OH-STRETCH/TORSION COUPLING AND QUANTUM YIELD EFFECTS IN THE $2\nu_{\mathrm{OH}}$ REGION OF THE *CIS-CIS* HOONO SPECTRUM

JULIANA L. FRY, ANDREW K. MOLLNER, MITCHIO OKUMURA, *Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125*; JOSEPH S. FRANCISCO, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*; and ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210*.

Peroxynitrous acid (HOONO) is a weakly bound isomer of nitric acid that is formed as a secondary product of the reaction of OH and NO_2. As the formation of nitric acid provides a sink for HO_x and NO_x in the atmosphere, the possibility of forming the less stable HOONO reduces the efficacy of this process. Recent spectroscopic studies of the intramolecularlly hydrogen-bonded *cis-cis* conformer of HOONO in the $2\nu_{\mathrm{OH}}$ region by Fry *et. al.*[a] and independently by Sinha and co-workers[b] indicated that the most intense feature in this region was 600 cm^{-1} to the blue of the feature that was assigned as the overtone.

This unusual intensity pattern led us to investigate a two-dimensional model of the potential and dipole moment surface for *cis-cis* HOONO. The potential was obtained at the CCSD(T)/cc-pVTZ level of theory/basis, while the dipole surface was evaluated at the QCISD/AUG-cc-pVTZ level of theory/basis. They were evaluated on a grid of 169 geometries with the four heavy atoms in a plane and the values of the six remaining coordinates chosen to minimize the electronic energy. The potential has a global minimum in the *cis-cis* conformation, but shows a broad shelf when the HOON torsion angle approaches 90°, the *cis-perp* conformation. Using this potential surface, the energies and wave functions were obtained and the wave functions were used, along with the dipole moment surface, to evaluate the intensities of the transitions. Excellent agreement between the experimental and calculated spectra are obtained when quantum yield effects are taken into account. It is found that the intense feature in the calculated spectrum reflect perpendicular transitions among the states that are just above the *cis-perp* shelf on the potential. In addition to a large increase in the density of states that are near-by in energy, the oscillator strength for these perpendicular transitions are larger than that for the overtone.

[a] J. L. Fry, S. A. Nizkorodov, M. Okumura, C. M. Roehl, J. S. Francisco and P. O. Wennberg, J. Chem. Phys. **121**, 1432 (2004).

[b] J. Matthews, A. Sinha and J. S. Francisco, J. Chem. Phys. **120**, 10543 (2004).