

Liquid Interfaces

KENNETH B. EISENTHAL

Chemistry Department, Columbia University, New York, New York 10027

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Interfaces are the boundary regions that separate different bulk regions of matter. They have special chemical, physical, and biological properties that have fascinated and drawn the attention of scientists and engineers from many different fields.¹ What makes the interface unique is the asymmetry in forces that is experienced by molecules and atomic species located there together with the almost two dimensional geometry of the interface. The chemical composition, the geometrical arrangement of the species, the equilibrium constants, pH, the motion of molecules, the thermodynamics and kinetics of ground- and excited-state chemical change, energy relaxation, and the phases and phase transitions of long-chain amphiphilic monolayers are among the fundamental manifestations of the unique characteristics of an interface.

Despite its importance and widespread interest, it remains difficult to probe the chemistry and physics of interfaces, and in particular liquid interfaces (vapor/liquid, liquid/liquid, liquid/solid) with traditional spectroscopic techniques. The reason is that the overwhelmingly large number of solute molecules in the bulk can dominate the signal originating from solute molecules in the interface. One way to circumvent this limiting characteristic of traditional methods is to use the techniques of second harmonic generation (SHG) and sum frequency generation (SFG), which can selectively probe an interface that separates centrosymmetric media.²⁻⁵ The key factor is that SHG and SFG are electric dipole forbidden in centrosymmetric media (bulk liquids, gases, centrosymmetric solids) but are allowed at the interface where inversion symmetry is broken. In second harmonic generation the incident light at a frequency ω interacts with the interface to generate radiation at 2ω , whereas the sum frequency generation the incident light, which consists of two sources, one at ω_1 and the other at ω_2 , generate radiation at the sum frequency $\omega_1 + \omega_2$. The second harmonic or sum frequency light field $E_{(\omega_1+\omega_2)}$ can be thought of as arising from the nonlinear polarization, $P_{\omega_1+\omega_2}^{(2)}$, induced in the interface by the incident light fields $E(\omega_1)$ and $E(\omega_2)$,

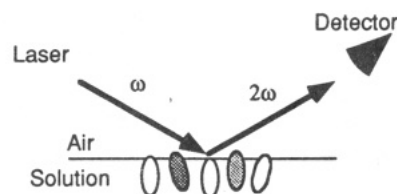
$$P_{\omega_1+\omega_2}^{(2)} = \chi_{\omega_1+\omega_2}^{(2)} E(\omega_1) E(\omega_2) \quad (1)$$

where $\chi_{\omega_1+\omega_2}^{(2)}$ is the second-order nonlinear susceptibility which contains all the information on the molecules at the interface. In this Account the focus of attention will be the work in our laboratory using second harmonic generation (SHG) and more recently sum frequency generation (SFG) to probe equilibrium and

dynamic properties of liquid interfaces. Although this Account is restricted to work in our laboratory, the reader is referred to reviews that reflect the impressive amount of fine research going on in this field.²⁻⁵

Orientalional Structure and Population at Interfaces

When I first learned about the interface specificity of SHG from a talk given by Y. R. Shen at a meeting in Alexandria, Egypt, organized by A. H. Zewail, the idea that raised my temperature was the possibility to actually "look at" the surface of a liquid, e.g., a solution or neat liquid/gas interface, something that had not been done before by a spectroscopic technique for reasons already noted. The system we chose to look at was the vapor/aqueous phenol solution interface.⁶ The second harmonic experimental setup is shown below.



We chose phenol because it had been extensively studied by surface tension and other methods and we wanted to compare SHG results with the results of other methods. Theoretical predictions indicated that the magnitude of the second harmonic field $E_{2\omega}$, which is the square root of the second harmonic signal $I_{2\omega}$, should be proportional to the number of phenol molecules in the surface area irradiated by the incident beam. However, there were all sorts of approximations behind this theoretical prediction. To find out if $E_{2\omega}$ was proportional to the phenol interface population, noting that the SHG from the interface water could be neglected at the wavelengths used in our experiments, we measured its adsorption isotherm, i.e., $E_{2\omega}$ vs bulk phenol concentration. We compared this curve with the phenol excess surface population, obtained from surface tension measurements, which is very close to being equal to the interface population for a highly surface active species, such as phenol.⁷ We were pleased

