

# Communicating Research to the General Public

---

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry 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, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded \$500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.



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.

**UW-Madison Department of Chemistry**  
**1101 University Avenue**  
**Madison, WI 53706-1396**  
**Contact: Prof. Bassam Z. Shakhshiri**  
**[bassam@chem.wisc.edu](mailto:bassam@chem.wisc.edu)**  
**[www.scifun.org](http://www.scifun.org)**

January 2011

Investigation of Proton Exchange Reactions between Acidic Gases  
and Protic Solvents Containing Dissolved Ions

by

Susan M. Brastad

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

Doctor of Philosophy

(Chemistry)

at the

UNIVERSITY OF WISCONSIN – MADISON

2010

## *Chapter 1*

### **An Introduction to Reactions of Gaseous DCI Molecules with Protic Liquids:**

#### **Controlling Reaction Pathways with Dissolved Ions**

##### **1.1. Overview**

This introductory chapter is divided into two sections: (1) a general public introduction and (2) a technical introduction for the scientific community. The goal of the first section is to introduce non-scientists to the research discussed in this thesis, focusing on the general results of the research and their implications. In the second section, we build a more detailed picture of liquid surfaces and discuss the effects of dissolved ions on interfacial reaction pathways found for gaseous DCI molecules. Each section is meant to stand alone, so do not feel obligated to read both—choose your own adventure.

##### **1.2. Introduction for Non-Scientists**

Gas-liquid interfaces are important in a variety of industrial, environmental, and biological systems. An interface occurs whenever there is a boundary between two different types of matter. For example, a glass of water has two unique interfaces: a solid-liquid interface where the liquid water is in contact with the solid glass, and a gas-liquid interface where the water is in contact with gas molecules in the air above it, as illustrated in Figure 1.1. Research in the Nathanson group focuses on chemical reactions that occur at the gas-liquid interface and how these reactions may be different from those in the bulk liquid (i.e. at the center of the glass of water). Our goal is to develop a “blow-by-blow” picture of the chemical processes at this

interface. Or, as Prof. Gil Nathanson says, “We want to ride on the back of a gas molecule and see what happens when it hits a liquid surface.”

While many of our research questions are motivated by environmentally important issues, we also focus on understanding the basic processes involved in gas entry into a liquid and potential chemical reactions that may occur at the gas-liquid interface. In this respect, we attempt to answer fundamental questions about what happens to a gas molecule when it hits a liquid surface: How many of the incoming gas molecules simply bounce off the surface and why does this happen? Can the gas molecules enter the liquid solution and, if so, how long do they stay in the solution? What happens if the incoming gas molecule can react with the liquid, and where do these reactions occur?

Reactions at gas-liquid interfaces depend on many factors, including the identity of the incoming gas molecule and the liquid surface. In order to investigate chemical reactions between gases and liquids, we need to first identify an interesting reaction. Generally, we look at how molecules dissociate or break apart into smaller pieces. One common reaction that we study is the dissociation of acidic molecules, such as hydrochloric acid (HCl). Hydrochloric acid is the major component of stomach acid and helps to break down proteins for digestion. Additionally, HCl is present in the atmosphere and is important in the production and removal of chlorine-containing molecules that destroy ozone. Here, we specifically study the dissociation of hydrochloric acid into protons ( $H^+$ ) and chloride ions ( $Cl^-$ ) according to the reaction



This dissociation reaction does not occur when HCl is isolated in the gas phase; it only happens when HCl is in contact with water-like liquids. Once dissociated, the  $H^+$  and  $Cl^-$  ions can react with each other to remake HCl, which can then evaporate from the liquid.

My research has focused on understanding the dissociation of HCl molecules in two different liquids: glycerol and water. As shown in Figure 1.2, glycerol is an organic molecule that is composed of carbon (C), oxygen (O), and hydrogen (H) atoms. Water, on the other hand, is smaller and just composed of oxygen and hydrogen atoms. The structures of these individual molecules dictate the properties of the bulk solution. Liquid glycerol is transparent, colorless and very thick (like honey); it is also non-toxic and can be found in food and beverages as a sweetener and humectant. Even though glycerol is chemically different from water, it can dissolve acids, bases, and salts just like water.

Figure 1.3 illustrates our main conclusions for reactions of gas phase HCl molecules with liquid glycerol. When we slam HCl molecules onto the liquid surface, we find that ~50% of those molecules simply bounce off the liquid surface, just like when you throw a tennis ball at a wall. The other half of the HCl molecules, however, stick to the liquid glycerol and do interesting things. A small number (10%) of those HCl molecules evaporate from the glycerol solution before reaction occurs, but most of them dissociate into  $H^+$  and  $Cl^-$ . Of the HCl molecules that stick to the solution, 87% of them remain in the glycerol for long times (seconds) and 3% recombine and leave the liquid in less than one millionth of a second (one microsecond). This short time limits the dissociation to occurring at the gas-liquid interface.

Earlier, we said that glycerol was a lot like water, but just how true is this statement? We know that glycerol is chemically different from water even though it dissolves acids like water. What does this mean for reactions of HCl molecules with water? Will we see similar reaction pathways for water as we do for glycerol? The answer is really yes and no. Figure 1.4 illustrates the reaction pathways we find for HCl molecules with an aqueous solution. Again, if we slam HCl molecules into the solution, we find that some bounce off and some stick, just like we found

for glycerol. However, roughly 90% of the HCl molecules stick to the aqueous solution, which is almost twice as many as glycerol! Of the ones that stick, we again see that a small fraction (12%) evaporate without dissociating while the majority of them fall apart to  $\text{H}^+$  and  $\text{Cl}^-$ . In this case, all of the dissociating HCl molecules stay in the aqueous solution for many seconds, and none recombine and evaporate at the gas-liquid interface.

