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Photoelectron spectroscopy and theoretical studies of UF₅⁻ and UF₆⁻

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The UF₅⁻ and UF₆⁻ anions are produced using electrospray ionization and investigated by photoelectron spectroscopy and relativistic quantum chemistry. An extensive vibrational progression is observed in the spectra of UF₅⁻, indicating significant geometry changes between the anion and neutral ground state. Franck-Condon factor simulations of the observed vibrational progression yield an adiabatic electron detachment energy of 3.82 ± 0.05 eV for UF₅⁻. Relativistic quantum calculations using density functional and *ab initio* theories are performed on UF₅⁻ and UF₆⁻ and their neutrals. The ground states of UF₅⁻ and UF₅ are found to have C_{4v} symmetry, but with a large U–F bond length change. The ground state of UF₅⁻ is a triplet state (³B₂) with the two 5f electrons occupying a $5f_{z^3}$ -based 8a₁ highest occupied molecular orbital (HOMO) and the $5f_{xyz}$ -based 2b₂ HOMO-1 orbital. The detachment cross section from the $5f_{xyz}$ orbital is observed to be extremely small and the detachment transition from the 2b₂ orbital is more than ten times weaker than that from the 8a₁ orbital at the photon energies available. The UF₆⁻ anion is found to be octahedral, similar to neutral UF₆ with the extra electron occupying the $5f_{xyz}$ -based a_{2u} orbital. Surprisingly, no photoelectron spectrum could be observed for UF₆⁻ due to the extremely low detachment cross section from the $5f_{xyz}$ -based HOMO of UF₆⁻. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4716182]

I. INTRODUCTION

Uranium hexafluoride (UF_6) has attracted much attention because of its importance in uranium enrichment for nuclear technology.¹ The U atom has its highest oxidation state of VI in UF₆ with a valence electron configuration of 5f⁰6d⁰, where the 5f and 6d orbitals can participate in back bonding with the ligands of ungerade and gerade symmetries, respectively.^{2,3} Single crystal neutron diffraction studies showed that UF₆ has an octahedral symmetry (O_h) with a mean U–F bond length of 1.995 \pm 0.002 Å at 293 K,4-6 and there is clear evidence of strong participation of the 5f orbitals in the chemical bonding.^{2,3,7,8} Furthermore, the short U-F bond has been suggested to have multiple-bond characters with U forming six σ bonds while being a good π acceptor.⁸ All six fundamental modes of vibration for the highly symmetric Oh UF6 are known from Raman and infrared spectroscopy.9-16 The electronic structure of UF₆ has also been well studied with absorption spectroscopy,^{17–19} electron impact spectroscopy,^{20,21} and photoelectron spectroscopy (PES).^{22,23} To understand these available experimental data, computational actinide chemistry has experienced a steady growth in developing better relativistic quantum chemistry methods.^{24–27} The electronic structure of UF₆ has been extensively studied theoretically.^{24,25,27–50} Similar to neutral UF₆, the UF₆⁻ anion in the Cs⁺[UF₆⁻] crystal has also been shown to possess the O_h symmetry.⁵¹ The ground state of UF_6^- has the neutral UF_6 electronic configuration^{33,52–57} with the additional electron populating the nonbonding a_{2u} orbital, which is mainly of U f_{xyz} character.^{29,58}

The structure of the isolated uranium pentafluoride (UF_5) is a product of photolysis of UF_6 in laser isotope separation.¹ Three infrared peaks at 584, 561, and 646 cm⁻¹ were observed for UF₅ in an argon matrix, confirming its C_{4v} symmetry.⁵⁹ Under the C_{4y} symmetry, the sevenfold degenerate 5f orbitals split into five sets of molecular orbitals (MOs), two of which are doubly degenerate.^{28,60} Both ligand field theory and ab initio theoretical calculations predicted the energy order of these MOs as: $b_2 < e < b_1 < a_1 < e^{28,60}$ Thus, the ground state of UF₅ is ²B₂, corresponding to the occupation of the b_2 MO, mainly of U f_{xyz} character.^{28,60} Thus, both UF₅ and UF₆⁻ share a similar f_{xyz}-based highest occupied molecular orbital (HOMO), despite their different symmetries. The absorption spectra of UF₅ are complicated, only revealing the energy separation between the ground state and the highest 5f orbital at about 14 647 cm⁻¹.⁶¹⁻⁶³ The overlapping vibronic manifolds from more than one electronic transition made it difficult to assign higher electronic transitions.^{60,62} This observation is consistent with the calculated electronic structure of UF5 including the spin-orbit (SO) coupling effects, which give rise to a high density of electronic states.⁶⁰ For example, the energy gap between the ground state and the next higher f orbital is only about 0.33 eV^{60} In contrast to UF₅, there is little experimental and theoretical work on the UF5⁻ anion. It would be interesting to see how adding an electron to the system will alter the electronic structure of the neutral UF₅ in the $5f^2$ UF₅⁻ system.

