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Photoelectron Spectroscopy of 4-Bromochlorobenzene Dimer and Trimer Anions

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Clusters are the aggregates of molecules or ions which have intrinsic properties that are not found in their monomer unit.[1] Their structure and charge distribution greatly affect the properties of the clusters. Charge resonance is the key factor that determines the structure of the cation clusters of aromatic hydrocarbons.[2] T. Shida and S. Iwata also calculated the charge resonance band and observed it experimentally.[3] With advances in molecular beam apparatus and quantum calculations, anion clusters have been extensively studied.[4-6] Benzene does not form a stable dimer anion in the gas phase, and naphthalene forms a dimer anion which may have T-shaped geometry due to the strong repulsion from the π-electron.[7] Dimer anions larger than naphthalene all have parallel-displaced (PD) geometries with charge resonance.[8-10] Sometimes homocluster anions show ion core switching with the increase of the cluster size.[8]

For the heterodimer anions, the geometry is determined by the differences in electronegativity of the molecules. Dimer anions with a large electronegativity difference have T-shaped geometries and those with a small electronegativity difference have PD geometries.[11]

Bromochlorobenzene (BCB) is able to accept an extra electron even though benzene monomer cannot. We found that an excess electron entered the anti-bonding orbital formed between C and Br atoms in bromochlorobenzene monomer anion that has the character of atomic Br.[12] Thus, the electron binding energy (EBE) is exceedingly large compared to that of other large aromatic hydrocarbon monomers. In this article, I report the photoelectron spectra and quantum calculation results for the dimer and trimer anions of 4-BCB, which are much different from those of the monomer anion.

The details of our experimental scheme have been described elsewhere.[13] Briefly, thermally evaporated 4-BCB molecules were co-expanded with 5 bar of Ar carrier gas through a pulsed solenoid valve to generate molecular clusters. Low energy secondary electrons were generated from the ionization of Ar with high energy electron from an electron gun (400 eV, 200 μA), which attached to the neutral molecules and turned them into anions. A Wiley-McLaren type time-of-flight mass spectrometer with a mass gate was used to select anions by their mass. The anions then entered a magnetic-bottle-type photoelectron spectrometer and were irradiated by the second harmonic output (532 nm) of a pulsed Nd:YAG laser. The kinetic energy of the ejected photoelectron was measured to yield the photoelectron spectrum by subtracting it from the incident photon energy.

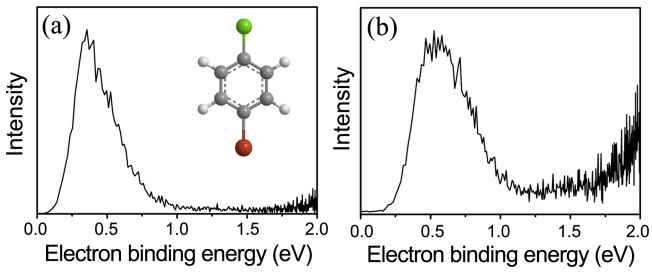

Figure 1. Photoelectron spectra of (a) $[4\text{-BCB}]_2^-$, and (b) $[4\text{-BCB}]_3^-$ obtained at 532 nm (inset: molecular structure of the 4-BCB).

In the mass spectrum of 4BCB cluster anions, the monomer anion has the largest peak intensity with the exception of the Br^- that comes from the dissociative electron attachment. The dimer anion has a significant intensity while the trimer and larger clusters have a very low intensity under our experimental conditions.[12]

Figure 1 shows the photoelectron spectra (PES) of (a) $[4\text{-BCB}]_2^-$, and (b) $[4\text{-BCB}]_3^-$ obtained at 532 nm. The PES of $[4\text{-BCB}]_2^-$ is quite different from that of $[4\text{-BCB}]_1^-$ in our previous study. It seems that there is only one broad peak that stands for the new valence ion formation. The vibrational progression for the neutral dimer molecule appears in the PES with 0.05 eV energy gaps. Surprisingly, the vertical detachment energy (VDE) of the $[4\text{-BCB}]_2^-$ greatly decreased to 0.36 eV while that of the monomer anion was 2.40 eV (Table 1).[12] This drastic decrease in the VDE can be explained with the change of the ion core. In the case of the monomer anion, an electron cannot be delocalized to the benzene ring due to the strong repulsion between the approaching electron and the π-electron. Thus, the excess electron is mostly localized to the Br atom. The singly occupied molecular orbital (SOMO) is anti-bonding in nature where the atomic Br character is dominant. As a