We think that some of the differences in reactions of HCl with glycerol and water arise from the viscosity (or thickness) of the liquids. Like we said earlier, glycerol is about as thick as honey, which means that movement of  $\text{H}^+$  and  $\text{Cl}^-$  ions in the liquid is relatively slow, like if you were wading through mud. However, if the mud becomes water, you can move through it easier and faster, just like  $\text{H}^+$  and  $\text{Cl}^-$  ions in water. The faster the ions are allowed to move, the easier it is for them to move away from each other. If  $\text{H}^+$  and  $\text{Cl}^-$  cannot find each other in the solution, they cannot recombine and evaporate.

Even though our investigation of HCl dissociation in glycerol and water has been motivated by fundamental questions, our results of HCl dissociation in aqueous solutions are atmospherically relevant. As mentioned earlier, there are small aqueous droplets in the atmosphere that can act as tiny chemical reactors. These droplets come from a variety of sources, including the ocean. Sea spray from ocean waves creates small aqueous droplets called marine aerosols, which are made up of salty water (similar to the ocean). The aerosols provide a medium for HCl (and other atmospheric gases) to dissociate and react with dissolved molecules to form gases that can eventually evaporate from the aerosol and destroy atmospheric ozone. We have shown that HCl enters and dissociates in an aqueous solution on almost every collision, implying that there is no barrier to entry. This observation may also be true for HCl entry into marine aerosols, although more experiments are necessary to confirm this.

### 1.3. A More Detailed Look at Reactions of DCl with Protic Liquids

Gas-liquid interfaces are prevalent in industrial, environmental, and biological systems. From gaseous sulfur dioxide removal by carbonate slurries to the uptake of oxygen by the surfactant-coated fluid found within the alveoli in the lungs, gas-liquid interfaces are important in our everyday lives. Our goal is to understand these complicated interactions by developing a “blow-by-blow” picture of chemical processes at gas-liquid interfaces. While many of our research questions are motivated by environmentally important issues, we focus on understanding the basic processes involved in gas uptake into a liquid and potential reaction pathways for incoming gas phase molecules. In this respect, we attempt to answer fundamental questions about what happens to a gas molecule when it hits a liquid surface: How many of the incoming gas molecules simply bounce off the surface and why does this happen? Can the gas molecules enter the liquid solution and, if so, how long do they stay in the solution? What happens if the incoming gas molecule can react with the liquid, and where do these reactions occur?

Reactions at gas-liquid interfaces depend on many factors, including the identity of incoming gas molecules and the liquid surface. For example, gaseous HCl molecules will behave differently when colliding with a liquid hydrocarbon surface (like squalane) than with a hydrogen bonding liquid (water). In order to understand these differences, it is useful to develop a microscopic picture of a liquid surface. Is the transition from a high-density liquid to a low-density vapor gradual or sharp? What part of the interfacial molecules “stick out” of the liquid?

We look to a variety of experimental and theoretical studies to answer these questions for a water/vapor interface. Braslau *et al.* have used X-ray reflectivity measurements to show that the surface roughness is  $\sim 3 \text{ \AA}$ ,<sup>1</sup> indicating that the transition from high-density liquid water to low-density vapor is relatively sharp, finite, and only a few molecular diameters in thickness. Recent advances in non-linear spectroscopy techniques and molecular dynamics simulations help us to understand the behavior of these surface water molecules, providing insight into their orientation and intermolecular forces. Sum frequency vibrational spectroscopy on neat water/vapor interfaces has shown that  $\sim 25\%$  of the surface monolayer is composed of dangling hydrogen bonds, where an H atom is directed towards the vapor phase.<sup>2</sup> The remaining interfacial water molecules form both a partially ordered and partially disordered hydrogen bonding network.<sup>2-4</sup> These features are also shown in snapshots from molecular dynamics simulations by Dang and coworkers of a water/vapor interface at 298 K (see Figure 1.5).<sup>5</sup>

We can alter the surface composition and structure of aqueous solutions in a variety of ways. Simply adding a surface active molecule to the solution significantly changes the composition of the surface; for instance, we can coat the surface of water with a hydrocarbon. A more subtle way to alter the surface, however, is to dissolve a salt in the liquid. This idea is somewhat surprising: Surface tension measurements of aqueous salt solutions show an increase in surface tension with increasing salt concentration, corresponding to an overall net depletion of ions in the interfacial region. Historically, this has been interpreted as a lack of ions at the surface of the liquid.<sup>6</sup> Figure 1.6 displays snapshots of molecular dynamics simulations of aqueous alkali halide solutions by Jungwirth and Tobias that show that this idea is not true: Large, polarizable anions can be readily found at the surface of aqueous solutions.<sup>6</sup> This region of high ion density is followed by region of low density that creates an overall net depletion in



the interfacial region. Recent sum frequency vibrational,<sup>4,7</sup> second harmonic generation,<sup>8,9</sup> and photoelectron<sup>10</sup> spectroscopy confirm the presence of dissolved ions in the surface region and explore the effects of these ions on the existing surface water structure.

