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Supporting Information

ABSTRACT: Uranium oxide clusters UO_x^- (x = 3-5) were produced by laser vaporization and characterized by photoelectron spectroscopy and quantum theory. Photoelectron spectra were obtained for UO_x^- at various photon energies with well-resolved detachment transitions and vibrational resolution for x = 3 and 4. The electron affinities of UO_x were measured as 1.12, 3.60, and 4.02 eV for x = 3, 4, and 5, respectively. The geometric and electronic structures of both



1. INTRODUCTION

The rich chemistry and bonding capacity of uranium have attracted extensive research interests.¹ Many uranium compounds have complicated electronic structures, owing to the soft 6p semicore-shell and to the spatially distributed 5f6d7s valence shells, resulting in diverse chemical-bonding tendencies. Uranium exhibits a broad range of oxidation states, but its most important ones in nature are IV and VI. The linear uranyl cation UO_2^{2+} , in which U is in its favorite oxidation state VI, is an extremely stable species that can form complexes with many different ligands in its equatorial plane.² The neutral UO₂ molecule, in which U is in its oxidation state IV, is also linear, but possesses very complicated electronic structures, owing to energetic near-degeneracy of the 5f6d7s shells and the large differences in their radial extensions. Interactions with adjacent atoms, even in noble gas matrices, can change the order of the lowest electronic states and occupation schemes of UO₂ within the U(5f6d7s)² superconfiguration.³⁻¹⁸

In a prior joint photoelectron spectroscopy (PES) and ab initio study, both the U^{IV}O₂ and U^{III}O₂⁻ molecules were found to be linear species with ${}^{3}\Phi_{u}[(5f\phi_{u})^{1}(7s\sigma_{e})^{1}]$ and

 ${}^{2}\Phi_{u}[(5f\phi_{u})^{1}(7s\sigma_{g})^{2}]$ ground states, respectively.¹⁹ More significantly, strong Coulomb-correlation and spin–orbit (SO) coupling effects were observed, leading to numerous shakeup transitions upon photodetachment from the dominant anionic $5f^{1}7s^{2}$ configuration with discernible spectral intensities. A subsequent high-resolution PES study of UO₂⁻ confirmed the previous observations and yielded much more accurate spectroscopic information.²⁰ Similar shakeup transitions were also observed in the PES of U¹F₂⁻, which has a dominant U ($5f^{3}7s^{2}$) configuration.²¹ A recent ab initio investigation of U^{II}O revealed strong configuration mixing by Coulomb-correlation and SO coupling within the U(5f6d7s)⁴ superconfiguration.²²

Received:November 19, 2015Revised:January 27, 2016Published:January 29, 2016

Here we report PES of $UO_x^{-}(x = 3-5)$ in conjunction with ab initio calculations to elucidate the trends and changes of the geometric and electronic structures and bonding mechanisms of the monouranium oxides with various O atoms. Wellresolved PES features were observed for all species, with vibrational resolution in the cases of UO_3^- and UO_4^- , and they were compared with theoretical data. The electron binding energies of UO_r^{-} were found to increase dramatically with the oxygen content. The theoretical studies show that the UO_x and UO, species mainly consist of an OUO uranyl unit, with additional O atoms building equatorially around the slightly bent OUO axis in O or O2 form. The oxidation state and formal charge on U increases with the oxygen content from the low value of I in UO⁻ stepwise up to its maximum value of VI. Interesting multicenter bonding is observed in the oxygen-rich systems. The current study provides both new experimental data valuable for benchmarking further theoretical development of actinide systems and new insights into the chemical bonding capacities of uranium.

2. EXPERIMENTAL METHODS

The experiments were carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which have been published elsewhere.³¹ In brief, a uranium disk target was used in the laser vaporization cluster source with a He carrier gas containing 5% Ar for better cooling.^{32,33} Oxygen-poor UO_x^{-1} ($x \le 3$) clusters could be produced due to the oxide impurity on the target surface without an external O source.^{19,20} To produce the oxygenricher clusters UO4- and UO5-, a He carrier gas seeded with 1% O₂ was used. The anionic clusters were extracted from the collimated cluster beam after a skimmer and analyzed in a timeof-fight mass spectrometer. The clusters of interest, UO_x^{-} (x = 3-5), were mass-selected and decelerated before being photodetached by a laser beam operated at 193 nm (6.424 eV) from an ArF excimer laser, or at 266 (4.661 eV), 355 (3.496 eV), and 532 nm (2.331 eV) from a Nd:YAG laser. Photoelectrons were collected at nearly 100% efficiency and analyzed in a 3.5 m long magnetic bottle time-of-flight PES analyzer. The resolution of the apparatus, $\Delta E_k/E_k$, was better than 2.5%, that is, \sim 25 meV for 1 eV electrons.

3. THEORETICAL METHODS

The geometric and electronic structures of UO_x^- and UO_x were first examined using approximate density functional theory (DFT) calculations, as implemented in the ADF 2013.01³⁴⁻³⁶ and Gaussian 09 programs.³⁷

In the ADF calculations, several functionals were applied, including the PBE density gradient approximation,³⁸ the B3LYP hybrid approximation,³⁹ and the statistically averaged orbital potential SAOP,⁴⁰ with the standard TZ2P basis sets in the ADF library, which represent Slater basis sets of polarized valence triple- ξ quality, [3s3p1d1f] for the O(2s2p) shell and [6s4p3d3f] for the U(5f6s6p6d7s) shell.⁴¹The orbitals of the $U[1s^2-5d^{10}]$ and $O[1s^2]$ cores from free atom calculations were ७७७стр different UO_x^0 and UO_x^- isomers with different electron configurations were optimized with various starting geometries at the scalar-relativistic (SR) zero-order-regular approximation (ZORA).⁴² SO coupling effects were taken into account for selected geometries by SO-ZORA. The structures were confirmed to be true minima by vibrational frequency calculations.

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Starting from these DFT-optimized structures, we reoptimized the lower energy states of UO_x and UO_x^- at the SR-ROHF-RCCSD(T) level,47 as implemented in the MOLPRO 2012.1 program using the same basis sets as in the G09 calculations.^{48,49} The first vertical detachment energy (VDE, here defined as the energy at maximum intensity) for each species was then computed as the total energy difference of the anionic and neutral species at the anionic geometry, at both the DFT and CCSD(T) levels. In the latter the O(2s)U(6s6p)semicore and O(2p)U(5f6d7s) valence shells were correlated. The first adiabatic detachment energy (ADE) for each species was calculated as the energy difference between the neutral and the anion at their respective optimized geometries. The energy of UO_3^- with a $U(5f^1)$ electron was determined by a CASSCF/ CCSD(T)/SI-SO approach using the above-mentioned effective core potential with SO coupling. The seven 5f type and one 7s type MOs in UO_3^- were included in the active space, which gives CAS(1e,80) and eight electronic states. The CAS(1e,80)-SCF wave functions were used for the off-diagonal SO matrix elements, and the CCSD(T) energies were used for the correlation-improved diagonal elements.⁵⁰⁻⁵⁵ The minor second-order SO correction of closed-shell UO₃ has been neglected.

The higher VDEs were calculated either with time-dependent (TD) DFT or by applying the Koopmans' Theorem (KT) approximation as generalized to the DFT approach, that is, by 祉i about -2 eV to the occupied orbital energies of the anion.^{56,57} TD-DFT for UO₃ with either SAOP or B3LYP potentials and KT-DFT-B3LYP for UO₃⁻ gave the same order of symmetry labels and similar PES patterns. For the UO₄ closed-shell ground-state species, TD-DFT with both SAOP and B3LYP functional yielded an incorrect negative excitation energy for the lowest excited triplet state and was not applied. Concerning the open-shell UO₅ species, the ADF and GAUSSIAN codes do not offer the option of SO-TD-DFT. Therefore, we applied only the KT-DFT-B3LYP approach for the VDEs of UO₄⁻ and UO_5^{-} . The energies of all stationary states were corrected for the harmonic vibrational zero-point effects at the DFT level. The respective corrections of energy differences were then added to the ADEs.

