

Anion Photoelectron Spectroscopy and Theoretical Calculation of the Hetero-dimers of Polycyclic Aromatic Hydrocarbons

Namdoo Kim^{†,*} and Sang Hak Lee^{†,*,*}

[†]Department of Chemistry, Seoul National University, Seoul 151-747, Korea. *E-mail: mandoo8100@gmail.com

^{*}Current address: Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801-3080, USA

*E-mail: shlee20467@gmail.com

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Hetero-dimer anions of naphthalene (Np), anthracene (An), phenanthrene (Ph) and pyrene (Py) were investigated using the time-of-flight mass spectrometer (TOF-MS), anion photoelectron spectroscopy (PES) and theoretical calculation. There are two possible geometries with their electron affinity (EA) difference: parallel displaced (PD) and T-shaped. Dispersion force plays a key role in PD structure with the formation of a new anionic core while π -hydrogen interaction plays a key role in T-shaped structure with the monomer anionic core. The optimized structures and charge distributions can simply be explained by the relative difference of EA.

Key Words : Anion photoelectron spectroscopy, Polycyclic aromatic hydrocarbon, π -hydrogen interaction, Dispersion force

Introduction

Small aromatic hydrocarbons like benzene (Bz) and naphthalene (Np) do not make stable monomer anion upon the attachment of an extra electron in the gas phase since they have negative EA. Incoming electron feels strong repulsion due to the rich π -electron in the small area.^{1,2} Only short-lived anionic species can exist in the gas phase for a very short time. The long-lived monomer anion was observed in the condensed phase.^{3,4} For example, Np⁻ can exist in solution because of the stabilization effect of the solvent and the counterion. Thus, their EA was estimated indirectly through the electron transmission spectrum or by extrapolation of the higher clusters' EA.⁵ However, stable monomer anion can be formed if the size of the molecule becomes bigger than naphthalene. The smallest stable monomer anion among polycyclic aromatic hydrocarbon (PAH) is a Ph⁻ with the vertical detachment energy (VDE) of 0.13 eV measured by our photoelectron spectroscopy apparatus. Otherwise, an unstable monomer anion becomes a stable cluster anion by making a complex with themselves (homo-cluster) or with other PAH molecules (hetero-cluster).

Structures of small homocluster cations and neutral counterparts were studied by theoretical calculation.⁶ They found that charge resonance phenomenon in cation was important to have a stacking structure. The charge resonance band of the PAH anion was also observed and theoretically calculated by T. Shida and S. Iwata.⁷ Homo-dimer anions of PAH larger than naphthalene all have parallel-displaced (PD) structure, so that the excess negative charge is delocalized between two molecules.⁸⁻¹⁰ In this case, the chromophore of the higher cluster anion is completely different from that of the monomer anion. Therefore, a new anionic core is generated upon electron attachment. An electrostatic interaction

like dispersion force acts as a key role in this stacking structure that stabilizes the repulsion from an excess electron. On the other hands, Np₂⁻ is thought to have T-shaped structure due to high repulsion between the π electron and excess negative charge.⁵

[Bz-Np]⁻ is the smallest stable hetero-dimer anion and its VDE was found to be 0.03 eV by PES.¹¹ Since the ring size of the benzene is not large enough to delocalize the excess negative charge, this complex adopts the T-shaped structure with a naphthalene monomer anionic core. Due to the solvation effect of the benzene molecule (-0.2 eV), a naphthalene monomer that has a negative EA (-0.19 eV) can form a stable valence anion complex. Two hydrogens in benzene are perpendicular to the naphthalene ring in order to have π -hydrogen interaction. However, there is no result that has been described on the large hetero-dimer anions.

In this article, we report the TOF-MS, PES and theoretical calculation of hetero-dimer anions of PAH to reveal the optimized structures, charge distribution and anionic cores of each complex with a rather simple EA concept.

