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論文内容の要旨

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 its 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 them information on microscopic solvation.

The purpose of this study is to get insights into the electron delocalizaion, 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 its ions as a function of number of solvent molecules. He also examined the solvated NH_4 radicals which are isoelectronic with alkali-metals.

2. Microscopic solvation process of alkali-atom in clusters; photoelectron and photoionization studies of $M(NH_3)_n$ and $M(H_2O)_n$(M=Li, Li^-, Na^-)

Photoelectron spectra(PESs) of $Li^-(NH_3)_n$ ($n\leq16$), $Na^-(NH_3)_n$ ($n\leq12$) and $Na^-(H_2O)_n$ ($n\leq7$), as well as the ionization potentials (IPs) of $Li(NH_3)_n$ ($n\leq28$) and $Li(H_2O)_n$ ($n\leq46$), are examined. PESs of $Li^-(NH_3)_n$ ($n\leq14$) exhibit three bands derived from the $Li(3^2S)$-$Li^-(^1S)$, $Li(2^2P)$-$Li^-(^1S)$, and $Li(2^2S)$-$Li^-(^1S)$ transitions. The vertical detachment energies (VDEs) of the 3^2S- and 2^2P-type states decrease dramatically with increasing n. In addition to these observations, he also finds the redshift of the neutral ground (2^2S) state with much slower rate. For $n\geq10$, the transitions to the ^2P-and ^2S-type states are almost superimposed each other. The similar spectral trends are also observed for the $Na(3^2P)$-$Na^-(^1S)$and $Na(3^2S)$-$Na^-(^1S)$ transitions of $Na^-(NH_3)_n$. On the other hand, the transitions of $Na^-(H_2O)_n$ exhibit an opposite shifts with maintaining the ^2P-^2S energy separation. As for $Li(H_2O)_n$, he finds a monotonous decrease in IPs with $n\leq4$ and a constant IP behavior for $n\geq5$. The limiting value for $n\rightarrow\infty$(3.12 eV) coincides with the photoelectric threshold of ice as in the case of $Cs(H_2O)_n$ and $Na(H_2O)_n$. Based on the results of *ab initio* calculations, he discusses these experimental findings in connection with the early stage of solvated-electron formation in finite clusters.

3. Microscopic solvation process of sodium dimer in ammonia clusters; photoelectron spectra of $Na_2(NH_3)_n^-$

Photoelectron spectra of $Na_2(NH_3)_n$ (n=0-8) are investigated in relation to the microscopic solvation process of sodium dimer in small ammonia clusters. $Na_2(NH_3)$ exhibits four bands at the vertical detachment energy (VDE) of 0.41, 1.36, 2.11 and 2.40 eV, corresponding to the transitions from the anion state to the neutral ground and excited states derived from the $X^1\Sigma_g^+$, $a^3\Sigma_u^+$, $b^3\Pi_u$, and $A^1\Sigma_u^+$ states of Na_2, respectively. The VDEs of the neutral ground state for $n\leq8$ are almost the same as that of $Na_2(^1\Sigma_g^+)$, while that of the first excited state derived from the $Na_2(^3\Sigma_u^+)$ increases gradually for $n\geq4$. In addition, the $^3\Pi_u$- and $^1\Sigma_u^+$-type transitions are found to shift rapidly to lower VDE and degenerate into the $^3\Sigma_u^+$-type transition. He discusses the solvation state of Na_2 in $(NH_3)_n$ with present results of experiments and theoretical calculations.

4. Formation and microscopic solvation process of NH_4 radical

NH_4 is a typical hypervalent Rydberg radical and its spectroscopic properties have been extensively studied since the first spectroscopic characterization by Herzberg. Although NH_4 was first well characterized with spectroscopy in the gas phase, the existence of mercury amalgam has long been anticipated. The possible existence of NH_4 radical in the reaction of the solvated electron and in electrochemistry has also been speculated on for many years. If NH_4 exists as solvated species in the condensed phase, an interesting question is raised how the Rydberg orbital is affected by the presence of large number of other molecules; the radical is expected to have a diffuse electronic structure. Since NH_4 is isoelectronic with alkali atoms, the ammoniated NH_4 clusters may serve as a new testing material to get further insight into the electron localization modes in the gas-phase clusters. Moreover, the study on the stability of these clusters as a function of the number of solvent molecules may provide them some clues to reveal the aforementioned long standing problems in bulk solution.

Formation process of NH_4 radical in ammonia clusters

Photochemical reaction of ammonia clusters in the first excited state is studied by a femtosecond pump-probe technique and a time-of-flight mass spectroscopy. Small ammonia clusters containing NH_4 radical are probed by resonance enhanced two-photon ionization method. NH_4 radical is formed within 0.5 ps and decomposes with a lifetime of 13 ps. The ammonia dimer ion is found to be formed mainly through the one-photon ionization of a new photolysis product such as an excited-state NH_4^*-NH_2. This intermediate may correspond to a cage product in the predissociation process of larger ammonia clusters and its formation and decay times are *ca.* 1 ps and < 1 ns, respectively. He also examined the lifetimes of $NH_4(NH_3)_n$ using the pump-probe technique with nanosecond lasers. The lifetime of NH_4 is found to be elongated more than 10^6

times in ammonia clusters. The mechanism of the formation and decay processes for these species are discussed on the basis of the present results in conjunction with the theoretical results in literatures.

