROUND
M=DIMENSION OF ARRAYS RS AND RB
AVE=CONTROL NUMBER FOR MAIN PROGRAM
SPECTRA WILL BE PLOTTED UNAVERAGED. IF AVE=0 THE FINAL
SPECTRUM WILL BE PLOTTED OF ALL THE SAMPLE RUNS.

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DIMENSION RS(M),RB(M)
AB=1.0E-10
THIS LINE SCALES THE FINAL PLOT FOR WEIGHTING OF X SAMPLES AND YBG
FACTOR=IX*G/IY
IF (AVE.EQ.0) GOTO 5
GOTO 7
FACTOR=G BECAUSE WE ARE RATIONING IBG AND ISAMPLE (AVE=0)
5 FACTOR=G
GOTO 8
7 FACTOR=IX*G/IY
8 CONTINUE
IF RS(1) OR RB(1) ARE LESS THAN 1.0×10^{-10} THEY ARE TAKEN AS ZERO
IF (RS(1).LT.AB.OR.RB(1).LT.AB) GOTO 2
RS(1)=(RS(1)*100.0)/(FACTOR*RB(1))
10 CONTINUE
DO 1 I=2,M
IF (RS(I).LT.AB.OR.RB(I).LT.AB) GOTO 3
IF RS(I) OR RB(I) ARE LESS THAN 1.0×10^{-10} THEY ARE TAKEN AS
RS(I-1) OR RB(I-1)
THIS IS A PRECAUTION TO REMOVE DUD POINTS
RS(I)=(RS(I)*100.0)/(FACTOR*RB(I))
THIS LOOP SUMS ALL RS(I) INTO FINI
1 CONTINUE
GOTO 4
2 RS(1)=0.0
GOTO 1
3 RS(I)=RS(I-1)
GOTO 1
4 RETURN
END

MIRCC302
MIRCC303
MIRCC304
MIRCC305
MIRCC306
MIRCC307
MIRCC308
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MIRCC310
MIRCC311
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MIRCC348
MIRCC349
MIRCC350

SUBROUTINE DOUT(J,ITAPE,G,AVE)
THIS SUBROUTINE WRITES THE TITLES TO THE PLOTS
IF UNRATIOED -----WRITES TAPE NUMBER AND (IF J=3) SAMPLE MODULUS:
IF UNRATIOED -----WRITES TAPE NUMBER AND (IF 4=4) BACKGROUND
MODULUS:
IF RATIOED AND AVERAGED WRITES FORMAT 103

WRITTEN BY D. W WADDINGTON AND IMPLEMENTED BY R. APPLEBY. 7/2/75.

IF RATIOED AND UNAVERAGED WRITES DORMAT 104
PARAMETERS

J=CONTROL-PARAMETER

J=3 SAMPLE DATA

J=4 BACKGROUND DATA

J=5 RATIOED SPECTRA

G=GAIN RATIO

AVE=CONTROLS AVERAGING FACILITIES

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100 FORMAT(///13H TAPE NUMBER ,I2//)
101 FORMAT(20H BACKGROUND MODULUS://)
102 FORMAT(16H SAMPLE MODULUS://)

I=J-4

IF (I) 1,2,3

1 WRITE(2,100) ITAPE

WRITE(2,102)

RETURN

2 WRITE(2,100) ITAPE

WRITE(2,101)

RETURN

3 WRITE(2,103) G

103 FORMAT(///14H GAIN RATIO = ,F8.4//)

RETURN

END

MIRCO3551
MIRCO3552
MIRCO3553
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MIRCO3584
MIRCO3585

DIMENSION IBUFFER(10), KHEAD(10), XINI(10), YINI(10)

DATA KHEAD/10H MOD 10H ALP 10H TRANS,

DATA IBUFFER/10H * 10H 10H

IN=10H

OCTAL CONSTANTS.....INTAR CONTAINS A * RIGHT JUSTIFIED ZERO FI

LL0.
ISPACE CONTAINS A * F.R.I. ZERO FILLED.

INTAR=479
ISPACE=555

GET THE DEVICE NUMBER.

LP=

GET THE NUMBER OF CHARACTERS PER INTEGER WORD.

NCHAR=10

END OF INITIALIZATION SECTION.

SELECT THE REQUIRED HEADINGS AND PRINT WITH THE TOP OF THE

MODULUS.

WRITE(1P,11)ITAP,INTAR,NP)

WRITE(1P,11)ISPACE

CLEAR THE AREA-WAIT EJECT.

WRITE(1P,11)

EXAMINE EACH ELEMENT OF Y IN TURN AND PLOT THE RELEVANT POINT.

DO 20 I=1,NP

EXPRESS EACH ELEMENT OF Y IN TERMS OF INCREMENTS FROM PRIM. THIS GIVES

THE REQUIRED POSITION.

ADIM=I*Y(I)-Y(1)+1

THIS VALUE MUST NOW BE OFFSET BECAUSE THE FIRST 3 LOCATIONS
OF THE BUFFER CONTAIN * WHICH FORMS PART OF A BORDER.

ICHA=INT(ADIM/INCH)

THE REQUIRED POSITION IS THE ICH+TH LOCATION OF
THE ARRAY ICH+1. THIS MUST NOW BE EXPRESSED IN TERMS OF WORDS

AND CHARACTERS.

IWORD=0
5 ICHAR=ICHAR-NCHARS
IWORD=IWORD+1
IF(ICHAR)10,10,5

10 ICHAR=ICHAR+NCHARS

THE REQUIRED POSITION IS THE ICHAR TH CHARACTER OF WORD
IBUFFR(IWORD).