Experimental

The details of our experimental scheme have been described elsewhere.¹² Briefly, we generated a molecular beam of mixed clusters by expanding a thermally evaporated sample seeded in 5 bar of Ar carrier gas through a pulsed solenoid valve that can be heated up to 200 °C. Since the melting points of four molecules are all different from each other, we never elevated the temperature of the sample mixture above the lower melting point. High-energy electron from an electron gun (400 eV, 200 μ A) produced low-energy secondary electrons, whose attachment to neutral molecules turned them into anions. These anions were extracted into a Wiley-

McLaren type time-of-flight mass spectrometer, where they were mass-selected by a mass gate before entering a magnetic-bottle-type photoelectron spectrometer. The irradiation of anions by the second harmonic output (532 nm) of a pulsed Nd:YAG laser or 508 nm laser from 355 nm pumped dye laser ejected photoelectrons whose kinetic energy was measured to yield the photoelectron spectrum by subtracting the electron kinetic energy from the incident photon energy.

Results and Discussion

PES of Hetero-dimer Anion of PAH. Figure 1 shows the mass spectrum of the mixture of An and Py, where the molar mass of An and Py are 178 and 202, respectively. There are two prominent peaks that correspond to the monomer anion of each molecule and two small peaks that correspond to homo-dimer anions. The intensities of these homo-dimer anions are 30 times smaller than that of the monomer anion. Besides homogeneous clusters, a 1:1 cluster appears between the peaks of homo-dimers that correspond to the hetero-dimer anion.

Figure 2 shows the PES of (a) An^- , (b) $[\text{Np-An}]^-$, (c) Py^- , (d) $[\text{Ph-Py}]^-$, and (e) $[\text{Np-Py}]^-$. The PES shape of $[\text{Np-An}]^-$ is similar to that of An^- except for the VDE (0.53 eV for An^- and 0.80 eV for $[\text{Np-An}]^-$). Symmetric vibration mode of An, ν_6 ($1408\text{ cm}^{-1} = 0.17\text{ eV}$) also appeared in both PES. Furthermore, a broad and featureless peak exists at the high electron binding energy (EBE). This peak does not come from direct electron detachment since it does not appear in the specific wavelengths of photodetachment photon. If we plot the electron kinetic energy (EKE) versus photoelectron intensity, this peak always appears at the same position regardless of the photon energy used. Thus, its origin is an autodetachment where the electron detachment occurs via some short-lived excited states. If the anion is excited to the

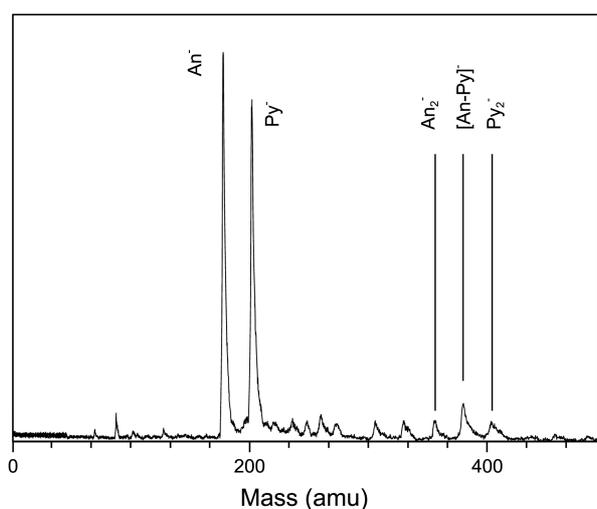


Figure 1. Mass spectrum of a mixed cluster of anthracene (An) and pyrene (Py). The most prominent species is monomer anion of each molecule. There are homo-dimer anions with smaller intensities. In addition, hetero-dimer anion is observed with significant intensity.

