

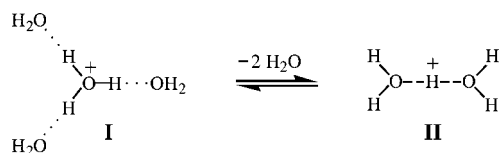
The Structure of the Hydrogen Ion (H_{aq}^+) in Water

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One of the oldest problems in chemistry is obtaining an accurate molecular description of the hydrogen ion (H_{aq}^+) produced when an acid ionizes in water.¹ The value of n in $H(H_2O)_n^+$ is poorly defined, and there has been a long debate over the relative importance of Eigen-type² $H_3O^+ \cdot 3H_2O$ (**I**) versus Zundel-type³ $H_5O_2^+$ (**II**) structures.^{4–19}



The Eigen ion **I** has three classical, unsymmetrical H bonds ($O \cdots O \approx 2.51 \text{ \AA}$),²⁰ while the Zundel ion **II** has a short, symmetrical H bond ($O \cdots O = 2.39\text{--}2.43 \text{ \AA}$)^{21–25} and a low barrier to proton movement within the double-well potential region of classical H bonding. Recent theory favors a kinetic description that blurs the distinction between these static structures. A distorted Eigen-type ion with one short $O \cdots O$ bond (the “special pair”) is the calculated energy minimum at short time scales.^{18,19} We now present experimental evidence that an adequate description of H_{aq}^+ requires its formulation as an $H(H_2O)_6^+$ ion. The IR spectrum of this ion matches neither the Eigen- nor Zundel-type ions.

The problem of developing an accurate molecular description of H_{aq}^+ from experimental data lies in the difficulty of establishing n in $H(H_2O)_n^+$, isolating its IR spectrum from that of bulk water, and interpreting its dauntingly broad features.^{3,26} IR spectroscopy is the method of choice because of its fast time scale and high sensitivity to H-bond formation. Mainly carborane acids²⁷ were chosen for this study because their large molecular weights allow quantitative measurements to be extended to low molarities, where strong acids are fully ionized. To optimize quantification, IR spectra were run in ATR mode, placing a drop of solution on a diamond window.

The IR spectrum of a strong aqueous acid consists of overlapping spectra from three types of water molecules: bulk water, water associated with H_{aq}^+ , and water perturbed by the anion. As shown in detail in the Supporting Information, the spectrum of water perturbed by the anion is readily subtracted using the spectrum of its equimolar alkali metal salt because the spectrum of a hydrated alkali metal cation, $M(H_2O)_n^+$, happens to coincide with that of bulk water.²⁸ The spectrum of bulk water can also be subtracted but will be oversubtracted by an amount equal to the number of water molecules included in the $H(H_2O)_n^+$ cation. This gives rise to a spectrum of $H(H_2O)_n^+$ that is distorted by negative peaks from bulk water at ~ 3400 and $\sim 1630 \text{ cm}^{-1}$. Using the +S/–S method,²⁹ the spectrum of bulk water is then added with a scaling factor that provides optimal removal of the spectral distortions. This leads not only to the true spectrum of the $H(H_2O)_n^+$ cation but also to the value of n (Table 1). For aqueous solutions of three different carborane acids and for perchloric acid, the average value of n was

Table 1. Stoichiometry of $H^+(H_2O)_n$ in Water Solutions of Carborane and Perchloric Acids

anion	molarity	n in $H^+(H_2O)_n$
$CHB_{11}Cl_{11}^-$	0.46	5.97
$CHB_{11}Cl_{11}^-$	0.330	5.7
CCD^-	0.427	6.06
$CHB_{11}I_{11}^-$	0.259	6.10
$CHB_{11}I_{11}^-$	0.22	6.15
$CHB_{11}I_{11}^-$	0.176	5.86; 6.10
ClO_4^-	0.5	5.98
ClO_4^-	0.75	5.95

