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Photelectron spectroscopy and the electronic structure of the uranyl tetrachloride dianion: \( \text{UO}_2\text{Cl}_4^{2-} \)

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The uranyl tetrachloride dianion (\( \text{UO}_2\text{Cl}_4^{2-} \)) is observed in the gas phase using electrospray ionization and investigated by photelectron spectroscopy and relativistic quantum chemical calculations. Photoelectron spectra of \( \text{UO}_2\text{Cl}_4^{2-} \) are obtained at various photon energies and congested spectral features are observed. The free \( \text{UO}_2\text{Cl}_4^{2-} \) dianion is found to be highly stable with an adiabatic electron binding energy of 2.40 eV. Ab initio calculations are carried out and used to interpret the photoelectron spectra and elucidate the electronic structure of \( \text{UO}_2\text{Cl}_4^{2-} \). The calculations show that the frontier molecular orbitals in \( \text{UO}_2\text{Cl}_4^{2-} \) are dominated by the ligand Cl 3p orbitals, while the U–O bonding orbitals are much more stable. The electronic structure of \( \text{UO}_2\text{Cl}_4^{2-} \) is compared with that of the recently reported \( \text{UO}_2\text{F}_4^{2-} \) [P. D. Dau, J. Su, H. T. Liu, J. B. Liu, D. L. Huang, J. Li, and L. S. Wang, Chem. Sci. 3 1137 (2012)]. The electron binding energy of \( \text{UO}_2\text{Cl}_4^{2-} \) is found to be 1.3 eV greater than that of \( \text{UO}_2\text{F}_4^{2-} \). The differences in the electronic stability and electronic structure between \( \text{UO}_2\text{Cl}_4^{2-} \) and \( \text{UO}_2\text{F}_4^{2-} \) are discussed. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4742062]

I. INTRODUCTION

The chemical and electronic properties of the actinyl ions remain an interesting research topic because of their relevance to the disposal of nuclear wastes. Considerable research efforts have been devoted to understanding the electronic structures of the actinyls and the actinide-oxygen bonding properties in the condensed phase.1–5 The uranyl dication (\( \text{UO}_2^{2+} \)) exists widely in uranium compounds,6 and its electronic structure and bonding properties have been reviewed recently by Denning.7 In \( \text{UO}_2^{2+} \), the U atom forms two strong U=O triple bonds with a linear geometry (\( D_{\text{shb}}, ^1\Sigma_g^+ \)).7–10 The occupied frontier bonding molecular orbitals (MOs) of \( \text{UO}_2^{2+} \) (\( \sigma_u, \sigma_g, \pi_g, \) and \( \pi_u \)) are mainly oxygen based, with the \( \sigma_u \) orbital being the highest occupied MO (HOMO). The lowest unoccupied MOs (LUMOs) are U-based 5f\( _\delta \) and 5f\( _\phi \) orbitals, which do not participate in chemical bonding with the O atoms in \( \text{UO}_2^{2+} \) due to symmetry constraints. The uranyl ions are usually coordinated equatorially by a variety of ligands, which have weaker interactions with U through the d- and f-type LUMOs. The U−ligand interactions can, in turn, significantly influence the electronic structure and bonding properties of \( \text{UO}_2^{2+} \).7,11–16 However, there is generally a scarce of experimental data about the uranyl-ligand interactions. We have recently studied the isolated \( \text{UO}_2\text{F}_2^{2-} \) species by combining photoelectron spectroscopy (PES) and \( \text{ab initio} \) calculations, revealing that the U−F bonding and the electrostatic repulsion from the F− ligands weaken the axial U−O bonds.17 The calculated U−O bond length in \( \text{UO}_2\text{F}_2^{2-} \) at the coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) level is about 1.81 Å, much longer than that in \( \text{UO}_2^{2+} \) (1.72 Å).18,19

