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CALCULATION OF LATTICE VIBRATION FREQUENCIES
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BY

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Abstract

CALCULATION OF LATTICE VIBRATION FREQUENCIES OF 4, 4' AZOXYDIANISOLE

by

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The 4, 4' azoxydianisole (PAA) crystal has twenty one far infrared and Raman active lattice vibrations. The frequencies of these vibrations have been calculated using a combined potential. This is expressed as a sum of two potentials, one representing the non-bonded atom-atom interactions, (van der Waals potential), and the other representing the dipole-dipole interactions. The parameters in the potential function are not adjusted but are transferred directily from other calculations. The results reproduce the observed infrared and Raman frequencies very well. They are discussed in terms of the intermolecular interactions responsible for the crystal phase as well for the nematic and isotropic phases.

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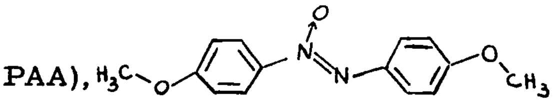
1. INTRODUCTION

4, 4' azoxydianisole (PAA),  , can be described in its solid phase as a molecular crystal. This means that the forces which hold the molecules together in the crystal are significantly weaker than the forces which bind the atoms into molecules.

When forming a solid the molecules preserve their individuality and behave as rigid bodies, in a first approximation. This characteristic permits one to do a convenient division of the vibrations of the crystal into:

Internal vibrations of intramolecular origin which are approximately the same in gaseous, solution and crystalline phases. The frequencies of these modes range from 250 to 3000 cm^{-1}. With these vibrations there is neither displacement of the center of mass of the molecule nor rotation of the molecule as a whole.

External or *lattice vibrations* which appear because of translational and rotational degrees of freedom of the molecules. The frequencies of these modes are smaller than the frequencies of the internal modes, generally falling in the region from 10 to 150 cm^{-1}.

Strictly speaking both types of vibrations can not be separated because between them there is an interaction, however this is often small and can be neglected. This approximation becomes progressively less valid as the size of the molecule is increased. Some of the internal vibrations may have low energies, particularly those corresponding to deformations or internal rotations, and may couple with the external vibrations.

PAA is an example for which a good separation between the two classes of vibrations should not be expected. It is a rather big molecule whose shape allows for torsions and deformations. Some experimental values corroborates this suspicion. The highest lattice vibration and the lowest internal vibration are very close, 150 and 180 cm^{-1} respectively [1].

On the other hand, the internal vibrations are found to obey selection rules consistent with the symmetry of the isolated molecule on its crystal site, rather than those of the factor group (unit cell group) of the crystal. This implies that while intermolecular interactions do take place, and low frequency internal vibrations are present, the factoring of the potential energy into internal and external blocks is approximately valid.

PAA presents, between 116° and 133° C, an intermediate phase. This is called the liquid crystal or mesomorphic phase [2-3]. As its name indicates, properties of both phases, liquid and solid, are simultaneously present.

In recent years a great number of papers dealing with the calculation of lattice vibrations of crystals have been published. It can be roughly said that there are two approaches to the problem. In one a limited number of force constants are taken and adjusted to give the best fit with the observed frequencies. The following crystals were treated in this way: pyrazine [4], uracil [5], diketopiperazine [5], cyanuric acid [5], cyanamide [6], benzene [7].

The second approach tries to determine a potential function, usually semiempirically, based on physical properties of the crystals. This treatment gives a better understanding of the intermolecular forces; it is more laborious, but not always possible. Some difficulties are associated either with the theoretical treatment, or with lack of sufficient experimental information, and in most cases with both. Benzene and naphthalene are probably the best examples where successful calculations were done [8-10]. Other examples include: chlorine [11], hexachlorobenzene [11], cyanogen [12], carbon dioxide [13]. Two comprehensive reviews, with an extensive list of references have been published [14-15].

In this thesis the lattice frequencies of solid PAA, at 25° C, were calculated. They were obtained from a proposed intermolecular potential. The first potential tried was a dipole-dipole interaction. It was shown that the contribution of this potential to the energy of the crystal is very small. The second potential tried was expressed as a sum of all possible non-bonded atom-atom interactions. This one gave very satisfactory results compared with the experimental values.

In these calculations the so called FG matrix method was used. The following approximations were made: the molecules were treated as rigid bodies, i.e. a complete separation between internal and external modes was assumed, and all anharmonic effects were neglected.

It is encouraging to see that it is possible to obtain good results with this simple, but powerful, method even for complex molecules such as PAA. The results shed considerable light on the interpretation of the existing experimental data.

2. CRYSTAL STRUCTURE AND SYMMETRY ELEMENTS

The X-ray crystal structure [16] of PAA at room temperature is known. It is a monoclinic crystal, space group C_{2h}^5 with cell dimensions:

$a = 15.78$ Å

$b = 8.11$ Å $\beta = 114.57^\circ$

$c = 11.02$ Å

A packing diagram is shown in figure 1.

There are four molecules in each unit cell, all of them differently oriented. The elements of the space group that leave the unit cell invariant constitute the factor group C_{2h}. They are : a two fold screw axis C_2, the inversion operator i, and a glide plane σ_h . The character table for this group is given in table 1.

Choosing a molecule at a cell corner as molecule I, the other three molecules can be obtained from I using the previously mentioned operations. Molecule II is obtained from I by a 180° rotation, C_2, molecule III by the inversion, and molecule IV by the reflection in a plane parallel to the xy plane, σ_h.

The crystal modes that are active in infrared and/or Raman spectra are those with very small values of the wavevector $\vec{k}$. At $\vec{k} = 0$

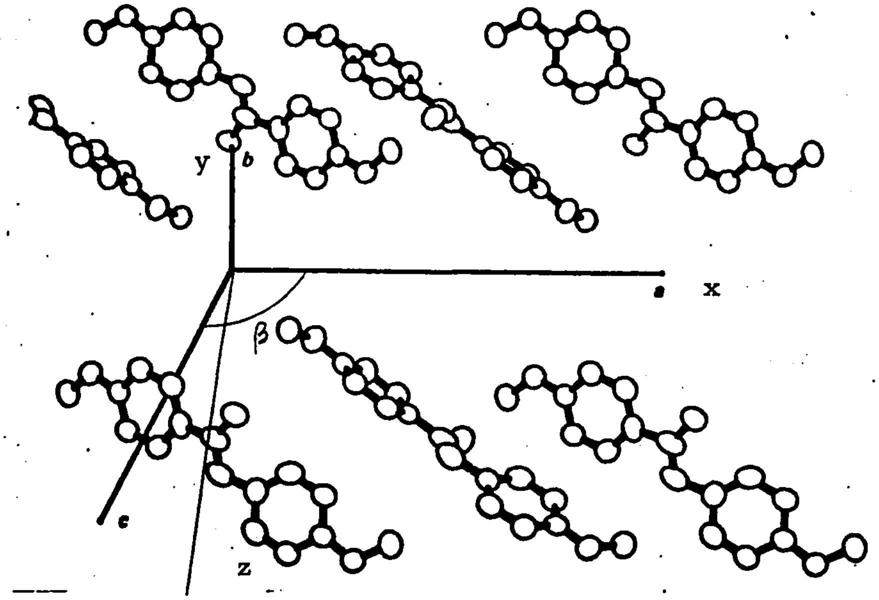


Fig. 1. PAA packing diagram (after Krigbaum et al. [16])

TABLE 1

CHARACTER TABLE FOR THE C_{2h} SYMMETRY GROUP

C_{2h}	Character table			
	E	C_2	i	σ_h
Ag	1	1	1	1
Au	1	1	-1	-1
Bg	1	-1	-1	-1
Bu	1	-1	-1	1

all the unit cells vibrate in phase and the displacements in each cell are identical. Thus, it is sufficient to consider the motion of a single unit cell to classify the spectroscopically active modes of the crystal.

There are six degrees of freedom per molecule or twenty four per unit cell. These correspond to twenty four lattice vibrations of which twenty one are optically active. The other three represent the acoustical translations with frequencies equal to zero.

Out of the twenty one, twelve are hindered rotations. They are divided among the four symmetry representations as follows:

3 Ag + 3 Bg + 3 Au + 3 Bu

The other nine vibrations are hindered translations. They belong to the following representations:

3 Ag + 2 Au + 3 Bg + Bu

The representations of the three acoustical modes are:

Au + 2 Bu

For an explanation of how these distributions are obtained, see Appendix I. Because the unit cell has a center of symmetry, all gerade modes are Raman active and all ungerade modes infrared active.

3. VIBRATIONS OF A LATTICE OF RIGID BODIES

Shimanouchi et al.[19] extended the well known FG matrix method of Wilson[20] for the calculation of internal vibrations of a molecule to vibrations of a lattice.

The following is a brief description of this method. It is a classical treatment, where the system considered is conservative, i.e. the potential energy is only a function of the position of the molecules.

The unit cell is approximated to a set of N rigid bodies that oscillate about their equilibrium positions. The kinetic energy of the system, at the equilibrium position can be expressed as:

$$2T = \sum_{i,j=1}^{3N} m_{ij}\dot{q}_i\dot{q}_j \tag{1}$$

the $\dot{q}_i$'s are the time derivatives of the coordinates and the coefficients m_{ij} are in general functions of the coordinates q_i. The m_{ij} must be symmetric ($m_{ij} = m_{ji}$).

The potential energy may be expressed in a Taylor series about the equilibrium position.

$$2V = 2V_o + 2\sum_{i=1}^{3N}\left(\frac{\partial V}{\partial q_i}\right)_o q_i + \sum_{i,j=1}^{3N}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_o q_i q_j + \text{higher order terms}$$

$$= 2V_o + 2\sum_{i=1}^{3N} f_i q_i + \sum_{i,j=1}^{3N} f_{ij} q_i q_j + \text{higher order terms} \qquad (2)$$

The $\left(\frac{\partial V}{\partial q_i}\right)_o$ are denoted by f_i, and the $\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_o$ by f_{ij}. The constants f_{ij} are also symmetrical ($f_{ij} = f_{ji}$).

V_o is the potential energy at the equilibrium position and can be taken arbitrarily as zero. The terms linear in q_i vanish because the energy must be a minimum at the equilibrium position.

Assuming very small vibrations, the higher order terms can be neglected, so the potential is approximated taking only the quadratic terms. Thus

$$2V = \sum_{i,j=1}^{3N} f_{ij} q_i q_j \qquad (3)$$

Newton's equations of motion can be written as

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_j} + \frac{\partial V}{\partial q_j} = 0 \qquad j = 1, 2, \ldots\ldots, 3N \qquad (4)$$

Substitution of the expressions for T and V in equation (4) yields

$$m_{ij}\ddot{q}_j + \sum_{i=1}^{3N} f_{ij}q_i = 0 \qquad j = 1, 2, \ldots, 3N \qquad (5)$$

A possible solution for this set of 3N simultaneous second order linear differential equations is:

$$q_i = A_i \cos(\lambda^{1/2} t + \epsilon) \qquad (6)$$

where A , λ , and ϵ are constants.

If the expressions (6) are substituted in equation (5) we get

$$\sum_{i=1}^{3N} (f_{ij} - \lambda m_{ij})A_i = 0 \qquad j = 1, 2, \ldots, 3N \qquad (7)$$

Equation (7) is a set of simultaneous linear equations that has non-vanishing solutions only for special values of λ. The special values of λ are those which satisfy the following secular equation:

$$\begin{vmatrix} f_{11} - \lambda m_{11} & f_{12} - \lambda m_{12} & \ldots\ldots\ldots & f_{1,3N} - \lambda m_{1,3N} \\ f_{12} - \lambda m_{12} & f_{22} - \lambda m_{22} & \ldots\ldots\ldots & f_{2,3N} - \lambda m_{2,3N} \\ \ldots\ldots & \ldots\ldots & \ldots\ldots\ldots & \ldots\ldots \\ f_{1,3N} - \lambda m_{1,3N} & f_{2,3N} - \lambda m_{2,3N} & & f_{3N,3N} - \lambda m_{3N,3N} \end{vmatrix} = 0 \qquad (8)$$

Equation (8) can also be written as

$$\left| F - G^{-1} \lambda \right| = 0 \qquad (9)$$

where F and G^{-1} are symmetric matrices given by $F_{ij} = f_{ij}$ and $G^{-1}_{ij} = m_{ij}$.

Multiplying equation (9) from left and right by $G^{1/2}$ we get

$$\left| G^{1/2} F G^{1/2} - \lambda E \right| = 0 \qquad \text{where} \tag{10}$$

E is the unit matrix.

The eigenvalues of the matrix $G^{1/2} F G^{1/2}$ give the lattice frequencies, including the three zeros corresponding to the three acoustical modes. The frequencies are related to the λ's by

$$\lambda = 4\pi^2 c^2 \nu^2 \tag{11}$$

where c is the velocity of light and ν the frequency expressed in cm^{-1}.

4. COORDINATE SYSTEM

To describe the translations of the molecule it is very convenient and simple to use Cartesian coordinates. The G^{-1} matrix has only elements along its diagonal. Thus

$$\left.\frac{\partial^2 T}{\partial \dot{q}_i \partial \dot{q}_j}\right|_o = \delta_{ij} G^{-1}_{ij} \qquad \begin{array}{l} \delta = 0 \text{ if } i \neq j \\ \\ \delta = 1 \text{ if } i = j \end{array} \tag{12}$$

But to express the rotations of a rigid body around a fixed point is not so simple. Some further considerations of this problem are necessary.

The most common set of parameters described in the literature are the Eulerian angles (θ , ϕ , ψ) [21]. The new coordinates of a point after a rotation, X, Y and Z, are obtained from the old coordinates, before rotation, x, y and z, by means of three successive rotations performed in a specific sequence, (see figure 2). Thus

$$\begin{aligned} X &= x(\cos\phi\cos\psi\cos\theta - \sin\phi\sin\psi) - y(\cos\phi\cos\theta\sin\psi \\ &\quad + \sin\phi\cos\psi) + z(\cos\phi\sin\theta) \\ Y &= x(\sin\phi\cos\theta\cos\psi + \cos\phi\sin\psi) + y(\cos\phi\cos\psi \\ &\quad - \sin\phi\cos\theta\sin\psi) + z(\sin\theta\sin\phi) \end{aligned} \tag{13}$$

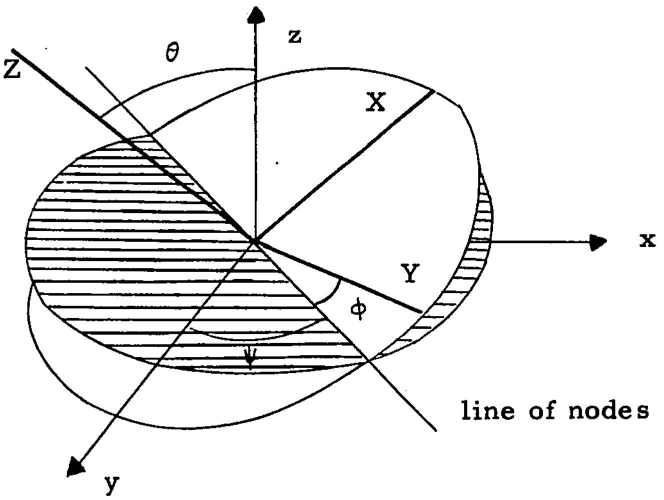


Fig. 2. Rotations defining the Eulerian angles.

$$Z = x\,(-\sin\theta\,\cos\psi) + y\,(\sin\theta\,\sin\psi) + z\cos\theta$$

The kinetic energy of the body is given by the following equation

$$2T = I_1\omega_x^2 + I_2\,\omega_y^2 + I_3\omega_z^2 \qquad (14)$$

where I_1, I_2 and I_3 are the principal moments of inertia, and ω_x, ω_y and ω_z are the components of the angular velocity of the body about the x, y and z axes respectively.

The angular velocity can be expressed in terms of the Euler angles as

$$\begin{aligned} \omega_x &= \dot{\theta}\sin\psi - \dot{\phi}\sin\theta\,\cos\psi \\ \omega_y &= \dot{\theta}\cos\psi - \dot{\phi}\sin\theta\,\sin\psi \\ \omega_z &= \dot{\psi} + \dot{\phi}\cos\theta \end{aligned} \qquad (15)$$

If expressions (15) are used in equation (14), one obtains

$$\begin{aligned} 2T = {} & I_1(\dot{\theta}\sin\psi - \dot{\phi}\sin\theta\,\cos\psi)^2 + I_2(\dot{\theta}\cos\psi - \dot{\phi}\sin\theta\,\sin\psi)^2 \\ & + I_3(\dot{\psi} + \dot{\phi}\cos\theta)^2 \end{aligned} \qquad (16)$$

The elements of the G^{-1} matrix are calculated as

$$m = \left.\frac{\partial^2 T}{\partial\dot{\theta}\,\partial\dot{\phi}}\right|_o \quad , \quad m = \left.\frac{\partial^2 T}{\partial\dot{\theta}^2}\right|_o \qquad \text{etc.}$$

These derivatives are evaluated at the equilibrium position, i.e. $\theta = \phi = \psi = 0$, or when the x, y, z and X, Y, Z axes coincide. See figure 2.

The G^{-1} obtained is:

$$G^{-1} = \begin{vmatrix} I_2 & 0 & 0 \\ 0 & I_3 & I_3 \\ 0 & I_3 & I_3 \end{vmatrix} \qquad (17)$$

It is important to note the following facts about the matrix:

1. No element is a function of I_1.
2. Its determinant is zero, therefore it is not an invertible matrix. It is also in contradiction with the definition of T which says: "T is a positive definite quadratic form in $\dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n$, and so satisfies the conditions that its determinant and the principal minors of every order of its determinant are positive". [21]

These two points show that the Eulerian angles are not appropriate for this particular situation. It was decided to try and use another system of coordinates, which are defined by Whittaker, [21], as follows.

