REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
12 June 1995

3. REPORT TYPE AND DATES COVERED
Technical 6/94-5/95

4. TITLE AND SUBTITLE
Molecular and Ionic Interactions at the Oil/Water Interface as Measured by Surface Second Harmonic Generation and Sum-Frequency Generation

5. FUNDING NUMBERS
ONR N00014089-J-1261
R&T Code 4131038

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8. PERFORMING ORGANIZATION REPORT NUMBER
ONR Technical Report #5

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
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800 North Quincy St.
Arlington, VA 22217-5000

10. SPONSORING/MONI
AGENCY REPORT NU

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19950616 121

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release: distribution unlimited

12b. DISTRIBUTION CO

13. ABSTRACT *(Maximum 200 words)*

Direct measurement of molecular properties of these fluid interfacial regions remains a challenging task. In recent years we have been applying two techniques to such problems, surface second harmonic generation (SHG) and sum-frequency generation (SFG). The success that we have had in making measurements of the structural and molecular properties of a variety of neat hydrocarbon/water interfaces and dichloroethane/water interfaces has come from employing a total intenal reflection geometry (TIR). We have examined interfacial order, molecular orientation and ionic adsorption at various oil/water interfaces with TIR SHG and TIR SFG. The results provide a valuable insight into how molecules and ions interact at these fluid interfaces.

DTIC QUALITY INSPECTED 5

14. SUBJECT TERMS
Sum Frequency Generation; Second Harmonic Generation; Oil/Water Interface Molecular and Ionic Interactions

15. NUMBER OF PAGES
2

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT

OFFICE OF NAVAL RESEARCH

Grant N00014-89-J-1261

R&T Code 4131038

Technical Report No. 5

"Molecular and Ionic Interactions at the Oil/Water Interface as Measured by Surface Second Harmonic Generation and Sum-Frequency Generation"

by

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Accepted, Proceedings of the Electrochemical Society, 1995

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June 1995

Molecular and Ionic Interactions at the Oil/Water Interface as Measured by Surface Second Harmonic Generation and Sum-Frequency Generation

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Research in this laboratory in recent years has focussed on developing nonlinear optical methods for studying the oil/water interface. Interest in characterization of the oil/water interfaces remains high because of the central role which they play in many areas of chemistry, physics and biology. However, direct measurement of molecular properties of these fluid interfacial regions remains a challenging task. We have been primarily directing our efforts on two nonlinear optical techniques, surface second harmonic generation (SHG) and sum-frequency generation (SFG). Because of their inherent interfacial sensitivity, such second order optical processes are uniquely suited for studying buried interfaces in general [1-3], and the liquid/liquid interface in particular [4,5]. However, due to the relatively low polarizability of many simple hydrocarbon/water systems, and the dynamic nature of the interface, the SHG or SFG response from the interface can be abysmally low. This is particularly true for the SHG measurements examining the structure and order of native hydrocarbon/water interface where optical resonances cannot be used to enhance the nonlinear response. Previously, the structural properties of oil/water interfaces have relied on placing a fluroescent or resonance enhanced probe molecule at the interface [6-8]. Our objective has been to measure the native interfacial properties in the absence of such a probe molecule. For the SFG measurements to be described, the vibrational spectroscopy of interfacial surfactant molecules is sought. Although such experiments involve a resonance between the incoming tunable infrared beam, the SFG response is still relatively low and the experiment requires a relatively high powered tunable infrared source.

In the studies to be described, optical SHG is used to study a number of immiscible systems including the alkane/water and water/1,2-dichloroethane (water/DCE) interfaces. In the alkane/water studies, important new insight is provided as to the relative order of these interfaces as a function of hydrocarbon structure and length. The results are then compared with similar measurements of the water/DCE system. The electrolytic water/DCE interface has also been examined and the SH response measured as a function of the applied potential. Although such experiments are difficult if not impossible to perform by SHG due to low signal levels, success in performing the studies described herein has come from using a unique total internal reflection (TIR) geometry to enhance the interfacial SH response. Figure 1 shows a schematic of the optical geometry and the TIR cell used in the experiments. With this geometry, a 10-100 fold increase in SHG is achievable as the incident angle approaches the critical angle [9].

To demonstrate the effect of using the TIR geometry to obtain the strong SH response, the dependence of the SH response on the incident angle of the fundamental light source at frequency ω is shown for the decane/water interface (Figure 2a). As the incident angle approaches the critical angle, the second harmonic response increases dramatically as seen in Figure 2a. The fundamental light (ω) at 532nm is incident upon the interface from the alkane side which possesses the higher index of refraction and the SH light (2ω) at 266nm is collected in reflection. The solid lines of Figure 2(a and b) represent the theoretically calculated SH intensity using a single adjustable parameter. The two maxima displayed in the theoretical and SH intensities are due to the TIR of the fundamental and SH at their respective critical angles; for decane/water the angles are 70.6° and 75.7°. Polarization measurements under the TIR geometry have been used to determine the relative molecular order of a series of alkanes. Using Kleinman symmetry rules, the polarization data clearly shows that the interface containing alkanes with an even number of carbon atoms (ie. hexane and octane) possesses a higher degree of order than the interface containing an odd number of carbon atoms (i.e. heptane and nonane).

