Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison chemistry Ph.D. candidates.

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The Uptake and Reactivity of Organic and Atmospheric Gases in Salty and Surfactant-Coated Water Microjets

By

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Preface

A Thesis Introduction for Non-Scientists

I write this introduction as a means to tell the people in my life, from my friends and family to my amazing wife-to-be, who are not chemists, what I do. This introduction is a thank you to them for listening to me explain my research for multiple years and for helping me to learn how to convey my research to a broad audience. So, who am I, and what do I do? My name is Tom Sobyra, and I am a surface scientist. I have spent the past five years exploring the dynamic interface that is the boundary between liquid water and the gas above it. My research focuses on understanding the behavior of gaseous molecules like acetic acid, the acid found in vinegar, and ethanol, the molecule in all alcoholic beverages, as they enter the surfaces of liquids. The gas-liquid interface is an important boundary that exists all around us. From sea spray droplets in our atmosphere that create clouds to fuel droplets in a jet engine to the gas-liquid interface closest to our heart, the thin liquid films in our lungs that control oxygen and carbon dioxide exchange (please excuse the terrible joke, I could not help myself).

These surfaces provide a unique area of study because of the lopsidedness that exits between the two halves. Molecules in the atmosphere around us are spread out and collide about 10 billion times every second, which sounds rather high, but in comparison, a molecule in liquid water is in constant random motion (diffusion) and is continuously colliding with a near-infinite collision rate with its surrounding water molecules. The transition between these two areas (phases) provides a unique region for reactions and interactions to take place that would not otherwise occur. It has been my pleasure to explore the power of water surfaces as they capture and transform gaseous molecules entering this boundary region.

In the Nathanson research group, I use a technique called gas-liquid scattering by creating a beam of molecules[1] (a molecular beam) and directing it at the surface of liquid water. These incoming molecules can
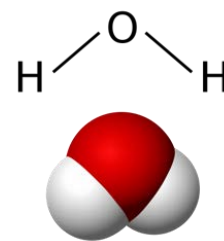
Molecule of Water[1]

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[1] A molecule is a group of two or more atoms held together by chemical bonds.

undergo several different interactions when they encounter the surface shown in the figure below. They could 1) scatter directly from the surface without actually entering the liquid, 2) hit the surface and hop along it before evaporating back into the gas phase, 3) enter solution and evaporate or react in the liquid to produce a new molecule which may then
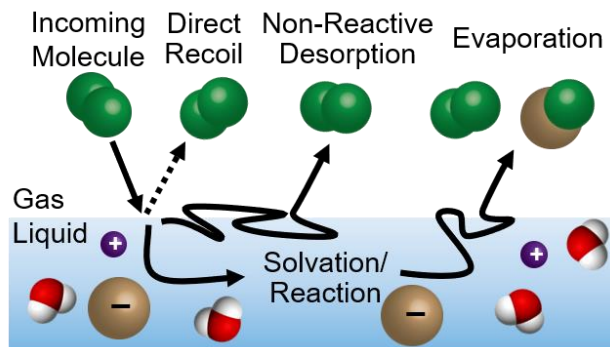
Sample Molecular Beam Pathways: The incoming molecule can 1) directly recoil, 2) hop along the surface and leave after a few bounces, 3) dissolve into the liquid and evaporate before or after reaction.

evaporate. All of these pathways are shown in the following figure. Any of the molecules that leave our water surface, either by scattering or by reaction and evaporation, are collected with a mass spectrometer, which is an instrument that filters molecules by their weight or number and type of atoms that make up the molecule.

In order to ensure that the molecules we are sending at the water surface reach without hitting other gas molecules, we perform the experiments inside a vacuum chamber. We lower the pressure in our chamber to about 1/100,000,000 of atmospheric pressure (14.7 psi or 1 atmosphere). Reducing the pressure by this massive amount decreases the amount of gas by a factor of one hundred million from its initial value and reduces the number of gas-gas collisions by the same factor from 10 billion times every second to about 100 every second; this dramatic decrease reduces the likelihood of gas-gas collisions in our vacuum chamber.

