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IR Spectroscopic Properties of $H(MeOH)_n^+$ Clusters in the Liquid Phase: Evidence for a Proton Wire

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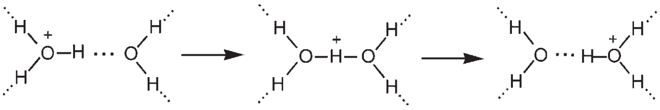
Abstract: The long-standing problem of understanding the nature of the "excess proton" in acidified water is simplified by studying the proton in methanol. The 3D network of hydrogen bonds in $H_{(aq)}^+$ is reduced to a 1D problem. Infrared spectroscopic characterization of linear chain methanol proton solvates in $H(CH_3OH)_n^+$ for $n=2–8$ provides insight into some of the puzzling IR spectral features associated with O-H-O vibrations. These include the virtual disappearance of otherwise strong bands from H-bonded methanol molecules adjacent to symmetrical O-H$^+$-O groups. The data indicate that a chain of up to four O−H···O bonds either side of this group can act as an electrical wire to separate positive charge. This suggests a refinement of the Grotthuss proton-hopping mechanism for explaining the anomalously high mobility of H$^+$ in H-bonded media.

Keywords: Grotthuss mechanism • hydrogen bonds • IR spectroscopy • proton solvate • proton wire

Introduction

One of the oldest unsolved problems in chemistry is obtaining an accurate molecular description of the "excess proton" in acidified water ($H_{(aq)}^+$) and using its structure to explain the high mobility of H$^+$ in water, proteins and other H-bonded media.[1] It was well established by 1905 that the mobility of H$^+$ in water was high compared to that of other unipositive ions, and Danneel[2] revived the 1806 idea of Grotthuss[3] that the movement of positive charge occurs via "proton hopping". The essential idea was that H$^+$ binds to one water molecule that immediately passes off one its H atoms to the next as H$^+$. Sequential proton hops along a chain of water molecules achieves rapid movement of positive charge over a large distance without the need for any particular proton to travel more than a short distance. Remarkably, the Grotthuss mechanism was proposed six years before Avogadro proved that water had the formula H_2O not HO.[1] The modern version of the Grotthuss mechanism (Scheme 1) is typically described in terms of proton transfer from H_3O^+ to H_2O within an Eigen-type[4] $H_3O^+\cdot 3H_2O$ ion (having three regular O−H···O hydrogen bonds) via a Zundel-type[5] $H_5O_2^+$ ion (having a unique, symmetrical O−H$^+$−O bond). These are limiting structures because a precise description of the proton in water has yet to be developed.[6–8]



Scheme 1. Representation of the Grotthuss proton-hopping mechanism from one Eigen-type ion to another, via a Zundel-type ion intermediate.

The problem of developing an accurate molecular description of H$^+$ in water lies in the difficulty of interpreting the very broad IR spectrum of $H_{(aq)}^+$ in terms of specific $H(H_2O)_n^+$ structure(s). This difficulty can be addressed using methanol as a water mimic and studying $H(CH_3OH)_n^+$ clusters. Methanol has the same hydrogen-bonding capability as water but, with only one OH group, propagates intermolecular O−H···O contacts in a simple linear rather than a more complex 3D fashion. This simplification allows the unique and often peculiar IR spectral fingerprints associated with O−H$^+$−O groupings to be identified in discrete $H(CH_3OH)_n^+$ clusters for $n \geq 2$. The same O−H$^+$−O groupings exist in protonated water clusters so that results in methanol should be useful for elucidating the structure of H$^+$ in bulk water. Moreover, like water, methanol supports anomalously high proton mobility.[9]

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Recent investigations on protonated methanol have focused on size-selected $H(CH_3OH)_n^+$ clusters in the gas phase.[10–13] It is proposed that these provide suitable models to unravel the molecular details of H-bonded networks in the liquid phase.[14] However, with the exception of recent studies of the $n=2$ ion,[13] $H(CH_3OH)_n^+$ clusters have only been studied in the OH stretch region ($>2500\,cm^{-1}$) by vibrational predissociation spectroscopy. This is a serious restriction since the stepwise formation of clusters is observed without registering absorptions from the $O{-}H^+{-}O$ core, making structural identification largely inferential and heavily reliant on theoretical modelling.

On the basis of observed νOH bands, it was deduced that gas phase $H(CH_3OH)_n^+$ clusters have linear chain structures up to $n=4$, that both linear and cyclic forms coexist for $n=5$ and 6, and at that only cyclic clusters are formed for $n\geq 7$.[10,11] The unfavorable entropy associated with the formation of rings is apparently overcome by the enthalpy of formation of additional hydrogen bonds by the terminal OH groups, even though this additional hydrogen bonding must be relatively weak because it involves four- rather than three-coordinate O atoms.

In the liquid phase, the terminal OH groups of $H(CH_3OH)_n^+$ clusters will be more readily solvated by the surrounding medium. Solution thermodynamics will favour linear chain structures. An illustration of this principle is provided by a comparison of the gas- and liquid-phase structures of neutral methanol clusters. In the gas phase,[15,16] cyclic $(CH_3OH)_n$ structures begin forming starting with $n=3$, whereas in liquid methanol only chain-like structures are observed[17] and calculated.[18] A second illustration is provided by comparing water with liquid HF. Whereas water propagates in three dimensions via cyclic clusters, HF forms linear $(HF)_n$ chains of average length $n\approx 7$.[19]

An additional concern with the suitability of gas-phase cluster studies as models for the liquid phase is the problem of the counterion. Gas-phase studies cannot take the influence of the anion into account even though ion pairing may play a significant role in determining the structural motif of the solvated H^+ core.