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Despite the importance of UF₆ and UF₅, their electron affinities (EAs) are not accurately known. Charge transfer experiments between UF₆ and alkali atoms led to the estimation of the EAs of UF₅ and UF₆ to be about 4.0 ± 0.4 eV and ≥ 5.1 eV, respectively.^{64,65} Charge transfer reaction between UF₆⁻ and BF₃ yielded an EA of about 4.9 ± 0.5 eV for UF₆.⁶⁶ Ion equilibrium studies suggested similar EA values, about 3.7 ± 0.2 eV for UF₅ and 5.1 ± 0.2 eV for UF₆.^{67,68}

Photoelectron spectroscopy is a powerful experimental technique to study the electronic structures of molecules. In principle, anion PES can provide accurate EA values for the corresponding neutrals, if the 0-0 transition in the PES spectra can be observed from vibrationally resolved data. Besides, anion PES can provide rich information about the ground and excited states of the neutral UF_x species. In the current paper, we report a combined PES and theoretical study on UF5⁻ and UF_6^- in the gas phase. Vibrationally resolved PES spectra have been observed for UF5⁻, yielding an EA of 3.82 \pm 0.05 eV for UF₅ on the bases of Franck-Condon simulations. Strong anion mass signals were observed for UF_6^- , but no photoelectron signals could be observed due to the extremely low detachment cross sections from the f_{xyz}based HOMO of UF₆⁻. Density functional theory (DFT) and ab initio wave function theory (WFT) calculations were performed on UF_5^- and UF_6^- to understand their electronic structures.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Electrospray and photoelectron spectroscopy

The experiment was carried out using a magnetic-bottle PES apparatus coupled with an electrospray ionization (ESI) source, details of which has been described previously.⁶⁹ The only modification for the current study was the shortening of the electron flight tube of the magnetic-bottle PES analyzer from 4.0 to 2.5 m. As shown below, the shorter flight tube does not affect the electron energy resolution significantly. To produce the UF_x⁻ species, we used an ESI solution prepared by adding a small amount of AgF to a 1 mM solution of depleted ²³⁸U(SO₄)₂ in acetonitrile. Anions from the ESI source were transferred to a Paul trap at room temperature by a radio frequency quadrupole ion guide. After being accumulated for 0.1 s in the Paul trap, the anions were pulsed into the extraction zone of a time-of-flight mass spectrometer. Three anionic species UO₂F₃⁻, UF₅⁻, and UF₆⁻ were observed from



FIG. 1. Electrospray mass spectrum for UO₂F₃⁻, UF₅⁻, and UF₆⁻.

our ESI source (Fig. 1). The $UO_2F_3^-$ anion was formed due to air contamination during the electrospray. Hence, nitrogen gas was used to purge the ESI zone to minimize the air contamination and enhance the ion signals of UF_5^- and UF_6^- . The anions of interest were selected by a mass gate and decelerated before being intercepted by a laser beam in the detachment region of the magnetic-bottle PES analyzer. An F₂ excimer laser (157 nm, 7.866 eV), the highest photon energy available to us, was used to probe a wide binding energy range. To enhance the spectral resolution, we performed PES experiments at lower photon energies, 213 nm (5.821 eV), 245 nm (5.061 eV), 275 nm (4.508 eV) from a dye laser and 266 nm (4.661 eV) from a Nd:YAG laser. The PES experiment was calibrated by the known spectra of Au⁻ and I⁻. The Au⁻ anion was produced by electrospray of a pyridine/methanol solution of PPh₃AuCl and NaSCH₃.⁷⁰ The electron kinetic energy resolution of the current magnetic-bottle photoelectron analyzer with the shortened electron flight tube was about 3%, i.e., 30 meV for 1 eV electrons.

