SPECTROSCOPIC EVALUATION OF THE STRUCTURE AND DYNAMICS OF THE HYDROGEN BONDS IN DIFFERENT CRYSTAL MODIFICATIONS OF POTASSIUM BIIODATE

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The $KIO_3 \cdot HIO_3$ crystals belong to the family of acidic iodate compounds which is well-known for its ferroelectric phase transitions and has four crystal modifications. Here we report the results of IR and Raman study of vibrational spectra (4000$-$60 cm^{-1}) of α and δ-modifications in the temperature range from 300 to 13 K. The α-$KIO_3 \cdot HIO_3$ crystal ($P2_1/b$ space group, z=4 at room temperature) is built of two nonequivalent sets of dimers $IO_3 \cdots H \cdots O_3I$, joined by strong symmetric hydrogen bond ($O \cdots O$ distance is about 2.5 Å). At 223 K (T_c) the ferroelectric phase transition occurs in this crystal. The stable δ-modification (space group $Fdd2$, z=24 at room temperature) is formed from structure units of three distinct types: I_2O_5 and $I_2O_5(OH)$, which are joined by the H-bond network. In order to understand the normal modes of vibrations in α-$KIO_3 \cdot HIO_3$ and δ-$KIO_3 \cdot HIO_3$, we have carried out lattice dynamics calculations using a generalized valence force field for the dimers $[H(IO_3)_2]^-$ and other structure units. The introduction of the translation and libration coordinates related to the normal coordinate analysis leads to a precise assignment of the frequencies and shows that both stretching and bending vibrations of IO_3 groups are strongly coupled with the translational vibrations of the hydrogen atom in case of α-modification. In the case of δ-modification those vibrations are localized on separate I$-$O bonds. A comparative analysis of the vibrational spectra and structure is presented. On the base of analysis of vibrational spectra and according to measurements[a] of pressure dependencies of the ^{127}I NQR spectra at 77 K it was concluded that the mechanism of ferroelectric phase transition in α-modification of potassium biiodate crystal involves the proton ordering in the double-well potential at T_c.

[a] A.I.Barabash, J. Mol. Struct., 270, 517 (1992).