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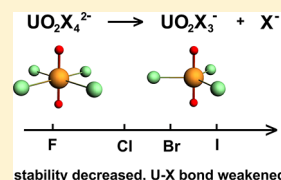
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S Supporting Information

ABSTRACT: While uranyl halide complexes $[\text{UO}_2(\text{halogen})_n]^{2-n}$ ($n = 1, 2, 4$) are ubiquitous, the tricoordinate species have been relatively unknown until very recently. Here photoelectron spectroscopy and relativistic quantum chemistry are used to investigate the bonding and stability of a series of gaseous tricoordinate uranyl complexes, UO_2X_3^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). Isolated UO_2X_3^- ions are produced by electrospray ionization and observed to be highly stable with very large adiabatic electron detachment energies: 6.25, 6.64, 6.27, and 5.60 eV for $\text{X} = \text{F}, \text{Cl}, \text{Br}$, and I , respectively. Theoretical calculations reveal that the frontier molecular orbitals are mainly of uranyl U–O bonding character in UO_2F_3^- , but they are from the ligand valence np lone pairs in the heavier halogen complexes. Extensive bonding analyses are carried out for UO_2X_3^- as well as for the doubly charged tetracoordinate complexes ($\text{UO}_2\text{X}_4^{2-}$), showing that the U–X bonds are dominated by ionic interactions with weak covalency. The U–X bond strength decreases down the periodic table from F to I. Coulomb barriers and dissociation energies of $\text{UO}_2\text{X}_4^{2-} \rightarrow \text{UO}_2\text{X}_3^- + \text{X}^-$ are calculated, revealing that all gaseous dianions are in fact metastable. The dielectric constant of the environment is shown to be the key in controlling the thermodynamic and kinetic stabilities of the tetracoordinate uranyl complexes via modulation of the ligand–ligand Coulomb repulsions.



1. INTRODUCTION

Uranyl dication (UO_2^{2+}) is the most stable form of uranium in nature and usually coordinated by ligands or solvent molecules. Investigations of uranyl complexes and their stabilities are important in understanding the chemical transformation and migration of nuclear wastes, as well as the coordination chemistry in recycling spent nuclear fuels.¹ Elucidating the nature of uranium–ligand chemical bonds is critical for evaluating the binding ability of various ligands^{2–4} and for development of new ligands for efficient and selective separation of fission products.^{5–15} Among numerous uranyl compounds with various inorganic and organic ligands, uranyl halides have been extensively investigated due to their important roles in the extraction of uranium into the aqueous phase as well as in serving as useful starting materials for syntheses of a wide variety of uranium compounds.^{16,17}

The uranyl dication is linear with two $\text{U}\equiv\text{O}$ triple bonds, $[\text{O}\equiv\text{U}\equiv\text{O}]^{2+}$, which is typically coordinated by 4–6 ligands in the equatorial plane.^{1,18} No isolated uranyl halides with fewer than four equatorial ligands have been observed in the condensed phases.¹ Extended X-ray absorption fine structure (EXAFS) and X-ray crystallography experiments have shown that uranyl usually has a saturated equatorial coordination number (CN_{eq}) of 4–6 by ligands and/or solvent molecules in condensed phases.^{19–21} In the solid state, multiply charged uranyl halides, $\text{UO}_2\text{F}_3^{3-}$ ²² and $\text{UO}_2\text{X}_4^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)^{23–26}

have been observed experimentally. Despite the syntheses of complexes formulated with $\text{UO}_2\text{F}_6^{4-}$ and $\text{UO}_2\text{F}_7^{5-}$,^{27,28} uranyl halides with more than 6 equatorial halogen ligands seem unlikely as the X-ray structure of the UO_2F_2 crystal shows that the $\text{UO}_2\text{F}_6^{4-}$ ion has a D_{3d} local symmetry with the six ligands arranged in a nonplanar zigzag crown along the equatorial plane.²⁹ The multiply charged complexes appear to be less stable in the solution than in the solid due to ligand exchanges. For example, an F^- ligand in the $\text{UO}_2\text{F}_5^{3-}$ trianion is substituted by a neutral solvent molecule (water or acetonitrile) to form the $\text{UO}_2\text{F}_4(\text{solvent})^{2-}$ dianions.^{30,31} EXAFS and UV–Vis absorption experiments show that the $\text{UO}_2\text{Cl}_4^{2-}$ dianion exists in organic solutions with high concentrations of Cl^- .³² The $\text{UO}_2\text{Br}_4^{2-}$ dianion has been observed to be stable in ionic liquids,³³ whereas high-energy X-ray scattering (HEXS) data have revealed an average U–Br CN_{eq} of 1.9 in concentrated aqueous hydrobromic acid solutions.²⁸ Uranyl species tend to retain low CN_{eq} in the gas phase due to increased Coulomb repulsion between the ligands. Indeed, uranyl complexes exist in low-temperature noble-gas matrices in the form of neutral UO_2X_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) species.^{34–36} Recently, Groenewold et al. measured the infrared multiphoton dissociation spectroscopy (IRMPD) of UO_2X_3^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) in the gas phase.¹³

Received: March 15, 2013

Published: May 10, 2013



We observed stable $\text{UO}_2\text{F}_4^{2-}$ and $\text{UO}_2\text{Cl}_4^{2-}$ dianions and their solvation complexes with water and acetonitrile molecules in the gas phase using electrospray ionization (ESI),^{37,38} but $\text{UO}_2\text{Br}_4^{2-}$ and $\text{UO}_2\text{I}_4^{2-}$ were not observed in these experiments.

The two strong $\text{U}\equiv\text{O}$ triple bonds in uranyl are formed between the U 5f/6d orbitals and the O 2p orbitals.³⁹ The resulting six frontier bonding orbitals (σ_w , π_w , π_g , and σ_g) are fully occupied with 12 valence electrons. The U 7s shell usually does not participate in bonding in uranyl complexes because of its high orbital energy in U(VI); the U 5f δ_w , 5f ϕ_w , and 6d δ_g orbitals remain nonbonding because their symmetries do not match with that of the O 2p orbitals. These occupied and nonbonding frontier orbitals are available for σ and π interactions with the equatorial ligands, thus weakening the $\text{U}\equiv\text{O}$ bond upon coordination.^{18,40} The CN_{eq} in uranyl complexes is a result of competition between the U–X bonding strength and the electrostatic Coulomb repulsion among the negatively charged X ligands. Photodissociation was not observed for UO_2F_3^- in the previous IRMPD experiment,¹³ implying that the U–F bond is the strongest among the UO_2X_3^- complexes. Recent experimental observations and investigations of $\text{UO}_2\text{X}_4^{2-}$ (X = F, Cl) and UO_2X_3^- (X = F, Cl, Br, I) in the gas phase indicate that there are rich chemistries in uranyl halides outside the condensed phases.