The appearance of ions at the interface has also been found to alter reactions between gas phase molecules and liquid solutions. Davidovits and coworkers have found that the uptake of gaseous  $\text{Cl}_2$  and  $\text{Br}_2$  increases in aqueous NaBr and NaI solutions due to the presence of interfacial  $\text{Br}^-$  and  $\text{I}^-$  ions.<sup>11</sup> This has also been found to be true for reactive uptake of OH radicals on aqueous NaCl aerosols.<sup>12</sup>

Our own studies on salty glycerol solutions have found that dissolved ions can alter interfacial reactions between acidic gases and protic liquids.<sup>13-16</sup> Much of our previous work has focused on reactions of acidic gases, such as deuterated hydrochloric acid (DCl), with liquid glycerol ( $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$ ), a low vapor pressure, protic liquid that dissolves acids, bases, and salts with water-like solubilities. Molecular dynamics simulations<sup>17</sup> of pure glycerol show that the surface is ~60% OH and ~40% CH and  $\text{CH}_2$  while sum frequency experiments<sup>18</sup> suggest that all of the surface OH groups in glycerol are hydrogen bonded with no dangling hydrogen bonds, which is in contrast to the dangling hydrogen bonds on liquid water surfaces. Ion scattering experiments on KI- and NaI-glycerol solutions indicate that dissolved ions are present at the liquid surface.<sup>19</sup>

We use molecular beam scattering techniques to understand how these dissolved ions affect proton transfer reactions at the surface of glycerol. To do this, we aim a beam of high energy DCl molecules at the surface of a pure or salty glycerol solution. We then use both time-of-flight detection of the DCl or HCl molecules that leave the liquid surface and gas uptake experiments to monitor gas-liquid energy transfer, interaction times, and reaction pathways.

Figure 1.7 illustrates the reaction pathways determined for collisions of high energy DCI molecules with pure and salty glycerol solutions. In pure glycerol, roughly half of the incident high energy DCI molecules inelastically scatter (pathway a in Figure 1.7) from the solution after one or a few collisions while the other half become trapped (b) on the surface of the liquid. We find that the majority (87%) of the trapped molecules enter the liquid as  $D^+$  and  $Cl^-$  (c) and emerge at later times ( $\sim 0.1$  s) as recombined HCl molecules that then evaporate from the liquid (d). Surprisingly, 10% of the thermalized DCI are rejected from entering or reacting with the liquid and leave almost immediately as intact DCI molecules (e). Even more astonishing is the fact that 3% of the thermalized DCI molecules undergo a rapid proton exchange reaction and desorb as HCl in less than  $10^{-6}$  s (f). It is this rapid, near-interfacial exchange pathway that continues to interest us to this day.

Molecular dynamics simulations of HCl at the surface of pure glycerol and in the bulk liquid help us to form a “blow-by-blow” picture of the DCI scattering pathways outlined above.<sup>20,21</sup> These simulations indicate that HCl dissociates to the contact ion pair when two hydrogen bonds are formed to Cl and one to H; this process is found to occur on the picosecond timescale. Our results suggest that  $\sim 10\%$  of thermalized DCI molecules cannot find enough hydrogen bonding sites at the surface to allow DCI to dissociate either at the surface or in the interfacial region; these DCI molecules then desorb from the liquid surface intact. Furthermore, molecular dynamics simulations predict that  $D^+/H^+$  diffuses away from  $Cl^-$  via a Grotthuss-like proton shuttling mechanism along the one-dimensional hydrogen bonding network found in bulk glycerol.<sup>21</sup> This mechanism accounts for the  $\sim 87\%$  of thermalized DCI molecules that become solvated in the bulk liquid. Figure 1.8 illustrates two possible mechanisms for rapid, near-interfacial exchange in pure glycerol. Panel a shows a concerted proton exchange involving

multiple glycerol molecules where DCI protonates one glycerol molecule while another glycerol molecule donates H to the Cl. Snapshots from a density functional theory calculation of two glycerol molecules and one HCl molecule (shown in panel b) provide evidence for this concerted mechanism, and show a contact ion pair transition state. In contrast, panel b shows that D→H exchange occurs after a thermal fluctuation causes a rotation about the C-O bond (steps a-d).

In our quest to control these interfacial reaction pathways—nonreactive DCI desorption and rapid, near-interfacial proton exchange—Annabel Muentert, and later Jennie DeZwaan, dissolved salts (LiI, KI, NaI, NaBr, and CaI<sub>2</sub>) in glycerol.<sup>15,16</sup> When added to glycerol in molar quantities (~2.5 M), all of the salts have been shown to affect the reaction pathways outlined in Figure 1.7 in similar ways: In the presence of dissolved ions, more thermalized DCI molecules desorb from the solution prior to reaction *and* more undergo rapid, near-interfacial proton exchange; these increases come at the expense of bulk solvation. We have postulated that these increases result from the ability of cations and anions to bind to glycerol molecules in the interfacial region. By pre-bonding to interfacial glycerol molecules, the ions remove binding sites for incoming DCI molecules. Additionally, the ions may also disrupt the hydrogen bonding network of glycerol, which prevents D<sup>+</sup>/H<sup>+</sup> from diffusing away from Cl<sup>-</sup>, as shown in Figure 1.8b steps e-f.

Jennie DeZwaan continued the salty glycerol work by studying the effects of salt concentration and cation charge.<sup>14</sup> These studies showed that both nonreactive DCI desorption and rapid, near-interfacial exchange increase linearly with increasing NaI or CaI<sub>2</sub> concentration. Additionally, we found that cation charge matters: Solutions containing the divalent Ca<sup>2+</sup> cation were much more effective at enhancing the interfacial reaction pathways than solutions

containing monovalent  $\text{Na}^+$  ions at the same  $\text{I}^-$  concentration. In this case, the higher charge density of  $\text{Ca}^{2+}$  most likely binds interfacial glycerol molecules more tightly than  $\text{Na}^+$  ions.