PLACE THE CHARACTER '*' IN THE RIGHT POSITION.
CALL PUTCH(IBUFFR(IWORD),ISTAR,ICHAR)

PRINT THE BUFFER.
WRITE(LP,102)IBUFFR,X(I),Y(I)

CLEAR THE BUFFER.
CALL PUTCH(IBUFFR(IWORD),ISPACE,ICHAR)

23 CONTINUE

FINISH OFF THE BORDER.
WRITE(LP,101)IBUFFR
WRITE(LP,100)IW,KHEAD(NF)

FORMAT STATEMENTS.
100 FORMAT(1H,2X,96(1H+),2X,2A10)
101 FORMAT(1H,10A10)
102 FORMAT(1H,10A10,F7.2,2X,F9.5)
103 FORMAT(1HQ)
104 FORMAT(1HR)

RESET THE AUTO PAGE EJECT.
WRITE(LP,104)

RETURN
END

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MIR00468
MIR00469
MIR00470
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MIR01000

SUBROUTINE PCARD(X,Y,M,NF,FW,WI,K)
THIS SUBROUTINE WILL GIVE PUNCHED CARD OUTPUT OF THE FINAL SPECTRUM
IF CARDS NOT EQUAL 0

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PARAMETERS

X FINAL WAVENUMBER VALUE
Y FINAL TRANSMISSION VALUE
M DIMENSION OF X AND Y
NF CONTROLS X OR Y PRINTOUT
DIMENSION X(M), Y(M)

100 FORMAT(6F9.3)
101 FORMAT(6F10.5)
102 FORMAT(F5.1,2X,F4.0,2X,I3,2X,I2,60X)
WRITE(3,102) FW,WI,M,K
WRITE(3,100) X
IF(NF-1) 1,2,2
1 WRITE(3,101) Y
GOTO 3
2 WRITE(3,100) Y
3 RETURN
END

MIRCO 06
MIRCO 07
MIRCO 08
MIRCO 09
MIRCO 10
MIRCO 11
MIRCO 12
MIRCO 13
MIRCO 14
MIRCO 15
MIRCO 16
MIRCO 17
MIRCO 18
MIRCO 19
MIRCO 20
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MIRCO 28
MIRCO 29
MIRCO 30
MIRCO 31

SUBROUTINE FFT(N,TR1,TI1,TR2,TI2,CS,AMOD,IS,M)
THIS SUBROUTINE PERFORMS THE INVERSE FOURIER COSINE TRANSFORM

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PARAMETERS

N=HALF NUMBER OF POINTS TO BE TRANSFORMED
TR1,TR2,TI1,TI2,ARRAYS DIMENSIONED N USED IN MANIPULATING DATA
CS ARRAY USED TO CONTAIN THE COSINE PART OF THE TRANSFORM
AMOD IS THE FINAL MODULUS OF EACH POINT
IS CONSTANT CALCULATED IN MAIN PROGRAMME
M=NUMBER OF OUTPUT POINTS

DIMENSION TR1(N),TI1(N),TR2(N),TI2(N),CS(N),AMOD(M)
DOUBLE PRECISION AI,AR,BI,BR,WI,WR,PI,F,F1

LOGICAL SW

SW=.TRUE.

NH=N/2

NQ=NH/2

PI=3.14159265358979

AI=NH

DO 1 I=1,N

TR1(I)=TR1(I)/AI

TI1(I)=0.0

F=PI/AI

DO 2 I=1,NQ

F1=(I-1)*F

CS(I)=DCOS(F1)

CS(NQ+1)=0.0

IH=NH

J=0

JK=(J/IH)*IH

J=J+1

L=J+NH

IP=J+JK

IQ=IP+IH

JQ=JK-NQ

IF (JQ) 21,21,22

21 WR=CS(JK+1)

WI=CS(1-JQ)

GOTO 23

22 WR=-CS(NH-JK+1)

WI=CS(JQ+1)

23 IF (.NOT. SW) GOTO 24

AR=TR1(IP)

AI=TI1(IP)

BR=TR1(IQ)*WR-TI1(IQ)*WI

BI=TR1(IQ)*WI+TI1(IQ)*WR

TR2(J)=AR+BR

TI2(J)=AI+BI

TR2(L)=AR-BR

TI2(L)=AI-BI

GOTO 25

24 AR=TR2(IP)

AI=TI2(IP)

BR=TR2(IQ)*WR-TI2(IQ)*WI

BI=TR2(IQ)*WI+TI2(IQ)*WR

TR1(J)=AR+BR

TI1(J)=AI+BI

TR1(L)=AR-BR

TI1(L)=AI-BI

25 IF (J-NH) 3,4,4

3 IH=IH/2

SW=.NOT. SW

IF (IH) 20,5,20

5 IF (SW) GOTO 6

DO 7 I=1,N

TR1(I)=TR2(I)

7 TI1(I)=TI2(I)

6 TR1(1)=0.5*TR1(1)

TI1(1)=0.5*TI1(1)

J=IS

DO 8 I=1,M

J=J+1

X=TR1(J)

Y=TI1(J)

AMOD IS CALCULATED FROM THE COMPLEX NUMBER S X AND Y

8 AMOD(I)=SQRT(X*X+Y*Y)

RETURN

MIRCO 669
MIRCO 670
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MIRCO 674
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MIRCO 840
MIRCO 841
MIRCO 842
MIRCO 843
MIRCO 844
MIRCO 845
MIRCO 846
MIRCO 847
MIRCO 848
MIRCO 849

SUBROUTINE APODIZE(E,I1,N)
 THIS SUBROUTINE APODIZES THE DATA USING A FUNCTION SIN SQUARED
 A ZERO IS ENCOUNTERED

WRITTEN BY D.H.WADDINGTON DOCUMENTED AND DEVELOPED BY
 R.APPELBY. LEICESTER UNIVERSITY 7/2/75

PARAMETERS

THE ORDER OF INPUT POINTS
 IS STARTING FROM DIMENSION OF 1
 TOTAL NUMBER OF ARRAY ELEMENTS INPUT = (15)

CALL APODIZE(E,I1,N)
 E(I1) = 0.0

SUBROUTINE APODIZE(E,I1,N)
 THIS SUBROUTINE APODIZES THE DATA USING A FUNCTION SIN SQUARED

WRITTEN BY D.H.WADDINGTON DOCUMENTED AND DEVELOPED BY
 R.APPELBY. LEICESTER UNIVERSITY 7/2/75

PARAMETERS

N=HALF NUMBER OF POINTS TO BE TRANSFORMED

E=ARRAY CONTAINING DATA

I1=DIMENSION OF E

DIMENSION E(I1)

DOUBLE PRECISION PI,F,X

PI=3.14159265358979

F=PI/(2*N)

J=-1

DO 1 I=1,I1

J=J+1

X=DSIN(J*F)

