

Chapter 1

INTRODUCTION

To everyone who was kind and patient enough to show the world to a curious girl, the first chapter is for you.

1.1 The initial conversation

After a seminar on the quantum mechanics of atomic clocks, I asked a visiting scientist how he explained the significance of his work to a stranger on a plane. To my great surprise, he replied, "British maritime history." To my puzzled look, he continued, "When the British ruled the seas, they had the best marine chronometer and could calculate longitudinal coordinates better than anyone else. If we want to lead in the future, we need to be able to know time to the utmost accuracy." His reply was true but far removed from his earlier talk. It captured the essence of science: the pursuit of basic knowledge with the imagination to see the same ideas in the everyday world.

The everyday world my research occupies is the atmosphere of our planet. The Earth's atmosphere can be divided into separate layers, with humans occupying the lowest level, the troposphere. In elementary school, we learned that the Earth's atmosphere consists mostly of nitrogen (78%) and oxygen (21%). What was not taught to us was that it is the minority of the species (often less than 1 part per million) that drives the chemistry of the atmosphere. The reactions of these few species determine whether we have clear skies or smog formation.

The quality of the air we breathe has been tied to both the quality of life and public health.¹⁻⁵ The issue is not just an "urban" problem, as winds can transport pollutants on both local and global scales.⁶ While many

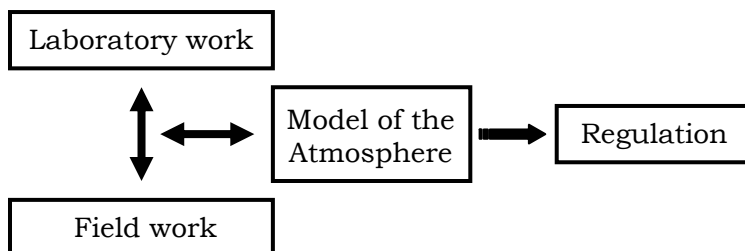


Figure 1.1. Diagram of the relationship among different branches of atmospheric chemistry. Parameters obtained in the experimental (laboratory/field) work are used by modelers to describe the chemistry of our atmosphere. The results are used by national and international governing bodies to better regulate the air quality.

reactions begin in the gas phase, the gas species can react further to form larger complexes until they begin to coagulate or form particles called secondary organic aerosols (SOA). These aerosols absorb or scatter energy from the sun, playing a major factor in determining the Earth's climate.⁷ Any regulation on global warming will have to involve understanding of the underlying gas phase chemistry forming these aerosols.

There has thus been both scientific and societal interest in accurately modeling the atmosphere of the Earth. The chemistry, however, is very complex with hundreds of reactions going on simultaneously. Considerable field work has been done to identify and measure concentrations of relevant species. *But where do these species come from? How fast do they form? How fast do they react? What do they form?*

Answering these questions requires complementary work in the laboratory, where the complex network of reactions can be isolated into individual reactions (Fig. 1.1). Some experiments focus on re-creating the atmosphere in a more controlled setting. Chamber experiments involve

adding known concentrations of gas phase species into a large Teflon bag and measuring product growth over long timescales. While such studies have provided useful data, there are often discrepancies in the measurements. Even a small percentage difference in the yields can lead to large errors in the atmospheric models. Accurate quantification of the parameters is thus critical.

Much of the discrepancy in the chamber experiments could be resolved by studying the reactions on shorter timescales. Due to the transient nature of the initiating species, the oxidation or reaction of the compounds occurs very quickly, ranging from the microsecond to millisecond timescale. The intermediates formed during oxidation can follow multiple pathways, resulting in a large range of products. If we could probe the intermediates directly, we could not only characterize the intermediate, but we could also conduct quantitative kinetic experiments, measuring the rate of reaction between the intermediate and gas species of interest and quantifying product yields of the various pathways.

Our initial conversation on the Earth's atmosphere has brought us to the laboratory to detect specific trace gas intermediates. That is the magic of science. The atmospheric problem is now a chemical physics problem. *How does one detect a species that is transient and exists only in low concentrations? How does one detect a species that has never been detected?* We explore the answers to these questions in the next section.

