LIBRATIONAL MODES OF SOLID N_2 AND CO

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CONTENTS: An intermolecular potential between two diatomic molecules consisting of quadrupole, dispersion and repulsive terms has been used to determine the librational modes of the molecules in the solid α phase. Fixed centers of mass of the molecules, i.e. no translational motion has been assumed and the calculation is carried out in the small angle approximation for both N_2 and CO. The calculated modes of nitrogen are used to study the temperature dependence of the nuclear quadrupole resonance frequency. The results are compared with Raman scattering and N.Q.R. experiments. An alternate approximation is included in the discussion.

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CHAPTER 1

INTRODUCTION

Although there is increasing interest on the part of solid state physicists in both the experimental and theoretical areas, in molecular crystals; a good understanding of how to approach the unique problem of such crystals, i.e. librational and rotational motion, has not yet been obtained. By the term "molecular crystal", we refer to those crystals which have complexes of tightly bound atoms such that the forces between these complexes is much less than the internal forces between the atoms in the complex. So it becomes apparent that there is a better co-ordinate scheme to describe the dynamics of such crystals than the usual lattice dynamics which assign three displacement co-ordinates to each atom. That is to assign three displacement co-ordinates to the molecular center of mass and all the internal vibrational modes of the molecule and to describe the last two co-ordinates as the angular orientation of the molecule. This becomes completely necessary on the realization that the molecules in such crystals actually rotate, so that the motion of a single atom may be some complex orbit about the center of mass of the molecule. This then is the nature of the unique problem of molecule crystals.

There are a number of things which may be learned as a result of the theoretical study of the dynamics of molecular crystals. In general the internal vibrational modes are of so much higher energy than the intermolecular energies that they are only slightly perturbed from their free molecular values. This is definitely the case for the diatomic molecules which this paper discusses. Thus something can be learned about the perturbation to the vibrational modes due to the solid environment, but this is only a second order effect. When we consider the intermolecular dynamics, a knowledge of the normal modes and molecular motions may lead to a better understanding of the intermolecular forces, particularly of the angular dependent nature of such forces which are poorly described by the study of such molecules in the gas phase. But more frequently, the intermolecular potential is already reasonably well understood from the gas data, and this can be used as a starting point for a study of the molecular motions in the solid. This is the course chosen by this present research. Eventually, as these types of crystals are better understood, the question of how the solid environment affects the intermolecular potential may be answered.

Another characteristic of molecular crystals is the existence of low temperature phase transitions for which there is considerable evidence that the cause is the beginning of hindered rotations of the molecules in the crystals.[1,2.] Although the formulations in this paper does not allow us to investigate this phenomena, this is certainly an important goal in the study of molecular crystals.

This present research considers several properties of solid nitrogen and attempts to calculate the librational frequencies of the molecules in the solid.

The second chapter is concerned with the static properties of the crystal. An intermolecular potential obtained from gas data is modified to give the correct lattice spacing at $T=0^{\circ}K$. Then the calculated binding energy is found to be in good agreement with the experimental heat of sublimation.

The third chapter is concerned with the crystal dynamics. The intermolecular potential is extended to form a crystal Hamiltonian. With the center of mass of the molecules fixed, the librational frequencies are calculated from the classical equations of motion in the small angle approximation. The calculated frequencies are compared with experimental values obtained from Raman scattering, and are found to be too high, an effect which can readily be understood from a consideration of the small angle, harmonic approximation.

In chapter four, the N.Q.R. experiments are discussed. The temperature dependence of the resonance frequency is considered to be due to the librational modes of vibration. It is found that the temperature dependence can be reasonably well understood using the quasi-harmonic approximation in which the temperature dependence of the librational frequencies is considered to be due to only the thermal expansion.

Chapter five, contains the results of an identical calculation for CO which is completely analogous to N_2. The results do not agree as well with experiment, a conclusion which is understood from the inadequacy of the potential for this case.

The sixth chapter is a general discussion of the various methods which have been used to attempt to solve the molecular crystal problem. The strengths and weaknesses of each are pointed out and a possible direction for further study is outlined.

CHAPTER 2

STATIC PROPERTIES OF THE NITROGEN CRYSTAL

A. The Intermolecular Potential

We begin with an intermolecular potential which is obtained from the study of nitrogen gas and which is consistent with the form of the molecule. It is essentially the potential of Kohin[3] with some slight corrections and consists of three parts: the quadrupole-quadrupole interaction, the attractive dispersion force, and the repulsive short range force.

The quadrupole-quadrupole interaction between two axially symmetric charge distributions is:

$$V_q = \frac{3}{4}\frac{Q^2}{R^5}\{1-5(\hat{n}_1\cdot\hat{n}_2)^2-5(\hat{n}_2\cdot\hat{r}_{12})^2+35(\hat{n}_1\cdot\hat{r}_{12})^2(\hat{n}_2\cdot\hat{r}_{12})^2$$

$$-20(\hat{n}_1\cdot\hat{n}_2)(\hat{n}_1\cdot\hat{r}_{12})(\hat{n}_2\cdot\hat{r}_{12})\}$$

where $\hat{n}_1$ and $\hat{n}_2$ are unit vectors along the symmetry axes of the two molecules and $\hat{r}_{12}$ is a unit vector in the direction of the line joining the molecular centers.

R is the distance between the molecular centers and Q is the quadrupole moment for a nitrogen molecule.

The attractive dispersion force, which is a type of London force [4], depends on the polarizability of the molecule and the parameters of the Lennard-Jones potential.

$$V_a = \frac{4\varepsilon\sigma^6}{R^6}\{-1 + \kappa[1 - \tfrac{3}{2}(\hat{n}_1\cdot\hat{r}_{12})^2 - \tfrac{3}{2}(\hat{n}_2\cdot\hat{r}_{12})^2] + \kappa^2[\tfrac{3}{2}(\hat{n}_1\cdot\hat{r}_{12})^2$$

$$+\tfrac{3}{2}(\hat{n}_2\cdot\hat{r}_{12})^2 - 13.5(\hat{n}_1\cdot\hat{r}_{12})^2(\hat{n}_2\cdot\hat{r}_{12})^2$$

$$+9(\hat{n}_1\cdot\hat{r}_{12})(\hat{n}_2\cdot\hat{r}_{12})(\hat{n}_1\cdot\hat{n}_2) - \tfrac{3}{2}(\hat{n}_1\cdot\hat{n}_2)^2]\}$$

where $\kappa = (\alpha_{zz} - \alpha_{xx}) / (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$, and ε and σ are the Lennard-Jones parameters, derived from experiments in the gas phase which have been fitted with the potential

$$V(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right].$$

The repulsive short range force is assumed to be proportional to R^{-12}. For this force the nitrogen molecule is assumed to be two nitrogen atoms at the correct nuclear separation of the molecule. (An assumption which seems quite well justified from the density distribution plots of Bader (1967) [5].) Each atom of the first molecule repels each atom of the second molecule with a potential $\frac{B}{r^{12}}$ where r is the separation between the atoms under consideration.

therefore: $V_r = B\ (\frac{1}{r_{ac}^{12}} + \frac{1}{r_{ad}^{12}} + \frac{1}{r_{bc}^{12}} + \frac{1}{r_{bd}^{12}})$ which can be expressed in terms of angles to first order in R^{-12} as:

$$V_r = \frac{4B}{R^{12}} \{1+6\,\frac{d^2}{R^2}\,[14(\hat{n}_1 \cdot \hat{r}_{12})^2 + 14(\hat{n}_2 \cdot \hat{r}_{12})^2 - 2]$$

$$+42\,\frac{d^4}{R^4}\,[\,1 - 16(\hat{n}_1 \cdot \hat{r}_{12})^2 - 16(\hat{n}_2 \cdot \hat{r}_{12})^2$$

$$+ 288(\hat{n}_1 \cdot \hat{r}_{12})^2 (\hat{n}_2 \cdot \hat{r}_{12})^2 + 2(\hat{n}_1 \cdot \hat{n}_2)^2$$

$$- 64(\hat{n}_1 \cdot \hat{r}_{12})(\hat{n}_2 \cdot \hat{r}_{12})(\hat{n}_1 \cdot \hat{n}_2)] + 42\,\frac{d^4}{R^4}\,[1-16(\hat{n}_1 \cdot \hat{r}_{12})^2$$

$$- 16(\hat{n}_2 \cdot \hat{r}_{12})^2 + 48(\hat{n}_1 \cdot \hat{r}_{12})^4 + 48(\hat{n}_1 \cdot \hat{r}_{12})^4]\}$$

where B is the repulsive potential parameter and d is one half of the internuclear separation. It should be noted here, that a correction has been made to Kohin's potential in the inclusion of the last five terms which she neglects.[4] While they are of the same order in the expansion parameter, the neglected terms do turn out to be small, introducing very little error in Kohin's work.

The repulsive potential parameter B in this paper has been determined such that the crystal will have minimum energy at the equilibrium lattice spacing and differs from Kohin's value, which is deduced from viscosity data, by 11%. The values of all parameters used in the calculations are included in Table 1.

B. The Crystal Structure

At low temperature, nitrogen solidifies in the α phase in which the molecular centers are found on a face centered cubic (fcc) lattice. There are four atoms per unit cell and four sublattices. Table 2 gives a list of the four sublattices, their positions and orientations. Figure 1 is a diagram of the unit cell[6]. The crystal symmetry is Pa3.

