EQUILIBRIUM FOCUSED APPROACHES FOR CALCULATING TUNNELING SPLITTINGS IN FORMIC ACID DIMER

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Formic Acid Dimer (FAD) is the smallest molecule that is held together by a double hydrogen bond. This interesting type of bonding structure is commonly found in large biological systems. Gaining a clear understanding of such systems is an important, though challenging, endeavor since high level theoretical treatments of such systems are currently computationally intractable. Through an in depth study of the FAD system, insight into the general class of double hydrogen bonded molecules may be gained. The tunneling splittings present in FAD are sensitive to the details of the potential energy surface and therefore serve as a good point of comparison between theory and experiment. Madeja and Havenith (J. Chem. Phys. **117**, 7162 (2002)) have measured these splittings for the ground state as well as the state with one quantum of CO stretch excitation. We have calculated a three dimensional reaction surface potential for FAD while treating all other degrees of freedom as a set of coupled harmonic oscillators. The "reaction coordinate" changes dramatically across this surface. In fact, the coordinate which represents the minimum energy path at the hydrogen tunneling transition state is one of the highest frequency motions at equilibrium. These dramatic changes across the surface lead to strong couplings between the degrees of freedom. By focusing on the equilibrium configuration, i.e. where the wavefunction is large, methods have been developed which produce small and efficient representations in which to approach this system. With such tools at our disposal, the effects of vibrational excitation on the calculated tunneling splittings is examined. The theoretical symmetric OH stretch Raman spectrum and energy decay pathways are also presented.