STRUCTURAL ASPECTS OF CERTAIN
INORGANIC SOLID-STATE MATERIALS

A THESIS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in the Faculty of Science

BY

PHILIP WILLIAM RUFF

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Statement

The work undertaken and recorded in this thesis is original in nature, unless otherwise acknowledged in the text or by reference. The work was carried out by the author at the Chemistry Department of the University of Leicester mainly between October 1981 to October 1984 and January 1986 to May 1987. This work has not been submitted for any other degree.

[Signature]

December 1988
A full introduction to the theory of phase transitions is presented which includes both thermodynamic and structural treatments of phase transitions. A literature review of the role of vibrational spectroscopy in the investigation of phase transitions is given for the period covering 1978 to 1987. Full experimental procedures are outlined covering the design and use of the diamond anvil cell (d.a.c.) utilised in the experimental investigations undertaken in this work.

The single crystal structure of Re(CO)₅I has been determined by x-ray diffraction techniques, together with a structural comparison with the other members of the Re(CO)₅X series (where X = Cl, Br).

Following on from the above, a vibrational investigation of the M(CO)₅X series (where M = Mn, Re; X = Cl, Br, I) is presented. An accompanying high-pressure Raman investigation of Re(CO)₅I is also shown.

The group I metal halate series MXO₃ (where M = K, Na; X = Cl, Br) have been investigated by infrared and Raman spectroscopy. High-pressure data are available for some of the series.

In continuation of earlier work a phase structural investigation, at high-pressure, of KClO₃ was performed using synchrotron radiation at the SRS, Daresbury.
Acknowledgments

There are numerous "thank you’s" to be made. Firstly, I must thank my supervisor, David Adams for his support and valued friendship over the years and to his wife, Marion for her excellent cooking.

Thanks are also due to the members of the Leicester High-Pressure Research Group, both past and present for their constant 'enthusiam' in the face of experimental failures (diamond anvils break with a sickeningly expensive sound!).

I am particularly proud to have classed the Chemistry Department at Leicester University as home and safe haven for so many years and my thanks go to all the members of staff for their help and friendship, in particular to Dr. David Russell for the hours we have spent thrashing a little green ball around a squash court and Professor John Holloway for a much needed kick in the rear to complete this thesis.

Special thanks are due to Andy Heath for helping to create the beginings of this thesis (and for being such a close friend) and to Mrs. Ann Crane, who has produced such excellent diagrams to accompany this text. The finished items bear little resemblance to the initial manic scriblings!

I must take time to thank all of my family (large as it is) for their support down the long years. I hope that they are as proud of my achievements as I am of them.

I cannot express adequately in words the help that my father has given me, nor the sadness I feel because my mother is not here to see this work completed.

Finally, and most importantly, I thank my wife Shamim, who has coped with the tempers, frustrations and general childishness that I’ve gone through in creating this thesis. I honestly could not have completed this work without her constant 'encouragement'.
Author's Comment

This thesis began its life as a hand-written manuscript, was then typed into the Leicester University WORD-11 word-processing system, transferred via ASCII text to an IBM PS-2 model 50 via the KERMIT protocol and thence onto several 3½ inch diskettes. From there, the text files were loaded into "ChemText™" (from Molecular Design) and converted into ChemText document files, with final output being on a postscript Apple laserwriter, spooled from a DEC microVAX Q6 machine. To bring the wheel round full-circle, the final editing was accomplished by hand.

And who said that producing a thesis was easy!!
To Shamim,
for her constant love and support

"You're my inspiration, my reason and my rhyme
From the first impressions, until the end of time
I'm telling you I love you, what else can I say?
'Cos you're my inspiration in every single way"

(Ian Dury)
To my Father and in memory of my Mother

"I am the one who guided you this far
All you know and all you feel.
Nobody must know my name,
For nobody would understand and you kill what you fear.
I call you for I must leave
You're on your own until the end.
You had a choice, but now it's gone
I said you wouldn't understand
Take what's yours and be damned."

(Genesis)
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Chapter One

An introduction to the theory of phase transitions

"I while the God's laugh
The worlds' vortex am;
Maelstrom of passions in that hidden sea
Whose waves of all-time lap the coasts of me
And in small compass the dark waters cram."

(Mervyn Peake)
CHAPTER 1

AN INTRODUCTION TO THE THEORY OF PHASE TRANSITIONS

1.1 WHY STUDY PHASE TRANSITIONS?

The study of phase transitions is of interest to a wide ranging section of the scientific community such as physicists, chemists, metallurgists and other workers in solid state science. It is also a subject of real technological importance, crossing the formal disciplinary subject boundaries. This is exemplified by the recent massive growth of the semiconductor industry, and is not just merely a topic of ("ivory-tower") academic interest. New phase systems are constantly being reported and the magnitude of the scientific literature reflects the tremendous growth in this particular area of science. The number of publications in the field now runs into several thousand per year on the study of phase transitions and its related areas. New concepts towards the understanding of the mechanisms of phase transitions are constantly being refined enabling theoreticians to improve their methods for the prediction of new structures and phases.

It is beyond the scope of this chapter to provide more than a brief insight into the enormous field of phase transitions and their study, but will hopefully serve to provide an overview of this fascinating field.

1.2 AN INTRODUCTION TO THE THEORY OF PHASE TRANSITIONS IN SOLIDS

Our knowledge of the crystal structure adopted under a given set of conditions is fundamental to our understanding of crystal chemistry. Changes in crystal structure arise from changes in intensive variables such as pressure, temperature, electric field, etc.

A solid, of known chemical composition, which changes form one crystal structure to another is deemed to have undergone a phase transition.
The crystal structure adopted by a compound at a given temperature and pressure is that with the minimum Gibbs free energy. The difference between the two structures may be dramatic or subtle, requiring a partial or total rearrangement of the atoms, or merely some minor re-adjustment of the atomic positions.

The occurrence of repeatable, reversible phase transitions suggests the possible existence of a mechanism connecting the structures of the two different phases. An understanding of such a mechanism is a pre-requisite to extending our knowledge of the occurrence and stability of different phases. There are two main types of phase transitions, namely first and second order transitions.

The distinction between the two, which is by no means apparent in the majority of cases, but which nevertheless remains of value, becomes apparent in the structural and thermodynamic classifications reviewed later in this chapter.

Second-order transitions are reasonably well understood from Landau’s theory (Landau, 1937, Landau and Lifshitz, 1958), which contains both thermodynamic and group theoretical elements.

In brief the theory describes a second-order transition in terms of order parameters, which transform according to the \( i^{th} \) representation of the phase with the higher symmetry. The possibility of the so-called soft mode as the trigger or driving force for second-order transitions is also discussed.

First-order phase transitions are more complicated to explain in symmetry terms, particularly those associated with volume changes. It can be shown that a relationship between phases can be fashioned and a mechanism deduced.

1.3 A THERMODYNAMIC CLASSIFICATION OF PHASE TRANSITIONS

A phase is only stable when its Gibbs free energy is at a minimum for a given set of thermodynamic conditions. If the Gibbs free energy is at a local minimum, then the phase is said to be metastable and an input of energy is necessary in order for the system to reach it’s most thermodynamically stable state (e.g. Diamond is metastable below 13.2 kbar).
As the pressure or temperature is varied, the Gibbs free energy of the system varies both continuously and smoothly. Above a certain pressure (or below a certain temperature) it is possible that the Gibbs free energy of a second and different phase is lower than that of its original state. Therefore, a phase transition will occur at the pressure (or temperature) at which the Gibbs free energies of both phases are equal. In other words, there is no discontinuous change in the Gibbs free energy at the transition point. As previously stated the structural differences between the phases may be large, requiring a complete molecular re-arrangement, or small, needing only slight shifts in the crystallographic fractional co-ordinates. The thermodynamic equilibrium existing between the two different phases may be represented by the Gibbs free energy function:

\[ G = H - TS = E + PV - TS \]

where:
- \( G \) Gibbs free energy
- \( H \) Enthalpy
- \( T \) Temperature
- \( S \) Entropy
- \( E \) Internal energy
- \( P \) Pressure
- \( V \) Volume

Ehrenfest (1933) has classified phase transitions as being of the same order as the derivative of the Gibbs free energy which displays a continuous change at the transition point.

**FIRST DERIVATIVES OF THE GIBBS FREE ENERGY, \( G \)**

\[ \frac{\Delta G}{\Delta P} = V \]

\[ \frac{\Delta G}{\Delta T} = -S \]
A Temperature-induced first order phase transition
Curves $G_I$, $G_{II}$ and $H_I$ and $H_{II}$ represent the variations in the Gibbs Free Energies and Enthalpies respectively of phases I and II at constant pressure.
The Gibbs Free Energy curves intersect at the transition temperature, $T_t$ where the II - I phase transition occurs. For temperatures greater than $T_t$, the variation in Gibbs Free Energy will be represented by the $G_I$ curve. Note that both phases co-exist at the transition temperature and are distinguishable by their differing enthalpies (and hence different structural details) at $T_t$.
The $G_I$ and $G_{II}$ curves may be meaningfully extrapolated, although to a limited extent, on either side of the transition temperature.
The curves correspond to the superheated and supercooled states respectively.

A Pressure-induced first order transition
$\Delta V$ is the discontinuous volume change and $P_t$ is the transition pressure. The extensions of curves $G_I$ and $G_{II}$ correspond to the supercompressed and superexpanded states respectively. (Rao and Rao, 1978).

A temperature-induced second-order phase transition.
At the transition temperature the slopes of the $G_I$ curves are equal. There is, however, a difference in the curvatures of $G_I$ and $G_{II}$. Volume and entropy are continuous.
SECOND DERIVATIVES OF THE GIBBS FREE ENERGY, $G$

\[ \Delta^2 G = \Delta V = -V\beta \]
\[ \Delta P^2 \Delta P \]

where $\beta$ is the compressibility

and

\[ \Delta^2 G = \Delta V = V\alpha \]
\[ \Delta P \Delta T \Delta T \]

where $\alpha$ is the volume thermal expansivity

and

\[ \Delta^2 G = -\Delta S = -C_p \]
\[ \Delta T^2 \Delta T \Delta T \]

where $C_p$ is the heat capacity.

Therefore, theoretically, a first-order phase transition displays a volume change when pressure-induced or an entropy change when temperature-induced. This is represented graphically in Fig 1.1 and 1.2. Over a confined pressure (or temperature) range, however, both phases are relatively stable and may co-exist in thermodynamic equilibrium. In practice it is entirely possible that one domain may have transformed to the new phase whilst its neighbour has not. This phenomenon of hysteresis is commonly associated with first-order phase transitions (either temperature or pressure induced), especially if it is accompanied by a large volume change. It manifests itself as a difference in $T_t$ or $T_p$ in the forward or reverse (Bridgman, 1932, Rao and Rao, 1966, Dornell et al, 1970). Observations of hysteresis suggest that the transition does not occur at the point where the free energies are exactly equal.

There are two possible causes for hysteresis:

i) The formation of a hybrid single crystal, where two phases co-exist within some general pattern of orientation. A full account of this theory has been given by Ubbelohde (1956, 1957, 1967).

ii) Kinetic reasons; although the free energies of the two phases become equal at the
FIG 1.4

The variation of enthalpy, $H$, with temperature, $T$, for a second-order transition occurring at $T_c$. Similar variations occur for volume, $V$, and entropy, $S$.

The variation of specific heat capacity, $C_p$, for a second-order temperature induced transition occurring at $T_c$.

The variation of the Landau parameter, $\xi_0$, with temperature for a second-order transition occurring at $T_c$.

The variation of the order parameter squared, $\xi_0^2$, with temperature for a second-order transition occurring at $T_c$. 

transition point (either $T_t$ or $T_p$), the new phase cannot nucleate because of the existence of kinetic barriers. Put simply, the nucleation of the new phase takes place under compression in one direction and under tension in the reverse direction. Therefore, it is reasonable to expect that the nucleation barriers and hence, $T_t$ or $T_p$, to be different in the different directions. This has been found to be true in the case of the ammonium halides (Thomas and Staveley, 1951), and other transitions (Rao and Rao, 1966).

Experimentally, however, the effects of hysteresis may be too small to be observable. In general, the two phases are structurally distinct with no obviously apparent symmetry relationship existing between them.

In a second-order transition the variation in $G$ occurs smoothly and continuously with temperature or pressure and the material consists solely of one phase at all times. The phenomenon of hysteresis therefore, is not associated with such transitions. Second-order phase transitions are often, although not necessarily, associated with an ordering process.

Second-order transitions involve discontinuous changes in either the heat capacity, $C_p$, if temperature induced, or the compressibility, $\beta$, if pressure induced. The variation of the Gibbs Free Energy with temperature is shown in Fig 1.3.

The variation of enthalpy, $H$, specific heat capacity, $C_p$, and order parameter, $\xi_0$, with temperature are represented in Fig 1.4.

Lambda transitions are sometimes referred to, incorrectly, as being second-order in nature. In reality they are transitions in which the heat capacity, $C_p$, of the system tends towards infinity as the transition temperature (usually referred to as the critical temperature, $T_c$) is approached. They derive their descriptive name from the characteristic shape of the graph of heat capacity plotted as a function of temperature. A classic example of a lambda transition is the transformation of crystalline quartz (Moser, 1936) as shown in Fig 1.5.

Another well studied series which display lambda transitions are the ammonium halides. The lambda transitions involve the loss of orientational order of the $\text{NH}_4^+$ ions. At temperatures below $T_\lambda$, $\text{NH}_4\text{Cl}$ has virtually all the $\text{NH}_4^+$ ions orientated parallel to one-another (i.e it is ferro-ordered), whereas in $\text{NH}_4\text{Br}$ they lie parallel along any one chain co-linear with the $c$-axis, but have an anti-parallel arrangement within the $ab$ plane (i.e
FIG 1.5

Curve of the variation of specific heat capacity, $C_p$, with temperature showing the lambda transition in crystalline quartz (after Moser, 1936).

FIG 1.6

A two-dimensional representation of the structure of CuZn alloy.

a) Above the transition temperature ($T_c$ approximately 730 K) Cu and Zn atoms are randomly distributed on two inter-penetrating cubic lattices (A and B), which together form a b.c.c. lattice.

b) Below the transition temperature, there is a preponderance of Cu atoms (open circles) on one sub-lattice (A). Complete order, as illustrated, is in principle attained at 0 K (Cochran, 1973)
antiferro-ordered). Above $T_\lambda$ the NH$_4^+$ ions are distributed essentially at random between the two possible orientations (Yurtseven, 1984). Many phase transitions exhibit both first- and second-order characteristics and may be classified as being of "mixed" type in accordance with Ehrenfest's scheme. This has inclined Ubbelohde (1957) to designate transitions as either "thermodynamically continuous" (or gradual) or as "thermodynamically discontinuous". The former are usually (but not necessarily) second-order, whereas the latter are usually first-order in nature.

### 1.4 A STRUCTURAL CLASSIFICATION OF PHASE TRANSITIONS

A thermodynamic treatment of phase transitions only presents a macroscopic view of the events taking place. Consequently, Buerger (1951, 1961, 1971a, 1971b) has classified them according to the criteria of the accompanying structural changes. At the transition point there is variation in the nature of either the first-nearest neighbours (primary co-ordination) or that of the second-nearest neighbours (secondary co-ordination). A change in primary co-ordination will involve a more dramatic energy variation than that required for secondary or, indeed, higher co-ordination. Thus, Buerger has classified phase transitions as being dependent upon primary or higher structural changes and also the transition speed or potential barrier to a transition.

(i) **Transformations involving primary co-ordination**

   (a) reconstructive (sluggish)
   
   Here the primary bonds are broken and reformed.

   (b) dilatational (rapid)

(ii) **Transformations involving secondary co-ordination**

   (a) reconstructive (sluggish)

   (b) displacive (rapid)

These involve a distortion of the primary bonds; in other words, each atom moves relative to its neighbours by an amount which is small in comparison with a unit cell dimension. Thus, the transition is from ordered structure to ordered structure, the low-pressure (or high-temperature) variant usually having a higher specific volume, specific
heat capacity and symmetry.

(iii) Transformations involving disorder

In this case the transition entropies are large in comparison to those of displacive transitions.

(a) substitutional (sluggish)
These are commonly found in metals and alloys.

(b) rotational (rapid)
These contain some of the characteristics of displacive transitions.

(iv) Transformations of bond type (sluggish)

Many phase transitions are of "mixed" type according to Buerger’s classification. It can be seen that certain parallels exist between Buerger’s structural classification and Ehrenfest’s thermodynamic treatment. In particular, reconstructive and bond type transformations are analogous, but not identical, to first-order phase transitions whilst displacive and disorder transitions bear semblance to second-order phase transitions. Reconstructive transitions give rise to large discontinuities in cell dimensions, symmetry, internal energy and so on. A typical example is the aragonite (Pnma) to calcite (R3c) transition in CaCO₃ (at 723 K), where the calcium co-ordination changes from 9 to 6.

1.5 ORDER PARAMETERS AND SOFT MODES

At a phase transition a certain long range order, which is absent in the first phase, may be considered to appear in the new phase. The transition can be described in terms of an order parameter, \( \xi \), which is non-zero below the transition temperature and becomes zero above it. The order parameter is selected to represent some change in a physical parameter, such as disorder, molecular rotation or partial rotation of a crystal lattice (e.g. octahedron rotations in perovskites). In a second-order structural transition the order parameter measures the mean extent to which the atomic configuration within the less symmetrical phase is displaced from that of the more symmetric phase.

The appropriateness of such a term becomes most apparent when considering, for...
example, a binary alloy such as CuZn. Above $T_e$ (approximately 730 K) the Cu and Zn atoms are randomly distributed on two interpenetrating simple cubic lattices, together forming a body-centered cubic lattice (Fig 1.6a). Below 730 K there is a predominance of copper atoms on one of the sub-lattices, denoted A. Complete ordering (Fig 1.6b) is theoretically obtained at zero kelvin.

The order parameter is defined by

$$\xi_0 = \frac{2N_A - N}{N}$$

Where $N_A$ is the number of Cu atoms on A sites
N is the total number of Cu atoms

For total disorder

$$N_A = \frac{1}{2} N$$

Thus, the order parameter tends to zero as the system becomes completely disordered.

Vibrational soft modes are associated with all second-order structural transitions. Thus, both displacive and order-disorder transitions involve soft modes. A soft mode, by definition, is a mode the square of whose frequency tends towards zero as the transition point is approached.

The only pre-war spectroscopic investigation undertaken was that of Raman and Nedungadi on quartz (1940). This investigation of the $\alpha$ to $\beta$ transition effectively pioneered the concept of the vibrational soft mode. In the same year, Saksena (1940) presented a lattice dynamical model of quartz which demonstrated the instability of one particular normal mode as the $\alpha$ to $\beta$ transition from $D_3^4$ ($P3_12$) to $D_6^5$ ($P6_22$) structure developed. Over the next twenty years little experimental work was done outside the USSR (Iakovlev et al, 1956, 1957).

Cochran (1960) proposed the now famous lattice dynamical theory. He demonstrated that for a simple cubic monatomic lattice, the stability requirements are that
the elastic coefficients satisfy the following general conditions:

\[
\begin{align*}
C_{11} &\geq 0 \\
C_{12} &\geq 0 \\
C_{11}^2 - C_{12}^2 &\geq 0 \\
C_{11} + 2C_{12} &\geq 0
\end{align*}
\]

and that for complex crystals these conditions are reduced to the requirement:

\[\omega_i \geq 0\]

for all \(i\), where \(\omega_i\) is the \(i^{th}\) normal mode frequency. Therefore, we see that \(\omega_i\) is equivalent to some generalised elastic coefficient becoming small. In the latter case the crystal's restoring force against some shear deformation is weak, and the crystal literally softens. This equivalence of \(\omega_i\) with some generalised elastic co-efficient \(C_{jk}\) is thus responsible for the term 'soft mode' applied to the normal mode for which \(\omega(T)\) tends to zero.

Cochran illustrates his lattice dynamical theory with a cubic diatomic crystal such as GeTe which is explained in depth in the following references (Scott, 1974, Bierly, 1963, Pawley, 1966).

Anharmonic theory of lattice dynamics has been extensively reviewed by Cowley (1963). He derives Cochran's soft mode equation from a microscopic approach, thus linking the macroscopic, thermodynamic approach of Landau, Devonshire (1949) and Cochran's lattice dynamical theory.

1.6 LANDAU'S CRITERION FOR SECOND-ORDER TRANSITIONS

By expanding the Gibbs free energy of a system in terms of the order parameter:

\[
\phi(P,T,\xi) = \phi(P,T) + A\xi_0 + B\xi_0^2 + C\xi_0^3 + ...
\]

Landau was to demonstrate, as Ehrenfest had deduced via a different route, that at
a second-order transition entropy is continuous while heat capacity, thermal expansivity and compressibility all undergo discontinuous change.

Landau also pioneered the application of group theoretical arguments to thermodynamics. He found no observable symmetry relationship between the parent and daughter phases for a first order phase transition. The order parameter varies continuously at the transition point for a second-order transition but the symmetry changes discontinuously, being higher for the high-temperature (or low-pressure) phase. However, this is not a thermodynamic law and, of course, exceptions are possible. Such an example is XeF$_6$ which, when cooled, undergoes a series of phase transitions, which have increasingly complex structures, none of which contain discrete XeF$_6$ molecules.

\begin{tabular}{|c|c|c|c|c|}
\hline
 & I & II & III & IV \\
Monoclinic & Orthorhombic & Monoclinic & Cubic \\
\hline
Z= & 8 & 16 & 64 & 144 \\
(+10°c) & (-25°) & (-180°) & \\
\hline
\end{tabular}

(After Wells, 1975).

Landau showed that the symmetry criteria for a second-order transition may be summarised as follows (Rao and Rao, 1978).

(i) The symmetry group (G$_i$) of the low-temperature (or high-pressure) phase is a subgroup of that (G$_o$) of the high-temperature (or low-pressure) phase.

(ii) The variation in crystal transformation should correspond to a single irreducible representation of G$_o$ (but not the identity representation). That is, a soft mode must be non-totally symmetric in the parent phase and become totally symmetric in the daughter phase.

(iii) When the Gibbs free energy is expanded in terms of the order parameter it cannot contain third order terms, since a polynomial of odd-order cannot correspond to a minimum in the thermodynamic potential. This condition has been extended by Hosoya (1977) to exclude all odd-order variants other than n1.

-10-
1.7 A BRIEF SURVEY OF SOME OF THE TECHNIQUES UTILISED IN THE STUDY OF PHASE TRANSITIONS

The range of techniques used by scientists in their studies of phase transitions is wide and varied. It seems that as soon as new techniques become available they are immediately pressed into service.

As temperature and pressure are the two most important thermodynamic variables in the field of phase transitions any studies would therefore involve measurements of properties as a function of temperature or pressure. Obviously in respect of the work undertaken in this thesis particular emphasis will be given to the high-pressure applications of the various techniques.

X-ray diffraction techniques (Jamieson et al, 1959, Block et al, 1965, Merrill and Bassett, 1974, Keller and Holzapfel, 1977) provide an essential part of any study and the literature contains many x-ray studies performed at variable temperatures and pressures. Single crystal measurements by either Laue or Weisenberg methods can provide valuable structural and mechanistic information in certain situations which preserve the crystal or the crystal axis through the transition(s). In most cases, however, due to the instability or unavailability of a single crystal, powder diffraction methods are routinely utilised. The recent emergence of synchrotron radiation facilities (outlined in a later chapter) has dramatically reduced the data collection time in, particularly, high-pressure powder diffraction phase transition studies.

This technique, in conjunction with computer simulations of spectra, is providing promising results in the field of high-pressure structure determination (Heath, 1986). Neutron diffraction studies are most significantly useful in the study of the positions of the lighter atoms and magnetic structures (Reitveld, 1969). Analogous powder diffraction analysis routines as mentioned above make neutron powder diffraction an extremely important technique in the study of phase transitions.

Thermal methods of analysis have been extensively applied to the identification and characterisation of phase transitions. Differential thermal analysis (DTA) (Rao and Rao, 1966, Natarajan et al, 1969) has been routinely employed to measure precise enthalpy changes and hence indicate the thermodynamic order of transitions. DTA has also been used to study thermal hysteresis in phase transitions (Rao and Rao, 1966).
Differential scanning calorimetry (DSC) has increased in popularity for obtaining heat capacity data and $\Delta H$ of phase transitions (the $\Delta H$ values obtained via DSC being more reliable than those obtained by DTA).

Optical spectroscopy in the UV/visible and infrared regions have been extensively employed to study solids undergoing phase transitions. Laser Raman spectroscopy is perhaps the commonest technique used in the characterisation of high-pressure phase transitions, particularly within the research group at Leicester.

Both neutron scattering and Raman spectroscopy can yield direct information concerning soft modes, an area of increasing importance in the study of phase transitions (Scott, 1974).

