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# Lattice Vibrations of Acenaphthene

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Lattice vibrations of acenaphthene have been calculated using the rigid-molecule approximation. The spectrum has been completed with two new bands observed at low temperature. The intensity of some of the observed Raman bands has been discussed.

## INTRODUCTION

The lattice dynamics of molecular crystals has been extensively studied in the last few years in the framework of crystal dynamics and intermolecular forces. Hydrocarbon crystals with only two types of atoms are especially suitable for such studies, since the number of parameters describing intermolecular potential functions is considerably reduced. This makes it possible to study lattices even with a large number of atoms, such as acenaphthene with 88 atoms in the unit cell distributed among four molecules. The experimental study of the lattice dynamics of the acenaphthene crystal was first performed by Mathieu *et al.*[1] Using vibrational analysis, they determined which of the two space groups ($D_{2h}^{5}$[2] or $C_{2v}^{2}$[3]) proposed by X-ray diffraction measurements corresponds to acenaphthene. Later, other experiments were performed in the Raman[4,5] and far IR spectrum.[6] In spite of the relatively good recordings in all measurements, the 21 bands anticipated by the group-theory treatment were not observed in the spectrum. Only 19 bands were observed at room temperature in the Raman[4,5] and far IR spectrum.[6] One band of symmetry species $A_1$ (85 cm$^{-1}$) active in the IR spectrum, was systematically missing from the Raman spectrum. The other two missing bands are of symmetry species $A_2$ and $B_2$. Experimental data obtained so far offer no satisfactory explanation of the absence of the first band in the Raman spectrum nor of the two missing bands in the Raman and far IR spectra. This problem could be explained only by normal-coordinate analysis.

Hawranek[7] has recently performed calculations for librational frequencies in the acenaphthene lattice using a model in which complete separation of rotational from translational modes is assumed. The absence of the inversion centrum in the lattice space group does not allow such an assumption.[8] Therefore, the frequencies obtained by this approximation are difficult to assign to the observed spectrum.

In order to explain the absence of the two bands in the spectra of acenaphthene observed so far,[1,4,5,6] we calculated the complete spectrum of external vibrations in this crystal and measured the Raman spectrum of a single crystal at low temperatures. The intermolecular potential functions proposed by Williams[9] and Kitaigorodskii[10] were used in our calculations for comparison.

## CRYSTAL SYMMETRY AND SELECTION RULES

Acenaphthene crystallizes in the orthorhombic system, space group $C_{2v}^2$ ($P_{cm}2_1$), with four molecules in the unit cell (Figure 1). The molecules are separated into two sets of crystallographically independent units. Each molecule occupies a site of symmetry $C_s$. Pairs of crystallographically dependent molecules are symmetrical with respect to the binary axes ($C_2^c$). As can be seen from Figure 1, the inertial axes of one set of molecules are parallel to the crystallographic axes (Set I), while the axes of the other set (Set II) are tilted against the crystal axes *a* at 62°. Since the molecules in both sets have the same site symmetry, they should satisfy the same selection rules derived by the group-theory treatment and the correlation of molecular, site, and factor symmetry group, as given in Table I.

The lattice vibrational spectrum contains 24 modes. The total irreducible representation of external vibrations is

$$\Gamma(\text{vib}) = 6A_1 + 6A_2 + 6B_1 + 6B_2.$$

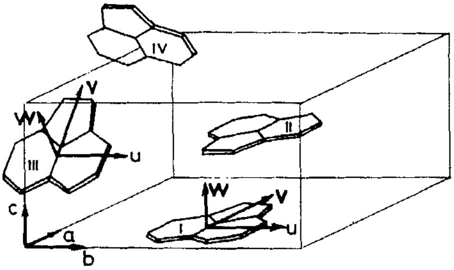

FIGURE 1 The unit cell of acenaphthene crystal.