Chemical bonding analyses were performed using Mulliken populations,⁵⁸ bond orders of Mayer⁵⁹ and of Nalewajski and Mrozek,^{60–63} and the adaptive natural density partitioning (AdNDP) approach of Boldyrev,⁶⁴ which is an extension of the NBO approach of Weinhold and Landis,⁶⁵ where one searches for an optimal decomposition of the one-electron density matrix into chemically intuitive localized orbital contributions. Thereby, one can recover, step-by-step, one-center core and valence lone pairs (1c-2e), then two-center (2c-2e), and then multicenter bond pairs (3c-2e, ...). A pair-density defect (i.e., < 2e) results if one aimed at a too strongly localized bonding picture. All molecular structures and valence MOs were visualized using the ADF 2013 GUI software.³⁶ The AdNDP results were visualized using GaussView 5.0.⁶⁶ The bond order analyses were carried out with the ADF 2013.1 package.³⁶

4. PHOTOELECTRON SPECTROSCOPY OF UO_x^- (x = 3-5)

The photoelectron spectra of UO_x^- at various photon energies are shown in Figures 1–3 for x = 3-5, respectively. The spectra



Figure 1. Photoelectron spectra of UO_3^- at (a) 532 (2.331 eV), (b) 355 (3.496 eV), (c) 266 (4.661), and (d) 193 nm (6.424 eV). The vertical lines in panel a indicate the vibrational progression. The vertical bars in panel d mark the theoretical VDE values. The first VDE was from ΔE -CCSD(T) and the higher energy VDEs were shifted SR-KT-DFT-B3LYP values (see Table 1).

obtained at high photon energies reveal more detachment transitions, and those obtained at low photon energies offer better spectral resolution for the low binding energy features. The observed PES bands are labeled with letters (X, A, B, ...), and the measured VDEs from the band maxima are given in Tables 1–3, where they are compared with the calculated VDEs. In each spectrum, the X band represents the transition from the anionic ground state to the electronic ground state of the corresponding neutral species with a similar geometric structure as the anion (not necessarily the global minimum).



Figure 2. Photoelectron spectra of UO_4^- at (a) 266 and (b) 193 nm. The vertical lines in panel a indicate the vibrational progression for band X. The vertical bars in panel b mark the theoretical VDEs. The first VDE is from ΔE -CCSD(T) and the higher energy VDEs are shifted SR-KT-DFT-B3LYP values (see Table 2). The weak feature * near ~1.47 eV is due to O⁻.



The higher binding energy PES bands (A, B, ...) denote transitions to excited states of the corresponding neutral species.

Table 1. UO ₃ ⁻ : Observed Vertical Electron Detachment Energies (VDE in eV) Compared with Calculated VDEs of	of $C_{2\nu}$ (² B ₂)
UO_3^- at SO-TD-DFT/SAOP&B3LYP, Koopmans DFT/B3LYP and ΔE -CCSD(T)/SO Levels at CCSD(T) Geome	tries, and
Dominant One-Electron Configuration States of the Detachments	

					TD-DFT		KT-DFT	
obs. band	VDE (obs) ^a	dominant configuration of final states at the SR level^b	final SO state	SAOP	aver. ^c	B3LYP	B3LYP ^d	
Xe	1.44(3)	$5a_1^2 \ 3b_1^2 \ 1a_2^2 \ 6a_1^2 \ 2b_2^2 \ 4b_1^2 \ 3b_2^2 \ 7a_1^2 \ 5b_1^2 \ 4b_2^0$	${}^{1}A_{1}$	1.22		1.62	ΔCC:1.60	
А	3.19(6)	$5a_1^2 \ 3b_1^2 \ 1a_2^2 \ 6a_1^2 \ 2b_2^2 \ 4b_1^2 \ 3b_2^2 \ 7a_1^2 \ 5b_1^1 \ 4b_2^1$	B_2	3.24		3.00	3.19	
			A_1	3.25	←3.28	3.05		
			A_2	3.30	3.07→	3.07		
			B_1	3.32		3.17		
В	3.81(6)	$5a_1^2 \ 3b_1^2 \ 1a_2^2 \ 6a_1^2 \ 2b_2^2 \ 4b_1^2 \ 3b_2^2 \ 7a_1^1 \ 5b_1^2 \ 4b_2^1$	B_1	3.71		3.70	3.75	
			A_2	3.74	←3.77	3.78		
			B_2	3.78	3.82→	3.82		
			A_1	3.85		3.98		
С	4.7(1)	$5a_1^2 \ 3b_1^2 \ 1a_2^2 \ 6a_1^2 \ 2b_2^2 \ 4b_1^2 \ 3b_2^1 \ 7a_1^2 \ 5b_1^2 \ 4b_2^1$	A_2	4.49		4.66	4.62	
			A_1	4.50	←4.55	4.66		
			A_2	4.54	4.71→	4.72		
			B_1	4.65		4.81		
D	5.1(1)	$5a_1^2 3b_1^2 1a_2^2 6a_1^2 2b_2^2 4b_1^1 3b_2^2 7a_1^2 5b_1^2 4b_2^1$	B ₂	4.88		5.11	5.05	
			A_2	4.92	←4.93	5.12		
			A_2	4.96	5.13→	5.12		
			A ₂	4.97		5.18		
		$5a_1^2 3b_1^2 1a_2^2 6a_1^2 2b_2^1 4b_1^2 3b_2^2 7a_1^2 5b_1^2 4b_2^1$	B_1	5.13		5.46	5.35	
			A_2	5.13	←5.16	5.46		
			B ₂	5.19	5.47→	5.47		
			A ₁	5.19		5.49		
Е	5.7-6.3	$5a_1^2 3b_1^2 1a_2^2 6a_1^1 2b_2^2 4b_1^2 3b_2^2 7a_1^2 5b_1^2 4b_2^1$	B ₁	5.41		5.71	5.66	
			A ₂	5.42	← 5.46	5.71		
			B ₂	5.45	5.75→	5.75		
			A ₁	5.54		5.85		
		$5a_1^2 3b_1^2 1a_2^1 6a_1^2 2b_2^2 4b_1^2 3b_2^2 7a_1^2 5b_1^2 4b_2^1$	B ₂	5.57		6.05	5.83	
			A ₂	5.57	←5.58	6.05		
			A ₁	5.58	6.05→	6.05		
			B ₁	5.58		6.06		
		$5a_1^2 3b_1^1 1a_2^2 6a_1^2 2b_2^2 4b_1^2 3b_2^2 7a_1^2 5b_1^2 4b_2^1$	B ₂	5.73		6.24	6.11	
			A ₁	5.74	←5.75	6.24		
			A ₂	5.75	6.24→	6.24		
			B ₁	5.76		6.24		
		$5a_1^{-1} 3b_1^{-2} 1a_2^{-2} 6a_1^{-2} 2b_2^{-2} 4b_1^{-2} 3b_2^{-2} 7a_1^{-2} 5b_1^{-2} 4b_2^{-1}$	A ₂	5.85		6.31	6.12	
		······································	B ₁	5.87	←5.87	6.34		
			В,	5.88	6.34→	6.35		
			Â,	5.89		6.36		

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4.2. UO_4^- . Because of its relatively high electron binding energies, UO_4^- was studied only at 266 and 193 nm detachment wavelengths, as shown in Figure 2. The X band