The uranyl tetrachloride dianion, \( \text{UO}_2\text{Cl}_4^{2-} \), is also an important uranyl complex in the condensed phase and has been the subject of detailed optical spectroscopy and theoretical studies both in the solid state as a Cs\( _2\text{UO}_2\text{Cl}_4 \) salt and in solutions.11–15,20–26 However, accurate interpretations of the optical spectra of \( \text{UO}_2\text{Cl}_4^{2-} \) in the condensed environments remain a challenging task in computational actinide chemistry.16,18,26–28 For instance, the explanation of the spectroscopic data of crystallized Cs\( _2\text{UO}_2\text{Cl}_4 \) still relies on empirical models or approximate qualitative analyses.25,29 Furthermore, due to prohibitive computational cost, high-level \( \text{ab initio} \) quantum chemistry calculations can only be applied to isolated actinyl species, such as \( \text{UO}_2^{2+}, \text{UO}_2\text{Cl}_4^{2-}, \) and \( \text{NpO}_2\text{Cl}_4^{2-} \).27–32 Gas-phase spectroscopy provides a unique opportunity to obtain experimental data without perturbation from the environmental effects in the condensed phases, allowing direct comparisons with high-level \( \text{ab initio} \) calculations. Previously, only one gas-phase vibrational spectroscopy study of singly charged uranyl halide anions has been reported.33 We are interested in probing the electronic structures of actinyl complexes using electrospray ionization (ESI) and PES in the gas phase. Following our recent work on \( \text{UO}_2\text{F}_2^{2-} \), here we report the observation of PES and \( \text{ab initio} \) calculations of the isolated tetrachloride dianion, \( \text{UO}_2\text{Cl}_4^{2-} \). We find that \( \text{UO}_2\text{Cl}_4^{2-} \) is even more electronically stable with an adiabatic electron binding energy (ADE) of 2.40 eV. Both density function theory (DFT) and wavefunction-based \( \text{ab initio} \) calculations are performed to help interpret the PES data and elucidate the electronic structure and bonding in

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UO₂Cl₄²⁻. Significant differences in the electronic structure and bonding are found between the two tetrahalide dianions. The PES data of UO₂Cl₄²⁻, as well as the recently reported data for UO₂F₂²⁻, provide valuable experimental results for benchmarking theoretical methods.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Electrospray ionization and photoelectron spectroscopy

The experiment was carried out using our ESI-PES apparatus, which was described in detail previously. The only modification was the shortening of the electron flight tube from 4.0 m to 2.5 m, resulting in a slight decrease of electron energy resolution. Briefly, the UO₂Cl₄²⁻ anion was produced by electrospraying of a 1 mM solution of UCl₄ in acetonitrile with a trace amount of water. A radio frequency-only quadrupole device guided the anions from the ESI source into a Paul trap operated at room temperature, where anions were accumulated for 0.1 s before being pulsed into the extraction zone of a time-of-flight mass spectrometer. Under our ESI condition, strong UO₂Cl₄²⁻ dianion signals were produced, presumably as a result of oxidation reactions of UCl₄ with O₂ and water during the ESI. The UO₂Cl₄²⁻ anions 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. Three different lasers were used for the PES experiment in the current work: 157 nm (7.866 eV) from an F₂ excimer laser, 213 nm (5.821 eV) and 245 nm (5.061) from a dye laser, and 266 nm (4.661 eV) from a Nd:YAG laser. The PES spectra were calibrated using the known spectra of Au⁺ and Au⁻. The Au⁺ anion was produced by electrospraying a pyridine solution of PPh₃AuCl with NaSCH₃ and a trace amount of CH₃OH. The Au⁻ anion was produced from a 0.1 mM NaCl solution in a mixed water-methanol solution. The electron kinetic energy resolution of the current magnetic-bottle photoelectron analyzer with the shortened electron flight tube was about 3%, i.e., 30 meV for 1 eV electrons.

B. Theoretical and computational methods

Theoretical studies were carried out using both DFT and \textit{ab initio} wavefunction theory (WFT) methods. DFT calculations were carried out on the UO₂Cl₄²⁻ dianion and UO₂Cl₄⁻ monoanion using the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and the hybrid functional known as B3LYP (Ref. 38) as implemented in the Amsterdam Density Functional (ADF 2010.01) program. The Slater basis sets with the quality of triple-ζ plus two polarization functions (TZ2P) (Ref. 42) were used, with the frozen core approximation applied to inner shells, \{1s^2-5d^{10}\} for U, \{1s^2\} for O, and \{1s^2-2p^6\} for Cl. The scalar relativistic (SR) and spin-orbit (SO) coupling effects were taken into account by the zero-order regular approximation (ZORA). Geometries were fully optimized at the SR-ZORA level and single-point energy calculations were performed with inclusion of the SO effects via the SO-ZORA approach.

