

A COMBINED GIGAHERTZ AND TERAHERTZ SYNCHROTRON-BASED FOURIER TRANSFORM INFRARED (TERAHERTZ) SPECTROSCOPIC INVESTIGATION OF META- AND ORTHO-D-PHENOL: OBSERVATION OF TUNNELING SWITCHING

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Tunneling switching is of fundamental interest for certain experiments aiming at detecting parity violation in chiral molecules.^{a,b} A particularly intriguing recent development is the theoretical prediction of prototypical tunneling switching in meta- and ortho-D-phenol (C₆H₄DOH) as opposed to phenol (C₆H₅OH)^c where only tunneling dominates the dynamics: For meta and 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 vibrational energy in the lowest quasiadiabatic channel. This effectively localizes the molecular wavefunction at either the *syn* or *anti* structure of meta- and ortho-D-phenol. At higher torsional states of meta- and ortho-D-phenol, tunneling becomes dominant, thus switching the dynamics to a delocalized quantum wavefunction. The pure rotational spectra of the meta- and ortho-D-phenol were recorded between 60 and 110 GHz using an experimental setup^d which we have improved somewhat whereas the rotationally resolved vibrational spectra in the THz and infrared region were collected in the range of 200 to 1000 cm⁻¹ using synchrotron-based FTIR spectroscopy.^e The detailed assignment of the new GHz spectra including excited vibrational states, whereas previously only microwave spectra of the ground state were known,^f shall be discussed, in terms of the experimental evidence demonstrating tunneling switching in the first overtone of the torsional vibration of meta-D-phenol.

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