Peroxynitrous acid (HOONO) is a weakly bound isomer of nitric acid that is formed as a secondary product of the reaction of OH and NO₂. As the formation of nitric acid provides a sink for HO₂ and NO₂ in the atmosphere, the possibility of forming the less stable HOONO reduces the efficacy of this process. Recent spectroscopic studies of the intramolecularly hydrogen-bonded cis-cis conformer of HOONO in the 2νOH region by Fry et al. and independently by Sinha and co-workers 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 reflects 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.

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**References**