To compare with the experimental results, \textit{ab initio} WFT calculations were done on UO₂Cl₄²⁻ using more advanced electron correlation methods in the MOLPRO 2008.1 program. Both the CCSD(T) and complete-active-space self-consistent field (CASSCF) methods were used in these calculations. The geometry of UO₂Cl₄²⁻ was optimized at the level of CCSD(T) with SR effects included. Single-point CCSD(T) energies of the ground and excited states of UO₂Cl₄⁻ were calculated at the optimized SR-CCSD(T) geometry of UO₂Cl₄²⁻, generating accurate state-specific SR energies for all the states. The electron detachment energies corresponding to one-electron transitions from the closed-shell ground state of UO₂Cl₄²⁻ to the ground and excited states of UO₂Cl₄⁻ were obtained using the CASSCF/CCSD(T)/SO approach, which has been shown to generate accurate excitation energies for molecules containing heavy elements. In this approach, the SO splittings were treated as a perturbation to the SR state energies and were calculated on the basis of CASSCF wavefunctions with the diagonal matrix elements replaced by the individual CCSD(T) state energies. SO splitting was calculated by using a state-interacting method with SO pseudopotentials. We also used the CASSCF/CR-EOM-CCSD(T)/SO approach, which completely renormalized equation-of-motion CCSD(T) (CR-EOM-CCSD(T)) energies, derived from the EOM-CCSD calculations with completely renormalized EOM-CCSD(T) corrections as implemented in NWChem 6.0, were used as the diagonal elements. In this approach, the CR-EOM-CCSD(T) calculations were performed on the monoanion at the optimized CCSD(T) geometry of the dianion to obtain the vertical energies of the excited states, with the CCSD(T) energy of the first state used as a reference. In the MOLPRO and NWChem calculations, we used the Stuttgart energy-consistent relativistic pseudopotential ECP60MBW (U) and the corresponding valence triple-ζ basis sets aug-cc-pVTZ for O and Cl. These basis sets and pseudopotential are shown to produce reasonably accurate results for excitation energies of actinide complexes.

III. EXPERIMENTAL RESULTS

Figure 1 displays the PES spectra of UO₂Cl₄²⁻ at four different photon energies. The 157 nm spectrum (Fig. 1(d)) reveals congested detachment features between 2 and 5 eV binding energies, as labeled from X to F. These features are all fairly broad, owing to either a large geometric change from the dianion to the monoanion states and/or overlaps of multiple detachment transitions. Thus, the labels are for the sake of discussion and cannot be viewed as representing single electronic transitions, as usually done. At 213 nm (Fig. 1(c)), bands X and A are better resolved. However, the relative intensities of bands B–F are significantly reduced, due to the repulsive Coulomb barrier (RCB) expected for a dianion. The RCB cuts off higher binding energy (low kinetic energy) features, when detachment photon energies (hv) are decreased. With a sharp cutoff, one can estimate the
FIG. 1. Photoelectron spectra of UO$_2$Cl$_4^{2−}$ at (a) 266 nm (4.661 eV), (b) 245 nm (5.061 eV), (c) 213 nm (5.821 eV), and (d) 157 nm (7.866 eV).

magnitude of the RCB ($\hbar\nu$—cutoff). However, because of electron tunneling, the RCB cannot define a sharp cutoff threshold and its height can only be estimated from the PES spectra at different photon energies. The 213 nm spectrum suggests that band D (vertical detachment energy (VDE): 4.1 eV) is probably near the barrier top, yielding a RCB $<\!\!\!<$ 2 eV.

At 245 nm (Fig. 1(b)), band D is cut off and the relative intensities of bands A–C are further reduced, consistent with the RCB estimated from the 213 nm spectrum. The sharp and intense double peaks around 3.6 eV in the 245 nm spectrum are due to detachment of Cl$^−$, originated from photodissociation of the UO$_2$Cl$_4^{2−}$ parent dianion at 245 nm through the reaction: UO$_2$Cl$_4^{2−}$ $\rightarrow$ UO$_2$Cl$_3^{−}$ + Cl$^−$. The electron binding energies of the UO$_2$Cl$_3^{−}$ fragment are too high for its photodetachment to be observed at 245 nm. Similar photodissociation is also observed at 266 nm (Fig. 1(a)), as shown by the observation of the sharp Cl$^−$ detachment signals. The photodissociations are most likely due to resonant absorption of a detachment photon, which does not seem to occur at 213 or 157 nm. At 266 nm, feature A is partially cut off at about 3 eV binding energy, which suggests a RCB of $\sim$1.7 eV (4.661 eV–3 eV). This RCB is lower than that estimated for UO$_2$F$_4^{2−}$ previously, in agreement with the smaller size and the higher intramolecular Coulomb repulsion of the tetrafluoride dianion. The ADE and VDE for the ground state transition from UO$_2$Cl$_4^{2−}$ to UO$_2$Cl$_3^{−}$ are determined from the X band as $2.40 \pm 0.08$ eV and $2.62 \pm 0.05$ eV, respectively. The VDE is measured from the maximum of band X. Because no vibrational structure is resolved, the ADE is determined by drawing a straight line along the leading edge of band X and then adding the instrumental resolution to the intersection to the binding energy axis. The ADE of UO$_2$Cl$_4^{2−}$ is much larger than that of UO$_2$F$_4^{2−}$ (1.10 eV), indicating that UO$_2$Cl$_4^{2−}$ is highly electronically stable in the gas phase.

