THE APPLICATION OF CAVITY RING-DOWN SPECTROSCOPY TO DETERMINE
NITRATE RADICAL CONCENTRATIONS IN THE ATMOSPHERE

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THE APPLICATION OF CAVITY RING-DOWN SPECTROSCOPY TO DETERMINE NITRATE RADICAL CONCENTRATIONS IN THE ATMOSPHERE

A

THESIS

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By

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Abstract

The nitrate radical, NO₃, is a potent atmospheric oxidant. Current NO₃ measurement methods average NO₃ concentrations over several kilometer pathlengths. Recent modeling studies predict that NO₃'s distribution is vertically inhomogeneous, causing previous NO₃ observations to not be representative of its atmospheric chemistry. In-situ measurements offer a test of these modeling predictions and a better understanding of NO₃ chemistry. In this thesis, we describe construction of an instrument capable of detecting NO₃ in-situ. This sensor is based upon cavity ring-down spectroscopy. Our initial work demonstrated that CRDS could sensitively detect NO₃. We then built and tested a field prototype during June 2001, successfully detecting NO₃ in the field. CRDS observations were compared to path averaged NO₃ observations. Similar time behavior of both signals indicated that the techniques were observing NO₃. A consistent difference in signal levels indicated that the two techniques were not sampling a homogeneous air mass.
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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Sinusoidal voltage component used to modulate laser frequency</td>
</tr>
<tr>
<td>AOM</td>
<td>Acousto-optic modulator</td>
</tr>
<tr>
<td>APD</td>
<td>Avalanche photodiode detector</td>
</tr>
<tr>
<td>AP</td>
<td>Anamorphic prism</td>
</tr>
<tr>
<td>CRDS</td>
<td>Cavity ring-down spectroscopy</td>
</tr>
<tr>
<td>CW-CRDS</td>
<td>Continuous-wave cavity ring-down spectroscopy</td>
</tr>
<tr>
<td>DC</td>
<td>Constant voltage component used to control laser frequency</td>
</tr>
<tr>
<td>DOAS</td>
<td>Differential optical absorption spectroscopy</td>
</tr>
<tr>
<td>ECDL</td>
<td>External cavity diode laser</td>
</tr>
<tr>
<td>FSR</td>
<td>Free spectral range</td>
</tr>
<tr>
<td>ID</td>
<td>Inner diameter</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperture</td>
</tr>
<tr>
<td>NBL</td>
<td>Nocturnal boundary layer</td>
</tr>
<tr>
<td>OD</td>
<td>Outer diameter</td>
</tr>
<tr>
<td>P-CRDS</td>
<td>Pulsed cavity ring-down spectroscopy</td>
</tr>
<tr>
<td>PHX 2001</td>
<td>Phoenix Sunrise Campaign 2001</td>
</tr>
<tr>
<td>PM</td>
<td>Polarization maintaining</td>
</tr>
<tr>
<td>SM</td>
<td>Single-mode</td>
</tr>
<tr>
<td>PFA</td>
<td>Perfluoro alkyl (a type of Teflon®)</td>
</tr>
<tr>
<td>PZT</td>
<td>Lead zirconate titanate Piezo-electric transducer</td>
</tr>
<tr>
<td>RDC</td>
<td>Ring-down cavity</td>
</tr>
<tr>
<td>RL</td>
<td>Residual Layer</td>
</tr>
<tr>
<td>TEM</td>
<td>Transverse electric and magnetic mode pattern of a resonator</td>
</tr>
<tr>
<td>UHP</td>
<td>Ultra high purity</td>
</tr>
</tbody>
</table>
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Chapter 1

Chemistry of the nitrate radical

1.1 Motivation for developing an in-situ NO$_3$ detector

Models of atmospheric chemistry, meteorology and deposition are the critical elements in the development and assessment of effective pollution control strategies. Accurate data on the spatial and temporal distribution of pollutants and other trace gases are necessary for testing these models. The ability of models to characterize correctly the behavior of atmospheric chemical systems rests on the data against which they are tested. Thus, it is critical that measurement techniques are sensitive, accurate, and capable of resolving the spatial and temporal variations of key chemical species.

The subject of this thesis is the application of a new, ultra-sensitive optical absorption technique, called cavity ring-down spectroscopy (CRDS), to measure free radical concentrations in the atmosphere. Free radicals (e.g. OH and NO$_3$) drive atmospheric oxidation chemistry by initiating the conversion of reduced compounds (i.e. NO and volatile organics) to more water-soluble products (i.e. acids) that are then deposited to the ground. Without free radical chemistry, the process of atmospheric oxidation would proceed exceedingly slow; therefore accurate data regarding free radical concentrations is important to understanding atmospheric oxidation chemistry. To demonstrate the application of CRDS to study free radical chemistry in the atmosphere, we have selected the nitrate radical, a potent oxidizer in the nighttime atmosphere.

While a large number of field and laboratory studies have been directed at understanding the role of NO$_3$ in the atmosphere, there remain a great number of questions to be answered. These questions arise, in part, due to a lack of adequate measurement techniques, and in part, due to the influence of nighttime meteorology. Thus, subsequent to this introduction, we outline the general reactions of the nitrate radical in the atmosphere in order to layout the uncertainties regarding NO$_3$ chemistry, the origin of these uncertainties, and how CRDS can help to resolve these problems.
Because CRDS is a relatively new spectroscopic technique, whose principles, and advantages over other spectroscopic methods, are not yet widely known to the scientific community, we describe the technique of cavity ring-down spectroscopy in chapter 2. In particular we detail how a CRDS measurement is converted to a molecular concentration, and consider some of the requirements of a CRDS setup that must be met in order to use the technique quantitatively. Because the atmosphere presents a mixture of interfering compounds and physical processes that pose challenges to any spectroscopic method, we consider the general difficulties associated with optically detecting the nitrate radical atmosphere in chapter 3.

At the point where we began these investigations, no molecular radical had been detected in ambient air using CRDS. We achieved this goal in 1999 by detecting NO$_3$ in ambient laboratory air. These efforts are discussed in chapter 4. We then began improving our laboratory system and designing a CRDS instrument for use in the field. Chapter 5 describes the design and quantification methods of our first field NO$_3$ sensor. Laboratory measurements of operational parameters for this field system are detailed in chapter 6.

During the summer of 2001, we deployed the instrument in conjunction with the Phoenix Sunrise 2001 campaign, sponsored by the U.S. Department of Energy. At this campaign, we successfully detected NO$_3$ in the urban atmosphere of downtown Phoenix, Arizona. In chapter 7, we present the data collected at this campaign and discuss the important implications of our results. In chapter 8, we present conclusions of this thesis and the NO$_3$ sensor development project to this point.

1.2 Introduction to nitrate radical chemistry

The nitrate radical (NO$_3$) impacts atmospheric chemistry in several ways. The nitrate radical is a potent oxidizer, and the major fate of many organic compounds in the nighttime atmosphere (e.g. isoprene and terpenes in rural regions or dimethylsulfide in marine environments). Reactions of the nitrate radical with organics provide a means of generating organic free radicals and subsequently hydroxyl radicals at night. Thus, the nitrate radical contributes directly and synergistically to the oxidizing capacity of the
atmosphere. Additionally, the NO₃ radical plays a role in the important nighttime conversion of NOₓ (NOₓ = NO + NO₂) to reservoirs of dinitrogen pentoxide (N₂O₅) and nitric acid (HNO₃). Both N₂O₅ and HNO₃ are readily removed from the atmosphere via wet and dry deposition processes, thus the nitrate radical can serve to control NOₓ at night. Several authors have detailed the chemistry of the nitrate radical [Heintz et al., 1996; Atkinson, 1997], and it is extensively reviewed by Wayne et al [1991]. In what follows, we present a general overview of nitrate radical chemistry in the atmosphere, and consider some of the outstanding questions that regard the role of NO₃ in the atmosphere.

1.3 Atmospheric sources and sinks of the nitrate radical

The dominant source of the nitrate radical in the atmosphere is the reaction between nitrogen dioxide (NO₂) and ozone (O₃),

\[ \text{NO}_2 + \text{O}_3 \xrightarrow{k_{1.1}} \text{NO}_3 + \text{O}_2 \]  

(1.1)

At 298 K, the rate constant is \( k_{1.1} (298 \text{ K}) = 3.2 \times 10^{17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [DeMore et al., 1997]. The rate of reaction 1.1 increases with the concentrations of NO₂ and O₃ and with increasing temperature. The temperature dependence is characterized by \( k_{1.1} (T) = 1.2 \times 10^{13} \exp(-2450/(T/\text{K})) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [DeMore et al., 1997]. Because the concentrations of both precursor species have increased in the industrial era, it is likely that role of NO₃ has become more important as a sink for primary pollutants [Wayne et al., 1991].

Substantial nitrate radical concentrations are only observed during the night because the NO₃ radical is rapidly photolyzed by visible light. For an overhead sun and clear sky conditions at sea level, the photolysis lifetime is approximately five seconds [Orlando and Calvert, 1993]. There are two photodissociation channels.

\[ \text{NO}_3 + h\nu (\lambda < 640 \text{ nm}) \xrightarrow{\phi_{1.2a}} \text{NO}_2 + \text{O} \]  

(1.2a)

\[ \xrightarrow{\phi_{1.2b}} \text{NO} + \text{O}_2. \]  

(1.2b)
Reaction 1.2a is the dominant pathway. Thus, most NO\textsubscript{3} that is present at sunrise leads to the formation of nitrogen dioxide and a ground state oxygen atom, which reforms ozone.

Significant concentrations of NO\textsubscript{3} will also build only in the absence of nitric oxide (NO), which reacts rapidly with NO\textsubscript{3} to form 2NO\textsubscript{2},

$$\text{NO} + \text{NO}_3 \rightarrow \text{2NO}_2. \quad (1.3)$$

At 298 K, \(k_{1.3}(298 \text{ K}) = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). The temperature dependent rate constant is \(k_{1.3}(T) = 1.5 \times 10^{-11} \exp(-170/(T/\text{K})) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{DeMore et al., 1997}].\)

Once the NO\textsubscript{3} radical is formed in the nighttime atmosphere, it rapidly establishes equilibrium with NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{5}.

$$\text{NO}_3 + \text{NO}_2 + \text{M} \leftrightarrow \text{K}_{eq} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (\text{M} = \text{third body}). \quad (1.4)$$

The value of the equilibrium constant at 298 K for the equilibrium reaction 1.4 is \(K_{eq} = 2.9 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1}\), and the temperature dependent equilibrium constant is \(K_{eq}(T) = 2.7 \times 10^{27} \exp(11000/(T/\text{K})) \text{ cm}^3 \text{ molecule}^{-1} [\text{DeMore et al., 1997}].\) For 1 ppbv of NO\textsubscript{2} and 50 pptv of NO\textsubscript{3} in equilibrium at 298 K and atmospheric pressure, the relaxation time (i.e. the time to reestablish equilibrium after some perturbation) is about 15 s. The high-pressure limit forward rate constant for reaction 1.4 at atmospheric pressure is \(k_{-1.4}(T) = 1.4 \times 10^{-12} ((T/\text{K})/300)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{DeMore et al., 1997}].\) Reaction 1.4 is the only known source of N\textsubscript{2}O\textsubscript{5}. Because N\textsubscript{2}O\textsubscript{5} is unstable at high temperatures, but relatively stable at lower temperatures, it can transport in cool air masses (i.e. at higher altitudes or latitudes). Upon re-warming it decomposes to form NO\textsubscript{3} and NO\textsubscript{2}. This process can serve as a source of NO\textsubscript{3} in the absence of sunlight, or a source of NO\textsubscript{x} during the day via the reverse of reaction 1.4 followed by reaction 1.2. Otherwise, loss processes of N\textsubscript{2}O\textsubscript{5} serve as indirect sinks of NO\textsubscript{3}. The major loss process for N\textsubscript{2}O\textsubscript{5} is heterogeneous hydrolysis on wet aerosols to form two molecules of nitric acid.

$$\text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(aq) \rightarrow \text{Aerosol} \rightarrow 2\text{HNO}_3(aq) \quad (1.5)$$
Reaction 1.4 and reaction 1.5 work in concert to remove NO₃ from the atmosphere. In effect, these reactions serve as a major removal process for NOₓ in wet, remote regions and contribute to the acidification of the atmosphere [Allan et al., 1999; Heintz et al., 1996; Platt et al., 1990].

The nitrate radical initiates the oxidation of organic compounds via either hydrogen abstraction, in the case of alkanes (RH), or by the addition to double bonds, in the case of alkenes (R₂C = CR₂).

\[ \text{NO}_3 + RH \longrightarrow \text{HNO}_3 + R \cdot \ldots \longrightarrow \text{oxidized products.} \quad (1.6) \]

\[ \text{NO}_3 + R_2C = CR_2 \longrightarrow R_2\cdot C - CR_2\text{ONO}_2 \ldots \longrightarrow \text{oxidized products.} \quad (1.7) \]

The reactions of NO₃ with many alkenes are fast and NO₃ serves as the main sink for these compounds in the atmosphere. Reactions between NO₃ and alkanes are slow, but directly lead to the formation of nitric acid (reaction 1.6). While these reactions have been studied extensively in the laboratory, their impact in the atmosphere is less certain as a result of limited field measurements.

1.4 Nitrate radical observations and outstanding questions

Nitrate radical concentrations are typically determined via some adaptation of differential optical absorption spectroscopy (DOAS) [Heintz et al., 1996]. DOAS measures the path-averaged concentration of a molecular species along a light path through the atmosphere (see chapter 3 for details of DOAS). Long pathlengths (1-15 km) are often required because NO₃ mixing ratios are typically low (e.g. 0 – 400 parts per trillion by volume (pptv)). For instance, Heintz and Platt (1996) observed an average NO₃ mixing ratio of 25 pptv in a long-term study performed in a clean environment. A DOAS instrument can be configured to measure either the total vertical column density of a molecule (i.e. the average concentration between the ground and the top of the atmosphere), or the average concentration of a molecule between two points on the earth. While the DOAS technique is robust, sensitive and capable of monitoring a couple of trace gas species at one time, practical limitations make it either difficult or impossible to
investigate many important postulates regarding the role NO$_3$ in the nighttime troposphere.

Path-averaged (e.g. DOAS) measurements of NO$_3$ concentrations are often difficult to compare with \textit{in-situ} measurements of other trace gas concentrations (e.g. NO$_2$, O$_3$, VOC and aerosols) because these techniques are observing different air masses. The spatial distribution of a chemical species is nearly impossible to decipher from a DOAS measurement due to the long pathlengths utilized in the observation. Thus, the chemistry determined through DOAS observations is path-averaged chemistry. Even comparing multiple species measured by DOAS can be problematic. For instance, an air mass could contain pockets of NO and NO$_3$ that are distributed along the DOAS light path. The path-averaged measurement would then predict that NO and NO$_3$ exist in the air mass, which cannot be the case due to reaction 1.3. The assumption of homogeneous air masses may be incorrect in many cases, and path-averaged concentrations may not be accurate indicators of the actual chemistry. This problem may be pronounced in the air over cities, where turbulence induced by tall structures causes the chemistry nearer to the city to differ from the chemistry in the open land surrounding the city.

Recently, vertical column measurements by Aliwell and Jones [1998] and Martinez and Perner [2000], and modeling results by Fish and Shallcross [1999], suggest that ground-based DOAS observations of the NO$_3$ radical are not likely representative of NO$_3$ concentrations throughout the lower nighttime atmosphere. Fish and Shallcross [1999] predict that the NO$_3$ concentration is greatest high above the surface layer. The origin of this effect lies in the vertical temperature structure of the near-surface atmosphere at night. During the day, chemicals emitted at the earth's surface are rapidly mixed by convection. During the night, radiative cooling at the surface results in the formation of a temperature inversion, corresponding to a stable nocturnal boundary layer (NBL), characterized by slow vertical mixing. Above this layer is the residual layer (RL) with near neutral stability. The RL contains the previous day's pollution that does not mix with the NBL. The NO$_3$ radical can be rapidly depleted in the near surface inversion layer (~300 m) \textit{via} reactions with surface emissions (\textit{i.e.} NO). As the surface emissions
do not transport vertically (i.e. they are essentially trapped or stratified in the NBL),
greater quantities of NO$_3$, aloft in the NBL, may be available to react with daytime
pollution that is trapped within the residual layer (300 m – 2 km). Consequently, ground-
level measurements may underestimate the oxidizing capacity of the atmosphere. High-
resolution vertical profiles of NO$_3$ are needed to test this hypothesis, and standard DOAS
measurements are not adequate.

An additional disadvantage of long-path absorption spectroscopy is that it cannot
explore the role of NO$_3$ chemistry indoors, which is thought to significantly contribute to
the mutagenicity of indoor air through the formation of nitro-polycyclic aromatic
hydrocarbons. Over a 24 hour period, Weschler and Shields [1997] found that indoor
NO$_2$ levels are normally between 20 and 50 ppbv, while O$_3$ levels were measured at
greater than 25 ppbv, indicating a production rate of NO$_3$ of ~2 ppbv per hour. Thus,
measurements of NO$_3$ precursors suggest that indoor production rates of NO$_3$ can be
comparable and even exceed outdoor NO$_3$ production rates. The NO$_3$ radical may turn
out to be very important with regard to indoor air pollution chemistry, but is yet to be
explored due to a lack of *in-situ* methods for NO$_3$ detection.

For these reasons, we are actively developing an *in-situ* technique, based on the
new ultrasensitive technique of cavity ring-down spectroscopy, to determine nitrate
radical concentrations in the atmosphere. Cavity ring-down spectroscopy achieves the
long effective pathlengths (20 km) that are required for sensitive detection, but in short
base pathlengths (1 m). CRDS achieves comparable sensitivities to DOAS, but with the
added feature of fast (e.g. averaging times on the order of seconds versus minutes in
DOAS), *in-situ* sampling and detection. An *in-situ* technique for nitrate radical detection
adds a new dimension to atmospheric chemistry research.
Chapter 2

Cavity ring-down spectroscopy (CRDS)

2.1 Introduction

Cavity ring-down spectroscopy (CRDS) is a sensitive absorption technique where the rate of light absorption rather than the magnitude of light absorption is used to determine molecular concentrations. Traditional absorption measurements require determination of two parameters: the initial power of the probe beam that passes through a sample \( P_0 \) and the power of the beam after it has been transmitted through the sample \( P_f \). The magnitude of transmitted power approaches \( P_0 \) as the concentration of the absorbing species decreases. The detection limit is reached when the two signals are statistically equal. By contrast, CRDS monitors the exponential decay of light that is introduced in an optical cavity composed of highly reflective mirrors. At a single wavelength, the lifetime associated with this exponential decay is related to the absorption coefficient of the gas contained in the cavity. The decay time is shortened for increased concentrations. Improvements in detection limits achieved in CRDS can be on the order of \( 10^3 \) or more compared to traditional optical absorption techniques for two primary reasons: (1) the absorption is determined from the time behavior of the signal and is thus independent of light source fluctuations, and (2) the sample pathlength is enhanced greatly (\( 10^4 \) times the base pathlength) by resonating the probe light in an optical cavity. Other attractive features of CRDS are its simplicity, and the absorption is measured on an absolute scale \( i.e. \) the method does not need calibration, just a knowledge of the molecules absorption cross section.

The origins of CRDS date back to the early 1980's. Herbelin et al. [1980] and Anderson et al. [1984] used an optical cavity to measure mirror reflectivities. These instruments were known commercially as cavity lossmeters. O'Keefe and Deacon [1988] were the first to use the CRDS concept for spectroscopy applications with gas phase samples. Prior to 1996, CRDS instruments employed pulsed lasers systems. In 1996,
Lehman proposed, and patented, the use of continuous-wave (CW) lasers in CRDS. Romanini et al. [1997] were the first to employ small, low-cost, CW diode lasers for CRDS. Several reviews of CRDS exist, including a comprehensive review that details the history of CRDS in a book dedicated to CRDS [Busch and Busch, 1999].

