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Structures of Thermal, Mass-Selected Water Clusters Probed with Hydrophobic Ion Tags and Infrared Photodissociation Spectroscopy

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Abstract: The structures of tetramethylammonium (TMA^+) and phenyltrimethylammonium ($PTMA^+$) with 1–8 water molecules attached were investigated using infrared photodissociation spectroscopy (IRPD), blackbody infrared radiative dissociation, and theory to elucidate the effects of ion–water interactions and water–water hydrogen bonding in clusters containing these hydrophobic ions. Several pieces of evidence suggest that these ions have only a small effect on water structure. The binding energy of a water molecule to TMA^+ is 44 kJ/mol, a value that is significantly lower than that reported for other cations and close to the condensation energy of bulk water. The OH asymmetric stretch of the water molecule in $TMA^+\cdot(H_2O)_1$ at 3718 cm^{-1} is less red-shifted from that of an isolated water molecule (3756 cm^{-1}) than for those of other cations, and water–water hydrogen bonding is extensive for all clusters with two or more water molecules. These results indicate that charge transfer from water to these hydrophobic ions is much less than that for other cations. There are two predominant structures for these ions with three water molecules: one in which water molecules form a chain and one with a cyclic structure analogous to that of neutral water trimer. With four water molecules attached, water forms a cyclic structure similar to that of neutral water tetramer. The spectra of the larger clusters follow trends reported for neutral water molecule clusters, which indicates that these hydrophobic ions have only a minimal effect on the structure of water in clusters with four or more water molecules. These results suggest that these hydrophobic ions can be used as “tags” that could make possible acquisition of IRPD spectra of even larger clusters, such as clathrates, for which precise mass selection of neutral clusters is not possible by other methods.

Introduction

The hydrogen-bonding structure of liquid water and perturbation of this structure due to solvation of hydrophilic and hydrophobic ions and molecules are of key interest in understanding chemistry in aqueous solutions. Competitive and cooperative interactions between water molecules and with solutes that affect the tetrahedral network of water–water hydrogen bonds have been implicated in Hofmeister series effects,[1] solute aggregation, protein folding, and the solvent shell structure of ions. Detailed study of the hydrogen-bonding network of bulk aqueous solutions at biologically relevant concentrations is difficult, because hydrogen bonds can be formed and broken on extremely short (picosecond) time scales and because water molecules outside the first few solvent shells often give very intense, broad background signal for a variety of spectroscopic methods. Isolated water oligomers and small hydrates of ions can serve as model systems for understanding these interactions, and small clusters can often be practically studied with high-level *ab initio* calculations.

The structures of isolated oligomers consisting of up to ~9 water molecules and of oligomers attached to benzene or in gas matrices have been examined in a number of studies using infrared spectroscopy and computational chemistry.[2–23] These studies show that the frequency of the OH stretch of a water molecule is a highly sensitive probe of its hydrogen-bonding environment. For example, distinct OH stretch bands, corresponding to subtly different hydrogen bond lengths and angles, have been observed in infrared spectra of water vapor samples containing oligomer sizes from the monomer through (at least)

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the hexamer.[2−8] Two experimental methods have proved particularly successful in assigning spectral bands to definite oligomer sizes. In one of these, the appearance of new features in OH stretch absorption spectra is correlated with increasing pressure of the water vapor in expansions that form the oligomers, hence, with oligomer size.[4,5] In the second method, the maximal scattering angles of a collimated water oligomer beam through a collision cell as a function of oligomer size is exploited to yield size-selected infrared action spectra.[6−8] These techniques, in combination with calculated oligomer structures and spectra, have enabled the assignment of many OH stretch bands to specific hydrogen-bonding structures. However, unambiguous assignment of some bands to specific cluster sizes is complicated by the difficulty in mass-selecting oligomers of a known size. Even in action spectroscopy studies where maximal scattering angles for different oligomer sizes are well separated, contributions to the spectrum assigned to oligomers as small as the hexamer from larger and smaller oligomers cannot be completely eliminated.[6,7] Composite OH stretch spectra of broad distributions of neutral water oligomers containing between tens and thousands of water molecules indicate that, across this size range, most spectral bands vary little in position and intensity and are attributable to contributions from both “crystalline” and amorphous hydrogen-bonding networks.[24−26]

In contrast to neutral clusters, ionic clusters can be readily *m*/*z* selected, so that bands in infrared action spectra of the resulting mass-selected clusters can then be unambiguously assigned to a population of ions of known cluster size. This technique has been used to study many hydrated ions, including e^-,[27] H^+,[28−31] alkali metal cations,[32−41] multivalent metal cations,[42−46] halide anions,[47−51] ammonium,[52−54] and numerous other ions.[42,55−66] Tagging these clusters with noble gas atoms that separate from the clusters easily upon laser irradiation[35−39,42,56,57] can result in distinct, narrow spectral bands. OH stretch spectra of these clusters often display trends that can be used to identify the gas-phase coordination number of the ion as well as preferred solvation shell geometries. Water−water hydrogen bonding has been observed for many of these systems, and in spectra of large metal cation water clusters, features very similar to those of bulk liquid water have been observed,[43−45] suggesting that the hydrogen-bond network in such clusters is liquid-like.

Spectra of hydrated alkali metal cations with and without the use of Ar tags have been recently reported, and these results indicate that the cluster size at which water−water hydrogen bonding is first observed decreases with increasing size of the metal cation.[34] Extensive water−water hydrogen bonding is observed for $Cs^+\cdot(H_2O)_4\cdot Ar$,[35] which has a structure resembling that of a neutral water tetramer, although such a structure is not observed for $Cs^+\cdot(H_2O)_4$.[34] Such a strong similarity between the spectra and structure of hydrated ions and those of neutral water clusters has not been reported for any other ions at a

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cluster size this small. This similarity is likely due to the weak interaction of Cs^+ with water molecules.[35]

Tetramethylammonium (TMA^+) is a monocation with a highly shielded charge that is at one extreme end of the Hofmeister series[1] and is known to have hydrophobic properties.[67−75] Neutron diffraction[71,72] and molecular dynamics[73−75] simulation studies indicate that water molecules in the first solvation shell of TMA^+ form a clathrate-like structure around TMA^+ with minimal distortion of the bulk water tetrahedral hydrogen-bonding network. Ammonium and alkali metal cations are thought to organize vicinal water molecules more strongly.[1] Because TMA^+ is a hydrophobic ion, it is intriguing to consider whether sequential solvation of TMA^+ will more closely resemble that of other monocations, such as alkali metal cations or ammonium, or whether water−water hydrogen bonding like that of neutral water oligomers will instead be observed. In order to address this question, we present here infrared action spectra of $TMA^+\cdot(H_2O)_{1-8}$ and of the closely related phenyltrimethylammonium$\cdot(H_2O)_{1-8}$ at 133 K as well as computational results for the smaller clusters.

