ROTATIONAL DEPENDENCE OF INTRAMOLECULAR DYNAMICS IN ACETYLENE AT LOW VIBRATIONAL EXCITATION AS DEDUCED FROM HIGH RESOLUTION SPECTROSCOPY

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The link between energy-resolved spectra and time-resolved dynamics is explored quantitatively for acetylene ($^{12}C_2H_2$), $\tilde{X}^1\Sigma_g^+$ with up to 8,600 cm^{-1} of vibrational energy. This comparison is based on the extensive knowledge of the vibration-rotation energy levels and on the model Hamiltonian used to fit them to high precision.[a] Simulated intensity borrowing features in high resolution absorption spectra and predicted survival probabilities for intramolecular vibrational redistribution (IVR) are first investigated for the $\nu_4 + \nu_5$ and ν_3 bright states, for $J = 2$, 30 and 100. The dependence of the results on the rotational quantum number and on the choice of vibrational bright state reflects the interplay of three kinds of off-diagonal resonances: anharmonic, rotational l—type, and Coriolis. The dynamical quantities used to characterize the calculated time-dependent dynamics are the dilution factor ϕ_d, the IVR lifetime τ_{IVR}, and the recurrence time τ_{rec}. For the two bright states $\nu_3 + 2\nu_4$ and $7\nu_4$, the collisionless dynamics for thermally averaged rotational distributions at $T = 27$, 270 and 500 K were calculated from the available spectroscopic data. For the $7\nu_4$ bright state, an apparent irreversible decay of is found. In all cases, the model Hamiltonian allows a detailed calculation of the energy flow among all of the coupled zeroth-order vibration-rotation states.

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[a]B. Amyay, S. Robert, M. Herman, A. Fayt, B. Raghavendra, A. Moudens, J. Thivin, B. Rowe, and R. Georges, J. Chem. Phys. <u>131</u>, 114301 (2009).