These studies have repeatedly shown that we can increase the nonreactive DCl desorption and rapid, near-interfacial exchange pathways, but can we turn them off? One possible way to turn off these pathways is to add ions that are *not* found in the interfacial region, such as  $\text{F}^-$  (see Figure 1.2). Based on this observation, Jennie began studying collisions of DCl molecules with 0-4 M KF-glycerol solutions, and I joined her for the final experiments. We found that dissolved  $\text{F}^-$  ions are very effective at reducing *both* nonreactive DCl desorption and rapid, near-interfacial D $\rightarrow$ H exchange; no D $\rightarrow$ H exchanged HCl molecules could be detected leaving (either via near-interfacial exchange or longtime bulk solvation followed by HCl evaporation) a 2.5 M or higher KF-glycerol solution. Instead, we find that dissolved  $\text{F}^-$  ions act as scavengers by binding with interfacial DCl molecules to form  $[\text{FDCl}]^-$ , which then decays into DF and  $\text{Cl}^-$ , followed by DF  $\rightarrow$  HF conversion and slow HF evaporation.<sup>13</sup>

After the KF experiments, we wanted to find a way to turn off the interfacial pathways without introducing a scavenger ion such as  $\text{F}^-$  or another bulk phase solute. We initially believed that coating the surface with a hydrocarbon would accomplish this by removing potential hydrogen bonding sites for incoming DCl molecules. We chose the ionic surfactant tetrahexylammonium bromide (THABr) for this purpose. Surface tension measurements and high energy argon atom scattering experiments indicate that a significant fraction (~55%) of the surface of a 0.03 M THABr-glycerol solution is covered with the  $\text{THA}^+$  cation.<sup>22</sup> Surprisingly, we found that this surfactant-coated solution also enhances both nonreactive DCl desorption *and* rapid, near-interfacial D $\rightarrow$ H exchange! These enhancements indicate that the hexyl chains of  $\text{THA}^+$  do not interact strongly with interfacial glycerol molecules and do not physically block

DCl entry. Additionally, the surfactant nature of  $\text{THA}^+$  requires that  $\text{Br}^-$  ions also populate the interfacial region, in concentrations that are comparable to the estimated surface  $\text{Br}^-$  concentration for a 2.7 M NaBr-glycerol solution. These studies confirm that interfacial ions control DCl entry and D $\rightarrow$ H exchange in the salty glycerol solutions.

By studying DCl dissociation and subsequent proton exchange reactions in pure and salty glycerol solutions, we have been able to learn about how acidic gases dissociate in protic liquids. Our discovery of nonreactive DCl desorption tells us that not every DCl molecule dissociates when in contact with the liquid surface, even though it may be thermodynamically favorable to do so. This observation implies that dissociation occurs prior to bulk entry. Additionally, the presence of a near-interfacial exchange pathway supports the idea that DCl dissociates in the interfacial region.

Are these general ideas valid for just glycerol or do they apply to other protic liquids, such as water? Pure water is an experimentally challenging liquid to use for molecular beam scattering experiments because of its high vapor pressure (18 Torr at 298 K). At this high vapor pressure, the incoming molecular beam is more likely to undergo collisions with evaporating water molecules instead of the liquid surface. This is not a trivial problem: Because these collisions occur between the incoming gas molecules and directly evaporating water vapor, simply increasing the pumping speed in the main reaction chamber will not solve this problem. Historically, we have avoided high vapor pressure liquids by using low vapor pressure hydrocarbons such as squalane ( $10^{-8}$  Torr), and then protic liquids like glycerol ( $10^{-4}$  Torr) and supercooled sulfuric acid ( $10^{-4}$ - $10^{-3}$  Torr). Here, we simultaneously confront the challenges associated with gas-vapor collisions and conduct our first experiments on a neutral aqueous solution by studying collisions of DCl molecules with a 7.5 molal LiBr-H<sub>2</sub>O solution at 212 K.

The high salt concentration of the LiBr-H<sub>2</sub>O solution helps us in two ways: (1) it allows us to cool the solution to 212 K where the vapor pressure is low enough for scattering experiments (~5 mTorr, our limit for the rotating wheel method), and (2) according to the glycerol studies, any interfacial proton exchange pathway should be enhanced in the salty solution. Our most important finding is that water is not like glycerol: We were unable to detect any fast proton exchange pathway in the cold, aqueous solution. This lack of an interfacial reaction pathway is most likely due to the increased solubility of HCl in low temperature water<sup>23</sup> and to an extensive hydrogen bonding network in water that allows H<sup>+</sup> to easily diffuse away from Cl<sup>-</sup>.<sup>24,25</sup> However, we have detected a nonreactive DCl desorption pathway, similar to what we find for collisions of DCl molecules with liquid glycerol. This observation implies that some DCl molecules cannot form enough hydrogen bonds to dissociate even though the bulk solubility is high.

### *Thesis Overview*

The following chapters discuss the final salty glycerol experiments using KF and THABr, the machine modifications necessary for the aqueous experiments, and our results from molecular beam scattering studies using an aqueous LiBr solution. The content of each chapter is briefly summarized below.

*Chapter 2* includes a detailed description of the experimental preparation—from solution preparation to pump down—for the cold, salty water solutions as well as machine maintenance and modifications. Most notably, this chapter discusses changes made to both the main reaction chamber and the liquid reservoir for the cold, salty water experiments (including drawings).

Additionally, the end of the chapter provides a detailed procedure for tuning the Extrel mass spectrometer and switching high-q heads.

*Chapter 3* describes the THABr-glycerol experiments and our conclusions about the role of interfacial ions in catalyzing D→H exchange.

*Chapter 4* is really the heart of this thesis. In it, we describe the challenges associated with molecular beam scattering experiments from relatively high vapor pressure aqueous solutions. Finally, this chapter thoroughly discusses all of the results found for water evaporation, argon atom scattering, and DCI/HCl scattering and uptake experiments.

*Chapter 5* summarizes a series of DCI → HCl exchange experiments conducted on a ~2.5 molal KI-ethylene glycol solution at 240 and 267 K. The initial goal of these experiments was to explore temperature effects on near-interfacial D→H exchange in a solvent similar to glycerol. We find no evidence for rapid D→H exchange at either temperature and attribute this observation to the low viscosity of the solution.

