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Laser Intensity and Ionic Strength Dependence of the Aqueous Nitrate and Carbonate Ion Raman Spectra

Samuel White
Western Kentucky University, samuel.white995@topper.wku.edu

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LASER INTENSITY AND IONIC STRENGTH DEPENDENCE OF THE AQUEOUS NITRATE AND CARBONATE ION RAMAN SPECTRA

A Capstone Experience/Thesis Project

Presented in Partial Fulfillment of the Requirements for

the Degree Bachelor of Science with

Honors College Graduate Distinction at Western Kentucky University

By

Samuel T. White

*****

Western Kentucky University
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CE/T Committee:

Dr. Matthew J. Nee, Advisor

Dr. Keith Andrew

Dr. Gordon Baylis

Approved by

____________________

Advisor

Department of Chemistry
ABSTRACT

The geometry (and hence vibrational modes) of aqueous nitrate ion, NO\textsubscript{3}\textsuperscript{-}, is known to depend on the solution composition—concentration, counter ions, etc. If a definite relationship between the vibrational spectrum and ionic strength of the solution could be established, it could be a useful monitor of solution composition over time. This would be valuable in studying the reaction rates and mechanisms of reactions involving nitrate in an aqueous environment, such as its photolysis in snow. Previous work in our lab observed a split peak at the symmetric-stretch mode of nitrate, though this mode does not usually show multiple peaks. The degree of peak splitting varied with time after photolysis (possibly indicating composition dependence) and also with the laser power of the spectrometer. In this project, Raman spectra of several different nitrate and carbonate solutions were collected over a range of laser powers, in order to relate the power-dependent peak splitting to the solution composition. To check results, the experiments were repeated on a second instrument. While the first spectrometer consistently showed peak-splitting, the effect was not reproducible on the second spectrometer, and so not likely to be useful as a probe of ionic strength.

Keywords: nitrate ion, vibrational spectroscopy, atmospheric chemistry, photolysis
This work is dedicated to the glory of the LORD God—Father, Son and Holy Spirit.

His name be praised.

1 Corinthians 10:31
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First and foremost, I would like to thank my primary advisor, Dr. Matthew Nee for all his contributions to this project: providing direction to my study, bearing patiently with my learning curve, pointing out ways to improve and check my experiments, reviewing everything I wrote, and cheerfully accepting disappointing results when they became evident. Also, I am grateful to my second reader, Dr. Keith Andrew, for his continued interest in my project and his everlasting excitement about science in general, and my third reader Dr. Gordon Baylis for his input and advice. I would like to thank the students who worked in this lab before me, whose work motivated this project.

No acknowledgment would be complete without mention of my parents—not only for their unfailing support, encouragement, and advice, but also for money, food, shelter, laundry, and the countless other things they provide; my brother and very best friend, Will; and the various and sundry friends who have wished me well in “shooting lasers at stuff”, listening to me explain my project even though I can’t image they found it very interesting.

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VITA

July 26, 1991.......................................................... Born-Paducah, Kentucky

2010............................................................... Firm Foundation Homeschool,
Scottsville, Kentucky

PUBLICATIONS


FIELDS OF STUDY

Major Field 1: Chemistry (ACS certified)

Major Field 2: Physics
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CHAPTER 1

INTRODUCTION

Our world is filled with chemical reactions and chemical equilibria in and among the earth, the air, and the water. Chemical phenomena shape all of nature, not independent of one another, but intricately interrelated. Like the pieces of a puzzle, natural reactions are all connected, and understanding any one piece adds to our understanding of the whole. In order to make use of, as well as protect and maintain, nature, it is necessary to understand, as fully as possible, the mechanisms and processes that shape our world, even to the smallest ions at the remotest corners of the earth. This thesis investigates properties of aqueous solutions of nitrate, in hopes of finding a new way to study the photolysis of nitrate in snow—an obscure-seeming reaction, perhaps, but an integral part of atmospheric chemistry as a whole.

1.1 NITRATE ION

Nitrogen is one of the most abundant elements on earth. Its molecular form, N₂, is the major component of our air, and its many other forms play important roles in biological and environmental processes, affecting earth, air, and water; plants, animals and humans (1,2). One important form of nitrogen is the polyatomic ion nitrate, NO₃⁻. Nitrate is an important fertilizer, and can also be found in the atmosphere and the oceans, even in snow and ice and at the Earth’s poles (2,3,4,5,6). One seemingly small yet important role of nitrate in nature is its photolysis in aqueous solution (4,5,7). Nitrate in
water or snow can be broken apart by UV light from the sun, producing reactive species like OH radical that can react with other molecules in the snow \((5,4,7)\). A complex series of reactions can lead to the release of small molecules into the air, affecting the polar atmosphere and eventually the global atmosphere \((4,5,8)\). As a part of the global nitrogen cycle, nitrate photolysis and its accompanying reactions are important to understand, particularly in modeling the reactions that take place in snow \((4,9,10)\). Mechanisms for these reactions have been proposed, but are not fully understood, and improvements could be made by better understanding of molecular structure \((7,11)\).

