A generalized reactive force field for nonlinear hydrogen bonds : hydrogen dynamics and transfer in malonaldehyde

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Using molecular dynamics (MD) simulations, the spectroscopy and dynamics of malonaldehyde is investigated. To this end, the recently proposed molecular mechanics with proton transfer (MMPT) potential is generalized to nonlinear hydrogen bonds. The calculated properties for malonaldehyde in both gas and condensed phases, including equilibrium geometries, infrared spectra, tunneling splittings, and hydrogen transfer rates, compare well with previous experimental and computational works. In particular, by using a harmonic bath averaged (HBA) Hamiltonian, which is based on a reaction path Hamiltonian, it is possible to estimate the tunneling splitting in an efficient manner. It is found that a zero point corrected barrier of 6.7 kcal/mol and effective masses of 1.234 (i.e., 23.4% larger than the mass of a physical H-atom) and 1.117 (for the physical D-atom) are consistent with the measured splittings of 21.6 and 2.9 cm(-1), respectively. The HBA Hamiltonian also yields a pair of hydrogen transfer fundamentals at 1573 and 1267 cm(-1), similar to results obtained with a reaction surface Hamiltonian on a MP2/6-31G(**) potential energy surface. This amounts to a substantial redshift of more than 1000 cm(-1) which can be rationalized by comparison with weakly (HCO(+): rare gas) and strongly (H(2)O-H(+)-OH(2)) proton-bound systems. Hydrogen transfer rates in vacuum and water were determined from the validated MMPT potential and it is found that the solvent enhances the rate by a factor of 5 at 300 K. The rates of 2.4/ns and 10/ns are commensurate with previous density functional tight binding ab initio MD studies.
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