

Anisotropy of rotational reorientations of cyclohexane near a phase transition

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(Submitted 15 August 1978)

Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 7, 465–468 (5 October 1978)

It is shown for the first time, using the temperature dependence of the phonon Raman spectra of anisotropic crystals of deuterocyclohexane, that the reorientation of the molecules around the C_3 axis is activated prior to the phase transition into a plastic crystal. The frequencies and waveforms of the lattice vibrations are calculated using atom-atom potentials.

PACS numbers: 63.20.Dj, 78.30.Jw, 64.70.Kb

Recent research revealed many examples of stagewise “melting” degrees of freedom of molecules in crystals, accompanied as a rule by phase transitions. Thus, the transition from a solid crystalline phase into a nematic liquid-crystal phase is due to “melting” of the translational degrees of freedom,¹ and the transition from the anisotropic (low-temperature) phase into the plastic (high-temperature) phase is the consequence of “melting” of the rotational degrees of freedom. In the latter case it is usually tacitly assumed that certain types of molecule rotations, by virtue of the singularities of their structure (for example, because of their disk-like shape), can be activated prior to others even in the anisotropic phase.

This stagewise “melting” of the rotational degrees of freedom might be revealed by the phonon spectra that are active and usually most intense in Raman scattering of light. The violation of the correlated rotational motion of molecules by individual reorientations of a definite type should lead to a broadening and relative decrease of the intensity of the phonon lines.²

To identify the type of rotations (librations) to which the frequencies belong it is necessary to have a reliably interpreted spectrum and data on the waveform of the oscillations.

In the present study we investigated the temperature dependence of the phonon spectrum of Raman scattering of cyclohexane and deuterocyclohexane in a wide range of temperatures, including the immediate vicinity of a phase transition (anisotropic crystal into a plastic crystal), and calculated the phonon spectrum of the low-temperature crystalline modification of these substances.

In the 40–200 cm^{-1} region, the Raman scattering (forward scattering) of crystalline cyclohexane and deuterocyclohexane were registered with a DFS-24 (LOMO Leningrad Optical & Mechanical Combine) spectrophotometer. The excitation was with the 488-nm line of an argon ion laser. The frequency measurement accuracy was $\pm 2 \text{ cm}^{-1}$. Ampoules with the substances were placed in a metallic vacuum cryostat, in which the copper sample holder with the heater was isolated from the nitrogen bath by a steel thin-wall transition piece, to permit accurate temperature measurements

($\pm 0.05^\circ$). In the 87–185 K interval the sample temperature was varied at a rate of $15^\circ/\text{hr}$ and in the vicinity of the phase transition at a rate $0.5^\circ/\text{hr}$.

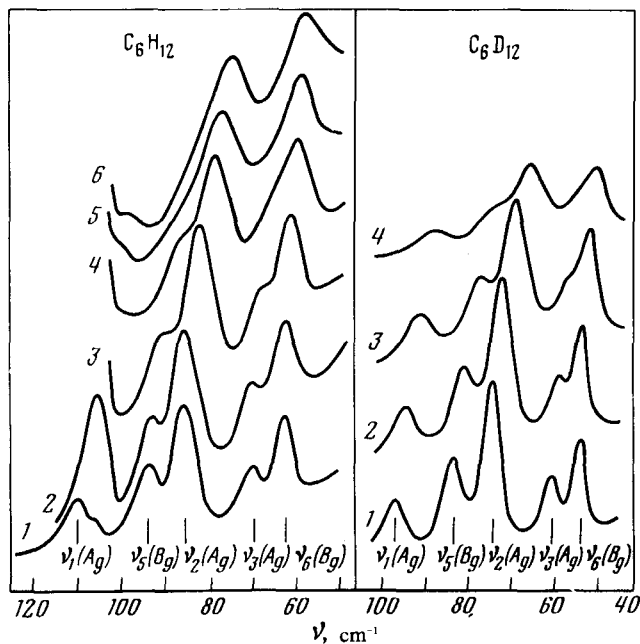


FIG. 1. Temperature dependence of the phonon Raman spectra of cyclohexane (C_6H_{12}): 1, 2–115; 3–140; 4–160; 5–170; 6–180 K and deuterocyclohexane (C_6D_{12}): 1–115; 2–140; 3–160; 4–180 K. Curve 1 (C_6H_{12}) was obtained with a filter to eliminate the plasma line (105 cm^{-1}).