TABLE I

Correlation of molecular, site, and factor symmetry group

| | Molecular group $C_{2v}$ | | | | | Site group $C_s$ | | Factor group | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Each set | Lattice (2 sets) |
| | $E$ | $C_2^V$ | $\sigma_U$ | $\sigma_W$ | | | $\sigma_U \equiv \sigma_b$ | | $E$ $C_2^c$ | $\sigma_U \equiv \sigma_b$ $\sigma_a$ |
| $a_1$ | 1 | 1 | 1 | 1 | $T_V$ | $A'$ | $T_V, T_W, R_U$ | $A_1$ | $(T_a, R_U) + T_c$ | $2(T_a, R_U) + T'_c - T_c$ |
| $a_2$ | 1 | 1 | −1 | −1 | | | $(T_a, T_c)$ | $A_2$ | $(T_b, R_V, R_W)$ | $2(T_b, R_V, R_W)$ |
| $b_1$ | 1 | −1 | 1 | −1 | $T_W, R_U$ | $A''$ | $T_U \equiv T_b$ | $B_1$ | $(T_c, R_U) + T_a$ | $2(T_c, R_U) + T'_a - T_a$ |
| $b_2$ | 1 | −1 | −1 | 1 | $T_U, R_W$ | | $R_V, R_W$ | $B_2$ | $(R_V, R_W) + T_b$ | $2(R_V, R_W) + T'_b - T_b$ |

$T_i$ = translational motions of molecules in a set
$T'_i$ = translational motions of two sets against each other

The acoustic modes are given by

$$\Gamma(AT) = 1A_1 + 1B_1 + 1B_2.$$

The presence of two sets of molecules in the lattice gives rise to two types of optical translational modes: the one ($OT$) describes translational vibrations of two molecules in a set, while the other ($OT'$) describes translations of two rigid sets against each other

$$\Gamma(OT) = 2A_1 + 2A_2 + 2B_1$$

and

$$\Gamma(OT') = 1A_1 + 1B_1 + 1B_2.$$

Finally, the optical librational modes are given by

$$\Gamma(OR) = 2A_1 + 2B_1 + 4A_2 + 4B_2.$$

The whole optical spectrum is given by

$$\Gamma(O) = 2A_1^R + 2B_1^R + 4A_2^R + 4B_2^R + 2A_1^T + 2B_1^T + 2A_2^T + 1A_1^{T'} + 1B_1^{T'} + 1B_2^{T'}.$$

## LOW-TEMPERATURE MEASUREMENTS

The calculations performed in this work are based on the Raman[4] spectrum and on the far IR spectra reported by Wyncke *et al.*[6] The relative intensities of bands were used from our previous measurements.[4] Low-frequency Raman spectra of a single crystal were taken at different temperatures in the range from room temperature to 40°K. Measurements were performed using a Coderg triple monochromator model T800. Figure 2 shows the observed frequencies plotted against temperature. The curves describing the frequency