Experimental Section

IRPD Spectroscopy. IRPD spectra of $TMA^+\cdot(H_2O)_n$ and $PTMA^+\cdot(H_2O)_n$, $n = 1-8$, were acquired using a 2.75 T Fourier transform ion cyclotron resonance mass spectrometer coupled to a tunable OPO/OPA laser system.[43,76−78] Hydrated ions are formed by nanoelectrospray ionization using borosilicate capillaries with tips pulled to an inner diameter of ~1 μm that are filled with 1 mM aqueous solutions of tetramethylammonium bromide (Aldrich Chemical Co., Milwaukee, WI, U.S.A.) or phenyltrimethylammonium chloride (Sigma-Aldrich GmbH, Steinheim, Germany). A platinum wire inserted into the capillary is in direct contact with the solution and is held at ~600 V relative to the heated metal capillary of the electrospray interface. Ions are guided to the ion cell through five stages of differential pumping using a series of electrostatic lenses. Surrounding the cell is a copper block which is cooled by a temperature-regulated flow of liquid nitrogen[78] to 133 K for at least 8 h prior to all experiments. Ion trapping and thermalization is enhanced with a ~5 s pulse of dry nitrogen gas (~10^{-6} Torr) and a ~6 s pumpdown to a pressure of ~10^{-8} Torr. Precursor clusters are isolated using stored waveform inverse Fourier transforms.

Photodissociation of mass-selected clusters is achieved by irradiating the ions with tunable infrared light in the OH stretch region (~3000−3900 cm^{-1}) from an OPO/OPA (LaserVision, Bellevue, WA, U.S.A.) pumped by the 1064 nm fundamental of a Nd:YAG laser (Continuum Surelight I-10, Santa Clara, CA, U.S.A.) at a 10 Hz repetition rate.[76] Irradiation times of 3−30 s are used in order to produce substantial but not complete fragmentation of the precursor clusters. First-order photodissociation rate constants are obtained as a function of laser frequency from the precursor and product ion abundances after irradiation and are corrected for variations in laser power over the frequency range studied as well as blackbody infrared radiative dissociation (BIRD), which occurs as a result of absorption of blackbody photons from the 133 K ion cell and cell jacket. First-order BIRD rate constants at 133 K are obtained from the abundances of precursor and product ions using up to 30 s of exposure to blackbody photons without laser irradiation. A MIDAS data system[79] is used to acquire all mass spectra.

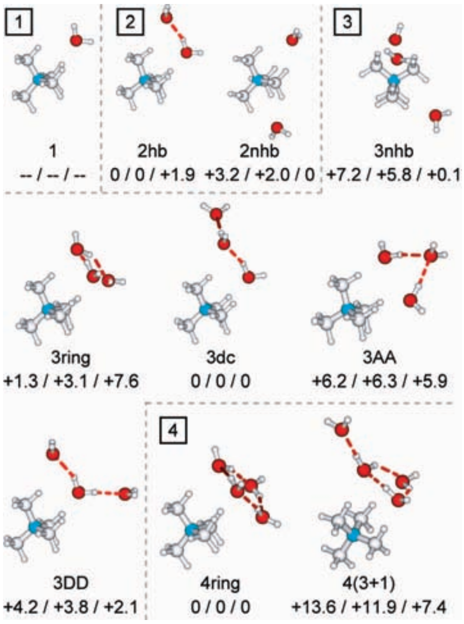

Figure 1. Candidate low-energy structures for $TMA^+\cdot(H_2O)_{1-4}$ and relative Gibbs free energies (kJ/mol) at 0/133/298 K calculated at the MP2/6-31++G(d,p) level of theory.

Computational Chemistry. A limited number of initial structures for $TMA^+\cdot(H_2O)_{0-4}$ were generated in Macromodel 8.1 (Schrödinger, Inc., Portland, OR, U.S.A.). For structures in which water−water hydrogen bonds exist, water clusters were built manually and positioned ~6 Å from the TMA^+ nitrogen atom in order to allow geometry relaxation during initial optimization. Initial structures were then optimized using the B3LYP/6-31G* level of theory in Jaguar v. 6.5 (Schrödinger, Inc., Portland, OR, U.S.A.). Geometries were further optimized, and harmonic oscillator vibrational frequencies and intensities were calculated using the MP2/6-31++G(d,p) level of theory in Q-Chem v. 3.1.[80] Vibrational frequencies in the calculated absorption spectra were scaled by 0.94. Calculated intensities for $TMA\cdot(H_2O)_{2,3}$ were convolved with a 15 and 30 cm^{-1} fwhm Lorentzian for the 3680−3900 and 3000−3680 cm^{-1} regions, respectively. For $TMA^+\cdot(H_2O)_4$, 15 and 70 cm^{-1} fwhm Lorentzians were used for these two regions. Zero-point energies as well as enthalpy and entropy corrections were calculated using unscaled frequencies. The structures and energetics of an isolated water molecule and of water dimer were calculated similarly from MP2/6-31++G(d,p) optimized structures.

Results

Calculated Structures. Candidate low-energy structures identified for $TMA^+\cdot(H_2O)_{1-4}$ are shown along with their relative Gibbs free energies at 0/133/298 K in Figure 1. Only one stable structure (**1**) was found for $TMA^+\cdot(H_2O)_1$. This structure has a

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C_s geometry in which the oxygen atom of the water molecule accepts a weak methyl hydrogen bond from each of three methyl groups (H$\cdots$O bond lengths 2.4–2.6 Å) and coordinates to a "face" of the tetrahedron formed by the four TMA$^+$ methyl groups. Initial structures in which the water molecule is at a "vertex" or along an "edge" of the TMA$^+$ tetrahedron either minimized to this structure or did not converge.

Two stable structures were identified for TMA$^+\cdot(H_2O)_2$. In one structure (**2nhb**), the two water molecules are bound to two "faces" of the TMA$^+$ tetrahedon and do not hydrogen bond to each other. In the second structure (**2hb**), one water molecule accepts one methyl hydrogen bond (2.3 Å) from each of two methyl groups and donates a hydrogen bond to the second water molecule, which accepts a methyl hydrogen bond (2.6 Å) from a third methyl group. The O–H$\cdots$O angle is 159°, as compared to 175° for an isolated water dimer at the same level of theory, and the O$\cdots$O distance measures 2.81 Å, indicating a strong, slightly perturbed water–water hydrogen bond. Structure **2hb** is more stable than structure **2nhb** at low temperature, but **2nhb** is more stable at 298 K, analogous to results reported for Cs$^+\cdot(H_2O)_2$.[36]

Five stable structures within ~10 kJ/mol of each other were identified for TMA$^+\cdot(H_2O)_3$, although additional structures likely exist. Structure **3dc**, in which the water molecules are hydrogen-bound in a "daisy-chain," is lowest in energy and has a geometry for the two water molecules closest to the TMA$^+$ similar to that of structure **2hb**. The third water molecule in **3dc** lies 4.4 Å away from the nearest methyl hydrogen, clearly occupying an outer solvent shell, and accepts a strong, essentially ideal hydrogen bond (O$\cdots$O distance 2.80 Å, O–H$\cdots$O bond angle 177°). In structure **3ring**, each water molecule accepts and donates one hydrogen bond to form a ring-like structure bound to a face of the TMA$^+$ tetrahedron. Each of the water–water hydrogen bonds measures 2.78 Å and 139°, indicating strong but highly perturbed hydrogen bonding compared to isolated water dimer. Structure **3DD** is very similar to **3dc**, except that the outer-shell water molecule accepts a hydrogen bond from the edge-bound water molecule, yielding a structure with a central donor–donor water molecule. Structure **3AA** has two inner-shell water molecules and one outer-shell water molecule, which accepts a nearly ideal hydrogen bond (2.92 Å and ~170°) from each of the inner shell water molecules and lies 4.4 Å from the nearest methyl hydrogens. Structure **3nhb**, analogous to **2nhb**, with the three water molecules bound to three different faces of the TMA$^+$ tetrahedron, was found to be similar in energy to **3AA** at 0 and 133 K and nearly isoenergetic with **3dc** at room temperature.

