Investigation of the Surface Properties of Aqueous Solutions

by

Anthony Melchiore Rizzuto

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Richard J. Saykally, Chair
Professor Ron C. Cohen
Professor Kranthi Mandadapu

Fall 2016
Abstract

Investigation of the Surface Properties of Aqueous Solutions

by

Anthony Melchiore Rizzuto

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Richard J. Saykally, Chair

Understanding the structure and composition of the air-water interfaces is of utmost important to many areas of scientific study. Aqueous interfaces are ubiquitous in nature and as such, are intimately involved in chemical processes ranging from those affecting atmospheric aerosols to those governing cellular structuring. The current state of the atmosphere in relation to climate change is of utmost importance, and surface sensitive spectroscopies are only now beginning to shed light on the chemical mechanisms involved. An understanding of how ions adsorb to the water surface will be invaluable in predicting and combatting the environmental chemistry which is central to climate change. Despite the importance of the air-water interface, it remains incompletely understood – particularly in the case of those solutions which contain ions and/or biomolecules – due to the experimental challenges involved in probing it. However, recent experimental and theoretical results have established the existence of certain anions that are preferentially adsorbed to the air-water interface. In this dissertation, I discuss my development of a broadband deep-UV sum frequency generation (DUV-SFG) spectroscopy experiment which was used to explicitly measure the adsorption of ions at the air-water interface. I also use a Raman thermometry experiment that, while it is not a surface specific probe, is a surface sensitive probe and so interfacial information can be drawn from those experiments.

In Chapter 2 I describe broadband DUV-SFG studies of the aqueous iodide ion wherein the first full interfacial charge-transfer-to-solvent (CTTS) spectrum of an ion was measured. Interestingly, the spectrum is redshifted by ~8 nm relative to the bulk spectrum as well as significant line narrowing – 17% for the $J = 1/2$ peak and 66% for the $J = 3/2$ peak. These results may indicate very interesting dynamics at the air-water interface as well as reporting on the hydration structure of those ions at the water surface.

A recent publication indicated that sodium nitrite adsorbs strongly to the interface as a contact ion pair, wherein the Gibbs free energy of adsorption to the air-water interface was found to be -17.8 kJ/mol. In Chapter 3 I describe broadband DUV-SFG studies on the aqueous sodium nitrite system in an attempt to confirm or deny the contact ion pairing hypothesis. It was found that despite elaborate attempts to purify the salt prior to studying it in solution, there was always a significant degree of hydrocarbon contamination. This contamination
likely resulted in the previous study’s misinterpretation of large SHG intensity as nitrite adsorption to the air-water interface. Interestingly, the broadband SFG experiment was found to be a good method for confirming sample purity by examining the nonresonant signal collected.

Clearly the development of nonlinear optical spectroscopies has greatly advanced the field of interfacial science, but there is still much to be learned. In Chapter 4 I describe what I feel are the most important future steps toward furthering our understanding of interfaces. I have outlined several experimental techniques that need to be developed or refined, as well as indicated the next steps for theoreticians. This chapter does not encompass all of what can or should be done, but it is a good starting point.

Nonlinear optical spectroscopies are incredibly powerful due to their interfacial specificity, but they are also quite difficult to utilize because they are naturally a low signal method and are very susceptible to contamination. In Chapter 5 I describe the use of Raman thermometry to study the evaporation rate of water from aqueous HCl droplets. By definition, evaporation is a process that occurs at the interface, and so despite Raman spectroscopy not being a surface specific probe, this experimental technique allows us to draw conclusions about interfacial properties. The kinetics and energetics of cloud droplet and aerosol formation in the atmosphere are highly governed by the evaporation and condensation rates of water, yet the magnitude and mechanism of evaporation remains incompletely characterized. Of particular import (and controversy) is the nature of interfacial water pH and its effect on the evaporation rate and environmental reactivity. Raman thermometry measurements of freely evaporating micro-droplets were used to determine evaporation coefficients ($\gamma$) for two different hydrochloric acid solutions, both which result in a significant deviation from $\gamma_{\text{water}}$. With a 95% confidence level, it is found that the evaporation coefficient for 1.0 M HCl is $0.24 \pm 0.04$ -- a ~60% decrease relative to pure water, and for 0.1 M HCl is $0.91 \pm 0.08$ -- a ~45% increase relative to pure water. These results suggest a large perturbation in the surface structure induced by hydronium at the water surface.
For Kelly
# Table of Contents

## Chapter 1: Introduction

1.1 Salts and the air-water interface  
1.2 Nonlinear optical spectroscopy  
1.3 References  

## Chapter 2: Broadband deep UV spectra of interfacial aqueous iodide

2.1 Introduction  
2.2 Experimental methods  
2.3 Results and discussion  
2.4 References  

## Chapter 3: Broadband spectra of nitrite salts at the air-water interface

3.1 Introduction  
3.2 Experimental methods  
3.3 Results and discussion  
3.4 Conclusions  
3.5 References  

## Chapter 4: Future directions in interfacial spectroscopy

4.1 Introduction  
4.2 Experimental efforts  
4.3 Computational efforts  
4.4 References  

## Chapter 5: Raman thermometry measurements of aqueous HCl droplets and the effect of pH on the evaporation coefficient

5.1 Introduction  
5.2 Experimental methods  
5.3 Results and discussion  
5.4 Conclusions  
5.5 References
Acknowledgements

First and foremost, I would like to thank Rich. He is exactly what I was looking for in and advisor when I began my graduate school career – he has been doing this for a long time and yet his passion and enthusiasm never wanes. He has passed that enthusiasm for science along to me, and he has given me the tools to pass it on to my own students in the future. He is a true mentor and friend.

Next I would like to thank the Saykally group. The group has changed a lot over the years, but every one of them helped me along this journey. Ali for introducing me to the obnoxious amount of optics to be used in a laser experiment, Jacob for being the only other person in the entire department who enjoys watching baseball, the rest of the Femto group for commiserating (and sometimes even celebrating) with me throughout the years, Royce for putting up with my computer technology ignorance, and Will and Michael for taking me away from the frustrations of the lab and to the frustrations of the golf course.

I would like to thank my friends and family, who truly are one and the same. Particularly The group who spent long nights at Roosevelt doing quantum homework and helping each other study for qualifying exams. I would not have made it past the first year here if it weren’t for Anna, Attar, Neel, Karla, Cooper, Frances, Buyanin (who does not actually suck by the way), and so many others. Thank you all. To my parents who supported me my entire life, and even pretended to be interested when they asked the obligatory, “Tell me about your research.”

Thank you to Karl Sienerth who has remained a mentor and friend to me since my time at Elon – especially considering the amount of times I’ve hit him with a racquetball. Sorry Karl.

A special thank you to the Molins, the finest in-laws a man could ask for. Thank you for welcoming me into your home and letting me marry your daughter.

Last of all, I would like to thank my wonderful wife, Kelly. You are nothing less than an inspiration to me. Thank you for all that you do (and for putting up with my graduate student salary for so long). We spent three long years apart, but darling, you were worth the wait.
1.1 Salts and the air-water interface:

Water is the most important substance on the planet. The famed complexity of water chemistry emanates from the unusually strong tetrahedral hydrogen bonding structure,\(^1\) and its ubiquitous nature has motivated investigation by scientific communities ranging from mathematicians to ecologists. While water is interesting in its own right, of particular import is the behavior of aqueous solutions. More specifically, the interfaces formed by aqueous solutions are of immense interest in many fields: in atmospheric chemistry, wherein cloud nucleation is governed by aerosol particles in the air;\(^2\)–\(^8\) in biology, wherein protein solvation and stability is powerfully affected by the Hofmeister series of ions;\(^9\)–\(^12\) in energy sciences and electrochemistry, wherein contact of water and ions at metal surfaces govern process efficiencies;\(^13\),\(^14\)– truly the importance of aqueous interfaces navigates across many different scientific fields.

For many years, it has been assumed that inorganic ions were repelled from the air-water interface. This was partially explained by Onsager and Samaras,\(^15\) who used the method of images\(^16\) to model ions as point charges and the interface as an intersection of two continuous dielectrics. Due to the necessary boundary conditions in this model, there must exist an image charge exactly equidistant from the phase boundary as the real charge. If the real charge exists in a medium with a dielectric constant smaller than the second medium, the image charge will have the opposite sign as the real charge resulting in image charge attraction. However, if the real charge exists in the higher dielectric medium, as is the case for the air-water interface, the image charge will be of the same sign as the real charge resulting in image charge repulsion:

\[
Z_{\text{image}} = Z_{\text{real}} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \tag{1}
\]

Thus, an image force is formed that in the case of the air-water interface, repels ions back into the bulk as shown in Figure 1.

The conclusions of Onsager and Samaras were supported by surface tension measurements, wherein the water surface tension increased with salt concentration.\(^17\)–\(^19\) This indicated a depletion of salt ions from the air-water interface, as indicated by the Gibbs adsorption equation:

\[
\Gamma = -\frac{1}{RT} \left( \frac{\delta \gamma}{\delta \ln C} \right) \tag{2}
\]

Here \(\Gamma\) is the surface excess of the solute, \(C\) is the bulk concentration of the solute, and \(\gamma\) is the surface tension of the solution. The Gibbs adsorption equation predicts a linear increase in surface tension with increasing bulk salt concentration. Interestingly, Jones and Ray\(^20\)–\(^23\) discovered 13 salts that actually exhibit a surface tension minimum near 1 mM
concentrations, a result that is in opposition to that of Onsager and Samaras and is now called the "Jones-Ray effect".

The Jones-Ray effect, in combination with numerous atmospheric chemistry experiments, sparked a reevaluation of the phenomenon of selective ion adsorption to the air-water interface.\textsuperscript{24–29} The past few decades have witnessed significant advances in surface sensitive spectroscopies as well as computational models. Two of the most prevalent surface sensitive spectroscopic methods are vibrational sum frequency generation (VSFG) and second harmonic generation (SHG) – both second-order nonlinear optical processes that are inherently surface specific.