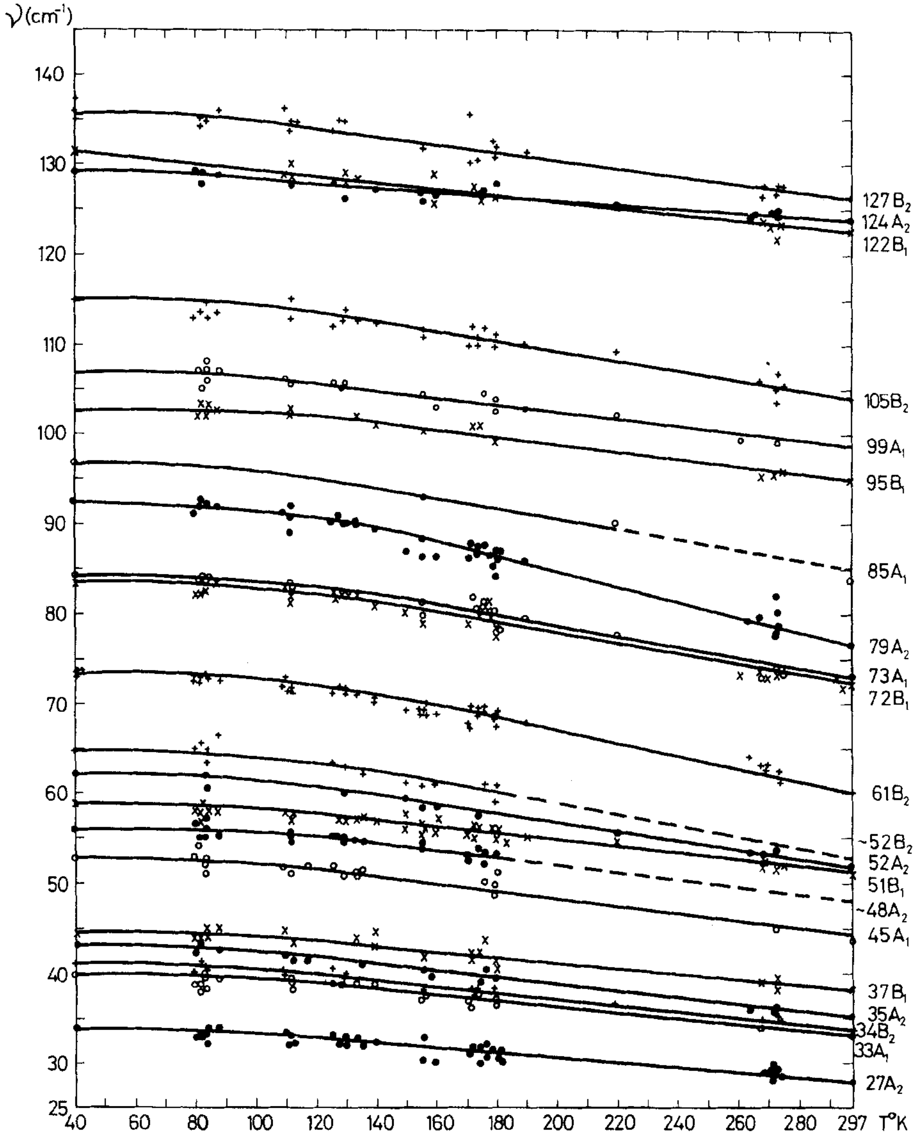

FIGURE 2 Temperature dependence of Raman frequencies.

dependence on temperature exhibit different slopes, especially at higher temperatures. Some of the bands were observed only at lower temperatures. Since all spectra were polarized, the three new bands were detected as being of symmetry species $A_2$, $B_2$, and $A_1$. Their frequencies at room temperature, obtained by approximate extrapolation, are 48, 52, and 85 $\text{cm}^{-1}$, respectively, as shown in Figure 2.

## NORMAL-MODE CALCULATIONS AND INTERMOLECULAR POTENTIAL FUNCTIONS

Normal-mode calculations were performed by the rigid-molecule approximation of Wilson's *GF*-matrix method, as given by Shimanouchi.[13] This method was particularly suitable for our purposes, since we wanted to give a description of lattice dynamics and to determine the degree of couplings between rotational and translational modes. The programme used was written for similar studies of the crystal lattice of benzoic acid.[14] In the present work the programme was extended and adapted for the computer UNIVAC 1106, by means of which all calculations were performed.

In calculating lattice vibrations in molecular crystals the main problem is to determine the force constants for intermolecular interactions. It is generally assumed that the packing of molecules and their mutual orientations in the lattice are determined by van der Waals and repulsion forces[3, 15, 16] and expressed as a sum of all unbonded atom–atom pair potentials. The potential-energy function of intermolecular interactions under these conditions is usually of the type of the so-called "6-exp" function

$$V = -\frac{A}{r^6} + B\exp(-Cr),$$

where $r$ is the distance between unbonded atoms of a pair of molecules. The parameters $A$, $B$, and $C$ are taken from the measurements performed by Williams[9] and Kitaigorodskii.[10] They studied the packing of molecules in aromatic crystals and obtained these parameters by minimizing the free energy of the lattice. Among several sets of such parameters proposed by Williams,[9] Set IV is the most suitable one for aromatic crystals. The values of the parameters $A$, $B$, and $C$, used in our calculations, are given in Table II. Calculations of vibrational spectra using the two sets of parameters[9,10] and for different cut-off points at distance $r$ enables us to compare the adequacy of these functions for the acenaphthene crystal. Calculations were performed using the Kitaigorodskii function for all nearest neighbours within 2.7 Å and then the range was increased up to 4.2 Å in steps of 0.1 Å. Calculations with the Williams function were performed at the cut-off points 3.8 Å and 4.2 Å.

