Surface Science in the Richmond Lab:

Vapor/Water Studies

Many of the Earth’s important atmospheric processes occur at the air-water boundary of oceans and aerosols and include adsorption, uptake, and reactions of gaseous pollutants. These interactions are affected by organics at the water surface, as well as by solution properties like temperature, ionic strength, and pH. Our studies focus on how such complex solution properties affect the behavior of interfacial molecular species as well as gas-surface interactions.

Recent investigations of small chain dicarboxylic acids show chain length dependence of properties important for subsequent surface chemical reactions. For example, malonic acid (one -CH₂- group between carboxylic groups) shows unique, weak solvation at the air/water interface. As the chain length increases, the carbonyl mode becomes more solvated and similar to bulk. The pH dependence shows that only the fully protonated species is surface active, indicating a single “surface” pKₐ unlike the bulk where there are two distinct pKₐ values.

We can probe the formation of gas-water surface complexes and investigate the uptake and reactivity of small gas-phase molecules, such as SO₂, CO₂, and HCl, at the surface. Past research explored the effect of temperature, acid, and organics in SO₂ adsorption to an aqueous interface. For instance, we know surface organics and salts affect interfacial water structure but have little affect on SO₂(g) adsorption. Currently, we are investigating HCl (g) surface adsorption onto organic coated and uncoated acidic solutions.

Computational Studies: Organics at Aqueous Surfaces

The behavior and optical properties of organic molecules at the air/water interface is investigated using a combination of classical molecular dynamics and density functional theory. Classical dynamics can provide otherwise inaccessible information on the conformations and orientations of molecules. This information along with quantum mechanical response tensors is used to generate vibrational sum frequency spectra, which can be directly compared with experiment.
Investigations of Environmental Systems

Liquid/Liquid Studies

The interface between hydrophobic fluids and water is found in a variety of systems in biology, the environment, and in industry. In particular, the oil/water interface is the site of processes such as protein adsorption, oil recovery, and emulsion stabilization. We are studying the behavior of species at the carbon tetrachloride/water (CCl₄/H₂O) interface as model systems for understanding different oil/water interfacial processes.

Surface Modified Nanoparticles

Self assembly of ligand-stabilized nanoparticles at the oil/water interface has attracted a lot of attention in the past few years due to their ability to stabilize emulsions and to form complex interfacial structures with new collective properties. In our lab, we are investigating the adsorption behavior of surface-modified nanoparticles at the CCl₄/H₂O interface. We find that particle adsorption is strongly influenced by particle hydrophobicity, size, and aqueous phase composition. Additionally, particle adsorption is a slow, diffusion driven process.

Tunable Polyelectrolytes

Polyelectrolyte adsorption to the interface between water and non-polar fluids is an important process for several biological, environmental, pharmaceutical, and industrial applications. We are studying a model polyelectrolyte, polymethacrylic acid (PMA), at the CCl₄/H₂O interface in order to better understand polyelectrolyte adsorption to oil-water interfaces. Current investigations include the effects of PMA charge density, specific isomer, and molecular weight as well as the presence of ions in solution on polyelectrolyte interfacial behavior.

Emulsion Studies: Characterization of Droplet Surfaces

Emulsions are comprised of either water droplets suspended in oil (reverse) or oil droplets suspended in water (regular). They are stabilized by chemical species such as amphiphilic surfactant molecules or nanoparticles. Emulsions are important for the food and cosmetic industry, water remediation, and nanoparticle synthesis. We would like to understand their local chemical environment at the oil-water interface in order to gain insight in their formation and stabilization. Sum Frequency Scattering (SFS) allows the vibrational modes of molecules at the curved oil-water interface to be probed where further information about their orientation and assembly can be determined on a molecular level.
Enhanced Photovoltaic Efficiency Through Heterojunction Assisted Impact Ionization

Solar energy is a renewable resource which can be harvested by photovoltaic systems to produce clean, local energy. The maximum theoretical efficiency of ~30% for a silicon solar cell can be overcome with the use of multiple absorbing layers. These heterojunction materials make better use of photons with energy much less or greater than the bandgap through processes such as multi-photon absorption or multiple electron-hole pair generation, respectively. The latter is the focus of this project, in which high energy photons \( (E_{hv} \geq 2E_g) \) can achieve a quantum efficiency >1 through heterojunction-assisted impact ionization (HAII).

**Impact Ionization**
Impact ionization is a process by which hot carriers lose their excess energy by excitation of additional electron-hole pairs. Through this process, two electron-hole pairs are generated using the energy provided by one high-energy photon. Impact ionization is promoted at heterojunctions by combining large bandgap thin films or nanostructures (harvesters) with small, indirect bandgap bulk materials (hosts).

**Band Diagram**
High energy photons are absorbed in the harvester, where they excite electron-hole pairs. The electrons diffuse into the host and excite additional electron-hole pairs by impact ionization.

**Laser Studies**
Electronic properties are analyzed using an ultrafast pump-probe laser experiment in which electron-hole pairs are generated by an energetic pump beam and monitored via free carrier absorption (FCA) of a low energy, time-delayed probe beam.

**What might we expect the transient spectrum to look like?**
- The pump beam is absorbed at time \( t=0 \), generating free carriers in the harvester.
- Free carriers diffuse into the host material.
- Carriers impact ionize to create additional electron-hole pairs as they diffuse into the host material.
- Carrier lifetimes are long in the indirect-bandgap host material.
Experimental Techniques

Vibrational Sum Frequency Spectroscopy

Our primary research technique is VSFS. This non-linear optical spectroscopy collects the vibrational spectra of surface molecules without interference from the bulk. More detail is obtained by using different polarization combinations of the incident and detected beams, to probe surface molecular orientation.

Laser Systems

Picosecond Laser Systems
- (3) Ekspla: Nd:YAG: 30 ps, 10/50 Hz, 1064 nm
- Spectra Physics: 2.6 ps, 1 kHz, 800 nm
- air/water, liquid/liquid, and solid/liquid interfaces
- Scanning IR from 2.3 – 16 µm, 5 cm⁻¹ resolution

Broad Bandwidth SFG
- BBSFG combines broad-bandwidth IR pulses (femtosecond) with narrow-bandwidth 800 nm pulses (picosecond) to generate broad bandwidth sum-frequency.
- Optimized for air/water studies and scattering experiments.
- 200 cm⁻¹ spectral window from 3 – 8 µm with 15 cm⁻¹ resolution

Surface Analytical Techniques

In addition to VSFS, we use a variety of other surface characterization methods:

Wilhelmy plate and optical surface tensiometry with ability to measure contact angles.

FTIR with PM-IRRAS module for air/liquid & solid/liquid studies

Additional Instrumentation:
- Temp. controlled Langmuir trough
- Confocal Raman Microscope
- Two nanopure water filters
- High accuracy warm walled oven
- Vacuum desicator cabinet
- Schlenk Line
- Light scattering instrument for size and zeta potential measurements.