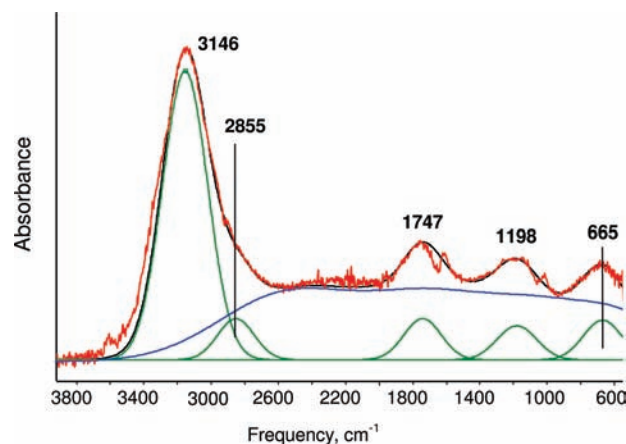


Figure 1. Isolated IR spectrum of $H(H_2O)_n^+$ from 0.330 M aqueous $H(CHB_{11}Cl_{11})$ (red). Also shown is the deconvolution into five bands (green), a continuous broad absorption (blue), and their summation (black). The points of inflection in the red spectrum near 1630 and 1050 cm^{-1} arise from the +S/–S subtraction process.

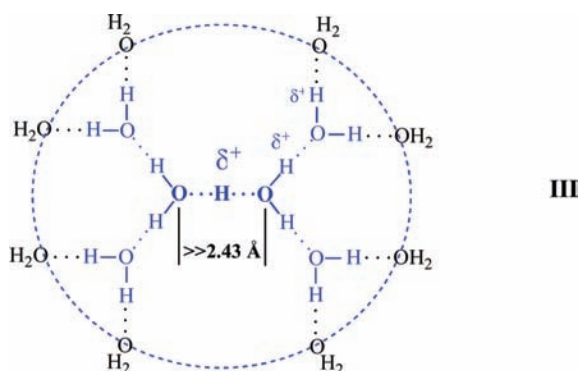
found to be 6.0 ± 0.3 . The apparent contradiction between this $H(H_2O)_6^+$ formulation and the distorted Eigen-type $H(H_2O)_4^+$ structure favored by theory^{18,19} can be reconciled by recognizing that shortening of one $O\text{--}H \cdots O$ bond in **I** to create the “special pair” attracts two outer-sphere water molecules closer to the Eigen core, converting it into an $H(H_2O)_6^+$ ion.

Deconvolution of the IR spectrum (Figure 1, red trace) gives the often-noted but poorly understood continuous broad absorption (cba) (blue trace) overlaid with Gaussian bands (green traces) having frequency variances for the four different acids of 3134 ± 12 , 2816 ± 40 , 1746 ± 11 , 1202 ± 4 , and $654 \pm 12 \text{ cm}^{-1}$. This spectrum for these 0.2–0.75 M acids refines those reported earlier for more concentrated acids,^{3,4,26} where only bands at ~ 1740 and $\sim 1200 \text{ cm}^{-1}$ could be identified with H_{aq}^+ . The small variation with the anion is ascribed to weak outer-sphere ion-pairing effects on the $H(H_2O)_6^+$ ion.

We conclude from these experiments that in aqueous solutions of strong acids, the H_{aq}^+ cation has six spectroscopically distinct water molecules that define the boundary of influence of the positive charge. Positive charge extends out onto the O atoms of the outer

hydration shell but not significantly enough to make their O–H stretching vibrations distinguishable from those of bulk water.