TABLE II
Parameters for the potential functions used

| | C—C | | | C—H | | | H—H | | |
|---|---|---|---|---|---|---|---|---|---|
| $A$ (kcal/mol · Å$^6$)<br>$B$ (kcal/mol)<br>$C$ (Å$^{-1}$) | $A$ | $B$ | $C$ | $A$ | $B$ | $C$ | $A$ | $B$ | $C$ |
| Kitaigorodskii[10] | 358.0 | 42 000 | 3.58 | 154 | 42 000 | 4.12 | 57.0 | 42 000 | 4.86 |
| Williams[9] | 568 | 83 630 | 360 | 125 | 8766 | 3.67 | 27.3 | 2654 | 3.74 |

## DISCUSSION

Table III summarizes the observed and calculated spectra. The Raman spectra observed previously[4] at room temperature are given in the first column. The intensities of all bands were measured relatively to the band 79 $A_2$ (the strongest band, of intensity 100) and are given in the parentheses. The next column gives the far IR spectrum[6] observed at room temperature and the Raman spectrum observed at a temperature of 40°K. The results obtained at the cut-off points of 4.2 Å for both functions used are given in the column of calculated spectra. The symmetry species were derived through symmetry coordinates and the assignment of molecular motions wes determined by the components of eigenvectors for each mode. According to the rigid-body approximation, individual molecules are considered to perform librational ($R$) and translational ($T$) motions. In the case of libration the subscript denotes the axis of inertia; in the case of translation it denotes the crystallographic axes (the components of eigenvectors were transformed into the crystallographic system). The superscript denotes the set of molecules contributing to the mode. The contributions from free molecular librations and translations to the real mode are expressed in percentage (eigenvectors are normalized) and given in the column of assignments. Due to the point group symmetry, the lattice mode might be pure rotational or translational motions of symmetrically equivalent molecules such as 95 $B_1$, 73 $A_1$, and 33 $A_1$. This space group also allows combined modes in which translational and rotational motions of molecules from different sets contribute together to build up two lattice modes, as in the case of 99 $A_1$ and 85 $A_1$. In the latter case, the same type of free molecular motions is active in the two modes, but with different amplitude distributions. Therefore, the splitting of such modes should be relatively small. Obviously, more complicated couplings can arise, giving lattice modes of a very complex nature, as can be seen in the column of assignments for our spectrum. In order to give a better description of some of the lattice modes, we tried to represent them by drawing translational and rotational components

