Cavity Enhanced Technique for the Study of Vibrational Overtone Transitions: Acetic Acid ν(OH) = 4

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Cavity Enhanced Technique for the Study of Vibrational
Overtone Transitions: Acetic Acid $v_{OH} = 4$

by

Stephen Brent Hinton

B.S. in Chemistry, University of Georgia, 2010
B.A. in Russian, University of Georgia, 2010

A thesis submitted to the
Faculty of the Graduate School of the
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2012
This thesis entitled:
Cavity Enhanced Technique for the Study of Vibrational Overtone Transitions: Acetic Acid $v_{OH} = 4$
written by Stephen Brent Hinton
has been approved for the Department of Chemistry and Biochemistry

_____________________________________
Veronica Vaida

_____________________________________
W. Carl Lineberger

Date _____________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Hinton, Stephen Brent (M.S., Chemistry)

Cavity Enhanced Technique for the Study of Vibrational Overtone Transitions: Acetic Acid

\[ v_{OH} = 4 \]

Thesis directed by Professor Veronica Vaida

Acetic acid is one of the most abundant organic acids in the atmosphere and it affects aerosol formation and composition. The purpose of this work was to develop spectroscopic methods to probe the anharmonic part of the potential energy spectrum and follow the chemistry of this molecule. Fundamental knowledge of acetic acid is required in order to fully comprehend its role in aerosols and radiative forcing. Cavity ring-down spectroscopy was used to observe vibrational overtones. In this experiment, the pressure of acetic was varied to probe for the effect concentration on the spectra, however, no effects were seen. In addition to studying dimer effects, this experiment provided the first extinction coefficient of acetic acid vapor.
Dedication

I dedicate this thesis to my niece, who constantly reminds me how awesome science can be.
Acknowledgements

I would like to thank my friends, family, and academic mentors for their support throughout my education. Their belief in me and my abilities is the leading factor for where I am today.
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Chapter 1

Introduction

The field of atmospheric chemistry is becoming ever more involved in defining the causes of climate change. As the error bars in the Intergovernmental Panel on Climate Change (IPCC) report show, the uncertainty in many climate forcing variables is still too high to accurately predict future changes.\textsuperscript{23} In order to reduce these error bars, the atmospheric community needs to reexamine which molecules significantly influence atmospheric chemistry and what interactions are involved. Interestingly, the IPCC report does not include contributions from organic molecules on aerosol mass and concentration. Organic molecules have been shown to influence aerosols,\textsuperscript{10} however, lack of fundamental understanding of these organic molecules impedes our knowledge of their role in aerosol chemistry. Low concentration species like acids and complexes are important in aerosol formation despite their small number densities. Studies have shown that organic acids help nucleate sulfuric acid aerosols\textsuperscript{40,13} which are the majority of aerosol particles in the atmosphere. Current atmospheric abundance models overestimate the concentration of acetic acid compared to observations.\textsuperscript{26} Acetic acid is a major emission from vegetation,\textsuperscript{28} and yet models do not account for all loss mechanisms for acetic acid occurring in the atmosphere. Atmospheric complexes, both van der Waal’s and hydrogen bonded, have been shown to have altered absorption cross-sections compared to the monomers.\textsuperscript{32,36,14} Studying the spectroscopy of acetic acid and its complexes can provide the groundwork for understanding the role of all acids in aerosol formation and determining new photo-dissociation mechanisms to update
current models. In addition to fundamental vibrational frequencies, there is a need to quantify the weaker absorptions in spectral regions previously thought to be atmospherically irrelevant\(^2\). Vibrational overtones are an example of weak yet important spectral features of molecules containing OH stretches. Weak overtone transitions contribute to solar radiation absorption and in some instances activate photo-dissociation pathways. Overtone induced photo-dissociation can occur through two different mechanisms. One method involves Intramolecular Vibration Energy Transfer (IVET)\(^3\). The photon energy energy absorbed by an OH stretch of a molecule can be transferred to a weaker bond within the molecule through IVET causing cleavage of that bond. The other mechanism is through a concerted reaction that goes through a transition state which defines the energy barrier for reaction. When an OH stretch absorbs several quanta of vibrational energy (i.e. overtone excitation), the large amplitude oscillations of the H atom can drive a reaction pathway whose reaction coordinate is along the OH stretching frequency.

As in many areas in science, conducting spectroscopy on relatively weak transitions is limited by the sensitivity of the instruments and experimental conditions. This thesis reports the use of a highly sensitive cavity enhanced technique to study weak overtone cross-sections. This technique is called Cavity Ring-Down Spectroscopy (CRDS) and provides highly sensitive measurements from the infrared (IR) to the ultraviolet (UV). In particular, I used CRDS to study the formally forbidden \(v_{OH} = 4\) and \(v_{OH} = 5\) overtones of acetic acid and its dimer in the visible spectral region. Chapter 2 of this thesis will discuss the various models used to describe molecular vibrations, vibrational overtones and their role in atmospheric chemistry. Chapter 3 will detail the CRDS instrument and explain the data analysis for this technique. Chapter 4 will briefly describe the spectroscopy of acetic acid in the literature and how my research ties into the previous work. Chapter 4 will also describe the experimental conditions during data collection. Finally, Chapter 5 will describe what future work can be done to improve on this experiment.
Atmospheric spectroscopy as a field aims to study the interaction of atmospheric species with light. My research studied the formally forbidden overtone transitions of atmospheric species. Overtone transitions occur at higher energy than fundamental transitions and can allow new pathways not seen through fundamental absorption. Photo-dissociation requires high-energy light, typically UV radiation. UV radiation causes electronic excitation that leads to bond cleavage. Visible light, next lowest in energy, also causes electronic transitions, however these transitions are not energetic enough to cause bond cleavage. In addition to electronic transitions, visible light can also excite vibrational energy levels of certain molecules. Overtone transitions are an example of visible light exciting vibrational energy levels. If the $\Delta E_{\text{transition}}$ for overtone absorption is great enough, it can cause dissociation of the molecule in the ground electronic state. The arrows in Figure 2.1 show the energy transition $\Delta E_{\text{transition}}$ for UV and visible-overtone absorptions. As depicted in the figure, absorption of UV radiation cause transitions to excited electronic levels, whereas overtone transitions remain in the ground electronic level.