Molecules have characteristic geometric shapes determined by the arrangement of bonds between atoms and the distribution of electrons \((12,13)\). However, these shapes are not rigid; they can be bent or stretched out of shape. Since nuclei and electrons are charged, the geometry can be affected by local electric fields, like those produced by polar molecules and ions or the electromagnetic waves of light. Isolated nitrate ion (Figure 1.1(a)) has a highly symmetric trigonal planar geometry \((14)\). All the N-O bonds are the same length and are separated by 120° angles. But in a polar solvent, like water, the nitrate geometry becomes distorted and its symmetry is broken \((15,16,17,18)\). Figure 1.1(b) shows one common geometry of aqueous nitrate—hydrogen-bonded to a water molecule. The nitrate oxygens involved in the hydrogen bonding are pulled slightly toward the water, increasing bond lengths and decreasing the angle between bonds. Other ions in solution have the potential to further distort the geometry of nitrate, so it could be related to ionic strength (a measure of the number of ions in solution) \((19,20,21)\). Carbonate is another polyatomic ion with the same geometry as nitrate \((13,22)\) (Figure 1.1(c)), and also experiences symmetry-breaking in solution \((17,18)\), so it
Figure 1.1. Isolated nitrate ion (a) has a $D_{3h}$ (trigonal planar) geometry. All the atoms lie in a plane with equal bond lengths and angles. In aqueous solution (b), nitrate’s geometry is distorted by hydrogen bonding, resulting in a less symmetric structure. Carbonate (c) also has a trigonal planar geometry.
might be expected to behave similarly with respect to ionic strength.

1.2 MOLECULAR VIBRATIONS

The atoms in a molecule can vibrate about their bonds, as though connected by springs. Any vibration is associated with a certain amount of energy. Quantum mechanics tells us that molecular vibrations can only occur at specific, “quantized” energy levels (23,24,25). These energy levels are specific to a given species and are closely related to molecular geometry. Changes in geometry, such as those accompanying solvation in water, can change the vibrational energy levels (16,17,18,19,21). These energy levels can be measured by vibrational spectroscopy (see Chapter 2), so it is possible to observe the effects of changes in geometry.

Two nitrate vibrational modes (22,26) are illustrated in Figure 1.2. The symmetric stretch (Figure 1.2(a)) is the vibration we investigate here. It consists of all three oxygen atoms vibrating in and out, in phase with each other. For comparison, the two asymmetric stretches (Figure 1.2(b)) are more complex, and less symmetric. In highly symmetric molecules, some vibrations can occur in more than one way with the same energy; these vibrations are said to be “degenerate”. If the molecule’s geometry is changed in such a way that its symmetry is “broken”, the degeneracy can be “lifted”, that is, the energies change relative to one another. Where before there were two states with the same energy level, the states now have different energies, and two different vibrational energy levels can be observed. This behavior has been observed for the asymmetric stretch of nitrate, which is degenerate. When nitrate is dissolved in water, its symmetry is broken as it forms hydrogen bonds with water (15,16) or ion pairs with other ions in solution (19).
Figure 1.2. Nitrate’s symmetric stretch vibration (a) is the focus of its study. All three oxygen atoms vibrate in and out of phase. For comparison, the two asymmetric stretches (b), are more complex and less symmetric.
This broken symmetry causes the energy level for the asymmetric stretch to be split into two, as has been observed in several studies of aqueous nitrate \((8,15,16,19,20)\). The symmetric stretch, on the other hand, is not degenerate, and is not usually observed to show energy level splitting \((15,16,19,20)\).

Since the precise vibrational energy levels and the degree of splitting in the asymmetric stretch depend on the solution geometry of nitrate (of which there are several possible \((15,16)\)) the vibrational spectrum (see Chapter 2) can be used to investigate the environment about nitrate. For example, Xu et al. \((19)\) used such spectral changes to measure the degree to which nitrate forms ion pairs with different counter ions. Similarly, Asher et al. \((8)\) used changes in the vibrational spectrum to observe changes in the crystal structure of solid sodium nitrate undergoing photolysis.

1.3 PREVIOUS WORK

Since nitrate photolysis and associated reactions involve changes in solution composition and ionic strength, the geometry of unphotolyzed nitrate molecules in solution could change slightly as the reactions proceed. But changes in geometry can cause changes in vibrational energy levels, which can be measured with vibrational spectroscopy. Therefore, it is possible to indirectly monitor aqueous nitrate photolysis through vibrational spectroscopy, as Asher et al. \((8)\) did for solid and aqueous sodium nitrate. They reported a decrease in intensity of the symmetric stretch peak (corresponding to a decrease in nitrate concentration) as it was photolyzed. Our group has further investigated the Raman spectrum of aqueous nitrate ion—particularly the shape and position of the symmetric stretch peak—in hopes of learning not only about
how the concentration of nitrate changes but also how its solution geometry changes during photolysis.

In a previous experiment in our lab, an aqueous nitrate solution was briefly illuminated with UV light to stimulate photolysis. Then, Raman spectra of the solution were collected at regular intervals over a three-hour period. Figure 1.3(a) shows several of the resulting spectra, zoomed in on the symmetric stretch peak. There are two interesting features: the peak appears to be “split”, composed of two overlapping peaks, and the relative sizes of these peaks change over time. To see how the spectrum changes with time, Figure 1.3(b) shows the areas of the two peaks as a function of time. Initially, the two peaks have similar areas. Over time, one shrinks while the other grows until there is essentially only one peak; but eventually they return to similar sizes.

This data presents two questions. First, why is the spectrum changing? Perhaps this represents changes in ionic strength over time, which would mean that Raman spectroscopy can be used to monitor nitrate photolysis, as hoped. Second, why are there two peaks? Since the symmetric stretch is not degenerate, the peak should not be split as a result of symmetry-breaking, nor have other studies of aqueous nitrate observed a split peak (15,16,17,18,19,20). One possibility is that the two peaks represent two different solvation geometries, each with a different energy. Another is that the peak splitting is due to some sort of AC Stark effect (27,28). The normal Stark effect (an electrical analog of the slightly better-known Zeeman effect) results from interactions between a molecule and a constant external electric field; a similar effect can be caused by an alternating (AC) electric field, such as is present in the electromagnetic waves of light (27,28). Since a Raman spectrometer probes the sample with a focused laser, such an AC electric field is
Figure 1.3. Previous data suggesting that the Raman spectrum of nitrate varies after exposure to UV light. An overlay of spectra collected at intervals after exposure (a) shows two peaks that vary with time. A plot of the peak areas vs. time (b) shows that they are similar at short and long times, but one dominates intermediately. Data collected and figures prepared by Elizabeth Fugate.
present, and could be interacting with the sample. If this is the case, the peak splitting should become more prominent as the laser power is increased—as the laser power increases, the strength of the electric field increases, and thus the strength of the effect of the field increases as well. To test this, spectra of a nitrate solution (not photolyzed) were collected at different laser powers. The results are shown in Figure 1.4. Again there are two peaks, and as predicted, the peak splitting increases with power. At low power, there is only one significant peak, but as power increases, a second peak begins to appear. Figure 1.4(b) shows that this effect is seen regardless of the counter ion used for nitrate.

