

### Benzonitrile: Electron affinity, excited states, and anion solvation

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We report a negative-ion photoelectron imaging study of benzonitrile and several of its hydrated, oxygenated, and homo-molecularly solvated cluster anions. The photodetachment from the unsolvated benzonitrile anion to the  $\tilde{X}^{1}A_{1}$  state of the neutral peaks at 58 ± 5 meV. This value is assigned as the vertical detachment energy (VDE) of the valence anion and the upper bound of adiabatic electron affinity (EA) of benzonitrile. The EA of the lowest excited electronic state of benzonitrile,  $\tilde{a}^{3}A_{1}$ , is determined as 3.41 ± 0.01 eV, corresponding to a 3.35 eV lower bound for the singlet-triplet splitting. The next excited state, the open-shell singlet  $\tilde{A}^{1}A_{1}$ , is found about an electron-volt above the triplet, with a VDE of  $4.45 \pm 0.01$  eV. These results are in good agreement with *ab initio* calculations for neutral benzonitrile and its valence anion but do not preclude the existence of a dipole-bound state of similar energy and geometry. The step-wise and cumulative solvation energies of benzonitrile anions by several types of species were determined, including homo-molecular solvation by benzonitrile, hydration by 1-3 waters, oxygenation by 1-3 oxygen molecules, and mixed solvation by various combinations of O<sub>2</sub>, H<sub>2</sub>O, and benzonitrile. The plausible structures of the dimer anion of benzonitrile were examined using density functional theory and compared to the experimental observations. It is predicted that the dimer anion favors a stacked geometry capitalizing on the  $\pi$ - $\pi$  interactions between the two partially charged benzonitrile moieties. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4931985]

#### I. INTRODUCTION

Benzonitrile (cyanobenzene) is the precursor molecule for numerous cyano-aromatic functionalities, which are of interest for their electronic properties and associated reactivity. In particular, they are often involved in intramolecular chargetransfer processes as electron acceptor moieties.<sup>1,2</sup> Benzonitrile ( $C_5H_5CN$ ), on the other hand, has been shown to act a donor in intermolecular charge-transfer transitions.<sup>3</sup>

Many conjugated molecules containing CN functional groups have been investigated as electron-transport systems.<sup>4–6</sup> Among them, benzonitrile has also been studied as a charge-transfer agent on carbon nano-tubes doped with transition metals, where the aromatic ring coordinates with the metal atom.<sup>7</sup> It is also known to form ordered surfaces on metals. Due to its bi-functionality, it can interact with surfaces both with the CN lone pair and the  $\pi$ -conjugated ring.<sup>8–10</sup> This makes it an appealing target for surface chemistry, functionalization, and molecular sensor design.

The chemistry of cyano-containing organics is also under investigation in the Titan atmosphere, where both benzene and HCN have been detected.<sup>11</sup> Under temperature conditions matching those on Titan, the formation of benzonitrile from these precursors proceeds rapidly and essentially to completion and has been predicted to occur even at temperatures of interstellar clouds.<sup>11,12</sup>

Despite the importance and relevance of benzonitrile, much remains unknown about its most essential properties. Electron affinity (EA) is of utmost importance for electron transfer, particularly for the function of electron acceptors. To this end, even the nature of the anion of benzonitrile is still unclear. Given its large dipole moment (>4 D),<sup>13</sup> the benzonitrile molecule is expected to support a dipole-bound anion<sup>14,15</sup> state, but valence anion states are possible as well. Measurements of electron affinity are the best way to shed light on this issue, but the most recent experimental determination of this property of benzonitrile dates back to 1983. In that work, using electron capture detection, the EA was determined—indirectly—to be  $0.26 \pm 0.10 \text{ eV}$ .<sup>16</sup> Despite the larger uncertainty, this result was in agreement with the 1975 also indirect measurement of EA =  $0.256 \pm 0.017 \text{ eV}^{17}$  and with the subsequent 1992 work that concluded the ground-state anion of benzonitrile was not observable by electron transmission spectroscopy, because it was "bound by a few tenths of an electron-volt."<sup>18</sup>

No direct spectroscopic determination of the EA of benzonitrile exists to this day and only limited details are known about the electronic structure and its effects on fluorescence and charge transfer.<sup>19</sup> An excited singlet state of benzonitrile was found 4.5 eV above the ground state and has been well studied.<sup>20,21</sup> A nearby dark state was suggested by an electricfield induced perturbation study, with some restrictions on its symmetry inferred indirectly.<sup>22</sup> However, this state has not been observed spectroscopically.

We report a photoelectron imaging study of the benzonitrile anion and its clusters with water,  $O_2$ , and additional benzonitrile moieties. The detachment energy to the ground state of the neutral as well as the adiabatic EA of the two lowest-lying excited states is determined from the photoelectron spectra. In addition, we report solvation energies for several solvent molecules and several states of benzonitrile and

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propose possible structures for the benzonitrile dimer anion which are consistent with the observed spectra.

#### **II. EXPERIMENTAL AND THEORETICAL METHODS**

Anion photoelectron imaging experiments were performed using the custom-built instrument described in detail elsewhere.<sup>23</sup> In short, benzonitrile vapor was seeded in argon by passing the carrier gas over a liquid sample kept at room temperature. The resulting mixture was expanded into the high-vacuum chamber through a pulsed supersonic nozzle (General Valve, Inc., Series 99). The expansion was crossed at a right angle by a 1 keV electron beam. Anions were formed in the resulting plasma via slow secondary electron attachment to neutral molecules and clusters.<sup>24</sup> The anions were then extracted into the Wiley-McLaren mass-spectrometer and separated according to their m/z ratios. Anions of selected mass were irradiated with pulsed linearly-polarized light, produced by a Spectra Physics LAB-130-50 Nd:YAG laser. The fundamental, frequency-doubled, tripled, or quadrupled output was used as the source of 1064, 532, 355, or 266 nm radiation, respectively. The ion and laser beams intersected at 90° within the velocity-map<sup>25</sup> photoelectron imaging<sup>26,27</sup> assembly.

The photodetached electrons were projected electrostatically in the direction perpendicular to both the light and ion beams, toward a 40 mm position-sensitive dual microchannel plate detector coupled to a P43 phosphorous screen (Burle, Inc.). Positions of electron impacts on the detector were recorded by a thermoelectrically cooled charge-coupled device camera (CoolSNAP Myo, Photometrics, Inc.). Images were typically collected for  $\sim 10^5 - 10^6$  experimental cycles and were analyzed by reconstructing the original 3D-electron distribution via the inverse Abel transformation<sup>26</sup> implemented in the BASEX software.<sup>28</sup> The resulting radial distributions were converted to photoelectron spectra using the well-known O<sup>-</sup> photodetachment transitions for calibration.<sup>29,30</sup> All spectra presented in this work are plotted with respect to electron binding energy (eBE), calculated as eBE = hv - eKE, where eKE is electron kinetic energy.

