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The Formation of $[TiO(H_2O)_n]^+$ Cluster Ions

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Gas phase $[TiO(H_2O)_n]^+$ clusters are produced by laser induced plasma reactions of titanium and water, and studied using a triple quadrupole mass spectrometer. More than 60 water molecules cluster onto TiO^+; but, no $[Ti(H_2O)_n]^+$ clusters are observed. The cluster size distributions of $[TiO(H_2O)_n]^+$ can be fit to log-normal curves. Considered in the context of other data reported herein for cluster distributions of $[NbO(H_2O)_n]^+$, it is concluded that the cluster formation and growth proceed *via* a coalescence mechanism between $[TiO(H_2O)_n]^+$ and water molecule(s), which may lead to the formation of solvation shells. *Ab initio* calculations were employed to gain insight into the structures and energetics of small $[TiO(H_2O)_n]^+$ clusters with n = 1–3. A charge donation from the water ligand to the TiO^+ ion is found, which indicates the existence of high binding energies between water and TiO^+. These experimental and theoretical results further contribute to an understanding of ion-induced nucleation in general, and hydration of TiO^+, in particular.

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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INTRODUCTION

Ion-water clusters play an important role in atmospheric condensation,[1] ion-induced nucleation,[2–4] and ion solvation,[5] and have been extensively studied for many years. Through measurements of the successive hydration energies by high-pressure mass spectrometry,[6–7] and bond dissociation energies obtained by collision induced dissociation mehtods,[8–11] and *ab initio* calculations,[12–18] it is found that the interactions between metal cations and water molecules are mainly electrostatic. The binding energies of the first water onto first row transition metal cations is about 125–167 kJ/mol.[11,17] However, the binding of a second water is stronger than that of the first one in the case of a number of first-row transition metal ions[17] such as V^+, Cr^+, Fe^+, and Cu^+. Theoretical studies also point out that in the case of Mg^+ and Al^+, all waters bind on the same side due to the polarization of the 3s orbital away from the ligand.[15] Additionally, for $[Mg(H_2O)_n]^+$ clusters, it is found that a dehydrogenation reaction occurs when n is larger than 4.[19]

However, by comparison, little is known about the hydration of metal oxide cations in either the gas phase or condensed phase, although it has been long known that metal oxide cations such as oxotitanium ions can exist in solutions.[20] It would be particularly instructive to know if metal oxide cations and metal cations have different hydration behavior. TiO_2 is a most useful oxide as a pigment, coating material and catalyst, and is known to be photocatalytically active. TiO^+ is a dominant species in the gas phase formed from reactions of titanium and traces of oxygen, and as a component in the vaporization of TiO_2.[21] Ground state Ti^+ also reacts readily with water vapor to form TiO^+.[22] It is also found that TiO^+ displays a significant difference from Ti^+ when clustering to N_2.[23] For these reasons, and to further elucidate their behavior, $[TiO(H_2O)_n]^+$ clusters are chosen as the objective of the present study. In the current investigation, these species are produced by laser induced plasma reactions of titanium and water.

Recently, it has been reported that size distributions of elemental clusters produced using laser chemistry or supersonic expansion can be fitted into log-normal curves,[24–28] which is often taken as being suggestive that the formation of these clusters proceeds through a coalescence growth mechanism. Log-normal distributions are widely used to describe the size distributions of the product of breaking, milling, and grinding processes. Such distributions also aptly describe the formation of new phase nuclei, and the ultimate size distributions arising from their further growth *via* association and coagulation.[29–32] The general time evolution of the size distribution can be represented by Smoluchowski's kinetic equation.[24] For cluster formation, this equation takes the general form of a second-order chemical reaction, and eventually, it can be represented by the following equation:

$$F(x) = (1x\sigma\sqrt{2\pi})\ \exp(-(1nx-\mu)^2/2\sigma^2)$$

$F(x)$ stands for the standard log-normal distribution function, μ and σ are the logarithm of the statistical median, and the geometric standard deviation, respectively. More recently, it was also found that the general form of these clusters which have log-normal distributions can be defined as $AB_nC_{m\ldots}$, where A is a charged cluster nucleus and B, C, … are neutral building blocks.[33] The first goal of the present studies is to examine if the size distribution of $[TiO(H_2O)_n]^+$ clusters can be fitted into this model, and to gain insight into the formation mechanism of these ion-water clusters; the second goal is to investigate the structures and energies of small $[TiO(H_2O)_n]^+$ (n = 1–3) clusters by employing *ab initio* calculations. Through the present studies, useful information related to ion-induced nucleation and ion hydration is provided and discussed.

