# 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.

Wisconsin Initiative for Science Literacy

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. Shakhashiri**
**bassam@chem.wisc.edu**
**www.scifun.org**

May 2014

# New Methods for Nonlinear Vibrational Spectroscopy of Materials and Biophysical Interfaces

By

**Jennifer E. Laaser**

A dissertation submitted in partial fulfillment of the

requirements for the degree of

Doctor of Philosophy

(Chemistry)

at the

**UNIVERSITY OF WISCONSIN – MADISON**

2013

Date of final oral examination: 8/23/2013

This dissertation is approved by the following members of the Final Oral Committee:
Martin T. Zanni, Professor, Chemistry
Robert J. Hamers, Professor, Chemistry
John C. Wright, Professor, Chemistry
Mark D. Ediger, Professor, Chemistry
Jordan R. Schmidt, Assistant Professor, Chemistry

# Appendix B

# Summary for the General Public

Interfaces are everywhere. The surface of the ocean is an interface between water and air. The surface of a cell is an interface between water and fatty lipid molecules in the cell membrane. And the circuits that make up modern-day electronics contain many interfaces between different types of metals and semiconductors. These are just a few examples of the many, many interfaces that surround us in our day-to-day lives.

Interfaces are important in many types of chemistry, because chemical reactions often happen differently at interfaces than they do elsewhere. For example, the proteins which make energy-storage molecules in our bodies have to be encased in fatty membranes to function. If you take them out of the membranes, they can no longer do their jobs. Similarly, generating electricity in a solar cell requires electrons to jump across the interface between two different types of conductive materials. If the materials are separated, no current can flow. And the reactions which get rid of toxic compounds in the catalytic converter of your car, or which produce important products like ammonia for fertilizers, often happen not in a bulk mixture of reactants, but on the surface of a small catalytic metal particle.

Understanding how molecules behave at interfaces is thus critically important to understanding and controlling all of these important chemistries. As experimentalists, however, we face several critical challenges in studying chemical processes at interfaces. Three aspects which make studying interfaces exceedingly difficult are:

1. measuring on fast enough timescales to watch chemical processes
2. getting information about molecular structures and environments
3. getting enough sensitivity to study the molecules at the interface (and *only* the molecules at the interface)

In the next section, I will discuss each of these challenges in more detail. I then will explain how ultrafast lasers can help us address all three of these problems. And finally, I will discuss a few of my research projects using lasers to study the structures and dynamics of a diverse range of interfaces ranging from those present in solar cells to proteins in cell membranes.

## B.1 Challenges faced in studying chemical processes at interfaces

### B.1.1 Timescales

The first challenge we face in studying chemical processes - whether at interfaces or in bulk systems - is measuring on fast enough timescales to watch these processes. Chemical processes happen on incredibly fast timescales, much faster than are accessible by most experimental techniques.

The timescales involved in a wide range of processes are shown in Figure B.1. Most events that we perceive in our day-to-day lives happen on a seconds- to milliseconds-timescale. If we want to watch a quarterback throw a 20-yard pass, for example, the football is in the air for about half a second. A single frame of film in a movie goes by in a $24^{\text{th}}$ of a second, or about 40 milliseconds.