Here we report the first gas-phase investigation of the electronic structures of UO_2X_3^- (X = F, Cl, Br, I) using photoelectron spectroscopy (PES) and relativistic quantum chemistry calculations. The ESI-PES technique developed in the Wang lab⁴¹ is uniquely suited to study negatively charged uranyl complexes. In the current study, the PES experiments are carried out on the series of UO_2X_3^- complexes (X = F, Cl, Br, I), which are produced by ESI. We find that all UO_2X_3^- species are highly stable electronically with adiabatic electron detachment energies (ADEs) ranging from 5.60 eV for UO_2I_3^- to as high as 6.64 eV for UO_2Cl_3^- . Calculations using density function theory (DFT) and ab initio wave function theory (WFT) are carried out to gain insight into the electronic structures and stabilities of these monoanions. The thermodynamic and kinetic stabilities of the $\text{UO}_2\text{X}_4^{2-}$ (X = F, Cl, Br, I) dianions are also explored in relation to the UO_2X_3^- monoanions. Extensive bonding analyses are performed to understand the nature of the U–X bonds in UO_2X_3^- and $\text{UO}_2\text{X}_4^{2-}$.

2. EXPERIMENTAL AND THEORETICAL METHODS

2.1. Electrospray and Photoelectron Spectroscopy. The experiment was performed using the ESI-PES apparatus developed in the Wang lab, as described in detail previously.⁴¹ Briefly, the UO_2X_3^- (X = Cl, Br, I) anions were produced by electrospray of a 1 mM solution of $\text{UO}_2(\text{CH}_3\text{CO}_2)_2\cdot 2\text{H}_2\text{O}$ mixed with the corresponding halogen acid (HX) in a methanol/water (90/10) mixed solvent. The pH of the solution was adjusted to be ~ 4 . The UO_2F_3^- complex was formed by adding an excess amount of AgF to a 1 mM solution of $\text{U}(\text{SO}_4)_2$ in acetonitrile. Anions from the ESI source were accumulated in an ion trap operated at 20 K for 0.1 s and then pulsed into the extraction zone of a time-of-flight mass spectrometer. Anions of interest were selected by a mass gate and decelerated before being intercepted by a laser beam in the detachment region of a magnetic-bottle photoelectron analyzer. In the current study, we used an F₂ excimer laser (157 nm, 7.866 eV) because of the very high electron binding energies of the uranyl halide complexes. The details of the cryogenically cooled ion trap developed by the Wang lab have been described previously.^{42a} Cold ions are essential to eliminate vibrational hot bands and achieve better spectral resolution and more accurate

ADE measurements.^{42b} PES experiments were calibrated using the known spectra of Au^- and I^- . Au^- atomic anion was produced by ESI of an acetonitrile solution of PPh_3AuCl with NaSCH_3 and a trace amount of CH_3OH .⁴³ The current electron flight tube is shortened from 4.0 to 2.5 m, leading to only a slight decrease of electron energy resolution.^{37,38} 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.^{42b,44}

2.2. Theoretical Methods. Theoretical studies were carried out using both DFT and WFT methods. DFT calculations were performed on both UO_2X_3^- and UO_2X_3 (X = F, Cl, Br, I) using the generalized gradient approximation (GGA) with the PBE exchange-correlation functional⁴⁵ as implemented in the Amsterdam Density Functional (ADF 2010.02) program.^{46–48} The Slater basis sets with the quality of triple- ζ plus two polarization functions (TZ2P)⁴⁹ were used, with the frozen core approximation applied to the inner shells [$1s^2\text{-}5d^{10}$] for U, [$1s^2$] for O and F, [$1s^2\text{-}2p^6$] for Cl, [$1s^2\text{-}3d^{10}$] for Br, and [$1s^2\text{-}4d^{10}$] for I. The scalar relativistic (SR) and spin–orbit (SO) coupling effects were taken into account by the zero-order regular approximation (ZORA).⁵⁰ Geometries were fully optimized at the SR-ZORA level, and single-point energies were calculated with inclusion of the SO effects via the SO-ZORA approach.

To compare with the experimental results, we further carried out ab initio WFT calculations using advanced electron correlation methods implemented in the MOLPRO 2008.1 program.⁵¹ The coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) and complete-active-space self-consistent field (CASSCF) methods were used. Structures of UO_2X_3^- (X = F, Cl, Br, I) were optimized at the level of CCSD(T) with the SR effects included. Single-point CCSD(T) energies of the ground and excited states of UO_2X_3^- (X = F, Cl, Br, I) were calculated at the optimized geometries of UO_2X_3^- , which accurately generated state-specific SR energies for all states. Electron binding energies corresponding to one-electron transitions from the closed-shell ground state of UO_2X_3^- (X = F, Cl, Br, I) to the ground and excited states of UO_2X_3 were obtained using the CASSCF/CCSD(T)/SO approach, which has been shown to produce highly accurate excitation energies for heavy-element systems.^{37,40,52–55} In this approach, SO coupling was accounted for using a state-interacting method with SO pseudopotentials, where SO splittings were determined as a perturbation to the SR state energies and calculated on the basis of CASSCF wave functions with the diagonal matrix elements replaced by the individual CCSD(T) state energies. We also used the CASSCF/CR-EOM-CCSD(T)/SO approach, where CR-EOM-CCSD(T)⁵⁶ energies obtained from the EOM-CCSD energies with completely renormalized EOM-CCSD(T) corrections as implemented in NWChem 6.0 were used as the diagonal elements.⁵⁷ In this approach, CR-EOM-CCSD(T) calculations were performed on the neutrals at the CCSD(T)-optimized geometry of the monoanions to obtain the energies of the excited states, with the CCSD(T) energy of the state corresponding to one electron removed from the HOMO ($4a_2''$) as reference. In the MOLPRO and NWChem calculations, we used the Stuttgart energy-consistent relativistic 32-valence-electron pseudopotentials ECP60MWB (U) and the corresponding ECP60MWB-SEG basis for U,^{58–60} the valence triple- ζ basis sets aug-cc-pVTZ for O, F, and Cl,^{61,62} the relativistic 25-valence-electron pseudopotential ECP10MDF (Br) and the corresponding aug-cc-pVTZ-PP basis set for Br,⁶³ and the relativistic 25-valence-electron pseudopotential ECP28MDF and the corresponding aug-cc-pVTZ-PP basis set for I.⁶⁴

