THEORY OF
LIBRATIONAL MOTION IN THE
α PHASE OF NITROGEN

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By

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SCOPE AND CONTENTS:

Librational motion in the α phase of solid nitrogen is studied theoretically, assuming the crystal structure to belong to the space group Pa3 and ignoring the translational motions entirely. A general expansion is written down for an arbitrary nonsingular potential function of the positions of two nitrogen molecules, and methods are presented for obtaining the expansion coefficients for some particular potential model. The crystal Hamiltonian is written down and the mean field approximation is briefly discussed. The eigenstates of the mean-field Hamiltonian, the oblate spheroidal wave functions, are shown to correspond formally to the eigenstates of the two-dimensional isotropic harmonic oscillator, and this correspondence is exploited to define boson creation and annihilation operators for excitations of a single molecule. The crystal Hamiltonian is second-quantized in terms of these operators, and the bilinear terms which result are diagonalized by an RPA treatment which is an extension of one given by Raich and Etters. The uniqueness of the present diagonalization scheme is established and explicit expressions are developed for the three-operator terms in the Hamiltonian, which are essential for the later consideration of spin-lattice relaxation. Numerical calculations of the Raman frequencies show that the potential models proposed by Kohin and by Raich and Mills do not exhibit the correct anisotropic behaviour, the computed Raman frequencies being 57% to 103% too high in the first case and 28% to 53% too high in the second. Without taking account of libron-libron interactions, it is possible to obtain temperature-dependent Raman frequencies, but this dependence is negligibly weak. The temperature dependence of the nuclear quadrupole resonance frequency is not well reproduced by the theory, although a potential which is constructed to fit the Raman frequencies is more successful than an a priori potential. Using an approach due originally to Van Kranendonk and Walker, an a priori theory of quadrupolar spin-lattice relaxation is developed. The direct and first-order Raman processes, and a process involving a three-libron vertex, are shown not to contribute to relaxation. The anharmonic Raman process is considered, using first-order perturbation theory and the expressions for the three-operator terms. The relaxation time is found to be in fair agreement with experiment above about 10 K, and it is argued that a direct process involving phonons would be the dominant relaxation mechanism at low temperatures.

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Finally, I owe a general and major debt of gratitude to my father, for showing me by his example the meaning of scholarship.

A. M. D. G.

qui fecit coelum et terram

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CHAPTER 1

INTRODUCTION

1.1 Background

At temperatures below 35.6 K, under its own vapour pressure, solid molecular nitrogen exists as an ordered cubic phase, known as the α phase, in which the mean orientations of the molecules lie along the four body diagonals of the cube (Jordan et al., 1964; Venables 1970). At high pressures (above 3500 atm. at low temperatures), the stable phase is an orientationally ordered tetragonal structure, the γ phase (Mills and Schuch 1969; Schuch and Mills 1970). Since the nitrogen molecule is not spherical, it can rotate as well as vibrate, and in the ordered phases, collective excitations of the rotational degrees of freedom will arise in which the molecules in the crystal undergo angular oscillations (librations) about their equilibrium orientations. We shall refer to these collective excitations as librons. In their physical origin, librons are therefore completely analogous to phonons, but there are some significant formal differences which will be brought out later.

The properties associated with the librons provide a sensitive test of models proposed for the energy of interaction between two nitrogen molecules (the intermolecular potential). This potential can be conceptually divided into two parts, an isotropic part (i.e., one not depending on the orientation in space of either molecule, but only on the distance between the centres of the molecules) and an anisotropic part (all the rest, depending on the orientation of one or both molecules, as well as their distance apart). It is evident that the orientational ordering of the α and γ phases, and consequently the existence of librons, must be due entirely to the anisotropic part of the potential, in the sense that these phenomena would not occur if the potential were completely isotropic. The most precise information about the anisotropic part of the potential comes from measurements of the properties of the librons. Many other properties of nitrogen give information about the intermolecular potential, but they tend to be sensitive mainly to the isotropic part and to give little information about the anisotropic part. For this reason it is of great interest to have a reliable theory of librational motion in nitrogen crystals in order to extract the information contained in the experimental data.

1.2 Object of the Calculation

A number of calculations of libron frequencies for the α crystal phase occur in the literature. These calculations may be divided into two main groups: those that employ some standard form of lattice dynamics, either harmonic lattice dynamics or self-consistent phonon theory, and which must therefore approximate the intermolecular potential by some sum of potentials between atoms (Kuan et al. 1970; Raich et al. 1974; Kjems and Dolling 1974; Zunger and Huler 1974), and those that employ more general intermolecular potentials and which consequently have to develop a suitable lattice dynamics (Goodings and Henkelman 1971; Jacobi and Schnepp 1972; Raich 1972; Harris and Coll 1972; Dunmore 1972; Mandell 1974).

The former type of calculation has two important advantages; first, the relevant theories of lattice dynamics, and programs embodying them, are well developed; and second, both phonon and libron spectra, and their mixing, are calculated together. The disadvantages stem from the fact that neither harmonic lattice dynamics nor self-consistent phonon theory is capable of handling a crystal parts of which are rotating as units, and it is therefore necessary to treat the nitrogen molecule as comprising two nitrogen atoms, with the interaction between two molecules being approximated as a sum of central forces between the constituent atoms. There does not appear to be any analysis of how well such a sum can approximate realistic intermolecular potentials, such as the quadrupole-quadrupole potential, but physically such a picture is unappealing. If the outer contours of the electron density calculations by Bader et al. (1967) are taken as a guide, a nitrogen molecule appears externally as a rather featureless prolate spheroid, in which the positions of the individual atoms cannot be discerned. Picturesquely expressed, one might say that atom-atom potentials implicitly regard the nitrogen molecule as looking like a dumb-bell, whereas in fact it looks much more like a football. An important technical problem with these potentials is that the two atoms belonging to a single molecule must be bound together with an additional intramolecular potential. When the molecules are as far apart as they are in the α phase, the intramolecular potential is very much stronger than the intermolecular potential, so that the two atoms in a molecule are very strongly correlated in their motion, as they must be. But, given the approximate nature of any lattice dynamics, the presence of such a strong potential could conceivably have spurious residual effects on the translational and librational modes. Indeed, Zunger and Huler (1974) found substantial shifts in the libron frequencies at zero wavevector when the atomic positions in the crystal were very slightly relaxed. Compared to the magnitude of the intermolecular potential, these shifts appear to be quite remarkably large, and it may be that they are an effect of the intramolecular potential.

We may remark also on a further objection to the use of conventional phonon theories in treating librational motion in α-nitrogen. This objection follows from the relatively large amplitude of the librational oscillations. Goodings and Henkelman (1971) gave a semi-classical estimate of 17.9° for the root-mean-square angular displacement of a molecule at zero temperature, and the estimates to be developed in this thesis are very close to that figure. This is such a large amplitude of motion that the harmonic approximation of conventional phonon theory is open to serious question. It is also sufficiently large that there is an appreciable probability of the molecule turning end-over-end: in an atomic description, there is a significant exchange probability for the two atoms in a molecule. The difficulties of large-amplitude motion and strongly correlated motion of the two atoms in a molecule can be largely overcome in a self-consistent phonon calculation with a Jastrow correlation factor, as has been done by Raich et al. (1974). However, the effects of exchange on the crystal wave function cannot be dealt with except by an additional exchange calculation.

The alternative approach is to use a molecule-molecule form for the intermolecular potential. By ignoring the internal structure of the molecule, this eliminates the strong intramolecular potential and the associated correlation problems. It can be cast, as here, in a form which does not assume the angular displacement to be small. Since the molecule is treated as a unit which can rotate, the exchange problem is handled automatically. (In a crystal of molecules as heavy and as far apart as the one we are dealing with, exchange of atoms belonging to different molecules is a completely negligible process.) However, one must develop a special lattice dynamics. Goodings and Henkelman (1971) presented a classical harmonic theory; Jacobi and Schnepp (1972) and Raich (1972) developed an exciton-like formalism which proved not to reduce to classical lattice dynamics in the appropriate limit (Dunmore 1972); and Dunmore (1972), Harris and Coll (1972) and Mandell (1974) have presented, in various guises, theories which are essentially versions of the random-phase approximation (Fetter and Walecka 1971). The present work is in this latter tradition, but is cast in such a way that the libron operators are exact bosons and that an explicit procedure is provided for proceeding beyond the random-phase approximation to consider libron-libron interactions. As an example of the power of the scheme, we calculate an effect (the spin-lattice relaxation of the nuclear quadrupole resonance) for which libron-libron interactions are essential and for which no a priori theory existed.

The essential disadvantage of the scheme is that the lattice vibrations, the phonons, are not included in the calculation (nor, to date, in any other calculation using molecule-molecule potentials). Although it is clear that this can be done, and we shall draw attention to the points at which the phonons would be incorporated in a complete lattice dynamics, such inclusion would seriously complicate the already somewhat involved formalism. The neglect of the phonons should not have a critical effect on calculations of effects which depend essentially on librational motion, but because phonons and librons mix together in general (so that the elementary excitations away from zero wavevector are neither phonons nor librons, but have both a vibrational and a librational character), we shall find that our calculations do show non-negligible discrepancies from experimental data which can be attributed to effects of the neglected phonons.

The objects of the calculation may be summarized as follows: to develop a formalism for treating librational motion in the α phase of nitrogen using arbitrary molecule-molecule potentials; to apply the formalism to calculate effects which depend essentially on the librons; and to investigate the validity of various model potentials.

1.3 Organization of the Thesis

In Chapter 2 we discuss the intermolecular potential. We present an expansion for an arbitrary potential and discuss the computation of the expansion coefficients for an arbitrary potential model, and describe some model potentials which appear in the literature.

Chapter 3 is concerned with employing the expansion for the intermolecular potential to generate the Hamiltonian for the crystal, and with discussing the motions of individual molecules in an independent-particle view of the crystal (the mean field model). A correspondence is shown between these single-molecule states and the states of a two-dimensional harmonic oscillator. This correspondence is exploited to define creation and annihilation operators for excitations of a single molecule.

In Chapter 4, we express the crystal Hamiltonian in terms of single-molecule creation and annihilation operators and present a series of transformations which convert these to libron creation and annihilation operators. We point out that the spheroidal wave function parameter, which characterizes the single-molecule states and is not otherwise determined, may be chosen so as to minimize the free energy of the crystal at each temperature, and that this process provides a mechanism for temperature-dependent libron frequencies even in a non-interacting libron model. We then briefly discuss the nature of the crystal state in which no librons are present, and finally develop explicit formulae for the three-operator terms in the crystal Hamiltonian.

In Chapter 5 we develop the theory of quadrupolar relaxation of the nuclear spins, and, using the three-operator terms developed in the preceding chapter, calculate the spin-lattice relaxation time.

To this point, the development is entirely formal. Numerical results are mentioned rarely and in passing. In Chapter 6, numerical results are presented for the theory, and are compared, where appropriate, with the results of other calculations appearing in the literature, and with experiment. Chapter 7 summarizes the theory that has been developed and draws conclusions as to the completeness of the theory and the status of the potential models considered.

The development, particularly in Chapters 4 and 5, is necessarily highly mathematical, and because of the complexity of the problem the notation is distinctly intimidating. Where an understanding of some mathematical development is not directly essential to an understanding of the physics, the author has not hesitated to deposit the offending material in an Appendix, where it may be consulted by any reader unfortunate enough to be required to read it. It is hoped that readers willing to take such material on faith will find the coherence of the main text to be enhanced by the absence of this material. In addition, in Chapters 4 and 5 and Appendices D and E, the author has introduced some conventions to simplify the appearance of the formulae required. These conventions are described early in Chapter 4. The reader may readily verify that an equation such as (4.37) would appear many times more complex than it does were these notational conventions not employed.

CHAPTER 2

THE INTERMOLECULAR POTENTIAL

2.1 Expansion of an Arbitrary Potential

We begin this chapter by considering the most general possible expansion of an arbitrary non-singular potential function of the position of two homonuclear nitrogen molecules. This expansion will be valid at the intermolecular distances of interest to us, but several of the potential models to be considered exhibit singularities at shorter distances, and the expansion will then diverge.

Following where possible the notation of Goodings and Henkelman (1971), we express the orientation of two molecules by sets of polar angles ω_1 and ω_2, taking the polar axis to be the line from the centre of molecule 1 to the centre of molecule 2. If R is the distance between the centres, then the interaction energy $V(R,\omega_1,\omega_2)$ can be expressed in the form

$$V(R,\omega_1,\omega_2) = \sum_{\ell_1=0}^{\infty} \sum_{m_1=-\ell_1}^{\ell_1} \sum_{\ell_2=0}^{\infty} \sum_{m_2=-\ell_2}^{\ell_2} A(R,\ell_1,\ell_2,m_1,m_2) \times Y_{\ell_1 m_1}(\omega_1) Y_{\ell_2 m_2}(\omega_2) \qquad (2.1)$$

where the functions $Y_{\ell m}$ are the spherical harmonics in the usual convention (Edmonds 1957; Messiah 1958).

The symmetries of the nitrogen molecules impose severe restrictions on the number of independent nonzero coefficients A. Since each molecule has inversion symmetry about its centre, the coefficients are nonzero only if ℓ_1 and ℓ_2 are even. The potential energy is unaltered if the pair of molecules is rotated about the polar axis, and so $m_2 = - m_1$. Further, the potential is real, so that

$$A(R,\ell_1,\ell_2,m_1,-m_1)^* = A(R,\ell_1,\ell_2,-m_1,m_1) \tag{2.2}$$

where the star denotes complex conjugation. The potential is invariant if the system is reflected in any plane containing the polar axis, and it is then trivial to show that

$$A(R,\ell_1,\ell_2,m_1,-m_1) = A(R,\ell_1,\ell_2,-m_1,m_1) \quad . \tag{2.3}$$

These latter two properties imply that all the A coefficients are real. Lastly, the potential is invariant if molecules 1 and 2 are renumbered (i.e., if R is replaced by - R). This leads to the relation

$$A(R,\ell_1,\ell_2,m_1,-m_1) = A(R,\ell_2,\ell_1,-m_1,m_1) \quad . \tag{2.4}$$

The first few nonzero terms in the expansion (2.1) may then be written

$$
\begin{aligned}
V(R,\omega_1,\omega_2) = {} & B_0(R) + B_1(R)[Y_{20}(\omega_1) + Y_{20}(\omega_2)] \\
& + \sum_{\mu=-2}^{2} A_\mu(R) Y_{2\mu}(\omega_1) Y_{2-\mu}(\omega_2) \\
& + D(R)[Y_{40}(\omega_1) + Y_{40}(\omega_2)] \\
& + \sum_{\mu=-2}^{2} E_\mu(R)[Y_{4\mu}(\omega_1) Y_{2-\mu}(\omega_2) \\
& + Y_{2-\mu}(\omega_1) Y_{4\mu}(\omega_2)] \\
& + \sum_{\mu=-4}^{4} F_\mu(R) Y_{4\mu}(\omega_1) Y_{4-\mu}(\omega_2) + \ldots \qquad (2.5)
\end{aligned}
$$

where $A(R,0,0,0,0) = 4\pi B_0(R)$, $A(R,2,0,0,0) = A(R,0,2,0,0) = \sqrt{4\pi}\, B_1(R)$, and so forth. All the coefficients in (2.5) are real, and they obey the symmetries $A_{-\mu}(R) = A_\mu(R)$, $E_{-\mu}(R) = E_\mu(R)$ and $F_{-\mu}(R) = F_\mu(R)$. By writing the expansion coefficients as asymptotic series in powers of R^{-1}, one may generate a multipole expansion similar to that presented by Mandell (1974). However, we do not take that step, since it offers no advantages in the present problem.

We now consider the determination of the coefficients in (2.5). Suppose that, for some fixed value of R, the potential $V(R,\omega_1,\omega_2)$ is known for various orientations, either from theoretical calculations or from some phenomenological model. The expansion coefficients corresponding to that particular value of R may be found in either of two ways.

If the potential is known at some specified set of orientations $\{\omega\} \equiv \{(\omega_1,\omega_2)\}$, one may minimize the quantity

$$\Delta = \sum_{\omega} \{V(\omega_1,\omega_2) - B_0 - B_1[Y_{20}(\omega_1) + Y_{20}(\omega_2)] - \sum_{\mu=-2}^{2} A_\mu Y_{2\mu}(\omega_1)Y_{2-\mu}(\omega_2) - \ldots\}^2 \quad (2.6)$$

with respect to the coefficients B_0, B_1, etc. (Since the radial dependence is not interesting, we have suppressed the argument R.) This is a conventional least-squares fitting procedure, which yields a set of linear equations in the desired coefficients.

If the potential energy may be calculated at any desired orientations, one may take advantage of the orthonormality of the spherical harmonics to write

$$A(\ell_1,\ell_2,m_1,-m_1) = \int d\omega_1 \int d\omega_2\, Y^*_{\ell_1 m_1}(\omega_1) Y^*_{\ell_2 -m_1}(\omega_2) \times V(\omega_1,\omega_2) \quad (2.7)$$

By the symmetries of V discussed above, one of the azimuthal integrals may be performed at once, and the remaining three-fold integrals may be restricted to the ranges $0 \leq \theta_1 \leq \frac{\pi}{2}$, $0 \leq \theta_2 \leq \frac{\pi}{2}$, $0 \leq \phi_2 \leq \pi$. These integrals may be evaluated numerically as three successive one-dimensional integrals.

As an example of the results obtained by different techniques, we have used the hard-core potential model of Raich and Mills (1971), a physical description of which will be given presently. The values of the expansion coefficients, at the nearest-neighbour distance appropriate to the α phase of nitrogen, are shown in Table 1. Various methods of computation were used, in an effort to determine the best method of evaluating the coefficients. This may be gauged by inspection of Table 1, using the consistency of various sets of results as a guide. The most accurate method is undoubtedly the use of a ten-point Gaussian integration formula to perform each of the one-dimensional integrals. This requires knowledge of the potential energy at 1000 orientations. However, the use of a five-point Gaussian formula gives results in generally close agreement with those from the ten-point formula, and a four-point formula is adequate for most of the larger coefficients. Fitting at the 61 special orientations mentioned in Table 1 is satisfactory for the A_μ coefficients, but not for some of the higher coefficients, while fitting at a set of 50

TABLE 1

EXPANSION COEFFICIENTS FOR THE RAICH-MILLS POTENTIAL MODEL, USING VARIOUS METHODS OF CALCULATION.

The intermolecular distance is 3.99 Å.

Coefficients are in cm^{-1}.

I. 10-point Gauss integration formula.

II. 5-point Gauss formula.

III. 4-point Gauss formula.

IV, V. Fits to different sets of 50 orientations chosen at random.

VI. Fit to the 61 distinct orientations which occur in the set $\theta_1 = 0, 30°, 45°, 60°, 90°$; $\phi_1 = 0$; $\theta_2 = 0, 30°, 45°, 60°, 90°$; $\phi_2 = 0, 30°, 45°, 90°, 143°, 180°$.

	I	II	III	IV	V	VI
B_0	-79.3	-79.3	-79.3	-79.5	-78.5	-79.8
B_1	56.7	56.7	56.6	57.5	60.2	56.4
A_0	290.5	290.5	289.9	288.7	298.1	292.7
A_1	116.1	116.1	116.4	118.9	121.9	113.4
A_2	14.7	15.0	11.8	16.1	18.2	15.3
D	19.6	19.6	18.8	20.7	20.2	20.2
E_0	37.0	36.8	35.0	41.5	39.1	45.5
E_1	10.4	10.5	11.0	12.5	14.2	11.0

TABLE 1 - continued

	I	II	III	IV	V	VI
E_2	1.1	1.1	0.6	-2.5	4.3	1.4
F_0	10.3	10.2	9.0	16.2	12.3	20.5
F_1	4.3	4.4	4.9	5.6	2.6	7.1
F_2	0.9	0.9	0.8	3.8	18.5	0.5
F_3	0.1	1.6	-11.4	2.3	9.7	0.9
F_4	0.0	-17.3	109.0	3.0	0.2	0.2

orientations chosen at random gives results which are not particularly accurate and which vary considerably if a new set of random orientations is selected. Except as otherwise noted in Chapter 6, calculations with model potentials were performed with a five-point Gaussian formula, since this appears to give satisfactory results without requiring a substantial amount of computer time.

2.2 Choice of a Potential Model

Obviously the most satisfactory potential to use for the lattice dynamics of nitrogen would be one derived from a reliable molecular orbital calculation. Such calculations now appear in the literature for hydrogen (England et al. 1974; and references therein) but not, to the author's knowledge, for nitrogen. Santry and Middlemiss (1974) performed such a calculation for the energy of an N_2-N_2 dimer at an intermolecular distance of 3.99 Å, using the CNDO (complete neglect of differential overlap) approximation of molecular orbital theory (Pople et al. 1965; Pople and Beveridge 1970). Unfortunately, the results of these calculations indicate that the two molecules have the lowest energy when lined up end-to-end, and all the A_μ coefficients turn out to be negative. This contrasts strikingly with the behaviour of a pair of quadrupolar charge distributions, which have the highest energy when lined up end-to-end, and for which all the A_μ coefficients are positive (Goodings and Henkelman 1971). The effect is that the calculations of Santry and Middlemiss would require the α-phase crystal structure to be unstable against reorientation of any molecule, and so we do not consider them further.

From the plethora of model potentials appearing in the literature (Kohin 1960; Ron and Schnepp 1967; Kuan et al. 1970; Raich and Mills 1971; Jacobi and Schnepp 1973; Kjems and Dolling 1974) we make a selection by rejecting all those which can be written as a sum of atom-atom potentials. This procedure is justified on the grounds that such potentials can be treated by standard theories of lattice dynamics (Born and Huang 1954; Werthamer 1969). There remain three model potentials: the quadrupole-quadrupole potential, the Kohin (1960) potential, and the potential of Raich and Mills (1971). We now consider these in turn.

The simplest model potential is obtained by assuming that the interaction between two nitrogen molecules is due entirely to the electrostatic energy of their charge distributions. Since the nitrogen molecule does not have a permanent dipole moment, this electrostatic energy is essentially the interaction energy of the two quadrupole moments. For this model of interacting point quadrupoles, the coefficients A_μ may be determined analytically (Goodings and Henkelman 1971), with the result

$$A_0 = \frac{24\pi}{5} Q^2/R^5 \quad , \quad A_1 = \frac{16\pi}{5} Q^2/R^5 \quad , \quad A_2 = \frac{4\pi}{5} Q^2/R^5 \tag{2.8}$$

where Q is the molecular quadrupole moment. All other expansion coefficients are zero. The currently accepted value of Q, derived from gas-phase data, is $Q = -1.4 \times 10^{-26}$ esu (Buckingham et al. 1968), but other values, notably $Q = -1.52 \times 10^{-26}$ esu (Stogryn and Stogryn 1966) have been used in many calculations in the literature.

The Kohin and Raich-Mills potentials contain, in addition to the quadrupole-quadrupole interaction, two further interaction mechanisms, namely the Van der Waals dispersive interaction and the repulsion due to overlap of the electron clouds. Because the polarizability of the nitrogen molecules is anisotropic, the dispersive interaction leads to an anisotropic attraction, considered by De Boer (1942) and Kohin (1960). Again, analytic expressions for the A_μ may be obtained, and are

$$A_0 = -\frac{48\pi}{5}\varepsilon\kappa^2(\sigma/R)^6 \qquad A_1 = -\frac{32\pi}{5}\varepsilon\kappa^2(\sigma/R)^6$$
$$A_2 = -\frac{16\pi}{5}\varepsilon\kappa^2(\sigma/R)^6 \quad . \tag{2.9}$$

Here ε is the strength parameter of the dispersive interaction, σ is its range, and κ is the anisotropy of the molecular polarizability.

It may be remarked here that the R^{-6} form of the dispersive forces, assumed by De Boer and subsequent workers, is not correct except at large separations. Jacobi and Csanak (1974) have considered the dispersive force between two helium atoms, and have shown that, at the minimum of the potential energy well for the He-He system, the dispersive force is only 65-75% of the value given by the R^{-6} formula, and that the discrepancy becomes larger at closer distances. This work is not directly applicable to the dispersive forces in an N_2-N_2 pair, but it leads to the suspicion that the De Boer form may lead to too strong an attraction, especially at small intermolecular separations. This might have an important effect, for example, on the repulsive part of the Raich-Mills potential, which was fitted to data at high pressures (i.e., small separations).

The choice of a satisfactory model for the repulsive part of the potential is the most difficult. Following De Boer (1942), Kohin (1960) used a potential of the form

$$V_r = B \sum_{n=1}^{4} r_n^{-12} \quad , \tag{2.10}$$

where r_n is the distance between one of the four pairs of atoms on different molecules. The contributions of this potential to the A_μ coefficients may be represented by an asymptotic series in powers of $(d/R)^2$, where 2d is the distance between the two nuclei in a single molecule: the first terms in these expansions were given by Goodings and Henkelman (1971). However, direct numerical calculations of these coefficients, using Eqs. (2.7) and (2.10), show that these analytic approximations are becoming very inaccurate at distances of the order of the nearest-neighbour distance. Figure 1 shows the ratio of the true value to the asymptotic value of the A_μ for the repulsive part (only) of the Kohin potential. It can be seen that at the nearest-neighbour distance of 4 Å, the Goodings and Henkelman expressions are too small by about 60%.

Raich and Mills (1971) showed that the full Kohin potential, comprising quadrupole, dispersive and the Kohin form of the repulsive interaction, was unsatisfactory at high pressures, being unable to explain the stability of the tetragonal γ phase of nitrogen. The electron density contours for a nitrogen molecule (Bader et al. 1967) show that the shape of the outer edge of the electron cloud is approximately a prolate spheroid, with the ratio of the major to minor axis being about 1.3:1. Since the repulsion is due to Pauli exclusion in the region of overlap of the electron clouds, Raich and Mills proposed that the repulsive potential should depend on the shortest distance between two prolate spheroids of the appropriate eccentricity. The form they chose was

Fig. 1: Ratio of the true A_μ coefficients to the approximate expressions derived by Goodings and Henkelman (1971), for the repulsive term of the Kohin (1960) potential. True A_μ values were determined with a 10-point Gaussian integration formula. ——— A_0. ····· A_1. ----- A_2.

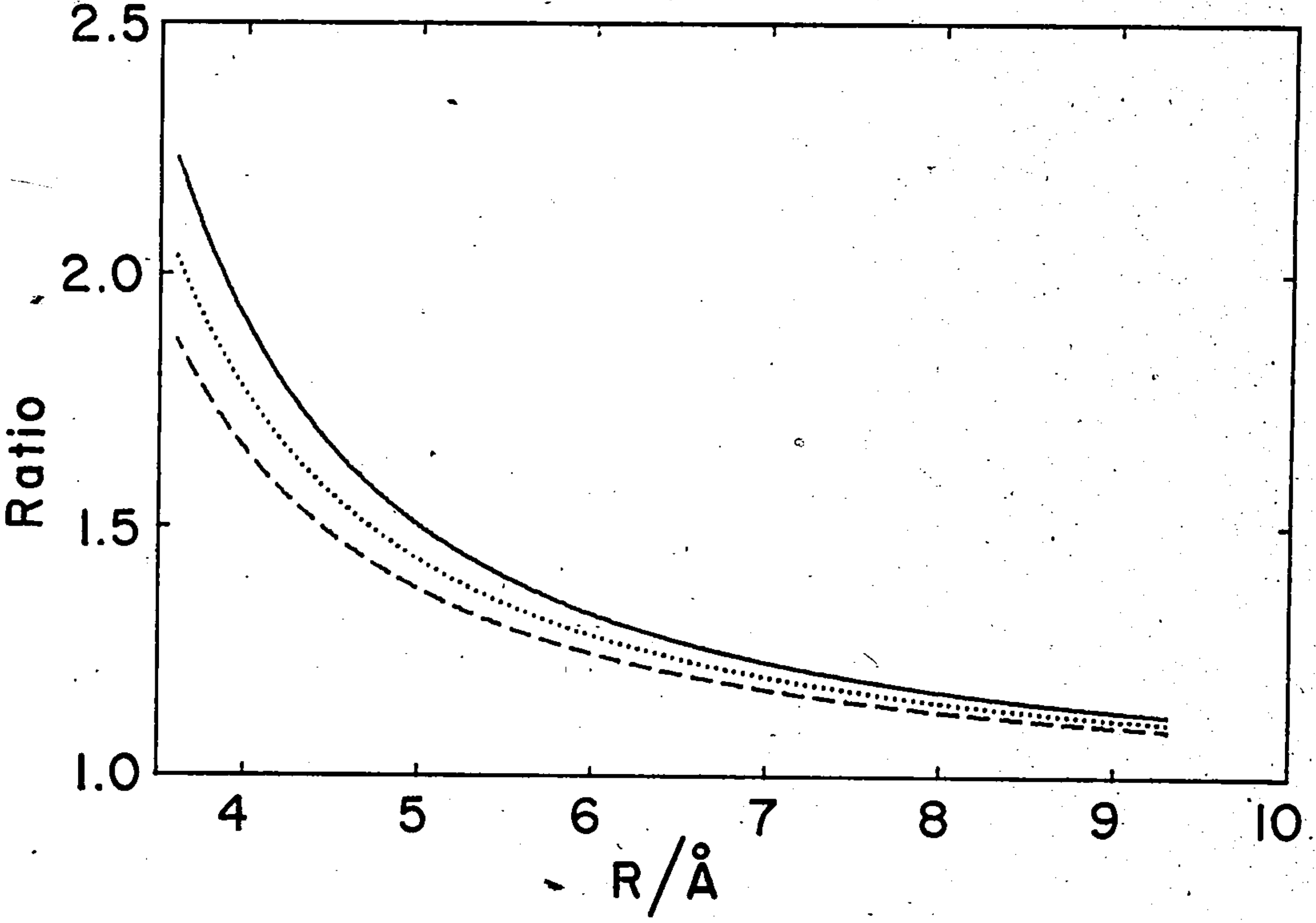

Fig. 1

$$V_r = Ar_m^{-\alpha} \quad , \tag{2.11}$$

where r_m is the shortest distance between two spheroids of major and minor axes 4.34s Å and 3.39s Å. A, α and the scale factor s were chosen as adjustable parameters, and were fitted to the heat of sublimation of the α phase of nitrogen and to the experimental p-V curve. This repulsive potential, together with the quadrupole-quadrupole and dispersive parts described previously, will be referred to as the Raich-Mills potential. Because this potential satisfactorily explains the stability of the γ phase of nitrogen, and because it appears to take account of the actual shape of the nitrogen molecule rather than treating it as a dumb-bell composed of two atoms, we judge it to be the most satisfactory phenomenological potential yet proposed for nitrogen.