These observations make the need for condensed-phase studies of the solvated proton more pressing. The attraction of gas-phase studies lies in the challenge of developing instrumental capability, coupled with the promise of higher resolution spectroscopy and corroboration by theory. While this is beginning to be realized, the degree to which gas-phase studies model the solvated proton in the liquid state remains an open question.

Results and Discussion

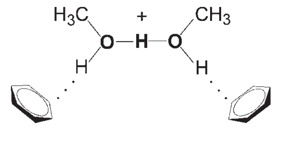
The methanol-solvated proton was studied in both benzene solution and neat methanol. Carborane acids, $H(CHB_{11}H_5Br_6)$ (**1a**) and $H(CHB_{11}Cl_{11})$ (**1b**), were chosen for these studies because, as members of the class of the strongest acids,[20] capable of protonating benzene,[21] their conjugate base anions are weaker bases than benzene. We therefore expected solvation of $H(CH_3OH)_n^+$ clusters by benzene (and methanol) would be competitive with ion pairing and that the anion would have a minimal effect on the structure of the cations.

We consider first the data gathered in benzene solution. The IR spectra of $H(CH_3OH)_n^+$ clusters and the values of n, as well as the total number of methanol molecules in one way or another associated with the clusters (N), were determined by quantitative spectral subtraction of free methanol (i.e. CH_3OH in benzene that is completely unaffected by the proton or the anion). For benzene solutions with methanol/acid mole ratios from 2 to 40, the value of N varies from 2 to 15.7 (Table 1). As will be shown below, $n=N$ for $N<8$.

Table 1. The constitution of 0.015 M benzene solutions of $H(CHB_{11}H_5Br_6)$ with different methanol concentrations.

$[MeOH]_{total}$	$[MeOH]_{free}$	N
0.03	0	2.04
0.0337	0	2.11
0.0375	0	2.5
0.0412	0	2.92
0.0487	0.0079	3.00
0.0562	0.0111	3.00
0.060	0.0168	3.06
0.07	0.0246	3.19
0.08	0.030	3.33
0.10	0.048	3.7
0.12	0.0582	4.12
0.15	0.0801	4.67
0.25	0.139	7.4
0.26	0.138	8.1
0.30	0.155	9.7
0.30	0.176	8.26
0.35	0.216	8.9
0.40	0.252	9.9
0.45	0.300	11.2
0.47	0.303	11.1
0.60	0.385	14.3
0.60	0.365	15.7

The IR spectrum of the cationic part of acids **1a**,**1b** in benzene solution with $N=2$ methanol molecules are fully coincident, indicating that the structure of the cation is not dependent of the nature of the carborane anion. The spectrum is shown in Figure 1 (green). (The monosolvates, **1a**,**b**·CH_3OH, are insoluble in benzene and therefore could not be observed). It corresponds to a disolvate of type **2** (Scheme 2) since the set of bands in the 1600–700 cm^{-1} region (Table 2) is associated with vibrations of a symmetrical O–H–O moiety.[13,22] The lack of dependency of νOH from the terminal OH groups (3377 cm^{-1}) on the nature of the carborane anion, and the increased intensity of combination bands of benzene at 1800–2000 cm^{-1}, indicate[23] OH···π hydrogen bonding to benzene,



Scheme 2. Structure of the $H(CH_3OH)_2^+$ ion in the proton disolvate **2**.

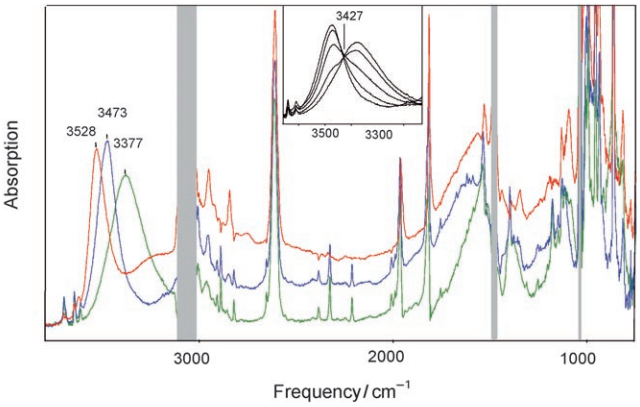


Figure 1. IR spectra of clusters **2** (green), **3** (blue), and **4** (red). The gradual change from **2** to **3** occurs with an isosbestic point at 3427 cm^{-1} (inset). Similarly, the change from **3** to **4** occurs with an isosbestic point at 3497 cm^{-1} (not shown). Gray regions are masked by strong solvent absorptions. The anion is $H_5Br_6^-$.

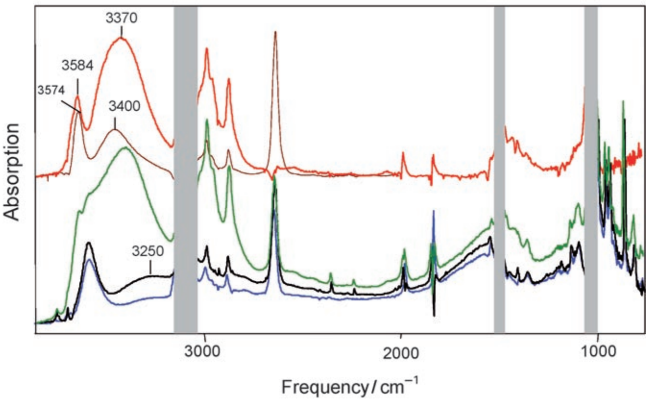


Figure 2. Lower: IR spectra of clusters with $N=4$ (**4**, blue), $N=8$ (**8**, black), and $N=16$ (**8** plus outer sphere methanol, green). The green/black difference spectrum with a scaling factor of 1 (red) belongs to outer-sphere methanol. The anion is $H_5Br_6^-$. The brown spectrum is the methanol-solvated Cs^+ salt.

