Observation of Magic Numbers for $(ROH)_nH_3O^+$ Heteroclusters (R = CH_3, CH_3CH_2, $(CH_3)_2CH$, and $CH_3CH_2CH_2$): Implications for Cluster Ion Structure

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Abstract: We report in this paper nearly identical ion intensity distribution curves for ROH/water heterocluster ions for a variety of alcohols. The cluster ions $(ROH)_9(H_2O)H^+$ and $(ROH)_{10}(H_2O)_2H^+$ were found to display enhanced stability for all of the alcohols studied. Heteroclusters with $n < 7$ could *not* be observed upon ionization of neat alcohol clusters and were generally found with low intensity from the mixed alcohol/water clusters. We will introduce in this paper a structural model which can account for both the stability of the $(ROH)_9(H_2O)H^+$ ions and the loss of water from clusters with $n < 7$. This model implies a "proton switch" at a specific cluster size, leading to what may be thought of as a central H_3O^+ ion completely solvated by a ring (or chain) of hydrogen-bonded alcohols. The stable structure formed for $(ROH)_9(H_2O)H^+$ consists of three fused five-membered rings, each consisting of 4 ROH's and a H_3O^+ hydrogen-bonded together. This structure is closely related to that proposed by Castleman and co-workers for the dodecahedral water cluster $((H_2O)_{21}H^+)$.

I. Introduction

Cluster science has grown and evolved at a prodigious rate during the last decade or so. There are at present a considerable number of groups pursuing a diverse range of investigations involving a large number of differing cluster systems.[1-16] One common theme in almost all of these studies has been the importance of the cluster's structure and its relationship to the properties of the isolated gas-phase atoms or molecules of which the cluster is composed. A firm understanding of the cluster's structure and its relationship to the properties of the isolated gas-phase atoms or molecules of which the cluster is composed is highly desirable since the forces and interactions which determine the structures of the finite clusters also give rise to the structures and properties of the bulk (solid and liquid) phases of matter.[17]

Water, alcohols, and their mixtures represent an extremely important class of solvents due to the importance of the interaction of hydrogen bonding, and many investigations of the properties of these clusters have been undertaken, including several involving the alcohol/water mixed clusters.[4,6,7,12] The mass spectra of cluster ions for both neat water and alcohol clusters as well as mixed heteroclusters are dominated by sequences of protonated clusters (i.e., $(ROH)_nH^+$, $(H_2O)_nH^+$, and $(ROH)_n(H_2O)_mH^+$) generated via intracluster ion-molecule reactions.[1] An important question regarding the heterocluster ions concerns the fate of the proton in the cluster. On which (if either?) molecule is the proton localized within the cluster? Are the properties of the mixed heteroclusters best understood by considering the ionic core to consist of a protonated alcohol molecule, as might be predicted on the basis of the larger gas-phase proton affinity of the alcohol? Or is the system more complex, with the location of the proton dependent on both the size of the cluster and the nature of the alcohol?

Several $(M)_n(H_2O)_mH^+$ cluster ion systems have been investigated for which M has a greater proton affinity than water. These systems are characterized by an apparent ligand preference switch from M to H_2O at some particular cluster size.[4,6,8,11,12,20] For the M = $(CH_3)_2O$[5] or CH_3CN[18,19] systems, it has been suggested[5] that the switch in solvent preference is accompanied by a "proton switch" as well. The cluster ion distributions of these $(M)_n(H_2O)_mH^+$ cluster ions are characterized by strong magic numbers which are easily explained in terms of structures in which protonated water and water clusters form the ion core. This behavior seems to be most often encountered when M is unable to act as a proton donor. Castleman et al. have, quite recently, taken advantage of this fact to "titrate" the free hydrogens of the dodecahedral $(H_2O)_{21}H^+$ cluster through the use of trimethylamine, $(CH_3)_3N$, thus providing convincing evidence of the structure for protonated water clusters.[9] For the case where M = NH_3, however, it has been shown that ammonia[20] is highly preferred in the first solvation shell, while water is favored beyond the first solvent shell. In this system NH_4^+ is regarded as the central ion core and the preference switch arises as a result of a change from hydrogen bonding interactions in the first solvation shell to weaker electrostatic interactions beyond. NH_3 is favored in the first solvation shell because of its higher PA whereas H_2O is favored beyond the first solvation shell because of its higher dipole moment and its ability to hydrogen bond.

Alcohol/water clusters represent a case intermediate in nature since the alcohols are capable of acting as both proton acceptors and donors. The question of the energetics of stepwise solvation of the proton in mixed alcohol/water cluster ions has been addressed by Kebarle and co-workers[12] and the thermodynamics for clustering in both the methanol/water and ethanol/water systems has been studied via high-pressure mass spectrometry (HPMS).