The rigid body is rotated through an angle ω about a line through the fixed origin, whose direction angles are α, β and γ. See figure 3. The coordinates X, Y and Z of the new position of any point whose orig-

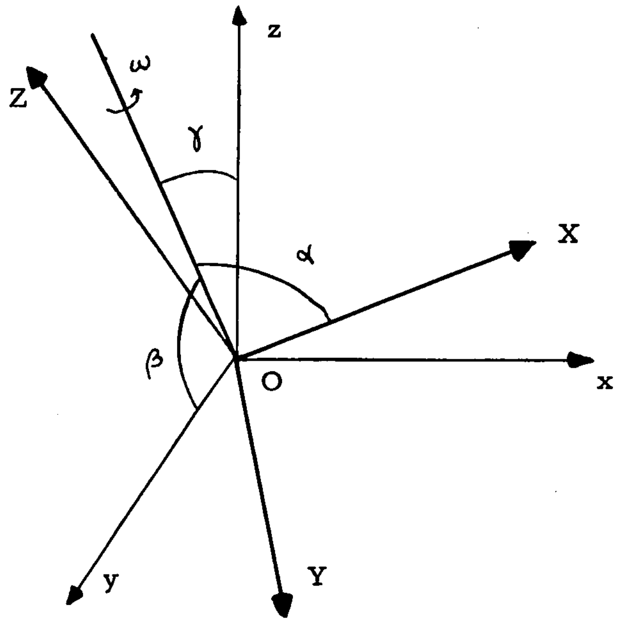


Fig. 3. Rotations and angles defining the symmetrical parameters.

inal coordinates were x, y and z are given by the equations:

$$\begin{aligned}
X &= x - 2\sin^2 \tfrac{1}{2}\omega\,(x \sin^2\alpha - y \cos\alpha \cos\beta - z \cos\alpha \cos\gamma) \\
&\quad + 2\sin\tfrac{1}{2}\omega \cos\tfrac{1}{2}\omega\,(z \cos\beta - y \cos\gamma) \\
Y &= y - 2\sin^2 \tfrac{1}{2}\omega\,(y \sin^2\beta - z \cos\beta \cos\gamma - x \cos\beta \cos\alpha) \\
&\quad + 2\sin\tfrac{1}{2}\omega \cos\tfrac{1}{2}\omega\,(x \cos\gamma - z \cos\alpha) \\
Z &= z - 2\sin^2 \tfrac{1}{2}\omega\,(z \sin^2\gamma - x \cos\alpha \cos\gamma - y \cos\beta \cos\gamma) \\
&\quad + 2\sin\tfrac{1}{2}\omega \cos\tfrac{1}{2}\omega\,(y \cos\alpha - x \cos\beta)
\end{aligned} \qquad (18)$$

Let us introduce new parameters ξ, η, ζ, χ, symmetrical parameters, defined by the equations:

$$\begin{aligned}
\xi &= \cos\alpha \sin \tfrac{1}{2}\omega \\
\eta &= \cos\beta \sin \tfrac{1}{2}\omega \\
\zeta &= \cos\gamma \sin \tfrac{1}{2}\omega \\
\chi &= \cos \tfrac{1}{2}\omega
\end{aligned} \qquad (19)$$

which satisfy the relation:

$$\xi^2 + \eta^2 + \zeta^2 + \chi^2 = 1 \qquad (20)$$

Using these symmetrical parameters in equation (18), one gets:

$$\begin{aligned}
X &= (\xi^2 - \eta^2 - \zeta^2 + \chi^2)\,x + 2(\xi\eta - \zeta\chi)\,y \\
&\quad + 2(\xi\zeta + \eta\chi)\,z \\
Y &= 2(\xi\eta + \zeta\chi)\,x + (-\xi^2 + \eta^2 - \zeta^2 + \chi^2)\,y \\
&\quad + 2(\eta\zeta - \xi\chi)\,z \\
Z &= 2(\xi\zeta - \eta\chi)\,x + 2(\eta\zeta + \xi\chi)\,y + (-\xi^2 - \eta^2 + \zeta^2 + \chi^2)\,z
\end{aligned} \qquad (21)$$

The angular velocity components ω_x, ω_y, ω_z can be expressed in terms of the symmetrical parameters as:

$$\begin{aligned} \omega_x &= 2(\chi \dot{\xi} + \zeta \dot{\eta} - \eta \dot{\zeta} - \xi \dot{\chi}) \\ \omega_y &= 2(- \zeta \dot{\xi} + \chi \dot{\eta} + \xi \dot{\zeta} - \eta \dot{\chi}) \\ \omega_z &= 2(\eta \dot{\xi} - \zeta \dot{\eta} + \chi \dot{\zeta} - \zeta \dot{\chi}) \end{aligned} \tag{22}$$

If expressions (22) are used in equation (14), one obtains:

$$\begin{aligned} T = {} & 2I_1(\chi \dot{\xi} + \zeta \dot{\eta} - \eta \dot{\zeta} - \xi \dot{\chi})^2 + 2I_2(- \zeta \dot{\xi} + \chi \dot{\eta} \\ & + \xi \dot{\zeta} - \eta \dot{\chi})^2 + 2I_3(\eta \dot{\xi} - \zeta \dot{\eta} + \chi \dot{\zeta} - \zeta \dot{\chi})^2 \end{aligned} \tag{23}$$

The equilibrium position corresponds to $\omega = 0$. From equation (19) it can be seen that at that position $\xi = \eta = \zeta = 0$ and $\chi = 1$.

If the elements of the G^{-1} matrix are calculated, as before, one obtains:

$$G^{-1} = 4 \begin{vmatrix} I_1 & 0 & 0 \\ 0 & I_2 & 0 \\ 0 & 0 & I_3 \end{vmatrix} \tag{24}$$

This G^{-1} is well-behaved. The three principal moments of inertia are present. It is an invertible matrix; its determinant and the principal minors of every order of its determinant are positive.

5. PAA SPECTRA

The low frequency, lattice vibration region, Raman [22] and far infrared spectra [1] of solid PAA have been reported. They are reproduced in figures 4, 5 and 6.

The Raman spectrum of the single crystal shows nine lattice modes,. Their values range from 16 cm^{-1} to 95 cm^{-1}. On the other hand the far infrared spectra of polycrystalline samples show six distinct frequencies, which values go from 50 cm^{-1} to 150 cm^{-1}. See table 2. Some of the far infrared absorption may be due to more than one mode, unresolved under the experimental conditions (2 cm^{-1} resolution). It is interesting to note that some coincidences exist between infrared and Raman spectra. Further discussion of these spectra isreserved for a later section of the thesis.

Certain spectral regions corresponding to internal vibrations show drastic changes as the substance goes from solid phase to nematic and liquid phases. These changes are noted in Raman [23], in the 1300 cm^{-1} to 1625 cm^{-1} and 1100 cm^{-1} to 1225 cm^{-1} regions, and near infrared [24], in the 1120 cm^{-1} to 1210 cm^{-1} regions. This is additional evidence that a non-negligible interaction exists between the internal and external modes.

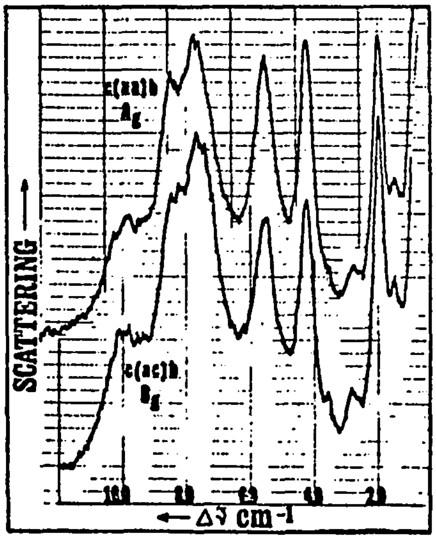


Fig. 4. Raman spectrum of single crystal of PAA at -90 °C.

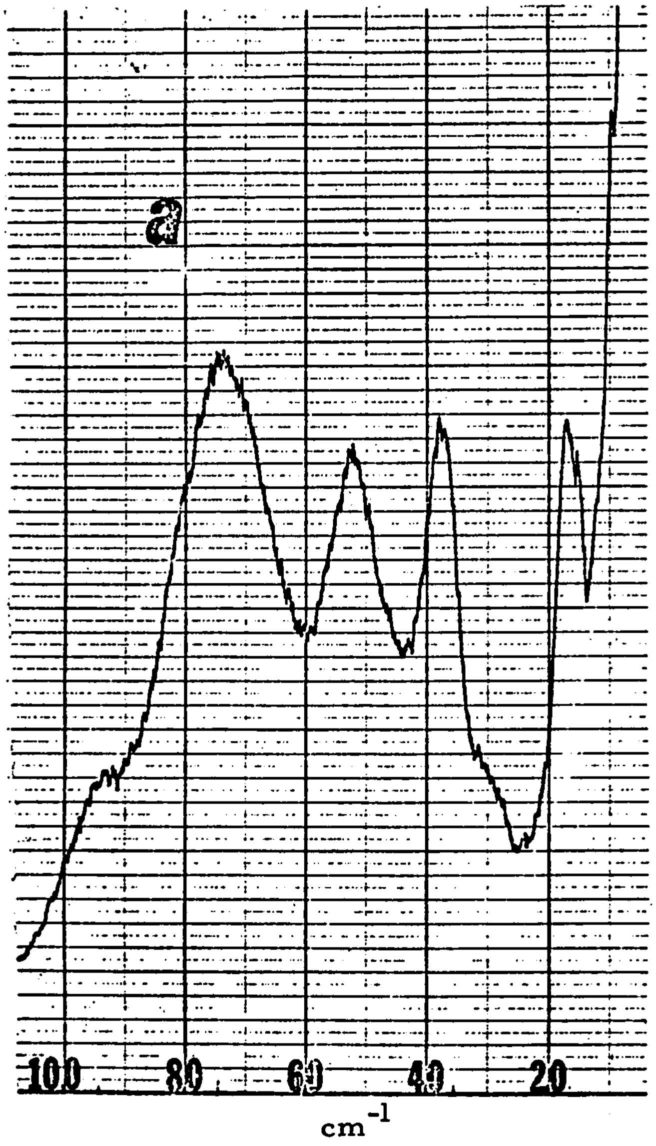


Fig. 5. Raman spectrum of PAA at 25 °C.

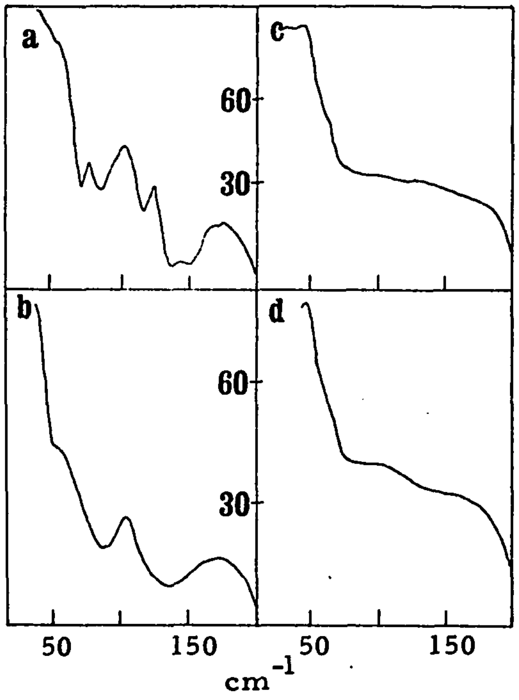


Fig. 6. Far infrared spectrum of solid PAA as a function of temperature: a) 25°, b) 90°, c) 116°, d) 117 °C.

TABLE 2

COMPARISON OF FAR INFRARED AND RAMAN FREQUENCIES (cm^{-1})

Far infrared[a]	Raman[a]	Raman[b]
	16	16
	30	30
	38	37
50	52	52
70	72	70
		74
84		
		90, 91
	94	95
115		
135		
150		

[a] Polycrystalline sample at 25 C.
[b] Single crystal sample at -90 C.

6. INTERMOLECULAR POTENTIALS

The total energy of the crystal lattice at absolute zero, E_o, is the sum of the potential energy of the lattice, V_o and the zero point energy, U_o, associated with the zero point vibration of the molecules in the lattice [25].

$$E_o = U_o + V_o = -H_o^{sub} \tag{25}$$

where H_o^{sub} is the heat of sublimation at 0°K. U_o is smaller than V_o by two orders of magnitude and is generally neglected [26]. Therefore

$$E_o = -H_o^{sub} = V_o \tag{26}$$

Equation (26) is valid, assuming U_o to be very small, at 0°K only. The potential energy of the lattice, however, can be calculated only at temperatures for which crystal structure data are available, 25°C for PAA crystals. At a temperature different from 0°K one can identify the heat of sublimation and the potential energy only if the crystal structure is not too different from that at 0°K.

Because it is believed that interactions between dipolar and highly polarizable groups are responsible for the stability of the mesomorphic phase of PAA [2], a dipole-dipole potential was the first intermolecular potential tried in our calculations.

A model of the PAA molecule with its three permanent dipoles is shown in figure 7. The dipole moment $\vec{\mu}$ is a vector quantity whose direction is that of a line joining the center of gravity of the positive electric charge with the center of gravity of the negative charge and whose magnitude is the length of that line multiplied by the total negative or the total positive charge, these being equal [20].

The intermolecular potential is expressed as a sum of all dipole-dipole interactions.

$$V = \sum V_{d-d} = \sum \text{(dipole-dipole interactions)} \qquad (27)$$

The V_{d-d} is expressed as [27]

$$V_{d-d} = \frac{\vec{\mu}\vec{\mu}'}{r^3}(\cos \epsilon - 3\cos\theta\cos\theta') \qquad (28)$$

where $\vec{\mu}$ and $\vec{\mu}'$ are the magnitudes of the dipoles, r is the distance between the dipoles, see figure 8,

$$r = \sqrt{(x - x')^2 + (y - y')^2 + (z - z')^2}$$

$$\cos\epsilon = ll' + mm' + nn'$$

$$\cos\theta = \frac{1}{r}\left(l(x - x') + m(y - y') + n(z - z')\right) \qquad (29)$$

$$\cos\theta' = \frac{1}{r}\left(l'(x - x') + m'(y - y') + n'(z - z')\right)$$

where l, m, n are the direction cosines of dipole $\vec{\mu}$, and l', m', n' are the direction cosines of dipole $\vec{\mu}'$.

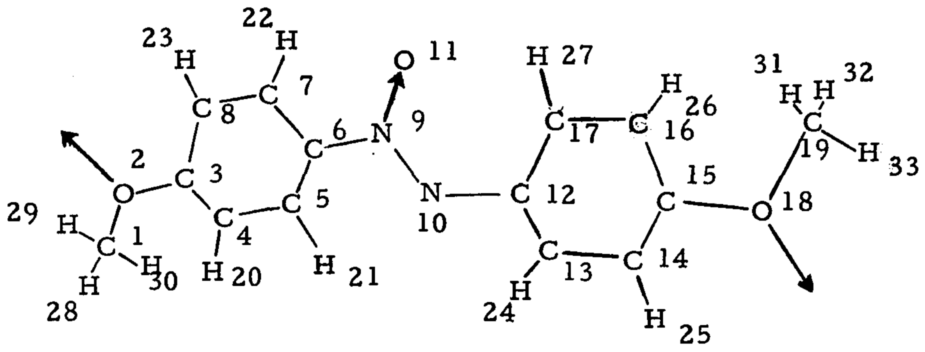


Fig. 7. Molecule of PAA with its permanent dipole moments.

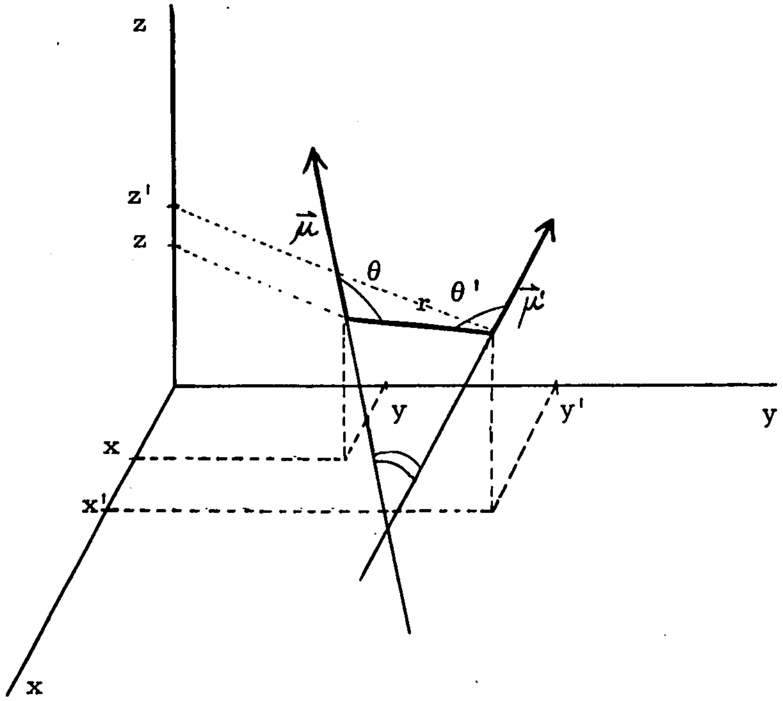


Fig. 8. Variables that define the dipole-dipole potential.

To be able to use expressions (27), (28) and (29) the coordinates of the atoms of the molecules that form the crystal are needed. From crystallographic data [16] the fractional atomic coordinates of a molecule are taken. They are given in table 3. For convenience this molecule was situated at a cell corner and named molecule I. The coordinates of all the atoms of molecules, other than I, can be generated from the coordinates of molecule I, the unit cell dimensions and the factor group of the crystal using the well known program ORTEP [28]. Appendix II shows an output of this program.

The coordinates given in table 3 as well the coordinates obtained from the ORTEP program are referred to the monoclinic system of the crystal and "normalized" to the unit cell dimentions. This means that the numbers in columns A', B' and C' in table 3 are dimensionless.

$$A' = A/a \qquad B' = B/b \qquad C' = C/c$$

where a, b and c are the dimension of the monoclinic cell as given in page 5. The monoclinic coordinates A, B and C are shown in figure 9 in relation to a Cartesian system.

