

# Microsolvation of small anions by aromatic molecules: An exploratory study

K. Le Barbu,<sup>a)</sup> J. Schiedt, R. Weinkauf,<sup>b)</sup> and E. W. Schlag

*Institute for Physical and Theoretical Chemistry, Technical University of Munich, 85747 Garching, Germany*

J. M. Nilles, S.-J. Xu, O. C. Thomas,<sup>c)</sup> and K. H. Bowen<sup>d)</sup>

*Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218*

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This work was motivated by the experimental finding that the  $O_2^-$ /benzene interaction energy is unexpectedly large. To further explore the interactions of small anions with aromatic molecules, anion photoelectron spectroscopy was utilized to measure interaction strengths of the seed anions,  $O_2^-$  and  $NO^-$ , complexed with several aromatic molecules, including benzene, naphthalene, pyridine, and pyrimidine. As in the case of  $O_2^-$  (benzene), the anion(aromatic)<sub>1</sub> binding energies for the other complexes studied were also higher than one might have anticipated. In addition, the interaction energy of  $O_2^-$  complexed with a given aromatic molecule was, in every case studied, higher (by a factor of  $\sim 1.5$ ) than that of  $NO^-$  complexed with the same aromatic. While the dependence of interaction strengths on solvent dipole moments and/or polarizabilities implied a substantial electrostatic component to the binding in these complexes, differences in the binding of  $O_2^-$  and  $NO^-$  with these aromatic molecules showed that there is a distinct covalent aspect to the interaction as well. A significant portion of this interaction was attributed to the fact that  $O_2^-$  and  $NO^-$  are both open-shell anions that are interacting with closed-shell aromatic molecules. In the accompanying paper [J. Chem. Phys. **116**, 9672 (2002)] calculations on  $O_2^-$  (benzene)<sub>1</sub> by Jalbout and Adamowicz shed additional light on the nature of small anion–aromatic molecule interactions. Last, results are also presented comparing the interaction energies of several multisolvated, anion–molecule complexes. © 2002 American Institute of Physics. [DOI: 10.1063/1.1475750]

## I. INTRODUCTION

Gas-phase studies of size-dependent microsolvation allow the observation of specific binding effects<sup>1</sup> as well as providing direct comparisons with theory. In the past, both our groups have investigated the microsolvation of small aromatic anions by water, i.e., the solvent stabilization of otherwise unstable anions.<sup>2,3</sup> In these, the excess charge was delocalized over the aromatic  $\pi$ -system, resulting in an extended electron cloud which was then weakly solvated by one or more water molecules. In the present work, we reverse the role of the aromatic molecules and use them to solvate the small anion seeds,  $NO^-$  and  $O_2^-$ . The solvation of anions by aromatic molecules had received little attention prior to the present study.

By contrast, the interactions of cations with aromatic molecules has been the subject of numerous studies.<sup>4–22</sup> Among these, transition metal cation/aromatic ligand binding and alkali metal cation/aromatic interactions are probably the most thoroughly investigated. Whereas the bonding in the former (pseudocoordination complexes) is largely covalent

in character, the latter is predominantly electrostatic. As a result, the bonds in transition metal cation/aromatic molecule coordination complexes can be quite strong. Interestingly, however, alkali cation– $\pi$  system interactions, despite their largely noncovalent character, exhibit considerable strength as well. There is, in fact, growing evidence that cation– $\pi$  system interactions may be of widespread importance in biological processes. From experiments, it has been found that nonpolar benzene competes favorably with water in the solvation of potassium cations. Interestingly, however, the reverse is the case for sodium cations, and it is thought that this difference in behavior may be the molecular basis for ion selectivity in potassium channels.<sup>11,12</sup> From theory, calculations on prototypical cation– $\pi$  systems suggest that they may also play important roles in molecular recognition in neuroreceptors, in the structural biology of proteins, in biologically relevant charge transfer systems, and in some biocatalytic processes.<sup>14–22</sup>

Intuitively, it is easy to imagine that a cation would interact attractively with the electron-rich,  $\pi$ -cloud of an aromatic molecule. When, however, one considers the prospects for anion–aromatic molecule binding, the same essentially electrostatic arguments suggest repulsive interactions, and this is perhaps the main reason that so little attention has been paid to them. Recently, however, the presumption of weak anion–aromatic molecule interactions was challenged by the observation of an unexpectedly large binding energy ( $\sim 0.6$  eV) between the homonuclear anion,  $O_2^-$ , and the

<sup>a)</sup>Present address: Laboratoire de Photophysique Moléculaire, Université Paris XI—Batiment 210, 91405 Orsay Cedex, France.

<sup>b)</sup>Present address: Institut fuer Physikalische Chemie und Elektrochemie, Heinrich-Heine Universitaet Duesseldorf, Universitaetstrasse 1, 40225 Duesseldorf, Germany. Electronic mail: weinkauf@uni-duesseldorf.de

<sup>c)</sup>Present address: Process Measurements Division, National Institutes of Standards and Technology, Gaithersburg, MD 20899.

<sup>d)</sup>Electronic mail: kitbowen@jhunix.hcf.jhu.edu

nonpolar molecule, benzene, in the complex,  $O_2^-(\text{benzene})_1$ . With neither component of this complex having a dipole moment, one might have expected a significantly smaller binding energy. The surprising strength of this interaction raises the possibility that anion–aromatic binding might also play a significant role in biological systems, where on average, there are as many anions present as cations.

In this work, we explore the microsolvation of the small anions,  $O_2^-$  and  $NO^-$ , by the aromatic molecules, benzene and naphthalene, as well as the conjugated heterocyclic molecules, pyridine and pyrimidine. Both  $O_2^-$  and  $NO^-$  play significant roles in biology. The superoxide ion,  $O_2^-$ , causes oxidative damage in biological systems,<sup>23</sup> while the nitroxyl anion,  $NO^-$ , along with neutral NO, mediate a variety of biological processes.<sup>24</sup> Our strategy in studying anion–aromatic interactions was to vary both the anion and the aromatic molecule in order to create a matrix of information that would facilitate comparisons, permit the recognition of trends, and provide benchmarks for theory. To insure that the location of the excess charge is well defined, we used only small aromatic molecules with negative adiabatic electron affinities. In this way, we were assured that excess negative charge was localized primarily on the similar-size anion seeds,  $O_2^-$  and  $NO^-$ .

Our two groups collaborated in this effort. The Technical University of Munich group, which had originally found the large  $O_2^-(\text{benzene})_1$  binding energy, utilized pulsed, anion photoelectron spectroscopy to measure the spectra of several  $O_2^-$ /aromatic molecule complexes, while the Johns Hopkins University group used continuous, anion photoelectron spectroscopy to record the spectra of several  $NO^-$  complexes with mostly the same aromatic molecules. Here, we present the results of this joint effort. Theoretical support was provided by Jalbout and Adamowicz. Their results on the  $O_2^-(\text{benzene})$  complex are presented in the accompanying paper, hereafter referred to as Paper II.

