

Chad Crigger, Bernard Wittmaack, Kelling Donald

Department of Chemistry, Gottwald Center for the Sciences, University of Richmond,  
Richmond, Virginia 23173

**Analysis of Competing Bonding Parameters in Heavy Analogues of Halomethanes:  
Conformational Energies and Dipole Moments**

**Abstract:**

Tetracoordinate square planar group 14 compounds are of large interest to theoretical structural chemists and are intriguing targets for synthetic chemists. To gain a better understanding of energetic and structural variations in the halomethanes and their group 14 analogues ( $MH_{4-n}X_n$ ) ( $M = Si, Ge, Sn, Pb$ ;  $X = F, Cl, Br, I$ ), we use computational (MP2) methods to study the energy profiles for linear transits from the preferred tetrahedral (Td) to square planar (Sq-pl) geometry of the  $MX_4$  molecules. For  $CF_4$ , the energy barrier is  $\sim 6.0$  eV. This barrier is much less for  $M = Si$  through to  $Pb$  ( $< 3.2$  eV). As  $X$  gets larger the energy barriers decrease somewhat for C, but increase by fractions of an eV for other group 14 elements. The dependence of the conformational energies on  $M$  and  $X$  are explained by a competition between geometrical and electronic parameters i) the  $X\cdots X$  (electrostatic) hard sphere repulsive interactions, and ii) differences in the  $M-X$  bond strengths, going from  $X = F$  to  $X = I$ . We touch on another remarkable characteristic of these systems. Peak in the dipole moments of  $MH_{4-n}X_n$  ( $n = 1$  to  $4$ ) at  $n = 2$  for  $X = F$ , have been confirmed for the C, Si and Ge series, and are predicted for the stannanes and plumbanes. The peaks are explained by a serendipitous combination of conditions, including a relatively constant charge at F in the fluorides. The peaks disappear going to  $X=I$  as the charge distribution generally decreases by a large amount with  $n$ .