CAN INTERNAL CONVERSION BE CONTROLLED BY MODE-SPECIFIC VIBRATIONAL EXCITATION IN POLYATOMIC MOLECULES

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Nonadiabatic processes, dominated by dynamic passage of reactive fluxes through conical intersections (CIs) are considered to be appealing means for manipulating reaction paths. One approach that is considered to be effective in controlling the course of dissociation processes is the selective excitation of vibrational modes containing a considerable component of motion. Here, we have chosen to study the predissociation of the model test molecule, methylamine and its deuterated isotopologues, excited to well-characterized quantum states on the first excited electronic state, S_1, by following the N-H(D) bond fission dynamics through sensitive H(D) photofragment probing. The branching ratios between slow and fast H(D) photofragments, the internal energies of their counter radical photofragments and the anisotropy parameters for fast H photofragments, confirm correlated anomalies for predissociation initiated from specific rovibronic states, reflecting the existence of a dynamic resonance in each molecule. This resonance strongly depends on the energy of the initially excited rovibronic states, the evolving vibrational mode on the repulsive S_1 part during N-H(D) bond elongation, and the manipulated passage through the CI that leads to radicals excited with C-N-H(D) bending and preferential perpendicular bond breaking, relative to the photolyzing laser polarization, in molecules containing the NH_2 group. The indicated resonance plays an important role in the bifurcation dynamics at the CI and can be foreseen to exist in other photoinitiated processes and to control their outcome.