1.2 Detection of transient species

We would like to detect the transient species in a non-invasive manner. Laser spectroscopic methods are ideal, as absorption of low energy photons of light does not change the chemical nature of the species but allows identification, as compounds absorb energies of light characteristic

to their molecular rotations, vibrations, and electronic transitions. A spectroscopic method that is fast and sensitive is also necessary, as the species of interest have lifetimes on the microsecond to millisecond timescale and are low in concentration. In our laboratory, we use the laser method cavity ringdown spectroscopy (CRDS).^{8,9}

The sensitivity of spectroscopic methods is related directly to the probability of photons interacting with the sample. The earliest atmospheric experiments gained sensitivity by maximizing the pathlength of detection. For example, many people are familiar with current efforts to measure ozone levels in the troposphere. These measurements however have a rich history. In 1881, Hartley measured the ozone absorption of ultraviolet (UV) light by pointing a spectrometer at the sun from mountain tops across Europe.¹⁰ In 1918, a mercury lamp was set in one town and a spectrometer was placed four miles away in another valley to measure ozone levels directly in the troposphere.¹¹

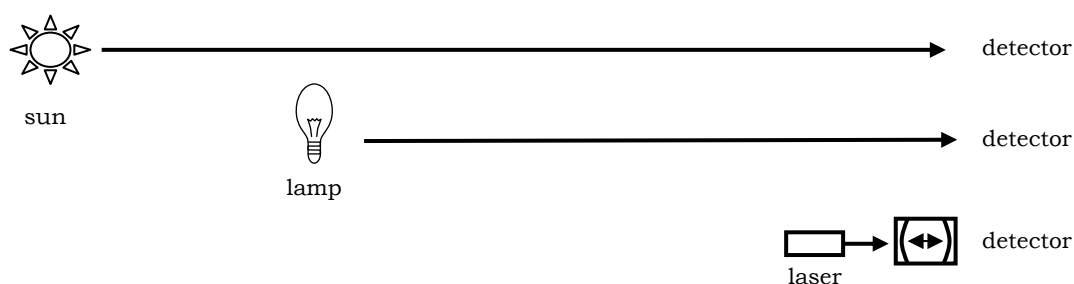


Figure 1.2. To achieve enough sensitivity to detect gas phase species in spectroscopic experiments, the detector and light source were historically placed kilometers apart. The optical cavity (shown on the bottom) is only a few centimeters in length. It uses highly reflective mirrors such that the effective pathlength the light propagates is equivalent to a few kilometers.

The measurements were amazing for their time, and there are still measurements being done today in which we point a laser to the sky and record the observations. These situations, however, are not ideal for a laboratory setting. One alternative is to place two highly reflective mirrors at the end of a sample cell. When laser light is injected into the cavity, the laser pulse is reflected back and forth such that the effective pathlength of the cell is equivalent to a few kilometers (Fig. 1.2). This is the underlying idea of CRDS.

CRDS allows for detection of species below 1 part per million. To truly appreciate the sensitivity of the technique, imagine measuring the height of Mt. Everest with a ruler. To match the relative sensitivity of CRDS, the measurement would have to be made with a precision of inches. CRDS also measures samples on the microsecond timescale, as the time of detection is related directly to the time it takes for light to be reflected about the cavity. Thus, CRDS is an ideal technique for directly probing the intermediates of atmospheric reactions.

Choosing the detection wavelength is governed by both the characteristic molecular trait by which we choose the species to be identified and the chemistry which we use to generate the species in the laboratory. The electromagnetic spectrum is shown in Fig. 1.3. Rotational, vibrational, and electronic transitions lie typically in the microwave, infrared (IR), and visible/UV regions, respectively. With commercial availability of sensitive detectors and high power laser sources, many experimental studies have been done in the visible and IR regions. While transitional energies are distinct to the species, many species absorb similar wavelengths of light. Overlapping spectral bands complicates individual identification and quantification of species.

In this work, we detect gas phase species in the near-infrared (NIR) region. Many species do not absorb photons in this region. Most intermediates of atmospheric reactions are highly reactive species called radicals. These radicals tend to have low-lying electronic transitions in the NIR. We run quantum mechanical calculations on the radical structure and electron density to predict the electronic transitional energies. The bands are then detected in the NIR using CRDS.

