CHARACTERIZATION OF PEROXYNITROUS ACID (HOONO) IN CIS-PERP CONFIGURATIONS

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The three-body association reaction OH + NO_2 + M → $HONO_2$ + M is a primary termination step for atmospheric hydroxyl (OH) and nitrogen dioxide (NO_2) species. Peroxynitrous acid (HOONO) is a secondary product of this reaction that has at least two stable conformers, namely, cis-cis and trans-perp. Recent focus on HOONO has rested on a possible third minimum in cis-perp (cp) configurations. An analysis of the two-dimensional HOONO potential including the OH stretch and HOON torsion modes indicates that some of the torsional states are localized primarily in the cp shelf region. In our experiments, HOONO is generated in the gas phase via photolysis of $HONO_2$ followed by recombination of OH and NO_2 and subsequent cooling in a pulsed supersonic expansion. An IR transition at 6996.2 cm^{-1} (origin), +25 cm^{-1} relative to the first OH overtone transition of trans-perp, was observed using high-resolution action spectroscopy. The band contour is well simulated using rotational constants predicted for cp-HOONO at ∼5 K with an *a*:*b*∼1:1 hybrid band type. The vibrational frequency and transition type are in good accord with theoretical predictions for an OH overtone transition involving torsional states with predominately cp character. Furthermore, an O-O bond energy of 17 kcal mol^{-1} is deduced from the OH product state distribution, which is consistent with *ab initio* values. Based on the vibrational frequency, rotational band structure, stability of the observed feature, and comparison with theoretical calculations, this near-IR spectral feature is attributed to HOONO in cp configurations.