Tunneling and tunneling switching dynamics in phenol, o-D-phenol and m-D-phenol: FTIR spectroscopy with synchrotron radiation and theory

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The understanding of tunneling in chemical reactions [1] is of fundamental interest. A particularly intriguing recent development is the theoretical prediction of tunneling switching in ortho- and meta-D-phenol (C_6H_4DOH) as opposed to phenol (C_6H_5OH) [2] where only tunneling dominates the dynamics. For ortho- and meta-D-phenol at low energy, tunneling is completely suppressed due to isotopic substitution, which introduces an asymmetry in the effective potential. It effectively localizes the molecular wavefunction at either the *syn* or the *anti* structure of ortho- and meta-D-phenol. At higher torsional states of ortho- and meta-D-phenol, tunneling becomes dominant, thus switching the dynamics to a delocalized quantum wavefunction. For that reason we have investigated the rotationally resolved THz and IR spectra of phenol, ortho- and meta-D-phenol in the range 200 to 1000 cm^{-1} measured with our FTIR setup at the Swiss Light Source (SLS) using synchrotron radiation [3,4,5]. We have been able to analyse the torsional fundamentals, the first and second overtones of the three isotopomers. A comparison of the spectra of phenol and meta-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- amd meta-D-phenol and the possible tunneling switching in torsional overtone region of meta-D-phenol. The results shall be also discussed in relation to the quasiadiabatic channel reaction path Hamiltonian approach [6] including time dependent multidimensional wavepacket dynamics.

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