Table 1. Vertical detachment energies (VDE) and adiabatic electron affinities (AEA) of $[4\text{-BCB}]_2^-$, and $[4\text{-BCB}]_3^-$ calculated at the B3LYP/6-31+G* level. These values were compared with the experimental VDE values.

	VDE	AEA	Experiment
$[4\text{-BCB}]_2^-$	0.36 eV	0.14 eV	0.36 eV
$[4\text{-BCB}]_3^-$	0.44 eV	0.24 eV	0.53 eV

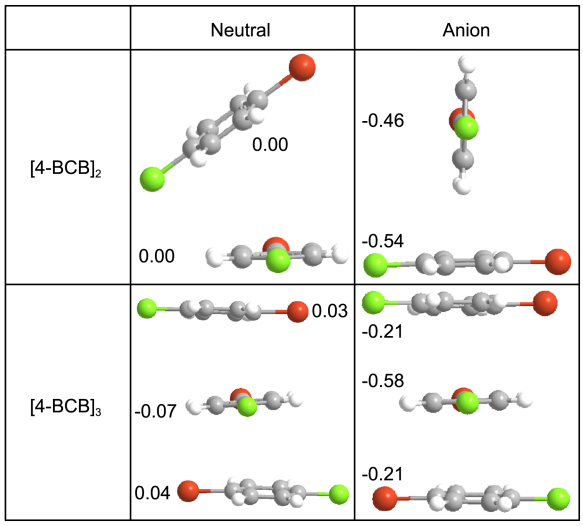

Figure 2. Optimized geometries and Mulliken charge analysis of (a) $[4\text{-BCB}]_2^-$, and (b) $[4\text{-BCB}]_3^-$ obtained by the B3LYP/6-31+G* level of calculation.

result, the VDE is quite large despite of the negative VDE of the benzene monomer anion (−1.12 eV).

In contrast, the excess electron can be delocalized over two 4-BCB molecules in $[4\text{-BCB}]_2^-$. A Mulliken charge analysis reveals that two 4-BCB molecules have -0.54e and -0.46e, respectively upon electron attachment.[14] The anion SOMO also verifies the delocalization of the excess electron throughout the entire cluster (Figure S1). The optimized geometries of the dimer are distorted PD (neutral) and T-shape (anion), respectively as seen in Figure 2.

The PES of $[4\text{-BCB}]_3^-$ is quite similar to that of $[4\text{-BCB}]_2^-$, thus allowing for the possibility that the trimer anion has a dimeric anion core. Furthermore, the VDE difference is 0.18 eV, which can be thought as the solvation effect of another 4-BCB molecule. However, the full-width at half maximum of the peak is larger than that of the dimer anion. In addition, the most stable geometry is totally different from that of the dimer anion. In both the neutral and anion states, $[4\text{-BCB}]_3$ has PD structures. Thus, the ion core of the trimer is not a dimeric core. However, delocalization of the excess electron is also expected by the Mulliken charge analysis and the SOMO of the anion. The moiety at the middle of the cluster has −0.58e and the remaining two moieties evenly share the residual negative charge (Figure 2). The SOMO is also extended to the entire cluster, thus verifying the delocalization of the excess charge (Figure S1). In addition, the nature of the electron delocalization is quite similar in the dimer and trimer anions. For both anions, most of the excess negative charge is delocalized over the benzene rings through the extended π-network (Table S2).

In conclusion, I investigated the electron attachment to 4-BCB dimer and trimer anions using anion photoelectron spectroscopy and theoretical calculations. I found that an excess electron can be delocalized to these clusters through extended π-network. However, the nature of the ion core is different for the dimer and trimer.

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