What is the structure of the $\text{H}(\text{H}_2\text{O})_6^+$ ion giving rise to the red spectrum in Figure 1? A static Eigen-type structure based on the C_{3v} -symmetric H_3O^+ ion is easily ruled out, as this would require $n = 4$ or 10 to preserve symmetry. Moreover, the IR spectrum of the $\text{H}_3\text{O}^+ \cdot 3\text{H}_2\text{O}$ cation in the X-ray structurally characterized carborane salt has no cba, and bands associated with the O–H \cdots O groups occur at ~ 2575 , 2290, and 1865 cm^{-1} ,³⁰ which are quite different from those of $\text{H}(\text{H}_2\text{O})_6^+$. There is a closer but still poor match to the spectra of symmetric $\text{H}_5\text{O}_2^+ \cdot 4\text{L}$ Zundel-type ions.²² In particular, the $\sim 1200\text{ cm}^{-1}$ band occurs at anomalously high frequency. This Zundel ion marker band, which is associated with proton oscillation along the O \cdots O trajectory of the central symmetrical O–H $^+$ –O group,^{22,31,32} occurs in the 840–1085 cm^{-1} range for gas-phase ions^{31,32} and at 1000–1160 cm^{-1} for condensed phases,²² where its frequency increases with the basicity of L. It is lowest (1084 cm^{-1}) for L = benzene, which is a weaker base than water,²² reaches 1140 cm^{-1} for tributylphosphate, whose basicity coincides with that of liquid water,³³ and increases to 1160 cm^{-1} for L = phosphine oxides, whose basicities exceed that of water.³⁴ The $\sim 1200\text{ cm}^{-1}$ frequency in $\text{H}(\text{H}_2\text{O})_6^+$ is out of line with this spectroscopic regularity. Since the O \cdots O distance in the central O–H–O group increases with increasing basicity of L because of positive-charge removal, an unexpected elongation of the O \cdots O separation would rationalize the 1200 cm^{-1} band for $\text{H}(\text{H}_2\text{O})_6^+$. Thus, we propose structure **III** for this cation, where the dotted circle passing through the O atoms of the outer-sphere hydration shell defines the extent of positive-charge delocalization:



This possibility 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 unlike all other Zundel-type structures, which have central O \cdots O separations in the range 2.39–2.42 Å,^{21–25} that in a centrosymmetric $\text{H}_{13}\text{O}_6^+$ ion is anomalously long (2.57 Å).³⁵ The difference between this $\text{H}_{13}\text{O}_6^+$ ion and those in all previously known Zundel ion-type structures appears to lie in their outer-sphere environments. Zundel ion structures have typically been characterized in relatively rigid, discrete cation/anion structures, whereas the $\text{H}_{13}\text{O}_6^+$ ion in $\text{H}(\text{CHB}_{11}\text{I}_{11}) \cdot 8\text{H}_2\text{O}$ is located in a nanotube of protonated water, much closer to the environment of liquid water. The positive charge is more delocalized, and the O \cdots O separation increases accordingly.

The simplicity of the four-band spectrum of the aquated $\text{H}_{13}\text{O}_6^+$ ion and the relatively narrow bandwidth of $\nu(\text{OH})$ at $\sim 3140\text{ cm}^{-1}$ are indicative of a high-symmetry structure. Distorted Eigen-type structures, such as the hydrated H_7O_3^+ ion,³⁰ various HCl hydrates,³⁶ etc., have more complex IR spectra. The distorted Eigen-

type structures favored by current theory^{18,19} have lifetimes that are shorter than the IR time scale and therefore could not be detected in the present experiments.

In summary, H_{aq}^+ is a unique entity requiring formulation as a hydrated $\text{H}_{13}\text{O}_6^+$ ion. This defines the boundary of delocalization of the positive charge and should become an essential part of mechanistic discussions involving H_{aq}^+ . Its IR spectrum matches neither that of a C_{3v} Eigen ion nor that of a typical Zundel ion with a short central O \cdots O distance. Delocalization of the positive charge is more extensive. The IR spectrum is consistent with a centrosymmetric structure, and the high frequency of the $\sim 1200\text{ cm}^{-1}$ band indicates an unexpectedly long O \cdots O separation. With its delocalized proton in the central O–H–O group, the $\text{H}_{13}\text{O}_6^+$ ion in water is quite distinct from the tetrahydrated Zundel ion $\text{H}_5\text{O}_2^+ \cdot 4\text{H}_2\text{O}$ in the solid state or gas phase, which bear only topological similarity. Liquid water is a unique environment for the hydrated proton.

