THE STRUCTURE AND DYNAMICS OF

MOLECULAR CRYSTALS

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Ph.D. Thesis

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Other people can talk about how to expand the destiny of mankind. I just want to talk about how to fix a motorcycle.

Robert M Pirsig.
I wish to express my gratitude to all those who have helped to make this work possible.

In particular, I am indebted to my supervisor, Dr. G.S. Fawley, for his continued guidance and encouragement.

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The research described in this thesis was the unaided work of the author, unless otherwise indicated. Where the research was done in collaboration with others, there was a significant contribution by the author.
Abstract

Structural and dynamical properties of a number of molecular crystals have been investigated by coherent inelastic neutron scattering, Raman scattering and neutron powder diffraction.

Measurements of the phonon dispersion relations in perdeuteronaphthalene have been assigned with the aid of a rigid molecule lattice dynamics calculation. The intermolecular forces were derived from semi-empirical potential functions which represented the interactions between non-bonded atoms. An attempt was made to improve the model by altering the potential function parameters to get a closer correspondence between observed and calculated frequencies.

The method of total profile refinement has been used in the analysis of neutron powder diffraction data from perfluorodiphenyl, octafluoronaphthalene and para-diiodo and para-dibromo-tetrafluorobenzene. It has been shown that it is possible, by means of reasonable constraints, to refine a molecular structure involving a large number of atoms. The Rietveld program for structure refinement was used for perfluorodiphenyl but the constraint facilities of this program have been found to be inadequate for the lower symmetry systems of interest. The development and use of a new refinement program, embodying more versatile constraint facilities is described.

The Raman spectrum of perfluorodiphenyl has been interpreted in terms of a simple polarisability model. The low frequency totally symmetric spectra are explained by the coupling of a lattice vibration with a torsional mode of the molecule.

The phase transition in octafluoronaphthalene has been investigated by Raman scattering and neutron powder diffraction. The weight of experimental evidence points to a unit cell doubling with no change in
space group symmetry. Lattice dynamics calculations support this, and indicate that an instability in a zone boundary acoustic mode, may be associated with the transition.
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CHAPTER 1

BRIEF REVIEW AND INTRODUCTION
1.1 Theoretical Models

The lattice dynamics of solids in which the basic structural units are individual atoms or ions is a well developed field in physics. The development of the theory is due mainly to Born and collaborators, and the standard reference work on the subject is that of Born and Huang (1954). In the Born-von Karman formalism, the procedure is to assign three positional degrees of freedom to each atom in the crystal, set up the equations of motion, and then solve them to obtain the vibrational frequencies and displacements of the atoms. There are, however, serious limitations in applying this method to more complicated systems in which the basic units are molecular groups. Such solids generally exhibit low crystal symmetry and have a large number of atoms in the primitive unit cell. This makes the solution of the dynamical problem computationally difficult because of the large number of degrees of freedom involved. More importantly, the physical picture of the molecular groups vibrating as whole units is lost, and can only be constructed retrospectively after the equations of motion have been solved.

The motion of the groups as whole units is a distinguishing feature of molecular crystals and arises from the fact that the forces between molecules are usually much weaker than those between the atoms within each molecule, so that the molecules essentially retain their free state character. Because of the existence of two strengths of interaction in molecular crystals, the normal modes may be divided into two types: the internal modes, and the external modes. The internal modes are those in which the atoms within the molecule move with respect to each other while the centre of mass of the molecule remains fixed. The frequencies of these modes are generally quite high, above, say, 3THz. Since the interaction between neighbouring
molecules is weak, the frequencies of the internal modes differ only slightly from the free state values and are very weakly dependent on \( g \), the phonon wavevector. The external modes are those in which the molecules move as whole units and generally have frequencies between 0 and about 3THz which are strongly dependent on \( g \). The motion consists of rotation, or libration, as well as translation, so that in general each molecule has six external degrees of freedom.

This division into two types of vibration is often called the separation approximation, the applicability of which can be judged by the difference in the vibrational frequencies of the two types of modes. In the rigid molecule approximation, the separation between the internal and external modes is assumed to be large. The lattice dynamics calculations then follow the standard Born-von Karman procedure using the molecular translational and rotational coordinates instead of the individual atomic coordinates. The effects of non-rigidity can be investigated subsequently by reintroducing the degrees of freedom corresponding to the internal modes.

The theoretical and experimental developments in molecular lattice dynamics have been discussed in the reviews by Venkataraman and Sahni (1970) and Schnepp and Jacobi (1972). The first complete lattice dynamical treatment of a molecular crystal was done by Cochran and Pawley (1964) for hexamethylenetetramine, HMT. This substance is of sufficiently high symmetry that the force constants could be treated as individual model parameters which were adjusted to fit the experimental data. Normally, however, the symmetry of molecular crystals is so low that the number of independent force constant parameters becomes exceedingly large. In these circumstances a different approach is required. The method adopted has been to postulate an intermolecular
potential from which all the required force constants may be derived. Pawley (1967) presented the first complete treatment of this kind in his model of the lattice dynamics of naphthalene and anthracene. The intermolecular potentials were represented by semi-empirical atom-atom pair potential functions of the form:

$$V(r) = A + B \exp(-\alpha r)$$

where $r$ is the distance between two atoms in different molecules and the parameters depend on the type of atom-atom contact considered.

This type of treatment has since been applied to several other molecular crystals including HMT (Dolling, Pawley and Powell 1970), para-dichlorobenzene (Reynolds, Kjems and White 1972) and most recently orthorhombic sulphur (Rinaldi 1973, Rinaldi and Pawley 1975). In most cases the calculations agree well with the available experimental data but it is hoped that the inadequacies in the model will become evident as more extensive data is obtained. A more sophisticated model which includes the molecular polarisability has been outlined by Luty and Pawley (1974) following the shell model which has been used for the lattice dynamics of ionic crystals (Woods et al 1960). The effect of the non-rigidity of the molecules has been investigated by Pawley and Cyvin (1970) who allowed the atoms within each molecule to move with respect to each other using force constants obtained from studies of the gaseous phase. The results of their calculation gave an indication of the effect on the internal modes due to the crystalline forces as well as the effect on the external modes due to the distortion of the molecules. The latter effect proved to be quite considerable for naphthalene being greater than the typical experimental errors in a neutron scattering experiment. The suggestion was made that experimental frequencies should be
adjusted in proportion to the predicted shifts so that a rigid molecule model may still be used in the model fitting procedure.

1.2 Experimental Techniques

Various techniques can be employed to investigate the vibrations in molecular crystals. Raman scattering and infrared absorption enable the modes with zero wavevector to be studied, while Brillouin scattering and ultrasonic velocity measurements are restricted to the region of very small wavevector. The thermal diffuse scattering of X-rays gives results for all wavevectors, but the extraction of the phonon frequencies is difficult. By far the most powerful technique is the coherent inelastic scattering of thermal neutrons, by which phonons, throughout the Brillouin zone may be measured directly. Incoherent inelastic scattering, on the other hand, provides only qualitative information about the frequency distribution of the normal modes.

Coherent inelastic neutron scattering measurements require relatively large single crystals of the material under investigation. In addition, any hydrogen in the material must be replaced by deuterium to avoid the strong incoherent scattering from hydrogen. Unfortunately, suitable samples are difficult to obtain and consequently, the number of molecular crystals which have been fully investigated by coherent scattering, is rather small. Of these, the most extensively studied is HMT, for which high quality measurements of the phonon dispersion curves exist (Dolling and Powell 1970). These results have been used for fitting a variety of dynamical models, both in the original paper and by Rafizadeh and Yip (1970) and Dolling, Pawley and Powell (1970). One of the most recent detailed investigations of a molecular crystal was that of orthorhombic sulphur (Rinaldi 1973
and Rinaldi and Pawley 1975). The advantage of studying this material is that it is made up of only one type of atom, and hence, the number of model parameters is small, since only one atom-atom potential function is required. Several branches of the phonon dispersion curves were measured, and these, together with the available Raman measurements, were compared with the results of model calculations using '6-exp' functions. Although the agreement between observed and calculated frequencies was good, it is hoped that the fit may be improved when a more sophisticated model, including the effects of molecular polarisability, is used.

The molecules mentioned so far have been relatively large. There is also considerable interest in the dynamics of small molecules such as CO$_2$, OCS and HCN. Only the first of these has been extensively investigated by coherent inelastic neutron scattering (Powell et al 1973). Preliminary measurements have been made on the deuterated form of HCN which has one linear molecule in the primitive unit cell, and hence, has only five external mode branches (Dietrich, Mackenzie and Pawley 1975). This makes the measurement and assignment of the phonon branches relatively simple since they are not confused by the overlapping which occurs in more complex structures. In addition, the crystal exhibits a structural phase transition from a high temperature tetragonal phase, to a low temperature orthorhombic phase. Lattice statics and dynamics calculations for HCN have been done by Rae (1969, 1972) who found that a transverse acoustic mode in the direction of the base diagonal had anomalous behaviour, indicating that an instability in such a mode might be associated with the phase transition. Although the sample used in the experiments was of poor quality, a mode of the predicted character was observed to decrease in frequency
as the phase transition was approached from above. Attempts to grow a better crystal proved unsuccessful however, and the results obtained so far are limited to those described in the preliminary report (Dietrich, Mackenzie and Pawley 1975). It is planned to use a variety of crystal growing techniques to obtain a sample suitable for more detailed measurements. The multi-crystalline nature of the samples used so far have caused incoherent scattering to obscure the details of the phonon spectra at low energy. It is hoped that a more perfect crystal will allow this region to be investigated, particularly at small values of the phonon wavevector $q$.

1.3 Structural Studies

A good knowledge of the structure of a crystal is normally a prerequisite for any dynamical study. This is particularly true, when some model is to be used to represent the crystalline forces since the model must predict the equilibrium positions of the atoms as well as their vibrational frequencies. Although the techniques of crystal structure determination, using single crystal specimens, are well developed, the extraction of meaningful structural information from powder diffraction data is a relatively new field of the study. Neutron powder diffraction offers a method of determining the structures of crystals for which single crystal measurements are either difficult or impossible. The technique is particularly useful in the study of substances which undergo phase transitions when the pressure or temperature is changed. Structural phase transitions are common in molecular systems and the study of such systems can give important information about the pressure and temperature dependence of the inter-molecular forces. Changes in crystal structure are often
accompanied by a breaking up of the crystal, which makes single crystal structure analysis impossible.

The structures most commonly found in molecular crystals tend to be of low symmetry, predominantly monoclinic, with fairly large unit cells. This gives rise to a large number of powder diffraction peaks, even at low angles. Thermal motion causes a rapid fall off in the intensity of the diffraction peaks as the scattering angle increases. In consequence, structural studies of such systems must rely on the limited amount of information contained in the low order peaks in the diffraction pattern. Much of the present work is concerned with the application of diffraction profile analysis to the refinement of molecular crystal structures. The development and the use of the computer programs for this purpose are described in detail in Chapter 4.

1.4 The Present Work

The experimental work described in this thesis includes both structural and dynamical investigations of several molecular crystals. The main subjects of study were the aromatic molecular crystals of perdeuteronaphthalene, perfluorodiphenyl and octafluoronaphthalene. The first of these was investigated using neutron coherent inelastic scattering, while the latter two were studied by Raman scattering and neutron powder diffraction. Studies of para-diiodo and para-dibromo-tetrafluorobenzene and orthorhombic sulphur are described more briefly as examples of the use of powder profile refinement and Raman scattering.
1.5 Frequency Units

Three different units are commonly used for vibrational frequencies. The particular unit used generally depends on the context and the experimental technique under consideration. Optical spectroscopists normally use the wavenumber (cm$^{-1}$) which is defined in terms of the shift in reciprocal wavelength of the light:

$$\nu = \frac{1}{\lambda_0} - \frac{1}{\lambda_1} \quad \text{where} \quad \lambda \text{ is in cm}$$

Neutron spectroscopists use either the milli-electron-volt (meV), a unit of energy, or the tera-Hertz (THz), a true frequency. The approximate relationships between these units are shown below:

6THz $-$ 25meV $-$ 200cm$^{-1}$
CHAPTER 2

LATTICE DYNAMICS OF MOLECULAR CRYSTALS
2.1 The potential function

As already mentioned in Chapter 1, the first full lattice dynamics calculation of a molecular crystal, hexamethylenetetramine, (Cochran and Pawley 1964) used force constants as the model parameters. The approach taken in later work, however, was to represent the intermolecular potential by a function of relatively few parameters from which all the force constants could be calculated. A simple pairwise interaction between molecules is inadequate since this does not represent the anisotropy in the system due to the shape of the molecules. A way to include the molecular shape in the model is to represent the interactions between atoms in different molecules by some explicit potential function. The intermolecular potential can be expressed as

\[ V = \sum_{ij} V_{ij}(r_{ij}) \]

where \( r_{ij} \) is the separation between the \( i \) and \( j \) atoms in the molecules \( n \) and \( m \) respectively.

The atom-atom potential function approach has been used by several authors in studies of crystal packing (Kitaigorodskii 1961 and 1966, Craig et al 1965, Liquori et al 1968, Williams 1966 and 1967). The most commonly used form is the Buckingham "6-exp" function:

\[ V_{ij} = -\frac{A_k}{6} \frac{1}{r_{ij}^6} + B_k \exp (-\alpha_k r_{ij}) \]

where the constants \( A_k, B_k \) and \( \alpha_k \) depend on the chemical nature of the atom pair under consideration.

The first term represents the attractive Van der Waals or induced dipole-dipole interaction. The second term is the short range repulsive interaction which can also be represented by an inverse twelfth term, \( C_k / r_{ij}^{12} \), (the Lennard-Jones potential). Mixed potentials involving central, multipole and atom-atom forces have also been used to represent the inter-
molecular interaction (Craig et al. 1965). A number of sets of parameters for the 6-exp potential for carbon and hydrogen atoms derived from studies of several aromatic and aliphatic hydrocarbons are listed in Table 2.1. Those derived by Kitaigorodskii (1966) were used by Pawley (1967) for the calculation of the lattice dynamics of naphthalene and were also used as the starting point for the analysis of the neutron measurements of perdeuteronaphthalene (Chapter 6).

The atom-atom interactions are summed between all non-bonded contacts for separations out to a maximum, R. It has been found by calculation (Pawley 1967) that a maximum separation of 5.5\(\AA\) introduces errors of less than 1% in the calculated phonon frequencies for naphthalene. The long range interactions are not ignored completely however. These are included in the crystal potential energy calculation by replacing the sum over i and j by an integral, assuming a homogeneous atomic density, so that the total potential energy of the crystal, \(\Phi\), is

\[
2\Phi = \sum_{i,j} \left\{ -\frac{A}{r_{ij}^6} + B \exp(-\alpha r_{ij}) \right\} + 2\Phi_{\text{distant}}
\]

where

\[
2\Phi_{\text{distant}} = -\left( A_{1-1} N_1^2 + 2A_{1-2} N_1 N_2 + A_{2-2} N_2^2 \right) \times \frac{N_{\text{cell}}}{V} \times \int_R^{\infty} \frac{d\pi r^2}{r^6} dr
\]

\[
= -\left( A_{1-1} N_1^2 + 2A_{1-2} N_1 N_2 + A_{2-2} N_2^2 \right) \frac{4\pi N_{\text{cell}}}{3V R^3}
\]

\(N_{\text{cell}}\) = number of molecules in cell

\(N_1\) = number of atoms type 1 per molecule

\(N_2\) = number of atoms type 2 per molecule

\(V\) = unit cell volume
Table 2.1

Parameters for the 6-exp potential for carbon and hydrogen atoms.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
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<tbody>
<tr>
<td>A&lt;sub&gt;C-C&lt;/sub&gt;</td>
<td>358.</td>
<td>568.</td>
<td>297.</td>
<td>535.</td>
</tr>
<tr>
<td>B&lt;sub&gt;C-C&lt;/sub&gt;</td>
<td>42000.</td>
<td>83630.</td>
<td>237000.</td>
<td>74460.</td>
</tr>
<tr>
<td>α&lt;sub&gt;C-C&lt;/sub&gt;</td>
<td>3.58</td>
<td>3.60</td>
<td>4.32</td>
<td>3.60</td>
</tr>
<tr>
<td>A&lt;sub&gt;C-H&lt;/sub&gt;</td>
<td>154.</td>
<td>125.</td>
<td>121.1</td>
<td>139.</td>
</tr>
<tr>
<td>B&lt;sub&gt;C-H&lt;/sub&gt;</td>
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<td>8766.</td>
<td>31390.</td>
<td>9411.</td>
</tr>
<tr>
<td>α&lt;sub&gt;C-H&lt;/sub&gt;</td>
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<td>3.67</td>
<td>4.20</td>
<td>3.67</td>
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<td>A&lt;sub&gt;H-H&lt;/sub&gt;</td>
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<td>27.3</td>
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<td>B&lt;sub&gt;H-H&lt;/sub&gt;</td>
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<td>2654.</td>
<td>6600.</td>
<td>4000.</td>
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<tr>
<td>α&lt;sub&gt;H-H&lt;/sub&gt;</td>
<td>4.86</td>
<td>3.74</td>
<td>4.08</td>
<td>3.74</td>
</tr>
</tbody>
</table>

(1) Kitaigorodskii(1966)
(2) Williams(1967)
(3) Liquori,Giglio and Mazzarella(1968)
(4) Williams(1966)

The units are: A kcal/mole A<sup>-6</sup>
B kcal/mole
α kcal/mole A<sup>-1</sup>
2.2 Basic equations

The formalism used for molecular lattice dynamics is an extension of the Born-von Karman theory (Born and Huang 1954) which has been reviewed by Cochran (1963) and Cochran and Cowley (1967). The summary presented here follows the treatment of Pawley (1972a) in which the differentials of the potential function are calculated from analytic expressions. This superseded the earlier method (Pawley 1967) in which the second stage was done numerically.

The treatment here is essentially classical. In the quantum mechanical treatment the displacements of the atoms are expressed in terms of creation and annihilation operators which act on simple harmonic oscillator functions. This is unnecessary for the present purpose though we note that the energy is quantised and we use the term 'phonon' to describe the quantum of lattice vibrational energy. The term libration is often used to describe a lattice vibration which involves rotational motion of the molecules. In this work the terms librational and rotational are, in general, synonymous.

The theory depends on two approximations:

(i) The Born-Oppenheimer (adiabatic) approximation that the electrons instantaneously take up configurations appropriate to the displaced atomic nuclei. This allows the potential energy of the crystal to be written as a power series involving the small displacements of the nuclei from their equilibrium positions.

(ii) The harmonic approximation, in which the terms in the potential energy expansion higher than quadratic are neglected. Within these two approximations the potential energy of the crystal can be written:

\[
\phi = \phi_0 + \sum_{\ell k i} \frac{\delta \phi}{\delta u_{\ell i}(\ell k)} u_{\ell i}(\ell k) + \frac{1}{2} \sum_{\ell k i} \sum_{\ell' k' j} \frac{\delta^2 \phi}{\delta u_{\ell i}(\ell k) \delta u_{\ell j}(\ell' k')} u_{\ell i}(\ell k) u_{\ell j}(\ell' k')
\]
where \( u_i(\ell k) \) is the \( i \)th component of the displacement of the \( k \)th molecule in the \( \ell \)th unit cell, and the differentials are evaluated at equilibrium. The displacement \( u \) is a six dimensional vector of which the first three components represent translations and the last three represent rotations. It should be noted that the translations form a polar vector while the rotations form an axial vector. This difference gives rise to different transformation properties. The first term of the expansion, \( \phi_0 \), is the arbitrary zero point of potential which can be chosen to be zero while the linear term involving \( \frac{\partial \phi}{\partial u} \) must be zero since the equilibrium position is defined as the minimum of \( \phi \). The only non-zero term is therefore the quadratic term.

The equations of motion for the molecule \((\ell'k')\) are:

\[
m_{ij} u_j(\ell'k') = \sum_{k,k'} \bar{\Phi}_{ij}(\ell k, \ell'k') \ u_j(\ell'k')
\]

where \( \bar{\Phi}_{ij}(\ell k, \ell'k') = \frac{\partial^2 \phi}{\partial u_i(\ell k) \partial u_j(\ell'k')} \)

and \( m_i \) is the molecular mass for \( i = 1, 2, 3 \) and the moment of inertia about the principal axes for \( i = 4, 5, 6 \). The displacements \( u(\ell k) \) are expressed in the principal inertial axes coordinate system of the molecule \((\ell k)\) so that care must be taken in evaluating the differentials. A travelling wave solution can be substituted for \( u(\ell k) \) in the normal way to obtain

\[
\omega^2(q) \ (\sqrt{m_i} U_i(\ell k)) = \sum_{k,k'} (\sqrt{m_j} U_j(\ell'k')) M_{ij}(kk'q)
\]

The matrix \( M \) is the mass reduced dynamical matrix whose elements are given by:

\[
M_{ij} = \sum_{\ell} \bar{\Phi}_{ij}(\ell k, \ell'k') \ \exp \left[ ig \cdot (r(\ell'k') - r(\ell k)) \right] \]

\[
x \sqrt{m_i} \ m_j
\]
The eigen-values of $M$ are the squared frequencies of the phonons, $\omega_{\mathbf{q}}^2$, and the matrix which diagonalises $M$ is the matrix of phonon eigenvectors. The problem of obtaining the phonon frequencies and eigenvectors then consists of constructing $M$ and diagonalising it.

2.3 The Force Constant Tensors

The dynamical matrix is constructed by evaluating the force constant tensors $\tilde{\Phi}(\mathbf{q}, \mathbf{q}')$, for each molecule-molecule pair under consideration, with each term multiplied by the appropriate exponential factor containing the wavevector. The $6\times6$ force constant tensors $\tilde{\Phi}$ relate the force-couple on the first molecule to the translation-rotation of the second molecule.

If atom-atom interactions are assumed, these may be written as:

$$\tilde{\Phi}(O,N) = \sum_{ij} \tilde{\Phi}(O_i,N_j)$$

where $i$ labels the atoms in molecule $O$ and $j$ labels the atoms in molecule $N$.

The $6\times6$ tensors can be considered as four $3\times3$ blocks representing translation-translation, translation-rotation, rotation-translation and rotation-rotation terms:

$$\tilde{\Phi}(O_i,N_j) = \begin{bmatrix} \phi_{tt}(O_i,N_j) & \phi_{tr}(O_i,N_j) \\ \phi_{rt}(O_i,N_j) & \phi_{rr}(O_i,N_j) \end{bmatrix}$$

The translation-translation tensor $\phi_{tt}$ can be expressed in terms of the derivatives with respect to separation $r_{ij}$ of the potential function $V_{ij}$ between the atoms $i$ and $j$:

$$\phi_{tt}(O_i,N_j) = e^{q_{O_i}} (V'' - V') e^{q_{N_j}}$$
where \( \mathbf{e} \) is a unit vector along the direction between atoms \( i \) and \( j \) and is expressed either as a row or a column vector. \( E \) and \( G \) represent the identity transformation and the transformation relating the coordinate system of molecule 0 to molecule \( N \) respectively. The subscripts on \( \mathbf{e} \) indicate the system in which the unit vector is expressed.

\( V' \) and \( V'' \) are the first and second derivatives of the interatomic potential with respect to the separation \( r_{ij} \).

The full 6x6 interaction tensor can then be written as

\[
\Phi(O_0, N_j) = \begin{bmatrix}
\varphi & \varphi_{R_{N_j}} \\
-R_{0i} \varphi & -R_{0i} \varphi_{R_{N_j}}
\end{bmatrix}
\]

where \( \varphi = \varphi^{tt}(O_0, N_j) \)

\[
R_{N_j} = \begin{bmatrix}
0 & r_{3,N_j} & -r_{2,N_j} \\
r_{3,N_j} & 0 & r_{1,N_j} \\
r_{2,N_j} & -r_{1,N_j} & 0
\end{bmatrix}
\]

and \( R_{0i} = \begin{bmatrix}
0 & r_{3,0i} & -r_{2,0i} \\
r_{3,0i} & 0 & r_{1,0i} \\
r_{2,0i} & -r_{1,0i} & 0
\end{bmatrix} \)

\( r_{\alpha,N_j} \) is the \( \alpha \)th component of the position vector of the \( j \)th atom in molecule \( N \) measured in the appropriate coordinate system.

The antisymmetric matrices \( R \) result from a consideration of the vector products which arise in evaluating the rotational terms in \( \Phi \).

The only interaction tensor which remains to be calculated is \( \Phi(0,0) \) which represents the force-couple on the basic molecule due to a translation-rotation of itself, such terms are called the self terms.

It can be shown by using the conditions of translational and rotational
invariance that the effect is equivalent to equal and opposite displace-
ments of all the other molecules:

$$-\Phi(0,0)U = \sum_N \Phi(0,N) \begin{bmatrix} G^{-1} & G^{-1}R_N \\ 0 & sG^{-1} \end{bmatrix} U$$

where s is the determinant of G which is +1 for a proper rotation and
-1 for an improper rotation.

2.4 The Dynamical Matrix

The elements of the mass reduced dynamical matrix are

$$M_{ij}(k,k',q) = (m_i m_j)^\frac{1}{2} \sum_{l} \Phi_{ij}(l, k, l') \exp iq(r(l'k') - r(lk))$$

The force constant tensors $\Phi_{ij}$ have been developed in terms of the inter-
actions between the molecule 0 at the origin and the neighbouring molecules
N at positions $r(l'k')$.

For a crystal with more than one molecule in the primitive unit

cell, the force constant tensors for interactions between each basic
molecule and its neighbours must be included in the dynamical matrix.
It has been shown by Pawley (1972a), however, that the force constant
tensors $\Phi(0,N)$ may be used, provided the phonon wavevector $q$ is trans-
formed accordingly.

The modified dynamical matrix is then composed of a total of $n^2$
6x6 blocks, where n is the number of molecule types. The edge size of the
matrix is therefore 6n. Diagonalisation then yields 6n eigenvalues $\omega_j^2(q)$
with the associated eigenvectors $U_j(q)$ whose 6n components specify how
the n molecules translate and librate in the mode $(\textbf{q}j)$. The dynamical
matrix is Hermitian and therefore the eigenvalues $\omega_j^2(q)$ must be real.
For the model to correspond to a stable crystal, however, the $\omega_j^2(q)$
must all be positive and so the dynamical matrix must be positive-definite.
A non-positive-definite dynamical matrix corresponds to a crystal which
is unstable with respect to certain displacements (Born and Huang 1954).

The eigenvectors $\mathbf{U}_j(q)$ are in general complex, reflecting the phase relationships between the motions of the molecules. In the particular case of a centrosymmetric structure in which the molecule centres occupy the centres of symmetry, there is a $\pi/2$ phase difference between the translational and rotational motion of the molecules. It can be shown that for such a structure the elements of the dynamical matrix are either purely real or purely imaginary, as a consequence of the different transformation properties of the translational and rotational terms. It is therefore possible to make the matrix purely real by introducing imaginary rotational coordinates. It follows that the eigenvectors are purely real and that the phase difference between rotational and translational parts is exactly $\pi/2$. Such a transformation was introduced by Cochran and Pawley (1964) in their treatment of hexamethylenetetramine which they assumed to be centrosymmetric to simplify the calculations.

The computer program based on the procedure outlined in this chapter uses the double Jacobi method of rotations (Wilkinson 1965) to diagonalise the dynamical matrix. The columns of the matrix used to rotate $\mathbf{M}$ in the diagonalisation process are then the eigenvectors of the phonon modes. The use of this program is illustrated in Chapter 6 in which calculations of the lattice dynamics of perdeuteronaphthalene are described.
CHAPTER 3

THERMAL NEUTRON SCATTERING
3.1 Introduction

The scattering of thermal neutrons is an invaluable technique in the investigation of the physical properties of solids. Because their wavelengths, typically a few Ångstroms, and energies, about 0.02 eV, are of the same order as the atomic spacings and the excitation energies in a crystal, neutrons can be used to study both the structure and dynamics. This is in contrast to electromagnetic radiation in which only one property, wavelength or energy, can be compatible at one time. For example, with X-rays the crystal structure may be measured whereas the phonon frequencies are unresolvable due to the much higher energy of the X-rays. With Raman scattering on the other hand, the energies of the crystal excitations may be resolved, but the long wavelength of light compared with the atomic spacings restricts the measurement to excitations of very long wavelength i.e. at the Brillouin zone centre.

The use of neutrons in structural studies can be seen as complementary to that of X-rays. Since the neutrons scatter from the atomic nuclei rather than from the atomic electron distributions, neutron diffraction can be used to determine accurately the nuclear positions. This is particularly useful in studies of hydrogenous substances because the hydrogen nuclear position does not necessarily correspond to the centre of the electron distribution. Neutron diffraction is also useful for determining the positions of light atoms in the presence of very heavy atoms and in distinguishing between atoms of similar atomic number. Such studies are difficult with X-ray diffraction since the scattering of X-rays is proportional to the atomic number.
Finally, it may be mentioned that neutrons have a magnetic moment and so can be used to obtain information on magnetic properties on the atomic scale. The work described here concerns neutron scattering from atoms with paired electrons, so no account of magnetic scattering is given.

3.2 Theory

The theory of thermal neutron scattering has been formulated by several authors (eg. Van Hove 1954, Marshall and Lovesey 1971) and here only a brief outline of the approach is given, along with an extension to the case of scattering from molecular crystals. The formulation depends on the fact that the neutron wavelength is much greater than the size of an atomic nucleus, and hence, only s-wave scattering which is isotropic and independent of neutron energy can occur.

We consider a process in which neutrons of wavevector $k_0$ are scattered to wavevector $k_1$, and the state of the scattering system changes from $|m\rangle$ to $|n\rangle$. The transition probability is then given by Fermi's Golden Rule (Schiff 1968):

$$w = \frac{2\pi}{\hbar} |\langle f|V|i\rangle|^2 \delta(E_i - E_f)$$

where $|i\rangle = |m\rangle \exp i \mathbf{k}_0 \cdot \mathbf{r}$

$|f\rangle = |n\rangle \exp i \mathbf{k}_1 \cdot \mathbf{r}$

and $V$ is the interaction potential.

The delta function represents conservation of energy.

In a neutron scattering experiment, the quantity which is measured is not a transition probability, but a cross section which represents the intensity of scattering into an energy interval $dE_1$ and a solid angle $d\Omega$ for a unit incident flux.
The partial differential cross section is:
\[
\frac{d^2 \sigma}{d\Omega dE_1} = \left( \frac{m_N}{2\pi h^2} \right)^2 \frac{k_1}{k_0} \sum_{n,m} p_m \left| \langle n | e^{-iQ \cdot \mathbf{r}} V e^{iQ \cdot \mathbf{r}} | m \rangle \right|^2 \delta(E_1 - E_f)
\]

The factor \( p_m \) is the statistical probability of the initial state \( |m\rangle \). The \( k_0 \) factor arises from the definition of the unit incident flux and the \( k_1 \) factor arises from a consideration of the density of possible final neutron states, \( m_N \) is the neutron mass.

The delta function may then be expressed in terms of neutron energy and change in crystal energy and the wavevector transfer \( Q = k_0 - k_1 \) introduced to give
\[
\frac{d^2 \sigma}{d\Omega dE_1} = \left( \frac{m_N}{2\pi h^2} \right)^2 \frac{k_1}{k_0} \sum_{n,m} p_m \left| \langle n | e^{iQ \cdot \mathbf{r}} V | m \rangle \right|^2 \delta \left( \frac{\hbar^2 k_0^2}{2m_N} - \frac{\hbar^2 k_1^2}{2m_N} + E_m - E_f \right)
\]

The neutron interacts with the nucleus by way of the strong nuclear force, and in such a case it is not strictly correct to use plane waves to represent the process, because the waves become severely distorted within the nucleus. However, Fermi showed that for neutrons with wavelengths much larger than the size of the nucleus, the scattering is the same as that calculated using plane waves with a delta function potential at the nuclear position.

The so called Fermi pseudopotential is
\[
v = \sum_{\ell} \frac{2m_n^2}{m_N} b_{\ell} \delta(\mathbf{r} - \mathbf{r}_{\ell})
\]
where \( \mathbf{r}_{\ell} \) is the position of the \( \ell \)th nucleus and \( b_{\ell} \) is its scattering length which depends on the type of nucleus and the total spin of the neutron-nucleus system.

The cross section is then
\[
\frac{d^2 \sigma}{d\Omega dE_1} = \frac{k_1}{k_0} \sum_{n,m} p_m \left| \langle n | \sum_{\ell} b_{\ell} \exp iQ \cdot \mathbf{r}_{\ell} | m \rangle \right|^2 \delta \left( \frac{\hbar^2 k_0^2}{2m_N} - \frac{\hbar^2 k_1^2}{2m_N} + E_m - E_f \right)
\]
It is conventional to divide this into two parts, coherent and incoherent, by considering the terms which result when the square is performed. The scattering lengths appear as product terms $b_\ell b_{\ell'}$, and a distinction can be made between terms which have $\ell = \ell'$ and those which have $\ell \neq \ell'$. The latter contain information on the correlation between different atoms and give rise to interference effects. The situation can be illustrated by considering a rigid monatomic lattice. The cross section is:

$$\frac{d\sigma}{d\Omega} = \left| \sum_{\ell} b_\ell \exp i \frac{Q \cdot r_\ell}{b_\ell} \right|^2$$

$$= \sum_{\ell, \ell'} b_\ell b_{\ell'} \exp i \frac{Q \cdot (r_\ell - r_{\ell'})}{b_\ell}$$

$$= \sum_{\ell} b_\ell^2 + \sum_{\ell, \ell'} b_\ell b_{\ell'} \exp i \frac{Q \cdot (r_\ell - r_{\ell'})}{b_\ell}$$

where $\sum_{\ell'}$ excludes $\ell = \ell'$

The first term is $N\langle b^2 \rangle$, where the brackets denote the average, and the second term is:

$$N \langle b \rangle^2 \sum_{\ell, \ell'} \exp i \frac{Q \cdot (r_\ell - r_{\ell'})}{b_\ell} = -N \langle b \rangle^2 + N \langle b \rangle^2 \sum_{\ell, \ell'} \exp i \frac{Q \cdot (r_\ell - r_{\ell'})}{b_\ell}$$

The cross section may therefore be written as:

$$\frac{d\sigma}{d\Omega} = N(\langle b^2 \rangle - \langle b \rangle^2) + N\langle b \rangle^2 \sum_{\ell, \ell'} \exp i \frac{Q \cdot (r_\ell - r_{\ell'})}{b_\ell}$$

The first term is the incoherent scattering and contains no information on the correlation between different atoms. The second term is the coherent scattering, and gives rise to interference effects which depend on the correlation between different atoms. This term has peaks at values of the wavevector transfer $Q$ equal to reciprocal lattice vectors because of the sum over $\ell$, and corresponds to Bragg scattering.

The incoherent scattering has no wavevector dependence, and is therefore isotropic, apart from the Debye-Waller factor which we have
neglected in this example, since the crystal is rigid.

It is convenient to define coherent and incoherent scattering lengths:

\[ b^{\text{coh}} = \langle b \rangle \]
\[ (b^{\text{inc}})^2 = (\langle b^2 \rangle - \langle b \rangle^2) \]

The scattering length depends, not only on the chemical species, but also on the isotope and the relative orientation of the neutron spin and the nuclear spin (if the latter exists). If all the nuclei are the same, and they have zero spin, then the scattering is completely coherent, because the incoherent scattering length is zero, whereas if different isotopes, or non-zero spin nuclei are present, then both coherent and incoherent scattering occur. Hydrogen is an example of an element which has very high incoherent scattering because of its non-zero nuclear spin. It is for this reason that it is necessary to substitute deuterium when coherent scattering measurements of hydrogenous materials are carried out, e.g. perdeuteronaphthalene, DCN. Another strong incoherent scatterer is vanadium which is often used in experiments because of this property. Inelastic incoherent scattering measurements are often done on hydrogenous materials however since this scattering can be related to the density of vibrational states. (White 1968, Pawley, Reynolds, Kjems and White 1971). In what follows the scattering length will be assumed to be \( b^{\text{coh}} \) since the present work is concerned only with coherent scattering.

