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# Temperature Dependence of the Low-Frequency Vibrational Spectrum of the Furane Crystal

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Infrared and Raman spectra of lattice vibrations of the furane crystal have been recorded at different temperatures ranging from 12 to 253 K. Because of the very low crystallization temperature of this solid, the spectra were recorded on a polycrystalline sample. However, since the selection rules for infrared (IR) and Raman transitions in the factor group $D_4$ are different, the interpretation of the lattice vibrational spectrum in the ordered phase could be given by comparison of the observed IR and Raman spectra with the calculated frequencies from the results of a normal-mode calculation.

## I INTRODUCTION

We have already reported preliminary results of our investigations of the low-frequency spectrum of the furane crystal.[1,2] Recently, we have performed some new measurements of the temperature dependence of IR and Raman spectra of this crystal; these enable us to give a more complete interpretation of this spectrum. The solid furane (below 187.55 K) possesses two crystalline modifications.[3] The first one (phase I) exhibits all characteristics of an orientationally disordered crystal (ODIC, usually called "plastic" crystals) and occurs in the temperature region of 187–150 K. Below this temperature, the furane crystal possesses an ordered phase (phase II).

Several investigations performed in the last few years have contributed to better understanding of the molecular dynamics of the furane crystal. The most important step was taken by Fourme,[4] who performed an X-ray analysis of both solid phases of this crystal. Information on the character of molecular motion was obtained by dielectric dispersion measurements,[5] NMR investigations,[6] and studies of IR and Raman band shapes.[7]

However, to the best of our knowledge, the low-frequency vibrational spectrum of furane has received little attention so far. In the present paper we observe and interpret the lattice vibrational spectrum of furane in the ordered phase using Raman and IR spectroscopic methods and a normal-mode calculation.[1] In our opinion, the complete interpretation of the lattice vibrational spectrum in the ordered phase and the study of the variations of the spectrum with temperature can be an important source of information in the effort to understand the dynamics of this molecule in its plastic phase.

## II THE CRYSTAL AND MOLECULAR STRUCTURE OF FURANE

The furane molecule ($C_4H_4O$), planar and of nearly perfect pentagonal shape, is of symmetry $C_{2v}$. The molecular structure of furane was determined using the electron-diffraction method[8] and microwave spectroscopy. The polymorphism of furane and its thermodynamic properties were extensively studied by Guthrie *et al.*[3] They also determined a small lambda point at 56 K, together with a transition at 150 K and fusion at 187.55 K. The same authors measured the head capacity, the heat of fusion, and the heat of the transition. The entropy of the transition was measured to be 3.26 e.u. Such a low entropy and the regular pentagonal shape of the molecule led Guthrie *et al.*[3] to the conclusion that the high-temperature phase is a plastic phase, in which the molecule can take five positions. This was supported by the entropy they calculated for such a conformational change, $\Delta S = R \ln 5 = 3.20$ e.u., which is close to the observed value 3.26 e.u. The study of molecular reorientation in the plastic phase using dielectric dispersion[5] furnished very high frequencies of reorientation, i.e., $\sim$2300 MHz at 154 K and $\sim$6250 MHz at 181 K. NMR investigations[6] confirmed the assumption of molecular reorientation and established that the reorientation occurred around an axis of order 2 or higher which was normal to the molecular plane.

The crystal structure analysis performed by Fourme[4] provided atomic positions for both high- and low-temperature phases. The lattice of the high-temperature phase (phase I) is orthorhombic, with four molecules in the unit cell. The dimensions of the lattice are $a = 8.65$, $b = 6.70$, and $c = 6.75$ Å. Two space groups were proposed for the furane crystal I: $D_{2h}^{18}$ (Cmca) or $C_{2v}^{17}$ (Aba2). Both of them allow four equivalent positions of the molecule at the site, which is in contrast to the earlier result.[3] The existence of four equivalent positions was also confirmed by calculations of the intermolecular potential.[10] The lattice of furane in the ordered phase (phase II) crystallizes in the tetragonal system, with four molecules in the unit cell. The lattice parameters are $a = 5.69$ Å and $c = 11.92$ Å. The corresponding space group is $D_4^4(P4_12_12)$ or $D_4^8$ ($P4_32_12$).

## III EXPERIMENTAL

Far-infrared (FIR) and Raman spectra were recorded at several temperatures in the region of 12–253 K, including the liquid, plastic, and ordered phases. The Raman spectra were recorded by three spectrometers, CODERG T800, SPEX 1401, and LOMO DFS 12. The FIR measurements were performed by means of a GRUBB PARSON and a CAMECA SI 36 type spectrometers. The accuracy of temperature measurements was different in each case, but was always better than $\pm 2$ K.

