

## THE $2\nu_{\text{OH}}$ OVERTONE SPECTRUM OF HOONO

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HOONO (peroxynitrous acid) is a minor but significant channel in the association reaction  $\text{OH} + \text{NO}_2$ . Formation of HOONO reduces the efficiency of this reaction for sinking radicals by reducing the yield of the major product nitric acid. HOONO was first detected via its first OH overtone spectrum, recorded by vibrational predissociation action spectroscopy at room temperature. This spectrum has many bands with anomalous intensity patterns, and their assignment remains uncertain. Three factors are believed to be important: quantum yield effects on the observed band intensities in the action spectrum, the presence of multiple conformers, and strong coupling of the OH stretch and HOON torsional modes. In this paper, we examine the first two factors. An experimental absorption spectrum is recorded by near infrared cavity ringdown spectroscopy (CRDS), to obtain intensities in the absence of quantum yield effects. The significant differences between the CRDS and action spectra demonstrate the importance of quantum yield on the action spectrum. A one-dimensional HOON torsional potential is calculated at the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ level, to predict the stability and existence of the low-lying *cis-perp* conformer relative to the lowest energy planar *cis-cis* conformer. These results allow us to assign the origin of the (*cis-cis*) isomer unambiguously, and suggest that much of the spectrum results from excitation out of torsionally hot states.