

Experimental Observation of a Very High Second Electron Affinity for ZrF_6 from Photodetachment of Gaseous ZrF_6^{2-} Doubly Charged Anions

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We report a photodetachment photoelectron spectroscopy study of a doubly charged anion, ZrF_6^{2-} , in the gas phase at two photon energies: 6.424 (193 nm) and 7.865 (157 nm) eV. The adiabatic detachment energy, i.e., the second electron affinity of ZrF_6 , was measured to be extremely high, 2.9(0.2) eV. The vertical detachment energy (VDE) was measured to be 3.4(0.1) eV. Two excited states were also observed for the ZrF_6^- singly charged anion with VDEs at 4.0 and 4.6 eV, respectively. The repulsive Coulomb barrier, and hence the intramolecular Coulomb repulsion in ZrF_6^{2-} , was estimated from the photon-energy-dependent spectra to be ~ 2.4 eV. The ZrF_6^{2-} dianion was observed to be metastable with a half-life of ~ 4 s under our experimental conditions, confirming theoretical predictions that ZrF_6^{2-} is thermodynamically unstable against loss of an F^- , despite its extremely high electronic stability. We also performed experiment for the singly charged ZrF_5^- , but could not observe photodetachment even at 157 nm, the highest photon energy available to us. Thus, we estimated that the electron affinity of ZrF_5 is larger than 7.8 eV, the highest electron affinity yet confirmed experimentally.

Introduction

Electron affinity (EA) is an important molecular property relevant to the electronic structure, chemical reactivity and stability of a molecule. Most neutral molecules and all radicals can bind an extra electron to form stable molecular anions, which have been extensively studied over the past three decades. Molecules with high EAs are strong oxidizing agents and form extremely stable anions.^{1–6} Since the recognition of the high oxidative power of PtF_6 , which can oxidize O_2 or Xe to form highly unusual ionic compounds of the form $\text{M}^+[\text{PtF}_6^-]$,⁷ there has been a significant interest in searching for molecules with extremely high EAs. Since halogen atoms are the most electronegative elements, research efforts have generally been focused on halogen compounds, especially fluorine complexes.^{8–11} The term “superhalogen” was coined to refer to molecules that have higher EAs than those of the halogen atoms,^{12,13} which have the highest EAs among all the atomic elements. Determination of high EAs was and still is challenging experimentally. Thus, there have been considerable theoretical efforts trying to understand and design molecules with extremely high EAs.^{14–16} EA values as high as 10–12 eV were predicted theoretically,^{17–19} though there have been no direct experimental confirmations of such high EAs. With such high first EAs, the possibility of such a molecule to bind a second electron was considered. Several molecules with positive second EAs were predicted.^{18–20} In particular, Gutsev and Boldyrev proposed that the highest possible second and higher values of EA should be among polynuclear species of the types $\text{M}_n\text{X}_{nk+2}$, $\text{M}_n\text{X}_{nk+3}$, etc., where $n > 1$, k is the maximal formal valency of M, and X is a monovalent electronegative ligand.¹⁸ Indeed, more recently, Cederbaum and co-workers have predicted very high second EAs for a series of alkali and alkali-earth halide systems with these stoichiometries.^{19,21,22}

For a molecule to have positive second or higher EAs, the corresponding dianion or multiply charged anion has to be electronically stable in the gas phase. Recently, many dianions have been theoretically predicted to be electronically stable,^{18–29} primarily by the groups of Cederbaum and Simons. Cederbaum and co-workers have proposed a so-called “construction principle” to design electronically stable multiply charged anions based on the alkali and alkali-earth halide systems.²² Boldyrev and Simons in fact have predicted that TeF_8^{2-} would have the largest electron detachment energy (5 eV) among the MX_n^{2-} type of dianions.²⁴ Simons et al. have also investigated a number of multiply charged anions involving heavy early transition metal-fluorine complexes.^{26–28} Of particular interest to our current work is the ZrF_6^{2-} dianion,^{26,27} which was predicted to possess a very high electron detachment energy, very close to that of TeF_8^{2-} .