It is convenient to transform the atomic coordinates to Cartesian coordinates, in order to simplify the calculation. From figure 9 the following relations are obtained

$$\begin{aligned} x &= A - C\sin\omega = A'\,15.78 - C'\,11.02\sin\omega \\ y &= B = B'\,8.11 \\ z &= C\cos\omega = C'\,11.02\cos\omega \end{aligned} \tag{30}$$

TABLE 3

ATOMIC COORDINATES

	A'	B'	C'
C(1)	−0·23311 (28)*	−0·04705 (54)	0·48652 (44)
O(2)	−0·18465 (17)	0·08853 (31)	0·46132 (25)
C(3)	−0·09467 (23)	0·11463 (39)	0·54570 (33)
C(4)	−0·04312 (25)	0·01732 (46)	0·65615 (34)
C(5)	0·04985 (26)	0·05669 (47)	0·73317 (35)
C(6)	0·08950 (24)	0·19123 (41)	0·69894 (34)
C(7)	0·03868 (28)	0·28628 (45)	0·58969 (40)
C(8)	−0·05281 (28)	0·24810 (46)	0·51327 (41)
N(9)	0·18922 (25)	0·23966 (35)	0·77533 (31)
N(10)	0·22817 (26)	0·15249 (37)	0·87293 (33)
O(11)	0·22030 (19)	0·36082 (30)	0·73160 (27)
C(12)	0·33006 (25)	0·18597 (44)	0·94867 (36)
C(13)	0·36329 (29)	0·10634 (47)	1·07232 (40)
C(14)	0·45643 (26)	0·10696 (45)	1·15318 (36)
C(15)	0·51990 (24)	0·18355 (38)	1·11352 (31)
C(16)	0·48810 (27)	0·26231 (45)	0·99162 (35)
C(17)	0·39226 (30)	0·26357 (50)	0·91016 (37)
O(18)	0·61080 (17)	0·17329 (32)	1·20136 (23)
C(19)	0·67989 (27)	0·24368 (55)	1·16339 (44)
H(20)	−0·0697 (33)	−0·0737 (65)	0·6834 (48)
H(21)	0·0863 (31)	−0·0217 (62)	0·8123 (47)
H(22)	0·0747 (33)	0·3827 (63)	0·5664 (48)
H(23)	0·0910 (35)	0·3180 (63)	0·4378 (50)
H(24)	0·3170 (33)	0·0437 (61)	1·0878 (47)
H(25)	0·4865 (32)	0·0490 (61)	1·2551 (48)
H(26)	0·5335 (33)	0·3178 (61)	0·9629 (48)
H(27)	0·3794 (33)	0·3193 (61)	0·8294 (49)
H(28)	−0·2364 (31)	−0·0303 (60)	0·5876 (48)
H(29)	−0·2952 (34)	−0·0426 (62)	0·4061 (49)
H(30)	−0·1986 (34)	−0·1634 (63)	0·4818 (48)
H(31)	0·6667 (33)	0·3659 (66)	1·1508 (48)
H(32)	0·6722 (33)	0·1934 (61)	1·0740 (51)
H(33)	0·7427 (30)	0·2020 (55)	1·2354 (43)

* Numbers in parentheses give the standard deviations in the last significant figures.

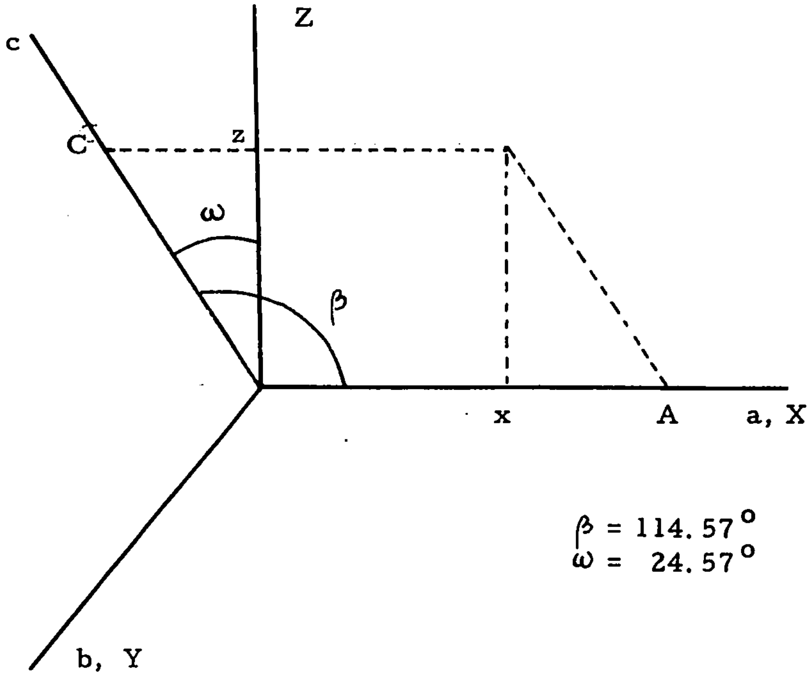


Fig. 9. Relation between Cartesian (X, Y, Z) and monoclinic (a, b, c) axes.

The values of the dipoles were taken from the literature. These are given in table 4.

The direction cosines needed in expressions (28) and (29) are calculated and evaluated in Appendix III.

For the present calculation as well as the calculations described in the next section the maximum distance used between atoms was 7 Å. The dipolar potential decreases with the distances as r^{-3}. Within this distance a sufficient number of interactions are included such that expression (27) is satisfied.

The calculated lattice energy that one gets summing all the dipole-dipole interactions up to 7 Å is 1. 13 kcal/mol. To our knowledge no sublimation energy for PAA has ever been reported. But considering the mass of the PAA molecule this is a very small value.

If this value is compared with the heats of sublimation of some long chain alcohols, it is seen that there is an enormous difference between them [31].

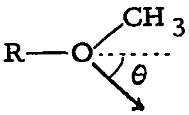
For example:

1- dodecanol	31. 1 kcal/mol
1- tetradecanol	34. 4 kcal/mol
1- octodecanol	44. 8 kcal/mol

Kitaigorodski [9] points out that the energy due to dipoles ranges between 5. 0 kcal/mol to -2. 5 kcal/mol. These energies are not small enough to be neglected, but indeed they are not big enough to explain the crystal stability.

TABLE 4

VALUES OF THE DIPOLE MOMENTS

Group	Dipole (Debye)	References
	1.35 $\theta = 55^{o}$	[29]
N⟶O	1.705	[30]

Searching for a new potential it was decided to try one that was defined by Pawley [10] as the pairwise sum of all possible non-bonded atom-atom interactions between a given pair of molecules.

$$2E\,(\text{lattice}) = \sum_n V_n = \sum_n (\text{pairwise interactions})_n \qquad (31)$$

This assumption is not clearly justified theoretically, especially when delocalized electrons are present. It is perhaps impotant to consider the contributions by electrons in collective states, as if they were also atom-atom in nature, for example delocalized π electron states [35].

Each V_n term can be expressed by semiempirical formulae of the Lennard-Jones (6-12) or Buckingham (6-exp) type. These potentials are represented by the form:

$$V_n = -\frac{A}{r^6} + \frac{B\,e^{-Cr}}{r^d} \qquad (32)$$

where r is the distance between two non-bonded atoms. A, B and C are constants. For C = 0 and d = 12 equation (32) becomes the Lennard-Jones. . For C $\neq$ 0 and d = 0 it becomes the Buckingham potential. In all of the calculations in this thesis, d was equal to zero.

We wish to make it clear that there is no theoretical justification for this. Other three parameter potentials with, e.g. C = 0 and d $\neq$ 0 might work equally well. The Buckingham potential is used because it has been parametrized for the atom-atom interactions, and the parameters have been well tested.

The $- A / r^6$ portion of the potential represents the attractive or long range forces, corresponding to instantaneous dipole-dipole polarizations. The repulsive or short range forces are expressed by the other portion of the potential. Its true form is very complicated and depends on the specific kind of interaction. The forms given above $B e^{-Cr}$, or B / r^{12} are useful oversimplifications.

In table 5 all the potentials found in the literature and used in our calculations are listed. For the $C \ldots CH_3$ interaction the following expression was found [32]:

$$(-1235 + 287900\, e^{-1.67\, r}) / r^6 \qquad (33)$$

We have used different combinations of the listed potentials to calculate the energy of the lattice. It does not matter what combination we used to get a minimum of energy, because all of them give it. This is a minimum with respect to all coordinates. Moreover the value of the energy does not change very much.

Some authors [33] think that probably the reason that very different parameters give such similar results is that calculations based on equilibrium structures may not be very sensitive to the choice of potential function, especially when it is represented by a very simple form as

TABLE 5

PARAMETERS IN THE ATOM-ATOM POTENTIALS

Atom pair	A(kcal. mol. A)	B(kcal.mol)	C(A)	References
H...H	36	4000	3.74	[8]
	57	42000	4.56	[9]
C...C	358	42000	3.58	[9]
	535	74500	3.60	[8]
C...H	39	9400	3.67	[8]
	154	42000	4.12	[9]
O...H	99.2	28100	4.32	[34]
	491.6	19820	3.84	[32]
N...H	99.2	28100	4.32	[34]
N...N	200	186400	4.55	[34]
	125.1	105700	4.61	[32]
N...O	200	186400	4.55	[34]
C...O	244	212100	4.44	[34]
C...N	244	212100	4.44	[34]
O...O	200	186400	4.55	[34]
$CH_3 \ldots CH_3$	2942	273900	3.33	[32]
$H \ldots CH_3$	2089	31905	3.20	[32]

the Buckingham type.

For the final combination of potentials the following were chosen:

for C. . . C Kitaigorodski's potential [9]
for C. . . H and H. . . H Williams' potentials [8]
for N. . . N and O. . . H Liquori's potentials [34]

This particular combination was arbitrarily selected because it gives the deepest minimum. The lattice energy obtained using this final selection is -59.0 kcal/mol. It is a reasonable value.

7. FORCE CONSTANT CALCULATIONS

To describe the lattice vibrations of the PAA crystal, 24 coordinates are needed. The unit cell has four molecules, and each molecule needs six coordinates, one for each degree of freedom, three are related to translations, (x, y, z), and the other three are related to rotations, (ξ, η, ζ). See figures 1 and 3.

The potential energy matrix, F, is a 24x24 symmetric matrix. See table 6. The analytical expressions for the different force constants are given in Appendix IV, part A.

For symmetry reasons the following relations are true:

$$f_{ij}^{11} = f_{ij}^{22} = f_{ij}^{33} = f_{ij}^{44} \tag{34}$$

$$f_{ij}^{12} = f_{ij}^{34} \qquad f_{ij}^{13} = f_{ij}^{24} \qquad f_{ij}^{14} = f_{ij}^{23}$$

where i and j can be either one of the coordinates x, y, ξ, η or ζ. The numbers indicate the molecules.

The kinetic energy matrix, G^{-1}, is also a 24x24 symmetric matrix. It has a diagonal form for the twelve elements associated with the translations. They are, all of them, equal to the mass of the molecule. See table 7. The elements associated with the rotations are the moments of inertia. Because the x, y and z molecular axes

TABLE 6

POTENTIAL ENERGY MATRIX F

$$\begin{array}{cccccccccccccccccccccccc}
x_1 & y_1 & z_1 & x_2 & y_2 & z_2 & x_3 & y_3 & z_3 & x_4 & y_4 & z_4 & \xi_1 & \eta_1 & \zeta_1 & \xi_2 & \eta_2 & \zeta_2 & \xi_3 & \eta_3 & \zeta_3 & \xi_4 & \eta_4 & \zeta_4 \\
f^{11}_{xx} & f^{11}_{xy} & f^{11}_{xz} & f^{12}_{xx} & f^{12}_{xy} & f^{12}_{xz} & f^{13}_{xx} & f^{13}_{xy} & f^{13}_{xz} & f^{14}_{xx} & f^{14}_{xy} & f^{14}_{xz} & f^{11}_{x\xi} & f^{11}_{x\eta} & f^{11}_{x\zeta} & f^{12}_{x\xi} & f^{12}_{x\eta} & f^{12}_{x\zeta} & f^{13}_{x\xi} & f^{13}_{x\eta} & f^{13}_{x\zeta} & f^{14}_{x\xi} & f^{14}_{x\eta} & f^{14}_{x\zeta} \\
 & f^{11}_{yy} & f^{11}_{yz} & f^{12}_{yx} & f^{12}_{yy} & f^{12}_{yz} & f^{13}_{yx} & f^{13}_{yy} & f^{13}_{yz} & f^{14}_{yx} & f^{14}_{yy} & f^{14}_{yz} & f^{11}_{y\xi} & f^{11}_{y\eta} & f^{11}_{y\zeta} & f^{12}_{y\xi} & f^{12}_{y\eta} & f^{12}_{y\zeta} & f^{13}_{y\xi} & f^{13}_{y\eta} & f^{13}_{y\zeta} & f^{14}_{y\xi} & f^{14}_{y\eta} & f^{14}_{y\zeta} \\
 & & f^{11}_{zz} & f^{12}_{zx} & f^{12}_{zy} & f^{12}_{zz} & f^{13}_{zx} & f^{13}_{zy} & f^{13}_{zz} & f^{14}_{zx} & f^{14}_{zy} & f^{14}_{zz} & f^{11}_{z\xi} & f^{11}_{z\eta} & f^{11}_{z\zeta} & f^{12}_{z\xi} & f^{12}_{z\eta} & f^{12}_{z\zeta} & f^{13}_{z\xi} & f^{13}_{z\eta} & f^{13}_{z\zeta} & f^{14}_{z\xi} & f^{14}_{z\eta} & f^{14}_{z\zeta} \\
 & & & f^{22}_{xx} & f^{22}_{xy} & f^{22}_{xz} & f^{23}_{xx} & f^{23}_{xy} & f^{23}_{xz} & f^{24}_{xx} & f^{24}_{xy} & f^{24}_{xz} & f^{21}_{x\xi} & f^{21}_{x\eta} & f^{21}_{x\zeta} & f^{22}_{x\xi} & f^{22}_{x\eta} & f^{22}_{x\zeta} & f^{23}_{x\xi} & f^{23}_{x\eta} & f^{23}_{x\zeta} & f^{24}_{x\xi} & f^{24}_{x\eta} & f^{24}_{x\zeta} \\
 & & & & f^{22}_{yy} & f^{22}_{yz} & f^{23}_{yx} & f^{23}_{yy} & f^{23}_{yz} & f^{24}_{yx} & f^{24}_{yy} & f^{24}_{yz} & f^{21}_{y\xi} & f^{21}_{y\eta} & f^{21}_{y\zeta} & f^{22}_{y\xi} & f^{22}_{y\eta} & f^{22}_{y\zeta} & f^{23}_{y\xi} & f^{23}_{y\eta} & f^{23}_{y\zeta} & f^{24}_{y\xi} & f^{24}_{y\eta} & f^{24}_{y\zeta} \\
 & & & & & f^{22}_{zz} & f^{23}_{zx} & f^{23}_{zy} & f^{23}_{zz} & f^{24}_{zx} & f^{24}_{zy} & f^{24}_{zz} & f^{21}_{z\xi} & f^{21}_{z\eta} & f^{21}_{z\zeta} & f^{22}_{z\xi} & f^{22}_{z\eta} & f^{22}_{z\zeta} & f^{23}_{z\xi} & f^{23}_{z\eta} & f^{23}_{z\zeta} & f^{24}_{z\xi} & f^{24}_{z\eta} & f^{24}_{z\zeta} \\
 & & & & & & f^{33}_{xx} & f^{33}_{xy} & f^{33}_{xz} & f^{34}_{xx} & f^{34}_{xy} & f^{34}_{xz} & f^{31}_{x\xi} & f^{31}_{x\eta} & f^{31}_{x\zeta} & f^{32}_{x\xi} & f^{32}_{x\eta} & f^{32}_{x\zeta} & f^{33}_{x\xi} & f^{33}_{x\eta} & f^{33}_{x\zeta} & f^{34}_{x\xi} & f^{34}_{x\eta} & f^{34}_{x\zeta} \\
 & & & & & & & f^{33}_{yy} & f^{33}_{yz} & f^{34}_{yx} & f^{34}_{yy} & f^{34}_{yz} & f^{31}_{y\xi} & f^{31}_{y\eta} & f^{31}_{y\zeta} & f^{32}_{y\xi} & f^{32}_{y\eta} & f^{32}_{y\zeta} & f^{33}_{y\xi} & f^{33}_{y\eta} & f^{33}_{y\zeta} & f^{34}_{y\xi} & f^{34}_{y\eta} & f^{34}_{y\zeta} \\
 & & & & & & & & f^{33}_{zz} & f^{34}_{zx} & f^{34}_{zy} & f^{34}_{zz} & f^{31}_{z\xi} & f^{31}_{z\eta} & f^{31}_{z\zeta} & f^{32}_{z\xi} & f^{32}_{z\eta} & f^{32}_{z\zeta} & f^{33}_{z\xi} & f^{33}_{z\eta} & f^{33}_{z\zeta} & f^{34}_{z\xi} & f^{34}_{z\eta} & f^{34}_{z\zeta} \\
 & & & & & & & & & f^{44}_{xx} & f^{44}_{xy} & f^{44}_{xz} & f^{41}_{x\xi} & f^{41}_{x\eta} & f^{41}_{x\zeta} & f^{42}_{x\xi} & f^{42}_{x\eta} & f^{42}_{x\zeta} & f^{43}_{x\xi} & f^{43}_{x\eta} & f^{43}_{x\zeta} & f^{44}_{x\xi} & f^{44}_{x\eta} & f^{44}_{x\zeta} \\
 & & & & & & & & & & f^{44}_{yy} & f^{44}_{yz} & f^{41}_{y\xi} & f^{41}_{y\eta} & f^{41}_{y\zeta} & f^{42}_{y\xi} & f^{42}_{y\eta} & f^{42}_{y\zeta} & f^{43}_{y\xi} & f^{43}_{y\eta} & f^{43}_{y\zeta} & f^{44}_{y\xi} & f^{44}_{y\eta} & f^{44}_{y\zeta} \\
 & & & & & & & & & & & f^{44}_{zz} & f^{41}_{z\xi} & f^{41}_{z\eta} & f^{41}_{z\zeta} & f^{42}_{z\xi} & f^{42}_{z\eta} & f^{42}_{z\zeta} & f^{43}_{z\xi} & f^{43}_{z\eta} & f^{43}_{z\zeta} & f^{44}_{z\xi} & f^{44}_{z\eta} & f^{44}_{z\zeta} \\
 & & & & & \text{Symmetric} & & & & & & & f^{11}_{\xi\xi} & f^{11}_{\xi\eta} & f^{11}_{\xi\zeta} & f^{12}_{\xi\xi} & f^{12}_{\xi\eta} & f^{12}_{\xi\zeta} & f^{13}_{\xi\xi} & f^{13}_{\xi\eta} & f^{13}_{\xi\zeta} & f^{14}_{\xi\xi} & f^{14}_{\xi\eta} & f^{14}_{\xi\zeta} \\
 & & & & & & & & & & & & & f^{11}_{\eta\eta} & f^{11}_{\eta\zeta} & f^{12}_{\eta\xi} & f^{12}_{\eta\eta} & f^{12}_{\eta\zeta} & f^{13}_{\eta\xi} & f^{13}_{\eta\eta} & f^{13}_{\eta\zeta} & f^{14}_{\eta\xi} & f^{14}_{\eta\eta} & f^{14}_{\eta\zeta} \\
 & & & & & & & & & & & & & & f^{11}_{\zeta\zeta} & f^{12}_{\zeta\xi} & f^{12}_{\zeta\eta} & f^{12}_{\zeta\zeta} & f^{13}_{\zeta\xi} & f^{13}_{\zeta\eta} & f^{13}_{\zeta\zeta} & f^{14}_{\zeta\xi} & f^{14}_{\zeta\eta} & f^{14}_{\zeta\zeta} \\
 & & & & & & & & & & & & & & & f^{22}_{\xi\xi} & f^{22}_{\xi\eta} & f^{22}_{\xi\zeta} & f^{23}_{\xi\xi} & f^{23}_{\xi\eta} & f^{23}_{\xi\zeta} & f^{24}_{\xi\xi} & f^{24}_{\xi\eta} & f^{24}_{\xi\zeta} \\
 & & & & & & & & & & & & & & & & f^{22}_{\eta\eta} & f^{22}_{\eta\zeta} & f^{23}_{\eta\xi} & f^{23}_{\eta\eta} & f^{23}_{\eta\zeta} & f^{24}_{\eta\xi} & f^{24}_{\eta\eta} & f^{24}_{\eta\zeta} \\
 & & & & & & & & & & & & & & & & & f^{22}_{\zeta\zeta} & f^{23}_{\zeta\xi} & f^{23}_{\zeta\eta} & f^{23}_{\zeta\zeta} & f^{24}_{\zeta\xi} & f^{24}_{\zeta\eta} & f^{24}_{\zeta\zeta} \\
 & & & & & & & & & & & & & & & & & & f^{33}_{\xi\xi} & f^{33}_{\xi\eta} & f^{33}_{\xi\zeta} & f^{34}_{\xi\xi} & f^{34}_{\xi\eta} & f^{34}_{\xi\zeta} \\
 & & & & & & & & & & & & & & & & & & & f^{33}_{\eta\eta} & f^{33}_{\eta\zeta} & f^{34}_{\eta\xi} & f^{34}_{\eta\eta} & f^{34}_{\eta\zeta} \\
 & & & & & & & & & & & & & & & & & & & & f^{33}_{\zeta\zeta} & f^{34}_{\zeta\xi} & f^{34}_{\zeta\eta} & f^{34}_{\zeta\zeta} \\
 & & & & & & & & & & & & & & & & & & & & & f^{44}_{\xi\xi} & f^{44}_{\xi\eta} & f^{44}_{\xi\zeta} \\
 & & & & & & & & & & & & & & & & & & & & & & f^{44}_{\eta\eta} & f^{44}_{\eta\zeta} \\
 & & & & & & & & & & & & & & & & & & & & & & & f^{44}_{\zeta\zeta}
\end{array}$$