**In summary**, the array of techniques available is substantial and growing steadily larger including the more "exotic" techniques such as Mössbauer spectroscopy, magnetic susceptibility measurements, electrical conductivity measurements, NMR, NQR, and ESR spectroscopies, x-ray photoelectron spectroscopy and more recently positron annihilation studies.
References for Chapter One


Cochran, W., in "Structural phase transitions and soft


Chapter Two

Vibrational spectroscopy at high-pressures:
A review covering the period 1978 to 1987

"Plagiarise, Plagiarise,
Let no-one's work evade your eyes."

(Tom Lehrer)
CHAPTER 2

VIBRATIONAL SPECTROSCOPY AT HIGH-PRESSURES: A REVIEW
COVERING THE PERIOD 1978 TO THE PRESENT

2.1 INTRODUCTION

The purpose of this review is to provide a resumé of the tremendous and varied amount of high-pressure investigations undertaken world-wide. It is apparent that certain key research groups are now established as ‘centres of excellence’ in the field of high-pressure technology and measurements.

The vast amount of high-pressure research literature has been selectively reduced in quantity by introducing the limitation of vibrational spectroscopy as a means of principal investigation. Clearly, such a limitation enables a sensible volume of data to be processed and provides a comprehensive database of use to the majority of high-pressure research groups, particularly within the U.K.

Other high-pressure investigative techniques have been outlined in chapters 1 and 5.

The remaining literature has been further sub-divided into major categories, again for ease of manipulation and reference. These categories are: Aqueous systems, Gases, Semiconductors, Minerals, Ice, Organics and Inorganics (of primary importance to the Leicester based High-Pressure Research Group). Despite these formal sub-divisions there is frequent interaction between the category types, particularly in the cases of Aqueous systems and Organics.

Each individual section will include reference to major work undertaken in that area, together with references to other research performed and given in a tabular form.
2.2 AQUEOUS SYSTEMS

A small, but nevertheless important, area of high-pressure investigations concerns the study of aqueous systems. This section will report the activity of the high-pressure community with water, and the interaction of water with other systems.

Manouvrier and Devaure (1) have used Raman spectroscopy as a means of investigating the pressure effects on the association between the thiocyanate ion and a selection of metallic cations, namely, Zn$^{2+}$, Mn$^{2+}$, Al$^{3+}$, In$^{3+}$, Th$^{4+}$ and Hg$^{2+}$. The $v$(C-S) stretching frequency of the anion was analysed because of its noted sensitivity to complexation. New $v$(C-S) peaks appear at frequencies distinct from that of the free $v$(C-S). The quantity of free SCN$^{-}$ in the system was determined from the intensity of the free $v$(C-S) peak and was used to calculate the formation constants for the following equilibrium:

$$M^{x+} nSCN^{(x-n)-} \rightleftharpoons M(SCN)_n$$

Values for the formation constants were obtained at ambient pressure and at 3 kbar. The mean value of the change in partial molar volume, $\Delta V$, for the complexation reaction between the two pressure extremes was calculated. The dissociation of the complex was found to be favoured by an increase in pressure, with positive $\Delta V$ values. The largest values of $\Delta V$ measured are interpreted as a change in the co-ordination number of the cation upon complexation.

A near-infrared study of H$_2$O at high-pressures has been carried out by Suzuki, Taniguchi and Tsuchiya (2). The study in pressure effects on the physiochemical properties of aqueous solutions of amphiphiles, and determined properties such as critical micelle concentration (CMC) and lower critical solution temperature (LCST). The lower critical solution temperatures for triethylene glycol hexyl ether and for partially acetylated polyvinyl alchohol were determined. The results tend to indicate the presence of a dense-ice structure of H$_2$O at pressures greater than 2 kbar.

Buback (3) has described the design of optical cells for infrared and Raman investigations of pure H$_2$O and aqueous solutions up to 5 Kbar and 720K. The experimental data for the integrated molar absorptivity and for the maximum O-H
stretching mode frequency demonstrate, that at supercritical temperatures, hydrogen-bonded structures are not important in pure H\textsubscript{2}O. From the infrared spectra of aqueous LiCl and NaClO\textsubscript{4} solutions Buback suggests that, for 1:1 electrolytes, a transition from water-like to melt-like behaviour occurs in a fairly narrow concentration region, usually between 10 and 15 molar percent salt. Raman spectroscopy proves to be particularly well suited to the determination of species in pure H\textsubscript{2}O and also in aqueous solutions, which may contain simple ions, complex ions and also uncharged complexes.

Klug and Whalley (4) have studied the integrated absorption intensity and frequency of the uncoupled O-H stretching vibration for a dilute solution of H\textsubscript{2}O in D\textsubscript{2}O, measured up to 189 kbar and 295K in a d.a.c.. The thickness of the sample was determined by the use of interference fringes, and pressure determined using the ruby fluorescence method. The frequency shift with pressure was nearly linear in the region of stability ice (VII), with a slope of -2.08 cm\textsuperscript{-1}Kbar\textsuperscript{-1}. The integrated intensity of the uncoupled O-H vibration increased by a factor of 2.8 in the pressure range 23-189 Kbar, corresponding to a change in the O-H-O bond length from 2.91 to 2.62 Å. The result obtained agrees well with a simple model proposed for integrated intensities.

Holmes \textit{et al} (5) have investigated spontaneous Raman scattering from shocked water. The O-H Raman stretching band of liquid water was observed at both high pressures and temperatures. A new single-pulse Raman technique was used to obtain spectra from water shocked up to 260 kbar and 1700K. Band shape changes over the range 75 to 260 kbar were fitted well by a two-component mixture model. Intermolecular hydrogen bonding, which is dominant at 120 kbar, is almost completely absent at 260 kbar. The Raman spectra point toward the transfer of H\textsuperscript{+} and OH\textsuperscript{-} ions as being the most probable mechanism for the electrical conductivity of shocked water.

Raman scattering of pyridine complexes in aqueous solution has been observed by Zakin \textit{et al} (6). The \nu\textsubscript{1} and \nu\textsubscript{12} ring-breathing vibrational modes of pyridine in aqueous solution have been studied both as a function of concentration (up to 12M) and pressure (up to 35 kbar in a d.a.c.). The pyridine isotopes -h\textsubscript{5} and -d\textsubscript{5} display marked differences in their behaviour. The pressure dependence of \nu\textsubscript{1} for the -h\textsubscript{5} isotope is virtually linear in nature, whereas it is distinctly curved for the -d\textsubscript{5} analogue, and this curvature has been shown to increase with decreasing concentration. This effect is attributed to the formation of pyridine-water complexes, involving both O-H...N and C-H...O-H bonds. The pressure dependency for \nu\textsubscript{12} does not vary with concentration, but has been shown to be at least
five times steeper for pyridine-h₅ than pyridine-d₅. At high concentrations υ₁ manifests itself as two distinct peaks, each with a different pressure dependency, indicative of the presence of both complexed and free pyridine. It was observed that for certain combinations of solvent and solute concentrations, a strong pressure dependent Fermi resonance between the υ₁ and υ₁₂ modes becomes visible. Similar experiments with DMF, a weakly associating solvent, and non-associating solvents such as PhMe and PhH were performed. For these systems the dependencies were not observed to vary with concentration. This, together with other results, tend to indicate the aspects of the aqueous solution results which can be assigned to pyridine-water and pyridine-pyridine complexes.

Further work on aqueous systems include:

<table>
<thead>
<tr>
<th>Material</th>
<th>Comments</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
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<td>aq.H₃PO₄, KH₂PO₄, Na₃PO₄</td>
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<td>H₂O</td>
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<td>As for reference 10.</td>
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<td>21</td>
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<tr>
<td>aq.LiNO$_3$, NaNO$_3$,KNO$_3$</td>
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<tr>
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<td>Pressure dependence of title molecule measured upto 26.1 kbar. Raman study.</td>
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<tr>
<td>aq.lysozyme</td>
<td>Pressure effects on Raman spectra of denatured proteins. Minor changes</td>
<td>24</td>
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</table>
occur up to 3.6 kbar. Irreversible
denaturation and precipitation occurs
at 5.5 kbar.

2.3 GASES

This section includes the generation of very high-pressures, put succinctly by the
premier high-pressure research group, namely that of Mao and Bell, as
'Ultrahigh-pressures'.

Hydrogen

Mao, Bell and Hemley (25) have carried out optical and Raman measurements on
hydrogen and deuterium at pressures up to 1.47 Mbar. Measurements on the intramolecular
stretching mode, or vibron, indicate an initial frequency increase followed by a sharp
decrease in frequency at pressures greater than 0.5 Mbar. At 1.14 Mbar the vibron
frequency had decreased to the zero pressure value, and at 1.47 Mbar the vibron has a
value 90 cm\(^{-1}\) below that of the vibrational mode in the isolated molecule. The pronounced
softening of the intramolecular stretching mode suggests the possibility of a strengthened
intermolecular interaction.

Wijngaarden et al (26) have also investigated the pressure dependence of the
vibron in solid hydrogen and deuterium up to 600 Kbar and at temperatures down to 5K in
a diamond anvil cell. A semi-empirical model was developed to describe the pressure
dependence of the transition frequency. The agreement between theoretical and
experimental results is good for the low-pressure region up to approximately 200 Kbar.
However, the deviations observed at higher pressures could not be explained in terms of
the proposed simple mean-field model.

Further investigations carried out on hydrogen and deuterium include:

<table>
<thead>
<tr>
<th>Material</th>
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<tbody>
<tr>
<td>n-H(_2)</td>
<td>Raman scattering study up to</td>
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</table>
631 kbar at room temperature.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-H₂, n-H₂</td>
<td>Near-IR absorption up to 12 kbar and 4.2 and 2 K. p-H₂ HCP in compressed solid to 12 kbar</td>
</tr>
<tr>
<td>p-H₂, o-D₂</td>
<td>Theoretical calculations of pressure-induced rotation-libration transitions.</td>
</tr>
<tr>
<td>n-H₂</td>
<td>Raman scattering study of ( E_{2g} ) transverse-optical phonon.</td>
</tr>
<tr>
<td>p-H₂, o-D₂</td>
<td>Comparison of experimental data with theoretical calculations for rotation-libration transition.</td>
</tr>
<tr>
<td>( H_2^6He ) mixture</td>
<td>Raman study up to 80 kbar at 300 K.</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>Raman study on solid ( H_2 ), and calculation of ( H_2 ) molecule frequency in a solid ( H_2 ) medium.</td>
</tr>
<tr>
<td>( H_2, D_2, N_2 )</td>
<td>Raman scattering study on vibron frequency shifts as a function of pressure. 1.8 Mbar maximum pressure recorded.</td>
</tr>
</tbody>
</table>

**Nitrogen**

Spectroscopic investigations performed on the diatomic gases are numerous. Le Sar *et al* (35) have undertaken a Raman spectroscopic study of solid nitrogen up to 374 kbar at room temperature in a d.a.c. Only the molecular stretching mode was observed. Between approximately 50 and 120 kbar, the Raman line splits into a second, higher frequency.
peak, which could be attributed to molecular ordering within the solid. Measurements of the broadening and splitting in the $R_1$ and $R_2$ ruby fluorescence lines give an indication that solid $N_2$ might be a useful pressure transmitting medium (refer to chapter 3).

A far-infrared and empirical intermolecular potential study for $\alpha$- and $\gamma$- nitrogen, under varying pressure, has been undertaken by Fondere et al (36). Far-infrared measurements of solid $N_2$ were collected in both the $\alpha$- and $\gamma$- phases. Pressure shifts, integrated intensities, and Grueneisen parameters were derived. Further work by the same group has been carried out down to liquid helium temperatures (37).

**Oxygen**

Nicol et al (38) have measured the Raman spectra of fluid and solid oxygen at temperatures near to 298K and pressures up to 180 kbar. At 298 K, fluid oxygen freezes at approximately 59 kbar. Solid-solid phase transitions were observed at approximately 95 and 99 kbar respectively.

Solid molecular oxygen has been investigated in a d.a.c. by means of Raman spectroscopy at pressures up to 140 kbar and temperatures from 6 to 300K by Jodl et al (39). Characteristic spectral features in the different crystal phases of oxygen have enabled conclusions to be drawn about the P-T phase diagram.

**Other diatomics**

Johannsen and Holzapfel (40) have performed a high-pressure Raman study on solid chlorine. Pressures up to 450 kbar were obtained using a d.a.c. They noticed that the accidental degeneracy of the $B_{3g}$ and $A_g$ lattice modes was lifted under pressure.

Further work undertaken includes:

<table>
<thead>
<tr>
<th>Material</th>
<th>Comments</th>
<th>Ref</th>
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<tbody>
<tr>
<td>$\alpha$-$N_2$</td>
<td>Far-IR study. Mode Grueneisen parameters reported and discussed.</td>
<td>41</td>
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<tr>
<td>solid $N_2$</td>
<td>Calculation of high-pressure phase</td>
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</tbody>
</table>

-24-
transitions in solid N$_2$.

solid O$_2$ Raman observation of librons and vibrons at low temps. and up to 60 kbar.

$\alpha$-O$_2$ Static and dynamic properties of solid O$_2$ calculated as functions of pressure at zero temperature. A soft-mode-induced phase transition from a monoclinic structure to an orthorhombic structure predicted at 60 kbar.

$\alpha$-N$_2$ Far-IR two-phonon absorption study under pressure.

### A-B diatomics

The A-B type diatomic gases have also been investigated. Fondere $et$ $al$ (46) have collected the Far-IR spectra of HCl and HBr in an argon matrix at 4.2 K and pressures up to 4.5 kbar. Further work by the same authors has been extended to include the numerical analysis of pressure frequency shifts using an intermolecular potential model (47).

Pure carbon monoxide has been investigated at supercritical temperatures between 293 and 500 K and pressures up to 2.8 kbar by Buback, Schweer and Tups (48). Band maxima positions and vibrational intensities between gaseous and liquid-like states have been tabulated and discussed.

Reference is also made to the following:

<table>
<thead>
<tr>
<th>Material</th>
<th>Comments</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Investigation by CARS at elevated temps. and pressures.</td>
<td>49</td>
</tr>
</tbody>
</table>

-25-
Triatomics

High-pressure spectroscopic investigations of triatomic gases appear to be confined mainly to carbon dioxide, with a few exceptions.

Jodl (52) has studied the effect of pressure (up to 8 kbar) on the Raman spectra of NO$_2$ isolated in Ar and KI matrixes at 77 and 4.2K.

Hanson and Jones (53) have made Infrared and Raman studies on the librational and internal modes of solid CO$_2$ at ambient temperature and pressure between 6 and 120 kbar. The Fermi-resonance of the system was investigated in detail. They observed that the stretching modes stiffen with pressure, whereas the bending mode softens with pressure. A simple theoretical model using gas phase anharmonic constants has been used to predict much of the observed behaviour.

An extended investigation by Hanson (54) presents evidence for a new phase (III) of solid CO$_2$ which occurs in the region of 180 kbar at ambient temperature. This new phase has a markedly different low-frequency Raman mode pattern from that of the well characterised Pa3 phase (I).

Further studies of interest include:

<table>
<thead>
<tr>
<th>Material</th>
<th>Comments</th>
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</tr>
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<tbody>
<tr>
<td>$\alpha$-CO$_2$</td>
<td>Molecular librations of solid $\alpha$-CO$_2$ were studied at high-pressures and 0 K in terms of Kihara models. Calculated libration frequencies show</td>
<td>55</td>
</tr>
</tbody>
</table>
agreement with observed Raman and neutron data.

\begin{tabular}{ll}
\textbf{CO}_2 & CO\textsubscript{2} and NH\textsubscript{3} studied to 110 kbar at ambient temp. in a d.a.c. by Raman spectroscopy. \\
\textbf{NH}_3 & \\
\textbf{CO}_2 & Raman spectrum of solid CO\textsubscript{2} at high-pressure recorded. Model calculations performed. \\
\textbf{CO}_2 & Comparison of experimental IR spectra with prediction models. Pressures of 800-1600 kbar reported. \\
\textbf{N}_2\textbf{O} & High-pressure Raman study of vibrational relaxation in N\textsubscript{2}O. Temp. range 298-423 K and pressure up to 2 kbar. \\
\textbf{CO}_2 & IR absorption study of CO\textsubscript{2} at high-pressure.
\end{tabular}

The final section of this catagory deals with high-pressure studies on methane, methane-d\textsubscript{4} and ammonia.

**Methane**

An exhaustive study of the phase relations of methane and methane-d\textsubscript{4} has been performed by various French workers over the period covering 1978-1985 (61-67).

During this period the phase diagram of methane (and methane-d\textsubscript{4}) has been extended as follows:-
These phases have been determined by a combination of Far-IR and Raman spectroscopic techniques. All measurements were performed at 4.2 K.

Ammonia

Bradly, Zerda and Jonas (68) have studied the vibrational relaxation of the $u_1 + 2u_4$ Fermi-resonance coupled modes of ammonia as a function of pressure (up to 2 Kbar) and temperature (273-373 K).

Other investigations include:

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<th>Material</th>
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<tbody>
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<tr>
<td>CH$_4$</td>
<td>Pressure shift and broadening study of CH$_4$ by Raman spectroscopy at 293K.</td>
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<tr>
<td>CH$_4$</td>
<td>Far-IR matrix isolation study at 4.2K. CH$_4$/Ar, CH$_4$/Xe and CH$_4$/Kr systems studied.</td>
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</tbody>
</table>
2.4 SEMICONDUCTORS

The role of semiconductors is an increasing one in today’s technology. The single largest growth area in scientific research is into semiconductor technology, and its associated spin-off projects. The emergence of techniques such as high-pressure x-ray diffraction and EXAFS, utilising synchrotron radiation sources (outlined in chapter 5), has aided the study of these extremely important materials.

Photoluminescence and resonance Raman techniques were used to study GaAs under hydrostatic pressures up to 72 kbar by Yu and Weber (73). From pressure dependencies obtained from the P.L. data, the pressure coefficient of the conduction band minimum in GaAs was derived. The pressure dependence of the band-edge phonon energies for GaAs were also reported.

Trommer et al (74) have measured the first- and second-order Raman spectra of InP in a d.a.c. as a function of pressure up to the reported phase transition at 100 kbar. The Gruneisen parameters of the LO and TO phonons, and also those for several optical and acoustical phonons were measured. The results obtained were interpreted in terms of band-orbital theory, and also that of a pseudopotential calculation of the dynamical charge as a function of lattice constants.

GaS has been studied to 200 kbar by Polian, Chervin and Besson (75). Line broadenings induced by pressure are discussed. The observed behaviour is interpreted as an intrinsic property of the crystal and is not due to inhomogeneous strain-broadening, as this is minimised in the experimental technique used. A structural phase transition above 190 kbar is reported. The new phase observed displays 3-dimensional bonded network behaviour.

Besson et al (76) have also investigated the effect of pressure on the optical properties of crystalline arsenic (III) sulphide. Raman scattering spectra reveals that the optical band gap red-shifts rapidly with increasing pressure decreasing from 2.7 eV at atmospheric pressure to 1.6 eV at 100 kbar. At high-pressures 2D-3D dimensionality effects are clearly observed in the vibrational Raman spectra. Pressure data was used to distinguish between the explicit (phonon-occupation-driven) and implicit (volume-driven) contributions of the dependence of the band gap and Raman-active phonon frequencies.
Amorphous orpiment ($\text{As}_2\text{S}_3$) has also been investigated by Besson and co-workers (77). High-pressure measurements of the absorption edge, and Raman spectra of crystalline (c-) and amorphous (a-) $\text{As}_2\text{S}_3$ were reported. The band gap of both materials red-shift rapidly with increasing pressure. These observations are interpreted as an enhancement of the interlayer interaction for c-$\text{As}_2\text{S}_3$. Similar behaviour for a-$\text{As}_2\text{S}_3$ suggests a layer-like macromolecular structure. The absorption edge for a-$\text{As}_2\text{S}_3$ increases strongly with pressure and this effect is discussed in terms of a theoretical model. Raman evidence points to a smooth transition from 2D to 3D behaviour under the influence of increasing pressure.

Minomura (78) has produced a review containing 34 references concerning the pressure-induced effects on the optical absorption edges, electrical resistivities, superconductivities, atomic structures, Raman-active phonon frequencies, and phase transitions to metallic states for amorphous chalcogenides and tetrahedral materials.

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pressure. Correlation of results to known neutron data.

**GaP**
- Raman scattering by **LO** and **TO** phonons measured up to 100 kbar.

**GaSb, InSb**
- First-order Raman scattering by **LO** InAs, and **TO** phonons observed up to their phase transitions.

**Bi₂Te₃**
- Lattice parameters, atomic parameters and shift in the Raman active vibrations in p-Bi₂Te₃ reported with variation in pressure. Structural investigation with Neutron diffraction.

**InAs**
- Pressure dependence of the **LO-TO** phonons investigated by Raman scattering in a d.a.c.. InAs undergoes a phase transition at 70±1 kbar, assumed to be to the NaCl-type structure.

**GaP**
- First-order Raman spectra of GaP at room temperature and 77K measured up to 70 kbar. **LO** and **TO** Gruneisen parameters calculated from pressure shifts.

**TlSe, TlInSe₂, TlInSe₂(1-x)S₂**
- Pressure coefficients of the direct and indirect energy gaps determined.
- Pressure up to 55 kbar applied.

**Pb₁₋ₓSnₓTe**
- High-pressure Far-IR study.

**Ga₁₋ₓInₓP, GaAsₓP₁₋ₓ**
- Behaviour of 'one-mode' and 'two-mode' mixed III-V alloys under
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\[ \text{Pb}_{1-x}\text{Sn}_x\text{Te} \] Far-IR measurements undertaken at very high-pressures to investigate pressure dependence of plasmon-phonon spectra in PbTe and In doped Pb\(_{1-x}\)Sn\(_x\)Te.

\[ \text{GaSb, InAs, InSb} \] Raman scattering study. Raman frequencies increase almost linearly while the \textit{LO-TO} splittings decrease with increasing pressure.

\[ \text{As}_2\text{S}_3 \] Low frequency light scattering study up to 30 kbar in a d.a.c.

### 2.5 MINERALS

The work reported in this section falls into the following categories: the rutile system, quartz, diamond and ‘others’. A brief synopsis of the most important work will be given for each case.

**Rutile**

Nicol and Hara (104, 105) have made a re-examination of the rutile system by Raman spectroscopy. The previously reported transition at 30 kbar was detected at 35±5 kbar as the splitting of the 460 cm\(^{-1}\) \textit{E}_g mode of rutile. Weak spectral features were also observed at 200, 300, 390 and 600 cm\(^{-1}\) and were consistent with previously reported spectra of TiO\(_2\) (II). No other transitions were discovered at pressures up to 155 kbar. At 56 kbar, the Raman spectrum is reported as being consistent with a 2-formula unit CaCl\(_2\) type structure, instead of the 4-formula unit a-PbO\(_2\) structure.

In contrast, Mammone and Sharma (106) have reported that TiO\(_2\) undergoes a high-pressure phase transition at 70±5 kbar under nearly hydrostatic conditions in a d.a.c.. The presence of shear stresses appears to lower the transition pressure quite considerably (down to approximately 30 kbar). They report that the structure of the new high-pressure
phase is not that of CaCl$_2$ but appears to be the a-PbO$_2$ type structure.

Raman spectra of anatase, at pressures of up to 60 kbar and at room temperature, have been reported by Ohsaka $et$ $al$ (107). A pressure-induced phase transition was observed at pressures > 25.6 kbar. The 197 cm$^{-1}$ mode is reported to exhibit anomalous pressure dependence in which its frequency decreases with increasing pressure.

**Quartz**

Dean, Sherman and Wilkinson (108) have investigated natural quartz both as a function of temperature from 77 to 300 K, and pressures up to 10 kbar. Cooling the sample increased the vibrational frequencies with corresponding reductions in spectral line width, and the soft mode at 206 cm$^{-1}$ was shown to be very strongly temperature dependent. New results were used to calculate the mode Gruneisen parameters, $\gamma_i$, for the three strongest vibrational modes. These are reported as 3.63, 0.64 and 1.55 for the 206, 464 and 128 cm$^{-1}$ respectively.

The pressure shift of the infrared bands of crystalline quartz has been proposed as an alternative to the ruby R-line method of pressure determination by Wong, Moffatt and Baudais (109). They have reported the infrared spectra of crystalline $\alpha$-quartz measured as a function of pressure up to 50.3 kbar. Large pressure-induced frequency shifts, increases in transverse-longitudinal optical (TO-LO) splittings and softening of various phonon bands were observed. The pressure dependencies of the mode Gruneisen parameters for selected phonons were calculated.

**Diamond**

A number of high-pressure studies on diamond have been performed. Hanfland and Syassen (110) have measured the first-order Raman spectra of diamonds used as anvils in a gasketed d.a.c. under applied load. They demonstrate that Raman spectroscopy provides $in$ $situ$ experimental information on the stress distribution within the diamond anvils. At pressures of up to 300 kbar the Raman profile, as measured at the centre of the diamond tip face, displays a linear dependence on pressure within the sample volume. The application of this pressure dependence as a means of pressure measurement has been forwarded.

