

Characterization of correlation-bound anions of perfluorinated molecules

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ABSTRACT

We characterize the anions of perfluorinated cage molecules and perfluorobenzene. These anions are correlation-bound, meaning that Hartree-Fock predicts a metastable anion with an unbound electron, while density functional theory predicts a stable anion with only bound electrons. Additionally, the cage molecules are said to be able to accommodate an electron inside the cage[1,2,3] in an orbital formed by overlapping anti-binding σ^* orbitals whose lobes point inside the cage.[1] Our study assesses the performance of eight different methods, including three density functionals, for the calculation of electron affinities, and characterizes the anionic states by means of electronic Fukui functions, Dyson orbitals, and electron localization functions. We performed all analyses at the optimized geometries of both the neutral and anionic state, to investigate if and how the anion changes character upon geometry relaxation. In case of a metastable state, the unbound electron was treated using the charge stabilization method.[4] Our results show that two of the density functionals perform at a comparable level as approximate coupled-cluster methods. Evidence for an electron inside the cage was found for perfluoroadamantane.

References

- [1] Irikura, K. K. Sigma Stellation: A Design Strategy for Electron Boxes. *The Journal of Physical Chemistry A* **2008**, *112*, 983–988.
- [2] Berski, S.; Gordon, A. J.; Latajka Z. Electron Localization Function Study on the Chemical Bonding in a Real Space for Tetrahedrane, Cubane, Adamantane, and Dodecahedrane and Their Perfluorinated Derivatives and Radical Anions. *The Journal of Physical Chemistry A* **2014**, *118*, 4147–4156.
- [3] Ghosh, A.; Conradie, J. The Perfluoro Cage Effect : A Search for Electron-Encapsulating Molecules. *ACS Omega* **2023**, *8*, 4972–4975.
- [4] Nestmann, B.; Peyerimhoff S. D. Calculation of the discrete component of resonance states in negative ions by variation of nuclear charges. *Journal of Physics B : Atomic and Molecular Physics* **1985**, *18*, 615–626.