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 (\(^{12}C_2H_2\)), \(^1\Sigma_g^+\) 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 \(\nu_5\) 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 \(I - I'\) type, and Coriolis. The dynamical quantities used to characterize the calculated time-dependent dynamics are the dilution factor \(\phi_{IVR}\), the IVR lifetime \(\tau_{IVR}\), and the recurrence time \(\tau_{rec}\). For the two bright states \(\nu_5 + 2\nu_4\) 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.