For dissociation of $\text{UO}_2\text{X}_4^{2-} \rightarrow \text{UO}_2\text{X}_3^- + \text{X}^-$, we did DFT/B3LYP calculations^{65,66} for the equilibrium geometries and vibrational spectra of the reactants, transition states, and products using Gaussian 09.⁶⁷ Basis sets used for O and X were the valence double- ζ basis sets aug-cc-pVDZ.^{61–64} Zero-point energies (ZPE) and free energy corrections were derived from the B3LYP frequency calculations. Single-point energies of the structures optimized at the B3LYP level were calculated using the CCSD(T) method with the same basis sets. Natural localized molecular orbitals (NLMO), natural population analyses, and natural resonance theory (NRT) bond order were calculated to understand the bonding and electronic structures of $\text{UO}_2\text{X}_4^{2-}$ and UO_2X_3^- based

on the B3LYP results using the natural bond orbital method,⁶⁸ implemented in the NBO 5.G program.⁶⁹ Linear transit (LT) calculations were performed by constrained optimizations at each LT coordinate along the $X \cdots \text{UO}_2\text{X}_3^-$ dissociation pathway using the DFT/PBE method at the SR level in ADF 2010.02.⁴⁶ Further bonding analyses were performed with the energy decomposition approach (EDA) to evaluate the relative importance of steric repulsion and the ionic and covalent bonding effects.^{70–72}

3. EXPERIMENTAL RESULTS

The 157 nm PES spectra of UO_2X_3^- ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) at 20 K are shown in Figure 1. The extremely high electron binding

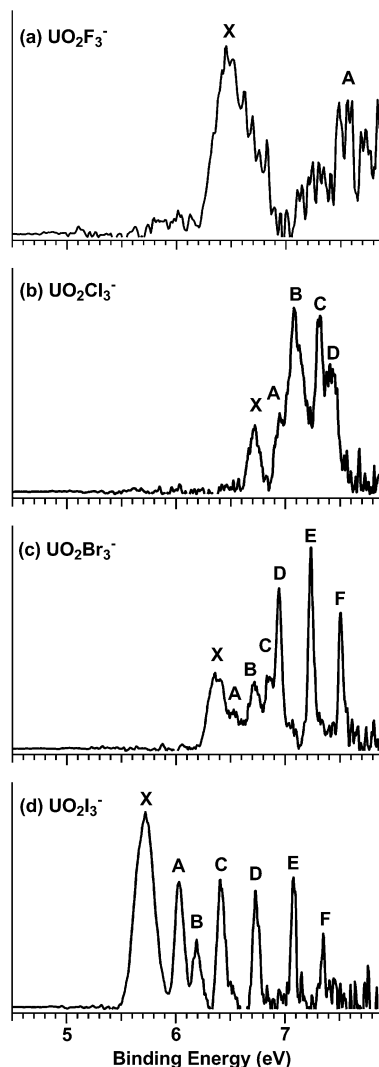


Figure 1. Photoelectron spectra of (a) UO_2F_3^- , (b) UO_2Cl_3^- , (c) UO_2Br_3^- , and (d) UO_2I_3^- at 20 K and 157 nm (7.866 eV).

energies of these species made it necessary for us to use the highest photon energy available in our lab at 157 nm, in particular for UO_2F_3^- and UO_2Cl_3^- .

3.1. UO_2F_3^- . We found it to be extremely challenging to obtain the spectrum of UO_2F_3^- because of its low detachment cross sections. Despite relatively strong ion intensities, very weak photoelectron signals were observed for UO_2F_3^- at 157 nm. The spectrum displayed in Figure 1a was accumulated for more than 20 h, but it still displays relatively poor signal-to-noise ratios, especially at high binding energies above 7 eV. A broad band was observed around 6.5 eV (X). The poor signal-

to-noise ratios prevented us from definitively assigning detachment transitions at higher binding energies. A band labeled as A was tentatively identified for the sake of discussion. Because of the elimination of vibrational hot bands, a relatively sharp onset was observed for the ground state band X, allowing us to measure the ADE or the electron affinity of neutral UO_2F_3 as 6.25 ± 0.05 eV. This quantity was obtained by drawing a straight line along the leading edge of the X band and then adding the instrumental resolution (0.05 eV) to the intersection with the binding energy axis. The vertical detachment energy (VDE) for band X was measured to be 6.53 ± 0.05 eV from the band maximum. The ADE and VDE for the X band are given in Table 1, where they are compared with the theoretical results.

Table 1. Observed and Calculated Adiabatic (ADE) and Vertical (VDE) Detachment Energies for UO_2X_3^- ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$)^a

		exp ^b	DFT/PBE		CCSD(T) ^d	
			SR	SO	SR	SO ^c
UO_2F_3^-	ADE	6.25 (S)	5.44	5.31	6.48	6.35
	VDE	6.53 (S)	5.62	5.52	6.81	6.71
UO_2Cl_3^-	ADE	6.64 (S)	5.47	5.41	6.82	6.76
	VDE	6.72 (S)	5.52	5.47	6.88	6.83
UO_2Br_3^-	ADE	6.27 (S)	5.24	5.18	6.45	6.39
	VDE	6.37 (S)	5.24	5.18	6.45	6.39
UO_2I_3^-	ADE	5.60 (S)	4.84	4.71	5.86	5.73
	VDE	5.72 (S)	4.85	4.72	5.86	5.73

^aAll energies are in eV. ^bNumbers in parentheses represent the experimental uncertainties in the last digit. ^cThese SO results are estimated using the SR CCSD(T) energies with the ad hoc SO corrections from the DFT/PBE calculations. ^dOptimized geometries of the UO_2X_3^- ($X = \text{Br}, \text{I}$) anions and their neutrals are so close that the calculated ADEs and VDEs are nearly identical, respectively.

