

# Non Intrusive Monitoring of Ocean Surfactants with Nonlinear Optics

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## LONG-TERM GOAL

Wind-wave coupling, wave damping, surface turbulence, and air/sea gas exchange along with the reflection, transmission, emission, and absorption of electromagnetic radiation at the air/sea interface are all dictated by the molecular level structure and chemical composition of the top several molecular layers which define this interface. This research effort is directed at obtaining and using knowledge of molecular level structure and composition of the air/sea interface to understand and predict macroscopic interfacial physicochemical properties.

## SCIENTIFIC OBJECTIVES

Surfactant (both soluble and insoluble) concentration gradients and dynamic perturbations (surface waves and interfacial flows) at the air/water interface lead to large measurable changes in the thermodynamic, electromagnetic, and fluid properties of this interface as well as changes in mass transport across this interface. In addition, the macroscopic perturbations on the interface (such as surface waves or interfacial flow) create and enhance the interfacial chemical and structural gradients. Knowledge of how these interfacial microscopic (molecular level) structural and chemical composition gradients correlate with macroscopic changes provides a first step in understanding and quantifying the relationships between these interfacial phenomena.

## APPROACH

Laser based second order nonlinear optical processes provide surface selective probes for studying the gas/liquid interface (Shen, 1989). There are a number of these second order techniques and each can be used to probe non intrusively and non destructively just the top several molecular layers of the air/sea interface. Work using two of these processes, reflected second harmonic generation (SHG) and reflected sum frequency generation (SFG), is described below. This research program has refined, adapted, and extended these techniques for in situ studies of the air/sea interface (Korenowski, 1997). These techniques have also been used for studying well defined interfacial dynamic processes in a laboratory setting (Hirsa et. al, 1997). Prof. A. Hirsa of Rensselaer, Dr. E. Bock of the Woods Hole Oceanographic Institution, and Dr. J. R. Saylor have contributed to providing well defined dynamic substrates (flow or waves at the air/water interface) for study.

With these probes, the detected signal arises from a nonlinear mixing of the electric field(s) from an impinging laser beam(s) in the surface layer molecules (these processes are electric-dipole forbidden in the bulk liquid). As a result, a single laser pulse of several nanosecond duration supplies information

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about the chemical composition and molecular structure of the interfacial molecules. As a result, these optical processes are ideally suited for studying dynamic events at the air/liquid interface. Molecular vibrational and electronic spectra of the interfacial molecules, their interfacial concentration, and their average orientation with respect to the interface are all obtained from studies with the probes. Until now, work with these techniques has been limited to point measurements. A program was undertaken to develop an imaging detection system for use with these techniques. An imaging detection system provides interfacial concentration and structural gradient information with a single laser pulse.

## **WORK COMPLETED**

An imaging detection system was constructed for imaging the SHG and SFG signal from an interface. This included the design and construction of the delivery and collection optical system. Part of the collection optical system is the image splitting component which delivers the separate reflected laser beam image and corresponding SHG signal image from the surface to the intensified, pulse gated, CCD camera. Preliminary software for processing the images to yield surface concentration profiles was developed. The imaging system was applied to image the surfactant concentration on a static water surface for predetermined surfactant concentrations. A second test of the imaging system was its use to determine the surfactant concentration on a well defined flowing substrate. This flow loop was designed, built, and its flow characterized by Prof. A. Hirska (Rensselaer) for this calibration experiment of the SHG area imaging system. A third test was performed as a collaborative experiment with Dr. J. R. Saylor (NRL). In this third experiment the imaging system was used to measure the relative surfactant concentrations at the crest and trough of circular capillary waves.

In addition to the imaging research, work continued on basic studies using point measurements. Based on our field work and subsequent laboratory studies, it was determined that water exhibits macroscopic structural anisotropy in the plane of the air/water interface. A study on the angular dependence and polarization dependence of SHG from a clean water surface, surfactant covered water surface, and electrolyte containing water surface was completed. This study was conducted to determine the extent of the "ice-like" character of the skin layer on a water surface and the effect that surfactants and electrolytes have on this macroscopic ordering (Judd, 1996). Related SHG studies were also completed for methanol and n-decane surfaces. In addition, we concluded a study with surface waves which indicate that this in-plane anisotropic response from a water surface is enhanced at the crest and trough of capillary waves implying that macroscopic movement or flow results in increase molecular level surface order at the air-water interface.

