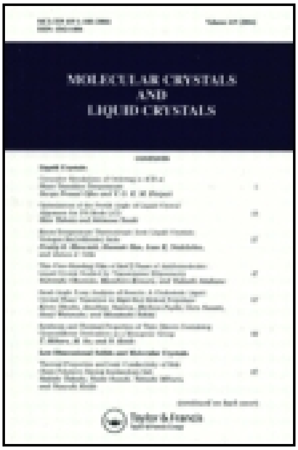

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Display of Stages in “Melting” of Molecular Rotational Degrees of Freedom of Some Anisotropic Organic Crystals via Their Raman Spectra

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The temperature dependence of Raman spectra (temperature maintained within ±0.01°) in the premelting region of naphthalene, benzene, thiophene, phenanthrene, anthracene and *p*-dichlorobenzene (β-modification) have been investigated. Normal-mode calculations have been performed using atom–atom potentials. The jump-like intensity decreasing and disappearance of $\nu_5(A_g)$ and $\nu_6(B_g)$ lines (librations around the axis close to the axis with the smallest moment of inertia) in comparison with other lines of the phonon spectrum have been observed in premelting region of naphthalene. This is due to the activation of naphthalene molecular reorientations about corresponding axis. Gradual broadening, decrease of intensity and disappearance of some lines in the phonon spectrum is characteristic of benzene and thiophene. Complete disappearance of the phonon spectrum of thiophene has been observed near the melting point. This is related to disorder of all molecular orientations in crystal. The phonon spectra of phenanthrene, anthracene and *p*-dichlorobenzene (β-modification) have not indicated preferable disappearance of any Raman lines in the premelting region.

INTRODUCTION

Information about the crystal state near the phase transition point is necessary to determine the polymorphic transformation mechanism.

This is of paticular interest because changes of the crystal structure occurring at this stage relate to their further evolution. Recently Raman and absorption spectroscopy in the far infra-red (FIR) region[1–4] have been used successfully for study of the transitions between crystals and the plastic or liquid crystal states. This is seen by the direct display in phonon spectra of the pretransition crystal states; this occurs before the stages of disorder due to rotational and transitional degrees of freedom.

It is known from NMR, neutron scattering data and other techniques that with increasing temperature some molecular rotational degrees of freedom may undergo "melting" within the limits of the anisotropic phase, not only during the transition into the plastic crystalline state but also for those substances which do not have plastic modifications at all.[5–7]

The lowering of the orientational barriers for certain molecules to values sufficient to permit activation of reorientational motion of molecules around certain axes may cause an increase of anharmonicity, anomalous expansion of the crystal lattice, and fluctuations of short-range order in the premelting region.

Such effects can be seen in Raman spectra as gradual line broadening, decrease of relative line intensities, and complete disappearance of corresponding phonon lines due to distortion of the correlated librational motion of the individual molecular reorientations of certain types.[2,8]

Nevertheless, the transformation of an anisotropic crystal phonon spectrum into the Rayleigh wing is usually supposed to take place simultaneously for all librational lines during the melting of the crystal.

In this paper we present results of a study of temperature dependences of Raman phonon spectra over a large temperature range for some nonplastic molecular crystals in which the premelting region may be expected as a stage in the activation of molecular reorientations, and particular or complete disappearance of rotational phonon spectrum. The calculation and assignment of frequencies were made using atom–atom potentials.

EXPERIMENTAL

The Raman spectra were measured on spectrometers DFS-12 and DFS-24 using 4416 Å and 5145 Å excitation lines from He–Cd and argon-ion lasers, respectively. The observed frequencies are believed to be accurate to within ±1 cm^{-1}. For study of the melting point, from room to higher temperatures a specially designed optical cell was used to allow heating of sample with a rate of 1 ÷ 2° K/h, and to maintain its temperatures within ±0.01° K. The temperature was measured by a calibrated platinum resistance thermometer. The time of sample equilibration at each temperature was 20 to 30 min. The conditions of the low temperature experiments were the same as described in Ref. 2.

