DEVELOPMENT OF AN INFRARED CAVITY RINGDOWN SPECTROSCOPY EXPERIMENT AND MEASUREMENTS OF WATER VAPOR CONTINUUM ABSORPTION

by

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A Thesis submitted in conformity with the requirements for the Degree of Doctor of Philosophy Graduate Department of Physics University of Toronto

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For My Mother and My Father
who surely would have, if given the chance
Abstract

The development of a quantitative infrared cavity ringdown spectroscopy experiment capable of measuring water vapor continuum absorption in the 1000 cm$^{-1}$ region is described. Cavity ringdown spectroscopy (CRDS) is a new high-performance technique in which laser pulses are injected into a stable, high-finesse optical cavity called the "ringdown cavity". Absorption coefficients are obtained from the difference in the decay time constant when an absorbing gas is added and then removed from the system. We determine the decay time constants from a nonlinear least squares analysis of individual decay events. Our CRDS experiment is designed around a 1-m long near-confocal ringdown cavity, and is novel in that it is a gas flow experiment in which we control the relative humidity from zero to near-saturation. Most CRDS experiments to date have been in the visible region, and so we describe some of the problems associated with infrared work.

There is no established theory for the water vapor continuum, and so all of our knowledge is empirically-derived. Our intercomparison of water vapor continuum measurements demonstrates that continuum absorption coefficients derived from conventional spectroscopic techniques have uncertainties $\geq 20\%$. We have made water vapor continuum absorption measurements with uncertainties $< 10\%$ for selected CO$_2$ laser transitions ranging from 931 - 969 cm$^{-1}$ near 296 K. Our measurements, analyzed in terms of the continuum coefficients of self- and foreign-broadening, are found to be in good agreement with the recently-developed far wing line shape theory of Ma and Tipping. We demonstrate that empirical models of the water vapor continuum, widely used in atmospheric radiative transfer applications, significantly overestimate the self-broadened continuum and do not properly account for the foreign-broadened continuum. The performance of the infrared CRDS experiment, sources of error, and proposed improvements are all discussed.
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Chapter 1

Introduction

1.1 Introduction

Water is probably the most important substance to understand. The most abundant compound on the surface of the Earth, water is essential to life as we know it. As the human body is nearly 80% water, the importance of liquid water is obvious. However, atmospheric water vapor, which barely accounts for 0.001% of the global water supply (Fig. 1.1), also plays a critical role in supporting life. This is because water vapor is the principal 'greenhouse gas,' responsible for about 2/3 of the Earth's natural global warming of 34 °C.

The many distinctive properties of water in the solid, liquid, and vapor phases are interpreted through our understanding of the water molecule. Much of what is known about the water molecule has been determined through spectroscopic investigation. Spectroscopy is a broad experimental field with the aim of understanding the nature of matter through the interaction of atoms and molecules with electromagnetic (EM) radiation. Atomic and molecular behavior may be revealed on many levels, from coarse-resolution spectroscopy of entire absorption bands down to high resolution spectroscopy of individual spectral lines. This thesis is concerned with the application of extremely sensitive gas-phase spectroscopy to a longstanding problem in atmospheric radiative transfer: the infrared water vapor continuum.

The subject of the infrared water vapor continuum has aspects which are highly practical, and aspects which relate to fundamental problems. An example of the former is found in connection with the measurement of sea surface temperatures (SST) from space. These measurements depend on
Figure 1.1 - The hydrologic cycle of the Earth, showing estimates of reservoir volumes and fluxes of water between them. Taken from American Geophysical Union [1995].
atmospheric 'windows,' which are spectral regions of high transparency. The most important window for SST measurements is the infrared window from 700 - 1250 cm$^{-1}$ [Barton, 1995]. In this window, atmospheric absorption is dominated by the water vapor continuum. The water vapor continuum can introduce a bias of up to 10 K in the SST measurement [Deschamps and Phulpin, 1980], because the remote instrument receives atmospheric emission from the water vapor continuum in addition to emission from the ocean surface. Another very relevant problem concerns the role of the water vapor continuum in the global climate, and this is discussed in greater detail in Sections 1.3 and 1.4.

The water vapor continuum is also related to more fundamental questions involving the nature of strong interactions between water molecules. Whether these interactions result from molecular collisions or the formation of bonds between water molecules is the subject of active debate, and this is explored in greater detail in Chapter 2. Improving our understanding of the water vapor continuum could, in principle, yield valuable insights into the formation of water clusters and ultimately, the existence of liquid water.

In the next section, the water vapor continuum is introduced in the form of a historical account. It is hoped that this will illustrate the close correlation between experimental advances and refinements in our understanding of the water vapor continuum. Cavity ringdown spectroscopy, discussed in depth in Sections 3.1 and 3.2, is a new high-performance technique which has not been applied to the problem of the water vapor continuum until now. Much of this thesis concerns the development of an infrared cavity ringdown experiment suitable for making quantitative measurements of the water vapor continuum. Our first measurements of the water vapor continuum, presented in Chapter 4, are an indication of the impressive potential of cavity ringdown spectroscopy.
1.2 The Water Vapor Continuum: A Historical Perspective

The study of infrared spectra was pioneered in the late 1800s by Langley, who used a large rock-salt prism to disperse solar and lunar energy. The dispersed energy fell onto a bolometer, which detected heat by measuring changes in resistance of a very thin strip of metal coated with lampblack. As director of the Allegheny Observatory at Pittsburgh, Langley discovered that the Earth’s atmosphere absorbs strongly for wavelengths between 5.0 and 7.7 μm, and is essentially completely transparent between 8.4 and 9.1 μm [Langley, 1888]. Despite the notoriously smoky atmosphere above Pittsburgh, Langley reported complete transparency for wavelengths of 8.8 and 10.7 μm up to an airmass factor of 3.8 (the airmass factor is the secant of the solar zenith angle, for direct solar viewing). Langley’s discovery of atmospheric absorption bands and a transparent infrared window disproved the longstanding belief, attributed to Fourier, that the Earth’s atmosphere absorbed uniformly at all wavelengths.

The first quantitative investigations of the absorption of atmospheric water vapor would be undertaken by Fowle nearly 30 years later [Fowle, 1915; Fowle, 1917]. At the Smithsonian Institution, Fowle measured the transmission of horizontal atmospheric paths through an open galvanized iron tube illuminated at one end with a bank of Nernst filaments. The spectrometer consisted of a rock-salt prism and an improved bolometer. Path lengths of 128.5 and 245.5 m were employed, along with a short 11.5 m path serving as a “dry” calibration. Fowle devised a spectroscopic technique for evaluating the amount of water vapor based on the intensities of three absorption bands at 0.935, 1.13, and 1.47 μm. Measurements of the absorption band intensities were correlated with humidity, which was obtained from wet- and dry-bulb thermometer readings. Fowle quantified water vapor amount in terms of precipitable water, which he defined as the thickness of the layer of liquid water which can be precipitated from the absorbing air column. (Note: Precipitable
water is a measure of the amount of water vapor, not the amount of absorption. Liquid water absorbs 10^3-10^4 times as much in the 10 \mu m region as the equivalent amount of water vapor [Carlon, 1970].

For longer optical paths, Fowle made atmospheric absorption measurements of solar radiation at the Mount Wilson Observatory. Finding no appreciable absorption in the 9 - 12 \mu m window region (or 830 - 1100 cm\(^{-1}\) in terms of the wavenumber \(\nu\)), Fowle agreed with Langley's conclusion that the atmosphere was effectively transparent in that region [Fowle, 1917].

In 1937, Randall and co-workers obtained one of the first resolved spectra of the strong far-infrared absorption band of water vapor in the laboratory using a reflection grating spectrometer [Randall et al., 1937]. The unprecedented resolution (0.5 cm\(^{-1}\)) of the experiment permitted 173 lines from 74 - 560 cm\(^{-1}\) to be resolved. Nearly all of the observed lines were identified as transitions between rotational levels, up to the rotational quantum number \(J = 11\). Randall et al. provided theoretical estimates of the corresponding intensities, which were not accurately measured. Soon after, Elsasser used the data of Randall et al. to predict the existence of continuous absorption in the region from 400 - 1000 cm\(^{-1}\) due to the accumulation of absorption from the far wings of the water vapor rotational lines [Elsasser, 1938]. Assuming the Lorentz theory of pressure broadening to be valid, Elsasser noted that the absorption in the far wings would be proportional to the half-widths of the rotational lines, which he estimated to be 0.25 cm\(^{-1}\). Because of the large number of spectral lines involved, Elsasser performed numerical calculations for only a few wavenumbers. The absorption coefficients \(k_c(\nu)\) for the continuum appeared to vary smoothly from \(k_c(400 \text{ cm}^{-1}) = 3.5 \text{ cm}^2/\text{g}\) to \(k_c(1000 \text{ cm}^{-1}) = 0.12 \text{ cm}^2/\text{g}\) (note: the absorption coefficient and its relationship to the extinction of electromagnetic radiation is described in Sections 2.1 and 2.2).

Assuming an atmospheric water vapor density of \(1.3 \times 10^5 \text{ g/cm}^3\) (50% relative humidity at 300 K) the absorption coefficients per unit pathlength range from \(k_c(400 \text{ cm}^{-1}) = 4.5 \times 10^5 \text{ cm}^{-1}\) to
$k_e(1000 \text{ cm}^{-1}) = 1.5 \times 10^6 \text{ cm}^{-1}$. Elsasser predicted the water vapor continuum would be difficult to observe in the laboratory, but could explain larger than expected atmospheric emission measurements. (Interestingly, if we interpret Elsasser’s continuum absorption coefficient at 1000 cm$^{-1}$ ($k_e = 0.12 \text{ cm}^2/\text{g}$) in terms of the continuum coefficient of foreign-broadening which is defined in Section 2.4 and has units of molecules$^{-1}$ cm$^2$ atm$^{-1}$, we find that Elsasser’s estimate of continuum absorption agrees with our measurements at 969 cm$^{-1}$ to within our experimental error).

One year later, Adel reported low-resolution (~ 10 cm$^{-1}$) atmospheric solar absorption measurements in the 700 - 1200 cm$^{-1}$ region at the Lowell Observatory [Adel, 1939]. Adel used a rock-salt prism spectrometer and Fowle’s methodology for determining water vapor amounts. However, the signal detection was improved through the use of a thermocouple coated with bismuth black and an amplifier. From measurements for several water vapor amounts, Adel found a smooth absorption spectrum that appeared to obey the Beer-Lambert law. This suggested that the spectrum was adequately resolved and was therefore truly continuous. The continuous spectrum, shown in Fig. 1.2, is roughly similar to that predicted by Elsasser. Given the reasonable agreement, Adel was encouraged to speculate that the increase in the observed absorption for $\nu > 1100 \text{ cm}^{-1}$ might be due to the far wings of the $\nu_2$ vibration-rotation band of water vapor centered at 1600 cm$^{-1}$, which Elsasser had not considered.

By the late 1950s, significant theoretical advances were being reported. Benedict and Kaplan, noting that only a handful of water vapor lines had been studied experimentally, applied Anderson’s general theory of collision line broadening to the problem of H$_2$O - N$_2$ collisions [Benedict and Kaplan, 1959]. The calculations for the pure rotation band indicated a general decrease in the nitrogen-broadened line width $\Gamma_n$ with increasing rotational energy, from $\Gamma_n = 0.111 \text{ cm}^{-1} \text{ atm}^{-1}$ for $\nu \approx 20 \text{ cm}^{-1}$ to $\Gamma_n = 0.032 \text{ cm}^{-1} \text{ atm}^{-1}$ for $\nu \approx 550 \text{ cm}^{-1}$. These results suggested that Randall’s observed
Figure 1.2 - Atmospheric absorption as a function of wavenumber for the solar absorption measurements of Adel (circles) and the water vapor far wing absorption calculations of Elsasser (crosses). Note that the absorption coefficients $\alpha_\nu$ reported by Adel are given in terms of absorption per cm of precipitable water $e$ and not the present-day convention of absorption per cm of path length in the gas. Adapted from Adel [1939].

\[ I_\nu = I_\nu^0 e^{-\alpha_\nu \ell} \]
line widths of 0.25 cm$^{-1}$ probably represented instrumental and not spectral line widths. In a later paper, the authors presented calculations of self-broadened line widths as well as oxygen-broadened line widths [Benedict and Kaplan, 1964]. Benedict and Kaplan determined that the ratio of self- to nitrogen- (or air-) broadened line widths for water vapor was roughly equal to 5. The dominance of self-broadening in water vapor was attributed to the large dipole moment of the water molecule. Thus, the dipole-dipole interaction in H$_2$O - H$_2$O collisions is stronger than the dipole-quadrupole interaction in H$_2$O - N$_2$ collisions.

Meanwhile, Roach and Goody published the results of more extensive field measurements of absorption and emission in several wide bands within the 770 - 1250 cm$^{-1}$ window [Roach and Goody, 1958]. In this work, they employed rock-salt prisms (7 cm$^{-1}$ resolution) and a Golay cell infrared detector. Absorption coefficients were derived from the variation of solar intensity with solar zenith angle, with water vapor amounts determined from daily radiosonde data. Roach and Goody began making measurements in London, but as absorption and emission were larger than expected, they suspected that the air was too polluted to measure the natural atmosphere. Consequently, the apparatus was moved to the countryside at Ascot, where they recorded an absorption spectrum that qualitatively resembled the one observed by Adel, with a minimum near 1100 cm$^{-1}$. While the data from Ascot tended to support Elsasser's hypothesis, Roach and Goody argued that the likeliest explanation for the higher extinction observed over London was the presence of aerosol particles. This argument was later challenged by Bignell [Bignell, 1970], who pointed out that there are diurnal variations to atmospheric humidity and while Roach and Goody made afternoon measurements in London, their observations at Ascot were made during the morning.

A few years later, Bignell studied the atmospheric infrared continuum at the Ascot site using a grating spectrometer (2.2 cm$^{-1}$ resolution) and Golay cell [Bignell et al., 1963]. Bignell obtained
solar absorption spectra in the window region of 790 - 1200 cm\(^{-1}\) using the same slant-path methodology as Roach and Goody. However, the water vapor amount was deduced from a measurement of the equivalent width of the rotation line at 871 cm\(^{-1}\). Bignell estimated this reduced the standard error in water vapor amount by a factor of 3 over the radiosonde data employed by Roach and Goody. The combined improvements in spectrometer resolution and humidity measurement enabled Bignell to demonstrate a mean correlation coefficient of \(r = 0.91\) between continuum absorption and water vapor amount. Bignell also recorded absorption spectra for the region between 480 - 720 cm\(^{-1}\) over a 400-m long horizontal path using a Nernst source. For these data, the water vapor amount was obtained from wet- and dry-bulb thermometer readings. In the horizontal path spectra, Bignell found a strong dependence of the absorption coefficient on the water vapor partial pressure. Bignell estimated the self-broadening effect to be 30 times larger than air-broadening. Finally, Bignell also compared his spectra to the calculated far wing continua for four different line shapes and found that none of the line shapes gave good agreement with the observed continuum.

Although it had long been argued on theoretical grounds that the Lorentz line shape was not valid in the far wings, verification for any gas presented a challenge because of the difficulty in measuring weak far wing absorption in the presence of strong selective absorption. A convenient region where far wing absorption could be studied was the high frequency wing of the asymmetric stretching mode (\(v_3\)) band of CO\(_2\) centered at 2350 cm\(^{-1}\). Winters measured the continuous absorption in the 2400 - 2600 cm\(^{-1}\) region and determined that the absorption was much less than predicted using the Lorentz profile for the distant CO\(_2\) lines [Winters et al., 1964]. By modifying the Lorentz line shape with an empirical factor \(\chi\) which was a function of the detuning \(|v - v_0|\), where \(v_0\) is the transition wavenumber and \(v\) is the observation wavenumber, Winters found that the correct line
shape for CO₂ had sub-Lorentzian wings (i.e. χ < 1). By 1966, the more extensive data of Burch also
revealed that far wing absorption depended on the wavelength, temperature and broadening gas in
ways which were not quantitatively explained by existing theories of collisional broadening [Burch
and Gryvnak, 1966].

The following year, Penner and Varanasi were studying the infrared absorption of high-
pressure steam in the laboratory at a resolution of ~ 3 cm⁻¹ when they made an important discovery.
Generating steam pressures up to 25 atm at temperatures ranging from 400 to 500 K, they noticed
an excess of absorption in the 650 - 1000 cm⁻¹ region which increased nonlinearly with steam
pressure [Penner and Varanasi, 1967]. Penner and Varanasi estimated that the far wing absorption
of the rotation band was not large enough to account for their observations, and also dismissed far
wing absorption on the grounds that they expected it to increase linearly with pressure. Shortly
afterward, Varanasi reported that the excess absorption increased with decreasing temperature,
consistent with the formation of intermolecular bonds [Varanasi et al., 1968]. Based on the
temperature dependence of the absorption, Varanasi estimated the intermolecular binding energy to
be 3 - 5 kcal/mole, which was in rough agreement with the hydrogen bond energy of 5 kcal/mole for
water vapor given by Pauling [1960]. Varanasi and Penner concluded that water vapor dimer
absorption was responsible for the continuum absorption they observed in steam, which was quickly
interpreted by Gebbie as evidence of the wide spectral extent of water vapor dimer absorption in the
Earth’s atmosphere [Gebbie et al., 1969].

One week after Gebbie’s paper was submitted, McCoy described the first use of laser
spectroscopy to investigate water vapor continuum absorption [McCoy et al., 1969]. The experiment
was performed with a CO₂ laser at the 10P(20) laser transition (944 cm⁻¹). The CO₂ laser generated
intense monochromatic radiation in the infrared window region, overcoming the traditional difficulty

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of weak signals in infrared spectroscopy. This permitted the use of a thermopile detector, which was less sensitive but more robust than Golay cells. McCoy made room-temperature transmission measurements of water vapor buffered with synthetic air (80% N₂, 20% O₂) in a 15-m long White cell with an effective path length of 980 m. Because of the long path length of the experiment, it was possible for the first time to measure water vapor continuum absorption without having to elevate the temperature in order to support more humidity in the cell. The methodology was first to evacuate the cell, then water vapor was slowly evaporated into the cell. When the water vapor pressure had stabilized, the cell was filled with synthetic air to a total pressure of 93 kPa. Following this, sufficient time had to be allowed for the gas mixture to stabilize before transmission measurements could be made. This was a serious drawback, as the gas in the 4400-liter White cell typically required 12-16 hours to stabilize sufficiently so that the water vapor continuum absorption could be measured. Nevertheless, McCoy's experiment was groundbreaking because it illustrated the strong, quadratic water vapor partial pressure dependence of the water vapor continuum in the infrared window region. The self- to air-broadening ratio was found to be ~ 200:1, much higher than the ratio of 5:1 found near line centers.

The following year, Bignell reported the results of a room-temperature laboratory study of the water vapor continuum [Bignell, 1970]. Bignell used a 15.5-m long White cell with an effective path length of 500 m, and the Nernst source and grating spectrometer from his previous experiment [Bignell et al., 1963]. Bignell studied the absorption spectrum of the water vapor continuum with moderate signal-to-noise (> 50) in eight windows from 480 to 1120 cm⁻¹ that were thought to be free of significant local line absorption. Despite problems with instrumental drift and unreliable observations at low values of humidity, the laboratory-derived continuum data demonstrated a quadratic dependence on the water vapor partial pressure. Bignell concluded that in addition to
foreign-broadening as given by the theory of collision-broadening, there was a second component to continuum absorption. Bignell called this "e-type absorption," because the absorption coefficient was proportional to the water vapor partial pressure, e. As shown in Fig. 1.3, the strength of e-type absorption relative to foreign-broadening appeared to increase rapidly with increasing wavenumber, from a ratio of ~ 35:1 at 500 cm\(^{-1}\) to ~ 150:1 at 1000 cm\(^{-1}\). Interestingly, the e-type absorption also had a pronounced negative temperature dependence, which Bignell estimated to be - 2%/°C based on his observations for temperatures in the range 21-45 °C. Bignell thought the strength of e-type absorption and its temperature dependence could not be explained in terms of self-broadening, and proposed that water vapor dimers were responsible for e-type absorption.

Since then, there has been a great deal of research, both experimental and theoretical, aimed at characterizing and understanding the mechanism(s) responsible for the infrared water vapor continuum. Unfortunately, review papers of the water vapor continuum suggest that little has been resolved conclusively [Varanasi, 1988; Grant, 1990; Aref'ev, 1991]. The uncertainty surrounding the origin of the water vapor continuum has led to different nomenclature being employed by various investigators. For example, the continuum absorption term dubbed "e-type absorption" or "dimer absorption" is referred to as "self-broadening" by other investigators who think that the far wings of self-broadened lines are responsible. In this work, the water vapor continuum is described in terms of self- and foreign-broadening, simply because it is more consistent. In Chapter 2, a more extensive discussion of the possible role of water vapor dimers and far wing absorption is presented.

The experimental data of the past 30 years are also reviewed in Chapter 2. These data reveal that there are large uncertainties in many aspects of the water vapor continuum. In particular, there are uncertainties of roughly 20% and 70% in the magnitude of the water vapor continuum coefficients of self- and foreign-broadening, respectively. Additionally, the temperature dependence
Figure 1.3 - Mass absorption coefficients for the foreign-broadened ($k_1$) and e-type ($k_2$) water vapor continuum, compiled by Bignell from various sources. Bignell’s $k_1$ and $k_2$ absorption coefficients are shown as ‘•’ and ‘⊙’, respectively. Taken from Bignell [1970].

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of the coefficients of self- and foreign-broadening are poorly known. These uncertainties in the water vapor continuum have grave implications for our understanding of the Earth's natural climate and impede our ability to assess the anthropogenic influence on the climate, to which we now turn our attention.

1.3 The Earth's Natural Climate

The Earth's climate, which may be simply defined as the average weather of the planet over a period of time, is a complex system incorporating the atmosphere, oceans, ice, land and biomass. The chief observable of the climate is the mean surface temperature, which depends on the balance of energy at the Earth's surface. In general, heat may be added to a thermodynamic system through conduction, convection, or radiation. Since the first two mechanisms require the presence of a medium and the Earth is surrounded by the vacuum of space, the sole input of energy is from the sun, which radiates like a blackbody at a temperature of 5780 K.

Satellite radiometer measurements indicate the solar irradiance at the top of the atmosphere is presently $S_0 = 1367 \pm 3 \text{ W/m}^2$ [Pap and Fröhlich, 1999]. The radiant flux density available to drive the Earth's climate is $S_0/4 = 342 \text{ W/m}^2$, where the geometrical factor of $1/4$ accounts for the ratio of the area of the Earth intercepting solar radiation to the total surface area of the planet. Similar measurements indicate that approximately 31% of the incident solar radiation is reflected by the planet back into space, leaving ~ 235 W/m$^2$ to be absorbed by the climate system. Meanwhile, the fundamental cooling mechanism of the climate system is outgoing longwave radiation (OLR) to space, which has been measured to be $235 \pm 5 \text{ W/m}^2$ according to the Earth Radiation Budget Experiment (ERBE) satellite observations [Ramanathan et al., 1989]. Thus, it appears that the Earth is roughly in thermal equilibrium. The Earth's radiation and energy balance is depicted in Fig. 1.4.
Figure 1.4 - The Earth’s radiation and energy balance. Taken from IPCC [1996].
While satellite instruments provide essential data on the overall energy budget of the climate system, it is more difficult to obtain adequate information on the surface energy budget. Radiative transfer models are constructed to test hypotheses describing how the intervening atmosphere alters the solar and terrestrial radiation fields. The spectroscopic input parameters to these radiative transfer models are best obtained through laboratory experiments, which are essential to quantify the infrared absorption of atmospheric gases such as water vapor, carbon dioxide, methane, and other trace gases. For concentrations representative of the Earth’s atmosphere, these gases absorb 90% of the infrared radiation emitted by the Earth’s surface. Water vapor alone accounts for 2/3 of the greenhouse gas absorption, by virtue of its abundance and numerous strong infrared absorption bands.

Two natural processes are responsible for the greenhouse effect, which is defined as the difference between the infrared emission from the surface and the top of the atmosphere. Nearly all of the infrared absorption takes place in the troposphere, which cools rapidly with altitude as can be seen in Fig. 1.5. This infrared absorption causes the atmosphere to warm until it emits as much as it absorbs and thermal equilibrium is restored. In addition, surface heating occurs because the greenhouse gases emit radiation isotropically, and the downward infrared emission of these gases is almost completely absorbed by the Earth’s surface. The natural greenhouse effect makes our planet habitable, elevating the mean surface temperature from 254 K to 288 K, a difference of +34 K.

Recently, clear-sky fluxes have been used to study the coupling between greenhouse absorption, sea surface temperature, and atmospheric water vapor [Raval and Ramanathan, 1989]. The greenhouse effect was obtained by subtracting ERBE measurements of the OLR from estimates of the radiation emitted by the ocean surface. Noteworthy for providing observational evidence of the greenhouse effect, the study also uncovered a non-linear increase of the greenhouse effect for surface temperatures greater than ~ 294 K, which can be seen in Fig. 1.6. Raval and Ramanathan
Figure 1.5 - The U.S. Standard Atmosphere [NOAA, 1976] model of the thermal structure of the atmosphere. The troposphere, which extends from 0 - 13 km altitude, contains nearly all of the atmospheric water vapor and is where nearly all atmospheric infrared absorption takes place.
raised the possibility that the observed nonlinear rise in the greenhouse effect for high surface temperatures might be due to the water vapor continuum. This was supported by line-by-line calculations which indicated that the contribution to the greenhouse effect due to the water vapor continuum increases rapidly with temperature. Further evidence was provided in a field experiment with a Fourier transform infrared (FTIR) spectrometer [Lubin, 1994]. The FTIR spectra demonstrated that the nonlinear increase in the greenhouse effect occurs primarily in the 800 - 1250 cm\(^{-1}\) infrared window, a region where the water vapor continuum is the dominant absorption mechanism. The super greenhouse effect, as it has become known, is a natural aspect of the Earth's climate which occurs because the water vapor continuum exhibits a quadratic dependence on the water vapor partial pressure, and also because the window region is relatively transparent. The net result is that an increase in the humidity leads to a disproportionate increase in atmospheric emissivity. The super greenhouse effect provides a compelling reason for accurately characterizing the water vapor continuum, especially when the possibility of global climate change is considered.

1.4 Global Climate Change

One of the most important questions of our time is whether the Earth's climate is changing as a result of human activity. Analysis of ancient air trapped in polar ice core samples suggests that increases in carbon dioxide and methane since the industrial revolution have led to atmospheric concentrations that are approximately 30% and 150% higher, respectively, than any levels experienced in the previous 150,000 years [Raynaud et al., 1993]. In its recent Third Assessment Report, the Intergovernmental Panel on Climate Change (IPCC) has projected that the increase in atmospheric greenhouse gases resulting from the continuation of such activities as deforestation and the burning of hydrocarbon fuels (coal, oil, natural gas, etc.) will lead to a global warming in the
Figure 1.6 - The greenhouse effect as a function of surface temperature [Raval and Ramanathan, 1989]. One hypothesis for the apparent nonlinear increase in the greenhouse effect that is observed in ERBE data for temperatures above ~ 295 K is the influence of the water vapor continuum. This hypothesis is supported by line-by-line calculations which indicate the contribution to the greenhouse effect due to the water vapor continuum increases rapidly with temperature.
range of 1.4 - 5.8 °C over the next century [IPCC, 2001]. While this may seem small compared to ordinary diurnal variations, it is believed such an increase in the global mean temperature may trigger dire consequences including a rise in the mean sea level, a more vigorous hydrological cycle, and a shift in the competitive balance among species of life.

Changes in the energy available to the Earth-atmosphere system are quantified in terms of the concept of radiative forcing, $\Delta F$ (W/m$^2$). The direct radiative forcing due to the increase in concentration of atmospheric CO$_2$ from pre-industrial times ($\sim$280 ppmv) to the present ($\sim$360 ppmv) has been calculated to be +1.6 W/m$^2$ [IPCC, 1996]. For small perturbations, the global mean surface temperature change $\Delta T_s$ will be approximately proportional to the radiative forcing, i.e.:

$$\Delta T_s = \lambda \Delta F$$

where $\lambda$ is the climate sensitivity (K (W/m$^2$)$^{-1}$). Presently, there are large uncertainties in the climate sensitivity ranging from 0.3 - 1.1 K (W/m$^2$)$^{-1}$ [Shine, 2000]. These are partially due to the complexities of climate feedback mechanisms as well as the observational problem resulting from the long time scales (decades) involved with changes in forcing and the consequent response.

The warming or cooling which results from a direct radiative forcing is modified by feedback processes, which may be positive or negative, depending on whether the feedback amplifies or diminishes the response to the forcing. Despite being greater in magnitude than most of the Earth’s climate forcings, the effect of water vapor is thought of as a feedback since no externally imposed change is involved. Water vapor feedback occurs because the warming resulting from a positive radiative forcing leads to increased evaporation from the oceans along with a greater saturation vapor pressure in the warmer troposphere [Manabe and Wetherald, 1967]. Water vapor feedback is positive, since an increase in the amount of atmospheric water vapor leads to greater infrared absorption and further warming. While it is well-known that there are uncertainties in the
distribution of atmospheric water vapor, it is not generally recognized that there are also substantial uncertainties in water vapor absorption coefficients. This is doubly significant, because the IPCC has cited uncertainty in cloud feedback as a major factor obstructing our ability to detect anthropogenic influences on the climate [IPCC, 2001]. Since clouds and water vapor are highly correlated in the atmosphere [Arking, 1999], it is necessary to isolate the radiative effects of water vapor from the radiative effects of clouds in order to develop an understanding of cloud feedback. This cannot be done adequately if there are substantial uncertainties in the magnitude of water vapor feedback.

An intercomparison of all available water vapor continuum data is presented in Section 2.7, which demonstrates that the uncertainties in the magnitude of the self- and foreign-broadened coefficients of the water vapor continuum are roughly 20% and 70%, respectively. The errors from the self- and foreign-broadened coefficients of the water vapor continuum will combine in a manner which depends on the relative magnitudes of the self- and foreign-broadened coefficients, as well as the temperature and water vapor and foreign gas partial pressures. For a mid-latitude summer atmospheric model with a surface temperature of 294 K and surface level water vapor partial pressure of 1.9 kPa, the combined uncertainty in the magnitude of the water vapor continuum is roughly 30%.

In a recent intercomparison of almost 40 infrared radiation codes used in climate models, the greenhouse effect due to the water vapor continuum was calculated to be 7.3 W/m² for a mid-latitude summer model atmosphere [Ellingson et al., 1991]. Thus, a 30% uncertainty in the magnitude of the water vapor continuum results in an uncertainty in the greenhouse effect of ± 2.2 W/m². Presently, the atmospheric concentration of CO₂ is increasing at a rate of 1.5 ppmv/yr [IPCC, 1996]. Over the next 30 years, the median radiative forcing due to the increase in atmospheric CO₂ is expected to be ~ 0.3 W/m² per decade [Wigley and Raper, 2001]. While it may prove possible to measure such a
small change in the radiative forcing (e.g. by observations of the downward longwave flux), we need a better understanding of the climate radiation budget before a change in radiative forcing could be attributed to a specific cause. In order to be able to ascribe the projected forcing of 0.3 W/m² per decade to increases in atmospheric CO₂, the level of uncertainty in water vapor continuum absorption would have to be reduced by an order of magnitude. Other factors that contribute to the overall uncertainty in radiative transfer might have to be reduced as well.

1.5 Thesis Motivation and Outline

The central purpose of this thesis is to reduce uncertainties in the magnitude of the water vapor continuum, which are currently ± 20% and ± 70% for the self- and foreign-broadened coefficients of the water vapor continuum, respectively. These uncertainties frustrate efforts to understand cloud feedback, and are themselves large enough to prevent the detection of anthropogenic forcing on the climate. Furthermore, there is evidence that the water vapor continuum is responsible for the super greenhouse effect, which could greatly amplify the response to an anthropogenic forcing [Raval and Ramanathan, 1989]. Cavity ringdown spectroscopy is a new laboratory technique which is highly sensitive to weak absorption, without sacrificing the accuracy of the absorption measurement. This thesis reports the development of a novel infrared cavity ringdown spectroscopy experiment and the first measurements of the water vapor continuum using cavity ringdown spectroscopy.

In Chapter 2, the water vapor continuum is defined and its distinctive properties are described in greater detail. In addition, two hypotheses concerning the origin of the water vapor continuum, water vapor dimer absorption and far-wing absorption, are discussed. Finally, water vapor continuum measurements from the past 30 years are compared.
Chapter 3 begins with an introduction to cavity ringdown spectroscopy and a discussion of its advantages over other spectroscopic techniques. Then, the infrared cavity ringdown experiment is described in detail. Special emphasis is placed on the stability issues encountered in making quantitative cavity ringdown spectroscopy measurements of the water vapor continuum.

The results are presented and discussed in Chapter 4. The water vapor continuum absorption coefficients are compared with continuum coefficients derived from a recent far wing theory, as well as empirical models of the water vapor continuum. Empirical models are routinely used in radiative transfer calculations because of their computational efficiency. The performance of the cavity ringdown experiment is also discussed.