The growth of furane single crystals is associated with difficulties due to the low temperature of fusion (187 K). The orientation and cutting of samples at this temperature would require a particular technique. Since the measurements of the spectra were performed on polycrystalline samples, no polarization analysis was possible either in Raman or in FIR spectra.

A selection of Raman spectra (Figure 1) and of FIR spectra (Figure 2), recorded at different temperatures, indicate changes occurring in the spectrum due to temperature increase and phase transitions. In both spectra of

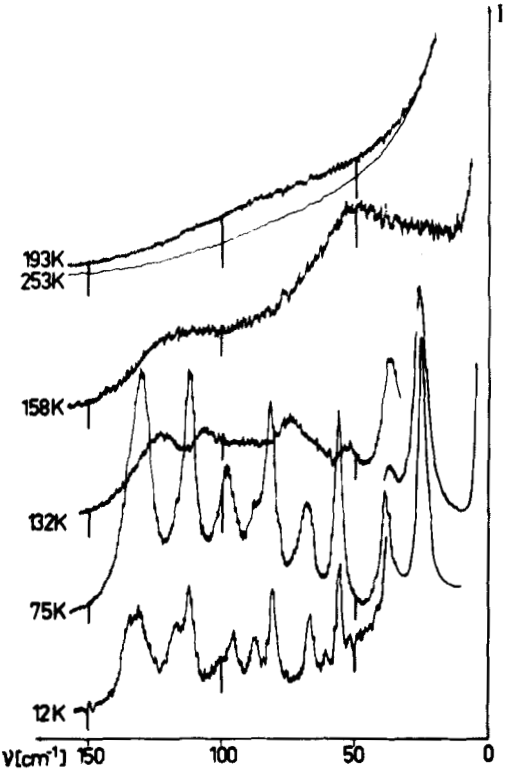


FIGURE 1 Selection of Raman spectra of furane recorded at different temperatures.

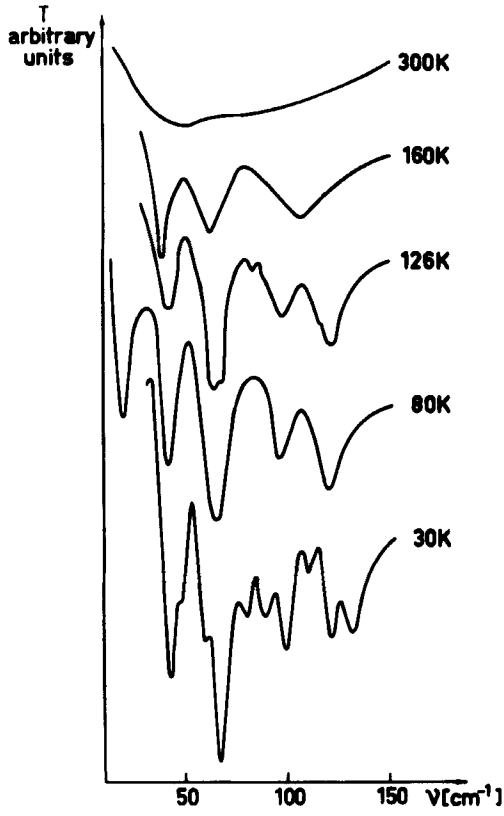


FIGURE 2 Selection of FIR spectra of furane recorded at different temperatures.

the ordered phase, the bands could be well resolved only at very low temperatures. With increasing temperature, both Raman and FIR bands exhibit a marked broadening, thus often screening weaker bands. Already at 100 K, most of the bands tend to form very broad spectral features whose peaks are difficult to determine with good accuracy. In addition, the recognition of the corresponding bands in the spectra recorded at different temperatures was rendered difficult because different modes exhibit different types of temperature dependence. This can be seen from the reproduced spectra, or still better from Figure 3, where all observed frequencies are plotted against temperature. The circles represent Raman frequencies, while the crosses represent FIR spectra. For very broad bands, apart from the peak frequency, the "broadness" of the band is roughly indicated by a bar. The symmetry of each band observed in the ordered phase is indicated on the left side of Figure 3. The lowest temperature for FIR measurements was

