

## Infrared Spectroscopic Study of the Hydrates of Hydrogen Chloride and Hydrogen Bromide

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**Summary** The i.r. spectra for  $\text{HX}, x\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $x = 1-4$ ) and evidence for the existence of the complex  $\text{HCl}, 4\text{H}_2\text{O}$  are reported; the spectra of the dihydrates show the presence of a very strong central hydrogen bond in  $\text{H}_5\text{O}_2^+$ , and other spectra indicate the presence of  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+$ , or  $\text{H}_5\text{O}_2^+$  units, consistent with X-ray crystal structures.

PHASE equilibria studies have shown the existence of three solid hydrates  $\text{HCl}, x\text{H}_2\text{O}$  ( $x = 1, 2$  and  $3$ )<sup>1</sup> in equilibrium with aqueous solutions of HCl and four analogous hydrates ( $x = 1-4$ )<sup>2</sup> in equilibrium with aqueous solutions of HBr.

The crystal structures of four of these compounds have been determined from X-ray diffraction data.  $\text{HCl}, \text{H}_3\text{O}^3$  and  $\text{HBr}, 4\text{H}_2\text{O}^4$  contain the hydronium ion  $\text{H}_3\text{O}^+$  as clearly defined units but the di-<sup>5</sup> and tri-<sup>6</sup> hydrates of hydrogen chloride possess the diaquo-hydrogen ion ( $\text{H}_2\text{O} \dots \text{H} \dots \text{OH}_2$ )<sup>+</sup> with a very strong hydrogen bond indicated by a short 'O...O' distance.

We report the i.r. spectra of all seven known hydrates as well as that of another complex which, from its spectrum, is probably  $\text{HCl}, 4\text{H}_2\text{O}$ . The different spectra were produced successively by loss of the hydrogen halide from the monohydrate, the latter having been formed by co-condensation of its constituents from the vapour phase onto an i.r.-transparent window cooled with liquid nitrogen.

The i.r. spectra are quite distinct from one another and reflect the differing complexity of these intermolecular compounds. The similarity of corresponding spectra originating from HCl and HBr indicates that each pair of hydrates is isostructural. In general the region of strongest absorption above  $2000 \text{ cm}^{-1}$  moves upward with increasing proportion of water in the complex. For the chlorides  $\nu(\text{OH})$  stretching vibrations are at lower frequencies and bending vibrations are at higher frequencies than for bromides, suggesting stronger hydrogen bonding for the chlorides. I.r. spectra from the hydrates of HCl, and from the deuterium-containing equivalents of the mono to trihydrates are shown in the figure.

Our spectra for monohydrates resemble those of Ferriso and Hornig<sup>7</sup> in most respects, having four broad and intense bands assignable to the fundamentals of a pyramidal  $\text{H}_3\text{O}^+$  ion.<sup>7,8</sup>

Several examples of the ion  $\text{H}_5\text{O}_2^+$  have been reported from X-ray crystallographic work. This ion is characterised by a very short,  $2.4-2.5 \text{ \AA}$ , 'OHO' bond, whose symmetry depends on the arrangement of the two outer water molecules. Both  $\text{HClO}_4, 2\text{H}_2\text{O}^9$  and  $\text{Co}(\text{en})_2\text{Cl}_2, \text{HCl}_2, 2\text{H}_2\text{O}^{10}$  ( $\text{en} = \text{ethylenediamine}$ ) contain  $\text{H}_5\text{O}_2^+$ , with a centre of symmetry about the central proton. However, i.r. spectra of these compounds are complicated by absorptions from counterions.<sup>11,12</sup> The 'OHO' bond in  $\text{HCl}, 2\text{H}_2\text{O}$  is again very short, *ca.*  $2.41 \text{ \AA}$ , but is asymmetric because the outer water groups are structurally non-equivalent. The spectra of the two dihydrates, and of samples of the chloride containing various amounts of deuterium, show that the central OHO

bond is of sufficient strength to make the  $\text{H}_5\text{O}_2^+$  ion vibrate as a discrete entity.