Two structures were calculated for TMA$^+\cdot(H_2O)_4$: **4(3 + 1)**, in which one water molecule in a structure similar to **3ring** donates a nearly ideal hydrogen bond to an outer-shell water molecule, and **4ring**, in which the water molecules each accept and donate one hydrogen bond to another water molecule. In structure **4ring**, one of the water molecules is not directly associated with any methyl hydrogens. A similar structure, in which the 4-member ring is bound to an edge of the TMA$^+$ tetrahedron with each oxygen atom coordinated to one methyl hydrogen, did not converge upon initial geometry optimization and was not pursued at the MP2 level of theory. The water–water hydrogen bond lengths and angles in **4ring** all measure 2.75 Å and between 154° and 158°, indicative of stronger, more ideal hydrogen bonds than those in either **3ring** or **4(3 + 1)**. Structure **4ring** is significantly more stable than **4(3 + 1)**. No other structures with single-acceptor water molecules were investigated, because no corresponding band at ~3640 cm^{-1} was observed in the experimental spectrum.

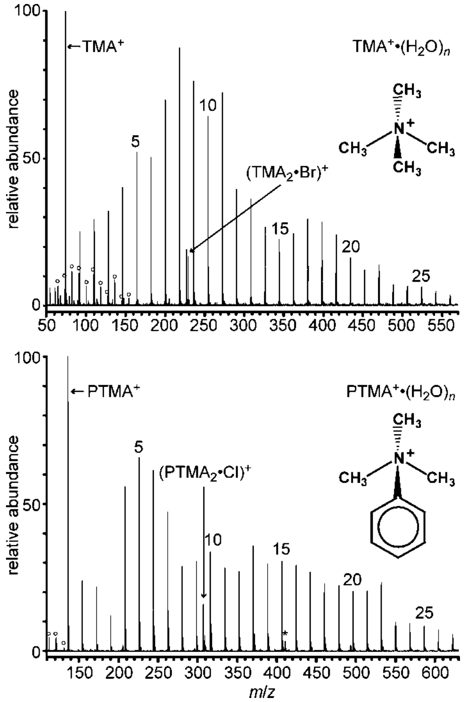

Figure 2. Electrospray ionization spectra of TMA$^+$ and PTMA$^+$ from aqueous solution. Circles (°) above peaks indicate harmonics, and the asterisk (*) denotes a noise peak.

ESI Mass Spectra and Cluster Stability. Hydrated ions can be readily formed by electrospray ionization (ESI),[81,82] and the extent of hydration can be changed by varying a number of parameters.[77] Typical ESI mass spectra of TMA$^+$- and PTMA$^+$-water clusters measured under identical conditions are shown in Figure 2. The most significant difference in the hydration of these two ions is the unusually low abundance of PTMA$^+\cdot(H_2O)_3$ compared to the abundance of the adjacent clusters. TMA$^+\cdot(H_2O)_{11}$ is unusually abundant under a wide range of conditions.

Because "magic numbers" in cluster mass spectra can occur either because a cluster is especially stable, or because an adjacent cluster is especially unstable, the cluster stabilities were investigated using BIRD.[78,83,84] The 133 K BIRD unimolecular rate constants for TMA$^+\cdot(H_2O)_{1-8}$ and PTMA$^+\cdot(H_2O)_{1-8}$ are shown in Figure 3. These rate constants increase monotonically for TMA$^+\cdot(H_2O)_{1-8}$ with increasing cluster size, consistent with the absence of any magic numbers for these cluster sizes. In contrast, both PTMA$^+\cdot(H_2O)_4$ and PTMA$^+\cdot(H_2O)_7$ are more stable than adjacent clusters. Direct comparison in these rate constants for TMA$^+$ versus PTMA$^+$ is complicated by the different number of vibrational modes that can exchange radiation with the blackbody field[83,84] for these ions. The small differences in the BIRD rate constant trends for TMA$^+\cdot(H_2O)_{1-8}$ and PTMA$^+\cdot(H_2O)_{1-8}$ indicate that the sequential water binding

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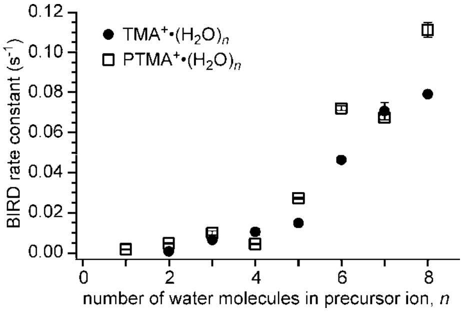

Figure 3. BIRD rate constants for $TMA^+{\bullet}(H_2O)_n$ and $PTMA^+{\bullet}(H_2O)_n$ at 133 K as a function of *n*. Error bars correspond to one standard deviation in the rate constant values.

Table 1. Calculated Binding Energies (Δ*H* kJ/mol) for the Reaction $TMA^+{\bullet}(H_2O)_n \rightarrow TMA^+{\bullet}(H_2O)_{n-1} + H_2O$

n	Δ*H* at 0 K	Δ*H* at 133 K	Δ*H* at 298 K
1	44	45	44
2	43	44	35
3	41	42	46
4	51	54	54

energies for these two ions differ slightly, due to interaction of water molecules with the phenyl ring of $PTMA^+$ or partial diffusion of the positive charge onto the phenyl ring.

