

## Photoelectron spectroscopy of naphthalene cluster anions

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Mass spectrometric and anion photoelectron spectroscopic studies of homogeneous naphthalene cluster anions,  $(\text{Nph})_{n=2-7}^-$ , were conducted to characterize the nature of their anionic cores. The smallest stable species in this series was found to be the naphthalene dimer anion. The vertical detachment energies of naphthalene clusters,  $n=2-7$ , were determined and found to increase smoothly with cluster size. By extrapolation, the vertical detachment energy of the isolated naphthalene molecule was found to be  $-0.18$  eV, in agreement with its adiabatic electron affinity value from literature. The strong similarity between the spectral profiles of  $(\text{Nph})_2^-$  and  $(\text{Nph})_1^-(\text{H}_2\text{O})_1$  implied that  $(\text{Nph})_2^-$  possesses a solvated monomeric anion core. All of the naphthalene cluster anions studied here were interpreted as having monomer anion cores. © 2002 American Institute of Physics. [DOI: 10.1063/1.1449869]

### INTRODUCTION

The naphthalene molecular anion is one of many negative ions which are unstable in isolation but which are nevertheless stable in condensed phases. In the gas phase, the bare naphthalene anion exists only as a temporary anion, its momentary presence being detected by the resonant scattering of low energy electrons. Analysis of its electron transmission spectrum by Burrow and Jordan<sup>1-3</sup> determined the vertical (as well as the adiabatic) electron affinity of naphthalene to be  $-0.19$  eV. Consistent with the instability of the isolated naphthalene anion, the pulsed electron, high pressure mass spectrometric experiments of Kebarle and co-workers,<sup>4</sup> which had set out to study the anions of naphthalene, were unable to observe its parent anion. In the condensed phase, on the other hand, the naphthalene anion has been detected by ESR,<sup>5-7</sup> electronic spectroscopy,<sup>8-10</sup> vibrational spectroscopy,<sup>11</sup> and polarography.<sup>12</sup> Moreover, the naphthalene anion is a common reagent in organic chemistry. Presumably, the stability of the naphthalene anion in solution is due to its energetic stabilization by environmental effects such as solvation and/or counterions. At the molecular level, the effect of solvation can be explored by forming gas-phase solvated anions, thereby mimicking some of the short range effects that are operative in condensed phases.

Solvation of otherwise unstable anions has now been studied in the gas phase by several research groups. Kondow and co-workers<sup>13</sup> observed this phenomena in their mass spectrometric studies of pyridine/water cluster anions. Schermann, Desfrancois *et al.*<sup>14,15</sup> studied it during their Rydberg electron transfer experiments on hydrated cluster anions of uracil, pyridine, pyridazine, pyrimidine, and pyrazine. Bowen and co-workers<sup>16,17</sup> utilized anion photoelectron spectroscopy to study hydrated cluster anions of naphthalene, py-

ridine, pyrimidine, uracil, dimethyluracil, methylcytosine, glycine, phenylalanine, and tryptophan. Weinkauff, Schlag *et al.*<sup>18,19</sup> used anion photoelectron spectroscopy to study hydrated cluster anions of uracil, cytosine, thymine, and naphthalene. Kim and co-workers employed anion photoelectron spectroscopy to study pyridine/carbon dioxide<sup>20</sup> and naphthalene/water cluster anions.<sup>21</sup> In addition to the heterogeneous systems which have been studied, Kim also studied the homogeneous cluster anions of pyridine,<sup>22,23</sup> and Bowen<sup>24</sup> investigated the homogeneous cluster anions of pyrimidine.

In the present paper, we jointly present our mass spectrometric and anion photoelectron spectroscopic studies of the homogeneous naphthalene cluster anions,  $(\text{Nph})_{n=2-7}^-$ . Our two groups were both motivated by an interest in characterizing the excess electron-carrying moieties within these species. In the simplest plausible case, the excess electron would be localized on a single naphthalene, with the other naphthalene molecules in the cluster acting to solvate this monomeric anion. Another possibility, however, is that the excess electron is delocalized over two or more naphthalene molecules, a dimeric subanion being the most likely. This latter case could be described as an example of charge resonance stabilization.