B. Theoretical and computational methods

The theoretical studies were carried out using both DFT and ab initio WFT methods. In the DFT calculations, we used the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁷¹ implemented in the Amsterdam Density Functional (ADF 2010.02) program.^{72–74} The Slater basis sets with the quality of triple- ζ plus two polarization functions (TZ2P) (Ref. 75) were used, with the frozen core approximation applied to the inner shells $[1s^2-5d^{10}]$ (Refs. 61, 76, and 77) for U and [1s²] for F. The zero-order-regular approximation (ZORA) (Ref. 26) was employed to accounted for the scalar relativistic (SR) and SO coupling effects. Geometry optimizations were performed at the SR-ZORA level, followed by singlepoint energy calculations with inclusion of the SO effects via the SO-ZORA approach, where the non-collinear relativistic method was used.

In the *ab initio* WFT calculations, we used the coupled cluster with singles, doubles, and perturbative triples [CCSD(T)] method, as implemented in the MOLPRO 2008.1 program.⁷⁸ Geometry optimizations were performed at the level of CCSD(T) with SR effects included via the relativistic effective core potentials (RECP). Single-point CCSD(T) energies of the ground and excited states of the neutrals were calculated at the optimized geometries of their anionic structures, which accurately generated state-specific SR energies for all the states.^{79–81} Stuttgart energy-consistent RECP, i.e., ECP60MWB,^{76,77} was applied for U, where the 1s²-4f¹⁴ core was chosen. We used the aug-cc-PVDZ basis set for F (Ref. 82) and the ECP60MWB-SEG basis set for U.

In addition to the Franck-Condon factor (FCF) analyses to be presented in Sec. IV, we also computed the profiles of the vibrational progression in the UF₅⁻ PES spectra using our own code that was written based on the Franck-Condon formulas of Fonger and Struck,⁸³ which have been successfully applied to the luminescence spectra simulation of uranyl and neptunyl compounds.^{84–86} In this approach, vibrational frequency changes from the ground state to the

excited states upon electronic transition were taken into account, but anharmonicities and Duschinsky rotations, which were expected to be small for the current case due to the identical point-group symmetry in the anion and neutral molecules, were neglected. In this paper, we only considered the in-phase symmetric stretching vibration of U-F, which accounts for the observed vibrational progression, and neglected the coupling with other vibrational modes. Groundstate geometry optimizations and frequency calculations of UF₅⁻ were also performed with DFT/PBE using GAUSSIAN 03 (G03) with the same basis sets as in the CCSD(T) calculations above.⁸⁷ The geometrical parameters from the CCSD(T) calculations, the vibrational frequency, and normal mode coordinates from DFT/PBE calculations by G03 were used in the simulation. Additionally, hot bands due to the U-F symmetric stretching mode of UF5⁻ were included using a vibrational temperature of 350 K, as deduced from the FCF simulation of the experimental data.

III. EXPERIMENTAL RESULTS

A. UF₆⁻

Under our ESI conditions, we observed three major anions at m/z = 327, 333, and 352, corresponding to $UO_2F_3^-$, UF_5^- , and UF_6^- , respectively, as shown in Fig. 1. The relative ion intensity for UF_6^- was much stronger compared to those of $UO_2F_3^-$ and UF_5^- . The focus of the current study was on UF_6^- and UF_5^- . However, we were unable to detect photoelectrons from UF_6^- at any detachment photon energies including the highest photon energy available: 7.866 eV (157 nm). This was surprising because all previous studies suggested that the EA of UF_6 should be less than 6 eV. As shown below, our theoretical calculations also predicted that the EA of UF_6 is less than 6 eV. The current observation was attributed to the extremely low detachment cross section of the extra electron in UF_6^- , which occupies a U f_{xyz}-based MO (*vide infra*).

B. UF₅⁻

We were only able to obtain the PES spectra of UF_5^- , as shown in Fig. 2 at four different photon energies: 275 nm, 266 nm, 245 nm, and 213 nm. We also measured the spectrum of UF_5^- at 157 nm, which is not presented in Fig. 1 because no additional features were observed in comparison to the 213 nm spectrum. At 213 nm (Fig. 2(d)), a very broad detachment band was observed, covering a spectral range of more than 1 eV from about 3.8 to 5.2 eV. The broadband suggested that there must be a large geometry change between the ground state of UF_5^- and that of its neutral. At 245 nm (Fig. 2(c)), vibrational fine features were resolved, but the high binding energy side appeared to be cut off due to the lower photon energy. The most intense vibrational feature in the 245 nm spectrum yielded a vertical detachment energy (VDE) of 4.40 eV for UF₅⁻. Figure 2(b) shows a better vibrationally resolved spectrum at 266 nm, but the higher binding energy side was clearly cut off. In order to resolve the lower binding energy side better, we also measured the spectrum at



FIG. 2. Photoelectron spectra of UF_5^- at (a) 275 nm (4.508 eV), (b) 266 nm (4.661 eV), (c) 245 nm (5.061 eV), and (d) 213 nm (5.821 eV). HB stands for hot band transitions.