Sequential Water Binding Energies and Photodissociation. Sequential water binding energies for $TMA^+{\bullet}(H_2O)_{0-4}$ were calculated from the lowest-energy structures for $TMA^+{\bullet}(H_2O)_{0-4}$ (Table 1). There is no significant trend in water binding energy with cluster size. The 298 K binding energies calculated for the first and fourth water molecules are 44 and 54 kJ/mol, respectively. These results are consistent with the measured 298 K binding energy of 38 kJ/mol and estimated value of 39 kJ/mol for the first and second water molecules, respectively.[85] By comparison, sequential binding energies at 298 K of 1 through 4 water molecules are 142, 109, 88, and 67 kJ/mol for Li^+, respectively, and 59, 50, 46, and 44 kJ/mol for Cs^+.[86] Sequential binding energies also decrease with cluster size for Me_3NH^+, from 61 to 42 kJ/mol for the first and third water molecule.[87] The lower values for $TMA^+{\bullet}(H_2O)_{1-3}$ are consistent with the greater extent of charge shielding expected for the large, nonpolar TMA^+ ion than for metal cations or Me_3NH^+. The binding energies for $TMA^+{\bullet}(H_2O)_{1-4}$ are all similar to the condensation energy of bulk water (44 kJ/mol).[88] The high, fourth water binding energy for TMA^+ can be attributed to the especially strong, cooperative water−water hydrogen bonds in the **4ring** structure, two of which must be broken for water molecule loss to occur. This increase in binding energy between $TMA^+{\bullet}(H_2O)_3$ and $TMA^+{\bullet}(H_2O)_4$ is consistent with a similar increase for neutral water clusters, for which the third and fourth sequential binding energies are calculated to be 34 and 40 kJ/mol, respectively, at 298 K.[12]

Because the sequential water binding energies to TMA^+ and $PTMA^+$ are so low, absorption of just one photon (∼36−47 kJ/mol for the range 3000−3900 cm^{-1}) can result in a significant increase in dissociation for these small clusters. Thus, the IRPD spectra may more closely reflect true absorption spectra as well as calculated spectra that include anharmonicity corrections than do action spectra where absorption of many photons is required to produce measurable dissociation.

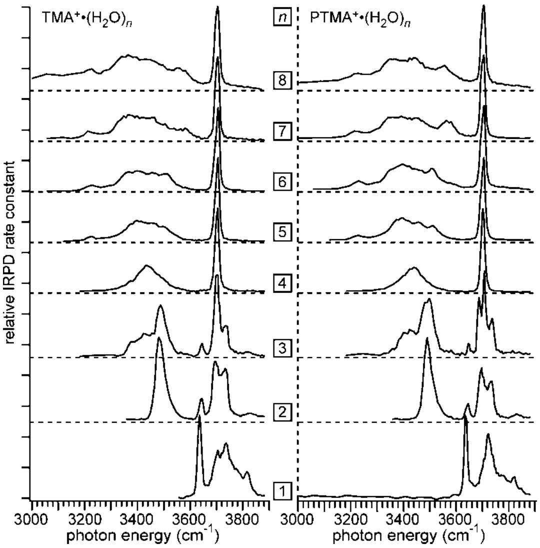

Figure 4. IRPD spectra of $TMA^+{\bullet}(H_2O)_{1-8}$ and $PTMA^+{\bullet}(H_2O)_{1-8}$ in the OH stretch region at 133 K

Infrared Action Spectra. Experimental spectra of $TMA^+{\bullet}(H_2O)_{1-8}$ and $PTMA^+{\bullet}(H_2O)_{1-8}$ in the OH stretch region (3000−3900 cm^{-1}) are shown in Figure 4, and peak assignments for these spectra are summarized in Table 2. The potential energy surface of a hydrogen bond can be very anharmonic, leading to difficulties in accurately calculating the absorption spectra of both water clusters and hydrated ions using a harmonic approximation.[89] CH stretch bands for all structures calculated here are extremely weak and occur at ∼3100 cm^{-1}, substantially lower in frequency than all of the peaks observed in the experimental spectra. The similarity of the TMA^+ and $PTMA^+$ spectra for each hydration state is striking and indicates that hydrations of these two ions are also similar. Because the phenyl group of $PTMA^+$ should prevent water molecules from completely surrounding this ion, the similar spectra of the hydrated $PTMA^+$ and TMA^+ even at $n = 5-8$ indicate that water does not isotropically solvate either ion at these cluster sizes. No strong perturbation due to the phenyl ring is evident, indicating that hydration of both ions up to this extent occurs on one "side" of the ion. Furthermore, the disappearance of acceptor-only (A-only) water symmetric stretch peaks near 3640 cm^{-1} for both ions with $n \geq 4$ suggests that hydration is contiguous and "closed," that is, all water molecules in clusters of these sizes donate at least one hydrogen bond to another water molecule, forming a single network of hydrogen-bonded water molecules. This situation is very different from hydration of metal ions, for which more "open" structures favoring peripheral A-only water molecules appear to dominate at small cluster sizes.[33,34,41,43,46,58]

A more detailed analysis of hydration of TMA^+ and $PTMA^+$ is possible from changes in these spectra as a function of the number of attached water molecules. Because precursor clusters are mass-selected, assignment of spectral bands in these spectra to distinct cluster sizes is unambiguous. Comparison of these

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Table 2. Observed OH Stretching Vibrations for $TMA^+ \cdot (H_2O)_n$ and $PTMA^+ \cdot (H_2O)_n$ and Assignments.

$TMA^+ \cdot (H_2O)_n$			$PTMA^+ \cdot (H_2O)_n$		
n	frequency (cm^{-1})	mode	n	frequency (cm^{-1})	mode
1	3815	comb. band	1	3815	comb. band
	3718	asym		3721	asym
	3634	sym		3634	sym
2	3820	comb. band	2	3822	comb. band
	3732	asym		3732	asym
	3696	free, AD		3696	free, AD
	3644	sym		3644	sym
	3480	HB, AD		3488	HB, AD
3	3732	asym	3	3735	asym
	3701	free, chain AD or cyclic AD		3708, 3685	free, chain AD or cyclic AD
	3644	sym		3644	sym
	3480	HB, cyclic AD		3488	HB, cyclic AD
	∼3350−3500	HB, chain AD		∼3350−3500	HB, chain AD
4	3704	free, cyclic AD	4	3701	free, cyclic AD
	3430	HB, cyclic AD		3438	HB, cyclic AD
5,6	3704	free, AD and AAD	5,6	3704	free, AD and AAD
	∼3300−3550	HB, AD		∼3300−3550	HB, AD
	3230	HB, AAD or bend overtone		3228	HB, AAD or bend overtone
7,8	3704	free, AD and AAD	7,8	3704	free, AD and AAD
	∼3500−3550	free/HB, ADD		∼3500−3550	free/HB, ADD
	∼3300−3500	HB, AD		∼3300−3500	HB, AD
	<3250	HB, AAD or bend overtone		<3250	HB, AAD or bend overtone

spectra to those of other hydrated ions and neutral water clusters as well as computed spectra aids in the assignment of spectral bands.

Discussion

$TMA^+ \cdot (H_2O)_1$. The spectrum of $TMA^+ \cdot (H_2O)_1$ has two primary bands: an asymmetric stretch (a.s.) at 3700−3750 cm^{-1}, divided into two subbands, and a symmetric stretch (s.s.) at 3634 cm^{-1}. The splitting between the two a.s. subbands is 28 cm^{-1} and may be attributable to two different water-binding structures for the complex or to rotational structure due to the weakly hindered motion of the water molecule with respect to the TMA^+ ion. Because no other stable structures were identified for this complex other than **1** (*vide supra*), the latter seems more likely. A band origin for the a.s. is estimated to be ∼3718 cm^{-1} from the average of these two frequencies. This is in good agreement with the a.s. band of $PTMA^+ \cdot (H_2O)_1$, which occurs as a singlet at 3721 cm^{-1}. Several factors contribute to the broadening of the $TMA^+ \cdot (H_2O)_1$ a.s., including the line width of the laser (∼3 cm^{-1}), finite temperature effects, the small axial rotational constant of the complex, a low barrier for rotation of the water molecule about the N−O axis, and possibly lifetime broadening due to rapid predissociation. Similar broadening of an a.s. has been observed for singly hydrated alkali metal cations[36−40] as well as $NH_4^+ \cdot H_2O$.[54] The sideband at 3815 cm^{-1} which overlaps with the a.s. is consistent with a combination band[58] arising from simultaneous excitation of the water a.s. and a low-frequency mode of the same symmetry in which, among other possibilities, the water molecule oscillates in the mirror plane of the complex and perpendicular to the N−O axis (∼65 cm^{-1} at the MP2/6-31++G(d,p) level of theory).

