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 20 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 dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Collisions and Reactions with Glycerol Films and Water Microjets: Exploring the Chemistry of Interfacial Ions

By

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Preface

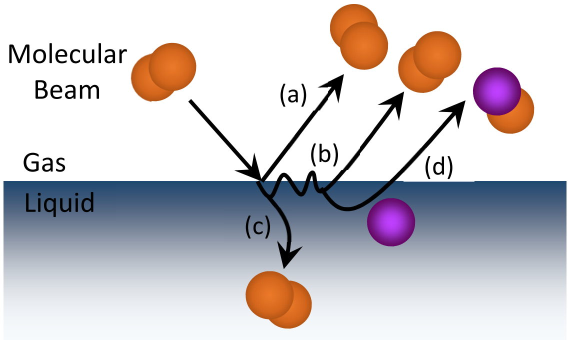
A Thesis Introduction for Non-Scientists

When I tell new acquaintances that I am studying chemistry, I usually receive one of two responses. Some groan and ask “Really?”, as if they are incredulous that anyone would ever want to pursue the subject. Others look intrigued and follow up with “What sort of chemistry?” This introduction is my attempt to address both questions—not only to explain the problems I have devoted five years of my life to exploring, but also to explain why I find these problems exciting and worthwhile.

I am a physical chemist, which means I use methods from physics to understand the properties of molecules and their reactions. My research focuses on understanding how gases behave at the surfaces of liquids. Gas-liquid interfaces (boundaries) are all around us: from fuel droplets in a jet engine for combustion, to thin liquid films in the lungs for oxygen and carbon dioxide exchange, to sea spray aerosol droplets in the atmosphere for cloud formation.

I find surfaces interesting because they behave differently from pure gases and pure liquids. Molecules in the air are dispersed; they react only if they collide in the proper orientation with the proper energy. In water, dissolved molecules (known as solutes) are surrounded on all sides by water (known as the solvent); these molecules are constantly and randomly moving (diffusing) as they bounce into one another. The surface, however, possesses a unique asymmetry because the gas on one side is so different from the liquid on the other. It is my goal to untangle the varied routes available for reactions at gas-liquid interfaces.

In my research group, we use a technique known as molecular beam scattering to fire a stream of gas molecules at a liquid surface. As shown below, the incoming molecules can either (a) scatter directly from the surface after one or two bounces, (b) spend more time on the surface before evaporating, (c) dissolve into the liquid, or (d) react near the interface. We detect scattered molecules and reaction products with a mass spectrometer, which is an instrument that can distinguish particles by weight.

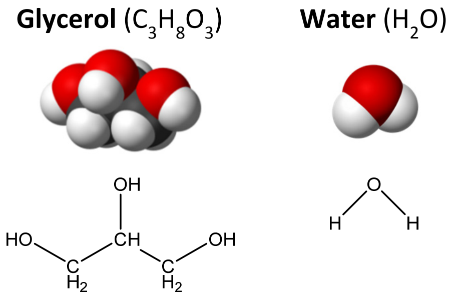


Molecular beam scattering pathways. A gas molecule that strikes a liquid surface can (a) directly recoil, (b) leave after a few bounces, (c) dissolve into the liquid, or (d) react near the interface and exit as a new molecule.

These experiments must be carried out inside a vacuum chamber. Out in the air, nitrogen, oxygen, and other gases would block our molecular beam from reaching the liquid surface. In our vacuum chamber, we pump out ambient air to prevent these undesirable gas-phase collisions.

However, background gas can also come from the liquid itself. Vapor (gas) evaporates from a liquid; you know this if you’ve ever opened a bottle of nail polish remover, rubbing alcohol, or vinegar. These are high vapor pressure liquids (containing acetone, isopropanol, and acetic acid, respectively) that you can smell because of the gas molecules that evaporate from the liquid and travel to the receptors in your nose. By our standards, even water is a high vapor pressure liquid, so we sometimes substitute glycerol instead. Glycerol is similar to water—both molecules have groups of oxygen and hydrogen atoms—but because the vapor pressure of glycerol is one hundred thousand times lower than that of water, we can use glycerol in our vacuum chamber without creating too much extra vapor.