It has been reported in the literature that the actual crystal structure deviates from that described above by a shift of the molecules along their symmetry axis (the three-fold axis of the crystal) by a distance of 0.17 Å which would reduce the symmetry to $P2_13$.[7] This would produce a small effect since this shift is only 3% of the lattice unit cell size. A theoretical investigation of this result is discussed in Chapter II, Part D, and since no evidence for such a shift is found there, we shall continue to assume the higher Pa3 symmetry with

TABLE I

PARAMETERS AND CONSTANTS FOR N_2

Quantity	Symbol	Value
Lattice parameter[8]	A_o	5.644 Å
One-half the internuclear distance[9]	d	0.552 Å
Quadrupole moment[10]	Q	1.29×10^{-26} esu
Lennard-Jones parameters[3]	ε	1.313×10^{-14} ergs
	σ	3.708 Å
Polarizability[3]	κ	0.189
Repulsive parameter	B	4.099×10^{-8} ergs/ $Å^{12}$
Moment of Inertia[9]	I	1.401×10^{-39} g cm^2
Transition Temperature[7]	T_o	35.6 °K
Plank's Constant[11]	$\hbar$	1.054×10^{-27} erg sec
Boltzmann's Constant[11]	k	1.3805×10^{-16} ergs /°K

TABLE 2

CRYSTAL STRUCTURE

Sublattice Number (arbitrarily defined)	Position*	Orientation (at equilibrium)
1	1 1 0	(-1,1,1)
2	1-1 0	(1,-1,1)
3	0 1-1	(1,1,-1)
4	0 0 0	(-1,-1,-1)

*This is with a unit cell of side 2 units.

NOTE: There is an arbitrariness of plus or minus in the equilibrium orientations, but this set is chosen so that the crystal appears identical from each sublattice position.

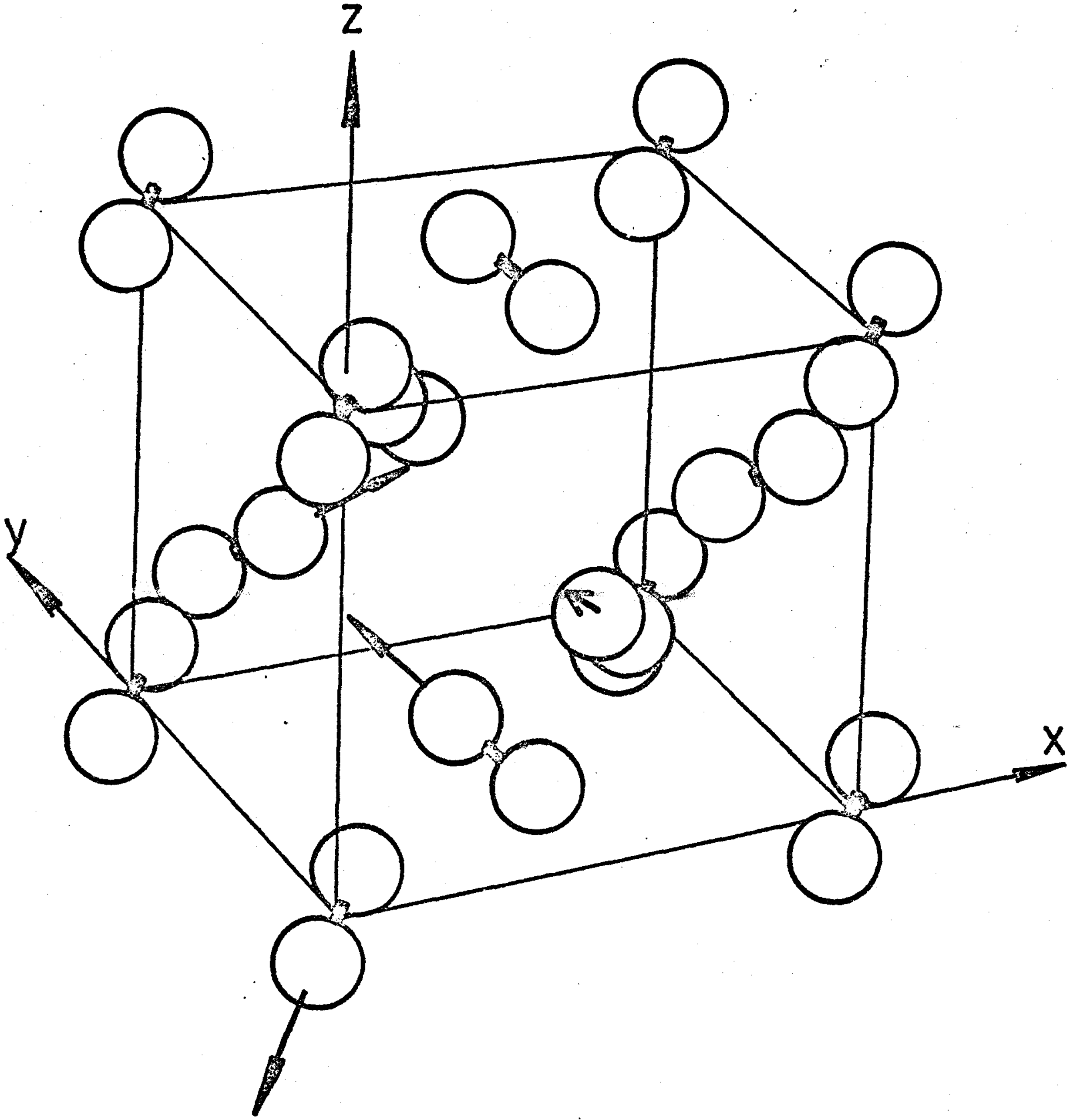

FIGURE 1

The crystal structure in a unit cell of αN_2 showing the f.c.c structure with Pa3 symmetry and showing the orientations of the 4 sublattices the assurance that any error introduced there by must indeed be small.

As the temperature is increased, the crystal undergoes a phase transition at 35.6°K to the β phase in which the crystal structure is hexagonalclose packed.[12] It is found that the molecules are oriented at 56.0° ± 2.5° with respect to the z axis. This result is consistent with the pure quadrupole resonance which vanishes in the β phase. But the quadrupole frequency [13] is proportional to $\left\langle P_2(\cos\theta) \right\rangle$ which is zero if $\theta=54^{\circ}44'$. It is not possible from the X-ray results to distinquish between precession about the axis and a random distribution of orientations.

A third solid phase of nitrogen (γphase) has been reported at high pressure[14], but is not of interest in the present research.

C. The Binding Energy

With a knowledge of the intermolecular potential and knowing the crystal structure it is possible to determine the binding energy of the crystal. We sum up the contributions of each of the three potentials for one molecule with each of its neighbours out to the sixth nearest neighbour. The contributions for further neighbours is less than 0.015% and is thus negligable.

The only parameter which is difficult to determine independently is the repulsive parameter B, since it can be determined only approximately from viscosity data. Therefore the molecular binding energy was calculated as a function of lattice parameter A_o and B was chosen so that $\frac{dE}{dA_o} = 0$ at A_o equal to the known experimental value at 4.2°K of 5.644 Å.[8] This gave a value of $B = 4.103 \times 10^{-8}$ ergs / $\mathring{A}^{12}$ which differs from Kohin's value by 11%[3].

We can compare the calculated binding energy / molecule with the heat of sublimation per mole by using the relation.

1 erg / molecule = 14.3937×10^{15} cal/mol.[11], and remembering to sum each interaction only once introducing a factor of ½. The results are recorded in Table 3. There results are in precise agreement with Kohin's calculations, recognizing the change in lattice parameter and including the previously neglected repulsive terms. To compare the total energy with the experimentally measured energy of -1652 cal/mole[3], it is necessary to include zero point energy corrections which have been estimated to be 213 cal/mole for the translational modes and 123 cal/mole for the librational modes[3]. The deviation from pairwise additivity has also been estimated by Lupton to

TABLE 3

CONTRIBUTIONS TO THE CRYSTAL ENERGY FOR N_2

Energy Term	Energy/Molecule $\times 10^{15}$ ergs	Crystal Energy cal/mole
Quadrupole Quadrupole	-34.76	-250.2
Attractive	-461.91	-3324.3
Repulsive	+227.84	+1636.1
Total	-269.33	-1938.3

Including effects of zero point energy	-336
and deviation from pairwise additivity	+ 30
The calculated sublimation energy	= 1632
The experimental sublimation energy	= 1652

And the deviation is 1.2%.

be -30 cal/mole [15]. Including these terms, the calculated value of the sublimation energy of 1631 cal/mole agrees well with the experimental value of 1652 cal/mole.

It should be noted here that both the attractive and repulsive terms in the potential can be divided into spherically symmetric and angularly dependent terms. From Kohin's work[3], the angularly dependent contributions are +88 cal/mole and -362 cal/mole respectively which are not small compared with the quadrupole terms of -251 cal/mole. Therefore any attempt to calculate the librational lattice dynamics using only a quadrupole-quadrupole interaction omits a large contribution to the angularly dependent potential and thus arrives at doubtful conclusions.

Also the work by Kuan, Warshel and Schnepp (1970)[16], which omits the quadrupole-quadrupole interaction, arrives at conclusions where a main part of the angularly dependent potential has been neglected. The parameters are also chosen to fit a set of librational frequencies which do not include the high frequency mode seen by Anderson et al (1970)[17]. This work differs from Schnepp's in that it considers the polarizability of the molecules in the attractive potential which Schnepp does not.

D. Shift of the Equilibrium Positions

As noted in the section on crystal structure, there has been some evidence from Xray diffraction that the equilibrium position of the molecules was shifted from the f.c.c. sites on the lattice along the four, three-fold axes of symmetry by 0.17Å.[7]. reducing the symmetry to $P2_13$.

This was investigated using the potential described in this chapter by calculating the total crystal energy as a function of shift distance and investigating the results for a minimum at 0.17Å. The molecules were shifted as described by Lipscomb (1964)[7] and the results are plotted in Figure 2. It can readily be seen that the lowest energy occurs for a crystal in which the molecules are not shifted and the higher symmetry of Pa3 describes the crystal.

