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Unusual behavior of benzoic acid at low temperature: Raman spectroscopic study



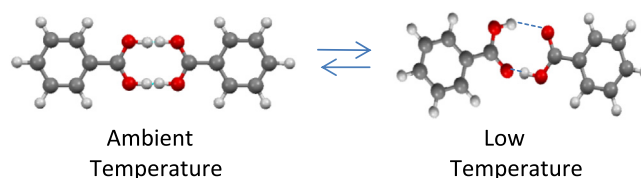
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HIGHLIGHTS

- Raman spectra of benzoic acid single crystals are taken in the temperature range of 5–300 K.
- One of two intra-dimer H-bond stretching modes disappears at $T < 60$ K due to loss of symmetry.
- The series of weak and narrow bands arises in the high-wavenumber region of 2500–3700 cm^{-1} at $T < 60$ K.
- A transition of two wells potential of H-bond to single well potential occurs at low temperature.
- The coupling of intramolecular and O–H stretching vibrations forms states, which resemble soliton states.

GRAPHICAL ABSTRACT



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ABSTRACT

The Raman spectra of benzoic acid single crystals have been measured in the temperature range of 5–300 K. At $T < 60$ K the spectra show at least two anomalous features, one of which is of direct relevance to intensity changes of the lattice modes in the low-wavenumber region. The intensity of modes at ~ 86 and ~ 146 cm^{-1} tends to zero at $T \rightarrow 0$ K. It is associated with appearance of two H-bonds of different length in the same α -tautomer, and with the loss of the inversion center in the dimer. The modes at ~ 86 and ~ 146 cm^{-1} are assigned to symmetric stretching intra-dimer vibrations of the O–H...O hydrogen bonds of the first and second order, respectively. The assignment is based on the measurements of spectral parameters as function of temperature. The other anomaly is that the series of weak and narrow bands arises in the high-wavenumber region of 2500–3700 cm^{-1} . The bands are assigned to combination tones of O–H hydrogen bonded stretching vibration and intramolecular modes. This effect results from a low-temperature transition of a conventional two wells potential of short H-bond in the α -tautomer to asymmetrical single well potential, and is due to a strong coupling of intramolecular vibrations to O–H stretching.

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Introduction

Benzoic acid is a classical object for vibrational and NMR spectroscopy. Primarily the interest of researchers was derived from an

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expectation to find out a strong symmetric hydrogen bonding at low temperature. When it became clear that the protons at the hydrogen bonds do not locate in the middle of the O...O distance at low temperature, the main attention switched to the processes of the protons ordering and tunneling.

Molecules of benzoic acid (BA) form dimers in the crystal, which is doubly hydrogen bonded through the carbonyl group (Fig. 1),

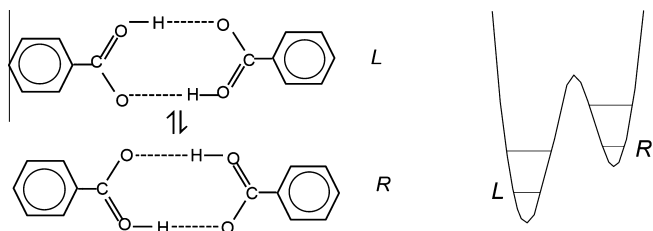


Fig. 1. The two tautomeric forms of the BA molecules labeled *L* and *R*, and schematic representation of the asymmetric double minimum potential.

and the crystal field in the solid state gives rise to the weak energy asymmetry of *L* and *R* tautomers. At elevated temperatures the system exhibits a dynamic disorder [1–8] and coordinated double proton transfer within the hydrogen bonds due to tunneling assisted by intra-dimer vibrations (that is, CO₂ rocking and stretch). The frequency of promoting modes corresponds well to the lowest activation energy calculated from the temperature dependence of the proton transfer rate [5]. The tunneling process gets slower at low temperature.

Vibrational spectrum of BA was studied in Refs. [9–15]. However, at $T = 0$ K the dimers are ordered in a unique configuration *L* (Fig. 1) throughout the crystal. How the ordering changes the vibrational spectrum of the crystal? Does the ordering affect the hydrogen bond strength? We will address these and some other questions in this paper.

Experimental

The crystalline samples were obtained from saturated alcohol solutions by B. Zakharov (Novosibirsk State University). The average crystal size was around 1 mm. The orientation of the crystallographic axes with respect to the external crystal edges and faces was determined by B. Zakharov using STOE IPDS equipment.

Polarized single-crystal Raman spectra were collected on a Lab-RAM Horiba single spectrometer with a CCD Symphony (Jobin Yvon) detector, that provided 2048 pixels along the abscissa. The laser line was used for wavenumber correction of the spectra. The laser power (488 nm line of an Ar⁺ laser) at the sample was typically 3 mW. The spectra at all temperatures were measured in 180° backscattering collection geometry with a Raman microscope. The BA crystals were wrapped in indium foil for better thermal contact, keeping an open area at the upper surface accessible for light, and fixed on a cold finger of the He-cryostat. All measurements were performed with a spectral resolution of 0.7 cm⁻¹.

