INFRARED SPECTROSCOPIC ESTIMATION OF H⁺ AND D⁺ POSITIONS IN THE STRUCTURE OF THE ORTHORHOMBIC CRYSTALS OF H₅O₂ClO₄⁻ AND D₅O₂ClO₄⁻

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The crystalline samples of the orthorhombic phase of H₅O₂ClO₄⁻ (I) and D₅O₂ClO₄⁻ (II) are examined by infrared (IR) absorption spectroscopy. Inaccuracies referring to the identification of II found in the literature are corrected. The work shows that a typical evidence of the crystallization of I is the doublet splitting ν(OH) at 3232 cm⁻¹ and 3340 cm⁻¹; and a typical evidence of the crystallization of II is a similar doublet splitting ν(OD) at 2391 cm⁻¹ and 2484 cm⁻¹. In order to determine the doublet origin and to make clear how it depends on the concentration of hydrogen isotopes, specially prepared isotopically mixed crystalline samples of the composition (HₓD_{1-x})₅O₂ClO₄⁻ (III, x = 0.17-0.90) are studied. Observations of the concentration dependence of the doublet splitting are used to check the quality of the existing variants of the crystal structure of I. Agreement in the experiments with the samples of III is obtained when the structural model of the cation with the H⁺ and D⁺ positions in the center of a strong H₂O…H⁺…OH₂ and D₂O…D⁺…OD₂ hydrogen bond (HB) is used. Although we do not exclude the possibility of a symmetrical statistical distribution of H⁺ and D⁺ between two potential energy minima. The results of the spectroscopic analysis agree with the known data of the X-ray crystallographic analysis, showing that the crystals of I have a space symmetry group Pnma. At the same time, they disagree with the recently published data of theoretical calculations of the crystal structure of I (P2₁2₁2₁), these data showing that H⁺ notably shifts from the center of the strong HB towards an oxygen atom of one of the two water molecules.

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INTRODUCTION

The peak of interest in the structural analysis of crystalline hydrates of perchloric acid and some other strong acids was in the second half of the last century. At that period, the structure of some crystalline hydrates of perchloric acid, including the H₅O₂ClO₄⁻ crystals with a melting point of 20.65 °C [1], was determined by the X-ray crystallography. At the final stage of the structure identification, the symmetry space groups Pnma and Pn2₁2₁2₁ were found to be equally possible: the R-factor of 0.114 and 0.108 respectively. A preference was given to the centrosymmetric group, though, in particular, its R-factor was higher. If there were the space group Pnma, then the H⁺ proton would be in the center of crystallographic inversion, and, consequently, in the center of a strong H₂O…H⁺…OH₂ hydrogen bond. However, in the final chapter of [1]...
and in the chapter, devoted to the X-ray crystallography data of [2], there was a note regarding the known limitations of the method used. This note indicates that the X-ray diffraction method does not allow the determination of the $H^+$ location: whether it is on the symmetry element or its opposite sides, occupying two statistically or dynamically related positions.

Using the single crystal X-ray diffraction (XRD) data of [1], the IR and Raman spectra of $\text{H}_2\text{O}_2\text{ClO}_4^-$ and of $\text{D}_2\text{O}_2\text{ClO}_4^-$ were interpreted in [3-5]; and crystal vibrations were analyzed, correspondingly, within the framework of the $D_{2h}$ factor-group.

Inelastic neutrons scatterings of $\text{H}_2\text{O}_2\text{ClO}_4^-$ are presented in [6]. The authors of the work used the data of [1] in the assignment of the $\text{H}_2\text{O}_2^+$ vibrational frequencies.

Calculations of the crystal structure of $\text{H}_2\text{O}_2\text{ClO}_4^-$ by the molecular dynamics methods and total energy density functional theory were carried out a few years ago and were presented in [7]. According to the calculations, the space group $Pnma$ corresponds to a saddle point and $P2_12_12_1$ corresponds to an energy minimum. On passing from the saddle point to the minimum, the reduction of symmetry of $\text{H}_2\text{O}_2^+$ is observed, which is accompanied by a shift of $H^+$ from the center of the strong HB. The authors of the abovementioned work calculated also the IR and inelastic scattering spectra of $\text{H}_2\text{O}_2\text{ClO}_4^-$. They used the spectra given in [2, 6] for comparison. The work [7] pretends to give a complete interpretation of the vibrational spectra of $\text{H}_2\text{O}_2\text{ClO}_4^-$. However, in our opinion, a difference between the theoretically calculated and experimentally measured spectra is too big.

Vibrational spectra are a very sensitive method to detect the reduction of symmetry [8]. Taking into account the existence of various points of view on the structure of $\text{H}_2\text{O}_2\text{ClO}_4^-$ crystals, we have carried out a series of experiments aimed to reveal the symmetry of $\text{H}_2\text{O}_2^+$ by IR spectroscopy. The obtained data are presented below.

**EXPERIMENTAL**

Information on the preparation of HClO$_4$·2H$_2$O and DCIO$_4$·2D$_2$O solutions with the aim of subsequent crystallization of $\text{H}_2\text{O}_2\text{ClO}_4^-$ и $\text{D}_2\text{O}_2\text{ClO}_4^-$ can be found here [9]. The content of a heavy hydrogen isotope in DCIO$_4$·2D$_2$O is 99 at. % D. Due to perchloric acid hygroscopicity, all operations with its concentrated solution were carried out in a dry box. A drop of the prepared solution was compressed between AgCl plates wrapped with a taut PVC ribbon around the perimeter. The sample was taken out of the box and placed into a vacuum IR cryostat with outer windows made of KBr. The AgCl plates with a film of the liquid phase were tightly pressed by means of buckles and screws to the copper cooling unit. A thin insulating lead gasket was used to prevent any reaction between the material of the plates and the metal unit.

The cryostat with the sample inside was filled up with dry nitrogen at room temperature. When the temperature of the unit with the sample was lowered to $-60^\circ$C--$-80^\circ$C, nitrogen was pumped out by a fore vacuum pump through a nitrogen trap; then the cryostat was filled up with liquid nitrogen. The cooling rate of the solution and the products of its crystallization varied from 4 °/min to 50 °/min. In some cases, glass transition of the liquid phase was observed instead of crystal formation. In order to cause crystallization, the glassy film was heated or kept at a fixed elevated temperature for some time; then the sample was cooled again with liquid nitrogen. The precipitated $\text{H}_2\text{O}_2\text{ClO}_4^-$ and $\text{D}_2\text{O}_2\text{ClO}_4^-$ crystals were exposed to cyclic heat treatment, i.e., the temperature was increased to the melting onset and it was lowered to the temperature near the liquid nitrogen boiling-point.

The operating copper–constantan junction thermocouple was fastened directly to the copper cooling unit. Due to the temperature gradient between the cooling unit and silver chloride, low heat conductivity of silver chloride, the IR irradiation of the plates in the cuvette chamber of the spectrophotometer, a minimum temperature of the examined crystalline samples was higher than the boiling-point of liquid nitrogen by nearly 40°.

In order to prepare the crystalline samples of $(\text{H}_{1-x}\text{D}_x)_2\text{O}_2\text{ClO}_4^-$, the HClO$_4$·2H$_2$O and DCIO$_4$·2D$_2$O solutions were mixed in the calculated ratio. All further operations with the samples (i.e., cooling, crystallization, recrystallization, heat treatment) do not differ from the abovementioned operations.