275 nm (Fig. 2(a)). Hot band transitions due to vibrationally excited UF_5^- anions were observed. The observed vibrational fine features consist of one single vibrational progression with an average spacing estimated as $650 \pm 50 \text{ cm}^{-1}$. However, we were not able to determine the adiabatic detachment energy (ADE) because we could not definitively identify the 0–0 transition on the low binding energy part of the spectrum due to the long vibrational progression and the limited spectral resolution. ADE is an important quantity, since it corresponds to the EA of neutral UF₅. The observed vibrational structures indicated that only one vibrational mode was active during the detachment transition and this mode was most likely the totally symmetric U–F stretching mode. This observation suggested that a FCF simulation was possible, which would yield a more reliable ADE.



FIG. 3. Frank-Condon simulation (blue solid line) for the ground-state detachment transition of UF_5^- using PESCAL (Ref. 84) compared with the 245 nm PES spectrum (dotted line). The vertical lines are the calculated Frank-Condon factors (blue: transitions from the vibrational ground state; red: transitions from vibrational hot bands).

IV. FRANCK-CONDON FACTOR ANALYSES

In order to determine the EA of UF₅ from the PES spectra of UF₅⁻, we performed a FCF simulation using the PESCAL program.⁸⁸ A single active vibrational mode with a frequency of 650 cm⁻¹ was considered on the basis of the resolved vibrational progression in the PES spectra (Fig. 2). The 245 nm spectrum was used to compare with the FCF simulation because it had a relatively good resolution and did not have the severe cutoff on the high binding energy side suffered in the 266 nm spectrum (Fig. 2(b)). For the UF₅⁻ initial state, a harmonic frequency of 534 cm⁻¹ was used from the DFT/PBE calculation (see below) because the hot band transitions were not well resolved in the PES spectra and could not be used to obtain the vibrational frequency for the anion. With the fixed vibrational frequencies for the initial and final states, we used the PESCAL program to obtain the best fit with the experimental spectrum, as shown in Fig. 3, by varying the ADE, the vibrational temperature of the anion, and the displacement of the normal mode. The FCF fitting yielded an ADE of 3.82 \pm 0.05 eV, a vibrational temperature for the anion of 350 K, and a normal model displacement of 0.901 Å (g/mol)^{1/2} from the anion ground state to that of the neutral, corresponding to the totally symmetric U–F stretching mode of the neutral UF₅ ground state. It is reasonable to fix some values when fitting a partially resolved spectrum,^{89–91} as is the case in the current study. The simulated spectrum in Fig. 3 was obtained by convoluting all calculated FCFs with 80 meV width Gaussian functions. This width (full width at half maximum) was considerably broader than the instrumental resolution, suggesting that other low frequency modes might also be active during the photodetachment transition. The obtained ADE and the measured VDE of UF₅⁻ are given in Table I and compared with theoretical calculations (*vide infra*).

V. THEORETICAL RESUTS

A. UF₅⁻

Table I shows the calculated ADEs and VDEs of UF₅⁻ compared with the experimental results. Theoretical calculations showed that the ground state of UF₅⁻ is a triplet state (³B₂) with two unpaired electrons, occupying the 5f-based 2b₂ and 8a₁ MOs, respectively (Figs. 4 and 5). The open-shell ground state of UF₅⁻ is expected to result in two close-lying detachment transitions. The ADEs and VDEs of these two detachment transitions from SR-CCSD(T) calculations and DFT/PBE are given in Table I, as ADE₁, ADE₂, VDE₁, and VDE₂. As we have observed before,⁹² the DFT/PBE values are smaller by almost 1 eV when compared with the CCSD(T) results. We note that the additional SO coupling corrections at the DFT/PBE level do not change much the SR values.