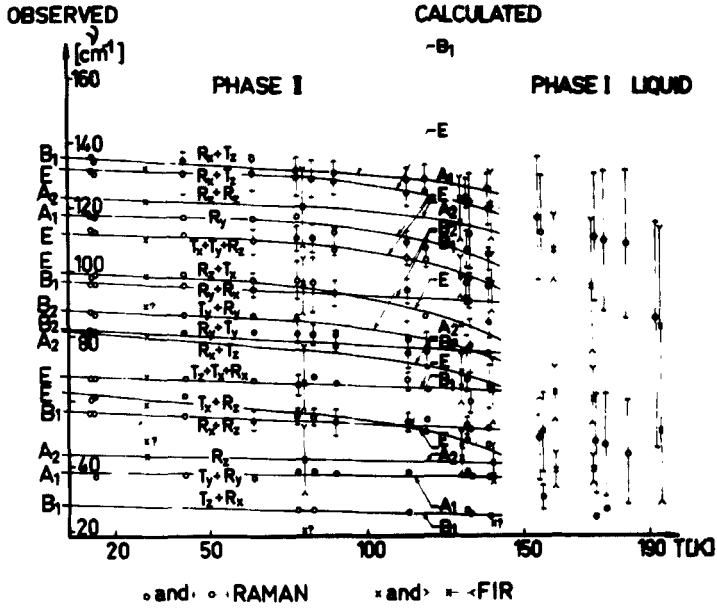


FIGURE 3 Temperature dependence of the low-frequency spectrum of furane.

30 K, while the Raman spectra were recorded at 12 K with a Spex spectrometer. This spectrometer did not allow us to resolve frequencies as low as 26 $cm^{-1}$, while the Coderg T800 spectrometer enabled us to separate this band at much higher temperature.

Owing to the relatively close temperatures of measurements, the correspondence between different spectra (Raman and FIR) at a particular temperature and between the same spectra at different temperatures could be established using the intensity of bands as a relevant parameter. While in the Raman spectra no excess of bands was observed, the number of observed frequencies in different FIR spectra varied and often exceeded the number of the eight bands expected. Thus, we could not assign the bands at 48 and 89 $cm^{-1}$ recorded at 30 K by a Grubb Parson spectrometer, nor the band at 20 $cm^{-1}$ observed at 80 and 140 K by a Cameca spectrometer.

At the temperature of the plastic phase, the Raman spectrum consisted of two very broad bands that were centered at about 115 and 50 $cm^{-1}$ and which indicated a relatively weak temperature dependence. A weak band at about 25 $cm^{-1}$ was observed at temperatures relatively distant from the transition to the ordered phase. The FIR spectrum of the plastic phase exhibited three distinct bands of frequencies 38, 62, and 106 $cm^{-1}$ at a temperature of 160 K. Some of them were very sensitive to temperature variations. In spite of the low accuracy of the frequency determinations of

such broad bands, it is evident from this investigation that the frequencies observed in the Raman and those observed in the FIR spectrum of the plastic phase of furane are different.

Above the temperature of fusion (187 K), the three bands in the Raman spectrum were replaced by a broad, unique band centered at about 80 $cm^{-1}$. This band disappeared almost completely at 257 K. The same feature was observed in the FIR spectrum at 300 K, but the observed band seemed to have another peak at about 50 $cm^{-1}$ (Figure 2).

## IV INTERPRETATION OF THE VIBRATIONAL SPECTRUM OF FURANE II

### A Vibrational analysis

As it has already been mentioned, in the ordered phase furane crystallizes in the tetragonal system, space group $D_4^4$ ($P4_12_12$) or $D_4^8$ ($P4_32_12$), with four molecules in the unit cell (Figure 4). The lattice vibrational spectrum contains 21 vibrations distributed into five classes in the following way:

$$\Gamma = 2A_1 + 3A_2 + 4B_1 + 2B_2 + 5E.$$

The selection rules for Raman and IR transitions in the symmetry group $D_4$ indicate that species $A_1$, $B_1$, and $B_2$ are active only in the Raman spectrum, species $A_2$ is active only in the IR spectrum, while $E$ modes are active both in the Raman and in the IR spectra. Assuming that the observed spectra were as complete as possible, mere comparison of the recorded Raman and FIR spectra was sufficient to isolate vibrations of species $E$ (active both in the Raman and in the IR spectra) and vibrations of species $A_2$ (active in FIR only). In this way, the bands 132, 112, 98, 67, and 62 $cm^{-1}$ in the spectra observed at the lowest temperature (Figures 1 and 2) could be assigned as species $E$, and the bands 123, 82, and 43 $cm^{-1}$ as species $A_2$. Since we did not perform the polarization analysis of the Raman spectra, we had no other experimental procedure at disposal to define the symmetry of the remaining eight transitions observed only in the Raman spectrum. However, since we had already determined the symmetry of eight out of sixteen bands, it was obvious that the rest of the spectrum could be assigned on the basis of a normal coordinate analysis. In this analysis, the bands already assigned could be used as reference bands to check the rest of the spectrum.

