Probing the electronic structures of low oxidation-state uranium fluoride molecules UF$_x$ ($x = 24$)
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Probing the electronic structures of low oxidation-state uranium fluoride molecules $\text{UF}_x^- (x = 2–4)$

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We report the experimental observation of gaseous $\text{UF}_x^- (x = 2–4)$ anions, which are investigated using photoelectron spectroscopy and relativistic quantum chemistry. Vibrationally resolved photoelectron spectra are obtained for all three species and the electron affinities of $\text{UF}_x^- (x = 2–4)$ are measured to be 1.16(3), 1.09(3), and 1.58(3) eV, respectively. Significant multi-electron transitions are observed in the photoelectron spectra of $\text{U}(5f^77s^2)\text{F}_2^-$, as a result of strong electron correlation effects of the two 7s electrons. The $\text{U}–\text{F}$ symmetric stretching vibrational modes are resolved for the ground states of all $\text{UF}_x^- (x = 2–4)$ neutrals. Theoretical calculations are performed to qualitatively understand the photoelectron spectra. The entire $\text{UF}_2^-$ and $\text{UF}_x^- (x = 1–6)$ series are considered theoretically to examine the trends of $\text{U}–\text{F}$ bonding and the electron affinities as a function of fluorine coordination. The increased $\text{U}–\text{F}$ bond lengths and decreased bond orders from $\text{UF}_2^-$ to $\text{UF}_4^-$ indicate that the $\text{U}–\text{F}$ bonding becomes weaker as the oxidation state of U increases from I to III.

I. INTRODUCTION

Actinide chemistry has attracted significant recent attention because of the importance of nuclear energy and the issues related to the disposal of nuclear wastes. Understanding the electronic structures and chemical bonding of uranium compounds is important for developing efficient extraction agents for nuclear waste management and advanced nuclear fuel cycle.¹ The most common and most important uranium fluoride is uranium hexafluoride ($\text{UF}_6$), which is used in the nuclear industry for isotope separation to produce $^{235}$U-enriched nuclear fuels. The $\text{UF}_6$ molecule in the gas phase has been extensively studied both experimentally and theoretically.²–⁴¹ It is a perfect octahedral molecule ($\text{O}_h$ symmetry) with a $\text{U}–\text{F}$ bond length of 1.996 ± 0.008 Å,² in which U is in its most stable oxidation state of VI. $\text{UF}_5$ is a photolysis product of $\text{UF}_6$ and can be produced by reactions of uranium with fluorine.⁵ The $\text{UF}_3$ molecule, which has $\text{C}_{4v}$ symmetry, has also been well characterized.⁵–⁷,31–35 Uranium tetrafluoride ($\text{UF}_4$) is a stable compound, in which U has an oxidation of $\text{U}^{4+}$ ($5\text{f}^2$). The $\text{UF}_4$ molecule in the gas phase has $\text{T}_d$ symmetry with a bond length of 2.056 ± 0.001 Å.³⁶,³⁷ However, there have been suggestions that $\text{UF}_4$ may have a distorted tetrahedral structure due to the Jahn-Teller effect.³⁸–⁴¹ More recent infrared spectroscopy data seem to support the $\text{T}_d$ symmetry in the gas phase.³⁷,⁴²

