RESEARCH IN PHYSICAL CHEMISTRY AND CHEMICAL EDUCATION:

Part A: Water Mediated Chemistry of Oxidized Atmospheric Compounds Part B: The Development of Surveying Tools to Determine How Effective Laboratory Experiments Contribute to Student Conceptual Understanding.

by

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Research in Physical Chemistry and Chemical Education: Part A: Water Mediated Chemistry of Oxidized Atmospheric Compounds Part B: The Development of Surveying Tools to Determine How Effective Laboratory Experiments Contribute to Student Conceptual Understanding.

Thesis directed by Professors Veronica Vaida and Robert Parson.

This dissertation is a combination of two research areas, experimental physical chemistry, Chapters I to V, and chemical education, Chapters VI to VII.

Chapters I to V describe research on the water-mediated chemistry of oxidized atmospheric molecules and the impact that water has on the spectra of these environmental systems. The role of water in the Earth's atmosphere has been of considerable interest due to its ability to impact chemistry and climate. Oxidized atmospheric molecules in the presence of water have the ability to form hydrogen bonded water complexes. The spectroscopic investigation of nitric acid-water complexes, outlined in Chapter III, was undertaken to characterize intermolecular hydrogen bonds in a water-restricted environment at ambient temperatures. Additionally, this characterization of nitric acid-water complexes allowed for the comparison of calculated overtone OH-stretching vibrational band frequencies, intensities, and anharmonicities of intermolecular hydrogen-bonded water complexes with experimental observations.

Oxidized organic molecules, such as aldehydes and ketones, in addition to forming hydrogen-bonded water complexes can undergo a hydration reaction of the carbonyl group and form germinal diols in the presence of water. This chemistry has been studied extensively in bulk aqueous media, however little is known about this process in the gas-phase at low water concentrations. The focus of the studies outlined in Chapters IV and V is motivated by the ability of pyruvic acid and formaldehyde to form germinal diols and water complexes in waterrestricted environment. This water-mediated chemistry changes the physical and chemical properties of these organic molecules, therefore, impacting the partitioning between gas and particle phase, as well as the chemistry and photochemistry of oxidized organic molecules in the Earth's atmosphere. The results presented in this dissertation may help resolve the significant discrepancy between atmospherically measured oxidized organic molecules and predictions of atmospheric models at different relative humidities.

The chemical education portion of this manuscript presented in Chapters VI and VII includes the development of a survey to determine how effective a laboratory experiment is in contributing to students' understanding of fundamental chemistry. The specific example used is an electrochemical cell. Our initial results showed that while most of our students could answer quantitative questions about the operation of the cell, their conceptual understanding of the microscopic processes that occur within the cell was inconsistent with the material presented in class. In particular, we noticed that while many students were able to correctly describe the events that take place at the surface of the anode and cathode, their understanding of the events that take place at the salt bridge was lacking.

In this investigation, we were able to confirm the misconceptions reported in previous studies. Our results suggest that a relatively modest, incremental revision of the experiment reduces these misconceptions and helped the students to develop a molecular-scale picture of the processes that occur within an electrochemical cell.

Dedication

This thesis is dedicated to my family, in Poland, Illinois and Colorado. Thank you for all your love and support through out the years.

"The most serious problem which can be urged against modern laboratory work in Physics is that it often degenerates into a servile following of directions, and thus loses all save a purely manipulative value. Important as is dexterity in the handling and adjustment of apparatus, it can not be too strongly emphasized that it is grasp of principles, not skill in manipulation, which should be the primary object of General Physics Courses."

Robert A. Millikan, 1903

"Our work is neither meaningful nor consequential until it is understood by others."

Lee S. Shulman

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Chapter I: Water-Mediated Chemistry of Oxidized Atmospheric Compounds

1.1 Motivation

In the presence of water oxidized atmospheric molecules have the ability to form hydrogen-bonded water complexes. These complexes have been of considerable interest, due to their potential role in atmospheric chemistry[1-5] and climate.[6-9] Vibrational spectra of these complexes, at ambient temperatures, are needed to assess their atmospheric importance.[1, 4, 6, 9-13] In addition to forming hydrogen-bonded water complexes, oxidized organic atmospheric molecules, such as aldehydes and to a lesser extant ketones, can undergo a hydration reaction of the carbonyl group and form geminal diols.[14-16] The formation of hydrogen-bonded complexes and geminal diols changes the physical and chemical properties of atmospheric molecules, therefore, impacting the partitioning between gas and particle phase,[17-19] as well as their chemistry and photochemistry in the atmosphere. The work presented here uses the combination of infrared spectroscopy and theoretical calculations to gain insight into the water-mediated chemistry of oxidized organic molecules at low water concentrations.

This hydration of oxidized organic molecules is well known in aqueous solutions,[15, 20-30] where this reaction occurs efficiently and is acid catalyzed. However the formation of geminal diols was not expected at low water concentrations due to the common belief that there is insufficient water present to favor hydration. The work in this thesis contradicts to this assumption and the experimental results suggest the possibility of water catalysis enhancing the extent of geminal diol formation. Our investigation of the hydration reaction of oxidized organic molecules has shown a dependence on the water concentration.[31-34]

A major consequence of this gas-phase water-mediated chemistry is that the formation of geminal diols will suppress the near-UV photochemistry due to absorbance of aldehydes, ketones and ketoacids electronic states. Traditionally, climate and chemical models only incorporate electronic excitation via ultraviolet (UV) light and subsequent dissociation as the predominant source of atmospheric photochemistry. The two alcohol groups in the diol provide an alternative photochemical pathway via overtone excitation of the OH chromophores.[36-38] Red light initiated chemistry by excitation of the OH vibrations overtones in the ground electronic state has been proposed to be significant for oxidized atmospheric species.[2, 7, 12, 13, 33, 39-48]

1.2 Characterization of Nitric Acid-Water Complex in the Mid- and Near-Infrared Regions at Ambient Temperatures in Carbon Tetrachloride

In this work we present the vibrational spectrum of a hydrogen-bonded complex, nitric acid-water, in the region 6000 cm⁻¹ to 11000 cm⁻¹ using Fourier-transform infrared spectroscopy. This study builds on previous observation of the nitric acid-water complex in the mid-infrared via a carbon tetrachloride matrix to investigate the vibrational overtone region of the complex at ambient conditions. Our experimental observations of $n_{\text{OH}} = 1$, 2 and 3 of the nitric acid-water complex provides a testing ground for the simple harmonically coupled anharmonic oscillator local-mode model treatment of OH-vibrational overtone spectra of hydrogen bonded complexes.

1.3 Hydration of Pyruvic Acid to its Geminal-Diol, 2,2-Dihydroxporanoic Acid, in a Water-Restricted Environment

In this work we present the spectroscopic characterization of 2,2-dihydroxypropanoic acid (CH₃C(OH)₂COOH) and its complexes with water. Based on the Fourier-transform mid-

infrared and nuclear magnetic resonance spectroscopy (NMR), the water-mediated hydration between pyruvic acid (CH₃COCOOH) and its geminal diol counterpart, 2,2-dihydroxypropanoic acid, was investigated at very low water concentration at ambient temperatures. By isolating pyruvic acid and water in a carbon tetrachloride matrix we determined the effect of water concentration on the extent of the hydration process. We experimentally observed large concentrations of 2,2-dihydroxypropanoic acid in the water-restricted environment of the carbon tetrachloride matrix, explained by the role of hydrogen-bonded water clusters in promoting the hydration of the carbonyl in pyruvic acid.

1.4 Gas-Phase Water Mediated Equilibrium Between Formaldehyde and Methanediol

In this work, we present the spectroscopic characterization of methanediol and its hydrated complexes in the gas phase. Based on our Fourier-transform mid-infrared spectroscopy we determined the water-mediated equilibrium between formaldehyde and methanediol at low relative humidity ($RH \le 5\%$) and ambient temperatures. The Gibbs energy determined in this study implies the possibility of gas-phase hydration of the carbonyl groups at ambient temperatures. Consequences of the hydration of formaldehyde for field measurements and atmospheric chemistry are discussed.

1.5 Dissertation overview Part A: Experimental Physical Chemistry

The work presented in this section of the dissertation is divided into four chapters and three appendices. Chapter II presents the experimental set-up for all spectroscopic studies. Chapter III presents the characterization of the nitric acid-water complex in the mid- and nearinfrared regions at ambient temperature via a carbon tetrachloride matrix. Chapter IV presents the extent of hydration of pyruvic acid to its geminal diol in a water-restricted environment. Chapter V presents the gas-phase water-mediated equilibrium between formaldehyde and methanediol. Appendix A out-lines the carbonic acid investigation and presents preliminary spectra and assignments. Appendix B out-lines new particle formation by nucleation of gas-phase methanediol experiments. Appendix C out-lines the photolysis experiments of methanediol in the gas-phase.

1.6 References for Chapter I

- 1. Vaida, V. and J.E. Headrick, *Physicochemical properties of hydrated complexes in the Earth's atmosphere*. Journal of Physical Chemistry A, 2000. **104**(23): p. 5401-5412.
- 2. Miller, Y., et al., *Photochemical processes induced by vibrational overtone excitations: Dynamics simulations for cis-HONO, trans-HONO, HNO3, and HNO3-H2O.* Journal of Physical Chemistry A, 2006. **110**(16): p. 5342-5354.
- 3. Staikova, M. and D.J. Donaldson, *Ab initio investigation of water complexes of some atmospherically important acids: HONO, HNO3 and HO2NO2.* Physical Chemistry Chemical Physics, 2001. **3**(11): p. 1999-2006.
- 4. Vaida, V., et al., Sunlight-initiated photochemistry: Excited vibrational states of atmospheric chromophores. International Journal of Photoenergy, 2008.
- 5. Frost, G. and V. Vaida, *Atmospheric implications of the photolysis of the ozone-water weakly-bound complex.* Journal of Geophysical Research-Atmospheres, 1995. **100**(D9): p. 18803-18809.
- 6. Vaida, V., et al., *Atmospheric absorption of near infrared and visible solar radiation by the hydrogen bonded water dimer.* Quarterly Journal of the Royal Meteorological Society, 2001. **127**(575): p. 1627-1643.
- Vaida, V., H.G. Kjaergaard, and K.J. Feierabend, *Hydrated complexes: Relevance to atmospheric chemistry and climate*. International Reviews in Physical Chemistry, 2003. 22(1): p. 203-219.
- 8. Headrick, J.E. and V. Vaida, *Significance of water complexes in the atmosphere*. Physics and Chemistry of the Earth Part C-Solar-Terrestial and Planetary Science, 2001. **26**(7): p. 479-486.
- 9. Daniel, J.S., et al., *Atmospheric water vapor complexes and the continuum*. Geophysical Research Letters, 2004. **31**(6): p. L06118.
- 10. Ptashnik, I.V., et al., *Laboratory measurements of water vapour continuum absorption in spectral region 5000-5600 cm(-1): Evidence for water dimers.* Quarterly Journal of the Royal Meteorological Society, 2004. **130**(602): p. 2391-2408.
- 11. Pfeilsticker, K., et al., *Atmospheric detection of water dimers via near-infrared absorption*. Science, 2003. **300**(5628): p. 2078-2080.
- 12. Donaldson, D.J., A.F. Tuck, and V. Vaida, *Atmospheric photochemistry via vibrational overtone absorption*. Chemical Reviews, 2003. **103**(12): p. 4717-4729.

- Miller, Y., R.B. Gerber, and V. Vaida, *Photodissociation yields for vibrationally excited states of sulfuric acid under atmospheric conditions*. Geophysical Research Letters, 2007. 34(16).
- 14. Kent, D.R., et al., *A theoretical study of the conversion of gas phase methanediol to formaldehyde.* Journal of Chemical Physics, 2003. **119**(10): p. 5117-5120.
- 15. Mugnai, M., et al., *Ab initio molecular dynamics study of aqueous formaldehyde and methanediol*. Molecular Physics, 2007. **105**(17-18): p. 2203-2210.
- 16. Krizner, H.E., D.O. De Haan, and J. Kua, *Thermodynamics and Kinetics of Methylglyoxal Dimer Formation: A Computational Study.* Journal of Physical Chemistry A, 2009. **113**(25): p. 6994-7001.
- 17. Bao, L., et al., *Gas/particle partitioning of low-molecular-weight dicarboxylic acids at a suburban site in Saitama, Japan.* Atmospheric Environment, 2009: p. Article in Press.
- 18. Matsunaga, S., M. Mochida, and K. Kawamura, Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Isaland in Japan. Journal of Geophysical Research, 2004. **109**: p. D04302.
- 19. Remorov, R.G. and C. George, *Analysis of chemical kinetics at the gas-aqueous interface for submicron aerosols.* Physical Chemistry Chemical Physics, 2006. **8**: p. 4897-4901.
- 20. Becker, M., *Uber magnetische kernesonanzspektren wassriger brenztrubensaurelosungen.* Berichte Der Bunsen-Gesellschaft Fur Physikalische Chemie, 1964. **68**(7): p. 669-676.
- 21. Cooper, A.J.L. and A.G. Redfield, *Proton Magnetic Resonance Studies of alpha keto acids*. The Journal of Biological Chemistry, 1975. **250**(2): p. 527-532.
- Buschmann, H.J., E. Dutkiewicz, and W. Knoche, *The Reversible Hydration of Carbonyl Compounds in Aqueous Solution.* 2. *The Kinetics of the Keto Gem-Diol Transition.* Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics, 1982. 86(2): p. 129-134.
- 23. Bezzi, S., et al., *Cinetica di formazione e scissione di macromolecole lineari ed equillri fra monomero e suol polimeri*. Gazz. Chim. Ital., 1951. **81**: p. 951.
- 24. Walker, F.J., Formaldehyde. 1964, New York: Reinhold.
- 25. Bell, R.P., *The Reversible Hydration of Carbonyl Compounds*. Adv. Phs. Org. Chem., 1966. **4**: p. 1-29.

- 26. Fischer, G., et al., *Carbon-13 NMR investigations on the structure of .alpha.-keto acids in aqueous solution.* The Journal of Organic Chemistry, 1988. **53**(1): p. 214-216.
- 27. Becker, M. and H. Strehlow, *Der einfuluss der hydratibiung auf das polarographische verhalten von alpha-oxocarbonsauren*. Zeitschrift Fur Elektrochemie, 1960. **64**(6): p. 813-817.
- 28. Buschmann, H.J., H.H. Fuldner, and W. Knoche, *Reversible hydration of carbonylcompounds in aqueous solution .1. Keto-gem-diol equilibrium.* Berichte Der Bunsen-Gesellschaft - Physical Chemistry Chemical Physics, 1980. **84**(1): p. 41-44.
- 29. Betterton, E.A. and M.R. Hoffmann, *Henry law constrans of some environmentally important aldehydes*. Environmental Science and Technology, 1988. **22**(12): p. 1415-1418.
- 30. Piret, E.L. and M.W. Hall, *Distillation principles of formaldehyde solutions Liquid Vapor equilibrium and effect of partial condensation*. Industrial and Engineering Chemistry, 1948. **40**(4): p. 661-672.
- 31. Maron, M.K., et al., *Hydration of Pyruvic Acid to its Geminal-Diol in a Water-Restricted Environment.* 2011: p. Submitted.
- 32. Maron, M.K. and V. Vaida, *Gas-Phase Water Mediated Equilibrium Between* Formaldehyde and Methanediol. TBA, 2011.
- 33. Plath, K.L., et al., *Gas-phase vibrational spectra of glyoxylic acid and its gem diol monohydrate. Implications for atmospheric chemistry.* Reaction Kinetics and Catalysis Letters, 2009. **96**(2): p. 209-224.
- 34. Axson, J.L., et al., *Gas-Phase Water Mediated Equilibrium Study Between Methylglyoxal and its Geminal Diol.* Proceedings of the National Academy of Sciences of the United States of America, 2010. **107**(15): p. 6687-6692.
- 35. Wolfe, S., et al., *Hydration of the Carbonyl Group A Theoretical Study of the Cooperative Mechanism.* Journal of the American Chemical Society, 1995. **117**(15): p. 4240-4260.
- 36. Carbajo, P.G., et al., *Ultraviolet Photolysis of HCHO: Absolute HCO Quantum Yield by Direct Detection of the HCO Radical Photoproduct.* Journal of Physical Chemistry A, 2008. **112**(48): p. 12437-12448.
- 37. Pope, F.D., et al., *Photochemistry of formaldehyde under troposhperic conditions*. Faraday Discussions, 2005. **130**: p. 59-72.
- 38. Gratien, A., et al., *UV and IR Absorption Cross-sections of HCHO, HCDO, and DCDO.* Journal of Physical Chemistry A, 2007. **111**(45): p. 11506-11513.

- 39. Plath, K.L., et al., *Fundamental and Overtone Vibrational Spectra of Gas-Phase Pyruvic Acid.* Journal of Physical Chemistry A, 2009. **113**(26): p. 7294-7303.
- 40. Takahashi, K., et al., *Dynamics of vibrational overtone excited pyruvic acid in the gas phase: Line broadening through hydrogen-atom chattering*. Journal of Physical Chemistry A, 2008. **112**(32): p. 7321-7331.
- 41. Hintze, P.E., et al., *Vibrational and electronic spectroscopy of sulfuric acid vapor*. Journal of Physical Chemistry A, 2003. **107**(8): p. 1112-1118.
- 42. Havey, D.K., et al., *Experimental and theoretical investigation of vibrational overtones of glycolic acid and its hydrogen bonding interactions with water*. Journal of Physical Chemistry A, 2006. **110**(20): p. 6439-6446.
- 43. Vaida, V., et al., *Photolysis of sulfuric acid vapor by visible solar radiation*. Science, 2003. **299**(5612): p. 1566-1568.
- 44. Vaida, V., Spectroscopy of Photoreactive Systems: Implications for Atmospheric Chemistry. Journal of Physical Chemistry A, 2009. **113**(1): p. 5-18.
- 45. Staikova, M., M. Oh, and D.J. Donaldson, *Overtone-induced decarboxylation: A potential sink for atmospheric diacids.* Journal of Physical Chemistry A, 2005. **109**(4): p. 597-602.
- 46. Matthews J, S.A., Francisco, J. S., *The importance of weak absorption features in promoting tropospheric radical production.* Proceedings of the National Academy of Sciences of the United States of America, 2005. **102**(21): p. 7449-7452.
- 47. Donaldson, D.J., et al., *Atmospheric radical production by excitation of vibrational overtones via absorption of visible light*. Geophysical Research Letters, 1997. **24**(21): p. 2651-2654.
- 48. Wennberg, P.O., et al., *Removal of stratospheric 03 by radicals in-situ measurements of OH, HO2, NO, NO2, CLO, and BRO.* Science, 1994. **266**(5184): p. 398-404.

Chapter II: Experimental Apparatus

2.1 Introduction

The experiments described in this dissertation involve Fourier-Transform Spectroscopy (FTS) and Nuclear Magnetic Resonance (NMR). This chapter reviews and outlines the spectroscopic technique FTS and NMR. The combination of FTS with an carbon tetrachloride matrix was used in the investigation of nitric acid,[1] pyruvic acid,[2] and carbonic acid. NMR was used in the investigation of pyruvic acid.[2] Formaldehyde[3] studies were performed in the gas-phase within a static cell using FTS. The FTS technique was employed to explore water-mediated chemistry, and to assign and analyze the effects of intra- and inter-molecular hydrogen bonding.

The spectroscopic methods in these experiments were used in conjunction with theory in order to analyze and interpret the vibrational spectra. In the last section the theoretical method that was used is described.

2.2 Fourier-Transform Spectroscopy

2.2.1 Background Information

The development of FTS would have been impossible without the Michelson interferometer[4-6] and Fast Fourier Transform (FFT).[7] A. A. Michelson invented this spectrometer in 1880,[4-6] and won the Nobel Prize in Physics in 1907 for using it to accurately measuring wavelengths of light. J. W. Cooley and J. W. Tukey invented the FFT algorithm,

which allowed for rapid calculations of the Fourier transforms required to convert an interferogram into a spectrum. Originally FTS was used to test the existence of a "luminiferous aether", a medium that allows for the propagation of light waves. Today most commonly FTS is used for optical spectroscopy in the mid- and near-infrared (IR), however it can be expanded to the visible and ultraviolet spectral (UV) regions. The discussion in this dissertation is limited to FTS in the mid- and near-IR, as the experimental investigations were not carried out in the visible or UV spectral regions. Two FTS instruments, Bruker IFS 66 v/s and Bruker Tensor 27, were used in our experimental investigations, the discussion in this chapter will be the general theory of FTS, while the individual chapters contain information regarding the set-up of the specific experimental presented in this dissertation. The books by P. R. Griffiths, et al.,[8] and B. C. Smith[9] were consulted during our FTS investigations.

To understand the advantages of FTS over other traditional absorption spectroscopic methods the design of an FTS spectrometer must be discussed. The design of many interferometers used for FTS is based on that of the two-beam Michelson interferometer,[4-6] shown in Figure 2.1. The Michelson interferometer consists of a broadband radiation source, beamsplitter, and two mutually perpendicular plane mirrors, one of which can move along an axis that is perpendicular to its plane. This interferometer divides a beam of radiation emitted from the source via the beamsplitter into two paths; one half is directed onto the fixed mirror and the other half reflects off the moving mirror. Then the two beams are recombined after a path difference has been introduced. The difference in distance traveled by these two light beam is



Figure 2.1 An optical diagram of a Michelson interferometer.

called the optical path difference, δ . When the beams return to the beamsplitter, they interfere and are again partially reflected and partially transmitted. Ultimately the beam is directed through the sample before reaching the detector, which provides the spectral information in a Fourier transform spectrometer.

The distance travelled by the two light beams is the same, when the moving mirror and fixed mirror are the same distance from the beam splitter. This is known as zero path distance (ZPD). Therefore, the distance that the moving mirror is moved from ZPD is known as the mirror displacement, Δ . The mirror displacement is measured with an internal HeNe laser.

When the two beams of light reflected from the fixed and moving mirror recombine at the beamsplitter at ZPD, they will be in phase. Therefore, the crests and troughs will constructively interfere, as shown in Figure 2.2. Constructive interference also occurs when the optical path



Figure 2.2 An illustration of the fixed mirror light beam (••••) and the moving mirror light beam (--••-) in a Michelson interferometer when the optical path difference is zero (ZPD). The two beams are completely in phase and constructively interfere, shown by the solid line, combing to give an intense light beam

difference is equal to multiples of the wavelength, λ . In these instances the light beam reflecting off the moving mirror has travelled a different distance then the light beam reflecting off the fixed mirror, but in the correct phase to lead to constructive interference. Constructive interference results in an intense light beam. In short constructive interference occurs for any value of δ where the two light beams are in phase, as summarized in Equation 2.1, where n = 0, 1, 2, Conversely, when the mirror displacement of the moving mirror is $\frac{1}{4}\lambda$ away of the ZPD,

2.1

the two light beams recombine at the beamsplitter and are completely out of phase. Therefore, the crests and troughs will destructively interfere, as shown in Figure 2.3, and will result in a

 $\delta = n\lambda$



Figure 2.3 An illustration of the fixed mirror light beam (••••) and the moving mirror light beam (--••-) in a Michelson interferometer when the optical path difference is $\frac{1}{2}$ of a wavelength of light. The two beams are completely our of phase and destructively interfere, shown by the solid line, combining to give a weak light beam.

weak beam. Destructive interference occurs for any multiple of an optical path difference of $\frac{1}{2}\lambda$,

as summarized in Equation 2.2, where n = 0, 1, 2, ... At distances between equations 2.1 and

$$\delta = (n + \frac{1}{2})\lambda \qquad 2.2$$

2.2 the interference is a combination between constructive and destructive interference and the intensity varies accordingly.

A plot of the light intensity as a function of optical path difference is called an interferogram, $I(\delta)$. The interferogram of a broadband source is shown in Figure 2.4.



optical path differnce (δ)

Figure 2.4 The interferogram of a broadband source. The centerburst is the sharp intensity spike at the ZPD, where all wavelengths are constructively interfering.

In a broadband source the light is a continuum of wavelengths, where each gives rise to its own unique cosine wave interferograms. The total interferogram is the summation of the interferograms from all the different wavelengths, which is given by Equation 2.3, where B(v) is the spectral intensity as a function of the wavenumber,

$$I(\delta) = \int_{-\infty}^{+\infty} B(v) \cos 2\pi v \delta \, dv \qquad 2.3$$

v. The interferogram has a sharp intensity (spike) at ZPD, which is called a centerburst, and low intensity at high optical path differences, which are called the wings of the interferograms, as can be seen in Figure 2.4. The interferogram, $I(\delta)$, is not yet a spectrum, it is a plot of detector response as a function of light path difference. The interferogram, $I(\delta)$, is converted to a spectrum, B(v), the intensity as a function of wavenumber, by performing a Fourier-Transform. The Fourier-Transform converts an independent variable of a function through the general integrals 2.4 F(k)functions. and 2.5. where f(x)and general are

$$f(x) = \int_{-\infty}^{+\infty} F(k) \exp(2\pi i k x) dk$$
 2.4

$$F(k) = \int_{-\infty}^{+\infty} f(x) \exp(-2\pi i kx) dx \qquad 2.5$$

Therefore, the interferogram, $I(\delta)$, as shown in equation 2.3 can be transformed to the spectrum, B(v), by equation 2.6

$$B(v) = \int_{-\infty}^{+\infty} I(\delta) \cos 2\pi v \delta \, d\delta \qquad 2.6$$

The performance of Fourier Transform spectrometers (FT) is ultimately determined by the resolution and signal-to-noise ratio (SNR). The spectral resolution is a measure of the ability of an FT to distinguish spectral features and is controlled by two parts of the interferometer, the optical path difference of the moving mirror, and the aperture diameter of the light beam. The larger the optical path difference the more opportunities for the instrument to distinguish between individual sinusoids of each wavelength. Therefore, as the optical path difference increases the easier it is for the FT to distinguish spectral features, this relationship is summarized in Equation 2.7. Increasing the optical path difference increases the time required to acquire

resolution
$$\propto \frac{1}{\delta}$$
 2.7

scan. A scan is defined by one cycle of the moving mirror, the moving mirror starts at ZPD, travels the requested optical path difference and returns to ZPD. Therefore, the greater the optical path difference the longer the time it takes to collect one scan, this relationship is summarized in Equation 2.8, where t is time. The diameter of the

resolution
$$\propto t$$
 2.8

aperture also effects the resolution, the smaller the aperture diameter the less dispersion in the source beam and therefore the better the resolution. Decreasing the aperture diameter allows less light to pass through the sample, and therefore lowers the SNR. To increase the SNR multiple scans are averaged together, this will in turn increase the time to acquire a spectrum. Thus, the FTS "trading rules", high resolution spectra are inherently noisier and take longer time to collect, but contain a lot of information. Low-resolution spectra are not as noisy and take less time to collect, but have lower information content.

As previously described, the interferogram in Figure 2.4, is a large number of sinusoidal signals added together. The Fourier transform calculates the infrared spectrum from the summed sinusoidal waves in the interferogram. This process requires performing a mathematical integral on the interferogram. The limits of this integral ideally would be $\pm \infty$, however it is impossible for the moving mirror to travel an infinite distance and to collect an infinite number of data

points to obtain an interferogram that will Fourier transform properly. Therefore, the interferogram and the integral is truncated at a finite point and the limits of integration are the ZPD and the desired optical path difference. Truncation of the interferogram and integral affects the spectrum by introducing sidelobes to peaks. An apodization function is employed to suppress these affects. A side effect of using apodization functions is that the spectral resolution is reduced. Suppressing the sidelobes causes an altering of the instrument lineshape and a widening of the observed transitions. Therefore, an apodization function must account for both the intensity and frequency resolution needs for a given experiment: the experiments presented here utilized a 3-term Blackman-Harris apodization function.[8]

The interferogram is symmetric around the centerburst, as can be seen in Figure 2.4. This is due to the moving mirror passing through every point twice in one scan. This process is both time and data intensive, therefore the FTS collects half of the interferogram. Now the interferogram is asymmetric and artifacts are introduced. An error is introduced to the intensity and frequency in the spectrum, along with a phase lag from various components in the instrument. A phase correction is used by the FTS software that accounts for these artifacts. A phase correction is a low-resolution scan (usually 4 cm⁻¹) in which both sides of the interferogram are collected and the asymmetry between the two sides are observed by the FTS software. The FTS software then creates a correction function from this data, and multiplies the interferogram in every subsequent scan, eliminating the need to use the entire interferogram. The phase correction is specific to the parameters of each experiment (i.e. aperture, wavelength range, light source, beam splitter, etc.).

The FTS has many advantages over other traditional absorption spectroscopy methods. All source wavelengths are measured simultaneously, also known as the Multiplex advantage. Thus, the complete spectrum is recorded rapidly, which allows for many scans to be averaged, as a result one has the ability to reduce the SNR. The energy throughput in FTS is much higher than in dispersive techniques, and therefore allow for more light to be absorbed by the sample, this is known as the Throughput advantage or the Jacquinot advantage. Additionally, due to the Connes advantage, the wavenumber scale of the interferometer is kept very stable and well characterized by the use of the a HeNe laser which serves as a internal reference. The FTS is a robust and versatile technique that can be used to obtain a large amount of data.

2.2.2 Detail of FTS Instrument in the Vaida Lab

The specific configuration for each experiment is provided in detail in the individual chapters. Here the two FTS instruments will be discussed that were used in this thesis; the Bruker IFS 66 v/s and the Bruker Tensor 27. The Bruker IFS 66 v/s allows the user to control the various parameters for each experiment and uses the Michelson interferometer that was described in the previous section, with an upper limit of a 0.10 cm⁻¹ resolution. The Bruker IFS 66 v/s has the possibility to change the light source, beamsplitter and detector to accommodate the spectral region of interest. The experiments performed in the mid-infrared (800 cm⁻¹ – 4000 cm⁻¹) used a globar light source with a KBr beamsplitter, a Mercury-Cadmium-Telluride (MCT) detector , and a resolution of 0.25 cm⁻¹ and 1 cm⁻¹. In the experiments performed in the near infrared (4000 cm⁻¹ – 8000 cm⁻¹) a quartz tungsten-halogen lamp, a CaF₂ beamsplitter, a Indium-Antimonide (InSb) detector, and a resolution of 1 cm⁻¹ was used. In both experimental set-ups the detectors were nitrogen cooled. To lower the trace absorbing species in the background the spectrometer was put under vacuum. The FTS was used both in the internal and external mode. In the internal mode the sample cell and detector are housed inside the spectrometer, in the
external mode they are on the outside of the spectrometer. In the external mode a nitrogen purged box is built around the set-up to lower the absorbing species in the background.

The Bruker Tensor 27 is a smaller and less diverse FTS instrument than the Bruker IFS 66 v/s. with a relatively lower resolution, 1 cm⁻¹. The experiments performed with the Bruker Tensor 27 were between 500 cm⁻¹ and 5000 cm⁻¹, using the globar light source with a KBr beamsplitter, and a MCT detector or a DTGS detector. The Bruker Tensor 27 uses a RockSolidTM cube corner interferometer. Unlike the Michelson interferometer, the RockSolidTM cube corner interferometer. Unlike the Michelson interferometer, the RockSolidTM cube corner interferometer. Although this type of interferometer limits the optical path difference it does allow the instrument to be less susceptible to vibrations in the lab, and the alignment is more stable than the Michelson interferometer.

2.3 Nuclear Magnetic Resonance

2.3.1 Background Information

Nuclear Magnetic Resonance (NMR) is a powerful technique that is available for the investigation of the structure of molecules. NMR is considered a type of absorption spectroscopy. It involves the absorption of radiowaves by the nuclei of molecules located in a magnetic field. Although, the energy of radiofrequency (RF) is low, it is great enough to affect the nuclear spin of electrons in a molecule. The fundamental property of spin is inherent to all protons, electrons, and neutrons as defined by quantum mechanics. Charged particles, such as protons and electrons, possess spin, which creates a magnetic field, such as produced by the NMR spectrometer and/or produced by surrounding electrons. In the presence of an applied magnetic field, nuclei with nuclear spin can exist in one of two discrete energy levels, as shown

in Figure 2.5. The energy levels are separated by ΔE . The lower energy level $(m = \frac{1}{2})$ has the nuclear magnetic moment aligned with the field. The higher energy level $(m = -\frac{1}{2})$ has the nuclear magnetic moment aligned against the field. Irradiating the sample with RF, the nuclei absorbs energy, and become excited. The spin is flipped from a lower potential energy level to a higher potential energy. Monitoring the frequencies that are absorbed by the nuclei in a magnetic field provides information about the chemical structure of the molecule.[10, 11]



Figure 2.5 Energy levels for a nucleus with a spin quantum number of 1/v.[11]

Modern NMR spectrometers use the Fourier Transform (FT), which allow for faster data acquisition and increase sensitivity compared to continuous wave NMRs. The fundamentals of FT spectroscopy and the advantages gained through the use of FT spectroscopy were discussed in Section 2.2.1. A schematic of a typical FT-NMR is shown in Figure 2.6. Brief periodic pulses of intense RF energy simultaneously excite all of the nuclei. Following the excitation

pulse, the nuclei relax and the free induction decay (FID) is detected. The frequencies, intensities, and line shapes of the excited nuclei are contained in the FID signal. FT converts the FID signal from a time-domain to the frequency-domain, which produces an absorption spectrum. The NMR spectra are commonly plotted as absorption intensity of RF radiation versus the chemical shift, δ . The chemical shift is a relative term, which is equal to 1 ppm of the



Figure 2.6 Schematic diagram of a typical FT-NMR spectrometer.

spectrometer operating frequency. The observed differences in chemical shifts are due to the small local magnetic fields of electrons surrounding the different nuclei present in the molecule. The magnitude of a chemical shift is dependent on the ability of the electrons to shield the nuclei from the applied magnetic field. Additionally, the nuclei can be affected by the magnetic field of adjoining nuclei in the molecule. This phenomenon is known as spin-spin splitting, and further

splits the observed peaks. The integrated peak area, regardless of its splitting pattern, is directly proportional to the number of nuclei that produces the particular peak.

The advantage of NMR spectroscopy is that it has the potential to detect and resolve every chemically distinct nucleus in a molecule. This provides structural information on a molecular level.[12] The major disadvantage of this spectroscopic technique is that it is relatively insensitive, due to the naturally low abundance of NMR-active nuclei.[13]

2.3.2 Detail of NMR Instrument at University of Colorado, Boulder

The NMR facility under the direction of Dr. Richard Shoemaker at the University of Colorado, Boulder, has several FT-NMR spectrometers. The NMR spectrometers range from 300 MHz to 800 MHz. Additionally, they are equipped with various probes, optimized for different nuclei including ¹H, ¹³C, ¹⁹F, and ³¹P. The specific NMR spectrometer parameters used for the experiments in this thesis are detailed in Section 2.4.2. The NMR studies were done with collaboration with Dr. Richard Shoemaker.

2.4 Sample Handling and Experiment Set-Up

2.4.1 Carbon Tetrachloride Experiments

The carbon tetrachloride (Aldrich, >99.5%, anhydrous) used for the investigation of nitric acid,[1] pyruvic acid,[2] and carbonic acid water interactions was dried with silica gel and purified with activated carbon within a closed reservoir. The specific preparation of the nitric acid, pyruvic acid and carbonic acid aqueous solutions is provided in detail in the individual chapters.

Stock carbon tetrachloride/aqueous acid solutions were prepared by vigorously mixing excess aqueous acid solution with dried carbon tetrachloride. The mixtures were then transferred

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to a closed reservoir and allowed to phase separate over night. After phase separation the carbon tetrachloride layer of each carbon tetrachloride/aqueous acid solution was transferred from each respective closed reservoir into a glass cell fitted with IR Quartz or Calcium Fluoride windows. Cell path length varied from 2.5 cm – 30 cm, in order to improve the signal to noise ratio, and increase the absorbance. The glass cell is shown in Figure 2.7.



Figure 2.7 A schematic of the glass cell used in carbon tetrachloride matrix experiments. The cell path length varied from 2.5 - 15 cm and was fitted with either IR Quartz or Calcium Fluoride windows. (A) Side view. (B) Front view.

The glass cell and all the glassware, including the IR Quartz windows, used in these experiments were salinized. This process was performed to prevent hydrogen bonding to the glass cell walls and IR Quartz windows, rendering the surfaces hydrophobic, and thereby eliminating spectroscopic artifacts. First the glassware was cleaned with concentrated sulfuric acid, and then soaked in Nanopure water (NERL reagent grade water 18 M Ω) overnight, in order to leach our any residual acid. The clean glassware was then soaked overnight in a silanol solution. The silanol solution is a 10% (v/v) dimethylethoxysilane (Gelest, Inc.) in ethanol, pH adjusted to 4.5 – 5.5 with acetic acid and potassium hydroxide. The silanol is decanted and the glassware was rinsed with ethanol and heated in an oven for 10 minutes at 110 °C, to drive off

the ethanol and to cure the saline layer. The preparation and conditioning of the glassware used was adapted from the salinization procedure provided by Kuo, M. H., et al.[14]

The infrared absorption spectra of the carbon tetrachloride/aqueous acid layers were measured at room temperature in the mid-infrared with two commercial Fourier Transform Spectrometers (FTS). A Bruker TENSOR 27 (DTLGS detector and resolution of 1 cm⁻¹) in the mid-infrared from 2800 cm⁻¹ – 4000 cm⁻¹ with 100 scans/spectrum and a Bruker IFS 66v (InGaAs detector and resolution of 0.25 cm⁻¹) in the mid- and near-infrared from 2800 cm⁻¹ – 4000 cm⁻¹.

2.4.2 NMR Experiments

Aqueous pyruvic acid solutions for ¹³C nuclear magnetic resonance (NMR) spectroscopic studies were prepared by appropriately diluting 98 wt.% pyruvic acid with Nanopure water by weight and were vigorously mixed. The mixtures were then transferred to NMR tubes for spectroscopic analysis.

