

UC Riverside

UC Riverside Previously Published Works

Title

The unique nature of H + in water

Permalink

<https://escholarship.org/uc/item/6sk610vn>

Journal

Chemical Science, 2(3)

ISSN

2041-6520

Authors

Stoyanov, Evgenii S
Stoyanova, Irina V
Reed, Christopher A

Publication Date

2011

DOI

10.1039/c0sc00415d

Peer reviewed

Cite this: *Chem. Sci.*, 2011, **2**, 462

www.rsc.org/chemicalscience

EDGE ARTICLE

The unique nature of H^+ in water†

Evgenii S. Stoyanov,* Irina V. Stoyanova and Christopher A. Reed*

Received 4th August 2010, Accepted 23rd November 2010

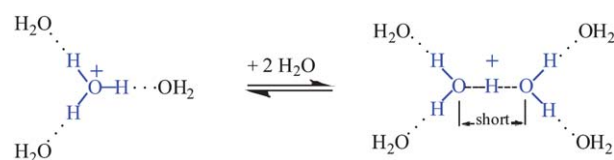
DOI: 10.1039/c0sc00415d

The $\text{H}^+(\text{aq})$ ion in ionized strong aqueous acids is an unexpectedly unique $\text{H}_{13}\text{O}_6^+$ entity, unlike those in gas phase $\text{H}^+(\text{H}_2\text{O})_n$ clusters or typical crystalline acid hydrates. IR spectroscopy indicates that the core structure has neither C_{3v} , H_3O^+ Eigen-like nor typical H_5O_2^+ Zundel-like character. Rather, extensive delocalization of the positive charge leads to a $\text{H}_{13}\text{O}_6^+$ ion having an unexpectedly long central $\text{O}\cdots\text{O}$ separation of ~ 2.57 Å and four conjugated $\text{O}\cdots\text{O}$ separations of ~ 2.7 Å. These dimensions are in conflict with the shorter $\text{O}\cdots\text{O}$ separations found in structures calculated by theory. Ultrafast dynamic properties of the five H atoms involved in these H-bonds lead to a substantial collapse of normal IR vibrations and the appearance of a continuous broad absorption (*cba*) across the entire IR spectrum. This *cba* is distinguishable from the broad IR bands associated with typical low-barrier H-bonds. The solvation shell outside of the $\text{H}_{13}\text{O}_6^+$ ion defines the boundary of positive charge delocalization. At low acid concentrations, the $\text{H}_{13}\text{O}_6^+$ ion is a constituent part of an ion pair that has contact with the first hydration shell of the conjugate base anion. At higher concentrations, or with weaker acids, one or two H_2O molecules of $\text{H}_{13}\text{O}_6^+$ cation are shared with the hydration shell of the anion. Even the strongest acids show evidence of ion pairing.

Introduction

The state of H^+ in water (frequently referred to as the “proton” or “excess proton” but more properly called the hydrogen ion) is one of the oldest unsolved problems in chemistry.¹ The earliest studies centered on the unusually fast mobility of H^+ in galvanic cells. In a remarkable tribute to the importance of ideas, the name of Grotthuss is associated with the proton hopping mechanism that grew out of his description of charge diffusion over 200 years ago,² at about the same time that Gay-Lussac confirmed that water was H_2O not $\text{HO}!$ ³ Mobility studies were used by Eigen⁴ in the mid 20th century to formulate $\text{H}^+(\text{aq})$ as a C_{3v} , trihydrated H_3O^+ ion and this formulation persists in textbooks today despite the rather restrictive conditions now known for its existence.^{5–7} With the availability of IR spectrometers in the 1950s, attempts were made to measure and interpret the IR spectrum of $\text{H}^+(\text{aq})$.^{8,9} These met with mixed success because it was not possible to cleanly isolate the spectrum of the $\text{H}^+(\text{aq})$ cation from that of water solvent and the evident broad absorptions in these qualitative spectra defied easy interpretation. Zundel put forward compelling arguments for the existence of an alternate structure for $\text{H}^+(\text{aq})$ based on the short, strong, symmetrical H-bonding in the H_5O_2^+ ion which now bears his name.⁸ Despite extensive experimental effort in

condensed phases into the 1970s, the true nature of $\text{H}^+(\text{aq})$ in water remained inconclusive. A rapid equilibrium between Eigen- and Zundel-type ions became a popular hypothesis.^{10–14}



Calculated ratios of Eigen *versus* Zundel ions of *ca.* 65 : 35^{15,16} or 75 : 25¹⁴ have been suggested. The isolation of crystalline forms of each of these ions in symmetrical anion environments lent credence to their proposed existence in the liquid phase and X-ray structure determinations defined their $\text{O}\cdots\text{O}$ separations: ~ 2.55 Å in Eigen-type ions^{17,18} and ~ 2.39 Å and ~ 2.52 Å in Zundel-type $\text{H}_5\text{O}_2^+ \cdot 4\text{H}_2\text{O}$ ion for the central and peripheral $\text{O}\cdots\text{O}$ separations, respectively.¹⁹

Meanwhile, theoretical and gas phase experimental methods for studying mass-isolated $\text{H}^+(\text{H}_2\text{O})_n$ clusters were advancing rapidly and these approaches have dominated research on the hydrated proton for the past couple of decades.^{16,20–28} Elegant experimental studies have been combined with theory to establish the gas phase structures and IR spectra of $\text{H}^+(\text{H}_2\text{O})_n$ clusters up to $n = 100$ values^{16,20–26,28} with the expectation that these results provide information relevant to H^+ in liquid water. The most recent theory^{29,30} for large clusters supports the predominant existence of a hybrid structure that can be described as an Eigen ion distorted towards a Zundel-type ion by having one

Department of Chemistry, University of California, Riverside, CA, 92521, USA. E-mail: evgeniis@ucr.edu; chris.reed@ucr.edu

† Electronic supplementary information (ESI) available: experimental details, IR spectra. See DOI: 10.1039/c0sc00415d

short O...O separation (the “special pair”). The short O...O bond fluctuates over all three Eigen-type O...O bonds on the picosecond timescale so IR spectroscopy, which has >100 ps timescale, is not expected to detect this asymmetry in normal mode vibrations.

We now bring these studies full circle by applying quantitative IR techniques to $\text{H}^+(\text{H}_2\text{O})_n$ in liquid water. We come to the surprising conclusion that the accumulated decades of circumstantial evidence for the structure of $\text{H}^+(\text{H}_2\text{O})_n$ in liquid water are inconsistent with our new IR and X-ray data. These data indicate that delocalization of positive charge in liquid water is more extensive than could have anticipated from gas or solid phase studies or by theory. This is evidenced by O...O bond elongation such that neither traditional Eigen nor Zundel structures are consistent with the data. Ion pairing is also more prevalent than previously believed.

The present work addresses the following questions.

(1) What is the value of n in $\text{H}^+(\text{H}_2\text{O})_n$ that adequately describes $\text{H}^+(\text{aq})$? Surprisingly, this question has not been addressed. It is synonymous with an enquiry into the extent of positive charge distribution over the hydrations shells of the $\text{H}^+(\text{aq})$ ion. We use the criterion that if the IR spectrum of a water molecule is different from that of bulk water, it is part of the solvation shell of an ion.

(2) What is the true IR spectrum of $\text{H}^+(\text{aq})$? What are the correct vibrational assignments of the bands and what is the origin of the mysterious continuous broad absorption (*cba*)? Theories developed during the 1970–80s to explain the *cba* are many. They include Zundel’s theory of strong OH^+O bond polarisability whereby the proton interacts with the fluctuating electric field of the surroundings,^{8,31} stochastic theory,^{32,33} combined transitions of the proton in H_5O_2^+ accompanied by multiple excitation of low frequency oscillators of the hydration shell,^{34,35} strong interaction between the $\nu(\text{O}-\text{H})$ and $\nu(\text{O}\cdots\text{H})$ vibrations,³⁶ anomalous amplification of a large number of overtones and combinations,^{37,38} and a rapid interconversion between H_3O^+ and H_5O_2^+ within a special OH^+O bond.³⁹ In the present paper, we redefine the *cba* and its origin based on new experimental data.

(3) What is the molecular structure of $\text{H}^+(\text{aq})$ giving rise to its IR spectrum? At a minimum, the locations of the oxygen atoms need to be determined and compared to Eigen- and Zundel-type ions.

(4) What is the role of ion pairing on the structure of ionized strong acids? We note that gas phase studies and, with few exceptions,^{40,41} theoretical calculations are carried out in the absence of anions. We have recently shown that in chlorocarbon solvents, where tight ion pairing is important, neither Eigen nor Zundel-type core ions exist for $\text{H}(\text{H}_2\text{O})_n^+$ ($n = 3-8$) clusters. Rather, the core ion is the H_7O_3^+ cation.⁴²

These questions are addressed by IR spectroscopy using quantitative methods where only qualitative had been applied previously.^{43,44} A method for determining the value of n in $\text{H}^+(\text{H}_2\text{O})_n$ was developed some time ago to determine the stoichiometry of $\text{H}^+(\text{aq})$ incorporated into the water core of reverse micelles.^{45,46} More recently, we communicated the results of applying this method to dilute aqueous solutions of carborane superacids and HClO_4 and found $n = 6$.⁴⁷ In the present work we extend these studies to common mineral acids such as HCl ,

HNO_3 and to higher concentrations of HClO_4 . Also in the recent communication, we published the first quantitatively reliable IR spectrum of $\text{H}^+(\text{aq})$ cation and offered a preliminary interpretation in terms of a unique $\text{H}_{13}\text{O}_6^+$ structural entity having O...O separations that are longer than those in either Eigen or Zundel ions, and longer than those predicted by theory. In the present paper, we offer a more complete analysis of the IR spectrum including a new explanation for the continuous broad absorption (*cba*). Finally, we relate these IR studies to the unique X-ray structure of the carborane acid $\text{H}(\text{CHB}_{11}\text{I}_{11})\cdot 8\text{H}_2\text{O}$ ⁴⁸ whose nanotubular structure appears to offer the first good structural model for $\text{H}^+(\text{aq})$. Unlike all other X-ray structures of $\text{H}^+(\text{H}_2\text{O})_n^+$ salts, it has O...O separations that reflect the delocalized, mobile nature of H^+ in liquid water. They are significantly longer than those found the more localized, static structures having traditional Eigen or Zundel character.

We use attenuated total reflectance (ATR) infrared spectroscopy because in transmission mode the spectrum of water has a very high molar absorptivity in the OH stretching vibration region, resulting in saturation. ATR is regarded as the best method for high-precision measurements in liquid water.^{49,50} The depth of IR penetration is a few microns. Effects of the diamond surface on dissolved electrolytes are confined to a few nanometers so they are not registered by ATR IR.

Experimental

HClO_4 , HNO_3 and HCl acid were used without additional purification. Acid concentrations were determined by titration with standardized NaOH solutions.

