

I-P Microscopic Solvation of Alkali Atom and Aggregates in Polar Solvent Clusters

The understanding of the structure and dynamics of solvated electron is of fundamental importance in the wide areas of chemistry, physics and biology. Clusters containing polar solvent molecules and a single alkali atom and/or aggregates can be regarded as a prototype for studying this intriguing subject. They are expected to give size dependent information on the spontaneous ionization of the alkali metal and the formation of the solvated electron. To elucidate the electronic nature of the clusters at the molecular level, we have carried out *ab initio* study in collaboration with the spectroscopic experiments.

I-P-1 Solvation Process of Na_m in Small Ammonia Clusters: Photoelectron Spectroscopy of $\text{Na}_m^-(\text{NH}_3)_n$ ($m \leq 3$)

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Photoelectron spectra (PESs) of $\text{Na}_m^-(\text{NH}_3)_n$ ($m \leq 3$) are investigated to explore the solvation of sodium atom and its aggregates in small ammonia clusters. For $\text{Na}^-(\text{NH}_3)_n$, we examine the PESs with an improved resolution and confirm the spontaneous ionization of Na atom in small clusters. As for $\text{Na}_2^-(\text{NH}_3)_n$ ($n \leq 8$), vertical detachment energy (VDE) of the transition from the anion to the neutral ground state is found to shift to the red with respect to that of $\text{Na}_2(\text{X}^1\Sigma_g^+)$, while that of the first excited state derived from $\text{Na}_2(\text{a}^3\Sigma_u^+)$ increases gradually for $n \geq 4$. In addition, the transitions to the higher-excited states derived from those correlated to the $3^2\text{S} + 3^2\text{P}$ asymptote are found to be shifted rapidly to the red and become almost degenerate with the $\text{a}^3\Sigma_u^+$ -type transition. The extensive spectral change is ascribed to the asymmetrical ammoniation and spontaneous ionization of Na_2 in small clusters. We also find the drastic change in the PESs of $\text{Na}_3^-(\text{NH}_3)_n$; the neutral ground ($^2\Sigma_u^+$ -type) and first excited ($^2\Sigma_g^+$ -type) states of these clusters become degenerate with each other as the number of NH_3 molecules increases. With the aide of the theoretical calculations, this spectral change is ascribed to the dissociation of Na_3^- core in clusters. This may be the first observation of the dissolution of metal aggregates in small clusters.

I-P-2 Theoretical Study of $[\text{Na}(\text{H}_2\text{O})_n]^-$ ($n = 1-4$) Clusters: Geometries, Vertical Detachment Energies and IR Spectra

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Geometries, vertical detachment energies (VDEs) and IR spectra of $[\text{Na}(\text{H}_2\text{O})_n]^-$ ($n = 1-4$) have been investigated by *ab initio* MO method at correlated level. Water molecules are bound to Na^- via Na-H as well as hydrogen bond interactions. The calculated VDEs are in good agreement with the recent photoelectron

spectroscopy and all observed bands are assignable to the $3^2\text{S}(\text{Na})-3^1\text{S}(\text{Na}^-)$ and $3^2\text{P}(\text{Na})-3^1\text{S}(\text{Na}^-)$ type transitions perturbed by hydration. They are shifted to higher energy with increasing n by keeping their separation almost unchanged, which reflects the hydration structure of Na^- . We also report the calculated IR spectra that are informative about the ionic Na-H bonds and the hydrogen-bond network among water molecules in the clusters.

I-P-3 Theoretical Study of $[\text{Na}(\text{NH}_3)_n]^-$ ($n = 1-4$)

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In connection with the recent photoelectron spectroscopy of negatively charged Na atom in ammonia clusters, the geometries, electronic state, vertical detachment energies, and harmonic frequencies of $[\text{Na}(\text{NH}_3)_n]^-$ ($n = 1-4$) have been studied by *ab initio* MO method. Structure having as many Na-N bonds as possible becomes more stable than other isomers as n grows. The Na 3s electrons are widely spread and delocalized in space outside the $[\text{Na}(\text{NH}_3)_n]^+$ core for $n \geq 2$. The dramatic red-shifts of the photoelectron band for the 3^2P -type transition with increasing n reflect the electronic change from an atomic state to one-center Rydberg-like states in the neutrals. The frequencies of the combined vibrations of the NH_3 ν_1 mode are nearly degenerate and are expected to coalesce into only one strong IR band in the NH stretch region irrespective of n .