

# UC Riverside

## UC Riverside Previously Published Works

### Title

Haq + Structures in Proton Wires inside Nanotubes

### Permalink

<https://escholarship.org/uc/item/7v12q1hc>

### Journal

Journal of the American Chemical Society, 131(48)

### ISSN

0002-7863

### Authors

Stoyanov, Evgenii S  
Stoyanova, Irina V  
Tham, Fook S  
et al.

### Publication Date

2009-12-09

### DOI

10.1021/ja907708g

Peer reviewed

## $H_{aq}^+$ 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

Received September 10, 2009; E-mail: evgeniis@ucr.edu; chris.reed@ucr.edu

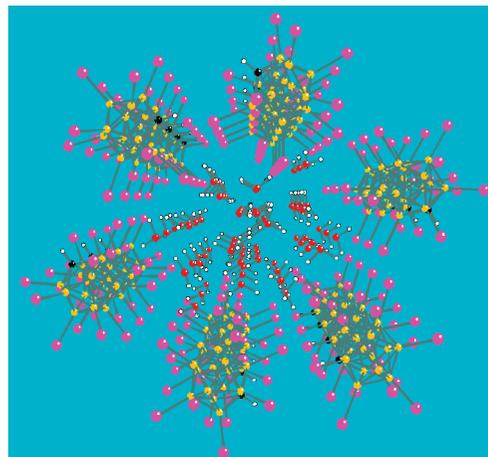
Nanoscale science focuses attention on how bulk properties are altered when substances are confined to small spaces and reduced dimensionality. For example, theory suggests that water takes on novel “ice” structures when confined inside carbon nanotubes.<sup>1</sup> Calculations also support the idea that confinement of  $H_{aq}^+$  to narrow channels creates a proton wire<sup>2</sup> having up to 40 times faster proton transport than in the bulk.<sup>3</sup> 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 transmembrane proteins involved in proton pumping and cellular pH control.<sup>4</sup> Counterintuitively, these protein channels are often lined with nonpolar residues, suggesting that nature may exploit special properties of hydrophobically confined chains of water molecules.<sup>5</sup>

Structurally well-defined channels containing  $H_{aq}^+$  are rare, so experimental opportunities to investigate these hypotheses are few.<sup>6</sup> Herein, we report several novel structural features of  $H_{aq}^+$  confined to a hydrophobic nanotube.

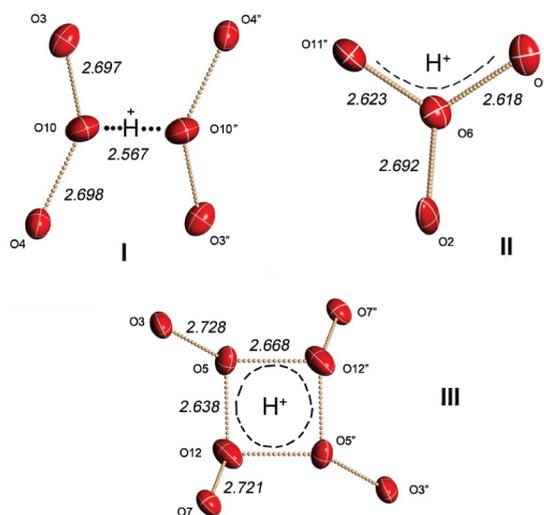
Saturated aqueous solutions of the carborane acid  $H(CHB_{11}I_{11})^7$  deposited crystals of the nominally octahydrated acid  $H(CHB_{11}I_{11}) \cdot 8H_2O$ , whose X-ray structure revealed  $1.1 \times 0.5$  nm diameter elliptical channels of  $H_{aq}^+$  encased by walls of carborane anions (Figure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

The unit cell contains six  $H^+$  cations, 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 an 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 to model 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  $O \cdots O$  separations: those shorter than the ones in hexagonal ice (2.76 Å)<sup>11</sup> or liquid water (2.85 Å)<sup>12</sup> are candidates for bridging  $H^+$ . The presently known range of  $O \cdots O$  distances for  $O-H \cdots O$  bonds considered to carry positive charge in  $H(H_2O)_n^+$  cations is 2.39–2.59 Å.<sup>7,13</sup> Short  $O \cdots O$  separations ( $\leq 2.42$  Å) are associated with symmetrical H bonding in Zundel-type  $H_5O_2^+$  ions,<sup>9,14</sup> while longer 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.<sup>8</sup>



**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 shown at the 50% probability level.

A survey of short  $O \cdots O$  separations in the unit cell of tube **A** (Figure 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  $O \cdots O$  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 two  $H_{aq}^+$  sites for tube **B**, and two symmetry-related  $H_7O_3^+$  ions of type **II** with  $O \cdots O$  separations of 2.582(13) and 2.573(9) Å are found among the ordered water molecules. There are no other short  $O \cdots O$  separations. The 4:2

partitioning of  $H^+$  between channels **A** and **B** corresponds to an average composition of six  $H_2O$  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**.

