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Binding Energy of the Benzene−Water Cluster Cation: An Ar-Mediated IR Photodissociation Study

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Infrared photodissociation spectra of (benzene−water−Ar)$^+$ in the 3 μm region were observed by monitoring benzene$^+$ and (benzene−water)$^+$ fragments. The spectral features showed that the Ar atom locates on the benzene ring, preserving the same structure as that of (benzene−water)$^+$, in which the water moiety is bound to the side of benzene$^+$ by the charge−dipole interaction and C−H···O hydrogen bonds. We evaluated the binding energy of (benzene−water)$^+$ to be D_0 = 3290 ± 120 cm^{-1} by analyzing the appearance energy dependence of the fragments. The binding energy of the cluster cation gave us the adiabatic ionization potential of the neutral (benzene−water) cluster, IP$_0$ = 72160 ± 150 cm^{-1}.

Introduction

In molecular cluster studies on intermolecular interactions, geometric structures and binding energies of the intermolecular bonds are the two most important observables. Recent development of quantum chemical calculations enables us to evaluate these quantities, especially for small-sized clusters.[1] While intermolecular structures have recently been well established in many cluster systems with development of various spectroscopic techniques,[2,3] there have been only a few experimental determinations of binding energies of clusters.[4−6] Quantum chemical calculations are still a unique method for the binding energy estimation in most clusters. To examine the reliability of calculation methods and levels, experimental data on binding energies are now highly required.

The (benzene−water)$^+$ cation, (Bz−W)$^+$, is one of the prototype systems to explore the charge−dipole interaction. Infrared (IR) spectroscopy and theoretical calculations of (Bz−W)$^+$ have revealed that the water molecule locates at the side of the benzene ring, and the charge−dipole interaction as well as C−H···O hydrogen bonds dominates the cluster structure.[7−13] In contrast, the cluster structure of the neutral, (Bz−W), is totally different from that of (Bz−W)$^+$; the neutral (Bz−W) cluster is known to have an on-top structure bound by π-hydrogen bonds.[14] Such a drastic change of cluster structures upon photoionization has been the subject of theoretical and experimental studies.[7−17] Theoretical calculations at B3LYP/6-31G(d,p), B3LYP/6-311G(d,p), and MP2/6-31G(d) predicted binding energies of 3290, 4410, and 4795 cm^{-1} (9.40, 12.6, and 13.7 kcal/mol), respectively.[7,9,12,13] Solcá and Dopfer experimentally evaluated the binding energy to be 4900 ± 1100 cm^{-1} (14 ± 3 kcal/mol) on the basis of the OH stretching frequency shifts of the water moiety.[9,10] Though this experimental value well agrees with the latter two theoretical predictions, their evaluation assumed a correlation between the binding energy and the free OH frequency shifts seen in typical hydrogen-bonded systems. Such a correlation may not be accurate in charge−dipole interaction systems, so the value should be examined by other experimental methods with more feasibility for the binding energy determination.

In this paper, we report an alternative experimental approach to the binding energy of (Bz−W)$^+$ on the basis of infrared photodissociation (IRPD) experiments using an “Ar messenger”. The attachment of an Ar atom to the cluster cation not only suppresses the internal energy of the cluster cation but also opens multiple dissociation channels for the vibrational predissociation process. We analyzed appearance energies of the dissociation channels observed in the IRPD spectra of the (Bz−W−Ar)$^+$ cluster cation with some postulates, and determined the binding energy with a high accuracy.

Experimental Section

We used a tandem quadrupole mass filter type spectrometer that has already been reported elsewhere in detail.[8] Briefly, a gaseous mixture of benzene, water, and Ar was expanded into a vacuum chamber through a pulsed nozzle with a stagnation pressure of about 2 atm. Bare benzene was resonantly ionized via the S_1−S_0 6^1_0 transition in the collisional region of the jet expansion[18] so that the benzene cation collided with water and Ar, leading to (Bz−W−Ar)$^+$. This cluster cation was mass-selected by the first quadrupole mass filter and was introduced into an octopole ion guide, where the cluster cation was irradiated by a counter propagating IR laser pulse. When the IR wavelength was resonant on a vibrational transition of the cluster cation, fragment ions were produced due to vibrational predissociation. We recorded a vibrational spectrum of (Bz−W−Ar)$^+$ by scanning the IR wavelength while detecting only a fragment cation mass-selected by the second quadrupole mass filter. In the present experiment, we monitored Bz$^+$ and (Bz−W)$^+$ fragments, and no (Bz−Ar)$^+$ fragment was observed. For a comparison of spectral features, we also measured an IRPD spectrum of (Bz−W)$^+$ by monitoring the Bz$^+$ fragment.

