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Photoelectron spectroscopy and theoretical studies of gaseous uranium hexachlorides in different oxidation states: UCl$_6$$^{q-}$ ($q = 0$–2)

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Uranium chlorides are important in actinide chemistry and nuclear industries, but their chemical bonding and many physical and chemical properties are not well understood yet. Here, we report the first experimental observation of two gaseous uranium hexachloride anions, UCl$_6$$^{-}$ and UCl$_6$$^{2-}$, which are probed by photoelectron spectroscopy in conjunction with quantum chemistry calculations. The electron affinity of UCl$_6$ is measured for the first time as +5.3 eV; its second electron affinity is measured to be +0.60 eV from the photoelectron spectra of UCl$_6$$^{2-}$. We observe that the detachment cross sections of the 5f electrons are extremely weak in the visible and UV energy ranges. It is found that the one-electron one-determinantal molecular orbital picture and Koopmans’ theorem break down for the strongly internally correlated U-5f$^2$ valence shell of tetravalent U$^{4+}$ in UCl$_6$$^{2-}$. The calculated adiabatic and vertical electron detachment energies from ab initio calculations agree well with the experimental observations. Electronic structure and chemical bonding in the uranium hexachloride species UCl$_6$$^{-}$ to UCl$_6$ are discussed as a function of the oxidation state of U. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4916399]

I. INTRODUCTION

Uranium halides play essential roles both in fundamental actinide chemistry and in nuclear technologies from uranium enrichment to separation. Among the most studied actinide complexes are the uranium hexahalides, possessing octahedral symmetry and thereby providing a well-defined platform for theoretical investigations.$^{1-3}$ The [UCl$_6$]$^{2-}$ dianion is the most important species when tetravalent uranium compound (U$^{4+}$)Cl$_6$ is dissolved in LiCl/KCl molten salt. It has been shown that trivalent U$^{3+}$ and pentavalent U$^{5+}$ are formed during redox processes.$^{4-6}$ The [UCl$_6$]$^{3-}$ and [UCl$_6$]$^{4-}$ species have also been observed in room-temperature ionic liquids.$^7$ Even though there have been many experimental and computational studies of [U(t$_2$)$^2$]Cl$_6$ in condensed phases,$^{1,8-16}$ the accurate account of the electronic structure of the [U(t$_2$)$^2$]Cl$_6$$^{-}$ species has been challenging owing to the highly complex $t^2$ system and the perturbations caused by interactions with the counterions in crystal and solution phases.$^{17-21}$

Anion photoelectron spectroscopy (PES) is a powerful experimental technique to probe the ground and excited states of neutral species, through electron detachment from singly charged anions. We have developed PES techniques to study solution-phase species, both singly charged and multiply charged anions, in the gas phase using electrospray ionization (ESI).$^{22}$ In particular, our recent development of a cryogenic ion trap has allowed the creation of vibrationally cold anions,$^{23}$ making it possible for high-resolution spectroscopic investigations of solution anions in the gas phase.$^{24}$ Relevant to the current uranium halides, we have successfully applied ESI-PES to probe the electronic structures of a series of uranyl and uranium halide anions in conjunction with relativistic quantum chemical calculations.$^{25-31}$ In particular, we have produced [UF$_3$]$^-$ and [UF$_6$]$^-$ using ESI and obtained the PES spectra of [UF$_3$]$^-$ both at room temperature and low temperature, which yielded an accurate electron affinity (EA) for UF$_5$ as 3.885 ± 0.015 eV.$^{28,29}$ The [U(t$_2$)$^2$F$_3$]$^-$ anion has a $C_{4v}$ symmetry with two unpaired 5f electrons, occupying $f_x$ and $f_{xyz}$ type orbitals, respectively. We found that the detachment cross section of the $f_{xyz}$ electron is at least a factor of ten smaller relative to that of the $f_x$ electron. Consequently, we were not able to obtain the PES spectrum of [UF$_5$]$^-$, because the extra electron occupies the $f_{xyz}$-type orbital of UF$_6$ and its detachment cross section is too weak to be observed at the available photon energies.$^{28}$ We have also recently reported a PES and computational study of [UCl$_6$]$^-$ that was produced using ESI.$^{31}$ In addition to weak detachment features from the 5f electrons, we were able to observe strong detachment features from the Cl 3p orbitals, whereas the electron binding energies of the F 2p electrons are too high to be observed at the available detachment photon energies in the case of [UF$_3$]$^-$.$^{28}$ The EA of UCl$_3$ was measured to be 4.76 ± 0.03 eV, significantly higher than that of UF$_3$.$^{32}$

In the current article, we report the first experimental observation and characterization of gaseous [UCl$_6$]$^{q-}$ and

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[UCl₆]²⁻ by ESI-PES, allowing us to measure successfully both the first and second EA of UCl₆. In addition, we have investigated the electron detachment energies of [UCl₆]⁹⁻ (q = 1, 2) theoretically using relativistically corrected density functional theory (DFT) and ab initio wavefunction theories (WFT) and compared the computational data with the experimental results. The observation of the [UCl₆]²⁻ dianion is particularly interesting, as it provides long-sought gas-phase information regarding the f² uranium(IV) hexahalides. The electronic structure and chemical bonding in the hexachlorides are investigated as a function of the uranium oxidation states from [(U⁴⁺)Cl₆]²⁻ → [(U⁵⁺)Cl₆]⁻ → [(U⁶⁺)Cl₆]⁰. The current results provide further insights into the chemical and physical properties of uranium chloride anionic species, which are common in high-temperature molten salts and electrolytes.³²

II. EXPERIMENTAL AND COMPUTATIONAL METHODOLOGY

A. Electrospray photoelectron spectroscopy with a temperature-controlled ion trap

The PES-ESI apparatus used for this study was described in detail previously.²² It consisted of an ESI source and a magnetic-bottle photoelectron analyzer (the magnetic field in the interaction zone was estimated to be ~800 gauss). It was modified by shortening the electron flight tube from 4.0 m to 2.5 m, only resulting in a slight decrease of the electron energy resolution.³³ The [UCl₆]⁻ and [UCl₆]²⁻ anions were produced by ESI, using a 1 mM solution of UCl₄ in acetonitrile. A radio frequency quadrupole device guided the anions from the ESI source into a cryogenically controlled ion trap,²³ where the anions were accumulated and cooled for 0.1 s before being pulsed into the extraction zone of a time-of-flight mass spectrometer. The ion trap can be cooled down to 4.4 K using a closed-cycle helium refrigerator²⁶ and was operated at 20 K for the current experiment. Under our ESI conditions, both the [UCl₆]⁻ and [UCl₆]²⁻ anions were readily observed. They 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. Four different laser wavelengths were used: 157 nm (7.866 eV) from an F₂ excimer laser, 213 nm (5.821 eV) from a dye laser, 266 nm (4.661 eV), and 355 nm (3.496 eV) from a Nd:YAG laser. The PES spectra were calibrated using the known spectra of Au⁻ (2.3086 eV) and I⁻ (3.0590 eV).³⁴,³⁵ The Au⁻ anion was produced by ESI of a pyridine solution of PPh₃AuCl and NaSCH₃ with a trace amount of CH₃OH.³⁶ The electron kinetic energy resolution of the current magnetic-bottle electron analyzer was about 3%, i.e., 30 meV for 1 eV electrons.³³

B. Computational details

The theoretical studies were performed using both DFT and WFT methods. The computational details of the two kinds of methods are described separately below.

