MODELING SPIN-ORBIT COUPLING IN THE MONOHALOCARBENES

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The monohalocarbenes CHX (X = F, Cl, Br, I) are model systems for examining carbene singlet-triplet energy gaps and spin-orbit coupling. In a series of studies, our group and others have used Single Vibronic Level (SVL) emission spectroscopy and Stimulated Emission Pumping (SEP) spectroscopy to probe the ground vibrational level structure in these carbenes, which has provided a wealth of spectroscopic information and clearly demonstrated the presence of perturbations involving the low-lying triplet state for X = Cl, Br, and I. To model these interactions in more detail, we used the structures, harmonic frequencies, and normal mode displacements from *ab initio* and DFT calculations to calculate the vibrational overlaps of the singlet and triplet state levels, incorporating the full effects of Dushinsky mixing. These results were then incorporated with the purely electronic spin-orbit matrix element into a matrix diagonalization routine which calculated the term energies of the mixed singlet-triplet levels, which were iteratively fit to the extensive experimental results from SVL emission and SEP spectroscopy for the carbenes and their deuterated isotopomers. These calculations have allowed many new assignments to be made, particularly for CHI, and provided improved estimates of the spin-orbit coupling matrix elements and singlet-triplet gaps.