TABLE 7

KINETIC ENERGY MATRIX G^{-1}

$$10^{-23}\left|\begin{array}{cccccccccccccccccccccccc}
x_1 & y_1 & z_1 & x_2 & y_2 & z_2 & x_3 & y_3 & z_3 & x_4 & y_4 & x_4 & \xi_1 & \eta_1 & \zeta_1 & \xi_2 & \eta_2 & \zeta_2 & \xi_3 & \eta_3 & \zeta_3 & \xi_4 & \eta_4 & \zeta_4 \\
42.62 &&&&&&&&&&&&&&&&&&&&&&& \\
& 42.62 &&&&&&&&&&&&&&&&&&&&&& \\
&& 42.62 &&&&&&&&&&&&&&&&&&&&& \\
&&& 42.62 &&&&&&&&&&&&&&&&&&&& \\
&&&& 42.62 &&&&&&&&&&&&&&&&&&& \\
&&&&& 42.62 &&&&&&&&&&&&&&&&&& \\
&&&&&& 42.62 &&&&&&&&&&&&&&&&& \\
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&&&&&&&& 42.62 &&&&&&&&&&&&&&& \\
&&&&&&&&& 42.62 &&&&&&&&&&&&&& \\
&&&&&&&&&& 42.62 &&&&&&&&&&&&& \\
&&&&&&&&&&& 42.62 &&&&&&&&&&&& \\
&&&&&&&&&&&& 1164 & -2459 & 0 &&&&&&&&& \\
&&&&&&&&&&&& -2459 & 2822 & -76 &&&&&&&&& \\
&&&&&&&&&&&& 0 & -76 & 1912 &&&&&&&&& \\
&&&&&&&&&&&&&&& 1164 & -2459 & 0 &&&&&& \\
&&&&&&&&&&&&&&& -2459 & 2822 & -76 &&&&&& \\
&&&&&&&&&&&&&&& 0 & -76 & 1912 &&&&&& \\
&&&&&&&&&&&&&&&&&& 1164 & -2459 & 0 &&& \\
&&&&&&&&&&&&&&&&&& -2459 & 2822 & -76 &&& \\
&&&&&&&&&&&&&&&&&& 0 & -76 & 1912 &&& \\
&&&&&&&&&&&&&&&&&&&&& 1164 & -2459 & 0 \\
&&&&&&&&&&&&&&&&&&&&& -2459 & 2822 & -76 \\
&&&&&&&&&&&&&&&&&&&&& 0 & -76 & 1912
\end{array}\right|$$

used did not coincide with the principal axes of inertia this part of the matrix presents off-diagonal elements different from zero.

It is necessary to have G^{-1} expressed in a diagonal form to be able to calculate the $G^{1/2}$ needed.

Let us call D, table 8, the orthogonal matrix that diagonalizes the kinetic energy matrix G^{-1}. Therefore

$$D^t G^{-1} D = G_d^{-1} \qquad (35)$$

where G_d^{-1} is a diagonal matrix whose elements associated with translations are the same as in G^{-1}, but its elements associated with rotations are the principal moments of inertia of the molecule, as is shown in table 9.

The same transformation has to be applied to the F matrix. Thus

$$\begin{aligned} \left| F - \lambda G^{-1} \right| &= 0 \text{ is equivalent to} \\ \left| D^t F D - \lambda (D^t G^{-1} D) \right| &= \left| D^t F D - \lambda G_d^{-1} \right| = 0 \end{aligned} \qquad (36)$$

The $G_d^{1/2}$ can be calculated. It is a diagonal matrix, whose elements are the inverse of the square roots of the corresponding elements of the G_d^{-1} matrix. See table 10 for the $G_d^{1/2}$ matrix.

$$\begin{aligned} G_d^{-1/2}\ G_d^{-1/2} &= G_d^{-1} \\ \text{and} \quad G_d^{1/2}\ G_d^{-1/2} &= E = \text{identity matrix} \end{aligned} \qquad (37)$$

Using $G_d^{1/2}$ in expression (36), it can be rewritten as:

TABLE 8

THE D MATRIX

$$
\begin{array}{*{24}{c}}
1 \\
& 1 \\
&& 1 \\
&&& 1 \\
&&&& 1 \\
&&&&& 1 \\
&&&&&& 1 \\
&&&&&&& 1 \\
&&&&&&&& 1 \\
&&&&&&&&& 1 \\
&&&&&&&&&& 1 \\
&&&&&&&&&&& 1 \\
&&&&&&&&&&&& 0.9894 & -0.1428 & -0.0250 \\
&&&&&&&&&&&& 0.1443 & 0.9866 & 0.0760 \\
&&&&&&&&&&&& 0.0138 & -0.0788 & 0.9968 \\
&&&&&&&&&&&&&&& 0.9894 & -0.1428 & -0.0250 \\
&&&&&&&&&&&&&&& 0.1443 & 0.9866 & 0.0760 \\
&&&&&&&&&&&&&&& 0.0138 & -0.0788 & 0.9968 \\
&&&&&&&&&&&&&&&&&& 0.9894 & -0.1428 & -0.0250 \\
&&&&&&&&&&&&&&&&&& 0.1443 & 0.9866 & 0.0760 \\
&&&&&&&&&&&&&&&&&& 0.0138 & -0.0788 & 0.9968 \\
&&&&&&&&&&&&&&&&&&&&& 0.9894 & -0.1428 & -0.0250 \\
&&&&&&&&&&&&&&&&&&&&& 0.1443 & 0.9866 & 0.0760 \\
&&&&&&&&&&&&&&&&&&&&& 0.0138 & -0.0788 & 0.9968
\end{array}
$$

TABLE 9

DIAGONALIZED KINETIC ENERGY MATRIX G_d^{-1}

$$10^{-23}\begin{vmatrix}
42.62 &&&&& &&&&& &&&&& &&&&& &&& \\
& 42.62 &&&&& &&&&& &&&&& &&&&& && \\
&& 42.62 &&&&& &&&&& &&&&& &&&&& & \\
&&& 42.62 &&&&& &&&&& &&&&& &&&&& \\
&&&& 42.62 &&&&& &&&&& &&&&& &&&& \\
&&&&& 42.62 &&&&& &&&&& &&&&& &&& \\
&&&&& & 42.62 &&&&& &&&&& &&&&& && \\
&&&&& && 42.62 &&&&& &&&&& &&&&& & \\
&&&&& &&& 42.62 &&&&& &&&&& &&&&& \\
&&&&& &&&& 42.62 &&&&& &&&&& &&&& \\
&&&&& &&&&& 42.62 &&&&& &&&&& &&& \\
&&&&& &&&&& & 42.62 &&&&& &&&&& && \\
&&&&& &&&&& && 1138 &&&&& &&&&& & \\
&&&&& &&&&& &&& 2863 &&&&& &&&&& \\
&&&&& &&&&& &&&& 1906 &&&&& &&&& \\
&&&&& &&&&& &&&&& 1138 &&&&& &&& \\
&&&&& &&&&& &&&&& & 2863 &&&&& && \\
&&&&& &&&&& &&&&& && 1906 &&&&& & \\
&&&&& &&&&& &&&&& &&& 1138 &&&&& \\
&&&&& &&&&& &&&&& &&&& 2863 &&&& \\
&&&&& &&&&& &&&&& &&&&& 1906 &&& \\
&&&&& &&&&& &&&&& &&&&& & 1138 && \\
&&&&& &&&&& &&&&& &&&&& && 2863 & \\
&&&&& &&&&& &&&&& &&&&& &&& 1906
\end{vmatrix}$$

TABLE 10

THE $G_d^{1/2}$ MATRIX

$$10^{23/2}\begin{vmatrix}
0.1532 \\
& 0.1532 \\
&& 0.1532 \\
&&& 0.1532 \\
&&&& 0.1532 \\
&&&&& 0.1532 \\
&&&&&& 0.1532 \\
&&&&&&& 0.1532 \\
&&&&&&&& 0.1532 \\
&&&&&&&&& 0.1532 \\
&&&&&&&&&& 0.1532 \\
&&&&&&&&&&& 0.1532 \\
&&&&&&&&&&&& 0.0298 \\
&&&&&&&&&&&&& 0.0187 \\
&&&&&&&&&&&&&& 0.0229 \\
&&&&&&&&&&&&&&& 0.0298 \\
&&&&&&&&&&&&&&&& 0.0187 \\
&&&&&&&&&&&&&&&&& 0.0229 \\
&&&&&&&&&&&&&&&&&& 0.0298 \\
&&&&&&&&&&&&&&&&&&& 0.0187 \\
&&&&&&&&&&&&&&&&&&&& 0.0229 \\
&&&&&&&&&&&&&&&&&&&&& 0.0298 \\
&&&&&&&&&&&&&&&&&&&&&& 0.0187 \\
&&&&&&&&&&&&&&&&&&&&&&& 0.0229
\end{vmatrix}$$

$$\left| G_d^{1/2} D^t F D G_d^{1/2} - \lambda (G_d^{1/2} G_d^{-1} G_d^{1/2}) \right| = 0$$

$$\text{or} \quad \left| G_d^{1/2} D^t F D G_d^{1/2} - \lambda E \right| = 0 \qquad (38)$$

The $(G_d^{1/2} D^t F D G_d^{1/2})$ matrix can be factored by a proper choice of symmetry coordinates S, which are given by:

$$S = UC$$

$$S = N \sum_R \chi_R^{\gamma} RC \qquad (39)$$

where χ is the trace of the operator R in the γ representation. In this case there are four operators E, C_2, i and σ, and also four representations Ag, Au, Bg and Bu. The C in expression (39) represents the Cartesian coordinates or symmetrical parameters, as defined on page 18. N is a normalization factor.

The transformation matrix U is listed in table 11. Of the translational coordinates, S_6, S_{10} and S_{11} represent uniform motion of the whole crystal, acoustical modes, and they are assumed to give rise to eigenvalues equal to zero.

Using the U matrix one obtains:

$$U G_d^{1/2} D^t F D G_d^{1/2} U^t = \text{four blocks of 6x6 elements each} \qquad (40)$$

Each block belongs to a different representation. It can be shown that the U and the $(G_d^{1/2} D^t)$ matrices commute. See Appendix V for proof. Equation (40) can be written using this property as:

TABLE 11

TRANSFORMATION MATRIX U

$$\frac{1}{2}\;\begin{array}{c|cccccccccccccccccccccccc|}
 & x_1&y_1&z_1&x_2&y_2&z_2&x_3&y_3&z_3&x_4&y_4&z_4&\xi_1&\eta_1&\zeta_1&\xi_2&\eta_2&\zeta_2&\xi_3&\eta_3&\zeta_3&\xi_4&\eta_4&\zeta_4 \\
\hline
s_1&1&&&1&&&1&&&1&&&&&&&&&&&&&& \\
s_2&&1&&&1&&&1&&&1&&&&&&&&&&&&& \\
s_3&&&1&&&1&&&1&&&1&&&&&&&&&&&& \\
s_4&1&&&1&&&-1&&&-1&&&&&&&&&&&&&& \\
s_5&&1&&&1&&&-1&&&-1&&&&&&&&&&&&& \\
s_6&&&1&&&1&&&-1&&&-1&&&&&&&&&&&& \\
s_7&1&&&-1&&&1&&&-1&&&&&&&&&&&&&& \\
s_8&&1&&&-1&&&1&&&-1&&&&&&&&&&&&& \\
s_9&&&1&&&-1&&&1&&&-1&&&&&&&&&&&& \\
s_{10}&1&&&-1&&&-1&&&1&&&&&&&&&&&&&& \\
s_{11}&&1&&&-1&&&-1&&&1&&&&&&&&&&&&& \\
s_{12}&&&1&&&-1&&&-1&&&1&&&&&&&&&&&& \\
s_{13}&&&&&&&&&&&&&1&&&1&&&1&&&1&& \\
s_{14}&&&&&&&&&&&&&&1&&&1&&&1&&&1& \\
s_{15}&&&&&&&&&&&&&&&1&&&1&&&1&&&1 \\
s_{16}&&&&&&&&&&&&&1&&&1&&&-1&&&-1&& \\
s_{17}&&&&&&&&&&&&&&1&&&1&&&-1&&&-1& \\
s_{18}&&&&&&&&&&&&&&&1&&&1&&&-1&&&-1 \\
s_{19}&&&&&&&&&&&&&1&&&-1&&&1&&&-1&& \\
s_{20}&&&&&&&&&&&&&&1&&&-1&&&1&&&-1& \\
s_{21}&&&&&&&&&&&&&&&1&&&-1&&&1&&&-1 \\
s_{22}&&&&&&&&&&&&&1&&&-1&&&-1&&&1&& \\
s_{23}&&&&&&&&&&&&&&1&&&-1&&&-1&&&1& \\
s_{24}&&&&&&&&&&&&&&&1&&&-1&&&-1&&&1
\end{array}$$

$$G_d^{1/2} D^t (U F U^t) D G_d^{1/2} \qquad (41)$$

This new order simplifies the calculations greatly. $(U F U^t)$ consists of four 6x6 blocks, and they have a general structure independent of the numerical value of each constant.

Thus the block that belongs to the Ag representation $(U F U^t)_{Ag}$ can be written as follows

$$\left|\begin{array}{cccccc} T_{xx} & T_{xy} & T_{xz} & TR_{x\xi} & TR_{x\eta} & TR_{x\zeta} \\ & T_{yy} & T_{yz} & TR_{y\xi} & TR_{y\eta} & TR_{y\zeta} \\ & & T_{zz} & TR_{z\xi} & TR_{z\eta} & TR_{z\zeta} \\ & \text{symmetric} & & R_{\xi\xi} & R_{\xi\eta} & R_{\xi\zeta} \\ & & & & R_{\eta\eta} & R_{\eta\zeta} \\ & & & & & R_{\zeta\zeta} \end{array}\right| \qquad (42)$$

where $T_{xy} = f_{xy}^{11} + f_{xy}^{12} + f_{xy}^{13} + f_{xy}^{14}$

$$TR_{z\xi} = f_{z\xi}^{11} + f_{z\xi}^{12} + f_{z\xi}^{13} + f_{z\xi}^{14} \qquad (43)$$

$$R_{\xi\eta} = f_{\xi\eta}^{11} + f_{\xi\eta}^{12} + f_{\xi\eta}^{13} + f_{\xi\eta}^{14}$$

For the Au representation we have $(U F U^t)_{Au}$

$$\left|\begin{array}{cccccc} T'_{xx} & T'_{xy} & 0 & TR'_{x\xi} & TR'_{x\eta} & TR'_{x\zeta} \\ & T'_{yy} & 0 & TR'_{y\xi} & TR'_{y\eta} & TR'_{y\zeta} \\ & & 0 & 0 & 0 & 0 \\ & \text{symmetric} & & R'_{\xi\xi} & R'_{\xi\eta} & R'_{\xi\zeta} \\ & & & & R'_{\eta\eta} & R'_{\eta\zeta} \\ & & & & & R'_{\zeta\zeta} \end{array}\right| \tag{44}$$

where $T'_{yz} = f^{11}_{yz} + f^{12}_{yz} - f^{13}_{yz} - f^{14}_{yz}$

$$TR'_{x\eta} = f^{11}_{x\eta} + f^{12}_{x\eta} - f^{13}_{x\eta} - f^{14}_{x\eta} \tag{45}$$

$R'_{\xi\zeta} = f^{11}_{\xi\zeta} + f^{12}_{\xi\zeta} - f^{13}_{\xi\zeta} - f^{14}_{\xi\zeta}$

The block representing the Bg representation is expressed as:

$$\left|\begin{array}{cccccc} T''_{xx} & T''_{xy} & T''_{xz} & TR''_{x\xi} & TR''_{x\eta} & TR''_{x\zeta} \\ & T''_{yy} & T''_{yz} & TR''_{y\xi} & TR''_{y\eta} & TR''_{y\zeta} \\ & & T''_{zz} & TR''_{z\xi} & TR''_{z\eta} & TR''_{z\zeta} \\ & \text{symmetric} & & R''_{\xi\xi} & R''_{\xi\eta} & R''_{\xi\zeta} \\ & & & & R''_{\eta\eta} & R''_{\eta\zeta} \\ & & & & & R''_{\zeta\zeta} \end{array}\right| \tag{46}$$

where $T''_{xz} = f^{11}_{xz} - f^{12}_{xz} + f^{13}_{xz} - f^{14}_{xz}$

$$TR''_{y\xi} = f^{11}_{y\xi} - f^{12}_{y\xi} + f^{13}_{y\xi} - f^{14}_{y\xi} \tag{47}$$

$R''_{\eta\eta} = f^{11}_{\eta\eta} - f^{12}_{\eta\eta} + f^{13}_{\eta\eta} - f^{14}_{\eta\eta}$

Finally for the Bu representation we have the $(U F U^t)$ block

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ & 0 & 0 & 0 & 0 & 0 \\ & & T'''_{zz} & TR'''_{z\xi} & TR'''_{z\eta} & TR'''_{z\zeta} \\ & \text{symmetric} & & R'''_{\xi\xi} & R'''_{\xi\eta} & R'''_{\xi\zeta} \\ & & & & R'''_{\eta\eta} & R'''_{\eta\zeta} \\ & & & & & R'''_{\zeta\zeta} \end{bmatrix} \tag{48}$$

where $T'''_{xx} = f^{11}_{xx} - f^{12}_{xx} - f^{13}_{xx} + f^{14}_{xx}$

$$RT'''_{y\zeta} = f^{11}_{y\zeta} - f^{12}_{y\zeta} - f^{13}_{y\zeta} + f^{14}_{y\zeta} \tag{49}$$

$R'''_{\xi\eta} = f^{11}_{\xi\eta} - f^{12}_{\xi\eta} - f^{13}_{\xi\eta} + f^{14}_{\xi\eta}$

If T_{xx} (Ag), T'_{xx} (Au), T''_{xx} (Bg) and T'''_{xx} (Bu) are compared, we see that the only difference between them is the sign in front of some of the force constants. Going back to table 1, it is noticed that the sign of the elements is equal to the sign of the trace of the related operation in the different representations.

