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Low-Frequency Vibrational Spectra of Molecular Crystals. XXII†

Cyclobutane-d_0 and Cyclobutane-d_8

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The Raman spectra (0–300 cm^{-1}) of the two crystal modifications of cyclobutane-d_0 and cyclobutane-d_8 were recorded at various temperatures. The infrared spectra (30 to 300 cm^{-1}) were also recorded at various temperatures. Lattice modes were observed at 109, 106, 93, 46 and 33 cm^{-1} for cyclobutane in crystal phase II at 20°K. From the shift factors with deuteration, it is concluded that the highest three bands are librational modes whereas the two bands of lowest frequency are optical translations. The number and activity of the lattice modes are consistent with the previously proposed crystal symmetry of C_{cca} (D_{2h}^{22}) with two molecules per primitive cell for phase II. The ring-puckering vibration is observed at 255 cm^{-1} and shifts to 201 cm^{-1} with deuteration. The temperature dependency of these bands is discussed and it is shown that the ring-puckering vibration is intimately involved in the phase transition II → I.

INTRODUCTION

The crystallization of many almost-spherical molecules (called globular molecules) leads to a new phase of matter which has been called a "plastic crystal" by Timmermans.[1–4] Timmermans noted that such compounds have an unusually low entropy of fusion on the order of R, which is the entropy of fusion of monatomic crystals. This fact suggests that only the centers of gravity of the molecules acquire mobility on melting, whereas the rotational degrees of freedom have become activated at lower temperatures. In all such cases, the melting point of the compound is much higher than expected (globular molecule, neopentane, melting point, −16°C; non-globular

† For part XXI, see *Mol. Cryst. Liq. Cryst.*, **31**, 185 (1975).

TABLE I

Low-frequency (cm^{-1}) Raman bands for phase II cyclobutane and cyclobutane-d_8 as a function of temperature (°K)

Cyclobutane-d_0				Cyclobutane-d_8				Shift factor	
20°	75°	110°	140°	20°	75°	110°	140°	at 20°K	Assignment
257	255	245	243	201	199	195.5	192	1.28	Ring-puckering
109	102	91	86	93	84	77.5	77	1.17	Librations
106				88				1.20	
93	89	79	76	77	73	69	65	1.21	Libration
46	45	38	37						Translation
33	32	23	20						Translation

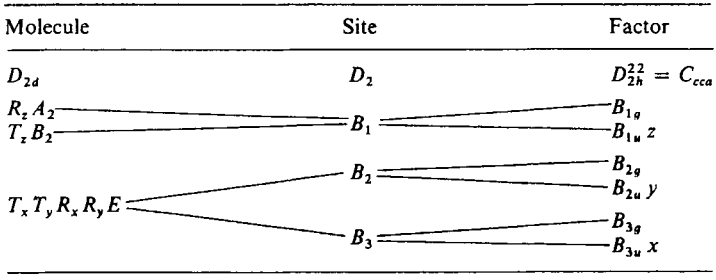
molecule, normal pentane, melting point −141°C) which indicates that the crystal is stable in spite of considerable mobility of the constituent molecules. Substances which form plastic crystals are very often polymorphic and phase I is of high crystallographic symmetry and usually cubic (phase I is the crystalline form which exists between the temperature of the transition II → I and the melting point). In fact, the X-ray radiation scattered "in-phase" from these plastic crystals comes from an electron distribution concentrated around the centers of gravity of the molecules. This behavior indicates that the molecules can either rotate more or less freely, which is the explanation that was initially given as the reason for the plastic phase, or they can assume a number of orientations of equivalent energy in the crystal by passing over a relatively low potential barrier. By knowing the van der Waals radii for the peripheral atoms of a molecule, one can estimate the volume of a sphere which will just circumscribe the freely rotating molecule. The diameter of this sphere is always found to be greater by roughly 15 to 20% than the distance between the centers of neighboring molecules in the plastic crystal,[5,6] and hence, free rotation is not reasonable.