¹³C NMR spectra of the aqueous pyruvic acid solutions were obtained with a Varian Inova-400 NMR spectrometer operating at 100.63 MHz. For quantization of the ¹³C NMR resonances, a 60° excitation pulse of 9.3 μs duration was used for acquisition with a recycle delay of 4.3 seconds for signal averaging. It was not necessary to use extraordinarily long relaxation delays because the T₁ relaxation time-constant should not change significantly with relative molar concentration. Internal ratios of similar peak intensities within each spectrum were used to determine the relative molar ratio of pyruvic and 2,2-dihydroxypropanoic acids. To eliminate relative intensity variation due to the Nuclear Overhauser Effect, broadband ¹H inverse-gated decoupling was used such that the decoupler was off during the 3.0 second relaxation delay. To achieve adequate digital resolution for peak integration, the time-domain NMR signal consisting of 64K complex points was zero-filled to 256K prior to application of the Fourier Transform.

2.4.3 Gas-Phase Experiments

Formaldehyde was prepared by heating *para*formadehyde (Aldrich, 95%, prills) to 110 °C, trapping the vapor at liquid N_2 temperature, then distilling the formaldehyde from a dry ice trap into a pressure controlled spectroscopic glass cell, as adapted from Khoshkhoo, H. et al.[15] Methanediol was prepared *in-situ*, by first introducing formaldehyde into a pressure controlled spectroscopic glass cell, then opening the cell to the room atmosphere until the internal pressure of the cell was equal to the room pressure. The spectroscopic glass cell used in these experiments had a 7.62 cm inner diameter, a path length of 62.23 cm and was fitted with KRS-5 windows. The initial internal partial pressure of the spectroscopic glass cell prior to introducing the sample was approximately 15 mTorr.

The infrared absorption spectra of formaldehyde and methanediol were measured at room temperature in the mid-infrared with a commercial Fourier Transform Spectrometer (FTS) in a glass static cell. A Bruker TENSOR 27 (mercury cadmium telluride (MCT) detector and resolution of 1 cm⁻¹) was used from 600 cm⁻¹ – 4000 cm⁻¹).

2.4.4 Photochemistry Experiments

Formaldehyde and methanediol were prepared as described in Section 2.4.3 Gas-Phase Experiments. The photolysis experiments were conducted using *in-situ* detection of the gas-phase products using a commercial Fourier Transform Spectrometer (FTS). A cross glass static cell was used for the photolysis experiments. The cross cell consisted of two cells, which were connected with a #50 Ace-Threds threaded glass joint. The upper glass cell had an inner diameter of 7.62 cm, a path length of 62.23 cm and was fitted with calcium fluoride (CaF₂)

windows. The lower glass cell had an inner diameter of 2.54 cm, a path length of 62.23 cm and was fitted with KRS-5 windows. The photolysis beam passed through the upper glass cell, while the mid-infrared beam passed through the lower glass cell. The glass cell is shown in Figure 2.8.



Figure 2.8 A schematic of the photolysis experimental set-up. The photolysis beam path is shown in yellow and the infrared beam path is shown in red.

The infrared absorption spectra of formaldehydes, methanediol and photoproducts were measured at room temperature in the mid-infrared with a commercial FTS. A Bruker TENSOR 27 (mercury cadmium telluride (MCT) detector and resolution of 1 cm⁻¹) was used from 600 cm⁻¹ – 4000 cm⁻¹).

2.5 Theoretical Calculations

Theoretical analysis was used in conjunction with spectroscopic methods to analyze and interpret the vibrational spectra in this thesis. All quantum chemistry calculations were performed at the B3LYP/6-311++G(3df,3pd)[16-21] level of theory using Gaussian03[21] quantum chemistry package. The structures of the compounds investigated were optimized and the normal mode frequencies were determined. Single point calculations were used to generate a one dimensional potential energy surface for the OH chromophores and their local mode vibrational frequencies were subsequently determined using the harmonically coupled anharmonic oscillator method. The detail of the harmonically coupled anharmonic oscillator (HCAO) method is described elsewhere. [22, 23] The potential energy curves with respect to the OH-stretching coordinate used for the local mode vibrational calculation, were obtained by displacing the OH bond length by ±0.2 Å from equilibrium in steps of 0.05 Å while keeping all other structural parameters fixed at their equilibrium values. The points were fit to a Morse potential and the local-mode OH-stretching frequency was determined from the second-, third-, and fourth-order derivatives of the potential energy curve according to the procedure given by Kjaergaard[22] and Howard et al.[24]

The oscillator strengths of each OH-stretching transition have been calculated within the HCAO local mode model with local mode parameters that were determined with an *ab initio* calculated dipole moment function as described by Low, G. R., et al.[25] The theoretical studies were performed with the advice from the Skodje group.

2.6 Conclusion

The work conducted in this thesis used spectroscopic techniques, FTS and NMR as well as theoretical calculations. The carbon tetrachloride matrix was used to study the vibrational spectra of nitric acid-water complexes, the water-mediated chemistry of pyruvic acid and 2,2-dihydroxypropanoic acid and the observation of carbonic acid, covered in Chapters III, IV and Appendix A. NMR was used to aid in the observation and characterization of 2,2-dihydroxypropanoic acid, covered in Chapter IV. The water-mediated chemistry of formaldehyde and methanediol, as well as the photolysis experiments were investigated in the gas-phase using vibrational spectroscopy, covered in Chapters V, VI and Appendix A and B. Theoretical calculations were used to aid in the assignment of spectroscopic features in all of the work conducted in this thesis.

2.7 References for Chapter II

- 1. Maron, M.K., M.J. Shultz, and V. Vaida, *Characterization of the nitric acid-water complex in the infrared and near-infrared region at ambient temperatures in carbon tetrachloride*. Chemical Physics Letters, 2008. **473**(4-6): p. 268-273.
- 2. Maron, M.K., et al., *Water Mediated Equilibrium Between Pyruvic and 2,2-Dihydroxypropanoic Acids* 2011: p. Submitted.
- 3. Maron, M.K. and V. Vaida, *Gas-Phase Water Mediated Equilibrium Between Formaldehyde and Methanediol.* TBA, 2011.
- 4. Livingston, D.M., *The Master of Light: A Biography of Albert Abraham Michelson*. 1973, Chicago: The University of Press of Chicago.
- 5. Michelson, A., Phil. Mag., 1891. **31**: p. 338.
- 6. Michelson, A., Phil. Mag., 1892. **34**: p. 280.
- 7. Cooley, J.W. and J.W. Tukey, Math. Comput., 1965. 19: p. 297.
- 8. Griffiths, P.R. and J.A.d. Haseth, *Fourier Transform Infrared Spectrometry*. 2nd ed. 1986, New York, NY: Wiley.
- 9. Smith, B.C., *Fourier Transform Infraraed Spectroscopy*. 1996, Boca Raton, FL: CRC Press.
- 10. Lambert, J.B. and E.P. Mazzola, *Nuclear Magnetic Resonance Spectroscopy: An Introduction to Princliples, Applications, and Experimental Methods.* 2004, Upper Saddle River: Pearson Education, Inc.
- 11. Robinson, J.W., E.M.S. Frame, and G.M.F. II, *Undergraduate Instrumental Analysis*. Vol. 6th. 2005, New York: Marcel Dekker.
- 12. Clore, G.M. and A.M. Groneborn, *NMR structure determination of proteins and protein complexes larger than 20 kDa. Current Opinion in Chemical Biology 2.* 1998: p. 564-570.
- 13. Nelson, J.H., *Nuclear Magnetic Resonance Spectroscopy*. 2003, Upper Saddle River: Pearson Education, Inc.
- 14. Kuo, M.H., et al., *Nitric acid Water interaction probed via isolation in carbon tetrachloride.* Journal of Physical Chemistry C, 2007. **111**(25): p. 8827-8831.
- 15. Khoshkhoo, H. and E.R. Nixon, *Infrared and Raman spectra of formaldehyde in argon and nitrogen matrices*. Spectrochimica Acta, 1973. **29A**: p. 603-612.

- 16. Becke, A.D., *Density-functional thermochemistry. III. The role of exact exchange.* Journal of Chemical Physics, 1992. **98**(7): p. 5648-5652.
- 17. Lee, C.T., W.T. Yang, and R.G. Parr, *Development of the colle-salvetti correlationenergy formula into a functional of the electron-density.* Physical Review B, 1988. **37**(2): p. 785-789.
- 18. McLean, A.D. and G.S. Chandler, *Contracted Gaussian-Basis Sets for molecular Calculations. I. 2nd row atoms, Z=11-18.* Journal of Chemical Physics, 1980. **72**(10): p. 5639-5648.
- 19. Krishnan, R., et al., *Self-consistent Molecular-Orbital Methods. XX. Basis set for Correlated Wave-Functions.* Journal of Chemical Physics, 1980. **72**(1): p. 650-654.
- 20. Clark, T., et al., *Efficient Diffuse Function-Augmented Basis-Sets for Anion Calculations*. *III. The 3-21+G Basis Set for 1st-Row Elements, Li-F.* Journal of Computational Chemistry, 1983. 4(3): p. 294-301.
- 21. Frisch, M.J., et al., Gaussian03, C.02 ed. Vol. 110. 2004, Gaussian Inc.: Wallingford, CT.
- 22. Kjaergaard, H.G., *Calculated OH-stretching vibrational transitions of the water-nitric acid complex.* Journal of Physical Chemistry A, 2002. **106**(12): p. 2979-2987.
- 23. Howard, D.L., P. Jorgensen, and H.G. Kjaergaard, *Weak intramolecular interactions in ethylene glycol identified by vapor phase OH-stretching overtone spectroscopy*. Journal of the American Chemical Society, 2005. **127**(48): p. 17096-17103.
- 24. Howard, D.L. and H.G. Kjaergaard, *Influence of intramolecular hydrogen bond strength* on OH-stretching overtones. Journal of Physical Chemistry A, 2006. **110**(34): p. 10245-10250.
- 25. Low, G.R. and H.G. Kjaergaard, *Calculation of OH-stretching band intensities of the water dimer and trimer*. Journal of Chemical Physics, 1999. **110**(18): p. 9104-9115.

Chapter III: Characterization of Nitric Acid-Water Complex in the Mid- and Near-Infrared Regions at Ambient Temperatures in Carbon Tetrachloride

3.1 Introduction

Hydrogen-bonded complexes, in particular water complexes, have been of considerable interest due to their impact in both biological and environmental systems. In this study, the nitric acid-water (HNO₃•H₂O) complex is investigated through spectroscopic analysis of the vibrational overtone region at ambient temperatures. The intent of our work is to provide spectroscopic results to allow for the comparison with calculated overtone OH-stretching vibrational band frequencies, intensities and anharmonicities of intermolecular hydrogen-bonded hydrated complexes.

Hydrated complexes have been proposed to play a potential role in atmospheric chemistry[1-5] and climate.[6-11] Vibrational spectra of these complexes, at ambient temperatures, are needed to assess their atmospheric importance.[1, 6, 7, 10-14] In this context, spectroscopic studies of the vibrational overtone transitions which are able to access the anharmonic part of the potential energy surface are required. Overtone-induced chemistry through the OH-stretch has been proposed as a viable pathway for photochemical processing of hydrates in the Earth's atmosphere.[2, 8, 12, 13, 15-18] While vibrational overtone transitions are significantly weaker than transition between electronic states, intensities of the OH-stretching vibrational overtone transitions.[19, 20] In the Earth's oxidizing atmosphere OH chromophores are excellent targets for a spectroscopic study. The low vapor pressures of oxidized species (acids, alcohols,

etc.) and the low cross section of OH-stretching overtone transitions challenges spectroscopic investigations of hydrogen-bonded hydrated complexes at atmospherically relevant temperatures. Theoretical treatment of fundamental molecular vibrations has been successful using the normalmode model.[21] However, the normal-mode model is less successful in treating vibrational overtone transitions. For XH-stretching modes (where X = O, C, N and S) in the vibrational overtone region the harmonically coupled anharmonic oscillator (HCAO) local-mode model has been developed and tested successfully for CH and more recently, OH containing molecules.[21-28] The simple HCAO local-model and ab initio-calculated dipole moment functions have been used to predict overtone OH-stretching vibrational band frequencies and intensities of intermolecular hydrogen-bonded nitric acid-water complex.[29] The simple HCAO local-mode model, also referred to as the anharmonic oscillator (AO) local-mode model, only includes OHstretching modes with no coupling to other vibrational modes. Previous work has shown the simple HCAO local-mode model is a good approximation for overtone transitions.[26, 30] Theoretical investigations have shown that the overtone transitions of the hydrogen-bonded OH bond in hydrates are sensitive to the ab inito basis set used. [19, 31, 32] However, testing of the theoretical predictions for hydrogen-bonded systems have been limited to intramolecular hydrogen bonded molecules since vibrational overtone spectra of intermolecular hydrogenbonded hydrated complexes are not available at ambient temperatures.[19, 33]

The work presented in this chapter describes the first spectroscopic characterization of an intermolecular hydrogen-bonded complex, $HNO_3 \cdot H_2O$, in the vibrational overtone region at atmospherically relevant temperatures. This spectroscopic investigation of the nitric acid hydrate builds on known fundamental information of the complex. The molecular structure of the $HNO_3 \cdot H_2O$ complex has been determined through microwave studies.[34] Nitric acid hydrates

have been extensively studied experimentally at low temperatures, and through theoretical treatments.[1-3, 29, 35-48] Interest in the characterization of the HNO₃•H₂O complex is in part due to its role in the chemistry of the upper and lower atmosphere and the strong hydrogen bonding interactions between water and nitric acid.[44] A recent study by Kuo et al.[49] investigated nitric acid-water interaction via isolation in carbon tetrachloride, in the mid-infrared from 3000 to 4000 cm⁻¹, at ambient conditions. This environment has been shown to be an effective method to investigate and characterize intermolecular hydrogen-bonded complexes, such as 1,4-butanediol with aprotic solvents[50] and *N*-methyldiacetamide with phenol derivatives.[51] In this work we have used this environment to extend the characterization of the HNO₃•H₂O complex as done by Kuo et al.[49] to the vibrational overtone region. Our investigation provides a testing ground for AO local-mode treatment of the nitric acid monohydrate.

3.2 Experimental

3.2.1 Materials and Sample Preparation

All materials were purchased from Sigma-Aldrich Chemical Co., Inc. Carbon tetrachloride (Aldrich, >99.5%, anhydrous) was dried with silica gel and activated carbon in a closed reservoir. Near 100 wt.% nitric acid was generated by the addition of 1:1 mole ratio of concentrated sulfuric acid (Aldrich, 95-98%, A.C.S. Reagent), at room temperature, to a potassium nitrate (Aldrich, 99+%, A.C.S. Reagent) reservoir, at 50-60 °C, within a simple distillation set-up held under vacuum. The nitric acid product was collected in a trap submerged in a dry ice/ethanol bath, at -75 to -80 °C. Aqueous nitric acid solutions were prepared from 70 wt.% nitric acid (Aldrich, A.C.S. reagent) and diluted with Nanopure water (NERL reagent grade water 18 MΩ).

Stock carbon tetrachloride/aqueous nitric acid solutions were prepared by vigorously mixing excess 70 and 49 wt.% nitric acid with dried carbon tetrachloride. The mixtures were then transferred to a closed reservoir using a vacuum line, and allowed to phase separate over night. The carbon tetrachloride/water solution was prepared similarly. The carbon tetrachloride/near 100 wt.% nitric acid solution was prepared by vigorously mixing 3 μ L of concentrated nitric acid with 30 mL of dried carbon tetrachloride.

After phase separation the carbon tetrachloride layer of each carbon tetrachloride/water and carbon tetrachloride/nitric acid solutions was transferred from each respective closed reservoir into a glass cell fitted with IR Quartz windows. Preparation and conditioning of the glass cell and all glassware used is described elsewhere.[49] Cell path length varied form 2.5 cm – 15 cm, in order to improve the signal to noise ratio, and increase the absorbance.

3.2.2 Spectroscopic Studies

The infrared absorption spectra of carbon tetrachloride/water and carbon tetrachloride/nitric acid solutions were measured at room temperature in the mid- and near-infrared with two commercial Fourier Transform (FTS) Spectrometers. A Thermo Nicolet Avatar 360 (DTGS KBr detector, 100 scans/spectrum, resolution 1.0 cm⁻¹) was used in the mid-infrared from 2500 to 4000 cm⁻¹. A Bruker IFS 66v (InGaAs detector, 100 scans/spectrum, resolution of 0.25 cm⁻¹) was used in the near infrared from 6000 to 11000 cm⁻¹.

3.3 Results and Discussion

In this work the OH-stretching frequency, $\tilde{\omega}$, and anharmonicity, $\tilde{\omega}x$, values were calculated for the OH bond in HNO₃ and the hydrogen bonded OH in the HNO₃ of the

HNO₃•H₂O complex, as described by Kjaergaard[29] and Howard et. al.[52] The $\tilde{\omega}$ and $\tilde{\omega}x$ values were determined using QCISD theory and the 6-311++G-(2d,2p) basis set. The localmode parameters calculated with the QCISD/6-311++G(2d,2p) method for HNO₃ and the HNO₃•H₂O complex are shown in Table 3.1. Using the HNO₃ experimental data we obtained the scaling factors 0.9546 and

Table 3.1 Calculated Local-Mode Frequencies $(cm^{-1})^a$ for Nitric Acid and Nitric Acid-Water Complex

	$ ilde{\omega}$	ѽх
HNO ₃	3621	71.4
$H_2O\bullet HNO_3$	3300	81.8

^{*a*} Calculated with the QCISD/6-311++G(2d,2p) method. The calculated frequencies and anharmonicities have been scaled by 0.9546 and 0.6659, respectively, for the OH in the HNO₃ unit

0.6659 for $\tilde{\omega}$ and $\tilde{\omega}x$, so that the theoretical values reproduced experimental results in an ambient CCl₄ matrix. The experimentally derived frequency and anharmonicity of the OH-stretching oscillator in HNO₃, in CCl₄ at room temperature, were found to be 3621 cm⁻¹ and 71.4 cm⁻¹, respectively, from our observed fundamental and $\Delta v_{OH} = 1$ -3 overtone transition frequencies. We have scaled the *ab initio*-calculated $\tilde{\omega}$ and $\tilde{\omega}x$ for the HNO₃•H₂O complex, with the scaling factors obtained from the HNO₃ experimental data. Appropriate scaling factors provided corrected OH-stretching frequencies and anharmonicities for comparison with spectrsocopically observed vibrational overtone transitions of the HNO₃•H₂O complex. The theoretical work completed in this chapter follows closely Kjaergaard[29] and Howard et. al.[52] The reported OH-stretching frequencies by Kjaergaard[29] were not used here because they were scaled to fit gas phase results.



An QCISD/6-311+G(2d,2p) optimized structure of HNO₃ and the HNO₃•H₂O complex is

Figure 3.1 QCISD/6-311+G(2d,2p) optimized structure of (a) HNO₃ and (b) the HNO₃ H_2O complex

transition frequencies for HNO_3 are given in Table 3.2. The ab initio-calculated and HNO_3 -scaled frequency and anharmonicity of the bonding OH in the HNO_3 of the $HNO_3 \bullet H_2O$ complex was determined to be 3300 cm⁻¹ and 81.8 cm⁻¹, respectively.

vibrational mode	<i>ab initio</i> calculated frequency (cm ⁻¹)	experimentally observed frequency (cm ⁻¹)
H_2O		
n ₁		$3617^c, 3617^d$
n 3		3708 ^c , 3709 ^d
2 n _{OH}		7161.60 ^{<i>c</i>}
$n_{1}+n_{3}$		7161.60 ^{<i>c</i>}
3 n _{OH}		10489.68 ^c
HNO_3		
2 n ₂		3360^c , 3358^d
n ₁	3478 ^{<i>a</i>}	3475 ^{<i>c</i>} , 3475 ^{<i>d</i>}
n 1+2 n 4		6065.38 ^c
2 n ₁ - n ₈		6275.36 ^{<i>c</i>}
2 n ₁ - n ₇		6351.60 ^{<i>c</i>}
2 n ₁ - n ₉		6440.80 [°]
2 n 1	6814 ^{<i>a</i>}	6826.04 ^c
$2 n_1 + n_4$		8052 ^c
$2 n_1 + n_3$		8066.78 ^c
2 n ₁ +2 n ₈		8681 ^c
3 n 1	10006 ^{<i>a</i>}	9996.45 ^c
$HNO_3 \bullet H_2O$		
free OH (H_2O)	3711 ^{<i>b</i>}	3706 ^{<i>c</i>} , 3708 ^{<i>d</i>}
donor $OH (H_2O)$	3617 ^{<i>b</i>}	3616 ^{<i>c</i>} , 3617 ^{<i>d</i>}
donor OH (HNO ₃)		
u = 1	3137 ^{<i>a</i>}	3119 ^c
u = 2	6111 ^{<i>a</i>}	6062 ^c
u = 3	8920 ^{<i>a</i>}	8851 ^c

Table 3.2 Experimentally Observed and ab initio Calculated H_2O , HNO_3 , and $HNO_3 \cdot H_2O$ Complex Resonances and Assignment of Observed Peaks from 3000 cm⁻¹ to 11000 cm⁻¹.

 a Our AO local-mode model calculated OH-stretching transitions with the QCISD/6-311++G(2d,2p) method, HNO_3-scaled

^b Escribano, R. et al. DFT level calculations were used to obtain the calculated frequencies, scaled by 0.958.[42]

^c Our experimentally observed OH-stretching transitions, at $T = 20^{\circ}C$

^d Kuo, M. H. et al. [49]

The experimental frequency and anharmonicity of the OH-stretching oscillator of the bonding OH in the HNO₃ of the HNO₃•H₂O complex were derived to be 3286 cm⁻¹ and 84.3 cm⁻¹

¹, respectively, from our observed fundamental and $\Delta v_{OH} = 1-3$ overtone transition frequencies.

Our experimentally observed and calculated OH transition frequencies for the $HNO_3 \cdot H_2O$ complex agree within the uncertainty in measured band frequencies, due to overlapping peaks. The agreement between observed and calculated OH-stretching transitions frequencies for the $HNO_3 \cdot H_2O$ complex is good, as illustrated with results in Table 3.2.

The vibrational overtone study of the HNO₃•H₂O complex has been motivated by the recent results of Kuo et al., [49] who explored the interactions between HNO₃ and H₂O dispersed within carbon tetrachloride at ambient temperatures in the mid-infrared from 3000 to 4000 cm⁻¹. Their results show that a carbon tetrachloride matrix is an effective method to investigate water complexes.[49] Addition of nitric acid to carbon tetrachloride created spectral features due to molecular nitric acid as well as hydrates: nitric acid monohydrate (NAM), nitric acid dihydrate (NAD), and nitric acid trihydrate (NAT). Figure 3.2 shows a comparison of our spectra of 49 wt.% HNO₃ aqueous solution and that of Kuo et al.[49] 53 wt.% HNO₃ aqueous solution, which are within excellent agreement. Figure 3.3 contains a comparison of the mid-infrared absorption spectra of the carbon tetrachloride layer of near to 100 wt.% HNO₃, 49 wt.% HNO₃ and 100 wt.% H₂O. The following is a summary of Kuo et. al.[49] results and peak assignments, and is presented in Table 3.2 and Figure 3.3. The peak at 3475 cm⁻ ¹ is attributed to n_1 OH stretch of molecular nitric acid.



Figure 3.2 A comparison of the Kuo et al.[49] mid-infrared absorption spectrum of 53 wt.% HNO_3 with the spectrum obtained in this work of 49 wt.% HNO_3 . Absorbance has been offset for clarity.



Figure 3.3 Observed mid-infrared absorption spectra of (a) 49 wt.%, (b) concentrated HNO₃, and (c) 100 wt.% H₂O in the carbon tetrachloride layer at a 1 cm⁻¹ resolution form 3000 cm⁻¹ to 4000 cm⁻¹. The presence of nitric acid complexes is confirmed by the broad peak marked with *, and doubled peaks marked with \bullet .

The peaks at 3617 cm⁻¹ and 3709 cm⁻¹ are assigned to the symmetric and antisymmetric stretch of molecular water, respectively. Evidence of nitric acid hydrates can be clearly observed in the spectrum of 49 wt.% HNO₃. A collection of broad peaks are observed between 3000 – 3300 cm⁻¹, which were assigned by Kuo et al.[49] to donor OH of HNO₃, in NAM, NAD and NAT. The peak at 3359 cm⁻¹ was previously assigned[49] to the donor OH in a water-water hydrogen bond, within a ring formed by nitric acid hydrates. We believe that this feature is due to an overtone hot band of HNO₃. This assignment is supported by the gas phase results of HNO₃ by Feierabend et al.[53] and the lack of H₂O concentration dependence, as can be seen in Figure 3.3. In addition to the appearance of the above-mentioned new spectral features, the water symmetric and antisymmetric stretch peaks develop a doublet structure, which was attributed[49] to the water molecule donating a hydrogen to nitric acid, therefore slightly red-shifting the symmetric and antisymmetric OH-stretch. The characterization of the infrared absorption spectra of water, nitric acid and the water-nitric acid complex in the mid-infrared at room temperature shows that the samples contain nitric acid hydrates.

In this chapter I have extended the characterization of the HNO₃•H₂O complex from the mid-infrared to the vibrational overtone region. Figure 3.4 shows a 0.25 cm⁻¹ resolution nearinfrared absorption spectrum of the carbon tetrachloride layer of 70 wt.% HNO₃ aqueous solution from 6000 to 11000 cm⁻¹. This spectral region is dominated by transitions due to overtones and combinations of the fundamental normal modes of water and nitric acid, which are summarized in Table 3.2. The most prominent features observed in the vibrational overtone region are the peaks at 6826 cm⁻¹ and a collection of broad peaks between 7000 – 7500 cm⁻¹, shown in Figure 3.4, which are assigned to $2n_1$ OH-stretch of molecular HNO₃ and to $2n_{OH}$ and the combination band n_1+n_3 of H₂O, respectively. The peak at 6062 cm⁻¹ is assigned to the



combination band n_1+2n_4 of HNO₃. The peaks at 6275.36 cm⁻¹, 6351.60 cm⁻¹ and 8681 cm⁻¹ are

Figure 3.4 Observed and fitted near-infrared absorption spectrum of 70 wt.% HNO₃ aqueous solution in the carbon tetrachloride layer at a 0.25 cm⁻¹ resolution from 6000 cm⁻¹ to 11000 cm⁻¹. The peaks at 6062 cm⁻¹ and 8851 cm⁻¹, marked with *, are assigned to v = 2 and v = 3 of the donor OH-stretch of nitric acid in the HNO₃•H₂O complex. T= 20 °C.

 $2n_1$ - n_7 and $2n_1$ + $2n_8$, respectively, of molecular HNO₃. Tentative assignments of transitions are based on vibrational frequencies of the normal modes of molecular nitric acid. These transitions have not been previously reported or assigned. The summary of the peaks observed in this work is shown in Table 3.2. The assignment of the observed peaks was done by comparison to gas phase results[49, 53] and theoretical predictions.[29, 42, 54] The noticeable 80 – 90 cm⁻¹ difference between OH-stretching frequencies for gas phase spectra and CCl₄ matrix spectra of molecular HNO₃ is due to matrix effects in the liquid phase.

Evidence of the $HNO_3 \cdot H_2O$ complex can be observed in Figure 3.4 by the small shoulders at 6062 cm⁻¹ and the peak at 8851 cm⁻¹, which are assigned to the first and second overtone of donor OH-stretch of HNO_3 within the $HNO_3 \cdot H_2O$ complex. A comparison of the

near-infrared absorption spectrum of the carbon tetrachloride layer of near 100 wt.% HNO₃ and 100 wt.% H₂O with 70 wt.% HNO₃ aqueous solutions is shown in Figure 3.5. The comparison of the spectra in Figure 3.5 allowed for observation of changes in spectral features due to hydration and our AO local-mode model calculated and scaled OH frequencies assisted in the assignment of the spectral features due to the HNO₃•H₂O complex. Our experimentally



Figure 3.5 Comparison of the observed near-infrared absorption spectra of H₂O, 70 wt.% HNO₃ aqueous with concentrated HNO₃ solutions in the carbon tetrachloride layer at a 0.25 cm⁻¹ resolution from 6000 - 11000 cm⁻¹. The red shift of the first OH-stretch overtone of H₂O in the HNO₃•H₂O complex has been marked with \bullet .

observed OH frequencies for the HNO₃•H₂O complex were slightly red shifted, 18 cm⁻¹, 49 cm⁻¹ and 69 cm⁻¹ when compared with our AO local-mode model calculated and scaled OH frequencies for n = 1, 2 and 3, respectively. This difference between theory and experimental OH frequencies for the HNO₃•H₂O complex emphasizes the effect on the anharmonicity of the complex, when compared to the anharmonicity of molecular HNO₃, due to intermolecular hydrogen bonding. The elongation of the OH bond length of HNO₃ and H₂O in the HNO₃•H₂O complex leads to a change of electron density and therefore a shallower, more anharmonic potential energy surface. This is supported by derived anharmonicities of 71.6 cm⁻¹ and 84.3 cm⁻¹, for the donor OH stretch of HNO₃ and the HNO₃•H₂O complex, respectively. The observed increase in anharmonicity of the HNO₃•H₂O complex compared with molecular HNO₃ is good agreement with theoretical calculations, presented by Kjaergaard[29] using the QCISD/6-311++G(2d,2p) method.

The presence of the HNO₃•H₂O complex can be more clearly observed by a slight 30 cm⁻¹ red shift of the $2n_{OH}$ OH-stretch of water, which is attributed to the presence of nitric acid monohydrate upon the addition of HNO₃ to H₂O to the carbon tetrachloride layer. The red-shift of the OH overtone stretching transitions of water are consistent with what is seen in the fundamental region, as discussed by Kuo, et al.[49] In agreement with observation, a similar red-shift of the OH-stretching transitions of H₂O in the overtone region can be observed upon the comparison of calculated spectra of H₂O and the HNO₃•H₂O complex.[29]

Previously, HCAO local-mode model treatments of molecular HNO₃ and H₂O, have shown that the donor OH bond length of HNO₃ and H₂O in the HNO₃•H₂O complex is increased by 16 mÅ and 4 mÅ, respectively.[29] It was argued that the observed bond angle for the donor OH of HNO₃ and the acceptor O of H₂O of 175.01°, supports the increased bond length and hydrogen bonding, as it was earlier implied.[46] The increase of bond length for the donor OH of HNO₃ and acceptor OH of H₂O in the HNO₃•H₂O complex is predicted to give rise to a significant red-shift of the OH-stretching transitions for the complex with respect to the molecular units OH-stretching transitions in the fundamental and overtone regions. The theoretical predictions of a red shift of the OH-stretching transitions agree well with our experimental results. In the fundamental region the red shift of the donor OH of HNO₃ in this work was observed to be 356 cm⁻¹ (3475 cm⁻¹ to 3119 cm⁻¹), whereas the acceptor OH of H₂O is only slightly red-shifted by 19 cm⁻¹ (3708 cm⁻¹ to 3689 cm⁻¹). Similar results are observed in the spectra of the vibrational overtone region. The donor OH of HNO₃ is red-shifted by 764 cm⁻¹ (6826 cm⁻¹ to 6062 cm⁻¹) and 1145 cm⁻¹ (9996 cm⁻¹ and 8851 cm⁻¹) for $\Delta v = 2$ and 3, respectively. The acceptor OH of H₂O is only slightly red-shifted by 36 cm⁻¹ (7162 cm⁻¹ to 7126 cm⁻¹) and 44 cm⁻¹ (10494 cm⁻¹ to 10450 cm⁻¹) for $\Delta v = 2$ and 3, respectively, in good agreement with the theoretical predictions.[29]

3.4 Summary

In this study we present vibrational spectra of the intermolecular hydrogen-bonded nitric acid-water complex. This investigation of the nitric acid-water complex builds on previous work[49] in the mid-infrared via a carbon tetrachloride matrix at ambient conditions. With this method we were able to observe new transitions for molecular nitric acid and its hydrate in the vibrational overtone region up to 11,000 cm⁻¹. The experimental observations of $n_{OH} = 2$ and 3 of the nitric acid-water complex at ambient temperatures provides the first report of vibrational overtone spectra of an intermolecular hydrogen-bonded hydrated complex.

The work presented in this chapter allowed for the comparison of experimental results at ambient temperatures with AO local-mode model treatment of intermolecular hydrogen-bonded complexes. The observed OH-stretch frequencies for molecular nitric acid are in excellent agreement with the theoretical AO local-mode model calculated frequencies. The AO local-mode model was in good agreement with the OH-stretch frequencies in the vibrational overtone region for the hydrated complex. As expected, larger experimental anharmonicity is found in spectra of OH frequencies for the HNO₃•H₂O complex.

3.5 References for Chapter III

- 1. Vaida, V. and J.E. Headrick, *Physicochemical properties of hydrated complexes in the Earth's atmosphere*. Journal of Physical Chemistry A, 2000. **104**(23): p. 5401-5412.
- 2. Miller, Y., et al., *Photochemical processes induced by vibrational overtone excitations: Dynamics simulations for cis-HONO, trans-HONO, HNO3, and HNO3-H2O.* Journal of Physical Chemistry A, 2006. **110**(16): p. 5342-5354.
- 3. Staikova, M. and D.J. Donaldson, *Ab initio investigation of water complexes of some atmospherically important acids: HONO, HNO3 and HO2NO2.* Physical Chemistry Chemical Physics, 2001. **3**(11): p. 1999-2006.
- 4. Vaida, V., et al., Sunlight-initiated photochemistry: Excited vibrational states of atmospheric chromophores. International Journal of Photoenergy, 2008.
- 5. Frost, G. and V. Vaida, *Atmospheric implications of the photolysis of the ozone-water weakly-bound complex.* Journal of Geophysical Research-Atmospheres, 1995. **100**(D9): p. 18803-18809.
- 6. Ptashnik, I.V., et al., *Laboratory measurements of water vapour continuum absorption in spectral region 5000-5600 cm(-1): Evidence for water dimers.* Quarterly Journal of the Royal Meteorological Society, 2004. **130**(602): p. 2391-2408.
- Vaida, V., et al., Atmospheric absorption of near infrared and visible solar radiation by the hydrogen bonded water dimer. Quarterly Journal of the Royal Meteorological Society, 2001. 127(575): p. 1627-1643.
- Vaida, V., H.G. Kjaergaard, and K.J. Feierabend, *Hydrated complexes: Relevance to atmospheric chemistry and climate*. International Reviews in Physical Chemistry, 2003. 22(1): p. 203-219.
- 9. Headrick, J.E. and V. Vaida, *Significance of water complexes in the atmosphere*. Physics and Chemistry of the Earth Part C-Solar-Terrestial and Planetary Science, 2001. **26**(7): p. 479-486.
- 10. Daniel, J.S., et al., *Atmospheric water vapor complexes and the continuum*. Geophysical Research Letters, 2004. **31**(6): p. L06118.
- 11. Pfeilsticker, K., et al., *Atmospheric detection of water dimers via near-infrared absorption*. Science, 2003. **300**(5628): p. 2078-2080.
- 12. Vaida, V., et al., *Sunligh-initiated photchemistry: excited vibrational states of atmospheric chromophores.* International Journal of Photenergy, 2008. 2008: p. 138091.

- 13. Donaldson, D.J., A.F. Tuck, and V. Vaida, *Atmospheric photochemistry via vibrational overtone absorption*. Chemical Reviews, 2003. **103**(12): p. 4717-4729.
- Miller, Y., R.B. Gerber, and V. Vaida, *Photodissociation yields for vibrationally excited states of sulfuric acid under atmospheric conditions*. Geophysical Research Letters, 2007. 34(16).
- 15. Donaldson, D.J., et al., *Atmospheric radical production by excitation of vibrational overtones via absorption of visible light*. Geophysical Research Letters, 1997. **24**(21): p. 2651-2654.
- 16. Staikova, M., M. Oh, and D.J. Donaldson, *Overtone-induced decarboxylation: A potential sink for atmospheric diacids*. Journal of Physical Chemistry A, 2005. **109**(4): p. 597-602.
- 17. Vaida, V., et al., *Photolysis of sulfuric acid vapor by visible solar radiation*. Science, 2003. **299**(5612): p. 1566-1568.
- 18. Vaida, V., *Review article: Sunlight initiated atmospheric photochemical reactions.* International Journal of Photoenergy, 2005. 7(2): p. 61-70.
- 19. Kjaergaard, H.G., et al., *OH- and CH-stretching overtone spectra of catechol*. Journal of Physical Chemistry A, 2002. **106**(2): p. 258-266.
- 20. Takahashi, K., *XH Stretching Vibrational Spectra, A Theoretical Perspective*. 2004, Keio University.
- 21. Henry, B.R., *Local modes in description of highly vibrationally excited molecules*. Accounts of Chemical Research, 1977. **10**(6): p. 207-213.
- 22. Henry, B.R. and H.G. Kjaergaard, *Local modes*. Canadian Journal of Chemistry-Revue Canadienne De Chimie, 2002. **80**(12): p. 1635-1642.
- 23. Mortensen, O.S., et al., *Intensities in loval mode overtone spectra dichlormethane and deuterated dichloromethane*. Journal of Chemical Physics, 1985. **82**(9): p. 3903-3911.
- 24. Findsen, L.A., et al., *Theoretical description of the overtone spectra of acetaldehyde using the local mode approach*. Journal of Chemical Physics, 1986. **84**(1): p. 16-27.
- 25. Kjaergaard, H.G., et al., *Intensities in local mode overtone spectra propane*. Journal of Chemical Physics, 1990. **93**(9): p. 6239-6248.
- 26. Kjaergaard, H.G., D.M. Turnbull, and B.R. Henry, *Intensities of CH-stretching and CD-stretching overtones in 1,3-butadiene and 1,3-butadiene-D6*. Journal of Chemical Physics, 1993. **99**(12): p. 9438-9452.

