The ability of fluorocarbons to form hydrogen bonds has been a subject of debate. For example, based on an analysis of structural databases, several authors concluded that C–F groups are very poor hydrogen bond acceptors.1–4 In particular, Dunitz and Taylor noted that out of 5947 C–F bonds reported in the Cambridge Structural Database, only two were definitively found to form hydrogen bonds.1 On the other hand, it is also known that C–H···F interactions in the crystals of fluorinated organic compounds have structurally directional properties which are analogous to those in other weak hydrogen-bonded systems.4–6 Furthermore, gas-phase complexes of water and methanol with partially fluorinated benzenes, e.g., monofluorobenzene, 1,4-difluorobenzene, and 1,2,4,5-tetrafluorobenzene, form cyclic hydrogen-bonded complexes with C–H···O–H···F–C structural motifs.7–10

By contrast, a fully fluorinated benzene molecule, i.e., hexafluorobenzene, and a water molecule do not interact to form a hydrogen bond. Calculations by Gallivan and Dougherty11 and by Danten et al.12 on the hexafluorobenzene-water complex both find an initially counternintuitive geometry in which the water molecule sits above the plane of the hexafluorobenzene molecule with its C2v axis perpendicular to the plane of hexafluorobenzene and with the lone pairs of oxygen pointing directly toward the hexafluorobenzene plane. Gallivan and Dougherty characterized their binding as primarily electrostatic with an attractive interaction between the dipole moment of water and the quadrupole moment of hexafluorobenzene. The same calculations also imply an absence of in-plane C–F···H–O hydrogen bonding interactions, even in face of the availability of hexafluorobenzene’s six C–F groups. In addition, circumstantial experimental evidence by Patwari and Lisy (infrared photodissociation in beams) and by Besnard et al. (infrared and Raman spectroscopy in solutions) is also consistent with this assessment.13,14 Using the atoms in molecules theoretical approach, Singh et al.15 recently showed that C–F groups in fluorinated benzenes lose their abilities to hydrogen bond when benzene is substituted with five or more fluorine atoms. This was attributed to a lowering of peripheral electron densities on the terminal fluorine atoms.16 In light of the foregoing, an intriguing question arose: Would hexafluorobenzene hydrogen bond to water if the electron density on its fluorine atoms were to be somehow increased? To tackle this question, we added an extra electron to hexafluorobenzene and studied the interaction of the resulting hexafluorobenzene anion with one and with two water molecules. This was accomplished by forming hexafluorobenzene anion-water complexes, \( \text{C}_6\text{F}_6^-(\text{H}_2\text{O})_{n=1,2} \), and measuring their photoelectron spectra. Complementing these experimental results, we also performed calculations which linked adiabatic electron affinities to the structures of the negatively charged species and their neutral counterparts. Neutral hexafluorobenzene-water complexes are not thought to be hydrogen bonded.
formed is aromatic and its solvent is a nonaromatic molecule, whereas in the latter cases, the roles are reversed.\textsuperscript{18}

**EXPERIMENTAL AND COMPUTATIONAL METHODS**

The experimental portion of this work consisted of generating the solvated cluster anions, $\text{C}_6\text{F}_6(\text{H}_2\text{O})_n$ ($n=0-2$), identifying them by mass spectrometry, mass selecting the species of interest, and measuring their anion photoelectron spectra. These cluster anions were produced by the coexpansion of $\text{C}_6\text{F}_6(\text{g})$, $\text{H}_2\text{O}(\text{g})$, and argon at a total pressure of 1–4 atm through a 20 $\mu$m nozzle into a high vacuum. The resultant jet was intercepted as it left the nozzle by a stream of electrons produced by a biased thoriated iridium filament. This resulted in the formation of a microplasma, which itself was confined by an axial magnetic field. The anionic clusters were then extracted, formed into a beam (focused), and mass analyzed by a 90° sector magnet. The ion of interest was then selected by tuning the magnetic field of the magnet and sent on into a chamber where it was irradiated with photons from an argon ion laser operating intracavity at 488 nm (2.54 eV). The resulting photodetached electrons were next energy analyzed with a hemispherical electron energy analyzer and counted. The photodetachment process is governed by the energy-conserving relationship $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. The experimental apparatus has been described in detail elsewhere.\textsuperscript{19} The computational portion of this work focused on calculating the ener-
gies of the optimized structures of both the anionic species and their neutral counterparts, thereby providing their corre-
sponding adiabatic electron affinities. These calculations were carried out at the MPW1PW91/6-311+G($d,p$) level of density functional theory using GAUSSIAN 98.\textsuperscript{20}