Other evidence favouring the higher symmetry is obtained from the fact that the $P2_13$ symmetry should result in some extra lines in the Raman spectra which have never been observed.[17] Anderson has suggested that the apparent shift is a result of strains occuring in the crystal since it was grown in a small capillary.[18] Adding to this the lack of any theoretical justification for such a shift, we will assume in the remainder of this paper that the crystal structure has Pa3 symmetry until

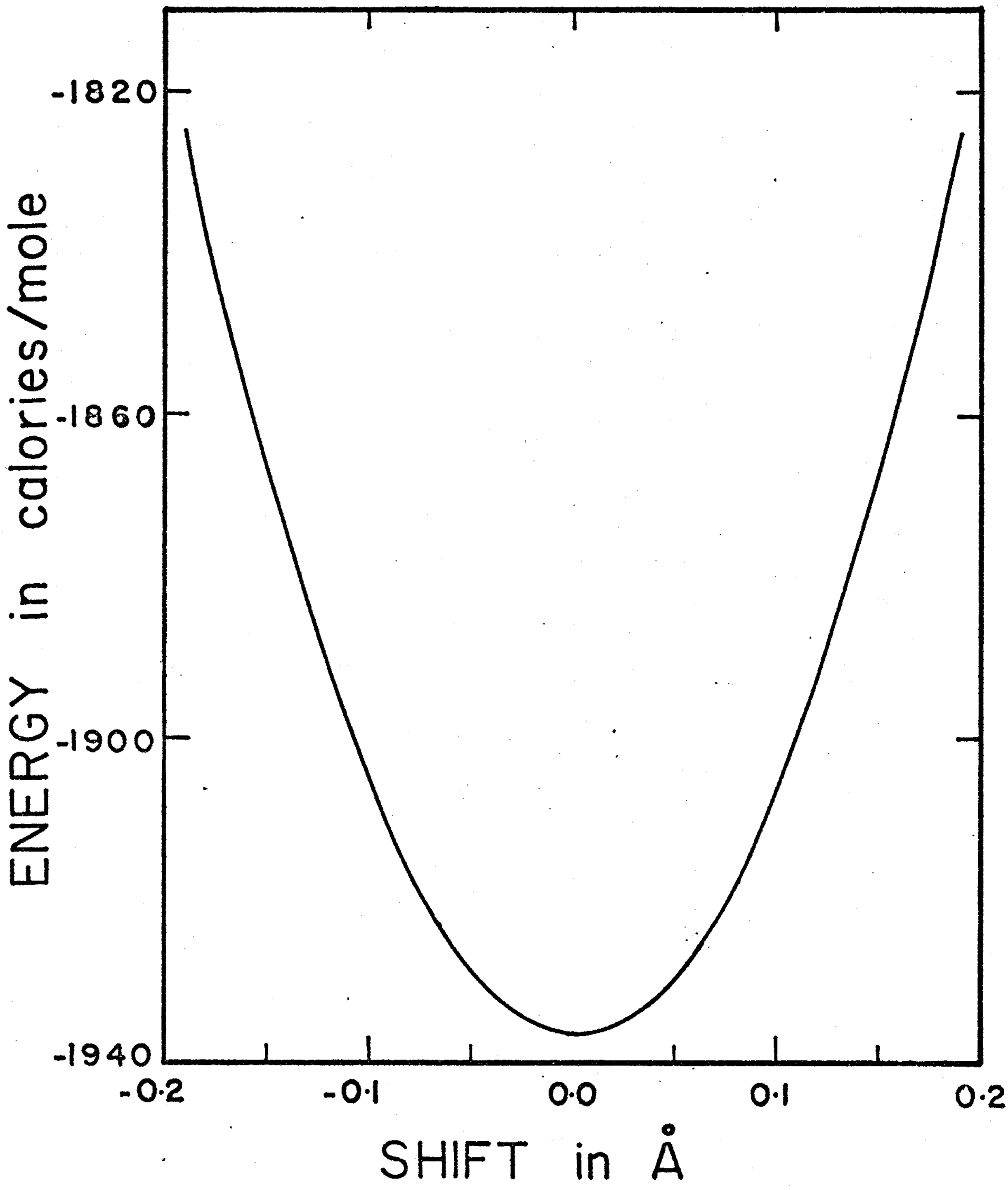

FIGURE 2

A calculation of the total crystal energy of an N_2 cystal vs the shift of the molecules along their 3-fold symmetry axis shows a minimum energy for zero shift implying that such a shift is not consistent with the theoretical potential.

further evidence is obtained to determine the question more exactly.

CHAPTER III

DYNAMICS OF THE LIBRATIONAL MODES OF THE CRYSTAL

A The Librational Hamiltonian

We have described in Chapter II an intermolecular potential between two nitrogen molecules in terms of the distance between the centers of mass and the relative angles. This potential can be expressed much more succintly in terms of spherical harmonics as defined by Edmonds.[19] It becomes

$$V_{12} = B_\circ + B_{1.} [Y_{20}(\omega_1) + Y_{20}(\omega_2)] + \sum_{\mu=-2}^{2} A_\mu Y_{2\mu}(\omega_1) Y_{2-\mu}(\omega_2)$$

$$+ D[Y_{40}(\omega_1) + Y_{40}(\omega_2)]$$

where

$$A_\circ = \frac{24\pi}{5} \left\{ \frac{Q^2}{R^5} - \frac{2\varepsilon\sigma^6}{R^6} \kappa^2 + \frac{227}{27} \; \frac{336Bd^4}{R^{16}} \right\}$$

$$A_1 = A_{-1} = \frac{16\pi}{5} \left\{ \frac{Q^2}{R^5} - \frac{2\varepsilon\sigma^6}{R^6} \kappa^2 + 5 \; \frac{336Bd^4}{R^{16}} \right\}$$

$$A_2 = A_{-2} = \frac{24\pi}{5} \left\{ \frac{Q^2}{R^5} - 2 \frac{2\varepsilon\sigma^6}{R^6} \kappa^2 + 2 \; \frac{336Bd^4}{R^{16}} \right\}$$

$$D = \frac{128}{35} \sqrt{\pi} \; \frac{336Bd^4}{R^{16}}$$

and ω_1 and ω_2 are the polar angles of the molecular axes of symmetry with respect to the intermolecular axis, and B_0 and B_1 are constants which are independent of all angular quantities.

Since we will be taking commutators of various operators with the Hamiltonian, the constant term B_0 does not contribute to the librational Hamiltonian. Also, as is shown in Appendix A, the term $Y_{20}(\omega_2)$ summed over all sites of any particular neighbouring shell is a constant and so can similarily be neglected since it will not contribute to the librational motion.

Now, rather than expressing each interaction between molecular pairs in terms of angles measured with respect to the intermolecular axis, we rotate the spherical harmonics and express them in terms of angles measured with respect to a crystal axis. The standard form of rotation of spherical harmonics is given by Edmond's equation (4.1.4)

$$Y^{\ell}_{m}(\omega_i) = \sum D^{\ell}_{m'm}(\alpha,\beta,\gamma)\; Y^{\ell}_{m'}(\Omega_i)$$

The terms in $Y^4{}_m$ are rotated directly to angles measured with respect to the equilibrium positions of the molecule. Then the effective potential can be written

$$V_{12} = \sum_{m_1 m_2} \sum_{\ell=0}^{4} [(4\pi)(2\ell+1)]^{\frac{1}{2}} \begin{pmatrix} 2 & 2 & \ell \\ m_1 & m_2 & -(m_1+m_2) \end{pmatrix}$$

$$\sum_{\mu} A_{\mu} \begin{pmatrix} 2 & 2 & \ell \\ \mu & -\mu & o \end{pmatrix} Y^{\ell}_{m_1+m_2}(\beta,\gamma) \; Y^{2}_{m_1}(\Omega_1)$$

$$Y^{2}_{m_2}(\Omega_2) + D \sum_{\mu} [D^{4}_{\mu o}(\alpha,\beta,\gamma)_{21} \; Y^{4}_{\mu}(\omega_1)$$

$$+ D^{4}_{\mu o}(\alpha,\beta,\gamma)_{12} \; Y^{4}_{\mu}(\omega_2)]$$

Several relations among the D^2 rotation matrixes have been used from Edmonds.

It is then possible to sum over the whole crystal, remembering to sum each interaction only once. Then if the spherical harmonics for each molecule are expressed in terms of angles from the equilibrium position as described in the crystal structure Chapter II, the Hamiltonian takes the form

$$H = \tfrac{1}{2} \sum_{ij} [\sum_{m'_1 m'_2} C_{ij}(m'_1 m'_2) \; Y^{*}_{2m'_1}(\omega_i) \; Y_{2m'_2}(\omega_j)]$$

$$+ \sum_{ji} D \sum_{\mu} D^{4}_{\mu o}(\alpha,\beta,\gamma)_{ji} \; Y^{4}_{\mu}(\omega_j)$$

and

$$C_{ij}(m'_1 m'_2) = (-1)^{m'_1} \sum_{m_1 m_2} \Big[\sum_{\ell=o}^{4} (4\pi(2\ell+1))^{\frac{1}{2}}$$

$$\begin{pmatrix} 2 & 2 & \ell \\ m_1 & m_2 & -(m_1+m_2) \end{pmatrix} \sum_{\mu=-2}^{2} A_\mu \begin{pmatrix} 2 & 2 & \ell \\ \mu & -\mu & o \end{pmatrix} \Big]$$

$$Y^{\ell}_{m_1+m_2}(\beta,\gamma)_{ij} \quad D^{2}_{-m'_1 m_1}(\alpha_i \beta_i \gamma_i)$$

$$D^{2}_{m'_1 m_2}(\alpha_j \beta_j \gamma_j)$$

In the above sums, i and j run independently over all the molecules in the crystal. m'_1, m'_2, m_1, and m_2 all sum independently from -2 to 2.

In the expression for H, ω_i is the angular polar co-ordinate of the molecular axis measured with respect to the equilibrium axis of molecule i which will in turn depend on the sublattice to which molecule i belongs. $(\alpha,\beta,\gamma)_{ji}$ are the Euler angles required to take the intermolecular axis between molecules j and i into the equilibrium axis for molecule j. And $D_{\mu o}$ is the rotation matrix as defined by Edmonds.[19]

The expression $\begin{pmatrix} 2 & 2 & \ell \\ m_1 & m_2 & -(m_1 + m_2) \end{pmatrix}$ is the usual "3_j" symbol. $(\beta,\gamma)_{ij}$ are the last two Euler angles (α

being arbitrary) required to align the intermolecular axis between molecules i and j with the crystal axis whereas $(\alpha_i,\beta_i,\gamma_i)$ are the Euler angles required to take the crystal axis into the equilibrium axis of molecule i.