Table 2. Absorption bands of the terminal OH group (±1 cm^{-1}), the central O$-$H$^+-$O group in **2, 4,** and H-$(CH_3OH)_n^+$, and the conjugated O···H$-$O$-$H···O group in **3** (±5 cm^{-1} and ±2 cm^{-1} for *c*) in benzene. The νOH_{term} for cations in solid state are given in brackets.

Cluster	*a*	*b*			*c*	*d*	νOH_{term}[a]
2-{H_5Br_6}	*862*[c]	977	1084	1158	1549	1376	3379 (3381)
2-{Cl_{11}}	*858*	984	1081	1125	1544	3388 (3462)	
3-{H_5Br_6}	*964*	1000w	[b]	[b]	1600	1361	3473 (3483)
3-{Cl_{11}}	*968*			[b]1633	1356	3522 (3560)	
4-{H_5Br_6}	947	*1009*	1088	[b]	1563	1344	3523 (3518)
4-{Cl_{11}}	*934*	1122			1583	[b]	3557 (3562)
$H(CH_3OH)_n^+$-{Cl_{11}}[d]	~850	*972*	[b]	[b]	1565	[b]	absent

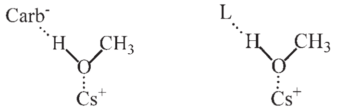
[a] νOH_{term} equals to 3537 cm^{-1} for **8**-{H_5Br_6} and 3577 cm^{-1} for **8**-{Cl_{11}}. [b] Cannot be determined. [c] The most intense band is in italics. [d] In neat methanol.

similar to that established for $H_5O_2^+$ in benzene where $\nu OH = 3390$ cm^{-1}.[22] Although the structure of **2** is ion pair (see later), the terminal OH groups are not involved.

A gradual increase in the mole ratio of methanol/acid from $N=2.0$ to 3.0 results in a smooth spectral transition from the disolvate **2** to the trisolvate **3** with an isosbestic point at 3427 cm^{-1}, indicating only two species are present (Figure 1 inset). The spectrum of **3** (Figure 1, blue) is notable for the continuous broad absorption across the entire 3200–1000 cm^{-1} region. Addition of further methanol to achieve $N=4$ occurs with smooth spectral change and an isosbestic point at 3497 cm^{-1}, indicating tetrasolvate formation, **4**. The distinctive spectral feature of **4** is an increase of the continuous broad absorption relative to **3**, biased towards high frequency (Figure 1, red). Continued gradual addition of methanol up to $N=8$ results in a weak increase of the continuous absorption in the high frequency region, without isosbestic points (Figure 2, blue to black). Thus, the $H(CH_3OH)_n^+$ ions with $n \geq 4$ are spectrally similar to each other. It is remarkable that the four added methanol molecules on going from **4** to **8** are nearly spectrally invisible.

For N from ≈9 to 16, the spectrum of self-associated methanol grows in, dominated by a broad, intense νOH band at 3370 cm^{-1} (Figure 2, green). The absorptions from the COH group (νCO and δCOH) differ from those of free methanol (which has been subtracted) even though their νCH_3 bands coincide. However, the νCH_3 frequencies of self-associated methanol are higher (by 11 cm^{-1} for $\nu_s CH_3$) than those in the $H(CH_3OH)_8^+$ cluster. Because the bands are narrow, this difference allows subtraction of the spectrum of the $H(CH_3OH)_8^+$ cluster from the $N=16$ spectrum until the cluster $\nu_s CH_3$ band disappears. The isolated spectrum then belongs to associated methanol (Figure 2, red). Full compensation of $H(CH_3OH)_8^+$ bands occurred with a scaling factor of unity relative to bands from the anion indicating that this associated methanol, while influenced by the cluster, is not a constituent part of the $H(CH_3OH)_n^+$ ions. Its spectrum does not develop any of the peculiarities of the protonated methanol clusters. Evidently, the specific sphere of influence of H^+ stops at the octasolvate level and additional methanol takes a less specific role of outer sphere solvation in the ion pair.

A distinguishing feature of the spectrum of this outer sphere methanol is a narrow νOH band at 3584 cm^{-1}. This is lower in frequency than that of the OH groups of free methanol that are π-H-bonded with benzene (3612 cm^{-1}) and may arise from CH_3OH that is H-bonded to the carborane anion. Support for this proposal comes from the spectrum of the methanol molecules involved in the solvation of $Cs(CHB_{11}H_5Br_{11})$ in benzene solution with 0.6 M CH_3OH (Figure 2, brown). Only two νOH bands are observed and these are assigned to the following two types of methanol molecules: a) CH_3OH that is O-atom coordinated to Cs^+ and H-bonded to the carborane anion (Scheme 3, left), giving rise to the narrow, high frequency νOH band at

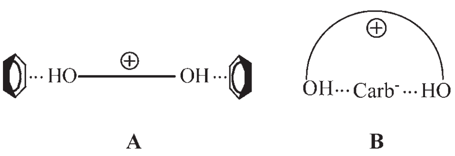


Scheme 3. The two types of hydrogen-bonded methanol in the solvation of $Cs(CHB_{11}H_5Br_6)$ in benzene solution (L = methanol).

3574 cm^{-1}, and b) CH_3OH that is O-atom coordinated to Cs^+ and H-bonded to another CH_3OH molecule (Scheme 3, right), giving rise to the broad, low-frequency band at 3400 cm^{-1} that is essentially indistinguishable from that of dissolved, self-associated methanol.

