LARGE-AMPLITUDE BENDING DYNAMICS OF ACETYLENE

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We have investigated the large-amplitude bending dynamics of acetylene, in its ground electronic state, using an effective Hamiltonian model that reproduces all relevant experimental data (84 vibrational levels), up to 15,000 cm^{-1} in internal energy, with 1.4 cm^{-1} accuracy (1σ). This investigation has been made possible by a numerical pattern recognition analysis of our dispersed fluorescence (DF) data set for the acetylene $\tilde{A}^1A_u \rightarrow \tilde{X}^1\Sigma_g^+$ system, which includes DF spectra recorded from five different vibrational levels of the $\tilde{A}^1A_u$ state. Through this pattern recognition analysis, polyad quantum numbers have been assigned to observed transitions in the DF spectra up to $E_{vib} = 15{,}000\ \mathrm{cm}^{-1}$. Our analysis of the "pure bending" polyads, which involve excitation exclusively in the *trans* and *cis* bending modes, has revealed a rich, but in many ways, suprisingly simple, dynamics at high internal energy ($> 10{,}000\ \mathrm{cm}^{-1}$). Among the conclusions of this analysis is that, in many ways, the observed bending dynamics is somewhat simpler at 15,000 cm^{-1} than it is at 10,000 cm^{-1}; this rather surprising result can be explained in terms of qualitative changes in the structures of the pure bending polyads as a function of increasing internal energy. In addition, the eigenfunctions of the effective Hamiltonian at high internal energy are classifiable in terms of "local bending" and "librational" motions; this observation implies that a localized model of the bending dynamics is more appropriate at high internal energy than a normal model model, and we have derived analytical expressions for converting between these two representations of the dynamics.