Results and Discussion

Parts a and b of Figure 1 show IR spectra of (Bz−W−Ar)$^+$ measured by monitoring Bz$^+$ and (Bz−W)$^+$ fragments, respectively. Spectrum c is an IR spectrum of the (Bz−W)$^+$ cluster cation by monitoring the Bz$^+$ fragment for a comparison with

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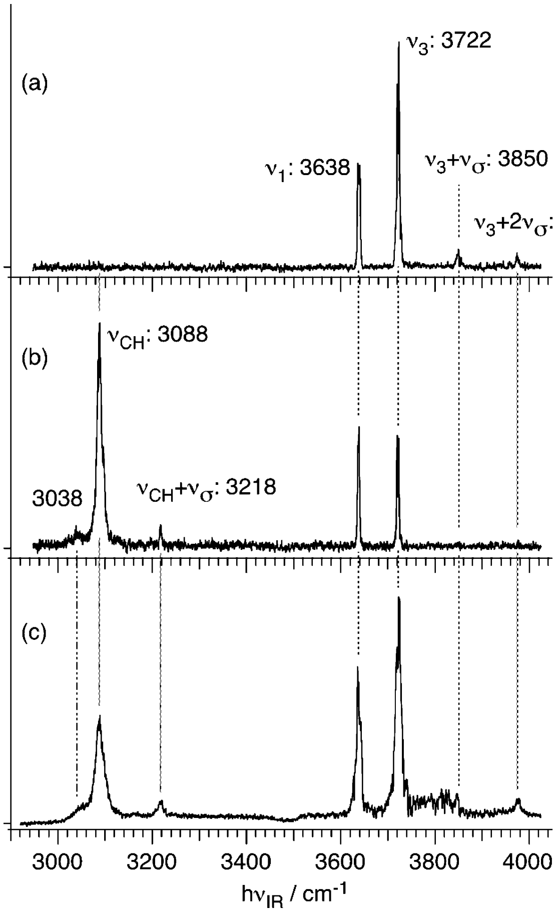

Figure 1. IR spectra of the (benzene−water−Ar)$^+$ cluster cation by monitoring (a) benzene$^+$ and (b) (benzene−water)$^+$ fragments, respectively. Spectrum c is an IR spectrum of the (benzene−water)$^+$ cluster cation measured by monitoring the benzene$^+$ fragment.

spectra a and b. In spectrum c, the two strong bands at 3638 and 3722 cm^{-1} are assigned to the symmetric (ν_1) and antisymmetric (ν_3) OH stretching vibrations of the water moiety, respectively, and another intense band at 3088 cm^{-1} is the CH stretching band (ν_{CH}) of the benzene cation moiety. Three weak bands, two of which associate with the ν_3 band and the other of which associates with the ν_{CH} band, are assigned to combination bands with the intermolecular stretching vibration (ν_σ). A small hump is seen at 3038 cm^{-1}, near the low-frequency tail of the ν_{CH} band. We tentatively assign this band to some hot bands because of its intensity enhancement under the hot ion conditions.

The IR spectrum of (Bz−W)$^+$ has been extensively analyzed in the previous studies,[7−10] and the "side" structure, where the water molecule is bound to the side of the benzene cation with the charge−dipole interaction and C−H···O hydrogen bonds, has been established.[7−13] Both the IR spectra of (Bz−W−Ar)$^+$ show the same features as those in the spectrum of (Bz−W)$^+$ except for the band intensities, which reflect the vibrational energy dependence of the dissociation yield. The Ar attachment does not perturb the OH stretch of the water moiety as well as the CH stretch of the benzene cation moiety. This means that the benzene cation and water moieties in (Bz−W−Ar)$^+$ hold the same side structure as in (Bz−W)$^+$, and the Ar atom locates on the benzene ring. The schematic cluster structure of (Bz−W−Ar)$^+$ is shown in Figure 2.

