

## Au as a Surrogate for F: The Case of $\text{UAu}_6$ vs $\text{UF}_6$

Rachel M. Harris, Zhaoguo Zhu, Deepika, Burak A. Tufekci, Kirk Peterson,\* Puru Jena,\* and Kit H. Bowen\*



Cite This: *J. Am. Chem. Soc.* 2022, 144, 19685–19688



Read Online

ACCESS |



Metrics & More



Article Recommendations



Supporting Information

**ABSTRACT:** Here, anion photoelectron spectroscopy and first-principles quantum chemistry are used to demonstrate to what degree Au can act as a surrogate for F in  $\text{UF}_6$  and its anion. Unlike  $\text{UF}_6$ ,  $\text{UAu}_6$  exhibits strong ligand–ligand, i.e., Au–Au, interactions, resulting in three low-lying isomers, two of which are three-dimensional while the third isomer has a ring-like quasi two-dimensional structure. Additionally, all the  $\text{UAu}_6$  isomers have open-shell electrons, which in nearly all cases are localized on the central U atom. The adiabatic electron affinity and vertical detachment energy are measured to be  $3.05 \pm 0.05$  and  $3.28 \pm 0.05$  eV, respectively, and are in very good agreement with calculations.

Uranium hexafluoride ( $\text{UF}_6$ ) is the most important molecule in the nuclear industry, as it is used for enriching uranium to produce fuels for nuclear reactors and fissile material for nuclear weapons. Consequently, there has been a substantial interest in understanding the chemistry of  $\text{UF}_6$  and its derivatives. Nevertheless, a deeper understanding of the chemistry of uranium-containing molecules continues to be challenging due to their complicated electronic structures, multiple oxidation states, and strong relativistic and spin–orbit coupling effects. For example, while both  $\text{UCl}_6^-$  and  $\text{UF}_6^-$  have been studied by anion photoelectron spectroscopy and the adiabatic electron affinity (EA) of  $\text{UCl}_6$  has been measured to be 5.3 eV, the EA of  $\text{UF}_6^-$  has not, even though it is likely higher.<sup>1,2</sup>

Here, we adopt an alternative approach to better understand  $\text{UF}_6$  and  $\text{UF}_6^-$  by using Au as a surrogate for F. Note that the EA of the Au atom (2.32 eV) is the highest among all metals in the periodic table; it is also one of the few metals that forms ionic bonds with metal atoms, such as Cs and Th.<sup>3–6</sup> That Au may mimic F in  $\text{UF}_6$  is consistent with Hoffmann’s isolobal principle, which suggests that species with similar symmetry and frontier orbital energies have similar bonding and reactivity.<sup>7</sup> It was previously predicted by theory that Au could behave like a halogen when interacting with U in  $\text{UAu}_4$ .<sup>8,9</sup> Recent joint experimental–theory studies on various thorium–gold anions, as well as the  $\text{Au}_2\text{F}$  molecule, have shown that indeed Au can behave very similarly to F.<sup>10,11</sup> In a computational pilot study of the  $\text{UAuF}$  trimer, we also found that Au mimics the chemistry of F (Section S2, and Figure S2 of the Supporting Information, SI).

In the present work, a synergistic approach involving anion photoelectron spectroscopy (PES) experiments and first-principles theory based on both density functional theory (DFT) and coupled cluster calculations shows that while  $\text{UAu}_6^-$  possesses some of the properties of  $\text{UF}_6^-$ , it also exhibits unique properties of its own.