CHAPTER 3

THE MEAN-FIELD MODEL

3.1 The Hamiltonian

In this thesis we are concerned with physical properties that depend on the librational motion. To calculate these properties it suffices, at least as a first approximation, to treat the molecules as having their centres fixed on a rigid lattice having the α-phase crystal structure. This approximation implies neglect of the phonons and of libron-phonon interactions, so that properties depending essentially on the phonons, such as the specific heat and the thermal expansion, cannot be calculated. We shall point out, as they occur, the places at which the existence of the phonons would be introduced if this theory were being extended to become a complete lattice dynamics for α-nitrogen.

We consider the classical interaction energy of a rigid lattice of nitrogen molecules whose centres are held fixed in the α crystal structure. Our next simplifying approximation is to truncate the expansion (2.5) for the intermolecular potential by assuming the potential to have the form

$$V_{jk} = B_0(R_{jk}) + B_1(R_{jk})[Y_{20}(\omega_j) + Y_{20}(\omega_k)]$$

$$+ \sum_{\mu=-2}^{2} A_\mu(R_{jk})Y_{2\mu}(\omega_j)Y_{2-\mu}(\omega_k) \qquad (3.1)$$

for the energy of interaction between molecules j and k. The additional terms could be treated in the same way as we shall treat the A_μ terms, at a cost in additional complexity of the Hamiltonian.

In order to discuss the form of the Hamiltonian, we must briefly describe the crystal structure. In theoretical calculations, the structure is generally supposed to be that of the space group Pa3. The experimental situation is somewhat confused, there being evidence both for the Pa3 structure (Schuch and Mills 1970; Goodings and Henkelman 1971; Venables and English 1974) and for the similar $P2_13$ structure (Jordan et al. 1964; Brookeman et al. 1971; Wachtel 1972); the difference between these two structures will be explained shortly. Venables and English (1974) reviewed the evidence and concluded that some of the data could be explained on the basis that twinning had occurred in the supposedly single crystals used, and that the remainder were qualitative and gave no indication of the extent of the distortion to the $P2_13$ structure, leading to the possibility that it might be explained by local strains in the crystal, surface effects, and such like. They concluded that the distortion was certainly less than 0.05 Å, which is small enough that we shall assume the simpler Pa3 crystal structure.

In the Pa3 structure, the Bravais lattice is simple cubic and the basis comprises four molecules, each of which is aligned along a different one of the four body diagonals of the cube. The molecular centres lie on a face-centred cubic lattice. If one molecule is taken to be at (0 0 0), the other three molecules in the basis are centred at the three $(\frac{1}{2}\,\frac{1}{2}\,0)$ positions. (The diagrams given by James and Raich (1967) give a fairly clear view of the Pa3 structure.) The $P2_13$ structure is similar except that the molecules are displaced along their axes, by 0.17 Å (Jordan et al. 1964) or < 0.05 Å (Venables and English 1974).

The term B_0 in Eq. (3.1) affects the phonons but not the orientational motions of the molecules and will henceforth be ignored. In addition, the terms involving B_1 yield a constant when summed over all the molecules in a Pa3 structure, and so they do not affect the librational motion (Goodings and Henkelman 1971). These terms would not sum to a constant if the Pa3 structure were distorted by the presence of a phonon of finite wavevector: thus they provide a mechanism for libron-phonon coupling. We do not consider these terms further.

In analysing the librational motions, the convenient coordinate system to use is that in which each molecule is in equilibrium at $\theta = 0$: thus there will be four coordinate systems, one for each sublattice. The spherical harmonics $Y_{2\mu}(\omega_j)$ and $Y_{2-\mu}(\omega_k)$ can be expressed, by a rotation of coordinates, in terms of harmonics $Y_{2m}(\theta_j,\phi_j)$ and $Y_{2m'}(\theta_k,\phi_k)$, where the angles (θ_j,ϕ_j) are measured in the equilibrium coordinate system of molecule j. The details of the rotation are described by Goodings and Henkelman (1971): the result is that the total energy is

$$V = \frac{1}{2} \sum_{jk} \sum_{m=-2}^{2} \sum_{m'=-2}^{2} C_{jk}(m,m') Y_{2m}(\theta_j,\phi_j) Y_{2m'}(\theta_k,\phi_k) \tag{3.2}$$

where expressions for the C_{jk} in terms of the A_μ are given by Goodings and Henkelman. (It is convenient to define $C_{jj}(m,m') = 0$.) The total classical energy of the system is then T+V, where T is the total rotational kinetic energy of the molecules.

We write the quantum-mechanical Hamiltonian by regarding $Y_{2m}(\theta_j,\phi_j)$ as the representation in polar coordinates of the components of a spherical tensor operator of rank 2, and replacing T by the quantum-mechanical kinetic energy operator. The Hamiltonian, expressed in the coordinate representation, is then

$$\mathcal{H} = B \sum_j \underline{J}_j^2 + \frac{1}{2} \sum_{jk} \sum_{mm'} C_{jk}(m,m') \times Y_{2m}(\theta_j,\phi_j) Y_{2m'}(\theta_k,\phi_k) \tag{3.3a}$$

where

$$\underline{J}_j^2 = - \frac{1}{\sin\theta_j} \frac{\partial}{\partial\theta_j} (\sin\theta_j \frac{\partial}{\partial\theta_j}) - \frac{1}{\sin^2\theta_j} \frac{\partial^2}{\partial\phi_j^2} \tag{3.3b}$$

and $B = \frac{\hbar^2}{2\mathcal{I}}$ is the rotational constant, $\mathcal{I}$ being the moment of inertia of a molecule.

The mean-field Hamiltonian is obtained by writing (3.3a) as

$$\mathcal{H} = \sum_j \mathcal{H}_j = \sum_j [B\underline{J}_j^2 + \frac{1}{2} \sum_k \sum_{mm'} C_{jk}(m,m') \times Y_{2m}(\theta_j,\phi_j) Y_{2m'}(\theta_k,\phi_k)] \tag{3.4}$$

and then supposing that each molecule moves independently under a Hamiltonian $\mathcal{H}_j$ in which the motion of the neighbours (described by $Y_{2m'}(\theta_k,\phi_k)$) is averaged out. The Hamiltonian that results is

$$\mathcal{H}_{MF} = B\underline{J}^2 - \sum_{m=-2}^{2} U_m Y_{2m}(\theta,\phi) \tag{3.5}$$

where U_m may be chosen self-consistently (James and Raich 1967) as

$$U_m = - \sum_k \sum_{m'=-2}^{2} C_{jk}(m,m') \langle Y_{2m'}(\theta_k,\phi_k) \rangle \qquad (3.6)$$

where the angle brackets denote an appropriate average. Equations (3.5) and (3.6) minimize the free energy within a single-molecule description of the crystal. Note that the factor of $\frac{1}{2}$ in (3.4) does not appear in (3.5) or (3.6). Because all the sublattices in the Pa3 structure are equivalent, U_m and hence $\mathcal{H}_{MF}$ do not depend explicitly on the central molecule j. Further, however, the crystal structure has 3-fold symmetry about the coordinate axis, and so the only non-zero U_m must be U_0. The eigenfunctions of the Hamiltonian (3.5) are then the spheroidal wave functions, to be discussed below, and the averages of Y_{21} and Y_{22} in any spheroidal wave function state can be shown to vanish. The mean-field Hamiltonian is then

$$\mathcal{H}_{MF} = B\underline{J}^2 - U_0 Y_{20}(\theta,\phi) \qquad (3.7)$$

where

$$U_0 = - \langle Y_{20}(\theta,\phi) \rangle \sum_k C_{jk}(0,0) \quad . \qquad (3.8)$$

3.2 The Spheroidal Wave Functions

By the normal technique of separation of variables, the eigenfunctions of $\mathcal{H}_{MF}$ may be found to be

$$W_{\ell m}(\theta,\phi) = \{[(2\ell+1)/4\pi][(\ell-m)!/(\ell+m)!]\}^{\frac{1}{2}} \times S_{\ell}^{m}(-ic;\cos\theta)e^{im\phi} \tag{3.9a}$$

where

$$c^2 = (45/16\pi)^{\frac{1}{2}} (U_0/B) \quad . \tag{3.9b}$$

The functions $S_{\ell}^{m}(-ic;\eta)$ are essentially the oblate spheroidal wave functions $S_{m\ell}(-ic;\eta)$ defined by Flammer (1957). However, we choose the phase so that $W_{\ell m}$ is a continuous function of c reducing to $Y_{\ell m}$ when $c = 0$, and the normalization so that the functions are normalized to unity over the unit sphere. For any finite value of c, the functions $W_{\ell m}(\theta,\phi)$ ($\ell = 0, 1, 2, \ldots; m = -\ell, \ldots, 0, \ldots, \ell$) form a complete orthonormal set of functions on the unit sphere. They are a generalization of the spherical harmonics, as the S_{ℓ}^{m} are a generalization of the associated Legendre functions (Erdélyi et al. 1953).

Since the defining Hamiltonian (3.7) has inversion symmetry, the $W_{\ell m}$ are functions with definite parity under inversion, and since $Y_{\ell m}$ has parity $(-1)^{\ell}$, this must be the parity of $W_{\ell m}$ also. If the nuclear spins are neglected, a homonuclear nitrogen molecule (e.g., ^{14}N-^{14}N) has inversion symmetry and any Hamiltonian which neglects the nuclear spins must leave the parity of the molecules' orientational wave function unaltered. As is true for hydrogen, nitrogen therefore exists in ortho and para spin species. In the case of ^{14}N-^{14}N, the ortho species has an even-parity orientational wave function and the para species has an odd-parity function, and conversion processes between the two species are expected to be slow. However, for the values of c appropriate to nitrogen (in the range of 11 to 17), the splitting in energy levels is so small (Curl et al. 1968) and the difference in the appropriate matrix elements is so slight that the existence of the two species may be ignored, and calculations may be performed on a pure crystal of either species, with identical results.

The computation of the spheroidal wave functions is not trivial. For our purposes, the best method is due to Hodge (1970), and the main details are presented in Appendix A. We express the functions as a series of the form

$$W_{\ell m}(\theta,\phi) = \sum_{q=0}^{\infty} D_q^{\ell m}(c)\, Y_{|m|+2q+s,m}(\theta,\phi) \qquad (3.10)$$

where (to give the correct parity) $s = 0$ if $\ell-m$ is even and $s = 1$ otherwise. The coefficients $D_q^{\ell m}$ are real and may be determined using a recurrence relation obtained from the defining differential equation. It may be remarked that the spheroidal wave functions are not hypergeometric functions and cannot be obtained from recurrence relations of the type satisfied by the Legendre functions (Flammer 1957).

The spheroidal wave functions will be used as basis functions with which to construct coherent excitations in the crystal, and they will enter the formalism only through the matrix elements of operators. If O is some operator, its matrix elements between $W_{\ell m}$ states are

$$\langle W_{\ell m}|O|W_{\ell' m'}\rangle = \sum_{qq'} D_q^{\ell m}(c) D_{q'}^{\ell' m'}(c) \times \langle Y_{|m|+2q+s,m}|O|Y_{|m'|+2q'+s',m'}\rangle \ . \tag{3.11}$$

The operators for which we wish to make such expansions are $\underset{\sim}{J}^2$ and the spherical harmonics, and in these cases explicit formulae for the matrix elements on the right-hand side of (3.11) are known (Edmonds 1957), and there are stringent selection rules which greatly simplify the summation.

3.3 Relation to the Two-Dimensional Oscillator

In Fig. 2 we present a typical energy-level diagram for $\mathcal{H}_{MF}$. It is strikingly similar to the corresponding diagram which could be constructed for the two-dimensional harmonic oscillator, and the similarity becomes closer for larger values of c. If one expands (3.7) for small θ and makes the substitutions $x = \theta\cos\phi$, $y = \theta\sin\phi$, one finds

$$\mathcal{H}_{MF} \approx - B\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \frac{3}{2}\sqrt{\frac{5}{\pi}}\, U_0 + \frac{9}{4}\sqrt{\frac{5}{\pi}}\, U_0 (x^2+y^2) \quad (3.12)$$

which is of the form of the Hamiltonian for the isotropic two-dimensional harmonic oscillator (Messiah 1958). The physics is that a very strong barrier (large U_0) constrains the molecule, in its low-energy states, to rotate only close to $\theta = 0$. If one examines the motion of one end of such a molecule, it is moving in a small section of a surface which appears almost plane on the scale of the allowed motions, and the leading terms in the potential constraining it are of course quadratic in the displacement. We take advantage of this correspondence to develop a quantization scheme which has both the tractable formal properties of the usual quantization of the harmonic oscillator and also the exact physics of the spheroidal wave function states. It is at this point that our treatment becomes inappropriate for the isostructural solid ortho-hydrogen, since the appropriate

Fig. 2: Energy-level diagram for the low-lying oblate spheroidal wave function states, for even ℓ. Spheroidal parameter $c = 11.0$. The diagram shows ℓ and m values, the $|n_+,n_->$ state assignments, and the total number of quanta $n = n_+ + n_-$. The dashed levels are the energy levels of the two-dimensional harmonic oscillator, where these differ appreciably from the corresponding spheroidal wave function levels. The diagram for odd ℓ is essentially degenerate with this one: the same assignments of the other quantum numbers hold.

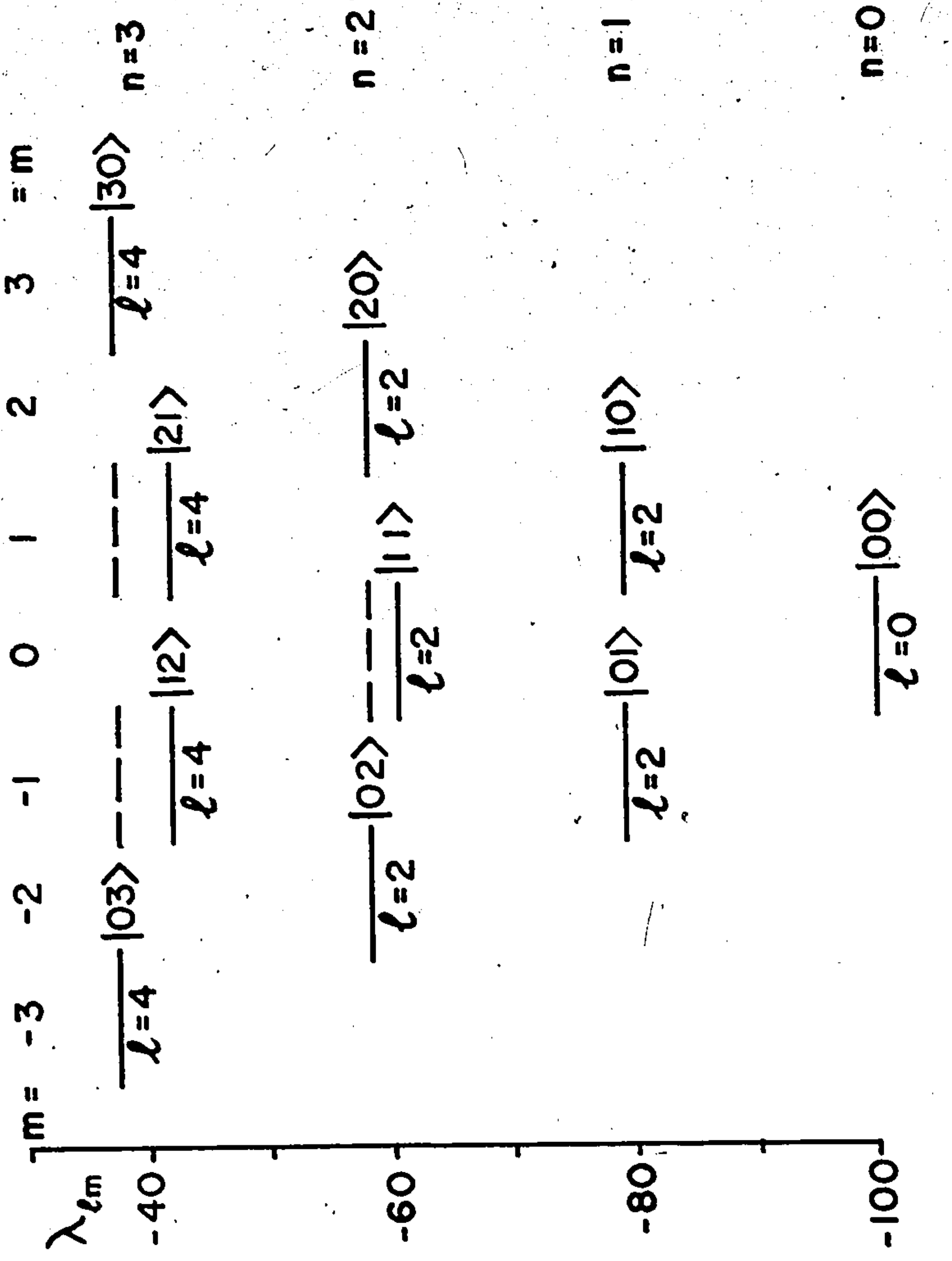
$\lambda_{\ell m}$
-40
-60
-80
-100
m = -3 -2 -1 0 1 2 3 = m
ℓ=4 |03⟩
ℓ=4 |12⟩
ℓ=4 |21⟩
ℓ=4 |30⟩
n=3
ℓ=2 |02⟩
ℓ=2 |11⟩
ℓ=2 |20⟩
n=2
ℓ=2 |01⟩
ℓ=2 |10⟩
n=1
ℓ=0 |00⟩
n=0

Fig. 2

spheroidal wave function states are almost free rotor states rather than almost harmonic oscillator states.

We begin by summarizing the results of a second quantized treatment of the two-dimensional isotropic harmonic oscillator (Messiah 1958). The Hamiltonian is quantized in terms of angular momentum raising and lowering operators

$$A_{\pm} = \frac{1}{\sqrt{2}}(a_x \mp ia_y) \qquad A_{\pm}^{\dagger} = \frac{1}{\sqrt{2}}(a_x^{\dagger} \pm ia_y^{\dagger}) \qquad (3.13)$$

where $a_x^{\dagger}$ and a_x create and annihilate excitations in the x direction, and $a_y^{\dagger}$ and a_y do the same in the y direction. The operators obey the commutation rules

$$[A_r,A_s] = [A_r^{\dagger},A_s^{\dagger}] = 0 \qquad [A_r,A_s^{\dagger}] = \delta_{rs} \quad . \qquad (3.14)$$

The states

$$|n_+,n_-> = (n_+!n_-!)^{-\frac{1}{2}} (A_+^{\dagger})^{n_+}(A_-^{\dagger})^{n_-}|0,0> \qquad (3.15)$$

are a complete orthonormal set. The number operators for the two types of excitations are $N_{\pm} = A_{\pm}^{\dagger}A_{\pm}$. The total number operator is $N = N_+ + N_-$ and the operator giving the z-component of angular momentum is $L = N_+ - N_-$. The energy of the state $|n_+,n_->$ is $(n_++n_-+1)\hbar\omega$ and its angular momentum is (n_+-n_-). Finally, the A operators obey the commutation rules for angular momentum raising and lowering operators, and $A_+^\dagger$ and A_- raise the z-component of angular momentum by one unit, while $A_-^\dagger$ and A_+ lower it by one unit.

We first seek a system of labelling the spheroidal wave functions by quantum numbers n_+ and n_- (rather than ℓ and m) to permit an asymptotic correspondence with the harmonic oscillator. The labelling turns out to be

$$n_\pm = [\frac{\ell\pm m}{2}] \tag{3.16a}$$

where [x] is the greatest integer not exceeding x, or, inversely

$$m = n_+ - n_- \qquad \ell = \begin{cases} 2\ [\frac{n_+ + n_- + 1}{2}] & \text{for even } \ell. \\ 2\ [\frac{n_+ + n_-}{2}] + 1 & \text{for odd } \ell. \end{cases} \tag{3.16b}$$

This labelling clearly gives the correct correspondence of the angular momentum. The correspondence of the energy levels may be inspected with the help of asymptotic expressions for the eigenvalues of the oblate spheroidal wave functions (Lowan 1965). If Eqs. (3.16b) are substituted in the asymptotic expansions, one finds that the energy is asymptotically proportional to $(n_+ + n_- + 1)$, with a relative splitting of $c^{-1}n_+n_-$, which goes to zero as $c \to \infty$. This verifies that the labelling (3.16) gives the correct correspondence to the harmonic oscillator in the limit $c \to \infty$, apart from possible phase factors. The problem with the phase factors is that the phase relations between the harmonic oscillator states are different from those among the spherical harmonics. Determining the correct phase relation involves examining the leading term in expansions about $\theta = 0$ and $x = y = 0$; this is done in Appendix B, where it is shown that there is a factor of $(-1)^{n_+}$ between $|n_+,n_->$ and the corresponding spheroidal wave function state.

We now have a set of states $|n_+,n_->$ which are complete and orthonormal on the unit sphere, which are identical to the $W_{\ell m}$ apart from their phases, and which reduce asymptotically as $c \to \infty$ to the eigenstates of the two-dimensional oscillator. We now invent operators analogous to the $A_\pm$ operators of the oscillator by defining

$$\begin{aligned}
A_+^\dagger &= \sum_{n_+=0}^{\infty} \sum_{n_-=0}^{\infty} (n_++1)^{\frac{1}{2}} \, |n_++1,n_-><n_+,n_-| \\
A_+ &= \sum_{n_+=0}^{\infty} \sum_{n_-=0}^{\infty} (n_++1)^{\frac{1}{2}} \, |n_+,n_-><n_++1,n_-| \, . \\
A_-^\dagger &= \sum_{n_+=0}^{\infty} \sum_{n_-=0}^{\infty} (n_-+1)^{\frac{1}{2}} \, |n_+,n_-+1><n_+,n_-| \\
A_- &= \sum_{n_+=0}^{\infty} \sum_{n_-=0}^{\infty} (n_-+1)^{\frac{1}{2}} \, |n_+,n_-><n_+,n_-+1| \, .
\end{aligned} \tag{3.17}$$

It is trivial to show that the operators so defined increase and decrease n_+ and n_- as required, that $N_\pm = A_\pm^\dagger A_\pm$ act as number operators for the $n_\pm$ quantum numbers, and that commutation rules (3.14) are obeyed. These operators therefore satisfy all the requirements for creation and annihilation operators, and we may then reinterpret the state $|n_+,n_->$, which we introduced as merely an alternative way of labelling the spheroidal wave function states $W_{\ell m}$, as being states containing n_+ excitations each carrying +1 unit of angular momentum and n_- excitations each carrying -1 unit. The operators $A_\pm^\dagger$ and $A_\pm$ are then regarded as creating and annihilating these excitations, which obey Bose statistics.

It may perhaps be stressed that no change in the physics has occurred as a result of the introduction of these operators. The scheme is an exact second quantization of the mean-field Hamiltonian (3.7), and not just of the harmonic oscillator Hamiltonian. The advantage of the scheme is that the two Hamiltonians are asymptotically equivalent as $c \to \infty$, and very closely related for values of c relevant to nitrogen, so that the anharmonic terms to be produced by the theory will vanish asymptotically and will be small in practice.

CHAPTER 4

THE SECOND-QUANTIZED HAMILTONIAN

4.1 Introduction

In the previous chapter, we presented the mean-field model in order to motivate the introduction of the spheroidal wave functions and the subsequent definition of operators which induce transitions among spheroidal wave function states. We now attack the main problem treated in this work: the use of these operators to effect a systematic second quantization of the Hamiltonian (3.3).

We begin by considering the expansions of $\underline{J}^2$ and the spherical harmonics in terms of the A operators. Since $\underline{J}^2$ does not alter the m quantum number of a state, while Y_{2M} increases it by M, and in view of the angular momentum properties of the A operators, the expansions take the general form

$$\underline{J}^2 = \alpha_1 + \alpha_2 A_+^\dagger A_+ + \alpha_3 A_-^\dagger A_- + \alpha_4 A_+^\dagger A_-^\dagger + \alpha_5 A_+ A_- + \text{quartic and higher terms} \qquad (4.1a)$$

$$Y_{20} = \beta_1 + \beta_2 A_+^\dagger A_+ + \beta_3 A_-^\dagger A_- + \beta_4 A_+^\dagger A_-^\dagger + \beta_5 A_+ A_- + \text{quartic and higher terms} \qquad (4.1b)$$

$$Y_{21} = \gamma_1 A_+^\dagger + \gamma_2 A_- + \gamma_3 A_+^\dagger A_+^\dagger A_-^\dagger + \gamma_4 A_+ A_- A_-$$

$$+ \gamma_5 A_+^\dagger A_-^\dagger A_- + \gamma_6 A_+^\dagger A_+ A_- + \gamma_7 A_+^\dagger A_+^\dagger A_+ + \gamma_8 A_-^\dagger A_- A_-$$

$$+ \text{quintic and higher terms} \qquad (4.1c)$$

$$Y_{22} = \delta_1 A_+^\dagger A_+^\dagger + \delta_2 A_- A_- + \delta_3 A_+^\dagger A_-$$

$$+ \text{quartic and higher terms} \quad . \qquad (4.1d)$$

Using the relation $Y_{2-m} = (-1)^m Y_{2m}^\dagger$, one may easily write down the expressions for Y_{2-1} and Y_{2-2} from Eqs. (4.1c) and (4.1d). We have kept only those terms involving three or fewer operators, because in the present work we shall not attempt to calculate effects depending on the four-operator terms in the Hamiltonian, such as the anharmonic corrections to the libron energies. Such terms may be written down without introducing any new difficulties in the formalism.

The coefficients appearing in the expansions (4.1) are related to the matrix elements of the operators $\underline{J}^2$ and Y_{2m}. The relations are given in Appendix C, where it is also shown that

$$\alpha_2 = \alpha_3 \qquad \alpha_4 = \alpha_5 \qquad \beta_2 = \beta_3 \qquad \beta_4 = \beta_5$$

$$\gamma_1 = \gamma_2 \qquad \gamma_3 = \gamma_4 \qquad \gamma_5 = \gamma_6 \qquad \gamma_7 = \gamma_8 \qquad (4.2)$$

$$\delta_1 = \delta_2$$

From their relation to the matrix elements of the operators in the representation of the spheroidal wave function states, these coefficients are readily evaluated numerically for any value of the spheroidal parameter c. From a logarithmic plot, one may then extract the power-law dependence of the coefficients as $c \to \infty$. This asymptotic dependence may be examined analytically, and the expressions so obtained provide a useful check on the numerical work. However, the derivation of these analytic expressions is not presented here, since it adds nothing of interest to the results obtained numerically. These results are

$$\alpha_1 \sim c \qquad \alpha_2 \sim c \qquad \alpha_4 \sim -c$$

$$\beta_1 \sim c^0 \qquad \beta_2 \sim -c^{-1} \qquad \beta_4 \sim -c^{-1}$$

$$\gamma_1 \sim -c^{-\frac{1}{2}} \qquad \gamma_3 \sim c^{-\frac{3}{2}} \qquad \gamma_5 \sim c^{-\frac{3}{2}} \qquad \gamma_7 \sim c^{-\frac{3}{2}} \tag{4.3}$$

$$\delta_1 \sim c^{-1} \qquad \delta_3 \sim c^{-1} \quad .$$

We shall classify terms by their powers of $c^{-\frac{1}{2}}$. All the coefficients of n-operator terms in the expansions of Y_{2m} behave as $(c^{-\frac{1}{2}})^n$ for large c. If we consider the mean-field Hamiltonian (3.7) and note that $U_0 \sim Bc^2$, then we see from (3.8) that the potential coefficients $C_{jk}(m,m')$

must be regarded as being of order Bc^2, since $\langle Y_{20}(\theta,\phi)\rangle$ is asymptotically constant. Hence, in the full Hamiltonian (3.3), all terms involving n operators are of order $Bc^2(c^{-\frac{1}{2}})^n$, except for α_1, which does not affect the librational excitations in any case. We again emphasize that the treatment is not appropriate for ortho-hydrogen, since the expansion coefficients do not fall off rapidly when c is very small, as it is in ortho-hydrogen.

In the remainder of this chapter, and throughout the next chapter and the associated appendices, some very formidable algebraic expressions will arise. To compress these expressions as far as practicable, the author proposes to use several conventions of notation. First, "spin" indices σ will take values + or - (or, where the context so requires, values of +1 or -1, so that 2σ would be ±2). Second, the crystallographic convention is adopted that a bar over a symbol is equivalent to a minus sign, so that $\bar{\sigma} = -\sigma$. Third, libron labels $(\underline{q}_1,\beta_1)$ will often be abbreviated as 1, so that $\xi_1\eta_2B_1^\dagger B_{\bar{2}}$ means $\xi_{\underline{q}_1\beta_1}\eta_{\underline{q}_2\beta_2}B^\dagger_{\underline{q}_1\beta_1}B_{\bar{\underline{q}}_2\beta_2}$. Fourth, any subscripts, superscripts or indices (including the numbers standing as abbreviations for libron labels) which occur on the right-hand side of an equation and not on the left-hand side are implicitly to be summed over. The author believes that neither the typist nor the reader is likely to regret the resulting compression of the formulae.

