

SPECTROSCOPIC CHARACTERIZATION OF HOONO AND ITS BINDING ENERGY VIA INFRARED ACTION SPECTROSCOPY

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The $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M}$ reaction is of fundamental importance in atmospheric chemistry because it is an important sink of reactive HO_x and NO_x radicals that directly affect the destruction of ozone in the stratosphere and the production of ozone in the troposphere. Peroxynitrous acid (HOONO), a secondary product of the $\text{OH} + \text{NO}_2$ reaction and a less stable isomer of HONO_2 , has been created in a pulsed supersonic free-jet expansion by reaction of photolytically generated OH radicals with NO_2 . An infrared pump-ultraviolet probe technique has been used to spectroscopically characterize the trans-perp (tp) conformer of HOONO. Infrared action spectra of tp-HOONO have been recorded in the OH overtone region near $1.4 \mu\text{m}$ using a single-mode optical parametric oscillator. Rotational structure of the pure OH overtone band has been observed at 6971.4 cm^{-1} (band origin). Experimental spectra have been assigned by comparison to simulated rotational band structure using rotational constants and estimated vibrational frequencies predicted by previous *ab initio* calculations. Infrared excitation of tp-HOONO in the OH overtone region provides sufficient energy to break the O–O bond leading to unimolecular dissociation into OH and NO_2 products in less than 6 ns (laser-limited). An OH ($v=0$) product state distribution was obtained following infrared overtone excitation. The highest populated OH $^2\Pi_{3/2}$ ($v=0$) state observed, $J = 15/2$, establishes a tp-HOONO binding energy of $D_0 \leq 17 \text{ kcal/mol}$, which is consistent with current theoretical estimates of the binding energy.