IV. THEORETICAL RESULTS

The calculated first ADE and VDE for UO$_2$Cl$_4^{2−}$ at the DFT/B3LYP and CCSD(T) levels are compared with the experimental data in Table I. The DFT/B3LYP binding energies are significantly lower than the experimental values, most likely due to the self-interaction error. The underestimated electronic binding energies of highly charged anions at DFT levels were also observed in our previous studies of Pt(CN)$_6^{2−}$ (Ref. 62) and UO$_2$F$_4^{2−}$. In as much as the frontier MOs are mainly from Cl 3p orbitals in both UO$_2$Cl$_4^{2−}$ and UO$_2$Cl$_4^{−}$, the SO relativistic effects are expected to be small. At the DFT/B3LYP level, inclusion of the SO coupling effects only improves the ADE and VDE of UO$_2$Cl$_4^{2−}$ by $\sim$0.05 eV. The calculated ADE (2.58 eV) and VDE (2.61 eV) at the SR-CCSD(T) level are in much better agreement with the experiment. In particular, the VDE is in excellent agreement with the experiment, although without SO corrections the SR-CCSD(T) method still overestimates the ADE for UO$_2$Cl$_4^{2−}$ by about 0.2 eV, which is similar to our previous finding for the case of UO$_2$F$_4^{2−}$. The optimized ground-state geometrical parameters of UO$_2$Cl$_4^{2−}$ and UO$_2$Cl$_4^{−}$ at the SR level are given in Table II. Upon electron detachment from UO$_2$Cl$_4^{2−}$, both

<table>
<thead>
<tr>
<th>Exp.</th>
<th>B3LYP</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADE</td>
<td>2.40 ± 0.08</td>
<td>1.75</td>
</tr>
<tr>
<td>VDE</td>
<td>2.62 ± 0.05</td>
<td>1.77</td>
</tr>
</tbody>
</table>

$^a$The ADE and VDE correspond to one-electron detachment from the 1$a_2$ orbital (see Figs. 2 and 3).
DFT and CCSD(T) calculations show that the U–Cl bonds are shortened by about 0.03–0.04 Å and the U–O bonds are slightly shortened by about 0.01 Å in the UO$_2$Cl$_4$$^{2-}$ monoanion.

The occupied valence MO levels for UO$_2$Cl$_4$$^{2-}$ are shown in Fig. 2 with SR and SO effects included, and details of the calculated VDEs for all the MOs by DFT/PBE can be found in Table III. Among these MOs, the 1$e_g$ and 2$e_u$ orbitals display strong SO effects (Fig. 2) due to contributions of the U 5$f\pi$ orbitals to the former and U 5$f\delta$ and 6$p$ orbitals to the latter. The 1$\alpha_{1g}$, 1$\epsilon_g$, 1$e_u$, and 1$\alpha_{2u}$ MOs are the U–O bonding orbitals, and the remaining MOs are primarily Cl 3$p$ type orbitals (Table III). The three-dimensional iso-surface contours of the occupied MOs for UO$_2$Cl$_4$$^{2-}$ from DFT calculations are presented in Fig. 3.

The calculated VDEs from all the valence MOs using the CASCF/CASSCF(CCSD(T)/SO) and CASSCF/CR-EOM-CCSD(T)/SO methods are given in Table IV. The simulated PES spectra of UO$_2$Cl$_4$$^{2-}$ using these calculated VDEs are shown in Fig. 4, where they are compared with the experimental spectrum at 157 nm.

### Table II. Optimized geometrical parameters of UO$_2$Cl$_4$$^{2-}$ and UO$_2$Cl$_4$$^{-}$ at the scalar relativistic level.

<table>
<thead>
<tr>
<th>Sym</th>
<th>GS</th>
<th>U–O (Å)</th>
<th>U–Cl (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT/PBE$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO$_2$Cl$_4$$^{2-}$</td>
<td>Da$_n$</td>
<td>1$\alpha_{1g}$</td>
<td>1.807</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DFT/B3LYP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CCSD(T)</td>
</tr>
<tr>
<td></td>
<td>UO$_2$Cl$_4$$^{-}$</td>
<td>Da$_n$</td>
<td>2$\alpha_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DFT/B3LYP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CCSD(T)</td>
</tr>
</tbody>
</table>

$^a$DFT/PBE method erroneously gives a 1$\alpha_{1g}$ state as the ground state (GS) of UO$_2$Cl$_4$$^{-}$, lower than the 1$\alpha_{2g}$ state by 0.12 eV, which is within the error of the DFT method used. The two states correspond to one-electron detachment from the 2$\alpha_{1u}$ and 1$\alpha_{2u}$ orbitals of UO$_2$Cl$_4$$^{2-}$, respectively. See Figs. 2 and 3.