In the case of DFT calculations, we used the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional,³⁷ as implemented in ADF 2010.02.³⁸–⁴⁰ Slater basis sets of triple-ζ plus two polarization functions (TZ2P)⁴¹ were applied. The frozen core approximation for the inner shells [1s²-5d⁶] of U (corresponding to 14 electrons in the 5f⁶-6s⁶-6p⁷ (semi-) valence shell) and [1s²-2p⁴] of Cl (with 7 electrons in the 3s³p valence shell) was applied by taking the core orbitals from free atom calculations. The scalar relativistic (SR) and spin-orbit (SO) coupling effects were taken into account by the zero order regular approximation (ZORA).⁴² The geometries were optimized at the SR-ZORA level, and single-point energy calculations were performed with inclusion of the SO coupling effects via the SO-ZORA approach. The vibrational frequencies of [UCl₆]⁹⁻ (q = 0–2) at their optimized octahedral structures were calculated at the SR DFT/PBE level. Preliminary SO-ZORA calculations show that the Jahn-Teller (JT) distortion of the open-shell species is quenched by SO interaction. For the vertical detachment energies (VDEs) of [UCl₆]⁻, the time-dependent DFT (TDDFT) approach was used to calculate the excited states of UCl₆ at the DFT/PBE ground state geometry of [UCl₆]⁻. In the TDDFT calculations, both the B3LYP potential⁴³,⁴⁴ and the “statistically averaged orbital potential” (SAOP) with the correct asymptotic 1/r behavior were used.⁴⁵

In the case of WFT calculations, we used the advanced ab initio electron correlation methods in the MOLPRO 2012.1 and NWChem 6.0 program packages.⁴⁶,⁴⁷ With MOLPRO, we used the coupled-cluster approach with single and double and perturbative triple substitutions [CCSD(T)]⁴⁸ and the complete-active-space multi-configuration approach with second-order perturbation theoretical correction (CASPT²).⁴⁹ With NWChem, we employed the completely renormalized equation-of-motion CCSD(T) [CR-EOM-CCSD(T)] approach to calculate the excited states.⁵⁰ For U, the Stuttgart energy-consistent relativistic small-core pseudopotential ECP60MWB (32 electrons in the 5s5p6s6p5f5d7s extended valence shell) was applied with the ECP60MWB-_SEG basis.⁵¹,⁵² For Cl, the all-electron augmented polarized valence-double-ζ basis set (aug-cc-pVDZ) was used.⁵³ The geometric structures of UCl₆⁻ and UCl₆⁻ were optimized at the SR-CCSD(T) level. All the product species resulting from vertical electron detachments were similarly calculated at those geometries. We determined the first vertical detachment energy (VDE₁) of UCl₆⁻ at the SR-CCSD(T) level as the ground-state energy difference between UCl₆⁻ and UCl₆⁻ both at the optimized ground-state geometry of UCl₆⁻. In the same way, the VDE₁ of UCl₆⁻ was determined at the SR-CCSD(T) level. To understand the ground and low-lying excited-states of UCl₆⁻ of 5f² type, we performed SR-CASPT² calculations using an active space of two electrons in the complete shell of the seven 5f orbitals as active space, denoted as CAS(2,7). Similar SR-CASPT² calculations using “CAS(1,7)” were applied to all the 5f⁵ states of UCl₆⁻. Besides, the CCSD(T) and CR-EOM-CCSD(T) methods at the SR level were used to calculate the 5f⁴ excited states of UCl₆⁻. We then determined the SO coupling effects of those species with configurations of U-5fⁿ (n = 1, 2). The small SO effects by the Cl atoms, estimated as a few 0.01 eV, were neglected. SO coupling was accounted by a state-interacting method with SO pseudopotentials,⁵⁵ where the SO splittings
were determined as a perturbation to the SR state energies and calculated from CASCCSF wavefunctions. The diagonal matrix elements were replaced by the individual CCSD(T) or CR-EOM-CCSD(T) or CASPT2 state energies at the SR level, which are denoted as CASCCSF/CCSD(T)/SO or CASCCSF/CAS/CRCASSCF/CCSD(T)/SO or CASCCSF/CASPT2/CCSD(T)/SO methods, respectively.\textsuperscript{25–27,56–60} In the CASCCSF/CR-EOM-CCSD(T)/SO calculation for \( \text{UCI}_6^- \), the CCSD(T) ground-state energy and the CR-EOM-CCSD(T) \( 5f^1 \) excited state energies were used as diagonal matrix elements of the SO coupling matrix. That is, the vertical excitation energies of \( \text{UCI}_6^- \) and \( \text{UCI}_6_{2-} \) at the SO level were calculated with the so-called CASCCSF/CAS(2,7)/PT2/CCSD(T)/SO and CASCCSF/CR-EOM-CCSD(T)/SO methods, respectively.

The SO effects on the ground-state energies of \( \text{UCI}_6^- \) and \( \text{UCI}_6_{2-} \) were calculated with the CAS(1,7)/SCF/CR-EOM-CCSD(T)/SO and CASCCSF/CAS(2,7)/PT2/CCSD(T)/SO approaches, including all \( 5f^1 \) and \( 5f^2 \) states, respectively, at the SR-CCSD(T) ground state geometries of \( \text{UCI}_6^- \). The SO-corrected VDE of \( \text{UCI}_6^- \) at the CCSD(T) level was obtained by adding the above SO corrections on the ground-state energies of \( \text{UCI}_6^- \) and \( \text{UCI}_6_{2-} \) to the SR-CCSD(T) VDE value of \( \text{UCI}_6^- \). Similarly, the SO-corrected VDE of \( \text{UCI}_6^- \) at the CCSD(T) level was estimated based on the SO correction on the ground-state energy of \( \text{UCI}_6^- \) from CAS(1,7)/SCF/CR-EOM-CCSD(T)/SO calculations at the SR-CCSD(T) ground state geometry of \( \text{UCI}_6^- \). It is worth mentioning that the ground-state energy of \( \text{UCI}_6^- \) is hardly affected by SO effects due to the closed-shell character.

Using the CASCCSF/CASPT2/CCSD(T)/SO approach with the CAS(7,10) active space, we calculated the lowest ligand-to-metal electron a charge transfer (LMCT) excited state of \( \text{UCI}_6^- \) at the CCSD(T) ground state geometries of \( \text{UCI}_6_{2-} \), corresponding to an electronic transition from the Cl-1t \( 1g \) orbital to the U-5f shell. The 10 active orbitals include the (Cl-3p)1t \( 1g \), and (U-5f)1a \( 2u \), 2t \( 2u \), and 3t \( 1u \) orbitals. SR-CASPT2 calculations were performed on the lowest 33 doublet and 33 quartet LMCT excited states of gerade symmetry in this active space. The SO-coupled LMCT state energies were obtained by CASCCSF/CAS(7,10)/PT2/CCSD(T)/SO approach, and the lowest LMCT excitation energies were obtained by subtracting the SO-coupled ground-state energy of \( \text{UCI}_6^- \) from the CASCCSF/CAS(1,7)/PT2/CCSD(T)/SO results with the whole 5f valence shell as active orbitals. In all the CASPT2 calculations, the ionization potential/electron affinity (IPEA) corrected zeroth-order Hamiltonian\textsuperscript{64} was used with an IPEA shift of 0.25 a.u.