3.2. UO_2X_3^- ($X = \text{Cl}, \text{Br}, \text{I}$). Better spectra were obtained for the heavier halogen complexes, UO_2X_3^- ($X = \text{Cl}, \text{Br}, \text{I}$), each with well-resolved spectral features, as shown in Figure 1b–d, respectively. The UO_2Cl_3^- complex exhibits the highest electron binding energies with five resolved detachment transitions (X, A–D). The ADE and VDE of the X band for UO_2Cl_3^- were measured to be 6.64 and 6.72 eV, respectively. Electron binding energies decrease systematically from UO_2Cl_3^- to UO_2I_3^- . In addition, more and sharper spectral features were observed for the heavier complexes, probably as a result of the SO splitting from detachment of the heavier halogen ligand orbitals. The ADE and VDE for the first bands for all UO_2X_3^- complexes are given in Table 1, where they are compared with theoretical results at different levels of theory. The VDEs for all detachment features are given in Tables 2 and 3, where they are compared with theoretical calculations from CASSCF/CCSD(T)/SO.

4. THEORETICAL RESULTS

4.1. Structures of UO_2X_3^- and UO_2X_3 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). Optimized ground state structural parameters and U–O symmetric vibrational frequencies for UO_2X_3^- and UO_2X_3 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) at the SR level are given in Table 4. Upon electron detachment from UO_2X_3^- , both DFT and CCSD(T) calculations indicate that the U–X bond lengths decrease as a result of the reduced intramolecular Coulomb repulsion, but the change becomes smaller from $X = \text{F}$ to I , suggesting the intramolecular Coulomb repulsion becomes weaker in the

Table 2. VDEs Observed and Calculated at the CASSCF/CCSD(T)/SO Level with the Corresponding MOs of UO_2X_3^- ($\text{X} = \text{F}, \text{Cl}$)^a

UO ₂ F ₃ [−]				UO ₂ Cl ₃ [−]			
obs features	VDE (expt) ^b	MO (SR)	VDE (theor)	obs features	VDE (expt) ^b	MO (SR)	VDE (theor)
X	6.53 (5)	4a ₂ '' (U–O σ _u)	6.69	X	6.72 (5)	4a ₂ '' (Cl 3p)	6.83
A	~7.5	5e' (U–O π _u)	7.55	A	6.95 (5)	2e'' (Cl 3p)	7.00
		2e'' (U–O π _g)	7.91			2e'' (Cl 3p)	7.00
		2e'' (U–O π _g)	7.92	B	7.08 (5)	5e' (Cl 3p)	7.04
		5e' (U–O π _u)	8.14	C	7.31 (5)	5e' (Cl 3p)	7.25
		5a ₁ ' (U–O σ _g)	8.33	D	7.41 (5)	1a ₂ ' (Cl 3p)	7.27
		4e'	8.87			4e' (Cl 3p)	7.85
		4e'	8.94			4e' (Cl 3p)	7.91
		1a ₂ '	9.16			5a ₁ ' (Cl 3p)	8.13
		3a ₂ ''	9.28			3a ₂ ''	8.45
		3e'	9.72			3e'	9.25
		3e'	9.75			3e'	9.46
		1e''	9.94			4a ₁ '	9.90
		1e''	9.95			1e''	10.10
		4a ₁ '	10.24			1e''	10.14

^aAll energies are in eV. ^bThe numbers in parentheses represent the experimental uncertainties in the last digit.

Table 3. VDEs Observed and Calculated at the CASSCF/CCSD(T)/SO Level with the Corresponding MOs of UO_2X_3^- ($\text{X} = \text{Br}, \text{I}$)^a

UO_2Br_3^-				UO_2I_3^-			
obs features	VDE (expt) ^b	MO (SR)	VDE (theor)	obs features	VDE (expt) ^b	MO (SR)	VDE (theor)
X	6.37 (5)	$2e''$ (Br 4p)	6.35	X	5.72 (5)	$2e''$ (I 5p)	5.62
		$4a_2''$ (Br 4p)	6.36			$2e''$ (I 5p)	5.63
		$2e''$ (Br 4p)	6.38			$4a_2''$ (I 5p)	5.71
A	6.53 (5)	$5e'$ (Br 4p)	6.64	A	6.03 (5)	$5e'$ (I 5p)	5.97
B	6.71 (5)	$1a_2'$ (Br 4p)	6.67	B	6.20 (5)	$1a_2'$ (I 5p)	6.07
C	6.86 (5)	$5e'$ (Br 4p)	6.79	C	6.41 (5)	$4e'$ (I 5p)	6.30
D	6.94 (5)	$4e'$ (Br 4p)	7.16	D	6.73 (5)	$5e'$ (I 5p)	6.58
E	7.24 (5)	$4e'$ (Br 4p)	7.43	E	7.08 (5)	$4e'$ (I 5p)	6.97
F	7.51 (5)	$5a_1'$ (Br 4p)	7.70	F	7.35 (5)	$5a_1'$ (I 5p)	7.25
		$3a_2''$	8.38			$3a_2''$	8.46
		$3e'$	9.37			$3e'$	9.53
		$3e'$	9.62			$3e'$	9.80
		$4a_1'$	9.98			$4a_1'$	10.10
		$1e''$	10.21			$1e''$	10.37
		$1e''$	10.25			$1e''$	10.41

^aAll energies are in eV. ^bNumbers in parentheses represent the experimental uncertainties in the last digit.

Table 4. Optimized Ground State (GS) Geometrical Parameters, Symmetries (Sym), and U–O Stretching Vibrational Frequencies (ν_s) for UO_2X_3^- and UO_2X_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) at the Scalar-Relativistic Level

complexes	sym	GS	DFT/PBE			CCSD(T)	
			U–O/Å	U–X/Å	$\nu_s(\text{U–O})/\text{cm}^{-1}$	U–O/Å	U–X/Å
UO_2F_3^-	D_{3h}	$1A_1'$	1.819	2.165	807	1.782	2.160
UO_2F_3	D_{3h}	$2A_2''$	1.814	2.083	783	1.794	2.055
UO_2Cl_3^-	D_{3h}	$1A_1'$	1.794	2.632	834	1.757	2.638
UO_2Cl_3	D_{3h}	$2A_2''$	1.783	2.580	846	1.751	2.571
UO_2Br_3^-	D_{3h}	$1A_1'$	1.789	2.803	840	1.752	2.796
UO_2Br_3	D_{3h}	$2E''$	1.782	2.804	861	1.751	2.786
UO_2I_3^-	D_{3h}	$1A_1'$	1.785	3.028	845	1.748	3.015
UO_2I_3	D_{3h}	$2E''$	1.780	3.025	862	1.748	3.000

heavier complexes. At the DFT level, U–O bond lengths in neutral UO_2X_3 are all predicted to be slightly decreased. However, at the CCSD(T) level, U–O bonds in UO_2F_3 are increased by 0.012 Å whereas U–O bonds in the three heavier

halogen complexes are unchanged or decreased slightly. CCSD(T) results are consistent with the trend of the U–O symmetrical stretching frequencies at the DFT/PBE level, suggesting weakened U–O bonding in neutral UO_2F_3 but

