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Intracluster Ion–Molecule Reactions in $M^+(CH_3OH)_N$ Where M = Na or Cs

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Abstract: The dehydration of methanol and three deuterated isotopomers (CH_3OD, CD_3OH, and CD_3OD) in $M^+(CH_3OH)_N$, M = Cs or Na, cluster ions has been studied. The cluster ions are produced by collision of large neutral methanol clusters formed in a supersonic expansion with alkali metal ions. The energy imparted to the cluster by the collision and subsequent solvation is sufficient to induce reaction. The reaction was followed by comparing the intensities of $M^+(CH_3OH)_{N-2}$ (H_2O) product peaks with the intensities of the parent $M^+(CH_3OH)_N$ peaks. A strong dependence of the extent of reaction on cluster size was observed. A minimum of twelve methanol molecules was necessary for the reaction to proceed in $Cs^+(CH_3OH)_N$ and a minimum of eight was necessary in $Na^+(CH_3OH)_N$. Isotopomers of methanol were used to confirm the identity of reaction products and to help suggest a reaction mechanism. When CH_3OH and CD_3OH clusters are produced, the exclusive products of dehydration are H_2O and CH_3OCH_3 and CD_3OCD_3, respectively. However, when CH_3OD and CD_3OD clusters are produced, the products are D_2O and the corresponding symmetric ethers. We propose a possible reaction mechanism for the alkali ion catalyzed dehydration of methanol in the cluster ions.

I. Introduction

Condensed phase chemical reactions depend strongly on the solvent in which they are carried out. Many organic reactions proceed through ionic intermediates or require ionic reactants. If the transition state has a higher charge density than the reactants, it will be stabilized by polar solvents resulting in a decreased activation energy and increased reaction rate. Although general trends in reactivity with changing solvent properties are well established, experiments measuring solvent effects on the molecular level are few. The unique environment of a van der Waals or hydrogen-bonded cluster offers an ideal medium for the study of stepwise solvation on chemical reactions.

Ion–molecule reactions occur readily in the gas phase. Association reactions between neutral molecules and ions have been reported for decades.[1] Mass spectrometric techniques such as ion cyclotron resonance (ICR)[2] and high-pressure mass spectrometry (HPMS)[3] have provided valuable information on the thermodynamics of ion–molecule equilibria. The kinetics of many gas-phase reactions have been explored by fast flow techniques such as flowing afterglow (FA)[4] and its variants such as selected ion flow tubes (SIFT).[5] Reactions involving negative ions acting as nucleophiles in S_N2 displacements have given us a clearer picture on the effect of solvation on reactive potential surfaces.[6] The most detailed information on gas-phase reactions has come from time-resolved experiments in which reactant molecules are prepared with well-known internal energies and product formation and state distribution are probed with ultrafast lasers.[7]

Reactions between neutral molecules can be richly enhanced by the presence of alkali cations. The interactions between molecules and alkali ions are purely electrostatic. The ion plays no chemical role in the reaction as is often seen for reactions involving transition metals. In a variable-temperature FA apparatus, Rowe et al.[8] studied the reactions of small neutral molecules in the presence of Li^+, Na^+, and K^+. Enormous rate enhancements in excess of nine orders of magnitude were measured relative to the collision rate constant. A combination of SIFT experiments and *ab initio* calculations[9] found reaction rates in the presence of the same ions to be enhanced by over 30 orders of magnitude. These extraordinary results were explained by three factors: (1) the interaction energy of the ions and neutrals exceeds the reaction activation barrier, (2) the ion alters the potential energy surface of the reaction, and (3) the collision complex is more stable with a charge present and the probability of reaction increases. It is no surprise that some unusual chemistry may be observed in alkali metal cluster ions.

The formation of ethers from alcohols and alkyl halides has been observed in a variety of places. In the Williamson reaction,[10] a textbook synthesis of ethers, alkali metal alkoxides attack alkyl halides to produce an ether. The methanol to gasoline conversion process[11,12] (reaction 1), patented by Mobil, proceeds via an initial methanol to dimethyl ether dehydration step and takes place within the cage of the zeolite, ZSM-5. Proposed reaction

$$2CH_3OH \overset{-H_2O}{\rightleftarrows} CH_3OCH_3 \xrightarrow{-H_2O} \text{olefins } (C_2\text{–}C_5) \rightarrow \text{large paraffins } (<C_{10}) \quad (1)$$

mechanisms involve catalysis by acidic sites within the zeolite superstructure where large electrostatic fields prevail. When the zeolites are exchanged with alkali metal cations, an increase in catalytic activity is observed and in fact increases as the electric