However, very little is known experimentally about the second or higher order EAs for any molecular species until very recently. Experimental determination of second or higher order EAs is an extremely difficult task. Although a number of multiply charged anions have been observed in the gas phase,^{6,19,30–33} no measurements of their electron binding energies have been done. To determine the second or higher order EAs, one not only has to produce multiply charged anions in the gas phase with reasonable intensity, but also has to perform photodetachment photoelectron spectroscopy (PES) experiments. We have recently developed a PES apparatus with an electro-spray ion source, specifically designed to investigate gaseous multiply charged anions.³⁴ As we have shown,³⁵ PES is a powerful experimental technique that is uniquely suitable to measure second or higher order EAs, because of the universal existence of a repulsive Coulomb barrier (RCB) against electron attachment to or detachment from a multiply charged anion. We have measured the PES spectra of several multiply charged

anions,^{36–41} ranging from organic species to inorganic species, among which the highest second EA was found for S_2O_8 (1.7 ± 0.2 eV).³⁷ In fact, we have observed negative electron binding energies in several multiply charged anions.^{40,41}

In the current work, we focus our attention on those hexafluoride complexes that were theoretically investigated by Simons et al. and were predicted to have very high second EAs.^{26–28} However, all of those multiply charged anions were predicted to be unstable thermodynamically against the loss of an F^- . Thus, it was not clear if any of those multiply charged species would have long enough lifetimes to be observed in our experiment. In this article, we report our successful observation of ZrF_6^{2-} . We present its photoelectron spectra, measured at 193 and 157 nm, and compare our experimental data to the theoretical calculations by Simons et al. We measured a vertical detachment energy of 3.4 eV, confirming the high detachment energy of ZrF_6^{2-} , predicted by theory, but also suggesting that the theory has substantially overestimated the detachment energy. We were also able to estimate the lifetime of ZrF_6^{2-} using our ion trap and obtained a decay half-life of about 4 s, confirming its thermodynamic metastability, as predicted theoretically.

Experimental Section

The experiment was performed with our magnetic-bottle time-of-flight (TOF) photoelectron apparatus equipped with an electrospray ion source and an ion trap TOF mass spectrometer. Details of the experiment have been published elsewhere³⁴ and only a brief description is given here. A 10^{-3} M Na_2ZrF_6 solution in a H_2O/CH_3OH (1/10 volume ratio) mixed solvent was used in the electrospray. Liquid droplets from the electrospray were fed into a desolvation capillary heated to 50 °C. The anionic species emerging from the desolvation capillary were guided by a radio frequency quadrupole ion-guide into a three-dimensional quadrupole ion trap. The ions were accumulated for 0.1 s in the trap before being pulsed out into the extraction zone of the TOF mass spectrometer for mass and charge analyses. The main anion signal was ZrF_6^{2-} with a small amount of ZrF_5^- also present. The ZrF_6^{2-} dianions, clearly identified by its mass/charge ratio and characteristic isotope pattern, was selected by a mass-gate and decelerated before being detached by a laser beam. Photoelectrons were collected with nearly 100% efficiency in a 4-meter long magnetic-bottle TOF electron analyzer. Photoelectron TOF spectra were collected and then converted to kinetic energy spectra, calibrated by the known spectra of I^- and O^- . The electron binding energy (BE) spectra presented were obtained by subtracting the kinetic energy spectra from the detachment photon energies. Both an excimer laser (193 and 157 nm) and a Nd:YAG laser (266 nm) were used for photodetachment. The experiments were done at 20 Hz with the ion beam off at alternating laser shots for background subtraction. The electron kinetic energy resolution was $\Delta E/E \sim 2\%$, i.e., 20 meV for 1 eV electrons. The 157 nm laser (F_2 excimer) newly equipped in our laboratory has significantly enhanced our capability to investigate anions with very high electron binding energies.

Results and Discussion

Figure 1 shows the PES spectra of ZrF_6^{2-} at (a) 193 nm (6.424 eV) and (b) 157 nm (7.865 eV). Two features (X and A) were observed in the 193 nm spectrum with vertical detachment energies (VDE's) at 3.4 and 4.0 eV, respectively. A third feature (B) was revealed at 157 nm at a VDE of 4.6 eV. The A feature is much stronger than the X and B features.

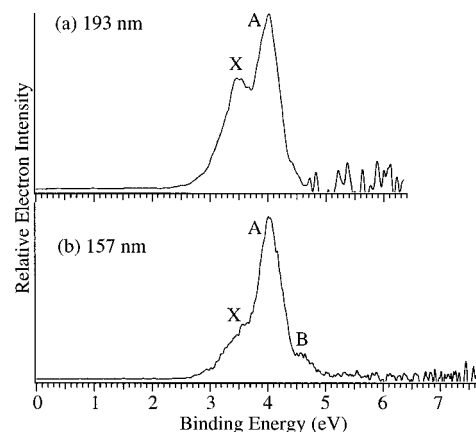


Figure 1. Photoelectron spectra of ZrF_6^{2-} at (a) 193 nm (6.424 eV) and (b) 157 nm (7.865 eV).