The νOH bands are sensitive to the nature of the H-bonded base (carborane or methanol) but are rather insensitive to interactions via the O atom. It is reasonable that the νOH frequency of outer sphere methanol in the protonated clusters (3584 cm^{-1}) would be about 10 cm^{-1} higher than in $Carb^-{\cdots}HOCH_3$ type bonding in the absence of cation influence. Possibly, it is anion solvation that initiates the formation of outer sphere methanol. Nevertheless, only a fraction of the outer sphere methanol molecules interact with the carborane anion. The majority are self-associated, indicating a very weak interaction with the $H(CH_3OH)_8^+$ ion. This situation is similar to that observed in the solvation of diacetate proton complexes by acetic acid, $[(AcO{-}H{-}OAc)^-{\cdot}n\,HOAc]{\cdot}m\,HOAc$, where seven to eight HOAc molecules (n) are involved in primary solvation and up to 12 (m) are involved in forming an outer sphere solvation shell.[24]

In the spectra of **3**, **4**, and **8**, the highest νOH frequencies are from the terminal OH groups (νOH_{term}). They are dependent on the nature of carborane anion, $CHB_{11}H_5Br_6^-$ versus $CHB_{11}Cl_{11}^-$ (abbreviated $\{H_5Br_6^-\}$ and $\{Cl_{11}^-\}$). This indicates the formation of ion-paired structures. Consistent with the higher basicity of the $H_5Br_6^-$ ion relative to the Cl_{11}^- ion,[25] the νOH_{term} frequencies of the former are always lower than the latter (Table 2). The other vibrations of the cations are not influenced within the limits of experimental error. The νOH_{term} bands for cations **3**–**8** develop as symmetrical bands indicating that the cations retain high symmetry. This suggests ion-paired structures where both terminal O–H groups have the same interaction with benzene or anion (structures **A** and **B** in Scheme 4).



Scheme 4. Representations of hydrogen bonding by the terminal OH groups in ion-paired structures of protonated methanol cations.

Based on the following evidence, we propose that cations with the $\{Cl_{11}^-\}$ ion have structure **A**, whereas those with the more basic $\{H_5Br_6^-\}$ ion have structure **B**. Cation **2** with the $\{Cl_{11}^-\}$ counterion has a significantly lower νOH_{term} frequency in benzene solution (3388 cm^{-1}) than in the solid state (3462 cm^{-1}) where, in the absence of benzene, the anion must be directly hydrogen-bonded to the cation. Similarly, cation **3** with $\{Cl_{11}^-\}$ as counterion has a lower νOH_{term} (3522 cm^{-1}) in benzene solution than in the solid state (3560 cm^{-1}) unsolvated by benzene. Thus, with the Cl_{11}^- counterion, $\Delta\nu OH_{term}$ between the solid and solution states decreases from 74 cm^{-1} for **2** to 38 cm^{-1} for **3** and practically disappears for **4** (5 cm^{-1}, but remains positive). On the other hand, there are essentially no differences between the solid- and solution-state values of νOH_{term} for these cations when the counterion is $H_5Br_6^-$ (Table 2). This indicates ion pairing of type **B** and is consistent with the near equivalence of basicity of $H_5Br_6^-$ and benzene.[26] With the less basic Cl_{11}^- ion, however, benzene must successfully compete for hydrogen bonding with the terminal O–H groups giving structure **A**.

Let us now analyze the spectra of **2**–**8** in more detail to highlight their peculiarities and more accurately detail the structures from which they rise.

The frequencies of the central $O{-}H^+{-}O$ group in **2** (Figure 3, Table 2) are consistent with those found in the entire family of symmetrical proton disolvates, including $H_5O_2^+$, and are designated *a, b, c* and *d*.[22] The broad, intense *a* and *b* bands at 861 and 977 cm^{-1}, respectively, are readily assigned to ν_{as}OHO in a symmetrical $O{-}H^+{-}O$

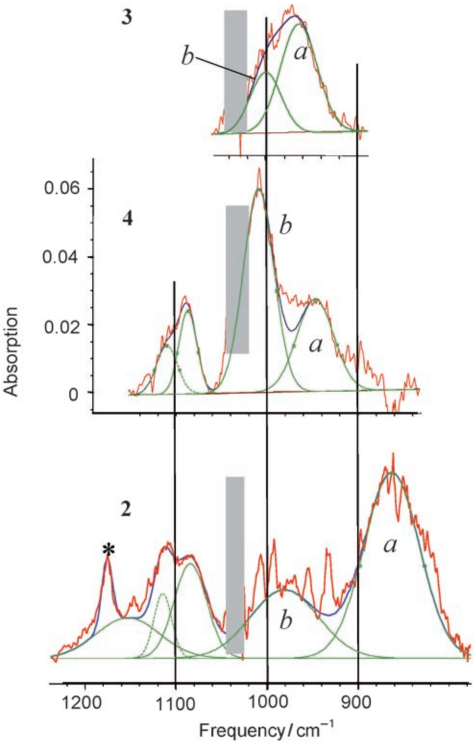
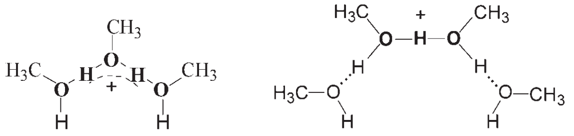


Figure 3. Deconvoluted IR spectra of clusters **2**, **4** and **3** in the OHO frequency region showing bands *a* and *b*. The band marked with an asterisk arises from incompletely subtracted benzene. The nature of the dashed band is uncertain. The anion is $H_5Br_6^-$.

moiety. The distinctive strong band *c*, whose exact assignment is not fully understood in condensed phases but is probably associated with ν_{as}OHO,[22] appears at 1549 cm^{-1}, whereas that in H(EtOH)$_2^+$ appears at 1507 cm^{-1}.[22] The medium band at 1376 cm^{-1} is attributed to the out-of-plane bend γOHO (band *d*), and the in-plane bend δOHO (band *e*), expected in the range 1400–1550 cm^{-1}, is apparently masked by the strong band *c*.