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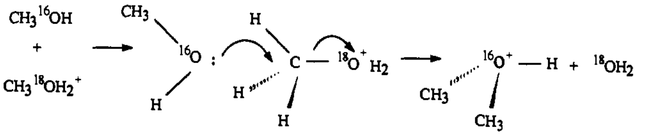
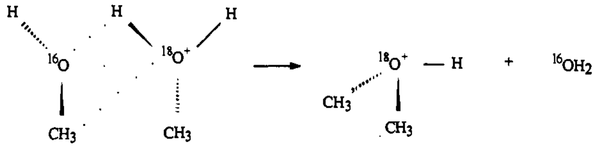
field of the cation increases (i.e. ionic radius decreases).[13] An isotope effect was observed when the acidic proton of the alcohol was deuterated.[13] The gas-phase reaction of protonated methanol with methanol (reaction 2) has been studied using HPMS, ICR, and SIFT apparatus.[14-25] Two basic mechanisms have been

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \quad (2)$$

proposed for reaction 2. The first involves the backside attack of the protonated methanol by a methanol molecule in an S_N2 type reaction (Scheme 1).[17]



The second involves a frontside attack as in Scheme 2.[16]



A recent SIFT experiment[24] suggests that rearrangement of a proton bound dimer of methanol to a methyl bound dimer is responsible for the dehydration channel. The methanol dehydration reaction was studied within small molecular cluster ions prepared by multiphoton ionization (MPI) in a molecular beam[26] and in a fast flow reactor with a SIFT ion source.[20] The dehydration reaction channel shows a dependence on cluster size. In the fast flow reactor, H_2O is lost from the cluster for $N \leq 7$ and $(CH_3)_2O$ is retained. Ether loss and water retention are observed for $N \geq 7$ in both the MPI and SIFT experiments. The reactions of alcohols on metal surfaces appear to proceed through a variety of mechanisms quite different from those we observe in our experiments. Alcohols adsorb reversibly to clean, nonreactive surfaces but dehydrate on preoxidized surfaces. An alkoxide intermediate decomposes by β-hydride elimination to yield an aldehyde. No ether formation has been observed in these reactions.[27]

In a previous publication, we reported the dehydration of methanol in solvated cesium ion clusters.[28] The onset of reaction at a cluster size of $N = 12$ in $Cs^+(CH_3OH)_N$ and observation of an isotope effect are confirmed in the present study. These reactions were recently observed by Zhang and Castleman[29] in a fast flow reactor for cesium and other alkali ions with onset behavior very similar to that reported for the Cs^+ ion.[28] Their attempts at carrying out switching reactions with deuterated analogs of reaction products for $N < 10$ were unsuccessful, confirming the assertion that reaction does not take place below this critical cluster size. In this report, we present results on Cs^+ and Na^+ ions solvated by methanol and the deuterated methanol molecules CH_3OD, CD_3OH, and CD_3OD. The isotopic substitution experiments confirm that the products do arise from the reaction of two methanol molecules within the cluster and not from background water vapor or solvent contamination. These experiments also permit a possible reaction mechanism to be formulated for the dehydration of alcohols in solvated alkali metal ion clusters.

II. Experimental Section

The same apparatus was used in these experiments as in our vibrational predissociation studies and has been described in previous publications.[30] A particular point of interest in these sets of experiments is the production of solvated alkali ion clusters, which will be highlighted here. Large neutral methanol clusters are formed in a seeded supersonic expansion of methanol in Ar. A conical nozzle 180 μm in diameter with an expanding cone of 30° and length of 1 cm was used to increase signals of very large clusters. Typical stagnation pressures were 250–300 Torr. About 8 mm downstream from the expansion, a thermionic emitter is positioned around the molecular beam axis. The emitter is biased at a potential of approximately 50 V above ground to facilitate ion emission. Assuming that the ions have an initial energy of 50 eV, calculations using SIMION[31] indicate that they are decelerated to an energy of about 25–35 eV in the laboratory frame at the interaction region with the molecular beam. The Cs^+ and Na^+ collide with the neutral clusters inelastically and are solvated. The collision and exothermicity of the solvation process rapidly increase the internal energy of the cluster ion. Much of the energy of the cluster is dissipated by evaporative cooling.[32] The quasistable ions are guided into a detector chamber by an array of electrostatic aperture lenses where they are mass selected by a quadrupole mass spectrometer (Extrel, 150 QC). Mass selected ions impact a conversion dynode biased at –5 kV where they are converted to a pulse of electrons and detected with a Channeltron electron multiplier (Galileo, Model 5816). Output of the CEM is processed using a multichannel scaler and digitized with a PDP LSI 11/73 microcomputer. Mass spectra were collected by computer controlled scanning of the quadrupole mass filter. Signal was collected at each mass step for 1 s and mass steps of 0.25 amu were used. The resolution of the mass spectrometer was kept at about 1.0 amu throughout the entire mass range so that the differentiation between the dehydration products H_2O (18 amu), HOD (19 amu), and D_2O (20 amu) could be clearly made. Five mass spectra were collected for each isotopomer except methanol-d_3 where the expense limited the number of mass spectra to one.

Methanol was obtained from Fisher Scientific as 99.9% pure and assayed as containing only 0.02% H_2O. The methanol was stored over 4A molecular sieve pellets. All containers were dried at 350 °C overnight before coming in contact with the solvents. Methanol-d_3 was purchased from Aldrich as 99 atom % D, methanol-d_1 and methanol-d_4 were purchased from Cambridge Isotope Labs as 99 atom % D and used without further purification.