The IR spectra of (Bz−W−Ar)$^+$ show rather sharper bandwidths in comparison with those of (Bz−W)$^+$. The attachment of Ar severely restricts the internal energy of (Bz−W−Ar)$^+$ because of the small binding energy of Ar to the benzene cation moiety and therefore reduces contributions of hot bands to the IR spectra. The Ar attachment substantially affects the band intensities depending on which fragment is monitored. Spectrum a, obtained by monitoring Bz$^+$, shows only the bands at higher frequency than the $\nu_{\mathrm{CH}} + \nu_\sigma$ band, while spectrum b, monitoring (Bz−W)$^+$, exhibits intensities only for the lower frequency region up to the ν_3 band. Only the ν_1 and ν_3 bands have intensities in both the Bz$^+$ and (Bz−W)$^+$ channels. The branching ratio of the Bz$^+$ channel to the (Bz−W)$^+$ channel at the ν_1 band was found to be about 2:1 to 3:2, weakly depending the ion source condition. That of the ν_3 band was about 5:1 to 3:1 (the band appearance/disappearance of the other bands in each dissociation channel did not depend on the source condition). The ordinates of Figure 1a,b are independently normalized with respect to the strongest band in each spectrum.

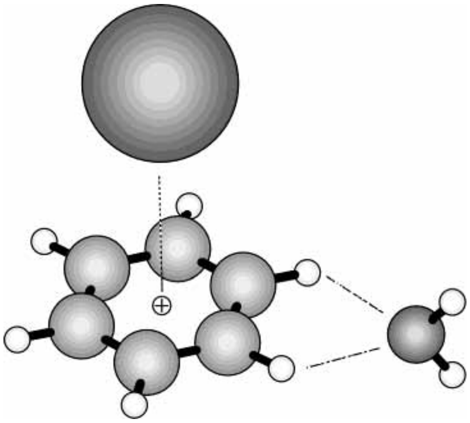

Figure 2. A schematic representation of the structure of the (benzene−water−Ar)$^+$ cluster cation.

On the basis of the intensity dependence described above, we estimated the binding energy of (Bz−W)$^+$ with the following postulates: (1) The binding energy of the Ar atom in (Bz−W−Ar)$^+$ is 500 ± 50 cm^{-1}. (2) According to postulate 1, the internal energy of (Bz−W−Ar)$^+$ is limited up to 500 cm^{-1}. Therefore, the initial internal energy of (Bz−W−Ar)$^+$ makes a distribution between 0 and 500 cm^{-1} including both the limiting values. (3) When an IR absorption occurs, the Ar atom dissociates first, and this process carries off 500 cm^{-1} from the internal energy of (Bz−W−Ar)$^+$. Then, the water molecule dissociates from the resulting (Bz−W)$^+$ cluster, if it is possible in energy. (4) The total dissociation yield is 100% whenever the internal energy exceeds the binding energy. (5) There is no kinetic release as the Ar atom dissociates. Postulate 1 is estimated on the basis of binding energies of (aromatic cation−Ar) clusters reported so far.[5,6] Postulate 3 is rationalized from the observation that no (Bz−Ar)$^+$ fragment was detected. Other conditions are postulated to simplify the analysis.

Figure 3a shows an energy scheme of the dissociation process of (Bz−W−Ar)$^+$ following an IR photon absorption of $h\nu_{\mathrm{IR}}$ cm^{-1}. (Bz−W−Ar)$^+$ with no initial internal energy obtains an internal energy of $h\nu_{\mathrm{IR}}$ cm^{-1} after the IR photon absorption, and then the dissociation of the Ar atom produces (Bz−W)$^+$ with an excess energy of $h\nu_{\mathrm{IR}} - 500$ cm^{-1}. On the other hand, (Bz−W−Ar)$^+$ having the maximum initial internal energy, 500 cm^{-1}, is excited to an energy level of $h\nu_{\mathrm{IR}} + 500$ cm^{-1}, and the following Ar dissociation results in the formation of (Bz−W)$^+$ with an excess energy of $(h\nu_{\mathrm{IR}} + 500) - 500 = h\nu_{\mathrm{IR}}$ cm^{-1}. Therefore, the excess energy distribution of (Bz−W)$^+$ created by the IR photoabsorption of (Bz−W−Ar)$^+$ should be in the