In a further study by the above authors and co-workers (111) the effect of pressure
upto 400 kbar on the fundamental Raman mode of diamond was determined. The mode frequency was shown to increase linearly with pressure as determined by the ruby line method. The mode frequency was calculated theoretically for extended pressures up to 600 kbar and was found to vary sub-linearly with pressure.

Boppart, Van Straaten and Silvera (112) have measured the first-order Raman spectrum of diamond upto 270 kbar. They report a shift of 0.287 cm\(^{-1}\) kbar\(^{-1}\) for the fundamental frequency with pressure.

A theoretical determination of the diamond Raman band as a high-pressure calibrant has been forwarded by Sherman (113). Using previously published results, and more precise equations than those employed by previous workers, the implications of this method for pressure determination are discussed.

Finally, for this section on diamond, Sharma et al (114) have utilised micro-Raman spectroscopy to measure first-order Raman spectra of diamonds under pressure in a d.a.c., using 180° and 135° scattering geometries. A linear pressure coefficient of 0.237 cm\(^{-1}\) kbar\(^{-1}\) has been determined for the high-frequency diamond Raman mode. The spectra obtained also provide useful information concerning stress distribution in the diamond anvil.

'Others'

Sharma, Virgo and Mysen (115) have determined the coordination of Al\(^{3+}\) in glasses of jadite composition synthesised at 1723 and 1823 K by Raman spectroscopy at pressures up to 40 kbar. The Raman spectra of the jadite glass is compared to that of SiO\(_2\) glass, with the Si-O stretching frequencies occurring at lower frequencies than those for SiO\(_2\) glass, and are weakly polarised in contrast to the depolarised bands in SiO\(_2\) glass. The shift of the Si-O bands to lower frequencies is attributed to Si(Al)-O coupled modes in the jadite glass. The weakly polarised bands may suggest that the local ordering in the jadite glass could resemble that of a-cristobalite. The Al\(^{3+}\) is reported to remain tetrahedrally co-ordinated over the pressure range investigated.

A high-pressure Raman study of spinels, Na\(_2\)MO\(_4\) (M = Mo and W) and Ag\(_2\)MO\(_4\), scheelites, M'\(_4\)MO\(_4\) (M' = Ca, Sr, Ba and Pb) and of scheelite-type rhenates, M'\(_4\)ReO\(_4\) (M' = Na, K, Rb, Ag and NH\(_4\)^+) has been carried out by Breitinger et al (116). The internal
modes for rhenates with high force constants displayed small or medium pressure dependencies, in contrast to the highly pressure dependent lattice modes. These pressure dependencies were correlated to vibrational amplitudes and anharmonicities.

Velde and Besson (117) have examined the Raman spectra of natural analcime upto 9.4 kbar. They report that the basic Si, Al-O network vibrations are affected only to a slight degree by pressure, even though significant volume changes and a minor phase transition occur. The bonded water in analcime appears to remain in the mineral at high-pressure. The bulk volume change, as determined previously by unit cell dimension measurements, can be attributed to a reduction of the size of the internal cavities in the structure. This is deduced from the fact that the Si-Al-O vibrations are display weak pressure dependence, whereas the O-H vibrations of water molecules found in the cavities are observed to be strongly pressure dependent.

Further work on minerals and mineral-type systems inculde the following:

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2.6 ICE

Ice is a unique material. At varying pressures and temperatures nine well characterised phases exist and evidence for a new phase, (X), has been formulated.

It is obvious that there is still a vast area of P-T space left unexplored. The work presented in this section will hopefully serve as a guide to this fascinating material.

Johari and Sivakumar (130) have studied the effect of pressure on the Raman spectrum of the translational lattice vibrations of ice 1. They observed that the frequency of the main peak, \( \nu_1 \), at 255.4±0.2 K, increases linearly with pressure from 214.2 cm\(^{-1}\) at 1 bar to 222.0 cm\(^{-1}\) at 1.57 kbar. The reported frequencies decrease almost linearly with increasing temperature in the range 250-266K. The pressure coefficient \((\delta \nu_1/\delta P)_T\) and temperature coefficient \((\delta \nu_1/\delta T)_P\) were determined as 4.77 cm\(^{-1}\) kbar\(^{-1}\) at 255K and -0.134 cm\(^{-1}\) K\(^{-1}\) at 1 bar. The two coefficients remained constant with variation in either temperature or pressure. Explicit temperature and volume effects were evaluated. The
Gruneisen constant, $\gamma = -\frac{\delta \ln \nu}{\delta \ln \rho}$ was calculated as 1.86 at 255 K.

Abbe and Walrafen (131) have investigated the pressure dependence of the Raman O-H stretching peak frequency over the entire ice VI phase region from approximately 9 to 21 kbar. The peak frequency is recorded as a linear function of pressure. The data yielded a slope of $7.2\pm0.2 \text{ cm}^{-1} \text{kbar}^{-1}$, a larger value than that previously recorded for liquid H$_2$O ($2 \text{ cm}^{-1} \text{kbar}^{-1}$).

An in-depth high-pressure investigation of the phases of ice has been carried out by Sukarova, Sherman and Wilkinson (132). The Raman spectra of ices I$_h$, II, III, V, VI and IX of H$_2$O, D$_2$O and 2% D$_2$O in H$_2$O were measured at pressures up to 6.5 kbar and temperatures down to 140 K. The Raman spectra of ices II and V were measured over a wide range of temperatures and pressures. The temperature dependence of ice VI was followed and an attempt made to detect the ice VI to ice VI' transition. Results for the ice III to ice IX disorder-order transition were obtained and compared to that previously obtained by dielectric methods.

Walrafen et al (133) collected Raman data for the ice VII phase upto 300 kbar, and x-ray lattice parameters up to 360 kbar, all at room temperature. Both the Raman O-H stretching frequency and the edge distance of the b.c.c. unit cell were observed to decrease with a decreasing rate with pressure. A value of $2.35(6) \text{ Å}$ for the nearest O-O nearest neighbour was determined. This compares favourably with the value $2.4 \text{ Å}$ found for the symmetrical O-H-O units in other materials.

The effects of pressure on the Raman spectra of ice VIII and the evidence for the existence of ice X has been given by Hirsch and Holzapfel (134). They measured the Raman spectra of H$_2$O and D$_2$O ice VIII up to 500 kbar and at a temperature of 100 K. The appearance of a new band, together with changes in peak positions and intensities above 400 kbar, indicate the existence of a new phase, ice X. A lattice dynamical analysis of the data up to 360 kbar suggests a second-order phase transition to symmetrical hydrogen bonds near 475 kbar. The observed changes in the lattice mode frequencies, however, indicate the new phase has already been formed by a first-order phase transition at 420 kbar.
Further work includes:

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## 2.7 ORGANICS

High-pressure investigations involving organic materials are numerous. Many diverse systems have been studied, from exceptionally simple organic compounds to large and complicated polymeric macromolecules. In certain instances, repeated studies have been undertaken on various organic systems. The major areas of interest, in terms of high-pressure research, are examined in sub-sections with the remainder tabulated as in previous category types.

**Benzene**

A Raman study of benzene-d$_6$ at high-pressure has been performed by Tanabe and Jonas (144). The totally symmetrical $v_1$ and $v_2$ bands, in addition to 5 degenerate modes ($v_{11}$, $v_{15}$, $v_{16}$, $v_{17}$ and $v_{18}$) were measured in liquid benzene-d$_6$ as a function of pressure up to 4 Kbar and between 30 - 120°C. The results obtained show that all bands have an increased vibrational relaxation width with increasing pressure, but that the variation with temperature appears to be specific for each individual band.

An investigation of benzene at pressures up to 1.53 GPa has been undertaken by Schmidt and co-workers (145, 146) using shock-compression techniques. The pressure-induced frequency shifts detected for the ring-breathing mode for neat benzene were found to be in agreement with previously obtained results. These were compared to benzene compressed isothermally in a d.a.c.. Evidence for nearest-neighbour effects on vibrational frequency shifts is discussed.
Asenbaum and Hochheimer (147) have recorded Brillouin scattering spectra at pressures up to 1.3 Kbar and at varying temperature. Various theoretical models are discussed in the interpretation of the results obtained.

Thiery et al (148) have obtained Raman spectra of solid benzene in a d.a.c. up to pressures of 15 GPa. The pressure dependencies of the intramolecular and lattice vibration modes were used to determine the different solid phases of benzene. Discontinuities observed at around 45 Kbar are believed to correspond to the previously reported II - III phase transition. The appearance of a new band at around 90 Kbar suggests the formation of a new phase, IV. A tentative phase diagram displaying the II - III, and the III - IV phase boundaries is presented.

Two further studies by Schmidt and co-workers have also been reported:

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Pyridine

Podini and Schnur (151) have used the technique of surface enhanced Raman spectroscopy (SERS) to observe pyridine at pressures up to 4 Kbar. A full description of the preparative techniques used in the study, together with the reliability of the measured parameters such as linewidth, frequency, and intensity are given.

A Raman study of pyridine at elevated hydrostatic pressures has been reported by Jia et al (152). The pressure behaviour of the vibrational modes above phase transitions were studied. They observed a type of crystalline - plastic phase transition in the region of 60 Kbar.

Heyns and Venter (153) have recorded two modifications of pyridine after solidification of the liquid at 10 Kbar and at 300 K in a d.a.c.. One modification is
crystalline in nature and is characterised by narrow and well-defined lattice modes, and undergoes a phase transition at 20 Kbar. The other has fewer, and broader, lattice modes. The Raman spectra obtained for these modifications are in conflict with the reported space group for solid pyridine obtained on cooling the liquid at atmospheric pressure. Pressure dependencies of the crystalline phase indicates its closeness in type to the monoclinic phase II in planar aromatic molecules, such as benzene. The second modification resembles a glassy phase previously reported from infrared experiments.

A semi-theoretical study on vibrational frequency shifts induced by molecular compression of pyridine in solution has been carried out by Zakin and Herschbach (154). Simplified theoretical models were used to calculate the pressure dependencies of the ring-breathing mode in varying solvents.

**Carbon disulphide**

Shimazu (155) has reported high-pressure Raman data on liquid and crystalline CS$_2$ to 45 Kbar. Pressure dependencies for the internal and 4 librational lattice modes are reported. The $\nu_1$ mode increases very little with pressure due to exceptionally strong S-C-S bonding. The $2\nu_2$ overtones of the bending modes in the liquid state are split by 18 cm$^{-1}$ into two cleanly resolved major peaks at the liquid-solid transition point (approximately 13 Kbar). Comparison of the Raman spectra of high-pressure crystals with those obtained at low-temperature at atmospheric pressure indicates a similarity in structure type.

The effects of pressure on both polarised and depolarised Raman spectra of liquid CS$_2$ for properties such as peak frequencies, bandwidths, and relative intensities of the allowed $\nu_1$ and $\nu_2$ bands, and the interaction-induced $\nu_2$ and $\nu_3$ bands were obtained at pressures up to 10 Kbar by Ikawa and Whalley (156). The $\nu_1$ band is reported to shift at the rate 0.16 ± 0.01 cm$^{-1}$ Kbar$^{-1}$. The shifts of the $\nu_1$ and $2\nu_2$ bands suggest that the C-S bond length decreases at the rate in the region of 2 x $10^{-4}$ Å Kbar$^{-1}$.

Agnew et al (157) have used the d.a.c. with a combination of spectroscopic techniques including Raman, infrared, and UV-visible-near IR absorption to analyse the behaviour of CS$_2$ at elevated pressures up to 10 GPa.

**The dihalomethanes**

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The dihalomethanes, $\text{CH}_2\text{X}_2$ (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been the centre of a series of investigations, using both Raman and FT-IR spectroscopies, undertaken by Shimizu (158-162). A summary of the work performed is as follows:

$\text{CH}_2\text{Cl}_2$, $\text{CH}_2\text{Br}_2$, $\text{CH}_2\text{I}_2$; studied up to 100 Kbar in a d.a.c.. The pressure dependencies of the internal and external (lattice) modes, pressure-induced phase transitions, and the pressure-tuning resonance between the internal and external modes have been recorded and discussed.

$\text{CH}_2\text{Cl}_2$; a high-pressure study to 85 Kbar. The $\nu_4$ symmetrical $\text{CCl}_2$ bending mode splits into 2 major components at 11.3 Kbar, the liquid - solid transition point. A second-order phase transition is reported at approximately 45 Kbar.

$\text{CH}_2\text{Br}_2$; A maximum pressure of 100 Kbar was achieved in a gasketed d.a.c. in this investigation. The $\nu_4$ symmetrical bending mode, and the pressure-sensitive vibrational mode were observed to cross at approximately 45 Kbar. Changes in peak intensities and frequency behaviour with pressure are discussed in terms of resonance interaction between two states of the same type (pressure-tuning resonance).

Other investigations on the dihalomethanes of note include:

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The trihalomethanes

Following on from the dihalomethanes are the trihalomethanes, or more commonly the haloforms, CHX$_3$ (where X = Cl, Br, I).

Shimizu (166, 167) has studied both CHCl$_3$, CHBr$_3$ and their deuterated analogues. CHCl$_3$ and CDCI$_3$ have been studied by Raman spectoscopy to pressures of 100 KBar at 300 K in a gasketed d.a.c.. The liquid - solid transition is observed to occur at 6 Kbar. The existance of a further pressure-induced phase transition is postulated in the region of 46 kbar.

CHBr$_3$ and CDBr$_3$ have been similarly studied. The solid - solid α - β phase transition is reported at 10 Kbar. The β - γ transition occurs at 42 kbar, with a mixture of β and γ phases existing between 35 to 55 Kbar. The γ phase is reported to be metastable at ambient conditions, becoming stable at pressures above 42 Kbar.

Zhao et al (168) have studied CHCl$_3$ and CHBr$_3$ in both the liquid and crystalline state by use of Raman spectroscopy at pressure of up to 102 Kbar and at room temperature. For CHCl$_3$, all of the E modes ($\nu_4$, $\nu_5$, and $\nu_6$) are split into 2 peaks at the liquid - solid transition point which occurs at 7.9 kbar. A further phase transition is suggested by discontinuities in (du/dP) for the internal modes and is observed in the region of 60 Kbar. CHBr$_3$ has been reported as having 3 pressure-induced phase transitions. The first, the liquid - solid (liquid - α) transition is observed at 3.3 Kbar. The α - β transition and the β + γ transition occur at 8 Kbar and 51.5 - 95 Kbar respectively. The pure β phase of CHBr$_3$ was obtained at pressures in excess of 95 Kbar.

Two other investigations of the haloforms include:

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The 'Rest'

Yacoby and Roth (171) have undertaken a resonant Raman scattering study of trans-polyacetylene. Spectra were obtained up tp 44 Kbar in a d.a.c.. Comparison of the pressure dependence of the 1295 cm⁻¹ band with the dependence on the photon energy of the laser exciting line enabled the detection of the pressure variation of the electronic energy gap. The results proved consistent with previous measurements of the absorption spectrum under hydrostatic conditions carried out to 13.5 Kbar. The gap is found to decrease with pressure. The results are consistent with a model in which chain - chain interactions play a dominant role.

Coter et al (172) have studied the 3 resonantly enhanced Raman lines of polyacetylene under hydrostatic conditions to 8 Kbar, using various laser excitation wavelengths. An interpretation of the results is proposed within the framework of the Amplitude Mode (AM) theory with varying interchain coupling.

Raman spectra of methanol and ethanol have been measured at pressures up to 100 Kbar at room temperature by Mammone, Sharma, and Nicol (173). Methanol is found to form either a glass or a crystalline phase at these pressures, whereas ethanol is always crystalline. The crystallisation pressure for methanol is reported as 35 ± 1 Kbar. Comparison of Raman spectra obtained from high-pressure crystals with those from low-temperature a-methanol suggests that the high-pressure structure is similar in type to the low-temperature form. Ethanol was found to crystallise at 17.8 ± 10 Kbar and its Raman spectra were interpreted in terms of the monoclinic space group, P̄c (Z = 4), of the low-temperature form.

A high-pressure infrared spectroscopic investigation of 1-hexanol has been undertaken by Schioeberg et al (174). The O-H stretching vibration of the H-bonded OH group splits into 2 bands at high-pressure, indicative of an O-H....O-H chain structure. Normal co-ordinate analysis of a linear chain gives rise to parameters such as force constants, and the correlation of the in-phase and out-of-phase O-H streching vibrations.

Ebisuzaki (175) has studied carbon tetrachloride, CCl₄, by Raman spectroscopy at high-pressures. Spectra of CCl₄ phase I and CCl₄ III, and the changes in Raman activity at the II-III phase transition are reported. CCl₄ II is characterised by low-intensity lattice
modes, and by the appearance of side bands on both the high- and low-energy sides of the internal modes, $v_2$ and $v_4$. These sidebands become Raman inactive at the II-III phase interface with an increase in the intensity of the lattice bands. The major lattice peaks appear to be Raman active in both phases. CCl$_4$ III is reported to be an ordered phase, whereas CCl$_4$ II appears to contain some orientationally disordered molecules.

The remainder of the references for this section are outlined below, with brief comments, as in previous sections:

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1,3,5-trinitro 1,3,5-triazo cyclohexane

Effect of temperature and pressure up to 30 Kbar on the Raman active internal and external modes.

Acetic acid

Detection of the phase diagram below 0°C and 2 Kbar. X-ray powder diffraction data and far-IR absorption spectrum of phase II at ~100 K.

Urea

Three polymorphic phases detected and investigated by Raman spectroscopy.

Napthalene, Napthalene-d₈

Influence of pressure on the lattice vibrations in single crystals. Raman study up to 8.5 Kbar.

d-Camphor

Raman and IR study of the carbonyl stretching mode as a function of temperature and pressure.

Acrylonitrile, poly-acrylonitrile

IR study to 50 Kbar. The liquid freezes at ~100 Kbar. A phase transition occurs near 27 Kbar.

Me₂CO

Raman study of the C=O stretching band as a function of pressure to 4 Kbar.

n-alkanes, n-perfluoro alkanes

Raman study on pressure effects to 6 Kbar.

C(Me)₄, Si(Me)₄, Ge(Me)₄, Sn(Me)

High-pressure investigation of vibrational relaxation in liquid group IV tetramethyl compounds. Maximum pressure achieved was 4 Kbar.
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DCOOD  Raman spectra of crystalline deuterated formic acid at pressures upto 100 Kbar in a gasketed d.a.c. A phase transition was observed near 45 Kbar.

Polyphenols  The IR spectra of polyphenols measured at pressures ≤ 50 Kbar.

Haeme-proteins  High-pressure study to 34 Kbar. Resonance Raman investigation of deoxy-, CO-Hb and deoxymyoglobin.

2-Adamant-anone  Pressure dependence of the Raman-active bands at pressures upto 21 Kbar. Large hysteresis was observed. Transitions were detected at 10±0.2 and 6.9±0.2 Kbar for the compression and decomposition cycles respectively.

2.8 INORGANICS

Without doubt, the largest single class of compounds studied in high-pressure investigations, according to the available literature, is that of the inorganics.

The sub-division ‘inorganics’ covers simple materials, such as the alkali metal halide systems MX (where M = Li, Na, K and Rb and X = Cl, Br and I) to extremely complex formula types overlapping with the formation of synthetic minerals.

Some of the work is repetitive, with workers re-checking previous work, either in the light of new investigations performed on the material or in comparison to work performed on analogous compounds.

As in previous sections, reference will be made to individual or group works undertaken with a comprehensive reference collection at its conclusion.
The ammonium halides have been the focus for intensive investigation. They are relatively simple structures with known crystal structures (an important factor in the interpretation of high-pressure vibrational spectra) and, most importantly, exhibit interesting phase behaviour with variance in both pressure and temperature.

The principal investigators of the ammonium halide systems are Hochheimer and Holzapfel.

Hochheimer reported Raman spectra of three CsCl-type phases of NH$_4$Br and NH$_4$I which exhibit differences in the orientation of the NH$_4$ tetrahedra (204). In phase (IV), which has T$_d$ symmetry, the tetrahedra are equally orientated. The two possible orientations allowed are randomly occupied in phase (II) having O$_h$ symmetry. The tetragonal phase (III) (D$_{4h}$ symmetry) has neighbouring tetrahedra equally orientated along the tetragonal axis. The Raman spectra of the three phases are reported to differ markedly. Phase diagrams for NH$_4$Br and NH$_4$I are postulated.

Hamman (205) has recorded the IR spectra of 33 polycrystalline ammonium salts (including the ammonium halides). The salts behave as though they have very strong hydrogen bonding.

Hochheimer et al. (206) have studied phases I, II, III and IV by Raman spectroscopy at pressures up to 7 kbar for NH$_4$Br and NH$_4$I. Pressure dependencies are reported for the lattice modes observed. Theoretical models are examined in relationship to the data obtained.

Heyns, Hirsch and Holzapfel have studied NH$_4$I and its deuterated analogue at high-pressure (207). Changes observed in the Raman spectra indicate the existence of a new phase. The phase occurs upon further compression of phase IV, which is ferro-ordered. The same type of transition is reported to occur in NH$_4$Cl and NH$_4$Br but at significantly higher pressures.

The same authors (208) have published a more detailed account of the above work. Pressures up to 130 kbar were employed. The II - IV transition is reported to occur at approximately 27 kbar at room temperature. At higher High-pressures in phase IV a volume effect becomes significant and this probably gives rise to the IV-V transition.
occuring at 54 kbar.

The effect of pressure on the Raman spectra of NH$_4$Cl has been studied by Heyns (209). The pressure range utilised was from 10.6 - 131 kbar. All measurements were made at room temperature. Above 110 kbar Heyns observed a large number of lattice modes and that some of the internal modes were altered. It is suggested that these features arise from the existence of phase V reported by previous work. As a final note, Heyns comments that the IV - V transition pressures appear to vary linearly with the anionic radius.

Further work by Heyns, Hirsch and Holzapfel (210) on NH$_4$I and ND$_4$I postulates further the existence of phase V in ammonium halides, but states that it's existence should not be confused with the, as yet, unsubstantiated phase 'V' in NH$_4$Br and NH$_4$Cl. The link between the IV-V transition pressures and anionic radii is further discussed. The assumption is that it is a volume effect that is primarily responsible for the transition to the 5th phase.

Schwake, Hirsch and Holzapfel (211) have further studied the effect of pressure on the $v_5(\text{TO})$ lattice mode in addition to the internal modes $v_1$, $v_3$ and $v_2 + v_4$ for phase IV of the NH$_4$Br at 100 K. The location of the IV-V transition boundary was determined by changes in the Raman spectra recorded in the temperature range 100 - 300 K at a constant pressure of 65 kbar. The II - IV phase transition displays a strong decrease of its pressure dependence indicating the existence of a triple point of the phases II - IV - V in the region of 350 K and 65 kbar.

Finally, for the ammonium halides, Zou et al (212) have studied NH$_4$F by Raman spectroscopy at pressures above 200 kbar. They report two new phases V and VI at 15 and 143 kbar respectively. Kinetic studies for the transition of the soft mode from phase V to VI in NH$_4$F at 143 kbar were also undertaken.

HgI$_2$ is a simple inorganic material commonly employed as a simple visual test of the anvil alignment in a d.a.c..

Adams and Appleby (213, 214) have reported far-IR and Raman data upto 400 K and 10 kbar in addition to single crystal reflectance and Raman spectra down to 80 K. They observed from differences observed in the spectra obtained that the
high-temperature and high-pressure yellow forms have different structures. No evidence was found to support the proposed temperature-induced transition to HgI$_2$ (IV). Pressure versus frequency plots show a possible II - III phase boundary at 610.5 kbar.

A later study by Khiliju, Sherman, Stadtmüller and Wilkinson (215) confirms the difference between the high-temperature and high-pressure yellow forms of HgI$_2$. Again, no evidence was found to support a III - IV phase transition. However, a previously unreported Raman spectrum of an orange phase of HgI$_2$ is discussed together with possible modifications to the known phase diagram.

Studies of $X_2$, IX and HX (where X is a halogen) have been undertaken by Holzapfel and fellow workers (216-219). Their results can be best summerised as follows.

1983: Solid Br$_2$ up to 330 kbar by Raman spectroscopy with overlap of the two intramolecular peaks occurring at 240 kbar.

1984: Raman study on HCl and HBr. The temperature range was 100 - 250 K, pressure up to 400 kbar. Ar and N$_2$ were used as the pressure media. A new phase was detected for HBr at 100 K and at pressures above 320 kbar.

1985: Cl$_2$, Br$_2$ and I$_2$ studied by Raman and energy dispersive x-ray techniques. Br$_2$ was studied up to 350 kbar and Cl$_2$ to 450 kbar. A comparison of the results with those previously obtained for I$_2$ gave estimated transition pressures of 450±10 kbar for Br$_2$ and 1300±200 kbar for Cl$_2$. Lattice dynamical calculations were shown to reproduce the Raman data reasonably well. This gave transition pressures of 500±100 kbar for Br$_2$ and 1200±200 kbar for Cl$_2$.