To understand the chemical bonding in \( \text{UCI}_6_{2-} \) \((q = 0–2)\), natural bond orbital analyses as developed by the Weinhold group were carried out. We performed NLMO (natural localized molecular orbital) and natural population analyses using the program NBO 5.0.\textsuperscript{62} and covalency analyses with NRT (natural resonance theory) using NBO 6.0.\textsuperscript{63} The electronic wavefunctions were obtained from single-point DFT/B3LYP\textsuperscript{33,40} calculations using Gaussian 09\textsuperscript{64} at the SR-DFT/PBE optimized geometries from ADF 2010.02 calculations. In the Gaussian 09 calculations, we used the same pseudopotentials for U and the same basis sets for U and Cl as in the MOLPRO calculations.

III. EXPERIMENTAL RESULTS

The photoelectron spectra of \( \text{UCI}_6^- \) and \( \text{UCI}_6_{2-} \) are shown in Figs. 1 and 2, respectively. All the observed VDEs for \( \text{UCI}_6^- \) and \( \text{UCI}_6_{2-} \) are given in Table I, where they are compared with the theoretical data. The transition from the ground state of \( \text{UCI}_6^- \) and \( \text{UCI}_6_{2-} \) to that of the corresponding final state is labeled as X and the letters (A, B, C,...) designate detachment transitions to the excited states of the final state.

A. \text{UCI}_6^- \( \text{UCI}_6^- \)

The photoelectron spectrum of \( \text{UCI}_6^- \) at 157 nm and 20 K is shown in Fig. 1(a). The simulated spectrum is shown in Fig. 1(b) for comparison and will be discussed later. Three intense bands (A, B, and C) are observed at very high binding energies, with VDEs of 7.04, 7.43, and 7.73 eV, respectively. Careful examination reveals an extremely weak band near 5.5 eV, labeled as X (see inset of Fig. 1(a)). This band is barely above the noise level and should correspond to electron detachment from the 5f electron in \( \text{UCI}_6^- \). The X band defines the EA for \( \text{UCI}_6^- \). However, the extremely weak signal and poor signal-to-noise ratio of this band prevent us from measuring an accurate electron binding energy. The VDE is estimated to be 5.5 ± 0.1 eV and the adiabatic detachment energy (ADE) or the EA of \( \text{UCI}_6^- \) is estimated to be 5.3 ± 0.2 eV.

The extremely weak detachment cross section of the X band suggests that the highest singly occupied molecular orbital (SOMO) of \( \text{UCI}_6^- \) is mainly of 5f\( _{xyz} \) character, which was shown previously to give rise to very low detachment cross sections for \( \text{UF}_5^- \) and \( \text{UCI}_6^- \).\textsuperscript{28,31} The current observation for \( \text{UCI}_6^- \) confirms unequivocally that we were not able to obtain the PES spectrum of \( \text{UF}_5^- \) previously.\textsuperscript{28} Without the strong...
detachment features from the Cl3p orbitals at the high binding energy side, to the bands A, B, and C (Fig. 1a), it would not be possible for us to observe the feeble detachment feature from the 5f SOMO of UCl$^{2-}$. In fact, we tried to take the spectrum of UCl$_6^{2-}$ at 213 nm (5.821 eV) and were not able to observe any signals for the X band above the noise level. In the case of UF$_6^{-}$, the binding energies of the F2p orbitals were too high to be observed at 157 nm, the highest photon energy available, thwarting our opportunity to directly measure the EA of the important UF$_6$ molecule.$^{28}$

B. UCl$_6^{2-}$

We were able to measure the photoelectron spectra of UCl$_6^{2-}$ at 20 K and four different photon energies, as shown in Figs. 2(a)-2(d). We also obtained the 266 nm spectrum at room temperature (red curve in Fig. 2(b)) for comparison. The simulated spectrum is shown in Fig. 2(e) to be discussed later. At 355 nm (Fig. 2(a)), two bands (X and A) are resolved with VDEs of 0.86 and 1.5 eV, respectively. From the onset of the X band, we estimate an ADE of 0.60 eV, which should correspond to the EA of the UCl$_6^{2-}$ anion or the second EA of neutral UCl$_6$. The UCl$_6$ molecule is among only a few species for which the second EAs have been measured. Band A is broad with strong signals ranging from 1.0 to 1.7 eV and even weaker signals around 2 eV (Fig. 2(b)). In fact, the higher binding energy side of band A is cut off by the repulsive Coulomb barrier (RCB) at 355 nm (vide infra). Following an energy gap, two weak features, B and C, are observed at 266 nm (Fig. 2(b)) and these two bands become the dominating features at higher photon energies. The weak signals of the B and C bands at 266 nm are due to electron tunneling through the RCB, as will be discussed below. In addition, we observe two sharp peaks at 266 nm due to detachment from Cl$^-$, corresponding to binding energies at 3.613 and 3.722 eV for the $^3P_{1/2}$ and $^3P_{1/2}$ final states of Cl, respectively.$^{66,67}$ The Cl$^-$ detachment features are significantly enhanced in the room temperature spectrum (red curve in Fig. 2(b)). Since the Cl$^-$ signals are not observed in the higher photon energy spectra, they are likely derived from photodissociation of UCl$_6^{2-}$ to UC$_5^-$ + Cl$^-$ upon photoabsorption at 266 nm, followed by detachment from a second photon. The electron detachment energy of the UC$_5^-$ fragment is above 4.7 eV and cannot be observed at 266 nm (4.661 eV).$^{31}$ The B and C bands are significantly enhanced at 213 nm (Fig. 2(c)), whereas the X and A bands become very weak. As will be shown below, the X and A bands are from detachment of 5f-based MOs, which have much lower detachment cross sections. A shoulder is observed on the higher binding energy side of band C at 213 nm, and it becomes a dominant band (D) at 157 nm (Fig. 2(d)). More features (E) are observed at higher binding energies in the 157 nm spectrum.

Comparing the spectrum at 213 nm (Fig. 2(c)) with that at 157 nm (Fig. 2(d)), one notes that band E is cut off in the lower photon energy spectrum and the relative intensity of band D is significantly reduced. This photon energy dependent spectral cutoff is a characteristic of PES of multiply charged anions and is a result of the RCB present universally for electron detachment from multiply charged anions.$^{68}$ From the 213 nm (5.821 eV) spectrum, we can see that the spectral cutoff is around 3.6 eV, which yields a RCB of ~2.2 eV ($hv$ - cutoff). The RCB sets the minimum kinetic energy for photoelectrons to be emitted without tunnelling. The estimated RCB of 2.2 eV is consistent with the spectral cutoff at 157 nm (7.866 eV), where no signals are observed in the high binding energy side above 5.5 eV. Therefore, at 266 nm (4.661 eV), the B and C bands are below the RCB and the weak signals observed for the B and C bands are results of electron tunnelling through the RCB (Fig. 2(b)).$^{65}$ In fact, the relative intensity and shape of band A at 355 nm (Fig. 2(a)) are also affected by the RCB.
TABLE I. Observed VDEs of UCl$_6^{q-}$ and UCl$_6^{q-}$ in comparison with calculated VDEs and the dominantly ionized MOs. All energies are in eV.

