

## AN OH IN FLUORINE'S CLOTHING - THE CURIOUS ROTATIONAL SPECTROSCOPY OF PERFLUOROPHENOL

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Perfluorophenol ( $C_6F_5OH$ ) is analogous to hexafluorobenzene ( $C_6F_6$ ), with one fluorine atom replaced by a hydroxyl group. This substitution has a threefold effect: it provides a permanent dipole moment, the molecule remains very close to the oblate symmetric top limit, and intramolecular hydrogen bonds between the H and adjacent fluorine atoms are formed. Hydrogen can tunnel through the barrier to internal rotation of the OH group, lifting the degeneracy of the torsional states. These factors result in the unusual case of a polar, tunneling, near-symmetric top.

To probe these effects, the 1 K rotational spectrum of perfluorophenol between 7.5 and 17.5 GHz has been measured using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy. The asymmetry parameter ( $\kappa$ ) was experimentally determined to be 0.944, in agreement with the near-oblate geometries predicted by MP2/6-311++G(d,p) calculations. Tunneling splitting was observed for both *a*-type and *b*-type transitions due to the C-O bond axis lying between the *a* and *b* inertial axes; a consequence of the near-symmetry of perfluorophenol. The energy difference between the split  $0^+$  and  $0^-$  tunnelling levels was established to be 24.850 MHz. Preliminary wB97XD/6-311++G\*\* calculations estimate a barrier to internal rotation ( $V_2$ ) of approximately  $1211\text{ cm}^{-1}$ . The observed energy splitting is much lower than might be expected of this barrier height when compared to other phenolic derivatives, the exact reason for which is still to be understood.