The phenomena of charge resonance has a rich literature.<sup>25-36</sup> Charge resonance is well known in several aromatic homogeneous dimer cations, where it is characterized by extra stabilization, unique absorption bands, and a charge distribution in which the excess positive charge is evenly distributed over the two aromatic moieties. In the case of the naphthalene dimer cation, for example, charge resonance was identified by Lewis and Singer<sup>25</sup> in its ESR spectrum through charge delocalization and by Nishi<sup>29-35</sup> in its gas-phase photodissociation spectrum<sup>31-33</sup> through the appearance of its absorption band. Charge resonance has also been observed in aromatic dimer anions. In the case of the

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matrix isolated anthracene dimer anion, for example, Shida and Iwata<sup>36</sup> observed its charge resonance absorption band directly. Thus, in the case of the naphthalene dimer anion, there exists the intriguing possibility that it too may be charge resonance stabilized, and that it may be the anion core in larger naphthalene cluster anions. Both monomeric and dimeric anion core possibilities will be considered below in light of our photoelectron spectral data on naphthalene cluster anions.

## EXPERIMENT

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. This is a direct approach to the determination of electron binding energies (EBE), relying as it does on the energy-conserving relationship,  $h\nu = \text{EBE} + \text{EKE}$ , in which  $h\nu$  is the photon energy, and EKE is the measured electron kinetic energy. In the collaborative experiments reported here, the Kim group utilized a pulsed, magnetic bottle anion photoelectron spectrometer, while the Bowen group used a continuous, hemispherical analyzer anion photoelectron spectrometer.

The details of the anion photoelectron spectroscopy apparatus in Kim's group have been described elsewhere.<sup>23</sup> In brief, naphthalene cluster anions were produced by the collisions of a 500 eV electron beam with a pulsed beam of naphthalene vapor in argon carrier gas. The secondary electrons produced in the ionization process were attached to neutral species to form anions. The resulting anions were then accelerated and mass analyzed by a 1.8-meter linear time-of-flight mass spectrometer. When recording a photoelectron spectrum, the anions were mass-selected with a mass gate prior to being photodetached by the fundamental (1064 nm, 1.165 eV) photons of an Nd:YAG laser. The photoelectrons were then energy-analyzed by a magnetic bottle electron energy analyzer. The spectra were calibrated against the well-known photoelectron spectrum of  $\text{O}_2^-$ .

The anion photoelectron spectrometer in Bowen's group has also been described elsewhere in detail.<sup>37</sup> Naphthalene cluster anions were generated in a supersonic expansion anion source in which naphthalene was heated to 90 °C and co-expanded with 4 atm of argon gas through a 25  $\mu\text{m}$  diameter nozzle. Relatively low energy electrons were injected directly into the high density portion of the expanding jet in the presence of weak axial magnetic fields, and negative ions were extracted from the resulting microplasma. The resulting cluster anions were mass selected with a Wien filter and photodetached with 514 nm (2.409 eV) photons from an argon ion laser, which was operated intracavity with a power of  $\sim 100$  circulating Watts. The photodetached electrons were then energy analyzed with a hemispherical energy analyzer having a resolution of  $\sim 30$  meV. The photoelectron spectra were calibrated against the well-known photoelectron spectra of  $\text{O}^-$  and  $\text{NO}^-$ .

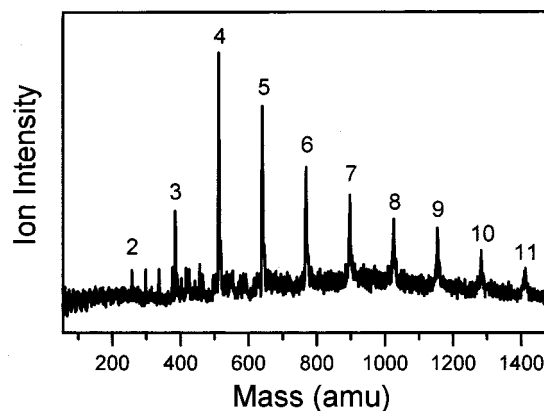


FIG. 1. Time-of-flight mass spectrum of naphthalene cluster anions  $(\text{Nph})_n^-$ .