1 E(I)=E(I)*X*X

RETURN

END

MIR 0.81
 MIR 0.80
 MIR 0.83
 MIR 0.84
 MIR 0.85
 MIR 0.86
 MIR 0.87
 MIR 0.88
 MIR 0.89
 MIR 0.90
 MIR 0.91
 MIR 0.92
 MIR 0.93
 MIR 0.94
 MIR 0.95
 MIR 0.96
 MIR 0.97
 MIR 0.98
 MIR 0.99
 MIR 1.00
 MIR 1.01
 MIR 1.02

```
SUBROUTINE INTAPE(N,Z,IC)
THIS SUBROUTINE  READS IN DATA 10F10.0
UNTIL A ZERO IS ENCOUNTERED
```

----- WRITTEN BY D.W. WADDINGTON DOCUMENTED AND DEVELOPED BY
R. APPELBY. LEICESTER UNIVERSITY 7/2/75

PARAMETERS

```

100 IC=NUMBER OF INPUT POINTS
101 N=2XNSTART(=2000) DIMENSION OF Z
102 DIMENSION Z(N)
103 FORMAT(40H TOTAL NUMBER OF ARRAY ELEMENTS INPUT = ,I5)
104 FORMAT(10F10.0)
105 IC=1
106 1 KK=IC+9
107 READ(8,101) (Z(J),J=IC,KK)
108 DO 5 J=IC, KK
109 IF (Z(J)) 2,2,5
110 5 CONTINUE
111 IC=IC+10
112 GOTO 1
113 2 IC=IC-1
114 WRITE(2,100) IC
115 RETURN
116 END

```


SUBROUTINE FUDGE(RS,IC,M)

THIS SUBROUTINE CAN SCALE THE FINAL PLOT.

WRITTEN BY R.APPLEBY. 3/12/76.

PARAMETERS.

FACTOR SCALING FACTOR READ FROM CARDS OR CALCULATED.

RS ARRAY CONTAINING DATA.

M DIMENSION OF RS(NO OF OUTPUT POINTS)

IC CONTROL PARAMETER IF 0 NO SCALING.

IF 1 SCALE PLOT TO FILL PAGE.

IF 2 READ SCALING FACTOR(F10.6)

DIMENSION RS(M)

IF (IC.EQ.0) GOTO 10

N=M-1

RMAX=0.0

RMIN=500.0

DO 20 I=1,N

J=I+1

IF (RS(I)-RS(J)) 30,30,40

20 CONTINUE

GOTO 50

30 IF (RS(I).LT.RMIN) RMIN=RS(I)

GOTO 20

40 IF (RS(I).GT.RMAX) RMAX=RS(I)

GOTO 20

50 SPAN=RMAX-RMIN

FACTOR=100/SPAN

IF (IC.EQ.1) GOTO 80

70 READ(7,200)FACTOR

80 DO 60 I=1,M

RS(I)=(RS(I)-RMIN)*FACTOR

WRITE(2,100)FACTOR

100 FORMAT(3H PLOT SCALED,SCALING FACTOR = ,F10.5)

200 FORMAT(F10.6)

10 RETURN

END

MIR0731
MIR0732
MIR0733
MIR0734
MIR0735
MIR0736
MIR0737
MIR0738
MIR0739
MIR0740
MIR0741
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MIR0743
MIR0744
MIR0745
MIR0746
MIR0747
MIR0748
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MIR0750
MIR0751
MIR0752
MIR0753
MIR0754
MIR0755
MIR0756
MIR0757
MIR0758
MIR0759
MIR0760
MIR0761
MIR0762
MIR0763
MIR0764
MIR0765
MIR0766
MIR0767
MIR0768
MIR0769

SUBROUTINE PLOTTA(W,RR,FACTOR,FW,WI,M,K,YMIN)
PLOTS UNRATIOED SPECTRA AT PLOTTER.

R. APPLEBY. 26/11/76.

```

DIMENSION RR(M),W(M),XX(500)
PARAMETERS.

```

M NO OF DUPUT POINTS.

FW FINAL WAVENUMBER.

WI INITIAL WAVENUMBER.

K NO OF PLOTS.

RR ARRAY CONTAINING DATA.

W ARRAY CONTAINING WAVENUMBERS.

```
DO 10 I=1,M
```

```
13 XX(I)=(RR(I)-YMIN)*FACTOR
```

```
WRITE (3, 110) FW, WI, M, K
```

```
WRITE (3,100) (W(I),I=1,M)
```

```
WRITE (3,100) (XX(I), I=1,M)
```

103 FORMAT(6F9.3)

```
110 FORMAT(F5.0,2X,F4.0,2X,I3,2X,I2,2X,58X)
```

PORTFOLIO RETURN

END

MIRG7770
MIRG7771
MIRG7772
MIRG7773
MIRG7774
MIRG7775
MIRG7776
MIRG7777
MIRG7778
MIRG7779
MIRG7800
MIRG7811
MIRG7822
MIRG7833
MIRG7844
MIRG7855
MIRG7866
MIRG7877
MIRG7888
MIRG7899
MIRG7900
MIRG7911
MIRG7922

SUBROUTINE PUTCH(IW,IC,ICH)

 MACHINE DEPENDENT SUBROUTINE CDC VERSION

AUTHOR G.G. TOLTON UNIVERSITY OF LEICESTER COMPUTER LAB.
 SEPTEMBER 1974.

PLACES A CHARACTER IC IN POSITION ICH OF WORD IW

IC CONTAINS A SINGLE CHAR. RIGHT JUSTIFIED ZERO FILLED.
 ICH THE REQUIRED POSITION IN IW (1 TO 10 FROM LEFT)

E.G. IF THE VARIABLE ICHAR=10HCHARACTERS AND IT WAS
 REQUIRED TO REPLACE THE P WITH T THEN

CALL PUTCH(ICCHAR,LETTER,7)

WHERE LETTER CONTAINS THE CHARACTER T RIGHT
 JUSTIFIED ZERO FILLED, WOULD RETURN ICHAR AS
 10HCHARACTERS.

NOTE... IC RETURNS UNMUTILATED.

SEE CDC FORTRAN EXTENDED VERSION 4 REFERENCE MANUAL FOR
 DETAILS OF FUNCTIONS SHIFT AND MASK. PART I-6-4.