The symmetric trisolvate **3** (Scheme 5) is expected to have vibrational frequencies of the conjugated O···H–O–H···O group (blue) different from those of the symmetric O–H–O group in **2**. Indeed, the spectrum of **3** does develop a continuous broad absorption typical of unsymmetrical O–H···O groupings[5] having O····O separations >2.45 Å.[27] Nevertheless, in the fingerprint region from 800–1400 cm^{-1}, similarity with **2** is retained. Bands consistent with *a* and *b* appear at 964 and 1000 cm^{-1} (Table 2, Figure 3) although their frequencies are somewhat merged and the total intensity more than halved. Band *c* at 1600 cm^{-1} is not only retained but has increased intensity, and band *d* has developed at 1361 cm^{-1}. So, in cation **3**, bands *a*, *b*, *c* and the continuous broad absorption are constituent parts of the O···H–O–H···O group stretch vibrations. In this case, all three *a*, *b*, and *c* bands will have a resonance nature and the OH stretching frequency is determined by the center of mass of *a*, *b*, *c* and the continuous broad absorption.



3 **4**

Scheme 5. Structure of the proton trisolvate **3** (left) and tetrasolvate **4** (right).

The spectrum of the tetrasolvate **4** with a symmetrical structure (Scheme 5) is readily understood in terms of a central, symmetrical O–H$^+$–O unit (blue) giving rise to *a*, *b* and *c* type bands (Table 2, Figure 3) and an approximate doubling of the continuous broad absorption intensity (relative to **3**) from the two flanking, unsymmetrical O–H···O groups. The continuous broad absorption is somewhat skewed towards the higher frequency region (2400–3400 cm^{-1}) and a new broad band with weak intensity is apparent at about 3240 cm^{-1} (Figure 1). The two terminal O–H groups have a common νOH centered at 3527 cm^{-1}. This frequency is considerably higher than that of **3** (3473 cm^{-1}), consistent with lower partial positive charge at the periphery of the larger cation.

The successive addition of 1–4 more methanol molecules to **4** giving penta-, hexa-, septa-, and octasolvated cations **5**, **6**, **7**, and **8** occurs with only gradual spectral changes in the frequency region higher than 1200 cm^{-1} (Figure 2). Since isosbestic points are absent, the individual spectra of cations **5**–**8** cannot be obtained. Their formation can be understood in terms of gradual solvation of **4** up to **8**, retaining the core OH$^+$O fragment. In the 700–1200 cm^{-1} region, the fingerprint of the central O–H$^+$–O unit vibrations, the difference spectrum between **4** and **8** yields a flat baseline at zero optical density. Thus, the bands of the O–H–O unit are unchanged in frequency *and* intensity, meaning that the positive charge on the O–H–O unit changes very little, if at all, when passing from clusters **4** to **8**. In the frequency range of the continuous broad absorption, the difference spectrum between **4** and **8** shows that the four new O–H···O bonds in **8** give rise to increased intensity in the high frequency region, resulting in broad bands at about 2680 cm^{-1} and 3250 cm^{-1} (Figure 4). The molar intensity of this band (4.15 arbitrary units), assigned to νOH in unsymmetrical O–H···O units, is anomalously low relative to that expected ($\geqslant$4) by comparison to the molar intensity of νOH band of the terminal OH groups (3535 cm^{-1}) which is 3.05. The other abnormality is the surprisingly small increase of the νOH frequency of the terminal OH groups, by only 8 cm^{-1}, when moving from **4** to **8**. This is discussed later. Collectively, these data indicate a linear growth of **4** with successive additional methanol molecules up to **8**.

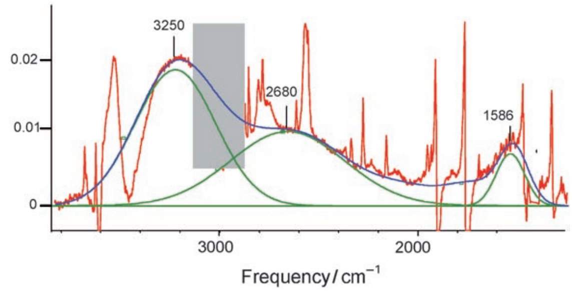
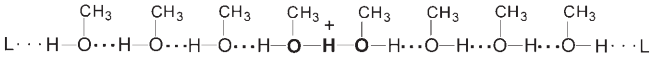


Figure 4. Enlarged absorbance scale spectrum of the blue/black difference spectrum of Figure 2 revealing absorptions from the four added methanol molecules upon going from **4** to **8**. The deconvolution is presented in green and the summation in blue.

The central O–H–O group (bold in Scheme 6) is symmetrical and responsible for bands *a*–*e*. The immediately flanking O–H···O groups are unsymmetrical and responsible for most of the continuous broad absorption. The additional methanol molecules (3rd and 4th distant from H$^+$) add unsymmetrical O–H···O groups which, having higher νOH frequencies, contribute a blue-skewed continuous broad absorption. The linear-chain structure is stabilized by benzene or carborane anion interactions with the terminal OH groups, by outer sphere methanol and presumably by ben-



$L\cdots H{-}\underset{}{\overset{CH_3}{O}}\cdots H{-}\overset{CH_3}{O}\cdots H{-}\overset{CH_3}{O}\cdots H{-}\overset{CH_3}{\mathbf{O}}{-}\overset{+}{\mathbf{H}}{-}\overset{CH_3}{\mathbf{O}}{-}H\cdots\overset{CH_3}{O}{-}H\cdots\overset{CH_3}{O}{-}H\cdots\overset{CH_3}{O}{-}H\cdots L$

8

Scheme 6. Representation of the structure of the octasolvate **8** (L = benzene or, for cyclic structure **B**, carborane anion).

zene. By contrast, in the absence of solvent and counterion, gas phase $H^+(CH_3OH)_n$ clusters with $n>4$ are beginning to cyclize and those with $n>7$ are cyclic only.[11]