Electronic structure calculations were carried out using the Q-Chem 4.0<sup>31</sup> and Gaussian 09<sup>32</sup> software packages. Q-Chem was used for geometry optimizations of benzonitrile and it anion at the couple-cluster theory level with single and double excitations (CCSD) and the augmented Dunning's correlation-consistent basis set of double- $\zeta$  quality (aug-ccpVDZ). The optimized structure of the anion was used for calculations of electron detachment energies using the equation-of-motion ionization-potential methodology combined with coupled-cluster theory (EOM-IP-CCSD).<sup>33</sup> In the Franck-Condon (FC) simulation of the photoelectron spectrum of bn<sup>-</sup>, vibrational modes were treated as independent harmonic oscillators with Duschinky rotations as implemented in the PESCAL 2010 program.<sup>34</sup> Calculations on cluster anions were performed with the Gaussian 09 software. Geometry optimizations for the anion and neutral species employed the M06-2X density functional. EAs were calculated as the difference in electronic energy (no ZPE correction) for the anion and neutral species calculated at the respective optimized geometries. Vertical detachment energies (VDEs)

were calculated as the difference in electronic energy (no ZPE correction) for the anion and neutral species, both calculated at the anion geometry.

#### **III. RESULTS**

Several types of anionic species containing benzonitrile (bn) were studied in this work: the unsolvated bn<sup>-</sup> anions; the hydrated cluster anions of benzonitrile bn<sup>-</sup>(H<sub>2</sub>O)<sub>n</sub>, n = 1-3; the oxygenated cluster anions bn<sup>-</sup>(O<sub>2</sub>)<sub>n</sub>, n = 1-3; the mixed hydrated-oxygenated cluster anions bn<sup>-</sup>(H<sub>2</sub>O)<sub>n</sub>(O<sub>2</sub>), n = 1-2; the homo-molecularly solvated cluster anions (bn)<sub>n</sub><sup>-</sup>, n = 2-4; and the corresponding mono-hydrated and mono-oxygenated species (bn)<sub>n</sub><sup>-</sup>(H<sub>2</sub>O), n = 2-3 and (bn)<sub>n</sub><sup>-</sup>(O<sub>2</sub>), n = 2-3.

#### A. Benzonitrile anion

The photoelectron images and corresponding spectra for the unsolvated benzonitrile anion, bn<sup>-</sup>, recorded at 1064, 532, 355, and 266 nm, are presented in Figures 1(a)-1(d), respectively. Band A, appearing in all spectra, corresponds to the lowest-energy photodetachment transition. Assignment of this band requires the knowledge of the nature of the anion state. For reasons discussed in Section IV, it is assigned as the  $\tilde{X}^2B_1 \rightarrow \tilde{X}^1A_1$  photodetachment transition of the valence



FIG. 1. Photoelectron images and spectra of the benzonitrile anion (bn<sup>-</sup>) at (a) 1064 nm; (b) 532 nm; (c) 355 nm; (d) 266 nm. Bands A–C are assigned as transitions to the  $\tilde{X}$ <sup>1</sup>A<sub>1</sub>,  $\tilde{a}$ <sup>3</sup>A<sub>1</sub>, and  $\tilde{A}$ <sup>1</sup>A<sub>1</sub> states of neutral bn, respectively. Band D is autodetachment. The direction of laser polarization is indicated by the double-sided arrow in (a).

anion of benzonitrile. We will refer to the  $\tilde{X}$  <sup>1</sup>A<sub>1</sub> ground state of neutral bn, for brevity, as "the singlet." Band D, which corresponds to the electron counts appearing near the 1064 nm image center, is attributed to autodetachment.

All spectra in Figure 1 indicate a small electron affinity of benzonitrile. The position of the first distinct peak of band A in the 1064 nm spectrum indicates a VDE of  $58 \pm 5$  meV. It also defines the upper bound of adiabatic electron affinity, EA  $\leq 58$  meV. This result contrasts the previous indirect determination of the EA by electron capture,  $0.26 \pm 0.10$  eV.<sup>16</sup>

Compared to 1064 nm (a), the 532 nm spectrum (b) in Figure 1 exhibits a complete loss of vibrational resolution for band A. The loss is not surprising due to the higher eKE. The 355 nm spectrum (c) reveals another transition, labeled B. This band is observed near the 355 nm image center, but unlike band D, it shifts away from the center at a shorter wavelength in (d). As discussed in Section IV, band B is assigned as the  $\tilde{X}^{2}B_{1} \rightarrow \tilde{a}^{3}A_{1}$  photodetachment transition. The  $\tilde{a}^{3}A_{1}$  neutral state, which is not accessible via optical excitation from the  $\tilde{X}^{1}A_{1}$  ground state of benzonitrile, will be referred to simply as "the triplet." Band B's onset at  $3.41 \pm 0.01$  eV, prominent at 355 nm in Figure 1(c), as well as at 266 nm in (d), corresponds to the adiabatic electron affinity of the triplet state. The corresponding singlet-triplet splitting (between the  $\tilde{X}^{1}A_{1}\tilde{a}^{3}A_{1}$ states) is therefore  $\geq$  3.35 eV. The VDE of band B is determined from the 266 nm spectrum, VDE =  $3.51 \pm 0.01$  eV.

In the 266 nm spectrum in Figure 1(d), yet another band (C) appears, assigned as the  $\tilde{X} \,{}^2B_1 \rightarrow \tilde{A} \,{}^1A_1$  photodetachment transition. As justified later, the  $\tilde{A} \,{}^1A_1$  neutral state of benzonitrile will be referred to as "the open-shell singlet." Band C peaks at VDE = 4.45 ± 0.01 eV. Taking into account the 0.058 eV VDE of band A, this value corresponds to a 4.39 eV vertical gap between the  $\tilde{X} \,{}^1A_1$  and  $\tilde{A} \,{}^1A_1$  neutral states at the anion geometry. This result agrees well with the previous measurements of the  $\tilde{X} \,{}^1A_1 \rightarrow \tilde{A} \,{}^1A_1$  optical excitation of neutral benzonitrile using UV absorption, observed just above 4.5 eV.<sup>20,21</sup>

# B. Hydrated and oxygenated cluster anions of benzonitrile

The photoelectron images and spectra of  $bn^{-}(H_2O)_{1-3}$  cluster anions are presented in Figure 2, with the corresponding unsolvated  $bn^{-}$  data reproduced for reference. The photoelectron images collected at 1064, 532, and 355 nm are presented, but only the 1064 nm spectra are shown, as the trends to be discussed are consistent throughout the spectra at all the wavelengths.