- 27. Takahashi, K., et al., *Dynamics of vibrational overtone excited pyruvic acid in the gas phase: Line broadening through hydrogen-atom chattering*. Journal of Physical Chemistry A, 2008. **112**(32): p. 7321-7331.
- 28. Dunn, M.E., et al., *Experimental and Theoretical Study of the OH Vibrational Spectra and Overtone Chemistry of Gas-Phase Vinylacetic Acid.* Journal of Physical Chemistry A, 2008. **112**(41): p. 10226-10235.
- 29. Kjaergaard, H.G., *Calculated OH-stretching vibrational transitions of the water-nitric acid complex.* Journal of Physical Chemistry A, 2002. **106**(12): p. 2979-2987.
- 30. Kjaergaard, H.G. and B.R. Henry, *The relative intensity contributions of axial and equatorial CH bonds in the local mode overtone spectra of cyclohexane.* Journal of Chemical Physics, 1992. **96**(7): p. 4841-4851.
- 31. Kjaergaard, H.G., et al., *Calculated OH-stretching vibrational transitions in the waternitrogen and water-oxygen complexes*. Journal of Physical Chemistry A, 2002. **106**(38): p. 8955-8962.
- 32. Low, G.R. and H.G. Kjaergaard, *Calculation of OH-stretching band intensities of the water dimer and trimer*. Journal of Chemical Physics, 1999. **110**(18): p. 9104-9115.
- 33. Howard, D.L. and H.G. Kjaergaard, *Influence of intramolecular hydrogen bond strength on OH-stretching overtones*. Journal of Physical Chemistry A, 2006. **110**(34): p. 10245-10250.
- 34. Canagaratna, M., et al., *The nitric acid-water complex: Microwave spectrum, structure, and tunneling.* Journal of Physical Chemistry A, 1998. **102**(9): p. 1489-1497.
- McCurdy, P.R., W.P. Hess, and S.S. Xantheas, *Nitric Acid-Water Complezes: Theoretical Calculations and Comparison to Experiment*. Journal of Physical Chemistry A, 2002. 106(33): p. 7628-7635.
- 36. Ritzhaupt, G. and J.P. Devlin, *Ionic vs. molecular nature of monomerix ammonium and hydronium nitrate. Infrared spectra of H3O+NO3- and NH4+NO3 solvated in argon matrices.* The Journal of Physical Chemistry, 1977. **81**(6).
- 37. Barnes, A.J., E. Lasson, and C.J. Nielsen, *Molecular complexes of nitric acid with various bases studied by matrix isolation infrared spectroscopy*. Journal of Molecular Structure, 1994. **322**: p. 165-174.
- 38. Tolbert, M.A., B.G. Koehler, and A.M. Middlebrook, *Spectroscopic studies of model polar stratospheric cloud films*. Spectrochimica Acta Part A: Molecular Spectroscopy, 1992. **48**(9): p. 1303-1313.

- 39. Koch, T.G., et al., *Low-temperature reflection/absorption IR study of thin films of nitric acid hydrates and ammonium nitrae adsorbed on gold foil.* Journal of the Chemical Society, Faraday Transactions, 1996. **92**(23): p. 4787-4792.
- 40. Escribano, R., et al., *The nitric acid hydrates: Ab initio molecular study, and RAIR spectra of the solids.* Journal of Physical Chemistry A, 2003. **107**(5): p. 651-661.
- 41. Callaghan, R., et al., *Laboratory simulation of polar stratospheric clouds*. Geophysical Research Letters, 1994. **21**(5): p. 373-376.
- 42. Miller, Y., G.M. Chaban, and R.B. Gerber, *Theoretical study of anharmonic vibrational spectra of HNO3, HNO3-H2O, HNO4: Fundamental, overtone and combination excitations.* Chemical Physics, 2005. **313**(1-3): p. 213-224.
- 43. Koller, J. and D. Hadzi, *AM1 and ab initio calculations on nitric acid mono- and trihyrates.* Journal of Molecular Structure, 1991. **247**: p. 225-236.
- 44. Tao, F.M., et al., *Structure, binding energy, and equilibrium constant of the nitric acid-water complex*. Geophysical Research Letters, 1996. **23**(14): p. 1797-1800.
- 45. Ying, L.M. and X.S. Zhao, *Theoretical studies of XONO2-H2O* (X = Cl, H) *complexes*. Journal of Physical Chemistry A, 1997. **101**(36): p. 6807-6812.
- 46. Toth, G., *Quantum chemical study of the different forms of nitric acid monohydrate.* Journal of Physical Chemistry A, 1997. **101**(47): p. 8871-8876.
- 47. Smith, R.H., M.T. Leu, and L.F. Keyser, *Infrared spectra of solid films formed from* vapors containing water and nitric acid. Journal of Physical Chemistry, 1991. **95**(15): p. 5924-5930.
- 48. Ritzhaupt, G. and J.P. Devlin, *Infrared spectra of nitric and hydrochloric acid hydrate thin films*. Journal of Physical Chemistry, 1991. **95**(1): p. 90-95.
- 49. Kuo, M.H., et al., *Nitric acid Water interaction probed via isolation in carbon tetrachloride*. Journal of Physical Chemistry C, 2007. **111**(25): p. 8827-8831.
- 50. Kleeberg, H., D. Klein, and W.A.P. Luck, *Quantitative Infrared Spectroscopic Investigations of Hydrogen-Bond Cooperativity*. Journal of Physical Chemistry, 1987. **91**(12): p. 3200-3203.
- 51. Leroux, N., C. Samyn, and T. Zeegers-Huyskens. *Mid- and near-IR study of the hydrogen bond interaction between N-methyldiacetamide and phenols*. 1998: Elsevier Science Bv.
- 52. Howard, D.L., P. Jorgensen, and H.G. Kjaergaard, *Weak intramolecular interactions in ethylene glycol identified by vapor phase OH-stretching overtone spectroscopy*. Journal of the American Chemical Society, 2005. **127**(48): p. 17096-17103.

- 53. Feierabend, K.J., D.K. Havey, and V. Vaida, *Gas phase spectroscopy of HNO3 in the region 2000-8500 cm(-1)*. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 2004. **60**(12): p. 2775-2781.
- 54. Donaldson, D.J., et al., *Absolute intensities of nitric acid overtones*. Journal of Physical Chemistry A, 1998. **102**(27): p. 5171-5174.

Chapter IV: Hydration of Pyruvic Acid to its Geminal-Diol, 2,2-Dihydroxypropanoic Acid, in a Water-Restricted Environment

4.1 Introduction

In the presence of water, aldehydes and to a lesser extent ketones have the ability to form geminal diols by the hydration of the carbonyl group.[1-3] This chemistry has been studied extensively in bulk aqueous media,[4-9] where this reaction occurs efficiently and is acid catalyzed. However, little is known about this process at low water concentrations where the acid catalyzed mechanism is not applicable. Significant discrepancies between atmospherically measured oxidized organic molecules and predictions of atmospheric models have been observed.[10] Spectroscopic studies of the hydration of oxidized organic molecules in water-restricted environments might contribute to assessments of their atmospheric importance.

This study investigates the hydration of pyruvic acid in a water-restricted environment at ambient temperatures using a carbon tetrachloride matrix. While well known in aqueous solutions, the formation of the geminal diol of pyruvic acid, 2,2-dihydroxypropanoic acid, was not expected in a water-restricted environment. Our present results suggest the possibility of water enhancing the extent of diol formation at low water concentrations.

Pyruvic acid has been previously characterized in the mid-infrared in a carbon tetrachloride matrix[11] and in the gas-phase.[12] However, no vibrational spectra of 2,2-dihydroxypropanoic acid, or water complexes of pyruvic and 2,2-dihydroxypropanoic acids, have been reported at ambient temperatures, prior to the present study. A matrix isolation study

of methanediol by Lugez, et al.[13] and recent works by Plath, et al.[14] and Axson, et al.[14, 15] provide the only infrared spectra of other geminal diols in the literature. The characterization of pyruvic acid hydrates, 2,2-dihydroxypropanoic acid and its hydrates provided in this chapter using infrared spectroscopy makes it possible to investigate the water mediated hydration between pyruvic acid and 2,2-dihydroxypropanoic acid at low water concentration.

The hydrophobic solvent, carbon tetrachloride, was chosen in this study because of its low water solubility. Additionally, pyruvic acid has been shown to stay as a monomer in non-polar solvents, such as carbon tetrachloride, due to its ability to form intramolecular hydrogen bonds.[6] Formation of intramolecular bonds weakens the tendency of this molecule to form dimers by intermolecular hydrogen bonds. Accordingly, the carbon tetrachloride matrix is a perfect medium for the observation and characterization of pyruvic acid-water interactions at ambient temperatures. This environment has been shown to be effective for investigating the rotational structure of water[16] and for characterizing intermolecular hydrogen-bonded complexes, such as 1,4-butanediol with aprotic solvents,[17] *N*-methyldiacetamide with phenol derivatives,[18] nitric acid-water complexes,[19, 20] ions[21], and water dimer.[22] As shown here, this medium made it possible to observe pyruvic and 2,2-dihydroxypropanoic acid-water complexes, adding to the literature on hydrogen bonded complexes.[16, 19-21, 23, 24]

Organic acids are important environmental constituents due to their possible impact on climate as a result of the contribution to organic aerosols and to the formation of cloud condensation nuclei.[25-29] Pyruvic acid is one of the most abundant keto acids in the atmosphere, where it is generated by photochemical oxidation of biogenically emitted organic compounds such as isoprene.[30, 31] Pyruvic acid has been observed in the gas-phase, in aerosols, and in rainwater in both remote continental and marine atmospheres.[32-41] The role

of pyruvic acid in secondary organic aerosol formation in both clouds and aerosols has led to investigations by field measurements,[32, 34-42] laboratory studies[43-45] and theoretical modeling.[33, 46] While, the contribution of all organics in secondary organic aerosol chemistry is underestimated by approximately an order of magnitude.[47, 48] Pyruvic acid's UV photochemistry in the gas phase, in clouds, aerosols and on ice, has been included in these models.[49, 50] The major sink for pyruvic acid in the atmosphere is considered to be UV photolysis.[51] Red light initiated chemistry by excitation of the OH vibration overtones in the ground electronic state has been proposed to be significant for oxidized atmospheric species.[12, 14, 52-63] OH vibrational overtone pumping through the absorption of visible solar photons may provide another pathway for loss of pyruvic and 2,2-dihydroxypropanoic acids in the atmosphere potentially leading to different photoproducts.[12]

4.2 Experimental

4.2.1 Materials and Sample Preparation

All materials were purchased from Sigma-Aldrich Chemical Co., Inc. Carbon tetrachloride (Aldrich, >99.5%, anhydrous) was dried with silica gel and activated carbon in a closed reservoir. The samples in this study were prepared using two different methods to allow for qualitative observations and quantitative interpretations (via infrared spectroscopy). For our qualitative analysis in the mid- and near-infrared spectroscopic studies the aqueous pyruvic acid solutions were prepared by diluting 98 wt.% pyruvic acid (Aldrich, 98%) with Nanopure water (NERL reagent grade water 18M Ω) by weight. Stock carbon tetrachloride/aqueous pyruvic acid solutions were prepared by vigorously mixing excess 45, 35, 24, 15, 5 and 0 wt.% pyruvic acid aqueous solutions with dried carbon tetrachloride. The mixtures were then transferred to a closed reservoir and allowed to phase separate over night. For our quantitative interpretations

the aqueous 16 and 8 wt.% pyruvic acid solutions were prepared by adding 0.5 or 1.0 μ L of pyruvic acid to 50 mL of carbon tetrachloride saturated with Nanopure water. The carbon tetrachloride/98 wt.% pyruvic acid solution was prepared by vigorously mixing 3 μ L of 98 wt.% pyruvic acid with 30 mL of dried carbon tetrachloride.

After phase separation, the carbon tetrachloride layer of each carbon tetrachloride/pyruvic acid solution was transferred from each respective closed reservoir into a glass cell, with a path length of 2.5 cm for the mid-infrared studies and 30 cm for the near-infrared studies, both fitted with calcium fluoride windows. Preparation and conditioning of the glass cell and all glassware used in this work is described elsewhere.[19]

Aqueous pyruvic acid solutions for ¹³C nuclear magnetic resonance (NMR) spectroscopic studies were prepared by appropriately diluting 98 wt.% pyruvic acid with Nanopure water by weight and were vigorously mixed. The mixtures were then transferred to NMR tubes for spectroscopic analysis.

4.2.2 Spectroscopic Studies

The infrared absorption spectra of the carbon tetrachloride/pyruvic acid layers were measured at room temperature in the mid- and near-infrared with two commercial Fourier Transform Spectrometers (FTS). A Bruker TENSOR 27 (DTLGS detector and resolution of 1 cm⁻¹) was used for 16 and 8 wt.% carbon tetrachloride/pyruvic acid solutions, in the mid-infrared from 2800 cm⁻¹ – 4000 cm⁻¹ with 100 scans/spectrum and a Bruker IFS 66v (InGaAs detector and resolution of 0.25 cm⁻¹) was used for 45, 35, 24, 15, 5 and 0 wt.% carbon tetrachloride/pyruvic acid solutions in the mid- and near-infrared from 2800 cm⁻¹ – 4000 cm⁻¹. The higher resolution spectrometer was used in the near-infrared

region in order to investigate the first overtone region of the aqueous pyruvic acid solutions, but was not necessary in the mid-infrared region.

¹³C NMR spectra of the aqueous pyruvic acid solutions were obtained with a Varian Inova-400 NMR spectrometer operating at 100.63 MHz. For quantization of the ¹³C NMR resonances, a 60° excitation pulse of 9.3 μs duration was used for acquisition with a recycle delay of 4.3 seconds for signal averaging. It was not necessary to use extraordinarily long relaxation delays because the T₁ relaxation time-constant should not change significantly with relative molar concentration. Internal ratios of similar peak intensities within each spectrum were used to determine the relative molar ratio of pyruvic and 2,2-dihydroxypropanoic acids. To eliminate relative intensity variation due to the Nuclear Overhauser Effect, broadband ¹H inverse-gated decoupling was used such that the decoupler was off during the 3.0 second relaxation delay. To achieve adequate digital resolution for peak integration, the time-domain NMR signal consisting of 64K complex points was zero-filled to 256K prior to application of the Fourier Transform.

4.2.3 Theoretical Calculations

The structures of formaldehyde and methanediol, as well as the fundamental vibrational mode OH frequencies of methanediol were calculated using the anharmonic oscillator localmode (AO) method with the B3LYP[64, 65] functional with 6-311++G(3df,3pd)[66-69] basis set on the Gaussian 03 program.[69] The detail of the harmonically coupled anharmonic oscillator (HCAO) method is described elsewhere.[70, 71] The potential energy curves with respect to the OH-stretching coordinate used for the local mode vibrational calculation, were obtained by displacing the OH bond length by ± 0.2 Å from equilibrium in steps of 0.05 Å while keeping all other structural parameters fixed at their equilibrium values. The points were fit to a Morse
potential and the local-mode OH-stretching frequency, $\tilde{\omega}$, and anharmonicity, $\tilde{\omega}x$, were determined from the second-, third-, and fourth-order derivatives of the potential energy curve according to the equations given by Kjaergaard[70] and Howard et al.[72] Peak assignments along with AO method calculated frequencies are presented in Table 4.1. The calculated oscillator strengths of each OH-stretching transition have been calculated within the HCAO local mode model with local mode parameters that were determined with an *ab initio* calculated dipole moment function, as described by Low, G. R., et al.[74]

vibrational mode	calculated frequency (cm ⁻¹)	experimentally observed frequency (cm ⁻¹)
H_2O	d	a b
n_1	3656	3616 [°] , 3616 [°]
<i>n</i> ₃	3755 ^a	3708 ^{<i>a</i>} , 3708 ^{<i>b</i>}
2 <i>n</i> _{OH}		7162 ^{<i>a</i>}
n_1+n_3		7162"
Isomer Tce		
u_{OH}^{acid}	3360 ^{<i>a</i>} 3494 ^{<i>c</i>}	3429^{a} 3430^{c}
$2u_{OH}^{acid}$	6633	6632
Isomer Tte	0055	0052
u_{OH}^{acid}	3557 ^a , 3602 ^c	3561 ^a , 3563 ^c
$2u_{OH}^{acid}$	6983	6872
Isomer Cte	0705	0072
u_{OH}^{acid}	3594 [°]	3561 ^a , 3563 ^c
Isomer E1		
u_{OH}^{acta}	3616	3561 ^a , 3573 ^c
u_{OH}^{enolic}		3514 [°] , 3516 [°]
$CH_3COCOOH \cdot H_2O$		
Conformer Tce	a	a
	2842	2975
Conformer Tte	а	а
	2808	2887
$CH_3C(OH)_2COOH$		
u_{OH}^{acid}	3487	3429
$u_{OH}^{bonding}$	2566	
UOH free	3300 ^a	2624
$2u_{on}^{free}$	3686	3634
	7175	7084
Conformer Tce		
u_{OH}^{acid}	2828^{a}	2929 ^a
$u_{OH}^{bonding}$	3386	_/_/
u _{OH} free	2660	2624
$2u_{OH}^{free}$	2009 a	
011	7149	/084

Table 4.1 Experimentally observed and calculated H_2O , $CH_3COCOOH$, $CH_3COCOOH \cdot H_2O$, $CH_3C(OH)_2COOH$ and $CH_3C(OH)_2COOH \cdot H_2O$ frequencies and assignment from 3300 cm⁻¹ to 3700 cm⁻¹ and 6500 cm⁻¹ to 7400 cm⁻¹.

^{*a*} Experimentally observed or calculated OH-stretching transitions presented in this work. HCAO local-mode model was used to obtain calculated OH-stretching transitions.

^{*b*} Kuo, M. H. et al.[19]

^c Raczynska, E. D. et al.[73]

^d Kjaergaard, H. G. HCAO local-mode model was used to obtain calculated OH-stretching transitions.[70]

4.3 Results and Discussion

4.3.1 Characterization of Vibrational Spectra in the Mid-Infrared

Pyruvic acid is an α -ketoacid, which is most stable in its ketone form,[11, 12, 43, 75-78] but can exist in its enol form via a keto-enol tautomerism. The flexibility of the C- $^{\alpha}$ C-C-O chain in the keto and O- $^{\alpha}$ C-C-O in the enol form allows for many possible conformations.[11] The three thermodynamically stable keto conformations, *Tce, Tte, Cte,* and the most stable enol form, *E1*, of pyruvic acid, have been previously observed within a carbon tetrachloride matrix and assigned by Raczyńska, E. D. et al.[11] The nomenclature for the keto conformations were taken from Yang, X. et al.[75] and the nomenclature for the enol form was taken from Raczyńska, E. D.





(g)

(h)

Figure 4.1 B3LYP/6-311++G(3df,3pd) optimized structures of (a) *Tce*- CH₃COCOOH, (b) *Tte*-CH₃COCOOH, (c) *Tce*-CH₃C(OH)₂COOH, (d) *Tte*-CH₃C(OH)₂COOH (e) *Tce*-CH₃COCOOH•H₂O (f) *Tte*-CH₃COCOOH•H₂O (g) *Tce*-CH₃C(OH)₂COOH•H₂O and (h) *Tte*-CH₃C(OH)₂COOH •H₂O.

et al.[11] In this investigation in addition to observing *Tce-*, *Tte-*, *Cte-* and *E1-*pyruvic acid conformers we have observed Tce-2,2-dihydroxypropanoic acid and the hydrates of Tce- and Tte-pyruvic acids and Tce-2,2-dihydroxypropanoic. The emphasis in this study is on the lowest energy, reactive *Tce*-pyruvic acid conformer.[12, 53] The *Tce*-pyruvic acid conformer is the most stable structure, due to strong intramolecular hydrogen bonding between the carbonyl C=O and the carboxylic OH functional groups.[76] The B3LYP/6-311++G(3df,3pd) optimized structures of the two most stable conformers of pyruvic acid, Tce-CH₃COCOOH and Tte-CH₃COCOOH, and the two structures of 2,2-dihydroxypropanoic acid, *Tce*-CH₃C(OH)₂COOH and Tte-CH₃C(OH)₂COOH, are shown in Figure 4.1. The Tce and Tte-pyruvic acid conformers differ by a *trans* and *cis* conformation of the carboxylic hydrogen atom and the carbonyl groups. The *Tte*-pyruvic acid conformer is stabilized by a weaker intramolecular hydrogen bond. Carbon tetrachloride matrix[11] and gas-phase[12] infrared spectra are available in the literature for pyruvic acid, but no vibrational spectra of pyruvic acid hydrates, 2,2-dihydroxypropanoic acid and its hydrates have been reported prior to the present study. Figure 4.2 contains the fundamental vibrational mid-infrared spectra of 45, 35, 24, 15 and 0 wt.% aqueous pyruvic acid solutions in carbon tetrachloride, at 20°C, obtained in this chapter.

To aid and support assignments of our mid- and near-infrared spectra we conducted a hydration investigation of pyruvic acid in aqueous phase via ¹³C NMR and performed theoretical calculations of the structures and fundamental vibrational mode frequencies for pyruvic acid, 2,2-dihydroxypropanoic acid and their



Figure 4.2 Observed mid-infrared absorption spectra of aqueous pyruvic acid solutions in the carbon tetrachloride layer are shown as a function of weight percent, at 0.25 cm^{-1} resolution from 2800 to 4000 cm⁻¹. *Tte-* and *Cte-*CH₃COCOOH and *E1* conformers of pyruvic acid are also present, but unmarked and spectra have been offset for clarity.

corresponding monohydrates of the most stable conformers. The ¹³C NMR spectra of aqueous pyruvic acid solutions, shown in Figure 4.3, indicate that at high water/pyruvic acid ratios new spectral features appear attributed to the presence of 2,2-dihydroxypropanoic acid. Vibrational peak assignments of the infrared spectra along with AO method calculated OH-stretching transitions are presented in Table 4.1.

The ability of pyruvic acid to hydrate its carbonyl group in the presence of water to form 2,2-dihydroxypropanoic acid and the distinct spectroscopic signatures of these two OH chromophores allows to investigate the extent of the water-mediated hydration. In aqueous solution, these acids could hydrolyze to give H_3O^+ , CH_3COCOO^- and $CH_3C(OH)_2COO^-$ ions; however, these species were not observed



Figure 4.3 ¹³C NMR spectra of aqueous pyruvic acid solutions are shown as a function of weight percent. Spectra have been offset for clarity. The features due to 2,2-dihyroxyporpanoic acid conformers have been indicated with green boxes.

in this experiment. The spectra shown in Figure 4.2, indicate that molecular pyruvic and 2,2dihydroxypropanoic acids and their hydrates are the primary constituents in this water-restricted environment. The spectral features at 3429 cm⁻¹, 3561 cm⁻¹ and 3514 cm⁻¹ are attributed to the OH-stretches of the four molecular pyruvic acid conformers *Tce, Tte, Cte* and *E1*, respectively, with the most stable *Tce*-pyruvic acid conformer appearing with the highest intensity as expected. The peak at 3561 cm⁻¹ is comprised of overlapped transitions for the *Tte-* and *Cte*-pyruvic acid conformers. Our observations of the OH-stretches of molecular *Tce-*, *Tte-*, *Cte-* and *E1*-pyruvic acid conformers in a carbon tetrachloride matrix are in excellent agreement with previous work in the same environment by Raczyńska, E. D. et al.[11, 73], which reported these features at 3430 cm⁻¹, 3563 cm⁻¹ and 3516 cm⁻¹ respectively. The OH-stretch of molecular *Tce-* and *Tte-*pyruvic acid has been observed in the gas-phase at 3467 cm⁻¹ and 3579 cm⁻¹, respectively.[12] The peaks at 3616 cm⁻¹ and 3708 cm⁻¹ are assigned to the symmetric and antisymmetric OH-stretch of molecular water, respectively. Previous work by Kuo et al.[19] has observed the symmetric and antisymmetric OH-stretch of H₂O in a carbon tetrachloride matrix at 3617 cm⁻¹ and 3708 cm⁻¹, respectively, and we follow their assignments for water.

At high water/pyruvic acid ratios, several new spectral features are observed. A new peak appears at 3634 cm⁻¹ and a broad spectrum develops between 2800 cm⁻¹ and 3100 cm⁻¹. We assign the peak at 3634 cm⁻¹ to overlapping free OH-stretching transitions of *Tce*-2,2-dihydroxypropanoic acid and its monohydrate. This assignment was aided by our theoretical calculations given in Table 4.1. Intermolecular hydrogen bonding is expected to produce a significant red-shift of the OH-stretching transitions in the complex.[12, 14, 59, 71, 73, 80-83] Therefore, we can assign the broad spectrum in the infrared between 2800 cm⁻¹ and 3100 cm⁻¹ to *Tce*- and *Tte*-pyruvic monohydrates (*Tce*- and *Tte*-CH₃COCOOH•H₂O) and *Tce*-2,2-dihydroxypropanoic acid monohydrate (*Tce*-CH₃C(OH)₂COOH•H₂O). We performed theoretical calculations to obtain structures of monohydrate clusters of *Tce*- and *Tte*-pyruvic and *Tce*-2,2-dihyroxypropanoic acids, as shown in Figure 4.1, as well as their fundamental OH peak positions, to get a firm assignment of the broad spectral feature. The monohydrate formation

leads to an increase in the acid OH bond length of Tce- and Tte-pyruvic and Tce-2,2dihydroxypropanoic acids. By comparing the values reported in Figure 4.1 we see a small increase in OH bond length of 13 mÅ, 22 mÅ and 17 mÅ for Tce- and Tte-pyruvic and Tce-2,2dihydroxypropanoic acids, respectively. The elongation of the OH bond length of the acid OH of *Tce*- and *Tte*-pyruvic and *Tce*-2,2-dihydroxypropanoic acid monohydrates is a characteristic of molecules complexed to water and is indicative of intermolecular hydrogen bonding. The most defined peaks centered at 2887 cm⁻¹, 2929 cm⁻¹ and 2975 cm⁻¹ are assigned to Tte-CH₃COCOOH•H₂O, *Tce*-CH₃C(OH)₂COOH•H₂O and *Tce*-CH₃COCOOH•H₂O respectively. These assignments were aided by the calculated vibrational frequencies for these monohydrates shown in Table 4.1. The noticeable difference between calculated and observed calculated frequencies is due to a matrix shift as well as the limited ability of theory to accurately predict intermolecular hydrogen bonded OH vibrations. In the fundamental region, the red-shift of the acid OH of Tte-CH₃COCOOH•H₂O, Tce-CH₃C(OH)₂COOH•H₂O and Tce-CH₃COCOOH•H₂O was observed to be 674 cm⁻¹ (3561 cm⁻¹ to 2887 cm⁻¹), 500 cm⁻¹ (3429 cm⁻¹ to 2929 cm⁻¹) and 518 cm⁻¹ (3429 cm⁻¹ to 2975 cm⁻¹), respectively. The theoretically predicted red-shifts of the acid OH-stretching transitions calculated in this study are expected to be 749 cm⁻¹ for Tte-CH₃COCOOH•H₂O, 659 cm⁻¹ for *Tce*-CH₃C(OH)₂COOH•H₂O and 518 cm⁻¹ for *Tce*-CH₃COCOOH•H₂O, in agreement with the experimental results.

4.3.2 Characterization of Vibrational Spectra in the Near-Infrared

We have extended our characterization of pyruvic acid, 2,2-dihydroxypropanoic acid and their corresponding monohydrates from the mid-infrared to the vibrational overtone (near infrared) region. Figure 4.4 shows a 0.25 cm⁻¹ resolution near-infrared absorption spectra of the

carbon tetrachloride layer of 98, 45, 24, 15 and 0 wt.% pyruvic acid aqueous solutions form 6400 cm⁻¹ to 7500 cm⁻¹. This spectral region is dominated by transitions due to overtones of the fundamental normal modes of water, pyruvic and 2,2-dihydroxypropanoic acids. The most prominent features observed in the vibrational overtone region are the peaks at 6632 cm⁻¹, 6872 cm⁻¹, 7227 cm⁻¹ and a collection of broad peaks between 7000 cm⁻¹ – 7500 cm⁻¹, as shown in Figure 4.4, which are assigned to $2n_1$ OH-stretch of molecular *Tce*- and *Tte*-CH₃COCOOH and to $2n_{OH}$ and the combination band n_1+n_3 of molecular H₂O, respectively. We assign the peak at 7088 cm⁻¹, which appears at high water/pyruvic acid ratios, to overlapping free OH-stretching transitions of *Tce*-2,2-hydroxypropanoic acid and its monohydrate, this assignment is supported by our calculated frequencies, as shown in Table 4.1.

The effect of intermolecular hydrogen bonding due the formation of *Tce*-pyruvic and *Tce*-2,2-dihydroxypropanoic acid monohydrates can be clearly observed by a slight 37 cm⁻¹ (7120 cm⁻¹ to 7083 cm⁻¹) red-shift of the $2n_{OH}$ OH-stretch of water in the vibrational overtone region, as shown Figure 4.4. The slight red-shift of the



Figure 4.4 Observed near-infrared absorption spectra of aqueous pyruvic acid solutions in the carbon tetrachloride layer are shown as a function of weight percent, at 0.25 cm⁻¹ resolution from 6400 to 7500 cm⁻¹. The peak at 7088cm⁻¹ is assigned to v = 2 of the free OH stretching transition in the *Tce*-CH₃C(OH)₂COOH and *Tce*-CH₃C(OH)₂COOH•H₂O complex. Spectra have been offset for clarity.

acceptor OH of H_2O and the appearance of small shoulders centered at 7116 cm⁻¹ are attributed to the presence of the *Tce*-pyruvic and *Tce*-2,2-dihydroxypropanoic acid hydrates. The red-shift of the OH overtone stretching transitions of water are consistent with what has been observed experimentally[20] and predicted theoretically[70] with the nitric acid-water monohydrate.

4.3.3.1. Water Mediated Hydration between Pyruvic and 2-2-dihydroxypropanoic Acids

Our spectroscopic results, as shown in Figures 4.2 and 4.3, allowed for qualitative observation and characterization of molecular *Tce-*, *Tte- Cte-* and *E1-*pyruvic and *Tce-*2,2-dihydroxypropanoic acids and *Tce-* and *Tte-*pyruvic and *Tce-*2,2-dihydroxypropanoic acid monohydrates within a water-restricted environment at ambient temperatures. In order to quantify the extent of the hydration of pyruvic acid to 2,2-dihydroxypropanoic acid, the concentrations of *Tce-*pyruvic acid and *Tce-*2,2-dihydroxypropanoic acid were required and were

determined by taking the ratio of the integrated area of the acid OH-stretching transition with the corresponding theoretical oscillator strength, shown by Eq. 1. Where OH_x represents the acid OH for *Tce*-pyruvic acid or the free OH for *Tce*-2,2-dihydroxypropanoic. The integrated areas of each OH-acid and free OH-stretching transitions were determined by fitting each spectrum in the appropriate region with Gaussian fits via IGOR Pro Version 6.02A, as shown in Figure 4.5.

$$\frac{\int_{\tilde{v}_{1}}^{\tilde{v}_{2}} \operatorname{Area}_{\operatorname{OH}_{x}} d\tilde{v}}{l \cdot \frac{N_{A} e^{2}}{4 \varepsilon_{0} m_{e} c^{2} \ln 10} f_{\operatorname{OH}_{x}}} = [CH_{3}COCOOH] \text{ or } [CH_{3}C(OH)_{2}COOH]$$
(1)

Due to the overlapping OH-stretching transitions of the free OH on *Tce*-2,2-dihyrdoxypropanoic acid and its monohydrate it was not possible to separate and determine their individual concentrations. Therefore the total geminal diol concentration was determined by taking the ratio of the integrated area of the free OH-stretching transition with the average of the theoretical oscillator strengths for *Tce*-2,2-dihyrdoxypropanoic acid and its monohydrate using Eq. 1. The integrated areas of the OH-stretching transitions, the theoretical oscillator strengths and the concentrations for both acids are summarized in Table 4.2.



Figure 4.5 Observed mid-infrared absorption spectra, shown in black, of 1.0 μ L (16 wt.%) pyruvic acid in carbon tetrachloride saturated with Nanopure water solutions, at 1 cm⁻¹ resolution (a) from 2800 cm⁻¹ to 3100 cm⁻¹ and (b) from 3300 cm⁻¹ to 4000 cm⁻¹. The pyruvic acid molecular and water complex peaks are indicated in red, the resolvable water peaks are in blue and the features due to 2,2-dihydroxyproponoic acid and water complex peaks are in green. The resonance centered at 3018 cm⁻¹ is an impurity.

Pyruvic acid wt.%		<i>Tce-</i> CH ₃ COCOOH	<i>Tce</i> - CH ₃ C(OH) ₂ COOH	<i>Tce</i> - CH ₃ C(OH) ₂ COOH ∙H ₂ O
	15	7.22689	0.860297	
Area*	24	15.9396	0.508982	
	35	33.4019	0.206982	
	45	49.2495	0.115478	
Oscillator Strength f_{01}^{**}		2.09×10^{-5}	5.75×10^{-6}	8.56×10^{-6}
			7.16×10^{-6}	
Concentration, M*	15	2.14×10^{-5}	2.04	× 10 ⁻⁵
	24	4.71×10^{-4}	1.21×10^{-5}	
	35	9.87×10^{-4}	4.92×10^{-6}	
	45	1.46×10^{-3}	8.50×10^{-6}	

Table 4.2 The integrated area of OH-stretching transitions, the calculated oscillator strengths and the determined concentrations of *Tce*-pyruvic acid and *Tce*-2,2-dihydroxypropanoic acid and its corresponding water complex are shown here.

* Due to the overlapping OH-stretching transitions of the free OH on *Tce-2,2-* dihyrdoxypropanoic acid and its monohydrate, the integrated area was obtained and concentration of the geminal diol was determined. ** In order to determine the total geminal diol concentration the average oscillator strengths of the free OH on *Tce-2,2-* dihydroxypropanoic acid and its monohydrate were used.

The extent of the hydration of pyruvic acid to 2,2-dihydroxypropanoic acid is denoted by *Q* and is given by Eq. 2. The *Q* determined for the 45, 35, 24, and 15

$$Q = \frac{[CH_3C(OH)_2COOH]}{[CH_3COCOOH]}$$
(2)

wt.% aqueous pyruvic acid solutions in carbon tetrachloride are 2.3×10^{-3} , 6.2×10^{-3} , 3.2×10^{-2} , and 1.2×10^{-1} , respectively. We note that this analysis depends on the accuracy of the calculated relative fundamental intensities of the two peaks. Previous studies have shown that B3LYP intensities give results within a factor of two of the experimental values. On the other hand, when relative intensities are considered, this discrepancy is much smaller, and we have

previously compared the B3LYP intensity ratios for the two conformers of pyruvic acid with CCSD(T) results and saw that it was off by less than 10%. Therefore, we believe that the above Q values are accurate only to the two digits that are reported. The dependence of Q on the water concentration suggests that water and water complexes play an important role in the hydration of pyruvic acid to 2,2-dihydroxypropanoic acid. The relative population of 2,2-dihydroxypropanoic acid is much grater than what is expected from the consideration of one water molecule and we believe that larger water clusters promote the hydration process. The importance of including water complexes in order to account for the observed water dependence in other hydration studies has been stated by Plath, et al.[14] and Axson, et al.[15] in the observation of the geminal diols of glyoxylic acid and methylglyoxal in the gas-phase, respectively. The work by Gandour, [79] and Wolfe, et al., [80] have proposed that the hydration of a carbonyl group proceeds in aqueous solution via a cyclic transition state containing two or three water molecules.[80] They suggest the formation of a cyclic six- or eight-membered reaction complex, with two or three protons moving more or less synchronously in the transition state. The formation of a cyclic reaction complex to lower the barrier for the similar hydration reaction of fluoromethanol was also shown by K. Takahashi, et al.[24]

4.4 Summary

The vibrational spectra of *Tce-*, *Tte-*, *Cte-* and *E1-*pyruvic acid conformers as well as *Tce*and *Tte-*2,2-dihydroxypropanoic acid and their monohydrates are reported here at ambient temperatures in a water restricted environment. With this method, we were able to make the first spectroscopic observation of 2,2-dihydroxypropanoic acid and monohydrates of *Tce-* and *Tte*pyruvic and *Tce-*2,2-dihydroxypropanoic acids in the mid- and near-infrared. The results from this study show that at ambient conditions in this water-restricted environment, pyruvic acid will undergo hydration to form 2,2-dihydroxypropanoic acid.

This investigation of the equilibrium between pyruvic and 2,2-dihydroxypropanoic acids showed that in order to explain the experimentally observed large concentration of 2,2-dihydroxypropanoic acid it was necessary to incorporate intermolecular hydrogen-bonded water complexes in the reaction mechanism. Our findings shows that the hydration equilibrium of pyruvic acid to 2,2-dihydroxypropanoic acid is dependent on the water concentration, supporting previous work[79, 80] suggesting that the hydration of a carbonyl group in aqueous solution proceeds via a cyclic transition state containing two to four water molecules.

We conclude that significant concentration of the geminal diol of pyruvic acid may form in water-restricted situations typical in environmental chemistry. 2,2-Dihydroxypropanoic acid has different chemical and physical properties than pyruvic acid. These results imply the importance of relative humidity on the partitioning between gas and particle phase. [30, 31, 81] Hydration of the carbonyl group will have important consequences to the photochemistry of pyruvic acid and other aldehydes and ketones in the atmosphere.