### B Normal-mode calculations

The normal-coordinate calculation for the ordered phase was performed using the crystallographic data given by Fourme.[4] The calculation was performed in the rigid-body approximation using the GF method as given by

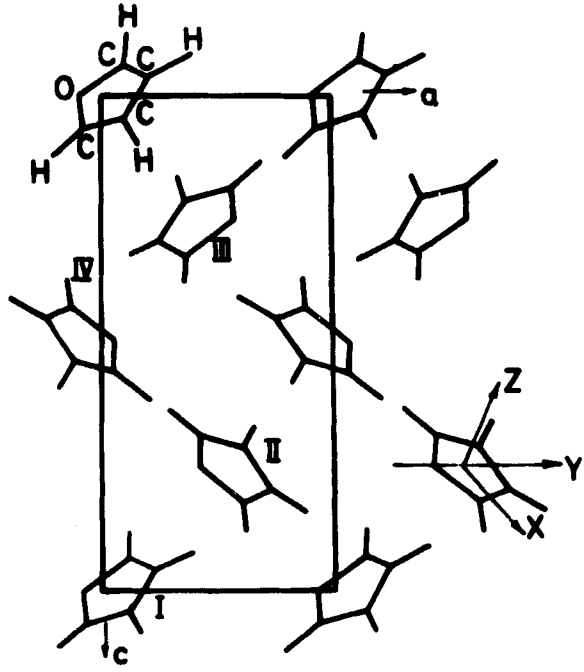


FIGURE 4 Unit cell of the furane II crystal.

Shimanouchi.[11] The large difference between the internal and external vibrational frequencies justifies the use of the rigid-body approximation. The highest observed lattice mode was about 135 $cm^{-1}$ at 10 K, while the lowest internal mode was at 602 $cm^{-1}$.[12] The intermolecular force field was described by the semiempirical atom-atom potential function of the exp-6 type, using the parameters given by Kitaigorodskii[13] and listed in Table I. The intermolecular interactions were described taking into account all contacts nonbonded atom pairs at distances shorter than 4.5 Å.

TABLE I

Parameters of the semiempirical potential function used.[a]

| Atom pair | $A$(kcal/mol Å$^6$) | $B$(kcal/mol) | $\alpha$(Å$^{-1}$) |
|---|---|---|---|
| C...C | 358 | 42,000 | 3.58 |
| H...H | 57 | 42,000 | 4.86 |
| C...H | 154 | 42,000 | 4.12 |
| O...O | 259.4 | 77,000 | 4.18 |
| C...O | 313.2 | 57,100 | 3.85 |
| O...H | 106 | 49,200 | 4.50 |

[a] Ref. 13.

TABLE II

The calculated and observed spectrum of the furane lattice.

| Calculated | | | Observed | | |
|---|---|---|---|---|---|
| Species | | Assignment[a] | Raman | | FIR |
| $A_1$ | 122 | $R_y + T_y$ | 108(117)[b] | | |
| | 27 | $T_y + R_y$ | 37(38) | | |
| | 121 | $R_x + R_z + T_z$ | | | 115(123) |
| $A_2$ | 79 | $R_x + T_z + T_x$ | | | 70(81) |
| | 43 | $R_x$ | | | 41(43) |
| | 169 | $R_x + T_z$ | 127(135) | | |
| $B_1$ | 112 | $R_z + T_x$ | 91(96) | | |
| | 67 | $T_x + R_z$ | 52(57) | | |
| | 21 | $T_z + R_x$ | 25(28) | | |
| $B_2$ | 112 | $R_y + T_y$ | 78(87) | | |
| | 78 | $T_y + R_y$ | 76(82) | | |
| | 143 | $R_x + T_z$ | | 123(132) | |
| | 122 | $T_x + T_y + R_z$ | | 101(112) | |
| $E$ | 97 | $R_y + R_x$ | | 86(98) | |
| | 71 | $T_z + R_x + T_x$ | | 64(67) | |
| | 45 | $R_z$ | | 50(62) | |

[a] Translational and liberational motions are related to the molecular inertial system. $y$ coincides with the molecular binary axis, $x$ is the second axis in the molecular plane, and $z$ is the axis normal to the molecular plane.