As indicated in the figure, band A in the  $bn^{-}(H_2O)$  spectrum, peaking at eBE = 0.38 eV, is shifted up by 0.32 eV, compared to unsolvated  $bn^{-}$ . This shift corresponds approximately to the solvation energy of the  $bn^{-}$  anion by one water



FIG. 2. Left to right: 355, 532, and 1064 nm photoelectron images and 1064 nm photoelectron spectra of hydrated  $bn^-$  cluster anions: (a) unsolvated  $bn^-$  reference, reproduced for comparison from Figure 1; (b)  $bn^-(H_2O)$ ; (c)  $bn^-(H_2O)_2$ ; (d)  $bn^-(H_2O)_3$ . The direction of laser polarization is indicated by the double-sided arrow in (d). Spectral band shifts calculated based on the VDEs for band A are indicated by dashed horizontal arrows. The values are in eV.

molecule. The magnitude of the interaction is on the lower end of typical hydration energies, but not unusual among highly conjugated cyano-anions, such as the anions of *trans*-1,2-dicyanoethylene (fumaronitrile)<sup>35</sup> and tetracyanoethylene.<sup>36</sup>

The bn<sup>-</sup>(H<sub>2</sub>O) system was previously investigated by Maeyama et al. using structurally sensitive infrared vibrational autodetachment spectroscopy.<sup>37</sup> Using DFT methods, the cluster was assigned a  $C_s$  symmetry structure with the water being singly hydrogen-bound to the CN functionality, the other bond dissecting the plane of the aromatic ring. While some discrepancies exist between the experiment and theory, our experimental results in Figure 2 are in good agreement with the measurements reported by Maeyama et al.<sup>37</sup> In particular, their adiabatic detachment energy of 0.31 eV is in excellent agreement with the first peak of band A in Figure 2. Their VDE = 0.50 eV is in good agreement with the band A's peak in our higher photon energy spectra (not pictured in Figure 2). The second and third water molecules in  $bn^{-}(H_2O)_2$ and  $bn^{-}(H_2O)_3$  have further stabilizing effects of progressively decreasing magnitudes (0.28 and 0.24 eV, respectively).

The monohydrated cluster, bn<sup>-</sup>(H<sub>2</sub>O) was additionally examined at 266 nm. The photoelectron image and spectrum are shown in Figure 3(b), where the bn<sup>-</sup> dataset for the same wavelength is reproduced for reference in (a). Band B in the bn<sup>-</sup>(H<sub>2</sub>O) spectrum is shifted relative to the bn<sup>-</sup> spectrum by 0.24 eV, which is smaller than the corresponding shift for band A, 0.32 eV in Figure 2(b). The difference is indicative of the different interaction strengths between the respective  $\tilde{a}^{3}A_{1}$  and  $\tilde{X}^{1}A_{1}$  states of neutral benzonitrile and water molecules. Band C, peaking at 4.45 eV in the bn<sup>-</sup> spectrum in Figure 3(a),



FIG. 3. Photoelectron images and spectra of (a)  $bn^-$ , (b)  $bn^-(H_2O)$ , and (c)  $bn^-(H_2O)$  collected at 266 nm. The results of the unsolvated anion (a) are reproduced for reference from Figure 1(d). The direction of light polarization is indicated by the double-sided arrow in (a). The band shifts are in eV.

is shifted beyond the 266 nm photon energy cutoff in the  $bn^{-}(H_2O)$  spectrum 3(b).

Cluster anions of benzonitrile solvated by 1-3 oxygen molecules were also studied. The 1064 nm photoelectron spectra of the  $bn^-(O_2)_{1-3}$  cluster anions are presented in Figures 4(b) and 4(c), in comparison to the corresponding data for unsolvated  $bn^-$  in Figure 4(a). Band A in the monooxygenated cluster is shifted by 0.35 eV, which is comparable to the 0.32 eV shift in the corresponding  $bn^-(H_2O)$  data in Figure 2(b). The effect of the second oxygenation in  $bn^-(O_2)_2$ , however, is only 0.21 eV [Figure 4(c)], smaller than the 0.28 eV effect of adding a second water molecule [Figure 2(c)]. Although mono-oxygenation appears to be slightly more effective than mono-hydration in stabilizing the  $bn^-$  anion, the trend is reversed when double-oxygenation is compared to double-hydration (a total of 0.56 eV for the addition of two O<sub>2</sub> molecules vs. 0.60 eV for two H<sub>2</sub>Os).

For further comparison, cluster anions of the mixed  $bn^-(O_2)$  (H<sub>2</sub>O)<sub>1-2</sub> composition were also examined. The 1064 nm spectrum of  $bn^-(O_2)$  (H<sub>2</sub>O) is shown in Figure 4(d). If this cluster is viewed as  $bn^-(O_2)$  with an H<sub>2</sub>O molecule added, then based on the band shift in Figure 4(d) vs. 4(b), the approximate binding energy of H<sub>2</sub>O to  $bn^-(O_2)$  is 0.27 eV. This value is similar to the binding energy of H<sub>2</sub>O to  $bn^-(H_2O)$  in Figure 2(c). On the other hand, if  $bn^-(O_2)$  (H<sub>2</sub>O) is viewed as



FIG. 4. The 1064 nm photoelectron spectra of the oxygenated and mixed hydrated-oxygenated cluster anions of benzonitrile. The results of the unsolvated anion in (a) are reproduced from Figure 1(a). The band shifts are indicated in eV.

bn<sup>-</sup>(H<sub>2</sub>O) additionally solvated by  $O_2$ , then comparison of the data in Figures 2(b) and 4(d) indicates that the approximate binding energy of  $O_2$  to bn<sup>-</sup>(H<sub>2</sub>O) is 0.30 eV, larger than the 0.21 eV binding energy of  $O_2$  to bn<sup>-</sup>(O<sub>2</sub>) revealed in Figure 4(c). These differences are likely to be due to aggregate many-body effects in solvation, but they also point to different modes of solvation by  $O_2$  or H<sub>2</sub>O. This conclusion is intuitive, given that the bn<sup>-</sup> is a relative large anion and H<sub>2</sub>O is polar, while  $O_2$  is not. Further discussion of possible structures is found in Section IV C.

