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Considerable Stability and Visible Absorption of the Benzene−Water Hexamer Cluster Anion

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Time-of-flight mass spectrometry and photodestruction spectroscopy have been carried out for cluster anions of benzene−water, $Bz_m(H_2O)_n^-$. We have found that a distinct magic number $n = 6$ is associated with all the species of $m = 1-8$ and that an intense photoabsorption of $Bz(H_2O)_6^-$ occurs in the visible region. The results indicate that there is a strong interaction between the excess electron and valence orbitals of benzene, suggesting that these cluster anions can be a new model for the scavenging process of solvated electrons in condensed phases.

1. Introduction

In condensed phases, the disappearance of solvated electrons induced by impurity trapping is called the "scavenging" effect.[1,2] It has been well-known that impurity molecules having not only positive but also negative electron affinity may act as electron scavengers. The electron-transfer mechanism has been considered to be feasible for such electron-scavenging processes. On the other hand, cluster anions of polar molecules, such as water or ammonia, are often considered to be a model of the solvated electrons in condensed phases. In this respect, therefore, it is interesting to investigate the electron-transfer process occurring in water cluster anions solvating an impurity molecule. The investigation will contribute to a microscopic view of the scavenging processes of hydrated electrons in condensed matter. In this Letter, we report the mass spectrometric and photodestruction spectroscopic investigation of cluster anions of water having benzene (Bz) molecule(s) as an impurity site; $Bz_m(H_2O)_n^-$, where the electron affinity of benzene[3,4] is known to be −1.14 eV in the gas phase. We find that a remarkable magic number for the water cluster size occurs at $n = 6$ and that an intense absorption band appears in the visible region with a peak at 2.2 ± 0.1 eV, suggesting a novel interaction between the hydrated electron and the benzene site.

2. Experiment

The experimental setup and procedures are the same as those described elsewhere.[5] Briefly, neutral clusters were formed in a supersonic jet of a gaseous mixture of benzene and water seeded in argon gas, and anions were generated by electron attachment to the neutrals. A zirconium metal surface was used as a electron source, from which photoejected electrons were prepared by the excitation with the fourth harmonic of a Nd:YAG laser. The cluster anions were mass-analyzed with a pulsed time-of-flight (TOF) mass spectrometer. To measure a photodestruction spectrum, we used an unfocused beam of either signal or idler outputs of an optical parametric oscillator (OPO; Spectra Physics MOPO 730) as a light source. Relative cross sections for photodestruction as a function of the photon energy were obtained by a logarithm plot of the depleted ion signal intensities. The fluence of the OPO pulse was kept around 10 mJ/cm^2 to avoid saturation effects and multiphoton processes.

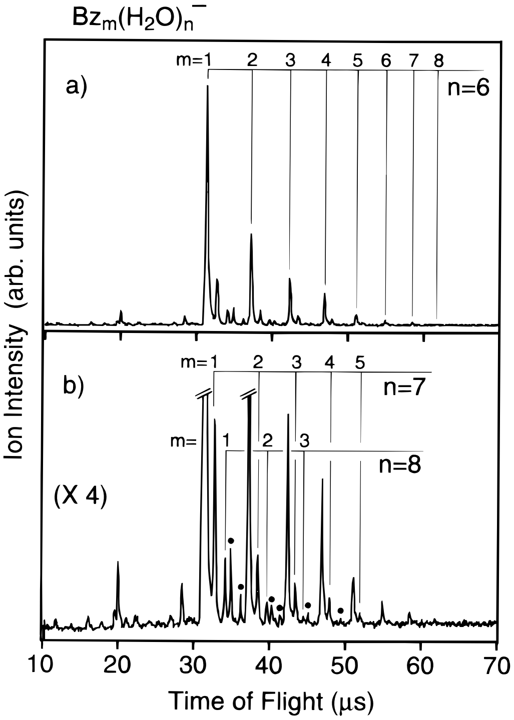

Figure 1. (a) Time-of-flight mass spectrum of cluster anions of the benzene−water mixture. The dominant progression is assigned to the $Bz_m(H_2O)_6^-$ clusters. (b) An expanded trace (×4) is given in the lower panel. Weak progressions of $Bz_m(H_2O)_n^-$, $n = 7$ and 8, are seen. Peaks marked by dots are due to complexes of an impurity molecule ($M = 47 \pm 1$ amu) with $Bz_m(H_2O)_n^-$, $n = 6$ and 7. Weak peaks in the range of flight-time less than 30 μs are attributed to impurities or product anions of dissociative electron attachment of benzene clusters.

3. Results and Discussion

It has been established by many investigators[5−9] that exclusive magic numbers of neat water cluster anions, $(H_2O)_n^-$, are $n = 2$, 6, 7, and 11 for small cluster size and that ion signal intensities for $n = 6$ and 7 are comparable irrespective of different experimental conditions. Figure 1 shows a mass spectrum of cluster anions of the benzene−water mixture, $Bz_m(H_2O)_n^-$. The dominant progression corresponding to $Bz_m(H_2O)_6^-$ is seen in the spectrum, which is considerably more intense compared with those of $n = 7$ and 8. The cluster anions of $n \leq 5$ and $n \geq 9$ were completely absent under several different conditions with respect to water vapor pressure. This result represents that the cluster anions involving a unit of water hexamer are substantially

