OH OVERTONE SPECTROSCOPY OF PEROXYNITROUS ACID (HOONO)

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The OH + NO_2 + M $\rightarrow$ $HONO_2$ + M reaction is a primary sink for reactive hydroxyl radical (OH) and nitrogen dioxide (NO_2) in the lower atmosphere. Peroxynitrous acid (HOONO), a secondary product of this reaction, has been generated via photolysis of $HONO_2$ followed by recombination of OH and NO_2, and then cooled in a pulsed supersonic expansion. Infrared spectra of HOONO in the first and second OH overtone regions were recorded using high-resolution action spectroscopy. The IR transition observed at 10195.3 cm^{-1} (origin) has been positively identified as the second OH overtone of the trans-perp conformer of HOONO based on its vibrational frequency, rotational constants, and transition type. The rotational constants show little change upon OH stretch excitation. Homogenous broadening was observed in rotational lines, and the apparent linewidth has been attributed to intramolecular vibrational redistribution. HOONO $(3\nu_{\mathrm{OH}})$ ultimately dissociates, producing primarily OH $(v = 0)$ products with a small contribution from $v = 1$. In addition, weaker features in the first overtone region provide valuable information on the torsional dynamics of HOONO.