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Supporting Information Available: Experimental details, including isolation of the IR spectrum of H_{aq}^+ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Cukierman, S. *Biochim. Biophys. Acta* **2006**, *1757*, 876.
- (2) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.
- (3) Zundel, G. In *The Hydrogen Bond: Recent Developments in Theory and Experiments*; Schuster, P.; Zundel, G.; Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Vol. 2.
- (4) Giguère, P. A.; Turrell, S. *Can. J. Chem.* **1976**, *54*, 3477.
- (5) Agmon, N. *J. Phys. Chem. A* **1998**, *102*, 192.
- (6) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature* **1999**, *397*, 601.
- (7) Vuilleumier, R.; Borgis, D. *J. Chem. Phys.* **1999**, *111*, 4251.
- (8) Schmidt, U. W.; Voth, G. A. *J. Chem. Phys.* **1999**, *111*, 9361.
- (9) Kim, J.; Schmitt, U. W.; Gruetzmacher, J. A.; Voth, G. A.; Scherer, N. E. *J. Chem. Phys.* **2002**, *116*, 737.
- (10) Marx, D. *ChemPhysChem* **2006**, *7*, 1848.
- (11) Voth, G. A. *Acc. Chem. Res.* **2006**, *39*, 143.
- (12) Woutersen, S.; Bakker, H. J. *Phys. Rev. Lett.* **2006**, *96*, 138305.
- (13) Smiechowski, M.; Stangret, J. *J. Chem. Phys.* **2006**, *125*, 204508.
- (14) Heuft, J. M.; Meijer, E. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3116.
- (15) Botti, A.; Bruni, F.; Ricci, M. A.; Soper, A. K. *J. Chem. Phys.* **2006**, *125*, 014508.
- (16) Cavalleri, M.; Näslund, L.; Edwards, D. C.; Wernet, P.; Ogasawara, H.; Myneni, S.; Ojamäe, L.; Odelius, M.; Nilsson, A.; Pettersson, L. G. M. *J. Chem. Phys.* **2006**, *124*, 194508.
- (17) Smiechowski, M.; Stangret, J. *J. Mol. Struct.* **2008**, *878*, 104.
- (18) Markovitch, O.; Chen, H.; Izvekoy, S.; Paesani, F.; Voth, G. A.; Agmon, N. *J. Phys. Chem. B* **2008**, *112*, 9456.
- (19) Swanson, J. M. J.; Simons, J. *J. Phys. Chem. B* **2009**, *113*, 5149.
- (20) Xie, Z.; Bau, R.; Reed, C. A. *Inorg. Chem.* **1995**, *34*, 5403.
- (21) Bell, R. A.; Christoph, G. G.; Fronczek, F. R.; Marsh, R. E. *Science* **1975**, *190*, 151.
- (22) Stoyanov, E. S.; Reed, C. A. *J. Phys. Chem. A* **2006**, *110*, 12992.
- (23) Lundgren, J. O.; Olovsson, I. *Acta Crystallogr.* **1967**, *23*, 966.
- (24) Ortwein, R.; Schmidt, A. Z. *Z. Anorg. Allg. Chem.* **1976**, *425*, 10.
- (25) Jones, D. J.; Roziere, J. *J. Mol. Struct.* **1989**, *195*, 283.
- (26) *The Hydrogen Bond*; Sokolov, N. D., Ed.; Nauka: Moscow, 1981.
- (27) Reed, C. A. *Chem. Commun.* **2005**, 1669.
- (28) Stangret, J. *J. Phys. Chem. A* **2002**, *106*, 5393.
- (29) Stoyanov, E. S. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2803.
- (30) Stoyanov, E. S.; Stoyanova, I. V.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 12128.
- (31) Headrick, J. M.; Dicken, E. G.; Walters, R. S.; Hammer, N. I.; Christie, R. A.; Cui, J.; Myshakin, E. M.; Duncan, M. A.; Johnson, M. A.; Jordan, K. D. *Science* **2005**, *308*, 1765.
- (32) Roscioli, J. R.; McCunn, L. R.; Johnson, M. A. *Science* **2007**, *316*, 249.
- (33) Stoyanov, E. S. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 4165.
- (34) Stoyanov, E. S.; Smirnov, I. V. *J. Mol. Struct.* **2005**, *740*, 9.
- (35) Stoyanov, E. S.; Stoyanova, I. V.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2009**, *131*, 17540.
- (36) Buch, V.; Dubrovskiy, A.; Mohamed, F.; Parrinello, M.; Sadlej, J.; Hammerich, A. D.; Devlin, J. P. *J. Phys. Chem. A* **2008**, *112*, 2144.

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