Finally, conclusions and future work are presented in Chapter 5.
Chapter 2

The Infrared Water Vapor Continuum

2.1 Infrared Atmospheric Spectroscopy

The carrier of information in a spectroscopic experiment is the electromagnetic (EM) field, represented by the electric field vector $E$ (it is not necessary to separately consider the magnetic field $H$, as it contains no additional information in this case). In this thesis, EM radiation is effectively assumed to propagate in the form of transverse, plane waves. For a plane wave propagating in the $z$-direction:

$$E = E_0 \hat{x} \sin(kz - \omega t) \tag{2.1}$$

where $E_0$ is the electric field amplitude ($\text{V/m}$), $k = k\hat{x}$ is the wave vector and $\omega$ is the angular frequency ($\text{rad/sec}$). The unit vector $\hat{x}$ indicates that the electric field is constrained to oscillate in the $x$-direction. Thus, the EM wave is said to be linearly polarized in the $x$-direction. The regions of the EM spectrum and the nature of the interactions involved are shown in Fig. 2.1. In infrared spectroscopy, EM waves are normally characterized by the inverse of the wavelength or wavenumber, $\nu$ ($\text{cm}^{-1}$), a convention which we adopt in this thesis.

Spectroscopic signals are typically observed with detectors which measure the intensity $I$ (i.e. the power) of the EM radiation. The intensity is defined as the time average of the amount of energy which crosses in unit time a unit area perpendicular to the direction of the energy flow. For a plane EM wave in a vacuum, the average intensity is:

$$I = \frac{c}{4\pi} \sqrt{\frac{\varepsilon_0}{\mu_0}} \langle E^2 \rangle \tag{2.2}$$
Figure 2.1 - The electromagnetic spectrum [Banwell, 1983]. Several processes by which electromagnetic energy can be absorbed and emitted in molecules are also shown.
where \( \varepsilon_0 \) is the permittivity of free space \( (\varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) \), \( \mu_0 \) is the permeability of free space \( (\mu_0 = 1.26 \times 10^{-6} \text{ W} \text{ A}^{-1} \text{ m}^{-1}) \), and \( c = \sqrt{\frac{1}{\varepsilon_0 \mu_0}} \) is the speed of light \( (c = 2.9979 \times 10^8 \text{ m/s}). \)

Molecules interact with an electromagnetic field through changes to their dipole moment. Generally, the intensity of EM radiation propagating in a real medium may be attenuated or augmented by several processes including absorption, emission, and scattering. In this thesis, we are concerned only with the absorption of the medium, which is a process whereby the energy of a photon is used to excite a molecule from a lower to a higher internal energy state. Two forms of internal energy are relevant in infrared spectroscopy: vibrational and rotational energy. On a molecular scale, energy is quantized, so that infrared spectra are characterized by sets of discrete transitions forming vibration, rotation, and vibration-rotation absorption bands.

The attenuation of EM radiation propagating through an absorbing medium is described by the **Beer-Lambert law**:

\[
\frac{dI(v)}{dz} = -\sigma(v)NI(v)
\]  

(2.3)

or, in its integrated form (assuming a homogenous medium):

\[
I(v, z) = I_0(v) \exp[-\sigma(v)NZ]
\]

(2.4)

where \( I_0(v) \) is the initial intensity (W cm\(^{-2}\)), \( \sigma(v) \) is the absorption cross-section (cm\(^2\) molecule\(^{-1}\)) at wavenumber \( v \), \( N \) is the number density (molecules cm\(^{-3}\)) and \( z \) is the path length (cm). Frequently, Eq. (2.4) is expressed in terms of the absorption coefficient \( k \) (cm\(^{-1}\)), where \( k(v) = \sigma(v)N \). It is apparent from Eq. (2.4) that the total absorption can be increased by increasing either the number density of the absorbers or the optical path length. The Beer-Lambert law is a powerful quantitative tool in spectroscopy, because the number density can be accurately measured if the absorption cross-
As can be seen from Fig. 2.1, infrared energies correspond to the vibrational or rotational transitions of molecules. Although all molecules rotate and vibrate, only those molecules whose dipole moments change as a result of rotational or vibrational transitions may interact with an infrared radiation field. Sometimes these molecules are called infrared-active. Examples of infrared-active molecules include H₂O and CO₂, while molecules with no infrared absorption bands include N₂ and O₂. Infrared absorption spectra reveal a great deal about the internal structure and dynamics of molecules, and are often considered molecular “fingerprints” because of their uniqueness. However, we are not overly concerned in this thesis with such “fingerprint” spectra, nor what they reveal about the internal structure or the dynamics of the water molecule. Rather, the focus of this thesis is on the nature of H₂O - H₂O and H₂O - N₂ molecular interactions, and the influence of these interactions on the transmission of radiation in the relatively transparent region between the infrared absorption bands of water vapor.

Molecular interactions are commonly observed in gas-phase spectroscopy, through the broadening of spectral lines. The most important broadening mechanism for pressures near 1 atm is collisional broadening. This occurs because molecular collisions slightly deform the molecules, perturbing the energy levels involved in vibrational and rotational transitions. The net result of the random molecular collisions which continually take place is a characteristic broadening, which is most often modeled using the Lorentz line shape [Liou, 1980]:

\[
    k_l(v) = \frac{NS}{\pi} \frac{\alpha_L}{(v - v_0)^2 + \alpha_L^2}
\]

where \( N \) is the absorber number density (molecules cm⁻³), \( v_0 \) is the transition wavenumber (cm⁻¹), \( \alpha_L \) is the half-width at half-maximum (cm⁻¹), and \( S \) is the line strength (cm² molecule⁻¹ cm⁻¹). The line
shape is normalized so that the line strength is defined by [Liou, 1980]:

\[ S = \frac{1}{N} \int_{-\infty}^{\infty} k_i(\nu) \, d\nu \]  

(2.6)

The Lorentz line shape is based on the impact approximation, which assumes that perturbing collisions are short compared to the time between them. Several reviews discuss the impact approximation and the range of detuning \( |\nu - \nu_0| \) where it is expected to be valid [Allard and Kielkopf, 1982; Szudy and Baylis, 1996]. Generally, it can be assumed that the Lorentz line shape is valid for \( |\nu - \nu_0| < (c \tau_{\text{coll}})^{-1} \), where \( \tau_{\text{coll}} \sim 10^{12} \) s is taken to be the effective duration of collision. Thus, the Lorentz line shape can only be applied for detunings \( |\nu - \nu_0| < 30 \) cm\(^{-1} \). This thesis investigates the role of collisional broadening in the water vapor continuum, through the application of a far wing line shape theory which is valid for \( |\nu - \nu_0| > 30 \) cm\(^{-1} \). We also investigate whether strong molecular interactions of another kind, the formation of bound water vapor dimers, play a role in the water vapor continuum. Far wing collisional broadening and water vapor dimers are discussed in greater detail in Section 2.6.

2.2 Spectroscopy of Water Vapor

The infrared spectrum of water vapor consists of vibrational and rotational absorption bands as well as a background continuous absorption phenomenon known as the water vapor continuum. Chemically, water consists of two hydrogen atoms and an oxygen atom. The nuclei of a water molecule form an isosceles triangle, with an obtuse angle \( \alpha_0 \) at the oxygen nucleus (cf. Fig. 2.2). In the ground state, \( \alpha_0 \) is about 104.5° and the O - H bond length is \( 0.957 \times 10^{-8} \) cm. Because of oxygen’s affinity for electrons, there is a high electron density distribution around the oxygen atom, which leads to a strong permanent dipole moment of \( \mu = 1.87 \) Debye (the Debye, or D, is a unit of...
Figure 2.2 - The normal modes of vibrations of H₂O. The bonds are represented by dashed lines. The arrows show the relative directions and displacements of the nuclei during a given vibration. Taken from Eisenberg and Kauzmann [1969].
electric dipole moment and has a value of $1\, \text{D} = 3.336 \times 10^{-30} \, \text{C m}$).

The water molecule has three normal modes of vibration, illustrated in Fig. 2.2. As rotational energy changes typically accompany vibrational transitions, vibration-rotation bands are formed. In the gas state, the vibrational-rotational spectrum involves combinations of the symmetric stretch ($v_1$), asymmetric stretch ($v_3$), and bending ($v_2$) modes of the molecule. Because of the permanent dipole moment, water vapor also has a pure rotation band which peaks around 200 cm$^{-1}$. The rotational spectrum of water vapor is dense and superficially irregular (Fig. 2.3, top panel), because the water molecule is an asymmetric top. The transitions extending into the 800 - 1000 cm$^{-1}$ window region have the highest rotational energies, and assignment has been difficult. Recently, it has also been reported that some of these transitions have uncertainties of 30% in line intensities and up to 0.8 cm$^{-1}$ in the line positions [Rothman et al., 1998].

Despite generally adequate knowledge of the vibrational and rotational spectrum of water vapor, the infrared absorption due to water vapor has remained a challenging experimental and theoretical problem. The normal practice has been to treat the absorption coefficient of water vapor as the sum of contributions from local lines and a weak, unstructured background known as the water vapor continuum:

$$k(v) = k_l(v) + k_c(v)$$

(2.7)

where $k_l$ and $k_c$ are the local line and continuum absorption coefficients (cm$^{-1}$), respectively. The continuum absorption coefficients are required to obtain agreement between line-by-line calculations and absorption measurements. The CKD 2.4 empirical model of the water vapor continuum is shown as a thick solid line in Fig. 2.3 (top panel). Despite the well-defined appearance of the CKD continuum, there is actually much uncertainty associated with the water vapor continuum. In the lower panel of Fig. 2.3 we have plotted the blackbody spectrum for 296 K to illustrate how the water
Figure 2.3 - The infrared spectrum of water vapor. In the top panel, the absorption cross sections are plotted from 0 to 2500 cm$^{-1}$ (data are taken from Rothman et al. [1998]). Two absorption bands dominate the water vapor spectrum: the pure rotation band which peaks near 200 cm$^{-1}$, and the $v_2$ ro-vibrational band centered near 1600 cm$^{-1}$. Between these absorption bands is a region of relative transparency from 700 - 1250 cm$^{-1}$ known as the infrared window. The CKD 2.4 empirical model of the water vapor continuum [Clough et al. 1989] is superimposed as a thick, dark curve. In the lower panel, the terrestrial emission spectrum is plotted, demonstrating that the presence of water vapor continuum absorption in the infrared window plays a critical role in the energy balance of the Earth.
vapor continuum plays a critical role in the energy balance of the Earth through its interaction with the terrestrial emission radiation field. The remainder of this chapter discusses the properties, hypotheses and uncertainties of the water vapor continuum. In the next section, we begin with the problem of defining the water vapor continuum.

2.3 Definition of the Water Vapor Continuum

The water vapor continuum is sometimes referred to as “excess” absorption (e.g. [Burch and Gryvnak, 1980]), because it is what remains of a water vapor absorption spectrum after local line absorption has been taken into account. Historically, there has been a need to distinguish between local lines and far-wing regimes for two reasons. First, it has been the practice to truncate absorption calculations in the far wings for reasons of computational efficiency. Second, line shapes based on the impact approximation are inapplicable for frequencies distant from line center.

Unfortunately, there is no established definition of “local line absorption”, and consequently no established definition of “continuum absorption”. For example, Varanasi reported measurements of the water vapor continuum using a grating spectrometer where the absorption from all lines within ± 25 cm⁻¹ of the measurement wavenumber was subtracted from the total to obtain the continuum absorption coefficient [Varanasi and Chudamani, 1987]. In another instance, Burch [Burch, 1981] made grating spectrometer measurements of the continuum in regions where the AFGL (precursor to HITRAN) line parameter database indicated there were no significant lines within the bandwidth of the spectrometer (~ 2 cm⁻¹). The absorption due to lines from 1 ≤ |ν-ν₀| ≤ 30 cm⁻¹ was calculated from the AFGL database assuming a Lorentz line shape and subtracted from the measured absorption. However, Burch’s definition is slightly complicated by the fact that the 30 cm⁻¹ bound is apodized, which is to say that the Lorentz profile is multiplied by a factor which varies linearly
from unity at $|v-v_0| = 20 \text{ cm}^{-1}$ to zero at $30 \text{ cm}^{-1}$.

It is important to establish a universally-accepted definition of the water vapor continuum. Differences in the definition introduce differences in the reported values of the continuum absorption coefficients. These differences are especially serious in regions of the spectrum where there are significant contributions from local lines, but they can also lead to discrepancies in measurements of the continuum within window regions. Coarse-resolution spectrometer measurements of the continuum are problematic in the thermal infrared window from 700 - 1250 cm$^{-1}$, which contains hundreds of weak water vapor lines. One advantage of CO$_2$ laser measurements is that there is negligible local line contribution for several CO$_2$ laser frequencies, which lessens the significance of the choice of definition for the water vapor continuum. In this thesis, we report continuum absorption coefficients that follow the definition of Varanasi. That is, the water vapor continuum is taken to be the absorption which remains after the absorption due to all lines within $\pm 25 \text{ cm}^{-1}$ of the measurement wavenumber are taken into account. This definition is also consistent with the recently developed far wing line shape theory of Ma and Tipping (cf. Section 2.6).

2.4 Properties of the Water Vapor Continuum

Our practical knowledge of the water vapor continuum is derived from experiments. These investigations have revealed that the excess absorption possesses several distinct characteristics. We now consider in greater detail three important properties of the water vapor continuum in the 700 - 1250 cm$^{-1}$ infrared window region: the quadratic dependence on the water vapor partial pressure, the spectral dependence of the continuum coefficients of self- and foreign-broadening, and the temperature dependence of the continuum coefficients.
2.4.1 Partial Pressure Dependence of the Water Vapor Continuum

The most well-established property of the continuum in the infrared window region is the quadratic water vapor partial pressure dependence. The possibility of a quadratic dependence was raised by Penner and Varanasi [Penner and Varanasi, 1967; Varanasi et al., 1968], although the first clear demonstration of the quadratic dependence of the continuum absorption on the water vapor partial pressure is found in the CO₂ laser absorption data of McCoy et al. [1969]. However, the significance of McCoy's work was apparently not recognized at that time, and Bignell is often credited with the discovery [Bignell, 1970]. Bignell proposed that the continuum absorption coefficient \( k_c \) (cm\(^{-1}\)) be written as a sum of contributions:

\[
k_c = \rho_e (k_1 p + k_2 e)
\]

(2.8)

where \( p \) is the foreign gas partial pressure (atm), \( e \) is the water vapor partial pressure (atm), and \( \rho_e \) is the density of water vapor (g cm\(^{-3}\)). Bignell called \( k_1 \) the "absorption coefficient for foreign-broadening" (cm\(^{-2}\) g\(^{-1}\) atm\(^{-1}\)) and \( k_2 \) the "absorption coefficient for e-type absorption" (cm\(^{-2}\) g\(^{-1}\) atm\(^{-1}\)). The mechanism of the e-type absorption was not understood at that time, and this led to much speculation about the role of water vapor dimers, a topic which is discussed in greater detail in Section 2.6. Since the early work of McCoy and Bignell, the data of Burch [Burch, 1972; Burch and Alt, 1984], Peterson [Peterson et al., 1979], Varanasi [Varanasi and Chudamani, 1987], and many other investigators, support the quadratic partial pressure dependence. As a result, the following formulation for the water vapor continuum is generally accepted:

\[
k_c(v, T) = \left( \frac{N_0}{P_{ref}} \right) \left( \frac{T_{ref}}{T} \right) [C_s(v, T) \times e^2 + C_f(v, T) \times e P_f]
\]

(2.9)

where \( P_{ref} \) is the reference pressure (1 atm), \( T_{ref} \) is the reference temperature (296 K), \( N_0 \) is the
number density of an ideal gas at the reference conditions (molecules cm\(^{-3}\)), \(e\) is the water vapor partial pressure (atm), \(P_f\) is the foreign gas partial pressure (atm), and \(C_c\) and \(C_f\) are known as the continuum coefficients for self- and foreign-broadening, respectively (molecules\(^{-1}\) cm\(^2\) atm\(^{-1}\)).

The nature of the partial pressure dependence of the water vapor continuum can only be elucidated in the laboratory, where the water vapor partial pressure can be effectively controlled and removed. However, the investigations cited above all rely on large multi-pass cells, for which it is difficult to rapidly change the water vapor partial pressure. One consequence is that for any given study, the analysis was based on absorption measurements for only a few values of the water vapor partial pressure. For example, the results obtained by Peterson using a White cell [Peterson et al., 1979] were based on absorption measurements for only 4 water vapor partial pressures. Undersampling of the partial pressure dependence probably contributes to the large uncertainties in the continuum coefficients of self- and foreign-broadening which are discussed in Section 2.7.

### 2.4.2 Spectral Dependence of the Continuum Coefficients

The spectral dependence of the water vapor continuum has been the subject of several investigations over the last 30 years [Burch et al., 1971; Burch et al., 1974; Burch and Alt, 1984; Roberts et al., 1976; Varanasi and Chudamani, 1987], and there is rough agreement on the absorption spectrum. In Fig. 2.4, the continuum coefficients of self-broadening from two spectrometer data sets are plotted along with \(C_c\) values from the CKD 2.4 empirical model of the continuum [Clough et al., 1989]. The scatter of the data is probably an indication of experimental noise rather than structure in the absorption spectrum.

The absorption spectrum due to the continuum of foreign-broadening is less well established. Like the continuum of self-broadening, the continuum of foreign-broadening appears to be strongest
Figure 2.4 - Empirical continuum coefficients of self- and foreign-broadening. '+' : data of Burch and Alt [1984], 'o' data of Varanasi and Chudamani [1987]. The solid curve represents the CKD 2.4 empirical model of the continuum [Clough et al., 1989]. The superscript '°' (i.e. $C_i^0$ vs. $C_i$) denotes that the data have been corrected to the reference temperature of 296 K.
within the vibrational and rotational absorption bands, and weakest in the window regions in between absorption bands. However, the continuum coefficients of foreign-broadening are much weaker than the coefficients of self-broadening in the 700-1250 cm$^{-1}$ window region, and so there are few reliable measurements of the continuum of foreign-broadening. The lower panel of Fig. 2.4 presents the data of Burch and Alt [Burch and Alt, 1984], which was the only set of continuum coefficients of foreign-broadening available to us. Interestingly, the CKD 2.4 coefficients of foreign-broadening [Clough et al., 1989] do not appear to agree with the experimental values of $C_f$ known to us.

**2.4.3 Temperature Dependence of the Continuum Coefficients**

The temperature dependence of the water vapor continuum of self-broadening from 250 - 500 K can be seen in Fig. 2.5. It is apparent that there are few reliable measurements of the temperature dependence over this range. However, it is especially important that the continuum is studied for temperatures that are representative of the Earth's atmosphere (i.e. from 250 - 310 K), because both the absorption and its temperature dependence at elevated temperatures are markedly different from those at atmospheric temperatures. Low-temperature experiments are very difficult and require high sensitivity because of the combination of low saturation vapor pressures for $T < 296$ K and small continuum absorption cross-sections. Although there are large uncertainties in the measurements, the low-temperature data in Fig. 2.6 indicate that $C_s$ has a strong negative temperature dependence. It has been suggested that the following empirical relation may be used to model temperature dependence of the continuum coefficients of self-broadening: [Roberts et al., 1976]

\[
C_s(v, T) = C_s^0 \exp \left[ T_0 \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right]
\]  

(2.10)
Figure 2.5 - Temperature dependence of the water vapor continuum coefficient of self-broadening in the 1000 cm\(^{-1}\) wavenumber region. Two of the data sets were obtained using photoacoustic spectroscopy [Loper et al., 1983; Hinderling et al., 1987]. One data set was obtained from field measurements using an aircraft-borne radiometer [Coffey, 1977]. The fourth data set was obtained using a multi-pass cell in the laboratory [Montgomery, 1978]. In all cases, the experimental error bars are those reported by the authors. Below approximately 400 K, there is a strong, negative temperature dependence, while at higher temperatures the temperature dependence appears to be small and positive.
Figure 2.6 - Expanded view of the low-temperature measurements of $C_s$, the continuum coefficient of self-broadening, near 1000 cm$^{-1}$. Three curves are shown illustrating the least squares fits of the three data sets to the temperature dependence model represented by Eq. (2.10): solid curve [Hinderling et al., 1987], dashed curve [Loper et al., 1983], dotted curve [Coffey, 1977].
where $C_s^0$ is the continuum coefficient of self-broadening at $T_{ref}$ (296 K), and $T_0$ is a characteristic temperature. In adopting Eq. (2.10) as a model of temperature dependence, we stress that it is an empirical model which is probably only adequate for small temperature corrections.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Samples</th>
<th>Mean Reported Error</th>
<th>$C_s^0$ [10^{-12} molecule^{-1} cm^2 atm^{-1}]</th>
<th>$T_0$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffey [1977]</td>
<td>5</td>
<td>2.15</td>
<td>$1.90 \pm 0.21$</td>
<td>$4010 \pm 400$</td>
</tr>
<tr>
<td>Loper et al. [1983]</td>
<td>4</td>
<td>0.64</td>
<td>$2.94 \pm 0.22$</td>
<td>$2480 \pm 270$</td>
</tr>
<tr>
<td>Hinderling et al. [1987]</td>
<td>7</td>
<td>0.35</td>
<td>$2.18 \pm 0.24$</td>
<td>$1900 \pm 270$</td>
</tr>
</tbody>
</table>

Table 2.1 - Analysis of the temperature dependence of the continuum coefficients of self-broadening for the three low-temperature data sets.

The results of least-squares fits to Eq. (2.10) for the three data sets in Fig. 2.6 are presented in Table 2.1. The data sets of Loper et al. [1983] and Hinderling et al. [1987] have somewhat lower errors in the fit coefficient $T_0$ than the data of Coffey [1977]. However, we note that Loper et al. were not able to determine absolute values of $C_s$ for the two lowest temperatures (273 and 263 K). Instead, estimates of $C_s$ were derived from the ratio of the absorption coefficients at these temperatures with those at the higher temperatures. Meanwhile, Hinderling et al. made the most measurements and also reported the lowest mean experimental error. Therefore the data set of Hinderling et al. seems to contain the best information we presently have on the temperature dependence of the water vapor continuum for temperatures in the range 250-300 K, and a temperature dependence equivalent to Eq. (2.10) with $T_0 = 1900$ K should be used for the self-broadened coefficient of the water vapor continuum until we have improved data.

Finally, we note that in the literature, it is generally assumed that the temperature dependence
of $C_f$ is small and positive. However, we did not find any experimental results reported in the literature to support (or contradict) this assumption.

2.4.4 Summary of Water Vapor Continuum Properties

The infrared water vapor continuum possesses several distinctive properties which may be summarized as follows:

1. The absorption varies slowly with wavenumber. The absorption spectrum appears to be fully resolved, having the nature of a true continuum.

2. Although the data are incomplete, the evidence suggests that water vapor continuum absorption is found in all spectral regions. The continuum absorption coefficients are largest within absorption bands, reaching a minimum in the window regions between absorption bands.

3. In window regions, continuum absorption is generally stronger than local line absorption.

4. The continuum absorption comprises two terms, as shown in Eq. (2.9). One term depends on the square of the water vapor partial pressure, and is referred to in this thesis as the **continuum of self-broadening**. The other term is linear in water vapor partial pressure. We refer to this as the **continuum of foreign-broadening**.

5. The continuum coefficients of self-broadening, $C_s$, are greater than the coefficients of foreign-broadening, $C_f$, for all spectral regions. We define the ratio $B = C_s / C_f$. Within absorption bands,
B ~ 5, and increases rapidly to B > 100 in window regions.

6. The continuum coefficient of self-broadening increases rapidly with decreasing temperature. Little is known about the temperature dependence of the continuum coefficient of foreign-broadening.

2.5 Water Vapor Continuum Bibliography

Although several reviews of the water vapor continuum have been published [Varanasi, 1988; Grant, 1990; Aref’ev, 1991], none has included a comprehensive bibliography. A water vapor continuum bibliography should prove useful, particularly as we have noticed that there is a great deal of experimental data on the water vapor continuum which are not actually used in modeling or theoretical studies.

Presently, the water vapor continuum bibliography includes more than 640 references covering many topics related to the water vapor continuum up to June 2001. These include experimental studies of water vapor absorption and emission in atmospheric window regions of the spectrum. Line shape studies are included when there is substantial discussion of far wing absorption. Theoretical and experimental works on water dimers (equilibrium and non-equilibrium), water clusters, ion clusters and van der Waals complexes are all included, as these have all been postulated as being responsible for the water vapor continuum. Applications of the water vapor continuum in fields such as radiative transfer and climate modeling are also included. Although we have attempted to be thorough, we recognize that the bibliography may have omissions and so the database is updated with any suggestions communicated to us.

A formatted version of the bibliography is available at www.watervaporcontinuum.com. We also maintain a searchable electronic version of the database (Reference Manager 9.5 format),
which includes over 50 keywords pertaining to the water vapor continuum (see Appendix A.). This adds a great deal of power to the bibliography, because multi-parameter searches can be used to efficiently extract interesting references from the database. For example, performing the keyword search "longwave AND photoacoustic" extracts the 18 references from the database that discuss thermal infrared measurements of the water vapor continuum using photoacoustic spectroscopy. The electronic database can also be obtained from the web page.

2.6 Hypotheses of the Water Vapor Continuum

Many mechanisms have been proposed as being responsible for water vapor continuum absorption, including the far wings of water monomer transitions, water dimers (equilibrium and non-equilibrium), water clusters, collision-induced absorption, and aerosols. In this section, we focus on the equilibrium water dimer and far wing hypotheses, because these two mechanisms are the most likely to be involved in the water vapor continuum and the respective theories are the most developed. However, we do not attempt to present a rigorous mathematical review of theories, but rather discuss in a mostly qualitative way the elements of dimer theory and far wing line shape theory which are applicable to the problem of the water vapor continuum. In Chapter 4, we discuss how our measurements indicate that most of the infrared continuum is likely due to far wing absorption, although there may also be water dimer absorption present near 930 cm$^{-1}$.

2.6.1 Far Wing Hypothesis

The far wing hypothesis states that the water vapor continuum absorption is the sum of the contributions from the hundreds of strong but distant water vapor monomer rotation and vibration-rotation lines, i.e.:
where $S_i$ is the strength of the i-th transition and the shape of the far wing is given by a function $f$ which depends on the detuning from line center ($v - v_0$). The water vapor continuum cannot result solely from lines within the 700 - 1250 cm$^{-1}$ window region, because the continuum absorption is stronger than most of the water vapor lines in that region. It has long been known that the Lorentz line shape, as well as other line shapes based on the impact approximation, are not valid for large detunings $|v - v_0| > \alpha_L$ [Allard and Kielkopf, 1982; Szudy and Baylis, 1996]. In addition, conventional line shapes do not have the strong negative temperature dependence required to model the water vapor continuum. Therefore, the recent development of far wing line shapes has been an important step in our understanding of the water vapor continuum. We note that the discussion that follows is restricted to the mechanism of collisional broadening, which is the dominant broadening mechanism in the lower troposphere, where more than 90% of atmospheric water vapor is found.

In an early attempt to model the continuum with a far wing line shape, Burch found that fairly good agreement with the continuum absorption spectrum could be obtained by modeling the far wings of the absorption lines in the AFGL database using an empirical line shape [Burch and Gryvnak, 1980]. The empirical line shape was obtained by multiplying a conventional line shape (e.g. Lorentz) by a factor $\chi$, which was a function of the detuning $|v - v_0|$. For self-broadened lines, the observed continuum absorption was "super-Lorentzian", i.e. $\chi > 1$, for detunings in the range $10$ cm$^{-1} \leq |v - v_0| \leq 400 - 500$ cm$^{-1}$, while for greater detunings the absorption became "sub-Lorentzian" ($\chi < 1$). For foreign-broadened lines, the detuning range for super-Lorentzian behavior was probably smaller, perhaps $10$ cm$^{-1} \leq |v - v_0| \leq 200 - 300$ cm$^{-1}$, although there were large uncertainties in the observed continuum of foreign-broadening. In other words, foreign-broadened
water vapor lines have a different shape from self-broadened lines. Burch saw no need to invoke another mechanism, such as water dimers, to explain the water vapor continuum, since conventional line shapes demonstrated the correct partial pressure dependence, i.e. self-broadening would contribute a term proportional to the square of the water vapor partial pressure. However, Burch was unable to show how a line shape could have a strong negative temperature dependence.

Thomas and Nordstrom were among the first to attempt to develop a far wing line shape theory in order to model the water vapor continuum [Nordstrom and Thomas, 1980; Thomas and Nordstrom, 1982a; Thomas and Nordstrom, 1982b]. Thomas and Nordstrom began with an intuitive picture of the relationship between the intermolecular potential, the correlation function and the line shape, shown in Fig. 2.7. The correlation function $C(\tau)$ describes the correlation of the state of a system as it evolves over time. In an ensemble of molecules, random collisions will tend to diminish the correlation of the state over time, as illustrated in Fig. 2.7. The correlation function is related to the line shape by the Fourier transform:

$$f(\Delta \omega) = \frac{1}{\pi} \Re \int_0^\infty d\tau \exp(-i \Delta \omega \tau) C(\tau)$$

(2.12)

where $\Delta \omega$ is the detuning. It is frequently assumed that the correlation function decreases over time in an exponential manner, i.e. $C(\tau) = \exp(-\alpha \tau)$. When this assumption is made, the Fourier transform is the familiar Lorentzian line shape of Eq. (2.5).

Thomas and Nordstrom proceeded by subdividing the correlation functions into three categories: short, intermediate, and long correlation times, corresponding to far wing, intermediate, and near line center regions, respectively. As is apparent from Fig. 2.7, the short correlation times characteristic of far wing absorption are the result of strong short-range interactions between molecules. The details of the line shape theory derived by Thomas and Nordstrom are not discussed.
Figure 2.7 - The relationship between the intermolecular potential $H(R)$, the correlation function $C(\tau)$, and the spectral line shape $f(\Delta \omega)$. $R$ is the intermolecular distance between the absorber and perturber, $\tau$ is the correlation time, and $\omega_0$ is the transition frequency. Adapted from Thomas and Nordstrom [1982a].
further, as it has been superceded by improved theories. However, we point out that the derived line shape had a total of 18 adjustable empirical parameters, some of which had no obvious physical meaning and could only be estimated. Nevertheless, Thomas and Nordstrom obtained reasonable agreement in magnitude and wavenumber dependence with laboratory continuum data. In addition, the semi-empirical far wing theory of Thomas and Nordstrom had a negative temperature dependence, although it was not as strong as the temperature dependence of the water vapor continuum.

Rosenkranz [1985; 1987] sought to solve the water vapor far wing line shape problem using the line shape theory of Fano [1963]. Fano’s approach treats the pressure-broadened line shape as a relaxation problem in statistical physics, and so the spectral density (or line shape) is calculated for a system consisting of an absorber molecule in a thermal bath. Mathematically, the theory of Fano is developed around the Liouville operator representation of density matrices. We do not describe this formalism further but note that according to Rosenkranz [1985], the key advantages are that it allows the transformation to the frequency domain to be made at an early stage, avoiding calculational difficulties in the time domain representation, and also because it permits overlapping lines to be considered.

Rosenkranz also adopted the quasistatic approximation. The quasistatic approximation is complementary to the impact approximation (which treats collisions as being instantaneous) because, in a sense, collisions are of infinite duration in the quasistatic approximation. In the quasistatic approximation, a statistical distribution of stationary molecules is assumed and the radiating molecule emits a frequency \( \omega_0 + \Delta \omega \) which is given by the energy difference between the states of the radiating molecule perturbed by its interaction \( V \) with a nearby molecule (binary collision approximation). This interaction depends upon \( R \), the distance between the centers of mass of the
two molecules, as well as Ω_a, the orientation of the active molecule, and Ω_b, the orientation of the perturber. In the quasistatic approximation, the intensity is proportional to the probability of finding a perturber at a specified distance and orientation. The statistical weight is given by the usual Boltzmann factor, exp(-V(R, Ω_a, Ω_b)/kT), times the number density of the bath molecules.

The interaction potential between molecules can be written as a sum of anisotropic and isotropic components, i.e.:

\[ V(R, Ω_a, Ω_b) = V_a(R, Ω_a, Ω_b) + V_s(R). \]  (2.13)

In solving for the far wing line shape, Rosenkranz used a Lennard-Jones model for the isotropic part of the intermolecular potential:

\[ V_s(R) = \frac{C}{\sigma^6} \left[ \left( \frac{\sigma}{R} \right)^2 - \left( \frac{\sigma}{R} \right)^6 \right] \]  (2.14)

where C, σ, and s are constants. For H_2O-H_2O interactions, Rosenkranz used the values C = 1.10 x 10^{-23} \text{ J nm}^6, σ = 0.313 \text{ nm}, and s = 48, while for H_2O-N_2 interactions the values C = 1.13 x 10^{-23} \text{ J nm}^6, σ = 0.294 \text{ nm}, and s = 9 were used. While the ability to derive a line shape from intermolecular potentials represented an advance in water vapor line shape theory, it must be stressed that large uncertainties exist in the short-range interactions, i.e. in the far wing region of Fig. 2.7. Typical intermolecular potentials are illustrated in Fig. 2.8.