<table>
<thead>
<tr>
<th></th>
<th>Cl-3p</th>
<th>1t$_{2u}$</th>
<th>1t$_{2g}$</th>
<th>1a$_{2u}$</th>
<th>1e$_{g}$</th>
<th>1g$_{e}$</th>
<th>Expt.</th>
<th>WFT$^{a}$/DFT$^{b}$</th>
<th>MO</th>
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<td>X 5.5 (1)</td>
<td>5.44</td>
<td>1a$_{2u}$-5/2</td>
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<td></td>
<td></td>
<td></td>
<td>0.86(8)</td>
<td>1a$_{2u}$-5/2</td>
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<tr>
<td>A 7.04(8)</td>
<td>6.00-7.07</td>
<td>1t$_{2g}$-3/2,1/2</td>
<td>1t$_{2u}$-3/2</td>
<td></td>
<td>1a$_{2u}$</td>
<td></td>
<td>3.14(8)</td>
<td>3.10-3.19</td>
<td>1t$_{2g}$-3/2,1/2</td>
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<tr>
<td>B 7.43(8)</td>
<td>7.47-7.53</td>
<td>1t$_{2g}$-3/2</td>
<td>1t$_{2u}$-3/2</td>
<td></td>
<td>1a$_{2u}$</td>
<td></td>
<td>3.50(15)</td>
<td>3.57-3.66</td>
<td>1t$_{2u}$-3/2,1/2</td>
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<tr>
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<td>7.84-7.84</td>
<td>1t$_{2g}$-3/2</td>
<td>1t$_{2u}$-3/2</td>
<td></td>
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<td></td>
<td>3.81(15)</td>
<td>3.70-3.78</td>
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<td>1g$_{e}$-3/2</td>
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$^a$TDFT of all SO-coupled states of UCl$_6$ corresponding to dominantly one-electron detachment from UCl$_6^{q-}$. The energy scale is shifted by –0.42 eV to match the experimental peak A with the onset at 7.00 eV shown in bold face.

$^b$The four VDEs corresponding to band A were calculated using WFT (CASSCF/CR-EOM-CCSD(T)/SO) as the energy difference between the ground state (E$_{Cl-3p}$) and the four SO-coupled 5f$^1$ excited states of UCl$_6^{q-}$ (see Table V).

$^c$The VDEs corresponding to detachment from ligand orbitals (band B and higher) are Kohn-Sham MO energies of π (Cl-3p,1t$_{2g}$,1u$_{2g}$,1a$_{1u}$) energy levels, assuming that the correlation and reorganization errors are always the same in the Cl-3p shell. The energy scale is shifted by –0.21 eV to match the experimental peak B with the onset at 3.10 eV shown in bold face. For the meaning of Kohn-Sham MO energies, see Ref. 96.

$^d$Obtained by subtracting the theoretical energy difference 2.25 eV between the ground state and the first charge-transfer excited state (Cl-3p,1t$_{1g}$ → U-5f) of UCl$_6^{q-}$ [according to CASSCF/CASPT2(7,10)/SO calculations] from the experimental 3.1 eV of the onset of the B band.

$^e$Singly occupied MO of UCl$_6^{q-}$.

resulting in the apparent high relative intensity of the X band compared with that in the 266 nm spectrum.

IV. THEORETICAL RESULTS

The calculated energies of the ground and excited states of UCl$_6^{q-}$ and UCl$_6^{q-}$ using ab initio WFT methods at the SR and SO levels are given in Tables II–V. The first ADE and VDE of UCl$_6^{q-}$ and UCl$_6^{q-}$, calculated at the CCSD(T) level with SR and SO coupling corrections, are given in Table VI and compared with the experimental data. The theoretical VDEs of UCl$_6^{q-}$ and UCl$_6^{q-}$ based on the combination of TDDFT and WFT calculations are presented in Tables SI and SII, respectively, and two different notations for the irreducible representations of double group O$_h$ are listed in Table III of the supplementary material.

The optimized structural properties for all three uranium hexachlorides UCl$_6^{q-}$ (q = 0–2) at the SR-CCSD(T) level of theory are given in Table VII. The lowest vertical excitation energies (ΔE in eV) from the U-5f level of UCl$_6^{q-}$ by CASSCF/CR-EOM-CCSD(T)/SO calculations and in UCl$_6^{q-}$ by CASSCF/CASPT2/SO calculations are reported in Table VIII and are compared with theoretical literature results and experimental vertical absorption band values measured in crystals or solutions.

A. The geometrical structures of UCl$_6^{q-}$ (q = 0–2)

All three molecules are found to have octahedral symmetry (O$_h$), regardless of their charge states. Table VII shows that upon filling electrons into the U-5f shell of UCl$_6^{q-}$, the U–Cl bond lengths increase by 8 pm in UCl$_6^{q-}$ and by 21 pm in UCl$_6^{q-}$ at the SR-CCSD(T) level, primarily as a result of the reduced effective charges on U and the increased intramolecular Coulomb repulsion in the anions. The trend of the calculated gas phase U–Cl bond lengths is consistent with the calculated (harmonic) symmetric stretching vibrational frequencies. The frequencies agree within a few percent with the experimental values.

B. Molecular orbitals (MOs) of UCl$_6^{q-}$ (q = 0–2)

The one-electron MO schemes of UCl$_6^{q-}$ (q = 0–2), based on DFT calculations with SR and SO coupling, are displayed in Fig. 3, where the dominant atomic character of each MO is indicated. For O$_h$ symmetry, the six Cl-3p AO give rise to MOs of a$_{1g}$, e$_g$, and t$_{1u}$ species; the twelve Cl-3p AO give rise to MOs of t$_{1g}$, t$_{2g}$, t$_{1u}$, and t$_{2u}$ species. The two sets of t$_{1u}$ MOs are σ–π mixed. The dative Cl-3p bonding is due to mixing of the 1e$_g$(σ) and 1t$_{2g}$(π) ligand orbitals with the U-6d shell, and of the 1t$_{1u}$(σ) and 1t$_{2u}$(π) ligand orbitals with the U-5f shell. Accordingly, the Cl-3π(1t$_{1g}$) and the U-5f(1a$_{2u}$)
Vertically excited singlet and triplet U-5f type terms of UCl$_6^{2-}$ [from scalar-relativistic CAS(2,7)/PT2 calculations] at the CCSD(T)-optimized $^3$T$_{1g}$ ($t_{2g}^2$) ground-state geometry: energies and $\Omega_{h}$-ligand-field split occupations of orbital-pairs.

