Published in final edited form as:
J Am Chem Soc. 2009 December 9; 131(48): 17540–17541. doi:10.1021/ja907708g.

H_{aq}^+ Structures in Proton Wires inside Nanotubes

Evgenii S. Stoyanov, **Irina V. Stoyanova**, **Fook S. Tham**, and **Christopher A. Reed**[*]
Department of Chemistry, University of California, Riverside, California 92521-0403.

Nanoscale science focuses attention on how bulk properties are altered when substances are confined to small spaces and reduced dimensionality. For example, theory suggests that water takes on novel "ice" structures when confined inside carbon nanotubes.[1] Calculations also support the idea that confinement of H_{aq}^+ to narrow channels creates a proton wire[2] having up to 40 times faster proton transport than in bulk.[3] These findings are relevant to proton mobility in nanoscale channels of fuel cell membranes and also to biological proton transport where chains of water molecules are found in channels of trans-membrane proteins involved in proton pumping and cellular pH control.[4] Counterintuitively, these protein channels are often lined with non-polar residues suggesting that nature may be exploiting special properties of hydrophobically-confined chains of water molecules.[5]

Structurally well-defined channels containing H_{aq}^+ are rare so experimental opportunities to investigate these hypotheses are few.[6] Herein, we report several novel structural features of H_{aq}^+ when it is confined to a hydrophobic nanotube.

Saturated aqueous solutions of the carborane acid $H(CHB_{11}I_{11})$[7] deposit crystals of the nominally octahydrated acid $H(CHB_{11}I_{11})\cdot 8H_2O$ whose X-ray structure reveals 1.1 × 0.5 nm diameter elliptical channels of H_{aq}^+ encased by walls of carborane anions (Fig. 1). This structural motif contrasts with the discrete ionic lattice structures of all other $[H(H_2O)_n^+]$ $[\text{carborane}^-]$ salts having smaller, less polarizable anions e.g., $[H_9O_4]-[CHB_{11}H_5Br_6]$,[8] $[H_5O_2][CHB_{11}Cl_{11}]$[9] and $[H_3O][CHB_{11}Cl_{11}]$.[10] Multiple inter-anion I····I distances (3.68-3.96 Å) are less than the sum of the van der Waals separation suggesting that I····I dispersion forces are important in creating the tubular structure.

The unit cell contains six H^+, six $CHB_{11}I_{11}^-$ anions and 48 water molecules. There are two crystallographically distinct water-filled tubes containing H_{aq}^+ cations, labeled **A** and **B**. The water structure in tube **A** is crystallographically ordered (a so-called "ice") while that in tube **B** is partially disordered, indicating weaker organizational forces and suggesting unequal H^+ distribution between the two tubes.

Direct X-ray determination of the locations of H^+ and the H atoms of water is not possible because of their low electron density. In addition, the standard procedures built into crystallographic software for modeling their locations fail because the dimensional constraints of normal H-bonding do not apply to H_{aq}^+ clusters. Nevertheless, the locations of the excess protons are revealed by the shortening of O····O separations. When shorter than those in hexagonal ice (2.76 Å)[11] or liquid water (2.85 Å)[12] they are candidates for bridging H^+. The presently known range of O····O distances for O–H···O bonds considered to carry positive charge in $H(H_2O)_n^+$ cations is 2.39-2.59 Å.[7,13] Short O····O separations (≤2.42 Å) are associated with symmetrical H-bonding in Zundel-type $H_5O_2^+$ ions[9,14] while longer

---

chris.reed@ucr.edu.