highly-excited state with the same spin multiplicity, internal vibrational relaxation occurs before the ejection of the photoelectron. The resulting anion mostly undergoes photodetachment at the second excited state due to the selection rule. Therefore, the EKE is independent of the photon energy used (details are in ref.12). The shape of the PES tells us the origin of the ion core. $[\text{Np-(H}_2\text{O)}_i]^-$ and $[\text{Np-Bz}]^-$ have same PES shapes, and the T-shaped geometries indicate they have a common Np^- monomer core.^{5,11} The PES of $[\text{Np-An}]^-$ is similar to that of An^- , however, neither $[\text{Np-(H}_2\text{O)}_i]^-$ nor $[\text{Np-Bz}]^-$ show similar spectra. Consequently, we can deduce that the anionic core of $[\text{Np-An}]^-$ is An^- . The role of a naphthalene molecule is a solvation of anthracene anion core to stabilize it about 0.27 eV. The same results were obtained in $[\text{Np-Py}]^-$ and $[\text{Ph-Py}]^-$. The PES of $[\text{Np-Py}]^-$ and $[\text{Ph-Py}]^-$ are similar to that of Py^- . Therefore, they have a common Py^- monomer core in the same context with $[\text{Np-An}]^-$.

Figure 3 shows the opposite to the case in Figure 2. The PES of (a) Py^- and (b) $[\text{An-Py}]^-$ are obtained at 532 nm (2.33 eV). At a glance, the shape of the PES (b) is much more different from that of Py^- . First, there are many vibrational progressions in (a) while no exist in (b). Second,

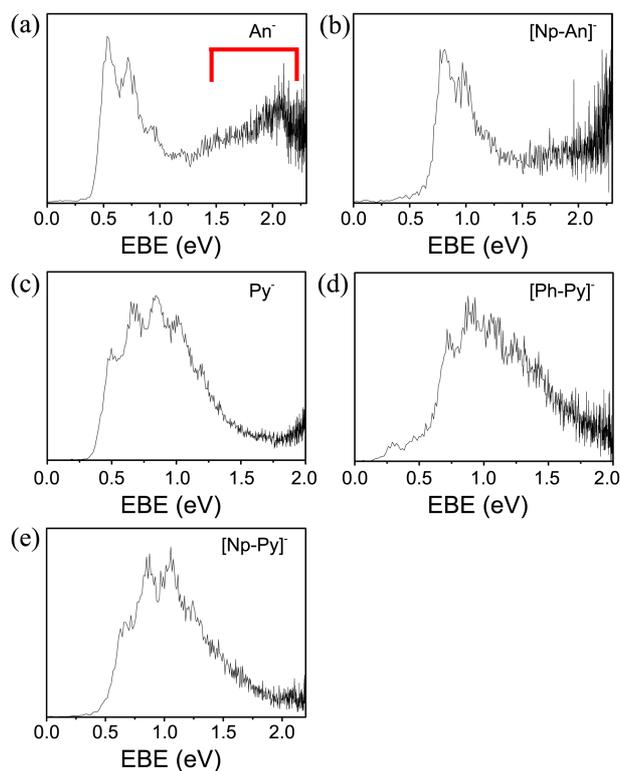


Figure 2. Photoelectron spectra of (a) anthracene monomer anion, (b) hetero-dimer anion of naphthalene-anthracene, (c) pyrene monomer anion, (d) hetero-dimer anion of phenanthrene-pyrene, and (e) hetero-dimer anion of naphthalene-pyrene. The PES shape in (b) is similar to that in (a), and those of (d) and (e) are similar to that in (c) indicating they have a monomer anionic core. Less electronegative naphthalene and phenanthrene act as a solvent to stabilize a monomer anionic core of more electronegative anthracene and pyrene. Red region in (a) denotes the photoelectron signals by autodetachment.