For example, the force constants with superscripts 12 are related to the C_2 operation. In the same way force constants with superscripts 13 are related to the i operation, and the force constants with superscripts 14 to the σ_h operation.

Using the parametrized potentials of table 5 and expression (33), the force constants given in table 12 were obtained.

TABLE 12

FORCE CONSTANTS

	f_{ij}^{11}			f_{ij}^{12}		
i \ j	x	y	z	x	y	z
x	52.86	-14.98	-30.14	0.01	0.01	-0.02
y	*	110.48	5.88	*	0.01	-0.02
z			90.56			0.02
i \ j	ξ	η	ζ	ξ	η	ζ
x	-119.67	-45.07	187.59	0.0	0.07	-0.04
y	159.66	33.26	-207.78	0.01	-0.01	-0.03
z	-155.46	41.05	76.41	-0.02	-0.02	0.01
i \ j	ξ	η	ζ	ξ	η	ζ
ξ	4317.6	-739.8	-3863.5	-0.03	-0.57	-0.29
η	*	8951.0	-1232.8	*	1.16	0.15
ζ			7020.2			-0.39

*Symmetric matrices.

TABLE 12 — Continued

	f_{ij}^{13}			f_{ij}^{14}		
j i	x	y	z	x	y	z
x	-10.25	12.55	2.56	-77.84	33.26	-15.28
y	*	-29.41	-9.79	*	-30.72	23.29
z			-8.79			-10.1
j i	ξ	η	ζ	ξ	η	ζ
x	76.47	77.79	-84.87	187.51	533.6	556.6
y	-158.22	-127.72	154.44	31.13	-430.7	-396.4
z	-31.88	-58.57	51.25	61.91	239.0	253.2
j i	ξ	η	ζ	ξ	η	ζ
ξ	-1217.5	-495.4	614.3	263.0	-971.1	-874.5
η		-929.9	800.6		-5658.2	-5751.1
ζ	*		-1737.6	*		-5644.5

*Symmetric matrices.

The calculated force constants f_{ij}^{12} have very small values. This indicates that the interactions between molecule I and II are very weak. The same applies to the interactions between molecules III and IV, according to relations (34). On the other hand there are strong interactions between molecules I. . . III, I. . . IV, II. . . IV and II. . . III.

Using the force constants given in table 12, the matrices shown in table 13 were obtained.

One of the matrices, $(U F U^t)_{Ag}$, has two negative elements in its diagonal. This means that this matrix has at least one negative eigenvalue, a very undesirable result when calculating frequencies of vibrations.

Each force constant is a sum of large number of interactions derived from several terms in the potential. Going back to the individual interactions, it was noticed that some of the force constants obtained from the $C \ldots CH_3$ potential were exceptionally large. For example:

$$f_{x\zeta}^{11} = 3614 \text{ kcal/mol.Å}$$

while the other potentials give for the same type of force constant, translation-rotation, values that range from 0 to 20 kcal/mol. Å.

No other expression for the $C \ldots CH_3$ was found in the literature. A new one, represented by the general expression:

$$\frac{-A}{r^6} + B\, e^{-Cr}$$

TABLE 13

THE (UFU^t) MATRICES

$(UFU^t)_{Ag}$					
-35.23	30.83	-42.86	144.3	566.3	659.3
	50.36	19.38	-29.7	-525.2	-449.8
		71.57	-125.4	221.5	380.9
Symmetric			2837.2	-2206.3	-4123.7
				2363.2	-6183.3
					-361.9

$(UFU^t)_{Au}$					
140.95	-60.79	0	-383.7	-656.5	-284.2
	170.62	0	349.0	591.7	34.2
		0	0	0	0
Symmetric			5798.1	726.7	-3603.3
				15539.0	3717.8
					14402.0

$(UFU^t)_{Bg}$					
120.45	-35.69	-12.3	-230.7	-500.9	-453.9
	111.80	-27.2	32.6	336.3	343.1
		91.9	-249.3	-256.6	-125.5
Symmetric			336.3	-264.1	-2374.6
				13680.0	5318.9
					10927.0

$(UFU^t)_{Bu}$					
0	0	0	0	0	0
	0	0	0	0	0
		89.25	-61.7	338.6	278.4
Symmetric			5272.1	-1215.5	-5352.3
				4223.1	-7784.4
					3113.3

is proposed herein, where A, B and C are combinations of the A's, B's and C's of the C...C and $CH_3...CH_3$ potentials. The Williams' C...H potential is similarly obtained from the C...C and H...H potentials [8]. In table 14 the new parameters for the $C...CH_3$ potential are obtained from an arithmetic mean approximation and also from a geometric mean approximation.

The force constants were recalculated. They are given in tables 15 and 16. The first shows the results obtained using the arithmetic average for the $C...CH_3$ parameters. The other using the geometric combination. The results are very similar.

The force constants given in tables 15 and 16 were used to calculate the (UFU^t) blocks. They are shown in tables 17 and 18. Notice that all the diagonal elements are positive.

It should be pointed out that the a_{ij} elements of the matrices in tables 13, 17 and 18 have different units. When i and j = 1, 2, 3 the units are kcal/mol.Å^2. When i = 1, 2, 3 and j = 4, 5, 6 or i = 4, 5, 6 and j = 1, 2, 3 the units are kcal/mol.Å. Finally when i and j = 4, 5, 6 the units are kcal/mol.

It is important to note the large values of many off-diagonal elements in these matrices. If our approximations are valid, this means that the vibrations are not nearly about and along the principal axes of inertia, and considerable mixing is present. In the past, it has been assumed that rotations occur about the principal axes, but as Pawley [10] points out there is not any physical reason for this to be so.

TABLE 14

NEW PARAMETERS FOR TWO

C...CH_3 POTENTIALS

A(kcal. A^6/mol)	B(kcal/mol)	C(A^{-1})
$\frac{^{A}C.C + {}^{A}CH_3.CH_3}{2} =$ 1650.0	$\frac{^{B}C.C + {}^{B}CH_3.CH_3}{2} =$ 157950.	$\frac{^{C}C.C + {}^{C}CH_3.CH_3}{2} =$ 3.45
$\overline{^{A}C.C\,{}^{A}CH_3.CH_3}$ 1026.2	$\overline{^{B}C.C\,{}^{B}CH_3.CH_3} =$ 107270.	$\frac{^{C}C.C + {}^{C}CH_3.CH_3}{2} =$ 3.45

TABLE 15

NEW FORCE CONSTANTS I

	f^{11}_{ij}			f^{12}_{ij}		
j / i	x	y	z	x	y	z
x	52.56	-14.76	-29.89	0.01	0.01	-0.02
y	*	111.47	1.26	*	0.01	-0.02
z			98.55			0.02
j / i	ξ	η	ζ	ξ	η	ζ
x	-105.3	-59.31	184.28	0.0	0.07	-0.01
y	153.1	73.49	-200.40	0.01	-0.01	-0.03
z	-123.8	-57.14	31.83	-0.01	-0.05	0.01
j / i	ξ	η	ζ	ξ	η	ζ
ξ	4391.8	-1187.8	-3948.2	-0.03	-0.57	-0.29
η	*	10140.3	-654.5	*	1.16	0.15
ζ			7141.5			-0.39

*Symmetric matrices

TABLE 15—Continued

	f_{ij}^{13}			f_{ij}^{14}		
$i \backslash j$	x	y	z	x	y	z
x	-10.25	12.55	2.56	-15.65	-12.69	10.53
y	*	-29.41	-9.79	*	-8.96	8.20
z			-8.79			-8.60
$i \backslash j$	ξ	η	ζ	ξ	η	ζ
x	76.47	77.79	-84.87	37.34	-99.0	-41.75
y	-158.22	-127.72	154.44	22.9	-51.6	-13.05
z	-31.88	-58.57	51.25	-30.45	59.6	14.52
$i \backslash j$	ξ	η	ζ	ξ	η	ζ
ξ	-1217.5	-487.7	613.1	-244.8	530.3	215.8
η	*	-929.9	790.7	*	-1267.0	-542.8
ζ			-1737.6			-171.8

*Symmetric matrices.

TABLE 16
NEW FORCE CONSTANTS II

	f_{ij}^{11}			f_{ij}^{12}		
i \ j	x	y	z	x	y	z
x	48.22	-14.09	-28.14	0.01	0.01	-0.02
y	*	106.72	0.14	*	0.01	-0.02
z			98.00			0.02
i \ j	ξ	η	ζ	ξ	η	ζ
x	-105.77	-63.23	180.8	0.0	0.07	-0.01
y	164.46	84.47	-216.96	0.01	-0.01	-0.03
z	-114.70	-45.37	21.30	-0.01	-0.05	0.01
i \ j	ξ	η	ζ	ξ	η	ζ
ξ	4248.7	-1264.9	-3766.1	-0.03	-0.57	-0.29
η	*	8796.0	-499.9	*	1.16	0.15
ζ			6834.8			-0.39

*Symmetric matrices.

TABLE 16 — Continued

	f^{13}_{ij}			f^{14}_{ij}		
i \ j	x	y	z	x	y	z
x	-9.32	12.73	2.07	-14.52	-12.31	10.18
y	*	-29.08	-9.68	*	-8.82	8.17
z			-8.81			-8.71
i \ j	ξ	η	ζ	ξ	η	ζ
x	75.09	70.40	-81.0	33.71	-86.18	-37.82
y	-156.7	-124.56	151.78	22.00	-47.79	-11.56
z	-31.08	-54.51	49.47	-30.12	57.85	14.07
i \ j	ξ	η	ζ	ξ	η	ζ
ξ	-1205.7	-486.5	601.1	-239.5	503.6	208.7
η	*	-867.5	758.4	*	-1166.0	-513.5
ζ			-1700.0			-190.9

*Symmetric matrices.

TABLE 17

NEW ((UFU^t)) MATRICES I*

$(UFU^t)_{Ag}$						$(UFU^t)_{Au}$					
26.66	-14.90	-16.80	8.49	-80.52	57.66	78.46	-14.62	0	-219.10	-38.1	310.9
	73.1	-0.33	18.07	-106.09	-59.01		149.84	0	288.03	253.8	-341.8
		81.16	-186.1	-56.1	97.6			0	0	0	0
Symmetric			2929.6	-1152.9	-3118.1	Symmetric			5854.0	-1222.7	-4778.2
				7943.4	-396.8					12337.0	-912.2
					5232.1						9051.0
$(UFU^t)_{Bg}$						$(UFU^t)_{Bu}$					
57.96	10.46	-37.86	-66.19	117.58	141.16	0	0	0	0	0	0
	91.02	-16.73	-28.41	-2.37	-32.91		0	0	0	0	0
		98.36	-125.23	-175.32	68.56			98.74	-122.37	61.0	-4.9
Symmetric			3419.1	-2213.5	-3549.6	Symmetric			5364.5	-162.1	-4346.7
				10477.0	688.9					9803.0	-1997.9
					5575.7						8707.3

---

* The arithmetic average potential was used in this calculations.

TABLE 18

NEW (UFU^t) MATRICES II*

$(UFU^t)_{Ag}$						$(UFU^t)_{Au}$					
24.38	-13.66	-15.90	2.83	-79.1	61.98	72.06	-14.51	0	-213.5	-47.4	299.7
	68.82	-1.37	30.66	-87.9	-76.74		144.6	0	299.5	256.9	-357.2
		80.50	-175.9	-42.0	84.84			0	0	0	0
Symmetric			2803.6	-1249.0	-2956.1	Symmetric			5688.0	-1283.0	-4575.0
				6762.	-265.0					10827.	-744.8
					4943.						8726.1
$(UFU^t)_{Bg}$						$(UFU^t)_{Bu}$					
53.4	10.45	-36.25	-64.42	93.38	137.7	0	0	0	0	0	0
	86.46	-17.71	-14.24	5.5	-53.61		0	0	0	0	0
		97.9	-115.6	-157.7	56.59			98.1	-113.8	65.95	-14.1
Symmetric			3281.	-2256.0	-3373.1	Symmetric			5214.5	-285.0	-4158.0
				9095.0	772.0					8497.	-1772.0
					5325.7						8342.9

---

*The geometric average potential was used in this calculations.

Finally the crystal potential was taken as the sum of the dipole-dipole and non-bonded atom-atom potentials, thus

$$\begin{aligned} V &= \sum V_n + \sum V_{d\text{-}d} \\ &= \sum (\text{pairwise interactions})_n + \sum (\text{dipolar interactions}) \end{aligned} \tag{50}$$

The force constants, that are obtained from this new potential, are expressed as the sum of the force constants due to both potentials, therefore,

$$f_{ij}^{ab} = (f_{ij}^{ab})_{\text{dipole}} + (f_{ij}^{ab})_{\text{atom-atom}} \tag{51}$$

Expressions for the dipolar force constants are given in Appendix IV, part B.

The (UFU^t) were recalculated using the new force constants. Table 19 gives the matrices obtained when the arithmetic average potential for the C... CH_3 interactions was used, and table 20 when the geometric average was used.

If table 17 is compared with table 19, and table 18 with table 20 it is noticed that the inclusion of the dipole-dipole potential introduces very small changes. This was expected considering the small energy calculated with this potential.

TABLE 19

NEW (UFU^t) MATRICES III*

$(UFU^t)_{Ag}$						$(UFU^t)_{Au}$					
27.56	-14.89	-15.35	8.27	-78.11	56.55	79.10	-14.06	0	-217.20	-33.07	307.5
	72.16	-0.35	17.89	-107.4	-55.35		148.4	0	288.5	244.5	-331.9
Symmetric		81.27	-183.7	-57.17	90.3	Symmetric		0	0	0	0
			2872.0	-1248.90	-2978.0				5851.0	-1264.0	-4575.0
				7738.0	-444.3					12140.0	-907.1
					5120.0						8916.0

$(UFU^t)_{Bg}$						$(UFU^t)_{Bu}$					
58.64	10.41	-36.43	-67.42	121.5	141.4	0	0	0	0	0	0
	90.00	-16.68	-28.01	-3.47	-29.1	0	0	0	0	0	0
		98.66	-121.5	-180.9	56.1			99.24	-119.1	53.0	-13.5
Symmetric			3363.0	-2173.0	-3409.	Symmetric			5360.0	-337.6	-4142.0
				10290.0	657.0					9578.0	-2009.1
					5453.0						8585.0

*The arithmetic average was used and the dipole-dipole interactions were included.

TABLE 20

NEW (UFU^t) MATRICES IV*

$(UFU^t)_{Ag}$					
25.28	-13.66	-14.44	2.81	-76.6	60.87
	67.88	-1.39	29.58	-89.2	-73.08
		80.59	-173.5	-43.1	77.54
Symmetric			2746.0	-1344.0	-2816.1
				6557.0	-302.5
					4831.0

$(UFU^t)_{Au}$					
72.70	-13.56	0	-212.6	-42.42	296.3
	143.2	0	299.6	248.3	-347.3
		0	0	0	0
Symmetric			5691.0	-1324.1	-4372.0
				10630.0	-739.6
					8591.0

$(UFU^t)_{Bg}$					
54.1	10.38	-34.82	-65.62	97.38	137.9
	85.44	-17.66	-13.83	6.60	-49.8
		98.20	-111.9	-163.3	44.2
			3227.0	-2215.0	-3233.1
Symmetric				8908.0	740.0
					5203.0

$(UFU^t)_{Bu}$					
0	0	0	0	0	0
	0	0	0	0	0
		98.6	-110.5	58.9	-22.7
			5210.0	-450.5	-3954.0
Symmetric				8272.0	-1783.
					8221.0

---

* The geometric average was used and the dipole-dipole interactions were included.

TABLE 21

CALCULATED FREQUENCIES (cm^{-1})

a	Arithmetic average + dipolar interactions						b	Geometric average + dipolar interactions					
Ag	29	57	63	22	76	98	Ag	28	55	62	20	69	94
Au	53	73	0	132	96	55	Au	51	69	0	130	89	55
Bg	38	61	72	26	85	107	Bg	37	60	69	25	82	101
Bu	0	0	67	121	85	52	Bu	0	0	67	119	78	52
c	Arithmetic average, no dipole interaction						d	Geometric average, no dipole interaction					
Ag	28	56	63	22	76	99	Ag	27	54	62	20	69	95
Au	55	73	0	134	97	53	Au	53	69	0	132	90	53
Bg	37	62	72	25	85	109	Bg	36	61	69	24	82	103
Bu	0	0	67	123	85	51	Bu	0	0	67	121	78	51

In Appendix VI the program used to calculate the value of the force constants is given.

The frequencies of vibrations corresponding to the force constants given in tables 17 to 20 are shown in table 21. The spectrum of frequencies shows a small contraction when the dipole-dipole potential is included (compare parts a with c, and b with d). As was expected, from the calculated energy and force constants, this is a small change.

The lattice energies obtained summing up all the van der Waals and dipole-dipole interactions are:

-60.6 kcal/mol, when the geometric average potential for the C... CH_3 interaction was used.

-61.3 kcal/mol, when the arithmetic average was used.

