PROTON TUNNELING ESTIMATES FOR MALONALDEHYDE VIBRATIONS FROM SUPERSONIC JET AND MATRIX QUENCHING EXPERIMENTS

T. N. WASSERMANN, M. A. SUHM, *Institut f. Physikalische Chemie, Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany*; D. LUCKHAUS, *Chemistry Departement, University of British Columbia, 6174 University Blvd., Vancouver, BC, Canada*; and S. COUSSAN, *Laboratoire Physique des Interactions Ioniques et Moléculaires, UMR 6633, Université de Provence-CNRS, Centre St-Jérôme, 13397 Marseille Cedex 20, France*.

Malonaldehyde (MA) in its stable enolic form is known as a prototype molecule for fast intramolecular proton transfer processes in a double minimum potential with a relatively large ground state splitting of 21.58 cm^{-1}.[a] Due to its moderate size it is a popular testing case for theoretical model calculations. So far, only few examples of vibrationally excited tunneling splittings are known experimentally.[b,c]

We provide several new experimental estimates for excited state tunneling splittings in MA obtained by adiabatic cooling and symmetry breaking experiments in three different molecular states (isolated, coated by Ar layers and embedded in bulk Ar matrices).[d] The application of a straightforward approach allows the estimate of the splittings by the joint interpretation of gas phase, supersonic jet and matrix FTIR data. Our results constitute an important step towards a complete mapping of the MA tunneling splittings as a function of vibrational excitation and thus facilitate the critical assessment of multidimensional dynamical approaches.

[a] S. L. Baughcum, Z. Smith, E. B. Wilson, R. W. Duerst, J. Am. Chem. Soc. 106, 2250 (1984).
[b] C. J. Seliskar, R. E. Hoffman, J. Mol. Spectrosc. 96, 146 (1982)
[c] C. Duan, D. Luckhaus, Chem. Phys. Lett. 391, 129 (2004)
[d] T. N. Wassermann, D. Luckhaus, S. Coussan, M. A. Suhm, Phys. Chem. Chem. Phys., submitted (2006)