

*AB INITIO* STUDIES OF SMALL FLUOROCARBONS

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Recent years have seen a resurgence of commercial interest in fully fluorinated saturated fluorocarbons. The new and unexpected reactivity of some saturated fluorocarbons, whereby the fluorine atoms in perfluorodecalin are displaced by arenethiolate nucleophiles in dipolar aprotic solvents [1], clearly demonstrates that our understanding of the electronic structure of these compounds is deficient.

Accordingly we report ab initio SCF geometry optimizations for several small perfluorocarbons in order to establish a reliable methodology for calculations on such systems [2]. Systems studied include perfluoromethane ( $CF_4$ ), perfluoroethane ( $C_2F_6$ ), perfluoropropane ( $C_3F_8$ ), perfluorocyclopropane ( $C_3F_6$ ) and perfluorospiro[2.2]pentane ( $C_5F_8$ ). We discuss in detail results obtained using different s/p basis sets and the effects of including polarization functions on carbon and/or fluorine. Small rings need to be treated differently from the acyclic molecules and this is linked to the hybridization of the carbon atoms.

Systematic structural variations from system to system are observed and these are interpreted using a very simple model which incorporates the charge on carbon as indicated by Mulliken population analyses. Possible connections between these variations and the reactivity of the perfluorocarbons are noted.

- 1 D. D. MacNicol and C. D. Robertson, Nature (London), **323**, 59 (1988).
- 2 D. L. Cooper, N. L. Allan and R. L. Powell, to be published.