Although there have been extensive investigations on the $\text{UF}_x (x = 4–6)$ molecules, much less is known about the lower oxidation-state $\text{UF}_x$ species, primarily because these are all transient species and are expected to be highly reactive. $\text{UF}_x^+ (x = 1–4)$ cations were observed by mass spectrometry.³² $\text{UF}_x^- (x = 1–3)$ species were proposed to exist in noble gas matrix,³³ but the absorption spectra attributed to UF and $\text{UF}_2$ were later reassigned to HF dimer and trimer, respectively.³²,³³ Only very recently, a spectroscopic and theoretical study is reported on the diatomic UF and $\text{UF}_4^+$.⁴³ Even though there have been a number of theoretical investigations on the geometries and vibration frequencies of $\text{UF}_x (x = 1–6)$ systematically,⁴⁴–⁴⁸ there is little experimental information available for low oxidation-state uranium fluoride species. The low oxidation state $\text{UF}_x$ species with unpaired 5f or 7s electrons are expected to exhibit more complicated electronic structures and possess rich spectroscopic information, which will provide better systems to compare with theoretical calculations and verify new computational methods. Our recent investigation on $\text{UO}_2^-$, which has a $(7\text{s})^2(5\text{f})$ electron configuration, illustrates an example that gives extremely rich photoelectron spectra due to strong electron correlation effects.⁴⁹ Accurate calculations involving both the initial and final states, with inclusion of electron correlation and spin-orbit coupling effects, are needed to interpret the observed spectra.

In this article, we report the first observation of gaseous $\text{UF}_x^- (x = 2–4)$ anionic species and their characterization using photoelectron spectroscopy (PES) and quantum chemical calculations. Vibrationally resolved photoelectron spectra have been obtained for each species at several photon energies. The photoelectron spectra show all three species have much lower electron binding energies than the previously

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observed UF$_5^-$ and UF$_6^-$. The adiabatic detachment energies (ADEs) of the anions or the electron affinities (EAs) of the corresponding neutral UF$_x$ ($x = 2$–$4$) species are accurately measured. The geometries, bond order indexes, and ADEs of the UF$_x^-$ ($x = 2$–$4$) species are calculated. The experimental spectra are qualitatively understood using the calculated electron configurations of UF$_x^-$ ($x = 2$–$4$).

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Photoelectron spectroscopy

The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which have been published in Ref. 50. In brief, a uranium plasma was generated by laser vaporization of a uranium disk target (Goodfellow Corporation) with a helium carrier gas containing a small amount of F$_2$. Plasma reactions between the laser-vaporized uranium atoms and F$_2$ produced the desired UF$_x^-$ ($x = 2$–$4$) species. The F$_2$ concentrations were adjusted to obtain a given UF$_x^-$ species by mixing a 0.05% F$_2$-in-helium gas with a 5% Ar-in-helium gas. Because of the high reactivity between U and F$_2$, stable UF$_2^-$ and UF$_3^-$ anion beams were produced with the residual F$_2$ in the gas line after exposure to the F$_2$ gas, whereas little UF$^-$ anion could be produced under our experimental conditions. The anions were entrained in the Ar/He carrier gas and underwent a supersonic expansion to form a cold and collimated molecular beam after passing a skimmer. Anions from the beam were extracted perpendicularly and analyzed by a time-of-flight mass spectrometer. The anions of interest were mass-selected and decelerated before being photodetached by a laser beam at 193 nm (6.424 eV) from an ArF excimer laser, and 266 nm (4.661 eV), 355 nm (3.496 eV), or 532 nm (2.331 eV) from a Nd-YAG laser. Photoelectrons were analyzed in a 3.5 m long flight tube and the photoelectron spectra were calibrated by the known spectra of Au$^-$ and Bi$^-$.

B. Theoretical methods

Theoretical calculations were carried out for UF$_x^-$ ($x = 1$–$6$) using spin-unrestricted Kohn-Sham density functional theory. The generalized-gradient approach with PBE exchange-correlation functional was used as implemented in the Amsterdam Density Functional program (ADF 2010.01). In these calculations, we used the PBE functional with zero-order-regular approximation (ZORA) for the scalar relativistic (SR) and spin-orbit (SO) effects. The frozen core approximation was applied to the $[1s^2]$ core of F and the $[1s^2]5d^{10}$ core of U, with the rest of the electrons explicitly treated variationally. The uncontracted Slater bases sets with triple-$\zeta$ plus two polarization functions (TZ2P) were used for the valence electrons. The geometries were fully optimized for various possible electron configurations and vibrational frequencies were computed analytically. Mulliken population analysis, Mayer bond order, Gopinathan-Jug (G-J) bond orders, and three-types of Naletwajski-Mrozek (N-M) bond orders, were performed to understand the U-F bonding in the UF$_x$ complexes. Because of the nearly degenerate spin multiplets, we also carried out geometry optimizations using the hybrid B3LYP functional and subsequent CCSD(T) single-point energy calculations with the NWChem program. In these calculations, the aug-cc-pVTZ (AVTZ hereafter) basis set was used for F, and SDD pseudopotential and basis set with 30 valence electrons were used for uranium, where the scalar relativistic effects were included through the quasi-relativistic pseudopotential.