With these conventions, and in the light of the Eqs. (4.2), the operator equations (4.1) may be condensed into the forms

$$\underline{J}^2 = \alpha_1 + \alpha_2 A_\sigma^\dagger A_\sigma + \alpha_4 (A_+^\dagger A_-^\dagger + A_+ A_-) \tag{4.4a}$$

$$\begin{aligned} Y_{2m} = {} & a_m + b_m^\sigma (A_\sigma^\dagger + A_{\bar\sigma}) + c_m^{\sigma_1\sigma_2} A_{\sigma_1}^\dagger A_{\sigma_2} \\ & + d_m^{\sigma_1\sigma_2} (A_{\sigma_1}^\dagger A_{\sigma_2}^\dagger + A_{\bar\sigma_2} A_{\bar\sigma_1}) \\ & + e_m^\sigma (A_\sigma^\dagger A_\sigma^\dagger A_{\bar\sigma}^\dagger + A_\sigma A_{\bar\sigma} A_{\bar\sigma}) \\ & + f_m^{\sigma_1\sigma_2} (A_{\sigma_1}^\dagger A_{\sigma_2}^\dagger A_{\sigma_2} + A_{\bar\sigma_2}^\dagger A_{\bar\sigma_2} A_{\bar\sigma_1}) \end{aligned} \tag{4.4b}$$

where

$$\begin{aligned} & a_m = \beta_1 \delta_{m0} \qquad b_m^\sigma = \sigma\gamma_1 \delta_{m\sigma} \\ & c_m^{\sigma_1\sigma_2} = \beta_2 \delta_{\sigma_1\sigma_2} \delta_{m0} + \delta_3 \delta_{\sigma_1\bar\sigma_2} \delta_{m,2\sigma_1} \\ & d_m^{\sigma_1\sigma_2} = \frac{1}{2} \beta_4 \delta_{\sigma_1\bar\sigma_2} \delta_{m0} + \delta_1 \delta_{\sigma_1\sigma_2} \delta_{m,2\sigma_1} \\ & e_m^\sigma = \sigma\gamma_3 \delta_{m\sigma} \qquad f_m^{\sigma_1\sigma_2} = \sigma_1 (\gamma_5 \delta_{\sigma_1\bar\sigma_2} + \gamma_7 \delta_{\sigma_1\sigma_2}) \delta_{m\sigma_1} \end{aligned} \tag{4.4c}$$

where δ_{jk} is the Kronecker delta.

4.2 The Linear and Quadratic Terms

To discuss the quantization of the Hamiltonian (3.3), we introduce operators $A^{\dagger}_{j\sigma}$, $A_{j\sigma}$ for each molecule j. Since the molecules are fixed to their lattice sites, they are distinguishable, and operators for different sites commute freely. Note that the coefficients in (4.4c) are the same for every site, so that we do not add a site index to them. From Eqs. (4.4), we can write down the parts of (3.3) which contain exactly one creation or annihilation operator, i.e., the terms of order $c^{\frac{3}{2}}$. These terms are

$$\mathcal{H}_1 = \frac{1}{2} C_{jk}(m,m')\{a_m b^{\sigma}_{m'}(A^{\dagger}_{k\sigma} + A_{k\bar{\sigma}}) + b^{\sigma}_{m}(A^{\dagger}_{j\sigma} + A_{j\bar{\sigma}})a_{m'}\} \tag{4.5a}$$

$$= \frac{1}{2} C_{jk}(0,m')\beta_1\sigma\gamma_1\delta_{m'\sigma}(A^{\dagger}_{k\sigma} + A_{k\bar{\sigma}})$$

$$+ \frac{1}{2} C_{jk}(m,0)\sigma\gamma_1\delta_{m\sigma}(A^{\dagger}_{j\sigma} + A_{j\bar{\sigma}})\beta_1 \quad . \tag{4.5b}$$

The first term vanishes because $\sum_j C_{jk}(0,m') = 0$ except for m' = 0 (Goodings and Henkelman 1971), while $\delta_{m'\sigma} = 0$ for m' = 0 since $\sigma = \pm 1$. The second term vanishes by a similar argument. The vanishing of $\mathcal{H}_1$ depends on the symmetry of the crystal, which is destroyed by the presence of phonons of finite wavevector. Thus, if our assumption of fixed molecular centres were relaxed, terms could arise containing one phonon and one libron operator, permitting phonons and librons to mix at finite wavevector. This mechanism is in addition to the one involving $B_1(R_{jk})$, mentioned in Section 3.1.

Before writing down the quadratic terms (those of order c), we examine the structure of the second term in Eq. (3.3). If we write (4.4b) in the form

$$Y_{2m}(\theta_j,\phi_j) = \sum_{\alpha} Y^{\alpha}_{jm} \tag{4.6}$$

then the sum is

$$\begin{aligned}
&\frac{1}{2}\sum_{jk}\sum_{mm'}\sum_{\alpha\beta} C_{jk}(m,m')Y^{\alpha}_{jm}Y^{\beta}_{km'} \\
&\quad = \frac{1}{2}\sum_{jk}\sum_{mm'}\sum_{\alpha} C_{jk}(m,m')Y^{\alpha}_{jm}Y^{\alpha}_{km'} \\
&\qquad + \sum_{jk}\sum_{mm'}\sum_{\alpha>\beta} C_{jk}(m,m')Y^{\alpha}_{jm}Y^{\beta}_{km} \quad .
\end{aligned} \tag{4.7}$$

In arriving at the second sum in (4.7), we have used the facts that $[Y^{\alpha}_{jm},Y^{\beta}_{km'}] = 0$ if $j \neq k$, that $C_{jk}(m,m') = 0$ if $j = k$, and that $C_{jk}(m,m') = C_{kj}(m',m)$.

Then the two-operator part of the potential energy is

$$\begin{aligned}
V_2 = C_{jk}(m,m')\{&\frac{1}{2}\, b_m^{\sigma_1} b_{m'}^{\sigma_2}(A^{\dagger}_{j\sigma_1}A^{\dagger}_{k\sigma_2} + A_{j\bar{\sigma}_1}A_{k\bar{\sigma}_2} \\
&+ 2A^{\dagger}_{j\sigma_1}A_{k\bar{\sigma}_2}) + a_{m'}c_m^{\sigma_1\sigma_2}A^{\dagger}_{j\sigma_1}A_{j\sigma_2} + \cdots
\end{aligned}$$

$$+ a_{m'} d_m^{\sigma_1\sigma_2} (A^\dagger_{j\sigma_1} A^\dagger_{j\sigma_2} + A_{j\bar{\sigma}_2} A_{j\bar{\sigma}_1}) \} \quad . \tag{4.8}$$

This expression can be simplified, using similar considerations to those applied to the treatment of $\mathcal{H}_1$. If the kinetic energy part is added in, the two-operator part of the Hamiltonian becomes

$$\begin{aligned}\mathcal{H}_2 = & \{\tfrac{1}{2} \gamma_1^2 \sigma_1 \sigma_2 C_{jk}(\sigma_1, \sigma_2) + \tfrac{1}{2} (B\alpha_4 - \beta_1\beta_4\Gamma) \delta_{jk} \delta_{\sigma_1\bar{\sigma}_2} \} \\ & \times \{A^\dagger_{j\sigma_1} A^\dagger_{k\sigma_2} + A_{j\bar{\sigma}_1} A_{k\bar{\sigma}_2} \} \\ & + \{\gamma_1^2 \sigma_1 \sigma_2 C_{jk}(\sigma_1, \alpha_2) + (B\alpha_2 - \beta_1\beta_2\Gamma) \delta_{jk} \delta_{\sigma_1\bar{\sigma}_2} \} \\ & \times A^\dagger_{j\sigma_1} A^\dagger_{k\bar{\sigma}_2}\end{aligned} \tag{4.9a}$$

where

$$- \sum_k C_{jk}(0,0) = \Gamma \tag{4.9b}$$

which is independent of j by translational symmetry and the equivalence of the sublattices.

To take advantage of the translational symmetry of the crystal, we introduce Fourier transformed operators $A^\dagger_{\underline{q}J\sigma}$ and $A_{\underline{q}J\sigma}$, defining

$$A^{\dagger}_{j\sigma} = N^{-\frac{1}{2}} \sum_{\underline{q}} \exp(-i\underline{q}\cdot\underline{R}_j)A^{\dagger}_{\underline{q}J\sigma} \qquad (j\varepsilon J) \qquad (4.10a)$$

$$A_{j\sigma} = N^{-\frac{1}{2}} \sum_{\underline{q}} \exp(i\underline{q}\cdot\underline{R}_j)A_{\underline{q}J\sigma}$$

$$= N^{-\frac{1}{2}} \sum_{\underline{q}} \exp(-i\underline{q}\cdot\underline{R}_j)A_{-\underline{q}J\sigma} \qquad (j\varepsilon J) \qquad (4.10b)$$

where $\underline{R}_j$ is the position vector of molecule j, and the notation jεJ indicates that molecule j lies on sublattice J (J = 1, 2, 3, 4). The numbering of the sublattices, which is arbitrary, was taken to be the same as that used by James and Raich (1967) and by Goodings and Henkelman (1971). N is the number of unit cells in the crystal: the number of molecules is 4N. The first form of (4.10b) shows that $A^{\dagger}_{\underline{q}J\sigma}$ is the hermitian adjoint of $A_{\underline{q}J\sigma}$, while the second form is the one to be actually substituted into Eq. (4.9a).

The Fourier-transformed operators are easily shown to obey the boson commutation rules

$$[A_{\underline{q}J\sigma},A_{\underline{q}'K\sigma'}] = [A^{\dagger}_{\underline{q}J\sigma},A^{\dagger}_{\underline{q}'K\sigma'}] = 0$$

$$[A_{\underline{q}J\sigma},A^{\dagger}_{\underline{q}'K\sigma'}] = \delta_{\underline{q}\underline{q}'}\delta_{JK}\delta_{\sigma\sigma'} \quad . \qquad (4.11)$$

We define the Fourier-transformed coefficients

$$C^{mm'}_{\underline{q}JK} = \frac{1}{N}\sum_{j\varepsilon J}\sum_{k\varepsilon K} C_{jk}(m,m')\exp\{-i\underline{q}\cdot(\underline{R}_j - \underline{R}_k)\} \quad . \qquad (4.12)$$

These coefficients exhibit a number of practically important symmetries, which are discussed in Appendix D. Substituting Eqs. (4.10) into (4.9a), we obtain the result

$$\mathcal{H}_2 = \{\tfrac{1}{2}\,\gamma_1^2\sigma_1\sigma_2 C^{\sigma_1\sigma_2}_{\underline{q}JK} + \tfrac{1}{2}\,(B\alpha_4 - \beta_1\beta_4\Gamma)\,\delta_{JK}\delta_{\sigma_1\bar{\sigma}_2}\}$$

$$\times\ \{A^{\dagger}_{\underline{q}J\sigma_1}A^{\dagger}_{\bar{\underline{q}}K\sigma_2} + A_{\bar{\underline{q}}J\bar{\sigma}_1}A_{\underline{q}K\bar{\sigma}_2}\}$$

$$+\ \{\gamma_1^2\sigma_1\sigma_2 C^{\sigma_1\sigma_2}_{\underline{q}JK} + (B\alpha_2 - \beta_1\beta_2\Gamma)\,\delta_{JK}\delta_{\sigma_1\bar{\sigma}_2}\}$$

$$\times\ A^{\dagger}_{\underline{q}J\sigma_1}A_{\underline{q}K\bar{\sigma}_2} \tag{4.13a}$$

$$= \theta A^{\dagger}_{\underline{q}J\sigma_1}A_{\underline{q}J\sigma_1} + W_{\underline{q}J\sigma_1K\sigma_2}\{A^{\dagger}_{\underline{q}J\sigma_1}A^{\dagger}_{\bar{\underline{q}}K\sigma_2}$$

$$+\ A_{\underline{q}K\bar{\sigma}_2}A_{\bar{\underline{q}}J\bar{\sigma}_1} + 2A^{\dagger}_{\underline{q}J\sigma_1}A_{\underline{q}K\bar{\sigma}_2}\} \tag{4.13b}$$

where

$$\theta = B(\alpha_2 - \alpha_4) - \beta_1(\beta_2 - \beta_4)\Gamma \tag{4.13c}$$

and

$$W_{\underline{q}J\sigma_1K\sigma_2} = \tfrac{1}{2}\,\gamma_1^2\sigma_1\sigma_2 C^{\sigma_1\sigma_2}_{\underline{q}JK} + \tfrac{1}{2}\,(B\alpha_4 - \beta_1\beta_4\Gamma)\,\delta_{JK}\delta_{\sigma_1\bar{\sigma}_2}\ . \tag{4.13d}$$

The diagonalization of the Bogoliubov Hamiltonian (4.13b) was treated by Raich and Etters (1968) in discussing librational motion in fcc ortho-hydrogen. However, Raich and Etters did not mention an important symmetry property of the eigenvectors (our Eq. (4.18), below) of which we shall make constant use. We therefore summarize in Appendix E the procedure for diagonalizing the Hamiltonian (4.13b). Libron creation and annihilation operators $B^\dagger_{\underline{q}\alpha}$ and $B_{\underline{q}\alpha}$, obeying boson commutation rules, are used to put $\mathcal{H}_2$ in the form

$$\mathcal{H}_2 = \epsilon_{\underline{q}\alpha} B^\dagger_{\underline{q}\alpha} B_{\underline{q}\alpha} \quad . \tag{4.14}$$

The A and B operators are related by the equations

$$A^\dagger_{\underline{q}J\sigma} = U^*_{\underline{q}J\sigma\alpha}(\xi_{\underline{q}\alpha} B^\dagger_{\underline{q}\alpha} + \eta_{\underline{q}\alpha} B_{\overline{\underline{q}}\alpha}) \tag{4.15a}$$

$$A_{\overline{\underline{q}}J\overline{\sigma}} = U^*_{\underline{q}J\sigma\alpha}(\eta_{\underline{q}\alpha} B^\dagger_{\underline{q}\alpha} + \xi_{\underline{q}\alpha} B_{\overline{\underline{q}}\alpha}) \quad . \tag{4.15b}$$

The composite index $J\sigma$ takes on eight values and the mode index α runs from 1 to 8. $U_{\underline{q}}$ is then an 8×8 matrix for each value of $\underline{q}$, and it is in fact the matrix of eigenvectors of the 8×8 hermitian matrix

$$M_{\underline{q}J\sigma K\sigma'} = \theta^2 \delta_{JK} \delta_{\sigma\sigma'} + 4\theta W_{\underline{q}J\sigma K\overline{\sigma}'} \tag{4.16}$$

subject to the unitarity conditions

$$\sum_{J\sigma} U^*_{\underline{q}J\sigma\alpha} U_{\underline{q}J\sigma\beta} = \delta_{\alpha\beta} \qquad \sum_{\alpha} U^*_{\underline{q}J\sigma\alpha} U_{\underline{q}K\sigma'\alpha} = \delta_{JK}\delta_{\sigma\sigma'} \tag{4.17}$$

and the symmetry property

$$U^*_{\underline{q}J\sigma\alpha} = U_{\underline{q}J\bar{\sigma}\alpha} \quad . \tag{4.18}$$

$\varepsilon^2_{\underline{q}\alpha}$ is the eigenvalue of $M_{\underline{q}}$ which corresponds to the eigenvector $U_{\underline{q}J\sigma\alpha}$. The real coefficients ξ and η are defined by

$$\begin{aligned} \xi_{\underline{q}\alpha} &= \frac{1}{2}\left(\theta\varepsilon_{\underline{q}\alpha}\right)^{-\frac{1}{2}}\left(\theta + \varepsilon_{\underline{q}\alpha}\right) \\ \eta_{\underline{q}\alpha} &= \frac{1}{2}\left(\theta\varepsilon_{\underline{q}\alpha}\right)^{-\frac{1}{2}}\left(\theta - \varepsilon_{\underline{q}\alpha}\right) \quad . \end{aligned} \tag{4.19}$$

The symmetry described by Eq. (4.18) is unusual and rather powerful. For a non-degenerate eigenvalue, it fixes the phase of the eigenvector to within an overall ± sign. For a degenerate subspace, it also eliminates the usual ambiguity in the choice of the eigenvectors, selecting out a special set. This property therefore ensures that the libron modes are uniquely defined, even at points in the Brillouin zone where degeneracies occur. The necessity of satisfying this symmetry causes some numerical complications in determining the eigenvectors.

We now have a scheme enabling us to determine the libron energies at any point in the Brillouin zone, and so we may compute the density of states of the librons. The most efficient procedure for doing this (Gilat and Raubenheimer 1966) involves also a knowledge of the gradients of the energies in $\underline{q}$ space. Since $\varepsilon^2_{\underline{q}\alpha}$ is the eigenvalue of $M_{\underline{q}}$ corresponding to $U_{\underline{q}J\sigma\alpha}$, we have

$$\nabla_{\underline{q}}(\varepsilon^2_{\underline{q}\alpha}) = \nabla_{\underline{q}}(U^*_{\underline{q}J\sigma\alpha} M_{\underline{q}J\sigma K\sigma'} U_{\underline{q}K\sigma'\alpha}) \tag{4.20a}$$

$$= U^*_{\underline{q}J\sigma\alpha} (\nabla_{\underline{q}} M_{\underline{q}J\sigma K\sigma'}) U_{\underline{q}K\sigma'\alpha} \quad , \tag{4.20b}$$

where the second step involves a certain amount of straightforward algebra. From (4.16) and (4.13d) we have that

$$\nabla_{\underline{q}} M_{\underline{q}J\sigma K\sigma'} = 2\theta\gamma^2_1 \sigma\sigma' \nabla_{\underline{q}} C^{\sigma\sigma'}_{\underline{q}JK} \tag{4.21}$$

and from (4.12) we can write down

$$\nabla_{\underline{q}} C^{mm'}_{\underline{q}JK} = -\frac{i}{N} \sum_{j\varepsilon J} \sum_{k\varepsilon K} (\underline{R}_k - \underline{R}_j) C_{jk}(m,m') \exp\{-i\underline{q}\cdot(\underline{R}_j - \underline{R}_k)\} \quad . \tag{4.22}$$

Equations (4.20) through (4.22) permit evaluation of $\nabla_{\underline{q}}\varepsilon_{\underline{q}\alpha}$ as well as $\varepsilon_{\underline{q}\alpha}$ at any point in the Brillouin zone, and so allow calculation of the libron density of states $D(\varepsilon)$.

Given the density of states, one may evaluate the partition function Z and hence the free energy (Landau and Lifshitz 1958),

$$F = -\frac{1}{\beta}\ln Z = E_0 + \frac{N}{\beta}\int_0^\infty \ln(1 - e^{-\beta\varepsilon})D(\varepsilon)d\varepsilon \qquad (4.23)$$

where the density of states is normalized so that

$$\int_0^\infty D(\varepsilon)d\varepsilon = 8 \quad . \qquad (4.24)$$

Here $\beta = (k_BT)^{-1}$, where k_B is Boltzmann's constant, and E_0 is the ground-state energy of the Hamiltonian (3.3), that is, those terms containing no libron operators. The terms are

$$\begin{aligned} E_0 &= B\sum_j \alpha_1 + \frac{1}{2}\sum_{jk} C_{jk}(m,m')a_m a_{m'} \\ &= 4N(B\alpha_1 - \frac{1}{2}\Gamma\beta_1^2) \end{aligned} \qquad (4.25)$$

since the number of molecules is 4N.

In the libron theory as developed so far in this chapter, the value to be assigned to the spheroidal wave function parameter c has nowhere been specified. The choice described by Eqs. (3.7), (3.8), and (3.9b) minimizes the free energy within the mean-field model (James and Raich 1967), but that is not obviously the appropriate choice within the libron model. We can therefore specify that c be chosen so as to minimize the libron free energy, Eq. (4.23). This choice will be temperature-dependent, and hence one obtains, within a non-interacting libron theory, a mechanism for the slight isochoric temperature dependence of the Raman frequencies (Medina and Daniels 1974).

This last remark draws attention to the fact that the non-interacting libron theory is formally quite different from conventional harmonic phonon theory, although it reduces to harmonic phonon theory in the "classical" limit $c \to \infty$ (Dunmore 1972). The differences arise from the peculiar topology of the underlying coordinate manifold, namely the unit sphere. The mean molecular displacements are sufficiently large (Goodings and Henkelman (1971) gave a semi-classical estimate of $\sqrt{\langle\theta^2\rangle} = 17.9°$ at $T = 0$; in Chapter 6 we shall present estimates of about 17.5°) that the curvature of the unit sphere becomes appreciable, and the symmetry (or antisymmetry) of the wave function under inversion becomes significant. These phenomena have no parallel in the case of the isotropic harmonic oscillator, and one cannot freely argue the formal properties of librons from those of phonons, although the two types of excitation have identical physical origins.

The final theoretical result which we shall attempt to extract from our non-interacting libron theory is the temperature dependence of the nuclear quadrupole resonance frequency ν_Q. Following DeReggi et al. (1969), we assume a quadrupole Hamiltonian with nuclear spin 1 (for the isotope ^{14}N) and zero asymmetry parameter, and assume that the temperature dependence of ν_Q comes from the molecular librations. Apart from some constant factors, the NQR frequency is then given by

$$\nu_Q \propto \langle Y_{20}(\theta,\phi)\rangle \tag{4.26}$$

where the angle brackets denote an appropriate thermal average. By the equivalence of the sublattices and the translational symmetry of the crystal, the expression should be the same for any particular molecule, and it is convenient to average over all the molecules on some sublattice J. Using (4.1b) and (4.2), we then write

$$\begin{aligned}\langle Y_{20}(J)\rangle &= \frac{1}{N}\sum_{j\epsilon J}\langle Y_{20}(\theta_j,\phi_j)\rangle\\ &= \beta_1 + \frac{1}{N}\beta_2\sum_{j\epsilon J}\langle A^{\dagger}_{j+}A_{j+} + A^{\dagger}_{j-}A_{j-}\rangle\\ &+ \frac{1}{N}\beta_4\sum_{j\epsilon J}\langle A^{\dagger}_{j+}A^{\dagger}_{j-} + A_{j+}A_{j-}\rangle \quad . \end{aligned} \tag{4.27}$$

We express the averages in terms of averages of libron operators, using (4.10) and (4.15). We find

$$
\begin{aligned}
\langle Y_{20}(J)\rangle = \beta_1 &+ N^{-2}\beta_2 \exp\{-i(\underline{q}+\underline{q}')\cdot\underline{R}_j) U^*_{\underline{q}J\sigma\alpha} U_{\underline{q}'J\sigma\beta} \\
&\times \langle(\xi_{\underline{q}\alpha} B^\dagger_{\underline{q}\alpha} + \eta_{\underline{q}\alpha} B_{\underline{\bar{q}}\alpha})(\eta_{\underline{q}'\beta} B^\dagger_{\underline{q}'\beta} + \xi_{\underline{q}'\beta} B_{\underline{\bar{q}}'\beta})\rangle \\
&+ N^{-2}\beta_4 \exp\{-i(\underline{q}+\underline{q}')\cdot\underline{R}_j\}\{U^*_{\underline{q}J+\alpha} U^*_{\underline{q}'J-\beta} \\
&\times \langle(\xi_{\underline{q}\alpha} B^\dagger_{\underline{q}\alpha} + \eta_{\underline{q}\alpha} B_{\underline{\bar{q}}\alpha})(\xi_{\underline{q}'\beta} B^\dagger_{\underline{q}'\beta} + \eta_{\underline{q}'\beta} B_{\underline{\bar{q}}'\beta})\rangle \\
&+ U_{\underline{q}J+\alpha} U_{\underline{q}'J+\beta} \langle(\eta_{\underline{q}\alpha} B^\dagger_{\underline{q}\alpha} + \xi_{\underline{q}\alpha} B_{\underline{\bar{q}}\alpha}) \\
&\times (\eta_{\underline{q}'\beta} B^\dagger_{\underline{q}'\beta} + \xi_{\underline{q}'\beta} B_{\underline{\bar{q}}'\beta})\rangle\} \qquad (4.28a)
\end{aligned}
$$

$$
\begin{aligned}
= \beta_1 &+ N^{-1}|U_{\underline{q}J\sigma\alpha}|^2\{(\beta_2 \xi^2_{\underline{q}\alpha} + \beta_4 \xi_{\underline{q}\alpha}\eta_{\underline{q}\alpha}) \\
&\times \langle B^\dagger_{\underline{q}\alpha} B_{\underline{q}\alpha}\rangle + (\beta_2 \eta^2_{\underline{q}\alpha} + \beta_4 \xi_{\underline{q}\alpha}\eta_{\underline{q}\alpha})\langle B_{\underline{\bar{q}}\alpha} B^\dagger_{\underline{\bar{q}}\alpha}\rangle\} . \qquad (4.28b)
\end{aligned}
$$

In obtaining (4.28b), we have used the symmetry (4.18), and have made use of the fact that the average is taken over non-interacting libron states, so that

$$\langle B^\dagger_{\underline{q}\alpha} B^\dagger_{\underline{q}'\beta}\rangle = \langle B_{\underline{q}\alpha} B_{\underline{q}'\beta}\rangle = 0 \qquad \langle B^\dagger_{\underline{q}\alpha} B_{\underline{q}'\beta}\rangle = \langle B^\dagger_{\underline{q}\alpha} B_{\underline{q}\beta}\rangle \delta_{\underline{q}\underline{q}'} \delta_{\alpha\beta} . \qquad (4.29)$$

But, since the librons obey boson commutation rules and hence Bose-Einstein statistics, we can write down

$$\langle B^{\dagger}_{\underline{q}\alpha} B_{\underline{q}\alpha} \rangle = \{\exp(\beta\epsilon_{\underline{q}\alpha}) - 1\}^{-1} \tag{4.30}$$

and

$$\langle B_{\underline{q}\alpha} B^{\dagger}_{\underline{q}\alpha} \rangle = \langle 1 + B^{\dagger}_{\underline{q}\alpha} B_{\underline{q}\alpha} \rangle = \exp(\beta\epsilon_{\underline{q}\alpha})\{\exp(\beta\epsilon_{\underline{q}\alpha}) - 1\}^{-1} . \tag{4.31}$$

Since $\epsilon_{\overline{\underline{q}}\alpha} = \epsilon_{\underline{q}\alpha}$ by the inversion symmetry of the crystal, we have finally

$$\begin{aligned} \langle Y_{20}(J) \rangle = \beta_1 + \frac{2}{N} |U_{\underline{q}J+\alpha}|^2 \{\exp(\beta\epsilon_{\underline{q}\alpha}) - 1\}^{-1} \\ \times \{(\beta_2 \xi^2_{\underline{q}\alpha} + \beta_4 \xi_{\underline{q}\alpha} \eta_{\underline{q}\alpha}) \\ + (\beta_2 \eta^2_{\underline{q}\alpha} + \beta_4 \xi_{\underline{q}\alpha} \eta_{\underline{q}\alpha}) \exp(\beta\epsilon_{\underline{q}\alpha})\} \end{aligned} \tag{4.32}$$

where symmetry (4.18) has again been invoked to replace the sum over σ by a factor of 2. The sum is easily evaluated over a convenient mesh of points in the Brillouin zone. The result must be independent of the sublattice J, which provides a useful check on the correctness of the numerical work. In addition to the explicit temperature dependence of (4.32), there is a further weak temperature dependence which enters through the temperature dependence of the spheroidal parameter c.

4.3 The Ground State

The ground state $|0\rangle$ of the non-interacting libron Hamiltonian is defined by the condition that it contain no librons: that is, that $B_{\underset{\sim}{q}\alpha}|0\rangle = 0$ for every $\underset{\sim}{q}$ and α. The set of states of the crystal which we implicitly used when quantizing the Hamiltonian are product states of single-molecule wave functions, and the ground state of this set, $|0'\rangle$, is the state in which every molecule in the crystal is in its ground state with $n_+ = n_- = 0$. It is easy to see that $|0'\rangle$ is not the ground state of the libron Hamiltonian, for the inverse equations to (4.10) and (4.15) show that $B_{\underset{\sim}{q}\alpha}$ may be expressed as a sum of $A^\dagger_{j\sigma}$ and $A_{j\sigma}$ operators. When applied to $|0'\rangle$, the $A_{j\sigma}$ operators give zero but the $A^\dagger_{j\sigma}$ operators do not. Hence $B_{\underset{\sim}{q}\alpha}|0'\rangle \neq 0$.

We do not attempt to express $|0\rangle$ in terms of single-molecule states, or indeed to give any physical description of its nature. We do note, however, two of its properties: it has exactly the same energy as does $|0'\rangle$, and it is (very slightly) less well ordered orientationally.

Neglecting the cubic and quartic ... terms in $\mathcal{H}$ (i.e., neglecting libron-libron interactions), we can write the ground-state energy in the libron representation as

$$\langle 0|\mathcal{H}|0\rangle = E_0 + \langle 0|\mathcal{H}_2|0\rangle \tag{4.33}$$

where E_0 represents the terms in $\mathcal{H}$ containing no libron operators. But $\langle 0|\mathcal{H}_2|0\rangle = 0$ from (4.14) and the definition of $|0\rangle$, so that the energy of $|0\rangle$ is just E_0.

The ground-state energy in the single-molecule representation is

$$\langle 0'|\mathcal{H}|0'\rangle = E_0 + \langle 0'|\mathcal{H}_2|0'\rangle \tag{4.34}$$

where E_0 represents the terms in $\mathcal{H}$ containing no single-molecule operators, and $\mathcal{H}_2$ is given in terms of single-molecule operators by (4.9a). Now the diagonalization of $\mathcal{H}_2$ did not generate any terms with no operators, so that E_0 is the same in (4.33) and (4.34). Also, from (4.9a), it is evident that $\langle 0'|\mathcal{H}_2|0'\rangle = 0$. Hence, in the non-interacting libron approximation (neglect of $\mathcal{H}_3$, $\mathcal{H}_4$, ...), the states $|0\rangle$ and $|0'\rangle$ have exactly the same energy E_0.

