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Possible manifestation of proton disorder in δ-$KIO_3 \cdot HIO_3$ crystal in its IR spectra

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Abstract

For getting more information about the behavior of hydrogen atoms in partially occupied sites in δ-$KIO_3 \cdot HIO_3$, we have measured temperature-dependent infrared spectra of this crystal at 14–300 K in the spectral range of OH stretching and bending vibrations. It was found that ν(OH) band (centered at ~2800 cm^{-1}) has complicated profile which, at temperatures below 220 K, includes weak low-frequency satellites at its low-frequency slope. At 14 K, we have main peak ν(OH) at 2766, satellites at 2606, 2485, and 2387 cm^{-1}, and strong 2δ(OH) overtone peak at 2274 cm^{-1} enhanced due to Fermi resonance. At the same time, the low-frequency slope of δ(OH) band (centered at 1189 cm^{-1}) shows equidistant satellites separated with period of approximately 25 cm^{-1}. The observed features suggest anharmonic coupling between OH high-frequency vibrations and various low-frequency motions of the crystal lattice.

Keywords: δ-$KIO_3 \cdot HIO_3$; H-bond; Phase transitions; FTIR spectra; Proton dynamics

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1. Introduction

Polymorphism of potassium biiodate, $KIO_3 \cdot HIO_3$, has been known for decades (see Ref. [1] and the literature cited therein). The stable delta polymorph of the title crystal, δ-$KIO_3 \cdot HIO_3$, was found to exhibit low temperature phase transition [1], non-linear dielectric and optical properties [1,2]; a dynamic jump type proton disorder was supposed for this polymorph [2,3]. The heavy atom part of the δ-$KIO_3 \cdot HIO_3$ crystal structure (K, I, O) was determined several times at room temperature from X-ray diffraction data [2–4] and refined in our previous work [5]. According to these works, the space group of the title crystal is *Fdd*2, with $Z = 24$. The lattice unit contains: three crystallographically non-equivalent pyramidal IO_3 groups, each in general position (16b), which gives 48 IO_3 groups; one K atom in general position (16b), and one K atom in a special position (8a) at C_2 axis, which gives 24 K atoms. From chemical structure, the unit cell should contain 24 hydrogen atoms; however, the crystal structure does not contain the sites of (8a) type suitable for occupation by hydrogen atoms, but it contains two such sites in general position (16b) which, at full occupation, would give 32 hydrogen atoms; therefore, at least one of these sites should be only partially occupied. One of these sites corresponds to short hydrogen bond ($O \cdots O$ distance equal to 267.1 pm) and seems to be fully occupied, while the other corresponds to greater $O \cdots O$ distance (290.7 pm) and could be partially occupied; for getting 24 hydrogen atoms, it should be one-half occupied. The resulting structure contains $O_{23}{-}H_1 \cdots O_{13} \cdots H_2{-}O_{33}$ fragments (Fig. 1), where one-half of H_2 atoms is absent. In Ref. [5], the coordinates of H_2 were reported as 0.023; 0.20; and 0.390; after correction, they are as follows: 0.020; 0.131; and 0.407. The structure can be described as consisting of $[I_3O_9H_{3/2}]^{3/2-}$ ions possibly originating from occupationally disordered $[I_3O_9H_2]^-$ and $[I_3O_9H]^{2-}$ anions (with short I–O contacts of IO_3 groups). These ions are connected via hydrogen bonds to form plane grids parallel to (100) with the K^+ ions placed between them. This agrees with the known structures of the oxosalts, oxoacids, and acid oxosalts of iodine(V), i.e. compounds of the types M^IIO_3, $H_n(IO_3)_n$, and $M^I_m(IO_3)_m \cdot H_n(IO_3)_n$, respectively, which

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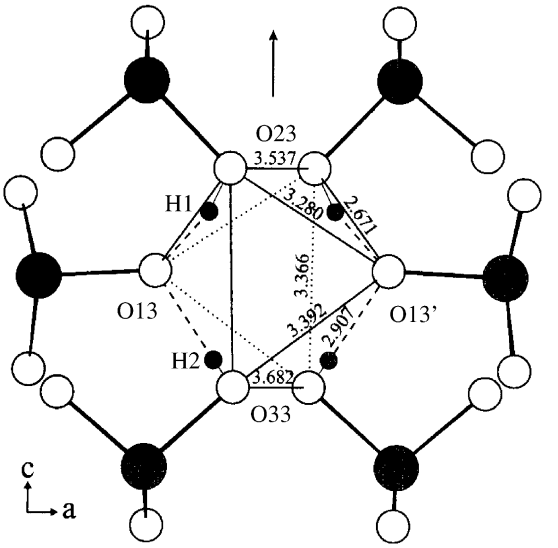