**EXPERIMENTAL RESULTS**

The mass spectrum exhibited strong ion intensities for $\text{C}_6\text{F}_6(\text{H}_2\text{O})_n$ at $n=0, 1, \text{and 2}$, only weak intensity at $n=3$, and no significant signal for $n>3$. The water cluster anion series ($\text{H}_2\text{O})_n$ appeared for $n>10$ and was the only series present at higher masses. The photoelectron spectra for $\text{C}_6\text{F}_6(\text{H}_2\text{O})_n$, $n=0-2$, are presented in Fig. 1, and all three exhibit broad spectral bands. Information extracted from these spectra is presented in Table I.

Our photoelectron spectrum of $\text{C}_6\text{F}_6$ agrees well with the previously published spectrum recorded by Nakajima et al.\textsuperscript{17} They reported a peak intensity maximum [vertical detachment energy (VDE)] of 1.56 eV and a threshold energy $E_T$ of 0.80 eV, while we measured a VDE of 1.55 eV and a $E_T$ of 0.7 eV. Our spectrum, however, is considerably better resolved, and the various peaks sticking up out of the otherwise broadband are real and reproducible vibrational features. Nevertheless, our attempts to provide a converged Franck-Condon fit to this spectrum were unsuccessful, probably due to the large number of modes with significant dis-
placements that were encountered. Thus, because of a lack of assignable structure in the spectrum, neither Nakajima et al. nor we were willing to report an adiabatic electron affinity $VDE$ value for $\text{C}_6\text{F}_6$, opting instead for giving VDE and $E_T$ values. Three $E_A$ values for $\text{C}_6\text{F}_6$, however, are reported in the literature. Using a flowing afterglow apparatus, Miller et al. determined its $E_A$ value to be 0.53 eV and also calculated it to be 0.45 eV.\textsuperscript{21} Two purely theoretical studies have also been published. Xie et al.\textsuperscript{22} reported an $E_A$ value for $\text{C}_6\text{F}_6$ of 0.69 eV, while Hou and Huang\textsuperscript{23} reported its value to be 0.72–0.76 eV. Still, even without a spectral assignment, if the structural difference between the anion and its corre-
sponding neutral is not too great and if the anions are rela-
tively cold, one would expect the electron binding energy of the $E_A$ value to be in the neighborhood of the $E_T$ value in an anion photoelectron spectrum, and our $E_T$ value is close to the calculated $E_A$ values of both Xie et al. and Hou and Huang. Nevertheless, because of the expected symmetry differ-
ence between neutral $\text{C}_6\text{F}_6$ and $\text{C}_6\text{F}_6$ and the lack of reliable information on the temperature of the anions, extracting an $E_A$ value for $\text{C}_6\text{F}_6$ from the photoelectron spectrum of $\text{C}_6\text{F}_6$ alone remains an uncertain endeavor.

**TABLE I. Measured vertical detachment energies, threshold energies, and sequential shifts.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Peak center VDE (eV)</th>
<th>Threshold energy $E_T$ (eV)</th>
<th>Sequential shift ΔVDE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{F}_6$</td>
<td>1.55</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_6\text{F}_6(\text{H}_2\text{O})$</td>
<td>1.78</td>
<td>1.1</td>
<td>0.23</td>
</tr>
<tr>
<td>$\text{C}_6\text{F}_6(\text{H}_2\text{O})_2$</td>
<td>1.93</td>
<td>1.2</td>
<td>0.15</td>
</tr>
</tbody>
</table>

FIG. 1. Photoelectron spectra of the $\text{C}_6\text{F}_6(\text{H}_2\text{O})_n$ ($n=0-2$) series.
While they have slightly narrower widths, the broad photoelectron spectral bands of \( C_6F_6(H_2O)_1 \) and \( C_6F_6(H_2O)_2 \) exhibit the same general shape as the photoelectron spectrum of \( C_6F_6 \), implying that the \( C_6F_6 \) subion is their chromophore for photodetachment and that \( C_6F_6(H_2O)_1 \) and \( C_6F_6(H_2O)_2 \) are both well described as anion-molecule complexes. Moreover, the spectra of \( C_6F_6(H_2O)_1 \) and \( C_6F_6(H_2O)_2 \) shift toward higher EBE values as \( n \) increases. This is due to the excess electron of \( C_6F_6 \) being progressively stabilized by solvation (hydration). These sequential shifts carry information about the stepwise solvation energy and then another water (solvent) molecules are added to the system. Such shifts are governed by the following relationship: 24