IR spectra were recorded in ATR mode by placing a drop of solution onto a diamond crystal using a Perkin Elmer Spectrum-100 spectrometer in the 4000–400 cm^{-1} frequency range. Raw spectra were corrected using the ATR algorithm⁵¹ and manipulated using GRAMMS software.

Results

Isolating the IR spectrum of $\text{H}^+(\text{H}_2\text{O})_n$

The IR spectrum of a strong aqueous acid consists of the spectrum of the anion and overlapping spectra from three types of water molecules: bulk water, water associated with H_{aq}^+ , and water perturbed by the anion. The spectrum of the anion and water perturbed by the anion can be readily subtracted using the spectrum of the corresponding alkali metal salt. Because the spectrum of the hydration shell of an alkali metal cation happens to coincide with that of bulk water⁵² it is successfully subtracted along with the solvent. In this manner, the spectra of the hydration shells of anions $\text{CHB}_{11}\text{Cl}_{11}^-$, ClO_4^- , NO_3^- and Cl^- (Fig. 1) have been isolated for aqueous solutions of their sodium and caesium salts. When normalized to unit concentration these spectra coincide, indicating that they are independent of the nature of cation (Na^+ or Cs^+) in the concentration range studied. This is illustrated for Cl^- in Fig. 2.

Since aquated anions, A_{aq}^- , have essentially no influence on the H-bonded network of liquid water beyond the primary hydration shell^{53,54} the spectra in Fig. 1 belong to their first hydration shell and are easily interpreted. The highest frequency

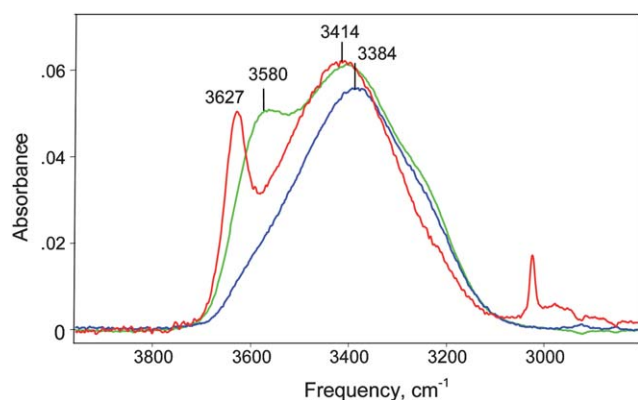


Fig. 1 IR spectra of the first hydration shells of anions Cl^- (blue), ClO_4^- (green) and $\text{CHB}_{11}\text{Cl}_{11}^-$ (red) normalized to unit concentration. These were obtained by subtracting the spectrum of bulk water from the spectra of water solutions of their sodium salts (1.5 M for Cl^- , ClO_4^- and 0.446 M for $\text{CHB}_{11}\text{Cl}_{11}^-$).

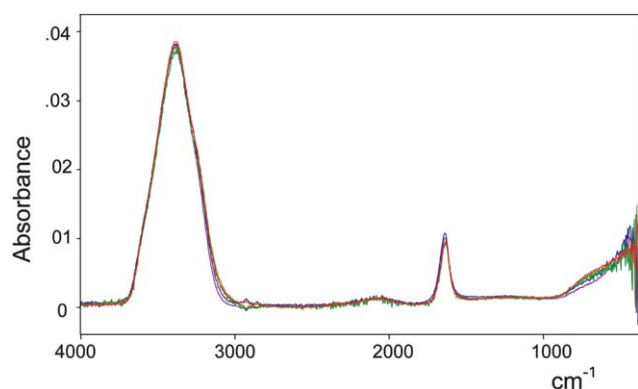
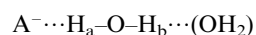


Fig. 2 IR spectra of the hydration shell of Cl^- obtained after subtracting the spectrum of bulk water from those of aqueous solutions of NaCl (1.0 and 2.0 M) and CsCl (0.5, 1.0 and 2.0 M). Spectra are normalized to unit concentration.

νOH band belongs to the $\text{O}-\text{H}_a$ group of water molecules directly H-bonded to anion:



The $\text{O}-\text{H}_b$ group is H-bonded with outer sphere water molecules and its frequency is practically indistinguishable from that of bulk water.⁵³

The νOH_a frequency reflects the proton acceptor properties of an anion and, as shown in Fig. 3, correlates very well with the $\Delta\nu\text{NH}$ basicity scale for anions based on trioctylammonium salt ion pairs.⁵⁵ For Cl_{aq}^- , the νOH_a frequency is the lowest compared to all other anions studied and strongly overlaps with νOH_b , giving rise to a single band at 3384 cm^{-1} . This confirms that Cl^- is the most basic anion of those studied and its conjugate acid in water is correspondingly the weakest.

These considerations allow the isolation of well-grounded spectra of $\text{H}^+(\text{H}_2\text{O})_n$ cations. There are two steps. First, from the spectrum of the acid HA solution (as illustrated for HNO_3 in Fig. 4, black), the spectrum of equimolar NaA is subtracted with

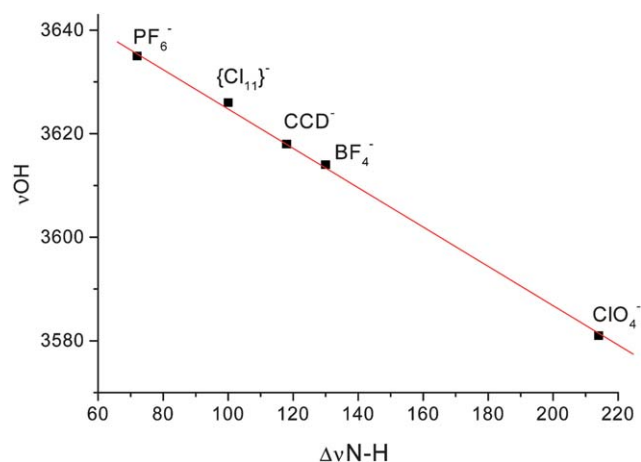


Fig. 3 The νOH_a frequency dependence of water bounded to anion on the $\Delta\nu\text{NH}$ scale basicity of anions⁵⁵

a scaling factor $f = 1$. This removes the spectra of bulk water, the anion and water associated with the anion. The resulting spectrum belongs to $\text{H}^+(\text{H}_2\text{O})_n$ but is distorted (Fig. 4, blue) because the spectrum of bulk water is over-subtracted by an amount equal to the number of water molecules involved in the $\text{H}(\text{H}_2\text{O})_n^+$ cation. Thus, in the second step, the spectrum of the bulk water is added with increasing scaling factor up to full removal of the spectral distortion. The criterion for full removal of the spectral distortion is strict compensation of the $\delta_{\text{H}_2\text{O}}$ band at 1632 cm^{-1} using the method^{45,46} of equality of areas $-S$ and $+S$ (Fig. 4 inset, barred regions in red spectrum). The resulting spectrum (Fig. 4, red) is the true spectrum of the $\text{H}^+(\text{H}_2\text{O})_n$ cation, blemished only by residual inflection point distortions from the $-S$ and $+S$

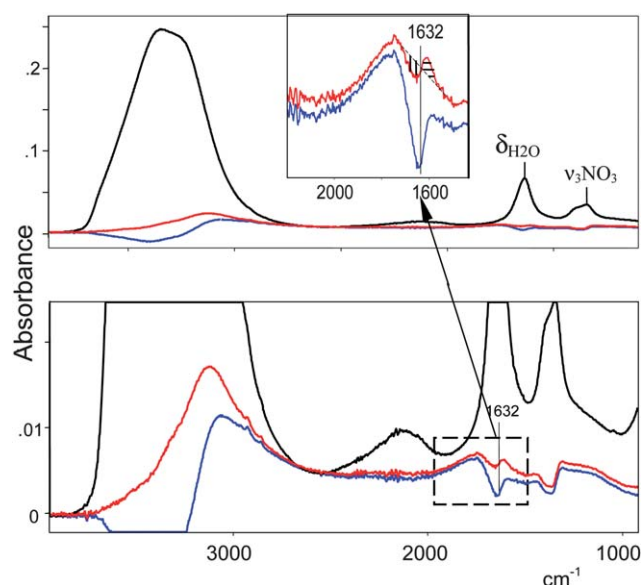


Fig. 4 The procedure for quantitative isolation of the IR spectrum of $\text{H}^+(\text{H}_2\text{O})_n$ cations illustrated for HNO_3 . From the spectrum of 0.75 M HNO_3 (black) was subtracted the spectrum of 0.75 M NaNO_3 resulting in spectrum (blue). Addition of the spectrum of water to (blue) up to equality of the intensities of $-S$ and $+S$ for the $\delta_{\text{H}_2\text{O}}$ band at 1632 cm^{-1} (inset) leads to spectrum (red), the true spectrum of the $\text{H}^+(\text{H}_2\text{O})_n$ cation.

subtraction process which reflect otherwise imperceptible changes in the IR spectrum of water molecules not included in the $\text{H}^+(\text{H}_2\text{O})_n$ formulation. Deconvolution of the IR spectrum (Fig. 5 red) gives the continuous broad absorption (*cba*, blue) overlaid with Gaussian bands (green) with frequency variances for all acids studied in dilute solution (≤ 0.5 M) of 3120 ± 20 , 2816 ± 40 , 1747 ± 5 , 1202 ± 5 and 654 ± 12 cm^{-1} .

Determination of n in $\text{H}^+(\text{H}_2\text{O})_n$

The isolation of the spectra of $\text{H}^+(\text{H}_2\text{O})_n$ cations allows simultaneous determination of the stoichiometry n . As previously described in Supp. Info.,^{47†} the concentration of water molecules

incorporated into the $\text{H}^+(\text{H}_2\text{O})_n$ cation can be determined from equation:

$$C_{\text{H}_2\text{O}}^{\text{bound}} = C_{\text{H}_2\text{O}}^{\text{HA}} - C_{\text{H}_2\text{O}}^{\text{NaA}} + 55.455 \times f \quad (1)$$

where $C_{\text{H}_2\text{O}}^{\text{HA}}$ is the molar concentration of water in the acid solution, $C_{\text{H}_2\text{O}}^{\text{NaA}}$ is the molar concentration of water in the salt solution, 55.455 is molar concentration of pure water and f is a scaling factor. The stoichiometry of $\text{H}^+(\text{H}_2\text{O})_n$ cations was determined as $n = C_{\text{H}_2\text{O}}^{\text{bound}}/C_{\text{HA}}$, where C_{HA} is the molar concentration of acid. The values $C_{\text{H}_2\text{O}}^{\text{HA}}$ and $C_{\text{H}_2\text{O}}^{\text{NaA}}$ for $\text{A}^- = \text{Cl}^-$, NO_3^- , ClO_4^- were taken from literature data.⁵⁶ Eqn (1) can be used with suitable accuracy up to 0.5–0.75 M HA concentration for low molecular weight acids such as HCl, HClO_4 and HNO_3 . In the case of high molecular weight carborane acids, it can be used up to 0.018 M.⁴⁷

As communicated earlier,⁴⁷ the value of n in the $\text{H}^+(\text{H}_2\text{O})_n$ cation was found to be equal to 6 for the strongest acids. This includes all carborane acids as well as HClO_4 at concentrations below 0.7 M. The n values are given in Table 1 for HClO_4 at higher concentrations and for HNO_3 and HCl acids. They show decreasing n values with increasing concentration. As discussed later, these are ascribed to ion pairing effects in these weaker acids.

