

Fully chlorinated hydrocarbons — not as simple as they seem

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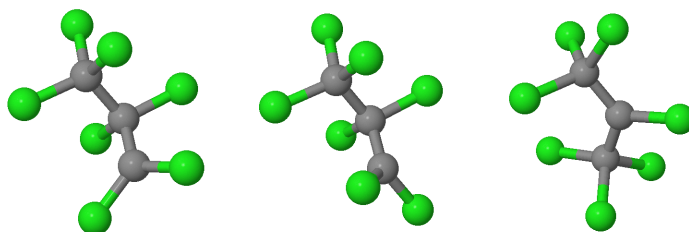
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Abstract

From an electronic structure point of view, the Cl—C bond is a surprisingly challenging beast [1]. Combined with the problem of the energetics of branching in hydrocarbons, the fully chlorinated hydrocarbons represent a class of seemingly simple, small molecules, which nevertheless require a very high level of theory in order to subdue to theoretical probing and investigation.

Here, it is shown that in order to correctly describe the bond cleavage energetics, as well as the energy difference between different branched isomers, electron correlation needs to be properly addressed. For this, extrapolations of both the basis set toward the basis set limit [2] and electron correlation toward the full configuration-interaction (FCI) limit are needed [3], with CCSD(T)/(aug-)cc-pVQZ calculations a prerequisite. The largest closed-shell CCSD(T) calculations thus employ 1450 basis functions, while the largest unrestricted CCSD(T) calculations employ 963 basis functions, in C₁ symmetry.

The benchmark, extrapolated complete-basis set limit FCI results are subsequently used as a basis for evaluating the performance of density functional theory (DFT) based methods. Standard functionals provide very unsatisfactory results. Dispersion effects are important and have to be included. Further, the open-shell species suffer from electron self-interaction, which needs to be corrected for in order to improve the DFT description. With a reliable and computationally feasible method established, larger molecules with active Cl—C bonds are open for future exploration.



- [1] J. Cioslowski, G. Liu, D. Moncrieff, "Thermochemistry of Homolytic C—C, C—H, and C—Cl Bond Dissociations in Polychloroethanes: Benchmark Electronic Structure Calculations", *J. Am. Chem. Soc.* **119** (1997) 11452.
- [2] A. Halkier *et al*, "Basis-set convergence in correlated calculations on Ne, N₂, and H₂O", *Chem. Phys. Lett.* **286** (1998) 243.
- [3] D.Z. Goodson, "Extrapolating the coupled-cluster sequence toward the full configuration-interaction limit", *J. Chem. Phys.* **116** (2002) 6948.