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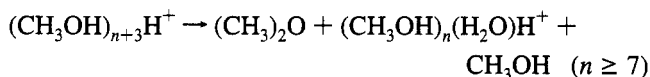
Dehydration Reactions of Metal Cations (Fe^+ and LaO^+) with Methanol ClustersWenyun Lu, Rongbin Huang,[†] and Shihe Yang*Department of Chemistry, The Hong Kong University of Science & Technology,
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Reaction of laser-generated metal cations (Fe^+ and LaO^+) with methanol clusters was studied in a molecular beam. The reaction products were analyzed by a time-of-flight mass spectrometer. A general reaction pattern is that of the methanol–methanol reaction which produces ether and water and which is induced by collision with the metal cations. However, very different reaction behaviors were found for Fe^+ and LaO^+ . For Fe^+ , there was a critical size ($n \geq 12$) for the reaction of methanol clusters $(\text{CH}_3\text{OH})_n$, with ether loss and H_2O retention. On the other hand, for LaO^+ , this critical size was 2, and the result was H_2O loss and ether retention. Multiple-ether formation was identified in a narrow cluster size region with the number of MeOHs ranging from 2 to 4. Furthermore, the series corresponding to $\text{LaO}^+(\text{MeOH})_n$ or $\text{LaO}^+(\text{Me}_2\text{O})(\text{MeOH})_{n-2}(\text{H}_2\text{O})$ suddenly appeared for $n \geq 12$. The two different reaction patterns are discussed in terms of electrostatic and covalent effects in the presence and absence of a solvation shell, respectively.

Introduction

It is well-known in solution chemistry that the solvation of ionic species participating in a given chemical reaction can greatly affect the dynamics of the reaction. However, the complexity of solution prevented even the most sophisticated experimental techniques from probing the detailed structures of solvated ions and ion/molecule reactions in the solution phase. Gas phase ion/solvent clusters provide a means to investigate the interaction between ions and solvent molecules as a function of the number of solvent molecules.¹

The exothermic reaction of CH_3OH_2^+ with CH_3OH (by 15.5 kcal/mol) has been studied under the controlled extent of solvation.² Earlier studies show that when CH_3OH_2^+ is solvated by a few methanol molecules, the reaction is quenched.³ However, further solvation of CH_3OH_2^+ by methanol molecules has been shown to promote the following intracuster reaction in a multiphoton ionization (MPI) study using a molecular beam and a fast flow reactor with a SIFT ion source:^{3,4}



Another study on the protonated methanol cluster ions under thermal conditions at low temperature (130 K) obtained the same results.⁵ Recently, by using the electron impact ionization method, a similar reaction was observed while this time it began when $n \geq 6$.⁶

Similar intracuster reactions of methanol clusters have been reported for alkali metal ions, such as Li, Na, K, Rb, and Cs.^{7,8} There appears to be a rather weak dependence of the critical methanol cluster size for reaction on the size of the alkali metal ion. For example, the product ions $\text{A}^+(\text{CH}_3\text{OH})_n(\text{H}_2\text{O})$ start to appear when n is around 8 for $\text{A} = \text{Li}, \text{Na}, \text{or K}$, whereas n is around 9 for $\text{A} = \text{Rb or Cs}$. More recently, an isotopic substitution experiment established that the H_2O product originates from the reaction of methanol molecules in the cluster.⁹ A mechanism was proposed for the intracuster reaction which essentially depends on the size of the first solvation shell of the ion.

So far, the study of the dehydration reaction in methanol clusters is limited to protonated methanol clusters and alkali metal ion-bound methanol clusters. It would be interesting to see whether other metal ions, particularly transition metal ions, can induce similar reactions. The study of the dehydration reaction with different metal cations could be illuminating on the role of the cations and the nature of interactions involved in the reaction. Here we present the results of the study of intracuster ion/molecule reactions in $\text{M}^+(\text{CH}_3\text{OH})_n$, where $\text{M} = \text{Fe or LaO}$. Although it seems more natural to compare the reaction patterns involving Fe^+ and La^+ , LaO^+ was found to be the most abundant species in the laser ablation source due to the unusually high strength of the La–O bond.

Experimental Section

Since the experimental setup has been described previously,¹⁰ only a brief description is given here. Metal or metal oxide samples were pressed and mounted on a sample load lock. An excimer laser (308 nm, XeCl) beam (28 ns duration) was weakly focused on a sample of Fe_2O_3 or La_2O_3 (laser power 10^7 – 10^8 W/cm²; beam spot size on the target 0.5×1.5 mm). The laser-vaporized metal ions perpendicularly crossed a supersonic methanol cluster beam 8 mm from the ablation target. The crossing region of the methanol cluster beam and laser-generated metal ion beam was 8 mm from the pulsed nozzle exit. The methanol cluster beam was generated by seeding methanol vapor at room temperature in He with a backing pressure of 5 atm. The seeded CH_3OH (>99.9% purity with <0.02% water impurity) supersonically expanded along with the He carrier gas and formed methanol clusters on exiting the 0.5 mm diameter hole of a pulsed nozzle. The He mass flow rate was 3 sccm, and the gas pulse width was $\sim 80 \mu\text{s}$. Laser-ablated metal ions reacted with the methanol clusters, and the products were carried by the pulsed He flow to the extraction region of a reflectron time-of-flight mass spectrometer (RTOFMS). The product cations were extracted and detected in the RTOFMS.

The source chamber and flight tube were differentially pumped by a 10 and a 6 in. diffusion pump, respectively. The operating pressures of the source chamber and flight tube were 10^{-5} and 10^{-7} Torr, respectively.

A typical experiment started with the opening of the pulsed nozzle. The ablation laser was fired 50 μs later. The extraction

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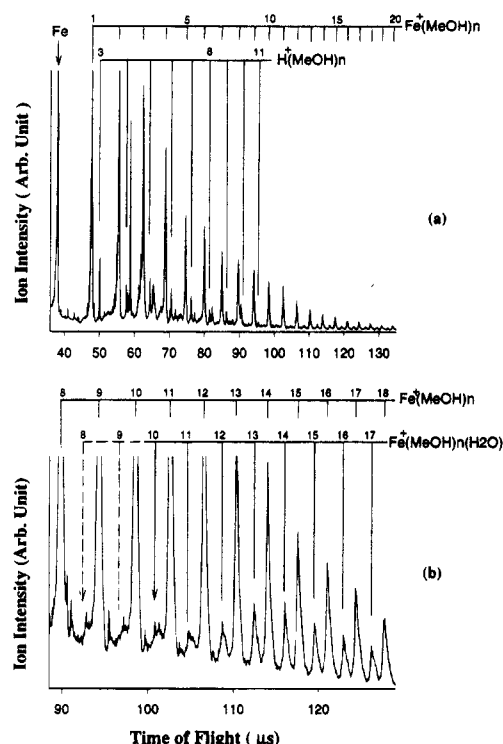


Figure 1. (a) Overall time-of-flight mass spectrum of $\text{Fe}^+(\text{CH}_3\text{OH})_n$. (b) TOF spectrum of $\text{Fe}^+(\text{CH}_3\text{OH})_n$ in the large cluster size portion.

high-voltage pulse was applied 100 μs after the laser firing when the reaction products traveled a 15 cm distance from the crossing region to the extraction region of the mass spectrometer. We expect that the methanol cluster formation is largely quenched after expansion through the 8 mm distance (16 nozzle diameters) to the crossing region. This is based on the fact that cluster formation requires three-body collisions. Since the frequency of three-body collisions scales as P^2D (P = pressure, D = nozzle diameter), the cluster formation rate in the crossing region is expected to be over 4 orders of magnitude smaller than that near the nozzle exit. Under a typical source condition, three-body collisions can be quenched in a few nozzle diameters for an axisymmetric expansion while two-body collisions can remain in an extended length scale (a few tens of nozzle diameters).¹¹ Therefore, the reaction of metal cations with methanol clusters could be separated from the cluster formation process.

The mass resolution of the mass spectrometer for this particular experiment is about 1 mass unit below $m/e = 600$. This mass resolution could be further increased for a specific mass window by optimizing the extraction and reflection voltage settings. A least-squares fitting procedure was routinely used for mass assignments, and this was facilitated by the regular sequences of the cluster species.

Results and Discussion

For $\text{Fe}^+(\text{CH}_3\text{OH})_n$, the time-of-flight mass spectrum is shown in Figure 1a. In general, the cluster signal intensity decreases as the cluster size increases. However, as shown in Figure 2, there appears to be some local intensity gaps around $n = 4$ and $n = 11$. The intensity gap has been found at $n = 2$ for a number of metal ions¹² with methanol clusters, but it is not obvious here for $\text{Fe}^+(\text{MeOH})_n$. The existence of intensity gap at $n = 4$ and $n = 11$ may indicate the formation of ion solvation shell or subshell. This is because clusters with a closed solvation shell or subshell should be more stable than those with open solvation shells. Consequently, immediate after the solvation shell closing the intensity of $\text{Fe}^+(\text{MeOH})_n$ will suddenly drop.

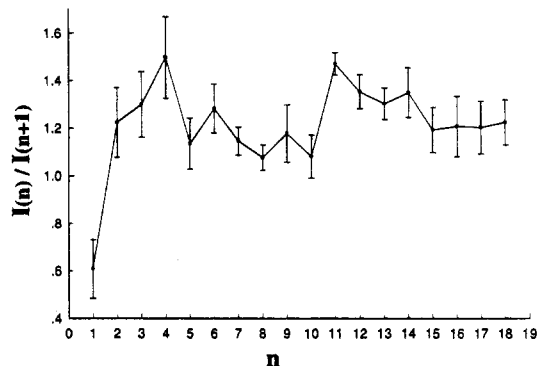


Figure 2. Plot of the intensity ratio of successive I_n/I_{n+1} versus the methanol cluster size n . The error bars are the standard deviations of the data from seven separate TOF mass spectra.

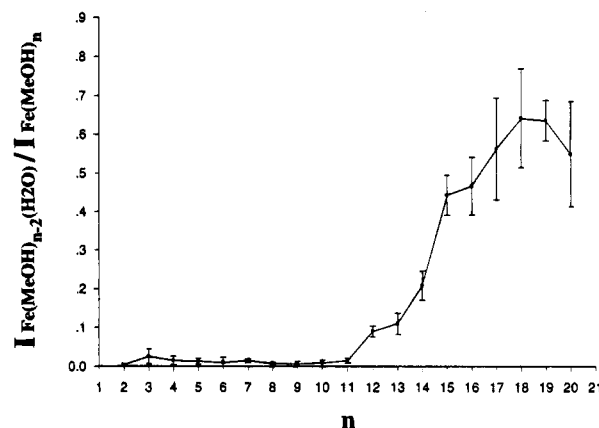
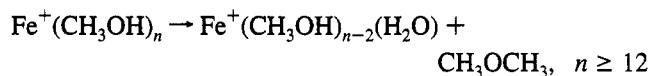
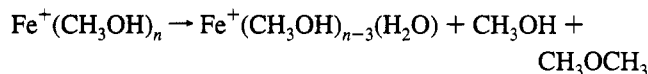


Figure 3. Plot of the relative peak intensity of $\text{Fe}^+(\text{CH}_3\text{OH})_{n-2}(\text{H}_2\text{O})$ as a function of the methanol cluster size n . The error bars are the standard deviations of the data from five separate TOF mass spectra.

Figure 1b reveals that another series of peaks exists for larger clusters with a formula of $\text{Fe}^+(\text{CH}_3\text{OH})_n(\text{H}_2\text{O})$, which can be attributed to the intracluster dehydration reaction. Interestingly, this dehydration reaction was found to occur when $n \geq 12$. That is,



This can be seen more clearly in Figure 3, which shows the relative intensity of the daughter ion $\text{Fe}^+(\text{CH}_3\text{OH})_{n-2}(\text{H}_2\text{O})$ with respect to the parent ion $\text{Fe}^+(\text{CH}_3\text{OH})_n$ as a function of the cluster size n . Of course, the reaction might also have been



In this case, one methanol molecule is evaporated to dispose of the reaction heat, and therefore $n \geq 13$. However, 12 is the minimum cluster size for the possible conversion of methanols to ether and water. It is surprising that this critical size of 12 is very similar to that found for alkali metal ions given the fact that a transition metal ion is normally considered more active in catalyzing organic reactions due to the availability of d electrons and orbitals. This suggests that the existence of a critical size for the intracluster ion/molecule reaction is the result of a purely electrostatic effect. This overwhelming electrostatic effect has been invoked to explain the similar critical cluster size ($n = 9-11$) for the intra-methanol cluster reactions catalyzed by either proton or alkali metal ions although the bonding properties of proton and alkali metal ions are very different.⁷ It follows that the mechanism of the intracluster ion/molecule reaction for transition metal ions such as Fe^+ seems to be similar to that for alkali metal ions and protons, which is

generally believed to occur after the solvation shell formation. Molecular dynamics simulation shows that the solvent shell formation is completed in as little as 1 ps upon a collision of Cs^+ with $(\text{CH}_3\text{OH})_n$, and the intracuster dehydration is much slower (microsecond time scale) than this time scale.^{9,13} More accurate data on the time scale of the proton-induced dehydration reaction is 1–15 μs estimated by Castleman and co-workers in a multiphoton ionization experiment.³ It is interesting to note that the critical size of $n = 12$ for the intracuster reaction of $\text{Fe}^+(\text{CH}_3\text{OH})_n$ is very close to the intensity gap at $n = 11$ shown in Figure 2, further suggesting that the reaction occurs after the solvation shell forms.

Also shown in Figure 1a is another series of small peaks attributed to $\text{H}^+(\text{MeOH})_n$. These species were probably produced by electron impact ionization of the neutral methanol clusters while the needed electrons were generated in the laser ablation process. Electron impact ionization has been one of the important techniques to produce protonated methanol clusters.^{2,6} While the electrons may also cause the ionization of $\text{Fe}(\text{MeOH})_n$, its contribution to $\text{Fe}^+(\text{MeOH})_n$ is likely to be minimal. First of all, the intensity of $\text{H}^+(\text{MeOH})_n$ from electron impact ionization is already very small compared to $\text{Fe}^+(\text{MeOH})_n$. Second, to produce $\text{Fe}^+(\text{MeOH})_n$ by electron impact ionization, $\text{Fe}(\text{MeOH})_n$ has to be formed in the first place.

Complexes in which transition metal ions are electrostatically bound to closed-shell atoms and molecules have been demonstrated by Brucat *et al.*¹⁴ in their photodissociation experiments. For example, the V^+-OH_2 stretching frequency has been determined in two different electronic configurations of the ion, and the electrostatic nature of the complex was confirmed by the excellent agreement between observed and calculated isotope shift. The ground state of V^+ has an open d shell corresponding to an electronic configuration $3d^4$. The dominant electrostatic nature of the V^+-OH_2 complex indicates that the electrons in the open shell of V^+ do not contribute significantly to the metal–molecule bonding. It is therefore reasonable to expect that Fe^+ with an open d shell electronic configuration $4s3d^6$ should also be electrostatically bound to the dipolar methanol molecules.

A series of beam experiments were conducted by Garvey and co-workers on the structure and reactivity of $(\text{MeOH})_n\text{H}^+$.¹⁵ They proposed that the appearance of magic numbers in the hydrogen-bonded cluster originates from the intrinsic stability of the individual clusters. A structure was suggested that incorporates H_3O^+ (or H_5O_2^+) as the core ion with the methanols forming several sets of fused five-membered hydrogen-bonded rings. Although it appears appropriate for protonated methanol clusters, this model does not explain why similar situation exists for alkali metal ions and now transition metal ions given the fact that the bonding properties of protons and metal ions are very different. An alternative is that the protons, alkali metal ions, or transition metal ions reside in the center of the shell and the H_2O is outside the shell. The preference of H_2O retention is simply a result of a larger ion–dipole interaction irrespective of the chemical nature of the ion. The small variation of solvation shell sizes for proton, alkali metal ions, and transition metal ions is roughly in parallel with the variation of the sizes of these ions. This model was considered by Lisy and co-workers.⁹

As for the reaction of LaO^+ with methanol clusters, the TOF mass spectrum is shown in Figures 4–6. It should be noted that in Figure 4 $\text{La}^+(\text{CH}_3\text{OH})_n$ ($n > 1$) is absent, and there is no dehydration product $\text{La}^+(\text{Me}_2\text{O})(\text{MeOH})_n$ or $\text{La}^+(\text{H}_2\text{O})(\text{MeOH})_n$. In addition, the signal intensity of La^+ is an order magnitude smaller than that of LaO^+ . Therefore, we only consider the reaction patterns involving LaO^+ . The reaction pattern of LaO^+ is in marked contrast to that of Fe^+ with methanol clusters. Several striking features can be pointed out:

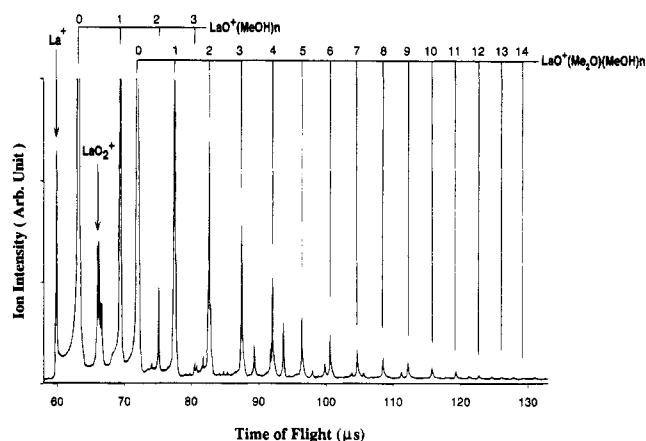


Figure 4. Time-of-flight mass spectrum of $\text{LaO}^+(\text{Me}_2\text{O})(\text{CH}_3\text{OH})_n$ showing the overall reaction pattern. The peak marked LaO_2^+ may also contain certain amounts of $\text{La}^+(\text{CH}_3\text{OH})$.

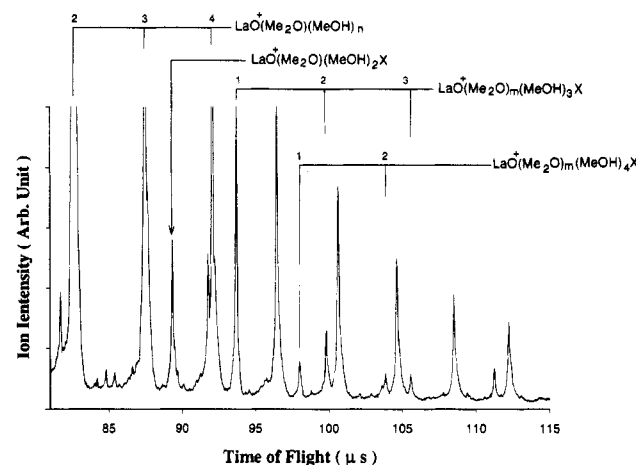


Figure 5. Time-of-flight mass spectrum of $\text{LaO}^+(\text{Me}_2\text{O})_m(\text{CH}_3\text{OH})_n$ for the middle cluster size region showing the multiple-ether formation. X is an unknown species with a mass of 44 amu.

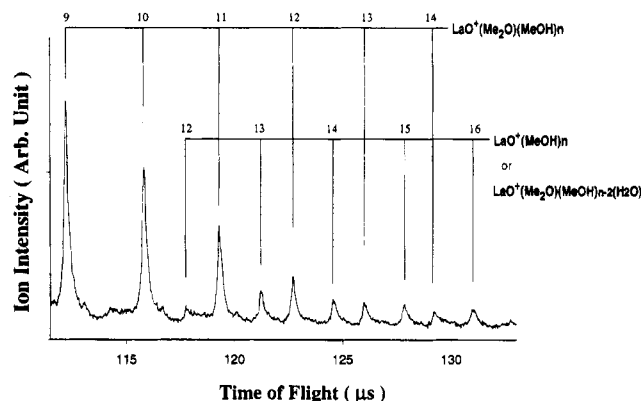
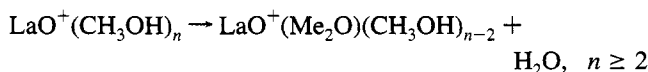


Figure 6. Time-of-flight mass spectrum showing the series corresponding to $\text{LaO}^+(\text{CH}_3\text{OH})_n$ or $\text{LaO}^+(\text{Me}_2\text{O})(\text{MeOH})_{n-2}(\text{H}_2\text{O})$. This series appeared abruptly around $n \geq 12$.

(1) The dominant series of peaks has a formula of $\text{LaO}^+(\text{MeOH})_n(\text{MeOMe})$ with n ranging from 0 to 15 (see Figure 4). The intensity decreases monotonically with cluster size. Although the peak of $\text{LaO}^+(\text{MeOH})_n$ for $n = 1$ is quite intense, that for $n \geq 2$ is negligibly small in comparison to $\text{LaO}^+(\text{MeOH})$. This indicates that the reaction requires at least two methanol molecules, and furthermore, as long as $n \geq 2$, the following reaction occurs spontaneously:



This reaction is similar to that catalyzed by Fe^+ and alkali metal ions, as well as protons in the sense that methanol molecules have been converted to ethers. However, in this case the ether is retained in the cluster and the H_2O is ejected. Moreover, the dehydration reaction catalyzed by LaO^+ exhibits a critical cluster size of $n = 2$, which is much smaller than that found in Fe^+ -catalyzed reactions, implying that the reaction occurs before the solvation shell forms.

(2) In the middle cluster size range, multiple-ether formation occurs as can be seen in Figure 5. The general formula for these products is $\text{LaO}^+(\text{Me}_2\text{O})_m(\text{MeOH})_n\text{X}$, where m ranges from 1 to 3, n ranges from 2 to 4, and X has a mass of 44, the same mass as a dehydrogenated ether. An intriguing observation is that the multiple-ether formation is always followed by the X . One possible explanation is that a MeOH in the hot complex $[\text{LaO}^+(\text{Me}_2\text{O})(\text{MeOH})_n]^*$ is dehydrogenated to form $\text{CH}_2=\text{O}$, which in turn reacts with other MeOH s by addition and dehydration reactions, producing $\text{CH}_3\text{OCH}_2\text{OCH}_3$. The product has a mass of X plus a MeOH . This reaction appears to be restricted to a narrow range of cluster sizes.

(3) For even larger clusters, the series $\text{LaO}^+(\text{MeOH})_n$ ($n \geq 12$) appears again although the series $\text{LaO}^+(\text{Me}_2\text{O})(\text{MeOH})_n$ still exists in this mass range (see Figure 6). It is not clear whether the species exist as $\text{LaO}^+(\text{Me}_2\text{O})(\text{H}_2\text{O})(\text{MeOH})_{n-2}$ or $\text{LaO}^+(\text{MeOH})_n$ since they have exactly the same mass. The presence of a sharp critical size for this series at $n = 12$ is suggestive of the completion of the first solvation shell. In contrast to Fe^+ -catalyzed reactions, this solvation shell may stabilize the complex from reaction by raising the activation barrier to the transition state. In this case the addition product $\text{LaO}^+(\text{MeOH})_n$ will form. Alternatively, the reaction products Me_2O and H_2O may be trapped in the solvent due to the cage effect, forming $\text{LaO}^+(\text{Me}_2\text{O})(\text{H}_2\text{O})(\text{MeOH})_{n-2}$. More work needs to be carried out to identify the reaction products.

It is quite clear that the catalytic mechanism for LaO^+ in methanol conversions is rather different from that for Fe^+ . First of all, the reaction occurs before the solvation shell forms. Therefore, the purely electrostatic effect present in the Fe^+ -catalyzed reaction is no longer predominant. Instead, to make some progress, the close-approach covalent interaction must be considered. Since pure electrostatic interaction is not important in this case, water is not necessarily retained. In just the opposite way, somehow ether retention is preferred. The preference of ether retention may be suggestive of the participation of covalent interaction. Covalent interactions of ScO^+ and YO^+ with solvents have been indicated in solvation studies of these ions.¹⁶

It should be noted that the laser-ablated metal ions may possess a broad kinetic energy distribution ranging from thermal energy to several tens of electronvolts.¹⁷ However, since the metal ion velocity is perpendicular to the supersonic methanol cluster beam direction facing the extraction region of the mass spectrometer, our experimental configuration preferentially samples the low-energy collisions. In addition, it is known that, at low collision energies and under multiple-collision conditions, addition products can be easily obtained for transition metal ions.¹⁸ Products from higher energy collisions may also be detected if upon collision the metal ion kinetic energy is taken away by evaporating methanol molecules from the methanol clusters.

One possible concern about the above experimental results is that the water-retaining mass peaks in the mass spectra could be due to trace amount of water impurities. The best way to resolve this problem is to carry out isotopic substitution experiments. In fact, Castleman *et al.* and Lisy *et al.* have done

that to exclude water impurity as the source of the series of water-retaining species in the dehydration reaction of alkali metal-methanol cluster cations.^{8,9} It seems unlikely that the water impurity can only be introduced to the cluster frame $\text{Fe}^+(\text{CH}_3\text{OH})_n$ as $n \geq 10$, a number remarkably close to the critical size of dehydration reaction in alkali metal-methanol cluster cations. Mixed water-methanol clusters would have been most abundant at small sizes were the water-retaining species $\text{Fe}^+(\text{CH}_3\text{OH})_m(\text{H}_2\text{O})$ due to trace amount of water impurity in the sample.¹⁹ Furthermore, we used spectrum grade methanol (<0.02% water impurity) in our experiment, and water impurity as a cluster source was minimized.

Summary and Conclusions

The experiment reported here has demonstrated two types of reactions of methanol clusters induced by Fe^+ and LaO^+ , which lead to the same products—ether and water. One is due to a purely electrostatic effect for a transition metal ion Fe^+ in a solvation shell with a critical size of $n = 12$, similar to the reaction catalyzed by alkali metal ions and protons. The other is due to a catalytic effect involving covalent interactions between LaO^+ and methanol clusters in the absence of a solvation shell for the rare earth metal oxide ion LaO^+ . Two methanol molecules are converted to ether and water spontaneously in the presence of LaO^+ with a critical cluster size of only 2. The purely electrostatic effect for the transition metal ion Fe^+ is remarkably similar to that of alkali metal ions and protons, which shows further that the catalytic effect in a solvation shell depends only slightly on the type of the ion in the center of the shell.

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References and Notes

- (1) Castleman Jr., A. W.; Keesee, R. G. *Chem. Rev.* **1986**, *86*, 589; *Science* **1988**, *241*, 36.
- (2) Morris, R. A.; Viggiano, A. A.; Paulson, J. F.; Henchman, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 5932.
- (3) Morgan, S.; Keesee, R. G.; Castleman Jr., A. W. *J. Am. Chem. Soc.* **1989**, *111*, 3841.
- (4) Morgan, S.; Castleman Jr., A. W. *J. Am. Chem. Soc.* **1987**, *109*, 2867.
- (5) Zhang, X.; Yang, X.; Castleman Jr., A. W. *Chem. Phys. Lett.* **1991**, *185*, 298.
- (6) El-Shall, M. S.; Marks, C.; Sieck, L. W.; Meot-Ner, M. *J. Phys. Chem.* **1992**, *96*, 2045.
- (7) Draves, J. A.; Lisy, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 9006.
- (8) Selegue, T. J.; Moe, N.; Draves, J. A.; Lisy, J. M. *J. Chem. Phys.* **1992**, *96*, 7268.
- (9) Zhang, X.; Castleman Jr., A. W. *J. Am. Chem. Soc.* **1992**, *114*, 8607.
- (10) Selegue, T. J.; Lisy, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 4874.
- (11) Huang, R. B.; Lu, W. Y.; Yang, S. H. *J. Phys. Chem.* **1995**, *102*, 189.
- (12) Huang, R. B.; Li, H. D.; Lin, Z. Y.; Yang, S. H. *J. Phys. Chem.* **1995**, *99*, 1418.
- (13) Lu, W. Y.; Huang, R. B.; Yang, S. H. *Chem. Phys. Lett.*, submitted.
- (14) Miller, D. R. In *Atomic and Molecular Beam Methods*; Scoles, G., Buck, D. B., Laine, D., Eds.; Oxford University Press: New York, 1988.
- (15) Kaya, T.; Horiki, Y.; Kobayashi, M.; Shinohara, H.; Sato, H. *Chem. Phys. Lett.* **1992**, *200*, 435.
- (16) Cabarcos, O. M.; Lisy, J. M. Private communication.
- (17) Lessen, D. E.; Asher, R. L.; Brucat, P. J. *J. Chem. Phys.* **1990**, *93*, 6102; **1991**, *95*, 1414.
- (18) Garvey, J. F.; Herron, W. J.; Vaidyanathan, G. *Chem. Rev.* **1994**, *94*, 1999 and references cited therein.
- (19) Wilson, K. L.; Buckner, S. W. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 848.
- (20) Sato, H. *Res. Chem. Intermed.* **1993**, *19*, 67.
- (21) Clemmer, D. E.; Chen, Y. M.; Khan, F. A.; Armentrout, P. B. *J. Phys. Chem.* **1994**, *98*, 6522.
- (22) Stace, A. J.; Shukla, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 5314.