III. Results and Discussion

The mass spectrum of a beam of $Na^+(CH_3OH)_N$ is shown in Figure 1. The series of large peaks correspond to pure methanol clusters with $1 \leq N \leq 24$. A smaller series of peaks begins to emerge near 250 amu. These peaks correspond to product cluster ions of the form $Na^+(CH_3OH)_M(H_2O)$. The mass spectrum of $Cs^+(CH_3OH)_N$ is shown in Figure 2. It is qualitatively similar to that recorded for $Na^+(CH_3OH)_N$. While the pure methanol

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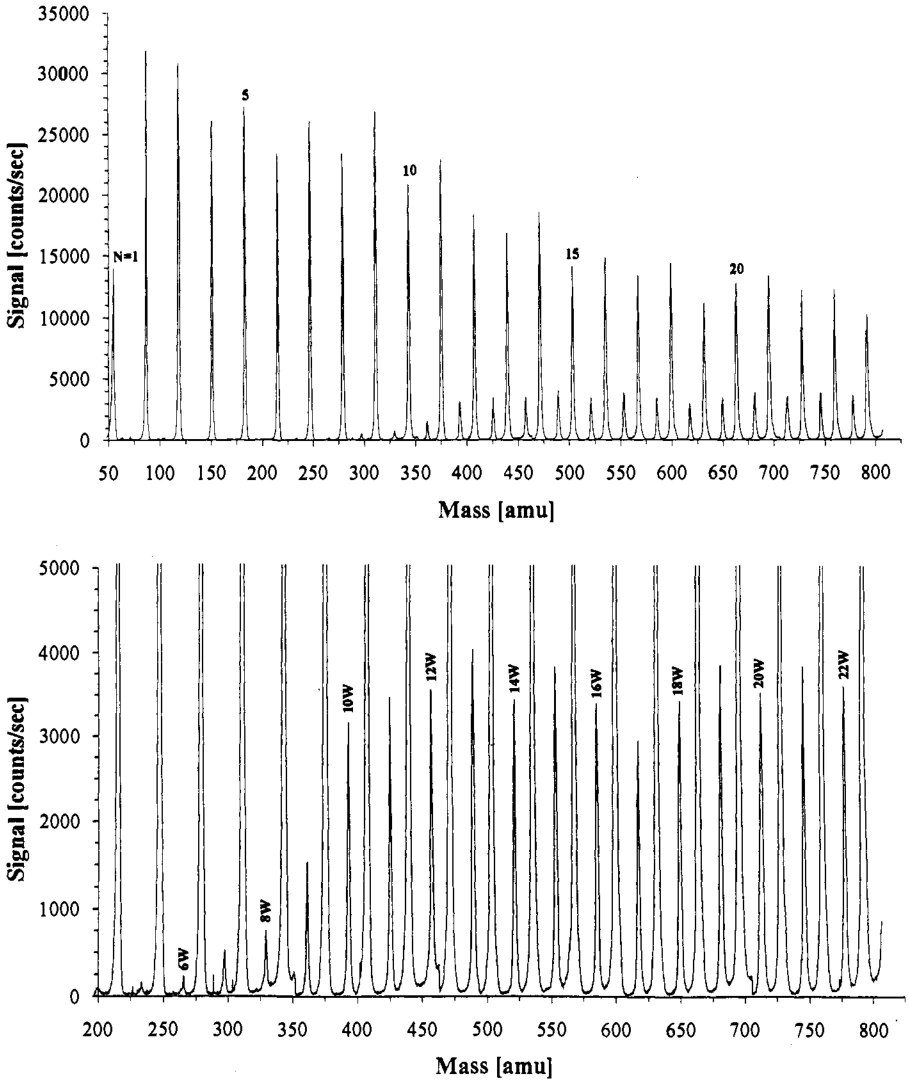
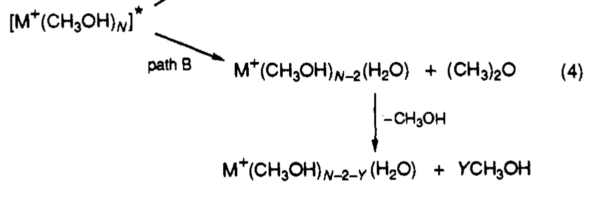


Figure 1. (a) Mass spectrum of a beam of $Na^+(CH_3OH)_N$. The signal from every fifth pure cluster ion $Na^+(CH_3OH)_N$ is labeled with an N value. (b) An expanded view of the mass spectrum in part a showing more clearly the product onset. The peaks of $Na^+(CH_3OH)_N(H_2O)$ with even N are labeled as NW.

cluster series shows a general decrease in peak intensity with increasing cluster size, the product peaks show a sharp increase. The first peak in the series $Na^+(CH_3OH)_N(H_2O)$ with significant intensity is $N = 6$ and the first significant peak in the $Cs^+(CH_3OH)_N(H_2O)$ series is $N = 10$. The products $M^+(CH_3OH)_{N-2}(H_2O)$ arise from the intracluster reaction shown below