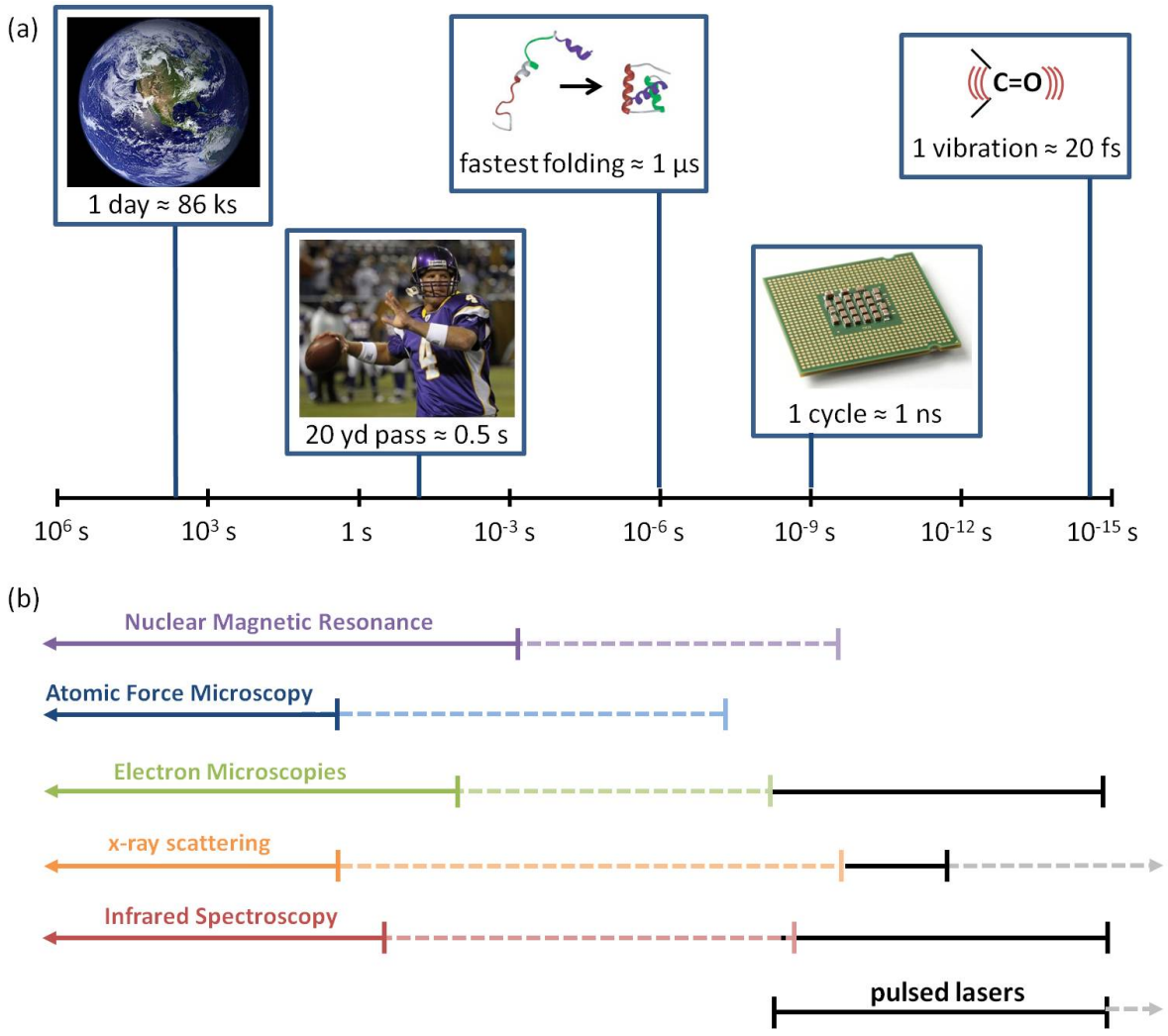


Figure B.1: Timescales of various processes, compared to timescales of available experimental techniques. Most experimental techniques can routinely investigate molecular structure and dynamics on 1 millisecond timescales (solid lines), and can get to timescales of about a nanosecond (dashed lines) with some modifications. Pulsed lasers can access shorter timescales, of femtoseconds to picoseconds. Combining laser-based methods with other techniques can push their timescales into this range as well (solid black lines).

If we want to watch most chemical processes, however, we have to be able to watch things happen much faster than this. For example, the fastest-folding proteins fold in about a microsecond, or a millionth of a second. If we want to be able to watch electrons flow, we have to be able to go at least a thousand times faster - a single cycle of a 1 GHz CPU, for example, takes just one nanosecond, or a billionth of a second. Electrons must be able to move even faster than this within the circuit as the transistors in the CPU switch on and off.

But if we want to watch what is going on in a single small molecule, we need to be able to look at even faster timescales. Individual chemical bonds in molecules vibrate back and forth in just a few tens of femtoseconds, or millionths of a billionth of a second. Thus, in order to monitor truly molecular processes, we really need to be able to monitor the molecule's dynamics on femtosecond timescales.

As I hope I've conveyed here, these timescales are incredibly, incredibly fast. To put this timescale in a slightly different perspective, a femtosecond is to a second as a second is to 32 million years. The problem we run into, though, is that most techniques for studying chemical systems can't monitor molecules' structures and behaviors nearly this quickly.

In the bottom half of Figure B.1, I've included a summary of the types of timescales accessible by different experimental techniques. The solid line depicts that timescales accessible in a normal, day-to-day experiment, while the dotted line shows how short a timescale you can look at if you really push either the electronics or your analysis methods. The key here is that it often takes significant effort to get to timescales below about a microsecond, and few (if any) of these techniques can really monitor processes faster than about a nanosecond. In large part, this is a fundamental limit of the electronics used in

most of these experiments.

Lasers, however, can generate pulses of light which are just tens of femtoseconds to a few nanoseconds long. The ultrafast laser in my lab, for example, puts out pulses of light that are only 45 fs in duration. If we can initiate a chemical process using a very short pulse of light, and then some time later come in and monitor that process with a second very short pulse of light, then we can effectively "watch" chemical processes happen on a timescale of just 50 or 100 femtoseconds.

So, now that we know that ultrafast lasers can monitor processes on these short timescales, how can we use pulses of light to initiate and monitor dynamics in chemical systems? The answer to this question lies in a technique called vibrational spectroscopy, which I will discuss in the next section.