### Table III. Calculated VDEs and the corresponding spinors of UO$_2$Cl$_4$$^{2-}$ from the SO-DFT/PBE level.

<table>
<thead>
<tr>
<th>VDE#</th>
<th>VDE (eV)</th>
<th>Spinor</th>
<th>Main component of SR MOs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.62$^a$</td>
<td>5$e_{12u}$</td>
<td>2$\alpha_{2u}$ Cl 3$p$</td>
</tr>
<tr>
<td>2</td>
<td>2.68</td>
<td>5$e_{12g}$</td>
<td>1$\alpha_{2g}$ Cl 3$p$</td>
</tr>
<tr>
<td>3</td>
<td>2.79</td>
<td>4$e_{32g}$</td>
<td>2$e_g$ Cl 3$p$</td>
</tr>
<tr>
<td>4</td>
<td>2.80</td>
<td>4$e_{12g}$</td>
<td>2$e_g$ Cl 3$p$</td>
</tr>
<tr>
<td>5</td>
<td>3.03</td>
<td>4$e_{12g}$</td>
<td>1$\beta_{2g}$ Cl 3$p$</td>
</tr>
<tr>
<td>6</td>
<td>3.13</td>
<td>3$e_{12u}$</td>
<td>2$e_u$ Cl 3$p$</td>
</tr>
<tr>
<td>7</td>
<td>3.14</td>
<td>4$e_{12g}$</td>
<td>3$e_{12g}$ Cl 3$p$</td>
</tr>
<tr>
<td>8</td>
<td>3.16</td>
<td>2$e_{12g}$</td>
<td>3$e_{12g}$ Cl 3$p$</td>
</tr>
<tr>
<td>9</td>
<td>3.36</td>
<td>3$e_{12u}$</td>
<td>2$e_u$ Cl 3$p$</td>
</tr>
<tr>
<td>10</td>
<td>3.67</td>
<td>3$e_{12u}$</td>
<td>1$\beta_{2g}$ Cl 3$p$</td>
</tr>
<tr>
<td>11</td>
<td>3.87</td>
<td>2$e_{12g}$</td>
<td>1$\alpha_{2u}$ U–O $\sigma_u$</td>
</tr>
<tr>
<td>12</td>
<td>3.99</td>
<td>3$e_{12g}$</td>
<td>2$\alpha_{1g}$ Cl 3$p$</td>
</tr>
<tr>
<td>13</td>
<td>4.14</td>
<td>2$e_{12g}$</td>
<td>1$\beta_{1g}$ Cl 3$p$</td>
</tr>
<tr>
<td>14</td>
<td>4.46</td>
<td>1$e_{12u}$</td>
<td>1$e_u$ U–O $\pi_o$</td>
</tr>
<tr>
<td>15</td>
<td>4.60</td>
<td>1$e_{12g}$</td>
<td>1$e_u$ U–O $\pi_o$</td>
</tr>
<tr>
<td>16</td>
<td>5.07</td>
<td>1$e_{12g}$</td>
<td>1$e_u$ U–O $\pi_f$</td>
</tr>
<tr>
<td>17</td>
<td>5.10</td>
<td>2$e_{12g}$</td>
<td>1$e_u$ U–O $\pi_f$</td>
</tr>
<tr>
<td>18</td>
<td>5.23</td>
<td>1$e_{12g}$</td>
<td>1$e_u$ U–O $\pi_f$</td>
</tr>
</tbody>
</table>

$^a$The VDE$_1$ calculated at SO-DFT/PBE level is 1.26 eV, which is underestimated relative to the experimental value. All VDEs listed are shifted by 1.36 eV to facilitate comparison with the experiment.
The contour diagrams of the occupied valence orbitals of UO$_2$Cl$_4^{2-}$ at the DFT/PBE level. The $2a_{2u}$ and $1a_{2g}$ orbitals are close in energy and compete for the HOMO.

$2a_{2u}$ orbital is nearly degenerate with the nonbonding $1a_{2g}$ orbital composed of pure Cl $3p$. Even with the inclusion of additional SO relativistic effects in the DFT calculations, the first two highest occupied MOs of UO$_2$Cl$_4^{2-}$, $2a_{2u}$ and $1a_{2g}$, remain close in energy (Fig. 2). In addition, the UO$_2$$^{2+}$ $\sigma_g$ orbital has a $\sigma$ bonding interaction with Cl $3p_{x,y}$ in the $1a_{1g}$ orbital, where the U $6d_\sigma$ has a small net overlap with the Cl $3p_{x,y}$ in the equatorial plane. The U $7s$ orbital contributes to the weak $\sigma$ bonding in the $2a_{1g}$ orbital with less than 2% contribution. Finally, the non-bonding U $5p_{\sigma_u}$ orbital has a very small overlap with the Cl $3p_{x,y}$ in the $3e_u$ orbital.