The IR spectra of the methanol molecules in cations **2–8** show other unusual features. Most striking is the disappearance of two bands: the νCO stretch, which is very intense in the spectrum of free methanol at 1021 cm^{-1}, and the δCOH bend (1338 cm^{-1} in free methanol). These bands have their normal appearance in the spectra of the outer sphere methanol associates, so this phenomenon is initiated by H^+ of the symmetrical $O{-}H^+{-}O$ group and is redistributed along the chains of CH_3OH molecules in higher solvates. It is not transmitted to the outer sphere molecules, which do not have hydrogen-bond connections with cluster **8**. The phenomenon of band disappearance has been observed in a number of proton disolvates when the O−H−O group is symmetrical.[22,28] It has been proposed that stochastic movements of the proton in the flat bottom potential function of a symmetrical O−H−O group induce an alternating electrical field that is transmitted to the nearest bonds, giving rise to additional modulation of their frequencies[28] but this is only one possible explanation for the unusual loss of band intensities.

While most pronounced for the vibrations of bonds immediately adjacent to the O−H−O group, this phenomenon also affects those that are two-bond distant. For example, consider the trends in frequency and intensity of ν_sCH_3 band shown in Figure 5 ($\nu_{as}CH_3$ behaves similarly). The frequency decreases nearly linearly for **2**, **3**, and **4**, consistent with expectations from a regularly increasing size/charge ratio. The positive charge is distributed over all carbon atoms, and the C−H bonds are strengthened. However, for cations **4–8**, the ν_sCH_3 (ca. 2841 cm^{-1}) appears scarcely to change (although it remains significantly higher than that of free methanol at 2831 cm^{-1}), as if the δ^+ positive charge on the CH_3 groups is not changing when passing from **4** to **8**. This is most unusual. A similar trend is shown by the integrated intensity of the ν_sCH_3 band (Figure 5b). From nearly zero intensity in **2** (ca. 0.06 that of free methanol), it increases regularly in **3** and **4**, where it is still 0.4 of that for free methanol. More unusual, the integrated intensity does not increase significantly in **5–8**. This means that the molar intensity of the νCH_3 bands actually decreases (by about half) when passing from **4** to **8**. This cannot be, so the only explanation is that the observed νCH_3 bands arise predominantly from the terminal methanol molecules and the contribution from the middle methanol molecules is very small. The essential disappearance of νCH_3 bands from the middle methanol molecules makes their contribution to the total observed intensity, as well as the influence on the band positions, negligible.

The final anomaly is the trend in νOH of the terminal OH group. As shown in Figure 6, νOH increases linearly (by 150 cm^{-1}) **2** through **4**, as expected from charge/size considerations. The trend is similar in the gas phase although the change in νOH is much less (24 cm^{-1}).[14] However, from **4** through **8**, νOH increases only 8 cm^{-1}, indicating that the partial positive charge on the terminal OH group becomes nearly independent of the length of the H-bonded methanol chain, for one to three methanol molecules. Consistent with this, the frequencies of bands *a*, *b*, and *c* from the central O−H−O unit remain unchanged **4** through **8**. The partial positive on H^+ in the O−H−O unit of **4** is not altered by attachment of additional methanol molecules. The remarkable effect is that the O−H···O chain acts as a wire to separate positive charge, practically as well for three methanol extensions as one. The same phenomenon that allows the O−H···O chain to act as a wire presumably causes the methyl groups of each added methanol in **5–8** to react as though

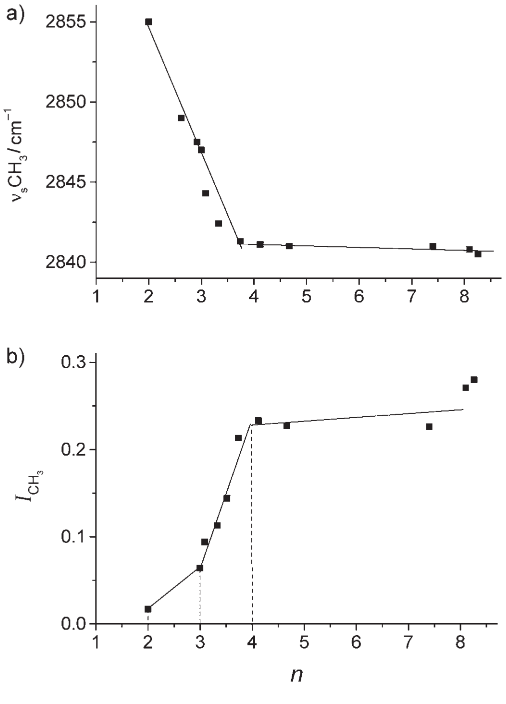


Figure 5. Dependence of a) ν_sCH_3 band frequency and b) absolute intensity (I_{CH_3} in arbitrary units) on the average number n in $H^+\cdot(CH_3OH)_n$ clusters for **2–8**. The anion is $\{H_5Br_6^-\}$.

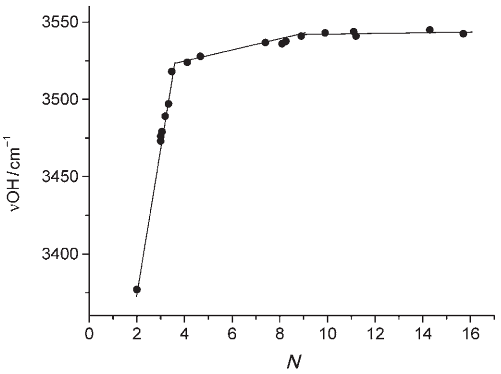


Figure 6. Dependence of νOH frequency of the terminal OH groups of clusters **2–8** on *N*. The anion is $\{H_5Br_6^-\}$.

they are in the same environment as those in **4**, losing the intensity of their IR bands.