Electronic structure and stability of $NH_4(NH_3)_n$

Ammoniated NH_4 radicals produced by an ArF excimer laser photolysis of ammonia clusters are studied by one-photon ionization and time-of-flight mass spectroscopy. The ionization potentials (IPs) of $NH_4(NH_3)_n$ (n=0-35) are determined by the photoionization threshold measurements. The binding energies of $NH_4(NH_3)_{n-1}$-NH_3(n=1-6) are estimated from IPs. The results indicate that the bonding between NH_4 and NH_3 is semi-ionic. The IPs for larger clusters are found to decrease monotonically with increasing n to a limit of 1.33 eV, which coincides with the photoemission threshold of liquid NH_3. This feature is similar to those found for alkali atoms-ammonia clusters.

Electronic structure and stability of $NH_4(NH_3)_m(H_2O)_n$

The photoionization process of $NH_4(NH_3)_m(H_2O)_n$ radicals produced by an ArF excimer laser photolysis of ammonia-water mixed clusters are examined using a time-of-flight mass spectroscopy. The ionization potentials (IPs) of $NH_4(NH_3)_m(H_2O)_n$ (m=0-4, n=0-3) are determined by the photoionization threshold measurements. A clear trend is found for the IPs; the clusters containing more water molecules have higher IP. This trend is ascribed to the large binding energy of NH_4^+-NH_3 comparing with that for NH_4^+-H_2O.

審査結果の要旨

本申請論文は、アルカリ原子及びそのイオン(Li, Li^-, Na^-)、ナトリウム原子2量体、NH_4ラジカルのアンモニア・クラスターあるいは水クラスターの光イオン化過程及び光電子スペクトルをクラスターサイズの関数として調べ、クラスター内での微視的溶媒和過程を考察したものである。

本論文は5章からなり、第一章では液体における電子あるいは金属イオンの溶媒和過程の研究の概説とこれまでの考え方の紹介の後、最近進歩した分子ビーム・クラスター法を用いれば、溶媒和過程をよりミクロな面から解明できることを概説し、論文全体の展望を行っている。第二章ではクラスターの光イオン化実験に用いた反射型TOF質量分析計および光電子スペクトル測定用の磁気ボトル型光電子分光計の概説を行っている。第三章では、$Li(NH_3)_n$、$Li(H_2O)_n$のイオン化ポテンシャルを測定し、アンモニア系ではnが増えるにつれ一定の値、ほぼ液体アンモニアの値に収斂すること、水の系ではnが4以上で一定の値になることを見いだした。また、$Li^-(NH_3)_n$、$Na^-(NH_3)_n$、$Na^-(H_2O)_n$の光電子スペクトルを測定し、アンモニアの系では、nが増えるにつれ電子励起状態が大きく安定化することを見いだした。これらの結果はクラスターが大きくなるにつれてSOMO電子がアルカリ金属原子上から周囲の溶媒和クラスターへ広がって行く溶媒和過程を表していると結論できる。第四章では、$Na_2(NH_3)_n^-$の光電子スペクトルを測定し、Na_2の電子状態がnの増加につれてどのようにシフトし分裂するかを調べ、その結果を溶媒和過程として考察したものである。第五章では二つに分かれ、最初、アルカリ金属原子と等電子構造を持つNH_4ラジカル・クラスターをフェムト秒ポンプ・プローブ法によりその生成、分解過程をしらべたものである。次に、同ラジカル・クラスターの光イオン化スペクトルを調べ、クラスターがどのように安定化するかを明らかにしたものである。

本研究は、アルカリ金属、アルカリ金属イオン、及びアルカリ金属と等電子構造を持つNH_4ラジカルのアンモニア及び水クラスターのイオン化ポテンシャル及び光電子スペクトルを詳細にしらべ、アルカリ原子のイオン化を伴う溶媒和の初期過程を電子状態、電子密度の変化などのミクロな過程として初めて明らかにしたものであり、溶媒和過程と言う化学の根本的問題に新しい研究方法を展開出来ることを示し、またそれについての新しい知見を明らかにした点で学問的に高い水準にあり、また、十分に価値のあるものである。以上に基づき審査委員会は、本申請論文が学位授与に値すると全員一致で判断した。

博士論文の審査終了後、関連する専門分野およびその基礎となる分野、すなわち、溶液化学、光化学、光電子分光、レーザー分光、電子構造論、量子化学、高真空技術などについて口述による試験を行った。これらに対して出題者は的確な対応を示した。なお、本論文は英文で書かれ、また、出題者はこれまでに5報の論文を十分なレベルの英文で発表しているので、出題者の英語能力は十分であると判断できる。また、出題者は公開の論文発表会において博士論文の主要点を分かりやすく、意欲的に報告するとともに、発表後の質疑応答においても十分な対応を示した。以上の結果、出題者は学位取得に十分な学識を有すると判断する。