Some people that I have described my research to remember a demonstration they once saw in a chemistry class where a glass of water is placed in a vacuum chamber. If you have not seen this, I suggest a quick browse of YouTube to see this demonstration, but if you do not have the time here is a brief description. As the vacuum is pulled around the liquid, you start to see the water in the vacuum turn to ice. What is happening is that water molecules in the liquid are evaporating and becoming water vapor (gaseous water). These molecules, as they leave the surface, take with them a small amount of energy from the liquid water. Eventually, the departing molecules take away enough energy that the liquid cools and then starts to freeze and

become ice. This phenomenon is similar to what happens just after you walk out of the shower. The water on your skin begins to evaporate, and when it does, it takes a small amount of energy away from your body, causing you to feel chilly. This experiment begs the question; how do you get liquid water into a vacuum chamber and prevent it from freezing?
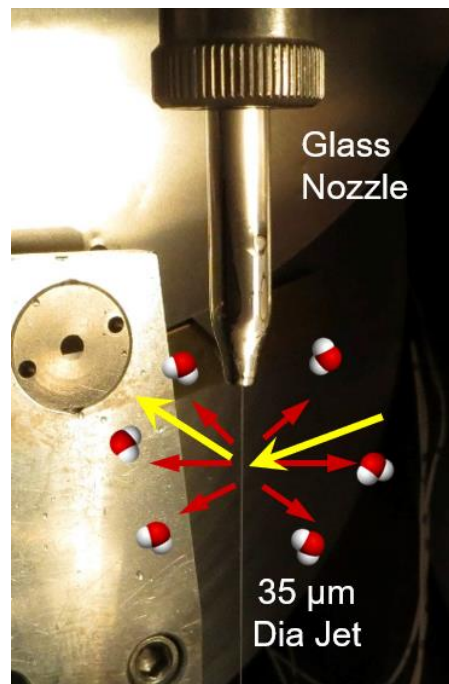
There is an excellent way to prevent water from freezing, and that is to introduce salt into the water to lower the point at which the water freezes (freezing point depression). If you have ever spent a winter in a region that regularly gets snow, you have seen this in action. Throughout the winter, salt will be thrown onto roads and driveways to melt ice on the ground. The act of throwing salt (NaCl) on the ice works because the salt breaks apart into ions, Na^+ and Cl^-. These ions intersperse among the water molecules and hinder them from getting close to each other, which reduces the freezing point of the ice on the ground and causes it to melt back into a liquid. In the lab, we introduce a salt at a high concentration that lowers the freezing point of the water we are using so that it stays a liquid when we introduce it into our vacuum chamber.

Using salty solutions, we can get liquid water into the vacuum chamber, but even salty water is a liquid with high vapor pressure. Meaning that even if we do place our salty solution into the vacuum chamber, it will still have many water molecules evaporating from the interface. Remember, we want to be able to get our gaseous molecules from our molecular beam to the surface of our solution to observe them interacting. If we were to place the salty water as is into our apparatus and direct our beam of molecules at the surface, it would be the equivalent of trying to enter a movie theater as hundreds of people were trying to exit after the previous show let out. You would undoubtedly be repelled by the mass of people pouring out of the theater and never make it in. In order to counteract this problem, what we can do is reduce the temperature of our salty water, which simultaneously lowers the vapor pressure of water above that solution (analogously, making people in the theater stick to their seats). The good news is that our added salt depresses the solution freezing point of water to as low as -78 °F, but this is far beyond where we would like to observe the interactions. Our goal is to study the reactions and interactions of atmospherically relevant molecules with water solutions that mimic aerosol

droplets in the troposphere (the region of the atmosphere where we live and breathe). The droplets we want to study are above freezing temperatures and comprised of water and sodium chloride at concentrations above seawater (due to evaporation of water that concentrates the particles as they travel upwards).

A simultaneous way we can tackle the theater problem of too many exiting moviegoers is to make the movie theater smaller and reduce the number of people exiting. Thanks to the previous graduate student, Jennifer Faust, our vacuum-based instrument system has been overhauled with a new experimental technique, liquid microjets, that solved this problem of water evaporation in precisely this way. A liquid microjet pictured on the right generates a thin stream of liquid that is approximately one third the size of a human hair (35 micrometers for our typical jets) by forcing the liquid through a glass nozzle tapered down to a small exit diameter. This liquid microjet flows continuously in our vacuum chamber and provides us with a continually refreshed surface. The other advantage of this technique is that we can cool the liquid salty solution entering the chamber. Cooling the water below freezing (32 °F) decreases the number of water molecules evaporating from the surface and limits the cloud of vapor molecules around the jet surface, ensuring that our incoming gas molecules and evaporating molecules from the water jet can enter and leave the jet without interacting with water vapor.