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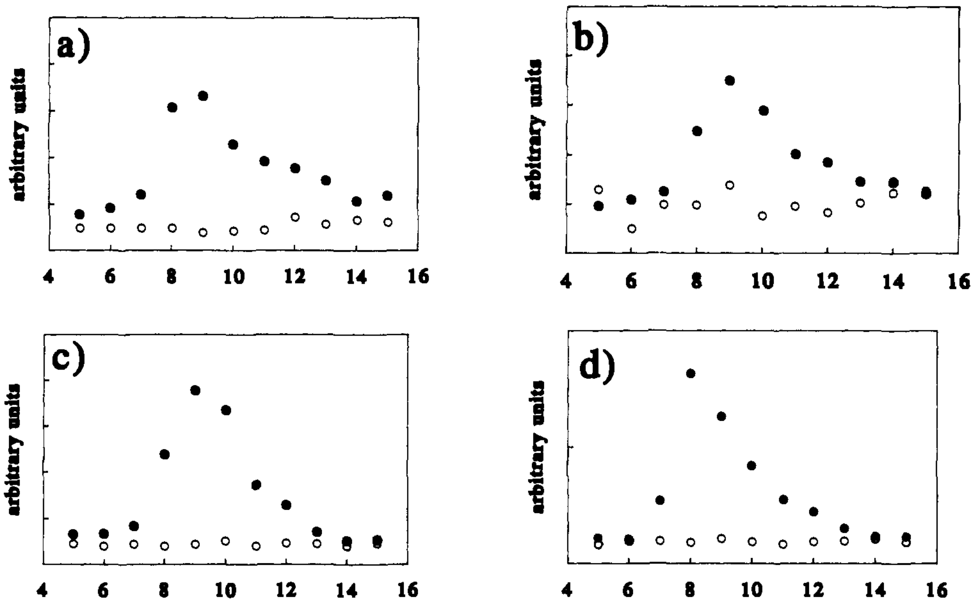

Figure 1. Plot of ion intensities vs cluster size for $(ROH)_n(H_2O)H^+$ at 50.0 eV electron energy for a neat alcohol expansion where ROH is (a) methanol, (b) ethanol, (c) *n*-propanol, and (d) 2-propanol. Solid circles represent the cluster ion intensity while the open circles represent typical background signal where no ion signal is observed (i.e., $(ROH)_n$ + 23 *m*/*z*).

In the size range of clusters amenable to study by HPMS ($n \leq 6$) they always found the alcohol to be the favored ligand. The degree to which the alcohol was favored was found to be a decreasing function of cluster size, implying that at some critical cluster size the addition of water to the protonated clusters would be favored over that of ROH. Kebarle et al. predicted this crossover point to occur at $n = 8$ for methanol and $n = 9$ for ethanol.

Stace and co-workers[4-6] have measured metastable dissociation branching ratios of a number of larger $(ROH)_n(H_2O)H^+$ clusters produced upon ionization of adiabatic expansions of alcohol/water vapor mixtures. They have found that water loss is the predominant loss channel for small cluster ions whereas the large clusters predominantly lose the alcohol. The point at which this switch in the dissociation behavior takes place again was determined to occur in the size range $n = 8$–10, depending on the particular alcohol; these determinations were not unambiguous, however, and errors of $n \pm 1$ were estimated.

We report in this paper nearly identical ion intensity distribution curves for cluster ions with the empirical formula $(ROH)_n(H_2O)H^+$ and $(ROH)_n(H_2O)_2H^+$ for several alcohols (methanol, ethanol, 1-propanol, and 2-propanol). Heterocluster ions, $(ROH)_9(H_2O)H^+$, were found to display enhanced stability for all of the alcohols studied. Mixed clusters with $n < 7$ could not be observed upon ionization of the neat alcohol clusters and were generally found with low intensity from mixed alcohol/water clusters. Ionization of mixed neutral clusters also gave rise to clusters of the type $(ROH)_n(H_2O)_2H^+$. The intensity distributions of these clusters all displayed a notable discontinuity at $n = 10$.