RESULTS AND DISCUSSION

Benzene. In the spectrum of benzene (space group Pbca, $z = 4$) twelve librational vibrations of four symmetry species ($3\ A_g + 3\ B_{1g} + 3_{2g} + 3_{3g}$) are active.[9] The reorientation barriers of solid benzene were estimated for two temperatures: $U_w = 3.2$ kcal/mol (138° K) and $U_w = 1.8$ kcal/mol (270° K).[10] Two other (U_v, U_u) barriers are very high. The corresponding barriers in the liquid near the solidification point are: $U_w \simeq 0$, $U_v \simeq U_u \simeq 1.35$ kcal/mol.[11] It is clear that in the premelting region the lowering of orientational barriers is sufficient for activation of reorientational molecular motion around their librational axes.

In Figure 1a and b are shown the temperature dependences of Raman Spectra of benzene-h_6 and benzene-d_6 polycrystals in the range of 112

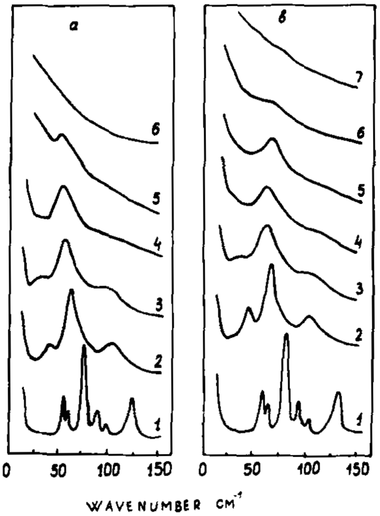

FIGURE 1 Temperature dependent Raman spectra for the polycrystals of: (a) benzene-d_6. 1—112.0; 2—223.0; 3—273.0; 4—277.0; 5—277.9; 6—279.0° K (liquid). (b) benzene-h_6; 1—112.0; 2—223.0; 3—273.0; 4—277.8; 5—277.9; 6—278.0; 7—279.0° K (liquid).

to 280° K. With increasing temperature, together with the general broadening of observed phonon lines, high-frequency and low-frequency parts of the spectrum (the groups of lines at 128 cm^{-1} and 60 cm^{-1}, $T = 112°$ K) at a temperature lower than the melting point are practically simultaneously broadened. Their intensities decrease and their transform looks like the Rayleigh line wing which is characteristic of disordered systems. It follows from the calculation that the maximum at 128 cm^{-1} is doubled and corresponds to two frequencies at 127 cm^{-1} (B_{3g}) and 128 cm^{-1} (B_{1g})-librations about the u' axis, close to the u axis of the smallest moment of inertia.[12,13] Evidently near the melting point this orientational barrier is a little lower than the barrier about the v' axis, which also lies practically in the plane of the molecule. The group of lines in the middle part of the spectrum corresponds to the librations around the v' axis. These lines (in form of a rather diffuse broad feature) remain distinct up to the temperature of about 0.1° K below the melting point. Evidently, the reorientations around the corresponding axis are substantially hindered by molecular packing in the crystal, so that their activation occurs only in the liquid state. The lowest frequency lines correspond to the librations about the w' axis, which is almost perpendicular to the plane of the molecule. Probably in this region of the spectrum there are more than two lines corresponding to the rotational oscillations around the w' axis. The quasielastic constants for the four symmetry species must be similar and the frequencies must practically coincide with weak intensity.[14] If librations of benzene occurred about the axes of inertia, the rotations around the C_6 axis would not cause a change of polarizability of the unit cell. As a result frequencies would have small Raman intensities. However numerous calculations[12-14] show considerable deflections of librational axes from the inertia axes of the molecule with the result that some librations around the w' axis appear in the spectrum. The NMR data show appreciable reorientation of benzene molecules around the w axis above 120° K,[15] but this motion cannot be seen from Raman spectra for reasons given above. Indeed, the spectrum of benzene rotational oscillations at temperatures in the range of 100–150° K changes insignificantly, and only in the premelting region, where overall correlation of the rotational molecular motion in crystalline benzene is strongly distorted. This results in the disappearance of phonon frequencies corresponding to the librational motion about the w' axis.

