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The Vibrational Spectrum of the Hydronium Ion in Hydronium Perchlorate

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RECEIVED APRIL 5, 1956

Raman spectra of large single crystals of hydronium perchlorate have been obtained at several temperatures between 25 and −50°. The results show that a transition occurs in this crystal at about −30° which is probably of the order–disorder type. Spectra obtained from the high temperature phase contained only the known bands of the perchlorate ion plus weak bands whose positions were in agreement with those expected for a pyramidal H_3O^+ ion. Three of the observed bands have been assigned as fundamentals and the position of the fourth fundamental estimated. On the basis of the assignment, valence force constants have been calculated and compared with the results of a similar calculation for the isoelectronic ammonia molecule. The comparison lends additional support to the correctness of the assignments.

Introduction

Ever since nuclear magnetic resonance measurements have furnished evidence that the crystalline monohydrates of several strong mineral acids contain true hydronium ions,[1,2] a renewed interest has been shown in the study of these compounds. In particular, spectroscopic work has been stimulated in an attempt to identify the characteristic vibrational frequencies of the hydronium ion itself. Thus far, infrared studies have been reported on the crystalline monohydrates of nitric acid and the hydrogen halides at low temperatures.[3,4] The spectra obtained were explained satisfactorily in terms of simple ionic structures and assignments of the fundamental vibrations of the hydronium ion were made. No Raman studies have been successful in locating hydronium ion frequencies in these particular compounds.

Chemical considerations indicate that, of the various compounds which might be used in such studies, crystalline perchloric acid monohydrate should be particularly suitable. Bethell and Sheppard mention the infrared spectrum of this compound in the discussion following their article on nitric acid monohydrate[3] but have published no data. Several Raman investigations have been made of liquid perchloric acid and its aqueous solutions[5–7] but no bands reported were assigned to the hydronium ion. Two brief references to the Raman spectrum of the crystal were found; no success was reported in the first[8] although hydronium bands were looked for specifically, while the second,[9] which appeared quite recently, lists the position of two rather broad and diffuse bands. The present communication reports on the Raman spectrum obtained from large single crystals of this substance over a range of temperatures. Spectra of aqueous solutions of perchloric acid and sodium perchlorate were also obtained as an aid in the interpretation of the results.

Experimental

The solid monohydrate of perchloric acid was obtained by generating an excess of anhydrous acid[10] and condensing it in redistilled constant boiling acid (72%). More purified constant boiling acid was added until the collected material in the receiver appeared to have solidified completely. (Melting point of the monohydrate is 49.9°.) This crude monohydrate was then melted and poured into a Pyrex glass tube 12 mm. in diameter which had been drawn out into a coarse capillary at the lower end and sealed off. The tube was tightly capped after filling. Large single crystals were obtained by lowering such tubes, capillary end first, through a heated hollow copper cylinder at the rate of about 3 cm. per day. If the crude monohydrate had a composition sufficiently close to the stoichiometric composition and a sharp temperature gradient was maintained at the bottom of the copper cylinder, it was possible to grow single crystals free from occlusions or gross defects about 5 cm. long and with a diameter equal to that of the glass tubing used. When a crystal of the desired size was obtained, the excess molten material was pipetted off leaving a clear, flat crystal face through which the scattered radiation could be passed with a minimum loss of light. Since hydronium perchlorate is exceedingly hygroscopic, precautions had to be taken to protect the crystal from atmospheric moisture. The solutions examined were prepared by dissolving known amounts of purified sodium perchlorate or anhydrous or constant boiling acid, in a known amount of water.

Since the bands of interest are weak and broad, it was necessary to use a low background source and filter the incident light heavily in addition to preparing the sample carefully. These details of the experimental arrangement have been described previously.[11] The positions of the sharp bands were measured with a comparator in conjunction with an argon comparison spectrum while the maxima of the more diffuse bands were measured on 26:1 enlarged microphotometer tracings made with a Leeds and Northrup instrument. The values reported in general represent the mean of several measurements and, except where otherwise noted, have estimated probable errors of approximately 1 cm.$^{-1}$.

Experimental Results

The spectra obtained from solutions of perchloric acid or sodium perchlorate in water confirmed the results of previous investigations of the perchlorate ion spectrum.[5–7] Molten monohydrate and solutions containing a stoichiometric excess of perchloric acid gave the spectrum of anhydrous perchloric acid superimposed on that of the perchlorate ion, as well as weak and very broad bands in the regions corresponding to the stretching and the bending of the hydroxyl bonds. No interpretation is given to the latter, since more than one distinct molecular species containing the hydroxyl bond is present in all the solutions.