obs. band	VDE (obs) ^a	dominant detachment	dominant final state configuration at the SR level^b	VDE (calc) ^c
X ^d	3.79(3)	$5b_1^{1\to 0}(\alpha)$	${}^{1}A_{1}$, $[6a_{1}^{2} 4b_{1}^{2} 7a_{1}^{2} 4b_{2}^{2} 2a_{2}^{2} 8a_{1}^{2} 5b_{2}^{2} 5b_{1}^{0}]$	ΔCC: 3.92
A^e	4.21(3)	$5b_2^{2 \to 1}(\beta)$	${}^{3}A_{2}$, $[6a_{1}{}^{2} 4b_{1}{}^{2} 7a_{1}{}^{2} 4b_{2}{}^{2} 2a_{2}{}^{2} 8a_{1}{}^{2} 5b_{2}{}^{1} 5b_{1}{}^{1}]$	4.14
В	4.40(5)	$5b_2^{2 \to 1}(\alpha)$	${}^{1}A_{1}$, $[6a_{1}{}^{2} 4b_{1}{}^{2} 7a_{1}{}^{2} 4b_{2}{}^{2} 2a_{2}{}^{2} 8a_{1}{}^{2} 5b_{2}{}^{1} 5b_{1}{}^{1}]$	4.33
С	5.0(1)	$2a_2^{2 \to 1}(\beta)$	${}^{3}B_{2}$, $[6a_{1}{}^{2} 4b_{1}{}^{2} 7a_{1}{}^{2} 4b_{2}{}^{2} 2a_{2}{}^{1} 8a_{1}{}^{2} 5b_{2}{}^{2} 5b_{1}{}^{1}]$	4.73
		$8a_1^{2 \to 1}(\beta)$	${}^{3}B_{1}$, $[6a_{1}{}^{2} 4b_{1}{}^{2} 7a_{1}{}^{2} 4b_{2}{}^{2} 2a_{2}{}^{2} 8a_{1}{}^{1} 5b_{2}{}^{2} 5b_{1}{}^{1}]$	4.81
		$8a_1^{2 \to 1}(\alpha)$	${}^{1}B_{1}$, $[6a_{1}^{2} 4b_{1}^{2} 7a_{1}^{2} 4b_{2}^{2} 2a_{2}^{2} 8a_{1}^{1} 5b_{2}^{2} 5b_{1}^{1}]$	4.91
D	5.57(8)	$4b_2^{2 \to 1}(\beta)$	${}^{3}A_{2}$, $[6a_{1}^{2} 4b_{1}^{2} 7a_{1}^{2} 4b_{2}^{1} 2a_{2}^{2} 8a_{1}^{2} 5b_{2}^{2} 5b_{1}^{1}]$	5.70
		$2a_2^{2 \to 1}(\alpha)$	${}^{1}B_{2}$, $[6a_{1}^{2} 4b_{1}^{2} 7a_{1}^{2} 4b_{2}^{2} 2a_{2}^{1} 8a_{1}^{2} 5b_{2}^{2} 5b_{1}^{1}]$	5.84
E	5.98(6)	$4b_1^{2 \to 1}(\beta)$	${}^{3}A_{1}$, $[6a_{1}^{2} 4b_{1}^{1} 7a_{1}^{2} 4b_{2}^{2} 2a_{2}^{2} 8a_{1}^{2} 5b_{2}^{2} 5b_{1}^{1}]$	5.91
		$4b_2^{2 \to 1}(\alpha)$	${}^{1}A_{2}$, $[6a_{1}^{2} 4b_{1}^{2} 7a_{1}^{2} 4b_{2}^{1} 2a_{2}^{2} 8a_{1}^{2} 5b_{2}^{2} 5b_{1}^{1}]$	5.96
F	~6.1(1)	$7a_1^{2 \to 1}(\beta)$	${}^{3}B_{1}$, $[6a_{1}{}^{2} 4b_{1}{}^{2} 7a_{1}{}^{1} 4b_{2}{}^{2} 2a_{2}{}^{2} 8a_{1}{}^{2} 5b_{2}{}^{2} 5b_{1}{}^{1}]$	6.11
		$6a_1^{2 \to 1}(\beta)$	${}^{3}B_{1}$, $[\mathbf{6a_{1}}^{1} 4b_{1}^{2} 7a_{1}^{2} 4b_{2}^{2} 2a_{2}^{2} 8a_{1}^{2} 5b_{2}^{2} \mathbf{5b_{1}}^{1}]$	6.36
		$7a_1^{2 \to 1}(\alpha)$	${}^{1}B_{1}$, $[6a_{1}{}^{2} 4b_{1}{}^{2} 7a_{1}{}^{1} 4b_{2}{}^{2} 2a_{2}{}^{2} 8a_{1}{}^{2} 5b_{2}{}^{2} 5b_{1}{}^{1}]$	6.49
		$4b_1^{2 \to 1}(\alpha)$	${}^{1}A_{1}$, $[6a_{1}^{2} 4b_{1}^{1} 7a_{1}^{2} 4b_{2}^{2} 2a_{2}^{2} 8a_{1}^{2} 5b_{2}^{2} 5b_{1}^{1}]$	6.55
		$6a_1^{2 \to 1}(\alpha)$	${}^{1}B_{1}$, $[\mathbf{6a_{1}}^{1} \ 4b_{1}^{2} \ 7a_{1}^{2} \ 4b_{2}^{2} \ 2a_{2}^{2} \ 8a_{1}^{2} \ 5b_{2}^{2} \ \mathbf{5b_{1}}^{1}]$	6.68

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obs. band	VDE (obs) ^b	dominant detachment from SR-MO	dominant final state configuration at the SR level	VDE (KT-DFT-B3LYP) ^c
X ^d	4.19(6)	7a″²	$6a''^2 \ 13a'^2 \ 14a'^2 \ 15a'^2 \ 7a''^1 \ 8a''^1$	4.36
				4.37
А	4.71(8)	15a' ²	$6a''^2 \ 13a'^2 \ 14a'^2 \ 15a'^1 \ 7a''^2 \ 8a''^1$	4.60
				4.76
В	5.2(1)	14a' ²	$6a''^2 \ 13a'^2 \ 14a'^1 \ 15a'^2 \ 7a''^2 \ 8a''^1$	5.31
С	5.5(1)			5.53
D	6.3(1)	13a' ²	$6a''^2 \mathbf{13a'}^1 \mathbf{14a'}^2 \mathbf{15a'}^2 \mathbf{7a''}^2 \mathbf{8a''}^1$	5.84
				5.91
		8a″1	6a" ² 13a' ² 14a' ² 15a' ² 7a" ² 8a" ⁰	5.89
		6a″²	$6a''^1 13a'^2 14a'^2 15a'^2 7a''^2 8a''^1$	6.28
				6.34
		12a'	$12a'^{1} 6a''^{2} (13-15)a'^{2} 7a''^{2} 8a''^{1}$	6.56
				6.68

in the 266 nm spectrum (Figure 2a) displayed a well-resolved vibrational progression with a frequency of 770 \pm 30 cm⁻¹, which should be due to the symmetric U-O stretching mode of the UO_4 final state. The respective ADE of UO_4^- , or EA of UO_4 , was readily measured from the 0–0 transition as 3.60 eV. The VDE of the X band, defined as the most intense vibrational peak $(0 \rightarrow 2)$, was 3.79 eV. We estimated a U–O bond length of ~6 pm using Franck-Condon simulation. A more intense partial vibrational progression (A), corresponding to an excited state of UO4, was observed, closely following band X. An average vibrational spacing of $810 \pm 50 \text{ cm}^{-1}$ was measured for band A. The ADE of band A was measured as 4.11 eV. Apparently, another band B, at the cutoff of the 266 nm detachment wavelength (4.661 eV) overlapped with band A, making it difficult to determine the VDEs of these two bands. Judging from the appearance of the two bands in the 193 nm

spectrum (Figure 2b), we assigned the $0 \rightarrow 1$ vibrational peak of the A band as the vertical transition with a VDE of 4.21 eV. The VDE of the B band was estimated to be 4.40 eV.

More detachment transitions were observed in the 193 nm spectrum (Figure 2b): a weak and broad band C (VDE: 5.0 eV), band D (VDE: 5.57 eV), and band E (VDE: 5.98 eV). The broad signals on the high binding energy side were tentatively labeled as band F with a VDE around 6.1 eV, which likely contained closely spaced detachment channels. A very weak peak (labeled as *) was observed in both spectra at a detachment energy of ~1.47 eV, consistent with the detachment energy of O⁻⁷². This observation suggested that there was a very minor channel of photodissociation of $UO_4^- \rightarrow UO_3 + O^-$ during the PES experiment, followed by detachment laser pulse.

4.3. UO_5^- . The photoelectron spectra at 266 and 193 nm are shown in Figure 3 and the binding energies of UO_5^- were found to be even higher. One relatively broad PES band (X) was observed at 266 nm with a VDE of 4.19 eV. Since no vibrational structure was resolved, the ADE was evaluated by drawing a straight line along the leading edge of band X and then adding the instrumental resolution to the intersection with the binding energy axis. The ADE so obtained was 4.02 eV, which also represents the EA of UO_5 .