To examine the orientational order, we see from (4.24) that $\langle 0'|Y_{20}|0'\rangle = \beta_1$. We can find $\langle 0|Y_{20}|0\rangle$ by considering the limit $T \to 0$ of (4.32): the result is evidently

$$\langle 0|Y_{20}(J)|0\rangle = \beta_1 + \frac{2}{N}\,|U_{\underline{g}J+\alpha}|^2(\beta_2\eta_{\underline{g}\alpha}^2 + \beta_4\xi_{\underline{g}\alpha}\eta_{\underline{g}\alpha}) \;. \tag{4.35}$$

Because the sign of $\eta_{\underline{q}\alpha}$ may be negative for some modes, it is difficult to make an unambiguous prediction about the sign of the correction term. Because the spheroidal matrix elements β_2 and β_4 are negative and nearly equal, one suspects that the correction will be negative, and this is borne out in practice. For the "fitted potential" (see Chapter 6) we find $\beta_1 = 0.552$ and $\langle 0|Y_{20}(J)|0\rangle = 0.549$. This indicates that the average angular displacement of the molecules from their classical equilibrium directions is very slightly larger in the state $|0\rangle$ than in the state $|0'\rangle$.

The conclusion to be drawn from this discussion is that, while the states $|0\rangle$ and $|0'\rangle$ are different, they have the same energy and very nearly the same degree of orientational ordering, so that the difference in their nature is probably very slight.

4.4 The Cubic Terms

We now present the terms in the Hamiltonian which contain three libron operators, i.e., those terms of order $Bo^{\frac{1}{2}}$. Since $\underline{J}^2$ contains no such terms, they arise only from the intermolecular potential. We note that the first sum in Eq. (4.7) can generate no terms with three operators, and we use the second sum in (4.7) to write down

$$\begin{aligned}\mathcal{H}_3 = C_{jk}(m,m')\{&a_m e^{\sigma}_{m'}(A^{\dagger}_{k\sigma}A^{\dagger}_{k\sigma}A^{\dagger}_{k\bar\sigma} + A_{k\sigma}A_{k\bar\sigma}A_{k\bar\sigma})\\ &+ a_m f^{\sigma_1\sigma_2}_{m'}(A^{\dagger}_{k\sigma_1}A^{\dagger}_{k\sigma_2}A_{k\sigma_2} + A^{\dagger}_{k\bar\sigma_2}A_{k\bar\sigma_2}A_{k\bar\sigma_1})\\ &+ b^{\sigma}_m(A^{\dagger}_{j\sigma} + A_{j\bar\sigma})c^{\sigma_1\bar\sigma_2}_{m'}(A^{\dagger}_{k\sigma_1}A_{k\bar\sigma_2})\\ &+ b^{\sigma}_m(A^{\dagger}_{j\sigma} + A_{j\bar\sigma})d^{\sigma_1\sigma_2}_{m'}(A^{\dagger}_{k\sigma_1}A^{\dagger}_{k\sigma_2} + A_{k\bar\sigma_2}A_{k\bar\sigma_1})\}. \quad (4.36)\end{aligned}$$

By a similar argument to that used on $\mathcal{H}_1$, one may show that the sums involving $e^{\sigma}_{m'}$ and $f^{\sigma_1\sigma_2}_{m'}$ both vanish. In the remaining terms, we replace the indices σ, σ_1, and σ_2 by σ_1, σ_2, and σ_3 respectively, obtaining

$$\begin{aligned}\mathcal{H}_3' = C_{jk}(m,m')b^{\sigma_1}_m\{&c^{\sigma_2\bar\sigma_3}_{m'}(A^{\dagger}_{j\sigma_1}A^{\dagger}_{k\sigma_1}A_{k\bar\sigma_2} + A^{\dagger}_{k\sigma_2}A_{k\bar\sigma_3}A_{j\bar\sigma_1})\\ &+ d^{\sigma_2\sigma_3}_{m'}(A^{\dagger}_{j\sigma_1}A^{\dagger}_{k\sigma_2}A^{\dagger}_{k\sigma_3} + A_{k\bar\sigma_3}A_{k\bar\sigma_2}A_{j\bar\sigma_1}\\ &+ A^{\dagger}_{j\sigma_1}A_{k\bar\sigma_2}A_{k\bar\sigma_3} + A^{\dagger}_{k\sigma_3}A^{\dagger}_{k\sigma_2}A_{j\bar\sigma_1})\} \quad . \qquad (4.37)\end{aligned}$$

We have made use of the commutation rules of the operators in arriving at (4.37). Note that j and k may be assumed to be different sites since $C_{jk}(m,m') = 0$ for $j = k$. We can make the expression more symmetrical by observing that

$$\sum_{\sigma_2\sigma_3} c^{\sigma_2\bar\sigma_3}_{m'}A^{\dagger}_{j\sigma_2}A_{j\bar\sigma_3} = \sum_{\sigma_2\sigma_3} c^{\sigma_2\bar\sigma_3}_{m'}A^{\dagger}_{j\sigma_3}A_{j\bar\sigma_2} \quad . \qquad (4.38)$$

In deriving Eq. (4.38), one makes use of the symmetry $c_{m'}^{\sigma_2\bar{\sigma}_3} = c_{m'}^{\sigma_3\bar{\sigma}_2}$, which follows easily from (4.4c).

We now rewrite $\mathcal{H}_3$ in terms of the libron operators $B_1^\dagger \equiv B_{\underline{q}_1\alpha_1}^\dagger$ etc., using Eqs. (4.12), (4.15), and (4.18). We find

$$\begin{aligned}\mathcal{H}_3 = N^{-\frac{1}{2}}\,\delta(\underline{q}_1+\underline{q}_2+\underline{q}_3)\,C_{\underline{q}_1JK}^{mm'}\,b_m^{\sigma_1}\,U^*_{\underline{q}_1J\sigma_1\alpha_1}U^*_{\underline{q}_2K\sigma_2\alpha_2}U^*_{\underline{q}_3K\sigma_3\alpha_3}\\
\times\,[c_{m'}^{\sigma_2\bar{\sigma}_3}\{((\xi_1B_1^\dagger+\eta_1B_{\bar{1}})(\xi_2B_2^\dagger+\eta_2B_{\bar{2}})(\eta_3B_3^\dagger+\xi_3B_{\bar{3}})\\
+\,(\xi_3B_3^\dagger+\eta_3B_{\bar{3}})(\eta_2B_2^\dagger+\xi_2B_{\bar{2}})(\eta_1B_1^\dagger+\xi_1B_{\bar{1}})\}\\
+\,d_{m'}^{\sigma_2\sigma_3}\{((\xi_1B_1^\dagger+\eta_1B_{\bar{1}})(\xi_2B_2^\dagger+\eta_2B_{\bar{2}})(\xi_3B_3^\dagger+\eta_3B_{\bar{3}})\\
+\,(\eta_3B_3^\dagger+\xi_3B_{\bar{3}})(\eta_2B_2^\dagger+\xi_2B_{\bar{2}})(\eta_1B_1^\dagger+\xi_1B_{\bar{1}})\\
+\,(\xi_1B_1^\dagger+\eta_1B_{\bar{1}})(\eta_2B_2^\dagger+\xi_2B_{\bar{2}})(\eta_3B_3^\dagger+\xi_3B_{\bar{3}})\\
+\,(\xi_3B_3^\dagger+\eta_3B_{\bar{3}})(\xi_2B_2^\dagger+\eta_2B_{\bar{2}})(\eta_1B_1^\dagger+\xi_1B_{\bar{1}})\}]\end{aligned} \qquad (4.39)$$

where

$$\delta(\underline{G}) = \begin{cases} 1 & \text{if } \underline{G} \text{ is a reciprocal lattice vector,} \\ 0 & \text{otherwise.} \end{cases}$$

When we expand these operator products and normally order the operators, placing creation operators before annihilation operators, some terms containing one operator will be thrown up by the commutation rules. For example,

$$B_1^\dagger B_{\overline{2}} B_3^\dagger = B_1^\dagger B_3^\dagger B_{\overline{2}} + B_1^\dagger \delta_{\overline{2}3} \quad . \qquad (4.40)$$

However, because such terms contain the additional Kronecker delta $\delta_{\overline{2}3} = \delta_{\overline{\underline{g}_2}\underline{g}_3}\delta_{\alpha_2\alpha_3}$, such terms are less numerous by a factor N than the three-operator terms. Also, because of the leading factor of $N^{-\frac{1}{2}}$ in $\mathcal{H}_3$, these terms are each smaller by a factor N than the corresponding terms which would arise in $\mathcal{H}_1$ if the crystal symmetry were slightly distorted to make $\mathcal{H}_1$ non-zero. In the limit of a large crystal, $N \to \infty$, we may therefore neglect these terms entirely, and we are therefore justified in commuting the B operators freely while passing to the normally ordered form. The form that results is

$$\begin{aligned}\mathcal{H}_3 = N^{-\frac{1}{2}}\,&\delta(\underline{g}_1+\underline{g}_2+\underline{g}_3)\,C^{mm'}_{\underline{g}_1JK}\,b_m^{\sigma_1}\,U^*_{\underline{g}_1J\sigma_1\alpha_1}U^*_{\underline{g}_2K\sigma_2\alpha_2}U^*_{\underline{g}_3K\sigma_3\alpha_3}\\ &\times[\{c_{m'}^{\sigma_2\overline{\sigma}_3}(\xi_1\xi_2\eta_3+\eta_1\eta_2\xi_3) + d_{m'}^{\sigma_2\sigma_3}(\xi_1+\eta_1)(\xi_2\xi_3+\eta_2\eta_3)\}\\ &\times\{B_1^\dagger B_2^\dagger B_3^\dagger + B_{\overline{3}}B_{\overline{2}}B_{\overline{1}}\} + \{c_{m'}^{\sigma_2\overline{\sigma}_3}(\xi_1\xi_2\xi_3+\eta_1\eta_2\eta_3)\\ &+ d_{m'}^{\sigma_2\sigma_3}(\xi_1+\eta_1)(\xi_2\eta_3+\eta_2\xi_3)\}\{B_1^\dagger B_2^\dagger B_{\overline{3}} + B_3^\dagger B_{\overline{2}}B_{\overline{1}}\} + \ldots\end{aligned}$$

$$+ \{c_{m'}^{\sigma_2\bar{\sigma}_3}(\xi_1\eta_2\eta_3+\eta_1\xi_2\xi_3) + d_{m'}^{\sigma_2\sigma_3}(\xi_1+\eta_1)(\eta_2\xi_3+\xi_2\eta_3)\}$$

$$\times \{B_1^\dagger B_3^\dagger B_{\bar{2}}+B_2^\dagger B_{\bar{3}}B_{\bar{1}}\}+\{c_{m'}^{\sigma_2\bar{\sigma}_3}(\eta_1\xi_2\eta_3+\xi_1\eta_2\xi_3)$$

$$+ d_{m'}^{\sigma_2\sigma_3}(\xi_1+\eta_1)(\xi_2\xi_3+\eta_2\eta_3)\}\{B_3^\dagger B_2^\dagger B_{\bar{1}}+B_1^\dagger B_{\bar{2}}B_{\bar{3}}\}] \quad . \tag{4.41}$$

The last three terms, those of the form $B^\dagger B^\dagger B+B^\dagger BB$, can be combined into a single term by a redefinition of the indices of summation. A symmetrical expression for $\mathcal{H}_3$ could be obtained by making the permutations 1→2→3→1 in the second such term and 1→3→2→1 in the last term. For numerical work, however, it is more important to have an expression containing few terms than to have one of high symmetry. We obtain the fewest terms, at the cost of asymmetrical expressions, by making the interchanges 2↔3, σ_2↔σ_3 and 1↔3, σ_1↔σ_3, J↔K respectively. The manipulations are straightforward but tedious, and one obtains the result

$$\mathcal{H}_3 = V_{123}^{3a}(B_1^\dagger B_2^\dagger B_3^\dagger+B_{\bar{3}}B_{\bar{2}}B_{\bar{1}}) + V_{123}^{3b}(B_1^\dagger B_2^\dagger B_{\bar{3}}+B_3^\dagger B_{\bar{2}}B_{\bar{1}}) \tag{4.42}$$

where $V_{123}^{3a} \equiv V^{3a}_{\underline{g}_1\alpha_1\underline{g}_2\alpha_2\underline{g}_3\alpha_3}$

$$= N^{-\frac{1}{2}}\,\delta(\underline{g}_1+\underline{g}_2+\underline{g}_3)\,C^{mm'}_{\underline{g}_1JK}b_m^{\sigma_1}U^*_{\underline{g}_1J\sigma_1\alpha_1}U^*_{\underline{g}_2K\sigma_2\alpha_2}U^*_{\underline{g}_3K\sigma_3\alpha_3}$$

$$\times \{c_{m'}^{\sigma_2\bar{\sigma}_3}(\xi_1\xi_2\eta_3+\eta_1\eta_2\xi_3)+d_{m'}^{\sigma_2\sigma_3}(\xi_1+\eta_1)(\xi_2\xi_3+\eta_2\eta_3)\} \tag{4.43a}$$

$$V^{3b}_{123} = N^{-\frac{1}{2}}\,\delta(q_1+q_2+q_3)\,U^*_{\underline{q}_1 J\sigma_1\alpha_1}U^*_{\underline{q}_2 K\sigma_2\alpha_2}U^*_{\underline{q}_3 K\sigma_3\alpha_3}$$

$$\times\ [C^{mm'}_{\underline{q}_1 JK}b_m^{\sigma_1}\{c_{m'}^{\sigma_2\overline{\sigma}_3}(\xi_1+\eta_1)(\xi_2\xi_3+\eta_2\eta_3)$$

$$+\ 2d_{m'}^{\sigma_2\sigma_3}(\xi_1+\eta_1)(\xi_2\eta_3+\eta_2\xi_3)\}$$

$$+\ C^{mm'}_{\underline{q}_3 KJ}b_m^{\sigma_3}\{c_{m'}^{\sigma_1\overline{\sigma}_2}(\eta_1\xi_2\eta_3+\xi_1\eta_2\xi_3)$$

$$+\ d_{m'}^{\sigma_1\sigma_2}(\xi_3+\eta_3)(\xi_1\xi_2+\eta_1\eta_2)\}]\ . \qquad (4.43b)$$

The Eqs. (4.4c) can be used to reduce the number of summations in these expressions. In considering V^{3a}, we do this by eliminating the sum on σ_3, writing out explicitly the terms with $\sigma_3 = \sigma_2$ and $\sigma_3 = \overline{\sigma}_2$. Then one finds

$$V^{3a}_{123} = N^{-\frac{1}{2}}\,\delta(q_1+q_2+q_3)\,\gamma_1\sigma_1 U^*_{\underline{q}_1 J\sigma_1\alpha_1}U^*_{\underline{q}_2 K\sigma_2\alpha_2}$$

$$\times\ \{C^{\sigma_1,2\sigma_2}_{\underline{q}_1 JK}U^*_{\underline{q}_3 K\sigma_2\alpha_3}[\delta_3(\xi_1\xi_2\eta_3+\eta_1\eta_2\xi_3)$$

$$+\ \delta_1(\xi_1+\eta_1)(\xi_2\xi_3+\eta_2\eta_3)] + C^{\sigma_1 0}_{\underline{q}_1 JK}U_{\underline{q}_3 K\sigma_2\alpha_3}$$

$$\times\ [\beta_2(\xi_1\xi_2\eta_3+\eta_1\eta_2\xi_3) + \frac{1}{2}\,\beta_4(\xi_1+\eta_1)(\xi_2\xi_3+\eta_2\eta_3)]\}. \qquad (4.44a)$$

(Only the subscripts on ξ and η are libron mode indices. γ_1 and the other coefficients are the numbers defined in Eq.

(4.1).) In going from (4.43a) to (4.44a), the number of terms in the summation has been reduced from 3200 to 64. In applying the same process to V^{3b}, we eliminate σ_3 in the first part of Eq. (4.43b) and σ_2 in the second part, obtaining

$$\begin{aligned}
V^{3b}_{123} = {} & N^{-\frac{1}{2}} \delta(q_1+q_2+q_3)\gamma_1 U^*_{\underline{q}_1 J\sigma_1\alpha_1} \Big(\sigma_1 U^*_{\underline{q}_2 K\sigma_2\alpha_2} \\
& \times \{C^{\sigma_1, 2\sigma_2}_{\underline{q}_1 JK} U^*_{\underline{q}_3 K\sigma_2\alpha_3} (\xi_1+\eta_1)[\delta_3(\xi_2\xi_3+\eta_2\eta_3) \\
& + 2\delta_1(\xi_2\eta_3+\eta_2\xi_3)] + C^{\sigma_1 0}_{\underline{q}_1 JK} U_{\underline{q}_3 K\sigma_2\alpha_3} (\xi_1+\eta_1) \\
& \times [\beta_2(\xi_2\xi_3+\eta_2\eta_3)+\beta_4(\xi_2\eta_3+\eta_2\xi_3)]\} + \sigma_3 U^*_{\underline{q}_3 K\sigma_3\alpha_3} \\
& \times \{C^{\sigma_3, 2\sigma_1}_{\underline{q}_3 KJ} U^*_{\underline{q}_2 K\sigma_1\alpha_2} [\delta_3(\eta_1\xi_2\eta_3+\xi_1\eta_2\xi_3) \\
& + \delta_1(\xi_3+\eta_3)(\xi_1\xi_2+\eta_1\eta_2)] + C^{\sigma_3 0}_{\underline{q}_3 KJ} U_{\underline{q}_2 K\sigma_1\alpha_2} \\
& \times [\beta_2(\eta_1\xi_2\eta_3+\xi_1\eta_2\xi_3) + \tfrac{1}{2}\beta_4(\xi_3+\eta_3)(\xi_1\xi_2+\eta_1\eta_2)]\}\Big).
\end{aligned} \tag{4.44b}$$

The coefficients V^{3a} and V^{3b} must have a number of symmetries, some of which are not obvious from the asymmetric expressions given here. Since some of the libron modes are equivalent in Eq. (4.42), we conclude that V^{3a}_{123} must be invariant under any permutation of its subscripts, and that $V^{3b}_{123} = V^{3b}_{213}$. Also, both sets of coefficients are invariant under any transformation of $\underline{q}_1$, $\underline{q}_2$, and $\underline{q}_3$ which leaves the $C_{\underline{q}}$ coefficients invariant and which still satisfies the delta function $\delta(\underline{q}_1+\underline{q}_2+\underline{q}_3)$, because all the other quantities in (4.44) depend on $\underline{q}$ only through $C_{\underline{q}}$. In particular, the inversion symmetry of the crystal implies that $C^{mm'}_{\bar{\underline{q}}JK} = C^{mm'}_{\underline{q}JK}$, and so we have $V^{3a}_{123} = V^{3a}_{\bar{1}\bar{2}\bar{3}}$ and $V^{3b}_{123} = V^{3b}_{\bar{1}\bar{2}\bar{3}}$. So we may rewrite (4.42) in the form

$$\mathcal{H}_3 = V^{3a}_{123}(B^\dagger_1 B^\dagger_2 B^\dagger_3 + B_3 B_2 B_1) + V^{3b}_{12\bar{3}}(B^\dagger_1 B^\dagger_2 B_3 + B^\dagger_3 B_2 B_1) \quad . \tag{4.45}$$

Finally, if this expression is to be hermitian, we require V^{3a} and V^{3b} to be real.

CHAPTER 5

APPLICATION OF THE CUBIC TERMS

- SPIN-LATTICE RELAXATION

5.1 Introduction

In this chapter, we present a calculation of an effect for which the three-operator terms in the Hamiltonian are essential. The example chosen, the temperature dependence of the spin-lattice relaxation time T_1, is one for which no theory presently exists. The experiments of DeReggi et al. (1969) were analysed in terms of a phenomenological theory due originally to Bayer (Bayer 1951; Woessner and Gutowsky 1963) which relates T_1 to the average lifetime τ_a for transitions between "torsional states" of a molecule. If one regards the motions of the molecules in a crystal as being coherent collective excitations (librons), such a description becomes physically unnatural. Further, the lifetime τ_a required to explain the T_1 measurements is itself strongly temperature-dependent. According to the results of DeReggi et al. (1969), T_1 varies as $T^{-3.5}$ over a wide temperature range, while τ_a varies roughly as $T^{-3.2}$. The Bayer theory therefore seems to contribute little to an understanding of relaxation in nitrogen.

We summarize briefly the basic theory of nuclear quadrupole resonance and spin-lattice relaxation in nitrogen (Abragam 1961; Slichter 1963; Scott 1962; Woessner and Gutowsky 1963; Van Kranendonk and Walker 1968). The abundant ^{14}N nucleus has spin $I = 1$ and a finite quadrupole moment eQ. In the rather open crystal structure of the α phase, most of the electric field gradient experienced by a nucleus is due to the molecule in which it resides, only about 0.1% being contributed by neighbouring molecules (McEnnan 1971). The field gradient eq due to the molecule is cylindrically symmetric, and the energy splitting between the $m_I = 0$ and the $m_I = \pm 1$ states is then

$$h\nu_Q = \frac{3}{4} e^2qQ \quad , \tag{5.1}$$

where ν_Q is the pure quadrupole resonance frequency. Equation (5.1) applies to a static molecule, but the molecules in a crystal are in fact librating, so that the field gradient experienced by the nucleus librates, at a frequency much larger than ν_Q.

This libration of the field gradient has two effects. First, it weakens the average field gradient experienced by the nucleus, so that the energy splitting is reduced to

$$h\nu_Q = \frac{3}{4} e^2qQ\langle P_2(\cos\theta)\rangle = \frac{3}{2}\sqrt{\frac{\pi}{5}}\, e^2qQ\langle Y_{20}(\theta,\phi)\rangle \quad . \tag{5.2}$$

Second, the fluctuations in the field gradient cause transitions between the spin states, causing the spin populations to approach thermal equilibrium. This transfers energy between the spin system and the molecular librations (i.e., the lattice), and is characterized by the spin-lattice relaxation time T_1. Quadrupole relaxation appears to be more effective than dipole relaxation in most cases where the nucleus has a non-zero quadrupole moment, and we shall assume it to be the dominant mechanism here.

5.2 General Formulation

The basic approach which we shall use in calculating T_1 is that of Van Kranendonk and Walker (1968). The spin-lattice Hamiltonian, which expresses the interaction between the quadrupole moments of the nuclei and the electric field gradients in which they are situated, is

$$\mathcal{H}_{s\ell} = \sum_{j} \sum_{m=-2}^{2} Q_j^{-m} F_j^{m} \qquad (5.3a)$$

where $Q^0 = \frac{1}{2} [3I_z^2 - I(I+1)]eQ$

$$Q^{\pm 1} = \frac{1}{4} \sqrt{6}\, [I_z I_\pm + I_\pm I_z]eQ \qquad (5.3b)$$

$$Q^{\pm 2} = \frac{1}{4} \sqrt{6}\, I_\pm^2 eQ$$

and

$$F^0 = \sqrt{\frac{\pi}{5}}\, eqY_{20}$$

$$F^{\pm 1} = \mp \sqrt{\frac{\pi}{5}}\, eqY_{2\pm 1} \qquad (5.3c)$$

$$F^{\pm 2} = \sqrt{\frac{\pi}{5}}\, eqY_{2\pm 2} \; .$$

Equations (5.3) are equivalent to the Hamiltonian used by Woessner and Gutowsky (1963), but are written for the case $I = 1$ and are cast in the form used by Van Kranendonk and Walker (1968). (The latter authors were concerned with relaxation by phonons in alkali halides, rather than by librons in molecular solids, and they consequently had different expressions for F_ℓ^m.)

If we define W_1 as the rate at which $\mathcal{H}_{s\ell}$ induces transitions from a state $m_I = 0$ to $m_I = 1$ (or from $m_I = 0$ to $m_I = -1$), then one finds from first-order perturbation theory that

$$W_1 = 4\pi\kappa \sum_{nn'} P_n |F_{nn'}|^2 \delta(E_{n'} - E_n - h\omega_Q) \qquad (5.4a)$$

where $\kappa = \frac{3}{8} e^2Q^2/\hbar$. Here $|n\rangle$ denotes a state of the lattice with energy E_n and occupation probability P_n, and, in the present case,

$$F_{nn'} = \langle n'|F^{+1}|n\rangle \quad . \tag{5.4b}$$

Equation (5.4a) is of the form used by Van Kranendonk and Walker (1968), but the more familiar form for a transition rate in the theory of relaxation processes is that of a correlation function (Abragam 1961). By using the well-known identity

$$2\pi\hbar\delta(E) = \int_{-\infty}^{\infty} \exp(iE\tau/\hbar)d\tau \tag{5.5}$$

it is a straightforward matter to cast (5.4a) in the form

$$W_1 = -\frac{3\pi}{20\hbar^2} e^4q^2Q^2 \int_{-\infty}^{\infty} \langle Y_{21}(t)Y_{2-1}(t+\tau)\rangle \exp(i\omega_Q\tau)d\tau \quad , \tag{5.6}$$

which is essentially the expression given by Woessner and Gutowsky (1963).

To determine T_1 in terms of W_1, one needs to consider the steady-state solution of the master equation for the nuclear spin state populations (Slichter 1963). One finds (DeRaggi et al. 1969) that $T_1 = 1/(3W_1)$.

We calculate the states $|n\rangle$ by first-order perturbation theory in $\mathcal{H}_3$ (Chapter 4), using multilibron states $|\{N_{q\alpha}\}\rangle$ as the unperturbed states, where $\{N_{q\alpha}\}$ is the set of occupation numbers for the libron modes. Then

$$|n\rangle = (1 + \frac{P}{E_n^0 - \mathcal{H}_2}\mathcal{H}_3)|\{N_{g\alpha}\}\rangle \qquad (5.7)$$

where $E_n^0 = \sum_{g\alpha} N_{g\alpha}\epsilon_{g\alpha}$ is the energy of the state $|\{N_{g\alpha}\}\rangle$, and P denotes the principal value. Also

$$E_n = E_n^0 + \langle\{N_{g\alpha}\}|\mathcal{H}_3|\{N_{g\alpha}\}\rangle = E_n^0 \qquad (5.8)$$

since the diagonal matrix elements of $\mathcal{H}_3$ clearly vanish. Then, to first order in $\mathcal{H}_3$, we have

$$\begin{aligned} F_{nn'} = \langle\{N'_{g\alpha}\}|F^{+1} &+ F^{+1}\frac{P}{E_n^0 - \mathcal{H}_2}\mathcal{H}_3 \\ &+ \mathcal{H}_3\frac{P}{E_{n'}^0 - \mathcal{H}_2}F^{+1}|\{N_{g\alpha}\}\rangle \end{aligned} \qquad (5.9)$$

where $\{N'_{g\alpha}\}$ is a different set of occupation numbers, and

$$W_1 = 4\pi\kappa P_n|F_{nn'}|^2\delta(E_{n'}^0 - E_n^0 - \hbar\omega_Q) \quad . \qquad (5.10)$$

In analysing the processes which contribute to W_1, it is important to recognise that the energies of the states $|\{N_{g\alpha}\}\rangle$ and $|\{N'_{g\alpha}\}\rangle$ must differ by the energy $\hbar\omega_Q$, which is about 10^{-4} cm^{-1}, compared to the lowest libron energies of some tens of wavenumbers. Because of the presence of this energy gap in the libron spectrum, a process in which a single libron is created or annihilated (the d process of

Fig. 3) cannot satisfy the energy delta function in Eq. (5.10) and so cannot contribute to W_1. Provided the libron dispersion is sufficient that the highest-energy librons have at least twice as much energy as the lowest-energy librons, then a three-libron process (identified by 3L in Fig. 3) would be possible in which two low-energy librons are created (annihilated) and one high-energy libron is annihilated (created). Depending on the potential used, this condition may or may not be satisfied (see the density of states results, Chapter 6), but in any case the phase space for such processes is clearly very small. In addition, a straightforward analysis of the matrix elements involved shows that such a process is of higher order in $c^{-\frac{1}{2}}$ than the anharmonic Raman process which we shall consider.

In Fig. 3 we present Feynman diagrams for the above two processes, and for two other processes discussed by Van Kranendonk and Walker, the first-order Raman (1R) process, and the anharmonic Raman (aR) process. The contribution of the 1R process to W_1 is obtained by setting $\mathscr{H}_3 = 0$ in Eq. (5.9) and evaluating the resulting matrix element $F_{nn'}$ between states which differ by precisely two librons. But this matrix element is rigorously zero because F^{+1} ($\sim Y_{21}$) does not contain any terms involving two libron operators, as may be seen from the expansion (4.1c).

Fig. 3: Diagrams for some elementary relaxation processes, after Van Kranendonk and Walker (1968). The solid lines denote spin states and the dotted lines represent librons. d: direct process (rigorously zero). 1R: first-order Raman process (rigorously zero). aR: anharmonic Raman process. 3L: three-libron process (assumed small because of phase-space restrictions).

