

Au as a surrogate for F: The case of UAu_6 vs UF_6 .

Rachel M. Harris^{1†}, Zhaoguo Zhu^{1†}, Deepika^{2†}, Burak A. Tufekci¹, Kirk Peterson^{3*}, Puru Jena^{2*} and Kit H. Bowen^{1*}

¹Department of Chemistry, Johns Hopkins University; Baltimore, MD 21218 USA.

²Department of Physics, Virginia Commonwealth University; Richmond, Virginia 23284 USA.

³Department of Chemistry, Washington State University; Pullman, Washington 99164 USA.

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 UF_6 and its anion. Unlike UF_6 , 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 UAu_6 isomers have open-shell electrons, which in nearly all cases are localized on the central U atom. The adiabatic electron affinity (EA) and vertical detachment energy (VDE) are measured to be 3.05 ± 0.05 and 3.28 ± 0.05 eV, respectively, and are in very good agreement with calculations.

Uranium hexafluoride (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 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 UCl_6^- and UF_6^- have been studied by anion photoelectron spectroscopy and the adiabatic electron affinity (EA) of UCl_6^- has been measured to be 5.3 eV, the EA of UF_6^- has not, even though it is likely higher^{1,2}.

Here, we adopt an alternative approach to better understand UF_6 and 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 Th³⁻⁶. That Au may mimic F in UF_6 is consistent with Hoffmann's isolobal principle, which suggests that species with similar symmetry and frontier orbital energies have similar bonding and reactivity⁷. It was previously predicted by theory that Au could behave like a halogen when interacting with U in UAu_4 ^{8,9}. Recent joint experimental-theory studies on various thorium-gold anions, as well as the Au_2F molecule, have shown that indeed Au can behave very similarly to F^{10,11}. In a computational pilot study of the 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 UAu_6^- possesses some of the properties of UF_6^- , it also exhibits its unique properties of its own.

The photoelectron spectra of UAu_6^- measured with 3.49 eV, 4.66 eV and 6.42 eV photons are displayed in Figure 1. The first peak observed in the 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 electron binding energy (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 UAu_6 of 3.05 ± 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 ± 0.05 eV for UAu_6^- .

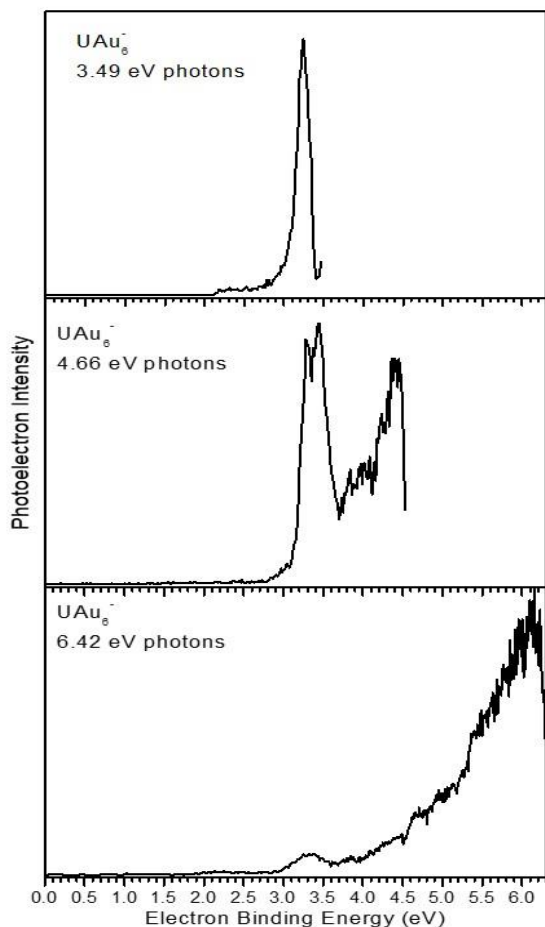


Figure 1. Photoelectron Spectrum of UAu_6^- taken with 3.49 eV, 4.66 eV, and 6.42 eV photons

Figure 2 presents the DFT optimized geometries of the nearly isoenergetic neutral and anionic 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 Å 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 UAu_6^- (isomer I) is more symmetric than that of neutral UAu_6 , with the U-Au bond length contracted 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 UAu_6 (Figure S3), analogous to the equilibrium geometry of 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 UAu_6 , isomer III is clearly the ground state. A natural population

analysis (NPA) showed that in all the neutral and anionic UAu_6 isomers, the U atom is positively charged. In neutral isomer I and II, all six Au atoms carry 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 UAu_6 , Au atoms behave like halogens. In the anion, the charge on the U atom is decreased by nearly $\frac{1}{2}$ 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.