Photograph of the liquid microjet inside the vacuum chamber: This glass nozzle generates a jet with a diameter of 35 μm. The red arrows indicate the evaporation of water molecules from the jet as it travels through the vacuum chamber and the yellow arrows show the pathway of molecules as they are directed at the jet and as they desorb from solution towards the detector.

Equipped with a liquid microjet and a vacuum chamber, my research over the past five years has been focused on expanding our fundamental understanding of atmospheric reactions on water droplets. I solve real-world problems using a fundamental approach to study how atoms

and molecules interact at water surfaces. During my time I have worked on three main projects measuring the uptake[2] of various molecules: 1) Organic (molecules primarily composed of carbon and hydrogen atoms) molecules into salty water, 2) Dinitrogen pentoxide (N_2O_5, an atmospherically relevant nitrogen oxide) into salty and organic coated water solutions, and 3) Nitric acid (HNO_3) into salty and organic coated water solutions.

As a start to my career in studying interactions at the surfaces of liquid microjets, I began by trying to determine the limitations of the microjet method. Liquid microjets were a relatively new undertaking in my research group, and we wanted to improve our technique, our results, and our repertoire of what we could measure. I decided to explore the collisions of a wide range of organic molecules with a range of different molecular components (functional groups). These functional groups are collections of atoms in a molecule that determine the behavior and reactivity of the molecule. We studied a diverse group of molecules ranging from carboxylic acids like acetic acid that contain a carboxyl group and are weak acids, to organic bases similar in structure to ammonia, to a host of other molecules with various functional groups. All these molecules are pictured in the figure on the next page. The way these molecules interact (through the four channels outlined earlier) with the surface of water is dictated by their functional groups. Our goal was to investigate the interactions and loss of these molecules to the surface of salty water to correlate the measurements to the chemical interactions they form in solution.
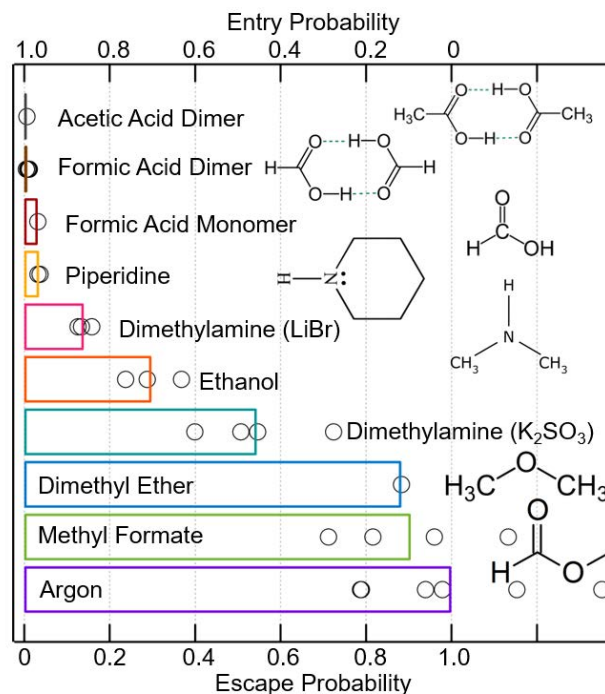
In this experiment, we required a method to determine the loss of a given molecule due to reaction or dissolution into water. We figured out a method to know how many molecules were exiting solution and the amount that was colliding with the solution and used it to measure the loss of the organic molecules (formic acid, acetic acid, piperidine, ethanol, dimethylamine, methyl formate, and dimethyl ether) to a lithium bromide (LiBr) solution at 253 K (-4 °F). Our results showed that the loss of molecules roughly followed the solubility of those molecules in solution (which is dictated by their chemical interactions with a liquid) and is shown in the

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[2] Uptake is the fraction of molecules that are permanently trapped by the solution versus the total number of molecules that interact with the solution.

histogram to the right (along with an image for every molecule). These results were a significant achievement and would ultimately setup up the remainder of my experiments during graduate school.