1.4 PROJECT OVERVIEW

Figure 1.5 illustrates the overall motivation for this project. Nitrate photolysis is important in environmental and atmospheric chemistry, but its mechanism is complex, and not fully understood. As photolysis proceeds, it is expected to cause changes in the ionic strength of the solution, as ions are formed or eliminated. These changes could affect the solvation geometry of nitrate ion, which determines the energies of its vibrational modes. These energies can be measured with Raman spectroscopy. The Raman spectrum shows a split peak which changes in time after photolysis and depends on the power of the spectrometer laser. Hopefully, this peak splitting can be related to the ionic strength of the solution, making it useful to monitor nitrate photolysis. Traditional methods for analyzing reactions and rates often involve removing aliquots of the sample from the reaction vessel and analyzing them with chromatography (7.29); this is time-consuming and difficult. Raman spectra, on the other hand, can be collected in a matter of seconds to minutes, allowing the reactions to be monitored almost in real time.
Figure 1.4. An overlay of spectra collected at different powers (a) shows two peaks that vary with power. A plot of the peak areas vs. laser power (b) shows that the secondary peak grows with power. The trend is seen regardless of the counter ion. Data collected and figures prepared by Heather Shockley.
Figure 1.5. An overview of background and motivation for the project. Nitrate photolysis has a complex mechanism involving ionic strength which may affect the solvation geometry of nitrate, which in turn affects the vibrational modes. The vibrational energy levels can be measured by Raman spectrometry; which reveals a peak-splitting that depends on laser power. Such an effect could be used to study nitrate photolysis.

*Mechanism table reproduced from reference (7).
The goal of this project is to investigate this power-dependent peak splitting, especially to relate it to ionic strength and, if possible, to determine its origin. This is accomplished by collecting Raman spectra of several nitrate solutions while varying the laser power, and looking for a relationship between the power-dependence and the solution composition.
CHAPTER 2

EXPERIMENTAL METHODS AND PROCEDURES

These experiments primarily investigate the Raman spectrum of aqueous nitrate ion (NO$_3^-$). This chapter will provide a brief overview of Raman spectroscopy and its relation to this project, then will describe the equipment and methods used to collect and process data.

2.1 RAMAN SPECTROMETRY

Spectroscopy in general studies the interaction of light with matter, particularly the spectrum (range of wavelengths) absorbed or emitted by a certain substance under certain circumstances. Quantum mechanics tells us that atoms and molecules cannot have any arbitrary amount of energy, but instead exist only in specific, quantized energy levels; a molecule can transition between these energy levels by gaining the requisite amount of energy from, or losing it to, its surroundings (24, 25). Since energy levels are discrete, the transitions are discrete as well; a given molecule can only gain or lose energy in fixed amounts. Many such energy-transfer processes involve interaction with light—the absorption, emission, or scattering of a photon (24). Spectroscopy, then, can be used to investigate the differences between energy levels of a sample.

The difference in energy between states corresponding to molecular vibrations is similar in magnitude to the energy of an infrared (IR) photon (25), so a molecule can be excited to vibrate by absorbing a specific wavelength of IR light. Figure 2.1(a) shows
an IR absorption event (24). A molecule, initially in the ground vibrational state, \( v = 0 \), absorbs a specific-wavelength photon, and is excited to a higher vibrational state \( v = 1 \). IR spectrometry measures how much light a sample absorbs at different wavelengths.

But there are other ways a molecule can interact with a photon. Figure 2.1(b) illustrates elastic (Rayleigh) scattering, a process in which a photon “bounces off” a molecule—the photon may change direction, but neither it nor the molecule change energy (24). This is in contrast with inelastic (Raman) scattering (Figure 2.1(c)). A photon scatters off a molecule, and transfers some energy to the molecule, exciting it, for instance, to a higher vibrational level. The photon is not absorbed but scatters away, though with less energy (24,30). In this case, the energy change of the molecule corresponds not to the frequency of the incident light, but to the change in frequency between the incident and scattered light. Raman spectrometry measures the change in frequency of the scattered light (30,31).

Figure 2.2 is a sample Raman spectrum, of 1.0-M aqueous KNO₃ solution. The dependent axis is intensity of scattered light; it corresponds to the number of scattered photons, which depends on concentration of the analyte molecule, intensity of the incident light, and the scattering cross-section for the vibration (31). The intensity units are “arbitrary”—most spectrometer detectors return a pure number related to the number of photons collected. For our purposes the actual value of intensity is not important, but only the relative intensities of different spectral components. The independent axis is Raman shift—the change in wavenumber (inverse wavelength) of scattered light, measured in cm\(^{-1}\) (by convention). The wavenumber shift is directly proportional to the change in energy (24,30). The range of wavenumbers observed in vibrational Raman
Figure 2.1. Several ways a molecule can interact with light. IR absorption (a): a molecule transitions from vibrational state $v=0$ to $v=1$ by absorbing specific frequency IR. Elastic scattering (b): a photon is scattered with no effect on the molecule. Inelastic (Raman) scattering (c): a photon is scattered, but transfers energy to the molecule, exciting it to state $v=1$. 
Figure 2.2. The Raman spectrum of 1-M KNO₃. A Raman spectrum is a plot of the intensity of scattered light vs. the change in wavenumber of scattered light (relative to incident light). We are interested in the symmetric-stretch peak at 1050 cm⁻¹.
is the same as in IR, since they both deal with vibrational energy changes.