Armed with a molecular beam and a vacuum chamber, I seek to expand our fundamental understanding of chemistry. I am motivated by real-world problems, but I am also driven by a general



Structures of glycerol and water.

curiosity to know how atoms and molecules behave. This type of research is known as basic or fundamental science because it is not directed toward inventing a particular commercial application. Over the course of my Ph.D., I focused on two chief goals: (a) characterizing chlorine to bromine conversion in salty glycerol, and (b) developing an experimental apparatus to study hydrochloric acid at the surface of water. However, research rarely follows a linear trajectory; in the middle of those two projects, I was sidetracked by the question of how gases evaporate from water. Here I will share a little of all three endeavors; consider it a *CliffsNotes* version of my thesis.

For my first research project, I investigated how chlorine gas (Cl_2) reacts with bromide ions[1] (Br^-) at the surface of salty glycerol to produce bromine gas (Br_2). This reaction is of interest because studies show that Br_2 originating from salty snowpack, sea spray, and sea ice in the Arctic destroys tropospheric ozone. Most people think of ozone as a good thing in the stratosphere, where the ozone layer blocks harmful UV radiation emanating from the sun. In contrast, closer to earth's surface, ozone is a pollutant that participates in complicated gas-phase chemistry. Understanding the concentrations of bromine and ozone will help climate modelers predict chemistry in the troposphere that may be affecting global climate.

On a more fundamental level, the Cl_2/Br^- reaction is a test case for the chemistry of ions at liquid surfaces. Scientists used to think that only solvent molecules occupied the outermost liquid layers. In the mid-1990s, a group of chemists from Boston discovered that they could not reconcile the Cl_2/Br^- reaction in water with normal models of chemistry.[2] They proposed that this

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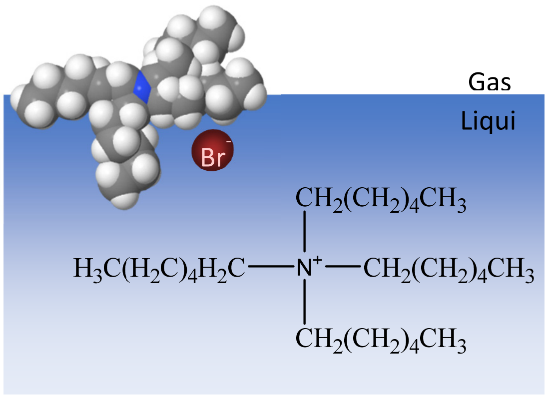
[1] An ion is an atom or molecule that is charged because it does not have an equal number of protons and electrons. You can think of it as a mini magnet.

[2] Hu, J. H.; Shi, Q.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. Reactive Uptake of $Cl_2(g)$ and $Br_2(g)$ by Aqueous Surfaces as a Function of Br^- and I^- Ion Concentration: The Effect of Chemical Reaction at the Interface. *J. Phys. Chem.* **1995,** *99*, 8768-8776.

reaction must include an interfacial, or near-surface, component. Further experimental and theoretical evidence emerged showing that many ions, including Br^-, can exist at liquid surfaces. However, the mechanism for the Cl_2/Br^- reaction remained unclear. What is the probability that a given Cl_2 molecule will react to form Br_2? Does Cl_2 begin to react right away when the molecule in the gas phase lands on top of the liquid? Does it travel down one layer of solvent molecules before reacting? Does it diffuse even deeper into the bulk? How long does it take for a Cl_2 molecule to be converted to Br_2? I spent the first two years of my graduate career addressing these questions with molecular beam scattering experiments in liquid glycerol.

I started by directing a beam of Cl_2 molecules at a reservoir containing sodium bromide (NaBr) dissolved in glycerol. NaBr is similar to table salt (NaCl), and it completely dissolves as Na^+ and Br^- ions in glycerol. I discovered that about 1 in 4 Cl_2 molecules that strike the surface of the liquid go on to react and form Br_2. Furthermore, we calculate that the Cl_2 molecule can travel no more than one or two layers of water molecules into the liquid on the timescale of our experiment. As a result, we have direct evidence that the Cl_2/Br^- reaction really does happen in the gas-liquid interfacial region.

