TOWARD AN AB INITIO UNDERSTANDING OF QUANTUM TUNNELING DYNAMICS IN VINYL RADICAL: A VIBRATIONALLY ADIABATIC APPROACH

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Large amplitude tunneling in vinyl radical over a C_{2v} planar transition state involves CCH bending excitation coupled to all other internal coordinates, resulting in a significant dependence of barrier height and shape on vibrational degrees of freedom at the zero point level. An ab initio potential surface for vinyl radical has been calculated at the CCSD(T) level (AVnZ; n=2,3,4,5) for vibrationally adiabatic 1D motion along the planar CCH bending tunneling coordinate, extrapolated to the complete basis set (CBS) limit and corrected for anharmonic zero point effects. The polyatomic reduced moment of inertia is calculated explicitly as a function of tunneling coordinate, with eigenvalues and tunneling splittings obtained from numerical solution of the resulting 1D Schroedinger equation. Linear scaling of the CBS potential to match predicted and observed tunneling splittings empirically yields an adiabatic barrier height of ΔE_{adiab} = 1696(20) cm^{-1}, which, when corrected for zero point energy contributions, translates into an effective barrier of ΔE_{eff} = 1602(20) cm^{-1} consistent with estimates (ΔE = 1580(100) cm^{-1}) by Tanaka and coworkers (J. Chem. Phys. 120, 3604 (2007)). These zero point corrected potential surfaces are used to predict tunneling dynamics in vibrationally excited states of vinyl radical, providing strong support for recent jet cooled high resolution infrared studies (Dong et al., J. Chem. Phys. 127 (in press)) in the symmetric CH_2 stretch mode.