Solvent-induced stabilization of the naphthalene anion by water molecules: A negative cluster ion photoelectron spectroscopic study

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We show that (a) only a single water molecule is needed to stabilize the naphthalene anion, (b) the EA_a of naphthalene is -0.20 eV, in agreement with determinations by electron transmission spectroscopy, (c) the energetics are consistent with the number of waters required to stabilize the naphthalene anion, and (d) the excess electron is located on the naphthalene moiety of $Nph_1^-(H_2O)_n$. © *2000 American Institute of Physics.* [S0021-9606(00)00915-6]

INTRODUCTION

There are many anions which are unstable in isolation but which are nevertheless stable in condensed phases. Such negative ions are often characterized as temporary anions in the gas phase by electron scattering techniques and as stable anions in condensed phases by a variety of spectroscopic techniques. Presumably, the reason for the occurrence of these anions in solutions and/or crystal lattices is that they have been energetically stabilized by environmental effects such as solvation and/or counterions. At the molecular level, the effect of solvation on anion stability can be explored by forming solvent-stabilized cluster anions, thereby mimicking some of the main effects that are operative in condensed phases.

The solvent-induced stabilization of otherwise unstable anions has now been observed in several cluster anion systems. It was implicit in the mass spectrometric studies of pyridine/water cluster anions by Kondow and co-workers[1,2] about ten years ago. Then, just a few years ago, the valence anion of uracil (which is either unstable or, at best, only marginally stable[3]) was observed to be stabilized by just one water molecule in the Rydberg electron transfer (RET) experiments of Schermann and co-workers,[4] in our negative ion photoelectron spectroscopic studies,[5–7] and in the anion photoelectron experiments of Weinkauf and co-workers.[8] More recently, we[7] have also utilized negative ion photoelectron spectroscopy to study the solvent-induced stabilization of dimethyluracil, 1-methylcytosine, pyridine, pyrimidine, and naphthalene anions by various numbers of water molecules; Desfrancois and co-workers[9] have conducted RET studies on pyridine, pyridazine, pyrimidine, and pyrazine anions solvent-stabilized by water, ammonia, and toluene molecules; and Kim and co-workers[10] have performed photoelectron studies on pyridine/carbon dioxide cluster anions systems. Other related work includes that of Schermann and co-workers[11] on phenol-pyridine dimer anions, that of Kim and co-workers[12] on homogeneous pyridine cluster anions,

that of Desfrancois and co-workers[13] on formamide and substituted methylformamide cluster anions, and that from our own group[7] on homogeneous naphthalene and on homogeneous pyrimidine cluster anions.

In this paper, we focus on the solvent-induced stabilization of the naphthalene anion by water molecules. The naphthalene negative ion is an example of an anion which is well known in condensed phases but which appears to be unstable in isolation. The naphthalene anion has been detected and characterized in the condensed phase by ESR,[14–16] electronic spectroscopy,[17–21] vibrational spectroscopy,[22] polarography,[23,24] and other techniques[25,26] (often both at 77 and 298 K). While it is chemically reactive there, it appears to be thermodynamically stable with respect to neutral naphthalene and a free electron. In regard to its gas phase stability, the preponderance of evidence indicates that the naphthalene anion is unstable in isolation, i.e., it has a negative electron affinity. Electron transmission spectroscopy (ETS) measurements gave a vertical electron affinity (EA_v) of -0.19 eV for naphthalene, and based on the observed vibrational structure in its spectrum, this was also interpreted as corresponding to its adiabatic electron affinity (EA_a).[27–29] In addition, pulsed electron, high-pressure mass spectrometric experiments that set out to measure the electron affinity of naphthalene were unable to observe its parent anion.[30] The observation of the naphthalene anion in the condensed phase is therefore most likely due to the stabilizing effect of the anion's interactions with its immediate surroundings.

To investigate the solvent-induced stabilization of the naphthalene anion, we recorded both the mass spectra and the photoelectron spectra of gas-phase, hydrated naphthalene anion clusters, $Nph_1^-(H_2O)_n$. In particular, we addressed the following questions: (a) how many water molecules are needed to stabilize the naphthalene anion? (b) What value of naphthalene's adiabatic electron affinity is implied by our data, and is this value consistent with the literature's value? (c) Are the energetics consistent with the number of water molecules needed to stabilize the naphthalene anion? (d) Is the excess electron localized onto the naphthalene moiety of the cluster, i.e., is "a naphthalene anion solvated by water molecules" a proper description of $Nph_1^-(H_2O)_n$? The answers to these questions provide a microscopic perspective

into the solvent-induced stabilization of the naphthalene anion by water and into the broader phenomena by which solvation is able to, in effect, ''breathe life'' into otherwise unstable anions.

