UNUSUAL ANHARMONICITIES IN ISOMERIZING SYSTEMS: THE $S_1$ STATE OF $C_2H_2$

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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.