Certain symmetry properties of the co-efficients $C_{ij}(m'_1,m'_2)$ are stated here without proof.

$$C_{ij}(m'_1,m'_2) = C^*_{ji}(m'_2,m'_1) \quad ,$$

$$C_{ij}(m'_1,m'_2) = (-1)^{m'_1+m'_2}\, C_{ji}(-m'_2,-m'_1) \quad ,$$

and therefore

$$C_{ij}(m'_1,m'_2) = C^*_{ij}(-m'_1,-m'_2)(-1)^{m'_1+m'_2} \quad .$$

These relations follow from the condition that the potential between two molecules be real.

Also, if the points j and j' are related by inversion symmetry

$$C_{ij}(m'_1,m'_2) = C_{ij'}(m'_1,\, m'_2) \quad .$$

The last relation, which is used several times in the following proof, is that

$$\sum_j C_{ij}(m,o) = \sum_j C_{ij}(o,m) = 0 \qquad \text{if } m\neq 0 \ .$$

This relation, which ensures the equilibrium of the crystal, is derived from a consideration of the transformation of these co-efficients under the three-fold rotational symmetry.

A partial check on the orientational equilibrium of a crystal described by this Hamiltonian has been made. Suppose all molecules in the crystal are fixed in their known equilibrium positions with the exception of molecule i. Then $\frac{\partial H}{\partial \theta_i}$ and $\frac{\partial H}{\partial \phi_i}$ should be zero for θ_i equal to zero, if the ith molecule is indeed to be found in its equilibrium position. This has been checked and is found to hold for this Hamiltonian. A more general investigation of Nagai and Nakamura (1960)[20] using a Hamiltonian derived from quadrupole-quadrupole interaction only (although it is easily extendable to this present Hamiltonian), shows that the structure described in Chapter II has the minimum possible energy of any orientation.

B. The Equations of Motion

It is desireable to have the time development of the librational motion of the molecules in the solid. Therefore we have chosen to consider the Heisenberg equations of motion.

1. The Quantum Mechanical Equations

If we consider the operators J_j^- and J_j^+ defined as in the Messiah, [21] $J_j^{\pm}=J_{xj}\pm iJ_{yj}$, where the subscript j refers to the j th molecule .

Then the Heisenberg equations of motions are:

$$i\hbar \frac{\partial J_j^{\pm}}{\partial t} = [J_j^{\pm}, H]$$

It should be noted here that H must be the total Hamiltonian: the potential energy V, plus the kinetic energy T. But since

$$T = \sum_i \frac{1}{2I_i} J_i^2$$

then: $[J_j^{\pm}, T] = 0$

and therefore the effective Hamiltonian is only the potential energy term and we shall ignore the kinetic energy term.

Using the relations from Messiah [21], the Heisenberg equations of motion become

$$i\hbar\frac{\partial J_j^{\pm}}{\partial t} = \tfrac{1}{2} \sum_{m_1 m_2} \sum_i \{- C_{ji}(m_1,m_2)[6-m_1(m_1\pm 1)]^{\frac{1}{2}} Y^{2*}_{m_1\pm 1}(\omega_j) Y^2_{m_2}(\omega_i) + C_{ij}(m_1,m_2) [6-m_2(m_2\pm 1)]^{\frac{1}{2}} Y^2_{m_1}(\omega_i) Y^2_{m_2\pm 1}(\omega_j) + \sum_i D \sum_\mu D^4_{\mu o}(\alpha,\beta,\gamma)_{ji} [20-\mu(\mu\pm 1)]^{\frac{1}{2}} Y^4_{\mu\pm 1}(\omega_j)$$

2. The Classical Equations of Motion

As has always been the case in lattice dynamics, the quantum mechanical equations of motion and the classical equations can be shown to be equivalent, and since the classical equations are often easier to solve, they are the equations which are used for calculation.

Starting from the Lagrange Equation

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_j} - \frac{\partial T}{\partial q_j} = - \frac{\partial V}{\partial q_j}$$

and using the classical expression for T

$$T = \tfrac{1}{2} (I) \sum_i \dot{\theta}_i^{\,2} + \tfrac{1}{2} \sum_i (I \quad \sin^2\theta_i)\dot{\phi}_i^{\,2}$$

we arrive at the final equations

$$\frac{d}{dt} [-I\overset{\pm i\phi_j}{e}(\dot{\theta}_j \pm i \sin \theta; \cos \theta_j \dot{\phi}_j)] = \tfrac{1}{2} \sum_{m_1 m_2} \quad \sum_i$$

$$(-C_{ji}(m_1,m_2)[6-m_1(m_1\pm 1)]^{\frac{1}{2}}\, Y^{2*}_{m_1\pm 1}(\omega_j)\ Y^2_{m_2}\ (\omega_i)$$

$$+ C_{ij}(m_1,m_2)[6-m_2(m_2\pm 1)]^{\frac{1}{2}}\, Y^{2*}_{m_1}\ (\omega_i)\ Y^2_{m_2\pm 1}\ (\omega_j)$$

$$\pm \sum_i D \quad \sum_\mu D^4_{\mu o}\ (\alpha,\beta,\gamma)_{ji}\ [20 - \mu(\mu\pm 1)]^{\frac{1}{2}}\, Y^4_{\mu\pm 1}(\omega_j)$$

The ± results from using the two different expressions for $\frac{\partial}{\partial\theta} Y^{\ell}_{m}(\theta,\phi)$ found in Messiah [21]

$$\frac{\partial}{\partial\theta} Y^{\ell}_{m} = [\ell(\ell+1) - m(m+1)]^{\frac{1}{2}} Y^{\ell}_{m+1} e^{-i\phi} + m \cot\theta\, Y^{\ell}_{m}$$

$$= -[\ell(\ell+1) - m(m-1)]^{\frac{1}{2}} Y^{\ell}_{m-1} e^{-i\phi} - m \cot\theta\, Y^{\ell}_{m}$$

and they are brought into this form by using the Lagrange equation of ϕ_j. Therefore these two θ_j equations are linearly dependent with the ϕ_j equation and may be used as the two fundamental equations of motion

3. Equivalence of the Quantum Mechanical and Classical Equations.

It can be seen immediately that if the association of the operators $i\hbar J^{\pm}_{j}$ is made with the classical expressions $Ie^{\pm i\phi_j}(\dot{\theta}_j \pm i \sin\theta_j \cos\theta_j \dot{\phi}_j)$, then the quantum and classical equations are identical. Further, it can be seen that the two equations in each pair are just Hermitian conjugate (or complex conjugate in the case of the classical set) which greatly simplifies the manipulation of these equations.

4. Discussion.

Up to this point, no terms have been neglected in the equations of motion, but to proceed further, some approximation must be made. Several approximations have been attempted in this research.

The first attempt made in this research was to express the Y^2 's in terms of their operator equivalents and and then, to solve the equations for $J_j^{\pm}$ after linearizing to first order in $J^{\pm}$. But the use of operator equivalents requires that the rotor be in a well defined J state. For molecules with as large a moment of inertia as N_2, the difference in kinetic energy between the different J rotational states is less than the interaction between nitrogen molecules. This means that the interaction will mix various J values, making the use of operator equivalents impossible. For a molecule such as H_2 this is not the case since the rotational states are well separated. Calculations of this type have been reported by Raich and Etters (1968)[22], for solid orthohydrogen.

A much poorer approximation, is to solve the classical equations in the harmonic approximation. This is a doubtful approximation since even the librational zero-point root mean spare amplitude is of the order of 10°. But the results do give qualitative agreement with experiment.

A discussion of other possible approximations in which to solve this problem will be returned to in Chapter VI.

C. Solution in the Harmonic Small Angle Approximation.

If we write out all the spherical harmonics, expand them in powers of θ, and keep only those terms which are linear in θ, the Lagrange equations become

$$
\begin{aligned}
I e^{\pm i\phi_j} \ddot{\theta}_j = \frac{15}{8\pi} \sum_i & -C_{ji}(\pm 1,\pm 1) e^{\pm i\phi_i} \theta_i + C_{ji}(\pm 1,\mp 1) e^{\mp i\phi_i} \theta_i \\
& + C_{ji}(0,0) e^{\pm i\phi_j} \theta_j + C_{ij}(0,0) e^{\pm i\phi_j} \theta_j \\
& + C_{ij}(\pm 1,\mp 1) e^{\mp i\phi_i} \theta_i - C_{ij}(\mp 1,\mp 1) e^{\pm i\phi_i} \theta_i \\
& + \left(\frac{900}{4\pi} \right)^{\frac{1}{2}} D \sum_i D^4_{oo} (\alpha,\beta,\gamma)_{ji} \; e^{\pm i\phi_j} \theta_j
\end{aligned}
$$

In writing the last term we have used the result that $\sum_i D^4_{\mu o} (\alpha,\beta,\gamma)_{ji} = 0$ if $\mu = 1$ which follows from the threefold rotation symmetry of the crystal.

A comment on the co-ordinates being used, is in order at this point. It is necessary to have two co-ordinates to specify the angular orientation of a molecule. We are using the independent co-ordinates $e^{+i\phi}\theta$ and

$e^{-i\phi}\theta$ where ϕ is assumed a constant and is also assumed non zero. If $\phi=0$, the two independent equations become identical and therefore ϕ must be chosen non zero.