Details of the optimized geometrical parameters of UF₅⁻ are summarized in Table II. The point group symmetries of the optimized ground state of UF₅⁻ and UF₅, as well as that of the lowest excited state of UF₅, are all found to be C_{4v}. For UF₅⁻, the axial and equatorial U–F bond lengths are found to be almost identical at both DFT/PBE and CCSD(T) levels. Furthermore, the two levels of theory give very similar U–F bond lengths for UF₅⁻, about 2.13 Å. Both DFT/PBE and CCSD(T) calculations of UF₅⁻ also give similar \angle F_{ax}UF_{eq} bond angles. The DFT/PBE and CCSD(T) calculations also give consistent geometrical parameters for the ground and excited state of UF₅. The neutral UF₅ shows a significantly shorter U–F bond in both its ground and excited states, about

TABLE I. The adiabatic (ADE) and vertical (VDE) detachment energies for UF_6^- and UF_5^- calculated at different levels of theory and comparison with experimental values for UF_5^- . All energies are in eV.

		UF ₆ -			UF ₅ -			
	DFT	/PBE	CCSD(T)	DFT/PBE		CCSD(T)		
	SR	SO	SR	SR	SO	SR	Exp.	
ADE ₁	4.06	4.07	5.20	2.63	2.63	3.48	3.82 ± 0.05^{a}	
ADE_2						3.95	4.29 ^b	
VDE ₁	4.43	4.46	5.72	3.13	3.14	4.20	4.40 ± 0.05	
VDE ₂			9.05 ^c			4.58	4.78 ^b	

^aThe average vibrational spacing for the detachment band is $650 \pm 50 \text{ cm}^{-1}$.

^bEstimated on the basis of the CCSD(T) results corrected by adding the difference between the experimental and CCSD(T) ADE₁ and VDE₁.

^cFrom Ref. 47



FIG. 4. Molecular orbital energy levels of UF_5^- from SR-DFT/PBE calculation. The $2b_2$ and $8a_1$ orbitals are singly occupied and the other higher lying 5f orbitals are unoccupied.



FIG. 5. The frontier molecular orbitals of UF_5^- at SR-DFT/PBE level. See Fig. 4 for the energy ordering. The two singly occupied molecular orbitals are $8a_1$ and $2b_2$, and the 8e, 7e, and $4b_1$ orbitals are unoccupied.

0.1 Å shorter than that in the UF_5^- anion. This is consistent with the experimental observation of an extensive vibrational progression in the totally symmetric vibrational mode in the PES spectra (Fig. 2). On the other hand, the DFT/PBE and CCSD(T) methods give slightly different $\angle F_{ax}UF_{eq}$ bond angles for the two neutral states of UF5. The DFT/PBE method seems to overestimate the bond angle change, whereas the CCST(D) method shows that the $\angle F_{ax}UF_{eq}$ bond angle of the two neutral states is very similar to that of the anion. We calculated the vibrational frequencies of the totally symmetric mode $[v_s(U-F)]$ at DFT/PBE and obtained 534 and 639 cm⁻¹ for the ground states of UF5⁻ and UF5, respectively, and 626 cm^{-1} for the lowest excited state of UF₅, as given in Table I. We used the calculated vibrational frequency for the UF₅⁻ anion in our FCF simulations in Sec. IV. The calculated symmetric frequency for the neutral ground state of UF₅ is in excellent agreement with the experimental observation $(650 \text{ cm}^{-1}).$

The energy levels of the valence MOs of UF_5^- are presented in Fig. 4 and the iso-contour surfaces of these orbitals are depicted in Fig. 5. The two singly occupied molecular orbitals are the $8a_1$ and $2b_2$ orbitals: the $8a_1$ MO is mainly of U $5f_{z^3}$ character with minor F 2p contributions while the $2b_2$ MO is the nonbonding U $5f_{xyz}$ orbital.

B. Franck-Condon factor calculations to access the contribution of the second detachment channel of $\rm UF_5^-$

According to our CCSD(T) calculations, a second detachment transition occurs at about 0.5 eV above the ground state of UF5, corresponding to the removal of the 2b2 electron with an ADE₂ of 3.95 eV (Table I). However, because of the large geometry changes between the ground state of UF_5^- and the two neutral final states, the corresponding detachment bands are expected to be broad and overlap with each other in the experimental PES spectra shown in Fig. 2. However, there is little evidence of the presence of an overlapping second detachment channel in the experimental PES data (Fig. 2). This observation suggests that the contribution or the relative intensity of the second detachment band must be very small or negligible. To access the possible contribution by this detachment channel, we carried out FCF calculations using the relevant experimental parameters obtained above, i.e., the vibrational temperature and ADE

TABLE II. Optimized geometrical parameters of UF_6^- and UF_5^- and their neutrals at both DFT and CCSD(T) levels of theory.