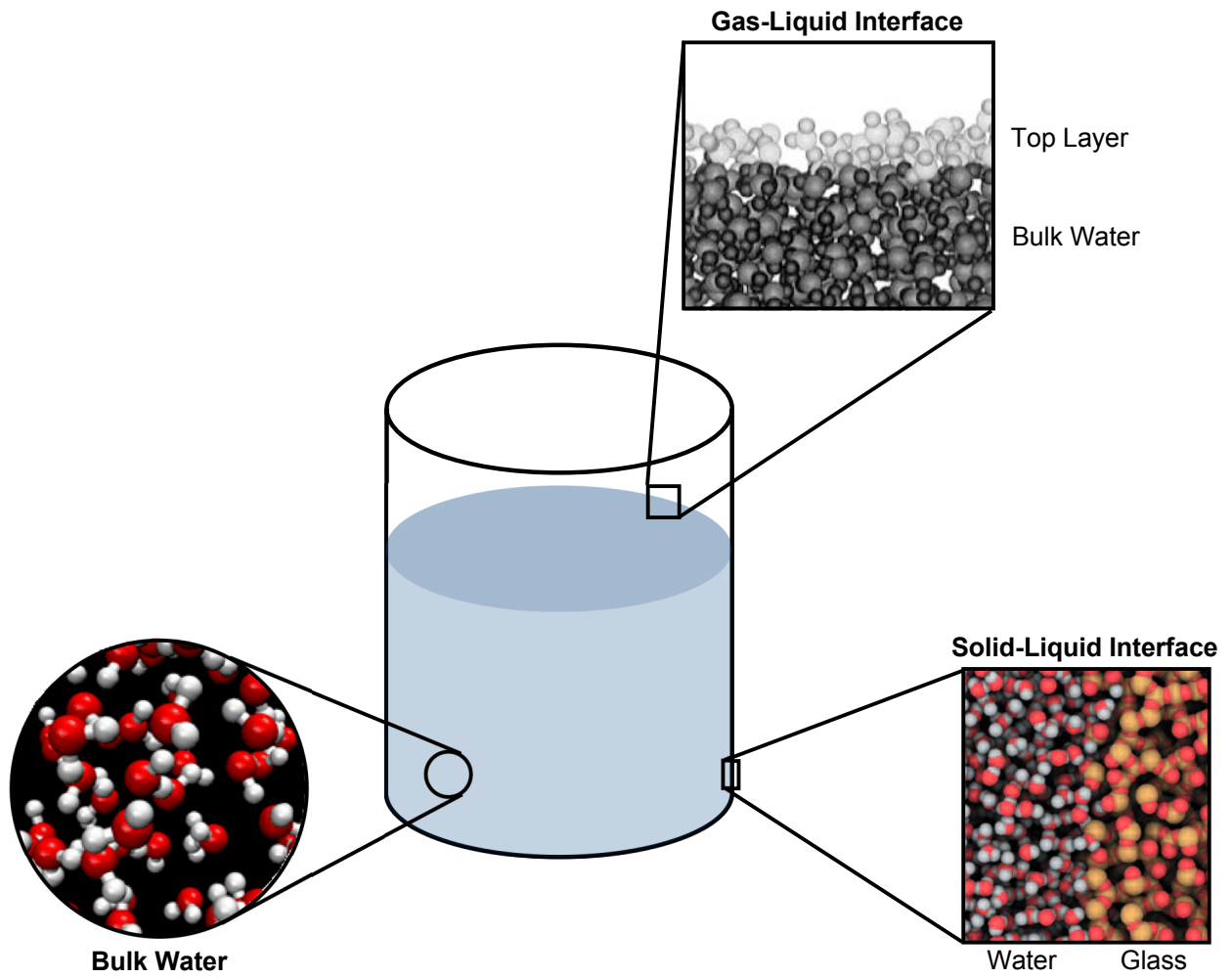
*Chapter 6* focuses on the effects of solution basicity on the DCI → HCl exchange reactions in salty glycerol solutions, specifically a 2.1 molal LiI-glycerol solution. This chapter also briefly comments on the KF-glycerol experiment and final results since most of the work has been previously outlined in Chapter 6 of Jennie DeZwaan's thesis.<sup>26</sup>