Since the mid-1980s, VSFG has been known to be a valuable surface specific technique.\textsuperscript{30,31} Specifically, it can be used as an indirect probe of aqueous solution surfaces by probing the interfacial vibrations of water as a function of increased salt concentration. In 2004 two important studies were conducted – the first being a study by Liu et al,\textsuperscript{32} who studied the halide series ranging from fluoride to iodide. They determined that both bromide and iodide exhibit enhanced concentrations at the air-water interface relative to their bulk concentrations, while chloride and fluoride exhibit no such effects. The second study, by Raymond et al,\textsuperscript{33} studied the same system but came to very different conclusions – namely, that fluoride is a “structure maker” compared to the “structure breakers,” chloride, bromide, and iodide. Their report concludes that the hydrogen bonding structure of water is impacted greatly by the larger halides, breaking the centrosymmetry of the bulk and effectively changing the second order VSFG response without actually necessitating interfacial ion enhancement.

Because VSFG is an indirect probe of the solute – water is being probed rather than the ions – the use of SHG to study aqueous interfaces became widely used around the same
SHG typically utilizes the charge-transfer-to-solvent (CTTS) transitions exhibited by all anions in aqueous solutions, thus those studies directly probe the ions themselves, rather than the surrounding water structure. In 2004, Petersen et al. confirmed surface enhancement of iodide in the millimolar regime supporting the surface tension observation by Jones and Ray. Additionally, Petersen et al. was able to measure surface enhancement of azide (not a Jones-Ray salt) at the molar concentration regime. In an attempt to answer the questions of whether the water surface is acidic or basic, Petersen et al performed a comparative SHG experiment studying hydroiodic acid (HI) and two alkali iodides (NaI and KI). They were able to determine that hydronium ions exist in much higher densities near the liquid surface than do the alkali ions, supporting the idea of an acidic interface. In keeping with the image charge repulsion model, it is largely assumed that only singly charged ions will adsorb to the air-water interface. In 2005, Petersen et al studied the enhancement of ferrocyanide anions and found that while those ions are not surface active at high concentrations, there is a strong attraction in the millimolar concentration range indicating that the image charge model does not fully describe the mechanism behind selective ion adsorption. Further studies that same year examined the adsorption of thiocyanate (SCN⁻) to the air-water interface using SHG in conjunction with MD simulations. That collaboration between Petersen et al and Mucha et al determined that thiocyanate is preferentially adsorbed to the interface because it is a polarizable anion which allowed the ion to overcome the image charge repulsion. Further supporting these findings are computational studies: Jungwirth and Tobias used molecular dynamics (MD) simulations to determine that the surface affinity of halides correlates with ion polarizability. Much of this work was reviewed in detail by Petersen and Saykally in 2006.

Other studies now support the idea of selective ion adsorption to the air-water interface, including an electrospray ionization mass spectrometry experiment that determined a relative surface affinity for several important ions: SCN⁻ > I⁻ > NO₃⁻ > Br⁻. While a complete mechanism remains elusive, it is now clear that many inorganic anions are not excluded from the air-water interface, but rather are preferentially adsorbed. The halide series is a very important one for understanding how ions are adsorbed to the interface, but they are also the simplest case as they are all spherical anions. In 2007, Otten et al studied the nitrate anion (NO₃⁻) and determined that appreciable, albeit small, concentrations of nitrate ions reside in the interfacial region. Onorato et al moved beyond the air-water interface in 2009 and studied thiocyanate adsorption to the dodecanol-water interface – a vastly important interface concerning atmospheric and environmental chemistry. They showed that concentrations up to 4 M exhibited identical free energies of adsorption as at the air-water interface, but at higher concentrations they see evidence for a drastic structural change in the interfacial region itself. Additional studies compared the adsorption of bromide at the air-water and dodecanol-water interfaces where they determined very slight ion enhancement at both interfaces. In an attempt to elucidate the underlying mechanism, Otten et al. performed temperature dependent SHG measurements on the thiocyanate anion. By doing so and fitting to a Langmuir isotherm model, they were not only able to calculate the Gibbs free energy of adsorption (ΔGₘₐₖ), but also they succeeded in separating the entropic and enthalpic contributions. They determine that ion adsorption to the air-water interface is enthalpically favorable, but entropically hindered – a result in stark contrast to most assumptions based on image charge repulsion models. To explain
this, MD simulations were used to show that weakly hydrogen bonded water molecules at the interface are displaced back into the bulk as the ion breaches the interface. Additionally, as the ion breaches the interface it sheds part of its solvation shell, allowing those water molecules to also form stronger interactions with bulk water. For weakly hydrated ions, the energetic loss of hydration shell waters is more than compensated by the reformation of strong bulk water hydrogen bonds, resulting in a favorable enthalpic contribution to $\Delta G_{\text{ads}}$. The entropic hindrance was explained by a suppression of interfacial capillary waves, but it is not significant enough to overcome the enthalpic energetics and cause ion repulsion from the interface. Very interestingly, in 2012 Otten et al studied the nitrite anion ($\text{NO}_2^-$) as a direct comparison to their previous nitrate studies.\textsuperscript{50} Despite being smaller and less polarizable, nitrite was shown to adsorb to the interface 20x more favorably than nitrate. This was explained by a Langmuir adsorption model in which the nitrite ion adsorbed to the interface as a contact ion pair with its counter ion ($\text{Na}^+$).

While traditional SHG spectroscopy is a powerful probe of ions at the air-water interface, it is rather ineffective in producing a meaningful spectrum in that it probes only a single wavelength at a time. For this reason, nearly all spectral information is lost including peak shifts, linewidth narrowing or broadening, and relative intensity variations. To address this, and to be able to produce a complete broadband spectrum of interfacial ions, a new experiment was developed by our group,\textsuperscript{51} building on advances by the Tahara group. Tahara and coworkers modified their existing VSFG experiment such that one pulse is in the visible or IR wavelength range, and the second pulse is a broadband ultrafast continuum ranging several hundred nanometers in spectral bandwidth. This “white light continuum” allowed them to probe and analyze the spectrum of a dye, Nile Blue, as it adsorbed to the air water interface.\textsuperscript{52} Using this technique, they were able to accurately determine intermolecular interactions at the interface by comparing both line shapes and peak locations. They further extended this technique to perform time-resolved experiments on dyes as well as to probe the vibrational dynamics of water at the interface,\textsuperscript{53} however all of the experiments have been limited to the visible and infrared wavelength ranges. Finally, the incorporation of heterodyne sum frequency generation (HD-SFG), developed by Shen and coworkers at Berkeley,\textsuperscript{54} provided the ability to separate out the complex and real components of the SFG signal by creating an interference pattern using a local oscillator. This technique provides a more informative analysis and even gives information on the orientation of ions and molecules at the air-water interface.\textsuperscript{55}

The question of exactly how deep into the bulk the interfacial region protrudes is paramount to understanding the data collected by various surface spectroscopies. MD simulations largely use the Gibbs dividing surface – the point at which the density of water becomes half of its bulk value – as the point where bulk becomes surface. In an attempt to address that question, x-ray photoelectron spectroscopy (XPS) was used to perform depth profiling experiments.\textsuperscript{56} These experiments confirmed a relative concentration enhancement of both bromide and iodide at the water surface, with the more polarizable iodide ion being much more enhanced than bromide. While they were qualitatively able to determine surface enhancement of the halides, they were not able to define a hard limit where bulk and interface interchange.

Ion adsorption to the air-water interface has now become a very active field. Much progress has been made in understanding the mechanism of selective ion adsorption, but a truly complete description remains to be developed. As a result of the work described in
this thesis, broadband deep UV spectra are now becoming possible to obtain, and will provide important new constraints and benchmarks for deducing the detailed behavior of ions at aqueous interfaces including lifetime effects, interfacial orientations, and hydration structure differences relative to bulk.

1.2 Nonlinear optical spectroscopy:

Most surface measurements over the past century have been performed using macroscopic techniques, with the result being used to infer information about the interfacial properties. In essence, those were bulk measurements lacking molecular specificity at the interface. With the advent of high-power, ultrafast lasers, the interfacial science community gained the ability to directly probe the interface using second-order spectroscopies, and with those advances the field has grown tremendously over the past decade. This section aims to describe the nonlinear optical processes that have been so valuable to surface scientists.

When light interacts with matter, it effects an instantaneous induced polarization. For a linear spectroscopy, this induced polarization is directly dependent on the magnitude of the electric field of the applied light source, however, for excitation with powerful laser sources, the material has smaller but significant responses to the higher orders of the electric field. As such, the polarization of a material, $P(t)$, is appropriately described by a power series expansion:

$$P(t) = P^{(1)}(t) + P^{(2)}(t) + P^3(t) + \cdots \quad (3)$$

Here $P^{(1)}(t)$ is the first order polarization of the material, $P^{(2)}(t)$ is the second order polarization, etc. The polarizations can be rewritten in terms of their corresponding molecular susceptibilities, $\chi^{(n)}$, and the magnitude of the electric field, $E$:

$$P(t) = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots \quad (4)$$

The second order molecular susceptibility, $\chi^{(2)}$, involves three electric fields, with three specific polarizations: $j$ and $k$ refer to the polarization of the incident electric fields (i.e. the incident laser pulses) and $i$ refers to the light generated at the frequency of the material response (i.e. the generated SFG beam). Because the response of the material can be different for each polarization component, $\chi^{(2)}_{ijk}$ is a third-rank, 27 element tensor. The higher order components of the polarization exhibit very weak responses, so in order to provide a measurable signal, the magnitude of the applied electric field must be very large. For this reason, ultrafast laser pulses (~100 fs) are utilized to take advantage of their high peak powers (~$10^7$ watts/pulse).