**B. Comparison with experiment**

Upon removal of one valence electron, theoretical calculations at the DFT/B3LYP and CCSD(T) levels give the ground state of UO$_2$Cl$_4$ as $2A_2g$ (Table II). This corresponds to electron detachment from the nonbonding $1a_{2g}$ orbital of pure Cl $3p$ character. This explains why all the U–O and U–Cl bond lengths do not change significantly between the ground states of the dianion and monoanion (Table II). The slightly shorter bond lengths in the UO$_2$Cl$_4$ monoanion are mainly due to the reduced intramolecular Coulomb repulsion.

Table IV. Calculated VDEs and the corresponding MOs of UO$_2$Cl$_4^{2-}$ at the CASSCF/CCSD(T)/SO and CASSCF/CR-EOM-CCSD(T)/SO levels.

<table>
<thead>
<tr>
<th>VDE#</th>
<th>VDE (eV)</th>
<th>MOs (SR)</th>
<th>VDE (eV)</th>
<th>MOs (SR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.61</td>
<td>$1a_{2g}$</td>
<td>2.61</td>
<td>$1a_{2g}$</td>
</tr>
<tr>
<td>2</td>
<td>2.85</td>
<td>$2a_{2u}$</td>
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<td>$2a_{2u}$</td>
</tr>
<tr>
<td>3</td>
<td>2.89</td>
<td>$2e_u$</td>
<td>2.66</td>
<td>$3e_u$</td>
</tr>
<tr>
<td>4</td>
<td>2.89</td>
<td>$2e_u$</td>
<td>2.68</td>
<td>$2e_u$</td>
</tr>
<tr>
<td>5</td>
<td>2.93</td>
<td>$3e_u$</td>
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<td>$2e_u$</td>
</tr>
<tr>
<td>6</td>
<td>3.09</td>
<td>$3e_u$</td>
<td>2.77</td>
<td>$3e_u$</td>
</tr>
<tr>
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The observed ADE of 2.40 eV indicates that $\text{UO}_2\text{Cl}_4^{2-}$ is a highly stable dianion in the gas phase. As seen in Table I, DFT calculations with or without SO effects significantly underestimate the electronic stability of the $\text{UO}_2\text{Cl}_4^{2-}$ dianion by $\sim$0.6 eV. The SR-CCSD(T) calculation yields a better ADE (2.58 eV) and an excellent VDE (2.61 eV) for $\text{UO}_2\text{Cl}_4^{2-}$, compared to the experimental values of 2.40 and 2.62 eV, respectively. The difference between the CCSD(T) and experimental ADE is likely due to high-order electron correlation and truncation errors of the atomic basis sets used.

The calculated VDEs at the CASSCF/CCSD(T)/SO and CASSCF/CR-EOM-CCSD(T)/SO levels (Table IV) are fitted with Gaussians to yield the simulated PES spectra in Fig. 4, where they are compared with the 157 nm experimental spectrum. The two levels of theory give similar spectral patterns with some slight energy differences in a few detachment channels. The simulated spectrum at the CASSCF/CCSD(T)/SO level is in excellent qualitative agreement with the experimental data, owing to the single-excitation character of the detachment transitions and the specifically optimized reference wavefunction in the CCSD(T) calculations. In addition to the detachment from the $1\alpha_{2g}$ orbital, which gives the ground state transition ($X$), electron detachments from the $2\alpha_{2u}, 2\epsilon_{u}, 2\epsilon_{g}, 3\epsilon_{u}$, and $1\beta_{2u}$ orbitals result in the congested bands A, B, C. Following a small energy gap, detachments from the $1\beta_{2g}, 2\alpha_{1g}, 1\alpha_{2u}$, and $1\beta_{1g}$ orbitals give rise to bands D and E. All these orbitals are Cl based and are expected to have higher relative detachment cross sections. Even the primarily U–O $1\alpha_{2g}$ orbital in this group contains significant contributions from Cl $p_x$. Detachments from the primarily $\text{UO}_2^{2+}$-based $1\epsilon_{u}$ orbitals are expected to have lower relative cross sections and should correspond to the weak signals around 5 eV (Fig. 4(c)). The VDEs for detachments from the $\text{UO}_2^{2+}$, $1\alpha_{1g}$, and $1\epsilon_{g}$ orbitals are too high and are cut off by the RCB in the 157 nm spectrum. The overall agreement between the CASSCF/CCSD(T)/SO calculations and the PES data for $\text{UO}_2\text{Cl}_4^{2-}$ seems to be better than in the case of $\text{UO}_2\text{F}_4^{2-}$ at the same level of theory.\textsuperscript{17}