The primary source of light that drives atmospheric chemistry is direct radiation from the Sun. Figure 2.2 shows the distribution of solar radiation intensity as a function of wavelength observed at the top of Earth’s atmosphere. The distribution follows the black body model of radiation at a temperature of 5780 K. Solar electromagnetic radiation ranges from high-energy UV to the IR, and earth receives all of these frequencies. Although high-
Figure 2.1: Comparison between UV (dashed line), visible (dotted line) and vibrational overtone (solid line) absorptions.
Figure 2.2: Solar spectrum in yellow. Red shows the radiation that penetrates to the ground.

Energy UV radiation reaches Earth’s atmosphere, most of this radiation is absorbed by \( \text{O}_2 \) and \( \text{O}_3 \) in the stratosphere. These two molecules essentially create a UV filter at wavelengths < 300 nm. This leaves little intensity in the lower atmosphere in the UV for photo-dissociation, nearly eliminating that reaction pathway. Visible light is the next candidate for causing photo-dissociation. The solar spectrum peaks in the visible (\( \approx 500 \text{ nm} \)) providing adequate intensities to induce dissociation. However, visible light is not energetic enough to dissociate most molecules. Table 2.1 compares the available energy of UV and visible light to typical bond dissociation enthalpies.

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>(2.5 \times 10^4 - 5.0 \times 10^4)</td>
</tr>
<tr>
<td>Visible</td>
<td>(1.25 \times 10^4 - 2.5 \times 10^4)</td>
</tr>
<tr>
<td>Compound</td>
<td>Bond Dissociation Energy (cm(^{-1}))</td>
</tr>
<tr>
<td>C=O</td>
<td>62,146</td>
</tr>
<tr>
<td>O−H</td>
<td>35,798</td>
</tr>
<tr>
<td>Methane C−H</td>
<td>36,384</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>41,570</td>
</tr>
</tbody>
</table>

Table 2.1: Energy of UV and Visible radiation compared to bond dissociation energies of various molecules. Energies are bond dissociation enthalpies from Peter Atkins 9th Edition.\(^1\)

Visible excitation is not energetic enough to cause excited electronic level dissociation, however, overtone absorption enables pathways to ground-state dissociation through high-
amplitude vibrations. In order for overtone transitions to occur, a molecule needs to contain certain high vibrational frequency functional groups (i.e. X–H, where X can be C, O or N). Next I will discuss the models that describe vibrational overtone spectra.

2.1 Harmonic Oscillator

For the following discussion, I will describe the properties a typical N-atom polyatomic molecule. The harmonic model assumes that each of the 3N-6 vibrational modes are uncoupled oscillators. This approach is based on a normal mode analysis of vibrations. Each vibration has a vibrational frequency that does not depend on the frequencies of other vibrations in the molecule. According to the harmonic model, the potential energy associated with the vibration of two atoms with mass (m) separated by a bond length (x) and bound together by a Hooke’s Law spring is given by Equation 2.1.

\[ V(x) = \frac{1}{2} kx^2 \]  

(2.1)

Hooke’s spring constant (k) is defined as \( k = \omega_e^2 m \). The available energy levels for a harmonic potential can be derived from the Schrödinger Equation and are found to be

\[ v_n = (n + \frac{1}{2})\hbar\omega_e \]  

(2.2)

In this equation, \( \omega_e \) is the equilibrium vibrational frequency, \( h \) is Plank’s constant divided by \( 2\pi \), \( n \) is the vibrational energy level in question, and \( v_n \) is the vibrational energy at level \( n \). For a transition to occur between two energy levels, there must be overlap between the wavefunctions for the two energy levels. For a harmonic potential, only adjacent energy levels have a non-zero overlap integral yielding the selection rule for vibrational transitions in a harmonic oscillator to be \( \Delta v = \pm 1 \).

2.2 Morse Oscillator

In reality, actual molecular vibrational behavior deviates from the harmonic oscillator model. This model under predicts the repulsive interactions of two atoms at small separation
and does not give rise to dissociation. An alternative model to describe molecular vibrations is the anharmonic model. Unlike the harmonic model, the anharmonic model includes terms that account for the deviations of actual molecular vibrations from harmonic behavior called the anharmonicity of the vibration. The anharmonic model predicts a bond dissociation energy, $D_e$ as well as decreasing spacing between adjacent vibrational energy levels as energy increases. The Morse potential is an example of an anharmonic treatment of molecular vibrations. The Morse potential has the form

$$V(r) = D_e(1 - e^{-a(r-r_e)})^2$$  \hspace{1cm} (2.3)

where $D_e$ is the ground electronic dissociation energy, $a$ corresponds to the steepness of the potential well, $r$ is the bond length, and $r_e$ is the equilibrium bond length. A plot of the potential as a function of bond length is shown in Figure 2.3. Figure 2.4 compares the Morse and harmonic potentials, showing diverging properties at large vibrational levels.