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(1) R. E. Richards and J. A. S. Smith, *Trans. Faraday Soc.*, **47**, 1261 (1951).

(2) (a) Y. Kakiuchi, H. Shono, H. Komatsu and K. Kigoshi, *J. Chem. Phys.*, **19**, 1069 (1951); (b) Y. Kakiuchi, *et al.*, *J. Phys. Soc. Japan*, **7**, 102, 380 (1952).

(3) D. E. Bethell and N. Sheppard, *J. chim. phys.*, **50**, C72 (1933).

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(6) R. Fonteyne, *Nature*, **138**, 886 (1936); *Natuurwet. Tijdschr.*, **20**, 112 (1938).

(7) O. Redlich, E. K. Holt and J. Bigeleisen, THIS JOURNAL, **66**, 13 (1944).

(8) D. J. Millen, *J. Chem. Soc.*, 2606 (1950).

(9) J. T. Mullhaupt and D. F. Hornig, *J. Chem. Phys.*, **24**, 169 (1956).

(10) G. F. Smith, THIS JOURNAL, **75**, 184 (1953).

(11) G. L. Vidale and R. C. Taylor, *ibid.*, **78**, 294 (1956).

The Raman spectrum of crystalline monohydrate was obtained at several temperatures. Tracings of spectra obtained from crystals at 20 and −21°, as well as comparison spectra obtained from molten monohydrate and from sodium perchlorate solutions are shown in Fig. 1. The measured frequencies of the observed bands are listed in Table I. As can be seen, the typical bands due to the perchlorate ion are present at both temperatures, and these have approximately the same width and frequency as the corresponding bands obtained from the Raman spectrum of the solutions. Since no bands are observed which can be attributed to un-ionized perchloric acid, it appears most probable that the remaining weak bands indicated by arrows in Fig. 1 must be assigned to the hydronium ion.

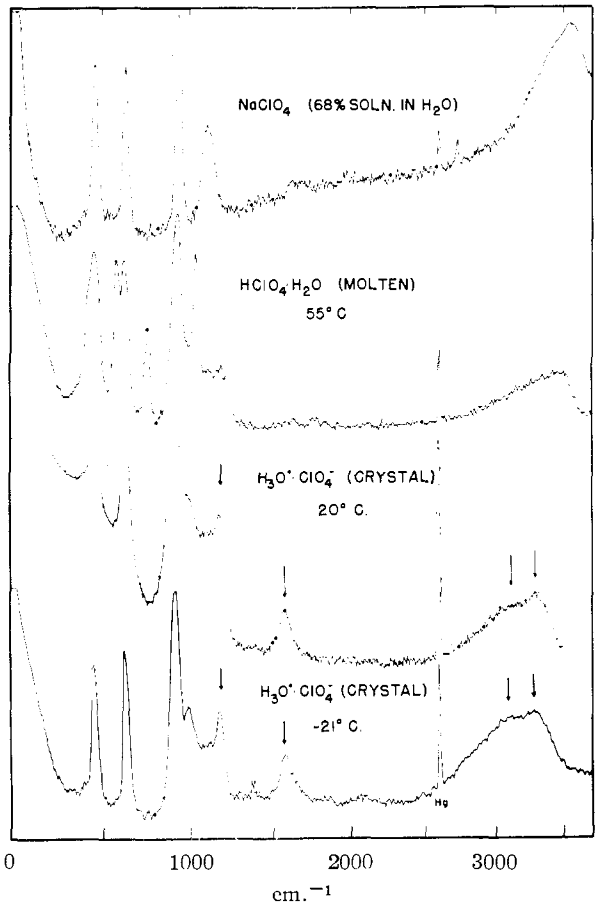

Fig. 1.—Raman spectra of $HClO_4 \cdot H_2O$ and of aqueous $NaClO_4$ at various temperatures.

Several attempts were made to obtain spectra from crystals at lower temperatures, but in every case the crystal shattered when the temperature reached approximately −30°. Spectra obtained from the broken crystals were of poor quality, but they did show that at this reduced temperature the rather broad degenerate fundamentals of the perchlorate ion were split into narrow components while the A_1 frequency became much sharper. Less can be said with certainty about the other bands because of their low intensity and diffuse nature. A tracing of a spectrum obtained at −50° is shown in Fig. 2 while the frequencies of those bands that could be measured reproducibly are included in Table I.