A structural model will be discussed which may account for both the stability of the $(ROH)_9(H_2O)H^+$ ions and the loss of water from clusters with $n < 7$. This model may be thought of as an H_3O^+ ion solvated by a ring of hydrogen-bonded alcohols. The stability of this structure comes from the formation of three fused five-membered rings, with each ring consisting of 4 ROH's and H_3O^+ hydrogen-bonded together. This structure is closely related to the structure observed for the dodecahedral water cluster $((H_2O)_{21}H^+)$, which is formed via hydrogen bonding of 12 fused five-member rings, solvating an H_3O^+ at the center.[9]

II. Experimental Section

The clusters were generated by expanding either a pure alcohol or a mixture of water and alcohol vapors in helium gas (Cryogenic Supply, 99.997%) through a 250-μm nozzle. The He carrier gas pressure was 2.0 atm for all experiments. In order to reduce the mixing ratio only a portion of the total carrier gas flow was directed through the reservoir containing the alcohol or alcohol/water mixtures. The diverted flow was then allowed to remix with the main flow of He prior to expansion. The alcohols utilized for these experiments were methanol (MeOH; 99.9% Fisher Scientific), ethanol (EtOH; 99.9% Quantum Chemical Corp.), 1-propanol (*n*-PrOH; 99.9% Fisher Scientific), and 2-propanol (*i*-PrOH; 99.9% J. T. Baker); the alcohols were used without further purification. Deionized water was used in preparing the alcohol/water solutions. Trimethylamine (TMA) was obtained in the form of a 23–25 wt % mixture with water (Aldrich). The alcohol/water solutions were prepared as ~19:1 (alcohol–water) volume mixtures. The ternary mixtures of TMA were prepared as ~2:1 (v/v) (methanol:water/TMA) mixture. All samples were subjected to several freeze–pump–thaw cycles to remove dissolved gases prior to each experiment.

The experimental setup has been described in detail previously[21] and consists of a continuous molecular beam cluster source of the Campargue design[22] coupled to a quadrupole mass spectrometer (Extrel C50, capable of unit resolution to 1400 amu). After being skimmed and collimated the neutral cluster beam passes into a collinear electron impact ion source where a fraction of the beam is ionized. All of the mass spectra presented herein were obtained at electron energies of 50 eV.

III. Results

$(ROH)_n(H_2O)H^+$ cluster ions were observed upon ionization of both neat alcohol and alcohol/water expansions. Figure 1 presents a portion of the ion intensity distributions of the $(ROH)_n(H_2O)H^+$ cluster ions observed from the neat expansions. The forms of the intensity distributions for all of the $(ROH)_n(H_2O)H^+$ ions from neat alcohol expansions were very similar and were found to be independent of electron energy down to 15 eV. Heteroclusters were observed only for $n \geq 7$, except in the cases of ethanol and the propanols where heterodimer ions, $(ROH)(H_2O)H^+$, were also observed. Figure 2 displays the intensity distributions of $(ROH)_n(H_2O)H^+$ observed from the mixed expansions. Addition of water leads to large increases in the intensity of the heterocluster ions, especially for methanol and ethanol, while the overall shape of the intensity distributions remains very similar and again independent of electron energy. The very large increases in the intensity of the $(ROH)_n(H_2O)H^+$ ions lead us to conclude that the observed intensity distributions arise as a consequence of the ion stabilities.

The ion intensity distributions displayed in Figures 1 and 2 either peak at or display enhanced intensity at $n = 9$ for methanol, ethanol, and 1-propanol while the 2-propanol distribution peaks at $n = 8$. In the case of 2-propanol, addition of water leads mainly

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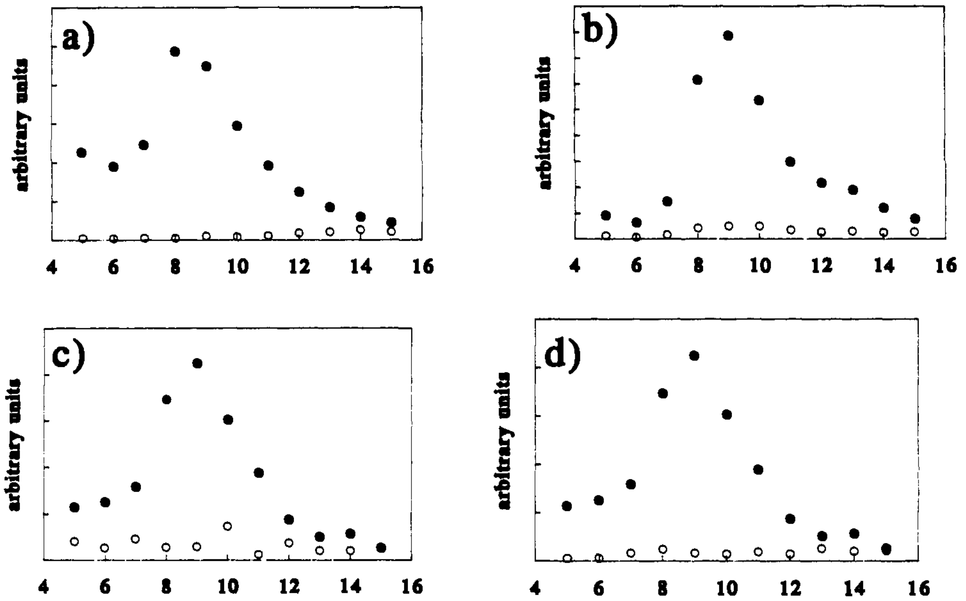

Figure 2. Plot of ion intensities vs cluster size for $(ROH)_n(H_2O)H^+$ at 50.0 eV electron energy for a 19:1 alcohol/water coexpansion where ROH is (a) methanol, (b) ethanol, (c) *n*-propanol, and (d) 2-propanol. Solid circles represent the cluster ion intensity while the open circles represent typical background signal where no ion signal is observed (i.e., $(ROH)_n + 23$ *m/z*).