![Figure 2.3: Morse potential showing the bond dissociation energy $D_e$ and the decrease in energy level spacing.](image)

Using the Schrödinger equation, the possible energy levels for the Morse potential are given by Equation 2.4. These new energy levels have different wavefunctions from the harmonic
model due to the anharmonicity, Figure 2.5. These anharmonic wavefunctions have overlap integrals $\neq 0$ with energy levels not bound by the selection rule $\Delta v = \pm 1$. Anharmonic potentials can therefore support transitions with $\Delta v > 1$, such as overtones.

$$v_n = \omega_e \hbar (n + \frac{1}{2}) - \frac{\omega_e^2 \hbar^2}{4D_e} (v + \frac{1}{2})^2 \quad (2.4)$$

It is through the overlap of these anharmonic wavefunctions that visible light can lead to overtone induced photo-dissociation. Although the radiation frequency for overtone absorption can be large enough to cause photo-dissociation, the cross-section for the particular overtone absorption needs to be large enough to allow an appreciable number of molecules to absorb the radiation and undergo photo-dissociation.

### 2.3 Overtone Absorption

Generally, in absorbing a photon of the correct wavelength, a molecular vibration can be excited from a thermally populated energy level, Figure 2.3, to an excited vibrational energy level. With an anharmonic model to describe molecular vibrations, it is possible to have vibrational transitions $\Delta v > \pm 1$. Such excitations are called overtones and can result in photo-dissociation if $E_{\text{transition}} > E_{\text{threshold}}$. The $E_{\text{threshold}}$ represents the energy required for
Figure 2.5: Born representation of probability for the Morse oscillator indicating overlap between non-adjacent energy levels. The x-axis is in arbitrary units of length, whereas the y-axis is in arbitrary units if energy.\textsuperscript{18}
dissociation which can be bond dissociation energies or transition state energies. Overtone transitions are required to excite molecules to energies $\approx E_{\text{threshold}}$ in the absence of UV radiation. All photon-induced transitions originate from a populated energy level regardless of the radiation type. The population of molecules in a given vibrational energy level is determined by Boltzmann statistics, Equation 2.5.

$$f_n = \frac{e^{-\beta hv(n+1/2)}}{q_{\text{vib}}}$$

(2.5)

Here, $\beta = \frac{1}{kT}$ where $k$ is Boltzmann’s constant and $T$ is temperature and $q_{\text{vib}}$ is the vibrational partition function defined as Equation 2.6.

$$q_{\text{vib}} = \frac{e^{-\beta hv/2}}{1 - e^{-\beta hv}}$$

(2.6)

Equation 2.5 shows that as the temperature of the molecule increases, higher vibrational states are available to the molecule. At atmospheric temperatures, 298K, only the first few vibrational energy levels are populated for most molecules. Using Equation 2.5, the fractional population of acetic acid molecules with various OH vibrational energy levels was calculated and is shown in Figure 2.6, assuming a harmonic oscillator. The transition state barrier for acetic acid was calculated in the literature\textsuperscript{33} to be 67 kcal/mol, the dissociation pathway therefore requires vibrational energy $\Delta E_{\text{transition}} \approx 23447$ cm$^{-1}$ ($v_{OH} = 7$). The temperature of the molecule would need to be quite high in order to populate $v_{OH} = 6$ to allow the harmonic transition $\Delta v = 1$ to $v_{OH} = 6$. For this reason overtone transitions are needed to attain vibrational energies $\approx E_{\text{threshold}}$.

In naming overtone transitions, it is helpful to recognize that a transition of $\Delta v_{OH} = 1$ is considered one quantum of the $v_{OH}$ stretch. The fundamental transition occurs between the ground state and the next highest energy level, with $\Delta v_{OH} = 1$. The first overtone corresponds to $\Delta v_{OH} = 2$, and the second overtone corresponds to $\Delta v_{OH} = 3$. Each overtone is named for the number of $v_{OH}$ quanta, excluding the fundamental, needed to make the transition. Overtone cross-sections are orders of magnitude smaller than their corresponding
Figure 2.6: Fraction of population occupying vibrational energy levels \(v\) at 298 and 7000 K. Populations calculated using Equation 2.5.
fundamental transitions and the frequency of an overtone depends on the anharmonicity of the vibration. Figure 2.7 shows general trends for overtones: 1) there is a reduction in intensity with increasing overtone, 2) the intensity for an overtone is generally the same for all compounds however the OH stretching overtone has the greatest intensities at all overtone numbers. The integrated cross-section of the third OH overtone of acetic acid was calculated to be $4.23 \times 10^{-24}$ cm molecule$^{-1}$ approximately $1.0 \times 10^{-21}$ cm molecule$^{-1}$. Even with such small cross-sections, overtone transitions are important atmospheric contributors because of the large number of OH containing acids in the atmosphere.