Fig. 1. Hydrogen bond system of δ-$KIO_3{\cdot}HIO_3$ with the octahedral surrounding of the 8a sites at 0 0 1/2. Dashed lines represent hydrogen bonds [5].

contain trigonal pyramidal IO_3^- ions or IO_2OH molecules, which tend to form dimeric or oligomeric species with intermolecular I···O contacts. Our previous results of infrared (IR) and Raman studies of δ-$KIO_3{\cdot}HIO_3$ [5] show that this species undergoes a second-order phase transition (without changes in its crystal structure) near 220 K, which manifests itself as a change in the slope of the temperature dependence of some spectral parameters and can be related to the proton sublattice. However, until now the mechanism of this phase transition is not clear due to the lack of experimental data in the OH stretching range. It is known [6,7] that in hydrogen bonded systems the profile and frequency shift of OH stretching band is correlated with both the intermolecular distance O···O, and the intramolecular bond length, and the temperature dependence of the bands related to the vibrations of O–H bonds can give valuable information concerning the dynamics of the proton subsystem. In the present work, we perform a comprehensive analysis of the temperature-dependent FTIR spectra of the δ-$KIO_3{\cdot}HIO_3$ crystal in the region of OH stretching and bending vibrations. The aim of this analysis is to characterize in more detail the lattice dynamics of δ-$KIO_3{\cdot}HIO_3$ crystal and to get insight into the mechanism of the phase behavior of this crystal.

2. Experimental

Specimens of the δ-$KIO_3{\cdot}HIO_3$ crystal were obtained according to Ref. [4] by slowly cooling down the concentrated solutions of KIO_3 and HIO_3 from 413 to 353 K during 3 months. The temperature-dependent IR spectra of the powdered crystal suspended in Nujol were recorded on the Bruker FTIR spectrometer IFS-88 model in 400–4000 cm^{-1} spectral range. Temperature dependencies of the IR spectra in the 14–300 K temperature range were measured using the ADP cryogenics closed-cycle helium refrigerator system, which allows one to maintain the temperature of the sample within 1 K. The measurements were performed with 10–30 K steps and a 20 min stabilization time for each temperature.

3. Results and discussion

The fragments of the temperature-dependent FTIR spectra of δ-$KIO_3{\cdot}HIO_3$ crystal recorded in the frequency range of OH stretching and bending vibrations (1800–3400 and 900–1300 cm^{-1}) are shown in Figs. 2 and 3, respectively. The lengths of the two types of the OH···O bonds in this crystal, as reported in Ref. [5], are 290.7 and 267.1 pm and, therefore, according to well-known Novak's classification [6,7], one can ascribe them to weak and medium strength hydrogen bonds. It is known [6,7] that for weak and medium strength hydrogen bonds one can distinguish three IR active modes corresponding to vibrations of OH···O fragments: (1) stretching modes ν(OH) with $3500 \geq \nu_{OH} \geq 2800\ cm^{-1}$; (2) in-plane bending modes δ(OH) with $1300 \geq \delta_{OH} \geq 1150\ cm^{-1}$; and (3) out-of-plane bending modes γ(OH) with $\gamma_{OH} \approx 550\ cm^{-1}$ [7]. The frequencies vary with the strength of the hydrogen bond and, within the series of similar compounds, they correlate with each other and with the strength