The peaks in a Raman spectrum correspond to molecular vibrations in the sample. The location of a peak corresponds to the energy change associated with exciting that vibration \((30)\). In Figure 2.2, the tall, narrow peak near 1050 cm\(^{-1}\) corresponds to the symmetric stretch vibration of NO\(_3^-\), and is the focus of this project. The low, broad peak near 1400 cm\(^{-1}\) was observed in all solutions investigated, and can be attributed to the cuvette used. The negative spike near 1200 cm\(^{-1}\) indicates a dead area on the spectrometer detector that consistently displays erratic behavior.

A Raman spectrometer is an instrument designed to collect Raman spectra. Figure 2.3 is the block diagram of a basic Raman spectrometer, such as those used in this experiment \((30,32)\). The incident light source is usually a laser, because laser radiation is monochromatic, intense, and simple to manipulate; the laser is directed to the sample with a fiber optic cable. The laser is focused into (or, in the case of a solid, onto the surface of) a sample. Backscattered light is collected and passed into a monochromator, which separates the collected light by wavelength, much like a prism. It is important that the light be collected off-axis from, or antiparallel to, the incident light, so that transmitted light does not overwhelm the signal. A detector measures intensity of the dispersed light at different points in space, corresponding to different wavelengths. The detector output is recorded and processed with a computer.

### 2.2 EQUIPMENT

This project involved two commercial Raman spectrometers. The first, which was used for previous projects and on which the effect discussed in Chapter 1 was observed, is a Raman Systems R3000 spectrometer. It uses a 785-nm laser with a range
Figure 2.3. A block diagram representing the R3000 and PeakSeeker spectrometers used in this experiment. Laser light and electrical signals are passed between the main unit and probe. The laser is focused into a sample at the end of the probe. Backscattered light is collected and dispersed onto a CCD detector.
of powers ~60-180 mW. Spectra were collected with a 60-s integration time divided into two 30-s frames. Data collection and processing is controlled with the program RSIScan. The second, purchased new at the beginning of this project, is an Agiltron Raman Systems PeakSeeker, which is basically a newer model of the same spectrometer. Like the R3000, it employs a 785-nm laser, but it can detect a wider range of wavenumber shifts and its power range is significantly larger: ~100-400 mW. Since the PeakSeeker has higher power and a better detector than the R300, the integration time was not required to be as long. A single 15-s or 8-s frame was used. Data collection and processing is controlled with RSIQ, a newer version of the RSIScan program.

Both spectrometers use a fiber optic probe to direct the excitation laser and collect backscattered light. This probe has two exchangeable tips of different lengths so that the focal point is at the tip (for solids) or a few millimeters beyond the tip (for liquids). All spectra were collected using a 1-cm glass cuvette, with the “liquid” tip on the spectrometer, and the probe tip placed flush against the cuvette.

The laser beam profile was measured near the focal point for each spectrometer. Figure 2.4 shows a top-down view of the setup for this measurement. The probe was mounted so that its beam fell on the power meter. Between the probe and power meter, a vertically-oriented razor blade was mounted on a micrometer-driven translation stage. The razor was moved into the path of the laser until a 10% decrease in its power was observed, and the razor’s horizontal position was noted. The razor was moved further until only 90% of the laser power was observed. The difference between the 10% and 90% positions was taken to be the “width” of the laser beam. This width was measured at different distances from the laser probe to find the width at the focal point.
Figure 2.4. The setup for measuring laser beam width, top-down perspective. A razor mounted to a translation stage is moved into the path of the laser beam, blocking part of the beam from reaching the power meter. The width of the beam at x is the difference in y between the positions where 10% and 90% of the power is blocked.
Throughout the project, laser power was measured before and after each spectrum with an Ophir radiant power meter. The probe was mounted to a ring stand so that the laser fell completely on the meter’s active area, and the spectrometer was set to “focus mode” (laser on continuously). The power was recorded after the reading had stabilized (a few seconds).

2.3 METHODOLOGY

All aqueous solutions were prepared by dissolving a known mass of salt in a known volume of 18-MΩ deionized water. Molarities were calculated assuming a negligible change in the water’s volume due to adding the solute. KNO₃ and NaCl were obtained from Sigma Aldrich, and K₂CO₃ and CCl₄ from Fisher Scientific; all were used without further preparation.

Most of the data in this thesis are sets of spectra collected over a range of laser powers. A solution was prepared, and a sample transferred to the cuvette. The spectrometer laser was set to its lowest power, the power was measured, and a spectrum was collected. The power was measured again after the run, and the power for that spectrum was assumed to be the average of the powers before and after data collection. The power was increased and measured, and another spectrum was collected. This was repeated until the maximum laser power was reached. A second set of spectra was collected for the same sample, but with the power decreased at each step, in order to differentiate a power-dependence from a time-dependence.

On the R3000, power was incremented in ~8-mW steps; spectra were collected with a 60-s integration time in 30-s or 10-s frames. Sets of spectra were collected for KNO₃ solutions of 1-M, 0.2-M, 0.2-M with 0.8-M NaCl, 1-M with 1-M NaCl, and 1-M
with 3-M NaCl; for K₂CO₃ solutions of 1-M, 0.5-M, and 0.5-M with 1.5-M NaCl; and for CCl₄ for comparison. On the PeakSeeker, power was incremented in ~20-mW steps; spectra were collected with a single-frame 8-s or 15-s integration. Sets of spectra were collected for KNO₃ solutions of 1 M, 0.2 M, 1 M with 1-M NaCl, and 1 M with 3-M NaCl.