The OH a.s. of $TMA^+ \cdot (H_2O)_1$ (3718 cm^{-1}) is slightly red-shifted relative to that of an isolated water molecule (3756 cm^{-1}). By comparison, the a.s. band origin of $M^+ \cdot (H_2O)_1 \cdot Ar$, M = Li, Na, K, and Cs is at 3696, 3707.0, 3710.0, and 3711.5 cm^{-1}, respectively.[35,37−39] The smaller shift for $TMA^+ \cdot (H_2O)_1$ compared to that of $M^+ \cdot (H_2O)_1 \cdot Ar$ indicates that the magnitude of charge transfer from the water molecule to the ion is significantly less for $TMA^+ \cdot (H_2O)_1$ than for the alkali metal ions. This is consistent with the substantially higher water binding energies at 298 K of $M^+ \cdot (H_2O)_1$, which are greater than that of $TMA^+ \cdot (H_2O)_1$ by 98 and 4 kJ/mol, for Li^+ and Cs^+, respectively.[86]

The s.s. band of $TMA^+ \cdot (H_2O)_1$ at 3634 cm^{-1} is also red-shifted relative to that an of isolated water molecule (3657 cm^{-1}). A similar ∼22 cm^{-1} red-shift of the s.s. occurs for $M^+ \cdot (H_2O)_1 \cdot Ar$, M = Li, Na, K, and Cs, where the correlation between the red-shift of the s.s. band and water binding energy as a function of metal ion size is very weak or absent.[37−39] Such a shift is notably smaller than that for singly hydrated ammonium, for which the s.s. band appears at 3610 cm^{-1}, likely due to the strong ionic hydrogen bond.[54] The frequencies of both the a.s. and s.s. for $TMA^+ \cdot (H_2O)_1$ are quite close to those of the water molecule in the spectrum of singly hydrated, protonated valine (3725 and 3640 cm^{-1}, respectively), where the water molecule is attached to the ammonium group, whose effective charge is lowered due to solvation by the carboxylic acid carbonyl oxygen.[60]

$TMA^+ \cdot (H_2O)_2$. The OH stretch spectrum of $TMA^+ \cdot (H_2O)_2$ has bands at 3480, 3644, 3696, and 3732 cm^{-1}. The 3644 and 3732 cm^{-1} bands are consistent with the stretch modes of an A-only water molecule and are significantly blue-shifted from the corresponding bands of $TMA^+ \cdot (H_2O)_1$, consistent with reduced charge transfer for this more extensively hydrated ion. Water molecule a.s. fundamentals at lower frequencies have been observed in ion−water clusters even for A-only water molecules outside the first solvation shell of the ion,[33−35,40,46,53] indicating a greater degree of charge transfer for such species. Thus, it is very likely this A-only water molecule in $TMA^+ \cdot (H_2O)_2$ does not interact strongly with the TMA^+ ion. The 3480 and 3696 cm^{-1} bands in the $TMA^+ \cdot (H_2O)_2$ spectrum are both too red-shifted to be A-only water molecule stretches and are instead attributed to acceptor−donor (AD) hydrogen-bonded (HB) and free OH stretches, respectively.

The spectra clearly show that the two water molecules in $TMA^+ \cdot (H_2O)_2$ interact via a single hydrogen bond for a majority of the ion population, i.e., water−water bonding is favorable over direct solvation of TMA^+ by two A-only water molecules.

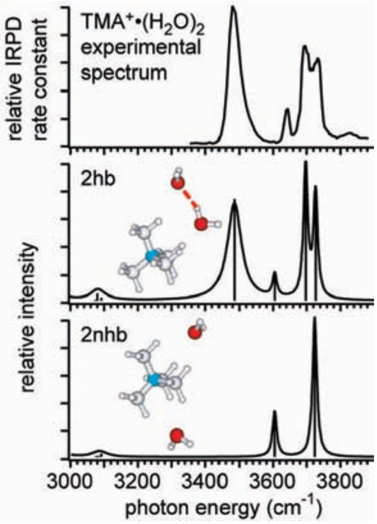

Figure 5. IRPD spectrum and MP2/6-31++G(d,p) calculated spectra for candidate structures of $TMA^+ \cdot (H_2O)_2$ in the OH stretch region.

A contribution from a structure with no water−water hydrogen bonding, such as **2nhb** (Figure 5), cannot be ruled out, because the a.s. and s.s. bands of the two water molecules are expected to fall in the same regions as those observed in the experimental spectrum. However, the intense HB band at 3480 cm^{-1} indicates that any contribution from such a structure must be small. This result is consistent with the calculations that indicate structure **2hb** is slightly lower in energy than **2nhb** at 133 K.

In comparison, water molecules bind on opposite sides of the alkali metal cation in $M^+ \cdot (H_2O)_2$ with and without an Ar tag.[34,35] Notably, the AD hydrogen-bound OH stretch of $TMA^+ \cdot (H_2O)_2$ lies further to the red than that of the HB stretch band in the spectrum of $Cs^+ \cdot (H_2O)_3 \cdot Ar$, which was assigned to a structure with a cyclic water trimer in which all of the water molecules are AD.[35] This indicates that the hydrogen bond between the two water molecules in $TMA^+ \cdot (H_2O)_2$ is stronger than those in $Cs^+ \cdot (H_2O)_3 \cdot Ar$, in agreement with the nearly ideal water−water hydrogen bond length and angle calculated for structure **2hb**. There is also a broad combination band at 3820 cm^{-1}.

It has been suggested that the "onset of water−water hydrogen bonding is a clear indication of the cation coordination number," by which definition the coordination number of Li^+, Na^+, and K^+ has been determined to be 4, and that of Cs^+ is 3.[34] The clear preference for structure **2hb** over **2nhb** observed here for TMA^+ indicates that, by this definition, the gas-phase coordination number of TMA^+ is 1 at 133 K.

