A QUANTUM CHEMICAL STUDY OF XH AND XH_2 (X=Be,C,N,O): $2s^2$ RECOUPLED PAIR BONDING

LU XU, D. E. WOON, and T. H. DUNNING, JR., *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

High level MRCI and RCCSD(T) calculations using large correlation consistent basis sets were used to study the low-lying states of the XH and XH_2 hydrides of the first row p block elements. Recoupled pair bonding is found in states such as the BeH $X^2\Sigma^+$ ground state, the BH $a^3\Pi$ excited state, the CH $a^4\Sigma^-$ excited state, the NH $A^3\Pi$ excited state, and OH $^2\Delta$ and $^2\Sigma^+$ excited states. The $2s^2$ recoupled bonding exhibited by these elements is similar to, but quantitatively different from, the $3p^2/3s^2$ recoupled pair bonding of the second row late p block elements (P, S, Cl). The differences arise from the well-understood distinction between the orbitals involved in recoupling. One of the dissimilarities between the two groups of elements is how favorable it is to form the second bond via covalent or recoupled pair bonding. In SF_2 and ClF_2, forming two recoupled pair bonds from the $3p^2$ pair is more stable than forming one recoupled bond and one covalent bond due to the antibonding character of the singly occupied orbital containing the electron left over from recoupling; using this orbital to form a second bond reduces the antibonding character and stabilizes the molecule. In B and C, the recoupled $2s^2$ pair is a set of lobe orbitals, and there is less driving force to bond to the second lobe than to the singly occupied 2p orbital that is also present. The X^2A_1 ground state of BH_2 and the X^3B_1 ground state of CH_2 are both therefore bent at about 130° with bonding that represents a linear combination of one recoupled bond and one covalent bond (the $X^1\Sigma_g^+$ ground state of BeH_2 is linear with two recoupled bonds because there is only one electron available in BeH($X^2\Sigma^+$)).