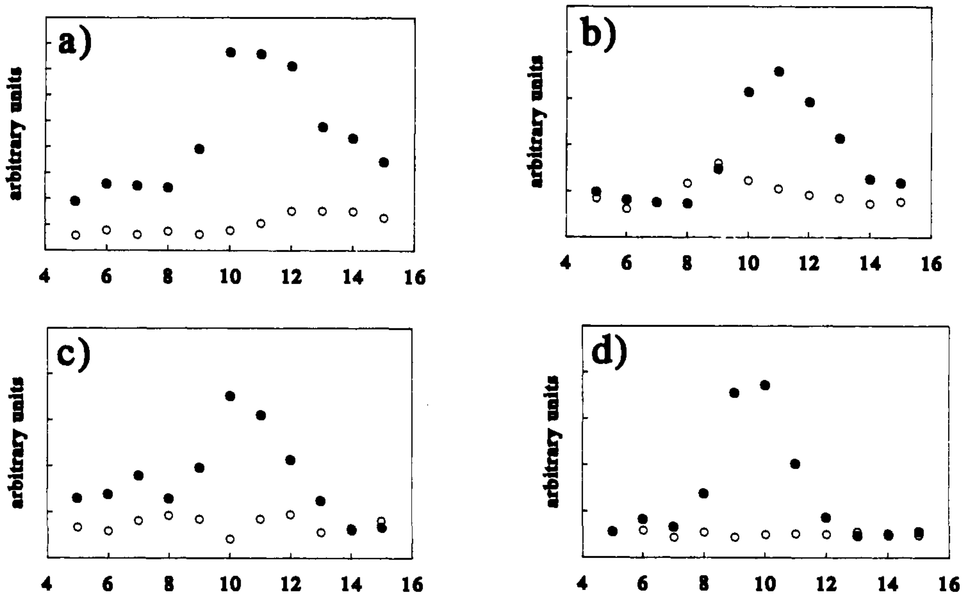

Figure 3. Plot of ion intensities vs cluster size for $(ROH)_n(H_2O)_2H^+$ at 50.0 eV electron energy for a 19:1 alcohol/water coexpansion where ROH is (a) methanol, (b) ethanol, (c) *n*-propanol, and (d) 2-propanol. Solid circles represent the cluster ion intensity while the open circles represent typical background signal where no ion signal is observed (i.e., $(ROH)_n + 23$ *m/z*).

to enhancement of the clusters with $n = 7$–9; these ions with $n > 9$ are not substantially enhanced.

Heterocluster ions containing two water molecules were obtained upon ionization of the alcohol/water mixtures (Figure 3). Once again, all of the distributions bear a close resemblance to each other. All of the $(ROH)_n(H_2O)_2H^+$ distributions display an anomaly at $n = 10$. For methanol, ethanol, and 1-propanol a sharp increase in ion intensity is observed between $n = 9$ and 10. In the case of 2-propanol, a sharp increase is observed between $n = 8$ and 9 while the intensity distribution peaks at $n = 10$. A very sharp decrease in ion intensity is observed between $n = 10$ and 11.

Lastly, we also report the results for a ternary mixture of trimethylamine (TMA = $(CH_3)_3N$), water, and methanol. The TMA (25% wt in water) was mixed with methanol in a 1:2 ratio. He at 2.0 atm of pressure was bubbled through a reservoir containing this mixture and expanded through our supersonic nozzle. We previously had observed the enhanced intensities of the $(ROH)_9H_3O^+$ and $(ROH)_{10}H_5O_2^+$ ions for the alcohol/water expansions. For the TMA/ROH/H_2O expansions, we now observe in Figure 4 enhanced intensities for the $(ROH)_7(H_3O)TMA^+$ and $(ROH)_8(H_5O_2)TMA^+$ ions. In both examples of mixed cluster ions where either a protonated water or water dimer was the central core ion, addition of a TMA molecule is accompanied by the loss of two methanol molecules.