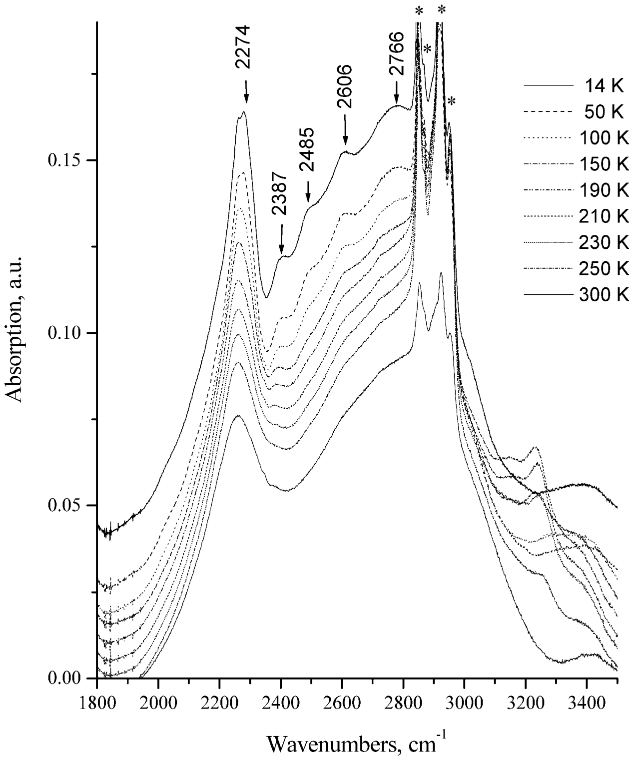

Fig. 2. Temperature evolution of FTIR spectra of polycrystalline δ-$KIO_3{\cdot}HIO_3$ (suspension in Nujol) in the region of ν(OH) stretching mode. Asterisks denote the Nujol absorption bands.

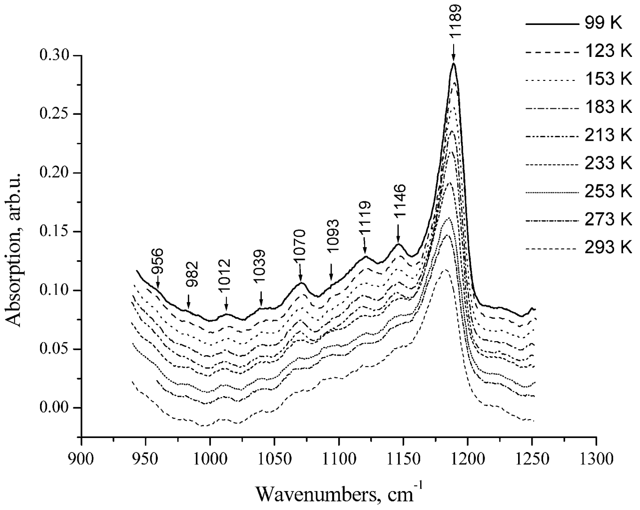

Fig. 3. Temperature evolution of FTIR spectra of polycrystalline δ-$KIO_3 \cdot HIO_3$ in NaCl pellet in the region of the δ(OH) in-plane bending mode.

and the $R_{O\cdots O}$ distance of the respective hydrogen bond. According to this classification, the OH stretching band of weaker hydrogen bond with O–H···O distance of 290.7 pm should be located at higher frequencies of about 3500 cm^{-1}. It was observed experimentally in our FTIR spectra at about 3585 cm^{-1}. It is also known that for medium strength H-bonds Fermi resonance often affects the ν(OH) band shape [8]. As it was mentioned above, a characteristic feature of δ-$KIO_3 \cdot HIO_3$ crystal structure is the presence of $K_{3/2}[I_3O_9H_{3/2}]$ moieties. The interatomic distances and hydrogen bond lengths in δ-$KIO_3 \cdot HIO_3$ are similar to those reported for α-HIO_3 crystal [9] where HIO_3 molecules are linked by chain-like H-bonds (see Table 1), and their low-frequency phonon spectra are similar, too [5,9]. This can be the reason for similarity of the spectral distribution observed in the region of ν(OH) stretching band in the spectra of these two crystals. Following [9], we assign a very strong broad band centered at 2800 cm^{-1} (at room temperature) and less intensive more narrow band centered at 2274 cm^{-1} to Fermi resonance doublet formed by ν(OH) stretching vibration and 2δ(OH) overtone. In the 1000–1300 cm^{-1} region, there is a band of middle intensity with peak position 1189 cm^{-1} at room temperature. Bands of similar frequencies were also observed in the IR spectra of the other H-bonded iodates [9,10], and they are usually assigned to in-plane bending modes δ(OH) of I–O–H···O–I fragments. Temperature evolution of the peak position and half-width of the δ(OH) band were measured in our previous work [5], and respective dependencies showed sharp changes in their slopes near 220 K, which was presumably attributed to a phase transition in the proton sublattice. In the present paper, we focused on the temperature evolution of the overall profile of the respective bands. First of all, one could see pronounced ‘modulation’ in the low-frequency slopes of the ν(OH) and δ(OH) bands, which clearly develops at lower temperatures. The frequencies of the δ(OH) band satellites at 99 K are 1146, 1119, 1093, 1070, 1039, 1012, 982, 956, and 932 cm^{-1}. The differences between the neighboring peaks in this progression are almost constant and equal to 27 ± 4 cm^{-1}. The ν(OH) band satellites in the spectra, which are more clearly seen on the low-frequency slope at the temperatures below 220 K, are located (14 K) at 2766 (main maximum), 2606, 2485, and 2387 cm^{-1}. The respective difference between the maxima are 160, 120, and 98 cm^{-1}, which correlates well with lattice phonons reported for the δ-$KIO_3 \cdot HIO_3$ crystal in Ref. [5]. When passing from 220 K to lower temperatures, all the satellite bands become sharper; however, they retain their relative positions and intensities. It is worth mentioning that the number of satellite bands observed in the OH bending mode region is three times greater than the number of corresponding satellites in the OH stretching region. Similar

