QUANTUM DYNAMICAL STUDY OF THE MULTI-STATE NONADIABATIC PHOTODISSOCIATION OF PYRROLE

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There has been a substantial amount of theoretical investigations on the photo-dynamics of pyrrole, often relying on surface hopping techniques or, if fully quantal, confining the study to the lowest two or three singlet states. In this study [1], we extend *ab initio* based quantum dynamical investigations to cover simultaneously the lowest five singlet states, two $\pi - \sigma^*$ and two $\pi - \pi^*$ excited states. The underlying potential energy surfaces are obtained from large-scale MRCI *ab initio* computations. These are used to extract linear and quadratic vibronic coupling constants employing the corresponding coupling models. For the N-H stretching mode Q24 an anharmonic treatment is necessary. Therefore, the vibronic coupling scheme is extended to more general functional forms of the diabatic potentials. The dynamical calculations rely on the multi-configurational time-dependent Hartree MCTDH approach [2]. In addition, a time-dependent picture of vibrational resonance Raman scattering [3], as well as a general scheme for the calculation of Raman excitation profiles within a MCTDH representation [4], will be presented. This scheme is built on improved relaxation approach suitable for calculation of the the excited vibrational states of the electronic ground state. Based on these dynamical calculations, Raman excitation profiles are computed including polarization effects. The calculated Raman-intensities and depolarization ratios are compared to the available experimental data.

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