1986: ICI and IBr studied by Raman spectroscopy at pressures up to 200 kbar in a d.a.c.. The IBr spectrum displayed drastic changes between 60 - 90 kbar representing a possible phase transition or transitions.

Adams and Hatton (220) studied the effect of pressure on Hg(CN)$_2$. They reported phase transitions near 2.5, 8.0, 19.0 and 60.0 kbar. The I - II transition was second-order. Use of Landau theory identified three possible structures for phase II, $S_4^2$ being identified as the most likely. Major reconstruction of the lattice is thought to occur at the II - III phase boundary with the co-ordination number of the Hg increasing to four. The structure
is presumed to be covalently bonded rather than molecular in nature. Phase IV displayed a Raman spectrum consistent with that for the cubic anticuprite structure. At pressures in excess of 60 kbar a brown polymeric phase V was observed to form irreversibly.

In contrast, a later paper by Wong (221) appears to have the two lower pressure transitions previously reported. Wong states that the v(CN) band appears as a singlet in the pressure range 0 - 16 kbar. It becomes a doublet, shifting to lower frequency at 20 kbar where the phase transition occurs (in agreement with Adams and Hatton). He records the existence of a second structural transition at 40 kbar.

Later work by Hatton (Ph.D. Thesis) substantiated the original findings given in (220).

The molecular Chalcogenides As$_4$S$_4$ and S$_4$N$_4$ have been investigated at pressure and temperature by Zallen, Slade and Lin (222). They report that the overall response to pressure of the phonons and S$_4$N$_4$ was qualitatively similar for both compounds. A systematic correlation between pressure sensitivity and mode frequency was found.

Crystalline P$_4$S$_3$ has also been studied. Chattopadhyay et al (223) have recorded Raman spectra for P$_4$S$_3$ as a function of temperature (10 - 320 K) at ambient pressure, and at elevated pressures upto 86 kbar at room temperature. The external modes, determined as being due to the librational modes of the molecules in the crystal, were observed to completely disappear at the crystal-plastic phase transition near 314 K. The external mode frequencies were reported to be strongly pressure-dependent. The internal mode frequencies appear to be less affected by pressure. Crystal field and Davydov splitting are revealed at sub-ambient temperatures because of line narrowing. These are enhanced at pressure because of stronger intermolecular interaction resulting from compression.

DeBeer and co-workers (224) have investigated the high-pressure and high-temperature phase relations and vibrational spectra of CsSbF$_6$. Under ambient conditions, CsSbF$_6$ phase II is trigonal having the space group D53d (R3-m). CsSbF$_6$ decomposes with the loss of fluorine at atmospheric pressure and elevated temperatures. Utilisation of high-pressure in conjunction with high-temperatures prevents the decomposition. Use of this technique has enabled the II - I phase boundary and melting curve to be determined for this compound. IR and Raman spectroscopies were employed as the main diagnostic tools.
An investigation on the pressure-induced reduction of Fe(III) salts has been carried out by Lewis and Whalley (225). They undertook a series of experiments to test whether the reported reduction of Fe(III) compounds under pressure was triggered by hydrostatic stresses or shear deformation. Firstly, the Raman spectrum of a single crystal of K₃[Fe(CN)₆] was recorded under hydrostatic pressure up to 19 kbar. The observed spectrum showed no evidence of reduction. A single crystal of K₃[Fe(CN)₆] was subjected to a hydrostatic pressure of 45 kbar. The crystal was recovered at zero pressure. Again, its Raman spectrum was unchanged. The reported reduction is said to occur with considerable hysteresis - and thus should have been easily detectable. In a final experiment, they subjected a single crystal of KCl, with K₃[Fe(CN)₆] dissolved in it, to repeated hydrostatic pressurisations up to 25 kbar. Its IR spectrum was recorded after each pressure cycle. They reported that pressures lower than that for the CsCl transition to occur caused no detectable change in the recorded spectra. Above this pressure, reduction to K₄[Fe(CN)₆] was observed and more reduction occurred with each pressure cycle. They concluded that the evidence supports reduction due to shear, rather than hydrostatic pressure.

Wong (226) has studied the effect of pressure on K₂Hg(CN)₄. The ferroelastic phase transition at 1.5 kbar and room temperature was observed to exhibit pseudo-second-order behaviour. In addition, two first-order structural transitions were observed near 5 and 12 kbar respectively. It is presumed that these transitions are driven by a soft-mode at 44 cm⁻¹ (1 kbar) and two at 38 and 44 cm⁻¹ (8.6 kbar).

High-pressure Raman spectra of KClO₃ in a d.a.c. were obtained by Heyns (227). The effects of pressure on the lattice modes were more pronounced than for the internal modes, which shifted at a lower rate with pressure in comparison. The I - II transition occurring at approximately 7 kbar was reported to be sluggish. The largest observable changes occurred in the ν(Cl-O) bands, namely ν₃ shifting from 982 to 943 cm⁻¹ and ν₁ from 943 to 934 cm⁻¹. The Raman spectra of KClO₃ II were observed to be similar in nature to those of RbClO₃ indicating the rhombohedral nature of phase II. Further work using synchrotron radiation as the principal investigative means is reported elsewhere (Chapter 4).

The use of nitrite and nitrate ions as potential pressure sensors is discussed by Klug and Whalley (228). Measurements of the antisymmetric stretching bands in dilute
solutions of NO$_2^-$ and NO$_3^-$ ions in NaBr were measured up to 186 kbar, relative to the established ruby fluorescence scale of pressure calibration. The pressure determination is related to the shift, $\Delta \nu$, of the frequency of the nitrite ion (at 295 K) from the zero-pressure value (1279.0 cm$^{-1}$) by the equation:

$$P/\text{kbar} = 2.35(\Delta \nu/\text{cm}^{-1}) - 1.334(\Delta \nu/\text{cm}^{-1}) \exp(-\Delta \nu/92\text{cm}^{-1})$$

Similarly for the nitrate ion (which has a zero-pressure value of 1401.3 cm$^{-1}$):

$$P/\text{kbar} = 1.775(\Delta \nu/\text{cm}^{-1}) - 0.7495(\Delta \nu/\text{cm}^{-1}) \exp(-\Delta \nu/78\text{cm}^{-1})$$

Both equations were refined by least-squares methods with the assumption that the errors lie in the pressure only. The reliability of the method is discussed.

Further investigations of inorganic systems are referenced below:

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and are resistant to pressure.

$\text{Co}_3(\text{CO})_9\text{COMClCp}_2$
(M = Ti, Zr, Hf),
$[\text{Co}_3(\text{CO})_9\text{CO}]_2\text{MCP}_2$
(M as above)

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4.5 and 27 Kbar respectively.

RbNO₃, CsNO₃  Mid-IR and Raman study upto 125 Kbar. CsNO₃ III-IV transition observed. CsNO₃ III/IV mixed phase occurs between 72-109 Kbar.

SiO₂  Raman spectra of pressure compacted fused SiO₂.

Cdₓ₂, PbFₓ (X=Cl,Br,I)  Pressure-dependencies of the Raman active modes of the title compounds were determined. Pressures upto 40 kbar were achieved.

K₂M(CN)₄ (M=Zn,Cd,Hg)  Each of the complex cyanides in the investigation display 2nd order phase transitions characterised by Raman spectroscopy. A summary of the recorded transition pressures is as follows:

M=Hg  1.5, 1.8 Kbar
M=Cd  3.0, 8.0 Kbar
M=Zn  4.0, 14.0 Kbar

M(NO₃)₃ (M=La,Pr,Nd)  Effects of temperature and pressure recorded by IR spectroscopy.

Phosphorous  A pressure study on the lattice vibrations. The rhombohedral to orthorhombic transition was observed at 52 Kbar.

BH₄⁻/RbI  The internal and external modes of the BH₄⁻ ion in RbI crystals were studied by Raman spectroscopy as a function of temperature and pressure.
Investigation of the lattice vibrations by Raman spectroscopy at pressures upto 180 Kbar.

A high-pressure Raman investigation on ZnS with transition metal impurities (Cr, Mn, Fe, Co and Ni) upto 40 Kbar. Theoretical calculations were carried out with the pressure-dependencies data obtained.

Pressures upto 450 Kbar. UV and IR study in a d.a.c.. The potential use of CsI as a pressure calibrant is also discussed.

An IR study of the effects of pressure (maximum achieved was 110 Kbar) on the crystal field splitting of the Co\textsuperscript{2+} in doped in CdTe.

Fe\textsuperscript{II} complexes investigated in a d.a.c. under hydrostatic conditions to 40 Kbar.

KNO\textsubscript{3} studied to 12 Kbar. The II-IV transition was observed at 4 Kbar. NH\textsubscript{4}NO\textsubscript{3} was also studied to 12 Kbar. The data suggests a phase transition near 6.5 Kbar.

High-pressure Raman, optical microscopy and electrical conductivity measurements performed.
The pressure-volume relation of Rb was investigated by high-pressure x-ray diffraction techniques up to 110 Kbar. Near-IR reflectivity data was collected up to 250 Kbar. The Rb(I) to Rb(II) phase transition (bcc to fcc) was observed at 70±2 Kbar. Other transitions were seen at 128, 160 and 190 Kbar respectively.

Rb

ZrS₃

Raman scattering results recorded as a function of hydrostatic pressure.

NH₄ReO₄

Pressure-dependencies of ν₂ and ν₄ were recorded. There were no observable phase transitions at pressures up to 15 Kbar.

Mn(CO)₅Br

Raman high-pressure study to 50 Kbar. A second-order transition was detected at 24±3 Kbar.

TlInSe₂, TlGaS₂, TlGaSe₂ and TlInS₂

Raman investigation as a function of pressure at constant temperatures. (300 and 110K)

LiTmF₆

Raman and IR reflection spectra in paramagnetic LiTmF₆ recorded at pressures up to 12 Kbar.

ZnSe

The pressure-dependencies of the Raman spectrum were recorded.

KN₃

A polarised Raman investigation on a single crystal and as a function of temperature and pressure (powder).
ZrO$_2$  
High-pressure Raman study obtained using (i) MeOH and (ii) NaCl as the pressure transmitting media. For MeOH a transition is recorded at 35 Kbar in comparison to 54 Kbar for the NaCl media.

Hg$_2$Cl$_2$ and Hg$_2$Br$_2$  
The pressure and temperature dependence of the Raman-active soft-mode in both of the title compounds was determined. The data obtained were compared to those found in an earlier study for Hg$_2$I$_2$.

K$_2$SeO$_4$  
The effect of uniaxial stress along the orthorhombic $c$ axis of single crystals was studied using Raman spectroscopy.

LiNH$_4$SO$_4$  
A single-crystal Raman scattering study under hydrostatic pressure conditions up to nearly 1 Kbar.

M(CO)$_6$  
(M=Cr,Mo,W)  
Re(CO)$_3$Br,  
M$_2$(CO)$_{10}$  
(M=Mn,Re)  
MnRe(CO)$_{10}$,  
Hg(CN)$_2$,  
K$_2$M(CN)$_4$  
(M=Zn,Cd,Hg)  
and K$_3$Cu(CN)$_4$  
Raman spectra were used to characterise the phase transitions of the title compounds. The structures of some of the phases were deduced from group theoretical methods.

BaTiO$_3$ and PbTiO$_3$  
A high-pressure Raman investigation of ferroelectric to paraelectric phase transitions. Transition pressures were 19 Kbar(Ba) and 110 Kbar(Pb).
<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCl₂</td>
<td>Raman study upto 80 Kbar. Grueneisen parameters are presented.</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>Raman studies of vitreous B₂O₃ between 8-700K and pressures upto 8 Kbar.</td>
</tr>
<tr>
<td>Sn₂P₂S₆</td>
<td>The effects of hydrostatic pressure on the ferroelectric Sn₂P₂S₆ were studied by Raman spectroscopy. A 2nd-order phase transition was observed at 2 Kbar.</td>
</tr>
<tr>
<td>NO₃⁻/KI</td>
<td>An extension of the study quoted in reference 74.</td>
</tr>
<tr>
<td>LaF₃</td>
<td>The first-order Raman spectrum was recorded upto 100 Kbar and between 60-900K. Anharmonicity calculations and mode Grueneisen parameters are presented from the data obtained.</td>
</tr>
<tr>
<td>BeO</td>
<td>The effect of pressure on the TO phonon modes was recorded for pressures upto 200 Kbar.</td>
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<td>CdS</td>
<td>A hydrostatic pressure study to 42 Kbar and temperatures down to 6K. Luminescence and Raman spectra were obtained.</td>
</tr>
<tr>
<td>HgTe</td>
<td>A pressure - temperature study to 8 Kbar and ≤ 80K. A Kramers-Kronig analysis of the data obtained was undertaken.</td>
</tr>
<tr>
<td>PbMoO₄ and PbWO₄</td>
<td>High-pressure Raman spectra obtained upto 100 Kbar. First-order transitions were observed at 90 Kbar for PbMoO₄ and PbWO₄</td>
</tr>
</tbody>
</table>
45 Kbar for PbWO₄.

RbNO₃ and CsNO₃

Raman spectra recorded upto 18 Kbar.

6H-PbI₂

A high-pressure Raman investigation of two solid phases of 6H-PbI₂ at ambient temperature. Maximum pressure achieved was 14 Kbar.

InS

The ferroelectric properties of InS were studied by Raman spectroscopy at 300K and at pressures upto 120 Kbar. The data obtained suggests a $D_{2h}^{12}$ to $D_{2h}^{17}$ phase transition at 70±15 Kbar.

Tl₂CO₃

Raman spectra obtained to 52 Kbar and IR data to 36 Kbar. Single crystal IR and Raman data are also presented.

InPS₄ and Cu₂PS₃I

A study by Raman spectroscopy on the effects of hydrostatic pressure on the title compounds. Potential energy curve calculations are presented.

α-LiIO₃

A Raman investigation as a function of temperature an pressure.

Hg(SCN)₂

High-pressure investigation by Raman spectroscopy. A new phase transition is observed near 35 Kbar which displays considerable hysteresis.

MnRe(CO)₁₀

Raman study. Two first-order phase transitions are observed near 7 and 13 Kbar. The changes in the spectra are
interpreted as staggered to eclipsed to staggered molecular geometry.

RbCN  Raman and Brillouin spectra obtained to a pressure of 80 Kbar and temperatures down to 80K.

A₂HgI₄  Raman spectra and phonon dependencies with pressure are presented. The data is summerised as follows:

\[
\begin{align*}
\text{Cu}_2\text{HgI}_4 & : 8, 25 \text{ Kbar} \\
\text{Tl}_2\text{HgI}_4 & : 11.5 \text{ Kbar} \\
\text{PbHgI}_4 & : 7, 14 \text{ Kbar} \\
\text{Ag}_2\text{HgI}_4 & : 3.3, 5.9 \text{ and } 8.1 \text{ Kbar}
\end{align*}
\]

CdI₂, SnS₂ and SnS₂  A Raman investigation. Also, x-ray diffraction measurements on CdI₂ are presented, giving the variation in lattice parameters with hydrostatic pressure.

ZnSiP₂  A Raman high-pressure study to 52 Kbar. Mode Gruneisen parameters for each Raman mode were obtained.

PbTiO₃  A raman study of the ferroelectric tetragonal PbTiO₃ as a function of pressure. Use of the Liddane-Sachs-Teller (LST) relataon results in then calculation of the static dielectric constant as a function of pressure.

CaWO₄, SrWO₄ and BaWO₄  High-pressure investigation to 90 Kbar in a d.a.c.. A reversible first-order transition was found near 65 Kbar for BaWO₄.
$\beta$-LiO$_3$  Continuing work begun in reference 110. The maximum pressure obtained was 90 Kbar. A new phase occurs beyond 50 Kbar.

GeS$_2$  Cryobaric Raman measurements are shown for amorphous GeS$_2$ at 13K and pressures upto 56 Kbar. Quasicrystallisation is observed to occur at 56 KBar.

K$_2$SO$_4$ and K$_2$SeO$_4$  Room-temperature polarised Raman spectra were collected upto 100 Kbar. Raman back-scattering configuration was employed.

NH$_4$NO$_3$  IR spectra were obtained at pressures $\leq 6$ Kbar. A P-T phase diagram for the $\lambda$-transition of NH$_4$NO$_3$ was obtained.

NaCOOH  The pressure dependencies of the Raman modes of NaCOOH were studied at 298K. Three different phases were identified up to 30 Kbar.

AlSb  The first-order Raman scattering of TO and LO phonons were measured under hydrostatic pressure.

AmI$_3$, CfBr$_3$, NdCl$_3$ and AmCl$_3$  A high-pressure study in a d.a.c. with pressures up to 300 Kbar achieved.

P$_4$Se$_4$  Raman spectra of crystalline $\alpha$-P$_4$Se$_4$ were obtained to pressures of 20.2 Kbar. Comparisons are drawn from a previous x-ray crystallographic study.
<table>
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<th>Compound</th>
<th>Description</th>
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</thead>
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<td>K,SbF$_6$, CsSbF$_6$</td>
<td>A polarised high-pressure Raman study. A comparison is made to results for both TlSbF$_6$ and CsSbF$_6$. Cationic effects are discussed.</td>
</tr>
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<td>a-S</td>
<td>An investigation of the effects of both hydrostatic and uniaxial pressure. The measurement of elastic constants and their variance with pressure were presented.</td>
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<td>(Bu$_4$N)$_2$Re$_2$Cl$_2$</td>
<td>Electronic absorption and resonance Raman data at pressures up to 150 Kbar is presented. The Re-Re vibrational frequency is observed to increase with increasing pressure.</td>
</tr>
<tr>
<td>PbI$_2$</td>
<td>The 2H-PbI$_2$ polytype undergoes pressure-induced phase transitions at 5 and 30 Kbar. The 4H-polytype displays transitions at 8 and 30 Kbar.</td>
</tr>
<tr>
<td>ZnP$_2$</td>
<td>A Raman study in a d.a.c. up to 150 Kbar. The interchain P modes are seen to exhibit strong pressure-dependencies. The low-frequency Zn-P modes are observed to soften slightly under pressure.</td>
</tr>
<tr>
<td>BaBiO$_3$</td>
<td>The compound shows a pressure-induced phase transition at 80-100 kbar. Changes in the Raman spectra indicate a transition from a nearly cubic to a nearly tetragonal lattice.</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>A Raman scattering investigation at</td>
</tr>
</tbody>
</table>

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high-pressure and under hydrostatic conditions. The $\beta$ to $\gamma$ phase transition occurs near 50 Kbar.

LiNbO$_3$, LiTaO$_3$ The pressure-dependencies for the optical phonons are presented for LiNbO$_3$ to 210 Kbar and LiTaO$_3$ to 100 Kbar.

In conclusion, this review presents information covering a representative sample of the vast amount of research undertaken within the high-pressure community. Although this particular work centres mainly on the use of the 'classical' investigative techniques such as Raman spectroscopy, many of the extracts quoted cite other techniques and clearly the underlying trend is now towards the use of multiple investigative methods to obtain the maximum possible information within a single study.

The work presented in this thesis crosses, in part, the boundary between the 'classical' i.e. vibrational spectroscopy and the newer emerging techniques, such as synchrotron radiation sources and attempts, where possible, to provide structural information about the systems studied.
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**Organics**


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Inorganics


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Chapter Three

Experimental Procedures

"Specialisation is for insects."

(Robert Heinlein)
CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 AN INTRODUCTION TO THE DESIGN AND USE OF THE DIAMOND ANVIL CELL

Many different types of experimental measurements have been made on materials at elevated pressures, and the interest in this field is constantly expanding. Merrill (1981) has reported in excess of three thousand papers published annually on the use of high-pressure techniques. The development of a diversified array of high-pressure cells for use with infrared, Raman and x-ray spectroscopies has spurred on activity in this field.

Stadtmüller (1976) has discussed over forty different types of high-pressure optical devices. Of these, the Bridgman opposed-anvil cell and the diamond anvil cell (d.a.c.) has proved the most versatile in achieving extremely high pressures (into the mega-bar regime). The so-called Bridgman era spanned from roughly 1910 to 1950 and was dominated by the Bridgman opposed anvil device developed for compressibility and electrical conductivity measurements. It is this single opposed anvil device which has spawned the present day d.a.c. in its many guises. Without doubt the d.a.c. is the simplest and most convenient device to use in high-pressure investigations. The same cell may, with appropriate modifications be used for experimental purposes in conjunction with Raman, IR (both mid- and far-) spectroscopies, and x-ray sources, and with the ability to work at both high- and low-temperatures, and is compact enough to be held in the palm of a hand. The highest pressure currently obtained by such a device is quoted as 4.6 Mbar (Goettle et al, 1986).

Typically, the sample volume in a gasketed d.a.c. experiment is less than twenty nanolitres, and with a cell transmission of as little as 1% (Adams and Sharma, 1977) the success of the system is by its correct manipulation and effective coupling to the relevant
FIG 3.1

Photograph of the 'Dynocell'.
FIG 3.2

Photograph of the 'Diacell'.
Diagramatic representation of the Dynocell.
Diagramatic representation of the Diacell.


3.2 AN OUTLINE OF D.A.C. DESIGN

An excellent account of the basic design of d.a.c.'s is available in Appleby (1977), with particular emphasis on the cells designed for use within the Leicester research group. Appleby also evaluated a structural analysis leading to the development of d.a.c.'s capable of generating much higher pressures. The development of the d.a.c. has progressed throughout the research group (Williams, 1980) and Shaw (1982) has published an excellent detailed account of a computer aided design study on the stress and deformations experienced by diamond anvils under pressure. This has given valuable insight into both diamond anvil and d.a.c. design within the group.

The high-pressure work undertaken in this thesis has been performed using a variety of cells, namely the MK II a d.a.c. (Hatton, 1983) and MK III 'Dynocell' (Fig 3.1) capable of extremely high-pressures (Fletcher, 1985). The main d.a.c. used for routine work up to 150 kbar is the 'Diacell' (Fig 3.2) (Diacell Products Ltd).

The sample is placed between the opposed diamond anvils, which are typically in the order of 0.7 mm to 1.2 mm in diameter at the working face. When the cell is assembled pressure is generated hydraulically and transmitted to the moving anvil holder (piston) via the lever arms and presser-plate, thus compressing the sample.

Assembled and 'exploded' views of the 'Dynocells' and 'Diacells' used are shown in Fig 3.3 and Fig 3.4 respectively. Light ports beneath each anvil permit the passage of radiation to be transmitted through the diamond anvils and the sample.

The 'Diacell' is made from stainless steel, AISI 310 and the 'Dynocell' is made from McCready’s NSOH steel (not oil-hardened). The anvil supports are fashioned from tooled-steel which is harder than stainless steel. Should extremely high pressures be required, the diamond anvils are mounted on tungsten carbide inserts.

3.3 SELECTION OF DIAMOND ANVILS

The selection of the diamonds used for the anvils in a d.a.c. depends upon the ultimate use of the cell and the technique(s) to which it is to be coupled. For
light-scattering techniques such as Raman spectroscopy diamonds with very low fluorescence levels (when excited with laser radiation) are required. Usually type II diamonds will satisfy this criterion (Adams, Payne and Martin, 1973, Adams and Sharma, 1977). However, a fluorescent anvil presents no problems with short wavelength radiation and thus type I diamonds are usually employed in x-ray diffraction experiments. Recent work has shown that certain type I stones can be selected for use in conjunction with Raman spectroscopy (Adams and Ruff, 1983). Typical fluorescence profiles of diamond anvils are shown in Williams, (1980). The choice of size and exact shape of the diamonds is dependent upon the pressure range which the experimenter wishes to exploit.

3.4 ANVIL MOUNTING

Within our research group at Leicester two methods of diamond anvil mounting have been developed (although they are essentially the same).

METHOD A

The diamond anvil is centered upon the light-port of the base hemisphere of the piston. Observation (with magnification) is via a monocular microscope. Thin strands of a slow-setting epoxy such as Araldite are then laid from one of the sides of the anvil to a previously mounted metal bar to one side of the light-port. Final positioning of the anvil over the light port is then carried out and the assembly is left to dry to hardness. Assuming that the anvil has not moved in the drying process, it can then be completely cemented in place by surrounding it with a jacket of Araldite. This process (assuming that there are no problems) can take 24-48 hours to complete in total. A full account of this mounting process can be found in Appleby, (1977), Williams, (1980) and Shaw, (1982).

METHOD B

A simple mounting assembly has been constructed to hold the anvil base plates securely in position. The diamond anvil is held in place over the light-port by a Perspex top plate.

Adjustment of the anvil's position over the light-port is achieved by the use of four Teflon screws. When the anvil is centered over the light-port the entire assembly is clamped down tightly and the anvil is completely cemented in place with rapid setting.
Araldite. This process takes in the region of thirty minutes and is considerably more precise and simple to use. It should be noted that before anvil mounting can take place the base plates are polished flat and the anvil bases are meticulously cleaned as imperfections in the mounting process can lead to catastrophic anvil failure as discussed in considerable depth by Williams, (1980).