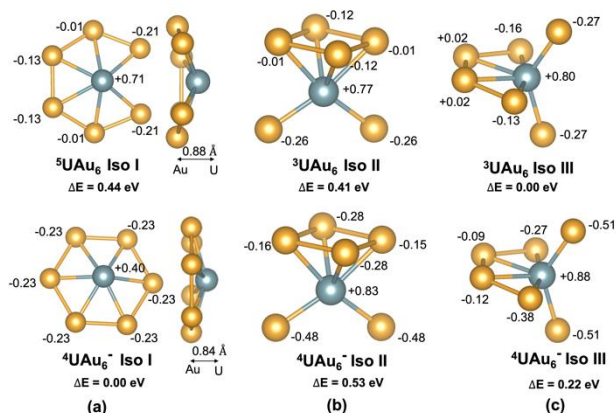


Figure 2. DFT optimized ground state geometries of the nearly isoenergetic isomers: (a) Ring isomer (I), (b) Distorted-octahedral isomer (II), and (c) Butterfly isomer (III) of neutrals, i.e., UAu_6 (top row) and anions, i.e., UAu_6^- (bottom row). Relative energies, ΔE , are given at the CCSD(T) level 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.

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 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) results for the VDE of isomer III is about 0.15 eV lower than that of isomer I. As shown in Fig. 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 Fig. 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.

Table 1. Experimental and CCSD(T) adiabatic electron affinities^a (EA) of UAu₆ and vertical detachment energies (VDE) of UAu₆⁻.

Species	EA (eV)		VDE (eV)	
	Expt.	Theory	Expt.	Theory
UAu ₆	3.05 ±0.05		3.28±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)

^aThe CCSD(T) values correspond to using aVTZ basis sets. See the text in the SI. DFT results are shown in parentheses.

Analogous to the bonding in UF₆, the bonding between U and Au in UAu₆ is primarily ionic. However, there are significant differences in the electronic structures of UF₆ and UAu₆ (and their anions). While UF₆ exhibits only two-center-two-electron (2c-2e) bonds, UAu₆ exhibits 3c-2e bonds (Figures S4-S6). In addition, UF₆ has a closed-shell singlet ground state with an octahedral structure, while UAu₆ 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 Au₂ and F₂ dimers. The DFT calculated Au₂ BDE of 1.96 eV (exp. 2.32 eV) is significantly larger than that of F₂, 1.61 eV (exp. 1.66 eV) with a significantly longer equilibrium bond distance, about 2.47 Å for Au₂ compared to 1.41 Å for F₂. This allows for ionic U-Au as well as Au-Au, interactions. In the octahedral geometry of singlet UAu₆ (Figure S3), the Au-Au bond lengths are 3.87 Å, which is much longer than the calculated equilibrium distance in Au₂ (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 UAu₆ range from 2.72 to 2.85 Å (Table S1). Thus, the three isomers of UAu₆ can be rationalized as structures with competing U-Au and Au-Au interactions. In UF₆ 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 UF₆ to +4 in UAu₆, yielding the open-shell spin states in the latter. An important difference between UF₆ and UAu₆ 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 UAu₆ as a building block of one dimensional ferromagnets, similar to the V₆(C₆H₆)₇ sandwich complexes which have been both predicted and experimentally confirmed^{12,13}. If so, this would be a case in which two metallic elements, that are intrinsically nonmagnetic in the bulk, give rise to a ferromagnet with constrained geometry and composition.

Realizing that Au with an outer electron configuration of 5d¹⁰6s¹ has versatile chemistry in that it behaves both as a

hydrogen atom and halogen atom, we used it as a surrogate of F to shed additional light on UF₆. We were able to photo-detach UAu₆⁻ and measure its adiabatic EA and VDE to be 3.05 ± 0.05 and 3.28 ± 0.05, eV, respectively, making UAu₆ a pseudo-halogen. 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 UF₆. However, theory also revealed properties of UAu₆ that are very different from that of UF₆. For example, the geometry of UF₆⁻ is an octahedron with no interaction between the F atoms while UAu₆⁻ 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 UAu₆ is a quintet with 3 μ_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. Materials and methods¹⁴⁻²⁸, supplementary discussion of the experimental mass spectrum, and the electronic structure and nature of bonding in UAuF and UAu₆. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Email: kbowen@jhu.edu (KHB), pjena@vcu.edu (PJ), and kippers@wsu.edu (KAP)

Author Contributions

The manuscript was written through contributions of all authors. †These authors contributed equally.