2.4 Overtone-Induced Photo-Dissociation Pathways

Two main mechanisms for overtone induced dissociation have been reported in the literature.$^{6,36,38}$ In both pathways, absorption of visible light, typically by the OH vibrational stretch of a molecule, provides the necessary energy for dissociation. Overtone absorption of visible light by the OH stretch excites the molecule to a high energy vibrational level. If the vibrational energy of the OH stretch is greater than the bond dissociation energy of an adjacent bond, then this vibrational energy can be transported to the weaker bond and cause bond cleavage. Typically the only bonds that are weak enough to be cleaved by the IVET pathway are N–N, N–O or O–O. For the typical OH vibrational frequency of 3600 cm$^{-1}$ and anharmonicity 80 cm$^{-1}$, the $v_{OH} = 6$ overtone absorption, the cross-section of which is easily excited by solar radiation, has an energy around 19000 cm$^{-1}$. Comparing the $v_{OH} = 6$ energy to the values in Table 2.1 indicates that only these weak bonds between nitrogen and oxygen can be cleaved through overtone induced photo-dissociation. An alternative pathway towards overtone photo-dissociation is through a concerted reaction where high amplitude OH vibrations cause molecular rearrangement followed by dissociation. The products of the concerted pathway are typically stable products, as opposed to radical species produced in the bond cleaving pathway. The activation energy or energy barrier for this pathway depends on the transition state energy for the reaction. Figure 2.8 depicts the energy barrier for the
Figure 2.7: Overtone intensities for various compounds as a function of overtone number.\textsuperscript{37}
Figure 2.8: Reaction pathway for thermal decomposition of acetic acid. Figure taken from Takahashi 2002.  

thermal decomposition reaction of acetic acid. Transition state energies are typically lower in energy than bond dissociation energies so the concerted mechanism provides a reaction pathway for molecules with no weak bonds. Table 2.2 shows some typical transition state energies for several molecules, including acetic acid. It is through this concerted reaction pathway that I would expect acetic acid to photo-dissociate in the atmosphere.

2.5 Atmospheric Consequences

Donaldson et al. showed the formation of OH from decomposition of HNO$_3$ and HNO$_4$ was possible through overtone excitation followed by IVET. Others have studied the decarboxylation of compounds such as malonic acid and vinylacetic acid which follows the concerted dissociation pathway. Of particular importance, Vaida et al. proposed the overtone induced dehydration reaction of H$_2$SO$_4$, Equation 2.7, which is the only pathway for the thermal dissociation of H$_2$SO$_4$ in the atmosphere.

$$\text{H}_2\text{SO}_4 \xrightleftharpoons{\text{Vis-Near-IR photons}} \text{H}_2\text{O} + \text{SO}_3$$  \hspace{1cm} (2.7)

Wennberg et al. suggested the overtone induced dissociation mechanism of HNO$_4$ was needed to match observed concentrations of HNO$_4$. Understanding the formation and loss mecha-
Table 2.2: Lowest energy barrier for reaction, reaction products and OH quanta exceeding barrier for various acids. Table taken from Vaida 2008.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lowest energy barrier for reaction (kcal/mol)</th>
<th>Reaction products</th>
<th>OH quanta exceeding barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid(^{14,16,20})</td>
<td>32 – 40</td>
<td>SO(_3), H(_2)O</td>
<td>(v_{OH} = 4)</td>
</tr>
<tr>
<td>Nitric acid(^{29})</td>
<td>47.7</td>
<td>NO(_2), OH</td>
<td>(v_{OH} = 5)</td>
</tr>
<tr>
<td>Pernitric acid(^{30})</td>
<td>21.1</td>
<td>HO(_2), NO(_2)</td>
<td>(v_{OH} = 3)</td>
</tr>
<tr>
<td>Formic acid (a)(^{27}) (b)(^{9})</td>
<td>(a)41.5, (b)63.0</td>
<td>CO, H(_2)O</td>
<td>(v_{OH} = 5, 7)</td>
</tr>
<tr>
<td>Glycolic acid(^{5})</td>
<td>50.9</td>
<td>H(_2)CO, CO, H(_2)O</td>
<td>(v_{OH} = 6)</td>
</tr>
<tr>
<td>Lactic acid(^{5})</td>
<td>47.4</td>
<td>HCOCH(_3), CO, H(_2)O</td>
<td>(v_{OH} = 5)</td>
</tr>
<tr>
<td>Malonic acid(^{31})</td>
<td>27.6</td>
<td>H(_2)CC(OH)(_2), CO(_2)</td>
<td>(v_{OH} = 3)</td>
</tr>
<tr>
<td>Acetic acid (c)(^{33}) (d)(^{19})</td>
<td>(c)67.01, (d)71.5</td>
<td>CH(_4), CO(_2)</td>
<td>(v_{OH} = 7, 8)</td>
</tr>
<tr>
<td>Trifluoroacetic acid(^{25})</td>
<td>50.3</td>
<td>CF(_2)CO(_2), HF</td>
<td>(v_{OH} = 6)</td>
</tr>
</tbody>
</table>