<table>
<thead>
<tr>
<th>Terms</th>
<th>Main contributions</th>
<th>$\Delta E$/eV</th>
<th>$\Delta \tilde{v}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^3T_{1g}$</td>
<td>45%$t_{2g}2s + 35%t_{2g}2p + 19%t_{1u}2p + 1%t_{1u}1d$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>$a^3T_{2g}$</td>
<td>73%$t_{1u}2p + 27%t_{2g}2p$</td>
<td>0.16</td>
<td>1309</td>
</tr>
<tr>
<td>$a^3T_{1g}$</td>
<td>42%$t_{2g}2s + 23%t_{2g}2p + 19%t_{1u}2p + 16%t_{1u}1d$</td>
<td>0.18</td>
<td>1479</td>
</tr>
<tr>
<td>$3^3E_g$</td>
<td>100%$t_{1u}1d$</td>
<td>0.26</td>
<td>2082</td>
</tr>
<tr>
<td>$b^3T_{1g}$</td>
<td>62%$t_{1u}2p + 20%t_{2g}2p + 11%t_{1u}2s + 7%t_{2g}1u$</td>
<td>0.67</td>
<td>5405</td>
</tr>
<tr>
<td>$b^3T_{2g}$</td>
<td>73%$t_{1u}2p + 27%t_{1u}2p$</td>
<td>0.67</td>
<td>5440</td>
</tr>
<tr>
<td>$3^3A_{2g}$</td>
<td>100%$t_{2g}1u$</td>
<td>0.77</td>
<td>6172</td>
</tr>
<tr>
<td>$a^3T_{1g}$</td>
<td>58%$t_{1u}2p + 42%t_{2g}2p$</td>
<td>0.65</td>
<td>5268</td>
</tr>
<tr>
<td>$a^3E_g$</td>
<td>85%$t_{2g}2s + 7%t_{1u}2p + 8%t_{2g}1u$</td>
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<td>5285</td>
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<tr>
<td>$a^3A_{1g}$</td>
<td>71%$a_{2g}2s + 28%t_{1u}2s$</td>
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<td>5609</td>
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<tr>
<td>$a^3T_{2g}$</td>
<td>36%$t_{2g}2s + 49%t_{1u}1d + 9%t_{2g}2p + 6%t_{1u}a_2u$</td>
<td>0.85</td>
<td>6852</td>
</tr>
<tr>
<td>$b^3T_{2g}$</td>
<td>56%$t_{1u}2p + 43%t_{1u}2p$</td>
<td>1.73</td>
<td>13990</td>
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<tr>
<td>$b^3E_g$</td>
<td>89%$t_{1u}2p + 7%t_{1u}2s + 4%t_{2g}2p$</td>
<td>1.99</td>
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<td>59%$t_{2g}2s + 23%t_{1u}2p + 18%a_{2u}2s$</td>
<td>2.30</td>
<td>18550</td>
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<tr>
<td>$b^3T_{1g}$</td>
<td>58%$t_{1u}2p + 42%t_{2g}2p$</td>
<td>2.33</td>
<td>18759</td>
</tr>
<tr>
<td>$c^3T_{2g}$</td>
<td>51%$t_{1u}2p + 34%t_{2g}2p + 11%t_{1u}2s + 5%t_{1u}a_2u$</td>
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<td>2.46</td>
<td>19854</td>
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<tr>
<td>$a^3A_{2g}$</td>
<td>100%$t_{2g}1u$</td>
<td>2.50</td>
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<tr>
<td>$d^3T_{2g}$</td>
<td>52%$t_{1u}2p + 46%t_{1u}1d + 2%t_{1u}2u$</td>
<td>2.66</td>
<td>21490</td>
</tr>
<tr>
<td>$c^3E_g$</td>
<td>86%$t_{1u}2s + 10%t_{2g}2s + 2%t_{2g}1u$</td>
<td>2.70</td>
<td>21739</td>
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<tr>
<td>$c^3A_{1g}$</td>
<td>49%$t_{1u}2u + 39%t_{2g}2u + 12%a_{2u}2s$</td>
<td>4.93</td>
<td>39799</td>
</tr>
</tbody>
</table>

The lowest seven SO-coupled states of UCl$_6^{2-}$ (from CASCCF/CAS(2,7)/PT2/SO calculations) at the geometry of $T^1_1$ (5f$^2$t$_{2g}^2$) as optimized by SR-CCSD(T). SO-mixing of LS-U-5f type $\Omega_h$-ligand-field configuration states. The SR leading term of each SO-coupled state is in boldface.
complexity in the PES spectra of the dianion, as will be discussed below. In Fig. 3, the $1t_{1g}$ Cl-3p HOMO is used as the zero energy reference for all three UCl$_6$$^q$- species. The common approximate exchange-correlation functionals are known to incorrectly reproduce the electron repulsion in compact orbital shells; therefore, the upper U-5f type MO levels of UCl$_6$$^2$- are predicted more than 0.5 eV too high by DFT.

The three-dimensional MO contour pictures of UCl$_6$$^q$- are shown in Fig. 4, where the occupation and bonding character for UCl$_6$$^q$- are given. It should be noted that the shapes of the $1t_{1g}$ and $2t_{1u}$ orbitals are interchanged from UCl$_6$ to UCl$_6$$^2$-.

C. The ground electronic states of UCl$_6$$^q$- ($q = 0$–2)

In UCl$_6$, U is in its highest oxidation state of +6 with a 5f$^6$ singlet ground state ($^1A_{1g}$). The UCl$_6$$^q$- anion has a doublet ground state ($^2A_{2u}$) with one 5f electron in the $1a_{2u}$ MO (Fig. 3). The UCl$_6$$^2$- dianion has two electrons, resulting in more complicated electronic structures due to strong Fermi, Coulomb, and SO correlation effects between the U-5f electrons. The states and energies derived for different spin and LS couplings and owing to mixing of different octahedral orbital configurations are given in Table II. At the SR-DFT level, the electronic ground term of UCl$_6$$^2$- is a degenerate $^3T_{1g}$ one with the two electrons occupying the $2t_{2u}$ U-5f shell at $O_h$ symmetry (Fig. 3). This state should be subject to static or dynamic Jahn-Teller distortion of the octahedral symmetry. The $^3T_{1g}(2t_{2u})$ ground term also dominates the CAS wavefunction, but contributes only 45%, with $2t_{2u}^11a_{2u}^1$ and $2t_{2u}^23t_{1u}^1$ configurations contributing 35% and 19%, respectively. It must be noted, however, that all atomic LS$^2$ terms are of open-shell single-configuration multi-determinant type with symmetry-fixed rational mixing coefficients. The ligand-field splitting of the U-5f shell in the UCl$_6$ species into $a_{2u}$, $t_{2u}$, and $t_{1u}$ by around $\pm$0.5 eV transforms these atomic single-configuration multi-determinant $^2$ functions into $(2a_{2u}1t_{1u}2t_{2u})$ multi-configuration functions with nearly rational mixing coefficients. With SO coupling, the electronic ground state of UCl$_6$$^2$- becomes a first-order Jahn-Teller non-active $A_{1g}$ state (Table III), thus rendering the regular octahedral structure of the dianion. The strongly pseudo-configuration-mixed $^3T_{1g}$ state contributes 93% to the SOCoupled $A_{1g}$ state, while the remaining 7% come from $1a_{2u}^2$ and $3t_{1u}^2$ configurations (for details, see Tables II and III). Our calculated SO-coupled excitation energies of UCl$_6$$^q$- at the SR-CCSD(T) ground-state geometry of UCl$_6$$^2$- are listed in Table V, and the higher VDEs of UCl$_6$$^q$- due to 5f electron detachment are obtained by reference to the first calculated VDE of peak X.