## II. 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 relationship,

$$h\nu = \text{EBE} + \text{EKE}, \quad (1)$$

in which  $h\nu$  is the photon energy, and EKE is the measured electron kinetic energy.

Both the TU-Munich and the Johns Hopkins anion photoelectron spectrometers have been described elsewhere in detail.<sup>25,26</sup> Briefly, in the Munich apparatus, anions were mass selected using a quadrupole mass spectrometer, photodetachment was accomplished with a pulsed laser beam, and electrons were energy-analyzed by measuring their flight times along a field-free pathway. In these experiments, the third harmonic (355 nm) of a Nd:YAG laser was normally used for photodetachment. While electron energy resolution is strongly energy dependent in time-of-flight energy analy-

sis, it was 3.5 meV (FWHM) at an electron kinetic energy of 40 meV in the apparatus used in these studies. Negative ions were generated by focusing a pulsed beam of energetic electrons into a pulsed supersonic expansion, where low-energy secondary electrons were produced, anions were formed and cooled, and anion–molecule complexes were prepared. The stagnation chamber of the pulsed nozzle source was heated to  $\sim 100^\circ\text{C}$ , as needed, to obtain a sufficient vapor pressure of a given aromatic sample, while its total pressure was maintained at 8 bar with a mixture of nitrogen and a small amount of oxygen. The diameter of the nozzle was  $\sim 200\ \mu\text{m}$ . Once the expansion had done its work, ions and neutrals alike drifted through a skimmer into the next chamber, where the anions were pulse extracted perpendicularly into the mass spectrometer.

In the Hopkins apparatus, anions were mass selected using a magnetic sector, photodetachment was accomplished with a continuous laser beam operated intracavity, and electrons were energy-analyzed with a hemispherical electrostatic energy analyzer. In these experiments,  $\sim 100$  circulating W of 488 nm (2.540 eV) light from an argon ion laser was used for photodetachment. The electron energy resolution of hemispherical analyzers is constant with electron energy and was 30 meV (FWHM) during these experiments. Photoelectron spectra were calibrated against the well-known spectrum of  $O^-$ . Negative ions were generated by injecting low-energy electrons from a biased filament directly into a continuous supersonic expansion in the presence of a weak, axial magnetic field and a secondary gas “pick-up” line. The diameter of the nozzle used in these experiments was  $\sim 20\ \mu\text{m}$ . The stagnation chamber of the source was heated to  $\sim 80^\circ\text{C}$ , as needed, to obtain a sufficient vapor pressure of aromatic sample, while its total backing pressure was maintained at 4 bar of argon gas. A small flow of  $N_2O$  gas was continuously introduced through the pick-up line to generate  $NO^-$  ions, thereby seeding them into the expansion. The resulting anions were extracted continuously and coaxially.

While the two apparatus used in these experiments differ in several ways, the photoelectron spectra that they are capable of measuring are essentially the same. The main opportunity for differences occurs in their source environments. There, one could imagine that differing source conditions might give rise to different isomers and thus to spectral differences. To check for this possibility, the photoelectron spectrum of both  $O_2^-(\text{benzene})_1$  and  $NO^-(\text{benzene})_1$  were measured on both the Munich and the Hopkins instruments. No significant spectral differences were found, leading us to believe that the two sources provide rather similar anion formation environments.

## III. RESULTS AND ANALYSIS

The seed anions in these experiments were  $NO^-$  or  $O_2^-$ . The photoelectron spectra of  $O_2^-$  and  $NO^-$  are both well known.<sup>27,28</sup> The nitric oxide anion was the first molecular anion to be studied by anion photoelectron spectroscopy, and as such, it has been well characterized. The photoelectron spectrum of  $NO^-$  shows a long progression in the neutral

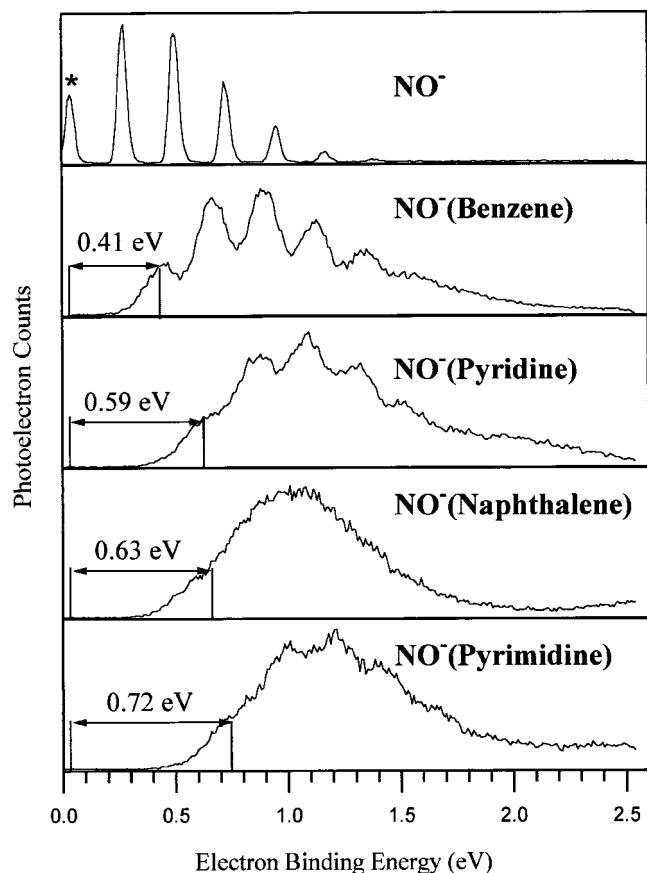


FIG. 1. Photoelectron spectra of  $\text{NO}^-$  and four  $\text{NO}^-$ (aromatic) $_1$  complexes. Spectral shifts from their  $\text{NO}^-$  seed ion are indicated for each complex.

ground-state vibration of  $1895\text{ cm}^{-1}$ . Its intensity pattern indicates a significant geometry difference between the neutral and its anion, i.e.,  $R_c = 1.151\text{ \AA}$  versus  $1.270\text{ \AA}$ , respectively. The lowest EBE peak in the  $\text{NO}^-$  photoelectron spectrum is the origin transition ( $v=0 \leftarrow v=0$ ). Due to vibrational autodetachment, this spectrum exhibits no vibrational hot bands. The adiabatic electron affinity of  $\text{NO}$  is given by the EBE of this peak which, after being corrected for rotational and spin-orbit effects, is  $0.026\text{ eV}$ . The photoelectron spectrum of  $\text{O}_2^-$  shows photodetachment transitions to both the ground state and the first excited ( $a^1\Delta$ ) state of neutral  $\text{O}_2$ . Each of these also shows long vibrational progressions, indicative of significant structural differences between the ground state of  $\text{O}_2^-$  and these two neutral states. In the absence of vibrational hot bands, the lowest EBE peak in the  $\text{O}_2^-$  spectrum is its origin transition, from which the adiabatic electron affinity of  $\text{O}_2$  has been determined to be  $0.451\text{ eV}$ .