\[
EA(XY_n) - EA(XY_{n-1}) = D[X\ Y_{n-1}\ldots Y] - D[XY_{n-1}\ldots Y],
\]

where \( EA(XY_n) \) is the adiabatic electron affinity of \( XY_n \), \( EA(XY_{n-1}) \) is the adiabatic electron affinity of \( XY_{n-1} \). \( D[X\ Y_{n-1}\ldots Y] \) is the dissociation energy for the \( X\ Y_n \) cluster anion to lose a single solvent molecule \( Y \) (i.e., the negative of the stepwise anion-neutral solvation/interaction energy), and \( D[XY_{n-1}\ldots Y] \) is the dissociation energy for the \( XY_n \) neutral cluster to lose a single solvent molecule \( Y \) (i.e., the negative of the stepwise neutral-neutral solvation/interaction energy).

Next, consider the relationship between VDE and \( EA_n \). The vertical detachment energy is equal to adiabatic electron affinity plus the neutral’s reorganization energy \( \lambda \), i.e.,

\[
\text{VDE} = EA_n + \lambda.
\]

While we did not measure \( EA_n \) per se, we did measure VDE values. The reorganization energies in all three \( C_6F_6(H_2O)_n \), \( n = 0-2 \), spectra are likely to be similar, both because the chromophore is the same in each case and because the spectral band shapes are empirically similar. Thus, if \( EA_n \) values in Eq. (1) are replaced by \( \text{VDE}-\lambda \), the \( \lambda \) values will roughly cancel, leaving the following sequential shift equation based on differences in VDE values for adjacent size cluster anions:

\[
\text{VDE}(XY_n) - \text{VDE}(XY_{n-1}) = D[X\ Y_{n-1}\ldots Y] - D[XY_{n-1}\ldots Y].
\]

As shown in Table I, we have measured VDE and \( E_F \) values for the photoelectron spectra of both \( C_6F_6(H_2O)_1 \) and \( C_6F_6(H_2O)_2 \). The VDE values in Table I lead to the sequential VDE shifts, \( \Delta \text{VDE} \), from the spectra of \( C_6F_6 \) to \( C_6F_6(H_2O)_1 \) and from the spectra of \( C_6F_6(H_2O)_1 \) to \( C_6F_6(H_2O)_2 \), and they are 0.23 and 0.15 eV, respectively.

The shift from the spectra of \( C_6F_6 \) to \( C_6F_6(H_2O)_1 \) is

\[
D[C_6F_6(H_2O)_1] - D[C_6F_6(H_2O)_2] = 0.23 \text{ eV.}
\]

Since Gallivan and Dougherty11 had calculated \( D[C_6F_6(H_2O)_2] \) to be 0.09 eV, \( D[C_6F_6(H_2O)_1] \) must be 0.32 eV or 7.4 kcal/mole. Thus, our estimate for the solvation (stabilization) energy of \( C_6F_6(H_2O)_1 \) by a single H2O molecule is ~7.4 kcal/mole. Likewise, the shift from the spectra of \( C_6F_6(H_2O)_1 \) to \( C_6F_6(H_2O)_2 \) is

\[
D[C_6F_6(H_2O)_1] - D[C_6F_6(H_2O)_2] = 0.15 \text{ eV.}
\]

Gallivan and Dougherty11 had also calculated \( D[C_6F_6(H_2O)_1] \) and found it to be 0.07 eV. Thus, \( D[C_6F_6(H_2O)_1] \) must be 0.22 eV or 5.1 kcal/mole. Thus, our estimate for the stepwise solvation energy of \( C_6F_6(H_2O)_1 \) by a second H2O molecule is ~5.1 kcal/mole.

**COMPUTATIONAL RESULTS**

The energies of the optimized structures of both the anionic species and their neutral counterparts are presented in Table II along with their adiabatic electron affinities and vertical detachment energies. Their corresponding geometries are shown in Fig. 2.