Discussion

The structure of $\text{H}^+(\text{H}_2\text{O})_n$ and its IR spectrum

The determined stoichiometry of the $\text{H}^+(\text{H}_2\text{O})_6$ cation in strong acids along with a preliminary interpretation of its IR spectrum led us to formulate H_{aq}^+ as a unique $\text{H}_{13}\text{O}_6^+$ ion having the structure shown schematically in 2D in Scheme 1 (blue).⁴⁷

Let us now discuss this in more detail with additional evidence. Obviously, the $n = 6$ result rules out formation of a C_{3v} Eigen-type $\text{H}_3\text{O}^+ \cdot 3\text{H}_2\text{O}$ ion because it has a stoichiometry of $n = 4$. Moreover, the IR spectrum of the $\text{H}^+(\text{H}_2\text{O})_6$ cation is quite different from that of Eigen-type ions. These include H_3O^+ bound to three water molecules in crystallographically characterized $[\text{H}_3\text{O}^+ \cdot 3\text{H}_2\text{O}][\text{CHB}_{11}\text{Cl}_{11}]^-$ ⁴² and H_3O^+ bound to three tributylphosphate molecules (TBP) in $[\text{H}_3\text{O}^+ \cdot 3\text{TBP}][\text{FeCl}_4]^-$.⁵⁷

The basicity of TBP is known to be very close to that of bulk water⁵⁷ so the IR spectra of these ions are expected to be very similar. As seen in Fig. 5a (blue, black), the central H_3O^+ group of these Eigen-type ions has a characteristic broad absorption in

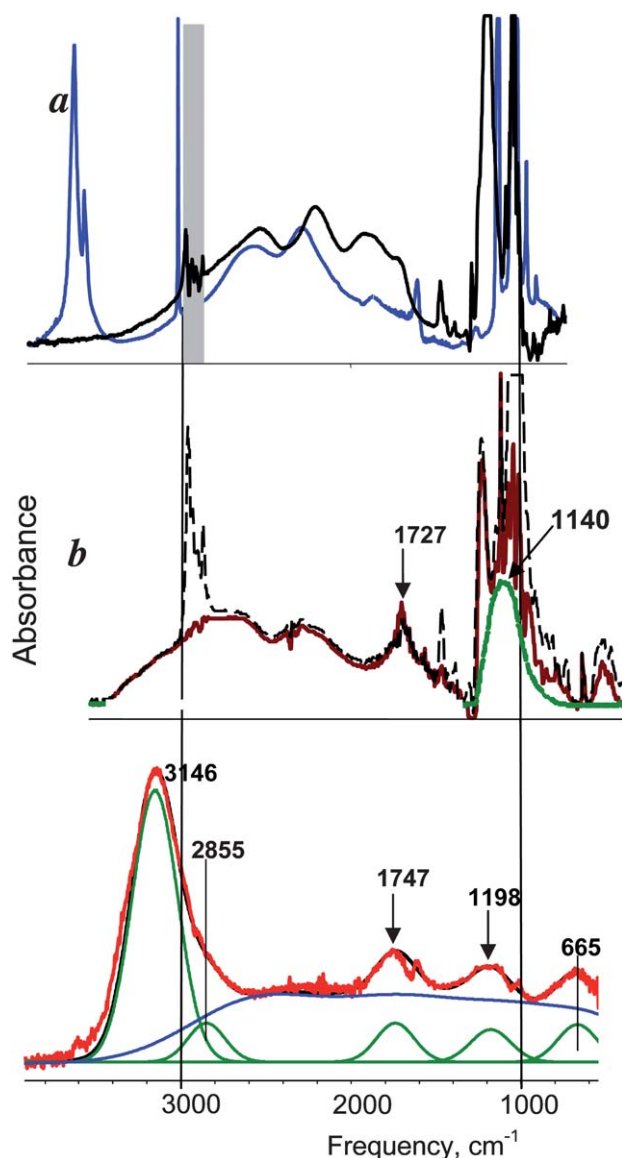
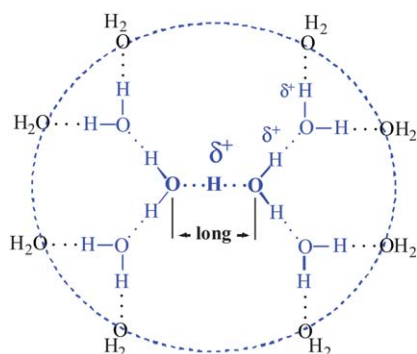


Fig. 5 IR spectrum of $\text{H}^+(\text{H}_2\text{O})_6$ cation in water (red) compared with those of: *a*) $\text{H}_3\text{O}^+ \cdot 3\text{H}_2\text{O}$ in crystal $\text{H}^+(\text{H}_2\text{O})_4\{\text{Cl}_{11}\}$ (blue) and $(\text{H}_3\text{O}^+ \cdot 3\text{TBP})\text{FeCl}_4^-$ in CCl_4 solution (black); *b*) $\text{H}_5\text{O}_2^+ \cdot 4\text{TBP}$ in TBP solutions of $\text{H}_5\text{O}_2^+\text{ClO}_4^-$ salt, initial (black dashed) and after subtraction of $\text{C}_4\text{H}_{12}\text{O}$ groups absorption of TBP.

Table 1 Stoichiometry n of $\text{H}^+(\text{H}_2\text{O})_n$ clusters formed in water solutions of HClO_4 , HNO_3 and HCl

Concentration, mol L ⁻¹	Acid		
	HClO_4	HNO_3	HCl
0.5	5.98	6.33	5.1
0.7	—	—	5.1
0.75	5.88	5.73	—
1.0	5.84	6.03	5.02
1.5	5.78	5.31	5.1
2.0	5.67	4.89	5.22
3.0	5.45	4.54	5.18
4.0	5.43	4.35	5.5



Scheme 1 Schematic 2D structure of the $\text{H}_{13}\text{O}_6^+$ ion.

the 1700–3000 cm^{-1} frequency range⁴² which is absent in the spectrum of the $\text{H}^+(\text{H}_2\text{O})_6$ cation (Fig. 5, red). Clearly, C_{3v} Eigen-type H_3O^+ ions do not exist in aqueous acid solutions.

Since the $n = 6$ stoichiometry of the $\text{H}^+(\text{H}_2\text{O})_6$ ion is compatible with a tetrahydrated Zundel-type $\text{H}_5\text{O}_2^+ \cdot 4\text{H}_2\text{O}$ ion, the appropriateness of a Zundel-type formulation for H_{aq}^+ must be made on the basis of spectral similarity. This is somewhat problematic because, while structurally characterized by X-ray crystallography,¹⁹ the IR spectrum of the Zundel-type $\text{H}_5\text{O}_2^+ \cdot 4\text{H}_2\text{O}$ ion has not been reported in condensed phases. Nevertheless, the IR spectrum of the H_5O_2^+ ion surrounded by four TBP molecules is known⁵⁷ and the close similarity of the basicity of TBP with that of bulk water leads to the expectation that the spectrum of $\text{H}_5\text{O}_2^+ \cdot 4\text{TBP}$ will be a good model for that of $\text{H}_5\text{O}_2^+ \cdot 4\text{H}_2\text{O}$. The comparison is shown in Fig. 5 (red vs. brown). There is a similarity, but also an important distinction. The similarity is the development of the two Zundel ion marker bands, in the ranges 1140–1200 and 1727–1747 cm^{-1} , which are associated with the vibrations of the central symmetric O–H–O group with strong H-bonds.⁵⁸ However, these frequencies for the $\text{H}^+(\text{H}_2\text{O})_6$ cation are significantly higher than those of the $\text{H}_5\text{O}_2^+ \cdot 4\text{TBP}$ cation.

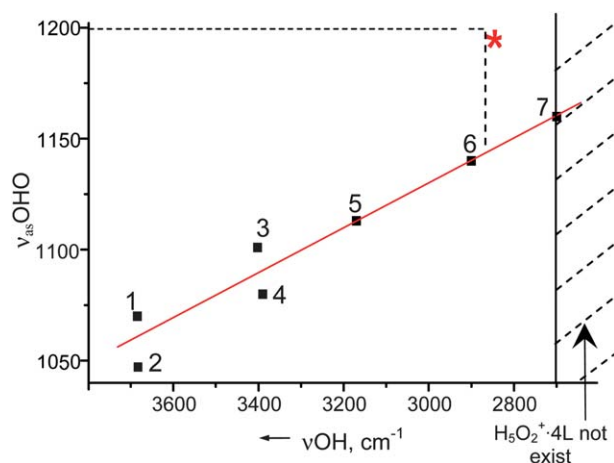


Fig. 6 The $\nu_{\text{as}}\text{OHO}$ dependence on basicity of L in $\text{H}_5\text{O}_2^+ \cdot 4\text{L}$ cations. 1, 2—bare in gas phase; 3— $\{\text{Cl}_{11}\}$ ion in solid state; 4— C_6H_6 in benzene solution; 5—diethyl ether in benzene solution; 6—tributyl phosphate in CCl_4 solution; 7—phosphin oxide in dichloroethane solution.

It is known that the frequencies of both Zundel ion marker bands increase linearly with increasing the basicity of L-ligands of $\text{H}_5\text{O}_2^+ \cdot 4\text{L}$ because of decreasing positive charge and decreasing H-bond strength at the central OHO group.⁵⁸ As shown in Fig. 6, the lower frequency band, $\nu_{\text{as}}\text{OHO}$, increases from $\sim 1060 \text{ cm}^{-1}$ in the bare (gas phase) H_5O_2^+ ion^{59,60} to 1140 cm^{-1} for L = tributylphosphate, whose basicity coincides with that of liquid water.⁵⁷ It increases further to 1160 cm^{-1} for L = phosphine oxides, whose basicities exceed that of water.⁶¹ This represents the limit of existence of $\text{H}_5\text{O}_2^+ \cdot 4\text{L}$ because with this L basicity there is an equilibrium with proton disolvate-type $\text{L}-\text{H}^+-\text{L}$ ion.⁶¹ If the basicity of L exceeds that of phosphine oxides, then only $\text{L}-\text{H}^+-\text{L}$ ions exist. The $\nu_{\text{as}}\text{OHO}$ value for $\text{H}^+(\text{H}_2\text{O})_6$ in water lies conspicuously off the basicity correlation in Fig. 6 (red asterisk). Its high frequency of 1198–1200 cm^{-1} corresponds to a region where typical Zundel-type H_5O_2^+ ions do not exist. The frequency indicates that the central O–H–O group has both anomalously low positive charge and an anomalously long O...O distance compared to typical Zundel-type ions.