$TMA^+ \cdot (H_2O)_3$. The spectrum of $TMA^+ \cdot (H_2O)_3$ has a broad, flat band between 3350 and ∼3500 cm^{-1}, superimposed with a sharp peak at 3488, and there are three more bands at 3644, 3701, and 3732 cm^{-1}. The 3644 and 3732 cm^{-1} bands are consistent with an A-only s.s. and a.s., respectively, and are essentially identical in frequency and relative intensity to the A-only peaks of $TMA^+ \cdot (H_2O)_2$. These bands indicate that the water molecules exist in three significantly different hydrogen-bonding environments. The intensity of the 3701 cm^{-1} peak relative to that at 3732 cm^{-1} is roughly double that of the AD free OH stretch to the A-only a.s. in the spectrum of $TMA^+ \cdot (H_2O)_2$, suggesting that the 3701 cm^{-1} peak may be a superposition of two or more closely spaced peaks. The intensity of the peak at 3488 cm^{-1} relative to that at 3732 cm^{-1} is also nearly identical to that of the AD-bound OH stretch versus the A-only a.s. in the $TMA^+ \cdot (H_2O)_2$ spectrum, suggesting that one of the superimposed peaks underlying the 3701 cm^{-1} feature is due to the free OH stretch of an AD water molecule in nearly the same hydrogen-bonding environment as that in $TMA^+ \cdot (H_2O)_2$. The more red-shifted broad band between 3350 and ∼3500 cm^{-1} and the remaining constituent peak underlying the 3701 cm^{-1} feature are assigned respectively as the HB and free OH stretches of water molecules that donate more linear hydrogen bonds.

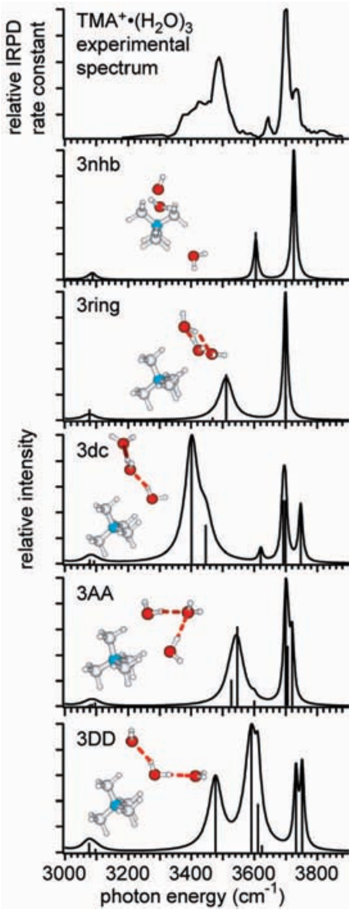

Figure 6. IRPD spectrum and MP2/6-31++G(d,p) calculated spectra for candidate structures of $TMA^+ \cdot (H_2O)_3$ in the OH stretch region.

Spectra of the candidate low-energy structures (Figure 1) are compared to the IRPD spectrum in Figure 6. The A-only bands in the $TMA^+ \cdot (H_2O)_3$ spectrum indicate the presence of a chain-like structure, such as **3AA** and **3dc**, which both have A-only and AD water molecules. The calculated spectrum for structure **3dc** is consistent with experiment, especially in the s.s. region. The HB stretches of the two AD water molecules are strongly coupled, and the floppiness of structure **3dc** may contribute to the observed s.s. broadening from 3350 to ∼3500 cm^{-1} in which the two HB stretches are indistinguishable. For structure **3AA**, the small frequency difference for the two AD symmetric and asymmetric stretches is attributable to the slight asymmetry in the way the two AD molecules bind to the methyl groups of the TMA^+ ion. This structure has no bands below 3500 cm^{-1}, and the A-only s.s. at 3600 cm^{-1} is a poor match to experiment. Thus, it is unlikely that this structure contributes substantially to the ion population. The calculated spectrum of structure **3ring** is consistent with a HB stretch occurring near 3500 cm^{-1} and a strong free OH stretch near 3700 cm^{-1}. Thus, although the frequency of the prominent HB feature for **3ring** is blue-shifted by ~22 cm^{-1} from the experimental peak 3488 cm^{-1}, these results suggest that this structure is also present. Added IRPD intensities of **3ring** and **3dc** account for the band intensities in the measured spectrum, consistent with the presence of significant populations of both structures. A small population of structure **3nhb** could also be present.

In comparison, an extensive computational study by Mó et al. of neutral water trimers indicates that the “homodromic” cyclic form, in which each water molecule accepts and donates one hydrogen bond, is most stable.[90] Several low-energy neutral water trimer conformations were found that include one or more double-donor water molecules. Because double-donor stretches observed in spectra of both neutral water and hydrated ionic species consistently appear blue-shifted relative to AD HB stretch peaks, it is unlikely that $TMA^+\cdot(H_2O)_3$ conformers analogous to these neutral water trimer conformers, such as **3DD**, contribute substantially to the experimental spectrum.

For $M^+\cdot(H_2O)_3\cdot Ar$, M = Li, Na, and K, structures with no hydrogen bonding are most stable, and a homodromic, cyclic structure dominates for M = Cs.[35] In the spectra of these complexes without Ar tags, this cyclic structure occurs only for M = Cs, where its OH stretches are dominated in intensity by structures with fewer water−water hydrogen bonds.[34] No structures analogous to **3dc** are observed for these triply hydrated alkali metal cations, with or without Ar tags.[34,35] Although the relatively small red-shifts in the A-only OH stretches for $TMA^+\cdot(H_2O)_{1-3}$ strongly indicate that interaction of the water molecules with the ion in these complexes is significantly weaker than for $M^+\cdot(H_2O)_{1-3}\cdot Ar$, M = Li, Na, and K, and for $M^+\cdot(H_2O)_{1-3}$, M = Li, Na, K, and Cs, the interaction of the water molecules with TMA^+ is strong enough to stabilize a chain-like water trimer over the cyclic form favored for a neutral water trimer. This chain-like water trimer has a large dipole moment and is calculated to be more stable than the homodromic, cyclic structure, in a weak electric field.[91] The greater propensity for TMA^+ to stabilize the chain-like structure compared to alkali metal cations may be attributed to the weaker interaction of the water molecules with TMA^+, enabling the water molecules to begin populating an outer solvation shell even in the $TMA^+\cdot(H_2O)_3$ complex.

$TMA^+\cdot(H_2O)_4$. Experimental and calculated spectra for $TMA^+\cdot(H_2O)_4$ are shown in Figure 7. The spectrum of $TMA^+\cdot(H_2O)_4$ is greatly simplified and has only two features: a nearly symmetrical, broad (fwhm ~100 cm^{-1}) band centered at ~3430 cm^{-1} and a sharp, narrow (fwhm ~15 cm^{-1}) band at 3704 cm^{-1}, consistent with the HB and free OH stretches, respectively, of four nearly identical AD water molecules. No A-only water stretch peaks are observed, which rules out many potential structures. The presence of four AD water molecules can be explained only by a $TMA^+\cdot(H_2O)_4$ structure in which water molecules are arranged in a homodromic, cyclic arrangement, as in structure **4ring**. Interestingly, the global minimum structure for neutral water tetramer is a homodromic, cyclic structure with dangling OH bonds pointing alternatingly above and below the plane of the ring (“*udud*”).[12,15,16,92] The HB stretch for this structure has been observed experimentally at 3416 cm^{-1},[2,7] remarkably close to that of $TMA^+\cdot(H_2O)_4$ (3430 cm^{-1}). For $TMA^+\cdot(H_2O)_4$, these dangling OH bonds all point away from the TMA^+ ion (“*uuuu*”) or lie in the plane of the ring (“*pppp*”), such that the hydrogen bonds are slightly perturbed from the *udud* structure of neutral water tetramer, and their HB stretches appear mildly blue-shifted. The *uuuu* and *pppp* structures for neutral water tetramer are expected to lie only ~9 and 12 kJ/mol above the *udud* structure,[16] respectively, and such structures can be preferentially stabilized by a weak electric field perpendicular to the water molecule ring.[91] Thus, a reordering of energies by as little as 9 kJ/mol occurs for water tetramer in the presence of TMA^+ versus in isolation.

