

**CAVITY RINGDOWN SPECTROSCOPY OF
THE NITRATE AND PEROXY RADICALS**

Thesis by

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In Partial Fulfillment of the Requirements

for the degree of

Doctor of Philosophy



California Institute of Technology

Pasadena, California

2011

(Defended May 23, 2011)

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ACKNOWLEDGEMENTS

I know that the Ph. D. journey can be difficult, but my years at Caltech have been some of my happiest, and I owe it to the incredible love and support that I have received from my family and Caltech family over the last years. I also would never have begun this journey without the love and support of past teachers and friends. I don't think that I was ever the normal child, but I was always a loved child, and for that I am eternally grateful.

To my mother, father, and brother: Thank you for supporting me, not only the past years in school, but throughout my entire life. You always let me be me. I was lucky to be born your daughter and sister, and I will always love you.

To my advisor Mitchio: I've learned to become a better scientist and mentor from our work together. Somewhere along the way, you became not only my advisor but my trusted friend. Thank you. I also thank your wife Laurie and the girls Mei-Li and Jinny for their laughter and smiles.

To my thesis committee, Geoff, Harry, and Rudy: I couldn't have asked for a merrier trio. You represent to me the spirit of the scientific community: the camaraderie, the knowledge, and the joy. Thank you.

To my fellow Okumurons: You were not only my research peers but were my friends and family outside of the lab. To all the current and past lab members, Aaron, Andrew, David, Julie, Andrei, Laurence, Dave, Kathleen, Sigrid, Kathryn, Leah, Thinh, Matt, Aileen, and Nathan, to all the summer students, Jonathan, Heather, Alex, Eric, Matthew, Geoff, and Marcus, and

to all the honorary Okumurons, Stan, Xu, Fred, Pin, and Ralph, thank you. Once an Okumuron, always an Okumuron. I'll always be yours.

To my friends at Caltech: There never was a girl who felt more loved. I apologize that I can't name everyone here individually, but thanks to the Potluck group, WMW, the floorball team, and the LA Dipoles. I also want to thank Jenelle and Adrienne. I've never had sisters, but you two are the best "older" sisters a girl could ever have. I also want to thank Laurence, who would have made an excellent twin.

To the various Caltech lab groups and collaborators: Thanks to the Blake, Barton, Sander, Wennberg, Seinfeld, and Rees groups for all the merriment and equipment. The gas phase and atmospheric communities have both been so kind. Anne, I owe you another Curious George book, and John, I make fun of you way too much. Terry and Ming-Wei, OSU was that much lovelier with your company

To Caltech staff: Thanks to Rick, Steve, Mike, and Tom for dealing with both me and the broken equipment, to Steve and Leah for orders, to Terry, Joe, and Ron for deliveries, to Carlette for fellowship work, to Linda, Anne, Agnes, Dian, and Laura for crazy paperwork, and to facilities for gas cylinders. Thanks also to Ernie, who is part of "Caltech staff" for me.

Finally, to my past teachers and friends: To my friends in high school and college, I learned from you how to be a better friend. To my teachers at Daniel and Prof. Darryl DesMarteau at Clemson, I learned from you how to be a better mentor. Thank you. To the University of Chicago, you gave me a chance to learn with the fellowship. It meant the world to me. And finally, to Prof. Laurie Butler and the Butler girls, you showed me the joys

of research. I never would have begun my journey without you. Thank you.

P.S. NSF and EPA: When I started the Ph. D. journey, I didn't even know that students get paid in graduate school. The fellowships gave me the freedom to pursue my dreams. I've made the best of my opportunities at Caltech and I have thoroughly enjoyed the journey. Thank you.

ABSTRACT

The chemistry of the Earth's atmosphere consists of complex networks of reactions. Photooxidation of volatile organic compounds (VOCs) in the atmosphere initiates free radical formation. These radicals attack other VOCs to form pollutants and secondary organic aerosols. Quantitative understanding of the radicals and reactions is needed for accurate modeling of the atmosphere. Many species are difficult to study due to low concentrations and short lifetimes. Spectroscopic methods in the ultraviolet and visible regions either do not have the sensitivity or the specificity to characterize these reactions. The work here examines the chemistry and physics of atmospheric radicals by using the sensitive and fast spectroscopic technique cavity ringdown spectroscopy (CRDS), to detect transient species in the near-infrared (NIR) region.

The nitrate radical NO_3 is a major nighttime oxidant in the troposphere. It is also a classic example of the breakdown of the Born-Oppenheimer approximation. The radical was first observed a century ago in atmospheric measurements. The structures of the three lowest electronic state however are still not well understood. Difficulties arise from the non-adiabatic Jahn Teller and Pseudo-Jahn-Teller effects. In Chapter 3, we examine the electronic-dipole forbidden $\tilde{A} \leftarrow \tilde{X}$ transition of NO_3 in the NIR to elucidate the \tilde{A} state of NO_3 . In Chapter 4, we examine the role of NO_3 in atmospheric reactions by detecting the peroxy radical intermediate of the oxidation of 2-butene by NO_3 .

The chlorine atom Cl is highly reactive and has been historically considered a coastal or marine layer oxidant. Studies now indicate that Cl atoms can play significant roles in urban mainland chemistry. Isoprene and 2-methyl-3-buten-2-ol (MBO232) are two important biogenic VOC

emissions. Isoprene alone is responsible for emissions of 500 Tg C y⁻¹. The peroxy radical intermediates of the oxidation of isoprene and MBO232 by Cl have never been detected using absorption spectroscopy. Chapter 5 includes the first preliminary CRD spectra of the $\tilde{A} \leftarrow \tilde{X}$ transition of Cl-isoprenyl and Cl-MBO232 peroxy radials in the NIR. We also outline kinetic experiments to measure the rates of reaction between the Cl-substituted peroxy radicals and nitric oxide (NO) and hydroperoxy radical (HO₂) under high and low NO_x conditions in the troposphere.

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