Table 1
I–O bond distances (pm) of α-HIO_3 and δ-$KIO_3 \cdot HIO_3$ to oxygen atoms acting as hydroxyl groups (I–OH), H-bond acceptors (I–O···H) or bridging atoms to neighbouring I atoms (O–I···O) with short (≤265 pm) I···O contacts, and O–H···O distances

	I–OH	I–O···H	O–I···O	I···O	O–H···O	Ref.
α-HIO_3	190	181	181	250	268	[10]
δ-$KIO_3 \cdot HIO_3$	193	181	182	235	267.1	[5]
	188	181	181	256	290.7	[5]

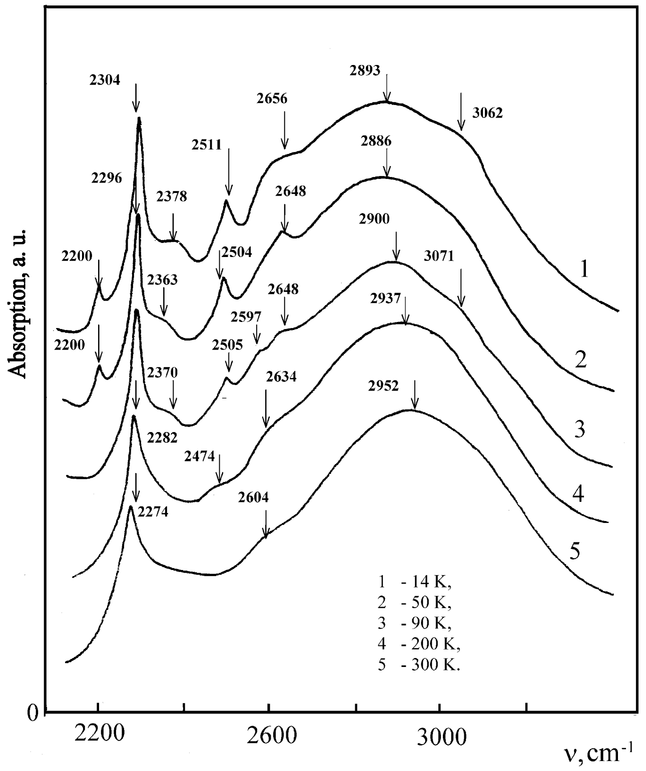

Fig. 4. Temperature-dependent IR spectra of single crystal α-HIO_3 (yz plane; E||Z thickness of plate ~5 μm in the region of ν(OH) stretching mode.