Sets of spectra were analyzed with a custom MatLab program. A set of (increasing or decreasing) power-dependent spectra is analyzed together. Each spectrum is zoomed to a window surrounding the peak of interest (1000-1120 cm⁻¹ for KNO₃, 1020-1140 cm⁻¹ for K₂CO₃). The endpoints within this window are pinned to an arbitrary intensity zero, to eliminate vertical offset of different spectra; and the area under the spectrum within the window is normalized to unity to account for differences in peak height due to different laser powers. Spectral overlay plots are created from eight of the spectra in a set, for visual comparison of peak shape. Each spectrum is fit to two overlapping Gaussian peaks using a custom-written MatLab subroutine (since preliminary data suggest that the spectrum is composed of two peaks). The areas of the two peaks are then plotted as a function of power. The relative peak areas are a measure of peak splitting, so these plots show the power-dependence of the effect we want to investigate.

For all the spectra measured, different solutions were investigated at different times or on different days. To isolate solution-dependence from any possible time dependence, four solutions were investigated quasi-simultaneously on the R3000—1-M KNO₃, 0.2-M KNO₃, 1-M KNO₃ with 1-M NaCl, and 0.5-M K₂CO₃. These particular solutions were selected because they cover a wide range of concentrations and ionic
strengths, and because they showed significantly different results in the earlier experiments. Starting at the lowest power, a spectrum was collected of each of the four solutions. The power was increased, and spectra were collected for all four solutions again, in the same order; this was repeated until the maximum power was reached. Since only two cuvettes were available, it was necessary to rinse the cuvette and use a fresh aliquot of sample for each spectrum (whereas before the same aliquot was used repeatedly).
R3000 DATA: POWER DEPENDENT PEAK SPLITTING

In order to determine whether the power-dependent peak splitting observed previously in our group (Figures 1.3 and 1.4) was real or an artifact, and, if real, how it is related to solution composition, Raman spectra of various nitrate and carbonate solutions were collected over a range of powers on the R3000 spectrometer.

3.1 NITRATE

Initial data agreed well with the previous results seen in our lab. Figure 3.1(a) shows an overlay of Raman spectra from the R3000 for 1-M KNO₃ (1-M ionic strength). Each curve is the spectrum at a different power. As seen before, the peak shape changes at the highest powers (near 170 mW); a shoulder begins to appear near 1070 cm⁻¹ (the main peak being at ~1050 cm⁻¹). This peak shape can be well described as the sum of two overlapping Gaussian peaks of different areas; fitting each spectrum to this model results in the accompanying plot of Integrated Peak Area vs. Power (Figure 3.1(b)). This plot shows that, for low powers, the main peak at 1050 cm⁻¹ is dominant while the peak at 1070 cm⁻¹ is negligible. At high power, however, the main peak begins to shrink while the secondary peak grows larger, resulting in the “splitting” observed in the spectra. As noted in Chapter 1, this splitting of the symmetric stretch peak does not agree with other studies of the aqueous nitrate ion (15,16,17,18,19,20,21), in which the symmetric...
Figure 3.1. Data for several KNO₃ solutions, collected on the R3000. In each case, peak splitting appears and is strongest at high power. Raman spectra (a) and peak area vs. power (b) for 1-M KNO₃ show a slight splitting at high power. Plots of 0.2-M KNO₃ (c) and 0.2-M KNO₃ with 0.8-M NaCl (d) are similar, though noisier. The same trends are observed when decreasing power (e-f).
stretch vibration showed only a single peak, though splitting of the asymmetric stretch peak was observed and attributed to symmetry-breaking.

Previous data suggested that the peak splitting also depends on solution composition (see Chapter 1, especially Figure 1.3). To test this, spectra were collected for solutions with different concentrations of nitrate and different ionic strengths. Figures 3.1(c) and 3.1(d) are, respectively, peak area plots for 0.2-M KNO$_3$ (0.2-M ionic strength), and 0.2-M KNO$_3$ with 0.8-M NaCl (1-M ionic strength). Both plots are more erratic than Figure 3.1(b); this is because the concentration of nitrate is lower by a factor of five, and the corresponding spectra are much noisier. The most prominent trend is still that strongest splitting occurs at highest power. Sets of spectra collected with the power decreased each scan (as opposed to increased) such as Figures 3.1(e) and 3.1(f), show the same trend—maximum splitting at high power. This is consistent with the idea that the splitting is due to the Stark effect: higher power corresponds to a stronger electric field and a more pronounced effect (28).

Among these three solutions (1-M KNO$_3$, 0.2-M KNO$_3$, and 0.2-M KNO$_3$ with 0.8-M NaCl) there is not a clear relationship between the peak-splitting and either the concentration of nitrate or the ionic strength. Though the peak area plots are not identical, the differences between plots for different solutions are similar in magnitude to the differences between plots for increasing vs. decreasing power (e.g. compare Figures 3.1(b) and (e) or (d) and (f)), suggesting that they are due to random noise. Overall, the magnitude of splitting is similar in all the solutions. It may be that the peak splitting is not dependent upon nitrate concentration or ionic strength, in which case it would not be as useful as a tool for investigating nitrate photolysis as originally hoped. On the other
hand, the effect of concentration or ionic strength might be present, but so weak that it is
masked by noise. For example, in a study that varied counter-ion and concentration of
nitrate solution, Xu et al. (19) reported variations in the peak position on the order of 1
cm⁻¹, which is smaller than we can measure with our resolution. Solutions with more
drastically different composition (carbonate instead of nitrate, and nitrate in very high
ionic strength) were investigated to help identify composition dependence.