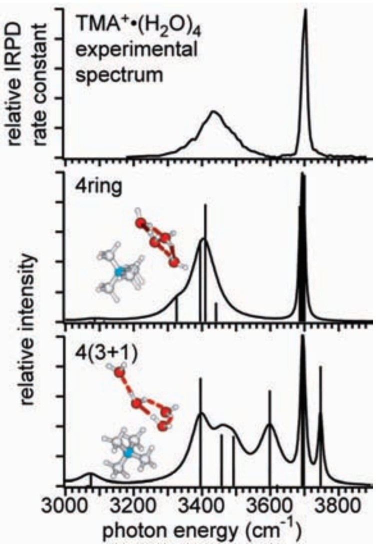

Figure 7. IRPD spectrum and MP2/6-31++G(d,p) calculated spectra for candidate structures of $TMA^+\cdot(H_2O)_4$ in the OH stretch region.

A similar *uuuu* structure analogous to **4ring** was deduced by Lisy and co-workers for $Cs^+\cdot(H_2O)_4\cdot Ar$,[35] which has a HB stretch feature centered at 3503.5 cm^{-1}. This band is significantly more blue-shifted from the HB stretch of neutral water tetramer (3416 cm^{-1}) than is the 3430 cm^{-1} band for $TMA^+\cdot(H_2O)_4$. The homodromic, cyclic structure for $Cs^+\cdot(H_2O)_4\cdot Ar$ is somewhat perturbed from that of neutral water tetramer, in agreement with its large observed HB stretch blue-shift. For $TMA^+\cdot(H_2O)_4$ structure **4ring**, the angles between the free OH bonds and the oxygen atom ring measure between 25° and 38°, very close to the calculated value (39.5°) for the *uuuu* structure of water tetramer.[16] These angles and the small observed HB stretch blue-shift indicate that the overall structure of the water molecule network in $TMA^+\cdot(H_2O)_4$ is much closer to that of neutral water tetramer than that in $Cs^+\cdot(H_2O)_4\cdot Ar$. By comparison, the cyclic water tetramer structure of $Cs^+\cdot(H_2O)_4$ without an Ar tag is not stable.[34]

The presence of the neutral water tetramer-like structure for $TMA^+\cdot(H_2O)_4$ indicates that, although the interaction of the bound water molecules with TMA^+ is strong enough to perturb the structure of $TMA^+\cdot(H_2O)_3$ relative to neutral water trimer, this perturbation is significantly less for $TMA^+\cdot(H_2O)_4$. The greater ring-strain energy of the cyclic structure in the trimer versus the tetramer results in a greater stabilization of the cyclic structure relative to a chain-like structure in the tetramer than in the trimer. This is also reflected in the large stabilization of structure **4ring** over structure **4(3 + 1)**. The latter structure does not make up a significant portion of the ion population, based on the absence of any A-only stretches in the experimental spectrum.

$TMA^+\cdot(H_2O)_{5-8}$. As for $TMA^+\cdot(H_2O)_4$, no peaks are observed between 3600 and 3657 cm^{-1} or above 3710 cm^{-1}, indicating that there is not a significant population of ions with

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A-only water molecules. Instead, a free OH band occurs at 3704 cm^{-1}, very close to that of neutral water tetramer and pentamer (both ~3714 cm^{-1}), which have homodromic, cyclic structures.[7] Significant photodissociation due to HB stretches occurs between 3300 and 3550 cm^{-1}, overlapping the region where AD HB stretches for neutral water pentamer have been observed (~3360 cm^{-1}, fwhm ~35 cm^{-1}).[7] Comparison of this spectrum to that of $TMA^+\cdot(H_2O)_2$ suggests that much of the photodissociation between ~3470 cm^{-1} and 3550 cm^{-1} is due to the slightly perturbed HB stretch of one or more AD water molecules. Photodissociation between 3300 and 3470 cm^{-1} can be assigned to the HB stretches of more ideally and strongly hydrogen-bound AD water molecules. The spectra of $TMA^+\cdot(H_2O)_{5,6}$ thus indicate substantial populations of slightly perturbed homodromic, cyclic water pentamer and hexamer structures, respectively, and similarly hydrogen-bonded water molecules are present for $TMA^+\cdot(H_2O)_{7,8}$. The HB stretch peak of isolated cyclic water hexamer has not yet been identified experimentally, but the striking similarity of $TMA^+\cdot(H_2O)_{5,6}$ suggests that this peak may not be substantially red-shifted from that of the pentamer, in agreement with results for cyclic water hexamer in liquid helium droplets.[21]

Significant contributions from water network structures other than homodromic, cyclic pentamer, and hexamer are also apparent from the spectra. The broader peak shape in both spectra compared to that observed for $TMA^+\cdot(H_2O)_4$ suggests that the AD water molecules in at least some of the $TMA^+\cdot(H_2O)_{5-8}$ population exist in a less symmetrical environment than the cyclic water tetramer in $TMA^+\cdot(H_2O)_4$. Along with the low-intensity peak at ~3230 cm^{-1}, consistent with the HB stretch of a water molecule that donates one and accepts two hydrogen bonds (AAD), the presence of nonequivalent AD water molecules indicates that substantial populations of these clusters have water molecules that are involved in more than two hydrogen bonds. Such structures indicate a transition from a quasi-planar arrangement of oxygen atoms in $TMA^+\cdot(H_2O)_4$ to more three-dimensional structures. This agrees well with calculations for isolated water oligomers, which suggest this transition takes place around $n = 6$.[12,14,92]

Low-energy three-dimensional water oligomer structures with no A-only water molecules include at least one ADD and one AAD water molecule. The OH stretches of an ADD water molecule should appear above 3500 cm^{-1}, based on assignments for large neutral water clusters.[6,8,24,26] No peaks are apparent in this region for $TMA^+\cdot(H_2O)_{5,6}$, although they are present for $TMA^+\cdot(H_2O)_{7,8}$. Unfortunately, a direct comparison with water hexamer cannot be made, because techniques previously used to obtain OH stretch spectra of isolated water hexamer are not sufficiently mass-selective to assign bands unambiguously to individual clusters.[4,7,21] The absence of HB stretches above 3500 cm^{-1} for $TMA^+\cdot(H_2O)_{5,6}$ may indicate a misassignment of neutral water oligomer spectra, or this mode may be unusually weak. In contrast, a band at ~3220−3230 cm^{-1} has been attributed in studies of neutral water oligomers to the HB stretch of AAD water molecules in an octahedral "cage" hexamer,[2−4,19,21] consistent with the peak at ~3230 cm^{-1} in the $TMA^+\cdot(H_2O)_{5-8}$ spectra. Photodissociation in this region may also be attributable to water-bending overtones, as suggested for other hydrated cations and anions,[27,45,47,93] although such overtone bands are expected to be weak.