The 532 nm photoelectron spectra of  $bn^-(O_2)$  (H<sub>2</sub>O) and  $bn^-(O_2)$  (H<sub>2</sub>O)<sub>2</sub> are presented in Figure 5, again in comparison with the corresponding data for  $bn^-$ . The combined 0.61 eV binding energy of O<sub>2</sub> and H<sub>2</sub>O in  $bn^-(O_2)$  (H<sub>2</sub>O) observed at this wavelength is similar to the 0.62 eV cumulative value from O<sub>2</sub> and H<sub>2</sub>O in the 1064 nm data in Figure 4. The overall O<sub>2</sub> and H<sub>2</sub>O stabilization of  $bn^-$  is also comparable to the corresponding values due to either two waters (0.60 eV in Figure 2) or two oxygen molecules (0.56 eV in Figure 4). The addition of a second water to  $bn^-(O_2)$  (H<sub>2</sub>O) shifts the band in  $bn^-(O_2)$  (H<sub>2</sub>O)<sub>2</sub> by only an additional 0.21 eV [Figure 5(c)], which is similar to the band shift between  $bn^-(H_2O)_2$  and  $bn^-(H_2O)_3$  in Figure 2(d). Thus, even though different solvent molecules may bind to the anion in different ways, the binding of additional solvents tends to be less efficient, as in the bulk.

#### C. Benzonitrile dimer, trimer, and tetramer anions

Some of the most intriguing observations in this work reflect on the properties of the homo-molecular cluster anions



FIG. 5. The 532 nm photoelectron spectra of mixed oxygenated and hyrdated cluster anions of benzonitrile. The results for unsolvated  $bn^-$  in (a) are reproduced from Figure 1(b) for comparison. The band shifts are indicated in eV.

of benzonitrile  $(bn)_n^-$ . The dimer, trimer, and tetramer anions were investigated using 1064, 532, and 355, and 266 nm light. The results for the dimer are presented in Figures 6(b)-6(e) and can be compared to the 1064 nm data for the monomer anion in Figure 6(a). Figure 7 shows the 532 nm spectra of  $(bn)_n^-$ , n = 1-4.

Based on these spectra, particularly the similarity of the 266 nm spectrum of  $(bn)_2^-$  in Figures 3(c) and 6(e) and the corresponding spectrum of bn<sup>-</sup> in Figure 3(a),  $(bn)_2^-$  is qualitatively best described as a monomer-anion solvated by a neutral bn molecule, i.e., bn<sup>-</sup> · bn. Similarly, the  $(bn)_n^-$ , n = 3-4 clusters also appear to involve monomer-anion cluster cores, solvated by (n - 1) predominantly neutral bn molecules and can be described as bn<sup>-</sup> · bn<sub>n-1</sub>. In this picture, the cluster anion photodetachment transitions correspond to those of the bn<sup>-</sup> cluster core, shifted by the approximate amounts of solvation-stabilization energy.

The lowest-energy photoelectron band of the dimer (band A) exhibits a stabilization of 0.54 eV relative to the monomer [Figures 6(b)-6(e) and 7(b)]. This large band shift indicates strong but predominantly non-covalent interactions with the bn<sup>-</sup> cluster core. The trimer and the tetramer exhibit gradually decreasing sequential solvation energies of 0.35 and 0.27 eV,



FIG. 6. Photoelectron imaging results for the  $(bn)_2^-$  dimer anion. (a) The Ref. 1064 nm data reproduced from Figure 1(a). (b)–(e) The 1064, 532, 355, and 266 nm  $(bn)_2^-$  results. The 266 nm  $(bn)_2^-$  spectrum of in (e) is from Figure 3(c). The band shifts are indicated in eV.



FIG. 7. The 532 nm photoelectron spectra of the (b) dimer, (c) trimer, and (d) tetramer anions of benzonitrile. The results in (a) for the monomer anion,  $bn^-$ , are reproduced from Figure 1(b). The band shifts are indicated in eV.

respectively [Figures 7(c) and 7(d)]. Band B in the 266 nm spectrum of the dimer [Figures 3(c) and 6(e)] corresponds to the triplet state of bn formed in the photodetachment of the  $bn^-$  cluster core. This band is shifted by 0.42 eV, relative to the



same band in the bn<sup>-</sup> spectrum, in contrast to the 0.54 eV shift of the A band. The decreased solvation-induced shift of band B in  $(bn)_2^-$  mirrors the similar effect observed in the bn<sup>-</sup>(H<sub>2</sub>O) spectrum [0.24 eV shift for band B in Figure 3(b) vs. 0.32 eV for band A in Figure 2(b)].

The observed band shifts are quite similar to those observed for other substituted aromatics. For example, the dimer and trimer anions of nitrobenzene (nb) were previously studied by photoelectron spectroscopy.<sup>38</sup> Compared to nb<sup>-</sup>, the dimer exhibited an approximate band shift of ~0.5 eV and the trimer—an additional ~0.3 eV. These solvation energies compare almost exactly to what is observed here for benzonitrile.

## D. Hydrated and oxygenated dimer and trimer anions of benzonitrile

Figure 8 displays the 532 nm spectra of the  $(bn)_n^{-}(H_2O)$ and  $(bn)_n^{-}(O_2)$ , n = 2-3 cluster anions. Arguments similar to those in Section III C suggest that these clusters are also based on the bn<sup>-</sup> monomer-anion cores, and their structures are therefore best described bn<sup>-</sup>(bn)\_{1-2} (H\_2O) and bn<sup>-</sup>(bn)\_{1-2}(O\_2).

In particular, the  $(bn)_n^{-}(O_2)$ , n = 2-3 photoelectron spectra in Figures 8(c) and 8(d) are inconsistent with a superoxide-based motif,  $O_2^{-}(bn)_n$ , n = 2-3. Similar arguments can also be made with regard to the data presented in Figures 4 and 5 for other oxygen-containing cluster anions studied in the work. The photodetachment of  $O_2^-$  has been extensively studied.<sup>39-45</sup> In particular, its 532 nm spectrum obtained under the experimental conditions similar to the present work exhibits resolved vibrational structure, with intensity peaking at an eBE  $\approx 1.0$  eV.<sup>46</sup> Although the vibrational structure is often lost due to solvation, the assumption of the  $O_2^{-}(bn)_2$ structure of the cluster examined in Figure 8(c) would imply a slightly negative band shift resulting from solvation of the O<sub>2</sub><sup>-</sup> core by two polar benzonitrile molecules. This assumption is inconsistent with the generally expected energetics of cluster formation. Moreover, band A in the  $(bn)_2^{-}(O_2)$  spectrum in Figure 8(c) exhibits very similar structure to band A in

FIG. 8. The 532 nm spectra of the hydrated and oxygenated dimer, (a) and (c), respectively, and trimer, (b) and (d), respectively, cluster anions of benzonitrile. The observed band shifts are reported in eV with respect to band A of the unsolvated anion.