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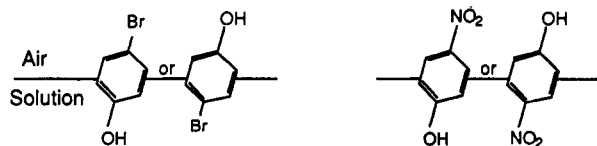
Kenneth B. Eisenenthal received a B.S. in chemistry from Brooklyn College and an M.A. in physics and a Ph.D. in chemical physics from Harvard University. He did postdoctoral research at UCLA and was at IBM Almaden before coming to Columbia University in 1975.

to learn that the two isotherms from low surface coverages (~ 0.05 monolayer) to beyond a monolayer coverage were identical. We now know that SHG can be used not only to obtain interface populations but also to obtain the free energies of molecular adsorption that determine the interface population. Furthermore, we saw that since it is a spectroscopic method, it can differentiate among the various interface species, that it is more sensitive than normal surface tension and other interface techniques, and that it can probe buried interfaces (liquid/solid and solid/solid interfaces) that normal methods cannot.

To complement the interface population measurements obtained from the amplitude of the SH electric field, we can use the polarization of the SH light to gain information on the orientation of molecules in the interface.² We learned that the orientation of phenol was $50 \pm 5^\circ$ using a simple model,⁶ and that its orientation did not change as its surface density increased, suggesting that the phenol orientation is determined chiefly by its interactions with the subphase water molecules and not by lateral phenol/phenol interactions.

Although the SH polarization measurements yield the molecular orientation, they cannot give the polar alignment of the molecules at the interface; i.e., are the molecules oriented with their dipole moments up or down with respect to the surface normal? For the vapor/aqueous phenol interface we are confident that the dipole moment is oriented "up", which corresponds to the hydroxy end of phenol pointing toward the bulk water phase and the hydrophobic phenyl ring toward the vapor. However, we surmise this by chemical reasoning and not by experimental measurement. We of course want a measurement that will yield the polar alignment for any polar molecule of interest at any interface of interest. The determination of the polar ordering became possible when it was recognized that the sign (more generally the phase) of $\chi^{(2)}$ in eq 1 is directly related to the polar alignment of the interface molecules.⁸

To obtain the phase of $\chi^{(2)}$ an interference method was used and was first applied to the vapor/aqueous phenol interface.⁸ The results confirmed the intuitive notion that the hydroxy group is directed toward the bulk water. We were now able to ask questions about other molecules; the ones we chose were the para-substituted phenols. In particular, what are the alignments of *p*-bromophenol and *p*-nitrophenol, two molecules which both have their permanent dipole moments pointing in the opposite sense to phenol? The results

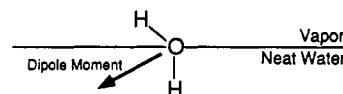


indicate that it is the hydroxy group that determines the polar alignment; all of these phenols have their hydroxy group pointing toward the bulk water.⁹

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What about the ubiquitous vapor/ neat water interface? Although the various surface potential measurements¹⁰⁻¹⁵ are not in agreement, the various calculations¹⁶⁻²² of the molecular water orientation indicate that the oxygen up orientation is the preferred one. From the phase measurements it was inferred that the preferred orientation of the water molecule is the one where its dipole moment is directed toward the bulk water, i.e., the oxygen is up.²³



The implication of the preferred alignment of the interface water molecules is that there are a larger number oriented with their permanent dipole moments down than up. What the net population difference is at the interface cannot be determined from the phase measurements since the net population is determined by the energy difference between water oriented "up", i.e., in the upper quadrant ($0-90^\circ$) versus "down", i.e., the lower angular quadrant ($90-180^\circ$). One way to gain information on the average "up" versus "down" energy difference is to measure the temperature dependence of the SH signal. Although our earlier SH measurements^{24a} indicated a temperature dependence over the temperature range from 15°C to 80°C , more recent experiments in our laboratory and SF experiments^{24b} over a similar range indicate a change of less than 10% in the SH and SF signals. One of two different possibilities consistent with the very weak temperature dependence and the relatively weak SH signal, considering the very high number density of water, is that there is a wide distribution of water orientations due to a very small orientational energy barrier. The effect of temperature in the range studied would not alter the overall orientational distribution. Alternatively the structural demands at the interface, e.g., hydrogen bonding as well as electrostatic interactions, could result in a favorable structure where the water molecules were oriented close to parallel to the interface. This would yield a small SH signal due to cancellations from oppositely oriented molecules, though the SF signal would be fairly large because the O-H groups pointing out of the water would be frequency shifted from those in the water and would therefore not cancel each other. In any event, more extensive temperature dependent studies are necessary to differentiate the low- and high-energy possibilities.

