VIBRATIONAL STATE DEPENDENT LARGE AMPLITUDE TUNNELING DYNAMICS IN MALONALDEHYDE

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The quantum dynamics of intramolecular proton transfer in malonaldehyde has represented a major challenge for first principles theoretical calculation, in large measure due to the highly concerted motion of all 9 nuclei throughout the tunneling event. This talk describes efforts to predict quantum state dependent tunneling rates from high level ab initio calculations, exploiting the large amplitude motion (LAM) Hamiltonian methods of Hougen, Bunker and Johns.[a] An effective adiabatic potential surface for the tunneling path is constructed from CCSD(T)/AVnZ-F12 calculations using explicitly correlated basis set methods and extrapolated to the complete basis set (CBS) limit. This potential is adiabatically corrected by zero point excitation in the remaining 3N-7 = 20 vibrational modes, with the multidimensional tunneling dependence of the effective mass explicitly taken into account[b] and numerically solved with Numerov methods. Of special importance, this method permits calculation of mode dependent tunneling splittings as a function of vibrational quantum state, which offers interesting prospects for comparison with recent FTIR slit jet cooled data of Suhm and coworkers.[c]

[a] J. T. Hougen, P. R. Bunker and J. W. C. Johns, J. Mol. Spectrosc. 34, 136 (1970). [b] D. J. Rush and K. B. Wiberg, J. Phys. Chem. A 101, 3143 (1997). [c] N. O. B. Luttschwager, T. N. Wassermann, S. Coussan and M. A. Suhm, Phys. Chem. Chem. Phys., DOI: 10.1039/c002345k (2010)