Second-order nonlinear optical processes most generally result from the combination of two ultrafast laser pulses with optical frequencies $\omega_1$ and $\omega_2$. The second order response of the material occurs at either the sum of those frequencies, $\omega_3 = \omega_1 + \omega_2$, or the difference of those frequencies, $\omega_3 = |\omega_1 - \omega_2|$ – former being referred to as sum frequency generation (SFG) and the latter as difference frequency generation (DFG). A specific case of SFG is when the two input frequencies are degenerate (usually coming from the same laser
source), in which case \( \omega_2 = 2\omega_1 \), referred to as second harmonic generation (SHG). This can be explained given the following:

\[
E_T = E_1 \cos(\omega_1 t) + E_2 \cos(\omega_2 t)
\]  

(5)

This equation defines the magnitude of the total electric field incident on a material when two laser pulses are used, as in an SFG experiment. The second order term requires us to square the electric field:

\[
E_T^2 = E_1^2 \cos^2(\omega_1 t) + E_2^2 \cos^2(\omega_2 t) + E_1 E_2 \cos(\omega_1 t)\cos(\omega_2 t)
\]  

(6)

Using a common trigonometry identity:

\[
E_1 E_2 \cos(\omega_1 t)\cos(\omega_2 t) = \frac{E_1 E_2}{2} \{\cos[(\omega_1 + \omega_2)t] + \cos[(\omega_1 - \omega_2)t]\}
\]  

(7)

In this equation, it is clear that two input laser beams generate a polarization oscillating as \( \cos[(\omega_1 + \omega_2)t] \) (SFG) and a polarization oscillating as \( \cos[(\omega_1 - \omega_2)t] \) (DFG). Additionally, this equation shows that the magnitude of the second order signal will be proportional to the electric field of each input laser pulse. As such, increasing the incident intensity of the fundamental beams will increase the SFG signal that is generated:

\[
I_3 \propto |\chi^{(2)}|^2 I_1 I_2
\]  

(8)

Nonlinear optical processes can be resonantly enhanced when the frequency of one input photon, or the sum of the frequencies of two input photons are close to that of an electronic or vibrational molecular transitions frequency. In the case of electronic sum frequency generation (ESFG), the sum of the two photons is tuned to be resonant with an electronic transition (such as the CTTS transition) the material being studied:

\[
\chi_{ESFG}^{(2)} \propto \frac{1}{\omega_{CTTS} - (\omega_1 + \omega_2) - i\Gamma_{CTTS}}
\]  

(9)

Here, \( \omega_{CTTS} \) is the frequency of the CTTS transition of an arbitrary anion in water, \((\omega_1 + \omega_2)\) is the sum of the two input frequencies from the incident laser pulses, and \( \Gamma_{CTTS} \) is the lifetime of the excited CTTS state. It is clear that the denominator will become small and the molecular susceptibility will become large when \((\omega_1 + \omega_2)\) and \( \omega_{CTTS} \) are similar or identical.

The reasoning behind using second order (or any even order) nonlinear optical processes to study interfaces derives from their inherent surface specificity. Specifically, under the dipole approximation \( \chi^{(2)} \) is only nonzero when there exists broken inversion symmetry. This is shown mathematically using an inversion operator, \( \hat{I} \). In the case of a centrosymmetric environment, we can show that inversion of the nonlinear susceptibility tensor returns the same value.
\[ \hat{\chi}_{ijk}^{(2)} = \tilde{\chi}_{-i-j-k}^{(2)} = \chi_{ijk}^{(2)} \] (10)

Inversion of the electric field changes its sign:

\[ \hat{E}_{jk} = E_{-j-k} = -E_{jk} \] (11)

Similarly, inversion of the polarization also changes its sign:

\[ \hat{\chi}_{ijk}^{(2)} = \tilde{\chi}_{ijk}^{(2)} \] (12)

However, the polarization is the product of the nonlinear susceptibility and the square of the electric field, which results in the following:

\[ \chi_{ijk}^{(2)}(-E_j)(-E_k) = -p_i^{(2)} \] (13)

This then necessitates that \( p_i^{(2)} = -p_i^{(2)} \), which can only be true in a centrosymmetric environment if \( \chi_{ijk}^{(2)} = 0 \). Thus, second order nonlinear optical processes can be used to selectively probe interfaces without any of the complications from a bulk contribution.

In the case of an aqueous sample, the bulk is usually a centrosymmetric environment, while the interface exhibits a plane of broken inversion symmetry. As such, aqueous interfaces can be probed quite explicitly using second order spectroscopies like sum frequency generation.
1.3 References:


(32) Liu, D.; Ma, G.; Levering, L. M.; Allen, H. C. Vibrational Spectroscopy of Aqueous Sodium Halide Solutions and Air–Liquid Interfaces: Observation of Increased


(48) Onorato, R. M.; Otten, D. E.; Saykally, R. J. Measurement of bromide ion affinities for the air/water and dodecanol/water interfaces at molar concentrations by UV


2.1 Introduction:

Conflicting with time-honored textbook models\(^1\)\(^-\)\(^4\), the counterintuitive concentration enhancement of ions at the air-water interface predicted by recent theory\(^5\)\(^-\)\(^8\), has been convincingly demonstrated for several anions, including thiocyanate (SCN\(^-\)), azide (N\(_3\))\(^-\), and several halides by surface-sensitive deep ultraviolet second harmonic generation spectroscopy (DUV-SHG) experiments\(^9\)\(^-\)\(^15\), exploiting the very strong charge-transfer-to-solvent (CTTS) transitions exhibited by anions in aqueous solution (Fig. 1).

![Fig. 1. Bulk charge-transfer-to-solvent (CTTS) absorption spectrum of aqueous iodide. The J = 1/2 peak is centered at 194 nm while the J = 3/2 peak is centered at 225 nm. Extinction coefficients of the J = 1/2 peak and J = 3/2 peak are 0.284 and 0.252, respectively.](image)

More recently, mass spectrometry and ultrafast vibrational sum frequency generation (VSFG) experiments have corroborated these findings\(^17\)\(^,\)\(^18\). The mechanism responsible for this concentration enhancement has been shown to involve a favorable change in enthalpy resulting from the displacement of weakly interacting waters from the interfacial region and from the solvation shell of the weakly hydrated ion into the bulk solution, hindered entropically by the suppression of capillary waves at the interface\(^9\). However, a complete mechanism accounting for counterion effects and surface electric fields remains to be
elaborated\textsuperscript{19–21}. The DUV-SHG measurements of surface vs. bulk ion concentrations were interpreted using simple Langmuir adsorption models to yield testable thermodynamic properties of the system. However, the CTTS spectra of the interfacial anions were themselves incompletely characterized by these pointwise spectroscopic measurements. Details of such spectra would provide another testable property of the system, and would aid in developing a more complete mechanism for interfacial ion adsorption.

2.2 Experimental methods:

Rather than the cumbersome and noisy pointwise spectral measurements employed in the prior work, we have extended the broadband electronic sum frequency generation (ESFG) method of Tahara et al\textsuperscript{22} into the deep ultraviolet in order to more completely measure the interfacial CTTS spectra of anions. Here we report the measurement of the interfacial CTTS spectrum of aqueous iodide using femtosecond broadband DUV-ESFG spectroscopy; the experimental set up is depicted in Figure 2. While both sodium and potassium iodide salts were studied, they produced essentially identical spectra, so only potassium iodide results are reported here.

\textbf{Fig. 2.} Schematic of the experimental design used for the broadband DUV-SFG experiment. The third harmonic generator is shown first with a BBO, followed a calcite delay plate (Δt), a half-wave plate (½ WP), and finally, a third harmonic generating BBO. The fundamental beams reflected off the sample are physically blocked and optically filtered out so as to not saturate the CCD.

The laser system consists of a commercial oscillator (Spectra Physics Mai Tai) seeding a regenerative amplifier (Spectra Physics Spitfire Ace). The output of the amplifier (800 nm, 4.2 mJ/pulse, 1 kHz, 100 fs, horizontal polarization) is split into two separate beams.
The first beam (ω₁) is the frequency tripled fundamental (266 nm). The third harmonic generator consists of a BBO crystal which doubles the 800 nm pulse to 400 nm with ~20% efficiency, a calcite delay plate to reestablish temporal overlap between the fundamental and second harmonic pulses, a half-wave plate to match the polarization, and finally, another BBO crystal is used for mixing the 800 nm fundamental with the 400 nm second harmonic pulses to generate 3 μJ of s-polarized 266 nm light with a bandwidth of 2 nm. The tripled pulse is then purified using optical filters and directed through a variable time delay before being focused at a 57° angle relative to normal onto the sample. The 266 nm spot size on the sample is 36 μm on the major axis and 20 μm on the minor axis. This slightly larger than usual spot size serves two purposes: (1) it mitigates heating and sample damage and (2) it ensures a more complete spatial overlap with the larger white light continuum spot.

The second beam (ω₂) is a white light continuum. White light generation is an optical phenomenon wherein a tightly focused ultrafast laser pulse is propagated through a transparent medium, resulting in a superbroadening of the spectrum. This superbroadening is primarily a result of self-phase modulation of the laser pulse, although other factors, such as self-steepening of the pulse, also contribute. Properties of the generated supercontinuum are governed principally by the medium through which the incident laser pulse is propagated, as well as the laser pulse wavelength and pulse duration 23. In this experiment, water that is constantly flowed through a 5 mm quartz cell serves as the supercontinuum generating medium. An 800 nm, p-polarized beam is focused to a 90 μm beam waist with a 30 mm Rayleigh length. Polarization is conserved throughout the white light continuum generation process, obviating the need for further polarization purification. The long Rayleigh length ensures that the quartz cell will not generate burn spots. After passing through the flow cell, the diverging supercontinuum beam is collimated with a curved mirror before being directed to and focused onto the sample via another curved mirror. Curved mirrors are used to direct the supercontinuum to eliminate chromatic aberrations. The generated white light continuum, which has a spectrum spanning 600 nm to 1400 nm, impinges on the sample at a 50° angle relative to the surface normal with a spot size that is 47 μm on the major axis and 30 μm on the minor axis.

The two incident laser beams are blocked after reflecting from the sample, while the generated s-polarized DUV-SFG signal is collected using a collimating curved mirror and directed into a spectrograph (Acton SpectraPro 300i). Optical filters were used to minimize background light contamination while the spectrum was collected with a CCD (Princeton Instruments, PIXIS). The spectral resolution of this experiment is limited by the bandwidth of the ω₁ pulse (2 nm).

The raw SFG spectrum is normalized with the DUV-SFG output from a reference GaAs sample to account for the intensity of the incident beams and for the inconsistent spectral density of the white light continuum. GaAs was chosen because it has no electronic resonance in the wavelength range being used 24. The actual |χ(2)⟩ interfacial spectrum is then obtained by normalizing the SFG spectrum from the sample to that of the GaAs reference, shown in Fig 3.