The 193 nm spectrum displayed a series of congested and broad PES bands. A broad band A was observed at a VDE of 4.71 eV, beyond which the spectrum was almost continuous. Three bands were labeled tentatively for the sake of discussion: band B at a VDE of 5.2 eV, band C at a VDE of 5.5 eV, and band D at a VDE of ~6.3 eV. Very weak signals at ~1.2 eV (labeled as *) and ~3.5 eV (labeled as **) were also observed in the 266 nm spectrum but were not present in the 193 nm spectrum. In comparison with Figure 1, these signals likely came from UO₃⁻. This observation suggested that the UO₅⁻ species might contain an O₂ unit and the UO₃⁻ species was derived from a minor channel of photodissociation at 266 nm: $UO_5^- \rightarrow UO_3^- + O_2$.

Table 4. Observed First Adiabatic (ADE) and Vertical (VDE) Detachment Energies (in eV) of UO_x^- (x = 3-5) Compared with Quantum Calculations at the SR/SO-CCSD(T) Level

			calc.: CC	CSD(T)
anion	process	obs. ^a	SO	SR
UO3-	ADE	1.12(3)	1.12 ^b	0.81
	VDE	1.44(3)	1.60 ^b	1.29
UO_4^-	ADE	3.60(3)	3.51 ^c	3.64
	VDE	3.79(3)	3.79 ^c	3.96
UO_5^-	ADE	4.02(6)	3.92 ^c	3.92
	VDE	4.19(6)	4.37 ^c	4.42

^{*a*}Numbers in parentheses are the uncertainties in the last digit. The first ADE represents the EA of the corresponding neutral. The experimental VDE refers to the intensity maximum in the PES. ^{*b*}Theoretical SO-coupled value of the VDE was obtained from CAS(1,8)SCF/CCSD(T)/SO calculations; the respective SO correction was then added to the SR value of the ADE. ^{*c*}SO corrections for ADE and VDE are from corresponding SO–DFT/B3LYP calculations.

5. THEORETICAL RESULTS AND INTERPRETATION OF THE PHOELECTRON SPECTRA

Previous experimental and theoretical investigations have established that both O and O₂ ligands in the UO_x species are possible, depending on the oxygen content.^{24,25,73} For Orich UO_x species, either η^1 -O₂ or η^2 -O₂ binding to U is possible. We have considered computationally different isomeric structures of UO_x and UO_x⁻ (x = 3–5), as shown in Figure 4.

5.1. UO₃ and UO₃⁻. The U atom has six valence electrons and can form a stable stoichiometric UO₃ molecule, in which U assumes its maximum oxidation state of VI. UO₃ was found to be a closed-shell molecule with $C_{2\nu}$ symmetry (3A in Figure 4), as previously known.^{16,27–29} It could be viewed as consisting of a uranyl-like UO₂ unit, deformed by the equatorial coordination

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The valence MO level diagram of UO_3^- is shown in Figure 5 祉holl of the section of the UO3 are similar to those of UO3 $^-$ except that the 4b2 MO is dominant $O(2p\sigma,\pi)$ character. The lower three MOs (5a₁, 3b₁, $1a_2$) contain ~15% U(6d), and the remaining six occupied MOs contain $\sim 20\%$ U(5f) on average. Seven of the lowest eight unoccupied MOs, including the 4b₂ LUMO, contain ~75% U(5f) on average and smaller amounts of U(6d) and O(2p), whereas one MO has ~65% U(7s). This MO of dominant U(7s) character is the upper $9a_1$ in UO₃, while in UO_3^- it is the lower $8a_1$, as shown in Figure 5 and Figure S1. It corresponds to the rule that in transition-metal atoms the nscomes energetically down, near to the (n-1)d or (n-2)f AOs, only if the atom carries significant negative physical charge. ७७соросссс UO_3^- are given in Table S3.

Because the highest singly occupied 4b₂ MO of UO₃⁻ is of compact U(5f) character, the first detachment band X, yielding the closed-shell ¹A₁ ground state of UO₃, had low relative intensity. The calculated VDE was 1.60 eV at the CCSD(T)/SO level and 1.22 eV at the SO-TDDFT/SAOP level, compared with the experimental value of 1.44 eV in Tables 1 and 4. The calculated symmetric U-O stretching frequency was 852 cm^{-1} compared with the observed vibrational frequency of 850 ± 30 cm⁻¹. All doubly occupied valence MOs are O(2p)-based and give intense detachment features of open-shell character $\{O(2p^1) \cup U(5f-4b_2)^1\}$ with four different final electronic states, split by the order of 0.1 to 0.2 eV due to Coulomb-exchange and SO couplings (Table 1), resulting in closely spaced detachment channels. Therefore, it was impossible to resolve any vibrational structures in the higher binding energy detachment bands, which correspond to single or several groups of one-electron detachment channels from the O(2p) shells, as shown in Table 1 and also plotted in Figure 1d. Overall, the computed VDEs are in excellent agreement with the experimental PES data.



∆ electronvolts.



Figure 5. Qualitative orbital energy level scheme for U, UO₃, and 3O, based on SR-DFT/PBE calculations. Two dots indicate the highest doubly occupied level, a single dot indicates (sets of) partially (singly) occupied levels. $5b_1$ is the doubly occupied O(2p) type HOMO of UO_3 and UO_3^- , and $4b_2$ is the singly occupied U(5f) type SOMO of UO_3^{-} . The U(7s) type MO is energetically rather low in the anion while it is above the U(6d) shell in the neutral.

for x > 3. Jahn–Teller effects may be active, which will reduce the symmetries of UO_{x^*} . In the UO_x^- anion for x > 3, the extra electron will enter a dominantly O(2p)-type LUMO, resulting in significantly higher EAs for the O-rich UO_x species than for O-poor UO_x species with dominantly U(5f)-type LUMOs.

There are several chemically reasonable options for adding an open-shell $O(2p^4)$ atom to the closed-shell UO_3 molecule. In the global minimum of UO_4 (4A in Figure 4), the O atom is

added to the equatorial O^{2-} oxide ligand, forming an $\eta^2 \cdot O_2^{2-}$ peroxide ligand and a $C_{2\nu}$ -symmetric complex with a ${}^{1}A_{1}$ spinsinglet state. This structure was also reported by Michelini et al. at the DFT level.²⁵ Structure 4B in Figure 1 is the next higher isomer at +0.7 eV, where the fourth O is directly bound to U, competing for binding electrons with the other three O atoms. We found a spin-singlet state with D_{2d} symmetry at both DFT and CCSD(T) levels of theory. A slightly higher energy structure 4C at +0.85 eV is similar to structure 4A but with a triplet spin state, in which a η^2 -O₂ superoxide ligand is weakly bonded to a uranyl (U^V) unit in a biradical fashion.

We found similar structural isomers for the UO₄⁻ anion at the CCSD(T)-SO level but with different ordering. The global minimum of UO₄⁻ shown in 4a of Figure 4 corresponds to the neutral 4B isomer with a $C_{2\nu}$ -²B₁ state and no O–O bond. The two isomers with η^2 peroxide (4b) and superoxide (4c) are much higher in energy for UO_4^- . Hence, the global minimum of UO₄ cannot be accessed via detachment of the most stable isomer of UO₄⁻. Its orbital level scheme is displayed in Figure 6, and the MO contours are given in Figure S2. We calculated a sufficiently high barrier between the neutral 4B and 4A structures (Figure S3) so that the 4B state is sufficiently longlived to allow experimentally resolvable vibrational structure (Figure 2). The calculated symmetric U–O vibrational frequency (759 cm⁻¹) agrees quite well with the experimental value of 770 \pm 30 cm⁻¹. The calculated U–O bond length contractions upon electron detachment (see 4a and 4B in Figure 4) are also consistent with the value derived from the Franck-Condon simulation for the observed vibrational progression of the X band in Figure 2 (average $\Delta R \approx 6$ to 7 pm).

Article



Figure 6. Qualitative orbital energy level scheme of U, UO_4^- , and 4O, from SR-DFT/PBE calculations. The Sb_1 orbital of dominant O(2p) character is singly occupied in UO_4^- . A dot indicates partially occupied levels.