ITEMP1=MASK(54)
 M=6*(10-ICH)
 IK=SHIFT(IC,M)
 ITEMP1=SHIFT(ITEMP1,M)
 ITEMP2=IW.AND.ITEMP1
 IW=ITEMP2.OR.IK

RETURN
 END

MI 6793
 MI 6794
 MI 6795
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 MI 6999
 MI 7000

(ii) The program used to plot all the far-i.r. spectra given in this thesis produced by MIRROR called PLOTTER.


```
PROGRAM PLOTTER(INPUT,OUTPUT,TAPE1,TAPE2=OUTPUT)
```

```
THIS PROGRAM PLOTS DATA PRODUCE BY THE FOURIER TRANSFORM
```

```
PROGRAM MIRROR.
```

```
DIMENSION X(500),Y(500)
```

```
WRITTEN BY R APPLEBY LEICESTER UNIVERSITY 22/4/75
```

PARAMETERS

```
M=NUMBER OF OUTPUT POINTS
```

```
FW=FINAL WAVENUMBER
```

```
WI=INITIAL WAVENUMBER
```

```
K=NO. OF DATA SETS.
```

FILES USED

```
INPUT CARD READER
```

```
OUTPUT=TAPE2 LINE PRINTER
```

```
TAPE1 DATA FILE OUTPUT BY MIRROR
```

```
A FILE CONTAINING THE PLOT CALLED GRIDFL IS CREATED BUT IS NOT  
SPECIFIED IN THE PROGRAM
```

CALLS

```
A SUBSET OF FORTRAN PLOTTING ROUTINES CALLED CGHOST AVAILABLE AT  
LEICESTER ARE USED IN THIS PROGRAM.
```

```
SUBROUTINES CALLED
```

```
PLOTTER, READER.
```

```
THE FOLLOWING SUBROUTINES ARE CALLED FROM CGHOST.
```

```
PAPER(1),GPSTOP,GREND,PSPACE,MAP,BORDER,BFOKEN,GRATIC,FULL,  
NSCURV,AXES,CTRSET,CTRMAG,READCS,POSITN,TYPECS,CTRORI,FRAME
```

```
READ(1,3)FW,WI,M,K
```

```
REWIND 1
```

```
3 FORMAT(F5.0,2X,F4.0,2X,I3,2X,I2,60X)
```

```
CALL PAPER(1)
```

```
CALL GPSTOP(11)
```

```
SETS FRAME LIMIT AT 11 FRAMES.
```

```
SWITCHES ON THE PLOTTER
```

```
DO 6 N=1,K
```

```
CALL READER(X,Y,M,FW,WI)
```

```
CALL PLOT(X,Y,M,FW,WI)
```

```
5 CONTINUE
```

```
CALL GREND
```

```
SWITCHES OFF THE PLOTTER
```

```
STOP
```

```
END
```

```
PLO00001  
PLO00002  
PLO00003  
PLO00004  
PLO00005  
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PLO00007  
PLO00008  
PLO00009  
PLO00010  
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PLO00050
```



```

SUBROUTINE PLOT(X,M,Y,M,FW,WI)
THIS SUBROUTINE PLOTS THE DATA READ IN BY READER.

  WRITTEN BY R APPLEBY LEICESTER UNIVERSITY 22/4/75

  DIMENSION X(M),Y(M),ITITLE(8),IX(2),IY(2)
  A IS A CONSTANT USED TO CHOOSE PSPACE FOR THE INTERVAL IN
  HAVENUMBERS / INCH
  A=(FW-WI)/40+1.0
  D=ASCALING FACTOR USED IN PSPACE
  D=2.54/30.0
  S CONTROLS THE POSITION FOR TYPING THE AXES HEADINGS
  S=WI+7.0
  CALL PSPACE(D,A*D,D,11.0*D)
  SET UP THE AREA OF PAPER TO BE USED
  CALL MAP(WI,FW,0.0,100.0)
  DEFINES THE SCALES
  CALL BORDER
  DRAWS A BORDER
  CALL BROKEN(10,10,10,10)
  CALL GRATIO
  DRAWS A BROKEN GRATIDULE THE COMPUTER CHOOSING THE POSITIONS
  CALL FULL
  REVERTS BACK TO FULL LINE
  CALL NSCURV(X,Y,1,M)
  JOINS THE POINTS HELD IN X,Y FITTING A CUBIC OVER 5 POINTS.
  CALL AXES
  AUTOMATICALLY ANNOTATES AXIS
  IX(1)=10HTRANSMISSI
  IX(2)=5HON % @
  SETS X AXIS HEADING
  IY(1)=10HFREQUENCY
  IY(2)=5H/C4 @
  SETS Y AXIS HEADING
  CALL CTRSET(5)
  CALL CTRMAG(10)
  USES CHARACTER SET 5
  CALL READCS(ITITLE)
  READS TITLE FROM CARDS
  CALL POSITN(S,97.0)
  CALL TYPECS(ITITLE,80)
  POSITIONS AND TYPES TITLE
  CALL POSITN(S,2.0)
  CALL TYPECS(IY,15)
  POSITIONS AND TYPES X AXIS HEADING
  CALL POSITN(S,60.0)
  CALL CTRORI(1.0)
  CALL TYPECS(IX,16)
  ROTATES AND TYPES Y AXIS HEADING
  CALL CTRORI(4.0)
  CALL FRAME
  MOVES ON TO NEXT FRAME
  RETURN
END

```

```

PLOC143
PLOC144
PLOC145
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PLOC1000

```

SUBROUTINE READER(X,Y,M,FW,WI)
 THIS SUBROUTINE READS DATA FOR PLOTTING WHICH HAS BEEN OUTPUT BY
 MIRROR AND CORRECTS ANY POINTS NOT BETWEEN 0 AND 100 PERCENT.

WRITTEN BY R APPLEBY LEICESTER UNIVERSITY 22/4/75

00000 C C	DIMENSION X(500),Y(500) READ(1,3)FW,WI,M 9 FORMAT(F5.0,2X,F4.0,2X,I3,64X) READ(1,10)(X(I),I=1,M) 10 FORMAT(6F9.3) READ(1,2)(Y(I),I=1,M) 2 FORMAT(6F9.3) THIS LOOP CONVERTS ALPHA TO PERCENTAGE TRANSMISSION AND CORRECTS ANY ERRORS DO 3 I=1,M IF(Y(I).GT.100.0) GOTO 4 IF(Y(I).LT.0.0) GOTO 5 GOTO 3 4 Y(I)=100.0 GOTO 3 5 Y(I)=0.0 3 CONTINUE RETURN END	PLOC102 PLOC103 PLOC104 PLOC105 PLOC106 PLOC107 PLOC108 PLOC109 PLOC110 PLOC111 PLOC112 PLOC113 PLOC114 PLOC115 PLOC116 PLOC117 PLOC118 PLOC119 PLOC120 PLOC121 PLOC122 PLOC123 PLOC124 PLOC125 PLOC126
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APPENDIX 2

(i) The program used to perform the analysis
on the temperature dependence of frequency.

