SIGNIFICANT RADICAL REACTIONS IN THE LOWER ATMOSPHERE: A NEW VIEW

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Significant production of peroxynitrous acid (HOONO), a weakly bound isomer of nitric acid and a secondary product of the OH + NO_2 association reaction, is predicted to have a profound impact on atmospheric models of NO_x chemistry as well as the ozone budgets of the troposphere and stratosphere. Recent spectroscopic studies in this laboratory have led to the definitive identification of the trans-perp conformer of HOONO under jet-cooled conditions. The first OH overtone transition (6971 cm^{-1}) exhibits clearly resolved rotational band structure characteristic of a near prolate asymmetric top, but with homogeneous broadening indicative of intramolecular vibrational redistribution. The second OH overtone transition (10195 cm^{-1}) shows substantially more broadening, but still displays a readily identifiable band contour. Infrared overtone excitation also induces unimolecular reaction dynamics, resulting in a nearly statistical OH product state distribution. This permits an experimental determination of the HOONO binding energy and an estimate for its yield under atmospheric conditions. Weaker spectroscopic features provide insight into the complex torsional motion and conformational dynamics of HOONO. [a] [b]

[a] Coworkers include I. M. Konen, E. X. J. Li, I. B. Pollack, and T. A. Stephenson.

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