566. *Raman Spectra and Constitution of Solid Hydrates. Hydroxonium Perchlorate, Nitrate, Hydrogen Sulphate, and Sulphate.*

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The Raman spectra of the monohydrates of perchloric, sulphuric, and nitric acids, and of the dihydrate of sulphuric acid have been examined. They are consistent with the ionic structures corresponding to the hydroxonium salts $(H_3O^+)(ClO_4^-)$, $(H_3O^+)(HSO_4^-)$, $(H_3O^+)(NO_3^-)$, and $(H_3O^+)_2(SO_4^{2-})$, respectively.

THE Raman spectrum of perchloric acid monohydrate [1] shows it to have the ionic constitution $(H_3O^+)(ClO_4^-)$. The present paper gives details of the investigation of this and other acid hydrates. The Raman spectrum of perchloric acid monohydrate at room temperature is difficult to record,[1] probably because of the unusual breadth of the lines, but this difficulty has been reduced by using a specially designed cell, with high intensity illumination, which allows spectra to be observed at liquid-air temperature.

Raman frequencies at —185°.

(Frequency separations in cm.$^{-1}$ from Hg 4358 Å.)

$HClO_4$ (anhyd.)	ClO_4^-	$HClO_4,H_2O$	$HClO_4$ (anhyd.)	ClO_4^-	$HClO_4,H_2O$
425 (w)	—	—	—	938 (vs)	926 (s)
—	461 (mw)	—	1032 (vs)	—	1030 (vw)
572 (m)	—	—	—	1073 (mw)	1065 (vw band)
585 (mw)	—	—	—	1121 (mw)	—
—	628 (m)	620 (mw)	1182—1312 (w)	—	—
738 (m)	—	—			

Intensities are indicated as vs = very strong, s = strong, ms = moderately strong, m = medium, mw = moderately weak, w = weak, vw = very weak.

Perchloric Acid Monohydrate.—In the Table the Raman frequencies of perchloric monohydrate at —185° are compared with those of anhydrous perchloric acid [2] and those of the perchlorate ion as observed [3] for solid potassium perchlorate.

The spectrum of the hydrate contains lines corresponding to the two strongest

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[1] Millen, *J.*, 1950, 2607.

[2] Redlich, Holt, and Bigeleisen, *J. Amer. Chem. Soc.*, 1944, **66**, 13.

[3] Millen, *J.*, 1950, 2611.

perchlorate ion fundamentals at 630 and 930 cm.$^{-1}$, and also an indication of the weak Fermi doublet at about 1065 cm.$^{-1}$. A few plates also recorded a very weak, broad line at about 1030 cm.$^{-1}$. This corresponds to the strongest fundamental of the perchloric acid molecule, possibly present owing to imperfect crystallisation. Whatever the origin of the weak line at 1030 cm.$^{-1}$, it can safely be concluded that the hydrate is ionic, being composed of perchlorate ions and, presumably, hydroxonium ions. The absence of the fourth fundamental of the perchlorate ion, at about 460 cm.$^{-1}$, can be attributed to the difficulty of detecting weak lines of low frequency displacement in the Raman spectrum of a powdered crystal. This interpretation of the spectrum is confirmed by conclusions reached from proton-resonance [4, 5] and from infrared [6] studies.

In several attempts to obtain the spectrum of the hydrate at room temperature, the same optical arrangement was used as for the work at low temperature. Even with very long exposures only one line was detected. This corresponds to the strongest perchlorate ion fundamental at about 930 cm.$^{-1}$. It appears probable that the difficulty of photographically recording the spectrum under these conditions is due, not to low intensity of the spectrum, but to a broadening of the lines. Possible causes of the broadening are excitation of lattice vibrations and reorientation of neighbouring hydroxonium ions, a process which has been suggested [4, 5] to account for the proton-resonance spectrum of the hydrate at room temperature.

Nitric Acid Monohydrate.—The Raman spectrum of the crystalline hydrate at −185° has a strong, sharp line at 1052 cm.$^{-1}$ which corresponds to the well-known breathing frequency of the nitrate ion; there was no sign of even the most strongly allowed frequency of molecular nitric acid. This is consistent with the ionic constitution $(H_3O^+)(NO_3^-)$ suggested from proton magnetic resonance studies [5] and spectroscopy,[6, 7] but contrary to the conclusion reached from an *X*-ray investigation.[8] The experimental errors quoted in the last work do not, however, exclude a structure in which nitrate and hydroxonium ions are hydrogen bonded in layers. In such a structure the two potential minima available to the proton between two oxygen atoms will be non-equivalent, and, consistently with this, Forsythe and Giauque [9] have found that the entropy of the hydrate approaches zero towards the absolute zero.

Sulphuric Acid Mono- and Di-hydrate.—In the Raman spectrum of the monohydrate at −185° a strong, sharp line was observed at 1028 cm.$^{-1}$. There was no indication of even the strongest Raman-active frequency of molecular sulphuric acid. The most characteristic frequency of the hydrogen sulphate ion is known from the study [10] of aqueous sulphuric acid to occur at about 1030 cm.$^{-1}$. It is concluded that the crystalline monohydrate has the ionic constitution $(H_3O^+)(HSO_4^-)$ in agreement with conclusions reached from nuclear magnetic resonance.[5]

The Raman spectrum of sulphuric acid dihydrate at −185° has a line at 986 cm.$^{-1}$. This corresponds to the most intense line of the sulphate ion. There are no indications of lines corresponding to frequencies of molecular acid or hydrogen sulphate ion. This clearly indicates that the solid has the ionic constitution $(H_3O^+)_2(SO_4^{2-})$.