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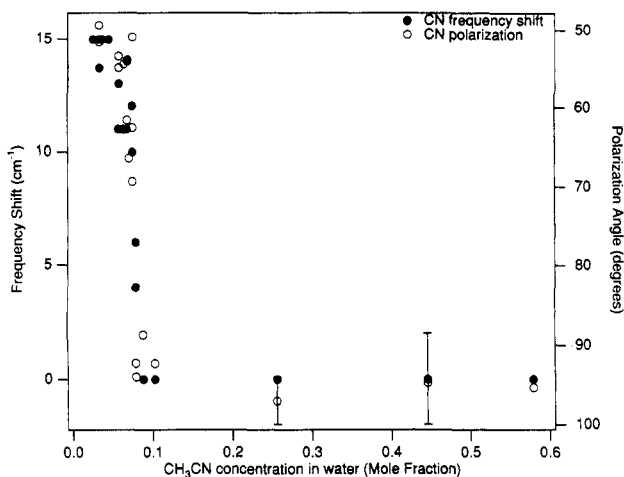


Figure 1. Compilation of frequency shifts of the resonance peak with respect to neat bulk acetonitrile absorption and polarization data for the CN transition of acetonitrile in the interface versus mole fraction of acetonitrile in the bulk water solution.

Surprising Phase Transition at the Air/Acetonitrile–Water Solution Interface

Infrared–visible sum frequency generation is a powerful analytical method for probing molecules at interfaces because it has the fingerprint sensitivity of vibrational spectroscopy.² It thus provides a valuable complement to second harmonic studies of interfacial molecular properties. Information on the orientation and environmental interactions of specific vibrational chromophores in a molecule can be obtained from measurements of the polarization of the SF light and from the frequencies of the vibrational transitions.^{2–5} Using the SFG method the orientational structure and environment of CD₃CN at the air/acetonitrile–water solution interface was investigated.²⁵ At low acetonitrile bulk concentrations the C≡N vibrational frequency was blue shifted with respect to neat bulk acetonitrile, which is consistent with the effects of hydrogen bonding and solvation on the vibrational frequencies of nitriles in bulk aqueous or alcohol solutions. The orientation of CD₃CN using a simple model was found to be about 40° to the interface normal below a CD₃CN bulk mole fraction of 0.07. Surprisingly, an abrupt change in both the orientation and chemical environment was observed above this. The frequency of the cyano SF signal showed a sharp red shift to a value close to that of the bulk acetonitrile interface, and at this same concentration a sharp change in the polarization of the SF occurred, corresponding to an orientation shift from about 40° to more than 70° (Figure 1). This sharp change was attributed to a phase transition in the interface, which appears to be the first case of a phase transition involving small mutually soluble molecules at a liquid interface.

Chemical Equilibria at Liquid Interfaces

In our first attempt to investigate how molecular forces at the liquid interface affect chemical equilibria, we used SHG to probe the acid–base reaction of

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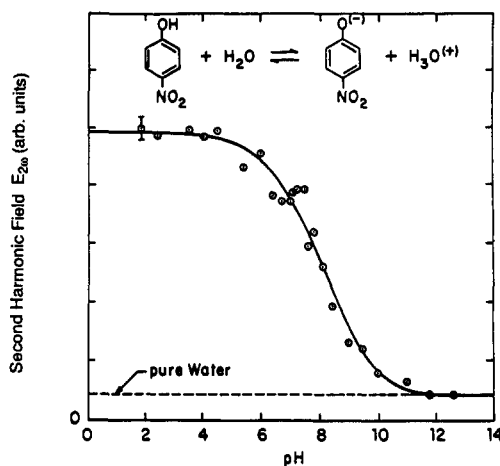