III. EXPERIMENTAL RESULTS

The photoelectron spectra of UF$_x^-$ ($x = 2$–$4$) at four different photon energies are shown in Figs. 1–3, respectively. The observed PES bands are labeled with letters (X, A, B, C, D) and the measured vertical detachment energies (VDEs), ADEs, and vibrational frequencies are summarized in Table I. The use of the Ar-seeded helium carrier gas was shown previously to produce very cold gold cluster anions. Very recently high resolution photoelectron imaging experiments showed that with the Ar-seeded helium carrier gas we could produce vibrationally cold Au$_4^-$ clusters, for which vibrational hot bands were completely eliminated. The sharp onset in the 532 nm spectra of UF$_2^-$ (Fig. 1(a)) and UF$_3^-$ (Fig. 2(a)) suggested that these anions were vibrationally cold. We only observed very weak vibrational hot band in the 532 nm spectrum of UF$_4^-$ (Fig. 3(a)). The cold anions and the vibrationally resolved photoelectron spectra at 532 nm were critical for us to evaluate the ADEs for the anions. In each spectrum, the X band represents the transition from the anionic ground electronic state to that of the neutral. The A, B, C, and D bands denote transitions from the anionic ground electronic state to the excited states of the neutrals. The weak broad features in the energy region from 2 to 4 eV in the UF$_2^-$ spectra are labeled with low-case letters $a$, $b$, $c$… and their peak positions are also listed in Table I.

A. Photoelectron spectra of UF$_2^-$

The photoelectron spectrum of UF$_2^-$ at 532 nm (Fig. 1(a)) shows a well-resolved features (X and A) in the low binding energy range and three weak peaks (B, C, D). The low binding energy features seem to consist of two vibrational progressions. The progression labeled as X has a VDE of $1.18 \pm 0.03$ eV with a vibrational spacing of $580 \pm 30$ cm$^{-1}$. Each vibrational peak has a splitting of about 20 meV, indicating excitation of another vibrational mode with a low frequency of about $160 \pm 30$ cm$^{-1}$. The ADE is defined by the 0-0 transition to be $1.16 \pm 0.03$ eV (Table I), which represents the EA of UF$_2$. The progression labeled with A has an origin at $1.31 \pm 0.03$ eV with an average vibrational spacing of $510 \pm 30$ cm$^{-1}$. Each vibrational peak of band A is also fairly broad, indicating unresolved low frequency vibrational features. Three weak and relatively sharp features labeled as B, C, and D are observed at $1.76 \pm 0.03$ eV, $1.84 \pm 0.03$ eV, and $1.90 \pm 0.03$ eV, respectively.
FIG. 1. Photoelectron spectra of UF$_2^-$ at (a) 532 nm, (b) 355 nm, (c) 266 nm, and (d) 193 nm. The vertical lines in the inset indicate vibrational structures.