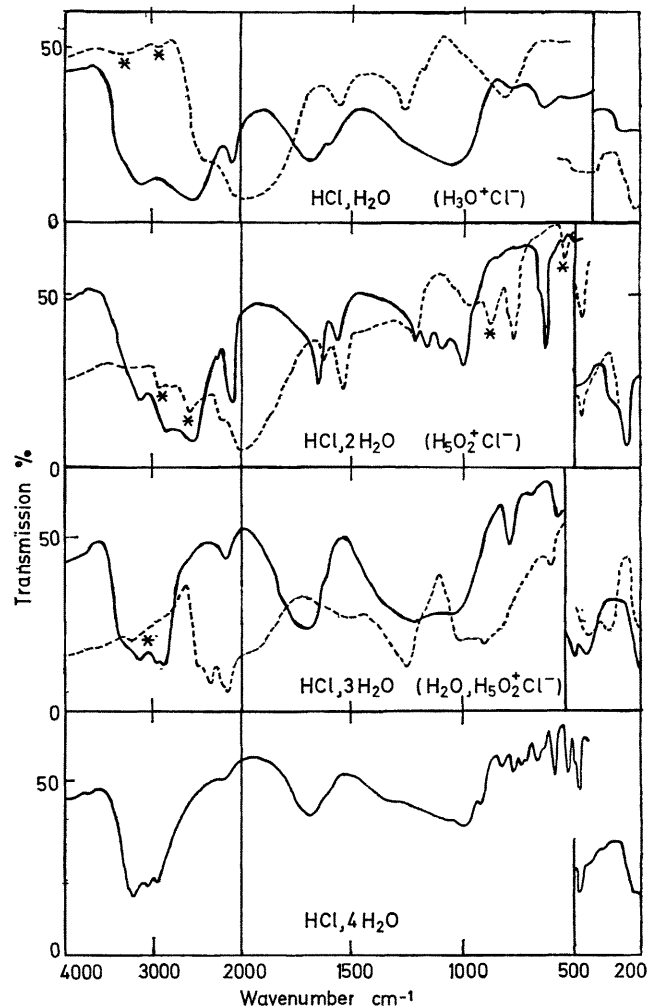


FIGURE. I.r. spectra for hydrates of HCl (solid lines) and their deuterium containing equivalents (dashed lines) with transmission scale expanded ( $\times 2$ ).

\* Absorption attributed either wholly or partially to residual hydrogen.

The spectra of the dihydrates, particularly the complexity in the region  $1200-800 \text{ cm}^{-1}$ , cannot be satisfactorily interpreted in terms of either a hydrated  $\text{H}_3\text{O}^+$  ion or two weakly coupled water molecules. Although the unit cells contain four  $[\text{H}_5\text{O}_2]^+$  entities these are separated from each other by  $\text{Cl}^-$  ions and are not likely to give rise to notable factor group splittings. For the chlorine compound the hydrogen stretching frequency of the 'OHO' bond is probably represented by the broad band centred in the  $1200-1000 \text{ cm}^{-1}$  region with a deuterium equivalent at

around 950—900  $\text{cm}^{-1}$ . Both its position and shift on deuteration are as expected for an asymmetric hydrogen bond of such length.

$\text{HCl}\cdot 3\text{H}_2\text{O}$  is formulated as  $[\text{H}_5\text{O}_2, \text{H}_2\text{O}]^+ \text{Cl}^-$  from its crystal structure.  $\text{H}_5\text{O}_2^+$  groups are joined together by 'H<sub>2</sub>O' molecules to form infinitely extending chains, *i.e.*  $\cdots \text{H}_5\text{O}_2^+ \cdots \text{H}_2\text{O} \cdots \text{H}_5\text{O}_2^+$ . Like the dihydrate it has a short asymmetric 'OHO' bond *ca.* 2.43 Å in length. The very broad and flat absorption we have observed between 1430 and 930  $\text{cm}^{-1}$  in the chloride (and from 1345 to 885  $\text{cm}^{-1}$  in the bromide) is considered to be largely due to the hydrogen stretching mode of the central OHO groups. On deuteration it shifts downward by a factor of *ca.* 1.23. It has a weaker sharper band at 1210  $\text{cm}^{-1}$  superimposed on it, which shows a more normal deuterium shift (to *ca.* 895  $\text{cm}^{-1}$ ) and may be an OHO(ODO) bending mode.

The spectrum of  $\text{HBr}\cdot 4\text{H}_2\text{O}$  was almost identical to that obtained by Rudolph and Zimmermann,<sup>13</sup> from a frozen 1 : 4 solution of hydrobromic acid. It reflects a complicated structure with two differently co-ordinated types of  $\text{H}_3\text{O}^+$ . The m.p./composition diagrams of Pickering do not show a phase corresponding to the chloride tetrahydrate although there were few experimental points in this composition range. This appears to be the first report of the existence of this compound. These spectra show numerous sharp bands below 1000  $\text{cm}^{-1}$ , which are probably to be assigned to torsional fundamentals of  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  entities and combinations of these with low frequency lattice modes.

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