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学位(専攻分野)	博士(理学)
学位記番号	総研大甲第102号
学位授与の日付	平成6年9月20日
学位授与の要件	数物科学研究科 機能分子科学専攻 学位規則第4条第1項該当
学位論文題目	Studies on Microscopic Solvation Dynamics for Clusters Containing Metal Atoms/Ions.
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## 1. Introduction.

Electrons and metal ions in fluids play important roles in many aspects of chemical phenomena and have been the subject of numerous investigations for many years. Although experimental and theoretical studies have attempted to understand the nature and the dynamics of solvation for these species, its microscopic aspect has not yet been fully understood. Recently, advances in molecular beam technique open new approaches to a microscopic investigation of the excess electrons and metal ions in fluids. The clusters containing neutral metal atoms and/or their ions have found to be easily produced in a beam. The study of successively large clusters is analogous to modeling the process of solvation and provides us information on microscopic solvation.

The purpose of this study is to get insights into the electron delocalization, the formation of solvation shell, and the fundamental interactions among ions, solvent molecules, and electrons *via* the observation of the physical and chemical properties of the gas-phase clusters containing metal atoms and their ions as a function of number of solvent molecules.

## 2. Photoionization processes of solvated alkali atom clusters.

Cesium atoms solvated with polar solvents,  $\text{Cs}(\text{H}_2\text{O})_n$ ,  $\text{Cs}(\text{NH}_3)_n$ , and  $\text{Cs}(\text{CH}_3\text{CN})_n$ , are studied by one-photon ionization and time-of-flight mass spectroscopy. The solvated Cs atom clusters are produced by a pickup type cluster source. Ionization potentials of these clusters are determined by the observation of photoionization efficiency curves as a function of the laser photon energy. The ionization potentials of  $\text{Cs}(\text{H}_2\text{O})_n$  and  $\text{Cs}(\text{CH}_3\text{CN})_n$  are found to be constant for  $n \geq 4$  (3.1eV) and  $n \geq 12$  (2.4eV), respectively, while that for  $\text{Cs}(\text{NH}_3)_n$  decreases monotonically with increasing  $n$  to a limit of 1.4eV, which coincides with the bulk value. These results are discussed in connection with the stability of solvated electrons in these polar solvents. Especially, the behavior of the ionization potentials for  $\text{Cs}(\text{H}_2\text{O})_n$ , which exhibit the bulk value only at  $n=4$ , is ascribed to the stabilization of an ion-pair state; a spontaneous ionization of metal atom occurs even in the small clusters.

## 3. Photodissociation processes of hydrated alkaline-earth metal ion clusters.

Ionic clusters are relevant to many chemical phenomena such as flame, catalysis, solvation, surfaces, and uncleanation. In particular, the clusters containing metal ions have studied extensively, because these clusters play an important role for the reactions both in the gas-phase and in solution. These ions are also observed as the constituents of the upper/lower atmosphere. Until

now, most of the studies on the solvated clusters containing metal ions have been devoted to determining the successive hydration energies by high-pressure mass spectrometry, and collision induced dissociation and photodissociation. While the spectroscopic study of clusters as a specific function of cluster size can also play a crucial role in understanding the above phenomena, however, the experimental studies have been quite limited.

In order to get insights into energetics and dynamics of solvation, the photodissociation processes of the hydrated alkaline-earth metal ion clusters,  $M^+(H_2O)_n$  for  $M=Mg$  and  $Ca$ , are investigated using a reflectron type time-of-flight mass spectrometer. Since the alkaline-earth metal ions have an isoelectronic structure with alkali atoms, these systems include the same issue on the electron delocalization in clusters as mentioned in the previous section. The photodissociation spectra and the branching fractions of the photofragment ions are measured for the size-selected  $M^+(H_2O)_n$  ions as a function of the photolysis energy. The time-dependent photodissociation is also carried out for  $n=2$ . On the basis of these results, the electronic structure, the solvation shell, and the photodissociation processes of these clusters are discussed in relation to the solvation in bulk fluids.