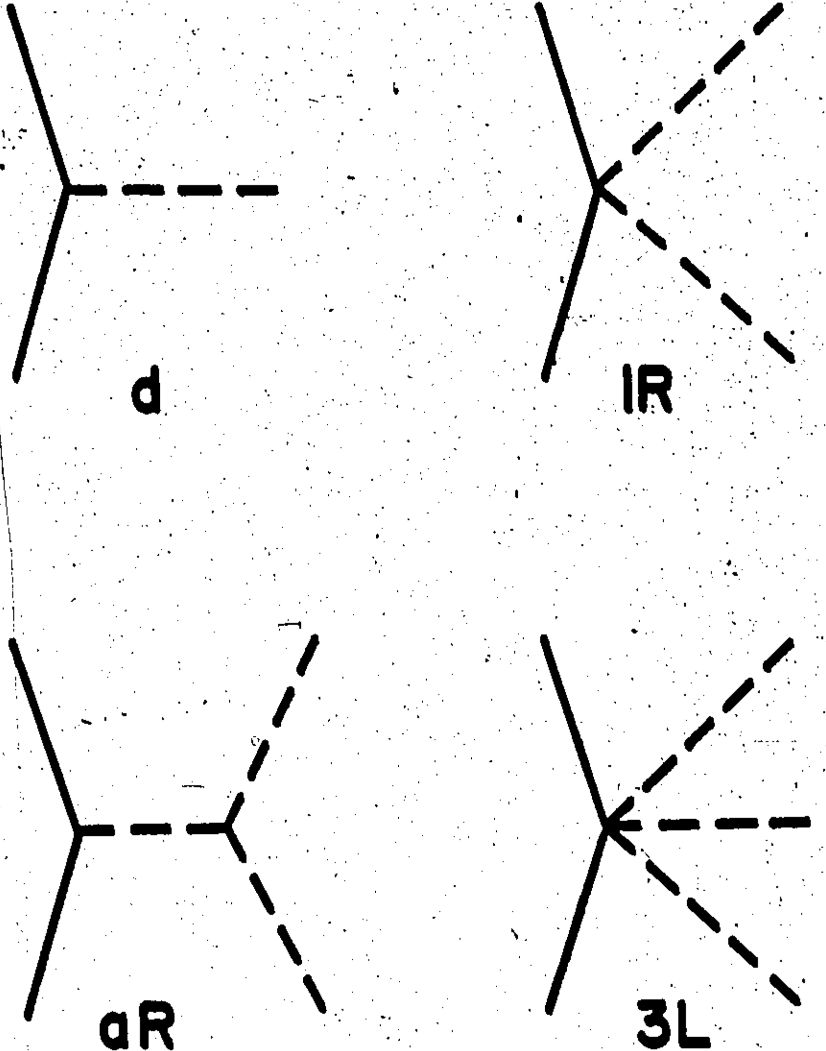

Fig. 3

The process which we shall calculate is the anharmonic Raman process, whose contribution to W_1 is obtained by setting

$$F^{+1} = -\sqrt{\frac{\pi}{5}}\, eqY_{21} = -\sqrt{\frac{\pi}{5}}\, eq\gamma_1 (A_+^\dagger + A_-) \tag{5.11}$$

in (5.9), and evaluating $F_{nn'}$ between states which differ by two librons of essentially equal energy, one being created and the other destroyed in the process. Note that the terms involving V^{3a} in Eq. (4.45) do not contribute to these matrix elements because, when combined with the one-operator terms of (5.11), they either create (annihilate) four librons or they create (annihilate) three librons and annihilate (create) one, with a net population difference between the initial and final states of four or two librons. The latter process could conserve energy if the single libron had as much energy as the other three together, but again we rule this out on phase-space grounds.

Using Eqs. (4.10) and (4.15), we write F^{+1} for a molecule on a particular sublattice J in the form

$$F_J^{+1} = -\sqrt{\frac{\pi}{5}}\, eq\gamma_1 N^{-\frac{1}{2}} U^*_{\underline{g}J+\alpha} (\xi_{\underline{g}\alpha} + \eta_{\underline{g}\alpha})(B^\dagger_{\underline{g}\alpha} + B_{\overline{\underline{g}}\alpha}) \tag{5.12a}$$

$$= -\sqrt{\frac{\pi}{5}}\, eqY_{\underline{g}J\alpha}(B^\dagger_{\underline{g}\alpha} + B_{\overline{\underline{g}}\alpha}) \tag{5.12b}$$

where

$$y_{\underline{g}J\alpha} = N_1^{-\frac{1}{2}} \gamma_1 U^*_{\underline{g}J+\alpha}(\xi_{\underline{g}\alpha} + \eta_{\underline{g}\alpha}) \quad . \qquad (5.12c)$$

By the inversion symmetry of the crystal, $y_{\bar{\underline{g}}J\alpha} = y_{\underline{g}J\alpha}$ and so one may omit the bar over the second term in Eq. (5.12b). These numbers, of course, are different for different sublattices J, but the final expression for W_1 must be independent of the sublattice and hence can be averaged over J. Until this is done, the expressions obtained will not have the full cubic symmetry, because the choice of a particular sublattice selects out a special [111] direction.

5.3 Calculation of W_1

We now evaluate W_1 for the aR process, using (5.9), (5.10), and (5.12b), assuming that the relaxing nucleus lies on sublattice J. We take the states $|\{N_{\underline{g}\alpha}\}\rangle$ and $|\{N'_{\underline{g}\alpha}\}\rangle$ to be $|N_2, N_3\rangle$ and $|N_2-1, N_3+1\rangle$ respectively. (The populations of all modes except $2 \equiv \underline{g}_2\alpha_2$ and $3 \equiv \underline{g}_3\alpha_3$ are unchanged and have been suppressed.) The corresponding $F_{nn'}$ will be written as $F_J(N_2, N_3)$.

We introduce a set of intermediate states in which the population of some mode $1 \equiv \underline{g}_1\alpha_1$ has been changed from N_1 to N_1'. Then we may write (5.9) in the form

$$F_J(N_2,N_3) = -\sqrt{\frac{\pi}{5}}\, eqy_{g_1 J\alpha_1} \sum_{N_1'} \Big(\langle N_1, N_2-1, N_3+1 | B_1^\dagger + B_1 | N_1', N_2-1, N_3+1 \rangle$$

$$\times \frac{\langle N_1', N_2-1, N_3+1 | V^{3b}_{45\bar{6}} (B_4^\dagger B_5^\dagger B_6 + B_6^\dagger B_5 B_4) | N_1, N_2, N_3 \rangle}{(N_1-N_1')\epsilon_1+\epsilon_2-\epsilon_3}$$

$$+ \frac{\langle N_1, N_2-1, N_3+1 | V^{3b}_{45\bar{6}} (B_4^\dagger B_5^\dagger B_6 + B_6^\dagger B_5 B_4) | N_1', N_2, N_3 \rangle}{(N_1-N_1')\epsilon_1-\epsilon_2+\epsilon_3}$$

$$\times \langle N_1', N_2, N_3 | B_1^\dagger + B_1 | N_1, N_2, N_3 \rangle \Big) \quad . \qquad (5.13)$$

The sum over the intermediate states involves a sum over both the occupation number N_1' (which has been made explicit) and a sum over the mode index 1 (which is implied by the summation convention outlined in Chapter 4). Although cases may arise in which mode 1 coincides with mode 2 or mode 3, we ignore these cases since they represent only about $\frac{1}{N}$th of the total number of terms. The matrix elements in (5.13) are

$$\langle N_1, N_2-1, N_3+1 | B_1^\dagger + B_1 | N_1', N_2-1, N_3+1 \rangle$$

$$= \sqrt{N_1}\,\delta_{N_1, N_1'+1} + \sqrt{(N_1+1)}\,\delta_{N_1, N_1'-1} \qquad (5.14)$$

$$\langle N_1', N_2-1, N_3+1 | B_4^\dagger B_5^\dagger B_6 + B_6^\dagger B_5 B_4 | N_1, N_2, N_3 \rangle$$

$$= \sqrt{N_2(N_3+1)}\,(\sqrt{(N_1+1)}\,\delta_{N_1,N_1'-1}(\delta_{14}\delta_{26}\delta_{35}+\delta_{15}\delta_{26}\delta_{34})$$

$$+ \sqrt{N_1}\,\delta_{N_1,N_1'+1}(\delta_{14}\delta_{25}\delta_{36}+\delta_{15}\delta_{24}\delta_{36})) \qquad (5.15)$$

with similar expressions for the other two matrix elements. $F_J(N_2,N_3)$ is then reduced to the form

$$F_J(N_2,N_3) = 2\sqrt{\frac{\pi}{5}}\, eqY_{\underline{g}_1 J\alpha_1}\sqrt{N_2(N_3+1)}$$

$$\times \left(\frac{V^{3b}_{12\bar{3}}}{\varepsilon_1+\varepsilon_2-\varepsilon_3} + \frac{V^{3b}_{13\bar{2}}}{\varepsilon_1-\varepsilon_2+\varepsilon_3}\right) . \qquad (5.16)$$

The factor of 2 arises when the symmetry $V^{3b}_{123} = V^{3b}_{213}$ (Chapter 4) is used to eliminate two of the V^{3b} coefficients. The population of mode 1 has disappeared from the expression because of a cancellation of the form $(N_1+1) - N_1$. Putting in the sums over the populations of all the levels, and including the weighting factor P_n, one obtains from Eq. (5.10) the transition rate for the aR process,

$$W_{aR}(J) = 4\pi\kappa\,\frac{4\pi}{5}\,e^2q^2 n(\varepsilon_2)(n(\varepsilon_3)+1)\,|Y_{\underline{g}_1 J\alpha_1}$$

$$\times \left(\frac{V^{3b}_{12\bar{3}}}{\varepsilon_1+\varepsilon_2-\varepsilon_3} + \frac{V^{3b}_{13\bar{2}}}{\varepsilon_1-\varepsilon_2+\varepsilon_3}\right)|^2\,\delta(\varepsilon_3-\varepsilon_2-\hbar\omega_Q) \qquad (5.17)$$

where $n(\epsilon) = (\exp(\beta\epsilon) - 1)^{-1}$ is the usual Bose-Einstein population factor. Since the energy delta function ensures that $|\epsilon_2 - \epsilon_3| = \hbar\omega_Q \sim 10^{-5}\, \epsilon_1$, and averaging over the sublattices, we obtain finally

$$W_{aR} = \frac{4}{5}\pi^2 e^2 q^2 \kappa \sum_{23} n(\epsilon_2)(n(\epsilon_3)+1)$$

$$\times \sum_{J} \Big| \sum_{1} \epsilon_1^{-1}\, Y_{\underline{q}_1 J \alpha_1}\, (V^{3b}_{12\bar{3}} + V^{3b}_{13\bar{2}}) \Big|^2\, \delta(\epsilon_3 - \epsilon_2 - \hbar\omega_Q) \quad . \tag{5.18}$$

(The sums have been written explicitly so as to show the order in which the sums and taking the absolute value are to be performed.) The sum on $\underline{q}_1$ actually contains only one term because of the momentum-conserving delta function which occurs in the definition of V^{3b}. The double Brillouin zone sum which remains is not easy to evaluate numerically. The sum over mode 2 need only be performed over the irreducible $\frac{1}{48}$th of the zone, but the sum over mode 3 must be performed over the entire zone, since any particular choice of $\underline{q}_2$ destroys the crystal symmetry by defining a preferred direction.

For numerical work, we certainly cannot claim to know the energies at any point in the Brillouin zone with an accuracy of parts in 10^6, so we shall not introduce any new error if we set $\hbar\omega_Q$ to zero in (5.18). It is convenient to measure $\underline{q}$ in units of $\frac{2\pi}{a}$, where a is the lattice spacing. The volume of the first Brillouin zone is then unity and it contains N $\underline{q}$ vectors, so that we can replace $\sum_{\underline{q}}$ by $N\iiint d^3\underline{q}$, which in turn we replace by

$$N \int_0^{\infty} d\epsilon \oiint |\nabla_{\underline{q}\alpha}(\epsilon)|^{-1}\, dS_{\underline{q}\alpha}(\epsilon) \quad ,$$

where $dS_{\underline{q}\alpha}(\epsilon)$ is an element of the surface in $\underline{q}$ space on which branch α has energy ϵ, and $\nabla_{\underline{q}\alpha}(\epsilon)$ is the $\underline{q}$-gradient of the energy of branch α at $dS_{\underline{q}\alpha}(\epsilon)$. We now define the quantity

$$|f_{2,3}|^2 = \frac{1}{4} N^2 \sum_J \Big| \sum_1 \epsilon_1^{-1}\, y_{\underline{q}_1 J\alpha_1} (V^{3b}_{12\bar{3}} + V^{3b}_{13\bar{2}}) \Big|^2 \tag{5.19}$$

Because we wish to distinguish sums over branches from integrals over $\underline{q}$, we will now write the composite mode subscripts, and the associated summations, explicitly. Using the energy-conserving delta function to eliminate one of the integrals over energy, we rewrite (5.18) in the form

$$W_{aR} = \frac{6\pi^2}{5\hbar} e^4 q^2 Q^2 \int_0^{\infty} d\epsilon\; n(\epsilon)(n(\epsilon)+1) \sum_{\alpha\alpha'} \oiint |\nabla_{\underline{q}\alpha}(\epsilon)|^{-1}$$
$$\times\, dS_{\underline{q}\alpha}(\epsilon) \oiint |\nabla_{\underline{q}'\alpha'}(\epsilon)|^{-1}\, dS_{\underline{q}'\alpha'}(\epsilon)\, |f_{\underline{q}\alpha;\underline{q}'\alpha'}|^2 \ . \tag{5.20}$$

The integrals lend themselves naturally to computation by the method of Gilat and Raubenheimer (1966). We use a shifted mesh of points in the Brillouin zone, from which $\underline{q}$ and $\underline{q}'$ points are selected, and a large number of energy bins of some suitably narrow width. We compute $|f_{\underline{q}\alpha,\underline{q}'\alpha'}|^2$ as an 8×8 matrix for the pair of points and (lacking any other tractable assumption) suppose it to be constant over the small cubes centred at the points $\underline{q}$ and $\underline{q}'$. Using the formulae presented by Gilat and Raubenheimer, we sweep through the pair of cubes, evaluating the contributions to the various energy bins of the surface elements

$$|\nabla_{\underline{q}\alpha}(\varepsilon)|^{-1}|\nabla_{\underline{q}'\alpha'}(\varepsilon)|^{-1}dS_{\underline{q}\alpha}(\varepsilon)\,dS_{\underline{q}'\alpha'}(\varepsilon) .$$

Finally we perform the integral over energy for a range of temperatures to obtain W_{aR} and hence T_1 as a function of temperature.

The drawback to the scheme is simply that computation of $|f_{\underline{q}\alpha,\underline{q}'\alpha'}|^2$ requires so much computer time (typically 5 to 10 seconds on the CDC 6400 for each $(\underline{q},\underline{q}')$ pair) that only a very coarse mesh can be used. However, the theory is similarly crude (notably in its neglect of the phonons and the libron-phonon coupling), so that we do not expect good quantitative agreement with experiment in any case, and the numerical work is probably sufficiently accurate to show the main trend of the results predicted by the theory.

Although we cannot evaluate W_{aR} analytically by examining Eq. (5.20), we can obtain the temperature dependence in the limits of high and low temperatures by putting in the thermal factors to obtain

$$W_{aR} \sim \int_0^\infty d\varepsilon\, e^{\beta\varepsilon}(e^{\beta\varepsilon} - 1)^{-2}\, \Phi(\varepsilon) \tag{5.21}$$

where Φ is some function of the libron energy. Since Φ is nonzero only in a band from about 40 K to 80 K (Chapter 6), one may extract the temperature factors in the limits $\beta\varepsilon \ll 1$ and $\beta\varepsilon \gg 1$. In the former case one finds $W_{aR} \sim \beta^{-2}$ and in the latter case one finds $W_{aR} \sim \exp(-\beta\varepsilon)$. As mentioned earlier, experiment gives $T_1 \sim T^{-3.5}$, i.e., $W_{aR} \sim \beta^{-3.5}$. The limit $\beta\varepsilon \ll 1$ (which is not applicable because the α phase is unstable above 35.6 K) therefore gives too weak a temperature dependence, while the limit $\beta\varepsilon \gg 1$ gives too strong a dependence. We may therefore hope that, in the regime $\beta\varepsilon \sim 1$, applicable at intermediate temperatures, the theory gives an approximately correct temperature dependence, but of course this depends on the exact form of Φ.

CHAPTER 6

RESULTS AND DISCUSSION

6.1 The Intermolecular Potential

In Figs. 4 through 8, we present graphs of the potential coefficients B_0, B_1, and A_μ as functions of R in the range spanning the first few neighbour shells in the Pa3 structure. (The arrows indicate the positions of these shells.) The potential models used are the Raich-Mills potential, the Kohin potential, the quadrupole-quadrupole potential, and the repulsive term of the Raich-Mills potential. The parameter values used are shown in column II of Table 2. Note that B_0 and B_1 vanish for the quadrupole potential.

It is evident from these graphs that the Kohin potential is very much harder than the Raich-Mills and the quadrupole-quadrupole potentials at small distances. This is not unexpected in view of the recent work of England et al. (1974) on the potential in H_2; these authors concluded that the 6-12 potential (essentially the Kohin form) was much harder than more physically realistic potentials.

Beyond about 5 Å, the repulsive parts of both the Kohin and the Raich-Mills potentials become negligible, and

Fig. 4: Intermolecular potential coefficient $B_0(R)$, calculated for various model potentials. The arrows at the top of the graph indicate the positions of the first 4 neighbour shells in the Pa3 crystal structure. ——— Full Raich-Mills potential. -·-·- Repulsive part of Raich-Mills potential. ······ Full Kohin potential (quadrupole moment = 1.52×10^{-26} esu). Note that $B_0(R)$ is zero for the quadrupole-quadrupole potential.

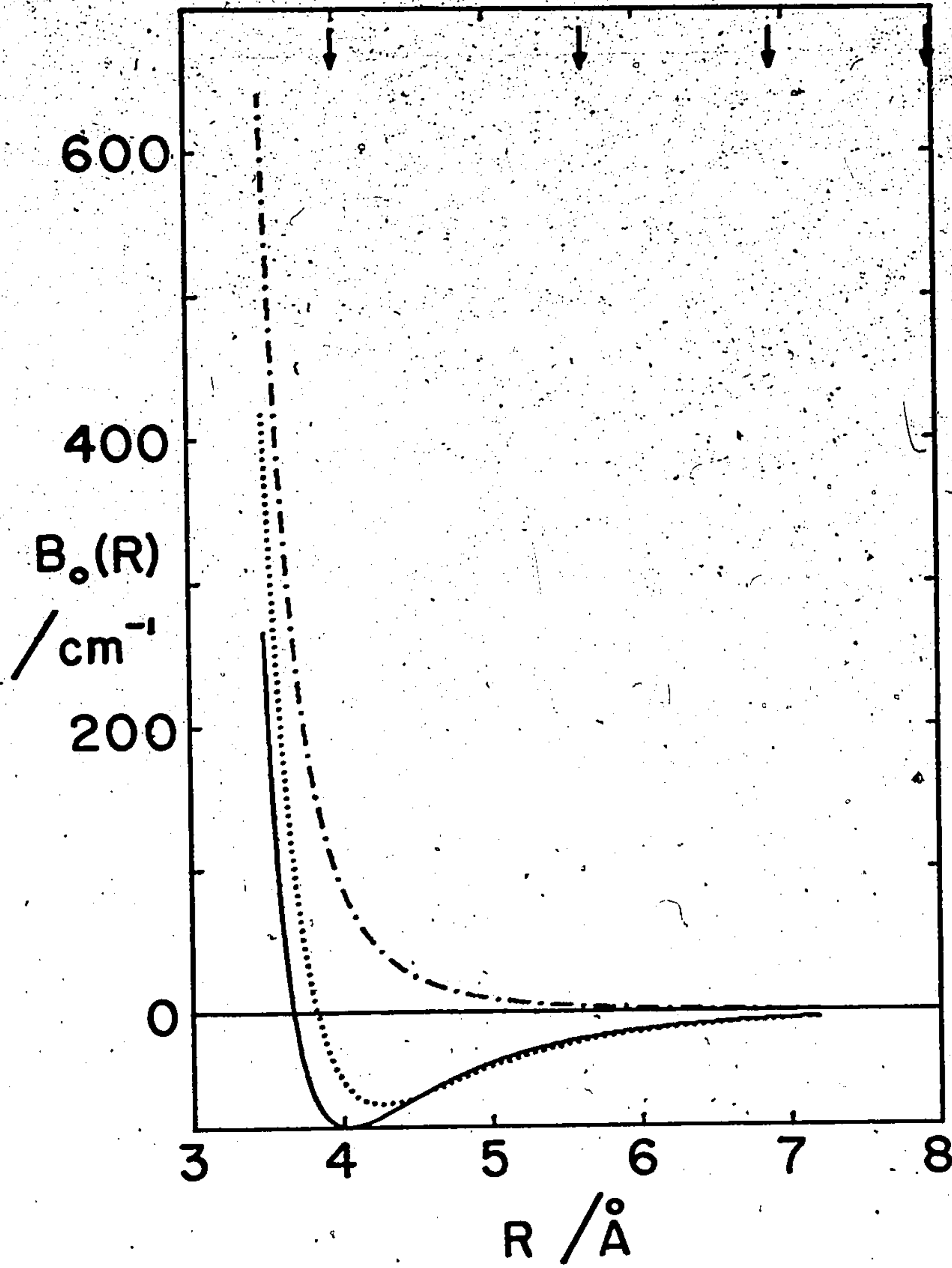

Fig. 4

Fig. 5: Intermolecular potential coefficient $B_l(R)$, calculated for various model potentials. The arrows at the top of the graph indicate the positions of the first 4 neighbour shells in the Pa3 crystal structure. ——— Full Raich-Mills potential. -·-·- Repulsive part of Raich-Mills potential. ····· Full Kohin potential (quadrupole moment = 1.52×10^{-26} esu). Note that $B_l(R)$ is zero for the quadrupole-quadrupole potential.

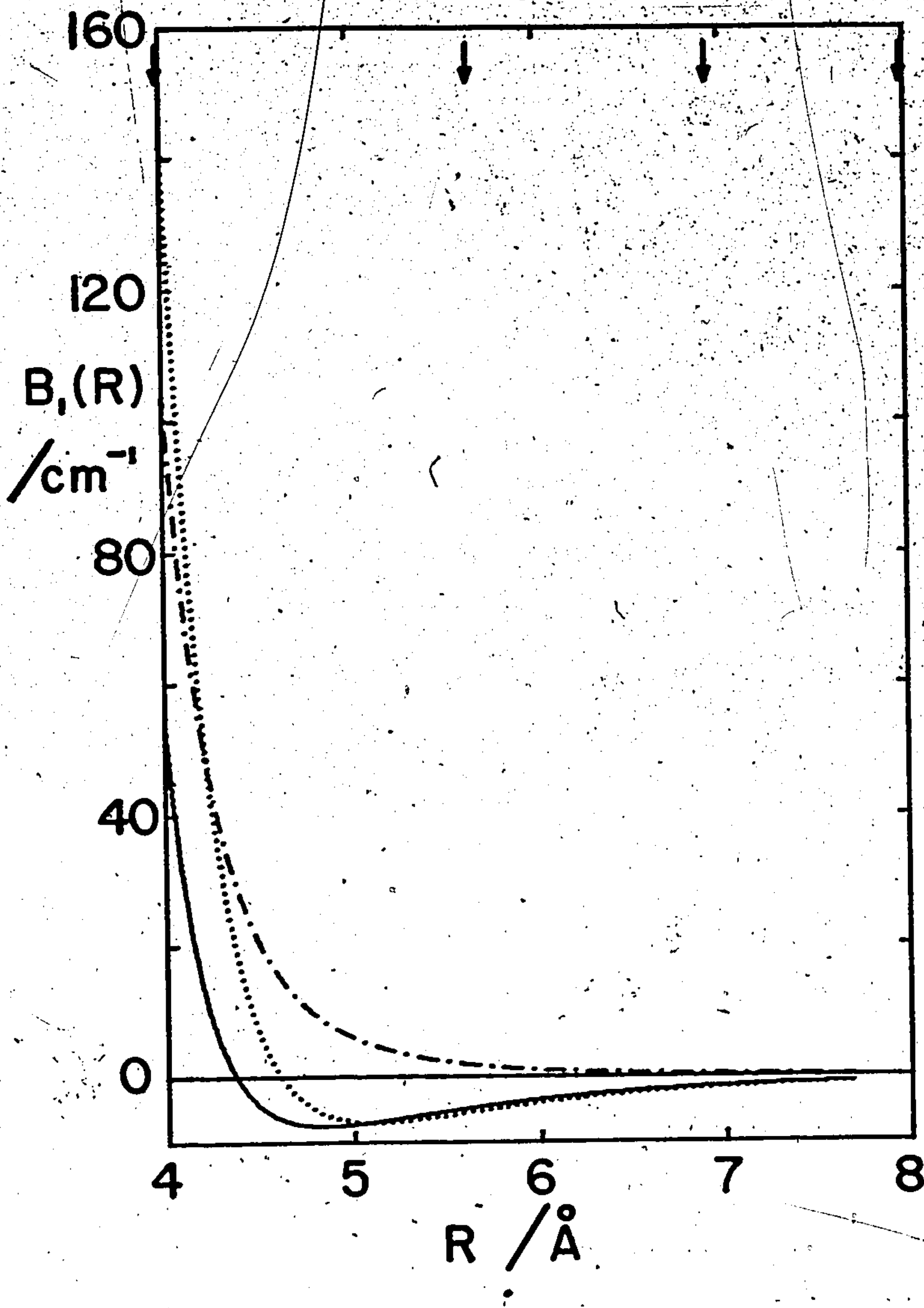

Fig. 5

Fig. 6: Potential coefficient $A_0(R)$, calculated for various model potentials. The arrows at the top of the graph indicate the positions of the first 4 neighbour shells in the Pa3 structure. ——— Full Raich-Mills potential. ---·- Repulsive part of Raich-Mills potential. ----- Quadrupole-quadrupole potential. ····· Full Kohin potential. The quadrupole moment was taken as 1.52×10^{-26} esu for all potential models.

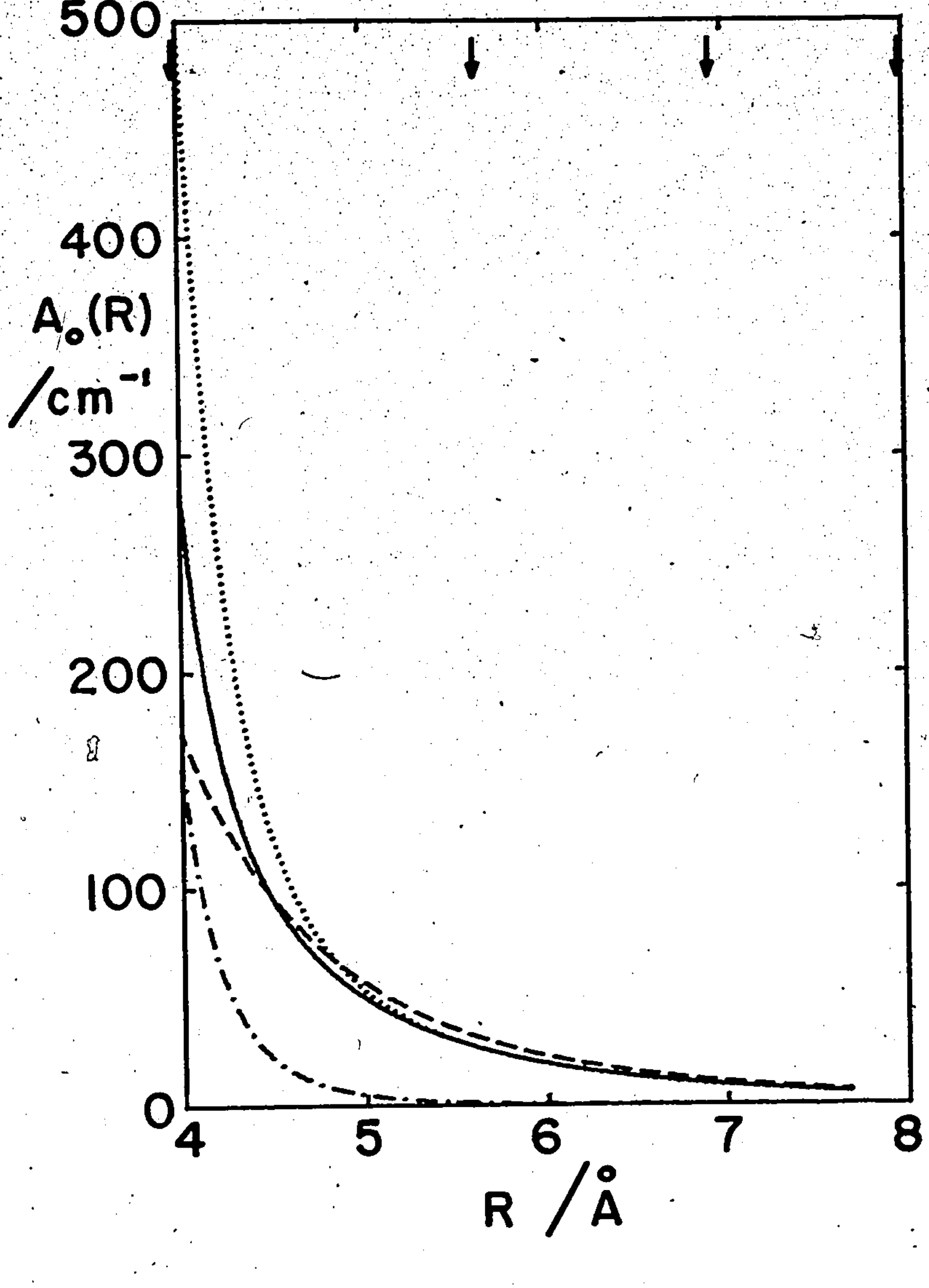

Fig. 6

Fig. 7: Potential coefficient $A_1(R)$, calculated for various model potentials. The arrows at the top of the graph indicate the positions of the first 4 neighbour shells in the Pa3 structure. ——— Full Raich-Mills potential. -·-·- Repulsive part of Raich-Mills potential. ----- Quadrupole-quadrupole potential. ····· Full Kohin potential. The quadrupole moment was taken as 1.52×10^{-26} esu for all potential models.