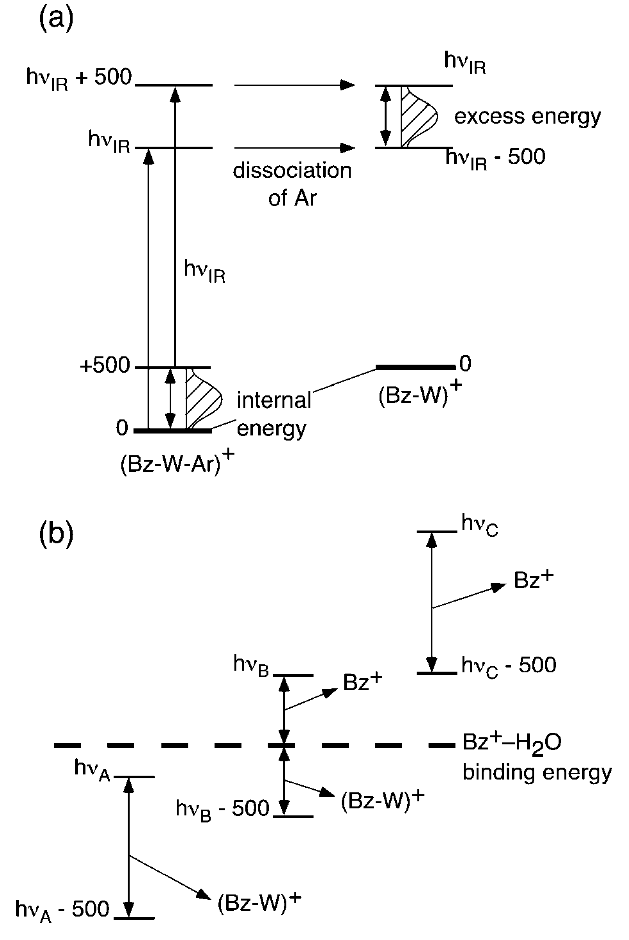

Figure 3. Energy schemes of the (a) dissociation process of (benzene−water−Ar)$^+$ following the IR light absorption of $h\nu_{IR}$ and (b) relation between the excess energy distribution and dissociation channels in (benzene−water)$^+$ produced by the dissociation of (benzene−water−Ar)$^+$ (see the text).

range of ($h\nu_{IR}$ − 500) to $h\nu_{IR}$ cm^{-1}. The relative energy balance between the excess energy and the binding energy of (Bz−W)$^+$ determines the band appearance in the IR spectrum by monitoring each fragment channel, as schematically shown in Figure 3b. When the excess energy of (Bz−W)$^+$ is lower than the binding energy, further dissociation does not occur (Figure 3b, the case of mode ν_A) and only the (Bz−W)$^+$ fragment is generated. On the other hand, when the excess energy is higher than the binding energy, (Bz−W)$^+$ completely dissociates further into the Bz$^+$ fragment (Figure 3b, the case of mode ν_C). Only when the excess energy distribution extends over the binding energy (Figure 3b, the case of mode ν_B), both of the (Bz−W)$^+$ and Bz$^+$ fragments are produced, and the relative ratio of the two fragment channels depends on the excess energy distribution.

