Evaluation of bonding, electron affinity, and optical properties of M@C28 (M = Zr, Hf, Th, and U): Role of d- and f-orbitals in endohedral fullerenes from relativistic DFT calculations

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The experimentally characterized endohedral metallic fullerenes involving the small C28 cage, has shown to be able to encapsulate zirconium, hafnium, and uranium atoms, among other elements. Here, we explore the formation and nature of concentric bonds from purely d- to f-block elements, given by Zr, Hf, and uranium, along a borderline metal between such blocks, thorium. We explore the interplay of d- and f-orbitals in the chemistry of the early actinides, where the features of a d- or f-block metal can be mixed. Our results indicate that the bonding of Th@C28 involves contributions from both d- and f-type bonds, as characteristic of this early actinide element. Even uranium in U@C28, also exhibits a contribution from d-type bonds in addition to its relevant f-block character. Electron affinity and optical properties were evaluated to gain more insights into the variation of these molecular properties in this small endohedral fullerene, along Zr, Hf, Th, and U. The current results, allows to unravel the role of (n ? 1)d and (n ? 2)f orbitals in confined elements ranging from d- to f-blocks, which can be useful to gain a deeper understanding of the bonding situation in other endohedral species. © 2016 Wiley Periodicals, Inc.

actinides

bonding

endohedral

thorium

Actinides

Bonding

Chemical bonds

Electron affinity

Fullerenes

Thorium

Uranium

Actinide elements

Block character

Bonding situation

DFT calculation

Endohedral fullerene

Endohedrals

Molecular properties

Uranium atom

Optical properties