It is now necessary to transform the linearized equation by a Fourier Transform in which each sublattice ν transforms independently according to

$$e^{i\phi\nu}\,\theta q\nu = \sum_{j \text{ on sublattice } \nu} e^{i\phi j}\theta_j\, e^{-i\hat{q}.\hat{R}j}$$

Then the linearized equation becomes

$$I e^{\pm i\phi\nu}\ddot{\theta}_{\hat{q}\nu} = \frac{15}{4\pi}\sum_{\mu}[-\,C_{\nu\mu}\,(\pm1,\pm1)\,e^{\pm i\phi\mu}\,\theta_{\hat{q}\mu}$$

$$+\,C_{\nu\mu}\,(\pm1,\mp1)\,e^{\mp i\phi\mu}\theta_{\hat{q}\mu} + C_{\nu}\,(0,0)\,e^{\pm i\phi\nu}\theta_{\hat{q}\nu}]$$

$$+\,\left(\frac{225}{\pi}\right)^{\frac{1}{2}} D'_{\nu}\; e^{\pm i\phi\nu}\theta_{\hat{q}\nu}$$

where $C_{\nu\mu}$ is the Fourier transform of C_{ij}

$D'_{\nu} = \sum_{i} D\, D^{4}_{oo}(\alpha,\beta,\gamma)_{\,ji}$ for j, a molecule of sublattice ν and

$$C_{\nu} = \sum_{i} C_{ji}(0,0)$$

This equation now describes the lattice motion in terms of eight independent variables $e^{\pm i\phi\nu}\theta_{\hat{q}\nu}$ where ν

runs from one to four. Furthermore, the equations are linear. If we therefore assume that each parameter varies as a $e^{i\omega t}$ we can solve for ω^2 and for the eigen vectors of the motion.

D. Numerical Results for Nitrogen

The frequencies have been calculated using the given potential parameters (Chapter II) and the corresponding energies are expressed in cm^{-1}. It is interesting to note that we can easily calculate the energies for quadrupole-quadrupole interaction only and that we obtain exact agreement with Donkersloot who uses a completely different formulation[23,17].

The calculation includes the interaction out to 6 nearest neighbours and since the difference between 5th and 6th nearest neighbours is less than 0.5%, this was considered sufficient accuracy. These results are recorded in Table 4.

All the above results are reported for the $\hat{q}=0$ modes of vibration. These are the modes which are measured in the Raman experiments. These modes are also pure librational modes and are uncoupled from the translational modes. A proof of this is given by Walmsley and Pople (1964)[24]. For $\hat{q}\neq 0$ the librational

TABLE 4

CONVERGENCE OF THE 6TH NEAREST NEIGHBOUR APPROXIMATION FOR NITROGEN FREQUENCIES

Frequency in cm^{-1}	5th nearest neithbour	6th nearest neighbour	Difference	%
$\nu 1$	54.558	54.377	.181	0.33%
$\nu 2$	62.800	62.643	.157	0.25%
$\nu 3$	80.526	80.403	.123	0.15%

modes couple with the translational modes as reported by Schnepp and Ron (1969)[25]. Therefore the diagram (Figure 3), of the $\hat{q}$ dependence of the librational modes has very little significance except to show that the modes depend only slightly on $\hat{q}$ and to justify the use of an Einstein approximation in Chapter IV.

These calculated modes are compared with the results of the Raman experiments as measured by Anderson et al (1970)[17], and are recorded in Table 5. It can be seen that the agreement is only qualitative and that all the frequencies are high. This is consistent with the use of the harmonic approximation when the librational modes are known to have considerable anharmonicity[25]. Also, whereas the harmonic potential is unbounded for large θ, the actual potential must be periodic in θ which would result in a lower experimental mode. Further, we expect the harmonic approximation to be worst for low energy modes which result from a shallow potential and therefore have large root mean square values of θ. This is indeed found to be the case in these calculations.

Further discussion of the harmonic small angle approximation will be left to Chapter VI.

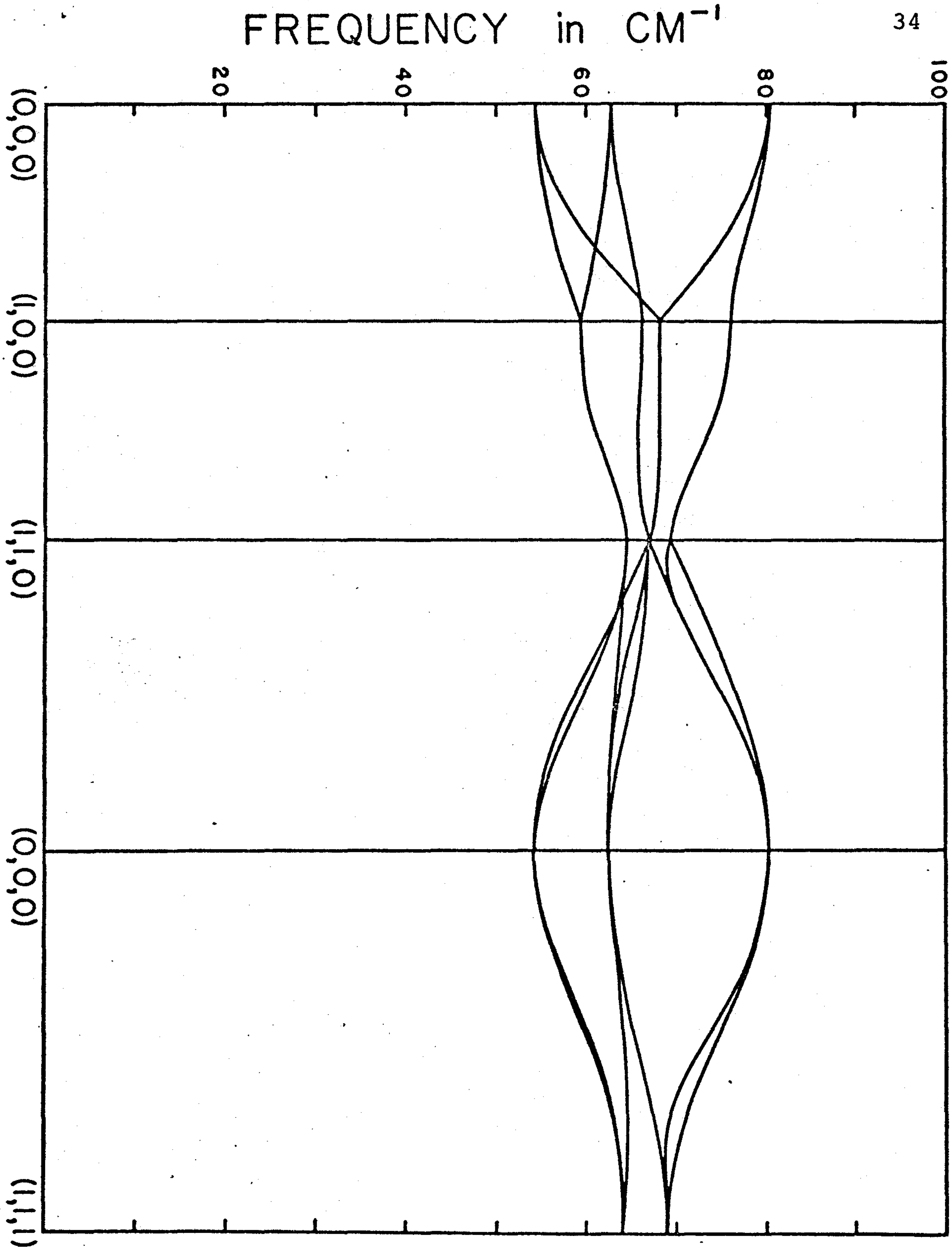

FIGURE 3

The q dependence of the librational modes of N_2 throughout the unit cell

TABLE 5

CALCULATED LIBRATIONAL FREQUENCIES FOR N_2

Mode	Degeneracy	Measured[17]	Calculated	Ratio	Calculated using Q-Q interaction only
E_g	(2)	32±1.5	54.4	1.70	30.4
T_g	(3)	36.5±1.5	62.6	1.72	39.2
T_g	(3)	60±4	80.4	1.34	64.4

CHAPTER IV

NUCLEAR QUADRUPOLE RESONANCE

A. Theory of Nuclear Quadrupole Resonance with Librations.

The frequency of the nuclear quadrupole resonance (N.Q.R.) which has been measured in solid nitrogen[26] depends on the librational motion of the molecules in the solid. It therefore serves as an experimental check on the calculated frequencies.

In general, any nucleus which has a permanent quadrupole moment (i.e. is not spherically symmetric) and which is situated in a non symmetric charge distribution, interacts with the charge distribution by the following Hamiltonian[13,27],

$$H_Q = \frac{eQq}{4I(2I-1)}[(3I_z^2 - I^2) + \tfrac{1}{2}\eta(I_+^2 + I_-^2)]$$

where I is the spin of the nucleus. I=1 for N^{14}.[28]
Q is the permanent quadrupole moment.

q is the electric field gradient of the charge distribution of the molecule in which the nucleus is situated. It is assumed that the contribution to q from neighbouring molecules is negligible.

$$q \equiv \int_{\tau_e} \frac{\rho(r_e)(3\cos^2\theta_e - 1)}{r_e^3}\, d\tau_e \equiv - \frac{\partial E_z}{\partial z}$$

where r_e and $_e$ are the polar co-ordinates of the electronic charge

$\eta = \left(\frac{\partial E_x}{\partial x} - \frac{\partial E_y}{\partial y} \right) / \frac{\partial E_z}{\partial z}$ and is called the assymmetry parameter. We assume for a nitrogen molecule in the crystal that $\eta = 0$ since the molecules are still expected to be axially symmetric.

Matrix elements for the various spin states are easily evaluated from this Hamiltonian.

$$\left\langle \pm 1 \,\middle|\, H_Q \,\middle|\, \pm 1 \right\rangle = +2\, \frac{eQq}{4}$$
$$\left\langle 0 \,\middle|\, H_Q \,\middle|\, 0 \right\rangle = -\, \frac{eQq}{4}$$

Thus, there are two levels separated by an energy of 3/4 eQ_q. Therefore only one N.Q.R. line is expected and only one is found in the experimental results[26].

Up to this point, we have been assuming a static lattice. This is definitely not the case, for even at 0°K the zero point energy allows for considerable librational motion. This orientational motion has a characteristic frequency which is much higher than the N.Q.R.

transition frequency, and therefore the N.Q.R. Hamiltonian experiences only an averaged field gradient q'.