### B.1.2 Molecular sensitivity

Even if they are too small for us to watch, molecules are constantly in motion. Molecules can move as complete units, moving from one place to the next. But molecules also have internal motions: a chemical bond can vibrate, the molecule can bend, or one part of the molecule might rotate around another.

In my work, I look at molecular vibrations. Chemical bonds are like springs, in that if you disturb them from their "natural" length, they will oscillate in and out, over and over, becoming shorter, then longer, then shorter again. The frequency of this oscillation depends on the structure of the molecule: put heavier atoms in (weights on the end of the spring) and the oscillation will slow down; bind the atoms tighter together (use a stiffer spring) and the oscillation will speed up.

By measuring the frequencies of these internal vibrations, then, we can obtain a lot

of information about the structure and environment of the molecule.

We do this using light. Molecular vibrations oscillate around 10 to 100 million million times per second. This frequency corresponds to the frequency of mid-infrared light – light which is just too far off the red side of the spectrum for us to see.

When we send infrared light into a sample, molecules whose vibrations match the frequency of the light will absorb some of that light. In our simplest experiments, we simply send light through the sample and look to see how much the molecules absorb at each frequency.

But these signals only tell us about the molecules' frequencies at a single point in time. In other experiments, called two-dimensional infrared (or 2D IR) experiments, we use a series of laser pulses to look at how the molecular frequencies change over time. We see rapid frequency fluctuations for molecules in dynamic environments, and slower frequency fluctuations for molecules in static environments.

Infrared spectroscopy, and 2D IR in particular, is thus a useful technique for getting information about the structure and dynamics of molecules on femtosecond timescales.

### B.1.3 Selectively probing interfaces

The final problem which we must address is how to monitor the molecules at the interface and *only* the molecules at the interface.

Techniques for studying interfaces have to be exquisitely sensitive, because far fewer molecules can pack into a single molecular layer at an interface than might be able to float around in a bulk solution, as depicted in Figure B.2a. The signals from an interface will correspondingly be much smaller than those from a bulk solution. If the interface is buried under such a solution, like in Figure B.2b, its signal will be overwhelmed by

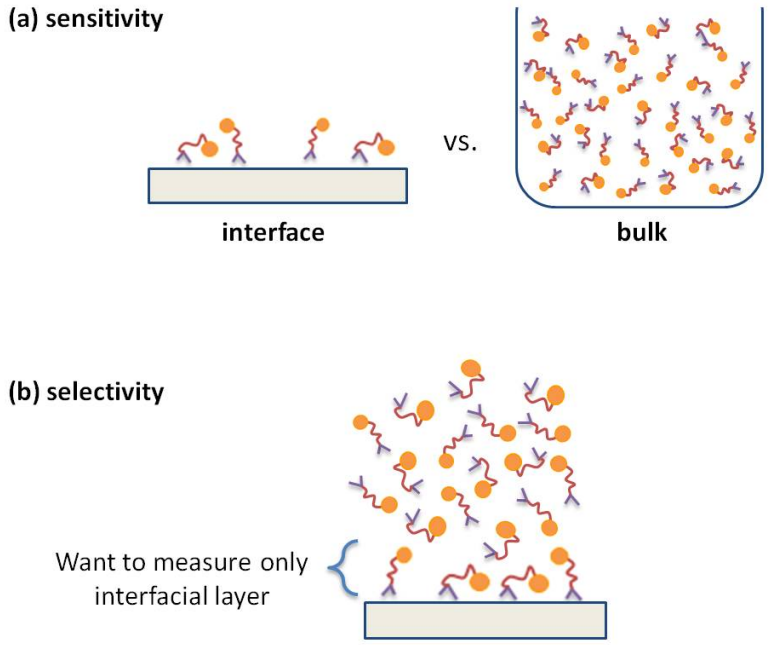


Figure B.2: Diagrams depicting (a) the difference in the number of molecules at an interface vs. in solution, and (b) the difficulties in detecting molecules at a buried interface.

that from the bulk. Ideally, we need a selective experimental technique that can *only* see molecules at the interface, and ignores those in the solution above it.

There is one easy way to bypass the sensitivity problem. In some of our experiments, we create many, many interfaces, so that we get a larger signal than we would from one interface alone.

But this approach only works for some types of interfaces, and also makes it very difficult to study molecular orientations. So, in much of our work, we instead solve both the sensitivity and selectivity problems by using a technique called vibrational sum frequency generation, or SFG.

In SFG, infrared and visible light are sent to the sample together. When the infrared light's frequency matches up with one of the vibrational frequencies of the molecules, the

infared and visible light sum together to give a signal. In our experiments, this signal comes out as red light.

