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**Analysis of competing bonding parameters in heavy analogues of halomethanes ($\text{MH}_{4-n}\text{X}_n$;
M=C, Si, Ge, Sn, Pb; X=F, Cl, Br, I; $n=1-4$)**

Abstract:

The bonding patterns and geometrical variations in halomethanes and their group 14 analogues ($\text{MH}_{4-n}\text{X}_n$, $n=1-4$; M=C, Si, Ge, Sn, Pb; X=F, Cl, Br, I) are analyzed using computed electronic parameters and a simple electrostatic model. *Ab initio* (full MP2) geometry optimizations have been performed for all twenty molecules, and the variations in the M—X bond lengths, X-M-X and other bond angles, are explained on the basis of a point charge model and bonding parameters obtained from an NBO analysis of the electron density in the molecule. A significant contraction in the M-X bond length with increasing n , is attributed to a competition for the electron density on M among the halide atoms and an increase in the Coulomb interaction between the X and M sites in the molecules. An increase in the X-M-X bond angles from $n=1$ to $n=4$ for M=Pb, Sn for all X is explained by an observed increase in the s contribution to the M hybrid orbitals. As the s character of the hybrid M orbitals increases the sp^n orbitals spread farther apart. For the smaller M atoms (M=C, Si, Ge) with the larger halides, a significant repulsion between larger X(= Cl, Br, I) atoms packing around the small M atom opposes this effect. Hence, the X-M-X bond angle starts out larger at $n = 2$ and decrease to 109.5 at $n = 4$. Extraordinary differences in the geometrical variations in the C compounds and the influence of the relatively low electronegativity of Si on bonding are discussed.