The possibility of such structural peculiarity in the $(\text{H}_{13}\text{O}_6^+)_{\text{aq}}$ cation was recently discovered in the X-ray structure of $\text{H}(\text{CHB}_{11}\text{I}_{11}) \cdot 8\text{H}_2\text{O}$, where three unusual types of protonated water clusters are formed in water filled nanotubes (Fig. 6b).⁴⁸ These are the $(\text{H}_{13}\text{O}_6^+)_{\text{aq}}$ ion (**I**), the $\text{H}_7\text{O}_3^+ \cdot \text{H}_2\text{O}$ ion (**II**) similar to that formed by ion-paired hydrated carborane acids in organic solvents⁴² and the previously unknown square-planar $(\text{H}_{17}\text{O}_8^+)_{\text{aq}}$ cluster (**III**). All clusters have unprecedented, long O...O distances. The IR spectrum of this crystal, which represents the overlapping spectra of these three cluster types, shows the same band at *ca.* 1200 cm^{-1} seen in the spectrum of $\text{H}_{13}\text{O}_6^+$ in an aqueous solution of $\text{H}(\text{CHB}_{11}\text{I}_{11})$ (Fig. 7). Does this band belong to only cluster **I** or do clusters **II** and **III** also contribute to this absorption? In Fig. 8 the spectrum of crystalline $\text{H}(\text{CHB}_{11}\text{I}_{11}) \cdot 8\text{H}_2\text{O}$ is compared to that of the $\text{H}_7\text{O}_3^+ \cdot 5\text{H}_2\text{O}$ cation formed in water-saturated dichloroethane solution of $\text{H}(\text{CHB}_{11}\text{I}_{11})$.⁴² One can see that the $\text{H}_7\text{O}_3^+ \cdot 5\text{H}_2\text{O}$ cation, which is topologically analogous to cluster **II** and has an O...O distance of $\sim 2.5 \text{ \AA}$,⁴² has no absorbance in the $\sim 1200 \text{ cm}^{-1}$ region. Since both clusters **II** and **III** have longer O...O distances of ~ 2.62 and

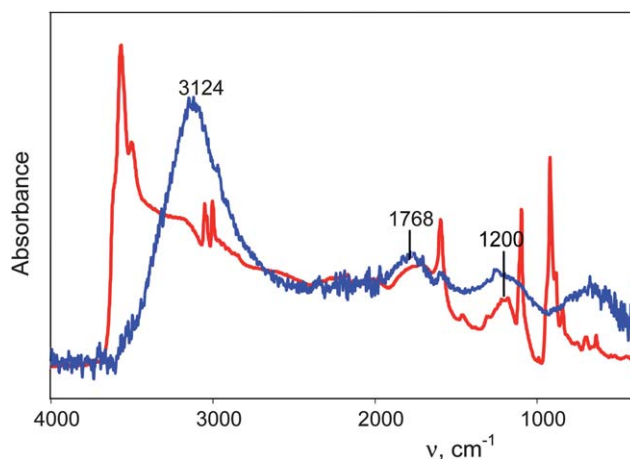


Fig. 7 IR spectrum of $\text{H}_{13}\text{O}_6^+$ in water solution of $\text{H}(\text{CHB}_{11}\text{I}_{11})$ acid (the absorption of anion is subtracted) (blue) in comparison with spectrum of crystal $\text{H}(\text{CHB}_{11}\text{I}_{11}) \cdot 8\text{H}_2\text{O}$ (red).

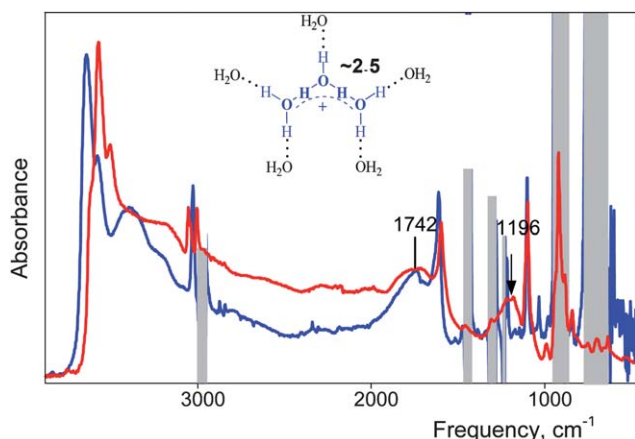


Fig. 8 IR spectrum of crystal $\text{H}(\text{CHB}_{11}\text{I}_{11}) \cdot 8\text{H}_2\text{O}$ (red) in comparison with spectrum of $[\text{H}_7\text{O}_3^+ \cdot 5\text{H}_2\text{O}](\text{CHB}_{11}\text{I}_{11})$ acid in dichloromethane solution (blue).

~ 2.64 Å, respectively, they too will not have absorptions in this region. Thus, we conclude that the ~ 1200 cm^{-1} band in the spectrum of crystalline $\text{H}(\text{CHB}_{11}\text{I}_{11}) \cdot 8\text{H}_2\text{O}$ arises from the $\nu_{\text{as}}\text{OHO}$ frequency of the central OHO group of cluster I. Since $\text{H}_{13}\text{O}_6^+$ ions in both this crystal and in liquid water are surrounded by water molecules and their $\nu_{\text{as}}\text{OHO}$ absorption have coincident frequency and similar width/shape, they must have a similar degree of positive charge delocalization and a similar central $\text{O} \cdots \text{O}$ and four conjugated $\text{O} \cdots \text{O}$ distances. This allows us to define the structure of the $\text{H}_{13}\text{O}_6^+(\text{aq})$ ion in Scheme 1 more exactly. Its key features are an unprecedented long central $\text{O} \cdots \text{O}$ distance of ~ 2.57 Å and $\text{O} \cdots \text{O}$ distances of four conjugated H-bonds with ~ 2.7 Å.

The other characteristic IR bands of the $(\text{H}_{13}\text{O}_6^+)_{\text{aq}}$ cation are readily interpreted by analogy to $\text{H}_5\text{O}_2^+ \cdot 4\text{L}$ cations: the 1768 cm^{-1} band, like that at ~ 1200 cm^{-1} , is associated with the central OHO group, the 2855 cm^{-1} band to the OH stretch of the two H_2O molecules forming the central H_5O_2 group and the 3146 cm^{-1} band is assigned to the OH stretch of the four peripheral H_2O molecules.

H/D comparison

A comparison of the band frequencies of protio and deutero forms of the $\text{H}_{13}\text{O}_6^+(\text{aq})$ cation (Table 2) shows that the H/D isotopic ratios for both OH stretching and torsional vibrations are close to 1.35, *i.e.* consistent with harmonic vibrations. However, the two bands arising from the central OHO group vibrations have lower H/D ratios indicating that they are

Table 2 IR frequencies of protio $\text{H}_{13}\text{O}_6^+$ and deutero $\text{D}_{13}\text{O}_6^+$ cations and isotopic H/D ratios

Vibrations	X = H	X = D	H/D
ν_{OX} peripheral	3146	2340	1.35
ν_{OX} of H_5O_2 group	2855	2111	1.35
δ_{OXO}	1747	1406	1.24
$\nu_{\text{as}}\text{OXO}$	1198	922	1.30
Torsion	672	491	1.36

anharmonic. This provides an additional criterion on which to judge the appropriateness of theoretical determinations of structure. We note that isotopic H/D ratios bands of the trihydrated Eigen ion (see Supp. Info.†) are all in the range common for harmonic vibrations (1.34–1.35).

Ion pairing effects

Infrared spectra of aqueous solutions of the studied acids as a function of concentration in the 0.2–4 M range show good isosbestic points. These occur at 3146 cm^{-1} for HCl , 3542 cm^{-1} for HNO_3 and at 3518 and 3072 cm^{-1} for HClO_4 (see Supp. Info.†). This might be taken as evidence that only one type of $\text{H}^+(\text{H}_2\text{O})_n$ cluster is present in these acids. However, isosbestic points are relatively insensitive to small changes in the intensities of bands. By careful attention to the quantitative subtraction of the spectrum of bulk water we find that n values decrease with increasing concentration for two acids, HNO_3 and HClO_4 . This is ascribed to ion pairing effects.

Increasing the HClO_4 and HNO_3 acid concentrations up to 4 M leads to gradual decreases in n from 6 to 5.4 and 4.3, respectively (Table 1). This indication of stronger ion pairing effects in HNO_3 relative to HClO_4 is consistent with the higher basicity of NO_3^- on the $\Delta\nu\text{NH}$ scale⁵⁵ and with the lower acid strength of HNO_3 ($\text{p}K_{\text{a}} -1.5$) relative to HClO_4 ($\text{p}K_{\text{a}} -8$). In their IR spectra, normalized to unit concentration, the change in n value is reflected mainly in a proportionate decrease in the intensity of the ν_{OH} absorption at 3120 – 3180 cm^{-1} , the band associated with the four peripheral H_2O molecules of the $\text{H}_{13}\text{O}_6^+$ ion. The remaining part of the H_{aq}^+ spectrum is insignificantly changed. This is illustrated for HNO_3 in Fig. 9. For HCl , the constant value of $n = 5$ and the invariability of the normalized IR spectra over the 1–4 M concentration range indicates constant ion pairing (Supp. Info.†).

Taken all together, these data suggest that ion pairing perturbs up to two of the four peripheral water molecules of the $\text{H}_{13}\text{O}_6^+$

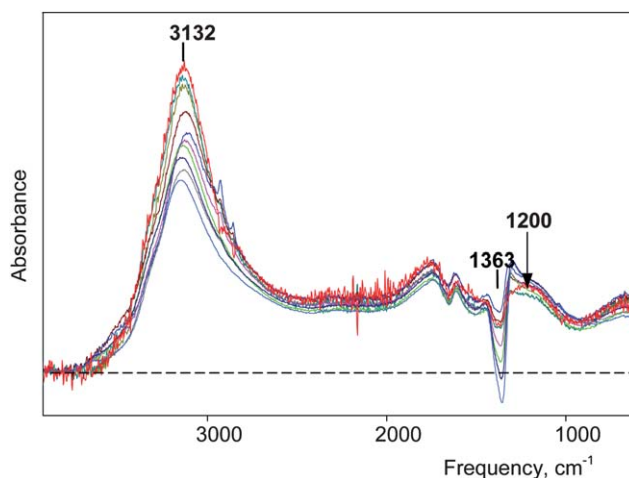


Fig. 9 IR spectra of $\text{H}(\text{H}_2\text{O})_n^+$ clusters normalized to unit concentration for HNO_3 water solutions with concentrations varied from 0.25 (red) to 4.0 M (blue). The inaccurate subtraction of $\nu_3\text{NO}_3$ band (over subtraction at 1363 cm^{-1}) arises because of different concentration dependence of the spectrum of NO_3^- anion for studied HNO_3 solutions and used for subtraction NaNO_3 solutions.

ion, removing their IR spectral peculiarity *i.e.*, restoring the distinctively absent $\delta\text{H}_2\text{O}$ band. As discussed in more detail later, absent IR bands are associated with ultrafast proton motion. Shared water molecules in an ion pair (Scheme 2) between $\text{H}(\text{H}_2\text{O})_n^+$ and the first hydration shell of the anion, where water mobility is slow,^{53,54,62} will immobilize these water molecules and restore their $\delta\text{H}_2\text{O}$ band. Thus, the spectrum of the shared water molecules is subtracted as the hydration shell of anion and the determined stoichiometry of $\text{H}^+(\text{H}_2\text{O})_n$ has $n < 6$.