VI. DISCUSSION

A. The electronic structure of $\text{UO}_2\text{Cl}_4^{2-}$ and intramolecular electrostatic interactions: $\text{UO}_2\text{Cl}_4^{2-}$ vs. $\text{UO}_2\text{F}_4^{2-}$

The measured ADE of 2.40 eV for $\text{UO}_2\text{Cl}_4^{2-}$ is 1.3 eV higher than that of $\text{UO}_2\text{F}_4^{2-}$.\textsuperscript{17} This large difference in electronic stability between the two dianions reflects the difference in their electronic structures, which are strongly influenced by the intramolecular electrostatic interactions. Both uranyl halide dianions have the same $D_{4h}$ symmetry and similar valence MOs, but the ordering of their valence MOs is very different: the frontier MOs of $\text{UO}_2\text{F}_4^{2-}$ are dominated by the U–O bonding orbitals of the $\text{UO}_2^{2+}$ moiety,\textsuperscript{17} while those of $\text{UO}_2\text{Cl}_4^{2-}$ are mainly from the Cl $3p$ orbitals (Figs. 2 and 3). Specifically, the ground state PES band of $\text{UO}_2\text{Cl}_4^{2-}$ arises from electron detachment from a nonbonding Cl $3p$ orbital ($1\alpha_{2g}$, Fig. 3), while the HOMO of $\text{UO}_2\text{F}_4^{2-}$ comes from the $\sigma_{\alpha}$ orbital of $\text{UO}_2^{2+}$. This difference in the ordering of valence MOs is due to the intramolecular electrostatic interactions and the strength of the U–ligand interactions in the two uranyl tetrahalide dianions. Because the U–F bond length (2.23 Å) (Ref. 17) in $\text{UO}_2\text{F}_4^{2-}$ are much shorter than the U–Cl bond lengths (2.73 Å, Table I) in $\text{UO}_2\text{Cl}_4^{2-}$, the intramolecular Coulomb repulsion should be stronger in $\text{UO}_2\text{F}_4^{2-}$. This is reflected in their respective RCBs: the observed RCB in $\text{UO}_2\text{F}_4^{2-}$ was estimated to be $\sim$2.0 eV,\textsuperscript{17} while that in $\text{UO}_2\text{Cl}_4^{2-}$ is estimated to be $\sim$1.7 eV in the current study. The high ADE of $\text{UO}_2\text{Cl}_4^{2-}$ is attributed to the high electron binding energy of the Cl$^-$ ligands and the smaller intramolecular Coulomb repulsion. On the other hand, the low ADE of $\text{UO}_2\text{F}_4^{2-}$ is presumably due to its smaller size and the increased intramolecular Coulomb repulsion in the dianion, as well as the strong U–F interactions (vide infra).

B. The U–Cl bond length changes between $\text{UO}_2\text{Cl}_4^{2-}$ and $\text{UO}_2\text{F}_4^{2-}$: Comparison with $\text{UO}_2\text{F}_4^{2-}/1\text{F}^-$

As shown in Table II, both DFT and CCSD(T) calculations show that the U–Cl bond lengths in $\text{UO}_2\text{Cl}_4^{2-}$ are about 2.73 Å, while the U–O bond lengths depend upon the computational methods. Because DFT calculations tend to overestimate the intramolecular Coulomb repulsion,\textsuperscript{17} the U–O bond length of 1.766 Å by CCSD(T) is more reliable. It is noteworthy that both the DFT and CCSD(T) calculations show that the geometrical changes upon electron detachment are rather different for $\text{UO}_2\text{F}_4^{2-}$ and $\text{UO}_2\text{Cl}_4^{2-}$. From the dianion to monooanion, the U–F bond length is decreased significantly by 0.123 Å,\textsuperscript{17} while the U–Cl bond length is only shortened by about 0.045 Å (Table II). This large difference in the U–F and U–Cl bonds upon electron detachment from the two uranyl tetrahalide complexes can be understood from both the intramolecular Coulomb repulsion and the nature of the HOMO, from which the electron is removed. The ground state of $\text{UO}_2\text{F}_4^{-}$ corresponds to the removal of an electron from the $2\alpha_{2u}$ orbital of $\text{UO}_2\text{F}_4^{2-}$, which represents anti-bonding interactions between the F 2p and the UO$^{2+}$ $\sigma_{\alpha}$ orbital. Hence, in addition to the reduced intramolecular Coulomb repulsion, the U–F bond is significantly enhanced by gaining more equatorial bonding character. In contrast, the ground state of the monooanion $\text{UO}_2\text{Cl}_4^{-}$ corresponds to the removal of an electron from the nonbonding $2\alpha_{2g}$ orbital, which is of pure Cl 3p character (Fig. 3). Hence, it is expected that the U–Cl bond lengths should not be affected significantly in the monooanion.