The spectra of UF$_2^-$ at 355 nm (Fig. 1(b)) and 266 nm (Fig. 1(c)) show weak and almost continuous signals in the 2–4 eV region. Three broad features can be tentatively identified as $a$ at $\sim 2.2$ eV, $b$ at $\sim 2.7$ eV, and $c$ at $\sim 3.2$ eV. Another feature $E$ is observed at $\sim 4.3$ eV in the 266 nm spectrum (Fig. 1(c)), but it became rather weak in the 193 nm spectrum (Fig. 1(d)), most likely due to the severe noise in the high binding energy range that resulted in poor signal to noise ratios after background subtraction. The continuous signals observed between 2 and 4 eV indicate a high density of electronic states in this energy region in neutral UF$_2$. They are similar to those observed in the photoelectron spectra of UO$_2^-$ observed recently, as a result of two-electron detachment transitions.$^{49}$

B. Photoelectron spectra of UF$_3^-$

The 532 nm spectrum of UF$_3^-$ (Fig. 2(a)) displays three broad features, an intense band X and two relatively weak bands A and B. The intense band X with a VDE of 1.16 $\pm$ 0.03 eV contains congested vibrational features. The ADE of band X is evaluated by drawing a tangential line along the leading edge and then adding the instrumental resolution to the intersection with the binding energy axis. The so
FIG. 3. Photoelectron spectra of UF$_4^-$ at (a) 532 nm, (b) 355 nm, (c) 266 nm, and (d) 193 nm. The vertical lines in the inset indicate vibrational structures.

obtained ADE for UF$_3^-$ is 1.09 $\pm$ 0.03 eV (Table I), which is also the EA of neutral UF$_3$. Band X contains two possible vibrational progressions, a long progression with a spacing of 530 $\pm$ 50 cm$^{-1}$ and tentatively a short progression with a spacing of 260 $\pm$ 50 cm$^{-1}$. The weak band A has an estimated VDE of $\sim$1.8 eV. At 355 nm (Fig. 2(b)), band B is observed to be quite broad, which may be due to extensive vibrational excitations or multiple detachment transitions. The VDE of band B is estimated to be $\sim$2.2 eV. Following a large energy gap, a broad band C is observed at a VDE of $\sim$4.5 eV in the 266 and 193 nm spectra.

C. Photoelectron spectra of UF$_4^-$

The 532 nm spectrum of UF$_4^-$ shown in Fig. 3(a) displays a nice vibrational progression. Each vibrational peak seems to be a doublet. Careful examination shows that there are two similar vibrational progressions, which should correspond to two nearly degenerate detachment channels. The ground state vibrational progression X has a slightly higher frequency of 620 $\pm$ 20 cm$^{-1}$, whereas the slightly higher energy progression A has a frequency of 600 $\pm$ 20 cm$^{-1}$. The 0–0 transition of band X defines an ADE of 1.58 $\pm$ 0.03 eV (Table I), which represents the EA of UF$_4$. A very weak hot band was observed around 1.50 eV. The ADE of band A is measured to be 1.61 $\pm$ 0.03 eV. The VDEs of bands X and A cannot be measured from the 532 nm, because of the cut-off in the high binding side. The 355 nm spectrum (Fig. 3(b)) shows that the v = 5 vibrational level defines the VDEs for bands X and A, which are measured from the 532 nm as 1.97 $\pm$ 0.03 eV and 1.98 $\pm$ 0.03 eV, respectively. The 355 nm spectrum (Fig. 3(b)) reveals a new band B also with an extensive vibrational progression that overlaps with those of bands X and A. The VDE of band B is estimated to be 2.50 $\pm$ 0.03 eV. The 266 nm spectrum (Fig. 3(c)) does not reveal additional bands, while the 193 nm spectrum (Fig. 3(d)) shows a broad feature C at a VDE of $\sim$5.1 eV following a large energy gap.

