TUNNELING AND TUNNELING SWITCHING DYNAMICS IN PHENOL AND ORTHO-D-PHENOL: FTIR SPECTROSCOPY WITH SYNCHROTRON RADIATION AND THEORY

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The understanding of tunneling in chemical reactions[a] is of fundamental interest. A particularly intriguing recent development is the theoretical prediction of tunneling switching in ortho-D-phenol (C_6H_4DOH) as opposed to phenol (C_6H_5OH)[b] where only tunneling dominates the dynamics. For ortho-D-phenol at low energy, tunneling is completely suppressed due to isotopic substitution, which introduces an asymmetry in the effective potential including zero point energy. This localizes the molecular wavefunction in either the syn or the anti structure of ortho-D-phenol. At higher torsional states of ortho-D-phenol, tunneling becomes dominant, thus switching the dynamics to a delocalized quantum wavefunction. Therefore, we have investigated the rotationally resolved THz and IR spectra of phenol and ortho-D-phenol measured with our FTIR setup at the Swiss Light Source (SLS)[c] using synchrotron radiation. We have been able to analyse the torsional fundamentals, the first and second overtones of both isotopomers. A comparison of the spectra of phenol and ortho-D-phenol indicates the theoretically predicted behavior of tunneling switching upon excitation of the torsional mode. In detail, we shall discuss the splitting of the torsional fundamental, of its first and second overtones of phenol as well as the fundamentals of syn- and anti- ortho-D-phenol and the possible tunneling switching in the torsional overtone region of ortho-D-phenol. The results shall be also discussed in relation to the quasiadiabatic channel Reaction Path Hamiltonian approach[d]. We shall also discuss the comparison with results for meta-D-phenol.

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[c] S. Albert and M. Quack, *ChemPhysChem*, **2007**, *8*, 1271-1281, S. Albert, K. Keppler Albert and M. Quack, *High Resolution Fourier Transform Infrared Spectroscopy* in *Handbook of High Resolution Spectroscopy*, Vol. 2 (Eds. M. Quack and F. Merkt), Wiley, Chicester **2011**, 965-1021, S. Albert, K.K. Albert, Ph. Lerch and M. Quack, *Faraday Discussions* **2011**, *150*, 71-99.

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