...
plexes between water and various atmospheric species can significantly alter the absorption spectrum of both substituents due to possible hydrogen bond formation. Stronger bonds between complex substituents induces greater shifts from monomer spectra. I studied the effects of dimerization of acetic acid on the previously unobserved $v_{OH} = 4$ overtone absorption. The hydrogen bonding between two acetic acid molecules is similar to the interactions between H$_2$O and various atmospheric species. Acetic acid dimer can orient in several geometries for the carbonyl and OH groups to form strong hydrogen bonds. Figure 2.9 shows the lowest energy conformer, which contains two hydrogen bonds and has a stabilization energy of $-56$ kJ mol$^{-1}$ compared to the monomer. The bonds between atoms involved in intermolecular bonding are the most affected. The OH stretching cross-section should show significant alteration since it takes part in the hydrogen bonding. Owing to the predicted significant alteration of the OH cross-sections and the fact that OH stretching overtone cross-section at $v_{OH} = 4$ is not in the literature, I made the $v_{OH} = 4$ OH stretching vibration the focus of this experiment.
Chapter 3

Method

3.1 CRDS

As mentioned in chapter 2, the overtone absorption features are low in intensity compared to the fundamental features. In order to observe these weak transitions, I used a cavity enhanced technique known as Cavity Ring-Down Spectroscopy (CRDS). The advantage of CRDS is its increased path length, giving it higher sensitivity compared to conventional absorption spectroscopies. A typical CRDS path length is $L \approx 200$ km compared to $L < 1$ m for traditional absorption techniques. Instead of a conventional cuvette cell, CRDS utilizes a high finesse optical cavity. High finesse cavities are typically linear in configuration and act as optical resonators by trapping light between two highly reflective mirrors. A typical reflectivity value ($R$) for a CRDS mirror is $R \approx 99.999\%$ at the wavelength maximum ($\lambda_{\text{max}}$) and falls off in either direction from $\lambda_{\text{max}}$, Figure 3.1. Referring to Figure 3.2 and Table 3.1,
light from a pulsed source is incident on mirror 1, component 10 in Figure 3.2, and a small amount of light (T) governed by Equation 3.1 passes through cavity mirror 1 and into the cavity, while the majority of the intensity (99.999%) is reflected away.

\[ T = 1 - R \]  (3.1)

Once inside the cavity, the light bounces between cavity mirrors 1 and 2 making several passes through the cell. The total number of passes the light makes governs the path length L of the high-finesse cavity and is described by \( L = \tau c \), where c is the speed of light, and \( \tau \) is the lifetime of the light pulse within the cavity. Each time the light pulse reflects off cavity mirror 2, another small percentage (0.0001%) of that light passes through the mirror and out the opposite side of the cavity towards the detector. The intensity of light from the cavity decreases as a single exponential and is detected by a Photon Multiplier Tube (PMT) detector. A data collection card digitizes the analog signal from the PMT and sends it to a computer. The computer then calculates and stores the decay lifetime of each light pulse as a function of wavelength. The decay lifetime of \( \tau \) is the amount of time required for the initial intensity \( I_0 \) to drop to \( \frac{I_0}{e} \), Figure 3.3. If an absorbing species is present within the cavity, the decay lifetime will be shorter, but will still have the form of a single exponential. By comparing the decay times between an empty cavity and one filled with sample, the extinction coefficient of an absorbing species at a particular wavelength \( \alpha(\lambda) \) can be determined, Equation 3.2. Since the PMT is only detecting the number of photons from the cavity and not the particular wavelength of each photon, the pulsed light source must be scanned through the spectral region of interest.

3.2 Data Analysis

The final data gathered from CRDS are decay lifetimes of light \( \tau(\lambda) \) within the cavity as a function of wavelength. The extinction coefficient \( \alpha(\lambda) \) as a function of wavelength can
Figure 3.2: Diagram of CRDS instrument in Dr. Veronica Vaida’s Laboratory as of June 2012.

<table>
<thead>
<tr>
<th>Component No</th>
<th>Description</th>
<th>Component No</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pulsed Nd:YAG Laser</td>
<td>9</td>
<td>Back turning mirror</td>
</tr>
<tr>
<td>2</td>
<td>Turning mirror</td>
<td>10</td>
<td>CRDS mirror mount 1</td>
</tr>
<tr>
<td>3</td>
<td>Cylindrical Lens</td>
<td>11</td>
<td>Glass Optical Cell</td>
</tr>
<tr>
<td>4</td>
<td>Dye Laser</td>
<td>12</td>
<td>CRDS mirror mount 2</td>
</tr>
<tr>
<td>5</td>
<td>Glan-Laser Calcite Polarizer</td>
<td>13</td>
<td>Turning mirror</td>
</tr>
<tr>
<td>6</td>
<td>Zero-Order Quartz Waveplate</td>
<td>14</td>
<td>Focusing lens</td>
</tr>
<tr>
<td>7</td>
<td>Lens : 50 cm focal length</td>
<td>15</td>
<td>PMT Detector</td>
</tr>
<tr>
<td>8</td>
<td>Front turning mirror</td>
<td>16</td>
<td>Computer/Data Acquisition Card</td>
</tr>
</tbody>
</table>

Table 3.1: List of CRDS components from Figure 3.2.
Figure 3.3: $\tau$ indicates the intensity of light from the CRDS cavity containing an absorbing species, while $\tau_0$ indicates the intensity of light in the absence of the absorbing species.
be calculated using Equation 3.2.

\[ \alpha = \frac{L}{c} \left( \frac{1}{\tau_0} - \frac{1}{\tau_{\text{sample}}} \right) \]  

(3.2)

A computer program was used to calculate \( \alpha(\lambda) \) at each wavelength yielding the extinction as a function of wavelength. From \( \alpha(\lambda) \) either the cross-section (\( \sigma \)) or the number density (\( N \)) can be calculated using Equation 3.3.

\[ \alpha(\lambda) = \sigma \cdot N \]  

(3.3)

To record a spectrum over a range of wavelengths, multiple \( \tau_0 \) and \( \tau \) values must be recorded and averaged at each wavelength step in the spectral region of interest. This time-consuming process makes CRDS inadequate for kinetic measurements for large spectral regions. The final data collected by a CRDS are decay times at each wavelength step for both the empty and sample containing cavities. The sensitivity of CRDS depends on the ability to distinguish \( \tau \) from \( \tau_0 \). The smallest difference between \( \tau \) and \( \tau_0 \) that can be distinguished is called \( \delta \tau \).