The 23 valence electrons of UO_4^- occupy the 12 O(2p)-type MOs, where the highest 5b₁ MO contains the unpaired electron (Figure 6 and Figure S2). We also found that there were some back-donations from O(2p) to the U(5f6d) shell. Because of exchange coupling with the anionic electron, the doubly occupied orbitals get split energies at the spin-unrestricted level (from $\Delta \varepsilon = 0.1$ eV for $8a_1$ up to $\Delta \varepsilon = 1.1$ eV for $2a_2$). Because the detachment MOs have dominant O(2p) character, the SO coupling plays a negligible role. Detachment of the single $5b_1$ electron from UO_4^- results in the ground electronic state of structure 4B (${}^{1}A_{1}$, $C_{2\nu}$, Figure 4). The calculated ADE of 3.60 eV and VDE of 3.92 eV at the CCSD(T) level agree well with the experimental values (Tables 2 and 4). The next detachment comes from the removal of a 5b₂ electron, which results in two channels removing a β or α electron. The computed VDEs at the DFT level are 4.14 and 4.33 eV, in good agreement with the measured VDEs of bands A (4.21 eV) and B (4.40 eV), as shown in Table 2. The next three detachment channels, $2a_2(\beta)$, $8a_1(\beta)$, $8a_1(\alpha)$, give close VDEs from 4.73 to 4.91 eV, in agreement with the broad band C. Following an energy gap, the higher binding energy detachment channels are very congested and almost continuous with calculated VDEs from 5.70 to 6.68 eV for the next nine detachment channels, consistent with the congested spectral features, as shown in Figure 2. The computed VDEs are also given as vertical bars in Figure 2b, and the overall agreement with experiment is reasonable.

5.3. UO₅ and UO₅⁻. The lowest energy structure of UO₅ (5A in Figure 4) contains a triplet O₂ weakly coordinated in the equatorial plane of UO₃ in η^1 fashion. The O–O distance (120 pm) is very similar to that of free O₂. The 5B structure is only +0.25 eV higher in energy, which contains an η^2 -O₂ in the equatorial plane. In structure 5B (³A', C_s), there is one unpaired spin on the equatorial O_{eq} (the 7a'' MO is mainly an O_{eq}(2p_z) orbital) and one unpaired spin on the O₂ unit (the 8a'' MO is mainly an O₂(π_{yz} *) orbital; see Figure S4), which are coupled through the U valence shell to a spin-triplet. Singlet structure 5C, in which all five O atoms are separated, is much higher in energy.

Again, for the UO_5^- anion, similar isomers were found as for neutral UO_5 , but the ordering is different. The global minimum structure Sa of UO_5^- corresponds to the neutral structure SB.



Figure 7. Qualitative orbital energy level scheme of UO₃, UO₅, and O₂ based on SR-DFT/B3LYP calculations. A single dot and a pair of dots indicate singly and doubly occupied levels, respectively. At the unrestricted KS-level, the 3a" and 8a" MOs of O₂(π,π^*) character are split by ±1 and ±2 eV, respectively. Accordingly the anionic 8a" electron is not the highest in energy, see Table 3 and Figure S4.

The lowest energy detachment from the UO₅⁻ ground state occurs by removing a β electron from the 7a" MO, leading (as mentioned) to the triplet structure 5B of neutral UO₅ with singly occupied 7a" and 8a" MOs. The calculated ADE at the CCSD(T) level for this channel was 3.92 eV, compared with the measured value of 4.02 eV (Table 4). The first VDE calculated at the KT-DFT-B3LP level was 4.36 eV. The detachment of an α electron gave a VDE of 4.37 eV for the final singlet state of UO₅. These two detachment channels gave very close VDEs, which were in reasonable agreement with the VDE of the X band (4.19 eV), as shown in Table 3. Hence, the X band of the photoelectron spectra of UO5- contains two overlapping detachment channels (Figure 3), making it impossible to resolve any vibrational structure. The next detachment takes place from the 15a' MO, which yielded a VDE of 4.60 eV for the triplet final state and 4.76 eV for the singlet final state. These two channels are in good agreement with the broad A band at 4.71 eV (Table 3). Following an energy gap, detachment from deeper MOs gave a series of closely lying detachment channels, consistent with the continuous spectral features observed in Figure 3b. All of the computed VDEs are compared with experiment in Table 3 and plotted as vertical bars in Figure 3b. Overall, the agreement between the computed VDEs and the observed PES is reasonable.

6. **DISCUSSION**

6.1. Chemical Bonding in UO_x (x = 3-5). UO₃ is a stable stoichiometric molecule with a large HOMO–LUMO gap, and it has the simplest electronic structure among the present three

monouranium oxides. AdNDP analyses revealed three lone pairs, one on each O atom, mainly O 2s electrons, as shown in Figure 8a. There are three dative-covalent $O(2s^{1/4}p_{\sigma}) \rightarrow$



Figure 8. Localized valence MOs from AdNDP analyses for (a) the UO_3 molecule and (b) the D_{2d} - UO_4 molecule. ON stands for occupation number.

U(Sf6d7s) pairs and six weakly dative $O(2p_{\pi}) \rightarrow U(Sf6d)$ pairs. Anticipating the results of the other UO_x molecules, three $O(\sigma)$ -pair donations throughout yield approximately U- $(Sf^46d^{1/2}7s^1)$, while the weaker $(2x) O(\pi)$ -pair donations approximately contribute another $U(Sf^{2/3}d^{1/3})$. The UO_3 molecule can be viewed as containing three dative U=O triple bonds.

The bonding in UO_4 and UO_5 is more complicated. The AdNDP analyses for the D_{2d} UO₄ are displayed in Figure 8b,

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and those of a closed shell isomer of UO_5 are shown in Figure S5. We again found a O(2sp) type lone pair on each O atom. In addition, we found weakly dative $O(2p\pi) \rightarrow U(5f6d)$ 2c-2e bonds, eight and ten, respectively, for UO_4 and UO_5 , similar to the 2c-2e π -pairs of UO_3 . Again three pairs for σ -electrons are left for four or five O(2sp) hybrids, resulting in multicenter bonding owing to the electron deficiency in $UO_{4,5}$. In UO_4 , we found two 3c-2e bonds and a totally delocalized 5c-2e bond (Figure 8b), and in the closed-shell 5C structure of UO_5 , we found one 3c-2e σ -bond on the O-U-O axis and two 4c-2e σ -bonds in the equatorial UO_3 plane (Figure S5).

We further analyzed the bond order indices from DFT calculations (covalent as defined by Mayer;⁵⁹ covalent + ionic as defined by Nalewajski and Mrozek^{60–63}) for UO_x and UO_x⁻ (x = 2-6), as summarized in Table 5. We included UO₂ and UO₆ in the bond order analyses for completeness and for comparison. The axial uranyl-like U=O bonds have covalent bond order values from 1.61 to 1.97 and covalent+ionic values from 2.27 to 2.78. In general, the axial bond orders in the anions are lower than in the neutrals because the anions have lower positive charge on the U atom and reduced coordinative interaction. The equivalent U–O bonds in D_{2d} -UO₄ and O_{h} -UO₆ are definitely weaker than typical polar U=O interactions in the uranyl-like fragments. The equatorial U-O bonds in UO_3 and UO_3^- and in 5A-UO₅ and UO_5^- are similar to the corresponding U– O_{ax} bonds, whereas the U– O_{eq} in UO₄⁻ and $5B-UO_5$ are weaker than those in the uranyl-like units. The U-O bond orders of Mayer and N-M for the O₂^q ligands are, respectively, 0.9 and 1.5 for q = 2-, half of that for q = 1-, and even smaller for q = 0. Conversely, the internal O-O bond orders vary from around 1 for O_2^{2-} to around 1.5 for O_2^{1-} to around 2 for O_2^0 .