## References

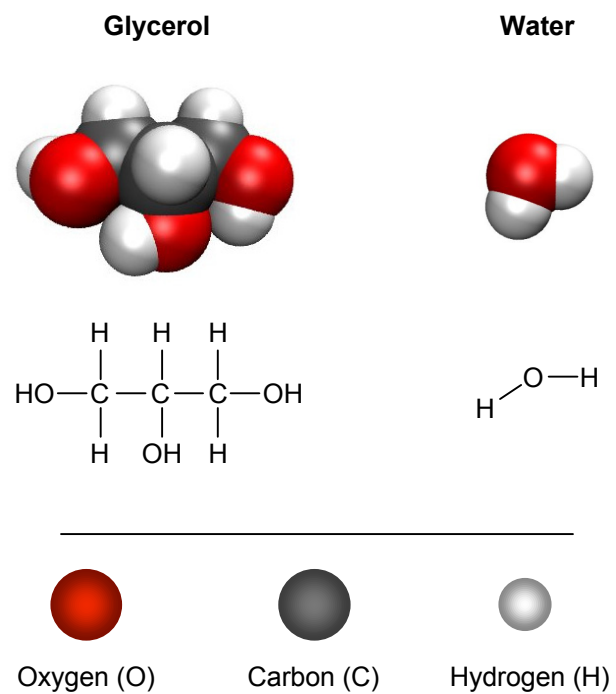
- (1) Braslau, A.; Deutsch, M.; Pershan, P. S.; Weiss, A. H.; Alsnielsen, J.; Bohr, J. *Phys. Rev. Lett.* **1985**, *54*, 114.
- (2) Shen, Y. R.; Ostroverkhov, V. *Chem. Rev.* **2006**, *106*, 1140.
- (3) Raymond, E. A.; Tarbuck, T. L.; Brown, M. G.; Richmond, G. L. *J. Phys. Chem. B* **2003**, *107*, 546.
- (4) Gopalakrishnan, S.; Liu, D.; Allen, H. C.; Kuo, M.; Shultz, M. J. *Chem. Rev.* **2006**, *106*, 1155.
- (5) Taylor, R. S.; Dang, L. X.; Garrett, B. C. *J. Phys. Chem.* **1996**, *100*, 11720.
- (6) Jungwirth, P.; Tobias, D. J. *Chem. Rev.* **2006**, *106*, 1259.
- (7) Ji, N.; Ostroverkhov, V.; Tian, C. S.; Shen, Y. R. *Phys. Rev. Lett.* **2008**, *100*, 096102.
- (8) Bian, H.-t.; Feng, R.-r.; Guo, Y.; Wang, H.-f. *J. Chem. Phys.* **2009**, *130*, 134709.
- (9) Peterson, P. B. *J. Phys. Chem. B* **2006**, *110*, 14060.
- (10) Winter, B.; Faubel, M. *Chem. Rev.* **2006**, *106*, 1176.
- (11) Hu, J. H.; Shi, Q.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1995**, *99*, 8768.
- (12) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301.
- (13) DeZwaan, J. L.; Brastad, S. M.; Nathanson, G. M. *J. Phys. Chem. C* **2008**, *112*, 15449.
- (14) DeZwaan, J. L.; Brastad, S. M.; Nathanson, G. M. *J. Phys. Chem. C* **2008**, *112*, 3008.
- (15) Muentzer, A. H.; DeZwaan, J. L.; Nathanson, G. M. *J. Phys. Chem. B* **2006**, *110*, 4881.
- (16) Muentzer, A. H.; DeZwaan, J. L.; Nathanson, G. M. *J. Phys. Chem. C* **2007**, *111*, 15043.
- (17) Benjamin, I.; Wilson, M. A.; Pohorille, A. *J. Chem. Phys.* **1994**, *100*, 6500.



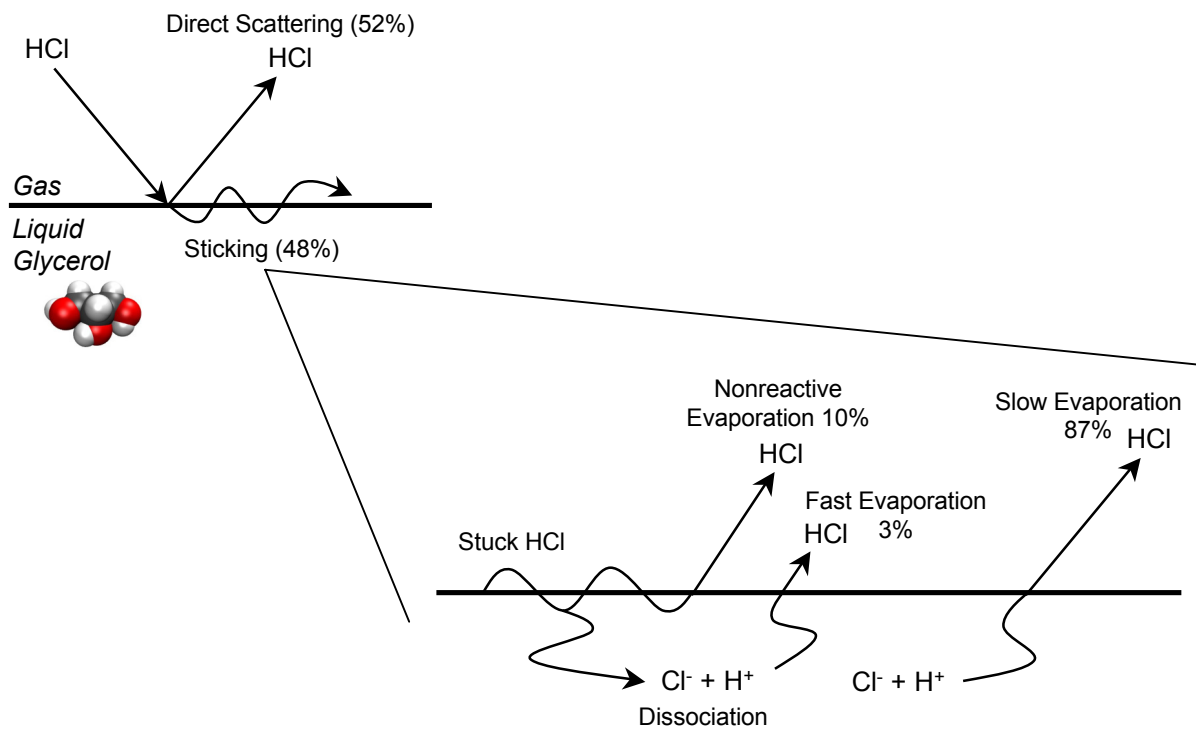
- (18) Baldelli, S.; Schnitzer, C.; Shultz, M. J.; Campbell, D. J. *J. Phys. Chem. B* **1997**, *101*, 4607.
- (19) Krebs, T.; Andersson, G.; Morgner, H., personal communication, results from ion scattering spectroscopy and neutral impact collision ion scattering spectroscopy experiments. For descriptions of these techniques, see Andersson, G.; Krebs, T.; Morgner, H. *Phys. Chem. Chem. Phys.* **2005**, *7*, 136 and Niehus, H.; Taglauer, E. *Surf. Sci. Rep.* **1993**, *17*, 213.
- (20) Chorny, I.; Benjamin, I.; Nathanson, G. M. *J. Phys. Chem. B* **2004**, *108*, 995.
- (21) Zhuang, W.; Dellago, C. *J. Phys. Chem. B* **2004**, *108*, 19647.
- (22) Brastad, S. M.; Albert, D. R.; Huang, M.; Nathanson, G. M. *J. Phys. Chem. A* **2009**, *113*, 7422.
- (23) Clegg, S. L.; Brimblecombe, P. *Atmos. Environ.* **1988**, *22*, 117.
- (24) *CRC Handbook of Chemistry and Physics*, 90th ed.; CRC Press: Boca Raton, 2009-2010.
- (25) Berkelbach, T. C.; Lee, H.-S.; Tuckerman, M. E. *Phys. Rev. Lett.* **2009**, *103*, 238302.
- (26) DeZwaan, J. L. *The Effects of Dissolved Ions on Near-Interfacial Proton Transfer in Liquid Glycerol*, University of Wisconsin, 2007.