		DFT/PBE ^a				CCSD(T)		
		U–F _{ax} (Å)	U–F _{eq} (Å)	$\angle F_{ax}UF_{eq}$ (°)	$\nu_{s}(U-F)^{b}(cm^{-1})$	U–F _{ax} (Å)	U–F _{eq} (Å)	$\angle F_{ax}UF_{eq}$ (°)
UF5	C_{4V}	2.130	2.127	102.3	534	2.136	2.138	103.1
$UF_5 (^2B_2)^c$	C_{4V}	2.034	2.037	95.8	639	2.032	2.032	99.6
$UF_5(^2A_1)^d$	C_{4V}	2.054	2.041	99.4	626	2.050	2.036	101.6
UF ₆	O _h	2.096				2.087		
UF ₆	O _h	2.024				2.008		

^aAs implemented in ADF 2010.2.

^bThe totally symmetric U-F stretching vibrational frequency.

^cThe ground state.

^dThe lowest excited state.

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TABLE III. Parameters for the Franck-Condon calculations for the two detachment bands of UF5.

	$\nu_{\rm s}({\rm U-F})^{\rm a}~({\rm cm}^{-1})$	ΔQ^{b} [Å (g/mol) ^{1/2}]	ADE (eV)	% Contribution ^c
UF_{5}^{-}	551	0	0	
$UF_5(^2B_2)$	650	0.909	3.82	91%
$UF_5(^2A_1)$	649	0.863	4.29	9%

^aThe values are based on DFT/PBE calculations using G03, corrected for the discrepancy between theory and experiment for the ground state of UF_5 .

 ${}^{b}\Delta Q$ is the normal coordinate displacement of UF₅ relative to UF₅.

^cPercentage of the contributions of the ground state and the lowest excited state of UF₅ to the observed PES spectrum at 213 nm (see Fig. 6(b)).

of UF₅⁻ and the vibrational frequency of UF₅. Details of these calculations are described in Sec. II B. For ADE₂, we scaled the calculated ADE₂ at the CCSD(T) level using the difference between the calculated and experimental ADE₁. Table III lists all the parameters used for the FCF calculations. Because the calculated $v_s(U-F)$ frequency from DFT/PBE in G03 was systematically smaller, it was scaled according to the experimental value of 650 cm⁻¹ for the ground state of UF₅ in the FCF calculations. The ground-state normal mode displacement ΔQ [in unit of Å (g/mol)^{1/2}] of UF₅ relative to UF₅⁻ was calculated to be 0.909, and 0.863 for the lowest excited state. The calculated normal mode displacement is in good agreement with that obtained from the FCF simulation (0.901 Å (g/mol)^{1/2}) using PESCAL (Sec. IV).

We used the 213 nm spectrum (Fig. 2(d)) to compare with the calculated FCFs because at this photon energy there was no cutoff in the high binding energy side. Fig. 4(a) shows a comparison of the FCF calculation (a 80 meV width Gaussian was convoluted to each calculated FCF) with the 213 nm PES spectrum, using only the ground-state transitions. We see that the agreement between the calculated spectrum and the experimental data is actually quite good, except that the high binding energy side displays a slight deviation, suggesting that there might be a very small contribution by the second detachment channel. Fig. 4(b) shows a comparison, where 9% of the first excited state was included, giving a slightly better agreement between the simulated spectrum and the experiment. These results suggest that the contribution by the first excited state is extremely small, i.e., the cross section for the second detachment channel of UF_5^- from the $2b_2$ MO was indeed very small, and it is almost negligible.

C. UF₆⁻

We also carried out calculations for UF_6^- and its neutral. The optimized geometrical parameters of UF_6 and UF_6^- are also given in Table II. Both the anion and the neutral UF_6 are found to have O_h symmetry, in agreement with previous studies.⁵¹ Again, both DFT/PBE and CCSD(T) calculations give similar U–F bond lengths for UF_6^- and UF_6^- . The average U–F bond lengths for UF₆ and UF_6^- from CCSD(T) and PBE calculations are 2.10 Å and 2.02 Å, respectively. The ADE and VDEs calculated for UF_6^- are also given in Table I. At the CCSD(T) level, we obtained an ADE of 5.2 eV for UF_6^- and VDE_1 of 5.72 eV, corresponding to the detachment of the extra electron in the anion. Similar to the case of UF_5^- and UF_5 , we again observed that the DFT/PBE values are significantly lower than the CCSD(T) values.

also computed the VDE₂ as 9.05 eV from a SO-coupled second-order perturbation theory based on a restricted active space self-consistent field reference wave function (RASPT2-SO).^{47,48}