## RESULTS AND SPECTRAL INTERPRETATION

A typical time-of-flight mass spectrum of naphthalene cluster anions is shown in Fig. 1. In both the TOF and the Wien filter mass spectra, the smallest naphthalene cluster anion detected was the dimer anion, with no trace of the monomer anion observed. The intensity of the dimer anion is weak compared to the other naphthalene cluster anions.

The photoelectron spectra of naphthalene cluster anions were taken at the two different photon energies, 1.165 and 2.409 eV. No differences in the resulting spectra were observed. The photoelectron spectra of naphthalene cluster anions,  $(\text{Nph})_{2-7}^-$ , are presented in Fig. 2. Each of them shifts to higher electron binding energies with increasing cluster size. The spectra of  $(\text{Nph})_{2-4}^-$  also show partially resolved vibrational structure, with the two evident peaks in each case being separated by 0.17 eV (1370  $\text{cm}^{-1}$ ). This energy most closely matches the  $\nu_5$  vibrational mode of neutral naphthalene, with reported literature values<sup>2,38-40</sup> of 1376  $\text{cm}^{-1}$ , 1383  $\text{cm}^{-1}$ , and 1417  $\text{cm}^{-1}$ . For the larger clusters,  $(\text{Nph})_{5-7}^-$ , vibrational structure is unresolved.

While all photodetachment transitions are, by their nature, vertical processes, when Franck-Condon overlap between the anion and its corresponding neutral ground state is sufficient, the  $(v=0 \leftarrow v=0)$  origin transition is mapped onto the photoelectron spectrum, and its energy is the adiabatic electron affinity (AEA) in the case of a molecule. In the case of a van der Waals complex, however, the energy of the origin transition cannot be generally equal to the AEA, unless the geometries of the anion and neutral complex are nearly alike over the entire set of coordinates, including the intermolecular ones. This is irrespective of the presence of a clearly identifiable chromophore for photodetachment. In the case of naphthalene clusters, the geometry of the anions turns out to be rather different from that of the corresponding neutrals, as will be discussed later.

All of the spectra presented here have steep, low electron binding energy onsets. While the spectra show no evidence of anion hot bands due to molecular vibrations, the presence of unresolved anion hot bands due to rotations is likely, and the presence of unresolved anion hot bands due to anion-neutral intermolecular vibrations is also a possibility. We do not expect major structural differences between these anion

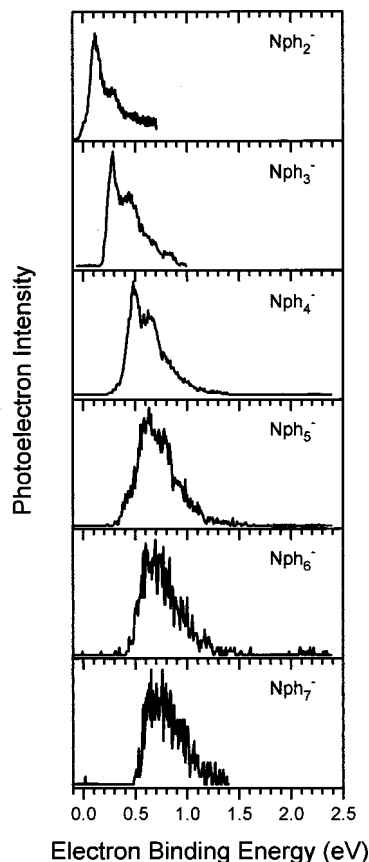


FIG. 2. Photoelectron spectra of naphthalene cluster anions  $(\text{Nph})_{2-7}^{-}$ .

*chromophores* and their neutral counterparts because the excess electron will be delocalized over the entire molecule, without causing a significant structural change. Therefore the origin-containing ( $v=0 \leftarrow v=0$ ) transition of the anion chromophore in each case is assignable. As mentioned before, however, we have assigned the origin-containing transition as the vertical detachment energy (VDE) rather than the AEA, since the latter requires a similar geometry for the cluster as a whole between the anion and the neutral counterpart. Because the spectral profiles of all of the spectra are similar to one another, the positions of the origins in the spectra of the larger naphthalene cluster anions,  $(\text{Nph})_{5-7}^{-}$ , were assigned by comparing the spectral profile of each spectrum, starting with that of  $(\text{Nph})_4^{-}$ , to that of the next larger one. The vertical detachment energies extracted from our photoelectron spectra are listed in Table I.