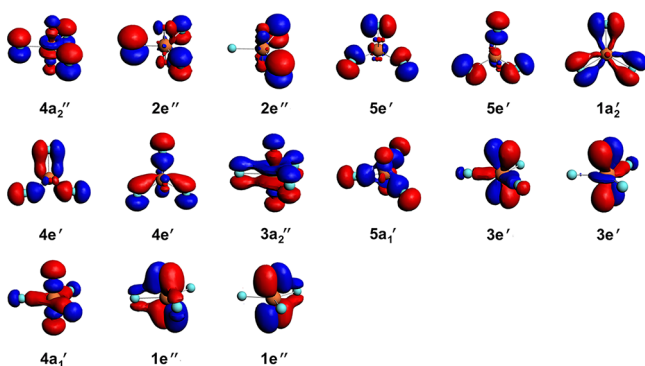


Figure 4. Contour plots of the occupied valence MOs of UO_2Cl_3^- at the DFT/PBE level; $4a_2''$ orbital is the HOMO.

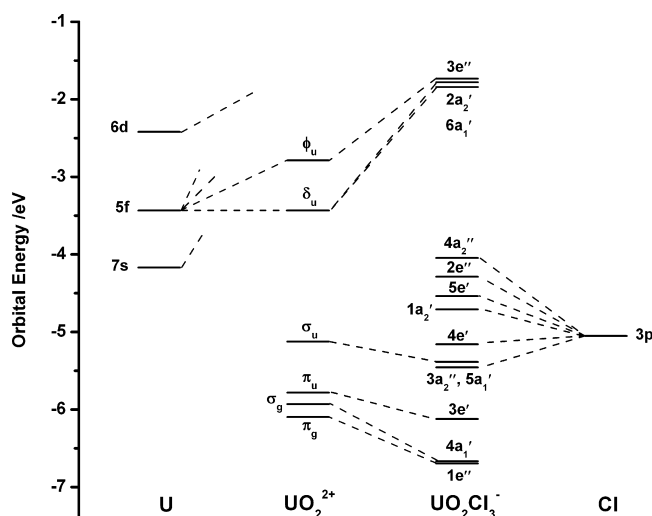


Figure 5. MO energy levels of UO_2Cl_3^- at the SR-DFT/PBE level; $4a_2''$ orbital is the HOMO, and $6a_1'$ orbital is the LUMO.

compounds.^{76,77} On the other hand, SO effects are negligible for the F 2p-type orbitals, while the $5e'$ U–O bonding orbital in UO_2F_3^- exhibits a large SO effect.

5. INTERPRETATION OF THE PHOTOELECTRON SPECTRA OF UO_2X_3^-

5.1. UO_2F_3^- . Calculated VDEs presented in Table 2 show that the first six detachment channels for UO_2F_3^- are from MOs of U–O bonding character (Figure 2). The HOMO ($4a_2''$) of UO_2F_3^- is mainly from the σ_u orbital of UO_2^{2+} with slight antibonding interactions with the F 2p_z orbitals (Figure 3). The calculated first VDE of 6.69 eV at the CASSCF/CCSD(T)/SO level agrees well with the experimental result of 6.53 eV. The CCSD(T) structural parameters given in Table 4 indicate that upon electron detachment from the HOMO the U–O bond lengths increase by 0.012 Å and the U–F bond lengths decrease by 0.105 Å in neutral UO_2F_3 . These large geometry changes are consistent with the broad ground state band (X) in the PES spectrum of UO_2F_3^- (Figure 1a). Calculated VDEs for the second to the fourth detachment channels are from the U–O π_u ($5e'$) and U–O π_g ($2e''$) MOs with calculated VDEs from 7.55 to 7.92 eV. Considering the fact that the first VDE was overestimated by 0.16 eV, we suspect that all three detachment channels should be accessible at the 157 nm detachment energy and contribute to the signals observed in the higher binding energy side in the spectrum of

UO_2F_3^- (Figure 1a). Unfortunately, the signal-to-noise ratios in the high binding energy side are too poor to allow any definitive assignments.

5.2. UO_2Cl_3^- . Calculated VDEs at the CASSCF/CCSD(T)/SO level and assignments for the PES features of UO_2Cl_3^- are also given in Table 2. In contrast to UO_2F_3^- , the frontier occupied MOs of UO_2Cl_3^- all have Cl 3p character (Figure 4), which are responsible for the top nine detachment channels. The VDEs for detachment from the U–O bonding orbitals have binding energies above 8.4 eV, too high to be accessed at 157 nm. Thus, all detachment bands observed for UO_2Cl_3^- in Figure 1b should be due to the Cl 3p ligand orbitals. In comparison, the detachment features observed for UO_2F_3^- are all from U–O bonding orbitals, which explains the low detachment cross sections for the fluoride complex. In a recent study on UF_6^- ,⁷³ we found that its detachment cross section at 157 nm for the U 5f HOMO was so small that we could not obtain its photoelectron spectrum.

The HOMO ($4a_2''$) of UO_2Cl_3^- has π antibonding character between the Cl 3p_z orbitals and the U–O σ_u orbital (Figure 4). Detachment from this MO gives rise to the X band in the PES spectra (Figure 1b). Calculated VDE of 6.83 eV is in good agreement with the experimental value of 6.72 eV (Table 2). Upon electron detachment, there is only a small contraction (0.067 Å) of the U–Cl bonds in neutral UO_2Cl_3 based on the CCSD(T) calculation (Table 4), consistent with the relatively sharp X band. The second detachment channel is from the $2e''$ orbital, which is mainly of Cl 3p_z character. The SO effect is negligible for this MO (Figure 2), and calculated VDEs of 7.00 eV for both SO channels are in good agreement with the 6.95 eV VDE measured for band A (Table 2). Bands B and C are in excellent agreement with the calculated VDEs of the SO split $5e'$ orbitals, whereas band D corresponds to detachment from the $1a_2'$ orbital. The VDEs for the two remaining Cl 3p-based ligand orbitals, $4e'$ and $5a_1'$ (Table 2), are too high to be accessed at 157 nm.