VI. DISCUSSION

A. UF_5^- : The detachment transition to the ground state of UF_5

In UF_5^- , U is in its oxidation state IV with a $5f^2$ configuration. As shown in Fig. 4, the seven 5f atomic orbitals split into $2b_2$, $8a_1$, $4b_1$, 7e, and 8e under C_{4v} symmetry. The two 5f electrons occupy the 2b₂ and 8a₁ MOs, giving rise to a triplet $({}^{3}B_{2})$ ground state for UF₅⁻. As shown in Fig. 5, the $8a_1$ HOMO is mainly of U $5f_{r^3}$ character with minor contributions from the F 2p orbital of the ligands. As the 8a1 HOMO is weakly antibonding, electron detachment from the 8a1 orbital of UF_5^- enhances bonding in neutral UF_5 (²B₂), resulting in the shortened U–F bonds and slightly reduced $\angle F_{ax}UF_{eq}$ bond angles (Table II). These theoretical predictions are consistent with the extensive vibrational progression observed in the PES spectra of UF_5^- (Fig. 2). The change in the U-F bond lengths leads to the extensive vibrational progression in the totally symmetric U-F stretching mode, whereas the slight bond angle change is in agreement with the broad line width, which suggests excitation of low frequency bending modes accompanying the stretching mode. The U-F bond lengths and $\angle F_{ax}UF_{eq}$ bond angles obtained from the current CCSD(T) calculations are in good agreement with the most recent theoretical study of UF5 by Batista and co-workers at the DFT/B3LYP level.⁴¹ Our current study also shows that the geometric parameters at DFT/PBE and CCSD(T) levels are similar (Table II).

However, the DFT/PBE method severely underestimates the electron detachment energies by more than 1 eV relative to the experiment, as shown in Table I.⁹² Our CCSD(T) value for ADE₁ of 3.48 eV is in good agreement with the observed ADE for the ground-state transition of 3.82 eV, although it is still lower by 0.34 eV in comparison to the experimental value due to the relatively small atomic basis sets and the negligence of the SO effects. The experimental ADE of 3.82 eV also represents the EA of UF₅. The current EA value is consistent with the estimate by Compton using charge transfer (4 \pm 0.4 eV)⁶⁴ or the 3.7 \pm 0.2 eV value from ion equilibrium studies.^{67,68}

The observed totally symmetric stretching vibrational frequency of $650 \pm 50 \text{ cm}^{-1}$ for the ground state of UF₅ is consistent with the v_1 mode (646 cm⁻¹) of UF₅ reported

by Jones and Ekberg.⁵⁹ Previous calculations suggested that the gas phase electronic spectrum of UF₅ might be complicated due to the presence of multiple electronic states and the fluxional character between D_{3h} and C_{4v}.^{61,93} However, our observation of one dominating U–F stretching mode rules out the D_{3h} symmetry for UF₅. Our calculated frequency at the DFT/PBE level for the v_s (U–F) mode of 639 cm⁻¹ is in good agreement with the experimental value. The smaller U–F stretching frequency calculated for UF₅⁻ is also consistent with the weakening of the U–F bonding in the anion.

B. UF₅⁻: The detachment transition to the excited state of UF₅

As mentioned above, electron detachment from the $2b_2$ HOMO-1 should result in the excited state of UF₅ ($^{2}A_{1}$). The 2b₂ MO is almost of pure U 5f_{xyz} character, as shown in Fig. 5. Our CCSD(T) calculations gave an ADE₂ of 3.95 eVand VDE_2 of 4.58 eV for this detachment channel (Table I). The geometrical parameters of the excited state are very similar to that of the UF₅ ground state. Thus, the detachment band was also expected to be as broad as that of the ground-state transition. The second detachment band would be completely overlapped with that of the ground-state band. However, the experimental PES spectra gave little hint about the presence of an overlapping band, suggesting that the detachment cross section from the 2b₂ MO is much smaller so that the contribution of this detachment channel to the PES spectra is negligibly small relative to that of the ground state. This conjecture was supported by our FCF calculations shown in Fig. 6, which indicate that the second detachment channel contributes no more than 9% to the observed PES spectrum at 213 nm (Fig. 6(b)). This suggests that the detachment cross section from the $5f_{xyz}$ -based $2b_2$ MO is at least ten times weaker than that from the $5f_{z^3}$ -based $8a_1$ orbital.