EXPERIMENT

Negative ion photoelectron spectroscopy is conducted by crossing a beam of mass-selected 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 relationship,

$$h\nu = EBE + EKE, \tag{1}$$

in which $h\nu$ is the photon energy, and EKE is the measured electron kinetic energy. Our apparatus has been described previously.[31] The spectra were calibrated against the well-known photoelectron spectra[32–34] of O^- and NO^-. The typical resolution (FWHM) of our electron energy analyzer was ~30 meV. In this work, 2.409, 2.540, and 2.708 eV photons were all used for photodetachment.

$Nph_1^-(H_2O)_n$ cluster anions were generated in our supersonic expansion nozzle ion source. To accomplish this, a naphthalene/water mixture was heated to 90 °C and coexpanded with 4 atm argon gas through a 15–20 μm nozzle orifice. Relatively low-energy electrons were then 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. Mass selection for these photodetachment experiments was accomplished with a Wien filter. In addition, we conducted complementary mass analysis with a quadrupole mass spectrometer in order to confirm mass assignments of cluster anions with unit mass resolution.

RESULTS

Mass spectra

A mass spectrum of $Nph_1^-(H_2O)_n$ clusters taken with our quadrupole mass spectrometer is shown in Fig. 1. The bare anion of naphthalene Nph_1^- (128 amu) is conspicuously absent from the mass spectrum. The first $Nph_1^-(H_2O)_n$ hydrated anion species to be observed occurs at $n = 1$, and the series continues uninterrupted, at least through $n = 24$. Naphthalene-containing peaks in the mass spectrum show the appropriate isotope patterns. The analysis of this and numerous other mass spectra recorded during these experiments revealed several persistent ion intensity patterns. The intensity of $Nph_1^-(H_2O)_1$, the first ion in the series, is always weak in comparison with that of $Nph_1^-(H_2O)_2$. In the other solvent-stabilized temporary anions that we have studied, the first cluster anion size to be observed, whatever size it may be, is also weaker in intensity than the next larger one. Presumably, this is related to its nascent stability. Under water-rich conditions, the intensity of $Nph_1^-(H_2O)_n$ clusters showed odd/even size alternations, with those clusters having an even number of water molecules exhibiting higher intensities. While this observation suggests that the even size cluster anions may have greater stability than their adjacent, odd
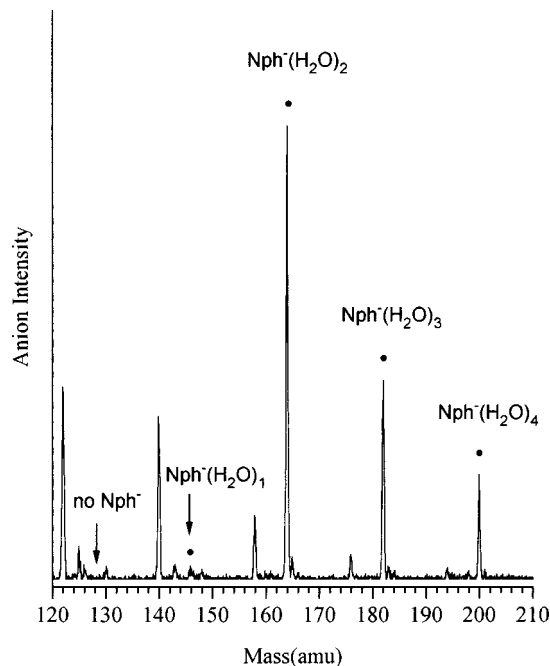

FIG. 1. Mass spectrum of $Nph_1^-(H_2O)_n$ cluster anions.

size counterparts, the photoelectron spectra do not mirror this size alternation and thus offer no clear clues in this regard. Under water-lean conditions, there was an abrupt decrease in intensity after $Nph_1^-(H_2O)_8$. The intensities of clusters containing multiple naphthalenes were substantially lower than the intensities of clusters having only one naphthalene molecule per cluster, $Nph_1^-(H_2O)_n$. Among the clusters containing more than one naphthalene per cluster, $Nph_2^-(H_2O)_4$ (equivalent in mass to $[Nph_1^-(H_2O)_2]_2$) routinely displayed a locally enhanced intensity relative to its immediately neighboring mass peaks.