The program is called ANHARM.

```

PROGRAM ANHARM(INPUT,OUTPUT,TAPE1=INPUT,TAPE2=OUTPUT)
DIMENSION T(20),V(20),V1(20),P(20),SKAP(20)
CALL DARRAY(20)
FUNCTION OF PROGRAM
-----

```

THIS PROGRAM HAS TWO MAIN FUNCTIONS

PART1

THE COMPRESSIBILITY AND VOLUME THERMAL EXPANSION ARE
CALCULATED FROM P,V,T DATA INPUT.

PART2

USING THE VARIABLES CALCULATED IN PART 1 THE RELATIONSHIP
BETWEEN FREQUENCY TEMPERATURE AND PRESSURE ARE ANALYSED.
(R.P.LOWHDES. PHYS.REV(3) 1971)

AUTHOR R.APPLEBY. 1977.

NOTE

----- THIS PROGRAM MAKES USE OF VOLUME AND DOESNT ACCOUNT
FOR THE SHAPE OF THE UNIT CELL.THERFORE P,V
AND V,T DATA SHOULD BE CHECKED FOR COINCIDENCE OF
VOLUME GIVEN CA ONE FIXED SIDE.

FILES USED

TAPE1=INPUT CARD READER
TAPE2=OUTPUT LINE PRINTER
A FILE CALLED GRIDFL CONTAINING PLOTS IS PRODUCED BUT NOT
SPECIFIED IN THE PROGRAM.

CALLS

A SUBSET OF FORTRAN PLOTTING ROUTINES IS CALLED AVAILABLE
AT LEICESTER UNDER THE NAME OF CGHOST.
PAPER(1),GPSTOP,GREND, CALLED FROM CGHOST.
VT,VP,ALP,ANH.

PARAMETERS

V VOLUME A CUBED
T TEMPERATURE K
N NUMBER OF V,T POINTS
P PRESSURE KBAR
V1 VOLUME A CUBED AT PRESSURE P
N1 NUMBER OF P,V1 POINTS
SKAP COMPRESSIBILITY
NMODES NUMBER OF MODES OF VIBRATION BEING COMPUTED

INITIALISE PLOTTER

```

CALL PAPER(1)
CALL OTRMAG(3)
READ(1,100)NIN
SET FRAME LIMIT
CALL GPSTOP(NIN)
100 FORMAT(I2)

```

```

CALL VT(V,T,H)
CALL ALP(V,T,N)
CALL VP(P,V1,N1,SKAP)

```

END PART 1

```

ANH00001
ANH00002
ANH00003
ANH00004
ANH00005
ANH00006
ANH00007
ANH00008
ANH00009
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ANH00100

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```
C
  READ(1,100)NMODES
  DO 10 I=1,NMODES
  WRITE(2,300)I
300  FORMAT(1H,1H,12H MODE NUMBER,1X,I2,1H,1H )
10  CALL ANH(V,T,N,P,V1,N1,SKAP)
    CALL GREND
    STOP
    END
```

```
ANH0066
ANH0067
ANH0068
ANH0069
ANH0070
ANH0071
ANH0072
ANH0073
ANH0074
```


SUBROUTINE VP(P,V,N,SKAP)
 COMMON A(20),B(20),C(20),D(20)
 A ROUTINE TO PLOT THE CHANGE IN COMPRESSIBILITY
 WITH PRESSURE. R.APPLEBY. 21 4 77

PARAMETERS

P PRESSURE KBAR
 V VOLUME A CUBED
 N NUMBER OF POINTS
 SKAP COMPRESSIBILITY AT PRESSURE P

CALLS

CALLS ROUTINES INDATA,FITFN,PLOT,DIFFUN.

DIMENSION P(20),V(20),V1(20),SKAP(20)
 DERVP=0.0
 CALL INDATA(P,V,N,C)
 ITITLE=10HVOL V PRES
 CALL FITFN(N,P,V,V1,1)
 CALL PLOT(P,V,V1,N,ITITLE,C)
 N1=N-1
 V(N)=V1(N)
 DO 10 I=1,N1
 V(I)=V1(I)

10 SKAP(I)=-B(I)/V(I)
 CONTINUE
 PN=P(N)-0.05
 CALL DIFFUN(P,V,N,PN,SKAP(N))
 ITITLE=10HP V COMP
 CALL PLOT(P,SKAP,SKAP,N1,ITITLE,C)
 RETURN
 END

ANH0075
 ANH0076
 ANH0077
 ANH0078
 ANH0079
 ANH0080
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 ANH0086
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 ANH0100
 ANH0101
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 ANH0106
 ANH0107
 ANH0108
 ANH0109
 ANH0110

```

REAL FUNCTION FUN(X)
  CALCULATES THE FUNCTION REQUIRED BY NAG ROUTINE D04AAF
  FROM THE COEFFICIENTS OF A CUBIC SPLINE GENERATED BY
  ROUTINE E03LF1.
  R. APPLEBY 18.4.77.
  THE COEFFICIENTS ARE PASSED THROUGH COMMON.
  COMMON A(20),B(20),C(20),D(20),V(20),N1
  DIMENSION V1(20)
  PARAMETERS
  -----
  A,B,C,D COEFFICIENTS OF A CUBIC SPLINE FITTED BY E03LF1.
  V1 REAL ARRAY USED IN CALCULATION

  NOTE
  ----
  MORE INFORMATION IS AVAILABLE IN N.A.G. MANUAL
  UNDER D04AAF AND IN LELIBF UNDER E03LF1.

  V REAL ARRAY CONTAINING X COORDINATES
  X IS THE POINT IN V AT WHICH THE FUNCTION IS REQUIRED
  N1 IS THE NUMBER OF DATA POINTS.
  RNEG=-1000000.0
  DO 10 I=1,N1
    SPOS=V(I)-X
    V1(I)=SPOS
    IF(SPOS) 15,15,10
15  CONTINUE
    IF (ABS(SPOS).LT.ABS(RNEG)) GOTO 30
    GOTO 10
30  RNEG=SPOS
10  CONTINUE
    DO 50 I=1,N1
      V1(I)=V1(I)-RNEG
      IF (V1(I).EQ.0.0) GOTO 60
      GOTO 50
60  I1=I
50  CONTINUE
      H=X-V(I1)
      FUN=D(I1)*H*H*H+C(I1)*H*H+B(I1)*H+A(I1)
70  RETURN
END