It is well known that ionization cross sections are strongly dependent on photon energies and the angular momenta of the orbitals, from which the electron is ionized.⁹⁴ The photon energy dependence of the ionization cross section of the U 5f orbital is not known. However, photoionization studies of Au showed that the ionization cross section of its 4f orbital is negligible near the ionization threshold and exhibits a very slow rise as a function of photon energy above the threshold.⁹⁵ Significant ionization cross section was observed only about 40 eV above the threshold. This behavior was understood on the basis of the high angular momentum of the 4f orbitals.⁹⁴ In the current case, while the $5f_{xyz}$ ($m_l = 2$) and $5f_z^3$ ($m_l = 0$) orbitals have the same high angular momentum (l = 3), they have very different projections in the z axis, which may be related to their very different detachment cross sections.

C. The electron affinity of UF_6 and the low detachment cross section of UF_6^-

Our CCSD(T) calculations yielded an ADE of 5.20 eV for UF₆⁻ (Table I). If we use the discrepancy (0.34 eV) between the CCSD(T) ADE and the experimental value for UF₅⁻, we estimate that the real ADE of UF₆⁻ would be around 5.5 eV, which is in line with the previous estimates of the EA of UF₆.^{64–68} Fig. 1 shows that we could produce



FIG. 6. Calculated photoelectron spectra (red) compared with the experimental photoelectron spectrum of UF_5^- at 213 nm (blue). (a) Only the ground-state transition is used. (b) Both the detachment transitions to the ground and first excited state of UF_5 are included. The contribution by the excited state is ~9%.

strong and stable ion signals for UF_6^- using our ESI source. Surprisingly, we were unable to observe any measurable photoelectron signals at 213 nm (5.821 eV) or our highest photon energy at 157 nm (7.866 eV).

The obvious question is why we could not observe any measurable photoelectrons for UF_6^- while the photon energies used were expected to be higher than its electron binding energy? The answer lies at the nature of the LUMO of UF_6 , in which the extra electron resides in UF_6^- . The ground state of UF_6 is closed shell (${}^{1}A_{1g}$) with a F-2p ligand-based valence electron configuration of $e_g{}^4t_{2g}{}^6t_{1u}{}^6a_{1g}{}^2t_{2u}{}^6t_{1g}{}^6t_{1u}{}^6$.^{58,96} The LUMO of UF_6 is an 5f-based a_{2u} orbital, where the extra electron resides in UF_6^- . The a_{2u} orbital is the nonbonding $5f_{xyz}$ orbital, essentially the same as the $2b_2$ orbital in UF_5^- (Fig. 5). As seen above, the $2b_2$ orbital of UF_5^- has an extremely low detachment cross section at the laser photon energies available to us. Hence, we attribute the failure to observe photoelectrons from UF_6^- to the extremely low detachment cross section of the $5f_{xyz}$ -based a_{2u} orbital.

VII. CONCLUSIONS

We report the observation of gaseous UF_5^- and $UF_6^$ anions using electrospray ionization and vibrationally resolved photoelectron spectra of UF_5^- at different photon energies. The electron affinity of UF_5 is determined to be 3.82

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 \pm 0.05 eV using Franck-Condon factor simulations of the observed photoelectron spectra. A vibrational frequency of 650 \pm 50 cm⁻¹ is measured from the vibrationally resolved PES spectra, corresponding to the totally symmetric U-F stretching mode. DFT and ab initio calculations are used to optimize the structures of UF5⁻, UF6⁻, and their neutrals. Both UF_5^- and UF_5 are found to have C_{4v} symmetry, but the U-F bond lengths in neutral UF₅ are significantly shortened. The ground state of UF_5^- is found to be triplet with the two unpaired electrons residing in the $5f_{z^3}$ -based $8a_1$ HOMO and the 5f_{xyz}-based 2b₂ HOMO-1. The detachment cross section of the $5f_{xyz}$ orbital is observed to be extremely small and the contribution of the 2b₂ detachment band is at least ten times weaker in comparison to that of the $8a_1$ band. The UF₆⁻ anion is found to be octahedral with the extra electron occupying the $5f_{xyz}$ -based LUMO of UF₆. The calculated ADE of UF₆⁻ is 5.20 eV and the EA of UF_6 is estimated to be about 5.5 eV. However, despite the strong ion signals observed for UF_6^- , we have not been able to obtain the photoelectron spectra of UF_6^- due to the extremely low detachment cross section of the $5f_{xyz}$ -based a_{2u} HOMO in UF_6^- , as also observed for the $5f_{xyz}$ -based HOMO-1 in UF₅⁻.

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