Path A corresponds to evaporation of methanol monomers from a hot methanol cluster ion. Path B corresponds to an intracluster condensation reaction in which two methanol molecules react to form dimethyl ether and water. The daughter ion can then continue to lose methanol molecules by evaporation. Since the cluster ion $M^+(CH_3OH)_{N-2}((CH_3)_2O)(H_2O)$ has the same mass to charge ratio as $M^+(CH_3OH)_N$, one of the reaction products must leave the cluster for the reaction to be observed with our mass spectrometer. We find that the dimethyl ether produced leaves the cluster exclusively and the water is retained. This finding is consistent with the previous results on dehydration in $Cs^+(CH_3OH)_N$ clusters[28] as well as protonated methanol clusters formed by both multiphoton ionization and electron impact ionization.[20,25,26] As mentioned above, cluster ions with composition $M^+(CH_3OH)_{N-2}((CH_3)_2O)(H_2O)$ have the same charge to mass ratio as $M^+(CH_3OH)_N$. We have investigated the possibility that the reaction has occurred, but without the loss of either product molecule. Neutral clusters $((CH_3)_2O)_N$, $N = 2$–4, have been observed to vibrationally predissociate following excitation of the OCO symmetric stretch of the dimethyl ether near 930 cm^{-1}.[33] Matrix isolation studies of the hydrogen-bonded $(CH_3)_2O\cdots HCl$ binary complex indicate that the OCO symmetric stretch is shifted 24 cm^{-1} to lower frequency.[34] A cluster ion containing a dimethyl ether molecule then could be expected to absorb in the 905–930-cm^{-1} region. Attempts to vibrationally predissociate clusters with charge to mass ratios of $M^+(CH_3OH)_N$ in the 910–960-cm^{-1} region (the P-branch of the $00^01 \rightarrow 10^00$ transition of the CO_2 laser) were unsuccessful. This failure is not due to a lack of sensitivity, as predissociation studies have been conducted on $M^+((CH_3)_2CO)_N(CH_3OH)$, $N = 2$–12, following excitation of the methanol CO stretch.[35] Therefore it

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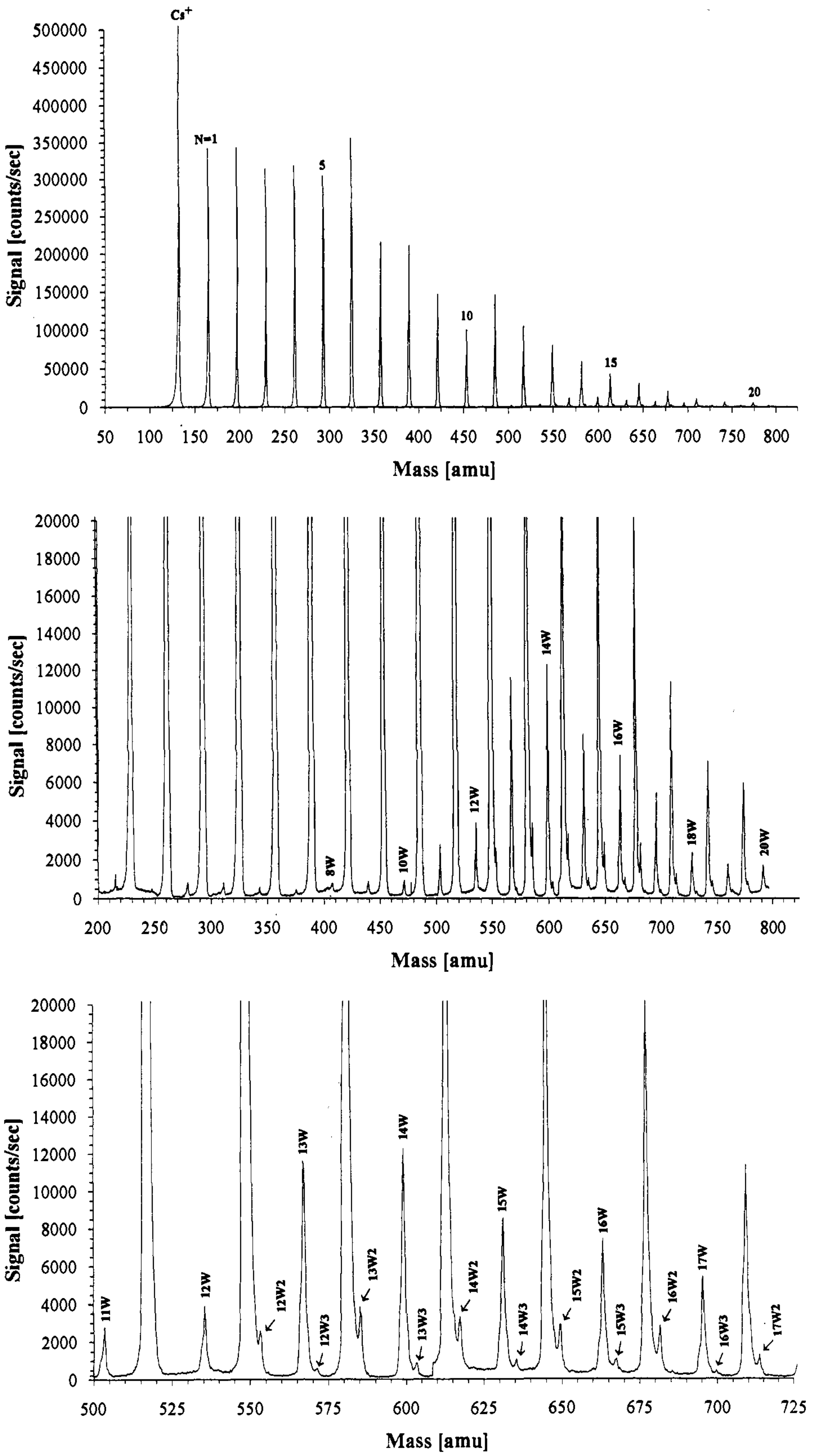