Supporting Information Available: X-ray crystallographic data for $H(CHB_{11}I_{11})\cdot 8H_2O$ with tables and CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

separations (2.52-2.55 Å) are typical of standard unsymmetrical H-bonds such as those in the $H_3O^+ \cdot 3H_2O$ Eigen-type ion.[8]

A survey of short O····O separations in the unit cell of tube **A** (Fig. 2) indicates three structurally different types of H_{aq}^+ clusters: cluster **I** with a single short O10–O10″ distance of 2.567(12) Å, two sites of cluster **II** with a pair of adjacent short O···O distances of 2.623(8) and 2.618(7) Å indicating an $H_7O_3^+$ core formulation, and an unprecedented cluster **III** with a nearly square O5–O12–O5″–O12″ arrangement having 2.636(8) and 2.668(8) Å rectangular sides. This stoichiometry leaves only 2 H_{aq}^+ sites for tube **B** and two symmetry-related $H_7O_3^+$ ions of type **II** with O···O separations of 2.582(13) and 2.573(9) Å are found amongst the ordered water molecules. There are no other short O····O separations. The 4:2 partitioning of H^+ between channels **A** and **B** corresponds to an average composition of 6 H_2O per H^+ in **A** and 12 H_2O per H^+ in **B** and is consistent with the disorder (and partial occupancy) of water molecules observed in channel **B**.

Cluster **I** is topologically a tetrahydrated $H_5O_2^+$ Zundel ion, but the O····O distances are quite anomalous. Sitting on a crystallographic center of symmetry, its central O····O distance of 2.57 Å is very long compared to those in other $H_5O_2^+$ cations (2.39-2.42 Å).[9,13,14] It is even longer than the O····O distances in the $H_3O^+ \cdot 3H_2O$ Eigen ion (2.52-2.55 Å).[8] The four O····O distances to the second sphere water molecules in **I** (2.70 Å) are also large compared to those in the $H_5O_2^+ \cdot 4H_2O$ ion (2.52 Å)[14] and only slightly below those in hexagonal ice (2.76 Å). This means that the positive charge of H^+ is significantly more delocalized in **I** than in classical Zundel-type $H_5O_2^+$ ions.

Cluster **II** is formulated as a hydrated $H_7O_3^+$ ion with the two central O····O distances that are equal within experimental error. It typically occurs when $H(H_2O)_n^+$ cations are ion paired[7] and is consistent with location of these clusters near the anion walls, removed from sites of crystallographic symmetry. One water molecule (O2) solvates the central O atom of the $H_7O_3^+$ core with a somewhat short O····O distance of 2.69 Å. This reflects delocalization of the positive charge onto this water molecule and illustrates the close relationship between monohydrated C_{2v} $H_7O_3^+$ ions and C_{3v} $H_9O_4^+$ Eigen-type ions. Four other water molecules (O4, O7, O8″ and O12″) solvate cluster **II** at O····O distances 2.77-3.03 Å.

Cluster **III** is unprecedented for a proton hydrate. Four O-atoms share H^+ in a nearly square arrangement whose center has crystallographic inversion symmetry. Four solvating water molecules are close enough to qualify for inclusion in the cluster (O7, O7″, O3, O3″ with O····O distances all close to 2.72 Å) leading to an $H_{17}O_8^+$ formulation. The next closest are O11 and O11″ at 3.03 Å but since these distances are even greater than that of liquid water (2.85 Å) they are not considered to carry positive charge from H^+. The novel structure of this ion must be the result of the electrostatic field peculiar to this inversion symmetry site within the tube. A related square core structure of eight water molecules, but having much longer O····O distances (2.91-3.02 Å) because an excess proton is absent, has been observed in the crystal structure of a hydrated lanthanide chelate.[15] The diversity of static H_{aq}^+ cluster structures trapped in the tubes is a reflection the highly dynamic nature of the excess proton in water.[16]

Clusters **I**, **II** and **III** all have much longer O····O separations than would be expected from the existing knowledge base of X-ray structures of crystalline acid hydrates[7-10,13,14] or the computed structures of gas phase ions, even those having greater than 20 water molecules.[17] This is compelling evidence for greater delocalization of positive charge in these clusters. It suggests that H_{aq}^+ in the present extended tubular environment (and presumably in liquid water) is uniquely different from the discrete $H(H_2O)_n^+$ ions in crystalline salts or the gas phase.