The partial differential cross section can now be extended to include more than one atom in the unit cell:

\[
\frac{\partial^2 \sigma}{\partial \Omega_i \partial E_i} = \frac{k_1}{k_0} \sum_{P \alpha \beta} \left| \langle n | \sum_{s} b_s \exp i \mathbf{Q} \cdot \mathbf{r}_s \mid m \rangle \right|^2 \delta \left( \frac{n^2 k_0^2}{2m_N} - \frac{n^2 k_1^2}{2m_N} + \frac{E - E_i}{m} \right)
\]

\[
= \frac{k_1}{k_0} \sum_{P \alpha \beta} \left| \langle n | \sum_{s} b_s \exp i \mathbf{Q} \cdot \mathbf{r}_s \sum_{l} \exp i(\mathbf{Q} \cdot \mathbf{r}_l + \mathbf{u}_{ls}) \mid m \rangle \right|^2 \delta(\ " " )
\]
where the position of the $s$th atom in the $\ell$th unit cell is
\[ r_{\ell s} = r_{\ell} + r_{s} + u_{\ell s} \]
Expansion of the exponential term containing the atomic displacements \( u_{\ell s} \), which are assumed small, yields terms which correspond to elastic scattering, one phonon scattering, two phonon scattering, and so on:
\[ \exp i \cdot u_{\ell s} = 1 + i \cdot u_{\ell s} - \frac{1}{2} (Q \cdot u_{\ell s})^2 \text{ etc.} \]
The procedure then is to represent the initial and final states of the crystal by simple harmonic oscillator functions and the atomic displacements in terms of phonon creation and annihilation operators, \( a^+ \) and \( a \) respectively. The effect of these operators is to increase or decrease the occupation number of the state by one, i.e.
\[ a^+ |n(qj)\rangle = (n(qj) + 1) \frac{1}{2} |n(qj) + 1\rangle \]
\[ a |n(qj)\rangle = (n(qj))^{\frac{1}{2}} |n(qj) - 1\rangle \]
The displacement of an atom is then
\[ u_{\ell s} = \sum_{j} \left\{ \frac{\hbar}{2M_j \omega_j} \right\} \left\{ a^+ e_{s}^{+}(q) \exp \left( i \cdot q \cdot (r_{\ell} + r_{s}) - i\omega_j t \right) \right. \\
\left. + a e_{s}^{+}(q) \exp \left( -i \cdot q \cdot (r_{\ell} + r_{s}) + i\omega_j t \right) \right\} \]
The well known Debye-Waller factor arises from pairs of \( e_{s} a^+ \) and is \( e^{-W} \) where \( W = \frac{1}{2} Q \cdot u^2 \). This factor is the same for elastic and inelastic, coherent and incoherent scattering.

The final expression for the one phonon coherent cross section is obtained by averaging over the initial states and summing over final states and is
\[ \frac{d^2 \sigma}{dE_1 dE_1'} = \frac{k_1}{k_0} \frac{(2\pi)^3}{V} \sum_{B} G_j(Q) \left| \frac{1}{2} \right. \frac{\hbar (n(qj) + \frac{1}{2} - \frac{1}{2}) \delta (Q + g - B) \delta (E_0 - E_1') h_{coh}(q) \rangle \frac{1}{2} \omega_j(q) \left| \right. \frac{1}{2} \omega_j(q) \right\}
where \( G_j(Q) \) is the inelastic structure factor given by
\[ G_j(Q) = \sum_{s} Q \cdot e_{s}^{+}(qj) h_{coh}^{s} \exp (i \cdot B \cdot r_{s}) \exp (-W) \]
The delta functions represent wavevector and energy conservation with the plus and minus signs in the latter corresponding to phonon annihilation (neutron energy gain) and phonon creation (neutron energy loss). The population factors associated with these processes, \((n(gj))\) and \((n(gj)+1)\) respectively, lead to differences in the cross sections. The occupation number of the phonon \((gj)\) is

\[n(gj) = \frac{1}{\exp(h\omega_j(g)/k_B T) - 1}\]

where \(k_B\) is Boltzmann's constant. At low temperatures this occupation number tends to zero so the cross section for phonon annihilation tends to zero. The cross section for the phonon creation process on the other hand tends to a finite value at low temperatures.

The above expression for the cross section follows the convention of Cochran (1963) in the definition of the inelastic structure factor and the wavevector conservation condition. The latter is dependent on the definition of the atomic displacement, \(\bar{u}\), and determines the direction of the phonon wavevector which in our case points towards the reciprocal lattice point for phonon creation (Figure 3.1). The expression derived by Marshall and Lovesey (1971) leads to the wavevector conservation conditions:

\[\delta(Q-g-B)\] phonon creation

\[\delta(Q+g-B)\] phonon annihilation

3.3 Extension to Molecular Crystals

Although the standard expression for the one phonon cross section is applicable to all crystals it is convenient to redefine the cross section for the particular case of molecular crystals. Essentially what is required is a redefinition of the eigenvector which occurs in the
Figure 3.1

Scattering diagram for phonon creation process with the wavevector conservation condition \( \mathbf{Q} = \mathbf{B} - \mathbf{q} \).
expression so that it corresponds to the rigid molecule type of motion in which we are interested. This involves describing the motion of the pth atom in the kth molecule of the \( \ell \)th unit cell in terms of the translational and rotational components \( U_k(qj) \) and \( \theta_k(qj) \) of the total eigenvector \( \nu_k(qj) \) of the kth molecule. \( \nu_k(qj) \) takes the place of \( e_s(qj) \) in the inelastic structure factor equation.

The total eigenvector is defined as

\[
\nu_k(qj) = U_k(qj) + \theta_k(qj) \times r_p
\]

where \( r_p \) is the position vector of atom p relative to the centre of mass of molecule k. The displacement of an atom is then

\[
u_{kp} = \nu_k(qj) \exp \left( ig \cdot (r_{k} + r_p) - i\omega_j(q) t \right)
\]

The phase factor \( \exp (ig \cdot r_p) \) between different atoms in the same molecule is not included in the wave motion since we are interested in rigid molecule motion. Instead, this factor is included in the eigenvector. This can be seen by comparing the above expression with that for the atomic displacement in a simple crystal:

\[
u_{es} = e_s(qj) \exp (ig \cdot (r_{e} + r_s) - i\omega_j(q) t)
\]

Thus we have

\[
e_s(qj) = \nu_k(qj) \exp (-ig \cdot r_p)
\]

Substitution of this expression into the inelastic structure factor then yields

\[
G_j(Q) = \sum_{kp} b_p Q \cdot \nu_k(qj) \exp (-ig \cdot r_p) \exp (iB \cdot (r_k + r_p)) \exp (-W_p)
\]

The calculation of the one phonon cross section using the above expression is included in the lattice dynamics program developed by Pawley (1972a) and described in Chapter 2. The use of this program in predicting neutron scattering intensities is described in Chapter 6.
in connection with the experiment on naphthalene.

3.4 **Experimental Neutron Spectroscopy**

The essential requirement for a neutron spectroscopy experiment is the ability to define the wavevector transfer $Q$ and the energy transfer $\hbar \omega$. Two methods can be used to do this:

(i) The energy and direction of the incident and scattered beams may be defined by Bragg scattering from single crystals of known plane spacing and orientation. The early development of this method has been reviewed by Iyengar (1965).

(ii) A pulsed neutron beam, either from a pulsed source (e.g. a LINAC) or from a steady state reactor, by way of choppers, can be used, and the time of flight of the neutrons scattered through a known angle measured. Time of flight methods have been reviewed by Brugger (1965).

Various spectrometers have been constructed utilising either of these methods, or combinations of the two, but by far the most popular instrument for the measurement of phonon dispersion curves, is the triple axis spectrometer (TAS) which was developed by Brockhouse (1961) at Chalk River, and it is this type of instrument with which we are concerned in the present work. The characteristics and operation of the triple axis spectrometer have been described in detail by many authors (e.g., Cochran and Cowley 1967, Dolling 1974, Iyengar 1965), so only a brief description of the instrument is included here.

A schematic diagram of a typical TAS is shown in Figure 3.2. A beam of neutrons with an approximately Maxwellian distribution of energies dependent on the reactor moderator temperature is allowed to escape through a hole in the reactor shielding. Most spectrometers in
Figure 3.2

Schematic diagram of a typical triple axis spectrometer, showing

R - reactor
M - monochromator
S - sample
A - analyser
C - Soller collimators
m - monitor counter
f - filter
d - detector
τ - reference reciprocal lattice vector.
use at the present time use neutrons from a moderator at about 300K but in some cases, hotter or colder moderators are used to shift the neutron energy distribution to higher or lower energies, and increase the neutron flux available at wavelengths appropriate to certain experiments.

Neutrons of a particular wavelength are Bragg reflected through the angle $2\theta_m$ by the monochromator crystal, and are incident on the sample. Those neutrons scattered through the angle $\phi$ are then reflected through the angle $2\theta_a$ at the analyser if their wavelengths satisfy the Bragg condition, they then pass into the detector and are counted. Mechanical half angling devices are used to ensure that the monochromator and analyser crystals remain in the reflecting orientation.

Several materials have been used for the monochromator and analyser crystals e.g. copper, lead, germanium, but recently, pyrolytic graphite has become very popular because of its high reflectivity and it was this material which was used in most of the experiments on naphthalene (Chapter 6). Pyrolytic graphite has a preferred orientation of the (00L) planes with the (hk0) planes aligned randomly. Due to this randomness, the primary extinction is much smaller than in single crystals and so the reflectivity is increased. The neutron flux can be increased further by bending the graphite monochromator to a cylindrical surface as suggested by Riste (1970). A disadvantage of pyrolytic graphite is that neutrons with wavelengths $\lambda/n$, for $n$ integral, are reflected as well as neutrons of the desired wavelength, $\lambda$. Higher order contamination can be removed to a great extent by using an oriented pyrolytic graphite filter (Shiran and Minkiewicz 1970). With the neutrons passing along the hexagonal $c$ direction, certain wavelengths pass through almost unattenuated
whereas other energies are scattered out of the beam. The transmission 'windows' commonly used are at wavelengths of 2.6 and 3.1 Å. The filter can be positioned before the sample, as in Figure 3.2, for experiments where the incident energy is kept fixed, or after the sample when the scattered energy is kept fixed. Polycrystalline Beryllium is also used as a filter. In this case the effect of scattering out of the beam is to cut off almost completely neutrons with wavelengths smaller than 3.92 Å. Cooling of the Beryllium improves the transmission by decreasing the amount of inelastic scattering of the first order neutrons. The characteristics of neutron filters have been described by Iyengar (1965).

The neutrons are collimated by parallel, equally spaced plates of cadmium plated steel commonly known as Soller slits. It is possible to vary the number and spacing of the slits so that different degrees of collimation of the four sections of the neutron beam in the instrument may be obtained.

The incident neutron flux is monitored by a low (about $10^{-4}$) efficiency fission counter. The efficiency is inversely proportional to neutron velocity and hence to neutron wavevector $k_0$. The monitor is normally used to determine the counting time at each point in an experimental scan. The $1/k_0$ dependence of the monitor efficiency is used to great advantage in scans in which the incident energy is varied, and the scattered energy is fixed. The measured cross section is then independent of the magnitudes of the incident and scattered wavevectors.

The neutrons reflected by the analyser crystal are normally detected by a $^{10}$BF$_3$ or a $^3$He gas detector. The former uses the $(n,\gamma)$ reaction and has been largely superseded by the more compact $^3$He
detector which uses the \((n,p)\) reaction. The technical details of neutron
detectors have been discussed by Cocking and Webb(1965).

A large amount of shielding is required particularly around the
monochromator, the analyser and the detector assemblies for both biological
and experimental reasons. The materials used for shielding vary between
instruments. The machines at Risø use a great deal of boron-10 impregnated
plastic. The plastic, having a high hydrogen content, has the effect of
thermalising fast neutrons while the \(^{10}\text{B}\) absorbs the resultant thermal
neutrons by way of the \((n,\gamma)\) reaction. Other materials used include wood,
cadmium, paraffin, wax and lead.

3.5 Operation of a Triple Axis Spectrometer

The wavevector and energy transfers for a particular experimental
configuration are determined by the angles \(\phi_M\), \(\phi\) and \(\phi_A\) and the plane
spacings of the monochromator and analyser crystals, \(d_M\) and \(d_A\) respectively.
The sample is oriented in such a way that a particular plane of reciprocal
space coincides with the scattering plane. The position of the wavevector
transfer in this plane is then defined by the angle \(\psi\).

The wavevector and energy conservation conditions imply that when
\(Q\) and \(E_0-E_1\) correspond to a point on the dispersion surface of the sample
a sharp resonance will be observed. This is broadened by resolution and
phonon lifetime effects to give the observed lineshape.

A path through \((Q,E)\) space can be traced out by varying the angles
described above. In modern spectrometers a computer is used to calculate
and set the angles to correspond to any point in this space within the
limits of the instrument. Only the zero settings of the four angles and
the plane spacings of the monochromator, analyser and sample need to be
specified beforehand. The zero settings are generally determined by a
preliminary calibration of the spectrometer using standard samples. The
degree of automation in triple axis spectrometers has increased considerably since the development of the first machine (Brockhouse 1961). Some machines e.g. those at ILL, Grenoble, use a large computer on a time sharing basis while others have small dedicated control computers. The first arrangement has the disadvantage that time which could be used for counting neutrons may be wasted while the instrument is waiting for the angles to be set. The best arrangement is probably to have a small dedicated computer with the ability to set all the angles simultaneously so that the time spent not counting neutrons is kept to a minimum. This method is used in the most recently constructed spectrometers e.g. TAS 4 and TAS 6 at Risø.

Two methods of scanning are commonly used in experiments with a triple axis spectrometer. The instrument can be operated to record the energy distribution at a particular value of the wavevector transfer $Q$ (the 'Constant $Q$' method), or to record the wavevector distribution at a fixed energy transfer (the 'Constant Energy' method).

In the Constant $Q$ method either the ingoing energy $E_0$ or the outgoing energy $E_1$ determined by $2\theta_M$ and $2\theta_A$ respectively may be kept fixed. The energy transfer is varied linearly by changing the remaining three angles in such a way that the wavevector transfer $Q$ remains fixed. The resulting peaks in the measured neutron distribution correspond to the energies of phonons at the wavevector $q$ determined by the conservation condition $Q + q = B$. In a monochromator scan with the outgoing energy fixed the observed neutron distribution is a direct measure of $G(Q)^2$ together with the appropriate population factor for energy gain or loss. The $1/k_0$ factor in the cross section is effectively cancelled out by the $1/V_0$ dependence of the monitor efficiency. With analyser scans on the other hand the measured distribution is actually the angular distribution at the analyser i.e. $\frac{d^2\sigma}{d\Omega dE_1}$ rather than $\frac{d^2\sigma}{d\Omega dE_1}$. In the latter case the
neutron distributions must be corrected particularly when the scattered intensity is of interest.

The Constant Energy technique is normally used when the dispersion is steeply sloping in $(Q,E)$ space. In this case a more sharply defined peak is obtained because of focusing effects (see section 3.6). The ingoing and outgoing energies $E_0$ and $E_1$ are chosen so that the correct energy transfer $\hbar \omega$ is selected. The monochromator and analyser remain fixed and the angles $\phi$ and $\psi$ are varied so that the end point of the wavevector transfer follows a straight line in a desired direction in reciprocal space. In this case peaks occur at the values of $Q$ which correspond to the wavevectors of phonons with the energy $\hbar \omega$.

3.6 Resolution and Focussing

The finite collimations of the neutron beams in the various directions together with the mosaic spreads of the crystals lead to a spread in the actual incident and scattered neutron wavevectors, both in magnitude and direction. In other words, although the instrument may be set up to measure the intensity of the scattering at a wavevector transfer $Q$ and energy transfer $E$ there is a finite probability of detecting neutrons which have undergone processes corresponding to $Q + \Delta Q$ and $E + \Delta E$. The probability distribution is called the resolution function and takes the form of an ellipsoid in 4-dimensional $(Q,E)$ space. The value of this function at each point in $(Q,E)$ space depends on whether the scattering at the monochromator, the sample and the analyser is to the left or the right as well as the various angles, the plane spacings, the mosaic spreads and the divergences of the Soller slit systems. The effects of these different components are highly correlated and the calculation of the resolution function is quite formidable. Analytic expressions have been devised for the resolution function (Cooper and Nathans 1967, Bjerrum-Møller and Nielsen 1969 and 1970) assuming Gaussian
mosaic spreads and collimator transmission functions.

An experimental scan can be considered as a process of passing the resolution function through the dispersion surfaces of the sample. A peak, or neutron group, occurs in the measured neutron distribution when the resolution function cuts a dispersion surface. The position and width of the measured neutron group obviously depends on the shape and the orientation of the resolution function in \((Q,E)\) space. If the largest principal axis of the ellipsoid is parallel to the dispersion surface at the point of intersection then the observed group will be narrow whereas if it is perpendicular to the dispersion surface the group will be broadened. In addition to this broadening effect the neutron peaks may be shifted so that the maximum in the measured neutron distribution at \((Q,E)\) does not correspond to the point \((q_j,h\omega_j)\) on the dispersion surface but to the point \((q_j+\delta q_j,h(\omega_j+\delta \omega))\). It is therefore helpful to know the shape and orientation of the resolution ellipsoid when carrying out an experiment to measure phonon dispersion curves so that the optimum conditions may be chosen. The spectrometer conditions chosen must inevitably be a compromise between resolution and intensity. The matching of the resolution function to the dispersion surface under investigation is known as focusing. Graphical and numerical methods have been developed for estimating the appropriate values for good focusing (Peckham et al., 1967). The resolution function itself can be calculated on a computer using an analytic formulation (Cooper and Nathans, 1967) and convoluted with some suitable approximation to the dispersion to give the expected peak widths. It is also possible to measure the resolution function experimentally.

The projection of the resolution ellipsoid on to the energy axis may be measured by doing an energy scan using a vanadium sample. The observed neutron distribution in this case is due to incoherent elastic
scattering. The intersections of the resolution function with the \((Q,E)\) planes can be measured by doing scans in various directions in the region of a Bragg point. Since the shape and orientation of the ellipsoid does not change appreciably with small changes in the spectrometer angles this method gives a good estimate of the resolution function for scans of relatively small energy transfer provided a suitable Bragg point is used as the probe. The reciprocal lattice vector of the reflection should be of about the same magnitude as the wavevector transfer to be used in the inelastic scan. Experimental measurements of the resolution ellipsoid should be made if subsequent corrections of the observed neutron groups for instrumental broadening and shifting are to be applied. This provides an important check on the parameters used in the calculation.

3.7 Spurious Processes

It is possible to observe peaks in the scattered neutron distribution which do not arise from the particular process under consideration. Neutrons which undergo processes other than coherent one phonon scattering with wavevector transfer \(Q\) and energy transfer \(\hbar \omega\) may be reflected by the analyser and counted. These spurious scattering processes often give rise to peaks of similar intensity and width to phonon peaks of the correct energy and so must be considered carefully when neutron inelastic data is analysed. Some of the important scattering processes which may lead to spurious peaks are listed below and illustrated by vector diagrams in Figure 3.3.

<table>
<thead>
<tr>
<th>Neutron scattered by monochromator</th>
<th>Energy transfer at specimen</th>
<th>Neutron scattered at analyser</th>
<th>Wavevector transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (k_o, E_o)</td>
<td>(\hbar \omega)</td>
<td>(k_1, E_1)</td>
<td>(k_o - k_1 = Q)</td>
</tr>
<tr>
<td>2. (k_o, E_o)</td>
<td>(\hbar \omega)</td>
<td>(2k_1, 4E_1)</td>
<td>(k_o - 2k_1 = Q')</td>
</tr>
<tr>
<td>3. (2k_o, 4E_o)</td>
<td>(\hbar \omega'')</td>
<td>(3k_1, 9E_1)</td>
<td>(2k_o - 2k_1 = Q'')</td>
</tr>
<tr>
<td>4. (k_o, E_o)</td>
<td>0</td>
<td>(</td>
<td>k_o</td>
</tr>
<tr>
<td>5. (</td>
<td>k_1</td>
<td>E_o, E_1)</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 3.3

Neutron scattering processes

(a) Process 1 - Normal one phonon process
(b) Process 2 - spurious
(c) Process 3 - spurious
(d) Process 4 - spurious
(e) Process 5 - spurious
Process 1 is the one phonon coherent scattering under investigation. Processes 2 and 3 involve elastic scattering of higher order neutrons either by the monochromator or the analyser and can occur if the energy and wavevector transfers, \((\hbar \omega', \mathbf{Q}')\) etc, happen to correspond to points on the phonon dispersion surface. Processes 4 and 5 involve Bragg scattering at the sample together with incoherent elastic or inelastic scattering at the analyser or monochromator respectively. The unit vectors \(\mathbf{e}_0\) and \(\mathbf{e}_1\) indicate the directions of \(\mathbf{k}_0\) and \(\mathbf{k}_1\).

Spurious peaks can also arise because of the extent of the resolution ellipsoid. This is particularly likely if scans are being performed in the vicinity of a Bragg point. In this case the measured group is usually much more intense and narrow than that expected from a normal one phonon process. The position of such a spurious peak is also highly dependent on the orientation of the resolution ellipsoid and would be expected to be shifted if the scan were repeated using a different spectrometer configuration.

The problem of higher order neutrons, which is due to the ability of the monochromator and analyser crystals to reflect neutrons of wave-lengths \(\lambda/2, \lambda/3\) etc as well as \(\lambda\), can be overcome in two ways:

(i) by using a filter e.g. pyrolytic graphite, to remove higher order neutrons from the beam. This method was used to a great extent in the work on naphthalene described in Chapter 6 and has already been described in Section 3.4.

(ii) by using monochromator and analyser crystal whose structure is such that scattering from higher order planes is zero. The (111) or (113) planes of germanium are suitable because the (222) and (226) reflections have zero structure factor so that \(\lambda/2\) neutrons are not reflected.

In many cases spurious processes of the types 2, and 3 are not possible because the energy transfer is outside the range of the phonon spectrum.
In general any dubious peaks in the measured neutron distribution should be checked for possible spurious nature by drawing scattering diagrams and repeating the experiment with different spectrometer conditions if necessary. The procedure used in the investigation of the phonons in naphthalene (Chapter 6) involved a comparison with the calculated intensities produced by the lattice dynamics and cross section program. A large number of scans were performed in different Brillouin zones using various spectrometer conditions. With this large amount of data it was possible to check all the neutron groups for reproducibility and consistency before assigning them to the phonon branches.
CHAPTER 4

NEUTRON POWDER DIFFRACTION AND CONSTRAINED REFINEMENT
4.1 Introduction

The conventional method of crystal structure refinement involves the measurement of integrated X-ray or neutron intensities of Bragg reflections from a single crystal diffraction experiment. The so-called structure amplitudes are then extracted from the data and a calculated structure is fitted using the least squares technique. There are disadvantages inherent in the single crystal method, particularly when structural phase transitions which accompany changes in a crystal's environment are investigated. In many cases it is difficult to obtain single crystals of the size necessary for neutron diffraction and, even when suitable samples are available, extinction, or the breakdown of the usual kinematic diffraction theory introduces systematic errors into single crystal data, making a proper interpretation of the diffracted intensities difficult. The devices used for controlling the crystal's environment, cryostats and pressure cells, are necessarily rather bulky and usually restrict the observations to one plane in reciprocal space. Such apparatus is therefore difficult to incorporate in the standard single crystal instrument, the four circle diffractometer. Structural phase transitions are often accompanied by a break-up of the crystal. This makes single crystal analysis of the structure almost impossible.

The problems associated with the single crystal method have led to a great interest in the extraction of structural information from powder diffraction data. The effects of extinction and sample break-up are not important in powder work and the inclusion of cryostats and pressure cells presents no great problem. Since all the diffraction information is contained in one plane there is no need for the complicated crystal orienting mechanism used in single crystal
experiments and a single counter scan is sufficient to collect all the data.

The major shortcoming of the powder method is the overlap of independent Bragg reflections, particularly at high scattering angles where the fine detail structural information is contained. There are two ways of refining crystal structures from such data: the integrated intensities of separate reflections or groups of reflections may be extracted or alternatively the entire diffraction profile may be fitted using some expression for the shape of a diffraction peak. The first method which has been used by Rietveld (1966) and more recently by Klein and Weitzel (1975) leads to the loss of information contained in the overlapping groups. The profile refinement method which was originally developed by Rietveld (1969) utilises all the available information and has proved to be very reliable. The principles of both methods of refinement and their application to the constrained refinement of molecular crystal structures are discussed in this chapter. Only neutron powder diffraction is discussed since the shape of the diffraction line can be easily parametrised. X-ray data could be treated similarly if some suitable expression for the lineshape were used.

4.2 The Intensity of Bragg Reflections

The intensity of a Bragg reflection occurring at a wavevector transfer \( \mathbf{Q} = \mathbf{B} \) (a reciprocal lattice vector) depends on the function \(|F(\mathbf{Q})|^2\), where \(F(\mathbf{Q})\) is the well known structure factor defined by

\[
F(\mathbf{Q}) = \sum_s b_s \exp(-W_s) \exp(i\mathbf{Q} \cdot \mathbf{r}_s)
\]

The summation is over all the atoms in the unit cell, \( \mathbf{r}_s \) is the position of the \( s \)th atom in fractional coordinates and \( b_s \) is its
coherent neutron scattering length. The factor \( \exp(-W_s(Q)) \) commonly known as the Debye-Waller factor takes account of the reduction in intensity due to the thermal motion. The expression for the structure factor is the same as that used for X-ray diffraction apart from the atomic scattering factor. In the X-ray case the scattering factors depend on the wavevector transfer \( Q \) because the scattering arises from the atomic electron distributions which are extended in space rather than from the nuclei which may be regarded as points.

The thermal motion of the atoms in a crystal is in general anisotropic and in the harmonic approximation may be represented by a probability ellipsoid. The anisotropic Debye-Waller factor may then be written as

\[
\exp\left(-\sum_{ij} \beta_{ij}^S h^2 + \beta_{12}^S k^2 + \beta_{33}^S l^2 + 2\beta_{12}^Shk + 2\beta_{23}^Skl + 2\beta_{31}^Skl \right)
\]

where the \( \beta_{ij}^S \) are the anisotropic temperature factors and \( h, k, l \) are the Miller indices of the Bragg reflection.

The \( \beta_{ij} \) may be expressed in terms of \( B_{ij} \) factors which are closely related to the actual vibrational amplitudes of the atoms:

\[
\beta_{ij} = \frac{1}{3} \sum_{a} a_i a_j B_{ij}
\]

Then \( B_{ij} = 8\pi^2 u_{ij}^2 \)

where \( u_{ij}^2 \) is an element of the mean square displacement tensor.

Because the thermal displacements of the atoms in a molecular crystal are mainly due to the external modes, it is possible to relate the \( u_{ij}^2 \) elements to each other. The model of Schomaker and Trueblood (1968) uses three tensors to describe the translational, librational and screw rotational motions of a rigid molecule. The thermal parameters may be constrained in the structure refinement according to this so called TLS model as described by Pawley (1972b).

No account has been taken of anisotropic thermal motion in the
present work, the refinement of molecular crystal structures from powder diffraction data, since only the large scale features of the structure were of interest. In this case the thermal motion can be described by an isotropic factor,

\[ B = 8\pi^2u^2 \]

where \( u^2 \) is the mean square atomic displacement.

In a single crystal diffraction experiment the observed quantities are the integrated intensities of the Bragg reflections measured along some direction in reciprocal space. Certain corrections must be applied to obtain the observed structure amplitudes \( F_{\text{obs}}^\text{h} \). These corrections are described in detail in the standard texts (Bacon 1962, Lipson and Cochran 1966) and include the effects of absorption, extinction, multiple reflection, polarisation (with X-rays) and the Lorentz factor. Only the last effect need be taken into account with neutron powder diffraction as the others are either negligible or isotropic. The Lorentz factor allows for the different lattice points to sweep through the reflecting sphere and is given by

\[ L = \frac{1}{\sin 2\theta_B} \quad \text{where } \theta_B \text{ is the Bragg angle.} \]

This factor applies to single crystal measurements when the axis of rotation is normal to the incident and scattering beam directions.

With powder diffraction a further correction factor arises from the dependence of the circumference of a Debye–Scherrer cone on the Bragg angle. The Lorentz factor for a powder diffraction measurement can therefore be taken as

\[ L = \frac{1}{\sin 2\theta_B \sin \theta_B} . \]

4.3 Experimental

The most commonly used instrument for performing neutron powder diffraction experiments is the two axis diffractometer. A monochromatic
beam is incident on the sample and the diffraction data is measured as a function of the scattering angle, $2\theta$, by scanning a detector through the successive diffracted cones. The counting efficiency of such a machine can be greatly increased by using multiple detectors which sample different parts of the diffraction pattern simultaneously. Another adaptation of the simple diffractometer is the introduction of an analysing crystal which selects only those neutrons which have been scattered elastically at the sample.

The time of flight method of powder diffractometry has recently received a great deal of attention due to the development of pulsed neutron sources such as the LINAC at AERE, Harwell. In this case a pulsed polychromatic beam of neutrons is scattered at the sample and the time distribution of the neutrons arriving at a fixed detector is recorded. The analysis of such data is still in the development stage and as yet only relatively simple structures have been investigated (Windsor and Sinclair 1976). It is hoped that this technique will prove useful in the future for obtaining high resolution powder diffraction data, particularly at high values of $\frac{\sin \theta}{\lambda}$.

The relative merits of the various techniques of neutron powder diffraction have been discussed by Hewat (1975) who concludes that the most efficient instrument at present is the conventional two axis diffractometer fitted with a multiple detector bank. In some cases, however, it may be advantageous to sacrifice efficiency for the quality of the measurement by using a triple axis spectrometer in the elastic mode. This technique leads to a reduction in the background counts from thermal diffuse scattering and incoherent inelastic scattering and may also give better angular resolution (Caglioti 1970). There is, of course, a reduction in the peak intensity due to the introduction of
the analyser but this loss can be offset to a great extent by using an analyser of pyrolitic graphite which has a very high reflectivity.

The lineshape of a powder diffraction peak is due to the convolution of the effects of the Soller collimators, the monochromator mosaic spread and the sample particle size. Although these do not all give Gaussian distributions individually, their convolution is almost exactly Gaussian with a full width at half width height which is a function of the scattering angle, $2\theta$, and can be easily parametrised (Caglioti, Paoletti and Ricci 1958). The peak width is ultimately limited by the particle size, or more correctly by the size of the individual perfect crystallites in the specimen. The contribution to the width by this effect is about $\cdot 1\circ$. It is possible to approach this limiting width by an appropriate choice of collimation and monochromator mosaic spread and take off angle, but in normal circumstances, a compromise between resolution and intensity is reached. These considerations are discussed in detail by Hewat (1975).

The powdered sample is normally contained in a metal cylinder about 2cm in diameter and about 5cm in height. The best material for this container is vanadium, the scattering from which is almost entirely incoherent and therefore does not give rise to unwanted peaks in the powder diffraction pattern. Most of the powder diffraction patterns reported in this work however were measured using aluminium cylinders since no vanadium containers were available. In some cases it has been necessary to exclude certain parts of the measured pattern from the refinement, because of the Bragg scattering from the container.
4.4 Crystallographic Least Squares Refinement

The conventional method of refining a crystal structure from diffraction measurements consists of minimising the function

\[ R = \sum_{h} W_h (F_{h}^{\text{obs}} - c F_{h}^{\text{calc}})^2 \]

by varying the positional and thermal parameters of the atoms in the unit cell.

- \( F_{h}^{\text{obs}} \) is the measured structure amplitude for the reflection \( h \).
- \( F_{h}^{\text{calc}} \) is the calculated structure amplitude.
- \( W_h \) is the statistical weight assigned to the reflection.
- \( c \) is a scale factor.

The summation is over all the measured Bragg reflections \( h \). The procedure for obtaining the minimum in the function is described by Lipson and Cochran (1966) and summarised by Pawley (1972b) in connection with constrained refinement. The structural and thermal parameters are represented by the set \( \{ P_i \} \) and the shifts required to obtain the best fit to the observations are represented by \( \{ \Delta P_i \} \).

It can be shown (Pawley 1972b) that the approximate parameter shifts are given by the expression

\[ \sum_{j} (\sum_{h} W_{h} F_{h}^{i} F_{h}^{j}) \Delta P_{j} = \sum_{h} W_{h} F_{h}^{i} \Delta F_{h} \]

\( F_{h}^{ij} \) is the derivative of the calculated structure amplitude with respect to the parameter \( P_j \),

\[ \left( \frac{\partial F_{h}^{i}}{\partial P_{j}} \right) \{ P_i \} \]

and \( \Delta F_{h} = F_{h}^{\text{obs}} - F_{h}^{\text{calc}} \)

The expression can be put in the form \( \sum_{j} M_{ij} \Delta P_{j} = V_i \) where \( M_{ij} \) and \( V_i \) are the least squares matrix and vector respectively. The procedure then involves setting up the matrix and vector, inverting the matrix.
and thus finding $\Delta P$. Because of the non-linearity of the problem
this must be done iteratively until convergence is reached. This is
easily done using a digital computer and many computer programs
have been written for this purpose. The most widely used of these
is probably ORFLS (Busing, Martin and Levy 1962) which has also been
adapted for constrained refinement (Pawley 1972b).

4.5 Constrained Refinement

In many cases the number of independant parameters may be reduced
considerably because certain aspects of the structure are relatively
well known or may be assumed. A particular example of this is in
molecular crystals where the molecules essentially retain their free
state character in the solid phase. Specific aspects of a crystal
structure may be studied whilst keeping other parameters constant.
For instance, as in the work described here, the atomic positions may
be constrained so that the molecular shape is kept constant while the
position and orientation of the molecule as a whole is refined.

Hamilton (1965) has discussed the use of statistical tests in deciding
the significance of the results of the constrained refinement. Such
significance tests can be used to decide between different models of a
structure by comparing the R-factors obtained in refinements run with
and without certain constraints. A knowledge of the number of
observations as well as the number of parameters is required so that
the number of degrees of freedom may be calculated. In the single
crystal case the number of observations is simply the number of
measured structure amplitudes used in the refinement, but with powder
profile refinement the number of observations is not well defined,
though it is presumably somewhat less than the number of
Bragg reflections which contribute to the pattern. It is planned to investigate the problem of the number of observations by comparing powder refinements and single crystal refinements of the same material.

The use of constraints on both the atomic positions and the thermal parameters has been described by Pawley (1972b). Only the former type of constraint is of relevance to the present work as constraints on the thermal parameters are probably more appropriate to high accuracy single crystal work such as that on perdeuteronaphthalene (Pawley and Yeats 1969a). The aim of the present work using powder diffraction data has been to obtain relatively low accuracy molecular positions and orientations with a view to investigating phase transitions in molecular crystals. It is planned however to investigate the possibility of using constraints on the anisotropic temperature factors in the analysis of high resolution powder diffraction data in the future.