So, it is seen from the temperature dependence of the Raman spectra of benzene-h_6 an benzene-d_6 crystals that near the melting point the activation of molecular rotations around the u' and w' axes takes place.

Thiophene. For thiophene, like benzene, the molecule is planar. Solid thiophene exists in four forms with transition points: 171° K (I–II), 138° K (II–III), and 112° K (III–IV).[16-20] X-ray study of the first form showed that orientations of the molecules are disordered.[18] This disorder is probably partial and related to the molecular rotations in their plane only.[19] However, the FIR study of the phase transitions in thiophene[19] has not revealed considerable difference in the spectra of its four modifications. This is understandable since the FIR spectra are more sensitive to changes in the molecular translational order but in the crystalline thiophene the disorder of the molecular orientations appears and is better seen in the Raman spectra. In Figure 2a are shown spectra of the four thiophene crystal forms in the lattice region. The spectrum of the phase IV (the most ordered form) differs substantially from spectra of the other phases. The phonon lines of thiophene IV are the most distinct. Considerable changes are also characteristic of the transition IV–III. It is seen from the temperature behavior of the phonon spectrum that the maximum at 120 cm^{-1} is noticeably broadened and completely disappears within the limits of phase I as the sample temperature reaches the melting point. This is analogous to the disappearance of the maximum at 128 cm^{-1} in crystalline benzene. With further heating one can see complete disappearance of the phonon spectrum of thiophene I. This is probably related to disorder of all molecular orientations in the crystal. Figure 3a shows that the impurities increase the disordered state temperature range. For pure samples the

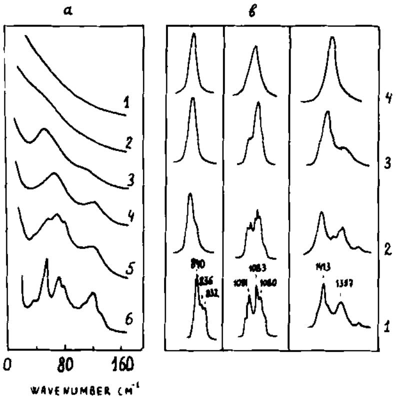

FIGURE 2 (a) Lattice region Raman spectra of the four thiophene crystal forms: 1—100.0 phase IV; 2—128.0 phase III; 3—158.0 phase II; 4—213.0 phase I; 5—233.5 phase I—completely disordered; 6—243.0° K—liquid. (b) Part of intramolecular Raman Spectra of the four tiophene crystal forms: 1—100.0 phase IV; 2—223.0 phase III; 3—163.0 phase II; 4—293.0° K (liquid).

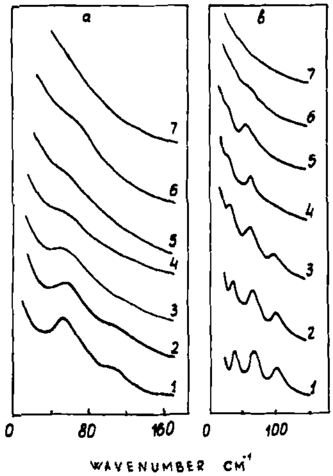

FIGURE 3 Temperature dependent Raman spectra for the polycrystals of: (a) thiophene—I. 1—215.0; 2—227.0; 3—230.0; 4—231.5; 5—233.3; 6—233.5; 7—235.0° K (liquid). (b) naphthalene. 1—352.0; 2—353.3; 3—353.5; 4—353.7; 5—353.9; 6—354.0; 7—355.2° K (liquid).

phonon spectrum (very weak) can be seen up to a few degrees below the melting point. Probably impurities make it easier for the initiation of orientational disorder of thiophene molecules in crystal sites. The existence of phase transitions in thiophene is confirmed by the intramolecular Raman spectra, Figure 2b, which agree with those reported previously.[20] Unfortunately the absence of structural data do not allow us to make the proper assignment of the phonon spectrum, and therefore determine the values of the orientational barriers.