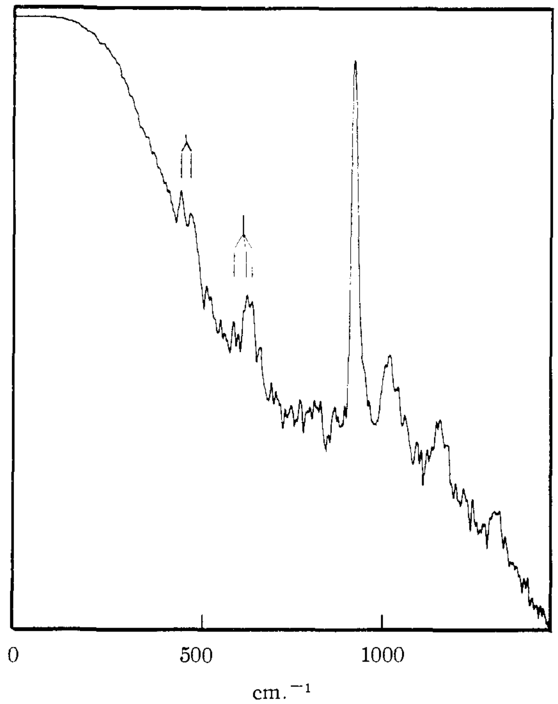

Fig. 2.—Raman spectrum derived from shattered crystal of $HClO_4 \cdot H_2O$ at −50°.

Discussion

The spectrum of single crystals of hydronium perchlorate at 20 and −21° is unexpectedly simple. Despite the low site symmetry of the orthorhombic lattice[12,13] and the probable large interaction between ions due to hydrogen bonding, no splitting of the perchlorate ion fundamentals is observed. This simplicity, together with the rather large breadth of the band envelopes, suggests that the crystalline phase being studied is a disordered phase. Such a conclusion is substantiated by the nuclear magnetic resonance studies in which a narrowing of the absorption line was observed to occur at −130°. The nature of the change indicated that at this temperature the H_3O^+ ions began reorienting their axes relative to each other at a rate comparable to the frequency line width, and that more than one axis was involved. No further change in the NMR spectrum was observed in the neighborhood of −30° where the physical behavior of the crystal and its Raman spectrum indicate a phase transition. The situation thus appears quite analogous to the case of the ammonium halides[14] for which the existence of a low temperature ordered phase and a high temperature disordered phase has been well established.

The nuclear magnetic resonance work has shown that the hydronium ion in perchloric acid monohydrate is pyramidal, and if it is assumed that it has

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(12) M. Volmer, *Ann.*, **440**, 200 (1924).

(13) L. J. Klinkenberg, *Rec. trav. chim. pays-bas*, **56**, 749 (1937).

(14) H. S. Gutowsky, G. E. Pake and R. Bersohn, *J. Chem. Phys.*, **22**, 643 (1954).

TABLE I

OBSERVED VIBRATIONAL FREQUENCIES OF CRYSTALLINE PERCHLORIC ACID MONOHYDRATE AND OF THE PERCHLORATE ION IN AQUEOUS SOLUTION (IN CM.$^{-1}$)

Assignment		ClO_4^- (lit. 5–7)	$NaClO_4$ soln.	$H_3O^+ \cdot ClO_4^-$ (cryst.)		
				20°	−21°	−50°
ClO_4^-						
ν_2	E	461–463	463	456	456	438 469
ν_4	F_2	626–632	631	627	628	615–636 with structure
ν_1	A_1	930–936	939	921	922	921
ν_3	F_2	1109–1120	1112 ± 3	....	1115 ± 6	...
H_3O^+						
ν_L or $2\nu_L$				....	995 ± 5	1021 ± 10
ν_2	A_1			1175 ± 2	1182 ± 2	1163 ± 10
ν_4	E			1577 ± 5	1577 ± 5	1600 ± 25
$2\nu_4$	A_1			3100 ± 50	3100 ± 50	....
ν_1	A_1			3285 ± 10	3285 ± 10	....
?				....	....	1322 ± 10