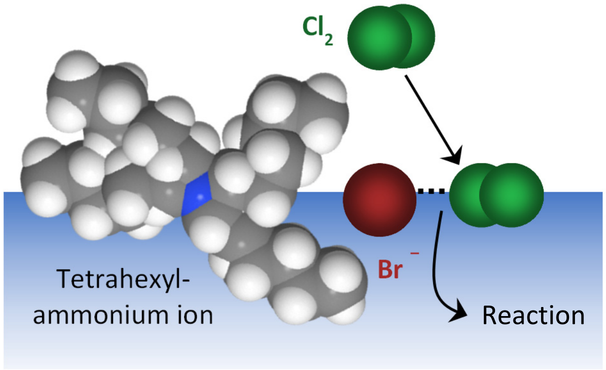


Tetrahexylammonium (THA^+) structure. THA^+ is an ionic surfactant, shown here with bromide, Br^-. Surfactants preferentially segregate to the gas-liquid interface.

I followed up on these findings by asking an even more complex question: what happens to the reaction probability if we add a bulky organic molecule to the liquid surface of the liquid? Surface-active agents, known as surfactants, are organic molecules and ions that contain water-like and oil-like components, as shown in the cartoon for my surfactant of choice: tetrahexylammonium

(THA$^+$). A variety of organic surfactants are present on liquid droplets in the atmosphere, but their chemical effects are complicated and often unclear.

When I added THA$^+$ to my glycerol solution, I expected fewer Cl_2 molecules to react because big, bulky THA$^+$ would block the incoming gaseous molecules. However, just the opposite occurred: THA$^+$ *increased* the reaction probability by more than three times! We hypothesized that this surprising enhancement occurs because THA$^+$ stabilizes both Br- and Cl_2, bringing them together within the "pocket" of the THA+ molecule, as pictured in the figure. In a sense, THA$^+$ teases Cl_2 into solution by grabbing it at the surface and bringing it into close contact with an interfacial Br^- ion. Clearly organic surfactants could exert a huge influence on how reactions occur in the atmosphere.



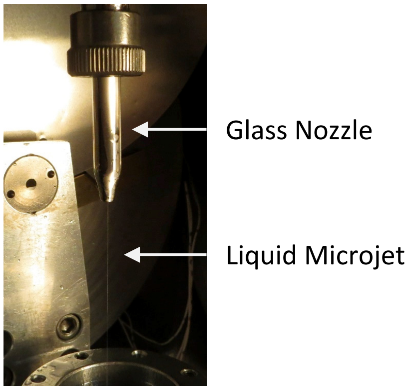
Tetrahexylammonium catalyzes the surface reaction. The surfactant stabilizes incoming Cl_2 molecules at the liquid surface during their initial reaction with bromide ions (Br^-).

However, my surfactant results are not directly transferrable to atmospheric systems. Clouds, the ocean, sea spray, and snowpack are all made of water, but our experimental setup limits us to glycerol. In order to study more relevant systems, we needed to devote time and money toward overhauling our apparatus, but being able to study water—the liquid of life—made the expense worthwhile. I devoted the next year and a half to making the transition to a new experimental technique: liquid microjets. Instead of inserting a box of glycerol in the vacuum chamber, we now create a thin stream of water, typically half the size of a human hair. (My hair happens to be 55 micrometers in diameter; I measured it with a microscope.) With such a small liquid surface exposed to the vacuum, we do not have to worry about collisions in the vapor.

Although their tiny size is the great advantage of liquid microjets, it is also their greatest challenge. We decreased the area of our liquid surface by a factor of 150 when changing from the glycerol box to the water jet, so we also increased the length of time required to collect data by that same factor of 150. A molecular beam experiment that we previously could have accomplished in ten minutes would now drag over a period of 25 hours (assuming we worked straight through without sleeping). Clearly this is not a sensible plan, so we detoured into some "easier" experiments to familiarize ourselves with microjets.