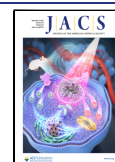
The photoelectron spectra of  $\text{UAu}_6^-$  measured with 3.49, 4.66, and 6.42 eV photons are displayed in Figure 1. The first

peak observed in the  $\text{UAu}_6^-$  spectrum has an onset around an electron binding energy (EBE) of 2.2 eV with a peak value at an EBE of 3.28 eV. In the 4.66 eV photon spectrum, this peak is seen to be split, with its higher EBE portion located at EBE = 3.43 eV. When there is sufficient Franck–Condon overlap between the ground state of the anion and the ground state of the neutral, and when vibrational hot bands are absent, the threshold EBE is the value of the adiabatic EA. Nevertheless, since vibrational temperatures for anions are difficult to estimate, and since some degree of vibrational excitation is not uncommon, the adiabatic EA value often lies between the threshold and the vertical detachment energy (VDE) value. As an approximation, we estimate the adiabatic EA as that corresponding to the EBE value at ~10% of the rising photoelectron intensity. Focusing primarily on the 3.49 eV photon spectrum, this yields an adiabatic EA value for  $\text{UAu}_6$  of  $3.05 \pm 0.05$  eV. The VDE is equal to the EBE value at the lowest EBE peak’s photoelectron intensity maximum and is found to be  $3.28 \pm 0.05$  eV for  $\text{UAu}_6^-$ .

Figure 2 presents the DFT optimized geometries of the nearly isoenergetic neutral and anionic  $\text{UAu}_6$  molecules. For isomer I, the six Au atoms are arranged in a ring with the U atom at its center but above its plane by 0.88 and 0.84 Å, respectively, for its neutral and anion geometries (Figure 2a). Isomer II (Figure 2b) has a three-dimensional geometry with four Au atoms forming a rectangular configuration, while the other two Au atoms are located on opposite sides of the U atom. Isomer III (Figure 2c) has a butterfly type geometry, where the U atom lies on a plane with four of the six Au atoms. The ring isomer of  $\text{UAu}_6^-$  (isomer I) is more symmetric than that of neutral  $\text{UAu}_6$ , with the U–Au bond length contracted

Received: August 3, 2022

Published: October 24, 2022



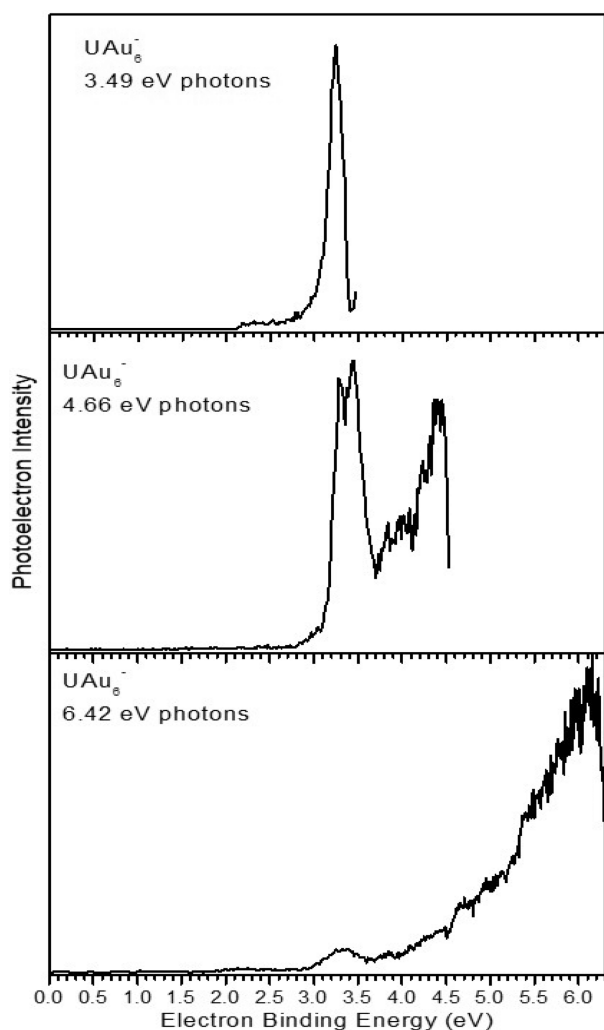


Figure 1. Photoelectron spectrum of  $\text{UAu}_6^-$  taken with 3.49, 4.66, and 6.42 eV photons.