All glassware in contact with the sample solution is soaked in a Nochromix/concentrated sulfuric acid solution for 24 hours prior to each experiment. All sample solutions are prepared with ultrapure water (18.2 MΩ cm) from a Millipore system and chemicals of reagent grade (≥99.5%) or better are used. Since the iodide solutions can
degrade when exposed to oxygen or light, new solutions were prepared for each experiment, and each individual sample was exposed to laser light for no longer than 60 seconds.

2.3 Results and Discussion:

Figure 1 shows the bulk CTTS absorption spectrum of aqueous KI. Figure 3a shows the raw (unnormalized) broadband DUV-SFG spectrum of 5 M aqueous potassium iodide at the air-water interface with the background subtracted. The background spectrum was obtained by temporally separating the two fundamental laser beams by 5 ps because such long delays generate no SFG contributions. The spectral window of the raw spectrum is dependent on the time delay between the two beams due to the temporal chirp in the white light continuum. In order to utilize the near-IR portion of the white light spectrum, the time delay was tuned so that $\omega_1$ arrived at the sample ~100 fs earlier than the 800 nm portion ($t_0$) of the supercontinuum. In this way, the measured spectrum overlaps with both the $J = 1/2$ and $J = 3/2$ iodine atom fine structure peaks as shown in Figure 1. Utilizing the near-IR spectrum requires a sacrifice in energy, as white light conversion is less efficient at longer wavelengths$^{23}$. This is compensated by the high power density of the 266 nm $\omega_1$ beam. GaAs was used as a reference spectrum because it has no electronic resonance in the wavelength range being used$^{24}$. The GaAs SFG reference spectrum was measured under identical conditions to that of the aqueous iodide and is shown in Figure 3b. Normalization of the raw iodide spectrum (Fig. 3a) using the GaAs reference spectrum reveals the true $|\chi^{(2)}|$ CTTS spectrum of interfacial aqueous iodide, shown in Figure 3c.
Fig. 3. Broadband DUV-SFG spectra of KI. (A) The unnormalized SFG spectrum of 5M aqueous iodide solution taken with ssp-polarization and generated by mixing 60 μJ of white-light continuum with 3 μJ of 266 nm light. Spectra measured in sps, ppp, and sss polarization configurations all show nearly identical spectra as that shown. The sharp intensity drop-off at 235 nm corresponds to where the accessible SFG wavelengths end due to the lack of white light intensity. (B) The nonresonant SFG reference spectrum of GaAs with ssp-polarization, generated under identical conditions to that in (A). (C) The broadband DUV-SFG spectrum of the CTTS transition for 5M aqueous iodide, normalized to the intensity profile of the nonresonant GaAs reference spectrum in (B).
Despite the relatively short acquisition time (60 sec), the $|\chi^{(2)}|$ spectrum of 5 M aqueous potassium iodide at the air-water interface shown in Figure 3c is of very high quality. For aqueous iodide, two spectral features are expected, the $J = 1/2$ and the $J = 3/2$ peaks$^{12,14,25,26}$, but at first glance it seems that only the $J = 3/2$ feature is observed. However, scaling the spectrum below 220 nm by 20x clearly reveals the presence of the $J = 1/2$ feature. This scaled spectrum, shown in Figure 4, exhibits two distinct peaks corresponding to both of the fine-structure transitions ($J = 1/2$ and $J = 3/2$) observed for the bulk solution. These features comprise the first complete charge-transfer-to-solvent (CTTS) spectrum observed for an interfacial ion.

![Graph showing the scaled spectrum of 5 M aqueous iodide.](image)

**Fig. 4.** Broadband DUV-SFG spectrum of 5 M aqueous iodide, with the $J = 1/2$ feature scaled up by a factor of twenty for easier comparison to the $J = 3/2$ feature. A factor of ~30 increase in the 3/2 to 1/2 intensity ratio relative to the bulk spectrum is apparent. The $J = 1/2$ peak exhibits an 8 nm red-shift (center $\lambda = 201$ nm) relative to the bulk spectrum. The $J = 3/2$ peak exhibits an 8 nm red-shift (center $\lambda = 233$ nm) relative to the bulk spectrum.

The first salient observation apparent in Figure 4 is the significant redshift of both peaks; the $J = 1/2$ peak is red-shifted by 8 nm (0.22 eV) and the $J = 3/2$ peak by 8 nm (0.17 eV) relative to the bulk spectrum. Red-shifted CTTS transitions at the interface have been previously reported for several ions, and attributed to the decreased polarity of the interface$^{14}$. However, due to the very limited spectral information obtained from pointwise DUV-SHG, the absolute shift has never been confirmed. Some studies have also revealed a blue-shift at higher ionic concentrations, and attribute this result to the sizeable electric field generated by the double layer$^{11,12}$. However, Bradforth and Jungwirth$^{27}$ showed that while both the ground state and excited CTTS state of iodide are stabilized at the interface, the CTTS state is stabilized 0.16 eV more, supporting the idea that iodide should exhibit a red-shift at the air-water interface. Our experimental data showing a 0.17 eV red-shift of
the J = 3/2 state agree well with their computational results. Our new measurement slightly revises the previous conclusion of Petersen et al\textsuperscript{12} who produced a pointwise UV-SHG spectrum of several iodide salts at high concentrations (3-5 M) which ostensibly indicated that the J = 3/2 state at the air-water interface is unshifted from bulk (~5.5 eV, 225 nm). Closer inspection of that UV-SHG pointwise spectrum shows that no measurements between 225 nm and 240 nm were taken, meaning that the actual center wavelength of the peak was never determined. The maximum intensity of the J = 1/2 peak observed at 201 nm indeed agrees with the results presented here.

A second defining characteristic of the new spectrum is the line-narrowing of the peaks. Figure 5a shows the J = 1/2 peak, which exhibits a FWHM of 15 nm at the air-water interface compared to 18 nm in bulk solution – a 17% reduction in the bandwidth. A more drastic difference is found for the J = 3/2 peak (Figure 5b) which exhibits a FWHM of only 7.5 nm at the air-water interface, compared to 22 nm in bulk solution – a 66% reduction in the bandwidth.
Fig. 5. Expanded view of Figure 3 with (A) showing the $J = 1/2$ peak. A Gaussian fit overlaid in blue, exhibits a FWHM of $\sim$15 nm and a center wavelength of $\sim$201 nm. (B) Shows the $J = 3/2$ peak. The Gaussian fit overlaid in blue exhibits a FWHM of $\sim$7.5 nm and a center wavelength of $\sim$233 nm.

The narrowing of the linewidth is a striking observation. The peaks fit a Gaussian profile quite well, indicating that inhomogeneous effects dominate the linewidth. The narrowing is likely due to the altered solvent environment the iodide experiences at the interface. When fit to a Voigt profile, only a minor Lorentzian component is observed, so while this may provide some new insight into altered CTTS dynamics at the air-water interface, the effect is likely small. If the narrowing in linewidth is due to homogeneous effects, this would imply a longer interfacial lifetime relative to the bulk. Interestingly, previous work by Sheu and Rossky$^{28}$ addressed an aqueous halide ion following two-photon excitation via nonadiabatic quantum molecular dynamics simulations. They found that the dynamics of the CTTS state at very early times ($<50$ fs) were determined by two relaxation channels: a minor channel involving direct electron detachment to a separated solvent void, and a dominant channel characterized by delayed adiabatic detachment.
through excited electronic states of the ion. They also determined that orbital symmetry plays a key role in the delayed detachment process, i.e. the detachment does not occur until the electron reaches the lowest excited state of the CTTS manifold (J = 3/2). The implication is that the J = 1/2 state has a much shorter lifetime than the J = 3/2 state, which agrees with our present result of a broader J = 1/2 peak. Also, Moskun et al\textsuperscript{25} previously used ultrafast pump-broadband probe spectroscopy to study the photodetachment dynamics of aqueous iodide. They reported the absence of a signature I (^2P_{1/2}) feature following 200 nm photodetachment of I\textsuperscript{-} (aq) and suggested that this could indicate a very fast electronic relaxation (sub 300 fs) of the excited CTTS state. The results reported here favor that hypothesis, as a much faster electronic relaxation from the second CTTS state (J=1/2) would be manifested as a significant broadening of that peak, relative to the first CTTS band (J=3/2), which is qualitatively what we observe.

The drastic change in the relative intensity of the J = 3/2 and J = 1/2 features apparent between the interfacial and bulk CTTS spectra probably involves these factors. In bulk solution, the extinction coefficients are roughly equal\textsuperscript{16}, as reflected in Figure 1, whereas in the interfacial spectrum the J = 3/2 peak is ~30x more intense than the J = 1/2 peak. The differing intensity ratios may be largely attributable to resonant enhancement effects. Because of the large redshift in the interfacial SFG spectrum, the J = 3/2 transition is actually doubly resonant, i.e. the 266 nm beam is resonant with the far wing of the J = 3/2 absorption line, and the sum of the white light frequency and the 266 nm light is broadly resonant with the peak center at 233 nm. In contrast, the 266 nm photons have essentially zero resonant overlap with the J = 1/2 transition at 201 nm, so only the broadband sum frequency light is resonant. While this would appear to generate a negligible contribution to the SFG intensity, the high power density of the $\omega_1$ pulse, viz. $\sim 10^{13}$ photons/pulse at 266 nm, may compensate for the very low extinction coefficient value in the far tail of the J = 3/2 transition. It is also possible that the J = 3/2 CTTS state has a significantly increased Franck-Condon overlap with the ground state, which would result in an enhancement in the peak intensity; finally, we note that large differences in the relaxation times of the final CTTS states in bulk solutions have been postulated\textsuperscript{27}. Further theoretical modeling is required to address these complex issues.
2.4 References:


(16) Fox, M. F.; Hayon, E. Far ultraviolet solution spectroscopy of the iodide ion. *J.


Chapter 3

Broadband UV spectra of nitrite salts at the air-water interface

3.1 Introduction:

The study of selective ion adsorption to the air-water interface has important implications for wide-ranging areas of science, including protein solubility and stability, electrochemistry, cloud formation and irradiation properties, and many more.1–9 The postulation that halide ions exist at the surface of sea salt aerosol particles in high concentration10,11 motivated several computational studies.10,12–16 Those studies were subsequently verified by deep-UV second harmonic generation (DUV-SHG) spectroscopy experiments,17,18 and later by x-ray photoelectron spectroscopy,19 electrospray ionization mass spectrometry,20,21 and further second harmonic and sum frequency generation spectroscopy efforts.22–26 The collective results of those studies have forced a reevaluation of traditional textbook explanations of the general phenomenon of ion adsorption to aqueous interfaces.