Figure 2. s-Polarized surface second harmonic field, $E_s^{2\omega}$ [$I_{\perp}^{1/2}(2\omega)$] of an aqueous solution of *p*-nitrophenol as a function of pH at 22 °C.

p-nitrophenol at the air/water interface.²⁸ The SH signal, which at low pH values was 100 times stronger than that of neat water, was observed to decrease as the bulk pH increased, (Figure 2). The surprising result occurred at high pH values (~12), where it was found that the SH signal had decreased to the value for the neat air/water interface. We thus learned that the anion (nitrophenolate) is not present at the air/water interface, but remains in the bulk water because the free energy of the bulk solvated anion is much lower.

Clearly it is not possible to measure the interface acid–base equilibrium constant when we cannot detect the population of the basic form. To overcome this problem, we lowered the surface free energy of the charged form by attaching hydrophobic groups to it, thereby forcing it to the interface. The systems chosen for study were para-substituted alkyl phenols and anilines.^{29,30} For the case of *p*-alkylphenols the bulk pH was adjusted so that the bulk contained only the phenolate form. It was found using SHG that not until the alkyl chain consisted of at least five carbons could the alkyl phenolate at the interface be detected. The dependence of the SH field on carbon chain length is shown in Figure 3 for both alkylphenolate and alkyl-anilinium ions. The increment in the SH field as the carbon chain length increases reflects the increase in the phenolate interface population. The interface population is determined, for a given bulk concentration, by the free energy of adsorption. If we view the adsorption process as the “reaction” of a bulk molecule with an empty surface “site” to give a filled “site”, and desorption as the reverse process, then we obtain the Langmuir adsorption equation,¹

$$N_s/N_{\max} = C/(C + a) \quad (2)$$

where N_s is the number/cm² of adsorbed solutes, N_{\max} is the maximum number in a monolayer, C is the bulk solute concentration, and $a = 55.5 \exp(\Delta G^{\circ}_{\text{ADS}}/RT)$, where 55.5 is the molarity of bulk water and $\Delta G^{\circ}_{\text{ADS}}$ is the adsorption free energy. For the adsorption of a charged molecule the $\Delta G^{\circ}_{\text{ADS}}$ consists of two parts. One

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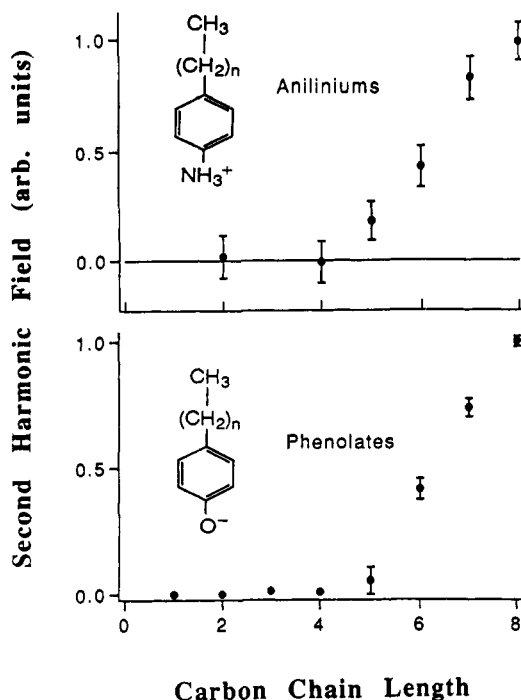


Figure 3. s-Polarized second harmonic field as a function of carbon chain length for phenolate and anilinium ions.

is an electrostatic part, ΔG°_{EL} , which is the reversible electrical work to bring a charge from the bulk, where the electrostatic potential is 0, to the interface, where the electrostatic potential is $\Phi(0)$. The remaining part is referred to as the chemical part, ΔG°_{CHEM} ,

$$\Delta G^{\circ}_{ADS} = \Delta G^{\circ}_{CHEM} + \Delta G^{\circ}_{EL} = \Delta G^{\circ}_{CHEM} + N_A z e \Phi(0) \quad (3)$$

where N_A is Avogadro's number and z is the valency of the adsorbed ion.