The sensitivity of a CRDS instrument, or the smallest measurable extinction coefficient \( \alpha_{\text{min}} \) is given by Equation 3.4.\(^4\)

\[ \alpha_{\text{min}} = \frac{R_L \delta \tau_0}{c \tau_0} \]  

(3.4)

\( \delta \tau \) can be decreased by increasing the reflectivity of cavity mirrors 1 and 2 at each wavelength \( R_{\text{mirror}}(\lambda) \), Figure 3.2. This effectively implies that the larger \( \tau_0 \) is compared to \( \tau \), the smaller \( \delta \tau \) is and therefore the greater the sensitivity. The CRDS in our lab is limited to the visible and near-infrared spectral regions. This limitation is due to the frequency limitations of the Nd:YAG pump laser. Other CRDS instruments that use pump lasers with different frequencies can work in the UV and far-infrared regions.

Aerosol formation inside the cavity can cause unpredictable broad absorption features that are typically constant over a wide range of wavelengths. This effect can cause a negative shift in the decay times over the entire spectral region. To reduce aerosol formation carrier gas flows were kept low enough to prevent particle-sized clusters from entering the optical cavity.
3.3  Maintenance

3.3.1  Start Up Procedure

The pump laser, dye laser, and the PMT detector need to be powered on 20 minutes prior to data collection. To power on the pump laser turn the key on the power supply and ensure the lasing button is not pressed. To power up the dye laser, simply flip the switch near the dye solution reservoir. To power up the PMT detector, first ensure the shutter is closed to protect the PMT from any accidental lasing. Next, flip the power switch on the PMT power supply and set the voltage gain to 100 V. Allow the setup to remain in this state for 20 minutes. Failure to follow the sequence can damage both lasers and the PMT detector. The computer and the gas flow to the mirror purges can be turned on at any time during this procedure.

3.3.2  Mirror Cleaning

CRDS cavity mirrors need to be cleaned periodically to provide a clean surface for maximum reflectivity. Mirror cleaning is most often performed during the alignment procedure before each mirror is placed into the mirror mounts. A sheet of aluminum foil is placed on the bench to provide a protective working surface. A 50/50 by volume mixture of methanol and acetone and optical lens paper are used to clean the mirrors. Using tweezers, hold the mirror in place on the foil and place a sheet of lens paper on the mirror. To clean using the swiping pattern, position the paper so the mirror is at one edge of the paper. Place one drop of the cleaning solution onto the lens paper and drag the paper over the mirror. To clean using the circular pattern, place a sheet of lens paper centered on the mirror. Place one drop of cleaning solution on the paper and make circular motions with the paper on the mirror. Each side of each mirror needs to be cleaned with 8 swiping patterns and 5 circular patterns.
3.3.3 Alignment

The high finesse cavity of CRDS requires precise alignment of the two highly reflective mirrors to achieve long path lengths and therefore high sensitivity. Cavity alignment needs to be completed each time the instrument is used in order to optimize ring-down times. The optics before and after the cavity need to be aligned only when placement has changed with the optics, lasers, or detector. The steps for aligning the CRDS cavity are as follows:

(1) Refer to Figure 3.2 for the following steps.

(2) Follow the Start up Procedure before aligning the cavity.

(3) Beginning with both cavity mirrors removed and the pump laser not lasing, place the alignment tools into the mirror mounts. The cross-hair tool goes in mirror mount 2 and the hole tool goes in mirror mount 1. See Figure 3.4 for description of alignment tools.

(4) Turn the pump laser on and adjust turning mirror 1 until the laser beam is centered on the hole tool and exits the cavity on the other end. Adjust turning mirror 2 until the laser beam is centered on the cross-hair tool.

(5) Iterate between steps 2 and 3 until the laser beam is centered on both the hole and cross-hair tools. Discontinue lasing.

(6) Replace the mirror at mirror position 2 on the cavity and begin lasing. Adjust cavity mirror mount 2 until the back reflected beam on turning mirror 2 is superimposed on the incoming beam. Discontinue lasing.

(7) Replace the mirror at mirror position 1 on the cavity and begin lasing. Adjust the mirror mount 1 knobs until the back reflected beam superimposes the incoming beam on turning mirror 1. Discontinue lasing.
(8) Open the shutter to the PMT detector and open the program “Time Series 4.”

(9) Begin lasing and press the play button in “Time Series 4.” Optimize the ring-down times ($\tau$) by adjusting the knobs on mirror mounts 1 and 2. Only adjust the vertical and horizontal knobs as small changes made using the diagonal adjustment knob are difficult to undo.