We also computed the effective atomic charges and spins for UO_x and UO_x^- (x = 2-6), as given in Table 6. As usual, Mulliken's electric charge populations⁵⁸ are about 1/3 of the formal charges. (The Voronoi charges⁷⁴ show similar trends, but are 2 to 3 times smaller.) For UO_x^- ($x \le 3$), the anionic electron is predominantly localized on the U atom, while for $x \ge 4$ it is localized on the O atoms. The formal chemical reduction of a metal cation reduces the effective charge on the metal only a bit (by $\sim 1/2$ e) but transfers quite some electronic

molecule ^b		U–O(1,2) axial uranyl			U–O(3,4) equatorial O			U < O ₂ equatorial O ₂			0-0			
formula	sym	term	mult	May	N–M	mult	May	N–M	mult	May	N–M	O_2^q	May	N–M
UO ₂	$D_{\infty h}$	${}^{3}\Phi_{u}$	$2 \times$	1.97										
UO_2^-	$D_{\infty h}$	${}^{2}\Phi_{u}$	$2 \times$	1.90										
UO ₃ (3A)	$C_{2\nu}$	${}^{1}A_{1}$	$2 \times$	1.92	2.78	$1 \times$	1.95	2.90						
$UO_{3}^{-}(3a)$	$C_{2\nu}$	${}^{2}B_{2}$	$2 \times$	1.78	2.71	$1 \times$	1.75	2.77						
UO ₄ (4A)	$C_{2\nu}$	${}^{1}A_{1}$	$2 \times$	1.91	2.75				$2 \times$	0.90	1.50	O_2^{2-}	0.98	1.23
UO_4 (4B)	D_{2d}	${}^{1}A_{1}$	4×	1.63	2.34									
UO_{4}^{-} (4a)	$C_{2\nu}$	${}^{2}B_{1}$	$2 \times$	1.61	2.27	$2 \times$	1.56	2.19						
UO_5 (5A)	C_s	³ A″	$2 \times$	1.90	2.71	$1 \times$	1.92	2.72	$1 \times$	0.15	0.28	$O_2^{\ 0}$	1.87	2.00
UO_5 (5B)	C_s	${}^{3}A'$	$2 \times$	1.85	2.66	$1 \times$	1.06	1.80	$2 \times$	0.46	0.75	O_2^{1-}	1.44	1.68
$UO_{5}^{-}(5a)$	C_s	$^{2}A''$	$2 \times$	1.81	2.55	$1 \times$	1.81	2.55	$2 \times$	0.36	0.60	O2 ¹⁻	1.43	1.74
UO ₆	O_h	${}^{1}A_{1g}$	6×	1.35										
$[UO_2](O_2)_2$	D_{2h}	${}^{3}A_{3u}$	$2 \times$	1.90					4×	0.46		O_2^{1-}	1.45	

Fable 6. Effective Atomic Mulliken	Charge (q) and Spin ((s) for I	UO _x and 1	UO_x^{-} ($(x=2-6)^a$
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molecule ^b				U axial O(1,2)			equatorial O(3,4)			equatorial O ₂				
formula	sym	term	9	5	mult	9	5	mult	9	5	O_2^q	mult	9	\$
UO ₂	$D_{\infty h}$	${}^{3}\Phi_{u}$	1.36	2.05	$2\times$	-0.68	-0.02							
UO_2^-	$D_{\infty h}$	${}^{2}\Phi_{u}$	0.50	1.07	$2 \times$	-0.75	-0.04							
UO ₃ (3A)	$C_{2\nu}$	${}^{1}A_{1}$	2.07	0	$2 \times$	-0.68	0	$1 \times$	-0.72	0				
$UO_{3}^{-}(3a)$	$C_{2\nu}$	${}^{2}B_{2}$	1.59	1.15	$2 \times$	-0.85	-0.05	$1 \times$	-0.90	-0.05				
UO ₄ (4A)	$C_{2\nu}$	${}^{1}A_{1}$	2.25	0	$2 \times$	-0.66	0				O_2^{2-}	$2 \times$	-0.46	0
UO_4 (4B)	D_{2d}	${}^{1}A_{1}$	2.46	0	4×	-0.61	0							
$UO_{4}^{-}(4a)$	$C_{2\nu}$	${}^{2}B_{1}$	2.12	-0.18	$2 \times$	-0.77	0.22	$2 \times$	-0.79	0.37				
UO_5 (5A)	C_s	³ A″	2.07	-0.02	$2 \times$	-0.69	0.01	$1 \times$	-0.73	0.02	$O_2^{\ 0}$	$1 \times$	-0.02;	0.89
													+0.05	1.08
UO_5 (5B)	C_s	³ A'	2.32	-0.11	$2 \times$	-0.64	0.07	$1 \times$	-0.53	0.92	O21-	$2 \times$	-0.26	0.52
$UO_{5}^{-}(5a)$	C_s	$^{2}A''$	2.06	-0.05	$2 \times$	-0.79	0.01	$1 \times$	-0.83	0.01	O_2^{1-}	$2 \times$	-0.32	0.51
UO ₆	O_h	${}^{1}A_{1g}$	3.04	0	6×	-0.51	0							
$[UO_2](O_2)_2$	D_{2h}	${}^{3}A_{3u}$	2.32	-0.08	$2 \times$	-0.64	0.01				O2 ¹⁻	4×	-0.26	0.52

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charge onto the basic ligands (here by -1/2 e). The spins are fully recovered by Mulliken's spin populations. In the case of UO_4^- , the spin is delocalized over all four O atoms. In the case UO_5 , the two spins sit either on the η^1 -O₂ ligand (structure 5A) or on each of the equatorial O_{eq} and the η^2 -O₂ ligand (structure 5B). As usual, the spin on the principal centers (U or the O atoms, respectively) is slightly larger than 1, with some small opposite spin polarization on the "opposite" atoms (i.e., the O or U atoms, respectively).

6.2. Sequential Oxidation of U in UO_x and UO_x⁻ (x = 1-6). The early actinides are relatively strong electropositive metals and can be easily oxidized by oxygen. Therefore, up to x= 3, the UO_x^{q} species are ordinary oxides with uranium in oxidation states +(2x + q) (i.e., \leq VI, the maximum oxidation state of U). The common energetic order of the uranium atomic orbitals in chemical compounds is $5f < 6d \ll 7s$. Only when U becomes "flooded" by negative electronic charges are the 5f and 6d orbitals pushed up into the vicinity of the 7s level. U and Np are the last actinides, where formally all 5f electrons can be easily transferred to electronegative ligands. The 6p⁶ semicore-shell can interact with low-lying valence orbitals of the ligands, such as 2s and 2p of oxygen, thereby transferring less or more SO-coupling strength, for instance, from the heavy element to the light element oxygen; however, formal oxidation of the 6p° semicore-shell appears impossible in stable chemical compounds. For the middle and later actinides, that is, Np, Pu, Am, Cm, and so on, it becomes less and less possible to formally oxidize even the whole valence shell.⁷

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Another interesting question concerns the assignment of the oxidation states. The D_{2d} UO₄ consists of U^{VI} and four equivalent O atoms, which must have a fractional oxidation state (O^{-1.5}). The $C_{2\nu}$ UO₄⁻ ground state is more problematic; it contains a U^{VI} and two slightly different pairs of O atoms. Neither simple option, $2O^{2-} + 2O^{-1.5}$ nor $4O^{-1.75}$, provides a satisfactory representation of the reality. The ground state of UO₅⁻ has a (η^2 -O₂⁻)UO₃ structure (5a in Figure 4). Because of the presence of two different O atoms around U, the detachment processes are interesting. As shown in Table 3, the first detachment channel is from the 7a'' MO, which is primarily a 2p orbital on the equatorial O_{eq} atom. This detachment would yield a (η^2 -O₂⁻)UO₃⁺ species, corresponding to 5B of UO₅ (Figure 4).

7. CONCLUSIONS

extended 5f6d7s valence shell of the early actinides as well as of the multifaceted oxidation tendency of oxygen.

The often so-called "principally exact" density functional theory with approximate exchange-correlation functionals is known to reach its limits when chemical accuracy is demanded for metal compounds from the upper range of the d-block and from the f-block. The early actinide elements, in particular, form a quantum-chemical challenge owing to the extended spdf semicore and valence shells, the vast near-degeneracy multiconfiguration mixing, and the strong scalar and spin-orbit relativistic effects. Relativistically corrected DFT approaches can only be used for first-step screening purposes. Modern quasi-relativistic multireference static-dynamic electron-correlation approaches are adequate to produce reliable results at the level of chemical demands (here within ± 0.2 eV) but are often not economic in terms of the computational costs. With the help of an empirical overall energy shift, we showed that even DFT results can help assign the experimental observations, again within about ± 0.2 eV. Accurate and sophisticated measurements are indispensible to guide theoretical efforts, while the combination of experiment and computation is essential to understand the electronic structures and chemical bonding of even the seemingly simple actinide molecules.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.Sb11354.