Two types of constraint have been used in the powder refinement programs: Lagrange undetermined multipliers and strict constraints. Although the Lagrange method is strict in that the relationships between the parameters may not be broken, the term 'strict' will be reserved for those constraints which bring about a direct reduction in the parameter set. The method of Lagrange undetermined multipliers has been used in classical mechanics (Goldstein 1959) and in statistical mechanics (Pointon 1967) but not extensively in crystallography. The total profile refinement program (Rietveld 1969) however makes use of the method to apply constraints which are in the form of linear and quadratic relations between the least squares parameters. The Lagrange constraint is expressed as a relationship between the
possible shifts on the parameters \( \{ P_j \} \)

\[
N \sum_{j=1}^N L_{jk} \Delta P_j = w_k, k=1, \ldots, n_c
\]

where \( L_{jk} \) and \( w_k \) are constants at the point \( \{ P_i \} \) and \( n_c \) is the number of constraints. The number of equations to be solved in the least squares process then becomes \( N+n_c \) rather than \( N \) in the unconstrained problem. These equations are

\[
\sum_{j=1}^N M_{ij} \Delta P_j \sum_{k=1}^{n_c} L_{ik} \gamma_k = \sum_{i=1}^N W_i F_i \Delta F_i \quad \text{and} \quad \sum_{j=1}^N L_{jk} \Delta P_j = w_k, k=1, \ldots, n_c
\]

This method is quite adequate for many problems, e.g. where bond lengths have to be fixed, but only in special circumstances is it suitable for constraining atomic positions to a molecular configuration.

A more general and easily understood way to specify relations between parameters is to use strict constraints as defined by Pawley (1972b). A constrained parameter set \( \{ P_j \} \) is used in the least squares refinement instead of the full parameter set \( \{ P_i \} \) and some relationship between these sets is specified:

\[
P_i = f_i ( \{ P_j \})
\]

In the case of a shape constraint for a molecular crystal, the full parameter set \( \{ P_i \} \) contains the coordinates of all the atoms in the asymmetric part of the unit cell, whereas the constrained set \( \{ P_j \} \) contains the coordinates of the asymmetric part of the molecule in the molecular frame together with three translational and three rotational coordinates. The full parameter set can be generated from the constrained set by the relationship \( f_i \) which applies the molecular symmetry and transforms the molecule into the crystal frame. The usual least squares matrix and vector are replaced by the constrained matrix and vector :
\[ m_{ij} = \sum_{h} \frac{\delta F_h}{\delta p_i} \frac{\delta F_h}{\delta p_j} \]

\[ v_j = \sum_{h} \frac{\delta F_h}{\delta p_j} \Delta F_h \]

where the differentials with respect to the constrained parameters are given by

\[ \frac{\delta F_h}{\delta p_j} = \sum_{i} \frac{\delta F_h}{\delta p_i} \frac{\delta p_i}{\delta p_j} \]

This procedure is easily incorporated in a refinement program by having a subroutine which creates the full parameter set, calculates the differentials with respect to the constrained parameter set and substitutes them into the appropriate places. The only other alteration required to the program is the conversion of the coordinate system from the usual crystallographic one using fractional coordinates to an orthogonal system in which all distances are measured in the same units. This alteration is not absolutely essential, but it does make a constrained refinement program much simpler by removing the need for multiplication by metric tensors apart from the initial transformation to the orthogonal system.

Strict constraints are used to a limited extent in the Rietveld program, which has a facility for assigning one least squares parameter to two or more of the structural parameters. This facility was used in the refinement of perfluorodiphenyl (Mackenzie, Pawley and Dietrich 1975, and Chapter 7) where only two parameters were required to define the \( z \) coordinates of the atoms in the molecule.

The application of strict constraints to the problem of powder
profile refinement has led to the need for a new refinement program based on the ORFLS program but using the profile intensities as the observed quantities (Section 4.8).

4.6 **Total Profile Refinement**

The method of fitting the measured profile of a neutron powder diffraction pattern was first developed by Rietveld (1967, 1969). In this procedure no attempt is made to separate the overlapping groups of reflections into individual peaks, instead, the detailed shape of the pattern is fitted point by point by the refinement program. This is possible because the neutron diffraction peak can be described almost exactly by a Gaussian function (Caglioti et al 1958). The full width of the peak at half maximum, \( H \), depends quadratically on the tangent of the Bragg angle:

\[
H^2 = u \tan^2 \Theta + v \tan \Theta + w
\]

where \( u, v, w \) are adjustable parameters. The positions of the peaks in a powder diffraction pattern are determined by the cell dimensions, the neutron wavelength and the counter zero angle while their integrated intensities depend on the crystal structure. The diffraction profile can therefore be parametrised and may be fitted using the least squares technique. The contribution from the \( h \) reflection at the position \( 2\Theta \) is

\[
Y_i = \frac{F_h^2 m_h L_h}{H_h \sqrt{\tau}} \frac{2 \sqrt{\ln 2}}{H_h} \exp\left\{ \frac{-4 \ln 2 \left( 2\Theta_i - 2\Theta_h \right)^2}{H_h^2} \right\}
\]

where \( F_h^2 = \) squared structure amplitude for the reflection \( h \)

\( m_h = \) the multiplicity of the reflection

\( L_h = \) the Lorentz factor = \( \frac{1}{\sin \Theta_h \sin 2\Theta_h} \)
\[ 2\theta_h \] = calculated position of the Bragg peak corrected for the zero error of the counter

\[ H_h \] = the full width at half maximum

\[ t \] = the counter step width

The Rietveld program includes corrections for preferred orientation of the powder, and for the peak asymmetry at low angles caused by the vertical divergence of the beam. The form of the latter correction has been criticised by Cooper and Sayer (1975) who suggest a more reasonable method of allowing for the effect. Neither of these corrections were necessary in the work described here.

Rietveld's procedure is to calculate the contribution at each point in the pattern from every reflection within a certain range. Because the Gaussian falls off rapidly to zero away from the peak position this range is taken as one and a half times the width, \( H_h \), of the appropriate reflection on either side of the peak position.

The expression for the intensity of the profile at the point \( 2\theta_i \) can be rewritten

\[ Y_i = W_{ih} \frac{F_h}{2} \]

where \[ W_{ih} = t_m L_h \frac{2\sqrt{\ln 2}}{H_h \sqrt{\pi}} \exp \left\{ -4 \ln 2 \left( \frac{2\theta_i - 2\theta_h}{H_h^2} \right)^2 \right\} \]

Then in the case when more than one Bragg reflection contributes to the profile intensity we have

\[ Y_i = \sum_h W_{ih} \frac{F_h^2}{H_h} \]

where the summation is over all peaks which can possibly contribute to the intensity at the particular point. The refinement program then adjusts the structural and profile parameters to minimise the quantity :
\[ \chi^2 = \sum w_i \left[ y_i \text{(obs)} - \frac{1}{c} y_i \text{(calc)} \right]^2 \]

where \( w_i = \frac{1}{\sigma_i^2} = \frac{1}{y_i \text{(obs)}} \) is a weighting factor.

The parameters in the refinement process can be divided into two types: the profile parameters, consisting of cell dimensions, halfwidth parameters and counter zero point and the structural parameters consisting of atomic positions and temperature factors. Both types of parameters may be refined at the same time, which is a great advantage when the unit cell of the substance under investigation is not known accurately. This is in contrast to the PERNOD program (Klein and Weitzel 1975) and the modification of ORFLS for profile refinement (Taylor and Cox 1973). In the former program the profile parameters are refined separately from the structural parameters while in the latter profile parameters are not refined at all.

The Rietveld program as it was used in this work is in two parts (Hewat 1973). The first part calculates the positions and halfwidths of the Bragg reflections which contribute to a diffraction pattern and determines which reflections can contribute at each point in the scan. The second part of the program then does the actual least squares refinement using a set of starting values for the structural and profile parameters, and the information from the first part of the program which is stored on a separate file. Each parameter is assigned a codeword which is non zero if the parameter is to be varied in the refinement. By means of these codewords, simple constraints between parameters may be set up by assigning the same codeword to separate parameters, this amounts to a strict constraint as defined by Pawley (1972b) as the parameter set is reduced. Only simple
relations may be specified in this way however, e.g. equality or definite ratios between parameters. For more complicated constraints the Rietveld program uses the method of Lagrange undetermined multipliers to specify linear and quadratic relations between the parameters. The quadratic constraint facility allows relations involving interatomic distances to be specified. The distance between two atoms in an orthogonal fractional coordinate system may be expressed as:

\[(ax_1 - ax_2)^2 + (by_1 - by_2)^2 + (cz_1 - cz_2)^2 = d^2\]

and on expanding this gives

\[a^2x_1^2 - 2a^2x_1x_2 + a^2x_2^2 + b^2y_1^2 - 2b^2y_1y_2 + b^2y_2^2 + c^2z_1^2 - 2c^2z_1z_2 + c^2z_2^2 = d^2\]

This expression must then be differentiated with respect to each variable parameter to give

\[2a^2x_1\delta x_1 - 2a^2x_1\delta x_2 - 2a^2x_2\delta x_1 + 2a^2x_2\delta x_2 + \text{etc} = 0\]

The quadratic relationship is specified to the program by the coefficients of the twelve terms in the above expression together with the distance, \(d\).

Unfortunately the present version of the Rietveld program (Hewat 1973) permits only nine terms in the above expression so that the method can only be used when some of the parameters are held constant, \(\delta x_1 = 0\). This is possible only in certain cases where the symmetry is favourable. Even more terms are obtained if a non-orthogonal system is used. Although, in principle, the program could be altered to permit more terms in the constraint, the structure of the program is such that the task would be quite considerable. Quadratic constraints are of limited use in any case and are certainly unsuited to many of the problems encountered in
molecular crystallography. Although a combination of linear and quadratic constraints did lead to a successful refinement of perfluorodiphenyl (Mackenzie, Pawley and Dietrich 1975), this must be regarded as a special case. It is more appropriate to use strict constraints (Pawley 1972b) for this type of problem and it is for this reason that a new program based on the ORFLS was developed (section 4.8).

4.7 Integrated Intensities Method

Before the advent of total profile refinement (Rietveld 1969) the method used for the analysis of powder data was that of taking integrated intensities and fitting structure amplitudes in the conventional way as with single crystal data. The structures of Ca₃UO₆ and Sr₃UO₆ were refined by Rietveld (1966) in this way. To overcome the problem of overlapping peaks he simply took the observable quantities to be the integrated intensities of separate groups with no attempt at separation of the individual Bragg reflections which contribute.

The quantity to be minimised was defined as

$$\sum_i w_i \left( \sum_h m_h F^2_{h \text{ obs}} - \sum_h m_h F^2_{h \text{ calc}} \right)^2$$

where $F_{h \text{ obs}}$ and $F_{h \text{ calc}}$ are the observed and calculated structure amplitudes, $m_h$ is the multiplicity of the reflection. The sum over $h$ represents an integration over all the reflections in one group and the sum over $i$ represents the sum over the groups where $w_i$ is the weight assigned to the $i$th group.

This method obviously leads to the loss of information contained within the overlapping groups. At high values of $\frac{\sin \theta}{\lambda}$ it is common for overlapping to be very severe so that few, if any, separate intensities can be measured. The number of observations used in these
refinements was relatively small, 33 and 38, for Ca$_3$UO$_6$ and Sr$_3$UO$_6$ respectively. The method is unsatisfactory for the following reasons:

a) overlapping reflections, even at low scattering angles, may contain considerable information about the structure

b) the small scale information contained in the high order reflections must be ignored except in very favourable circumstances where the overlapping is not too severe.

A variation of this procedure was developed by Klein and Weitzel (1975) though in a somewhat concealed form. Their program, called PERNOD (Pulver-Einkristall, Rontgen-und-Neutronen beugungs -ORFLS - Darmstadt), uses the well known ORFLS single crystal refinement program (Busing, Martin and Levy 1962) to refine the atomic parameters with the addition of a profile refinement to fit only the cell dimensions, peak width and counter zero point. The observed quantities, at least for the structure refinement, are still integrated intensities but an attempt is made to 'separate' the observed intensities of the overlapping groups into intensities contributed by single reflections in proportion to preliminary calculated intensities. The 'observed' intensity of the $g$th reflection in the group $G$ is then given by

$$I_{obs}^g = \frac{I_{G}^G}{I_{calc}^G} I_{calc}^g$$

Superficially it would seem that the overlapping reflections are accounted for in this way. However it is easy to show that no extra information is gained, and in fact the function to be minimised turns out to be almost exactly the same as that in the early method of Rietveld (1966).
The function to be minimised by Rietveld's program was:

\[ \chi_R^2 = \sum_g w_g (\sum_I^{\text{obs}} - \sum_I^{\text{calc}})^2 \]

The corresponding function in the PERNOD program is:

\[ \chi_P^2 = \sum_h w_h (\sum_I^{\text{obs}} - \sum_I^{\text{calc}})^2 \]

The expression can be rewritten

\[ \chi_P^2 = \sum_h \frac{I^{\text{calc}}}{\sum_g I^{\text{calc}}} \left( \sum_g I^{\text{obs}} - \sum_g I^{\text{calc}} \right)^2 \]

with the weights set to unity. The summation over \( h \), all reflections in the scan, is then separated into summations over \( G \) and \( g \), giving:

\[ \chi_P^2 = \sum_G \frac{\left( \sum_g I^{\text{calc}} \right)^2}{\left( \sum_g I^{\text{calc}} \right)^2} \left( \sum_g I^{\text{obs}} - \sum_g I^{\text{calc}} \right)^2 = \sum_G \sum_h w_1 (\sum_g I^{\text{obs}} - \sum_g I^{\text{calc}})^2 \]

Thus \( \chi_P^2 \sim \chi_R^2 \) with different weighting.

The PERNOD program also refines the profile parameters but this is done separately from the structure refinement in contrast to the total profile refinement method (Rietveld 1969) where the structural and profile parameters are refined simultaneously. It has been found by experience that the latter approach is to be preferred, particularly when relatively unknown structures are being refined.

Considerable effort was put into adapting the PERNOD program for the molecular crystal constraints before the shortcomings were realised. There was a considerable advantage in using a refinement program based on ORFLS since the necessary constraint routines were available (Pawley 1972b). The only major alteration to PERNOD
involved the change of coordinate system to an orthogonal Ångstrom one as described by Pawley (1972b).

The adapted program was run with the test data for CuWO₄ and gave substantially the same result as the original version of PERNOD, simply confirming that the change of coordinate system was in order. Perfluorodiphenyl provided a good test for the program's ability to refine molecular crystal structures as this structure had already been refined successfully using the Rietveld program (Mackenzie, Pawley and Dietrich 1975). The program was run with initial values of the parameters identical to those used in the successful Rietveld program run. The refinement proved to be unstable however and no minimum was reached. Attempts were also made to refine the structures of octafluoronaphthalene (room temperature phase), para-diiodo and para-dibromo-tetrafluorobenzene, all without success. The program was consequently abandoned.

4.8 The Development of a New Program: EDINP

The successful refinement of the structure of perfluorodiphenyl using the Rietveld program showed that the total profile refinement technique, with reasonable constraints, could be used to obtain meaningful information about molecular crystals. The application of the technique to molecular crystals of lower symmetry such as octafluoronaphthalene however requires the use of strict constraints. The structure of the Rietveld program is such that the introduction of such constraint facilities is impractical. It was therefore decided to develop a new program for powder profile refinement. This program, EDINP, is based on the ORFLS program (Busing et al. 1962) adapted for orthogonal coordinates by Pawley (1972b). The main
difference in this case is that the quantities necessary for the construction of the least squares matrix and vector are the differentials of the profile intensities at each point with respect to the parameters instead of the differentials of the structure amplitudes. The least squares matrix is:

\[ \sum_j M_{ij} \Delta P_j = V_i \]

where \( M_{ij} = \sum_s w_s \frac{\partial y_s}{\partial P_i} \frac{\partial y_s}{\partial P_j} \)

\[ V_i = \sum_s w_s \frac{\partial y_s}{\partial P_i} \Delta y_s \]

\[ \Delta y_s = y_{s \text{obs}} - y_{s \text{calc}} \]

i and j label the least squares parameters and s labels the scan points.

The procedure adopted in EDINP is to calculate the appropriate differentials for the various reflections, \( h \), in turn, then to sum the contributions to obtain the total differentials with respect to each parameter at each point in the scan. To save computer storage space, this is done in blocks of 100 scan points and as each block of differentials is completed the contributions are summed to form the matrix and vector. This procedure is different from that used in the Rietveld program in which all the reflections which can possibly contribute at each point are first calculated by a preparation program. This information is then stored on a magnetic tape or disc file and must be accessed on each refinement cycle. The Rietveld preparation information must be updated when the profile parameters are varied, since the contributing reflections at certain scan points are likely to change. The procedure adopted by the new program is
clearly to be preferred, both from the convenience, and the efficiency point of view.

The calculated intensity at the point i may be written:

\[ y_{i}^{\text{calc}} = \sum_{h} \left( \frac{F_{h}^{\text{calc}}}{h} \right)^{2} \frac{m_{h}}{\sin \theta \sin 2\theta H_{h}} \exp \left( -\frac{g \Delta^{2}}{H_{h}^{2}} \right) \]

where \( H_{h}^{2} = u \tan^{2} + v \tan + w \)

\[ \theta = \theta_{h}^{\text{calc}} \]

\[ g = 4 \ln 2 \]

\[ \Delta = 2\theta_{i}^{\text{obs}} - 2\theta_{i}^{\text{zero}} - 2\theta_{h}^{\text{calc}} \]

\( c \) is a scale factor

The differentials necessary for the least squares matrix and vector were obtained by differentiating the above expression with respect to the structure and profile parameters.

The goodness of fit may be judged by the R-factor which defined as

\[ R = 100 \cdot \frac{\sum_{i} | y_{i}^{\text{obs}} - y_{i}^{\text{calc}} |}{\sum_{i} y_{i}^{\text{obs}}} \%

This differs from the R-factor defined in the Rietveld (1969) program.

In the EDINP R-factor, the summation is over all observed points i, including the background region, whereas in the Rietveld program the summation is only over those points where there is a calculated contribution from a peak. The EDINP R-factor will therefore be increased if there is a peak with no corresponding calculated peak - the R-factor reflects the reliability of the whole scan.

The program was used to refine the structures of the two similar molecular crystals para-diiodo and para-dibromo tetrafluorobenzene.
Further use of the program is described in Chapters 7 and 8 in connection with perfluorodiphenyl and octafluoronaphthalene respectively.

Since EDINF uses a system of constraints identical to the single crystal refinement program (Pawley 1972b), the results of the two types of refinement can be compared directly. It is hoped to gain more insight into the profile refinement method and in particular into the problem of the significance testing by doing constrained refinements of several structures with both single crystal and powder data.
4.9 Constrained Refinement of p-diiodo and p-dibromo tetrafluorobenzene

The structures chosen for the first refinements using EDINP are very similar to p-dichlorobenzene which shows an interesting phase transition (Housty 1957, Reynolds, Kjems and White 1973). They are para-diiodo and para-dibromo tetrafluorobenzene. Differential thermal analysis has shown that the former has a phase change at approximately 85°C. The melting points of the two materials are approximately 107°C and 80°C respectively. Only the room temperature phases have been studied thoroughly. The powder diffraction data were measured at 300 and 150 K on the TAS 2 spectrometer at Risø using neutrons of wavelength 2.36 Å. Pyrolytic graphite was used as the monochromator and analyser and the higher order neutrons were removed from the beam with a pyrolytic graphite filter.

The high temperature phase of $p$-C$_6$F$_4$I$_2$ gave a poor diffraction pattern in a later experiment on the PANDA diffractometer at AERE, Harwell and this scan was confused by a great deal of scattering from the furnace, mainly from tantalum. Although the high temperature data could not be used to determine the structure, the scan did confirm the DTA results. Both the powder measurements and the DTA show that the substance remains in the high temperature phase after cooling well below the transition temperature. In fact, no further evidence of a phase transition was found in the DTA measurement even when the sample was cooled to liquid nitrogen temperature. Because of the nature of this phase transition it should be possible to measure the diffraction pattern of the high temperature phase without a furnace by first heating the sample then cooling to room temperature.

The unit cells of both $p$-C$_6$F$_4$I$_2$ and $p$-C$_6$F$_4$Br$_2$ were measured from single crystal X-ray photographs although, in principle, this could
have been done from the powder scans since there was no overlapping in the four lowest orders. The symmetry of the cells was also deduced from the photographs to be $P2_1/c$.

From the remarkable similarity of the powder diffraction patterns both materials were clearly isostructural, and, as a first step in solving the structure, a three dimensional model was constructed with cardboard molecules which were adjusted to give the most favourable packing. This structure was then fed into the first part of the lattice dynamics program (Pawley 1972a) which found a potential minimum after a slight readjustment of the molecular orientation. This structure was then used as the starting point for both refinements.

Both structures were refined using EDIN with strict constraints. The molecule was constrained to be planar at all times, and the final values of the atomic coordinates within this plane are listed in table 4.1. The $mmm$ symmetry of the molecule was retained by transformation of these coordinates. The centre of the molecule was placed on a centre of symmetry and its orientation was determined by the rotation matrix $R(\phi, \theta, \psi)$ where the three Euler angles were allowed to vary. The final atomic coordinates in the orthogonal cell and the final values of the Euler angles are given in table 4.2. The orthogonal axes $x$ and $y$ parallel the monoclinic axes $a$ and $b$ while the $z$ axis parallels $c$.

The parameters varied in the scan were:

1. overall scale factor
2. overall temperature factor
3. Euler angles
4. for the CC bond
5. for the CF bond
for the unit cell
1 for the zero angle of the scan
3 for the peak width
The final values of these parameters, apart from the three bond length parameters, are listed in table 4.3 along with the final R-factors.

Two regions of each scan were excluded from the refinement because there was a considerable contribution to the scattering from the aluminium sample container ((111) and (200) reflections).

The monoclinic angle $\beta$ is very close to $90^\circ$ in both structures and the preliminary measurement of the unit cell from the X-ray photographs was not sufficiently accurate to determine whether the angle was greater or less than $90^\circ$. With one choice of the angle, say $92.5^\circ$, the other possible structure, corresponding to $\beta = 87.5^\circ$, is obtained by altering the molecular orientation angle $\psi$ by $\pi$. The smooth refinement of $\psi$ through $90^\circ$ is impossible since this corresponds to a reindexing of the reflections. The value of $R$ in such a refinement would have to go through a large intermediate value in going from the false to the true minimum. The choice between the two possible structures was easy to make however by comparing the calculated and observed intensities of certain pairs of reflections $(h,k,\pm \ell)$, one of which was weak while the other was strong.

In the first refinement of each structure it was found that the final CBr and CI bond lengths were chemically unreasonable, being equal to the CF bond length. Since the scattering lengths of the substituent atoms are all of the same order (between 0.5 and 0.7) the bromine or iodine atoms could be positioned at any of the three independent positions around the benzene ring without greatly affecting the diffraction pattern. These different orientations
correspond to differences of $\pi/3$ in the Euler angle $\phi$. Refinement of the three possibilities showed that the first result was in a false minimum and at true minimum the bond lengths became chemically reasonable; namely:

\[
\begin{align*}
\text{CF} &= 1.36 (2) \text{ Å} \\
\text{CBr} &= 1.81 (1) \text{ Å} \\
\text{CI} &= 2.00 (3) \text{ Å}
\end{align*}
\]

P-C$_6$F$_4$Br$_2$

\[
\begin{align*}
\text{CF} &= 1.46 (4) \text{ Å} \\
\text{CL} &= 2.00 (3) \text{ Å}
\end{align*}
\]

P-C$_6$F$_4$I$_2$

The true minimum and the two false minima are shown for p - C$_6$F$_4$Br$_2$ in Figure 4.1. The R-factor was calculated at intermediate points, allowing the scale factor, $\theta$ and $\psi$ to vary, keeping $\phi$ fixed. This shows the size of the barrier between the true and false minima. Although it would be impossible for $\phi$ to refine through one of these barriers, the true minimum could be reached smoothly if all three substituent atoms were allowed to move independently, each with a variable scattering length.

Figure 4.2 shows the position of the p - C$_6$F$_4$I$_2$ molecule before the refinement and the shift into the false minimum. Some of the shifts in atomic positions exceed 1 Å. It is highly unlikely that such shifts in the positional parameters would be possible without constraints, because of the likelihood of reaching false minima.

Figure 4.3 shows the projection on to the (010) plane of the structure of p - C$_6$F$_4$Br$_2$. The structure of p - C$_6$F$_4$I$_2$ is very similar, so that a second diagram is unnecessary. Figure 4.4 (a) and (b) show the observed and fitted profiles for p - C$_6$F$_4$Br$_2$ and p - C$_6$F$_4$I$_2$ respectively.
The final coordinates of the atoms in the two molecules in $\mathcal{R}$, before the rotation to the crystalline orientation.

<table>
<thead>
<tr>
<th></th>
<th>$x_{\text{planar}}$</th>
<th>$y_{\text{planar}}$</th>
<th>$z_{\text{planar}}$</th>
</tr>
</thead>
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<tr>
<td>both structures</td>
<td>C</td>
<td>1.209</td>
<td>0.702</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.000</td>
<td>1.400</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>2.402(14)</td>
<td>1.352(12)</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>0.000</td>
<td>3.208(14)</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>2.446(26)</td>
<td>1.484(22)</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>0.000</td>
<td>3.399(31)</td>
</tr>
</tbody>
</table>

Table 4.2

Final coordinates of the atoms in the two structures with respect to the orthogonal Ångstrom system.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
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<tr>
<td>p-C$_6$F$_4$Br$_2$</td>
<td>C</td>
<td>-0.461</td>
<td>-1.185</td>
<td>-0.581</td>
<td>-0.481</td>
<td>-1.142</td>
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<tr>
<td></td>
<td>C</td>
<td>0.780</td>
<td>-0.664</td>
<td>-0.954</td>
<td>0.764</td>
<td>-0.616</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>-1.242</td>
<td>-0.520</td>
<td>0.375</td>
<td>-1.247</td>
<td>-0.525</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.938</td>
<td>-2.335</td>
<td>-1.125</td>
<td>-0.959</td>
<td>-2.391</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-2.445</td>
<td>-1.053</td>
<td>0.718</td>
<td>-2.614</td>
<td>-1.056</td>
</tr>
<tr>
<td></td>
<td>Br or I</td>
<td>1.787</td>
<td>-1.521</td>
<td>-2.187</td>
<td>1.836</td>
<td>-1.480</td>
</tr>
<tr>
<td>p-C$_6$F$_4$I$_2$</td>
<td>C</td>
<td>-0.481</td>
<td>-1.142</td>
<td>-0.647</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.764</td>
<td>-0.616</td>
<td>-0.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>-1.247</td>
<td>-0.525</td>
<td>0.354</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>F</td>
<td>-0.959</td>
<td>-2.391</td>
<td>-1.386</td>
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<td></td>
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<tr>
<td></td>
<td>F</td>
<td>-2.614</td>
<td>-1.056</td>
<td>0.779</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Br or I</td>
<td>1.836</td>
<td>-1.480</td>
<td>-2.401</td>
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Final values of the Euler angles for the two structures (in radians).

<table>
<thead>
<tr>
<th></th>
<th>$\phi$</th>
<th>$\theta$</th>
<th>$\psi$</th>
</tr>
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<tr>
<td>p-C$_6$F$_4$Br$_2$</td>
<td>-0.124(4)</td>
<td>0.757(1)</td>
<td>2.446(2)</td>
</tr>
<tr>
<td>p-C$_6$F$_4$I$_2$</td>
<td>-0.161(8)</td>
<td>0.805(3)</td>
<td>2.489(4)</td>
</tr>
</tbody>
</table>
Table 4.3

Final parameters and R-factors for both structure refinements.

<table>
<thead>
<tr>
<th></th>
<th>p-C$_6$F$_4$Br$_2$</th>
<th>p-C$_6$F$_4$I$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>scale factor</td>
<td>1.71(2)</td>
<td>1.55(4)</td>
</tr>
<tr>
<td>counter zero</td>
<td>-0.028(5)</td>
<td>-0.010(10)</td>
</tr>
<tr>
<td>u, peak shape</td>
<td>1.26(22)</td>
<td>3.70(78)</td>
</tr>
<tr>
<td>v, parameters</td>
<td>-0.48(15)</td>
<td>-0.98(49)</td>
</tr>
<tr>
<td>w, (degrees)$^2$</td>
<td>0.296(25)</td>
<td>0.377(74)</td>
</tr>
<tr>
<td>a, unit cell</td>
<td>6.090(1)</td>
<td>6.268(3)</td>
</tr>
<tr>
<td>b, parameters</td>
<td>11.412(3)</td>
<td>11.641(5)</td>
</tr>
<tr>
<td>c, (Å and degrees)</td>
<td>5.4042(2)</td>
<td>9.30(3)</td>
</tr>
<tr>
<td>B,</td>
<td>93.12(1)</td>
<td>92.70(3)</td>
</tr>
<tr>
<td>B, R-factor %</td>
<td>2.42(22)</td>
<td>5.66(49)</td>
</tr>
<tr>
<td>R-factor %</td>
<td>9.6</td>
<td>14.0</td>
</tr>
<tr>
<td>Temperature of measurement (K)</td>
<td>150</td>
<td>300</td>
</tr>
</tbody>
</table>
Figure 4.1.

The variation of the R-factor with $\phi$, showing the true minimum in the centre and the two false minima $\pm 3$ on either side. Intermediate R-factors were calculated varying the scale factor, $\Theta$ and $\Psi$, holding $\phi$ constant.

Figure 4.2

The position of the p-$C_6F_4I_2$ molecule before the first refinement cycle and its position in the false minimum. The view is down the $\gamma$-axis.
Projection on the (010) plane of the structure of $C_6F_4Br_2$. The largest circles are the bromine atoms. The structure of $C_6F_4I_2$ differs imperceptibly from that of $C_6F_4Br_2$. 
Figure 4.4

The observed and calculated scans for (a) $\text{C}_6\text{F}_4\text{Br}_2$ and (b) $\text{C}_6\text{F}_4\text{I}_2$ with the background removed. The zeros in the observed scans just above $2\theta = 60^\circ$ and $70^\circ$ are the parts of the scans removed because of the presence of (111) and (200) Al scattering. The scan ends just before $2\theta = 80^\circ$. 
\[ p-\text{Br}_2 \text{C}_6\text{F}_4 \]

\[ p-\text{I}_2 \text{C}_6\text{F}_4 \]
CHAPTER 5

RAMAN SCATTERING
5.1 Introduction

Raman scattering is the inelastic scattering of light by excitations. Photons of energy $\hbar \omega_0$ and wavevector $k_0$, incident on some system, are scattered to give photons of energy $\hbar \omega_1$ and wavevector $k_1$. Energy and wavevector conservation are satisfied by taking into account the change in state of the scattering system. In the present work the interaction of light with crystal vibrations or phonons is considered although the term Raman scattering is also applied to scattering from other types of excitations such as plasmons, excitons and magnons. The scattering from acoustic phonons is normally referred to as Brillouin scattering, the term Raman scattering being reserved for scattering from the optic modes.

The Raman effect in crystals has been understood qualitatively since the late 1920's but it was not until the development of the laser in the 1960's that it became a widespread technique for investigating excitations. The advantage of the laser is that it provides a high intensity, well collimated beam of light with definite polarisation and a very small spread in wavelength. The latter property is essential in the investigation of the low frequency excitations commonly found in crystals.

5.2 The Polarisability Model

Although the interaction between electromagnetic radiation and matter is an extremely complex problem, great simplifications can be made in the case of Raman scattering. The polarisability approach was formulated quantum mechanically by Placzek (1934) and the theory has been reviewed by Chantry (1971). The application to Raman scattering in crystals is described by Cowley (1971). Only the essential features of the model will be outlined here.

Because the wavelengths of the incident and scattered light are much greater than the size of atoms and the fact that the electric
component of the light interacts with the scattering system the interaction Hamiltonian may be expressed in terms of the polarisability:

\[ H = \sum_{\alpha/\beta} P_{\alpha/\beta}(k_0, i, k_1, f) E_{\alpha}(0) E_{\beta}(1) \]

where \( \alpha/\beta \) are Cartesian coordinates

\( i, f \) label the initial and final states of the crystal

\( E(0), E(1) \) are the electric vectors of the incident and scattered light

\( P_{\alpha/\beta} \) is an element of the crystal polarisability tensor.

The scattering probability can then be calculated using Fermi's Golden Rule:

\[ W = \frac{2\pi}{\hbar} \rho(\omega_1) \left| H(k_0, i, k_1, f) \right|^2 \delta(\omega_0 - \omega_1 + E_i - E_f) \]

where the density of final photon states is

\[ \rho(\omega_1) d\omega_1 d\Omega = \left( \frac{L}{2\pi c} \right)^3 \frac{\omega_1^2}{\hbar} d\omega_1 d\Omega \]  
(normalised in a box of side L)

This leads to an expression for the number of photons scattered per unit time into the solid angle \( d\Omega \) and the wavevector \( k_1 \) corresponding to the transition \( |i\rangle \) to \( |f\rangle \) in the crystal:

\[ W d\Omega = \frac{\omega_1^3}{2\pi^2 E_0 c^3} \sum_{\alpha/\beta} P_{\alpha/\beta}^{*if} E_{\alpha} E_{\beta} E \cdot \xi \xi(n(k_1) + 1) \]  
(5.1)

where \( \xi \) is the polarisation vector of the light

\( n(k_1) \) is the photon occupation number of the state labelled \( k_1 \). This is zero for the normal Raman effect considered here and greater than zero for the stimulated Raman effect.

\( P_{\alpha/\beta}^{if} \) is the matrix element \( \langle f | P_{\alpha/\beta}(k_0, k_1) | i \rangle \)

At optical frequencies (\( 10^{15} \) Hz) far beyond the vibrational spectrum of the crystal (\( 10^{12} \) Hz), the main contribution to the crystal polarisability is from the electrons. In the adiabatic approximation of lattice dynamics the electron states are functions of the nuclear coordinates.

It follows that the electronic polarisability is also a function of the
nuclear coordinates and the Raman scattering results from a modulation of this electronic polarisability by phonons. The matrix element $I_{\alpha\beta}^{\text{if}}$ can be written

$$I_{\alpha\beta}^{\text{if}}(k_0, k_1) = \langle \theta_f | \alpha_{\beta}^{(k_0, k_1)} | \theta_i v_1 \rangle$$

where $\theta$ labels the electronic states of the crystal.

$v$ labels the phonon states of the crystal.

In insulating crystals the electrons are assumed to be in ground states and the dependence of these states on the nuclear coordinates $r$ can be included in the polarisability, to give:

$$I_{\alpha\beta}^{\text{if}}(k_0, k_1) = \langle v_f | \alpha_{\beta}^{(k_0, k_1)} | v_1 \rangle$$

(5.2)

For small displacements the polarisability may be expanded as

$$I_{\alpha\beta}^{\text{if}}(k_0, k_1, r) = I_{\alpha\beta}^{\text{if}}(k_0, k_1) + \sum_{l, s} I_{\alpha\beta}^{l, s} \left| u(l, s) \right| + \text{higher order terms}$$

where $l$ labels the lattice points and $s$ combines indices for the atoms in the unit cell and for $x, y$ and $z$.

In terms of normal coordinates this gives

$$I_{\alpha\beta}^{(k_0, k_1, r)} = I_{\alpha\beta}^{(k_0, k_1)} + \sum_{q, j} A(q_j) \sum_{s} e_s(q_j) \left| \frac{p_{l, s}^{(k_0, k_1)}}{N_m} \right| + \sum_{q, j} e_s(q_j) \exp iq \cdot r(l)$$

where $e_s(q_j)$ is a component of the eigenvector of the $j$th phonon branch with wavevector $q$.

We now take the wavevector dependence of the polarisability into account by writing

$$I_{\alpha\beta}^{l, s} = I_{\alpha\beta}^{l, s} \exp iQ \cdot r(l)$$

The wave vector transfer is defined by $Q = k_0 - k_1$. 
Then after summing over \( \ell \) we obtain

\[
P_{\alpha \beta}(k_0, k_1, R) = P_0^{\alpha}(k_0, k_1) + \sum_j \lambda(q, j) e^{\alpha j}(j, k_0) \delta(q - g - B)
\]

where \( e^{1/2} (j, k_0) = \frac{1}{\sqrt{m_s}} \sum_s \sum \epsilon_s (q, j) P_{\alpha \beta} (s, k_0) \)

The delta function expresses conservation of wavevector as in the neutron case. In first order Raman scattering the wavevector transfer is very much smaller than a reciprocal lattice vector so that effectively \( q = 0 \).