The basicity of the O-atoms of the shared water molecules should increase slightly compared to that of the remaining unshared peripheral water molecules of the $\text{H}^+(\text{H}_2\text{O})_n$ cation because, as indicated by Fig. 1, H-bonding with Cl^- , NO_3^- or ClO_4^- anion is weaker than with outer sphere water molecules. However, this change in O-basicity is apparently too weak to notably influence the spectrum of $\text{H}^+(\text{H}_2\text{O})_n$ cation when passing from $n = 6$ to 5 or 4, other than decreasing the intensity of the νOH band at $\sim 3100\text{--}3200\text{ cm}^{-1}$ (Fig. 9). This indicates that the $n = 4$ cation retains high spectral and structural similarity with $n = 5$ and 6.

While the $\delta\text{H}_2\text{O}$ bands of the shared and peripheral water molecules are insensitive to their nonequivalence, the OH stretches are much more sensitive. The νOH bands of the shared water molecules should lie between that of the unshared peripheral H_2O molecules ($3100\text{--}3200\text{ cm}^{-1}$) and νOH of unshared water molecules bound to the anion. Thus, these bands will not be perfectly subtracted. This is detected as a weak distortion on the high frequency side of the νOH absorption at $\sim 3100\text{--}3200\text{ cm}^{-1}$ (Fig. 9). As expected, the distortion increases with decreasing n in $\text{H}^+(\text{H}_2\text{O})_n$.

Corroborating evidence for ion pair formation is found in the IR spectrum of anion, most sensitively with the NO_3^- anion. The decrease in its symmetry under the influence of a unidirectional electrostatic interaction splits the doubly degenerate $\nu_3\text{NO}_3$ stretching band. The stronger this interaction, the larger is the $\Delta\nu_3$ splitting. As shown in Fig. 10, $\Delta\nu_3$ increases with increasing HNO_3 concentration starting at *ca.* 0.6 M. This is consistent with decreasing average stoichiometry in $\text{H}^+(\text{H}_2\text{O})_6$ below 6. At HNO_3 concentrations below 0.6 M, where only the $n = 6$ cation is formed, $\Delta\nu_3$ appears to be concentration independent. Nevertheless, the residual $\Delta\nu_3$ splitting ($\sim 54\text{ cm}^{-1}$) indicates that ion pairing must still be present. A model that accommodates these data is shown in Scheme 3. The $\text{H}_{13}\text{O}_6^+$

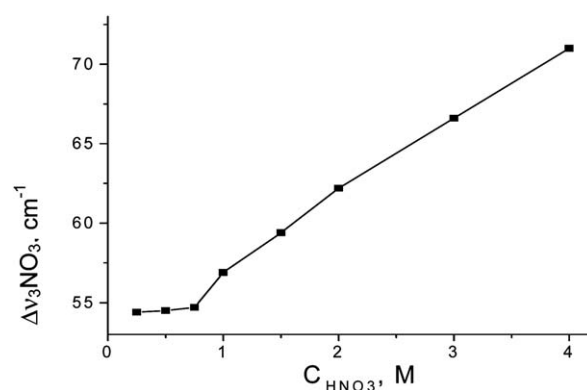


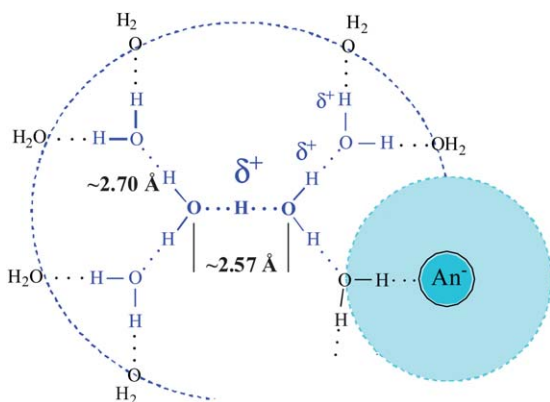
Fig. 10 Dependences of $\Delta\nu_3\text{NO}_3$ splitting on HNO_3 concentration.

cation and inner solvation shells of the anion remain intact but electrostatic contact is sufficient to perturb the D_{3h} symmetry of NO_3^- anion.

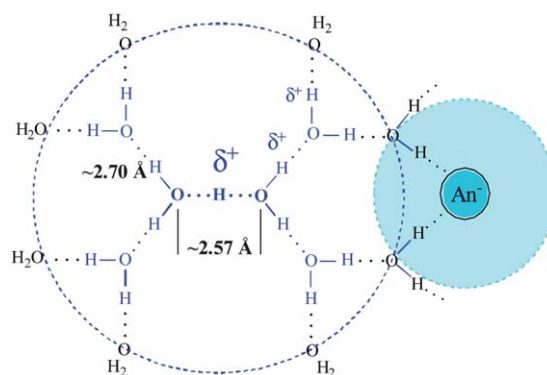
The triple degenerate ν_3 stretch of the ClO_4^- anion changes with increasing perchloric acid concentration in a similar manner to the $\nu_3\text{NO}_3$ band although the splitting is less pronounced. This indicates the same type of ion pairing is occurring.

Carborane superacids are the strongest known acids⁶³ so ion pairing is expected to be the weakest or non-existent. Indeed, the IR spectrum of the carborane anion is not detectably dependent on acid concentration and only $\text{H}_{13}\text{O}_6^+$ cations are formed. Nevertheless, the νOH frequency of the four peripheral H_2O molecules of the $\text{H}_{13}\text{O}_6^+$ cation shows a small dependence on the nature of carborane anion⁴⁷ that exceeds the error of νOH determination. Thus, even ionized carborane acids, $(\text{H}_{13}\text{O}_6^+)\text{Carb}^-_{\text{aq}}$, appear to be ion paired in the manner of Scheme 3. It is likely that all acids, no matter how strong, have ion pairing of this type.

For dilute solutions of mineral acids ($< 0.7\text{ M}$), the intensity of νOH bands (I_{OH}) can be measured more precisely than the determination of n in $\text{H}^+(\text{H}_2\text{O})_n$. That is why the dependence of I_{OH} on C_{HA} can give more precise information about composition of H_{aq}^+ at low concentrations, where stoichiometry cannot be accurately determined, and where n starts to change from 6 to 5. The I_{OH} dependences on acid concentration (C_{HA}) for HCl , HNO_3 and HClO_4 are given in Fig. 11. They show more sharply that ion pairing of the type in Scheme 2 with $n = 5$ begins at ~ 0.5 for HNO_3 and $\sim 0.9\text{ M}$ (HClO_4). Below these concentrations, ion



Scheme 2 Ion pairing with shared water molecule.



Scheme 3 Ion pairing in dilute solution.

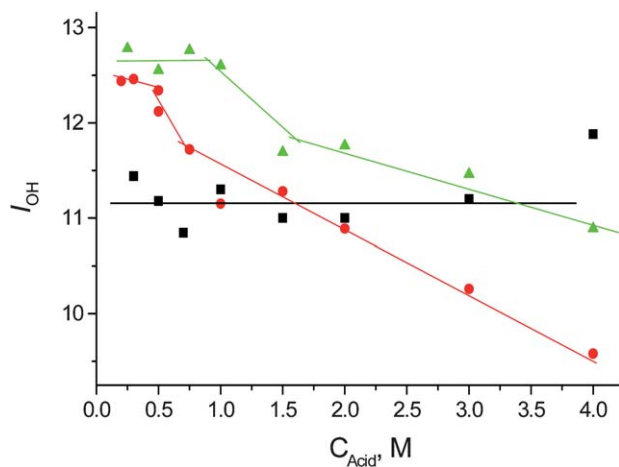


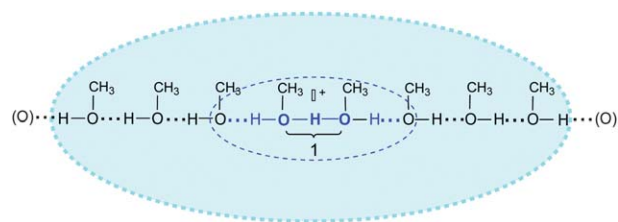
Fig. 11 Dependences of OH stretch intensities (I_{OH}) on acids concentration. Green— HClO_4 ; red— HNO_3 ; black— HCl .

pairing only occurs with the $n = 6$ cation according to Scheme 3. In the case of HCl , from as low as 0.3 M and up to 4 M concentration, only ion pairing with $n = 5$ is observed (Scheme 2). Thus, in spite of the leveling of acid strength in dilute solutions of these strong acids, measurable differences in ion pairing formation with $n = 5$ or 6 nevertheless reflects their relative acid strengths: $\text{H}(\text{carborane}) > \text{HClO}_4 > \text{HNO}_3 > \text{HCl}$.

The uniqueness of $\text{H}^+(\text{H}_2\text{O})_6$ cation

This is best revealed by comparison to the protonated methanol cluster, $\text{H}^+(\text{CH}_3\text{OH})_8$, formed when a strong acid ionizes in neat methanol.⁶⁴ The 3D-structured $\text{H}^+(\text{H}_2\text{O})_6$ cation has important similarities, as well as important distinctions, from 1D-structured $\text{H}^+(\text{CH}_3\text{OH})_8$ cation shown in Scheme 4.

The similarities in their IR spectra (Fig. 12) are: (i) both cations have characteristic bands at 1567–1747 and 958–1197 cm^{-1} arising from the central OHO group vibrations and ν_{OH} stretch frequencies of all other OH groups in the 2500–3200 cm^{-1} region, and (ii) bands from δCOH bending and νCO stretching vibrations of $\text{H}^+(\text{CH}_3\text{OH})_8$ are absent in its IR spectrum just as the $\delta\text{H}_2\text{O}$ bands are absent in the spectrum of $\text{H}(\text{H}_2\text{O})_6^+$. These similarities are common to all proton disolvates $\text{L}-\text{H}^+-\text{L}$, including $\text{H}_5\text{O}_2^+ \cdot 4\text{L}$ (L = nonprotic base) and have been discussed earlier.^{58,64–66} This peculiar absence of bands defines the sharp boundary between the eight CH_3OH molecules in $\text{H}^+(\text{CH}_3\text{OH})_8$ or the six H_2O molecules in $\text{H}_{13}\text{O}_6^+$ and the surrounding molecules of bulk methanol or water, respectively. Absent CO stretch and COH bend vibrations bands in



Scheme 4 Representation of $\text{H}(\text{CH}_3\text{OH})_8^+$ cation structure in neat methanol.