IV. THEORETICAL RESULTS

The symmetries, ground-state electron configurations, and structural parameters for UF$_x$ and UF$_x^-$ ($x = 1–6$) are summarized in Table II, where the calculated first ADEs for the anions are also given. The geometry optimizations were performed on UF$_x^-$ ($x = 1–6$) with various electron configurations. The most stable configurations for UF$_x^-$ ($x = 1–6$) anions are U(5f)$^3$(7s)$^2$(6d)$^1$, U(5f)$^3$(7s)$^2$, U(5f)$^3$(7s)$^2$, U(5f)$^3$(7s)$^1$, (5f)$^3$, U(5f)$^2$, and U(5f)$^1$, respectively. While these electron configurations and molecular symmetries are consistent with previous calculations on the neutral species,$^{44}$ they should be considered as tentative because of the complexity arising from the strong electron correlation and configuration-mixing due

<table>
<thead>
<tr>
<th>Observed features</th>
<th>UF$_2^-$</th>
<th>UF$_3^-$</th>
<th>UF$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VDEs (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>1.18(3)</td>
<td>1.16(3)</td>
<td>1.97(3)</td>
</tr>
<tr>
<td>A</td>
<td>1.31(3)</td>
<td>$\sim$1.8</td>
<td>1.98(3)</td>
</tr>
<tr>
<td>B</td>
<td>1.76(3)</td>
<td>$\sim$2.2</td>
<td>2.50(3)</td>
</tr>
<tr>
<td>C</td>
<td>1.84(3)</td>
<td>$\sim$4.5</td>
<td>$\sim$5.1</td>
</tr>
<tr>
<td>D</td>
<td>1.90(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>$\sim$4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>$\sim$2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>$\sim$2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>$\sim$3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADE (eV)$^b$</td>
<td>1.16(3)</td>
<td>1.09(3)</td>
<td>1.58(3)</td>
</tr>
<tr>
<td>Frequency (cm$^{-1}$)</td>
<td>580(30)</td>
<td>530(50)</td>
<td>620(20)</td>
</tr>
</tbody>
</table>

$^a$Numbers in parentheses represent the uncertainty in the last digits. $^b$This also represents the electron affinity of the neutral UF$_x$ species.
to spin-orbit coupling. For instance, theoretical analyses with only SR effects cannot resolve the debate regarding the geometry of the UF₄ molecule because its \((t_2)^2\) electron configuration is in principle subject to a Jahn-Teller distortion. With spin-orbit coupling the \(t_2\) MOs under \(T_d\) symmetry transform into \(u_{3/2} + e_{5/2}\) spinors in double-group symmetry. Our preliminary SO-ZORA calculations with PBE functional show that the quadruply degenerate \(u_{3/2}\) spinor is well below the \(e_{5/2}\) spinor (by \(\sim 0.63\) eV), implying a \((u_{3/2})^2\) ground state electron configuration, which is still Jahn-Teller active. Therefore, the geometry slightly distorts into \(D_{2d}\) symmetry even with spin-orbit coupling, but the distortion is nearly negligible relative to \(T_d\) symmetry because of the weak coupling between the \(5f\) states, as shown in Table II. For UF₃⁻, the most stable configuration at SR level is \(5f^4\). However, with inclusion of SO effects, the most stable configuration is \(5f^27s^1\). It is likely that the ground state of UF₃⁻ involves a strong mixing of the \(5f^3\) and \(5f^27s^1\) configurations.

V. DISCUSSION

Figure 4 depicts the contours of the occupied valence molecular orbitals of UFₙ⁻ \((x = 2–4)\) based on SR calculations. Quantitative assignments of the PES spectra of these open-shell species to specific electronic states of the neutrals are challenging because of the strong electron correlation and spin-orbit effects in the initial and final states involved in the electron detachment, as demonstrated in our recent detailed study of UO₂⁻.⁴⁹ Here we propose qualitative assignments of the photoelectron spectra on the basis of the MO configurations and the drastically different detachment cross sections for the \(5f\) or \(7s\)-based MOs. Our previous PES studies on UF₅⁻ and UCl₅⁻ show that the detachment cross sections for the \(5f\)-based MOs are much smaller relative to those of the ligand-based MOs.⁵¹,⁶⁹

