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S. A. Shchukarev, S. N. Andreev, and T. G. Balicheva

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Abstract

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Vibrational Spectra of Perchloric Acid in the Liquid and Gaseous States

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One of the principal spectroscopic manifestations of hydrogen bonding is the shift of the frequency of the valence X—H vibrations, characteristic of isolated molecules, to the low-frequency side by several hundred cm^{-1}, which indicates a sharp decrease in the force constant and in the bond energy. The present work is devoted to studying the state of the OH bond in molecules of perchloric acid present in the gas phase, in anhydrous 100% $HClO_4$, and in the form of solid $HClO_4 \cdot H_2O$, in the region of the fundamental tone of the valence OH vibrations.

The spectra of the above-mentioned substances were studied by us on a two-beam recording infrared spectrometer IKS-14 and on a non-recording infrared spectrometer IKS-6, with LiF prisms, the radiation sources being, respectively, a globar and a Nernst glower; the radiation detectors were a bolometer and a thermoelement. Calibration was carried out using the vibration–rotation spectra of NH_3, HCl, HBr, CO, CH_4, and C_6H_6. The stability of the calibration was checked against the spectrum of a polyethylene film. In the investigations, standard gas cells with LiF windows and quartz plates 0.5 mm thick were used. Anhydrous perchloric acid was obtained by vacuum distillation (30 mm Hg) of $HClO_4$, prepared by heating a mixture of solid $KClO_4$ and concentrated H_2SO_4 ([1], [2]). The $HClO_4$, slightly colored yellow by chlorine oxides, was redistilled in a flask with a reflux condenser 20 cm long at $t = 45$–$50°C$ and a vacuum of 40–50 mm Hg. In a receiver cooled with a cooling mixture—ice with NaCl—a transparent, colorless liquid, strongly fuming in air, was collected; this liquid was either immediately subjected to investigation or, by addition of a calculated amount of distilled water, converted into $HClO_4 \cdot H_2O$ or diluted aqueous $HClO_4$.

The vibrational spectra obtained by us are shown in Fig. 1. The vibrational spectrum of gaseous $HClO_4$, investigated at 20° and $P = 18$ mm Hg, is characterized by a single, rather intense narrow band with a maximum at 3560 cm^{-1}. The presence of only this band in a strongly diluted 0.001 M solution of anhydrous $HClO_4$ in CCl_4 indicates the existence of $HClO_4$ in the vapor in the form of a monomer. This conclusion agrees with the data of an X-ray study of gaseous $HClO_4$ by P. A. Akishin, L. V. Vilkov, and V. Ya. Rosolovskii ([3]). The vibrational spectrum of anhydrous $HClO_4$, investigated by us immediately

after its preparation, is characterized by an absorption band with a maximum lying at 3390 cm^{-1} (Fig. 1b). Simon ([4]), in the Raman spectrum of anhydrous $HClO_4$, obtained a diffuse band lying in the interval 3425–3243 cm^{-1}.

The vibrational spectrum of anhydrous $HClO_4$ is shifted, in comparison with the spectrum of isolated $HClO_4$ molecules, by 170 cm^{-1} into the low-frequency region, owing to association of perchloric-acid molecules through the formation of hydrogen bonds of the type $HClO_4 \cdots HClO_4$. The considerably weaker shift in comparison with that for water ($\Delta\tilde{\nu} = \tilde{\nu}_{gas} - \tilde{\nu}_{assoc} = 3750 - 3420 = 330$ cm^{-1}) and the greater volatility of perchloric acid already at room temperature indicate a significantly lower strength of the bonds.

$HClO_4 \cdots HClO_4$ compared with $H_2O \cdots H_2O$ bonds. Numerous studies ([7]) give an approximate proportionality between the frequency shift $\Delta\tilde{\nu} = \tilde{\nu}_{gas} - \tilde{\nu}_{assoc}$ and the energy of the hydrogen bond. Our approximate estimate of the hydrogen-bond energy in the $HClO_4 \cdots HClO_4$ complex gives a value of 3 kcal (for water $\varepsilon = 4.5$ kcal).