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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 UF₅⁻ and UF₆⁻. *J. Chem. Phys.* **2012**, *136* (19), 194304. <https://doi.org/10.1063/1.4716182>.

- (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: UCl_6q^- ($q = 0-2$). *J. Chem. Phys.* **2015**, *142* (13), 134308. <https://doi.org/10.1063/1.4916399>.
- (3) Heiz, U.; Vayloyan, A.; Schumacher, E.; Yeretian, C.; Stener, M.; Gisdakis, P.; Rösch, N. NaxAu and CsxAu Bimetal Clusters: Finite Size Analogs of Sodium–Gold and Cesium–Gold Compounds. *J. Chem. Phys.* **1996**, *105* (13), 5574–5585. <https://doi.org/10.1063/1.472397>.
- (4) Zhu, Z.; Marshall, M.; Harris, R. M.; Bowen, K. H.; Vasiliu, M.; Dixon, D. A. Th_2O^- , Th_2Au^- , 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. <https://doi.org/10.1021/acs.jpca.0c09766>.
- (5) Pyykkö, P.; Taubert, S. Saturnenes Like $\text{Th@Au}_6\text{D6h}$: Ring-Current Evidence for Au–Au Bonding Along the Gold Ring. *Israel Journal of Chemistry* **2022**, *62* (1–2), e202100139.
- (6) Pyykkö, P. Theoretical Chemistry of Gold. III. *Chem. Soc. Rev.* **2008**, *37* (9), 1967–1997. <https://doi.org/10.1039/B708613J>.
- (7) Hoffmann, R. Building Bridges Between Inorganic and Organic Chemistry (Nobel Lecture). *Angewandte Chemie International Edition in English* **1982**, *21* (10), 711–724. <https://doi.org/10.1002/anie.198207113>.
- (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 MAu_4 ($M = \text{Ti, Zr, and Hf}$). *Chemistry – An Asian Journal* **2011**, *6* (3), 868–872. <https://doi.org/10.1002/asia.201000742>.
- (9) Gagliardi, L. When Does Gold Behave as a Halogen? Predicted Uranium Tetraauride and Other MAu_4 Tetrahedral Species, ($M = \text{Ti, Zr, Hf, Th}$). *J. Am. Chem. Soc.* **2003**, *125* (25), 7504–7505. <https://doi.org/10.1021/ja035385a>.
- (10) Zhu, Z.; Marshall, M.; Bowen, K. H.; Peterson, K. A. ThAu_2^- , ThAu_2O^- , and ThAuOH^- Anions: Photoelectron Spectroscopic and Theoretical Characterization. *J. Chem. Phys.* **2022**, *156* (5), 054305. <https://doi.org/10.1063/5.0079795>.
- (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. <https://doi.org/10.1021/acs.jpclett.2c00910>.
- (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. <https://doi.org/10.1063/1.1738632>.
- (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. <https://doi.org/10.1021/ja043807q>.
- (14) Glendening, E. D.; Landis, C. R.; Weinhold, F. NBO 7.0: New Vistas in Localized and Delocalized Chemical Bonding Theory. *Journal of Computational Chemistry* **2019**, *40* (25), 2234–2241. <https://doi.org/10.1002/jcc.25873>.
- (15) Gerhards, M.; Thomas, O. C.; Nilles, J. M.; Zheng, W.-J.; Bowen, K. H. Cobalt–Benzene Cluster Anions: Mass Spectrometry and Negative Ion Photoelectron Spectroscopy. *J. Chem. Phys.* **2002**, *116* (23), 10247–10252. <https://doi.org/10.1063/1.1477924>.
- (16) Ho, J.; Ervin, K. M.; Lineberger, W. C. Photoelectron Spectroscopy of Metal Cluster Anions: Cu_n^- , Ag_n^- , and Au_n^- . *J. Chem. Phys.* **1990**, *93* (10), 6987–7002. <https://doi.org/10.1063/1.459475>.
- (17) Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
- (18) Werner, H.-J.; Knowles, P. J.; Manby, F. R.; Black, J. A.; Doll, K.; Heßelmann, A.; Kats, D.; Köhn, A.; Korona, T.; Kreplin, D. A.; Ma, Q.; Miller, T. F.; Mitrushchenkov, A.; Peterson, K. A.; Polyak, I.; Rauhut, G.; Sibaev, M. The Molpro Quantum Chemistry Package. *J. Chem. Phys.* **2020**, *152* (14), 144107. <https://doi.org/10.1063/5.0005081>.
- (19) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. Molpro: A General-Purpose Quantum Chemistry Program Package. *WIREs Computational Molecular Science* **2012**, *2* (2), 242–253. <https://doi.org/10.1002/wcms.82>.
- (20) Becke, A. D. Density-functional Thermochemistry. II. The Effect of the Perdew–Wang Generalized-gradient Correlation Correction. *J. Chem. Phys.* **1992**, *97* (12), 9173–9177. <https://doi.org/10.1063/1.463343>.
- (21) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652. <https://doi.org/10.1063/1.464913>.
- (22) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104. <https://doi.org/10.1063/1.3382344>.
- (23) Peterson, K. A.; Puzzarini, C. Systematically Convergent Basis Sets for Transition Metals. II. Pseudopotential-Based Correlation Consistent Basis Sets for the Group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) Elements. *Theor Chem Acc* **2005**, *114* (4), 283–296. <https://doi.org/10.1007/s00214-005-0681-9>.
- (24) Peterson, K. A. Correlation Consistent Basis Sets for Actinides. I. The Th and U Atoms. *J. Chem. Phys.* **2015**, *142* (7), 074105. <https://doi.org/10.1063/1.4907596>.
- (25) Dolg, M.; Cao, X. Accurate Relativistic Small-Core Pseudopotentials for Actinides. Energy Adjustment for Uranium