EXPERIMENTAL

The apparatus used in this work is a triple quadrupole mass spectrometer coupled with a laser vaporization source. A detailed description of the experimental procedure and this apparatus is given elsewhere.[34] In brief, the second harmonic output of a Nd:YAG laser is used to ablate the surface of a rotating titanium rod. Then, $[TiO(H_2O)_n]^+$ clusters are produced through a plasma reaction between metal and water with a concentration of 0.5% mixed in the helium carrier gas. Related experiments are also conducted with niobium. In some experiments D_2O is used in place of H_2O to facilitate mass identification of the peaks; no difference in behavior between the two isotope species was found. After exiting the source and passing the skimmer with a 5 mm diameter, the cluster beam is deflected and focused several times. Thereafter, it enters the quadrupole mass spectrometers, where the clusters are analyzed and detected by a channeltron electron multiplier.

Calculational Methods

Gaussian-92 software[35] is used in performing all the calculations of energies and structures of $[TiO(H_2O)_n]^+$ clusters reported herein. The standard STO-SG* basis set was used in all calculations and geometry optimizations are carried out at the CISD/STO-3G* level. In all cluster geometric optimizations, it is assumed that the water structure remains unchanged; the experimental values[36] of 0.957 Å for the O–H bond length and 104.5° for the H–O–H bond angle are used. All the calculations were carried out in our laboratory on an IBM RISC 6000 model 550 work station.

RESULTS AND DISCUSSION

The mass spectrum resulting from the laser induced plasma reactions of titanium with D_2O is displayed in Figure 1. By comparison with mass spec-