While the effect has now been studied extensively, the exact mechanism of selective ion adsorption remains unexplained.22,27 It has been shown that ion adsorption closely follows the Hofmeister effect,28–30 and the importance of polarizability and hydration strength of the ions in question have received much attention.13,31,32 In order to elucidate the thermodynamic properties of the interfacial adsorption process, Otten et al used second harmonic generation spectroscopy to study the adsorption of thiocyanate to the air-water interface as a function of temperature.33 In this way, the Gibbs free energy of adsorption (ΔG_{ads}) of the ion to the interface was able to be separated into its enthalpic and entropic components. They determined the enthalpic contribution to be favorable due to the shedding of weakly hydrating waters and formation of strong water hydrogen bonds, and the entropic contribution to be unfavorable due to the suppression of interfacial capillary waves – a result that was counter to the hypothesis at the time. A principle missing component of the mechanism for selective ion adsorption is the effect of counter-ions. SHG studies take advantage of the very strong, broad ultraviolet charge-transfer-to-solvent (CTTS) transitions exhibited by every anion in water.34 However, simple aqueous cations generally have a closed shell, and so they do not have such intense and easily accessible transitions. As such, they are notoriously difficult to probe directly. To address cation effects, Petersen et al26 studied the adsorption of iodide salts (KI, NaI, and HI) using SHG spectroscopy and observed very minimal differences between the two alkali salts, but evidenced a substantial increase in the hydronium density at the air-water interface.

In 2012, Otten et al used resonant DUV-SHG spectroscopy to study ion adsorption in sodium nitrite solutions.35 They observed an exceptionally large adsorption free energy (ΔG_{ads} = -17.8 kJ/mol) – a value that far exceeds the adsorption free energy of nitrate (ΔG_{ads} ≈ 0 kJ/mol),36 despite nitrate being more polarizable and more weakly hydrated. The authors attributed this dramatic difference to the sodium and nitrite ions adsorbing to the interface as a contact ion pair, and explain the mechanism using a bimolecular Langmuir adsorption model described by the equilibrium expression:
This equilibrium corresponds to a surface concentration \( (N_i) \) expression as a function of bulk concentration:

\[
N_S = \frac{([NO_2^-][Na^+])S_{max}}{[W]K^{-1} + [NO_2^-][Na^+]}
\]

Here \([SNa^+ \cdot NO_2^-]\) is the concentration of the surface sites, \(S\), that are occupied by the contact ion pair, \((Na^+ \cdot NO_2^-)\), and \(S_{max}\) is the maximum number of surface sites available.

The idea of contact ion pairing has been addressed by Collins et al.\(^2,30,37\) concluding that ions with similar free energies of hydration will tend to form contact ion pairs in solution – this is called the "law of matching water affinities," and has since been supported by 2D-IR spectroscopy studies\(^38\) and x-ray spectroscopy\(^39,40\). The idea of a contact ion pair adsorbing strongly to the air-water interface would agree well with the predictions of Onsager and Samaras\(^41\) and their use of the method of images\(^42\) to explain the typical dearth of ions at the liquid-vapor boundary. In this way, rather than a full image charge repulsion – the magnitude of which is proportional to \(\frac{1}{r^2}\) – there would exist something akin to an image dipole repulsion – the magnitude of which is proportional to \(\frac{1}{r^3}\).
Despite the detailed Langmuir modeling, Otten et al’s SHG experiments on NaNO₂ were only conducted at three separate wavelengths (Fig. 1.), as it is far too time intensive to produce extensive pointwise SHG spectra. Because of this limitation, a great deal of information about the mechanism is lost, and it is reasonable to surmise that a more complete spectrum would inform on the nature of contact ion pair formation at the air-water interface. To this end, the present study employs a newly-developed broadband sum frequency generation experiment that is extended from the visible to the deep ultraviolet range⁴³ to examine the electronic spectra of nitrite salts at the air-water interface.

3.2 Experimental methods:

Rather than the cumbersome and noisy pointwise spectral measurements employed in the Otten et al study, we have extended the broadband electronic sum frequency generation (ESFG) method of Tahara et al into the deep ultraviolet in order to more accurately measure
the interfacial spectra of the nitrite ion. The experimental setup is depicted in Figure 2. While both sodium and potassium nitrite salts were studied, they produced essentially identical spectra, so only sodium nitrite results are explicitly reported here.

![Experimental setup diagram](image)

**Fig. 2.** Schematic of the experimental design used for the broadband DUV-SFG experiment. The OPA was used to generate wavelengths ranging from 800 nm to 300 nm, depending on which wavelength range the experiment required. The fundamental beams reflected off the sample were physically blocked and optically filtered out so as to not saturate the CCD.

The laser system consists of a commercial oscillator (Spectra Physics Mai Tai) seeding a regenerative amplifier (Spectra Physics Spitfire Ace). The output of the amplifier (800 nm, 4.2 mJ/pulse, 1 kHz, 100 fs, horizontal polarization) is split into two separate beams. The first beam ($\omega_1$) is directed to an optical parametric amplifier (Spectra Physics TOPAS Prime) wherein the desired $\omega_1$ frequency (800 nm – 300 nm, depending on the experiment) is selected. The energy incident on the sample was controlled using neutral density filters to be ~3 μJ, and the polarization was set to p using a $\lambda/2$ waveplate and an optical polarizer. Depending on the wavelength chosen, the $\omega_1$ beam had a spectral bandwidth of ~4 nm. The pulse was then purified using optical filters and directed through a variable time delay before being focused onto the sample at a 57° angle relative to normal. The $\omega_1$ spot size on the sample was 55 μm on the major axis and 30 μm on the minor axis. This slightly larger than usual spot size serves two purposes: (1) it mitigates heating and sample damage and (2) it ensures a more complete spatial overlap with the larger white light continuum spot.

The second beam ($\omega_2$) is a white light continuum. White light generation is an optical phenomenon wherein a tightly focused ultrafast laser pulse is propagated through a transparent medium, resulting in a superbroadening of the spectrum. This superbroadening
is primarily a result of self-phase modulation of the laser pulse, although other factors, such as self-steepening of the pulse, also contribute. Properties of the generated supercontinuum are governed principally by the medium through which the incident laser pulse is propagated, as well as the laser pulse wavelength and pulse duration. In this experiment, water that is constantly flowed through a 5 mm quartz cell serves as the supercontinuum generating medium. An 800 nm, p-polarized beam is focused to a 90 μm beam waist with a 30 mm Rayleigh length. Polarization is conserved throughout the white light continuum generation process, obviating the need for further polarization purification. The long Rayleigh length ensures that the quartz cell will not generate burn spots. After passing through the flow cell, the diverging supercontinuum beam is collimated with a curved mirror before being directed to and focused onto the sample via another curved mirror. Curved mirrors are used to direct the supercontinuum to eliminate chromatic aberrations. The generated white light continuum, which has a spectrum spanning 600 nm to 1400 nm, impinges on the sample at a 50° angle relative to the surface normal with a spot size that is 47 μm on the major axis and 30 μm on the minor axis.

The two incident laser beams are blocked after reflecting from the sample, while the generated s-polarized SFG signal is collected using a collimating curved mirror and directed into a spectrograph (Acton SpectraPro 300i). Optical filters were used to minimize background light contamination while the spectrum was collected with a CCD (Princeton Instruments, PIXIS). The spectral resolution of this experiment is limited by the bandwidth of the ω1 pulse (4 nm).

The raw SFG spectrum is normalized with the SFG output from a nonresonant reference sample to account for the intensity of the incident beams and for the inconsistent spectral density of the white light continuum. This normalization allows for the actual |χ(2)| interfacial spectrum to be obtained. GaAs is chosen to normalize deep-UV (λ < 300 nm) spectra because it has no electronic resonance in that wavelength range, however, GaAs cannot be used for normalization of the higher-wavelength (λ > 300 nm) UV SFG spectra, because its absorption spectrum is no longer featureless. As such, pure water is used for the normalization of spectra in that region.

All glassware in contact with the sample solution is soaked in a Nochromix/concentrated sulfuric acid solution for 24 hours prior to each experiment. All sample solutions are prepared with ultrapure water (18.2 MΩ cm) from a Millipore system and chemicals of reagent grade (≥99.5%) or better are used. To mitigate photodegradation of the sample, new solutions were prepared for each experiment, and each individual sample was exposed to laser light for no longer than 60 seconds.

3.3 Results and Discussion:

Figure 3 shows the bulk absorption spectrum of aqueous sodium nitrite. There are two clear absorptions, a weak n→π* transition centered at ~360 nm and a strong π→π* transition centered at ~210 nm.
Fig. 3. The bulk UV-vis absorption spectrum of aqueous nitrite as adapted from Strickler et al. The feature at ~350 nm corresponds to an n→π* transition, and the feature at ~210 nm corresponds to a π→π* transition.46

Strikingly, the molar absorptivity of the π→π* transition is two orders of magnitude larger than the n→π* transition; generally, it is more desirable to probe this transition for such low-signal experiments as second order nonlinear spectroscopies. However, this study attempted to probe both wavelength ranges in order to determine the mechanism behind the significant ion adsorption observed by Otten et al.

Figures 4 and 5 show two different broadband SFG spectra for solutions of 2 M NaNO2 – Figure 4 shows the SFG spectrum in the wavelength range corresponding to the π→π* transition that was previously studied by Otten et al, and Figure 5 shows the SFG spectrum in the wavelength range corresponding to the weak n→π* transition.
Fig. 4. Broadband SFG spectrum of 2 M NaNO₂ taken with ppp polarization and generated by mixing 60 μJ of white light continuum with 3 μJ of 357 nm light. This energy range corresponds to the bulk π→π* transition of aqueous nitrite. The inset shows the nonresonant SFG reference spectrum of GaAs with ppp polarization, generated under identical conditions to the aqueous nitrite sample.