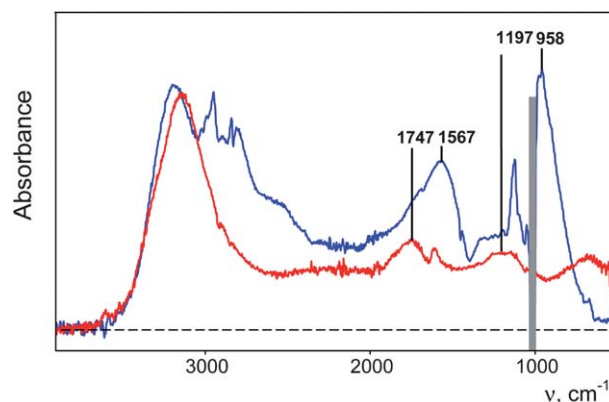


Fig. 12 IR spectra of 0.4 M $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ solutions in water (red, anion absorption is subtracted) and methanol (blue).

$\text{H}^+(\text{CH}_3\text{OH})_n$ cations are characteristic of chain-linked methanol molecules conjugated with the central $\text{O}-\text{H}^+-\text{O}$ group.⁶⁴ Even the CH stretching vibrations of the methyl groups are affected. Compared to the intensity of common CH_3OH molecules, their intensity decreases by 94% for those associated with the central $\text{O}-\text{H}^+-\text{O}$ group and 60% for those associated with the conjugated $\text{O}-\text{H}\cdots\text{O}$ groups. To date, this has not been addressed by theory but must be connected with special dynamic properties of the central OHO group.

Regarding the important distinctions between 3D $\text{H}(\text{H}_2\text{O})_6^+$ and 1D $\text{H}^+(\text{CH}_3\text{OH})_8$ clusters, these are mainly concerned with the central $\text{O}-\text{H}-\text{O}$ group and its response to conjugated peripheral molecules. In the case of $\text{H}^+(\text{CH}_3\text{OH})_n$ clusters when passing from $n = 2$ to 4, ν_{asOHO} increases from 950 to 1010 cm^{-1} without changing in intensity (Table 3). This occurs because of partial delocalization of the positive charge onto the two new $\text{O}-\text{H}\cdots\text{O}$ groups, accompanied by decreasing charge on the central OHO group and increasing $\text{O}\cdots\text{O}$ distance. For the next increases of n up to 8, there is practically no more influence on the central $\text{O}-\text{H}^+-\text{O}$ group (ν_{as} and I_{OHO} are constant). However, replacement of benzene solvent with methanol for the cluster with $n = 8$ returns ν_{as} to the initial value of 950 cm^{-1} as seen in the $n = 2$ cluster, i.e., the positive charge and $\text{O}\cdots\text{O}$ distance are restored. In the case of $\text{H}(\text{H}_2\text{O})_n^+$ clusters the situation is the opposite. Increasing n from 2 in benzene to 6 in water results in a high frequency shift of $\Delta\nu_{\text{asOHO}}$ by 170 cm^{-1} whereas there is no shift for the corresponding $\text{H}^+(\text{CH}_3\text{OH})_n$ clusters with $n = 2$ in benzene and $n = 8$ in methanol (Table 4). It is clear that the 3D water cluster structure favors positive charge delocalization from the central OHO group much more than the 1D methanol structure. The difference lies in their outer sphere solvation and ion pairing. The 3D water cluster has eight H-bonded outer sphere water molecules onto whose O-atoms the positive charge

Table 3 The ν_{asOHO} frequency and intensity (I_{OHO}) dependence on the n number of methanol molecules in $\text{H}^+(\text{CH}_3\text{OH})_n$ clusters

n	Solvent	ν_{asOHO}	I_{OHO}
2	Benzene	~ 950	3.1
4	Benzene	~1010	2.9
8	Benzene	~1010	3.3
8	Methanol	950	4.2

Table 4 The $\nu_{\text{as}}\text{OHO}$ frequency and intensity (I_{OHO}) dependence on the n number of water molecules in $\text{H}^+(\text{H}_2\text{O})_n$ clusters

n	Solvent	$\nu_{\text{as}}\text{OHO}$	I_{OHO}
2	Benzene	1028	3.25
6	Water	1198	0.90
6	Crystal	1198	4.2

can be delocalized whereas methanol clusters are restricted to charge delocalization in 1D and rely on greater accessibility of the central $\text{O}-\text{H}^+-\text{O}$ group to ion pairing and electrostatic solvation with outer sphere methanol.⁶⁴ This makes the $\text{H}_{13}\text{O}_6^+_{\text{aq}}$ ion unique and causes an unprecedented increase in the $\text{O}\cdots\text{O}$ distance of the central OHO group.

Another important distinction follows from the intensities of the $\nu_{\text{as}}\text{OHO}$ band (I_{OHO}). In the case of $\text{H}^+(\text{CH}_3\text{OH})_n$ clusters, increasing n from 2 to 8 does not change I_{OHO} significantly (Table 3). The same is true when passing from $\text{H}_5\text{O}_2^+\cdot 4\text{C}_6\text{H}_6$ in benzene solution to $\text{H}(\text{H}_2\text{O})_6^+$ in solid state (Table 4). However, for $\text{H}(\text{H}_2\text{O})_6^+$ in aqueous solution, I_{OHO} is more than a factor of three lower (Table 4) and it is accompanied by the appearance of the continuous broad absorption (*cba*). In other words, only about 30% of absorption of $\text{H}(\text{H}_2\text{O})_6^+_{\text{aq}}$ is observed as absorption bands due to normal vibrations, the other 70% appears to be developed as a continuum. In contrast, the $\text{H}^+(\text{CH}_3\text{OH})_8$ cation in neat methanol develops normal I_{OHO} intensity for $\text{O}-\text{H}^+-\text{O}$ group vibrations and does not develop a *cba*, only a broad absorption from multiple OH vibrations that is often mistakenly named a *cba*.

The continuous broad absorption (*cba*)

These observations allow us to give definition to the *cba* and ascertain its nature. The *cba* is an unstructured continuous absorption that develops in IR spectra of acidic water solutions across the entire $3000\text{--}50\text{ cm}^{-1}$ frequency range (Fig. 5, blue). Attempts to divide it into separate broad bands⁶⁷ are unconvincing. Such *cba* is not observed in the IR spectra of $\text{H}_3\text{O}^+\cdot 3\text{L}$, $\text{H}_5\text{O}_2^+\cdot 3\text{L}$ and $\text{H}_7\text{O}_3^+\cdot 5\text{L}$ cations with L = organic basics or H_2O , in the solid state or in solutions of organic solvents.^{5,42,48,58} When the basicity of L in these species is high (H_2O , tributylphosphate, phosphine oxides), their stretching OH vibrations develop as very broad overlapping bands in the $3000\text{--}1200\text{ cm}^{-1}$ frequency range having the so-called ABC structure⁶⁸ which has often been mistaken for *cba*. This is common to all species with asymmetric $\text{O}-\text{H}\cdots\text{O}$ groups having $\text{O}\cdots\text{O}$ distance *ca.* $2.5\text{--}2.6\text{ \AA}$.⁴² These broad absorptions are quite distinct from the *cba* of acidic water solutions by not being continuous and featureless. They can be deconvoluted into separate bands. To the best of our knowledge, *cba* is a specific spectroscopic feature found only in aqueous $\text{H}(\text{H}_2\text{O})_n^+$ clusters in liquid water. The spectrum of the $\text{H}(\text{H}_2\text{O})_6^+$ cluster in the solid state has no *cba* and the intensity of the absorption bands from normal vibrations is undiminished (Table 4). Similarly, such intensity conversion from *cba* to normal mode vibrations has been detected by Raman spectroscopy when 4M aqueous HCl or HBr form glasses at liquid nitrogen temperature. The *cba* intensity significantly decreases with temperature and is accompanied by a simultaneous increase in the intensity of the band at $\sim 1200\text{ cm}^{-1}$.⁶⁹ These observations indicate that the *cba* is associated with the dynamic properties of

excess proton. At low temperature in a glacial state ($-180\text{ }^\circ\text{C}$), or in the crystalline state at room temperature, the translational movements of the protons in the $\text{H}(\text{H}_2\text{O})_6^+$ cation are suppressed and the cluster develops normal vibrations. On the other hand, at room temperature in liquid water, proton dynamics are comparable to the timescale of vibrational transitions.¹³ As a consequence, the rates of vibrational transitions involving the five internal H-atoms of $\text{H}(\text{H}_2\text{O})_6^+$ exceed the lifetimes of their fixed positions. On the IR timescale, the location of these five H-atoms becomes uncertain and a continuous absorption develops instead of line spectra from normal vibrations. Since the intensity of the absorption bands of H_{aq}^+ in water corresponds to $\sim 30\%$ of that for normal vibrations (Table 4), on average only in $\sim 30\%$ of $\text{H}_{13}\text{O}_6^+$ clusters do the 5 H-atoms have lifetimes of their fixed positions sufficient to produce normal vibrations. The other $\sim 70\%$ of $\text{H}_{13}\text{O}_6^+$ clusters develop a *cba*. Shifting the equilibrium percentages between the line spectrum and the *cba* requires a significant temperature change that exceeds the liquid range of water. That is why small increases in temperature of water solutions from 293 to 313 K ⁶⁷ or 363 K ⁷⁰ do not reveal changes in the *cba*.

Dynamic properties of the excess proton may also be responsible for the disappearance of the $\delta\text{H}_2\text{O}$ band at $\sim 1630\text{ cm}^{-1}$ for all 6 H_2O molecules in the $\text{H}_{13}\text{O}_6^+$ cation, as well as the νCO and δCOH bands of $\text{H}^+(\text{CH}_3\text{OH})_n$ clusters and related bands in proton disolvates H^+L_2 .^{58,61,64–66} This effect is observed only in species having a symmetrical $\text{O}-\text{H}^+-\text{O}$ group with a flat-bottomed proton potential function. It was initially discovered in crystalline di(methylphenyl)phosphoric or di(chlorophenyl)phosphoric acid dimers, where the both $\nu_{\text{as}}\text{POO}$ and $\nu_{\text{s}}\text{POO}$ bands disappear in the IR spectra and the equivalency of the O-atoms in the $\text{O}-\text{H}^+-\text{O}$ group was established by X-ray crystallography.^{71–73} The phenomenon is not dependent on $\text{O}\cdots\text{O}$ distance since they differ significantly in these two acid dimers, $2.512\text{ \AA}$ ⁷² and $2.398\text{ \AA}$ respectively.⁷⁴ In contrast, strong bands from νPOO are observed in the IR spectra of dimeric dialkylphosphorous or dialkylphosphinic acids where the OHO groups are unsymmetrical.^{71,72} Similarly, the δHOH frequencies disappear in symmetric H_5O_2^+ ⁵⁸ but not in H_3O^+ or H_7O_3^+ cations with asymmetric $\text{O}-\text{H}\cdots\text{O}$ groups.^{5,42} It follows from these data that the disappearance of the $\delta\text{H}_2\text{O}$ bands of all six H_2O molecules in the $\text{H}_{13}\text{O}_6^+$ cation is indicative of high symmetry of the central OHO group with a flat-bottomed H^+ potential function and distribution of its dynamic properties over the 4 neighboring H-bonds. Breaking the symmetry should result in the reappearance of these bands.