an effective C_{3v} symmetry in the disordered crystal, the following assignment of the bands indicated in Fig. 1 can be made. In the hydrogen stretching region, the band has a maximum at 3285 cm.$^{-1}$ and a weaker shoulder centered around 3100 cm.$^{-1}$. The maximum is almost certainly the A_1 band while the weaker shoulder could be due either to the degenerate fundamental ν_3 or to the first overtone of the bending fundamental at 1577 cm.$^{-1}$ strengthened by Fermi resonance with ν_1. In view of the agreement between 2 × 1577 and 3100, and of the high probability of strong resonance between the first overtone of the bending frequency and the stretching frequency of the same hydrogen atoms, the latter alternative appears the more likely possibility. By analogy to ammonia and also to the work on the other hydronium compounds, the band at 1577 cm.$^{-1}$ is readily assigned to the degenerate bending fundamental ν_4.

Assignment of frequencies in the 1000–1200 cm.$^{-1}$ region requires somewhat more discussion. From a cursory inspection of Fig. 1, one would tend to identify the 1182 cm.$^{-1}$ band with ν_3 of the perchlorate ion leaving the 995 cm.$^{-1}$ band to be assigned to the A_1 bending mode of the hydronium ion and, indeed, this assignment was made initially in the present work. However, comparison of the measured value of the frequencies in Table I shows that this assignment results in a 70 cm.$^{-1}$ shift in the position of ν_3 between the solution and crystal spectra. This appears quite unreasonable in the light of the shifts observed for the other perchlorate ion fundamentals. A more critical examination of the crystal spectra in Fig. 1 reveals that the scattering in the region between the 995 and 1182 cm.$^{-1}$ bands does not drop to as low a value as one would expect from the sharpness of these two bands and suggests the presence of another weak and rather broad band which is partially overlaid. In longer exposures than those shown in Fig. 1, a small maximum can be distinguished with its center at about 1115 cm.$^{-1}$. Since this agrees with the position of ν_3 of the perchlorate ion in solution, the location of this frequency in the crystal spectrum appears established and the 995 and 1182 cm.$^{-1}$ bands are left as possibilities for assignment as ν_2 of the hydronium ion. The latter agrees better with the reported values in the infrared spectra of the nitrate and chloride and is assigned to this mode.

The remaining frequency at 995 cm.$^{-1}$ can be disposed of less satisfactorily. There appear to be two alternatives which can profitably be discussed. The first is to assign the 995 cm.$^{-1}$ band as the overtone of ν_2 of the perchlorate ion which has been strengthened by Fermi resonance with the ν_1 fundamental of the same ion. There are several criticisms of this assignment however which make it unsatisfactory. For example, twice the value of the ν_2 fundamental is 912 cm.$^{-1}$ which is less than the value 921 cm.$^{-1}$ measured for the ν_1 fundamental. One would therefore expect the overtone to appear on the low frequency rather than on the high frequency side of this band. In addition, both the sharpness and position of the 995 cm.$^{-1}$ band appear rather markedly temperature sensitive to the extent that the band was not resolved at all in the spectra obtained at 20°. This does not seem reasonable for a perchlorate ion overtone. Strange, too, is the fact that resonance between this overtone and fundamental should occur in the crystal with enhancement of the overtone intensity while in the solution spectrum of the perchlorate ion where the coincidence is practically the same, no indication of a satellite is seen.

The other alternative is to attribute the 995 cm.$^{-1}$ band to a librational lattice motion of the H_3O^+ ion. This assignment agrees with the general behavior and appearance of this band and about the only serious objection is that it is unusually high in frequency for this type of motion. However, in the infrared spectra of the hydronium halides[4] this assignment has been made for bands in the 750–800 cm.$^{-1}$ range and in view of the fact that the hydronium ion is more likely to be strongly hydrogen bonded in the perchlorate than in the halides, it would appear that a value of 995 cm.$^{-1}$ is not completely out of reason. In ice, a value of 820 cm.$^{-1}$ has been reported for the librational lattice mode.[15] A more certain assignment of the band in question does not appear possible without additional information such as that supplied by deuterium substitution. No other bands were observed at lower

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(15) P. A. Giguere and K. B. Harvey, *Can. J. Chem.*, **34**, 798 (1956).

frequencies which could be attributed to lattice modes.