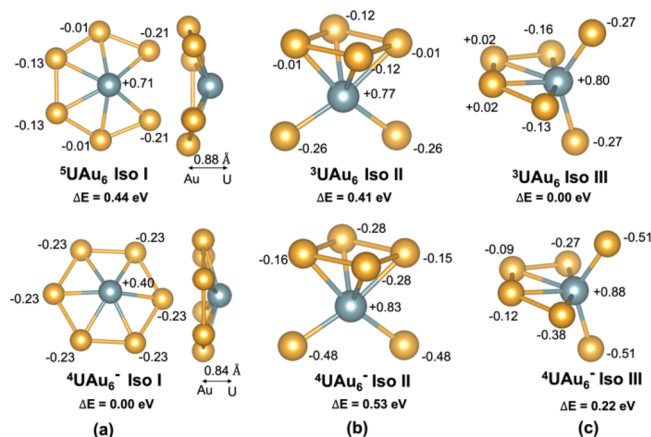


Figure 2. DFT optimized ground state geometries of the nearly isoenergetic isomers: (a) ring isomer (I), (b) distorted-octahedral isomer (II), and (c) butterfly isomer (III) of neutrals, i.e.,  $\text{UAu}_6$  (top row), and anions, i.e.,  $\text{UAu}_6^-$  (bottom row). Relative energies,  $\Delta E$ , are given at the CCSD(T) level of theory with NPA charges from the DFT density given next to the atoms. The superscript on the U atom represents the spin multiplicity of the molecule.

and Au–Au bond length expanded in the anion. At the CCSD(T) level of theory, using the DFT geometries, these three isomers differ in energy by at most 0.44 eV for the neutrals and 0.53 eV for the anions. The DFT relative energetics were smaller by about 0.2 eV. An octahedral structure for  $\text{UAu}_6$  (Figure S3), analogous to the equilibrium geometry of  $\text{UF}_6$ , was calculated to be unstable with respect to distortion to isomers II and III. The ground state of the anion is calculated by CCSD(T) to correspond to the ring type geometry (isomer I in Figure 2a) with isomer III lying 0.22 eV higher in energy. As shown in Table S3, before adding additional diffuse functions to the basis set on Au at the triple- $\zeta$  level, this separation was just 0.10 eV. For neutral  $\text{UAu}_6$ , isomer III is clearly the ground state. A natural population analysis (NPA) showed that in all the neutral and anionic  $\text{UAu}_6$  isomers, the U atom is positively charged. In neutral isomers I and II, all six Au atoms carry a negative charge (Figure 2), while in neutral isomer III four Au atoms are charged negatively and two are barely positive. This is consistent with the fact that the adiabatic EA of the U atom (0.31 eV) is significantly less than that of the Au atom, and thus in  $\text{UAu}_6$ , Au atoms behave like halogens. In the anion, the charge on the U atom is decreased by nearly 1/2 in the ring isomer (I), while it becomes slightly more positive in the other two isomers. In nearly all these six cases, the open-shell electrons reside on the U atom as 5f electrons, as indicated by their orbital character and the natural spin density. The one exception is the quintet state of the neutral ring isomer, where one unpaired electron is spread over the Au atoms.

Comparing the theoretical energetics with experiment, the calculated VDE and adiabatic EA of isomer I at both the DFT and CCSD(T) levels of theory agree well with the experimental values, cf., Table 1. The DFT values are about

Table 1. Experimental and CCSD(T) Adiabatic Electron Affinities<sup>a</sup> (EA) of  $\text{UAu}_6$  and Vertical Detachment Energies (VDE) of  $\text{UAu}_6^-$

species	EA (eV)		VDE (eV)	
	expt	theory	expt	theory
$\text{UAu}_6$	$3.05 \pm 0.05$		$3.28 \pm 0.05$	
isomer I		3.15 (2.99)		3.34 (3.18)
isomer II		2.59 (3.04)		3.12 (3.34)
isomer III		2.62 (3.07)		3.16 (3.40)

<sup>a</sup>The CCSD(T) values correspond to using a VTZ basis sets. See the text in the SI. DFT results are shown in parentheses.