TABLE I. The vertical detachment energies (VDE) of the naphthalene clusters  $(\text{Nph})_{n=2-7}^{-}$ .

$n$	VDE (eV)
1	-0.18 <sup>a</sup>
2	0.11
3	0.28
4	0.48
5	0.62
6	0.63
7	0.65

<sup>a</sup>Value estimated from extrapolation.

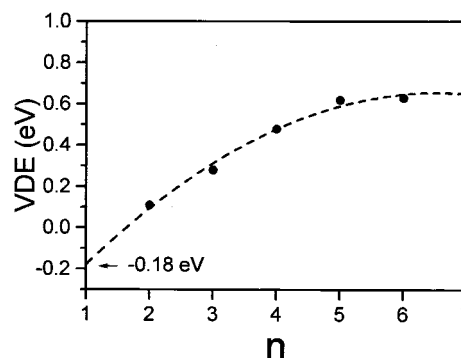


FIG. 3. Second order polynomial fit of the vertical detachment energies of naphthalene clusters vs  $n$  and its extrapolation to  $n=1$ . Typical error bars on these data points are  $\pm 30$  meV.

## DISCUSSION

### Electron affinity of naphthalene

Figure 3 plots the VDEs of naphthalene clusters vs their sizes,  $n$ , showing that their VDEs generally increase with cluster size. It is clear, however, that the relationship between VDE and cluster size is not linear, and that the sequential increase in VDE gradually decreases with increasing cluster size.

As mentioned earlier, analysis of electron transmission spectra put the AEA of the naphthalene molecule at  $-0.19$  eV. Here, we have made a second order polynomial fit to the data in Fig. 3 (see dashed line) and extended it to  $n=1$  in order to estimate the VDE of the naphthalene molecule from our data. The VDE gives an upper bound for the AEA. This procedure gives a VDE for naphthalene of  $-0.18$  eV, which is very close to the electron affinity value from electron transmission spectroscopy.<sup>1,2</sup> It is also nicely consistent with previous extrapolations of electron affinity vs size data on  $(\text{Nph})^{-}(\text{H}_2\text{O})_n$  by Bowen *et al.* ( $-0.20$  eV)<sup>16</sup> and by Weinkauff, Schlag, and co-workers ( $-0.20$  eV).<sup>19</sup> The VDE and the AEA are different in clusters as the intermolecular geometries are often different between the anion and the neutral. In the monomer, however, there is no intermolecular coordinates, and thus the VDE and the electron affinity can be nearly identical in case the molecular geometry does not change greatly between the anion and the neutral, as in the present case of naphthalene.

### The nature of the anionic core

Here, we consider the question of whether the core anion in the naphthalene cluster anions studied here is a monomeric or a dimeric anion. If it is the former, the monomer anion is the most stable excess electron carrier in the cluster, and it is simply solvated by neutral naphthalene molecules. If it is the latter, the dimer anion might well derive its special stability from charge resonance effects.

Charge resonance is characterized by extra stabilization, unique absorption bands, and in a dimer, a charge distribution in which the excess charge is evenly distributed over the two moieties. As for the first of these, no direct energetic information can be drawn from experiment alone in the

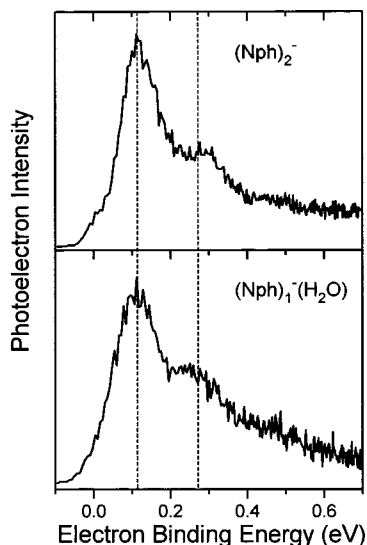


FIG. 4. Comparison of the photoelectron spectra of  $(\text{Nph})_2^-$  and  $(\text{Nph})_1^-(\text{H}_2\text{O})_1$ .

present case because of the inequality between the VDE and the electron affinity for clusters. Other direct evidence for a charge resonance interaction is seemingly lacking as well because, for example, there is no detectable absorption bands in the naphthalene anion clusters.