```

```

ANH0111
ANH0112
ANH0113
ANH0114
ANH0115
ANH0116
ANH0117
ANH0118
ANH0119
ANH0120
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ANH0123
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ANH0148
ANH0149
ANH0150

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```

SUBROUTINE DIFFUN(X,Y,N,Z1,DER)
COMMON A(20),B(20),C(20),D(20),V(20),N1
DIMENSION X(20),Y(20),DER(14),EREST(14)
EXTERNAL FUN

```

```

CALL DARRAY(20)

```

```

THIS ROUTINE CALCULATES THE DERIVATIVE AT A POINT Z1
IN THE X,Y FUNCTION Z1 HAS A VALUE OF X.
N.A.G. LIBRARY D04AAF IS USED TO PERFORM THE DIFFERENTIATION
DER CONTAINS THE FIRST 14 DERIVATIVES AND EREST AN ESTIMATE
OF THE ERROR.
ONLY THE FIRST DERIVATIVE IS USED BEING PUT INTO DRR.
THE N.A.G. ROUTINE IS CALLED SEVERAL TIMES AND THE BEST VALUE
OF DRR CHOSEN BY EXAMINATION OF EREST AUTOMATICALLY.

```

```

R. APPLEBY 19.4.77.

```

```

Z=Z1
DRR=0.0
ERP=1000.0
HBP=(X(N)-Z)/19
HBM=(Z-X(1))/19
IF (HBP-HBM) 60,70,70
60 HBASE=HBP
   GOTO 80
70 HBASE=HBM
80 CONTINUE
   N1=N
   DO 10 I=1,7
     HBASE=HBASE/2
     IFAIL=1
     CALL D04AAF(Z,-1,HBASE,DER,EREST,FUN,IFAIL)
     IF (IFAIL) 20,50,20
50 IF (EREST(1).LT.ERR) GOTO 15
     GOTO 10
15 ERR=EREST(1)
   DRR=DER(1)
10 CONTINUE
   DER(1)=DRR
   GOTO 40
20 WRITE(3,100)
   GOTO 30
40 CONTINUE
   WRITE(2,200)Z,DER(1),EREST(1)
30 CONTINUE
100 FORMAT(25H FAILED IN ROUTINE D04AAF)
200 FORMAT(14H DERIVATIVE AT,F10.5,3H IS,F10.5,17H WITH AN EREST OF,F10.5,28H EREST IS POSITIVE VALUE OK.)
RETURN
END

```

```

ANH0179
ANH0180
ANH0181
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ANH0226
ANH0227

```

```

SUBROUTINE WP(P,W,N,P3,SKAP,N3)
COMMON A(20),B(20),C(20),D(20),DUM(20),N2
THIS SUBROUTINE CALCULATES DW/DP AFTER READING W AND P
DIMENSION P(20),W(20),W1(20),W2(20),P3(20),B1(20),SKAP(20)

```

R. APPLEBY. 19.4.77.

PARAMETERS

```

P PRESSURE KBAR
W FREQUENCY CM-1
N NUMBER OF POINTS
SKAP COMPRESSIBILITY

```

CALLS

FITFN, PLOT, INDATA

THE GRUNEISEN PARAMETER $D(LNW)/DP$ AT VARIOUS PRESSURES
IS CALCULATED AND PLOTTED V PRESSURE.

```

CALL INDATA(P,W,N,0)
CALL FITFN(N,P,W,W1,1)
ITITLE=10HF V FREQ
CALL PLOT(P,W,W1,N,ITITLE,0)
DO 10 I=1,N
W(I)=W1(I)
10 W2(I)=ALOG(W(I))
CALL FITFN(N,P,W2,W1,0)
N1=N-1
ITITLE=10H GAMMA V P
DO 20 I=1,N1
20 B1(I)=B(I)
N2=N3
CALL FITFN(N3,P3,SKAP,W1,0)
DO 30 I=1,N1
30 B1(I)=B1(I)/FUN(P(I))
CALL PLOT(P,B1,B1,N1,ITITLE,0)
RETURN
END

```

```

ANH0223
ANH0229
ANH0230
ANH0231
ANH0232
ANH0233
ANH0234
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ANH0236
ANH0237
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ANH0240
ANH0241
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ANH0260
ANH0261
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ANH0264
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ANH0268

```

SUBROUTINE WT(T,W,DWDT,N)
 A SUBROUTINE TO CALCULATE A FUNCTION FITTING W AND T
 AND DW/DT THE CHAGE IN FREQUENCY FROM GK TO T K.
 DIMENSION T(20),W(20),DWDT(20),WT0(210),W1(20),T1(20),W2(20)

R. APPLEBY 1977.

PARAMETERS

T TEMPERATURE K
 W FREQUENCY CM-1
 DW/DT SHIFT IN CM-1 FROM FREQUENCY AT GK

NAG ROUTINE E01AAF IS USED TO CALCULATE FREQUENCY AT GK
 BY EXTRAPOLATION.

NOTE

 ONLY THE 4 POINTS CLOSEST TO GK ARE CONSIDERED
 AS THIS IS A LINEAR EXTRAPOLATION AND W,T IS
 USUALLY A CURVE.

CALLS

INDATA,FITEN,PLOT
 E01AAF (NAG)
 CALL INDATA(T,W,N,0)
 CALL FITEN(N,T,W,W1,1)
 ITITLE=10HT V FREQ
 CALL PLOT(T,W,W1,N,ITITLE,0)

N3=N
 N=4
 ONLY 4 POINTS CONSIDERED IN EXTRAPOLATION

N1=N
 N=N-1
 N2=N*(N+1)/2
 CALL E01AAF(T,W,WT0,N1,N2,N,0.0)
 N=N3

DO 20 I=1,N
 J=I+1
 W2(J)=W1(I)
 20 T1(J)=T(I)
 N=N+1
 W2(1)=WT0(N2)
 T1(1)=0.0

DO 10 I=1,N
 W1(I)=W2(I)
 T(I)=T1(I)
 W(I)=W1(I)
 10 DWDT(I)=W1(I)-W1(1)
 ITITLE=10HDELTA W V T
 CALL PLOT(T,DWDT,DWDT,N,ITITLE,1)
 RETURN
 END

