Formation and Photoelectron Spectroscopy of Nanoscale Cluster Anions of Biphenyl, $(BP)_n^-$ ($n = 2$–100)

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Evolution of electronic structures of nanoscale biphenyl cluster anions, $(BP)_n^-$ ($n = 2$–100), have been studied by photoelectron spectroscopy in a size-selective fashion. The energetics of vertical detachment energy (VDE) revealed negative electron affinity of a biphenyl molecule and substantial cluster reorganizations via electron attachment. Comparison of the VDE energetics with naphthalene cluster anions implied that the freezing (and/or melting) temperatures of the BP clusters may be much lower than those of naphthalene clusters.

Clusters, i.e., finite aggregates containing 2–10^4 particles, exhibit unique physical and chemical phenomena and provide ways to explore the gradual transition of the structural, electronic, and thermodynamic characteristics from molecular to condensed matter systems. In fact, size-selective study on broad size range of clusters has realized a bridge between molecular and condensed phase phenomena.[1]

Recently, we have developed the production method of negatively charged clusters consisting of several hundreds molecules with the use of a high-pressure, high-temperature, and ultra-short pulsed valve[2] combined with electron attachment.[3] Moreover, we have size-selectively traced the evolution of electronic structures of cluster anions up to several nanometers in diameter by using photoelectron spectroscopy[3–7] and discovered a novel anionic isomer coexistence phenomenon for the nanoscale cluster anions of oligoacene compounds such as naphthalene (Nph) and anthracene.[6] In this letter, we report a size-selected photoelectron spectroscopic study on the nanoscale cluster anions of biphenyl (BP) which is the simplest oligophenyl compound possessing a similar-sized aromatic frame with Nph. Comparison of the energetics between the BP and Nph cluster anions is also carried out to gain insight into the state (phase) of nano-aggregates of BP.

Details of the experimental apparatus have been previously described elsewhere.[8] The sample vapor was entrained in helium carrier gas at a stagnation pressure of ca. 50 atm and was pulsed out through an Even–Lavie valve.[2] The cluster anions, produced by electron impact ionization at the condensation region in a free jet, were coaxially extracted by applying a pulsed electric field and were detected with an in-line Wiley–McLaren-type TOF-MS ($M/\Delta M \approx 150$).

The photoelectron spectra were acquired by the fundamental (1064 nm, 1.17 eV) and second harmonic (532 nm, 2.33 eV) outputs of an Nd^{3+}: YAG laser. Each spectrum presented in this study represents accumulation of 6000–20000 laser shots. The energy resolution was ca. 50 meV full width at half maximum at 1 eV electron kinetic energy. The photoelectron spectrometer was calibrated with the $^1S_0 \rightarrow {}^2S_{1/2}$ and $^1S_0 \rightarrow {}^2D_{5/2}$ transitions of the gold atomic anion.

In a typical mass spectrum of biphenyl cluster anions, $(BP)_n^-$, the smallest cluster anion observed was the dimer anion and its intensity is extremely weak compared to the other cluster anions. Besides, no trace of a BP monomer anion was observed under any source conditions.

The photoelectron spectra of $(BP)_n^-$ clusters were taken at the photodetachment energies of 1064 nm for $n = 2$–20 and 532 nm for $n = 2$–100, some of which are presented in Figure 1.

In the spectra of $(BP)_{2-6}^-$, the partially resolved vibrational feature is observed with a peak-spacing of ca. 0.16 eV which agrees well with the energy of the inter-ring C–C stretching mode of neutral BP molecule.[9] For the larger clusters, this vibrational structure is unresolved because the larger number of low-frequency intermolecular vibrational modes are excited in the photodetachment process as the cluster size increases. The vertical detachment energy (VDE) of the observed peak gradually shifts to higher electron binding energy with increasing the clus-

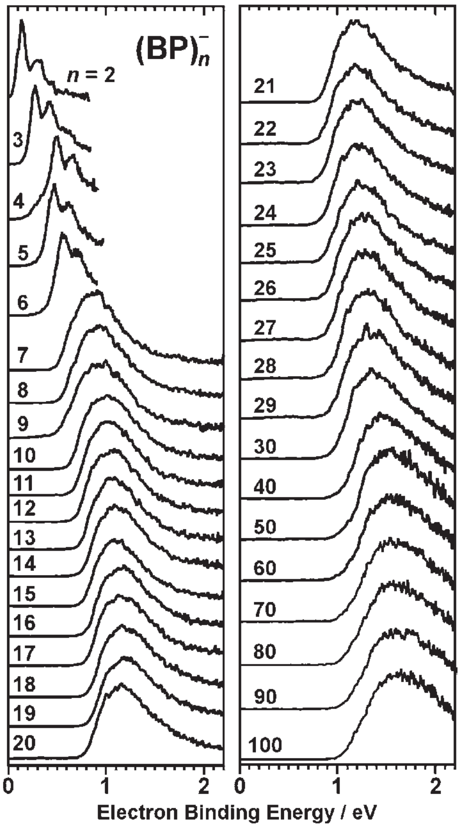

Figure 1. Photoelectron spectra of biphenyl cluster anions, $(BP)_n^-$ ($n = 2$–100), measured at 1064 nm for $n = 2$–6 and 532 nm for $n = 7$–100.

ter size. It is noted that no other spectral feature was observed when the source conditions were varied.

