ACETYLENE DYNAMICS AT ENERGIES UP TO 13,000 cm^{-1}

JONATHAN MARTENS, DAVID S. PERRY, *Department of Chemistry, The University of Akron, OH 44325-3601*; MICHEL HERMAN, BADR AMYAY, *Laboratoire de Chimie quantique et Photophysique, Universite libre de Bruxelles, B-1050, Belgium*.

The rotation-vibration Hamiltonian of acetylene is known in detail up to 13,000 cm^{-1} in the electronic ground state and allows the calculation of time-dependent dynamics for postulated excitations of certain bright states. The spectroscopic Hamiltonian, derived by Herman[a], includes four types of off-diagonal interactions: vibrational l-resonances, rotational l-resonances, anharmonic coupling, and Coriolis coupling. At high energies, hundreds of states may be coupled in each polyad and the rate and extent of intramolecular vibrational redistribution (IVR) increase substantially with rotational excitation. As each coupling mechanism becomes active, a hierarchical, sequential flow of probability through the different regions of phase space occurs on timescales ranging from 20 fs to 10 ps. As the energy is increased from one polyad to the next, the dynamics of similar bright states are similar; however, the dynamics depend critically on the nature of the bright state excited within a given polyad. The rotationally-mediated dynamics of the local CH stretch, the local bender and counter-rotator bright states are qualitatively similar to their normal mode counterparts.

[a]Didriche, K. Herman, M., Chem. Phys. Lett. 496, 1-7 (2010)