Figure 1 shows the temperature dependence of the phonon spectra of Raman scattering of cyclohexane and deuterocyclohexane in the region 115–180 K. It shows also a calculation-based interpretation of the transitions, which was verified against the isotopic relations. The phonon spectra of cyclohexane and deuterocyclohexane were calculated atom–atom potentials, which were previously used for a number of molecular crystals.³ The interaction potential was chosen in the form 6-exp. The structural data determined at 115 K with sufficient accuracy ($R = 0.061$) were taken from Ref. 4, and the radius for the intermolecular atom–atom interactions was 10 \AA . The best agreement between the calculated and experimental spectra is obtained with a Williams potential.⁵ The lattice energy $E_{\text{calc}} = -11.5\text{ kcal/mole}$ calculated at 115 K by using this potential agrees well with the experimental $U_{\text{exp}} = -11\text{ kcal/mole}$ obtained at 186 K.⁶

It is seen first of all from the temperature dependence that the lines ν_3 and ν_5 of cyclohexane, and the analogous pair in the spectrum of the deuterocyclohexane, broaden more rapidly than the rest, and decrease in intensity when the phase transition is approached. They become practically unobservable at temperatures 160–170 K, 20–30° ahead of the phase-transition point ($T_m = 186\text{ K}$).

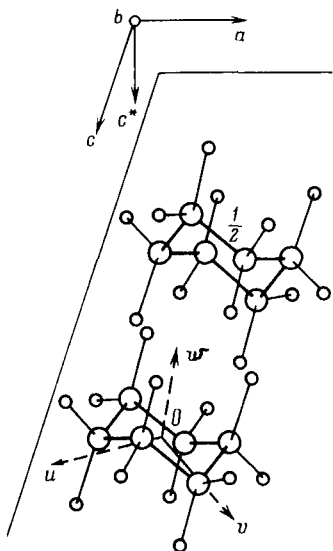


FIG. 2. Fragment of crystallographic cell of cyclohexane. The large and small circles are carbon and hydrogen atoms, respectively.

It follows from the calculation of the waveform of the vibrations that the $\nu_3(A_g)$ and $\nu_5(B_g)$ lines pertain to vibrations with substantial participation of rotations about the w axis (C_3 in the free molecule) (Fig. 2), which is close to the crystallographic c^* axis. It appears that the barrier of the rotational reorientations relative to this axis (≈ 2 kcal/mole, Ref. 2) is lower than that relative to the axes u and v , as a result of which the decrease of the intensities and the broadening of the corresponding phonon lines takes place long before the transition.

The lines $\nu_1(A_g)$, rotation around the u axis), $\nu_2(A_g)$, rotation around the v axis), and $\nu_6(B_g)$, rotation around the u axis) are clearly preserved in the spectrum up to temperatures that differ from the transition point by not more than 0.2° . These reorientations are substantially hindered by the packing of the molecules in the crystal (Fig. 2). They are "liberated" only after the transition into the plastic crystal. In this case all the Raman lines of the spectrum, shown in Fig. 1, go over into a structureless Rayleigh-scattering wing. It is assumed that all the reorientations are activated in the high-temperature plastic phase, since the entropy of the melting of the crystal is very low and corresponds only to "melting" of the translational degrees of freedom. The data obtained by us allows us to state that the phase transition into a plastic crystal "liberates" only the reorientations of the molecules relative to the axes u and v , whereas reorientations about w are activated in the anisotropic crystal long before the transition. A similar conclusion was drawn on the basis of NMR spectra.⁷

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