UNDERSTANDING THE MOLECULAR PROPERTIES OF ClF_n (n =1-7) SPECIES: AN APPLICATION OF THE RECOUPLED PAIR BONDING MODEL FOR HYPERVALENT BONDS

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Recently, new insight into the nature of hypervalent behavior led us to develop a model called recoupled pair bonding. In this model, two hypervalent bonds can be formed by decoupling a valence p^2 or s^2 electron pair. However, energy must be expended to decouple an electron pair, and the first bond is weakened as a consequence. The recoupled pair bonding model has been proven successful in our initial study of the SF_n (n =1-7) species. To further examine the applicability of this new model, this study explored the molecular properties of the ClF_n (n =1-7) series. Optimized ground state structures, bond energies, and spectral properties of these molecules were obtained by employing high level ab initio calculations [MRCI, CCSD(T)] with correlation consistent basis sets. Because of recoupled pair bonding, there are unanticipated low-lying excited states such as ClF ($^3\Pi$) and ClF_2 ($^2\Pi$,$^4\Sigma$). We also systematically explored the bond formation processes, adding F atoms one at a time to the optimized ClF_n ($1 \leq n \leq 6$) molecules. We find the bond energies for F addition to form ClF_2, ClF_4, and ClF_6 are much lower than those leading to ClF, ClF_3 and ClF_5. This oscillating trend is analogous to what is seen in the SF_n species, though the bond energies of the SF_n species are considerably greater than the ones for ClF_n. The lower bond energies of the even n species in the ClF_n series reflects the cost of decoupling paired electrons of the central atom, and the difference between ClF_n and SF_n reflects the fact that more energy is needed to decouple each of the $3p^2$ pairs of electrons of Cl than the single $3p^2$ pair of S. This behavior and other trends observed in ClF_n species demonstrate the improved predictive ability of the recoupled pair bonding model over other models for describing hypervalent bonding.