The delocalization of positive charge has another interesting consequence. Clusters **I** and **III** in tube **A** form an infinite chain of short O····O separations i.e., a true proton wire (Fig. 3). These clusters lie along the central axis of the tube and contain individual centers of symmetry. They are linked by common atoms (O3 and O3″) whose O····O distances of 2.70 Å and 2.72 Å to the core O atoms of the clusters are shorter than those of liquid water or hexagonal ice. This indicates an infinite 1D delocalization of positive charge. It is tempting to speculate that H^+ mobility would be especially fast along this chain.

In summary, three structural types of $H_{aq}{}^+$ have been identified in nanotubular crystals of $H(CHB_{11}I_{11})\cdot 8H_2O$. One is without precedent and all have unexpectedly long O····O separations compared to those in discrete $H(H_2O)_n{}^+$ moieties, reflecting more extensive positive charge delocalization. The confined centrosymmetric $H(H_2O)_n{}^+$ cations aggregate into infinite proton wires whose short inter-cation distances suggest a mechanism for enhanced one-dimensional H^+ mobility.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by NIH grant GM023851.

REFERENCES

1. Koga K, Gao GT, Tanaka H, Zeng XC. Nature 2001;412:802–805. [PubMed: 11518961]
2. Nagle JF, Morowitz HJ. Proc. Natl. Acad. Sci. USA 1978;75:298–302. [PubMed: 272644]
3. (a) Pomès R, Roux B. Biophys. J 1998;75:33–40. [PubMed: 9649365] (b) Brewer ML, Schmitt UW, Voth GA. Biophys. J 2001;80:1691–1702. [PubMed: 11259283] (c) Dellago C, Naor MM, Hummer G. Phys. Rev. Lett 2003;90:105902. [PubMed: 12689010]
4. (a) DeCoursey TE. Physiol. Rev 2003;83:475–579. [PubMed: 12663866] (b) Mathias G, Marx D. Proc. Natl. Acad. Sci. USA 2007;104:6980–6985. [PubMed: 17438299]
5. Hummer G. Molec. Phys 2007;105:201–207.
6. (a) Maniva Y, Kataura H, Abe M, Suzuki S, Achiba Y, Kira H, Matsuda K. J. Phys. Soc. Japan 2002;71:2863–2866. (b) Fromm KM, Gueneau ED, Goesmann H, Bochet CGZ. Anorg. Allg. Chem 2003;629:597–600. (c) Dułak M, Bergougnant R, Fromm KM, Hagemann HR, Robin AY, Wesołowski TA. Spectrochim. Acta A 2006;64:532–548.
7. Stoyanov ES, Stoyanova IV, Tham FS, Reed CA. J. Am. Chem. Soc 2008;130:12128–12138. [PubMed: 18700768]
8. Zie Z, Bau R, Reed CA. Inorg. Chem 1995;34:5403–5404.
9. Stoyanov ES, Reed CA. J. Phys. Chem . A 2006;110:12992–13002. [PubMed: 17134158]
10. Stoyanov ES, Hoffmann SP, Kim K-C, Tham FS, Reed CA. J. Am. Chem. Soc 2005;127:7664–7665. [PubMed: 15913341]
11. Kuhs WF, Lehmann MS. J. Phys. Chem 1983;87:4312–4313.
12. Narten AH, Thiessen WE, Blum L. Science 1982;217:1033. [PubMed: 17839340]
13. Lungdren, J-O.; Ollovsson, I. The Hydrogen Bond: II. Structure and Spectroscopy. Schuster, P.; Zundel, G.; Sandorfy, C., editors. Amsterdam; North-Holland: 1976. Chap. 10
14. Bell RA, Christoph GG, Fronczek FR, Marsh RE. Science 1975;190:151–152.
15. Neogi S, Savitha G, Bharadwaj PK. Inorg. Chem 2004;43:3771–3773. [PubMed: 15206849]
16. Marx D, Tuckerman ME, Hutter J, Parrinello M. Nature 1999;397:601–604.
17. Iyengar SS, Day TJF, Voth GA. Intl. J. Mass. Spect 2005;241:197–204.