C. Influence of U–O bonding by equatorial ligands: Cl$^-$ vs. F$^-$

Upon electron detachment, the axial U–O bonding in $\text{UO}_2\text{Cl}_4^{2-}$ is not significantly changed (Table I), and the same was observed in $\text{UO}_2\text{F}_4^{2-}$.\textsuperscript{17} The U–O bond length in $\text{UO}_2\text{F}_4^{2-}$ is slightly longer in the gas phase (1.83 Å) (Ref. 17) than that in solution (1.800 Å) (Ref. 19 and 64) or in solid (1.780 Å).\textsuperscript{55} For $\text{UO}_2\text{Cl}_4^{2-}$, the calculated U–O bond length is 1.76 Å (Table I), which is close to the result of 1.774 Å from the crystal structure of Cs$\text{UO}_2\text{Cl}_4$.\textsuperscript{21} These observations can be understood by the different equatorial ligand bonding in $\text{UO}_2\text{F}_4^{2-}$ and $\text{UO}_2\text{Cl}_4^{2-}$. In the previous
study of UO₂F₄²⁻,¹⁷ we found that its frontier MOs show π-interactions between the U 5fπ orbital and the equatorial ligands. Denning suggested that this π-interaction renders the U–F bonds in UO₂F₄²⁻ some multiple bonding characters.¹⁷ This observation is consistent with the U–F bonding in UF₆ (1.996 Å), which is also suggested to possess multiple bonding characters.⁶⁶,⁶⁷ At this short equatorial distance, the F 2p orbitals can have better interactions with the U–O orbitals, as reflected in the frontier MOs of UO₂F₄²⁻. However, the strong electrostatic repulsion from the F⁻ ligands can destabilize the U–O bonding. In the condensed phase, the solvent or counter cations alleviate the intramolecular Coulomb repulsion effects on the U–O bonds within UO₂F₄²⁻. In the gas phase, the intramolecular Coulomb repulsion can fully exert its influence on the U–O bonds. For the case of UO₂Cl₄²⁻, the third-row non-metal elements in the periodic table cannot efficiently form multiple bonds with U because of the Pauli repulsion from the inner shell orbitals. Hence, at the equatorial distance of 2.73 Å, there is a smaller net overlap between Cl 3p and the MOs of the UO₂²⁺ moiety. Consequently, the U–O bonds are not affected significantly from the intramolecular Coulomb repulsion in the gas phase.

VII. CONCLUSIONS

We report the observation and characterization of the doubly charged UO₂Cl₄²⁻ anion in the gas phase. Photoelectron spectroscopy and ab initio CCSD(T) theoretical calculations are used to probe the stability of UO₂Cl₄²⁻ and its electronic structure. The UO₂Cl₄²⁻ dianion is observed to have high electronic stability with an adiabic electron detachment energy of 2.40 eV. Theoretical calculations show that the frontier MOs of UO₂Cl₄²⁻ are mainly composed of Cl 3p orbitals. The simulated spectrum at the CCSD(T) level is found to be in good agreement with the experimental data. The comparison of UO₂Cl₄²⁻ with UO₂F₄²⁻ reveals interesting differences due to their different electrostatic interactions between the uranyl and the halide ligands. The much higher electron detachment energy of UO₂Cl₄²⁻ relative to UO₂F₄²⁻ is largely a result of its larger size and reduced intramolecular Coulomb repulsion, as well as the stronger uranyl-F interaction in the latter. The gas-phase PES results of uranyl complexes provide ideal experimental data for benchmarking theoretical methodologies of relativistic quantum chemistry involving strong electron correlations.

ACKNOWLEDGMENTS

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³¹ V. V. Zhurov, E. A. Zhurova, and A. A. Pinkerton, Inorg. Chem. 50, 6530 (2011).
53See http://www.theochem.uni-stuttgart.de/pseudopotentials for the pseudopotential and basis sets of uranium.
61The UO2Cl3− anion can also be produced directly by ESI. We measured its photoelectron spectrum at 157 nm and found its ADE to be more than 6.5 eV.