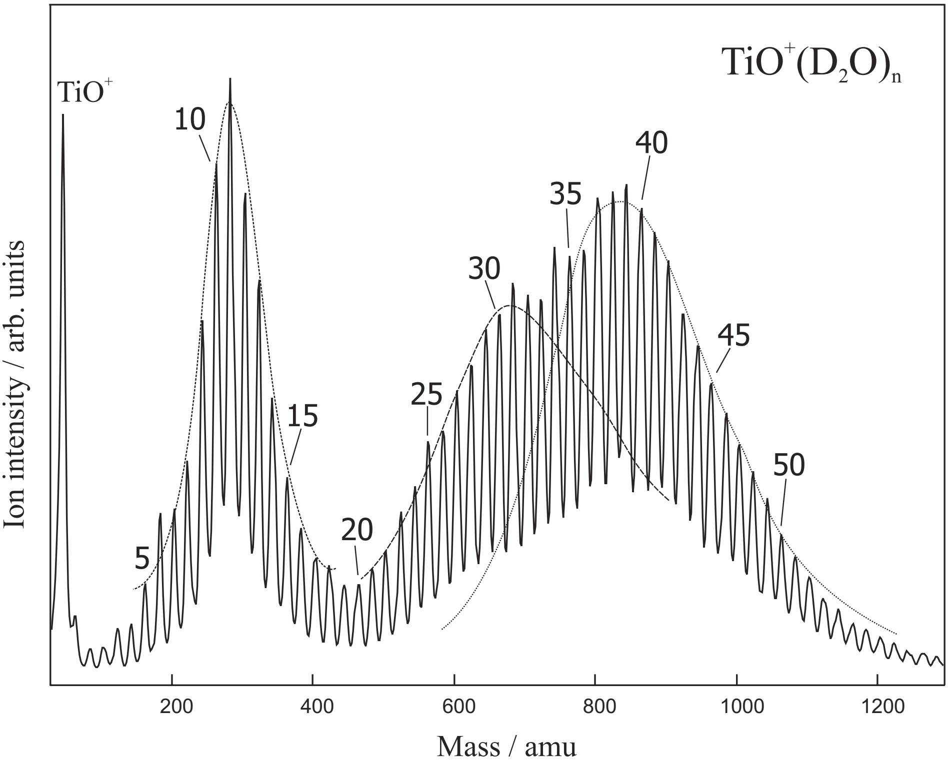

Figure 1. Size distribution of $[TiO(H_2O)_n]^+$ clusters and fitted log-normal curves.

tra we have taken of $[TiO(H_2O)_n]^+$, the peaks in Figure 1 can be accurately assigned. More than 60 waters are found to cluster onto the TiO^+ ion. But no peaks assignable to $[Ti(H_2O)_n]^+$ or $[TiO_2(H_2O)_n]^+$ are observed under the present experimental conditions.

It is evident that the peaks of $[TiO(D_2O)_n]^+$ in Figure 1 can be represented as being composed of two humps with each displaying a Gaussian type peak distribution. Using a curve-fitting method, the first hump can be accurately fitted into one log-normal curve, but the second hump needs two log-normal curves to be well represented. The fitted log-normal curves are also displayed in Figure 1. It can be noticed that small peaks, namely $[TiO(D_2O)_{1-4}]^+$, are not well fit by a log-normal curve. Studies on carbon clusters[27] suggest that clusters which can be fitted into one log-normal curve should possess similar structures and stabilities. Hence, it is probable that the structures of $[TiO(D_2O)_{1-4}]^+$ are different from $[TiO(D_2O)_5]^+$ to $[TiO(D_2O)_{20}]^+$ where those in the first hump can be well fitted into one log-normal curve. This can be understood in considering the interactions in these clusters. For the small species, ion-dipole interactions are dominant for the formation of the clusters. With increasing numbers of ligands, ligand-repulsion starts to become appreciable. The cluster structures can rearrange to form a solvation shell, in which hydrogen bonding is dominant.

In order to probe the structures and energetics of the small $[TiO(D_2O)_{1–4}]^+$ clusters, *ab initio* calculations are employed. It is found by CASSCF calculations that the bonding in TiO is through a polarized double bond, and the ground state is a $^3\Delta$ state.[37] In the present calculations, we assumed that the formation of $[TiO(H_2O)_n]^+$ comes from the ground state of TiO^+, which is a doublet state. The geometries and energies of $[TiO(H_2O)_{1–3}]^+$ are calculated at the CISD/STO-3G* level. The calculational results are listed in Table I.

TABLE I

Energies and geometries of $[TiO(D_2O)_{1–3}]^+$ clusters

	HF energy a.u.	Bonding length of Ti–O$^+$ / Å	Charges on titanium	Charges on oxygen of TiO
$TiO^+(H_2O)$	994.19	1.551	0.915	–0.250
$TiO^+(H_2O)_2$	1069.87	1.559	0.720	–0.330
$TiO^+(H_2O)_3$	1145.55	1.561	0.631	–0.408

In comparison with the energies of H_2O and TiO^+ calculated by the same method, it is found that the energy for binding the first water onto TiO^+ and the second water onto $[Ti(H_2O)_1]^+$ are similar, about 2.61 eV. Although the low basis sets used in this calculation may cause an overestimation of these binding energies, these values still indicated that the bonding between TiO^+ and water molecules is very strong. These unusually high binding energies come from the contribution of electrostatic interactions and charge transfer between TiO^+ and the water molecules. This can be seen from Table I which shows that the charge state of titanium decreases as the number of waters increases. Unlike the structure of $[Ti(H_2O)_2]^+$ which is linear, $[TiO(H_2O)_1]^+$ has a bent structure with a O–Ti–O angle of 108° for producing more overlap between the 2p orbitals of water and 3d orbitals of titanium. When the second water approaches $[TiO(H_2O)_1]^+$, a $[TiO(H_2O)_2]^+$ cluster with C_{2v} symmetry is formed. The bond lengths between TiO^+ and water(s) are 1.938 Å and 1.955 Å for $[TiO(H_2O)_1]^+$ and $[TiO(H_2O)_2]^+$, respectively. The binding of the third water onto $[TiO(H_2O)_2]^+$ leads to a significant change of cluster structure from two dimensions to three dimensions with a non-symmetrical structure