Due to dispersion, a transmitted as well as a reflected SH field is produced by the nonlinear polarization induced at the interface, even when the fundamental is under total internal reflection. We have used this geometry to study the water/DCE interface.(Figure 2b insert) The frequency dependent refractive indices of the liquids results in the SH at 2ω achieving TIR at an incidence angle larger than the critical angle of the fundamental at ω. The transmitted SH response shows the same dramatic increase over a very small incident angle distribution as a result of the TIR of the fundamental field. The SH signal disappears abruptly at an incident angle of 72° as the transmitted SH component becomes totally internally reflected. For the data in Figure 2b, the 532nm light is propagated through the DCE and is reflected. The transmitted SH is propagated through the water and collected in transmission. Collecting the SH light in transmission is critical for measuring the potential dependent SH response from this ITIES composed of an aqueous phase of LiCl and an organic phase of TBATPB in DCE. In the reflection TIR geometry where the 266nm light passes through the organic phase, no SH response can be measured due to the adsorption of the light by both the DCE and TBATPB. Not only does the transmitted SH light pass through the aqueous solution with minimal attenuation, but one can monitor the adsorption of TPB- at the interface since the SH response from this ion is resonance enhanced at 2ω. This resonance has made possible the first direct optical measurement of the potential dependent adsorption of TPB^- at the DCE/water interface [10,11]. This has never been achieved by any other optical method.

The final portion of the talk will describe our recent use of the TIR geometry to perform SFG measurements of surfactants at the oil/water interface. In these experiments we have focussed on the measurement of the C-H stretching modes of surfactants at the interface between D_2O and carbon tetrachloride. A tunable infrared beam is coincident with the visible (532 nm) beam operated in a TIR geometry. This is the first spectroscopic measurement of the vibrational modes of a simple surfactant at an interface. Previous studies of such surfactants have involved electronic excitation of chromophores or other dye molecules. The molecular orientation of the surfactants studied as a function of concentration will be discussed.

Acknowledgements: The authors gratefully acknowledge the National Science Foundation (Chemistry) and the Office of Naval Research for their support of this project.

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10. J.C. Conboy and G.L. Richmond, *Electrochim. Acta*, submitted.
11. To be discussed in detail in the related talk by J.C. Conboy entitled "Total Internal Reflection Second Harmonic Generation from the Interface Between Two Immiscible Electrolyte Solutions."

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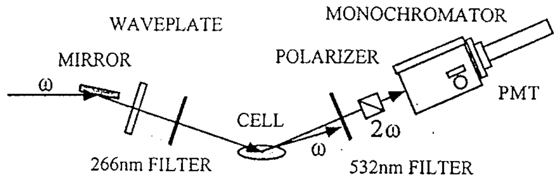
Experimental Setup.



Optical Cell

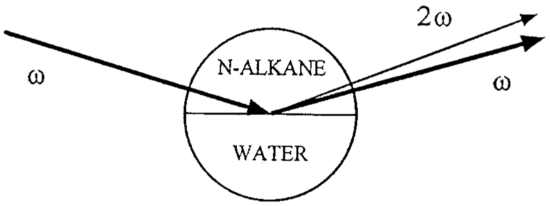


Figure 1. (upper)Experimental diagram for the TIR SHG studies. (lower) Optical cell geometry showing the incident and reflected fundamental (ω_{in} and ω_{ref}) and the reflected and transmitted SH fields ($2\omega_{ref}$ and $2\omega_{tran}$). Also shown are the fundamental incident angle (θ) and the input polarization angle (γ). ($\gamma = 0^o$, 180^o is *p*; $\gamma = 90^o$ is *s* and $\gamma = 45^o$ is mixed).

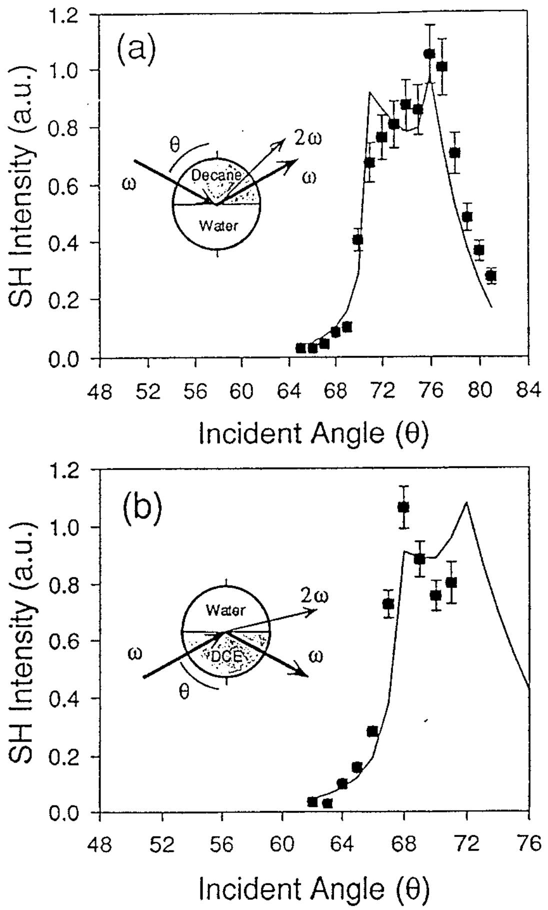


Figure 2. SH intensity (P_{in} , P_{out} polarization combination) versus incident angle (θ) for (a) decane/water in reflection and (b) water/DCE in transmission. The solid lines in each plot represent the SH response calculated from theory.