Figure 2. (a) Mass spectrum of a beam of $Cs^+(CH_3OH)_N$. The signal from bare cesium ion is labeled as Cs^+ and every fifth pure cluster ion $Cs^+(CH_3OH)_N$ is labeled with an N value. (b) An expanded view of the mass spectrum in part a showing more clearly the product onset. The peaks $Cs^+(CH_3OH)_N(H_2O)$ with even N are labeled as NW. (c) A further expansion of the mass spectrum in part a that illustrates the onset of cluster ions containing multiple water molecules. The peaks $Cs^+(CH_3OH)_N(H_2O)_2$ are labeled as NW2 and the peaks $Cs^+(CH_3OH)_N(H_2O)_3$ are labeled as NW3.

appears to be unlikely that cluster ions with both reaction products exist in the beam. Recent attempts by Zhang and Castleman[29] at switching reactions between the reacting cluster ions and isotopomers of the ether product in a fast flow reactor further demonstrated that no cluster ions of the form $M^+(CH_3OH)_{N-2}(CH_3OCH_3)(H_2O)$ exist.

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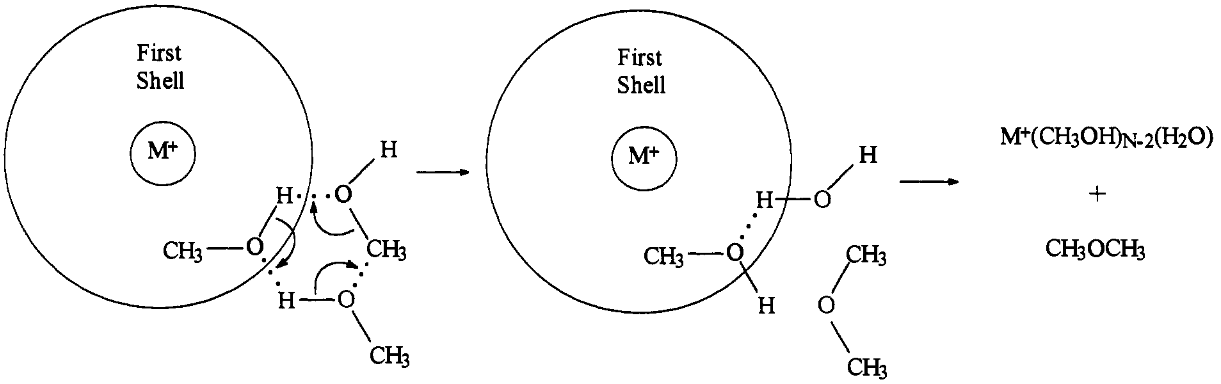

Figure 3. A graphical depiction of our proposed reaction mechanism. The circle about the central ion represents the filled first solvation shell of methanol molecules. Methanols residing in the second solvation shell and hydrogen bonded to the first are in a position to react.

The origin of the water produced in the dehydration reaction was found by clustering the alkali ions with deuterated variants of methanol. If water indeed arises from reaction between methanol subunits, the product D_2O or HOD should be produced when the methanol is fully or partially deuteriated. When CD_3OD was used as solvent, the cluster ions produced were $M^+(CD_3OD)_{N-2}(D_2O)$, as evidenced by a product peak appearing 20 amu rather than 18 amu above a pure solvent peak. Important information was obtained from experiments using CH_3OD and CD_3OH as solvents. When CH_3OD was used, the product was exclusively $M^+(CH_3OD)_{N-2}(D_2O)$. No H_2O or HOD was observed. Alternatively, when CD_3OH was used, the product was exclusively $M^+(CD_3OH)_{N-2}(H_2O)$. Again, we saw no evidence of D_2O or HOD in the mass spectrum. It is clear from these experiments that the water bound to the cluster ions arises from intracluster reaction. Background water vapor in the apparatus would give the same product regardless of choice of solvent. If the mixed clusters arise from trace impurity in the solvents used, a small amount of mixed HOD clusters might be expected but is not observed.