A. UF₂⁻ and strong multi-electron transitions

The UF₂⁻ anion has an electron configurations of U(5f)³(7s)² and neutral UF₂ has a U(5f)³(7s)¹ configuration, as shown in Table II and Fig. 4(a). Hence, the first detachment channel should correspond to removal of a \(7s\) electron, resulting in both a quintet and triplet final state. At the SR level, the triplet neutral state is 0.075 eV higher than the quintet state. This energy difference is in good agreement with the experimental energy separation between the X and A bands in the photoelectron spectra of UF₂⁻ (\(\sim 0.13\) eV in Table I). Thus, the ground state of UF₂ should correspond to the quintet state and the A band should correspond to the triplet final state. The relatively high intensities of the X and A bands are consistent with electron detachment from 5f-based MOs. Electron detachments from the three unpaired 5f-based MOs should each produce a triplet final state with close energies and should correspond to the weak and relatively sharp features B, C, and D. The very weak intensities of these peaks relative to the X and A bands are consistent with electron detachment from \(5f\)-based MOs. Electron detachment from the ligand-based F₂p MOs should have high electron binding energies, corresponding to the relatively broad band E at \(\sim 4.3\) eV. As will be seen below, the

TABLE II. Molecular symmetries, electron configurations, geometries, and energies of UFₓ and UFₓ⁻ \((x = 1–6)\).

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Configuration</th>
<th>U-F bond length (Å)</th>
<th>ΘBUF (deg)</th>
<th>ADESO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF₁⁻→O₀</td>
<td>(5f)⁰(7s)⁰</td>
<td>2.095</td>
<td>90.0</td>
<td>4.07</td>
</tr>
<tr>
<td>UF₁⁻→C₁</td>
<td>(5f)⁰(7s)⁰</td>
<td>2.128(e), 2.125(e)</td>
<td>102.6, 87.3</td>
<td>2.63</td>
</tr>
<tr>
<td>UF₂⁻→D₂</td>
<td>(5f)²(7s)²</td>
<td>2.147</td>
<td>106.6, 110.0</td>
<td>1.66</td>
</tr>
<tr>
<td>UF₂⁻→C₁</td>
<td>(5f)³(7s)³</td>
<td>2.136</td>
<td>110.0</td>
<td>0.89</td>
</tr>
<tr>
<td>UF₂⁻→C₂</td>
<td>(5f)³(7s)³</td>
<td>2.092</td>
<td>105.2</td>
<td>0.88</td>
</tr>
<tr>
<td>UF⁻→C₃+</td>
<td>(5f)³(7s)³(6d)¹</td>
<td>2.075</td>
<td>...</td>
<td>0.25</td>
</tr>
<tr>
<td>UF₆⁻→O₀</td>
<td>(5f)⁰(7s)⁰</td>
<td>2.021</td>
<td>90.0</td>
<td>3.1</td>
</tr>
<tr>
<td>UF₃⁻→C₁</td>
<td>(5f)³(7s)³</td>
<td>2.052(a), 2.036(e)</td>
<td>95.89(ae), 89.4(ee)</td>
<td></td>
</tr>
<tr>
<td>UF₄⁻→D₂</td>
<td>(5f)²(7s)²</td>
<td>2.067</td>
<td>109.2, 109.8</td>
<td>0.89</td>
</tr>
<tr>
<td>UF₃⁻→C₁</td>
<td>(5f)³(7s)³</td>
<td>2.066</td>
<td>102.0</td>
<td>0.89</td>
</tr>
<tr>
<td>UF₃⁻→C₂</td>
<td>(5f)³(7s)³</td>
<td>2.054</td>
<td>101.7</td>
<td>0.89</td>
</tr>
<tr>
<td>UF⁻→C₃+</td>
<td>(5f)³(7s)³</td>
<td>2.022</td>
<td>...</td>
<td>0.25</td>
</tr>
</tbody>
</table>


—a All the electron configurations, bond lengths, and bond angles are calculated using PBE functional with SO-ZORA Hamiltonian.

—b and c denote axial and equatorial ligands, respectively.