TABLE I. Observed solvation-induced shifts of band A, corresponding to approximate solvation energies. Band B shifts are also indicated for  $bn^-$  solvated by bn or H<sub>2</sub>O only (explicitly labeled with letter B). All values are in eV. The numerals and letters in parentheses indicate the datasets (figure numbers), where the reported shifts are observed.

Reference species	Added solvent molecule <sup>a</sup>				
	bn	H <sub>2</sub> O	O <sub>2</sub>		
bn <sup>-</sup>	0.54 (6b,7b) B: 0.42	0.32 (2b) B: 0.24	0.35 (4b)		
	(3c)	(3b)			
bn <sup>-</sup> (H <sub>2</sub> O)	0.45 (8a)	0.28 (2c)	0.30 (4d)		
$bn^{-}(H_2O)_2$		0.24 (2d)	0.22 (5c)		
$bn^{-}(O_2)$	0.43 (8c)	0.27 (4d)	0.21 (4c)		
$bn^{-}(H_2O)(O_2)$		0.21 (5c)			
(bn) <sub>2</sub> <sup>-</sup>	0.35 (7c)	0.23 (8a)	0.24 (8c)		
(bn) <sub>3</sub> <sup>-</sup>	0.27 (7d)	0.14 (8b)	0.20 (8d)		
(bn)2 <sup>-</sup> (H2O)	0.26 (8b)				
$(bn)_2^-(O_2)$	0.31 (8d)				

<sup>a</sup>Heterogeneously solvated cluster anions of the general composition  $X^-(Y)_m(Z)_n$ , where  $Y \neq Z$ , can be viewed as resulting either from addition of Y to  $X^-(Y)_{m-1}(Z)_n$ or from the addition of Z to  $X^-(Y)_m(Z)_{n-1}$ . For example, the  $bn^-(O_2)$  (H<sub>2</sub>O) data presented in Figure 4(d) results in two separate but related entries in the table: H<sub>2</sub>O added to  $bn^-(O_2)$  and O<sub>2</sub> added to  $bn^-(H_2O)$ . This analysis does not take into account the structural solvation motifs of these clusters. For example, no consideration is given which solvent molecule is the "primary" (more strongly bound) solvation agent.

 $(bn)_2^-$  (H<sub>2</sub>O) photodetachment, Figure 8(a), suggesting the same type of anionic cluster core in both cases.

With that, the origin of the lower-eBE bands (to the left of band A) in the  $(bn)_2^-(H_2O)$ ,  $(bn)_3^-(H_2O)$ , and  $(bn)_3^-(O_2)$ spectra in Figures 8(a), 8(b), and 8(d), respectively, is unclear. One may speculate that these bands are due to metastable decay of the parent clusters, resulting in the photodetachment of smaller species. However, detailed analysis and confirmation of this hypothesis are outside the scope of this work.

Based on the observed band shifts, the binding energies of water or oxygen to the benzonitrile dimer and trimer anions are indicated in the respective spectra in Figure 8. All reported solvation energies, approximately determined based on the spectral shifts of band A in benzonitrile cluster anions are summarized in Table I.

#### **IV. DISCUSSION**

#### A. The benzonitrile anion

Two qualitatively different electronic structures can be proposed for the benzonitrile anion,  $bn^-$ : (i) the valence anion (<sup>2</sup>B<sub>1</sub> electronic state), with the excess electron occupying the lowest vacant valance orbital of benzonitrile, which is the 4b<sub>1</sub> ( $\pi^*$ ) orbital shown in Figures 9(b) and 9(c) and (ii) the dipolebound anion (<sup>2</sup>A<sub>1</sub> state), where the diffuse electron with a totally symmetric wavefunction is loosely bound to the electrostatic dipole moment of neutral bn.

The *ab initio* calculations for the valence anion discussed below predict a VDE of 0.047 eV, which is in adequate agreement with the observed maximum of band A (0.058 eV). The dipole-bound anion is presently under the theoretical investigation by Kirnosov and Adamowicz and their preliminary results indicate a VDE = 0.0186 eV.<sup>13</sup> Although this value is slightly below the experimentally observed band maximum, the small



FIG. 9. (a) Selected structural parameters of neutral benzonitrile (regular font) and its anion (italic font) optimized with the CCSD/aug-cc-pVDZ method and basis. Both the neutral and anion structures are of  $C_{2v}$  symmetry. Complete structures are included in the supplementary material.<sup>65</sup> (b) and (c) The singly occupied 4b<sub>1</sub> HOMO of bn<sup>-</sup> shown from two different viewing angles.

discreapancy alone is not sufficient to draw a definitive conclusion about the qualitative structure of the anions observed in this work.

Hence, bn<sup>-</sup> presents an interesting theoretical and experimental problem. The existence of two states is anticipated, with close energetics and similar geometric structures, but very different electronic wavefunctions. Because of the energetic proximity and similar geometries, inter-conversion between the two types of anions is possible and even likely. In particular, the dipole-bound state may serve as a gateway to the valence structure. Similar processes have been hypothesized before, but usually involving valence and dipole-bound states of similar energies but different geometries, such as in HCCCN<sup>-</sup>.<sup>47–49</sup> The possibility of such inter-conversion in bn<sup>-</sup>, where the two states overlap not only in energy but also in the configuration space, is both interesting and intriguing. This possible process is under current theoretical investigation.<sup>13</sup>

There are several indications that the transitions observed in this work should be assigned primarily to the valence anion. First, the low-energy band A in Figure 1(a) shows evidence of a vibrational progression, consistent with a perhaps small, but nonetheless non-trivial geometry difference between the valence anion and the neutral. It is less consistent with a dipolebound anion, because photoelectron spectra of such species are usually dominated by single sharp transitions,<sup>50–52</sup> reflecting almost no equilibrium geometry change of the neutral core upon the photodetachment.

