A QUANTUM CHEMICAL STUDY OF FAMILIAR AND EXOTIC LOW-LYING SINGLET AND TRIPLET STATES OF CH_2, CF_2, AND CHF

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High level MRCI and RCCSD(T) calculations using triple and quadruple zeta quality correlation consistent basis sets were used to study the low-lying singlet and triplet states of CH_2, CF_2, and CHF. The bonding in carbon was found to be very similar to that of sulfur, where there is also a competition between states that form through normal covalent bonding and recoupled pair bonding. The recoupled pair bonding model was used to investigate these states systematically to see how closely they resemble the behavior of SF_2, which has a $^1A_1$ ground state and $^3B_1$ and $^3A_2$ excited states. In addition to accounting for the separations and ordering of the lowest singlet and triplet states of each species, the less-studied $^3A_2$ states of CH_2 and CF_2 and the $^3A''$ state of CHF were investigated and compared to gain insight into the underlying reasons for the energetic and bonding differences between these species. Interestingly, the $^3A_2$ state of CH_2 is a cyclic structure, the $^3A_2$ state of CF_2 is bent but not cyclic (resembling the same state of SF_2), and the analogous minimum structure on the $^3A''$ surface of CHF is a C—HF complex.