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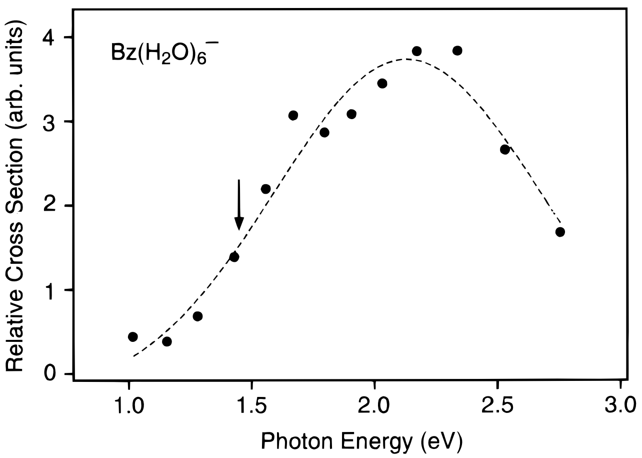

Figure 2. Photodestruction spectrum of $Bz(H_2O)_6^-$. The broken line represents the least-squares fit of the Gaussian line-shape function. The arrow indicates the VDE value (1.45 eV) obtained by Negishi et al. (ref 10).

stabilized with respect to the other sizes. Among them, the considerable stability of $Bz(H_2O)_6^-$ suggests a novel electronic interaction in the cluster anion of $n = 6$. Very recently, in fact, Nakajima and co-workers[10] measured photoelectron spectra of $Bz(H_2O)_n^-$. They found that vertical detachment energies (VDE's) for $n = 6$, 7, and 8 are 1.45 ± 0.1, 0.4 ± 0.1, and 0.75 ± 0.1 eV, respectively, indicating the characteristic stability for $n = 6$.

Despite many theoretical predictions,[11,12] the question concerning the binding nature of the excess electron in $(H_2O)_n^-$ is still a subject of debate.[13] Recent ab initio calculations[12] for $(H_2O)_6^-$ suggested that the stable structure with respect to intermolecular hydrogen bonds is an isomer with the prism-type form and the excess electron distribution is localized around dangling hydrogen atoms of the cluster anion. In the $Bz_m(H_2O)_n$ system, however, the binding characteristics of the electron seem to be different from that of the neat water system, because the $n = 6$ anions are preferentially stabilized. Since benzene is a highly polarizable molecule and its aromatic ring is known to act as an effective acceptor for π-hydrogen bonding,[14−16] it is feasible that the cluster form of the $(H_2O)_6^-$ moiety in $Bz_m(H_2O)_6^-$ is substantially modified by interaction with benzene molecule(s). In this respect, it is highly desirable that the cluster form is investigated by precise ab initio calculations including more extensive polarization functions as the basis sets.

To investigate the electronic structure, we measured a photodestruction spectrum of $Bz(H_2O)_6^-$, which is reproduced in Figure 2. A broad absorption spectrum occurs in the visible region with a peak at 2.2 ± 0.1 eV. The spectrum is totally different from that of the neat water hexamer anion, $(H_2O)_6^-$,[5,6] for which the peak position lies in the infrared region. The spectrum is also quite different from that of the benzene anion, which was observed under matrix-isolated conditions by Shida and co-workers.[17] The peak position of the absorption of $Bz(H_2O)_6^-$ is considerably higher than its VDE value (1.45 ± 0.1 eV).[10] Moreover, the absorption intensity was found to be quite large; the absorption cross section at the peak position is estimated to be of the order of 10^{-17} cm^2 by comparing the signal intensity with those obtained for systems with known cross sections.[5] This suggests that the absorption is not due to a direct electron detachment but to a bound-to-bound transition leading to an autodetachment process.

For the neat water cluster anions, $(H_2O)_n^-$, it has been observed that the absorption tends to shift to the high-energy side with increasing n, as reported by Johnson's group[6] as well as by our group.[5] The shifts are attributed to deepening of the electron binding potential with increasing cluster size, which leads to the electron localization.[11] In this sense, we first assumed for $Bz(H_2O)_6^-$ that the electron localization is accelerated by solvation with a benzene molecule. Although it agrees with the considerable stability of $Bz(H_2O)_6^-$, it cannot cause the bound-to-bound absorption with the energy being above the VDE, since an electron-bound excited state resulting from the electron localization should lie just below the detachment threshold. We therefore have to consider another assignment.

As such an intense transition, in the present case, one may easily expect an intracluster electron-transfer transition between the two moieties:

$$Bz\cdot(H_2O)_6^- + h\nu \rightarrow Bz^-\cdot(H_2O)_6$$

The transition of the excess electron bound in the $(H_2O)_6^-$ site takes place to the lowest antibonding π^* orbitals of the benzene site. Since the electron affinity of benzene is not positive,[3,4] the excess electron transferred from the $(H_2O)_6^-$ site is unstable and is readily released from the benzene moiety. Energetically, it is expected that the π^* orbitals of the benzene are in the continuum and the bound electron in the $(H_2O)_6^-$ site is slightly below it. The onset of the absorption represents the energy difference between the two, and the peak corresponds to the maximum of the Franck−Condon overlap for the electron-transfer transition. To confirm this, it would be necessary to observe more detailed photodestruction spectra covering the IR and UV region.

Finally, we note that the present work may provide a new insight onto the "scavenging" effect in condensed phases. Since solutions are considered as an ensemble of different size of clusters, the excess electron in the solution may be trapped not only by a solute molecule site but also by a cluster site of a suitable size, such as $Bz(H_2O)_6$. This "cluster-trapping" mechanism seems to be in good agreement with the fact that an impurity molecule having a negative electron affinity even acts as an electron scavenger.

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