After both anvils are mounted on their respective halves of the central insert (piston/cylinder arrangement) the opposed anvils are then aligned for parallelism.

3.5 DIAMOND ANVIL ALIGNMENT

After final mounting the opposing anvil faces must be made parallel to each other. Adjustment to the parallelism of the two anvils can be made via the three adjusting screws on the hemispherical base plate assembly. Newton’s fringes are used to determine the parallelism of the faces. Adjustments are made until only a single fringe can be observed across the faces of the anvils viewed through a x40 binocular microscope. A diagramatical representation of this process of alignment can be found in Williams, (1980).

3.6 PRESSURE TESTING AND STABILITY

After mounting and aligning the anvils, the complete cell is assembled in the ungasketed fashion and is pressure tested.

Visual phase transitions, induced by pressure, are observed through a microscope to determine the quality of the final alignment of the cell. As there is a parabolic pressure distribution across the anvil faces when pressure is applied, theoretically if the cell is perfectly aligned, then a phase transition should occur at the centre of the diamond anvils where the pressure distribution is at a maximum and then propagates outwards towards the edges of the faces. This gives rise to concentric phase boundaries. If this is not observed then the cell is deassembled and re-aligned using the method outlined in section 3.5.

Two compounds are commonly used to visually determine the alignment quality of the d.a.c..

(i) Mercuric (II) iodide, HgI\textsubscript{2}, which transforms from the low-pressure red form to the high-pressure yellow phase at approximately 13 kbar (Fig 3.5(i)).
1) Optical transition in HgI₂. The red (low-pressure) form transforms to the yellow (high-pressure) form at approximately 13 kbar. The darkening at the centre of the anvils is due to band shifting.

2) Optical pressure induced transitions in AgI. Pressure at the centre of the anvils is approximately 100 kbar.
TABLE 3.1

Some pressure media and their useful ranges

<table>
<thead>
<tr>
<th>Medium</th>
<th>Freezing Pressure at RT (kbar)</th>
<th>Pressure range of nearly hydrostatic (kbar)</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol/ethanol</td>
<td>104</td>
<td>~200</td>
<td>Easy</td>
<td>Piermarini, Block and</td>
</tr>
<tr>
<td>4:1</td>
<td></td>
<td>Barnett (1973)</td>
<td></td>
<td>1973</td>
</tr>
<tr>
<td>methanol/ethanol/water</td>
<td>145</td>
<td>~200</td>
<td></td>
<td>Fujishiro et al</td>
</tr>
<tr>
<td>16:3:1</td>
<td></td>
<td></td>
<td></td>
<td>(1981)</td>
</tr>
<tr>
<td>He</td>
<td>118</td>
<td>&gt;600</td>
<td>Cryogenic</td>
<td>Mao and Bell</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1982)</td>
</tr>
<tr>
<td>Ne</td>
<td>47</td>
<td>160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>12</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>300</td>
<td></td>
<td>Cooling</td>
<td>Leibenberg below</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1979) 165 K</td>
</tr>
<tr>
<td>H₂</td>
<td>57</td>
<td>&gt;600</td>
<td>Cryogenic</td>
<td>Mao and Bell etc</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1979)</td>
</tr>
<tr>
<td>D₂</td>
<td>53±2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>24</td>
<td>130</td>
<td>Cryogenic</td>
<td>Le Sar et al filling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1979)</td>
</tr>
<tr>
<td>O₂</td>
<td>59</td>
<td></td>
<td></td>
<td>Nicol et al</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1979)</td>
</tr>
</tbody>
</table>
(ii) Silver (I) iodide, AgI, which has transitions at approximately 4 and 98 kbar (Fig 3.5(ii)).

The cell is then left for several hours under pressure (preferably overnight) in order to test its long term stability at high pressure.

3.7 GASKETING

The use of a simple gasket in the experimental set-up allows the d.a.c. to become a quantitative tool for high-pressure research. As previously stated, a material merely placed between the bare opposed faces of the diamond anvils is subject to shear-stresses rather than hydrostatic ones. Use of the d.a.c. in the ungasketed mode leads to parabolic pressure gradients and hence mixed phases will occur when pressure is applied. Also, phenomena such as peak broadening are observed when the pressurised d.a.c. is used in conjunction with, for example, the technique of Raman spectroscopy.

By constraining the sample between the anvil faces in a convenient "sample chamber" together with a suitable hydrostatic pressure-transmitting medium and a pressure sensor (see later sections) all of the above problems can be overcome.

The gasket is made from a metal foil, usually inconel, tungsten or molybdenum, with a thickness in the region of 0.05-0.075 mm for use with infrared spectroscopy (Adams and Sharma) and typically 0.2-0.4 mm for Raman spectroscopy. A hole of about 0.2-0.35 mm is drilled through the centre of the gasket, which is then seated over the centre of the lower (cylinder) anvil face. The cell is then assembled and a modest pressure generated to pre-indent the gasket to the shape of the anvil.

Into this compressed gasket hole are placed the sample, the pressure-transmitting medium, and a chip of ruby; the latter acts as a pressure sensor.

The gasket, as well as providing a containment area for the sample, also extrudes around the diamond anvils, in effect acting as an additional supporting ring and thus reducing the stresses on the edges of the diamond faces, therefore helping to reduce the possibility of catastrophic anvil failure.
3.8 PRESSURE CALIBRATION

Forman et al (1972) first reported that the intense R₁ and R₂ ruby line doublet at 6927 and 6942 Å respectively, shift linearly with pressure. Further development has enabled the ruby fluorescence method to become a very rapid and convenient means of pressure determination (Barnett et al., 1973). A small chip of ruby (typically 5-10 μ in dimensions) is placed in the sample compartment along with the sample and pressure transmitting medium. By following the shifts in the R₁ and R₂ lines from the ambient positions, and by observing the separation between the two lines as pressure is increased, both the pressure and a reasonable estimate of the hydrostaticity of the system can be obtained.

The accepted value for the ruby R-line shift is 0.753 cm⁻¹kbar⁻¹, and the linearity of the scale has been shown up to 300 kbar (Piermarini et al., 1973).

Mao et al., (1978) have evaluated the reliability of the ruby line scale into the megabar range and have proposed that

\[
P(\text{Mbar}) = 3.808 \left( (\Delta \lambda + 1)^{5/2} - 1 \right)_{6942}
\]

The estimated error in pressure determination at one megabar is stated as being less than three percent. The ruby R-line scale, founded on reliable experimental data, remains the accepted pressure calibrant until such a time as a better scale at greatly elevated pressures is evolved (Bean et al., 1982).

3.9 PRESSURE MEDIA

The commonest pressure transmitting medium employed (and used within the Leicester research group) is a 4:1 mixture of methanol and ethanol which, according to Piermarini (1973) remains hydrostatic up to 104 kbar. The addition of a small amount of water in the proportion 16:3:1 (the latter water) extends the useful pressure range to 145 kbar.

Increasingly, the trend is now towards the use of condensed gases as hydrostatic pressure media, although these necessitate special filling techniques. Table 3.1 shows the commonest media currently in use, their useful pressure ranges and their relative ease of
Principal ray-paths through a d.a.c. used in Raman spectroscopy.
FIG 3.7

Schematic of the collecting optics used to couple a
d.a.c. to a Coderg T800 triple monochromator Raman
spectrometer.

1 Pre-sample focussing lens.

2 Gasket.

3 Diamond anvils.

4 Off-axis ellipsoidal mirror.

5 Collecting lens.
use. Such techniques are currently being evaluated for use within the Leicester high-pressure research group.

### 3.10 OPTICS OF THE DAC

Fig 3.6 shows the principal ray paths through a d.a.c. used in Raman spectroscopy. The incident laser beam is focused such that the focus is at the sample contained within the d.a.c. The size of the sample (i.e., very small) means that it can be effectively treated as a point source.

The Raman scatter from the sample in a cone of apex semi-angle of 25° will be collected and transmitted by the diamond anvil (Adams et al., 1976). It is apparent that the most crucial limitation is that set by the geometry of the anvil support material. Obviously, some compromise must be made between the need for the necessary mechanical strength of the anvil support, and a desirable large half-angle for the cone.

In Fig 3.6, the half-angle of the emergent beam $\theta$ is the angle of a ray to the normal in diamond. For $r = 0.455$ mm and $h = 2.0$ mm, only rays having $\theta \geq 5.8^\circ$ will pass directly through the cell (e.g., ray $\alpha$), but that others such that $5.8^\circ \leq \theta \leq 12.7^\circ$ will be collected after reflection from the walls of the anvil support (e.g., rays $\beta$ and $\gamma$).

### 3.11 COLLECTION OF RADIATION

Fig 3.7 shows the collecting optics used to couple the d.a.c. to a Coderg T800 Raman spectrometer (Williams, 1980).

To this effect, an ellipsoidal mirror of numerical aperture 0.7 is used. A hole of diameter 4.0 mm, drilled into the mirror with its axis parallel to the major axis of the ellipsoid, permits passage of the laser beam through it in either $0^\circ$ or $180^\circ$ scattering geometry.

The mirror turns the scattered light through $90^\circ$ in both scattering geometries.
References for Chapter Three


Diacell Products Ltd., 54, Ash Tree Road, Oadby, Leicester.

Fletcher, P.J., Unpublished Results.


Goettel, K.A., Williams, C.M., Reichlin, R. and Martin,


Merril, L., Bibliography on High-Pressure Research, Brigham-Young University, (1981).


Chapter Four

A single crystal x-ray structural investigation of rhenium pentacarbonyl iodide, Re(CO)$_5$I

"And if I only could I'd make a deal with God
And I'd get him to swap our places,
Be running up that road, be running up that hill
With no problems."

(Kate Bush)
CHAPTER 4

A SINGLE CRYSTAL X-RAY STRUCTURAL DETERMINATION OF RHENIUM PENTACARBONYL IODIDE, Re(CO)₅I

4.1 INTRODUCTION

During the low-frequency infrared and high-pressure Raman spectroscopic investigations of the rhenium pentacarbonyl halides the lack of detailed structural information became apparent. Therefore a single crystal x-ray diffraction study was undertaken on rhenium pentacarbonyl iodide, Re(CO)₅I. Concurrently, and unknown to us, Cotton and Daniels (1983) were determining the crystal structure of rhenium pentacarbonyl chloride, Re(CO)₅Cl, and these results were kindly forwarded by the authors for comparison prior to publication. Where possible comparisons are drawn between the determined structure of Re(CO)₅I and the analogous chloride and bromide.

4.2 EXPERIMENTAL

Rhenium pentacarbonyl iodide, Re(CO)₅I, was prepared from the reaction of dirhenium decacarbonyl, Re₂(CO)₁₀ and iodine in carbon tetrachloride under a nitrogen atmosphere (Darst and Lukehart, 1979). The dirhenium decacarbonyl was resublimed before use.

The crude Re(CO)₅I, which was contaminated with the dimer species [Re(CO)₄I]₂ was purified by several successive sublimations. Its Raman spectrum compared favourably with that previously reported in the literature (Hyams, 1967). Single crystals suitable for x-ray diffraction were obtained by placing a small quantity of the purified rhenium pentacarbonyl iodide in a sublimation apparatus under a vacuum of approx. 10⁻⁵ torr, and maintaining the temperature of the 'cold finger' of the apparatus one or two °C lower than that of its surrounding jacket. The assembly was left undisturbed for one week before crystal selection.
4.3 STRUCTURAL INVESTIGATION

A suitable single crystal was selected from those grown from the sublimation process. Crystals over a certain size tended to display twinning; consequently a small crystal was chosen. Oscillation, Wiensenberg and precession photographs were taken to determine the cell constants, crystal orientation and space group, systematic absences indicating \textit{Cmcm} (D\textsubscript{2h}, no.63) as the appropriate choice.

4.4 CRYSTAL DATA

Re(CO)\textsubscript{3}I  formula weight = 453.16

Space group  \textit{Cmcm} (no.63)

\begin{align*}
a &= 7.7422 \text{ Å} \\
b &= 10.9852 \text{ Å} \\
c &= 10.981 \text{ Å}
\end{align*}

\begin{align*}
\alpha &= \beta = \gamma = 90^\circ \\
F(000) &= 791.81
\end{align*}

Volume of unit cell = 933.9 Å\textsuperscript{3}

\textit{Z} = 4

Crystal size = 0.14 mm x 0.16 mm x 0.24 mm

\begin{align*}
\lambda &= 0.71069 \text{ Å} \\
\mu &= 155.5 \text{ cm}^{-1} \text{ (Mo Ka)}
\end{align*}

4.5 COLLECTION OF INTENSITY DATA

All intensity data were collected on a PDP-8 controlled Stoë 2-circle diffractometer using the \(\omega\) scan method. A total of 1139 unique reflections was measured. After corrections for Lorentz, polarisation, and absorption effects and merging, 633 reflections were obtained having \(I/\sigma(I) \geq 3\). Transmission coefficients varied between
Table 4.1

TABLE OF POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

<table>
<thead>
<tr>
<th>ATOM</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>0.5000</td>
<td>0.63987(7)</td>
<td>0.2500</td>
</tr>
<tr>
<td>I</td>
<td>0.5000</td>
<td>0.38693(15)</td>
<td>0.2500</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.5000</td>
<td>0.9188 (15)</td>
<td>0.2500</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.7936(17)</td>
<td>0.6264 (15)</td>
<td>0.493 (13)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.5000</td>
<td>0.818 (2)</td>
<td>0.2500</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.6862(17)</td>
<td>0.6308 (10)</td>
<td>0.1214(13)</td>
</tr>
</tbody>
</table>
### Table 4.2

**TABLE OF ANISOTROPIC THERMAL PARAMETERS - \( U_{(i,j)} \)'s**

<table>
<thead>
<tr>
<th>ATOM</th>
<th>( U(1,1) )</th>
<th>( U(2,2) )</th>
<th>( U(3,3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>0.0461(6)</td>
<td>0.0326(5)</td>
<td>0.0505(6)</td>
</tr>
<tr>
<td>I</td>
<td>0.0568(9)</td>
<td>0.0336(8)</td>
<td>0.0810(11)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.114(18)</td>
<td>0.010(6)</td>
<td>0.160(20)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.078(8)</td>
<td>0.078(7)</td>
<td>0.076(6)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.045(10)</td>
<td>0.048(11)</td>
<td>0.051(10)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.058(7)</td>
<td>0.054(6)</td>
<td>0.062(7)</td>
</tr>
<tr>
<td></td>
<td>( U(1,3) )</td>
<td>( U(2,3) )</td>
<td>( U(3,1) )</td>
</tr>
<tr>
<td>Re</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>I</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O(2)</td>
<td>-0.006(4)</td>
<td>0.030(6)</td>
<td>-0.066(4)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.006(5)</td>
<td>0.001(6)</td>
<td>0.006(4)</td>
</tr>
</tbody>
</table>

The form of the anisotropic thermal parameter is:

\[
\exp[-2*(a*U(1,1) + 2*h*k*a*U(1,2))]
\]
Table 4.3

TABLE OF BOND LENGTHS IN ANGSTROMS

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re - I</td>
<td>2.779(2)</td>
</tr>
<tr>
<td>Re - C(1)</td>
<td>1.96 (3)</td>
</tr>
<tr>
<td>Re - C(2)</td>
<td>2.021(14)</td>
</tr>
<tr>
<td>C(1) - O(1)</td>
<td>1.10 (3)</td>
</tr>
<tr>
<td>C(2) - O(2)</td>
<td>1.149(16)</td>
</tr>
</tbody>
</table>

(Numbers in parentheses are estimated standard deviations in the least significant digits).

Table 4.4

TABLE OF BOND ANGLES IN DEGREES

<table>
<thead>
<tr>
<th>Angle</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-Re-I</td>
<td>180.0</td>
</tr>
<tr>
<td>C(2)-Re-I</td>
<td>87.2(0.3)</td>
</tr>
<tr>
<td>C(2)-Re-C(1)</td>
<td>92.8(0.3)</td>
</tr>
<tr>
<td>O(1)-C(1)-Re</td>
<td>180.0</td>
</tr>
<tr>
<td>O(2)-C(2)-Re</td>
<td>179.0(1.2)</td>
</tr>
<tr>
<td>C(2)-Re-C(2')</td>
<td>91.0(0.8)</td>
</tr>
<tr>
<td>C(2)-Re-C(2')</td>
<td>88.7(1.8)</td>
</tr>
</tbody>
</table>
Fig 4.1

An ORTEP view of the molecular structure of Re(CO)₅I, showing the atom numbering scheme. The projection is rotated about the equatorial plane by 45°.
0.1994 and 0.0945.

Check reflection measurements, taken every 50 reflections, indicated no observable decay of the crystal during diffraction.

4.6 SOLUTION OF THE STRUCTURE

The computer program SHELX76 (Sheldrick, 1976), running on a CDC Cyber 73 machine, was used in the structure solution. The heavy atom method of determination was adopted.

Standard Patterson techniques enabled the location of the central rhenium atom, while successive difference Fourier syntheses elucidated the positions of the remaining atoms.

A full-matrix least-squares refinement of the atomic positional parameters was undertaken. The criteria used in the refinement were that anisotropic thermal parameters for the rhenium, carbon and oxygen atoms were allowed, and the application of a weighting scheme resulted in the following:

\[ R = 5.96\% \]
\[ R_w = 6.24\% \]

(for 633 reflections)

where

\[ R = \frac{\sum|F_o|-|F_c|}{\sum|F_o|} \]

and

\[ R_w = \frac{\sum w((|F_o|-|F_c|)^2)}{\sum w|F_o|^2}^{\frac{1}{2}} \]

\[ w = \frac{2.0529}{\sigma^2(|F_o|) + 0.006371|F_o|^2} \]

The final positional and thermal parameters for all the atoms are given in Tables 4.1 and 4.2.

4.7 DISCUSSION

The molecular structure of the rhenium pentacarbonyl iodide is as expected (Fig 4.1). The interatomic distances and bond angles are given in Tables 4.3 and 4.4 respectively.

-113-
### Table 4.5

**OPTIMUM M(CO)_5 GEOMETRIES**

<table>
<thead>
<tr>
<th>d^n configuration</th>
<th>Optimum symmetry</th>
<th>V, degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>C₄ᵥ</td>
<td>120</td>
</tr>
<tr>
<td>1</td>
<td>C₄ᵥ</td>
<td>116</td>
</tr>
<tr>
<td>2</td>
<td>C₄ᵥ</td>
<td>116</td>
</tr>
<tr>
<td>3</td>
<td>D₃h</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>D₃h</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C₄ᵥ</td>
<td>94</td>
</tr>
<tr>
<td>6</td>
<td>C₄ᵥ</td>
<td>93</td>
</tr>
<tr>
<td>7</td>
<td>C₄ᵥ</td>
<td>98</td>
</tr>
<tr>
<td>8</td>
<td>D₃h</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>D₃h</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>D₃h</td>
<td></td>
</tr>
</tbody>
</table>
Fig 4.2

Diagram showing the energy levels a square pyramidal M(CO)$_5$ fragment as a function of $\theta$. The orbital levels include the $d$ orbitals which contributes the most, which is not to imply that these orbitals are entirely localised on the metal. The orbital entering at the upper left-hand side of the figure is another $e$ level.

Fig 4.3

Diagram to show the possible orbital interactions for C$_{3v}$ and C$_{4v}$ M(CO)$_n$ fragments (where $n = 4$ or 5).

(After Elian and Hoffmann)
Predictably, the molecule displays an octahedral distribution of ligands around the central rhenium atom (the molecule itself having approximate $C_{4v}$ symmetry in the solid state). The I-Re-C(1)-O(1) axis of the molecule is rigidly linear, whilst the equatorial carbonyl ligands are bent away from the axial carbonyl group (and thus, away from equatorial planarity) towards the iodine atom.

This phenomenon has been observed in other metal carbonyl systems (Bailey, 1965, Darst, 1980, Churchill, 1981, Cotton, 1983, Albers, 1984, de Boer, 1984, Harris, 1984, Poli, 1985) and has been explained in depth by Elian and Hoffman (1974). In an elegant paper, Elian and Hoffman outline the electronic factors influencing the angular distribution of ligands around a central transition metal atom for a range of species, including $M(CO)_{5}L$ types.

**Fig 4.2** displays the energy levels of a $C_{4v}$ $M(CO)_{5}$ fragment as a function of $\nu$, the angle between apical and basal carbonyl ligands. The minimum energy for the system rests not at the expected 90° but at some slightly greater angle, this being dependant upon the d-electron configuration of the system. **Table 4.5** shows the optimum $M(CO)_{5}$ fragment geometries, $d^a$ configuration and angle $\nu$.

It can be shown from both symmetry arguments and more formal metal-ligand interaction schemes that the orbital hybridisation produced is such as to be maximised when pointing away from the apical ligand. In the case of carbon monoxide as a ligand, a secondary beneficial effect is conferred by metal-basal ligand $\pi$-antibonding, leading to an enhancement of the above effect.

In conclusion, for $M(CO)_{4}L$ and $M(CO)_{2}L$ systems, Elian and Hoffman state that if $L$ is a better donor than carbon monoxide, then this will lead to an increased stabilisation of the right-hand side of **Fig 4.3**. In other words, the equatorial carbonyl groups bend towards the apical ligand.

The prediction from **Table 4.5** is such that for a $d^6 C_{4v}$ system the angle $\nu$ expected between the axial and equatorial carbonyl ligands is 93°.

This is borne out in the light of our experimental observations in the Re(CO)$_5$I, a $d^6 C_{4v}$ system where $\nu$ is 92.8°.
Fig 4.4

The molecular structure of Re$_2$(CO)$_{10}$. 
The molecular structure of [Re₂(CO)₉F].
The molecular structure of \([\text{Re(CO)}_4\pi]_2\).
The mean equatorial metal-carbon distances are greater than that for the axial metal-carbon bond length. This is generally to the fact that there is a greater contribution of M\(\pi\)-CO\(\pi\)* bonding to the axial carbonyl group than to the equatorial carbonyl groups (Hall, 1975).

In other rhenium carbonyl systems containing iodine, such as \([\text{Re(CO)}_4\text{I}]_2\), the rhenium-carbon distances \(\text{trans}\)- to the iodine are shorter than other rhenium-carbon distances. This \(\text{trans}\)- effect is expected since the high polarisability of the iodine increases the Re-C d\(\pi\)-p\(\pi\) bonding to the equatorial carbonyl ligand as outlined above. The expected trend is indeed observed, with the mean equatorial rhenium-carbon distance being 2.021(14) \(\text{Å}\) and that of the axial rhenium-carbon distance being determined at 1.96(3) \(\text{Å}\).

Implicit in the Hall M\(\pi\)-CO\(\pi\)* explanation for the observed difference in the metal-carbon bond lengths is that the carbon-oxygen bond in the axial carbonyl group should be longer than that of its equatorial counterparts. This is also clearly seen with the mean equatorial carbon-oxygen bond length being 1.10(3) \(\text{Å}\). This is shorter than the observed 1.149(16) \(\text{Å}\) carbon-oxygen distance for the axial carbonyl group.

These trends are also observable in the 'parent' system dirhenium decacarbonyl, \(\text{Re}_2(\text{CO})_{10}\), (Churchill, 1981) (Fig 4.4) and conforms to the accepted theories for metal-carbon bonding and is interpreted as the net result of competition for d\(\pi\) electron density between mutually trans-pairs of equatorial carbonyl ligands.

The rhenium-iodine bond length in \(\text{Re(CO)}_5\text{I}\) is appreciably shorter at 2.779 \(\text{Å}\), in our determination, than in other recorded rhenium-iodine bonding distances. Thus, in \([\text{Re}_2(\text{CO})_9\text{I}]^+\) (Poli, 1985) (Fig 4.5) it is 2.833 \(\text{Å}\), and in the dimeric species \([\text{Re(CO)}_4\text{I}]_2\) (Fig 4.6) where the average rhenium-iodine distance is 2.82 \(\text{Å}\), for the iodine atoms bridging between the two \(\text{Re(CO)}_4\) fragments (Darst, 1980).