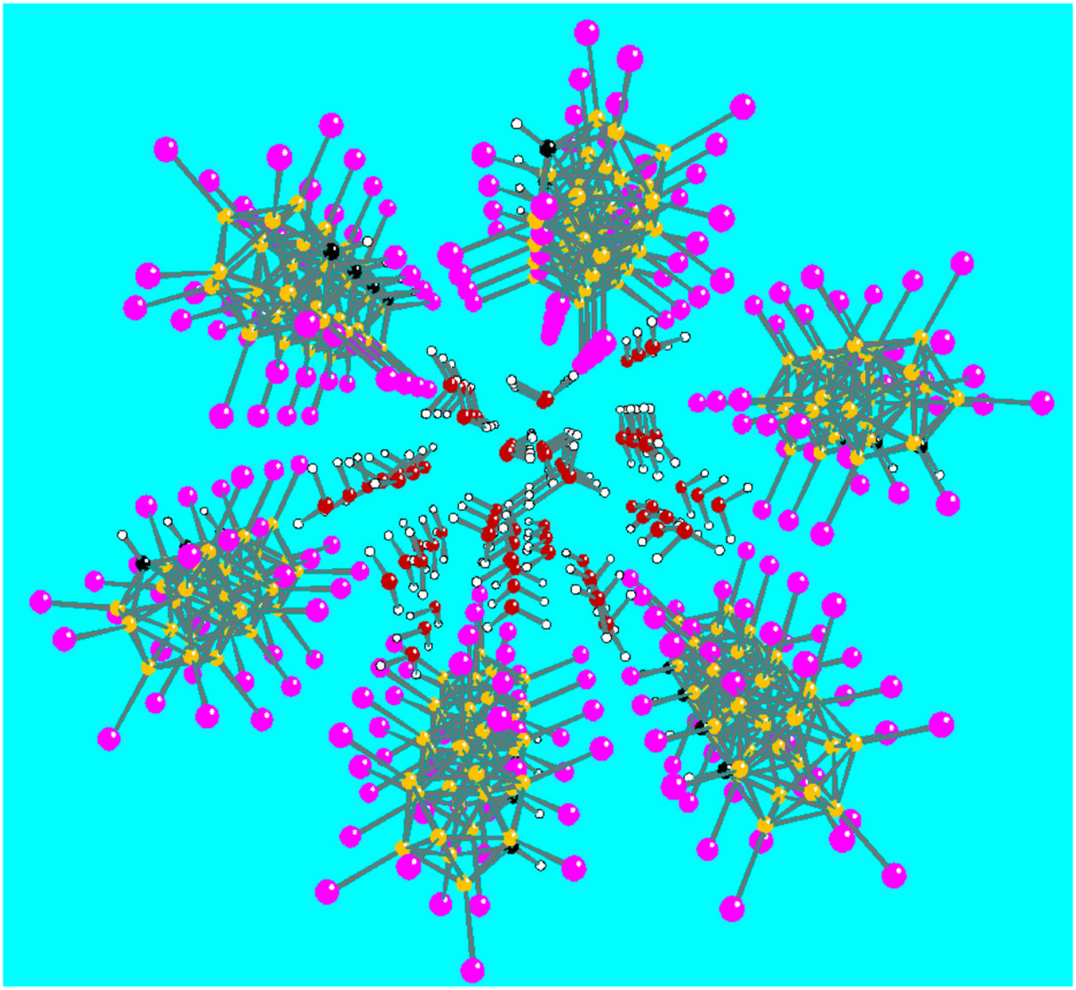

Figure 1.

Four unit cells of the tubular structure of $H(H_2O)_n^+$ cations (red, white) enclosed by $CHB_{11}I_{11}^-$ anions (black, yellow, magenta) in tube **A** of $H(CHB_{11}I_{11})\cdot 8H_2O$.

