

**CAVITY RINGDOWN SPECTROSCOPY STUDIES OF
ATMOSPHERIC REACTIONS: PEROXYNITROUS ACID
FORMATION AND ALKOXY RADICAL ISOMERIZATION**

Thesis by

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Abstract

This thesis describes laboratory experiments investigating atmospheric reactions using cavity ringdown spectroscopy (CRDS). The reactions studied were the formation of peroxyxynitrous acid (HOONO) in the termolecular association reaction $\text{OH} + \text{NO}_2$ (R1) and the isomerization of alkoxy radicals. Experiments were conducted in a gas flow cell combining UV photolysis to initiate reactions with infrared CRDS for the detection of products.

Formation of the weakly bound HOONO in the atmosphere reduces the yield of nitric acid (HONO_2) from R1 and lowers the efficiency of R1 as a sink for radicals. The *cis-cis* conformer of HOONO was detected through its fundamental ν_1 (OH-stretch) spectrum centered at 3306 cm^{-1} . The integrated absorbance of the ν_1 bands for HOONO and HONO_2 were measured with CRDS and used to calculate the branching ratio ($\text{BR} = k_{\text{HOONO}} / k_{\text{HONO}_2}$) of R1. Initial experiments using a microwave discharge to initiate R1 measured BR at 298 K and 14 torr, but were limited to low pressures by the discharge. BR was then reinvestigated using pulsed laser photolysis to initiate R1. BR was measured over the range 20–760 torr at 298 K.

In support of these branching ratio measurements, a detailed study of the spectroscopy of HONO_2 was conducted. CRDS experiments with moderate resolution (1 cm^{-1}) are known to give incorrect absorbances and line shapes when measuring spectral features with much narrower linewidths. However, the magnitude of these CRDS errors when probing a highly congested spectrum such as that of HONO_2 was unknown. We

observed reductions in the HONO₂ integrated intensity up to 60% and quantified these errors as a function of concentration and pressure.

Alkoxy radicals (RO) are an important class of intermediates in the oxidation of hydrocarbons, and they react via several mechanisms. For longer chain RO isomerization (forming HOR) becomes a major pathway, but isomerization rates have never been directly measured. Continuing work described in Eva Garland's thesis, we measured the infrared spectrum of alkoxy radical isomerization products (HOR and HORO₂) formed within 100 μs. We then used this spectrum to measure the relative rate of isomerization to reaction with oxygen for n-butoxy and 2-pentoxy radicals.

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