It has still remained unclear whether the adiabatic electron affinity ($\mathrm{EA_a}$) of BP molecule is positive or negative. For example, the upper limit of the $\mathrm{EA_a}$ for BP as determined by the electron capture detector method is 0.130 ± 0.035 eV.[10] However, it was theoretically shown that the $\mathrm{EA_a}$ of BP is nearly zero and its sign strongly depended on the level of theory used.[11] In this study, the VDE values of $(\mathrm{BP})_{n = 2,\,3,\,\text{and}\,4}{}^-$ are determined to be 0.13 ± 0.02, 0.28 ± 0.02, and 0.50 ± 0.02 eV, respectively, which are very close to those of Nph dimer, trimer, and tetramer anions, i.e. 0.11, 0.28, and 0.48 eV, respectively.[12] Since BP and Nph are similar-sized aromatic systems, these agreements suggest that BP has nearly the same $\mathrm{EA_a}$ with Nph. As is well known, the $\mathrm{EA_a}$ of Nph is negative (i.e. -0.19 eV).[13] Thus, the $\mathrm{EA_a}$ of BP can be considered to be negative, which is consistent with no trace of BP monomer anion observed in the mass spectrum.

The cluster size n can be related to the radius of the spherical cluster (R) by $R = r_s n^{1/3}$, where r_s is the effective radius of a constituent molecule,[1] and thus VDE obtained from photoelectron spectra are plotted against $n^{-1/3}$ corresponding to R^{-1}. Figure 2 displays the plot of VDEs as a function of $n^{-1/3}$ for $(\mathrm{BP})_n{}^-$ with $n = 2$–100.

The VDEs of $n \geq 7$ are well fitted linearly against $n^{-1/3}$ and solid line in Figure 2 represents the least square fit of the VDE data: $\mathrm{VDE} = 2.12 - 2.57 n^{-1/3}$ (correlation coefficient; 0.994).

The extrapolated value of VDE, i.e. VDE(∞), is given by $\mathrm{EA_a} + P - \lambda$, where P and λ represent the polarization energy and total reorganization energy, respectively.[6,7] Here we assume that the $\mathrm{EA_a}$ of BP is the same with that of Nph (i.e. -0.19 eV) and $P = 1.1$ eV,[14] and then the λ value is approximately estimated to be ca. 1.2 eV. This large reorganization energy indicates that substantial structural rearrangements occur to form the equilibrium anion configurations. Thus, the electron attachment might occur to relatively warm, liquid-like clusters because the higher internal energy allows constituent molecules to be rearranged.

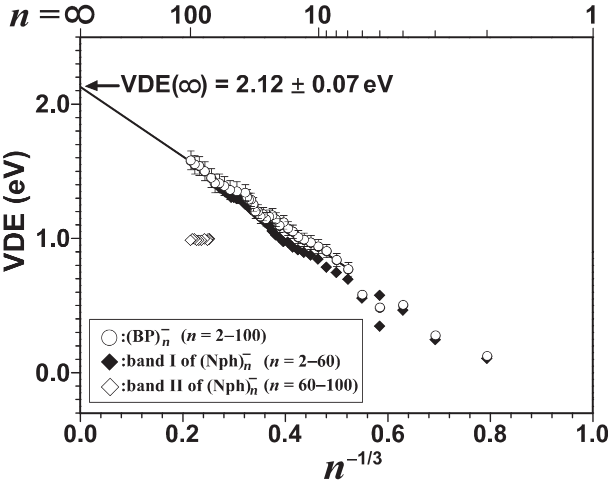

Figure 2. Plot of VDEs of $(\mathrm{BP})_n{}^-$ ($n = 2$–100) as a function of $n^{-1/3}$, together with VDE plots of bands I ($n = 2$–60) and II ($n = 60$–100) of $(\mathrm{Nph})_n{}^-$. The VDEs for $n = 7$–100 are well fitted linearly with $n^{-1/3}$ and are extrapolated to intercept [VDE(∞)] of 2.12 ± 0.07 eV.

In the Nph cluster anions with $n \geq 27$, the second band originated from crystal-like isomers (band II), which are formed by very small structural rearrangements from the corresponding neutral clusters, has emerged on the lower binding energy side of the band representing large structural rearrangements from the neutral clusters (band I).[6] The VDE energetics of the $(\mathrm{BP})_n{}^-$ clusters observed is very similar to that of the isomers yielding "band I" of the Nph cluster anions. However, for the $(\mathrm{BP})_n{}^-$ clusters, no crystal-like anionic isomers were observed up to $n = 100$ under any source conditions. Therefore, this result implies that the freezing (and/or melting) temperatures of the BP clusters may be much lower than those of the Nph clusters, irrespective of their almost the same bulk melting temperatures ($\approx$350 K). In contrast to Nph, a BP molecule has the degrees of freedom of intramolecular rotation by the angle τ around a single C–C bond between two phenyl rings, and the molecular conformation is thus influenced by crystal packing. In gas phase, a BP molecule is nonplanar with $\tau \approx 45^\circ$, whereas in the crystals BP molecules take slightly twisted conformations ($\tau \sim 10^\circ$) according to the packing effect.[15] In the BP cluster anions examined in this study, the packing effect may not be enough to form a planar crystal-like conformation because of the large surface to volume ratio in the clusters. Consequently, it is conceivable that the crystal-like isomers are thermo-dynamically unstable for the nanoclusters ($n \approx 100$) of BP.

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