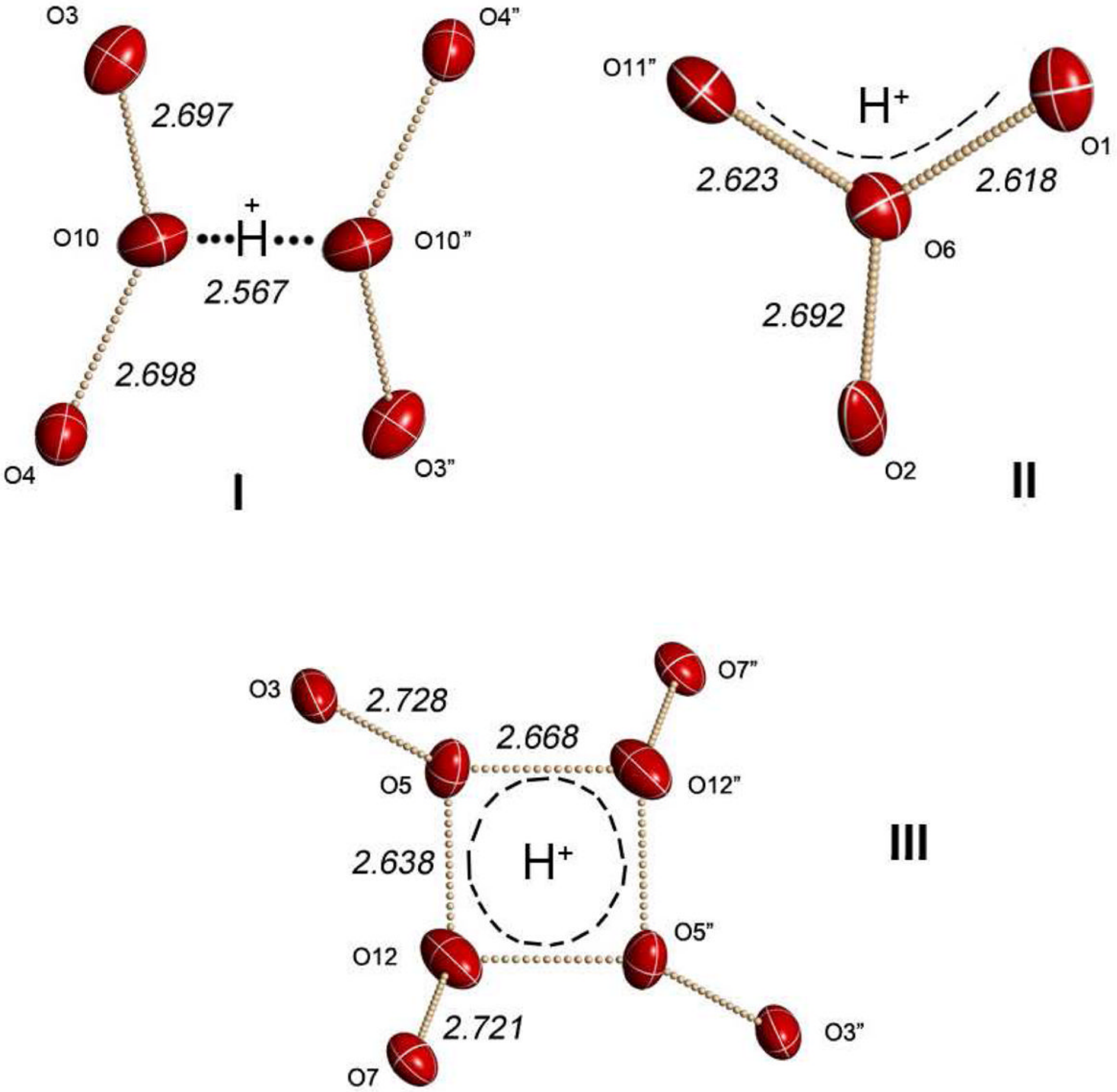

Figure 2.

