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Raman spectra of terephthalic acid crystals in the temperature range 5 K–300 K

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ABSTRACT

Raman spectra of terephthalic acid crystals were taken in the temperature range 5 K–300 K. The temperature dependence of the vibrational frequency of the O⋯O hydrogen bond is found to contain information on the mechanism of the proton motion along the bond (hopping and/or tunneling). Onset temperatures of both tunneling and ordering (termination of the hopping) process are determined. Triplet exciton bands observed in the high-wavenumber spectral range also exhibit the relation with proton motions between oxygen atoms. The energy spectra of molecular chains of terephthalic acid, the proton potential energy along the bond, and the probabilities of tunneling as a function of the hydrogen bond lengths are calculated.

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1. Introduction

In crystals, terephthalic acid (TPA) molecules form chains whose fragments are shown in Fig. 1.

Two O—H⋯O hydrogen bonds and carboxyl groups form a six-membered ring in which the left (*L*) and right (*R*) tautomers are identical. The identity of TPA tautomers allows the double proton transfer from one oxygen atom to another along the bonds. This phenomenon is called the proton tautomerism. The structures of compounds allowing the proton tautomerism are diverse and include crystals with infinite chains, dimers, trimers, and tetramers [1]. Moreover, both one type (O—H⋯O, N—H⋯N) and different type (O—H⋯N, N—H⋯O) atoms can serve as donors and acceptors of tautomeric hydrogen bonds (further, for simplicity, τ-bonds).

The proton potential function along the τ-bonds is represented by a curve with two identical minima (Fig. 2).

At sufficiently high barriers the U_0 proton transfers along the τ-bond are performed either by hopping over the potential barrier with the help of lattice vibrations (phonon-assisted jumping) or tunneling. The tunneling probability exponentially depends on both barrier height and distance between the minima

$$D = D_0 e^{-\left(\frac{2}{\hbar} \int\limits_{x_1}^{x_2} \sqrt{2m(U(x)-E)}dx \right)},\qquad(1)$$

where *D* is the barrier transparency, D_0 is the constant of about 1, *m* is the proton mass, $U(x)$ is the hydrogen bond potential, x_1, x_2 are the coordinates of the proton energy minima on the τ-bond. Thus, at cooling down the crystalline vibrations are 'frozen out' and the τ-bond becomes shorter. It causes a reducing of the jumping rate and an increasing of the tunneling probability.

There is a principal distinction in the quantum mechanical description of hopping and tunneling. In hopping, the proton is only in one minimum at each time instant, but changes its location with a certain frequency. There is one proton wave function and its square for each of the minima at any given moment. In tunneling, the proton wave function and the distribution density simultaneously cover both minima [2]. Therefore the proton jumps cause disorder in the crystals (structural parameters of the whole six-membered ring are violated) unlike tunneling because the proton happens to be near both atoms forming the τ-bond at the same time.

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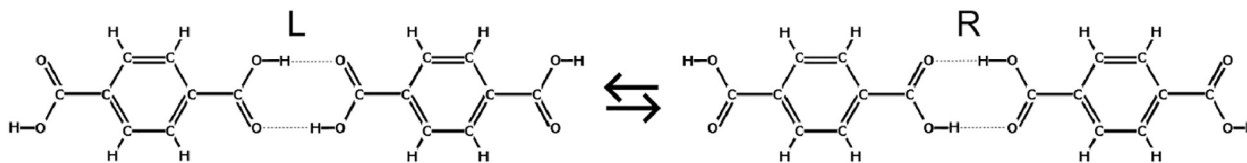*E-mail address:* kolesov@niic.nsc.ru (B.A. Kolesov).

Fig. 1. Fragment of a chain of TPA molecules in the crystal and different molecular tautomers.

Both mechanisms (tunneling and hopping) are formally not related to each other and their temperature characteristics are determined by the thermal occupancy of vibrational states different for each of them. Thus, tunneling turns out to be dependent on the population of vibrations that mainly change the donor-acceptor distance, and hopping depends on the population of those vibrations that change the fragment structure in favor of hopping.

In this work, we tried to elucidate how different mechanism of the proton motion are manifested in Raman spectra and how informative the data are that can be obtained from the measurement of the temperature dependence of the Raman spectra of terephthalic acid crystals in which chains are formed via τ-bonds. The greatest attention was paid to the vibrations of the O···O hydrogen bond in the low-wavenumber spectral region of crystal modes.