Table 2
Frequencies of ν(OH) and δ(OH) bands of HIO$_3$ and δ-KIO$_3$·HIO$_3$ at 300 and 14 K

α-HIO$_3$		δ-KIO$_3$·HIO$_3$		Assignment
300 K	14 K	300 K	14 K	
2274	2304	2263	2274	2δ(OH)
	2378		2407	Two-phonon excitations
	2511		2490	
2604	2656	2606	2606	
2952	2893	2858	2774	ν(OH)
	3062			
200 K	77 K	293 K	99 K	
1155	1165	1183	1189	δ(OH)
		1146	1146	
		1119	1119	
		1093	1093	
		1070	1070	
1060	1063	–	–	2γ(OH)
		1039	1039	
		1012	1012	
		982	982	
		956	956	

(but less regular) band progressions were also observed for ν(OH) band in the spectra of α-HIO$_3$ [9] (see Fig. 4) and α-KIO$_3$·HIO$_3$ [11] crystals, as well as for other systems [12–14]. The frequencies of ν(OH) and δ(OH) bands are presented in Table 2. The observed extra bands can be ascribed to strong anharmonic coupling between the high-frequency vibrational modes of hydrogen bonds and low-frequency lattice phonons as described in Ref. [15]. According to the theoretical model proposed in Ref. [15], for solids containing strong hydrogen bonds one can expect the appearance of a multiband substructure developed at the low-frequency slope of the ν(OH) absorption band in the IR spectra. To understand the origin of the fine structure of ν(OH) band which emerges when cooling the crystal (Fig. 4), it is worth mentioning that for α-HIO$_3$ crystal the submaxima observed in the 2300–2700 cm^{-1} region correspond to the gaps of the polariton branch in the Raman spectra on polaritons [16], and therefore the submaxima were attributed to dipole active two-particle states. This suggests that the observed structure is caused by resonant or quasiresonant interaction between the two-particle excitation zones and the one-particle state ν(OH) which leads to formation of coupled or quasicoupled pairs of phonons. The observed fine structure can be also connected with distribution of the density of states, as well as with excitation of the type $2\delta(\mathrm{OH}) + \omega_s$, where ω_s corresponds to low-frequency lattice vibrations.

Moreover, with account for rather complicated crystal structure of the δ-KIO$_3$·HIO$_3$ crystal ($Z = 24$) and presumed proton disordering, one should consider contribution of proton sublattice into the lattice dynamics of the studied crystal. It is well known that solids with hydrogen atoms or protons demonstrate a peculiar lattice dynamics. Of special importance are the recent studies performed by Fillaux and co-authors [17–19]. Using the incoherent inelastic neutron scattering technique, they have investigated the vibrational dynamics for protons in various solids and revealed that proton dynamics is almost totally decoupled from the surrounding heavy atoms. In addition, Fillaux notes that the proton subsystem demonstrates collective dynamics. By studying electronic absorption spectra in the benzoic acids crystal, Rambaud and Trommsdorff [20] have observed the cooperative proton transfer and tunneling (motion of four protons). Similar four-position protonic moieties can be selected in the δ-KIO$_3$·HIO$_3$ crystal (Fig. 1). For α-HIO$_3$ crystal, which at room temperature belongs to the orthorhombic shape group $P2_12_12_1$ with four formula per unit cell [9], there are also evidences [21] that the protons are randomly distributed in general positions between the oxygen atoms belonging to different iodate groups. So one can expect collective vibrations of protons in certain structures formed by statically disordered hydrogen atoms, whose vibrations are only weakly coupled with the vibrations of the neighboring hydrogen atoms (and which would be absent for ideally ordered proton subsystem). As it follows from our data [5], the OH bending vibration band is more sensitive to proton disorder than the OH stretching band. Therefore, the satellite bands observed on the low-frequency slope of δ(OH) band can be assigned to oscillations of disordered OH groups forming a periodic structure in the crystal. The resulting spectral distribution in the OH bending and stretching vibration regions is determined by the interplay between the adiabatic coupling between the high-frequency OH stretching/bending and the low-frequency lattice phonons and resonance interaction between the respective OH fundamental and various combination modes.

4. Conclusions

The detailed temperature variable FTIR spectroscopic study of the δ-KIO$_3$·HIO$_3$ crystal has been performed in the spectral range of OH stretching and bending vibrations at temperatures down to 14 K. Powder FTIR spectra of the title crystal show a series of submaxima, which are developed at the temperatures below 220 K and are superimposed on the carrying OH stretching or bending absorption band. We associate the presence of this extra bands in the IR spectra with anharmonic coupling between OH high-frequency vibrations and collective vibrations of disordered hydrogen atoms in proton sublattice of the crystal, with possible participation of lattice phonons.

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