

**CAVITY RINGDOWN SPECTROSCOPY, KINETICS, AND QUANTUM
CHEMISTRY OF ATMOSPHERICALLY RELEVANT REACTIONS**

Thesis by

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Acknowledgements

In front of you is a huge book, a thesis full of research results. (Well, if you are anything like me, it's an electronic file instead of a book...) This book is a culmination of my graduate research: seven years of work packed into one tome. But really, there is far more than seven years of work that has gone into this thesis. And most of it has not come at my hands: the wonderful people in my life for the last 28 years have shaped everything that you will read about here. If you are reading this, you know my style: very precise, detailed, and perhaps long-winded. So bear with me as I spend a few pages thanking everyone that has helped make this thesis possible.

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Abstract

This thesis describes laboratory experiments and electronic structure calculations on three chemical systems relevant to tropospheric ozone chemistry: peroxyxynitrous acid (HOONO), hydroxymethylperoxy radical formed from $\text{HO}_2 + \text{HCHO}$ (R1), and products of alkoxy isomerization (R2). R1 and R2 were studied experimentally using a gas flow cell that combined UV photolysis with cavity ringdown spectroscopy (CRDS). All chemical systems were studied using electronic structure calculations and kinetics modeling.

HOONO is one of the products of the reaction $\text{OH} + \text{NO}_2$, and acts as a temporary reservoir for HO_x and NO_x in the atmosphere. Torsional excitation of HOONO will break its internal hydrogen bond, leading to sequence band formation in the OH stretch spectrum. Chapter 3 describes a calculated 3-dimensional potential energy surface to examine torsional mode coupling and sequence band formation. We apply these results to previous CRDS kinetics studies of HOONO.

The reaction of HO_2 with carbonyls is believed to be a major sink of HO_x and carbonyl compounds at reduced temperatures. R1 is the simplest of these reactions. Despite numerous previous studies, considerable uncertainty exists on the activation energy and rate constant of R1. Chapters 4–6 describe CRDS and electronic structure studies on the isomerization product, hydroxymethylperoxy. CRDS was used to make the first measurements of the OH stretch and A-X electronic spectra, and the kinetics of hydroxymethylperoxy chemistry. Electronic structure calculations were used to simulate the spectroscopic bands and examine the conformers of hydroxymethylperoxy and 2-hydroxyisopropylperoxy.

Atmospheric alkoxy radicals can isomerize or react with O₂, and each pathway has a different impact on ozone chemistry. Chapters 7–10 describe cavity ringdown spectroscopy, kinetics, and electronic structure calculations on the *n*-butoxy and 2-pentoxy isomerization products, specifically $\delta\text{-HOC}_4\text{H}_8\bullet$, $\delta\text{-HOC}_4\text{H}_8\text{OO}\bullet$, $\delta\text{-HO-1-C}_5\text{H}_{10}\bullet$, and $\delta\text{-HO-1-C}_5\text{H}_{10}\text{OO}\bullet$. CRDS was used to make the first measurements of the A-X electronic spectrum of $\delta\text{-HOC}_4\text{H}_8\text{OO}\bullet$ and clean OH stretch spectra of all four radicals. Relative kinetics data previously obtained using CRDS were reanalyzed to include the effects of additional alkoxy reactions. Electronic structure calculations were performed to explain the observations that the OH stretch absorption cross section differs between HOR \bullet and HOROO \bullet .

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