2. Experimental

The crystalline samples were obtained from saturated alcohol solutions. Polarized single crystal Raman spectra were collected on a LabRAM Horiba single spectrometer with a CCD Symphony (Jobin Yvon) detector that provided 2048 pixels along the abscissa. The laser line was used for the wavenumber correction of the spectra. The laser power (488 nm line of an Ar$^+$ laser or 633 nm line of He-Ne laser) at the sample was typically <3 mW. The spectra at all temperatures were measured in a 180° backscattering collection geometry with a Raman microscope. The 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 closed cycle He-cryostat. All measurements were performed with a spectral resolution of 0.7 cm^{-1}.

2.1. Quantum Chemical Calculations

The geometries and harmonic vibrational frequencies of terephthalic acid, its dimers and tetramers in a gas phase were calculated at the M06-2X [3] and B3LYP levels [4] of theory with the 6-31+G(d) and 6-311+(d,p) basis sets [5]. All equilibrium structures were ascertained to be minima on the potential energy surfaces. Relaxed potential energy surfaces for the moving of protons relatively center of O—O distance in tetramers were performed using the B3LYP/6-311+G(d,p) method. In these type of calculations O—O distance was equal to 2.75, 2.66, 2.58, 2.50 and 2.41 Å. For all calculations the *GAUSSIAN09* suit of programs [6] has been employed.
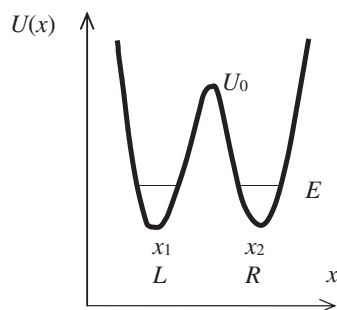
3. Results and Discussion

3.1. Crystal Vibrations

In the calculated vibrational spectrum of a chain of TPA molecules the 114 cm^{-1} mode (the wavenumber value is given without a correcting factor) in which the neighboring molecules shift to each other corresponds to the τ-bond vibrations. The total calculation of MOs and the vibrational spectrum is presented in the Supplement.

The experimental Raman spectra of TPA crystalline vibrations at different temperatures are shown in Fig. 3. The 106 cm^{-1} mode is polarized along the molecular chain (Fig. 4), and this fact together with the calculation results enable their assignment to τ-bond vibrations.

Fig. 5 depicts the temperature dependences of the peak position and half-width of the 106 cm^{-1} mode. When the temperature decreases, the slope ω(T) changes, the onset of the slope change being at T ~ 200 K, i.e. the temperature at which the average vibrational quantum number n of the 106 cm^{-1} mode becomes less than unity (shown in the inset).

The proton potential function on the τ-bond depends on the O···O distance. Fig. 6 illustrates the results of the calculation of the proton potential function $U(x)$ for terephthalic acid at different $d_{O···O}$ values. It is seen the distance between the minima and the barrier height U_0 substantially decrease with decreasing $d_{O···O}$ value.

The presented functions enable the calculation of the barrier transparency by expression (1) where the energy $\hbar\omega_{str}/2$ of proton zeroth vibrations should be taken as the proton energy E in the minimum. To estimate the former we used the results of Ref. [8] which determine the relationship between the length of the O—H···O hydrogen bond and the wavenumber ω_{str} of the proton stretching vibrations on the bond. Fig. 7 shows the results of the calculation of the barrier transparency. At $d_{O···O} = 2.411$ Å the barrier transparency (more precisely, D/D_0) was taken to be unity rather than calculated because in this case, the barrier height U_0 is so low that it becomes less than the energy of proton zero point motions. This means that at sufficiently short O···O distances
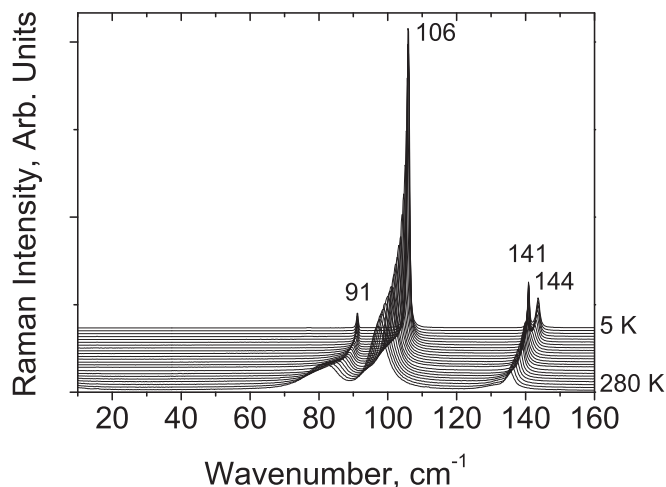

Fig. 2. Proton potential energy in the tautomeric hydrogen bond.

Fig. 3. Spectra of TPA crystalline vibrations at different temperatures.