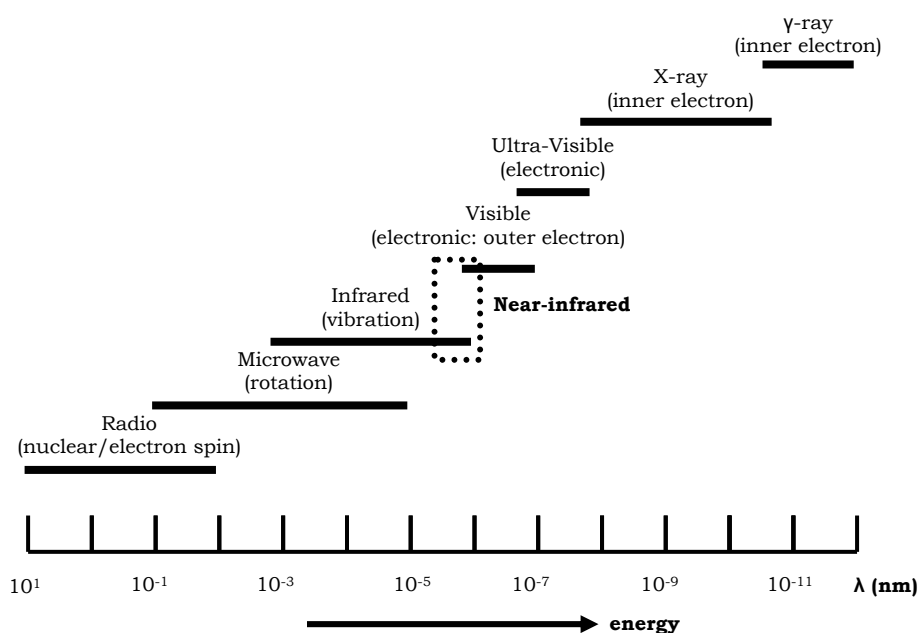


Figure 1.3. Diagram of the electromagnetic spectrum. As the wavelength gets shorter, each photon of light has more energy. For each region, the corresponding molecular transition is written in the parentheses. We conduct our experiments in the near-infrared, examining the rovibronic transitions of various gas phase species.

Before we conduct any experiments, the radical species must be generated in the laboratory. Often there are many ways to generate radicals. The ideal chemical method produces a high concentration of radicals with minimal secondary chemistry. Byproducts of the radical formation can have consequences for both detection and kinetic experiments. Products may absorb in the NIR and interfere with detection. They or subsequent products may react with the radical and complicate measurements of the

reaction rates. The physical manner in which we produce these radicals must also be considered. Thermal heat, electric discharge, laser photolysis, and chemical reactions are only a few examples of how radicals have been generated in the laboratory. Each approach requires a different set of chemicals and equipment.

The chemical methodology we choose is dependent on the purpose of the experiment. If the goal is to detect and characterize the radical, the method that produces the most abundant radical concentration without spectral interference is chosen. If the goal is to measure the kinetic rate constants, the method that minimizes secondary chemistry is chosen. For kinetic experiments, the physical method of radical production has to also allow for time resolution, as it is critical to measure the precise moment the radical is formed and begins to react with other gas species.

The ultimate goal of all experiments is to reproduce the most atmosphere-like conditions in the laboratory such that measurements made in the laboratory can be directly input to the atmospheric model. Many of the ideas behind the chemical methodologies originate from chemical reactions in the atmosphere. Thus, we now discuss the chemistry of the atmosphere.

1.3 The chemistry of the atmosphere: the role of the peroxy radical

The majority of atmospheric reactions are initiated by the sun. Stable compounds absorb solar energy and break apart into reactive species called radicals. These radicals attack other compounds to generate new species. The new species can continue to react in the gas phase or form SOA. Transport of species from different geographic locations and different atmospheric layers plays an important role in the atmosphere.¹² We focus on the chemical reactions in this work. Only a brief overview of

the chemistry is given here, as there are excellent books written on this subject.^{13,14}

Many of the compounds involved in the reactions are volatile organic compounds (VOCs).^{15,16} VOCs include hydrocarbon and oxygenated species from both biogenic and anthropogenic sources. Global biogenic VOC emissions contribute more than 1150 Tg (C) yr⁻¹, while anthropogenic VOC emissions contribute 100 Tg (C) yr⁻¹.¹⁷ In urban areas, anthropogenic sources still dominate.

The largest biogenic non-methane VOC emission is isoprene (Fig 1.4). Isoprene is naturally released by deciduous trees and contributes ~500 Tg (C) yr⁻¹.¹⁴ With two double bonds and multiple attack sites, isoprene is very reactive and can form a variety of products from oxidation by atmospheric radicals. The majority of anthropogenic VOC emissions are hydrocarbons from car exhaust and petrochemical plants. A breakdown of non-methane VOCs in an urban city such as Los Angeles showed VOC contributions from alkane (40-45%), alkene (10%), aromatic hydrocarbons (20%), oxygenated species (10-15%), and a small percentage of yet to be identified VOCs.¹⁸

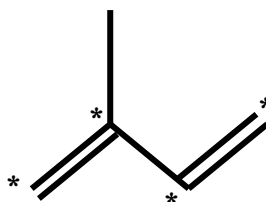
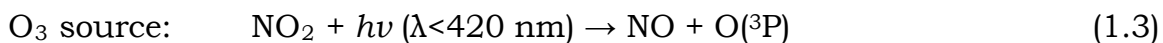
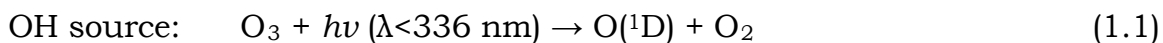


Figure 1.4. Isoprene is the most abundant non-methane VOC in the atmosphere. Upon oxidation, various products are formed. The asterisk (*) labels the various oxidation sites of isoprene.