The final expression for the Raman scattering probability is determined by evaluating the matrix elements between phonon states (equation 5.2) and substituting in equation 5.1 to get

\[
wd\omega = \frac{\omega^3}{4\pi^2 E_0 c^3} \sum_j \frac{n_j}{\omega_j} \left[ (n(\omega_j) + 1) \delta(\omega_0 - \omega_1 - \omega_j) + n(\omega_j) \delta(\omega_0 - \omega_1 + \omega_j) \right]
\]

\[
x (n(k_1) + 1)
\]

\[
\times \sum_{\alpha \beta \delta \gamma} P_{\alpha \beta}^{1/2} (j, k_0) P_{\delta \gamma}^{1/2} (j, k_0) E_\delta E_\gamma E_\delta E_\gamma
\]

The first term in the square brackets/ photon energy loss i.e. phonon creation. The second term represents photon energy gain i.e. phonon annihilation. These two types of scattering are often called Stokes and Anti-Stokes respectively.

In experimental situations the polarisation of the light is normally arranged to be along crystallographic axes. This results in a simplification of the expression above:

\[
\sum_{\alpha \beta} P_{\alpha \beta}^{1/2} P_{\delta \gamma}^{1/2} E_\delta E_\gamma E_\delta E_\gamma \Rightarrow \sum_{\alpha \beta} E_\delta E_\gamma P_{\alpha \beta}^{1/2} E_\delta |E_\gamma|^2
\]

We can obtain information on the eigenvectors of the phonons in a particular polarised Raman spectrum by considering the symmetry properties of the corresponding scattering tensor element \( P_{\alpha \beta}^{1/2} \) under the operations
of the crystallographic point group. \( P_{4/3}^1 \) transforms like a symmetric second rank tensor (i.e. like \( x^2, y^2, z^2, xy, yz, zx \)) so that the various spectra obtained correspond to irreducible representations of the point group. Phonons can give rise to 1st order Raman scattering only if they transform according to the same irreducible representation as the element of the scattering tensor concerned. Thus the frequencies of modes measured in a Raman scattering experiment may be assigned to phonons which have particular transformation properties under the operations of the crystal symmetry group.

Further information on the phonon eigenvectors can only be obtained if we have some knowledge of the form of the crystal polarisability and how it depends on the various atomic displacements. This is only possible in the particular case of molecular crystals.

5.3 Molecular Crystals - The Oriented Gas Model

Information about the eigenvectors as well as the frequencies and symmetry properties of phonons may be obtained from the Raman spectra of molecular crystals. This is because it is possible to write down an approximate expression for the molecular polarisability and hence calculate the crystal polarisability. The oriented gas approximation of Kastler and Rousset (1941) treats the crystal as a gas of oriented molecules and ignores the intermolecular forces which are assumed to be insufficient to perturb the electronic configuration of the molecules. The Raman scattering is then attributed to the modulation of the crystal polarisability due to librations of large optically anisotropic molecules. This approach has been used to discuss the Raman spectra of such crystals as naphthalene, anthracene and biphenyl (Ito et al 1968). A basic assumption in this earlier work has been that the normal modes consist of librations about only one principal axis of the molecule. This
assumption has been criticised by Pawley (1967) who found in his calculation of the lattice dynamics of naphthalene and anthracene that the rotation axes may be as much as 30° from the principle axes. In the present work we have made no assumptions about the rotation axes since our aim has been to obtain information about the zone centre eigenvectors using the relative intensities measured in the Raman spectra.

The validity of the oriented gas model for molecular crystals has been discussed recently by Arthur (1976) who derived expressions for the Raman scattering intensity when the interaction between induced dipoles are taken into account. The resultant expressions are more complicated than those for the simple oriented gas model and lead to differences in the relative intensities of the modes not predicted by the simple model. In special cases, however, the intensities within the same polarisation spectrum are not affected and the simple model still provides a good description of the Raman spectrum.

5.4 The Cross Section

The only essential information necessary to formulate the Raman scattering cross section in the oriented gas model is the crystal structure and the shape of the molecule. If the polarisability of the molecule is \( \alpha_m \), in diagonal form, then its contribution to the crystal polarisability is

\[
\alpha_c = \frac{1}{v} \alpha_m R
\]

where the orthogonal transformation \( R \) relates the molecular principal axis system to the crystal axes and \( v \) is the volume of the primitive cell.

Now we consider a libration of the molecule of amount \( \delta \Theta \) about some axis \( \bar{x} \) defined in the molecular axis system:

\[
\delta \Theta = \delta \Theta (x_1,x_2,x_3) = (\delta \Theta_1, \delta \Theta_2, \delta \Theta_3)
\]
This leads to a modified polarisability of the form
\[ \alpha'_m = [1+\Omega] \alpha_m [1-\Omega] + 0\theta^2 \]
where \( \Omega = \begin{bmatrix} 0 & -\delta \theta_3 & \delta \theta_2 \\ \delta \theta_3 & 0 & -\delta \theta_1 \\ -\delta \theta_2 & \delta \theta_1 & 0 \end{bmatrix} \)

To first order in \( \delta \theta \) this modified polarisability is
\[ \alpha'_m = \alpha_m + [\Omega \alpha_m - \alpha_m] \]

The term is the brackets is the change in polarisability due to the libration. The change in the crystal polarisability needed for the calculation of the cross section is therefore
\[ [\delta \alpha]_{\alpha \beta} = \sum_{klm} R_{k\alpha} R_{l\beta} \epsilon_{klm} (\alpha_{kk} - \alpha_{kl}) \delta \theta_m \] (5.4)

(where \( \epsilon_{klm} \) is the Levi-Civita tensor)

This expression can be used with equation 5.3 to give an expression for the integrated intensity due to the mode \( j \):
\[ I_{j \alpha \beta} = \gamma \sum_{j', mm'} \frac{n(j') + 1}{\omega_{j'}} \frac{e_{mm}^j e_{m'm'}^j}{(I_{mm} I_{m'm'})^{1/2}} \]

(5.5)

\[ = \frac{1}{\omega_j} (n(\omega_j) + 1)(P \alpha \beta)^2 \]

where \( \gamma \) is a scale factor

and \( P \alpha \beta = \sum_{m} \frac{P_{\alpha \beta}}{\sqrt{I_{mm}}} e_{m}^j \)

The librational components of the eigenvectors have been defined here as
\[ \delta \theta_m = \frac{e_{m}^j}{\sqrt{I_{mm}}} \]
where $I_{mm}$ is the moment of inertia about the axis $m$.

A weighted sum of the intensities in the spectrum ($\alpha\beta$) can be defined as

$$
\sum (\alpha\beta) = \sum_j \frac{\omega_j}{n(\omega_j)^2} n(\omega_j) \alpha\beta
$$

(5.6)

Through the orthonormality relations of the eigenvectors this reduces to

$$
\sum (\alpha\beta) = \sum_m \frac{(E^m_{\alpha\beta})^2}{I_{mm}}
$$

(5.7)

The experimental integrated intensity (equation 5.6) can therefore be compared with the calculation of the oriented gas model (equation 5.7).

In theory a measurement of the six $\sum (\alpha\beta)$ terms from spectra of carefully correlated intensities should make it possible to determine the magnitudes of the $\alpha_{kk} - \alpha_{ee}$ terms in equation 5.4. These latter quantities can then be used to calculate the eigenvectors for each mode by substituting into equation 5.5.

The eigenvectors have been related to the scattered intensity by using the molecular polarisability $\alpha_m$. The latter can take three forms depending on the symmetry of the molecule. If the molecule is isotropic then the quantities $E^m_{\alpha\beta}$ are zero and there is no first order Raman spectrum (e.g., HMT), if it is uniaxial there is one adjustable parameter and if it is biaxial there are two adjustable parameters.

The above description has dealt with only one molecule in the unit cell but there is no difficulty in accounting for more than one molecule provided these are related by space group symmetry to the first molecule. The contribution from the other molecules is similar to that from the first apart from possible differences in sign.

This model has been used in the analysis of the spectra of sulphur (Arthur and Mackenzie 1974, Arthur 1974) and perfluorodiphenyl (Arthur 1974, Arthur and Mackenzie 1976). Some inconsistencies between the
calculations and the observed spectra led to a re-examination of the model and its extension by including the effect of the induced dipoles on the local field (Arthur 1976). As already mentioned this more involved theory predicts differences between the polarisation spectra not accounted for by the simple theory but at the cost of greatly increased computational complexity. The comparison of relative intensities of modes within the same spectrum is only valid when the polarisability depends on motion of the molecules about one axis as in the case of sulphur. When more than one libration axis is involved as with perfluorodiphenyl (Arthur and Mackenzie 1976) relative intensities within the same spectrum are also affected.

5.5 Experimental

The technique of Raman scattering is similar to that already described for neutron inelastic scattering in that we require a source of monochromatic radiation, an oriented single crystal sample and a means of analysing the scattered radiation. The problem is very much simplified in light scattering since we are only concerned with phonons at the zone centre so we do not require to determine the wavevector of the scattered radiation. In most cases a right angle scattering geometry is used although sometimes it is necessary to use a 180° or backscattering geometry.

Four independent spectra may be obtained for any particular orientation of the crystal by using the different combinations of incident and scattered light polarisations. The spectra are labelled according to the directions of propagation and polarisation of the incident and scattered light with respect to the crystallographic axes. For the crystal orientation shown in Figure 5.1 the four possibilities are:
Figure 5.1

Relative orientation of crystal axes and light propagation and polarisation directions for a typical 90° scattering experiment.
The first and last symbols indicate the propagation directions of the incident and scattered beams and the second and third symbols indicate the polarization directions of the incident and scattered light. In brevity are sufficient to identify the species, just being associated with the successive element of the spectrum. The small deviation used in this way be necessary to normalize the data. If any deviation of the model is to be taken. This can be adjusted by the half wave plate and the monochromator. The scattering system can be detected with a split or three photodetectors which may be studied. The detector must be used to study the spectrum of this kind in a photomultiplier. A schematic diagram of a typical set is shown in Figure 6. The polarization of the incident light can be rotated through 90° using a half wave plate and the polarization of the scattered light entering the spectrometer may be selected by a plane.
The first and last symbols indicate the propagation directions of the incident and scattered beams and the second and third symbols indicate the polarisation directions. Normally the symbols in brackets are sufficient to identify the spectra, these being associated with the corresponding element of the scattering tensor. The notation used is due to Damen et al (1966).

The various polarisation spectra are measured under different intensity conditions since the transmission properties of the crystal are generally different in each orientation and the incident intensity is reduced by the half wave plate in half of the spectra. For this reason it is necessary to normalise the spectra if any comparison of intensities between spectra is to be made. This can be done easily by correlating similar off diagonal spectra in different orientations. Such a standardisation was carried out in the analysis of the sulphur and perfluorodiphenyl data and is described further in Chapter 7.

The ideal source of radiation is unquestionably the laser. This delivers light in an intense well collimated beam with well defined polarisation and an extremely narrow bandwidth. The analysing system normally employed is a grating monochromator with two or three monochromator stages to discriminate against the exciting frequency so that low lying excitations may be studied. The detector most commonly used in systems of this kind is a photomultiplier. A schematic diagram of a typical set up is shown in Figure 5.2. The polarisation of the incident light can be rotated through 90° using a half wave plate and the polarisation of the scattered light entering the spectrometer may be selected by a piece
Figure 5.2

Configuration of a typical Raman spectrometer showing:

PR - polarisation rotator
NDF - neutral density filter
PA - polarisation analyser
PS - polarisation scrambler
PM - photomultiplier
TO PHOTON COUNTING ELECTRONICS

GRATING MONOCHROMATOR

P.M.

P.S.

P.A.

LASER

P.R.

N.D.F.

SAMPLE

The particular experimental system used in the collection of the data reported in this work has been described in detail in Miller et al. (1974) and Miller and Lazenby (1974). The system consists of a double grating monochromator with a photomultiplier tube as the light detector and a sample under study as the source of scattered light. The spectra were excited using a Spectra Physics model 130 argon ion laser. The data was processed using a Spectra Physics model 130 argon ion laser.
of polaroid before the entrance slit. In this way the four polarisation combinations possible for one crystal orientation can be measured. It is necessary to pass the light through a polarisation scrambler before entering the monochromator since the reflection efficiency of the gratings is dependent on polarisation.

The particular experimental systems used in the collection of the data reported in this work have been described in detail by Arthur (1974) and Arthur and Lockwood (1974). The three systems offered varying degrees of sophistication and flexibility:

System I: Spex Ramalab double grating monochromator with a programmable multi-scan facility and output to a multi-channel scaler, graphplotter and paper tape.

System II: Spex 1400 double grating monochromator with a programmable single scan control and output to chart recorder and paper tape.

System III: A Coderg T800 triple grating monochromator controlled by an on-line PDP11 computer. This system was the most sophisticated of those used and had the facility for preliminary processing of the spectral data which was stored on magnetic disc. The data could be transferred to magnetic tape for input to the main computer on which most of the analysis was done.

The spectra were excited using a Spectra Physics Helium-Neon laser (λ = 6328Å) with System II and a Coherent Radiation Argon Ion laser (λ = 4880Å, 5145Å) with Systems I and III.

The data was processed using a systems of programs specially developed by J.W. Arthur (1974 and 1976b). This system included subroutines for peak finding, integration, fitting, subtraction and addition of spectra and graphplotting.
5.6 Sulphur: an example

The analysis of the Raman spectrum of orthorhombic sulphur has been described elsewhere (Arthur and Mackenzie 1974, Arthur 1974) and only a brief summary of the work is included here. Orthorhombic sulphur, \( \alpha S_8 \), is a molecular crystal consisting of puckered octagonal rings. The crystal has been the subject of a considerable amount of research involving structure refinement (Pawley and Rinaldi 1972) neutron inelastic scattering measurements and lattice dynamics calculations. (Rinaldi 1973, Rinaldi and Pawley 1975).

The Raman measurements described here were made to provide extra comparison with the calculated frequencies at the zone centre. Three recent Raman studies of \( \alpha S_8 \) (Ozin 1969, Anderson and Loh 1969, Gorelik et al 1971) had been reported at the time of our experiment but only in the work of Ozin (1969) was there any assignment of the lattice modes. These assignments were rather incomplete and it was felt that a remeasurement was required.

Orthorhombic sulphur crystallises in the space group Fddd with 4 primitive molecules in the unit cell. The 12 Raman active lattice vibrations transform according to the irreducible representations of the point group \( \text{mmm} \) (\( D_{2h} \)) as

\[
2A_g + 2B_{1g} + 4B_{2g} + 4B_{3g}
\]

with the \( A_g \) appearing in \( xx, yy \) and \( zz \) spectra

\[
\begin{align*}
B_{1g} & : xy \\
B_{2g} & : zx \\
B_{3g} & : zy
\end{align*}
\]

An arbitrary division between librational and translational modes was made at this stage in the first report of the work (Arthur and Mackenzie 1974). The model calculations (Rinaldi 1973) have shown, however,
that the zone centre eigenvectors have rotational and translational character so that the above division is not justified.

The measurements were made on a 6x4x3mm crystal with faces cut and polished perpendicular to the crystallographic axes. System II was used to collect the data which was taken at room temperature for three orientations covering all polarisations.

The analysis of the data involved subtraction of linear combinations of different spectra to obtain reasonably pure polarisation spectra. This was necessary because of the considerable amount of polarisation leakthrough present in some crystal orientations due to the optical properties of the crystal. Although group theory predicts two Raman active \( A_g \) modes, only one was observed in the experiment. This was interpreted (Arthur and Mackenzie 1974) as being a consequence of the translational character of the second \( A_g \) mode since only rotational motion is assumed to contribute to the change in polarisability in the first approximation. The results of the dynamical calculation (Rinaldi and Pawley 1975) however lead to a different interpretation. The two totally symmetric \( (A_g) \) modes at the zone centre are calculated to have frequencies which are very close, 50.7 cm\(^{-1}\) and 52.7 with almost equal components of translational and rotational motion.

<table>
<thead>
<tr>
<th>( A_g(1) )</th>
<th>Translation*</th>
<th>Rotation*</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.360</td>
<td>0.346</td>
<td>50.7 cm(^{-1})</td>
</tr>
<tr>
<td>( A_g(2) )</td>
<td>-0.346</td>
<td>0.360</td>
<td>52.7 cm(^{-1})</td>
</tr>
</tbody>
</table>

It would seem therefore that a more correct interpretation of the observed \( A_g \) spectrum is that the two modes are so close as to be unresolvable.

The calculated (Rinaldi and Pawley 1975) and measured (Arthur and Mackenzie 1974) frequencies are shown in Table 5.1.

* mass and moment of inertia reduced and normalised eigenvector components.
The agreement between observed and calculated frequencies is very good apart from modes $B_{2g}(4)$ and $B_{3g}(4)$. Both of these modes are in the frequency region where the internal and external vibration spectra overlap and it is impossible to classify these modes as purely external in character.

The Raman intensities for sulphur were calculated by Arthur (1974) using the simple oriented gas model and the zone centre eigenvectors from the dynamical calculation of Rinaldi (1973). A good agreement with the measured integrated intensities was obtained but it was found necessary to adjust the values of the molecular polarisability components for each polarisation spectrum. The inclusion of the interactions between induced molecular dipoles (Arthur 1976) leads to more complicated expressions for the scattering tensors. It is hoped that calculations based on this extended oriented gas model will lead to consistent values for the molecular polarisability.
The observed Raman frequencies (Arthur and Mackenzie 1974) together with the corresponding model predicted frequencies (Rinaldi and Pawley 1975).

<table>
<thead>
<tr>
<th>Representation</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g ) (1)</td>
<td>51.1 cm(^{-1} )</td>
<td>50.7 cm(^{-1} )</td>
</tr>
<tr>
<td>(2)</td>
<td>51.1</td>
<td>52.7</td>
</tr>
<tr>
<td>( B_{1g} ) (1)</td>
<td>40.0</td>
<td>38.0</td>
</tr>
<tr>
<td>(2)</td>
<td>54.0</td>
<td>55.3</td>
</tr>
<tr>
<td>( B_{2g} ) (1)</td>
<td>29.0</td>
<td>26.0</td>
</tr>
<tr>
<td>(2)</td>
<td>49.0</td>
<td>51.3</td>
</tr>
<tr>
<td>(3)</td>
<td>60.8</td>
<td>62.7</td>
</tr>
<tr>
<td>(4)</td>
<td>73.8</td>
<td>92.3</td>
</tr>
<tr>
<td>( B_{3g} ) (1)</td>
<td>26.5</td>
<td>19.3</td>
</tr>
<tr>
<td>(2)</td>
<td>42.3</td>
<td>37.0</td>
</tr>
<tr>
<td>(3)</td>
<td>53.3</td>
<td>54.3</td>
</tr>
<tr>
<td>(4)</td>
<td>64.5</td>
<td>71.0</td>
</tr>
</tbody>
</table>
CHAPTER 6

PERDEUTERONAPHTHALENE
6.1 Introduction

In this chapter an investigation of the phonon dispersion relations in perdeuteronaphthalene, \( \text{C}_{10}\text{D}_8 \), by neutron coherent inelastic scattering and lattice dynamics calculations, is described. The crystal structure is very similar to naphthalene, \( \text{C}_{10}\text{H}_8 \) (Cruickshank 1957) being monoclinic with the space group \( \text{P2}_1/\alpha \) and having two molecules in the unit cell lying on the centres of symmetry (Pawley and Yeats 1969a). The deuterated form was used in order to avoid the strong incoherent neutron scattering from hydrogen.

The phonon frequencies of naphthalene throughout the Brillouin zone were first calculated by Pawley (1967) using the rigid molecule lattice dynamics model described in Chapter 2, although in this early calculation the second stage of differentiation was performed numerically. This model was used, subsequently, in the analysis of a limited set of neutron inelastic scattering data and several branches of the phonon dispersion curves were fitted by varying the parameters of the '6-exp' atom-atom potential function (Yeats 1971). Some neutron groups which were believed to correspond to phonons of anomalously low frequency were observed in an early study (Pawley and Yeats 1969b) but these have since been shown to be due to spurious scattering processes.

A considerable amount of neutron inelastic scattering data has been accumulated since the early studies, and the aim of the present work has been to analyse all the available data and to attempt to assign the measurement groups to the various phonon branches. This assignment was done with the aid of a preliminary lattice dynamics and dynamical structure factor calculation which was used to predict the intensity of scattering due to each phonon branch at the appropriate points in reciprocal space. Although the calculated eigenfrequencies
may not correspond closely to the actual phonon frequencies, it is assumed in this work that the phonon eigenvectors, and hence the neutron scattering intensities, are not strongly model dependent. This assumption has been borne out in most cases, but it breaks down in situations where two branches of the same symmetry representation approach each other closely. When this occurs, a mixing of mode character may result, with a corresponding transfer of scattering intensity from one branch to another. This makes the assignment of the observed groups rather difficult, since the separation between certain branches is strongly dependent on the model used. For this reason it has not been possible to assign certain measurements to particular branches. An unambiguous assignment will only be possible when the model has been improved by fitting those branches which have been definitely measured.

An attempt has been made to improve the model by changing the potential function parameters. A closer correspondence between observed and calculated dispersion curves was obtained but, because of the extremely high correlation between the parameters, no significance can be attached to the individual parameter values obtained. The improved model should be regarded more as a further aid in analysing the measured neutron distributions, rather than as a better representation of the intermolecular forces.

6.2 Labelling of the Modes of Vibration

There is only one symmetry direction in the monoclinic structure, along the screw diad axis in the crystallographic b direction, and all the calculations and measurements described here correspond to phonons with wavevectors along this direction. There are two molecules in the unit cell of the crystal, and so there are twelve modes of vibration.
in general. At zero wavevector, there are six purely translational and six purely rotational modes, while at the zone boundary there are six doubly degenerate modes. For a general value of the wavevector along the \( \mathbf{b} \) direction, each of the twelve modes is a combination of translational and rotational components which can be shown to be \( \pi/2 \) out of phase with each other, as pointed out in Chapter 2.

The modes at the various points in the Brillouin zone may be classified in the normal way, according to the appropriate symmetry group. At the zone centre, \( \Gamma \), there are three modes of vibration which are totally symmetric. These modes involve motions which do not break the crystal symmetry, whereas, all the other modes do break some of this symmetry. The classification of these \( q=0 \) modes may be summarised by Table 6.1 which is the character table for the point group \( 2/m \).

<table>
<thead>
<tr>
<th>( )</th>
<th>( E )</th>
<th>( 2 )</th>
<th>( i )</th>
<th>( c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g' \Gamma^+_S )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( B_g' \Gamma^+_A )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( A_u' \Gamma^-_S )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( B_u' \Gamma^-_A )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

An entry 1 under an operation denotes that the mode is symmetric under the operation and -1 denotes that it is antisymmetric. Two labels are shown for each representation, the first being the one normally used in optical spectroscopy.

For values of the phonon wavevector between the zone centre, \( \Gamma \), and the zone boundary, \( \Sigma \), there are two representations which can be regarded as symmetric and antisymmetric with respect to the 2-fold screw
operation. This is not exact, however, since there is a phase difference of \( \frac{\mathbf{a} \cdot \mathbf{b}}{2} \) between the motions of the molecule at the origin and the one related by the screw diad. Because of this phase difference, all modes away from the zone centre break the \( 2 \) symmetry. This type of difficulty, which arises with non-symmorphic space groups, those containing screw or glide operations, can be overcome using the formalism of multiplier groups (Montgomery 1969). The operations in a multiplier group differ from those in the underlying group in that their multiplication table includes numerical factors. An operator can be defined which includes the phase factor. The modes of vibration may be classified according to their symmetry under this new operation, and it can be shown that the concept of symmetric and antisymmetric branches is still valid. These will be labelled \( \Delta_S \) and \( \Delta_A \) respectively, with additional numerical subscripts to distinguish the various branches of the same representation. At the zone boundary the \( \Delta_S \) and \( \Delta_A \) modes become degenerate and there is only one representation which will be labelled \( Y \), again with numerical subscripts to identify the separate modes. The symmetry properties of the modes of vibration will be discussed further in the next section.

6.3 Preliminary Calculation

The details of the crystal structure used in the dynamical calculation are presented in table 6.2. The parameters correspond to the results of the single crystal structure refinement of \( \text{C}_{10} \text{D}_8 \) (Pawley and Yeats 1969a). Only the coordinates of the basic molecule, centred at the origin, are given. The other molecule in the unit cell, centred at \( (1,1,0) \), is generated by the 2-fold screw symmetry which is represented by the transformation:
Table 6.2

Coordinates of atoms in molecule before potential minimisation. Nine atoms are shown, the remaining nine being related by inversion symmetry. The coordinates are in Å units measured with respect to orthogonal axes of which \( x \) and \( y \) parallel the monoclinic axes and \( z \) parallels \( c^* \).

<table>
<thead>
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<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
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<td>2.3628</td>
</tr>
<tr>
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<td>1.1219</td>
<td>-1.8468</td>
</tr>
<tr>
<td>-0.0897</td>
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<td>1.5990</td>
</tr>
<tr>
<td>0.9857</td>
<td>1.4833</td>
<td>-0.5698</td>
</tr>
<tr>
<td>0.2235</td>
<td>0.6153</td>
<td>0.2551</td>
</tr>
<tr>
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<td>3.3891</td>
</tr>
<tr>
<td>1.8810</td>
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<td>-2.4668</td>
</tr>
<tr>
<td>0.2599</td>
<td>1.9066</td>
<td>2.0002</td>
</tr>
<tr>
<td>1.3366</td>
<td>2.4348</td>
<td>-0.1693</td>
</tr>
</tbody>
</table>

Unit cell parameters.

\( a = 8.235\,\text{Å} \quad b = 6.003\,\text{Å} \quad c = 8.658\,\text{Å} \quad \beta = 122.917^\circ \)
### Table 6.3


Model parameters.

<table>
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<th>z</th>
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</tr>
</thead>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
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<td>1.0146</td>
<td>1.5493</td>
<td></td>
</tr>
<tr>
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<td>-0.6208</td>
<td></td>
</tr>
<tr>
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<td>0.6435</td>
<td>0.2296</td>
<td></td>
</tr>
<tr>
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<tr>
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<td>-2.5128</td>
<td></td>
</tr>
<tr>
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<td>2.0122</td>
<td>1.9110</td>
<td></td>
</tr>
<tr>
<td>1.1261</td>
<td>2.5314</td>
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<td></td>
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Unit cell parameters

\[ a = 7.674\text{Å} \quad b = 6.088\text{Å} \quad c = 8.557\text{Å} \quad \beta = 122.975^\circ \]

#### b) Coordinates of atoms after potential minimisation, Model 2 (see Section 6.7)

<table>
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<th>z</th>
<th>Mean deviation from Table 6.2 positions</th>
</tr>
</thead>
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<td>2.3481</td>
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</tr>
<tr>
<td>1.2330</td>
<td>1.1241</td>
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<td></td>
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<td>-0.1734</td>
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<td>0.1780</td>
<td>0.6400</td>
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<td></td>
</tr>
<tr>
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<td>0.1056</td>
<td>2.0077</td>
<td>1.9134</td>
<td></td>
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<tr>
<td>1.1691</td>
<td>2.5109</td>
<td>-0.2685</td>
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</tr>
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</table>

Unit cell parameters

\[ a = 8.040\text{Å} \quad b = 6.165\text{Å} \quad c = 8.630\text{Å} \quad \beta = 123.072^\circ \]
\[ x_2 = Rx_1 + T \]

where \( R = \begin{bmatrix} -1 & \ 1 \\ 1 & -1 \end{bmatrix}, T = \begin{bmatrix} 1 \\ \pi/2 \end{bmatrix} \)

The atom-atom potential functions used in the calculation were of the '6 exp' type with the parameters of Kitaigorodskii (1966) which were also used in the original calculation of the lattice dynamics of naphthalene (Pawley 1967). These parameters are:

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>( A ) (kcal / mole ( R^6 ))</th>
<th>( B ) (kcal / mole)</th>
<th>( (\AA^{-1}) )</th>
</tr>
</thead>
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<td>C-C</td>
<td>358</td>
<td>42000</td>
<td>3.58</td>
</tr>
<tr>
<td>C-H</td>
<td>154</td>
<td>42000</td>
<td>4.12</td>
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<tr>
<td>H-H</td>
<td>57</td>
<td>42000</td>
<td>4.86</td>
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</tbody>
</table>

The crystal potential was obtained by summing over all non-bonded atom-atom pairs within a distance of 5.5\( \AA \). It has been shown (Pawley 1967) that the error in the calculated frequencies obtained is less than 1% if this limit on the number of interactions is chosen.

In the first part of the program, the orientation of the molecule and the unit cell parameters \( a, b, c \) and \( \beta \) were adjusted until a minimum of the crystal potential was reached. This is necessary to ensure that the calculation of the dynamics is done with the crystal in equilibrium. The atomic coordinates, \( x'_1 \), and the cell parameters corresponding to this potential minimum are shown in Table 6.3. Ideally the knowledge of the crystal structure should be included at this stage, so that the model structure does not differ significantly from physical reality. This could be done by constraining the potential parameters in some way, so that the potential minimum occurs at the true structure. Such a procedure was adopted in the work on orthorhombic sulphur (Rinaldi and Pawley 1972) where there is only one type of atom-atom contact, and hence, only three parameters. The problem is more difficult in the
present case, with nine parameters, and as yet, no attempt has been made to constrain the model parameters so that the structure corresponds to the known one.

The calculated frequencies and eigenvectors for the reduced wave-vectors \( q_z = \frac{2\pi}{b} q = 0.0, 0.1 \) and 0.5 are shown in Tables 6.4, 6.5 and 6.6 with the various modes labelled according to the scheme described above. The labelling was done by a simple inspection of the eigenvector components. It can be seen from these results that the modes at the zone centre, \( \Gamma \), are either purely rotational, or purely translational, whereas at other points, the modes are a mixture of both characters. The \( \pi/2 \) phase difference between the rotational and translational components is clear from the separation of the real and imaginary parts of the eigenvector. The components of the eigenvector are given in the principal inertial axis frame of the molecule. It is clear that at the zone centre, the librations do not occur about the principal axes, as was assumed by earlier workers (Kastler and Rousset 1941, Ito et al 1968), in the interpretation of Raman spectra. This fact was first pointed out by Pawley (1967).

The full dispersion curves for \( q \) along the \( b^* \) direction are presented in Figure 6.1 with the symmetric \( \Delta_s \) branches to the left and the antisymmetric \( \Delta_a \) branches to the right of the Brillouin zone boundary. The unfolded picture of the dispersion curves is useful in illustrating some of the symmetry properties of the modes and also leads to less confusion when the measured frequencies are presented. The modes on the extreme left of the figure at \( q = 0 \) involve motions which do not break the 2-fold screw symmetry. These are the modes labelled \( \Delta_{s}^{+} \) and \( \Delta_{s}^{-} \) (or \( A_{s}^{+} \) and \( A_{s}^{-} \) in the optical notation). The phase difference between the molecules related by the screw diad symmetry
Tables 6.4 to 6.6

Calculated frequencies and eigenvectors obtained using the set of potential parameters given by Kitaigorodskii (1966). The frequencies in THz are listed in column 2.

T - translational components \{ subscripts indicate
R - rotational components \} molecule 1 or 2
%R - percentage rotational character

<table>
<thead>
<tr>
<th>Table</th>
<th>Reduced wavevector</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
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</tr>
<tr>
<td>6.5</td>
<td>0.1</td>
</tr>
<tr>
<td>6.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Calculated dispersion curves for the set of potential function parameters given by Kitaigorodskii (1966).
$C_{10}D_8$ CALCULATED DISPERSION CURVES

ENERGY (meV)

$\Delta_{S0}$ $\Delta_{S5}$ $\Delta_{S4}$ $\Delta_{A5}$ $\Delta_{S3}$ $\Delta_{A4}$ $\Delta_{S2}$ $\Delta_{A3}$ $\Delta_{S1}$ $\Delta_{A2}$ $\Delta_{A1}$

REDUCED WAVEVECTOR $(0, q, 0)$
is \( \frac{b}{2} \) so that for small \( q \) there is a small phase difference between the motions of these molecules. This phase difference builds up as the phonon wavevector approaches the zone boundary, \( Y \), where \( q = \frac{\pi}{b} \). The phase difference between the molecules is then \( \frac{\pi}{2} \). At \( q = \frac{2\pi}{b} \) the phase difference is \( \pi \) so that the two molecules are moving exactly in antiphase and the modes are antisymmetric with respect to the screw diad.

An important point which may be noted from Figure 6.1 is that none of the branches cross each other, since otherwise they would break the rules of group theory. When two branches approach each other, as the first and second symmetric branches and the second and third antisymmetric branches do, the eigenvectors become mixed and the mode character is transferred between branches. The mixing of mode character should not be taken to mean "mixing (or interaction) of modes" which would suggest anharmonic interactions. All the calculations described here were based on the harmonic approximation in which the independent nature of the modes is essential. This transfer of mode character is reflected in the neutron scattering intensity which is highly dependent on the eigenvector. In the course of an experiment, it is usual to follow particular branches through the Brillouin zone by performing 'constant-\( Q \)' scans, and the transfer of intensity from one branch to another is readily observed.

The neutron scattering intensities for the model were calculated in the final part of the program. These are listed in Tables 6.7, 6.8 and 6.9 for \( q = 0.0, 0.1 \) and 0.5. The strong dependence of the scattering intensity of each mode on the wavevector transfer \( Q \) can be clearly seen. This dependence can be exploited to overcome the problem of overlapping peaks in the neutron distributions by choosing the
Tables 6.7 to 6.9

Calculated neutron scattering intensities corresponding to the frequencies and eigenvectors listed in Tables 6.4 to 6.6. The column headed RELP indicates the reciprocal lattice point corresponding to the vector $\mathbf{B}$ which appears in the wavevector conservation condition $\mathbf{Q} = \mathbf{B} - \mathbf{q}$.

<table>
<thead>
<tr>
<th>Table</th>
<th>Reduced wavevector</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>0.0</td>
</tr>
<tr>
<td>6.8</td>
<td>0.1</td>
</tr>
<tr>
<td>6.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>
appropriate regions of reciprocal space in which to perform the experimental scans. A model of this kind is, in fact, essential for the interpretation of a neutron experiment on such a complicated system as naphthalene in which there are a large number of phonon branches.

6.4 Deformable Molecule Correction

The lattice dynamical calculation described in the previous section was based on the assumption that the molecules move as rigid bodies. The validity of this approximation has been investigated by Pawley and Cyvin (1970) who performed dynamical calculations for naphthalene which included the effect of molecular non-rigidity. The forces between atoms within each molecule were obtained by fitting the measured internal mode frequencies of the molecule in the gas phase. These forces were then combined with the interactions between non-bonded atoms, and the resulting dynamical matrix solved, to give the frequencies of all the modes in the system. The results showed that the external mode frequencies are shifted substantially from the rigid molecule values. In some cases, the shift is as much as 1 meV which is larger than the typical experimental uncertainty in a neutron inelastic measurement. Consequently, account must be taken of this effect if a rigid molecule model is to be compared with measured frequencies. Pawley and Cyvin (1970) suggest that the experimental frequencies should be altered systematically so that they correspond more closely to rigid molecule values. The effect of the non-rigidity is to decrease the external mode frequencies by varying amounts, depending on the mode eigenvector. The experimental frequencies should therefore be increased in proportion to the calculated shift, and the modified set of measurements used in the rigid molecule fit. Since the shifts depend on
Table 6.10

Predicted shifts in meV on $C_{10}D_8$ external mode branches due to non-rigidity of molecule (Pawley and Cyvin 1970.) The experimental frequencies should be 'stiffened' by these amounts so that they correspond to the rigid-molecule case.