It is now known that even in plastic crystals, the energy barrier to molecular rotation is seldom so small or the space sufficient so that the molecules can be said to rotate in the literal sense. However, if the barrier between two positions of minimum potential energy is small enough for the molecule to be able to convert with comparative rapidity from one orientation to another, then the molecules in the plastic phase can have a random distribution between different possible orientations. The evidence for this comes from a consideration of the spatial relations in the crystal,[6] the thermodynamic properties,[7] dielectric measurements[8,9] and NMR studies.[10,11]

Cyclobutane is a cyclic hydrocarbon, C_4H_8, which has been shown to have a plastic phase[12,13] between the phase transition II → I at 145.7°K and the melting point at 182.4°K. In the X-ray investigation[14] of phase I cyclobutane, only the [110] and [200] reflections were observed which showed

TABLE II

Factor group analysis of the lattice modes of crystalline phase II cyclobutane



that the unit cell must be body-centered cubic with $a = 6.06 \pm 0.03$ Å and two molecules per unit cell. If the origin is chosen at the center of gravity of one molecule, then the second molecule must be at the body center. To achieve this cubic symmetry, the two molecules must have either static or dynamic rotational disorder. Since the intermolecular distance between centers is 5.25 Å, it was concluded by Carter and Templeton[14] that this distance is substantially smaller than the largest van der Waals diameter of cyclobutane[15,16] and hence, the rotations must be hindered.

In the X-ray investigation[14] of the low-temperature phase (II) of cyclobutane, it was not possible to solve the structure but the authors concluded that it was not cubic. Recently, Castellucci *et al.*[17] investigated the molecular packing of solid phase II cyclobutane and cyclobutane-d_8 by means of intramolecular spectroscopic data and concluded that the crystal was orthorhombic with space group C_{cca} (D_{2h}^{22}) with two molecules per primitive cell. In this study, three lattice modes (84, 96 and 103 cm^{-1}) were reported in the Raman spectrum and two (81.4 and 94.6 cm^{-1}) were reported in the infrared spectrum. These data were taken at liquid nitrogen temperature (77°K). A Raman line at 249 cm^{-1} was assigned to the ring-puckering vibration. Miller *et al.*[18] have also reported the Raman spectrum of phase II solid cyclobutane at 113°K and reported lattice modes at 127, 144 and 245 cm^{-1} with the ring-puckering mode being assigned to the Raman line at 144 cm^{-1}. Thus, the Raman data are inconsistent between these two investigations and we have therefore undertaken a Raman and infrared investigation in the low-frequency region of solid cyclobutane. The results of this study are reported herein.

EXPERIMENTAL

Cyclobutane-d_0 and cyclobutane-d_8 were purchased from Merck, Sharp & Dohme and were purified using a low-pressure, low-temperature fractionating column.

The Raman spectra were recorded using a Cary Model 82 spectrophotometer with 5145 Å excitation from a Spectra Physics model 171 argon ion laser. The far infrared spectra were recorded with a Digilab FTS-15B Fourier transform interferometer using 6.25 μ and 25 μ Mylar beamsplitters and a high pressure Hg arc lamp source. Measured frequencies are expected to be accurate to at least ± 2 cm^{-1}.

The Raman data for solid cyclobutane were obtained by condensing the sample onto a brass plate maintained at 20°K in a Cryogenics Technology Inc. Spectrim cryostat equipped with a Lake Shore Cryotronics Model DTL 500 high-precision temperature controller. The sample was annealed by allowing the temperature to increase to 140°K and then quickly lowering it to $\sim$20°K. The spectra were then recorded at various temperatures ranging from 20°K to 150°K. The infrared data were obtained in the same manner except that a silicon plate was substituted for the far infrared region.

RESULTS AND DISCUSSION

From an inspection of the Raman spectrum of C_4H_8 shown in Figure 1A, one can clearly discern six pronounced lines at 257, 109, 106, 93, 46 and 33 cm^{-1}. Miller *et al.*[18] had previously reported the Raman spectrum of this compound in the solid state at 113°K which is close to our spectrum recorded at 110°K (Figure 1C). We found no evidence of the lines at 220, 144 and 127 cm^{-1} as reported by Miller *et al.*[18] and we have concluded that these are either impurities or their sample was not sufficiently annealed to give the phase II crystal which is the stable form at 113°K. It is noted that the 144 cm^{-1} Raman line was reported[18] to be 75% the intensity of the 245 cm^{-1} line and there are simply no Raman lines in the 91 to 245 cm^{-1} region (Figure 1C) of even 5% of the intensity of the 245 cm^{-1} line.

