INVESTIGATION OF THE MECHANISM OF INTERSYSTEM CROSSING IN S_1 ACETYLENE

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The simultaneously recorded Surface Electron Ejection by Laser-Excited Metastables (SEELEM, abbreviated LEM) and Laser-Induced Fluorescence (LIF) spectra of C_2H_2 provide information about the manifold of triplet states near-degenerate with the first excited singlet electronic state of this molecule. SEELEM detects states with long lifetimes due to large fractional triplet character (and less than 0.01 singlet character), and LIF detects states with short lifetimes due to large fractional singlet character. Therefore, SEELEM and LIF in combination allow one to study the intersystem crossing in C_2H_2 from a mechanistic point of view. SEELEM and LIF spectra have been subjected to a statistical analysis technique that has been developed to extract both qualitative and quantitative information about the nature of the singlet $\sim$ triplet coupling in S_1 acetylene. The new statistical method eliminates the need for assignment and fitting of all observed eigenstates. The type of questions related to the mechanism of intersystem crossing in C_2H_2 that the analysis technique addresses will be outlined. We will propose several optimized statistical schemes for processing either LIF spectra alone or the LIF/LEM combination, which enable the first step toward mechanism beyond the standard model of a bright state interacting with a statistical bath of dark states.