ANHC269
 ANHC270
 ANHC271
 ANHC272
 ANHC273
 ANHC274
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 ANHC320
 ANHC321

```

SUBROUTINE ANH(V1,T1,N2,P3,V3,N3,SKAP)
SUBROUTINE COMPLETES ANALYSIS ON TEMPERATURE DATA.
CONSTRUCTING THE DERIVATIVES FOR SOLUTION OF EQUATION
GIVEN BY R.P. LOWHDES. R. APPLEBY. 19.4.77
(D(LNWI)/DT)P=(D(LN(WI)/DT)V+(D(LNWI)/DP)T(OP/D(LNV))T
(D(LNV)/DT)P

```

USING DATA CALCULATED IN PART 1 OF THE PROGRAM

PARAMETERS

V1 VOLUME AT PARTICULAR TEMPERATURE T1 THERE ARE N2 POINTS
V3 VOLUME AT PARTICULAR PRESSURE P3 THERE ARE N3 POINTS
VOLUME A CUBED TEMPERATURE K PRESSURE KBAR.
SKAP COMPRESSIBILITY AT P3

CALLS

FITFN,WT,WP,PLOT

```

COMMON A(20),R(20),C(20),D(20),ZZ(20),IC
DIMENSION T(20),W(20),DWT(20),T1(20),V1(20),V2(20),DELTAV(20)
1,P(20),W1(20),W2(20),DELTA(20),DERWTP(20),DELTAP(20),P3(20),V3
1(20),V4(20),SKAP(20)
CALL WP(P,W1,N1,P3,SKAP,N3)
CALL WT(T,W,DWT,N)
CALL FITFN(N2,T1,V1,V2,0)
DO 10 I=1,N
X=T(I)
IC=N2
DELTAV(I)=FUN(X)
10 DELTAV(I)=DELTAV(I)-V1(1)
DELTAV CHANGE IN VOLUME FROM ZERO K.
IC=N3
CALL FITFN(N3,V3,P3,V4,0)
DO 20 I=1,N
DELTAV(I)=V3(1)-DELTAV(I)
20 DELTAP(I)=FUN(DELTAV(I))
CALL FITFN(N1,P,W1,W2,0)
DO 30 I=1,N
IC=N1
DELTW(I)=FUN(DELTAP(I))
ITITLE=10H T V DELW
30 DELTW(I)=DELTW(I)-W1(1)
CALL PLOT(T,DELTW,DELTW,N,ITITLE,1)
DO 40 I=1,N
40 DERWTP(I)=DWT(I)+DELTW(I)
ITITLE=10H T V (WT)V
CALL PLOT(T,DERWTP,DERWTP,N,ITITLE,1)
RETURN
END

```

```

ANH0322
ANH0323
ANH0324
ANH0325
ANH0326
ANH0327
ANH0328
ANH0329
ANH0330
ANH0331
ANH0332
ANH0333
ANH0334
ANH0335
ANH0336
ANH0337
ANH0338
ANH0339
ANH0340
ANH0341
ANH0342
ANH0343
ANH0344
ANH0345
ANH0346
ANH0347
ANH0348
ANH0349
ANH0350
ANH0351
ANH0352
ANH0353
ANH0354
ANH0355
ANH0356
ANH0357
ANH0358
ANH0359
ANH0360
ANH0361
ANH0362
ANH0363
ANH0364
ANH0365
ANH0366
ANH0367
ANH0368
ANH0369
ANH0370
ANH0371
ANH0372
ANH0373

```



```

SUBROUTINE PLOT(X,Y,F,N,ITITLE,NUM)
DIMENSION X(20),Y(20),F(20)
THIS SUBROUTINE WILL PLOT THE FUNCTION F(N) AND THE POINTS
HELD IN X(N),Y(N). THE PLOT IS GIVEN A TITLE ITITLE
AND THE DATA OUTPUT ON THE LINE PRINTER.

```

R.APPLEBY. 1.4.77.

CALLS

THE FOLLOWING CGHOST ROUTINES ARE CALLED FOR PLOTTING
MAP,BORDER,AXES,PTPLOT,NSCURV,PCSEND,FRAME

```

WRITE(2,100)ITITLE
WRITE(2,150)(X(I),Y(I),I=1,N)
100 FORMAT(1H ,A10)
150 FORMAT(1H ,2F10.6/)
YMIN=1000000.0
YMAX=-1000000.0
IF (NUM) 40,40,50
50 YMAX=20.0
YMIN=-20.0
GOTO 60
40 CONTINUE

DO 10 I=1,N
IF (Y(I).GT.YMAX) YMAX=Y(I)
IF (Y(I).LT.YMIN) YMIN=Y(I)
10 CONTINUE
60 CALL PSPACE(0.0,0.17,0.1,0.27)
CALL MAP(X(1),X(N),YMIN,YMAX)
CALL BORDER
CALL AXES
CALL PTPLOT(X,Y,1,N,34)
CALL NSCURV(X,F,1,N)
CALL PCSEND(X(N),Y(N),ITITLE,10)
CALL FRAME
RETURN
END

```

ANH0374
ANH0375
ANH0376
ANH0377
ANH0378
ANH0379
ANH0380
ANH0381
ANH0382
ANH0383
ANH0384
ANH0385
ANH0386
ANH0387
ANH0388
ANH0389
ANH0390
ANH0391
ANH0392
ANH0393
ANH0394
ANH0395
ANH0396
ANH0397
ANH0398
ANH0399
ANH0400
ANH0401
ANH0402
ANH0403
ANH0404
ANH0405
ANH0406
ANH0407
ANH0408
ANH0409
ANH0410
ANH0411
ANH0412

SUBROUTINE VT(V,T,N)

THIS SUBROUTINE CALCULATES THE VOLUME AT 0K AND FITS
A FUNCTION TO THE V AND T DATA FOR USE LATER.
NAG ROUTINE E01AAF IS CALLED TO EXTRAPOLATE TO 0K.
A SMOOTHING FUNCTION IS APPLIED TO THE DATA AND THE
NEW FUNCTION CALCULATED BY E03LF1. COURTESY OF K.BRODLE.
WRITTEN BY R.APPLEBY.1.4.77.