Consistent with this, the $\delta\text{H}_2\text{O}$ band reappears for peripheral water molecules of the $\text{H}_{13}\text{O}_6^+$ cation when they are shared with the solvation shell of the anion. As discussed above with respect to ion pairing, shared water molecules have decreased proton mobility and the local symmetry of the cation is lowered.

Conclusions

The ionized proton of a strong acid in liquid water, $\text{H}^+(\text{aq})$, is an entirely unique species. On the IR timescale, a single species exists having constant composition, $\text{H}^+(\text{H}_2\text{O})_6$, and a well-defined boundary of positive charge delocalization. Suggestions of an equilibrium between two types of cations such as Eigen-type

$\text{H}_3\text{O} \cdot 3\text{H}_2\text{O}^+$ or Zundel-type H_5O_2^+ ions^{10–15,75,76} are not supported by experiment.

The distinctive IR spectrum of $\text{H}^+(\text{aq})$, which is a combination of a continuous broad absorption (*cba*) and a relatively simple line spectrum, is not found in any gas phase $\text{H}^+(\text{H}_2\text{O})_n$ cluster, even up to $n > 100$.²⁸ This may be because in gas phase $\text{H}^+(\text{H}_2\text{O})_n$ clusters, the 3D network structure promoted by a single H^+ extends over the whole cluster network up to $n = 100$ (a “nucleation” effect)²⁸ whereas in bulk water the excess proton changes the H-bonding network only up to $n = 6$. In addition, the excess proton locates itself near the surface of the gas-phase cluster^{23,25,26,77–81} where the environment has lower symmetry and where proton mobility is lower than in bulk water. For want of a better term, these gas phase clusters experience a microscopic “surface tension” that makes their environment different from bulk water. For the same reasons, *i.e.* lower symmetry and lower proton mobility, the structures of $\text{H}^+(\text{H}_2\text{O})_n$ clusters in organic solvents and in crystals are distinctly different from those in liquid water. The only exception is found in crystals of $\text{H}(\text{CHB}_{11}\text{I}_{11}) \cdot 8\text{H}_2\text{O}$ ⁴⁸ where columns of centrosymmetrically located $\text{H}^+(\text{H}_2\text{O})_6$ cations find themselves in a nanotubular environment akin to liquid water.

The uniqueness of $\text{H}_{13}\text{O}_6^+(\text{aq})$ lies in the unusual degree of delocalization of positive charge away from the central O–H–O group. Unlike typical Zundel-type H_5O_2^+ cations, there is an unusually effective redistribution of charge onto peripheral parts of the $\text{H}_{13}\text{O}_6^+$ cation and even out onto the O-atoms of eight outer-sphere water molecules not included in the $n = 6$ formulation. This results in a marked elongation of the central OHO group from ~ 2.40 Å in Zundel-type ions to ~ 2.57 Å in the $\text{H}_{13}\text{O}_6^+(\text{aq})$ ion. There is concomitant lengthening in the four contiguous OHO groups from ~ 2.52 Å in the Zundel-type $\text{H}_5\text{O}_2 \cdot 4\text{H}_2\text{O}$ structure¹⁹ to ~ 2.7 Å in $\text{H}_{13}\text{O}_6^+(\text{aq})$. The $\text{H}_{13}\text{O}_6^+(\text{aq})$ cation is not representative of an aquated Zundel-like H_5O_2^+ cation. Rather, it is a unique $\text{H}_{13}\text{O}_6^+(\text{aq})$ entity existing only in liquid water or in an environment similar to liquid water.

The unprecedented long $\text{O} \cdots \text{O}$ distance of ~ 2.57 Å for the central O–H–O group in $\text{H}_{13}\text{O}_6^+(\text{aq})$ cation raises a number of interesting questions. Where is the central H-atom located? On the IR timescale, the data indicate a symmetric distribution but cannot distinguish between a predominant mid-point location and a time-averaged distribution of asymmetric H-bonds with a nearly flat-bottomed, double-well H^+ potential. Calculations at shorter timescales favor the predominance of an asymmetric structure^{29,30} but these calculations are done with short $\text{O} \cdots \text{O}$ distances typical of less delocalized cations, quite unlike the ~ 2.57 Å indicated by the present experiments.

Another issue is the origin of the *cba*. Is there a connection between the unusual elongation of the central O–H–O group and the appearance of the *cba*, a feature found *only* in IR spectrum of $\text{H}^+(\text{aq})$ clusters? This phenomenon is clearly associated with the fast dynamics of protons in these clusters and a challenge for theory to reproduce. The finding that at room temperature $\sim 30\%$ of the IR spectrum of $\text{H}^+(\text{aq})$ appears as a line spectrum whereas the remaining $\sim 70\%$ appears as *cba* provides a critical test of the veracity of, or calibration for, such calculations.

A related problem is to understand the disappearance of the $\delta\text{H}_2\text{O}$ band in the line spectrum of $\text{H}^+(\text{aq})$ clusters, as well as the

νCO and δCOH bands of $\text{H}^+(\text{CH}_3\text{OH})_n$ clusters⁶⁴ and related bands in proton disolvates H^+L_2 .^{58,61,65,66} This phenomenon is clearly related to the proximity of atoms to low-barrier H-bonds whose rapid fluctuations apparently lead to dramatically diminished intensities of associated vibrations.

Finally, we comment on the prevalence of ion pairing, even in the strongest acids. This may come as a surprise to many readers since strong acids are typically viewed in terms complete ionization, without ion pairing, and are treated as ideal electrolytes. Ionized strong acids can be considered as contact ion pairs. The $\text{H}_{13}\text{O}_6^+$ cation has contact with the first hydration shell of the anion and they are not separated by bulk water molecules. Carborane acids show a slight dependence of their IR spectra on the nature of the carborane anion⁴⁷ which is assigned to ion pairing effects (Scheme 3). With weaker acids such as HCl, or increasingly concentrated solutions of strong acids such as HNO_3 and HClO_4 , one or two peripheral water molecules of the $n = 6$ cation can be shared with the first solvation of the anion in contact ion pairs with reduced overall water content (Scheme 2). The influence on the IR spectrum is mainly in changes in band intensities. Our results obtained for dilute HCl solutions do not contradict those of Agmon⁸² in highly concentrated HCl solutions (≥ 8 M) where a Zundel-type $\text{H}_5\text{O}_2^+ \cdot 4\text{H}_2\text{O}$ ion surrounded by Cl-anions and a short central 2.40 Å $\text{O} \cdots \text{O}$ distance was established. This proposed structure is very similar to that found by Marsh *et al.* in the crystal state¹⁹ and can be viewed as a H_5O_2^+ cation in contact with the first hydration shells of neighboring Cl_{aq}^- anions. This removes the unique properties of the aqueous $\text{H}_{13}\text{O}_6^+$ cation and the core reverts to the common Zundel-type H_5O_2^+ cation.

Ion pairing is the underlying reason why the structure of the $\text{H}^+(\text{H}_2\text{O})_6$ cation in aqueous solution changes to $\text{H}_7\text{O}_3^+ \cdot n\text{H}_2\text{O}$ in weakly basic organic solvents such as benzene and chlorinated hydrocarbons.⁴² In organic solvents of low permittivity, diminished hydration of the anion leads to the formation of more intimate ion pairs with the hydrated proton. The stronger polarizing influence of the anion on the hydrated proton distorts its core to a H_7O_3^+ cation. Tighter ion pairing suppresses positive charge delocalization so unlike the $\text{H}_{13}\text{O}_6^+$ cation in aqueous solution, the $\text{O} \cdots \text{O}$ distances are typical of a static hydrated H_7O_3^+ cation.

This phenomenon plays out in a parallel manner in the nanotubular structure of $\text{H}(\text{CHB}_{11}\text{I}_{11}) \cdot 8\text{H}_2\text{O}$, but with an important difference. $\text{H}(\text{H}_2\text{O})_6^+$ clusters located in the center of the tube adopt the long $\text{O} \cdots \text{O}$ bonded, centrosymmetric $\text{H}_{13}\text{O}_6^+$ structure found in aqueous solution whereas those near the anionic walls of the tube have a distorted core that approaches the H_7O_3^+ motif. Notably, the core of this ion has $\text{O} \cdots \text{O}$ distances that are unusually long (~ 2.62 Å)⁴⁸ compared to those of typical $\text{H}_7\text{O}_3^+ \cdot n\text{H}_2\text{O}$ cations in crystals or organic solutions (~ 2.50 Å).⁴² Just as the longer $\text{O} \cdots \text{O}$ bonded central H_5O_2 group of the centrosymmetric $\text{H}_{13}\text{O}_6^+$ ion retains topographical similarity to H_5O_2^+ , so this H_7O_3 group with longer bond lengths retains a topographical similarity to the H_7O_3^+ ion. The difference lies in the surrounding environment. $\text{H}(\text{H}_2\text{O})_6^+$ clusters in the nanotubular structure are more hydrated and less tightly ion paired than the shorter $\text{O} \cdots \text{O}$ bonded $\text{H}_7\text{O}_3^+ \cdot n\text{H}_2\text{O}$ clusters in crystals or organic solvents because the positive charge is more delocalized. The tube environment is more akin to liquid water.

This is the *sine qua non* of our findings. Liquid water provides a special environment for H^+ that leads to greater delocalization of positive charge than previously suspected.

Acknowledgements

This work was supported by NIH Grant GM023851.