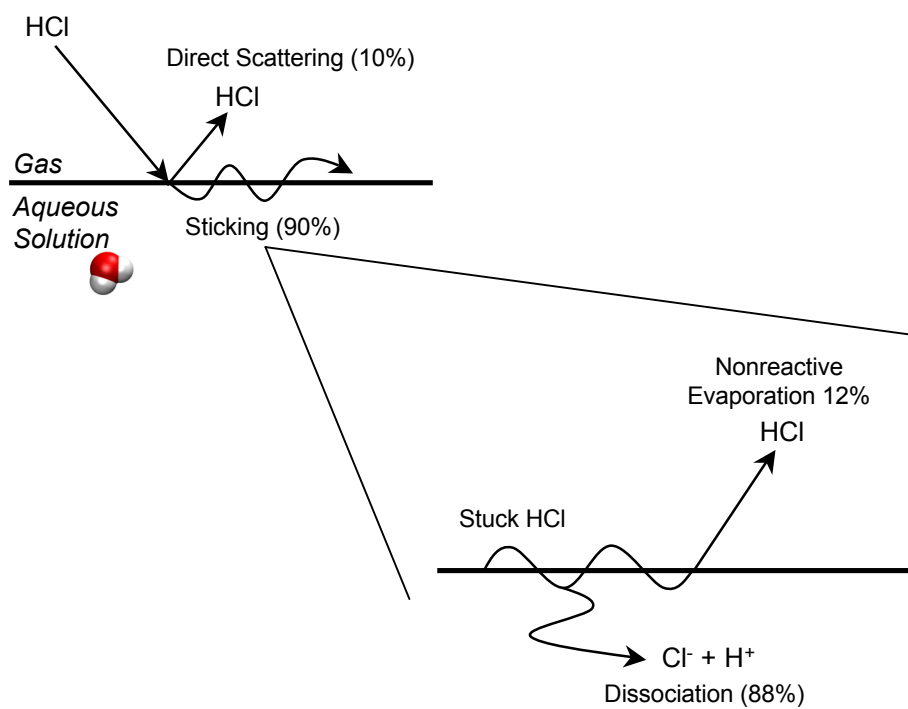
**Figure 1.1.** A glass of water demonstrates both a solid-liquid interface and a gas-liquid interface.



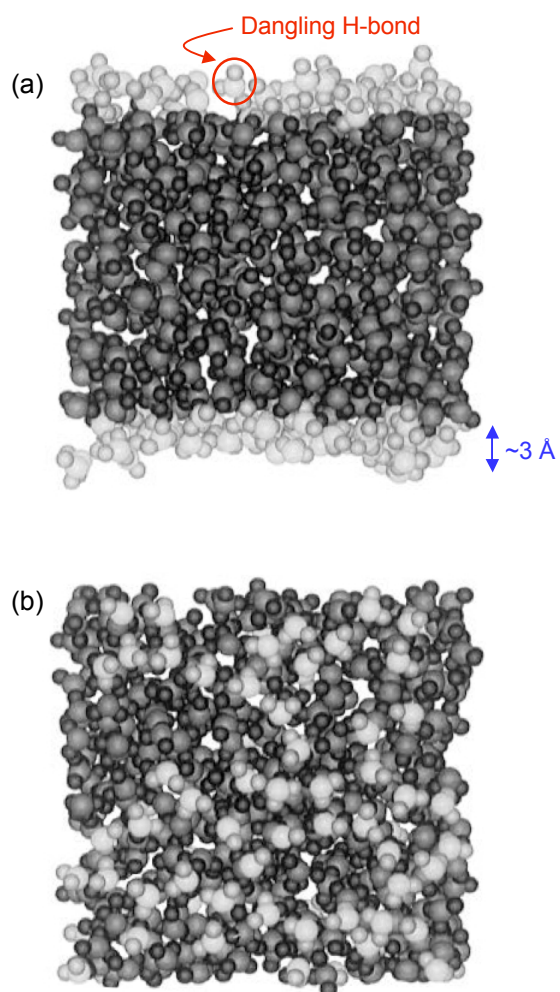
**Figure 1.2.** Glycerol and water molecules.



