THEORETICAL PREDICTIONS OF THE STRUCTURES AND ENERGETICS OF $ClF_n^{+/-}$(n=1−5) IONS: EXTENDED STUDIES OF HYPERVALENT SPECIES USING THE RECOUPLED PAIR BONDING MODEL

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Following studies of the nature of covalent and recoupled pair bonding in PF_n(n=1−5), SF_n(n=1−6), and ClF_n(n=1−7), we have used the recoupled pair bonding model to investigate the $ClF_n^{+/-}$(n=1−5) ions. The behavior of the cation series parallels the SF_n series to great extent, while the behavior of the anion series would parallel that of ArF_n if those species were bound. In the present research, we predict experimentally measurable properties, such as the electron affinities (EA) and ionization energies (IE) of the associated neutral ClF_n species. The optimized ground state structures, bond energies, and spectral properties of $ClF_n^{+/-}$ were obtained by employing high level *ab initio* calculations (MRCI, CCSD(T)) with correlation consistent basis sets. Our predictions agree well with the structures of experimentally observed species, including ClF_2^+, ClF_2^-, ClF_4^+, and ClF_4^-. Low-lying excited states of $ClF^+(^4\Sigma^-)$ and $ClF_2^+(^3B_1)$, were also identified. We found the excited $^3B_1$ state of ClF_2^+ is bent with an angle of 154.8° and a bond length of 1.596 $\AA$ at the RCCSD(T)/AVQZ level. We also found a major difference between SF_2 and ClF_2^+: the $^3A_2$ state of SF_2 is bound while the same state of ClF_2^+ is repulsive. Second, we systematically explored the bond formation processes, adding F atoms one at a time to the optimized $ClF_n^{+/-}$($1 \leq n \leq 5$) ions. We found the ionization energies and the electronic affinities both exhibit an oscillating trend as seen in the bond energies of the neutral ClF_n species. The structural and energetic data obtained by our calculations might help spectroscopists to identify new $ClF_n^{+/-}$ species or to detect new electronic states of known species.