Now, we apply this scheme to the observed spectra, that is, the fragmentation pattern with respect to the excitation of the ν_{CH}, $\nu_{CH} + \nu_\sigma$, ν_1, ν_3, $\nu_3 + \nu_\sigma$, and $\nu_3 + 2\nu_\sigma$ bands. The observed vibrational energy dependence of the dissociation channels is summed up in Figure 4. The ν_{CH} and $\nu_{CH} + \nu_\sigma$ bands appear only in the IR spectrum monitoring (Bz−W)$^+$ (spectrum b in Figure 1), and it is clear that the binding energy between the benzene cation and the water molecule lies above $h\nu_{CH} + h\nu_\sigma$, i.e., 3220 cm^{-1}. In addition, the binding energy should be lower than $h\nu_3 + \nu_\sigma - 500$ cm^{-1}, i.e., 3350 cm^{-1}, because the $\nu_3 + \nu_\sigma$ and $\nu_3 + 2\nu_\sigma$ modes are seen only in the Bz$^+$ fragment channel (spectrum a in Figure 1). Therefore, we safely restrict the range of the binding energy between $h\nu_{CH} + h\nu_\sigma$ and $h\nu_3 + h\nu_\sigma - 500$ cm^{-1} (3220 cm^{-1} $\leq D_0 \leq$ 3350 cm^{-1}). The ν_1 and ν_3 excitations result in the fragmentation to both the Bz$^+$ and (Bz−W)$^+$ channels, indicating the binding energy is between $h\nu_3 - 500$ and $h\nu_1$ cm^{-1} (3220 cm^{-1} $\leq D_0 \leq$ 3640 cm^{-1}). This is consistent with the estimation by the combination bands. Finally, including the estimation error of the binding energy of the Ar atom of ±50 cm^{-1}, we determine the binding energy of (Bz−W)$^+$ to be D_0 = 3290 ± 120 cm^{-1} (9.40 ± 0.34 kcal/mol).[19]

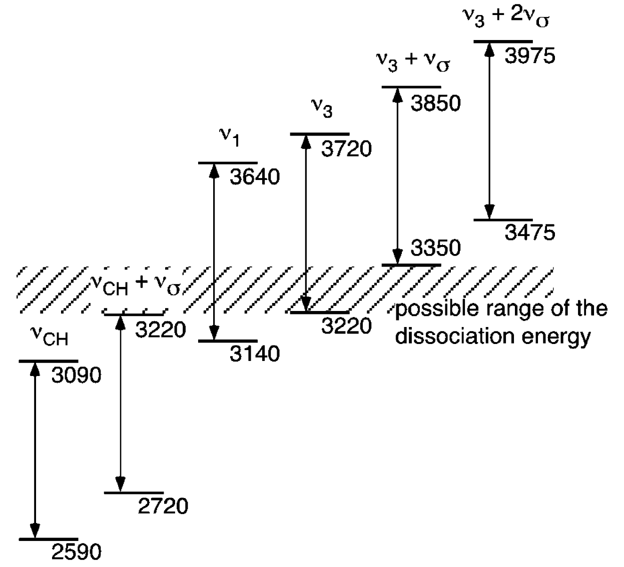

Figure 4. Excess energy distribution of (benzene−water)$^+$ following the vibrational excitation of (benzene−water−Ar)$^+$.

In the present analysis, we postulated the zero kinetic release for the dissociation of the Ar atom. If it is not negligible, this effect can be regarded as an increase of the dissociation energy of the Ar atom (500 cm^{-1}, in the default calculation). Such a correction reduces the low-energy limit of the excess energy distribution of the (Bz−W)$^+$ fragment, but the high-energy limit of the distribution is not affected. Therefore, the lower limit of the binding energy is not affected even in consideration of the kinetic release, because the lower limit of the binding energy is determined by the high-energy limit of the excess energy in the $\nu_{CH} + \nu_\sigma$ mode excitation. On the other hand, the upper limit of the binding energy is reduced with a decrease of the low-energy limit of the excess energy in the $\nu_3 + \nu_\sigma$ mode excitation. As a result, the possible range of the binding energy is narrowed with the inclusion of the kinetic energy release. Moreover, when the kinetic release is larger than 130 cm^{-1}, the low-energy limit of the excess energy in the $\nu_3 + \nu_\sigma$ mode excitation is below the high-energy limit of the excess energy in the $\nu_{CH} + \nu_\sigma$ mode excitation. In such a case, the $\nu_3 + \nu_\sigma$ band must appear in the spectrum by monitoring the (Bz−W)$^+$ fragment. However, the observed spectrum (spectrum b in Figure 1) clearly denies such an expectation. Therefore, the kinetic energy release associated with the Ar atom dissociation is within 130 cm^{-1}, and we neglected it.