TABLE III

The observed and calculated spectra

| Species | Observed | | | Calculated | | Assignment | | Assignment[4] |
|---|---|---|---|---|---|---|---|---|
| | Room temperature | | $T$ = 40°K | Kitai-gorodskii[10] | Williams[9] | | | |
| | Raman[4] | IR[6] | Raman | | | | | |
| $B_2$ | 127 (15) | — | 135.5 | 97.9 | 95.5 | $R_V^{II}(71\%) + R_V^{I}(24\%)$ | $R_V^{II} + R_V^{I}$ | $R_V^{II}$ |
| $A_2$ | 124 (12) | Inactive | 129 | 93.9 | 93.1 | $R_V^{I}(58\%) + R_W^{II}(23\%) + R_V^{II}(17\%)$ | $R_V^{I} + R_W^{II} + R_V^{II}$ | $R_V^{II}$ |
| $B_1$ | 122 (21) | — | 131 | 116.5 | 117.7 | $T_c^{I}(56\%) + R_U^{I}(44\%)$ | $T_c^{I} + R_U^{I}$ | $T_c^{I} + R_U^{I}$ |
| $B_2$ | 105 (57) | — | 115 | 76.6 | 76.5 | $R_W^{II}(51\%) + R_V^{I}(25\%) + R_V^{II}(11\%)$ | $R_W^{II} + R_V^{I} + R_V^{II}$ | $R_V$ |
| $A_1$ | 99 (w; w; 0) | 98m | 107 | 88.2 | 90.9 | $T_a^{II}(82\%) + R_U^{I}(16\%)$ | $T_a^{II} + R_U^{I}$ | $T_a^{I} + R_U^{I}$ |
| $B_1$ | 95 (26) | 94s | 102.5 | 85.4 | 84.2 | $R_U^{II}(98.8\%)$ | $R_U^{II}$ | $T_c^{I} + R_U^{I}$ |
| $A_1$ | — | 85s | 97 | 93.3 | 85.9 | $R_U^{I}(80\%) + T_a^{II}(14\%)$ | $R_U^{I} + T_a^{II}$ | $T_a^{I} + R_U^{I}$ |
| $A_2$ | 79 (100) | — | 92.5 | 79.0 | 76.5 | $R_V^{II}(59\%) + R_W^{I}(24\%) + R_V^{I}(14\%)$ | $R_V^{II} + R_W^{I} + R_V^{I}$ | $T_b + R_W$ |
| $A_1$ | 73 (S; 0; vS) | 73m. | 84 | 72.2 | 70.4 | $R_U^{II}(96.8\%)$ | $R_U^{II}$ | $T_a^{II} + R_U^{II}$ |
| $B_1$ | 72 (33) | 74m | 83.5 | 63.8 | 65.7 | $T_c^{II}(70\%) + R_U^{I}(15\%)$ | $T_c^{II} + R_U^{I}$ | $T_c + R_U$ |
| $B_2$ | 61 (59) | — | 73.5 | 56.2 | 55.8 | $R_W^{I}(59\%) + T_b^{I'}(18\%) + T_b^{II'}(18\%)$ | $T_W^{I} + T_b'$ | $T_b + R_W^{II}$ |
| $B_2$ | ~ 52 | — | 64.5 | 45.6 | 48.7 | $T_b^{I'}(26\%) + T_b^{II'}(26\%) + R_W^{I}(36\%)$ | $T_b' + R_W^{I}$ | |
| $B_1$ | 51 (47) | 51m | 59 | 47.6 | 48.6 | $T_a^{I'}(38\%) + T_a^{II'}(38\%) + R_U^{I}(14\%)$ | $T_a' + R_U^{I}$ | $T_c + R_U$ |
| $A_2$ | 52 (5) | Inactive | 62 | 52.7 | 53.4 | $T_b^{I}(46\%) + R_W^{I}(22\%) + T_b^{II}(9\%)$ | $T_b^{I} + R_W^{I} + T_b^{II}$ | $T_b + R_W$ |
| $A_2$ | ~ 48 | Inactive | 56 | 49.8 | 50.6 | $T_b^{II}(59\%) + R_W^{II}(27\%) + R_V^{I}(11\%)$ | $T_b^{II} + R_W^{II} + R_V^{I}$ | |
| $A_1$ | 45 (m; w; 0) | 48w | 53 | 45.7 | 45.0 | $T_c^{I'}(42\%) + T_c^{II'}(42\%) + T_a^{I}(12\%)$ | $T_c' + T_a^{I}$ | $T_a^{II} + R_U^{II}$ |
| $B_1$ | 37 (10) | 38w | 44.5 | 35.4 | 39.9 | $T_c^{II}(29\%) + R_U^{I}(27\%) + T_c^{I}(24\%)$ | $T_c^{II} + R_U^{I} + T_c^{I}$ | $T_a'$ |
| $A_2$ | 35 (11) | Inactive | 43 | 37.5 | 38.9 | $T_b^{I}(46\%) + R_W^{II}(28\%)$ | $T_b^{I} + R_W^{II}$ | $T_b + R_W$ |
| $B_2$ | 34 (38) | 34w | 41 | 25.4 | 25.2 | $R_W^{II}(45\%) + R_V^{I}(44\%)$ | $R_W^{II} + R_V^{I}$ | $T_b' + R_W^{II}$ |
| $A_1$ | — | 33w | 40 | 38.8 | 38.4 | $T_a^{I}(82\%)$ | $T_a^{I}$ | $T_c^{I}$ |
| $A_2$ | 27 (32) | Inactive | 34 | 33.2 | 35.7 | $R_W^{I}(43\%) + R_V^{II}(16\%) + T_b^{II}(21\%) + R_W^{II}(15\%)$ | $R_W^{I} + R_V^{II} + T_b^{II} + R_W^{II}$ | $T_b + R_W$ |

Numbers in parentheses indicate the relative intensity.

of eigenvectors. Comparison between the observed and calculated spectrum, regardless of the potential function used, shows rather good agreement except for the modes of highest frequencies. The values calculated for these modes are systematically lower than the observed ones. This is particularly true of some modes assigned to rotational motions. Such an aberation might be due to couplings between lattice modes of highest frequency and molecular torsional vibrations of very low frequency.[5] One could also discuss the type of the potential functions used, but our intention was to investigate the adequacy of these functions in the case of acenaphthene.