**Photodissociation of  $Mg^+(H_2O)_n$  for  $n=1-5$ .** Photodissociation spectra of  $Mg^+(H_2O)_n$  for  $n=1-5$  are examined in the wavelength region from 250 to 720nm by monitoring the total yields of the fragment ions. The absorption bands exhibit redshifts as large as  $17000\text{cm}^{-1}$  with respect to the  $^2P(3p)-^2S(3s)$  resonance line of the free  $Mg^+$  ion and are explained by the shift of this transition as a result of hydration. The spectra also exhibit clear evolution of solvation shell closing at  $n=3$ , being consistent with the theoretical prediction. As for the larger clusters, the spectral features are almost the same as that for  $n=3$ . These results indicate that the effect of the second-shell waters on the electronic structure of the  $Mg^+$  ion is quite small.

The mass spectra of the fragment ions show the existence of two dissociation processes: the evaporation of water molecules and the photoinduced intracluster reaction to produce the hydrated  $MgOH^+$  ion,  $MgOH^+(H_2O)_n$ , with an H-atom elimination. The intracluster reaction is found to depend strongly on the cluster size and the photolysis wavelength. The energetics and dynamics of these dissociation processes are discussed in conjunction with the results of *ab initio* calculations.

**Photodissociation of  $Ca^+(H_2O)_n$  for  $n=1-6$ .** The photodissociation of size-selected  $Ca^+(H_2O)_n$  ions are investigated for  $n=1-6$ . The photodissociation spectra are recorded in the wavelength region from 335 to 1440nm. The spectra for this entire series of clusters show large redshifts as large as  $\sim 18000\text{cm}^{-1}$  relative to the atomic resonance lines of  $Ca^+$  near 395nm. In contrast to  $Mg^+$

$(\text{H}_2\text{O})_n$ , the absorption bands redshift monotonically with increasing cluster size for  $n$  up to 6. This discrepancy is attributed to the difference in the number of solvent molecules filling the first solvation shell, because of an  $sd\sigma$  hybridization for the latter ion: The first shell of the  $\text{Ca}^+(\text{H}_2\text{O})_n$  may be filled at  $n \sim 6$ . In the case of  $\text{Ca}^+$ , the  $^2\text{D}(3d)$  state lies between the electronic ground  $^2\text{s}(4s)$  state and the  $2\text{P}(4p)$  state. The electronic structures of these clusters are discussed including the mixing of these states.

As in the  $\text{Mg}^+-\text{H}_2\text{O}$  system, the dehydrogenation reactions to produce the hydrated  $\text{CaOH}^+$  ions are also observed for  $\text{Ca}^+-\text{H}_2\text{O}$  system. However the size-dependence of the reaction for  $\text{Ca}^+(\text{H}_2\text{O})_n$  is found to be different from that for  $\text{Mg}^+(\text{H}_2\text{O})_n$ . The results are discussed in relation to the electronic character of these cluster ions.

#### 4. Reaction of singly charged alkaline-earth metal ions with water clusters.

In the previous sections, they discussed the geometrical structure, electronic structure and reactivity of the  $\text{M}^+(\text{H}_2\text{O})_n$  clusters. In order to understand the solvation dynamics of metal ions, the investigation of the reaction between the metal ions and water clusters is also important.

In the present study, they study the reactions of  $\text{Mg}^+$  and  $\text{Ca}^+$  ions with water clusters using the reflectron time-of-flight mass spectrometer combined with the laser vaporization technique. Both the  $\text{M}^+(\text{H}_2\text{O})_n$  and  $\text{MOH}^+(\text{H}_2\text{O})_{n-1}$  ( $\text{M}=\text{Mg}$  and  $\text{Ca}$ ) ions are found to form as the reaction products with characteristic size distribution: the latter ions are produced via an H-atom elimination reaction (oxidation of  $\text{M}^+$ ). As for the  $\text{Mg}^+$  ion, the  $\text{Mg}^+(\text{H}_2\text{O})_n$  ions are dominantly produced for  $1 \leq n \leq 5$  and  $n \geq 15$ , while  $\text{MgOH}^+(\text{H}_2\text{O})_{n-1}$  are exclusively observed for  $6 \leq n \leq 14$  in the mass spectrum. The similar product distributions are also observed for  $\text{Mg}^+-\text{D}_2\text{O}$ ,  $\text{Ca}^+-\text{H}_2\text{O}$  and  $\text{Ca}^+-\text{D}_2\text{O}$  systems, though they are found to be affected by deuterium and metal substitutions. They also reexamine the photodissociation processes of the mass-selected  $\text{Mg}^+(\text{H}_2\text{O})_n$  ( $n=1-5$ ) ions, in which the photoexcitation induces both the H-atom elimination reaction and the evaporation of water molecules. On the basis of these results, the first product switching at  $n=5$  for  $\text{Mg}^+$  ( $n=4$  for  $\text{Ca}^+$ ) is ascribed to the difference in the successive hydration energies of the  $\text{M}^+$  and  $\text{MOH}^+$  ions. As for the second product switching, two possible mechanisms are proposed such as the stabilization of a Rydberg-type ion-pair state and the involvement of a new product.