IV. Discussion

As can be seen from Figures 1 and 2, the distributions of $(ROH)_n(H_2O)H^+$ ions arising from ionization of either neat alcohol or alcohol/water clusters are quite similar showing the same general intensity distributions for sizes $n \geq 7$. In the case of methanol clusters the distribution of $(CH_3OH)_n(H_2O)H^+$ clusters has been attributed to "size-selective" chemistry within the protonated alcohol clusters.[8] The protonated dimer ion is known to undergo a dehydration reaction giving rise to a protonated dimethyl ether ion

$$(CH_3OH)_2H^+ \rightarrow (CH_3)_2OH^+ + H_2O \qquad (1)$$

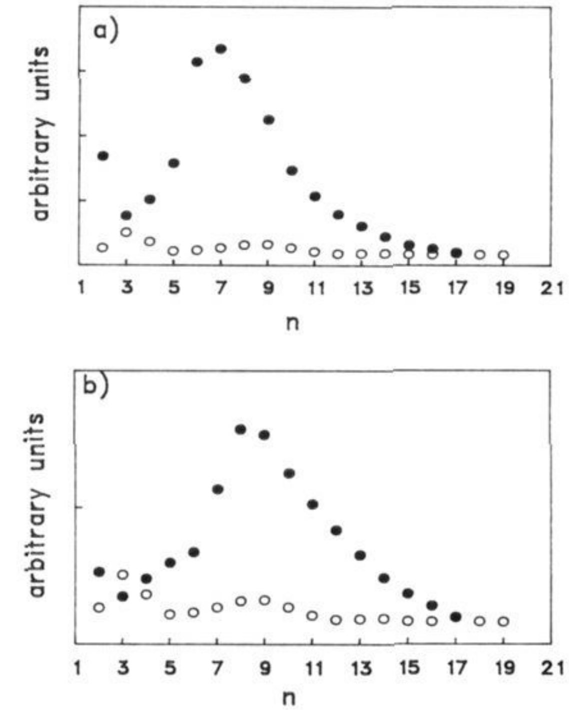

Figure 4. Plot of ion intensities vs cluster size for $(TMA)(CH_3OH)_n(H_2O)_mH^+$ at 50.0 eV electron energy for a 2:1 methanol/water–TMA coexpansion where (a) $m = 1$ and (b) $m = 2$. We note the appearance of prominent magic numbers for $(TMA)(CH_3OH)_7(H_2O)H^+$ and $(TMA)(CH_3OH)_8(H_2O)_2H^+$. Solid circles represent the cluster ion intensity while the open circles represent typical background signal where no ion signal is observed (i.e., $(ROH)_n$ + 23 m/z).

and is observed to be quenched in trimer and larger alcohol clusters. A new reaction channel, however, opens up in larger clusters which corresponds to loss of dimethyl ether and incorporation of the water into the cluster. The smallest cluster that was observed from this reaction is $(CH_3OH)_7(H_2O)H^+$. The smallest alcohol cluster that could be responsible for this reaction would be the protonated 9-mer

$$(CH_3OH)_9H^+ \rightarrow (CH_3OH)_7(H_2O)H^+ + (CH_3)_2O \quad (2)$$

The fact that reaction 1 is quenched in clusters larger than the dimer ion has been attributed to the fact that formation of the intermediate, a methyl-bound complex, is not facile in clusters larger than the dimer.[8] The implication of this reasoning, then, is that the formation of the intermediate necessary for reaction 2 is only facile in clusters of size $n \geq 9$.

The anomalies in the distributions of $(ROH)_n(H_2O)H^+$ clusters produced via ionization of neutral alcohol/water clusters most likely arise as a result of the intrinsic stabilities of the individual ion clusters. These results strongly suggest the possibility of a direct correlation between the structure of the $(ROH)_n(H_2O)H^+$ clusters and the size selective chemistry of the alcohol clusters. Mautner has measured the thermodynamics of clustering in the methanol/water system for small clusters[23] and explained his observations on the basis of the proton affinity difference between water and methanol. A protonated methanol would always be the central ion core of the cluster ions, such that on the basis of proton affinity alone CH_3OH will form stronger hydrogen bonds with itself than with water, forming an infinite hydrogen-bonding network. It was suggested that $(CH_3OH)_n(H_2O)H^+$ clusters then take the form of a $CH_3OH_2^+$ central ion with methanol molecules in the inner solvation shells and the water relegated to the outermost solvation shell, i.e. a chain of methanols with water at the end.

This model does not seem capable of explaining the ligand preference switch implied by the present experimental results and observed by Stace et al.[4,6] If the water molecules are always to be found in the outermost solvation shell, it is not at all clear why a preference switch takes place. To explain the ligand preference switch, Stace has suggested a structural model in which the methanol molecules hydrogen bond to form a chain; in his model, however, the water is placed in a non-hydrogen-bonding position near the ion core where it is bound by ion–dipole forces; water would be favored in such a position because of its higher dipole moment. It is expected that as methanol is added to positions further from the ion core the strength of the hydrogen bonds will decrease and the switch in ligand preference will then occur when the strength of the ion–dipole bond of water exceeds that of the terminal hydrogen bond.

