

14<sup>th</sup> June 2013 – 12:30  
 CFEL-bldg. 99, seminar room IV (O1.111)

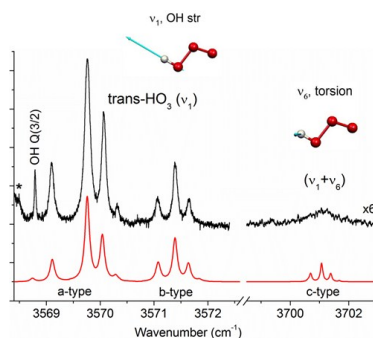
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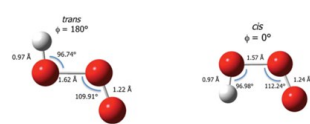
## Spectroscopy of the hydroxyl radical and HO-(O<sub>2</sub>)<sub>n</sub> clusters in helium nanodroplets

We are exploring the low temperature (0.4 K) *in-situ* association reactions between the hydroxyl radical (OH) and other small molecules, such as O<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>O. For example, upon sequential pick-up and solvation of OH and O<sub>2</sub>, the infrared spectrum in the 3500-3700 cm<sup>-1</sup> region reveals features that are assigned to the ν<sub>1</sub> (OH stretch) fundamental and ν<sub>1</sub>+ν<sub>6</sub> (OH stretch plus torsion) combination bands of the covalently bound *trans*-HO<sub>3</sub> isomer. Despite the characteristic low temperature and rapid cooling of helium droplets, there is no evidence for the formation of a previously predicted, weakly bound OH-O<sub>2</sub> van der Waals complex, which implies the absence of a kinetically significant barrier in the entrance channel of the reaction.

There is also no spectroscopic evidence for the formation of *cis*-HO<sub>3</sub>, which is predicted by theory to be nearly isoenergetic to the *trans* isomer. Stark spectroscopy of the *trans*-HO<sub>3</sub> species provides



$$H_{r,\phi} = -\frac{\hbar^2}{2} \frac{d}{dr} \theta_{rr} \frac{d}{dr} - \frac{\hbar^2}{2} \frac{d}{d\phi} \theta_{\phi\phi} \frac{d}{d\phi} + V(r, \phi)$$



vibrationally averaged dipole moment components that qualitatively disagree with predictions obtained from CCSD(T) computations at the equilibrium, planar geometry, indicating a floppy complex undergoing significant large-amplitude motion. A Hamiltonian in internal bond-angle coordinates is derived to account for this large-amplitude motion, and the expectation values of the inertial dipole moment components are compared to those obtained from the Stark spectra, revealing a fundamental error in the underlying single-reference CCSD(T) potential energy surface.