STRUCTURAL ANALYSIS 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*.

Peroxynitrous acid (HOONO) is a significant secondary product of the three-body OH + NO_2 + M $\rightarrow$ $HONO_2$ + M reaction, one of the most important processes in the chemistry of the lower atmosphere. We have photolytically generated HOONO in a pulsed supersonic expansion and determined the structure of the trans-perp (tp) conformer of HOONO using high-resolution (0.02 cm^{-1}) infrared action spectroscopy. Recent improvements in the production of HOONO and reduction of IR laser intensity to avoid power broadening have revealed extensive rotational band structure associated with the OH overtone transition of tp-HOONO at 6971.35(1) cm^{-1} (origin), which was previously hidden in the noise.[a] Subsequent analysis of the rotational band structure has yielded the ground and excited vibrational state rotational constants from a least-squares fit. Furthermore, the OH overtone transition dipole moment has been derived from the relative intensities of spectral lines arising from *a*- and *c*-type transitions. The spectral data is best simulated with a 0.2 cm^{-1} Lorentzian linewidth (at 4 K), which is attributed to lifetime broadening. Both the rotational constants and transition dipole moment are in good accord with *ab initio* values, confirming the spectroscopic identification of tp-HOONO. These quantities enable us to predict the spectral appearance of tp-HOONO under various experimental conditions, including atmospheric conditions.

[a] I. B. Pollack, I. M. Konen, E. X. J. Li and M. I. Lester, *J. Chem. Phys.* **119** (19), 9981 (2003).