To quantify this argument, we performed a FC simulation of the lowest-energy photodetachment band of bn<sup>-</sup>, assuming the valance-bound anion structure. The valence anion and neutral bn geometries were optimized in Q-Chem at the CCSD level using the aug-cc-pVDZ basis. The resulting structures are presented in Figure 9(a); they are similar to the corresponding B3LYP/6-31+G(d,p) geometries reported by Maeyama *et al.*<sup>37</sup> Both the anion and neutral structures in Figure 9(a) are of  $C_{2v}$ symmetry and, aside from a slight puckering of the ring in the anion, very similar. This is consistent with the experimental VDE of bn<sup>-</sup> (band A) being near the apparent onset of the band.

Next, the vibrational frequencies of neutral benzonitrile in the ground electronic state were calculated in Gaussian using the M06-2X density functional and the aug-cc-pVTZ basis set. The vibrational modes were treated as independent harmonic oscillators with Duschinky rotations in the PESCAL 2010 program.<sup>34</sup> The eBEs and intensities of the resulting photodetachment transitions are shown as a FC stick spectrum in Figure 10, superimposed with the 1064 nm experimental spectrum from the data in Figure 1(a). The eBE of the 0-0 simulated transition was set to the experimentally determined VDE and no further adjustments were necessary.

The stick spectrum was convoluted with a Gaussian function of a 5 meV full width at half-maximum, intentionally chosen to underestimate the experimental broadening. No anharmonicities or hot bands were included. The convoluted FC spectrum is shown in Figure 10 as a smooth blue line. The simulation clearly captures all of the major features of experimental band A, including the decline of intensity at ~0.8 eV. Band D in the 1064 nm spectrum, assigned as autodetachment, is not part of the FC simulation. The agreement clearly shows that the valence anion geometry is consistent with the experimentally observed band profile.

The second indication in favor of the valance structure of the anions studied in this work is the persistence of the overall features of band A with solvation. This is particularly clear in the  $bn^{-}(O_2)$  case in Figure 4(b). Band A shifts by 0.35 eV upon the addition of  $O_2$ , while its overall spectral structure remains



FIG. 10. Franck-Condon (FC) simulation of the  $\tilde{X} {}^{2}B_{1} \rightarrow \tilde{X} {}^{1}A_{1}$  photoelectron spectrum of bn<sup>-</sup>. Red vertical lines: the FC stick spectrum computed as described in the text. Continuous blue line: the FC stick spectrum convoluted with a Gaussian function (FWHM = 5 meV). Filled symbols: the expanded 1064 nm experimental spectrum from Figure 1(a).

mostly unchanged. In the dipole-bound anion, the attached electron wavefunction is defused and extended far from the core.<sup>14,15,53</sup> The solvation of such an anion by an O<sub>2</sub> molecule would likely lead to the formation of superoxide,<sup>39,42,45</sup> solvated by bn. The spectrum in Figure 4(b) is not consistent with  $O_2^{-}$ (bn).

The third indication is that past experiments on other systems have indicated that the photoelectron angular distributions in the photodetachment of dipole-bound anions tend to be predominantly parallel to the direction of the laser polarization.<sup>54</sup> This is contrary to the slightly perpendicular angular distributions of band A seen in the photoelectron images in Figure 1, particularly (a)–(c). On the other hand, the observed angular distributions are consistent with the  $\pi^*$  character of the valence anion HOMO (4b<sub>1</sub>) shown in Figures 9(b) and 9(c).<sup>27,55</sup>

We conclude that the transitions observed in our experiments are most consistent with the valance structure of the  $bn^-$  anion. This conclusion neither preclude the existence of the dipole-bound species nor does it negate their presence in our experiments. It is possible that the dipole-bound signal is overwhelmed by the valence transitions in the same energy range, particularly if the photodetachment cross section for the dipole-bound species is smaller than that for the valance anion.

#### B. The low-lying electronic states of benzonitrile

To aid in the assignment of all observed photodetachment transitions, the  $bn^-$  anions and the low-lying electronic states of neutral benzonitrile were investigated using the coupled-cluster and equation-of-motion electronic-structure methods, specifically targeting the anion photodetachment. All calculations described in this subsection were carried out using Q-Chem 4.0.<sup>31</sup>

To meet the needs of the EOM calculations, the anion and neutral geometries were optimized at the CCSD level using the aug-cc-pVDZ basis. As already mentioned in Section IV A, the resulting structures are shown in Figure 9(a). The ground and excited electronic states of neutral benzonitrile were then accessed with single-point EOM-IP-CCSD calculations starting from the anion reference at the optimized anion geometry. The properties of the resulting neutral states are summarized in Table II.

The lowest-energy vertical transition corresponds to detachment from the  $4b_1$  HOMO of the anion, resulting in

TABLE II. Benzonitrile anion photodetachment transitions and the corresponding neutral states determined using the EOM-IP-CCSD/aug-cc-pVDZ calculations starting from the anion reference and geometry optimized at the CCSD/aug-cc-pVDZ level of theory. The nominal electron configuration of  $bn^-$  is  $\tilde{X}^2B_1$ : ...(8a\_1)^2(8b\_2)^2(1a\_2)^2(3b\_1)^2(4b\_1)^1.

Nominal detachment orbital	Neutral state	Predicted VDE/eV	Experimental VDE/eV	Observed transition
α-4b <sub>1</sub>	$ ilde{X}$ $^{1}A_{1}$	0.047	0.058(5)	Band A
β-3b <sub>1</sub>	$\tilde{a}^{3}A_{1}$	3.358	3.51(1)	Band B
α-3b <sub>1</sub>	$ ilde{A}$ $^{1}A_{1}$	4.281	4.45(1)	Band C
β-1a <sub>2</sub>	$ ilde{b}{}^3\mathrm{B}_2$	4.711		
α-1a <sub>2</sub>	$\tilde{B}^{1}B_{2}$	4.897		

the closed-shell singlet neutral state. The calculated transition energy, VDE = 0.047 eV, is in agreement with the experimental value of 0.058 eV for band A. Photodetachment from HOMO-1 (3b<sub>1</sub>) yields two neutral states: the lowest triplet,  $\tilde{a}^{3}A_{1}$ , and the open-shell singlet,  $\tilde{A}^{1}A_{1}$ . The triplet is predicted to lie (vertically) 3.358 eV above the anion, which also compares very well to the observed VDE of band B, 3.51 eV [Figure 1(d)]. The  $\tilde{A}^{1}A_{1}$  state is predicted to be at 4.281 eV above the anion. For comparison, the experimental VDE of band C is 4.45 eV. The slight discrepancies between the observed detachment energies and the calculated energetics of the  $\tilde{a}^{3}A_{1}$  and  $\tilde{A}^{1}A_{1}$  states are not surprising in light of the complexity of the molecule, the limited double- $\zeta$  basis set, and the non-inclusion of triple excitations in the coupled-cluster calculations. These limitations notwithstanding the predicted vertical gap between the  $\tilde{a}^{3}A_{1}$  and  $\tilde{A}^{1}A_{1}$  states of bn, 0.923 eV, are in remarkable agreement with the difference between the experimental VDEs of bands B and C:  $\Delta VDE = 0.94(2) \text{ eV}$ .