Figure 2(a) shows the computed structure of neutral hexafluorobenzene. Addition of an electron to hexafluorobenzene distorts the regular hexagon \( (D_{6h}) \) structure of the neutral molecule, resulting in a boatlike structure with \( C_2v \) symmetry as shown in Fig. 2(b). The most notable structural change upon forming the hexafluorobenzene anion is the bending of the two \( C-F \) bonds out of plane by as much as 27°. Furthermore, the carbon skeleton is also slightly distorted, changing the internal dihedral angles of the ring by 2.3°. The structural difference between the neutral and its anion is responsible for the broad Franck-Condon envelope (band) seen in the photoelectron spectrum of \( C_6F_6 \). This same structural difference is also likely to be the primary reason for the width of the bands in the spectra of \( C_6F_6(H_2O)_1 \) and \( C_6F_6(H_2O)_2 \), since \( C_6F_6 \) is the chromophore in both. The adiabatic electron affinity that we calculated for \( C_6F_6 \) is 0.72 eV, in good agreement with the calculated values of Xie et al.22 and Hou and Huang.23 The vertical detachment energy that we calculated for \( C_6F_6 \) is 1.78 eV, in reasonable accord with our experimental value of 1.55 eV.

The computed structure of neutral hexafluorobenzene-water complex is presented in Fig. 2(c). It shows the water molecule binding above the plane of \( C_6F_6 \) with the oxygen atom of the water molecule pointing directly toward the \( \pi \)

---

**TABLE II. Calculated energies of optimized anionic and neutral structures plus adiabatic electron affinities and vertical detachment energies.**

<table>
<thead>
<tr>
<th>Species</th>
<th>( E ) (a.u.)</th>
<th>ZPE (a.u.)</th>
<th>( E + \text{ZPE} ) (eV)</th>
<th>( EA_n ) (eV)</th>
<th>VDE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6F_6 )</td>
<td>-827.668</td>
<td>0.052</td>
<td>-22520.748</td>
<td>0.724</td>
<td>1.78</td>
</tr>
<tr>
<td>( C_6F_6 )</td>
<td>-827.690</td>
<td>0.047</td>
<td>-22521.472</td>
<td>0.947</td>
<td>1.78</td>
</tr>
<tr>
<td>( C_6F_6(H_2O)_1 )</td>
<td>-904.107</td>
<td>0.075</td>
<td>-24600.159</td>
<td>0.947</td>
<td>2.23</td>
</tr>
<tr>
<td>( C_6F_6(H_2O)_2 )</td>
<td>-904.139</td>
<td>0.072</td>
<td>-24601.106</td>
<td>0.947</td>
<td>2.23</td>
</tr>
<tr>
<td>( C_6F_6(H_2O)_3 ) (i)</td>
<td>-980.553</td>
<td>0.100</td>
<td>-26679.697</td>
<td>1.001</td>
<td>2.52</td>
</tr>
<tr>
<td>( C_6F_6(H_2O)_2 ) (ii)</td>
<td>-980.545</td>
<td>0.097</td>
<td>-26679.544</td>
<td>1.155</td>
<td>2.52</td>
</tr>
<tr>
<td>( C_6F_6(H_2O)_2 ) (ii)</td>
<td>-980.585</td>
<td>0.095</td>
<td>-26680.699</td>
<td>1.205</td>
<td>2.52</td>
</tr>
</tbody>
</table>
molecules are bound one above and one below the ring
mizes into two structures. In the first one, the two water
that shown in Fig. 2
agreement with our experimental value of 1.78 eV. Moreover,
robenzene and the formation of two O–H
bonds. The adiabatic electron affinity that we calculated for
 was 0.36 eV, where in the case of
hexafluorobenzene anion case, C6F6–H2O2, both water mol-
ecules are also hydrogen bonded to the hexafluorobenzene
anion but on opposite sides. Thus, even though neutral
hexafluorobenzene-water complexes are not bound by hydro-
gen bonding, their anionic hexafluorobenzene-water com-
plexes are, i.e., a hexafluorobenzene molecule hydrogen
bonds with water in the presence of an excess electron.

FIG. 2. Optimized anionic and neutral structures: (A) C6F6−, (B) C6F6−, (C) C6F6(H2O)1, (D) C6F6(H2O)1, (E) C6F6(H2O)2, and (F) C6F6(H2O)2.

system of the hexafluorobenzene, in agreement with the structure reported in the literature.\(^{11,12}\) Starting from the neutral complex, the structural optimization of the hexafluorobenzene-water anionic complex leads to the mig-
ratio of the water molecule into the plane of hexafluoro-
benzene and the formation of two O–H···F hydrogen
bonds. The adiabatic electron affinity that we calculated for
 was 0.95 eV. The vertical detachment energy that we calculated for
was 2.23 eV, in acceptable agreement with our experimental value of 1.78 eV.