It is of interest to estimate, at least approximately, the change in the force constant and the interatomic distance of the OH bond in going from $HClO_4$ (gas) to $HClO_4$ (liquid). The calculation was carried out using the formula for vibrations of a harmonic oscillator ([5])

$$F = 5.889 \cdot 10^{-2} \cdot \frac{m_1 m_2}{m_1 + m_2} \tilde{\nu}^2$$

and Badger' s formula ([6])

$$r = \sqrt[3]{\frac{C_{ij}}{F}} + D_{ij}.$$

The values of the constants C_{ij} and D_{ij} were taken by us as applicable to H and O atoms, equal to: $C_{ij} = 57.1$, $D_{ij} = 0.335$. The results obtained are summarized in Table 1.

Table 1

Substance	State	$\tilde{\nu}$, cm^{-1}	$\Delta\tilde{\nu}$, cm^{-1}	$F \cdot 10^5$, $dyn \cdot cm^{-1}$	r_{O-H}, Å
$HClO_4$	Gas	3560		7.0	0.978
$HClO_4$	Liquid, 100%	3390	170	6.4	0.997
$HClO_4 \cdot H_2O$	Solid	3320	240	–	–
$HClO_4 \cdot H_2O$	Solid	2930	630	–	–

Fig. 1

Figure 1: Fig. 1

Since $HClO_4$ is most often used in the form of aqueous solutions, it is of interest to determine to what extent the vibrational spectrum of this acid is affected not only by the $HClO_4 \cdots HClO_4$ hydrogen bond, but also by the intermolecular interaction of $HClO_4$ with H_2O molecules.

Fig. 1. *a*—Vibrational absorption spectrum of gaseous $HClO_4$. Cell length 11.5 cm. $P = 18$ mm Hg; t room temperature; *b*—absorption spectrum of anhydrous $HClO_4$; *c*—absorption spectrum of a polycrystalline film of $HClO_4 \cdot H_2O$ at $t = -10°$.

For this purpose we studied the $HClO_4$—H_2O system at a component ratio of 1:1, which has attracted the attention of many authors because of the unusual nature of its chemical behavior. The monohydrate of perchloric acid, first obtained by Serullas ([8]), unlike its other hydrates, is a crystalline substance with m.p. 50°. Folmer ([9]), having established radiographically the isostructurality of NH_4ClO_4 and $HClO_4 \cdot H_2O$ crystals, proposed that $HClO_4 \cdot H_2O$ be regarded as oxonium perchlorate. Richards and Smith et al. ([10]), using nuclear magnetic resonance, proved the existence of the H_3O^+ ion in solid $HClO_4 \cdot H_2O$. The H_3O^+ ion has the form of a regular flat pyramid with an OH-bond length of 1.02 Å and an angle $\angle HOH = 115°$. Such a flat pyramidal ion should have 4 frequencies active in the Raman and infrared spectra ([11], [12]), two of which should lie in the region of stretching OH vibrations. Mulhaupt and Hornig ([11]) observed, in the 2460–3600 cm^{-1} region of the combination-scattering spectrum of $HClO_4 \cdot H_2O$ crystals at room temperature, a broad diffuse band with a more intense high-frequency part from 3390 to 2960 cm^{-1}, which they therefore assign to the symmetric OH vibration in H_3O^+.

The spectrum of the polycrystalline $HClO_4 \cdot H_2O$ film shown in Fig. 1, *c*, repeatedly obtained with constant cooling of the samples to −10°, −20°, clearly has a complex structure with main maxima at 3320 cm^{-1} and 2930 cm^{-1} and a very weak one at 3260 cm^{-1}.

The molecular reorientation undergone by the H_3O^+ ion in the crystal lattice of $HClO_4 \cdot H_2O$ already at 0°, found by NMR by Richards and Smith [10], is probably the cause that has greatly complicated spectral studies, as a result of which most authors obtained a broad absorption band, strongly smeared out into the low-frequency region, characteristic of H_3O^+ in concentrated acid solutions.

Leningrad State University
named after A. A. Zhdanov

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Note: Figure translations are in progress. See original paper for figures.