The inset in Figure 4 shows the nonresonant SFG signal obtained from GaAs using 357 nm as ω₁ and the white light continuum for ω₂, resulting in accessible SFG wavelengths ranging from ~230-260 nm. GaAs is used as the standard because it has a strong |χ(2)| signal and the absorption spectrum in this region is flat. Notably, the shapes of the nonresonant SFG signal from the GaAs and the nitrite sample are virtually identical, implying that the SFG signal generated from the solution surface is entirely nonresonant, despite the molecular transition supposedly residing in this energy range. These results conflict with those of Otten et al, as they observed a substantially larger SHG intensity at 247 nm than at 255 nm, indicating a significant resonant enhancement effect.
Fig. 5. Broadband SFG spectrum of 2 M NaNO₂ taken with ppp polarization and generated by mixing 60 μJ of white light continuum with 3 μJ of 800 nm light. This energy range corresponds to the bulk n→π* transition of aqueous nitrite. The inset shows the nonresonant SFG reference spectrum of water with ppp polarization, generated under identical conditions to the aqueous nitrite sample.

The spectrum in Figure 5 was obtained by mixing 800 nm (ω₁) with the white light continuum (ω₂) to probe the region ranging from ~350-410 nm. The inset shows the nonresonant SFG signal obtained from pure water – GaAs is not used as the standard for this SFG configuration because its absorption spectrum is no longer featureless around the wavelength range of interest. It is again notable that the shape of the nonresonant water SFG spectrum is identical to that of the spectrum obtained from the nitrite sample, despite the molecular transition that should reside in this energy range. Otten et al did not study the wavelength range of the nitrite n→π* transition, so a direct comparison to SHG is impossible.

It is important to note that the wavelength ranges probed were chosen to be consistent with the molecular transitions of bulk aqueous nitrite, but it has been shown quite convincingly that interfacial spectra exhibit significant deviations from their bulk counterparts. However, this experiment probes over 30 nm (0.622 eV) of spectral bandwidth in the π→π* transition wavelength range (Figure 4) and over 60 nm (0.518 eV) of spectral bandwidth in the n→π* transition wavelength range (Figure 5), and it is unlikely that there are such enormous energetic shifts between bulk and interfacial species.

In order to ascertain the origin of the sizable surface enhancement reported by Otten et al, the effect of the interfacial nitrite spectrum was studied as a function of time exposed to laser light under ambient atmospheric conditions. The results of this study are shown in Figure 6.
Fig. 6. Broadband UV-SFG spectra of 2 M NaNO₂. (A) Spectrum collected with a 10-minute acquisition time. The inset shows the nonresonant SFG reference spectrum of GaAs, generated under identical conditions to the aqueous nitrite sample. (B) Resultant spectrum from averaging five 2-minute acquisitions, each on freshly prepared aqueous nitrite samples.
Figure 6A shows the broadband UV-SFG spectrum of 2 M NaNO\textsubscript{2} collected using a 10-minute acquisition time. Clearly a large nonresonant feature is visible at ~255 nm, which is consistent with the results shown in Figure 4. Figure 6B shows the broadband UV-SFG spectrum obtained by averaging five 2-minute acquisitions, changing out the sample between each individual scan so that the maximum time spent under laser light and in ambient environment is two minutes for each sample. The nonresonant signal, while present, is significantly diminished relative to the 10-minute acquisition spectrum. These results indicate a significant degree of contamination in the samples – a problem that is likely compounded by the impinging laser light and induced photodamage of the contaminant. It is most probable that there is hydrocarbon contamination in the salt prior to preparing the solutions because great care is taken to acid-wash each piece of glassware as well as using ultrapure water for the solvent. It is well known that hydrocarbons will coat the surface of water, which is likely the source of the large nonresonant signal. Additionally, we postulate that the nonresonant signal grows with increased time under laser light due to photolysis of the interfacial hydrocarbons, which can then react with a number of species, including the nearby nitrite anions. Confirmation of the presence of hydrocarbons is given by vibrational sum frequency generation (VSFG) measurements on the nitrite solutions, shown in Figure 7.

Fig. 7. Vibrational SFG spectrum of 6 M NaNO\textsubscript{2} taken with ssp polarization is shown in red. The VSFG spectrum of pure water under identical conditions is shown in black. The sharp features at 2870 cm\textsuperscript{-1} and 2933 cm\textsuperscript{-1}, as well as the weaker feature at 3075 cm\textsuperscript{-1} confirm the presence of hydrocarbons. Figure used with permission from Magnus Johnson.
Shown in black is the VSFG spectrum of pure water. It is a very clean spectrum with the symmetric -OH stretching vibrations present from 3000-3600 cm\(^{-1}\), as well as the dangling interfacial -OH stretch at 3708 cm\(^{-1}\). Shown in red is the VSFG spectrum of 6 M NaNO\(_2\). If there were no hydrocarbons present in the sample, the spectrum would look virtually identical to that of pure water (there would likely be some small spectral shifts as well as intensity differences due to the effect of nitrite ions on the interfacial hydrogen bonding network of water). However, the spectrum looks quite similar to that of an all-trans hydrocarbon chain, with the sharp feature at 2870 cm\(^{-1}\) being due to the CH\(_3\) symmetric stretch and its Fermi resonance at 2933 cm\(^{-1}\). The weak feature at 3075 cm\(^{-1}\) could indicate the presence of an aromatic group, and the lack of a dangling -OH stretch is indicative of full surface coverage of the water by the hydrocarbon contaminants.

3.4 Conclusions:

Measurement of the broadband SFG spectrum of aqueous sodium nitrite (NaNO\(_2\)) was attempted both in the visible range, where there exists an n→π* transition, and in the ultraviolet, where there exists a π→π* transition. A large signal was detected in both of those wavelength ranges, however the broadband signal was determined to be entirely nonresonant, which is consistent with a large degree of hydrocarbon contamination. The invocation of hydrocarbon contamination was supported by temporal broadband SFG studies, and subsequently confirmed by vibrational SFG spectra. Despite closely mimicking the sample preparation reported by Otten et al, we are unable to eliminate the issue of hydrocarbon contamination. It is likely that the large signal obtained by Otten et al is due to the hydrocarbon contamination in their own samples rather than the proposed adsorption of sodium nitrite to the air-water interface as a contact ion pair. Recently, Smith et al\(^{47}\) used MD simulations in conjunction with x-ray absorption spectroscopy on sodium nitrite and sodium nitrate in order to compare ion pairing propensities. They found the hydration properties of the two salts to be very similar, with neither ion exhibiting a detectable propensity for ion pairing. Allen and coworkers performed an extensive study on the effect of salt purity on interfacial spectra,\(^{48}\) and they show that certain salts need to be baked at over 500°C to ensure that all hydrocarbons are eliminated from the sample. Because sodium nitrite melts at 271°C, this is impractical and future studies should consider recrystallization as a method to ensure hydrocarbon-free samples.
3.5 References:


(16) Jungwirth, P.; Tobias, D. J. Molecular structure of salt solutions: A new view of the


Chapter 4

Future directions in interfacial spectroscopy

4.1 Introduction:

The use of second-order nonlinear optical processes has rapidly become the preferred method for selectively probing liquid interfaces due to the symmetry constraints which necessitate $|\chi^{(2)}| = 0$ in centrosymmetric environments (in the dipole approximation).\textsuperscript{1–3} Over the past decade, vibrational sum frequency generation (VSFG)\textsuperscript{4–8} and ultraviolet second harmonic generation (UV-SHG)\textsuperscript{9–11} have been used extensively to probe the surface of aqueous solutions, interfaces between electrodes and electrolytes,\textsuperscript{12} hydrophilic-hydrophobic interfaces,\textsuperscript{13,14} and many more. More recently, broadband SFG experiments have been developed and are being used to measure interfacial spectra in their entirety, rather than just obtaining pointwise estimates.\textsuperscript{15–18} Despite these advances, the properties of many interfaces – especially aqueous interfaces – remain incompletely characterized. This overview describes future efforts that must be explored in order to answer century-old questions about interfaces.

4.2 Experimental efforts:

Charge-transfer-to-solvent (CTTS) transitions are often utilized to study interfacial anions because they are broad and very intense transitions, making them amenable to experiments which naturally suffer from low S/N (e.g. second-order spectroscopies).\textsuperscript{19} Those groups carrying out UV-SHG spectroscopy experiments have largely relied upon CTTS transitions, but due to the complexity of those experiments, usually only a few wavelengths were studied for a given ion.\textsuperscript{20–24} The development of broadband ultraviolet sum frequency generation (UV-SFG) has opened new avenues for the study of ions at the air-water interface, because this method allows one to probe a large wavelength range in a single laser shot, thus eliminating the need for the difficult and time-consuming pointwise measurements used in the past.\textsuperscript{15} Recently, the full CTTS spectrum of interfacial aqueous iodide was reported using this method.\textsuperscript{18} Future studies should concentrate on acquiring full CTTS spectra for the rest of the halide series, as well as for other interesting ions such as thiocyanate (SCN$^-$), azide (N$_3^-$), and perchlorate (ClO$_4^-$). Access to the full interfacial CTTS spectra of ions will provide necessary insight into the hydration environment at the interface due to the intimate relationship between the CTTS state and the solvent environment (density, polarity, etc.) Furthermore, the information gained by understanding peak shifts and line narrowing/broadening can provide information regarding timescales of the lifetime of the interfacial CTTS state – knowledge of which would have profound importance when considering cloud irradiation properties, redox chemistry at hydrophobic interfaces, and many more. Additionally, the broadband SFG method should be extended to include the study of molecular transitions in the near-UV and visible energy ranges in order to further investigate hydration properties of ions at the interface.

Chemical dynamics at interfaces are of paramount importance to numerous chemical processes. In order to investigate surface dynamics, time-resolved SFG and/or SHG should
be employed. Recently, Tahara et al developed this technique and were able to study the photochemical dynamics of the dye, Rhodamine 800.\textsuperscript{25} It will be interesting to expand this time-resolved technique to the deep ultraviolet in order to investigate the ultrafast dynamics of the excited CTTS states of ions at the air water interface. Recent experiments using broadband DUV-SFG indicate possible interesting dynamics of the $J = 1/2$ and $J = 3/2$ CTTS states of aqueous interfacial iodide. The narrowing of both CTTS peaks observed by Rizzuto et al\textsuperscript{26} could be partially attributed to an enhanced – albeit unequally so – lifetime of those CTTS states, but only a time-resolved measurement can fully answer this question. Additionally, the CTTS state is often viewed as a precursor to the formation of a solvated electron.\textsuperscript{27–29} This prototypical anion species is of great interest to the field, particularly regarding its behavior at the air-water interface. The solvated electron has a resonance at ~700 nm, so a time-resolved measurement using a UV pump – visible probe would elucidate the lifetime and dynamical properties of interfacial electrons.