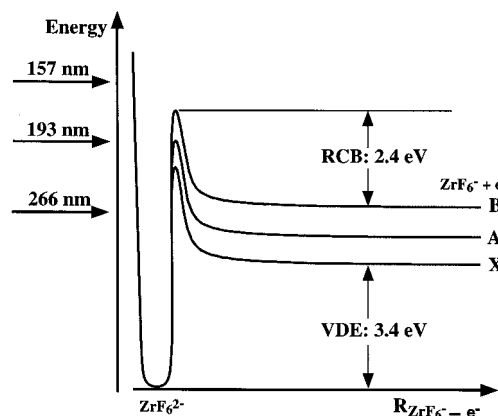


Figure 2. Schematics of the potential energy curves showing the repulsive Coulomb barriers (RCB) of ZrF_6^{2-} with respect to the three different final states (X, A, and B) of the singly charged anion ZrF_6^- . The vertical binding energy and the estimated RCB in eV are shown. The relative positions of the photon energies used are also indicated.

Since the VDE's of all the PES features are lower than the 266 nm (4.661 eV) photon energy, we also performed photodetachment experiment at 266 nm. But no measurable photoelectron signals were detected.

The observed photoelectron features represent detachment transitions from the ground state of the dianion to the ground and excited states of the singly charged anion (ZrF_6^-). The adiabatic detachment energy (ADE) of the X feature would be equivalent to the EA of ZrF_6^- or the second EA of the ZrF_6 neutral. The substantial width of the X feature, indicative of significant geometry changes between the dianion and the monoanion ground state, makes it difficult to obtain the ADE. We estimated an ADE of 2.9 (0.2) eV, based on the onset of the detachment feature. This value should be viewed probably as an upper limit for the true ADE.

The photon energy dependence of the detachment features, due to the repulsive Coulomb barrier, clearly indicates the doubly charged nature of the anions. Such photon-energy dependence is a universal characteristic of photodetachment of multiply charged anions and allows us to estimate the magnitude of the RCB.^{35–41} Figure 2 shows schematically the potential energy curves and the RCB's for photodetachment of ZrF_6^{2-} to the three final states (X, A, and B) of the singly charged anion ZrF_6^- . The appearance of the B feature at 157 nm and its disappearance at 193 nm suggest that the RCB should be smaller than ~ 3.2 eV (the 157 nm photon energy minus the

TABLE 1: Measured Vertical Electron Detachment Energies (in eV) of ZrF_6^{2-} , Compared to the Calculated Ones Using Different Methods from Reference 27

final states	OVGF	MP2	B3LYP	exptl
$X(^2T_{1g})$	5.11	3.58	2.69	3.4(0.1)
$A(^2T_{1u})$	5.39			4.0(0.1)
$B(^2T_{2u})$	5.51			4.6(0.1)

VDE of the B feature) and larger than 1.8 eV (the 193 nm photon energy minus the VDE of the B feature). The strong signal of the A feature in the 193 nm spectrum suggests that the RCB should be smaller than ~ 2.4 eV (193 nm photon energy minus the VDE of the A feature). Hence the RCB should be: $1.8 \text{ eV} < \text{RCB} < 2.4 \text{ eV}$. In fact, the photoelectron signal of the A feature relative to that of the X feature at 193 nm is significantly reduced, which may suggest that the 193 nm photon energy is near the barrier top of the A state. Thus, we estimated that the RCB should be around 2.4 eV. With such a high RCB, it is easy to understand why there were no photoelectron signals observed at 266 nm because it is way below the barrier of even the X state, as indicated in Figure 2.

In Table 1, we compare the measured VDE's of ZrF_6^{2-} to the calculated values by Simons et al. using different methods.²⁷ Clearly, the MP2 value has the best agreement with the experiment. The B3LYP value underestimated the VDE by almost 1 eV. More surprisingly, the OVGF value, which was used as indication of the high second EA for ZrF_6 , overestimated the VDE by 1.7 eV. This overestimation by OVGF is consistent with the theoretical result on F^- .²⁷

ZrF_6^{2-} is an octahedral and closed-shell dianion,^{26,27} with a ground-state configuration of $\dots(1t_{2u})^6(7t_{1u})^6(1t_{1g})^6(3t_{2g})^0(5e_g)^0$. The Zr atom has a formal oxidation state of IV, leaving the $3t_{2g}$ and $5e_g$ orbitals (primarily of 4d character) empty. The three detachment features should correspond to removal of an electron from the three highest occupied molecular orbitals (HOMO), among which the $1t_{1g}$ (HOMO) and $1t_{2u}$ (HOMO-2) are nonbonding MOs, purely of ligand p characters. The $7t_{1u}$ (HOMO-1) is also a ligand-dominated MO, but with significant contributions from the center metal d orbitals. The high VDE of the ZrF_6^{2-} dianion is due to the fact that the excess electron is delocalized over the six highly electronegative and symmetry-equivalent ligands. This is quite different from the hexahalo-genometalate doubly charged anions of the late 5d metals that we investigated recently.³⁹ In the latter, the HOMO is composed of 5d orbitals and they all have relatively low second EAs. The calculated VDEs for the three detachment channels using OVGF are given in Table 1 and compared to the experimental measurements. The relative intensities of the X, A, and B features observed in the PES spectra (Figure 1) support these assignments. Since the X and B features are due to detaching an electron from nonbonding F-based MOs, they are expected to have similar and weak intensities. The stronger intensity of the A feature is a result of the mixing of metal d orbitals in the $7t_{1u}$ MO. All the three occupied MOs of ZrF_6^{2-} are degenerate, suggesting that there would be Jahn–Teller distortions upon detachment of an electron from these MOs, consistent with the relatively broad widths of the detachment features.