Before interpreting our results, we wish to point out some considerations concerning the intensity of the Raman bands in the lattice vibrational spectrum. The oriented-gas approximation for calculating band intensities in the Raman spectrum can yield information on the relative distributions of terms in intensity matrices of different lattice modes. In this model, lattice vibrations were considered to come from motions of rigid molecules the symmetry of which is not deformed by the crystal field. Consequently, the inensity of each mode is a function of geometrical and optical parameters of the molecules in the lattice. Using this approximation, the intensity matrices of librational modes in the Raman spectrum can be calculated by the method of Kastler and Rousset.[17,18] As the geometry of the lattice is an essential parameter, it is obvious that the intensity matrices for the two sets of molecules are different in our case. The intensity matrices for acenaphthene calculated by this method are given in Table IV. From these results it may be concluded that three bands corresponding to librations of molecules I around their axes $U$,

TABLE IV

Intensity matrices for librational modes calculated by the "oriented-gas" approximation

| | $E_a^2$ | $E_b^2$ | $E_c^2$ | $R_U = 2(A_1 + B_1)$ | | $E_a^2$ | $E_b^2$ | $E_c^2$ |
|---|---|---|---|---|---|---|---|---|
| $P_a^2$ | 0 | 0 | 1 | | $P_a^2$ | 0.7 | 0 | 0.3 |
| $P_b^2$ | 0 | 0 | 0 | | $P_b^2$ | 0 | 0 | 0 |
| $P_c^2$ | 1 | 0 | 0 | | $P_c^2$ | 0.3 | 0 | 0.7 |
| | $E_a^2$ | $E_b^2$ | $E_c^2$ | $R_V = 2(A_2 + B_2)$ | | $E_a^2$ | $E_b^2$ | $E_c^2$ |
| $P_a^2$ | 0 | 0 | 0 | | $P_a^2$ | 0 | 0.77 | 0 |
| $P_b^2$ | 0 | 0 | 1 | | $P_b^2$ | 0.77 | 0 | 0.23 |
| $P_c^2$ | 0 | 1 | 0 | | $P_c^2$ | 0 | 0.23 | 0 |
| | $E_a^2$ | $E_b^2$ | $E_c^2$ | $R_W = 2(A_2 + B_2)$ | | $E_a^2$ | $E_b^2$ | $E_c^2$ |
| $P_a^2$ | 0 | 1 | 0 | | $P_a^2$ | 0 | 0.23 | 0 |
| $P_b^2$ | 1 | 0 | 0 | | $P_b^2$ | 0.23 | 0 | 0.77 |
| $P_c^2$ | 0 | 0 | 0 | | $P_c^2$ | 0 | 0.77 | 0 |

*V*, and *W* are expected to be missing from the Raman spectrum, namely, their intensities must be zero. However, as we emphasized earlier, we observed that only one of these bands was missing from the Raman spectrum. It is clear that the conditions imposed by the method of Kastler and Rousset are not satisfied in all librational modes.

## RESULTS

The discussion of our results can be carried out classifying transitions by symmetry species. In our further considerations we refer to frequencies of the spectrum observed at room temperature. In the case of the calculated spectrum frequencies were obtained using the Kitaigorodskii potential functions, if not stated otherwise.

### Species $A_1$ : 2 rotational + 3 translational modes

Rotational modes in this species are related to the *U*-axis of the molecule and two translations are related to the crystallographic *a*-axis. The third translational mode $T_c'$ describes the relative motion of two sets along the *c*-axis. The rotational mode $R_U^{II}$, observed as the 73 $A_1$ band, is a pure (96.8%) librational mode (see Figure 3). The validity of the Kastler-Rousset treatment is confirmed in this case by agreement between the calculated (0.7, 0, 0.7) and the observed (*S*, 0, *vS*) form of the intensity matrix. The $R_U^I$ motion in Set I is slightly coupled to the translation $T_a$ of molecules II (see Figure 4). The local crystal field of molecules I is not deformed by these translations. The corresponding calculated frequencies are 93 and 85 cm$^{-1}$. The observed

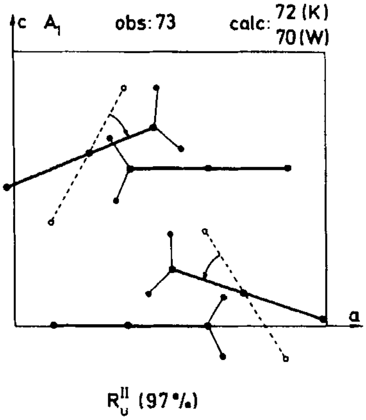

FIGURE 3 Pure rotational mode in species $A_1$.