<table>
<thead>
<tr>
<th>branch</th>
<th>0</th>
<th>.1</th>
<th>.2</th>
<th>.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>A2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>S1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>S2</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>A3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>A4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>S3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>A5</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>S4</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>S5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>S6</td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>A6</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>
the eigenvectors, they may be assumed to be largely insensitive to the
intermolecular force model. When the best rigid molecule model is found,
by fitting the modified dispersion curves, the full non-rigid calculation
can be done, and the frequency shifts adjusted if necessary.

The intermolecular potentials used by Pawley and Cyvin (1970)
were the same as those used in the preliminary calculation described in
the previous section. The calculated shifts for several wavevectors are
listed in Table 6.10. These shifts were used to modify the experimental
frequencies used in the fitting process described in Section 6.7.

6.5 Experimental

The neutron inelastic scattering measurements described in this
chapter were collected over a number of years by Pawley and Dietrich
(unpublished) and more recently by the author. All the experiments were
performed using the triple axis spectrometers at AEK, Risø, operating
in the "constant Q" mode. Two different crystals of C\textsubscript{10}D\textsubscript{8} were used in
the work, both having been grown by Dr J Sherwood of Strathclyde
University. The crystal used in the earlier set of experiments had a
relatively small mosaic spread of about 0.5° and allowed accurate
measurement of the acoustic modes. This crystal was rather small in size
however, and the scattered intensity was not sufficient for the
measurement of the higher frequency optic modes which have much smaller
dynamical structure factors. The larger sample used in later experiments
allowed the weak branches to be measured, but the resolution was poorer
because of the existence of two separate single crystals in the
specimen which produced an effective mosaic of about 2°.

Various combinations of incident and scattered neutron energy and
spectrometer configuration were employed in the experiments. In this
way, the measured neutron distributions could be checked for reproducibility, and peaks which were due to spurious processes could be identified and eliminated from the analysis. All measurements were made with the crystal at liquid nitrogen temperature, 77K, so that the effects of phonon lifetime could be minimized with a consequent sharpening of the phonon peaks.

Typical experimental resolution functions for both series of experiments are shown in Figures 6.2(a) and (b). These were mapped out by performing energy and wavevector scans in the vicinity of a Bragg point. If an ideally perfect crystal were used, such a measurement would result in a direct estimate of the instrumental resolution at zero energy transfer, with the sample crystal acting essentially as delta function probe. The crystals used in the present experiment were far from ideal and there is an additional contribution from the mosaic spread of the sample. The double ellipsoidal shape of (b) arises from the fact that two separate crystals were present. The slope of the ellipsoid in $E-q$ space at zero energy transfer is generally dependent on the magnitude of the neutron wavevector. In the present case, with $kN^2.4\AA^{-1}$, the slope is about 10 meV. which corresponds closely to the slopes of the acoustic mode branches in naphthalene. With the correct spectrometer configuration, it is therefore possible to exploit this gradient matching to achieve optional focussing of the measured neutron groups.

Figure 6.3 shows the result of a constant Q scan with the neutron energy transfer between -3 and 3 meV, showing neutron energy gain and neutron energy loss respectively. The experimental configuration was chosen so that focussing occurred for neutron energy loss, with defocussing for neutron energy gain. This is clearly borne out by the measured neutron distribution in which two phonons are well resolved in the energy loss
Figure 6.2

Typical experimental resolution functions for both crystals used in the experiments. In both cases the neutron wavevector was \( 2.34 \, \text{Å}^{-1} \) and \( \Delta q \) was along \( b^* \).

(a) Crystal 1. Measured at (210).

(b) Crystal 2. Measured at (200).
Figure 6.3

Result of a constant-$Q$ scan at $Q = (2,0.85,0)$

The neutron energy gain and neutron energy loss regions are on the left and right respectively. The circles represent the measured neutron intensities and the continuous line is a fit using Gaussian functions. The broad peak around zero energy transfer is due to incoherent elastic scattering.
region while a broad peak is observed for neutron energy gain.

6.6 Observations

Several typical neutron distributions at the Brillouin zone centre and boundary are shown in Figures 6.4 to 6.13 with the appropriate calculated intensities from the preliminary model calculation listed on the left hand page in each case. The continuous curves in these figures represent fitted Gaussian profiles but, because of the low quality of the data, in most cases, the fitted positions cannot be relied upon. In general, the peak positions were estimated by visual inspection and by comparing the peak positions in independent measurements of each branch. Figures 6.14 to 6.16 show three sets of scans between the centres and boundaries of the Brillouin zones, centred at (030), (040) and (320). Again the calculated intensities are shown opposite for comparison.

With the large amount of data measured under various conditions, the frequencies of most of the phonon branches have been determined, and only three branches remain unassigned. These are \( \Delta_{S2} \), \( \Delta_{A3} \) and \( \Delta_{A4} \). The calculated eigenvector of the first of these is such that the intensity is very low at all points in reciprocal space, for wavevectors \( q_r = 0 \) to about 0.3. Between 0.4 and 0.5 the branch has been definitely assigned, however. This is due to the change in the character of the mode \( \Delta_{S2} \) when it comes close to the lower frequency symmetric branch \( \Delta_{S1} \) around \( q_r = 0.3 \). The higher frequency branch then takes on the character of the acoustic mode, and vice versa, with a consequent transfer of scattering intensity.

The difficulty in measuring the branches \( \Delta_{A3} \) and \( \Delta_{A4} \) is due to their extreme closeness and the model dependent nature of their
Figures 6.4 to 6.13

Constant Q scans with neutron energy loss at zone centres and boundaries. The calculated intensities for each scan are shown on the left hand pages.

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<tr>
<th>Figure</th>
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<tr>
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<td>6.6</td>
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<td>(5,0,0)</td>
<td>0</td>
</tr>
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<tr>
<td>6.9</td>
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<td>0</td>
</tr>
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</tr>
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<td>6.12</td>
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<td>0.5</td>
</tr>
<tr>
<td>6.13</td>
<td>(3,2,0)</td>
<td>0.5</td>
</tr>
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<td>S2</td>
<td>A3</td>
<td>A4</td>
</tr>
<tr>
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<td>----</td>
<td>----</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
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| 25 | 600 | 612 | 241 | 4247 | 1692 | 1361 | 35 | 24 |
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(3, 1, 0) \( q=0 \)
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(5, 0, 0) q=0
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The graph shows energy levels across different $x$ values, with peaks at various energy levels.
Figures 6.14 to 6.16

Three sets of Constant-Q scans at wavevectors between the zone centre and the zone boundary. The continuous line drawn between the points is included as a guide to the eye. Calculated intensities are shown on the left hand facing pages in each case.

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ENERGY (meV)
Figure 6.17

(a) Calculated dispersion curves for the branches $\Delta_{A3}$ and $\Delta_{A4}$. The solid and broken line represent the results of the preliminary calculation, using the Kitaigorodskii (1966) parameters, and the improved model respectively.

(b) Calculated neutron intensity of $\Delta_{A3}$ and $\Delta_{A4}$ in the zone centred at $(0,3,0)$ for both models.
Table 6.11

Measured external mode frequencies in meV.

Errors of .2 meV on acoustic modes and .3 meV on optic modes should be assumed.

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<td>$\Gamma_{S6}$</td>
<td>$\Gamma_{A6}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.12

Raman frequencies of $C_{10}D_8$ in meV

(Ito et al 1968).
Figure 6.18

Measured phonon frequencies. The solid lines are guides to the eye. The estimated positions of the unassigned branches are indicated by broken lines and the Raman measurements of Ito et al (1968) are indicated by triangles.
C_{10}D_8  OBSERVED DISPERSION CURVES

ENERGY (meV)

REDUCED WAVEVECTOR (0, q, 0)
eigenvectors. Although the calculated scattering intensity for these modes is high at many points in reciprocal space, in most cases they appear together and cannot be resolved. The calculated frequencies and scattering intensities for these two branches for two different sets of potential function parameters are shown in Figures 6.17(a) and (b). It is hoped that the frequencies of the two branches may be determined at a later stage when the model has been improved by fitting the other branches which have been definitely assigned.

The definitely assigned frequencies are listed in Table 6.11 and plotted in Figure 6.18. The approximate estimated positions of the unmeasured branch $\Delta_{s2}$ and the unresolved branches $\Delta_{A3}$ and $\Delta_{A4}$ are included for comparison. The Raman scattering results of Ito et al. (1968) are listed in Table 6.12 and included in the plot of measured frequencies, Figure 6.18. These latter results confirm the assignments of the neutron measurements.

6.7 Improvement of the Model

With the measured peaks in the neutron spectra assigned to the various phonon branches, the next stage in the investigation was to improve the model calculation by varying the parameters of the potential functions to obtain a closer fit to the measured frequencies. This involved minimising the quantity

$$\chi^2 = \sum_i w_i (\omega_{obs}^i - \omega_{calc}^i)^2$$

where $w_i$ is a weight assigned to the $i$th measured frequency.

In such a fitting procedure it is necessary to ensure that the appropriate experimental and calculated frequencies are compared at all times. Fortunately, with naphthalene, this is quite straightforward since there are only two irreducible representations in the interior of the zone, and two modes of the same representation cannot cross. The procedure adopted was to read in the measured frequencies in two sets,
symmetric and antisymmetric, and to select the appropriate calculated mode frequency by examining the eigenvector for symmetry or antisymmetry. The differences were then either \( \omega_{S}^{\text{obs}} - \omega_{S}^{\text{calc}} \) or \( \omega_{A}^{\text{obs}} - \omega_{A}^{\text{calc}} \). This assumes that the ordering of the frequencies in one representation does not change. The only case where the ordering of the frequencies is in doubt is in the two lowest antisymmetric optic branches. These modes are very close throughout the zone, and may exchange rotational - translational character when the potential functions are altered.

As already mentioned in connection with the potential minimisation, a model calculation of this type should take into account the known structural and thermodynamic measurements. In the analysis of the neutron inelastic data for orthorhombic sulphur, Rinaldi and Pawley (1975) used the known crystal structure and the sublimation energy to constrain the potential function parameters. By choosing one variable parameter, the other two were fixed by the constraint, and the fitting of the calculated frequencies to the observations, was relatively straightforward. In the present work however, there are nine variable parameters, and the fitting of the dispersion curves is quite a complex problem. The number of independent parameters can be reduced from nine to six, by assuming that the C–H potential parameters are related to the C–C and H–H parameters as follows:

\[
\begin{align*}
A_{C-H} &= \sqrt{A_{C-C} \cdot A_{H-H}} \\
B_{C-H} &= \sqrt{B_{C-C} \cdot B_{H-H}} \\
\alpha_{C-H} &= \frac{\alpha_{C-C} + \alpha_{H-H}}{2}
\end{align*}
\]

As a first step in the improvement of the model, the six independent potential parameters were each shifted by small amounts
Figures 6.19 to 6.24

Variation of zone centre and zone boundary frequencies with individual model parameters.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Variable parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.19</td>
<td>$A_{C-C}$</td>
</tr>
<tr>
<td>6.20</td>
<td>$B_{C-C}$</td>
</tr>
<tr>
<td>6.21</td>
<td>$\alpha_{C-C}$</td>
</tr>
<tr>
<td>6.22</td>
<td>$A_{H-H}$</td>
</tr>
<tr>
<td>6.23</td>
<td>$B_{H-H}$</td>
</tr>
<tr>
<td>6.24</td>
<td>$\alpha_{H-H}$</td>
</tr>
</tbody>
</table>
ZONE BOUNDARY MODES

ZONE CENTRE MODES

ENERGY (eV)

ENERGY (eV)

% CHANGE IN $\alpha(C-C)$

% CHANGE IN $\alpha(C-C)$
ZONE BOUNDARY MODES

ENERGY (MeV)

ZONE CENTRE MODES

ENERGY (MeV)

% CHANGE IN B(H-H)
while keeping the others constant. The dependence of the calculated frequencies on the parameters A,B and $\alpha$ for C-C and H-H interactions, is shown graphically in Figures 6.19 to 6.24. The similarity between these curves illustrates the high degree of correlation between the potential parameters which makes the process of fitting the calculated frequencies to the measurements difficult.

An attempt was made to improve the model parameters by varying each one in turn until a minimum in the quantity $\chi^2$ was reached. The 'observed' frequencies used were those for $q = 0$, 0.1, 0.2 and 0.5, modified to correspond to rigid molecule values according to the shifts, listed in Table 6.10. The final values of the potential function parameters were:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>351.25</td>
<td>31175</td>
<td>3.33</td>
</tr>
<tr>
<td>C-H</td>
<td>124.49</td>
<td>31237</td>
<td>4.06</td>
</tr>
<tr>
<td>H-H</td>
<td>44.13</td>
<td>31300</td>
<td>4.79</td>
</tr>
</tbody>
</table>

The calculated dispersion curves for this set of parameters are presented in Figure 6.25. Very little significance can be attached to the values of the parameters, since they were optimised independently. The improved set of mode frequencies and neutron scattering intensities were, however, of some help in clarifying the assignments of the measured neutron groups.

It is planned to improve the model further, by an automatic least squares process in which the differentials of the frequencies, with respect to the various parameters, are calculated analytically. Pawley (1972a) has described how this may be done, by making additions to the dynamics program. The squared frequencies $\omega_i^2$ are the eigenvalues of the dynamical matrix $M$ and are obtained by diagonalising
Calculated dispersion curves for the improved model parameters (Model 2).
C_{10}D_{8}  CALCULATED DISPERSION CURVES

ENERGY (meV)

REDUCED WAVEVECTOR (0, q, 0)
M using the matrix of eigenvectors \( R \):

\[
R M R^{-1} = \sum
\]
giving \( \omega_i^2 \) as the diagonal elements.

The differentials required for the least squares equation are \( \frac{\Delta \Omega_{ii}}{\Delta P_j} \), where the \( P_j \) are the parameters of the potential function, \( A_j \) and \( \alpha \).

The dynamical matrix depends on the \( P_j \) through the quantities \( V' \) and \( V'' \), the first and second derivatives of the potential with respect to the interatomic distance. These differentials are simple to derive analytically and are included in the lattice dynamics program. If the differentials of \( V' \) and \( V'' \) with respect to the \( P_j \) are substituted, then the differential dynamical matrix \( \frac{\partial M}{\partial P_j} \) is formed instead of \( M \). For small parameter shifts, \( \Delta P_j \to 0 \), the transformation which diagonalises the differential matrix tends to \( R \), and we have:

\[
\frac{\Delta \Omega}{\Delta P_j} = R \frac{\partial M}{\partial P_j} R^{-1}
\]

The diagonal elements of the resulting matrix are the \( \frac{\partial \omega_i^2}{\partial P_j} \) required for the least squares matrix and vector. It is convenient at this stage, however, to convert to differentials of the frequency in the appropriate units, in the present case meV. The \( \frac{\partial \omega_i}{\partial P_j} \) are then used to form the matrix and vector:

\[
A_{ij} = \sum_k w_k \frac{\partial \omega_i}{\partial P_j} \frac{\partial \omega_k}{\partial P_j}
\]

\[
V_i = \sum_k w_k \frac{\partial \omega_i}{\partial P_k} \Delta \omega_k
\]

where \( \Delta \omega_k = \omega_{k,\text{obs}} - \omega_{k,\text{calc}} \)

The parameter shifts can then be found in the normal way by premultiplying the vector \( V \) by the inverse of the matrix \( A \).
It is hoped that the fitting process described above will lead to an improved model which will allow further analysis of the measured neutron distributions. It is possible, however, that the definite assignment of the branches $\Delta_{A3}$ and $\Delta_{A4}$ will require further experimental measurement with improved energy resolution. Definite measurement of the low frequency optic mode $\Delta_{S2}$ is unlikely on the other hand, since the calculated scattering intensity appears to be very low in all Brillouin zones.
CHAPTER 7

PERFLUORODIPHENYL
7.1 Introduction

The molecular crystal perfluorodiphenyl, \( C_{12}F_{10} \), is interesting, both structurally, because of its high symmetry, and dynamically, because of the low torsional rigidity of the molecule. In this chapter, investigations of the structure and dynamics, using the techniques of neutron powder diffraction and Raman scattering, are described.

The molecule consists of two fluorine substituted phenyl rings connected by a single C-C bond, Figure 7.1. The two ring systems are not coplanar and the interplanar angle \( \phi \) has been the subject of some discussion. (Boden et al 1964, Steele et al 1965, Almenningen et al 1968). In the hydrogenous molecule diphenyl \( C_{12}H_{10} \), the rings are not coplanar in the liquid and gas states but planar in the solid state. The equilibrium value of the interplanar angle, \( \phi \), can be regarded as the result of the competition between the attractive interaction between the de-localised \( \pi \)-electron systems on each ring and the interaction between non-bonded atoms (Fischer - Hjalmars 1963). The main contribution of the latter type presumably comes from the atoms adjacent to the central bond, but intermolecular forces must also play an important part since these are sufficient to make diphenyl planar in the crystal.

The determination of the interplanar angle in the solid phase of perfluorodiphenyl was one of the main aims of the structure refinement which is described in section 7.3. The value of this angle is also important in the interpretation of the Raman spectrum described in Section 7.5 to 7.8.

The crystal structure of perfluorodiphenyl was reported briefly by Neronova (1968). The space group is \( Fdd2 \) and the eight molecules in the unit cell are positioned on the diad axes along the C-axis at the
Figure 7.1

The conformation of the perfluorodiphenyl molecule.
\begin{center}

\includegraphics{diagram}

\end{center}

\textbf{FLUORINE}

\textbf{CARBON}
Figure 7.2

Projection of the unit cell structure of perfluorodiphenyl on to the (001) plane, after Neronova (1968).
special positions (0,0,0), (1,1,1) etc. A diagram of the crystal structure projected on to the ab plane is shown in Figure 7.2 The long molecular axis lies in the ab plane at an angle, \( \gamma \), to the \( a \)-axis. Neronova gives this angle as 38°. The size of the interplanar angle is not clear from Neronova's paper, where she states that the phenyl rings are rotated through 60° with respect to each other. This was originally assumed to mean \( \phi = 60^\circ \), but in the light of the results of the structure refinement, to be described in this chapter, it is likely that \( \phi = 120^\circ \) was intended.

### 7.2 Neutron Powder Diffraction Experiment

The neutron powder diffraction pattern of \( C_{12}F_{10} \) was measured on the TAS 4 spectrometer at Risø, using neutrons of wavelength 2.37\( \AA \) from a pyrolytic graphite monochromator with a pyrolytic graphite filter to remove \( \lambda/2 \). The machine was operated, with no analyser, as a conventional two axis diffractometer and the data was recorded in 0.2° intervals between \( 2\theta = 10^\circ \) and 90° counting for eleven minutes at each point.

### 7.3 Structure Refinement Using the Rietveld Program

The powder diffraction pattern was first analysed using the Rietveld (1969) program for total profile refinement. The aim of the study was two fold: firstly to determine more accurately the values of the structural parameters \( \phi, \Psi, r \), and secondly and more importantly, to assess the method of profile refinement when applied to molecular crystals. The problem required the use of a relatively complicated system of constraints employing all three methods embodied in the Rietveld program. These different types of constraints have already been described in Chapter 4.

The least squares refinement involved 11 independent atomic
positions, giving 33 positional parameters. The number of degrees of freedom in the problem was reduced from 33 to 3, corresponding to $\Psi$, $\phi$ and the central bond length $r$ (defined in Figure 7.1), by using a combination of linear, quadratic and substitutional constraints which amounted to 30 constraints in all. The choice of such constraints is not unique, and several combinations were tried before the refinement worked successfully. The unsuccessful attempts were due to instabilities in the program, caused by certain parameters being overconstrained. This latter problem was easily revealed by removing one constraint. The program then ran without failure, but with four degrees of freedom instead of three. The successful constraint system consisted of 19 quadratic constraint functions, which defined the interatomic distances shown in Figure 7.3. Because of the two fold crystal symmetry, the long axis of the molecule lies in the ab plane so that the $z$-coordinates of the atoms which lie along this axis can be fixed at 0. The $z$-coordinates of the other atoms are also related, and these were constrained using the codewords which define the least squares parameters, so that only two parameters represented the $z$-coordinates of the remaining 8 atoms. One linear constraint between the two $z$-coordinate parameters related the $z$-coordinates of the carbon and fluorine atoms. One additional quadratic constraint was used to apply the colinearity condition between the two carbon atoms along the molecular axis. These constraints are summarised below using the numbering of atoms defined in Figure 7.4.
Figure 7.3

Interatomic distances constrained by quadratic functions in the Rietveld program refinement.

Figure 7.4

Numbering of the atoms in the asymmetric part of the molecule.
Interatomic distances defined in Figure 7.3.

\[ z_3 = z_6 = z_9 = 0 \]  
\[ z_1 = z_2 = z_4 = -z_5 \]  
\[ z_7 = z_8 = -z_{10} = -z_{11} \]  
\[ \frac{z_4}{z_7} = \text{constant} \]  
\[ \frac{x_6}{x_3} = \frac{y_6}{y_3} \]  

Total number of constraints = 30
Number of degrees of freedom = 33 - 30 = 3

This system of constraints then allowed the variation in the atomic positions to be governed by three parameters only, \( \Psi \), \( \phi \) and \( r \). The interatomic bond lengths used were those reported by Neronova; the phenyl rings were assumed to have a regular hexagonal shape. The initial parameter values were \( r = 1.41 \text{Å}, \phi = 60^\circ \text{ and } \Psi = 38^\circ \). These were allowed to vary along with a scale factor, a counter zero point, the three orthogonal cell parameters and an overall temperature factor. The variation of \( r \), \( \phi \) and \( \Psi \) with each cycle of the refinement is shown graphically in Figure 7.5 with the corresponding variation in the R-factor in Figure 7.6. When the final R-factor of 17.3% was reached, the parameters had the values listed below.

\[ r = 1.63 \quad (6) \text{Å} \]
\[ \phi = 120.7 \quad (5) \text{°} \]
\[ \Psi = 37.9 \quad (5) \text{°} \]
\[ a = 13.48 \quad (1) \text{Å} \]
\[ b = 26.52 \quad (1) \text{Å} \]
\[ c = 6.29 \quad (1) \text{Å} \]
\[ B = 6.1 \quad (9) \text{Å}^2 \]
\[ \text{scale} = 6.7 \quad (1) \]
\[ \text{zero angle} = -0.02 \quad (2) \text{°} \]
Figure 7.5

The variation of the structural parameters $r$, $\phi$ and $\Theta$ with each cycle of the refinement with the Rietveld program.

Figure 7.6

Variation of the R-factor with each cycle of the refinement with the Rietveld program.
Figure 7.7

The observed powder profile (dots) and the best calculated fit (continuous line) for the Rietveld program refinement.

Figure 7.8

Comparison of experiment (dots) and calculated fit (continuous line) for the case when $\phi = 60^\circ$. 
The observed and calculated profiles for these parameter values are shown in Figure 7.7 and a similar diagram for the case when \( \phi \) was 60\(^\circ\), the starting value, is shown in Figure 7.8. The interplanar angle was initially in error by about 60\(^\circ\) and it is clear that the calculated fit with the final value of \( \phi \) gives much better agreement with experiment. It is evident from Figure 7.5 that the most important parameter in fitting the observed profile was, in fact, \( \phi \) since the other two parameters, \( \psi \) and \( r \), do not change appreciably. Although \( r \) shows some correlation with \( \phi \) it returns to a value not too different from its starting value. The error in the initial specification of \( \phi \) was quite fortuitous since it illustrated that the profile refinement program is capable of converging to a reasonable minimum even when the shifts on the atomic positions are quite large.

The fit becomes poorer at higher scattering but this is to be expected, as the parameters varied correspond to low atomic resolution. Any molecular distortion which might be present cannot be detected with the type of constraints used here. A more detailed structure refinement would require either single crystal diffraction data or high resolution powder diffraction data at high scattering angles. Both types of data would be analysed using the method of strict constraints (Pawley 1972b) as described in Chapter 4.

7.4 Structure Refinement using Strict Constraints

The inadequacies of the Rietveld method of applying constraints have been pointed out in Chapter 4 and the cumbersome nature of the constraint procedure is evident from the previous section. The development of the new program for profile refinement, EDINP, using strict constraints overcame the problems associated with the Rietveld program. It is interesting to compare the performance of EDINP with that of the Rietveld
Figure 7.9

The variation of the structural parameters $r$, $\phi$ and $\theta$ with each cycle of the refinement with EDINP.

Figure 7.10

The variation of the R-factor with each cycle of the refinement with EDINP.
program. This was done by refining the structure of $\text{C}_{12}\text{F}_{10}$ with the new program, with starting values of the parameters similar to those used with the Rietveld program. The variation of the parameters $r, \phi$ and $\Psi$, and of the R-factor are shown in Figures 7.9 and 7.10. These may be compared with Figures 7.5 and 7.6 which refer to the results of the Rietveld program.

Further refinement of the structure, with all profile parameters allowed to vary, led to a final R-factor of 19%. The final parameter values are listed below.

$r = 1.59 (1) \, \text{Å}$

$\phi = 122.5 (2) \, ^\circ$

$\Psi = 39.0 (3) \, ^\circ$

$a = 13.48 (1) \, \text{Å}$

$b = 26.50 (1) \, \text{Å}$

$c = 6.29 (1) \, \text{Å}$

$B = 7.1 (8) \, \text{Å}^2$

scale factor = 0.425 (13)

counter zero = 0.019 (15)°

$u = 2.4 (11)$

$v = -0.84 (73)$

$w = 0.23 (11)$

7.5 Raman Scattering Experiment

The single crystal sample used in the experiment was grown from the melt using the technique of zone melting. A small section of single crystal was produced and this was cut and polished with faces perpendicular to the crystallographic axes. The preliminary orientation was
done using a polarising microscope and the crystallographic axes were later identified by taking X-ray oscillation photographs. The crystal faces were found to deteriorate gradually due to sublimation of the surface layer and occasional repolishing was necessary. Although the sample was quite colourless and transparent it was found that local surface heating by the laser beam caused further deterioration by pitting. This was overcome by mounting the sample on a glass slide using a thin film of silicone oil to form an optical contact and in this way the transmission of the incident beam into the sample was greatly enhanced.

The experiments were performed on System II using the 6328Å line of the Helium Neon laser to excite the spectra and repeated using System I with the 5145Å line of the Argon Ion laser. The larger light throughput and blue sensitivity of this latter system gave nearly an order of magnitude increase in signal, enabling the weak internal modes to be measured. In both cases the measurements were made at room temperature over the frequency range 5-250 cm⁻¹. The spectra were measured in all polarisations with three separate orientations of the crystal giving twelve spectra in all:

\[ xx_1 \quad xy_1 \quad zy_1 \quad zx_1 \]
\[ yy_2 \quad yz_2 \quad xz_2 \quad xy_2 \]
\[ zz_3 \quad zx_3 \quad yx_3 \quad yz_3 \]

The spectra measured in different orientations were of dissimilar gain conditions but the intensities could be normalised by correlating the similar off diagonal spectra. This type of standardisation is necessary if the intensities of the diagonal spectra are to be compared since only one of these spectra can be measured in any one crystal orientation. In practice it was found that the normalisation was consistent within about 10%.
The data obtained were processed by computer with the aid of a variety of routines for intensity measurement, peak finding, band fitting and graphical output (Arthur 1974 and 1976b). The spectra of the external vibration 0-100 cm\(^{-1}\) are shown in Figures 7.11 to 7.13 and the observations are presented in numerical form in Table 7.1. Where integrated intensities under peaks were required the data were fitted with damped simple harmonic oscillator functions of the form:

\[
I_j = \frac{1}{\pi} \frac{\omega_j^2 \Gamma_j}{(\omega^2 - \omega_j^2)^2 + \omega_j^4 \Gamma_j^2} S_j
\]

The parameters \(\omega_j\) and \(\Gamma_j\) are the frequency and damping of the mode \(j\), and \(S_j\) is its 'strength'. The forms of equation 5.5 and 5.6 are then replaced by

\[
S_j(\alpha\beta) = \gamma_j (\pi_j)^2
\]

and

\[
\sum(\alpha\beta) = \sum_j \omega_j^2 S_j(\alpha\beta)
\]

These parameters for the totally symmetric Raman spectra, \(A_1(xx,yy,zz)\), are listed in Table 7.2 and these are used in the calculations described in section 7.8.

The possibility of low frequency internal modes in \(\text{C}_{12}\text{F}_{10}\) has been treated by Almenningen et al (1968) and Steele (1969). Steele's calculation (based on a molecule of \(\text{mmm} (D_{2h})\) symmetry) shows that perhaps 4 low frequency modes lie below 130 cm\(^{-1}\). Most of the other internal mode frequencies have been reported by Steele (1969) and Steele et al (1965) but nothing was reported of the modes below 130 cm\(^{-1}\). As a subsidiary experiment to check on the existence of low frequency internal modes, the Raman spectrum of liquid perfluorodiphenyl was measured and the result is shown in Figure 7.14. A peak is observed at 54 cm\(^{-1}\) with a width of about 21 cm\(^{-1}\), as determined by fitting. This is assumed to be due to the torsional
<table>
<thead>
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<th>Frequency (cm(^{-1}))</th>
<th>Representation</th>
<th>Actual Peak Height</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>xx</td>
<td>yy</td>
</tr>
<tr>
<td>32.9</td>
<td>(B_1^C)</td>
<td></td>
</tr>
<tr>
<td>33.4</td>
<td>(A_2^C)</td>
<td></td>
</tr>
<tr>
<td>38.0</td>
<td>(B_2^C)</td>
<td></td>
</tr>
<tr>
<td>38.8</td>
<td>(B_1^C)</td>
<td></td>
</tr>
<tr>
<td>47.1</td>
<td>(B_2^C)</td>
<td></td>
</tr>
<tr>
<td>48.1(^1), 48.7(^2)</td>
<td>(A_1^C)</td>
<td>(72380^2)</td>
</tr>
<tr>
<td>49.3</td>
<td>(A_2^C)</td>
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</tr>
<tr>
<td>52.8</td>
<td>(B_1^C)</td>
<td></td>
</tr>
<tr>
<td>54.4</td>
<td>(B_1^m, A_1^C)</td>
<td>(sh)</td>
</tr>
<tr>
<td>58.9</td>
<td>(A_2^C)</td>
<td></td>
</tr>
<tr>
<td>61.9</td>
<td>(B_2^C)</td>
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</tr>
<tr>
<td>64.3</td>
<td>(B_1^C)</td>
<td></td>
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<tr>
<td>66.4(^1), 67.1(^2)</td>
<td>(A_1^C)</td>
<td>(18600^1)</td>
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<tr>
<td>70.8</td>
<td>(A_2^C)</td>
<td></td>
</tr>
</tbody>
</table>

\(w =\) weak, \(sh =\) shoulder, superscripts 1 and 2 indicate slightly different frequencies in \(xx, yy\) and \(zz\)
Table 7.2

Fitted parameters for the $A^c_1$ spectrum. The data are corrected for different scattering efficiencies.

Experiment on System I

<table>
<thead>
<tr>
<th></th>
<th>$\omega_1$</th>
<th>$\Gamma_1$</th>
<th>$S_1$</th>
<th>$\omega_2$</th>
<th>$\Gamma_2$</th>
<th>$S_2$</th>
<th>$S_2/S_1$</th>
<th>$\Sigma \times 10^{-6}$</th>
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<tbody>
<tr>
<td>xx</td>
<td>48.8</td>
<td>7.6</td>
<td>2212</td>
<td>68.2</td>
<td>15.0</td>
<td>950</td>
<td>0.430</td>
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<td>yy</td>
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<td>8.0</td>
<td>4870</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>11.70</td>
<td></td>
</tr>
<tr>
<td>zz</td>
<td>48.0</td>
<td>6.7</td>
<td>1142</td>
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<td>13.8</td>
<td>2083</td>
<td>1.82</td>
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</table>

Experiment on System II

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<th>$S_1$</th>
<th>$\omega_2$</th>
<th>$\Gamma_2$</th>
<th>$S_2$</th>
<th>$S_2/S_1$</th>
<th>$\Sigma \times 10^{-5}$</th>
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<tbody>
<tr>
<td>xx</td>
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<td>6.6</td>
<td>164</td>
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<td>80.2</td>
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<td>7.4</td>
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<td>-</td>
<td>-</td>
<td>0</td>
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<tr>
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<td>6.5</td>
<td>103</td>
<td>69.4</td>
<td>14.2</td>
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</tr>
</tbody>
</table>
mode of the molecule. This mode, being infra-red inactive, could not have been detected by Steele's infra-red techniques.

7.6 Group Theory

A picture of the symmetry properties of the vibrations in $C_{12}F_{10}$ can be built up by considering in turn the vibrations of the individual rings, the molecules and the crystal. Although the present work is primarily concerned with the low frequency external modes, it is helpful to consider all the internal modes. A fuller discussion of the internal modes and an interpretation of the high frequency Raman spectrum has been presented elsewhere (Arthur 1974, Arthur and Mackenzie 1976).

The molecule can be treated as two planar perfluorophenyl, $C_6F_5$, rings each having $mm2 (C_{2v})$ symmetry. The low frequency vibrations come about from the twisting and bending of the C-C bond joining these relatively massive units. The modes of vibration of the individual rings may be classified under the irreducible representations of the point group $C_{2v}$ as

$$10A_1^r + 3A_2^r + 9B_1^r + 5B_2^r$$

$$+ A_1^r + B_1^r + B_2^r \quad \text{pure translations}$$

$$+ A_2^r + B_1^r + B_2^r \quad \text{pure rotations}$$

The superscript 'r' indicates a representation of the point group of the rings, 'm' and 'c' will be used to denote the representations of the molecule and the crystal point groups respectively.

In the molecule pairs of equivalent ring vibrations interact weakly to become vibrations of the molecule. The complete set of molecular vibrations transform according to the irreducible representations of $D_2$ as

$$15A_1^m + 16B_1^m + 16B_2^m + 13B_3^m$$
In the crystal the internal modes are pairwise linear combinations of the modes of the two molecules in the primitive cell and if the intermolecular forces are weak the frequencies of these modes will be only slightly shifted from the free state values. The ring originated vibrations occur in quartets, each component of which has a different symmetry and so appears in a different polarisation.

In the crystal the six external degrees of freedom of each of the molecules in the cell give rise to nine optical lattice vibrations at the zone centre, assuming rigid molecules. These modes transform under $C_{2v}$ as

$$A_1^C + 2A_2^C + 3B_1^C + 3B_2^C$$

An important result of this classification is that only one totally symmetric mode $A_1^C$ is predicted. This mode involves only vibrations of the molecules about the z-axis. Such a mode would be expected to contribute equally to the $xx$ and $yy$ spectra with zero contribution to the $zz$ spectrum. The measured $A_1^C$ spectra do not show this behaviour and it has been necessary to include the torsional mode of the molecule in the explanation of the spectra.

### 7.7 Interpretation of the $A_1$ Low Frequency Spectra

The $xx$, $yy$ and $zz$ spectra (Figures 7.11 and 7.12) show two modes at $48 \text{ cm}^{-1}$ and $67 \text{ cm}^{-1}$ neither of which has the predicted character of the $A_1^C$ lattice mode. In fact the mode at $67 \text{ cm}^{-1}$ is seen in $xx$ and $yy$ but not in $zz$. This contrast with the expected behaviour of separate lattice and molecular vibrations leads to the assumption that the vibrations in the crystal are combinations of the two. This is then taken into account in the model of the crystal polarisability.