Photodetachment from HOMO–2 (1a<sub>2</sub>) yields a higherlying pair of triplet and open-shell singlet states:  $\tilde{b}^{3}B_{2}$  and  $\tilde{B}^{1}B_{2}$ . The predicted transition energies, 4.711 and 4.897 eV, respectively (Table II), fall outside the experimental energy range. With that, all observed spectroscopic features are accounted for by theory.

#### C. Solvated benzonitrile cluster anions

The overall appearance of band A in the photoelectron spectra persists upon the addition of one of two solvent molecules to  $bn^-$  (Figures 2-5). This indicates that  $bn^-$  preserves its identity upon solvation. The structure of  $bn^-(H_2O)$  was previously investigated by Maeyama *et al.*<sup>37</sup> Using B3LYP/6-31+G(d,p) calculations, they determined the optimized cluster geometry, whereas the H<sub>2</sub>O molecule is singly hydrogenbound to the CN group of  $bn^-$ . The VDE of  $bn^-(H_2O)$  was predicted to be 0.678 eV,<sup>37</sup> compared to our experimental value of 0.38 eV [Figure 2(b)].

Since no structural information concerning the oxygenated bn<sup>-</sup> clusters exists in the literature, we attempted to optimize the  $bn^{-}(O_2)$  cluster anion geometry using the M06-2X density functional in Gaussian 09, paired with the aug-ccpVDZ basis set. The functional was chosen for its proven performance for long-distance interactions in molecular complexes and clusters.<sup>56–58</sup> These attempts resulted in the excess charge localized predominantly on the oxygen, i.e., the O<sub>2</sub><sup>-(bn)</sup> cluster motif rather than  $bn^{-}(O_2)$ . This is not surprising, since  $O_2$  has a greater EA compared to bn. However, this computational result contrasts the experimental observations, which clearly show the bn<sup>-</sup> core anion. It is likely that the observed  $bn^{-}(O_2)$  cluster anions are formed by attachment of  $O_2$  to the initially formed bn<sup>-</sup>, resulting in a cluster trapped in a local potential minimum. Similar arguments apply to the structures of all others water and oxygen clusters of bn<sup>-</sup> which retain the features of band A.

#### D. The benzonitrile dimer anion

The experimentally determined band shifts summarized in Table I reveal that the strongest interactions among all the clusters studied are observed when a second bn moiety is added to bn<sup>-</sup> or to a cluster anion already containing one moiety of benzonitrile. The interaction of bn<sup>-</sup> with bn is stronger than with any other solvent studied, including water. We now examine the dimer anion structures that may be responsible for this effect.

Stronger-than-hydration, non-covalent effects are a hallmark of ion- $\pi$  and  $\pi$ - $\pi$  stacking interactions.<sup>59–62</sup> The results summarized in Table I suggest the involvement of the  $\pi$  system of benzonitrile in the intermolecular bonding. This would also be consistent with the results for the nitrobenzene dimer anion,<sup>38</sup> as similar solvation energies in the two cases suggest that the underlying interaction is not unique the cyano- or nitrogroup.

In its neutral state, benzonitrile forms a dimer complex with hydrogen bonds between the cyano-group of one molecule and the othro-hydrogen of the other in a planar  $C_{2h}$  symmetry geometry.<sup>9,63,64</sup> However, neutral intermolecular interactions are weaker and there is no reason to expect that the structure of the dimer anion should follow the neutral complex motif. Case in point, Maeyama *et al.* showed clearly that the  $bn^{-}(H_2O)$  anion has a different hydrogen-bonding scheme than the corresponding neutral.<sup>37</sup>

We carried out exploratory calculations on several plausible  $(bn)_2^-$  structures, using the M06-2X density functional. Due to the size of the system, complete  $(bn)_2^-$  geometry optimization presented a challenge, which was addressed using the following approach. Initially, the structures of the neutral bn molecule and the bn<sup>-</sup> anion were optimized separately with the aug-cc-pVDZ basis set. Next, crude potential energy scans, consisting of single-point energy calculations with the smaller 6-311+G\* basis, were carried out by changing the relative positions of the frozen bn and bn<sup>-</sup> structures (optimized above), until an energy minimum with respect to the intermolecular coordinates was found. The resulting  $(bn)_2^-$  geometry was then used as the starting point of a complete geometry optimization with the 6-311++G\*\* basis. This approach yielded several plausible structures of the benzonitrile dimer anion. For each  $(bn)_2^-$  structure, the solvation/interaction energy was calculated as the difference between the sum of the isolated bn<sup>-</sup> and bn energies calculated using the same theory and basis, and the  $(bn)_2^-$  dimer anion energy.

Three major structural motifs have emerged. The first corresponds to a planar structure shown in Figure 11(a) with the two bn moieties laid end to end, maintaining an overall  $C_{2v}$  symmetry in collinear sigma-bonded geometry. The solvation energy for this structure is calculated to be 0.47 eV (without accounting for the zero-point vibrational energy correction or the neutral van der Waals interactions). The Milliken charge distribution (-0.07/-0.93 for the top/bottom bn moieties in the figure) indicates a predominantly ion-dipole motif and a bn<sup>-</sup> · bn solvated-anion structure.