2.2 Basic CRDS principles

The optical cavity in CRDS is often referred to as the ring-down cavity (RDC). Light introduced into the RDC is stored between the mirrors in the form of oscillating magnetic and electric fields for a period of time that is dependent on cavity loss processes (described below). In general, the RDC consists of \( n \) mirrors with reflectivity, \( R \), and transmission, \( T \). Optical cavities are referred to as "stable" when the light is refocused within the cavity after successive reflections from the mirrors. A cavity is termed "unstable" when the light escapes after some number of reflections. In CRDS, the mirrors are separated at a distance such that a stable resonator is formed. There are many possible stable cavity configurations, constrained by the resonator \( g \) factor as defined by Siegman [Siegman, 1986]. In the case of a linear cavity of mirror separation, \( l \), and radius of curvature, \( r_c \), \( g = 1 - (l/r_c) \). Stable cavities have a resonator \( g \) factor that is between \(-1\) and \(+1\), where \( g = -1 \) is the concentric limit, \( g = 0 \) is the confocal limit, and \( g = 1 \) is the near planar resonator. For ring cavities, an analogous linear cavity can be used to analyze stability.

A CRDS measurement begins by injecting light into the RDC through the back of one the cavity mirrors. Introducing light into the resonator can be accomplished with either a pulsed laser (Pulsed-CRDS) or a continuous-wave (CW) laser (CW-CRDS). Because our application is CW-CRDS, we consider the later case. Figure 2.1 illustrates the sequence of single measurement. For a finite period of time, light from a CW laser is coupled into the resonator. During this "build-up" time, the intra-cavity power increases. A detector monitors the small fraction (~10\(^{-5}\)) of intra-cavity power that leaks through the output mirror. Once the transmitted power reaches a predetermined value, called the detection threshold, \( P_0 \) (Watts), the input beam is deflected via the action of an acousto
Figure 2.1 A block-diagram of a basic CW-CRDS setup. The ring-down cavity (RDC) is excited by the light from an external cavity diode laser (ECDL). An acousto-optic modulator (AOM) deflects the ECDL beam to terminate the build-up. A detector placed behind one RDC mirror monitors the decay transient.
optic modulator (AOM). The intra-cavity power, $P_{\text{cav}}$, decays in time as the beam circulates back and forth between the cavity mirrors. For an evacuated cavity, $P_{\text{cav}}$ is attenuated by a factor of $1 - R$ each time the beam strikes a cavity mirror. If the response of the intra-cavity medium is linear, the decay process is first order and thus exponential in time.

In general, the detected power as a function of time, $t$ (s), is

$$P(t) = P_0 e^{-rt}, \quad (2.1)$$

where $r$ (cm$^{-1}$) is the fraction of light intensity decrease per distance traveled in the RDC, and $c$ is the speed of light (cm s$^{-1}$). The decay profile is characterized by the ring-down time, $\tau$ (s), where $\tau = (rc)^{-1}$. Figure 2.2 shows a decay curve for $\tau = 60 \mu s$ (typical in ambient air for our RDC described later). The detected power (left axis) is plotted versus time (bottom axis). The upper axis shows the distance that the light has traveled within the resonator. At 60 $\mu$s, the effective sample pathlength is 18 km.

The ring-down time is dependent on the sum of cavity loss process, which occur through two mechanisms: (a) the mirrors fail to reflect some of the light intensity, and (b) particles and gases present in the cavity absorb and scatter light intensity. We refer to $b$ (cm$^{-1}$) as the fraction of light intensity lost per distance traveled due to extinction processes between the mirrors. Mirror loss is a result of scattering, $S$, absorption, $A$, and transmission, $T$, by each mirror. The sum of all mirror loss and reflection is unity, $T + S + A + R = 1$. Ring-down cavities typically use mirrors, with $R > 99.9\%$.

It is often convenient to consider cavity losses in terms of the unitless round-trip loss, $L_{rt} = l_{rt}r$, where $l_{rt}$ (cm) is the round trip length of the cavity. The total cavity round-trip loss of light intensity including the absorption by molecule, $X$, present inside the resonator at concentration, $[X]$ (molecules cm$^{-3}$), is

$$L_{rt} = [n(T + S + A) + bl_{rt}] + \sigma[X]l_{rt}. \quad (2.2)$$

where $\sigma$ (cm$^2$ molecule$^{-1}$) is the molecule's absorption cross section at the laser wavelength. We refer to the sum of the first two terms, $n(T + S + A) + bl_{rt}$, as the fraction
Figure 2.2 A calculated ring-down trace for $\tau = 60 \mu s$. The detector response (left axis) is plotted versus time (bottom axis). The distance traveled by the detection beam (top axis) is also shown.
of light intensity lost per round-trip in the absence of X, or baseline loss, $L_B$. We refer to the last term, $\sigma[X]l_{rt}$, as the round-trip absorber loss, $L_X$. The total round-trip cavity loss is $L_{rt} = L_B + L_X$. Measuring $L_{rt}$ and $L_B$, allows one to determine $L_X = \sigma[X]l_{rt}$. Thus, knowing the value of $\sigma$ at the laser wavelength allows direct calculation of $[X]$, the molecular concentration. Note that in cases where the spectrum of interest has rotational or vibrational resolution, $\sigma$ and $[X]$ should refer to the absorption cross section and concentration of the molecules in the state corresponding to the absorption transition (see section later).

Occasionally, we refer to the absorption coefficient, $\alpha$ (cm$^{-1}$), which is just the product of the absorption cross section, $\sigma(\lambda)$, and the molecular concentration in units of molecules cm$^{-3}$.

In the absence of absorbing molecules, X, we often refer to the ring-down time as the baseline ring-down time, $\tau_o$, where $\tau_o = l_{rt}/L_Bc$. We can define a fundamental limit on the baseline ring-down time by considering the case where mirror transmission is the only loss (i.e. $A = S = 0$), and the baseline extinction is zero (i.e. $b = 0$). Thus,

$$\tau_B \leq \frac{l_{rt}}{nTc}.$$  \hspace{1cm} (2.3)

This limit is seldom achieved because most mirrors scatter a significant fraction of the light.

2.3 Coupling light into the RDC

To use a CW laser as a light source in CRDS, it is necessary to build energy within the resonator. Optical cavities act as narrow frequency filters with transmission peaks at regularly spaced intervals. The set of allowed frequencies that can propagate inside the cavity are called "modes" of the resonator. The properties of optical cavities in CRDS have been discussed in detail by Hodges et al. [1996], Lehman and Romanini [1996], Zalicki and Zare [1995], and Busch and Busch [1999].
A linear optical cavity of mirror distance $l$ has both longitudinal and transverse modes, which are characterized by the mode indices $p$, $m$, and $n$. The frequency of a TEM$_{mn}$ (transverse electric and magnetic) mode having a longitudinal index $p$ and transverse indices $m$, $n$ is given by

$$\nu_{qmn} = \frac{c}{l_{rt}} \left[ p + (m + n + 1) \cos^{-1} (\pm g) \right].$$

(2.4)

Thus, the longitudinal mode spacing, also called the free spectral range (FSR) is

$$\nu_{\text{longitudinal}} = \nu_{p+1,mn} - \nu_{p,mn} = \frac{c}{l_{rt}}.$$

(2.5)

The transverse mode spacing is

$$\Delta \nu_{\text{transverse}} = \nu_{p,m+n+1} - \nu_{p,m+n} = \frac{c}{l_{rt}} \left[ \cos^{-1} (\pm g) \right].$$

(2.6)

The resonator modes can be regarded as the electric field distribution associated with any geometrical ray that follows a closed path in the resonator. Resonator mode patterns are labeled according to the number of nodes that are encountered when the beam profile is scanned horizontally and then vertically. The TEM$_{00}$ mode (the fundamental mode) propagates along the cavity axis with zero nodes across the beam profile (i.e. the profile is continuous). The beam profile is characterized by a Gaussian intensity distribution. Higher order modes (transverse modes) posses node(s) across the beam profile and resonate at a fixed frequency offset for the TEM$_{00}$ mode with the same longitudinal mode number, $p$. Thus, transverse modes appear as satellite peaks to the sides of the TEM$_{00}$ mode pattern. For instance, the TEM$_{11}$ mode possesses a node along the x-axis and a node along the y-axis. Thus, the profile of a beam propagating in the TEM$_{11}$ mode appears as four spots symmetric about the cavity axis (looking down the cavity).

Because the mirror reflectivity is not perfectly continuous across the entire mirror, higher order modes posses different ring-down times (they strike the RDC mirrors at different locations). Thus, it is important to selectively excite a single mode in the resonator to observe a reproducible ring-down time. Maximum overlap between the diode laser and the RDC is achieved by using the TEM$_{00}$ mode of the cavity because the ECDL beam is
nearly 100% TEM$_{00}$. Thus, efforts are made to align the beam in the resonator such that we maximize overlap with the TEM$_{00}$ modes of the RDC, and suppress excitation of higher order modes.

For the confocal resonator, where $g = 0$, equation (2.4) predicts that the transverse mode spacing is exactly one half of the longitudinal mode spacing. All modes where $2p+m+n$ is the same are degenerate and oscillate at the same frequency. Our cavity is designed to be shorter than confocal geometry to avoid overlap of high order transverse modes with the TEM$_{00}$ mode. Figure 2.3 illustrates the mode structure for a cavity that is designed shorter than confocal geometry, and aligned to suppress excitation of the higher order modes of the resonator.

Paldus et al. [1998] demonstrated that is possible to frequency lock the RDC to the laser source. The cavity-locked approach ensures single mode excitation with data acquisition rates limited only by the ring-down and buildup constants of the resonator. Romainini et al. [1996] demonstrated a simpler approach, where they scan the cavity modes (using a piezoelectric translator on one cavity mirror) back and forth across the laser frequency and chopping the light input when the cavity achieved resonance with the laser. We use a variant of this approach, where we scan the laser frequency over the cavity resonant modes to achieve a match between the laser and ring-down cavity. This frequency-matched approach was first demonstrated by Shultz and Simpson [1998]. The laser frequency is modulated by slightly more than one FSR to ensure that there is always at least one buildup and ring-down event in the modulation window. This method of mode matching is illustrated in figure 2.4(a). The final approach, which we describe in chapter 6, is to decrease the amplitude of the modulated laser frequency such that the laser frequency is modulating around just one of the cavities longitudinal modes (figure 2.4(b)). Decreasing the modulation amplitude (for equal scanning frequencies), allows the laser frequency to be in resonance with the cavity mode for a longer period of time compared to scanning the FSR. Thus, larger signals are observed at the detector.
Figure 2.3 An illustration showing the cavity mode structure of a linear optical resonator arranged shorter than confocal geometry. Transverse modes are degenerate for equal values of $m+n$. The resonator is aligned such that the laser $\text{TEM}_{00}$ mode overlaps the cavity $\text{TEM}_{00}$ modes, suppressing excitation of higher modes.
Figure 2.4 Two methods of coupling CW-laser light into the ring-down cavity. In case A, the laser frequency is scanned slightly greater than one free spectral range (FSR). In case B, the modulation amplitude of the laser is reduced, increasing the amount of time that the laser is resonance with a single TEM$_{00}$ mode.
Because the cavity mode structure shifts as a result of vibrations and temperature changes that change the cavity length, the cavity mode drifts outside the modulation window. Therefore, a tracking circuit (described in chapter 6) must be employed to follow these changes.

2.4 Photocycling in CRDS

Ring-down cavities (~ 1 m base pathlength) commonly achieve effective pathlengths on the order of $10^4$ m. The small mode volume of the optical resonator used in CRDS leads to a much smaller detection volume compared to other long-path techniques (see table 2.1). Therefore, the effect of passing a laser beam many times through a relatively small number of molecules is a concern. To preserve the quantitative nature of the CRDS measurement, the laser beam must not alter the molecules in the detection volume. Photoalteration of the molecules will lead to errors in measurements of atmospheric trace gas concentrations, absorption cross sections, rate constants, and photochemistry. To address possible photoalteration artifacts, we introduce the photocycling number, $n_c$, that is used to determine conditions when CRDS can be used for quantitative absorption measurements.

The photocycling number is defined as the number of photons absorbed per molecule during a ring-down transient. When $n_c << 1$, CRDS will not suffer any experimental artifacts because only a small fraction ($n_c$) of the molecules absorb a photon. In this low photocycling case ($n_c << 1$), the ground-state concentration of molecules is not significantly altered by the absorption of light. Therefore, the loss of light intensity caused by molecular absorption is constant and the ring-down transient is purely an exponential decay. When $n_c \geq 1$, molecules must sequentially absorb photons and relax many times for CRDS to maintain the ground state concentration and thus the exponential character of the ring-down decay profile.

There are two types of photocycling behavior that could result in non-exponential ring-down transients for a value of $n_c$ not much less than one photon per molecule. In
Table 2.1 A comparison of long-path absorption techniques.

<table>
<thead>
<tr>
<th>Spectroscopic Technique</th>
<th>Base pathlength (m)</th>
<th>Effective pathlength (m)</th>
<th>Detection volume (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOAS</td>
<td>$10^3$-$10^4$</td>
<td>$10^3$-$10^4$</td>
<td>$10^3$-$10^3$</td>
</tr>
<tr>
<td>Multipass absorption</td>
<td>~1</td>
<td>$10^{-3}$-$10^3$</td>
<td>$10^{-5}$-$10^3$</td>
</tr>
<tr>
<td>Cavity ring-down</td>
<td>~1</td>
<td>$10^3$-$10^6$</td>
<td>$10^7$-$10^6$</td>
</tr>
</tbody>
</table>
the first case, the molecules undergo a chemical change on absorption of photons (e.g. photolysis or rearrangement). If the total quantum yield for photodestruction (photodissociation, photochemical reaction, etc.), $\phi$, is known for the molecules, and $\phi n_c << 1$, then only a negligible fraction of molecules are destroyed during a ring-down transient. Thus, CRDS may be applied. In the second case, the relaxation time of the molecules is long enough for the molecules to remain in the excited state, depleting the ground-state population. Thus, a photocycling number that is not significantly smaller than one photon per molecule may indicate saturation. Saturation effects have been recently observed in CW-CRDS of jet-cooled NO$_2$ molecules [Romanini et al., 1999]. In many cases it is possible to minimize $n_c$ through the experimental setup and ensure that the decay of light within the cavity is purely exponential.

Zalicki and Zare [1995] have addressed other mechanisms that lead to nonlinearity in CRDS. They found that the laser linewidth must be narrower than the absorption feature in order for the decay to be purely exponential. Because our primary application in this paper is CW-CRDS, where the laser linewidth is nearly always narrower than the absorption feature being measured, we do not suffer from nonlinearity of the type described by Zalicki and Zare [1995]. This section describes another mechanism by which CRDS measurements may be corrupted. Therefore, we only consider photocycling in this section with the caveat that both mechanisms should be considered in the general case.

2.5 Derivation of the photocycling number

In deriving our expressions for $n_c$, we assume that the molecules in the detection volume at the start of a ring-down transient remain within the detection volume for the duration of the ring-down transient. For typical values of the ring-down time and at atmospheric pressure, this static gas assumption is justified (see discussion). Thus, the number of molecules exposed to the laser beam is $[X]V$, where $V$ (cm$^3$) is the beam volume. These molecules absorb some of the light energy that has been injected into the cavity. We term this energy $E_x$. The energy absorbed by the molecules can be
converted to the number of photons absorbed by the molecules, $N_X$, through Plank's relation. The number of photons absorbed is

$$N_X = \left(\frac{\lambda}{hc}\right)E_X,$$

(2.7)

where $h$ (J s) is Plank's constant, and $\lambda$ (m) is the laser wavelength. For an arbitrary molecule, X, the photocycling number is equal to the ratio of the total number of photons absorbed to the total number of molecules exposed to the laser beam,

$$n_c = \frac{N_X}{[X]V} = \frac{\lambda E_X}{hc[X]V}.$$

(2.8)

To calculate $E_X$, we consider the energy absorbed by X molecules, which is equal to the initial energy deposited into the cavity, $E_0$, multiplied by the fraction of light intensity lost via molecular absorption. The fraction of light intensity lost via molecular absorption is simply equal to the ratio of the round-trip absorber loss, $L_X$, to the total round-trip loss, $L$,

$$E_X = \frac{L_X}{L}E_0.$$

(2.9)

The intra-cavity energy at the beginning of the ring-down transient is given by the product of the intra-cavity power ($P_0/T$), where $T$ is the mirror transmission) times the round-trip time, $t_R$ (s),

$$E_0 = \left(\frac{P_0}{T}\right)t_R.$$

(2.10)

The round-trip time is equal to $l_r/c$, thus we can express $E_0$ in terms of the cavity round-trip length,

$$E_0 = \frac{P_0}{T} \frac{l_r}{c}.$$

(2.11)
Substituting equation (2.11) into equation (2.7) and then into equation (2.8), and expressing cavity losses in their full structure, leads to an explicit form of the concentration dependent expression for $n_c$,

$$n_c = \left( \frac{\lambda n_0 P_0}{\hbar c^2 T} \right) \left( \frac{\sigma [X] J}{\sigma [X] J_t + L_B} \right) \left( \frac{1}{[X] V} \right). \quad (2.12)$$

We have written equation (2.12) in a form where each term in parenthesis has an understandable physical meaning. The first term expresses the number of photons initially inside the cavity, $N_0$, at the beginning of a ring-down transient,

$$N_0 = \frac{\lambda n_0 P_0}{\hbar c^2 T}. \quad (2.13)$$

The initial number of photons injected into the ring-down cavity is dependent on the detection threshold, cavity length, laser wavelength, and output mirror transmission. The second term is the fraction of light intensity lost via analyte absorption. The last term simply expresses the inverse dependence of $n_c$ on the number of molecules in the laser beam.

Substitution of $N_0$, and cancellation of $[X]$ in equation (2.12), simplifies the concentration dependent expression for $n_c$,

$$n_c = \left( \frac{N_0}{V} \right) \left( \frac{\sigma l}{\sigma [X] J_t + L_B} \right). \quad (2.14)$$

In the weak absorber limit (where $\sigma [X] J_t \ll L_B$), the dominant loss of light intensity is baseline cavity loss. Dropping $\sigma [X] J_t$ in the denominator of equation (2.14), and substituting $L_B = l_t / c \tau_o$, results in the low concentration limit expression for $n_c$,

$$n_c = \frac{N_0 \sigma c \tau_o}{V}. \quad (2.15)$$

Equation (2.15) succinctly describes the nature of the photocycling number in the limit of low concentration.
2.6 Discussion

Having derived explicit equations for the photocycling number, we can now consider the dependence of $n_c$ on absorber concentration, cavity geometry, molecular motion, and experimental noise.

2.6.1 Concentration dependence

To explore the dependence of $n_c$ on concentration, we used equation (2.14) to calculate the photocycling of the NO$_3$ radical under our experimental conditions (as described later) for various baseline ring-down times. Four curves, shown in figure 2.5, each of which corresponds to a different baseline ring-down time, describe the relation between $n_c$ and concentration. Each line approaches a limit as $[X]$ approaches zero, and the photocycling increases with increasing baseline ring-down time.

A cursory inspection of equation (2.8) would seem to indicate that $n_c$ is inversely related to the concentration of molecular absorbers, $[X]$. But as $[X]$ approaches zero, the energy lost to these molecules, $E_x$, also approaches zero. The resulting concentration dependence is weak and is of the form shown below,

$$n_c \propto \frac{1}{[X]+C},$$

(2.16)

where $C$ is an experimental constant, and equal to $L_B/\langle \sigma l \rangle$, obtained by dividing through by $\sigma l$ in equation (2.14). The concentration dependence is weaker than $1/[X]$, as equation (2.8) seemed to indicate. Thus, the photocycling number is inversely proportional to the sum of the absorber concentration and a constant originating from baseline loss processes. Notice that as the concentration decreases, the number of photons that a single molecule would have to absorb to maintain an exponential ring-down transient increases. At very low concentrations of $X$, most photons are lost to baseline loss processes, limiting the photocycling of these molecules. As $[X] \to 0$, $n_c \to 1/C$, leading to the photocycling number limit expressed in equation (2.15). Thus,
Figure 2.5 Photocycling curves of $n_c$ versus nitrate radical concentration are plotted for four values of the baseline ring-down time. The value of $n_c$ was calculated with equation (2.14).
at the low concentration limit, \( n_c \propto 1/C \), and \( n_c \) is limited by the round-trip baseline loss. Consequently, in the low concentration limit, anything that decreases \( L_B \), or equivalently, increases the baseline ring-down time, increases the photocycling number.

2.6.2 Cavity geometry and design

Equation (2.15) states that \( n_c \) is proportional to the number of photons initially trapped within the cavity, \( N_0 \), and inversely proportional to the beam volume, \( V \). Both \( N_0 \) and \( V \) are controlled through the experimental setup via detector sensitivity, mirror characteristics and cavity geometry. In order to illustrate the effect of component quality, we assume a fixed baseline ring-down time. Furthermore, because baseline loss is typically dominated by mirror loss (i.e. \( S + T + A \gg bl_{rt} \)), we take the case where \( bl_{rt} = 0 \) for further discussion. The baseline ring-down time is now solely determined by the cavity round trip length and mirror reflectivity.

Consider \( N_0 \) in equation (2.13). For fixed round-trip length, \( l_{rt} \), \( N_0 \) depends on the initial power circulating within the cavity, \( P_0/T \). Therefore, to obtain low values of \( n_c \) it is desirable to have sensitive detectors that allow low values of \( P_0 \) to be achieved. It is also advantageous to increase mirror transmission, \( T \), subject to the constraint that mirror reflectivity achieves a sufficient baseline ring-down time. Therefore, high quality mirrors, where \( S \) and \( A \) are small, will have higher transmission than mirrors with the same total loss, but significant scatter and absorption loss. These high quality mirrors reduce \( n_c \), relative to lower quality mirrors that achieve the same \( \tau_0 \). In summary, \( N_0 \) is controlled by mirror quality and detector sensitivity. High quality components lead to lower values of the photocycling number.

Equation (2.15) also states that \( n_c \) is inversely proportional to the beam volume, \( V \). The beam volume is equal to the beam area integrated over the cavity length. The beam area varies as a function of position in the cavity, and can be approximated by the top-hat area, \( A \). The top-hat area refers to the approximation of a Gaussian beam with a
cylindrical beam of equivalent peak intensity and same total power. The top-hat equation is

\[ A = \frac{\pi \omega^2}{2}, \]  

(2.17)

where \( \omega \) is the Gaussian beam waist parameter as defined by Siegman [Siegman, 1986].

For cavities with a resonator \( g \) factor varying between 1 and -0.4, the beam spot size can be approximated by the simpler planar cavity case. For a cavity composed of 1 m radius of curvature mirrors, these limits on \( g \) correspond to cavity spacing, \( l \), between 0 and 1.4 m. Making the planar cavity approximation,

\[ \omega^2 \approx \left( \frac{\lambda}{\pi} \right) \sqrt{\frac{l_r}{2}}. \]  

(2.18)

Over this range of \( g \) values, the approximation results in less than 10% error.

Substitution of equation (2.18) into equation (2.17), shows that the beam area is directly proportional to the square root of the mirror radius of curvature and directly proportional to the square root of the cavity length. Letting \( V = AI_{\text{r}} \) in equation (2.15), writing the expression for the top hat area, and dropping the constants that are not dependent on \( l_r \) or \( r_c \) in equation (2.18), yields

\[ n_c \propto \frac{1}{\sqrt{\frac{l_r}{r_c} \frac{1}{L_B}}}. \]  

(2.19)

The round trip length, \( l_r \), is a multiple of \( l \), depending on the cavity geometry. Therefore, \( l \) has been replaced with \( l_r \) in equation (2.19).

For fixed round-trip baseline loss, \( L_B \) (i.e. a specific mirror quality), the photocycling number is controlled by changing \( l_r \) or \( r_c \) only. Equation (2.18) indicates that increasing the mirror radius of curvature increases the beam waist, and thus beam volume. Increasing the beam volume, \( V \), by increasing the mirror radius of curvature, \( r_c \), reduces the value of \( n_c \) because the number of photons in the beam remains the same, while the number of molecules available for absorption increases. In effect, it is dilution of the photons into a larger volume of molecules.
Alternatively, increasing the volume by increasing the cavity length raises the value of $n_c$. The length dependence of $n_c$ comes from a number of factors. Examining equation (2.15), $n_c$ is directly proportional to $N_0$ and $\tau_B$, which are both linearly dependent on the cavity length, $l$. After cancellation of all length terms in equation (2.15), the resulting dependence of $n_c$ on the cavity round-trip length is $\sqrt{l}$, which is a relatively weak dependence on cavity length.

2.6.3 Diffusion and pre-exposure

In deriving our expressions for $n_c$, we did not take into account the motion of the molecules, or the exposure of molecules to the detection beam during build up of light intensity in cavity. Here, we explain our rational for choosing the static gas assumption and discuss the effects of molecular diffusion, mass flow and pre-exposure on the value of the photocycling number. The extent to which these processes affect the value of $n_c$ will vary depending on the specifics of the experimental design. Thus, all subsequent discussion will refer to our laboratory spectrometer [King et al., 2000] and apply to the nitrate radical (see Section 2.6.6 Examples).

If sample molecule exchange, between molecules in the beam volume and the bulk sample, is faster than the time scale of the ring-down transient, our calculation of $n_c$ is invalid because the number of ground-state molecules available for absorption is greater than $[X]V$. However, when the distance traversed by typical molecules during the ring-down time is significantly less than the diameter of the laser beam, the static gas assumption will be justified.

The estimated diffusion coefficient for the nitrate radical, calculated by the method of Fuller et al. (1966), is 0.13 cm$^2$s$^{-1}$ at standard temperature and pressure (1 atm, 273 K). According to random walk theory [Atkinson, 1997], the average distance traveled for a NO$_3$ molecule is 20 μm in 30 μs. The top-hat beam diameter for our RDC is on the order of 450 μm, the diffusion of exposed molecules leaving the beam is not dominant. When sample is drawn through the cavity at a linear flow rate of 1 m s$^{-1}$, a
molecule traverses 30 \( \mu m \) in 30 \( \mu s \). In both cases, the distance traversed by the gas molecules is not dominant for typical values of \( \tau \). Thus, the static gas assumption is justified under these conditions. For extreme flow rates (i.e. sampling in an airplane, rapid flow tube, supersonic beam or at low pressure), mass flow may be great enough to affect the actual value of \( n_e \). When sample molecule exchange is significant, the calculated value of \( n_e \) is higher than the actual value of \( n_e \).

In CW-CRDS, the time the molecules in the detection volume are irradiated with the laser beam before a measurement begins, is termed pre-exposure. Absorption by molecules during build-up can degrade the sample molecules. For our experimental set up, we have measured the ratio of total exposure (build-up and decay) to post-exposure (decay) to be on the order of a factor of two. Thus, the actual value of \( n_e \) is roughly double the calculated value of \( n_e \) where only post-exposure was considered. Pre-exposure can be significant in the case of well-locked cavities, where the intra-cavity power is allowed to build to high levels, and should be minimized when photocycling is calculated to be a problem.

2.6.4 Baseline noise and signal averaging

The noise equivalent concentration, \( [X]_{\text{Neq}} \) (molecules m\(^{-3}\)), is given by

\[
[X]_{\text{Neq}} = \frac{U_r}{l_{\text{eff}} \sigma},
\]  

(2.20)

where \( U_r \) (representing the uncertainty in \( \tau \)) is the standard deviation of multiple determinations of the ring-down time divided by the ring-down time, termed \( \sigma_r / \tau \) by Paldus [Paldus et al., 1998]. The effective pathlength, \( l_{\text{eff}} \), is equal to \( c\tau_o \). There are two methods of achieving a lower detection limit; (a) obtain a lower value of \( U_r \), or (b) achieve a longer effective path length. These two methods have different implications for photocycling. The former method of decreasing \( U_r \) will not effect the baseline ring-down time, thus, \( n_e \) is unchanged. Using the later method of achieving a longer effective
Figure 2.6 Photocycling curves are plotted for four different baseline ring-down times at low concentration. The value of $n_c$ was calculated with equation (2.14), the full expression for $n_c$. Photocycling curves of $n_c$ versus NO$_3$ radical concentration as a function of $\tau_0$ are shown as solid lines with $\tau_0$ labeling the curve. Photocycling curves of $n_c$ versus noise equivalent concentrations of the NO$_3$ radical as a function of system noise ($U_T$) are shown as dashed lines with the value of $U_T$ labeling the curve. See text for detail.
pathlength will improve the detection limit, but raise the baseline ring-down time, $\tau_o$, and the value of the photocycling number.

Figure 2.6 plots the same relationship between $n_c$ and $[X]$ as shown in figure 2.5, but focusing on lower concentration. Four cases (solid lines) that are representative of different baseline ring-down times are shown. Additionally, figure 2.6 plots the value of $n_c$ versus noise equivalent concentration. These curves were obtained by solving equation (2.14) for the required baseline ring-down time as a function of $[X]_{\text{neq}}$, and inserting the baseline ring-down time into the low-concentration photocycling number expression, equation (2.16). Because this relationship depends on an assumed $U_T$, we have plotted four curves corresponding to different values of $U_T$ in figure 2.6.

Figure 2.6 can be used to determine the noise equivalent concentration for a CRDS system by finding the crossing point between the curve of $n_c$ versus $[X]$ (for the experimental $\tau_B$) and the curve of $n_c$ versus $[X]_{\text{Neq}}$ (for the experimental $U_T$). The noise equivalent concentration is the x-axis value of the crossing point, and the photocycling present in the system is the y-axis value of the crossing point.

We illustrate an example by referring to the curve where $U_T = 0.02$. A ring-down time of 30 $\mu$s corresponds to a noise equivalent concentration of $1 \times 10^{15}$ (molecules m$^{-3}$). To decrease the detection limit by a factor of two, we can either decrease $U_T$ by a factor of two through improved electronics or signal averaging, or increase the baseline ring-down time to 60 $\mu$s. In the first case, the detection limit is reduced without altering the photocycling number. In the second case, the photocycling number roughly doubles.

### 2.6.5 Pulsed CRDS

In pulsed CRDS (P-CRDS), the calculation of $E_0$ is more complicated than in the CW-CRDS case. One might assume that the initially trapped energy, $E_0$, is equal to the
pulse energy, $E_p$, multiplied by the mirror transmission, but not all frequencies present in the laser pulse are capable of circulating in the cavity. Therefore, the actual relationship is very complex. One way to overcome this problem is to measure $P_0$ (the optical power at the detector) at the start of the ring-down transient, and apply CW-CRDS formulas. The analysis of P-CRDS systems, with regard to photocycling, is additionally complicated because the laser may be coupled into several transverse modes, making the determination of the beam volume difficult. The beam volume, in general, will not be the volume of the TEM$_{00}$ mode, and equations (2.18 – 2.20) will be invalid. However, the energy deposited into an RDC by a pulsed laser is typically small, and there is no pre-exposure in P-CRDS, thus photocycling is typically expected to be less of a concern.

2.6.6 Examples

To obtain an understanding of typical photocycling values, we calculated $n_c$ for four molecules with absorption features varying in wavelength between the near-UV and the near-IR (see table 2.2). We selected the nitrate radical, bromine monoxide, nitrogen dioxide, and methane. The experimental parameters used to evaluate $n_c$ are picked to match our laboratory spectrometer with reasonable assumptions for mirror and detector properties at varying wavelengths. The bow-tie cavity round-trip length is 1.8 m, and the mirror radius of curvature 1 m. Our detection threshold is set at 0.24 V (typical of our experiment) and converted to an optical power using the detector sensitivities in Table 3. We have also calculated a noise equivalent concentration for each molecule based upon an assumed value of $U_e$ equal to 0.01.

These cases demonstrate that photocycling is typically < 1, indicating that CRDS does not induce photoalteration artifacts. For other molecules or other cavity geometries, one should apply equation (2.14) to the actual situation. Also, the assumption of a static gas should be questioned, particularly for low-pressure experiments.
Table 2.2 The photocycling number calculated for four molecules at one-third the maximum ring-down time for cavity geometry described in 2.6.6.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Absorption cross section (cm² molecule⁻¹)</th>
<th>Mirror transmission</th>
<th>Wavelength (nm)</th>
<th>Detector sensitivity (Volts/Watt)</th>
<th>Initial photons (N_0)</th>
<th>(n_e) (photons molecule⁻¹)</th>
<th>Noise equivalent concentration (molecules cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃</td>
<td>(2.10 \times 10^{-17}) (i)</td>
<td>(1 \times 10^{-5})</td>
<td>662</td>
<td>(1.0 \times 10^6)</td>
<td>(4.8 \times 10^8)</td>
<td>0.064</td>
<td>(2.6 \times 10^8)</td>
</tr>
<tr>
<td>BrO</td>
<td>(1.6 \times 10^{-17}) (i)</td>
<td>(1 \times 10^{-4})</td>
<td>338</td>
<td>(2.0 \times 10^5)</td>
<td>(1.2 \times 10^8)</td>
<td>0.002</td>
<td>(4.2 \times 10^9)</td>
</tr>
<tr>
<td>CH₄</td>
<td>(7.00 \times 10^{-21}) (ii)</td>
<td>(1 \times 10^{-5})</td>
<td>1650</td>
<td>(1.4 \times 10^3)</td>
<td>(8.3 \times 10^{11})</td>
<td>0.004</td>
<td>(3.4 \times 10^{12})</td>
</tr>
<tr>
<td>NO₂</td>
<td>(6.00 \times 10^{-19}) (i)</td>
<td>(1 \times 10^{-5})</td>
<td>400</td>
<td>(3.0 \times 10^5)</td>
<td>(9.6 \times 10^8)</td>
<td>0.006</td>
<td>(9.4 \times 10^9)</td>
</tr>
</tbody>
</table>

iii. NO₃ and NO₂ were calculated for baseline ring-down times of 60 μs. BrO and CH₄ were calculated for 5 μs and 15 μs baseline ring-down times respectively. The CH₄ baseline ring-down time is limited by typical atmospheric concentrations and the BrO ring-down time is limited by the mirror transmission.
A recent publication has demonstrated nonlinear effects in CW-CRDS \cite{Romanini_1999}. These saturation effects must have resulted from photocycling greater than one photon per molecule. This example demonstrates that photocycling can be observed in CW-CRDS. Saturation was only observed for hot band transitions originating from a vibrationally excited sub-population of the molecules. Because the concentration of these molecules is smaller than the population of molecules present in the ground state, the photocycling was larger and saturation was observed. This observation points out the necessity of using consistent absorption cross sections and concentrations of molecules capable of absorbing the laser light. Unfortunately, application of the formulas in this chapter to the \textit{Romanini et al.} \cite{1999} example were not possible because the absorption cross-section and concentration of molecules are unknown and the static gas assumption was not valid in their supersonic jet experiment.

\section*{2.7 Conclusions}

We have defined a figure of merit, the photocycling number ($n_c$), and derived exact formulas for calculating $n_c$ in the static gas case. These equations are applicable to any gas phase molecule, and show that in the limit of low concentration, the photocycling number is independent of concentration because most photons are lost through baseline processes. Increasing the baseline ring-down time, or equivalently reducing baseline losses, raises the value of the photocycling number. Therefore, at short baseline ring-down times, photocycling is not a problem, but CRDS is not sensitive in this case. Clearly, the baseline ring-down time affects both sensitivity and photocycling, where long baseline ring-down times lead to high sensitivity at the cost of high photocycling.

Another contribution to CRDS sensitivity is the ability to determine accurately the ring-down time, which can be expressed as the fractional standard deviation of the ring-down time, $U_T$. Lowering $U_T$ improves the detection limit without changing the baseline ring-down time, thus without increasing photocycling requirements on the molecules. Therefore, signal averaging, which improves $U_T$ can lower detection limits
without increasing photocycling requirements. Additionally, improving
detection electronics and system design to achieve a low single shot $U_x$ is clearly a way
for lowering detection limits.

For CW-CRDS, $n_c$ is inversely proportional to the square root of the mirror
radius of curvature. Thus, longer radius of curvature mirrors reduce photocycling.
Detector sensitivity and cavity throughput determine $n_c$ by controlling the number of
photons initially circulating within the cavity. High sensitivity detectors and high quality
mirrors, where mirror scattering and absorption are low, increase the number of photons
observed at detector and thus allow the detector threshold to be lowered, decreasing the
photocycling.

For our cavity geometry, $n_c$ is less than one photon per molecule for the
molecules NO$_3$, BrO, NO$_2$, and CH$_4$. Thus, photocycling is not a problem for these
molecules under these experimental conditions. For high sample molecular motion or
well-locked cavities, a model of the individual system may need to be constructed in
order to determine accurately the photocycling present in the system.
Chapter 3

Spectroscopy of the nitrate radical in the atmosphere

3.1 Introduction

Detecting the nitrate radical (NO$_3$) in the atmosphere poses many challenges to an analytical technique. To quantify NO$_3$ mixing ratios requires that the analytical technique be sensitive because the maximum atmospheric NO$_3$ mixing ratio seldom exceeds 100 parts per trillion by volume (pptv). Sensitive detection of the nitrate radical in the atmosphere is complicated by the presence of a mixture of many interfering compounds that can be highly variable in magnitude (e.g. aerosol, water vapor, ozone and nitrogen dioxide). The method must therefore be selective and capable of resolving the complex environment of the NO$_3$ radical. In addition, an instrument operating in the atmosphere will be exposed to conditions not typically present in the laboratory that can degrade the sensitivity of an analytical method or make an instrument inoperable (i.e. mechanical vibrations and temperature changes can easily destroy the alignment of a traditional multipass (White) cell. The reactivity of the nitrate radical further complicates the task, bringing-forth the issue of sampling artifacts (i.e. a change in the molecular concentration due to sampling procedure). It is also desirable that the method possesses good time resolution in order to follow the expected fast time-scale processes that make NO$_3$ mixing ratios variable. Finally, it is desirable that the instrument be portable with good spatial resolution to characterize the vertical structure of NO$_3$ in the troposphere.

In this chapter, we focus on the light attenuation processes in the atmosphere that affect optical detection of the NO$_3$ radical. While visible and infrared spectroscopy, laser induced fluorescence, mass spectrometry, and electron spin resonance have been employed to study NO$_3$ in the laboratory, only long path differential optical absorption spectroscopy (DOAS) is routinely employed to measure atmospheric mixing ratios of NO$_3$, at the present time [Wayne et al., 1991]. Thus, we consider the DOAS technique, applied to NO$_3$ detection, in the context of the light attenuation processes that complicate optical spectroscopy of the NO$_3$ radical in the atmosphere.
3.2 NO$_3$ optical properties

The NO$_3$ radical exhibits strong optical absorption features in the visible region of the electromagnetic spectrum, and can thus potentially be detected via its electronic absorption spectrum. The prominent features in the NO$_3$ spectrum are two intense bands centered at 623 nm and 662 nm. Wayne et al. [1991] has reviewed the literature regarding the nitrate radical absorption spectrum, and recommends values of the absorption cross section by averaging the data from obtained by Ravishankara and Mauldin [1986], Sander [1986], Cantrell et al. [1987], and Canosa-Mas et al. [1987].

The recommended value at 662 nm is $\sigma = (2.10 \pm 0.20) \times 10^{-17}$ cm$^2$ molecule$^{-1}$ (298 K, 1 atm). The recommended temperature-independent cross sections (298K, 1 atm) in the wavelength range 550 – 691 nm are plotted in figure 3.1 (resolution 1 nm). The cross sections in figure 3.1 are calculated from the study by Sander [1986], but normalized to the recommended value of $\sigma$ at 662 nm [Wayne et al., 1991].

Several investigators have found that the NO$_3$ absorption cross section exhibits some temperature dependence. Though the issue is not currently resolved, a recommended "temperature-dependent" absorption cross section at 662 nm is proposed by Wayne et al. [1991] based on the data of Ravishankara and Mauldin [1986], Sander [1986] and Cantrell et al. [1987]. The temperature-dependent absorption cross section at 662 nm, $\sigma(T)$, is given by

$$\sigma(T) = 3.63 \times 10^{-17} - (5.13 \times 10^{-20} \times (T/K)) \text{ cm}^2 \text{ molecule}^{-1}. \quad (3.1)$$

The NO$_3$ radical possesses a non-zero quantum yield for dissociation for $\lambda < 640$ nm. Nitrate radical photolysis proceeds along two reaction channels, which were introduced in chapter 1. The primary quantum yield for dissociation via channel 1.2b ($\phi_{1.2b}$) produces nitric oxide (NO) and molecular oxygen. The primary quantum yield for dissociation via channel 1.2a ($\phi_{1.2a}$) produces nitrogen dioxide (NO$_2$) and a ground state oxygen atom. The total quantum yield, $\phi_{tot}$, is the sum of the two primary quantum yields. The photolysis quantum yields (298 K) are plotted in figure 3.1. The values of the quantum yields are from Johnston et al. [1996], reproduced in Finlayson-Pitts and Pitts [2000]. The total quantum yield for photolysis approaches unity for excitation
Figure 3.1 The nitrate radical absorption spectrum (298 K) and photolysis quantum yields. The total photolysis quantum yield is plotted together with the quantum yields for NO + O₂ production and NO₂ + O production. The absorption cross sections are from Wayne et al. [1991].
wavelengths $\lambda < 625$ nm and is zero for $\lambda > 640$ nm. At our detection wavelength (662.2 nm) the total quantum yield is within the measurement error of zero.

### 3.3 Optical spectroscopy in the atmosphere applied to NO$_3$ detection

A light beam traversing the atmosphere is attenuated as a result of particles and gases that scatter and absorb the beam along the light path. The mechanisms that attenuate the beam are generally referred to as extinction processes, and include particle absorption ($b_{ap}$), particle scattering ($b_{sp}$), gas scattering ($b_{sg}$), and gas absorption ($b_{ag}$). The sum of these processes is termed the total extinction coefficient ($b$), and can be defined as the fraction of light that is attenuated per distance traveled by the light beam.

Let the initial intensity of the beam be $I_0(\lambda)$ at wavelength $\lambda$. After the beam traverses a distance $L$ (cm), the attenuated intensity, $I(\lambda)$, is given by equation (3.2) for conditions where the Beer-Lambert's law is valid,

$$I(\lambda) = I_0(\lambda)\exp(-b(\lambda)L)$$  \hspace{1cm} (3.2)

The total extinction coefficient, $b$ (cm$^{-1}$), can be split into its component terms, and we can rewrite equation (3.2) for a specific wavelength to make the contribution of each process explicit,

$$\ln \left( \frac{I}{I_0} \right) = -bL = -L\left(b_{ap} + b_{sp} + b_{sg} + b_{ag}\right)$$  \hspace{1cm} (3.3)

The sum of absorption by various gases ($b_{ag}$) can be decomposed to highlight the absorption contribution of the species of interest,

$$b_{ag} = \sum_i \sigma_i N_i = \sigma_1 N_1 + \sigma_2 N_2 + ...$$  \hspace{1cm} (3.4)

where $\sigma_i$ (cm$^2$ molecule$^{-1}$) is the absorption cross section of the $i$th molecular species that is present at a concentration $N_i$. Gas and particle scattering is typically much less wavelength dependent than molecular absorption by many molecules. Thus, a raw open-air spectrum contains the imprint of molecular absorption on top of the broadband extinction characteristic of scattering by gases (Rayleigh), scattering by particles (Mie), and absorption by particles. For species with banded absorption spectra, it is possible to subtract their spectrum from the total extinction spectrum.
The extinction coefficients, relevant to NO$_3$ detection, are plotted in figure 3.2 using some typical values in the red spectral region. Extinction due to NO$_3$ absorption is plotted onto the graph for comparison. The NO$_3$ extinction spectrum was computed using an atmospheric mixing ratio of 100 pptv NO$_3$ (298 K, 1 atm). The extinction coefficient for Rayleigh scattering ($b_{sg}$) is calculable, and dependent on $\lambda^{-4}$. The plot of the Rayleigh extinction coefficient was constructed using the equation,

$$b_{sg} = 1.02 \times 10^4 \left( \frac{1}{(\lambda/\text{nm})^4} \right) \text{cm}^{-1},$$

(3.5)

where $N = 2.46 \times 10^{25}$ molecules m$^{-3}$ is the molecular density of air (298 K, 1 atm) and $n$ is the refractive index of air (298 K, 1 atm) at wavelength $\lambda$ (m) [Eckbreth, 1996]. The extinction coefficients for particle scattering and particle absorption are more complex and depend on the size distribution, chemical composition, and concentration of particles in the sampled air mass. These factors vary geographically, seasonally, diurnally and on the short time-scales in the troposphere. Values for $b_{sp}$ measured in ambient air typically range from $\sim 10^{-3}$ m$^{-1}$ ($10^{-5}$ cm$^{-1}$) in highly polluted urban areas to $\sim 10^{-7}$ m$^{-1}$ ($10^{-9}$ cm$^{-1}$) in remote locations [Finlayson-Pitts and Pitts, 2000]. A value of $1.5 \times 10^{-8}$ cm$^{-1}$ was selected to plot in figure 3.2. The extinction coefficient for particle absorption, generally ranges from $\sim 10^{-4}$ to $< 10^{-8}$ m$^{-1}$ ($10^{-6} - 10^{-10}$ cm$^{-1}$) [Finlayson-Pitts and Pitts, 2000]. A value of $1.5 \times 10^{-9}$ cm$^{-1}$ for $b_{ap}$ was selected to plot in figure 3.2. Both NO$_2$ and O$_3$ posses structured absorption bands in the visible region, thus their extinction spectra are shown in figure 3.2. The NO$_2$ extinction spectrum was constructed assuming a mixing ratio of 0.5 ppbv and using the cross section data (298 K) of Schneider et al. [1987]. The ozone extinction spectrum was constructed assuming a mixing ratio of 40 ppbv and using the cross section data (298 K) of Burkholder et al. [1994]. The water vapor extinction spectrum is plotted assuming a mixing ratio of 1 mole percent (~50 % RH at room temperature). The fine water structure is obvious in figure 3.2. Figure 3.3 shows the high-resolution NO$_3$ absorption cross section of Marinelli et al. [1982] plotted on a linear scale along with the pressure-broadened water spectrum in this region on a separate axis. The water absorption cross section was simulated using the HITRAN database for 1
Figure 3.2 Light extinction spectra for absorption and scattering mechanisms in the red spectral region. The extinction spectra of NO$_2$, NO$_3$, O$_3$, and H$_2$O were calculated using assumed mixing ratios of 0.5 ppbv, 100 pptv, 40 ppbv, 1 mole percent, respectively. Rayleigh scattering (b$_{sp}$) is calculated for 1 atmosphere pressure. Particle absorption (b$_{ap}$) and particle scattering (b$_{sp}$) are plotted for reasonable values discussed in the text.
Figure 3.3 An expanded plot of the water vapor absorption spectrum near the 662-nm absorption peak of the nitrate radical. The high-resolution NO$_3$ absorption spectrum is from Marinelli et al. (1982). The water absorption spectrum was simulated (298 K, 1 atm) as described in text.
atmosphere pressure and 298 K. It is clear from figures 3.2 and figure 3.3 that water vapor must be carefully considered in an instrument that detects NO₃.

3.4 Differential optical absorption spectroscopy (DOAS)

DOAS measures the average concentration of a chemical species along a light path through the atmosphere. The light path is typically ~10 km and defined by the line between a spectrometer, which records the transmitted intensity, and the light source, which can be natural (i.e. a star, the sun or moon) or artificial (i.e. a lamp). Determining the background spectrum in open-air is unachievable because it requires removing the chemical species from the light path. DOAS measures absorption by measuring the differential absorption between a peak and trough in the spectrum of molecule.

Figure 3.4 illustrates the DOAS technique for a molecule with a structured absorption peak at wavelength \( \lambda_1 \). The molecule does not absorb at \( \lambda_2 \). The intensity of the transmitted beam, as measured by a detector at the end of the light path, is denoted \( I_0' \), and slopes due to the wavelength dependent scattering processes. These broadband scattering processes prevent measurement of the true initial intensity, \( I_0 \), shown by the top line in figure 3.4. The transmitted intensity at \( \lambda_2 \) is the transmitted intensity in the absence of the structured absorption, \( I_0' \). The concentration of the molecular absorber can thus determined by replacing \( I_0 \) with \( I_0' \) in equation (3.2). In practice, a mathematical fitting procedure allows extracting the narrow spectral transitions ascribed to molecular absorption contained in the spectrum. The fitting procedure is based on the fact that the decrease in light intensity due to scattering in the optical path is much less wavelength dependent compared to the molecular absorption features of the sample. The extracted molecular absorption spectrum is then fitted to reference spectrum form the laboratory, and then the concentrations of the absorbing species is derived. Because ambient air contains a variety of light absorbing species, a multivariate fit must be used to obtain the contributions from various molecules to the observed absorption spectrum.

The DOAS technique is used often to determine atmospheric mixing ratios of NO₃. In chapter 1, we stated problems associated with path-averaged concentrations, which motivated our development of CRDS for NO₃ detection. Here we discuss
Figure 3.4 The method of determining the concentration of a molecular species in differential optical absorption spectroscopy. The molecule absorbs at $\lambda_1$ and does not absorb at $\lambda_2$. The true background signal is indicated by $I_0$, which can not be determined. Thus, the intensity measured at $\lambda_2$ is used to calculate the molecular concentration through the Beer-Lambert law.
spectroscopic difficulties associated with the DOAS technique, which are due primarily to water vapor absorption in the red spectral region where NO$_3$ absorbs.

In DOAS, it is necessary to account accurately for the water vapor contribution to the open-air spectrum in order to extract accurate NO$_3$ mixing ratios. Daytime spectra typically serve as reference spectra for water absorption during NO$_3$ measurements at night. A variable water vapor concentration is often problematic because the daytime spectrum is not fully representative of the nighttime water spectrum. Additionally, the water absorption lines often become optically saturated, thus a non-linear relationship between the observed spectrum and the water vapor mixing ratio develops. This relationship induces fitting artifacts, and complicates the analysis, ultimately degrading the sensitivity. Clearly, water vapor is a primary interference in the spectral region where NO$_3$ absorbs, and must be carefully considered with any spectroscopic technique.

3.5 Conclusions

The nitrate radical possesses a banded absorption spectrum in the visible region with strong absorption peaks near 623 and 662 nm, making it an ideal candidate for detection by absorption spectroscopy. Unfortunately, optical interference (i.e. particle scattering and water vapor absorption) complicates NO$_3$ spectroscopy in the atmosphere, posing rigorous requirements for an NO$_3$ detection method (i.e. sensitive, selective and robust). While DOAS is successful at measuring path-averaged NO$_3$ concentrations, an in-situ method is desirable for comparing NO$_3$ concentrations with other chemical species measured in-situ. In subsequent chapters we discuss the application of CRDS to NO$_3$ detection, and present our methods of dealing with the optical interferences and the difficulties associated with NO$_3$ detection put forth in this chapter.
Chapter 4

First application of CRDS to detect NO₃

4.1 Introduction

In this chapter we demonstrate the first application of cavity ring-down spectroscopy (CRDS) for nitrate radical (NO₃) detection by recording an absorption spectrum of NO₃ in ambient laboratory air that had been dosed with the NO₃ precursor, dinitrogen pentoxide (N₂O₅). This work represents the first time NO₃ has been detected via CRDS and led to the publication of King et al. [2000]. Additionally, we present data to confirm that our experimental arrangement does not suffer from saturation artifacts as discussed in detail in chapter 2.

4.2 Method

A flow cell constructed with two sheets of crown glass supported by two aluminum sidewalls was used to channel a flow of room air that was drawn by four small computer fans. The cell measured 364 mm in the direction of the laser propagation by 420 mm in the flow direction by 30 mm high. The RDC mirrors (Research Electro-Optics, R > 99.996%) were arranged in a bow-tie configuration and were enclosed by aluminum boxes to allow purging with bottled dry nitrogen. Purging was necessary to prevent dust settling on the mirrors, an effect that reduces the ring-down time of the cavity. The flow cell and the purge chambers for the mirrors were connected by 8 mm diameter holes to allow the laser beam to pass through the flow region. The linear flow velocity within the cell was estimated to be 0.5-1 m s⁻¹. Flow streamlines observed using condensed water vapor from a dewar of liquid nitrogen visually confirmed laminar flow. The CRDS optical system is described in a previous paper [Schulz and Simpson, 1998].

The NO₃ radical was generated in the flow cell from the thermal decomposition of previously synthesized N₂O₅,

\[ \text{N}_2\text{O}_5 + \text{M} \leftrightarrow \text{NO}_2 + \text{NO}_3 + \text{M.} \]  

A stream of N₂O₅ diluted in nitrogen was added to the flow cell through six nozzles upstream of the RDC. The flow of N₂O₅ in nitrogen was generated by passing a small
flow of nitrogen through a Pyrex trap containing N$_2$O$_5$ at $-250$ K and adding to a flow of nitrogen at $-11$ min$^{-1}$. The N$_2$O$_5$ was further diluted by the flow of room air ($-400$ l min$^{-1}$ estimated) upon entering the flow cell.

The laser was tuned between 657 nm and 668 nm in steps of approximately 1 nm. At every third step, the laser wavelength was set equal to 662 nm, the NO$_3$ absorption maximum. The laser frequency was recorded using a spectrometer calibrated with a Neon lamp. For each laser frequency, the flow of N$_2$O$_5$/N$_2$ was switched on and off. When no N$_2$O$_5$/N$_2$ was flowing, the measured light loss rate was taken as a baseline representing all cavity losses present for the cavity filled with flowing room air. The corresponding ring-down time is denoted $\tau_0$. The absorbance due to the addition of N$_2$O$_5$/N$_2$ is measured by subtracting the baseline measurement from the light loss rate measured while flowing the mixture. In terms of the cavity decay rate, $1/\tau$, introduced in chapter 2, the effective nitrate radical concentration is

$$[NO_3] = \frac{1}{c\sigma} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right),$$

where $\sigma$ is the absorption cross section (cm$^2$ molecule$^{-1}$) at the laser wavelength, and $c$ is the speed of light in units cm s$^{-1}$.

4.3 Results

Figure 4.1 shows a time series of light-loss-rate measurements at 662 nm. Each point represents a single CRDS measurement. Some points show larger losses that are probably caused by atmospheric particulate absorption and scattering. We have removed some of these outlying points by eliminating points more than two standard deviations from the median of each N$_2$O$_5$-on or N$_2$O$_5$-off cycle. The gaps between on and off states are equilibration times (30 s) where no ring-down events were recorded and flows were allowed to stabilize. We see that the light loss rate is increased by addition of the sample gas. It is also clear that the source is not stable. The right axis represents an equivalent mixing ratio of NO$_3$ based upon the linestrength $2.1\times10^{-17}$ cm$^2$ molecule$^{-1}$ at 662 nm (Wayne et al., 1991) and converted to a mixing ratio at 1 atmosphere, 25°C. Note that this mixing ratio is corrected for pathlength decrease (18%) caused by lack of absorption.
Figure 4.1 Time series of CRDS-measured loss rate, $r$ measured at 662 nm. The added flow of N$_2$O$_5$/N$_2$ is modulated off and on. The right hand axis represents an equivalent NO$_3$ mixing ratio as described in text. Gaps between on and off states are equilibration times where no ring-down transients were recorded.
in the mirror purge chambers. Possible losses of the NO$_3$ radical upstream of the detection point are unknown at this time.

Because the source of the NO$_3$ radical was not constant, a relative spectrum was recorded where the absorbance, $\alpha$ (cm$^{-1}$), was normalized to its value at 662nm, which was repeated regularly, (i.e. a plot of $\alpha/\alpha_{\lambda=662}$ was graphed versus wavelength, $\lambda$). The absorption coefficient, $\alpha$, is equal to the product of the absorption cross section, $\sigma$ (cm$^2$ molecule$^{-1}$) at the laser wavelength, and the nitrate radical concentration, [NO$_3$] (molecules cm$^{-3}$). The recorded spectrum is displayed in figure 4.2. Also displayed for comparison, is a high-resolution spectrum of the NO$_3$ radical recorded under ideal spectroscopic conditions [Marinelli et al., 1982].

4.4 Discussion

Figure 4.2 shows that the CRDS spectrum agrees with the spectrum of Marinelli et al. [1982], especially considering the NO$_3$ radicals were generated in ambient room air and the source of NO$_3$ was not constant. Our spectrum shows that we are detecting the NO$_3$ radical in our experiment, and figure 4.1 demonstrates our ability to detect NO$_3$ in real time.

By using the median of the $N_2O_5$-off data, we improve upon the single-shot noise at the expense of time resolution. A baseline loss measurement consists of approximately 150 ring-down events and requires approximately 30 s with this prototype instrument. The standard deviation of the replicate 30 second baseline loss measurements is $1\times10^9$ cm$^{-1}$. Subsequent improvements in the instrumental ring-down event rate decreased this noise through averaging and reduce the analysis time.

Possible interfering absorbers that could affect this technique are NO$_2$, O$_3$, and H$_2$O. Table 4.1 displays our CRDS noise-equivalent mixing ratio (assuming a baseline noise of $1\times10^9$ cm$^{-1}$) for each of these species in the wavelength region around 662 nm. At reasonable atmospheric mixing ratios, the instrument described here is insensitive to NO$_2$ and only slightly sensitive to O$_3$ interference.
Figure 4.2 Relative spectrum of the NO$_3$ radical recorded by CW-CRDS. Open circles represent CRDS-derived data and the solid line is from the laboratory spectrum of Marinelli et al. (1982).
Table 4.1 Noise equivalent mixing ratios of some potential interfering compounds assuming a baseline noise of $1 \times 10^{-9}$ cm$^{-1}$ in 30 seconds. Typical atmospheric mixing ratios are representative of relatively clean air, and the NO$_3$ mixing ratio is from Heintz et al. [1996].

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>$\sigma / 10^{-20}$ (cm$^2$ molecule$^{-1}$)</th>
<th>Typical atmospheric mixing ratio (ppbv)</th>
<th>Noise equivalent mixing ratio (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3$</td>
<td>$2.1 \times 10^3$</td>
<td>0.008</td>
<td>0.002</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.4</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>O$_3$</td>
<td>0.2</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>H$_2$O (min dip)</td>
<td>$1 \times 10^{-7}$</td>
<td>$1 \times 10^7$</td>
<td>$4 \times 10^7$</td>
</tr>
<tr>
<td>(662.2 nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O (strong line)</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^7$</td>
<td>$4 \times 10^4$</td>
</tr>
<tr>
<td>(657.7 nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Water vapor absorption lines also appear in this spectral region. Our CRDS technique easily resolves these pressure-broadened rotational lines [Schulz and Simpson, 1998]. Tuning the laser to a strong line allows sensitive detection of water vapor, as indicated by the 657.7 nm entry in Table 4.1. Tuning the laser to 662.2 nm, a dip between water lines, makes our instrument insensitive to water vapor, as indicated in Table 4.1. It is possible that the water-vapor continuum absorbance at this wavelength increases the cross section; therefore the instrument may be slightly sensitive to water vapor even at the minimum absorbance. Detection of NO$_3$ at 662.2 nm (very close to its absorption maximum) is possible by measuring the change in absorbance between ambient air and air that has had NO$_3$ chemically removed. Photolysis of the sample air can remove NO$_3$ without changing the water vapor or ozone mixing ratio. Thereby, the subtraction procedure would remove any residual absorption by water vapor, increasing our immunity to water interference. Additionally, tuning the probe laser by a few wavenumbers would detect underlying water vapor absorption and allow us to avoid problematic detection frequencies. Taking the difference between successive zero measurements and sample measurements is expected to increase the noise by $\sqrt{2}$, therefore a zero-based instrument would be expected to have a 1-$\sigma$ detection limit of 3 pptv.

### 4.5 Photocycling tests

Previously, in chapter 2, we derived an expression to calculate the number of photons that must be absorbed per molecule for the light intensity loss caused by the molecules to remain constant during the ring-down transient. To demonstrate that we do not suffer these saturation artifacts, we recorded the cavity loss rate in the presence of the NO$_3$ radical for a range of detection thresholds, where the detection threshold corresponds to the initial power circulating within the RDC. If the light intensity loss is not constant during the ring-down event, the CRDS signal will be non-exponential, destroying the linearity of the technique. The measured light loss rate was recorded at 662 nm for a series of detection thresholds ranging between 0.05 to 0.5 V (i.e. increasing the intra-cavity power by a factor of ten). Figure 4.3 plots the ratio of the light loss rate
Figure 4.3 The relative light loss rate, $r$ versus detection threshold. Saturation behavior would be indicated by a decrease in the light loss rate with increasing detection threshold, which corresponds to the intra-cavity power.
(proportional to the NO₃ concentration) at the corresponding detection threshold to the light loss rate at a detection of 0.20 V. The relative light loss rate was again plotted due to a fluctuating NO₃ concentration arising from an unstable NO₃ source. The error bars shown on the plot are 1-σ. If we were suffering from saturation artifacts we would observe a decrease in the relative light loss rate with increasing detection threshold (or intra-cavity power) as a result of a depleting ground state of NO₃ molecules in the detection beam. Clearly this effect is not observed and the light loss rate plotted is constant of the detection threshold range currently achievable within error.

4.6 Conclusions

We have demonstrated the capability to detect the NO₃ radical in room air by recording an absorption spectrum. In the current instrumental configuration, the baseline noise is 1x10⁻⁹ cm⁻¹ in a 30 s acquisition time. This noise is equivalent to a mixing ratio of 2 pptv for NO₃. Improvements in the instrument can easily increase the rate of ring-down events, decreasing the detection limit through averaging and shortening the acquisition time. Use of a chemical zero to modulate the NO₃ concentration without affecting other gases would allow differential detection eliminating water vapor and ozone interferences. Our current demonstration indicates that CRDS can be used to detect the NO₃ radical in ambient air at atmospheric mixing ratios. These measurements represent the first in-situ measurements of NO₃ radical at fast timescales.
Chapter 5

Instrument design principles and field data evaluation methods

5.1 Introduction

The primary advantage of using cavity ring-down spectroscopy (CRDS) for the atmospheric detection of the nitrate radical (NO$_3^-$) is that the measurement is conducted in-situ and can be compared easily with in-situ measurements of other compounds in the same air mass (e.g. ozone, water vapor, nitrogen oxides, hydrocarbons, and aerosol properties). Previously, we measured NO$_3^-$ in the laboratory by dosing the ambient air with the NO$_3^-$ precursor, dinitrogen pentoxide (N$_2$O$_5$). We simply modulated the N$_2$O$_5$ source flow on and off, allowing us to determine the cavity decay rate, $1/\tau$ (s$^{-1}$), with and without the NO$_3^-$ absorption contribution. The difference between NO$_3^-$ on and off measurements can be directly converted to a concentration. To measure the NO$_3^-$ concentration in the field requires a method of eliminating the NO$_3^-$ contribution to the total cavity decay rate. We refer to this removal procedure as zeroing. In this chapter, we discuss different zeroing methods as they pertain to the construction of a field instrument.

Processing the atmospheric air sample requires a sampling method to transport the air into the CRDS detection beam. Because the nitrate radical is reactive, reactions between NO$_3^-$ and the sampling inlet may destroy NO$_3^-$ prior to detection. We must therefore consider the effect of the sampling procedure on the quantitative determination of NO$_3^-$ concentrations.

In addition to the problems associated with zeroing and sampling, we consider several other factors that go into determining the ambient NO$_3^-$ concentration from a complete CRDS measurement. These correction factors, when combined, yield the final equation used for data reduction of the field measurements taken during the Phoenix Sunrise 2001 field campaign.
5.2 Overview of the prototype instrument

Figure 5.1 shows a block diagram of the field instrument used during the Phoenix Sunrise 2001 campaign (described in chapter 7). The boxes above the main diagram convey the regions over which the sample passes. The sample stream is continuously pulled from the atmosphere by the action of a vacuum pump. Ambient air enters the inlet through a section of glass tubing, labeled "inlet – region A" in Figure 5.1. The sample passes next to a region labeled "zero – region B" that represents the volume of the inlet that is sometimes used to remove NO₃ from the sampled air stream. The inlet extends through a chamber that houses the ring-down cavity (RDC) mirrors. This purge chamber protects the mirrors from accumulating particulates present in the sampled air. As the air exits the zero volume, it enters a glass cell that is referred to by "detection – region C" in the block diagram atop Figure 3.1. Here, the sample interacts with well-defined beam volume of the laser. Lastly, the sample is drawn to the pump and exhausted a long distance away from the instrument inlet.

Throughout this chapter, we are concerned with the time that an air parcel spends in a given region illustrated by the blocks above Figure 5.1. We generally define the time that an air parcel spends in a particular a stage of the sampling cycle in terms of the residence time for that process, which is easily calculated if the flow system parameters known. For instance, the total residence time through the system (i.e. to beginning of region D) is determined from the total system volume and the volumetric flow rate. The system volume is approximately 1.0 l and the volumetric flow rate through the inlet is approximately 85 l min⁻¹, yielding a total residence time of 0.70 s (i.e. this the time it takes a sample molecule to travel through the system). Because the flow is turbulent, all flow calculations assume a plug flow, where the velocity profile and concentration profile are constant across a cross section of the inlet.

5.3 Converting the CRDS signal to a detected NO₃ concentration

Analysis of the decay transient observed during a single CRDS measurement yields the ring-down time, τ (s). For a ring-down cavity (RDC) filled with a homogenous atmospheric sample that includes the nitrate radical, τ is given by
Figure 5.1 A block diagram overview of the field prototype instrument. Shaded areas indicate volumes where the atmospheric sample passes. The regions labeled on top of the instrument figure indicate stages that the atmospheric sample undergoes during transport through the instrument.
\[
\tau = \frac{I}{c[(1 - R) + b(\lambda) + \sigma[N\text{O}_3](\lambda)]},
\]

(5.1)

where \( R \) is the mirror reflectivity, \( c \) (cm s\(^{-1}\)) is the speed of light, \( I \) (cm) is the mirror-to-mirror distance of the resonator, and \( b(\lambda) \) (cm\(^{-1}\)) is the extinction coefficient of the air mass without the contribution of the NO\(_3\) absorption, \( \sigma(\lambda)[\text{NO}_3](\text{cm}^{-1}) \). Thus, we measure the product \( \sigma[N\text{O}_3] \) (i.e. the NO\(_3\) absorption coefficient) at 662.2 nm, and calculate the nitrate radical concentration using laboratory measurements of \( \sigma \) at 662.2 nm. The wavelength dependence is omitted from the following text and it should be assumed that wavelength dependent values correspond to the laser wavelength (662.2 nm).

We refer to the ring-down time in the absence of NO\(_3\) absorption as the baseline ring-down time, denoted \( \tau_b \) (i.e. removing the term \( \sigma[N\text{O}_3]/ \) in equation (5.1)). Thus, the baseline ring-down time accounts for all background extinction that is a result of both imperfect mirror reflection (1-\( R \)) and extinction due to particles and gases, other than NO\(_3\), that scatter and absorb radiation in the path of the probe beam. Successively measuring the baseline ring-down time, \( \tau_b \) (s), and the ring-down time in the presence of the NO\(_3\) absorber, \( \tau \) (s), allows one to directly determine the nitrate radical concentration by subtracting the baseline decay rate, \( 1/\tau_b \) (s\(^{-1}\)), from the total decay rate, \( 1/\tau \) (s\(^{-1}\)). Thus, the detected nitrate radical concentration, \([\text{NO}_3]_{\text{det}}\), is given by

\[
[\text{NO}_3]_{\text{det}} = \frac{1}{c\sigma} \left( \frac{1}{\tau} - \frac{1}{\tau_b} \right).
\]

(5.2)

In the field, it is difficult to determine \( \tau_b \), so we use a zeroing method to determine a very close approximation of \( \tau_b \).

5.4 Zeroing methods

5.4.1 General considerations

Zeroing the instrument in the field could be accomplished by either differential spectroscopy (i.e. measuring \( \tau \) on and off the absorption line similar to DOAS) or by
processing the sampled air to remove NO$_3$ and measure the cavity decay time at a single wavelength. We refer to the later method as a chemical zero, and the former method as a spectroscopic zero. The spectroscopic zero requires determination of the decay constant of at the maximum NO$_3$ absorption and then at a nearby wavelength where the NO$_3$ radical does not absorb. Alternately switching between two wavelengths requires either tuning the laser on and off the absorption line, which introduces the issue of the laser wavelength repeatability, or employing two lasers operating at nearby wavelengths, which requires a more complex and expensive setup. Additionally, the quantitative accuracy of using a spectroscopic zero assumes that the mirror reflectivity and the extinction coefficient of the air mass are the same at both wavelengths. The red spectral region is plagued with water lines as discussed in chapter 3. If the water absorption is not equal at these two wavelengths, the instrument will have a water interference. We can ensure that both measurements, $\tau$ and $\tau_0$, include the same water vapor contribution by using a chemical zeroing at a single wavelength near the NO$_3$ absorption maximum. Thus, we investigated the use of a chemical zeroing method to remove the NO$_3$ radical from the detection beam to accurately reproduce the baseline ring-down time, $\tau_0$. Both photolysis (i.e. selective destruction of sample molecules by light absorption), and chemical titration (i.e. selectively destroying the sample molecules via the chemical reaction with another compound) were investigated for use in the field instrument.

Two properties are desired from a chemical zeroing method. First the method should modulate the NO$_3$ concentration on and off without modulating baseline absorption (i.e. other absorbing gases present in the sample stream). Additionally, the method should be sufficiently fast (i.e. rapidly turn the NO$_3$ radical concentration on and off) such that the background extinction can be followed periodically. The total cavity decay time ($\tau$) fluctuates during a sampling period as a result of physical and chemical changes in the sampled air mass (i.e. decreased or increased extinction of the 662-nm detection beam caused by changing particulate loading, temperature or pressure, or fluctuating NO$_3$ absorption). Due to the fluctuating properties of a sampled air mass, it is important to measure $\tau_0$ frequently, determining the contribution of the extinction
coefficient to the total cavity decay time. This type of differential detection scheme eliminates interference by gases that absorb in the 662 nm region (e.g., O₃, and H₂O) and particles that absorb and scatter the radiation at 662 nm region, allowing one to determined the NO₃ concentration on top of a changing background. Modulation of NO₃ typically affects NO₂, but the absorption cross section of NO₂ is approximately four orders of magnitude smaller than that of NO₃, so the NO₂ modulation has a very small effect on the absorption signal modulation. Next, we consider the efficiency of a particular zeroing method.

5.4.2 Zeroing efficiency correction

Figure 5.2 shows two hypothetical time series of the ring-down time determined at 662.2 nm near the maximum absorption of the nitrate radical. The upper trace shows a constant baseline ring-down time, labeled by τ₀, which has been given the value of 85 μs; this is the cavity decay time in the absence of nitrate radical absorption, [NO₃] = 0. Addition of NO₃ to the RDC results in the shortest ring-down time on the plot, labeled by τ, which has a value of 60 μs; the ring-down time is shortened as a result of NO₃ absorption. The nitrate radical concentration used to construct Figure 5.2 is 7.78 x 10⁻⁹ molecules cm⁻³ (316 pptv), which can be determined from equation (5.2) using the absorption cross section at 662 nm (σ = 2.10 x 10⁻¹⁷ cm² molecule⁻¹). The middle trace, labeled by τ₂, has a value of 70 μs and corresponds to times during the sampling period where we chemically zero the instrument, but residual NO₃ prevents measurement of τ₀ (i.e. the zeroing method is not 100% effective in removing the NO₃ from the RDC). The modulated trace that is cycling between 70 and 60 μs represents a modulated NO₃ signal that would be observed in the field. The concentration determined from the modulated trace, [NO₃]_{mod}, is 3.78 x 10⁻⁹ molecules cm⁻³ (153 pptv), using equation (5.2), and replacing τ₀ with τ₂, the baseline ring-down is determined by the zeroing procedure. The previous calculation underestimates the actual NO₃ concentration because the calculation does not consider the imperfect zeroing efficiency used in this example.
Figure 5.2 Theoretical zeroing efficiency concept. A time series of the ring-down time in the absence of NO$_3$ ($\tau_0$), during titrant addition ($\tau_z$), and in the presence of NO$_3$ absorption ($\tau$).
To correct for imperfect modulation of NO₃, we define the zero efficiency of the method, \( z \), as the fraction of NO₃ radicals destroyed during the baseline measurement. The zeroing efficiency can be directly calculated from the plot via the following equation,

\[
z = \frac{[NO₃]_{\text{mod}}}{[NO₃]_{\text{det}}} = \frac{(1 - \frac{\tau}{\tau_z})}{(1 - \frac{\tau}{\tau_o})},
\]

where \([NO₃]_{\text{mod}}\) is the nitrate radical concentration determined from the modulated NO₃ signal (\( \tau \)) and the zero measurement (\( \tau_z \)), and \([NO₃]_{\text{det}}\) is the again the detected concentration as determined from \( \tau \) and \( \tau_o \). The value of \( z \) is 0.486 in figure 5.2. The detected NO₃ concentration, \([NO₃]_{\text{det}}\), is related to the NO₃ concentration determined via the zero measurement, \([NO₃]_{\text{mod}}\), by

\[
[NO₃]_{\text{det}} = \left( \frac{1}{z} \right)[NO₃]_{\text{mod}}.
\]

Using this formula we predict that

\[
[NO₃]_{\text{det}} = \left( \frac{1}{0.486} \right)(3.78 \times 10^{-9} \text{ molecules cm}^{-3}) = 7.78 \times 10^{-9} \text{ molecules cm}^{-3},
\]

in agreement with the assumed NO₃ concentration. Clearly having a near 100% zeroing efficiency is important to detecting NO₃ with high sensitivity. Otherwise, having a low zero efficiency degrades the instrument sensitivity by magnifying the baseline noise.

### 5.4.3 Photolytic zeroing

Photolysis of NO₃ (<630 nm) provides one means of measuring a chemical zero. Illuminating the atmospheric sample prior to reaching the detection region, will remove NO₃ from the sample stream. Thus, the NO₃ concentration is modulated on and off by modulating a photolysis beam off and on. Photolysis experiments utilized a transverse flow direction, as shown in figure 5.3. In this setup, the air is drawn through a rectangular sample inlet constructed of aluminum sidewalls and glass plates on the top and bottom. A photolysis lamp is modulated on and off with a mechanical shutter.

The theoretical zeroing efficiency, \( z \), in the case of photolysis is given by

\[
z = \frac{[NO₃]_{\text{mod}}}{[NO₃]_{\text{det}}} = \exp(-k_p t_p),
\]
Figure 5.3 A block diagram overview for transverse flow configuration. A photolysis beam is modulated on and off via the shutter shown above.
where $k_p \, (s^{-1})$ is the photolytic rate constant and $t_p$ is the photolysis residence time (i.e. the time that the sample spends in the photolysis region). The gray region in figure 5.3 indicates the photolysis region. The photolytic rate constant is determined by

$$k_p (s^{-1}) = \int \sigma(\lambda) \phi(\lambda) J(\lambda) d\lambda,$$

where $\sigma(\lambda)$ is absorption cross section, $\phi(\lambda)$ is the quantum yield, and $J(\lambda)$ is the photon flux in units photons cm$^{-2}$ s$^{-1}$ nm$^{-1}$. Measuring the visible power of the lamp and then normalizing the lamp's output spectrum over the same region allows one to determine the photon flux.

Figure 5.4 shows the results of one experiment, and plots the ring-down time in the presence and absence of the NO$_3$ radical. This NO$_3$ sample was generated in the laboratory using N$_2$O$_5$ as previously discussed in chapter 4. The gray regions indicate times for which the photolysis lamp is on. Thus, modulating the photolysis beam results in a modulated NO$_3$ signal. Because photolysis is incomplete, the lamp-on state of the upper trace contains residual NO$_3$ and is offset from the actual baseline cavity loss. The average baseline ring-down time (i.e. when NO$_3$ is not being added to the flow) is 47.4 $\mu$s. The ring-down time in the presence of NO$_3$ ($\tau$) is 39.8 $\mu$s. The modulated concentration determined by photolysis is thus $4.32 \times 10^9$ molecules cm$^{-3}$ (176 pptv). The detected concentration determined by averaging the surrounding baseline measurements (44.6 $\mu$s), and the detected concentration using $\tau$ and $\tau_0$ is $6.43 \times 10^9$ molecules cm$^{-3}$ (261 pptv). The zeroing efficiency determined from the plot in Figure 5.4 is 0.672.

While the photolytic zeroing efficiency can be improved by increasing the lamp power (increasing $k_p$), by reflecting the beam multiple times over the photolysis region (increasing $k_p$), or by increasing the system residence time (increasing the photolysis time $t_p$), it is difficult to adapt the transverse flow configuration for field measurements because a large, rectangular inlet is needed. Additionally, a slow flow rate (or long residence time) through the chamber is required to allow sufficient time for photolysis (>1 s) for reasonable lamp powers in the visible region. Because it was our general
Figure 5.4 Photolytic zeroing example. Hatched regions indicate times where the photolysis lamp is on. The upper trace corresponds to times when NO$_3$ is not being added to the flow cell.
design principle to keep the residence time $<1\, \text{s}$, in order to minimize the contact time between NO$_3$ and the inlet walls, employing the transverse flow configuration with the photolysis zeroing system was not practical. Additionally, the photolysis system itself is bulky, requires power and is potentially difficult to locate in particular sampling locations.

5.4.4 Chemical zeroing

As presented in chapter 1, nitric oxide (NO) reacts rapidly with NO$_3$ to form 2NO$_2$. Figure 5.5 shows a modulating NO$_3$ signal that is the result of NO to the sample stream to destroy the NO$_3$ radical. The NO is added upstream of the detection cell (section B in Figure 5.1). It is clear from the plot that the zero efficiency is near 100%, and accurately reproduces $\tau_0$. Thus, this chemical zeroing method was chosen for the field instrument. The actual modulation depth of the field instrument is discussed in chapter 6. Additionally, the chemical zeroing method allows us to flow the sample along the cavity axis, similar to figure 5.1, using a series of tubes, which makes it easier to locate the sampling inlet in the field.

5.5 Pathlength correction

The NO$_3$ concentration is calculated by converting the CRDS observation to a zero-efficiency corrected concentration, $[\text{NO}_3]_{\text{det}}$ (equation (5.4)). The calculation assumes that the NO$_3$ is homogeneously distributed along the entire CRDS beam path, which is not usually the case for a field CRDS instrument. In practice, the NO$_3$ is not uniformly distributed because the mirrors need to be housed inside purge chambers to protect them from the atmosphere. The detection beam passes through a sampling cell containing NO$_3$ and the purge chambers do not contain NO$_3$, only a purge gas. Therefore, only a fraction of the cavity length contains NO$_3$ molecules. In reference to figure 5.1, the length over which the probe beam illuminates the sample gas is termed $l_a$ (cm), and the entire length of the beam is shown as $l$ (cm).
Figure 5.5 Chemical zeroing example. The arrows indicate times were the NO titrant is used to destroy the NO$_3$ radical, the times when NO is not being added, and times when NO$_3$ is not being added to the sample stream.
The nitrate radical concentration as a function of distance, $N(x)$, traveled in the absorption cell is

$$\int_{0}^{l} N(x) \, dx.$$  \hspace{1cm} (5.7)

For a nitrate radical concentration that is constant in time (or equivalently in terms of the distance traveled through the cell), the integral in equation (5.7) is simply evaluated to $Nl_a$. Substituting $Nl_a$ for $NI$ in equation (5.1), and subtracting the two decay rates (equation (5.2)) results in the factor, $l/l_a$ (i.e. the ratio of the mirror-to-mirror distance to the beam pathlength containing $NO_3$. Therefore, the ambient $NO_3$ concentration inferred from the CRDS measurement, $[NO_3]_{det}$, is less than the $NO_3$ concentration present in the absorption cell (section C in figure 5.1) by a constant factor, $(l_a/l)$. Notice that if the length of the sample cell is the cavity length (i.e. the CRDS mirrors form the windows of the absorption cell), then $l = l_a$, and we reproduce equation (5.2) exactly. The detected concentration corrected for $z$ and the beam pathlength is

$$[NO_3]_{det} = \left( \frac{l_a}{l} \right) [NO_3]_{cell}.$$  \hspace{1cm} (5.8)

Typical purge geometries allow 60 - 90% of the CRDS pathlength to contain $NO_3$ molecules, resulting in a significant, but easily quantifiable correction factor.

### 5.6 Dilution correction

Previously, we mentioned that the CRDS mirrors are housed inside chambers to prevent particles from collecting on the mirror surface. This precaution is important because the sensitivity of the CRDS technique is degraded as the mirror reflectivity is reduced. To help prevent degradation of the mirror reflectivity, a flow (typically 2 slpm) of breathing quality air is passed over the mirror surface and adds through each side of the detection region (figure 5.1). The purge flow adds to the sample stream as it enters the absorption cell and thus dilutes the detected $NO_3$ concentration. If there are leaks in the purge boxes, as was the case during PHX 2001, this flow will also dilute the sampled $NO_3$ concentration. Taking into account the total dilution, the sum of added flow by
purge and leaking air into the system, results in the following equation for the NO$_3$ concentration in the cell,

$$\left[\text{NO}_3\right]_{\text{cell}} = \left(\frac{F_{\text{inlet}}}{F_{\text{inlet}} + F_{\text{dilute}}}\right)\left[\text{NO}_3\right]_{\text{cell inlet}},$$  \hspace{1cm} (5.9)

where $F_{\text{inlet}}$ (l min$^{-1}$) is the inlet flow rate and $F_{\text{dilute}}$ (l min$^{-1}$) is the rate of flow into the system that dilutes the [NO$_3$], and [NO$_3$]$_{\text{cell inlet}}$ is the NO$_3$ radical concentration prior to entering the absorption cell.

5.7 **Surface loss correction**

Sampling artifacts are induced when the sampling technique alters the composition of the atmospheric sample in some way. In the specific case of the NO$_3$ radical, the sampling operation can lead to inaccurate quantification of the ambient NO$_3$ concentration via two chemical pathways. First, reactions between NO$_3$ and the instrument walls may remove NO$_3$ molecules during transport through the system. A second NO$_3$ loss mechanism is the reactions of dinitrogen pentoxide (N$_2$O$_5$) with the water adsorbed to the inlet surface, leading to NO$_3$ loss as a result of a reestablishing the NO$_2$/NO$_3$/N$_2$O$_5$ equilibrium. Under reasonable atmospheric conditions (i.e. N$_2$O$_5$ concentration in the parts per billion by volume range), the relaxation time to reform N$_2$O$_5$ is on the order of several seconds for N$_2$O$_5$ concentrations on the order of $10^{-11}$ molecules cm$^{-3}$. Keeping the system residence time short (<1 s) leads to a small loss of the NO$_3$ via the N$_2$O$_5$ loss pathway, as well as minimizing the contact time for an NO$_3$ molecule in the inlet. Hence, we are primarily concerned with the direct loss of NO$_3$.

We denote the atmospheric concentration of NO$_3$ as [NO$_3$]$_{\text{ambient}}$, which is drawn into the inlet (region A) in figure 5.1. If the nitrate radical is lost during transport through the system, then the concentration will be changing in time during detection. We designate the average nitrate radical concentration determined in the detection region (region C) by [NO$_3$]$_{\text{cell inlet}}$. Specifying the fraction of molecules removed during transport through the instrument by $L$, we can write the ambient concentration prior to entering the inlet as
\[
\frac{[\text{NO}_3]_{\text{ambient}}}{[\text{NO}_3]_{\text{cell inlet}}} = \frac{[\text{NO}_3]_{\text{cell inlet}}}{(1 - L)}.
\]

(5.10)

In the absence of sample loss, \(L = 0\) and \([\text{NO}_3]_{\text{ambient}} = [\text{NO}_3]_{\text{cell inlet}}\). Otherwise, the presence of sample loss (\(L > 0\)) degrades the sensitivity of the technique because the resulting \(\text{NO}_3\) measurements and baseline noise are magnified by \((1 - L)^{-1}\).

We can analyze this situation by assuming that the rate of removal of \(\text{NO}_3\) from the sample stream is a first order process (the rate of removal is proportional to the concentration). The concentration of \(\text{NO}_3\) as a function of time in the flow system is given by

\[
[\text{NO}_3](t) = [\text{NO}_3]_{\text{ambient}} \exp(-kt),
\]

(5.11)

where and \(k\) (s\(^{-1}\)) is the pseudo first-order rate constant for the reaction between \(\text{NO}_3\) and the instrument wall or surface (shown below) and \(t\) is the time that the \(\text{NO}_3\) molecules have been in contact with the walls,

\[
[\text{NO}_3]_{+ \text{wall}} \rightarrow \text{products}.
\]

(5.12)

Our detector is not a true "point" detector, and we detect the concentration of \(\text{NO}_3\) over some region of wall contact times. Thus, the effective wall loss is given by

\[
L = \int_{t_c}^{t_d} (1 - e^{-kt}) dt
\]

(5.13)

where \(t_c\) is the time at which \(\text{NO}_3\) molecules enter the sample cell and \(t_d\) is the time where the \(\text{NO}_3\) molecules exits the sample cell.

The fraction of molecules removed during transport to the end of the absorption cell, \(L\), can be determined in the laboratory by adding \(\text{NO}_3\) to the sample stream for a series of residence times to determine the loss rate \(k\). An additional method of measuring the loss rate is to measure the \(\text{NO}_3\) concentration in the field as a function of residence time by varying the sampling flow rate. A difficulty with the later experiment is that it requires a large, stable \(\text{NO}_3\) concentration during the course of an experiment. In chapter 6 we discuss in detail the method for determining the loss rate for the configuration used during the Phoenix Sunrise Campaign 2001.
5.8 Conclusions

Each of the proceeding correction factors represented transmission factors for the fraction of NO₃ that is detected compared to what is present in the ambient atmosphere, thus we can combine all of these factors into a single equation. The ambient NO₃ concentration is related to the detected concentration by the following equation,

\[
[NO₃]_{\text{ambient}} = [NO₃]_{\text{mod}} \left( \frac{1}{z} \right) \left( \frac{I}{I_o} \right) \left( \frac{F_{\text{inlet}} + F_{\text{dilute}}}{F_{\text{inlet}}} \right) \left( \frac{1}{1 - L} \right),
\]  

(5.14)

where \([NO₃]_{\text{mod}}\) is determined, real-time, by measuring \(\tau\) and \(\tau_z\).

\[
[NO₃]_{\text{mod}} = \frac{1}{c \sigma} \left( \frac{1 - \frac{1}{\tau}}{\tau_z} \right).
\]  

(5.15)

In the following chapter, we will quantify all of these factors and derive an overall equation relating the measurement to NO₃ ambient concentrations. In the following chapter, often we convert \([NO₃]\) (molecules cm⁻³) to a mixing ratio in air using the density of air molecules at the cavity temperature and pressure (typically room temperature and 1 atm). The product of these correction factors magnifies the noise and degrades the sensitivity of the technique (i.e. the baseline noise must be multiplied the total correction factor).
Chapter 6

Field Instrument design and quantification of correction factors

6.1 Introduction

In this chapter, we describe the configuration of the field CRDS instrument that was used to determine NO$_3$ concentrations during the Phoenix Sunrise 2001 campaign (described in chapter 7). The instrument is split into two parts coupled by optical fibers to carry the laser beam and detected CRDS signal to and from the ring-down cavity (RDC). The detection side contains the RDC and the sampling inlet. The electronics side contains the laser and data acquisition electronics.

During our testing of the instrument in the laboratory, we generate the nitrate radical using the thermal decomposition of dinitrogen pentoxide. Thus, we consider some of the details associated with this method of NO$_3$ generation used to quantify the correction factors that were discussed in Chapter 5. We discuss the chemical zeroing method used for the field measurements and the corresponding zero efficiency of the method. We also present the method by which we determine the surface loss correction factor, the flow dilution correction factor, and the beam pathlength correction factor for the field instrument. Finally, we present the overall correction factor that is applied to the NO$_3$ data from Phoenix Sunrise Campaign presented in chapter 7.

6.2 Field-prototype configuration

6.2.1 Instrument design

The external cavity diode laser (ECDL) (Environmental Optical Sensors, model 2010) and the beam launching optics are mounted on a small optical breadboard (18" × 24" × 2") (figure 6.1). The ECDL outputs an elliptical beam that is directed onto an anamorphic prism beam expander (CVI Laser, AP-3X series), which circularizes the beam by reducing the long dimension of the elliptical beam. The circularized beam (~800 µm diameter) is directed onto an acousto-optic modulator (AOM) (Isomet, model IMD 80H-776B), which acts as a fast (<1 μs) optical switch, interrupting the laser beam during acquisition of the ring-down decay. The first-order diffracted beam from the
Figure 6.1 The laser optics platform. The components are the external cavity diode laser (ECDL), the anamorphic prism beam expander (AP), the acousto-optic modulator (AOM), and the fiber port used to couple the ECDL into the optical fiber.
AOM (~80% of the beam power striking the AOM) is focused into a single-mode (SM), polarization maintaining (PM) optical fiber (FCPP-10-670-FC/APC/APC) with the aid of a micro-positioning mount and focusing optic (\( f = 2.0 \) mm) (OFR, PAF-X FiberPort series). The un-diffracted zero'th order beam that passes through the AOM when the AOM power is off does not couple into the fiber. The fiber-coupling efficiency is typically 12-25%. The alignment holds for long periods of time in a stable environment.

The ring-down cavity optics and the sampling inlet are mounted on a separate lightweight optical breadboard (23" × 35" × 2") (figure 6.2 and figure 6.3) without any particular vibration isolation mechanisms. The optical components are housed in two chambers. The chamber walls are constructed from aluminum bar stock, and are bolted to the optical breadboard. Two Plexiglas sheets bolt to the top of the sidewalls to form the chamber tops. Rubber gaskets on the top and bottom of the walls form a seal. The fiber carrying the laser beam to the RDC enters through a hole in the input beam chamber sealed with a slotted rubber stopper. The beam exiting the SM-PM optical fiber is collimated with a lens (OFR, CFC-5-660) and aligned onto the input RDC mirror via an optical mount (CVI Laser, 160-10). The four RDC mirrors (Research Electro-Optics, R>99.996%) are arranged in a bowtie configuration. The length of bowtie is 43 cm and the width between the mirrors is 5 cm. The mirrors are plano concave with a radius of curvature of 1 m. The cavity mirrors are held in optical mounts (CVI Laser, 160-10). The cavity is optically stable (refer to chapter 2). Each chamber is subdivided to accommodate a slow flow of breathing quality air that is passed around the RDC mirrors. The stream of air helps purge the mirrors of dust and particles. The line for the purge air is 1/4" OD PFA Teflon tubing. The tubing enters each chamber through a Swagelok fitting. The flow rate to each purge chamber is controlled independently with standard variable area flow meters. The flow rate of the purge air is typically 2 standard liters per minute (slpm) per purge chamber. The light intensity that leaks through the output mirror is focused into a multi-mode optical fiber (200 \( \mu \)m Silica/Silica, NA = 0.22) with a focusing lens (\( f = 15 \) cm). The signal is transmitted through the 10 m fiber optic and
Figure 6.2 A block diagram overview of the CRDS field prototype instrument. The data acquisition electronics (DAQ) and mass flow controller (MFC) are housed in a box separate from the rest of the instrument. The external cavity diode laser (ECDL) and avalanche photodiode detector (APD) are mounted on a small optical breadboard along with the laser optics (see figure 6.1). The detection platform is connected to the laser platform via fiber optic cables.
**Figure 6.3** An expanded view of the detection platform. The sample flow path is along the long axis of the glass cell. The flow is drawn through the system via the action of a pump. Plexiglas tops cover the chambers that house the optics.
focused onto a silicon avalanche photodiode (APD) (Hamamatsu C5460), mounted on the
breadboard with the beam launching optics.

A glass cell (13" × 2.875" × 0.375") encloses the space between the input and
output beam chambers. The laser beam passes between the two chambers and through the
glass cell via four 1/4" OD holes in the walls of the chambers. The cell is clamped
between the chambers. Rubber gaskets form the seal on both ends of the cell. Air enters
the detection region through a 9.5" length, 1/2" ID glass tube that slips through an
UltraTorr fitting in the beam output chamber. The tube is input through a hole in the
sidewall, positioned between the two RDC mirrors. The sampled air stream is drawn
through the glass cell by a vacuum pump that connects to the system through an
UltraTorr fitting in a small aluminum block located between the sampling cell and input
beam chamber. Different inlet configurations can be utilized by attaching glass pieces
that connect to each other with o-ring sealed glass joints.

6.2.2 Data acquisition

The instrument is controlled by a personal computer (Dell Dimension L600r)
runtime LabVIEW (National Instruments) software. An avalanche photodiode detector
(APD) (Hamamatsu, model C5460) monitors the energy within the resonator by detecting
the small fraction (∼10⁻⁵) of the intra-cavity power that is transmitted through the output
mirror. LabVIEW triggers the acquisition once the APD detector signal reaches a
software-set threshold value by triggering the AOM to deflect the input beam. The APD
signal is recorded by a 12-bit, 1.25 MHz digitizer board (National Instruments PCI-MIO-
16E-1). The data are collected at 200 kHz. The program default is to collect 128 points
(buffer size), which corresponds to 640 μs of data. The ring-down transient (128 points)
is transferred to the computer for analysis after each scan.

The cavity decay time (τ) is determined from a weighted least-squares regression
to single ring-down transient curves [Bevington, 1992]. Subtracting the baseline offset
from the transient is required prior to analyzing the data. The value of the baseline signal
is determined by averaging the final 40% of the transient data. The baseline is
represented by the last 256 $\mu$s of the sampling interval. The baseline value is subtracted from each point along the initial 60% of the decay. For a 70 $\mu$s ring-down time, data encompasses approximately 6 ring-down times ensuring that the baseline is free of residual signal. The baseline-corrected data are transformed by taking the natural logarithm of each point along the ring-down transient. At some point late in the transient, noise drives the signal negative, which means that the natural logarithm of the signal is undefined. We truncate the baseline corrected data at the first negative data point prior to weighted-linear fitting. Typically, 4-5 lifetimes get analyzed ($\sim 280 - 350 \mu$s). A best estimate of the variance is used to weight each point along the ring-down transient [Bevington, 1992]. This algorithm will work to $\sim 75 \mu$s ring-down times. Longer ring-down times will lead to non-zero signal during the baseline determination. The ring-down time is extracted from the best-fit slope.

6.2.3 Cavity tracking circuit

In measuring the NO$_3$ absorption spectrum (chapter 4) we modulated the laser frequency by one free spectral range (FSR) to ensure that the laser would come into resonance with ring-down cavity (RDC), allowing build up and observation of a ring-down transient. An increased repetition rate is obtained when the ring-down events are centered with respect to a modulation amplitude that is smaller than the cavity FSR. While this changed modulation pattern improves the data rate on a short time-scale, vibrations and temperature fluctuations cause the cavity length to change and result in a cavity mode structure that jitters or drifts outside of the modulation window.

To compensate for the shifting mode structure of the RDC, we constructed a feedback circuit that provides a DC bias voltage to the piezoelectric transducer of the laser. The DC bias voltage centers each new AC modulation cycle on the frequency at which the previous ring-down event occurred. In this way we track the position of a single TEM$_{00}$ mode, significantly improving the data rate. Using this tracking scheme, we typically obtain data rates on the order of 20 to 40 Hz using a modulation frequency of 100 Hz and amplitude that is 19% of the cavity FSR, and flowing ambient laboratory air. The cavity FSR for the field instrument is 174 MHz, thus the modulation width is 33
MHz for this case. For our specific setup, the PZT modulation width (amplitude) is 8 mV, and the FSR of the bow-tie cavity is 40 mV.

LabVIEW controls the frequency and amplitude of the AC component of the ECDL scanning pattern. Occasionally, the “tracked” cavity mode will move outside the modulation window as a result of fast time-scale disturbances (i.e. mechanical shock) that rapidly change the mirror-to-mirror distance, or events that interrupt the laser beam. When this fault occurs, LabVIEW initiates a routine that generates a large modulation window (>1 FSR) that exponentially decays; each cycle steps down until the operating amplitude is reached. During each step, a new modulation window is centered with respect to the frequency of the registered ring-down events.

Ideally, a build-up and ring-down transient should be observed twice per modulation cycle, but in practice a reduced hit rate for passing through the trigger threshold is observed because the cavity does not always build intensity above threshold. Reducing the modulation amplitude increases the repetition rate because the laser scans across the TEM$_{00}$ mode slower at smaller amplitude modulation. For instance, consider modulating the laser frequency with a triangle wave of amplitude 174 MHz. If the modulation frequency is $10 \text{ Hz}$, it takes 50 ms to span one FSR (174 MHz). The slew rate is defined as the frequency change per unit time. For this example, the slew rate is 3.5 MHz/ms. The linewidth of a TEM$_{00}$ mode of the cavity is on the order of 100 kHz. Thus, the laser is in resonance with the cavity for $28 \mu$s. The previous exampled scanned a FSR. Next, consider scanning 19% of the FSR, or 33 MHz (and 10 Hz). The slew rate in this case is 0.66 MHz/ms; thus the laser is in resonance for 152 $\mu$s, achieving larger build-ups inside the resonator.

In general, the ability of the circuit to track a drifting TEM$_{00}$ mode is improved for a wide modulation window because the laser frequency scans a larger frequency range. The scanning frequency represents a compromise between having enough time to build energy within the resonator and fast enough so that the circuit can track shifts in the RDC mode structure. Operating at too fast of a modulation frequency does not allow the laser frequency to match the cavity mode frequency for a sufficient length of time. And
scanning the laser's frequency too slow to follow the changing mode structure of the cavity, causes the circuit to continually lose lock. Thus, in practice, the amplitude and frequency are adjusted to have the compromise of repetition rate and ring-down signal intensity.

6.3 Nitrate radical generation

In all laboratory experiments, the nitrate radical is generated from the thermal decomposition of previously synthesized dinitrogen pentoxide (N$_2$O$_5$). The N$_2$O$_5$ was synthesized by trapping the product of the gas-phase reaction of NO$_2$ with excess ozone in a glass trap at 198 K. This is the method of described by Canosa-Mas et al. [1999], an adaptation of the synthesis by Davidson et al. [1978]. The N$_2$O$_5$ solid adsorbed in the glass trap is stored in a freezer at -45 °C when not in use.

Production of the nitrate radical begins by passing a slow flow, at ambient pressure (~1 atm), of ultra high purity (UHP) nitrogen (N$_2$) through the glass trap containing the solid N$_2$O$_5$ crystals. The volume of the trap is ~500 mL. The temperature of the trap is maintained during a single experiment by partially submerging the trap into a constant temperature bath, composed of either dry ice and trichloroethylene (-78 °C), or acetone slush (-95 °C). The bath temperature determines the vapor pressure of N$_2$O$_5$ that is entrained in the nitrogen flow. Consequently, the flow rate of N$_2$ through the trap is adjusted for each experiment depending on the particular bath. The N$_2$O$_5$ is picked up in a 1 L min$^{-1}$ flow of N$_2$ for experiments that utilize the colder acetone slush bath. The corresponding residence time in the trap is 30 s. When generating NO$_3$ from the dry ice bath, the N$_2$ flow rate ranges between 0.01 and 0.25 L min$^{-1}$. The corresponding trap residence time ranges between 50 s and 2 min. Because the N$_2$O$_5$ vapor pressure is larger in the dry ice bath, the resultant flow from the trap is diluted prior to being added to the instrument inlet. The N$_2$O$_5$ in N$_2$ stream from the trap is added to a secondary flow (~1 L min$^{-1}$) of nitrogen.

Prior to being added to the main flow of the instrument, the N$_2$O$_5$ in N$_2$ stream is heated. The heated section consists of 0.32 cm ID PFA tubing wrapped in a heating tape and insulated with glass wool. The length of heated region is 56 cm. The air exiting the
heated PFA tube is ~71 °C. The total residence time through the heated region is 0.4 s at 1 L min⁻¹ flow. Calculations indicate that these conditions are sufficient to convert the N₂O₅ to NO₃ and NO₂ prior to dilution by the main sample stream of the instrument (see calculations below). The additional dilution at 298 K prevents NO₃ and NO₂ from reacting to re-form N₂O₅. In the discussion that follows, we reference the following reactions that are involved in NO₃ generation:

\[
\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5 \quad k_f \\
\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3 \quad k_r \\
\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5 \quad K_{eq} = k_f / k_r
\] (6.1-6.3)

Assuming that the source is free of contaminants (i.e. nitric acid or excess NO₂), we can calculate the fraction of N₂O₅ dissociate at the exit of the tube by considering the NO₃/NO₂/N₂O₅ equilibrium. Temperature dependent values for the forward rate constant (Reaction 6.1) and for the equilibrium constant (Reaction 6.3) are obtained from NASA JPL data [DeMore et al., 1997]. The rate constants are listed in chapter 1.

At dry ice temperature (~78 °C), the N₂O₅ mixing ratio in the glass trap is ~4 parts per million by volume (ppmv), determined by extrapolation of the vapor pressure data of McDaniels et al. [1988]. The resultant N₂O₅ stream (0.01 L min⁻¹) that exits the glass trap is picked up in the secondary flow of nitrogen (1 L min⁻¹). The new N₂O₅ mixing ratio is ~40 parts per billion by volume (ppbv) as a result of dilution. During transport through the heated region (0.4 s at 71 °C), we calculate that ~95% of the N₂O₅ has dissociated prior to exiting PFA inlet. The calculated lifetime for reaction 6.2 is ~0.14 s. Thus, there is ample time to reach equilibrium, and a constant addition of NO₃ and NO₂ occurs in the main instrument flow.

The NO₃ and NO₂ mixture is diluted at 298 K upon entrainment into the main system flow (~500 pptv using a system flow rate of 85 slpm). The dilution kinetically prevents the back reaction between NO₃ and NO₂ (i.e. the forward lifetime is 89 s and the reverse lifetime is 21 s). Both lifetimes far exceed the residence time in the cell used for determining the loss rate (<4 s). A similar analysis applied to the upper N₂ flow rate limit (0.25 L min⁻¹) of the dry ice experiments that results in a larger initial amount of N₂O₅.
(~800 ppbv) passing through the heated region, and in only 50% dissociation. When this flow is diluted into the main system flow, the forward lifetime (to reform N$_2$O$_5$) is ~16 s at 298 K, and is still longer than the residence time through the system. Thus, throughout the entire N$_2$ flow range, a constant addition is made to the sample stream of air. The kinetics are slow compared to the residence in the system.

In our experience with this procedure for generating NO$_3$, the amount of NO$_3$ detected is always much smaller (3 – 30 times smaller) than predicted by this model. Possible reasons for this discrepancy are first that the N$_2$O$_5$ vapor pressure calculation is wrong because the vapor pressure cannot be extrapolated to such cold temperatures. At these low temperatures, the vapor pressure of impurities in the trap like N$_2$O$_4$ may be larger than the N$_2$O$_5$ vapor pressure. Second, excess NO$_2$ will slow the dissociation kinetics to produce NO$_3$ and NO$_2$ via Le Chatelier's principle. The NO$_2$ may be present as an impurity in the N$_2$O$_5$ trap or created during the trap residence via reaction between the small, equilibrated amount of NO$_3$ in the top of the trap (not submerged in constant temperature bath) to form NO and O$_2$. The reaction between NO$_3$ and NO produces 2NO$_2$. The N$_2$O$_5$ may dissociate completely during the residence time of the heated inlet, but an excess concentration of NO$_2$ compared to NO$_3$ promotes the back reaction to reform N$_2$O$_5$ at the exit of the heated region, appearing as a loss of NO$_3$. Lastly, nitric acid formation from N$_2$O$_5$ reacting with water in the system will decrease the initial concentration of N$_2$O$_5$ that is added to the nitrogen flow out of the trap.

### 6.4 Zeroing efficiency

Nitrate radical concentrations are determined from successive measurements of the cavity decay time in the presence ($\tau$) and near absence ($\tau_z$) of the NO$_3$ radical (equation (5.15)). To measure baseline absorption ($\tau_z$) we selectively destroy the NO$_3$ radical by adding a small concentration of nitric oxide (NO) to the sample stream. The reaction produces two nitrogen dioxide (NO$_2$) molecules, a weak absorber in the 662-nm region,

$$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2.$$  \hspace{1cm} (6.4)
The absorption cross section is nearly 4 orders of magnitude smaller than the NO$_3$ absorption cross section at 662 nm.

To zero the instrument in the field, a 30.3 parts per million (ppmv) standard of NO in N$_2$ gas is added upstream of the cell inlet at a flow rate of 0.8 L min$^{-1}$. A mass flow controller (Tylan General, FC-280 series) delivers the NO gas to the system through a solenoid valve that modulates the NO gas on or off by passing it to the system or to a dump distant from the inlet. This flow is diluted into the total system flow (~85 slpm in the field). The resulting mixing ratio is approximately 30 ppbv. Using the bimolecular rate constant for reaction (6.4) at standard temperature (see chapter 1), and making the pseudo-first order approximation, we calculate that the NO$_3$ lifetime is ~0.05 s.

The residence time from the point of addition to the beginning of the detection region is about 0.2 s, or 4 times the reaction lifetime. To ensure that this addition was sufficient to destroy the nitrate radical we performed a series of experiments to determine the zeroing efficiency, $z$, of this chemical zeroing method.

Figure 6.4 shows a time series of the ring-down time for one zeroing experiment. Each point is the median of 25 CRDS measurements. The entire plot is divided into regions A, B, and C for the purpose of discussion. Each region corresponds to a different NO mixing ratio that is added to a sample containing the NO$_3$ radical. Region A corresponds to 0.1 ppmv of NO used for zeroing. The ring-down time in the absence of NO addition (source off) is 53 $\mu$s. Addition of NO (source on), results in $\tau_{21} = 55.2$ $\mu$s for modulation cycle A. Region B corresponds to 30 ppmv NO added (field conditions). The ring-down time during NO addition is $\tau_{22} = 58.7$ $\mu$s for modulated trace B. During region C, NO$_3$ is not being added to the system, and the value of the ring-down time is $\tau_o = 58.8$ $\mu$s. Using equation (5.3), we can calculate that the zeroing efficiency in the case of modulation A is 0.404. In the case of modulation B (field conditions), $z = 0.984$. Thus, in the notation of chapter 4,

$$\left[\text{NO}_3\right]_{\text{det}} = \left(\frac{1}{z}\right)\left[\text{NO}_3\right]_{\text{mod}} = \left(\frac{1}{0.984}\right)\left[\text{NO}_3\right]_{\text{mod}}.$$ (6.5)
Figure 6.4 Chemical zeroing experimental plot. Chemical zeroing is accomplished via the addition of nitric oxide to the sample stream. Region B corresponds to the addition of 30 ppbv NO to the sample stream containing NO₃. For region C, the NO₃ source was shut off.
The concentration of NO$_3$ detected as determined from the plot is 2.95 $\times$ 10$^9$ molecules cm$^{-3}$ (120 pptv).

Figure 6.5 illustrates how the zeroing efficiency depends on the mixing ratio of NO added. The zeroing efficiency increases for increasing NO mixing ratio. Correspondingly, the NO$_3$ lifetime, with respect to NO, decreases. Our operating parameters, 30.3 ppbv NO, are well within the region where $z = 1$.

6.5 Surface loss correction

To investigate the effect of sampling on the ambient NO$_3$ concentration we conducted a series of experiments to determine the pseudo first order loss rate for NO$_3$ on the walls. The loss rate is determined by changing the flow rate through the system, which changes the residence time and consequently the time that the NO$_3$ molecules are in contact with the walls. A single experiment consists of varying the inlet flow rate while adding a constant amount NO$_3$ to inlet flow. The inlet flow is varied over the range of $\sim$20 L min$^{-1}$ to 85 L min$^{-1}$.

Including a first order loss rate, $k$ (s$^{-1}$), the NO$_3$ concentration as a function of time, [NO$_3$](t), is

$$[\text{NO}_3](t) = \left( \frac{F_{\text{add}}}{F_{\text{total}}} \right) [\text{NO}_3]_i \exp(-kt),$$

where [NO$_3$]$_i$ is the initial NO$_3$ concentration added to the system, $F_{\text{add}}$ is flow rate of the NO$_3$ stream exiting the heated inlet (1 L min$^{-1}$), and $F_{\text{total}}$ is the sum of the inlet flow plus $F_{\text{add}}$. The ratio of $F_{\text{add}}$ to $F_{\text{total}}$ corrects for the dilution that occurs at the point of addition. The dilution varies with $F_{\text{total}}$, which is changed during the experiment.

A parcel of air resides in the detection region (i.e. the cell volume) for a time equal to $t_{\text{res}} - ft_{\text{res}}$, where $ft_{\text{res}}$ is some fraction of the total residence time, $t_{\text{res}}$. The average concentration detected in the cell, $\bar{[\text{NO}_3]}$, is

$$\bar{[\text{NO}_3]} = \frac{\int [\text{NO}_3](t)dt}{t_r - ft_r}.$$
Figure 6.5 Zeroing efficiency as a function of added titrant concentration. The NO mixing ratio was increased and the corresponding modulation depth (defined in text) was determined. Field conditions corresponded to NO mixing ratio of 30 ppbv.
Substituting for $[\text{NO}_3](t)$ in Equation (6.7) with the form of Equation (6.6), and integrating Equation (6.7) between the limits $f_{tr}$ and $t_r$ yields the following expression for the mean concentration of NO$_3$ in the detection cell,

$$\bar{[\text{NO}_3]} = \frac{F_{\text{add}}[\text{NO}_3]}{F_{\text{total}} k_{tr}(1 - f)} \left[\exp(-k_{tr}) - \exp(-k_{tr})\right].$$  \hspace{1cm} (6.9)

During a single experiment, the NO$_3$ concentration is recorded for a series of inlet flows. The data are then fit using a non-linear fitting routine to determine $k(s^{-1})$, the pseudo first order rate constant for reaction (6.5). The parameters of our experimental setup are such that the inlet volume and cell volume are equal. Thus, the total time that a gas molecule spends in the detection cell is half of the total residence time, thus the value of $f$ in equation (6.8) is 0.50. The total residence time is calculated from the system volume and the volumetric flow rate that is varied during the experiment.

Figure 6.6 shows the data from three experiments, which were performed at different initial concentrations of NO$_3$. Each experiment consists of measuring the NO$_3$ concentration via the chemical zeroing method described previously. The experiments exhibit slight concentration dependence. This could be explained by excess NO$_2$ concentration originating from the source, which reacts with NO$_3$ to form N$_2$O$_5$ during the system residence time. Increasing the flow through the N$_2$O$_5$ trap produces a larger initial value of N$_2$O$_5$ and may also produce a larger value of the initial NO$_2$ concentration, which is consistent with the trend of the data. Thus, the loss rate determined by our experiment may be considered as the sum of two losses, $k_f + k_{\text{loss}}$, where $k_f(s^{-1})$ is the forward rate constant for N$_2$O$_5$ production (reaction 6.1). Alternately, if the N$_2$O$_5$ concentration is increased to an amount such that the fraction of non-dissociated N$_2$O$_5$ exiting the heated region is large enough to source NO$_3$ during the system residence time, then $k_{\text{loss}}$ will be reduced. Adding N$_2$O$_5$ to the system with the heated inlet off showed no NO$_3$ signal in the detection region, indicating that the N$_2$O$_5$ are too slow to produce NO$_3$ within the residence times of our system. Thus, we take our loss rate to represent an upper limit.
Figure 6.6 Inlet loss calibration. The open circles represent the experimental data and the solid line is the best fit determined via a non-linear fitting routine. The three plots correspond to different initial NO$_3$ mixing ratios. The inlet flow rate is expressed in units of cubic feet per minute (cfm).
Ten experiments total were performed using the PFA Teflon heated inlet and dry ice bath described previously. Four experiments were performed using the acetone slush bath, yielding similar results. The detected NO$_3$ concentrations for a set of inlet flow rates were analyzed by a non-linear least-square regression, performed in Igor (Wavemetrics). The theoretical curves are shown as the lines in figure 6.6, and the data are shown as open circles. The average value of $k$ (s$^{-1}$) for the series of experiments is 1.11 (+/- 0.26) s$^{-1}$ (1 $\sigma$ error). Using the system operating values of the Phoenix Sunrise 2001 campaign, the fraction $(1-L)$ is calculated to 0.50 (+/- 0.08) (1 $\sigma$ error). The value of $(1 - L)$ is actually determined through a fitting procedure in Igor. In the notation of Equation (5.10),

$$[NO_3]_{ambient} = \frac{[NO_3]_{cell\ inlet}}{(1-L)} = \frac{[NO_3]_{cell\ inlet}}{0.50}.$$  
(6.10)

The surface loss model described above specifically assumes that the sample is well mixed within the detection cell, leading to the simple exponential loss of NO$_3$ in time. If the detection cell is not well mixed, it is possible that more of the NO$_3$ is lost along the outer paths of the bow-tie CRDS beam pattern than the amount of NO$_3$ lost on the crossing paths. We do not have sufficient detail on the actual flow within the detection volume to warrant creation of a more complex model for the surface loss process; therefore, we estimate an extreme case of inhomogeneous NO$_3$ distribution within the detection cell. In the case where the outer two paths have complete loss of NO$_3$, and only the two crossing paths contain NO$_3$, NO$_3$ would be detected in half the assumed pathlength, and the surface loss correction factor could be twice as large as compared to the simple model. One might expect that inhomogeneous distribution of NO$_3$ within the detection cell would make the data deviate from the simple exponential loss form. We do see some evidence for deviations from the simple model, but these deviations are fairly small. Therefore, we will retain the assumption of exponential surface loss, and calculate the loss correction using this simple assumption.
6.6 Flow dilution correction

The system flow rate is measured with a standard variable area flow meter prior to the pump. The pump metered flow is corrected for operating temperature and pressure. We found that the total flow rate was not equal to the sum of the purge flow rate and inlet flow rate (measured in the inlet). The additional flow was found to be a result of air leaking between the seals of the chamber. The ratio of the inlet flow rate to the pump flow rate while purging the RDC chambers is 0.73, thus \( F_{\text{inlet}} = 0.73F_{\text{total}} \). We assume half of the purge air flow and half of the leak flow occur at the inlet purge chamber, while the other half occurs at the output purge chamber, thus the inlet air is diluted by a flow of \( F_{\text{dilute}} = (1-0.73)/2) F_{\text{total}} = (0.135)F_{\text{total}} \). Thus, the flow correction factor \( (F_{\text{inlet}} + F_{\text{dilute}})/F_{\text{inlet}} = 1.185 \). We neglect the effect of dilution at the other purge chamber because this leak goes straight to the pump and does not dilute the air prior to the measurement.

6.7 Beam pathlength correction

To correct for the fact that only a portion of the beam is exposed the NO\(_3\) sample, we have to adjust the detected NO\(_3\) concentration as detailed in chapter 5. In the field configuration, the mirror-to-mirror distance of the ring-down cavity is 43 cm. The length of the sampling cell is 33.0 cm. In the notation of chapter 5, the ratio \( l/l_0 \) is equal to 0.767.

6.8 Conclusions

We can now rewrite Equation (5.14) to include all of the correction factors that are applied to the data obtained during the Phoenix Sunrise 2001 field campaign,

\[
[NO_3]_{\text{ambient}} = [NO_3]_{\text{mod}} \left( \frac{1}{z} \left( \frac{I}{I_a} \right) \left( \frac{F_{\text{inlet}} + F_{\text{dilute}}}{F_{\text{inlet}}} \right) \left( \frac{1}{1-L} \right) \right). \tag{6.11}
\]

These values are tabulated in Table 6.1. Equation (6.11) indicates that with the experimental configuration used for the field measurements, the ambient NO\(_3\) concentration is 3.14 times the concentration that is directly determined by the measurement. Thus, all measurements from the field campaign are subsequently multiplied by this overall correction factor.
Table 6.1 A summary of correction factors.

<table>
<thead>
<tr>
<th>Applied Correction</th>
<th>Value</th>
<th>±σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeroing efficiency, ( z )</td>
<td>1.016</td>
<td>0.01*</td>
</tr>
<tr>
<td>Pathlength, ( l/l_0 )</td>
<td>1.303</td>
<td>0.01*</td>
</tr>
<tr>
<td>Dilution, ( (F_{inlet} + F_{dilute})/F_{inlet} )</td>
<td>1.185</td>
<td>0.02*</td>
</tr>
<tr>
<td>Inlet loss, ( 1/(1-L) )</td>
<td>2.000</td>
<td>0.32</td>
</tr>
<tr>
<td>Accumulated correction factor</td>
<td>3.138</td>
<td>0.52</td>
</tr>
</tbody>
</table>

* indicates estimated error
Chapter 7

Field observations of NO₃

7.1 Introduction

In this chapter, we present nitrate radical observations made with the CRDS prototype from a skyscraper in downtown Phoenix, Arizona. These observations were made in conjunction with the U.S. Department of Energy's Phoenix Sunrise Campaign during June of 2001 (PHX 2001). The aim of the campaign was to study the early morning chemical and meteorological transition period as an urban atmosphere develops from a stable to a convective state. Our goal was to observe ambient mixing ratios of NO₃, and evaluate the CRDS prototype in the field so as to guide further refinement of the system. The field site provided many opportunities not afforded by other possible sites, including the comparison of in-situ NO₃ observations to path-averaged NO₃ mixing ratios determined by DOAS.

7.2 Motivation

7.2.1 Laboratory observations

One major aim of the field test was to evaluate the performance of the CRDS instrument under field conditions, where the instrument is susceptible to noise sources different from the laboratory and Fairbanks, Alaska. For long periods of time, the optical system was observed to be stable in the laboratory, requiring only a fine-alignment, every few days. The instrument was routinely powered-on and operated with fast data rates and low signal noise (i.e. the data rates typically ranged from 10 – 30 Hz and $\sigma/\tau$ was typically 1 – 5% while flowing unfiltered room air). Evaluating the stability of the optical system would guide further development or improvements to the instrument.

Noise induced by particulate scattering far outweighed other noise sources in the laboratory (i.e. electronic and optical), and was expected to dominate in the field, though the magnitude of the effect was to be determined. Understanding the effect of particulates in a real, "polluted" environment with NO₃ was of special interest, because the magnitude and character of the particulate effect determines whether it is beneficial to
filter the atmospheric air sample. Filtering the atmospheric sample was not possible within the design of the CRDS prototype, at the time. Laboratory studies with filters indicated that pressure drop induced by the filter was too large for our operating parameters (flow rates of 85 slpm through 1/2" ID tubing). Some experiments were performed in outside air in Fairbanks, Alaska, indicating that the CRDS system would operate outside. But the aerosol distribution in Fairbanks was expected to be different from the sampling location in Phoenix.

Prior to, and after, the field experiment, a considerable amount of effort was directed toward determining the loss of NO$_3$ to the sample inlet in the laboratory. While we believe we determined an upper limit for this reaction (chapter 6), it is considered suspect and a large error is associated the value (table 6.1). The most accurate measurement of inlet loss is to determine the inlet loss rate at the field site by measuring the NO$_3$ mixing ratio as a function of the inlet flow rate, which allows determination of the pseudo first-order loss rate as discussed in chapters 5 and 6. This method of determining the loss rate requires a relatively stable NO$_3$ mixing ratio in the sampled air mass. Large and relatively constant NO$_3$ concentrations were hoped for based on the meteorology of the field site.

7.2.2 Field site motivation

The CRDS sampling point was located on the observation deck (39th floor) of the Bank One building in downtown Phoenix, approximately 139 m above ground level (AGL). The Bank One observations, in general, were one component of an extensive set of measurements to characterize the vertical structure of the lower urban atmosphere (i.e. the same suite of measurements were made on the 16th floor). Observations from the CRDS sampling location were expected to characterize the chemistry of the upper nocturnal boundary layer (NBL). As discussed in chapter 1, modeling studies and observations suggest that NO$_3$ abundances are larger aloft in the NBL. Additional factors that suggested large NO$_3$ abundances at the field site were the warm temperatures and dry climate characteristic of Phoenix, Arizona during June. Warm temperatures promote the thermal dissociation of N$_2$O$_5$ to form NO$_3$ (equation 1.4), and the dry
environment makes the contribution of NO₃ loss via the heterogeneous reaction between N₂O₅ and water to form nitric acid small (equation 1.5).

Several measurements were performed next to the CRDS sampling inlet, which was located approximately 0.6 m from one face of the building wall. Ancillary in-situ measurements included NO₂, O₃, NO, dew point temperature, particle scattering, ambient temperature, and RH. A DOAS instrument was mounted on the observation deck to study the vertical distribution of trace gases over the city. Three arrays of retro reflectors were mounted at a distance of 3.4 km at heights of 10 m, 40 m, and 120 m AGL. The retro reflectors were placed on the tops of other buildings in uptown Phoenix. The telescope of the DOAS system was directed between the arrays, resulting in a gas profile every 20 min. DOAS measurements included NO₃.

7.3 Results and discussion

Aerosol scattering was clearly the dominant source of noise at PHX 2001. The noise (σt/τ) on a 300-point ensemble of ring-down times was 10 to 15%, compared to <1% for times where we were only flowing purge air into the system. The aerosol concentration was variable on all time scales. The particle signal would sometimes accidentally correspond to our NO-modulation frequency, leading to false positive and negative signal. The origin of this modulated particle effect is not fully clear, but it is not induced by our sampling method as it was observed during times where the NO modulation was shut off. A likely origin of the particle modulation is simply that the natural variation of the aerosols sometimes matched the NO modulation frequency. To remove these spikes, we averaged successive observation of NO₃, which degrades time resolution but decreases the effect of this interference. It is clear that the instrument is operable without filtering particulates, but filtering is desirable to remove this dominant source of noise, and improve the time resolution and sensitivity.

The optical system required fine alignment or "tweaking" approximately twice per day. This alignment procedure was likely needed due the diurnal variation in temperature within the observation deck. The temperature variation would slowly bring the optical alignment away from and then back to the alignment corresponding the temperature
under which the initial alignment took place. Despite efforts by portable air-conditioning units and insulation on the windows of the observation deck, the indoor temperature remained equal to, and sometimes exceeded the ambient outside temperature, which typically reached 45 °C during the day and decreased to ~35 °C by early morning.

Data rates during the campaign were 2 – 10 Hz, compared to 10 – 30 Hz under laboratory conditions. The slower data rates are believed to be the result of the warmer operating environment of the external cavity diode laser (ECDL). The data rate limitation was directly the result of low detected signal intensity exiting the RDC. While a good, clean TEM$_{00}$ mode structure was observed for the cavity on an oscilloscope, the intensity of each peak was significantly smaller than normal (by a factor of 10). The laser power was frequently checked during the campaign, and observed to be robust and typical of powers in the laboratory. Observation of the ECDL output spectrum, using a low resolution (1 nm) spectrometer, indicated that the ECDL might have been operating in multiple modes. Thus, the laser power was not concentrated in a single longitudinal mode, but distributed among different resonant frequencies. Although mode matching is still achievable, the energy stored in a single ECDL mode is smaller in magnitude than if the ECDL were operating in a single mode. These observations imply that laser environment should be maintained at reasonable temperature.

A second consideration regarding the slow data rates observed at the field site is effect of mechanical vibrations on the data rate. Mechanical vibrations on the time scale of build-up time would limit the time that the laser and RDC were resonant. Mechanical vibrations change the cavity length and could terminate the coupling of light into RDC, preventing the larger build-up intensities observed under laboratory conditions. The effect of mechanical vibrations is yet to be fully addressed, but can be circumvented by mounting the system on vibration-isolation legs.

Figure 7.1 shows the CRDS-NO$_3$ mixing ratio data for 6 nights and 2 days that were collected between June 17 and June 23. The data have been adjusted for the correction factors quantified in chapter 6. The corrected NO$_3$ mixing ratio is plotted on the left axis. The time (lower axis) is expressed in terms of the fractional day of year.
Figure 7.1 CRDS-derived NO$_3$ mixing ratios observed over the entire field test. The data are plotted for 60 point time averages (~1 hr time resolution). The days and nights that are labeled "glass inlet" refer to the system described in chapters 5 and 6. For doy 172 to 174, a Teflon inlet was utilized for sampling, but has not been characterized for inlet loss, as discussed in the text. The binary trace represents times for which there was sun.
(fdoy), where doy 168.0 corresponds to the midnight between June 16 and June 17, doy 168.5 corresponds to noon of June 17, etc. Each data point in figure 7.1 represents the average of 60 determinations of the NO$_3$ mixing ratio, and roughly corresponds to 1 hr (i.e. hourly averages). The error bars are ± 1 sigma and equal to ± ~5 pptv in terms of the NO$_3$ mixing ratio. The errors are magnified by the correction factors discussed in chapter 5. The right axis of the plot corresponds to night (0) and day (1), which are indicated by the binary trace in the figure. The first three nights (169.0, 170.0, and 171.0) utilized the glass inlet system discussed in chapters 5 and 6. The remaining set of measurements (times 171.8 to 174.8) utilized a Teflon inlet that has not been characterized for inlet loss. There was a test during the night of June 22 (labeled null test in figure 7.1) where we did not add any nitric oxide to the sample inlet to see if there was a sampling artifact. The mean nighttime NO$_3$ mixing ratio for this test night was 1.40 (±1.55) pptv, thus within error of zero (1 sigma). Only doy 168/169 shows large NO$_3$ mixing ratios, though doy 171 shows a mean nighttime average of NO$_3$ of 4.21 (±1.95), and doy 172 shows a mean nighttime average of 3.53 (±0.98). All other days and nights are within error of zero (1 sigma).

Figure 7.2 shows a comparison between DOAS (lower plot) and CRDS (upper plot) for all days. The DOAS data are re-averaged at 1-hour time resolution. The large error bars associated with 1-hour time averages are due to variability in the NO$_3$ mixing ratio, and are not representative of the actual measurement error (shown in figure 7.3). The data in the CRDS plot are hourly averages and there is variability included in these error bars also. Both sets of data show that the nitrate radical is most abundant on doy 168/169. Thus, we next focus on this night. The night of June 17 and early morning of June 18 are blown up figure 7.3 for a closer comparison of the data.

The DOAS data (right axis) and the CRDS data (left axis) are plotted for 20-minute averages in figure 7.3. Twenty minutes was the best time resolution achieved by DOAS during the campaign due to the fact that they were alternating between three light paths. From figure 7.3, the CRDS-nitrate radical mixing ratio rapidly increases from near zero to 57 pptv shortly before midnight, and stays elevated throughout the night. Shortly
Figure 7.2 A comparison of DOAS and CRDS-determined NO$_3$ mixing ratios. The data for both techniques are plotted for ~1 hr time averages. The DOAS error bars are not representative of measurement due to variability of the NO$_3$ concentrations (see figure 7.3 for the actual error).
Figure 7.3 A comparison of DOAS and CRDS-determined NO₃ mixing ratios for the night of June 17/18, 2001. The circles represent CRDS derived mixing ratios, and the crosses represent DOAS derived mixing ratios.
after the first NO$_3$ spike begins to settle, and second jump in the NO$_3$ mixing ratio occurs. The CRDS-NO$_3$ spikes line up well with the DOAS observations. The time difference between the second CRDS-NO$_3$ spike and the second DOAS spike is roughly 20 min, which is a reasonable transport time. While the time behavior is a strong indicator that we are looking at the same compound, the CRDS signal is much smaller than the observed DOAS-NO$_3$. Additional evidence that we were observing NO$_3$ is presented shortly, but first we consider the possibilities that could account for smaller NO$_3$ mixing ratios observed by CRDS.

An obvious first reason for the lower CRDS-NO$_3$ mixing ratio is that our inlet loss calibration is grossly in error. Though we are confident that our inlet loss measurements represent an upper limit for the inlet loss rate of the CRDS prototype, we cannot fully rule out this possibility at the time. As discussed in chapter 6, it is possible that the flow within the detection cell is not well mixed, which could lead to approximately a factor of two increase in the surface loss correction factor. If this were the case, the CRDS observation would still be smaller than the DOAS observations, although the extent of disagreement would be smaller. Other reasons for the discrepancy highlight the problem of comparing in-situ measurements with path-averaged measurements, and are considered more likely.

Because the NO$_3$ radical is reactive, it is possible that there is a NO$_3$ gradient that is low near the building wall and increases with distance from the building due to reactions of NO$_3$ with the building surface. Additionally, turbulence induced by the building would cause mixing of the air below the inlet with air at our sampling altitude, possibly reducing the effective altitude of the sampling point. The depth of this building-induced mixing layer is not known, but would result in a diluted NO$_3$ mixing ratio at our altitude. DOAS observations showed strong NO$_3$ vertical gradients throughout the night of doy 167/168, therefore mixing lower altitude air would lead to lower observed NO$_3$ mixing ratios.

The observation that the DOAS and NO$_3$ data appear to follow each other (figure 7.3) on doy 168/169, may be evidence that our observations showed lower NO$_3$ mixing
ratios due to the mixing effect described above and NO$_3$ loss to the building walls. The length scale of this effect (i.e. the perimeter of turbulent mixing that extends from the building) is not known. The DOAS technique cannot observe the building influence at the CRDS site of the DOAS lamp or at the site of the beam reflector, because the DOAS observations are averaged over several kilometers.

Figure 7.4 plots the ozone, NO, and NO$_y$ measurements for comparison with our CRDS observations on doy 168/169. The initial NO$_3$ spike happens just after a NO incursion that can be seen in the lower trace. The CRDS-NO$_3$ stays up until a morning NO incursion happens, which is the result of the onset of convective mixing and morning traffic in the downtown Phoenix area. These observations are consistent with the fact that NO$_3$ and NO should not be observed in the same air mass. DOAS gradient data suggests strong gradients throughout the night, which are believed to be caused by NO emissions at the ground. The NO burst could also be the result of eddies that come from street canyon below our sampling point. Whatever the meteorology, the fact that we only observe NO$_3$ during times where NO is not present is additional evidence showing that we were detecting NO$_3$. The fact that DOAS-NO$_3$ is nonzero during the time of the NO incursion shows how DOAS averages-out the effects of localized chemistry.

7.4 Conclusions

The CRDS prototype operated successfully during the Phoenix Sunrise Campaign of 2001. The data rates obtained during the campaign were smaller than data rates typical of the lab because of the extreme temperatures and possible vibrations of the sampling location. These data suggest that the CRDS system temperature should be maintained at moderate levels, though the stabilization requirements are probable not too rigid as we were able to operate in the variable and warm climate of the observation deck. Particulate scattering was the dominate source of noise, and sometimes induced false positive and false negative NO$_3$ mixing ratio data, which had to be resolved through signal averaging, leading to a reduced time resolution. These observations suggest that filtering would be beneficial to improve the time resolution of the method.
Figure 7.4 A comparison of NO, NO\textsubscript{y}, O\textsubscript{3} and CRDS-derived NO\textsubscript{3} mixing ratios for the night of June 17/18, 2001.
While these problems are easily addressed, the more significant issues are the differences and similarities between the CRDS-NO$_3$ observations and the DOAS-NO$_3$ observations.

The largest NO$_3$ abundances were observed on the night of June 17/18 by both CRDS and DOAS. The largest CRDS-NO$_3$ mixing ratio observed was ~5 times smaller than the largest DOAS-NO$_3$ signal. The initial jump in the NO$_3$ concentration, observed for both techniques, is a strong indicator that our sampling location (and the DOAS upper light path altitude) entered a new layer, either in higher in the NBL or even possibly extending into the residual layer (RL). The RL is composed of the previous day's convective layer and neutrally stable and well mixed throughout. It is likely that the residual layer would be characterized by less spiky NO$_3$ data, which both CRDS and DOAS indicate is not the case. Although, one cannot rule out the horizontal mixing of air masses, which could produce similar effects. It is likely that we moved aloft in the NBL. The NBL is stably stratified and not well mixed. Formation of the nitrate radical is most likely to occur aloft in the NBL, where NO rarely reaches as it is consumed primarily at ground level by reaction with ozone (see figure 7.4 plots). Ancillary measurements of nitric oxide suggest that eddies from the street below may have penetrated to our altitude (130 m) shortly before midnight, where the CRDS-NO$_3$ signal was within error of zero (1 sigma). The NO spikes resolved themselves prior to positive CRDS-NO$_3$ signals.

Possibly, turbulent mixing near the building boundary causes the CRDS inlet to be at an effective altitude that is lower in the nocturnal boundary layer. Thus, the effect of sampling near a building may influence the measurements. These results suggest that boundary layer meteorology control NO$_3$ abundances. DOAS observations cannot resolve these inhomogeneities in the air mass as they are averaged-out in the long paths. Though we do not presently know the length scales of these effects, it is likely that other inhomogeneities exist throughout the DOAS light path. Therefore, the question of whether path-averaged chemistry is really representative of what is occurring chemically in the air mass is highlighted by these observations.
Chapter 8

Conclusions

Deficiencies associated with current NO$_3$ detection schemes prevent exploring many aspects of NO$_3$ chemistry, like the vertical structure of NO$_3$ in the nighttime atmosphere. Cavity ring-down spectroscopy (CRDS) offers many advantages that overcome the limitations associated with path-averaged measurements by providing the potential for fast time-scale and short-length scale *in-situ* NO$_3$ measurements.

We first demonstrated the application of CRDS to nitrate radical detection by detecting NO$_3$ in laboratory air that had been dosed with the NO$_3$ precursor, dinitrogen pentoxide (N$_2$O$_5$). We achieved good detection limits (2 pptv) with good time resolution (30 s). Instrument modifications subsequent to this demonstration included increased data rates, the development of a sampling method, and finally the construction of portable field prototype. The CRDS field prototype was tested during one week of June 2001 in conjunction with the Phoenix Sunrise Campaign sponsored by the U.S. Department of Energy.

The field prototype uses a chemical zeroing method that allows us to eliminate the effect of interfering gases (*i.e.* water vapor and ozone) that complicate nitrate radical spectroscopy in the atmosphere. While this zeroing method is robust, several other instrumental improvements were suggested by the field test. These improvements include moderate temperature control of the optical system, filtering of the inlet air to remove the effect of particulates that dominated other sources of noise in the field, and new inlet coatings eliminate inlet losses of NO$_3$. Despite these problems, most of which are easily addressed and straightforward to implement, the instrument successfully operated during the campaign, and we were able to detect NO$_3$.

The Phoenix Sunrise campaign provided the opportunity to evaluate our technique in conjunction with path-averaged DOAS-NO$_3$ observations. The DOAS-NO$_3$ signal was integrated across light path that originated from a skyscraper in downtown Phoenix and was reflected back to a spectrometer (total pathlength = 7 km). The CRDS instrument
was located at the origin of the DOAS light path, ~130 m above ground level. Only one night during our observation period (6 nights) did both techniques show large NO₃ concentrations in the urban atmosphere. The CRDS-NO₃ signals and the DOAS signal both peaked shortly before midnight, and then stayed up throughout the remainder of the night. This time behavior is a strong indicator that we were both observing the same compound, though the CRDS-NO₃ signal was considerably smaller (5x) than the DOAS-NO₃ signal. These differences are likely due to sampling different air masses, with our air mass characteristic of the air directly in the vicinity of the building. The length-scale of this effect is not known, but strongly suggests that path-averaged concentrations and in-situ measurements are not comparable, which is often assumed in NO₃ chemistry.

Additional evidence to support our NO₃ observations include ancillary measurement of nitric oxide, which is not found in the same air mass as NO₃. This finding is consistent with the (NO + NO₃) fast reaction to form 2NO₂. While the CRDS observations were consistent with this reaction, the DOAS instrument showed nonzero NO₃ concentrations during the time of an NO incursion. This observation further illustrates the idea that both instruments were sampling different air masses, and the problem of comparing path-averaged measurements with in-situ measurements of other trace gases.

In the future, we look forward to using the new technique of CRDS-NO₃ detection to understand the chemistry of this reactive radical in the ambient atmosphere.
Literature Cited