There are two further assumptions to the theory of Rosenkranz: 1. The frequency ω at which the absorption coefficient is calculated is much larger than the transition frequency (i.e. ω > ω_0), sometimes called the high-frequency limit, and 2. ω is large compared to the differences between the frequencies of strong resonances in the gas, called the narrow-band approximation [Ma and Tipping, 1990]. This permitted Rosenkranz to replace the frequency-dependent coefficients of line coupling with a band-averaged broadening parameter. Rosenkranz expressed the absorption
Figure 2.8 - Typical Lennard-Jones intermolecular potentials for $\text{H}_2\text{O-H}_2\text{O}$ and $\text{H}_2\text{O-N}_2$ interactions. Values of the constants used to derive these curves were taken from Rosenkranz [1987].

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coefficient as:

\[ k(v) = N \sum_i \frac{v \sinh(h c v_i / 2 k T)}{v_i \sinh(h c v_i / 2 k T)} S_i [\hat{f}(v - v_i) + \hat{f}(-v - v_i)] \]  

(2.15)

where the spectral density is given by:

\[ \hat{f}(\Delta v) = \pi^{-1} \frac{\langle \hat{M}''(\Delta v) \rangle}{(\Delta v)^2 + \langle \hat{M}''(\Delta v) \rangle^2} . \]  

(2.16)

It is interesting to note the similarity of the expression for the spectral density to Eq. (2.5), the Lorentz line shape. However, in Eq. (2.16) the line width is given by \( \langle \hat{M}''(\Delta v) \rangle \), the symmetrized average relaxation parameter, which is no longer a constant value but instead depends on the detuning \( \Delta v \) from resonance. In the far wing region, \( \Delta v \gg \langle \hat{M}''(\Delta v) \rangle \), and so Eq. (2.16) can be approximated by:

\[ \hat{f}(\Delta v) \approx \pi^{-1} \frac{\langle \hat{M}''(\Delta v) \rangle}{(\Delta v)^2} . \]  

(2.17)

The dependence of \( \langle \hat{M}''(\Delta v) \rangle \) on the detuning is shown in Fig. 2.9. The enhanced broadening for detunings in the range of 50 - 300 cm\(^{-1}\) arises from the attractive terms in the intermolecular potentials, while the rapid drop in the broadening parameters for larger detunings is due to the repulsive term of the intermolecular potential [Rosenkranz, 1987]. The far wing absorption coefficients obtained by Rosenkranz generally agreed well with the empirical continuum data of Burch in the 300 - 1100 cm\(^{-1}\) region. Most significantly, Rosenkranz demonstrated that a properly formulated far wing line shape theory would have a strong negative temperature dependence.

Beginning with the basic formulation of Rosenkranz, but proceeding in a different way, Ma and Tipping have recently developed an improved far wing line shape theory [Tipping and Ma, 1995;...
Figure 2.9 - Symmetrized average broadening parameters as functions of detuning, for two different temperatures. Adapted from Rosenkranz [1987].
Ma et al., 1998; Ma and Tipping, 1999; Ma and Tipping, 2000]. The basic assumptions of the theory of Ma and Tipping are still the binary collision approximation and the quasistatic approximation. However, many of the limitations of the original Rosenkranz formulation have been overcome.

For example, the theory of Rosenkranz makes assumptions about the radiation frequency which limit the application of the theory to the high-frequency wings of absorption bands. Thus, the far wing calculations of Rosenkranz for the 300 - 1100 cm\(^{-1}\) region are based only on the pure rotational band and do not take into account the \(v_2\) rotation-vibration band centered near 1600 cm\(^{-1}\). The algorithm adopted by Ma and Tipping lifts the high-frequency restriction. Another serious problem encountered by Rosenkranz was the need to diagonalize the total Hamiltonian for the system. Because the number of possible states in an asymmetric top rotor increases rapidly with J, the angular momentum quantum number, Rosenkranz was forced to truncate the Hamiltonian matrix so that only values of \(J \leq 4\) were included in the calculation. Ma and Tipping expressed the density matrix in the coordinate representation basis set, in which the intermolecular potential is already diagonal [Ma and Tipping, 1999]. Thus, all states are included in the calculations of Ma and Tipping.

Results of the most recent far wing calculations for water vapor are presented in Fig. 2.10. The continuum absorption coefficients derived from these far wing line shapes are in good agreement with the empirical continuum data of Burch and others. In Chapter 4, we demonstrate that our measurements of the water vapor continuum are also in good agreement with the theory of Ma and Tipping.

Finally, we note that at present, the theory of Ma and Tipping is fundamentally limited by the accuracy of the intermolecular potential, especially the short-range anisotropic components [Tipping, 2001]. It is hoped that accurate measurements of water vapor continuum absorption can be used to improve our understanding of the intermolecular potential.
Figure 2.10 - The self-broadened far wing line shape of H$_2$O as a function of wavenumber for $T = 296, 338,$ and $430$ K (solid, dashed, and dotted lines, respectively). Taken from Ma and Tipping [1999].
2.6.2 Dimer Hypothesis

The water vapor dimer is a gas-phase species consisting of two water molecules joined by a hydrogen bond. Over the years, much theoretical interest in the dimer was fueled by the desire to understand the complex phenomenon of hydrogen bonding, and ultimately to develop a theory of liquid water [Coker et al., 1982]. Although the hydrogen bond was first discussed in 1920 [Latimer and Rodebush, 1920], our understanding of the potential role of water dimers in atmospheric radiative transfer has been comparatively slow to develop. Viktorova and Zhevakin were among the first to present a theoretical analysis of water dimer absorption for atmospheric conditions [Viktorova and Zhevakin, 1967]. The number density of dimers was estimated to be 0.1% of the water vapor monomer number density, for a temperature of 293 K and an absolute humidity of 7.5 g/m³. Interpreting the dimer structure to be that of a symmetric top rotator, Viktorova and Zhevakin calculated a regularly-spaced rotational spectrum with the most intense transitions in the far infrared and submillimeter region of the spectrum for \( \nu \leq 100 \text{ cm}^{-1} \).

In 1969, Gebbie studied water vapor absorption in the window regions of 6 - 9 cm\(^{-1}\) using a Fourier transform spectrometer and a multi-pass cell [Gebbie et al., 1969]. Gebbie reported finding a discrete absorption feature at 7.5 cm\(^{-1}\) which exhibited a quadratic dependence on the water vapor partial pressure, and which appeared to coincide with the prediction of a dimer rotational transition at 7.1 cm\(^{-1}\) [Viktorova and Zhevakin, 1967]. In a second experiment, quantitative measurements of water vapor absorption were made using a HCN maser source. In the window region near 30 cm\(^{-1}\), Gebbie observed continuum absorption with a strong negative temperature dependence over the range 293 - 320 K. From these measurements, Gebbie calculated the dimer binding energy to be \( E_2 = 5.2 \pm 1.5 \text{ kcal/mole}, \) in good agreement with the value of 5.0 kcal/mole predicted by Pauling.
for a water dimer with an open linear structure containing a single hydrogen bond [Pauling, 1960]. Gebbie concluded, citing the steam absorption experiments of Penner and Varanasi [1967], that dimer absorption in the atmosphere extends from the 7 cm\(^{-1}\) submillimeter wave region to the 1000 cm\(^{-1}\) infrared region.

The assumption of many investigators that water dimers were responsible for the infrared water vapor continuum (e.g. [Penner and Varanasi, 1967; Varanasi et al., 1968; Bignell, 1970; Gebbie et al., 1969]) was quickly adopted by the atmospheric physics community [Liou, 1980; Houghton, 1986]. The hypothesis that water dimers were responsible for the infrared continuum absorption was mainly based on the quadratic dependence on water vapor partial pressure and the strong negative temperature dependence. Models of the equilibrium concentration of water dimers vary in sophistication, but all predict a temperature dependence in the form of the well-known Boltzmann factor \(\exp(-E_2/RT)\), where \(E_2\) is the dimer binding energy.

The popularity of the dimer hypothesis has also been partly due to the fact that until recently, line shape theories have been unable to account for the observed continuum and were based on approximations that were inapplicable in the far wings. Unfortunately, the recognized deficiencies of conventional line shapes in the far wing region led many investigators to mistakenly dismiss the important role of self-broadened far wing absorption in the water vapor continuum. However, it is clear from Eq. (2.3) that quantitative spectroscopy requires knowledge of both the absorption cross-section, \(\sigma(\nu)\), and the number density, \(N\). In the case of the water dimer, little is known about either the number density or the absorption spectrum in the 700 - 1250 cm\(^{-1}\) region. Therefore, there has never been a spectroscopic basis to favor the dimer hypothesis of the infrared water vapor continuum.

Despite the absence of spectroscopic proof of the role of dimer absorption in the water vapor
continuum, proponents of the dimer hypothesis have continued to advance possibilities. In 1978, Wolynes and Roberts claimed that the continuum absorption in the 8-12 μm region could be explained by a librational (i.e. hindered rotational) motion about the hydrogen bond of the dimer [Wolynes and Roberts, 1978]. The idea that out-of-plane hydrogen-bond bending in the water dimer caused the water vapor continuum was given further support the following year by Suck and co-workers [Suck et al., 1979]. The position taken by Suck et al. was that the restoring force provided by the hydrogen bond would increase the frequency of motion into the infrared window region. In order to explain the observed continuum, they posited that the rotational fine structure of the dimer spectrum would be smeared by collisions, resulting in a continuum-like absorption. However, the authors of these studies never quantified the dimer absorption they predicted.

Spectroscopy has provided valuable information on the water dimer in other spectral regions. For example, Dyke observed radio frequency and microwave transitions of the water dimer in a molecular beam using electric resonance spectroscopy [Dyke et al., 1977]. From the rotational spectrum, Dyke identified the lowest energy equilibrium structure of the water vapor dimer as trans-linear, with a plane of symmetry and a linear hydrogen bond (Fig. 2.11). The elucidation of the dimer structure, in turn, has made it possible to identify 6 high-frequency intra-molecular and 6 low-frequency intermolecular vibrational modes associated with the water dimer. The intermolecular vibrational modes are illustrated in Fig. 2.12.

Spectroscopic measurements of water dimer infrared absorption are rare. The absorption bands of the intra-molecular normal modes of the water dimer have been observed in matrix isolation experiments [Tursi and Nixon, 1970; Bentwood et al., 1980], and recently in a supersonic expansion jet using cavity ringdown spectroscopy [Paul et al., 1999]. In these experiments, the wavenumber shifts of dimer bands with respect to the corresponding monomer bands was much less than the
Figure 2.11 - Trans-linear configuration of the water dimer. The solid line indicates the orientation of the hydrogen bond. Adapted from Chaplin [2001].
widths of the absorption bands. Thus, dimer intra-molecular absorption bands are very difficult to
directly observe for atmospheric conditions, given that they are almost entirely overlapped by
monomer absorption bands and that the equilibrium ratio of water vapor dimers to monomers is
$10^2 - 10^3$ for atmospheric temperatures [Chýlek and Geldart, 1997].

Large uncertainties remain in the intermolecular vibrational spectrum of the water dimer,
because the far infrared portion of the spectrum is completely obscured by the intense monomer
rotational band (cf. Fig. 2.3). As far as we know, there have been no observations of the water dimer
intermolecular spectrum from 200 - 1000 cm$^{-1}$ and only the translational vibration mode at
$\nu = 147$ cm$^{-1}$ has been observed experimentally [Dyke et al., 1977]. The best information we
presently have on the other modes may be the theoretical predictions made by Vigasin for the
positions and relative intensities of the intermolecular modes [Vigasin, 1983], which are shown in
Fig. 2.13. Interestingly, we also see in Fig. 2.13 the locations of various overtone and combination
bands in the 600 - 1000 cm$^{-1}$ region. Vigasin thought that these bands might form a quasi-continuum
which could explain the water vapor continuum. In Chapter 4, we discuss the possibility that our
absorption measurements provide evidence of a weak dimer combination band near 930 cm$^{-1}$.

2.7 Intercomparison of Water Vapor Continuum Measurements

Over the past 30 years, investigators have studied the water vapor continuum in the thermal
infrared window by a variety of techniques in both the field as well as the laboratory. In our survey
of the problem, we have found large uncertainties in the water vapor continuum absorption
coefficients when all available data were compared. This section describes an intercomparison of
measurements of water vapor continuum absorption coefficients. The goals of the intercomparison
are as follows. First, the overall level of uncertainty in water vapor continuum measurements is
Figure 2.12 - The intermolecular vibrational modes of the water dimer. Modes 1-4 are librational modes, 5 is a translational mode and 6 is a torsional mode. Adapted from Owicki [1975].
Figure 2.13 - Integrated intensity of intermolecular water dimer vibrations (vertical line segments in relative units). The numbers in parentheses identify the vibrational modes of Fig. 2.12. The possible positions of overtone and combination bands in the 600 - 1000 cm\(^{-1}\) region are also shown. Adapted from Vigasin [1983].
established. Second, data are grouped according to experimental technique, in order to identify the strengths and weaknesses of each technique. Finally, we propose a multi-technique approach to develop the most complete and accurate picture of the water vapor continuum.

Although this is not the first critical review of water vapor absorption in the thermal infrared window [Grant, 1990; Aref'ev, 1991], we believe our review represents a significant advance for three reasons. First, we have included the greatest number of water vapor continuum measurements. Second, data are compared for fixed conditions of wavenumber and temperature. By taking into account the observed dependence of the continuum on wavenumber and temperature, some of the confusion and ambiguity of previous intercomparisons is eliminated. Third, we have chosen to compare self- and foreign-broadened coefficients, rather than transmission or optical depth. The self- and foreign-broadened coefficients of the water vapor continuum can be thought of as absorption cross-sections, and so represent more intrinsic properties of an ensemble of water vapor molecules than the transmission or optical depth.

The first task was to select the wavenumber and temperature which permitted the greatest number of measurements to be compared. The majority of water vapor continuum measurements have been made in the thermal infrared window region ranging from 700 - 1250 cm\(^{-1}\), because of the strength of the continuum absorption relative to local line absorption. As mentioned in Section 1.2, the CO\(_2\) laser has been an important tool for infrared investigation, because of the intense infrared radiation emitted by these devices. Many of the transitions of the line-tunable CO\(_2\) laser are in regions devoid of significant water vapor line absorption, and are therefore ideal for quantitative studies of the water vapor continuum. The dominant transition of the CO\(_2\) laser is the 10P(20) transition at a wavenumber of 944.195 cm\(^{-1}\), and so we chose this wavenumber for our intercomparison. Since most laboratory experiments take place at or near the HITRAN reference
temperature \( T_{ref} = 296 \text{ K} \), we chose this temperature for the intercomparison.

The next step was to decide which data to include in the intercomparison. Our goal was to compare as many measurements as possible, provided that we did not compromise the accuracy of the data. This was a concern because the observations were reported at slightly different wavenumbers or temperatures in many instances. If the authors made no observations at 944.195 cm\(^{-1}\), we obtained a value of the continuum absorption coefficient at 944.195 cm\(^{-1}\) through a least squares fit of their data to a function of the form:

\[
C^0_s(v) = a_1 + a_2 \exp(a_3|v - a_4|)
\]

(2.18)

where \( a_1, a_2, a_3, \) and \( a_4 \) are fit coefficients. An example of such a fit is seen in Fig. 2.14 with the data of Varanasi and Chudamani [1987]. Given the typical scatter of spectrometer data which is evident from Fig. 2.14, we assume that the choice of empirical model does not contribute significantly to the uncertainty of the value at 944.195 cm\(^{-1}\). To test this hypothesis, we have fit continuum absorption coefficients derived from the far wing line shape theory of Ma and Tipping [1999]. It must be stressed that Eq. (2.18) is simply an empirical relation which provides a good fit to the data in the 700 - 1250 cm\(^{-1}\) region. However, as Fig. 2.15 demonstrates, the fit to the theoretical continuum absorption coefficients of Ma and Tipping is generally excellent, with a mean relative error less than 1%. Finally, we note that none of the data included in the intercomparison were obtained by extrapolation from outside the 700 - 1250 cm\(^{-1}\) window region.

Similarly, if the authors made measurements at several temperatures other than 296 K, we have used their temperature dependence data to obtain a value for the continuum absorption coefficient at 296 K. For many experiments (including our own), results were reported near 296 K but the temperature dependence was not studied. In order to correct for temperature, we have relied on the data of Hinderling \textit{et al.} [1987], from which we found a temperature dependence of...
Figure 2.14 - Data of Varanasi and Chudamani [1987] and the least squares fit to Eq. (2.18) used to obtain a value of $C_s^0$ for $v = 944.195 \text{ cm}^{-1}$. 

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Figure 2.15 - The least squares fit of Eq. (2.18) to the continuum coefficients derived from the far wing line shape theory of Ma and Tipping [1999]. In the 700 - 1250 cm⁻¹ window, Eq. (2.18) models the far wing continuum coefficients with a mean error less than 1%, as shown in the lower panel.
\[ T_0 = 1900 \pm 270 \text{ K (cf. Section 2.4). For experimental temperatures in the range } 296 \pm 10 \text{ K, the } \]
application of the above temperature correction adds less than 3\% to the uncertainty of the reported absorption coefficient. Thus, we believe it is better to apply a temperature correction when comparing data than to ignore the strong negative temperature dependence.

Some experimental results which were made at or near the intercomparison conditions of \( v = 944.195 \text{ cm}^{-1} \) and \( T = 296 \text{ K} \) are not included in this intercomparison. For example, in the field measurements of Han et al. [1997] and Barton [1991], there was insufficient reporting of data for us to derive self- and foreign-broadened coefficients. While there was good reporting of the atmospheric conditions in the transmission measurements of Ben-Shalom et al. [1980], the water vapor partial pressure dependence was not adequately sampled for us to derive unique values of the self- and foreign-broadened coefficients. In other instances, such as the aircraft radiometer measurements of Kilsby et al. [1992] and Rudman et al. [1994], the spectral response of the instrument was too broad for us to uniquely determine the self- and foreign-broadened coefficients from the observed radiances.

Water vapor continuum coefficients of self- and foreign-broadening may be directly compared when they are at the same wavenumber and temperature. Table 2.2 is a comparison of 26 measurements of the water vapor continuum coefficient of self-broadening, \( C_s^0 \), as well as 16 measurements of the water vapor continuum coefficient of foreign-broadening, \( C_f^0 \). When all of the data are considered, we find:

\[
C_s^0 = 2.09 \pm 0.35 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1} \text{ atm}^{-1}
\]
\[
C_f^0 = 1.02 \pm 0.75 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1} \text{ atm}^{-1}
\]

where the error estimates are the standard deviations of the 26 \( C_s^0 \) measurements and 16 \( C_f^0 \) measurements, respectively. Thus, the continuum coefficients of self-broadening have a relative
uncertainty of about ± 17%, while the continuum coefficients of foreign-broadening have an uncertainty of ± 74%. Recalling the discussions in Sections 1.3 and 1.4, it is clear that the overall uncertainties in the magnitude of the water vapor continuum inhibit our understanding of the natural climate and our ability to predict the anthropogenic influence on the climate.

We compare the accuracy of the continuum coefficients of self-broadening in terms of the experimental techniques that have been employed, as shown in Table 2.3. The following mnemonics identify the experimental technique:

Field: field measurements
LMPS: laboratory measurements, multi-pass cell and spectrometer
LMPL: laboratory measurements, multi-pass cell and CO₂ laser
LPAL: laboratory measurements, photoacoustic spectroscopy

2.7.1 Field Measurements

We begin our discussion of the measurement intercomparison with field techniques. Field observations provided the earliest evidence that there was significant extinction in the thermal infrared window. Direct observations of atmospheric radiation are also important for validating theories of radiative transfer. The greatest advantage of field observations is the very long optical path lengths that are possible. Whether the technique involves solar absorption or horizontal path measurements, the optical path lengths are often several km long. The mean and median values of Cₜ⁰ from field measurements are both close to the respective values for all measurements, as is apparent in Table 2.3. However, the relative uncertainty (which we define as the standard deviation divided by the mean) of continuum absorption coefficients obtained through field techniques is rather high, ± 19%.
Many factors likely contribute to the apparent lack of consistency. One of the biggest problems of field measurements arises from its greatest strength: the very long optical path, which is impossible to control and difficult to characterize. Two important factors are uncertainties in the composition of the path and the state variables. In order to derive accurate continuum absorption coefficients from atmospheric measurements, the issue of potential interference from other atmospheric constituents must be addressed with great care. Atmospheric constituents which may interfere with water vapor continuum measurements include fogs, clouds, hazes, dusts, aerosols, carbon dioxide and ozone. Also, many trace gases are powerful absorbers of infrared radiation.

The state of the atmosphere must also be well known. Typically, atmospheric state variables such as temperature and pressure are undersampled. In the case of vertical or slant atmospheric paths, atmospheric models are used to interpolate or extrapolate observational data, when it exists, over the optical path. An even more serious error may result from the uncertainty in the humidity over the optical path, because of the quadratic dependence on water vapor partial pressure. Moreover, even if the humidity in the optical path is well-characterized it cannot be conveniently removed, which makes it impractical to determine the experimental baseline. Nevertheless, the problem of the water vapor continuum impacts most heavily upon the area of atmospheric radiative transfer, and so field measurements provide important validation for laboratory results.

2.7.2 Laboratory Measurements

One of the biggest advantages of making laboratory measurements is experimental control over the gas composition and the state variables. In addition, it is generally not a problem to remove the humidity from the optical path in order to establish the experimental baseline. Curiously, the perceived advantages of laboratory experiments are not apparent in the relative uncertainty of all
laboratory data, which at ± 15% is only a slight improvement over field techniques. We were therefore led to investigate whether there were trade-offs in employing the sensitive spectroscopic techniques that are necessary to make measurements of the water vapor continuum in the restricted space of the laboratory. Such techniques can be broadly categorized into those which measure the absorption directly, and those which infer the absorption coefficient from the observation of another physical process. First, we consider direct absorption techniques, in which multi-pass cells are used to increase the total optical path length.

2.7.2.1 Multi-Pass Cell Techniques

In order to directly measure the absorption, it is generally necessary to increase either the optical path length, the absorber amount, or both. Early laboratory measurements of water vapor absorption in the infrared window region were made using steam [Hettner, 1918; Benedict et al., 1952; Penner and Varanasi, 1967; Varanasi et al., 1968], since the saturation vapor pressure of water is governed by an exponential function of temperature and it is relatively easy to increase the temperature above ambient. However, more recent experimental work has shown that the temperature dependence of the continuum at elevated temperatures is very different from that at atmospheric temperatures [Montgomery, 1978]. Therefore, it is now generally accepted that in order to understand the role of the water vapor continuum in the Earth’s atmosphere, it must be studied at temperatures representative of the atmosphere.

Efforts to increase the optical path length have centered around the multi-pass cell design first proposed by White [1942]. As the water vapor continuum has an absorption coefficient of order $10^{-6}$ cm$^{-1}$ in the thermal infrared window for $T \sim 296$ K, path lengths of order 1 km are needed to provide adequate optical depths. Unfortunately, a number of technical issues specific to infrared
work, such as alignment difficulties, mirror quality and low signal-to-noise ratio, impose a relatively low limit on the practical number of reflections. Consequently, White cells used to measure the room-temperature water vapor continuum tend to be very large, with base paths ranging from 15 m [McCoy et al., 1969] up to 50 m [Arefev et al., 1975]. The size of these White cells makes them expensive and rare, and also poses a difficult problem for experimental control. Thermal gradients and cell flexing are common problems with White cells, which makes it difficult to significantly vary the cell temperature and pressure. Furthermore, in the case of water vapor continuum measurements, one typically has to wait 12 hours or more for the cell humidity to stabilize sufficiently to make a single absorption measurement [McCoy et al., 1969; Peterson et al., 1979; Burch and Alt, 1984]. These issues notwithstanding, White cells have until now represented the primary method of directly measuring the water vapor continuum absorption in the laboratory.

When the values of \( C_s^0 \) derived from all laboratory multi-pass experiments are compared (LMPS+LMPL in Table 2.3), they demonstrate a relative uncertainty of ±14%. However, we have found a dramatic difference in the results when this technique is further subdivided into those made using a broadband source or tunable laser (LMPS) and those using CO\(_2\) lasers as the source (LMPL). In the former category, LMPS, the relative uncertainty is about ±17%, slightly higher than the

average for all multi-pass measurements. By contrast, the standard deviation for the LMPL technique is the lowest of all the measurement techniques, corresponding to a relative uncertainty of ±3%.

We believe there are a number of factors which account for the significant difference in standard deviation of these two experimental approaches. We begin by noting that the radiation must be dispersed when a broadband source is employed. In all but one experiment this was done by imaging a slit onto a diffraction grating. In the other experiment, \( C_s^0 \) was measured using a Fourier transform infrared spectrometer (FTIR), and a Horn-Pimentel multi-pass cell design with a
maximum optical path of 400 m [Kulp and Shinn, 1994]. While the use of a broadband source permits smooth spectral coverage, the power spectral density is much lower than when a CO₂ laser is used, and consequently the signal-to-noise ratio will be much lower as well. In addition to the higher standard deviation we note that the mean and median values of $C_s^0$ are 10% higher for experiments using a broadband source rather than a CO₂ laser. If there is line absorption within the optical bandwidth of the experiment which is not accounted for, then the measured value of the continuum absorption coefficient will be higher than the true value. As the probability of this occurrence should be proportional to the optical bandwidth, we expect it to be a greater problem with grating spectrometer experiments, which typically employ slit widths $\sim 1$ cm$^{-1}$, compared to CO₂ laser experiments where the laser bandwidth is less than the pressure broadened widths of water vapor lines line widths (typically $\sim 0.05 - 0.10$ cm$^{-1}$). Finally, we note that the temporal stability of the broadband source limits the reproducibility of the baseline in grating spectrometers. This is a particular concern in water vapor continuum experiments, because variations in the experimental baseline are easily misinterpreted as continuum absorption. While this effect could increase the standard deviation of the measurements, it is unlikely to produce a systematic bias of 10% in the measurements.

2.7.2.2 Photoacoustic Spectroscopy

The last technique which we consider is photoacoustic spectroscopy (LPAL). In photoacoustic spectroscopy, a laser beam is chopped at an acoustic frequency and injected into a small-volume cell. The absorption due to the gas in the cell causes cyclic local heating at the chopping frequency, which in turn leads to a density wave that is detected with a microphone. Because of the very high sensitivity of microphones, photoacoustic spectroscopy is capable of
detecting weak continuum absorption over optical paths as short as 20 cm. The main advantage of the small-volume cells typical of LPAL is the ease with which experimental parameters such as temperature and pressure may be controlled. However, the LPAL results have the highest relative uncertainty (± 19%), suggesting that this technique may not be very accurate.

In order to obtain absolute absorption coefficients with LPAL, it is necessary to calibrate the signal with a gas that has a known absorption coefficient. In one experiment, the calibration was performed by comparing the absorption coefficient of a water vapor absorption line at the 10R(20) line of the CO$_2$ laser to the value obtained with a White cell in the same laboratory [Peterson et al., 1979]. In the remaining LPAL experiments which we consider, the calibration has been performed with ethylene (C$_2$H$_4$). Ethylene has a strong vibrational band centered at 949.2 cm$^{-1}$ which overlaps the 10P(14) line of the CO$_2$ laser at $\nu = 949.480$ cm$^{-1}$. As the LPAL investigators used C$_2$H$_4$ absorption coefficients which varied from 29.1 - 34.8 cm$^{-1}$ atm$^{-1}$, we wondered whether the lack of agreement in $C_s^0$ values was due to the different calibration absorption coefficients. We tested this possibility by recalibrating the continuum absorption coefficients and recalculating $C_s^0$ and $C_f^0$. The new values, $C_s^0 = 2.16 \pm 0.27 \times 10^{-22}$ cm$^2$ molecule$^{-1}$ atm$^{-1}$ do seem to be more consistent, with a significantly lower standard deviation. However, we believe there are further problems which compromise the accuracy of LPAL results. Concerns with contamination were cited by some of the investigators. This is a possible explanation, as the recalibrated values of $C_s^0$ are also significantly higher than the values obtained using a CO$_2$ laser and multi-pass cell. Other factors have also been cited as concerns, such as synchronous mirror heating, laser beam alignment, and water vapor adsorption on the cell walls.

2.7.3 Summary of Measurement Intercomparison
The results of the intercomparison of continuum coefficients of self-broadening can be summarized as follows. Every experimental technique possesses distinct advantages which should be utilized in order to obtain the most accurate information about the water vapor continuum. Field measurements achieve very long optical paths, and also provide important validation of radiative transfer models. However, they are complicated by a non-uniform optical path and the need to disentangle the contributions to the observed absorption from many atmospheric constituents. Laboratory measurements generally permit better path characterization and offer a higher degree of control over the experimental parameters and gas composition, but are not necessarily more accurate. The highest accuracy (~ 3%) is obtained in the laboratory with a CO₂ laser and a multi-pass cell. However, most CO₂ lasers are only line-tunable over the range 930 - 1080 cm⁻¹, and so broadband sources are still required to give full spectral coverage in the thermal infrared window region. Furthermore, conventional multi-pass cells are very large and lack adequate sensitivity for low-temperature measurements. Finally, while photoacoustic spectroscopy combines high sensitivity with a small-volume cell, it is not a direct absorption technique and may be less accurate than other experimental methods.

Applying the same conventions, we have also performed a measurement intercomparison of the water vapor continuum coefficients of foreign-broadening. While the relative uncertainties are much higher, the general conclusions remain the same. The lowest uncertainties (± 33%) are found for laboratory measurements employing a multi-pass cell and CO₂ laser.

In the next chapter, we demonstrate that a relatively new technique, cavity ringdown spectroscopy, represents the best possible combination of experimental advantages. Cavity ringdown spectroscopy combines the inherent accuracy of a direct absorption technique with high sensitivity, all in a small-volume multi-pass cell.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>$C_1^\circ$ ($\times 10^{22}$) [molecules$^{-1}$ cm$^2$ atm$^{-1}$]</th>
<th>$C_1^\circ$ ($\times 10^{26}$) [molecules$^{-1}$ cm$^2$ atm$^{-1}$]</th>
<th>T [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kulp and Shinn [1994]</td>
<td>LMPS</td>
<td>1.89</td>
<td>-</td>
<td>297</td>
</tr>
<tr>
<td>Thériault et al. [1994]</td>
<td>Field</td>
<td>2.20</td>
<td>-</td>
<td>296</td>
</tr>
<tr>
<td>Fukabori et al. [1992]</td>
<td>Field</td>
<td>2.21</td>
<td>-</td>
<td>296</td>
</tr>
<tr>
<td>Hagan [1988]</td>
<td>Field</td>
<td>2.02</td>
<td>-</td>
<td>293</td>
</tr>
<tr>
<td>Devir et al. [1987]</td>
<td>Field</td>
<td>1.79</td>
<td>-</td>
<td>296</td>
</tr>
<tr>
<td>Hinderling et al. [1987]</td>
<td>LPAL</td>
<td>2.26</td>
<td>0.32</td>
<td>296</td>
</tr>
<tr>
<td>Varanasi and Chudamani [1987]</td>
<td>LMPS</td>
<td>2.13</td>
<td>-</td>
<td>333</td>
</tr>
<tr>
<td>Cutten [1985]</td>
<td>Field</td>
<td>1.31</td>
<td>-</td>
<td>296</td>
</tr>
<tr>
<td>Burch and Alt [1984]</td>
<td>LMPS</td>
<td>1.80</td>
<td>0.32</td>
<td>296</td>
</tr>
<tr>
<td>Aref'ev et al. [1983]</td>
<td>LMPL</td>
<td>1.95</td>
<td>0.80</td>
<td>296</td>
</tr>
<tr>
<td>Loper et al. [1983]</td>
<td>LPAL</td>
<td>2.56</td>
<td>0.47</td>
<td>300</td>
</tr>
<tr>
<td>Ryan et al. [1983; 1984]</td>
<td>LPAL</td>
<td>1.82</td>
<td>0.85</td>
<td>296</td>
</tr>
<tr>
<td>Eng and Mantz [1980]</td>
<td>LMPS</td>
<td>2.24</td>
<td>-</td>
<td>296</td>
</tr>
<tr>
<td>Horton [1979]</td>
<td>Field</td>
<td>1.94</td>
<td>0.31</td>
<td>297</td>
</tr>
<tr>
<td>Peterson et al. [1979]</td>
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<td>0.59</td>
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<tr>
<td>Peterson et al. [1979]</td>
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<td>297</td>
</tr>
<tr>
<td>Nordstrom et al. [1978]</td>
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<td>0.65</td>
<td>296</td>
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<tr>
<td>Aref'ev and Dianov-Klokov [1977]</td>
<td>LMPL</td>
<td>2.01</td>
<td>1.28</td>
<td>296</td>
</tr>
<tr>
<td>Coffey [1977]</td>
<td>Field</td>
<td>1.77</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>Roberts et al. [1976]</td>
<td>LMPS</td>
<td>2.24</td>
<td>-</td>
<td>296</td>
</tr>
<tr>
<td>Shumate et al. [1976]</td>
<td>LPAL</td>
<td>1.58</td>
<td>1.62</td>
<td>300</td>
</tr>
<tr>
<td>Tomasi et al. [1974]</td>
<td>Field</td>
<td>2.78</td>
<td>1.63</td>
<td>303</td>
</tr>
<tr>
<td>Lee [1973]</td>
<td>Field</td>
<td>2.50</td>
<td>2.87</td>
<td>296</td>
</tr>
<tr>
<td>Platt [1972]</td>
<td>Field</td>
<td>2.23</td>
<td>0.51</td>
<td>288</td>
</tr>
<tr>
<td>Bignell [1970]</td>
<td>LMPS</td>
<td>2.96</td>
<td>2.33</td>
<td>303</td>
</tr>
<tr>
<td>McCoy et al. [1969]</td>
<td>LMPL</td>
<td>1.94</td>
<td>1.01</td>
<td>296</td>
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</tbody>
</table>

Table 2.2 - Measurements of the water vapor continuum coefficients of self- and foreign-broadening, for $\nu = 944$ cm$^{-1}$ and $T = 296$ K.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Number of Measurements</th>
<th>Mean</th>
<th>Median</th>
<th>Standard Deviation</th>
<th>Relative Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>26</td>
<td>2.09</td>
<td>2.02</td>
<td>0.35</td>
<td>17</td>
</tr>
<tr>
<td>Field</td>
<td>10</td>
<td>2.08</td>
<td>2.11</td>
<td>0.39</td>
<td>19</td>
</tr>
<tr>
<td>Laboratory</td>
<td>16</td>
<td>2.10</td>
<td>2.02</td>
<td>0.32</td>
<td>15</td>
</tr>
<tr>
<td>LMPS + LMPL</td>
<td>11</td>
<td>2.12</td>
<td>2.02</td>
<td>0.30</td>
<td>14</td>
</tr>
<tr>
<td>LMPS</td>
<td>6</td>
<td>2.21</td>
<td>2.19</td>
<td>0.37</td>
<td>17</td>
</tr>
<tr>
<td>LMPL</td>
<td>5</td>
<td>2.01</td>
<td>2.01</td>
<td>0.07</td>
<td>3</td>
</tr>
<tr>
<td>LPAL</td>
<td>5</td>
<td>2.05</td>
<td>2.02</td>
<td>0.38</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 2.3 - Analysis of $C_s^0$ measurements grouped according to experimental technique. Values of $C_s^0$ are in units of $10^{-22}$ molecule$^{-1}$ cm$^2$ atm$^{-1}$.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Number of Measurements</th>
<th>Mean</th>
<th>Median</th>
<th>Standard Deviation</th>
<th>Relative Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>16</td>
<td>1.02</td>
<td>0.77</td>
<td>0.75</td>
<td>74</td>
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<tr>
<td>Field</td>
<td>5</td>
<td>1.53</td>
<td>1.63</td>
<td>1.12</td>
<td>73</td>
</tr>
<tr>
<td>Laboratory</td>
<td>11</td>
<td>0.79</td>
<td>0.74</td>
<td>0.40</td>
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</tr>
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<td>LMPL</td>
<td>5</td>
<td>0.87</td>
<td>0.80</td>
<td>0.28</td>
<td>33</td>
</tr>
<tr>
<td>LPAL</td>
<td>5</td>
<td>0.80</td>
<td>0.74</td>
<td>0.50</td>
<td>63</td>
</tr>
</tbody>
</table>

Table 2.4 - Analysis of $C_r^0$ measurements grouped according to experimental technique. Values of $C_r^0$ are in units of $10^{-24}$ molecule$^{-1}$ cm$^2$ atm$^{-1}$.
Chapter 3
Experimental

3.1 Introduction

The development and performance of the infrared cavity ringdown experiment is discussed in this chapter. We begin with a review of the principles of cavity ringdown spectroscopy. The design requirements and the construction of the apparatus are discussed in Section 3.3, while the novel methodology for making water vapor continuum absorption measurements is discussed in Section 3.4. Finally, in Section 3.5, we discuss the performance of the experiment. Particular attention is paid to the problem of the long-term drift of time constants, the various hypotheses to explain the drifts, and the operational solution which was eventually adopted.