It is supposed that the single totally symmetric lattice vibration
Figures 7.11 to 7.13

Low frequency polarised Raman spectra of perfluorodiphenyl.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Polarisation</th>
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<tbody>
<tr>
<td>7.11</td>
<td>xx and yy</td>
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<tr>
<td>7.12</td>
<td>zz and xy</td>
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<tr>
<td>7.13</td>
<td>yz and xz</td>
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Figure 7.14

Raman spectrum of liquid perfluorodiphenyl.
mixes with the symmetric torsional mode of the molecule. If the latter has a differential polarisability at least comparable to the lattice vibration, there would be a significant redistribution of the intensities in the \( xx \), \( yy \) and \( zz \) spectra caused by interference. The only other low frequency internal mode which could couple with the totally symmetric lattice vibration is the \( B_{1}^{m} \) bending mode. Such a mode could only affect the intensity distribution in \( xx \) and \( yy \) spectra since it has zero contribution to the \( zz \) spectrum. In the \( xx \) and \( yy \) spectra there is in fact a very weak shoulder at 54 cm\(^{-1}\) and this may well be due to the \( B_{1}^{m} \) mode, but we conclude that it is not included in the mixing since there is no trace of it in the \( zz \) spectrum.

7.8 The Polarisability Model

The equations for the oriented gas model given in Chapter 5 apply to a rigid molecule. The observed low frequency spectra show that the molecule cannot be treated as rigid and here a polarisability model is developed specifically for \( C_{12}F_{10} \) to take into account the torsional mode of vibration. This model is based on the assumption that the molecule can be treated as a pair of independent phenyl rings. The justification is that such a model gives a reasonable description of the observed \( A_{1}^{c} \) spectra. The \( A_{2}^{c} \), \( B_{1}^{c} \), and \( B_{2}^{c} \) spectra are, however, too complicated to treat in such detail and they are discussed no further.

The two halves of the molecule are assumed to make separate and identical contributions to the polarisability of the form

\[
\alpha = \begin{bmatrix} 
\alpha_{xx} & \alpha_{yy}' & \alpha_{zz}' \\
\alpha_{yy}' & \alpha_{xx} & \alpha_{zz}' \\
\alpha_{zz}' & \alpha_{yy}' & \alpha_{xx}
\end{bmatrix}
\]

referring to principal axes \( x \) along the C-C bond, \( z' \) perpendicular to
the plane of the ring and \( \gamma' \) lying in the plane. The two rings are rotated by \( \pm \phi \) about the \( x \) axis giving individual contributions to the molecular polarisability of

\[
\alpha(\pm \phi) = \begin{bmatrix}
\alpha_1 & 0 & 0 \\
0 & \alpha_2 + \cos \phi \alpha_3 & \pm \sin \phi \alpha_3 \\
0 & \pm \sin \phi \alpha_3 & \alpha_2 - \cos \phi \alpha_3
\end{bmatrix}
\]

with \( \alpha_1 = \alpha_{xx}, \alpha_2 = \frac{1}{4}(\alpha_{yy} + \alpha_{zz}'), \alpha_3 = \frac{1}{4}(\alpha_{yy}' - \alpha_{zz}') \)

The total contribution to \( \alpha_m \), the polarisability of the molecule, is the sum of the two parts for \( + \phi \) and \( - \phi \):

\[
\alpha_m = \begin{bmatrix}
\alpha_1 & 0 & 0 \\
0 & \alpha_2 + \cos \phi \alpha_3 & 0 \\
0 & 0 & \alpha_2 - \cos \phi \alpha_3
\end{bmatrix}
\]

This crude model gives an estimate of the \( \phi \) dependence of \( \alpha_m \) without the introduction of extra unknown parameters. The equations for the polarisability differential can now be written in terms of the oriented gas model described in Chapter 5. Equation 5.4 gives

\[
\delta \alpha = \begin{bmatrix}
\sin 2\psi \alpha_{\psi} & 0 & 0 \\
0 & -\sin 2\psi & 0 \\
0 & 0 & 0
\end{bmatrix} \delta \psi + \begin{bmatrix}
\alpha_{\phi}(1-\cos 2\psi) & 0 & 0 \\
0 & \alpha_{\phi}(1+\cos 2\psi) & 0 \\
0 & 0 & -2\alpha_{\phi}
\end{bmatrix} \frac{\delta \phi}{2} + \begin{bmatrix}
0 & \cos 2\psi & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix} \delta \psi + \begin{bmatrix}
0 & \sin 2\psi \alpha_{\phi} & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix} \frac{\delta \phi}{2}
\]

\[
\text{As } A_1, A_2
\]
The contributions from the two molecules in the unit cell have been included in the expression above. Only the \( A_1^c \) contribution is of interest here. The parameters \( \alpha \) and \( \phi \) replace \( \alpha_1, \alpha_2 \) and \( \alpha_3 \) as unknowns, \( \psi \) is 38° and \( \phi \) is 120°.

Eigenvectors for the coupled internal–external modes in the \( A_1^c \) spectrum may be defined as follows:

\[
\hat{e}_j = \frac{e^{i \phi}}{\sqrt{I_{zz}}} \delta \psi + \frac{e^{i \phi}}{\sqrt{I_{zz}}} \delta \phi
\]

for \( j = 1 \) and 2. These eigenvectors are orthogonal so that the components may be written as

\[
e_1 = e_2 = c, \quad e_1 = -e_2 = -s
\]

where \( s \) and \( c \) are the sine and cosine of some angle. Applying the equations of Chapter 5 with these eigenvectors, results in expressions for the experimental intensity parameters

\[
S_1(\beta \beta) = \frac{1}{\omega_1^2} \left( c \delta \alpha_{\phi} + s \delta \alpha_{\psi} \right)^2, \quad S_2(\beta \beta) = \frac{1}{\omega_2^2} \left( s \delta \alpha_{\psi} + c \delta \alpha_{\phi} \right)^2
\]

When \( c \) is near unity and \( s \) is small, the modes are unmixed and only one peak is seen in the zz spectrum since \( \delta \alpha_{\psi}^{zz} \) equals zero. Otherwise, two peaks will be seen in the zz spectrum, as is indeed the case here. There may also be values of \( s \) and \( c \) such that one of the terms in brackets vanishes, in which case, only one peak appears, as in the observed yy spectrum.

The parameters in the above expressions can now be evaluated using the integrated intensities determined by fitting the observed spectra. Firstly, using the fact that \( \delta \alpha_{\psi}^{zz} \) is zero we have

\[
\frac{c}{s} = \frac{\omega_2}{\omega_1} \frac{S_2(zz)}{S_1(zz)}
\]
Secondly, since $S_2(\psi)$ is effectively zero, there must be cancellation of terms in equation 7.1 giving

$$\frac{\alpha \psi}{\alpha \phi} = -\frac{c}{s} \sqrt{\frac{I_{zz}}{I_{xx}}} \frac{S_{xy}}{S_{xx}} = -\frac{c}{s} \sqrt{\frac{I_{zz}}{I_{xx}}} \left( \frac{1+\cos^2\psi}{\sin^2\psi} \right)$$

The numerical values for these parameters, using the results of the two experiments (System I and System II) and a value of 2.857 for $I_{zz}/I_{xx}$, are then

$$c/s = -1.93 \text{ and } -2.0$$

$$\frac{\alpha \psi}{\alpha \phi} = 4.16 \text{ and } 4.32$$

The ratio $S_2(\psi)/S_1(\psi)$ can then be calculated from these values and compared with the experimental values thus providing a consistency check on the model. The calculated ratios from the two sets of data are 0.51 and 0.47; these agree well with the observed ratios of 0.43 and 0.49. The calculated weighted intensity sums do not compare so favourably with the observations however. Using the values for the parameters $c/s$ and $\alpha \psi/\alpha \phi$ determined above, the ratios $\Sigma(\psi)/\Sigma(\psi):\Sigma(\psi):\Sigma(\psi)$ are 1:1.15:0.64 and 1:1.14:0.59 for the two sets of data whereas the actual measured intensities yield the ratios 1:1.21:1.28 and 1:1.17:1.60. This result illustrates the fact that the intensity correlations are unreliable and, more importantly that the oriented gas model accounts only crudely for the polarisability.

7.9 Discussion

The low frequency, totally symmetric Raman spectrum has been described in terms of a mixed lattice vibration and a torsional molecular vibration. The simple oriented gas model provides a satisfactory interpretation for the observed intensities of the two strong peaks in
the spectrum, and gives numerical values for the proportion of internal and external rotational character of the two modes. The numbers $c^2$ and $s^2$ represent the division of energy between the internal and external components. For the lower frequency mode, 80% is contributed by the lattice vibration, while 20% is due to the torsional vibration. The reverse is the case for the higher frequency mode. The higher frequency mode is therefore still primarily of internal character and the lower frequency mode still of external character. The mixing of mode character, however, is sufficient to greatly change the Raman spectrum from that expected in the uncoupled case. The simple oriented gas model appears to be successful in describing the relative intensities in spectra of the same polarisation, but when spectra of different polarisations are compared, there are discrepancies. Although some of the discrepancies are due to the errors involved in correcting for different scattering efficiencies, the main source of error is in the model itself. It is hoped that future calculations will take into account the interaction between induced dipoles following the extended oriented gas model put forward by Arthur (1976).

The mixing of internal and external modes shows that the molecule cannot be treated as rigid. It would still be possible, however, to do lattice dynamics calculations using the rigid molecule program (Pawley 1972a) provided that the perfluorophenyl rings were treated as the molecules. The usual interactions between non-bonded atoms would be considered, with the addition of a force constant for C-C bond bending, and a potential to represent the interaction between the de-localised $\pi$-electrons on the rings. The form of the latter contribution has been investigated by Fischer-Hjalmars (1963) in a study of the conformation of biphenyl, $C_{12}H_{10}$. This interaction is commonly known as conjugation
and can be described by a potential which depends on the interplanar angle $\phi$

$$V_{\text{conj}}(\phi) = V_{\text{conj}}(0) \cos^2 \phi$$

The result of combining non-bonded interactions and conjugation for biphenyl is to produce a 'W' shaped potential, with respect to variations in the angle $\phi$ with minima corresponding to the equilibrium value of $\phi$.

The conjugation potential parameter could be estimated by doing calculations for the free molecule and comparing the observed and calculated values of the equilibrium interplanar angle and the torsional frequency.

It is hoped that a full lattice dynamics calculation for perfluorodiphenyl will be done in the future, so a comparison may be made with the results of the Raman scattering study. An inelastic neutron scattering study is not contemplated, however. Although it would be relatively easy to grow a large single crystal by zone melting, the number of phonon branches would make analysis of the measured neutron distributions very difficult.
CHAPTER 8

OCTAFLUORONAPHTHALENE
8.1 Introduction

The crystal structure of octafluoronaphthalene, C_{10}F_8, at room temperature is very similar to that of naphthalene, however there is a structural phase transition just below room temperature. This chapter is concerned with an investigation of the phase transition and the low temperature structure using the experimental techniques of Raman scattering and neutron powder diffraction.

The first crystal structure study of C_{10}F_8 was by Del Pra (1972) who used X-ray techniques to determine the approximate orientations of the molecules at room temperature. Del Pra found that the molecules were approximately parallel to the \( (112) \) direction, a result which he confirmed by analysis of the thermal diffuse scattering. The overall temperature factor was found to have rather a high value, \( B=10 \), indicating a large amount of thermal motion in the crystal at room temperature.

The phase transition in C_{10}F_8 was discovered by Pawley and Dietrich (1975) while cooling a large crystal before attempting to measure phonon spectra by neutron inelastic scattering. The shattering of the crystal made phonon measurements impossible because of the large mosaic spread of the crystal, about \( 6^\circ \). Neutron powder diffraction measurements of both phases were measured and it was hoped that the structure of the low temperature phase could be solved using the profile refinement method. A considerable effort was put into indexing the low temperature pattern but no consistent set of unit cell parameters could be found. A single crystal structural investigation was therefore initiated. It turned out that the difficulty in indexing the lower phase powder pattern was due to the very close coincidence of two low order reflections. The structures of both phases were refined using the single crystal diffraction data. The refinement showed that the structure in both phases is very similar and assumed that there is no change in the space group symmetry.
or in the number of molecules in the unit cell (Pawley and Dietrich 1975).

The quality of the fit to low temperature phase data was rather poor and it was hoped that the refinement of the structure could be continued using the powder diffraction data. The unit cell of the low temperature phase which had been determined in the single crystal experiment was used to index the pattern successfully apart from a few relatively weak peaks. Figure 8.1 shows the measured neutron diffraction pattern of the low temperature phase along with the profile calculated on the basis of the structure determined by Pawley and Dietrich (1975), the unindexed peaks are particularly evident around $2\theta=30^\circ$ and $42^\circ$. These peaks could only be indexed using half integral Miller indices. This implied that the true unit cell of the low temperature phase was in fact a multiple of the unit cell determined in the single crystal experiment. The positions of reflections corresponding to half integral Miller indices $h$, $k$ and $l$ were compared with the measured diffraction pattern. From this comparison it seemed that the most likely direction for a doubling of the unit cell was the $a$ direction since the previously unindexed peaks matched the positions of $h/2$, $k$, $l$ reflections reasonably well.

A Raman scattering study was undertaken in an attempt to obtain more information on the phase transition, in particular to see if any evidence of unit cell doubling could be found. Since the crystal shatters on going through the phase transition, it was necessary to measure the Raman spectrum of the powder for a comparison of both phases. The spectra of the liquid and the single crystal were also measured but no assignment of modes was possible in the latter because of the poor quality and unfavourable orientation of the sample.
Figure 8.1

Observed neutron powder diffraction pattern of the low temperature phase (dots) with the calculated profile (continuous line) corresponding to the single unit cell structure. Note the regions around $2\theta = 30^\circ$ and $42^\circ$ where the unfitted peaks occur.
8.2 Raman Scattering Experiments

The spectra were measured on the Coderg T 800 spectrometer (System III) using the 5145Å and 4880Å lines of the Argon ion laser in different instances.

Although several pieces of single crystal were available (grown by Dr. J. Sherwood of Strathclyde University) we were unable to cut and orient a piece of the quality necessary for a full polarisation study of the Raman spectrum. This was due to the extreme softness of the material. We did however succeed in obtaining some degree of polarisation separation using a rough piece of crystal of unknown orientation and having one reasonably smooth face by measuring the Raman spectrum in the back-scattering geometry. Only one good face is required in such a configuration but it is necessary to have the crystallographic b axis and one other principal axis of the optical indicatrix in the plane if the A_1g and B_2g spectra are to be separated. If the incident and scattered light polarisations are parallel then the A_1g spectrum is obtained and if they are perpendicular the B_2g spectrum is obtained. With any other orientation of the crystal mixed spectra are obtained because of rotation of the Raman tensors and accidental depolarisation effects. The sample orientation was adjusted until the best possible depolarisation was found, but later X-ray photographs showed the orientation to be nonetheless completely general. Therefore it is not possible to give assignments of the peaks, but the results are sufficient to show more clearly the details of the phonon spectra at the Brillouin zone centre.

The main part of the Raman experiment involved the measurement of the spectrum of powdered C_{10}F_{8} at temperatures above and below the phase transition. For this purpose a novel sample holder was constructed which allowed adequate temperature control without serious frosting of the sample or of the optical components in its vicinity, Figure 8.2.
Figure 8.2

Powder Raman scattering apparatus, showing
(a) brass block containing sample (dotted)
(b) 45° tilted mirror
(c) illumination optics
(d) collection optics
(e) spectrometer entrance slit
(f) thermocouple
(g) heater
(h) nitrogen gas flow
(j) laser beam
The arrangement is similar to that used by Stenman (1970, and private communication) to measure the Raman spectrum of powdered naphthalene, but in the present case the sample is cooled by blowing nitrogen through holes in the brass sample block. The temperature was measured by a thermocouple embedded in the sample and controlled by a Thor 3010 temperature controller connected to a heater coil in the stream of nitrogen. Although the sample was open to the air, temperatures as low as -40°C were reached, without appreciable icing up, due to the constant flow of dry nitrogen. The laser beam was focussed onto the face of the sample and the light scattered at 180° was collected in the spectrometer by a 45° tilted mirror.

The Raman spectrum of the liquid was measured in order to obtain a better insight into the internal mode spectrum. The measurement was made just above the melting point (87 - 88°C) using a 90° scattering geometry.

8.3 Group Theory

Internal Modes

The normal modes of the C_{10}F_{8} molecule may be classified under the irreducible representations of the point group mmm(D_{2h}) as:

\[ 9A_{g}^{m} + 3B_{1g}^{m} + 4B_{2g}^{m} + 8B_{3g}^{m} + 4A_{u}^{m} + 8B_{1u}^{m} + 8B_{2u}^{m} + 4B_{3u}^{m} \]

\[ +(B_{1u} + B_{2u} + B_{3u}) \quad \text{pure translations} \]

\[ +(B_{1g} + B_{2g} + B_{3g}) \quad \text{rigid rotations} \]

The m superscript indicates representations of the molecular point group, c will be used for representations of the crystal point group.

In the crystal the internal modes are linear combinations of the normal modes of the molecules in the unit cell and are classified according to the irreducible representations of the point group 2/m (C_{2h}). In the
case where there are two molecules in the unit cell, each even (gerade) mode of the molecule splits into \( A_g^c \) and \( B_g^c \) in the crystal and the odd (ungerade) modes split into \( A_u^c \) and \( B_u^c \). The \( A_g^c \) and \( B_g^c \) representations correspond to combinations which are symmetric and antisymmetric with respect to the 2 fold screw-rotation axis. The even modes are active only in the Raman spectrum while the odd modes are active only in the infra-red spectrum because of the usual selection rules.

**External Modes**

The external modes at the Brillouin zone centre are classified according to the irreducible representations of the point group \( 2/m (C_{2h}) \).

If there are two molecules in the unit cell then the modes transform as:

\[
(3A_g + 3B_g + 2A_u + B_u) + (A_u + 2B_u)
\]

- optic modes
- acoustic modes

The six even modes are active in the Raman spectrum with \( A_g \) appearing in \( xx, yy, zz \) and \( xz \) polarisations and \( B_g \) appearing in \( xy \) and \( yz \). All of these modes are purely rotational in character since translations of the molecules break the inversion symmetry.

8.4 **Raman Scattering Observations**

**Internal Modes**

The spectra of the powder at room temperature and at \(-30^\circ C\), and of the liquid at about \(90^\circ C\) were measured between 0 and 3000 \( cm^{-1} \). A large number of peaks were found between 100 \( cm^{-1} \) and 1700 \( cm^{-1} \) with the lowest frequency peak of the liquid spectrum at 120 \( cm^{-1} \). These spectra are shown in Figures 8.3 to 8.5. The identification of the peaks corresponding to the internal modes was more difficult in this case than, for example, with perfluorodiphenyl (Arthur and Mackenzie 1976) for here there is no polarisation separation. The peak positions are listed in
Figure 8.3

Raman spectrum of the liquid 100-1500 cm$^{-1}$
Figure 8.4

Internal mode spectrum, 291 K, 100-1500 cm\(^{-1}\)
Figure 8.5

Internal mode spectrum, 243 K, 100-1500 cm$^{-1}$
<table>
<thead>
<tr>
<th>Liquid</th>
<th>Room Temp.</th>
<th>Low Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>105(^1)</td>
<td>134</td>
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<td>157</td>
<td>130</td>
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<td>184</td>
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<tr>
<td>282(^2)</td>
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\(^1\)from single crystal experiment, \(^2\)show splitting 1:2:4
Table 8.1 for the various spectra including the room temperature single crystal spectra which were measured over a shorter range. A complete enumeration and assignment of the internal modes must be left until a full polarisation study with a properly oriented single crystal can be done.

The splitting of the internal mode frequencies due to combinations from the different molecules in the unit cell is expected to be very small, and one would normally require accurate polarised single crystal data to observe it as with perfluorodiphenyl. In the present work it appears to be just possible to detect this splitting in one band in the spectra, namely the band near 280 cm\(^{-1}\). The appropriate regions of the liquid, room temperature and low temperature spectra were fitted with Lorentzian response functions. The results are presented graphically in Figures 8.6, 8.7 and 8.8. The 280 cm\(^{-1}\) band was fitted by one, two and four peaks in the liquid, room temperature and low temperature spectra respectively. This result is consistent with the existence of two and four molecules in the unit cells of the room temperature and low temperature phases respectively.

The External Modes

Since the lowest observed peak in the liquid spectrum lies at 120 cm\(^{-1}\) and the corresponding peak in the room temperature spectrum is seen at 105 cm\(^{-1}\) it is assumed that only the external modes contribute to the spectrum below 100 cm\(^{-1}\). Clearly the six Raman active modes cannot be resolved in the room temperature powder spectrum (Figure 8.9) because of the lack of polarisation separation. Three spectra of different polarisations from the single crystal measurements are shown in Figure 8.10. For reasons described in section 8.2 the A\(_g\) and B\(_g\) modes were not separable and consequently the modes are still not resolved and no assignment is possible.
Figures 8.6 to 8.8

Fitted bands of the liquid, room temperature and low temperature spectra showing the components of the band near 280 cm\(^{-1}\). The observed intensities are shown by circles and the fit is shown by a continuous line.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Spectrum</th>
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<tbody>
<tr>
<td>8.6</td>
<td>Liquid</td>
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<td>8.7</td>
<td>Room Temperature (291 K)</td>
</tr>
<tr>
<td>8.8</td>
<td>Low Temperature (243 K)</td>
</tr>
</tbody>
</table>
Titled Band of the Liquid Spectrum

12000
10000
8000
6000
4000
2000

INTENSITY

FREQUENCY (cm\(^{-1}\))
Figure 8.9

Powder Raman spectrum of room temperature phase, 5-100 cm$^{-1}$
Figure 8.10

Single crystal spectra of room temperature phase, 5-100 cm$^{-1}$, showing three sets of data measured with different polarisation conditions.
The Raman spectrum of the powder was measured as a function of temperature. Two sets of data were recorded: Figure 8.11 with the temperature decreasing and Figure 8.12 with the temperature increasing through the phase transition. The most noticeable change in the spectra on going into the lower phase is the appearance of two low frequency peaks at 11 cm\(^{-1}\) and 22 cm\(^{-1}\).

Several measurements were made at -30°C and it was found that the intensities of the two low frequency peaks increased considerably over a period of an hour or so after cooling to this temperature. The time dependence was investigated in detail by cooling the sample rapidly to -30°C and measuring the intensity of the 22 cm\(^{-1}\) peak as a function of time. Relatively wide spectrometer slits were used so that the count rate represented the integrated intensity of the peak. This was done several times and found to be different in each case. This is presumably because of the effects of particle size and strain which are changed each time the sample goes through the transition. The result of one time scan is shown in Figure 8.13. The intensity reached a steady level after a period of about two hours by which time it may be assumed that all the material is in the lower phase. On one occasion the sample was kept below the phase transition temperature for twenty four hours and indeed no further change in the spectrum was found. A much smaller time lag was observed when the temperature was increased above the transition temperature: the intensity reached a steady level after about five minutes.

The spectrum which is taken as representative of the low temperature phase (Figure 8.14) was measured at -30°C, 4\(\frac{1}{2}\) hours after cooling. In this spectrum there is evidence of at least seven Raman active modes in the frequency region below 100 cm\(^{-1}\). Only six modes would be expected in this region if both the space group symmetry and the number of molecules in the unit cell were the same as in the room temperature phase. The extra features in the low temperature spectrum below 100 cm\(^{-1}\) must be entirely
Figure 8.11

Powder Raman spectra, 5-100 cm$^{-1}$, measured with temperature decreasing from 291 K to 248 K.
POWDER SPECTRA : TEMPERATURE DECREASING
Figure 8.12

Powder Raman spectra, 5-100 cm$^{-1}$, measured with temperature increasing from 248 K to 291 K.
Figure 8.13

Integrated intensity of the 22 cm$^{-1}$ peak measured as a function of time after cooling to 243 K.
Figure 8.14

Powder Raman spectrum of the low temperature phase, 5-100 cm$^{-1}$, measured at 243 K, 4.5 hours after cooling.
Powder Spectrum at -30°C

Intensity

Frequency (cm⁻¹)
due to external lattice vibrations since the spectra of both phases are almost identical above 100 cm$^{-1}$ apart from the very slight splitting described in the previous section. This led to the conclusion that the structure of the low temperature phase must therefore be different from that determined in the 'single crystal' neutron diffraction experiment (Pawley and Dietrich 1975).

8.5 Lattice Dynamics Calculations

The phonon frequencies throughout the Brillouin zone were calculated using the rigid molecule lattice dynamics program (Pawley 1972a) which was used for naphthalene in Chapter 6. The potential parameters used were those of Kitaigorodski for carbon and hydrogen interactions. The use of these particular potential parameters can be justified by the relatively good agreement between the calculated frequencies and the approximate positions of the peaks in the Raman spectra. The structural data for both phases were taken from the results of the single crystal structure refinement (Pawley and Dietrich 1975). In the latter work the lattice statics part of the program was used to calculate the potential minima of both structures with respect to molecular orientation. The calculated molecular positions were very close to those obtained from the structure refinement. Although such a result may lend credence to the structure, it does not necessarily mean that the structure is stable. The stability of a structure can only be tested by doing the full lattice dynamics calculation with suitable frequencies which are real for all wavevectors in the Brillouin zone. Imaginary frequencies are obtained if the dynamical matrix is non-positive-definite in which case the structure is unstable with respect to certain displacements (Born and Huang 1954).

The calculations of Pawley and Dietrich (1975) were therefore
extended by calculating the phonon frequencies at the appropriate potential minima. For the room temperature phase the frequencies were found to be imaginary at the \( a^* \) and \( c^* \) zone boundaries showing that the structure was unstable with the potential functions used. A lower potential minimum was found however by allowing the cell parameters \( a, b, c \) and \( \beta \) to vary along with the molecular orientation. The frequencies obtained in this case were real throughout the zone. The mean deviation of the atomic positions from the previously refined values was \( \pm 2\sigma \) with a 10% increase in \( a, b \) and \( c \), and a 1% decrease in \( \beta \). In spite of the difference in the structure the frequencies obtained did compare favourably with the Raman scattering measurements, giving some justification for the calculation.

The calculation was also done for the low temperature structure, again using the refined atom positions and the unit cell determined by Pawley and Dietrich (1975) and the same atom-atom potential parameters. In this case the agreement between the structures determined by refinement and potential minimisation (including unit cell distortion) was much better. The mean deviation of the atom positions from the refined values was \( 0.08\sigma \) and the changes in the cell parameters were all less than 1%.

The dynamics calculation gave imaginary frequencies at wavevectors between the zone centre and \( 0.4b^* \) and at the \( a^* \) and \( c^* \) zone boundaries. At the \( a^* \) boundary two non-degenerate modes with 100% rotational character had imaginary frequencies while at \( 0.5c^* \) a doubly degenerate mode with 90% rotational character had an imaginary frequency. This result, although inconclusive if taken on its own, would tend to suggest that instabilities are likely to occur at the \( a^* \) and \( c^* \) zone boundaries. In particular an \( a^* \) zone boundary instability leading to a doubling of the unit cell, would produce two low frequency Raman active modes along with an increase in the number of modes at higher frequencies. A consideration of the symmetry
of the eigenvectors of these modes showed that an instability in one would be associated with a \( P_{21}^c \) structure while an instability in the other would be associated with a \( P_{21}^n \) structure, with the molecules remaining on the unit cell centres of symmetry in both cases.

8.6 The Possible Structures of the Low Temperature Phase

Four different structures may be associated with the doubled unit cell resulting from an instability at the \( \bar{a} \) zone boundary: two with symmetry \( P_{21}^c \) and two with symmetry \( P_{21}^n \) with the molecules lying on or off the unit cells centres of symmetry in each case. The lattice dynamics calculations suggest that the rotational modes are likely to be unstable and as already pointed out such instabilities would be associated with structures in which the molecules lie on the centres of symmetry. We cannot however discount the possibility that some translation is also involved in the transition so structures in which the molecules are displaced from the unit cell centres of symmetry must also be considered. The four possible structures are therefore:

Model 1 : space group \( P_{21}^n \) molecules on centres
Model 2 : space group \( P_{21}^c \) molecules on centres
Model 3 : space group \( P_{21}^n \) molecules off centres
Model 4 : space group \( P_{21}^c \) molecules off centres

These structures can be visualised by considering the appropriate space group diagrams. The space group diagram for the low phase structure determined by Pawley and Dietrich (1975) is shown in Figure 8.15. The centres of the molecules are situated on the centres of symmetry at \((0,0,0)\) and \((0,\frac{1}{4},\frac{1}{4})\). The four possible structures listed above correspond to the four ways reducing the number of symmetry elements in the unit cell by half and the space group diagrams for these are shown in Figures 8.16 to 8.19.
Figure 8.15

Space group diagram for single unit cell structure as determined by Pawley and Dietrich (1975).
Figures 8.16 to 8.19

Space group diagrams for the four possible doubled unit cell structures.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.16</td>
<td>Model 1</td>
</tr>
<tr>
<td>8.17</td>
<td>Model 2</td>
</tr>
<tr>
<td>8.18</td>
<td>Model 3</td>
</tr>
<tr>
<td>8.19</td>
<td>Model 4</td>
</tr>
</tbody>
</table>
The single crystal electron diffraction was repeated using the
previously obtained data and a glide plane was pos-
tible since the whole cell of the single crystal structure (Dorset and Shattock 1975) was now identified.

The results were

Models 1 and 2.

Models 3 and 4.

Single unit cell.

The difficulties in distinguishing between the possible structures. This is to be expected
since the exact ray of the single cell is polarized and by a slight
distortion the molecular projection from the single unit cell structure
The relative intensities of the single crystal reflections
of one to the whole unit cell are expected to be quite small
in such cases. The reflections which are not equal when the characteristics
are those which are not measured in the single crystal
experiment and which are not included in the powder
diffraction pattern and correspond to three peaks which could not
be seen originally.
The single crystal structure refinement was repeated using the
doubled unit cell. No distinction between the c and n glide planes was
possible since only those reflections appropriate to the single unit
cell had been measured. The reflections which contain the information
relevant to the glide planes are those with odd values of h (indexed
on the double unit cell) or half integral h (indexed on the single unit
cell).

These refinements may be compared with the refinement of the
single unit cell structure (Pawley and Dietrich 1975) using the R-factor
which is defined by

\[ R = 100 \sum \left| \frac{F_{\text{obs}} - F_{\text{calc}}}{F_{\text{calc}}} \right| \%
\]

where \( F_{\text{obs}} \) and \( F_{\text{calc}} \) are the observed and calculated structure
amplitudes.

The results were:

Models 1 and 2 \hspace{1cm} R = 46.4%
Models 3 and 4 \hspace{1cm} R = 44.2%
Single unit cell \hspace{1cm} R = 44.3%

The difference between these R-factors is not sufficient to
distinguish between the possible structures. This is to be expected
since the doubling of the unit cell is presumably caused by a slight
distortion of the molecular positions from the single unit cell structure.
The relative changes in the intensities of the single crystal reflections
corresponding to the single unit cell are expected to be quite small
in such a case. The reflections which are most sensitive to the distorted
structure are those which were not measured in the single crystal
experiment. These reflections are of course present in the powder
diffraction pattern and correspond to those peaks which could not be
indexed originally.
8.7 Powder Profile Refinement

The structure of \( \text{C}_{10}\text{F}_8 \) could not be refined using the powder diffraction data because of the inadequacies of the Rietveld program which have already been described. The development of EDINP however has made it possible to use the same type of constraint as was used in the single crystal refinement (Pawley and Dietrich 1975). The details of this constraint procedure have already been described in connection with the refinement of the structures of \( \text{p-I}_2\text{C}_6\text{F}_4 \) and \( \text{p-Br}_2\text{C}_6\text{F}_4 \) in Chapter 4 and need no further discussion.

The aim of the refinement of the low temperature phase structure of \( \text{C}_{10}\text{F}_8 \) was to determine whether Model 2 or Model 4 gave the best fit to the powder diffraction pattern. Models 1 and 3 can be ruled out since the reflections corresponding to the space group \( \text{P2}_1/\text{n} \) do not index the pattern. The program was run separately for the two models since the definition of the parameters was different. The starting structure for each model was the same however, namely the structure determined by the single crystal refinement. The observed and calculated profiles for this starting structure are shown in Figure 8.1 where the extra reflections which correspond to cell doubling can clearly be seen.

Model 2 required 6 Euler angles to define the orientations of the two independent molecules while Model 4 required 3 Euler angles and 3 centre of gravity components to define the position and orientation of the one molecule lying off the centre of symmetry. The parameters varied in the refinement were:

- 1 overall scale factor
- 1 overall temperature factor
- 6 Euler angles (Model 2) or 3 Euler angles (Model 4) and 3 centre of gravity components
- 1 zero angle
3 halfwidth parameters
4 unit cell parameters.

The full neutron diffraction scan from 10° to 90° in 2° intervals was used and structure was refined by allowing the parameters listed above to vary. The refinements were stable for both models and minima were soon reached with R-factors of 23% and 29% for Models 2 and 4 respectively. The fits to the measured profile were rather poor at scattering angles above 55° and in subsequent runs only the data below this angle was used.

The best fit to the measured profile was obtained using Model 2 with the fluorine atoms allowed to move in the molecular plane while still preserving the mmm symmetry of the molecule. An extra isotropic temperature factor on the fluorine atoms was introduced to take into account the difference in the thermal motion of the fluorines and carbons. The R-factor for this refinement was 17%. The corresponding value for Model 4 with similar degrees of freedom was 21%. In both cases however the C-F bond lengths were larger than would be expected on chemical grounds. Although some distortion of the molecule from the initial structure used in these refinements is likely, the existing data is not of sufficiently high resolution to justify a refinement at this level. The most reliable estimate of the structure must therefore be obtained by a refinement in which the atomic positions within the molecule remain constrained. With the fluorine atoms again constrained to their original positions R-factors of 20% and 25% were obtained for Models 2 and 4 respectively.

In each of the comparable refinements Model 2 gave a substantially lower R-factor than Model 4. It is therefore clear that a P21/c structure with the molecules occupying the centres of symmetry provides the best description of the powder diffraction pattern. The final parameters
for the most reliable fit (Model 2, R=20%) are listed in Tables 82, 3, and 4 and Figure 8.20 shows the structure of the unit cell projected onto the (010) plane. The observed and calculated profiles are shown in Figure 8.21. The corresponding Model 4 fit (R=25%) is shown in Figure 8.22 for comparison.

Very little reliability can be placed on the positions of the fluorine atoms or the temperature factors obtained in the refinement since the diffraction data corresponds to low atomic resolution. The large amount of thermal motion makes an analysis of the high angle data very difficult. A better determination of the structure at an atomic level could be achieved by taking measurements at a temperature well below the phase transition where the thermal motion is considerably reduced. It is unlikely however that the molecular orientations would change appreciably from the values determined in the low resolution study described here.

8.8 Conclusion

At the outset of this study the only evidence which hinted at the possibility of unit cell doubling was the existence of several unindexed peaks in the low temperature neutron powder diffraction pattern. As the work progressed however new pieces of information were obtained all of which were consistent with a doubling of the unit cell along the a direction. These were: the observation of four components in one band of the low temperature internal mode spectrum, the appearance of more than the expected number of modes in the low temperature external mode spectrum, and the results of a lattice dynamics calculation. Finally it has been shown that the neutron powder diffraction pattern is more readily accounted for using a structure which, although similar to that determined by the earlier single crystal refinement (Pawley and
Dietrich 1975) has a unit cell which is doubled along the a direction. The loss of symmetry between the molecules, originally related by the unit cell translation a, can be associated with the instability of one of the a * zone boundary acoustic modes of totally librational character. The dynamics calculations have shown that there are two such modes, and we conclude that these become Raman active when the unit cell doubles, so producing the two low frequency peaks observed in the low temperature Raman spectrum. This study illustrates the advantages of using the method of constrained refinement in the analysis of neutron powder diffraction data, and, together with a measurement of the Raman spectrum of the powder has elucidated the nature of a remarkable phase transition in which there is no change in space group symmetry.
The final values of the least squares parameters for the MODEL 2 fit with R=20%. The wavelength was 2.373 Å and the temperature of measurement was 260 K.

