ThH₅: An Actinide-Containing Superhalogen Molecule


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, ThH₃, and Th₂H₅, 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 C₅ᵥ 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, PtF₄, demonstrating that the once-believed inert gas can be reactive. With an electron affinity of ~6.8 eV, the PtF₄ molecule had behaved like an ultra-halogen.[7] 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, MXₗ₊₁, where the ligand, X, is a halogen atom and l is the nominal valence of the central electropositive metal M.[8] Jena later extended the definition of superhalogens, showing that they can exist without halogen atoms.[3–5] Thus, some hydrides, e.g., AlH₅⁻ 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.[9] The superconductivity parameters of ThH₂ and Th₂H₅, 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 XHₙ (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 ThHCl₂.[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 ThHₓ⁻ (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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maximum at EBE band, feature X, which begins at EBE = 4.52 eV. There is also a weaker
feature B peaks at 4.52 eV. The dissociation energy for ThH$_5^-$ 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 ThH$_5^-$ are presented in Table 1.

The calculated VDE values of ThH$_5^-$ 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 ThH$_5^-$ and the triplet state of ThH$_5^-$. The calculated VDE value of the ThH$_5^-$ anion is 0.72 eV, which is close to what is observed experimentally. The calculated structure of ThH$_5^-$ is presented as Figure S1. However, the VDE value of the triplet state of ThH$_5^-$ is 1.32 eV, drastically different from the peak X. Peak X in the photoelectron spectrum is therefore assigned to the ThH$_5^-$ anion. The agreement between the calculated and experimental VDE values of ThH$_5^-$ (0.72 eV and 0.88 eV, respectively) and that of the singlet state of ThH$_5^-$ (4.11 and 4.09 eV, respectively) indicate that both anions are present in the PES. Photodissociation of hydrides and loss of H$_2$ during the photoelectron spectroscopy is not uncommon in our
in good agreement with the experimental second VDE transition (4.52 eV), further confirming the presence of ThH$_5^-$.

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 ThH$_5^-$ 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 ThH$_5$ molecule in Figure 3, which displays a H$_2$ molecule weakly attached to ThH$_3$. 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 ThH$_5^-$, we performed the adaptive natural density partitioning (AdNDP) analysis of ThH$_5^-$ (Figure 4) at the B3LYP/aug-cc-pvTZ/ECPI60MDF level of theory. Five Th–H σ bonds in ThH$_5^-$ 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$_{n-1}^-$, where k is the number of valence electrons of M.$^{21}$ Since the Th atom has a [Rn]6d$^2$7s$^2$ electronic configuration with 4 valence electrons, ThH$_3^-$ with five Th–H σ bonds, is a superhalogen. The high VDE of ThH$_5^-$ also confirms the superhalogen nature of ThH$_3^-$. The frontier molecular orbitals and their corresponding energy levels of ThH$_3^-$ involving the Th–H bonds are presented in Figure S2. It is apparent that the σ 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 ThH$_5^-$ anion by anion photoelectron spectroscopy and computational studies. ThH$_5^-$ has C$_{6v}$ structure with five Th–H single bonds contributing to the experimentally observed photoelectron spectrum. Both the singlet ThH$_5^-$ anion and the photodissociation product ThH$_5^-$ 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 ThH$_5^-$ 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.

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