Figure 1 presents the photoelectron spectrum of  $\text{NO}^-$  along with the photoelectron spectra of  $\text{NO}^-$  complexed with benzene, pyridine, naphthalene, and pyrimidine, while Fig. 2 presents the spectrum of  $\text{O}_2^-$  along with the spectra of  $\text{O}_2^-$  complexed with benzene, pyridine, and naphthalene. Notice that the spectral envelopes (shapes and widths) of free  $\text{NO}^-$  and  $\text{O}_2^-$ , while shifted to higher EBEs, nevertheless coincide rather well (especially on their low EBE sides) with the spectral profiles of their corresponding anion-neutral complexes. These observations imply that, at least to first order, the excess electrons on the seed anions,  $\text{NO}^-$  and  $\text{O}_2^-$ ,

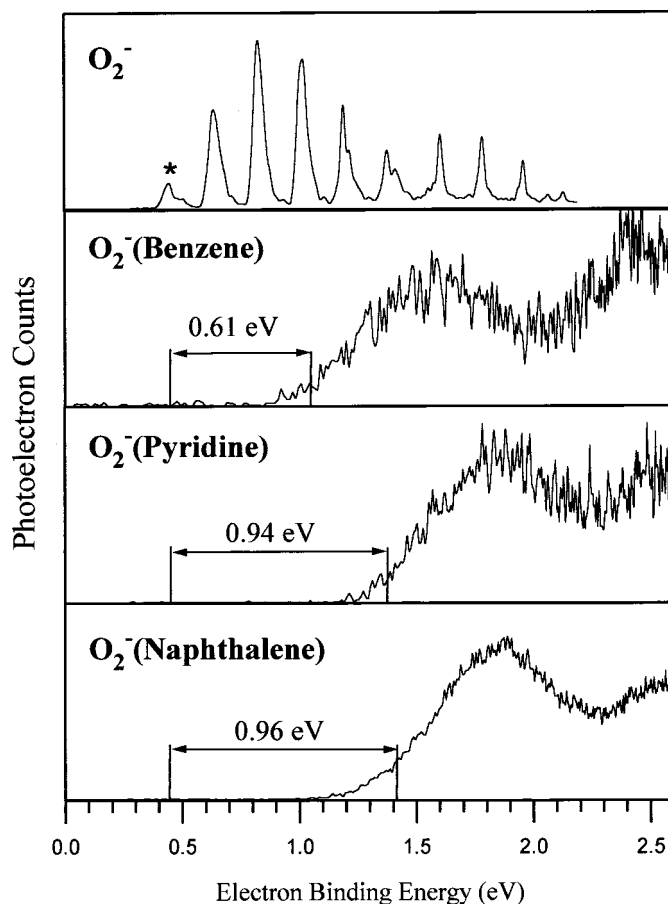


FIG. 2. Photoelectron spectra of  $\text{O}_2^-$  and three  $\text{O}_2^-$ (aromatic) $_1$  complexes. Spectral shifts from their  $\text{O}_2^-$  seed ion are indicated for each complex.

remain localized on them in the anion-molecule complexes studied here. Thus, these complexes are made up of intact seed anions and the neutral aromatic molecules that solvate them, with the seed anions acting as the primary chromophores for photodetachment. Also, notice that in the cases of  $\text{NO}^-$ (benzene) $_1$ ,  $\text{NO}^-$ (pyridine) $_1$ , and to a residual extent, in  $\text{NO}^-$ (pyrimidine) $_1$ , the vibrational structure of the free  $\text{NO}^-$  spectrum, although broadened, is preserved. Notice, on the other hand, that the vibrational structure of the free  $\text{O}_2^-$  spectrum is not preserved in any of the  $\text{O}_2^-$ (aromatic) spectra, showing that there are significant differences in the solvation of  $\text{O}_2^-$  and  $\text{NO}^-$ . We now consider how adiabatic electron affinities, E.A., were determined for the anion complexes studied, and how spectral shifts between E.A.-determining spectral features were used to determine anion-neutral interaction energies.

### A. Electron affinity determinations and solvent-induced spectral shifts

While in vibrationally resolved photoelectron spectra with assigned origin transitions the determination of adiabatic electron affinities is straightforward, this is not the case when the spectra are unresolved. Below, we describe a procedure which allows us to determine adiabatic electron affinities, to a good approximation, for complexes whose anion photoelectron spectra exhibit various degrees of spectral broadening.

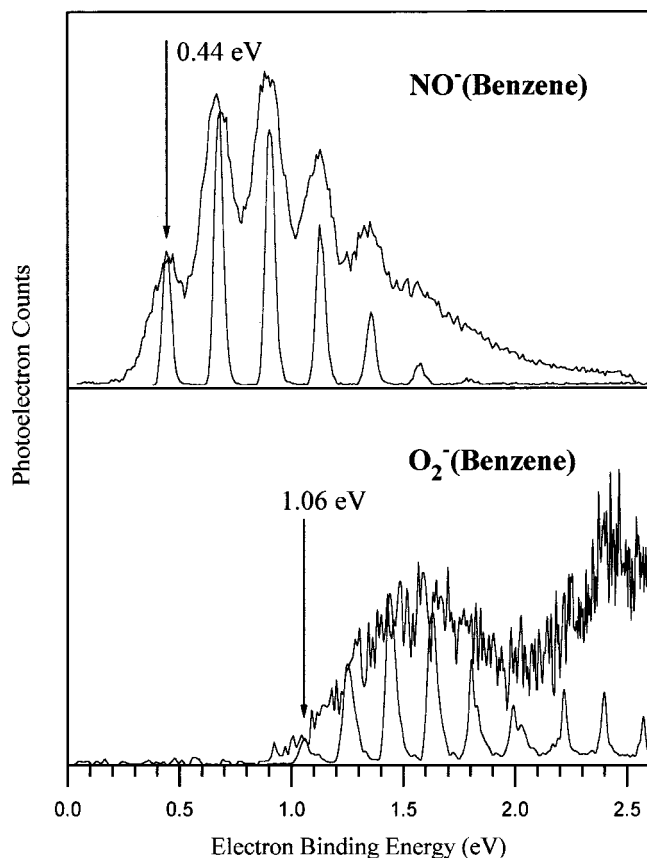


FIG. 3. Comparison of spectral profiles of  $\text{NO}^-$  vs  $\text{NO}^-(\text{benzene})_1$  in the top panel and  $\text{O}_2^-$  vs  $\text{O}_2^-(\text{benzene})_1$  in the bottom panel. The E.A. values of the complexes are indicated on their panels.