0.1 eV below while the CCSD(T) values are about 0.1 eV above. Not surprisingly, the calculated adiabatic EA and VDE values of isomers II and III are also similar to the experimental values. In particular, the CCSD(T) result for the VDE of isomer III is about 0.15 eV lower than that of isomer I. As shown in Figure 2, these two isomers are nearly isoenergetic, and thus these two VDEs could clearly account for the doublet structure in the experimental spectrum shown in Figure 1. Isomer III could also be present in the spectrum, although to a lesser extent since this anion lies higher in energy by about 0.5 eV. A comparison of all the DFT and CCSD(T) calculations of this work can be found in Tables S1–S3.

Analogous to the bonding in  $\text{UF}_6$ , the bonding between U and Au in  $\text{UAu}_6$  is primarily ionic. However, there are significant differences in the electronic structures of  $\text{UF}_6$  and  $\text{UAu}_6$  (and their anions). While  $\text{UF}_6$  exhibits only two-center-

two-electron ( $2c-2e$ ) bonds,  $UAu_6$  exhibits  $3c-2e$  bonds (Figures S4–S6). In addition,  $UF_6$  has a closed-shell singlet ground state with an octahedral structure, while  $UAu_6$  has an open-shell ground state (quintet or triplet) with somewhat unsymmetrical structures. The origin of these differences in the geometries can be traced to the relative bond dissociation energies (BDE) of the  $Au_2$  and  $F_2$  dimers. The DFT calculated  $Au_2$  BDE of 1.96 eV (expt 2.32 eV) is significantly larger than that of  $F_2$ , 1.61 eV (expt 1.66 eV) with a significantly longer equilibrium bond distance, about 2.47 Å for  $Au_2$  compared to 1.41 Å for  $F_2$ . This allows for ionic U–Au as well as Au–Au interactions. In the octahedral geometry of singlet  $UAu_6$  (Figure S3), the Au–Au bond lengths are 3.87 Å, which is much longer than the calculated equilibrium distance in  $Au_2$  (2.56 Å); hence there can be very little interaction between the Au atoms in this structure. Both isomers II and III arise from simple distortions from the octahedral geometry to allow for Au–Au interactions, and the average Au–Au distance in the three isomers of  $UAu_6$  range from 2.72 to 2.85 Å (Table S1). Thus, the three isomers of  $UAu_6$  can be rationalized as structures with competing U–Au and Au–Au interactions. In  $UF_6$  the ionic U–F interaction dominates and the geometry is then determined by maximizing the numbers of U–F bonds; hence the geometry adopts a perfect  $O_h$  symmetry. In addition, the existence of strong Au–Au interactions leads to a reduction in the oxidation state of U from +6 in  $UF_6$  to +4 in  $UAu_6$ , yielding the open-shell spin states in the latter. An important difference between  $UF_6$  and  $UAu_6$  that can have scientific and technological importance is that the latter is magnetic with a large magnetic moment localized at the U site. It may be possible to use  $UAu_6$  as a building block of one-dimensional ferromagnets, similar to the  $V_6(C_6H_6)_7$  sandwich complexes, which have been both predicted and experimentally confirmed.<sup>12,13</sup> If so, this would be a case in which two metallic elements, which are intrinsically nonmagnetic in the bulk, give rise to a ferromagnet with constrained geometry and composition.