Histogram of Escape/Entry Probability: The likihood that a molecule escapes from aqueous solution is dependent on its interactions with the water molecules and ions in solution. Molecules with high escape probabilities and low entry probabilities have less interactions with the solution.

One of the most notable results we found was the irreversible loss of weak acids (formic and acetic acid) and bases (piperidine and dimethylamine) on almost every collision with the LiBr solution. Even when we created a beam of formic acid and acetic acid dimers,[3] the dimers would break up upon entering the interface and be lost to solution for long periods of time. The second notable result we found is that the ions in solution could have dramatic effects on the solubility of molecules entering solution. We observed increased uptake of dimethylamine (an organic base) when using a solution of LiBr versus potassium sulfate (K_2SO_3) due to the coordination of Li^+ ions with ammonia like molecules. The interaction difference is shown in the histogram figure above, where the bar for the dimethylamine is smaller when measuring the uptake to LiBr versus K_2SO_3. The surface of salty water appears to be a nearly perfect doorway into solution for small organic molecules with oxygen or nitrogen functional groups, perhaps through the formation of just one gas-water interaction. This is important in the atmosphere where small organic molecules, like the ones used in this study, are removed by aerosol droplets. Breathing these organic molecules can have long-term health impacts, so it is crucial to understand the

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[3] A dimer is when two molecules of the same type are bonded with each other. For formic acid and acetic acid these molecules form a cyclic ring by hydrogen bonding with each other (see histogram figure).

generation and loss of these molecules in the atmosphere.

Ultimately these experiments set up the technique of measuring the entrapment of molecules to a salty water interface, and with this established, we decided to probe more atmospherically relevant molecules. As we burn fossil fuels, we produce nitrogen oxide compounds (NO and NO_2) that rise into the atmosphere and undergo some fascinating chemistry. These nitrogen oxides react with sunlight in the troposphere to produce ozone (O_3) and hydroxyl radicals (OH). Ozone molecules are being produced in the area of the atmosphere where we live (the troposphere) and are harmful to human health. The hydroxyl radicals that are produced react with greenhouse gases like methane and remove it from the atmosphere. At night all this sunlight-driven chemistry shuts off, and the nitrogen oxides react with the generated ozone to create N_2O_5. The N_2O_5 hangs around in the atmosphere at nighttime and dissolves and reacts in aerosol droplets. The disappearance of N_2O_5 into aerosol droplets at night is the dominant pathway for the removal of nitrogen oxides in the atmosphere, with up to 50% of the nitrogen oxides produced during the day being removed by N_2O_5 loss to aerosols at night. The values of N_2O_5 uptake into these droplets have been measured to be anywhere between 1 in 10,000 and 1 in 5 collisions leading to loss of N_2O_5 to the surface of an aerosol. If you alter the uptake of N_2O_5 from 1 in 10,000 to 1 in 5, there is a 15% change in the amount of ozone and hydroxyl radicals that are produced in our atmosphere and a two year difference in the ten year lifetime of methane.[4] The nighttime reactive uptake of N_2O_5 to aerosols has significant impacts on atmospheric gases.

My research on this topic focused on the reactive uptake of N_2O_5 to sea spray aerosols. So, what are sea spray aerosols, and what are they comprised of? As ocean waves break, bubbles are introduced into the water, and when those bubbles rise back up to the ocean surface, they pop and create sea spray aerosols. These aerosols are not just sodium chloride (NaCl) and water, but actually contain a large number of organic molecules. The top one millimeter of the ocean is

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[4] Macintyre, H. L.; Evans, M. J. Sensitivity of a Global Model to the Uptake of N_2O_5 by Tropospheric Aerosol. *Atmos. Chem. Phys.* **2010**, *10*, 7409-7414.

enriched in organic material and is referred to as the sea surface

microlayer (SSML). As plants and fish die and as

phytoplankton (microscopic marine algae) bloom and feed on

surrounding material, organic soap-like molecules

(surfactants[5]) are produced and rise to the surface of the ocean.