The fate of VOCs in the troposphere is tied directly to the formation of the peroxy radical intermediate.¹⁹ The hydroxyl radical (OH) and ozone (O₃) are formed during the day:



The radical (X = OH, O₃) can abstract either a H-atom or react with the VOC to form an alkyl radical (R). In the presence of oxygen, the alkyl radical is immediately converted to a peroxy radical.



Peroxy radicals can follow many chemical pathways after formation (Fig 1.5). They can react with other peroxy radicals to form carbonyl compounds (RHO), hydroperoxides (ROOH), and alcohols (ROH). They can also react with nitric oxide (NO) to form alkoxy radicals (RO), which can initiate their own complex network of reactions.^{20,21} The chemistry of the troposphere is often categorized into two domains: low and high NO_x conditions, in which NO_x includes compounds NO, NO₂, and NO₃. In rural environments with low NO_x conditions, the peroxy-peroxy reaction pathways dominate. In urban environments with high NO_x conditions, the peroxy-NO reaction pathways dominate.

The significance of peroxy radicals can also be understood by their relation to other atmospheric networks. One of the most important

questions in tropospheric chemistry is whether we can accurately model ozone concentrations. There is a tendency in popular literature to use the misleading terminologies "good" and "bad" ozone. The "good/bad" refers not to the chemical composition of ozone (O_3) but to the different roles ozone plays in the atmosphere. In the stratosphere, ozone absorbs harmful UV rays. In the troposphere, ozone or inhalation of ozone is adverse to human health.²²⁻²⁵

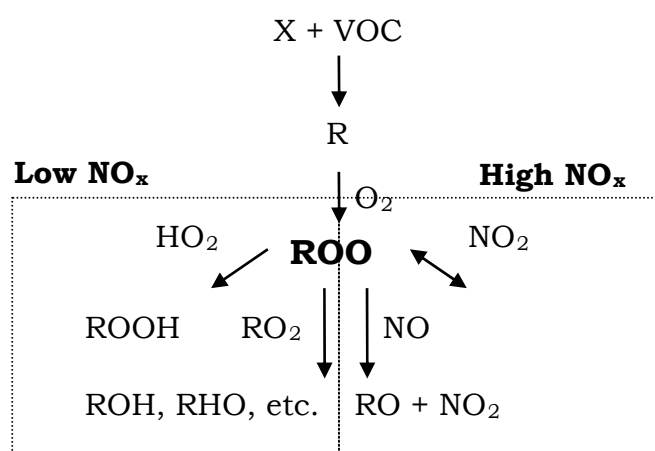


Figure 1.5. Schematic of the formation and subsequent chemistry of peroxy radicals. The peroxy radical can follow multiple pathways. Observed products can be grouped under low and high NO_x conditions. Measurement of the kinetic rate constants of the various species with ROO is critical for accurate modeling of the atmosphere.

In a polluted high NO_x environment, peroxy radicals react with NO to form alkoxy radicals and nitrogen dioxide (NO_2):



NO_2 can be photolyzed to form ozone (reactions 1.3-1.4). Thus, the two networks are connected. Peroxy radicals indirectly lead to ozone formation, while ozone-initiated oxidation of VOCs leads to peroxy radical formation. There has thus been much effort to characterize the peroxy radicals and their chemistry in the atmosphere. The simplest peroxy radicals include the hydroperoxyl (HO_2), methyl peroxy (CH_3O_2), and ethyl

peroxy ($\text{C}_2\text{H}_5\text{O}_2$) radicals. Rate constants for these radicals with HO_2 and NO have been measured to model low and high NO_x conditions, respectively.^{26,27}

In some cases, the radical can directly add to the VOC to form a substituted peroxy radical:



The substituted peroxy radicals can undergo similar reactions with NO and other peroxy radicals. There is, however, considerably less work on the kinetics and detection of substituted intermediates. Questions have risen with respect to the mechanism and yields of these addition reactions. *Does the radical addition lead to formation of substituted peroxy radical or is the adduct in quasi-equilibrium with the reactants? Are there new reaction pathways that need to be considered? Does the substituent on the peroxy radical affect its reactivity with other peroxy radicals and NO ?* These issues need to be resolved to gain a full picture of the peroxy and substituted peroxy radical chemistry in the atmosphere.

