

Charge Saturation and Neutral Substitutions in Halomethanes and their Group 14 Analogues

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A computational analysis of the charge distribution in halomethanes and their heavy analogues (MH_4-nX_n : $M = C, Si, Ge, Sn, \text{ and } Pb$; $X = F, Cl, Br, \text{ and } I$) as a function of n uncovers a previously unidentified saturation limit for fluorides when $M \equiv C$. We examine the electron densities obtained at the CCSD, MP2(full), B3PW91, and HF levels of theory for eighty molecules for four different basis sets. A previously observed substituent independent charge at F in fluoromethanes is shown to be a move towards saturation that is restricted by the low polarizability of C. This limitation fades into irrelevance for the more polarizable M central atoms such that a genuine F saturation is realized in those cases. A conceptual model leads to a function of the form $[q_M(n') - q_M(n)] = a[\chi_{A'} - \chi_A] + b$ that links the electronegativities (χ) of incoming and leaving atoms (e.g. $A' = X$ and $A = H$ for the halogenation of MH_4-nX_n) and the associated charge shift at M. We show that the phenomenon in which the charge at the central atom, q_M , is itself independent of n (e.g. at carbon in CH_4-nBr_n) is best described as an 'M-neutral substitution' – not saturation. Implications of the observed X saturation and M-neutral substitutions for larger organic and inorganic halogenated molecules and polymeric materials are identified.