This organic material is introduced into aerosols when the

bubbles burst at the surface, causing aerosols to be a diverse

mix of water and salt with an organic coating. This organic

coating can have a dramatic effect on the reactive uptake of

N_2O_5. The organic coating may block the entry of the

molecules as they try to penetrate the thick coating and dissolve
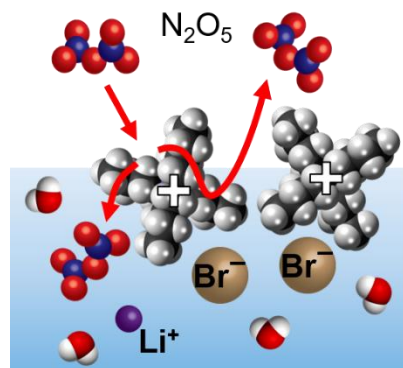
Entry of N2O5 to Surfactant Surface: Surfactant can block entry of N2O5 and other gaseous species from entering the solution. A charged surfactant will bring reactive ions to the surface for N2O5 to react with.

in the water below. If the coating is thinner, the organic molecules may enhance reaction by

bringing reactive ions to the surface for N_2O_5 to interact with (as shown in the figure to the right

for reactive bromide ions (Br^-), dragged to the surface by attraction to the oppositely charged

organic ion). Our research in this next project focused on answering two questions: 1) Can we

measure the reactive uptake (or entry probability) of N_2O_5 to solution and 2) What is the effect of

surfactants on the entry and reactivity of N_2O_5.

Since our previous attempts to measure the uptake of various organic molecules was

successful, we set out to measure the reactive uptake of this other atmospherically relevant

molecule to a concentrated LiBr solution. This goal began a two year trial of attempting to

measure the uptake of N_2O_5 which is reported to happen on fewer than 1 in 5 collisions and on

average occurs in less than 3 out of 100 collisions with a water surface. Along the way, we

stumbled across a few hurdles that would complicate our analysis, including the presence of a

highly reactive impurity, nitric acid (HNO_3), that is impossible to remove entirely from our

synthesized samples of N_2O_5. After removing the impurity from our data, we were able to

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[5] A surfactant is a molecule that contains both a water-like (hydrophilic) and an oil-like (hydrophobic) region. These molecules typically rise to the surface of water and are generally used as soap or detergents because of their ability to grab grease and dissolve it in water.

measure the reactive uptake of N_2O_5 to be -5%. Now, the negative number does not make sense because it is saying we actively made molecules. These results show the difficulty of these experiments, but what does come out of them is that the reactivity of N_2O_5 is not more than the highest reported value, implying that N_2O_5 disappears into our LiBr solutions in fewer than 1 in 5 collisions. A low value for the uptake of N_2O_5 means a shorter lifetime for the greenhouse gas methane in our atmosphere but a higher concentration of the health hazard, ozone, in the air we breathe.

Our second goal in these studies was to measure the effect of organic soap-like surfactant molecules on the reactivity of N_2O_5 in aqueous solutions. Having ruled out the ability to measure a difference in the reactive uptake, we instead turned to the observation of a product molecule. N_2O_5 in solution reacts with water to produce nitric acid and with ions like chloride (Cl^-) and bromide (Br^-) to produce nitryl chloride ($ClNO_2$) or bromine (Br_2). The reaction with chloride ions is prevalent in sea spray aerosols at the coasts, whereas the reaction with bromide ions is prevalent in the artic where large amounts of bromide are present. The molecules formed ($ClNO_2$ and Br_2) evaporate from the aerosols into the gas phase and react with sunlight to create highly reactive species that destroy methane and other volatile organic molecules.[6] We hoped to measure the production of Br_2 when scattering N_2O_5 from the surface of our LiBr water solution.[7] In a first for microjet scattering, we were able to observe the formation and evaporation of a gaseous molecule Br_2, upon scattering a different gas molecule, N_2O_5, from a microjet. Measurement of a product of reaction was a huge accomplishment in our lab and set us up with a means to measure the reactivity of N_2O_5 in the presence of surfactants.

We can now use Br_2 as a gauge to understand the effects of adding surfactant to the surface on the likelihood of N_2O_5 reaction in solution. Two surfactant molecules, butanol and tetrabutylammonium (TBA^+) were chosen, the former has the formula $CH_3CH_2CH_2CH_2OH$

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[6] Volatile organic compounds (VOCs) are organic molecules that have a high vapor pressure (meaning you can smell them at room temperature) and are varied and numerous in their structure and functional groups.