Notes and references

- 1 S. Cukierman, *Biochim. Biophys. Acta, Bioenerg.*, 2006, **1756**, 876.
- 2 C. J. T. Grotthuss, *Ann. Chim.*, 1806, **LVIII**, 54.
- 3 L. J-Gay-Lussac and A. Humboldt, *Ann. Chim.*, 1805, **LIII**, 239.
- 4 M. Eigen, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 1.
- 5 E. S. Stoyanov, C. K-Kim and C. A. Reed, *J. Am. Chem. Soc.*, 2006, **128**, 1948.
- 6 O. F. Mohammed, D. Pines, J. Dreyer, E. Pines and E. T. J. Nibbering, *Science*, 2005, **310**, 83.
- 7 O. F. Mohammed, D. Pines, E. Pines and E. T. J. Nibbering, *Chem. Phys.*, 2007, **341**, 240.
- 8 G. Zundel in *The Hydrogen Bond: Recent Developments in Theory and Experiments*, Schuster, P.; Zundel, G.; Sandorfy, C.; ed.; North-Holland: Amsterdam, 1976; Vol. 2.
- 9 *Hydrogen Bond (Vodorodnaya Sviaz')*; Ed.: N. D. Sokolov, Moscow, Nauka, 1981.
- 10 J. Kim, U. W. Schmitt, J. A. Gruetzmacher, G. A. Voth and N. E. Scherer, *J. Chem. Phys.*, 2002, **116**, 737.
- 11 R. Vuilleumier and D. Borgis, *J. Chem. Phys.*, 1999, **8**, 3116.
- 12 J. M. Heuft and E. J. Meijer, *Phys. Chem. Chem. Phys.*, 2006, **35**, 3523.
- 13 S. Woutersen and H. J. Bakker, *Phys. Rev. Lett.*, 2006, **96**, 138305.
- 14 A. Botti, F. Bruni and M. A. Ricci, *J. Chem. Phys.*, 2006, **125**, 014508.
- 15 G. A. Voth, *Acc. Chem. Res.*, 2006, **39**, 143.
- 16 A. Likholyot, K. H. Lemke, J. K. Hovey and T. M. Seward, *Geochim. Cosmochim. Acta*, 2007, **71**, 2436.
- 17 B. Krebs, S. Bonmann and K. Erpenstein, *Z. Naturforsch.*, 1991, **468**, 919.
- 18 Z. Xie, R. Bau and C. A. Reed, *Inorg. Chem.*, 1995, **34**, 5403.
- 19 R. Bell, G. Christopher, F. R. Fronczek and R. E. Marsh, *Science*, 1975, **190**, 151.
- 20 M. Okumura, L. I. Yeh, J. D. Myers and Y. T. Lee, *J. Phys. Chem.*, 1990, **94**, 3416.
- 21 J.-C. Jiang, Y.-S. Wang, H.-C. Chang, S. H. Lin, Y. T. Lee and G. Niedner-Schatteburg, *J. Am. Chem. Soc.*, 2000, **122**, 1398.
- 22 M. Miyazaki, A. Fujii, T. Ebata and N. Mikami, *Science*, 2004, **304**, 1134.
- 23 J.-W. Shin, N. I. Hammer, E. G. Diken, M. A. Johnson, R. S. Walters, T. D. Jaeger, M. A. Duncan, R. A. Christie and K. D. Jordan, *Science*, 2004, **304**, 1134.
- 24 C.-K. Lin, C.-C. Wu, Y.-S. Wang, Y. T. Lee, H.-C. Chang, J.-L. Kuo and M. L. Klein, *Phys. Chem. Chem. Phys.*, 2005, **7**, 938.
- 25 H.-C. Chang, C.-C. Wu and J.-L. Kuo, *Int. Rev. Phys. Chem.*, 2005, **24**, 553.
- 26 C.-C. Wu, C.-K. Lin, H.-C. Chang, J.-C. Jiang, J.-L. Kuo and M. L. Klein, *J. Chem. Phys.*, 2005, **122**, 074315.
- 27 J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson and K. D. Jordan, *Science*, 2005, **308**, 1765.
- 28 K. Mizuse, A. Fujii and N. Mikami, *J. Chem. Phys.*, 2007, **126**, 231101.
- 29 M. Tuckerman, K. Laasonen, M. Sprik and M. Parrinello, *J. Chem. Phys.*, 1995, **103**, 150.
- 30 O. Markovitch, H. Chen, S. Izvekov, F. Paesani, G. Voth and N. Agmon, *J. Phys. Chem. B*, 2008, **112**, 9456.
- 31 G. Zundel and M. Eckert, *J. Mol. Struct.*, 1989, **200**, 73.
- 32 S. Bratos and H. F. Ratajczak, *Chem. Phys.*, 1982, **73**, 77.
- 33 H. Romanovsky and L. Sobezek, *Chem. Phys.*, 1977, **19**, 361.
- 34 N. B. Librovich, V. P. Sakun and N. D. Sokolov, *Chem. Phys.*, 1979, **39**, 351.
- 35 N. B. Librovich, V. P. Sakun and N. D. Sokolov, In: *Vodorodnaya Sviaz' (Hydrogen Bond)*, Moscow, Nauka, 1981, p.174.
- 36 G. L. Hofacker, Y. Marechal and M. A. Ratner, In: *The Hydrogen Bond. Recent Developments in Theory and Experiments*. ed.: P. Schuster, G. Zundel and C. Sandorfy. V.1, North-Holland, Amsterdam, 1976.
- 37 G. V. Yukhnevich and E. G. Tarakanova, *J. Mol. Struct.*, 1988, **177**, 495.
- 38 G. V. Yukhnevich, E. G. Tarakanova, V. D. Mayorov and N. B. Librovich, *J. Mol. Struct.*, 1992, **265**, 234.
- 39 R. Vuilleumier and D. Borgis, *J. Chem. Phys.*, 1999, **111**, 4251.
- 40 K. E. Laasonen and M. L. Klein, *J. Phys. Chem. A*, 1997, **101**, 98.
- 41 A. J. Sillanpaa and K. E. Laasonen, *Phys. Chem. Chem. Phys.*, 2004, **6**, 555.
- 42 E. S. Stoyanov, I. V. Stoyanova, F. S. Tham and C. A. Reed, *J. Am. Chem. Soc.*, 2008, **130**, 12128.
- 43 K. Rahmelow and W. Hübner, *Appl. Spectrosc.*, 1997, **51**, 160.
- 44 J.-J. Max and C. Chapados, *Appl. Spectrosc.*, 1998, **52**, 963.
- 45 E. S. Stoyanov, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2803.
- 46 E. S. Stoyanov, *Phys. Chem. Chem. Phys.*, 1999, **1**, 2961.
- 47 E. S. Stoyanov, I. V. Stoyanova and C. A. Reed, *J. Am. Chem. Soc.*, 2010, **132**, 1484.
- 48 E. S. Stoyanov, I. V. Stoyanova, F. S. Tham and C. A. Reed, *J. Am. Chem. Soc.*, 2009, **131**, 17540.
- 49 Y. Maréchal, *J. Chem. Phys.*, 1991, **95**, 5565.
- 50 J. E. Bertie and Z. Lan, *Appl. Spectrosc.*, 1996, **50**, 1047.
- 51 S. Nunn and K. Nishikida, *Application Note: 50581: Advanced ATR Correction Algorithm*, Thermo Fisher Scientific Inc. Madison, WI, USA, 2008 (http://www.thermo.com/eThermo/CMA/PDFs/Articles/articlesFile_7217.pdf).
- 52 J. Stangret and J. Gampe, *J. Phys. Chem. A*, 2002, **106**, 5393.
- 53 A. W. Omta, M. F. Kropman, S. Woutersen and H. J. Bakker, *Science*, 2003, **301**, 347.
- 54 J. D. Smith, R. J. Saykally and P. L. Geissler, *J. Am. Chem. Soc.*, 2007, **129**, 13847.
- 55 E. S. Stoyanov, C. K-Kim and C. A. Reed, *J. Am. Chem. Soc.*, 2006, **128**, 8500.
- 56 For English version, see *Handbook of Chemist (Spravochnik Himika)*, Ed.: B. P. Nikol'skii, Moscow-Leningrad, 1964, Vol. 3, 2nd edition (Russian). http://molbiol.ru/eng/protocol/01_23.html.
- 57 E. S. Stoyanov, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 4165.
- 58 E. S. Stoyanov and C. A. Reed, *J. Phys. Chem. A*, 2006, **110**, 12992. Note: While band frequencies often decrease with increasing bond length, especially those arising from symmetric vibrations, the Zundel ion marker band is an asymmetric stretch and empirically follows an inverse relationship to bond length.
- 59 N. I. Hammer, E. G. Diken, J. R. Roscioli, M. A. Johnson, E. M. Myshakin, K. D. Jordan, A. B. McCoy, X. Huang, J. M. Bowman and S. Carter, *J. Chem. Phys.*, 2005, **122**, 244301.
- 60 J. R. Roscioli, L. R. McCunn and M. A. Johnson, *Science*, 2007, **316**, 249.
- 61 E. S. Stoyanov and I. V. Smirnov, *J. Mol. Struct.*, 2005, **740**, 9.
- 62 M. F. Kropman and H. J. Bakker, *Science*, 2001, **291**, 2118.
- 63 M. Juhasz, S. Hoffmann, E. Stoyanov, K.-C. Kim and C. A. Reed, *Angew. Chem., Int. Ed.*, 2004, **43**, 5352.
- 64 E. S. Stoyanov, I. V. Stoyanova and C. A. Reed, *Chem.-Eur. J.*, 2008, **14**, 3596.
- 65 E. S. Stoyanov, *Mendeleev Commun.*, 1999, 190.
- 66 E. S. Stoyanov, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1137.
- 67 M. Smiechowsky and J. Stangret, *J. Mol. Struct.*, 2008, **878**, 104.
- 68 D. Hadzi and N. Kobilarov, *J. Chem. Soc. A*, 1966, 439.
- 69 H. Kanno and J. Hiraishi, *Chem. Phys. Lett.*, 1984, **107**, 438.
- 70 D. Schiöberg and G. Zundel, *Chem. Phys. Lett.*, 1976, **38**, 334.
- 71 L. I. Katzin, G. W. Mason and D. F. Peppard, *Spectrochim. Acta*, 1978, **34A**, 51.
- 72 E. Gebert, A. H. Reis, S. W. Peterson, L. I. Katzin, G. W. Mason and D. F. Peppard, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1451.
- 73 D. Hadzi and A. Novak, *Proc. Chem. Soc.*, 1960, 241.
- 74 M. Callery and J. C. Speakman, *Acta Crystallogr.*, 1964, **17**, 1097.
- 75 D. Marx, M. E. Tuckerman, J. Hutter and M. Parrinello, *Nature*, 1999, **397**, 601.
- 76 M. Cavalleri, L.-Å. Näslund, D. C. Edwards, P. Wernet, H. Ogasawara, S. Myneni, L. Ojamäe, M. Odelius, A. Nilsson and L. G. M. Pettersson, *J. Chem. Phys.*, 2006, **124**, 194508.
- 77 J.-L. Kuo and M. L. Klein, *J. Chem. Phys.*, 2005, **122**, 024516.
- 78 T. James and D. J. Wales, *J. Chem. Phys.*, 2005, **122**, 134306.
- 79 S. S. Iyengar, M. K. Petersen, T. J. F. Day, C. J. Burnham, V. E. Teige and G. A. Voth, *J. Chem. Phys.*, 2005, **123**, 084309.
- 80 C. J. Burnham, M. K. Petersen, T. J. F. Day, S. S. Iyengar and G. A. Voth, *J. Chem. Phys.*, 2006, **124**, 024327.
- 81 N. J. Singh, M. Park, S. K. Min, S. B. Suh and K. S. Kim, *Angew. Chem., Int. Ed.*, 2006, **45**, 3795.
- 82 N. Agmon, *J. Phys. Chem. A*, 1998, **102**, 192.