<table>
<thead>
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<th>Value</th>
<th>Error</th>
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<td>Counter zeropoint (degrees)</td>
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<td>(30)</td>
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<td>u halfwidth</td>
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<td>(17)</td>
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<td>v parameters</td>
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<td>(89)</td>
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<tr>
<td>w (degree)²</td>
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<td>(110)</td>
</tr>
<tr>
<td>a unit</td>
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<td>(27)</td>
</tr>
<tr>
<td>b cell</td>
<td>4.674</td>
<td>(36)</td>
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<tr>
<td>c parameters</td>
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<td>(11)</td>
</tr>
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<td>β (Å and degrees)</td>
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<td>(57)</td>
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<td>BC isotropic temperature</td>
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<td>(15)</td>
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<tr>
<td>BF factors</td>
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<td>(15)</td>
</tr>
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</tr>
<tr>
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<td>(7)</td>
</tr>
<tr>
<td>Ψ₁ in radians</td>
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</tr>
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<td>φ₂ Euler angles</td>
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<td>(20)</td>
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<td>θ₂ for molecule 2</td>
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</tr>
<tr>
<td>Ψ₂ in radians</td>
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<td>(12)</td>
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Table 8.3
Planar coordinates of atoms in Å for asymmetric part of molecule before transformation to the crystalline orientation.

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<th></th>
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<th>y</th>
<th>z</th>
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<td>1.400</td>
<td>0.000</td>
</tr>
<tr>
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<td>0.707</td>
<td>0.000</td>
</tr>
<tr>
<td>C</td>
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<td>0.705</td>
<td>0.000</td>
</tr>
<tr>
<td>F</td>
<td>3.630</td>
<td>1.400</td>
<td>0.000</td>
</tr>
<tr>
<td>F</td>
<td>1.225</td>
<td>2.880</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Table 8.4
Final coordinates of atoms in both molecules with respect to the orthogonal cell in Å. The axes x and y parallel the monoclinic axes while z is along c.

The interplanar distance between molecules related by a b translation is 3.61 Å for molecules of type 1 and 2.69 Å for molecules of type 2.

<table>
<thead>
<tr>
<th></th>
<th>Molecule 1</th>
<th></th>
<th>Molecule 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>x</td>
</tr>
<tr>
<td>C</td>
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<td>0.647</td>
<td>1.539</td>
<td>9.948</td>
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<tr>
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<td>-0.603</td>
<td>9.603</td>
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<tr>
<td>F</td>
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<tr>
<td>F</td>
<td>3.591</td>
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<td>0.296</td>
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<td>F</td>
<td>1.685</td>
<td>-1.918</td>
<td>-1.680</td>
<td>9.414</td>
</tr>
</tbody>
</table>
Figure 8.20

Projection of the low temperature phase structure on to the (010) plane. Molecules drawn with open circles are displaced by \( \frac{2b}{3} \) towards the observer.
Figure 8.21

The observed powder profile (dots) and the calculated fit of the Model 2 refinement with $R = 20\%$ (continuous line).

Figure 8.22

The observed powder profile (dots) and the calculated fit of the Model 4 refinement with $R = 25\%$ (continuous line).
References


Born, M. and Huang, K. (1954) "Dynamical Theory of Crystal Lattices" (Oxford U.P.)


APPENDIX

PUBLICATIONS


THE EXTERNAL LATTICE VIBRATIONS OF ORTHORHOMBIC SULPHUR

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(Received 18 February, 1974)

Abstract. The Raman spectrum of orthorhombic sulphur has been measured in the frequency range 0-100 cm\(^{-1}\) for all polarisations. The \(A_{1g}(zz)\) and \(B_{1g}(xy)\) spectra have been clarified by later subtraction of unwanted scattering belonging to other polarisations. Definite assignments are made for all but one \(A_{1g}\) and one \(B_{1g}\) mode. An interpretation of the intensities observed in the \(A_{1g}\) and \(B_{1g}\) spectra is given in terms of the rotational motion of the \(S_8\) molecules affecting their contribution to the crystal polarisability.

1. Introduction

Orthorhombic sulphur, \(\alpha S_8\), has been studied in many Raman experiments [1–3], and notably Ozin [4] has given results in all polarisations for the single crystal.

As an example of a molecular crystal it has also recently been the subject of structural and dynamical calculations [5–8]. The model for these calculations assumes a crystal of rigid \(S_8\) molecules bound by a weak '6-exp' atom-atom potential. In order to compare calculations with experiment, neutron scattering measurements were made giving refinements on the structure and phonon frequencies at points throughout the Brillouin zone. The purpose of this work is to make comparison between model and experiment clearer by providing, as far as is possible by Raman scattering, accurate information about frequencies and assignments of the lattice modes at the zone centre.

The technique involved automatic digital recording of the spectra on paper tape. It was later possible to improve some of the spectra, the \(A_{1g}(zz)\) and \(B_{1g}(xy)\), by computer analysis, as described in Section 4.

In Section 5 we give an approximate calculation of relative intensities based on the properties of the free rigid molecule, thereby gaining some additional information on the dynamics of the molecules in orthorhombic sulphur.

2. Group Theory

Sulphur is a molecular crystal of point group \(D_{2h}\). There are four molecules in the primitive cell. The point group of the free molecules is \(D_{4d}\) and each molecule has a \(C_2^\perp\) axis aligned with the crystal \(z\) axis. Labelling the molecules as 1, 2, 3 and 4, 2 is related to 1 by \(C_{2x}\) and 3 and 4 are related to 1 and 2 by a centre of inversion.

The six degrees of freedom of the rigid molecule transform under \(D_{4d}\) as

\[
B_2 + E_1 \quad (x \text{ and } (y, z))
\]

\[
A_2 + E_3 \quad (R_x \text{ and } (R_y, R_z)),
\]

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where, after Pawley and Rinaldi [6], we take the molecular x axis as the \( C_4 \) axis and the z axis as the \( C'_2 \) axis aligned with the crystal z axis. In the crystal these give rise to 12 external lattice vibrations which are Raman active, transforming as:

\[
A_{1g} + B_{1g} + 2B_{2g} + 2B_{3g}: \text{translational}
\]

\[
A_{1g} + B_{1g} + 2B_{2g} + 2B_{3g}: \text{rotational}.
\]

The arbitrary division between rotational and translational parts has been made for later convenience.

Although group theory predicts two Raman active \( A_{1g}(Ag) \) lattice modes, Ozin [4] has reported seeing only one, a very intense peak in the \( xx \) and \( yy \) spectra at 52 cm\(^{-1}\). In the \( zz \) spectrum, also \( A_{1g} \), the intensity is very much weaker and any peak is obscured by additional small peaks attributable to admixtures from spectra of other polarisations. This is an experimental difficulty arising from the anisotropic optical properties of the crystal and strong internal ‘scattering’ of the laser light within the sample. The former problem has been discussed for the uniaxial crystal calcite by Porto et al. [9], but his solution is technically difficult. The approach taken here was to try and remove the unwanted peaks by subtracting portions of the other spectra suspected of contributing. By finding the correct proportions to take away only the proper spectrum should remain. The assumption is that the observed spectra are simply linear combinations of the true spectra for other orientations. This kind of technique is quite suitable when it is possible to use a computer for the analysis of the data, as was the case here.

A similar problem is encountered with the \( B_{1g}(xy) \) spectrum. Here the seriousness of the problem was found to be greater with some crystal orientations than with others. The same subtraction technique proved useful.

The ‘leak-through’ of intensity from peaks in other spectra presents difficulties in identifying peaks and making assignments, but another problem arises in sulphur because the lattice mode spectrum merges with the internal vibration spectrum in the region 70–90 cm\(^{-1}\). There is no easy solution to this problem because in this region there is no clear division between internal and external modes. The true modes will have the character of both.

3. Experimental

The experimental configuration involved a digitally controlled Spex 1400 double monochromator with data collection on paper tape and point plotter [10]. The paper tape was processed by computer with a variety of routines for conversion to wavenumber, intensity measurement, peak finding, band fitting and graphic output. Spectra were recorded for three different orientations of the crystal, measuring one diagonal and all three off-diagonal components in each case. By correlating intensities in the off-diagonal components for different crystal orientations it was possible to correct for different scattering efficiencies in each case. Wavenumber calibration was checked against the plasma lines of the helium-neon laser and the rotational spectrum of air to be ±0.2 cm\(^{-1}\) over the range of measurement.
4. Analysis

As a first step in the computer analysis the peak positions were determined as accurately as possible in all the spectra. The results agree well with those of Ozin, but the additional accuracy was occasionally important in identifying a peak from one spectrum to another. Secondly, treating each spectrum separately an attempt was made to identify the proper peaks in the spectra associated with each orientation.

4.1. The $A_{1g}$ ($xx$ and $yy$) Spectra

In both these spectra very intense peaks of comparable intensity are observed at 51 cm$^{-1}$ (Figure 1). The well separated peak at 89 cm$^{-1}$ is undoubtedly an internal mode, and the lineshape of the 51 cm$^{-1}$ peak was found to be well represented by a single Lorentzian function. As to the question of the presence of a second $A_{1g}$ mode we have to conclude that it is not to be seen in either of these spectra.

4.2. The $A_{1g}$ ($zz$) Spectrum

The initial reason for trying to remove the unwanted peaks in this spectrum was that it was thought possible that the second $A_{1g}$ mode might be revealed. Peak positions at 27, 42, 49, 53, and 62 cm$^{-1}$ correlate well with those observed in the $xz$ and $yz$ spectra. The spectrum, $S_{zz}$, say, was therefore compared with a linear combination of $S_{xz}$ and $S_{yz}$ thus:

$$S_{zz}^{\text{experiment}} \sim S_{zz}' = \alpha S_{xz} + \beta S_{yz}$$

and $\alpha$ and $\beta$ were chosen to minimise the difference between $S_{zz}^{\text{exp}}$ and $S_{zz}'$, and the 'corrected' spectrum $S_{zz} = (S_{zz}^{\text{exp}} - S_{zz}')$ was formed. Figure 2 shows this result. It is clear that the only peak remaining in the lattice mode region is a very weak contribution from the 51 cm$^{-1}$ peak seen in $xx$ and $yy$. Again we conclude that no second $A_{1g}$ mode is to be seen.

4.3. The $B_{1g}$ ($xy$) Spectrum

This spectrum should also show two peaks whereas possibly six are seen in some results. Applying the same subtraction procedure proportions of the $xz$ and $xx$ spectra were removed leaving two peaks at 40 and 54 cm$^{-1}$ (Figure 3). There are no peaks with matching frequencies in the other spectra. We believe that here we have been successful in isolating the proper peaks in the spectrum.

4.4. The $B_{2g}$ ($xz$) Spectrum

Here the spectrum is fairly intense with little evidence of breakthrough (Figure 4). The only problem is that of the nature of the peak at 74 cm$^{-1}$. This peak would be expected to arise from the 80 cm$^{-1}$ $E_2$ mode of the sulphur molecule [4]. In this particular spectrum the frequency of the mode has been considerably depressed so that it overlaps with the lattice frequencies. Here the distinction between internal and external vibrations stops, and any mode in this region may have the character of both. We can con-
clude nothing firmer from the spectrum alone, but a calculation of the molecular frequencies in the crystal by Pawley and Kurittu [11] may resolve the problem.

4.5. THE $B_{3g}(yz)$ SPECTRUM
In this case matters are quite straightforward. A very weak peak at 65 cm$^{-1}$ appears to complete the expected quartet of lines (Figure 5). Table I shows the measured frequencies and assignments of all the modes.
TABLE I

Frequencies and assignments of the external modes

<table>
<thead>
<tr>
<th></th>
<th>$A_{1g}$</th>
<th>$B_{1g}$</th>
<th>$B_{2g}$</th>
<th>$B_{3g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>51.1</td>
<td>40.0</td>
<td>29.0</td>
<td>26.5</td>
</tr>
<tr>
<td>2</td>
<td>not seen</td>
<td>54</td>
<td>49.0</td>
<td>42.3</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>60.8</td>
<td>53.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>73.8$^a$</td>
<td>64.5</td>
</tr>
</tbody>
</table>

$^a$ See Section 4.4.

$A_{1g}$ (zz) Spectrum

Experimental $-\cdots$  
$\alpha S_{xz} + \beta S_{yz} -\cdots- $  
Resulting $S_{zz} -\cdots- $
5. Discussion

In this section we account for the basic features of the $A_{1g}$ and $B_{1g}$ spectra. The discussion would also be applicable to $B_{2g}$ and $B_{3g}$ modes but with increased complexity since there are four modes to consider. It is assumed that the lowest order contribution to fluctuations in the crystal polarisability arises from rotatory displacement of the
S₈ molecules. In this approximation translatory motion of the molecules does not modify the crystal polarisability.

Starting with a molecular polarisability of the form:

\[ \alpha_m = \begin{bmatrix} a & b \\ b & c \end{bmatrix} \]
with the molecular $x(C_4)$ axis rotated by $\phi$ off the crystal $x$ axis, the contributions to the crystal polarisability for molecules type 1 and 2 are respectively:

$$\alpha_c^1 = \begin{bmatrix} \lambda & v \\ v & \mu \end{bmatrix} \quad \alpha_c^2 = \begin{bmatrix} \lambda & -v \\ -v & \mu \end{bmatrix}.$$
where
\[
\lambda = \cos^2 \phi a + \sin^2 \phi b \\
\mu = \cos^2 \phi b + \sin^2 \phi a \\
v = 2 \sin \phi \cos \phi (a - b).
\]

Symmetry coordinates for the \( A_{1g} \) and \( B_{1g} \) modes may be introduced as follows:

<table>
<thead>
<tr>
<th>( x^1 )</th>
<th>( y^1 )</th>
<th>( z^1 )</th>
<th>( R_x^1 )</th>
<th>( R_y^1 )</th>
<th>( R_z^1 )</th>
<th>( x^2 )</th>
<th>( y^2 )</th>
<th>( z^2 )</th>
<th>( R_x^2 )</th>
<th>( R_y^2 )</th>
<th>( R_z^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>0</td>
<td>0</td>
<td>+( \delta z )</td>
<td>0</td>
<td>0</td>
<td>+( \delta \phi )</td>
<td>0</td>
<td>0</td>
<td>-( \delta z )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>0</td>
<td>0</td>
<td>+( \delta z )</td>
<td>0</td>
<td>0</td>
<td>+( \delta \phi )</td>
<td>0</td>
<td>0</td>
<td>+( \delta z )</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Since molecules 3 and 4 are related to 1 and 2 by a centre of inversion, and only even modes are Raman active, they give an identical contribution and need not be considered further.

It can be seen that these modes correspond to in-phase and out-of-phase rotatory oscillations about the \( z \) axis, together with a displacement along the \( z \) axis which we may ignore. The oscillations, \( \delta \phi \), produce a change in the polarisability as follows:

\[
\delta z \propto \delta \phi \sin 2\phi \begin{bmatrix} a - b & 0 \\ 0 & a - b \end{bmatrix} \text{ Rotations in phase}
\]
\[
\delta z \propto \delta \phi \cos 2\phi \begin{bmatrix} a - b & 0 \\ 0 & 0 \end{bmatrix} \text{ Rotations antiphase}
\]

Thus
\[
\langle \delta z^2 \rangle \sim \langle \delta \phi^2 \rangle \sin^2 2\phi \ldots A_{1g}
\]
\[
\sim \langle \delta \phi^2 \rangle \cos^2 2\phi \ldots B_{1g}
\]

These expressions show that no intensity is expected in the \( zz \) spectrum whereas equal intensities are expected in \( xx \) and \( yy \). This is indeed what is observed, even if the \( xx \) and \( yy \) intensities are not quite identical. The fact that the peak at 89 cm\(^{-1}\) remains with strong intensity in \( zz \) shows that it does not have the character of an external mode for which the above analysis applies. It is therefore unambiguously identified as an internal mode.

Since the intensities of the \( A_{1g} \) modes are both approximately proportional to \( \langle \delta \phi^2 \rangle \) intensity will be seen from only one mode when the eigenvectors of these modes are respectively pure translatory and pure rotatory. We interpret the observation of only one \( A_{1g} \) mode as a demonstration of this behaviour.

A similar argument applies to the \( B_{1g} \) modes. Here the lower frequency mode should have the larger rotational component. The intensities are approximately in the ratio 3.5:1 so that the rotational components of the eigenvectors, \( \delta \phi \), are in the ratio 2.3:1.

In addition we can compare the intensities for the \( A_{1g} \) and \( B_{1g} \) modes by the ratio...
\[ \sin^2 \phi / \cos^2 \phi \text{ where } \phi = 141^\circ 18' \] [6]. This gives a ratio of 20:1. The experimental results lie between 13:1 and 20:1, which is in reasonable agreement.

6. Conclusion

The assignments of the lattice frequencies have been clarified by applying simple computer aided methods to the spectra. The manipulated \( A_{1g} (zz) \) spectrum showed no peak in the lattice region of any significance. That this fact should be borne out by a theoretical analysis provides a good test of the effectiveness of the technique. We therefore have confidence in applying it to the \( B_{1g} \) spectrum. A similar subtraction technique has also proved successful in separating the \( A_1 \) and \( E \) modes in cubic crystals [12].

Both the \( A_{1g} \) and \( B_{1g} \) spectra can be described by a simple model based on the molecule preserving its identity within the crystal. This bears out the central assumption that sulphur can be treated dynamically as a crystal of rigid molecules except where the lattice and internal vibration spectra overlap. The information gained about the rotational components of the \( A_{1g} \) and \( B_{1g} \) mode eigenvectors should be of use in further comparison with lattice dynamical calculations.

Acknowledgements

The authors are indebted to Dr R. P. Rinaldi and Dr G. S. Pawley of this department for many helpful discussions about the dynamics of sulphur; to Dr J. Sherwood, Strathclyde University, who provided the sample; to Dr T. Luty who suggested the calculation. The work was supported by the S.R.C.

References

LETTER TO THE EDITOR

The structural phase transition in solid DCN

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Abstract. Neutron scattering measurements on deuterated hydrogen cyanide have shown
that the structural phase change from a tetragonal to an orthorhombic form at 160 K
is a first-order transition. A transverse acoustic phonon mode, which has the symmetry
of the phase change, was observed at very low energies and showed ‘softening’ as the
transition temperature was approached from above.

In recent years there has been considerable interest in revealing the ‘driving force’ of
structural phase transitions on the basis of the softening of dynamical lattice modes and
the anharmonicity of interatomic forces. Most of the work so far has dealt with ionic or
metallic crystals, but many molecular crystals also exhibit structural phase transitions
which may well be explained on the same basis. However, the complexity of molecular
lattice dynamics, due to many degrees of freedom in a unit cell and weak intermolecular
forces, is often an obstacle for experimental investigation. There are, nevertheless, a few
molecular crystals which are relatively simple but still undergo structural phase transitions;
among them is hydrogen cyanide, which has a transition from a high temperature tetra-
gonal to a low temperature orthorhombic phase. The existence of a transition in HCN
was first discovered as an anomaly in the specific heat at 170·4 K by Giaquie and Rue-
hrwin (1939). The temperature resolution in their experiments was not sufficient to show
any width of the anomaly, but from the rate of cooling it seemed likely that the transition
region was finite, although narrow (less than 0·5 K). Later Dulmage and Lipscomb (1951)
made an x-ray determination of the crystal structures of both forms. The molecule is
linear and aligned along the c axis of the body-centred tetragonal or body-centred
orthorhombic unit cells. By the lowering of the symmetry from tetragonal to orthorhom-
bic the crystal is subject to a twinning (to which we return later) but it was observed in
the x-ray work that the transition was reversible and a single tetragonal crystal could be
recovered. Rae (1969,1972) has calculated the lattice energy and lattice dynamics for
both phases, based on an assumed intermolecular potential. Not surprisingly, he found
that the static energy was nearly equal for the two structures and the potential barrier
between them was very low. More interesting was the observation that the acoustic shear
mode in the direction of the base diagonal, (110), which relates the two structures, had
an anomalous behaviour where the calculated frequencies were imaginary. Rae suggested

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that the phase change is of second order and associated with an instability of the transverse acoustic phonon with wavevector in this direction.

We have undertaken an experimental study of deuterated hydrogen cyanide using the coherent inelastic neutron scattering technique. The reason for using the deuterated form is to avoid the large incoherent neutron scattering of hydrogen. The ultimate aim of this work is to reveal the 'driving force' of the phase transition. This goal is not yet achieved, but we report on some preliminary observations on the structural and dynamical behaviour of DCN.

A sample of 25 ml of DCN (melting point 13.8 °C, boiling point 26 °C) was prepared by dropping a molar solution of sodium cyanide in heavy water (99.7% isotopic deuterium abundance) on to phosphorus pentoxide. The sodium cyanide and the phosphorus pentoxide were thoroughly dried before the process, but in order to ensure the highest possible isotopic enrichment of deuterium, the gas was bubbled several times through heavy water and dried immediately afterwards in two calcium chloride lines. This is necessary since water catalyzes polymerization. A spectroscopic measurement showed a 95% enrichment of the final material. The sample was sealed under a vacuum in a 1 in diameter, 2 in long cylindrical quartz tube with the bottom end specially designed for single crystal growth. This was mounted in a cryostat such that the bottom and top could be heated or cooled independently in order to create a gradient, which would allow a single crystal to grow smoothly either from the melt at the bottom, or by sublimation from the top. Unfortunately, in about ten attempts with various growing rates and temperature gradients we never obtained a good single crystal of fair size and low mosaic width. Only in three cases could small single crystals be selected and oriented with the tetragonal plane horizontal; the best of these had a mosaic spread of about 2 degrees. Although the size of these pieces was too small to allow a full scale inelastic neutron scattering study, inelastic measurements limited to small energy transfers, and therefore large neutron scattering cross sections, were possible. After a crystal was grown

![Figure 1. Domain structure of the low temperature orthorhombic phase in the a*b* plane of reciprocal space. One or other of the base diagonals, (110) or (110), are retained in length and direction from the high temperature tetragonal phase, giving rise to the four domains A, B, C and D. The angles and relative lengths in the figure are drawn to scale.](image-url)
and the temperature gradient over the sample was eliminated, a temperature controller kept the temperature constant to an accuracy of about 0.05 K. The cryostat was mounted on a triple-axis crystal spectrometer at the DR 3 reactor, Risø, operated with pyrolytic graphite monochromator and analyser at an incident wavelength of 2.39 Å. A graphite filter was mounted in the monochromatic beam to reduce the λ/2 contamination.

It is known from the x-ray data (Dulmage and Lipscomb 1951), that the twinning of the hydrogen cyanide crystal in the orthorhombic phase is of the common type for this structure, as shown in figure 1. The drawing represents the $a^*b^*$ plane in reciprocal space and the thick lines marked (110) and (110) are the base diagonals in the tetragonal phase. In the orthorhombic phase, one or other of these base diagonals retains its direction in space and approximate length, thus giving rise to the four possible domain configurations denoted A, B, C and D in the figure. By this twinning the (020) reflection becomes a quadruplet and the (110) reflection becomes a triplet. The domain structure is most easily observed in an elastic intensity scan along the dotted line in figure 1. Such scans are shown in figure 2 for temperatures in the close vicinity of the phase transition. The upper curves at $T = 160.2$ K are obtained in the tetragonal phase and the lower curves at $T = 159.9$ K and $T = 159.0$ K in the orthorhombic phase. It is evident from figure 2 that the transition is very sharp. The small hump in the centre of the (020) scan at $T = 159.9$ K indicates coexistence of both phases, but this might be due to a small temperature gradient over the single crystal, which was long and thin. We passed the transition several times and found no hysteresis effects. Moreover, all intensities were regained, even the ratio of 3 to 2 of the two domains in the (020) scans of figure 2. The two other domains (C and D in figure 1) had peak intensities of about 5000 counts per 3 seconds.

![Figure 2. Neutron elastic scattering along the dotted line in figure 1. The orthorhombic domain structure produces a triplet (110) reflection and a quadruplet (020) reflection, as observed below 160.0 K.](image-url)
We have measured the positions of the (110) and (020) reflections over a wide temperature range and determined the temperature variations of the lattice spacings $a$ and $b$. The results are shown in figure 3, where we have plotted $a$, $b$ and $d_{110}$ relative to their values at 223.5 K, which are $a = b = 4.63$ Å and $d_{110} = 3.27$ Å (at 77 K, $a = 4.10$ Å and $b = 4.80$ Å). It is seen that $d_{110}$ varies smoothly and almost unaffected through the transition, whereas $a$ and $b$ show a characteristic behaviour of a first-order transition at $T_c = 160.0 \pm 0.1$ K. The initial bending of the $a$ and $b$ curves just below $T_c$ indicates, however, that the first-order transition happens 'accidentally' while the system is on its way to a second-order transition, which might have occurred near 180 K. It is interesting to notice that the transition in the deuterated sample occurs 10 K below the transition in the hydrogenous sample. This isotope effect is much smaller and opposite in sign to the temperature shifts observed in the strongly hydrogen bonded ferroelectrics, eg KDP. This observation leads us to believe that the hydrogen bond itself plays a minor role in the phase transition in hydrogen cyanide, and that the decrease in transition temperature is rather a consequence of the lowering of some lattice mode frequencies with the increase of the molecular mass.

Following the suggestion of Rae (1972), that the phase transition is associated with an instability in a transverse acoustic phonon with a wavevector $q$ in a direction close to (110), we have performed neutron energy scans for constant $q$ directed along (110) in the (110) Brillouin zone (dotted line in figure 1). Some results for various temperatures at two $q$ values are shown in figure 4, where $q_{max}$ refers to the zone boundary in that direction. In general we observed a three-peaked intensity function, as shown for $T = 135.0$ K at $q/q_{max} = 0.875$. The central peak, however, was found at all $q$ vectors. This is believed to arise from the incoherent elastic scattering collected from the whole of the illuminated part of the sample, not just from the single crystal piece. We have subtracted the central peak from the other scans in figure 4, marking the corrected intensities with a filled rather
than an open circle and using broken lines as guides to the eye. The measurements confirm Rae's calculation of a very low energy phonon branch in this direction, the two peaks being due to creation and annihilation of a phonon. We have observed this scattering also in other Brillouin zones, but the dynamical structure factor is largest in the (110) zone; two other single crystals with larger mosaic widths gave consistent results. The scans in the low temperature orthorhombic phase are obscured by the domain structure, as can be envisaged from figures 1 and 2. In the high temperature tetragonal phase, the scans at both \( q \) vectors seem to indicate a softening of the mode (about 25\%) between 225 K and 178 K, but no further softening towards the transition at 160 K. We plan to attempt to grow by other techniques a larger and more perfect single crystal that will enable us to resolve the transverse acoustic mode at smaller \( q \) vectors, and to observe if this mode couples to other lattice modes.

The deuterated hydrogen cyanide was prepared by O Jørgensen of the Chemistry Department, Risø. We owe our sincere thanks to him and to B Skytte Jensen, Head of the Chemistry Department, for their expert help in handling this poisonous material.

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Neutron powder diffraction analysis and constrained refinement of perfluorodiphenyl. By G. A. Mackenzie and G. S. Pawley, Physics Department, Edinburgh University, Scotland, and O. W. Dietrich, Physics Department, A.E.K., Risa, Roskilde, DK4000, Denmark.

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It is shown that with the small amount of data available in the neutron powder diffraction method, it is possible, by means of reasonable constraints, to refine a molecular structure involving a large number of atoms. The method has been used to refine the crystal structure of perfluorodiphenyl. Although the asymmetric unit contains 11 atoms, only three parameters are used to govern their positions, namely the central bond length, the orientation of the two rings about this bond, and the orientation of the whole molecule about the crystallographic c axis. The refinement procedure proved to be quite stable and a good fit to the observations was obtained. This procedure is clearly of value in the study of phase transitions in molecular crystals.

Introduction

The neutron powder profile method for the refinement of crystal structures has received a great deal of attention in recent years. A computer program (Rietveld, 1968) has been used extensively for the accurate determination of the positions of a small number of the atoms in the unit cell as in the case of hydrogen atoms in hydrogen-bonded ferroelectrics (Hewat, 1973). The method is here applied to a molecular crystal in which all the atomic positions are to be varied. By using a number of constraint functions the number of degrees of freedom in the problem is reduced to three. The method of Lagrange undetermined multipliers, which is incorporated in Rietveld's program, is used to apply the constraints, though for such a highly constrained problem the method of strict constraints is more appropriate (Pawley, 1972).

The molecule of perfluorodiphenyl, C_{12}F_{10}, consists of two fluorine-substituted phenyl rings connected by a single C-C bond, Fig. 1. The two ring systems are not coplanar, and the interplanar angle \( \phi \) has been the subject of some discussion (Almenningen, Hartmann & Seip, 1968). It is important in the consideration of the dynamics of the crystal, as shown by the interpretation of the Raman spectrum (Arthur & Mackenzie, in preparation). The determination of \( \phi \) and the length of the central bond were the principal structural aims of the present work.

The crystal structure was reported briefly by Neronova (1968). The space group is Fdd2 and the eight molecules in the unit cell are positioned on the diaz axes along the c axis at the special positions (0,0,0), (1,1,1) etc., Fig. 2. The long molecular axis lies in the ab plane at an angle \( \psi_{a} = 38^\circ \) to the a axis. Neronova gives an angle of 60\(^\circ\) as the rotation of the phenyl rings, and this we deduce to be the angle with respect to the ab plane; this is not clear from her paper, but is consistent with our final result.

Fig. 1. The molecule of perfluorodiphenyl and the definition of \( r \) and \( \phi \). The ring C-C bonds are 1.37 A and the C-F bonds are 1.38 A, being the values used by Neronova (1968).

Fig. 2. The crystal structure of perfluorodiphenyl, after Neronova (1968).
Experiment and analysis

The neutron powder diffraction pattern was measured using the triple-axis spectrometer TAS-4 at Riso, Denmark, with the analyser removed. Neutrons of wavelength 2.374 Å were used and the diffraction data recorded at intervals of 0.2° of 2θ between 10° and 90°, counting for 11 min at each point in the scan. The sample was wrapped in aluminum foil to make a cylinder, and only one aluminum powder line was detectable. The measurements were made at room temperature.

The least-squares structure refinement involved 11 independent atomic positions, giving 33 positional parameters. The facility of the Rietveld computer program for linear and quadratic constraints allowed the variations in these coordinates to be governed by three parameters only. These parameters were the central bond length, r, the angle ψ between the two phenyl rings measured so that 1/2ψ is the angle with the ab plane, and the angle ωz. The interatomic bond lengths used were those reported by Neronova; the phenyl rings were assumed to have a regular hexagonal shape. The initial parameter values were r = 1.41 Å, ψ = 60°, ωz = 38°. These were allowed to vary, along with the three orthorhombic cell parameters and an overall temperature parameter, and the refinement was stable at all times. When a minimum was reached the parameters had the following values: r = 1.62(6) Å, ψ = 120.7(5)°, ωz = 37.8(5)°, a = 13.48(1), b = 26.52(1), c = 6.29(1) Å. Overall temperature factor B = 6.1(9) Å².

The observed and calculated profiles are shown in Fig. 3, where the background counts have been subtracted. Fig. 4 shows a similar comparison where the calculated profile is that corresponding to the initial values of r, ψz, and ωz. The angle ψ was in error by about 60° initially, and it is clear that the calculated fit with the final value of ψ gives much the better agreement with experiment. The fit becomes poorer at higher scattering angles where there is considerable overlapping of the diffraction peaks, but this is to be expected as the parameters varied correspond to low atomic resolution. Any molecular distortion which might be present cannot be detected with this procedure, and it is planned to continue the investigation of the structure of this material using single-crystal four-circle diffractometer measurements and strict constrained refinement methods. Such an analysis will enable us to examine the thermal motion in the structure, as very little reliance can be put on the temperature factor obtained in the present low-resolution work.

Conclusion

It has been shown that the method of powder profile refinement can be used to obtain low-resolution information about the structure of molecular crystals. With the correct choice of constraints the large number of degrees of freedom of the system can be considerably reduced so that large scale features of the structure, such as molecular orientation, may be investigated. Such large-scale features are of dominant importance in the phase transitions of molecular crystals, and hence this method will have considerable value in such studies.

For the molecule of perfluorodiphenyl it is shown that the angle ψ between the two ring systems is 120° ± 7° with an error of perhaps ± 5°. The bond between the two rings is 1.62 Å, but as this is highly correlated to structural features which were held fixed, no good estimate of an error is possible. The error given above of 0.06 Å should be interpreted as the error between the centres of the two rings.

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THE ORIENTED GAS APPROXIMATION AND THE LATTICE VIBRATIONS OF MOLECULAR CRYSTALS: THEORY AND APPLICATION TO PERFLUOROBIPHENYL

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Abstract. The oriented gas model of the polarisability of a molecular crystal provides a basis for the discussion of its Raman spectrum. This model is examined with a view to deriving information about eigenvectors of the zone centre lattice vibrations in these crystals. The theory of the general case is much simplified by symmetry conditions in certain instances. This is applied to the molecular crystal perfluorobiphenyl, C_{12}F_{18}, of recent interest. For this crystal it is found necessary to extend the theory to include the coupling of internal vibrations with the lattice vibrations. A simple model is found to account for this and the extent of the coupling is thereby estimated.

1. Introduction

The first order Raman spectrum of a harmonic crystal contains information about the frequencies and eigenvectors of the lattice vibrations. The spectrum is related to a particular normal mode by the way that mode modulates the crystal polarisability. The frequency of the normal mode may be determined from the frequency of the corresponding peak in the Raman spectrum, and the wavevector, though very small, can be worked out from geometrical considerations, but information about the eigenvector can only be obtained from a knowledge of the crystal polarisability.

Group theory provides a first qualitative step in determining the eigenvector [1] because it allows the most general form of scattering tensor of a normal mode of a particular symmetry (and hence with a particular form of eigenvector) to be written down. The application of this requires single crystal spectra with incident and scattered light polarised in specific directions. To go any further, a model of the crystal polarisability must be found. The oriented gas model of Kastler and Rousset [2] is applicable to molecular crystals in which libration of large optically anisotropic molecules modulates the crystal polarisability. This approach has been used to discuss the Raman spectra of such molecular crystals as napthalene, anthracene and others [2], [3], but under the assumption that the rotational part of an eigenvector involves only libration about one principal axis of inertia of the molecule. In certain cases, symmetry considerations may dictate that this be so, but in general this is an unjustifiable assumption. For example, it is clear from the work of the present authors on sulphur [4], that it is quite unsatisfactory. Here, however, we make no such assumption because our aim is to derive information about the rotational components of the eigenvector using relative intensities measured in the Raman spectrum.

Before we examine the oriented gas model in detail, it must be pointed out that
there is uncertainty as to its accuracy. It describes a crystal of infinite small induced dipoles in which the polarisability, \( \alpha_c \), is simply the cell average of the molecular polarisabilities. This neglects completely the effects of the macroscopic polarisation and the local field. Even if one replaces the applied field by the effective field in the crystal (i.e. take the refractive index into account), the exciting field is actually the local field which, unfortunately, varies throughout the cell in both magnitude and direction. A calculation of the local field is outside the scope of this work, but it is found that the oriented gas approximation leads to a useful analysis of the lattice vibrations of crystals such as sulphur [4], and, here, perfluorobiphenyl.