V. THE CALCULATED ELECTRON BINDING ENERGIES AND INTERPRETATION OF THE OBSERVED PHOTOELECTRON SPECTRA

To interpret the PES spectra of UCl$_6$$^q$- and UCl$_6$$^q$2-, we calculated the electron binding energies and simulated the PES spectra based on the calculated VDEs. Several electronic states were calculated at a high level of correlated, quasi-relativistic SO-coupled theory. The calculated first ADE and VDE for UCl$_6$$^q$- and UCl$_6$$^q$2- are compared with the experimental values in Table VI. The theoretical results with SO corrections agree within about 0.3 eV of the experimental values. The calculated EA for UCl$_6$ at both SO-CCSD(T) (5.53 eV) and SR-CCSD(T) (5.26 eV) levels agrees with the observed value (5.3 ± 0.2 eV) within the large experimental uncertainty. We recently calculated an EA of 5.20 eV at the SR-CCSD(T) level for UF$_6$28 even though we were not able to measure the photoelectron spectrum of UF$_6$. The current study suggests that the previous theoretical EA for UF$_6$ is reasonable.

A. UCl$_6$$^q$-

Electronic detachment from the doublet ground state of UCl$_6$$^q$- yields singlet and triplet final states of UCl$_6$$^0$. The
VDEs were computed as excitations from the singlet ground state of UCl₆ to its singlet and triplet excited states using TDDFT at both the SAOP and B3LYP levels (Table SI). The two levels of theory yielded similar VDEs; the values from the SAOP level are compared with the experimental data in Table I and are used to produce the simulated PES spectra for UCl₆⁻ in Fig. 1(b). The simulated spectrum was obtained by representing the calculated VDEs for each Cl-3p MO detachment by a unit Gaussian of width 0.14 eV. The detachment features from the much more compact, and therefore much weaker U-5f type MOs are simply indicated by short bars in Fig. 1(b). The qualitative similarity of the simulated and observed PES spectrum for UCl₆⁻ lends considerable confidence for the reliability of the spectral assignments.

As shown in Fig. 1(b) and Table I, the observed four bands, X, A, B, and C correspond to one-electron detachments from orbitals or spinors of the following types: X from U-5f(1a₂₋₋₅/₂), A from SO-components Cl-3p(111/g₋₋₅/₂,1/₂), B from SO-components Cl-3p(21u₋₋₅/₂) and Cl-3p(11u₋₋₅/₂,1/₂), and C from Cl-3p(21u₋₋₁/₂) and Cl-3p(11u₋₋₁/₂). The detachment energy of the SO-component of Cl-3p(11u₋₋₁/₂) is already above the 157 nm excitation photon energy limit (7.866 eV). The SOMO of UCl₆⁻ (5fₕ₋₋₅/₂₋₋₁a₂) is comparably compact (Fig. 4), which explains why the detachment cross section of the X band is so weak in agreement with our previous experiment for UF₅⁻ and UF₆⁻.²⁸

### B. UCl₆²⁻

Without SO coupling, electron detachment from the UCl₆²⁻ triplet ground state can result in doublet and quartet final states of UCl₆⁻. Similar to the strong correlation effects observed in the electron detachment from U(f⁵)O₂⁻,⁷⁷ the electron detachment from U(f⁷)Cl₂⁻ is also complicated by the interplay of strong SO coupling and multi-configurational electron correlations. The detachment channels are schematically illustrated in Fig. 5. The computed VDEs are given in Table SI⁻⁹⁻ and compared with the experimental data in Table I and the simulated spectrum in Fig. 2(e). The simulated spectrum for UCl₆²⁻ was obtained by representing the calculated VDEs of each Cl-3p MO detachment feature by a unit Gaussian of width 0.28 eV. The detachment features of the much weaker U-5f type MOs are indicated by short bars in Fig. 2(e). The good agreement between the simulated and observed PES spectra for UCl₆²⁻ again confirms the reliability of the spectral assignments.

As shown in Table II, the leading configuration of the ground state of UCl₆²⁻ (3T₁g) is 2t₂₋₋₁ (45%). Single electron detachment from this orbital should only result in two detachment channels with the final state configurations of 2t₂₋₋₁ and 2t₂₋₋₅/₂, corresponding to VDE₂ and VDE₃ in Fig. 5. However, the 3T₁g ground state of UCl₆²⁻ also consists of 35% 2t₂₋₋₁ 1a₂⁻⁻⁻ and 19% 2t₂₋₋₅/₂, which lead to final state configurations of 1a₂⁻⁻⁻ (VDE₁) and 3t₁⁻⁻⁻ (VDE₄).

### TABLE VII. Geometric symmetry, electronic ground state with the leading configuration, bond lengths (R(U–Cl) in pm), and symmetric stretching vibrational frequencies (ν₃(U–Cl) in cm⁻¹) calculated for UCl₆, UCl₆⁻, and UCl₆²⁻ in vacuum at the SR-CCDD(T) and SR-DFT levels, and experimental bond lengths in the crystal phase.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Symmetry</th>
<th>Ground state</th>
<th>R(U–Cl) (SR-CCDD(T))</th>
<th>R(U–Cl) (SR-DFT)</th>
<th>ν₃(U–Cl) (Expt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCl₆</td>
<td>Oh</td>
<td>1A₁u(5f⁷)</td>
<td>245.4</td>
<td>241-251</td>
<td>247.1</td>
</tr>
<tr>
<td>UCl₆⁻</td>
<td>Oh</td>
<td>2A₂u(1-1a₂)</td>
<td>253.7</td>
<td>247.252-256</td>
<td>254.6</td>
</tr>
<tr>
<td>UCl₆²⁻</td>
<td>Oh</td>
<td>3T₁g(2t₂₋₋₁)</td>
<td>266.9</td>
<td>258-264</td>
<td>266.9</td>
</tr>
</tbody>
</table>

²⁸References 77-83.
²⁹References 84 and 85.
⁰Harmonic approximation.
¹The 2g₂⁻⁻ configuration contributes only 45% to the f₂ manifold; the 3T₁g LS state contributes 93% to the SO coupled ground state (Tables II and III). In the CCSD(T) calculations, the Abelian D₃h subgroup symmetry is used for electronic wavefunctions. The degenerate state 3T₁g(2t₂₋₋₁) in Oh symmetry was calculated as a 1B₁g(1b₂₁,1b₃₁) state in D₃h symmetry, i, j, k = 1, 2, 3.