4.5 References for Chapter IV

- 1. Mugnai, M., et al., *Ab initio molecular dynamics study of aqueous formaldehyde and methanediol.* Molecular Physics, 2007. **105**(17-18): p. 2203-2210.
- Krizner, H.E., D.O. De Haan, and J. Kua, *Thermodynamics and Kinetics of Methylglyoxal Dimer Formation: A Computational Study*. Journal of Physical Chemistry A, 2009. 113(25): p. 6994-7001.
- 3. Kent, D.R., et al., *A theoretical study of the conversion of gas phase methanediol to formaldehyde.* Journal of Chemical Physics, 2003. **119**(10): p. 5117-5120.
- 4. Cooper, A.J.L. and A.G. Redfield, *Proton Magnetic Resonance Studies of alpha keto acids*. The Journal of Biological Chemistry, 1975. **250**(2): p. 527-532.
- Buschmann, H.J., E. Dutkiewicz, and W. Knoche, *The Reversible Hydration of Carbonyl Compounds in Aqueous Solution.* 2. *The Kinetics of the Keto Gem-Diol Transition.* Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics, 1982. 86(2): p. 129-134.
- 6. Fischer, G., et al., *Carbon-13 NMR investigations on the structure of .alpha.-keto acids in aqueous solution.* The Journal of Organic Chemistry, 1988. **53**(1): p. 214-216.
- 7. Becker, M., *Uber magnetische kernesonanzspektren wassriger brenztrubensaurelosungen.* Berichte Der Bunsen-Gesellschaft Fur Physikalische Chemie, 1964. **68**(7): p. 669-676.
- 8. Becker, M. and H. Strehlow, *Der einfuluss der hydratibiung auf das polarographische verhalten von alpha-oxocarbonsauren*. Zeitschrift Fur Elektrochemie, 1960. **64**(6): p. 813-817.
- 9. Buschmann, H.J., H.H. Fuldner, and W. Knoche, *Reversible hydration of carbonylcompounds in aqueous solution .1. Keto-gem-diol equilibrium.* Berichte Der Bunsen-Gesellschaft - Physical Chemistry Chemical Physics, 1980. **84**(1): p. 41-44.
- 10. Hodzic, A., et al., *Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation.* Atmospheric Chemistry and Physics, 2010. **10**(12): p. 5491-5514.
- 11. Raczynska, E.D., K. Duczmal, and M. Darowska, *Experimental (FT-IR) and theoretical (DFT-IR) studies of keto-enol tautomerism in pyruvic acid.* Vibrational Spectroscopy, 2005. **39**(1): p. 37-45.
- 12. Takahashi, K., et al., *Dynamics of vibrational overtone excited pyruvic acid in the gas phase: Line broadening through hydrogen-atom chattering*. Journal of Physical Chemistry A, 2008. **112**(32): p. 7321-7331.

- 13. Lugez, C., et al., A matrix-isolation infrared spectroscopic study of the reactions of methane and methanol with ozone. Chemical Physics, 1994. **181**(1-2): p. 129-146.
- 14. Plath, K.L., et al., *Gas-phase vibrational spectra of glyoxylic acid and its gem diol monohydrate. Implications for atmospheric chemistry.* Reaction Kinetics and Catalysis Letters, 2009. **96**(2): p. 209-224.
- 15. Axson, J.L., et al., *Gas-Phase Water Mediated Equilibrium Study Between MEthylglyoxal and its Geminal Diol.* Proceedings of the National Academy of Sciences of the United States of America, 2009. **107**(15): p. 6687-6692.
- Kuo, M., N. Kamelamela, and M.J. Shultz, *Rotational structure of water in a hydrophobic environment: Carbon tetrachloride.* Journal of Physical Chemistry A, 2008. 112(6): p. 1214-1218.
- Kleeberg, H., D. Klein, and W.A.P. Luck, *Quantitative Infrared Spectroscopic Investigations of Hydrogen-Bond Cooperativity*. Journal of Physical Chemistry, 1987. 91(12): p. 3200-3203.
- 18. Leroux, N., C. Samyn, and T. Zeegers-Huyskens. *Mid- and near-IR study of the hydrogen bond interaction between N-methyldiacetamide and phenols*. 1998: Elsevier Science Bv.
- 19. Kuo, M.H., et al., *Nitric acid Water interaction probed via isolation in carbon tetrachloride.* Journal of Physical Chemistry C, 2007. **111**(25): p. 8827-8831.
- 20. Maron, M.K., M.J. Shultz, and V. Vaida, *Characterization of the nitric acid-water complex in the infrared and near-infrared region at ambient temperatures in carbon tetrachloride*. Chemical Physics Letters, 2008. **473**(4-6): p. 268-273.
- 21. Bisson, P., et al., *Ions and Hydrogen Bonding in a Hydrophobic Environment: CCl4.* Journal of Physical Chemistry A, 2010. **114**(12): p. 4051-4057.
- 22. Nicolaisen, F.M., *IR absorption spectrum (4200-3100 cm(-1)) of H2O and (H2O)(2) in CCl4. Estimates of the equilibrium constant and evidence that the atompsheric water absorption continuum is due to the water dimer.* Journal of Quantitative Spectroscopy and Radiative Transfer, 2009. **110**(18): p. 2060-2076.
- 23. Hammerich, A.D. and V. Buch, *An alternative near-neighbor definition of hydrogen bonding in water*. Journal of Chemical Physics, 2008. **128**(11): p. 111101.
- 24. Takahashi, K., et al., Vibrational overtone induced elimination reactions within hydrogen-bonded molecular clusters: the dynamics of water catalyzed reactions in CH2FOH center dot(H2O). Physical Chemistry Chemical Physics, 2007. 9(29): p. 3864-3871.

- 25. Solomon, S., et al., *Climate Change 2007: The Physical Science Basis*, in *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. 2007: Cambridge, United Kingdom and New York, NY, USA. p. 996.
- 26. Novakov, T. and J.E. Penner, *Large Contribution of ORganic Aerosols to clund-condensation nuclei concentrations*. Nature, 1993. **365**(6449): p. 823-826.
- 27. Kanakidou, M., et al., *Organic aerosol and global climate modelling: a review*. Atmospheric Chemistry and Physics, 2005. **5**: p. 1053-1123.
- 28. Rincon, A.G., et al., *Optical Absorptivity versus Molecular Composisiton of Model Organic Aerosol Matter.* Journal of Physical Chemistry A, 2009. **113**(39): p. 10512-10520.
- 29. De Gouw, J. and J. Jimenez, *Organic Aerosols in the Earth's Atmosphere*. Environmental Science and Technology, 2009. **43**(20): p. 7614-7618.
- 30. Matsunaga, S., M. Mochida, and K. Kawamura, Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Isaland in Japan. Journal of Geophysical Research, 2004. **109**: p. D04302.
- 31. Bao, L., et al., *Gas/particle partitioning of low-mlocular-weight dicarboxylic acids at a suburban site in Saitama, Japan.* Atmospheric Environment, 2009: p. Article in Press.
- 32. Guzman, M.I., A.J. Colussi, and M.R. Hoffmann, *Photoinduced oligomerization of aqueous pyruvic acid.* Journal of Physical Chemistry A, 2006. **110**(10): p. 3619-3626.
- 33. Ervens, B., et al., A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production. Journal of Geophysical Research Atmospheres, 2004. **109**(D15): p. D15205.
- Talbot, R.W., et al., Sources and sinks of formic, acetic and pyruvic aicds over central amazonia. 2. wet season. Journal of Geophysical Research-Atmospheres, 1990. 95(D10): p. 16799-16811.
- Moran, M.A. and R.G. Zepp, Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnology and Oceanography, 1997.
 42(6): p. 1307-1316.
- 36. Miller, W.L. and R.G. Zepp, *Photochemical production of dissolved inorganic carbon from terrestrial organic matter significance to the ocieanic organic carbon cycle.* Geophysical Research Letters, 1995. **22**(4): p. 417-420.
- 37. Kawamura, K. and O. Yasui, *Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere.* Atmospheric Environment, 2005. **39**(10): p. 1945-1960.

- 38. Kawamura, K., Y. Imai, and L.A. Barrie, *Photochemical production and loss of organic acids in high Arctic aerosols during long-range transport and polar sunrise ozone depletion events*. Atmospheric Environment, 2005. **39**(4): p. 599-614.
- Fisseha R, D.J., Sax M, Paulsen D, Kalberer M, Maurer R, Hofler F, Weingartner E, Baltensperger U, *Identification of organic acids in secondary organic aerosol and the corresponding gas phase from chamber experiments*. Analytical Chemistry, 2004. 76(22): p. 6535-6540.
- 40. Baboukas, E.D., M. Kanakidou, and N. Mihalopoulos, *Carboxylic acids in gas and particulate phase above the Atlantic Ocean*. Journal of Geophysical Research Atmospheres, 2000. **105**(D11): p. 14459-14471.
- 41. Kawamura, K., et al., *A Greenland ice core record of low molecular weight dicarboxylic acids, ketocarboxylic acids, and alpha-dicarbonyls: A trend from Little Ice Age to the present (1540 to 1989 AD).* Journal of Geophysical Research-Atmospheres, 2001. **106**(D1): p. 1331-1345.
- 42. Andreae, M.O., R.W. Talbot, and S.M. Li, *Atmospheric Measurements of Pyruvic and Formic Acid.* Journal of Geophysical Research Atmospheres, 1987. **92**(D6): p. 6635-6641.
- 43. Reva, I.D., et al., *Combined FTIR matrix isolation and ab initio studies of pyruvic acid: Proof for existence of the second conformer.* Journal of Physical Chemistry A, 2001. **105**(19): p. 4773-4780.
- 44. Schellenberger, A., W. Beer, and G. Oehme, *Untersuchungen zur theorie der alpha ketosauren .11. IR spektroskopische untersuchungen an alpha ketosauren im gaszustand.* Spectrochimica Acta, 1965. **21**(7): p. 1345.
- 45. Hollenstein, H., F. Akermann, and H.H. Gunthard, *Vibrational analysis of pyruvic-acid* and D-labeled, C-13-lanelled and O-18-labelled species - Matrix spectra, assignments, valence force-filed and noraml coordinate analysis. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 1978. **34**(11): p. 1041-1063.
- 46. Ervens, B., S. Gligorovski, and H. Herrmann, *Temperature-dependent rate constants for hydroxyl radical reactions with organic compounds in aqueous solutions*. Physical Chemistry Chemical Physics, 2003. **5**(9): p. 1811-1824.
- 47. Volkamer, R., et al., *Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected.* Geophysical Research Letters, 2006. **33**(17): p. L17811.
- 48. de Gouw JA, M.A., Warneke C, Goldan PD, Kuster WC, Roberts JM, Fehsenfeld FC, Worsnop DR, Canagaratna MR, Pszenny AAP, Keene WC, Marchewka M, Bertman SB, Bates TS, *Budget of organic carbon in a polluted atmosphere: Results from the New*

England Air Quality Study in 2002. Journal of Geophysical Research - Atmospheres, 2005. **110**(D16): p. D16305.

- 49. Guzman, M.I., A.J. Colussi, and M.R. Hoffmann, *Photogeneration of distant radical pairs in aqueous pyruvic acid glasses*. Journal of Physical Chemistry A, 2006. **110**(3): p. 931-935.
- 50. Guzman, M.I., M.R. Hoffmann, and A.J. Colussi, *Photolysis of pyruvic acid in ice: Possible relevance to CO and CO2 ice core record anomalies.* Journal of Geophysical Research-Atmospheres, 2007. **112**(D10).
- 51. Mellouki, A. and Y.J. Mu, *On the atmospheric degradation of pyruvic acid in the gas phase.* Journal of Photochemistry and Photobiology a-Chemistry, 2003. **157**(2-3): p. 295-300.
- Miller, Y., R.B. Gerber, and V. Vaida, *Photodissociation yields for vibrationally excited states of sulfuric acid under atmospheric conditions*. Geophysical Research Letters, 2007. 34(16): p. L16820.
- 53. Plath, K.L., et al., *Fundamental and Overtone Vibrational Spectra of Gas-Phase Pyruvic Acid.* Journal of Physical Chemistry A, 2009. **113**(26): p. 7294-7303.
- 54. Vaida, V., H.G. Kjaergaard, and K.J. Feierabend, *Hydrated complexes: Relevance to atmospheric chemistry and climate.* International Reviews in Physical Chemistry, 2003. **22**(1): p. 203-219.
- 55. Hintze, P.E., et al., *Vibrational and electronic spectroscopy of sulfuric acid vapor*. Journal of Physical Chemistry A, 2003. **107**(8): p. 1112-1118.
- 56. Havey, D.K., et al., *Experimental and theoretical investigation of vibrational overtones of glycolic acid and its hydrogen bonding interactions with water.* Journal of Physical Chemistry A, 2006. **110**(20): p. 6439-6446.
- 57. Vaida, V., et al., *Photolysis of sulfuric acid vapor by visible solar radiation*. Science, 2003. **299**(5612): p. 1566-1568.
- 58. Vaida, V., Spectroscopy of Photoreactive Systems: Implications for Atmospheric Chemistry. Journal of Physical Chemistry A, 2009. **113**(1): p. 5-18.
- 59. Staikova, M., M. Oh, and D.J. Donaldson, *Overtone-induced decarboxylation: A potential sink for atmospheric diacids.* Journal of Physical Chemistry A, 2005. **109**(4): p. 597-602.
- 60. Donaldson, D.J., A.F. Tuck, and V. Vaida, *Atmospheric photochemistry via vibrational overtone absorption*. Chemical Reviews, 2003. **103**(12): p. 4717-4729.

- 61. Matthews J, S.A., Francisco, J. S., *The importance of weak absorption features in promoting tropospheric radical production.* Proceedings of the National Academy of Sciences of the United States of America, 2005. **102**(21): p. 7449-7452.
- 62. Donaldson, D.J., et al., Atmospheric radical production by excitation of vibrational overtones via absorption of visible light. Geophysical Research Letters, 1997. 24(21): p. 2651-2654.
- 63. Wennberg, P.O., et al., *Removal of stratospheric 03 by radicals in-situ measurements of OH, HO2, NO, NO2, CLO, and BRO.* Science, 1994. **266**(5184): p. 398-404.
- 64. Becke, A.D., *Density-functional thermochemistry. III. The role of exact exchange.* Journal of Chemical Physics, 1992. **98**(7): p. 5648-5652.
- 65. Lee, C.T., W.T. Yang, and R.G. Parr, *Development of the colle-salvetti correlationenergy formula into a functional of the electron-density.* Physical Review B, 1988. **37**(2): p. 785-789.
- 66. McLean, A.D. and G.S. Chandler, *Contracted Gaussian-Basis Sets for molecular Calculations. I. 2nd row atoms*, Z=11-18. Journal of Chemical Physics, 1980. 72(10): p. 5639-5648.
- 67. Krishnan, R., et al., *Self-consistent Molecular-Orbital Methods. XX. Basis set for Correlated Wave-Functions.* Journal of Chemical Physics, 1980. **72**(1): p. 650-654.
- 68. Clark, T., et al., *Efficient Diffuse Function-Augmented Basis-Sets for Anion Calculations*. *III. The 3-21+G Basis Set for 1st-Row Elements, Li-F.* Journal of Computational Chemistry, 1983. 4(3): p. 294-301.
- 69. Frisch, M.J., et al., *Gaussian03, C.02 ed.* Vol. 110. 2004, Gaussian Inc.: Wallingford, CT.
- 70. Kjaergaard, H.G., *Calculated OH-stretching vibrational transitions of the water-nitric acid complex.* Journal of Physical Chemistry A, 2002. **106**(12): p. 2979-2987.
- 71. Howard, D.L., P. Jorgensen, and H.G. Kjaergaard, *Weak intramolecular interactions in ethylene glycol identified by vapor phase OH-stretching overtone spectroscopy*. Journal of the American Chemical Society, 2005. **127**(48): p. 17096-17103.
- 72. Howard, D.L. and H.G. Kjaergaard, *Influence of intramolecular hydrogen bond strength* on OH-stretching overtones. Journal of Physical Chemistry A, 2006. **110**(34): p. 10245-10250.
- 73. Raczynska, E.D., K. Duczmal, and M. Darowska, *Keto-enol tautomerism in pyruvic acid* - *Theoretical (HF, MP2 and DFT in the Vacuo) studies*. Polish Journal of Chemistry, 2005. **79**(4): p. 689-697.

- 74. Low, G.R. and H.G. Kjaergaard, *Calculation of OH-stretching band intensities of the water dimer and trimer*. Journal of Chemical Physics, 1999. **110**(18): p. 9104-9115.
- 75. Yang, X., et al., *A DFT study on the radical, monomer and dimer of alpha-keto pyruvic acid: equilibrium structures and vibrational analysis of stable conformers.* Chemical Physics Letters, 2003. **380**(1-2): p. 34-41.
- 76. Chen, C. and S.F. Shyu, *Theoretical study of glyoxylic and pyruvic acids: rotamers and intramolecular hydrogen bonding*. Journal of Molecular Structure-Theochem, 2000. **503**(3): p. 201-211.
- 77. Zhou, Z.Y., D.M. Du, and A.P. Fu, *Structures and vibrational frequencies of pyruvic acid: density functional theory study.* Vibrational Spectroscopy, 2000. **23**(2): p. 181-186.
- 78. Tarakeshwar, P. and S. Manogaran, *An ab initio study of pyruvic acid*. Theochem-Journal of Molecular Structure, 1998. **430**: p. 51-56.
- 79. Gandour, R.D., *Structural requirements for intramolecular proton transfers*. Tetrahedron Letters, 1974. **3**: p. 295-298.
- 80. Wolfe, S., et al., *Hydration of the Carbonyl Group A Theoretical Study of the Cooperative Mechanism.* Journal of the American Chemical Society, 1995. **117**(15): p. 4240-4260.
- 81. Remorov, R.G. and C. George, *Analysis of chemical kinetics at the gas-aqueous interface for submicron aerosols.* Physical Chemistry Chemical Physics, 2006. **8**: p. 4897-4901.

Chapter V: Gas-Phase Mediated Equilibrium Between Formaldehyde and Methanediol

5.1 Introduction

Formaldehyde is known to be the photochemical oxidation product of methane and nonmethane volatile organic compounds (NMVOCs) in ambient air. It is one of the most abundant carbonyl compounds[1] and the smallest member of the aldehyde family. The hydration of formaldehyde to methanediol has been studied extensively in bulk aqueous media.[2-10] While hydration is well known in aqueous solutions where it proceeds by acid catalysis, this chemistry was not expected in gas-phase due to the common belief that there is insufficient water present to favor hydration. Our observation of methanediol in this work, through the hydration of formaldehyde in the gas-phase at low water concentrations contradicts this belief. Similar results were obtained for gas-phase hydration of glyoxylic acid[11] and methylglyoxal,[12] and in the hydration of pyruvic acid in a carbon tetrachloride matrix in an environment of low water concentration.[13] The products of this chemistry, the geminal diol, has different the physical and chemical properties than the aldehyde. These results might explain the variability between field measurements of oxidized organic molecules, such as formaldehyde, and atmospheric models.[14-19]

This study investigates the hydration of formaldehyde at low water concentrations in the gas-phase at ambient temperatures using a combination of Fourier transform spectroscopy (FTS) and theory. Characterization of formaldehyde, methanediol, and their water clusters provided in this work allowed for the determination of the water mediated gas-phase equilibrium between

formaldehyde and methanediol. The equilibrium constant, K_p , for Reaction 1 (R1) is calculated using spectrsocopically determined concentrations of formaldehyde, methanediol, and water. This investigation shows the gas-phase hydration of formaldehyde occurs under relatively dry environmental conditions and is water mediated.

$$H_2CO + H_2O \leftrightarrow H_2C(OH)_2$$
 R1

5.2 Experimental

5.2.1 Materials and Sample Preparation

All materials were purchased from Sigma-Aldrich Chemical Co., Inc. Formaldehyde was prepared by heating *para*formadehyde (Aldrich, 95%, prills) to 110 °C, trapping the vapor at liquid N₂ temperature, then distilling the formaldehyde from a dry ice trap into a pressure controlled spectroscopic glass cell, as adapted from Khoshkhoo, H. et al.[20] Methanediol was prepared *in situ*, by first introducing formaldehyde into a pressure controlled spectroscopic glass cell, then opening the cell to the room atmosphere until the internal pressure of the cell was equal to the room pressure. The spectroscopic glass cell used in these experiments had a path length of 62.23 cm and was fitted with KRS-5 windows. The initial internal pressure of the spectroscopic glass cell was approximately 15 mTorr.

5.2.2 Spectroscopic Studies

The infrared absorption spectra of formaldehyde and methanediol were measured at room temperature in the mid-infrared with a commercial Fourier Transform Spectrometer (FTS) in a glass static cell. A Bruker TENSOR 27 (mercury cadmium telluride (MCT) detector and resolution of 1 cm⁻¹) was used from 600 cm⁻¹ – 4000 cm⁻¹.

5.2.3 Theoretical Calculation

The structures of formaldehyde, methanediol, and the monohydrate methanediol complex were optimized and normal mode frequencies were determined for each compound at the B3LYP/6-311++G(3df,3pd)[21-26] level of theory using the Gaussian03[26] quantum chemistry package. Single point calculations were used to generate a one dimensional potential energy surface for the OH chromophores and their local mode vibrational frequencies were subsequently determined using the harmonically coupled anharmonic oscillator method. The detail of the harmonically coupled anharmonic oscillator (HCAO) method is described elsewhere.[27, 28] The potential energy curves with respect to the OH-stretching coordinate used for the local mode vibrational calculation, were obtained by displacing the OH bond length by ± 0.2 Å from equilibrium in steps of 0.05 Å while keeping all other structural parameters fixed at their equilibrium values. The points were fit to a Morse potential and the local-mode OH-stretching frequency was determined from the second-, third-, and fourth-order derivatives of the potential energy curve according to the procedure given by Kjaergaard[27] and Howard et al.[29] Peak assignments along with AO method calculated frequencies are presented in Table 5.1.

vibrational mode	calculated frequency (cm ⁻¹)	experimentally observed frequency (cm ⁻¹)
H_2CO		
n_1	2886	2800^a , 2797.1 ^b
n_2	1821	1745^{a} , 1742.0^{b}
$2n_2$		3471 ^{<i>a</i>}
n ₃	1531	1501 ^{<i>a</i>} , 1498.8 ^{<i>b</i>}
n_4	2944	$2800^{a}, 2863.0^{b}$
<i>n</i> ₆	1201, 1265	1165 ^{<i>a</i>} , 1167.3 ^{<i>b</i>}
$H_2C(OH)_2$		
n_1	3033	2926 ^{<i>a</i>}
n_2	1369	1476 ^{<i>a</i>}
<i>n</i> ₃	1444	1238^{a}
n_4	3081	2979^{a}
<i>n</i> 5	1035	934 ^{<i>a</i>}
<i>n</i> ₆	1050	934 ^{<i>a</i>}
n _{OH free}	3640 ^{<i>a</i>}	
$H_2C(OH)_2$ H_2O		
n_1	3041	2926 ^{<i>a</i>}
n_2	1370	1238 ^{<i>a</i>}
<i>n</i> 3	1083	1094 ^{<i>a</i>}
n_4	3092	2979^{a}
n_5	1023	1003 ^{<i>a</i>}
<i>n</i> ₆	985	914 ^{<i>a</i>}
n_7	701	634 ^{<i>a</i>}
n _{OH free}		
N OH bonding		3100-3400 ^a

Table 5.1 Experimentally Observed and Calculated formaldehyde (H₂CO), methanediol (H₂C(OH)₂), and methanediol-water complex (H₂C(OH)₂ H₂O) Resonances and Assignment of Observed Peaks from 1350 cm⁻¹ to 3700 cm⁻¹.

^a Experimentally observed or calculated transitions presented in this work. HCAO local-mode model was used to obtain calculated OH-stretching transitions.
 ^b Khoshkhoo, H., et al.[20]

The oscillator strengths of each OH-stretching transition have been calculated within the HCAO local mode model with local mode parameters that were determined with an *ab initio* calculated dipole moment function as described by Low, G. R., et al.[30]

The calculated transition state theory (TST)[31] rate constants for the hydration of formaldehyde and the calculated equilibrium constants for the hydrated formaldehyde cluster evaporation reactions required the optimized geometries, energies, and vibrational frequencies of water, the hydrated formaldehyde clusters, $H_2CO^{\bullet}(H_2O)_n$ for n = 0, 1, 2, 3, and 4, and the associated hydration transition states. These quantities were computed at the B3LYP/6-31+G(d,p)[21-23, 25, 32-34] level of theory. Where the n=3 and n=4 hydrated formaldehyde clusters had more than one stable conformation, only the most stable cluster was included in the calculation for the rate constant and the equilibrium constants and exclusion of the less stable cluster geometries is not expected to dramatically affect the results. The most stable cluster via the minimum energy path through the "ring" transition states to the corresponding most stable, "ring", methanediol hydrated clusters. The formaldehyde clusters used are shown in Figure 5.1.

5.3 Results and Discussion

The theoretical calculations performed and shown in this section were performed and analyzed by Zeb C. Kramer.

5.3.1 Characterization of Vibrational Spectra in the Mid-Infrared

The optimized structure of formaldehyde is shown in Figure 5.2. The two stable methanediol conformations are *trans*- and *tilt*-methanediol, the B3LYP/6-311++G(3df,3pd) optimized structure of the *trans* conformer is shown in Figure 5.2. In this work we only considered the *trans*-methanediol conformation as we expect it to be the dominant conformer at room temperature.

Figure 5.3A contains the fundamental vibrational mid-infrared spectrum of formaldehyde at room temperature. Our calculated frequencies and literature

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Figure 5.1 The most stable equilibrium hydrated formaldehyde clusters and their corresponding hydration transition states and methanediol products calculated at the B3LYP/6-31+G(d,p) level of theory.



Figure 5.2 The B3LYP/6-311++G(3df,3pd) optimized structures of (a) formaldehyde, (b) *trans*-methanediol and (c) *trans*-methanediol monohydrate.

values[20] were used to assist in the assignment of the spectral features of formaldehyde. The spectral features at 1165 cm⁻¹ and 1501 cm⁻¹ are attributed to the wagging, v_6 , and scissoring, v_3 , vibrations of CH₂ in formaldehyde, respectively. The C=O stretching transition, v_2 , of formaldehyde has been assigned to the spectral feature at 1745 cm⁻¹. The congested spectral feature centered at 2800 cm⁻¹ is comprised of overlapped symmetric, v_1 , and antisymmetric, v_4 , stretching transitions of CH₂ in formaldehyde. Our observation of the vibrational modes of formaldehyde are in excellent agreement with previous work by Khoshkhoo, H., et al.[20] We attribute the spectral feature at 3471 cm⁻¹ to the first overtone of the C=O stretching transition, $2v_2$. These assignments as well as the calculated frequencies are summarized in Table 5.1.

Upon the addition of water to formaldehyde in the gas-phase at room temperature several new spectral features are observed, as shown in Figure 5.3B.



Figure 5.3 Observed mid-infrared absorption spectra of gas-phase (A) formaldehyde and (B) formaldehyde, methanediol and water mixture, at 1 cm⁻¹ resolution form 600 cm⁻¹ to 3700 cm⁻¹. The spectral features assigned to formaldehyde, methanediol and methanediol hydrate are labeled in black, green ,and blue, respectively

New peaks appear between 600 cm⁻¹ and 1300cm⁻¹, the congested spectral feature centered at 2800 cm⁻¹ is enhanced between 2900 cm⁻¹ and 3000 cm⁻¹ and a broad spectrum develops between 3100 cm⁻¹ and 3400 cm⁻¹. Based on our calculated frequencies of methanediol and the methanediol water-complex we assign the peak centered at 934 cm⁻¹ to the symmetric, v₅, and anti-symmetric, v₆, C–O stretching transitions in molecular methanediol. The peak at 1238 cm⁻¹ we assign to the CH₂ rock and free OH symmetric wag, v₃, in methanediol. The peak centered at 1476 cm⁻¹ we attribute to the CH₂ and free OH symmetric wag, v₂, in methanediol. The enhancement of the congested spectral feature between 2900 cm⁻¹ to 3000 cm⁻¹ we assign to the CH₂ symmetric, v₄, stretch of both methanediol and methanediol water-complexes. The peak at 634 cm⁻¹ we associate with the OH wag, v₇, of the bonding OH in

methanediol water-complexes. The peaks centered at 914 cm⁻¹ and 1094 cm⁻¹ we assign to the free, v_6 , and bonding, v_3 , C–O stretch in the methanediol water-complex. We assign the peaks centered at 1003 cm⁻¹ and 1238 cm⁻¹ to the CH₂ rock and free OH symmetric, v_5 , and anti-symmetric, v_2 , wag in the methanediol water-complex. The broad spectrum between 3100 cm⁻¹ and 3400 cm⁻¹ we assign to the bonding OH stretching transition, $v_{OH bonding}$, in methanediol water-complexes. Our assignment of all the spectral features were determined with our calculated vibrational frequencies of methanediol and methanediol water-complex as shown in Table 5.1. This work provides the first IR spectrum of methanediol and methanediol water complexes at room temperature.

5.3.2 Determination of Water, Formaldehyde, and Methanediol Concentrations

The spectroscopic characterization of the vibrational spectra in the mid-infrared allowed us to quantify the amount of water, formaldehyde, and methanediol present in each spectrum as shown below.

5.3.3 Partial Pressure of Water

Experimentally observed spectroscopic water lines were compared with high-resolution transmission molecular absorption database (HITRAN) water lines and line strengths to determine the partial pressure of water, as summarized in Table 5.2. Two water lines at 1918 cm⁻¹ and 3920 cm⁻¹ were isolated and analyzed. The H₂O number density (N/v) was determined via Equation 1:

$$\frac{N}{v} = \frac{\text{Abs.}}{L \times \sigma_{\text{H},0}}$$
(1)

The path length of the spectroscopic glass cell, *L*, was 62.23 cm and σ_{H_2O} (cm molecule⁻¹) is the HITRAN line strength for each water line. The partial pressure of water, *p*H₂O, was determined using the average *N*/*v* from the two water lines and then using the ideal gas law to convert to the vapor pressure of water.

Experiment	int abs 1918 cm ⁻¹	int abs 3920 cm^{-1}	Avg N/v , molecule cm ⁻³	$p_{\rm H2O}$, atm
1	0.02264	0.02356	1.3×10^{16}	5.4×10^{-4}
2	0.02308	0.01732	$1.2 imes 10^{16}$	4.7×10^{-4}
3	0.02415	0.02381	$1.4 imes 10^{16}$	5.6×10^{-4}
4	0.01427	0.00728	6.2×10^{15}	2.5×10^{-4}

 Table 5.2 Partial Pressure of Water

Partial pressures, $p_{\rm H2O}$, of water determined from experimental spectra and HITRAN. Integrated absorbance (int abs) for each experimental water lines were used. Water lines 1918 cm⁻¹ and 3920 cm⁻¹ had the following cross-sections: 2.93×10^{20} and 2.61×10^{20} cm moleculue⁻¹.[45]

5.3.4 Partial Pressure of Formaldehyde

The partial pressure of formaldehyde, pH_2CO , for each experiment was determined spectroscopically using the integrated absorbance of the formaldehyde C=O stretch, $2v_2$, from 3466 cm⁻¹ to 3473 cm⁻¹ and a cross-section of 8.29×10^{-20} cm molecule⁻¹, derived from the experimentally determined cross-section for the formaldehyde C=O stretch, v_2 , by Klotz, B. et al.,[35] as summarized in Table 5.3. The formaldehyde *N*/*v* was determined using Equation 1 and the *p*H₂CO was obtained using the ideal gas law.

Table 5.3 Partial Pressure of Formaldehyde

Experiment	int abs, cm ⁻¹	Avg N/v , molecule cm ⁻³	p_{H2CO} , atm
1	1.77	1.49×10^{17}	5.95×10^{-3}
2	1.79	1.51×10^{17}	6.03×10^{-3}
3	1.81	1.52×10^{17}	6.09×10^{-3}
4	1.66	1.40×10^{17}	5.58×10^{-3}

Partial pressures of formaldehyde, p_{H2CO} , determined from experimental spectra. Integrated absorbance (int abs) for the formaldehyde C=O stretch, $2v_2$, at 3471 cm⁻¹ was used. The experimentally derived $\sigma_{\text{C=O}}$ of 8.29 × 10²⁰ cm molecule⁻¹ was used.

5.3.5 Partial Pressure of Methanediol

The partial pressure of methanediol, $pH_2C(OH)_2$, was determined spectroscopically using the symmetric C–O stretch, v₅, at 914 cm⁻¹ and a theoretically calculated methanediol crosssection, $\sigma_{H_2C(OH)_2}$, of 1.54×10^{-17} cm molecule⁻¹. The integrated absorbance along with the calculated cross-section was used in Equation 1 to determine the methanediol N/v and the $pH_2C(OH)_2$ was then obtained using the ideal gas law. The experimentally obtained partial pressures are shown in Table 5.4.

Experiment	int abs, cm ⁻¹	Avg N/v , molecule cm ⁻³	$p_{\rm H2C(OH)2}$, at
1	2.05	9.25×10^{14}	3.69×10^{-5}
2	1.69	$7.62 imes 10^{14}$	3.04×10^{-5}
3	1.82	8.21×10^{14}	3.28×10^{-5}
4	0.93	4.20×10^{14}	1.68×10^{-5}

 Table 5.4 Partial Pressure of Methanediol

Partial pressure of methanediol, $p_{\rm H2C(OH)2}$, determined from experimental spectra integrated absorbance (int abs) for the methanediol C–O stretch at 914 cm⁻¹ was taken. Theoretically calculated $\sigma_{\rm C-O} 1.54 \times 10^{-17}$ cm molecule⁻¹ is used.

5.3.6 Water-Mediated Gas-Phase Equilibrium Constant

In the gas phase equilibrium, the most abundant species will be free formaldehyde, free water, and free methanediol so that the equilibrium constant, K_p , can be obtained from the partial pressures derived from our spectra using Eq. 2.

$$K_{p} = \frac{p_{\rm H_{2}C(OH)_{2}}}{p_{\rm H_{2}O} \cdot p_{\rm H_{2}CO}}$$
(2)

The K_p mean value for the four experiments, as summarized in Table 5.5, 11.0 ± 1.1 . Due to the limitations of our experimental set-up the water concentration was not varied over a large range. Although, we were able to observe the formation of methanediol-water complexes in our spectra, as shown in Figure 3b, we were not able to quantify the partial pressure of complexes in our experiments. The Gibbs energy (ΔG°) was calculated from K_p using Eq. 3.

$$\Delta G^{\circ} = -RT(\ln K_p) \tag{3}$$

Our mean experimentally determined ΔG° , are summarized in Table 5.5, -1.40 ± 0.06 kcal mol⁻¹.

Experiment	$p_{\rm H2O}$, atm	$p_{\rm H2CO}$, atm	$p_{\rm H2C(OH)2}$, atm
1	5.4×10^{-4}	5.95×10^{-3}	3.69×10^{-5}
2	$4.7 imes 10^{-4}$	6.03×10^{-3}	3.04×10^{-5}
3	5.6×10^{-4}	6.09×10^{-3}	3.28×10^{-5}
4	2.5×10^{-4}	5.58×10^{-3}	1.68×10^{-5}
Experiment	K_p	ΔG° , kcal mol ⁻¹	
1	11.5	-1.42	
2	10.8	-1.39	
3	9.67	-1.32	
4	12.2	-1.46	

 Table 5.5 Experimental equilibrium constant and Gibbs energy.

Experimentally determined gas-phase water-mediated equilibrium constant, K_p , values calculated using Eq. 3 for reaction R1 between formaldehyde and methanediol and the experimentally determined Gibbs energy, ΔG° , kcal mol⁻¹, values calculated using Eq. 4. Temperature was 293.15 K. K_p values have and error of ± 1.1 and , ΔG° values have an error of ± 0.06 kcal mol⁻¹. Previous investigations of the hydration of formaldehyde have been performed in the bulk aqueous media.[2-10] These investigations determined the Gibbs energy for R1 to be -4.6 kcal mol⁻¹,[10] with an equilibrium constant of 2000, corresponding to more then 80% of the aqueous formaldehyde solution being methanediol. Our gas-phase determined Gibbs energy and equilibrium constant for R1 are significantly smaller, but are not unreasonable. For comparison, methylglyoxal[12] was shown to hydrate to form its geminal diol counterpart in the gas-phase, with a ΔG° of -3.09 kcal mol⁻¹.[12] Therefore, our experimental gas-phase determination of Gibbs energy change of -1.40 ± 0.06 kcal mol⁻¹, R1, suggests the production of methanediol can proceed under very dry conditions (RH% < 5%). This observation is in agreement with previous investigations of the hydration of the carbonyl group in the gas-phase of glyoxylic acid[11] and methylglyoxal[12] and the hydration of pyruvic acid[13] in a carbon tetrachloride matrix with low water concentrations. Our investigation of the hydration of formaldehyde at higher water concentration have found that the spectral features are diminished due to water. The high solubility if these diols in water is consistent with other systems in the literature.[36]

The presence of excess water molecules in R1 catalyzes the thermal hydration of formaldehyde by significantly lowering the energy of the transition state relative to the reactants.[37, 38] Similar observations of "single molecule" catalysis was observed in the literature,[36, 39-41] in an investigation of water catalysis of acetaldehyde reaction with OH. This barrier lowering occurs via the formation of a hydrogen-bonded network manifested as a 6, 8, or 10 membered ring. The ring conformation properly orients the reactant complex for the reaction process and so reduces the steric strain and distance of the hydrogen transfer at the transition state. The hydration reaction then proceeds as a concerted hydrogen transfer along the hydrogen bonded network as the water oxygen and formaldehyde carbon simultaneously form a
bond. The dramatic effect of the presence of catalytic water can be seen from the transition state theory rate constants shown in Table 5.6 and Figure 5.4 at the ambient temperature of 298 K. There is essentially no reaction for the formaldehyde monohydrate complex at this temperature as a result of the high energy transition state. The presence of one catalytic water in the formaldehyde dihydrate lowers the activation energy by over 16 kcal mol⁻¹ and increases the calculated rate constant by more than 10 orders of magnitude. Additional catalytic waters in the reaction complex lower the activation energy even further. For the three and four water hydrated conformation is clusters, the ring present only not at the

Table 5.6 Unimolecular Transition State Theory Rate Constants, Activation Energies, and Preexponential Factors at 298 K for the Reaction $H_2CO^{\bullet}(H_2O)_n \rightarrow H_2C(OH)_2^{\bullet}(H_2O)_{n-1}$

1		=	
Reaction	k_{TST} , s ⁻¹	E _a , kcal mol ⁻¹	A, s^{-1}
n=1	$8.81 imes 10^{-18}$	37.95	1.28×10^{10}
n=2	8.16×10^{-6}	21.23	2.18×10^{9}
n=3	1.52×10^{-1}	14.29	$1.78 imes 10^8$
n=4	3.99×10^{2}	8.54	1.91×10^{7}

All calculations for the barrier energies, frequencies, and reactant and transition state geometries necessary to determine the TST rate constant were performed at the B3LYP/6-31+G(d,p) level of theory. Although several different conformations exist for the equilibrium clusters $H_2CO^{\bullet}(H_2O)_n$ for n=3 and 4, we account only for those directly connected through the transition state via the minimum energy path to the most stable "ring" hydrated conformers of the methanediol clusters.