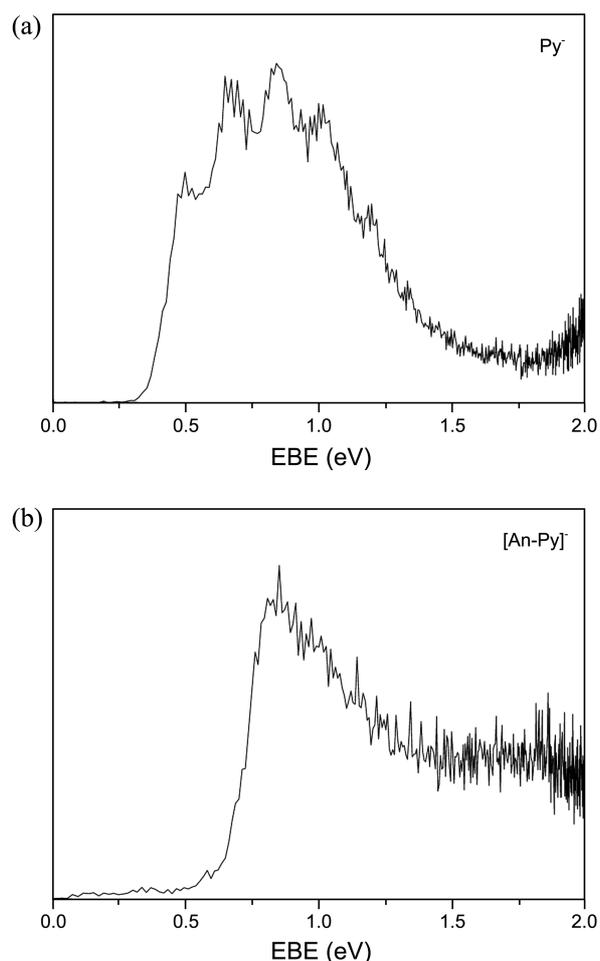


Figure 3. Photoelectron spectra of (a) pyrene monomer anion and (b) hetero-dimer anion of pyrene-anthracene at 532 nm. The shape of the PES in (b) is differs from that in (a) and (a) in Figure 2 indicating new anion core is formed.

the width of the band in (a) is much broader than that of (b). However, the PES shape of $[\text{An-Py}]^-$ is similar to that of An^- except for the absence of the vibrational progressions. We deconvoluted the PES with Gaussian functions for the comparison, and found that the intervals between peaks are not consistent with those in the PES of An^- . Thus, PES of (b) comes from a totally new anionic core rather than from Py^- or An^- . Further evidence for the generation of a new ionic core will be discussed in the next theoretical calculation section.

Theoretical Calculation of the Optimized Structure and Charge Distribution of Hetero-dimer Anion of PAH. To obtain the optimized structure and charge distribution of each hetero-dimer anion, we carried out a theoretical calculation with the density functional B3LYP method at the 6-31++G** level using Gaussian 03 package.¹³ Geometries were fully optimized and the frequencies checked to confirm that the obtained structure is lying on the global minimum point in the potential energy surface. VDE values were calculated to be compared with the experimentally obtained VDE values. Theoretical VDE for $[\text{Np-An}]^-$, $[\text{Np-Py}]^-$, $[\text{An-Py}]^-$

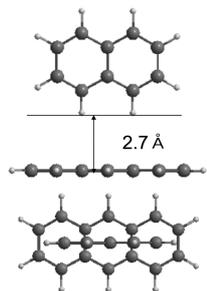
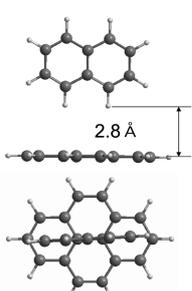
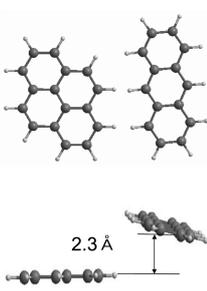
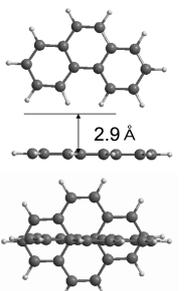
	$[\text{Np-An}]^-$	$[\text{Np-Py}]^-$
Geometry		
Charge	NP : -0.01 An : -0.99	NP : -0.22 Py : -0.78
	$[\text{An-Py}]^-$	$[\text{Ph-Py}]^-$
Geometry		
Charge	An : -0.56 Py : -0.44	Ph : -0.25 Py : -0.75