This approach has three main advantages. First, it only works in samples in which the molecules are ordered. Bulk solutions, which usually contain a random distribution of molecular orientations, yield no light at the summed frequency, while interfaces, which contain a much narrower distribution of orientations, do. Second, none of the input beams have the same color as the output light, which makes the output easier to detect. And third, because SFG lets us measure single, flat interfaces, we can use the polarization of the light to get information about the orientations of the molecules on the surface.

In my graduate research, I have developed several improvements to the vibrational sum frequency generation technique, including one which combines the capabilities of our 2D IR measurements with the interface selectivity of SFG. In the next section, I will describe some of the scientific problems we have tackled with these techniques.

## B.2 Selected research highlights

My research projects over the past five years have fallen into two broad categories: materials interfaces, and biophysical interfaces. Some of our results in both of these areas are described below.

### B.2.1 Electron transfer at the organic-inorganic interface

My first research goal has been to study how electrons move in dye-sensitized solar cells. In these solar cells, a molecule stuck to the surface absorbs light from the sun. Then, it releases an electron, which hops to the surface, and can flow out into a circuit to do

useful work.

How quickly the electron moves from the molecule to the surface is one of the many factors which controls the efficiency of the solar cell. Understanding the molecular structures which speed up or slow down the electron transfer may eventually help us figure out how to design more efficient cells. But these systems are also good models for many other so-called "organic-inorganic" interfaces, which play a role in everything from catalysts which turn carbon dioxide into useful fuel, to electronics like transistors and LEDs. Understanding how electrons move across these organic-inorganic interfaces is thus relevant in many problems in materials science.

We studied this process by using a pulse of visible light to start the electron-transfer, followed by a pulse of infrared light to find out where the electron was some time later. In one part of this project, we explored how different molecular structures affected the speed at which the electron moved to the surface. We found that electron transfer was fast in molecules with short "spacers" between the molecule and the surface, but slowed down when the spacer was longer. Replacing the spacer with a structure designed to work as a "molecular wire," however, sped the electron transfer up again.

In another part of this project, we used our 2D IR technique to look at how molecules were distributed on the surface. We found that the molecular layer isn't uniform, and that molecules on the surface are close enough together that they interact with each other. And by combining these measurements with the electron-transfer measurements, we showed that different subsets of the molecules on the surface transferred their electrons at different rates.

Through this work, we showed that heterogeneity in the molecular layer affects electron transfer across organic-inorganic interfaces. Controlling the structure and ordering

of the molecular layer might be a useful way to control the electrical performance of future devices which depend on electron transfer across these interfaces.

### B.2.2 Protein structures at biophysical interfaces

My second research goal has been to develop new ways to study the structure and dynamics of small proteins stuck to different types of interfaces.

Proteins (and their smaller counterparts, peptides) often do their jobs at the surfaces of cells, where they are embedded in the cell membrane. Some membrane proteins, for example, act as channels that shuttle necessary molecules and ions in and out of the cell. Others act as antimicrobials, destroying the cell walls of bacteria and killing them. These are only some of the many functions of membrane proteins in our bodies.

But peptides and proteins on surfaces are important not just in biochemistry, but in biotechnology as well. Proteins stuck to electrodes can be used as detectors for enzymes, molecules produced by cells, and even metal ions. And coating surfaces with the right protein layer can help prevent other proteins and cells from sticking to the surface. Preventing this process, called biofouling, might help medical implants last longer and improve their compatibility in the body.

In one of my research projects, done in collaboration with researchers at the University of Michigan, we studied the structure of a small antimicrobial peptide, ovispirin, stuck to surfaces like polystyrene (a plastic) and mock cell membranes. We showed that we can detect small chemical labels inserted into the peptide, and get extra information about the protein's structure if we do. We also showed that the models scientists have used to analyze experiments on these proteins may be too simple, and that using these labels lets us use more accurate models. We hope this will influence the way these experiments

are designed and analyzed in the future.

In another one of my research projects, we developed a new technique which we used to study the structure of a small peptide stuck to a gold surface. We know that this peptide wraps itself up into a nice helix when it's dissolved in water, and we showed that it keeps much of this helical structure when it deposits on the surface. Because there are very few good ways to look at peptide structures on surfaces, we anticipate that our technique will become a useful new method for investigating these systems.

## B.3 Conclusions and final remarks

Two-dimensional infrared spectroscopy and vibrational sum frequency generation are useful techniques for measuring structures and dynamics of molecules at interfaces. In my graduate research, I developed several new versions of these techniques with new capabilities, and used them to look at a range of materials and biophysical problems. While I haven't described them here, I also developed many new theoretical models which help us interpret these measurements and design new experiments. I hope that other scientists will build on these techniques to answer many questions about the fascinating chemistry of interfaces in the years to come.