Figure 5.4 The logarithm of the unimolecular formaldehyde hydration rate constant at 298 K is shown versus the number of water molecules in the hydrated formaldehyde reactant complex. waters in the reaction complex lower the activation energy even further. For the three and four water hydrated clusters, the ring conformation is present not only at the transition state but as a stable equilibrium point. The experimental study of Winkelman and coworkers report the

activation energy and the pre-exponential factor of the hydration of formaldehyde in an aqueous solution to be 5.8 kcal mol⁻¹ and 2.04×10^5 s⁻¹, respectively.[42] The results from Table 6 seem to imply a convergence to this solution phase limit as the number of waters in the formaldehyde cluster increases. The theoretical calculations of Wolfe et al.[37] and the molecular dynamics simulations of Nielsen et al.[6] have led those authors to postulate that the hydration of formaldehyde in solution is preceded by the formation of three and four water reactant ring complexes.[42] The rate constant calculations in this work, in agreement with Williams et al.[38] and Wolfe et al.[37], suggest that the gas phase hydration of formaldehyde must *also* be preceded by the complexation of at least two waters for any marked reaction to occur. Likely the most significant reaction pathway at ambient temperatures proceeds through the complexation of at least three or more water molecules. To summarize, in order for methanediol formation to occur in gas phase, the formaldehyde must first complex with two or more waters.

For given partial pressures of formaldehyde and water vapor, an equilibrium distribution of hydrated formaldehyde complexes will form. The relevant calculated equilibrium constants for the formation of these complexes are shown in Table 5.7 for a temperature of 298 K. The equilibrium constant for the evaporation of the monohydrate complex is large and implies that free formaldehyde and water is largely favored over the complex. In fact, it is not until three or four waters have been added to the cluster, so the stable ring complex configurations may form, that the energy stabilization from the formation of hydrogen bonds begins to balance the loss of

Table 5.7 Calculated Hydrated Formaldehyde Cluster Evaporation Pressure, Standard State 1 atm, Equilibrium Constants $H_2CO^{\bullet}(H_2O)_n \rightarrow H_2CO^{\bullet}(H_2O)_{n-1} + H_2O$.

Reaction	K _p
n=1	1.39×10^{2}
n=2	3.96×10^{1}
n=3	1.43
n=4	1.60×10^{1}

All energy, frequency, and geometry calculations necessary to compute the equilibrium constants were performed at the B3LYP/6-31+G(d,p) level of theory. The n=3 and n=4 cluster geometries were chosen to be the most stable, "ring", configurations found.

entropy and an addition of a free water molecule to the complex is less unfavorable. This result has a significant implication for the formation of methanediol. In order to form a substantial amount of hydrated complexes necessary for the conversion to methanediol, the water and formaldehyde reactants must be present in considerable amounts to form complexes to proceed to form the diol. In Figure 5.5, the percent of formaldehyde present in hydrated form at equilibrium at 298 K is plotted as the concentration of water is varied and clearly illustrates the necessity of a substantial water concentration to cause complexation. The rate of methanediol production is, therefore, expected to strongly depend upon the partial pressure of water and the formation of a significant amount of hydrated formaldehyde clusters is suggested to be a limiting step in the reaction. The presence of large amounts of water poses an experimental challenge in the detection of methanediol and its formation kinetics in the gas phase as absorption due to water and the hydrated complexes of methanediol and formaldehyde are difficult, if not impossible, to resolve. Abundance of water essentially "washes out" the spectrum. Our observation of methanediol in the gas phase proves that the hydration of formaldehyde indeed occurs but further kinetic work will be necessary to validate any proposed mechanism.



Figure 5.5 The percent of 6.00×10^{-3} atm of gas phase formaldehyde found as a hydrated complex, $H_2CO^{\bullet}(H_2O)_n$, in equilibrium and at temperature of 298 K is shown as the partial pressure of water is varied. The curve was calculated from a complex equilibrium scheme using the theoretical equilibrium constants shown in Table 5.7

5.4 Summary

Formaldehyde is an important atmospheric compound that is formed in the photochemical oxidation of methane and other higher hydrocarbons of both natural and anthropogenic origins. In this investigation, we obtained and assigned the gas-phase IR vibrational spectra of formaldehyde, *trans*-methanediol and *trans*-methanediol monohydrate, and observed that formaldehyde will undergo hydration to form methanediol at low relative humidity < 5%.

The predominant atmospheric sinks for formaldehyde are UV photolysis, oxidation by OH, and dry and wet deposition.[43] A major consequence of this gas-phase water-mediated chemistry is that the conversion of formaldehyde to methanediol will suppress the near-UV photochemistry due to absorbance of formaldehyde electronic states. The two alcohol groups in

the diol provide an alternative photochemical pathway via overtone excitation of the OH chromophores of the methanediol.[58-60] Red light initiated chemistry by excitation of the OH vibration overtones in the ground electronic state has been proposed to be significant for oxidized atmospheric species.[11, 44-57] The OH chromophores of the diol have the ability to undergo red light initiated chemistry by excitation of the OH vibration overtones in the ground electronic state, which has been suggested for other oxidized atmospheric species[11, 44-57] In addition, these results provide a insight into the discrepancies between measurements of oxidized organic molecules in the field and in atmospheric models.[14-19]

The gas-phase water-mediated equilibrium constant K_p was determined using the spectral features of formaldehyde, methanediol and water. The observed K_p implies that the gas-phase formation of the diol is possible in the atmosphere at low water concentrations and therefore has the possibility to affect the gas-particle partitioning of formaldehyde and its ability to form secondary organic aerosols (SOA). Results of field measurements and atmospheric models find that the formation pathways of SOA is highly speculative which leads to uncertainties in prediction of atmospheric models.[15, 17, 61] Atmospheric models have shown that a significant SOA source is missing when comparing the model prediction to simultaneous field measurements of volatile organic compounds (VOCs) and aerosol particles.[14, 15, 17, 62, 63] The results of this work point to the role that methanediol could play in the formation of SOA, due to its lower vapor pressure and tendency to form intermolecular hydrogen bonds.

5.5 References for Chapter V

- 1. Anderson, L.G., et al., *Sources and sinks of formaldehyde and acetaldehyde: An analysis of Denver's ambient concentration data.* Atmospheric Environment, 1996. **30**: p. 2113.
- 2. Betterton, E.A. and M.R. Hoffmann, *Henry law constants of some environmentally important aldehydes*. Environmental Science and Technology, 1988. **22**: p. 1415.
- 3. Bezzi, S., et al., *Cinetica di formazione e scissione di macromolecole lineari ed equillri fra monomero e suol polimeri*. Gazz. Chim. Ital., 1951. **81**: p. 951.
- 4. Walker, F.J., *Formaldehyde*. 1964, New York: Reinhold.
- 5. Piret, E.L. and M.W. Hall, *Distillation principles of formaldehyde solutions Liquid Vapor equilibrium and effect of partial condensation.* Ind. Eng. Chem., 1948. **40**: p. 661.
- 6. Mugnai, M., et al., *Ab initio molecular dynamics study of aqueous formaldehyde and methanediol.* Molecular Physics, 2007. **105**.
- 7. Bell, R.P., *The Reversible Hydration of Carbonyl Compounds*. Adv. Phs. Org. Chem., 1966. **4**: p. 1-29.
- 8. Bell, R.P. and P.G. Evans, *Kinetics of the dehydration of methylene glycol in aqueous solution*. Proc. R. Soc., 1966. **A291**: p. 297-323.
- 9. Hasse, H. and F. Maurer, *Kinetics of the Poly(oxymethylene) Glycol Formation in Aqueous Formaldehyde Solutions.* Ind. Eng. Chem. Res., 1991. **30**: p. 2195-2200.
- 10. Zavitsas, A.A., et al., *The reversible hydration of formaldehyde. Thermodynamic parameters.* The Journal of Physical Chemistry, 1970. **74**(14): p. 2746-2750.
- 11. Plath, K.L., et al., *Gas-phase vibrational spectra of glyoxylic acid and its gem diol monohydrate. Implications for atmospheric chemistry.* Reaction Kinetics and Catalysis Letters, 2009. **96**(2): p. 209-224.
- 12. Axson, J.L., et al., *Gas-Phase Water Mediated Equilibrium Study Between MEthylglyoxal and its Geminal Diol.* Proceedings of the National Academy of Sciences of the United States of America, 2009. **107**(15): p. 6687-6692.
- 13. Maron, M.K., et al., *Hydration of Pyruvic Acid to its Geminal-Diol in a Water-Restricted Environment.* 2011: p. Submitted.
- 14. Hodzic, A., et al., Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary

organic aerosol formation. Atmospheric Chemistry and Physics, 2010. 10(12): p. 5491-5514.

- 15. Heald, C.L., et al., *A large organic aerosol source in the free troposphere missing form current models.* Geophysical Research Letters, 2005. **32**: p. 4.
- 16. Ervens, B. and R. Volkamer, *Glyoxal processing by aerosol multiphase chemistry:* towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles. Atmospheric Chemistry and Physics, 2010. **10**(17): p. 8219-8244.
- 17. Volkamer, R., et al., Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected. Geophysical Research Letters, 2006. 33(17): p. L17811.
- 18. Volkamer, R., et al., *A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol.* Geophysical Research Letters, 2007. **34**(19): p. L19807.
- 19. Finalyson-Pitts, B.J., *Reactions at surfaces in the atmopshere: intergration of experiments and theory as necessary (but no necessarily sufficient) for prediciting the physical chemistry of aerosols.* Physical Chemistry Chemical Physics, 2009. **11**(36): p. 7760-7779.
- 20. Khoshkhoo, H. and E.R. Nixon, *Infrared and Raman spectra of formaldehyde in argon and nitrogen matrices*. Spectrochimica Acta, 1973. **29A**: p. 603-612.
- 21. Becke, A.D., *Density-functional thermochemistry*. *III. The role of exact exchange*. Journal of Chemical Physics, 1992. **98**(7): p. 5648-5652.
- 22. Lee, C.T., W.T. Yang, and R.G. Parr, *Development of the colle-salvetti correlationenergy formula into a functional of the electron-density.* Physical Review B, 1988. **37**(2): p. 785-789.
- 23. McLean, A.D. and G.S. Chandler, *Contracted Gaussian-Basis Sets for molecular Calculations. I. 2nd row atoms*, Z=11-18. Journal of Chemical Physics, 1980. 72(10): p. 5639-5648.
- 24. Krishnan, R., et al., *Self-consistent Molecular-Orbital Methods. XX. Basis set for Correlated Wave-Functions.* Journal of Chemical Physics, 1980. **72**(1): p. 650-654.
- 25. Clark, T., et al., *Efficient Diffuse Function-Augmented Basis-Sets for Anion Calculations*. *III. The 3-21+G Basis Set for 1st-Row Elements, Li-F.* Journal of Computational Chemistry, 1983. **4**(3): p. 294-301.
- 26. Frisch, M.J., et al., *Gaussian03, C.02 ed.* Vol. 110. 2004, Gaussian Inc.: Wallingford, CT.

- 27. Kjaergaard, H.G., *Calculated OH-stretching vibrational transitions of the water-nitric acid complex.* Journal of Physical Chemistry A, 2002. **106**(12): p. 2979-2987.
- 28. Howard, D.L., P. Jorgensen, and H.G. Kjaergaard, *Weak intramolecular interactions in ethylene glycol identified by vapor phase OH-stretching overtone spectroscopy*. Journal of the American Chemical Society, 2005. **127**(48): p. 17096-17103.
- 29. Howard, D.L. and H.G. Kjaergaard, *Influence of intramolecular hydrogen bond strength* on OH-stretching overtones. Journal of Physical Chemistry A, 2006. **110**(34): p. 10245-10250.
- 30. Low, G.R. and H.G. Kjaergaard, *Calculation of OH-stretching band intensities of the water dimer and trimer*. Journal of Chemical Physics, 1999. **110**(18): p. 9104-9115.
- 31. Eyring, H., J. Chem. Phys., 1935. **3**: p. 107.
- 32. Hehre, W.J., R. Ditchfield, and J.A. Pople, J. Chem. Phys., 1971. 56: p. 2257.
- 33. Hariharan, P.C. and J.A. Pople, Theor. Chim. Acta., 1973. 28: p. 213.
- 34. Francl, M.M., et al., J. Chem. Phys., 1982. 77: p. 3654.
- Klotz, B., I. Barnes, and T. Imamura, *Product study of the gas-phase reactions of O3, OH and NO3 radicals with methyl vinyl ether*. Physical Chemistry Chemical Physics, 2004.
 6: p. 1725-1734.
- 36. Vohringer-Martinez, E., et al., *Water Catalysis of a Radical-Molecule Gas-Phase Reaction*. Science, 2007. **315**: p. 497-501.
- 37. Wolfe, S., et al., *Hydration of the Carbonyl Group A Theoretical Study of the Cooperative Mechanism.* Journal of the American Chemical Society, 1995. **117**(15): p. 4240-4260.
- 38. WIlliams, I.H., et al., *Theoretical models for solvation and catalysis in carbonyl addition*. J. Am. Chem. Soc., 1983. **105**(1): p. 31-40.
- 39. Smith, I.W.M., *Single-molecule catalysis*. Science, 2007. **315**: p. 470-471.
- 40. Aloisio, S. and J.S. Francisco, *Radical-Water Complexes in Earth's Atmosphere*. Accounts of Chemical Research, 2000. **33**: p. 825-830.
- 41. Anglada, J.M. and J. Gonzalez, *Different catalytic effects of a single water molecule: The gas-phase reaction of formic acid with hydroxyl radial in water vapor.* Chemphyschem, 2009. **10**(17): p. 3034-3035.

- 42. Winkelman, J.G.M., et al., *Kinetics and chemical equilibrium of the hydration of formaldehyde*. Chemical Engineering Science, 2002. **57**: p. 4067-4076.
- 43. Stavrakou, T., et al., *Evaluating the performance of pyrogenic and biogenic emission inventories against one decade of space-based formaldehyde columns.* Atmos. Chem. Phys., 2009. **9**: p. 1037-1060.
- 44. Plath, K.L., et al., *Fundamental and Overtone Vibrational Spectra of Gas-Phase Pyruvic Acid.* Journal of Physical Chemistry A, 2009. **113**: p. 7294-7303.
- 45. Takahashi, K., et al., *Dynamics of vibrational overtone excited pyruvic acid in the gas phase: Line broadening through hydrogen-atom chattering*. Journal of Physical Chemistry A, 2008. **112**(32): p. 7321-7331.
- Vaida, V., H.G. Kjaergaard, and K.J. Feierabend, *Hydrated complexes: Relevance to atmospheric chemistry and climate*. International Reviews in Physical Chemistry, 2003. 22(1): p. 203-219.
- 47. Hintze, P.E., et al., *Vibrational and electronic spectroscopy of sulfuric acid vapor*. Journal of Physical Chemistry A, 2003. **107**(8): p. 1112-1118.
- 48. Havey, D.K., et al., *Experimental and theoretical investigation of vibrational overtones of glycolic acid and its hydrogen bonding interactions with water*. Journal of Physical Chemistry A, 2006. **110**(20): p. 6439-6446.
- Miller, Y., R.B. Gerber, and V. Vaida, *Photodissociation yields for vibrationally excited states of sulfuric acid under atmospheric conditions*. Geophysical Research Letters, 2007. 34(16).
- 50. Vaida, V., et al., *Photolysis of sulfuric acid vapor by visible solar radiation*. Science, 2003. **299**(5612): p. 1566-1568.
- 51. Vaida, V., Spectroscopy of Photoreactive Systems: Implications for Atmospheric Chemistry. Journal of Physical Chemistry A, 2009. **113**(1): p. 5-18.
- 52. Staikova, M., M. Oh, and D.J. Donaldson, *Overtone-induced decarboxylation: A potential sink for atmospheric diacids*. Journal of Physical Chemistry A, 2005. **109**(4): p. 597-602.
- 53. Donaldson, D.J., A.F. Tuck, and V. Vaida, *Atmospheric photochemistry via vibrational overtone absorption*. Chemical Reviews, 2003. **103**(12): p. 4717-4729.
- 54. Matthews J, S.A., Francisco, J. S., *The importance of weak absorption features in promoting tropospheric radical production.* Proceedings of the National Academy of Sciences of the United States of America, 2005. **102**(21): p. 7449-7452.

- 55. Miller, Y., et al., *Photochemical processes induced by vibrational overtone excitations: Dynamics simulations for cis-HONO, trans-HONO, HNO3, and HNO3-H2O.* Journal of Physical Chemistry A, 2006. **110**(16): p. 5342-5354.
- 56. Donaldson, D.J., et al., *Atmospheric radical production by excitation of vibrational overtones via absorption of visible light*. Geophysical Research Letters, 1997. **24**(21): p. 2651-2654.
- 57. Wennberg, P.O., et al., *Removal of stratospheric 03 by radicals in-situ measurements of OH, HO2, NO, NO2, CLO, and BRO.* Science, 1994. **266**(5184): p. 398-404.
- 58. Carbajo, P.G., et al., Ultraviolet Photolysis of HCHO: Absolute HCO Quantum Yield by Direct Detection of the HCO Radical Photoproduct. J. Phys. Chem. A, 2008. **112**: p. 12437-12448.
- 59. Pope, F.D., et al., *Photochemistry of formaldehyde under troposhperic conditions*. Faraday Discussions, 2005. **130**: p. 59-72.
- 60. Gratien, A., et al., *UV and IR Absorption Cross-sections of HCHO, HCDO, and DCDO.* J. Phys. Chem. A, 2007. **111**: p. 11506-11513.
- 61. Finlayson-Pitts, B.J., Reactions at surfaces in the atomsphere: Intergration of experiments and theory as necessary (but necessarily sufficient) for predicting the physical chemistry of aerosols. Physical Chemistry Chemical Physics, 2009. **11**(36): p. 7760 7779.
- 62. J. Fast, e.a., Evaluating simulated primary anthropogenic and biomass burning organic aerosols during MILAGRO: Implications for assessing treaments of secondary organic aerosols. Atmos. Chem. Phys., 2009. 9(16): p. 6191-6215.
- 63. de Gouw JA, M.A., Warneke C, Goldan PD, Kuster WC, Roberts JM, Fehsenfeld FC, Worsnop DR, Canagaratna MR, Pszenny AAP, Keene WC, Marchewka M, Bertman SB, Bates TS, *Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002.* Journal of Geophysical Research Atmospheres, 2005. **110**(D16): p. D16305.

Chapter VI: The Development of Assessment Tools to Determine Student Learning in Undergraduate Chemistry

6.1 Motivation

The classroom discourse in university and college courses and laboratory classrooms has significantly changed over the last two decades. At many institutions, traditional lectures and recitations have been supplemented or replaced by a variety of interactive engagement strategies, while traditional verification or "cookbook" laboratory exercises have been replaced with guided inquiry experiments. The goal of these transformations has been to place students at the center of learning. A student-centered environment focuses on the delivery of material presented to students rather than just the content of the material. The importance of this approach was highlighted in two reports from the American Association for the Advancement of Science (AAAS).[1, 2] These studies concluded that listening alone is not sufficient for meaningful learning; instead students need to engage in discussions, write, and read as well as to reinforce their understanding through problem solving.[1, 2] Based upon these observations about how students learn[3-9], a wide variety of science courses, ranging from the environmental sciences to physical chemistry, have incorporated student-centered environments.[10-16]

Along with these important transformations in science education comes a need for valid and reliable assessment tools, so as to ensure that the transformations are truly effective. The work presented in this thesis focuses on assessment in two areas: the first-year chemistry laboratory and the upper-division physical chemistry lecture course.

6.2 Student Understanding of the Electrochemical Cell and the Salt Bridge

For many years, laboratory exercises in lower-division science courses have predominantly followed the "verification" model. The goal of a verification lab is to demonstrate an established scientific principle - to show that some fact or relationship presented in lecture is true. Students are given a detailed procedure to follow, and are instructed to analyze their data using relationships that they have been given ahead of time. This approach to laboratory instruction has been heavily criticized, on multiple grounds. Observations of student discourse in the laboratory setting have shown that students are often so preoccupied with "getting through" the prescribed laboratory procedure that they devote little attention to what is actually going on.[3,4] The emphasis upon verification of prescribed results means that the laboratory experience has little resemblance to an authentic research environment. Taken together this evidence suggests that traditional laboratory exercises do not appreciably help students to understand the underlying concepts, and do not contribute to student understanding of the scientific method

The ineffectiveness of the traditional laboratory format has led educators to explore a variety of alternatives, which have been broadly described as "inquiry-based " or "discovery-based" laboratory exercises. At one extreme - so-called "open inquiry" labs - students are expected not only to devise the procedures that they will use to answer particular research questions but also to create research questions that are appropriate for the concepts that they are studying. In between the extremes of open inquiry and traditional verification labs fall a number of approaches that have been described as "structured inquiry" or "guided inquiry". These approaches allow students to establish relationships among the variables through the analysis of

their own data, although students are still given some specific experimental directions.[17, 18] Education researchers have described the difficulties that are associated with teaching inquiry laboratory courses, and have provided suggestions about how to overcome such difficulties [17, 18]. A primary focus of investigations concerning the adoption of guided-inquiry experiments has been linking student attitudes and achievements[19-24] as well as student perceptions of such experiments.[25] In contrast, less research has directly addressed the impact of the laboratory on student conceptual understanding.

Over the past few years, the General Chemistry program at the University of Colorado has been engaged in a critical examination and revision of the general chemistry laboratory courses, The revisions have been incremental rather than radical, incorporating elements of guided inquiry within traditional exercises. Up till now, however, no assessment tools have been developed to quantify the effect of these changes on student learning.

In Chapter VII of this thesis we investigate the impact of an electrochemistry laboratory exercise on student understanding. Electrochemistry was chosen based on an extensive literature that describes the difficulties that students have with the subject matter [26-31]. In the first phase of this project, free-response questionnaires were developed and administered to a sample of students. These pilot surveys showed that while most of our students could answer quantitative questions about the operation of an electrochemical cell, their conceptual understanding of the microscopic processes that occur within the cell was inconsistent and incomplete. The student responses were then used to construct a laboratory post-test that was administered to a larger sample of students in Spring 2010 and again in Spring 2011. In between the two terms, the laboratory exercise was revised so as to better address the difficulties revealed by the pilot surveys. After the revisions a substantial improvement on the post-test was found,

suggesting that the relatively modest changes to the laboratory procedure helped the students to develop a more consistent picture of the processes that occur within an electrochemical cell.

6.3 Transforming Upper-Division Physical Chemistry Teaching Based on Education Research

Quantum mechanics links many of the conceptual ideas to which students are introduced during their first years in college-level science education. Student difficulties have been observed throughout quantum mechanics, at both the undergraduate[32-42]and graduate levels.[43] A major project in this area has recently been carried out in the Physics department at the University of Colorado. As a part of this project, interactive simulations [44, 45] and assessment tools[40, 46] been developed and used in undergraduate quantum physics courses.

Physics and chemistry students typically have a different background in mathematics, as well as different problem-solving skills. The insights developed in studies of physics students may not, therefore, be directly applicable to chemistry courses. Recent work in chemical education has identified some of the reasons that chemistry students have difficulty with quantum mechanics. Most chemistry students lack the fundamental physical concepts necessary to construct the advanced concepts that are central to a quantum mechanics applications,[47, 48], and they usually do not have the mathematical background that is expected.[49] As a result, the previously developed assessment tools need to be adapted, and new pedagogical tools need to be developed, to fit the specific needs of chemistry students.

In this part of the thesis we have investigated the effects of new interactive teaching tools on student understanding in quantum mechanics. We assessed student attitudes and beliefs about science using the Chem-CLASS (Colorado Learning Attitudes about Science Survey) instrument[50]. The Chem-CLASS consists of fifty statements to which students respond using a five-point Likert scale. In addition, we adapted a quantum mechanics concept survey that was originally developed for an upper-division physics course for use in chemistry. Both surveys were administered at the beginning and at the end of a second-semester Physical Chemistry course so that we could measure the incoming knowledge of students and the knowledge that was gained as a consequence of completing the course.

6.4 Dissertation Overview Part B: Chemical Education

The work presented in this section of the dissertation consists of one chapter and two appendices. Chapter VII describes the electrochemistry laboratory project. Appendix C contains the supplementary material for Chapter VII, the pre- and post-electrochemistry pilot surveys, the electrochemistry post-test, and the voltaic cell laboratory exercises for the Spring 2010 and 2011 semesters. Appendix D outlines the quantum mechanics education project and provides the assessment surveys.

6.5 References for Chapter VI

- 1. AAAS, Science for all Americans: A Project 2061 report on literacy goals in science, mathematics, and technology. (AAAS, Washington, DC, 1989).
- 2. AAAS, *The Liberal Art of Science*. (AAAS, Washington, DC, 1990).
- 3. Bransford, J., A. Brown, and R. Cocking, *How people learn: brain, mind, experience and school.* . 2000, Washington, D. C.: National Academy Press.
- 4. Bransford, J. and M. Donovan, *How students learn: history, mathematics, and science in the classroom.* 2005, Washington, D. C.: National Academy Press.
- 5. Siebert, E.D., *In College Pathways to the Science Education Standards*. 2001: NSTA Press: Arlington, VA.
- 6. Browne, L.M. and E.V. Blackburn, *Teaching introductory organic chemistry: a problemsolving and collaborative-learning approach*. Journal of Chemical Education, 1999. **76**(8): p. 1104-1107.
- 7. *National Science Education Standards*. National Research Council. 1996: National Academy Press: Washington, DC.
- 8. *Science Teaching Reconsidered: A Handbook.* National Research Council. 1997: National Academy Press: Washington, DC.
- 9. Boyer, E., *Scholarhsip reconsidered: Priorities of the professorate.* (The Carnegie Foundation for the Advancement of Teaching, Stanford, CA, 1990).
- 10. Spencer, J.N., R.S. Moog, and J.J. Farrell, *Physical Chemistry: A Guided Inquiry*. (Houghton Mifflin, New York, 2004).
- 11. Lunsford, S.K. and W. Slattery, *An interactive environmental science course for education science majors.* Journal of Chemical Education, 2006. **83**(2): p. 233-236.
- 12. Grant, A. and D. Latimer, *Bromination and debromination of cholesterol: an inquirybased lab involving structure eludcidation, reaction mechanism, and 1H NMR.* Journal of Chemical Education, 2003. **80**(6): p. 670-671.
- 13. Vaksman, M.A. and J.W. Lane, *Using guided inquiry to study optical activity and optical rotatory dispersion in a cross-disciplinary chemistry lab.* Journal of Chemical Education, 2001. **78**(11): p. 1507-1509.
- 14. Durick, M.A., *The study of chemistry by guided inquiry method using microcomputerbased laboratories.* Journal of Chemical Education, 2001. **78**(5): p. 574-575.

- 15. Kimbrough, D.R., M.A. Magoun, and M. Langfur, *A laboratory experiment investigation different aspects of catalase activity in an inquiry -based approach*. Journal of Chemical Education, 1997. **74**(2): p. 210-212.
- 16. Cummins, R.H., W.J. Green, and C. Elliott, "Prompted" inquiry-based learning in the introductory chemistry labratory. Journal of Chemical Education, 2004. **81**(2): p. 239-241.
- 17. Abraham, M.R., *In Chemists' Guide to Effective Teaching*. Inquiry and the Learning Cycle Approach, ed. N.J. Pienta, M.M. Cooper, and T.J. Greenbow. 2004, Upper Saddle River, NJ. 41-52.
- 18. Martin-Hansen, I., *Defining inquiry*. The Science Teacher, 2002. **69**(2): p. 34-37.
- 19. Lawson, A.E., *Managing the inquiry classroom: problems and solutions*. The American Biology Teacher, 2000. **62**(9): p. 641-648.
- 20. Chin, C., Success with investigations. The Science Teacher, 2003. 70(2): p. 34-40.
- 21. Deters, K.M., *Inquiry in the chemistry classroom*. The Science Teacher, 2004. **71**(10): p. 42-45.
- 22. Chatterjee, S., et al., *Surveying students' attitudes and perceptions toward guided-inquiry and open-inquiry laboratories*. Journal of Chemical Education, 2009. **86**(2): p. 1427-1432.
- 23. Freedman, M.P., *Relationship among laboratory instruction, attitude toward science, and achievement in science knowledge.* J. Res. Sci. Teach, 1997. **34**(4): p. 343-357.
- 24. House, J.D., Res. Higher Ed., 2003. **36**: p. 473-490.
- 25. Deters, K.M., *Student opinions regarding inquiry-based labs*. Journal of Chemical Education, 2005. **82**(8): p. 1178-1180.
- 26. Ogude, A.N. and J.D. Bradley, *Ionic conduction and electrical neutrality in operating electrochemical cells*. Journal of Chemical Education, 1994. **71**(1): p. 29-34.
- 27. Sanger, M.J. and T.J. Greenbowe, *Common student misconceptions in electrochemistry: galvanic, electrolytic, and concentration cells.* Journal of Research in Science Teaching, 1997. **34**(4): p. 377-398.
- 28. Garnett, P.J. and D.F. Treagust, *Conceptual difficulties experienced by senior high school students of electrochemistry: Electrochemical (galvanic) and electrolytic cells.* Journal of Research in Science Teaching, 1992. **29**(10): p. 1079-1099.

- 29. Garnett, P.J. and D.F. Treagust, *Conceptual difficulties experienced by senior high school students of electrochemistry: Electric circuits and oxidation-reduction equations.* Journal of Research in Science Teaching, 1992. **29**(2): p. 121-142.
- 30. Hamza, K.M. and P.O. Wickman, *Describing and analyzing learning in action: An empirical study of the importance of misconceptions in learning science*. Science Education, 2008. **92**(1): p. 141-164.
- Sanger, M.J. and T.J. Greenbowe, Student's misconceptions in electrochemistry: current flow in electrolyte solutions and the salt bridge. Journal of Chemical Education, 1997. 74(7): p. 819-823.
- 32. Ambrose, B.S. A repeat performance? Challenges in developing a robust conceptual understanding in quantum mechanics. in Physical Education Research Conference Proceedings 2005.
- 33. Ambrose, B.S. *Investigation of student understanding of the wave-like properties of light and matter.* Ph. D. Thesis 1999. University of Washington.
- 34. Bao, L., *Dynamics of student modeling: A theory, algorithms, and application to quantum mechanics.* Ph. D. Thesis 1999: University of Maryland.
- 35. Morgan, J.T. and M.C. Wittman. *Examining the evolution of student ideas about quantum tunneling*. in *Physics Education Research Conference Proceedings*. 2006.
- 36. Steinberg, R.N., G.E. Oberem, and L.C. McDermott, *Development of computer-based tutorial on the photoelectric effect.* . American Journal of Physics, 1996. **64**: p. 1370-1379.
- 37. Steinberg, R.N. and G.E. Oberem, *Research-based instructional software in modern physics*. Journal of Computational Math and Science Teaching, 2000. **19**: p. 115-136.
- 38. Wittmann, M.C., J.T. Morgan, and L. Bao, *Addressing student models of energy loss in quantum tunneling*. European Journal of Physics, 2005. **26**: p. 939-950.
- 39. Wittmann, M.C., R.N. Steinberg, and E.F. Redish, *Investigating student understanding of quantum physics: Spontaneous models of conductivity.* . American Journal of Physics, 2002. **70**: p. 218-226.
- 40. McKagan, S.B. and C.E. Wieman. *Exploring student understanding of energy through the Quantum Mechanics Conceptual Survey*. in *Physics Education Research Conference Proceedings*. 2006.
- 41. Singh, C., *Student understanding of quantum mechanics*. American Journal of Physics, 2001. **69**: p. 885-895.

- 42. Bao, S.H. and L. Bao. *Student difficulties in understanding probability in quantum mechanics*. in *Physics Education Research Conference Proceedings* 2005.
- 43. Snigh, C. Assessing and improving student understanding of quantum mechanics. in *Physics Education Research Conference Proceedings* 2006.
- 44. Belloni, M., W. Christian, and A.J. Cox, *Physlet quantum physics: An interactive introduction*. 2005: Prenstice Hall.
- 45. McKagan, S.B., et al., *Developing and researching PhET simulations for teaching quantum mechanics*. American Journal of Physics, 2008. **76**: p. 406-417.
- 46. Cataloglu, E. and R.W. Robinett, *Testing the development of student conceptual and visualization understanding in quantum mechanics through the undergraduate career.* . American Journal of Physics, 2002. **70**: p. 238-251.
- 47. Zoller, U., Students' misunderstandings and misconceptions in college freshmen chemistry (general and organic) Comment. Journal of Research in Science Teaching, 1990. 27: p. 1053-1065.
- 48. Nakiboglu, C., Instructional misconceptions of Turkish prospective chemistry teachers about atomic orbitals and hybridization. Chemical Education Research Practices, 2003.
 4: p. 171-178.
- 49. Pauling, L. and Wilson Jr., E.B., *Introduction to quantum mechanics with applications to chemistry*. 1935, New York: McGraw-Hill.
- 50. Barbera, J., Combining research in physical chemistry and chemical education: Part A. The femtosecond molecular dynamics of small gas-phase anion clusters. Part B. Surveying student beliefs about chemistry and the development of physical chemistry learning tutorials, in Chemistry. Ph. D. Thesis 2007, University of Colorado: Boulder.

Chapter VII: Student Understanding of the Electrochemical Cell and the Salt Bridge

7.1 Introduction

Laboratory experiments attempt to provide a hands-on environment for students that allows them to practice and apply the chemistry concepts presented in lecture. However, the extent to which laboratory experiments actually contribute to students' understanding is not clear. The work presented here investigates the impact of laboratory exercise involving electrochemical cells on students' understanding of the microscopic processes that occur within the electrochemical cell.

Research in science education has shown that students express many misconceptions in their understanding of scientific phenomena.[1] Here we use the term "misconception" to describe a student's expression of a "nonscientific idea" in reasoning about an observed scientific process. Identifying and understanding the sources of student misconceptions is important in students' learning science. It has even been stated that student misconceptions characterize science learning.[2] Many studies have argued that in order for students to achieve meaningful learning, their misconceptions have to be supplemented with valid conceptions, otherwise new learning is distorted. These conclusions are based upon common patterns of student difficulties that have been observed in physics,[4] biology,[5] and chemistry[6], at a wide variety of educational institutions extending across several continents. Since student misconceptions do not exist in isolation from the contexts in which they appear, identifying and measuring to what extent students' learning is constrained or influenced by particular misconceptions is difficult. Deeply rooted misconceptions can be extraordinarily difficult to dislodge - many decades of experience have shown that merely correcting the students in a classroom or laboratory situation is insufficient. A more productive strategy is to design an environment within which students are forced to confront and resolve the inconsistencies in their reasoning on their own.

In this chapter, we describe an investigation of student conceptual understanding of electrochemistry in the context of a first-year general chemistry course at a large state-supported research university. We chose to focus on elementary electrochemistry for two reasons. First, there is a substantial body of research literature dealing with student difficulties in this area[7-17]; second, the instructors in the general chemistry program at this University had suggested, based upon their own observations of students, that the laboratory procedure in this subject area needed to be improved. Previous investigations have identified a number of particular student difficulties in electrochemistry.[12-17] One prominent misconception found in both high school and college students is the idea that electrons flow through the salt bridge from the anode to the cathode to complete the circuit.[12, 17] More generally, the research shows that many students can solve conventional numerical problems in electrochemistry without being able to answer qualitative questions related to the same underlying concepts.[12]

Our study reproduces the observations of earlier investigations [12-17] For example, we found that many students were able to use standard reduction potentials in order to predict the direction of the chemical reaction, but were unable to develop a schematic of an electrochemical cell [9], and that many students were unable to describe the function of the salt bridge. An analysis of the laboratory manual for this exercise revealed that relatively little attention was devoted to qualitative issues such as the role of the salt bridge. This led us to revise the

experimental procedure by incorporating questions and operations designed to stimulate critical thinking within the laboratory environment. The results of a laboratory post-test suggest that these changes have led to an improvement in conceptual understanding.

7.2 Methodology

7.2.1 General Outline of Project

This investigation is based on previously observed student difficulties regarding the qualitative interpretation of the microscopic processes within an electrochemical cell. The investigation spanned two academic years. The subjects involved in this study were studying electrochemistry in an introductory general chemistry freshmen level course at the University of Colorado, Boulder. The investigation was conducted in four phases, as described below.