We first proposed the experiment in March 1995 as a way to make accurate low-temperature measurements of the water vapor continuum in the 10 μm wavelength region. At that time, cavity ringdown spectroscopy (CRDS) was still a very new technique, and no infrared CRDS experiments had been reported. Since then, there have been a few published accounts of infrared CRDS [Scherer et al., 1995; Mürtz et al., 1999; Bucher et al., 2000]. However we are unaware of any published reports of infrared CRDS which are quantitative, despite the potential usefulness of the technique in the infrared region. Although the general principles of CRDS apply to all regions of the spectrum, experimental work in the infrared has proven more difficult for reasons which are discussed in Section 3.2.3.

There was no pre-existing expertise on CRDS at the University of Toronto, nor was there the equipment necessary for us to perform the experiment. Furthermore, we were initially misled by
prevailing misconceptions concerning coherence effects in CRDS experiments. In particular, it had been reported that if short laser pulses were injected into a ringdown cavity (where a "short" pulse is one which is shorter than the time required for the radiation to travel twice the length of the cavity), problems associated with the formation of the cavity mode structure could be avoided (e.g. [Scherer et al., 1995]). For a 1-m long ringdown cavity, this implied that we needed to use a CO$_2$ laser pulse width shorter than ~ 6.7 nsec, which could not be generated from commercial CO$_2$ lasers.

It is possible, in principle, to generate sufficiently short optical pulses using a technique known as cavity-dumping (sometimes also called coupling modulation) [Kiefer et al., 1972]. In cavity-dumping, an electro-optic modulator (EOM) is inserted inside the cavity of a continuous-wave gas laser. When voltage is applied to the EOM, an orthogonally polarized component of the circulating energy is generated that is coupled out of the cavity by reflection from the gas cell Brewster window nearest to the EOM. The magnitude of the orthogonal component is a function of the voltage applied to the electro-optic crystal. When the EOM is operated at the half-wave voltage, the polarization vector of incident light is rotated by 90°, and nearly all of the circulating energy is coupled out of the laser cavity. Electro-optic modulators are very fast devices that can be switched ON/OFF in the time that it takes light to travel the return trip inside a typical CO$_2$ laser cavity. Thus, cavity-dumping is capable of producing the short optical pulses that we thought would be required to perform CRDS.

However, Lehmann and Romanini [1996] presented an analysis based on linear systems theory which demonstrated that short pulses were not necessary in a CRDS experiment (cf. Section 3.2). Since we had already purchased the CO$_2$ laser and EOM, we positioned the EOM in the output beam of the laser so that in combination with a polarization analyzer, it formed an amplitude modulator. This gave us control over the depth of modulation and the pulse width, and we attempted
to perform CRDS this way. By 1999, after a great deal of work and analysis, it was apparent that the presence of after-pulse “ringing” in the EOM (illustrated in the bottom panel of Fig. 3.12) corrupted our ringdown signals and made it impossible for us to make meaningful measurements with our CRDS experiment. We overcame this challenge by using an acousto-optic modulator (AOM) instead. Thus, the quantitative infrared CRDS experiment which is discussed below is based on the use of an AOM to generate well-defined CO₂ laser pulses.

3.2 Quantitative CRDS

We begin this section by discussing the spatial and spectral properties of optical cavity modes and their role in a CRDS experiment. Then, we discuss the principles and the advantages of making infrared absorption measurements using single-mode CRDS. Finally, we discuss some issues which are particularly relevant to infrared work.

3.2.1 Principles of CRDS

Introduced in 1988 [O'Keefe and Deacon, 1988], CRDS has developed into a powerful technique for the quantitative measurement of weak gas absorption [Romanini and Lehmann, 1993; Zalicki and Zare, 1995; Jongma et al., 1995; Hodges et al., 1996; Lehmann and Romanini, 1996; Looney et al., 1999; van Zee et al., 1999]. In the most general sense, CRDS is a technique in which a laser pulse is injected into a high-finesse, stable optical cavity (the ringdown cavity) via the transmission loss of the front mirror, and the time evolution of the energy circulating inside the ringdown cavity is observed through the transmission loss of the back mirror (Fig. 3.1). An important variation of the technique is single-mode CRDS, in which a single optical mode of the ringdown cavity is excited. It will be shown that single mode CRDS is characterized by high sensitivity to
Figure 3.1 - Conceptual model of CRDS. The ringdown cavity is formed by two concave, high reflectivity mirrors spaced a distance $L$. The front mirror is taken to be the one upon which the laser pulse is initially incident. The time evolution of the radiation which is injected into the ringdown cavity is sensed via the transmission loss of the back mirror.
weak absorption as well as high spectral resolution. Although independently developed, many of the principles behind our single mode CRDS experiment are similar to those recently reported by van Zee et al. [1999].

3.2.1.1 Optical Modes

In CRDS, stable optical cavities are normally formed through the use of concave, spherical mirrors which satisfy the criterion [Yariv, 1975]:

\[
0 \leq \left( 1 - \frac{L}{r_1} \right) \left( 1 - \frac{L}{r_2} \right) \leq 1
\]

(3.1)

where \( r_1 \) and \( r_2 \) are the radii of curvature of the mirrors, and \( L \) is the mirror separation. The stability criterion is illustrated in Fig. 3.2. Often, such optical cavities are referred to as open cavities or open resonators, because the sides are open. The EM field inside an open spherical cavity is known (e.g. [Boyd and Gordon, 1961]), and we do not derive the solutions in this thesis. For our purposes, it is sufficient to note that self-reproducing stable field patterns, called optical modes, exist inside a ringdown cavity. Simply put, these eigenmodes are configurations of the EM field which satisfy Maxwell’s equations for the boundary conditions imposed by the mirrors.

The cavity eigenmodes are transverse electro-magnetic (TEM) modes, which to good approximations are given by the product of Hermite and Gaussian functions when Cartesian coordinates are used. The transverse mode orders in the \( x \)- and \( y \)-directions are identified by the positive integers \( m \) and \( n \), respectively. The modes are often referred to as “TEM\(_{mn}\)” modes so that the lowest-order transverse mode is the TEM\(_{00}\) mode, followed by the TEM\(_{01}\) mode, etc. The scalar electric field amplitude \( E_{mn}(x,y,z) \) describing the transverse profile of the propagating Gaussian beam can be written as [Yariv, 1975]:

-80-

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Figure 3.2 - The stability diagram for a two-mirror optical cavity. The shaded areas of the graph are the stable regions, where the mirrors correspond to a stable periodic focusing system. Adapted from Siegman (1986).
\[ E_{mn} = E_0 \frac{w_0}{w(z)} H_m \left( \sqrt{2} \frac{x}{w(z)} \right) H_n \left( \sqrt{2} \frac{y}{w(z)} \right) \exp \left( -\frac{x^2 + y^2}{w(z)} - \frac{k(x^2 + y^2)}{2R_f(z)} \right) \exp(-i\theta) \]  (3.2)

where \( w(z) \) is the beam width at \( z \), \( w_0 \) is the beam waist (a local minimum of the beam width), \( E_0 \) is the electric field amplitude at the beam waist, \( H_m \) is the Hermite polynomial of order \( m \), and \( R_f(z) \) is the radius of curvature of the phase fronts. The beam waist is determined by the cavity geometry [Yariv, 1975]:

\[ w_0 = \sqrt{\frac{\lambda z_0}{\pi n_0}} \]  (3.3)

where \( n_0 \) is the index of refraction of the medium and \( z_0 \) is known as the confocal length. For a symmetrical mirror cavity (i.e. \( r_1 = r_2 = r \)):

\[ z_0 = \sqrt{\frac{(2r - L)L}{4}} \]  (3.4)

where \( r \) is the radius of curvature of the mirrors and \( L \) is the cavity length. Finally, we note that a Gaussian beam will expand from the beam waist (where \( z = 0 \)) according to:

\[ w(z) = w_0 \sqrt{1 + \left( \frac{\lambda z}{\pi w_0^2 n_0} \right)^2} \]  (3.5)

where \( w_0 \) is given by Eq. (3.3) and \( \lambda \) is the wavelength. Thus, the beam width of an ideal propagating Gaussian beam is defined by the beam waist and the wavelength.

In Fig. 3.3, we illustrate how the Gaussian intensity distribution of the TEM\(_{00}\) mode varies along the \( z \)-axis of a 1-m long ringdown cavity. It is also interesting to see how the intensity distributions differ for higher-order modes. The intensity distributions at the mirrors for a few low-order TEM modes of our cavity are shown in Fig. 3.4.

We now turn our attention to the corresponding eigenfrequencies. In Eq. (3.2), \( \theta \) is a phase
shift given by:

\[
\theta(z) = kz - (m + n + 1) \arctan\left(\frac{z}{z_0}\right). 
\]  

(3.6)

The eigenfrequencies of the optical cavity are determined by the requirement that the phase shift from one mirror to the other is a multiple of \(\pi\). For a symmetrical cavity with mirrors at \(z = \pm L/2\), the resonance requirement is:

\[
\theta(z = +L/2) - \theta(z = -L/2) = q\pi 
\]

(3.7)

where \(q\) is a (large) positive integer denoting the axial (sometimes called longitudinal) mode index.

After substituting Eq. (3.6) into Eq. (3.7), we obtain with some algebraic manipulation the solution for the eigenfrequencies:

\[
f_{mnq} = \frac{c}{2n_0 L} \left[ q + \frac{2}{\pi} (m + n + 1) \arctan\left(\sqrt{\frac{L}{2r - L}}\right) \right] 
\]

(3.8)

where \(f_{mnq}\) is the resonant frequency (in Hz) of the TEM\(_{mnq}\) mode.

The free spectral range (FSR) is the frequency spacing between the axial cavity modes (i.e. \(\Delta q = 1\)). From Eq. (3.8), we see that the FSR is \(\Delta f_q = c/(2n_0 L)\). As an example, a 1.025-m long cavity will have a FSR of \(\Delta f_q = 146.3\) MHz when the cavity is evacuated. The mode spacing will change slightly when the cavity medium is air rather than a vacuum; however, that is not important to this discussion. Meanwhile, we see from Eq. (3.8) that the transverse mode spacing \(\Delta f_{mn}\) depends on the cavity geometry. Consider a typical cavity with the parameters \(L = 1.0\) m and \(r = 1.5\) m. For such a cavity we calculate a transverse mode spacing of \(\Delta f_{mn} = 58.8\) MHz. This means that the TEM\(_{01q}\) mode is separated from TEM\(_{00q}\) by +58.8 MHz, TEM\(_{02q}\) is +58.8 MHz from TEM\(_{01q}\), and +117.6 MHz from TEM\(_{00q}\), etc. The spectrum of cavity modes for this example is depicted in Fig. 3.5.
Figure 3.3 - Intensity distribution of the TEM$_{00}$ mode along the optical axis (z-axis) of a 1-m long ringdown cavity with mirrors at $z = \pm 500$ mm. The beam width is largest at the mirrors ($w = 1.8$ mm) and smallest in the center of the cavity, where the beam waist is $w_0 = 1.3$ mm. Meanwhile, the peak intensity is highest in the center of the cavity. Note that the axes are not drawn to the same scale.
Figure 3.4 - The intensity distributions of some low-order transverse electro-magnetic (TEM) modes. The horizontal axis is the x-axis, while the vertical axis is the y-axis, in units of mm. The spatial dimensions are calculated at the mirrors of a 1-m long cavity for $\lambda = 10.6 \, \mu m$ radiation.
Figure 3.5 - Spectrum of modes for a typical optical cavity, having the parameters $L = 1.0$ m and $r = 1.5$ m. Frequencies are relative to the $\text{TEM}_{00q}$ mode. Amplitudes are shown to decrease with mode order for greater clarity and also because the finite spatial cross-section of a given incident laser beam will result in a lesser degree of excitation for high-order modes (c.f. Section 3.3.5).
Several modes may be excited simultaneously in a ringdown cavity, depending on the bandwidth and spatial dimensions of the incident laser pulse. A typical situation is illustrated in Fig. 3.5, where several higher-order modes are excited to lesser and lesser degrees because of the finite spatial cross-section of the incident laser pulse. The excitation of several modes at once is highly undesirable in quantitative CRDS because the energy in different cavity modes may not decay at the same rate. Additionally, the ringdown decay signal (a typical ringdown decay signal is shown in Fig. 4.2) may be modulated by beat frequencies between modes, complicating the determination of the decay rate. In order to minimize the transmission peak amplitude of higher-order modes, the incident laser beam is \textit{mode-matched} to the TEM$_{00}$ mode of the ringdown cavity. A practical description of the optical technique of mode-matching is discussed separately in Section 3.4.1.

Once the incident laser beam is mode-matched to the ringdown cavity, a single cavity mode may be exclusively excited if the excitation optical bandwidth is less than the FSR of the ringdown cavity. The excitation of a single cavity mode is presented in Fig. 3.6. In the top panel, we depict the situation where the bandwidth (determined by the Fourier transform of the pulse in the time domain) of a 2-nsec Gaussian laser pulse is broader than the FSR of the ringdown cavity, resulting in the excitation of several cavity modes. In the bottom panel, we have plotted the bandwidth of a 5-μsec long laser pulse, which is sufficiently narrow that a single cavity mode may be excited. As we have shown it, the laser bandwidth does not overlap a ringdown cavity mode. However, the relative resonant frequency between the laser and ringdown cavity may be adjusted so that the laser bandwidth overlaps a single mode of the ringdown cavity. This is the basis for single-mode CRDS.

Finally, we note that the transmission peaks of the ringdown cavity are not actually delta functions. Rather, the transmission of a Fabry-Perot interferometer or a ringdown cavity is given by the Airy function [Born and Wolf, 1980]:

\begin{equation}
\text{Airy function}
\end{equation}
Figure 3.6 - Laser bandwidth and single-mode CRDS. In both panels, the comb-like series of transmission peaks corresponds to the longitudinal modes of a 1-m long ringdown cavity. In the top panel, the large bandwidth of a 2-nsec long Gaussian laser pulse overlaps several longitudinal modes of the ringdown cavity. In the bottom panel, the narrow laser bandwidth (indicated by the arrow) corresponds to a 5-μsec long laser pulse. By adjusting the relative resonant frequency between the laser and the ringdown cavity, the laser bandwidth can be tuned to overlap a single ringdown cavity transmission peak.
\[ \frac{I}{I_0} = \frac{1}{1 + F \sin^2 \frac{\delta}{2}} \]  

(3.9)

where \( \delta = 2\pi(\Delta f/\Delta f_0) \) is the phase shift of the detuning \( \Delta f \) from resonance, and \( F = 4R/(1 - R)^2 \). The full width at half-maximum (FWHM) of the transmission peaks is given by:

\[ \Delta f_{FWHM} = \frac{c (1 - R)}{2\pi n_0 L \sqrt{R}} \]  

(3.10)

where \( L \) is the cavity length, \( R \) is the mirror reflectivity, and \( c \) is the speed of light. For a 1-m long cavity with mirror reflectivity \( R = 0.995 \), \( \Delta f_{FWHM} = 240 \text{ kHz} \). Thus, it is possible to make absorption measurements with a very high spectral resolution using single-mode CRDS.

### 3.2.1.2 Absorption Measurement in CRDS

Consider a laser pulse that has been coupled into the fundamental (i.e. TEM\(_{00}\)) mode of the ringdown cavity. The modal energy in the cavity slowly decays until it has completely dissipated, through the imperfect reflectance of the mirrors and the scattering and/or absorption due to the gas between the mirrors. Taking \( I_0 \) to be the initial intensity of radiation at the output of the ringdown cavity following the injection of a laser pulse, we find that for an unsaturated medium:

\[ I(v, t) = I_0(v) \exp[-t/\tau(v)] \]  

(3.11)

where \( \tau(v) \) is the decay time constant. In general, the decay constant \( \tau \) is a function of the wavenumber \( v \) of the radiation. Eq. (3.11) can be related to the Beer-Lambert law, Eq. (2.4), through the speed of light, \( c \).

Originally, CRDS was seen as a way to make sensitive absorption measurements using pulsed lasers, because the decay time constant would be insensitive to pulse-to-pulse amplitude fluctuations. However, the analysis of Lehmann and Romanini which we referred to at the beginning
of this chapter is based on linear systems theory and demonstrates that a short pulse is not required to perform CRDS; it is only necessary that the fall time of the laser pulse is short compared to the decay time constant of the ringdown cavity. This realization opened up CRDS to the use of continuous-wave (cw) lasers switched with acousto-optic or electro-optic modulators. This is highly advantageous, as the narrow bandwidths typical of cw laser systems permit efficient excitation of a single mode of the ringdown cavity.

In single-mode CRDS, the decay time constant is a function of the cavity losses. The cavity losses can be split into three terms. One loss term represents the cavity loss per pass due to the mirrors and is equal to \((1-R(V))\), where \(R(V)\) is taken to be the effective reflectivity of the mirrors. Two additional loss terms are needed when a gas is present in the ringdown cavity. The term \(k(V)\cdot L\) describes the loss per pass due to the absorption of the gas, while \(k_{bg}(V)\cdot L\) represents any other loss mechanism associated with the medium (e.g. Rayleigh scattering or trace gas contamination). Combining these terms gives the following equation for the decay time constant:

\[
\tau(V) = \frac{L}{c[(1 - R(V)) + k_{bg}(V)\cdot L + k(V)\cdot L]}
\]

where \(L\) is the ringdown cavity mirror separation and \(c\) is the speed of light.

Because of the continuous nature of the water vapor continuum absorption, it is not possible to detune the experiment from an absorption peak in order to obtain the empty-cell decay constant (i.e. \(k_c(V) \neq 0\), for any \(V\)). Therefore, we have developed a novel experimental approach to CRDS, which consists of a nitrogen flow experiment where we control the amount of water vapor in the flow from zero to near saturation. Since the water vapor accounts for a small fraction of the total gas pressure (0-2%, at room temperature), we make the assumption that any background loss associated with the medium is taken into account in the dry nitrogen flow. In other words, the dry flow decay
constant $\tau_0$ is given by:

$$
\tau_0(v) = \frac{L}{c[(1 - R) + k_{bg}(v)L]}.
$$

(3.13)

From consideration of Eq. (3.12) and (3.13), we obtain the following simple expression for the absorption coefficient:

$$
k(v) = \frac{\tau_0(v) - \tau(v)}{c\tau_0(v)\tau(v)}.
$$

(3.14)

It is apparent from Eq. (3.14) that the absorption coefficient $k$ is directly determined from measurements of the decay constant alone, and in particular does not require separate measurements of the length of the ringdown cavity and the effective reflectivity of the mirrors.

We now consider the high sensitivity to weak absorption that is possible using single-mode CRDS. By differentiating and rearranging Eq. (3.12), we obtain the following expression for the minimum detectable absorption coefficient $k_{\text{min}}$:

$$
k_{\text{min}} = \frac{\sigma_\tau}{\tau} \times \frac{1}{L} \times [(1 - R) + k_{bg}L + kL].
$$

(3.15)

In the limit of small losses due to the presence of a medium (i.e. $k_{bg}$ and $k \to 0$), Eq. (3.15) reduces to:

$$
k_{\text{min}} = \frac{\sigma_\tau}{\tau} \times \frac{1}{L} \times (1 - R)
$$

(3.16)

where $\sigma_\tau$, the noise in the decay time constants, is the minimum resolvable change in the decay constant. For a 100-cm long cavity with mirrors of reflectivity $R = 0.995$ and assuming $\sigma_\tau/\tau = 0.002$, we obtain $k_{\text{min}} = 10^{-7}$ cm$^{-1}$. Thus, infrared CRDS has greater sensitivity to weak absorption than practical White cell experiments, which tend to have a sensitivity limit of $k_{\text{min}} \sim 10^{-6}$ cm$^{-1}$ [Lehmann
and Romanini, 1994]. Our present sensitivity of $k_{\text{min}} = 10^{-7}$ cm$^{-1}$ is comparable to real detection limits that have been reported for infrared photoacoustic spectroscopy experiments [Loper et al., 1983; Hinderling et al., 1987].

3.2.2 Advantages of CRDS

For our application, CRDS has distinct advantages over conventional spectroscopic techniques. In particular, CRDS provides a direct measure of the absorption coefficient in terms of observed ring-down times, and can be realized with high sensitivity using relatively small sample volumes. Recent work in the near-infrared region with mirrors of reflectivity $R > 0.9999$ has confirmed that CRDS is very sensitive to weak absorption, with a noise-equivalent absorption coefficient of $5 \times 10^{-10}$ cm$^{-1}$ for a 1-second measurement [van Zee et al., 1999]. Our results demonstrate that high sensitivity is also possible in the thermal infrared region of the spectrum with mirrors of more modest reflectivity.

The impressive sensitivity of CRDS is achieved through accurate measurement of the decay time constant, rather than measurement of transmission. To first order, the decay time constant is insensitive to pulse-to-pulse laser intensity fluctuations, which limit the sensitivity of conventional laser spectroscopy. Furthermore, CRDS combines high sensitivity with a compact volume cell design. For instance, our ringdown cavity has a gas volume of 6 liters and an effective path length of 720 m. The compact volume of a CRDS cell greatly facilitates gas handling and control compared to White cells, which tend to be very large (15-50 m long with gas volumes of 4000 - 40000 liters) in experiments to measure the water vapor continuum. Finally, we note that unlike photoacoustic spectroscopy, which is also a compact, highly-sensitive spectroscopic technique, CRDS directly measures the absorption coefficient and requires no signal calibration.
3.2.3 Infrared CRDS

There are a number of issues particular to infrared work which have to be considered in a CRDS experiment. These include optical alignment and mode matching, mirror quality, and detector nonlinearity. Below we briefly discuss the significance of these issues.

3.2.3.1 Optical Alignment and Mode Matching

Because the infrared laser beam cannot be seen, the use of a visible laser is necessary in order to align the optics. Generally, this is not a serious problem, although we note that it is only possible to do a rough alignment of the ringdown cavity mirrors using the visible laser beam. Another problem arises because measurements of the laser beam profile are necessary in order to do mode-matching (cf. Section 3.4.1). However, infrared beam profilers tend to be costly and not easily available. In Section 3.4.1 we discuss our attempts at infrared beam characterization.

3.2.3.2 Mirror Reflectivity

While mirrors of reflectivity \( R \approx 0.9999 \) are now regularly used in CRDS experiments in the visible region, infrared mirror technology is not as advanced. At \( \nu = 944 \, \text{cm}^{-1} \), standard high-reflectivity mirrors have \( R = 0.995 \). The relatively low reflectivity of the infrared mirrors ultimately limits the performance of an infrared CRDS experiment, because the sensitivity to absorption depends on the factor \((1 - R)\), as we have demonstrated in Eq. (3.15). Additionally, the low reflectivity of the infrared mirrors leads to relatively low decay time constants. For example, \( \tau_0 = 0.66 \, \mu\text{sec} \) for a 1-m long ringdown cavity with \( R = 0.995 \) mirrors. However, the same cavity with high-quality visible mirrors of \( R = 0.9999 \) would have a decay constant of 33 \( \mu\text{sec} \). Because a given digitizer will generate more samples over a longer decay event than it will over a shorter decay event, a longer
decay time constant can be determined with greater precision. Thus, mirror reflectivity is a very important factor in the sensitivity of CRDS. Another issue which must be appreciated in infrared CRDS work is that the mirrors are relatively expensive, and the substrate material (typically ZnSe) is soft and prone to scratches.

### 3.2.3.3 Detector Nonlinearity

We note from Eq. (3.10) that one seeks to measure an exponential signal in CRDS. Thus, it is important that the detector have a linear signal response over a wide range of signal levels. For infrared radiation in the 5 - 20 μm region, the most suitable detector is the liquid-nitrogen (LN₂) cooled HgCdTe detector. This is a photon detector which can be designed to operate based on the photoconductive (PC) or photovoltaic (PV) effects. Briefly, a PC HgCdTe detector is a low-impedance device in which incident infrared photons are absorbed, producing free charge carriers that change the electrical conductivity of the detector element. The output signals of these detectors are inherently nonlinear for all signal levels [Griffiths, 1986] and particularly at high signal levels, and so we do not recommend their use for quantitative CRDS. In our experiment, we use a PV HgCdTe detector. The PV HgCdTe detector is built as a p-n semiconductor junction. Infrared photons which are absorbed near the junction are separated by the junction, producing electron-hole pairs whose flow constitutes an external electrical current. Thus, the PV HgCdTe detector is considered to be a linear device in the sense that the current is proportional to number of incident infrared photons. However, we have found that the power response of our detector becomes nonlinear at high signal levels. The problem of detector linearity is discussed further in Section 3.5.2.
3.3 Apparatus

In this section, we describe in detail the apparatus used in the experiment, beginning with an overview of the experiment (Section 3.3.1). The major components include the ringdown cavity (Section 3.3.2), the CO$_2$ laser (Section 3.3.3), the acousto-optic modulator (Section 3.3.4), and the infrared detector and data acquisition system (Section 3.3.5). In Section 3.3.6 we discuss various ancillary instrumentation including pressure, temperature, and humidity sensors.

3.3.1 Overview

The layout of the experiment is depicted schematically in Fig. 3.7. First, we discuss the optical components, then we discuss the gas handling components. The cw CO$_2$ laser is shown in the upper right hand side of Fig. 3.7, with an infrared beam (indicated as heavy arrows) generally propagating in a counter-clockwise direction around the schematic. At the output of the laser, a portion of the laser beam is diverted to a power meter and a diffraction grating spectrum analyzer via two beam-splitters. The function of the spectrum analyzer is to measure the frequency of the laser radiation. The remainder of the beam is then attenuated, because the CO$_2$ laser generates more optical power than is necessary for the CRDS experiment. We use a polarizer-analyzer-attenuator (PAA) to provide continuously variable attenuation of the horizontally-polarized CO$_2$ laser beam. The PAA consists of 6 ZnSe plates (i.e. 12 surfaces) oriented at Brewster's angle ($\theta_B = 67.4^\circ$ at $\lambda = 10.6 \mu$m) to the laser beam and rotatable about the axis of the beam. From Fresnel's equations [Born and Wolf, 1980], we find that each surface transmits 50.3% of light that is polarized perpendicular to the plane of incidence. Therefore, the PAA has a theoretical maximum extinction ratio of about 3700:1.

The laser beam is then directed at the acousto-optic modulator (AOM), which is used to form
Figure 3.7 - Infrared cavity ringdown spectroscopy experiment.
pulses from the cw laser beam. A well-defined electronic pulse is used to switch the modulator radio-frequency (rf) power on and off, so that the first-order diffracted beam exiting the AOM is also a well-defined optical pulse having a 10-90% rise/fall time of ~ 500 nsec. The optical pulses exiting the AOM are then reflected by beam-steering mirrors toward the ringdown cavity. Before entering the ringdown cavity, the optical pulses are shaped with a mode-matching lens so that the laser pulse energy is efficiently coupled into the TEM$^{00}$ mode of the ringdown cavity. An infrared detector at the output of the ringdown cavity measures the decay of energy leaking out of the ringdown cavity. The signal from the detector is digitized and stored for later analysis. As the infrared pulses cannot be seen, we use a visible HeNe laser for alignment purposes. The visible laser is reflected into the infrared beam path using a dichroic optical flat (not shown in Fig. 3.7), and carefully aligned so that it is coaxial with the infrared beam.

Because of the continuous nature of the water vapor continuum absorption spectrum, our CRDS experiments are conducted in a novel way. We have developed a gas flow experiment in which we are able to control the humidity in the flow from zero to near-saturation. A cylinder of nitrogen provides the dry gas supply, which is humidified by diverting a portion of the flow over a vessel of distilled water. Needle valves in the "dry" and "wet" flow paths are used to control the amount of humidity in the recombined flow which enters the ringdown cavity. A total of seven inlet gas ports along the length of the ringdown cavity ensure that the gas in the ringdown cavity is well-mixed. Inside the ringdown cavity, the pressure is measured with a capacitance manometer, temperature with thermocouple sensors, and humidity with a chilled mirror dewpoint sensor. The gas flow through the ringdown cavity is exhausted to the laboratory via an outlet port located in the center of the ringdown cavity. Accurate measurements of the water vapor continuum absorption coefficients are obtained from the differences in the decay time constants for dry and humid flows.
More details on the experimental methodology can be found in Section 3.4.

3.3.2 Ringdown Cavity

The heart of a CRDS experiment is the ringdown cavity. A ringdown cavity serves as the gas cell of the experiment, and also acts as a stable optical cavity capable of long optical path lengths in a compact volume. We now discuss the practical requirements and design of our ringdown cavity.

3.3.2.1 Practical Requirements

The practical requirements for the ringdown cavity can be grouped into four categories: dimensions, optical, mechanical and gas-handling requirements. These are discussed separately in the subsections below.

3.3.2.1.1 Optimal Dimensions

We note from Eq. (3.16) that the sensitivity of CRDS experiments to weak absorption is directly related to the length of the optical cavity. For example, a 2-m long cavity has twice the sensitivity to weak absorption of a 1-m long cavity. For this reason, it is desirable to have as long a ringdown cavity as possible. The practical limitation is usually determined by the length of the optical table, which is often 2.4 or 3.0 m. While the length should be as long as possible, the cross-sectional area of a ringdown cavity is relatively unimportant, provided that it is large enough to accommodate the ringdown cavity mirrors. These mirrors are usually laser mirrors with diameters in the range 1.2 - 2.5 cm. Thus, ringdown cavities may have very small cross-sections.