The three fundamentals of the hydronium ion assigned in the present work are in reasonable agreement with the previous results[3,4] considering the differences in crystal structures and probable ionic interactions. The degenerate stretching frequency ν_3 was not identified in the present spectra, either because it was of too low intensity in the Raman effect or because it was overlaid by the rather broad band assigned to ν_1. The infrared workers have suggested a band in the neighborhood of 2600 cm.$^{-1}$ for this fundamental; however, the whole hydrogen stretching region was not too clearly resolved in the infrared work and this value seems much lower than one might expect. From a comparison of the stretching frequencies of H_2O and of such molecules as NH_3, PH_3 and AsH_3, one would expect the E mode to have a frequency not too far removed from the A_1 frequency and probably on the high frequency side.

It is perhaps of some interest to carry out a normal coördinate treatment of the H_3O^+ ion and to compare the results from the present data with those which have been obtained for the isoelectronic ammonia molecule in the crystal.[16] In view of the uncertainty in the value for ν_3, the results necessarily must be approximate and the uncertainty is further contributed to by a lack of knowledge of the angle parameter. The Japanese workers have listed a value of 1.58 Å. as an experimental H–H distance from their nuclear magnetic resonance work; assuming an O–H bond distance of 0.98 Å. and a pyramidal structure, the H–O–H angle is calculated to be slightly in excess of 107°. On the other hand, the English workers[1] give 1.70 Å. as the H–H distance at 90°K. from the same type of experiment. This figure implies a rather flat pyramid which is consistent with an angle of 115° and the longer bond distance of 1.02 Å. It is not clear whether the 1.58 Å. estimate was for the room temperature or low temperature phase.

The analysis was carried out using the now familiar FG method of Wilson, the *G* matrix elements being evaluated from the tables of Decius.[17] The symmetry coördinates used are

$$A_1:\quad S_1 = 1/\sqrt{3}(\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$S_2 = 1/\sqrt{3}(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31})$$

$$E:\quad S_3 = 1/\sqrt{2}(\Delta r_2 - \Delta r_3)$$

$$S_4 = 1/\sqrt{2}(\Delta\alpha_{31} - \Delta\alpha_{12})$$

For purposes of the calculation, a value of 3400 cm.$^{-1}$ was assumed for ν_3; although this choice is rather arbitrary, it is about what one would expect from other comparisons. In order to examine the effect of the angle parameter on the numerical values obtained for the force constants, the calculations were carried out for three different values using the bond distance 0.98 Å. The potential function used has been given previously[16]; bond length–bond angle interaction terms were not found necessary and were set equal to zero. The three sets of force constants, all of which reproduced the experimental values at −21° and the value of 3400 cm.$^{-1}$ for ν_3 within 1 cm.$^{-1}$, are listed in Table II. Also included are the force constants of the isoelectronic ammonia molecule in the crystal.[16] The comparison gives additional support for the correctness of the assignments, and, to whatever extent the comparison is valid, perhaps indicates a slight preference for the 107° angle.

TABLE II

FORCE CONSTANTS FOR THE HYDRONIUM ION (IN MILLIDYNES PER Å.)

	Symmetry force constants				Valence force constants			
α	107°	111°	115°		107°	111°	115°	NH_3[16]
F_1	6.24	6.29	6.34	f_r	6.31	6.31	6.31	6.13
F_2	0.61	0.80	1.31	f_{rr}	−0.033	−0.007	0.019	−0.071
F_3	6.34	6.31	6.29	f_α	0.59	.63	.77	.58
F_4	0.58	0.54	0.50	$f_{\alpha\alpha}$	0.010	.087	.270	− .049

The poor quality of the spectra obtained at −50° makes other than qualitative statements about the low temperature phase unwarranted. However, the doubly degenerate band of the perchlorate ion at 456 cm.$^{-1}$ is clearly split into two components of about equal intensity while the triply degenerate band at 628 cm.$^{-1}$ appears to have at least two and possibly three components. No statements can be made about the other triply degenerate band of the perchlorate ion nor of the degenerate band assigned to the hydronium ion. These splittings indicate that at temperatures below −30° the perchlorate ion is located in a crystal field which does not possess the tetrahedral symmetry of the free ion. Unfortunately, neither X-ray nor thermal data are available to indicate whether the transition at 30° is first or second order. However the spectral evidence does indicate that the low temperature phase is an ordered phase with the ions located in positions of rather low site symmetry.

Acknowledgment.—G. L. V. wishes to thank the Corning Glass Foundation for a postdoctoral fellowship which made possible this study.

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[16] F. P. Reding and D. F. Hornig, *J. Chem. Phys.*, **19**, 594 (1951).

[17] J. C. Decius, *ibid.*, **16**, 1025 (1948).