Under the assumption of an intact anion chromophore within the anion–molecule complex, one can make the approximation that the E.A. of the complex is the energy difference between the solvent-stabilized (solvated) anion and its solvent-stabilized neutral. This can be accomplished by identifying the spectral origin transition of the free anion within the spectral profile of the corresponding anion–molecule complex and taking the EBE of that point or feature on the complex’s spectrum as the E.A. of the complex. Since the equilibrium structures of the anion–neutral complex and its corresponding neutral–neutral complex may not be the same, the application of this perturbative approximation can lead to an overestimation of the E.A. of a binary complex by an energy that is of the magnitude of the neutral–neutral interaction energy. Most of the complexes studied here are expected to have neutral–neutral interaction energies which are small in comparison with the specific effects observed.

This procedure for determining electron affinities of complexes is illustrated in Fig. 3, where in the top panel the spectrum of free  $\text{NO}^-$  is overlaid onto the spectrum of  $\text{NO}^-(\text{benzene})_1$ , and where in the bottom panel the spectrum of free  $\text{O}_2^-$  is overlaid onto that of  $\text{O}_2^-(\text{benzene})_1$ . In the spectrum of  $\text{NO}^-(\text{benzene})_1$ , its partially resolved vibrational features correspond well, in terms of both spacings and intensities, with those in the spectrum of free  $\text{NO}^-$ . The origin transition in the  $\text{NO}^-$  spectrum is marked in Fig. 1

TABLE I. Electron affinities and spectral shifts for  $\text{O}_2^-$ (aromatic) and  $\text{NO}^-$ (aromatic) complexes. All values in eV.

a)		
$\text{O}_2^-$ (aromatic)	E.A.	Shift relative to $\text{O}_2^-$
$\text{O}_2^-$ (benzene)	1.06	0.61
$\text{O}_2^-$ (pyridine)	1.39	0.94
$\text{O}_2^-$ (pyridine)( $\text{H}_2\text{O}$ )	1.87	1.42
$\text{O}_2^-$ (naphthalene)	1.41	0.96
$\text{O}_2^-$ (naphthalene)( $\text{H}_2\text{O}$ )	2.09	1.64
$\text{O}_2^-$ (naphthalene)( $\text{H}_2\text{O}$ ) <sub>2</sub>	2.72	2.27
b)		
$\text{NO}^-$ (aromatic)	E.A.	Shift relative to $\text{NO}^-$
$\text{NO}^-$ (benzene)	0.44	0.41
$\text{NO}^-$ (benzene) <sub>2</sub>	0.79	0.76
$\text{NO}^-$ (pyridine)	0.62	0.59
$\text{NO}^-$ (naphthalene)	0.66	0.63
$\text{NO}^-$ (naphthalene) <sub>2</sub>	1.06	1.03
$\text{NO}^-$ (pyrimidine)	0.75	0.72

with an asterisk. Because of their matching profiles, one can recognize the same origin transition in the spectrum of  $\text{NO}^-(\text{benzene})_1$ , assign it as such, and determine from it the E.A. of  $\text{NO}^-(\text{benzene})_1$ . This was found to be 0.44 eV, as is indicated in Fig. 3. Thus, the solvent-induced shift between the spectra of  $\text{NO}^-$  and  $\text{NO}^-(\text{benzene})_1$ , i.e., the E.A. difference between  $\text{NO}$  and  $\text{NO}^-(\text{benzene})_1$ , is 0.41 eV. While remnants of free  $\text{O}_2^-$  vibrational structure are not evident in the spectrum of  $\text{O}_2^-(\text{benzene})_1$ , there is nevertheless a good match between the spectral envelopes (shapes and widths) of the lower EBE electronic bands in  $\text{O}_2^-$  and  $\text{O}_2^-(\text{benzene})_1$ . The origin transition in the free  $\text{O}_2^-$  spectrum is marked in Fig. 2 with an asterisk. By aligning the spectrum of  $\text{O}_2^-$  under the spectrum of  $\text{O}_2^-(\text{benzene})_1$  until the best graphical fit is achieved, one can locate the point on the spectral profile of  $\text{O}_2^-(\text{benzene})_1$  that corresponds to its estimated origin transition. The EBE of this location provides the E.A. of  $\text{O}_2^-(\text{benzene})_1$ . This was found to be 1.06 eV, as is indicated on Fig. 3. Thus, the solvent-induced shift between the spectra of  $\text{O}_2^-$  and  $\text{O}_2^-(\text{benzene})_1$ , i.e., the E.A. difference between  $\text{O}_2$  and  $\text{O}_2^-(\text{benzene})_1$ , is 0.61 eV. The ability to match the spectral envelope of the seed anion with that of its corresponding complexes provides a rationale for assigning origin transitions for these complexes and thus for determining electron affinities. All electron affinities and spectral shifts in this work were determined by this procedure. Both quantities are given in Table I. Spectral shifts, relative to their corresponding free seed anion spectrum, are marked in Figs. 1, 2, 4, and 5.

## B. Anion–neutral interaction energy determinations

For anion–molecule complexes,  $\text{X}^-(\text{Y})_n$ , where  $\text{X}^-$  is the seed anion and  $\text{Y}$  is a solvent, the following relationship holds:<sup>26</sup>

$$\begin{aligned} \text{E.A.}_a[\text{X}(\text{Y})_n] - \text{E.A.}_a[\text{X}(\text{Y})_{n-1}] \\ = D_{\text{anion}}[\text{X}^-(\text{Y})_{n-1} - \text{Y}] - D_{\text{neutral}}[\text{X}(\text{Y})_{n-1} - \text{Y}], \quad (2) \end{aligned}$$

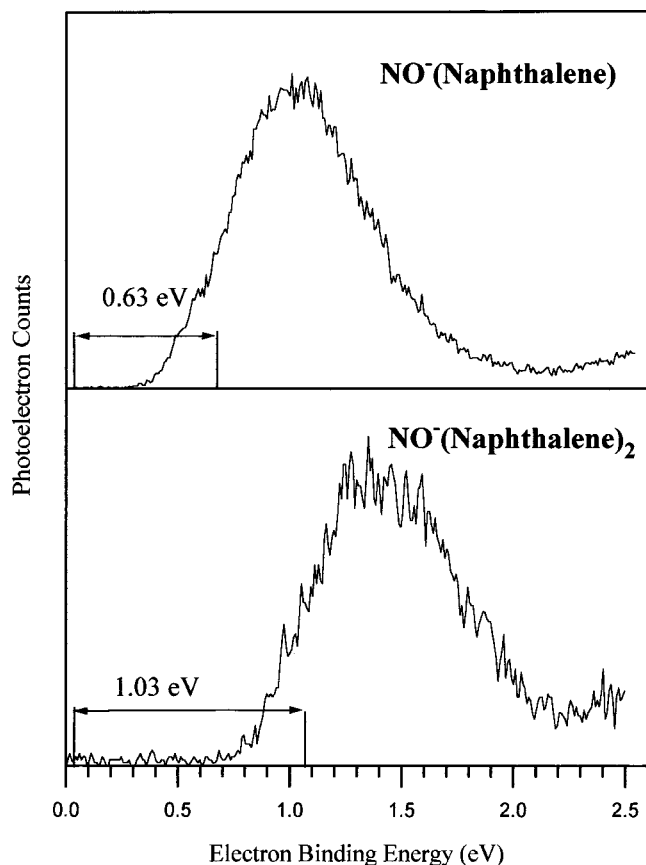


FIG. 4. Photoelectron spectra of  $\text{NO}^-$ (naphthalene)<sub>1</sub> and  $\text{NO}^-$ (naphthalene)<sub>2</sub>. Spectral shifts relative to  $\text{NO}^-$  are indicated for each.