The 3.4 eV VDE of ZrF_6^{2-} and the 2.9 eV second EA for ZrF_6 are the highest that we have observed so far, although even higher VDEs have been predicted theoretically in a number of doubly charged anions. The first EA of ZrF_6 was predicated to be 7.1 eV, which is lower than the 157 nm photon energy. Thus, it was possible to observe detachment features from the ZrF_6^- product anion in the 157 nm PES spectrum of ZrF_6^{2-} (Figure 1b) through absorption of a second photon. However, the 157

nm spectrum showed no detectable features at the higher binding energy side, suggesting that the first EA of ZrF_6 is probably even higher than the theoretical prediction.

We further performed photodetachment experiments on ZrF_5^- , which was also produced from our electrospray source. No detectable photoelectron signals were observed, suggesting that ZrF_5 has an EA value higher than the 157 nm photon energy. Taking into account of the experimental difficulty in observing electrons with very low kinetic energies, we estimated that the EA of ZrF_5 should be >7.8 eV. A previous theoretical calculation yielded a VDE of 11.4 eV for ZrF_5^- at the Koopmans' theorem level.²⁶ At the same level of theory, the VDE of ZrF_6^{2-} was estimated to be 6.31 eV, which was 2.91 eV higher than our current experimental measurement. Taking into account of this overestimation at the Koopmans' theorem level, we obtained a VDE of ~ 8.5 eV for ZrF_5^- , consistent with our experimental observation. Previously, the highest EA species was thought to be AuF_6 by Bartlett, who estimated an EA of >7.8 eV for this species.⁷ Sidorov subsequently estimated the EA of AuF_6 to be ~ 7.5 eV.¹¹ But there have been no direct experimental measurements of the high EA of AuF_6 , although indirect support for the high EA of AuF_6 was reported.^{8b} The highest EA that has been directly measured previously appeared to be for PtF_6 , for which an EA of 7.00 (0.35) eV was reported by Sidorov.^{10,11} Therefore, despite the fact that molecules with even higher EAs have been predicted, the extremely high EA of ZrF_5 seems to be the highest EA yet to be confirmed experimentally. ZrF_5^- belongs to a class of superhalogens^{12,18} and its high EA is not surprising. Recently, we have obtained the PES spectrum of YCl_4^- and measured a very high EA of 7.05 eV for YCl_4 .⁴² Compared to YCl_4^- in which Y has +3 oxidation state, ZrCl_5^- , in which Zr has +4 oxidation state, is expected to have a higher electron binding energy. Indeed, we failed to measure the PES spectrum of ZrCl_5^- at 157 nm, despite very intense mass signals and the high photon energy. In general the F-containing complexes all have higher EAs than the corresponding Cl-containing species. Therefore, the extremely high EA that we confirmed here for ZrF_5 is expected and reasonable.

Finally, we comment on the thermodynamic stability of the ZrF_6^{2-} dianions. Theoretical calculations^{26,27} indicate that ZrF_6^{2-} is thermodynamically unstable with respect to unimolecular fragmentation: $\text{ZrF}_6^{2-} \rightarrow \text{ZrF}_5^- + \text{F}^-$, due to the strong Coulomb repulsion, which must be larger than the Zr–F bond strength. Thus, ZrF_6^{2-} is expected to be metastable with a finite lifetime. We carried out lifetime measurements using our ion trap by monitoring the ion intensity as a function of trapping time. The half-lives of metastable species can be estimated using this technique.⁴¹ Indeed, we found that ZrF_6^{2-} only has a half-life of ~ 4 s, consistent with its metastability, as predicted theoretically. We also confirmed the above fragmentation channel by observing simultaneous enhancement of the ZrF_5^- signals. Simons et al.²⁶ estimated a 56.6 kJ/mol (0.6 eV) exothermicity for the loss of an F^- . Using our estimated intramolecular Coulomb repulsion energy (the estimated RCB) of ~ 2.4 eV, we obtained an estimate of the Zr–F bond energy in ZrF_6^{2-} to be ~ 1.8 eV (~ 41 kcal/mol).

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