The spectra of water pentamer and hexamer in the presence of TMA^+ differ somewhat from the inferred experimental spectra of isolated water pentamer and hexamer. This may be due to structures similar to, but not identical with, those of the neutral oligomers, or it may be due to misassignment of the neutral spectra to specific cluster sizes. The more extensive photodissociation below 3250 cm^{-1} as well as the HB stretch bands between 3500 and 3550 cm^{-1} observed for $TMA^+\cdot(H_2O)_{7,8}$ are consistent with three-dimensional, contiguous water networks with no A-only water molecules and perhaps several ADD and AAD water molecules. The $TMA^+\cdot(H_2O)_7$ spectrum is consistent with the reported spectrum of water heptamer,[6] albeit with much broader features and relatively less intensity for the ADD water molecules. Thus, $TMA^+\cdot(H_2O)_7$ may have a structure like that of neutral water heptamer, which has been assigned a quasi-prismatic structure,[6] and $TMA^+\cdot(H_2O)_8$ may be very similar.

$PTMA^+\cdot(H_2O)_{1-8}$. Whereas previous studies have shown that hydrogen-bonding of a water molecule to the π-system of an aromatic ring significantly perturbs the frequency of the π-bound OH stretching mode,[23] the single water molecule hydrates of TMA^+ and $PTMA^+$ are nearly identical, suggesting that the water molecule in $PTMA^+\cdot(H_2O)_1$ does not interact strongly with the phenyl ring. The coalescence of the two bands observed for the a.s. of $TMA^+\cdot(H_2O)_1$ into a single band at 3721 cm^{-1} for $PTMA^+\cdot(H_2O)_1$ supports the assigned a.s. band origin of ~3718 cm^{-1} for $TMA^+\cdot(H_2O)_1$. That the bands at ~3815 and ~3820 cm^{-1} observed for $TMA^+\cdot(H_2O)_{1,2}$, respectively, are also present for $PTMA^+\cdot(H_2O)_{1,2}$ confirms their assignment as vibrational combination bands rather than rotational features and shows that any perturbation caused by the phenyl ring is minor.

For neutral water dimer, the s.s. band of the acceptor water molecule has yet to be observed experimentally, although its position has been extrapolated from matrix data to be ~3660 cm^{-1},[6] relatively close to the peak clearly observed in both the $TMA^+\cdot(H_2O)_2$ and $PTMA^+\cdot(H_2O)_2$ spectra. The inability to observe this band for neutral water dimer has been attributed to low signal-to-noise in combination with the calculated 7−19 × lower intensity of this mode relative to that of the HB stretch mode.[94] For $TMA^+\cdot(H_2O)_2$ and $PTMA^+\cdot(H_2O)_2$, the ratios of the integrated relative intensities for the corresponding bands are ~4.8:1 and ~5.7:1, respectively, in reasonable agreement with the ratio calculated for water dimer.

Whereas the HB and A-only s.s. and a.s. bands for $TMA^+\cdot(H_2O)_3$ and $PTMA^+\cdot(H_2O)_3$ are essentially identical, the spectrum of $PTMA^+\cdot(H_2O)_3$ has two distinct bands at 3685 and 3708 cm^{-1} instead of a single band at ~3701 cm^{-1} as for $TMA^+\cdot(H_2O)_3$. These bands are attributed to AD free OH stretches. This difference suggests a greater disparity in the chemical environments of the two AD water molecules in $PTMA^+\cdot(H_2O)_3$ than in $TMA^+\cdot(H_2O)_3$. This may be due to the lower effective charge of the $PTMA^+$ ion, so that only the water molecule directly attached to the $PTMA^+$ ion experiences appreciable charge transfer, resulting in less red-shifting of the free OH stretch in the "middle" water molecule as compared to that of an AD molecule in a neutral water oligomer. Alternatively, it may be due to a very weak interaction with the phenyl ring that slightly perturbs the water hydrogen-bonding structure.

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Conclusions

Because OH stretch modes of water molecules depend strongly on both hydrogen-bonding environment and electric fields, infrared photodissociation spectroscopy of both neutral and ionic water-containing complexes in the spectral region from 3000−3900 cm^{-1} is a highly sensitive probe of structure. IRPD spectra of $TMA^+ \cdot (H_2O)_n$ and $PTMA^+ \cdot (H_2O)_n$, $n = 1-8$, show that these hydrophobic ions perturb the orientation of water molecules somewhat compared to that for neutral water molecule clusters for $n \leq 3$, but for complexes with $n \geq 4$, the structure of water in these ionic complexes is strikingly similar to that in neutral water clusters. Neutral water trimer forms a cyclic structure, whereas both a cyclic and a chain-like structure are observed for $TMA^+ \cdot (H_2O)_3$ and $PTMA^+ \cdot (H_2O)_3$. The chain structure has a larger dipole moment than a cyclic structure that is stabilized by the electric field of the ion. In contrast, a cyclic structure similar to that of neutral water tetramer is formed for complexes with four water molecules.

The OH stretch bands in these ionic clusters are only minimally shifted from those of neutral water molecule clusters and change only slightly with increasing cluster size. By comparison, these bands for hydrated alkali metal ions are considerably shifted from those of neutral water clusters at small cluster size. Spectra for $n \geq 4$ bear marked resemblance to those of the corresponding neutral water clusters and indicate that these ions are effectively excluded from the developing water cluster. These results strongly suggest that the disruption of the hydrogen-bond network in neutral water clusters by these hydrophobic ions is minimal in these larger clusters.

“Tagging” ions with noble gas atoms in IRPD spectroscopy can facilitate dissociation and can have a relatively small effect on ion structure. Using this technique, sharp spectral features can be obtained even for ions which would require the absorption of many photons to dissociate without the noble gas tag.[95] In our experiments, TMA^+ and $PTMA^+$ act as hydrophobic ion tags that minimally perturb the structures of water clusters at large sizes. Because ions can be readily stored, thermalized, and mass-selected, these results suggest that structures of sequentially larger water clusters could be obtained by “tagging” these clusters with hydrophobic ions, such as TMA^+ or $PTMA^+$. In contrast to clusters formed by some other methods where kinetic trapping of higher-energy structures may occur, ions in these experiments are equilibrated to the temperature of the ion cell over several seconds so that effects of temperature on water structure could be measured. Hydrophobic ion tagging may be particularly useful to obtain information about much larger water clusters, such as clathrates, for which precise mass selection of neutral clusters is not possible by other methods. In combination with noble gas atom tags, much higher resolution spectra of larger water clusters could be obtained. Such studies could also provide useful information about how water organizes around hydrophobic residues in proteins. Similarly, hydrophobic ion tags may be useful to obtain mass-selective IRPD spectra of other minimally perturbed neutral molecules or oligomers with unambiguous assignment of spectral bands to a given oligomer size.

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