Figure 4. Optimized geometries and charge distributions of four hetero-dimer anions. The complex that has small differences in electron affinity shows PD structure ($[\text{An-Py}]^-$) and shares nearly half of the excess negative charge. However, those that have large differences in electron affinity show T-shaped structure ($[\text{Np-An}]^-$, $[\text{Np-Py}]^-$, and $[\text{Ph-Py}]^-$) and the excess negative charge is localized to the more electronegative molecule.

$[\text{Py}]^-$ and $[\text{Ph-Py}]^-$ are 0.80 eV, 0.69 eV, 0.94 eV and 0.72 eV, respectively, which well agree with the experimental values.

Figure 4 represents the theoretically obtained structures for hetero-dimer anions. There are three anions with T-shaped structure and one with parallel-displaced structure. These numbers coincide with the results of PES. There are three hetero-dimer anions that have the same shapes with one of the monomer anions ($[\text{Np-An}]^-$, $[\text{Np-Py}]^-$ and $[\text{Ph-Py}]^-$), and there is a hetero-dimer anion that form a totally different anionic core ($[\text{An-Py}]^-$). The three hetero-dimer anions that adopted a T-shaped structure have monomeric anion cores (An^- in $[\text{Np-An}]^-$, Py^- in $[\text{Np-Py}]^-$ and $[\text{Ph-Py}]^-$) while the other molecule stabilizes the ion core (Np^- in $[\text{Np-An}]^-$ and $[\text{Np-Py}]^-$, Ph^- in $[\text{Ph-Py}]^-$). In the T-shaped structure, hydrogen atoms in the less electronegative molecule are perpendicular to the face of the more electronegative anion core, which results in stabilization by π -hydrogen interaction like $[\text{Bz-Np}]^-$. The distance between these hydrogens and the anion core molecule ranges 2.7 Å–3.0 Å.

Most excess negative charge is localized to the more electronegative molecule. This tendency becomes obvious with the increase of the difference in EA value (–0.19 eV for Np,

0.13 eV for Ph, 0.53 eV for An and 0.45 eV for Py). Our molecular orbital (MO) calculation revealed that the singly occupied molecular orbital (SOMO) of these hetero-dimers are the same as those of anionic core, which verifies the results of PES, T-shaped structure and charge localization.

On the other hand, two molecules lie together in a dislocated position to be stabilized by dispersion forces like anthracene dimer anion.⁸ Since the two molecules (An and Py) have similar EA value, excess negative charge is almost evenly delocalized between the two molecules in [An-Py]⁻. There might be local minimums with T-shaped structures. Thus, we applied several T-shaped structures to obtain local minimum structures. However, we could not find any local minimum, and every T-shaped structure finally converged to PD structure. Thus, there is no local minimum with T-shaped structure. In MO calculation, the singly occupied molecular orbital (SOMO) of these hetero-dimers are different from those of any parent molecule and are evenly distributed over the complex which also verifies the results of PES, PD structure and charge delocalization.

Conclusion

In conclusion, the nature of the hetero-dimer of PAH anions was investigated by mass-selected anion photoelectron spectroscopy and theoretical calculation. A complex between molecules with comparable electron affinity becomes a parallel-displaced structure due to the electrostatic interaction like dispersion force between two moieties with the delocalized negative charge distribution. In contrast, the T-shaped structure with a monomer anionic core is dominant when the electron affinity of the two molecules differs from each other. In this case, the π -hydrogen interaction becomes more important and the excess negative charge is localized to the more electronegative molecule.

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