Structures of the three $H(H_2O)_n^+$ clusters I, II and III. Thermal ellipsoids are at 50% probability level.

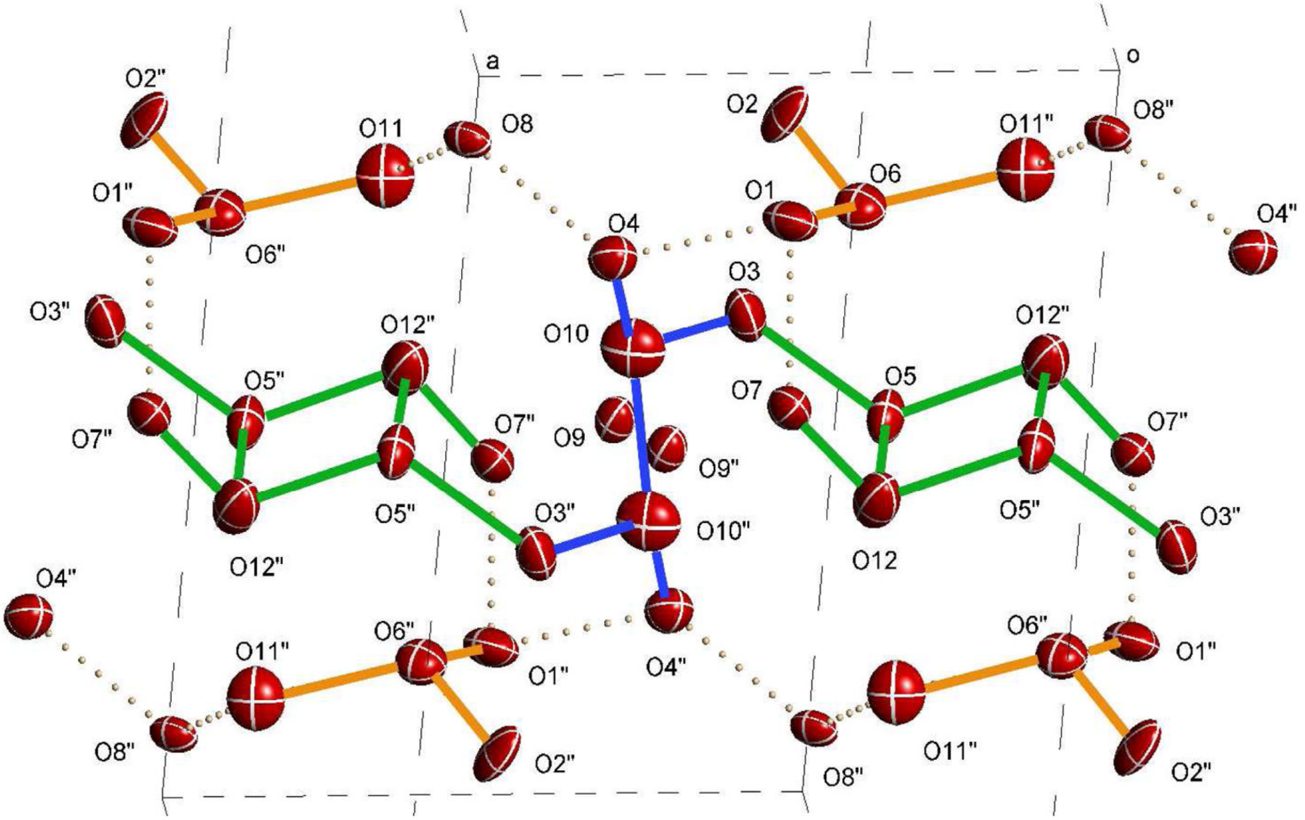

Figure 3.

Portion of a proton wire comprised of type **I** (blue) and **III** (green) $H(H_2O)_n^+$ clusters in tube **A** with O····O separations < 2.72 Å. Dotted bonds represent O····O separations > 2.72 Å. Cluster **II**, depicted in orange, is not part of the proton wire. Thermal ellipsoids at 50%.