8. DISCUSSION

In table 22 calculated and observed frequencies are compared. The agreement between them is quite satisfactory. Before the frequencies and their assigments are discussed, it is important to consider several points that we think are fundamental.

In the present calculation we have used potentials that have been obtained or calculated for the same atom-atom, atom-group or group-group interactions in different molecules. It has been a transference of potentials, the same way there are transferences of force constants in the calculations of internal vibrations.

The ability to reproduce experimental data using transferred potentials is one of the points of this work. Only more work can prove if this is a good general method to treat lattice vibrations. The future work has to be complemented with wide experimental information.

We also feel strongly that more theoretical work is needed to justify the usual approximations, (rigid body, zero wavevector $\vec{k} = 0$, harmonic oscillations), taken in calculations of this kind, especially when large organic molecules are involved. It has to be better understood how these assumptions affect the results, when they can not be used and more refined conditions are needed.

TABLE 22

OBSERVED[1] AND CALCULATED LATTICE VIBRATION FREQUENCIES

Symmetry Species	Translatory[2]			Rotatory[2]		
Ag						
observed	30	52	70	16	74	91
calculated (3)	28	55	62	20	69	94
calculated (4)	29	57	63	22	76	98
Bg						
observed	30, 37	52	70	16	74, 90	95
calculated (3)	37	60	69	25	82	101
calculated (4)	38	61	72	26	85	107
Au						
observed	50	70		135, 150	84	50?
calculated (3)	51	69	0[5]	130	89	55
calculated (4)	53	73	0[5]	132	96	55
Bu						
observed			70?	115	84?	50?
calculated (3)	0[5]	0[5]	67	119	78	52
calculated (4)	0[5]	0[5]	67	121	85	52

---

1. Raman data from ref. [22], single crystal frequencies at -90° C. Far infrared data from ref. [1], polycrystalline sample at 25°C.

2. Modes are primarily rotatory or translatory in nature, however, the translation-rotation force constants are not negligible.

3. See table 21, part c.

4. See table 21, part a.

5. Acoustical modes.

Considering the approximations used and ignoring their influence in the results, we decided not to vary any of the parameters of the potentials, see table 5, in order to improve the calculated frequencies.

Two intermolecular potentials have been used for the PAA crystal, a dipole-dipole and van der Waals type interactions. The last one plays a dominant role. The reason is the great number of interactions of this kind compared with the few of dipolar character.

The relative importance of one potential vs. the other could be leveled out in the nematic phase if there were a considerable increase in volume as the crystal passes to the nematic phase. The increase in the interatomic distances would then affect more intensely the Buckingham potentials, functions of r^{-6}, than the dipole-dipole potential, function of r^{-3}. Unfortunately, the experimental data on the volume change are contradictory [32-33]. It appears that the volume change is small, however, so no major change in potential on this basis is predicted.

Going back to the results shown in table 21, the frequencies are separated in translatory and rotatory modes. This is a convenient division, but only approximate, because of the non-negligible translation-rotation force constants.

Let us propose a model that will allow us to discuss and understand the obtained results.

Consider a PAA molecule in a crystal before the specific interactions have been "turned on". This model can be described as a "frozen gas". In this case the lattice vibrations could be represented schematically by the energy level diagram shown in figure 10 a. Experimentally, this situation might be simulated by examining the vibrations of a PAA molecule in a rare gas matrix. There will be three rotatory vibrations, with frequencies determinated by the moments of inertia. In addition, there will be three translatory vibrations. However, because we have assumed the potential to be the same in all directions, these translatory vibrations will be degenerate, with a frequency determinated by the molecular weight.

Let us now allow for anisotropy in the crystal field. The effect of this is shown in figure 10 b. The translatory modes will split by this anisotropy into three modes along x, y and z directions. The rotatory modes will be slighly shifted. We denote this level of approximation as the "anisotropic mean field" model. It is artificial in that one might view it as being a crystal with one molecule per unit cell.

Now let us consider the actual crystal with four molecules per unit cell. The molecules interact between them and as a result each of the 6 levels shown in figure 10 b will split into a maximun of 4 energy levels. The magnitude of these splittings will depend on the strength of those interactions. The stronger the interactions are, the larger will be the splittings. These 24 energy levels are shown schematically in figure 10 c.

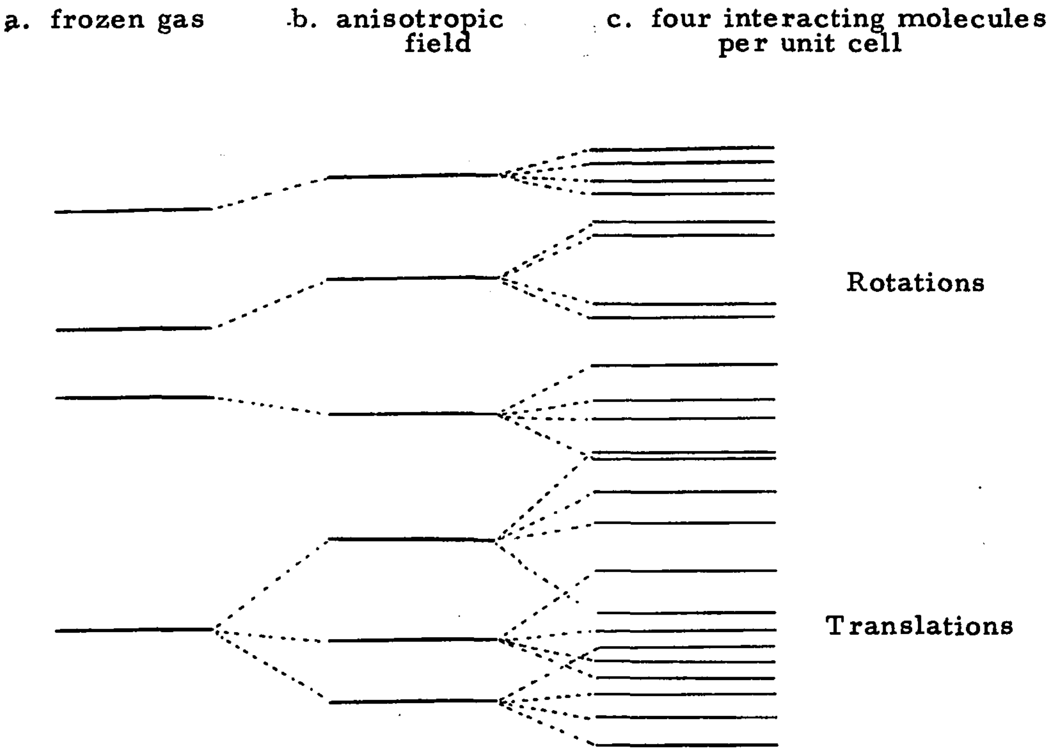

Fig. 10. Energy levels for three crystal models. A number of possible splitting patterns are shown schematically in (c).

These six groups of four energy levels each correspond to the calculated values in the six columns of table 22. We can now see the significance of these columns. The frequencies in each column represent different combinations of the same motion. As was pointed out above, the numbers will indicate what type of coupling exists between the molecules. A weak intermolecular coupling, that is a small splitting, will give similar numerical values for the frequencies. For example the translations along the z axis, and the rotations about the y axis, (η coordinate). Because of this weak coupling the motions can easily become free. Experimentally, it has been noticed that a gradual disappearance of a mode in the 70-80 cm^{-1} region occurs in the Raman, as the temperature of the sample is increased and reaches the transition point [22].

On the other hand, very different numbers in the same column indicate a strong intermolecular coupling. For example rotations along the x, (ξ coordinate), and the z, (ζ coordinate), axes. The predicted rotations along the last axis are the only vibrations for which the Raman values are higher than the infrared. These motions are so strongly coupled that they probably are present in the nematic phase. Stated another way, the nematic phase exists because of the presence of these pseudo-lattice modes that maintain certain order in the phase. The experimental data available support this point. Far infrared spectra of the nematic phase show frequencies in the 100 cm^{-1} region. Far infrared spectra of aligned nematic substances have indicated that this band is probably of rotatory origin [1].

The other two columns, representing translations along x and y, show what can be called an intermediate coupling.

Other qualitative aspects that have been noted from the spectra are supported by the calculated results such as : the most intense infrared active lattice modes are at higher frequency than the Raman active modes. The observed band in the 30-40 cm $^{-1}$ region in the Raman spectrum was assigned as a translation along the x or z axes. The calculated frequency, 37 cm^{-1}, is a translation along the x axis.

APPENDIX I

Classification of lattice vibrations according to irreducible representations of the symmetry group of the crystal

It is simple to classify lattice vibrations according to the irreducible representations of the symmetry group of the crystal and to establish the behavior of them in infrared and Raman spectra.

The characters of the reducible representations of the rotations, translations and acoustical translations of the crystal for wavevector k = 0 are obtained from the following relations [17]:

$$\begin{aligned} \chi(\mathrm{Rot})_M &= U_M(\,1 \pm 2\cos\theta) \\ \chi(\mathrm{Trans})_M &= \chi(\mathrm{ac.\,Trans})_M + \chi(\mathrm{op.\,Trans})_M \\ &= U_M(\,\pm 1 + 2\cos\theta) \\ \chi(\mathrm{ac.\,Trans})_M &= \pm 1 + 2\cos\theta \end{aligned} \tag{52}$$

U_M represents the number of molecules left invariant when operation M is applied to the unit cell. The + sign is used with "proper" operations, and the - sign with "improper" operations. A proper operation represents a rotation about an axis. An improper operation represents a rotation followed by a reflection in a plane perpendicular to the rotation axis. The angle θ is the angle of rotation associated with the operation M.

The factor group for PAA, C_{2h}, has four operations, E, C_2, i and σ_h. E and C_2 are "proper" operations and i and σ_h are "improper". The identity operation, E, is the only operation that leaves the four molecules of the unit cell invariant i.e. $U_E = 4$. All the molecules exchange places when the other operations are applied i.e. $U_{C_2} = U_i = U_{\sigma_h} = 0$.

As an example let us calculate the character of the reducible representation for the acoustical translations

$$\begin{aligned}
\chi(\text{ac. Trans})_E &= 1 + 2\cos 2\pi = 3 \\
\chi(\text{ac. Trans})_{C_2} &= 1 + 2\cos \pi = -1 \\
\chi(\text{ac. Trans})_i &= -1 + 2\cos \pi = -3 \\
\chi(\text{ac. Trans})_{\sigma_h} &= -1 + 2\cos 2\pi = 1
\end{aligned} \qquad (53)$$

The reducible representations for the other vibrations are obtained similarly, their numerical values are :

	E	C_2	i	σ_h
Γ (Rot)	12	0	0	0
Γ (Trans)	12	0	0	0

The character χ_M of a reducible representation can be expressed as a sum of the characters of various irreducible representations of which it is compased [18]. Thus it can be written as:

$$\chi_M = \sum a_j \chi_M^j$$

For each operation M, χ_M^j is the character of the irreducible representation Γ^j, and a_j is the number of times the irreducible representation j is present.

It can be proven [18] that the a_j can be expressed as:

$$a_j = \frac{1}{h} \sum_M \chi_M \chi_M^j \qquad (54)$$

where h is the number of operations in the group.

Using this last expression one obtains:

Γ (Rot) = 3 Ag + 3 Bg + 3 Au + 3 Bu

Γ (Trans) = 3 Ag + 3 Bg + 3 Au + 3 Bu

Γ (ac. Trans) = Au + 2 Bu

Γ (op. Trans) = 3 Ag + 3 Bg + 2 Au + Bu

APPENDIX II

Output obtained from the ORTEP program

This program was used to obtain the atomic coordinates of the PAA molecules that form the crystal. Table 23 shows part of an output. In this case the distances between H_{20} in molecule I and the surrounded atoms are given.

All the atoms in the PAA molecule were numered according to figure 7. The atoms are identified by the numbers given between parenthesis. Take for example the code number (20, 55501). The numbers in front of the comma designate the atom, in this case 20 refers to a H, see figure 7. In the case of the PAA molecule this number can take any value from 1 to 33, because there are 33 atoms in the molecule.

The three numbers that follow the comma identify the unit cell. They represent crystal lattice translations along edges a, b and c respectively. The origin cell is represented as 555. A translation by one unit cell in the a direction is represented as 655, the same translation but in opposite direction gives 455.

Finally the last two numbers represent the symmetry operators. In this particular case there are only four operators. The E is represented by 01, the C_2 by 02, the i by 03 and the σ_h by 04.

For a different example , atom designation code (8, 47502) refers to atom 8, C_8, moved through symmetry operation 02, then translated -1 cell translation along a, +2 cell translations along b and 0 cell translation along c.

The columns designated as A', B' and C' give the fractional atomic coordinates. They are called fractional because they are normalized to the unit cell dimensions. They are dimensionless and referred to the monoclinic axes.

The next and last column gives the distance, in Å, between the two atoms considered.

TABLE 23

ORTEP OUTPUT

```
                                                                              A'      B'      C'
VECTORS FROM ATOM  ( 20,55501)       TO ATOMS   1 THROUGH  33
   H20     C4      ( 20,55501) -,0697 -,0737  ,6834    (  4,55501) -,0431  ,0173  ,6560       D =  ,958
   H20     C5                                          (  5,55501)  ,0498  ,0570  ,7330       D = 2,030
   H20     C3                                          (  3,55501) -,0950  ,1150  ,5460       D = 2,072
   H20     H21                                         ( 21,55501)  ,0863 -,0217  ,8123       D = 2,312
   H20     H23                                         ( 23,55503) -,0910 -,3180  ,5622       D = 2,334
   H20     H30                                         ( 30,55501) -,1956 -,1634  ,4818       D = 2,417
   H20     H28                                         ( 28,55501) -,2364 -,0303  ,5876       D = 2,418
   H20     C1                                          (  1,55501) -,2330 -,0470  ,4670       D = 2,595
   H20     O18                                         ( 18,54602) -,1110 -,3270  ,8000       D = 2,644
   H20     O2                                          (  2,55501) -,1850  ,0385  ,4610       D = 2,709
   H20     C15                                         ( 15,54602) -,0200 -,3160  ,8900       D = 2,859
   H20     H31                                         ( 31,54602) -,1667 -,1341  ,8492       D = 2,872
   H20     H27                                         ( 27,45504) -,1206  ,1807  ,8294       D = 2,927
   H20     C14                                         ( 14,54602)  ,0440 -,3930  ,8470       D = 3,238
   H20     C6                                          (  6,55501)  ,0690  ,1910  ,6990       D = 3,246
   H20     C19                                         ( 19,54602) -,1800 -,2570  ,8400       D = 3,273
   H20     H25                                         ( 25,54602)  ,0135 -,4510  ,7449       D = 3,287
   H20     C8                                          (  8,55501) -,0530  ,2480  ,5130       D = 3,298
   H20     H26                                         ( 26,45504)  ,0335  ,1812  ,9629       D = 3,499
   H20     C16                                         ( 16,54602)  ,0120 -,2380 1,0090       D = 3,531
   H20     H29                                         ( 29,55501) -,2952 -,0426  ,4061       D = 3,608
   H20     C7                                          (  7,55503) -,0397 -,2460  ,4100       D = 3,675
   H20     H33                                         ( 33,54602) -,2427 -,2980  ,7646       D = 3,687
   H20     H22                                         ( 22,55503) -,0747 -,3827  ,4336       D = 3,699
   H20     C8                                          (  8,55503)  ,0530 -,2480  ,4870       D = 3,730
   H20     C7                                          (  7,55501)  ,0387  ,2460  ,5900       D = 3,736
   H20     C17                                         ( 17,45504) -,1076  ,2360  ,9100       D = 3,762
   H20     H26                                         ( 26,54602) -,0335 -,1912 1,0371       D = 3,798
   H20     O11                                         ( 11,45504) -,2600  ,1390  ,7320       D = 3,969
   H20     C16                                         ( 16,45504) -,0120  ,2380  ,9910       D = 4,018
   H20     H32                                         ( 32,54602) -,1722 -,3066  ,9260       D = 4,114
   H20     C13                                         ( 13,54602)  ,1370 -,3940  ,9300       D = 4,171
   H20     C6                                          (  6,55503) -,0890 -,1910  ,3010       D = 4,206
   H20     H29                                         ( 29,44502) -,2048 -,5426  ,5939       D = 4,279
   H20     C3                                          (  3,55503)  ,0950 -,1150  ,4540       D = 4,327
   H20     C17                                         ( 17,54602)  ,1078 -,2360 1,0900       D = 4,384
   H20     O2                                          (  2,44502) -,3150 -,4115  ,5390       D = 4,461
   H20     N9                                          (  9,55501)  ,1890  ,2400  ,7750       D = 4,553
   H20     N10                                         ( 10,55501)  ,2280  ,1520  ,8730       D = 4,650
   H20     C12                                         ( 12,54602)  ,1700 -,3140 1,0510       D = 4,666
   H20     H30                                         ( 30,45502) -,3014  ,3366  ,5182       D = 4,714
   H20     H29                                         ( 29,45502) -,2048  ,4574  ,5939       D = 4,725
```

APPENDIX III

Calculation of the direction cosines of the dipole moment vectors

The angles a vector makes with the x, y and z axes are frequently called its direction angles α, β and γ; $\cos\alpha$, $\cos\beta$, $\cos\gamma$, are called the direction cosines, they are expressed as:

$$\cos\alpha = l = \frac{x - x'}{\sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2}}$$

$$\cos\beta = m = \frac{y - y'}{\sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2}} \qquad (55)$$

$$\cos\gamma = n = \frac{z - z'}{\sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2}}$$

In this case the vector is $\vec{\mu} = (x-x')\vec{i} + (y-y')\vec{j} + (z-z')\vec{k}$.

1. Direction cosines of the N→O dipole.

$$r = \sqrt{(x_O - x_N)^2 + (y_O - y_N)^2 + (z_O - z_N)^2} = 1.273 \text{ Å}$$

$$l = \frac{x_O - x_N}{r} \qquad m = \frac{y_O - y_N}{r} \qquad n = \frac{z_O - z_N}{r}$$

$(x_O - x_N) = (A'_O - A'_N)\, 15.78 - (C'_O - C'_N)\, 11.02 \sin 24.57^{\circ}$

$(y_O - y_N) = (B'_O - B'_N)\, 8.11$

$(z_O - z_N) = (C'_O - C'_N)\, 11.02 \cos 24.57^{\circ}$

$l = 0.534$ $m = 0.772$ $n = -0.338$

The A' 's, B' 's and C' 's are the atomic coordinates from crystallographic data [16].

2. The calculation of the direction cosines of the $O_{(2)}$—CH_3 and $O_{(18)}$—CH_3 dipole vectors is a little more complicated because the coordinates of the dipole are not known.

