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

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The OH + NO_2 + M $\rightarrow$ $HONO_2$ + 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 OH + 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 μm 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 $D_0 \leq 17$ kcal/mol, which is consistent with current theoretical estimates of the binding energy.