Ground-state geometries of the UO_x^{q} species, additional results on UO_3 and UO_3^{-} from SR/SO-CCSD(T) calculations, MO contours for UO_x^{-} (x = 3-5), a schematic of the potential energy curves for the detachment processes of UO_4^{-} , and localized valence MOs from AdNDP analyses for the $C_{2\nu}$ -UO₅ (SC) molecule. (PDF)

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Notes

The authors declare no competing financial interest

ACKNOWLEDGMENTS

REFERENCES

(1) Grenthe, I.; Drożdżyński, J.; Fujino, T.; Buck, E. C.; Albrecht-Schmitt, T. E.; Wolf, S. F.: Uranium. In *The Chemistry of the Actinide and Transactinide Elements*; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Vol. 1, pp 253–698.

(2) Pepper, M.; Bursten, B. E. The Electronic Structure of Actinide-Containing Molecules: A Challenge to Applied Quantum Chemistry. *Chem. Rev.* **1991**, *91*, 719–741.

(3) Han, J. D.; Kaledin, L. A.; Goncharov, V.; Komissarov, A. V.; Heaven, M. C. Accurate Ionization Potentials for UO and UO_2 : A Rigorous Test of Relativistic Quantum Chemistry Calculations. *J. Am. Chem. Soc.* **2003**, *125*, 7176–7177.

(4) Han, J. D.; Goncharov, V.; Kaledin, L. A.; Komissarov, A. V.; Heaven, M. C. Electronic Spectroscopy and Ionization Potential of UO₂ in the Gas Phase. *J. Chem. Phys.* **2004**, *120*, 5155–5163.

(5) Lue, C. J.; Jin, J.; Ortiz, M. J.; Rienstra-Kiracofe, J. C.; Heaven, M. C. Electronic Spectroscopy of UO₂ Isolated in a Solid Ar Matrix. *J. Am. Chem. Soc.* **2004**, *126*, 1812–1815.

(6) Gagliardi, L.; Heaven, M. C.; Krogh, J. W.; Roos, B. O. The Electronic Spectrum of the UO_2 Molecule. *J. Am. Chem. Soc.* 2005, 127, 86–91.

(7) Zhou, M. F.; Andrews, L.; Ismail, N.; Marsden, C. Infrared Spectra of UO_2 , UO_2^+ , and UO_2^- in Solid Neon. J. Phys. Chem. A **2000**, 104, 5495–5502.

(8) Li, J.; Bursten, B. E.; Andrews, L.; Marsden, C. J. On the Electronic Structure of Molecular UO_2 in the Presence of Ar Atoms: Evidence for Direct U-Ar Bonding. *J. Am. Chem. Soc.* **2004**, *126*, 3424–3425.

(9) Gagliardi, L.; Roos, B. O.; Malmqvist, P. A.; Dyke, J. M. On the Electronic Structure of the UO_2 Molecule. *J. Phys. Chem. A* **2001**, *105*, 10602–10606.

(10) Chang, Q. Ab Initio Calculations on UO_2 . Master's Thesis, The Ohio State University, 2002.

(11) Fleig, T.; Jensen, H. J. A.; Olsen, J.; Visscher, L. The Generalized Active Space Concept for the Relativistic Treatment of Electron Correlation. III. Large-scale Configuration Interaction and Multi-configuration Self-Consistent-Field Four-Component Methods with Application to UO_2 . J. Chem. Phys. **2006**, 124, 104106.

(12) Infante, I.; Eliav, E.; Vilkas, M. J.; Ishikawa, Y.; Kaldor, U.; Visscher, L. A Fock Space Coupled Cluster Study on the Electronic Structure of the UO_2 , UO_2^+ , U_4^+ , and U_5^+ Species. *J. Chem. Phys.* **2007**, *127*, 124308.

(13) Clavaguera-Sarrio, C.; Vallet, V.; Maynau, D.; Marsden, C. J. Can Density Functional Methods Be Used for Open-Shell Actinide Molecules? Comparison with Multiconfigurational Spin-Orbit Studies. *J. Chem. Phys.* **2004**, *121*, 5312–5321.

(14) Gabelnick, S. D.; Reedy, G. T.; Chasanov, M. G. Infrared Spectra of Matrix-Isolated Uranium Oxide Species. 1. The Stretching Region. J. Chem. Phys. **1973**, 58, 4468–4475.

(15) Gabelnick, S. D.; Reedy, G. T.; Chasanov, M. G. Infrared Spectra of Matrix-Isolated Uranium Oxide Species. 2. Spectral Interpretation and Structure of UO_3 . *J. Chem. Phys.* **1973**, *59*, 6397–6404.

(16) Hunt, R. D.; Andrews, L. Reactions of Pulsed-Laser Evaporated Uranium Atoms with Molecular Oxygen: Infrared Spectra of UO, UO_2 , UO_3 , UO_2^+ , UO_2^{2+} , and UO_3 - O_2 in Solid Argon. J. Chem. Phys. **1993**, 98, 3690–3696.

(17) Merritt, J. M.; Han, J.; Heaven, M. C. Spectroscopy of the UO_2^+ Cation and the Delayed Ionization of UO_2 . *J. Chem. Phys.* **2008**, *128*, 084304.

(18) Infante, I.; Andrews, L.; Wang, X. F.; Gagliardi, L. Noble Gas Matrices May Change the Electronic Structure of Trapped Molecules: The $UO_2(Ng)_4$ (Ng = Ne, Ar) Case. *Chem. - Eur. J.* **2010**, *16*, 12804–12807.

(19) Li, W.-L.; Su, J.; Jian, T.; Lopez, G. V.; Hu, H.-S.; Cao, G.-J.; Li, J.; Wang, L.-S. Strong Electron Correlation in UO_2^{-1} : A Photoelectron Spectroscopy and Relativistic Quantum Chemistry Study. *J. Chem. Phys.* **2014**, 140, 094306.

(20) Czekner, J.; Lopez, G. V.; Wang, L. S. High Resolution Photoelectron Imaging of UO⁻ and UO₂⁻ and the Low-Lying Electronic States and Vibrational Frequencies of UO and UO₂. *J. Chem. Phys.* **2014**, *141*, 244302.

(21) Li, W. L.; Hu, H. S.; Jian, T.; Lopez, A. G.; Su, J.; Li, J.; Wang, L. S. Probing the Electronic Structures of Low Oxidation-State Uranium Fluoride Molecules UF_x^- (x = 2–4). *J. Chem. Phys.* **2013**, *139*, 244303.

(22) Tyagi, R.; Zhang, Z. Y.; Pitzer, R. M. Electronic Spectrum of the UO and UO⁺ Molecules. *J. Phys. Chem. A* **2014**, *118*, 11758–11767.

⑪'Pí

(25) (a) Michelini, M. d. C.; Marçalo, J.; Russo, N.; Gibson, J. K. Gas-Phase Reactions of Uranate Ions, UO_2^- , UO_3^- , UO_4^- , and UO_4H^- , with Methanol: A Convergence of Experiment and Theory. *Inorg. Chem.* **2010**, *49*, 3836–3850. (b) Sokalska, M.; Prussakowska, M.; Hoffmann, M.; Gierczyk, B.; Frański, R. Unusual Ion UO_4^- Formed Upon Collision Induced Dissociation of $[UO_2(NO_3)_3]^-$, $[UO_2(CIO_4)_3]^-$, $[UO_2(CH_3COO)_3]^-$ Ions. *J. Am. Soc. Mass Spectrom.* **2010**, *21*, 1789–1794.

(26) Ricks, A. M.; Gagliardi, L.; Duncan, M. A. Uranium Oxo and Superoxo Cations Revealed Using Infrared Spectroscopy in the Gas Phase. J. Phys. Chem. Lett. 2011, 2, 1662–1666.

(27) Odoh, S. O.; Schreckenbach, G. Performance of Relativistic Effective Core Potentials in DFT Calculations on Actinide Compounds. J. Phys. Chem. A **2010**, 114, 1957–1963.

(28) Bross, D. H.; Peterson, K. A. Composite Thermochemistry of Gas Phase U(VI)-Containing Molecules. J. Chem. Phys. 2014, 141, 244308.

(29) Li, P.; Jia, T. T.; Gao, T.; Li, G. The Structural and Spectroscopic Properties for Uranium Oxides. *Chin. Phys. B* 2012, 21, 043301.