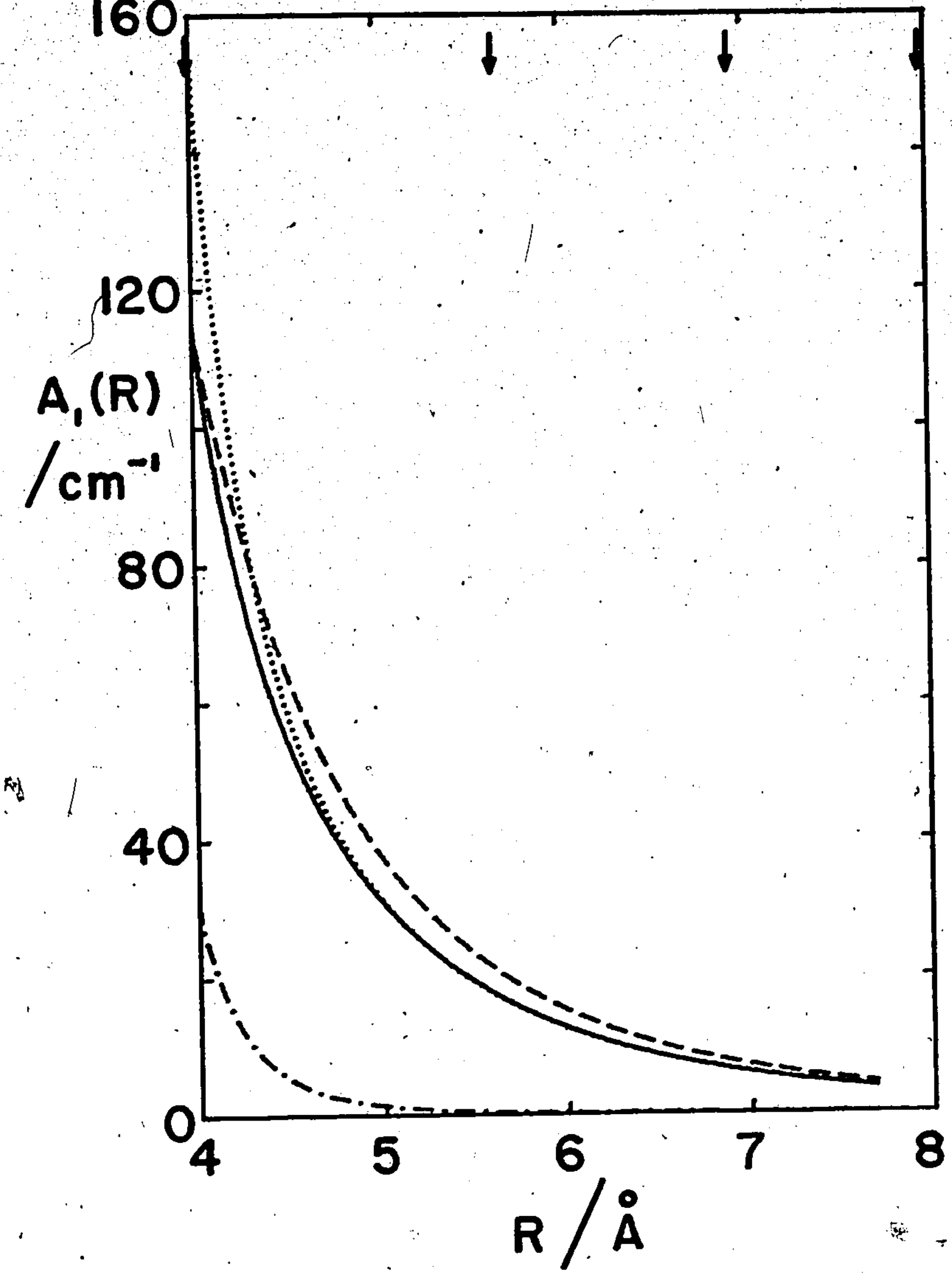

Fig. 7

Fig. 8: Potential coefficient $A_2(R)$, calculated for various model potentials. The arrows at the top of the graph indicate the positions of the first 4 neighbour shells in the Pa3 structure. ——— Full Raich-Mills potential. -·-·- Repulsive part of Raich-Mills potential. ----- Quadrupole-quadrupole potential. ····· Full Kohin potential. The quadrupole moment was taken as 1.52×10^{-26} esu for all potential models.

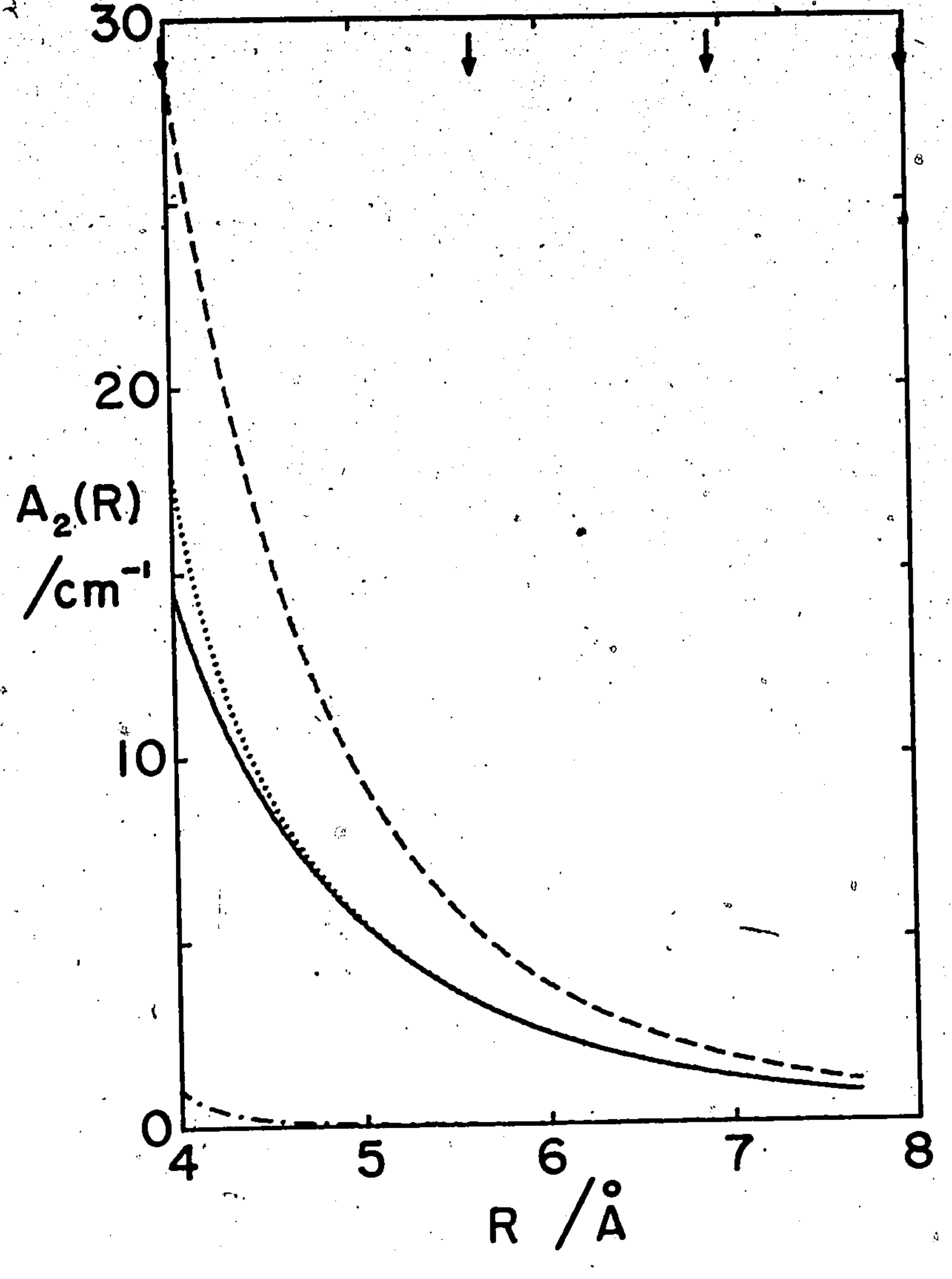

Fig. 8

TABLE 2

PARAMETER VALUES FOR THE MODEL INTERMOLECULAR POTENTIALS.

Values in the column headed I use the value of the quadrupole moment recommended by Buckingham et al. (1968). Values in column II are based on the older value reported by Stogryn and Stogryn (1966). Values are taken from Goodings and Henkelman (1971), Dunmore (1972) and Raich and Mills (1971).

Parameter	Symbol	units	I	II
Quadrupole moment	Q	e.s.u.	-1.4×10^{-26}	-1.52×10^{-26}
Anisotropy of polarizability	κ	-	0.189	0.189
Strength of dispersive interaction	ε	erg	1.313×10^{-14}	1.313×10^{-14}
Range of dispersive interaction	σ	Å	3.708	3.708
Kohin repulsive parameter	B	erg Å^{12}	4.142×10^{-8}	4.193×10^{-8}
Half the intramolecular bond length	d	Å	0.552	0.552
Raich-Mills repulsive parameter	A	erg Å$^{\alpha}$	-	6.361×10^{-14}
Scale factor for spheroids	s	-	-	0.70
Raich-Mills exponent	α	-	-	4.09

the two potentials reduce to the sum of quadrupole-quadrupole and dispersive interactions only. The difference between these coincident curves and the quadrupole-quadrupole curves then gives a measure of the strength of the dispersive interaction in this region. It may be seen that this is substantially weaker than the quadrupole-quadrupole interaction in its effect on A_0 and A_1, which, being the largest of the A_μ coefficients, are mainly responsible for determining the libron frequencies. Hence the dispersive interaction should have a relatively small effect on the libron frequencies, but a rather larger effect on the phonon frequencies (dominated by B_0). It is notable that the repulsive part of the Raich-Mills potential makes a relatively small contribution to A_1 and almost none to A_2 at the distances of interest.

The remaining noteworthy feature of these graphs is the very rapid variation of A_0 at the nearest-neighbour distance. This suggests that small differences in the potential form or parameters are likely to have a particularly acute effect on A_0, and hence have a substantial effect on the libron frequencies. This provides a graphic understanding of the difficulty which has been encountered (Goodings and Henkelman 1971; Dunmore 1972) in fitting the libron frequencies with a potential model whose parameters are determined by other data (generally data which is most sensitive to the spherically symmetric part of the interaction, such as the crystal binding energy). One is then led to the conclusion that a more reasonable way to perform calculations which depend on the librons, such as the temperature dependence of the NQR frequency, would be to use a potential in which the A_μ coefficients have been fitted directly to the observed libron frequencies, so that at least the librons are correctly described to begin with.

6.2 Librons at Zero Temperature

The frequencies of librons at zero wavevector are shown in Table 3, for all the potential models considered in this work. Where reasonably comparable calculations appear in the literature, their results are also presented in the table. Finally, some experimental observations of these frequencies are presented.

Comparison of the experimental and theoretical results in the table shows clearly that the best theoretical model for predicting the libron frequencies is the quadrupole-quadrupole potential with the value of the quadrupole moment recommended by Buckingham et al. (1968). This model (model I) gets the energies of the two T_g modes essentially correct and underestimates the E_g energy by only about 3 cm^{-1}. The models which attempt to include the dispersive and repulsive

TABLE 3

LIBRON FREQUENCIES AT ZERO WAVEVECTOR, THEORETICAL AND EXPERIMENTAL.

Where no author reference is given for a potential model calculation, the calculation is that of the present work. Potential models are those of Table 2. The experimental data of Kjems and Dolling are obtained from neutron scattering; other experimental data are obtained from Raman scattering. All energies in cm^{-1}.

Theoretical	E_g	T_g	T_g
Raich-Mills potential	46.4	55.7	76.6
Quadrupolar potential, model I	28.8	36.8	60.7
Quadrupolar potential, model II	31.4	40.2	66.1
- Goodings and Henkelman (1971)	35	45	74
- Harris and Coll (1972)	30.4	39.2	64.3
- Dunmore (1972)	31.5	40.3	66.4
- Jacobi and Schnepp (1972)	34.5	41.3	69.9
Kohin potential, model I	65.0	73.9	94.1
- Dunmore (1972) (see note below)	45.7	54.4	73.5
Kohin potential, model II	66.7	76.2	98.3
- Goodings and Henkelman (1971) (see note below)	50.5	61	85
- Dunmore (1972) (see note below)	47.8	57.2	78.7

continued...

TABLE 3 - continued

Experimental	E_g	T_g	T_g
Brith et al. (1969) (12K)	31.5	35.8	-
Cahill and Leroi (1969) (16K)	33.5	37.5	-
Anderson et al. (1970) (18K)	32 ±1.5	36.5±1.5	60 ±4
Mathai and Allin (1971) (4K)	31.5	36.0	59.8
Medina and Daniels (1974) (8K)	32.8	37.0	60.5
Kjems and Dolling (1974) (15K)	32.3±0.8	36.3±0.8	59.7±1.5

<u>Note</u>: Except for the present work, all calculations using the Kohin potential were based on Goodings and Henkelman's (1971) asymptotic expansion, which is seriously incorrect. The results of previous calculations are shown here only to indicate the magnitude of the error which was thereby introduced into these calculations.

forces, which physically must be present, fail strikingly to explain the observed libron energies. For the Raich-Mills potential, the theoretical energies are 28% to 53% too high. Using the quadrupole moment recommended by Buckingham et al. (1968), one finds for the Kohin potential (model I) libron energies which are too high by 57% to 103%, and the Kohin potential with the older parameter values (model II) is even worse.

As was noted in the previous section, the values of A_μ, and hence the librational frequencies, are an extremely sensitive test of the form of a potential model. Both the Raich-Mills and the Kohin potentials fail this test, the latter the more spectacularly. Because the Raich-Mills potential is physically the more appealing of the two, and because it reproduces the libron energies less badly, we shall use it as an a priori potential model in a number of subsequent calculations. However, we shall encounter some uncertainty as to whether a disagreement with experiment is due to the failings of the theory or to the failings of the potential, and it will then be useful to have available a potential model which at least fits the libron energies correctly. Rather than using the unrealistic quadrupole model for this purpose, the author proposes to introduce a "partial potential", to be described now.

We make no attempt to specify B_0 or B_1, since they have no influence on the libron energies. We further assume that all the A_μ coefficients are zero except between nearest neighbours, an assumption which may be justified by examining Figs. 6, 7, and 8, where it may be seen that the A_μ for second neighbours are already much smaller than for nearest neighbours. This leaves us three A_μ coefficients with which to fit the three libron energies – not a difficult task. Taking the experimental energies to be 32 cm^{-1}, 36.5 cm^{-1}, and 60 cm^{-1}, we can fit these energies to rather better than 1% with the choices $A_0 = 173.5\ cm^{-1}$, $A_1 = 90.4\ cm^{-1}$, and $A_2 = 29.4\ cm^{-1}$. (We could easily extend this model by choosing the derivatives dA_μ/dR so as to fit the volume dependence of the Raman energies reported by Medina and Daniels (1974), but this would lead to no new possible calculations, and so we do not take this step.) The "potential" thus constructed by fitting the $\underline{q} = 0$ libron energies will be referred to as the "fitted potential". Obviously we make no claims for physical realism for this potential.

The other obvious calculations which can be performed at T = 0 are those of dispersion curves and of densities of states. We stress that these are model calculations only, since the librons and phonons must mix in a real crystal away from $\underline{q} = 0$ (Walmsley and Pople 1964), and calculations by Schnepp and Ron (1969) indicate that this mixing significantly affects the quasi-librational modes.

Dispersion curves calculated with the Raich-Mills potential are shown in Fig. 9. The curves are drawn in the [100], [110], and [111] symmetry directions. Densities of states for the Raich-Mills potential, the fitted potential, the Kohin potential and the quadrupole potential are plotted in Figs. 10 and 11. The curves are normalized so that the total area under each is 8, the number of modes per unit cell. The densities of states were computed by the method of Gilat and Raubenheimer (1966), using 200 energy channels for each spectrum and 220 points in the irreducible $\frac{1}{48}$th of the first Brillouin zone. Some of the small irregular peaks in the spectra are undoubtedly caused by this limited number of q points, since they change when this number is altered. However, there seemed little point in spending the large amount of computer time which would have been required to eliminate them altogether.

The main interest of the density of states curves is in the discussion of some of the relaxation processes mentioned in Chapter 5. For example, it was argued there that energy-conserving processes in which one libron is created and two are annihilated are not possible. It can be seen from the densities of states that this is true for all potential models except the quadrupole-quadrupole, where a tiny number of such processes is allowed.

Fig. 9: Dispersion curves in the [100], [110], and [111] directions, computed using the Raich-Mills potential.

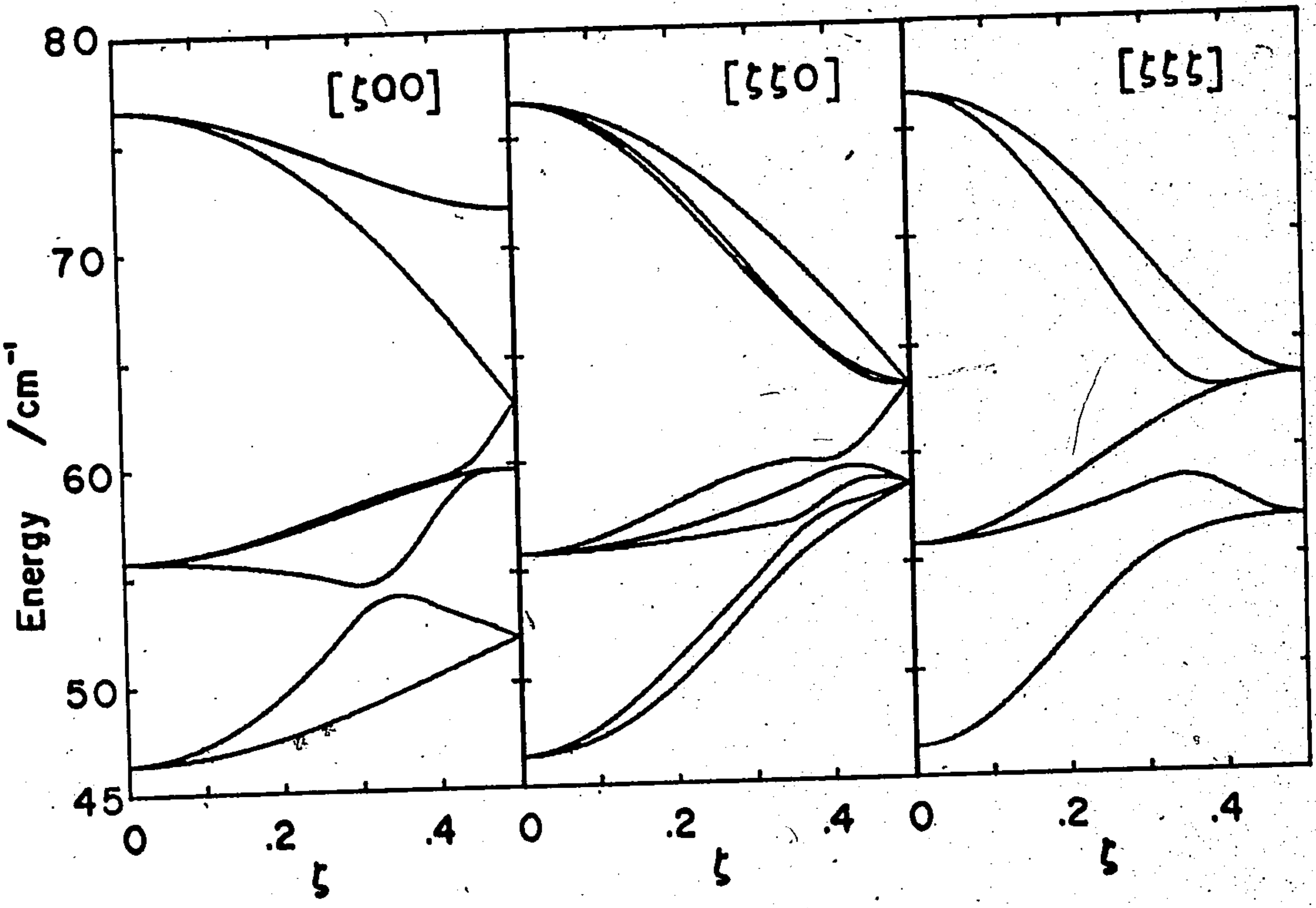

Fig. 9

Fig. 10: Libron densities of states. ——— Raich-Mills potential. ····· Fitted potential.

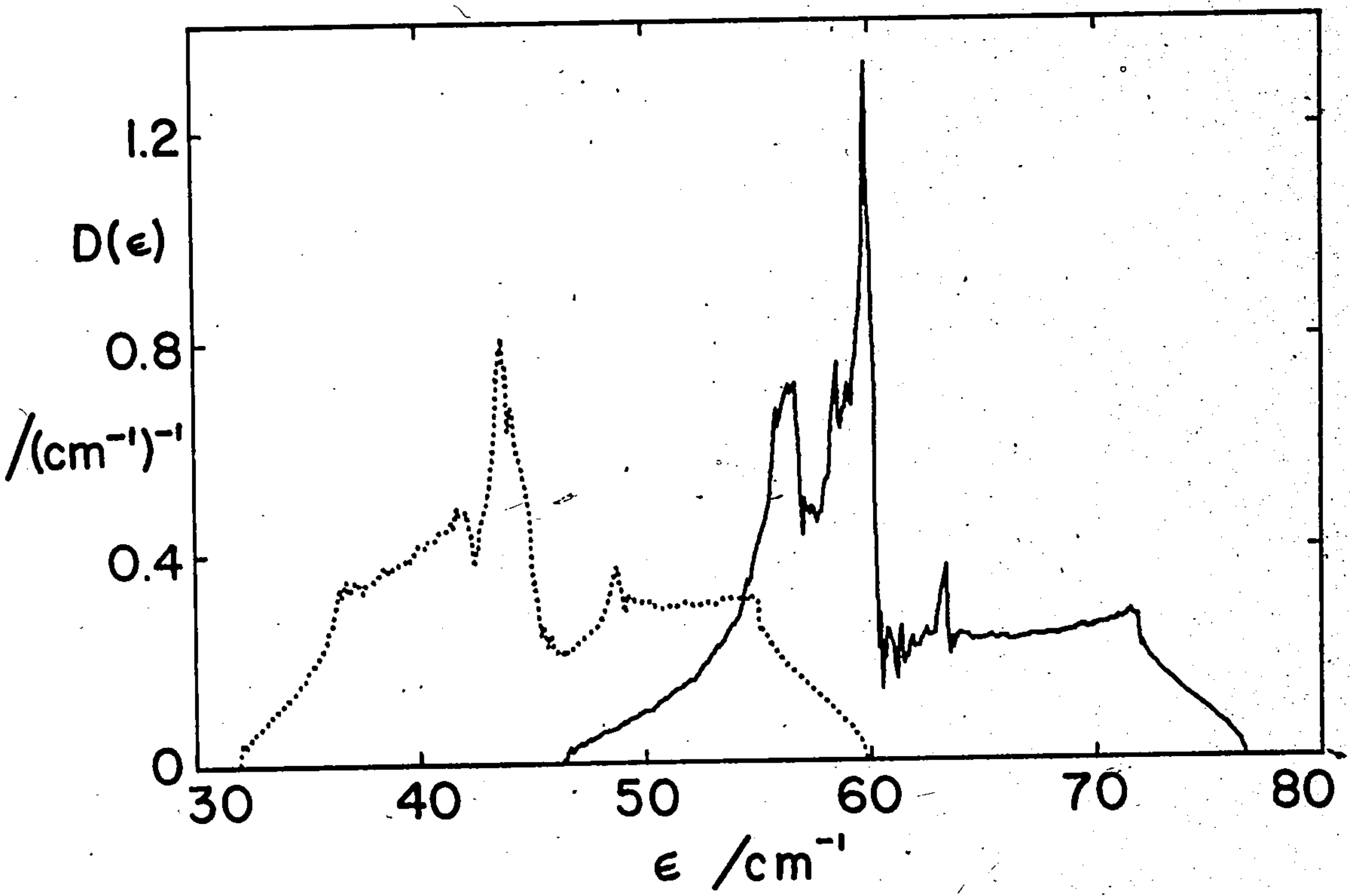

Fig. 10

Fig. 11: Libron densities of states. ——— Kohin potential.
······ Quadrupole-quadrupole potential.
Quadrupole moment = 1.4×10^{-26} esu.

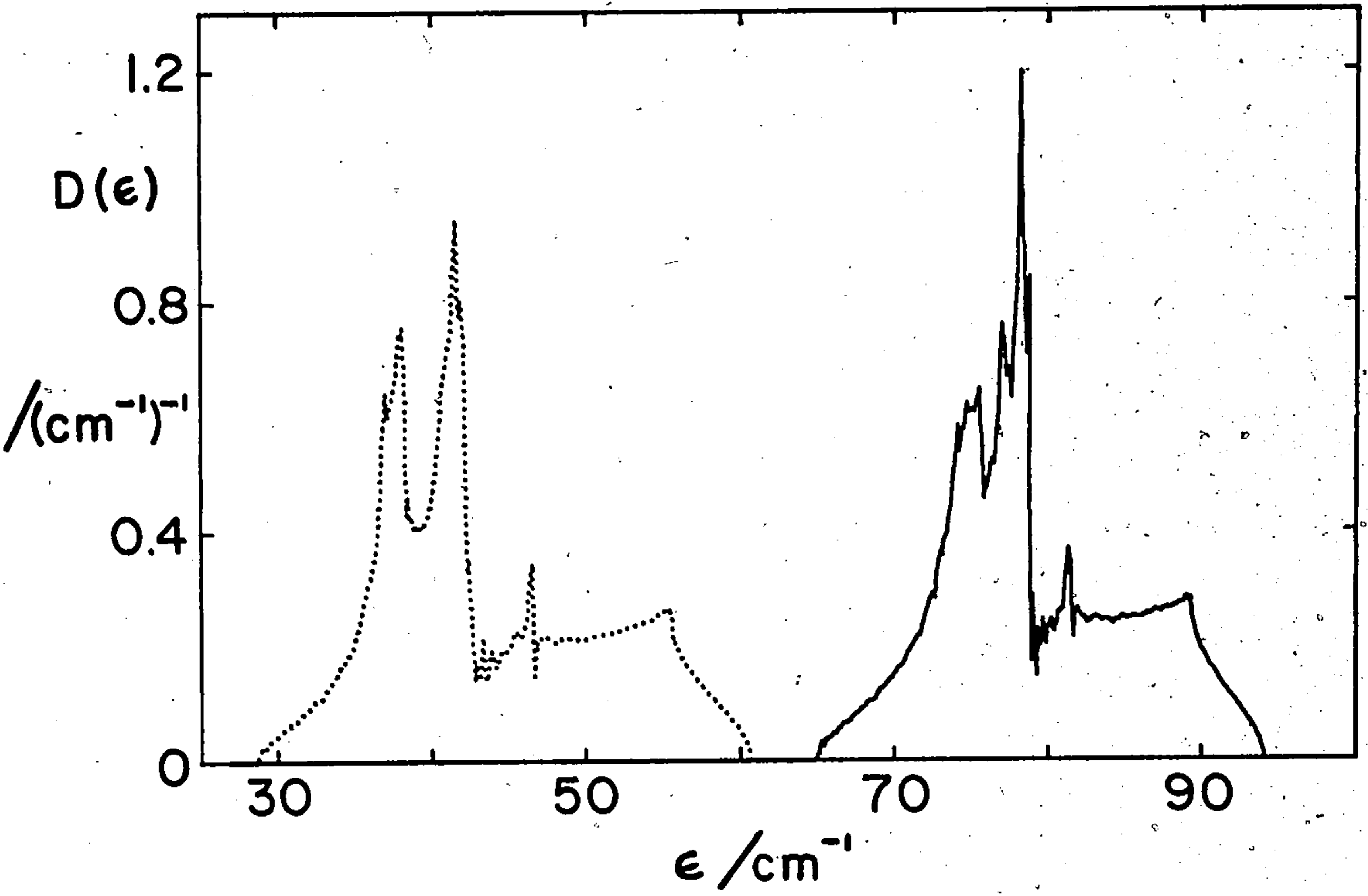

Fig. 11

6.3 Librons at Finite Temperature

Except for the T_1 calculations discussed in the next section, we have not attempted to investigate the effects of thermal expansion on the librational properties of α-nitrogen, but have confined ourselves to calculations of isochoric thermal effects. The experimental data mentioned in this section were all taken under conditions of constant volume.

From the density of states curves presented in the previous section, the free energy may be computed as discussed in Chapter 4. Free energy curves against temperature are shown in Fig. 12. As mentioned in Chapter 4, these curves may be computed for various values of the spheroidal parameter c, and a temperature-dependent c chosen to give the minimum free energy at each temperature. It turns out that the minimum is rather shallow, and the resulting value of c is not strongly temperature-dependent. A few typical values are given in Table 4 for the fitted potential, together with the $\underline{q} = 0$ libron energies to which they give rise, and the isochoric temperature dependence of the Raman lines reported by Medina and Daniels (1974). It will be seen that, although a temperature dependence occurs theoretically, it is far too weak to explain the observations, and is in fact sufficiently weak that we shall neglect it in all subsequent calculations.

We present in Fig. 13 theoretical and experimental curves showing the temperature dependence of the NQR frequency

Fig. 12: Free energy as a function of temperature. ——— Raich-Mills potential. ····· Fitted potential. Note the break in the vertical scale.