Castellucci *et al.*[17] reported Raman lines at 249, 220, 103, 96 and 84 cm^{-1} for cyclobutane in phase II at 77°K. At this temperature (75°K) we found lines at 255, 102, 89, 45 and 32 cm^{-1} with no indication of a line at 220 cm^{-1} nor a third line between 80 and 105 cm^{-1}. However, the spectral data reported by Castellucci *et al.*[17] are in better agreement with our data than the data reported by Miller *et al.*[18] Similarly our data on cyclobutane-d_8 (Figure 2A) agrees well with that reported by Castellucci *et al.*[17] for this isotope except that we did not observe the very weak line at 144 cm^{-1} nor the weak broad line at 55 cm^{-1}. However, in our initial investigation we observed a weak line at 65 cm^{-1} which disappeared with further purification of the sample. We found no evidence for Raman lines at 116 and 124 cm^{-1} as reported by Miller *et al.*[18]

The number and species of the intermolecular vibrations to be expected

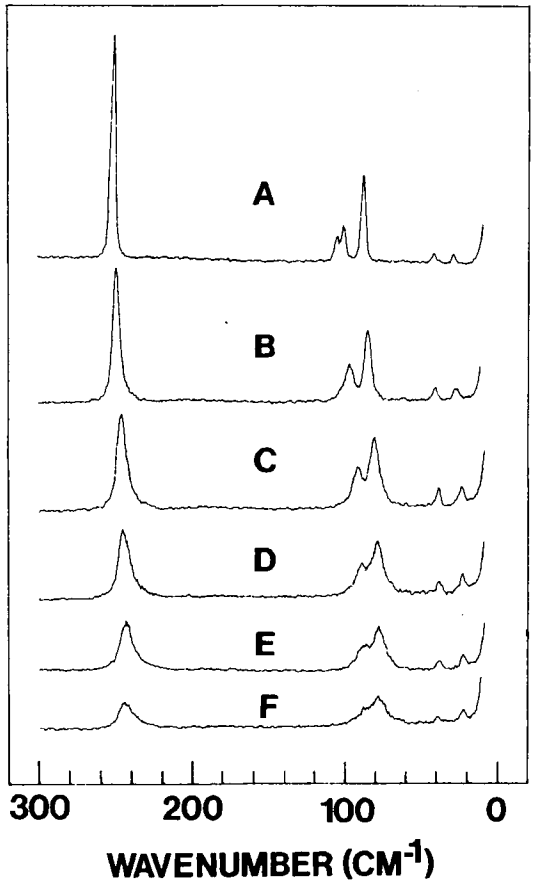


FIGURE 1 The Raman spectrum of cyclobutane-d_0 in solid phase II taken at various temperatures (°K). (A) 20°; (B) 75°; (C) 110°; (D) 120°; (E) 130°; (F) 140°.

from solid cyclobutane in solid phase II can be predicted in a straightforward manner by using the theoretical treatment proposed by Halford and Hornig.[19,20] The results for a C_{cca} (D_{2h}^{22}) system with two molecules per primitive cell are given below (see Table II). The total irreducible external vibrational representation is:

$$\Gamma(\text{total}) = 2B_{1g} + 2B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$$

for the twelve degrees of freedom. The acoustical modes are given by:

$$\Gamma(\text{AT}) = B_{1u} + B_{2u} + B_{3u}.$$

The optical translational modes are then:

$$\Gamma(\text{OT}) = B_{1g} + B_{2g} + B_{3g}$$

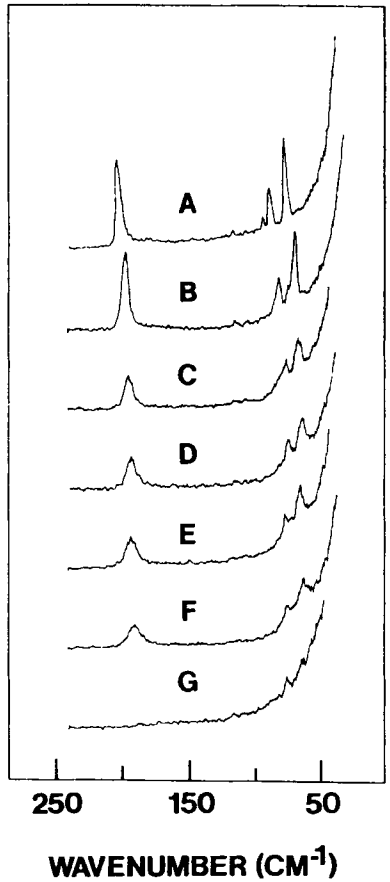


FIGURE 2 The Raman spectrum of cyclobutane-d_8 in solid phase II taken at various temperatures (°K). (A) 20°; (B) 75°; (C) 110°; (D) 120° (E) 130°; (F) 140°; (G) 150° and phase I. The increased scattering in the lower frequency region of these spectra is the result of the degradation of the surfaces of the mirrors in the monochromator.

whereas the optic librational modes are found to be:

$$\Gamma(\mathrm{OL}) = B_{1g} + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}.$$

The Raman active modes are the gerade species whereas the infrared active ones are all the ungerade species. Thus, one expects three optical librations and three optical translations in the Raman effect and only three optical librations in the infrared spectrum. The intermolecular fundamentals may be distinguished by analyzing the observed frequency shift of a motion upon deuteration of the molecule. The shift factor for a translation upon deuteration of cyclobutane should be proportional to the square root of the mass of

C_4D_8 to that of C_4H_8 or 1.08. Similarly, the shift factors associated with the librations depend upon the moments of inertia around the principal axes of a molecule and its isotopic species. The principal moments of inertia of cyclobutane were calculated from the structural data obtained from the electron diffraction investigations,[15,16] and the dihedral angle was obtained from the vibrational study of the ring-puckering motion.[21-23] Therefore the theoretical shift factor for libration around the figure axis is 1.14, whereas the librations perpendicular to the figure axis should have shift factors of 1.19. The ring-puckering mode was found to shift by a factor of 1.27 in the gas phase with deuteration.[18] Therefore the 257 cm^{-1} line is confidently assigned to the ring-puckering motion whereas the 109, 106 and 93 cm^{-1} lines are assigned as optical librations. The shift factor for the 109 cm^{-1} line indicates that this band is due to a libration around the figure axis. The shift factors for the 106 and 93 cm^{-1} lines are consistent with the fact that these lines arise from librations perpendicular to the figure axis. The much weaker lines at 46 and 33 cm^{-1} are assigned as optical translations. Thus, all but one of the lattice modes expected in the Raman spectrum have been observed. These assignments are summarized in Table I.

The far infrared spectra were not as definitive as the Raman spectra; however, the data were reasonably consistent with that previously reported by Castellucci *et al.*[17] For example, in the far infrared spectrum of the "light" compound, pronounced bands were observed at 100.3 and 86.7 cm^{-1} with a possible additional one at 81.2 cm^{-1}. These data were taken at 20°K and the frequencies for the two pronounced bands are about 5 cm^{-1} higher than those reported previously[17] in which the spectrum was recorded with the sample at 77°K. These bands appeared to shift to 86.8, 75 and $\sim$69 cm^{-1} with deuteration. The shift factors are consistent with these three bands being the infrared active librational modes. In the spectra taken at higher temperatures the band centers were less discernible because of the increased bandwidths. These data on the lattice modes are consistent with the proposed crystal structure of C_{cca} (D_{2h}^{22}) with two molecules per primitive cell.

An inspection of the frequency shift and linewidth of the ring-puckering mode (see Figures 1 and 2) as a function of temperature indicates that the ring is becoming less rigid as the crystal approaches phase I. In fact, the ring-puckering mode becomes so weak in phase I that it is almost impossible to detect its frequency. We interpret this behavior to be due to the ring undergoing inversion with sufficient rapidity that the effect on crystal phase I is the same as if the molecule were rotating perpendicular to the figure axis by 180°. Therefore, the ring inversion, with the accompanying very low potential, is giving rise to the plasticity of the cyclobutane crystal. This inversion also explains the X-ray observation that the crystal phase I has either a dynamic or static rotational disorder since the inversion gives

a crystal which is indistinguishable from one with molecules which are randomly rotated by 180°. Therefore, the dynamic inversion of the ring gives rise to the high cubic crystal symmetry of phase I. It is also believed that ring inversions cause plasticity in structurally related molecules such as cyclopentane. These results imply that four-membered ring molecules with high barriers to inversion should not have a plastic crystal phase.

Acknowledgement

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