Interfacial water in the vicinity of lipids and proteins plays an integral role in many biological processes, including protein solvation and ion transport.\textsuperscript{30–33} Therefore, molecular-level characterization of the properties of water at those interfaces is of much importance. A valuable method of studying those interactions is two-dimensional spectroscopy. Tahara and coworkers have developed a two-dimensional heterodyne-detected vibrational sum frequency generation (2D HD-VSFG) spectroscopy experiment to study vibrational dynamics at charged and lipid interfaces.\textsuperscript{34,35} Future work should expand this experiment to study ions at those interfaces to directly probe the dynamics of biological processes. In this way, the relationship between the Hofmeister series of ions and selective ion adsorption may be further clarified.

The development of heterodyne-detected sum frequency generation (HD-SFG) has advanced the field immensely.\textsuperscript{36} By utilizing a local oscillator to generate an interference pattern and Fourier transforming the resultant spectrum, the imaginary and real components of the molecular susceptibility, $|\chi^{(2)}|$, can be isolated from one another. The imaginary component can then provide information about both the number density of ions at the interface as well as interfacial orientations. Future broadband HD-SFG studies should be extended to the deep ultraviolet, where the complex phase will give further insight to the mechanism of selective ion adsorption. Of particular interest are aspherical ions such as azide, thiocyanate, nitrite, nitrate, etc. The mechanism governing how those ions adsorb to the interface, specifically their orientation, could drastically effect the chemistry occurring at the interface. For example, if thiocyanate approaches the interface with the sulfur, rather than the nitrogen, pointed toward the vapor phase, the chemical reactions available in atmospheric aerosols might be very different. Broadband deep UV HD-SFG experiments will be able to address those issues and provide answers to such important questions which have remained unanswered for decades.

While SFG and SHG have been widely used to investigate interfacial properties, there is no definite figure for how deep second-order spectroscopies probe, i.e. where does the interface end and the bulk begin? Most computational studies define the Gibbs dividing surface as that point, but experimentally, $|\chi^{(2)}|$ remains nonzero as long as there exists broken inversion symmetry. This question needs to be addressed by performing depth profiling studies such as an ultraviolet modification to XPS.

The idea that $|\chi^{(2)}|$ is zero in centrosymmetric media relies upon the validity of the dipole approximation. However, recent studies have shown that the magnetic dipole and the
electric quadrupole may slightly, but significantly, affect SFG spectra.\textsuperscript{37,38} To address this, thorough experimental investigations and mathematical treatments of the magnetic dipole and electric quadrupoles need to be done. These effects could force a reevaluation of the results from all second-order nonlinear optical spectroscopy experiments from the past several decades.

4.3 Computational efforts:

Despite the fact that interfacial spectroscopies have been prevalent for several decades, relatively few computational studies of the spectra have been conducted. Notably, Otten et al used molecular dynamics simulations to explain the favorable enthalpic and unfavorable entropic contributions to the adsorption of an iodide ion to the air-water interface.\textsuperscript{24} Bradforth and coworkers computed the energetics of the CTTS state of iodide at the air-water interface using a combination of classical MD simulations and \textit{ab initio} calculations.\textsuperscript{28} Their work was subsequently supported by SFG spectroscopy when Rizzuto et al\textsuperscript{18} produced the interfacial CTTS spectrum of aqueous iodide and determined the peak locations to be in very good agreement with the simulation results. However, a detailed calculation predicting the full spectrum of interfacial aqueous ions remains elusive. Being able to predict such spectra will be invaluable in elucidating the complete mechanism of selective ion adsorption to aqueous interfaces.
4.4 References:

(15) Yamaguchi, S.; Tahara, T. Precise electronic Chi 2 spectra of molecules adsorbed at


5.1 Introduction

Understanding the detailed mechanism of water evaporation and condensation remains an unsolved fundamental problem. Such processes occurring on the surfaces of micron sized droplets are vital for atmospheric science, governing cloud droplet growth kinetics and in turn, aerosol formation and cloud radiation properties in our atmosphere.1–4 Despite decades of study, the rates of water evaporation and condensation remain controversial, particularly in the case of aerosol droplets containing ions and surfactant molecules.5–9

The kinetics of evaporation and condensation processes are governed by the evaporation ($\gamma$) and condensation ($\alpha$) coefficients. Those coefficients are empirically determined ratios of the observed molecular flux evaporating from or condensing onto the liquid surface to the theoretical maximum value permitted by gas kinetic theory. For evaporation, this is described by the Hertz-Knudsen equation:

$$ J_e = \gamma \frac{p_{sat}}{\sqrt{2\pi mk_BT_{surf}}} $$

Here, $J_e$ is the evaporative flux, $p_{sat}$ is the saturation vapor pressure of the liquid, $T_{surf}$ is the surface temperature of the liquid, $m$ is the molecular mass of the evaporating molecule, $k_B$ is the Boltzmann constant, and $\gamma$ is the evaporation coefficient. Because the present work only concerns the study of evaporation rates, we will eliminate the condensation coefficient and mass accommodation flux from further discussion except to note that there is an analogous equation for condensation. It is also important to note that microscopic reversibility requires that condensation and evaporation coefficients for a single system be equal, so this study implicitly also reports on the condensation rate.

An evaporation coefficient of unity describes a system with no energetic or entropic barrier to evaporation. An evaporation coefficient of less than unity then describes a system with some kinetic or thermodynamic barrier such as proceeding through a transition state or a specific orientation that has an associated barrier. As such, determining an accurate value for $\gamma$ can give valuable insight into the molecular mechanism of evaporation.

Experimental measurements of $\gamma$ are challenging, and reported values for pure water span several orders of magnitude.10,11 An extensive review of the measurements made over the past century is provided by Marek and Stroud.11 It is important to note that different experimental techniques tend to yield different results, and values of $\gamma$ reported to be less than 0.1 are likely due to surface impurities, as those experiments were performed on stagnant surfaces. Additionally, it is difficult to ensure that evaporation events occur without concomitant recondensation under ambient conditions. Our experimental technique avoids those complications by employing a liquid microjet modified to form a regular droplet train that is injected into vacuum. This provides a clean droplet surface and
also ensures condensation-free evaporation. Using this technique, we have previously measured the evaporation coefficient of pure water (both H\textsubscript{2}O and D\textsubscript{2}O) to be 0.62 ± 0.09, a value which indicates a small kinetic or energetic barrier to the evaporation process.\textsuperscript{12,13} This technique was also used to study the effect of several inorganic ions on the evaporation rate.\textsuperscript{14,15} Duffey et al studied the evaporation rate of aqueous acetic acid solutions in an attempt to investigate the effects of hydrocarbon surfactants, but observed no deviation from that of neat water.\textsuperscript{16} In fact, the only aqueous solution exhibiting statistically significant decrease relative to pure water was 4 M sodium perchlorate, which exhibited $\gamma = 0.47 \pm 0.02$ – a ~25% decrease.\textsuperscript{14}

In addition to experimental studies, computational modeling has been performed by many groups. Since evaporation is a very rare event, studies have exploited the microscopic reversibility of the system to determine a mass accommodation coefficient. Interestingly, molecular dynamics (MD) simulations determine that there is no kinetic barrier to condensation – and by extension, to evaporation – of pure water such that the value of $\gamma$ necessarily is unity.\textsuperscript{17–20} Varilly and Chandler\textsuperscript{21} employed transition path sampling to study water evaporation and concluded that evaporation events become more frequent when the surface site exhibits a predominantly negative mean curvature. They also find that the evaporation is well explained by a simple model of ballistic escape from a deep potential well, with no additional barrier to evaporation beyond the cohesive strength of the liquid. These results are consistent with other simulation results providing an evaporation coefficient of near-unity. Recently, Nagata et al\textsuperscript{22} used MD simulations at the water-air interface to show that the evaporation of water is enabled by concerted, ultrafast hydrogen bond dynamics of interfacial water. They conclude that the high kinetic energy of an evaporated water molecule is enabled by well-timed making and breaking of hydrogen bonds involving at least three water molecules at the interface, the recoil of which allows one of the molecules to escape.

The pH of the air-water interface is of fundamental significance, as well as of particular interest to atmospheric and environmental sciences. Much effort has addressed this fiercely debated topic, but with very conflicting results.\textsuperscript{23} Beattie and coworkers conclude that hydroxide is preferentially adsorbed to the interface versus hydronium because of its strong effect on the relative permittivity, as well as having a small region of reduced solvent polarization fluctuations.\textsuperscript{24} Mishra et al\textsuperscript{25} used electrospray ionization mass spectrometry (ESI-MS) to study the proton-transfer mechanism of gaseous carboxylic acids, concluding that these proton-transfer reactions confirm the presence of hydroxide ions on the surface of water even at very acidic pH levels (pH > 2). Contrarily, classical molecular dynamics simulations by Mucha et al\textsuperscript{26} indicate a propensity for hydronium ions to accumulate at the water surface rather than hydroxide. These results were supported by \textit{ab initio} MD\textsuperscript{27,28} simulations. Second harmonic generation spectroscopy studies by Petersen et al\textsuperscript{29} find evidence for enhanced hydronium concentration at the air-water interface, and a phase-sensitive electronic sum frequency generation experiment performed by Tahara and coworkers determined the interfacial pH of water to be lower than that of the bulk by 1.7.\textsuperscript{30} Shen and coworkers\textsuperscript{31} used phase-sensitive vibrational sum frequency generation to study the water surface upon the addition of 1.2 M HCl, HI, and NaOH. The find that the surface of the acidic solutions is populated by hydronium ions which affect the interfacial hydrogen bonding structure and reorients the interfacial water molecules which contributes to an ice-like water structure. The basic solution indicates a small
preference for hydroxide adsorption to the interface, but how the ion contributes to the interfacial hydrogen bonding structure remains unclear.