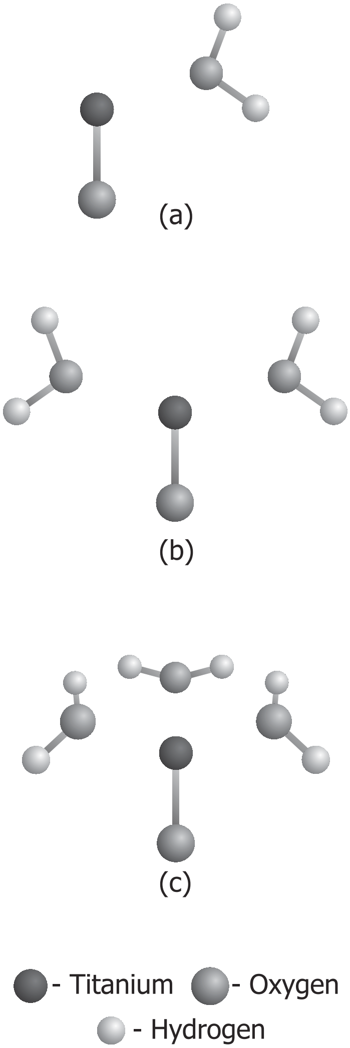

Figure 2. The optimized geometric structures of $[TiO(H_2O)_n]^+$; (a) $[TiO(H_2O)]^+$, (b) $[TiO(H_2O)_2]^+$, (c) $[TiO(H_2O)_3]^+$.

of $[TiO(H_2O)_3]^+$. The optimized geometric structures for $[TiO(H_2O)_{1-3}]^+$ are displayed in Figure 2(a-c). Optimizations of geometric structures for $[TiO(H_2O)_{4-5}]^+$ are not achieved. This may simply imply that the fourth water can only attach to $[TiO(H_2O)_3]^+$ by forming hydrogen bonds with water molecules. More reliable calculations and measurements of bonding dissociation energies are expected in the future.

For the $[TiO(H_2O)_n]^+$ clusters with n being larger than 3, the cluster size distribution can be fit to log-normal curves. As mentioned above, log-normal distributions are expected to result in cases where nucleation and irreversible coalescence processes are operative. Using fractal and kinetic equations, Chaiken *et al.* have established a kinetic model in accounting for this type of formation mechanism.[24] In this model, the cluster distribution can be determined by two kinetic parameters, the dimerization rate constant and homogeneity exponent ω. The homogeneity exponent ω is related to two factors: (1) the scaling equation $K_{\lambda_i \lambda_j} = \lambda^{2\omega} K_{ij}$, where λ is a scaling exponent and K_{ij} is the rate constant of formation of $(i + j)$-mers from i-mers and j-mers; and (2) the cluster distribution, $k_m/\langle k\rangle = 2\omega(2\omega - 1)$, in which k_m and $\langle k\rangle$ stand for the most probable cluster size and the average cluster size, respectively. Assuming that the formation of water clusters is through hydrogen bonding, it might be considered that every incoming water molecule takes up one site of the cluster surface, and provides two sites enabling further hydrogen bonding and associated accommodation of additional water molecules. Therefore, this formation process will lead to the extremely extended system with the small fractal dimension of the cluster.[24] Although the value of the homogeneity exponent ω for the size distribution of water clusters is not available, it is expected that this value could be more negative than for other cluster systems which display a log-normal size distribution. Using the log-normal distribution of $[TiO(H_2O)_n]^+$, we found that the homogeneity exponent ω is approximately –3.5 for the size distribution of $[TiO(H_2O)_n]^+$, which is consistent with theoretical expectations.[24]

Previous reports on the size distributions of water clusters have always revealed that cluster distributions are skewed to smaller cluster sizes. However, the size distribution of $[TiO(H_2O)_n]^+$ is much more symmetric as seen in Figure 1. The formation of large $[TiO(H_2O)_n]^+$ clusters could proceed through $[TiO(H_2O)_3]^+$, which has three water molecules and can further bond 6 water molecules. Thereafter, the $[TiO(H_2O)_9]^+$ cluster can associate another 12 water molecules and lead to the formation of the $[TiO(H_2O)_{21}]^+$ cluster. A distribution is observed in Figure 1, in which the size distribution of $[TiO(H_2O)_{320}]^+$ clusters can be fit to one log-normal curve. For elemental clusters, usually only one log-normal curve is found to fit the cluster distribution. However, three log-normal curves are required in the size distribution of $[TiO(H_2O)_n]^+$ clusters. It is still unclear how these larger clusters are formed, but the results are suggestive of a kinetically controlled growth process.

The same general type of cluster size distribution is also observed for $[NbO(D_2O)_n]^+$, which is displayed in Figure 3 along with fitted log-normal curves. No $[NbO(D_2O)_n]^+$ clusters with $n < 20$ are observed under similar ex-

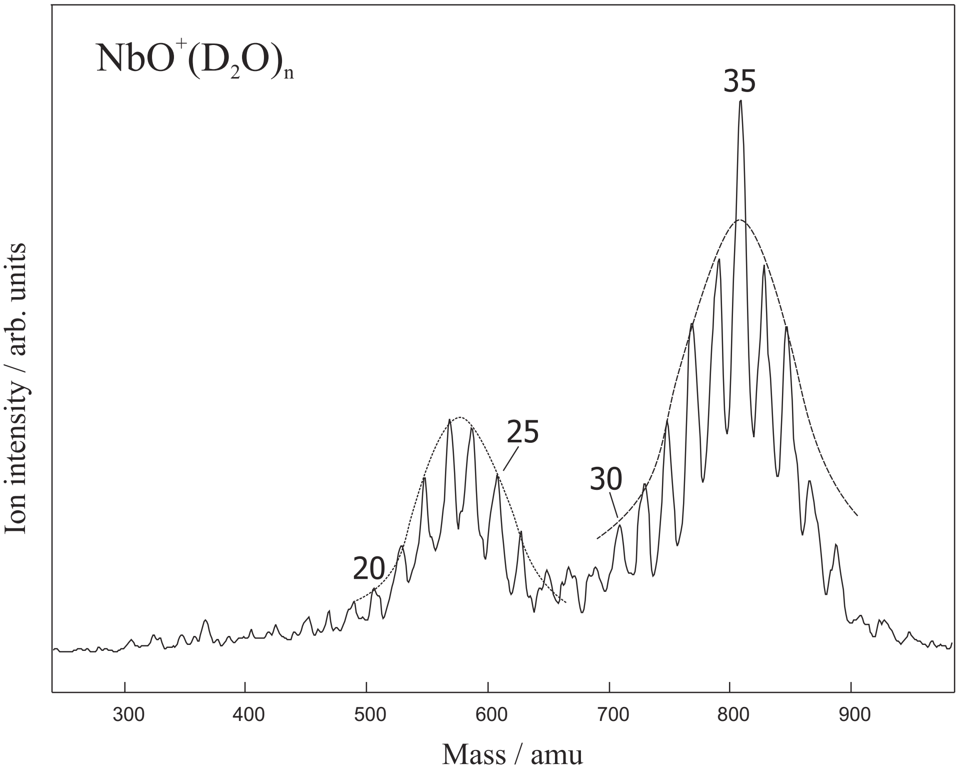

Figure 3. Size distribution of $[NbO(D_2O)_n]^+$ clusters and fitted log-normal curves.

perimental conditions, which implies that the formation of the larger clusters is more facile than in the case of $[TiO(D_2O)_n]^+$. The size distribution of $[NbO(H_2O)_n]^+$ is influenced by the experimental conditions. It is found that increasing the time that the pulse valve is open for the reactant gas at the same water concentration leads to a new cluster distribution such as that displayed in Figure 4.

The above results clearly indicate that the formation of $[TiO(H_2O)_n]^+$ and $[NbO(H_2O)_n]^+$ is purely a kinetic nucleation event. The formation process may happen in the supersonic expansion, in which the internal temperature can be significantly decreased, and where the clusters have low kinetic energy. When these hydrated ion clusters collide at low kinetic energy with other water clusters, subsequent cooling collisions can take place which enable needed removal of the internal energy and reduce the probability of metastable decay, thereby resulting in cluster distributions that can be fitted into log-normal curves. The variation of experimental conditions can greatly change the cluster size distribution which indicates that the formation of these ion-water clusters is kinetically controlled.

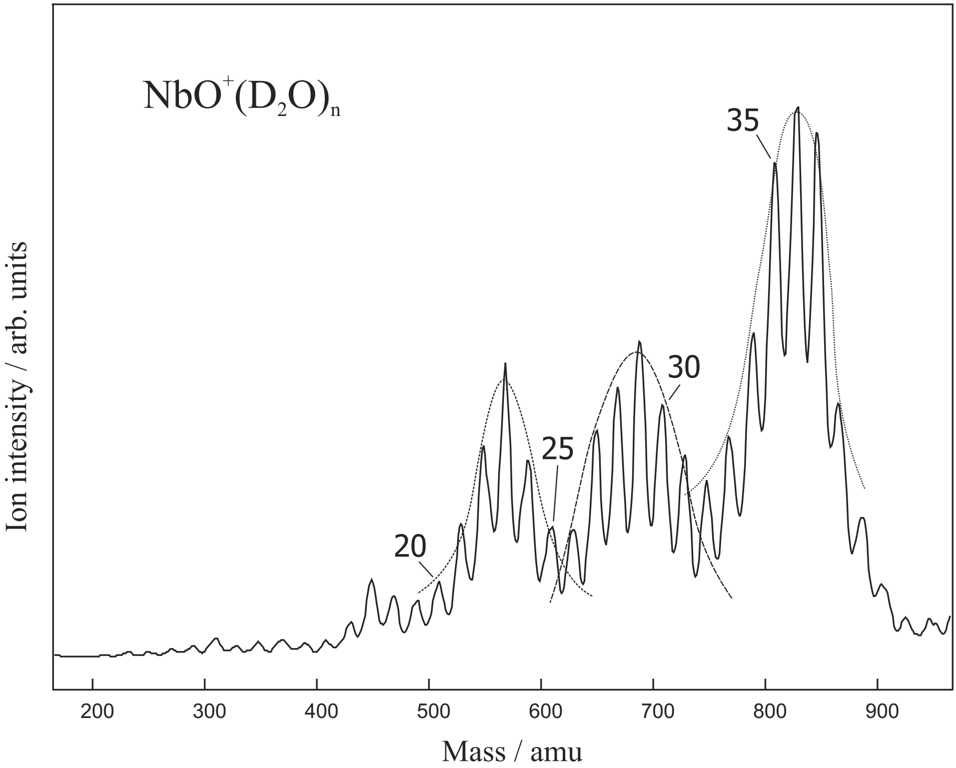

Figure 4. Size distribution of $[NbO(D_2O)_n]^+$ clusters and fitted log-normal curves at a higher source pressure of D_2O.

Beside these cluster size distributions, there are two more interesting experimental results worth discussing. First, although there is a strong interaction between Ti^+ and water, about 1.6 eV,[11,17] no $[Ti(H_2O)_n]^+$ clusters are observed under the present experimental conditions. The formation of TiO^+ is through the reaction of Ti^+ with water,[23,37–39] and can be represented by the following equation:

$$Ti^+ + H_2O \rightarrow H\text{–}Ti^+\text{–}OH \rightarrow TiO^+ + H_2 + 104\ \text{kJ/mol}$$

In addition, the intermediate is irreversible to $Ti^+\text{–}H_2O$.

Second, a difference is noticed between the ion-molecule reaction of TiO^+ with N_2 and the present experimental results. The ion-molecule reaction of TiO^+ with N_2 leads to a cluster distribution truncation[22] at $n = 5$, but the nozzle beam expansion in the present work leads to a log-normal distribution of large $[TiO(H_2O)_n]^+$ clusters. This is due to the nature of the bonding in the nitrogen complex as well as the internal energy in the nozzle beam expansion being much lower than that in the case of the reported ion-molecule reactions involving water.

CONCLUSIONS

$[TiO(H_2O)_n]^+$ clusters are produced by laser induced plasma reactions of Ti with water. The cluster distribution can be fitted into log-normal curves, which suggests that the formation of $[TiO(H_2O)_n]^+$ clusters may be dominated by a coalescence growth mechanism. The energies and structures of small $[TiO(H_2O)_{1-3}]^+$ are given and discussed in terms of *ab initio* calculations. $[TiO(H_2O)]^+$ has a bent structure with the O–Ti–O angle of 108°, and $[TiO(H_2O)_2]^+$ has a C_{2v} symmetry. The high bonding energies between TiO^+ and water(s) come from the contributions of charge transfer from water to titanium and electrostatic interactions.

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REFERENCES

1. B. Y. H. Liu, K. T. Whitby, and H. H. S. Yu, *J. Colloid Interface Sci.* **23** (1967) 367–378.
2. A. C. Zettelmoyer (Ed.), *Nucleation,* Dekker, New York, 1969, Chaps. 1–3.
3. F. F. Abraham and J. V. Dave, *J. Chem. Phys.* **55** (1971) 1587–1597.
4. A. W. Castleman, Jr. and I. N. Tang, *J. Chem. Phys.* **57** (1972) 3629–3638.
5. S. Goldman and R. G. Bates, *J. Am. Chem. Soc.* **94** (1972) 1476–1484.
6. P. Kebarle, *Ann. Rev. Phys. Chem.* **28** (1977) 445–476.
7. P. W. Holland and A. W. Castleman, Jr., *J. Chem Phys.* **76** (1982) 4195–4205.
8. P. J. Marinelli and R. R. Squires, *J. Am. Chem. Soc.* **111** (1989) 4101–4103.
9. T. F. Magnera, D. E. David, and J. Michl, *J. Am. Chem. Soc.* **111** (1989) 4100–4101.
10. T. F. Magnera, D. E. David, D. Stulik, R. G. Orth, H. T. Jonkman, and J. Michl, *J. Am. Chem. Soc.* **111** (1989) 5036–5043.
11. N. F. Dalleska, K. Honma, L. S. Sunderlin, and P. B. Armentrout, *J. Am. Chem. Soc.* **116** (1994) 3519–3528.
12. H. Watanabe, M. Aoki, and S. Iwata, *Bull. Chem. Soc. Jpn.* **66** (1993) 3245–3252.
13. C. W. Bauschlicher, S. R. Langhoff, H. Partridge, J. E. Rice, and A. J. Komormicki, *J. Chem. Phys.* **95** (1991) 5142–5148.

14. C. W. Bauschlicher and H. Partridge, *J. Phys. Chem.* **95** (1991) 3946–3950.
15. C. W. Bauschlicher and H. Partridge, *J. Phys. Chem.* **95** (1991) 9694–9698.
16. E. D. Glendening and D. Feller, *J. Phys. Chem.* **99** (1995) 3060–3067.
17. M. Rosi and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **90** (1989) 7264–7272.
18. M. Rosi and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **92** (1990) 1876–1878.
19. A. C. Harms, S. N. Khanna, B. Chen, and A. W. Castleman, Jr., *J. Chem. Phys.* **100** (1994) 3540–3544.
20. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, New York, Pergamon Press, 1984, Chap. 21.
21. Z. Y. Chen, G. J. Walder, and A. W. Castleman, Jr., *Phys. Rev. B* **49** (1994) 2739–2752.
22. E. M. Snyder, J. Purnell, S. Wei, S. A. Buzza, and A. W. Castleman, Jr., *Chem. Phys.* **207** (1996) 355–366.
23. G. M. Daly and M. S. El-Shall, *J. Chem. Phys.* **100** (1994) 1771–1772.
24. M. Villarica, M. J. Casey, J. Goodisman, and J. Chaiken, *J. Chem. Phys.* **98** (1993) 4610–4625.
25. I. Pocsik, *Z. Phys. D* **20** (1991) 395–397.
26. C. R. Wang, R. B. Huang, Z. Y. Liu, and L. S. Zheng, *Chem. Phys. Lett.* **227** (1994) 103–108.
27. C. R. Wang, R. B. Huang, Z. Y. Liu, and L. S. Zheng, *Chem. Phys. Lett.* **227** (1994) 109–114.
28. R. Botet and R. Jullien, *J. Phys. A: Math. Gen.* **17** (1984) 2517–2530.
29. G. C. Lindauer and A. W. Castleman, Jr., *Nucl. Sci. Eng.* **43** (1971) 212–217.
30. G. C. Lindauer and A. W. Castleman, Jr., *J. Aerosol Sci.* **2** (1971) 85–91.
31. J. Aitchison and J. A. C. Brown, *The Log-normal Distribution*, Cambridge University Press, Cambridge, 1973.
32. T. Allen, *Particle Size Measurements*, Powder Techn. Series, Chapman and Hall, London, 1981.
33. C. R. Wang, R. B. Huang, Z. Y. Liu, and L. S. Zheng, *Chem. Phys.* **201** (1995) 23–34.
34. K. P. Kerns, B. C. Guo, H. T. Deng, and A. W. Castleman, Jr., *J. Chem. Phys.* **101** (1994) 8529–8534.
35. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gompers, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *Gaussian 92,* Revision A, Gaussian Inc., Pittsburgh, PA, 1992.
36. W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24** (1956) 1139–1165.
37. C. W. Bauschlicher, P. S. Bagus, and C. J. Nelin, *Chem. Phys. Lett.* **101** (1983) 229–234.
38. B. C. Gou, K. P. Kerns, and A. W. Castleman, Jr., *J. Phys. Chem.* **96** (1992) 4879–4883.
39. Y. M. Chen, D. E. Clemmer, and P. B. Armentrout, *J. Phys. Chem.* **98** (1994) 11490–11498.
40. R. S. MacTaylor, W. D. Vann, and A. W. Castleman, Jr., *J. Phys. Chem.* **100** (1996) 5329–5333.

SAŽETAK

Nastajanje klusterskog iona $[TiO(H_2O)_n]^+$

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Klusteri $[TiO(H_2O)_n]^+$ u plinskoj fazi proizvedeni su reakcijama titanija i vode u plazmi induciranoj laserom, te proučavani primjenom trostrukoga kvadrupolnog masenog spektrometra. Više od 60 molekula vode bilo je vezano u kluster s TiO^+, dok klusteri $[TiO(H_2O)_n]^+$ nisu opaženi. Prikazane su raspodjele veličine klustera $[TiO(H_2O)_n]^+$. Uzimajući u obzir postojeće podatke o distribuciji klustera $[NbO(H_2O)_n]^+$, zaključeno je da se nastajanje i rast klustera u istraživanom sustavu zbiva mehanizmom koalescencije između $[TiO(H_2O)_n]^+$ i molekula vode što može dovesti do stvaranja solvatacijskih ovojnica. Primijenjeni su računi *ab initio* da se dobije uvid u strukture i energetiku malih klustera $[TiO(H_2O)_n]^+$, $n = 1$ do 3. Opažen je prijenos naboja s liganda vode na ion TiO^+, što ukazuje na visoku energiju vezanja između vode i TiO^+. Ti eksperimentalni i teorijski rezultati dodatno pridonose razumijevanju nukleacije inducirane ionom, te hidratacije iona TiO^+.