FIG. 4. Contours of the scalar-relativistic valence molecular orbitals of (a) UF₂⁻→(C₁), (b) UF⁻→(C₂), and (c) UF₁⁻→(D₂).
binding energies for electron detachment from the F2p based MOs all have similarly high binding energies in the UF$_3^-$ and UF$_4^-$ cases as well.

Hence, no more one-electron detachment channels are expected between 2 and 4 eV. However, almost continuous transitions are observed in this photoelectron spectral region, as seen in Fig. 1 (bands labeled as a, b, c). These observations are reminiscent of the photoelectron spectra of the linear UO$_2^-$ anion, which has a U(7s$^2$5f$^1$) electron configuration. Because of the strong correlation between the pair of 7s electrons, an unprecedented number of two-electron transitions were observed as a result of getting one 7s electron and simultaneous excitation of the other 7s electron to higher-lying unoccupied 7f orbitals. Such strong electronic correlation effects between electrons in s-type orbitals have been commonly observed in photoionization processes.

Our calculated ADE for UF$_2^-$ is 0.88 eV (Table II), in reasonable agreement with the experimental value of 1.16 eV. We have shown previously that DFT calculations tend to underestimate the electron binding energies for U-containing complexes. The U–F symmetric stretching frequency of the neutral UF$_2$ was calculated to be 554 cm$^{-1}$ previously, in good agreement with the measured frequency for the ground state band X (580 cm$^{-1}$). The U–F bond length decreases slightly (by 0.038 Å) in UF$_2$ relative to the anion (Table II), consistent with the short U–F vibrational progression observed in the X band (Fig. 1(a)). The X-FUF angle in UF$_2$ is decreased by 3.5$^\circ$, in agreement with the observed low-frequency vibrational excitation in the X band, which should be due to the bending mode.

**B. UF$_3^-$**

The UF$_3^-$ anion has a quintet ground state with a U(5f$^3$7s$^2$) electronic configuration while neutral UF$_3$ has a U(5f$^3$7s$^0$) configuration (Table II and Fig. 4(b)). The first detachment channel is then from removal of the 7s-based $a_1$ electron (Fig. 4(b)), resulting in the ground state band X (Fig. 2). The strong relative intensity of this band is consistent with detachment from a 7s-based orbital. The next detachment channel should correspond to the removal of the 5f-based $a_1$ electron, corresponding to the weak band A. Detachment from the degenerate 5f-based $e_1$ orbital (Fig. 4(b)) should correspond to the broad band B. The width of band B is likely a result of the Jahn-Teller effect, expected from detachment from the degenerate $e_1$ orbital. The relative weak intensities of bands A and B are consistent with their 5f characters. The broad band C at 4.45 eV should come from detachment of F2p-based MOs. It is interesting to note that all the observed PES bands for UF$_3^-$ correspond to one-electron detachment transitions. Unlike the UF$_2^-$ case above, there is no evidence of multi-electron transitions. This observation provides indirect confirmation for the U(5f$^3$7s$^2$) electron configuration of UF$_3^-$. We would expect strong multi-electron transitions for a U(5f$^3$7s$^2$) configuration because of the strong correlation effects of the 7s electrons, as observed for UF$_2^-$ above and UO$_2^-$ previously.

The ADE of UF$_3^-$ is calculated to be 0.89 eV, again underestimated in comparison with the experimental value of 1.09 eV (Table I). Both the ground states of UF$_3^-$ and UF$_2$ have C$_3v$ symmetry, but the U–F bond length and X-FUF bond angle decrease significantly in the neutral (Table II), suggesting a long vibrational progression in the symmetric vibrational mode and also major Franck-Condon activities in the umbrella mode. These structural changes are in agreement with the broad and congested PES band observed for the ground state transition (Fig. 2(a)). The frequency of the totally symmetric U–F breathing mode of UF$_3$ was calculated to be 543 cm$^{-1}$ previously, in good agreement with the main vibrational progression of 530 cm$^{-1}$. The extensive Franck-Condon activities in both the stretching and bending modes of UF$_3$ would be expected to produce a very complicated and congested ground state vibrational progression, as observed experimentally.