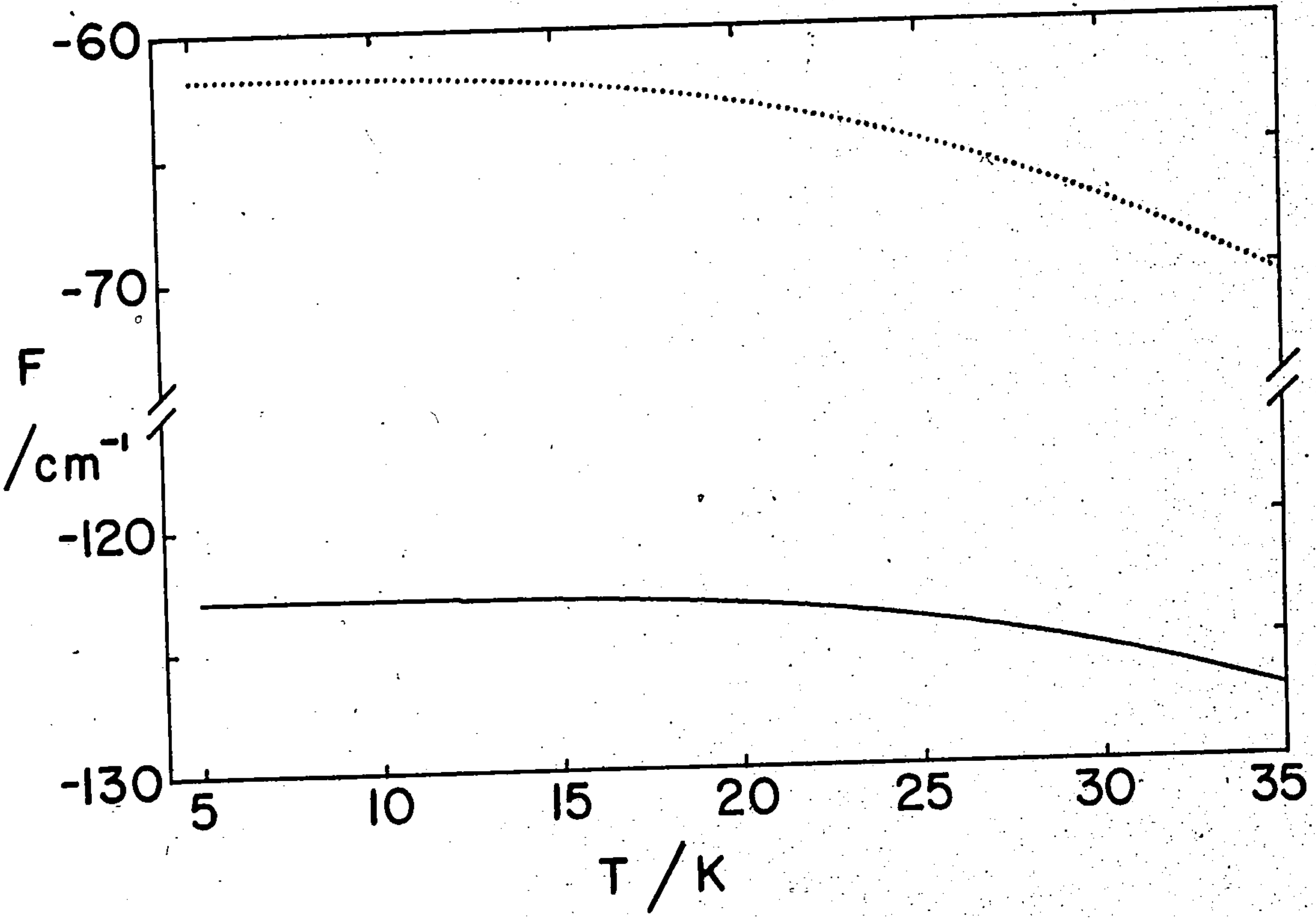

Fig. 12

TABLE 4

VARIATION OF LIBRON ENERGIES WITH TEMPERATURE, USING THE FITTED POTENTIAL.

The experimental data by Medina and Daniels (1974) were taken at a molar volume of 26.9 cm^3, i.e., a lattice parameter of 5.632 Å, slightly less than the zero-pressure value of 5.644 Å used in the calculations. All energies in cm^{-1}.

T(K)	Experiment			Theory			
	E_g	T_g	T_g	c	E_g	T_g	T_g
8	33.3	37.5	61.3	11.95	32.00	36.48	59.96
18	33	37.2	61	11.88	31.99	36.47	59.93
35	32.3	....	....	11.59	31.95	36.42	59.80

Fig. 13: Temperature dependence of the nuclear quadrupole resonance frequency, normalized to unity at T = 0. ——— Experimental results of Brookeman et al. (1971). ····· Raich-Mills potential. ----- Fitted potential.

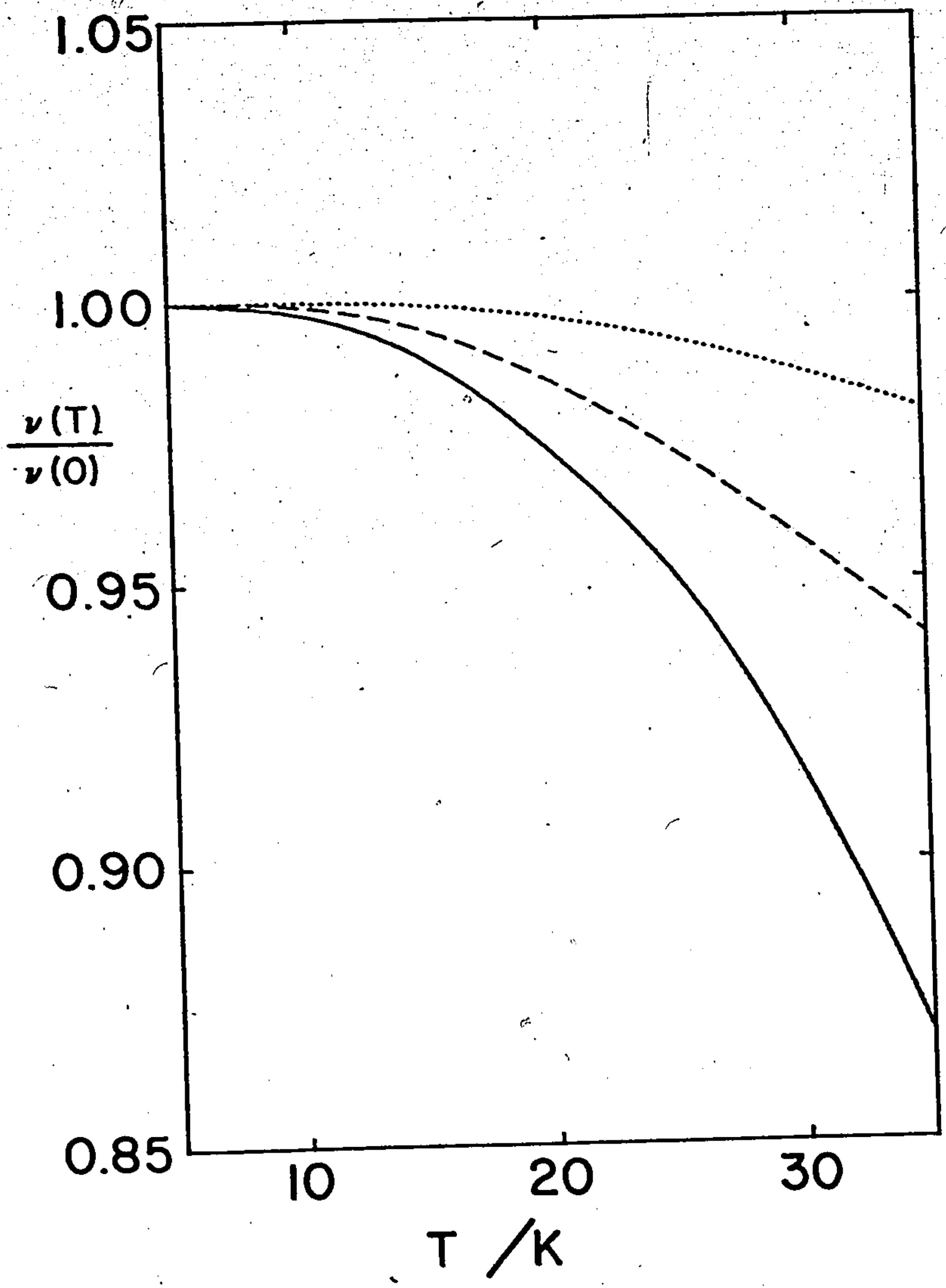

Fig. 13

(equivalently, the order parameter $<Y_{20}>$), normalized to unity at T = 0. The experimental data were read directly off a graph by Brookeman et al. (1971), and may be somewhat in error. The theoretical curves were calculated as described in Chapter 4, with the sums taken over 500 points in half of the Brillouin zone. It can be seen that neither the Raich-Mills potential nor the fitted potential can satisfactorily explain the observed temperature dependence, although the latter potential is much more nearly successful than the former.

One would expect that the introduction of libron-phonon and perhaps libron-libron interactions would improve the agreement between theory and experiment, both for the NQR frequency and for the libron frequencies. By "smearing out" the molecular positions and thereby weakening the effective anisotropy of the interactions (an effect which would be more pronounced at higher temperatures when more phonons are present), the presence of phonons would reduce the libron and NQR frequencies at higher temperatures. Libron-libron interactions would have a similar effect by directly increasing the disorder of the molecular orientations, again weakening the effective anisotropy of the interaction.

Because the field gradient eq is not independently known, the experimental NQR frequency cannot be used to determine $<Y_{20}>$. However, we can present theoretical estimates of this quantity and hence of the r.m.s. angular deviation $\sqrt{<\theta^2>}$ of the molecules from their equilibrium directions. This connection is easily made, since

$$<Y_{20}> = \frac{1}{4}\sqrt{\frac{5}{\pi}}\,(3<\cos^2\theta> - 1) \qquad (6.1a)$$

$$= \frac{1}{2}\sqrt{\frac{5}{\pi}} - \frac{3}{4}\sqrt{\frac{5}{\pi}}<\theta^2> + \frac{1}{4}\sqrt{\frac{5}{\pi}}<\theta^4> - \ldots \qquad (6.1b)$$

so that

$$<\theta^2> \doteq \frac{2}{3} - \frac{4}{3}\sqrt{\frac{\pi}{5}}<Y_{20}> + \frac{1}{3}<\theta^4> \quad . \qquad (6.1c)$$

Since the $<\theta^4>$ term is in practice a small correction, it will suffice for our purposes to estimate it roughly. For a probability distribution of the form $P(\theta) = ae^{-k\theta^2}$ (which is very roughly true for the lowest spheroidal wave function state), one may easily show that $<\theta^4> = 3<\theta^2>^2$, and we use this estimate for the last term in (6.1c). We neglect higher moments altogether.

Using the fitted potential, we find $<Y_{20}> = 0.5494$ at T = 5 K and 0.5163 at 35 K. These correspond to values of $\sqrt{<\theta^2>} = 17.5°$ at 5 K and 21.1° at 35 K. If we assume the estimate at 5 K to be correct, and use the experimental change in the NQR frequency to determine $<Y_{20}>$, we find $<Y_{20}> = 0.4758$ at 35 K, leading to $\sqrt{<\theta^2>} = 25.0°$.

It may be noted that the estimate of $\sqrt{<\theta^2>}$ at 5 K is very close to the semiclassical estimate of 17.9° made by Goodings and Henkelman (1971).

6.4 Spin-Lattice Relaxation

Figure 14 shows the spin-lattice relaxation time plotted against temperature. The experimental data were read directly off a graph by DeReggi et al. (1969), and may be somewhat in error. It should be noted also that T_1 was measured at essentially zero pressure, rather than at constant volume, while the calculations were performed at constant volume. The two theoretical calculations used the Raich-Mills and the fitted potential, using 300 energy channels and 64 points in the Brillouin zone. Considerations of computer time discouraged us from repeating the calculations with 216 points, but calculations with 8 points for the Raich-Mills potential gave results differing by less than a factor of 2 from those reported here, and this is presumably a rough upper bound on the error caused by the coarseness of the mesh.

In view of the very rough approximations made in the theory - the neglect of the phonons, the inclusion of only a single relaxation mechanism, and that only in first order of perturbation theory, the neglect of volume corrections, and

Fig. 14: Spin-lattice relaxation time T_1 as a function of temperature. ——— Experimental results of DeReggi et al. (1969). ····· Raich-Mills potential. ----- Fitted potential.

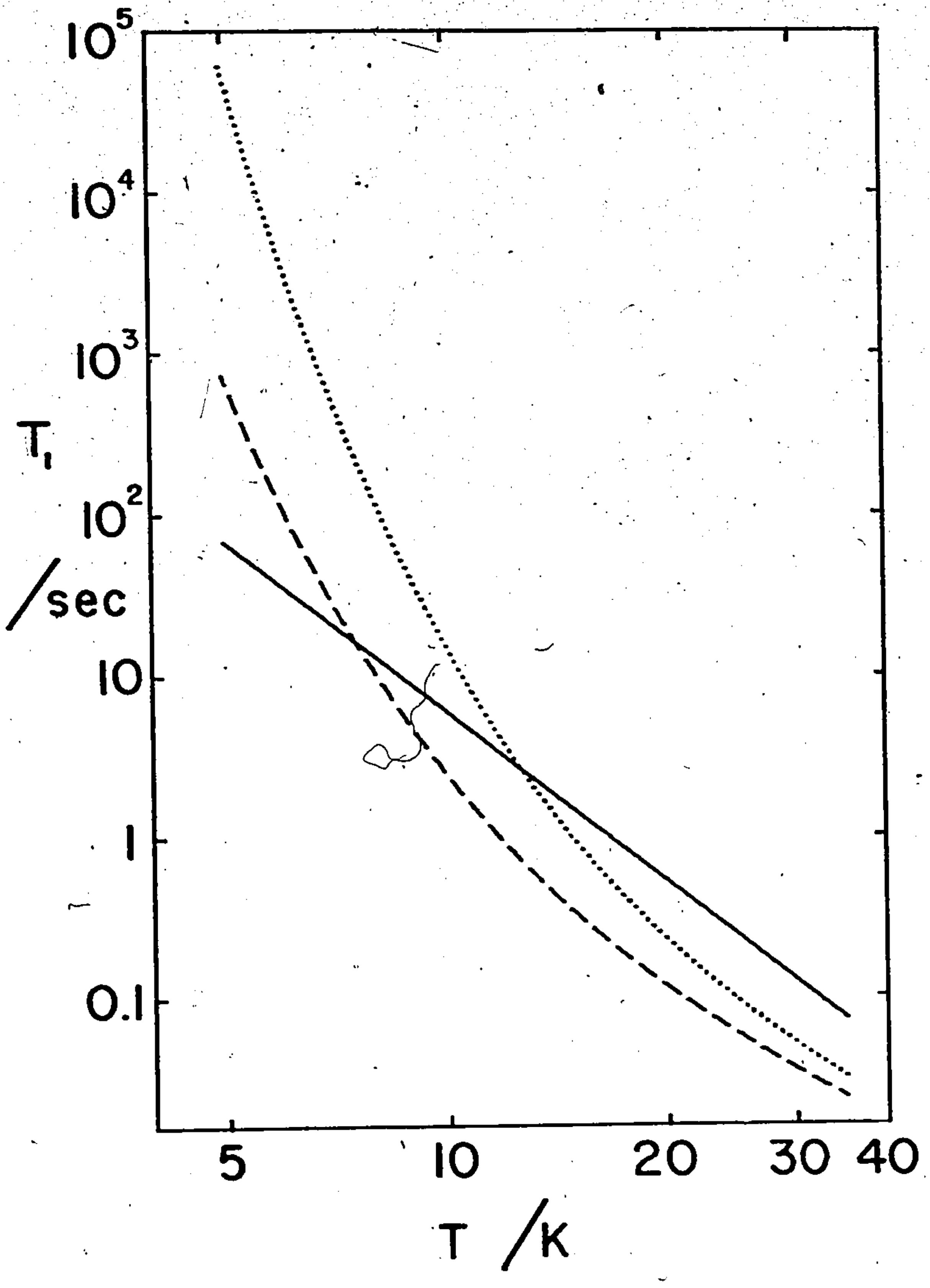

Fig. 14

finally the crudeness of the numerical work itself - the agreement between theory and experiment exhibited by Fig. 14 may be considered quite satisfactory. The effect of the thermal expansion has been estimated roughly, using the thermal expansion data of Heberlein et al. (1970). They show the relative increase in length of a nitrogen crystal at 35 K to be 6.8×10^{-3} (this value was read from a graph and may be somewhat inaccurate). This indicates a lattice parameter of 1.0068×5.644 Å = 5.682 Å at 35 K. We therefore repeated the T_1 calculation for the Raich-Mills potential, using a lattice parameter of 5.682 Å. At 35 K, the value of T_1 was found to alter from 3.1×10^{-2} sec to 5.7×10^{-3} sec.

The phonons provide an obvious explanation for why the calculated T_1 values become too large at low temperatures. Although at $\underline{q} = 0$ there is no mixing of phonons and librons, so that the phonons do not contribute to relaxation, away from but close to $\underline{q} = 0$ the phonons will be weakly mixed with the librons and will contribute weakly to the relaxation. This contribution will be negligible if the temperature is high enough that the libron states themselves are significantly populated, but at low temperatures only the acoustic phonon modes close to $\underline{q} = 0$ are appreciably populated and so they must provide the dominant relaxation mechanism. A calculation which neglects the phonons therefore may be expected to give too little relaxation (i.e., too long a T_1) at low temperatures. If the libron modes are lower in energy, they will provide the dominant mechanism for relaxation down to lower temperatures, and the too-high value of T_1 will occur at lower temperatures. This can be seen in Fig. 14, where the value of T_1 from the fitted potential (which gives lower libron energies) does not begin to rise sharply above experiment until several degrees lower than the value from the Raich-Mills potential.

CHAPTER 7

SUMMARY AND CONCLUSIONS

In this thesis we have been concerned with the nature and effects of the librational motions which occur in the α phase of nitrogen. We have presented a general expansion for an arbitrary anisotropic non-singular potential function of the positions of two nitrogen molecules, and shown how the coefficients in such an expansion may be calculated for a given model potential. We have pointed out that expressions for these coefficients which were obtained by Goodings and Henkelman (1971) for a particular potential model, the Kohin potential, were seriously in error.

In considering the interactions in a crystal, we used the ideas of the mean field model to introduce the spheroidal wave functions and then showed that, apart from a trivial phase factor, these functions may be relabelled to exhibit a formal correspondence between them and the states of a two-dimensional harmonic oscillator. Taking advantage of this correspondence, we were able to introduce raising and lowering operators for the spheroidal wave functions having exactly the same formal properties as the raising and lowering operators normally used for the harmonic oscillator.

We next expressed the operators which enter into the kinetic and potential energy in terms of these raising and lowering operators, and Fourier transformed to take advantage of the translational symmetry of the crystal. The resulting Hamiltonian contained no terms with one operator, and the terms containing two operators could be diagonalized exactly in terms of operators which create and annihilate librons. The ground state of the crystal, the state which contains no librons, was shown to be different from, but very close in its properties to, a state in which each molecule in the crystal is in its lowest-lying spheroidal wave function state. We then developed explicit expressions for those terms in the Hamiltonian which contain three libron operators.

In the final chapter outlining the formalism of the problem, we examined the libron contribution to the spin-lattice relaxation time T_1, considering quadrupolar relaxation in a formalism developed originally by Van Kranendonk and Walker (1968). We considered several elementary spin-libron interaction processes and showed that, of the processes considered, the only one which could contribute to the relaxation was the one which Van Kranendonk and Walker called the anharmonic Raman process. In this process, the three-libron terms in the Hamiltonian are crucial to the relaxation mechanism. Using first-order perturbation theory and the expressions previously developed for the three-libron terms, we calculated the spin-lattice relaxation time.

Finally, we presented numerical results for the theory which had been developed. We observed that the anisotropic terms in the expansion of the potential were very sensitive to the form of the potential and often not well defined by "static" data commonly used for fitting parameters in potential models. Hence a model which appeared otherwise satisfactory might give very poor predictions of the libron energies. Our calculations of the libron energies for two different potential models, the Raich-Mills potential and the Kohin potential, showed that this was indeed the case. The energies predicted by the Raich-Mills potential were 28% to 53% too high, and the energies predicted by the Kohin potential were 57% to 103% too high. The quadrupole-quadrupole potential gave almost the right energies but is known to be a completely unrealistic potential. We introduced a "fitted potential" in which we made no attempt to construct a complete potential model, but simply fitted the A_μ expansion coefficients to the experimental libron energies. In subsequent calculations, comparison of the results of the "fitted potential" with those of a potential model gave some indication of where there were shortcomings in the theory, as distinct from errors in a particular potential model.

We presented model dispersion curves and libron densities of states. These calculations were particularly unrealistic because the phonons, neglected in all the calculations in this thesis, are known to have a significant effect on the dispersion curves. We computed the free energy as a function of temperature, and by minimizing the free energy at each temperature we obtained a temperature-dependent spheroidal parameter and temperature-dependent libron energies. This temperature dependence turned out to be far too weak to explain the experimental results, however, and we surmised that libron-phonon and libron-libron interactions would have to be considered in order to explain the data.

The temperature dependence calculated for the nuclear quadrupole resonance frequency also turned out to be much weaker than the experimental data, and again libron-phonon and libron-libron interactions were suggested as a possible reason. We calculated the r.m.s. angular deviation of a molecule from its equilibrium direction to be $\sqrt{\langle\theta^2\rangle} = 17.5°$ at 5 K, very close to a previous semiclassical estimate of 17.9° (Goodings and Henkelman 1971).

Finally we presented the calculated temperature dependence of the spin-lattice relaxation time. In view of the crude nature of the approximations made, the results from 10 K to 35 K were felt to be in fairly good agreement with experiment. At lower temperatures, the calculated results were too high, probably reflecting the neglect of the phonons in the calculation.

In summary, the formalism presented here is a systematic way of treating librational motions in a manner which uses exact boson operators and is susceptible of systematic treatment by perturbation theory. The most serious drawback is the rigid lattice assumption, and the formalism will have to be extended by inclusion of phonons before a satisfactory treatment of the lattice dynamics of α-nitrogen will be possible by this method. However, were this to be done, the method would be superior to self-consistent phonon theory in that it would be capable of dealing with arbitrary intermolecular potentials.

It is clear also that neither the Kohin potential nor the potential of Raich and Mills exhibits the correct anisotropic behaviour, and further work on developing realistic and physically plausible model potentials is called for.

APPENDIX A

COMPUTATION OF THE SPHEROIDAL WAVE FUNCTIONS

The Schrödinger equation for the Hamiltonian in Eq. (3.7) is

$$\{B\underline{J}^2 - U_0 Y_{20}(\theta,\phi) - E_{\ell m}\} W(\theta,\phi) = 0 \tag{A.1}$$

where $\underline{J}^2$ is given by (3.3b) and

$$Y_{20}(\theta,\phi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\,(3\cos^2\theta - 1) \quad . \tag{A.2}$$

By separating the variables, one easily finds that the solution has the form given in Eq. (3.9), where m must be an integer if the solution is single-valued, an arbitrary normalization constant is written in the front, and $S_\ell^m(-ic;\cos\theta)$ satisfies the equation

$$\frac{1}{\sin^2\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{dS_\ell^m}{d\theta}\right) + \left\{\frac{1}{4}\sqrt{\frac{5}{\pi}}\,\frac{U_0}{B}\,(3\cos^2\theta - 1) + \frac{E_{\ell m}}{B} - \frac{m^2}{\sin^2\theta}\,S_\ell^m\right\} = 0 \quad . \tag{A.3}$$

If one makes the substitution $\eta = \cos\theta$ and identifies

$c^2 = -\frac{3}{4}\sqrt{\frac{5}{\pi}}\frac{U_0}{B}$ and $E_{\ell m} = \frac{1}{4}\sqrt{\frac{5}{\pi}}U_0 + B\lambda_{m\ell}$, this equation becomes identical to the oblate spheroidal wave equation (Flammer 1957; Hodge 1970). An expansion may be made in the form

$$S_\ell^m(-ic;\eta) = \sum_{q=0}^{\infty} d_q^{\ell m}(c)P^m_{|m|+2q+s}(\eta) \tag{A.4}$$

and from the recurrence relations for the Legendre functions (Erdélyi et al. 1953) and the differential equation for S_ℓ^m one obtains a three-term recurrence relation for the $d_q^{\ell m}(c)$. The recurrence relation involves $\lambda_{m\ell}$, and Hodge (1970) shows that it may be cast in such a form that the various $\lambda_{m\ell}$ ($\ell = |m|+s, |m|+s+2, \ldots$) emerge as the eigenvalues of a symmetric tridiagonal matrix. Rapid and stable algorithms exist for finding such eigenvalues (Wilkinson 1965), and with the $\lambda_{m\ell}$ determined, the recurrence relation is then used to compute the $d_q^{\ell m}(c)$ to within an overall normalization and phase.

In view of the relation in Eq. (3.9), and the similar relation which exists between the spherical harmonics and the associated Legendre functions (Edmonds 1957; Messiah 1958; but note that we use the Legendre functions in the convention of Erdélyi et al. (1953), which differs by a factor of $(-1)^m$ from that of the former authors), we may write a similar expansion to (A.4) in the form (3.10), where

$$D_q^{\ell m}(c) = \left[\frac{2\ell+1}{2|m|+4q+2s+1} \cdot \frac{(\ell-m)!}{(\ell+m)!} \cdot \frac{(|m|+m+2q+s)!}{(|m|-m+2q+s)!}\right]^{\frac{1}{2}}$$

$$\times\ d_q^{\ell m}(c)\ . \qquad \text{(A.5)}$$

The normalization is determined by requiring $W_{\ell m}$ to be normalized to unity on the unit sphere. Using (3.10) and the orthonormality of the spherical harmonics, one obtains the condition

$$\sum_{q=0}^{\infty} [D_q^{\ell m}(c)]^2 = 1\ . \qquad \text{(A.6)}$$

The phase is determined by requiring that the behaviour of $W_{\ell m}$ around $\theta = 0$ should have the same sign as that of $Y_{\ell m}$. From the formula for the behaviour of $P_\ell^m(x)$ around $x = 1$ (Erdélyi et al. 1953), namely

$$P_\ell^m(x) \doteqdot (-1)^m \frac{(\ell+m)!}{m!(\ell-m)!} \left(\frac{1-x}{2}\right)^{\frac{m}{2}} \quad \text{for} \quad m \geq 0 \qquad \text{(A.7)}$$

and putting $x = \cos\theta \doteqdot 1 - \frac{1}{2}\theta^2$ one finds that, for small θ,

$$Y_{\ell m}(\theta,\phi) \doteqdot (-1)^m \left[\frac{(2\ell+1)}{4\pi} \frac{(\ell+m)!}{(\ell-m)!}\right]^{\frac{1}{2}} \frac{1}{2^m\ m!}\ \theta^m e^{im\phi}$$

$$\text{for} \quad m \geq 0\ . \qquad \text{(A.8)}$$

Hence one obtains the behaviour of $W_{\ell m}$ for small θ,

$$W_{\ell m}(\theta,\phi) \doteq \frac{(-1)^m}{2^m\, m!}\,\theta^m e^{im\phi} \sum_{q=0}^{\infty} D_q^{\ell m}(c)$$

$$\times \left[\frac{(2m+4q+2s+1)}{4\pi} \cdot \frac{(2m+2q+s)!}{(2q+s)!}\right]^{\frac{1}{2}}$$

$$\text{for} \quad m \geq 0 \ . \qquad \text{(A.9)}$$

Consequently, the phase convention that $W_{\ell m}$ be a continuous function of c requires that the overall sign of the $D_q^{\ell m}(c)$ be chosen so that

$$\sum_{q=0}^{\infty} D_q^{\ell m}(c)\left[(2m+4q+2s+1)\ \frac{(2m+2q+s)!}{(2q+s)!}\right]^{\frac{1}{2}} > 0 \quad \text{for} \quad m \geq 0 \ . \qquad \text{(A.10)}$$

For m < 0, the phase is determined by requiring the conjugation symmetry

$$W_{\ell-m}(\theta,\phi) = (-1)^m\, W^*_{\ell m}(\theta,\phi) \qquad \text{(A.11)}$$

in agreement with the corresponding formula for the spherical harmonics.

APPENDIX B

PHASE RELATIONS BETWEEN SPHEROIDAL AND OSCILLATOR STATES

The behaviour of the spheroidal functions for small θ has been investigated in Appendix A. Here we consider the behaviour of the eigenfunctions of the two-dimensional isotropic harmonic oscillator near $x = y = 0$. The dimensionless Hamiltonian is

$$\mathcal{H} = -\frac{1}{4}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + (x^2+y^2) \tag{B.1}$$

and we introduce the usual creation and annihilation operators for x

$$a_x^\dagger = x - \frac{1}{2}\frac{\partial}{\partial x} \qquad a_x = x + \frac{1}{2}\frac{\partial}{\partial x} \tag{B.2}$$

and similar operators for y. The operators in (3.13) are then expressed in terms of x and y as

$$\begin{aligned} A_\pm^\dagger &= \frac{1}{\sqrt{2}}(x\pm iy) - \frac{1}{\sqrt{8}}\left(\frac{\partial}{\partial x} \pm i\frac{\partial}{\partial y}\right) \\ A_\pm &= \frac{1}{\sqrt{2}}(x\mp iy) + \frac{1}{\sqrt{8}}\left(\frac{\partial}{\partial x} \mp i\frac{\partial}{\partial y}\right) . \end{aligned} \tag{B.3}$$

Rather than using Cartesian coordinates, we work in polar coordinates (r,ϕ), for which

$$A_{\pm}^{\dagger} = e^{\pm i\phi}\left(\frac{1}{\sqrt{2}}\, r - \frac{1}{\sqrt{8}}\frac{\partial}{\partial r} \mp \frac{i}{\sqrt{8}}\frac{1}{r}\frac{\partial}{\partial \phi}\right)$$

$$A_{\pm} = e^{\mp i\phi}\left(\frac{1}{\sqrt{2}}\, r + \frac{1}{\sqrt{8}}\frac{\partial}{\partial r} \mp \frac{i}{\sqrt{8}}\frac{1}{r}\frac{\partial}{\partial \phi}\right) \qquad \text{(B.4)}$$

The normalized ground-state wave function is

$$|0,0\rangle = \sqrt{\frac{2}{\pi}}\, e^{-r^2} \qquad \text{(B.5)}$$

as may be seen by applying the operators $A_{\pm}$ to it. We write the states $|j,k\rangle$ in the form

$$|j,k\rangle = \sqrt{\frac{2}{\pi}}\, f_{jk}(r) e^{-r^2}\; e^{i(j-k)\phi} \qquad \text{(B.6)}$$

and by the relations

$$A_{+}^{\dagger}|j,k\rangle = \sqrt{j+1}\;|j+1,k\rangle \qquad A_{-}^{\dagger}|j,k\rangle = \sqrt{k+1}\;|j,k+1\rangle \qquad \text{(B.7)}$$

one easily derives the recurrence formulae

$$f_{j+1,k}(r) = \sqrt{\frac{2}{j+1}}\,\left\{\left(r + \frac{j-k}{4r}\right) f_{jk}(r) - \frac{1}{4}\, f'_{jk}(r)\right\}$$

$$f_{j,k+1}(r) = \sqrt{\frac{2}{k+1}}\,\left\{\left(r + \frac{k-j}{4r}\right) f_{jk}(r) - \frac{1}{4}\, f'_{jk}(r)\right\} . \qquad \text{(B.8)}$$

From the symmetry of these formulae it may be noted that $f_{jk} = f_{kj}$. Starting from $f_{00}(r) = 1$, it is easy to show by mathematical induction that

$$f_{j0}(r) = \{2^j/j!\}^{\frac{1}{2}}\, r^j \tag{B.9}$$

and hence that

$$f_{jk}(r) = (-1)^k \frac{\{j!k!2^{j-k}\}^{\frac{1}{2}}}{(j-k)!}\, r^{j-k} + O(r^{j-k+2})$$

$$\text{for} \quad j \geq k \quad . \tag{B.10}$$

Comparing this with Eq. (A.8), which is used to define the phase of the $W_{\ell m}$, we see that the phase of $W_{\ell m}$ differs from that of the corresponding $|n_+,n_->$ state by $(-1)^{n_-+m} = (-1)^{n_+}$ if $n_+ \geq n_-$. If $n_+ \leq n_-$, we use (A.11) and the symmetry $f_{jk} = f_{kj}$ to conclude that the phase difference in this case is $(-1)^{n_+}$ also.