5.3. UO_2X_3^- (X = Br and I). PES spectra of UO_2Br_3^- and UO_2I_3^- are very similar to each other (Figure 1); MOs of the two heavier halogen complexes are similar to those of UO_2Cl_3^- , as shown in Figure 4. PES spectra in Figure 1 reveal that electron binding energies of UO_2Cl_3^- are the highest and decrease from Cl to I. The major difference between the PES spectra of the two heavier complexes and that of UO_2Cl_3^- is the SO effects (Figure 2), which are responsible for the well-resolved PES spectral features for the Br and I complexes. Detailed spectral assignments for these two complexes are given in Table 3, which shows that, because of the reduced electron binding energies, all PES bands are due to the ligand-based valence MOs, while the U–O-based MOs all have too high binding energies to be accessed at 157 nm.

CASSCF/CCSD(T)/SO calculations indicate that the VDEs for the top two MOs ($2e''$ and $4a_2''$) for UO_2Br_3^- and UO_2I_3^- are very close in each system (Table 3), in excellent agreement with the broad X band in both spectra. Except for the C and D bands, all higher binding energy features for both systems also have a one-to-one correspondence, as shown in Table 3. In general, the calculated VDEs for UO_2I_3^- are in very good agreement with the experimental data with discrepancies within 0.1 eV. Calculated VDEs for the higher detachment channels for UO_2Br_3^- display a slightly larger error (~ 0.2 eV) in comparison with the experimental data.

5.4. Inadequacy of DFT GGA Energies and Importance of Spin–Orbit Effects. The ADEs of UO_2X_3^- (X = F, Cl, Br,

Table 5. Theoretical Analyses of the U–X Bonds in UO_2X_3^- and $\text{UO}_2\text{X}_4^{2-}$ (X = F, Cl, Br and I) at the DFT/B3LYP Level^a

	U–X/Å	Q(U)	Q(X)	NLMO		π	BO _{N–M}	BO _{NRT}	Cov.(NRT)
				σ					
UO ₂ X ₃ [–]									
F	2.161	2.15	–0.63	9.1% U(s ^{0.24} p ^{0.01} d ^{1.89} f) + 90.8% F(sp ^{1.82})		5.5% U(d ^{0.81} f) + 94.4% F(p)	1.549	1.026	9.0%
Cl	2.650	1.61	–0.48	14.2% U(s ^{0.76} d ^{2.33} f) + 85.5% Cl(sp ^{2.55})		7.3% U(d ^{1.15} f) + 92.6% Cl(p)	1.429	0.965	15.1%
Br	2.813	1.52	–0.45	15.3% U(s ^{0.97} d ^{2.62} f) + 84.3% Br(sp ^{3.52})		7.7% U(d ^{1.24} f) + 92.1% Br(p)	1.411	0.990	16.3%
I	3.043	1.42	–0.42	16.9% U(s ^{1.31} d ^{3.09} f) + 82.5% I(sp ^{4.55})		7.9% U(d ^{1.37} f) + 91.9% I(p)	1.384	0.952	19.0%
UO ₂ X ₄ ^{2–}									
F	2.236	2.05	–0.66	8.5% U(s ^{0.20} d ^{1.03} f) + 91.4% F(sp ^{1.35})		4.8% U(d ^{0.79} f) + 95.1% F(p)	1.452	0.994	10.2%
Cl	2.755	1.43	–0.55	13.1% U(s ^{0.51} d ^{1.52} f) + 86.6% Cl(sp ^{2.14})		5.4% U(d ^{1.00} f) + 94.2% Cl(p)	1.263	0.990	15.5%
Br	2.922	1.34	–0.53	14.3% U(s ^{0.63} p ^{0.01} d ^{1.71} f) + 85.3% Br(sp ^{3.07})		5.8% U(d ^{1.06} f) + 94.2% Br(p)	1.236	0.988	16.9%
I	3.166	1.27	–0.51	15.9% U(s ^{0.81} p ^{0.01} d ^{2.00} f) + 83.7% I(sp ^{4.13})		5.6% U(d ^{1.11} f) + 94.3% I(p)	1.182	0.983	18.3%

^aU–X: U–X bond lengths. Q(U) and Q(X): natural charges on atoms U and O, respectively. NLMO: natural localized molecular orbitals. $\text{BO}_{\text{N-M}}$: Nalewajski–Mrozek (N–M) bond order with the trace $(\Delta P)^2$ as N–M bond index referred to as a 4-index set. BO_{NRT} : natural resonance theory bond orders. Cov.(NRT): contribution of covalency to the BO_{NRT} .

I) or the electron affinities of the corresponding neutral UO_2X_3 are very large (Table 1), suggesting that the UO_2X_3^- monoanions are electronically highly stable gaseous species. The ADE of UO_2Cl_3^- is the highest in the series, consistent with the fact that the electron affinity of Cl is the highest among the halogen atoms. The UO_2X_3^- species can be considered as a new class of superhalogens,⁷⁸ because their ADEs far exceed those of the halogen anions. DFT calculations with approximate GGA exchange-correlation functionals significantly underestimate the electronic stabilities of the UO_2X_3^- complexes by about 0.7–1.2 eV, as shown in Table 1. This result is consistent with previous findings that GGA functionals usually underestimate VDEs and ADEs and hybrid functionals tend to improve the agreement with experiment.⁷⁹ High-level ab initio calculations like CCSD(T) are thus needed.³⁸ Without SO corrections, even the CCSD(T) calculations at the SR level overestimate the first ADEs by about 0.2–0.4 eV. Using the SO corrections from the DFT/PBE calculations to the SR CCSD(T) results, the resulting ADEs agree much better with the experimental data with an error of ~0.1 eV (Table 1). Such an ad hoc SO correction to the VDEs (Table 1) also gives results that are comparable to those from the more accurate CASSCF/CCSD(T)/SO calculations (Tables 2 and 3). These results suggest that SO corrections from DFT calculations can be used as initial estimates of the SO effects for the more expensive ab initio calculations.