The Raman bands were fitted using a PseudoVoigt1 or Lorentz function to determine their spectral parameters, i.e., wavenumber, bandwidth and integral intensity. The integral intensity of the bands at around 1000 cm⁻¹ was used as a reference for intensity calibration. These modes are not involved into intermolecular motions, and a relatively large energy of the modes makes the temperature-dependence of their Raman intensity negligible.

Results and discussion

Figs. 2–4 show the spectra of BA crystals in low-, mid- and high-wavenumber region respectively at different temperatures. These spectra demonstrate two distinctive features (among the others), one of which associated with anomalous behavior of some lattice modes in the range 80–150 cm⁻¹ (Fig. 2; unless specified otherwise, the wavenumbers of the vibrational modes mentioned in the text correspond to 5 K), and the other one – with the appearance of a band series in high-wavenumber region 2500–3700 cm⁻¹ characteristic of O–H and C–H stretches (Fig. 4). Both

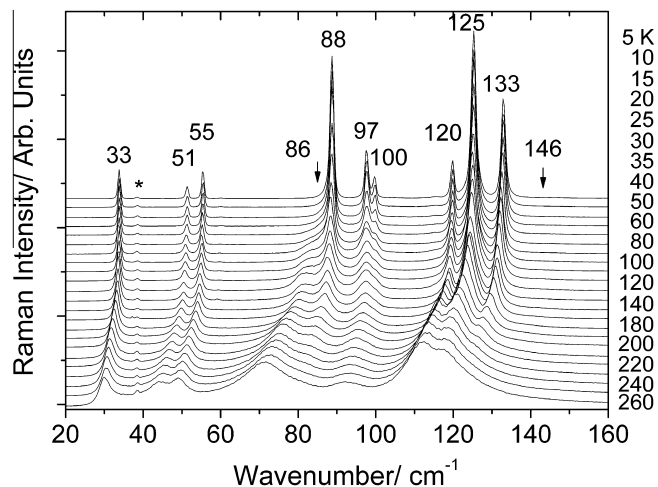


Fig. 2. Raman spectra of BA crystals in low-wavenumber region at different temperatures. Asterisk in Fig. 2a denotes a plasma line of Ar⁺ ion laser.

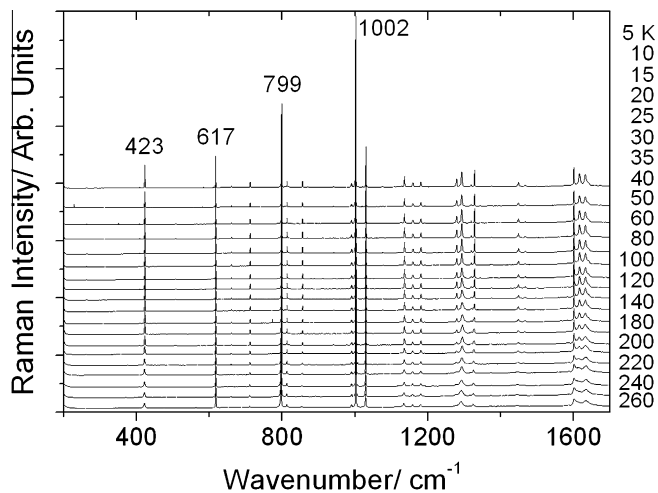


Fig. 3. Raman spectra of BA crystals in mid-wavenumber region at different temperatures.

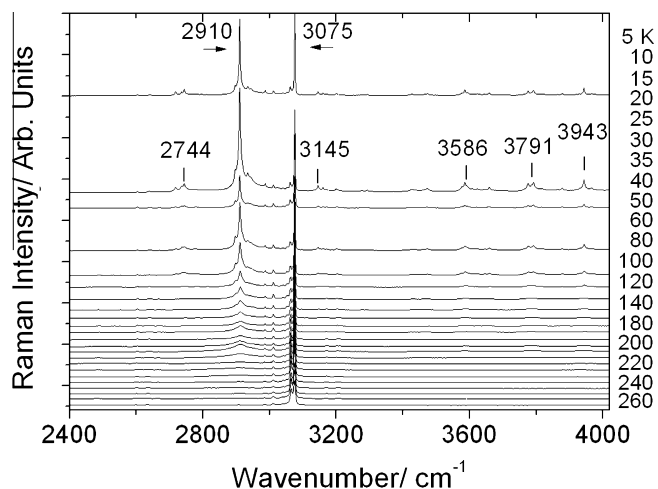


Fig. 4. Raman spectra of BA crystals in high-wavenumber region at different temperatures.

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