RAMAN SPECTRA AND THERMAL DISORDERING OF THE CRYSTALLINE STRUCTURE OF BENZENE

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Disordering of rotational degrees of freedom of molecules in a benzene crystal is investigated from Raman spectra. Nonuniform smearing of the spectrum of librational vibrations to the wing of the Rayleigh line is established. The changes observed are interpreted on the basis of calculations of frequencies, intensities, vibration modes, and barriers to molecular reorientations in the crystal by the method of atom-atom potentials. The line broadening in the spectrum of external vibrations by reorientations of molecules in the crystal as a function of their mode is analyzed.

Key words: Raman spectrum, structural disordering, isotropic reorientation of molecules, atom-atom potential.

Introduction. Crystalline benzene has three modifications [1, 2]. Of them, only phase I exists at normal pressure. The mobility of the molecules in phases II and III, which exist only at high pressure, is hindered substantially, while in phase I, according to data of different methods, it increases significantly with temperature [3-5]. At normal pressure, a benzene crystal experiences no phase transitions. However, the narrowing of the nuclear-magnetic-resonance signal in benzene I and its deuterio analog between 90 and 120 K (i.e., long before the phase transition to the liquid state, T_melt = 278.5 K) indicates the abrupt appearance of rather fast molecular reorientations in the plane of the benzene ring in the crystal [6]. The second moment decreases abruptly from 9.73 G² (90 K) to 1.6 G² (120 K) [5, 6]. According to different data, the activation energy of this motion is 2.1-4.2 kcal/mole (see [5]). Rotational reorientations of benzene in the molecular plane also reveal themselves in the temperature dependence of the times of spin-lattice relaxation T_{1p} and T_{1D} (T_{1D} is the dipole-relaxation time) [7, 8]. Furthermore, the sharp increase in T_{1D} at temperatures above 230 K indicates the presence of significant translational molecular diffusion in the crystal in the vicinity of the melting point. The activation energy of this motion is 21.2-22.6 kcal/mole [8].

Thus, the benzene crystal is an example of a structure with dissimilar types of dynamic molecular disorder. However, in spite of numerous works on investigating the mobility of the molecules in a crystal of benzene (or its deuterio analog) performed mainly by the nuclear-magnetic-resonance method (detailed surveys of the investigations are given in [3-5]), thermal disordering of its structure was not studied in detail from Raman spectra in the region of the frequencies of librational lattice vibrations sensitive to reorientational molecular motion.

Experimental Procedure. Raman spectra were recorded with a modernized DFS-24 spectrometer in excitation by a 0.05-W 514.5-nm line of an ILA-120 argon laser. The specimens for the investigations were cleaned by multiple distillation in vacuum. The parameters of the spectral lines were determined with the use of the software described in [9]. The spectra were processed in such a manner that the area of the total theoretical contour differed
The accuracy of determining the line widths by this method was 0.3 cm⁻¹. The barriers to molecular reorientation in the crystal and the frequencies, intensities, and modes of lattice vibrations of benzene were calculated by the method of atom-atom potentials (AAPs). The computational procedure and the parameters of the potentials are described in monograph [10].

Experimental Results and Their Discussion. The structure of phase I of benzene was determined by the x-ray method at 270 K [11, 12] and by the method of neutron diffraction at 218 and 138 K [13]. The elementary cell of the crystal belongs to a rhombic system (the spatial group $P_{6_{2}c}$) and contains four variously oriented molecules that occupy the positions $C_i$. Two planes (practically perpendicular to each other) that coincide with the planes of the benzene rings of the molecules and make a nearly 45° angle with the crystallographic axes $a$ and $c$ are pronounced in the crystal structure.

According to a group-theoretic analysis, 21 optical vibrations are active in the region of external vibrations in the vibrational spectrum of crystal I. Because of the alternative prohibition, 9 translational vibrations ($3A_u + 2B_{1u} + 2B_{2u} + 2B_{3u}$) are active only in IR absorption while 12 librational vibrations ($3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g}$) are active only in Raman scattering [14, 15].

Figure 1 shows Raman spectra of external vibrations (EVs) of crystals of benzene and its deutero analog at different temperatures. The temperature dependence of the experimentally observed frequencies and widths of some lines that correspond, according to our calculations (Table 1), to molecular librations about the $W'$ axis, which is close to the $W$ axis perpendicular to the benzene-ring plane, is given in Fig. 2. First of all, it can be seen that in the interval of 90-120 K, in which, according to data of nuclear magnetic resonance, molecular reorientation in the plane of the benzene ring is found, no substantial changes in the Raman spectra are observed. However as the temperature increases further, the high- and low-frequency parts of the spectrum (groups of lines at 130-140 cm⁻¹ and 55-65 cm⁻¹, $T = 77$ K) are broadened more substantially and decrease in intensity as compared to the lines in the middle part of the spectrum. A few degrees before the melting point they have the form of the practically structureless wing of the Rayleigh line, which is characteristic of disordered crystal systems. The group of lines in