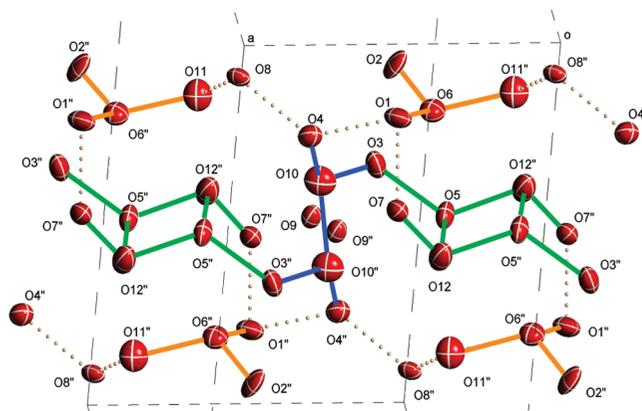
Cluster **I** is topologically a tetrahydrated  $H_5O_2^+$  Zundel ion, but the  $O\cdots O$  distances are quite anomalous. Sitting on a crystallographic center of symmetry, its central  $O\cdots O$  distance of 2.57 Å is very long compared to those in other  $H_5O_2^+$  cations (2.39–2.42 Å).<sup>9,13,14</sup> It is even longer than the  $O\cdots O$  distances in the  $H_3O^+ \cdot 3H_2O$  Eigen ion (2.52–2.55 Å).<sup>8</sup> The four  $O\cdots O$  distances to the second-sphere water molecules in **I** (2.70 Å) are also long compared with those in the  $H_5O_2^+ \cdot 4H_2O$  ion (2.52 Å)<sup>14</sup> and only slightly shorter than 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 having two central  $O\cdots O$  distances that are equal within experimental error. It typically occurs when  $H(H_2O)_n^+$  cations are ion-paired<sup>7</sup> and is consistent with the 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  $O\cdots O$  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  $O\cdots O$  distances of 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, and O3''), all with  $O\cdots O$  distances 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 in 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, in which the  $O\cdots O$  distances are much longer (2.91–3.02 Å) because the excess proton is absent, has been observed in the crystal structure of a hydrated lanthanide chelate.<sup>15</sup> The diversity of static  $H_{aq}^+$  cluster structures trapped in the tubes is a reflection of the highly dynamic nature of the excess proton in water.<sup>16</sup>

Clusters **I**, **II**, and **III** all have much longer  $O\cdots O$  separations than would be expected from the existing knowledge base of X-ray structures of crystalline acid hydrates<sup>7–10,13,14</sup> or the computed structures of gas-phase ions, even those having greater than 20 water molecules.<sup>17</sup> 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 with short  $O\cdots O$  separations, i.e., a true proton wire (Figure 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  $O\cdots O$  distances of 2.70 and 2.72 Å to the core O atoms of the clusters are shorter than those in liquid water or hexagonal ice. This indicates an infinite one-dimensional



**Figure 3.** Portion of a proton wire composed of types **I** (blue) and **III** (green)  $H(H_2O)_n^+$  clusters in tube **A** with  $O\cdots O$  separations of  $<2.72$  Å. Dotted bonds represent  $O\cdots O$  separations of  $>2.72$  Å. Cluster **II**, depicted in orange, is not part of the proton wire. Thermal ellipsoids are shown at the 50% probability level.

delocalization of positive charge. It is tempting to speculate that the  $H^+$  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  $O\cdots O$  separations that are unexpectedly long compared with 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 intercation distances suggest a mechanism for enhanced one-dimensional  $H^+$  mobility.

**Acknowledgment.** This work was supported by NIH Grant GM023851.

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

## References

- (1) Koga, K.; Gao, G. T.; Tanaka, H.; Zeng, X. C. *Nature* **2001**, *412*, 802.
- (2) Nagle, J. F.; Morowitz, H. J. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 298.
- (3) (a) Pomès, R.; Roux, B. *Biophys. J.* **1998**, *75*, 33. (b) Brewer, M. L.; Schmitt, U. W.; Voth, G. A. *Biophys. J.* **2001**, *80*, 1691. (c) Dellago, C.; Naor, M. M.; Hummer, G. *Phys. Rev. Lett.* **2003**, *90*, 105902.
- (4) (a) DeCoursey, T. E. *Physiol. Rev.* **2003**, *83*, 475. (b) Mathias, G.; Marx, D. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6980.
- (5) Hummer, G. *Mol. Phys.* **2007**, *105*, 201.
- (6) (a) Maniva, Y.; Kataura, H.; Abe, M.; Suzuki, S.; Achiba, Y.; Kira, H.; Matsuda, K. *J. Phys. Soc. Jpn.* **2002**, *71*, 2863. (b) Fromm, K. M.; Gueneau, E. D.; Goesmann, H.; Bochet, C. G. *Z. Anorg. Allg. Chem.* **2003**, *629*, 597. (c) Dułak, M.; Bergougnant, R.; Fromm, K. M.; Hagemann, H. R.; Robin, A. Y.; Wesolowski, T. A. *Spectrochim. Acta* **2006**, *A64*, 532. (d) Fromm, K. M.; Bergougnant, R. D. *Solid State Sci.* **2007**, *9*, 580.
- (7) Stoyanov, E. S.; Stoyanova, I. V.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 12128.
- (8) Zie, Z.; Bau, R.; Reed, C. A. *Inorg. Chem.* **1995**, *34*, 5403.
- (9) Stoyanov, E. S.; Reed, C. A. *J. Phys. Chem. A* **2006**, *110*, 12992.
- (10) Stoyanov, E. S.; Hoffmann, S. P.; Kim, K.-C.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 7664.
- (11) Kuhs, W. F.; Lehmann, M. S. *J. Phys. Chem.* **1983**, *87*, 4312.
- (12) Narten, A. H.; Thiessen, W. E.; Blum, L. *Science* **1982**, *217*, 1033.
- (13) Lundgren, J.-O.; Ollovsson, I. In *The Hydrogen Bond: II. Structure and Spectroscopy*; Schuster, P.; Zundel, G.; Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Chapter 10.
- (14) Bell, R. A.; Christoph, G. G.; Fronczek, F. R.; Marsh, R. E. *Science* **1975**, *190*, 151.
- (15) Neogi, S.; Savitha, G.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 3771.
- (16) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature* **1999**, *397*, 601.
- (17) Iyengar, S. S.; Day, T. J. F.; Voth, G. A. *Int. J. Mass. Spectrom.* **2005**, *241*, 197.

JA907708G