VIBRATIONAL OVERTONE SPECTROSCOPY OF HOONO UNDER SUPERSONIC JET-COOLED CONDITIONS

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Peroxynitrous acid (HOONO) has been stabilized in a pulsed supersonic free-jet expansion following reaction of OH and NO_2 radicals. Both OH and NO_2 are photolytically generated inside a quartz capillary tube attached to a pulsed valve assembly. A dramatic increase in HOONO yield and decrease in unreacted OH have been achieved since our initial publication by varying the photolysis conditions. A spectroscopic search for HOONO vibrational features was then conducted in the OH overtone region using an infrared pump-ultraviolet probe technique. The resulting infrared action spectrum reveals an intense feature, previously identified as the OH overtone transition of the trans-perp (tp) conformer of HOONO, as well as several significantly weaker vibrational bands. A higher resolution scan reveals extensive rotational substructure for the tp-HOONO overtone that was previously hidden in the noise. Unfortunately, the weaker vibrational bands display no discernable rotational band structure. Therefore, possible band assignments are based on comparison of the observed vibrational frequencies with anharmonic frequencies calculated at the MP2/6-311G(d,p) level using Gaussian 03. This comparison suggests that the observed features arise from various hot band and combination band transitions of tp-HOONO. The OH overtone band arising from the more stable cis-cis (cc) conformer is not observed under these jet-cooled conditions, as expected from current estimates of its transition frequency and binding energy.