

## Spectroscopy of the Hydroxyl Radical, HOOO, and OH-C<sub>2</sub>H<sub>2</sub> in Helium Nanodroplets

Paul L. Raston<sup>a,b</sup>, Tao Liang<sup>a</sup>, Gary E. Douberly<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA,  
douberly@uga.edu

<sup>b</sup> School of Chemistry & Physics, The University of Adelaide, South Australia, 5005,  
paul.raston@adelaide.edu.au

The  $X^2\Pi_{3/2}$  hydroxyl (OH) radical has been isolated in superfluid <sup>4</sup>He nanodroplets and probed with infrared (IR) laser depletion spectroscopy. From an analysis of the Stark spectrum of the  $Q(3/2)$  transition, the  $\Lambda$ -doublet splittings are determined to be 0.198(3) and 0.369(2) cm<sup>-1</sup> in the ground and first excited vibrational states, respectively. These splittings are 3.6 and 7.2 times larger than their respective gas phase values, which can be compared to the factor of 1.5 increase previously observed for NO by Havenith and co-workers [1]. A model is presented that assumes a realistic parity dependence of the rotor's effective moment of inertia and predicts a factor of 3.6 increase in the OH ground state ( $J=3/2$ )  $\Lambda$ -doubling when the  $B_0^e$  and  $B_0^f$  rotational constants differ by less than one percent.

We have also explored the low temperature (0.4 K) *in-situ* association reactions between 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. Following the sequential pick-up and solvation of OH and O<sub>2</sub>, the IR spectrum in the 3500-3700 cm<sup>-1</sup> region reveals bands that are assigned to the  $\nu_1$  (OH stretch) fundamental and  $\nu_1+\nu_6$  (OH stretch plus torsion) combination band of the covalently bound *trans*-HOOO isomer. Despite the characteristic low temperature and rapid cooling of helium droplets, there is no evidence for the formation of the 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*-HOOO, which is predicted by theory to be nearly isoenergetic to the *trans* isomer.

Stark spectroscopy of the *trans*-HOOO species provides 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.

The ro-vibrational *a*- (OH) and *b*-type (CH) stretching bands of the T-shaped OH-C<sub>2</sub>H<sub>2</sub> complex reveal the effects of partially quenched electronic angular momentum. A model is presented, which accounts for this quenching phenomenon upon complex formation, along with a discussion of the expected He-solvation effects.

[1] K. von Haeften, A. Metzethin, S. Rudolph, V. Staemmler, and M. Havenith, Phys. Rev. Lett. 95, 215301 (2005).