3.2 CARBONATE

Similar data were collected for carbonate solutions. Carbonate has a similar
geometry to nitrate, and also experiences symmetry breaking in solution, so if the effect
in nitrate is due to geometry changes, carbonate might be expected to display a similar
effect. Figures 3.2(a) and 3.2(b) show the results for 1-M K₂CO₃ (3-M ionic strength).
The expected peak splitting does appear, but it is much less pronounced than in 1-M
KNO₃. A very small hump appears near 1090 cm⁻¹ (the main peak being at 1070 cm⁻¹)
and is only apparent at the highest power. 0.5-M K₂CO₃ (1.5-M ionic strength) with
increasing power (Figure 3.2(c)) behaved similarly, but 0.5-M K₂CO₃ with 1.5-M NaCl
(3-M ionic strength, Figure 3.2(d)) shows stronger peak splitting overall and occurring at
lower powers. This is in contrast to the nitrate spectra, which showed little concentration
or ionic strength dependence.

The spectra collected with decreasing power (that is, power decreased on
consecutive scans) for the 1-M solution (not shown) were very similar to those with
increasing power. The other two, however, were notably different. 0.5-M with
decreasing power (Figure 3.2(e)) displayed stronger peak splitting and at lower powers,
like the 0.5-M with NaCl at increasing powers. On the other hand, 0.5-M K₂CO₃ with
Figure 3.2. Data for several $\text{K}_2\text{CO}_3$ solutions, on the R3000. Peak splitting is less prominent, but still greatest at high power. Raman spectra (a) and peak area vs. power (b) for 1-M $\text{K}_2\text{CO}_3$ show a very slight splitting, and only at very high power. 0.5-M $\text{K}_2\text{CO}_3$ (c) is similar. 0.5-M $\text{K}_2\text{CO}_3$ with 1.5-M NaCl (d) appears to have stronger splitting (still increasing with power), but may just have more noise. The decreasing power spectra for 0.5-M $\text{K}_2\text{CO}_3$ (e) and 0.5-M $\text{K}_2\text{CO}_3$ with 1.5-M NaCl (f) have slightly different shapes.
NaCl and decreasing power had significant splitting, but did not increase strictly with power, varying some but staying flat on average. These discrepancies between sets of spectra collected while increasing the power vs. decreasing the power are more pronounced than in the nitrate spectra. They probably are due to random noise, since they are worse in the lower-concentration solutions, which have a lower signal-to-noise ratio.

Overall, the carbonate solutions show a similar effect to that seen in nitrate, with a second peak growing in, with increasing power, at a higher wavenumber. The solutions 0.5-M in carbonate have more noticeable splitting and power dependence than the 1-M, but the increasing/decreasing agreement is poorer in these solutions and the spectra themselves are noisier due to lower analyte concentration. As with nitrate, then, it is difficult to draw a definite relationship between the peak splitting and the solution composition.

3.3 HIGH IONIC STRENGTH

Since these data did not definitely establish a connection between the laser-power peak-splitting effect and ionic strength, as would be expected if it arose from geometry changes, sets of spectra were collected for nitrate solutions with much higher ionic strengths: 1-M KNO₃ with 1-M NaCl (2-M ionic strength) and 1-M KNO₃ with 3-M NaCl (4-M ionic strength). The results are shown in Figure 3.3. In both cases, the peak splitting is much more pronounced than in any of the preceding solutions, with the second peak much larger relative to the first. However, the difference between these two solutions is smaller than might have been expected if the effect were linear; that is, since the solution with 1-M NaCl had twice the ionic strength of 1-M KNO₃, and that with 3-M
Figure 3.3. Data for nitrate solutions with very high ionic strength, on the R3000. Peak splitting is very strong, but trends with power are not consistent. Raman spectra and peak area vs. power for 1-M KNO$_3$ with 1-M NaCl (a-b) and for 1-M KNO$_3$ with 3-M NaCl (c-d) clearly show two peaks, but the smaller peak does not strictly increase with power, nor are power trends consistent between the solutions. Decreasing power plots (e-f) are consistent with increasing.
NaCl had four times the ionic strength, it might be predicted (to a first approximation) that whatever difference appeared between the former and the 1-M solution would have been doubled in the latter. This is not the case, so the ratio of peak heights does not vary linearly with ionic strength. Instead, there appears to be a large change in relative peak heights between 1-M and 2-M ionic strength, but very small changes from 0.2-M to 1-M and from 2-M to 4-M.

Comparing Figures 3.3(a) and 3.3(c) with Figure 3.1(a), it appears that in addition to the second peak being taller in the high ionic strength solutions, the peaks are also in a slightly different position. In the 1-M KNO₃ (Figure 3.1(a)) and other moderate ionic strength nitrate solutions, the major peak is at ~1050 cm⁻¹ and the minor peak at ~1080 cm⁻¹. For 1-M KNO₃ with 1-M NaCl (Figure 3.3(a)) the peaks are shifted slightly to lower wavenumbers—the major peak is nearer 1040 cm⁻¹ and the minor peak nearer 1070 cm⁻¹. For 1-M KNO₃ with 3-M NaCl (Figure 3.3(b)) the peaks are slightly more resolved—the major peak is near 1040 cm⁻¹, as for 1-M KNO₃ with 1-M NaCl, but the minor peak is almost to 1080 cm⁻¹, as for most of the moderate ionic strength solutions. However, there is some variability (~5 cm⁻¹) in peak position even within a set of spectra, so these may not be significant. Xu, et al. (19) reported that the symmetric stretch peak of NaNO₃ solutions shifted to larger wavenumbers at high concentrations; but over a very large concentration range (~0.2 to ~10 molal) the shift was only ~5 cm⁻¹, which is on the order of random variations on our instrument, so we do not expect to be able to observe that effect.