Translational motion of the molecules has no direct effect on the N.Q.R. frequencies since it displaces both the nucleus and the field gradient without reorientation. Only in the coupling of the translational and librational motion, does the translation affect the N.Q.R. frequencies but this is a second order effect. We note in passing, however, that this is the main mechanism contributing to the spin lattice relaxation time T_1.

The effective field gradient is

$$q' = q \left\langle P_2(\cos\theta) \right\rangle$$

where the angular brackets $\langle\ \rangle$, refer to a time average and an ensemble average. But since all our work is in a small angle approximation, expressed to first order in θ^2

$$q' = q\ [1 - 3/2 \left\langle \theta^2 \right\rangle\ ]$$

This expression can be comsidered to be implicitly temperature dependent. It is too laborious to do an exact ensemble average and would be unwarranted considering the use of the small angle approximation. Therefore we assume the three modes to be the modes of an Einstein oscillator.

i.e. The frequency of each mode is assumed to be a constant, independent of $\hat{q}$. The constant is chosen to be the calculated value at $\hat{q}=0$ given in Table 5. Since the $\hat{q}$ dependence of the modes is reasonably flat (see Figure 3), this is probably a justifiable assumption.

Now if we consider these frequencies in the harmonic approximation and set the classical maximum potential energy equal to the energy of the quantum mechanical mode using a Bose-Einstein distribution

$$\tfrac{1}{2}\,\omega_i^2 I \theta_{i\max}^2 = \hbar\omega_i \left(\tfrac{1}{2} + \frac{1}{e^{x_i} - 1}\right)$$

where $\theta_{i\max}$ is the amplitude of the ith libration and is equal to $2\left\langle \theta_i^2 \right\rangle^{\frac{1}{2}}$. X_i is the temperature dependent term and is equal to $\frac{\hbar\omega_i}{kT}$.

We include all 8 modes by noting that in the classical small angle approximation,

$$\left\langle \theta^2 \right\rangle = \sum_{i=1}^{8} \left\langle \theta_i^2 \right\rangle$$

A proof of this result is given in Appendix B.

Therefore, the N.Q.R. frequency can be written as a temperature dependent function of the 8 modes of libration

$$\nu_Q = \nu_o \left[1 - 3/2 \sum_i \frac{\hbar}{I\omega_i} \left(\tfrac{1}{2} + \frac{1}{e^{\hbar\omega_i/kT} - 1}\right)\right]$$

This is essentially the theory first derived by Bayer (1951)[29] with some mod~~e~~ifications to include several modes.

B. Results.

The above expression has been calculated as a function of temperature using the calculated frequencies of Chapter III. The calculated frequencies are used because the work must be done consistently in the small angle harmonic approximation.

The value of ν_o is determined by fitting the calculated curve to the extrapolated experimental frequency of 3.489 MH_z at $T=0^oK$. This gives a deduced value of 5.50 MH_z for $\frac{3}{4}$ eqQ, which agrees with the value cited by De Reggi (1968)[26] of 5.55 MH_z.

The results are plotted in Figure 4 along with the experimental results of De Reggi et al (1968)[26]. It can be seen that the curves agree only very qualitatively.

C. Temperature Dependence of Librational Modes.

In the above calculation, the librational modes have been assumed to be temperature independent but it is known from experiment that this is not the case[30]. To calculate the temperature dependence of the

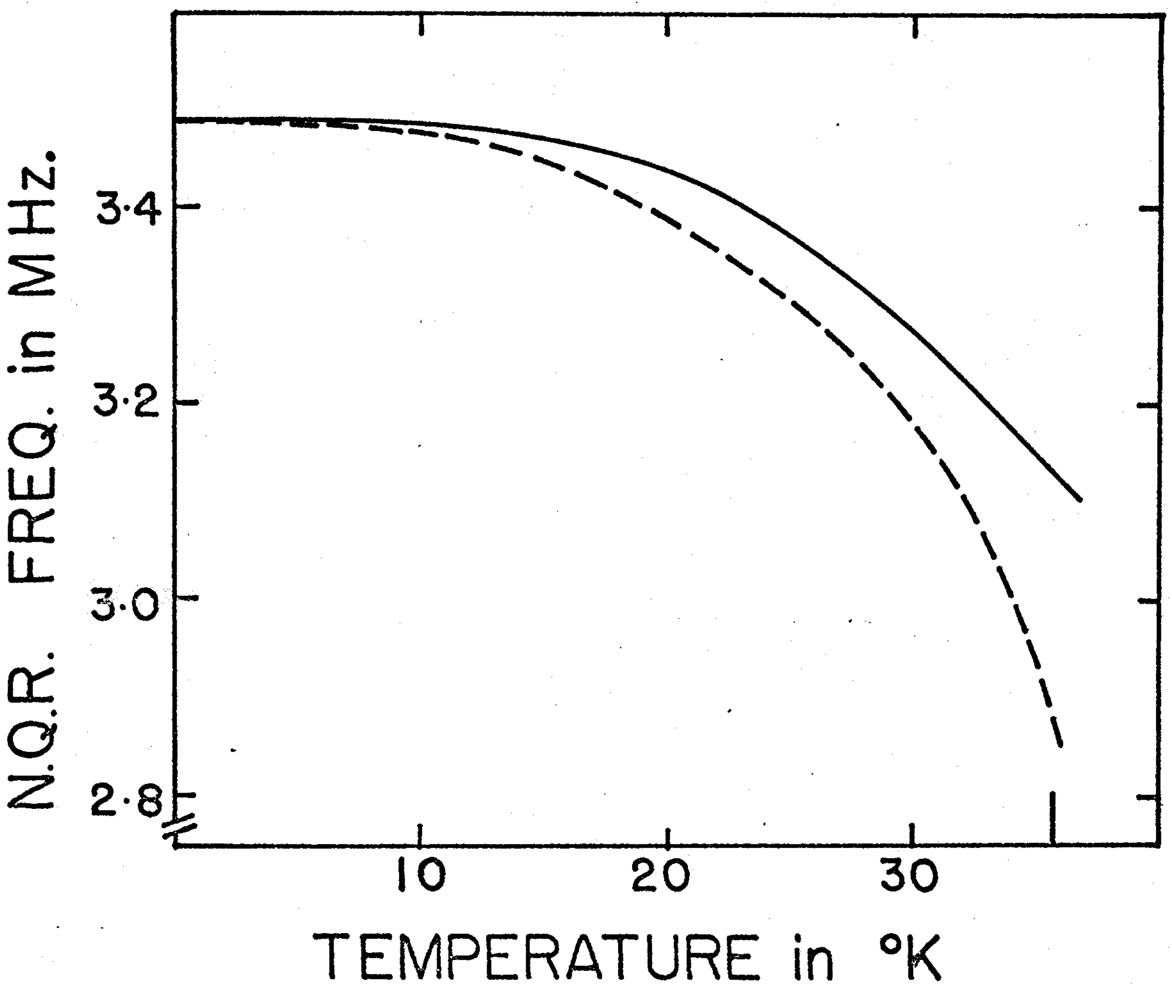

FIGURE 4

N.Q.R. frequencies calculated using temperature independent modes of libration (———) and compared with the experimentally measured frequencies (— — — —)

modes involves the introduction of anharmonic terms in the potential and phonon-phonon interactions. But it has been shown for Aluminum by Gilat and Nicklow (1965)[31] that the anharmonic effects can be quite well represented by considering them to be due to volume expansion alone. So that while N_2 is a very different system, we attempt this approximation to the temperature dependence of the modes.

The thermal expansion of solid nitrogen has been measured by Heberlein et al (1970) [32] and their results are included in Figure 5. From these experimental results which give the lattice parameter as a function of temperature, it is possible , by calculating the frequencies for various lattice parameters, to give the librational frequencies as a function of temperature. This has been done and the agreement with the measured temperature dependence is impressive, showing that even in this case the temperature dependence can be well accounted for by the thermal expansion.

In Figure 6, a calculated curve for librational frequency vs temperature is drawn through the experimental points of St. Louis and Schnepp (1969)[30] to which it is normalized.

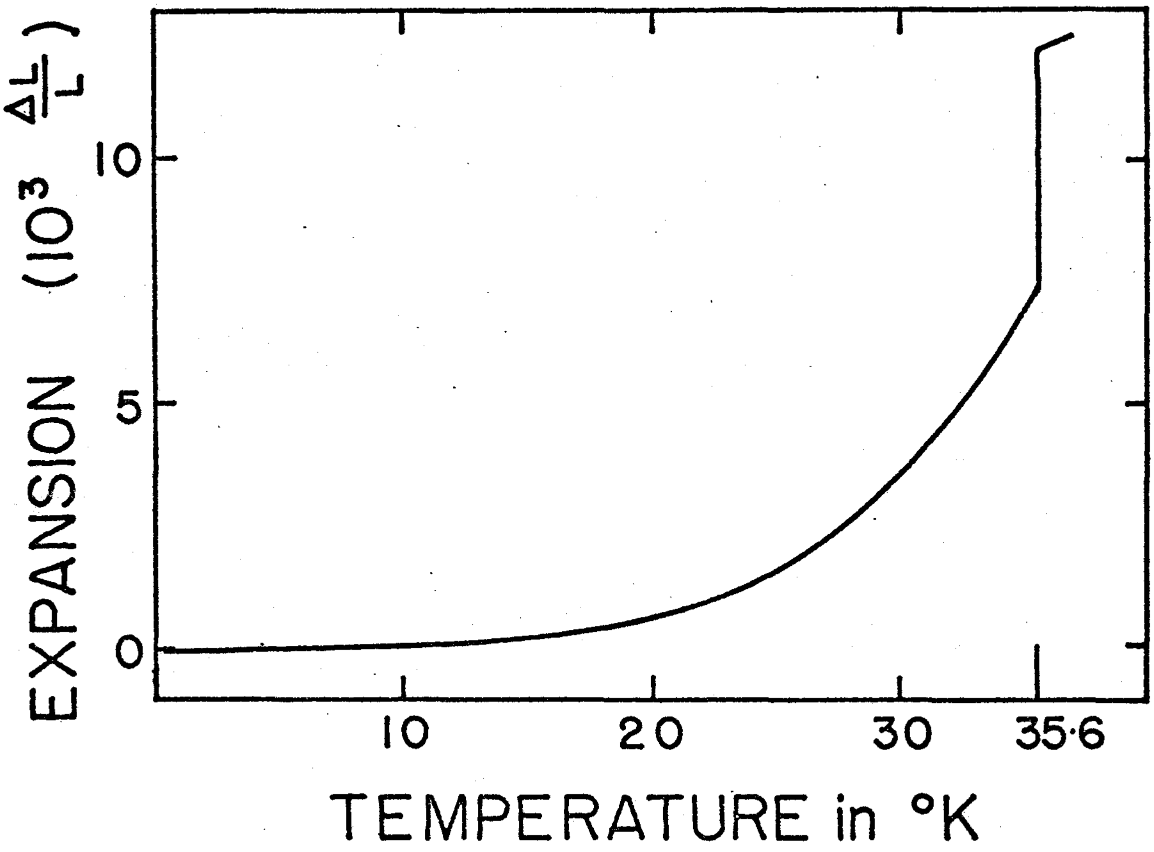

FIGURE 5

Experimental measurement of Thermal Expansion in solid α-N_2 up to the transition point 36.5°K.