In the following section we sketch the theory in general, after which in Section 3 we describe the experiment on perfluorobiphenyl. The observed spectra are then compared with group theoretical predictions in Section 4, and subsequently in Section 5 a fuller analysis is given in terms of our polarisability model. Conclusions are presented in Section 6.

2. The Oriented Gas Model for Polarisability and Scattering Tensors

Here we give an outline of the model as required for the calculation of eigenvectors and note some general observations in regard to the interpretation of the spectra. At first we treat only one molecule in the primitive cell and then extend this by a simple method, where symmetry conditions permit, to more than one molecule.

The molecular polarisability we denote by \( \alpha_m \) expressed in diagonal form. The molecular symmetry can be helpful in determining the required principal axes. These axes are related to the crystallographic axes by an orthogonal transformation, and therefore the crystalline polarisability \( \alpha_c \) is given in the oriented gas approximation by

\[
\alpha_c = R^+ \alpha_m R, \tag{2.1}
\]

where \( R \) is usually obtainable just from a knowledge of the crystal structure. If the molecule librates with an amplitude \( \delta \theta \) about an axis \( \kappa \) and we express this vectorially in the molecular coordinate system as:

\[
\delta \theta = \delta \theta \begin{bmatrix} x_1, x_2, x_3 \end{bmatrix} = \begin{bmatrix} \delta \theta_1, \delta \theta_2, \delta \theta_3 \end{bmatrix}, \tag{2.2}
\]

then we have a change in polarisability

\[
\alpha_m' = [1 + \Omega] \alpha_m [1 - \Omega] + O(\delta \theta^2), \tag{2.3}
\]

where

\[
\Omega = \begin{bmatrix} 0 & -\delta \theta_3 & \delta \theta_2 \\ \delta \theta_3 & 0 & -\delta \theta_1 \\ -\delta \theta_2 & \delta \theta_1 & 0 \end{bmatrix}. \tag{2.4}
\]

To first order in \( \delta \theta \), Equation (2.3) becomes

\[
\alpha_m' = \alpha_m + [\Omega \alpha_m - \alpha_m \Omega]. \tag{2.5}
\]

The term in square brackets is the polarisability differential from which we may find...
the scattering tensor. We require this expressed in crystal coordinates, however, giving

\[
\delta \varepsilon \mathcal{C}_{\beta \gamma} = \sum_{k\ell m} R_{\beta\gamma} R_{\ell\gamma} \delta \Theta_m \delta \Theta_{\ell m},
\]

where \( \delta \varepsilon \mathcal{C}_{\beta \gamma} \) is the Levi-Cevitta matrix. To derive the scattering tensor \( \mathcal{E}_{\beta \gamma} \) must be expressed in terms of normal modes and Equation (2.7) substituted in the usual scattering formula [5]. For our purposes this results in the expression for integrated intensities in Stokes' scattering

\[
I(\omega_j)_{\beta \gamma} = \eta \sum_m \frac{n(\omega_j) + 1}{\omega_j} \frac{e^I_m e^I_{m'} \mathcal{P}_{\beta \gamma}^{m m'}}{\sqrt{I_{m m'}}},
\]

where

\[
(P_j)_{\beta \gamma} = \frac{1}{\omega_j} \sum_m \frac{e^I_{m}}{\sqrt{I_{m m'}}} e^I_j
\]

\( I(\omega_j)_{\beta \gamma} \) is the intensity of the mode \( j \) of frequency \( \omega_j \) in the Stoke's spectrum with polarisation \( \beta \gamma \). The \( m \)th librational component of the eigenvector of the mode \( j \) is \( e^I_{m} \); \( I_{m m} \) is the corresponding moment of inertia, and \( \eta \) is simply a scale factor. 

The application of (2.8) to the analysis of a spectrum depends first of all on the form of the molecular polarisability.

There are three cases to consider in which the molecules are either optically isotropic, uniaxial, or biaxial. In the first case all of the \( (\varepsilon_{kk} - \varepsilon_{ii}) \) vanish and there is no first order spectrum, as for example in hexamethylene tetramine [6]. In the second case there is a first order spectrum and there is only one non zero value of \( (\varepsilon_{kk} - \varepsilon_{ii}) \), implying that there are no adjustable parameters as far as relative intensities are concerned. In the last case, however, there are two adjustable parameters. In theory it is possible to fix values for these by measuring integrated intensities over all modes in the lattice vibration region. We define this summation of intensities as

\[
\Sigma(\beta \gamma) = \sum_{\beta \gamma} \frac{\omega_j}{n(\omega_j) + 1} I_{\beta \gamma}(\omega_j).
\]

The orthogonality of the eigenvectors makes them disappear from this sum leaving

\[
\Sigma(\beta \gamma) = \eta \sum_m \frac{(P^m_{\beta \gamma})^2}{I_{m m}},
\]

\[
= \eta \sum_{k\ell m} \frac{R^2_{\alpha k} R^2_{\alpha \ell}}{I_{m m}} \delta_{k\ell} (\varepsilon_{kk} - \varepsilon_{ii})^2.
\]
Using six different combinations of the incident and scattered light polarisations which determine $\beta \gamma$, (2.13) yields six equations for the unknowns $(\alpha_{kk} - \alpha_{ll})^2$. In practice the problem of measuring spectra of different polarisations under the same gain conditions makes it difficult to measure these sums with sufficient accuracy, and it is often necessary to keep the molecular polarisability parameters as variables. Nevertheless, useful information may still be extracted from the spectra as will be seen here with perfluorobiphenyl.

Lastly, we come to the case where there is more than one molecule in the primitive cell. Equations (2.6)–(2.10) are formally easy to extend, but they become very complicated. Where the molecules are related by symmetry, however, there is much simplification, for the various $R$ and $A$ matrices are all similar. For crystals of symmetry not higher than orthorhombic in which all the molecules are related to one another by space group operations there is particular simplification. If the matrices $I_n^m$ are calculated for just one chosen molecule, it is found that the other molecules contribute similarly except for possible differences in signs. Because the eigenvectors are also related by the symmetry of the crystal, it is found that on forming the scattering tensor $(P_j)_{\beta \gamma}$ in (2.10) the effect of the other molecules is to cancel out all contributions except that which occurs under the same irreducible representation as the eigenvector $j$. Taking, for example, sulphur, the scattering tensor can be decomposed under the irreducible representations of $D_{2h}$ as:

\[
\begin{bmatrix}
  a \\
  b \\
  c \\
  d
\end{bmatrix}
\cdot
\begin{bmatrix}
  e \\
  f
\end{bmatrix}
\]

There are four molecules in the primitive cell and $P_n^m \delta \theta_m$ for one of them is found to be of the form:

\[
\begin{bmatrix}
  a \\
  b \\
  c \\
  d
\end{bmatrix}
\cdot
\begin{bmatrix}
  e \\
  f
\end{bmatrix}
\]

Following (2.14) we write this as

\[
\begin{bmatrix}
  a \\
  b \\
  c \\
  d
\end{bmatrix}
\cdot
\begin{bmatrix}
  e \\
  f
\end{bmatrix}
\]

These are the required scattering tensors, $P_j^j$, including the effect of all the molecules. The eigenvectors require only the components for the chosen molecule, but the rest are easily constructed from symmetry coordinate considerations. The infrared active
modes are known to give no contribution to the scattering and it is seen that they are immediately eliminated by this treatment. This simplified method will be applied in Section 4 to perfluorobiphenyl where there are two symmetry related molecules in the primitive cell. There is no such simple method for crystals of higher symmetry.

3. Experimental

A single crystal of perfluorobiphenyl, which we hereafter simply refer to by its formula C₁₂F₁₀, was obtained by zone refinement. It was cut and polished with faces perpendicular to the crystallographic axes, which are also the optic axes of the crystal, to a size of about 3 × 5 × 7 mm. The crystal faces were found to gradually deteriorate due to sublimation of the surface layer and occasional repolishing was necessary. To improve transmission of the focused laser beam into the sample it was mounted on a glass slide using a thin film of silicone oil to form an optical contact. The proper orientation of the crystal for each spectrum was finely adjusted to give minimum depolarisation of the transmitted laser beam, Figure 1. This is an important point for obtaining spectra free of accidental depolarisation, although in such birefringent crystals it still occurs to some extent. The experiments were performed initially on a Spex
Fig. 2. $xx$ spectrum: dotted line shows fit.

Fig. 3. $yy$ spectrum: dotted line shows fit.
Fig. 4. $zz$ spectrum; dotted line shows fit.

Fig. 5. $yz$ spectrum, X - accidental.
Fig. 6. $xz$ spectrum. X - accidental.

Fig. 7. $xy$ spectrum.
Peak frequencies and assignments. The peak heights are the data of System I; they are uncorrected for differing scattering intensities and are intended only to indicate relative strengths.

<table>
<thead>
<tr>
<th>Frequency at peak (cm(^{-1}))</th>
<th>Representation</th>
<th>Actual Peak Height</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(xx)</td>
</tr>
<tr>
<td>32.9</td>
<td>(B_1^x)</td>
<td></td>
</tr>
<tr>
<td>33.4</td>
<td>(A_1^x)</td>
<td></td>
</tr>
<tr>
<td>38.0</td>
<td>(B_1^x)</td>
<td></td>
</tr>
<tr>
<td>38.8</td>
<td>(B_1^x)</td>
<td></td>
</tr>
<tr>
<td>47.1</td>
<td>(B_1^y)</td>
<td>72380</td>
</tr>
<tr>
<td>48.1(^a), 48.7(^b)</td>
<td>(A_1^y)</td>
<td></td>
</tr>
<tr>
<td>49.3</td>
<td>(A_1^y)</td>
<td></td>
</tr>
<tr>
<td>52.8</td>
<td>(B_1^z)</td>
<td></td>
</tr>
<tr>
<td>54.4</td>
<td>(B_1^z)</td>
<td></td>
</tr>
<tr>
<td>54.4</td>
<td>(B_1^z)</td>
<td>sh</td>
</tr>
<tr>
<td>58.9</td>
<td>(A_1^z)</td>
<td></td>
</tr>
<tr>
<td>61.9</td>
<td>(B_1^z)</td>
<td></td>
</tr>
<tr>
<td>64.3</td>
<td>(A_2^z)</td>
<td>13660</td>
</tr>
<tr>
<td>65.4(^b), 67.1(^a)</td>
<td>(A_1^z)</td>
<td>18600</td>
</tr>
<tr>
<td>70.8</td>
<td>(A_1^z)</td>
<td></td>
</tr>
<tr>
<td>72.9</td>
<td>(A_1^z)</td>
<td>18600</td>
</tr>
<tr>
<td>126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>144.8</td>
<td>(B_1^z), (B_1^y)</td>
<td></td>
</tr>
<tr>
<td>146.3</td>
<td>(B_1^z), (B_1^y)</td>
<td></td>
</tr>
<tr>
<td>151.1</td>
<td>(A_2^z), (A_1^y)</td>
<td>2236</td>
</tr>
<tr>
<td>152.5</td>
<td>(A_2^z), (A_1^y)</td>
<td></td>
</tr>
<tr>
<td>183.5</td>
<td>(B_1^z), (A_1^y)</td>
<td>3883</td>
</tr>
<tr>
<td>185.4</td>
<td>(A_2^z), (A_1^y)</td>
<td>4916(^b)</td>
</tr>
<tr>
<td>186.1</td>
<td>(B_1^z), (B_1^y)</td>
<td>4916(^b)</td>
</tr>
<tr>
<td>186.6</td>
<td>(A_2^z), (A_1^y)</td>
<td>4916(^b)</td>
</tr>
<tr>
<td>234.1(^a), 234.8(^b)</td>
<td>(B_1^z), (A_1^y)</td>
<td>4916(^b)</td>
</tr>
<tr>
<td>234.8</td>
<td>(B_1^z), (A_1^y)</td>
<td>4916(^b)</td>
</tr>
<tr>
<td>240.6</td>
<td>(B_1^z), (B_1^y)</td>
<td>223</td>
</tr>
<tr>
<td>241.6</td>
<td>(B_1^z), (B_1^y)</td>
<td>223</td>
</tr>
</tbody>
</table>

X = accidental; \(^a\, ^b\) = slightly different frequencies for \(xx\), \(yy\) and \(zz\); w = weak; sh = shoulder.

1400 double monochromator with data collection on paper tape and point plotter (System II, [7]). The spectra were excited using the 632.8 nm line of Hg-Ne laser operating at about 80 mW output. For comparison the experiments were repeated on a Spex Ramalab (System I, [7]) with similar digital control, using in this case the 514.5 nm line of the argon ion laser. In both cases the spectra were measured at room temperature using a slit width of 2.5 cm\(^{-1}\) over a range 5–250 cm\(^{-1}\). Three separate orientations of the crystal were used each giving one diagonal and the three off-diagonal spectra under similar gain conditions. The spectra of the three different orientations were of dissimilar gain conditions, but since the same off-diagonal spectra occur in each, a correlation of intensities was possible. This correlation is necessary for an
intensity standardisation of the diagonal spectra. In practice it was possible to correlate intensities within an error of about 10% (as shown by inconsistency in the correlation of the various off-diagonal spectra).

The data obtained were processed by computer with the aid of a variety of routines for intensity measurement, peak finding, band fitting and graphical output [8]. The spectra are shown in Figures 2 to 7 and observations are presented in tabular form in Table I. Where integrated intensities under peaks were required the data were fitted to damped simple harmonic oscillator lineshapes [5] of the form

\[
I_j(\omega) = \frac{1}{\pi} \omega (\omega (\omega + 1)) \frac{\omega_j^2 \Gamma_j}{(\omega^2 - \omega_j^2)^2 + \omega_j^2 \Gamma_j^2} S_j. \tag{3.1}
\]

The parameters \(\omega_j\) and \(\Gamma_j\) are the frequency and damping of the mode \(j\), and \(S_j\) is its 'strength'. The forms of Equations (2.9) and (2.11) are then replaced by, for experimental purposes:

\[
S_j(\beta \gamma) = \eta (P_j) \frac{\omega_j^2}{\beta \gamma}, \tag{3.2}
\]

and

\[
\Sigma (\beta \gamma) = \sum_j \omega_j^2 S_j (\beta \gamma). \tag{3.3}
\]

Table II gives these fitted parameters for the \(A_x^c\) \(xx\), \(yy\) and \(zz\) spectra. Use will be made of them in the calculations of section 5.

**TABLE II**

Fitted parameters for the \(A_x^c\) spectrum. The data are corrected for differing scattering efficiencies.

<table>
<thead>
<tr>
<th>Experiment on System I</th>
<th>(\omega_1)</th>
<th>(\Gamma_1)</th>
<th>(S_1)</th>
<th>(\omega_2)</th>
<th>(\Gamma_2)</th>
<th>(S_2)</th>
<th>(S_2/S_1)</th>
<th>(\Sigma \times 10^{-6})</th>
</tr>
</thead>
<tbody>
<tr>
<td>xx</td>
<td>48.8</td>
<td>7.6</td>
<td>2212</td>
<td>68.2</td>
<td>15.0</td>
<td>950</td>
<td>0.430</td>
<td>9.70</td>
</tr>
<tr>
<td>yy</td>
<td>49.0</td>
<td>8.0</td>
<td>4870</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.0</td>
<td>11.70</td>
</tr>
<tr>
<td>zz</td>
<td>48.0</td>
<td>6.7</td>
<td>1142</td>
<td>68.5</td>
<td>13.8</td>
<td>2083</td>
<td>1.82</td>
<td>12.41</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment on System II</th>
<th>(\omega_1)</th>
<th>(\Gamma_1)</th>
<th>(S_1)</th>
<th>(\omega_2)</th>
<th>(\Gamma_2)</th>
<th>(S_2)</th>
<th>(S_2/S_1)</th>
<th>(\Sigma \times 10^{-5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>xx</td>
<td>49.1</td>
<td>6.6</td>
<td>164</td>
<td>68.3</td>
<td>14.4</td>
<td>80.2</td>
<td>0.489</td>
<td>7.70</td>
</tr>
<tr>
<td>yy</td>
<td>48.1</td>
<td>7.4</td>
<td>356</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.0</td>
<td>8.24</td>
</tr>
<tr>
<td>zz</td>
<td>48.4</td>
<td>6.5</td>
<td>103</td>
<td>69.4</td>
<td>14.2</td>
<td>204</td>
<td>1.98</td>
<td>12.30</td>
</tr>
</tbody>
</table>

| cm\(^{-1}\) | cm\(^{-1}\) | cm\(^{-1}\) | cm\(^{-1}\) |

4. Group Theory

The crystal structure of \(C_{12}F_{10}\) has been determined by Neronova [9] and refined by Mackenzie et al. [10]. Other work on the substance relates to the properties of the molecule, the structure of which is shown in Figure 8. The angle between the rings is 120° in the crystal [10], and the molecule has point group 222 (\(D_2\)).
the axes in the figure identifies the representations of the point group. As for the
crystal, the space group is Fdd2(C14) with two molecules in the primitive cell, located
at sites of C2 symmetry, Figure 9. This is in contrast with biphenyl, C12H10, which is
monoclinic with planar molecules.

4.1. Internal modes of vibration of the C12F10 molecule
The possibility of low frequency internal modes in C12F10 has been treated by
Almenningen et al. [11] and Steele [12]. Steele gives a calculation, based however
on a planar molecule, which shows that perhaps four low frequency modes exist below
130 cm⁻¹. Most of the internal modes at frequencies higher than this have been re-
ported by Steele [12] and Steele et al. [13]; but nothing was reported of the modes of
lower frequency. As a subsidiary experiment to check on this, the Raman spectrum
of molten C12F10 was measured and the result is shown in Figure 10. A peak is ob-
served at 54 cm⁻¹ with a width of about 21 cm⁻¹, as determined by fitting, and we
suppose this to be due to the symmetric torsional mode of the molecule. This mode,
being infrared inactive, could not have been seen by Steele’s infrared techniques in
any case. (Massey and Steele [12], however, have observed a band at 60 cm⁻¹ in
the infrared spectrum of C12F5H2 in which it would be active.) The evidence then
definitely points to the existence of at least one low frequency internal mode, pro-

bably the torsional mode.

For the treatment here we take the molecule as two planar perfluorophenyl rings,
C6F5, each having C2v symmetry. The low frequency vibrations come about from the
twisting and bending of the C–C bond joining these relatively massive rings. The
modes of vibration of the individual rings are different in character from these and
have higher frequencies. They may be classified under the irreducible representations of $C_{2v}$ as:

$$
10A'^r + 3A'^r + 9B'^r + 5B'^r \\
+ (A'^r + B'^r + B'^r) \text{ pure translations,} \\
+ (A'^r + B'^r + B'^r) \text{ rigid rotations.}
$$

(4.1)

The superscripts $r$, $m$, and $c$ are necessary to distinguish between the notations of the point groups of the rings, molecules and crystals respectively.

Fig. 9. The crystal structure showing the relationship between the crystal and molecular axis systems.

In the actual molecule pairs of equivalent ring vibrations interact weakly to become vibrations of the molecule classified under $D_2$ symmetry as follows:

$$
2A'^r \rightarrow A'^m + B'^3, \\
2A'^r \rightarrow A'^m + B'^3, \\
2B'^r \rightarrow B'^m + B'^3, \\
2B'^r \rightarrow B'^m + B'^3.
$$

(4.2)

The frequencies of most of these modes are expected to occur above, say, 100 cm$^{-1}$. The rigid rotations and translations of the rings, however, combine to produce the remaining six modes which stretch, twist, and bend the molecule about the central C–C bond. These modes are classified as

$$
2A'^m + 2B'^m + 2B'^m.
$$

(4.3)

The $A'^m$ modes twist and stretch the molecule whereas the $B'^m$ and $B'^m$ modes bend it about the $z$ and $y$ axes respectively. Apart from the $A'^m$ stretching mode these are
presumably the low frequency modes not yet observed. Combining (4.1) and (4.2) the entire set of molecular vibrations transform as

\[ 15A''' + 16B'''_1 + 16B'''_2 + 13B'''_3. \]  

(4.4)

Proceeding now to the crystal, the internal modes of vibration are pairwise linear combinations of the modes of the two molecules in the primitive cell. If the modes interact only weakly, as is to be expected, their vibrations will change only slightly.

**TABLE III**

<table>
<thead>
<tr>
<th>Molecule $D_2$</th>
<th>Crystal $C_{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\begin{bmatrix} a &amp; b \ c &amp; d \end{bmatrix}$</td>
<td>$R^+ \rightarrow \begin{bmatrix} c^2a + s^2b \ s^2a + c^2b \end{bmatrix}$</td>
</tr>
<tr>
<td>$2 \times A'''$</td>
<td>$A''_1 + A''_2$</td>
</tr>
<tr>
<td>$\begin{bmatrix} e \ f \end{bmatrix}$</td>
<td>$R^+ \rightarrow \begin{bmatrix} 0 &amp; s \end{bmatrix}$</td>
</tr>
<tr>
<td>$2 \times B'''_2$</td>
<td>$B''_1 + B''_2$</td>
</tr>
<tr>
<td>$\begin{bmatrix} c &amp; s \ -s &amp; c \end{bmatrix}$</td>
<td>$s = \sin 38^\circ$</td>
</tr>
</tbody>
</table>

Table III shows how each of the different molecular vibrations are affected and how their scattering tensors transform in the crystal. This is helpful in deducing the polarisation dependence of the internal mode spectrum and relating it to the original molecular vibrations. Figure 11 summarises this discussion of the internal mode spectrum and shows that the ring-originated vibrations occur in nearby quartets, each component of which has a different symmetry and so appears in a different polarisation.

4.2. **THE LATTICE VIBRATIONS**

In the crystal the six external degrees of freedom of each of the molecules in the cell give rise to nine optical lattice vibrations at the zone centre, assuming rigid molecules.
These modes transform under $C_{2v}$ as

$$A_1^e + 2A_2^e + 3B_1^e + 3B_2^e.$$  \hspace{1cm} (4.5)

The symmetry coordinates and scattering tensors for these modes are shown in Table IV below. An important observation is that there is only one totally symmetric mode, $A_1^e$, predicted, and it involves only vibrations of the molecules about the $z$ axis.

4.3. Comparison with the spectra

The internal vibration spectrum is not the main interest here, but it is necessary as far as possible to eliminate internal vibrations from the observed spectra to clarify the picture of the lattice vibrations.

Referring to Table I, and recalling the observation in Section 3.1 that ring-originated internal vibrations should occur in quartets of lines appearing in different polarisations, we see that this is indeed the case for the modes observed in the region above 130 cm$^{-1}$. We conclude that these are indeed ring-originated molecular vibrations.

Fig. 10. The Raman spectrum of the melt: dotted line shows fit.
Symmetry coordinates referred to the molecular axes. We relate the coordinate system of molecule 2 to that of molecule 1 by the $\sigma(xz)$ glide plane. Acoustic modes are discarded, and the coordinates under $\phi$ refer to the internal torsional mode of the molecule involving the interplanar angle

<table>
<thead>
<tr>
<th>$x^1$</th>
<th>$y^1$</th>
<th>$z^1$</th>
<th>$\theta^1_x$</th>
<th>$\theta^1_y$</th>
<th>$\theta^1_z$</th>
<th>$\delta^1$</th>
<th>$x^2$</th>
<th>$y^2$</th>
<th>$z^2$</th>
<th>$\theta^2_x$</th>
<th>$\theta^2_y$</th>
<th>$\theta^2_z$</th>
<th>$\phi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1^1$</td>
<td>$\gamma$</td>
<td>$\delta$</td>
<td>$\gamma$</td>
<td>$\delta$</td>
<td>$-c$</td>
<td>$-\gamma$</td>
<td>$-\delta$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_2^1$</td>
<td>$c$</td>
<td>$\gamma$</td>
<td>$\delta$</td>
<td>$-c$</td>
<td>$-\gamma$</td>
<td>$-\delta$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_1^1$</td>
<td>$b$</td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$-b$</td>
<td>$\alpha$</td>
<td>$-\beta$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_2^1$</td>
<td>$a$</td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$-a$</td>
<td>$-\alpha$</td>
<td>$\beta$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Scattering tensors:

\[
\begin{bmatrix}
  a & b & c \\
  d & e & f \\
  f & g & h
\end{bmatrix}
\]

**Fig. 11.** Internal ring vibrations in the molecular and crystal environments.
In the frequency region below 130 cm\(^{-1}\) there is first of all a weak feature of dubious origin appearing at 126 cm\(^{-1}\). For this we have no plausible assignment. Below this the observed modes fall into tightly packed bands in the region 30 to 70 cm\(^{-1}\). More peaks are observed in these spectra than the numbers predicted for lattice vibrations alone (4.5). Therefore, although all of these may be definitely assigned with respect to their symmetry, it is not clear as to what their origins are; lattice or molecular vibrations. There are ten expected low frequency internal vibrations, ignoring the two involving C–C stretch, and these must be presumed to overlap the lattice vibration spectrum. The combined lattice and low frequency internal vibration spectrum would then include the following modes

\[
5A^e_1 + 6A^e_2 + 5B^e_1 + 5B^e_2.
\]  

(4.6)

If we turn specifically to the \(A^e_1\) spectrum of \(xx\), \(yy\) and \(zz\) polarisations, we see from Figures 2 that there are two modes clearly visible and that neither of them has the predicted character of the single \(A^e_1\) lattice mode, that is, visible in \(xx\) and \(yy\) but not in \(zz\). In fact, the mode at 66.5 cm\(^{-1}\) is seen in \(xx\) and \(zz\) but not in \(yy\). This contrast with the behaviour predicted of separate lattice and molecular vibrations leads us to believe that the vibrations in the crystal are a combination of the two. This then we take into account in our model.

We suppose that the single totally symmetric lattice vibration mixes with the symmetric torsional mode of the molecule. If the latter mode has a differential polarisability at least comparable to the lattice vibration, there would be a significant redistribution of the intensities in the \(xx\), \(yy\) and \(zz\) spectra caused by interference. We presume it is the torsional mode which is involved because the only other possibility, a \(B^m_1\) bending mode, could only affect the distribution in the \(xx\) and \(yy\) spectra: it has no contribution to the \(zz\) spectrum. In the \(xx\) and \(yy\) spectra there is actually observed a very weak shoulder at 54 cm\(^{-1}\). This may well be due to a \(B^m_1\) mode, but we conclude that it is not included in the mixing since there is no trace of it in the \(zz\).

5. The Polarisability Model

The equations of Section 2 apply to a rigid molecule. The evidence of the observed spectra is that the molecule cannot be treated as rigid and we here derive a polarisability model specifically for C\(_{12}\)F\(_{16}\) to take into account the torsional \(A^m\) mode of vibration. The model is based on the assumption that to some extent the molecule may be treated as a pair of independent phenyl rings. We justify this after the fact by the satisfactory description it gives of the observed \(A^e_1\) spectra. The \(A^e_2\), \(B^e_1\), and \(B^e_2\) spectra are however too complicated to treat in such detail and they are discussed no further.

The two halves of the molecule are assumed to make separate and identical contributions to the polarisability of the form

\[
\alpha^r = \begin{bmatrix}
\alpha_{xx}^r & \alpha_{xy}^r & \alpha_{xz}^r \\
\alpha_{xy}^r & \alpha_{yy}^r & \alpha_{yz}^r \\
\alpha_{xz}^r & \alpha_{yz}^r & \alpha_{zz}^r
\end{bmatrix},
\]  

(5.1)
referring to principal axes $x$ along the $C-C$ bond, $z'$ perpendicular to the plane of the ring, and $y'$ lying in it. The two rings are rotated by $\pm \phi/2$ about the $x$ axis respectively giving individual contributions to the molecular polarisability of

$$\alpha(\pm \phi) = \begin{bmatrix}
\alpha & 0 & 0 \\
0 & \alpha_2 + \cos \phi \alpha_3 & \pm \sin \phi \alpha_3 \\
0 & \pm \sin \phi \alpha_3 & \alpha_2 - \cos \phi \alpha_3
\end{bmatrix},$$

(5.2)

with

$$\alpha_1 = \alpha_{xx}, \quad \alpha_2 = \frac{1}{2}(\alpha_{yy} + \alpha_{zz}), \quad \alpha_3 = \frac{1}{2}(\alpha_{yy} + \alpha_{zz})$$

The total contribution to $\alpha_m$ the polarisability of the molecule, is the sum of the two parts for $+\phi$ and $-\phi$:

$$\alpha_m = \begin{bmatrix}
\alpha_1 & \alpha_2 + \cos \phi \alpha_3 \\
\alpha_2 - \cos \phi \alpha_3 & \alpha_3
\end{bmatrix}.$$  

(5.3)

This crude model gives an estimate of the $\phi$ dependence of $\alpha_m$ without the introduction of extra unknown parameters. Analogously to (2.6) we can write down equations for the polarisability differential, this time including $\phi$.

$$\delta \alpha = \begin{bmatrix}
\sin 2\theta \alpha_0 & - \sin 2\theta \alpha_0 & 0 \\
\alpha_\phi (1 - \cos 2\theta) & \alpha_\phi (1 + \cos 2\theta) & 2\alpha_\phi \\
\cos 2\theta \alpha_0 & 0 & 0 \\
\sin 2\theta \alpha_\phi & 0 & 0
\end{bmatrix} \begin{bmatrix}
\delta \theta \\
\delta \phi \\
\delta \theta \\
\delta \phi
\end{bmatrix}.$$

(5.4)

This has been separated according to our rule for more than one molecule into contributions to the $A_1^c$ and $A_2^c$ spectra, but only the former contribution is of interest. The parameters $\alpha_\phi$ and $\alpha_\phi$ replace $\alpha_1$, $\alpha_2$ and $\alpha_3$ as unknowns, $2\theta$ is $76^\circ$ and $\phi$ is $120^\circ$ [10].

Eigenvectors for the coupled internal-external modes in the $A_1^c$ spectrum may be defined as follows:

$$e_j = \frac{e_j^1}{\sqrt{I_{zz}}} = \frac{e_j^3}{\sqrt{I_{xx}}} \left(\frac{\delta \phi}{2}\right),$$

(5.5)

for $j=1$ and 2. Since these eigenvectors are orthogonal we have

$$e_j^1 = e_j^2 = c \quad e_j^1 = - e_j^2 = - s.$$  

(5.6)
where \( s \) and \( c \) are the sine and cosine of some angle. Applying the equations of Section 2 to (5.4) with the eigenvectors so defined results in expressions for the experimental intensity parameters of (3.2) as follows:

\[
S_1 (\beta \beta) = \frac{\eta}{\omega_1} \left( c \cos \beta \theta - s \sin \beta \theta \right)^2 \\sqrt{I_{zz}} \div \sqrt{I_{xx}},
\]

\[
S_2 (\beta \beta) = \frac{\eta}{\omega_2} \left( s \cos \beta \theta + c \sin \beta \theta \right)^2 \\sqrt{I_{zz}} \div \sqrt{I_{xx}}. \tag{5.7}
\]

When \( c \) is near unity and \( s \) is small, the modes are unmixed and only one peak is seen in the \( zz \) spectrum since \( \delta \theta^2_{zz} \) equals zero. Otherwise there will generally appear two peaks in the \( zz \) spectrum as is indeed the case here. Further, there may be values of \( s \) and \( c \) such that one of the terms in brackets in (5.7) vanishes: then only one peak is observed as in \( yy \).

We now determine the values of the parameters in (5.7) which are in accord with the observed spectra. The ratios of the \( S \) factors \( S_2 (\beta \beta)/S_1 (\beta \beta) \) are different in the \( xx \), \( yy \) and \( zz \) spectra and we may therefore derive equations for these parameters from this. Firstly, using the fact that \( \delta \theta^2_{zz} \) is zero we find from (5.4):

\[
\frac{s}{c} = \frac{\omega_2}{\omega_1} \sqrt{\frac{S_2 (zz)}{S_1 (zz)}}. \tag{5.8}
\]

Secondly, since \( S_2 (yy) \) is observed to be effectively zero, there must be cancellation of terms in (5.7) giving

\[
\frac{\alpha_0}{\alpha_\phi} = -\frac{c}{s} \sqrt{\frac{I_{zz}}{I_{xx}}} \frac{\delta \theta^2_{yy}}{\delta \theta^2_{xy}} = -\frac{c}{s} \sqrt{\frac{I_{zz}}{I_{xx}}} \left( \frac{1 + \cos 2\theta}{\sin 2\theta} \right). \tag{5.9}
\]

The numerical values for these parameters, as determined from the results of the two experiments given in Table 11 and a value of 2.857 for \( I_{zz}/I_{xx} \), are then

\[
c/s = -1.93 \quad \text{and} \quad -2.0, \quad \alpha_0/\alpha_\phi = 4.16 \quad \text{and} \quad 4.32. \tag{5.10}
\]

With these values we may calculate from (5.7) the ratio \( S_2 (xx)/S_1 (xx) \) and compare it directly with the observed value. We have not yet used information from the \( xx \) spectrum in the calculations and this therefore provides a good consistency check. The calculated ratios are 0.51 and 0.47 respectively: this agrees very well with the observed ratios 0.43 and 0.49 encouraging us to believe that our model is along the right lines.

The results for the sum rule are not so encouraging. We have

\[
\Sigma (\beta \beta) = \omega_1^2 S_1 (\beta \beta) + \omega_2^2 S_2 (\beta \beta) = \frac{\left( \delta \theta^2_{\phi} \right)^2}{I_{zz}} + \frac{\left( \delta \theta^2_{\phi} \right)^2}{I_{xx}}. \tag{5.11}
\]

Using the parameters of (5.10) this gives ratios for \( \Sigma (xx) : \Sigma (yy) : \Sigma (zz) \) of 1 : 1.15 : 0.64.
The appearing which ring described correlations and the ability. \( E(zz) \) of 1:1.14:0.59 and 1:1.17:1.60. \( \Sigma(xx) \) and \( \Sigma(yy) \) are in the correct sort of ratio but \( \Sigma(zz) \) is much larger than calculated. This result stresses the unreliability of intensity correlations and that the oriented gas model accounts only crudely for the polarizability.

6. Conclusions

The spectrum of vibrations of the molecular crystal perfluorobiphenyl may be described in terms of high frequency ring originated vibrations, and low frequency ring-ring vibrations and lattice vibrations. Although the first category of vibrations, which have frequencies above 100 cm\(^{-1}\), are clearly discernible as quartets of lines appearing in different polarisations, the low frequency internal vibrations and lattice vibrations overlap and cannot be distinguished. The low frequency \( A_f \) spectrum has however been unravelled and described in terms of a mixed symmetric lattice vibration and a torsional molecular vibration. An oriented gas model has been found to satisfactorily account for the observed intensities of the two strong peaks in the spectrum and give numerical values for the eigenvector of the modes. The numbers obtained \( c^2 \) and \( s^2 \) represent the division of energy between the internal and external components of the modes so that we may state our result in the following way: 79–80\% of the energy of the \( A_f \) mode at 48 cm\(^{-1}\) is contributed by the external vibration and 21–20\% is contributed by the internal vibration. For the mode at 68 cm\(^{-1}\) the reverse holds. The higher frequency mode is therefore still primarily of internal character and the lower frequency mode still of external character. The extent of the coupling is enough to greatly change the spectrum from that expected in the uncoupled case, even though the internal mode has a relatively smaller polarisability. The oriented gas approximation appears to be successful for describing relative intensities in spectra of the same polarisation but for different polarisations there are discrepancies in correlated intensities. Some of the discrepancy is attributable to error in correlation of the experimental results, but we feel that it mainly originates from the fact that the macroscopic polarisation is not accounted for. A possible extension of the model to deal with this has been put forward [8].

The coupling of lattice and internal modes shows that the molecule is certainly non-rigid; any lattice dynamical calculation would have to take this into account. A possible way of doing this would be to treat the crystal as if it comprised four independent phenyl rings rather than two molecules. The usual forces [14] between all the rings would be considered, and the bonded rings would be taken into account through an additional force to represent the C–C bond and conjugation interaction [15].

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