(10) Once the ring-down times are optimized to desired values the cavity is aligned and ready for data collection.
Figure 3.4: Alignment tools used in aligning the CRDS cavity.
Acetic Acid Spectroscopy

4.1 Experimental Conditions

I chose acetic acid to study the effects of dimerization on OH overtone absorption because it contains an OH and carbonyl group both able to form hydrogen bonds with another acetic acid molecule, Figure 2.9. It was predicted that this molecule would show changes in its vibrational absorption cross-sections with dimerization. The equilibrium constant for acetic acid dimerization was determined experimentally\textsuperscript{24} at various temperatures and fit to a formula given by Equation 4.1.

\[
K_p = \frac{P_D}{[P_M]^2} = 7.1 \times 10^{-9} \exp\left(\frac{7705}{T}\right)
\] (4.1)

I used the above mentioned CRDS instrument to conduct this experiment. Our CRDS instrument was optimized for probing transitions in the visible spectral region. In particular, the reflectivity of the CRDS mirrors was centered at 755 nm and the dye laser was pumping a \(4.5 \times 10^{-5}\) M LDS 759 dye solution. The largest ring-down time, occurring at \(\lambda_{\text{max}}\), was recorded at 162 \(\mu\)s using Equation 3.4, the sensitivity of the CRDS using these mirrors was calculated to be \(1.29 \times 10^{-14}\) cm\(^{-1}\). This configuration enabled spectroscopic viewing in a region from 720 to 800 nm. The acetic acid sample was introduced into the optical cavity (length: 87 cm, diameter 2.5 cm) by flowing helium over a temperature controlled volume of glacial acetic acid using mass flow controller 1, Figure 4.1. An additional purge flow diluted the acetic acid/helium mixture before entering the optical cavity, see Flow Controller 2 in
Figure 4.1: Additional CRDS instrument figure depicting the sample inlet configuration.
Figure 4.1. The sample and dilution helium flows were controlled using two Alicat mass flow controllers. During the experiments, the total flow entering the cavity was held constant at 0.138 standard liters per minute (SLPM). The CRDS cavity was maintained at room temperature throughout the experiment, however, the temperature of the acetic acid sample was varied to increase the vapor pressure entering the cavity. Spectra were taken at various acetic acid temperatures ranging from $-3$ to $78^\circ$C. By varying the temperature of the glacial acetic acid, I was able to change the vapor pressure above the solution.

### 4.2 Results and Comparison to Previous Work

The presence of acetic acid in daily life, vinegar for cooking and cleaning, as well as the fact that it is one of the most abundant organic acids emitted by vegetation,\textsuperscript{28} has motivated many fundamental studies on the molecule. The first spectroscopic studies of acetic acid were done on solid crystals and liquid samples of acetic acid. These studies focused on the fundamental vibrational spectroscopy.\textsuperscript{11} The fundamental spectrum of acetic acid contains many overlapping peaks caused by acetic acid monomer and dimer absorptions, Figure 4.2. Attempts were made to deconvolve the overlapping OH dimer stretch from the monomer peaks using isotope substitution.\textsuperscript{17} The monomer OH stretch of acetic acid is shown in Figure 4.2 occurring at $3583$ cm$^{-1}$ whereas the dimer OH fundamental stretch occurs at $3000$ cm$^{-1}$. This indicated that the dimer fundamental OH stretch is red-shifted from the
monomer Oh fundamental stretch by \( \approx 600 \text{ cm}^{-1} \). This alteration in the fundamental can provide an estimate to the frequency of the dimer \( v_{OH} = 4 \) stretch.

The \( v_{OH} = 4 \) overtone absorption studied in this experiment is less ambiguous to assign since it occurs in a relatively unpopulated spectral region compared to the fundamental. Any changes to the absorption cross-section that occur due to complex formation should be easily observed. The large anharmonicity of the OH stretch provides substantial absorption intensity for the \( v_{OH} = 4 \) transition, Equation 2.7. OH overtones 1-4 have been assigned in the literature.\(^3\)\(^12\) The \( v_{OH} = 4 \) spectrum from the PhD thesis by Headrick was taken using photoacoustic spectroscopy and only gives the relative intensity for the transition, Figure 4.3. The extinction coefficients obtained in this experiment can yield the cross-section of the transition or the number density of acetic acid if one term is known, Equation 3.3. Using the experimental conditions described above, ring-down times for various solution temperatures of acetic acid were obtained. These ring-down times are given in Figure 4.4. The spectra of ring-down times corresponding to acetic acid temperatures \(-3\) through \(3^\circ\) C all lie on the same baseline. Spectra corresponding to 62 and 78\(^\circ\)C have baselines shifted towards lower times. This suggests that aerosols were formed at these higher temperatures. A similar shift was seen by Begashaw et al. at \( v_{OH} = 5 \). They corrected the ring-down times by shifting the spectra until the baselines aligned. A similar procedure was performed here to produce
The equilibrium constant for acetic acid dimer formation is given by Equation 4.1. It was believed that by increasing the temperature of the acetic acid sample and therefore increasing the vapor pressure of the acid above the liquid, more acetic acid would enter into the CRDS cavity. As seen by Equation 4.1, increasing the acetic acid monomer pressure should have increased the dimer partial pressure which should have caused alterations to the overtone cross-section. During this experiment, the monomer partial pressure within the CRDS cavity could not be measured directly so the actual concentration of acetic acid dimer within the CRDS cavity at any given time could not be determined.