[7] In solution, a salt like LiBr dissociates into ions, a cation with a positive charge (Li^+) and an anion with a negative charge (Br^-).

(butanol has 2 more carbons than ethanol), and the latter has the formula $(CH_3CH_2CH_2CH_2)_4N^+$. Both molecules are shown in the figure to the right and to see a picture of what these surfactant molecules look like on the surface of water, see the below image. Butanol is representative of simple organic molecules that are introduced into sea spray droplets. Tetrabutylammonium is a more complex

1-Butanol   **Tetrabutylammonium**
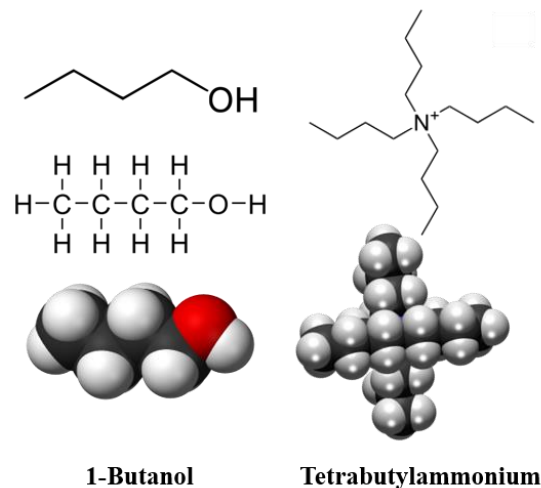
positively charged surfactant (TBA$^+$) representative of a group of more complex, charged organics that exist in sea spray droplets. TBA$^+$ acts like a magnet, it draws another magnet of the opposite charge when it moves, so when TBA$^+$ rises to the surface of our solution, it drags some of the bromide ions from solution with it. We hypothesize that TBA$^+$ should increase the amount of Br$_2$ produced from N$_2$O$_5$ reaction.

Scattering N$_2$O$_5$ and comparing the amount of Br$_2$ evaporating from both surfactant surfaces produced exciting results. When the butanol molecules cover about 40% of the surface (as shown in the figure to the right), they decrease the amount of bromine produced by about 35%. Butanol molecules are blocking the N$_2$O$_5$ from hitting the surface. Think of these surfactants like ropes or locks blocking of some doorways to a building. When 40% of the doors are closed, we see about 35% fewer people exit the building. In contrast, when about 60% of the surface is covered by TBA$^+$ (shown in the figure to the right), the Br$_2$ signal disappears entirely. In terms of the analogy, even though we have only blocked off a handful of more doors, we have completely stopped people from exiting the building. When the coverage of TBA$^+$ is

(a)
- C
- H
- I$^-$
- H$_2$O

(b)
1-butanol
Na$^+$ I$^-$
H$_2$O
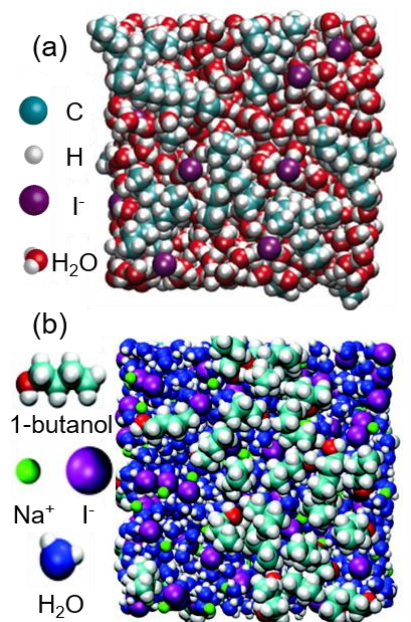
Snapshots of Surfactant Surfaces: Surface of (a) a tetrabutylammonium (TBA$^+$) and (b) a butanol surfactant layer on the surface of a solution of water.