6. U–X BONDING IN UO_2X_3^- (X = F, Cl, Br, I)

The bonding interactions between U(VI) and the halogen ligands have been extensively investigated both theoretically^{3–8} and experimentally.^{9–14} To understand the relative roles of the U 7s, 6p, 5f, and 6d orbitals and their chemical bonding with the halogen ligands, we have done a series of theoretical analyses on the uranyl halide complexes, UO_2X_3^- and $\text{UO}_2\text{X}_4^{2-}$, as shown in Table 5. This table presents the U–X bond lengths at the B3LYP level, natural charges, natural localized molecular orbitals (NLMOs), bond order analyses by the Nalewajski–Mrozek method ($\text{BO}_{\text{N-M}}$),⁸⁰ natural resonance theory (NRT) (BO_{NRT}), and covalency contributions to the BO_{NRT} [Cov.(NRT)].^{81–83} B3LYP U–X bond lengths given in Table 5 are consistent with those from the CCSD(T) calculations in Table 4. Natural population analysis⁸⁴ reveals that U carries a large positive charge and the halogen ligands carry considerable negative charges in these U(VI) complexes, indicating that the U–X bonds are mainly due to ionic

interactions. Our EDA results for $\text{UO}_2\text{X}_3^- \rightarrow \text{UO}_2^{2+} + \text{X}_3^{3-}$ (Table 6) show that while the Pauli repulsion and covalent

Table 6. Energy Decomposition Analyses (EDA) for $\text{UO}_2\text{X}_3^- \rightarrow \text{UO}_2^{2+} + \text{X}_3^{3-}$ (X = F, Cl, Br, I) from DFT/PBE calculations. All energies are in eV

X	steric interaction			orbital interaction	total bonding energy	steric % ^b
	electrostatic	Pauli	sum ^a			
F	−44.67	12.60	−32.07	−10.59	−42.66	75.2%
Cl	−36.26	10.54	−25.72	−9.73	−35.45	72.6%
Br	−33.03	9.52	−23.50	−10.00	−33.51	70.1%
I	−29.40	8.27	−21.13	−10.43	−31.56	67.0%

^aSteric interaction is the sum of electrostatic and Pauli interactions.

^bPercentage of steric interaction in total bonding energy.

orbital interactions change slightly from X = F to I, the electrostatic ionic interactions are the major contributions to the total bonding energies, consistent with the ionic character of the U–X bonds. NRT analyses show that UO_2X_3^- can be described by a dominant Lewis resonance structure (DLRS) with a single U–X bond, and the DLRS weight amounts to 56%, 58%, 52%, and 56% for UO_2X_3^- (X = F, Cl, Br, and I, respectively). BO_{NRT} values of U–X are between 1.03 and 0.95, with covalent contributions between 9.0% and 19.0%. $\text{BO}_{\text{N-M}}$ values are larger than the BO_{NRT} values by ~0.46 systematically as the former contains partial ionicity. Of particular importance is the trend that when the halogen ligands become heavier, the U–X bond order and total binding energies (Table 6) generally decrease but with increased covalency. This opposite trend indicates that enhanced covalency of the U–X bonds from X = F to I does not indicate stronger bonding because the U–X bonds are dominated by ionic bonding that gradually decreases from X = F to I.

In addition, calculated NLMOs reveal that U–X bonding has very weak σ character between U $d_{f\sigma}$ and X $sp\sigma$ hybrid orbitals and π -type conjugation interactions between the U $d_{f\pi}$ and the X $p\pi$ orbitals. As observed in other uranium halogen compounds,^{6,8} the U 6d contribution in the U–X bonding increases from X = F to I, showing the important role of the U 6d participation for covalent interactions. There is also significant participation of U 5f δ and 5f ϕ orbitals in the U–X bonding, as is the case of $\text{UO}_2(\text{HCO}_3)_3^-$.⁸⁵ The increase of the

U–X bond covalency from $X = \text{F}$ to I to a large extent comes from the better energy level matching between the U 6d and the X sp orbitals. Overall, the U–X bonding of UO_2X_3^- is strongest for $X = \text{F}$ and becomes weaker for $X = \text{Cl}, \text{Br}, \text{I}$, consistent with the conclusions from the previous IRMPD experiment.¹³ In $\text{UO}_2\text{F}_4^{2-}$ and UO_2F_3^- species, U–O orbitals are destabilized to become the frontier occupied MOs through mixing with the F 2p orbitals because the fluorine ligands have very low orbital energies in comparison with oxygen. In contrast, U–O orbitals are stabilized so that they lie below the halogen lone-pair orbitals in the heavier UO_2X_3^- ($X = \text{Cl}, \text{Br}, \text{I}$) species.

7. STABILITY OF $\text{UO}_2\text{X}_4^{2-}$: COULOMB REPULSION VS U–X BONDING STRENGTH

We recently observed and studied two tetrahalide dianion complexes, $\text{UO}_2\text{X}_4^{2-}$ ($X = \text{F}, \text{Cl}$).^{37,38} However, we were not able to observe $\text{UO}_2\text{Br}_4^{2-}$ and $\text{UO}_2\text{I}_4^{2-}$ even at very low temperatures. To understand the stability of $\text{UO}_2\text{X}_4^{2-}$, we calculated the linear transit (LT) energy curves for $\text{X}^- \cdots \text{UO}_2\text{X}_3^- \rightarrow \text{UO}_2\text{X}_3^- + \text{X}^-$, as shown in Figure 6. There

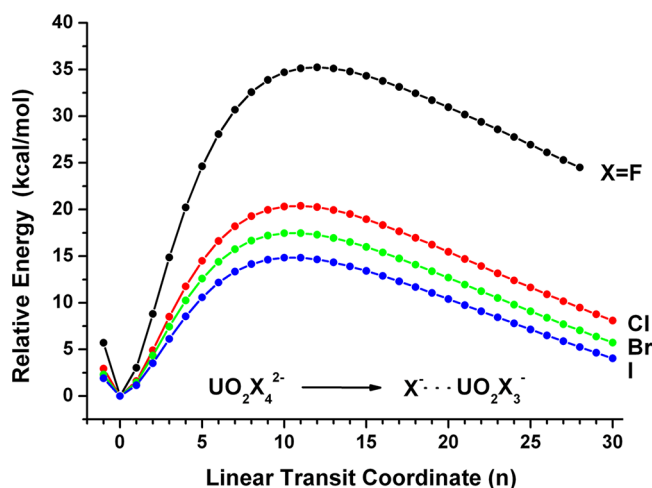


Figure 6. Linear transit (LT) energy curves illustrating dissociation of $\text{UO}_2\text{X}_4^{2-} \rightarrow \text{UO}_2\text{X}_3^- + \text{X}^-$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). Energies are obtained from DFT/PBE calculations. $\text{X}^- \cdots \text{UO}_2\text{X}_3^-$ distance $R_n = R_0 + 0.2n$ ($n = -1, 0, 1, \dots, 30$), where $R_0 = 2.234, 2.734, 2.910$, and 3.143 \AA for $X = \text{F}, \text{Cl}, \text{Br}$, and I , respectively.