The IR spectrum of a carborane acid in 100 % methanol is made up of three types of overlapping spectra. These arise from a) bulk methanol, undisturbed by acid, b) methanol incorporated into $H(CH_3OH)_n^+$ ions, and c) methanol that is solvating the carborane ions. Outer sphere methanol that is solvating the $H(CH_3OH)_n^+$ ions, as discussed previously for benzene solutions, is indistinguishable from that of free self-associated methanol. Thus, to isolate the spectrum of an $H(CH_3OH)_n^+$ ion from the initial observed spectrum, it is necessary to subtract the spectra of both bulk methanol and anion-solvated methanol. Figure 7 shows the spectra of $H\{H_5Br_6\}$ and $H\{Cl_{11}\}$ solutions after simple subtraction of only bulk methanol with equal scaling factors. The absence of well-defined subtraction criteria did not allow the contour of the νOH band to be accurately defined (in the area shadowed by gray in Figure 7). Nevertheless, the results allow the conclusion that the OH groups at the terminus of influence of the proton in the $H(CH_3OH)_n^+$ chain have νOH frequency at about 3190 cm^{-1} that is independent on the nature of anion. At the same time, the methanol molecules whose OH groups are involved in anion solvation are readily pronounced by separate narrow νOH bands at 3564 and 3597 cm^{-1} for $\{H_5Br_6^-\}$ and $\{Cl_{11}^-\}$ respectively (Figure 7).

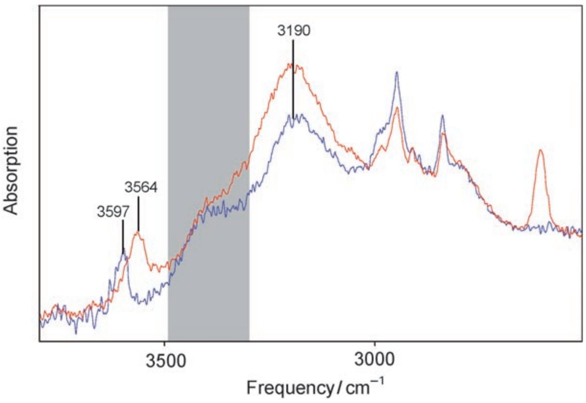


Figure 7. ATR FT-IR spectra of 0.25 M $H\{H_5Br_6\}$ (red) and 0.20 M $H\{Cl_{11}\}$ (blue) in pure methanol after subtraction of bulk methanol with a scaling factor of 0.9.

To determine that these anion-associated methanol molecules are not influenced by the proton and to obtain a more precise spectrum of $H(CH_3OH)_n^+$ in methanol we have taken the difference spectrum of H(carborane) and Cs(carborane) at equal concentration. Since the spectra of the cesium salts show the same narrow νOH bands with exectly the same frequencies, and the absorption from methanol molecules involved in the solvation of the Cs^+ ion is essentially indistinguishable from that of bulk methanol, they both are fully subtracted. After compensating for the "free" methanol concentration difference that arises because some portion of methanol is involved in proton solvation, the spectrum of the $H(CH_3OH)_n^+$ ion only is obtained (Figure 8, red).

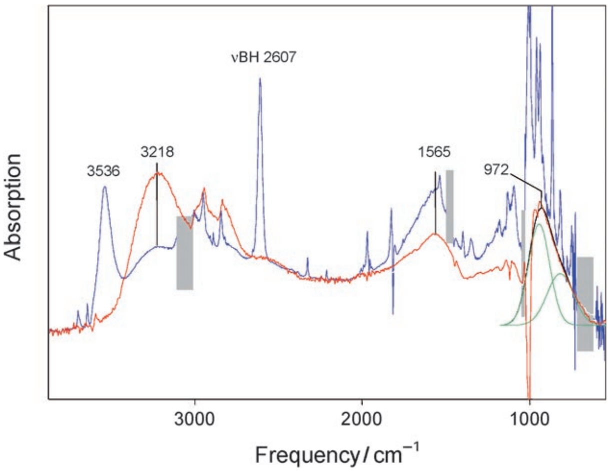
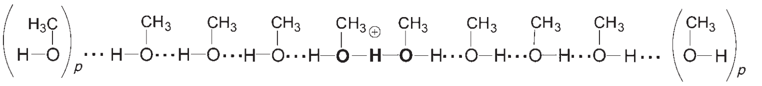


Figure 8. ATR FT-IR spectrum of $H(CH_3OH)_n^+$ (red), derived from the difference spectrum between 0.25 M $H\{Cl_{11}^-\}$ and $Cs\{Cl_{11}^-\}$ in methanol, compared to cation **8** in benzene solution with $\{H_5Br_6^-\}$ ion. The spectra are scaled to continuous broad absorption intensity. Regions of benzene nontransparency are shaded.

Figure 8 compares the spectrum of the $H(CH_3OH)_n^+$ cation in 100 % methanol (red) with that for **8** in benzene with $\{H_5Br_6^-\}$ ion (blue) to show spectral similarities in the cations. Sharp bands in the blue spectrum, such as νBH at 2607 cm^{-1} as well as νBB and νBBr near 1000 cm^{-1}, arise from the anion. These do not appear in the red spectrum because they have been subtracted. The $H(CH_3OH)_n^+$ ion in methanol shows an intense *b* band at 972 cm^{-1} from the central $O{-}H^+{-}O$ group with a higher frequency *a* component, as well as a strong *c* band at 1565 cm^{-1} (Table 2), continuous broad absorption and νOH at ≈3200 cm^{-1} very close to that for 3rd distant methanol from H^+ in **8** (Figure 8). The other unusual peculiarities of spectrum **8**, namely the absence of an intense νCO stretching band and strongly decreased $\nu_{as}CH_3$ and ν_sCH_3 band intensities are also well pronounced in the methanol solution spectrum of $H(CH_3OH)_n^+$, indicating a definite value for *n*. As expected, the $H(CH_3OH)_n^+$ spectrum does not show the νOH band from terminal OH group of **8** (at 3536 cm^{-1}) because, in the more basic solvent, they will be hydrogen-bonded to the methanol rather than anion. As a result, the relative intensity of νOH at ≈3200 cm^{-1} increases. The fact that this frequency is limited to this low frequency rather than showing gradual increase up to 3320 cm^{-1} for bulk methanol, indicates that the positive charge in the $H(CH_3OH)_n^+$ ion is redistributed along the H-bonded chain within a defined number of methanol molecules *n* that show all of the above disscussed spectral peculiarities. More distant hydrogen-bonded methanol molecules, however, are practically no longer distinguishable from bulk methanol. Judging from the relative intensities of the νOH bands, and knowing that the two terminal OH groups of **8** in benzene (3536 cm^{-1}) are converted to