## (論文審査結果)

本学位論文では、レーザー分光法と質量分析法を用いて金属原子または金属イオンを含む溶媒クラスターの幾何構造、電子構造と反応性を検討し、溶液化学を理解する上で重要な電子や金属イオンと溶媒分子間の基本的な相互作用および溶媒和ダイナミックスの微視的研究を行っている。電子の溶媒和過程との関連で極性溶媒の配位したセシウム原子 ( $\text{Cs}(\text{H}_2\text{O})_n$ ,  $\text{Cs}(\text{NH}_3)_n$ ,  $\text{Cs}(\text{CH}_3\text{CN})_n$ ) のイオン化ポテンシャルを調べた。この結果、 $\text{Cs}(\text{H}_2\text{O})_n$  では4個の水分子が配位するとイオン化ポテンシャルが凝縮相の仕事関数に収束することを見出し、溶媒和電子生成の初期過程でイオン対状態、 $\text{Cs}^+(\text{H}_2\text{O})_n^-$  の安定化が非常にサイズの小さいクラスターで起こることを示した。一方、金属イオンの水和ダイナミックスを明らかにするために、アルカリ土類金属原子の1価イオンを含む水クラスター [ $\text{M}^+(\text{H}_2\text{O})_n$  ( $\text{M}=\text{Mg}$ ,  $\text{Ca}$ )] について、電子スペクトルと励起状態ダイナミックスを光解離法を用いて系統的に調べた。この結果、 $\text{Mg}^+$  イオンでは3個、 $\text{Ca}^+$  イオンでは5~6個の水分子が配位すると第一水和殻が閉殻になることを見出した。また光解離スペクトルの解析により、基底状態および励起状態における金属イオンと水分子との相互作用は主に静電相互作用であることを明らかにした。

これらの分子の光解離生成物の解析により、光励起によって水素原子の脱離を伴った金属イオンの酸化反応が誘起され、 $\text{MOH}^+$  イオンが生成することを初めて見出した。この反応の励起エネルギー依存性の検討から、 $\text{Mg}^+(\text{H}_2\text{O})_n$  について  $n=1$  では基底状態で反応が進行するが、 $n=2$ 、 $3$  では励起状態からの反応経路が新たに開かれ、 $n=4$  と  $5$  では再び基底状態経路が優位となる特異的な反応過程のサイズ依存性を見出した。この反応機構のスイッチングは、水和エネルギーの変化と配位子間の相互作用により説明した。さらに、クラスター内でのミクロな水和過程を調べるために、 $\text{Mg}^+$  や  $\text{Ca}^+$  イオンと水クラスターとの衝突実験を行い、生成物イオン [ $\text{M}^+(\text{H}_2\text{O})_n$  と  $\text{MOH}^+(\text{H}_2\text{O})_n$  ( $\text{M}=\text{Mg}^+$ ,  $\text{Ca}^+$ )] が非常に特異的なサイズ分布を持って生成することを見出した。この現象を解明するために金属イオンと水クラスターの反応の衝突エネルギー依存性の実験を行い、生成物中の金属イオンの酸化状態が配位水の増加に伴って進行することを実証した。これらの一連の結果は、クラスター内での反応を伴うエネルギー散逸過程のダイナミックスを明らかにした数少ない例であり、バルクでの水和ダイナミックスを微視的に理解する上で重要な基礎的情報を提供する。