Figure 5. Proposed structure for the $(CH_3OH)_9(H_2O)H^+$ cluster ion. This species is the most prevalent of all cluster ions in the series $(CH_3OH)_n(H_2O)H^+$ and is believed to be a H_3O^+ cation surrounded by a complete solvation shell of methanols. The dark circles correspond to carbon atoms, the shaded circles correspond to oxygen atoms, and the open circles are hydrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. This structure is somewhat "flattened" in order to highlight the hydrogen-bonding rings.

It is not clear, however, whether it is reasonable to expect the alcohol cluster ions to take the form of very long chains of molecules. A growing body of evidence suggests that ring structures are favored over long chains for a number of systems. In the case of *neutral* methanol clusters[14,15] there is evidence to suggest that cyclic structures are found for all clusters with $n \geq 5$. Large $(H_2O)_nH^+$ clusters[9,10] appear to be constructed of networks of rings which fuse into hollow spheres. The ligand preference switch encountered in the alcohol/water clusters could therefore reflect a transition from linear to ring structures. If the bonding outside of the ring is dominated by weaker electrostatic interactions, such as ion–dipole forces, water might be favored because of its higher dipole moment. The main difficulty with this hypothesis is that ring formation would appear to be energetically favorable for clusters as small as $n = 5$ and 6, yet the preference switch does not take place until $n \geq 7$. This model also does not provide any good explanation for the apparent stability of the $(ROH)_9(H_2O)H^+$ and $(ROH)_{10}(H_2O)_2H^+$ clusters.

As an alternative to the models considered above, we would suggest the structures shown in Figures 5–7 for the $(ROH)_9(H_2O)H^+$, $(ROH)_7(H_2O)H^+$, and $(ROH)_{10}(H_2O)_2H^+$ clusters. These structures differ from those discussed above in so much as they incorporate H_3O^+ or $H_5O_2^+$ ions as the core ion with the alcohols forming respectively 3 and 4 sets of fused five-membered rings via hydrogen bonding. The structural models proposed here, unlike those discussed above, readily explain the observed magic numbers. In addition, a proton affinity switch would readily explain the observed ligand preference switch since in the larger clusters water would become the core ion. As a result, the $(ROH)_7(H_2O)H^+$ cluster ion is first observed because it is the smallest cluster ion which can have an H_3O^+ core with an open

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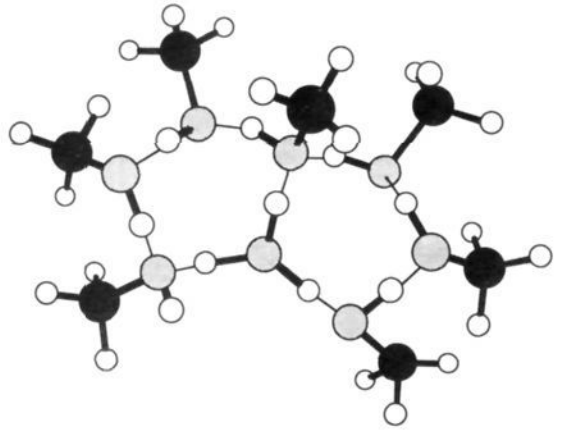

Figure 6. Proposed structure for the $(CH_3OH)_7(H_2O)H^+$ cluster ion. This species is the first of the cluster ions observed in the series $(CH_3OH)_n(H_2O)H^+$ and is believed to be a H_3O^+ cation surrounded by an incomplete ring of methanols, which are still capable of making 3 separate hydrogen bonds to the central cation. The dark circles correspond to carbon atoms, the shaded circles correspond to oxygen atoms, and the open circles are hydrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. This structure is somewhat "flattened" in order to highlight the hydrogen-bonding rings.

