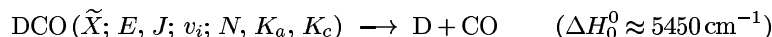


STIMULATED EMISSION PUMPING STUDIES OF HIGHLY VIBRATIONALLY EXCITED DCO (\tilde{X}^2A'): FROM SPECTRA TO UNIMOLECULAR DYNAMICS

F. TEMPS, *Institut für Physikalische Chemie, Universität Kiel, Olshausenstr., 24098 Kiel, Germany.*

The deuterated formyl radical, DCO (\tilde{X}^2A'), and its unimolecular dissociation reaction according to



provide a nearly ideal model system for investigating the unimolecular dissociation dynamics of highly vibrationally excited molecules at a fully quantum state resolved level. Stimulated Emission Pumping (SEP) experiments yield precise energies and widths, *i.e.* state-specific unimolecular decay rates, of ≥ 100 short-lived “resonance states” of the radical up to excitation energies of $18\,200 \text{ cm}^{-1}$, *i.e.* very far above the asymptotic dissociation limit. Great importance arises from an almost perfect 1 : 1 : 2 degeneracy between the radical’s three vibrational modes. Recent analyses of the measured spectra provide extraordinarily rich insight into the unimolecular dynamics. Focusing on these new results, observed spectra of DCO (\tilde{X}) are analyzed and assigned using an effective Hamiltonian based on a local mode, anharmonic oscillator, vibrational polyad model. The model calculations are in excellent agreement with the available experimental data *and* with the available quantum dynamics calculations. A one-to-one correspondence between the different data is established. The fitted parameters of the effective Hamiltonian reflect fundamental features of the PES and reveal the coupling between the conserved and disappearing oscillators during the dissociation. The calculated vibrational eigenfunctions are examined regarding their compositions in terms of chemically meaningful basis functions and regarding the fractionation of the bright state character (the CO stretching mode) among the other modes. The eigenfunctions are used furthermore to explore intramolecular energy redistribution rates and pathways. The state-specific unimolecular decay rates exhibit fluctuations over 4-5 orders of magnitude. Using the calculated wavefunctions from the polyad model, attempts are made to rationalize these fluctuations. Furthermore, the model in principle predicts *all* existing resonance states, giving direct access to the density of states in the continuum region of the PES above the D-CO dissociation limit. Results are compared with calculations employing classical phase space integration. Last but not least, the measured decay rates are compared with predictions by statistical unimolecular rate theory.