4.8 A STRUCTURAL COMPARISON OF THE Re(CO)_5X SERIES

(WHERE X = I, Br, Cl)

The pentacarbonyl halides of rhenium and manganese have been extensively studied by spectroscopic means, as outlined in chapter 6. Significantly, little structural
Table 4.6

COMPARISON OF CRYSTALLOGRAPHIC DATA FOR THE Re(CO)$_5$X SERIES
(X = Cl, Br, I)

<table>
<thead>
<tr>
<th></th>
<th>Re(CO)$_5$Cl</th>
<th>Re(CO)$_5$Br</th>
<th>Re(CO)$_5$I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Pnma ($D_{2h}^{16}$)</td>
<td>Pnma</td>
<td>Cmcm ($D_{2h}^{17}$)</td>
</tr>
<tr>
<td>$\alpha = \beta = \gamma$</td>
<td>90.0</td>
<td>90.0</td>
<td>90.0</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>11.686</td>
<td>11.898</td>
<td>7.7422</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>11.661</td>
<td>11.656</td>
<td>10.9852</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>6.069</td>
<td>6.189</td>
<td>10.981</td>
</tr>
<tr>
<td>cell vol. Å$^3$</td>
<td>827.03</td>
<td>858.31</td>
<td>933.93</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
### Table 4.7

**COMPARISON OF SOME BOND LENGTHS (Å) FOR THE Re(CO)$_5$X SERIES**  
*(WHERE X = Cl, Br, I)*

<table>
<thead>
<tr>
<th></th>
<th>Re(CO)$_5$Cl</th>
<th>Re(CO)$_5$Br</th>
<th>Re(CO)$_5$I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re-C(ax)</td>
<td>1.912(14)</td>
<td>2.04 (3)</td>
<td>1.96(3)</td>
</tr>
<tr>
<td>Mean Re-C(eq)</td>
<td>2.018(13)</td>
<td>1.935(3)</td>
<td>2.021(14)</td>
</tr>
<tr>
<td>Re-X</td>
<td>2.515(2)</td>
<td>2.62(1)</td>
<td>2.779(2)</td>
</tr>
<tr>
<td>C-O(ax)</td>
<td>1.189(15)</td>
<td>1.12(3)</td>
<td>1.149(16)</td>
</tr>
<tr>
<td>Mean C-O(eq)</td>
<td>1.112(9)</td>
<td>1.23(3)</td>
<td>1.10(3)</td>
</tr>
<tr>
<td>D((M-X)-r(X))</td>
<td>1.53</td>
<td>1.14</td>
<td>1.379</td>
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</table>
Table 4.8

COMPARISON OF SOME BOND ANGLES (DEGREES) FOR THE Re(CO)$_5$X SERIES
(WHERE X = Cl, Br, I)

<table>
<thead>
<tr>
<th></th>
<th>Re(CO)$_5$Cl</th>
<th>Re(CO)$_5$Br</th>
<th>Re(CO)$_5$I</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-Re-C(1)</td>
<td>179.9(3)</td>
<td>172.0(20)</td>
<td>180.0</td>
</tr>
<tr>
<td>X-Re-C(2)</td>
<td>89.0(2)</td>
<td>92.0(20)</td>
<td>87.20(3)</td>
</tr>
<tr>
<td>X-Re-C(3)</td>
<td>88.7(2)</td>
<td>88.0(20)</td>
<td></td>
</tr>
<tr>
<td>C(1)-Re-C(2)</td>
<td>91.0(3)</td>
<td>83.0(20)</td>
<td>92.80(3)</td>
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<tr>
<td>C(1)-Re-C(3)</td>
<td>91.3(3)</td>
<td>97.0(20)</td>
<td></td>
</tr>
<tr>
<td>C(2)-Re-C(2')</td>
<td>89.5(4)</td>
<td>92.0(20)</td>
<td>91.00(8)</td>
</tr>
<tr>
<td>C(2)-Re-C(3')</td>
<td>177.7(3)</td>
<td>178.0(20)</td>
<td></td>
</tr>
<tr>
<td>C(3)-Re-C(3')</td>
<td>90.5(4)</td>
<td>95.0(20)</td>
<td>88.70(8)</td>
</tr>
<tr>
<td>Re-C(1)-O(1)</td>
<td>179.7(9)</td>
<td>151.0(40)</td>
<td>180.0</td>
</tr>
<tr>
<td>Re-C(2)-O(2)</td>
<td>177.9(7)</td>
<td>171.0(40)</td>
<td>179.0(12)</td>
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<tr>
<td>Re-C(3)-O(3)</td>
<td>175.9(6)</td>
<td>175.0(40)</td>
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</tr>
</tbody>
</table>

(Numbers in parentheses are the estimated standard deviations in the least significant digit)
Fig 4.7

ORTEP projections of molecular Re(CO)$_5$Cl showing bond lengths (Angstroms) and angles (Degrees).

60° rotation about the equatorial CO plane

Side view of the molecule showing the bending of the equatorial carbonyls towards the chlorine.

Top view, looking approximately down the C(1)-Re-Cl axis of the molecule.
Fig 4.8

ORTEP projections of molecular Re(CO)$_3$Br showing bond lengths (Angstroms) and angles (Degrees).

$60^\circ$ rotation about the equatorial CO plane

Side view of the molecule showing the bending of the equatorial carbonyls towards the bromine.

Top view, looking approximately down the C(1)-Re-Br axis of the molecule.
Fig 3.9

ORTEP projections of molecular Re(CO)$_3$I showing bond lengths (Angstroms) and angles (Degrees).

$60^\circ$ rotation about the equatorial CO plane

Side view of the molecule showing the bending of the equatorial carbonyls towards the iodine.

Top view, looking approximately down the C(1)-Re-I axis of the molecule.
work has been undertaken on this series of compounds. The only pentacarbonyl halide structural determination for manganese is that of pentacarbonyl manganese chloride, Mn(CO)$_5$Cl (Greene and Bryan, 1971).

The structural determination for rhenium pentacarbonyl iodide, Re(CO)$_5$I completes the crystal structural information for the chloride, bromide and iodide series of the pentacarbonyl rhenium series.

An attempt at comparison, and where possible, rationalisation of the structures displayed will be undertaken within the experimental constraints of these determinations.

4.9 DISCUSSION

The molecular geometries for Re(CO)$_5$Cl, Re(CO)$_5$Br and Re(CO)$_5$I are shown in Figs 4.7, 4.8, and 4.9 respectively.

Re(CO)$_5$Br (Couldwell and Simpson, 1977) and Re(CO)$_5$Cl (Cotton and Daniels, 1983) crystallise, at ambient temperature and pressure, in the orthorhombic space group Pnma (D$_{2h}$, no.62), whereas Re(CO)$_5$I, as determined in this study, crystallises in the centrosymmetric orthorhombic space group Cmcm (D$_{2h}$, no.63). Table 4.6 shows a comparison of crystallographic data for the Re(CO)$_5$X series.

All have unit cells containing four molecules, with the iodide having the largest volume at 933.93 Å. The series displays an increase in cell volume from the chloride through to the iodide, presumably due to increase in halogen size progressing down the halide series in the Periodic Table. It is interesting to note, en passant, that for the chloride and bromide systems the $a$ axis is approximately equal to the $b$ axis in length, whereas the iodide has the $b$ axis approximately equal in length to the $c$ axis.

As can be seen from Tables 4.7 and 4.8, the structural data obtained for Re(CO)$_5$Br contains significantly large errors in comparison to that presented for Re(CO)$_5$Cl and Re(CO)$_5$I, thus hampering attempts at comparisons.

The comparative molecular data of bond lengths and bond angles for the series is displayed in Tables 4.9 and 4.10. The observed trend for the increase in the metal-halogen distances can be rationalised as being due to the increase in covalent radius size.
### Table 4.9

**TABLE OF COMPARATIVE PARAMETERS FOR THE Re(CO)$_5$X SERIES**  
($X = \text{Cl, Br, I}$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Re(CO)$_5$Cl</th>
<th>Re(CO)$_5$Br</th>
<th>Re(CO)$_5$I</th>
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<tbody>
<tr>
<td>Volume, Å$^3$</td>
<td>827.03</td>
<td>858.31</td>
<td>933.93</td>
</tr>
<tr>
<td>Volume Difference, Å$^3$</td>
<td>0.0</td>
<td>31.28</td>
<td>75.62</td>
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<tr>
<td>% volume change</td>
<td>0.0</td>
<td>3.78</td>
<td>8.81</td>
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<tr>
<td>van de Waals Radius of halogen, Å$^3$</td>
<td>1.79</td>
<td>2.01</td>
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<tr>
<td>Ratio of halogen radii</td>
<td>1.0</td>
<td>1.123</td>
<td>1.094</td>
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<tr>
<td>Ratio of Cell volumes</td>
<td>1.0</td>
<td>1.038</td>
<td>1.088</td>
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</table>
### Table 4.10

**TABLE OF INTERNUCLEAR NON-BONDED CONTACT DISTANCES**

*(RANGE 0.2 < 4.0 Å + SUM OF VAN DER WAALS RADII)*

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<tr>
<th></th>
<th>I</th>
<th>Br</th>
<th>&quot;Br/I&quot;</th>
<th>Cl</th>
<th>&quot;Cl/I&quot;</th>
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<td>4.289</td>
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<td>6.086</td>
<td>6.045</td>
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<td>X...O(1)</td>
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<td>5.685</td>
<td>5.844</td>
<td>5.616</td>
<td>5.880</td>
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</table>

* I = Re(CO)₅I, Br = Re(CO)₃Br, "Br/I" = Re(CO)₃Br/Re(CO)₅I
  Cl = Re(CO)₅Cl and "Cl/I" = Re(CO)₅Cl/Re(CO)₅I
Fig 4.10

Packing diagram of Re(CO)$_5$Cl viewed in the $ab$ plane.
Fig 4.11

Packing diagram of Re(CO)$_5$Br viewed in the $ab$ plane.
Fig 4.12

Packing diagram of Re(CO)\textsubscript{5}I viewed in the $ab$ plane.
Fig 4.13

ORTEP stereograms of:-

Re(CO)$_5$Cl

Re(CO)$_5$Br

Re(CO)$_5$I

All projections have been rotated by 30° about the rhenium-halogen molecular axis.

All projections are viewed in the $ab$ plane.
Fig 4.14

ORTEP projections of the packing in Re(CO)$_5$Cl and Re(CO)$_5$Br in the $ab$, $bc$ and $ac$ planes.
ORTEP projections of the packing in Re(CO)$_5$I in the $ab$, $bc$ and $ac$ planes.
of the halogen from chloride to iodide. Concomitant with this is an observable decrease in the determined covalent radius of rhenium obtained from the rhenium-halogen bond lengths from 1.53 Å for the chloride to 1.379 Å for the iodide with, predictably, an intermediate value of 1.41 Å for the bromide. It has been suggested that the observable differences are due to an increased p bonding contribution of the halogen to the metal-halogen bond (Cotton, 1982).

From factors outlined previously in the discussion of the molecular structure of Re(\text{CO})_5\text{I}, the axial metal-carbon distance is expected to increase down the group series from chloride to iodide. The expected value for the axial metal carbon distance should fall between the observed 1.912 Å for the chloride and 1.96 Å for the iodide but is considerably longer at 2.04 Å. The mean metal-carbon equatorial distance is also significantly shorter for the bromide system at 1.935 Å in comparison to the "average" mean values of approximately 2.02 Å for Re(\text{CO})_5\text{Cl} and Re(\text{CO})_5\text{I}. The increasing trans-effect of the halogen progressing from chloride to iodide should lead to a shortening of the axial carbon-oxygen bond length. This is displayed for the chloride and iodide having bond lengths of 1.189 Å and 1.149 Å respectively but once again the bromide shows an anomaly with a determined bond length of 1.12 Å.

The bond angles for Re(\text{CO})_5\text{Br} also display considerable deviation from those expected as typified by the value for the bromide-metal-axial carbon (Cl) determined at 172°, compared with expected co-linearity as found in Re(\text{CO})_5\text{Cl} and Re(\text{CO})_5\text{I}. Most significantly deviant is that of the rhenium-C(1)-O(1) axial carbonyl angle determined to be 151°, in contrast to the observed values of 179.7° and 180° for Re(\text{CO})_5\text{Cl} and Re(\text{CO})_5\text{I} respectively.

4.10 COMPARISON BETWEEN PACKING ARRANGEMENTS FOR Re(\text{CO})_5\text{X} SERIES (X = Cl, Br, I)

The most striking difference occurs in the method adopted of unit cell packing. This is particularly well displayed through Figs 4.10, 4.11, 4.12, and 4.13 respectively. The chloride and bromide systems, sharing a common space group, exhibit the same type of molecular packing. The iodide structure basically consists of two discrete molecules disposed about the centre of the unit cell orientated halogen to rhenium. It is also worth noting that the iodine-rhenium-axial carbonyl axis of the molecule is orientated along the longest axis of the unit cell. Table 4.9 shows comparative parameters for the Re(\text{CO})_5\text{X}
series Figs 4.14 and 4.15 display the relative packing types adopted by the chloride and bromide systems, as opposed to that shown by the iodide.

On initial inspection there is no apparent rationale for the quite dramatic difference displayed between the two packing types.

The anticipated difference in cell volumes on going from Re(CO)₅Br to Re(CO)₅I (Table 4.9), based upon the variation in the van der Waals radii of the halogen, is approximately twice that of the observed difference between the two cell volumes. However, on reflection, this fact is not as surprising as it would at first appear, as the only parameter changing is that of the van der Waals radius of the halogen, the rest of the molecule remaining unchanged.

The largest observed differences between the two packing types are in the inter-molecular non-bonded contact distances, given in Table 4.10. There are clearly-defined breaks, for certain contact distances, on progressing from the chloride/bromide structure to the iodide structure.

To enable a clearer comparison to be made between the two structure types, a series of non-bonded contact distances were generated, using the FORTRAN 77 program 'GEOM' (Russell, 1983), for both Re(CO)₅Cl and Re(CO)₅Br in their 'normal' structure type with the appropriate halogen radius substituted for the covalent radius of iodine. All relevant fractional atomic co-ordinates were corrected by simple ratioing methods.

The Re...halogen contact distances increase dramatically from the Re(CO)₅Br to Re(CO)₅I, having followed an approximate trend of increasing slightly from Re(CO)₅Cl to Re(CO)₅Br. The generated Re...halogen non-bonded contact distances for the "corrected" Re(CO)₅Cl and Re(CO)₅Br are decreased, as expected, by the halogen atom radius.

Large changes are also observable on progression across the series Cl<Br<<I for the Re...C(1), Re...O(2) and halogen...C(1) contact distances.

It would appear that the environment of the halogen plays a significant role in the determination of the packing adopted in these systems, such as to maximise the internuclear non-bonded contact distances for the halogen atoms.
Electrostatic forces may also be of significance between the two packing types. The electronegativities of the halogen atoms, and thus the Re...halogen bond polarisation, may cause some type of preferential packing alignment in Re(CO)₅Cl and Re(CO)₅Br, compared with that of Re(CO)₅I, which has the longest Re...halogen bond length, and the least electronegative halogen of the series.

Further investigation of these structures by such means as lattice dynamical calculations and energy minimisation techniques may provide further insight into the characteristics of the packing structure adopted.

**4.11 CONCLUSIONS**

Within the experimental errors observed, the structural trends expected are displayed. The comparatively perfunctory determination of Re(CO)₅Br leads to a significant reduction in the reliability of the trends recorded.

High anisotropic thermal parameters were observed in the Re(CO)₅I determination, especially for the oxygen of the axial carbonyl group, and are manifest throughout the series indicating that this particular structural series would benefit from low-temperature determinations.
Observed and calculated structure factors for Re(CO)$_5$I, after absorption and extinction corrections.
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<th>FO</th>
<th>FC</th>
<th>H</th>
<th>K</th>
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<td>1</td>
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... (the rest of the table continues in a similar format)
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|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 7  | 9  | 3  | 40 | 38 | 7  | 11 | 4  | 21 | -31| 7  | 3  | 6  | 66 | 59 | 12 | 4  | 40 | -23| 12 | 4  | 31 | -24| 12 |
| 0  | 10 | 3  | 16 | 10 | 0  | 12 | 4  | 46 | -42| 0  | 4  | 6  | 35 | 32 | 18 | 4  | 46 | -42| 18 | 4  | 35 | -32| 18 |
| 1  | 10 | 3  | 36 | 32 | 2  | 12 | 4  | 49 | -45| 2  | 4  | 6  | 35 | 32 | 24 | 4  | 49 | -45| 24 | 4  | 35 | -32| 24 |
| 2  | 10 | 3  | 72 | -70| 0  | 22 | 4  | 24 | 22| 0  | 4  | 6  | 35 | 32 | 24 | 4  | 49 | -45| 24 | 4  | 35 | -32| 24 |
| 3  | 10 | 3  | 63 | -59| 1  | 22 | 4  | 24 | 22| 1  | 4  | 6  | 35 | 32 | 24 | 4  | 49 | -45| 24 | 4  | 35 | -32| 24 |
| 4  | 11 | 3  | 39 | -41| 1  | 22 | 4  | 24 | 22| 1  | 4  | 6  | 35 | 32 | 24 | 4  | 49 | -45| 24 | 4  | 35 | -32| 24 |
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Structure factors for Re(CO)$_5$I with deviations greater than 2 sigma, after absorption and extinction corrections.
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**DEVIANCTIONS GREATER THAN 2 SIGMA**

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References for Chapter Four


Russell, D.R., The University of Leicester, GEOM - a program to calculate non-bonded contact distances.


Chapter Five

A high-pressure investigation of potassium chlorate, KClO₃, by energy dispersive x-ray diffraction using synchrotron radiation

"Day after day alone on a hill
The man with a thousand faces keeping perfectly still
And nobody wants to know him
They can see that he's just a fool
And nobody has to like him
He's the fool on the hill
And the eyes in his head see the world spinning round

(The Beatles)
CHAPTER 5

A HIGH-PRESSURE INVESTIGATION OF POTASSIUM CHLORATE, KClO₃,
BY ENERGY DISPERSIVE X-RAY DIFFRACTION USING SYNCHROTRON
RADIATION

5.1 INTRODUCTION

The first realisation of the importance of Synchrotron radiation as an alternative energy source was by Buras, Olsen and Gerward, (1976) who combined the Energy Dispersive Diffraction technique with synchrotron radiation in powder diffraction studies.

The first high-pressure measurements utilising synchrotron sources (and a d.a.c.) were performed by Buras, Staun Olsen, Gerward, Will and Hinze, (1977). From these initial experiments the d.a.c. has become the standard investigative tool for the high-pressure synchrotron studies reported thus far.

Recent work by Spain and Black (1985), Staun Olsen, Gerward and Benedict, (1985), Yagi et al, (1985), Skelton et al, (1985) and Spain, (1984) serve to outline the importance of synchrotron radiation in the still developing field of high-pressure structural investigations.

The aim of the study presented in this chapter is to use the energy dispersive x-ray diffraction (EDXRD) technique, employing synchrotron radiation as the x-ray source, to obtain structural information (where possible) on the various phases exhibited by potassium chlorate, KClO₃, whilst subjected to high-pressures. In this respect, x-ray diffraction is potentially a precise method for obtaining general structural data at elevated pressures.

The use of conventional x-ray sources make the EDXRD technique extremely slow requiring, usually, several days of actual data collection time, although some excellent work has been reported by Hochheimer (1986) and Hausermann (1986) with much shorter data collection times employing rotating anode x-ray sources.
FIG 5.1

Diagram to show the synchrotron profile of the SRS facility, Daresbury Laboratory.

FIG 5.2

Energy profiles of various synchrotron sources, including the SRS in comparison to other SR facilities available.
3-pole wiggler 5T field

Normal bending magnet 1.2T field

Intensity/photons s\(^{-1}\) mrad\(^{-1}\) (0.1% band pass)\(^{-1}\)

Photon energy/keV

Wavelength Å
The utilisation of synchrotron sources has enabled x-ray powder patterns to be obtained within seconds (Hatton, 1986).

It is intended that the EDXRD experiment should provide complementary structural information to that given by conventional means such as Raman spectroscopy. The relative ease of data analysis should enable this technique to be further developed into a highly productive method for high-pressure structural investigations.

5.2 SYNCHROTRON RADIATION

Synchrotron radiation is the intense, 'white', source of electromagnetic radiation produced by the acceleration of charged particles, to speeds where relativistic effects become important, around circular accelerators e.g. synchrotrons and storage rings which allow the propagation of the radiation.

Ideally, the synchrotron radiation source (SRS) is a storage ring where, after their capture in the orbit of the accelerator, electrons are restrained at fixed energy by constant magnetic fields for long periods, typically several hours. The gradual electron energy loss from the beam is replenished using the RF power from a Klystron. This is coupled to the main beam via RF cavities located at discrete intervals around the storage ring.

The ensuing radiation produced has several unique attributes which makes it preferentially desirable as a radiation source for experimental purposes.

Intensity: Currently available synchrotron sources produce beams with intensity in the order of $10^4-10^6$ times greater than conventional x-ray sources. The beam can, therefore, be stopped down without unreasonable losses in intensity.

Tunability: The SRS provides a continuous spectrum of electromagnetic radiation ranging from hard x-rays down to microwaves (Fig 5.1). Also, most importantly, the SR profile is smooth, whereas that obtained by conventional sources is usually punctuated by characteristic emission lines (Fig 5.2).

Collimation: The beam produced is highly collimated, in other words displaying a very narrow angular divergence in the plane of the beam orbit, typically 0.01
Periodicity: The RF coupling effectively punctuates the electron beam into 'packets' of electrons called 'bunches', so that the radiation is emitted as a series of pulses with a period of less than $10^{-9}$ seconds.

### 5.3 Experimental Theory

As previously outlined, synchrotron radiation constitutes all wavelengths. In the EDXRD experiment each set of crystal planes $hkl$ interact with incident 'white' light photons of energy, $E_{hkl}$ in accordance with the following relationship:

$$E_{hkl} = \frac{hc}{2d_{hkl}\sin\theta}$$

Where:

- $d_{hkl}$ = d-space (E)
- $h$ = Planck's constant
- $c$ = Velocity of light
- $\theta$ = Fixed diffraction angle, $2\theta$

Several excellent, and more detailed, accounts covering the theory of synchrotron radiation can be found in Buras (1979), and references therein.

### 5.4 Experimental Procedure

The high-pressure EDXRD experiment was carried out using the S.E.R.C. SRS facility, at the Daresbury Laboratory. In particular, the experiment utilised the hard x-rays produced from the so-called 'wiggler' line. In essence, the 'wiggler' consists of one 5 and two 2.5 Tesla magnets which introduce a perturbation in the circular motion of the electron beam. This sudden decrease in the radius of curvature of the beam causes the electrons, which are attempting to conserve momentum, to emit high-energy photons.
FIG 5.3

Schematic representation of station 9.1, at the SRS at Daresbury, in the Energy Dispersive mode.
FIG 5.4

Germanium detector calibration plot of MCA channel number versus energy (KeV).

FIG 5.5

The phase diagram of KCIO$_3$ (after Pistorius).
which correspond to the wavelength of hard x-rays. The 'wiggler' line at the SRS facility produces a hard x-ray beam down to 0.1 Å.

**Fig 5.3** is a schematic representation of a typical EDXRD experimental set-up. The high intensity, 'white' x-ray beam is stopped down via a pair of mutually perpendicular tantalum slits, to a 'spot-size' of approximately 6 x 10 microns, and is then passed through a gasketed d.a.c. containing the sample. The emergent beam is diffracted through a fixed angle, 2θ, by the sample. The x-rays fall upon a pure germanium solid-state detector (cooled to LN temperatures) which produces electrical signals. After appropriate amplification, these signals are passed into a multi-channel analyser (MCA). Typical data collection for a high-pressure experiment takes approximately twenty minutes to complete.

The Ge detector requires calibration of MCA channel number to actual energy. This is done at regular intervals during an experimental session. A radioactive dial source is used to produce known fluorescence energies for each of six different elements. The resulting peak positions, in MCA channel numbers, are then fitted to their respective accurately known energies via a least-squares fit. A typical detector calibration plot is shown in **Fig 5.4**. The correlation has been shown to be repeatably linear within experimental error.

The experimental station used is completely enclosed (when in use) due to the nature of the radiation used. The d.a.c. is manipulated within the beam by remotely controlled stepper motors to ensure the optimum signal/noise and removal of unwanted fluorescence or diffraction lines due to the cell or gasket material used.

Pressure determinations were performed using the ruby fluorescence method as outlined in Chapter 3. The d.a.c. was coupled to a one-third metre scan-controlled monochromator with appropriate focussing optics. Incident laser light, in either 180° back-scatter or straight-through geometries, was provided by either a He/Ne or air-cooled argon ion laser.

All data acquisition at the experimental station is undertaken by a dedicated microVAX II computer. An extensive suite of menu-driven data analysis software has been developed to run on the station microVAX and the Leicester University mainframe DEC (Digital Equipment Corporation) VAX cluster systems (Heath, 1986). This also
EDXRD powder patterns of KClO$_3$ at varying pressures showing different phases.
Phase II
P = 3.36 GPa

Phase I + II
P = 1.02 GPa

Phase I
P = 0.0001 GPa

Energy (KeV)
includes facilities for remote site file transfer via the JANET network, calculation of predicted EDXRD spectra, and a sub-suite of interactive graphical programs for spectral manipulation.

5.5 RESULTS

Structural differences have been observed, using the EDXRD method, between the two known phases of potassium chlorate, KClO₃. Earlier work by Raman spectroscopy (Heyns, 1982) and single crystal determinations (Zachariasen, 1929, Aravindakshan, 1958, Wyckoff, 1964, Pistorius, 1972 and Danielsen, 1982) have confirmed the phase diagram for KClO₃ as shown in Fig 5.5.