- (1) Identification of subject of study; Electrochemistry
- (2) Exploration of student difficulties and identification of misconceptions
- (3) Instrument design and identification of the possible sources of the misunderstanding
- (4) Modification of laboratory experiment and collection of student responses

7.2.2 The Laboratory Program

Each general chemistry course at the University of Colorado, Boulder includes 4 credit hours of lecture and recitation and 1 credit hour of lab. Although the students are required to enroll into the lecture, recitation, and lab sessions simultaneously, the three sections run independently of one another. Course lecturers are involved with the teaching of lab, in order to present chemical concepts in lecture consistent to those covered in the laboratory experiments. Each term of the general chemistry laboratory course consists of either 9 or 12 verification or guided-inquiry laboratory experiments. The students attend a 3 hour weekly lab session, which contains 18 - 21 students per one graduate student teaching assistant (TA). Lab sessions are scheduled at 1:00 -4:00 PM on Monday through Friday, at 9:00-12:00 AM on Tuesday and Thursday, and 6:00-9:00 PM on Tuesday evening. The TA introduces the laboratory experiment in a 15 - 30 minute lecture, which may include but is not limited to the background of the chemical concepts explored in the experiment and any relevant laboratory techniques to the students. Prior to entering the lab the students are required to complete a pre-laboratory assignment, which may ask quantitative, qualitative, and/or procedural questions that apply to the particular experiment.

7.2.3 Participants

Study participants were students enrolled in general chemistry courses in the spring semesters of 2010 and 2011. This study included 211 students, 106 students in the spring semester of 2010 and 105 students in the spring semester of 2011. The course instructor and laboratory instructor was the same for each year, as were all of the student assignments aside from the laboratory itself. Furthermore, the time line for the course and the laboratory experiments was the same. Table 7.1 presents the time line for the lecture and laboratory.

Lecture and Laboratory Time-Line	Week Number
Electrochemistry Lecture	8 - 9
Electrochemistry WebAssign (Homework Set)	9
Laboratory Exercise 6 - Voltaic Electrochemical Cells	9
Post Laboratory Exercise 6 Assignment Due	10
Electrochemistry Questionnaire	10
Exam II (Including electrochemistry)	10

Table 7.1 Electrochemistry time-line in the lecture and laboratory.

The Exam takes place on Thursday evening, after all but one of the laboratory sections have taken place. For this study, students were selected from the Monday-Thursday afternoon sections

and from Tuesday and Thursday morning sections. One section from each of these time periods was selected.

7.2.4 Instrument

The instrument used in this study consisted of a 7-item list of multiple-choice questions, shown in Figures 1a and 1b. This questionnaire was constructed on the basis of responses to previous open response questionnaires on electrochemical cells, which identified misconceptions that the students in this course had. The 7-item questionnaire was given after the post laboratory assignment for the Laboratory Exercise 6 – Voltaic Electrochemical Cells was turned in. The students had one week to complete the post laboratory assignment after completing the exercise in the laboratory. The 7-item questionnaire consisted of three parts. Part 1 asked students to identify the events that take place at the salt bridge in a voltaic cell similar to one that the students explored in the laboratory exercise. Part 2 asked student to identify the microscopic processes that the salt bridge allows; the results from this part are not included in this discussion due to the possible ambiguity of the question and answer choices. Part 3 contained attitude questions.

7.3 **Results and Discussion**

7.3.1 Pilot Studies

The pilot studies consisted of a pair of open-response surveys, administered before and after the laboratory exercise, but after classroom instruction in electrochemistry. Each survey contains two questions, one qualitative and the other quantitative, both associated with a single concept. In both of the surveys the qualitative question asks the student to schematically explain the microscopic phenomena at the anode and cathode, and at the ends of salt bridge in the anode and cathode half-cell compartments. The quantitative question in the pre-lab survey asks the student to calculate the standard cell potential for the voltaic cell, while the question in the postlab survey asks for the cell potential for a concentration cell. The detailed pre- and post-lab surveys are included in Appendix C.

7.3.1.1 Scoring Rubric

The pre- and post-lab surveys were scored using the rubric shown in Table 7.2. A rubric is used to score the pre- and post-surveys on a five-point scale. A poor match between the student's answer and an expert's response is denoted by a low numerical value, while a good match between the two answers is denoted by a high numerical value. The rubric and scoring definitions have been adapted from the work of J. Barbera.[18]

Rubric Score	Criterion
Rublic Score	Criterion
0	Student has no idea or student response is totally incorrect or irrelevant as compared to the expert response on the central concept(s)
1	Student response includes some aspects of the expert response on the central concept(s) but major aspects of the expert response on the central concept(s) are missing or incorrect
2	Student response matches expert response on the central concept(s) but with one important aspect of the central concept(s) missing or incorrect.
3	Student response essentially matches expert response on the central concept(s) but some of the details concerning the central concept(s) are missing or incorrect.
4	Student response matches the expert response on the central concept(s).

Table 7.2 Grading rubric used for detailed pre- and post-survey.*

^{*} Rubric and scoring definition have been adapted from the work by J. Barbera.[18]

7.3.1.2 Pre-lab Survey

To gauge the incoming knowledge of students we administered a pre-lab survey. Students were given 10 minutes to complete this survey individually prior to starting the laboratory exercise. This survey contained material that the students would perform in the laboratory exercise. The laboratory exercise and pre-survey were tied to the course material. This allowed us to measure the students' incoming knowledge after possibly completing homework problems, attending lectures and reading the textbook.

Score	Anode	Cathode	Salt-bridge anode	Salt-bridge cathode	Cell potential
0	35 %	35 %	59 %	61 %	23 %
1	9 %	10 %	25 %	23 %	3 %
2	32 %	32 %	10 %	10 %	0 %
3	20 %	20 %	4 %	4 %	0 %
4	4 %	3 %	1 %	1 %	74 %

 Table 7.3 Pre-lab survey results.
 69 students participated in total.

The pre-lab survey for electrochemistry assesses students' incoming knowledge of the microscopic processes that take place within a voltaic cell. A copy of the survey can be seen in Appendix C. The first question shows a diagram of a voltaic cell and asks students to explain on a molecular level what is happening in each half-cell, at the salt bridge and anode/cathode metal ends and the metal wire connecting the anode and cathode, with as much detail as possible. Students are also asked to write out any chemical reactions, if they apply. The second question on the survey asks student to calculate the standard cell potential for the above voltaic cell.

The results of the pre-lab survey are shown in Table 7.3. Most (74%) of the students were able to correctly calculate the standard cell potential, regardless if they were able to explain on a molecular level the events that occur within the voltaic cell. The 23% of students that did

not correctly calculate the standard cell potential mostly switched that anode and cathode. The 3% of students that received a score of 1, had the anode and cathode correctly assigned, but reversed the sign of the standard cell potential. Students in general were able to explain the events that occur at the anode and cathode ends in the half-cell compartments, as can be seen in Table 7.1. Most students used a chemical reaction to explain the events. However, many of these students had troubles in describing the microscopic processes that occurred at the salt bridge in either the anode or cathode half-cell compartment. In agreement with previous observations, student responses showed the flow of electrons through the salt bridge, as shown in Figure 7.1.



Figure 7.1 Students schematic description of the micro processes that occur within an electrochemical cell.

7.3.1.3 Post-lab Survey

To measure the effect that the voltaic cell laboratory exercise on student knowledge in regard to electrochemistry we administered a post-lab survey. Students were given 10 minutes to complete this survey individually, prior to starting the next laboratory exercise. This survey was given to students one week after completing the voltaic cell laboratory exercise and immediately after they turned in the post-laboratory assignment. The survey contained material that students performed in the voltaic laboratory exercise. The survey was tied to the course material.

Score	Anode	Cathode	Salt-bridge anode	Salt-bridge cathode	Cell potential
0	52 %	52 %	73 %	73 %	31 %
1	8 %	8 %	11 %	11 %	0 %
2	16 %	16 %	5 %	5 %	0 %
3	11 %	11 %	2 %	2 %	0 %
4	13 %	13 %	10 %	10 %	69 %

 Table 7.4 Post-electrochemistry survey results.
 63 students participated in total.

The post-lab survey for electrochemistry assesses students' knowledge of the microscopic processes that take place within a voltaic cell after the completion of the voltaic cell laboratory exercise and post-laboratory assignment. A copy of the survey can be seen in Appendix C. The first question shows a diagram of a concentration voltaic cell and asks students to explain on a molecular level what is happening in each half-cell, at the salt bridge and anode/cathode metal ends and the metal wire connecting the anode and cathode, with as much detail as possible. Students are also asked to write out any chemical reactions, if they apply. The second question on the survey asks student to calculate the cell potential for the above concentration voltaic cell.

The results of the survey are shown in Table 7.4. In general there was no net gain in knowledge by students after completing the laboratory exercise and post-laboratory assignment. Consistent with the results of the pre-lab survey, 69% of students were able to correctly calculate the standard cell potential, irrespective of whether they were able to explain on a molecular level the events that occur within the voltaic cell. The remaining 31% of students were not able to set-up the cell potential equation correctly. Students' responses reflected the same understanding of the events that occur at the anode and cathode ends in the half-cell compartments, as can be seen in Table 7.1. Most students used a chemical reaction to explain the events. However, just as in the pre-lab survey many of these students had trouble describing the microscopic processes that occurred at the salt bridge in either the anode or cathode half-cell compartment.

7.3.2 Electrochemistry Post-Lab test

On the basis of our student observations and student responses to the pilot surveys, a 7 item electrochemistry post-lab test was developed. The test focused on the microscopic processes that occur at the salt bridge in both the anode and cathode half-cell compartments, as shown in Appendix C. It also included questions designed to measure student' confidence concerning their understanding of the role of the salt-bridge in particular, and of electrochemistry in general. In the Spring 2010 semester of general chemistry, students took the test in order to confirm our previous observations of the pilot studies. The laboratory exercise was also examined for possible sources of misunderstanding. In the analysis of the laboratory exercise we identified that the written procedure devoted little attention to developing a qualitative understanding of processes taking place at the salt bridge. The procedure instructed students about how to

construct the salt bridge, but the students were not asked to explore its function or its role in the electrochemical cell.

7.3.3 Modifications to the Voltaic Cell Laboratory Exercise

In the fourth phase of our study modifications to the voltaic cell laboratory exercise were made. The changes were centered on the salt bridge and its function. Students were instructed to explore the behavior of an electrochemical cell with and without a salt bridge. In addition, they were asked to answer questions about its function, both during the laboratory period and as a part of their pre- and post-laboratory questions. The voltaic cell laboratory exercise for Spring 2010 and 2011 semesters can be seen in the Appendix C. After the Spring 2011 students turned in their post laboratory assignment, they were then given the same 7-item lab post-test that was given to students in Spring 2010. The total number and percentage of students in spring 2010 and 2011 that identified the correct process that occurs at the anode and cathode half-cell of the electrochemical cell is summarized in Table 7.5. In addition, Table 7.3 shows the total number and percentage of students in spring 2010 and 2011 that identified that electrons either enter or exit the salt bridge in the anode and cathode half-cell compartments of the electrochemical cell. We observed that the average percentage of students that identified electrons flowing through the salt bridge in Spring 2010 was 34% while in Spring 2011 the percentage of students was 23%. We believe that the decrease of 11% of students identifying the flow of electrons through the salt bridge between the semesters is a positive response to the changes made to the laboratory procedure. Student responses also showed that they were making more sophisticated choices in the later semester. In Spring 2010 only 18% of the students identified that while potassium ions (choice C) would be flowing out of the salt bridge into the cathode half-cell compartment, nitrate ions (choice B) would be flowing into the salt bridge. In Spring 2011 27% of the students

identified this phenomenon. Our observation of students making more educated choices was also reflected in the percentage of students making more than three choices in answering either the cathode or anode half-cell compartment question. In 2010

Table 7.5 Distribution of Results of the Electrochemistry Questions Regarding the Microscopic

 Processes that Occur at the Salt Bridge.

Year	Question	G and H, %	Only C, %	Only B and C, %	Only A, %	Only A and L,%
2010*	1 (cathode)	33, 31 %	66, 62 %	19, 18 %		
2010	2 (anode)	35, 33 %			61, 58 %	7,7%
2011**	1 (cathode)	22, 21 %	65, 62 %	28, 27 %		
2011**	2 (anode)	23, 22 %			68, 65 %	10, 10%

* 106 students participated in the 2010 spring semester. ** 105 students participated in the 2011 spring semester

an average of 11% of the students selected more than three choices to answer question 1 and 2, while in the Spring 2011 semester an average of 6% of students selected more than three choices in answering the same questions. We conjecture that students who were making more then three choices per questions were guessing rather than thinking about their response. The decrease in the number of students identifying the flow of electrons through the salt bridge and the increase in the number making more sophisticated choices suggests that students were thinking more about the micro processes that occurred at the salt bridge, and/or the role of the salt bridge within the electrochemical cell.

Student responses also revealed that the modifications to the laboratory exercise improved student confidence in their understanding of electrochemistry in general as well as in the role of the salt bridge. There is a dramatic positive shift between students in the Spring 2010 semester and the Spring 2011 semester. Table 7.6 summarizes the attitude responses from total number and percentage of students in spring 2010 and 2011.

Spring Semester Year	Question	1	2	3
2010*	4 (electrochemistry)	8,8%	16, 15 %	25, 25 %
2010	5 (Salt Bridge)	4,4%	13, 12 %	29, 27 %
2011**	4 (electrochemistry)	4,4%	11, 10 %	18, 17 %
2011	5 (Salt Bridge)	0,0%	4,4%	18, 17 %
Spring Semester Year	Question	4	5	6
Spring Semester Year	Question 4 (electrochemistry)	4 35, 33 %	5 20, 19%	6 1, 1%
Spring Semester Year 2010*	Question 4 (electrochemistry) 5 (Salt Bridge)	4 35, 33 % 31, 29 %	5 20, 19% 19, 18 %	6 1, 1% 9, 8 %
Spring Semester Year 2010*	Question 4 (electrochemistry) 5 (Salt Bridge) 4 (electrochemistry)	4 35, 33 % 31, 29 % 45, 43 %	5 20, 19% 19, 18 % 23, 22 %	6 1, 1% 9, 8% 3, 3%

Table 7.6 Distribution of Results of Attitude Responses Regarding Student Confidence in Understanding Electrochemistry and the Role of the Salt Bridge in the Electrochemical Cell.

The scale ranges from 1 - 6, where 1 represents very little confidence and 6 represents a lot of confidence. * 106 students participated in the 2010 spring semester. ** 105 students participated in the 2011 spring semester.

7.4 Summary

In our investigation, we reproduced several key observations made by previous studies of student conceptual understanding of electrochemistry, which showed that successful performance on conventional numerical problems is not always accompanied by a qualitative understanding of the underlying phenomena. In particular, we found that even after lecture, recitation, homework and a traditional verification lab, a significant fraction of students did not understand the function of the salt bridge. Student performance on a conceptual post-test improved after the laboratory exercise was revised so as to more closely engage the students in thinking about the molecular-scale phenomena responsible for the macroscopic observations, suggesting that more students were developing a consistent molecular-scale picture of the processes occurring in an electrochemical cell. This suggests that incremental, low-cost

revisions to traditional laboratory procedures can reduce the prevalence of student misconceptions and improve student conceptual understanding.

7.5 References for Chapter VII

- 1. Driever, R., et al., *Making sense of secondary science: Research in children's ideas.* London: Routledge, 1994.
- 2. Vosniadou, S., Conceptual change research and the teaching of science. In H. Behrendt, H. Dahncke, R. Duit, W. Graberm M. Komorek, A. Kross, and P. Reiska (Eds.), Research in science education - Past, present, and future. Dordrecht: Kluwer, 2001: p. 177-188.
- 3. Novak, J.D., *Meaningful learning: The essential factor for conceptual change in limited or inappropriate propositional hierarchies leading to empowerment of learners.* Science Education, 2002. **86**: p. 548 571.
- 4. Hammer, D., *Student resources for learning introductory physics*. American Journal of Physics, 2000. **68**: p. 52-59.
- Songer, C.J. and J.J. Mintzes, Understanding cellular respiration: An analysis of conceptual change in college bilology. Journal fo Research in Science Teaching, 1994.
 31: p. 621-637.
- 6. Ozmen, H., *Some student misconceptions in chemistry: A literature of chemical bonding.* Journal of Science Education and Technology, 2004. **13**: p. 147-159.
- 7. Carter, C., *Ph. D. Thesis*. 1987, Purdue University.
- 8. Johnstone, A.H., *Chemical education research: facts findings and consequences*. Chemical Society Reviews, 1980. **9**: p. 365-380.
- 9. Allsop, R.T. and N.H. George, Educ. Chem., 1982. 19: p. 57-59.
- 10. Schmidt, H.J., A. Marohn, and A.G. Harrison, *Factors that prevent learning in electrochemistry*. Journal of Research in Science Teaching, 2007. **44**(2): p. 258-283.
- 11. Moran, P.J. and E. Gileadi, *Alleviating the common confusion caused by polarity in electrochemistry*. Journal of Chemical Education, 1989. **66**(11): p. 912-916.
- 12. Ogude, A.N. and J.D. Bradley, *Ionic conduction and electrical neutrality in operating electrochemical cells*. Journal of Chemical Education, 1994. **71**(1): p. 29-34.
- 13. Sanger, M.J. and T.J. Greenbowe, *Common student misconceptions in electrochemistry: galvanic, electrolytic, and concentration cells.* Journal of Research in Science Teaching, 1997. **34**(4): p. 377-398.
- 14. Garnett, P.J. and D.F. Treagust, *Conceptual difficulties experienced by senior high school students of electrochemistry: Electrochemical (galvanic) and electrolytic cells.* Journal of Research in Science Teaching, 1992. **29**(10): p. 1079-1099.

- 15. Garnett, P.J. and D.F. Treagust, *Conceptual difficulties experienced by senior high school students of electrochemistry: Electric circuits and oxidation-reduction equations.* Journal of Research in Science Teaching, 1992. **29**(2): p. 121-142.
- 16. Hamza, K.M. and P.O. Wickman, *Describing and analyzing learning in action: An empirical study of the importance of misconceptions in learning science*. Science Education, 2008. **92**(1): p. 141-164.
- Sanger, M.J. and T.J. Greenbowe, Student's misconceptions in electrochemistry: current flow in electrolyte solutions and the salt bridge. Journal of Chemical Education, 1997. 74(7): p. 819-823.
- 18. Barbera, J., Combining research in physical chemistry and chemical education: Part A. The femtosecond molecular dynamics of small gas-phase anion clusters. Part B. Surveying student beliefs about chemistry and the development of physical chemistry learning tutorials, in Chemistry. Ph. D. Thesis 2007, University of Colorado: Boulder.
Bibliography

- AAAS, Science for all Americans: A Project 2061 report on literacy goals in science, mathematics, and technology. (AAAS, Washington, DC, 1989).
- AAAS, The Liberal Art of Science. (AAAS, Washington, DC, 1990).
- Abraham, M. R., In Chemists' Guide to Effective Teaching. Inquiry and the Learning Cycle Approach, ed. N. J. Pienta, M. M. Cooper, and T. J. Greenbow. 2004, Upper Saddle River, NJ. 41-52.
- Allsop, R.T. and N.H. George, Educ. Chem., 1982. 19: p. 57-59.
- Aloisio, S. and J.S. Francisco, *Radical-Water Complexes in Earth's Atmosphere*. Accounts of Chemical Research, 2000. **33**: p. 825-830.
- Ambrose, B.S. A repeat performance? Challenges in developing a robust conceptual understanding in quantum mechanics. in Physical Education Research Conference Proceedings 2005.
- Ambrose, B.S. *Investigation of student understanding of the wave-like properties of light and matter.* Ph. D. Thesis. 1999. University of Washington.
- Anderson, L.G., et al., Sources and sinks of formaldehyde and acetaldehyde: An analysis of Denver's ambient concentration data. Atmospheric Environment, 1996. **30**: p. 2113.
- Andreae, M.O., R.W. Talbot, and S.M. Li, *Atmospheric Measurements of Pyruvic and Formic Acid.* Journal of Geophysical Research - Atmospheres, 1987. **92**(D6): p. 6635-6641.
- Anglada, J.M. and J. Gonzalez, *Different catalytic effects of a single water molecule: The gasphase reaction of formic acid with hydroxyl radial in water vapor.* Chemphyschem, 2009. **10**(17): p. 3034-3035.
- Axson, J.L., et al., Gas-Phase Water Mediated Equilibrium Study Between Methylglyoxal and its Geminal Diol. Proceedings of the National Academy of Sciences of the United States of America, 2010. 107(15): p. 6687-6692.
- Baboukas, E.D., M. Kanakidou, and N. Mihalopoulos, *Carboxylic acids in gas and particulate phase above the Atlantic Ocean*. Journal of Geophysical Research Atmospheres, 2000. 105(D11): p. 14459-14471.
- Bao, L., Dynamics of student modeling: A theory, algorithms, and application to quantum mechanics. Ph. D. Thesis. 1999: University of Maryland.
- Bao, L., et al., *Gas/particle partitioning of low-mlocular-weight dicarboxylic acids at a suburban site in Saitama, Japan.* Atmospheric Environment, 2009: p. Article in Press.

- Bao, S.H. and L. Bao. *Student difficulties in understanding probability in quantum mechanics*. in *Physics Education Research Conference Proceedings* 2005.
- Barbera, J., Combining research in physical chemistry and chemical education: Part A. The femtosecond molecular dynamics of small gas-phase anion clusters. Part B. Surveying student beliefs about chemistry and the development of physical chemistry learning tutorials, in Chemistry. Ph. D. Thesis 2007, University of Colorado: Boulder.
- Barnes, A.J., E. Lasson, and C.J. Nielsen, *Molecular complexes of nitric acid with various bases studied by matrix isolation infrared spectroscopy*. Journal of Molecular Structure, 1994.
 322: p. 165-174.
- Becke, A.D., *Density-functional thermochemistry. III. The role of exact exchange.* Journal of Chemical Physics, 1992. **98**(7): p. 5648-5652.
- Becker, M. and H. Strehlow, *Der einfuluss der hydratibiung auf das polarographische verhalten von alpha-oxocarbonsauren.* Zeitschrift Fur Elektrochemie, 1960. **64**(6): p. 813-817.
- Becker, M., *Uber magnetische kernesonanzspektren wassriger brenztrubensaurelosungen*. Berichte Der Bunsen-Gesellschaft Fur Physikalische Chemie, 1964. **68**(7): p. 669-676.
- Bell, R.P. and P.G. Evans, *Kinetics of the dehydration of methylene glycol in aqueous solution*. Proc. R. Soc., 1966. A291: p. 297-323.
- Bell, R.P., *The Reversible Hydration of Carbonyl Compounds*. Adv. Phs. Org. Chem., 1966. **4**: p. 1-29.
- Belloni, M., W. Christian, and A.J. Cox, *Physlet quantum physics: An interactive introduction*. 2005: Prenstice Hall.
- Betterton, E.A. and M.R. Hoffmann, *Henry law constrans of some environmentally important aldehydes*. Environmental Science and Technology, 1988. **22**(12): p. 1415-1418.
- Bezzi, S., et al., Cinetica di formazione e scissione di macromolecole lineari ed equillri fra monomero e suol polimeri. Gazz. Chim. Ital., 1951. 81: p. 951.
- Bisson, P., et al., *Ions and Hydrogen Bonding in a Hydrophobic Environment: CCl4.* Journal of Physical Chemistry A, 2010. **114**(12): p. 4051-4057.
- Boyer, E., *Scholarhsip reconsidered: Priorities of the professorate.* (The Carnegie Foundation for the Advancement of Teaching, Stanford, CA, 1990).
- Bransford, J. and M. Donovan, *How students learn: history, mathematics, and science in the classroom.* 2005, Washington, D. C.: National Academy Press.

- Bransford, J., A. Brown, and R. Cocking, *How people learn: brain, mind, experience and school.* . 2000, Washington, D. C.: National Academy Press.
- Browne, L.M. and E.V. Blackburn, *Teaching introductory organic chemistry: a problem-solving and collaborative-learning approach*. Journal of Chemical Education, 1999. **76**(8): p. 1104-1107.
- Buschmann, H.J., E. Dutkiewicz, and W. Knoche, *The Reversible Hydration of Carbonyl Compounds in Aqueous Solution.* 2. *The Kinetics of the Keto Gem-Diol Transition.* Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics, 1982. 86(2): p. 129-134.
- Buschmann, H.J., H.H. Fuldner, and W. Knoche, *Reversible hydration of carbonyl-compounds in aqueous solution .1. Keto-gem-diol equilibrium.* Berichte Der Bunsen-Gesellschaft Physical Chemistry Chemical Physics, 1980. **84**(1): p. 41-44.
- Callaghan, R., et al., *Laboratory simulation of polar stratospheric clouds*. Geophysical Research Letters, 1994. **21**(5): p. 373-376.
- Canagaratna, M., et al., *The nitric acid-water complex: Microwave spectrum, structure, and tunneling*. Journal of Physical Chemistry A, 1998. **102**(9): p. 1489-1497.
- Carbajo, P.G., et al., Ultraviolet Photolysis of HCHO: Absolute HCO Quantum Yield by Direct Detection of the HCO Radical Photoproduct. Journal of Physical Chemistry A, 2008. **112**(48): p. 12437-12448.
- Carbajo, P.G., et al., Ultraviolet Photolysis of HCHO: Absolute HCO Quantum Yield by Direct Detection of the HCO Radical Photoproduct. J. Phys. Chem. A, 2008. **112**: p. 12437-12448.
- Carter, C., Ph. D. Thesis. 1987, Purdue University.
- Cataloglu, E. and R.W. Robinett, *Testing the development of student conceptual and visualization understanding in quantum mechanics through the undergraduate career*. American Journal of Physics, 2002. **70**: p. 238-251.
- Chatterjee, S., et al., *Surveying students' attitudes and perceptions toward guided-inquiry and open-inquiry laboratories.* Journal of Chemical Education, 2009. **86**(2): p. 1427-1432.
- Chen, C. and S.F. Shyu, *Theoretical study of glyoxylic and pyruvic acids: rotamers and intramolecular hydrogen bonding*. Journal of Molecular Structure-Theochem, 2000. **503**(3): p. 201-211.
- Chin, C., Success with investigations. The Science Teacher, 2003. 70(2): p. 34-40.

- Clark, T., et al., *Efficient Diffuse Function-Augmented Basis-Sets for Anion Calculations. III. The 3-21+G Basis Set for 1st-Row Elements, Li-F.* Journal of Computational Chemistry, 1983. **4**(3): p. 294-301.
- Clore, G.M. and A.M. Groneborn, *NMR structure determination of proteins and protein complexes larger than 20 kDa. Current Opinion in Chemical Biology 2.* 1998: p. 564-570.
- Cooley, J.W. and J.W. Tukey, Math. Comput., 1965. 19: p. 297.
- Cooper, A.J.L. and A.G. Redfield, *Proton Magnetic Resonance Studies of alpha keto acids*. The Journal of Biological Chemistry, 1975. **250**(2): p. 527-532.
- Cummins, R.H., W.J. Green, and C. Elliott, "Prompted" inquiry-based learning in the introductory chemistry labratory. Journal of Chemical Education, 2004. 81(2): p. 239-241.
- Daniel, J.S., et al., *Atmospheric water vapor complexes and the continuum*. Geophysical Research Letters, 2004. **31**(6): p. L06118.
- De Gouw JA, M.A., Warneke C, Goldan PD, Kuster WC, Roberts JM, Fehsenfeld FC, Worsnop DR, Canagaratna MR, Pszenny AAP, Keene WC, Marchewka M, Bertman SB, Bates TS, Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002. Journal of Geophysical Research Atmospheres, 2005. 110(D16): p. D16305.
- De Gouw, J. and J. Jimenez, Organic Aerosols in the Earth's Atmosphere. Environmental Science and Technology, 2009. **43**(20): p. 7614-7618.
- Deters, K.M., Inquiry in the chemistry classroom. The Science Teacher, 2004. 71(10): p. 42-45.
- Deters, K.M., *Student opinions regarding inquiry-based labs*. Journal of Chemical Education, 2005. **82**(8): p. 1178-1180.
- Donaldson, D.J., A.F. Tuck, and V. Vaida, *Atmospheric photochemistry via vibrational overtone absorption*. Chemical Reviews, 2003. **103**(12): p. 4717-4729.
- Donaldson, D.J., et al., *Absolute intensities of nitric acid overtones*. Journal of Physical Chemistry A, 1998. **102**(27): p. 5171-5174.
- Donaldson, D.J., et al., *Atmospheric radical production by excitation of vibrational overtones via absorption of visible light*. Geophysical Research Letters, 1997. **24**(21): p. 2651-2654.
- Driever, R., et al., Making sense of secondary science: Research in children's ideas. London: Routledge, 1994.

- Dunn, M.E., et al., *Experimental and Theoretical Study of the OH Vibrational Spectra and Overtone Chemistry of Gas-Phase Vinylacetic Acid.* Journal of Physical Chemistry A, 2008. **112**(41): p. 10226-10235.
- Durick, M.A., *The study of chemistry by guided inquiry method using microcomputer-based laboratories*. Journal of Chemical Education, 2001. **78**(5): p. 574-575.
- Ervens, B. and R. Volkamer, *Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles.* Atmospheric Chemistry and Physics, 2010. **10**(17): p. 8219-8244.
- Ervens, B., et al., A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production. Journal of Geophysical Research Atmospheres, 2004. **109**(D15): p. D15205.
- Ervens, B., S. Gligorovski, and H. Herrmann, *Temperature-dependent rate constants for hydroxyl radical reactions with organic compounds in aqueous solutions*. Physical Chemistry Chemical Physics, 2003. **5**(9): p. 1811-1824.
- Escribano, R., et al., *The nitric acid hydrates: Ab initio molecular study, and RAIR spectra of the solids.* Journal of Physical Chemistry A, 2003. **107**(5): p. 651-661.
- Eyring, H., J. Chem. Phys., 1935. 3: p. 107.
- Feierabend, K.J., D.K. Havey, and V. Vaida, Gas phase spectroscopy of HNO3 in the region 2000-8500 cm(-1). Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 2004. 60(12): p. 2775-2781.
- Finalyson-Pitts, B.J., *Reactions at surfaces in the atmopshere: intergration of experiments and theory as necessary (but no necessarily sufficient) for prediciting the physical chemistry of aerosols.* Physical Chemistry Chemical Physics, 2009. **11**(36): p. 7760-7779.
- Findsen, L.A., et al., *Theoretical description of the overtone spectra of acetaldehyde using the local mode approach*. Journal of Chemical Physics, 1986. **84**(1): p. 16-27.
- Fischer, G., et al., Carbon-13 NMR investigations on the structure of .alpha.-keto acids in aqueous solution. The Journal of Organic Chemistry, 1988. 53(1): p. 214-216.
- Fisseha R, D.J., Sax M, Paulsen D, Kalberer M, Maurer R, Hofler F, Weingartner E, Baltensperger U, *Identification of organic acids in secondary organic aerosol and the corresponding gas phase from chamber experiments*. Analytical Chemistry, 2004. 76(22): p. 6535-6540.
- Francisco, J.S. and I.H. Williams, *Reaction pathways for gas-phase hydrolysis of formyl compounds HXCO (X = H, F, and Cl)*. Journal of the American Chemical Society, 1993. 115: p. 3746-3751.

Francl, M.M., et al., J. Chem. Phys., 1982. 77: p. 3654.

- Freedman, M.P., *Relationship among laboratory instruction, attitude toward science, and achievement in science knowledge.* J. Res. Sci. Teach, 1997. **34**(4): p. 343-357.
- Frisch, M.J., et al., Gaussian03, C.02 ed. Vol. 110. 2004, Gaussian Inc.: Wallingford, CT.
- Frost, G. and V. Vaida, Atmospheric implications of the photolysis of the ozone-water weaklybound complex. Journal of Geophysical Research-Atmospheres, 1995. 100(D9): p. 18803-18809.
- Gandour, R.D., *Structural requirements for intramolecular proton transfers*. Tetrahedron Letters, 1974. **3**: p. 295-298.
- Garnett, P.J. and D.F. Treagust, *Conceptual difficulties experienced by senior high school students of electrochemistry: Electrochemical (galvanic) and electrolytic cells.* Journal of Research in Science Teaching, 1992. **29**(10): p. 1079-1099.
- Garnett, P.J. and D.F. Treagust, *Conceptual difficulties experienced by senior high school students of electrochemistry: Electric circuits and oxidation-reduction equations.* Journal of Research in Science Teaching, 1992. **29**(2): p. 121-142.
- Grant, A. and D. Latimer, *Bromination and debromination of cholesterol: an inquiry-based lab involving structure eludcidation, reaction mechanism, and 1H NMR*. Journal of Chemical Education, 2003. **80**(6): p. 670-671.
- Gratien, A., et al., *UV and IR Absorption Cross-sections of HCHO, HCDO, and DCDO*. Journal of Physical Chemistry A, 2007. **111**(45): p. 11506-11513.
- Griffiths, P.R. and J.A.d. Haseth, *Fourier Transform Infrared Spectrometry*. 2nd ed. 1986, New York, NY: Wiley.
- Guzman, M.I., A.J. Colussi, and M.R. Hoffmann, *Photogeneration of distant radical pairs in aqueous pyruvic acid glasses*. Journal of Physical Chemistry A, 2006. **110**(3): p. 931-935.
- Guzman, M.I., A.J. Colussi, and M.R. Hoffmann, *Photoinduced oligomerization of aqueous pyruvic acid.* Journal of Physical Chemistry A, 2006. **110**(10): p. 3619-3626.
- Guzman, M.I., M.R. Hoffmann, and A.J. Colussi, *Photolysis of pyruvic acid in ice: Possible relevance to CO and CO2 ice core record anomalies.* Journal of Geophysical Research-Atmospheres, 2007. **112**(D10).
- Hammer, D., *Student resources for learning introductory physics*. American Journal of Physics, 2000. **68**: p. 52-59.

- Hammerich, A.D. and V. Buch, An alternative near-neighbor definition of hydrogen bonding in water. Journal of Chemical Physics, 2008. 128(11): p. 111101.
- Hamza, K.M. and P.O. Wickman, Describing and analyzing learning in action: An empirical study of the importance of misconceptions in learning science. Science Education, 2008. 92(1): p. 141-164.
- Hariharan, P.C. and J.A. Pople, Theor. Chim. Acta., 1973. 28: p. 213.
- Hasse, H. and F. Maurer, *Kinetics of the Poly(oxymethylene) Glycol Formation in Aqueous Formaldehyde Solutions.* Ind. Eng. Chem. Res., 1991. **30**: p. 2195-2200.
- Havey, D.K., et al., *Experimental and theoretical investigation of vibrational overtones of glycolic acid and its hydrogen bonding interactions with water*. Journal of Physical Chemistry A, 2006. **110**(20): p. 6439-6446.
- Headrick, J.E. and V. Vaida, *Significance of water complexes in the atmosphere*. Physics and Chemistry of the Earth Part C-Solar-Terrestial and Planetary Science, 2001. **26**(7): p. 479-486.
- Heald, C.L., et al., *A large organic aerosol source in the fre troposphere missing form current models*. Geophysical Research Letters, 2005. **32**: p. 4.
- Hehre, W.J., R. Ditchfield, and J.A. Pople, J. Chem. Phys., 1971. 56: p. 2257.
- Henry, B.R. and H.G. Kjaergaard, *Local modes*. Canadian Journal of Chemistry-Revue Canadienne De Chimie, 2002. **80**(12): p. 1635-1642.
- Henry, B.R., *Local modes in description of highly vibrationally excited molecules*. Accounts of Chemical Research, 1977. **10**(6): p. 207-213.
- Hintze, P.E., et al., *Vibrational and electronic spectroscopy of sulfuric acid vapor*. Journal of Physical Chemistry A, 2003. **107**(8): p. 1112-1118.
- Hodzic, A., et al., *Modeling organic aerosols in a megacity: potential contribution of semivolatile and intermediate volatility primary organic compounds to secondary organic aerosol formation.* Atmospheric Chemistry and Physics, 2010. **10**(12): p. 5491-5514.
- Hollenstein, H., F. Akermann, and H.H. Gunthard, Vibrational analysis of pyruvic-acid and Dlabeled, C-13-lanelled and O-18-labelled species - Matrix spectra, assignments, valence force-filed and noraml coordinate analysis. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 1978. 34(11): p. 1041-1063.

House, J.D., Res. Higher Ed., 2003. 36: p. 473-490.

Howard, D.L. and H.G. Kjaergaard, *Influence of intramolecular hydrogen bond strength on OHstretching overtones.* Journal of Physical Chemistry A, 2006. **110**(34): p. 10245-10250.