We have thus far mentioned VOC oxidation by OH and ozone. Along the marine coast, halogens (I , Br , Cl) also influence the chemistry of the atmosphere. Halogens are very reactive, and it is only their general low abundance in the atmosphere that limits their importance to non-coastal environments. Recent reports however may change this picture, as relatively high levels of nitryl chloride (ClNO_2) have been reported inland.^{19,28,29} ClNO_2 can photolyze to form both Cl atoms and NO_2 . We have already discussed the impact of NO_2 on ozone levels. Cl -initiated oxidation of VOCs must also be well-characterized.

At nighttime, there are no longer photolytic sources for OH, ozone, or Cl. Instead, another radical, the nitrate radical (NO_3), dominates the nighttime chemistry. NO_3 is very reactive and oxidizes VOCs as rapidly as other atmospheric radicals. During the daytime, however, NO_3 is destroyed by sunlight:



At nighttime, NO_3 becomes the most abundant oxidant in the troposphere. The reaction rates of NO_3 with various VOCs have been measured.^{30,31} NO_3 -substituted peroxy radicals, however, have never been detected in the gas phase.

NO_3 also has a rich history with other scientific communities and has proven to be an equally interesting and challenging problem in itself. We discuss in the next section how the nitrate radical has entertained experimentalists and theorists alike in the physical chemistry community.

1.4 A puzzle for many: the nitrate radical

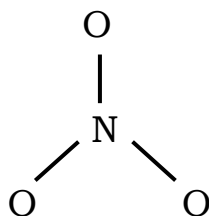


Figure 1.6. Picture of the NO_3 radical. This deceptively simple radical has proven to be a spectroscopic and theoretical puzzle for over a century.

Spectroscopic signatures of NO_3 were obtained in the visible region as early as 1880.³² Consisting of only four atoms, NO_3 appeared to be a simple system to calculate its electronic structures (Fig. 1.6). Modeling

the states of NO_3 is particularly important for accurate simulations of NO_3 oxidation of VOCs.

The Born-Oppenheimer (BO) approximation is often invoked to simplify quantum mechanical calculations. The approximation states that as electrons are very light in mass compared to nuclei in a compound, they should be able to instantaneously adjust to positional changes in the nuclei to minimize the overall energy of the compound. Mathematically, the wavefunction describing the electronic and nuclear motion of a molecular system can be separated into two functions. For NO_3 , however, this approximation is no longer valid. Thus, the quantum calculations becomes very challenging, and new theoretical approaches must be developed.

To test and push the development of accurate quantum models, quantitative features of the electronic states of NO_3 must be measured for comparison. NO_3 has been detected in the visible region; however it has been difficult to retrieve structural information from these spectra. Considerably less work has been done on NO_3 in the NIR region. We therefore use CRDS to probe NO_3 in the NIR region to elucidate the non-adiabatic effects of NO_3 .

1.5 Summary

We began with a simple conversation on the composition of the Earth's atmosphere and how it was the minority of the gas species that drives the chemistry of the atmosphere. The effect of air quality on public health and the role of aerosols in climate change make modeling the atmosphere both a scientific and societal issue. In order to model the atmosphere accurately, the complex network of reactions has to be studied in the controlled setting of a laboratory. We use the fast and sensitive

spectroscopic method CRDS to study the intermediates of VOC oxidation and measure their kinetic rate constants with other atmospheric species.

In particular, we are interested in the tropospheric peroxy and nitrate radicals. The *peroxy radical* is formed upon VOC oxidation and can follow many chemical pathways. Subsequent products have large consequences for the atmosphere, including ozone and smog formation. The *nitrate radical* is the primary initiator of VOC oxidation at night and can form substituted peroxy radicals. Although a small radical, NO_3 is proving very difficult to simulate, and more data is needed to better understand its non-adiabatic effects.

In the next chapter, we discuss the method of CRDS in more technical terms and provide details of our apparatus. In Chapter 3, we describe the non-adiabatic effects of NO_3 and the information we learned from the NO_3 spectra obtained in the NIR region. In Chapter 4, we discuss detection of the NO_3 substituted peroxy radicals in the NIR region using CRDS. Finally, in Chapter 5, we outline preliminary efforts to detect and conduct kinetic experiments on Cl-substituted peroxy radicals.

1.6 References

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