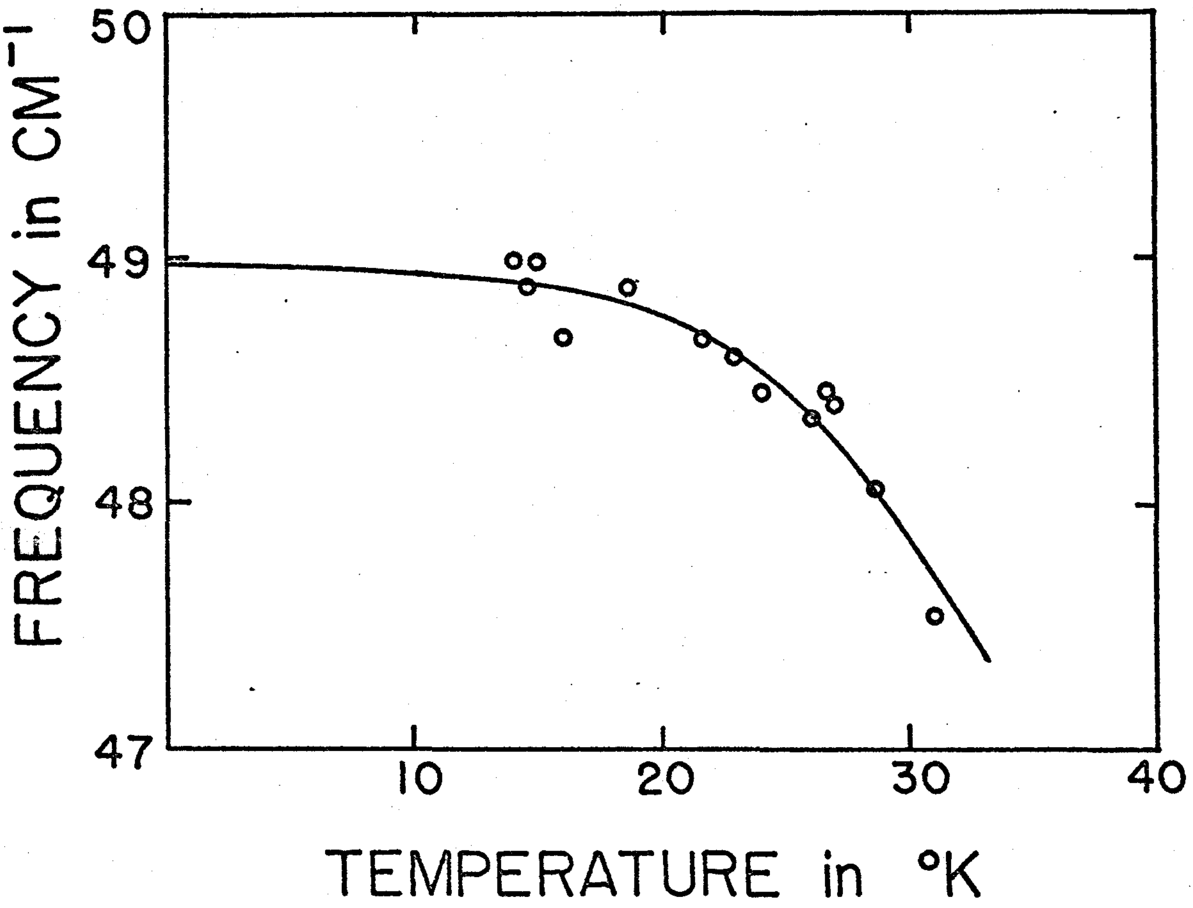

FIGURE 6

The temperature dependence of a librational mode using the thermal expansion only (———). Experimental points are included (o) to which the librational frequency is normalized.

These temperature dependent modes have been used to calculate the N.Q.R. frequency as a function of temperature with the results plotted in Figure 7. There is a significant improvement in the agreement with experiment from the use of temperature independent modes as in Figure 4.

The calculated frequencies are still higher than the measured frequencies and this is believed to be due to the use of the small angle approximation. The agreement becomes worst nearing the transition point, which is to be expected if the transition does indeed represent the beginning of hindered rotations.

But in spite of the considerable approximations made in the use of a small angle assumption, this work does give a qualitative understanding of the nuclear quadrupole resonance results in solid nitrogen.

D. Spin Lattice Relaxation.

As measurements have been made on the spin lattice relaxation time (T_1) in α-N_2, it would be of interest to calculate T_1 from a theoretical starting point, since De Reggi et al (1968)[26] find that T_1 varies with the temperature approximately as $T^{3.5}$. But

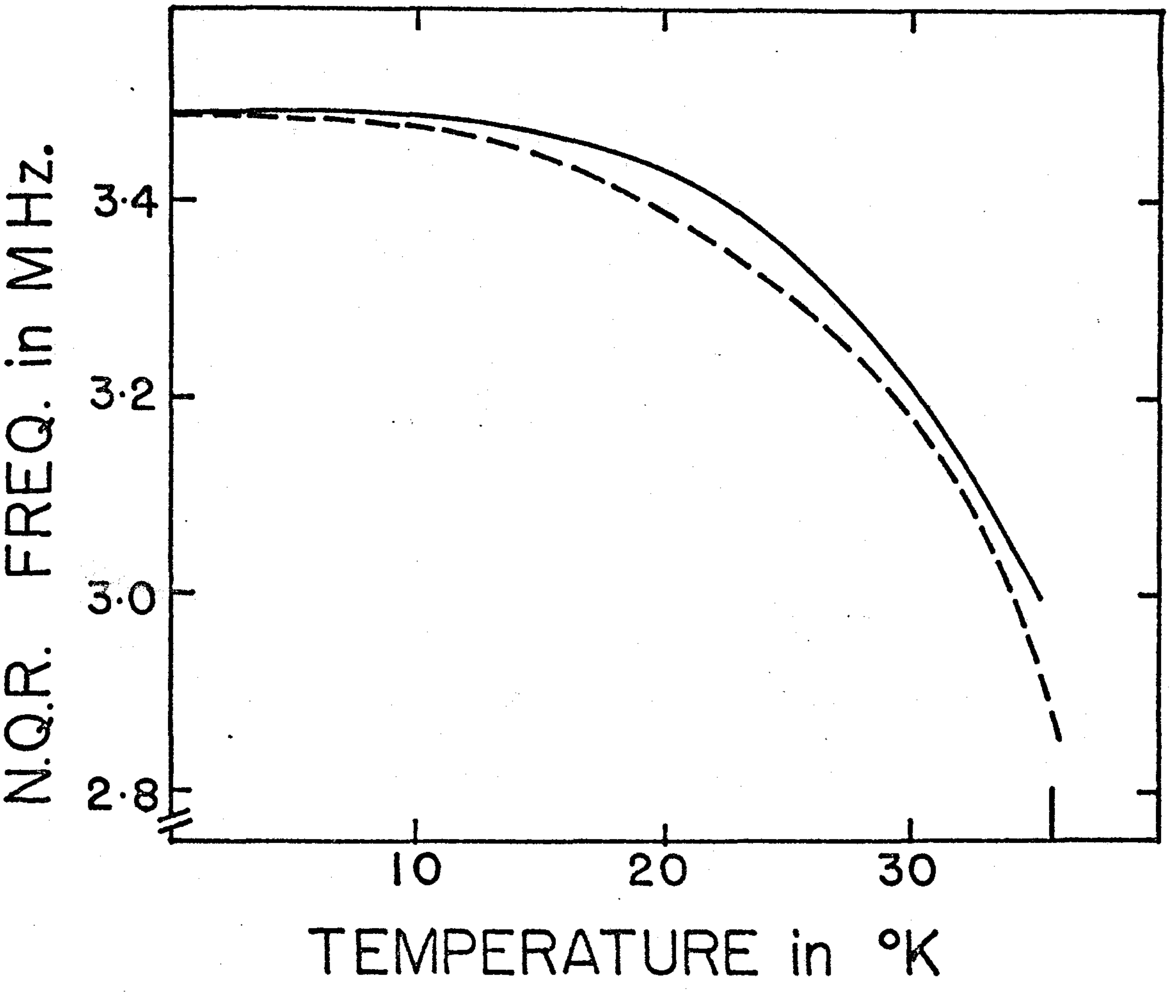

FIGURE 7

N.Q.R. frequencies as in Figure 4 are calculated but using the temperature dependent librational frequencies.

T_1 depends primarily on fluctuations in the librational motion and on the decay times of the librational states. The main contribution to this is probably the coupling between the translational and librational states, but since this has been neglected in the calculations, no theoretical estimate of T_1 can be given from this work.