3.3.2.1.2 Optical
A ringdown cavity must be a stable optical cavity, as defined by Eq. (3.1). However, there is a wide range of possibilities for cavity geometry satisfying the stability requirement (cf. Fig. 3.2). Restricting ourselves to symmetrical cavities, stable cavity geometries range from concentric ($r = L/2$), to confocal ($r = L$), to planar ($r = \infty$). Near-planar cavities are difficult to align properly, because the centers of curvature of the mirrors are far out beyond the ends of the resonators [Siegman, 1986]. Near-concentric cavities are also difficult to align because in this configuration, the centers of curvature of the mirrors are very close to one another and so large optical axis misalignments arise from small mirror misalignments. However, near-confocal cavities are relatively insensitive to misalignment, because a small mirror tilt still leaves the center of curvature on the other mirror surface. In choosing the cavity geometry, we note it is undesirable in a quantitative CRDS experiment to have the ringdown cavity exactly confocal, as any higher-order TEM modes which were excited would overlap in the spectrum (with even-orders at the TEM$_{00}$ frequencies and odd-orders at the TEM$_{01}$ frequencies), making it more difficult to discern their presence or prevent their excitation. We also caution that care must be taken with near-confocal cavities when the radii of curvature of the mirrors are not identical (i.e. $r_1 \neq r_2$), because the cavity will be unstable for $r_{\text{min}} < L < r_{\text{max}}$, as can be seen from Eq. (3.1). Nevertheless, we conclude that a near-confocal cavity is probably the best choice for our experiment, because it is desirable to make infrared alignment as easy as possible.

3.3.2.1.3 Mechanical

It is very important that the decay time constant not change significantly over the course of the experiment as a result of mechanical instability of the ringdown cavity. This is especially important when measuring broadband absorption like the water vapor continuum, where it is not
possible to obtain the experimental baseline by tuning away from an absorption peak. The problem of accurately measuring the experimental baseline in a water vapor continuum experiment is a difficult task, regardless of spectroscopic technique. In our case, the experimental baseline must be obtained by removing the water vapor from the cell and measuring the dry-cell decay constant. If there are significant temporal variations in the cavity alignment, or if misalignment is induced by the action of removing the water vapor, then it will not be possible to accurately measure the experimental baseline. For example, we estimate from Eq. (3.16) that in order to measure an absorption coefficient $k_c = 10^6 \text{ cm}^{-1}$ to an accuracy of 10% in a 1-m long ringdown cavity with $R = 0.995$ mirrors, the uncertainty in the decay constant must be $\sigma_\tau \leq 1.3 \text{ nsec}$, for $\tau = 660 \text{ nsec}$.

The procedures for building stable ringdown cavities are generally the same as for building stable Fabry-Perot etalons, and follow well-established principles. For example, the ringdown cavity length should be fixed with a low-thermal expansion spacer material and the mirror mounts themselves should be firmly mounted to the cavity spacer assembly (yet still capable of mirror tilt adjustments). Changes to the mirror alignment may also arise from pressure changes inside the cell if the ringdown cavity mirrors are used as cell windows, which is a common design. In our system the ringdown cavity is kinematically mounted inside a gas cell with separate entrance/exit windows. In addition to these considerations, it is also necessary to be able to make fine adjustments of the mirror separation, because the narrow optical bandwidth of our laser will generally not overlap a ringdown cavity mode. A standard way of doing this is by mounting one of the mirrors onto a piezoelectric transducer (PZT).

### 3.3.2.1.4 Gas Handling

In a general sense, the gas handling requirement for the ringdown cavity is to have controlled
amounts of water vapor inside the cell, ranging from zero to near-saturation. Thus, input and output
gas ports are required, along with sensors for monitoring temperature, pressure and humidity within
the cell, and external gas handling equipment. Additionally, our experiment requires that the action
of adding or removing water vapor from the cell does not compromise the mechanical stability of
the ringdown cavity.

3.3.2.2 Design

A cross-section schematic of our ringdown cavity design is shown in Fig. 3.8 (some of the
smaller parts of the ringdown cavity assembly have been omitted for clarity). The ringdown cavity
assembly is mounted inside the gas cell on a 3-point kinematic mount. The gas cell is constructed
from a 110-cm long and 10-cm diameter tube of electropolished stainless steel which has a wall
thickness of 3 mm. The ends of the cell are sealed with ConFlat flanges and viton gaskets. ZnSe
windows (which are wedged and antireflection-coated) are mounted on the flanges to permit infrared
radiation to enter and exit the gas cell. A total of six gas inlet ports are distributed along the length
of the gas cell in the vertical plane, with a single outlet port in the horizontal plane allowing gas to
flow over the dewpoint sensor before exhausting into the laboratory. The gas cell rests on two
brackets which are mounted on lab jacks (not shown in Fig. 3.8). Thus, during the alignment stage
of the experiment, the two ends of the ringdown gas cell may be moved in all directions before the
cell is locked down to the optical table.

Inside the gas cell, three 1.6-cm diameter rods of Zerodur, which is a commercially-available
low thermal-expansion ceramic ($\alpha = 0.00 \pm 0.02 \times 10^{-6}/K$, over the range 0 - 50 °C), are used to fix
the cavity length at $L = 102.5$ cm. The Zerodur rods are mounted onto two spacer end caps which
are machined from stainless steel. Grooves machined on the bottom surfaces of the spacer end caps

-101-
Figure 3.8 - Cross-section schematic diagram of the ringdown cavity. The cavity spacer end-pieces and mirror mounts are made from stainless steel, while the spacers are made from zero-expansion Zerodur. The entire cavity-spacer assembly rests on a 3-point kinematic base at the bottom of the cell. For clarity, the retaining leaf springs for the mirror mounts have been omitted. Diagram is not drawn to scale.
permit the entire ringdown cavity assembly to rest on the kinematic mounts at the bottom of the gas cell. The stainless steel mirror mounts are mounted to the spacer end caps with phosphor bronze leaf springs. In addition, coil springs are used to increase the rigidity of the mirror mounts against the cavity end spacers. Teflon inserts are used in the mirror mounts to protect the mirrors from damage. Horizontal and vertical tilt adjustments of the mirror mounts are made with precision alignment screws. One of the mirrors is first mounted on a PZT, which itself is mounted onto the mirror mount. The PZT permits fine adjustments of the cavity length up to about 6 μm. The range of displacement of the PZT is sufficient for the cavity to be scanned over one free spectral range for infrared wavelengths near 10 μm.

The ringdown cavity mirrors are 2.54 cm in diameter and have reflectivity \( R = 0.995 \) and radii of curvature \( r = 1.0 \) m. Thus, the ringdown cavity is a near-confocal geometry, with a beam waist of 1.3 mm at the center of the cavity and beam widths of 1.8 mm at the mirrors.

### 3.3.3 CO₂ Laser

In this section, we describe the principles of operation and the performance of the Ultra Lasertech model number 5822 CO₂ laser we have employed in this experiment.

#### 3.3.3.1 Principles of Operation

The CO₂ laser we have used in this experiment is a cw laser with an output beam polarized in the horizontal direction, because of the orientation of the Brewster windows of the gas tube. The output wavenumber of the laser is line-tunable from 920 - 1090 cm\(^{-1}\), and the normal operating wavenumber is 944.195 cm\(^{-1}\). The total reflector is a diffraction grating on a gimbal mount, permitting the laser frequency to be adjusted by rotating the grating in the horizontal plane. The
Figure 3.9 - Transitions of the CO$_2$ laser and their approximate output powers. Note that because the (100) and (020) bands of CO$_2$ are almost exactly 50/50 mixed by Fermi resonance, the lower state of the laser bands cannot be unambiguously assigned.
output frequency of the laser is measured by a CO$_2$ laser spectrum analyzer, which is a reflection grating spectrometer that images the slit onto a thermal imaging plate with a calibrated frequency scale. The CO$_2$ laser transitions and their approximate output power levels are shown in Fig. 3.9. The state of the CO$_2$ molecule is denoted by $(v_1,v_2,v_3)$, where $v_1$ is the symmetric stretch vibrational quantum number, $v_2$ is the symmetric bend quantum number, and $v_3$ is the asymmetric stretch quantum number.

The CO$_2$ laser is a sealed-tube laser with a CO$_2$ - N$_2$ - He gas mixture at a low total pressure. The gain medium is excited into a plasma by the application of a high-voltage (~10 kV), low-current (~6 mA) DC discharge. The presence of nitrogen in the gas discharge is very important to the high efficiency of CO$_2$ lasers (the efficiency, defined as the ratio of output optical power over input electrical power, is typically greater than 10% for CO$_2$ lasers). Nitrogen molecules are excited from the ground state to the $v = 1$ level by electron impact from the discharge. Because the excitation energy is nearly the same for the $v = 1$ level of the N$_2$ molecule and the (001) level of the CO$_2$ molecule, collisional transfer of vibrational energy from N$_2$ ($v = 1$) to ground state CO$_2$ molecules is particularly efficient. The CO$_2$ molecule may then emit radiation in the 9.6 and 10.6 µm regions by radiatively decaying either to the (100) or the (020) band. However, because these bands are almost exactly 50/50 mixed by Fermi resonance [Herzberg, 1945], the lower state of the laser bands cannot be unambiguously assigned. Finally, the role of helium in the discharge is to accelerate the de-excitation of CO$_2$ molecules in the (010) level, where a “bottleneck” is formed.

3.3.3.2 Performance

The CO$_2$ laser has several desirable properties for its use in a CRDS experiment. The CO$_2$ laser has excellent spectral purity with a short-term (order seconds) optical bandwidth $\leq$ 250 kHz.
Figure 3.10 - Three-dimensional intensity map of the laser beam profile at a distance of 3 m from the laser output coupler. The image was reconstructed from 20 individual horizontal scans of the laser beam taken at 1-mm intervals along the vertical, or y-axis. The darker shades denote higher intensity.
The laser also exhibits good long-term frequency stability, despite the fact that there is no active stabilization of the laser frequency. In addition, the transverse profile of the output laser beam is very nearly Gaussian, which facilitates the task of mode-matching. A three-dimensional intensity map of the laser beam at a distance of 3 m from the laser output coupler is shown in Fig. 3.10. This image is a composite of 20 horizontal scans using an infrared detector mounted on a translation stage driven by a linear actuator, taken at 1-mm intervals in the vertical axis.

While this approach has yielded our best information on the shape and propagation characteristics of the laser beam, it does have its drawbacks. For instance, the rate of travel of the linear actuator is a function of the voltage applied to the motor. In order to measure beam widths, it is necessary to determine the rate of travel for a given applied voltage. We found that the actuator velocity, which was measured using a stopwatch and traveling microscope, could not be determined to better than 5%. Thus, there is about a 5% uncertainty in our measurements of beam widths. However, a more serious drawback of this approach to imaging the beam is the time required: the data used in Fig. 3.10 were obtained over a 2-hour period. In order to properly characterize the laser beam, this procedure would have to be repeated for several distances from the laser output coupler. A more quantitative analysis of the propagation of the laser beam can be found in Section 3.4.1.

Despite the many advantages, operation of the CO₂ laser has proven troublesome. We have found mechanical faults with the original laser, and the sealed gas tube is prone to frequent failure. The symptoms which we have observed were the onset of output power fluctuations, followed by laser frequency instability and a tendency of the laser to fall into rf-discharge mode. Before long, it becomes impossible to operate the laser. Our investigation into the problems suggest that there may be problems with the seals of the Brewster windows, permitting air to slowly leak into the gas tube. Another possibility is that the gain becomes spoiled by ion sputtering from the discharge cathode.
onto the Brewster windows. Although we attempted to repair and refill the gas tube ourselves, our refills proved to be short-lived, and we eventually had to find a competent commercial supplier of CO₂ laser gas tubes. Unfortunately, the laser problems have led to more than one year of “down-time” for the experiment.

3.3.4 Acousto-Optic Modulator

In this section, we discuss the principles of operation and the performance of the Isomet acousto-optic modulator (AOM), which is used to generate clean optical pulses from the cw CO₂ laser beam.

3.3.4.1 Principles of Operation

The principle behind an AOM is the Bragg diffraction of light by acoustic waves. Radio frequency (rf) sound waves are launched into a solid transparent material via a PZT and produce a periodic change in the refractive index of the material. This periodic variation in the index is effectively a sinusoidal grating which is capable of diffracting incident light. In an AOM, the wavelength \( \Lambda \) of sound in the medium is analogous to the line spacing of a diffraction grating. We operate the AOM in the Bragg regime, where \( L > \Lambda^2/\lambda \) and the laser beam enters the crystal at the Bragg angle, \( \theta_B = \lambda/(2\Lambda) \). In the Bragg regime, light that is diffracted is mostly diffracted into the first order [Chang, 1995]. The first order is separated from the zeroth-order by an angle of \( \lambda/\Lambda \), as illustrated in Fig. 3.11.

Our AOM uses a germanium crystal (index of refraction \( n_0 = 4.00 \), velocity of sound \( v_s = 5.5 \times 10^5 \text{ cm/sec} \)) with a light-sound interaction length \( L = 19 \text{ mm} \) and a height \( H = 6 \text{ mm} \). The PZT is dithered at a frequency of 40 MHz, and so the sound wavelength is \( \Lambda = 0.14 \text{ mm} \). The
Figure 3.11 - Basic schematic of an acousto-optic modulator. A piezoelectric transducer is dithered at a high frequency, creating sound waves in the crystal that act as a diffraction grating for the incident light. In our AOM, the crystal material is germanium with a light-sound interaction length $L$ of 19mm. The PZT is dithered at a radio frequency of 40 MHz. At the end opposite to the PZT, an acoustic absorber is used to prevent the reflection of sound waves (not shown).
efficiency of the diffraction of light into the first order is given by [Chang, 1995]:

\[
\frac{I_1}{I_0} = \sin^2 \left( \frac{\pi}{2\lambda} \sqrt{2 \left( \frac{L}{H} \right) M_2 P_a} \right)
\]

(3.17)

where \(L/H\) is the aspect ratio of the sound field, \(M_2\) is a material figure of merit (\(M_2 = 815\) for germanium), and \(P_a\) is the acoustic power. \(P_a\) is normally chosen so that the maximum amount of light is diffracted into the first order. Practical AOM devices can have efficiencies of \(I_1/I_0 = 0.8\) or better.

3.3.4.2 Performance

Under optimal conditions, over 80% of the incident infrared radiation can be diffracted into the first order. By simply switching the acoustic energy source on and off, the AOM can form well-defined optical pulses in the deflected beam. When the acoustic energy source is switched off, we are unable to detect any infrared radiation diffracted into the first order, and so the contrast ratio of the optical pulses against the background is very high (greater than 1000:1).

The only practical limitation on the optical pulse-forming capabilities of the AOM is the time required for the acoustic wave field to be switched on and off in the volume of germanium traversed by the laser beam. That is, the transit time of the acoustic wave across the diameter \(d\) of the laser beam, \(t_{\text{trans}} = d/v_s\), determines how fast the deflected beam can be switched on or off. For an unfocused laser beam of diameter \(d = 3.6\) mm, the transit time is \(t_{\text{trans}} \approx 600\) nsec. Often, the 10-90\% rise/fall time is defined as 0.64 \(t_{\text{trans}}\). Thus, the minimum pulse width of our AOM is about 1 \(\mu\)sec. There is no upper bound to the AOM pulse width, which is capable of cw deflection (in fact, this is very useful for alignment purposes). A typical optical pulse formed from our AOM is shown in Fig. 3.12. The vertical scale is expanded so that we can clearly see the behavior in the after-pulse...
Figure 3.12 - Typical after-pulse characteristics of the optical pulses formed by the acousto-optic modulator (top panel) and the electro-optic modulator (bottom panel). Note that we have normalized the AOM and EOM pulse amplitudes to unity and expanded the vertical scale so that the after-pulse regions can be clearly seen. The AOM produces clean optical pulses with none of the after-pulse ringing of the EOM (cf. Section 3.1).
region. In the lower panel, we have shown a typical optical pulse formed with our electro-optic modulator (EOM), which we discussed briefly in Section 3.1. This permits us to see how the AOM produces clean optical pulses with none of the after-pulse ringing we observed in the optical pulses that were formed using the EOM. Although we have not yet sought to publish our data concerning the after-pulse ringing in our CdTe EOM, interested readers should note that this problem appears to be related to that described by Wang et al. [1990] for LiNbO₃ electro-optic modulators.

Finally, we note that because the acoustic wave travels across the optical beam, the optical frequency is Doppler-shifted by an amount equal to the acoustic frequency. Thus, in our experiment, there is a frequency shift of +40 MHz in the deflected optical beam. However, this shift is not significant for measurements of broadband absorption, such as the water vapor continuum.

3.3.5 Infrared Detector and Data Acquisition

In this section we discuss the equipment involved in the detection of the CRDS signals, which includes the infrared detector and the data acquisition hardware.

3.3.5.1 Infrared Detector

The infrared detector for this experiment is a Kolmar KMPV50-.5-J2 photovoltaic (PV) HgCdTe detector. This is a photon detector built as a p-n semiconductor junction (i.e. a photodiode). Infrared photons which are absorbed near the junction are separated by the junction, producing an external electrical current. Thus, the PV HgCdTe detector is considered to be a linear device, in the sense that the current is proportional to number of incident infrared photons. The responsive element (0.5 mm × 0.5 mm) of the detector is mounted on a side-looking liquid nitrogen (LN₂) dewar flask with a 12-hour hold time. Because the detector is cooled to LN₂ temperatures, the responsive element
must be kept in vacuum, and so the Kolmar unit has a wedged ZnSe window which has an antireflection coating that is effective from 2 - 12 μm.

The detector may be characterized by the detectivity $D^*$ (called "D-star"), which is the reciprocal of the noise equivalent power normalized to unit area and unit bandwidth:

$$D^* = \frac{1}{\text{NEP}} \sqrt{A_d \Delta f}$$  \hspace{1cm} (3.18)

where NEP is the noise equivalent power (W), $A_d$ is the responsive element area (cm$^2$), and $\Delta f$ is the effective noise bandwidth (Hz). The manufacturer’s specification for the detectivity of our detector is $D^* = 3 \times 10^{10} \text{ W}^{-1} \text{ cm Hz}^{1/2}$, for radiation near 10.6 μm. For the manufacturer’s reported test conditions ($\Delta f = 10$ kHz) and $A_d = 0.0025 \text{ cm}^2$, we calculate the noise equivalent power $\text{NEP} = 0.17 \text{ nW}$. Another useful figure of merit is the responsivity $R$, defined as the output signal per unit incident radiant power. Our detector has responsivity $R = 5.5 \text{ A/W}$ near 10.6 μm. The photodiode signal is coupled to a transimpedance amplifier, which has a gain of 4000 V/A and an electrical bandwidth of 50 MHz.

3.3.5.2 Data Acquisition Hardware

The signal from the DC-coupled output of the infrared detector is sent to a Datel model PCI-416H DAQ on the lab computer. The PCI-416H has one 12-bit differential input channel which can sample data at a maximum rate of 10 MHz. Very rapid sampling rates are possible because the DAQ relies on flash A/D converters, in which a bank of comparators and encoding logic are used to obtain the output code in a single step. The PCI-416H also has an output TTL trigger which we use to trigger the formation of the optical pulse. The DAQ trigger signal is sent to a separate electronic pulse generator, which in turn sends a specified pulse to the AOM digital input module.
Thus, the AOM forms an optical pulse on demand from the DAQ.

The on-board FIFO (First-In First-Out) memory buffer stores up to 8k of samples. However, the buffer is transferred to the computer when it is half-filled. Thus, we say that a buffer of ringdown data contains 4000 sample data points. Typically, we store 160 samples per trigger event (corresponding to a single ringdown decay event), for a total of 25 individual ringdown decay events per buffer. More details on data processing can be found in Chapter 4.

3.3.6 Ancillary Instrumentation

In this section, we briefly discuss the dewpoint hygrometer, pressure transducer and the temperature sensors in the ringdown cavity. The signals from these ancillary instruments are sent to 16-bit analog input channels of a National Instruments PCI-6035E DAQ configured in the differential mode and archived with the corresponding ringdown data on the lab computer.

3.3.6.1 Dew Point Hygrometer

The humidity in the cell is sampled at the output port of the ringdown cavity using an EdgeTech Model 200 DewTrak chilled mirror dew point hygrometer. The dew point hygrometer uses a thermo-electrically cooled, optically sensed mirror to directly measure the dew point. The dew point is the temperature to which a humid gas must be cooled in order that it is saturated with respect to water (when the dew point is below 0 °C, the saturation is measured with respect to ice). A dew point hygrometer is a primary instrument for measuring humidity, because the sensor directly measures the dew point. Once the dew point is known, the partial pressure of water vapor can be calculated from thermodynamic equations [Wexler, 1976; Wexler, 1977]. The relationship between the dew point and the water vapor partial pressure is illustrated in Fig. 3.13.
Figure 3.13 - Water vapor partial pressure as a function of the dew point. Below 0 °C, the saturation vapor pressure above ice is plotted.
The EdgeTech dew point sensor is calibrated against the NIST humidity standard, and has a measurement accuracy of ± 0.5 K. This corresponds to a water vapor partial pressure uncertainty ranging from ± 0.008 kPa for humidities near 0.13 kPa to ± 0.044 kPa for humidities near 1.3 kPa. Thus, the absolute error of the sensor increases with humidity, while the relative error decreases from 6% near 0.13 kPa of water vapor to 3.3% near 1.3 kPa of water vapor.

3.3.6.2 Pressure Transducer

The pressure in the ringdown cavity is measured using a MKS Baratron Type 120 capacitance manometer, which operates in the range 0 - 133 kPa. A capacitance manometer has a flexible metal diaphragm separating the unknown pressure from a vacuum. The capacitance between the diaphragm and fixed electrodes is inversely proportional to the distance between them, which is determined by the gas pressure. Capacitance manometers measure pressure independent of gas or vapor composition, and are accurate devices for measuring absolute pressure.

The MKS pressure sensor has a relative measurement accuracy of ± 0.12% of the reading. Since the measurements we report on in this thesis were all made for total cell pressures around 107 kPa, we take the measurement accuracy of the sensor to be ± 0.13 kPa.

3.3.6.3 Temperature Sensors

The temperature of the gas inside the ringdown cavity is measured using two T-type (copper-constantan) thermocouple junctions. One junction is located near the center of the ringdown cavity and the other junction is near one end of the cell. A thermocouple junction, formed by joining two dissimilar metal alloys, produces a voltage change $\Delta V$ that is nearly proportional to the change in temperature $\Delta T$ (the so-called Seebeck effect). The thermocouple junctions are connected to a
Stanford Research Systems SR630 thermocouple monitor, and the measured temperature is sent via the analog output channels from this monitor to the PCI-6035 DAQ.

The T-Type thermocouples have a measurement accuracy of ±0.5 K. We have tested for the presence of temperature gradients inside the ringdown cell, which are a problem with large volume White cells. To do this, we have conducted experiments with two thermocouples inside the ringdown cavity located near one end flange and in the output gas port in the center of the ringdown cavity. The temperatures at the two locations agree with one another to within the measurement accuracy, and so we have concluded there are no measurable temperature gradients inside the ringdown cell.

3.4 Methodology

In this section we discuss the methodology of our experiment. We begin with a discussion of infrared mode matching (Section 3.4.1). Then, we discuss gas-handling and water vapor generation (Section 3.4.2). In Section 3.4.3, we discuss the computer software that controls the experiment. Finally, in Section 3.4.4, we detail our methodology for making water vapor absorption measurements.

3.4.1 Infrared Mode Matching

Mode matching is important in quantitative CRDS in order to remove any uncertainty in the determination of absorption coefficients that might be related to the excitation of higher order modes in the ringdown cavity. The different higher order modes will in general have different decay time constants. This can lead to erroneous measurements of the absorption coefficients if the TEM_{00} mode of the ringdown cavity is not consistently probed. Thus, the goal of mode matching in our experiment is to preferentially excite the TEM_{00} mode of the ringdown cavity in such a way that no
Figure 3.14 - Examples of ABCD matrices for the propagation of a Gaussian beam through free space, and also through a thin lens.
higher order modes are mistakenly probed.

3.4.1.1 Gaussian Beam Propagation

In Section 3.3.3, we presented a three-dimensional intensity plot of the laser beam profile that illustrated the Gaussian nature of our laser beam. A Gaussian beam satisfies the equation [Yariv, 1975]:

\[
\frac{1}{q(z)} = \frac{1}{R_f(z)} - i \frac{\lambda}{\pi n_0 w^2(z)}
\]  

(3.19)

where \( q(z) \) is called the Gaussian beam parameter, \( R_f(z) \) is the radius of curvature of the phase fronts, \( w(z) \) is the beam width (sometimes called the spot size), and \( n_0 \) is the index of refraction. As a Gaussian beam propagates, it will be transformed according to the so-called ABCD law [Yariv, 1975]:

\[
q_2 = \frac{Aq_1 + B}{Cq_1 + D}
\]

(3.20)

where \( q_1 \) is the initial Gaussian beam parameter, and \( q_2 \) is the beam parameter following transformation by the 2 x 2 ray (or ABCD) matrix having elements A, B, C, D which characterizes the medium. Examples of ABCD matrices which are relevant to the problem of optical mode-matching are presented in Fig. 3.14. The ABCD law is a very useful tool because it makes it possible to develop simple algorithms that have the capability to calculate the propagation of Gaussian beams through any number of lenses.

3.4.1.2 Laser Beam Characterization and Mode Matching

In mode-matching, the aim is to have the laser beam width \( w(z) \) overlap as closely as possible
Figure 3.15 - Intensity profile of laser beam at a distance of 3 m from the laser output coupler. In the top panel, we have plotted the data (thick solid line) along with the best Gaussian fit (dashed line), which has width $w = 6.0$ mm. In the bottom panel, we plot the residuals to the fit, which are generally less than 5% of the signal intensity. This demonstrates that the CO$_2$ laser beam is highly Gaussian, which facilitates the task of mode-matching the laser to the ringdown cavity.
the beam width \( w(z) \) of the TEM\(_{00} \) mode in a given cavity. Although we demonstrated with Eq. (3.5) that the expansion of an ideal propagating Gaussian beam can be expressed in terms of the wavelength and the beam waist, a real laser beam may expand according to an effective beam waist \( w_0' \), rather than the actual beam waist \( w_0 \). Therefore, the expansion of the laser beam as it propagates must be experimentally characterized. As we mentioned briefly in Section 3.3.3.2, some of our characterizations of the laser beam profile involved scanning a detector horizontally across the beam. By repeating the scans for different vertical positions, we demonstrated it is possible to construct useful three-dimensional intensity maps of the infrared laser beam. It is then possible to fit the intensity profiles to a Gaussian and solve for the beam width, \( w(z) \), as we demonstrate in Fig. 3.15. For a propagation distance of \( z = 3.0 \) m from the laser beam waist, we measure a beam width of 6.0 mm.

We have supplemented this beam width measurement with data obtained from a simpler technique. The power transmission of a Gaussian beam which passes through the middle of a circular aperture of diameter \( 2a \) is given by [Siegman, 1986]:

\[
T_{power} = \frac{2}{\pi w^2} \int_0^a 2\pi r \exp(-2r^2/w^2) dr = 1 - \exp(-2a^2/w^2). \tag{3.21}
\]

When the aperture radius \( a = w \), the power transmission is 86.5%. Thus, by positioning a variable iris in front of a power meter and restricting the aperture until the power reading is 86.5\% of the original power, we can obtain the beam width from a vernier caliper measurement of the aperture diameter. In applying the variable iris technique, we first verified our results against the measurements we made using the intensity profiles. Then, we repeated the variable iris beam width measurement for several other propagation distances from the beam waist, which are shown in Fig. 3.16, along with the least squares fit to Eq. (3.5). The sole fit parameter is the effective beam waist,
Figure 3.16 - Expansion of Gaussian laser beam as a function of propagation distance, obtained by the variable iris technique. The solid curve is the least squares fit to Eq. (3.5), where the beam waist $w_0$ is the only fit parameter. These beam expansion measurements indicate $w_0 = 1.8$ mm, a parameter which we then use to mode-match the laser beam to the ringdown cavity.
for which the best fit is \( w_0' = 1.8 \text{ mm} \). This value is in excellent agreement with the calculated beam waist, \( w_0 = 1.8 \text{ mm} \), for the cavity geometry of our CO\(_2\) laser.

Once the effective beam waist is known, we apply the mode-matching technique of Kogelnik [1964]. Kogelnik showed that a single lens of focal length \( f > f_0 \) may be used to match the incident beam to the TEM\(_{00}\) mode of the optical cavity, where \( f_0 = \pi w_1 w_2 / \lambda \) and \( w_1 = 1.8 \text{ mm} \) and \( w_2 = 1.3 \text{ mm} \) are the waists of the laser cavity and ringdown cavity, respectively. For our experiment, we find \( f_0 = 69.4 \text{ cm} \), and so we selected a lens of \( f = 75 \text{ cm} \) for mode matching. However, we cannot use the convenient equations Kogelnik derived to determine the position of the lens with respect to the two cavity waists, because they do not consider the lens-like effect of the curved ringdown cavity mirrors. Instead, we iteratively solve for the propagation of the beam according to the ABCD law in order to minimize the beam mismatch inside the ringdown cavity. As we demonstrate in Fig. 3.17, the beam mismatch is minimized when the mode matching lens is positioned at a distance of 2893 mm from the laser output coupler \((z = 0)\), and the front mirror of the ringdown cavity is 3560 mm from the laser output coupler (and 3560 - 2893 = 667 mm from the mode matching lens). The dashed line illustrates the propagation of the beam if the mode matching lens were removed.

The effectiveness of mode matching is readily seen when the ringdown cavity PZT is scanned for conditions of no mode matching (Fig. 3.18, top panel) and mode matching (Fig. 3.18, bottom panel). When no mode matching lens is used, the pattern of modes that are excited in the ringdown cavity is complex and difficult to understand. The narrow transmission peaks in the top panel probably represent various transverse modes of the ringdown cavity, while the wider peaks may be the result of multiple reflections from other surfaces inside the ringdown cell. In the bottom panel, the mode matching lens is in place, and only a few peaks persist. Most of the incident laser pulse energy is channeled into the TEM\(_{00}\) mode of the ringdown cavity, with some residual energy.
Figure 3.17 - ABCD law calculations of the expansion of our Gaussian laser beam with (solid line) and without (dashed line) the mode matching lens. The mode-matching lens (f = 75 cm) has been positioned a distance of 2893 mm from the laser beam waist (z = 0 mm). The laser beam width exactly matches the width of the ringdown cavity TEM$_{00}$ mode (solid thick line). When the mode matching lens is removed, we see from the dashed line that the incident beam overfills the TEM$_{00}$ mode of the ringdown cavity, which will lead to the excitation of multiple transverse modes in the ringdown cavity.
Figure 3.18 - Ringdown cavity PZT scans for conditions of no mode matching (top panel) and mode matching (bottom panel). When no mode matching lens is used, numerous peaks are clearly visible in the scans. The narrow peaks in the top panel probably represent various transverse modes of the ringdown cavity, while the wider peaks may be the result of multiple reflections from other surfaces inside the ringdown cell. In the bottom panel, the mode matching lens is in place, and only a few peaks persist. Most of the incident laser pulse energy is channeled into the TEM$_{00}$ mode of the ringdown cavity, with some residual energy coupling into the TEM$_{01}$ mode.
coupling into the TEM$_{01}$ mode. Because the transmission peaks of the TEM$_{00}$ mode are much higher in amplitude than the TEM$_{01}$ mode, we are able to unambiguously identify the TEM$_{00}$ mode and tune the ringdown cavity so that this mode is resonant with the laser frequency.

3.4.2 Water Vapor Generation and Gas-Handling

We believe the present CRDS experiment is novel in that it is designed as a gas flow experiment, and we will shortly describe this methodology in greater detail. However, our initial attempts to measure the water vapor continuum were made with the ringdown cavity acting as a static gas cell, and we first briefly describe some of the results from these experiments. In this configuration, we first evacuated the ringdown cell to obtain the experimental baseline, and then we measured the time constant difference when the ringdown cell was refilled with humid gas. For this gas-handling methodology, it was necessary to have a vacuum system capable of fully evacuating the water vapor from the ringdown cell, and so we used a turbomolecular pump backed with a mechanical rotary pump. The vacuum system was connected to the ringdown cell via flexible stainless steel bellows that were rigidly affixed to the laboratory floor in order to channel pump vibrations away from the ringdown cavity.

Despite these measures, we were unable to obtain adequate stability of time constants. In Fig. 3.19, we present an example of a static cell CRDS experiment where the ringdown cell is alternately evacuated and refilled to a pressure of 1 atm with dry nitrogen. For greater clarity, we present buffer-averaged values for the decay time constant and cell pressure, where each buffer of data contains 40 individual decay events. In principle, the decay time constants should be the same for nitrogen-filled and evacuated cell conditions, since nitrogen does not absorb infrared radiation near 1000 cm$^{-1}$. However, we observe greater variability in the decay time constants when the
Figure 3.19 - Example of a static cell CRDS experiment to test system repeatability for a sequence of alternating dry nitrogen fills and evacuation. The experiment begins with the cell filled to approximately 101 kPa of dry nitrogen, and is evacuated and refilled 4 times. The time constants are shown as squares and the cell pressures are shown as a solid line. For greater clarity, we present buffer-averaged values of the decay time constant and cell pressure, where one buffer contains 40 individual decay events. The inconsistent behavior of the time constants prohibited quantitative measurements of water vapor continuum absorption.
ringdown cell is evacuated or refilled than we do when the cell conditions remain fixed. A similar behavior was observed by Bucher et al. [Bucher et al., 2000], in a CRDS experiment that used a CO₂ laser operating near 942 cm⁻¹. Bucher et al. reported that the decay time constant went from 536 nsec to 736 nsec when their air-filled cavity was evacuated, which they attributed to the water vapor continuum. However, this effect is too large to be explained by water vapor continuum absorption, which lowers our observed decay time constants by about 10 nsec (cf. Chapter 4).

Believing that pump vibrations were responsible for the apparent instability of the ringdown cavity, we redesigned our CRDS experiment as a flow experiment. That is, in the present configuration, gas continuously flows through the ringdown cell from the nitrogen cylinder and is then exhausted into the laboratory. One of the main advantages of this gas-handling methodology is that the pumps are no longer necessary. We are able to humidify the gas flow in a controlled way from zero to near-saturation by diverting a portion of the flow over a body of distilled water. The fraction of the gas flow which passes over the body of distilled water is controlled with two needle valves in the "dry" and "wet" flow paths. The split flow is then recombined, and directed to the ringdown cell. Removal of the humidity from the ringdown cell is accomplished by shutting the flow over the body of distilled water. This dry-purging is both efficient and effective at removing the water vapor from the ringdown cell. We have found the dew point sensor settles to a new value of the dew point within approximately two minutes following an adjustment of the needle valves.

Another advantage of this methodology has to do with the chilled mirror dew point sensor. This sensor takes a long time to stabilize in the static environment of the ringdown cell following evacuation or refilling with humid gas. In a gas flow experiment, by contrast, the dew point sensor rapidly converges on the dew point. A disadvantage with this approach is that it is not possible to study the absorption of pure water vapor. However, this is not a serious limitation to our experiment,
because the continuum absorption is easily separated into terms corresponding to the self- and foreign-broadened water vapor continuum.

In practice, the cell pressure is limited to values above ambient atmospheric pressure, and so most of our water vapor continuum measurements were made at a total cell pressure between 107 - 109 kPa. Finally, we note that in order to avoid problems associated with saturation such as condensation of moisture on surfaces inside the ringdown cell, we are careful to restrict the relative humidity to values less than about 80%. For example, the saturation vapor pressure at 296 K (the mean temperature of our measurements) is 2.8 kPa, and so we are careful not to exceed a vapor pressure of about 2.2 kPa in our experiments. This roughly corresponds to the saturation vapor pressure of water at 292.5 K, and so this gives us about a 3 K margin in the temperature in case there are any exposed surfaces cooler than our measurements of gas temperature.

3.4.3 Computer Software

We have designed several LabVIEW programs to control various aspects of the CRDS experiment. Because LabVIEW programs consist of graphical rather than text instructions, we do not include the code in this thesis, but rather describe some of the most important functions of these programs. Our general experimental methodology is to first scan the ringdown cavity to determine the PZT voltage corresponding to the transmission peak of the TEM_{00} mode of the cavity. Then, we launch the data collection program. In this section, we discuss the two programs that control these functions, and defer our discussion of the data analysis programs to Chapter 4.

3.4.3.1 Scan Program

A small but useful LabVIEW program is our scan program. The front panel of scan.vi is
Figure 3.20 - LabVIEW front panel for scan.vi. This program scans the ringdown cavity PZT and displays the transmission peak amplitudes as a function of the PZT voltage. The bottom plot is the current scan, and the top plot is the previous scan. The user selects the start and end voltages, and the number of points per scan.
shown in Fig. 3.20. The function of the scan program is to ramp the PZT voltage and plot the amplitude response of the ringdown cavity as a function of the applied voltage. User inputs include the start and end voltages, and the number of voltage increments per scan. The voltage ramp from scan.vi is sent to a high voltage amplifier via the 0-5 V analog output of the PCI-6035 DAQ, and the HV amplifier output is sent to the PZT. For each voltage increment, the program reads a buffer of ringdown data (see section 3.4.3.2) and outputs the buffer-averaged amplitude as a function of the PZT voltage. This permits us to scan over the free spectral range of the ringdown cavity and determine which optical cavity modes are excited. The scan program can be operated in either single-scan or continuous-scan mode.

3.4.3.2 Data Collection Program

The most important LabVIEW program is picard.vi, the central program which runs the CRDS experiment. Because the volume of data is too large to be fully analyzed in real-time, the main function of picard.vi is to collect and archive data, which can be later analyzed. Picard.vi begins by sending a series of commands to the Datel DAQ to initialize the card and prepare it for the acquisition of data. The front panel interface (Fig. 3.21) allows the user to select the pulse trigger rate for the experiment, as well as the number of ringdown decay events to acquire per buffer of data. Once the Datel card is initialized, it automatically triggers the formation of optical pulses at the user-defined repetition rate. The number of data points per decay event is automatically set by dividing the buffer size (4000 data points) by the number of traces per buffer. Typically, we choose a pulse repetition rate of 2 kHz and 25 traces per buffer (and therefore, 4000/25 = 160 data points per decay event).

The main loop of picard.vi continuously collects buffers of ringdown data. Several displays
Figure 3.21 - LabVIEW front panel for picard.vi, which controls the CRDS experiment. The user selects experimental parameters such as the pulse repetition rate, number of samples per ringdown event, and the selection criteria for saving data. As the ringdown cavity is tuned into resonance with the laser frequency, the signal from the ringdown event increases in amplitude, as seen in the lower left plot (the data are plotted on a logarithmic scale in the lower right plot). The upper left plot shows the initial intensity, $I_0$ in Eq. (3.11), for the 25 individual decay events in the buffer of data, along with the mean and standard deviation. Also shown are the buffer-averaged time constants of previously saved data buffers (upper right) and a number of ancillary measurements (center).
on the front panel of picard.vi are updated for each buffer. The execution time for the main loop is \( \sim 0.5 \text{ sec} \), and so new buffer information is displayed on the screen roughly twice per second. One of the most useful pieces of real-time information is the graph of the buffer-averaged ringdown decay event. In our CRDS experiment, the ringdown cavity PZT is manually tuned into resonance with the laser frequency. If the signal intensity of the buffer-averaged ringdown decay event drops, this is usually a sign that the ringdown cavity frequency is becoming detuned with respect to the laser frequency, and we adjust the PZT voltage accordingly.

A buffer of data is saved to disk when the buffer-averaged initial intensity, \( I_0 \) of Eq. (3.11), falls within a user-selected range. Note that \( I_0 \) is not the peak signal in the ringdown event, which is normally a saturated signal from the 12-bit ADC (i.e. a value of +2048 counts). The high and low intensity limits are determined from the consideration of several experimental factors, which we discuss in greater detail in Section 3.5. If the observed initial intensity falls outside the desired range (which may occur if laser power varies over time), then the optical pulse power can be adjusted using the polarizer-analyzer-attenuator.

Often, we also use the standard deviation of the values of \( I_0 \) in a buffer as an additional criterion for data saving. We have observed a small 120 Hz frequency modulation in the apparatus, which probably originates from the laser power supply. When the ringdown cavity is probed with pulses from a narrow band laser source, the frequency modulation of the source is observed as amplitude modulation at the cavity output. This amplitude modulation approaches a minimum when the ringdown cavity is resonant with the laser frequency, and grows as the ringdown cavity is detuned. Thus, the criterion of low standard deviation in the values of \( I_0 \) within a buffer of data helps to ensure that only high quality data at the transmission peak of the ringdown cavity are saved.

Picard.vi also collects a variety of ancillary data including the temperature, pressure and
humidity inside the ringdown cell, and the laser power. These experimental parameters are stored, along with a date and time stamp, in a formatted header for the buffer of data stored to disk.

### 3.4.4 Water Vapor Absorption Measurements

In this section we discuss the methodology we have developed for making water vapor absorption measurements with our CRDS experiment. We do not present the results of our experiments to measure the water vapor continuum, which are discussed separately in Chapter 4.

Once the ringdown cavity is mode matched to the laser beam so that the $\text{TE}_{00}$ mode is the dominant mode excited in scans of the ringdown cavity PZT, then it is possible to see how the ringdown decay constants corresponding to this mode change under the influence of cell humidity. We initially thought the turbulent gas flow through the ringdown cavity would degrade our ringdown signals and prevent us from measuring the decay constant while the gas was flowing. As we illustrate in Fig. 3.22, there is a measurable increase in the standard deviation of the decay time constants, but it does not prevent us from making accurate measurements. In Fig. 3.22, each data set consists of 2000 individual ringdown events collected over the course of about one minute. In both cases, only dry nitrogen was used and the total pressure was maintained at 108 kPa.

The methodology we initially adopted for absorption measurements was a dry - humid - dry flow sequence. In other words, we begin with a dry ringdown cell, and collect 80 buffers of ringdown data for a total of 2000 ringdown events. We then use the needle valves to divert part of the flow from the nitrogen cylinder over the body of distilled water. Once the dew point sensor has stabilized, we collect the ringdown data for the humidified flow. Finally, we purge the water vapor from the system with dry nitrogen flow, and when the dew point sensor has stabilized once again, we repeat the dry cell measurements. A typical dry - humid - dry sequence is presented in Fig. 3.23. These data

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Figure 3.22 - Sample ringdown data sets for flow (top) and no flow (bottom) conditions. This illustrates that the influence of the gas flow (roughly 0.5 liter/sec) introduces some noise to the decay time constant measurements, but does not affect the accuracy of these measurements.
Figure 3.23 - Three data sets obtained at $v = 944$ cm$^{-1}$, corresponding to the experimental sequence of dry-humid-dry flows (left to right). Each data set consists of 2000 individual decay events. The first data set was obtained with a dry-nitrogen flow, the second with a humidified nitrogen flow ($e = 1.6$ kPa), and finally another data set with dry-nitrogen flow. The vertical dashed lines indicate the boundaries between data sets.
were taken using a laser output frequency of 944.195 cm\(^{-1}\). The 13.7 nsec drop in the decay time constant when 1.6 kPa of water vapor is added to the nitrogen flow is due to the water vapor continuum absorption. We note that the time elapsed between the data sets is variable and generally depends on a number of factors, including the time required for the dew point sensor to stabilize. However, the third data set in Fig. 3.23 was collected two days after the first two data sets. We stress it was not necessary to wait two days for the system to stabilize. In fact, we have chosen to use these data because they offer an effective illustration of the impressive stability of our CRDS experiment.

As a result of the long-term stability demonstrated in our data, we concluded that it was possible to measure water vapor continuum absorption in an even more efficient manner. Therefore, the methodology we have employed for all of the data we present in Chapter 4 is the following. We first obtain our experimental baseline by collecting several ringdown data sets for dry flow conditions at the beginning of the measurement run. Then we proceed to make water vapor continuum absorption measurements by adding humidity to the gas flow. When the dew point sensor reports a stable value of humidity (typically, this takes less than 5 minutes following an adjustment to the needle valves), we collect 2000 ringdown events in the manner described above. Then, the humidity level is changed, and the procedure is repeated. An experimental run typically takes 4-5 hours, and during this time we have found it possible to make water vapor continuum measurements for over 40 different humidity levels. When we completed the water vapor absorption measurements, we flushed out the cell with dry gas and collected a few buffers of ringdown data to assure ourselves that the dry decay time constants had not shifted. As we have mentioned in Chapter 2, White cell measurements of the water vapor continuum are very tedious because of the very large gas volume of these cells, and so a typical time required to make continuum measurements for a single value of humidity is at least 12 hours [McCoy et al., 1969]. Therefore, by comparison with
previous experimental techniques, our CRDS experiment is capable of efficiently measuring water vapor continuum absorption.

3.5 System Performance

In this section, we discuss some issues pertaining to the performance of our CRDS experiment. We begin with the most important and challenging issue, which was the long-term drift of the decay time constants (Section 3.5.1). We discuss the manifestations of long-term drift, our hypotheses for the long-term drift, and the operational solution we eventually adopted. Following this, we discuss two other performance issues, namely infrared detector linearity (Section 3.5.2) and baseline modulation (Section 3.5.3). Lastly, in Section 3.5.4, we summarize the experimental capabilities of our system.

3.5.1 Long-Term Drift

The long-term drift of the apparatus is the most important problem we faced, because the water vapor continuum is similar to an experimental baseline. If our experimental baseline varies significantly during the course of an experiment, the accuracy of our measurements of continuum absorption coefficients will be compromised. We begin by presenting some of our observations of long-term drift, then we discuss our hypotheses for the long-term drift. Unfortunately, the problem of long-term drift proved to be very difficult to overcome, and many months were spent trying to understand this problem. Much of our success is due to a serendipitous discovery that pointed to an unforeseen role played by our detector in the long-term drift. We conclude this section with a qualitative model of the problem of long-term drift in our experiment and the operational solution to long-term drift we adopted following this discovery.
3.5.1.1 Description of Long-Term Drift

Because of the difficulty of the problem, an intensive study of the long-term drift of our system was required. In order to do this, we modified our scan program so that it would scan continuously, and compute the decay time constant for the buffer of data corresponding to the transmission peak of the PZT scans. This automated the task of data collection and was also useful because it permitted us to slow down the stream of data to manageable levels, which was necessary for real-time data processing. The modified scan program scanned the cavity approximately once every 30 seconds, and would save to disk the mean time constant of the buffer of data corresponding to the ringdown cavity transmission peak.

In Fig. 3.24 and Fig. 3.25, we present two typical examples of long-term drift, taken on Feb. 2, 2001, and Jan. 22, 2001, respectively. In both cases, the ringdown cell was filled with 1 atm of dry nitrogen and there was no flow through the cell. The experiment was run for about 6 hours in the former case and 10 hours in the latter case. The lack of reproducibility to the drift patterns exhibited in Fig. 3.24 and Fig. 3.25 illustrates the complexity of the problem. The long-term drift was unpredictable, with the decay time constants sometimes drifting more rapidly and other times more slowly. In Fig. 3.26, we show the cell temperature and pressure for the data set in Fig. 3.25. The variation is about ±0.2% for both temperature and pressure, and neither the trends nor the magnitude of variation could account for the ± 3% variation in decay time constants. We also established early on that variations in the laser output power were not responsible for the long-term drift. As we discuss in greater detail in the next section, we have been unable to correlate long-term drift with any known variable.

The long time scales of this problem suggested a possible thermal explanation, while the variation of the decay time constants pointed to instability in the ringdown cavity apparatus. We
Figure 3.24 - Example of long-term drift of the CRDS experiment, from Feb. 2, 2001. The ringdown cell contains 1 atm of dry nitrogen, in a static (i.e. no-flow) condition. The time constants vary in an unpredictable way over the course of the experiment. The decay time constant statistics for this data set are $\tau = 648 \pm 30$ nsec.
Figure 3.25 - Another example of the long-term drift in our CRDS experiment, this time from Jan. 22, 2001. The ringdown cell contains 1 atm of dry nitrogen, in a static (i.e. no-flow) condition. Once again, the time constants vary in an unpredictable way over the course of the experiment, sometimes varying slowly and sometimes varying rapidly. The decay time constant statistics for this data set are $\tau = 625 \pm 19$ nsec.
Figure 3.26 - Measurements of temperature and pressure inside the ringdown cell for the long-term data set presented in Fig. 3.25. The variation is about ± 0.2% for both temperature and pressure, and neither the trends nor the magnitude of variation could account for the ± 3% variation in decay time constants.
needed an experimental solution to the problem, because we could not make meaningful measurements of the water vapor continuum absorption. The uncertainty in decay time constants introduced by the presence of long-term drift was larger than the expected change in decay time constants due to the introduction of water vapor in the ringdown cell. For example, the data set presented in Fig. 3.25 has a mean decay time constant $\tau = 625$ nsec with a standard deviation $\sigma_\tau = 19$ nsec. Referring back to the data of Fig. 3.23 (note: these data were collected after we solved the long-term drift problem), we find that adding 1.6 kPa of water vapor to the dry nitrogen lowers the decay time constant by only 13.7 nsec. Thus, in order to measure such decay constant drops (and consequently, continuum absorption coefficients) to 10% accuracy, the long-term drift had to be reduced by at least an order of magnitude.

3.5.1.2 Hypotheses for Long-Term Drift

We advanced a wide variety of hypotheses to explain the long-term drift behavior of our CRDS experiment. When we ran out of ideas, we solicited the advice of several people, both inside and outside the physics department, who had experience with lasers and/or optical cavities. The various hypotheses which we considered are categorized in terms of optical, mechanical, gas-related or miscellaneous hypotheses, and briefly described below.

A. Optical

A1. Electro-optic modulator. We determined that the after-pulse ringing of the EOM contributed additional noise to the decay time constants. In addition, we observed that significant infrared radiation leaked through the EOM + analyzer pulse-forming system and into the ringdown cavity.
Figure 3.27 - Effect of tuning PZT voltage by one free spectral range on the decay time constants. In the lower panel the PZT voltage is plotted for the data buffer number. The buffer-averaged decay time constant is plotted in the top panel. The decay time constants do not exhibit a significant shift when the PZT is tuned 1 FSR, which demonstrates that PZT tilt cannot be responsible for the long-term drift of decay time constants.
when the EOM was off. Unfortunately, the long-term drift of decay constants was not due to the
EOM, because the problem was still observed when the acousto-optic modulator was used to form
optical pulses.

A2. **PZT misalignment of ringdown cavity.** Because one of the ringdown cavity mirrors is mounted
on a PZT, we thought that cavity misalignment might occur if there is a tilting of the PZT as it
expands or contracts. However, we demonstrate in Fig. 3.27 that when the PZT voltage is adjusted
so that the cavity resonant mode is shifted by one free spectral range, the decay time constants are
not significantly affected.

A3. **Laser beam wander.** We considered laser beam pointing instability (arising from the laser cavity
or from the acousto-optic modulator) as a possible cause of long-term drift in the decay time
constants. We tested this hypothesis by using pinholes to eliminate potential laser beam wander.
Although we found that we were able to influence the coupling efficiency to the TEM$_{\infty}$ mode of the
ringdown cavity, we concluded that laser beam pointing was not a factor in the long-term drift of
decay time constants.

**B. Mechanical**

B1. **Pump vibrations.** As we have already discussed, we suspected pump vibrations were causing the
instability in decay time constants. We first tried to suppress the coupling of pump vibrations into
the ringdown cavity, and eventually redesigned the experiment without pumps. However, the long-
term drift remained.
B2. **Mirror mount relaxation.** In the original design of our ringdown cavity, the mirror mounts were retained against the cavity spacer assembly only through the action of the leaf springs. Sensing this might be the cause of decay time constant instability, we supplemented the retention provided by the leaf springs with several coil springs. While this made the cavity very rigid, it did not solve the problem of long-term drift.

C. **Gas**

C1. **Pressure or refractive index variations.** As we illustrated in Fig. 3.26, we found no correlation between pressure, temperature, or index of refraction and the variations in the decay time constant. In addition, the good stability of the cell temperature led us to dismiss potential effects due to cavity thermal expansion. This conclusion is supported by our measurements of the drift in the cavity resonant frequency, which is generally less than 20-30 MHz. In Section 3.5.3, we do discuss a small variation in decay time constants which we have observed when we pressure scan the cavity, but this does not appear to be a pure pressure effect and its magnitude is much smaller than the long-term drift with which we are presently concerned.

C2. **Gas contamination.** The commercial nitrogen cylinders we use are rated as 99.998% purity, and so we wondered whether our CRDS experiment, which is designed to be highly sensitive to weak absorption, might be responding to trace hydrocarbon contamination in the gas supply. We tested this hypothesis two ways. First, we employed a cold trap in the inlet stream to condense any hydrocarbon vapors before they reached the ringdown cavity. Second, we tuned the CO$_2$ laser to different frequencies and looked to see if we could influence the long-term drift, since hydrocarbon
absorption bands are not continuous like the water vapor continuum. However, the long-term drift persisted.

D. Miscellaneous

D1. Electrical noise. We received anecdotal reports that certain sensitive laser experiments in the physics building were thought to be adversely influenced by the proximity of heavy transient electrical loads. Specific examples cited included nearby subways and public transit streetcars, as well as arc welding equipment used by the mechanical workshop of the physics department. We attempted to correlate drops in line voltage with decay time constant variations, but we found it difficult to precisely measure the small changes in line voltage, and the results of this study are inconclusive.

D2. Time of day. We were also told that we might reduce experimental noise if we worked in the evening or overnight. Despite the fact that our experiment is on an optical table with pneumatic legs to provide vibration isolation, it was argued that the low-frequency building vibrations could still be transmitted to the apparatus. We tested this hypothesis with several runs during the evening and one overnight run, and found the time of day explanation wanting. However, an unusual event occurred on the overnight run, and this led us to develop an operational solution to the problem of long-term drift.

3.5.1.3 Operational Solution To Long-Term Drift

We now describe the nature of our serendipitous discovery and the operational solution to
Figure 3.28 - Long-term drift of decay time constants for data collected on March 12, 2001. The arrow denotes the point at which the infrared detector dewar was refilled with LN$_2$. 

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the problem of long-term drift we eventually adopted. At 1pm on March 12, 2001, we began another long-term run to collect data through the afternoon and into the evening and overnight. Our goal was to see if there was any change in the behavior of the long-term drift as a function of the time of day. During the course of the run, it became necessary for the first time ever to refill the infrared detector dewar with LN$_2$ while the experiment was running. In Fig. 3.28, we have plotted the decay time constants from this run, with an arrow to indicate the time of the detector dewar refill. There is an unmistakable change in the pattern of long-term drift following the LN$_2$ refill. After further testing, we discovered we were able to consistently induce rapid variations in the decay time constants by the action of refilling the detector dewar.

The configuration of our CRDS experiment during that period was slightly different than depicted in Fig. 3.7. At that time, we used an $f = 9$ cm lens to focus the energy exiting the ringdown cavity onto the detector element. This fact, and the apparent influence on the long-term drift by the action of dewar refilling, led us to speculate that the detector element, which is mounted on the inner wall of the dewar, is capable of motion. When the detector is refilled with LN$_2$, motion is induced in the detector element, perhaps as a result of thermal gradients within the dewar or else mechanically, through the addition of mass to the dewar. Because it is difficult to perfectly mode match the infrared radiation to the ringdown cavity, we initially thought there may be a chance that some of the energy incident on the ringdown cavity was being coupled into higher order transverse modes. This raised the possibility that the energy exiting the ringdown cavity may have decayed in a way which exhibited a transverse spatial dependence. Thus, our hypothesis was that the slow motion of the detector element led to variations in the spatial sampling of the energy exiting the ringdown cavity.

To test this hypothesis, we simply removed the focusing lens in order to reduce the sensitivity
Figure 3.29 - Long-term study of the decay time constant following the removal of the focusing lens. Note that we have made the vertical scale similar to our previous plots of long-term drift so that a direct comparison may be made. No long-term drift is apparent over a 4-hour period. This level of stability is adequate for making water vapor continuum measurements.
of the decay constants to the transverse position of the detector element. The results of a 4-hour study of the decay time constants is presented in Fig. 3.29. No long-term drift is apparent over the course of the experiment, demonstrating our success at suppressing long-term drift in our system. The level of stability demonstrated in Fig. 3.29 is adequate for making water vapor continuum measurements.

More recently, we have received new insights into our long-term drift problem from the external examiner of this thesis [Lehmann, 2002]. Lehmann made the suggestion that a second, badly mode-matched cavity may be formed from the detector element (R ~ 40%) and output mirror of the ringdown cavity. Radiation circulating within this second cavity will interfere with the radiation field exiting the ringdown cavity. Whether the interference is constructive or destructive depends on the phase of the radiation in the second cavity relative to radiation exiting the ringdown cavity, and will switch from constructive to destructive for cavity length changes of λ/4. The rapid oscillations we observed in the decay time constants during LN2 filling of the detector dewar (cf. Fig. 3.28) could be explained by the thermal contraction of the detector dewar wall (ΔL ~ 10 - 20 μm, for ΔT ~ 200 K). Meanwhile, the expansion/contraction of the optical table (ΔL ~ 2 - 4 μm, for ΔT ~ 1 K) as a result of normal laboratory changes in ambient temperature may be sufficient to account for the long-term drift in the decay time constants. Because the amount of interference (and consequently the magnitude of the variation in decay time constants) is determined by the amount of energy circulating in the second cavity, the effect of removing the focusing lens may have been to greatly reduce the coupling efficiency of the second cavity, thereby eliminating the long-term drift in decay time constants.

3.5.2 Infrared Detector Linearity

In photoconductive (PC) HgCdTe detectors, the recorded signal is usually a nonlinear
function of the incident photon flux. This well-known problem in infrared spectroscopy arises because the detector element, which has resistance inversely proportional to the photon flux, is operated in series with a bias voltage and load resistor. It is frequently assumed that photovoltaic (PV) HgCdTe detectors are linear devices, because photons incident on the $pn$ junction produce free electron-hole pairs that are separated by the electric field of the junction, causing a current to flow in proportion to the photon flux. However, we are unaware of any experimental data in the literature which supports the assumption of linearity for PV HgCdTe detectors at all signal levels. We therefore attempted to measure the power response of our PV HgCdTe infrared detector, using a commercial blackbody source that was controllable from 50 - 1000 °C.

In this experiment, we measured the detector signal as a function of the blackbody temperature, in steps of 25 °C. We then calculated the blackbody power spectrum, divided by the solid angle subtended by the detector element. Once we determined the power spectrum incident on the detector, we used the detector spectral response curve (Fig. 3.30) to calculate the total power sensed by the detector. The power sensed by the detector was then multiplied by the responsivity of the detector ($R = 2.28 \times 10^4 \text{ V/W}$) in order to obtain the expected detector output signal. The expected detector output signal could then be compared to our measured values of the detector output, as a function of the incident power (Fig. 3.31). The close correspondence between the expected detector output and the measured detector output is an indication that the detector power response is linear, at least up to an incident power of 50 μW.

Unfortunately, it is easy to have power levels much higher than 50 μW incident on the detector when a CO$_2$ laser source is used. This can put us into a regime where the power response of the detector is nonlinear, as shown in Fig. 3.32. Here, we plot decay time constants as a function of the power incident on the detector. For all incident power levels below about 110 μW, the mean
Figure 3.30 - The spectral response of our PV HgCdTe infrared detector (data supplied by manufacturer).
Figure 3.31 - Expected detector output (solid line) versus the measured detector output ('x') as a function of the incident power from a blackbody source. The close correspondence between the expected and measured detector output values indicates that the infrared detector power response is approximately linear, at least up to an incident power of 50 \( \mu \text{W} \). The small but clearly systematic deviation from linearity may be due to an incorrect spectral response profile for the infrared detector.
Figure 3.32 - Decay time constants as a function of the power incident on the detector. For incident power levels below about 110 μW, the mean decay time constant is approximately the same (roughly 546 nsec), but the noise in the decay constants increases as the power on the detector decreases. This occurs primarily because the influence of digitization noise is more significant at the lower incident power levels. Thus, the best signal-to-noise ratio in our experiment is found when the power incident on the detector is in the range 90 - 110 μW. Above 110 μW, the decay time constants begin to increase because of the nonlinear power response of the detector.
decay time constant is approximately constant (roughly 546 nsec), although the noise in the decay constants increases as the power incident on the detector decreases. This occurs primarily because the lower incident power levels result in a decrease of the signal-to-noise ratio, making the influence of digitization noise more significant. Thus, the best signal-to-noise ratio in our experiment is found when the power incident on the detector is in the range 90 - 110 μW. However, above 110 μW, the decay time constants begin to increase. When we examined the residuals to the exponential fits, it became apparent to us that the decay constants were rising because the detector was exhibiting a nonlinear power response.

It appears that even photovoltaic HgCdTe detectors have nonlinear power response at high incident power levels. When the power response of the detector is important, as it is in quantitative CRDS, then care must be taken to avoid high photon fluxes with HgCdTe detectors. It has been suggested that this occurs because there is a decline in the lifetime of charge carriers in HgCdTe as a result of Auger recombination [Bartoli et al., 1974]. In measurements using a CO₂ laser, Bartoli et al. found that this effect became significant for photon fluxes above 10^{18} photons cm⁻² sec⁻¹, and our findings appear to support this observation. For an incident power level of 110 μW on a detector element of size 0.05 cm × 0.05 cm, the photon flux for λ = 10.6 μm is 2 × 10^{18} photons cm⁻² sec⁻¹. Therefore, we stress that it should not be assumed that photovoltaic HgCdTe detectors behave as linear devices (although they are certainly more linear than photoconductive HgCdTe detectors), particularly when CO₂ lasers are used as the source of radiation.

3.5.3 Baseline Modulation

As we have already discussed, it is necessary to have an accurate characterization of the experimental baseline in order to make accurate water vapor continuum measurements. Because we
do not hold the pressure constant in our experiments, we decided to investigate whether the dry-cell decay time constants exhibited any dependence on the cell pressure. To study the pressure dependence, we scanned the cell pressure around the typical experiment pressure of 108 kPa in several discrete steps of roughly 0.13 kPa each. By scanning the pressure in our cavity, the resonant frequency is shifted so that a change to the PZT voltage is required to bring the cavity into resonance with the laser frequency.

The data we collected for $\nu = 944$ cm$^{-1}$ are plotted in Fig. 3.33. In the top panel, we show the relationship between pressure and PZT voltage. Note that around 107 kPa, we have adjusted the PZT voltage by $\sim 3.5$ V so that the cavity resonant frequency is shifted by one free spectral range (FSR), which is approximately 146 MHz. In the bottom panel, we plot the decay time constants as a function of the PZT voltage. A sinusoidal modulation with an amplitude $\sim 1.5$ nsec and a period approximately equal to the FSR of the cavity is clearly visible. We also observe a similar modulation having roughly the same period and amplitude when we tune the laser to other frequencies.

We are not sure of the cause of this baseline modulation. Our current experimental configuration makes it difficult to precisely measure the period of the baseline modulation. First of all, the pressure adjustment and the PZT voltage adjustment are both done manually. Secondly, we are unable to scan the PZT over several FSR. We have estimated the period by fitting the baseline modulation to a sine function (the fit to these data is shown in Fig. 4.11). The data are well-modeled by a sine function having a period of 3.4 V, which agrees with our measurement of the ringdown cavity FSR to within a 5% experimental error. Therefore, the baseline modulation might be an etalon effect involving the back surface of one ringdown cavity mirror and the high-reflectivity surface from the second cavity mirror, because the FSR of such a cavity would be slightly less than the FSR of the ringdown cavity. We are investigating this problem further.
Figure 3.33 - Baseline modulation in our CRDS experiment. By scanning the pressure in our cavity, the resonant frequency is shifted so that a change to the PZT voltage is required to bring the cavity into resonance with the laser frequency. In the top panel, we show the relationship between pressure and PZT voltage. Note that at 107.3 kPa, we have tuned the PZT voltage so that the cavity resonant frequency is shifted by one free spectral range. In the bottom panel, we plot the decay time constants as a function of the PZT voltage, showing a clear modulation of the decay constants having a period approximately equal to the free spectral range of the cavity. This modulation in the experimental baseline must be accounted for in a quantitative CRDS experiment.
In order to account for this baseline modulation in our measurements of the water vapor continuum, we do a dry-cell pressure scan over the range of the piezo and compute the mean decay time constant from the data. Unfortunately, it is not practical to do this for every water vapor absorption measurement we make, and so these decay time constants are uncorrected for the baseline modulation. However, this does not affect the accuracy of the continuum coefficients of self- and foreign-broadening we report in Chapter 4. This is because each water vapor absorption measurement involves changing the humidity and/or the total pressure of the gas stream in such a way that the resonant frequency (and therefore the PZT voltage) changes in an essentially random way. As we have typically made measurements for 40 or more different values of the humidity, it is reasonable to assume that any systematic error due to the baseline modulation is effectively washed out.

3.5.4 Experimental Capabilities

In this section we briefly review the capabilities of our apparatus, in terms of the spectral range, the minimum detectable absorption, and trace gas detection.

3.5.4.1 Spectral Range

The spectral range of our experiment appears to be limited by the range of the CO₂ laser, which is line tunable from 920 - 1090 cm⁻¹. Although the ZnSe mirror coatings are optimized for maximum reflectivity near 944 cm⁻¹, spectrophotometer tests conducted by the manufacturer indicate that the region of high reflectivity where a sensitive CRDS experiment should be possible extends fully through the wavenumber range of the CO₂ laser. We have successfully made CRDS measurements from 931 - 969 cm⁻¹, and we are planning to extend this range.
3.5.4.2 Minimum Detectable Absorption

The minimum detectable absorption coefficient, $k_{\text{min}}$, is a useful measure of the sensitivity of a spectroscopic experiment to weak absorption. Our CRDS experiment has a sensitivity equivalent to $k_{\text{min}} \approx 10^{-7} \text{ cm}^{-1}$, using Eq. (3.16) and the experimental parameters $R = 0.994$ and $\sigma_{c}/\tau = 0.002$. This is about an order of magnitude more sensitive than is possible with large-volume White cell spectroscopy, and is comparable to photoacoustic spectroscopy experiments at a similar level of development. We anticipate that proposed modifications to our experiment will substantially improve the sensitivity.

3.5.4.3 Trace Gas Detection

Many trace gases absorb infrared radiation within the spectral range of our experiment. We have conducted initial testing of the capability of our CRDS experiment to detect trace gases, and the results are encouraging. As an example, we have found that our system is capable of detecting a concentration of about 200 pptv of SF$_6$. One of the most powerful greenhouse gases on a per molecule basis, SF$_6$ has a radiative forcing of $0.64 \text{ W m}^{-2}/\text{ppbv}$ (compared to $1.8 \times 10^{-5} \text{ W m}^{-2}/\text{ppbv}$ for CO$_2$), and is believed to be increasing in the atmosphere at a rate of about 7% per annum [IPCC, 1996]. While the SF$_6$ detection limit of our experiment is an order of magnitude higher than present day atmospheric concentrations, we anticipate that proposed improvements to our apparatus will enhance our detection capability.
Chapter 4

Results and Discussion

This Chapter provides a detailed analysis of ringdown data and presents our measurements of the infrared water vapor continuum. In Section 4.1, we begin with a description of the data collected in our experiment and our method of analysis. Our measurements of the water vapor continuum are presented in Section 4.2. In Section 4.3, we establish the accuracy of our results by comparison with data obtained in experiments using CO₂ lasers and White cells. Then our results are compared to far wing theory and two empirical models of the continuum. We conclude with a discussion of recommended improvements for the experiment.

4.1 Ringdown Decay Analysis

In this section, we describe the ringdown data and our methods of analysis. We begin in Section 4.1.1 with an illustration of a typical ringdown event, and explain the various portions of a ringdown event. This is followed in Section 4.1.2 by a thorough description of our methodology for analyzing the individual decay events. In Section 4.1.3, we look at the analysis of an ensemble of ringdown events constituting a measurement data set. Then, we conclude in Section 4.1.4 with a discussion of the shortcomings of alternative analyses from the point of view of a quantitative CRDS experiment.

4.1.1 Introduction to Ringdown Data

In Section 3.4.4, we described how data are collected in our experiment. Briefly, once a
Figure 4.1 - A typical ringdown event as a function of time (top panel). For comparison, a typical laser pulse is plotted in the bottom panel. The ringdown signal begins to rise rapidly around 2 µsec, corresponding to the leading edge of the laser pulse. The digitized ringdown signal appears flat roughly between 3.3 - 7.6 µsec because the detector output voltage exceeds the 5-V digitization limit of the ADC. We see from the bottom panel that the laser pulse has terminated and the signal has returned to the background level by the time $t = 8.0$ µsec. Note that we attenuated the laser pulse more heavily before it was sensed by the detector, and so the ADC signal in the bottom panel does not saturate. In the top panel, the least squares fit to the exponentially-decaying signal is shown as a solid line beginning at time $t = 8.1$ µsec. When the energy inside the ringdown cavity has completely decayed, the ringdown signal returns to the pre-pulse background level.
stable humidity is reached inside the ringdown cell, data may be collected for analysis. This is accomplished by manually tuning the ringdown cavity PZT so that the TEM\textsubscript{00} mode becomes resonant with the laser frequency. As a buffer of data is collected, data are tested against predetermined "save" criteria, such as the mean and standard deviation of the values of the initial intensity \( I_0 \) of the decay events. When the predetermined save criteria are met, the entire buffer of 25 individual ringdown events is saved to disk, along with a header file of ancillary information. The chief observable of a CRDS experiment, the decay time constant, is then determined by analysis of the individual decay events in a measurement data set.

A typical ringdown event as a function of time is plotted in Fig. 4.1 (top panel). For comparison, we have plotted a typical laser pulse in the bottom panel. The initial portion of the event is a 2 \( \mu \)sec-long pretrigger sample representing the quiescent background signal of the infrared detector. The ringdown signal begins to rise rapidly around 2 \( \mu \)sec, corresponding to the leading edge of the laser pulse being injected in the ringdown cavity. The digitized ringdown signal appears flat roughly between 3.3 - 7.6 \( \mu \)sec because the detector output voltage exceeds the \(+5 \) V digitization limit of the ADC. This overload is permitted so as to maximize the signal-to-noise ratio over the decay portion of the ringdown event. A typical laser pulse is plotted in the bottom panel of Fig. 4.1, from which we see that the laser pulse has terminated and the signal has returned to the background level by the time \( t = 8.0 \) \( \mu \)sec. (Note that we attenuated the laser pulse more heavily before it was sensed by the detector, and so the ADC signal in the bottom panel does not saturate.) It is necessary to wait until the AOM shutter has fully closed and the ringdown signal is an exponential decay before beginning the fitting. In the top panel, the least squares fit to the exponentially-decaying signal is shown as a solid line beginning at time \( t = 8.1 \) \( \mu \)sec. Finally, we see that when the energy inside the ringdown cavity has completely decayed (i.e. for \( t \geq 11 \) \( \mu \)sec), the ringdown signal returns to the
pre-pulse background level.

4.1.2 Analysis of Individual Decay Events

We use the Levenberg-Marquardt least-squares minimization algorithm [Press et al., 1992] to fit a fixed portion of each decay curve to the following equation:

\[ I(t) = I_0 \exp \left( -\frac{t}{\tau} \right) + b \]  

(4.1)

where \( I_0 \) is the initial intensity, \( \tau \) is the decay time constant, and \( b \) is the background signal. All three variables are free fit parameters to Eq. (4.1). In contrast to some practices that have been reported for CRDS analysis, we do not average (or "stack") decay events before solving for the decay time constant, nor do we subtract an estimated background signal prior to the fit or take the logarithm of the data. In Section 4.1.4, we discuss some of the pitfalls of such practices to quantitative CRDS. We also note that the data used in the fit are unweighted, in the sense that we assume the standard deviation of the signal, \( \sigma_s \), does not depend on the signal. As we demonstrate below, this assumption appears to be valid based on the residuals to the fit.

For the data we present in this thesis, we have taken the starting point of the fit to be 8.1 \( \mu \)sec from the beginning of the ringdown event, as indicated in Fig. 4.1. A total of 25 data points are used in each fit, so that the fit time window, \( \Delta t \), is 2.4 \( \mu \)sec long. Thus, the effective optical path length of our experiment is \( L_{\text{eff}} = c\Delta t = 720 \text{ m} \). The fit time window corresponds to about \( \Delta t \sim 4\tau \) for most of the data, which is adequate for accurately determining the decay time constant. While the fit time window could be extended further, we have found that our results are not significantly changed except that the analysis takes longer. In Fig. 4.2, we have plotted the portion of the ringdown data from Fig. 4.1 that is used for decay analysis, along with the best fit to Eq. (4.1). For these data, the value of the reduced \( \chi^2 \) is 1.096. The reduced \( \chi^2 \) is given by [Bevington, 1969]:

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Figure 4.2 - In the top panel we plot the decay portion of the ringdown event illustrated in
Fig. 4.1. The data are shown as circles, and the solid line is the least squares fit to Eq. (4.1). The
residuals to the fit are plotted in the lower panel. The value of the reduced $\chi^2 = 1.096$ and the
normal scatter in the residuals indicate that the ringdown data are modeled well by Eq. (4.1) and
display no evidence of systematic effects.
reduced \( \chi^2 = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{\Delta_i}{\sigma_i} \right)^2 \)

where \( n \) is the degrees of freedom, \( \Delta_i \) is the deviation from fit, and \( \sigma_i \) (\( = 1.02 \) ADC counts) is the measured uncertainty of the data. Along with the normal scatter of the residuals (lower panel of Fig. 4.2) having a mean \( \mu_r = 0.0 \) counts and standard deviation \( \sigma_r = 1.0 \) counts, this indicates that the data are modeled well by Eq. (4.1) and display no evidence of systematic effects.

### 4.1.3 Analysis of Ringdown Data Sets

We now turn our attention to a typical measurement data set. The data set we consider consists of an ensemble of 2000 decay events which were obtained in a flow configuration for dry cell conditions at a wavenumber \( \nu = 944.195 \) cm\(^{-1}\). Once the ringdown decay events in a measurement data set have been analyzed, there are several ways to visualize the results so that we can assess the quality of the data. In Fig. 4.3, we present the sequence of 2000 decay constants. The ensemble of decay constants has mean \( \tau = 548.2 \) nsec and standard deviation \( \sigma_\tau = 1.1 \) nsec. The mean value of the uncertainty in decay time constants for the 2000 decay events is \( \langle \sigma_\tau \rangle = 1.0 \) nsec. This agreement between the ensemble statistics and the mean uncertainty of the 2000 decay events is an indication that there are no significant systematic effects evident in the data sets. In Fig. 4.4, the same data are presented in the form of a time series, illustrating that the data were collected over a period of about 150 sec. The 80 vertical striations that can be seen in Fig. 4.4 are the result of the method by which we collect data, and represent the 80 buffers of data in the data set.

In Fig. 4.5, we plot the cumulative probability distribution (CPD) for the decay time constants in the sample data set (circles). The CPD of the decay time constant is the fraction of a set of
Figure 4.3 - Sequence of the 2000 decay time constants for the sample measurement data set. The ensemble of decay constants has mean $\tau = 548.2$ nsec and standard deviation $\sigma_\tau = 1.1$ nsec.
Figure 4.4 - Time series of the 2000 decay time constants for the sample measurement data set. Typically, a measurement data set is collected over a 2-3 minute period. There are 80 vertical striations corresponding to 80 buffers of data, because each buffer of data is given a unique time stamp.
Figure 4.5 - Cumulative probability distribution (CPD) for the decay time constants in the sample data set (circles). The CPD of the decay time constant is the fraction of a set of measurements with a value equal to or less than a given value of $\tau$ as a function of $\tau$. In the top panel, the solid line is the CPD for a normal distribution with mean $\tau = 548.2$ nsec and standard deviation $\sigma_{\tau} = 1.1$ nsec. In the bottom panel, we obtain the Kolmogorov-Smirnov statistic, $D = 0.012$, which indicates that there is less than a 1% probability that the observed distribution of decay time constants is not normal.
Figure 4.6 - Histogram of 50000 residuals (data - fit), corresponding to the 2000 decays × 25 points/decay. The residuals are normally distributed with a mean of 0.0 counts and a standard deviation of 0.94 counts.
Figure 4.7 - Decay time constants for the sample measurement data set, plotted as a function of the signal amplitude. Over a wide range of signal amplitudes, there are no systematic effects apparent in the decay time constants.
measurements with a value equal to or less than a given value of $\tau$ as a function of $\tau$. Also shown in Fig. 4.5 is the calculated CPD for a normal distribution with mean $\tau = 548.2$ nsec and standard deviation $\sigma_{\tau} = 1.1$ nsec (solid line). The level of agreement between the measured and calculated distributions is quantified using the Kolmogorov-Smirnov statistic, $D$, which is defined as the maximum absolute difference between the two distributions [Press et al., 1992]. We find $D = 0.012$, which indicates that there is less than a 1% probability that the measured distribution is not normal. The residuals (data - fit) are also normally distributed, as we show in Fig. 4.6. Note that this plot is a histogram of 50000 residuals, corresponding to 2000 decays $\times$ 25 points/decay.

We also scrutinize our data for correlations between experimental variables. For example, it has recently been reported that an inverse correlation was observed between the decay time constant and the signal amplitude [Bucher et al., 2000]. As we demonstrate in Fig. 4.7, there is no evidence of such a systematic effect in our measurement data sets. We have already discussed a relationship between amplitude and decay time constant at high photon fluxes (cf. Section 3.5.2), but this is clearly a positive correlation which may be related to Auger recombination of charge carriers in HgCdTe infrared detectors. It may also be due to nonlinearity in the detector preamplifier. In any event, this effect is not evident in our data because we attenuate the laser beam in order to avoid the nonlinear signal regime.

### 4.1.4 Alternative Methods of Analysis

Several methods of analyzing ringdown data have been discussed by other investigators. While these methods are often easy to implement and can be efficient ways to obtain a decay time constant, we demonstrate that this is usually at the expense of accuracy and precision, which is paramount in a quantitative CRDS experiment.
One method of analysis involves taking the natural logarithm of the signal after subtracting an estimated background signal, and then obtaining the decay time constant from the slope of a least squares linear fit [Jongma et al., 1995; van Zee et al., 1999]. Using our sample measurement data set, we have calculated decay time constants from the equation:

$$\log(S(t) - b') = a - m \times t$$

(4.3)

where $S(t)$ is the CRDS signal, $b'$ is the estimated background signal, and $a$ and $m$ are the intercept and slope of the least squares fit to a straight line. The decay time constants, $\tau = 1/m$, are plotted in Fig. 4.8 along with the results we obtained using Eq. (4.1). The statistics for the two sets of decay time constants are:

(a.) least squares fit to Eq. (4.1): $\tau = 548.2 \pm 1.1$ nsec

(b.) least squares fit to Eq. (4.3): $\tau = 542.3 \pm 4.8$ nsec

The difference in the values of the decay time constants for cases (a.) and (b.) is significant, and appear to be due to an erroneous estimation of the background signal when Eq. (4.3) is used. In case (b.), we used the quiescent pre-trigger signal to estimate the background, but this value is on average 0.68 counts higher than the fitted background signal ($\sim 50$ counts) we obtain when we fit the data to Eq. (4.1). In case (c.), the estimate of the background signal is taken to be the fitted value obtained using Eq. (4.1):

(c.) least squares fit to Eq. (4.3): $\tau = 548.4 \pm 1.5$ nsec

These results demonstrate that when the correct background is subtracted from the signal, the method of Eq. (4.3) is approximately equivalent to the method of Eq. (4.1). However, we caution that great care must be taken to estimate the background signal properly when Eq. (4.3) is used, since the decay time constant is very sensitive to the background signal estimate.

Another method of analysis involves integrating the CRDS signal in two separate time
Figure 4.8 - Decay time constants for the sample measurement data set, determined by two methods. The solid line represents the original decay time constants determined from Eq. (4.1), while the circles are the decay time constants determined by subtracting an estimated baseline, taking the logarithm of the signal, and fitting a straight line to the data. The latter method leads to an erroneous value of the decay time constant. Also, the data are clearly noisier which limits the performance of the CRDS experiment.
windows along the decay curve [Romanini and Lehmann, 1993]. The decay time constant is then given by:

\[ \tau = -\frac{\Delta t}{\log \left( I(t_A)/I(t_B) \right)} \]  

(4.4)

where \( I(t_A) \) and \( I(t_B) \) are the background-subtracted integrated signals in windows “A” and “B”, which are separated by a time \( \Delta t \). Here, note that window “B” precedes window “A” in time. Following Romanini and Lehmann, we have taken \( \Delta t = 2\tau \) and computed the decay time constants of our measurement data set, using as our estimate of the background signal the fit parameter from the method of Eq. (4.1). Our results are:

(d.) two-window signal integration: \( \tau = 548.2 \pm 1.2 \) nsec

Thus, the two-window signal integration method of obtaining the decay time constant appears to give similar results to the method of Eq. (4.1) and can be very useful when digitization of the signal is not practical. However, the method suffers from the same problem as the method of Eq. (4.3): the decay time constant will be very sensitive to the estimate of the background signal, and erroneous results will be obtained if great care is not taken to estimate the background signal properly.

To summarize, we have developed an approach for the analysis of ringdown data which is based on the principle of individual analysis of CRDS decay events in linear space (as opposed to logarithmic space), by finding the nonlinear least squares fit to an exponential function. This approach is integral to the success of the quantitative infrared CRDS experiment, as our application requires us to carefully characterize our experimental signals in order to extract the decay time constant with both high accuracy and precision. None of the alternative methods of analysis we have considered would have been entirely satisfactory for measurements of the water vapor continuum. However, our approach is not the easiest to implement. For example, in order to analyze a large data
set of individual decay events, we require a DAQ which can adequately sample the decay waveforms at a high repetition rate, and also transfer a high volume of data to a PC hard drive in near real-time.

4.2 Water Vapor Absorption Measurements

In this section, we present water vapor absorption measurements made using the infrared CRDS experiment. We begin with a brief review of our methodology, followed by a description of our method of analysis. Following this, we present our measurements for the 10P(34), 10P(20), and 10R(10) lines of the CO₂ laser. Our results are summarized in Section 4.2.5.

4.2.1 Introduction to the Measurements

During the testing phase of the infrared CRDS experiment, we established that the decay time constants dropped by a realistic amount when water vapor was introduced in the nitrogen gas flow through the ringdown cell, based on previous measurements of water vapor continuum absorption by other investigators near 944 cm⁻¹. In addition, we found that when we purged the ringdown cell by switching to a dry nitrogen flow, the mean decay time constant returned to the original value. Satisfied that the apparatus was stable, we adopted an efficient methodology for absorption measurements whereby we primarily characterize the dry decay time constants prior to making a series of water vapor absorption measurements. We did purge the cell and measure the dry decay time constants following our water vapor absorption measurements at the end of each day. These dry-cell measurements were made at a single cell pressure (rather than the full pressure scans described in Section 3.5.3) because they were simply intended to confirm that there had not been a shift in the dry decay time constants.

The experimental baseline was obtained by pressure scanning the ringdown cavity over
several values of pressure. By scanning the pressure in our cavity, the resonant frequency is shifted so that a change to the PZT voltage is required to bring the cavity into resonance with the laser frequency. The dry decay time constants, which are a function of PZT voltage, were then fitted to a sine function:

\[
\tau(V_{PZT}) = \tau_0 + A_\tau \sin \left( \frac{2\pi V_{PZT}}{V_{2\pi}} + \phi_\tau \right) \tag{4.5}
\]

where \(\tau_0\) is the DC offset to the baseline modulation, \(A_\tau\) is the amplitude of the modulation, \(V_{2\pi}\) is the period of the modulation and \(\phi_\tau\) is the phase of the modulation with respect to \(V_{PZT} = 0\). It is not possible to obtain a function \(\tau_0(V_{PZT})\) which can be universally applied, because the CO₂ laser PZT has to be occasionally tuned to maintain peak laser power and mode quality. Unfortunately, once the laser PZT is adjusted, the function \(\tau_0(V_{PZT})\) is no longer applicable as the phase \(\phi_\tau\) will have shifted. Our procedure, therefore, has been to quickly scan the dry cavity (i.e. before a laser PZT adjustment is required) in order to obtain data to fit to Eq. (4.5), as shown in Fig. 4.9. We then take \(\tau_0\) to be the mean dry decay time constant for our measurements.

Ideally, the same procedure should be followed with the humid values of decay time constants, which are similarly modulated. However, it is impractical to follow this procedure with our apparatus for every measurement we make. As a result, any humid data set of decay time constants is obtained on a pseudo-random part of the sine function. While this inevitably introduces a small systematic bias to any single absorption coefficient determined from Eq. (3.14), it is nevertheless possible to determine \(C_s^0\) and \(C_n^0\) from Eq. (2.9) without significant bias provided that enough humid data sets are collected. To test this assumption, we recalculated our results at 944 cm⁻¹ (cf. Section 4.2.3) using only every other data point, and found the recalculated values \(C_s^{0*}\) and \(C_n^{0*}\) were within 5% of the values of \(C_s^0\) and \(C_n^0\) we determined using all of our data.
As we have already discussed, each humid data set is derived from 2000 decay events. Once these events have been individually analyzed, we calculate the mean decay time constant of the ensemble. The mean decay time constant is then used in Eq. (3.14) to determine the mean absorption coefficient $k$ of the measurement. Each absorption coefficient is associated with mean values of total pressure $p$, water vapor partial pressure $e$, and temperature $T$, which were measured inside the ringdown cell.

The water vapor absorption coefficient $k(e,p,T)$ is the sum of continuum and local line absorption coefficients, as we discussed in Section 2.2. While we have deliberately chosen CO$_2$ laser wavenumbers where local line absorption is weak relative to continuum absorption, it is nevertheless necessary to subtract local line absorption from the measured absorption coefficient. We have performed line-by-line absorption calculations using water vapor line parameters from the HITRAN 2000 database within $\pm 25$ cm$^{-1}$ of the laser wavenumber, and subtracted the computed local line absorption from the measured absorption to obtain $k_c(e,p,T)$, the continuum absorption coefficient. Based on reported water vapor line strength uncertainties in the 700 - 1250 cm$^{-1}$ region [Rothman et al., 1998], the local line absorption coefficient has an approximate uncertainty of $\pm 20\%$.

Once we have a set of continuum absorption coefficients $k_c(e,p,T)$, our next step is to analyze the data in terms of the $C_s^0$ and $C_n^0$, the continuum coefficients of self- and nitrogen-broadening at 296 K. We do this by solving a system of linear equations of the form given by Eq. (2.9), where we explicitly include the temperature dependence of the continuum coefficients. For the self-broadened continuum, we adopt the temperature dependence model of Eq. (2.10) with the characteristic temperature $T_0 = 1900$ K. Meanwhile, the temperature dependence of the nitrogen-broadened continuum is believed to be small and so we assume $C_n = C_n^0$ for the small deviations from 296 K of our experiment. Finally, we note that our solution to the system of linear equations of the form
given by Eq. (2.9) is entirely in terms of $C_s^0$ and $C_a^0$. There are no other free parameters involved in the solution.

The discrete nature of CO$_2$ laser transitions prevents us from observing the complete continuum spectrum. However, it is reasonable to assume that the water vapor continuum varies slowly with wavenumber, and so the continuum spectrum can be adequately characterized from observations at relatively coarse wavenumber intervals. We now present our measurements of the water vapor continuum, which were made at three different wavenumbers: 931, 944, and 969 cm$^{-1}$.

4.2.2 Continuum Absorption at 931 cm$^{-1}$

We have measured the water vapor continuum with the CO$_2$ laser tuned to the 10P(34) line, which has a wavenumber of 931.002 cm$^{-1}$. The data which we have used to determine the experimental baseline are shown in Fig. 4.9. When these data are fitted to Eq. (4.5), we find that the DC offset is 529.7 nsec and the amplitude of the baseline modulation is 1.3 nsec. Thus, we take the mean dry decay time constant to be $\tau_0 = 529.7 \pm 1.3$ nsec.

We have made a total of 39 measurements of water vapor continuum absorption at 931 cm$^{-1}$, at a mean temperature of 297.5 ± 0.5 K and with total cell pressures ranging from 107 - 108 kPa (1.057 - 1.068 atm). Each measurement corresponds to a different value of the water vapor partial pressure in the gas flow, which was systematically varied from 0.21 - 2.25 kPa (0.0021 - 0.022 atm), corresponding to relative humidities from 7 - 73%.

Our measured absorption coefficients are plotted in Fig. 4.10 as a function of the water vapor partial pressure. Representative 1-$\sigma$ error bars are shown which correspond to the uncertainty in the absorption coefficients due to the decay time constant measurements. The thick solid curve is the best fit of the data to Eq. (2.9), while the dashed line represents local line absorption. The continuum

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Figure 4.9 - Experimental baseline for the water vapor continuum absorption measurements at 931.002 cm$^{-1}$. The mean dry decay time constant is $\tau_0 = 529.7$ nsec.
Figure 4.10 - Water vapor continuum absorption coefficients for 931.002 cm\(^{-1}\) and 297.5 K. The ‘X’ are the measured continuum absorption coefficients \(k_c\), while the dashed line is the calculated local line absorption coefficient \(k_l\). The thin solid line indicates the zero point of the absorption axis. The thick solid line is the least squares fit of the measured absorption coefficients to Eq. (2.9). 1-\(\sigma\) experimental error bars are shown for low and high humidities. We note the appearance of a sinusoidal variation in the absorption coefficients (see also Fig. 4.14), which is due to the uncorrected effect of baseline modulation on the humid decay time constants (see text).
coefficients of self- and nitrogen-broadening, corrected to 296 K, are found to be:

\[ C_v^0(931 \text{ cm}^{-1}) = 2.25 \pm 0.18 \times 10^{-22} \text{ molecules}^{-1} \text{ cm}^2 \text{ atm}^{-1} \]

\[ C_n^0(931 \text{ cm}^{-1}) = 1.22 \pm 0.29 \times 10^{-24} \text{ molecules}^{-1} \text{ cm}^2 \text{ atm}^{-1} \]

where the uncertainties are the standard deviations of the coefficients to the fit.

### 4.2.3 Continuum Absorption at 944 cm\(^{-1}\)

We have measured the water vapor continuum with the CO\(_2\) laser tuned to the 10P(20) line, which has a wavenumber of 944.195 cm\(^{-1}\). The data which we have used to determine the experimental baseline are plotted in Fig. 4.11. When these data are fitted to Eq. (4.5), we obtain a mean dry decay time constant of \( \tau_0 = 547.7 \pm 1.5 \text{ nsec} \).

We have made a total of 88 measurements of water vapor continuum absorption at 944 cm\(^{-1}\), at a mean temperature of 294.2 ± 0.5 K and with total cell pressures ranging from 107 - 109 kPa (1.054 - 1.074 atm). Each measurement corresponds to a different value of the water vapor partial pressure in the gas flow, which was systematically varied from 0.13 - 1.75 kPa (0.0014 - 0.017 atm), corresponding to relative humidities from 5 - 69%.

Our measured absorption coefficients are plotted in Fig. 4.12 as a function of the water vapor partial pressure. The thick solid curve is the best fit of the data to Eq. (2.9), while the dashed line represents local line absorption. The continuum coefficients of self- and nitrogen-broadening, corrected to 296 K, are found to be:

\[ C_v^0(944 \text{ cm}^{-1}) = 2.01 \pm 0.14 \times 10^{-22} \text{ molecules}^{-1} \text{ cm}^2 \text{ atm}^{-1} \]

\[ C_n^0(944 \text{ cm}^{-1}) = 0.85 \pm 0.17 \times 10^{-24} \text{ molecules}^{-1} \text{ cm}^2 \text{ atm}^{-1} \]
Figure 4.11 - Experimental baseline for the water vapor continuum absorption measurements at 944.195 cm$^{-1}$ (these data are the same we presented in Fig. 3.37). The mean dry decay time constant is $\tau_0 = 547.7$ nsec.
Figure 4.12 - Water vapor continuum absorption coefficients for 944.195 cm\(^{-1}\) and 294.2 K. The 'X' are the measured continuum absorption coefficients \(k_c\), while the dashed line is the calculated local line absorption coefficient \(k_l\). The thin solid line indicates the zero point of the absorption axis. The thick solid line is the least squares fit of the measured absorption coefficients to Eq. (2.9). \(1-\sigma\) experimental error bars are shown for low and high humidities.
4.2.4 Continuum Absorption at 969 cm\(^{-1}\)

We have measured the water vapor continuum with the CO\(_2\) laser tuned to the 10R(10) line, which has a wavenumber of 969.104 cm\(^{-1}\). The data which we have used to determine the experimental baseline are plotted in Fig. 4.13. When these data are fitted to Eq. (4.5), we obtain a mean dry decay time constant of \(\tau_0 = 514.2 \pm 1.4\) nsec.

We have made a total of 39 measurements of water vapor continuum absorption at 969 cm\(^{-1}\), at a mean temperature of 295.1 \(\pm\) 0.5 K and with total cell pressures ranging from 108 - 109 kPa (1.071 - 1.078 atm). Each measurement corresponds to a different value of the water vapor partial pressure in the gas flow, which was systematically varied from 0.19 - 1.96 kPa (0.0019 - 0.019 atm), corresponding to relative humidities from 7 - 74%.

Our measured absorption coefficients are plotted in Fig. 4.14 as a function of the water vapor partial pressure. The thick solid curve is the best fit of the data to Eq. (2.9), while the dashed line represents local line absorption. The continuum coefficients of self- and nitrogen-broadening, corrected to 296 K, are found to be:

\[
C_s^0(969\text{ cm}^{-1}) = 1.80 \pm 0.19 \times 10^{-22}\text{ molecules}^{-1}\text{ cm}^2\text{ atm}^{-1}
\]

\[
C_n^0(969\text{ cm}^{-1}) = 0.53 \pm 0.27 \times 10^{-24}\text{ molecules}^{-1}\text{ cm}^2\text{ atm}^{-1}
\]

4.2.5 Summary of results

Our objective was to develop a quantitative infrared CRDS experiment capable of making accurate room-temperature measurements of water vapor continuum absorption in the thermal infrared window region. As we discussed in Section 2.7, we have compiled an intercomparison of the water vapor continuum measurements known to us. In the intercomparison, we found measurement uncertainties of 18% and 71% for the continuum coefficients of self- and foreign-
Figure 4.13 - Experimental baseline for the water vapor continuum absorption measurements at 969.104 cm⁻¹. The mean dry decay time constant is $\tau_0 = 514.2$ nsec.
Figure 4.14 - Water vapor continuum absorption coefficients for 969.104 cm$^{-1}$ and 295.1 K. The 'X' are the measured continuum absorption coefficients $k_c$, while the dashed line is the calculated local line absorption coefficient $k_l$. The thin solid line indicates the zero point of the absorption axis. The thick solid line is the least squares fit of the measured absorption coefficients to Eq. (2.9). 1-$\sigma$ experimental error bars are shown for low and high humidities. We note the appearance of a sinusoidal variation in the absorption coefficients (see also Fig. 4.10), which is due to the uncorrected effect of baseline modulation on the humid decay time constants (see text).
broadening, respectively. We have measured the water vapor continuum using infrared CRDS for three wavenumbers ranging from 931 - 969 cm$^{-1}$. Our results are summarized in Table 4.1. Our continuum coefficients of self- and nitrogen-broadening at 944 cm$^{-1}$ have approximate uncertainties of 7% and 20%, respectively, demonstrating that CRDS is capable of making high precision measurements of the infrared water vapor continuum.

4.3 Discussion

Other investigators have demonstrated that CRDS is a high performance spectroscopic technique in the visible region of the spectrum that is capable of high accuracy and sensitivity to weak absorption [van Zee, 1999]. However, the infrared region of the spectrum is the most important for atmospheric radiative transfer applications. With the development of our infrared CRDS experiment, we have successfully extended the range of CRDS into the thermal infrared region near 1000 cm$^{-1}$. Our measurements of water vapor continuum absorption demonstrate that CRDS can be a powerful tool for quantitative infrared spectroscopy.

In this section, we discuss the significance of our measurements. We begin with a discussion of the accuracy of our measurements (Section 4.3.1). In Section 4.3.2, our results are plotted along with continuum coefficients derived from the far wing line shape theory of Ma and Tipping. The generally good agreement with our measured values suggests that far wing absorption is the primary mechanism of the water vapor continuum. However, in Section 4.3.3, we present evidence that the excess absorption we observe near 930 cm$^{-1}$ may be due to water vapor dimers. Finally, in Section 4.3.4, we demonstrate that so-called empirical models of the water vapor continuum are not in agreement with our observations.
<table>
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<th>v [cm⁻¹]</th>
<th>Number of Measurements</th>
<th>T [K]</th>
<th>Range of Water Vapor Partial Pressures [kPa]</th>
<th>Cₗ₀ [10⁻²² molecules⁻¹ cm⁻² atm⁻¹]</th>
<th>Cₐ₀ [10⁻²⁴ molecules⁻¹ cm⁻² atm⁻¹]</th>
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<td>39</td>
<td>297.5</td>
<td>0.21 - 2.26</td>
<td>2.25 ± 0.18</td>
<td>1.22 ± 0.29</td>
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<td>88</td>
<td>294.2</td>
<td>0.14 - 1.75</td>
<td>2.01 ± 0.14</td>
<td>0.85 ± 0.17</td>
</tr>
<tr>
<td>10R(10)</td>
<td>969.104</td>
<td>39</td>
<td>295.1</td>
<td>0.19 - 1.95</td>
<td>1.80 ± 0.19</td>
<td>0.53 ± 0.27</td>
</tr>
</tbody>
</table>

Table 4.1 - Summary of water vapor continuum absorption measurements.
4.3.1 Accuracy of Measurements

It is difficult to establish our experimental accuracy by comparison with calculations, as there is no ab initio theory of the water vapor continuum. However, it is possible to estimate the accuracy of our measurements by comparing our data with the results from other experiments. In Section 2.7, we presented the results of an intercomparison of all water vapor continuum measurements known to us, near 296 K and 944 cm⁻¹. From this intercomparison, we determined that the water vapor continuum absorption measurements with the highest accuracy (and also the ones most similar to our own) were likely to be those involving a CO₂ laser and a multi-pass cell. In Table 4.2, we compare data from these experiments with our results. Note that we have not included error estimates for the measurements of other investigators, because none were provided in the references we cite. The uncertainties in the LMPL mean values of C₅₀ and C₆₀ are the standard deviations of the LMPL measurements.

The continuum coefficients of self- and nitrogen-broadening derived from experiments employing CO₂ lasers and multi-pass cells are both found to be in excellent agreement with our measured values. Our value of C₅₀ = 2.01 × 10⁻²² molecule⁻¹ cm² atm⁻¹ is in exact agreement with the LMPL mean, while our value of C₆₀ = 0.85 × 10⁻²⁴ molecule⁻¹ cm² atm⁻¹ is within 3% of the LMPL mean value. We consider this to be excellent agreement because the nitrogen-broadened continuum absorption is of order 10⁷ cm⁻¹ for typical atmospheric conditions, and this is very close to the detection limit for most White cell experiments. Based on the agreement of continuum coefficients of self- and nitrogen-broadening with LMPL data, we conclude that our absorption coefficient measurements are probably accurate to within the uncertainty of our measurements, ± 1 × 10⁻⁷ cm⁻¹. This is a significant achievement, since the volume of our ringdown cell is a fraction of the volume of the White cells used in the LMPL experiments.
Table 4.2 - Comparison of our results at 944 cm⁻¹ with independent results from the LMPL technique. Also shown are the cell volumes and effective path lengths of the experiments. We have not included uncertainties for the individual LMPL measurements of $C^0_s$ and $C^0_n$ because the investigators did not report their measurement errors. The uncertainty in the mean values of the LMPL data represents the standard deviation of the reported coefficients, not experimental error.
Finally, we point out that we are unaware of any data from other experiments using CO$_2$ lasers and multi-pass cells to compare with our results at 931 and 969 cm$^{-1}$. However, there is no reason why the accuracy of our infrared CRDS experiment at 944 cm$^{-1}$ should not extend to other wavenumbers accessible to our apparatus.

