BIRTH OF NEW VIBRATIONAL MODES IN BIFURCATIONS OF HIGHLY EXCITED NORMAL MODES

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At low energies, molecular vibrational motion is described by the normal modes model. This "standard model" breaks down at higher energy, with strong coupling between normal modes, and onset of chaotic dynamics. New anharmonic modes are born in bifurcations, or branchings of the normal modes. Knowledge of these new modes is obtained through the window of frequency-domain spectroscopy, using techniques of nonlinear classical dynamics. Spectra of highly excited C_2H_2 bends are analyzed starting with the effective polyad Hamiltonian used to fit experimental spectra. A semiclassical correspondence is used to obtain a reduced classical polyad Hamiltonian. Bifurcation analysis of the new modes born in bifurcations is performed using an analytical critical points method, without the necessity to integrate Hamilton's equations. Four new anharmonic modes are found which differ drastically from the ordinary normal modes of acetylene. Vivid animations show the dramatically different character of the new modes.

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