PARAMETERS

V VOLUME A CUBED
T TEMPERATURE K
N NUMBER OF V,T POINTS

CALLS

FITFN, PLOT
E01AAF (NAG)

NOTE

A CUBIC SPLINE IS FITTED TO V,T AS V,T IS EXPONENTIAL
THIS IS NOT ENTIRELY SATISFACTORY AND SPURIOUS VALUES
OF ALPHA $D(\ln V)/DT$ MAY RESULT. A ROUTINE TO FIT AN
EXPONENTIAL IS BEING DEVELOPED.

DIMENSION V(20),V1(20),T(20),V0(210),T1(20)

CALL INDATA(T,V,N,1)
EXTRAPOLATE TO ZERO K.

N=N-1
DO 20 I=1,N

J=I+1

T1(I)=T(J)

V1(I)=V(J)

N3=N

N=4

ONLY 4 POINTS CONSIDERED IN EXTRAPOLATION.
SEE ROUTINE WT.

N=N-1

N1=N+1

N2=N*(N+1)/2

CALL E01AAF(T1,V1,V0,N1,N2,N,0.0)

V(1)=V0(N2)

T(1)=T(N2)

FIT FUNCTION AND PLOT

N=N3+1

CALL FITFN(N,T,V,V1,1)

ITITLE='CHVOL V TEMP'

CALL PLOT(T,V,V1,N,ITITLE,0)

TRANSFER SMOOTHED DATA TO ORIGINAL ARRAY

DO 10 I=1,N

V(I)=V1(I)

RETURN

END

ANH0413
ANH0414
ANH0415
ANH0416
ANH0417
ANH0418
ANH0419
ANH0420
ANH0421
ANH0422
ANH0423
ANH0424
ANH0425
ANH0426
ANH0427
ANH0428
ANH0429
ANH0430
ANH0431
ANH0432
ANH0433
ANH0434
ANH0435
ANH0436
ANH0437
ANH0438
ANH0439
ANH0440
ANH0441
ANH0442
ANH0443
ANH0444
ANH0445
ANH0446
ANH0447
ANH0448
ANH0449
ANH0450
ANH0451
ANH0452
ANH0453
ANH0454
ANH0455
ANH0456
ANH0457
ANH0458
ANH0459
ANH0460
ANH0461
ANH0462
ANH0463
ANH0464
ANH0465
ANH0466
ANH0467
ANH0468
ANH0469
ANH0470
ANH0471
ANH0472
ANH0473
ANH0474
ANH0475
ANH0476
ANH0477
ANH0478
ANH0479
ANH0480
ANH0481
ANH0482
ANH0483
ANH0484
ANH0485
ANH0486
ANH0487
ANH0488
ANH0489
ANH0490
ANH0491
ANH0492
ANH0493
ANH0494
ANH0495
ANH0496
ANH0497
ANH0498
ANH0499
ANH0500

SUBROUTINE FITFN(N,X,Y,Z,ID)
THIS SUBROUTINE FITS A FUNCTION TO THE POINTS HELD IN
REAL ARRAYS X,Y.
Z WILL CONTAIN THE SMOOTHED DATA.

R.APPLEBY. 17.2.77.

PARAMETERS

X,Y FUNCTION TO BE FITTED AND SMOOTHED
X,Z CALCD FUNCTION FITTING X,Y SMOOTHED
SD CONTROLS THE AMOUNT OF SMOOTHING
IF 0 CALCD FUNC. PASSES THROUGH ALL INPUT POINTS
IF 100 CALCD FUN. WILL BE A STRAIGHT LINE FIT TO X,Y
CALLS

EC3LF1 CALLED FROM LELIBF ALIB AVAILABLE AT LEIC.

COMMON A(20),B(20),C(20),D(20),X1(20),NDUM

DIMENSION X(20),Y(20),Z(20),DY(20),W(154)

DO 30 I=1,20

A(I)=0.0

B(I)=0.0

C(I)=0.0

D(I)=0.0

30 X1(I)=0.0

IF (ID) 40,40,50

50 READ(1,100) SD

GOTO 60

40 SD=0.0

60 DO 20 I=1,N

10 DY(I)=SD

100 FORNAT(F10.5)

S=FLOAT(N)

CALL EC3LF1(N,X,Y,DY,S,A,B,C,D,W)

DO 20 I=1,N

X1(I)=X(I)

20 Z(I)=A(I)

RETURN

END

ANH0466
ANH0467
ANH0468
ANH0469
ANH0470
ANH0471
ANH0472
ANH0473
ANH0474
ANH0475
ANH0476
ANH0477
ANH0478
ANH0479
ANH0480
ANH0481
ANH0482
ANH0483
ANH0484
ANH0485
ANH0486
ANH0487
ANH0488
ANH0489
ANH0490
ANH0491
ANH0492
ANH0493
ANH0494
ANH0495
ANH0496
ANH0497
ANH0498
ANH0499
ANH0500
ANH0501
ANH0502
ANH0503
ANH0504

ABSTRACTVIBRATIONAL SPECTROSCOPY AT HIGH PRESSURESROGER APPLEBY

A review is given with over 100 references of equipment for and results obtained in the field of vibrational spectroscopy at high pressures in the period June, 1975 to June, 1977. The device used in this thesis, the Diamond Anvil Cell (DAC), is analysed in detail and redesigned. A full discussion is given of earlier designs. The complex problems that arise in optical coupling of the DAC to i.r. and Raman spectrometers are also studied.

Pressure calibration using the R fluorescence lines of Ruby is fully discussed and the problems of low temperature high pressure experiments investigated, and a calibration proposed.

Three classes of compound are investigated: (i) organic (benzene), (ii) inorganic molecular (mercuric halides), and (iii) inorganic ionic (CsNiCl_3). For benzene the same sample held under hydrostatic pressure in a gasketed DAC was examined by Raman, far-i.r. and mid-i.r. spectroscopy. Spectra of the solid phases of I and II were recorded and evidence for the elusive phase III obtained. The Raman spectra compared well with those obtained by Nicol using a much larger sample in a Drickamer cell whilst the i.r. results are entirely new.

HgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been studied in detail up to ca. 40 kbar and almost all known phases characterised by Raman and i.r. spectroscopy and structures proposed for several phases of hitherto unknown structure. In particular the high pressure form of yellow HgI_2 is shown to differ from the yellow high temperature modification.

Raman and i.r. spectra of CsNiCl_3 at various temperatures and pressures have been obtained and analysed, using compressibility and thermal expansion data determined as part of the study, in terms of anharmonic parameters.