The Quantum Yield of NO_2 from Photodissociation of Peroxynitric Acid (HO_2NO_2)

Coleen M. Roehl, Stanley P. Sander, and Randall R. Friedl

Chemical Kinetics and Photochemistry Group
Jet Propulsion Laboratory
California Institute of Technology
M/S 183-901
4800 Oak Grove Drive
Pasadena, CA 91109

Investigations of the potential impacts of commercial operation of stratospheric aircraft on the chemistry of the upper atmosphere have mainly focused on the possibility of stratospheric ozone depletion by increased levels of nitrogen oxides. Model calculations have proven to be particularly sensitive to additional chemical processes which affect the partitioning between reactive and reservoir odd nitrogen species (NO_y) and a complete and accurate data base for NO_y is clearly necessary for a quantitative assessment of potential atmospheric effects. One nitrogen oxide specie that has still not been fully characterized is peroxynitric acid (HO_2NO_2), which is formed by the combination of HO_2 radical with NO_2 in the atmosphere. In the lower stratosphere, photolysis is a predominant loss process for HO_2NO_2, yet uncertainties exist in the product quantum yields. As an initial step to understanding the primary photochemical pathways of peroxynitric acid, the quantum yield of NO_2 was determined using laser photolysis of HO_2NO_2 at 248 nm followed by laser induced fluorescence of the NO_2 product. High purity peroxynitric acid was synthesized by the reaction of neat 90% H_2O_2 with NO_2BF_4 and concentrations were determined by UV absorption measurements taken at 214 nm in a cell located directly upstream of the photolysis chamber. The production of NO_2 from a measured concentration of HO_2NO_2 was compared to the NO_2 produced from the photolysis of a known amount of HNO_3 under identical experimental conditions,