dropped to just 9%, we see that the bromine signal returns but only to about 15% of what we see with no surfactant. What about this TBA^+ surfactant solution causes this extra drop in Br_2 signal? Blocking entry at a fraction of doors with TBA^+ decreases the number of pedestrians leaving to 20% of the number able to exit when the doors were roped off with butanol. An additional effect is going on in solution (the building) that is trapping Br_2 (the pedestrians) from exiting. We believe that bromine formed in solution reacts with an additional bromide ion to form tribromide. The formation of this ion increases the solubility of Br_2 in solution and prevents it from evaporating out of the microjet. In terms of our previous analogy, it means that while the number of people entering the surface was not reduced, the people trying to exit were slowed down. For example, when you go to a museum or amusement park, but are forced to exit through a gift shop. In this case, the people trying to leave are held up by shopping in the gift shop and spend extra time in the park/museum. The results from the butanol and the TBA^+ surface show that surfactants and organic molecules on the surface of an aerosol can have a dramatic effect on the reactivity of N_2O_5 and prevent the evaporation of species (Br_2) that can go on to remove greenhouse gases like methane from the atmosphere.

For my last project in graduate school, I focused on looking into the reactive uptake (entry probability) of nitric acid (HNO_3) into our salty solutions. HNO_3 is an important atmospheric gas that acidifies droplets in the troposphere and is one source of acid rain. The reactive uptake of HNO_3 into aerosol droplets is also another major pathway for the removal of nitrogen oxides from the atmosphere. Our initial hypothesis was that the entry probability of this strong acid should be close to one (every collision leads to disappearance), just as it is for the weak acids formic and acetic acid and the strong acid, hydrochloric acid. In the literature, measurements of the nitric acid uptake have shown it to be a difficult quantity to measure, and the most reliable values put the number between 20 and 70%.[8] If the value of the uptake were 50%, this would dramatically change the results of our N_2O_5 uptake experiment as the molecules

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[8] Guimbaud, C.; Arens, F.; Gutzwiller, L.; Gaggeler, H. W.; Ammann, M. Uptake of HNO_3 to Deliquescent Sea-Salt Particles: A Study Using the Short-Lived Radioactive Isotope Tracer ^{13}N. *Atm. Chem. Phys.* **2002**, *2*, 249-257.

exiting the microjet solution would not only be N_2O_5 but could also be the HNO_3 impurity. This would explain the discrepancy in our measured uptake of -5% from the literature value of 3%.

Our first goal was to determine what the reactive uptake of HNO_3 in our system is and then use it to determine a correction factor for our N_2O_5 uptake measurement. Measurements using our method results in an HNO_3 uptake into concentrated $LiBr/H_2O$ solutions of 59%, which is in line with the literature measurements. This means that during our experiments measuring N_2O_5 uptake only about 3 out of every 5 collisions of the nitric acid impurity lead to dissolution of the strong acid. The remaining acid evaporated from solution and was detected by our mass spectrometer and counted in the N_2O_5 signal. This would be analogous to counting people with coats leaving a building but counting people with either a coat or sweater leaving. If we correct for this additional signal in our measurement for the uptake and entry of N_2O_5 the value rises from -5% to 4%, a value that is close to the reported 3% seen on most salty solutions.

Our next goal is to understand how organic soap-like surfactants impact the uptake of HNO_3 as it enters solution in an effort to understand how organics on the surface of aerosols impact the acidification of aerosol droplets. We are using a similar 60% covered tetrabutylammonium solution to test the impact of a surfactant on the entry of HNO_3. Addition of the surfactant lowers the entrance of HNO_3 to solution 0%. This is an astonishing drop in the entrance of a major acidifying species to aerosol droplets. In the context of the previous building analogy, we have blocked 3/5ths of the doorways into the building, but nobody is able to enter as a result. This would be the equivalent of blocking all the public entrances to a museum which prevents anyone from entering.

During my time at the University of Wisconsin-Madison, I have had the opportunity to extensively learn about gas transfer across the gas-liquid interface. I have shown it is possible to measure the uptake of various molecules using a liquid microjet system and used this technique to observe the interactions of atmospherically relevant molecules, N_2O_5 and HNO_3, on the surface of salty and surfactant coated solutions, as well as a host of organic molecules composed of different functional groups. Throughout this process, I have learned valuable skills in problem

solving and communication. I hope this intro serves as an easy, accessible answer to the question, "what is your research?"

      This section was written with the guidance and editorial support of my advisor, Prof. Gil Nathanson, and the science communications program of the Wisconsin Initiative for Science Literacy.