EDXRD powder patterns for both phases are shown in Fig 5.6. The powder patterns in each phase were indexed from previous structural data (Bridgman, 1944 and Pistorius, 1972). The experimental data were found to fit with previously reported work (Pistorius, 1972) and refined well in the high-pressure phase using a rhombohedral system. The alkali metal halates have been investigated in some detail and the results obtained thus far with the EDXRD method fits the known behaviour of these compounds.

Accurate measurements of the spectra resulted in a series of indexed d-spacings for each pressure measurement. The d-spacings for each phase were fitted to a set of calculated d_{hkl} via a non-linear least-squares refinement. The actual function minimised was the difference between the squares of the calculated and observed reciprocal d_{hkl} i.e.

\[ \Delta = d_{c}^{*2} - d_{o}^{*2} \]

(where \( \Delta \) is the function to be minimised)

Therefore, a minimum is encountered when

\[ w \cdot \frac{\delta \Delta}{\delta u_j} = 0 \]

(where \( u_j \) is the set of parameters to be minimised and \( w \) is the weighting factor and is proportional to \( d^2 \) )
FIG 5.7

Bulk compressibility plot for KClO$_3$ II.

(Standard errors are shown in parentheses).

FIG 5.8

Uniaxial compressibility plot for the lattice vector, $a$, of KClO$_3$ II (rhombohedral).

(Standard errors are shown in parentheses).
This least-squares refinement was performed using the computer program VARVEC (Heath, 1987), which refines a total set of data from various pressure measurements and calculates dependence of crystal lattice parameters (e.g. $a$, $b$, $c$, and $\beta$ for a monoclinic system) with pressure. Hence, the overall compressibility is simply calculated as a function of varying unit cell volume.

The compressibility of the high-pressure phase II of KClO$_3$ was determined as $2.36(25) \times 10^{-2}$ GPa$^{-1}$ and the uniaxial compression of the lattice vector, $a$, was found to be $3.4(4) \times 10^{-2}$ GPa$^{-1}$.

These results are graphically represented in Figs 5.7 and 5.8. The standard errors found in these measurements were comparable to those of previous investigations (Adams et al., 1987).

### 4.6 DISCUSSION

The results obtained for the bulk compressibility of KClO$_3$ II compare favorably with that found by Bridgman (1944) who found a value of $2.7(1) \times 10^{-2}$ GPa$^{-1}$ which is within statistical error of the value found in this determination.

Bridgman's data was produced by hydraulic pressure measurements, using a large amount of sample and without very accurate pressure determinations. Table 5.1 shows data obtained by Bridgman using the above experimental technique. Table 5.2 gives similar volume data obtained by the EDXRD method.

Obviously, the EDXRD determination suffers in the reliability of the least squares refinement due to the relatively small number of d-spacings measured and indexed for each pressure. There has to be at least one more d-spacing than there are degrees of freedom in a crystal system otherwise iterative methods will fail. However, the number of degrees of freedom demanded by a rhombohedral system is only two (i.e. $a$ and $\alpha$) and hence, all spectra of varying pressures could be analysed.

The relatively poor quality of the spectra obtained in terms of resolution of Bragg peaks, large background and low count rates reduce the reliability of the data and had phase II been anything other than rhombohedral problems may have been encountered.
**TABLE 5.1**

Bridgman compressibility data for KClO$_3$ II

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>V/V$_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>0.1044</td>
</tr>
<tr>
<td>1.47</td>
<td>0.1217</td>
</tr>
<tr>
<td>1.96</td>
<td>0.1362</td>
</tr>
<tr>
<td>2.45</td>
<td>0.1483</td>
</tr>
</tbody>
</table>

(Pressure units converted from Bridgman's original Kgcm$^{-2}$)

Bulk compressibility = 2.7(1)x10$^{-2}$ GPa$^{-1}$

**TABLE 5.2**

Compressibility data for KClO$_3$ II determined by the EDXRD method

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>V/V$_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96</td>
<td>0.9942</td>
</tr>
<tr>
<td>1.02</td>
<td>0.9893</td>
</tr>
<tr>
<td>2.02</td>
<td>0.9679</td>
</tr>
<tr>
<td>3.38</td>
<td>0.9386</td>
</tr>
</tbody>
</table>

Bulk compressibility = 2.36(25)x10$^{-2}$ GPa$^{-1}$
Fig 5.9

i) ORTEP projection of the packing arrangement for the ambient phase I of KClO₃

ii) ORTEP projection of the packing arrangement of phase II of KClO₃.
The computer analysis takes the above factors into account by weighting the indexed d-spacings proportionally to their magnitude. This means that data encountered at high energies is given less significance because of poorer detector resolution and, of course, the number of high-indexed data is greater.

The quality of the powder diffraction spectra observed decreases as the pressure is increased. This phenomenon arises from the fact that the sample thickness decreases between the diamond anvil faces and therefore the scattering power is reduced, hence lower count rates are observed and the signal/noise decreases.

\(\text{KClO}_3\) undergoes a transition from the distorted B1 NaCl-type structure to the distorted B2 CsCl-type structure at approximately 7 kbar (Bridgman, 1944). Phase II adopts the rhombohedral space group R\(\bar{3}m\), and is isostructural with KBrO\(_3\) (Zachariasen, 1929). In phase II, the K and Cl atoms occupy special positions at 0,0,0 and \(\frac{1}{3},\frac{1}{3},\frac{1}{3}\) respectively (the other atomic positions are of approximate values due to the nature of the structural investigation (Pistorius, 1976)). Thus, the unit cell occupancy is one, with the chlorate group at the approximate centre of the cell, and the cell corners bounded by potassiums (Fig 5.9). For the rhombohedral system, \(a = b = c\), and \(\alpha = \beta = \gamma\), and the structure adopted is accordingly highly symmetrical, with all of the chlorate groups displaying the same direction of orientation.

The ambient phase, \(\text{KClO}_3\) I, crystallises in the monoclinic space group P2\(_i\)/m with two formula units per unit cell (Fig 5.9). The origin is at an inversion point, and \(b\) is the unique axis (Zachariasen, 1929). Two K, two Cl, and two O atoms occupy positions on a mirror plane corresponding to the set of coordinates, 2\(e\). The remaining oxygens are found on general positions, 4\(f\). Each potassium is surrounded by six chlorate groups. Although the crystal system is monoclinic the chlorate groups possess a high degree of symmetry themselves, and this is reflected in the x-ray data obtained (Aravinarshan, 1958) as well as in infrared (Ramadas, 1952) and Raman (Shantakuman, 1950) data previously presented.

Comparative parameters for the two systems are given below:

<table>
<thead>
<tr>
<th></th>
<th>I (P2(_i)/m)</th>
<th>II (R(\bar{3}m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>4.647</td>
<td>4.270</td>
</tr>
<tr>
<td>(b)</td>
<td>5.585</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

-128-
The largest changes occur in the \( b \) and \( c \) lattice parameters. The average K...O non-bonded contact distance for phase I is 2.92 Å, and 2.89 Å for the high-pressure phase. The corresponding K...Cl non-bonded contact distance is 3.74 Å in phase I and 3.59 Å in phase II. There is a slight reduction in these distances in going from the ambient phase to the high-pressure phase (as might be reasonably be expected), and this is displayed in the packing considerations adopted by the different structures.

### 5.7 CONCLUSION

Further results at higher pressures (extending the pressure range into the tens of GPa region) would improve both the reliability of the data and its ultimate analysis. Improved experimental methods including the use of monochromatic angle scanning diffraction and position sensitive detectors would improve the resolution obtained by an order of magnitude. This would allow a greater quantity of data to be reliably indexed.

It is apparent that the EDXRD method provides a reasonably fast and accurate determination of phase systems with the added advantage of offering structural information which is completely inaccessible by vibrational spectroscopic means (e.g. bulk compressibility and lattice parameter calculation).

The use of the d.a.c. itself introduces statistical problems, in that an extremely small amount of sample is used (refer to chapter 3). This means that only a relatively small number of sample crystallites give rise to the diffracted radiation. This is reflected in the non-reproducibility of Bragg peak intensities with variation of pressure. It is these intensities that hold the total structural information concerning atomic positions within the unit cell. It is therefore impossible to obtain the complete crystal structure from these high-pressure powder patterns using standard analysis methods such as Rietveld refinement. Use of a larger sample volume (e.g. as in neutron time-of-flight diffraction) gives reliable intensity information and hence, allows a complete structural refinement to

\[
\begin{align*}
c & = 7.085 \\
\alpha & = 90.0 \\
\beta & = 109.65 \\
\gamma & = 90.0 \\
Z & = 2 \\
\rho & = 2.26 \\
\end{align*}
\]
be undertaken (Worlton et al, 1986). However, the use of a larger sample precludes the possibility of very high-pressures being obtained.

Finally, it should be stated that there are both advantages and disadvantages to be gained from the use of the EDXRD technique and Raman spectoscopy. The principal advantages of the EDXRD experiment are its speed and direct structural information offered as outlined above. Its main disadvantages are that the experiment can only be performed (with such speed) at a synchrotron source, and then only in certain allocated experimental sessions. It is also an extremely high-cost experiment! Raman spectroscopy, in contrast, can be performed without having to travel from the home laboratory and has the added advantage of more 'sociable' user time. The most serious disadvantage of Raman spectroscopy is in terms of information accessible to the experimenter. It must be stressed that the application of group theory and factor group analysis to experimental Raman data rarely leads to an unambiguous assignment of data, as these methods apply properly only to perfect systems and this is unlikely to be achieved in an experiment.

In summary, the maximum possible amount of information can be obtained by utilising both techniques, with Raman spectroscopy continuing to provide the main bulk of experimental data for phase diagram determinations, and the EDXRD method contributing structural information inaccessible by vibrational spectroscopic means.
References for Chapter Five


Yagi, T., Shimomura, O., Yamaoka, S., Takemura, K. and Akimoto,


-133-
A low-frequency vibrational study of the M(CO)₅X series (M=Mn, Re; X= Cl, Br, I) and high-pressure investigation of rhenium pentacarbonyl iodide, Re(CO)₅I

"Climbing up on Solsbury hill I could see the city lights
Wind was blowing time stood still
Eagle flew out of the night
He was something to observe, came in close I heard a voice
Standing, stretching every nerve
I had to listen had no choice
I did not believe the information, I just had to trust imagination
Son, he said, grab your things I've come to take you home."

(Peter Gabriel)
CHAPTER 6

A LOW FREQUENCY VIBRATIONAL STUDY OF THE M(CO)\textsubscript{5}X SERIES (M = Mn, Re; X = Cl, I) AND HIGH-PRESSURE INVESTIGATION OF RHENIUM PENTACARBONYL IODIDE, Re(CO)\textsubscript{5}I

6.1 INTRODUCTION

The vibrational spectra of the pentacarbonyl halides M(CO)\textsubscript{5}X (where M = Mn, Re; X = Cl, Br, I) have been investigated quite extensively in relation to the study of bonding in certain metal carbonyl systems. The infrared and Raman spectra of certain metal carbonyls have been investigated in detail (Hyams et al., 1967; Wozniak and Sheline, 1972; Caesar et al., 1974; Hall, 1975; Wrighton et al., 1976). Kariuki and Kettle (1976, 1978) have used mixed crystals of pentacarbonyl halides in order to investigate the coupling of modes in the solid state. The two bromides of this series have been studied as single crystals in various orientations in polarised light, resulting in reasonably secure vibrational assignments (Adams and Taylor, 1982).

In comparison, far less complete vibrational assignments exist for the chlorides and iodides. Indeed there are few reports of low-frequency data, and almost none obtained at the temperatures required for the resolution of spectral components by the removal of 'hot' bands.

This chapter details new low-frequency infrared and some Raman data obtained for the rhenium and manganese pentacarbonyl chlorides and iodides at low-temperature.

6.2 EXPERIMENTAL

Samples of Mn(CO)\textsubscript{5}Cl, Mn(CO)\textsubscript{5}I, Re(CO)\textsubscript{5}Cl and Re(CO)\textsubscript{5}I were prepared by standard literature methods (Darst and Lukehart, 1976). All samples were purified by several successive sublimations before use.
Table 6.1

Factor group analysis for Re(CO)$_2$I

<table>
<thead>
<tr>
<th>$D_{2h}^{17}$</th>
<th>$N_T^a$</th>
<th>$T_A$</th>
<th>$T$</th>
<th>$R$</th>
<th>$\Gamma_{vib}$</th>
<th>Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>10</td>
<td>1</td>
<td></td>
<td>9</td>
<td>$Ra$</td>
<td></td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>8</td>
<td>$Ra$</td>
<td></td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>6</td>
<td>1</td>
<td></td>
<td>5</td>
<td>$Ra$</td>
<td></td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>8</td>
<td>$Ra$</td>
<td></td>
</tr>
<tr>
<td>$A_u$</td>
<td>6</td>
<td>1</td>
<td></td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>8</td>
<td>$ir$</td>
<td></td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>10</td>
<td>1</td>
<td></td>
<td>9</td>
<td>$ir$</td>
<td></td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>8</td>
<td>$ir$</td>
<td></td>
</tr>
</tbody>
</table>

$N_T = $ total number of unit-cell modes
$T_A = $ acoustic modes
$T = $ Optic branch modes
$R = $ libratory modes
$\Gamma_{vib} = $ internal modes
Table 6.2

correlation scheme for Re(CO)₅I

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Site</th>
<th>Unit cell&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;4v&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2v&lt;/sub&gt;(σ&lt;sub&gt;d&lt;/sub&gt;) × 2</td>
<td>D&lt;sub&gt;2h&lt;/sub&gt;¹⁷</td>
</tr>
<tr>
<td>7A₁</td>
<td>9A₁</td>
<td>9(A&lt;sub&gt;g&lt;/sub&gt;+B&lt;sub&gt;2u&lt;/sub&gt;)</td>
</tr>
<tr>
<td>A₂</td>
<td>5A₂</td>
<td>5(B&lt;sub&gt;2g&lt;/sub&gt;+A&lt;sub&gt;u&lt;/sub&gt;)</td>
</tr>
<tr>
<td>4B₁</td>
<td>8B₁</td>
<td>8(B&lt;sub&gt;3g&lt;/sub&gt;+B&lt;sub&gt;1u&lt;/sub&gt;)</td>
</tr>
<tr>
<td>2B₂</td>
<td>8B₂</td>
<td>8(B&lt;sub&gt;1g&lt;/sub&gt;+B&lt;sub&gt;3u&lt;/sub&gt;)</td>
</tr>
</tbody>
</table>

<sup>b</sup> This column is identical with Γ<sub>vib</sub>
## Table 6.3

Factor group analysis for $\text{M(CO)}_3\text{X}$ ($\text{M} = \text{Mn, Re}; \text{X} = \text{Cl, Br}$)

<table>
<thead>
<tr>
<th>$D_{2h}^{17}$</th>
<th>$N_T^a$</th>
<th>$T_A$</th>
<th>$T$</th>
<th>$R$</th>
<th>$\Gamma_{\text{vib}}$</th>
<th>Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>20</td>
<td>2</td>
<td>1</td>
<td>17</td>
<td></td>
<td>Ra</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>16</td>
<td>1</td>
<td>2</td>
<td>13</td>
<td></td>
<td>Ra</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>20</td>
<td>2</td>
<td>1</td>
<td>17</td>
<td></td>
<td>Ra</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>16</td>
<td>1</td>
<td>2</td>
<td>13</td>
<td></td>
<td>Ra</td>
</tr>
<tr>
<td>$A_u$</td>
<td>16</td>
<td>1</td>
<td>2</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>20</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>17</td>
<td>ir</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>16</td>
<td>1</td>
<td>2</td>
<td>17</td>
<td></td>
<td>ir</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>20</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>17</td>
<td>ir</td>
</tr>
</tbody>
</table>

$^a$ $N_T = \text{total number of unit-cell modes}$  
$T_A = \text{acoustic modes}$  
$T = \text{Optic branch modes}$  
$R = \text{libratory modes}$  
$\Gamma_{\text{vib}} = \text{internal modes}$
Table 6.4

Correlation scheme for $M(CO)_gX$ ($M = \text{Mn, Re}; X = \text{Cl, Br}$)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Site</th>
<th>Unit cell$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4v$</td>
<td>$C_5(\sigma_d)$</td>
<td>$D_{2h}^{16}$</td>
</tr>
<tr>
<td>7$A_1$</td>
<td>$17A'$</td>
<td>$17(A_g+B_{2g}+B_{1u}+B_{3u})$</td>
</tr>
<tr>
<td>A$_2$</td>
<td>$13A''$</td>
<td>$13(B_{1g}+B_{3g}+A_u+B_{2u})$</td>
</tr>
<tr>
<td>4$B_1$</td>
<td>$13A''$</td>
<td></td>
</tr>
<tr>
<td>2$B_2$</td>
<td>$13A''$</td>
<td></td>
</tr>
<tr>
<td>8$E$</td>
<td>$13A''$</td>
<td></td>
</tr>
</tbody>
</table>
Infrared spectrum of Mn(CO)$_5$Cl below 400 cm$^{-1}$. The spectrum was recorded at approximately 100 K. (Resolution $\sim$ 1 cm$^{-1}$).
Fig 6.2

Infrared spectrum of Re(CO)$_3$Cl below 400 cm$^{-1}$. The spectrum was recorded at approximately 100 K. (Resolution ~ 1 cm$^{-1}$).
Infrared spectrum of Mn(CO)$_5$I below 400 cm$^{-1}$. The spectrum was recorded at approximately 100 K. (Resolution $\sim 1$ cm$^{-1}$).
Fig 6.4

Infrared spectrum of Re(CO)$_5$I below 400 cm$^{-1}$. The spectrum was recorded at approximately 100 K. (Resolution $\sim$ 1 cm$^{-1}$).
All far-infrared spectra were recorded on a Beckman RIIC FS-720 Fourier transform infrared spectrometer using a room-temperature pneumatic golay detector.

The spectrometer itself was under the control of an Apple II microcomputer running a suite of interactive BASIC programs which performed routine data-logging, general spectral manipulation, and the actual fast Fourier transform (FFT) utilising a modified Cooley-Tukey algorithm.

Low-temperature infrared spectra at approximately 100 K were obtained by use of in-house manufactured cryostats used in conjunction with the above equipment.

Low-temperature Raman spectra of Re(CO)₅I were obtained using an Oxford Instruments model 704 liquid nitrogen cryostat coupled to a Coderg T800 triple monochromator Raman spectrometer.

Incident Raman scattering was achieved by using the 514.5 and 488.0 nm emission lines of a Spectra-Physics model 163 Argon ion laser, at powers of up to 0.25W at the sample.

6.3 RESULTS AND DISCUSSION - THE REGION BELOW 300 cm⁻¹

The factor group analysis (FGA) and corelation scheme for rhenium pentacarbonyl iodide are given in Tables 6.1 and 6.2 respectively. A similar correlation scheme for M(CO)₅X (M= Mn, Re; X= Cl,Br) is given in Tables 6.3 and 6.4 respectively.

The pentacarbonyl halides adopt two different structure types. Full details for each structure can be found in chapter 4.

Infrared data

It can be seen that from combination of the new infrared data with those obtained by Adams and Taylor for M = Mn, Re; X = Br, a consistent interpretation is observable. This is shown in Tables 6.5 and 6.6. Low-frequency, low-temperature infrared spectra are shown in Figs 6.1 to 6.4. The assignments for the pentacarbonyl bromides are reasonably secure in that they rest upon both infrared and Raman single crystal polarization data. The
### Table 6.5

Vibrational data (cm⁻¹) for Mn(CO)₅X, (X = Cl, Br, I) in the low-frequency region

<table>
<thead>
<tr>
<th></th>
<th>X=Cl</th>
<th>X=Br</th>
<th>X=I</th>
<th>Assignment</th>
<th>X=I(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ir (100K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>292</td>
<td>237</td>
<td>189</td>
<td></td>
<td>A₁,ν₆</td>
<td>ν(M-X)</td>
</tr>
<tr>
<td>146</td>
<td>139</td>
<td>142</td>
<td></td>
<td>B₂,ν₁₄</td>
<td>133</td>
</tr>
<tr>
<td>130</td>
<td>126</td>
<td>121</td>
<td></td>
<td>A₁,ν₇</td>
<td>122</td>
</tr>
<tr>
<td>120sh</td>
<td>119</td>
<td>107</td>
<td></td>
<td>E,ν₂₀</td>
<td>δ(C-M-C)</td>
</tr>
<tr>
<td>104</td>
<td>103</td>
<td>102</td>
<td></td>
<td>E,ν₂₁</td>
<td></td>
</tr>
<tr>
<td>94</td>
<td>78</td>
<td>80</td>
<td></td>
<td>B₁,ν₁₂</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>86</td>
<td>67</td>
<td></td>
<td>E,ν₂₂</td>
<td>δ(M-X)</td>
</tr>
<tr>
<td>83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>54</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>40</td>
<td>40</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Adams and Taylor, 1982

\(^b\) Butler and Spendijan, 1969
Table 6.6

Vibrational data (cm\(^{-1}\)) for Re(CO)\(_5\)X, (X = Cl, Br, I) in the low-frequency region

<table>
<thead>
<tr>
<th></th>
<th>X=Cl</th>
<th>X=Br</th>
<th>X=I</th>
<th>Assignment</th>
<th>X=I</th>
</tr>
</thead>
<tbody>
<tr>
<td>ir (100K)</td>
<td>296</td>
<td>216</td>
<td>164</td>
<td>(A_1,\nu_6)</td>
<td>(\nu(M-X))</td>
</tr>
<tr>
<td>Raman(100K)</td>
<td>290</td>
<td></td>
<td></td>
<td>(\delta(C-M-C))</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>142</td>
<td>133</td>
<td>111</td>
<td>(B_2,\nu_{14})</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>120</td>
<td>136</td>
<td>(A_1,\nu_7)</td>
<td>132.4</td>
</tr>
<tr>
<td></td>
<td>115</td>
<td>111</td>
<td>114</td>
<td>(E,\nu_{20})</td>
<td>(\delta(M-X))</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>104</td>
<td></td>
<td>(E,\nu_{21})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>83</td>
<td>84</td>
<td>97</td>
<td>(B_1,\nu_{12})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>165</td>
<td>94</td>
<td>88</td>
<td>(E,\nu_{22})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>66</td>
<td>62</td>
<td></td>
<td>58.6</td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>54</td>
<td>39</td>
<td>(\nu_L)</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>40</td>
<td></td>
<td></td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td></td>
<td></td>
<td>15.5</td>
</tr>
</tbody>
</table>
new data for the pentacarbonyl chlorides and iodides are assigned by direct comparison, with the following points being worthy of note.

The selection rules applicable, in this instance, are those of molecular $C_{4v}$. There is no apparent indication that any of the E mode degeneracies are lifted by the site field, in either the $M(CO)_5\text{Cl}$ or the $M(CO)_5\text{I}$ structure types. However, the $B_1, \nu_{12}$ and $B_2, \nu_{14}$ modes (which are also site allowed from being only Raman active in $C_{4v}$) do reveal themselves, although not always with any great intensity.

The most complicating feature of these spectra is the E, $\nu_{20}$ mode which is $\delta(M-X)$ in type. For both chlorides a band was observed at 165 cm$^{-1}$ attributed to this origin. This is not unreasonable as $A_1, \nu_6, \nu(Mn-Cl)$ is at 296 cm$^{-1}$, as is $\nu(Re-Cl)$. For comparison:

\[
\begin{array}{ccc}
\text{Cs}_2[\text{ReCl}_6] & \text{Cs}_2[\text{ReBr}_6] \\
\nu_3 & 313 \text{ cm}^{-1} & 217 \text{ cm}^{-1} \\
\nu_4 & 172 \text{ cm}^{-1} & 110 \text{ cm}^{-1}
\end{array}
\]

Corresponding values of $\nu_{20}$ in the bromides and iodides of the $M(CO)_5X$ series follow by analogy, although there must be some degree of mode mixing in the E-block.

The assignments shown in Tables 6.5 and 6.6 account for all six modes predicted on the basis of molecular $C_{4v}$ selection rules.

The lattice mode predictions for the two structure types adopted are quite different. For the pentacarbonyl iodides no translatory modes are permitted, with only two libratory modes allowed; one of these libratory modes has been observed. In contrast, six possible translatory and libratory modes are allowable for the pentacarbonyl chloride structure; up to four of them have been detected in particular cases.

Raman data

The new Raman data presented for Re(CO)$_5$I compares well with that previously offered by Butler and Spendjian (1969) for Mn(CO)$_5$I at ambient temperature. The new
Fig 6.5

Pressure versus frequency plot for the lattice region of Re(CO)$_3$I.
Fig 6.6

Pressure versus frequency plot for the metal-carbon region of Re(CO)$_5$I.
Fig 6.7

Pressure versus frequency plot for the carbonyl region of Re(CO)₅I.
Stacked pressure plot showing the movement of the lattice Raman bands of Re(CO)$_5$I with increasing pressure.
Stacked pressure plot showing the movement of the metal-carbon Raman bands of Re(CO)$_5$I with increasing pressure.
Fig 6.10

Stacked pressure plot showing the movement of the carbonyl Raman bands of Re(CO)$_5$I with increasing pressure.
data, obtained at low-temperature displays greater resolution of structure than that
previously reported.