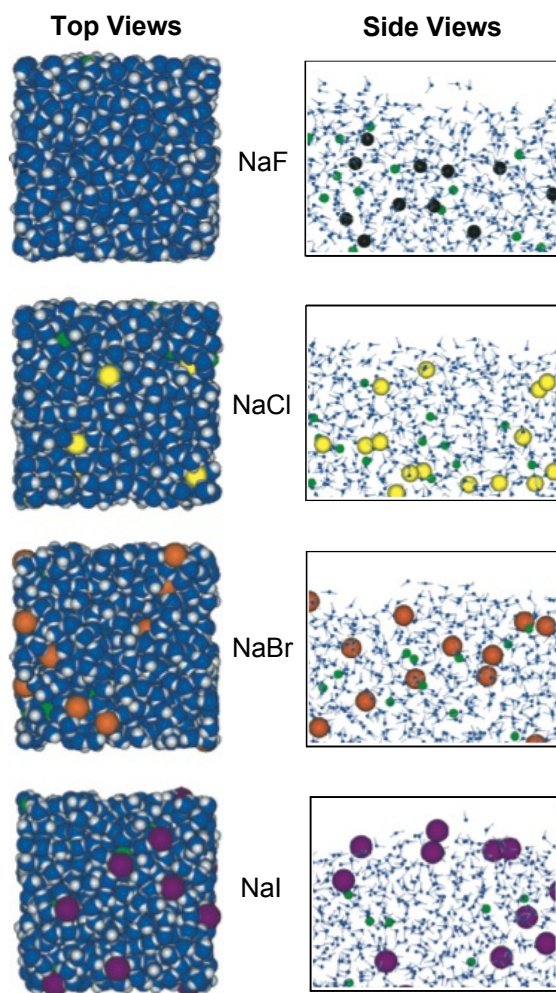
**Figure 1.3.** Reactions of HCl in liquid glycerol.



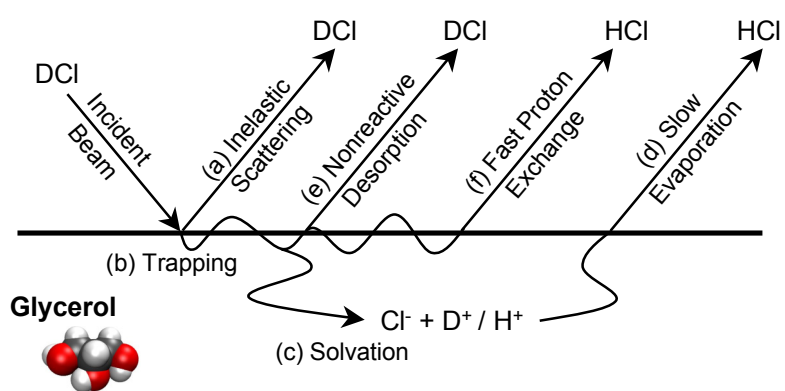
**Figure 1.4.** Reactions of HCl in an aqueous solution.



**Figure 1.5.** Molecular dynamics simulation snapshots of  $\text{H}_2\text{O}$  at 298 K from ref 5. The light gray  $\text{H}_2\text{O}$  molecules are surface molecules. (a) Side view. (b) Top view.

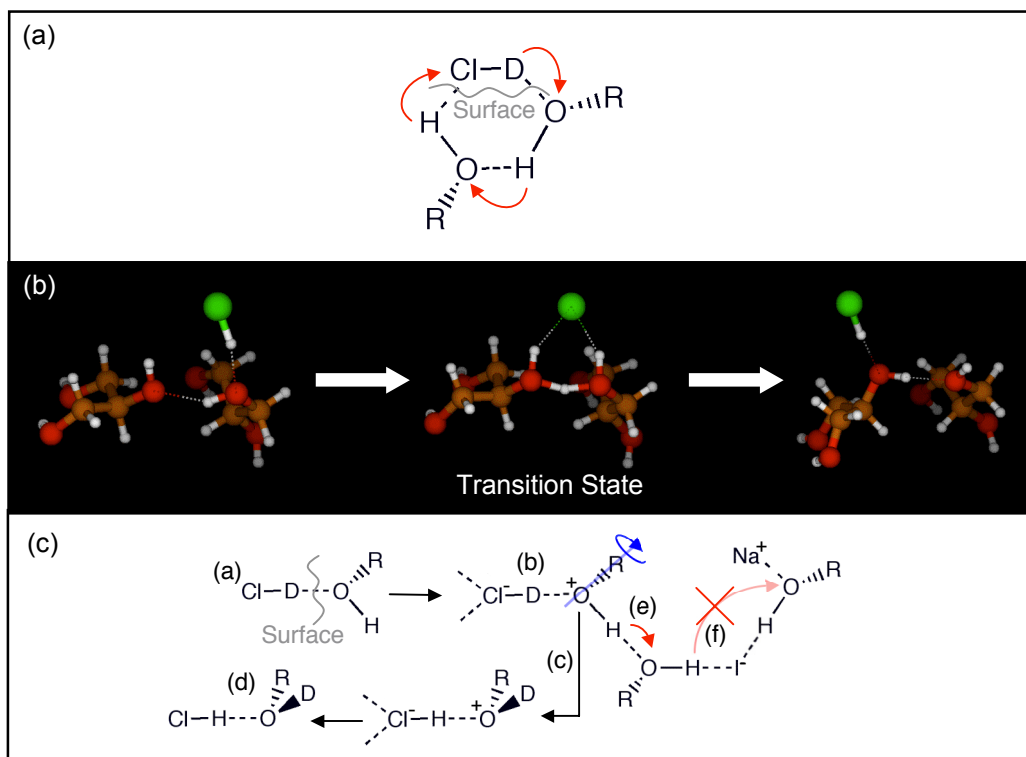


**Figure 1.6.** Molecular dynamics simulation snapshots of 1.2 M aqueous sodium halide solutions from ref 6.



**Figure 1.7.** Observed reaction pathways for high energy DCI molecules with a liquid glycerol solution.





**Figure 1.8.** (a) A possible concerted mechanism for fast D→H exchange. (b) Snapshots from a DFT calculation showing a contact ion pair transition state. (c) A second proposed reaction mechanism for rapid, near-interfacial exchange in a salty glycerol solution.