where  $E.A._a[\text{X}(\text{Y})_n]$  and  $E.A._a[\text{X}(\text{Y})_{n-1}]$  denote the adiabatic electron affinities of the  $\text{X}(\text{Y})_n$  and the  $\text{X}(\text{Y})_{n-1}$  clusters.  $D_{\text{anion}}[\text{X}^-(\text{Y})_{n-1}-\text{Y}]$  is the anion dissociation energy for the loss of a single neutral solvent molecule, Y, from  $\text{X}^-(\text{Y})_n$ , and  $D_{\text{neutral}}[\text{X}(\text{Y})_{n-1}-\text{Y}]$  is the weak-bond, neutral-neutral dissociation energy for the loss of a single solvent molecule, Y, from  $\text{X}(\text{Y})_n$ . Especially pertinent here is the case where  $n=1$ . Under these circumstances, the above relationship becomes

$$E.A._a[\text{X}(\text{Y})_1] - E.A._a[\text{X}] = D_{\text{anion}}[\text{X}^- - \text{Y}] - D_{\text{neutral}}[\text{X} - \text{Y}], \quad (3)$$

where the difference between electron affinities is the spectral shift described above. Since anion dissociation energies are usually somewhat larger than weak-bond, neutral-neutral interaction energies, the following approximation can often be applied:

$$E.A._a[\text{X}(\text{Y})_1] - E.A._a[\text{X}] \approx D_{\text{anion}}[\text{X}^- - \text{Y}]. \quad (4)$$

This gives an estimate of  $D_{\text{anion}}[\text{X}^- - \text{Y}]$ , which is also the interaction energy between the anion,  $\text{X}^-$  and its neutral solvent molecule, Y. The assumption that the neutral binding energy is small is valid to a good approximation for the complexes investigated here. For example, the  $\text{O}_2^-$ -benzene (neutral-neutral) dissociation energy is known to be about 0.05 eV.<sup>29-31</sup> This value can be neglected in comparison with the magnitudes of the spectral shifts (E.A. differences) encountered here. Also, while NO has a dipole moment, it is

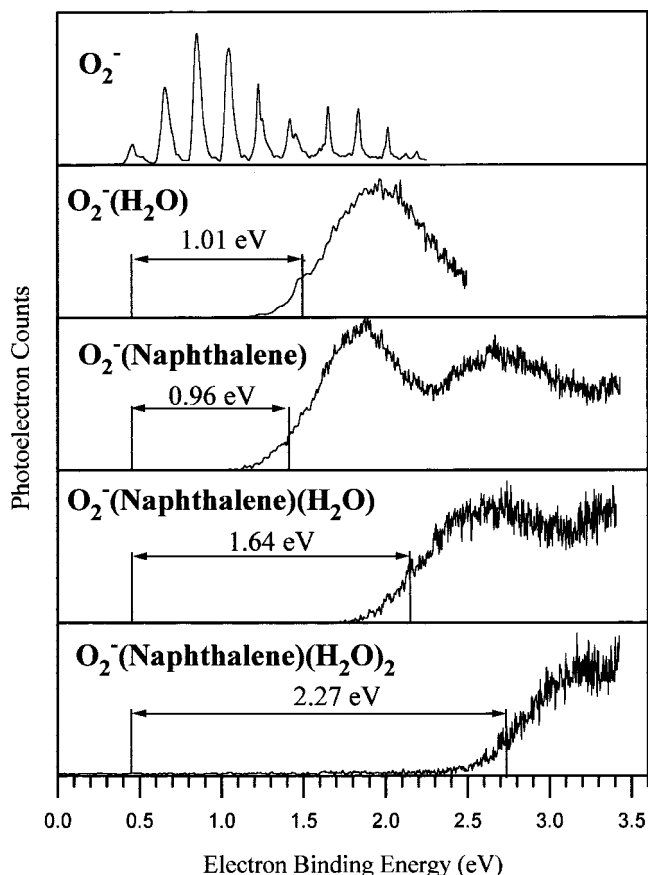


FIG. 5. Photoelectron spectra of  $\text{O}_2^-$ ,  $\text{O}_2^-$ ( $\text{H}_2\text{O}$ ),  $\text{O}_2^-$ (naphthalene),  $\text{O}_2^-$ (naphthalene)( $\text{H}_2\text{O}$ )<sub>1</sub> and  $\text{O}_2^-$ (naphthalene)( $\text{H}_2\text{O}$ )<sub>2</sub>, along with their spectral shifts from their seed anion,  $\text{O}_2^-$ .

quite small ( $\mu=0.159$  D), and the same conclusion for neutral NO/neutral aromatic complexes is also likely to be valid. Furthermore, the E.A. value extracted from the spectrum of a given binary anion-molecule complex is likely, as was pointed out above, to overestimate the actual E.A. by an amount on the order of  $D_{\text{neutral}}[\text{X}-\text{Y}]$ , improving Eq. (4) as an approximation still further. Thus, for each of the  $\text{O}_2^-$ (aromatic)<sub>1</sub> and  $\text{NO}^-$ (aromatic)<sub>1</sub> photoelectron spectra studied here, the vast majority of the observed spectral shift is due to the attractive interaction between the anion and the aromatic molecule. Therefore, equating the observed spectral shift to  $D_{\text{anion}}[\text{X}^- - \text{Y}]$  is a reasonable approximation. The spectral shifts shown in Table I for binary complexes are therefore also anion-neutral interaction energies.

When the complex contains more than two components, and the observed spectral shift is measured relative to the spectrum of the free seed anion, the following energetic relationship holds:<sup>26</sup>

$$E.A._a[\text{X}(\text{Y})_n] - E.A._a[\text{X}] = \sum_{m=0}^{n-1} D_{\text{anion}}[\text{X}^-(\text{Y})_m - \text{Y}] - \sum_{m=0}^{n-1} D_{\text{neutral}}[\text{X}(\text{Y})_m - \text{Y}]. \quad (5)$$

For those anion-neutral complexes, the spectral shifts are due to the sum of the individual anion-neutral interaction

energies minus the sum of the individual neutral–neutral interaction energies. Again, if the latter can be neglected, the spectral shift is predominantly due to the anion–neutral interaction energies present. In the case of complexes where water is a component, however, this approximation is weakened due to the strength of hydrogen bonding. In addition to spectral shifts for binary anion–molecule complexes, Table I also lists spectral shifts for multicomponent complexes referenced to the spectra of their free seed anion.