The other important point of the plots in Figure 3.3 is that the clear power-dependence, which was the most consistent feature in all the above plots, is not present.
The degree of peak-splitting does not increase with power, nor does the strongest splitting occur at the highest powers. This casts doubt on the hypothesis of a Stark effect, which predicts a strict power-dependence.

3.4 ARTIFACT CHECKING

Figure 3.4 shows the results of some initial artifact checking, to ensure that the effect is not something artificial introduced by the spectrometer. Figure 3.4(a) is an overlay of CCl₄ spectra collected at different powers. There is only one peak, with no splitting and no power dependence (the small changes in baseline and peak position are not significant on this instrument), proving that the splitting effect is not observed for all analytes. Of course, it could still be that the effect is an artifact specific to the 1000-1100 cm⁻¹ range of the spectrometer.

In addition to power-dependent sets of spectra, some constant-power spectra were collected on the R3000. The sample was prepared and placed in the cuvette holder, and the spectrometer was set to collect spectra at fixed time intervals. The power was measured at the beginning and end of the collection period, but not between each run. Figures 3.4(b) and 3.4(c) represent spectra of a 1-M KNO₃ solution collected at a constant 180-mW power over ~30 min in ~3-min intervals. The time is measured in minutes from the start of the hour. They show that, in this time interval, the spectrum does not change significantly, but the peak constantly has a slight shoulder around 1070 cm⁻¹, the usual peak-splitting.

3.5 SUMMARY

The R300 data show two peaks in the symmetric-stretch region of the nitrate and carbonate spectra. For moderate ionic strength solutions, one peak is very small, but
increases with laser power. In nitrate solutions with high ionic strength, the peak splitting is much more prominent, but does not show the clear power-dependence of the others. Initial artifact checking supports the belief that the effect is real; CCl₄ spectra show no power-dependence, and nitrate spectra show no time-dependence over a 30 min. interval.
Figure 3.4. Results of initial artifact testing, suggesting that the effect is real. Spectra of CCl$_4$ (a) do not show a power-dependence or any peak-splitting. Nor do spectra of 1-M KNO$_3$ (b) collected over a 30-min. period at a constant power; the peak areas (c) are constant in time.
CHAPTER 4

PEAKSEEKER DATA AND FURTHER INVESTIGATIONS

All of the nitrate and carbonate spectra collected with the R3000 spectrometer showed some form of splitting in the symmetric-stretch peak. In many cases, the peak splitting only appeared near maximum power (see especially Figures 3.1 and 3.2), suggesting that the effect might be better seen if the power could be increased further.

For this reason, and to validate the R3000 data, sets of nitrate spectra were also collected with the newer and more powerful PeakSeeker spectrometer. The results are shown in Figure 4.1. Figure 4.1(a) is an overlay of spectra for 1-M KNO₃. There is no discernable peak splitting or power dependence, even though the range of powers used is much larger than before. Figures 4.1(b) through 4.1(f) are peak area vs. power plots for several other nitrate solutions. In every case, a single peak near 1050 cm⁻¹ dominates. The spectrum is composed of only one peak—fitting the spectrum to two peaks results in one peak having negligible area. Furthermore, the plots are constant with power, the relative peak intensities having no power dependence. Variation in the plot for 0.2-M KNO₃ (Figure 4.1(e)) is due to a lower signal (resulting from decreased analyte concentration).

The fact that none of the PeakSeeker spectra display the peak splitting effect which was so apparent in the R3000 spectra, combined with the fact that the symmetric stretch is not expected to have two peaks at all (see Chapter 1), casts serious doubt on the
Figure 4.1. Nitrate data collected on the PeakSeeker. There is no peak splitting and no power dependence for 1-M KNO₃ (a-b), 1-M KNO₃ with 1-M NaCl (c), 1-M KNO₃ with 3-M NaCl (c), or 0.2-M KNO₃. Attempts to fit to two peaks result in one peak having negligible area. Decreasing power spectra (f) show the same trends.
validity of the R3000 data. Given that the two spectrometers give such drastically
different results (compare, for example, Figures 4.1(d) and 3.3(d)) we are left with two
possible conclusions: 1) The peak splitting, as originally supposed, corresponds to some
real physical phenomenon. In this case, there must be some difference in the
spectrometers that physically affects the sample. 2) One of the spectrometers is in error,
introducing some artifact via hardware or software. In this case, it is much more likely
that the newer PeakSeeker, which agrees with expectations, is functioning properly while
the older R3000, which displays an otherwise unreported effect, is in error.

Regarding the first possible explanation, the only way in which the spectrometer
interacts with the sample is through its laser. One possible difference between the
spectrometer lasers, which could account for the observed effect, is how tightly their
beams are focused. If the laser in the R3000 is focused to a much smaller spot, the local
electric field (and thus the effect on a given molecule) would be stronger than on the
PeakSeeker, even though the R3000’s overall power is less. If the peak splitting effect
we observe is, in fact, due to electrically induced molecular perturbation, such an increase
in local electric field strength could explain the differences between spectrometers. The
beam widths of the two lasers were measured along the beam axis (see Chapter 2).
Figure 4.2 shows the beam profiles for the two instruments. Their narrowest points were
found to be 89 ± 2 μm for the R3000 and 74 ± 2 μm for the PeakSeeker (average values
near the focus ± one standard deviation). These are relatively close, and the PeakSeeker
actually has the tighter focus, so beam width cannot account for the observed difference.

