THE LOW-LYING STATES OF SF_n SPECIES (n=1–6): INSIGHTS INTO HYPERVALENCY FROM THE RECOUPLED PAIR BONDING MODEL

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High level MRCI and RCCSD(T) calculations with correlation consistent basis sets were used to characterize SF_n species. By examining both the stable structures and the bonding processes that occur during SF_n + F $\rightarrow$ SF_{n+1} additions, we have derived a new model for describing hypervalent behavior that we call recoupled pair bonding, in which a pair of electrons on S can be decoupled to allow formation of a bond with F. The new model accounts for the origin of hypervalency, the presence of low-lying excited states, and the structures and spectral properties of neutral and ionic SF_n species; it has more predictive capability than other models. For example, while SF and SF_2 both have covalently bonded ground states, they each have low-lying excited states with at least one recoupled pair bond. To the best of our knowledge, the SF($^4\Sigma^-$), SF_2($^3B_1$), and SF_2($^3A_2$) states have not yet been observed experimentally.