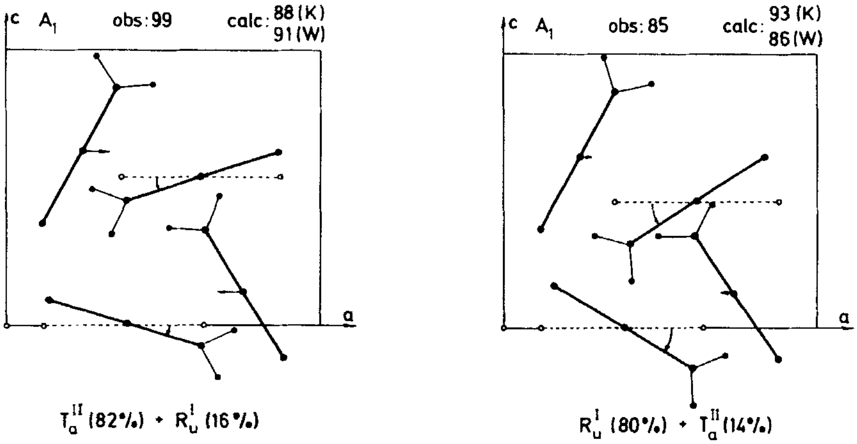

FIGURE 4 Two modes of species $A_1$ with couplings of translational and rotational motions.

spectrum indicates that the conditions for application of the method of Kastler and Rousset are also satisfied. In fact, from the calculated intensity matrix (Table IV) it follows that the corresponding Raman band must be of zero intensity. The 85 $A_1$ band is the only band that is missing from the Raman spectrum; it is therefore assigned to the lattice mode, in agreement with the calculated frequencies and with the Kastler–Rousset treatment. A weak band was observed at lower temperature in this region of the Raman spectrum, and it was assigned to the 85 cm$^{-1}$ band by extrapolation at room temperature. It is interesting to note that this band was observed only in the $P_{cc}$ component. The observed 99 $A_1$ band (see Figure 4) corresponds to the rotational mode $R_U^I$ but with a higher contribution of the translational motion, as can be seen from Table III. It is interesting to note the differences in frequences calculated for the two modes (85 and 99 $A_1$) using the different type of potential functions: The frequency obtained by the Kitaigorodskii function is higher for the predominantly librational mode (93 cm$^{-1}$) than for the predominantly translational mode (88 cm$^{-1}$). On the other hand, the Williams potential function gives the opposite distribution (86, 91), which is in very good argeement with the observed frequencies 85 and 99 cm$^{-1}$. This is also the highest aberation between the two calculated spectra.

The translational mode 33 $A_1$ is assigned to the pure translational mode of Set I, while the mode 45 cm$^{-1}$ corresponds to the relative motion of two crystallographically independent sets along the *c* axis.

### Species $B_1$: 2 rotational + 3 translational modes

Motions of molecules of species $B_1$ are related to the same axes as in class $A_1$. The only pure rotational mode (98.8%) in this species is related to the lattice mode $R_U^{II}$ and was assigned to the observed band 95 $B_1$. The other librational modes are coupled to translations. The observed band 51 cm$^{-1}$ is a predominantly translational mode in which two sets move rigidly against each other along the a axis. The highest frequency mode of symmetry $B_1$, namely, the band observed at 122 cm$^{-1}$, is in better agreement with the calculated frequencies (116 and 117 cm$^{-1}$) than the other bands in the upper part of the spectrum. It is also interesting to notice that this mode is a predominantly translational one, and is the only mode of the translational type in this energy region.