Photoelectron spectra

The photoelectron spectra of $Nph_1^-(H_2O)_n$, $n = 1-8$ are presented in Fig. 2. The photoelectron spectrum of $Nph_1^-(H_2O)_1$ displays two prominent peaks that are separated from one another by 178 ± 9 meV (1435 ± 72 cm^{-1}). The photoelectron spectrum of the next larger cluster in the series, $Nph_1^-(H_2O)_2$, resembles that of $Nph_1^-(H_2O)_1$. While it is shifted to higher EBE and slightly broadened, the general profile is nevertheless preserved. The spacing between the two main peaks in this spectrum measures 165 ± 9 meV (1331 ± 72 cm^{-1}). Even though resolved structure disappears in the photoelectron spectra of the larger clusters, $Nph_1^-(H_2O)_{n \geqslant 3}$, their spectral profiles remain locally similar to one another throughout the series.

The photoelectron spectrum of $Nph_1^-(H_2O)_1$ has a very step spectral onset, starting from a threshold electron binding energy of only 0.035 eV. While this spectrum shows no evidence of anion hot bands due to molecular vibrations, the presence of unresolved anion hot bands due to rotations is quite likely, and the presence of unresolved anion hot bands due to anion–neutral molecule vibrations is also a possibility. Given these circumstances, we have assigned the lowest
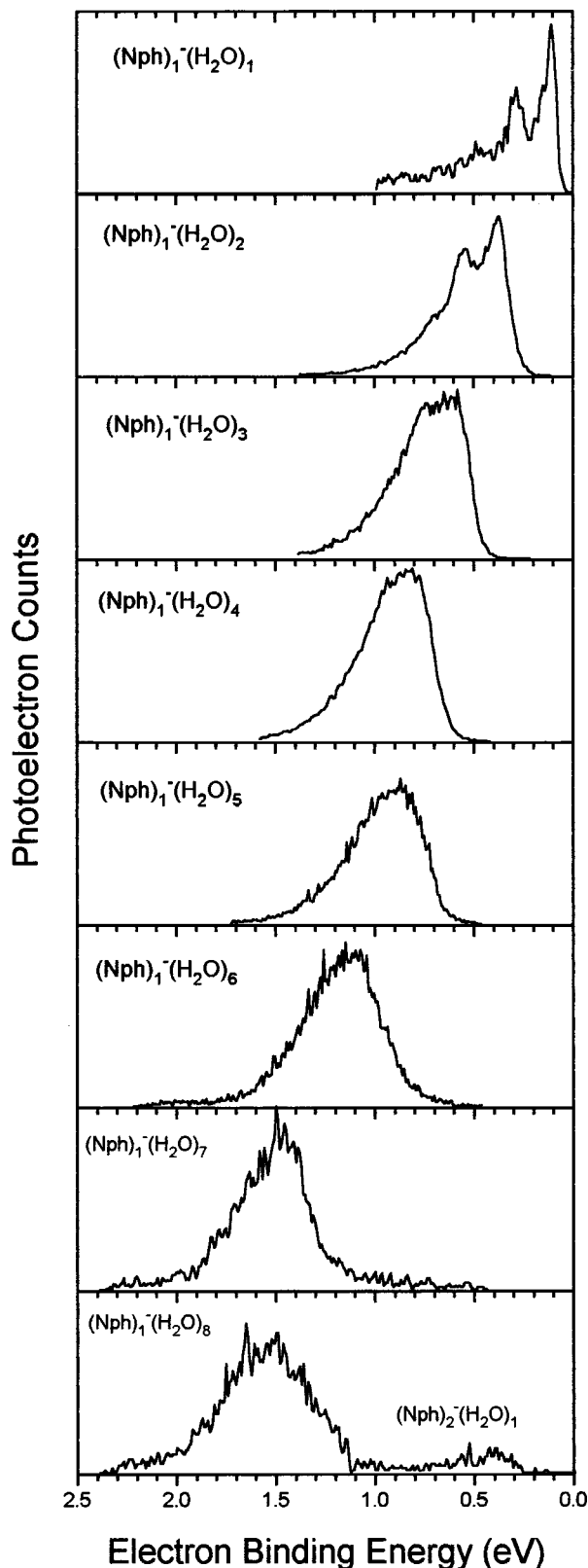
FIG. 2. Photoelectron spectra of $Nph_1^-(H_2O)_n$, $n=1-8$, recorded with 2.409 eV photons.

TABLE I. The adiabatic electron affinities (EA_a) of hydrated naphthalene clusters $Nph_1(H_2O)_n$, their stepwise increase ($\Delta EA_a = EA_{a(n)} - EA_{a(n-1)}$), and the threshold energies (E_{th}) of their negative ion photoelectron spectra. All energy values are in eV.

n	E_{th}	EA_a	ΔEA_a
1	0.035	0.11	$\cdots$
2	0.21	0.37	0.26
3	0.4	0.57	0.20
4	0.6	0.76	0.19
5	0.6	0.85	0.09
6	0.6	1.1	0.25
7	1.0	1.4	0.3
8	1.1	1.5	0.1

are all similar to one another, the positions of the origins of the larger $Nph_1^-(H_2O)_n$ cluster anions were assigned by comparing the spectral profile of each spectrum to that of the next larger one, i.e., by overlaying the spectral profiles of pairs such as $n=1,2$; $n=2,3$; $n=3,4$, etc. We believe this procedure to be largely equivalent to, but more accurate than, comparing the spectral profiles of each larger cluster anion in the series to that of $n=1$. The values so obtained for EA_a's and sequential spectral shifts (ΔEA_a's between adjacent cluster sizes) as well as those for threshold EBEs (E_{th}'s) are listed in Table I. The values of EA_a vs n are plotted in Fig. 3.

Sequential spectral shifts reflect the following general energetic relationship:

$$\Delta EA_a = EA[X(Y)_n] - EA[X(Y)_{n-1}]$$
$$= D[X^-(Y)_{n-1}\cdots Y] - D_{WB}[X(Y)_{n-1}\cdots Y], \quad (2)$$

where $EA[X(Y)_n]$ denotes the adiabatic electron affinity of the $X(Y)_n$ cluster, $D[X^-(Y)_{n-1}\cdots Y]$ is the ion–neutral dissociation energy for the loss of a single neutral solvent molecule, Y, from $X^-(Y)_n$, and $D_{WB}[X(Y)_{n-1}\cdots Y]$ is the weak-bond, neutral–neutral dissociation energy for the loss of a single solvent molecule, Y, from the same size neutral cluster, $X(Y)_n$. In most instances, ion–neutral dissociation energies can be expected to be larger than weak-bond, neutral–neutral dissociation energies.
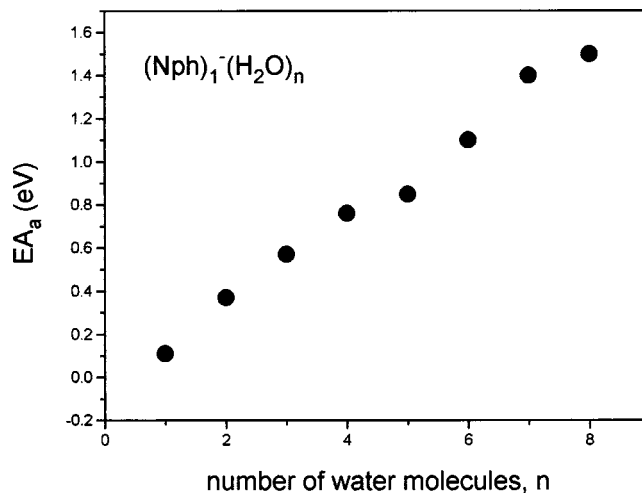

FIG. 3. Plot of the adiabatic electron affinities (EA_a) of hydrated naphthalene clusters as a function of cluster size, n.

EBE and most prominent peak in this spectrum as the origin-containing transition, with the EBE of the peak center being taken as the EA_a of the corresponding neutral cluster. Because the spectral profiles of the $Nph_1^-(H_2O)_n$ cluster anions
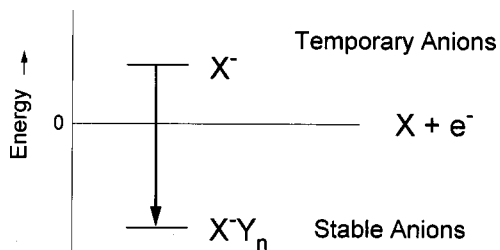
FIG. 4. Schematic showing energetics of solvent-induced stabilization of temporary anions.

In addition to photoelectron spectra taken with 2.409 eV photons, we also recorded spectra of $Nph_1^-(H_2O)_{n=2,3,4}$ with 2.540 and 2.708 eV photons.[7] While the lower-energy photons (2.409 and 2.540 eV) gave very similar photoelectron spectra, an additional feature emerged between 1.2 and 2.2 eV EBE in the 2.708 eV photon spectra of all three of these systems. It is probably due to the access, at that photon energy, of an anion resonance.

DISCUSSION

How many water molecules are needed to stabilize the naphthalene anion?

The answer to this question is evident from the mass spectrum of the naphthalene/water cluster anion system (see Fig. 1); only one water molecule is required to stabilize the naphthalene anion. As a broader issue, the more negative the electron affinity of a given temporary anion, X^- (the higher the energy of X^- is above that of $X+e^-$), the more solvent molecules, Y, of a given kind are presumably required to lower its energy into stability (see Fig. 4). When the sequential spectral shifts for various anion/solvent combinations are comparable, this hypothesis implies a linear relationship between the absolute values of the adiabatic (thermodynamic) electron affinities of temporary anions and the minimal number of solvents required to lower them into stability.

Sequential photoelectron spectral shifts for anion–neutral complexes are usually dominated by sequential anion–neutral solvent interaction energies, and these depend, among other things, on the excess charge density on the anions. In addition to the naphthalene anion, we have also investigated the solvent stabilization of several other temporary anions by water molecules. These anions, i.e., those of styrene, uracil, pyrimidine, and pyridine, all are relatively small molecules with ring structures, and, as such, their excess negative charge densities are probably not vastly different. Thus, our basic picture of temporary anion solvent stabilization can be tested, at least tentatively, via these five hydrated anion systems.

Electron transmission spectroscopy (ETS) has provided most of the presently available information about the electron affinities of these systems, and our mass spectral studies have supplied values for the minimal number of solvent molecules required to stabilize their temporary anions. As mentioned earlier, ETS has measured the vertical electron affinity (EA_v) of naphthalene to be -0.19 eV, and based on the observed vibrational structure in its spectrum, this value was

also interpreted as corresponding to its adiabatic electron affinity (EA_a).[27–29] For styrene, ETS has measured its EA_v to be -0.25 eV, and as in the case of naphthalene, this value was also interpreted as corresponding to its EA_a.[35] For pyrimidine, ETS has measured its EA_v to be -0.38 eV, but based on an assignment of its lowest lying vibrational feature, the value of its EA_a was interpreted to be -0.26 eV.[36] The case of uracil is less clear. ETS found its EA_v to be -0.22 eV, but a lack of vibrational structure made a determination of its EA_a problematic.[37] In any case, the EA_a values of naphthalene, styrene, and pyrimidine are all around -0.2 eV, and the EA_a of uracil is either the same or less negative. In each of these four systems, the minimal number of water molecules required to stabilize their temporary anions was found in our mass spectral studies to be one. Next, consider pyridine. ETS measured its lowest lying vibrational feature at -0.59 eV, which was interpreted as corresponding to both its EA_v and its EA_a values.[38] In our, as well as Kondow's,[1,2] mass spectral study of hydrated pyridine anions, a minimum of three water molecules were found to be needed to stabilize the pyridine anion. To summarize, when their EA_a's are about -0.2 eV, only one water is required to stabilize them, but when EA_a is three times more negative (about -0.6 eV), fully three water molecules are needed. Thus, from the data that we have so far, there appears to be a roughly linear relationship between $|EA_a|$ and the minimal number of solvent molecules required to lower temporary anions into stability. Viewed from another perspective, the process of offering successive numbers of solvent molecules to a given temporary anion until stability is achieved can be viewed as a kind of ''titration'' for estimating negative EA_a values, with the minimal number of solvents required for stabilization being its ''end point.''

What value for naphthalene's EA_a is implied by our data?

Our data implies a value for the EA_a of naphthalene, and, thus, a comparison of our value with that determined from ETS measurements serves as a check on both. Three methods for extracting an EA_a value from our data present themselves: the ''titration'' method using other systems as calibrants, a linear extrapolation of the EA_a vs n plot in Fig. 3 to $n=0$, and an extrapolation of our ΔEA_a vs n data to $n=1$ (see Fig. 5). The ''titration'' approach provides only a rough estimate; both of the other methods are more quantitative. The disadvantage of the ''linear extrapolation of the EA_a vs n'' method lies in the fact that it is not and should not be linear. The sequential (stepwise) spectral shift between adjacent size cluster anions (here, ΔEA_a) is not constant but tends to decrease slowly as n increases. This makes the EA_a vs n plot in Fig. 3 curve to the right, at least for the smaller sizes for which the error bars on the data are smallest. Such behavior is typical of most anion–neutral complexes, the few exceptions involving structural or electronic pathologies. If, however, one were to employ this method, a linear extrapolation of the first three data points in Fig. 3 would imply an EA_a for bare naphthalene of -0.11 eV, while a linear extrapolation using the first four points would imply an EA_a of -0.085 eV. Given the curvature of the plot in Fig. 3, how-
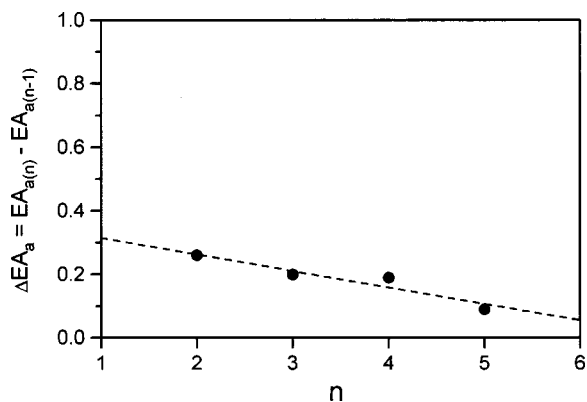
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FIG. 5. Plot of the sequential spectral shifts (ΔEA_a) of $Nph_1^-(H_2O)_n$ photoelectron spectra as a function of cluster size, n, and their extrapolation to $n=1$.

ever, the real EA_a for naphthalene is likely to have a more negative value. The third method involves an extrapolation of a plot of ΔEA_a vs n to $n=1$. Since this plot is not linear either, one would like to fit it to a monotonic curve and then to extend that curve to $n=1$ in order to determine the ΔEA_a there. However, because such a fit is problematic, we choose instead to make a linear extrapolation of the first several data points in our ΔEA_a vs n plot (see Fig. 5). Essentially, this is a second-order linear fit of the data, and its extrapolation to $n=1$ implies that $EA_a(n=1) - EA_a(n=0) = 0.31$ eV. Since $EA_a(n=1) = 0.11$ eV, this implies that $EA_a(n=0) = -0.20$ eV. This value for the EA_a of naphthalene (-0.20 eV) is in excellent agreement with the ETS result (-0.19 eV) of Burrow and Jordan.[27–29] Of the three methods we have described, this is the most accurate for the determination of the EA_a of naphthalene from our data.

Are the energetics consistent with the number of water molecules required?

With the value for EA_a of naphthalene confirmed as being about -0.2 eV, and with the stabilization energy in going from bare Nph_1^- to $Nph_1^-(H_2O)_1$ estimated by extrapolation as being ~ 0.3 eV, a consistent picture emerges for the energetics of naphthalene anion solvent stabilization. Since the bare naphthalene anion sits ~ 0.2 eV in energy above the neutral naphthalene plus free electron asymptote, a stabilization energy of ~ 0.3 eV, due mostly to the interaction of the naphthalene anion and a water molecule, is enough to pull the energy of the system down into stability. It is therefore reasonable that a single water molecule should be able to stabilize the naphthalene anion. The energetics of this problem are thus consistent with the observed number of water molecules required. An additional consequence of these energetics is that one water molecule should just barely stabilize the naphthalene anion, leading to the expectation that the EA_a of $Nph(H_2O)_1$ should be quite small. This too conforms to our observations. The EA_a of $Nph(H_2O)_1$ is only 0.11 eV, and its threshold (E_{th}) in the photoelectron spectrum of $Nph_1^-(H_2O)_1$ occurs at an EBE of only 0.035 eV. Subsequent water solvents just continue to stabilize the system further, although by not as much per solvent step.