Naphthalene. Among the molecular crystals naphthalene is one of the most studied. It is especially valuable for the investigation of premelting phenomena. Its Raman and FIR spectra have been studied widely over a large temperature range.[21-25] Naphthalene crystalizes in monoclinic space group $P2_1/c$, $z = 2$. In the Raman spectra of the lattice region six librational modes are active ($3A_g + 3B_g$). The axes of librations and axes of inertia do not coincide. The lines in the spectrum group in pairs and at 2° K they have the following frequencies (cm^{-1}): 57, 68 (ν_1, ν_2), 83, 89 (ν_3, ν_4) and 121, 141 (ν_5, ν_6).[24] By increasing the temperature the convergence of the corresponding pairs into broad bands occurs. The ν_5 (A_g) and ν_6 (B_g) lines, corresponding to the librations about the u' axis close to the u axis, the axis with the smallest moment of inertia, are much broader than the others. Their widths depend exponentially upon temperature.[21,24] It was speculated previously[21] that this is related to the reorientations of naphthalene molecules around the u axis. The barrier of reorientation determined was 4.5 ± 0.3 kcal/mol. It is pointed out[24] that such considerable broadening of the ν_5 and ν_6 lines is the result of strong vibrational anharmonicity. This is confirmed by a considerable discrepancy in the observed and calculated temperature dependences of the ν_5 and ν_6 frequencies.[24,25] The remaining width changes are insignificant and are nearly linearly dependent upon temperature. It is difficult at the moment to understand the true reason for such anomalous broadening. There is probably a large deformation of the potential function as a result of which the reorientational motion of naphthalene molecules occurs around the u' axis, thus increasing the anharmonicity of these vibrations. In any case such anomalous behavior of the ν_5 and ν_6 line widths, in comparison with other lines, should be displayed in Raman spectra especially in the premelting stage. Figure 4 shows the temperature dependence of the

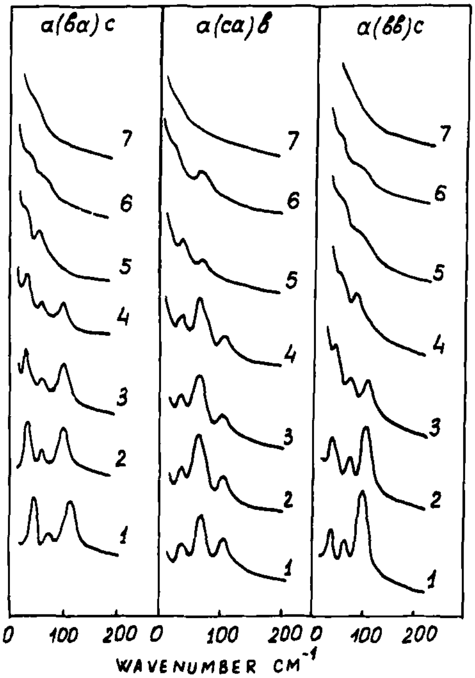

FIGURE 4 Polarized Raman spectra of naphthalene single crystals near the melting point. a (ba) c. 1—352.6; 2—353.6; 3—353.65; 4—353.70; 5—353.75; 6—353.8; 7—354.0° K (liquid). a (ca) b. 1—348.0; 2—352.7; 3—353.1; 4—353.5; 5—353.6; 6—353.9; 7—354.0° K (liquid). a (bb) c. 1—350.0; 2—353.6; 3—353.65; 4—353.70; 5—353.75; 6—353.9; 7—354.0° K (liquid).

polarized phonon spectra of naphthalene single crystal near the melting point. It is seen that the ν_5 and ν_6 lines are broadening and decreasing in intensity much more markedly with increasing temperature than are the others (Figure 5). They completely disappear near the melting point. Their complete disappearance occurs in a temperature interval ~0.2° K. At about 0.25° K below the melting point they become practically unobservable while the other lines (librations around the axes, close to the axes of the largest and medium moments of inertia) are still clearly observable. On cooling the sample from 353.8 to 353.6° K the ν_5 and ν_6 lines reappear in the spectrum.