In figure 11 the methoxy and its dipole are represented. The values of the ω and θ are known [29]. Then,

$\omega = 118^{\circ}$ $\theta = 55^{\circ}$ $\theta' = 180^{\circ} - 55^{\circ} = 125^{\circ}$

The coordinates of point A are necessary in order to be able to calculate the direction cosines. From figure 11 one gets

$$\vec{r} = \vec{r}_1 + \frac{(r_2 - r_1)}{|r_2 - r_1|}\, d \cos\theta' + \frac{U}{|U|}\, d \sin\theta' , \text{ where} \qquad (56)$$

$U = a(r_2 - r_1) - b\,(r_3 - r_1)$, where a and b are two coefficients.

If U is multiplied by $(r_2 - r_1)$ one obtains:

$U\,(r_2 - r_1) = a\,(r_2 - r_1)^2 - b\,(r_3 - r_1)(r_2 - r_1) = 0$ because

$$U \perp (r_2 - r_1)$$

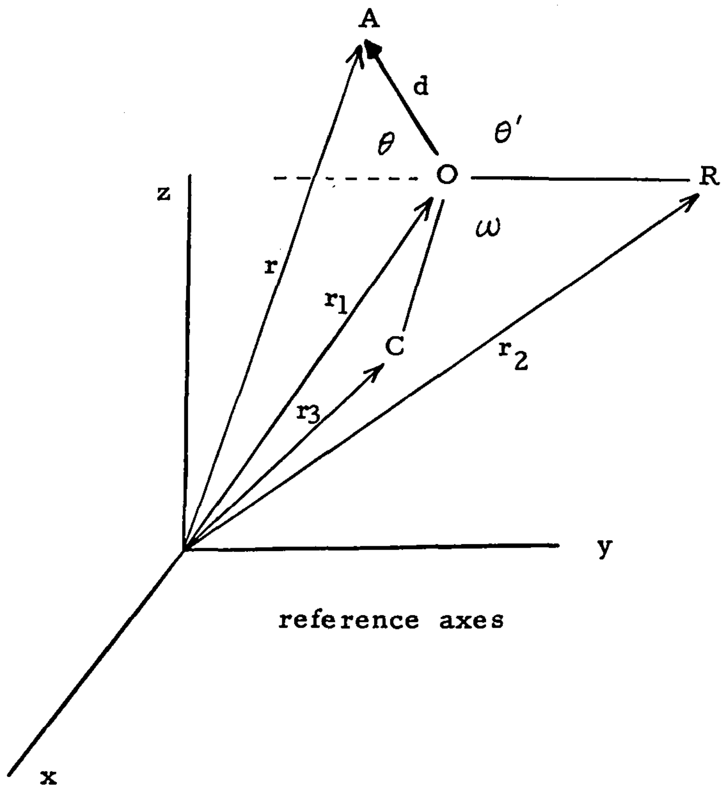

Fig. 11. Methoxy group and its dipole moment.

If b = 1, then $a = \dfrac{(r_3 - r_1)(r_2 - r_1)}{|r_2 - r_1|^2}$ and the U can be written as (58)

$$U = \frac{(r_3 - r_1)(r_2 - r_1)^2}{|r_2 - r_1|^2} - (r_3 - r_1) \qquad (59)$$

$$|U|^2 = \frac{((r_3 - r_1)(r_2 - r_1))^2}{|r_2 - r_1|^2} - 2\,\frac{((r_3 - r_1)(r_2 - r_1))^2}{|r_2 - r_1|^2} + (r_3 - r_1)^2 \qquad (60)$$

$$= (r_3 - r_1)^2 - \frac{((r_3 - r_1)(r_2 - r_1))^2}{|r_2 - r_1|^2}$$

but from figure 11 we see that $\cos\omega = \dfrac{(r_2 - r_1)(r_3 - r_1)}{|r_2 - r_1||r_3 - r_1|}$ (61)

$$|U|^2 = (r_3 - r_1)^2 (1 - \cos^2\omega) \qquad (62)$$

$$|U| = |r_3 - r_1| \sin\omega \qquad (63)$$

$$\frac{U}{|U|} = \frac{(r_3 - r_1)(r_2 - r_1)^2}{|r_2 - r_1|^2 |r_3 - r_1| \sin\omega} - \frac{(r_3 - r_1)}{|r_3 - r_1| \sin\omega}$$

using expression (61) one obtains

$$\frac{U}{|U|} = \frac{(r_2 - r_1)\cos\omega}{|r_2 - r_1| \sin\omega} - \frac{(r_3 - r_1)}{|r_3 - r_1| \sin\omega} \qquad (64)$$

If $\frac{U}{|U|}$ is substituted in expression (56), one gets:

$$\vec{r} = \vec{r}_1 + \frac{(r_2-r_1)}{|r_2-r_1|} d\cos\theta' + \left(\frac{\cos\omega(r_2-r_1)}{\sin\omega|r_2-r_1|} - \frac{(r_3-r_1)}{|r_3-r_1|\sin\omega}\right) d\sin\theta'$$

$$= \vec{r}_1 + d(\cos\theta' + \sin\theta'\frac{\cos\omega}{\sin\omega})\frac{(r_2-r_1)}{|r_2-r_1|} - d\,\frac{(r_3-r_1)\sin\theta'}{|r_3-r_1|\sin\omega} \qquad (65)$$

Finally the expressions for the direction cosines are:

$$l = \frac{x-x'}{d} = \frac{(x_2-x_1)}{|r_2-r_1|}\left(\cos\theta' + \frac{\cos\omega\sin\theta'}{\sin\omega}\right) - \frac{(x_3-x_1)\sin\theta'}{|r_3-r_1|\sin\omega}$$

$$m = \frac{y-y'}{d} = \frac{(y_2-y_1)}{|r_2-r_1|}\left(\cos\theta' + \frac{\cos\omega\sin\theta'}{\sin\omega}\right) - \frac{(y_3-y_1)\sin\theta'}{|r_3-r_1|\sin\omega} \qquad (66)$$

$$n = \frac{z-z'}{d} = \frac{(z_2-z_1)}{|r_2-r_1|}\left(\cos\theta' + \frac{\cos\omega\sin\theta'}{\sin\omega}\right) - \frac{(z_3-z_1)\sin\theta'}{|r_3-r_1|\sin\omega}$$

Substituting the corresponding values of the coordinates the following direction cosines are obtained:

a. For the $O_{(2)}-CH_3$ dipole

$l = -0.267$ $m = 0.552$ $n = -0.797$

b. For the $O_{(18)}-CH_3$ dipole

$l = -0.060$ $m = -0.430$ $n = 0.911$

The direction cosines for the other three molecules in the unit cell are easily obtained from molecule I.

$$
\begin{aligned}
l^{I} &= -l^{II} = -l^{III} = l^{IV} \\
m^{I} &= m^{II} = -m^{III} = -m^{IV} \qquad (67) \\
n^{I} &= -n^{II} = -n^{III} = n^{IV}
\end{aligned}
$$

APPENDIX IV

A. Some expressions for the force constants obtained from the atom-atom interactions.

$$W = -\frac{A}{r^6} + B\, e^{-Cr}$$

$$\left(\frac{\partial^2 W}{\partial x^2}\right)_o = f^{11}_{xx} = \frac{6A}{r^8}\left(1 - \frac{8(x-x')^2}{r^2}\right) + \frac{BCe^{-Cr}}{r}\left(-1 + \frac{C(x-x')^2}{r} + \frac{(x-x')^2}{r^2}\right)$$

$$\left(\frac{\partial^2 W}{\partial y^2}\right)_o = f^{11}_{yy} = \frac{6A}{r^8}\left(1 - \frac{8(y-y')^2}{r^2}\right) + \frac{BCe^{-Cr}}{r}\left(-1 + \frac{C(y-y')^2}{r} + \frac{(y-y')^2}{r^2}\right)$$

$$\left(\frac{\partial^2 W}{\partial z^2}\right)_o = f^{11}_{zz} = \frac{6A}{r^8}\left(1 - \frac{8(z-z')^2}{r^2}\right) + \frac{BCe^{-Cr}}{r}\left(-1 + \frac{C(z-z')^2}{r} + \frac{(z-z')^2}{r^2}\right)$$

$$\left(\frac{\partial^2 W}{\partial x\, \partial y}\right)_o = f^{11}_{xy} = \frac{(x-x')(y-y')}{r^2}\left(-\frac{48A}{r^8} + BCe^{-Cr}\left(C + \frac{1}{r}\right)\right)$$

$$\left(\frac{{}^2 W}{\partial x\, \partial z}\right)_o = f^{11}_{xz} = \frac{(x-x')(z-z')}{r^2}\left(-\frac{48A}{r^8} + BCe^{-Cr}\left(C + \frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial y\,\partial z}\right)_o = f^{11}_{yz} = \frac{(y-y')(z-z')}{r^2}\left(-\frac{48A}{r^8} + BCe^{-Cr}\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial x\,\partial x'}\right)_o = f^{1a*}_{xx'} = \frac{6A}{r^8}\left(-1+\frac{8(x-x')^2}{r^2}\right) + \frac{BCe^{-Cr}}{r}\left(1-(x-x')^2\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial y\,\partial y'}\right)_o = f^{1a}_{yy'} = \frac{6A}{r^8}\left(-1+\frac{8(y-y')^2}{r^2}\right) + \frac{BCe^{-Cr}}{r}\left(1-(y-y')^2\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial z\,\partial z'}\right)_o = f^{1a}_{zz'} = \frac{6A}{r^8}\left(-1+\frac{8(z-z')^2}{r^2}\right) + \frac{BCe^{-Cr}}{r}\left(1-(z-z')^2\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial x\,\partial y'}\right)_o = f^{1a}_{xy'} = \frac{(x-x')(y-y')}{r^2}\left(\frac{48A}{r^8} - BCe^{-Cr}\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial x\,\partial z'}\right)_o = f^{1a}_{xz'} = \frac{(x-x')(z-z')}{r^2}\left(\frac{48A}{r^8} - BCe^{-Cr}\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial y\,\partial z'}\right)_o = f^{1a}_{yz'} = \frac{(y-y')(z-z')}{r^2}\left(\frac{48A}{r^8} - BCe^{-Cr}\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial \xi\,\partial x}\right)_o = f^{11}_{x\xi} = \frac{(zy'-yz')(x-x')}{r^2}\left(-\frac{96A}{r^8} + 2BCe^{-Cr}\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial \xi\,\partial y}\right)_o = f^{11}_{y\xi} = -\frac{12Az}{r^8} + \frac{(zy'-yz')}{r^2}\left(-\frac{96A}{r^8} + 2BCe^{-Cr}\left(C+\frac{1}{r}\right)\right)$$

$$-\frac{2BCe^{-Cr}z}{r}$$

---

[*] The a can be 2, 3 or 4 depending in what molecule is x'.

$$\left(\frac{\partial^2 W}{\partial\xi\,\partial z}\right)_o = f^{11}_{z\xi} = \frac{12Ay}{r^8} + \frac{(zy'-yz')(z-z')}{r^2}\left(-\frac{96A}{r^8} + 2BCe^{-Cr}\left(C+\frac{1}{r}\right)\right) - \frac{2BCe^{-Cr}y}{r}$$

$$\left(\frac{\partial^2 W}{\partial\eta\,\partial x}\right)_o = f^{11}_{x\eta} = \frac{12Az}{r^8} + \frac{(xz'-x'z)(x-x')}{r^2}\left(-\frac{96A}{r^8} + 2BCe^{-Cr}\left(C+\frac{1}{r}\right)\right) - \frac{2BCe^{-Cr}z}{r}$$

$$\left(\frac{\partial^2 W}{\partial\eta\,\partial y}\right)_o = f^{11}_{y\eta} = \frac{(z'x-x'z)(y-y')}{r^2}\left(-\frac{96A}{r^8} + 2BCe^{-Cr}\left(C+\frac{1}{r}\right)\right)$$

$$\left(\frac{\partial^2 W}{\partial\eta\,\partial z}\right)_o = f^{11}_{z\eta} = -\frac{12Ax}{r^8} + \frac{(z'x-x'z)(z-z')}{r^2}\left(-\frac{96A}{r^8} + 2BCe^{-Cr}\left(C+\frac{1}{r}\right)\right) + \frac{2BCe^{-Cr}x}{r}$$

$$\left(\frac{\partial^2 W}{\partial\xi^2}\right)_o = f^{11}_{\xi\xi} = \frac{24A}{r^8}\left(yy'+zz'-\frac{8(y'z-z'y)^2}{r^2}\right) + \frac{4BCe^{-Cr}}{r}\left(\left(C\left(\frac{y'z-yz'}{r}\right)^2\right) + \frac{(yz'-y'z)^2}{r^2} - (yy'+zz')\right)$$

$$\left(\frac{\partial^2 W}{\partial\eta^2}\right)_o = f^{11}_{\eta\eta} = \frac{24A}{r^8}\left(xx'+zz'-\frac{8(x'z-z'x)^2}{r^2}\right) + \frac{4BCe^{-Cr}}{r}\left(\left(C\frac{(x'z-xz')^2}{r}\right) + \frac{(x'z-xz')^2}{r^2} - (xx'+zz')\right)$$

$$\left(\frac{\partial^2 W}{\partial \zeta^2}\right)_o = f^{11}_{\zeta\zeta} = \frac{24A}{r^8}\left(yy' + xx' - \frac{8\,(x'y-y'x)^2}{r^2}\right) + \frac{4BCe^{-Cr}}{r}\Big((C$$

$$\frac{(xy'-x'y)^2)}{r} + \frac{(xy'-x'y)^2}{r^2} - (xx'-yy')\Big)$$

$$\left(\frac{\partial^2 W}{\partial \eta\,\partial \xi}\right)_o = f^{11}_{\eta\xi} = -\frac{24A}{r^8}\left(\frac{x'y+xy'}{2} + \frac{8}{r^2}(zy'-yz')(xz'-x'z)\right) + \frac{4BCe^{-Cr}}{r}$$

$$\left(\frac{(y'z-yz')(xz'-zx')}{r}\left(C+\frac{1}{r}\right) + \frac{(xy'+yx')}{2}\right)$$

$$\left(\frac{\partial^2 W}{\partial \zeta\,\partial \xi}\right)_o = f^{11}_{\xi\zeta} = -\frac{12A}{r^8}\left(x'z+z'x + \frac{16\,(zy'-yz')(x'y+y'x)}{r^2}\right) +$$

$$\frac{4BCe^{-Cr}}{r}\left(\frac{(zy'-yz')(yx'-y'x)}{r}\left(C+\frac{1}{r}\right) + \frac{(zx'+z'x)}{2}\right)$$

B. Some expressions for the force constants obtained from the dipole-dipole potential.

$$V = \frac{\mu\mu'}{r^3}(\cos\varepsilon - \cos\theta\cos\theta')$$

$$\left(\frac{\partial^2 V}{\partial x^2}\right)_o = f^{11}_{xx} = \frac{\mu\mu'}{r^5}\Big(-6ll' - 3\cos\varepsilon + 15\cos\theta\cos\theta' + \frac{30(x-x')}{r}$$

$$(l\cos\theta' + l'\cos\theta) + \frac{15}{r^2}(\cos\varepsilon - 7\cos\theta\cos\theta')(x-x')^2\Big)$$

$$\left(\frac{\partial^2 V}{\partial z^2}\right)_o = f^{11}_{zz} = \frac{\mu\mu'}{r^5}\Big(-6nn' - 3\cos\varepsilon + 15\cos\theta\cos\theta' + \frac{30(z-z')}{r}$$

$$(n\cos\theta' + n'\cos\theta) + \frac{15(z-z')^2}{r^2}(\cos\varepsilon - 7\cos\theta'\cos\theta)\Big)$$

$$\left(\frac{\partial^2 V}{\partial x\,\partial y}\right)_o = f^{11}_{xy} = \frac{\mu\mu'}{r^5}\Big(-3(lm'+l'm) + 15\Big(\frac{(x-x')(m\cos\theta' + m'\cos\theta)}{r} +$$

$$\frac{(y-y')(l\cos\theta' + l'\cos\theta)}{r}\Big) + \frac{15(x-x')(y-y')(\cos\varepsilon - 7\cos\theta\cos\theta')}{r^2}\Big)$$

$$\left(\frac{\partial^2 V}{\partial y\,\partial \eta}\right)_o = f^{11}_{y\eta} = \frac{6\mu\mu'}{r^5}\Big(-(y-y')(l'n-n'l) - m'(z'l-x'n) - m(l'z-$$

$$n'x) + \frac{5}{r}(y-y')(\cos\theta(l'z-n'x) + \cos\theta'(z'l-x'n))$$

$$+ 5(y-y')(xz'-zx')(\cos\varepsilon + m\cos\theta' + m'\cos\theta -$$

$$7\cos\theta\cos\theta')\frac{1}{r^2}\Big)$$

$$\left(\frac{\partial^2 V}{\partial x\,\partial\zeta}\right)_o = f^{11}_{x\zeta} = \frac{6\mu\mu'}{r^4}\Big(m\cos\theta' + \frac{1}{r}\Big((\cos\varepsilon - 5\cos\theta\cos\theta')y - (x-x')(m'l-l'm) -$$
$$l(xm'-l'y) - l'(mx'-ly')\Big) + \frac{5}{r^2}\Big((x-x')(\cos\theta'(mx'-ly') + \cos\theta$$
$$(xm'-l'y)) + (yx'-xy')(l\cos\theta'+l'\cos\theta)\Big) + \frac{5}{r^3}(x-x')(yx'-xy')$$
$$(\cos\varepsilon - 7\cos\theta\cos\theta')\Big)$$

$$\left(\frac{\partial^2 V}{\partial\eta^2}\right)_o = f^{11}_{\eta\eta} = \frac{4\mu\mu'}{r^3}\Big(-ll' - nn' + \frac{3}{r}\Big(\cos\theta(n'z+l'x) - \cos\theta'(lx'+nz')\Big) - \frac{3}{r^2}$$
$$\Big(\cos\varepsilon(xx'+zz') + 2(xz'-x'z)(l'n-ln') + 2(lz'-nx')(l'z-n'x)$$
$$- 5\cos\theta\cos\theta'(xx'+zz')\Big) + \frac{30}{r^3}(xz'-x'z)\Big(\cos\theta'(lz'-nx')$$
$$+\cos\theta(l'z-n'x)\Big) + \frac{15}{r^4}(xz'-x'z)^2(\cos\varepsilon - 7\cos\theta\cos\theta')\Big)$$

$$\left(\frac{\partial^2 V}{\partial\xi\,\partial\zeta}\right)_o = f^{11}_{\xi\zeta} = \frac{2\mu\mu'}{r^3}\Big(nl' + n'l + \frac{3}{r}(\cos\theta'(nx'+lz') - \cos\theta(l'z+n'x)) + \frac{3}{r^2}$$
$$\Big(\cos\varepsilon(x'z+z'x) - 2(yx'-y'x)(mn'-nm') - 2(zy'-yz')$$
$$(lm'-ml') - 5\cos\theta\cos\theta'(zx'+z'x) - 2(ny'-mz')(l'y-m'x)$$
$$- 2(mx'-ly')(m'z-yn')\Big) + \frac{30}{r^3}\Big((yx'-y'x)(\cos\theta'(ny'-mz')$$
$$+ \cos\theta(n'y-m'z)) + (zy'-z'y)(\cos\theta'(mx'-ly') + \cos\theta$$
$$(m'x-l'y))\Big) + \frac{30}{r^4}(zy'-yz')(yx'-y'x)(\cos\varepsilon - 7\cos\theta\cos\theta')\Big)$$

APPENDIX V

Commutation of matrices U and $(G_d^{1/2} D^t)$

In trying to prove the relation

$$U(G_d^{1/2} D^t) = (G_d^{1/2} D^t)U \qquad (68)$$

it is convenient to proceed by steps so as to avoid unnecessary computations.