Even without extrapolating to the stabilization energy, $EA_a(n=1) - EA_a(n=0)$, one could reach the same conclusion by noticing that the typical sequential spectral shift per water molecule in small hydrated naphthalene cluster anions (see the ΔEA_a values in Table I) is roughly 0.2 eV. Thus, with an EA_a for naphthalene of -0.19 eV, it is evident that only a single water solvent molecule would be needed to lower the energy of the naphthalene anion to the edge of stability. Taken together, these energetics help to rationalize how species with negative electron affinities can occur as stable anions in liquid or solid phase environments.

Is the excess electron located on the naphthalene moiety of the cluster?

In condensed phases, ESR studies make it clear that the naphthalene anion exists as a *bona fide* anion. The question then arises as to whether it exists as such in the smallest $Nph_1^-(H_2O)_n$ cluster anions, i.e., has the excess electron localized itself onto the naphthalene moiety of the cluster to form an intact naphthalene anion?

For several reasons, it is likely that the excess electron is associated with naphthalene rather than with the water molecule(s) in these clusters. First, while water and naphthalene both have negative adiabatic electron affinities, the EA_a of naphthalene is much less negative than that of water. Second, the photoelectron spectra of $Nph_1^-(H_2O)_n$ show little similarity to those of $(H_2O)_n^-$. In the relevant size range only the $(H_2O)_n^-$ species at sizes, $n=2$, 6, and 7 are easy to make, and the photoelectron spectrum of size, $n=2$ looks rather different than those of sizes, $n=6$ and 7. All of the $Nph_1^-(H_2O)_n$ species, on the other hand, form relatively easily and continuously from size, $n=1$ up through at least 24, and all of those that we measured have similar photoelectron spectral profiles. None of these resemble those of $(H_2O)_n^-$ photoelectron spectra.[39,40]

The most compelling reason to interpret the excess electron as residing on naphthalene in $Nph_1^-(H_2O)_n$, however, is the structure observed in the first two $Nph_1^-(H_2O)_n$ photoelectron spectra. In the spectra of both $Nph_1^-(H_2O)_1$ and $Nph_1^-(H_2O)_2$, at least two distinct peaks are observed. As mentioned previously, in $Nph_1^-(H_2O)_1$, they are separated by 1435 ± 72 cm^{-1}, while in $Nph_1^-(H_2O)_2$, they are separated by 1331 ± 72 cm^{-1}, essentially the same number for present purposes. This splitting is very similar to some of the vibrational frequencies in neutral naphthalene, and we interpret it, in both cases, as being due to them. Neutral naphthalene has vibrational frequencies[41–43] at 1460 cm^{-1} (ν_4) and at 1376 cm^{-1} (ν_5), and since both are of A_g symmetry, both are allowed in photoelectron spectra. The splitting in $Nph_1^-(H_2O)_1$ is closer to the frequency of ν_4, while the splitting in $Nph_1^-(H_2O)_2$ is closer to that of ν_5, but both of these may well be represented in the spectra to one degree or another in both cases. The observation of a naphthalene vibration(s) in the central profile of our photoelectron spectra is symptomatic of a naphthalene anion ''chromophore'' in these clusters and thus of the presence of an intact naphthalene anion within the cluster. We should also point out that this same splitting is seen in our photoelectron spectra of

homogeneous naphthalene cluster anions, where, of course, no water is present. Taken together, all of this implies that ''a naphthalene anion solvated by water molecules'' is a proper description of $Nph_1^-(H_2O)_n$ clusters, including even their smallest viable member, $Nph_1^-(H_2O)_1$.

One final issue concerns the excess charge density on the naphthalene anion. Given that the excess electron is closely associated with naphthalene in $Nph_1^-(H_2O)_n$, can we discern more about how localized (or delocalized) it is there? The magnitudes of sequential spectral shifts offer useful clues. For the first few $Nph_1^-(H_2O)_n$ clusters, the shifts tend to be $\sim 0.2-0.3$ eV, and for the hydrated anthracene anion,[44] a related system, it is about the same. These are in contrast, however, with sequential spectral shifts in cluster anions such as $NO^-(H_2O)_n$ and $Cl^-(H_2O)_n$, where the shifts are from two to four times larger for the same cluster number, n.[45,46] Since sequential shifts are usually dominated by ion–neutral interaction energies, the small spectral shifts seen in hydrated naphthalene cluster anions probably mean, in accord with intuition, that the excess charge density on the naphthalene anion is substantially lower than on NO^- and Cl^-, and thus, that the excess electron on naphthalene is highly delocalized.

ACKNOWLEDGMENTS

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