### TABLE VIII. The lowest vertical excitation energies (∆E in eV) within the U-5f shell of UCl₆⁻, from CASSCF/CR-EOM-CCSD(T)/SO, and of UCl₆²⁻ from CASSCF/CASPT2/SO calculations, at the SR-CCSD(T) optimized ground-state geometries with R(U–Cl) bond lengths of 2.537 and 2.669 Å, respectively, in the gas phase, and comparison with reported theoretical results and experimental vertical absorption bands measured in crystals or solutions.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Level</th>
<th>XE₅/₂a</th>
<th>aU₅/₂a</th>
<th>aE₅/₂a</th>
<th>bU₅/₂a</th>
<th>aE₁/₂a</th>
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</thead>
<tbody>
<tr>
<td>UCl₆⁻</td>
<td>∆E</td>
<td>-0.09</td>
<td>0.39</td>
<td>0.73</td>
<td>1.13</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>Eₜₑ</td>
<td>-0.04-0.47</td>
<td>0.84-0.91</td>
<td>1.16-1.39</td>
<td>1.33-1.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Eₜ₂</td>
<td>-0.9-0.5</td>
<td>-0.85</td>
<td>-1.2</td>
<td>-1.45</td>
<td></td>
</tr>
<tr>
<td>Dianion</td>
<td>Level</td>
<td>XA₁g</td>
<td>aT₁g</td>
<td>aE₁g</td>
<td>aT₂g</td>
<td>bT₁g</td>
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<tr>
<td>UCl₆²⁻</td>
<td>∆E</td>
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<td>0.14</td>
<td>0.24</td>
<td>0.66</td>
<td>0.66</td>
</tr>
</tbody>
</table>

²Active space of 2-electrons in 7-orbitals, CAS(2,7).
²²From SO-CASSCF and SO-CASPT2 calculations in Refs. 9 and 70.
²¹From Refs. 8, 11, and 71.
²²From Refs. 72-76.
FIG. 3. SR and SO-coupled energies of the valence orbitals of UCl$_6$\(^{q-}\) ($q = 0-2$) from relativistic DFT/PBE calculations (nb, nonbonding).

and VDE$_5$). These detachments’ transitions can be viewed as two-electron processes, which are direct manifestation of the strong electron correlation (or open-shell determinantal mixing) effects of the two 5f electrons in UCl$_6^{2-}$, thus leading to the breakdown of Koopmans’ single-determinantal theorem. The intensities of these transitions are expected to be low, especially for the VDE$_4$ and VDE$_5$ channels, due to the low percentage of the 2t$_{2u}^1$3t$_{1u}^1$ configuration (19%). As assigned in Table I, the VDE$_1$ corresponding to U5f(1a$_{2u}$–5/2) is assigned to the observed X band. The two detachment channels leading to U-5f(2t$_{2u}$5/2,3/2) should correspond to the more intense broad band A. The two channels leading to U5f(3t$_{1u}$3/2,1/2) should have very low relative intensities and should correspond to very weak signals on the higher binding energy side of band A (VDE$_4$ and VDE$_5$ in Fig. 5, but not shown in Fig. 2(e)). The strong band B then corresponds to one-electron detachment from Cl-3p(1t$_{1g}$3/2,1/2). The higher binding energy detachment bands (C, D, and E) are assigned to higher Cl-3p based ligand orbitals (Table I and Fig. 2(e)).

FIG. 4. Pictures of the relevant valence orbitals of UCl$_6$\(^{q-}\) from DFT calculations and the orbital characters (b, bonding; w, weakly bonding; n, nonbonding; a, antibonding).
One of the two $t_{1u}$ MOs has some anti-bonding contribution from the strongly SO-affected U-6p$^6$ core shell and is thus significantly SO-split due to the large SO splitting constant of U-6p (Figs. 3 and 4). The two SO components correspond to $t_{1u}$-1/2 and $t_{1u}$-3/2 ($e_1/2u$ and $u_3/2u$ in double-group representation, Fig. 3). The softness of the outer noble-gas core shells is well known for the bottom rows of the periodic table,25-27,31,88,89 where the heavy noble-gas shells have an influence on the valency of the heavy metal atoms from the s- and early f-blocks. Without accounting for the SO splitting of the Cl-3p $t_{1u}$ MOs of 0.4 eV, the spectral simulations would become visibly worse for both UCl$_6^-$ and UCl$_6^{2-}$, indicating the valence participation of the Rn-6p noble-gas shell.

VI. DISCUSSION

A. The origin of the PES band widths

The experimental PES bands are all quite broad (Figs. 1 and 2), as a result of both overlapping detachment transitions, and extended Franck-Condon envelopes due to the geometry changes upon electron detachment (Table VII). These geometry changes result mainly from changes in the ionic core shell and electron correlation effects. The instrumental resolution is much smaller, as indicated by the PES features of Cl$^-$ in Fig. 2(b). The band widths of our low temperature PES spectra without thermal broadening are around 0.1–0.15 eV for the spectrum of UCl$_6^-$ (Fig. 1) and 0.25–0.30 eV for UCl$_6^{2-}$ (Fig. 2). The energy difference between the observed first ADE and VDE of UCl$_6^{2-}$ is ~0.26 eV, which should be roughly the width of band X. The calculated harmonic U–Cl stretching vibrational frequencies of UCl$_6^-$ and UCl$_6$ are around 330 cm$^{-1}$ (Table VII), suggesting Huang-Rhys factors of $S = \Delta E/h\nu = \approx 7$ and 4, respectively, for UCl$_6^-$ and UCl$_6$, with $\Delta E = 0.26$ and 0.15 eV (i.e., the experimental and theoretical PES band widths). These relations follow from the theory of bond-length-change $\Delta R$ (vibrational-band-width of highly symmetric molecules AX$_n$ upon electronic excitation, $\Delta R = 821 \times [S(\nu u^2 M_k)]^{1/2}$, where $S = M_k$ is the mass of a single ligand X in amu (e.g., 35.5 for Cl), $\nu$ is the symmetric breathing vibrational frequency of the final species in cm$^{-1}$, and $w$ is the often mistakenly overlooked topological factor (for AX$_n$ complexes of Os symmetry, $w = 6$). For one-electron detachment from UCl$_6^{2-}$, we obtained $\Delta R$ (U–Cl) $\approx 20$ pm without the $w$ factor, and with $w$ we have $\Delta R \approx 8$ pm. This experimentally derived value using Eq. (1) agrees much better with the theoretical $\Delta R$ value in Table VII. This result suggests that one can evaluate the PES band widths ($\Delta E$) using the optimized U–Cl bond-length change ($\Delta R$).