In conclusion, realizing that Au, with an outer electron configuration of  $5d^{10}6s^1$ , has versatile chemistry in that it behaves as both a hydrogen atom and halogen atom, we used it as a surrogate of F to shed additional light on  $UF_6$ . We were able to photodetach  $UAu_6^-$  and measure its adiabatic EA and VDE to be  $3.05 \pm 0.05$  and  $3.28 \pm 0.05$  eV, respectively, making  $UAu_6$  a pseudohalogen. Theoretical studies based on first-principles theory provided results in good agreement with experiment and evidence that the spectrum has contributions from at least two nearly isoenergetic isomers with the bonding dominated by ionic interactions between U and Au, similar to the bonding in  $UF_6$ . However, theory also revealed properties of  $UAu_6$  that are very different from that of  $UF_6$ . For example, the geometry of  $UF_6^-$  is an octahedron with no interaction between the F atoms, while  $UAu_6^-$  exhibits three nearly isoenergetic isomers with ring, quasi-octahedral, and butterfly geometries, all having coupling between the Au atoms. An intriguing difference is that the spin multiplicity of the ring isomer of neutral  $UAu_6$  is a quintet with  $3 \mu_B$  of the magnetic moment localized at the U site. Thus, while Au can be used as a surrogate for F, one must be aware that Au–Au interactions can cause interesting deviations from fluorine's behavior.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c08231>.

Materials and methods, supplementary discussion of the experimental mass spectrum, and the electronic structure and nature of bonding in  $UAuF$  and  $UAu_6$  (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

Kit H. Bowen – Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States; [orcid.org/0000-0002-2858-6352](https://orcid.org/0000-0002-2858-6352); Email: [kbowen@jhu.edu](mailto:kbowen@jhu.edu)

Puru Jena – Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, United States; [orcid.org/0000-0002-2316-859X](https://orcid.org/0000-0002-2316-859X); Email: [pjena@vcu.edu](mailto:pjena@vcu.edu)

Kirk Peterson – Department of Chemistry, Washington State University, Pullman, Washington 99164, United States; [orcid.org/0000-0003-4901-3235](https://orcid.org/0000-0003-4901-3235); Email: [kipeters@wsu.edu](mailto:kipeters@wsu.edu)

### Authors

Rachel M. Harris – Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States; [orcid.org/0000-0002-3585-5258](https://orcid.org/0000-0002-3585-5258)

Zhaoguo Zhu – Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States; [orcid.org/0000-0002-4395-9102](https://orcid.org/0000-0002-4395-9102)

Deepika – Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, United States

Burak A. Tufekci – Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.2c08231>

### Author Contributions

The manuscript was written through contributions of all authors. R.M.H., Z.Z., and D. contributed equally.

### Funding

We thank the U.S. Department of Energy for their support under grants DE-SC0019317 (K.H.B.), DE-SC0008501 (K.A.P.), and DE-FG02-96ER45579 (P.J.).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Support of the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Heavy Element Chemistry program [Grant Nos. DE-SC0022977 (K.H.B.) and DE-SC0008501 (K.A.P.)], is gratefully acknowledged. Resources of the National Energy Research Scientific Computing Center supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 are also acknowledged.

## ■ REFERENCES

- (1) Dau, P. D.; Su, J.; Liu, H.-T.; Huang, D.-L.; Wei, F.; Li, J.; Wang, L.-S. Photoelectron Spectroscopy and Theoretical Studies of  $UF_5^-$  and  $UF_6^-$ . *J. Chem. Phys.* **2012**, *136* (19), 194304.

(2) Su, J.; Dau, P. D.; Liu, H.-T.; Huang, D.-L.; Wei, F.; Schwarz, W. H. E.; Li, J.; Wang, L.-S. Photoelectron Spectroscopy and Theoretical Studies of Gaseous Uranium Hexachlorides in Different Oxidation States:  $\text{UCl}_6^q$  ( $q = 0-2$ ). *J. Chem. Phys.* **2015**, *142* (13), 134308.

(3) Heiz, U.; Vayloyan, A.; Schumacher, E.; Yerezian, C.; Stener, M.; Gisdakis, P.; Rösch, N.  $\text{NaxAu}$  and  $\text{CsxAu}$  Bimetal Clusters: Finite Size Analogs of Sodium-Gold and Cesium-Gold Compounds. *J. Chem. Phys.* **1996**, *105* (13), 5574–5585.

