SPECTROSCOPIC IDENTIFICATION OF TRANS-PERP HOONO

EUNICE X.J. LI, ILANA B. POLLACK, IAN M. KONEN, and MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323*.

The three-body OH + NO_2 + M $\rightarrow$ HNO_3 + M reaction is important in stratospheric ozone depletion because it converts reactive hydroxyl radical (OH) and nitrogen dioxide (NO_2) species into inactive nitric acid (HNO_3). Peroxynitrous acid (HOONO) is a less stable, secondary product of this reaction that competes with the production of HNO_3. At least two conformations of HOONO, cis-cis and trans-perp, are predicted to be stable. Although both are near prolate tops, they are predicted to have very different geometries, OH vibrational frequencies, and rotational constants. Asymmetric top rotational band simulations have been generated for both conformers using structural parameters from previous *ab initio* calculations.[a,b] Transition moments for the first overtone of the OH stretch were assumed to lie along the O–H bond. In our experiment, HOONO was generated in a supersonic expansion by photolysis of HNO_3 in argon carrier gas. An IR pump-UV probe technique was employed to obtain infrared action spectra of HOONO in the OH overtone region near 1.4 μm. The pure OH overtone was observed at 6971.4 cm^{-1} (band origin), and consists of four distinct features. The observed rotational band structure is in excellent accord with a simulation of trans-perp HOONO at 20 K having equal parts of a- and c-type transitions.

[a] S. A. Nizkorodov and P. O. Wennberg, *J. Phys. Chem. A* **106**, 855 (2002).
[b] M. P. McGrath and F. S. Rowland, *J. Phys. Chem.* **98**, 1061 (1994).