The $\nu$(CO) region for the iodides agree in showing only three (very intense)
principal bands, in contrast to the much more complex carbonyl stretching region
exhibited by their chloride and bromide counterparts. The bands are readily assigned to the
$\nu_1$ and $\nu_2$, $A_1$-type modes, and to $\nu_{15}$, $E$.

Since the primitive unit cell of the iodide is bimolecular, no factor group splitting
is possible in the Raman spectra of these solids, in marked contrast to their congeners
which adopt a tetramolecular primitive unit cell (refer to Chapter 4). However, both the
$\nu_9$, $B_1$ and the second component of the $\nu_{15}$, $E$ mode are absent, being accidentally weak,
showing that in this instance even the site group rules do not apply for these materials. It
may be significant in this case that the C-Re-X angle is approximately $2^\circ$ less in
Re(CO)$_3$I than in Re(CO)$_3$Cl.

In the very low-frequency region, there is a group of strong bands in Re(CO)$_5$I
between 120 and 160 cm$^{-1}$ which are attributed to $\delta$(C-Re-C), and then nothing observable
until ca 60 cm$^{-1}$ and lower. In contrast, the chlorides and bromides display far richer
Raman spectra throughout the region below 150 cm$^{-1}$

Single-crystal Raman data for M(CO)$_3$Br (M = Mn, Re) has shown that in the
powder specimens about half the factor group analysis permitted number of bands were
observed, each generally being a supposition of two correlation components. If this is also
the case for the iodide structure type, we might reasonably expect three lattice mode
bands rather than the six required by the full factor group analysis. There are bands at
43.0, 37.0 and 15.5 cm$^{-1}$ in Re(CO)$_5$I which are almost certainly of this origin, with a
further band found near 60 cm$^{-1}$ which is assigned as $\nu_{22}$, $E$, $\delta$(Re-I) and which is observed
to have an infrared counterpart.
### Table 6.7

<table>
<thead>
<tr>
<th>$\nu_i$</th>
<th>$\delta\nu/\delta P$</th>
<th>$1/\nu_i \Delta\nu/\Delta P \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5</td>
<td>0.63</td>
<td>4.7</td>
</tr>
<tr>
<td>33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40.5</td>
<td>0.62</td>
<td>1.53</td>
</tr>
<tr>
<td>56</td>
<td>0.36</td>
<td>0.64</td>
</tr>
<tr>
<td>120</td>
<td>0.43</td>
<td>0.36</td>
</tr>
<tr>
<td>128</td>
<td>1.38</td>
<td>1.1</td>
</tr>
<tr>
<td>&lt;b&gt;160&lt;/b&gt;</td>
<td>&lt;b&gt;-&lt;/b&gt;</td>
<td>&lt;b&gt;-&lt;/b&gt;</td>
</tr>
<tr>
<td>163</td>
<td>0.34</td>
<td>0.21</td>
</tr>
<tr>
<td>355</td>
<td>0.46</td>
<td>0.13</td>
</tr>
<tr>
<td>370.5</td>
<td>0.76</td>
<td>0.21</td>
</tr>
<tr>
<td>412.5</td>
<td>0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>440</td>
<td>0.47</td>
<td>0.11</td>
</tr>
<tr>
<td>475</td>
<td>0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>495.5</td>
<td>0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>549</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>579</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>589</td>
<td>0.16</td>
<td>0.03</td>
</tr>
<tr>
<td>1984</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2074</td>
<td>0.28</td>
<td>0.014</td>
</tr>
<tr>
<td>2150</td>
<td>0.43</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* curve • estimated
Table 6.8
Pressure-sensitivities of the Raman-active modes of $M(CO)_{5}X$ ($M = Mn, Re; X = Br, I$)*

<table>
<thead>
<tr>
<th>$\nu_{(CO)}$</th>
<th>$M(CO)_{5}Br$</th>
<th>Re($CO)_{5}Br$</th>
<th>Re($CO)_{5}I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{1}$</td>
<td>0.0065</td>
<td>0.014</td>
<td>0.020</td>
</tr>
<tr>
<td>$\nu_{9}$</td>
<td>0.016</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>$\nu_{15}$</td>
<td>0.008</td>
<td>0.008</td>
<td>0.014</td>
</tr>
<tr>
<td>$\nu_{2}$</td>
<td>-</td>
<td>0.005(4)</td>
<td>0</td>
</tr>
<tr>
<td>$\nu_{(M-X)}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{1,\nu_{6}}$</td>
<td>0.32</td>
<td>0.20</td>
<td>0.30</td>
</tr>
</tbody>
</table>

$\bullet$ $1 \times 10^2 \frac{\Delta \nu_{i} \times 10^2}{\nu_{i} \Delta P}$ in cm$^{-1}$Kbar$^{-1}$
Table 6.9
Pressure-sensitivities for M(CO)₅X (M = Mn, Re; X = Br, I) with vibrational assignment

<table>
<thead>
<tr>
<th>υ₁</th>
<th>Re(CO)₂Br</th>
<th>(Δυ₁/ΔP)</th>
<th>(1/υ₁,[Δυ₁/ΔP] x 10²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>591</td>
<td>A₁,υ₃</td>
<td>0.08</td>
<td>0.014</td>
</tr>
<tr>
<td>586</td>
<td>υ₁₆</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>556</td>
<td>υ₁₇</td>
<td>0.1</td>
<td>0.018</td>
</tr>
<tr>
<td>501</td>
<td>υ₁₀</td>
<td>0.37</td>
<td>0.074</td>
</tr>
<tr>
<td>487.5</td>
<td>υ₁₃</td>
<td>0.1</td>
<td>0.021</td>
</tr>
<tr>
<td>442.5</td>
<td>υ₄</td>
<td>0.46</td>
<td>0.10</td>
</tr>
<tr>
<td>412</td>
<td>υ₅</td>
<td>0.09</td>
<td>0.022</td>
</tr>
<tr>
<td>369</td>
<td>υ₁₁</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>351</td>
<td>υ₁₉</td>
<td>0.48</td>
<td>0.140</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>υ₁</th>
<th>Re(CO)₂Br</th>
<th>(Δυ₁/ΔP)</th>
<th>(1/υ₁,[Δυ₁/ΔP] x 10²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>589</td>
<td>A₁,υ₃</td>
<td>0.16</td>
<td>0.027</td>
</tr>
<tr>
<td>579</td>
<td>υ₁₆</td>
<td>0.08</td>
<td>0.014</td>
</tr>
<tr>
<td>548</td>
<td>υ₁₇</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>495</td>
<td>υ₁₀</td>
<td>0.20</td>
<td>0.040</td>
</tr>
<tr>
<td>475</td>
<td>υ₁₃</td>
<td>0.20</td>
<td>0.042</td>
</tr>
<tr>
<td>440</td>
<td>υ₄</td>
<td>0.47</td>
<td>0.110</td>
</tr>
<tr>
<td>413</td>
<td>υ₅</td>
<td>0.12</td>
<td>0.029</td>
</tr>
<tr>
<td>371</td>
<td>υ₁₁</td>
<td>0.76</td>
<td>0.200</td>
</tr>
<tr>
<td>355</td>
<td>υ₁₉</td>
<td>0.46</td>
<td>0.130</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>υ₁</th>
<th>Mn(CO)₃Br</th>
<th>(Δυ₁/ΔP)</th>
<th>(1/υ₁,[Δυ₁/ΔP] x 10²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td></td>
<td>0.645</td>
<td>0.140</td>
</tr>
<tr>
<td>383.5</td>
<td></td>
<td>0.928</td>
<td>0.24</td>
</tr>
<tr>
<td>414</td>
<td></td>
<td>0.719</td>
<td>0.170</td>
</tr>
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</table>
Crossover point associated with the $\nu(\lambda\epsilon-I)$ and one of the $\delta(C-\lambda\epsilon-C)$ modes.
Factor Group Analysis (FGA) details are given in tables 6.1 and 6.3.

6.7 DISCUSSION

The spectra

The pressure against frequency plots display the usual hardening of mode frequencies associated with increasing pressure. The plots are continuous, with no observable breaks or changes of slope typically indicative of a phase transition. The same is true for Re(CO)$_5$Br.

Analysis of the Re(CO)$_5$I spectra reveal a crossover point associated with the $\nu$(Re-I) and one of the $\delta$(C-Re-C) modes observed initially at 163 and 128 cm$^{-1}$ respectively, as shown in figure 6.11. The sharper $\nu$(Re-I) band appears to merge into, and then crosses behind the deformational mode with increasing pressure. However, it should be noted that this deformational mode region is complex, comprising several contributions which could be resolved at low-temperatures and by use of appropriate single crystal techniques (Taylor, 1983), including one of A1 symmetry. This symmetric component should be repelled by the same symmetry A1, $\nu$(Re-I) mode. From the data observed it is uncertain as to whether or not this is, in fact, the case. This ambiguity could be resolved by employing the use of low-temperatures in conjunction with high-pressures. With increasing pressure, several weak bands are observed to appear in the region 70 - 100 cm$^{-1}$ which are present in low-temperature capillary spectra, although not in ambient temperature spectra. In addition, there is a low-intensity band, which is definitely not observable at ambient pressure even at 80 K, which first appears at approximately 11 kbar and then shifts rapidly with increasing pressure ($\gamma_1^* = 1.12$). It is unlikely that this feature is a fundamental mode, but it is conceivable that it may be a combination of a $\delta$(C-Re-C) mode with a librational lattice mode. This would account for its large observed high pressure-sensitivity.

The lattice modes (below 40 cm$^{-1}$) display large $\gamma_1^*$ values, typical for such modes in molecular crystals, and are comparable with those for Mn(CO)$_5$Br (Adams and Ekijuba, 1982).
6.8 COMPARISON OF PRESSURE SHIFTS FOR M(CO)$_5X$ (WHERE M = Mn, Re; X = Br, I)

The general effect of increasing pressure on a molecular solid is to raise the internal and lattice mode frequencies. However, in the case of metal-carbonyl complexes a special bonding situation occurs in that the weakest bonds present are metal-carbon, and consequently they are likely to undergo the greatest shifts with pressure. Because of the well characterised dπ-π* back-bonding arrangement in such systems, compression of the metal-carbon bonds will consequently be accompanied by a lowering of the υ(CO) modes due to an increase in population of the anti-bonding orbital. Hence, the observed pressure-shift of a υ(CO) mode in a metal-carbonyl system will be the resultant of the increase due to lattice compression, less the decrease due to increased metal-carbon back-bonding.

In comparison of data obtained for Re(CO)$_5$I and Re(CO)$_5$Br with those for Mn(CO)$_5$Br, it is important to compare only those data of a similar nature. Due to differing band intensities, all modes present in the ambient powder spectra were not directly evident at elevated pressures in a d.a.c. The most readily assigned and observable are those of the A$_1$ (C$_{4v}$) symmetry. Thus, for Re(CO)$_5$I, the A$_1$ υ(CO) modes υ$_1$ and υ$_2$ have an average $\gamma^*_1$ ($\gamma^*_1 = \gamma^*_2 = 1/\nu(Q_1/\Delta P)$) of 0.01, whereas the corresponding υ(Re-C) modes υ$_4$ and υ$_5$ have $\gamma^*_i = 0.07$. Very similar values are obtained for Re(CO)$_5$Br (0.01 and 0.06 respectively), but those values obtained for Mn(CO)$_5$Br are approximately three times greater than those derived for the two rhenium analogues, and the converse applies to the υ(CO) modes. This leads to the conclusion that increased pressure leads to a significant enhancement of dπ-π* back-bonding for the manganese compound over the rhenium ones. The υ(CO) modes in Mn(CO)$_5$Br are, therefore, lowered with increased pressure although, as previously explained, due to general compression of the lattice, most of them actually exhibit slight positive trends.

For both rhenium compounds the lower bands in the υ(Re-C), δ(Re-C-O) region show larger $\gamma^*_i$ values, associated with having greater Re-C stretching contributions.

6.9 CONCLUSIONS

The main conclusion drawn from this investigation is that the observed effects of pressure on the Raman spectra of M(CO)$_5X$ compounds (where M = Mn, Re; X = Br, I)
are chiefly dependent upon the nature of the central metal atom, rather than by the adoption of a different crystal structure by the bromides to that of the iodide, as discussed in chapter 3. Differing crystal structures may well reveal differing solid-solid phase transitions under pressure, and these materials may well exhibit such phase relational behaviour at pressures greater than those achieved in this study. Nevertheless, the results obtained are indicative of how the molecular internal bonding of a solid-state structure responds with the application of increasing pressure.
References for Chapter Six


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Chapter Seven

An infrared, Raman and high-pressure study of MXO$_3$
(where M=Na, K; X=Cl, Br)

"There's an angel standing in the sun
And he's crying with a loud voice
This is the supper of the almighty one
The Lord of Lord's, King of King's
Has returned to lead his children home
To take them to the new Jerusalem."

(Genesis)
CHAPTER 7

AN INFRARED, RAMAN AND HIGH-PRESSURE RAMAN STUDY OF MXO₃
(M = Na, K; X = Cl, Br)

7.1 INTRODUCTION

As part of a continuing program of investigation into the structural principles inherent in complex ionic salts: KCN (Adams and Sharma, 1978), NaNO₂ (Adams and Sharma, 1971), KNO₂ (Adams et al, 1988), KNO₃ (Adams and Sharma, 1981; Adams et al., 1988) and MSCN (Adams and Pogson, 1988), a vibrational study of certain metal halate salts was undertaken.

These salts exhibit a variety of related structures under ambient conditions (Table 7.1) and, where they have been investigated, display quite complex phase behaviour.

Table 7.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Unit-cell occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₃</td>
<td>P2₁3 = T⁴</td>
<td>Z = 4</td>
</tr>
<tr>
<td>NaBrO₃</td>
<td>isostructural with NaClO₃</td>
<td></td>
</tr>
<tr>
<td>KBrO₃</td>
<td>R₃m = C₃ᵥ ⁵</td>
<td>Z = 1</td>
</tr>
<tr>
<td>KClO₃</td>
<td>P2₁/m = C₂ᵥ ²</td>
<td>Z = 2</td>
</tr>
</tbody>
</table>

7.2 EXPERIMENTAL

Analar materials were dried before use. High-pressure Raman spectra were recorded as described in chapter 2 using a Coderg T800 instrument with 488.0 and 515.5
Fig 7.1

Phase diagram for NaClO$_3$. 
Table 7.2
Factor group analysis for NaClO$_3$

<table>
<thead>
<tr>
<th>T'</th>
<th>A</th>
<th>E</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>Na</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4a</td>
<td>Cl</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>12b</td>
<td>O</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>N_T</th>
<th>T_A</th>
<th>T</th>
<th>R(ClO$_3^-$)</th>
<th>T$_{vib}$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>2</td>
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</tr>
<tr>
<td></td>
<td>15</td>
<td>1</td>
<td>5</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 7.3
Correlation table for NaClO$_3$

ClO$_3^-$ site unit cell

\[ C_{3v} \rightarrow C_3 \rightarrow T' \]

\[ 2A_1, \nu_1, \nu_2 \rightarrow 2A \rightarrow 2(A+T) \]

\[ 2E, \nu_3, \nu_4 \rightarrow 2E \rightarrow 2(E+2T) \]
Fig 7.2

Frequency versus pressure plot for the lattice region of NaClO₃.
Fig 7.3

Frequency versus pressure plot for the Cl-O stretching region of NaClO$_3$. 

nm excitation. Far-ir spectra were recorded on a Bruker 113v FT-IR instrument at the Department of Chemistry, University College of London. Low-temperature Raman spectra were obtained using an Oxford Instruments model DN 704 cryostat.

7.3 RESULTS AND DISCUSSION

NaClO₃

Bridgman (1945) studied the compressibility of NaClO₃ from 300 to 470 K, and at pressures up to 50 kbar. He reported the phase diagram shown in Fig 7.1. Three other phases were discovered to exist at varying temperatures and pressures in addition to the stable phase (I) at ambient conditions. Bridgman recorded the stability regions of two of these phases down to ambient temperatures with observed transition pressures of 16 and 36 kbar respectively. The third high-temperature phase was assigned to that of liquid NaClO₃ by Rappaport (1967).

At ambient pressures, NaClO₃ crystalises in the non-centrosymmetric space group T₄ (P2₁3) (Wycoff, 1964) with four molecules occupying the primitive cell. All optic phonons are thus active for this structure. The Raman spectrum of this ambient phase has been investigated and assigned by Hartwig et al (1969).

Table 7.2 shows the factor group analysis for NaClO₃. Table 7.3 shows the correlation table for the same compound.

Frequency shift versus pressure plots for NaClO₃ can be seen in Fig 7.2 and Fig 7.3.

Although NaClO₃ is reported to undergo a transition from phase (I) to phase (II) near 16 Kbar, no observable change is detected in the Raman spectra. A phase transition is tentatively assigned in the region of 36 kbar as per Bridgman and Nicol et al (1977). The transition is characterised by the emergence of a new band (or bands) in the ν(Cl-O) region. These new peaks can only be due to a lower symmetry in the new phase, lifting some of the degeneracies of the cubic structure.

The reported volume changes by Bridgman for the two ambient temperature phases are 3.5 x 10⁻⁴ cm³g⁻¹ and 3 x 10⁻³ cm³g⁻¹² at 16 and 36 kbar respectively. Thus, the
Diagrammatical representation of the Raman and Far-IR spectra for NaClO₃, showing the mode assignment. Spectra were recorded at approximately 100 K.
Fig 7.5

Diagramatical representation of the Raman and Far-IR spectra for NaBrO$_3$, showing the mode assignment.
Spectra were recorded at approximately 100 K.
Fig 7.6

Frequency versus pressure plots for NaBrO$_3$ in the region 0 - 300 cm$^{-1}$. 
Fig 7.7

Frequency versus pressure plots for NaBrO\textsubscript{3} in the region 350 - 500 cm\textsuperscript{-1}. 
Fig 7.8

Frequency versus pressure plots for NaBrO₃ in the region 720 - 920 cm⁻¹.
volume change recorded for the first transition is clearly small, and might correspond to a more nearly second-order transition, which is more difficult to detect using vibrational spectroscopic techniques.

This work confirms that of Nicol and co-workers in not detecting a phase transition at 16 kbar. The reported phase change at ~36 kbar is observed. However, the spectra obtained during this study were of poor quality due to high fluorescence backgrounds from the diamond anvils and the poor Raman scattering observed from NaClO₃ which rapidly becomes transparent under the application of pressure.

**NaBrO₃**

The vibrational spectra of NaBrO₃ are poorly documented, and there appear to be no reports of its far-ir spectrum. This material is isostructural with NaClO₃ (see Table 7.1) for which a full vibrational assignment has been made by Hartwig et al (1969). Thus, by analogy, NaBrO₃ is assigned using NaClO₃ as a model. The Raman spectrum of NaBrO₃ strongly resembles that of its chlorate counterpart. The spectra are complex in nature because the cell is both tetramolecular and non-centric. Accordingly, the Raman spectra show both $lo$ and $to$ components for the $T$ species modes, as they carry both i.r. and Raman activity.

**Figure 7.4** shows Raman spectra of NaClO₃ at ambient and LN temperatures together with the assignment of Hartwig et al (Table 7.4).

**Figure 7.5** shows Raman and far-ir spectra of NaBrO₃ at ambient (Raman) and LN (Raman and far-ir) temperatures. The assignment of the spectrum is given in table together with that for NaClO₃ (Table 7.5).

**Figures 7.6** to 7.8 show frequency shift versus pressure plots for NaBrO₃. The observed high-pressure Raman spectra give rise to a clear change in slope in the pressure plots indicative of a phase transition at ~24 kbar. Beyond 40 Kbar NaBrO₃ phase (II) remains stable to at least 100 Kbar, but the region from 25 to 40 kbar is difficult to interpret on the vibrational evidence alone. The data admit the possibility of a further structural change near 40 kbar but, equally, might represent a region of intergrowth between phases (I) and (II). Diffraction data are required to clarify the events occurring within this region.
Table 7.4
Optical phonons of NaClO₃

<table>
<thead>
<tr>
<th>Raman</th>
<th>A</th>
<th>E</th>
<th>T_{lo}</th>
<th>T_{to}</th>
<th>Assignment</th>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>v₃</td>
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<td></td>
<td>595</td>
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<td>990</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>938</td>
<td>937</td>
<td>943</td>
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<td>v₁</td>
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<td>933.4¹</td>
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¹ = isotope frequencies
² = assignment from Hartwig et al
³ = assignment from Miller et al combined
⁴ = this data
### Table 7.5

**Optical phonons of NaBrO₃**

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>E</th>
<th>( T_{lo} )</th>
<th>( T'_{lo} )</th>
<th>i.r</th>
<th>Assignment</th>
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</table>
Fig 7.9

Frequency versus pressure plots for KBrO$_3$ in the region 100 - 260 cm$^{-1}$.
Fig 7.10

Frequency versus pressure plots for KBrO$_3$ in the region 350 - 400 cm$^{-1}$.
Fig 7.11

Frequency versus pressure plots for KBrO₃ in the region 420 - 470 cm⁻¹.
KBrO$_3$
Fig 7.12

Frequency versus pressure plots for KBrO₃ in the region 750 - 900 cm⁻¹.
### Table 7.7
Assignment for KBrO$_3$

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<tr>
<th>Raman</th>
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<td>$\nu_2 (A_1)$</td>
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<tr>
<td>369</td>
<td>lo</td>
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<tr>
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<td>to</td>
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<td>112</td>
<td>sh</td>
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</tr>
</tbody>
</table>
KBrO₃

There appears to be no high-pressure data recorded for KBrO₃ in the literature, not even by Bridgman.

The reported ambient crystal structure is R3m (C₃ᵥ) with Z = 1, or possibly R3m (D₃d) with Z = 1, (see Hartwig et al and references therein) but there is no spectroscopic evidence which is not readily accommodated on this basis. In view of this ambiguity an investigation to establish the crystal structure was undertaken (Heath and Russell, 1988) and confirmed that the symmetry is R3m (C₃ᵥ) with Z = 1. Thus it should display a simple vibrational spectrum as indicated by the factor group analysis shown in Table 7.6. Because the group is non-centric and both A₁ and E species carry both i.r. and Raman activity, the Raman spectrum may also show lo modes. As in other non-centric solids (eg. NaN₂O₂, NaClO₃), Raman phonon frequencies may be strongly dependent upon the propagation direction in the crystal, with any preferred crystal orientations in the sample generating extra peaks.

All of these factors appear to be contributory in the Raman spectrum of KBrO₃. The clearest region is that of the (A₁), (E), δ(Br-O) modes. Here the Raman spectrum shows a doublet for each, the higher component in each case being the lo component; the to component agrees within experimental error with the i.r. equivalent.

The υ(Br-O) region has υ₁(A₁) and υ₃(E) co-incident in solution but showing the expected four lo and to components in the solid (plus an isotopic component).

There should be three i.r. active lattice modes: These were found (112, 126 and 170 cm⁻¹ - LN data). They have Raman analogies as shown in Table 7.7.

The high-pressure Raman data indicate the presence of a phase transition near 19 Kbars, seen as breaks or changes in slope in frequency shifts versus pressure plots, as shown in Figures 7.9 to 7.12. It is difficult, in particular, to account for the appearance of the spectra in the 350 - 450 cm⁻¹ region (υ₂, A₁, υ₄, E) on the basis of a unimolecular unit cell due to the reasons outlined above.
7.4 CONCLUSIONS

The data presented in this section extends the work previously performed on complex ionic salts. New phase transitions have been observed for NaBrO₃ and KBrO₃, low-frequency vibrational spectra are displayed and a vibrational assignment is given for NaBrO₃ based on previous reported work. The investigation of NaClO₃ confirms earlier work performed by Nicol and co-workers.
References for Chapter Seven


ABSTRACT

An introduction to the theory of phase transitions is presented which includes both thermodynamic and structural treatments of phase transitions. A literature review of the role of vibrational spectroscopy in the investigation of phase transitions is given for the period covering 1978 to 1987.

Full experimental procedures are outlined covering the design and use of the diamond anvil cell (d.a.c.) utilised in the experimental investigations undertaken in this work.

The single crystal structure of Re(CO)$_3$I has been determined by x-ray diffraction techniques, together with a structural comparison with the other members of the Re(CO)$_3$X series (where X = Cl, Br).

Following on from the above, a vibrational investigation of the M(CO)$_3$X series (where M = Mn, Re; X = Cl, Br, I) is presented. An accompanying high-pressure Raman investigation of Re(CO)$_3$I is also shown.

The group I metal halate series MXO$_3$ (where M = K, Na; X = Cl, Br) have been investigated by infrared and Raman spectroscopy. High-pressure data are available for some of the series.

In continuation of earlier work a phase structural investigation, at high-pressure, of KClO$_3$ was performed using synchrotron radiation at the SRS, Daresbury.