Hierarchies of Intramolecular Vibration-Rotation Dynamical Processes in Acetylene up to 13,000 cm^{-1}

David S. Perry [a], Jonathan Martens [a], Badr Amyay [b], and Michel Herman [b]

[a] Department of Chemistry, The University of Akron, Akron, OH, USA,
Tel.: 330-972-6825, E-mail: dperry@uakron.edu, jonmartens66@gmail.com;
[b] Laboratoire de Chimie quantique et Photophysique CP160/09, Université Libre de Bruxelles,
B-1050, Belgium, Tel.: 32-2-650-2417, E-mail: mherman@ulb.ac.be, badr.amyay@gmail.com

The vibration-rotation dynamics of $^1\Sigma_g^+$ acetylene are computed from a spectroscopic Hamiltonian with 468 parameters fit to 19,582 vibration-rotation transitions up to 13,000 cm^{-1} of vibrational energy. In this energy range, both the bending and the CH stretching vibrations can reach large amplitudes, but the maximum energy remains below the threshold for isomerization to vinylidene.

In contrast to the behavior at energies below 5,000 cm^{-1} [1], excitation of single bright states leads, in almost all cases, to computed intramolecular vibrational redistribution (IVR) that is irreversible on the timescales investigated [2]. Hierarchies of IVR processes on timescales ranging from 20 fs to 20 ps result when different bright states are excited. Different parts of the vibrational quantum number space are explored as a result of the four different classes of coupling terms:

(a) vibrational *l*-type resonance,
(b) anharmonic resonances, including DD4455 and DD1133,
(c) rotational *l*-type resonance, and
(d) Coriolis couplings.

The initial IVR rates are very different depending on whether the bright states are bending states or stretching states, normal modes or local modes, edge states or interior states. However, the rates of the rotationally mediated couplings do not depend substantially on these distinctions. Notably, the local bender bright state does not show special stability against the rotationally mediated couplings. The local bender involves motion along a coordinate that, at higher energy, becomes the reaction coordinate connecting acetylene to vinylidene.

The volume of phase space explored increases steadily over three decades of time for most bending bright states, showing a more-or-less linear increase on a logarithmic time scale. Different patterns are seen for *cis*-bend and CH-stretch bright states. The total volume of phase space explored depends strongly on the level of rotational excitation and also on the nature of the bright state.

[1] D. S. Perry, A. Miller, B. Amyay, A. Fayt, M. Herman, M. *Mol. Phys.* **108**, 1115 (2010).
[2] D. S. Perry, J. Martens, B. Amyay, and M. Herman, Hierarchies of Intramolecular Vibration-Rotation Dynamical Processes in Acetylene up to 13,000 cm^{-1}, *Mol. Phys.* **110**, 2687-2705 (2012).