VIBRATIONAL DYNAMICS AROUND THE CONICAL INTERSECTION OF METHOXY

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The stimulated emission pumping (SEP) spectrum of the methoxy molecule resulting from the transition from the $\tilde{A}^2A_1$ to the $\tilde{X}^2E$ state is calculated and compared to experiment. This work builds on the results of the talk by Nagesh and Sibert in which force fields for these surfaces are calculated and the vibrational states are calculated variationally using a curvilinear normal mode zero order representation. The role of the Jahn-Teller distortion on the increased spectral complexity is examined for this system as well as simple model systems. Specifically, a model Hamiltonian consisting of two vibrational degrees of freedom and the coupling between them is presented in a diabatic representation of the doubly degenerate electronic degrees of freedom. The observed complex dynamics are understood in terms of the multiple timescales that arise as the initial wave packet passes through the conical intersection. This time-dependent approach is extended to interpret the SEP spectrum of methoxy.