All the matrices involved here act on a 24 dimensional space which splits naturally in 12 coordinates pertaining to translations and 12 to rotations. Moreover there is a further splitting in 4 groups of 3 coordinates each among the rotational parameters. These splittings are apparent in matrices U, $G_d^{1/2}$ and D^t. See tables 11, 10 and 8 respectively.

First observe that in the "translation subspace" both D^t and $G_d^{1/2}$, and therefore its product $G_d^{1/2} D^t$ are scalar matrices and thus relation (68) is trivially true in this subspace.

In the orthogonal complement to this subspace, that is to say the subspace of "rotational coordinates" the product $G_d^{1/2} D^t$ takes the form

$$G_d^{1/2} D^t = \begin{vmatrix} A & O & O & O \\ O & A & O & O \\ O & O & A & O \\ O & O & O & A \end{vmatrix}$$

where the O stands for a 3x3 null matrix and the A for

$$\begin{vmatrix} 0.0298 & 0 & 0 \\ 0 & 0.0187 & 0 \\ 0 & 0 & 0.0229 \end{vmatrix} \begin{vmatrix} 0.9894 & 0.1443 & 0.0138 \\ -0.1428 & 0.9866 & -0.0788 \\ -0.025 & 0.076 & 0.9968 \end{vmatrix}$$

In this same subspace U takes the form

$$\begin{vmatrix} I & I & I & I \\ I & I & -I & -I \\ I & -I & I & -I \\ I & -I & -I & I \end{vmatrix}$$

where I is a 3x3 identity matrix. Now a direct computation shows that both $(G_d^{1/2} D^t)U$ and $U(G_d^{1/2} D^t)$ are equal to

$$\begin{vmatrix} A & A & A & A \\ A & A & -A & -A \\ A & -A & A & -A \\ A & -A & -A & A \end{vmatrix}$$

APPENDIX VI

Program used to calculate the force constants

The F matrix, as is shown in table 6, represents the potential energy; its elements are the force constants. Each element is a sum of a large number of interactions between the atoms of a molecule with the atoms of the molecules around it. It was explained before that all possible interactions within a distance of 7 Å were considered.

The program can be described by the following steps. See table 24.

1. One atom-atom potential is chosen, for example the one that describes C. . . C interactions. The A, B and C parameters for that potential are read.

2. The atomic coordinates, (D, E, F), of one atom are read. Let us call it C_1. These coordinates are transformed to Cartesian coordinates by the equations:

$$x = D\ 15.78 - F\ 11.02 \times 0.417 + 0.394$$

$$y = E\ 8.11 - 1.381$$

$$z = F\ 11.02 \times 0.908 - 8.23$$

3. The atomic coordinates, (T, P, R), of a C atom in another molecule are read. They are also transformed to Cartesian coordinates by similar equations.

4. The distance between the atoms is calculated.

5. The values for the different force constants are calculated.

$$DXX = \frac{\partial^2 V}{\partial x^2}, \; DYY = \frac{\partial^2 V}{\partial y^2}, \; DXY = \frac{\partial^2 V}{\partial x \, \partial y}, \text{etc.}$$

6. Those results are stored in the memory as SUXX, SUYY, SUXY, etc.

7. The statement GO TO 110 sends the calculation back to step 3, where the coordinates of a new atom are read. Steps 4 and 5 are repeated. In step 6 the new calculated values are added to the previous values.

This sequence is repeated for all possible C atoms that interact with C_1. When no more interactions with this specific atom can be found, the statement GO TO 100, step 8, sends the calculation back to step 2. Another C atom, located in the same molecule as C_1, is considered. All the steps followed with C_1 are repeated.

9. Once all the possible C...C interactions are considered the partial values for the force constants are printed.

10. The next statement, GO TO 130, sends the calculation to step 1. A new set of A, B and C parameters are read. They describe the Buckingham potential for another kind of atom-atom interaction.

The program ends when all the potentials and interactions are considered. The desired force constants are obtained from the sum of all individual force constants.

TABLE 24

FORCE CONSTANT PROGRAM

```
            SUXX= 0.
            SUYY = 0.0
            SUZZ = 0.0
            SUXY = 0.0
            SUXZ = 0.0
            SUYZ = 0.0
            SUXN = 0.0
            SUXM = 0.0
            SUXO = 0.0
            SUYN = 0.0
            SUYM = 0.0
            SUYO = 0.0
            SUZN = 0.0
            SUZM = 0.0
            SUZO = 0.0
            SUNN = 0.0
            SUMM = 0.0
            SUOO = 0.0
            SUNM = 0.0
            SUNO =0.0
            SUMO = 0.0
       130 READ 1, A,B,C
         1 FORMAT (F8.1,F8.0,F8.5)
  1         IF(A.EQ.1.) GO TO 140
            PRINT 4, A,B,C
         4 FORMAT(3X,2HA=,F8.1,5X,2HB=,F8.0,5X,2HC=,F8.5)
       100 READ 2, D,E,F
         2 FORMAT (3F8.5)
  2         IF (D.EQ.99.0) GOTO 120
            X = D* 15.78 -F*11.02* 0.417 + .394
            Y = E*8.11 -1.381
            Z = F *11.02* 0.9063 - 8.23
       110 READ 3, T,P,Q
         3 FORMAT (3F8.5)
  3         IF (T.EQ.0.0) GO TO 100 ——————————→ 8
            XI =T*15.78 -Q*11.02* 0.417 +    .394
            YI = P*8.11 - 1.381
            ZI = Q*0.91 *11.02 - 8.23
            DELX = X-XI
            DELY = Y-YI
  4         DELZ = Z-ZI
            R= SQRT(DELX**2+ DELY**2+ DELZ**2)
            PRINT 5,R
         5 FORMAT (5X,F10.5)
            S = R**8
           DXX= 6.*A*(1.-8.*(X-XI)**2/R**2)/S + B*C* (-1.+ C*(X-XI)**2/R+
          1(X-XI)**2/R**2)/ (R*(2.718**(C*R)))
           DYY= 6.*A*(1.-8.*(Y-YI)**2/R**2)/S + B*C* (-1.+ C*(Y-YI)**2/R+
          1(Y-YI)**2/R**2)/ (R*(2.718**(C*R)))
           DZZ= 6.*A*(1.-8.*(Z-ZI)**2/R**2)/S + B*C* (-1.+ C*(Z-ZI)**2/R+
          1(Z-ZI)**2/R**2)/ (R*(2.718**(C*R)))
           DXY = (X-XI)*(Y-YI)*(-48.*A/S + B*C*(C+1./R)/(2.718**(C*R)))/(R**2
          1)
           DXZ = (X-XI)*(Z-ZI)*(-48.*A/S + B*C*(C+1./R)/(2.718**(C*R)))/(R**2
          1)
           DYZ = (Y-YI)*(Z-ZI)*(-48.*A/S + B*C*(C+1./R)/(2.718**(C*R)))/(R**2
          1)
```

```
       DXN=(Z*YI-Y*ZI)*(X-XI)*(-A*96./S+ 2.*B*C*(1./R+C)/(2.718**(R*C)))/
      1(R**2)
       DXM= A*12.*Z/R**8+(ZI*X-XI*Z)*(X-XI)*(-A*96./S+2.*B*C*(1./R+C)/
      1(2.718**(R*C)))/R**2  - 2.*B*C*Z/(2.718**(C*R)*(R))
       DXO=-A*12.*Y/R**8+(XI*Y-X*YI)*(X-XI)*(-A*96./S+2.*B*C*(1./R+C)/
      1(2.718**(R*C)))/R**2  + 2.*B*C*Y/(2.718**(C*R)*(R))
       DYN=-A*12.*Z/R**8+(Z*YI-Y*ZI)*(Y-YI)*(-A*96./S+2.*B*C*(1./R+C)/
      1(2.718**(R*C)))/R**2  + 2.*B*C*Z/(2.718**(C*R)*(R))
       DYM=(ZI*X-XI*Z)*(Y-YI)*(-A*96./S+ 2.*B*C*(1./R+C)/(2.718**(R*C)))/
      1(R**2)
       DYO= A*12.*X/R**8+(XI*Y-X*YI)*(Y-YI)*(-A*96./S+2.*B*C*(1./R+C)/
      1(2.718**(R*C)))/R**2  - 2.*B*C*X/(2.718**(C*R)*(R))
       DZN= A*12.*Y/R**8+(Z*YI-Y*ZI)*(Z-ZI)*(-A*96./S+2.*B*C*(1./R+C)/
      1(2.718**(R*C)))/R**2  - 2.*B*C*Y/(2.718**(C*R)*(R))
5      DZM=-A*12.*X/R**8+(ZI*X-XI*Z)*(Z-ZI)*(-A*96./S+2.*B*C*(1./R+C)/
      1(2.718**(R*C)))/R**2  + 2.*B*C*X/(2.718**(C*R)*(R))
       DZO=(XI*Y-YI*X)*(Z-ZI)*(-A*96./S+ 2.*B*C*(1./R+C)/(2.718**(R*C)))/
      1(R**2)
       DNN= A*24.*(Y*YI+ Z*ZI- 8.*(YI*Z-ZI*Y)**2/R**2)/(R** 8)+ 4.*B*C*
      1(((YI*Z-ZI*Y)**2)*(C+1./R)/R -(Y*YI+Z*ZI))/((2.718**(C*R))*(R))
       DMM= A*24.*(X*XI+ Z*ZI- 8.*(XI*Z-ZI*X)**2/R**2)/(R** 8)+ 4.*B*C*
      1(((XI*Z-ZI*Y)**2)*(C+1./R)/R -(X*XI+Z*ZI))/((2.718**(C*R))*(R))
       DOO= A*24.*(Y*YI+ X*XI- 8.*(YI*X-XI*Y)**2/R**2)/(R** 8)+ 4.*B*C*
      1(((YI*X-XI*Y)**2)*(C+1./R)/R -(Y*YI+X*XI))/((2.718**(C*R))*(R))
       DNM =-A*24.*((XI*Y+X*YI)/2.+ 8.*(Z*YI-Y*ZI)*(X*ZI-XI*Z)/(R**2))/S
      1 + 4.*B*C*((YI*Z-Y*ZI)*(X*ZI-Z*XI)*(C+ 1./R)/R + (X*YI+Y*XI)/2.) /
      2((2.718**(C*R))*(R))
       DNO =-A*24.*((XI*Z+X*ZI)/2.+ 8.*(Z*YI-Y*ZI)*(XI*Y-X*YI)/(R**2))/S
      1 + 4.*B*C*((YI*Z-Y*ZI)*(Y*XI-YI*X)*(C+ 1./R)/R + (Z*XI+ZI*X)/2.)/
      2((2.718**(C*R))*(R))
       DMO= -A*24.*((Y*ZI+Z*YI)/2.+ 8.*(Y*XI-X*YI)*(X*ZI-Z*XI)/(R**2))/S
      1 + 4.*B*C*((Y*XI-X*YI)*(X*ZI-Z*XI)*(C+1./R)/R +(Y*ZI+Z*YI)/2.)/
      2((2.718**(C*R))*(R))
       SUXX = SLXX + DXX
       SUYY = SLYY + DYY
       SUZZ = SLZZ + DZZ
       SUXY = SLXY + DXY
       SUXZ = SLXZ + DXZ
       SUYZ = SLYZ + DYZ
       SUXN = SLXN + DXN
       SUZO = SLZO + DZO
6      SUYM = SLYM + DYM
       SUXM = SLXM + DXM
       SUXO = SLXO + DXO
       SUYN = SLYN + DYN
       SUYO = SLYO + DYO
       SUZN = SLZN+ DZN
       SUZM = SLZM + DZM
       SUNN = SLNN + DNN
       SUMM = SLMM + DMM
       SUOO = SLOO + DOO
       SUNM = SLNM + DNM
       SUNO = SLNO + DNO
       SUMO = SLMO + DMO
7  ->  GO TO 110
   120 PRINT 12,SUXX,SUYY,SUZZ,SUXY,SUXZ,SUYZ
    12 FORMAT (5X,5HSUXX=,E16.5,5X,5HSUYY=,E16.5,5X,5HSUZZ=,E16.5/5X,5HSU
      1XY=,E16.5,5X,5HSUXZ=,E16.5,5X,5HSUYZ=,E16.5)
       PRINT 13, SUXN,SUXM,SUXO,SUYN,SUYM,SUYO,SUZN,SUZM,SUZO
9   13 FORMAT(7X,5HSUXN=,E16.5,5X,5HSUXM=,E16.5,5X,5HSUXO=,E16.5/5X,6HSU
      1YN=,E16.5,5X,5HSUYM=,E16.5,5X,5HSUYO=,E16.5/5X,5HSUZN=,E16.5,5X,5H
      2SUZM=,E16.5,5X,5HSUZO=,E16.5)
       PRINT 14,SUNN,SUMM,SUOO,SUNM,SUNO,SUMO
    14 FORMAT(7X,5HSUNN=,E16.5,5X,5HSUMM=,E16.5,5X,5HSUOO=,E16.5/5X,5HSUN
      1M=,E16.5,5X,5HSUNO=,E16.5,5X,5HSUMO=,E16.5)
10 ->  GO TO 130
   140 CALL EXIT
       END
```

LIST OF REFERENCES

1. B. J. Bulkin, W. B. Lok, J. Phys. Chem., 77, 326, (1973).
2. D. DuPre, E. Samulski, A. Tobolsky, "Polymer Science and Molecules". Edited by A. Tobolsky and H. Mark. John Wiley & Sons, Inc., 1971.
3. G. W. Gray, "Molecular Structure and Properties of Liquid Crystals". Academic Press, New York, 1962.
4. M. Ito, T. Shigeoka, J. Chem. Phys., 44, 1001, (1966).
5. T. Shimanouchi, I. Harada, J. Chem. Phys., 2651, (1964).
6. J. Durig, M. Walker, F. Baglin, J. Chem. Phys., 48, 4675, (1968).
7. I. Harada, T. Shimanouchi, J. Chem. Phys., 44, 2016, (1966).
8. D. Williams, J. Chem. Phys., 45, 3770, (1966).
9. A. Kitaigorodski, J. Chim. Phys., 63, 6, (1966).
10. G. Pawley, Phys. State Solid, 20, 347, (1967).
11. J. B. Bates, W. Busing, Chem. Div. Ann. Progr. Rept. for Period Ending May 20, 1973.
12. P. Richardson, E. Nixon, J. Chem. Phys., 49, 4276, (1968).
13. S. H. Walmsley, J. A. Pople, Molecular Physics, 8, 345, (1969).

14. G. Venkataraman, V. Sahni, Rev. Modern Phys., 42, 409, (1970).

15. G. Taddei, S. Califaro, Rivista del Nuovo Cimento, 1, 547, (1969).

16. W. Krigbaum, Y. Chatani, P. Barber, Acta Cryst., B26, 97, (1970).

17. S. Bhagavantam, K. Venkatarayudu, "Theory of Groups and its Applications to Physical Problems", 2d ed., Andhra Univ., Waltair, India, 1951.

18. F. A. Cotton, "Chemical Applications of Group Theory", Interscience Publishers. John Wiley & Sons, Inc., New York, 1963.

19. T. Shimanouchi, M. Tsuboi, T. Miyazawa, J. Chem. Phys., 35, 1597, (1961).

20. E. Wilson, J. Decius, P. Cross, "Molecular Vibrations", McGraw Hill, New York, 1955.

21. E. Whittaker, "A Treatise on the Analytical Dynamics of Particles and Rigid Bodies". Cambridge University Press, 1965.

22. B. J. Bulkin, F. Prochaska, J. Chem. Phys., 54, 635, (1971).

23. N. Amer, Y. Shen, J. Chem. Phys., 56, 2654, (1972).

24. B. J. Bulkin, D. Grunbaum, A. Santoro, J. Chem. Phys., 51, 1602, (1969).

25. J. O. Hirshfelder, C. F. Curtiss, R. B. Bird, "Molecular Theory of Gases and Liquids". John Wiley & Sons, Inc., New York, Chapman & Hall Limited, London, 1954.

26. K. Banerjee, L. Salem, Molecular Phys., 11, 405, (1966).

27. J. H. Jeans, "The Mathematical Theory of Electricity and Magnetism", 5th ed., Cambridge Univ. Press, 1925.

28. C. Johnson, OR TEP, Oak Ridge National Laboratory, 1965.

29. C. Smyth, "Dielectric Behavior and Structure", McGraw Hill, New York, 1955.

30. J. Smith, "Electric Dipole Moments", Butterworths Scientific Publications, London, 1955.

31. M. Davis, B. Kybett, Trans. Faraday Soc., 61, 1608, (1965).

32. P. De Santis, E. Giglio, A. Liquori, A. Ripamonti, Nature, 206, 456, (1965).

33. R. Mason, in "Perspectives in Structure Chemistry III". Edited by J. Dunitz and J. Ibers. John Wiley & Sons, New York, 1967.

34. A. Liquori, in "Symmetry and Function of Biological Systems at the Macromolecular Level". Nobel Symposium, 11th Sodergarn, 1968. Edited by A. Engstrom and B. Strandberg. Stockholm, New York, London. Wiley Interscience.

35. H. Longuet Higgins, Disc. Faraday Soc., 40, 7, (1965).

36. E. Bauer, J. Bernamont, J. Phys. Radium, 7, 19, (1936).

37. R. Porter, J. Johnson, J. Appl., 34, 51, (1963).

38. H. Arnold, Z. Phys. Chem. (DDR), 226, 146, (1964).