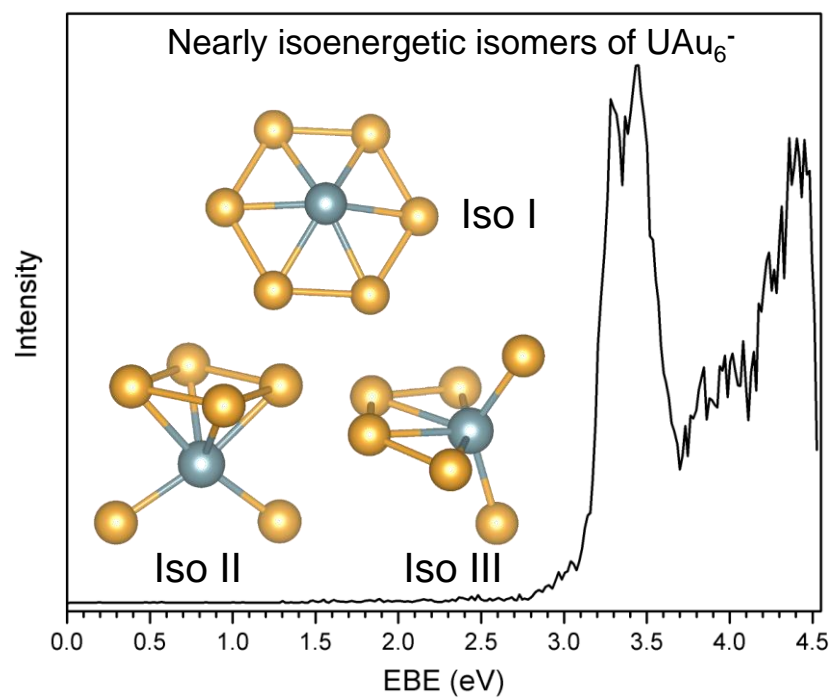
and First Applications to Uranium Hydride. *J. Phys. Chem. A* **2009**, *113* (45), 12573–12581. <https://doi.org/10.1021/jp9044594>.

(26) Figgen, D.; Rauhut, G.; Dolg, M.; Stoll, H. Energy-Consistent Pseudopotentials for Group 11 and 12 Atoms: Adjustment to Multi-Configuration Dirac–Hartree–Fock Data. *Chemical Physics* **2005**, *311* (1), 227–244. <https://doi.org/10.1016/j.chemphys.2004.10.005>.

(27) Knowles, P. J.; Hampel, C.; Werner, H. Coupled Cluster Theory for High Spin, Open Shell Reference Wave Functions. *J. Chem. Phys.* **1993**, *99* (7), 5219–5227. <https://doi.org/10.1063/1.465990>.

(28) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. *Journal of Computational Chemistry* **2012**, *33* (5), 580–592. <https://doi.org/10.1002/jcc.22885>.

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