LARGE AMPLITUDE MOTIONS AND INFORMATION TRANSFER ALONG CONJUGATED BONDS: THE CASE OF PARATOLUALDEHYDE

HILKKA SAAL, JENS-UWE GRABOW, *Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Callinstraße 3A, D-30167 Hannover, Germany*; ANGELA R. HIGHT-WALKER, JON T. HOUGEN, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA*; WALTHER CAMINATI, *Universita di Bologna, Dipartimento di Chimica G. Ciamician, via F. Selmi 2, 40126 Bologna, Italia*; ISABELLE KLEINER, *Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS et Universités Paris 7 et Paris 12, 61 av. Général de Gaulle, 94010, Créteil, France.*

Historically, barriers to large amplitude motions are often related, using steric hinderance arguments, to the local atom arrangement. More recently, large changes have been found in the barrier inhibiting methyl rotation, when electronic excitation or ionization of a substituted toluene occurs,[a] suggesting molecular orbital occupancy as a dominant factor in aromatic molecules. Theoretically, the relation can also be made to the molecular orbital and electron density structure.

Experimentally, we examine the situation by comparing toluene with paratolualdehyde. In particular, the barrier in toluene, $CH_3 - C_6H_5$, is six-fold by symmetry. In paratolualdehyde, $CH_3 - C_6H_4 - CHO$, the aldehyde group is far enough from the methyl rotor that direct through-space interactions should be rather small. Thus, a three-fold contribution to the barrier would leave electron orbital effects in the π-system as the primary causal agent.

Microwave spectroscopy is well suited for discriminating between V_3 and V_6 contributions - but only if torsionally exited states can be accessed which typically requires temperatures much higher that than those encountered in pulsed-jet expansions. Thus, the supersonic-jet FT-MW spectrometers in Hannover and Gaithersburg as well as the free-jet CW mm-wave spectrometer in Bologna were needed to take the spectra. Analyzing 5 torsional species using the Belgi program, the barrier was found to vastly be dominated by the V_3 vs. a minor V_6 contribution, thus revealing the information transfer though conjugated π-electron systems.

[a] L. H. Spangler, J Rev. Phys. Chem. 48 (1997) 481-510