- Howard, D.L., P. Jorgensen, and H.G. Kjaergaard, Weak intramolecular interactions in ethylene glycol identified by vapor phase OH-stretching overtone spectroscopy. Journal of the American Chemical Society, 2005. 127(48): p. 17096-17103.
- J. Fast, e.a., *Evaluating simulated primary anthropogenic and biomass burning organic aerosols during MILAGRO: Implications for assessing treaments of secondary organic aerosols.* Atmos. Chem. Phys., 2009. **9**(16): p. 6191-6215.
- Johnstone, A.H., *Chemical education research: facts findings and consequences*. Chemical Society Reviews, 1980. **9**: p. 365-380.
- Kanakidou, M., et al., *Organic aerosol and global climate modelling: a review*. Atmospheric Chemistry and Physics, 2005. **5**: p. 1053-1123.
- Kawamura, K. and O. Yasui, *Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere.* Atmospheric Environment, 2005. **39**(10): p. 1945-1960.
- Kawamura, K., et al., A Greenland ice core record of low molecular weight dicarboxylic acids, ketocarboxylic acids, and alpha-dicarbonyls: A trend from Little Ice Age to the present (1540 to 1989 AD). Journal of Geophysical Research-Atmospheres, 2001. 106(D1): p. 1331-1345.
- Kawamura, K., Y. Imai, and L.A. Barrie, *Photochemical production and loss of organic acids in high Arctic aerosols during long-range transport and polar sunrise ozone depletion events.* Atmospheric Environment, 2005. **39**(4): p. 599-614.
- Kent, D.R., et al., A theoretical study of the conversion of gas phase methanediol to formaldehyde. Journal of Chemical Physics, 2003. **119**(10): p. 5117-5120.
- Khoshkhoo, H. and E.R. Nixon, *Infrared and Raman spectra of formaldehyde in argon and nitrogen matrices*. Spectrochimica Acta, 1973. **29A**: p. 603-612.
- Kimbrough, D.R., M.A. Magoun, and M. Langfur, *A laboratory experiment investigation different aspects of catalase activity in an inquiry -based approach*. Journal of Chemical Education, 1997. **74**(2): p. 210-212.
- Kjaergaard, H.G. and B.R. Henry, *The relative intensity contributions of axial and equatorial CH bonds in the local mode overtone spectra of cyclohexane.* Journal of Chemical Physics, 1992. **96**(7): p. 4841-4851.
- Kjaergaard, H.G., *Calculated OH-stretching vibrational transitions of the water-nitric acid complex.* Journal of Physical Chemistry A, 2002. **106**(12): p. 2979-2987.

- Kjaergaard, H.G., D.M. Turnbull, and B.R. Henry, *Intensities of CH-stretching and CD-stretching overtones in 1,3-butadiene and 1,3-butadiene-D6*. Journal of Chemical Physics, 1993. **99**(12): p. 9438-9452.
- Kjaergaard, H.G., et al., *Calculated OH-stretching vibrational transitions in the water-nitrogen and water-oxygen complexes.* Journal of Physical Chemistry A, 2002. **106**(38): p. 8955-8962.
- Kjaergaard, H.G., et al., *Intensities in local mode overtone spectra propane*. Journal of Chemical Physics, 1990. **93**(9): p. 6239-6248.
- Kjaergaard, H.G., et al., *OH- and CH-stretching overtone spectra of catechol.* Journal of Physical Chemistry A, 2002. **106**(2): p. 258-266.
- Kleeberg, H., D. Klein, and W.A.P. Luck, *Quantitative Infrared Spectroscopic Investigations of Hydrogen-Bond Cooperativity*. Journal of Physical Chemistry, 1987. **91**(12): p. 3200-3203.
- Klotz, B., I. Barnes, and T. Imamura, *Product study of the gas-phase reactions of O3, OH and NO3 radicals with methyl vinyl ether.* Physical Chemistry Chemical Physics, 2004. **6**: p. 1725-1734.
- Koch, T.G., et al., Low-temperature reflection/absorption IR study of thin films of nitric acid hydrates and ammonium nitrae adsorbed on gold foil. Journal of the Chemical Society, Faraday Transactions, 1996. **92**(23): p. 4787-4792.
- Koller, J. and D. Hadzi, *AM1 and ab initio calculations on nitric acid mono- and trihyrates*. Journal of Molecular Structure, 1991. **247**: p. 225-236.
- Krishnan, R., et al., Self-consistent Molecular-Orbital Methods. XX. Basis set for Correlated Wave-Functions. Journal of Chemical Physics, 1980. 72(1): p. 650-654.
- Krizner, H.E., D.O. De Haan, and J. Kua, *Thermodynamics and Kinetics of Methylglyoxal Dimer* Formation: A Computational Study. Journal of Physical Chemistry A, 2009. **113**(25): p. 6994-7001.
- Kuo, M., N. Kamelamela, and M.J. Shultz, *Rotational structure of water in a hydrophobic environment: Carbon tetrachloride*. Journal of Physical Chemistry A, 2008. **112**(6): p. 1214-1218.
- Kuo, M.H., et al., *Nitric acid Water interaction probed via isolation in carbon tetrachloride*. Journal of Physical Chemistry C, 2007. **111**(25): p. 8827-8831.
- Lambert, J.B. and E.P. Mazzola, *Nuclear Magnetic Resonance Spectroscopy: An Introduction to Princliples, Applications, and Experimental Methods.* 2004, Upper Saddle River: Pearson Education, Inc.

- Lawson, A.E., *Managing the inquiry classroom: problems and solutions*. The American Biology Teacher, 2000. **62**(9): p. 641-648.
- Lee, C.T., W.T. Yang, and R.G. Parr, *Development of the colle-salvetti correlation-energy* formula into a functional of the electron-density. Physical Review B, 1988. **37**(2): p. 785-789.
- Lemke, K.H. and T.M. Seward, *Ab initio investigation of the structure, stability, and atmospheric distribution of molecular clusters containing H2O, CO2, and N2O.* Journal of Geophysical Research, 2008. **113**: p. D19304.
- Leroux, N., C. Samyn, and T. Zeegers-Huyskens. *Mid- and near-IR study of the hydrogen bond interaction between N-methyldiacetamide and phenols*. 1998: Elsevier Science Bv.
- Livingston, D.M., *The Master of Light: A Biography of Albert Abraham Michelson*. 1973, Chicago: The University of Press of Chicago.
- Low, G.R. and H.G. Kjaergaard, *Calculation of OH-stretching band intensities of the water dimer and trimer*. Journal of Chemical Physics, 1999. **110**(18): p. 9104-9115.
- Lugez, C., et al., *A matrix-isolation infrared spectroscopic study of the reactions of methane and methanol with ozone*. Chemical Physics, 1994. **181**(1-2): p. 129-146.
- Lunsford, S.K. and W. Slattery, *An interactive environmental science course for education science majors*. Journal of Chemical Education, 2006. **83**(2): p. 233-236.
- Maes, G. and Graindourze, Matrix isolation vibrational spectra of alkyl chalcogenides complexed with HCl : Structure of alkyl sulfide and alkyl selenide complexes with hydrochloric acid in ar matrices from infrared spectra. Journal of Molecular Spectroscopy, 1985. **113**(2): p. 410-425.
- Maron, M.K. and V. Vaida, *Gas-Phase Water Mediated Equilibrium Between Formaldehyde and Methanediol. In preparation*, 2011.
- Maron, M.K., et al., *Hydration of Pyruvic Acid to its Geminal-Diol in a Water-Restricted Environment.* 2011: p. Submitted.
- Maron, M.K., M.J. Shultz, and V. Vaida, *Characterization of the nitric acid-water complex in the infrared and near-infrared region at ambient temperatures in carbon tetrachloride.* Chemical Physics Letters, 2008. **473**(4-6): p. 268-273.
- Martin-Hansen, I., Defining inquiry. The Science Teacher, 2002. 69(2): p. 34-37.
- Matsunaga, S., M. Mochida, and K. Kawamura, Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at

Moshiri, Hokkaido Isaland in Japan. Journal of Geophysical Research, 2004. 109: p. D04302.

- Matthews J, S.A., Francisco, J. S., *The importance of weak absorption features in promoting tropospheric radical production.* Proceedings of the National Academy of Sciences of the United States of America, 2005. **102**(21): p. 7449-7452.
- McCurdy, P.R., W.P. Hess, and S.S. Xantheas, Nitric Acid-Water Complexes: Theoretical Calculations and Comparison to Experiment. Journal of Physical Chemistry A, 2002. 106(33): p. 7628-7635.
- McKagan, S.B. and C.E. Wieman. Exploring student understanding of energy through the Quantum Mechanics Conceptual Survey. in Physics Education Research Conference Proceedings. 2006.
- McKagan, S.B., et al., *Developing and researching PhET simulations for teaching quantum mechanics*. American Journal of Physics, 2008. **76**: p. 406-417.
- McLean, A.D. and G.S. Chandler, *Contracted Gaussian-Basis Sets for molecular Calculations. I.* 2nd row atoms, Z=11-18. Journal of Chemical Physics, 1980. 72(10): p. 5639-5648.
- Mellouki, A. and Y.J. Mu, *On the atmospheric degradation of pyruvic acid in the gas phase*. Journal of Photochemistry and Photobiology a-Chemistry, 2003. **157**(2-3): p. 295-300.
- Michelson, A., Phil. Mag., 1891. **31**: p. 338.
- Michelson, A., Phil. Mag., 1892. 34: p. 280.
- Miller, W.L. and R.G. Zepp, *Photochemical production of dissolved inorganic carbon from terrestrial organic matter - significance to the ocieanic organic carbon cycle.* Geophysical Research Letters, 1995. **22**(4): p. 417-420.
- Miller, Y., et al., *Photochemical processes induced by vibrational overtone excitations: Dynamics simulations for cis-HONO, trans-HONO, HNO3, and HNO3-H2O.* Journal of Physical Chemistry A, 2006. **110**(16): p. 5342-5354.
- Miller, Y., G.M. Chaban, and R.B. Gerber, *Theoretical study of anharmonic vibrational spectra* of HNO3, HNO3-H2O, HNO4: Fundamental, overtone and combination excitations. Chemical Physics, 2005. **313**(1-3): p. 213-224.
- Miller, Y., R.B. Gerber, and V. Vaida, *Photodissociation yields for vibrationally excited states of sulfuric acid under atmospheric conditions*. Geophysical Research Letters, 2007. **34**(16).
- Moore, M.H. and R.K. Khanna, *Infrared and mass spectral studies of proton irradiated H2O* + *CO2 ice: evidence for carbonic acid.* Spectrochimica Acta, 1991. **47A**(2): p. 255-262.

- Moran, M.A. and R.G. Zepp, *Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter*. Limnology and Oceanography, 1997. **42**(6): p. 1307-1316.
- Moran, P.J. and E. Gileadi, *Alleviating the common confusion caused by polarity in electrochemistry*. Journal of Chemical Education, 1989. **66**(11): p. 912-916.
- Morgan, J.T. and M.C. Wittman. *Examining the evolution of student ideas about quantum tunneling*. in *Physics Education Research Conference Proceedings*. 2006.
- Mortensen, O.S., et al., Intensities in loval mode overtone spectra dichlormethane and deuterated dichloromethane. Journal of Chemical Physics, 1985. **82**(9): p. 3903-3911.
- Mugnai, M., et al., *Ab initio molecular dynamics study of aqueous formaldehyde and methanediol.* Molecular Physics, 2007. **105**(17-18): p. 2203-2210.
- Nakiboglu, C., Instructional misconceptions of Turkish prospective chemistry teachers about atomic orbitals and hybridization. Chemical Education Research Practices, 2003. 4: p. 171-178.
- National Science Education Standards. National Research Council. 1996: National Academy Press: Washington, DC.
- Nelson, J.H., Nuclear Magnetic Resonance Spectroscopy. 2003, Upper Saddle River: Pearson Education, Inc.
- Nguyen, M.T. and T.K. Ha, *Theoretical study of the formation of carbonic acid from the hydration of carbon dioxide: A case of active solvent catalysis.* J. Am. Chem. Soc., 1984. **106**(599-602): p. 599.
- Nicolaisen, F.M., *IR absorption spectrum (4200-3100 cm(-1)) of H2O and (H2O)(2) in CCl4. Estimates of the equilibrium constant and evidence that the atompsheric water absorption continuum is due to the water dimer.* Journal of Quantitative Spectroscopy and Radiative Transfer, 2009. **110**(18): p. 2060-2076.
- Novak, J.D., Meaningful learning: The essential factor for conceptual change in limited or inappropriate propositional hierarchies leading to empowerment of learners. Science Education, 2002. 86: p. 548 - 571.
- Novakov, T. and J.E. Penner, *Large Contribution of ORganic Aerosols to clund-condensation nuclei concentrations*. Nature, 1993. **365**(6449): p. 823-826.
- Ogude, A.N. and J.D. Bradley, *Ionic conduction and electrical neutrality in operating electrochemical cells.* Journal of Chemical Education, 1994. **71**(1): p. 29-34.
- Ozmen, H., *Some student misconceptions in chemistry: A literature of chemical bonding*. Journal of Science Education and Technology, 2004. **13**: p. 147-159.

- Pauling, L. and Wilson, Jr., E. B. Introduction to quantum mechanics with applications to chemistry. 1935, New York: McGraw-Hill.
- Pfeilsticker, K., et al., Atmospheric detection of water dimers via near-infrared absorption. Science, 2003. **300**(5628): p. 2078-2080.
- Piret, E.L. and M.W. Hall, *Distillation principles of formaldehyde solutions Liquid Vapor equilibrium and effect of partial condensation*. Industrial and Engineering Chemistry, 1948. **40**(4): p. 661-672.
- Piret, E.L. and M.W. Hall, *Distillation principles of formaldehyde solutions Liquid Vapor equilibrium and effect of partial condensation*. Ind. Eng. Chem., 1948. **40**: p. 661.
- Plath, K.L., et al., *Fundamental and Overtone Vibrational Spectra of Gas-Phase Pyruvic Acid.* Journal of Physical Chemistry A, 2009. **113**(26): p. 7294-7303.
- Plath, K.L., et al., Gas-phase vibrational spectra of glyoxylic acid and its gem diol monohydrate. Implications for atmospheric chemistry. Reaction Kinetics and Catalysis Letters, 2009. 96(2): p. 209-224.
- Pope, F.D., et al., *Photochemistry of formaldehyde under troposhperic conditions*. Faraday Discussions, 2005. **130**: p. 59-72.
- Ptashnik, I.V., et al., Laboratory measurements of water vapour continuum absorption in spectral region 5000-5600 cm(-1): Evidence for water dimers. Quarterly Journal of the Royal Meteorological Society, 2004. **130**(602): p. 2391-2408.
- Raczynska, E.D., K. Duczmal, and M. Darowska, *Experimental (FT-IR) and theoretical (DFT-IR) studies of keto-enol tautomerism in pyruvic acid.* Vibrational Spectroscopy, 2005. 39(1): p. 37-45.
- Raczynska, E.D., K. Duczmal, and M. Darowska, *Keto-enol tautomerism in pyruvic acid Theoretical (HF, MP2 and DFT in the Vacuo) studies*. Polish Journal of Chemistry, 2005. 79(4): p. 689-697.
- Remorov, R.G. and C. George, *Analysis of chemical kinetics at the gas-aqueous interface for submicron aerosols*. Physical Chemistry Chemical Physics, 2006. **8**: p. 4897-4901.
- Reva, I.D., et al., Combined FTIR matrix isolation and ab initio studies of pyruvic acid: Proof for existence of the second conformer. Journal of Physical Chemistry A, 2001. 105(19): p. 4773-4780.
- Rincon, A.G., et al., *Optical Absorptivity versus Molecular Composisiton of Model Organic Aerosol Matter.* Journal of Physical Chemistry A, 2009. **113**(39): p. 10512-10520.

- Ritzhaupt, G. and J.P. Devlin, *Infrared spectra of nitric and hydrochloric acid hydrate thin films*. Journal of Physical Chemistry, 1991. **95**(1): p. 90-95.
- Ritzhaupt, G. and J.P. Devlin, *Ionic vs. molecular nature of monomerix ammonium and hydronium nitrate. Infrared spectra of H3O+NO3- and NH4+NO3 solvated in argon matrices.* The Journal of Physical Chemistry, 1977. **81**(6).
- Robinson, J.W., E.M.S. Frame, and G.M.F. II, *Undergraduate Instrumental Analysis*. Vol. 6th. 2005, New York: Marcel Dekker.
- Sanger, M.J. and T.J. Greenbowe, Common student misconceptions in electrochemistry: galvanic, electrolytic, and concentration cells. Journal of Research in Science Teaching, 1997. 34(4): p. 377-398.
- Sanger, M.J. and T.J. Greenbowe, *Student's misconceptions in electrochemistry: current flow in electrolyte solutions and the salt bridge*. Journal of Chemical Education, 1997. **74**(7): p. 819-823.
- Scharge, T., D. Luckhaus, and M.A. Suhm, Observation and quantification of the hydrogen bond effect on O–H overtone intensities in an alcohol dimer. Chemical Physics, 2008. 346(1-3): p. 167-175.
- Schellenberger, A., W. Beer, and G. Oehme, Untersuchungen zur theorie der alpha ketosauren .11. IR spektroskopische untersuchungen an alpha ketosauren im gaszustand. Spectrochimica Acta, 1965. 21(7): p. 1345.
- Schmidt, H.J., A. Marohn, and A.G. Harrison, *Factors that prevent learning in electrochemistry*. Journal of Research in Science Teaching, 2007. **44**(2): p. 258-283.
- Science Teaching Reconsidered: A Handbook. National Research Council. 1997: National Academy Press: Washington, DC.
- Siebert, E.D., In College Pathways to the Science Education Standards. 2001: NSTA Press: Arlington, VA.
- Singh, C., *Student understanding of quantum mechanics*. American Journal of Physics, 2001. **69**: p. 885-895.
- Smith, B.C., Fourier Transform Infraraed Spectroscopy. 1996, Boca Raton, FL: CRC Press.
- Smith, I.W.M., Single-molecule catalysis. Science, 2007. 315: p. 470-471.
- Smith, R.H., M.T. Leu, and L.F. Keyser, *Infrared spectra of solid films formed from vapors containing water and nitric acid.* Journal of Physical Chemistry, 1991. 95(15): p. 5924-5930.

- Snigh, C. Assessing and improving student understanding of quantum mechanics. in Physics Education Research Conference Proceedings 2006.
- Solomon, S., et al., Climate Change 2007: The Physical Science Basis, in Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. 2007: Cambridge, United Kingdom and New York, NY, USA. p. 996.
- Songer, C.J. and J.J. Mintzes, *Understanding cellular respiration: An analysis of conceptual change in college bilology.* Journal fo Research in Science Teaching, 1994. **31**: p. 621-637.
- Spencer, J.N., R.S. Moog, and J.J. Farrell, *Physical Chemistry: A Guided Inquiry*. (Houghton Mifflin, New York, 2004).
- Staikova, M. and D.J. Donaldson, Ab initio investigation of water complexes of some atmospherically important acids: HONO, HNO3 and HO2NO2. Physical Chemistry Chemical Physics, 2001. 3(11): p. 1999-2006.
- Staikova, M., M. Oh, and D.J. Donaldson, *Overtone-induced decarboxylation: A potential sink for atmospheric diacids.* Journal of Physical Chemistry A, 2005. **109**(4): p. 597-602.
- Stavrakou, T., et al., *Evaluating the performance of pyrogenic and biogenic emission inventories against one decade of space-based formaldehyde columns*. Atmos. Chem. Phys., 2009. 9: p. 1037-1060.
- Steinberg, R.N. and G.E. Oberem, *Research-based instructional software in modern physics*. Journal of Computational Math and Science Teaching, 2000. **19**: p. 115-136.
- Takahashi, K., et al., *Dynamics of vibrational overtone excited pyruvic acid in the gas phase: Line broadening through hydrogen-atom chattering.* Journal of Physical Chemistry A, 2008. **112**(32): p. 7321-7331.
- Takahashi, K., et al., *Vibrational overtone induced elimination reactions within hydrogenbonded molecular clusters: the dynamics of water catalyzed reactions in CH2FOH center dot(H2O).* Physical Chemistry Chemical Physics, 2007. **9**(29): p. 3864-3871.
- Takahashi, K., Theoretical study on the effect of intramolecular hydrogen bonding on OH stretching overtone decay lifetime of ethylene glycol, 1,3-propanediol, and 1,4-butanediol. Physical Chemistry Chemical Physics, 2010. 12(42): p. 13950-13961.
- Takahashi, K., XH Stretching Vibrational Spectra, A Theoretical Perspective. 2004, Keio University.
- Talbot, R.W., et al., Sources and sinks of formic, acetic and pyruvic aicds over central amazonia.
 2. wet season. Journal of Geophysical Research-Atmospheres, 1990. 95(D10): p. 16799-16811.

- Tao, F.M., et al., *Structure, binding energy, and equilibrium constant of the nitric acid-water complex.* Geophysical Research Letters, 1996. **23**(14): p. 1797-1800.
- Tarakeshwar, P. and S. Manogaran, *An ab initio study of pyruvic acid.* Theochem-Journal of Molecular Structure, 1998. **430**: p. 51-56.
- Tautermann, C.S., et al., Towards the experimental decomposition rate of carbonic acid (H2CO3) in aqueous solution. Chem. Eur. J., 2002. 8(1): p. 66-73.
- Tolbert, M.A., B.G. Koehler, and A.M. Middlebrook, Spectroscopic studies of model polar stratospheric cloud films. Spectrochimica Acta Part A: Molecular Spectroscopy, 1992. 48(9): p. 1303-1313.
- Toth, G., *Quantum chemical study of the different forms of nitric acid monohydrate*. Journal of Physical Chemistry A, 1997. **101**(47): p. 8871-8876.
- Vaida, V. and J.E. Headrick, *Physicochemical properties of hydrated complexes in the Earth's atmosphere*. Journal of Physical Chemistry A, 2000. **104**(23): p. 5401-5412.
- Vaida, V., et al., Atmospheric absorption of near infrared and visible solar radiation by the hydrogen bonded water dimer. Quarterly Journal of the Royal Meteorological Society, 2001. 127(575): p. 1627-1643.
- Vaida, V., et al., *Photolysis of sulfuric acid vapor by visible solar radiation*. Science, 2003. **299**(5612): p. 1566-1568.
- Vaida, V., et al., Sunligh-initiated photchemistry: excited vibrational states of atmospheric chromophores. International Journal of Photenergy, 2008. 2008: p. 138091.
- Vaida, V., et al., Sunlight-initiated photochemistry: Excited vibrational states of atmospheric chromophores. International Journal of Photoenergy, 2008.
- Vaida, V., H.G. Kjaergaard, and K.J. Feierabend, *Hydrated complexes: Relevance to atmospheric chemistry and climate*. International Reviews in Physical Chemistry, 2003. 22(1): p. 203-219.
- Vaida, V., *Review article: Sunlight initiated atmospheric photochemical reactions*. International Journal of Photoenergy, 2005. 7(2): p. 61-70.
- Vaida, V., Spectroscopy of Photoreactive Systems: Implications for Atmospheric Chemistry. Journal of Physical Chemistry A, 2009. **113**(1): p. 5-18.
- Vaksman, M.A. and J.W. Lane, *Using guided inquiry to study optical activity and optical rotatory dispersion in a cross-disciplinary chemistry lab.* Journal of Chemical Education, 2001. **78**(11): p. 1507-1509.

- Veres P, R.J., Warneke C, Welsh-Bon D, Zahniser M, Herndon S, Fall R, de Gouw J, Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere. International Journal of Mass Spectrometry, 2008. 274(1-3): p. 48-55.
- Vohringer-Martinez, E., et al., *Water Catalysis of a Radical-Molecule Gas-Phase Reaction*. Science, 2007. **315**: p. 497-501.
- Volkamer, R., et al., A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol. Geophysical Research Letters, 2007. 34(19): p. L19807.
- Volkamer, R., et al., Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected. Geophysical Research Letters, 2006. **33**(17): p. L17811.
- Vosniadou, S., Conceptual change research and the teaching of science. In H. Behrendt, H. Dahncke, R. Duit, W. Graberm M. Komorek, A. Kross, and P. Reiska (Eds.), Research in science education Past, present, and future. Dordrecht: Kluwer, 2001: p. 177-188.
- Walker, F.J., Formaldehyde. 1964, New York: Reinhold.
- Wennberg, P.O., et al., *Removal of stratospheric 03 by radicals in-situ measurements of OH,* HO2, NO, NO2, CLO, and BRO. Science, 1994. **266**(5184): p. 398-404.
- WIlliams, I.H., et al., *Theoretical models for solvation and catalysis in carbonyl addition*. J. Am. Chem. Soc., 1983. **105**(1): p. 31-40.
- Winkelman, J.G.M., et al., *Kinetics and chemical equilibrium of the hydration of formaldehyde*. Chemical Engineering Science, 2002. **57**: p. 4067-4076.
- Wittmann, M.C., R.N. Steinberg, and E.F. Redish, *Investigating student understanding of quantum physics: Spontaneous models of conductivity.* . American Journal of Physics, 2002. **70**: p. 218-226.
- Wolfe, S., et al., *Hydration of the Carbonyl Group A Theoretical Study of the Cooperative Mechanism.* Journal of the American Chemical Society, 1995. **117**(15): p. 4240-4260.
- Yang, X., et al., *A DFT study on the radical, monomer and dimer of alpha-keto pyruvic acid: equilibrium structures and vibrational analysis of stable conformers.* Chemical Physics Letters, 2003. **380**(1-2): p. 34-41.
- Ying, L.M. and X.S. Zhao, *Theoretical studies of XONO2-H2O (X = Cl, H) complexes*. Journal of Physical Chemistry A, 1997. **101**(36): p. 6807-6812.
- Zavitsas, A.A., et al., *The reversible hydration of formaldehyde. Thermodynamic parameters.* The Journal of Physical Chemistry, 1970. **74**(14): p. 2746-2750.

- Zhou, Z.Y., D.M. Du, and A.P. Fu, *Structures and vibrational frequencies of pyruvic acid: density functional theory study.* Vibrational Spectroscopy, 2000. **23**(2): p. 181-186.
- Zoller, U., Student misunderstandings and misconceptions in college freshmen chemistry (general and organic) Comment. Journal of Research in Science Teaching, 1990. 27: p. 1053-1065.

Appendix A: Mid-Infrared Spectra of Carbonic Acid

A.1 Experimental

A.1.1 Spectroscopic Studies

Infrared absorption spectra were obtained at room temperature with a commercial Fourier Transform (FTS) Spectrometer. A Bruker IFS 66v (MCT detector, 100 scans/spectrum, resolution of 0.25 cm⁻¹) was used in the mid-infrared from 1700 cm⁻¹ to 4500 cm⁻¹. The instrument was held under vacuum before and during data collection.

A glass cell was used to obtain the mid-infrared spectra of carbon tetrachloride/water solutions. The cell path length varied from 2.5 - 15 cm in order to improve the signal to noise ratio, and to increase the absorbance. The glass cell was fitted with IR quartz windows. Special conditioning of the glass cell and all glassware was done to prevent hydrogen bonding. Preparation and conditioning of the glass cell and all glassware used is described in Chapter II Section 2.4.1.

A.1.2 Materials and Sample Preparation

All materials were purchased from Sigma-Aldrich Chemical Co., Inc. Carbon tetrachloride (Aldrich, >99.5%, anhydrous) was dried with silica gel and activated carbon in a closed reservoir. The saturated water spectrum was prepared by mixing Nanopure water (NERL reagent grade water 18 M Ω) with dried carbon tetrachloride and allowed to phase separate. The spectrum was taken of the carbon tetrachloride layer only. The stock solution was prepared by

filling a 10 μ L syringe with Nanopure water, weighing it, adding the contents to 100 mL volumetric flask of dried carbon tetrachloride, and then mixing vigorously using a sonicator. Dilutions were made by transferring a known volume of stock solution from the stock solution volumetric flask to the IR glass cell, taking a spectrum, and diluting the stock solution volumetric flask with a known volume of dried carbon tetrachloride. These procedures were repeated to obtain the spectra in this work.

A.2 Results



Figure A.1. Observed mid-infrared absorption spectra of carbon tetrachloride/water solutions at 0.25 cm^{-1} resolution from 1750 cm⁻¹ to 4500 cm⁻¹. The spectrum marked with the dashed line represents carbon tetrachloride saturated with Nanopure water. The spectrum with the solid black line represents the carbon tetrachloride with a low water concentration.

The presence of carbonic acid is confirmed with the appearance of the C=O stretch at 1810 cm^{-1} and OH stretch at 3180 cm^{-1} . The spectral features have been assigned with assistance of work by Moore, M. H., et al.[2] It should be noted that there is a shoulder that appears at lower water concentration, this could be due to intermolecular hydrogen bonding between carbonic acid and water. Additionally, a peak at 2825 cm^{-1} is present at high water concentration, but has not been assigned here.



Figure A.2. Observed mid-infrared absorption spectrum of dried carbon tetrachloride at 0.25 cm⁻¹ resolution from 3200 cm⁻¹ to 4300 cm⁻¹.

The presence of carbonic acid is confirmed with the appearance of the first overtone of the C=O stretch at 3590 cm⁻¹. The peak at 4220 cm⁻¹ is tentatively assigned to a combination band of the OH stretch with the C-O symmetric stretch of carbonic acid. The combination band was assigned with assistance of work by Moore, M. H., et al.[2] The peaks at 3590 cm⁻¹ and 4220 cm⁻¹ are not present at high water concentration, where carbonic acid is not expected to be stable.

Table A.1 Experimentally Observed H_2O and H_2CO_3 Resonances and Assignment of Observed Peaks from 1700 cm⁻¹ to 4500 cm⁻¹.

vibrational mode	literature frequency (cm ⁻¹)	experimentally observed frequency (cm ⁻¹)
H_2O		
n ₁	3617^{b}	3617 ^{<i>a</i>}
n 3	3709^{b}	3708^{a}
H_2CO_3		
n _{OH}	3030 ^c	3180 ^{<i>a</i>}
n _{C=O}	1705 ^c	1810 ^a
2n _{C=0}		3590 ^a

a Our experimentally observed stretching transitions, at room temperature

b Kuo, M. H., et al.[1]

c Moore, M. H., et al.[2]

A.2 References for Appendix A

- 1. Kuo, M.H., et al., *Nitric acid Water interaction probed via isolation in carbon tetrachloride*. Journal of Physical Chemistry C, 2007. **111**(25): p. 8827-8831.
- 2. Moore, M.H. and R.K. Khanna, *Infrared and mass spectral studies of proton irradiated* H2O + CO2 ice: evidence for carbonic acid. Spectrochimica Acta, 1991. **47A**(2): p. 255-262.
- 3. Tautermann, C.S., et al., *Towards the experimental decomposition rate of carbonic acid* (H2CO3) in aqueous solution. Chem. Eur. J., 2002. **8**(1): p. 66-73.
- 4. Nguyen, M.T. and T.K. Ha, *Theoretical study of the formation of carbonic acid from the hydration of carbon dioxide: A case of active solvent catalysis.* J. Am. Chem. Soc., 1984. **106**(599-602): p. 599.
- 5. Lemke, K.H. and T.M. Seward, *Ab initio investigation of the structure, stability, and atmospheric distribution of molecular clusters containing H2O, CO2, and N2O.* Journal of Geophysical Research, 2008. **113**: p. D19304.

Appendix B: Photochemical Reaction Pathways of Gas-Phase Methanediol

B.1 Experimental

B.1.1 Spectroscopic Studies

Infrared absorption spectra were obtained at room temperature with a commercial Fourier Transform (FTS) spectrometer. A Bruker TENSOR 27 (mercury cadmium telluride (MCT) detector and resolution of 1 cm⁻¹) was used in the mid-infrared from 600 cm⁻¹ – 4000 cm⁻¹. The instrument was purged with dry and carbon dioxide free air before and during data collection.

A cross glass static cell was used to obtain the mid-infrared spectra and for the photolysis experiments. The cross cell consisted of two cells, which were connected with a #50 Ace-Threds threaded glass joint. The upper glass cell had an inner diameter of 7.62 cm, a path length of 62.23 cm and was fitted with calcium fluoride (CaF₂) windows. The lower glass cell had an inner diameter of 2.54 cm, a path length of 62.23 cm and was fitted with KRS-5 windows. The photolysis beam passed through the upper glass cell, while the mid-infrared beam passed through the lower glass cell. The glass cell schematic is shown in Chapter II Section 2.4.4 Figure 2.8. A purge box, which was purged with dry and carbon dioxide air before and during data collection, was built around the cross glass cell and the detector.

B.1.2. Materials and Sample Preparation

All materials were purchased from Sigma-Aldrich Chemical CO., Inc. Formaldehyde was prepared by heating *para*formadehyde (Aldrich, 95%, prills) to 110 °C, trapping the vapor at liquid N₂ temperature, then distilling the formaldehyde from a dry ice trap into a pressure controlled spectroscopic glass cell, as adapted from Khoshkhoo, H. et al.[1] Methanediol was prepared *in-situ*, by first introducing formaldehyde into a pressure controlled spectroscopic glass cell, then opening the cell to the room atmosphere until the internal pressure of the cell was equal to the room pressure. The initial internal pressure of the spectroscopic glass cell was approximately 15 mTorr.

The hydration of formaldehyde to methanediol was allowed for one hour. The hydration reaction was monitored by taking a spectrum (100 scans with 1 cm⁻¹) every five minutes of the sample in the lower glass cell. After one hour the photolysis beam was allowed to pass through the upper glass cell for three hours. As the photolysis beam was passing through the sample, the photolysis reactions were monitored by taking a spectrum every five minutes using FTS of the lower glass cell. A spectrum (100 scans with 1 cm⁻¹) was taken every five minutes for three hours.

B.2 Results



Figure B.1. Observed infrared absorption spectra of formaldehyde, methandiol, water, carbon dioxide in the gas-phase at 1 cm^{-1} resolution from 800 cm⁻¹ to 7000 cm⁻¹. The spectrum in the black is the sample prior to exposure to the photolysis beam and the spectrum in the blue is after the sample was exposed to the photolysis beam for three hours. No difference in the spectra was observed

B.3 Summary

A major consequence of this gas-phase water-mediated chemistry is that the conversion of formaldehyde to methanediol will suppress the near-UV photochemistry due to absorbance of formaldehyde electronic states. The major atmospheric sinks for formaldehyde are UV photolysis, oxidation by OH, and dry and wet deposition.[2] Red light initiated chemistry by excitation of the OH vibration overtones in the ground electronic state has been proposed to be significant for oxidized atmospheric species.[3-17] The two alcohol groups in the diol provide an alternative photochemical pathway via overtone excitation of the OH chromophores of the methanediol.[18-20] The OH chromophores of the diol have the ability to undergo red light initiated chemistry by excitation of the OH vibration overtones in the ground electronic state, which has been suggested for other oxidized atmospheric species[3-17]

The theoretical study of by J. S. Francisco, et al.[21] showed methanediol has a sufficiently long lifetime to allow further decomposition reactions. However the barriers to elimination of hydrogen gas to form formic acid and elimination of water to form a carbene are too high to be of significance. The proposed reaction pathways of formaldehyde are shown in Figure B.2. While our photolysis experiments did not provide spectroscopic evidence of formic acid we believe or experiment was limited by the low sensitivity of our FTS and low water concentrations. The presence of excess water molecules has been suggested to catalyze photoreactions due to the formation of hydrogen-bonded complexes.[12, 22] The intermolecular hydrogen bonding in hydrogen-bonded complex elongates the OH bond length, therefore changing the electron density leading to a shallower, more anharmonic potential energy surface. Future photolysis investigations should be performed at higher water concentrations to determine the significance of methanediol light initiated reactions. We suggest using in these experiments with a cavity enhanced techniques, which are significantly more sensitive than FTS.





Figure B.2. Reaction pathway scheme for gas-phase hydrolysis of formaldehyde. Proposed by J. S. Francisco, et al.[21]

B.4 References for Appendix B

- 1. Khoshkhoo, H. and E.R. Nixon, *Infrared and Raman spectra of formaldehyde in argon and nitrogen matrices*. Spectrochimica Acta, 1973. 29A: p. 603-612.
- 2. Stavrakou, T., et al., *Evaluating the performance of pyrogenic and biogenic emission inventories against one decade of space-based formaldehyde columns.* Atmos. Chem. Phys., 2009. 9: p. 1037-1060.
- 3. Plath, K.L., et al., *Fundamental and Overtone Vibrational Spectra of Gas-Phase Pyruvic Acid.* Journal of Physical Chemistry A, 2009. 113: p. 7294-7303.
- 4. Plath, K.L., et al., *Gas-phase vibrational spectra of glyoxylic acid and its gem diol monohydrate. Implications for atmospheric chemistry.* Reaction Kinetics and Catalysis Letters, 2009. 96(2): p. 209-224.
- 5. Takahashi, K., et al., *Dynamics of vibrational overtone excited pyruvic acid in the gas phase: Line broadening through hydrogen-atom chattering*. Journal of Physical Chemistry A, 2008. 112(32): p. 7321-7331.
- 6. Vaida, V., H.G. Kjaergaard, and K.J. Feierabend, *Hydrated complexes: Relevance to atmospheric chemistry and climate.* International Reviews in Physical Chemistry, 2003. 22(1): p. 203-219.
- 7. Hintze, P.E., et al., *Vibrational and electronic spectroscopy of sulfuric acid vapor*. Journal of Physical Chemistry A, 2003. 107(8): p. 1112-1118.
- 8. Havey, D.K., et al., *Experimental and theoretical investigation of vibrational overtones of glycolic acid and its hydrogen bonding interactions with water*. Journal of Physical Chemistry A, 2006. 110(20): p. 6439-6446.
- 9. Miller, Y., R.B. Gerber, and V. Vaida, *Photodissociation yields for vibrationally excited states of sulfuric acid under atmospheric conditions*. Geophysical Research Letters, 2007. 34(16).
- 10. Vaida, V., et al., *Photolysis of sulfuric acid vapor by visible solar radiation*. Science, 2003. 299(5612): p. 1566-1568.
- 11. Vaida, V., Spectroscopy of Photoreactive Systems: Implications for Atmospheric Chemistry. Journal of Physical Chemistry A, 2009. 113(1): p. 5-18.
- 12. Staikova, M., M. Oh, and D.J. Donaldson, *Overtone-induced decarboxylation: A potential sink for atmospheric diacids*. Journal of Physical Chemistry A, 2005. 109(4): p. 597-602.