The binding energy of 3290 ± 120 cm^{-1} for (Bz−W)$^+$ estimated in the present work is 30% smaller than the previous experimental values (4900 ± 1050 cm^{-1}) by Solcá and Dopfer.[9] The previous estimation referred to a correlation between the binding energy and the free OH frequency shifts in the typical hydrogen-bonded cationic clusters. The present result is based on the firmer physical basis, and the large deviation of the previous estimation suggests that the correlation between the binding energy and the free OH frequency shifts would depend on the systems. The present experimental value just agrees with that of the previous calculation at B3LYP/6-31G(d,p) (3290 cm^{-1}).[7] Accidental cancellation of calculation errors, however, may contribute to this very nice agreement, because the calculations at the relatively higher levels, B3LYP/6-311G(d,p) and MP2/6-31G(d), overestimated the binding energy by 20−30%.[9,12,13] The present result offers a benchmark to check the validity of quantum chemical calculations for charge−dipole interaction systems.

The determination of the binding energy of $(Bz-W)^+$ also enables us to evaluate the adiabatic ionization potential of the neutral (Bz−W) cluster, $IP_0(Bz-W)$. Because (Bz−W) drastically changes its intermolecular structure upon ionization, it has no Franck−Condon overlap between the zero-point levels in the neutral and cationic ground states.[11,12,15,17] Therefore, it is impossible to determine the $IP_0(Bz-W)$ by a direct photoionization experiment. The binding energy of the neutral ground state, however, has been determined to be $D_0(Bz-W) = 890 \pm 32\ cm^{-1}$ using the appearance energy of the dissociative ionization of (Bz−W), $AP[(Bz-W) \rightarrow Bz^+ + W]$, and a thermodynamic relation, $D_0(Bz-W) = AP[(Bz-W) \rightarrow Bz^+ + W] - IP_0(Bz)$.[11] This binding energy in the neutral ground state well corresponds to the value $D_0(Bz-W) = 1014 \pm 70\ cm^{-1}$ from a high-level ab initio calculation.[20] In combination with the thermodynamic relation $IP_0(Bz) - IP_0(Bz-W) = D_0[(Bz-W)^+] - D_0(Bz-W)$, the ionization potential of (Bz−W) is evaluated as $IP_0(Bz-W) = 72160 \pm 150\ cm^{-1}$. Here, we used the values $D_0[(Bz-W)^+] = 3290\ cm^{-1}$, $D_0(Bz-W) = 890\ cm^{-1}$, and $IP_0(Bz) = 74555.5\ cm^{-1}$. [21]

Conclusion

In the present study we carried out IR photodissociation spectroscopy of $(Bz\text{-}W-Ar)^+$ by monitoring both the Bz^+ and $(Bz-W)^+$ fragments in the 3 μm region. All the band positions of the spectra in $(Bz-W-Ar)^+$ are the same as those of $(Bz-W)^+$, though the bandwidths are remarkably narrowed as a result of a restriction of the cluster internal energy due to the Ar attachment. The same IR spectral feature in these spectra demonstrated that the Ar atom locates on the benzene ring while the benzene cation and water moieties hold the side structure as the $(Bz-W)^+$ cluster. The branching ratio of the two dissociation fragments shows a remarkable vibrational energy dependence. The Bz^+ fragment channel is open only in the higher frequency region, while the $(Bz-W)^+$ channel is closed with an increase of the vibrational energy. The binding energy of $(Bz-W)^+$ was evaluated as $D_0 = 3290 \pm 120\ cm^{-1}$ by analyzing the vibrational energy dependence of the dissociation of $(Bz-W-Ar)^+$ under the postulates with respect to the Ar dissociation. In combination with a thermodynamic energy cycle, the adiabatic ionization potential of (Bz−W) was estimated to be $72160 \pm 150\ cm^{-1}$. This value is lower by about 2400 cm^{-1} than that of bare benzene.

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(19) The vibrational energy of ν_{CH} is lower than this binding energy. This band appears in the IR dissociation spectrum of $(benzene-water)^+$ (Figure 1c) because of the higher internal energy of $(benzene-water)^+$ than that of $(benzene-water-Ar)^+$.

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