**C. UF$_4^-$**

The ground state electron configuration of the UF$_4^-$ anion is more complicated. At the SR level, it has a 5f$^6$ configuration in its ground state. However, when SO coupling is included, the configuration becomes 5f$^2$7s$^4$. It is possible that the ground state of UF$_4^-$ is multi-configurational with strong mixing of the two configurations. The relatively strong intensities of all the three observed PES bands at low binding energies are consistent with strong contributions of 7s characters in each of the detachment channel. The broad band C at $\sim$5.1 eV should come from detachment of F2p-based orbitals. There is a slight increase of the binding energies of this detachment feature from UF$_2^-$ to UF$_4^-$ (Figs. 1–3). The ADE of UF$_4^-$ is calculated to be 1.66 eV, in good agreement with the measured value of 1.58 eV (Table I). There is a large U–F bond length reduction in the neutral UF$_4$ ground state (by 0.08 Å) and little change in the X-FUF bond angles, in excellent agreement with the long vibrational progression (Fig. 3(a)), which should be due to the totally symmetric stretching mode with no discernible activity of any bending modes. The previously calculated frequency for the U–F breathing mode was 598 cm$^{-1}$, close to the experimentally measured frequency of 620 cm$^{-1}$. Our experiment indicates that the first excited state of UF$_4$ (band A) is nearly degenerate with the ground state (band X) and they have similar structures. In fact, the observation of a simple stretching vibrational progression for the ground state detachment transition without any hint of bending excitation suggests that both UF$_4^-$ and UF$_4$ in their ground states may possess the high symmetry Td structure, even though our current DFT calculations suggest a very slight distortion to a D$_{2d}$ structure for both the anion and neutral uranium tetra-fluoride.

The low oxidation-state UF$_4^-$ species with open 5f and 7s shells are challenging electronic systems. Advanced \textit{ab initio} wavefunction calculations with both dynamic and static electron correlations and relativistic effects (including
TABLE III. The calculated Mulliken charges and bond orders of UF$_x^-$ (x = 1–6) based on different bonding index schemes.

<table>
<thead>
<tr>
<th>Charge</th>
<th>Bond order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q(U)</td>
</tr>
<tr>
<td>UF$_2^-$</td>
<td>2.32</td>
</tr>
<tr>
<td>UF$_3^-$</td>
<td>1.90</td>
</tr>
<tr>
<td>UF$_4^-$</td>
<td>1.19</td>
</tr>
<tr>
<td>UF$_5^-$</td>
<td>0.51</td>
</tr>
<tr>
<td>UF$_6^-$</td>
<td>-0.25</td>
</tr>
<tr>
<td>UF$_7^-$</td>
<td>-0.62</td>
</tr>
</tbody>
</table>

spin–orbit coupling) are necessary to provide quantitative interpretations of the PES data. The rich electronic structure information would be ideal for verifying new computational methods for accurate treatments of the electronic structures of open-shell actinide compounds.

VI. CONCLUSIONS

The low oxidation-state UF$_x^-$ (x = 2–4) species are observed and investigated using photoelectron spectroscopy and theoretical calculations. Vibrationally resolved photoelectron spectra are reported for all three species and the electron affinities of the three neutral UF$_x$ (x = 2–4) species are accurately measured. The observed spectral features are qualitatively understood on the basis of the calculated electron configurations and the large differences of detachment cross sections from 5f or 7s-based orbitals. The electron binding energies of F$_2$p-based orbitals are quite high and increases steadily from x = 2–4. Strong multi-electron transitions are observed for UF$_5^-$, due to its 5f$^3$7s$^2$ configuration. As the F coordination increases in UF$_x^-$, the U–F bond lengths increase and the bond strengths decrease, consistent with the calculated bond orders. The low oxidation-state UF$_x^-$ species possess rich electronic structures and are ideal test cases to verify computational methods for accurate treatment of actinide compounds.

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