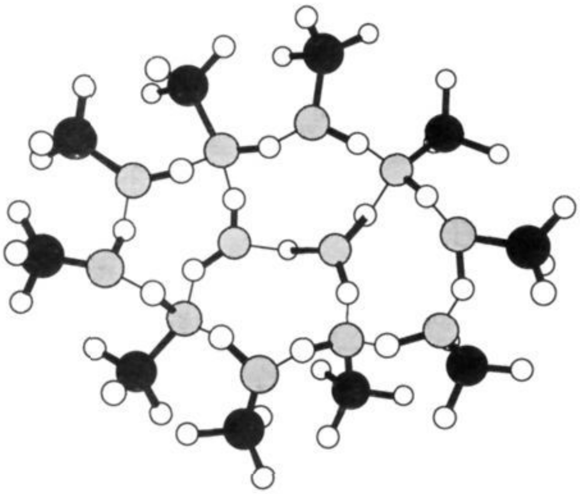

Figure 7. Proposed structure for the $(CH_3OH)_{10}(H_2O)_2H^+$ cluster ion. This species is the first of the cluster ions observed in the series $(CH_3OH)_n(H_2O)_2H^+$ and is believed to be a $H_5O_2^+$ cation surrounded by a complete solvation shell of methanols. The dark circles correspond to carbon atoms, the shaded circles correspond to oxygen atoms, and the open circles are hydrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines. This structure is somewhat "flattened" in order to highlight the hydrogen-bonding rings.

"ring" of alcohols completely solvating the 3 protons.

There is ample evidence to suggest that such proton affinity switches do take place in protonated cluster ions. Deakyne and co-workers[24] have studied the thermodynamics of clustering in the acetonitrile/water system. For this system it was shown that the $(CH_3CN)_2(H_2O)H^+$ ion undergoes a proton affinity switch, i.e. the ion may be considered to be $(CH_3CN)_2H_3O^+$ even though the proton affinity of CH_3CN is 21.7 kcal·mol^{-1} greater than that of water. This effect was attributed to the fact that in these systems the only way in which all of the components could be bound by strong hydrogen bonds is to incorporate a protonated water or water cluster as the central ionic moiety of the cluster. The cluster ion mass spectra of all these systems are characterized by prominent magic number ions, $(M)_n(H_2O)_mH^+$, when $n = m + 2$. This result is also best explained in terms of an intracluster proton-transfer reaction.

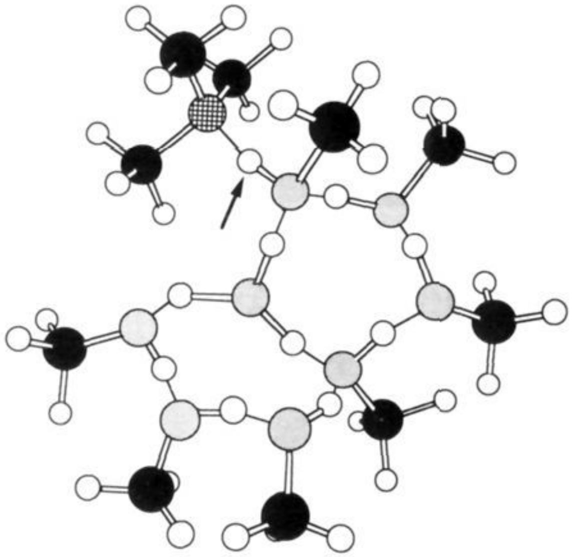

Figure 8. Proposed structure for the $(TMA)(CH_3OH)_7(H_2O)H^+$ cluster ion. The TMA molecule is hydrogen bonded to an available proton on the methanol (indicated by an arrow). The dark circles correspond to carbon atoms, the shaded circles correspond to oxygen atoms, the open circles are hydrogen atoms, and the crosshatched circles correspond to nitrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines.

The energetically favored structure for these clusters is thus the one that (1) maximizes the number of hydrogen bonds and (2) minimizes the distances between the alcohol molecules and the ion core. It is our contention that the overall structures of alcohol/water clusters are governed by the same principles which determine the structure of neat water clusters. Once again, one may expect a hydrogen-bond network constructed of fused five-membered rings to be favored. The magic numbers observed for alcohol/water clusters may be rationalized in terms of closed shell structures directly derived from the dodecahedral 20/21-mer of water clusters.[9,10]

In summary, the distributions of the $(ROH)_n(H_2O)H^+$ clusters all share three characteristics: (1) they all either peak or show an enhanced intensity at $n = 9$, (2) heterocluster ions are *only observed strongly for* $n \geq 7$, *and* (3) *this behavior is independent* of alcohol type up to isopropyl alcohol. Although it is possible to construct a number of structures for the $(ROH)_9(H_2O)H^+$ ions, it seems quite logical to consider the bonding in these clusters to be similar to that of the neat water clusters since the alkyl group only blocks one of the hydrogen-bonding sites. On this basis we propose that the $(ROH)_9(H_2O)H^+$ clusters possess the structure displayed in Figure 5. This structure effectively represents "half" of a dodecahedron.

We also note that since the alkyl groups are outside of the hydrogen-bonded rings, the identity of the alcohol does not affect the hydrogen bonding occurring around the H_3O^+ cation. This has been confirmed through the use of CPK models with which we have constructed models of $\{(CH_3)_2CHOH\}_9H_3O^+$ and observed that all the methyl groups can easily accommodate each other. As a result it is consistent with our proposed structure that it is independent of alcohol identity.