The computed structure of neutral C6F6(H2O)2 mini-
mizes into two structures. In the first one, the two water
molecules are bound one above and one below the ring [see
Fig. 2(E)]. In the other structure, one water molecule is bound to the \(\pi\) system of the hexafluorobenzene, and the other water molecule is hydrogen bonded to it [see Fig. 2
(E)]. This structure can also be viewed as a water dimer
bound to hexafluorobenzene, and in any case, it is the most
stable structure. Starting from either neutral geometry, how-
ever, the structural optimization of C6F6(H2O)2 converges to
that shown in Fig. 2(f). There, both water molecules are hydro-
gen bonded to the hexafluorobenzene anion but on oppo-
site ends. The adiabatic electron affinity that we calculated for
was 1.16 eV. The vertical detachment energy that we calculated for
 was 2.52 eV, in rough ac-
cord with our experimental value of 1.93 eV. Furthermore,
in the cases of both C6F6(H2O)1 and C6F6(H2O)2, our cal-
culations show their hexafluorobenzene anion moieties re-
taining their nonplanar structures.

**DISCUSSION**

Our calculations link adiabatic electron affinities and vertical detachment energies to the optimized geometries of the three anionic species we studied and their neutral counterparts. The locations of these calculated EA\(_a\) values are marked on each of our photoelectron spectra in Fig. 1. In all three cases, they are seen to lie quite close to the spectral threshold energies \(E_T\) (see Table I). Especially in light of the fact that our measured \(E_T\) value from the photoelectron spec-
trum of C6F6 is close to all three calculated \(E_T\) values for the
EA\(_a\) of C6F6 (Xie et al.\(^{25}\), Hou and Huang,\(^{23}\) and this work), we see our calculated EA\(_a\) values for the three systems we studied as being consistent with their measured anion photo-
electron spectra. Likewise, our measured and calculated vertical detachment energies are consistent with one another. Thus, the experimental results authenticate the computed geo-
metries and thereby support our structural assignments.

In the case of the hexafluorobenzene-water anionic com-
plex, C6F6−(H2O)1, the water molecule is seen to lie in the
plane of hexafluorobenzene anion, bound by two O–H···F ionic hydrogen bonds, whereas in the case of the dihydrated hexafluorobenzene anion case, C6F6−(H2O)2, both water mol-
ecules are also hydrogen bonded to the hexafluorobenzene
anion but on opposite sides. Thus, even though neutral
hexafluorobenzene-water complexes are not bound by hydro-
gen bonding, their anionic hexafluorobenzene-water com-
plexes are, i.e., a hexafluorobenzene molecule hydrogen
bonds with water in the presence of an excess electron.

One can describe the role of the excess electron in two ways: (1) As causing an enhancement of electron density on the fluorine atoms of hexafluorobenzene or (2) as a monopole-dipole interaction due to electron attachment to hexafluorobenzene and the formation of the C6F6 anion. While these two pictures are not incompatible, the simple monopole-dipole model no doubt misses much of the struc-
tural detail of the interaction. Also, the fact that an anion interacts with a hydrogen atom (or atoms) at the positive end of a molecular dipole does not negate it having hydrogen bonding character. An example is the case of H+(NH3), where the hydride anion interacts with one (according to theory) of the ammonia molecule’s hydrogen atoms, largely through ionic hydrogen bonding.\(^{25}\) There, the interaction energy was measured to be 0.36 eV, where in the case of
was 0.32 eV, and in the case of
 was 0.22 eV.

Qualitatively, the present study reaches the conclusion that hexafluorobenzene does indeed hydrogen bond with wa-
ter in the presence of an excess electron, while quantitatively, it provides values for interaction energies. In the companion paper by Schneider et al.\(^{26}\) on the infrared spectroscopy of anionic hydrated fluorobenzenes, they and we reach the same conclusion as to the geometric structure of the hexafluorobenzene-monohydrate anion, C6F6−(H2O)1. Lastly,
it is interesting to imagine how additional water molecules will add to C₆F₆⁻, especially once the in-plane sites are filled. Will the first solvent shell exhibit both in-plane, hydrogen bonded and out-of-plane, non-hydrogen-bonded (dipole-quadrupole/lone pair π cloud) interactions?

ACKNOWLEDGMENTS

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16 Peripheral electron density here pertains to the electron density at the hypothetical bond critical point for penta- and hexafluorobenzenes.