APPENDIX C

THE EXPANSION COEFFICIENTS FOR $\underline{J}^2$ AND Y_{2m}

Using the Eqs. (4.1) and the matrix elements

$$\begin{aligned} \langle i,j|A_+^\dagger|k,\ell\rangle &= \sqrt{i}\ \delta_{i,k+1}\delta_{j\ell} \\ \langle i,j|A_-^\dagger|k,\ell\rangle &= \sqrt{j}\ \delta_{ik}\delta_{j,\ell+1} \end{aligned} \tag{C.1}$$

and their adjoint relations, which are implied by the definitions (3.17) of the creation and annihilation operators, we may obtain expressions for the matrix elements, in the $|n_+,n_-\rangle$ representation, of the operators $\underline{J}^2$ and Y_{2m}. We find

$$\begin{aligned} \langle 0,0|\underline{J}^2|0,0\rangle &= \alpha_1 & \langle 1,0|\underline{J}^2|1,0\rangle &= \alpha_1 + \alpha_2 \\ \langle 0,1|\underline{J}^2|0,1\rangle &= \alpha_1 + \alpha_3 & \langle 1,1|\underline{J}^2|0,0\rangle &= \alpha_4 \\ \langle 0,0|\underline{J}^2|1,1\rangle &= \alpha_5 & \langle 1,0|Y_{21}|0,0\rangle &= \gamma_1 \\ \langle 0,0|Y_{21}|0,1\rangle &= \gamma_2 & \langle 2,1|Y_{21}|0,0\rangle &= \sqrt{2}\ \gamma_3 \end{aligned} \tag{C.2}$$

$$\begin{aligned}
&\langle 0,0|Y_{21}|1,2\rangle = \sqrt{2}\,\gamma_4 && \langle 1,1|Y_{21}|0,1\rangle = \gamma_1 + \gamma_5 \\
&\langle 1,0|Y_{21}|1,1\rangle = \gamma_2 + \gamma_6 && \langle 2,0|Y_{21}|1,0\rangle = \sqrt{2}\,(\gamma_1+\gamma_7) \\
&\langle 0,1|Y_{21}|0,2\rangle = \sqrt{2}\,(\gamma_2+\gamma_8) && \langle 2,0|Y_{22}|0,0\rangle = \sqrt{2}\,\delta_1 \\
&\langle 0,0|Y_{22}|0,2\rangle = \sqrt{2}\,\delta_2 && \langle 1,0|Y_{22}|0,1\rangle = \delta_3 \ .
\end{aligned} \tag{C.2}$$

The expressions for Y_{20} are exactly as for $\underline{J}^2$, with α_j replaced by β_j.

Not all of these matrix elements are independent. From the expression (3.11) for the matrix elements of an operator in spheroidal wave function states, using the fact that the $D_q^{\ell m}$ are all real, and using the symmetry (A.11) and the properties of the matrix elements of $\underline{J}^2$ and Y_{2m} in spherical harmonic states (Edmonds 1957), one easily finds the relations

$$\langle W_{\ell_1 m_1}|Y_{2M}|W_{\ell_2 m_2}\rangle = (-1)^M \langle W_{\ell_2 -m_2}|Y_{2M}|W_{\ell_1 -m_1}\rangle \tag{C.3a}$$

$$\langle W_{\ell_1 m}|\underline{J}^2|W_{\ell_2 m}\rangle = \langle W_{\ell_2 -m}|\underline{J}^2|W_{\ell_1 -m}\rangle \ . \tag{C.3b}$$

Because of the phase factor of $(-1)^{n_+}$ between $W_{\ell m}$ and the corresponding $|n_+,n_-\rangle$ state (Appendix B), these relations obviously may be written

$$\langle i,j|Y_{2M}|k,\ell\rangle = \langle \ell,k|Y_{2M}|j,i\rangle \tag{C.4a}$$

$$\langle i,j|\underline{J}^2|k,\ell\rangle = \langle \ell,k|\underline{J}^2|j,i\rangle \tag{C.4b}$$

Equations (C.2) and (C.4) lead at once to the Eqs. (4.2).

APPENDIX D

SOME SYMMETRIES OF THE $C_{\underline{q}}$ COEFFICIENTS

Because the 400×N coefficients $C_{\underline{q}JK}^{mm'}$ are derived ultimately from only a small number of A_μ coefficients, it is clear that there must be many relations between them. This appendix deals with some symmetries which are simple enough to be of practical importance for numerical work (and which in some cases are of theoretical importance also).

The easiest symmetries to write down are those which follow from the symmetry properties of the $C_{jk}(m,m')$ which were pointed out by Goodings and Henkelman (1971). From their work, and the defining Eq. (4.12), it follows at once that

$$C_{\underline{q}JK}^{mm'} = C_{\underline{q}KJ}^{m'm} \tag{D.1a}$$

$$C_{\underline{q}JK}^{mm'} = (-1)^{m+m'}(C_{\underline{q}JK}^{\bar{m}\bar{m}'})^* \tag{D.1b}$$

$$C_{\underline{q}JK}^{mm'} = C_{\overline{\underline{q}}JK}^{mm'} \tag{D.1c}$$

Equation (D.1a) expresses the condition that $V_{jk} = V_{kj}$, while Eq. (D.1b) ensures that the potential is real and (D.1c) takes account of the inversion symmetry of the crystal. This latter symmetry is of the greatest theoretical importance, since all the quantities which depend on $C_{\underline{q}}$ are then invariant under the transformation $\underline{q} \rightarrow \bar{\underline{q}}$. This property is used frequently in Chapters 4 and 5.

To discuss other symmetries of the $C_{\underline{q}}$ coefficients, it is necessary to specify the coordinate systems more carefully than has hitherto been done. The set of equilibrium coordinate axes for the four sublattices is chosen to give a consistent view of the crystal, in the sense that the four sublattices are explicitly equivalent. As seen from any molecule in that molecule's coordinate frame, the twelve nearest neighbours lie on three sublattices, A, B, and C, with four molecules on each sublattice, and the properties shown in Table 5. The choice of coordinate axes and sublattice numbers which yields this result is shown in Table 6.

The potential energy of the crystal is

$$V = C_{jk}^{mm'} \; Y_{2m}(\theta_j,\phi_j) Y_{2m'}(\theta_k,\phi_k) \tag{D.2a}$$

$$= C_{\underline{q}JK}^{mm'} \; Y_{\bar{\underline{q}}J}^{m} \; Y_{\underline{q}K}^{m'} \tag{D.2b}$$

where we have defined

TABLE 5

PROPERTIES OF THE NEAREST NEIGHBOURS OF ANY MOLECULE.

All coordinates are expressed in the equilibrium coordinate frame of the central molecule.

The lattice parameter is a.

Sublattice	Positions of the 4 molecules on this sublattice	x axis direction	z axis direction
A	$(0, \pm \frac{a}{\sqrt{6}}, \mp \frac{a}{\sqrt{3}})$ $(\pm \frac{a}{\sqrt{2}}, 0, 0)$	$(0, - \frac{1}{\sqrt{3}}, \sqrt{\frac{2}{3}})$	$(\sqrt{\frac{2}{3}}, - \frac{1}{3} \sqrt{2}, - \frac{1}{3})$
B	$(\pm \frac{a}{2\sqrt{2}}, \mp \frac{a}{2\sqrt{6}}, \mp \frac{a}{\sqrt{3}})$ $(\pm \frac{a}{2\sqrt{2}}, \pm \frac{a}{2} \sqrt{\frac{3}{2}}, 0)$	$(0, \frac{1}{\sqrt{3}}, - \sqrt{\frac{2}{3}})$	$(- \sqrt{\frac{2}{3}}, - \frac{1}{3} \sqrt{2}, - \frac{1}{3})$
C	$(\pm \frac{a}{2\sqrt{2}}, \pm \frac{a}{2\sqrt{6}}, \pm \frac{a}{\sqrt{3}})$ $(\pm \frac{a}{2\sqrt{2}}, \mp \frac{a}{2} \sqrt{\frac{3}{2}}, 0)$	$(-1, 0, 0)$	$(0, \frac{2}{3} \sqrt{2}, - \frac{1}{3})$

TABLE 6

THE EQUILIBRIUM COORDINATE SYSTEMS FOR THE FOUR SUBLATTICES.

Vectors are expressed in crystal coordinates.

Sublattice	x axis	y axis	z axis	A	B	C
1	$\frac{1}{\sqrt{2}}(-1, -1, 0)$	$\frac{1}{\sqrt{6}}(1, -1, 2)$	$\frac{1}{\sqrt{3}}(-1, 1, 1)$	4	3	2
2	$\frac{1}{\sqrt{2}}(1, 1, 0)$	$\frac{1}{\sqrt{6}}(-1, 1, 2)$	$\frac{1}{\sqrt{3}}(1, -1, 1)$	3	4	1
3	$\frac{1}{\sqrt{2}}(1, -1, 0)$	$\frac{1}{\sqrt{6}}(-1, -1, -2)$	$\frac{1}{\sqrt{3}}(1, 1, -1)$	2	1	4
4	$\frac{1}{\sqrt{2}}(-1, 1, 0)$	$\frac{1}{\sqrt{6}}(1, 1, -2)$	$\frac{1}{\sqrt{3}}(-1, -1, -1)$	1	2	3

$$Y^m_{\underline{q}J} = N^{-\frac{1}{2}} \sum_{j\epsilon J} \exp(-i\underline{q}\cdot\underline{R}_j) Y_{2m}(\theta_j,\phi_j) \quad . \qquad \text{(D.3)}$$

Suppose there is some disturbance from equilibrium in the crystal characterized by a single wavevector $\underline{q}$. The energy of interaction between all the molecules on sublattice J and all the molecules on sublattice K is then

$$V_{JK}(\underline{q}) = C^{mm'}_{\underline{q}JK} \, Y^m_{\underline{q}J} \, Y^{m'}_{\underline{q}K} \quad . \qquad \text{(D.4)}$$

Now let us rotate and translate the crystal, disturbance and all, so that the molecules of sublattice J end up in the positions originally occupied by the molecules of some sublattice J', with their equilibrium coordinate systems realigned accordingly. Because of the equivalence of the sublattices, this transformation will map sublattice K into some sublattice K'. The wavevector $\underline{q}$ is of course transformed into some $\underline{q}'$.

If $\underline{x}_J$, $\underline{y}_J$, and $\underline{z}_J$ are the unit column vectors giving (in crystal coordinates) the directions of the axes of the coordinate system for sublattice J (these are the vectors in Table 6), then the matrix which describes the rotation part of the transformation is defined by

$$R(J,J')(\underline{x}_J, \underline{y}_J, \underline{z}_J) = (\underline{x}_{J'}, \underline{y}_{J'}, \underline{z}_{J'}) \qquad \text{(D.5a)}$$

or

$$R(J,J') = (\underline{x}_{J'}, \underline{y}_{J'}, \underline{z}_{J'}) \begin{pmatrix} \underline{x}_J^T \\ \underline{y}_J^T \\ \underline{z}_J^T \end{pmatrix} \qquad \text{(D.5b)}$$

where the superscript T denotes the transpose. For the choice of coordinates used here, there are only four distinct matrices, all of them diagonal. They are

$$R(1,1) = R(2,2) = R(3,3) = R(4,4) = \mathrm{diag}(1,1,1) \qquad \text{(D.6a)}$$

$$R(1,2) = R(2,1) = R(3,4) = R(4,3) = \mathrm{diag}(\bar{1},\bar{1},1) \qquad \text{(D.6b)}$$

$$R(1,3) = R(2,4) = R(3,1) = R(4,2) = \mathrm{diag}(\bar{1},1,\bar{1}) \qquad \text{(D.6c)}$$

$$R(1,4) = R(2,3) = R(3,2) = R(4,1) = \mathrm{diag}(1,\bar{1},\bar{1}) \; . \qquad \text{(D.6d)}$$

If $\underline{\Delta}(J,J')$ is the translation vector for the transformation, it follows easily from the definition (D.4) that

$$Y^m_{\underline{q}'J'} = \exp(-i\underline{q}'\cdot\underline{\Delta}(J,J'))\,Y^m_{\underline{q}J} \; . \qquad \text{(D.7)}$$

Since the relations between the molecules have not been altered by the transformation of the crystal, the potential energy must be the same, so that

$$\sum_{mm'} C^{mm'}_{\underline{q}JK} Y^{m}_{\underline{q}J} Y^{m'}_{\underline{q}K} = \sum_{mm'} C^{mm'}_{\underline{q}'J'K'} Y^{m}_{\underline{q}'J'} Y^{m'}_{\underline{q}'K'} \tag{D.8a}$$

$$= \sum_{mm'} C^{mm'}_{\underline{q}'J'K'} Y^{m}_{\underline{q}J} Y^{m'}_{\underline{q}K} , \tag{D.8b}$$

where the last step has used (D.7). So we have the symmetries

$$C^{mm'}_{\underline{q}JK} = C^{mm'}_{\underline{q}'J'K'} \tag{D.9}$$

which connect the coefficients in different octants of the Brillouin zone. Including the effect of the inversion symmetry, Eq. (D.1c), we may state the results as follows:

(i) If the sign of q_x is changed, then sublattices 1 and 4 are interchanged, and 2 and 3 are interchanged.

(ii) If the sign of q_y is changed, then 1 and 3 are interchanged, and 2 and 4 are interchanged.

(iii) If the sign of q_z is changed, then 1 and 2 are interchanged, and 3 and 4 are interchanged.

Because the eigenvectors $U_{\underset{\sim}{q}J\sigma\alpha}$ are determined by the $C_{\underset{\sim}{q}}$ coefficients in the manner stated in Chapter 4, rules (i) - (iii) above apply also to these eigenvectors.

APPENDIX E

DIAGONALIZATION OF THE LIBRON HAMILTONIAN

In this appendix, we discuss the diagonalization of the Hamiltonian (4.13) and sketch the derivation of Eqs. (4.15) through (4.19). The approach is the same as that of Raich and Etters (1968), but we shall go into rather more detail in order to emphasize the uniqueness of the transformation, which is necessary if the librons so obtained are to have any physical credibility. As a notational convenience, and to make the 8×8 structure of the matrices more evident, we shall abbreviate the composite index $J\sigma$ by the single index λ, and shall write $\overline{\lambda}$ in place of $J\overline{\sigma}$. Equation (4.13b) is then

$$\mathcal{H}_2 = \theta A^{\dagger}_{\underline{q}\lambda} A_{\underline{q}\lambda} + W_{\underline{q}\lambda\mu}\{A^{\dagger}_{\underline{q}\lambda} A^{\dagger}_{\overline{\underline{q}}\mu} + A_{\underline{q}\overline{\mu}} A_{\overline{\underline{q}}\overline{\lambda}} + 2A^{\dagger}_{\underline{q}\lambda} A_{\underline{q}\overline{\mu}}\} \ . \quad \text{(E.1)}$$

We seek to diagonalize $\mathcal{H}_2$ in the form (4.14), where the B operators are bosons and so have the commutation rules

$$[B_{\underline{q}\alpha}, \mathcal{H}_2] = \varepsilon_{\underline{q}\alpha} B_{\underline{q}\alpha} \qquad [B^{\dagger}_{\underline{q}\alpha}, \mathcal{H}_2] = -\varepsilon_{\underline{q}\alpha} B^{\dagger}_{\underline{q}\alpha} \quad \text{(E.2)}$$

and hence

$$[[B_{\underline{q}\alpha}, \mathcal{H}_2], \mathcal{H}_2] = \varepsilon^2_{\underline{q}\alpha} B_{\underline{q}\alpha} \quad [[B^{\dagger}_{\underline{q}\alpha}, \mathcal{H}_2], \mathcal{H}_2] = \varepsilon^2_{\underline{q}\alpha} B^{\dagger}_{\underline{q}\alpha} \ . \text{(E.3)}$$

The cubic crystal symmetry requires $\varepsilon^2_{\bar{\underline{q}}\alpha} = \varepsilon^2_{\underline{q}\alpha}$, and when we obtain an expression for $\varepsilon^2_{\underline{q}\alpha}$ it will be apparent that this condition is satisfied. For the moment, we assume it, and so if we define the operators

$$C^\dagger_{\underline{q}\alpha} = \xi_{\underline{q}\alpha} B^\dagger_{\underline{q}\alpha} + \eta_{\underline{q}\alpha} B_{\bar{\underline{q}}\alpha} \qquad C_{\underline{q}\alpha} = \eta^*_{\underline{q}\alpha} B^\dagger_{\bar{\underline{q}}\alpha} + \xi^*_{\underline{q}\alpha} B_{\underline{q}\alpha} \tag{E.4}$$

then it follows that the C operators have double commutators with $\mathcal{H}_2$ of the same form as (E.3). The inverse transformation is

$$B^\dagger_{\underline{q}\alpha} = (\xi_{\underline{q}\alpha}\xi^*_{\bar{\underline{q}}\alpha} - \eta_{\underline{q}\alpha}\eta^*_{\bar{\underline{q}}\alpha})^{-1}(\xi^*_{\bar{\underline{q}}\alpha} C^\dagger_{\underline{q}\alpha} - \eta_{\underline{q}\alpha} C_{\bar{\underline{q}}\alpha}) \tag{E.5a}$$

$$B_{\underline{q}\alpha} = (\xi^*_{\underline{q}\alpha}\xi_{\bar{\underline{q}}\alpha} - \eta^*_{\underline{q}\alpha}\eta_{\bar{\underline{q}}\alpha})^{-1}(-\eta^*_{\underline{q}\alpha} C^\dagger_{\bar{\underline{q}}\alpha} + \xi_{\bar{\underline{q}}\alpha} C_{\underline{q}\alpha}) \ . \tag{E.5b}$$

We propose to make the transformation in the two stages A → C → B. We shall require the C operators to be bosons and to be related to the B operators by (E.4) and to the A operators by

$$C^\dagger_{\underline{q}\alpha} = U_{\underline{q}\lambda\alpha} A^\dagger_{\underline{q}\lambda} \qquad\qquad C_{\underline{q}\alpha} = U^*_{\underline{q}\lambda\alpha} A_{\underline{q}\lambda} \ . \tag{E.6}$$

We first extract some conditions on ξ and η which ensure that the C operators are bosons if and only if the B operators are bosons. Assuming the C operators to be bosons, we find

$$[B^{\dagger}_{\underline{q}\alpha}, B^{\dagger}_{\underline{q}'\beta}] = \delta_{\underline{q}\bar{\underline{q}}'}\delta_{\alpha\beta}(\xi_{\underline{q}\alpha}\xi^{*}_{\bar{\underline{q}}\alpha} - \eta_{\underline{q}\alpha}\eta^{*}_{\bar{\underline{q}}\alpha})^{-1}$$

$$\times\ (\xi_{\bar{\underline{q}}\alpha}\xi^{*}_{\underline{q}\alpha} - \eta_{\bar{\underline{q}}\alpha}\eta^{*}_{\underline{q}\alpha})^{-1}(\xi^{*}_{\bar{\underline{q}}\alpha}\eta_{\bar{\underline{q}}\alpha} - \eta_{\underline{q}\alpha}\xi^{*}_{\underline{q}\alpha}) \tag{E.7}$$

and the B operators can be bosons only if

$$\xi^{*}_{\bar{\underline{q}}\alpha}\eta_{\bar{\underline{q}}\alpha} = \eta_{\underline{q}\alpha}\xi^{*}_{\underline{q}\alpha} \quad . \tag{E.8}$$

If the B operators are bosons, then we find

$$[C^{\dagger}_{\underline{q}\alpha}, C^{\dagger}_{\underline{q}'\beta}] = \delta_{\underline{q}\bar{\underline{q}}'}\delta_{\alpha\beta}(\eta_{\underline{q}\alpha}\xi_{\bar{\underline{q}}\alpha} - \eta_{\bar{\underline{q}}\alpha}\xi_{\underline{q}\alpha}) \tag{E.9}$$

and the C operators can be bosons only if

$$\eta_{\underline{q}\alpha}\xi_{\bar{\underline{q}}\alpha} = \eta_{\bar{\underline{q}}\alpha}\xi_{\underline{q}\alpha} \quad . \tag{E.10}$$

Comparing (E.8) and (E.10), we find that $|\xi_{\bar{\underline{q}}\alpha}|^2 = |\xi_{\underline{q}\alpha}|^2$ (assuming $\eta_{\underline{q}\alpha} \neq 0$). So we must have

$$\xi_{\bar{\underline{q}}\alpha} = e^{i\zeta}\ \xi_{\underline{q}\alpha} \qquad\qquad \eta_{\bar{\underline{q}}\alpha} = e^{i\zeta}\ \eta_{\underline{q}\alpha} \tag{E.11}$$

where we have suppressed the implied subscripts on the real number ζ. The remaining commutator of importance is

$$[B_{\underline{q}\alpha}, B^{\dagger}_{\underline{q}'\beta}] = \delta_{\underline{q}\underline{q}'}\delta_{\alpha\beta}\{|\xi_{\underline{q}\alpha}|^2 - |\eta_{\underline{q}\alpha}|^2\} \tag{E.12}$$

which leads to the further condition

$$|\xi_{\underline{q}\alpha}|^2 - |\eta_{\underline{q}\alpha}|^2 = 1 \quad . \tag{E.13}$$

The commutator $[C_{\underline{q}\alpha}, C^{\dagger}_{\underline{q}'\beta}]$ turns out to add no new information.

We now see what can be learned about the matrix $U_{\underline{q}}$ from Eq. (E.6). We note that

$$\sum_{\lambda} U_{\underline{q}\lambda\alpha}[[A^{\dagger}_{\underline{q}\lambda}, \mathcal{H}_2], \mathcal{H}_2] = [[C^{\dagger}_{\underline{q}\alpha}, \mathcal{H}_2], \mathcal{H}_2] = \epsilon^2_{\underline{q}\alpha} \sum_{\lambda} U_{\underline{q}\lambda\alpha} A^{\dagger}_{\underline{q}\lambda} \quad . \tag{E.14}$$

It is straightforward to evaluate the double commutator, using (E.1) and (4.11): one finds

$$[[A^{\dagger}_{\underline{q}\lambda}, \mathcal{H}_2], \mathcal{H}_2] = \theta^2 A^{\dagger}_{\underline{q}\lambda} + 4\theta W_{\underline{q}\mu\bar{\lambda}} A^{\dagger}_{\underline{q}\mu} \tag{E.15}$$

where one requires the symmetry property $W_{\underline{q}\mu\bar{\lambda}} = W_{\underline{q}\bar{\mu}\lambda}$, which follows from (4.13d). Equating the coefficients of $A^{\dagger}_{\underline{q}\lambda}$ in (E.14) then gives the condition

$$\epsilon^2_{\underline{q}\alpha} U_{\underline{q}\lambda\alpha} = (\theta^2 \delta_{\lambda\mu} + 4\theta W_{\underline{q}\lambda\bar{\mu}}) U_{\underline{q}\mu\alpha} \quad . \tag{E.16}$$

So we have identified $\epsilon^2_{\underline{q}\alpha}$ as an eigenvalue and $U_{\underline{q}\lambda\alpha}$ as the corresponding eigenvector of the matrix $M_{\underline{q}}$ defined by (4.16). From (4.13d), one finds $W^*_{\underline{q}\lambda\mu} = W_{\underline{q}\bar{\lambda}\bar{\mu}}$, so that $M_{\underline{q}}$ is hermitian and $\epsilon^2_{\underline{q}\alpha}$ is real, and the eigenvector matrix can be made unitary. That we must make it unitary can be seen by considering

$$[C_{\underline{q}\alpha}, C^{\dagger}_{\underline{q}'\beta}] = \delta_{\underline{q}\underline{q}'} U^*_{\underline{q}\lambda\alpha} U_{\underline{q}\lambda\beta} \quad , \tag{E.17}$$

from (E.6). Hence the C operators can be bosons only if $\sum_{\lambda} U^*_{\underline{q}\lambda\alpha} U_{\underline{q}\lambda\beta} = \delta_{\alpha\beta}$. The other part of the unitarity condition (4.17) is obtained by considering $[A_{\underline{q}\lambda}, A^{\dagger}_{\underline{q}'\mu}]$. The other commutators are obviously zero and add no information.

The symmetry (4.18) is obtained by writing (E.16) in the form

$$\epsilon^2_{\underline{q}\alpha} U_{\underline{q}\bar{\lambda}\alpha} = (\theta^2 \delta_{\lambda\mu} + 4\theta W_{\underline{q}\bar{\lambda}\mu}) U_{\underline{q}\bar{\mu}\alpha} \tag{E.18a}$$

$$= (\theta^2 \delta_{\lambda\mu} + 4\theta W_{\underline{q}\lambda\bar{\mu}})^* \, U_{\underline{q}\bar{\mu}\alpha} \tag{E.18b}$$

so that $U_{\underline{q}\bar{\lambda}\alpha}$ is the eigenvector of $M^*_{\underline{q}}$ corresponding to the eigenvalue $\epsilon^2_{\underline{q}\alpha}$; hence (4.18) follows.

We now can obtain expressions for ξ and η. If we evaluate $[C_{\underline{q}\alpha}, \mathscr{H}_2]$ using (E.6) and the properties of $U_{\underline{q}}$ which we have found, we discover that

$$[C_{\underline{q}\alpha},\mathcal{H}_2] = (2\theta)^{-1}(\theta^2 + \varepsilon^2_{\underline{q}\alpha})C_{\underline{q}\alpha} - (2\theta)^{-1}(\theta^2 - \varepsilon^2_{\underline{q}\alpha})C^\dagger_{\underline{q}\alpha} \; . \qquad \text{(E.19a)}$$

However, if we evaluate the same commutator using (E.4), we find

$$[C_{\underline{q}\alpha},\mathcal{H}_2] = \varepsilon_{\underline{q}\alpha}(|\xi_{\underline{q}\alpha}|^2 + |\eta_{\underline{q}\alpha}|^2)C_{\underline{q}\alpha}$$

$$- 2\varepsilon_{\underline{q}\alpha}\, e^{-i\zeta}\, \eta^*_{\underline{q}\alpha}\xi^*_{\underline{q}\alpha}\, C^\dagger_{\underline{q}\alpha} \; . \qquad \text{(E.19b)}$$

Comparing the coefficients of $C^\dagger_{\underline{q}\alpha}$ in these expressions, we see that $e^{-i\zeta}\,\eta^*_{\underline{q}\alpha}\xi^*_{\underline{q}\alpha}$ must be real. So we write

$$\xi_{\underline{q}\alpha} = |\xi_{\underline{q}\alpha}|e^{i\psi} \qquad \eta_{\underline{q}\alpha} = |\eta_{\underline{q}\alpha}|e^{-i(\psi+\zeta)} \qquad \text{(E.20)}$$

where we have again suppressed the subscripts on the real number ψ. If we put (E.11), (E.13), and (E.20) into (E.5), we obtain

$$B^\dagger_{\underline{q}\alpha} = e^{-i\psi}(|\xi_{\underline{q}\alpha}|C^\dagger_{\underline{q}\alpha} - |\eta_{\underline{q}\alpha}|C_{\underline{q}\alpha}) \qquad \text{(E.21a)}$$

$$B_{\underline{q}\alpha} = e^{i\psi}(- |\eta_{\underline{q}\alpha}|C^\dagger_{\underline{q}\alpha} + |\xi_{\underline{q}\alpha}|C_{\underline{q}\alpha}) \qquad \text{(E.21b)}$$

But the only conditions that we wish to impose on the B operators are that they be bosons and that they put $\mathcal{H}_2$

in the form (4.14), and these conditions clearly leave the operators undefined by just such a phase as appears in (E.21). So we are at liberty to pick $\psi = 0$, and since ζ does not enter into the relation (E.21) between B and C, we may pick $\zeta = 0$ also. Then $\xi_{\underline{g}\alpha}$ and $\eta_{\underline{g}\alpha}$ are real numbers satisfying $\xi_{\bar{\underline{g}}\alpha} = \xi_{\underline{g}\alpha}$ and $\eta_{\bar{\underline{g}}\alpha} = \eta_{\underline{g}\alpha}$, and by comparing coefficients in (E.19) and taking account of (E.13), we obtain the equations (4.19).

Finally, since $U_{\underline{g}}$ is unitary, the inverse transformation to (E.6) is

$$A^{\dagger}_{\underline{g}\lambda} = U^{*}_{\underline{g}\lambda\alpha}C^{\dagger}_{\underline{g}\alpha} \qquad A_{\underline{g}\lambda} = U_{\underline{g}\lambda\alpha}C_{\underline{g}\alpha} \tag{E.22}$$

and with the use of (E.4) we then obtain (4.15).

This completes the demonstration of Eqs. (4.15) through (4.19). We have shown that the transformation is unique to within an arbitrary phase factor having no physical significance, and that the various conditions are necessary and sufficient for the transformation to map bosons to bosons while diagonalizing $\mathcal{H}_2$.

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