REDUCED DIMENSION ROVIBRATIONAL VARIATIONAL CALCULATIONS OF THE S_1 STATE OF C_2H_2

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The bending and torsional degrees of freedom in S_1 acetylene, C_2H_2, are subject to severe vibrational resonances and rovibrational interactions, which result in the low-energy vibrational polyad structure of these modes. As the internal energy approaches that of the barrier to *cis-trans* isomerization, these energy level patterns undergo further large-scale reorganization that cannot be satisfactorily treated by traditional models tied to local equilibrium geometries. Experimental spectra in the region near the *cis-trans* transition state exhibit these complicated new patterns. In order to rationalize our near-barrier observations and predict the detailed effects of *cis-trans* isomerization on the rovibrational energy structure, we have performed reduced dimension rovibrational variational calculations of the S_1 state. Our calculation uses a high accuracy *ab initio* potential surface and a fully symmetrized extended-CNPI group theoretical treatment of a multivalued internal coordinate system that is appropriate for bending and torsional large amplitude motions. We will discuss these results and the insights they offer on understanding both large-scale features and spectroscopic details, such as tunneling staggerings, of barrier-proximal rovibrational levels of the S_1 state. We will also discuss spectral features by which barriers can be located and characterized in general polyatomic systems.