The Hydroxonium Ion.—For all the hydrates examined, the observed lines can be attributed to anions derived from the acids, except in the case of perchloric acid hydrate where one line corresponds to a frequency of the acid molecule. In no case were any lines observed which could be attributed to a cation, although proton resonance [4, 5] and infrared studies [6, 11] provide strong evidence for the occurrence of the hydroxonium ion in a number of acid hydrates. In both infrared investigations [6, 11] the lines attributed to the hydroxonium ion were found to be unusually broad, having half-widths of about 150—300 cm.$^{-1}$, even at low temperatures. The breadth of the lines undoubtedly contributes

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[4] Kakiuchi, Shono, Komatsu, and Kigoshi, *J. Chem. Phys.*, 1951, **19**, 1069.

[5] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261.

[6] Bethell and Sheppard, *J. Chem. Phys.*, 1953, **21**, 1421; *J. Chim. phys.*, 1953, **50**, c72.

[7] Simon and Hopner, *Kolloid Z.*, 1938, **85**, 8.

[8] Luzatti, *Compt. rend.*, 1950, **233**, 101; *Acta Cryst.*, 1951, **4**, 239.

[9] Forsythe and Giauque, *J. Amer. Chem. Soc.*, 1942, **64**, 48.

[10] Woodward and Horner, *Proc. Roy. Soc.*, 1934, **144**, *A*, 129.

[11] Ferriso and Hornig, *J. Amer. Chem. Soc.*, 1953, **75**, 4113; *J. Chem. Phys.*, 1955, **23**, 1464.

to the difficulty of their photographic detection in Raman spectra.* However, this effect seems unlikely to be the only reason for the absence of these lines from our spectra. In the case of hydroxonium perchlorate the spectra include the weakest characteristic of the perchlorate ion, namely a very weak, broad band at about 1065 cm.$^{-1}$. That even the strongest line of the hydroxonium ion should be more difficult to record than the very weak, broad line of the perchlorate ion probably indicates that the polarisability of the hydroxonium ion does not change appreciably during a vibration.

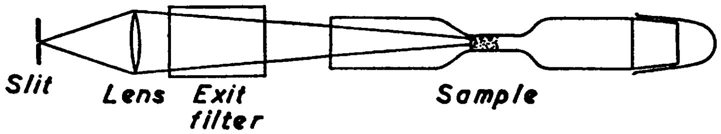
The unusually large line-breadth is found for both the degenerate and the non-degenerate vibrations of the hydroxonium ion and so it appears that it may be due, in part, at any rate, to some special mechanism. Possibly it arises from a splitting of the vibrational levels due to proton tunnelling between the potential minima corresponding to $H_3O^+A^-$ and $H_2O{\cdot}HA$. In the vibrational ground state tunnelling is evidently slight, for the spectra are essentially those of anions. However, the weak appearance, in the spectrum of hydroxonium perchlorate, of a line due to the perchloric acid molecule may be an indication that tunnelling in the ground state is not negligible. An appreciably larger effect for the upper states involved in vibrational transitions could contribute to the appearance of broad lines.

EXPERIMENTAL

In order to obtain high sensitivity in photographing spectra of powdered solids we used a Hilger E612 Raman spectrograph with a camera lens of relative aperture $F/1{\cdot}5$, a high-intensity low-pressure mercury arc (15 A maximum; water-cooled anode) source, and a specially designed cell. To overcome a main problem in the design of a cell for use with powdered solids, namely loss of incident light, by reflections at crystal faces, before it reaches the region which is effective in scattering Raman radiation into the spectrograph, we concentrated the effective scattering region into a small volume and reduced the thickness of powdered crystal in the path of the incident light as far as possible consistent with ease of alignment. The cell consisted of an optical window 3 mm. × 25 mm. sealed into a tube as shown in the Figure, which is a section through the narrow dimension.

In operation, the cell was used vertically in a vacuum flask similar to that used by Sutherland,[12] except that it was partially silvered and had a window for the entry of incident radiation. The cell was aligned by using a method similar to that described by Poole.[13] About 0·5 ml. of liquid acid hydrate was run into the cell and was cooled slowly and stirred with a glass rod to avoid supercooling. This gave a translucent crystalline mass, suitable for obtaining Raman spectra. Rapid cooling often resulted in a sudden solidification to a " glass " and fracture of the cell. The end of the tube was closed with a ground-glass cap, sealed with metaphosphoric acid.

Section through narrow dimension of rectangular cell formed in a circular tube, showing simplified method of use.



An entry filter of cobalt thiocyanate and an exit filter of *o*-nitrophenol were used as described previously.[14] Spectra were recorded on Kodak O–aO plates.

The authors thank Professor C. K. Ingold, F.R.S., for his interest.

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[*Received, March 6th,* 1956.]

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* [*Added* 18·6·56.] Mullhaupt and Hornig (*J. Chem. Phys.*, 1956, **24**, 169) have succeeded in recording photoelectrically two bands in the Raman spectrum of a single crystal of hydroxonium perchlorate. These bands are indeed very broad, stretching from 1500 to 1690 and from 2460 to 3600 cm.$^{-1}$.

[12] Sutherland, *Proc. Roy. Soc.*, 1933, **141**, *A*, 535.

[13] Poole, *J.*, 1946, 251.

[14] Ingold, Millen, and Poole, *J.*, 1950, 2577.