

Does the Reaction of HO₂ with NO Produce HONO₂ and HOONO?

by

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HO_x (HO₂ and OH) and NO_x (NO₂ and NO) radicals are key intermediates in chemistry throughout the atmosphere; the HO_x and NO_x cycles catalyze ozone depletion in the stratosphere and ozone and photochemical smog production in the troposphere. Interconversion within the HO_x family and within the NO_x family happens continuously, partially through the reaction of HO₂ and NO to form OH and NO₂. Since these radicals are continually recycled, even a small branching yield of nitric acid (HONO₂) from the reaction of HO₂ with NO would impact radical concentrations predicted in the troposphere and stratosphere, by cumulatively sequestering radicals in a stable reservoir species.

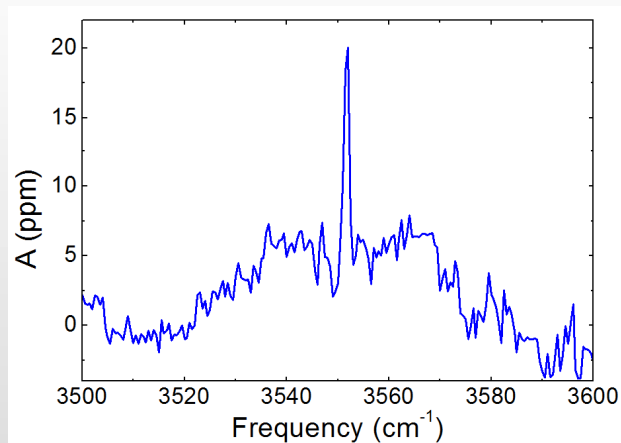


Fig. 1: Spectrum of pure HONO₂ ($4.0 \times 10^{12} \text{ cm}^{-3}$) at room temperature. HONO₂ was purified by vacuum distilling a mixture of HONO₂ (70% in water) and concentrated H₂SO₄ and added to the cell with (87 ± 2) torr of N₂.

Butkovskaya *et al.* observed a small yield of HONO₂ from the reaction of HO₂ with NO (0.5% at 1 atm and 298K) in a turbulent flow reactor using Chemical-Ionization Mass Spectrometry. We investigated this reaction by an alternative method: directly detecting the HONO₂ – as well as its weakly bound isomer HOONO – with Pulsed-Cavity Ringdown spectroscopy. HO₂ radicals were produced by Pulsed Laser Photolysis of Cl₂ in a slow flow cell, in the presence of methanol. Addition of 700 Torr of CO prevented unwanted HONO₂ formation from the reaction of OH and NO₂ and recycled HO₂. Our experiments provide a complementary approach, allowing detection of products spectroscopically on short time-scales (2.5 ms) in the absence of any wall reactions.