### Species $A_2$: 4 rotational + 2 translational modes

In species $A_2$ and $B_2$, couplings occur predominantly between rotational motions $R_V$ and $R_W$. For example, the 79 cm$^{-1}$ band, the most intense band in the Raman spectrum, is assigned to the calculated 79 $A_2$ mode in which all molecules in the lattice perform rotational motions about their $V$ and $W$ axes. The $A_2$ component of the $R_V^I$ libration, which should be absent from the Raman spectrum according to our intensity calculations, is present in all spectra observed. In fact, the $R_V^I$ and $R_W^I$ librations do not conserve the symmetry of the local field. In addition, the rotational $R_V^I$ motion is strongly coupled to other librations. It is seen from Table III that $R_V^I$ is a component belonging to the librational modes 79 $A_2$ and 124 $A_2$. Therefore, the above method of intensity calculations is not applicable in the case of the $R_V^I$ component. It should also be emphasized that the most important discrepancies between the calculated and observed spectra are found in transitions of symmetry species $A_2$ and $B_2$. These correspond mostly to rotational modes. The band of symmetry $A_2$, which is missing from the spectra observed so far, is one of the bands assigned to the doublet arising from coupling of rotations $R_W^I$ and $R_W^{II}$ to translations $T_b$. From low-temperature measurements it was possible to identify this band and to extrapolate its frequency of about 48 cm$^{-1}$ at room temperature.

### Species $B_2$: 4 rotational + 1 translational modes

The mixing of individual molecular motions which leads to real lattice modes is particularly characteristic of this species. There is no mode of this group in which only one type of motion would be active. The relative motion of two rigid sets ($T_b'$) which are active in this species is strongly coupled to $R_W^I$ librations. These motions give rise to a doublet of bands for which the calculated frequencies are 56 and 46 cm$^{-1}$. In this spectral region only one, relatively strong band was observed in the Raman spectrum at 61 cm$^{-1}$. This band was not observed in the IR spectrum. Since the 61 cm$^{-1}$ band becomes very fine at low temperature, a weak band of symmetry $B_2$ appears. Its frequency at room temperature is about 52 $cm^{-1}$, as seen from Figure 2.

## CONCLUSION

The rigid-body approximation, applied in this study, is particularly suitable for description of the lattice dynamics of molecular crystals. However, it is less successful in determining real transition energies of different modes. The discrepancies occurring in the determination of transition energies could probably be reduced by taking into account possible couplings of internal and external molecular modes or by using another type of intermolecular potential function. In this work we were interested in the dynamics rather than in the transition energies of the lattice. Therefore, we restricted our study to the rigid-body approximation, even though some of the calculated frequencies are not in very good agreement with the observed spectra.

The bands missing from the observed IR and Raman spectra can be explained by the overlap of doublets. The absence of the band in the Raman spectrum is due to the form of intensity matrices. The new bands we observed are the bands 48 $A_2$ and 52 $B_2$. The first band forms part of a doublet arising from the couplings of rotational motions $R_W$ and translational motions $T_b$. The difference in frequency between the two modes is small, which explains the overlapping of the corresponding bands at room temperature. The 52 $cm^{-1}$ band belongs to a doublet arising from the couplings of $R_W^1$ with the translations of both sets $T_b'$. In this case the two modes exhibit a difference in frequency which is somewhat larger (61–52 $cm^{-1}$) than that for the 48 $A_2$ band but the difference in intensity of the Raman bands is much more pronounced. In IR spectra, either the 48 $A_2$ band or the 52 $B_2$ band was observed.

As we emphasized previously, the application of the method of Kastler and Rousset for calculating the intensity matrices of Raman bands indicates the existence of three (Raman) bands with intensity zero. Comparison of the observed and calculated spectra indicates only one such band (85 $A_1$). The nature of the corresponding modes shows that the method is valid only in the cases in which the symmetry of the local field is rigorously conserved. In these cases even the distribution of terms in the intensity matrix is very well predicted, as can be seen from the band 73 $A_1$.

The last column of Table III shows an earlier[4] assignment made on the basis of symmetry considerations. In some cases this assignment is in relatively good agreement with that obtained by calculation. Omitting some errors in symmetry species from the observed spectrum used by Hawranek *et al.*,[7] the spectrum calculated by the same[7] authors is in agreement with our assignment only for pure rotational modes 95 $B_1$ and 73 $A_1$, as expected.

The study of the two intermolecular potential functions used does not allow us to draw conclusions which of the two functions would be more appropriate to our considerations. It may, however, be concluded that a longer range should be taken in the case of the Williams potential function because of its slow convergency.

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