Our isotropic substitution experiments also help to suggest a possible reaction mechanism for the dehydration. Since H_2O is the sole product when CH_3OH and CD_3OH are used as solvents and D_2O is produced when CH_3OD and CD_3OD are used, it appears that the two protons or deuterons in the water product come from the labile protons bound to oxygen in the two methanol molecules. The deuteration of the methyl group does not change the labeling of the water product nor does it lead to HOD production. We propose the reaction mechanism shown in Figure 3 for the dehydration channel (reaction 4). The six-centered structure is similar to the structure of $(CH_3OH)_3$, which is known to be cyclic,[36] but with a rotation of one methanol about a hydrogen bond to achieve the $O\cdots CH_3$ orientation. As mentioned earlier, neutral methanol clusters are formed in the molecular beam and alkali metal ions impact after expansion. The ions are translationally energetic, about 25 to 35 eV in the laboratory frame, at the point of impact. No low lying excited ion states are accessible so electronic contributions can be ruled out. The center of mass collision energy between a Cs^+ ion and a large neutral cluster (assumed to be moving at the velocity of the carrier gas) is about 1500 kJ/mol. Some of this energy will be channeled into translation of the collision complex but a substantial amount will be partitioned among internal degrees of freedom. The activation barrier of the reaction in large clusters such as these is unknown. The corresponding activation barrier in the dehydration of the protonated methanol dimer is 110 kJ/mol. With ion–methanol binding energies in the range of 35–50 kJ/mol, a competition between dehydration and monomer evaporation is expected. The excess energy given to the cluster during collision, however, should be enough to promote the reaction. A lowering of the activation barrier by the presence of the ion and the solvation by other methanol molecules may also be expected. The daughter cluster ion then loses the dimethyl ether and retains the water to give the final product ion. Because water can more extensively hydrogen bond with the methanol molecules in the cluster than dimethyl ether, it is no surprise that the dimethyl ether is preferentially lost from the cluster. If enough internal energy remains, the daughter ion can fragment further or react a second time to give a product with two water molecules. Because of the intracluster geometry of the methanol molecules in the region beyond the first solvation shell, a frontside nucleophilic attack similar to that proposed in Scheme 2 might appear to be the most probable interaction, since it leads to production of the symmetric ether and a water molecule in which the acidic protons of the two reacting methanol molecules are incorporated. Since the cluster is bound by a metal ion rather than a proton, the resulting four-centered structure and an ion–dimethyl ether complex seem unlikely. The backside attack S_N2 mechanism of Scheme 1 appears to be more likely, provided more than two methanol molecules are involved. Otherwise, the distant hydrogen could simply escape from the cluster rather than becoming entrained in the product.

In the $Cs^+(CH_3OH)_N$ mass spectrum in Figure 2, a second series of product peaks of the form $Cs^+(CH_3OH)_N(H_2O)_2$ is observed beginning at $N = 12$. As four methanol molecules are necessary to produce the two water molecules, the parent cluster ion for this product is $N = 16$. It also appears that both dimethyl ether molecules are lost subsequent to the multiple reaction. A much weaker series of peaks corresponding to $Cs^+(CH_3OH)_N(H_2O)_3$ also begins at $N = 12$. Similarly, the parent ion for this product would be $N = 18$. This effect was not seen in the mass spectra of Cs^+ with the isotopomers of methanol nor was it seen with the Na^+ ion, although overlapping peaks may have masked the detection of additional water in the case of methanol isotopomers.

The explanation for the strong dependence of the extent of reaction on cluster size is not clear. To try to forward an answer, we collected five mass spectra for $Cs^+(CH_3OH)_N$ and each of the isotopomers and five for $Na^+(CH_3OH)_N$. The intensity of the product peak $M^+(CH_3OH)_{N-2}(H_2O)$ was ratioed to the parent peak intensity, $M^+(CH_3OH)_N$ according to our proposed mechanism, and plotted versus N. The reaction dependence ratios for $Cs^+(CH_3OH)_N$ and its isotopomers are shown in Figure 4. The ratio of product to parent peak intensity is near zero in each system until a cluster size of $N = 12$ is reached, at which point it increases sharply. The ratio continues to increase through $N \approx 20$. The corresponding plot for $Na^+(CH_3OH)_N$ is shown in Figure 5. The onset at $N = 8$ is seen for the reaction involving the Na^+ ion, albeit less dramatic. Again, the ratio continues to increase through $N = 25$. Working within our proposed mechanism, these data indicate that a minimum cluster size of $N = 12$ is necessary for reaction to occur in $Cs^+(CH_3OH)_N$ and

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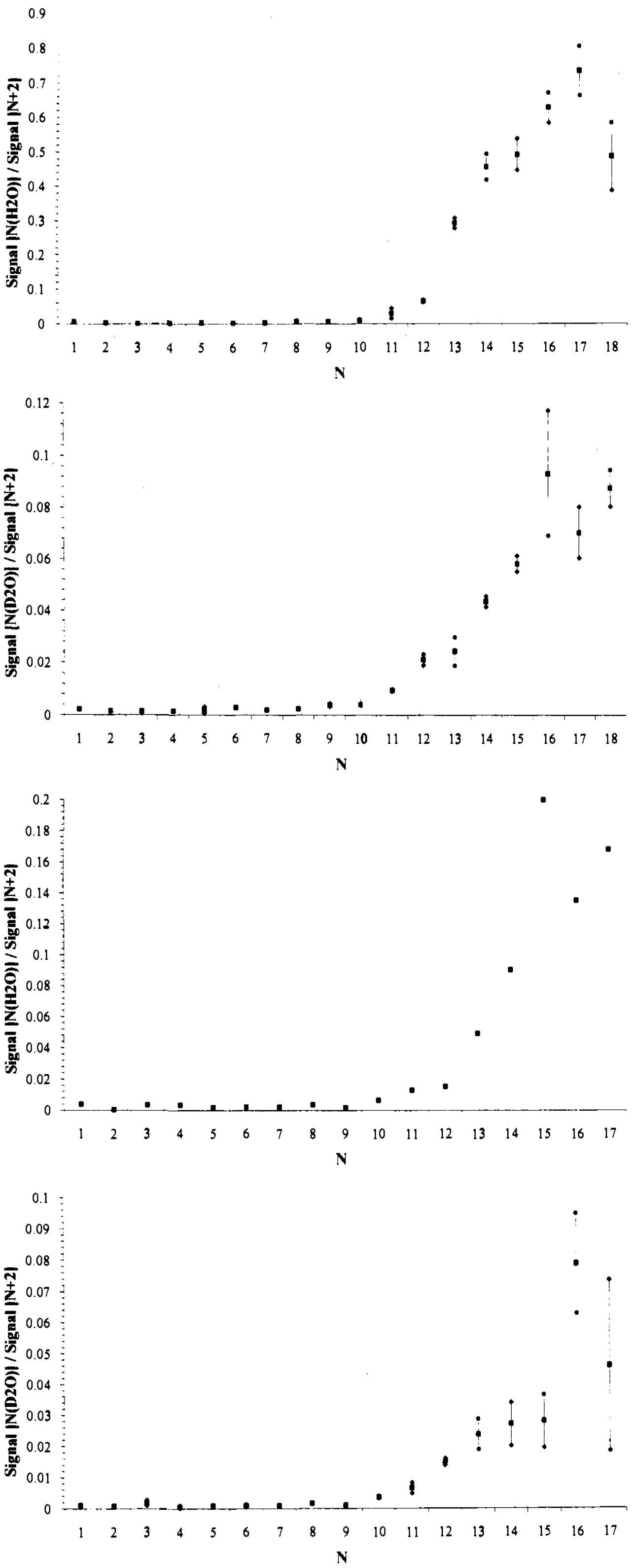

Figure 4. Reaction onset ratios for (a) $Cs^+(CH_3OH)_N$, (b) $Cs^+(CH_3OD)_N$, (c) $Cs^+(CD_3OH)_N$, and (d) $Cs^+(CD_3OD)_N$. The ratio of the intensity of the product peak Cs^+(methanol)$_{N-2}$(water) to its parent peak Cs^+(methanol)$_N$ intensity is plotted versus N. Error bars represent $\pm\sigma$.

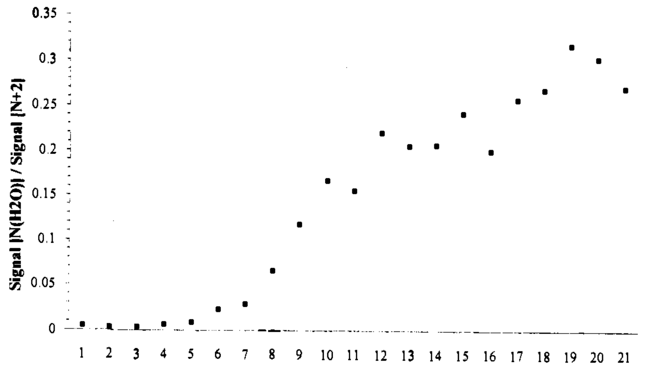

Figure 5. Reaction onset ratio for $Na^+(CH_3OH)_N$. The ratio of the intensity of the product peak Na^+(methanol)$_{N-2}$(water) to its parent peak Na^+(methanol)$_N$(methanol)$_N$ intensity is plotted versus N. Error bars represent $\pm\sigma$.

$N = 8$ is necessary for $Na^+(CH_3OH)_N$. The probability that the intracluster reaction occurs for N less than these minimum values is small and no reaction is observed. Once this minimum size is reached, the reaction occurs more readily with each successive solvation step. Zhang and Castleman[29] report an onset of $Na^+(CH_3OH)_MH_2O$ and $Cs^+(CH_3OH)_MH_2O$ for $M = 8$ and 9, respectively, when the reaction is carried out under thermal conditions. If the mechanism of the reaction observed in their experiments is the same as the one we suggest here, this would increase their minimum cluster size for reaction when $N \geq 10$ for Na^+ and $N \geq 11$ for Cs^+. These values are very consistent with those that we report.

An interplay between several factors involving solvation shell structure may be responsible for the onset of reactivity at a critical cluster size. The point at which the dehydration reaction in Na^+ and Cs^+ cluster ions is switched on corresponds quite closely to the filling of the first solvation shell of these ions with methanol. The Cs^+ ion has a first solvation shell of ten methanol molecules and the Na^+ ion has a first solvation shell of six.[30] The onset of reaction in $Na^+(CH_3OH)_N$ at $N = 8$ and in $Cs^+(CH_3OH)_N$ at $N = 12$ means that two methanol molecules are occupying a second solvation shell in each case. The mechanism suggested in Figure 3 depicts this graphically. When the first solvation shell is filled or partially filled, no reaction is detected. When two methanol molecules reside in a second solvation shell, they can react to give products. The orientation of the molecules in the second shell relative to one another is important in determining whether they will react. The methanol molecules must be oriented such that O–H and O–CH_3 interactions are possible. Hydrogen bonding between methanol molecules in the cluster acts to structure the second solvation shell. Monte Carlo calculations on $Cs^+(CH_3OH)_N$ and $Na^+(CH_3OH)_N$[30] have shown that there is hydrogen bonding taking place between molecules in the first and second solvation shells. The interaction between a molecule in the first shell and two in the second induces a local structure that allows the molecules to react. The result is a water molecule that is hydrogen bonded to a first shell methanol and a weakly bound dimethyl ether that is free to leave the cluster. When enough methanols are present in the second shell, and enough energy is present in the cluster, multiple reaction sites can be set up at the surface of the first shell and more than one reaction can occur. As the size of the cluster increases, the activation energy for the reaction is likely to be lowered and the reaction proceeds more easily. This is a probable explanation for the increase in reactivity through the higher cluster sizes measured.

Solvation shell formation and intracluster reaction both occur during the formation of an energized cluster ion and their relative time scales must be addressed. The mechanism that we suggest in Figure 3 assumes that the dehydration reaction occurs within the framework of fully formed solvation shells. If the reaction occurs on a time scale faster than solvent shell formation, this assumption would be invalid. The rate at which the dehydration reaction occurs in our experiment is not known precisely. The flight time of the cluster ions in our apparatus to the quadrupole mass filter is about 25 μs, establishing a lower limit on reaction lifetime. Following multiphoton ionization in a time-of-flight mass spectrometer, Castleman[26] observed reaction followed by loss of dimethyl ether on a 1 to 15 μs time scale in $H^+(CH_3OH)_N$, $N = 4$–9. Clusters with $N > 7$ were reported to react more rapidly. These data suggest that the time scale of the dehydration reaction in cluster ions is within a factor of 10–100 of the flight time, but may decrease with increasing solvation. To address the question of time scale of solvent shell formation, we carried out a series of molecular dynamics simulations on the collision of a translationally energetic Cs^+ ion with an equilibrated, internally cold (25 K) methanol cluster. The full results of the simulations will be presented in a forthcoming publication.[37] Initial results show that after the impact between a Cs^+ ion and a methanol cluster with relative translational energies of 0–20 eV, extensive cluster fragmentation (loss of solvent molecules) occurs. Evidence of the formation of solvent shells by the remaining methanol molecules is seen at as little as 1 ps following collision. If the structure of a cluster ion is determined within the first few picoseconds of the formation process and the dehydration reaction is not significantly accelerated from those observed by Castleman,[26] the mechanism of Figure 3 is reasonable. Further investigation into the process of solvent shell formation is underway in our laboratory.

IV. Conclusions

The dehydration of methanol to produce dimethyl ether and water is catalyzed by an alkali ion in solvated ion clusters. The energy to overcome the activation barrier to the reaction is supplied by the collision of an alkali ion with a neutral methanol cluster and subsequent solvation during cluster ion formation. Critical cluster sizes of $N = 12$ and 8 are necessary for significant reaction to be observed in Cs^+ and Na^+ cluster ions, respectively. Once this threshold is reached, the reaction proceeds more readily with each additional methanol. Isotopic substitution experiments suggest a mechanism for the dehydration in which two methanols interact and their acidic protons (or deuterons) form the water molecule produced regardless of the degree of deuteration of the methyl group. Although the interactions between methanol molecules within our metal ion clusters and in protonated methanol clusters are similar, the fundamental mechanism that we propose is rather different. The structuring effect of hydrogen bonding within the cluster ions may be responsible for the sharp increase in reactivity at a minimum cluster size. Initial molecular dynamics results suggest that solvation shell formation occurs on a much faster time scale than the dehydration reaction. This validates the mechanism in which reaction takes place in a formed solvent shell environment.

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[37] Cabarcos, O. M.; Lisy, J. M. Manuscript in preparation.