The second is a hydrogen-bonded structure shown in Figure 11(b), with the nitrogen of the cyano-groups ~2.7 Å from the ortho-hydrogen of the other ring. This structure is very similar to that previously reported by Borst *et al.* for the neutral van der Waals dimer.<sup>64</sup> The solvation energy is estimated to be 0.32 eV, indicating a weaker interaction than in the ion-dipole motif (a). We must consider, however, that



FIG. 11. Five relaxed  $(bn)_2^-$  structures optimized using the M06-2X functional with the 6-311++G\*\* basis set (see the text for details). The solvation/interaction energies corresponding to each of the structures are summarized in the inset in the bottom left corner of the figure. The negative values next to the angular brackets in (a) indicate the Mulliken charges of the two bn moieties. In (b)-(e), the excess charge is approximately equally shared between the monomers. The average separation between the two moieties in the stacked geometries (c)-(e) is 3.2–3.4 Å. Complete structural details are included in the supplementary material.<sup>65</sup>

a high degree of delocalization of the excess charge in each moiety and across the structure (Milliken analysis indicates the charge is evenly shared) mutes the benefits of an anion participating in a hydrogen bond. Second, the strong dipole of the neutral and anion predicted at this level of theory (4.7 and 4.4 D, respectively) may favor the ion-dipole interaction.

Other plausible  $(bn)_2^-$  structures that were discovered involved  $\pi$ - $\pi$  stacking interactions, with the charge shared approximately equally between two monomer moieties sandwiched approximately parallel to each other, with an intermoiety separation in the 3.2–3.5 Å range. The salient features of three stacked local-minimum structures are illustrated in Figures 11(c)-11(e), while the complete structural details are included in the supplementary material.<sup>65</sup> The primary distinction between structures (c)–(e) is in the relative orientation of the cyano-groups with respect to each other, as described by the eclipse angle. In (c), the CN groups of the two bn moieties are aligned in nearly the same direction (the eclipse angle is nearly zero). In structure (d), the CN eclipse angle is 180°, while structure (e) corresponds to an intermediate arrangement (eclipse angle ~90°).

Such  $\pi$ - $\pi$  stacking structural motifs are quite common in dimers and dimer-anions of conjugated molecules. Structure (e), in particular, is reminiscent of the uracil dimer anion.<sup>66</sup> The respective solvation stabilization energies of structures (c)–(e) in Figure 11, determined at the M06-2X/6-311++G\*\* level of theory, are 0.58, 0.79, and 0.79 eV. While it is impossible to say definitively which (bn)<sub>2</sub><sup>-</sup> structure, (d) or (e), is most

stable, it is clear that structure (c), corresponding to the two CN groups nearly eclipsing each other, is most unstable of the three stacked geometries (c)–(e). It has been shown that  $\pi$ - $\pi$  stacking interactions of substituted benzenes are destabilized when the substituents are close enough to interact directly through their local environment.<sup>67</sup> The (bn)<sub>2</sub><sup>-</sup> results presented here are in direct agreement with this observation. These results strongly support the importance of the  $\pi$ - $\pi$  interactions in stabilizing the dimer anion and indicate that the corresponding structural motif favors minimizing the direct interaction between the CN substituent groups.

Similar to the water and O<sub>2</sub> clusters, band A of the  $(bn)_2^-$  shown in Figure 6(b) has somewhat similar features to the spectrum of bare bn<sup>-</sup>, despite the increase in the eBE. However, there is significant broadening, indicating solvent rearrangement upon  $(bn)_2^-$  photodetachment. To shed light on the expected geometry changes, we optimized  $(M06-2X/6-311++G^{**})$  the neutral dimer structures using the anion geometries in Figures 11(d) and 11(e), reproduced in Figures 12(a) and 12(b), respectively, as the starting points. The results are shown in Figure 12, right, while complete details are included in the supplementary material.<sup>65</sup> Both optimized neutral structures show an increase in the average distance between the moieties by 0.2–0.3 Å, compared to the anions. The structural changes of each moiety upon electron detachment from the dimer are quite small, similar to those in the detachment of bare bn<sup>-</sup>. This result is consistent with the preservation of the overall features of band A and also





FIG. 12. Left, (a) and (b): the  $(bn)_2^$ dimer anion structures reproduced from Figures 11(d) and 11(e), respectively. Right, (a) and (b): the neutral structures obtained by M06-2X/6-311++G\*\* optimization using the anionic structures on the left as respective starting points. The average separation distance between the neutral stacked moieties is 3.4–3.6 Å. Full structural details are included in the supplementary material.<sup>65</sup>

with the greater broadening of the dimer-anion band compared to the mono-solvated water or oxygen clusters, since the (intermolecular) geometry change is larger for  $(bn)_2^-$  than any

other cluster studied. The neutral energies corresponding to the initial and final geometries shown in Figure 12, in conjunction with the optimized anion energies, allowed for the calculation of the corresponding VDEs and EAs. The EAs corresponding to dimer structures (a) and (b) in Figure 12, right, are 0.513 and 0.514 eV, respectively. This result is-again-consistent with the local substituent environment being the main factor in  $\pi$ - $\pi$  interactions of substituted benzenes. The predicted VDEs of dimer anions (d) and (e) in Figure 11, corresponding to Figures 12(a) and 12(b), left, are 0.763 eV and 0.756 eV, respectively. Although the agreement between the predicted solvent stabilization energies and the experimental band shifts in the dimer anion (Table I) is not perfect, it can hardly be expected given the limitations of these calculations. Charge sharing between the two monomer moieties is clearly advantageous from the dimer bonding perspective.

#### V. SUMMARY

We have reported a negative-ion photoelectron imaging study of benzonitrile and several of its hydrated, oxygenated, and homo-molecularly solvated cluster anions. Benzonitrile is found to have a very small electron affinity. The photodetachment transition from the ground state of the anion to the  $\tilde{X}$  <sup>1</sup>A<sub>1</sub> state of the neutral peaks at a VDE = 58 ± 5 meV. This transition is assigned to the <sup>2</sup>B<sub>1</sub> valence anion, but the existence of a dipole-bound state of similar energy and geometry cannot be excluded and is in fact likely.<sup>13</sup> The above VDE value is also assigned as the upper bound of the adiabatic EA of benzonitrile, improving over previous indirect methods. The EA of the first excited electronic state, the  $\tilde{a}^{3}A_{1}$  state, was determined to be  $3.41 \pm 0.01$  eV. The next excited state, the open-shell singlet  $\tilde{A}^{1}A_{1}$ , corresponds to an anion VDE =  $4.45 \pm 0.01$  eV. These results are in good agreement with the predictions of theory. The step-wise and cumulative solvation energies of benzonitrile anions by several types of species were also determined. The strongest intermolecular interactions are observed between two benzonitrile moieties. The magnitude of these homo-molecular interactions exceeds the hydration or oxygenation energies. Theoretical modeling of the benzonitrile dimer anion using density functional theory predicts that the dimer anion favors a stacked structural motif, capitalizing on the  $\pi$ - $\pi$  interactions between the two benzonitrile moieties.

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