## **RESULTS**

A preliminary result for imaging a surface SHG signal from circular capillary waves is shown in Figure 1. Monolayers of hemicyanine (insoluble surfactant) were spread on a water surface in the a circular tank mounted on a shaker. The reflected second harmonic signal at 266 nm was generated at the water surface from an unfocused (5.5 mm diameter) incident 532 nm laser beam. The reflected second harmonic signal (collinear with the reflected 532 nm pump beam) was passed through the image splitting optics where the 266 nm and 532 nm signals were displaced from each other but continued on in parallel paths. A quartz Nikon lens system then imaged the two beams on to the intensified pulse gated CCD camera. The simultaneous images of the reflected pump laser pulse and the surface second harmonic signal were recorded and used to convert the images into a map of relative surface concentrations. Using the squared dependence of the SHG signal on both the incident pump beam

intensity and surfactant concentration, the SHG image was converted to the concentration map of the surface presented. In the system, the largest amplitude was at the center of the circular tank and the amplitude decrease as one moves from the center to the rim of the tank. The extracted relative surfactant concentrations showed the anticipated behavior of surfactant compression at the peaks and surfactant dilation in the troughs with the center peak giving the highest surfactant concentration and the first trough (trough adjacent to center peak) yielding the lowest surfactant concentration.

Experiments on the angular dependence of the SHG signal from clean water and the polarization dependence of the signal unambiguously imply that macroscopic anisotropic structure exists in the plane of the water surface on the nanosecond time scale of the laser pulse. This anisotropic in-plane ordering results in unexpectedly large SHG signals for an experimental arrangement of a nearly normal incident probe laser beam. For probing under non resonant conditions (far from molecular resonance frequencies) in this geometry, this enhanced signal suggests that the surface layer possesses larger than expected optical dielectric constants in comparison to that of an isotropic water surface. The anisotropy or in-plane ordering was found to extend over the dimension of the laser beam footprint. These results are in direct disagreement with theoretical models which predict correlation lengths for in-plane structure of only one or two water molecule diameters. The exact nature of the structure (possession of what particular symmetry elements) was not determined in these Phase One experiments. Nevertheless, it was determined that the interface is not perfectly ordered and that there is a significant isotropic in-plane component as well. For comparison, identical studies were performed on methanol and n-decane. The results from these studies imply that this interfacial ordering is not unique to water but that it appears to be a phenomenon related to the strength of hydrogen-bonding in the liquid. In-plane interfacial order was observed for methanol but the degree of the anisotropy was significantly smaller than that observed for water. It was also found that electrolytes in the bulk water and their negative surface excess concentration can increase this ordering, however, no simple trends related to ion size were found. Experiments were also performed on the effects of insoluble monolayers on this in-plane order of the interfacial water molecules. Stearyl alcohol and stearic acid, identical except for the polar head group, were found to have different effects on the anisotropy. A stearyl alcohol film (less polar head group) had no observable effect whereas a stearic acid film alters the interfacial structure of the water surface. Surface flow was found to play an important role in inducing the interfacial structure.

Capillary waves induce additional surface order which increased the signal by a factor of four to six hundred indicating a several order of magnitude change in the surface nonlinear dielectric constant in the presence of surface capillary waves.



*Figure 1. Concentration of surfactant on circular wave peak and troughs.*

## **IMPACT/APPLICATION**

The surface imaging system offers the first surface specific, chemically selective, imaging probe for studying the air/liquid interface and opens a new possibilities for studying surfactant effects on interfacial fluid flow and wave dynamics. It is also capable of being used in situ for studies on the ocean surface. The structure found at a water surface totally changes our view of liquid surfaces. In addition, it would indicate that hydrogen bonded liquid aerosols may exhibit anomalous dielectric properties.

## **TRANSITIONS**

The surface SHG and SFG imaging system can immediately be applied to problems concerning surfactant effects on free surface turbulence both in the laboratory setting and in situ on the ocean surface. It can also be used in imaging surface concentration and structural gradients on other interfaces (e.g. solid surfaces) and applications to microelectronics, adhesion, and corrosion problems are straightforward. It also offers a scaled down laboratory equivalent to coherent Radar imaging. In addition, these surface probes offer a potentially new method for studying the surface composition and dielectric properties of liquid aerosol droplets.

## **RELATED PROJECTS**

Collaborations with Prof. A. Hirska of Rensselaer and Dr. E. Bock of the WHOI continue. Well defined surface flows and surface wave structures are supplied for study by these collaborators. A collaboration with Dr. J. Saylor of the Naval Research Laboratory was initiated in which the SHG imaging system is used to study surfactant distributions on well defined surface capillary waves.

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