O–H···O groups in 100% methanol ($\approx$3200 cm^{-1}), n in $H(CH_3OH)_n^+$ is estimated to be 8–10. So, the $H(CH_3OH)_n^+$ ion has a long chain structure of methanol molecules, at least eight of which are influenced by H^+, while the others are indistinguishable from bulk methanol and can be considered as solvating this cation. These are shown as $(CH_3OH)_p$ in Scheme 7.



Scheme 7. Representation of the $H(CH_3OH)_n^+$ structure in neat methanol.

Conclusion

Infrared data on $H(CH_3OH)_n^+$ indicate that the influence of the proton extends in a linear chain up to four methanol molecules either side of the proton. This is coincident with a recent ab initio molecular dynamics study that finds an average chain length of six to eight methanol molecules.[18] Remarkably, in benzene solution, the terminal νOH frequencies increase by only 8 cm^{-1} from $n=4$ to $n=8$, indicating that the partial positive charge on the terminal O–H group is nearly independent of the length of the hydrogen-bonded methanol chain, for one to three O–H···O groupings. Such transfer of positive charge along a molecular chain resembles charge conduction in a wire. H-bonded chains of water molecules are increasingly referred to as "proton wires". The present work provides the first experimental evidence that this description may be appropriate in the electrical sense, where charge separation is independent of the length of the wire.

The present observations suggest that high proton mobility in hydrogen-bonded solvents may be dependent not only on proton hopping in linear chain clusters[18] but also on wire-like charge separation in oligomeric molecular units. In methanol, the proton is most stable in a Zundel-like symmetrical O–H$^+$–O unit with three or four flanking methanol molecules on each side. Grothuss proton hopping can then be viewed as occurring between $H(CH_3OH)_n^+$ units with $n \geq 8$ and linear hydrogen-bonded methanol as shown in Scheme 8.

Such charge transfer implies near synchronous, concerted proton transfers within $[H(CH_3OH)_n^+]$ ions via low-barrier hydrogen bonds. This is expected to occur more rapidly than in the stepwise proton hops of the classical Grotthuss mechanism[1,7] and can be accommodated within calculations of proton diffusion in methanol.[9,18] It offers an additional rationale for the anomalous high mobility of the proton in hydrogen-bonding media. The possibility of synchronous double proton transfer has been explored theoretically in the solvated $H_7O_3^+$ ion[29] and the coupled motion of protons in delocalized, symmetrical hydrogen-bonded systems is discussed by Zundel in his interpretation of the continuous broad absorption phenomenon.[5] The present work indicates that previously unrecognized special effects extend either side of a symmetrical O–H$^+$–O unit to at least three added H-O units. A similar phenomenon should exist in water.

Finally, we note that the protonated methanol structural unit written $CH_3OH_2^+$, analogous to H_3O^+, has no existence in methanol solution. Rather, the symmetrical O–H$^+$–O unit prevails. This also suggests that a deeper study of the proton in water is in order.

Experimental Section

Carborane acids were prepared as previously described.[20] Benzene was purified and dried according to the literature methods.[30] Methanol from Acros (extra dry, water <50 ppm) was used without additional purification. Benzene solutions of $H\{H_5Br_6\}$ and $H\{Cl_{11}\}$ acids (0.015 M) with variable methanol concentration (0.03–0.6 M) were prepared by dissolving a weighed quantity of acid in benzene with predetermined methanol concentrations. All operations were performed in a Vacuum Atmospheres Corp. glovebox under He (O_2, H_2O < 0.5 ppm). IR spectra in the 4000–450 cm^{-1} range were run on a Shimadzu-8300 FT-IR spectrometer housed inside a glovebox. A cell with Si windows having 0.036 mm separation at the beam transmission point was used. To avoid interference effects, the cell configuration was wedge-shaped. ATR FT IR spectra in the 4000–600 cm^{-1} frequency range were run on a Perkin Elmer Spectrum 100 spectrometer housed inside a glovebox. IR data were manipulated using GRAMMS software. Additional figures (S1-S4) describing the subtraction procedure used to obtain the spectrum of $H(CH_3OH)_n^+$ in methanol as well as the anion dependence of the spectra of **4** and **8** are available as Supporting Information.

Acknowledgements

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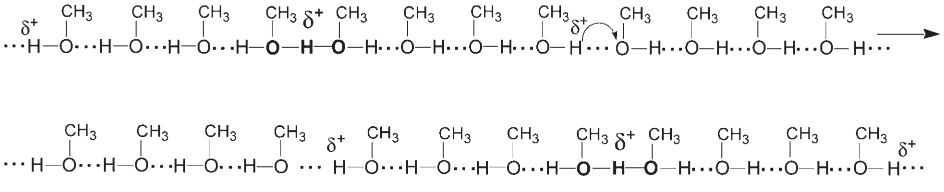

Scheme 8. Representation of proton hopping in methanol.

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