(30) Bryantsev, V. S.; Jong, W. A. d.; Cossel, K. C.; Diallo, M. S.; Goddard, W. A.; Groenewold, G. S.; Chien, W.; van Stipdonk, M. J. Two-Electron Three-Centered Bond in Side-On (η^2) Uranyl(V) Superoxo Complexes. J. Phys. Chem. A **2008**, 112, 5777–5780.

(31) Wang, L. S.; Cheng, H. S.; Fan, J. W. Photoelectron Spectroscopy of Size-Selected Transition Metal Clusters: Fe_n^- , n = 3-24. J. Chem. Phys. **1995**, 102, 9480–8493.

(32) Akola, J.; Manninen, M.; Hakkinen, H.; Landman, U.; Li, X.; Wang, L. S. Photoelectron Spectra of Aluminum Cluster Anions: Temperature Effects and Ab Initio Simulations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *60*, 11297–11300.

(33) Huang, W.; Wang, L. S. Probing the 2D to 3D Structural Transition in Gold Cluster Anions Using Argon Tagging. *Phys. Rev. Lett.* **2009**, *102*, 153401.

(34) Fonseca Guerra, C.; Snijders, J.; te Velde, G.; Baerends, E. J. Towards an Order-N DFT Method. *Theor. Chem. Acc.* **1998**, *99*, 391–403.

⑪, 'God', '

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2010.

(38) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(39) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

७७७९

(42) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic Regular Two-Component Hamiltonians. J. Chem. Phys. **1993**, 99, 4597–4610.

(44) Cao, X.; Dolg, M.; Stoll, H. Valence Basis Sets for Relativistic Energy-Consistent Small-Core Actinide Pseudopotentials. *J. Chem. Phys.* **2003**, *118*, 487–496.

(45) Cao, X.; Dolg, M. Segmented Contraction Scheme for Small-Core Actinide Pseudopotential Basis Sets. *J. Mol. Struct.: THEOCHEM* **2004**, *673*, 203–209.

(46) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron Affinities of the First-Row Atoms Revisited. Systematic Basis Sets and Wave Functions. J. Chem. Phys. **1992**, *96*, 6796–6806.

(47) Knowles, P. J.; Hampel, C.; Werner, H.-J. Coupled Cluster Theory for High Spin, Open Shell Reference Wave Functions. *J. Chem. Phys.* **1993**, *99*, 5219–5227.

(48) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. Molpro: A General-Purpose Quantum Chemistry Program Package. *WIREs Comput. Mol. Sci.* **2012**, *2*, 242–253.

(49) Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G. et al. *MOLPRO*, version 2012.1, a package of ab initio programs, 2012.

⑪ඖ

(52) Su, J.; Wang, Z.; Pan, D.; Li, J. Excited States and Luminescent Properties of UO_2F_2 and Its Solvated Complexes in Aqueous Solution. *Inorg. Chem.* **2014**, *53*, 7340–7350.

(53) Dau, P. D.; Su, J.; Liu, H. T.; Liu, J. B.; Huang, D. L.; Li, J.; Wang, L. S. Observation and investigation of the uranyl tetrafluoride dianion $(UO_2F_4^{2-})$ and its solvation complexes with water and acetonitrile. *Chem. Sci.* **2012**, *3*, 1137–1146.

(54) Malmqvist, P. Å.; Roos, B. O.; Schimmelpfennig, B. The Restricted Active Space (RAS) State Interaction Approach with Spin– Orbit Coupling. *Chem. Phys. Lett.* **2002**, *357*, 230–240.

(55) Roos, B. O.; Malmqvist, P. Å. Relativistic Quantum Chemistry: The Multiconfigurational Approach. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2919–2927.

(56) Tozer, D. J.; Handy, N. C. Improving Virtual Kohn–Sham Orbitals and Eigenvalues: Application to Excitation Energies and Static Polarizabilities. *J. Chem. Phys.* **1998**, *109*, 10180–10189.

(57) van Meer, R.; Gritsenko, O. V.; Baerends, E. J. Physical Meaning of Virtual Kohn-Sham Orbitals and Orbital Energies: An Ideal Basis for the Description of Molecular Excitations. *J. Chem. Theory Comput.* **2014**, *10*, 4432–4441.

(58) Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. J. Chem. Phys. **1955**, 23, 1833-1840.

(59) Mayer, I. Charge, Bond Order and Valence in the Ab Initio SCF theory. *Chem. Phys. Lett.* **1983**, *97*, 270–274.

(60) Michalak, A.; Dekock, R. L.; Ziegler, T. Bond Multiplicity in Transition-Metal Complexes: Applications of Two-Electron Valence Indices. *J. Phys. Chem. A* **2008**, *112*, 7256–7263.

(61) Nalewajski, R. F.; Mrozek, J. Modified Valence Indices from the Two-Particle Density Matrix. *Int. J. Quantum Chem.* **1994**, *51*, 187–200.

(62) Nalewajski, R. F.; Mrozek, J.; Michalak, A. Int. J. Quantum Chem. 1997, 61, 589. Nalewajski, R. F.; Mrozek, J.; Michalak, A. Exploring Bonding Patterns of Molecular Systems Using Quantum Mechanical Bond Multiplicities. *Polish J. Chem.* **1998**, 72, 1779–1791.

(63) Nalewajski, R. F.; Mrozek, J.; Mazur, G. Quantum Chemical Valence Indices from the One-Determinantal Difference Approach. *Can. J. Chem.* **1996**, *74*, 1121–1130.

७७९९९९

(65) Weinhold, F.; Landis, C. R. Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective; Cambridge University Press: Cambridge, U. K., 2005.

(66) Dennington, R.; Keith, T.; Millam, J. *GaussView*, Version 5; Semichem, Inc.: Shawnee Mission, KS, 2009.

(67) Ervin, K. M. PESCAL Fortran Programs for Franck-Condon Analysis of Molecular Electronic Spectra; University of Reno, 2010

(68) Su, J.; Wei, F.; Schwarz, W. H. E.; Li, J. Deduction of Bond Length Changes of Symmetric Molecules from Experimental Vibrational Progressions, Including a Topological Mass Factor. J. Phys. Chem. A 2012, 116, 12299–12304.

(69) Dau, P. D.; Su, J.; Liu, H. T.; Huang, D. L.; Wei, F.; Li, J.; Wang, L. S. Photoelectron Spectroscopy and Theoretical Studies of UF_5^- and UF_6^- . J. Chem. Phys. **2012**, 136, 194304.

(70) Su, J.; Dau, P. D.; Xu, C. F.; Huang, D. L.; Liu, H. T.; Wei, F.; Wang, L. S.; Li, J. A Joint Photoelectron Spectroscopy and Theoretical Study on the Electronic Structure of UCl_5^- and UCl_5 . *Chem. - Asian J.* **2013**, *8*, 2489–2496.

(71) Su, J.; Dau, P. D.; Liu, H. T.; Huang, D. L.; Wei, F.; Schwarz, W. H. E.; Li, J.; Wang, L. S. Photoelectron Spectroscopy and Theoretical Studies of Gaseous Uranium Hexachlorides in Different Oxidation States: UCl_6^{q-1} (q = 0-2). J. Chem. Phys. **2015**, 142, 134308.

(72) Neumark, D. M.; Lykke, K.; Andersen, R. T.; Lineberger, W. C. Laser Photodetachment Measurement of the Electron Affinity of Atomic Oxygen. *Phys. Rev. A: At., Mol., Opt. Phys.* **1985**, 32, 1890–1892.

(73) Xiao, H.; Hu, H.-S.; Schwarz, W. H. E.; Li, J. Theoretical Investigations of Geometry, Electronic Structure and Stability of UO₆: Octahedral Uranium Hexoxide and Its Isomers. *J. Phys. Chem. A* **2010**, *114*, 8837–8844.

(74) Fonseca Guerra, C.; Handgraaf, J.-W.; Baerends, E. J.; Bickelhaupt, F. M. Voronoi Deformation Density (VDD) Charges: Assessment of the Mulliken, Bader, Hirshfeld, Weinhold, and VDD Methods for Charge Analysis. *J. Comput. Chem.* **2004**, *25*, 189–210.

(75) Zaitsevskii, A. Plutonium and Transplutonium Element Trioxides: Molecular Structures, Chemical Bonding, and Isomers. *Phys. Chem. Chem. Phys.* **2015**, *17*, 24831–24836.