CHAPTER V

SIMILAR CALCULATIONS FOR CARBON MONOXIDE

As a further check on the theory, a calculation of the librational modes of CO is carried out. The structure of α-CO is identical to the structure of α-N_2 except that without the inversion symmetry the space group is reduced to $P2_13$.[17] Therefore, if dipole-dipole interactions (which are known to be small)[33] are neglected and if the attractive and repulsive potentials are assumed identical between C-C and C-O and 0-0 atoms, the same theory can be applied for α-CO. But it is noted at this point, that the results are not expected to agree with experiment as well as for N_2 due to these assumptions which are only partially justified.

The values of the physical parameters are listed in Table 6. Again the repulsive parameter is chosen to minimize the crystal energy at the known lattice spacing. The total crystal energy is compared with the heat of sublimation in Table 7, and is found to be higher by 1.2%

TABLE 6

PARAMETERS FOR CO

Quantity	Symbol	Value
Lattice Parameter[8]	A_o	5.64 Å
One-half the internuclear[9] distance	d	0.564 Å
Quadrupole Moment[3]	Q	1.62×10^{-26} esu
Lennard-Jones parameters[3]	ε	1.382×10^{-14} ergs
	σ	3.769 Å
Polarizability[3]	κ	0.168
Repulsive Parameter	B	4.752×10^{-8} ergs / Å^{12}
Moment of Inertia[9]	I	14.49×10^{-39} g cm^2
Transition Temperature[34]	T_o	61.6 °K

TABLE 7

CONTRIBUTIONS TO THE CRYSTAL ENERGY FOR CO

Energy term	Energy/molecule x10^{15} ergs	Crystal Energy cal/mole
Quadrupole-Quadrupole	-55.02	-396.0
Attractive	271.58	1954.5
Repulsive	-541.64	-3898.1
Total	-325.08	2339.5

Including effects of zero point energy -359

and deviation from pairwise

additivity +30

The calculated sublimation energy =2011

The experimental sublimation energy[3] =1987

and the deviation is 1.2%.

Using these physical parameters, the frequency of the librational modes is calculated for $\hat{q}=0$. These are reported in Table 8, along with the calculated values using quadrupole-quadrupole coupling only and with the experimentally measured values from Raman scattering experiments[17].

The calculated frequencies can be seen to show the same type of agreement with the experimental frequencies as the N_2 results with all the frequencies being too high and the best agreement occuring for the high frequency modes.

There are no experimental N.Q.R. results for CO since experiments have not been done using O^{17} and C^{13} which are stable and have permanent quadrupole moments.

Similar calculations could be carried out for CO_2 and N_2O since they also have the same structure, but slight modifications to include the repulsion between the center atoms which do not contribute to the moment of inertia would have to be included. These calculations have as yet not been done.

TABLE 8

CALCULATED LIBRATIONAL FREQUENCIES FOR CO

Mode	Measured[7]	Calculated	Ratio	Calculated using Q-Q interaction only
E_q	44	63.8	1.45	33.9
T_q	52	73.7	1.42	43.8
T_q	90.5	98.3	1.09	71.8

CHAPTER VI

DISCUSSION OF THE THEORY

A. Criticism of the Small Angle Approximation

As has been pointed out all through this paper, the main source of error is the small angle approximation. The zero point motion of the molecules is of the order of 10° which cannot be considered as a small angle.

Furthermore, any small angle theory cannot be expected to give results near the transition point if the transition is indeed due to the commencement of hindered rotations.

Therefore, we concluded that it is difficult to decide the merits of the various Hamiltonians used, (quadrupole-quadrupole[17]; anisotropic Lennard-Jones[16]; and the present work) while they are all used in a theory which is based on the small angle approximation.

B. Suggestions from the Hydrogen papers

The most apparent way to consider this librational motion (other than to include higher order terms in the expansion in θ which will not help near the transition) is to consider the angular wave function of the molecule as a sum of spherical-harmonics.

The work of James and Raich (1967)[35] on ortho-hydrogen provides leadership in this area. Their original paper, which is based on the self-consistent molecular field approximation is easier than a similar theory for Nitrogen because it is possible in Hydrogen to restrict interest to a single J state (i.e. J= 1 in H_2).

Although the molecular field approximation does not follow the correlation of neighbouring molecules as well as a theory which allows for q-dependent modes, it is found by Raich and Etters (1968)[22] to give results which are similar to the q-dependent model which is analogous to spin waves. Although the energy levels for molecular field and the spin wave model are quite different, the statistical average of $P_2(\cos\theta)$ differs only by 2%.

We note here for interest that the small angle approximation in H_2 (which physically is unjustifiable) yields the same energy levels for the three librational frequencies (to the order of the accuracy of the results compared, 0.1%) as the Tyablikov decoupling of Raich and Etters in the non-linear spin wave treatment. It has not been determined whether the results are equivalent or whether the agreement is fortuitous.

However, there is reason to believe that the molecular field approximation in N_2 may yield useful results.

C. Self Consistent Molecular Field Approximation.

It has already been noted, that, due to the necessity of a mixture of J states in N_2, the formulation of James and Raich cannot be used. A self consistent molecular field theory can be formulated following the Hartree theory for atoms.

We write the total wave functions of the crystal as a product of angular wavefunctions for each molecule which, by symmetry are identical for the ground state. There is no need to antisymmetrize, since the rotors are spatially separated.

$$\therefore \quad \Psi_{total} = \prod_{i=1}^{N} \psi(i)$$

And the crystal energy is $E = \Psi H \Psi$

where the Hamiltonian H is given by $H = \sum_i T_i + \sum_{ij} V_{ij}$

Now we assume that the angular wavefunction can be written as a sum over a finite number of J states. The higher J states do not mix because of their large kinetic energy.

$$\therefore\ \psi(i) = \sum_{J,M} c_{JM}\, Y^J_M$$

Then,

$$E = N \sum_{JM} c_{JM}{}^2 \left\langle Y^J_M \middle| T_i \middle| Y^J_M \right\rangle$$

$$+ N \left\langle \psi_{(i)} \middle| \sum_{jJMJ'M'} c_{JM} c_{J'M'} \left\langle Y^{J'}_{M'(j)} \right. \right.$$

$$\left. \left. \middle| V_{ij} \middle| Y^J_{M(j)} \right\rangle \middle| \psi_{(i)} \right\rangle$$

Minimization of E by variation of the c_{JM} coefficients will result in a ground state.

The excited states can be obtained by minimizing E with the c_{JM} restricted to be orthogonal to the ground state. To obtain the correct number of excited states the four sublattices would have to be treated independently.

This formulation is expected to give results which should complement the small angle approximation well. This theory can be extended to higher temperatures and should yield some information about the transition point. It should also give results which allow better calculations of statistical averages. It does not seem possible to include translational interactions in the librational frequencies as is possible with the small angle approximation.

It is felt by the author that a new formulation of the molecular crystal problem which is neither an extension of molecular field calculations nor small angle calculations, is needed. Such a theory should allow for large amplitude of librational motion and for well correlated modes.

APPENDIX A

Theorem: For any shell in an f.c.c. lattice, that is all 48 points equivalent to $\{k,m,n\}$ which are at a distance $\sqrt{k^2+m^2+n^2}$ from the origin,

$$\sum_{i=1}^{48} \cos^2\theta_i = \text{const},$$ where θ_i is the angle between lattice point i and the arbitrary direction (a,b,c,). (We assume $a^2+b^2+c^2=1$)

Proof:

$$\sqrt{k^2+m^2+n^2}\,\cos\theta_i = ka+mb+nc$$

$$\therefore (k^2+m^2+n^2)\cos^2\theta_i = k^2a^2+m^2b^2+n^2c^2+2kamb+2mbnc+2kanc$$

$$\therefore (k^2+m^2+n^2)\sum_{i=1}^{48}\cos^2\theta_i = 8(k^2a^2+m^2b^2+n^2c^2)$$

$$+8(k^2a^2+n^2b^2+m^2c^2)\ +8(m^2a^2+k^2b^2+n^2c^2)$$

$$+8(m^2a^2+n^2b^2+k^2c^2)\ +8(n^2a^2+k^2b^2+m^2c^2)$$

$$+8(n^2a^2+m^2b^2+k^2c^2)$$

$$\therefore \sum_{i=1}^{48}\cos^2\theta_i = 16(a^2+b^2+c^2) = 16$$

Note: In some cases, i.e. when k,m, or n = 0, the set of 48 equivalent points is degenerate, but the proof is identical with the degenerate points counted twice.

APPENDIX B

A proof of the result that $\left\langle \theta^2 \right\rangle = \sum_{i=1}^{8} \left\langle \theta_i^2 \right\rangle$ comes from considering the eigenvectors of the motion.

For the two fold degenerate mode, the eigenvectors describe motions in which all molecules vibrate with the same amplitude in each of two orthogonal directions which we denote as θ_x and θ_y. Now if we consider a unit vector along the z axis which is rotated by θ_x about the x axis, and then θ_y about the y axis, the angle between resulting direction and the z axis is given by

$$\cos\theta = (\cos\theta_y - \sin^2\theta_x) / \cos\theta_x$$

Then: $$\sin^2\theta = \frac{\cos^2\theta_x - \cos^2\theta_y + 2\cos\theta_y \sin^2\theta_x - \sin^4\theta_x}{\cos^2\theta_x}$$

And if all angles are assumed small so that the first terms of the trigonometric expansions are adequate, then to second order in the angles $\theta^2 = \theta_x^2 + \theta_y^2$

$$\therefore \left\langle \theta^2 \right\rangle = \left\langle \theta_x^2 \right\rangle + \left\langle \theta_y^2 \right\rangle$$

The three fold degenerate modes are treated analogously except that the eigenvectors describe modes which are at an angle of 60° to each other rather than orthogonal.

Therefore, when all the modes are considered,

$$\left\langle \theta^2 \right\rangle = \sum_{i=1}^{8} \left\langle \theta_i^2 \right\rangle$$

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