B. The electronic structures of UCl$_6^{q-}$ ($q = 1, 2$)

The extra electron in UCl$_6^-$ occupies the non-degenerate 1a$_{2u}$ MO (Fig. 3), which is not split by SO coupling and does not induce first-order JT distortion of the octahedral complex. We have verified computationally that no pseudo-JT distortion occurs either. The U-5f orbitals are split by the O$_5$ ligand field and the SO-coupling in the UCl$_6^-$ anion into five levels (Table VIII), spanning a range of nearly 1.5 eV. Optically dipole-forbidden, vibrationally induced transitions from 5f(3a$_{2u}$) to 5f(1a$_{2u}$) would appear in the near and mid-IR regions. The lowest excitation $E_{5/2a} \rightarrow aU_{5/3a}$ has indeed been observed near 0.5 eV in the IR spectra of various U(V)X$_6^-$ species in condensed phases,8,11,71 in reasonable comparison with 0.39 eV calculated in the current study (Table VIII). For the next three 5f-5f excitation energies of UCl$_6^{2-}$, our theoretical data agree with the experimental data in the condensed phase within ~0.15 eV, i.e., slightly better than the reported SO-CASSCF and SO-CASPT2 results in the literature9,70 (deviations within 0.26 eV). The observed gap of 0.6 eV between bands X and A in the PES of UCl$_6^{2-}$ corresponds approximately to the mean energy of transitions in UCl$_6^-$ from the $E_{5/2a}$ ground state to the SO split levels $aU_{5/2a}$ and $E_{5/2a}$ at the ground-state geometry of UCl$_6^{2-}$. In the case of octahedral UCl$_6^{q-}$ with two 5f electrons, the lowest energy with minimal electron repulsion is obtained for two f electrons in two different MOs of 2t$_{2u}$ symmetry (Fig. 3). The atomic f$^2$ configuration gives rise to 91 determinantal wavefunctions, and all symmetry adapted states are heavily determinant-mixed. Further mixing is induced by the strong 2e-Coulomb, SO, and ligand-field interactions (Tables II and III). The SO-coupled ground state is of $A_{1g}$ type and has AO populations corresponding to U-5f$^2$ (1a$_{2u}$, 3a$_{2u}$, 1t$_{1u}$, 0.23). This $A_{1g}$ ground state is not subject to pseudo-JT distortion; our investigation on D$_3h$ and D$_h$ distortions at the SR-DFT/PBE level revealed little U–Cl bond length and angle changes. The lowest energy detachments...
of the $X_{A_{1g}}$ ground state of $U(f^2)Cl_6^{2−}$ yield the lowest final states of $U(f^3)Cl_6^{3−}$: $X E_{5/2a}(1_{a_{2u}}{5/2})$, $\alpha U_{3/2a}(f-2_{2u}{5/2})$, $\alpha E_{5/2a}(f-2_{2u}{5/2})$, $\beta U_{3/2a}(f-3_{1u}{5/2})$, and $\alpha E_{1/2a}(f-3_{1u}{1/2})$ (Fig. 5 and Table V). Since the final $3_{1u}{1/2}$ states ($\beta U_{3/2a}$ and $\alpha E_{3/2a}$, indicated by dotted lines in Fig. 5) are of shake-up type and have low intensities in the PES, the gap of 0.6 eV between the observed PES bands X and A in Fig. 2 corresponds to the energy gap between spinor $1_{a_{2u}}{5/2}$ and the average of $2_{2u}{3/2,5/2}$ of $UCl_6^{2−}$, representing the average of the first and second excitation energies of $UCl_6^{6−}$, which are calculated at the ground-state geometry of $UCl_6^{2−}$ as 0.34 eV and 0.73 eV (Table V), and observed as 0.5 and 0.85 eV in the IR region (Table VIII).

C. Chemical bonding in $UCl_6^{6−}$ ($q = 0−2$)

The results of chemical bonding analyses are presented in Table IX. We have investigated two questions. First, how do the added electrons distribute over the molecules in the series $UCl_6 → UCl_6^{q−} → UCl_6^{q−−}$? The expectation is that they go into the inner $U-5f$ shell. We applied two different procedures to assign formal or effective electronic charges to the atoms. In the Voronoi procedure, $91$ the bond is cut in the geometric middle of the bond line. Most of the added electronic charge goes to the outer region of the U atom, where the Cl atoms are overlapping (Table IX). As a result, by decreasing the oxidation state of $U$ by 1 formal unit from $U^{4+}$ to $U^{3+}$ to $U^{2+}$, the positive Voronoi charge on the U atom decreases only by a small amount, i.e., by 0.09[e] and 0.23[e], respectively, while the added electronic charge is dominantly assigned to the Cl anions, which become more negative by nearly $−1/6$.

In the NBO procedure, $92$ the electronic charge is assigned to the overlapping AOs. Here, the charge on the Cl atoms even varies slightly more than by $−e/6$ upon reduction of the U cation by 1 formal unit. In other words, oxidizing the uranium halides implies removing electronic charge from the ligands rather than from the formally oxidized central metal.

This result suggests the second interesting aspect: how do ionicity and covalency change from $UCl_6 → UCl_6^{q−} → UCl_6^{q−−}$ upon sequential reduction? The covalent bond orders of Mayer $93$ and of Gopinathan-Jug $94$ decrease in this order. In contrast, the overall (covalent and ionic) bond order of Nalewajski-Mrozek $95$ and the NBO of Weinhold et al. $92$ do not vary much, indicating a remarkable increase of ionic bonding in the counterintuitive order. Namely, from $U(−6) → U(−5) → U(−4)$, the effective positive charge on $U$ varies little, but the effective negative charge on the chlorine ligands increases substantially, so that the effective ionic product $Q_{Cl−Cl}$ increases from $U^{4+}$ ($Cl^{−6}$ to $U^{3+}$ ($Cl^{−6}$), counter-intuitively, independent of the charge definition (Voronoi or NBO). Also the NLMOs become more polar towards Cl, when electrons are formally added into the $U-5f$ shell, thereby reducing the electron affinity of the central atom. The $U-5f$ AOs have much larger percentage contribution in both $\sigma$ and $\pi$ dative bonding than the $U-6d$ AOs, while the latter are more important in orbital overlap.

As shown in Fig. 3, the energies of the Cl-3p and U-5f valence shells approach each other upon oxidation from $U^{4+}$ to $U^{1+}$. Namely, increasing the oxidation state of $U$ lowers the energies of the metal orbitals and provides better chances for $U−Cl$ interactions. $8,17$ Oxidation of $UCl_6^{q−−}$ reduces the negative charge on the ligands and also the Coulomb repulsion between the ligands, thereby leading to shorter bond lengths (Table IX) and better orbital overlap. As a result, the $U−Cl$ covalency increases from 26% in $UCl_6^{q−−}$ to 41% in $UCl_6^{q−}$; i.e., uranium with higher oxidation state possesses larger covalent bonding.

VII. CONCLUSIONS

We report the first experimental observation of $UCl_6^{−}$ and $UCl_6^{2−}$ in the gas phase and the investigation of their electronic structures by low-temperature photoelectron spectroscopy and by $ab$ initio calculations. Both the first and second electron affinities of $UCl_6$ are measured for the first time, as 5.3 eV and 0.60 eV, respectively. The open 5f shell together with the high electronegativity of the ligands contributes to the large electron affinity of $UCl_6$. The detachment cross section of the single 5f electron ($5f_{xyzz}$) in $UCl_6^{−}$ was observed to be extremely small.
UC\textsubscript{6}Cl\textsubscript{6}\textsuperscript{2−} with two 5f electrons is found to possess a strong multi-determinantal ground state, giving rise to multiple detachment features beyond Koopmans’ theorem. Multi-reference WFT \textit{ab initio} methods with spin-orbit coupling are necessary to accurately interpret the detailed electronic structures of these uranium hexachloride species. The U–Cl covalency is found to decrease upon reduction of formal ionicity from [(U\textsuperscript{6+}Cl\textsubscript{6}) \rightarrow [(U\textsuperscript{5+}Cl\textsubscript{6}) \rightarrow [(U\textsuperscript{4+}Cl\textsubscript{6})\textsuperscript{2−}.

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69See supplementary material at dx.doi.org/10.1063/1.4916399 for the listing of the calculated VDEs for UCl$_6^-$ and UCl$_6^{2-}$ and two different notations for the irreducible representations of double group O$_{h}$.