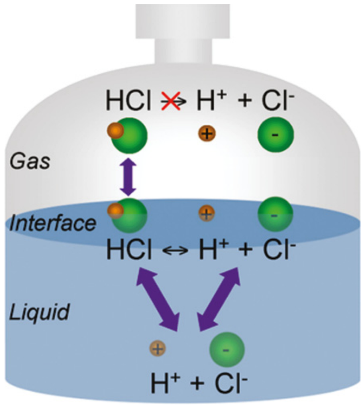
One of the neat things about fundamental research is that if you stumble across something scientifically intriguing, you are free to pursue that curiosity even if it is not part of your initial research direction. In our case, we noticed that dissolved helium atoms were evaporating out of our salty water microjets with up to 70% more energy than expected. Watching gases evaporate from a microjet is slightly simpler than our original scattering experiments, so we decided to systematically study helium evaporation in a year-long digression.

You've seen macroscopic evidence of gas evaporation from water if you've ever opened a bottle of seltzer and released a stream of carbon dioxide bubbles. We observe the same phenomenon on a microscopic level when we detect the evaporation of dissolved helium atoms bursting out of water microjets, except that the helium atoms evaporate at comparatively higher energies than the carbon dioxide molecules in your soda. We were so surprised by



Liquid microjet inside the vacuum chamber. The liquid stream is typically 2x thinner than a human hair.

what we termed the "ballistic evaporation" of helium atoms that we recruited our colleagues in theoretical chemistry, Prof. Jim Skinner and his student Zak Kann, to conduct computer simulations of helium evaporation. Zak calculated an evaporation energy 60% higher than normal for cold salty water, confirming our experimental results. Furthermore, Zak can follow the trajectory of each single helium atom as it evaporates from water. Although there is no practical application for the helium project at this time, it does offer a dynamic glimpse into the structure and motions of molecules at the gas-liquid interface.



Bottle of hydrochloric acid (HCl). In the liquid, hydrochloric acid exists as H^+ and Cl^- ions. In the gas space on top, HCl exists only as intact molecules. What happens at the interface?

Meanwhile, as we were monitoring helium evaporation, we were also designing changes to our experimental setup so that we could move forward with molecular beam scattering.[3] Our goal was to answer a deceptively simple, fundamental question: how do acids dissolve in water? Consider hydrochloric acid (HCl). In liquid water, all HCl molecules spontaneously dissociate (split) into H^+ and Cl^- ions. In contrast, hydrochloric acid molecules in the gas phase exist only as intact HCl. What happens to a gaseous HCl molecule when it reaches the gas-liquid interface—that nebulous zone that is neither fully gas nor fully liquid? Do all HCl molecules that land on the surface of water dissolve? Do the HCl molecules break apart into H^+ and Cl^- ions on top of the water surface? Or do they travel one layer of water molecules down before breaking apart? Two layers down? Even deeper? Can the ions come back together in time for HCl to reform and evaporate from solution? So much could be happening to such a small molecule!

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[3] I never imagined chemists could spend so much time thinking about welds and bolt circles and screw threads.

The previous four generations of graduate students in the Nathanson group explored HCl dissolution in glycerol, and the culmination of twenty years of such research finally led to my experiments with HCl and water. Unfortunately, by the time we had ironed out most of the initial experimental difficulties with liquid microjets, my thesis defense date was less than one month away, so we rushed to collect as much data as possible. Our picture of how HCl dissolves in water remains incomplete, but my initial results suggest that temperature strongly controls how much HCl ionizes at the surface of salty water. In short, we now have evidence that HCl molecules fall apart into H^+ and Cl^- ions near the surface of cold salty water but do not evaporate back out of solution until a long time has passed. To hear the full story about HCl in water, you will have to wait for the thesis of my successor Tom Sobyra in about four years, but you can see a sneak preview in this thesis.

Over the course of my own five years in graduate school, I've learned a lot about three very different gas-liquid systems—the transformation of chlorine to bromine at the surface of glycerol, helium atom evaporation from salty water microjets, and the dissolution of hydrochloric acid in water. As I was uncovering fundamental features of chemical reactions, I also learned about problem solving, perseverance, and critical thinking along the way. Because my Ph.D. work encompasses such a broad mix of lessons, there is no simple answer to questions about "what sort of chemistry" I study. I hope I have at least given you a taste of my own particular brand of science, and I encourage you to keep asking questions!