In this experiment, there are two places in the spectra to determine whether dimerization has indeed affected the overtone cross-sections of acetic acid. One place to observe alterations is the OH stretch of acetic acid monomer. By recording spectra at varying acetic acid monomer pressures within the CRDS cavity, the percent dimer of the total acetic acid pressure within the CRDS cavity would also vary by Equation 4.1. Comparing the monomer OH stretch cross-sections at various acetic acid pressures, Figure 4.5, could show changes to the monomer cross-section due to dimerization. However, since the acetic acid monomer concentration could not be determined in this experiment, these changes could not be determined.

The second place to study in the overtone spectra of acetic acid is at the dimer OH stretch...
stretch region. If the fundamental dimer OH stretch seen in Figure 4.2 is projected to $v_{OH} = 4$ it should occur around 850 nm. The CRDS mirror and laser dye combination used during this experiment limited the spectral range of the instrument between 720 and 800 nm. If the projected frequency of the dimer OH stretch is correct then this peak would occur outside the spectra obtained during this experiment. Even if the dimer OH stretch occurred within the spectral range of the instrument, lifetime broadening of the peak would flatten the peak making detection difficult. The energy absorbed during the 3rd OH overtone transition for acetic acid is 34 kcal/mol whereas the dissociation energy of the dimer to form two acetic acid monomers is 14 kcal/mol. Since the overtone energy is greater than the dimerization energy, some of the absorbed overtone energy can flow into other modes of the dimer causing dissociation. This dissociation of the dimer will cause the lifetime broadening of the $v_{OH} = 4$ cross-section.

To validate whether the transition I see from this experiment is, in fact, the 3rd OH stretching overtone, I plotted the difference in overtone frequency ($\Delta G$) between vibrational states $v$ and $v+1$ as a function of $1 + v$. As can be seen from Figure 4.6, the plot shows that the 3rd overtone frequency, indicated by the blue circle, lies on the line of literature overtone peaks. The anharmonicity of the $v_{OH}$ stretch is equal to one-half the slope of the best fit line in Figure 4.6. The anharmonicity obtained from this plot was 80.9 cm$^{-1}$ and the literature value$^{15}$ is 83.1 cm$^{-1}$. The agreement between literature and experimental anharmonicity
indicates that the absorption feature in Figure 4.5 is the $v_{OH} = 4$ overtone transition. Donaldson explained that the chemical threshold for vibrational overtone induced dissociation occurs when the $\Delta E$ of an overtone transition is equal to $\Delta E_{\text{threshold}}$. Takahashi calculated the energy threshold for acetic acid decomposing to methane (CH$_4$) and carbon dioxide (CO$_2$) to be 67.01 kcal/mol. The light used in this experiment (755 nm $\approx$ 37.8 kcal/mol) was not energetic enough to cause dissociation and was not predicted to do so. Referring back to Table 2.2, probing the sixth overtone transition (i.e. $v_{OH} = 7$) could possibly induce photo-dissociation, however the small cross-section ($4.23 \times 10^{-24}$ cm molecule$^{-1}$) would limit this pathway.

During this experiment, I also planned to study the $v_{OH} = 5$ region of acetic acid. Performance issues with the CRDS prevented me from completing this study. While performing the maintenance procedure for aligning and cleaning the CRDS cavity that I used for the $v_{OH} = 4$ region, I was unable to optimize the ring-down times greater than 75 $\mu$s, which corresponds to a low sensitivity. Also, instead of using mass flow controllers to carry acetic acid vapor into the CRDS cavity, the vial of acetic acid was attached directly to the cavity.
and I controlled the temperature of the water bath in order to drive more vapor pressure into
the cavity. Both the sensitivity and the number density of acetic acid in the cavity could
have played a role in not observing $v_{OH} = 5$ transition of acetic acid.

4.3 Conclusion

Unfortunately, the data from this experiment do not determine whether acetic acid
dimer formation affects overtone cross-sections. The inability to measure the concentration
of acetic acid monomer in the CRDS cavity restricted the information about dimerization
effects on the OH overtone cross-sections that potentially could have be obtained from the
spectra recorded in this experiment. This experiment presents the previously unreported in
the literature $v_{OH} = 4$ extinction coefficient of acetic acid.
Chapter 5

Future Work

Future experiments on acetic acid overtone spectroscopy could benefit by incorporating an additional absorption cell in the CRDS setup to measure the acetic acid monomer concentration within the CRDS cavity. This would allow the user to determine the absolute cross-section of the $v_{OH} = 4$ transition instead of just the extinction coefficient. The additional optical cell would allow one to quantify the changes in monomer OH cross-section as the acetic acid vapor pressure is varied within the CRDS cavity. Quantifying these changes would allow one to determine the effects of acetic acid dimerization on the $v_{OH} = 4$ cross-section of acetic acid. Adjusting the spectral region of the instrument to observe the dimer $v_{OH} = 4$ transition at 850 nm could be done, however, the lifetime broadening of the peak might make detection impossible. Another option would be to adjust the spectral region of the instrument to study the 1st OH overtone of acetic acid, since the absorption energy of this overtone is less than the dimer dissociation energy and lifetime broadening of the dimer peak would be minimal. After optimizing the CRDS to detect acetic acid dimer overtone cross-sections, the next step would be to study the effects on overtone cross-sections when acetic acid and water form a complex.
Bibliography