is a Coulomb barrier for dissociation to two negative charges, similar to electron detachment from a multiply charged anion.^{86,87} Figure 6 shows that the Coulomb barrier decreases from $X = \text{F}$ to I , suggesting that the dynamic stability of $\text{UO}_2\text{X}_4^{2-}$ decreases in the same direction. Table 7 lists the activation energies (E_a), reaction energies (ΔE), and reaction

free energies (ΔG) from both B3LYP and CCSD(T) calculations, showing that the dissociation reactions are highly exothermic and all $\text{UO}_2\text{X}_4^{2-}$ complexes are thermodynamically unstable. Therefore, all $\text{UO}_2\text{X}_4^{2-}$ species are only kinetically stable (metastable), and their lifetimes are dependent on the barrier heights. The lower barriers and relatively high exothermicity of the dissociation reactions probably made $\text{UO}_2\text{X}_4^{2-}$ ($X = \text{Br}$ and I) too fragile to be observed experimentally.

Coulomb barriers and stabilities of $\text{UO}_2\text{X}_4^{2-}$ are determined by the balance between the short-range U–X bonding and the long-range Coulomb repulsion between X^- and UO_2X_3^- , also similar to the electronic stability of multiply charged anions.⁸⁸ Theoretical analyses of the U–X bonds in $\text{UO}_2\text{X}_4^{2-}$ are also given in Table 5, which shows that the U–X bonding patterns are very similar to those in UO_2X_3^- . However, the U–X bonding in $\text{UO}_2\text{X}_4^{2-}$ is weaker, as can be seen in their longer U–X bond lengths, due to the intramolecular Coulomb repulsion in the dianion complexes. Therefore, the competition between the U–X bond strength and the Coulomb repulsions determines the dynamic stabilities of $\text{UO}_2\text{X}_4^{2-}$. Because of the ionic nature of the U–X bonds, the dielectric constants (ϵ_0) of the medium should be critical in determining the stability of the $\text{UO}_2\text{X}_4^{2-}$ dianion complexes. Our preliminary calculations on dissociation of $\text{UO}_2\text{F}_4^{2-} \rightarrow \text{UO}_2\text{F}_3^- + \text{F}^-$ show that in the gas phase ($\epsilon_0 = 1$) $\text{UO}_2\text{F}_4^{2-}$ is metastable with $\Delta E = -19.7 \text{ kcal/mol}$. However, in aqueous solution ($\epsilon_0 = 80$) $\text{UO}_2\text{F}_4^{2-}$ is highly stable with $\Delta E = 24.5 \text{ kcal/mol}$. Thus, less X^- ligands can be accommodated in the equatorial plane of uranyl in the gas phase than in the condensed phase because of the increased Coulomb repulsion in the former.

8. CONCLUSIONS

Photoelectron spectroscopy and relativistic quantum chemistry are used to probe the stabilities of gaseous UO_2X_3^- ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and their electronic structures. Low-temperature photoelectron spectra of all four UO_2X_3^- complexes are obtained at 20 K, and the uranyl trihalides are observed to be electronically highly stable with extremely high electron binding energies. The frontier occupied MOs in UO_2F_3^- are shown to mainly consist of U–O bonding orbitals, very different from those in the heavier UO_2X_3^- ($X = \text{Cl}, \text{Br}, \text{I}$) species, which consist of primarily ligand np -type valence orbitals. DFT calculations are shown to give poor results due to its overestimation of the Coulomb repulsion in UO_2X_3^- , whereas CCSD(T) calculations with inclusion of SO effects are in good agreement with the experimental data. Systematic analyses of the U–X bonding in UO_2X_3^- and $\text{UO}_2\text{X}_4^{2-}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) show that the U–X bonds are dominated by ionic interactions with weak covalency, which increases from $X = \text{F}$ to I . Further calculations reveal that the gaseous doubly charged $\text{UO}_2\text{X}_4^{2-}$

Table 7. Activation Energies (E_a), Reaction Energies (ΔE), and Reaction Free Energies (ΔG) (in kcal/mol) for $\text{UO}_2\text{X}_4^{2-} \rightarrow \text{X}^- + \text{UO}_2\text{X}_3^-$ Reactions

X	B3LYP ^a				CCSD(T) ^b			
	F	Cl	Br	I	F	Cl	Br	I
E_a	33.0	19.3	16.7	14.0	37.0	24.3	22.2	20.5
ΔE	−19.7	−29.8	−30.9	−31.4	−16.2	−24.4	−24.9	−24.4
ΔG	−27.8	−37.6	−38.7	−39.1	−24.3	−32.2	−32.7	−32.1

^aZero-point energy (ZPE) corrections are included in the energies. ^bSingle-point CCSD(T) energy calculations at the B3LYP-optimized geometries with inclusion of ZPE corrections and thermal free energy corrections from B3LYP calculation.

complexes are thermodynamically unstable against dissociation to $\text{UO}_2\text{X}_3^- + \text{X}^-$ with decreasing dynamic stability from $\text{X} = \text{F}$ to I . The competition between the U–X bonding and the Coulomb repulsions determines the kinetic stabilities of gaseous $\text{UO}_2\text{X}_4^{2-}$.

■ ASSOCIATED CONTENT

■ Supporting Information

Complete ref 67 and calculated VDEs of UO_2X_3^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) from the SO-DFT/PBE and CASSCF/CR-EOM-CCSD(T)/SO methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant No. DE-FG02-11ER16261. P.D.D. would like to thank the Nahigian Gift to the Department of Chemistry at Brown University for partial support for this work. Theoretical work was supported by NSFC (20933003, 11079006, 91026003) to J.L. and NSFC (21201106) and the China Postdoctoral Science Foundation (2012M520297) to J.S. Calculations were performed at the Supercomputer Center of the Computer Network Information Center, Chinese Academy of Sciences, Tsinghua National Laboratory for Information Science and Technology, and Shanghai Supercomputing Center. A portion of the calculations was performed using EMSL, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory.

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