UNUSUAL ANHARMONICITIES IN ISOMERIZING SYSTEMS: THE S_1 STATE OF C_2H_2

J. H. BARABAN, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; J. F. STANTON, *Institute for Theoretical Chemistry, Departments 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.*

Low-barrier *cis-trans* isomerization profoundly affects the $\tilde{A}$-$\tilde{X}$ spectrum of acetylene. We present extensions of the usual effective Hamiltonian model that capture these effects, and thereby enable fits of the complete $\tilde{A}\ ^1A_u$ state $J = K = 0$ level structure up to 4300 cm^{-1} above the *trans* zero point level. The relationship between these new additions to the model and spectroscopic indicators of the transition state energy will also be discussed. One dimensional models will be used to illustrate both the effects of the isomerization dynamics on the spectrum and how they can be exploited to reveal the isomerization barrier height.