The experiment was repeated with two monocrystalline samples at four orientations of the single crystals. In each case there was observed the disappearance of the ν_5 and ν_6 lines near the melting point while the remainder were present. The data obtained permit us to conclude that, near the transition point "anisotropic crystal–isotropic liquid," reorientations of naphthalene molecules occur about the axis close to the axis of the smallest moment of inertia.

However one must also consider the possibility that such anomalous behavior may be caused by the depolarization of these lines as the temperature of the crystal approaches the melting point. At this stage, the single crystal sample becomes a polycrystalline one. An additional investigation was made on the polycrystalline sample. Changes in the phonon spectra of polycrystal are given in Figure 3b. The ν_5 and ν_6 lines in the premelting region are much more broad than those observed for single crystal samples. They are unresolved but it is clearly seen that they have the same temperature dependence. It should be also mentioned that the DTA curves of naphthalene melting and solidifying show discontinuous jumps.[26] Thus, for crystalline naphthalene, which

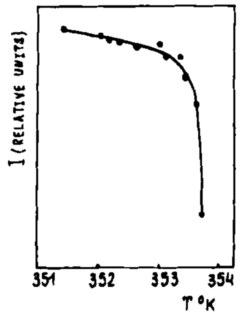

FIGURE 5 Integral intensity for the ν_5 single crystal line vs. temperature (°K) in the premelting region.

does not have a plastic phase, rotational degrees of molecular freedom occur with melting.

It was interesting to estimate the reorientational barriers around the *u′* and *w′* axes in the crystal. We made the calculations using atom–atom potentials. The results proved to be rather disappointing in comparison with the experiment. They are given in Figure 6. It is seen that orientational barriers hindering the rotational motion around the *u′* and *v′* axes have at room temperature such high values that a reorientational mechanism could be in no way responsible for the broadening of the ν_5 and ν_6 lines. It should be emphasized that the calculation of the potential barriers by this method near the melting point is probably unacceptable because of the strong anharmonicity and presence of numerous crystal defects in this range of temperatures. At the same time the angular dependence of molecular potential energy for the rotation around the *w′* axis has several local minima, with corresponding orientational barriers of about 16 kcal/mol.

CONCLUSION

The investigation of the premelting region of some molecular crystals, having no plastic phase, by Raman spectroscopy showed that near the melting point there can be activation of certain reorientations. Gradual

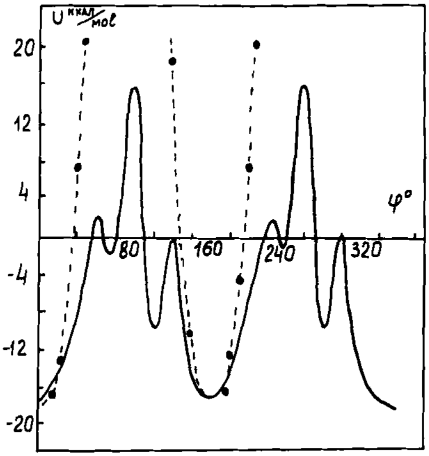

FIGURE 6 Intermolecular potential energy, *V* (kcal/mol) vs. rotation angle, φ for rotation around the *w′* (solid line) and *v′* (broken line) axes. For rotation around the *u′* axis $V = 215.8$ kcal/mol when $\varphi = 40°$.

broadening, decrease of intensity and disappearance of some lines in phonon spectra is characteristic of benzene and thiophene, while for naphthalene, anthracene and *p*-dichlorobenzene (*β*-modification) we could not find preferable disappearance of any librational phonon frequencies near the melting point. This confirms the fact that the rotational volumes of these substances are also insufficient for the molecular reorientation around any axis of inertia.[6]