[b] The frequencies listed were read out from Figure 3 for a temperature of 123 K. The values in the parentheses are the mean values of frequencies observed at the lowest temperatures.

In Table II the results of the calculations are listed, and the frequency and vibrational character of the modes together with the assignment of the observed bands are indicated. Since the crystallographic data were measured at a temperature of 123 K, the frequencies listed in Table II are those read out from the curves in Figure 3 for this temperature. In addition, we list the mean values of frequencies observed at very low temperatures. In assigning the observed bands to the calculated frequencies we started from the bands of symmetry species $E$ and $A_2$. The rest of the bands approximately follow the frequency distribution as obtained by the normal-mode calculation in each class. In some cases in which this distribution was not unambiguous, we took into account the fact that the temperature dependence of librational modes is more pronounced.[14,15] For all modes below 100 $cm^{-1}$, the discrepancy between the observed and calculated frequencies was less than 20 $cm^{-1}$, which is satisfactory for this type of calculations. Above 100 $cm^{-1}$, the discrepancy between the observed and calculated frequency increased, as observed in similar studies for some molecular crystals (e.g., benzoic acid,[16] acenaphthene,[17] and phenanthrene.)[18] However, while in pure

hydrocarbon crystals the calculated frequencies are lower than the observed ones,[17,18] the calculated frequencies for several highest modes of furane exceed the observed ones. This feature may be due to the excessively large and probably unrealistic value of the force constant corresponding to a short O...H intermolecular contact of 2.5 Å, as given for the crystal structure.[4] This assumption is supported by the fact that the largest calculated frequencies correspond to the librational modes involving predominantly the motion of the oxygen and hydrogen atoms at the apex of the molecule. It is worthwhile to mention that similar, excessively high calculated frequencies were obtained for the 1-M-tymin crystal spectrum, in which a short O...H intermolecular distance was also present.[19] These results indicate that the repulsive part of the potential function used for O...H contacts is probably too "steep" and that the corresponding parameters should be corrected. However, keeping in mind the procedure used by Kitiagorodskii,[13] Williams,[20] and other authors to determine these parameters, it seems that these should not be adapted to each particular case.

## V DISCUSSION

The abundant experimental data and the specific selection rules for IR and Raman transitions present advantages of this study. The calculated normal-mode frequencies allow the interpretation of the observed vibrational spectrum of the furane II lattice even for a polycrystalline sample. Investigations of the IR and Raman spectra performed in a wide range of temperatures including the liquid and two solid phases can be a tool for further study of the dynamics of the furane molecule.

The most important conclusion drawn from this investigation for the spectrum of the plastic phase is the existence of three bands in both the IR and Raman spectra, and the fact that the frequencies of the six bands observed are completely different. This separation probably supports the choice of the factor group $D_{2h}$ proposed by Fourme.[4]

Both spectra of the liquid phase indicate low-frequency molecular motion, which is typical of globular or regularly shaped molecules. This observation is in agreement with the data obtained by molecular reorientation measurements.[21]

We have paid special attention to the temperature dependence of the frequencies in the ordered phase of furane. The bands exhibit various temperature dependence (Figure 3). These differences, particularly marked at high temperatures, indicate different degrees of anharmonicity for different modes. Consequently, as can be seen from Table II, the agreement between the observed and calculated frequencies would probably be better if the

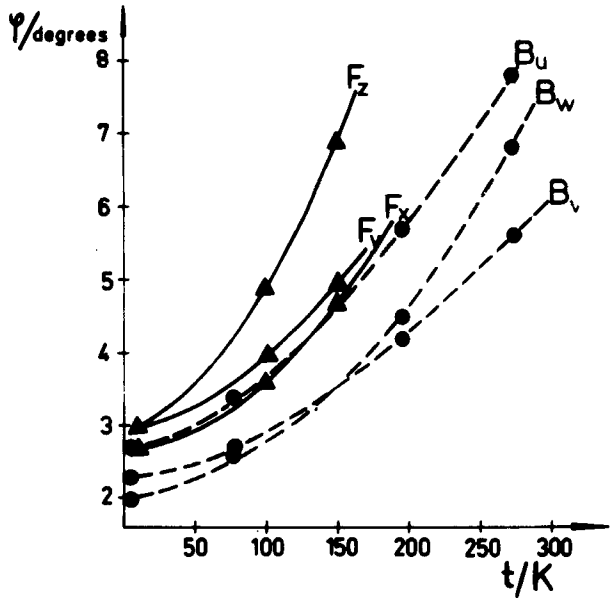


FIGURE 5 Root mean square amplitudes of librations calculated for the furane molecule ($F_i$) (full line) and the benzene molecule ($B_i$)[23] (dashed line).