4.3.2 Origin of the Water Vapor Continuum

The origin of the water vapor continuum has been the subject of debate for more than 30 years [Varanasi, 1988]. There are probably two major reasons why the issue has been unresolved until now. First, there has been a real lack of accurate experimental data and second, advances in far wing line shape theories have been slow to develop. In Section 2.6, we discussed two competing hypotheses of the water vapor continuum: the far wing and dimer hypotheses. Proponents of the dimer hypothesis argue that water vapor dimers form under atmospheric conditions, and that they exhibit a continuum-like absorption in the 800 - 1200 cm$^{-1}$ region. Meanwhile, proponents of the far wing hypothesis maintain that the far wings of the water vapor lines in the pure rotational and vibration-rotation bands on either side of the infrared window accumulate to form the water vapor continuum absorption.

Recently, there has been significant progress in the development of line shape theories based on the quasistatic approximation [Tipping and Ma, 1995; Ma and Tipping, 1999; Ma and Tipping, 2000]. We have already discussed the line shape theory in Section 2.6, and so we simply point out that while the impact approximation assumes collisions are instantaneous, the quasistatic approximation assumes collisions of infinite duration. They are therefore complementary approximations, as line shape theories (e.g. Lorentz) based on the impact approximation are valid near the centers of absorption lines, while line shape theories based on the quasistatic approximation...
are applicable in the far wings.

While dimer absorption has received a great deal of attention (e.g. [Gebbie et al., 1969]), it unfortunately remains a mostly qualitative theory based on the assumption that the strong negative temperature dependence and quadratic partial pressure dependence of the self-broadened continuum can only be explained by the presence of atmospheric water dimers. As we discussed in Section 2.6, predictions of water dimer concentrations for atmospheric temperatures range over two orders of magnitude, and little is known about the spectrum of the water dimer in the 1000 cm$^{-1}$ window region. Therefore, we cannot make a quantitative comparison of our data with predictions from the dimer model.

In Fig. 4.15, we compare our measurements of the continuum coefficients of self-broadening to the self-broadened far wing line shape theory of Ma and Tipping [Ma and Tipping, 1999]. The square datum at 944 cm$^{-1}$ represents the mean LMPL value. Also shown are calculations of the Lorentz far wing absorption (dotted line), demonstrating that the simpler impact approximation theories do not reproduce the observed continuum. However, the theory of Ma and Tipping, based on the quasistatic approximation, is in very good agreement with our results. This is a strong indication that far wing absorption, and not dimer absorption, is the correct explanation of the water vapor continuum. The discrepancy between our results and Ma and Tipping near 930 cm$^{-1}$ is interesting, and we shall return to this point in Section 4.3.3.

In Fig. 4.16, we plot our measurements of the continuum coefficients of nitrogen-broadening along with the nitrogen-broadened far wing line shape theory of Ma and Tipping [Ma and Tipping, 2000]. Again, we have included the mean LMPL value at 944 cm$^{-1}$, along with calculations of the nitrogen-broadened Lorentz wing absorption. The far wing theory of Ma and Tipping predicts significantly less absorption than we observe, and does not drop as rapidly with wavenumber as our
Figure 4.15 - Continuum coefficients of self-broadening in the 900 - 1000 cm⁻¹ region. Our measurements are shown as '*' with accompanying error bars. The square at 944 cm⁻¹ denotes the mean LMPL value. The solid line represents the far wing line shape theory of Ma and Tipping [1999]. For comparison, we have included the Lorentz far wing continuum (dotted line), demonstrating that the Lorentz line shape does not model the observed self-broadened continuum.
Figure 4.16 - Continuum coefficients of nitrogen-broadening in the 900 - 1000 cm\(^{-1}\) region. Our measurements are shown as '*' with accompanying error bars. The square at 944 cm\(^{-1}\) denotes the mean LMPL value. The solid line represents the far wing line shape theory of Ma and Tipping [2000]. For comparison, we have included the Lorentz far wing continuum (dotted line), demonstrating that the Lorentz line shape does not model the observed nitrogen-broadened continuum.
measurements. The agreement between theory and our data is not as convincing as it is for the self-
broadened continuum. Nonetheless, water dimer absorption has no role in the nitrogen-broadened
continuum, and it is unlikely to result from any mechanism other than far wing absorption. Clearly,
there are large experimental errors associated with the nitrogen-broadened data, and these
uncertainties need to be reduced with improved experimental techniques. However, there are also
large uncertainties in the nitrogen-broadened far wing theory of Ma and Tipping, and the theory
should be re-examined to see if improvements can be made to give better agreement with the best
available data in the 900 - 1000 cm\(^{-1}\) region.

4.3.3 Possible Water Dimer Absorption Near 930 cm\(^{-1}\)

To the best of our knowledge, no absorption feature in the 900 - 1000 cm\(^{-1}\) region has ever
been assigned to a water dimer transition. However, the divergence of our absorption measurement
near 930 cm\(^{-1}\) with the far wing theory which can be seen in Fig. 4.15 is interesting, because the
discrepancy may be the result of a combination band of the water vapor dimer. Given that there are
6 high-frequency intra-molecular and 6 low-frequency intermolecular vibrational bands associated
with the water dimer (cf. Section 2.6.2), numerous combination bands are likely to exist. Theoretical
estimates of the wavenumbers and relative intensities of the water vapor dimer absorption bands
have been made by Vigasin [Vigasin, 1983]. One interesting combination involves the relatively
intense \(v_2\) intra-molecular band at 1600 cm\(^{-1}\) and the \(v_{12}\) and \(v_{14}\) intermolecular librational bands
at 383 and 287 cm\(^{-1}\). Consider a combination band of the form \(\Omega_{cb} = \Omega_i - (\Omega + \Omega')\), where \(\Omega_{cb}\) is the
combination band center (cm\(^{-1}\)), \(\Omega_i\) is the intra-molecular vibration band center (cm\(^{-1}\)), and \(\Omega\) and
\(\Omega'\) are intermolecular vibration band centers (cm\(^{-1}\)). Substituting the values above, we obtain:

\[\Omega_{cb} = 1600 - (383 + 287) = 930 \text{ cm}^{-1}\]
suggesting there might be a dimer combination band centered near 930 cm\(^{-1}\). However, we note that there is a significant uncertainty associated with our prediction of the combination band position, as we are unaware of any experimental data confirming the librational band centers.

If such a dimer absorption band existed, it would have the same quadratic partial pressure dependence as the self-broadened far wing continuum. Additional measurements in the vicinity of 930 cm\(^{-1}\) are necessary to make our finding more conclusive and to better determine the width and center of the possible dimer band. If further observations support the existence of a dimer absorption band near 930 cm\(^{-1}\), it would be very significant as it would represent the first time an experiment has positively identified both dimer and far wing contributions to the water vapor continuum.

On the other hand, some of the apparent discrepancy between our observations and the far wing continuum could be due to uncertainties in the intermolecular potential of water. This is because the wavenumber dependence of the quasistatic far wing line shape theory is sensitive to uncertainties in the intermolecular potential of water [Ma, 2001]. This possibility needs to be investigated further.

### 4.3.4 Empirical Models of the Water Vapor Continuum

Empirical models of the water vapor continuum are normally used in atmospheric radiative transfer calculations for two main reasons. First, they are computationally efficient compared to line-by-line far wing absorption calculations. Second, it is generally recognized that the far wings of conventional line shapes (e.g. Lorentz) do not model the water vapor continuum in a realistic way, as we have demonstrated in Fig. 4.15 and Fig. 4.16. In the absence of a validated theory of the water vapor continuum, the empirical models were intended to generate continuum absorption coefficients which were in agreement with observations of continuum absorption for radiative transfer codes.
Two empirical models of the water vapor continuum are in widespread use. One model [Roberts et al., 1976], hereafter RSB, is mostly derived from the early laboratory spectrometer data of Burch. The main virtue of the RSB empirical model is its simplicity: only two formulae are used to describe water vapor continuum absorption. In the RSB model, the spectral dependence of the self-broadened continuum is given by:

\[ Q^0(\nu) = a + b \exp(-\beta \nu) \]  

(4.6)

where the fit parameters are:

\[ a = 1.25 \times 10^{-22} \text{ molecules}^{-1} \text{ cm}^2 \text{ atm}^{-1} \]

\[ b = 1.67 \times 10^{-19} \text{ molecules}^{-1} \text{ cm}^2 \text{ atm}^{-1} \]

and

\[ \beta = 7.87 \times 10^{-3} \text{ cm}. \]

The RSB model includes the temperature dependence of Eq. (2.10), with the characteristic temperature \( T_0 = 1800 \text{ K} \). Notably absent from the RSB model are expressions for the continuum coefficients of foreign-broadening. This is because when the model was developed, little was known about the foreign-broadened continuum. Finally, we note that the RSB model is only valid in the 800 - 1200 cm\(^{-1}\) region.

The more recent CKD model [Clough et al., 1989] is also largely based on Burch’s data, but various unspecified field observations have been used to refine the model. Therefore, neither model appears to incorporate the results from LMPL experiments, which we found to be the most accurate data in the intercomparison we presented in Section 2.7. In the CKD model, the water vapor continuum is modeled as the accumulation of Lorentzian lines which are modified in the far wings by an empirical \( \chi \)-factor. The empirical line shape, derived from a best fit to data in various regions of the spectrum below 2500 cm\(^{-1}\), is assumed to be applicable throughout the spectrum. Rather than
providing computationally intensive formulae, the CKD model provides fast look-up tables of continuum absorption coefficients. The CKD model includes both self- and foreign-broadened continua. In order to model the temperature dependence of the self-broadened continuum, the CKD model extrapolates continuum coefficients obtained at 296 and 338 K down to 260 K.

As we demonstrate in Fig. 4.17, both the RSB and CKD models have continuum coefficients of self-broadening which are significantly larger than our measured values. The dashed line is the CKD 2.4 model, while the dotted line is the RSB model. The CKD model appears to have the correct wavenumber dependence in the 900 - 1000 cm\(^{-1}\) region, but the self-broadened absorption coefficients in CKD would have to be scaled down by factors of 0.88 to give the best agreement with experimental data. The RSB model does not appear to have the correct wavenumber dependence, and the self-broadened absorption coefficients are roughly 9% higher than the experimental data.

In Fig. 4.18, we see that the situation is even worse when we compare our continuum coefficients of nitrogen-broadening with the empirical models. The dashed line is the CKD 2.4 model, while the RSB model is not shown as it does not include nitrogen-broadening. In this case, the agreement with experimental data is so poor we have plotted the data on a logarithmic scale. The CKD model appears to have roughly the correct wavenumber dependence in the 900 - 1000 cm\(^{-1}\) region, but the nitrogen-broadened absorption coefficients in CKD need to be multiplied by a factor of approximately 200 in order to give reasonable agreement with experimental data.

In Chapter 1, we discussed an application of radiative transfer calculations using an empirical model, where it was suggested that the observed nonlinear rise in the greenhouse effect with surface temperature may be due to the water vapor continuum. Given the seriousness of the problems that are being addressed with radiative transfer calculations and the practical necessity (at least for the time being) of employing empirical models of the water vapor continuum, it is imperative that these
Figure 4.17 - Comparison of our continuum coefficients of self-broadening with empirical models of the water vapor continuum. The dashed line is the CKD 2.4 model [Clough et al., 1989], while the dotted line is the RSB model [Roberts et al., 1976]. The CKD model appears to have the correct wavenumber dependence in the 900-1000 cm\(^{-1}\) region, but the self-broadened absorption coefficients in CKD should be lowered by 12% to give the best agreement with experimental data. The RSB model does not appear to have the correct wavenumber dependence, and the self-broadened absorption coefficients are roughly 9% higher than the experimental data.
Figure 4.18 - Comparison of our continuum coefficients of nitrogen-broadening with empirical models of the water vapor continuum. The dashed line is the CKD 2.4 model [Clough et al., 1989], while the RSB model [Roberts et al., 1976] does not include nitrogen-broadening. In this case, the agreement with experimental data is so poor we have plotted the data on a logarithmic scale. The CKD model has roughly the correct wavenumber dependence in the 900 - 1000 cm$^{-1}$ region, but the nitrogen-broadened absorption coefficients in CKD need to be multiplied by 210 in order to give the best agreement with experimental data.
empirical models are as accurate as possible. One obvious way to improve the empirical models would be to incorporate more accurate data into the existing models. An alternative approach might be to develop a new empirical model based on the Ma and Tipping far wing line shape. Such a model would have the advantage that, like CKD, it could be applied across the spectrum. And based on the comparisons we have presented with our experimental data, an empirical model based on the Ma and Tipping theory would fare better than the existing models. While this model would naturally not include any dimer absorption, this could always be added as an additional term if further investigations succeed in quantifying dimer absorption.

4.4 Recommended Improvements

There are several possible areas for improvement of the infrared CRDS experiment. One of the easiest improvements to implement involves replacing the existing mirrors (R = 0.994) with new mirrors (R = 0.998). Based on the longer decay constants we would obtain, making this simple improvement has the potential to lower the minimum detectable absorption coefficient of the experiment by an order of magnitude:

\[
R = 0.994 \text{ mirrors: } k_{\text{min}} = 1.4 \times 10^7 \text{ cm}^{-1}
\]
\[
R = 0.998 \text{ mirrors: } k_{\text{min}} = 1.5 \times 10^8 \text{ cm}^{-1}
\]

In the photoacoustic spectroscopy experiments of Hinderling et al. [1987], these authors reported having attained a sensitivity limit of \( k_{\text{min}} = 3 \times 10^8 \text{ cm}^{-1} \). Thus, the expected sensitivity of our improved CRDS experiment would exceed the best reported value we have found for a spectroscopy experiment near 1000 cm\(^{-1}\). In addition, mirrors of higher reflectivity have the potential to further improve our sensitivity through a reduction of the decay time constant noise. If the baseline modulation we have observed in our apparatus is an etalon effect caused by reflections from the back

-202-
surfaces of the mirrors, then using higher reflectivity mirrors may result in proportionately less intra-cavity energy being available to reflect off of the secondary mirror surfaces. We have recently received a new set of $R = 0.998$ mirrors, and expect to install them in our apparatus soon.

The sensitivity gains we anticipate from our new mirrors should permit us to investigate some interesting and poorly-characterized aspects of the water vapor continuum. For example, the foreign-broadened water vapor continuum could be studied quantitatively. Few experiments have demonstrated the required sensitivity to measure the foreign-broadened continuum, and we are only aware of a single experiment that attempted to determine the influence of oxygen on foreign-broadening [Nordstrom et al., 1978]. However, these measurements would be essential for radiative transfer applications, as there are many regions of the atmosphere where the foreign-broadened continuum tends to dominate over the self-broadened continuum, such as the mid-latitudes and the upper troposphere. Such data are especially important since the foreign-broadened continuum is not properly accounted for in empirical models of the water vapor continuum, and significant discrepancies still exist between far wing line shape theories and existing data.

The performance of the experiment may also be improved in other ways. For example, it would be desirable to have the ringdown cavity frequency automatically track the long-term drift of the CO$_2$ laser frequency. Presently, the ringdown cavity frequency is tuned by manual adjustment of the PZT voltage. The easiest way to automatically track the laser frequency is to have the computer scan the ringdown cavity PZT and locate the TEM$^{00}$ transmission peak. We have already experimented with modifications to the scan program that permit it to collect and record ringdown data while it scans over a narrow range of PZT voltages centered about the TEM$^{00}$ peak voltage. Unfortunately, the volume of data collected is low because only a single buffer of data is saved per scan, and each scan of the PZT takes roughly 10 sec. This contrasts with manual PZT tuning, where
data can be collected and stored at a rate of 2-3 buffers/sec.

Nevertheless, we are interested in making further improvements to the frequency tracking capability of our apparatus. This would permit CRDS signals to be more easily monitored in dynamic situations, such as when we make adjustments to the humidity in the ringdown cell. This could accelerate data collection in water vapor continuum absorption experiments even further, because the system would be capable of continuously recording decay time constants as the cell humidity is varied.

In addition to automating the frequency tracking, we are considering automating the humidity control in the gas stream. Presently, the humidity is controlled by adjusting two manual hand valves in the dry and humid gas paths. We have found it difficult to obtain exactly the desired humidity in the gas stream, because the humidity level in the ringdown cell is rather sensitive to adjustments of the hand valves. As a result of this, the humidity values of our water vapor continuum data sets are not evenly separated and there are gaps where it would have been desirable to obtain better coverage. We think we can improve our humidity sampling by replacing the hand valves with two mass flow controllers. The output flow rate of the mass flow controllers is determined by an input voltage that can easily be computer-controlled via the analog output channels of the PCI-6035E DAQ. Having the ability to make fine adjustments to the humidity in the gas stream would facilitate the task of frequency tracking, since the refractive index changes would not be so abrupt. It could also help us to get adequate coverage of humidity when we make our anticipated low-temperature measurements of the water vapor continuum.

One of the ultimate objectives of our experiment is to make accurate measurements of the temperature dependence of the water vapor continuum for realistic atmospheric temperatures. It is important to accurately characterize the temperature dependence because the atmosphere is not held
at a fixed temperature. The water vapor continuum makes its most significant contribution to radiative transfer in the troposphere, where temperatures range from about 250 - 310 K. Such low-temperature measurements require especially high sensitivity, because the saturation vapor pressure of water is an exponential function of temperature (cf. Fig. 3.13). We are only aware of two laboratory investigations of the water vapor continuum spanning the range 260 - 300 K [Loper et al., 1983; Hinderling et al., 1987]. These data, shown in Fig. 2.6 along with the lone atmospheric data set, constitute all that is known about the temperature dependence of the water vapor continuum. However, the photoacoustic spectroscopy data suffer from large uncertainties as well as questions about the accuracy of the technique.

Presently, our infrared CRDS experiment lacks temperature control, which limits us to collecting our data at the ambient laboratory temperature. The problem of temperature control is a very difficult one for the large volume White cells that have been used to measure continuum absorption, and these experiments are almost always restricted to making room-temperature measurements. Fortunately, it is not especially difficult to control the temperature inside a small-volume spectroscopic cell. One way of cooling the ringdown cell would be to wrap it in a loop of copper tubing, and circulate a low-temperature coolant such as ethylene glycol. This could be done using the RTE-140 Neslab chiller, which is capable of controlling the temperature to within 0.1 K over the desired temperature range for the experiment. A potential problem we might face when cooling the cell is the presence of gas temperature gradients inside the ringdown cell, because our CRDS experiment is designed as a flow experiment. With the gas supply and the cell at the ambient laboratory temperature, this is presently not a problem. If we see evidence of temperature gradients, it will be necessary to control the temperature of the supply of dry gas as well.
Chapter 5

Conclusions

In this chapter, we summarize our achievements, absorption measurements, and offer several recommendations for further research.

5.1 Achievements

We have designed, built, and tested a novel infrared quantitative CRDS experiment that has successfully measured the water vapor continuum absorption in the 1000 cm$^{-1}$ region. CRDS is a new high-performance spectroscopic technique in which laser pulses are injected into a stable, high-finesse optical cavity. Accurate measurements of the absorption coefficient of the gas are obtained from the difference in the decay time constant when an absorbing gas is added and then removed from the system. Our infrared CRDS experiment is designed around a 1-m long near-confocal ringdown cavity. Well-defined infrared laser pulses are formed from a cw CO$_2$ laser by rapidly switching on/off the deflected beam of an acousto-optic modulator. The pulsed, Gaussian infrared beam is mode-matched using a single lens before it is injected into the ringdown cavity. The noise in our decay time constants is $\sigma_\tau/\tau = 0.2 \%$, which is comparable to the lowest noise levels reported for CRDS and we are unaware of a lower noise level reported for an infrared CRDS experiment.

CRDS is a powerful spectroscopic technique that is capable of high sensitivity to weak absorption, high spectral resolution, and high measurement accuracy. Despite these advantages, few infrared CRDS experiments exist at present and we are unaware of any other quantitative experiments near 1000 cm$^{-1}$. We were faced with a wide variety of technical challenges as our
experiment was developed, many of which were related to infrared work. The most significant obstacles we have encountered in the development of our quantitative infrared CRDS experiment are the following:

- **Generation of clean infrared pulses.** If electro-optic modulators are used, great care must be taken to ensure that the acoustic waves that tend to propagate in such devices are properly damped. These acoustic waves propagate following the main optical pulse and so are detrimental to CRDS signals. We demonstrated that this problem can be avoided by using an acousto-optic modulator instead of an electro-optic modulator.

- **Infrared mode-matching.** A proper characterization of the infrared laser beam, necessary to successfully implement mode-matching, is difficult because we lacked an infrared beam imager. However, we have demonstrated that the combination of a home-made horizontal scanner and simple pinhole power reduction technique can be used to obtain accurate information on the laser beam. We were then able to mode-match the laser beam to the TEM$_{00}$ mode of the ringdown cavity.

- **Nonlinear signal response of detector.** The signal nonlinearity of photoconductive HgCdTe infrared detectors is well known, and it is widely assumed that this problem is avoided when a photovoltaic (PV) HgCdTe infrared detector is used instead. However, we have demonstrated that even PV HgCdTe detectors can respond in a nonlinear fashion to high photon fluxes, in our case above $10^{18}$ photons cm$^{-2}$ sec$^{-1}$. Care must be taken to maintain photon fluxes below $10^{18}$ photons cm$^{-2}$ sec$^{-1}$ over the decay portion of the CRDS signal.

  We also encountered difficulties specific to our objective of measuring the water vapor continuum. Although the water vapor continuum plays a critical role in the Earth climate system, it is considered weak absorption over short path lengths. Furthermore, the continuum spectrum resembles the experimental baseline that one often seeks to remove in absorption spectra. For this
reason, we need an accurate characterization of the baseline in our infrared CRDS experiment. Until recently, we observed a slow, but unpredictable long-term drift in decay time constants that was larger than the difference we expected to observe due to water vapor continuum absorption. This long-term drift, which had frustrated our attempts to measure the water vapor continuum, was eliminated by removing the lens which focused radiation exiting the ringdown cavity onto the infrared detector.

Because it is not possible to detune the experiment from an absorption peak when we are measuring continuum absorption, we developed a methodology based on a gas flow experiment. Nitrogen gas continuously flows through the ringdown cavity and is exhausted into the laboratory. By diverting a portion of the inlet gas stream over a body of distilled water, we demonstrated that we can generate humidities in the ringdown cavity ranging from zero to near-saturation. A major advantage of our methodology is that it is possible to make water vapor absorption measurements for several different cell humidities in a short amount of time.

Finally, the work described in this thesis represents the personal achievements of this author. I conceived of, and was the principal investigator of, the infrared CRDS experiment. Although I was fortunate to have received help along the way from a number of people, no one else worked full-time on the infrared CRDS experiment.

5.2 Summary of Results

We have made an intercomparison of the existing body of water vapor continuum measurements for conditions of $T = 296\,\text{K}$ and $v = 944\,\text{cm}^{-1}$, and we have found uncertainties of $\pm 17\%$ and $\pm 74\%$ for the continuum coefficients of self- and foreign-broadening, respectively. These uncertainties contribute significantly to the overall uncertainty in the atmospheric radiative transfer
of the Earth. One consequence, discussed in the introduction to this thesis, is that such uncertainties obscure our ability to detect and ascribe global climate change to anthropogenic influences. Additionally, uncertainties in the water vapor continuum frustrate our understanding of the radiative transfer of clouds. This is because clouds are thought to absorb and emit infrared radiation in continuous spectra similar to blackbodies [Houghton, 1986]. Furthermore, clouds are associated with atmospheric conditions of high humidity in satellite data [Arking, 1999], which is also where the influence of the water vapor continuum is strongest. Therefore, it will be difficult to develop a better understanding of cloud radiative transfer before we have accurately characterized and understood the water vapor continuum.

In this thesis, we report measurements of the water vapor continuum using our infrared CRDS experiment for CO$_2$ laser wavenumbers ranging from 931 - 969 cm$^{-1}$ for temperatures near 296 K. In this experiment, we systematically varied the partial pressure of water vapor from 0 - 2.3 kPa (0 - 0.022 atm), with the total cell pressure ranging between 107 - 109 kPa (1.05 - 1.08 atm). All of our measurements have been analyzed in terms of the continuum coefficients of self- and nitrogen-broadening, and are summarized in Table 4.1. We compared our results at 944 cm$^{-1}$, where the most data are available for comparison, against the values obtained by investigators using CO$_2$ lasers and White cell spectroscopy (Table 4.2). Our data at 944 cm$^{-1}$ are:

$$C_s^0 = 2.01 \pm 0.14 \times 10^{-22} \text{ molecule}^{-1} \text{ cm}^2 \text{ atm}^{-1}$$

$$C_n^0 = 0.85 \pm 0.17 \times 10^{-24} \text{ molecule}^{-1} \text{ cm}^2 \text{ atm}^{-1}$$

Both of these coefficients were found to be in excellent agreement with data from other experiments. We found no data to compare with our measurements at other wavenumbers, but we see no reason why the demonstrated accuracy of our apparatus should not extend to these wavenumbers as well.

Our continuum absorption coefficients are found to be in very good agreement with the far
wing line shape theory of Ma and Tipping. We interpret this as strong evidence that the accumulated far wing absorption of water vapor lines, and not dimer absorption, is the primary mechanism responsible for the water vapor continuum. Thus, for the first time, there exists a theoretical framework capable of explaining the infrared water vapor continuum, as well as validation from accurate experimental data.

We also think there may be some significance to the discrepancy between our results and the far wing theory at 931 cm$^{-1}$. One possibility is that the excess absorption we observe is due to a nearby water vapor dimer combination band. Although such a band was predicted by Vigasin [Vigasin and Chlenova, 1984], we are unaware of any observations of dimer absorption in the thermal infrared window. On the other hand, the discrepancy might be partly attributable to uncertainties in the intermolecular potential of water, which is used in the quasistatic far wing line shape theory. This could be a very significant discovery and should be investigated further.

Finally, we note that our measurements differ significantly from two empirical models of the water vapor continuum. This is a matter of great concern, as empirical models are routinely used in radiative transfer calculations because of their computational efficiency. For the RSB [Roberts et al., 1976] and CKD [Clough et al., 1989] models to agree with our continuum coefficients of self-broadening in the 900 - 1000 cm$^{-1}$ region, they would have to be scaled down by factors of ~ 0.91 and ~ 0.88, respectively. Meanwhile, the disagreement between the empirical models and our data is much more pronounced for the nitrogen-broadened continuum. The RSB model has no nitrogen-broadened continuum, whereas the nitrogen-broadened coefficients in the CKD model must be multiplied by over 200 to give agreement with our observations. We believe that these models rely on data which are inaccurate and derived from techniques with inadequate sensitivity to detect the weak nitrogen-broadened continuum. However, the details of how the empirical models should be
corrected is an urgent matter that must be addressed by the modelers.

5.3 Recommendations and Further Research

In Section 4.4, we discussed several possible areas for improvement of the infrared CRDS experiment. One of the easiest improvements to implement involves replacing the existing mirrors (R = 0.994) with new mirrors (R = 0.998). This improvement has the potential to lower the minimum detectable absorption coefficient of the experiment an order of magnitude, to $k_{\text{min}} = 1.5 \times 10^{-8} \text{ cm}^{-1}$ or better. The expected sensitivity of our improved CRDS experiment would exceed any reported values known to us for a spectroscopic experiment near 1000 cm$^{-1}$.

The infrared CRDS experiment offers many possibilities for further research. An obvious possibility is to extend our study of the water vapor continuum over the full spectral range of the CO$_2$ laser. Given the failure of empirical models to properly account for accurate observations of the water vapor continuum, providing such data is critical to radiative transfer applications. Extending the spectral coverage of our continuum measurements would also permit a better validation of the far wing line shape theory and may uncover some other areas in the window region where there are discrepancies between theory and observation, such as the possible dimer absorption band we have found near 930 cm$^{-1}$.

Another interesting experiment would involve studying the water vapor absorption at the R(20) line of the CO$_2$ laser (975.930 cm$^{-1}$), because it has been reported that this CO$_2$ laser transition is nearly coincident with a high J-number pure rotational line of water vapor [Hinderling et al., 1987]. In addition to comparing our measured absorption cross-section with that reported by others, our data could also provide independent confirmation of the dew point sensor measurements.

The sensitivity gains we anticipate from the new R = 0.998 mirrors should permit us to
investigate some interesting and poorly-characterized aspects of the water vapor continuum. For example, the foreign-broadened water vapor continuum could be studied quantitatively. Few experiments have had the required sensitivity to measure the foreign-broadened continuum, and we are only aware of a single experiment that attempted to determine the influence of oxygen on foreign-broadening [Nordstrom et al., 1978]. Such measurements are vital for radiative transfer applications as there are many regions of the atmosphere where the foreign-broadened continuum tends to dominate over the self-broadened continuum, such as the mid-latitudes and the upper troposphere. Such data are especially important since the foreign-broadened continuum is not properly accounted for in empirical models of the water vapor continuum, and there are significant discrepancies between far wing line shape theories and existing data.

We are also looking into adding temperature control capabilities to our apparatus. Presently, our infrared CRDS experiment lacks temperature control, and so all of our data have been collected at the ambient laboratory temperature. We are investigating how to proceed with temperature control over the range 250 - 310 K. One of the ultimate objectives of our experiment is to make accurate measurements of the temperature dependence of the water vapor continuum for realistic atmospheric temperatures. It is important to accurately characterize the temperature dependence because the atmosphere is not held at a fixed temperature. The water vapor continuum makes its most significant contribution to radiative transfer in the troposphere, where temperatures range from about 250 - 310 K. Such low-temperature measurements require especially high sensitivity, because the saturation vapor pressure of water is an exponential function of temperature. We are only aware of two laboratory investigations of the water vapor continuum spanning the range 260 - 300 K, which were obtained using photoacoustic spectroscopy. However, there are large uncertainties associated with the data from this technique, which are due to inaccuracies in the calibration along with other
experimental problems.

Our CRDS experiment has proven to be capable of making precise and accurate measurements of the infrared water vapor continuum. Accurate measurements of the water vapor continuum are important because the continuum represents a major source of uncertainty in atmospheric radiative transfer models. However, we also see many possibilities for measuring the absorption of gases other than water vapor. For example, we have already made some preliminary measurements of SF₆ absorption. SF₆ is one of the most powerful greenhouse gases on a per molecule basis, and is believed to be increasing in the atmosphere at a rate of about 7% per annum. Our survey of published data on SF₆ absorption suggests there are uncertainties of 20% or greater in the absorption coefficients. Furthermore, infrared CRDS has already found applications in supersonic expansion jets [Paul et al., 1997] and nonlinear spectroscopy [Bucher et al., 2000]. Thus, there are many possibilities for further research and development with our infrared CRDS experiment.
Appendix A

Water Vapor Continuum Electronic Database Keywords

aerosol - aerosol absorption (includes hazes, fogs)
carbon dioxide - carbon dioxide continuum
climate - role of water vapor continuum in climate studies
clouds - anomalous cloud absorption
cluster - water molecule or ion aggregates
CO2 laser - experimental work utilizing a CO2 laser
collision-induced absorption - collision-induced continuum absorption
dimer - water vapor equilibrium and non-equilibrium dimers (H2O)2
experimental - experimental results
Fabry-Perot - experimental technique
far wing - far wing line absorption
FASCODE - radiative transfer modeling code
field - field experimental results
foreign-broadening - continuum absorption term proportional to foreign gas pressure
Fourier transform - type of spectrometer
frequency dependence - frequency dependence of continuum absorption
grating - type of spectrometer
HITRAN - molecular line absorption database
horizontal - horizontal optical path field measurements
hydrogen bond - role of hydrogen bond in continuum absorption

intermolecular potential - concerning water - water intermolecular potential

laboratory - laboratory experimental results

laser - experimental work utilizing a laser source

LBLRTM - radiative transfer modeling code

line absorption - line absorption results related to water vapor continuum

line shape - spectral line shapes

longwave - results from thermal infrared region of spectrum

LOWTRAN - radiative transfer modeling code

matrix isolation - experimental technique

microwave - results from microwave region of spectrum

millimeter wave - results from millimeter and sub-millimeter wave region of spectrum

modeling - methodology for representing water vapor continuum in climate studies

multipass cell - laboratory experimental technique

photoacoustic - experimental results obtained utilizing photoacoustic spectroscopy

prism - type of spectrometer

radiometer - experimental use of radiometer

remote sounding - role of continuum in window regions targeted by remote sounding/sensing

review - reviews of water vapor continuum

saturation - saturated or supersaturated water vapor and continuum absorption

sea surface temperature - role of continuum in remote sensing of sea surface temperature

self-broadening - continuum absorption term proportional to water vapor pressure

shortwave - results from solar infrared region of spectrum
spectrometer - experimental results obtained with a spectrometer and broadband source

spectroscopy - results obtained by any spectroscopic technique

steam - experimental results obtained using steam

temperature dependence - temperature dependence of continuum absorption

theoretical - theoretical results

thermodynamic - results derived from thermodynamic or acoustic properties of air

transmission - field transmission results

van der Waals - role of van der Waals complexes in continuum absorption

vertical - vertical optical path field measurements

water vapor - water vapor continuum

White cell - laboratory experimental technique
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