(4) Zhu, Z.; Marshall, M.; Harris, R. M.; Bowen, K. H.; Vasiliu, M.; Dixon, D. A.  $\text{Th}_2\text{O}^-$ ,  $\text{Th}_2\text{Au}^-$ , and  $\text{Th}_2\text{AuO}_{1,2}^-$  Anions: Photoelectron Spectroscopic and Computational Characterization of Energetics and Bonding. *J. Phys. Chem. A* **2021**, *125* (1), 258–271.

(5) Pyykkö, P.; Taubert, S. Saturnenes Like  $\text{Th@Au}_6\text{D6h}$ : Ring-Current Evidence for Au–Au Bonding Along the Gold Ring. *Isr. J. Chem.* **2022**, *62* (1–2), No. e202100139.

(6) Pyykkö, P. Theoretical Chemistry of Gold. III. *Chem. Soc. Rev.* **2008**, *37* (9), 1967–1997.

(7) Hoffmann, R. Building Bridges Between Inorganic and Organic Chemistry (Nobel Lecture). *Angewandte Chemie International Edition in English* **1982**, *21* (10), 711–724.

(8) Jung, J.; Kim, H.; Kim, J. C.; Park, M. H.; Han, Y.-K. Gold Behaves as Hydrogen in the Intermolecular Self-Interaction of Metal Aurides  $\text{MAu}_4$  ( $M = \text{Ti, Zr, and Hf}$ ). *Chemistry - An Asian Journal* **2011**, *6* (3), 868–872.

(9) Gagliardi, L. When Does Gold Behave as a Halogen? Predicted Uranium Tetraauride and Other  $\text{MAu}_4$  Tetrahedral Species, ( $M = \text{Ti, Zr, Hf, Th}$ ). *J. Am. Chem. Soc.* **2003**, *125* (25), 7504–7505.

(10) Zhu, Z.; Marshall, M.; Bowen, K. H.; Peterson, K. A.  $\text{ThAu}_2^-$ ,  $\text{ThAu}_2\text{O}^-$ , and  $\text{ThAuOH}^-$  Anions: Photoelectron Spectroscopic and Theoretical Characterization. *J. Chem. Phys.* **2022**, *156* (5), 054305.

(11) Shah, A.; Banjade, H.; Long, Z.-C.; Gao, Z.-O.; Xu, H.-G.; Zheng, W.; Jena, P. Signature of Au as a Halogen. *J. Phys. Chem. Lett.* **2022**, *13* (21), 4721–4728.

(12) Kandalam, A. K.; Rao, B. K.; Jena, P.; Pandey, R. Geometry and Electronic Structure of  $\text{Vn}(\text{Bz})_m$  Complexes. *J. Chem. Phys.* **2004**, *120* (22), 10414–10422.

(13) Wang, J.; Acioli, P. H.; Jellinek, J. Structure and Magnetism of  $\text{VnBzn}+1$  Sandwich Clusters. *J. Am. Chem. Soc.* **2005**, *127* (9), 2812–2813.

## Recommended by ACS

### Stabilized Nitrogen Framework Anions in the Ga–N System

Hang Zhai, Yanming Ma, *et al.*

NOVEMBER 17, 2022  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

### Evidence for Water Antibonding Orbital Mixing in the Hydrated Electron from Its Oxygen 1s X-ray Absorption Spectrum

Xingpin Li, William J. Glover, *et al.*

OCTOBER 17, 2022  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

### The Chromium Dimer: Closing a Chapter of Quantum Chemistry

Henrik R. Larsson, Garnet Kin-Lic Chan, *et al.*

AUGUST 24, 2022  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

### Disassembly Mechanisms and Energetics of Polymetallic Rings and Rotaxanes

Niklas Geue, Perdita E. Barran, *et al.*

DECEMBER 02, 2022  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

READ 

Get More Suggestions >