References

1. N. I. Afanasyeva, V. M. Burlakov, G. N. Zhizhin, *Zh. Exp. Teor. Fiz. Pisma*, **23**, 506 (1976).
2. E. I. Mukhtarov, V. N. Rogovoi, Ju. N. Krasjukov, G. N. Zhizhin, *Optika i Spektroskopiya* (*USSR*), **46**, 920 (1979).
3. V. N. Rogovoi, G. N. Zhizhin, *Sov. Phys. Solid State*, **17**, 376 (1975).
4. L. A. Leites, S. S. Bukalow, *J. Raman Spectroscopy*, **7**, 235 (1978).
5. E. F. Westrum, Jr. and J. P. McCullough, in "Physics and Chemistry of the Organic Solid State" (D. Fox, M. Labes, and A. Weissberger, eds.) Vol. I, pp. 89–101 Wiley (*Interscience*), New York, 1963.
6. A. R. Ubbelohde, *Melting and Crystal Structure* (Oxford Clarendon Press, 1965).
7. N. G. Parsonage, L. A. K. Staveley, *Disorder in Crystals* (Oxford Clarendon Press, 1978).
8. G. N. Zhizhin, N. V. Sidorov, *Optika i Spektroskopiya* (USSR), **47**, 405 (1979).
9. I. Harada, T. Shimanoychi, *J. Chem. Phys.*, **46**, 2016 (1966).
10. R. K. Boyd, C. A. Fyfe, D. A. Wright, *J. Phys. Chem. Solids*, **35**, 1355 (1974).
11. M. V. Vuks, *Optika i Spektroskopiya* (*USSR*), **9**, 92 (1960).
12. G. Taddei, H. Bonadeo, M. P. Marzocchi, S. Califano, *J. Chem. Phys.*, **58**, 966 (1973).
13. W. D. Ellenson, M. Nicol, *J. Chem. Phys.*, **61**, 1387 (1974).
14. Y. A. Sataty, A. Ron, *J. Chem. Phys.*, **65**, 1578 (1976).
15. E. R. Andrew, *J. Chem. Phys.*, **18**, 607 (1950).
16. G. Waddington, J. W. Knowlton, *J. Amer. Chem. Soc.*, **77**, 797 (1949).
17. G. Brum, G. Nata, *R. C. Acad. Lincei* (*6*), **11**, 929 (1930).
18. S. S. Abrahams, W. N. Lipscomb, *Acta Crystallogr.*, **5**, 93 (1952).
19. G. N. Zhizhin, M. S. Moskaleva, V. N. Rogovoi, *J. Struct. Chem., USSR*, **14**, 656 (1973).
20. P. S. Salvi, G. G. Mighorini, *Mo. Spectr. of Dense Phase.* Proceedings of the 12th European Congress on Molecular Spectroscopy. p. 275 (Strasbourg, France, 1975).
21. P. A. Bazhulin, A. A. Rakhimov, *Sov. Phys. Solid State*, **7**, 94, 2088 (1965).
22. M. Suzuki, T. Yokoama, I. Ito, *Spectrochim, Acta*, **24A**, 1091 (1968).
23. M. Ito, M. Suzuki, T. Yokoyama, "Excitons, Magnons and Phonons in Molecular Crystals," Ch. I (Cambridge Univ. Press 1968).
24. J. C. Bellows, P. N. Prasad. *J. Chem. Phys.*, **70**, 1864 (1976).
25. A. I. Kitaigorodsky, *Molekularnyje Kristaly* (Izd. Nauka, Moscow, 1971).
26. G. Kirsanov, A. A. Artamonov, A. V. Sechkarev, *Spectroscopiya i Jeje Primenenije v Geophisike i Khimii* (Izd. Nauka, Sibirskoje Otdelenije, 1975).