If the effect is artificial, introduced in error by the spectrometer, it is surprising
that it should depend on the ionic strength of solution (compare 1-M KNO₃ with and
Figure 4.2. Beam profiles for the R3000 (a) and PeakSeeker (b) spectrometer lasers. The two lines respectively represent positions of the razor where 10% or 90% of the laser’s power is blocked. Their widths are similar, but the PeakSeeker is slightly narrower. The “fit” lines do not have numerical significance, but are only for visual aid.
without 1-M NaCl, Figures 3.1(a) and 3.3(a)). It is more likely to depend on time, as an issue with spectrometer might fluctuate in time or be sensitive to the environment, in which case the spectral differences would be due not to changing solution composition but to collecting data on different days and times. To distinguish solution-dependence from time-dependence, sets of spectra for four different solutions were collected on the R3000 quasi-simultaneously by exchanging samples after each scan (see Chapter 2 for a more detailed explanation). The results are shown in Figure 4.3.

Figure 4.3(a) shows the spectra for 1-M KNO₃, collected on the R3000. Peak splitting is again observed, but the peak shape is strikingly different from all earlier spectra. In all previous cases, the dominant peak was at the lower wavenumber, near 1050 cm⁻¹ in nitrate solutions and 1070 cm⁻¹ in carbonate. But here the dominant peak is at higher wavenumber, near 1070 cm⁻¹ in nitrate and 1080 cm⁻¹ in carbonate. The peak area plots (Figures 4.3(b) to 4.3(e)) show that this is true for all four solutions. More importantly, the four peak area plots show “power” dependence very similar to each other, but very different from previous data on the same solutions. In each of these four plots, the areas of the two peaks are very close at 60 mW, but one rapidly grows larger and the other shrinks. At ~90 mW, the peaks again have similar areas. At higher powers the peaks become more stable, with one definitely larger. Yet a comparison to other spectra of the same solutions (e.g. compare Figures 4.3(b) and 3.1(b), both 1-M KNO₃) reveals much less consistency.

So we see that spectra of different solutions collected on the same day are more consistent than spectra of the same solutions collected on different days. This strongly
Figure 4.3. Sets of spectra of 1-M KNO₃ (a-b), 0.2-M KNO₃ (c), 1-M KNO₃ with 1-M NaCl (d), and 0.5-M K₂CO₃ (e), collected at the same time on the R3000. These are different from all previous spectra in that the higher-wavenumber peak dominates. All four peak area plots show similar trends with power.
suggests that the supposed peak splitting effect is an artifact of the spectrometer that varies over time. To confirm this time-dependence, spectra of 1-M KNO₃ were collected at constant 177-mW power over a period of six hours in ~13-min intervals. As for other constant-power measurements (Chapter 3) the power was measured at the beginning and end of the collection period, but not between each run. The results of two separate runs are shown in Figure 4.4. Again, there is a peak splitting, and it varies with time. In both trials, peak splitting is significant at short times, but goes away over time.

In summary, data from the PeakSeeker show that the power-dependent peak splitting is not observed on all instruments. The simultaneously collected spectra and long-time constant-power spectra show that peak splitting depends more consistently on time than on solution composition or laser power. Taken together, these facts prevent this effect from being a useful monitor of solution composition, as was originally hoped. In fact, they strongly suggest that the supposed effect is merely an artifact introduced by the R3000 spectrometer.
Figure 4.4. The spectrum of 1-M KNO₃ over a long period of time (~6 hours). There are significant changes over time. Two peaks appear at short times, but one disappears over time. (a-b) and (c-d) are for two separate trials. Also, the higher-wavenumber peak dominates, which is inconsistent with the majority of the data.
CHAPTER 5

SUMMARY AND CONCLUSION

The photolysis of nitrate in snow is important in atmospheric chemistry because it affects the polar atmosphere (4,5), but its reaction mechanism is not fully understood (7). As the reactions proceed, the solution composition changes (7), affecting the geometry and vibrations of nitrate, which can be measured with vibrational spectroscopy (16,19).

We hoped to study the reactions accompanying photolysis by monitoring the solution geometry of nitrate through Raman spectroscopy. In preliminary experiments, the Raman spectrum of nitrate was observed to change over time after photolysis, possibly showing a change in solution composition. Other experiments showed a previously unreported power-dependent peak splitting in the spectrum.

The aim of this project was to investigate this peak splitting effect, in hopes of relating it to ionic strength of the solution. Spectra of nitrate, carbonate, and nitrate with large amounts of sodium chloride all showed the same peak splitting; in most cases, the splitting increased with power, though this trend was not observed in all solutions. Similar spectra of carbon tetrachloride did not show a peak splitting, and spectra collected over a 30-min. period did show significant change in time, providing some evidence that the effect represented a real physical phenomenon.

However, similar data collected on a newer and better spectrometer showed no power dependence and no peak splitting regardless of solution composition.
Furthermore, spectra of different solutions collected quasi-simultaneously on the old spectrometer were remarkably similar, despite their marked differences when collected on separate days. Also, long-time, constant-power spectra on the old spectrometer showed significant variation over time.

Considering that the new spectrometer has a higher laser power, a better detector, and a tighter focus, and that its results agree better with those observed by others (15,16,17,18,19,20,21), it is clear that the power-dependent peak splitting investigated under investigation is an artifact introduced by hardware or software issues on the old spectrometer, making it useless as a monitor of solution composition and probe of reaction mechanisms, as was originally hoped. This artifact varies over time, as evidenced by the constant-power data. It is unlikely that such an artifact truly depends on solution composition, so the variation observed likely indicates that the artifact varies by day and time, and possibly by spectral region, as it did not appear in the carbon tetrachloride data.

Though we were unable to use this effect to study nitrate solutions, this project has been of value, particularly in uncovering a significant error in the old spectrometer which, if not identified, could potentially have interfered with other projects. Future work to be done on this project could involve investigating this artifact further, to determine whether the spectrometer can be repaired or the software updated.
REFERENCES


