

## REDUCED DIMENSION ROVIBRATIONAL VARIATIONAL CALCULATIONS OF THE $S_1$ STATE OF $C_2H_2$

P. B. CHANGALA, J. H. BARABAN, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; J. F. STANTON, *Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*; A. J. MERER, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*; *Department of Chemistry, University of British Columbia, B.C. V6T 1Z1, Canada.*

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.