- 13. Donaldson, D.J., A.F. Tuck, and V. Vaida, *Atmospheric photochemistry via vibrational overtone absorption*. Chemical Reviews, 2003. 103(12): p. 4717-4729.
- 14. Matthews J, S.A., Francisco, J. S., *The importance of weak absorption features in promoting tropospheric radical production.* Proceedings of the National Academy of Sciences of the United States of America, 2005. 102(21): p. 7449-7452.
- 15. Miller, Y., et al., *Photochemical processes induced by vibrational overtone excitations: Dynamics simulations for cis-HONO, trans-HONO, HNO3, and HNO3-H2O.* Journal of Physical Chemistry A, 2006. 110(16): p. 5342-5354.
- 16. Donaldson, D.J., et al., *Atmospheric radical production by excitation of vibrational overtones via absorption of visible light*. Geophysical Research Letters, 1997. 24(21): p. 2651-2654.
- 17. Wennberg, P.O., et al., *Removal of stratospheric 03 by radicals in-situ measurements of OH, HO2, NO, NO2, CLO, and BRO.* Science, 1994. 266(5184): p. 398-404.
- 18. Carbajo, P.G., et al., Ultraviolet Photolysis of HCHO: Absolute HCO Quantum Yield by Direct Detection of the HCO Radical Photoproduct. J. Phys. Chem. A, 2008. 112: p. 12437-12448.
- 19. Pope, F.D., et al., *Photochemistry of formaldehyde under troposhperic conditions*. Faraday Discussions, 2005. 130: p. 59-72.
- 20. Gratien, A., et al., *UV and IR Absorption Cross-sections of HCHO, HCDO, and DCDO.* J. Phys. Chem. A, 2007. 111: p. 11506-11513.
- 21. Francisco, J.S. and I.H. Williams, *Reaction pathways for gas-phase hydrolysis of formyl compounds HXCO (X = H, F, and Cl)*. Journal of the American Chemical Society, 1993. 115: p. 3746-3751.
- 22. Takahashi, K., et al., Vibrational overtone induced elimination reactions within hydrogen-bonded molecular clusters: the dynamics of water catalyzed reactions in CH2FOH center dot(H2O). Physical Chemistry Chemical Physics, 2007. 9(29): p. 3864-3871.

Appendix C: Electrochemical Cell Surveys and Questionnaire

C.1 Electrochemical Cell Pre-Survey



Over the weekend, you and a couple of your friends from CHEM 1131 got together to study and go over some of the material for the upcoming exam. Upon coming across some questions on electrochemistry some of your friends in the group got stuck on the following question.

An electrochemical cell is composed of Zn metal in a 1.0 M ZnSO₄ solution, Cu metal in a 1.0 M Cu(NO₃)₂ solution and a 10 M KNO₃ salt bridge. Find the E°_{cell} for this system.

Half-Reaction	$E^{\circ}_{cell}(V)$
$Cu \rightarrow Cu^{2+} + 2 e^{-}$	- 0.34
$Zn \rightarrow Zn^{2+} + 2e^{-}$	+0.74

Use the diagram below to describe how you would explain to your friends what is happening on a molecular level in each half-cell reaction, at the salt bridge and anode/cathode metal ends and the metal wire connecting the anode and cathode, with as much detail as possible. Write out any chemical reactions, if they apply.



C.2 Electrochemical Cell Post-Survey

Name:

While writing up your Voltaic Electrochemical Cells laboratory report, you noticed that for your measured potential, for compartment I. and V., you recorded 0V, for *Part 3. Concentration Cell Potentials.*

You were given the following information in your laboratory experiment:

Part 3. Concentration Cell Potentials

In addition to cell compartment I from Part 1, prepare the following cell compartments

- V. $\operatorname{Cu} \text{ in } 0.1 \text{ M} \operatorname{Cu} (\operatorname{NO}_3)_2$
- VI. Cu in 0.01 M Cu $(NO_3)_2$
- VII. Cu in 0.001 M Cu (NO₃)₂

Measure and record the potentials and electrode polarities (red or black, cathode or anode) for cells composed of compartment I and each of the other compartments (V, VI and VII)

(The compartment information from Part 1 is as follows)

I. Cu in 1 M Cu (NO₃)₂

In the space below, explain what might have happened during your experiment and how that would result in a 0V measured potential?

Name:

Given the information above, what would you expect for the measured potential be for compartment I. and V.

Half-Reaction	E°_{cell}
$Cu \rightarrow Cu^{2+} + 2 e^{-}$	- 0.34

Before doing any calculations, use the diagram below to describe what you think is happening on a molecular level in each half-cell reaction, at the salt bridge and anode/cathode metal ends and the metal wire connecting the anode and cathode.



C.3 Conceptual questioner (questions 1-2) concerning the salt bridge within an electrochemical cell.


C.4 Conceptual questioner (questions 3 - 7) concerning the salt bridge within an electrochemical cell.



C.5 Laboratory Experiment Spring Semester 2010 Laboratory Exercise 6

VOLTAIC ELECTROCHEMICAL CELLS

OBJECTIVES

- To construct a variety of voltaic cells and measure their cell potentials.
- To investigate the influence of concentration on cell potentials.

INTRODUCTION

Review your text and class notes for background on voltaic cells. This introduction will address how voltaic cells will be made and used in this lab exercise.

A voltaic electrochemical cell consists of two cell compartments that are in electrical contact by means of a salt bridge. The cell potential is measured by attaching wires (leads) to the two electrodes and connecting these wires to a voltmeter. See Figure 1:



In this lab exercise, each cell compartment will consist of a small beaker, partially filled with an aqueous metal solution (e.g., $Cu(NO_3)_2$) and a metal strip (the same metal as in the solution) that serves as the electrode, either the anode or the cathode.

The salt bridge is a glass U-tube filled with 1 M KNO₃ and supporting strips of filter papers (moistened with the KNO₃ solution) at the two ends of the tubes using corks. The U-tube hangs between the two beakers with its ends immersed in the solution.

The voltmeter for this lab exercise is a modified pH meter.

PROCEDURE

NOTES: A strip of lead metal will be one of the electrodes. Wear gloves when handling.

Part 1. Preparation and Set up

- **1.1 Cell compartments:** Clean several 50 or 100 mL beakers. Label each one and place about 10 mL of each of the following solutions:
 - I. Cu in $1.0 \text{ M Cu}(\text{NO}_3)_2$
 - II. Zn in 1.0 M ZnSO₄
 - III. Pb in $1.0 \text{ M Pb}(\text{NO}_3)_2$
 - IV. Fe in 1.0 M FeSO₄

NOTE: Only a small amount of solution is needed, just enough to cover the bottom of your smallest beakers and moisten the filter paper of the salt bridge when it is inserted.

- **1.2 Salt bridge construction:** Based on the description in the introduction and the TAs instructions, construct the salt bridge.
- **1.3 Electrodes:** Copper and iron rods, zinc and lead strips, and carbon rods will be used as electrodes. In order to obtain meaningful cell potentials, it is important that the surfaces of these electrodes are clean. The copper, zinc, lead and iron electrodes can be cleaned with emery cloth or steel wool followed by rinsing the electrodes briefly in 1M HNO₃ and then in distilled water. The carbon rods can be cleaned by brief immersion in 1M H₂SO₄, followed by a thorough rinsing with distilled water. The carbon rods should be kept in distilled water between experiments.

CAUTION: nitric and sulfuric acids are severe skin irritants. If you spill any on your skin, immediately wash the affected area with plenty of water.

1.4 Voltmeter: Connect the electrode leads to the coaxial plug on the back of the voltmeter (pH meter). After turning on the voltmeter, press mode twice, so that the display shows "mV" in the upper left-hand corner. When the two leads are touched together, the display should read "0mV".

Part 2. Measuring Standard Cells Potentials

Use cell compartments I and II ($Cu(NO_3)_3$ and $ZnSO_4$). Insert the corresponding metal rod or strip into each beaker. Place the salt bridge over the two beakers; ensure that the ends of the salt bridge are in the solution. Add more solution if necessary. Attach the voltmeter leads to the metal

with alligator clips so that a positive cell potential is read; if the potential is negative, switch the leads. For this cell, the copper electrode is the cathode (positive) and the zinc electrode is the anode (negative). Record the color of the lead (red or black) going to copper and going to zinc; based on this association between lead color and electrode type, you will be able in subsequent cell measurements to identify the cathode and the anode for the cell.

When the cell potential is measured and recorded, remove the salt bridge, rinse the ends with distilled water and shake off the excess. Do this after each measurement. If you notice a precipitate in a half cell, it is caused by contamination from an inadequately rinsed salt bridge.

Now measure the cell potential of all other combinations of the four compartments. Connect the leads to the electrodes so that the cell potential reading is positive indicating a spontaneous redox event. Knowing the association between the color of the lead and the electrode type, you can determine which electrode is the cathode and which is the anode. If the display reads a negative potential, switch the leads to get a positive potential. Record in your notebook which lead (red or black) goes to which metal when the cell potential is positive; identify each metal as either the cathode (+) or the anode (-).

When all combinations of cells have been measured, discard the contents of cells II, III, and IV in the appropriate waste container, retaining compartment I for use in Part 3. Rinse the electrodes with distilled water and dry them with a Kimwipe.

Part 3. Concentration Cell Potentials

In addition to cell compartment I from Part 1, prepare the following cell compartments:

V.	Cu in	0.1	$M Cu(NO_3)_2$
v.	Cum	0.1	$M Cu(MO3)_2$

VI. Cu in 0.01 M Cu(NO₃)₂

VII. Cu in $0.001 \text{ M Cu}(\text{NO}_3)_2$

Measure and record the potentials and electrode polarities (red or black, cathode or anode) for cells composed of compartment I and each of the other compartments (V, VI and VII.)

Retain compartment I for use in Part 4; discard the solutions from cell compartments V, VI and VII. Rinse the electrodes with distilled water and dry them with a Kimwipe.

Part 4. Effect of Concentration on the Cells Containing the Fe³⁺/Fe²⁺ Couple

Prepare the following cell compartments:

- IX. Carbon in a solution containing equal portions of 1.0 M FeSO₄ and 1.0 M FeCl₃
- X. Carbon in a solution containing equal portions of 1.0 M FeSO₄ and **0.1 M** FeCl₃
- XI. Carbon in a solution containing equal portions of **0.1 M** FeSO₄ and 1.0 M FeCl₃

Measure and record the potentials and electrode polarities for cells composed of compartment I and compartments IX, X and XI.

STUDENT ASSIGNMENTS

I. Pre-laboratory Preparation

Prior to attending the laboratory and recitation period, complete the following activities in an organized manner your laboratory notebook. This assignment is due at the beginning of the recitation period.

A. Introductory Statement

In one paragraph, summarize in <u>your own words</u> (not the lab manual's), the purpose, theory and procedure for this laboratory exercise.

B. Pre-laboratory Questions / Activities

- 1. Which electrodes will be used to measure the potential of the Fe^{3+}/Fe^{2+} couple?
- 2. Explain what a concentration cell is. What is the value of E° for a concentration cell containing different concentrations of Ag^{+} in contact with Ag electrodes. Explain your answer.
- 3. Consider a cell Cu(s) | Cu^{2+} , 0.10 M || Cu^{2+} , 0.10 M | Cu(s). What would the cell potential be for this cell?

C. Prepare Data Section for lab

Prior to the start of lab, prepare the data collection section of the notebook, beginning with the next page after the pre-lab questions/activities. Format this section for the collection of data during the lab, using the procedure section of the lab write-up and the Data Collection section below as a guide for the data fields. Note that <u>you will not turn in the empty data pages</u> as part of the prelab (Introductory statement and Pre-lab questions/activities), but the data page(s) must be formatted prior coming to lab.

II. Data Collection

In your laboratory notebook, format the data section so that you can record data during the lab. Leave room in order to compensate for mistakes, multiple trials, and/or additional data that should be recorded during the lab.

Part 2. Standard Cell Potentials

For each of the 6 cells constructed in Part 2, state the color and sign (+ or -) of both the cathode and the anode. Then create a table with the following headers and enter the pertinent data when a positive cell potential was obtained. The first cell is entered as an example.

Cathode: Color of lead: Anode: Color of lead:		Sign: Sign:		
Cell	Cathode	Anode	Cell Potential, mV	
I + II	Cu	Zn	725	

Part 3. Concentration Cell Potentials

Record data from these cells as for Part 2.

Part 4. Effect of Concentration of Fe³⁺/Fe²⁺ Couple Cells

Record data from these cells as for Part 2.

III. Calculations

Begin calculations on the next page after the data section in your laboratory notebook. You must **SHOW ALL WORK** for calculations made in order to obtain a result. The following list will guide your work but other calculations may be necessary in order to substantiate results. Be sure to label all results clearly and always include units.

• Calculated cell potentials

Using the table of standard reduction potentials (in acidic solution) in your textbook, calculate the cell potentials for each of the voltaic cells in Part 2. Compare these calculated cell potentials to the measured values. Explain any differences in sign or magnitude.

• Concentration cell calculations

Use the Nernst equation and concentrations of Cu^{2+} to calculate the cell potentials for the cells that constructed in Part 3 using cell compartment I with each of cell compartments V, VI, and VII. In each case, calculate the percent error between the values you calculate and the cell potential value measured for each cell.

• Graphical analysis of Fe³⁺/Fe²⁺ Cells

The relationship between cell potential and concentration of cell components can be analyzed graphically. The Nernst equation

$$E_{cell} = E^{\circ}_{cell} - (RT/nF) \ln Q = E^{\circ}_{cell} - (0.0592V/n) \log Q$$

can be algebraically rearranged in a straight-line equation form of y = mx + b:

$$E_{cell} = -(0.0592/n) \log Q + E^{\circ}_{cell}$$

where $y = E_{cell}$, m (slope) = -(0.0592/n), x = log(Q), and E °_{cell} is b.

And for the Fe(III)/Fe(II) cell in Part 4 where

$$2 \operatorname{Fe}^{3+} + \operatorname{Cu} \rightarrow 2 \operatorname{Fe}^{2+} + \operatorname{Cu}^{2+}.$$

 $E_{\text{coll}} = -(0.0592 / n) \log ([\text{Fe}^{2+}]^2 / [\text{Fe}^{3+}]^2) + E_{\text{coll}}^\circ$

the exact form of the Nernst equation becomes:

or

$$E_{cell} = -2 (0.0592 / n) \log ([Fe^{2+}] / [Fe^{3+}]) + E^{\circ}_{cell}$$

The factor of 2 comes from the stoichiometry of the balanced equation.

- Make a graph of E_{cell} vs. log([Fe²⁺]/[Fe³⁺]) using the three data points from Part 4 data. Refer to Silberberg, Figure 21.11 and the graphing appendix in this lab manual. Use graphing software to make the plot and determine the equation of the best-fit line.
- From the equation of the best fit line calculate the value of n for the overall reaction and E° for the cell. Hint: The E°_{cell} obtained from the graph is with respect to E° for the oxidation of Cu to Cu²⁺ (-0.34V); therefore, a negative 0.34V must be subtracted from E° cell to get the Fe³⁺ to Fe²⁺ half cell potential referenced to the standard hydrogen electrode (SHE).

IV. Post-Laboratory Assignment

There are no post-lab activities or questions for this lab exercise.

V. Results and Conclusion

Write a paragraph summarizing your results and what you determined during the exercises you participated in. Make sure to discuss your results. Include errors that occurred (human error will not be accepted) as well as interesting or significant implications of the information you obtained.

C.6 Laboratory Experiment Spring Semester 2011 Laboratory Exercise 6

VOLTAIC ELECTROCHEMICAL CELLS

OBJECTIVES

- To construct a variety of voltaic cells and measure their cell potentials.
- To investigate the influence of concentration on cell potentials.

INTRODUCTION

Review your text and class notes for background on voltaic cells. This introduction will address how voltaic cells will be made and used in this lab exercise.

A voltaic electrochemical cell consists of two cell compartments that are in electrical contact by means of a salt bridge. The cell potential is measured by attaching wires (leads) to the two electrodes and connecting these wires to a voltmeter. See Figure 1:



Figure 1: A Voltaic Cell Setup

Source: http://www.uq.edu.au/_School_Science_Lessons/UNChem2b.html

In this lab exercise, each cell compartment will consist of a small beaker, partially filled with an aqueous metal solution (e.g., $Cu(NO_3)_2$) and a metal strip (the same metal as in the solution) that serves as the electrode, either the anode or the cathode.

The salt bridge is a glass U-tube filled with 1 M KNO₃ and supporting strips of filter papers (moistened with the KNO₃ solution) at the two ends of the tubes using corks. The U-tube hangs between the two beakers with its ends immersed in the solution.

The voltmeter for this lab exercise is a modified pH meter.

PROCEDURE

NOTES: A strip of lead metal will be one of the electrodes. Wear gloves when handling.

Part 1. Preparation and Set up

- **1.5 Cell compartments:** Clean several 50 or 100 mL beakers. Label each one and place about 10 mL of each of the following solutions:
 - I. Cu in $1.0 \text{ M Cu}(\text{NO}_3)_2$
 - II. Zn in 1.0 M ZnSO₄
 - III. Pb in $1.0 \text{ M Pb}(\text{NO}_3)_2$
 - IV. Fe in 1.0 M FeSO₄

NOTE: Only a small amount of solution is needed, just enough to cover the bottom of your smallest beakers and moisten the filter paper of the salt bridge when it is inserted.

- **1.6 Salt bridge construction:** Based on the description in the introduction and the TAs instructions, construct the salt bridge.
- **1.7 Electrodes:** Copper and iron rods, zinc and lead strips, and carbon rods will be used as electrodes. In order to obtain meaningful cell potentials, it is important that the surfaces of these electrodes are clean. The copper, zinc, lead and iron electrodes can be cleaned with emery cloth or steel wool followed by rinsing the electrodes briefly in 1M HNO₃ and then in distilled water. The carbon rods can be cleaned by brief immersion in 1M H₂SO₄, followed by a thorough rinsing with distilled water. The carbon rods should be kept in distilled water between experiments.

CAUTION: nitric and sulfuric acids are severe skin irritants. If you spill any on your skin, immediately wash the affected area with plenty of water.

1.8 Voltmeter: Connect the electrode leads to the coaxial plug on the back of the voltmeter (pH meter). After turning on the voltmeter, press mode twice, so that the display shows "mV" in the upper left-hand corner. When the two leads are touched together, the display should read "0mV".

Part 2. Measuring Standard Cells Potentials

Use cell compartments I and II ($Cu(NO_3)_3$ and $ZnSO_4$). Insert the corresponding metal rod or strip into each beaker. Place the salt bridge over the two beakers; ensure that the ends of the salt

bridge are in the solution. Add more solution if necessary. Attach the voltmeter leads to the metal with alligator clips so that a positive cell potential is read; if the potential is negative, switch the leads. For this cell, the copper electrode is the cathode (positive) and the zinc electrode is the anode (negative). Record the color of the lead (red or black) going to copper and going to zinc; based on this association between lead color and electrode type, you will be able in subsequent cell measurements to identify the cathode and the anode for the cell.

When the cell potential is measured and recorded, remove the salt bridge, rinse the ends with distilled water and shake off the excess. Do this after each measurement. If you notice a precipitate in a half cell, it is caused by contamination from an inadequately rinsed salt bridge.

Now measure the cell potential of all other combinations of the four compartments. Connect the leads to the electrodes so that the cell potential reading is positive indicating a spontaneous redox event. Knowing the association between the color of the lead and the electrode type, you can determine which electrode is the cathode and which is the anode. If the display reads a negative potential, switch the leads to get a positive potential. Record in your notebook which lead (red or black) goes to which metal when the cell potential is positive; identify each metal as either the cathode (+) or the anode (-).

When all combinations of cells have been measured, discard the contents of cells II, III, and IV in the appropriate waste container, retaining compartment I for use in Part 3. Rinse the electrodes with distilled water and dry them with a Kimwipe.

Part 3. Concentration Cell Potentials

In addition to cell compartment I from Part 1, prepare the following cell compartments:

V	Cu	in	01	М	$Cu(NO_2)_2$
v .	Cu	111	0.1	1.11	

VI. Cu in $0.01 \text{ M Cu}(\text{NO}_3)_2$

VII. Cu in 0.001 M Cu(NO₃)₂

Measure and record the potentials and electrode polarities (red or black, cathode or anode) for cells composed of compartment I and each of the other compartments (V, VI and VII.)

Retain compartment I for use in Part 4; discard the solutions from cell compartments V, VI and VII. Rinse the electrodes with distilled water and dry them with a Kimwipe.

Part 4. Effect of Concentration on the Cells Containing the Fe³⁺/Fe²⁺ Couple

Prepare the following cell compartments:

- IX. Carbon in a solution containing equal portions of 1.0 M FeSO₄ and 1.0 M FeCl₃
- X. Carbon in a solution containing equal portions of 1.0 M FeSO₄ and **0.1 M** FeCl₃
- XI. Carbon in a solution containing equal portions of **0.1 M** FeSO₄ and 1.0 M FeCl₃

Measure and record the potentials and electrode polarities for cells composed of compartment I and compartments IX, X and XI.

STUDENT ASSIGNMENTS

I. Pre-laboratory Preparation

Prior to attending the laboratory and recitation period, complete the following activities in an organized manner your laboratory notebook. This assignment is due at the beginning of the recitation period.

A. Introductory Statement

In one paragraph, summarize in <u>your own words</u> (not the lab manual's), the purpose, theory and procedure for this laboratory exercise.

B. Pre-laboratory Questions / Activities

- 1. Which electrodes will be used to measure the potential of the Fe^{3+}/Fe^{2+} couple?
- 2. Explain what a concentration cell is. What is the value of E° for a concentration cell containing different concentrations of Ag^{+} in contact with Ag electrodes. Explain your answer.
- 3. Consider a cell Cu(s) | Cu^{2+} , 0.10 M || Cu^{2+} , 0.10 M | Cu(s). What would the cell potential be for this cell?

C. Prepare Data Section for lab

Prior to the start of lab, prepare the data collection section of the notebook, beginning with the next page after the pre-lab questions/activities. Format this section for the collection of data during the lab, using the procedure section of the lab write-up and the Data Collection section below as a guide for the data fields. Note that <u>you will not turn in the empty data pages</u> as part of the prelab (Introductory statement and Pre-lab questions/activities), but the data page(s) must be formatted prior coming to lab.

II. Data Collection

In your laboratory notebook, format the data section so that you can record data during the lab. Leave room in order to compensate for mistakes, multiple trials, and/or additional data that should be recorded during the lab.

Part 2. Standard Cell Potentials

For each of the 6 cells constructed in Part 2, state the color and sign (+ or -) of both the cathode and the anode. Then create a table with the following headers and enter the pertinent data when a positive cell potential was obtained. The first cell is entered as an example.

Cathode: Color of lead: Anode: Color of lead:		Sign: Sign:		
Cell	Cathode	Anode	Cell Potential, mV	
I + II	Cu	Zn	725	

Part 3. Concentration Cell Potentials

Record data from these cells as for Part 2.

Part 4. Effect of Concentration of Fe³⁺/Fe²⁺ Couple Cells

Record data from these cells as for Part 2.

III. Calculations

Begin calculations on the next page after the data section in your laboratory notebook. You must **SHOW ALL WORK** for calculations made in order to obtain a result. The following list will guide your work but other calculations may be necessary in order to substantiate results. Be sure to label all results clearly and always include units.

• Calculated cell potentials

Using the table of standard reduction potentials (in acidic solution) in your textbook, calculate the cell potentials for each of the voltaic cells in Part 2. Compare these calculated cell potentials to the measured values. Explain any differences in sign or magnitude.

• Concentration cell calculations

Use the Nernst equation and concentrations of Cu^{2+} to calculate the cell potentials for the cells that constructed in Part 3 using cell compartment I with each of cell compartments V, VI, and VII. In each case, calculate the percent error between the values you calculate and the cell potential value measured for each cell.

• Graphical analysis of Fe³⁺/Fe²⁺ Cells

The relationship between cell potential and concentration of cell components can be analyzed graphically. The Nernst equation

$$E_{cell} = E^{\circ}_{cell} - (RT/nF) \ln Q = E^{\circ}_{cell} - (0.0592V/n) \log Q$$

can be algebraically rearranged in a straight-line equation form of y = mx + b:

$$E_{cell} = -(0.0592/n) \log Q + E^{\circ}_{cell}$$

where $y = E_{cell}$, m (slope) = -(0.0592/n), x = log(Q), and E °_{cell} is b.

And for the Fe(III)/Fe(II) cell in Part 4 where

$$2 \operatorname{Fe}^{3+} + \operatorname{Cu} \rightarrow 2 \operatorname{Fe}^{2+} + \operatorname{Cu}^{2+}.$$

 $E_{cell} = -(0.0592 / n) \log ([Fe^{2+}]^2 / [Fe^{3+}]^2) + E_{cell}^{\circ}$

the exact form of the Nernst equation becomes:

or

 $E_{cell} = -2 (0.0592 / n) \log ([Fe^{2+}] / [Fe^{3+}]) + E^{\circ}_{cell}$

The factor of 2 comes from the stoichiometry of the balanced equation.

- Make a graph of E_{cell} vs. log([Fe²⁺]/[Fe³⁺]) using the three data points from Part 4 data. Refer to Silberberg, Figure 21.11 and the graphing appendix in this lab manual. Use graphing software to make the plot and determine the equation of the best-fit line.
- From the equation of the best fit line calculate the value of n for the overall reaction and E° for the cell. Hint: The E°_{cell} obtained from the graph is with respect to E° for the oxidation of Cu to Cu²⁺ (-0.34V); therefore, a negative 0.34V must be subtracted from E° cell to get the Fe³⁺ to Fe²⁺ half cell potential referenced to the standard hydrogen electrode (SHE).

IV. Post-Laboratory Assignment

There are no post-lab activities or questions for this lab exercise.

V. Results and Conclusion

Write a paragraph summarizing your results and what you determined during the exercises you participated in. Make sure to discuss your results. Include errors that occurred (human error will not be accepted) as well as interesting or significant implications of the information you obtained.

Appendix D: Transforming Upper-Division Physical Chemistry Teaching Based on Education Research

D.1 Summary

Research in science education has helped to identify the key difficulties that students encounter when learning quantum mechanics. These difficulties show up at both the undergraduate [1-11]and graduate[12] level. Most of this research has involved observations of physics students. Since physics and chemistry student typically have different backgrounds in mathematics, as well as different problem-solving skills, the insights developed in these studies may not be directly applicable to chemistry students. The overall goal of this project was to create new pedagogical tools for use in the classroom, and to create instruments to assess the effect of these new pedagogical tools on student learning in an upper division physical chemistry course. The project was carried out in three stages. First, learning goals were defined for the course. Next, the instrument was developed and used to measure the impact of the changes made to the course. Finally, the results of the assessment were used as feedback to further improve student learning. This appendix focuses on the development of the pre- and post-quantum mechanics concept survey.

The quantum mechanics concept surveys were adapted from an instrument that had been developed for an upper-division physics course. Two surveys were given to students, one at the beginning of the course and one at the end; these are included in appendices E.2 and E.3, respectively. At the University of Colorado, the quantum mechanics is taught in the second semester of a two-semester Physical Chemistry sequence. The "pre-survey" was administered at the beginning of the first lecture, in order to measure the knowledge of students coming into the course. This survey was divided into three parts. The first part (questions 1 - 8) was focused on mathematical manipulations and dimensional analysis. This portion of the survey was developed to give the instructor insight into the students' mathematical ability. The second part of the presurvey (questions 9 - 15) covered concepts that the students may have been exposed to in their previous classes, such as general chemistry or introductory physics courses. The third part of the pre-survey (questions 16 - 20) was intended to measure the attitudes and beliefs that students coming into the course had about quantum mechanics and its applications.

The "post-survey" was administered at the beginning of the final lecture of the same course. It was intended to measure the knowledge gained by students as a consequence of completing the course. This survey was also divided into three parts. The first part (questions 1 and 2) was focused on dimensional analysis. The second part (questions 3 - 14) was devoted to concepts that had been covered in the course, with an emphasis on quantum mechanics. Some of the questions in this section of the post-survey were the same as the questions in the pre-survey, while others were new. By asking students the same questions in the pre- and post-survey we were able to measure if student conceptual understanding improved as a consequence of completing the course. The new questions in the post-survey were intended to measure the extent to which students were able to understand new concepts introduced in the course itself. The third part of the post-survey (questions 15 - 19) was intended to measure the extent to which student attitudes and beliefs toward quantum mechanics and its application had changed after completing the course.

D.2 Mathematics and Quantum Mechanics Pre Conceptual Survey

Mathematics and Quantum Mechanics Pre Conceptual Survey for use in Physical Chemistry II Your performance on this exam will not affect your grade. Your professor will not see your individual score on this exam, only the aggregate scores of the class as a whole. Note that some questions may deal with topics that have not been explicitly covered in your class. Don't worry about this; just do your best to figure out the answer based on what you know. Mark all answers on your sheet. Please answer all questions. Your answers should reflect what you personally think. Plan to finish the 20 questions in 30 minutes. Thank you!

1. A complex number z is a number of the form z = x + iy, where $i = \sqrt{-1}$. Which of the following statements are false. A. ... x is a real number and y is a imaginary number. B. ... if $y \neq 0$, then z is an imaginary number. C. ... if x = 0 and $y \neq 0$ then z is a imaginary number. D. ... real and imaginary numbers are special cases of complex numbers. E. ... the complex conjugate of z is given by $z^* = x - iy$. 2. Which of the following statements in the context of vector algebra is false, where A, B are vectors and *m*, *n* are scalars. A. $\dots \mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A}$ B. ... A + (B + C) = (A + B) + CC. ... *m***A** ≠ **A***m* D. ... $m(n\mathbf{A}) = (mn)\mathbf{A}$ E. ... $(m + n)\mathbf{A} = m\mathbf{A} + n\mathbf{A}$ 3. Which of the following statements in the context of the dot product or scalar product are **false**, where **A**, **B**, **C** are vectors and *m* is a scalar. A. ... $\mathbf{A} \cdot \mathbf{B} = \mathbf{B} \cdot \mathbf{A}$, and the result of the dot product is a vector. B. ... $\mathbf{A} \cdot (\mathbf{B} + \mathbf{C}) = \mathbf{A} \cdot \mathbf{B} + \mathbf{A} \cdot \mathbf{C}$ C. ... $m(\mathbf{A} \cdot \mathbf{B}) = (m \mathbf{A}) \cdot \mathbf{B} = \mathbf{A} \cdot (m\mathbf{B}) = (\mathbf{A} \cdot \mathbf{B})m$ D. ... if $\mathbf{A} \cdot \mathbf{B} = 0$ and \mathbf{A} and \mathbf{B} are not null vectors, then \mathbf{A} and \mathbf{B} are parallel. 4. Which of the following statements regarding matrix addition and scalar multplication is **false**, where A, B are $m \times n$ matrices. A. ... the matrix -A is called the negative of the matrix A; -A = (-1)A. B. ... the matrix A - B is called the difference of A and B; A - B = A + (-B)C. ... the sum of matrixes with different sizes in defined as A + B. D. ... the product of the matrix A by a scalar k, written kA, is the matrix obtained by multiplying each element of A by k.

5. $\hat{D} = \frac{d}{dx}$ is an example of an operator. Which of the following statements about operators are <u>false</u>, where \hat{A} , \hat{B} are operators

- A. ... a operator is a rule that transforms a given function into another function.
- B. ... the sum two linear operators is defined by $(\hat{A} + \hat{B})f(x) = \hat{A}f(x) + \hat{B}f(x)$.
- C. ... $\hat{A}\hat{B} = \hat{B}\hat{A}$
- D. ... the product of two operators is defined by $\hat{A}\hat{B}f(x) = \hat{A}[\hat{B}f(x)]$.
- E. ... the commutator of two operators is defined by $[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} \hat{B}\hat{A}$.
- F. ... if $\hat{A}\hat{B} = \hat{B}\hat{A}$ and as a consequence $[\hat{A},\hat{B}] = 0$, we say that \hat{A} and \hat{B} do not commute.
- 6. Which of the following functions satisfies the differential eqaution $a \frac{\partial f}{\partial x} + b = 0$.

A.
$$f = \frac{-be^{x}}{a}$$

B.
$$f = -bx \ln(a)$$

C.
$$f = \frac{-xb}{a}$$

D.
$$f = b(\log_{a} x)$$

E.
$$f = \frac{e^{-bx}}{ab}$$

- 7. A typical radius of isolated neutral atoms typically ranges between ...
 - A. $0.3 3 \text{ cm}^{-1}$ B. 0.3 - 3 ÅC. 0.3 - 3 pmD. 0.3 - 3 fm
- 8. Kinetic energy has dimensions of ...
 - A. ... joules
 - B. ... kilograms times meters squared per second squared
 - C. ... mass times length squared per time squared
 - D. ... cm⁻¹







18. You can find examples of implications of quantum mechanics in your everyday life.

- A. 5 ... strongly agree.
- B. 4
 C. 3
 D. 2
 E. 1
- F. 0 ... strongly disagree.

19. Quantum mechanics is used in the interpretation of spectrocopic results.

- A. 5 ... strongly agree.
- B. 4 C. 3
- D. 2
- E. 1
- F. 0 ... strongly disagree.

20. I am interested in quantum mechanics and its applications.

- A. 5 ... strongly agree.
- B. 4
- C. 3 D. 2
- E. 1
- F. 0 ... strongly disagree.

D.3	Mathematics and Quantum Mechanics Post Conceptual Survey

Mathematics and Quantum Mechanics Post Conceptual Survey

for use in Physical Chemistry II

Your performance on this exam will <u>not</u> affect your grade. Your professor will not see your individual score on this exam, only the aggregate scores of the class as a whole.

Note that some questions may deal with topics that have not been explicitly covered in your class. Don't worry about this; answer all questions to the best of your ability.

Mark all answers on your sheet.

Please answer all questions.

Your answers should reflect what you personally think.

Plan to finish the 19 questions in 30 minutes.

Thank you!

1. A typical radius of isolated neutral atoms typically ranges between ...

- A. 0.3 3 cm⁻¹
- B. 0.3 3 Å
- C. 0.3 3 pm
- D. 0.3 3 fm
- 2. Kinetic energy has dimensions of ...
 - A. ... joules
 - B. ... kiolgrams times meters squared per second squared
 - C. ... mass times length squared per time squared
 - D. ... cm⁻¹
- 3. The diagram at right shows the electronic energy levels in an atom with an electron at energy level E_m . When this electron moves from energy level E_m to E_n , light is emitted. The greater the energy difference between the electronic energy levels E_m and E_n ...



- A. ...the more photons emitted.
- B. ...the brighter (higher intensity) the light emitted.
- C. ...the longer the wavelength (the more red) of the light emitted.
- D. ...the shorter the wavelength (the more blue) of the light emitted.
- E. More than one of the above answers is correct.
- 4. The electron in a hydrogen atom is in its ground state. You measure the distance of the electron from the nucleus. What will be the result of this measurement?
 - A. You will measure the distance to be the Bohr radius.
 - B. You could measure any distance between zero and infinity with equal probability.
 - C. You are most likely to measure the distance to be the Bohr radius, but there is a range of other distances that you could possibly measure.
 - D. There is an equal probability of finding the electron at any distance within a range from a little bit less than the Bohr radius to a little bit more than the Bohr radius.
- 5. True or False: In the absence of external forces, electrons move along sinusoidal paths.
 - A. True
 - B. False









16. Quantum mechanics allows for the description/prediction of molecular structure and behavior of molecules. A. 5 ... strongly agree. B. 4 C. 3 D. 2 E. 1 F. 0 ... strongly disagree. 17. You can find examples of implications of quantum mechanics in your everyday life. A. 5 ... strongly agree. B. 4 C. 3 D. 2 E. 1 F. 0 ... strongly disagree. 18. Quantum mechanics is used in the interpretation of spectrocopic results. A. 5 ... strongly agree. B. 4 C. 3 D. 2 E. 1 F. 0 ... strongly disagree. 19. I am interested in quantum mechanics and its applications. A. 5 ... strongly agree. B. 4 C. 3 D. 2 E. 1 F. 0 ... strongly disagree

D.4 References for Appendix D

- 1. Ambrose, B.S. A repeat performance? Challenges in developing a robust conceptual understanding in quantum mechanics. in Physical Education Research Conference Proceedings 2005.
- 2. Ambrose, B.S. *Investigation of student understanding of the wave-like properties of light and matter.* . 1999. University of Washington.
- 3. Bao, L., Dynamics of student modeling: A theory, algorithms, and application to quantum mechanics. 1999: University of Maryland.
- 4. Morgan, J.T. and M.C. Wittman. *Examining the evolution of student ideas about quantum tunneling.* in *Physics Education Research Conference Proceedings.* 2006.
- 5. Steinberg, R.N., G.E. Oberem, and L.C. McDermott, *Development of computer-based tutorial on the photoelectric effect.* . American Journal of Physics, 1996. **64**: p. 1370-1379.
- 6. Steinberg, R.N. and G.E. Oberem, *Research-based instructional software in modern physics*. Journal of Computational Math and Science Teaching, 2000. **19**: p. 115-136.
- 7. Wittmann, M.C., J.T. Morgan, and L. Bao, *Addressing student models of energy loss in quantum tunneling*. European Journal of Physics, 2005. **26**: p. 939-950.
- 8. Wittmann, M.C., R.N. Steinberg, and E.F. Redish, *Investigating student understanding of quantum physics: Spontaneous models of conductivity.* . American Journal of Physics, 2002. **70**: p. 218-226.
- 9. McKagan, S.B. and C.E. Wieman. *Exploring student understanding of energy through the Quantum Mechanics Conceptual Survey*. in *Physics Education Research Conference Proceedings*. 2006.
- 10. Singh, C., *Student understanding of quantum mechanics*. American Journal of Physics, 2001. **69**: p. 885-895.
- 11. Bao, S.H. and L. Bao. *Student difficulties in understanding probability in quantum mechanics.* in *Physics Education Research Conference Proceedings* 2005.
- 12. Snigh, C. Assessing and improving student understanding of quantum mechanics. in *Physics Education Research Conference Proceedings* 2006.