Establishing the chemical details governing water evaporation rate is of central interest, as is the related question of the pH of the water surface. The present study addresses the effect of bulk pH on the evaporation rate of water, and in doing so provides insight into the controversial subject of the water surface pH.

5.2 Experimental Methods:

Sample Preparation:

Hydrochloric acid solutions were prepared volumetrically with 12.1 M HCl stock solution (EMD Millipore) and ultrapure water (18.2 MΩ·cm) from a Millipore system.

Experimental Apparatus:

The experimental apparatus schematic is shown in Figure 1. The droplet train is generated by driving the liquid sample at high pressure (~100 atm) through a 10 ± 1 μm inner diameter fused silica capillary (New Objective). The liquid microjet is mounted on a piezoelectric ceramic which acts as a vibrating orifice aerosol generator (VOAG) and an applied square-wave voltage results in the generation of a regular and uniform droplet train. The microdroplet assembly is mounted to an XYZ-manipulator and attached via bellows to a cubical vacuum chamber with the droplet train propagating downward. The vacuum chamber is evacuated to <100 mTorr by a roughing pump (Varian SD-300). The droplet train is then intersected by an Ar⁺ laser beam (Innova 300, Coherent) operating at ~200 mW at 514.5 nm in the orthogonal direction. The scattered Raman signal is detected at 90 degrees from the incident laser beam and directed to a liquid nitrogen-cooled CCD detector (Princeton Instruments) via an optical fiber. The droplet train is monitored throughout the experiment by measuring the laser light with a photodiode after it passes through the droplet train, which is displayed on an oscilloscope. As each droplet intersects the laser beam there is a dip in signal from the photodiode, resulting in a sinusoidal signal corresponding to the applied square-wave voltage. After the droplets pass through the interaction region, they are frozen onto a liquid nitrogen trap.
Raman Thermometry:

It has been previously demonstrated that the position and line shape of the –OH stretch in the Raman spectrum of liquid water is highly sensitive to temperature.\textsuperscript{32,33} Consequently one can utilize this feature to measure the temperature of the droplets via a calibrated Raman spectrum. A temperature calibration curve is obtained by collecting the Raman scattering intensity as a function of temperature over the range 0 – 30 °C. The calibration temperature is measured using a thermocouple (Sper Scientific) operating at atmospheric pressure. The resulting spectra are baseline corrected and area normalized. The spectra are then divided into two portions: the “low energy stretches” (data below the energy of the isosbestic point) and the “high energy stretches” (data above the energy of the isosbestic point). The two portions of data are individually integrated and a calibration curve is constructed by plotting the logarithm of the ratios of the integrated portions ($I_{\omega=\text{high}}/I_{\omega=\text{low}}$) against the inverse temperature (K\textsuperscript{-1}). Plots of log[$I_{\omega=\text{high}}/I_{\omega=\text{low}}$] vs K\textsuperscript{-1} always exhibit a linear relationship, enabling the straightforward measurement of the temperature of even supercooled water in the droplet train.\textsuperscript{34,35}

The residence time in vacuum for each droplet is carefully controlled by adjusting the vertical offset of the microdroplet assembly. By raising the assembly vertically, each
droplet resides longer in the vacuum before being probed by the laser. Multiple spectra are recorded at each vertical position of the assembly, assuring reproducibility. Those spectra are then analyzed in the same way as the calibration spectra – they are baseline corrected and area normalized, then the logarithm of the ratio of the integrated peak areas are determined and compared to the calibration plot. Knowing the vertical distance between the jet aperture and the intersecting laser beam in addition to the liquid flow velocity allows for a precise calculation of the droplet’s residence time in vacuum. From these data, as well as the initial droplet size (governed by the orifice inner diameter and the VOAG frequency, as well as the flow rate) a cooling curve is generated to be compared with the computational model.

Cooling Model:

The cooling model has previously been described in detail. Briefly the evaporation rate is described without complication due to condensation, as the jet diameter is much smaller than the mean free path of evaporating water molecules. Heat transfer is assumed to occur via conduction only, and the droplet is divided into 20 spherical shells allowing for a temperature gradient to form. The surface of the droplet cools as a function of the evaporative flux given by the following equation:

$$\frac{dT}{dt} = -\gamma \frac{p_{sat}}{\sqrt{2\pi mk_BT}} \frac{\Delta H_{vap}}{C_p} \frac{3r_0^2}{(r_0^3 - r_1^3)\rho}$$  \hspace{1cm} (2)

where $\Delta H_{vap}$ is the enthalpy of vaporization, $C_p$ and $\rho$ are the heat capacity and density of the surface shell, and $r$ is the radius with the subscripts indicating each subshell ($r_0$ being the outermost shell). Heat is then conducted outward from each sub-shell of the droplet:

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dr}$$  \hspace{1cm} (3)

where $Q$ is heat, $\kappa$ is the thermal conductivity, and $A$ is the surface area of the subshell. The two equations are numerically integrated and the physical parameters are adjusted at each time step as a function of temperature.

5.3 Results and discussion:

Cooling curves were obtained for both 1.0 M and 0.1 M HCl, with droplet radii ranging from 7-10 μm. The evaporation coefficients determined for these experiments are $0.24 \pm 0.04$ for 1.0 M HCl and $0.91 \pm 0.08$ for 0.1 M HCl; the reported errors reflect the 95% confidence interval. Figure 2 shows typical experimental cooling curves for 1.0 M HCl (red circles) and 0.1 M HCl (blue diamonds). The overlaid curves correspond to the curves produced using our cooling model, and exhibit very good agreement with the experimental data collected for each solution. The middle curve in the figure corresponds to the cooling curve for pure water ($\gamma = 0.62 \pm 0.9$). Clearly, the cooling curves for both HCl solutions deviate drastically from that of pure water, a result which suggests that
Hydronium ions significantly perturb the surface properties of water, and in turn the evaporation rate.

**Fig. 2.** Evaporative cooling curves for 1.0 M HCl (red circles), 0.1 M HCl (blue diamonds), and neat water (black). Cooling curves shown for the HCl solutions are from an individual data set. The initial droplet radii were 9.0128 μm and 7.9859 μm for 1.0 M and 0.1 M HCl, respectively. The generated curves from the cooling model are overlaid showing good agreement between the experiment and the model. The modeled curve for a pure water droplet initialized with a radius of 9 μm at 300 K is included for reference. The shaded region represents the previously reported uncertainty.

Each experiment has a different initial droplet temperature depending on the ambient temperature in the room the day the experiment was performed. To ensure that the apparent difference in gamma values for the solutions studied is not an artifact of the variable starting temperature, the cooling model was run for the three gamma values of interest. These data are shown in Figure 3, and it is clear that even with an identical initial droplet temperature, the generated cooling curves are significantly different for each modeled solution.
Interestingly, the two solutions drive the evaporation coefficient in opposite directions. While the 0.1 M HCl solution stimulates an increase in the rate of evaporation ($\gamma_{0.1\text{M HCl}}$ is ~45% greater than $\gamma_{\text{water}}$), the 1.0 M HCl solution reduces that rate ($\gamma_{1.0\text{M HCl}}$ is ~60% lower than $\gamma_{\text{water}}$). These effects can be rationalized if the presence of hydronium significantly perturbs the droplet’s interfacial hydrogen bond structure. Voth and coworkers\textsuperscript{37} employed quantum-based molecular dynamics simulations to study the molecular details governing hydronium adsorption to the air-water interface. They found that hydronium is preferentially adsorbed to the air-water interface, and this adsorption results in the pinning of instantaneous surface height fluctuations of water. The pinning was found to affect the surface region encompassed by a ~6 Å radius around the hydronium ion. The decrease in the entropy from suppressed surface fluctuations agrees well with other computational studies\textsuperscript{38}, and the effect on the interfacial hydrogen bonding network supports our findings here. This suggests that in a 1.0 M HCl solution, the hydronium at the surface will pin ~10% of the interfacial water molecules. This significant amount of interfacial pinning severely dampens the instantaneous surface fluctuations and is the likely source of the drastic decrease in the evaporation rate observed in this study. By comparison, a 0.1 M HCl solution would only result in pinning ~1% of interfacial water molecules – a number which is insufficient to dampen the instantaneous surface fluctuations to the point of depressing the evaporation rate. However, those surface enhanced hydronium ions may be sufficient to disrupt the regular hydrogen bonding network of water, making it more thermodynamically favorable for an evaporation event to occur. This increased probability
of a water molecule being ejected into the vapor would manifest as an *increase* in the observed evaporation rate. This analysis is also consistent with the findings of Nagata et al, which emphasize the importance of ultrafast hydrogen-bond dynamics of interfacial water.\(^\text{22}\)

An alternative explanation deals with the complex issue of ion pairing.\(^\text{39,40}\) Some studies have suggested a significant degree of ion pairing between hard acids and soft bases in aqueous solutions.\(^\text{41}\) In particular, Mundy and coworkers\(^\text{42}\) report that $\text{Cl}^- \cdots \text{H}_3\text{O}^+$ contact ion pair structure persists through a large concentration range at the air-water interface. The adsorption of the $\text{Cl}^- \cdots \text{H}_3\text{O}^+$ contact ion pair moiety to the air-water interface in large quantities is supported by the thermodynamic prediction put forth by Onsager and Samaras.\(^\text{43}\) While the work by Mundy and coworkers supports our findings here, they did not study HCl solutions at concentrations near 0.1 M, and so we cannot compare our results for that system.

### 5.4 Conclusions:

We describe the first experimental study using the liquid jet Raman thermometry method to identify an aqueous solution with an evaporation coefficient that exhibits a significant deviation from that of pure water. We find that as the concentration of HCl is increased to 0.1 M, the gamma value *increases* by ~45% relative to pure water, indicating a decrease in the barrier to free evaporation of water molecules. If the concentration of HCl is increased further, to 1.0 M, the gamma value *decreases* by ~60% relative to pure water, indicating a large increase in the barrier to free evaporation of water molecules. These results imply a significant penchant for hydronium to adsorb to the droplet surface, either as a lone ion, or in the form of a contact ion pair with its counter-ion, Cl$. Further theoretical calculations need to be performed in order to elucidate the exact mechanism.
5.5 References:


