

ThH₅: An Actinide-Containing Superhalogen Molecule

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Thorium and its compounds have been widely investigated as important nuclear materials. Previous research focused on the potential use of thorium hydrides, such as ThH₂, ThH₄, and Th₄H₁₅, as nuclear fuels. Here, we report studies of the anion, ThH₅⁻, by anion photoelectron spectroscopy and computations. The resulting experimental and theoretical vertical detachment energies (VDE) for ThH₅⁻ are 4.09 eV and 4.11 eV, respectively. These values and the agreement between theory and experiment facilitated the characterization of the structure of the ThH₅⁻ anion and showed its neutral counterpart, ThH₅ to be a superhalogen. ThH₅⁻, which exhibits a C_{4v} structure with five Th–H single bonds, possesses the largest known H/M ratio among the actinide elements, M. The adaptive natural density partitioning (AdNDP) method was used to further analyze the chemical bonding of ThH₅⁻ and to confirm the existence of five Th–H single bonds in the ThH₅⁻ molecular anion.

In the 1960's, Neil Bartlett carried out the reaction between the noble gas, xenon, and the powerful oxidizing agent, PtF₆, demonstrating that the once-believed inert gas can be reactive. With an electron affinity of ~6.8 eV, the PtF₆ molecule had behaved like an ultra-halogen.^[1] Gutsev and Boldyrev later coined the term "superhalogen" to describe the class of compounds that behave chemically like halogens yet possess much higher electron affinities. Generally, superhalogens are molecules or clusters having electron affinities that are greater than that of chlorine, the element with the highest electron affinity in the periodic table. Superhalogens are of the form, MX_{k+1}, where the ligand, X, is a halogen atom and k is the nominal valence of the central electropositive metal M.^[2] Jena later extended the definition of superhalogens, showing that they can exist without halogen atoms.^[3–5] Thus, some hydrides, e.g., AlH₄, came to be classified as superhalogens, since as such, they readily formed their anionic counterparts, i.e., AlH₄⁻.^[6] Superhalogens have been reported for both main group

elements and transition metals, but to the best of our knowledge, they have not been extended to Th.

Interest in thorium hydrides stems not only from their potential as fuels for nuclear reactors, but also from indications that they are superconducting materials. Relative to thorium oxides, thorium hydrides possess higher thorium metal densities, this being an attribute in power reactors.^[7] The superconductivity parameters of ThH₂ and Th₄H₁₅, both of which are metallic solids, are well known^[8,9] and both compounds have been characterized by nuclear magnetic resonance.^[10,11] Several computational studies have also predicted that the superhydrides XH_n (n > 5) possess high superconducting transitions.^[12–15] Furthermore, given their high hydrogen-to-metal ratio, some thorium hydrides have been considered as candidate materials for hydrogen storage.^[16] Because of the radioactivity and toxicity of some actinides, the ability to conduct accurate theoretical calculations is quite important. Owing to electron correlation and relativistic effects, accurate calculations on actinides and actinide compounds are still very challenging. While thorium is only mildly radioactive and modestly toxic compared to trans-uranium actinides, calculations on thorium compounds provide valuable benchmarks for computations on heavier actinides. Theoretical calculations on thorium hydride systems have included ThH₄^[17–19] and HTHCl₃.^[20]

The present work investigates the thorium penta-hydride anion, ThH₅⁻, using anion photoelectron spectroscopy (PES) and quantum chemical calculations. ThH₅ is shown to be a superhalogen, whose anion, ThH₅⁻, exhibits the highest H/M ratio among other actinide compounds. Detailed experimental and theoretical methods are provided in the supporting information (SI).

Figure 1 shows the mass spectrum containing ThH₅⁻. No other hydrides ThH_x⁻ (x ≠ 5) were observed. This phenomenon is uncommon for mass spectrometric studies of metal hydrides, since there are almost always diverse combinations of hydrogen atoms attached to the metal atoms as shown in previous reports.^[21–23] When a cluster ion exhibits unusually high intensity relative to its neighbors in the mass spectrum, it might well possess some particular property that facilitates its abundance and by implication, its stability. Clusters of this type are often declared the "magic clusters",^[24] and examples of such clusters include the famous discovery of C₆₀.^[25]

Figure 2 shows the photoelectron spectrum for ThH₅⁻ taken with a 266 nm (4.66 eV) laser. Three features marked as A, B and X are observed in the spectrum. Feature A has an onset at an electron binding energy (EBE) of 3.71 eV ranging up to 4.35 eV, with an intensity maximum at 4.09 eV. The vertical detachment energy (VDE) is the transition at which the Franck-Condon overlap between the wave function of the ground state and

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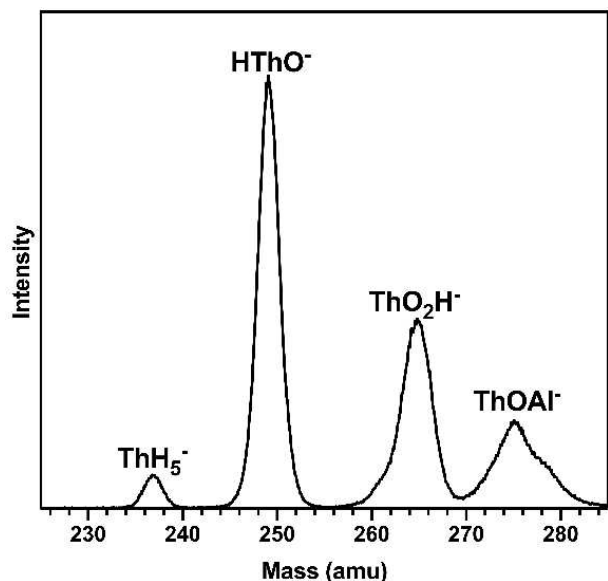


Figure 1. The mass spectrum obtained from the pulsed arc cluster ion source using thorium powder pressed into an aluminium rod with H₂ backing gas.

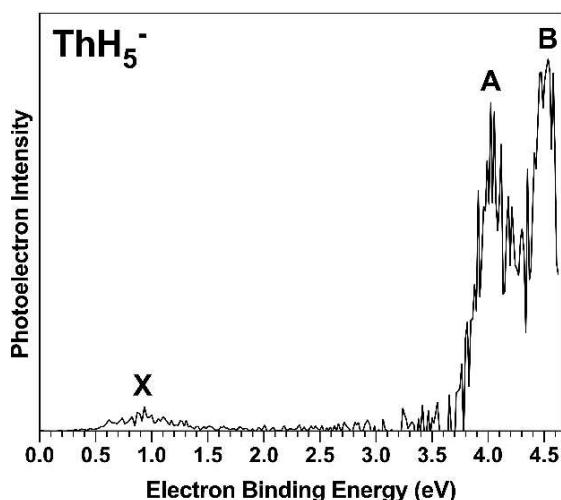


Figure 2. Photoelectron spectrum of ThH₅⁻ measured with a 266 nm laser.

that of its neutral counterpart in the structure of the anion is maximal. The VDE value for ThH₅⁻ is determined to be 4.09 eV. In addition, feature B peaks at 4.52 eV. There is also a weaker EBE band, feature X, which begins at EBE = 0.58 eV, reaching its maximum at EBE = 0.88 eV. This feature corresponds to ThH₃⁻. The 4.66 eV photons have enough energy to photodissociate ThH₅⁻ into ThH₃⁻ + H₂, with a second photon photodetaching an electron from ThH₃⁻. This is a two-photon phenomenon, which was also seen in the spectrum PtH₅⁻.^[21] These values are tabulated in Table 1, where they are compared with corresponding theoretical values.

To better understand the ThH₅⁻ anion, we used quantum theoretical methods to compare with the experimental results (details provided in the SI). Figure 3 presents the calculated

Table 1. Experimental and theoretical vertical detachment energies (VDE) values (eV) for ThH₃⁻ and ThH₅⁻ at the different levels of theory. The aug-ccpVTZ/ECP60MDF basis sets are used for all methods.

System	Expt. VDE	Theo. VDE	Expt. 2 nd VDE	Theo. 2 nd VDE
ThH ₃ ⁻	0.88 (X)	0.72 ^[a]	–	–
ThH ₅ ⁻⁰ (singlet)	4.09 (A)	4.11 ^[a] , 3.82 ^[b] , 4.06 ^[c] , 3.89 ^[d] , 3.97 ^[e] , 4.34 ^[f]	4.52 (B)	4.66 ^[a]
ThH ₅ ⁻⁰ (triplet)	–	1.32 ^[a]	–	–

[a] B3LYP, [b] PBE, [c] PBE0, [d] tpss, [e] tpssh, [f] CCSD(t)

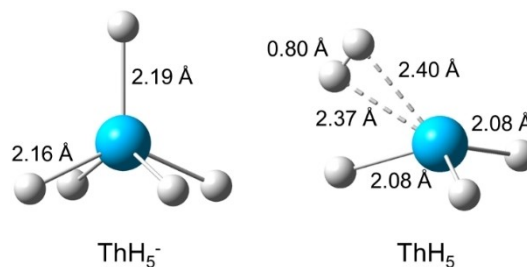


Figure 3. Geometrical structures and bond lengths (in Å) of the ThH₅⁻⁰ molecules optimized at the B3LYP/aug-ccpVTZ/ECP60MDF level of theory. The thorium atom is blue, and hydrogen atom is white.

geometric structures and bond lengths of ThH₅⁻. The anion geometry converged to C_{4v} symmetry. The optimization of the singlet and triplet states of ThH₅⁻ determines that the singlet state is more stable. The Cartesian coordinates of the calculated structures are shown in Table S1. The ThH₅⁻ anion was optimized at several density theory functionals including PBE, PBE0, B3LYP, TPSS, TPSSH, as well as CCSD(T) level of theory. The aug-ccpVTZ basis set was applied to the hydrogen atoms, and the relativistic pseudopotential ECP60MDF was used for Th in all calculations. The VDE values calculated at different levels for ThH₅⁻ are presented in Table 1.

The calculated VDE values of ThH₅⁻ agree well among each other and are also in good agreement with the experimental results (4.09 eV, peak A). To identify the weaker peak observed at 0.88 eV (peak X), we optimized both the singlet ThH₃⁻ anion and the triplet state of ThH₅⁻. The calculated VDE value of the ThH₃⁻ anion is 0.72 eV, which is close to what is observed experimentally. The calculated structure of ThH₃⁻ is presented as Figure S1. However, the VDE value of the triplet state of ThH₅⁻ is 1.32 eV, drastically different from the peak X. Peak X in the photoelectron spectrum is therefore assigned to the ThH₃⁻ anion. The agreement between the calculated and experimental VDE values of ThH₃⁻ (0.72 eV and 0.88 eV, respectively) and that of the singlet state of ThH₅⁻ (4.11 and 4.09 eV, respectively) indicate that both anions are present in the PES. Photodissociation of ThH₅⁻ by the photodetachment laser after mass selection is the likely source of ThH₃⁻ anions in the ion beam. The dissociation energy for the reaction ThH₅⁻ → ThH₃⁻ + H₂ is calculated to be 1.76 eV, well below the photon energy used for photodetachment. Photodissociation of hydrides and loss of H₂ during the photoelectron spectroscopy is not uncommon in our

experiments.^[21] In addition, the high-energy (peak B) transition for ThH₅⁻ (peak B, 4.66 eV) is also in good agreement with the experimental second VDE transition (4.52 eV), further confirming the presence of ThH₅⁻.

The calculated VDE depends on the computational methods and basis sets, and they range from 3.82 to 4.34 eV in the methods that we used. The experimental VDE value of 4.09 eV for the ThH₅⁻ anion is within the range of our theoretical estimates. The VDE values obtained at the B3LYP (4.11 eV) and PBE0 (4.06 eV) levels of theory are the closest to the experimental value. Based on reasonable agreement between experiment and theory, we conclude that the theoretical methods used are reliable.

We have also presented the structure of the neutral ThH₅ molecule in Figure 3, which displays a H₂ molecule weakly attached to ThH₃. Since there is a large structural difference between the neutral and the anion, the Franck-Condon overlap between these two states is not sufficient enough to facilitate the experimental observation of the adiabatic electron affinity (AEA), therefore, here we could only report the calculated value, 2.23 eV.

To further investigate the chemical bonding of ThH₅⁻, we performed the adaptive natural density partitioning (AdNDP)^[23] analysis of ThH₅⁻ (Figure 4) at the B3LYP/aug-ccpvtz/ECP60MDF level of theory. Five Th–H σ bonds in ThH₅⁻ with occupation number (ON) values of 2.00 |e| are observed. According to Gutsev and Boldyrev, the general formula for a typical superhalogen anion is MX_{k+1}⁻, where k is the number of valence electrons of M.^[2] Since the Th atom has a [Rn]6d²7s² electronic configuration with 4 valence electrons, ThH₅⁻ with five Th–H σ bonds, is a superhalogen. The high VDE of ThH₅⁻ also confirms the superhalogen nature of ThH₅. The frontier molecular orbitals and their corresponding energy levels of ThH₅⁻ involving the Th–H bonds are presented in Figure S2. It is apparent that the s and d orbitals of Th participates in the formation of the Th–H bonds. There is no clear evidence of the involvement of f orbitals.

To conclude, we have investigated the structural and electronic properties, as well as the chemical bonding, of the ThH₅⁻ anion by anion photoelectron spectroscopy and compu-

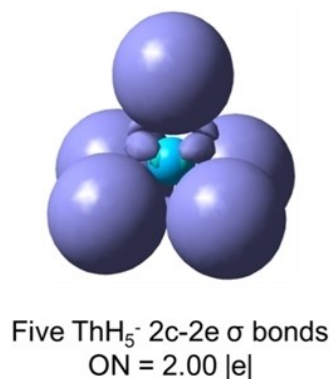


Figure 4. Summary of the AdNDP analysis of the ThH₅⁻ anion at the B3LYP/aug-ccpVTZ/ECP60MDF level of theory.

tational studies. ThH₅⁻ has C_{4v} structure with five Th–H single bonds contributing to the experimentally observed photoelectron spectrum. Both the singlet ThH₅⁻ anion and the photodissociation product ThH₃⁻ are observed in the photoelectron spectrum. The AdNDP analysis reveals five Th–H single bonds with occupation numbers of almost 2.0. Based on the current study, we extend superhalogens to the actinide element, Th, and the ThH₅⁻ anion has the greatest H/M ration among all actinide compounds.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: actinides · anion photoelectron spectroscopy · hydrides · superhalogen · thorium

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