A similar situation is likely to pertain in the case of $(ROH)_n(H_2O)_2H^+$ clusters. The distributions of these ions are characterized by a magic number at $n = 10$. The structure proposed for these ions is given, for the case of methanol, in Figure 6. This structure assumes an $H_5O_2^+$ core ion solvated by a ring of methanol molecules in analogy to that proposed for $(ROH)_9(H_2O)H^+$.

To obtain some further, although indirect, structural evidence for the model presented, further experiments have been conducted with a ternary mixture of trimethylamine, water, and methanol.

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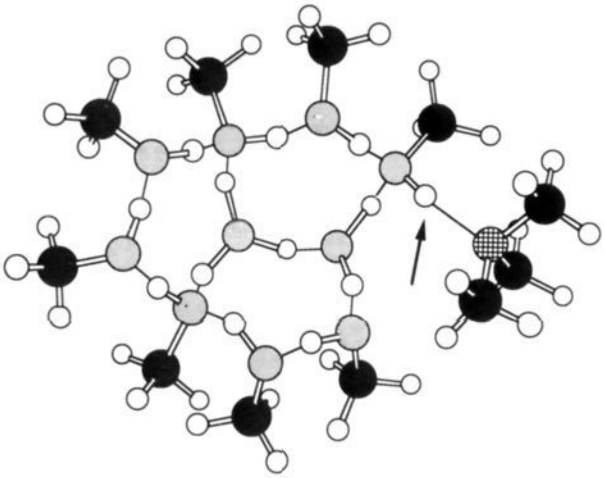

Figure 9. Proposed structure for the $(TMA)(CH_3OH)_8(H_2O)_2H^+$ cluster ion. The TMA molecule is hydrogen bonded to an available proton on the methanol (indicated by an arrow). The dark circles correspond to carbon atoms, the shaded circles correspond to oxygen atoms, the open circles are hydrogen atoms, and the crosshatched circles correspond to nitrogen atoms. Chemical bonds are indicated by "sticks" while hydrogen bonds are indicated by thin lines.

Because the trimethylamine molecule is such a good proton acceptor, one would expect the TMA's to selectively tie up any available hydrogens on the cluster ion. Castleman and co-workers[9] have demonstrated good success using this molecule to "titrate" their neat water clusters showing that indeed the TMA's do selectively bind to any available protons on the cluster ion structure. In contrast to the enhanced intensities we observed for $(ROH)_9H_3O^+$ and $(ROH)_{10}H_5O_2^+$ ions in the alcohol/water expansions, we now observe for the TMA/ROH/H_2O expansions enhanced intensities for the $(ROH)_7(H_3O)TMA^+$ and $(ROH)_8(H_5O_2)TMA^+$ ions (Figure 4). This is not inconsistent with our proposed model where the species with the higher proton affinity will be found close to the charge center. The magic number shifts shown in Figure 4 can be explained by invoking that the TMA being a good proton acceptor directly binds to the "dangling proton" on the methanol for both $(CH_3OH)_7H_3O^+$ and $(CH_3OH)_8(H_2O)_2H^+$ as shown in Figures 8 and 9.[25]

Lastly, direct comparison between the structures found for gas-phase cluster ions and the bulk solution phases is difficult. In terms of the solvation energies, it may be noted that the energy of the H_3O^+ ion solvated by methanols, as depicted in Figure 5, would be expected to be lower than if it was solvated by water molecules. This is a consequence of the greater polarizability of the methanol molecule.[23] Thus the structures presented here are not inconsistent with an increase in the free energy of solvation of the hydronium ion in alcohol solutions.

V. Conclusion

To summarize, we may draw some generalized conclusions concerning the factors that are important in determining the possible structures of a heterocluster ion: the proton will typically reside on the molecule which will maximize the amount of hydrogen bonding within the structure, regardless of proton affinities, provided that cation is completely solvated; structures constructed of fused five-membered rings can be expected to be favored since this geometry maximizes the number of hydrogen bonds and minimizes the number of "dangling" bonds, while maintaining favorable bonding geometries.

This work highlights the unique structural and chemical differences between gas-phase clusters and condensed-phase materials while suggesting that it is possible to construct models that may be applied to both the clustered and bulk condensed phases of matter. Such an understanding should prove useful in understanding not only the structure of matter but also its chemical reactivity. We are now actively pursuing this area by studying other hydrogen-bonded heterocluster systems in order to demonstrate the generality of these conclusions.

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[25] As pointed out by a reviewer of this manuscript, other structures for these species are also possible. Our proposed structure for $(ROH)_7(H_3O)$-TMA^+ is postulated because it is consistent with the ROH/H_3O^+ work presented in this paper.