ABSTRACT

RESONANT TWO-PHOTON IONIZATION STUDIES OF NON COVALENT INTERACTIONS IN HALO AROMATIC CLUSTERS AND SPIN-ORBIT COUPLING MODELING IN MONO-HALOCARBENES

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Non-covalent interactions in bromobenzene have been studied here using resonance two-photon ionization (R2PI) spectroscopy combined with a linear TOF-mass spectrometer. Bromobenzene clusters were created in a supersonic expansion with helium as a carrier gas. The general trend observed in the R2PI spectra of all the clusters is the broadness and a red-shift relative to the monomer absorption. A few minimum energy dimers and trimmers have been found by density functional theory method, M06-2x/aug-cc-pVDZ. TD-DFT calculations of the different cluster conformers have been carried out, the excitation energies obtained confirms the experimental absorptions to cover a broad energy range. The broadness have been mainly attributed to the presence of different cluster isomers that can be present at the same time in a molecular beam. In the second part of this dissertation, we report a global analysis of spin-orbit coupling in the mono-halocarbenes, CH(D)X, where X = Cl, Br, I. The mono-halocarbenes are model systems for examining carbene singlet-triplet energy gaps and spin-orbit coupling. Experiments probing the ground vibrational levels in these carbenes have clearly demonstrated the presence of perturbations involving the low-lying triplet. To model these interactions more globally, we used a diabatic treatment of the spin-orbit coupling, where the matrix elements are written in terms of a purely electronic spin-orbit matrix element which is independent of nuclear coordinates, and an integral representing the overlap of the singlet and triplet vibrational wavefunctions. In this way, the structures, harmonic frequencies, and normal mode displacements from ab initio and DFT calculations were used to calculate the vibrational overlaps of the singlet and triplet state levels, incorporating the full effects of Duschinsky mixing. These results were then incorporated with the electronic spin-orbit matrix element into a matrix diagonalization routine that 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 halocarbenes and their deuterated isotopomers. These calculations have allowed many new assignments to be made, particularly for CHI, and provided spin-orbit coupling matrix elements and improved values for the singlet-triplet gaps.