### C. Specific observations

In Fig. 1, one observes that  $\text{NO}^-(\text{aromatic})_1$  interaction strengths (spectral shifts relative to the spectrum of free  $\text{NO}^-$ ) increase in the order,  $\text{NO}^-(\text{benzene})_1$ ,  $\text{NO}^-(\text{pyridine})_1$ ,  $\text{NO}^-(\text{naphthalene})_1$ ,  $\text{NO}^-(\text{pyrimidine})_1$ , i.e., by 0.41, 0.59, 0.63, 0.72 eV, respectively. Likewise, in Fig. 2, one notices that  $\text{O}_2^-(\text{aromatic})_1$  interaction strengths (spectral shifts relative to the spectrum of free  $\text{O}_2^-$ ) increase in the order,  $\text{O}_2^-(\text{benzene})_1$ ,  $\text{O}_2^-(\text{pyridine})_1$ , and  $\text{O}_2^-(\text{naphthalene})_1$ , i.e., by 0.61, 0.94, and 0.96 eV, respectively. Interaction strengths evidently increase in going from benzene to pyridine to naphthalene, whether the seed anion is  $\text{O}_2^-$  or  $\text{NO}^-$ . Also, in comparing the spectra of  $\text{NO}^-(\text{aromatic})_1$  with those of  $\text{O}_2^-(\text{aromatic})_1$ , one notices that the spectral shift observed for each  $\text{O}_2^-(\text{aromatic})_1$  is larger than the spectral shift seen for its corresponding  $\text{NO}^-(\text{aromatic})_1$  complex. Interestingly, there is a persistent 3:2 ratio between them. Thus, despite similarities between  $\text{O}_2^-$  and  $\text{NO}^-$ , it is clear that these two diatomic anions behave differently when solvated by aromatic molecules.

Another important observation can also be made from a comparison of Figs. 1 and 2. Spectral broadening, as measured by the degree of loss of seed anion vibrational structure, is correlated with increasing interaction strengths, as measured by spectral shifts. This is seen by comparing corresponding spectra of  $\text{NO}^-(\text{aromatic})_1$  and  $\text{O}_2^-(\text{aromatic})_1$ , where the  $\text{NO}^-(\text{aromatic})_1$  complexes, which exhibit smaller interaction strengths than the  $\text{O}_2^-(\text{aromatic})_1$  complexes, retain some free  $\text{NO}^-$  vibrational structure in most cases, while all  $\text{O}_2^-(\text{aromatic})_1$  complexes studied here have lost their free  $\text{O}_2^-$  vibrational structure. This same correlation can be seen by comparing the spectra of  $\text{NO}^-(\text{N}_2\text{O})_1$  and  $\text{NO}^-(\text{H}_2\text{O})_1$ , both recorded in previous studies.<sup>26,32</sup> [In the present study, the only exception to this correlation appears to be the comparison between  $\text{NO}^-(\text{naphthalene})_1$  and  $\text{NO}^-(\text{pyrimidine})_1$ .] The spectral broadening of the photoelectron structures is caused by progressions of low-frequency intermolecular vibrations which are not resolved in our machines. They superimpose the intramolecular vibrational transitions leading to a broad envelope. The correlation observed here points to a decreasing intermolecular Franck–Condon overlap with increasing anion–neutral interaction (coupling) strength.

Interesting observations may also be made about multicomponent anion–molecule complexes. Consider, for example, the trimer anion made up of one NO molecule, two naphthalene molecules, and an excess electron. In principle, it could be  $\text{NO}^-(\text{naphthalene})_2$ ,  $\text{NO}(\text{naphthalene})_2^-$ , or

$(\text{naphthalene})^-\text{NO}(\text{naphthalene})$ . The dimer anion,  $(\text{naphthalene})_2^-$  is known,<sup>33</sup> and the monomer anion,  $(\text{naphthalene})^-$  can be stabilized by solvation.<sup>2,3</sup> The electron affinities of their corresponding neutrals, however, are +0.11 and –0.18 eV, respectively. Thus, both the second and third possibilities above are quite unlikely, since their solvent(s) would not be able to shift their seed anion electron binding energies to the relatively large energy at which it is actually observed (see below). The trimer anion in question is therefore  $\text{NO}^-(\text{naphthalene})_2$ .

Figure 4 compares the spectra of  $\text{NO}^-(\text{naphthalene})_1$  and  $\text{NO}^-(\text{naphthalene})_2$ . Whereas the solvent shift for  $\text{NO}^-(\text{naphthalene})_1$  is 0.63 eV, the solvent shift for  $\text{NO}^-(\text{naphthalene})_2$ , relative to  $\text{NO}^-$ , is 1.03 eV, and this is significantly less than two times 0.63 eV. This is a nonadditive effect; each successive solvent stabilizes the cluster anion against electron loss less than the one before it, i.e., sequential interaction (solvation) energies tend to decrease with cluster size. To one extent or another, this nonadditive effect usually occurs in ion solvation. For comparison, solvation of  $\text{NO}^-$  by one water molecule shifts the E.A. by 0.72 eV, while solvation by a second water molecule shifts it by an additional 0.68 eV.<sup>32</sup> In this particular case, the non-additive effect is much less drastic than in  $\text{NO}^-(\text{naphthalene})_{1,2}$ , even though it is still apparent. In most instances, sequential shift, nonadditivity is probably due to a reduction in the available electrostatic interaction with the seed anion as subsequent solvents are added. At a rudimentary level, this can be envisioned either in terms of a partial cancellation of the charge on the seed anion by the partial (opposite) charges of nearby solvent(s) [present due to either a permanent or an induced charge asymmetry] or by partial charge transfer to the solvent(s). In either case, the more solvents are attached, the less effective charge is left localized on the anion seed. Of course, once a solvation shell is filled, dielectric shielding further reduces the available electrostatic interaction between the seed anion and additional solvents, but this effect is not in play here, where only small numbers of solvents are being considered.

Next, consider the multicomponent anion–molecule complexes,  $\text{O}_2^-(\text{naphthalene})_1(\text{H}_2\text{O})_1$ , and  $\text{O}_2^-(\text{naphthalene})_1(\text{H}_2\text{O})_2$ . The excess electrons on these anion complexes are no doubt located as indicated by the formulas,  $\text{O}_2^-(\text{naphthalene})_1(\text{H}_2\text{O})_1$ , and  $\text{O}_2^-(\text{naphthalene})_1(\text{H}_2\text{O})_2$ . While the species,  $(\text{H}_2\text{O})_2^-$ ,  $(\text{naphthalene})^-(\text{H}_2\text{O})_1$ , and  $(\text{naphthalene})^-(\text{H}_2\text{O})_2$  are known,<sup>2,3,34</sup> the electron affinities of their corresponding neutrals are again much too small to permit them to be shifted by their putative solvent(s) to the electron binding energies at which  $\text{O}_2^-(\text{naphthalene})_1(\text{H}_2\text{O})_1$  and  $\text{O}_2^-(\text{naphthalene})_1(\text{H}_2\text{O})_2$  are actually observed spectroscopically (see Table Ia and Fig. 5). Hence, the surplus charge is on the  $\text{O}_2^-$  moiety, while water and naphthalene act as solvents.

Figure 5 compares the spectra of  $\text{O}_2^-$ ,  $\text{O}_2^-(\text{H}_2\text{O})_1$ ,  $\text{O}_2^-(\text{naphthalene})_1$ ,  $\text{O}_2^-(\text{naphthalene})_1(\text{H}_2\text{O})_1$ , and  $\text{O}_2^-(\text{naphthalene})_1(\text{H}_2\text{O})_2$ . The origin transition in the spectrum of  $\text{O}_2^-(\text{H}_2\text{O})_1$  is shifted relative to the origin in the spectrum of bare  $\text{O}_2^-$  by 1.01 eV.<sup>35</sup> The water– $\text{O}_2^-$  interaction

is quite strong, and it has been interpreted by Weber and Johnson in terms of the interaction of the  $\pi^*$  orbital of  $O_2^-$  with  $H_2O$ .<sup>35</sup> Interestingly, the spectral shift of  $O_2^-$  interacting with a single water molecule is similar in magnitude to the spectral shift of  $O_2^-$  interacting with a single naphthalene molecule (0.96 eV). However, when a water molecule is added to  $O_2^-$ (naphthalene)<sub>1</sub> to form  $O_2^-$ (naphthalene)<sub>1</sub>( $H_2O$ )<sub>1</sub>, the incremental shift due to the added water molecule is only 0.68 eV, which is considerably less than the interaction energy between bare  $O_2^-$  and a water molecule. This is another example of a strongly nonadditive, ion solvation effect. On the other hand, when still another water molecule is added to form  $O_2^-$ (naphthalene)<sub>1</sub>( $H_2O$ )<sub>2</sub>, the sequential shift is 0.63 eV, which, while nonadditive, is only slightly less than the 0.68 eV observed for the first water. Perhaps, this means that the second water molecule has geometric access to the seed anion in a way that is similar to that enjoyed by the first water molecule. While the spectra presented here may well be signatures of specific cluster structures, it does not follow that we can determine them directly from such spectra, and absent theoretical support beyond binary complexes, we resist the temptation to speculate further about their structures.

#### IV. DISCUSSION

While using our data to shed light on the structures of these anion–molecule complexes may be out of reach, making a contribution toward elucidating the nature of their interactions may not. For this purpose, we focus on the binary anion–molecule complexes that we have studied, considering both electrostatic and chemical aspects of their binding. Obvious interactions which may be responsible for anion–neutral binding include ion–dipole, ion–quadrupole, ion-induced dipole (polarizability) interactions as well as covalent bonding. Because anion–dipole interactions can be expected to be significant, we will separate our discussion of specific solvents according to whether or not they have a permanent dipole moment. Then, we will ponder the role of seed anion electronic structure in understanding why the interactions are as strong as they are, and why the binding is different between  $NO^-$  and  $O_2^-$  complexed with the same aromatic molecule.

##### A. Nonpolar solvent interactions

The two nonpolar solvents that we utilized in this work are benzene and naphthalene. In binary complexes of these solvents with  $NO^-$  and  $O_2^-$ , one observes that the interaction energy between  $NO^-$  and naphthalene is greater than the interaction energy between  $NO^-$  and benzene, and that the interaction energy between  $O_2^-$  and naphthalene is greater than the interaction energy between  $O_2^-$  and benzene. For a given seed anion, the larger aromatic solvent has the higher interaction strength. Qualitatively, this suggests that the polarizabilities of these aromatic solvents may play a role in the strength of these interactions. To explore this further, we plot, in Fig. 6, various binary anion–neutral interaction strengths (spectral shifts) versus the polarizabilities of their solvents. Benchmarks at small polarizabilities are provided

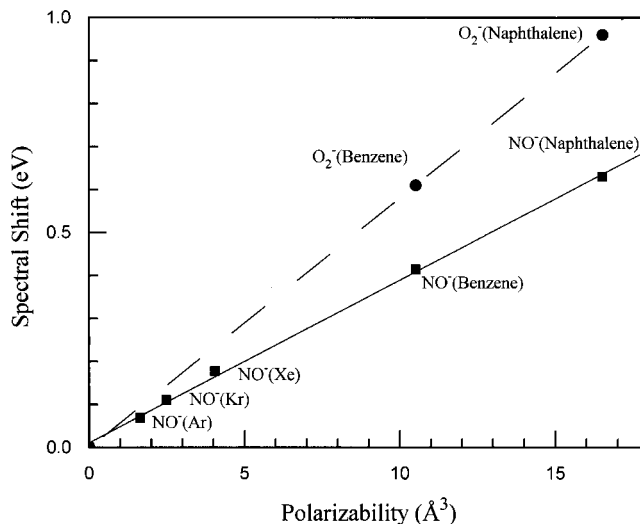


FIG. 6. A plot of spectral shifts vs solvent polarizabilities for selected  $O_2^-$  and  $NO^-$  complexes.

by the photoelectron spectral shifts of  $NO^-(Ar)_1$ ,  $NO^-(Kr)_1$ , and  $NO^-(Xe)_1$ .<sup>36</sup> Interestingly, linear dependences with polarizability are found for each seed anion, confirming the important role of polarizability in these interactions. Of just as much interest, however, is the fact that their slopes are different. Given that the seed anions,  $O_2^-$  and  $NO^-$ , are of similar size and that the dipole moment of  $NO^-$  is probably of little consequence, a linear dependence on polarizability with a single slope would be expected in a purely electrostatic interaction. The fact that the dependence is linear in each case but that the slopes are different implies that the interaction is not only electrostatic. The chemical identities of the two seed anions count; they are interacting with the aromatic molecules differently.

Theoretical calculations by Jalbout and Adamowicz on the  $O_2^-$ (benzene)<sub>1</sub> anion–aromatic molecule complex provide important insights into the structures of anion–aromatic molecule complexes and the nature of their interactions (see Paper II). Their calculations find a planar structure for the  $O_2^-$ (benzene)<sub>1</sub> complex, with the anion avoiding direct interaction with the  $\pi$ -cloud of benzene. Specifically, they find the axis of the  $O_2^-$  molecular anion to be oriented alongside the benzene molecule so as to maximize interaction between its two oxygen atoms and two of the hydrogen atoms on the perimeter of the benzene ring, i.e., it is predicted to be a side-by-side structure with two contact sites. Important insight was also gained regarding the nature of the interaction. While they found the charge-induced dipole interaction to be the dominant binding mechanism, their analysis of the  $O_2^-$ (benzene)<sub>1</sub> wave function also showed significant delocalization of the excess electron onto the  $\sigma$  electron region of the benzene. They further commented that these features are also likely to appear in other complexes involving small covalent anions interacting with aromatic molecules. In addition, we note that their results may carry over into the structures of multicomponent complexes, such as  $O_2^-$ (benzene)<sub>2</sub>, where one might expect a planar, two-sided structure, viz. (benzene) $O_2^-$ (benzene) in analogy to  $O_2^-$ ( $H_2O$ )<sub>n</sub> clusters.<sup>35</sup>

## B. Polar solvent interactions

The two polar, aromatic solvents that we utilized in this work are pyridine and pyrimidine. Both have comparable and relatively large dipole moments, at  $\mu=2.2$  D for pyridine and  $\mu=2.3$  D for pyrimidine, and thus, one would expect anion–dipole interactions to play a major role in governing the magnitudes of interaction strengths. Against the backdrop of this electrostatic expectation, several observations can be made. The spectral shift exhibited by  $\text{NO}^-$ (pyrimidine)<sub>1</sub> is significantly greater than that exhibited by  $\text{NO}^-$ (pyridine)<sub>1</sub>, while the dipole moment of pyrimidine is only slightly greater than that of pyridine. The spectral shift exhibited by  $\text{O}_2^-$ (pyridine)<sub>1</sub> is slightly smaller than that exhibited by  $\text{O}_2^-$ (H<sub>2</sub>O)<sub>1</sub>, even though pyridine has a somewhat larger dipole moment than water ( $\mu=1.84$  D). Likewise, the spectral shift exhibited by  $\text{NO}^-$ (pyridine)<sub>1</sub> is significantly smaller than that exhibited by  $\text{NO}^-$ (H<sub>2</sub>O)<sub>1</sub> [cf. 0.72 eV],<sup>32</sup> despite the ratio of the dipole moments of their solvents. Most striking of all, however, are the observations that the spectral shift of  $\text{O}_2^-$ (pyridine)<sub>1</sub> is very similar to that of  $\text{O}_2^-$ (naphthalene)<sub>1</sub>, and that the spectral shifts of  $\text{NO}^-$ (pyridine)<sub>1</sub> and  $\text{NO}^-$ (pyrimidine)<sub>1</sub> bracket the spectral shift value of  $\text{NO}^-$ (naphthalene)<sub>1</sub>, even though naphthalene has no dipole moment. Thus, while anion–dipole interactions are probably important, clearly they alone do not govern the magnitudes of the interaction strengths measured in these experiments. These observations provide additional evidence implicating an important role for covalency in anion–aromatic molecule interactions. Covalency, in fact, appears to be a significant part of the reason for the unexpected strength of small anion–aromatic molecule interactions.

## C. The role of the electronic structures of $\text{O}_2^-$ and $\text{NO}^-$

There are two major observations emerging from this work. They are (1) the interactions between the small anions and aromatic molecules studied here are unexpectedly strong, and (2) when  $\text{O}_2^-$  interacts with an aromatic molecule and  $\text{NO}^-$  interacts with the same aromatic molecule, their interaction strengths differ substantially, with the former being the larger.

Consider observation (1). Both  $\text{O}_2^-$  and  $\text{NO}^-$  are open-shell anions, and all of the aromatic molecules studied here are closed shells. To empirically investigate the effect of an open-shell anion on the interaction strengths of anion–aromatic complexes, it would be useful to compare them with closed-shell anion/aromatic interaction strengths. To our knowledge, the only example of a closed-shell anion/aromatic complex to have been studied is  $\text{Cl}^-$ (anthracene)<sub>1</sub>.<sup>37</sup> While anthracene has a positive E.A. (0.53 eV), the much larger E.A. of the chlorine atom (3.6 eV) essentially guarantees that  $\text{Cl}^-$  will be the anion seed in this complex, confirming its proper description as  $\text{Cl}^-$ (anthracene)<sub>1</sub>. The spectral shift between the photoelectron spectrum of  $\text{Cl}^-$  and that of  $\text{Cl}^-$ (anthracene)<sub>1</sub> is 0.4 eV, making this a good approximation to the interaction energy between the closed-shell anion,  $\text{Cl}^-$  and anthracene. At first glance, this interaction energy seems comparable to that of

complexes we have studied here, e.g., it was 0.44 eV in  $\text{NO}^-$ (benzene)<sub>1</sub>. This, however, is not a fair comparison, because the spectral shifts of both  $\text{O}_2^-$ (aromatic)<sub>1</sub> and  $\text{NO}^-$ (aromatic)<sub>1</sub> complexes increase significantly with the size and polarizability of a given aromatic. Anthracene is larger than any aromatic molecule utilized in our study, and yet the  $\text{Cl}^-$ /anthracene interaction energy remains modest in comparison to the other complexes studied here. This suggests that the relatively high interaction strengths seen in this work are in part due to  $\text{O}_2^-$  and  $\text{NO}^-$  being open-shell anions. For  $\text{O}_2^-$  solvated by H<sub>2</sub>O, covalent binding to the partially occupied  $\pi^*$  orbital has, in fact, been observed.<sup>35</sup>

Next, consider observation (2). The key to understanding the differences in the binding of  $\text{O}_2^-$ (aromatic) versus  $\text{NO}^-$ (aromatic) complexes must reside in the differences between the electronic structures of the two seed anions and how these impact the covalent bonding contribution in each case. Hence, one should consider their molecular orbitals and their electron occupations. The electron configuration of ground state  $\text{O}_2^-$  is  $\dots\sigma^2\pi^4\pi^{*3}$ , while that of ground state  $\text{NO}^-$  is  $\dots\pi^4\sigma^2\pi^{*2}$ . (Note the difference in the number of electrons in the  $\pi^*$  orbital in each case and the reversal in energy ordering between the  $\sigma$  and  $\pi$  orbitals in each anion.) As consequences of these electron configurations, the ground states of  $\text{O}_2^-$  and  $\text{NO}^-$  are thus  $^2\Pi$  and  $^3\Sigma$  states, respectively, while the ground states of  $\text{O}_2$  and  $\text{NO}$  are  $^3\Sigma_g^-$  and  $^2\Pi$  states, respectively. Again, because of differing electron configurations, the roles of  $^2\Pi$  and  $^3\Sigma$  states in the anions and their corresponding neutrals are exchanged in these systems.

The most obvious qualitative difference between the electronic structures of  $\text{O}_2^-$  and  $\text{NO}^-$  are the numbers of electrons in their  $\pi^*$  orbitals, i.e., 3 versus 2, respectively. Curiously, this corresponds to the persistently observed 3:2 ratio in  $\text{O}_2^-$ (aromatic)<sub>1</sub> versus  $\text{NO}^-$ (aromatic)<sub>1</sub> spectral shifts that we described above. The question is whether this is accidental or a clue to the interplay between the electronic structures of these seed anions and the binding of their anion–aromatic molecule complexes. Unfortunately, our experimental results alone are insufficient to answer this question. The accompanying paper by Jalbout and Adamowicz (paper II) is the beginning of a partnership with theory, which we hope will address this question.

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