On the other hand, spectral band profiles can provide a crucial clue to the character of the anionic core of a complex anion. We note that the band shapes of the photoelectron spectra observed for  $(\text{Nph})_2^-$  and  $(\text{Nph})_1^-(\text{H}_2\text{O})_1$  are strikingly similar, as shown in Fig. 4. This indicates that these anions share a common anionic core, which must be the monomeric anion  $(\text{Nph})_1^-$ . The absence of reports of a charge resonance absorption band in solutions containing naphthalene anions also supports the monomeric anion core in the naphthalene cluster anions. Given the observation that the shape of the  $(\text{Nph})_1^-(\text{H}_2\text{O})_1$  and  $(\text{Nph})_2^-$  spectrum is also similar to those of larger naphthalene cluster anions, the monomer anion is probably also the anionic core in  $(\text{Nph})_{n=3-7}^-$  as well. In addition, the photoelectron spectra of  $(\text{Nph})_{2-7}^-$  bear a significant resemblance to those of  $(\text{Nph})_1^-(\text{H}_2\text{O})_{1-8}$ , further suggesting that the chromophores in both families of cluster anions are naphthalene monomer anions. It is also worth noting that while the photodissociation experiments of Brauman<sup>41</sup> on the toluquinone dimer anion were initially interpreted in terms of a charge resonance transition, his subsequent theoretical analysis, using the treatments of Simons<sup>28</sup> and of Schatz,<sup>42</sup> led to the conclusion that its excess electron is actually highly localized. Finality in answering the question of charge localization versus delocalization in anionic complexes has often been elusive.

### The geometry of the dimer anion

While the charge resonance stabilized, naphthalene dimer cation is thought to possess a structure with cofacial moieties that partially overlap,<sup>29</sup> the geometry of the naphthalene dimer anion can be totally different, as, for instance,

in a nonparallel structure with little orbital overlap. We carried out a cursory *ab initio* calculation that showed that the binding energy of a neutral T-shaped naphthalene dimer is as large as 70% of that of a cofacial dimer. The main contribution to the binding energy of the former was the electrostatic interaction between the delocalized  $\pi$  orbital of a naphthalene moiety and the two hydrogen atoms of the other naphthalene.<sup>43</sup> In the *anion* systems, the electrostatic interaction is expected to play an even more important role in the stabilization of the naphthalene dimer because of the extra charge. Recently Weinkauff, Schlag, and co-workers reported a stable geometry for  $[(\text{Nph})_1(\text{H}_2\text{O})_1]^-$  by an *ab initio* calculation, which showed that the two hydrogen atoms of water tend to form two hydrogen bonds with the naphthalene anion.<sup>19</sup>

We suggest that such hydrogen bonding scheme may operate in the case of naphthalene dimer anion as well, with two hydrogen atoms of one naphthalene molecule strongly interacting with the  $\pi$  orbital of the other molecule that contains most of the excess charge. In a parallel structure, the electrons in the  $\pi$  orbital of a naphthalene molecule would interact unfavorably with that of the other molecule with a negative charge. We find that the current model of a monomer anion solvated by a neutral naphthalene molecule is more consistent with a T-shaped naphthalene dimer anion structure than with a parallel structure. A more detailed study of the core structure and the geometry of naphthalene cluster anions may require high-level theoretical calculations.

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- <sup>43</sup>The *ab initio* calculation was carried out for the naphthalene dimer at the level of MP2/6-31G\*(0.25) designed for more diffuse *d*-polarization functions of carbon atom. To take the BSSE correction into account, all the stationary points of a geometry were searched by the point-by-point method. The result of the calculation showed that the parallel-displaced geometry is the most stable structure for the neutral naphthalene dimer with a stabilization energy of 7.63 kcal/mol (0.33 eV). Our preliminary *ab initio* calculation has failed to produce reliable results for the anion.

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