PHASE SPACE EXPLORATION OF ACETYLENE AT ENERGIES UP TO 13,000 cm^{-1}

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The rotation-vibration Hamiltonian of acetylene is known in detail up to 13,000 cm^{-1} in the electronic ground state, allows the calculation of time-dependent dynamics for postulated excitations of certain bright states. Three different measures of phase space exploration are examined including the participation number, Gruebele's dispersion, and the Shannon entropy. The time scales for phase space exploration span the range from 20 fs to 10 ps. The volume of phase space explored by the dynamics increases with energy and the rotational quantum number, J reaching about 90% of the (GOE) statistical limit at 12,000 cm^{-1} and J = 100. At low and intermediate J, the extent of phase space exploration is reduced for the local bender and counter-rotator bright states as compared to their normal mode counterparts. However, the phase space exploration of the local mode CH stretch state is similar to that of the corresponding normal mode vibration. These calculations shed light on the applicability of the energy randomization assumption that is at the heart of the Rice-Rampsberger-Kassel-Marcus (RRKM) theory of unimolecular reactions.