crystallographic data were given for a lower temperature. In order to investigate the dynamics of the furane molecule at different temperatures, we applied the procedure given by Cruickshank[22] to investigate the variation of amplitudes of libration with temperature by calculating the mean square amplitudes of libration around each of the molecular axis of inertia. Since the lattice modes in furane are considerably mixed, we performed a rough calculation using a simplified formula given by Ito:[23]

$$\Phi_I^2 = \frac{h}{8\pi^2} \sum_i \frac{1}{Iv_i} \coth\left(\frac{hv_i}{2kT}\right),$$

where $n$ is the number of molecules per unit cell, and $I$ is the moment of inertia of the molecule. The values of frequencies are taken from Figure 3 at temperatures of 10, 100, and 150 K. Only those modes were considered for which the eigenvector indicated a predominantly librational character. The values obtained for the mean square amplitudes of libration are plotted against temperature in Figure 5. For comparison, we give the values for benzene obtained by Ito.[23] Even though the amplitudes of libration in the furane molecule are of the same magnitude as those for benzene, it is important to note the marked difference between the amplitudes of libration around the axes in the molecular plane and the amplitudes of libration

around the axis normal to the molecular plane. These results are in good agreement with all earlier studies of the molecular motion in furane and are a further confirmation of the large amplitude oscillations of this molecule around the normal axis.



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## References

1. D. Kirin and L. Colombo, *Proc. Vth Internat. Conf. on Raman Spectroscopy*, ed., by E. D. Schmid *et al.*, Freiberg (1976), p. 530.
2. L. Colombo, *Proc. VIth Internat. Conf. on Raman Spectroscopy*, ed., by E. D. Schmid *et al.*, Bangalore (1978),Vol. 1, p. 295.
3. G. B. Guthrie, Jr., D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCullough, M. E. Gross, K. D. Williamson, and G. Waddington, *J. Am. Chem. Soc.*, **74**, 4662 (1952).
4. R. Fourme, *Acta Cryst.*, **B28**, 2984 (1972).
5. F. Fried and B. Lassier, *J. Chim. Phys.*, **1**, 75 (1966).
6. F. Fried, *C. R. Acad. Sci., Paris*, **262C**, 1497 (1966).
7. J. P. Pinan-Lucarre, J. Loisel, and J. Vincent-Geisse, *Mol. Cryst. Liq. Cryst.*, **28**, 237 (1974).
8. J. Y. Beach, *J. Chem. Phys.*, **9**, 54 (1941).
9. B. Bak, L. Hansen, and J. Rastrup-Andersen, *Discussions Faraday Soc.*, **19**, 30 (1955).
10. F. Fried, Thèse, Université de Nice (1974), p. 130.
11. T. Shimanouchi and I. Harada, *J. Chem. Phys.*, **41**, 2651 (1964).
12. L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, *Kolebatel'nie spektri mnogoatomnih molekul*, (Nauka, Moskva, 1970), p. 452.
13. A. I. Kitaigorodskii, *Molecular Crystals and Molecules* (Academic Press, New York, 1973).
14. G. G. Dumas, *Spectrochim. Acta* **30A**, 1623 (1974).
15. A. I. Kitaigorodskii and E. I. Mukhatarov, *Soviet Phys. Cryst.*, **14**, 678 (1970).
16. K. Furić and L. Colombo, *Phonons*, ed., by M. A. Nusumovici, Rennes (1971), p. 254.
17. A. Turković, L. Colombo, K. Furić, and D. Kirin, *Mol. Cryst. Liq. Cryst.*, **29**, 5 (1974).
18. J. Godec and L. Colombo, *J. Chem. Phys.*, **65**, 4693 (1976)
19. D. Kirin, L. Colombo, and K. Furić, *Spectrochim. Acta*, **31A**, 1721 (1975).
20. D. E. Williams, *J. Chem. Phys.*, **47**, 4680 (1967).
21. F. Fried, Thèse, Université de Nice (1974), p. 96.
22. D. W. Cruikshank, *Acta Cryst.*, **9**, 1005 (1956).
23. M. Ito and T. Shigeoka, *Spectrochim. Acta*, **22**, 1029 (1966).