For all of the alkylphenolates and alkyaniliniums studied (carbon chain lengths from 6 through 8), the adsorption isotherms yielded excellent fits to a Langmuir adsorption equation. The relation between the alkylphenolate and alkyanilinium interface charge densities and the interface potential $\Phi(0)$ was obtained using the Gouy-Chapman model¹ of the charged interface, a model which is known to be applicable under the conditions of our experiments.³¹ From the fit are obtained the ΔG°_{CHEM} and the interface potential (Figure 4).

With the interface potential $\Phi(0)$, the surface population of hydronium ions, which is needed for the determination of the equilibrium constant, can be calculated using the Boltzmann equation,

$$(H_3O^+)_s = (H_3O^+)_B e^{-e\Phi/kT} \quad (4)$$

where the subscripts s and B refer to the surface and bulk regions. The equilibrium pK_A at the interface,

$$pK_a = pH_s + \log[(HA)/(A^-)] \quad (5)$$

is obtained from SH measurements that yield the population ratio $(HA)/(A^-)$ together with a determination of the interface charge density (A^-), which then yields the interface pH_s using eq 4. With this approach the interface pK_a of hexadecylanilinium $CH_3(CH_2)_{15}C_6H_4NH_3^+$ was found to be 3.6, which is a factor of 50

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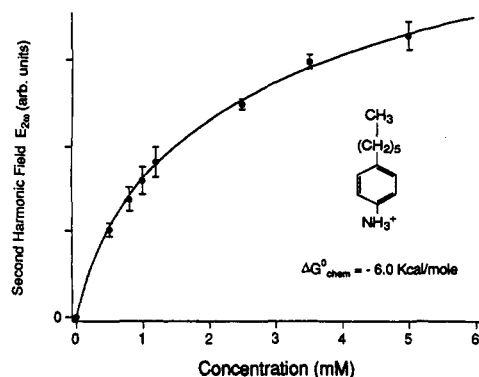
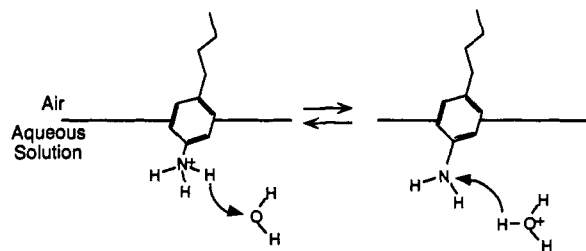


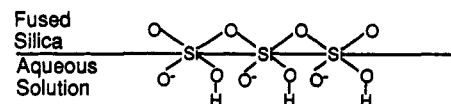
Figure 4. p-Hexylanilinium adsorption isotherm. The line represents the best fit to the Langmuir equation including the electrostatic term.



more acidic than the bulk equilibria where the pK_a is 5.3. In contrast to the anilinium case, it was found for the long-chain phenol $CH_3(CH_2)_{17}C_6H_4OH$ that the acidity decreased by a factor of 100. The pK_a at the interface is 12 versus 10 in the bulk. The observed decrease in acidity of the phenol derivative is attributed to the lower free energy of the neutral acidic form (HA) of the molecule versus its charged basic form (A^-) at the interface, whereas the acidic form of aniline (HA^+) is charged and has a higher free energy than its neutral basic form at the interface.

Acid-Base Equilibria at a Solid/Water Interface: Polarization of Water Molecules

In seeking to extend our studies of acid-base reactions and electrostatic potentials to other liquid interfaces, we decided to investigate the silica/water interface because of its widespread interest and importance.³²



The acidic moieties are the silanol groups (SiOH) that terminate the silica surface. The approach we used was the same as for the alkylphenols and alkyanilines at the air/water interface, namely, to measure the SH signal as a function of bulk pH and to relate this to the ratio of the charged to the uncharged populations. As can be seen from Figure 5 there are two plateaus in the SH electric field vs bulk pH, which suggests the presence of two silanol sites having different pK_a values. The very large increase (10^2) in the SH signal ($\sim |E_{2\omega}|^2$) as the pH increases indicates that the nonlinear polarizability of the SiO^- form is much greater than that of the neutral acidic form SiOH. These various inferences seemed just fine until we measured the dependence of

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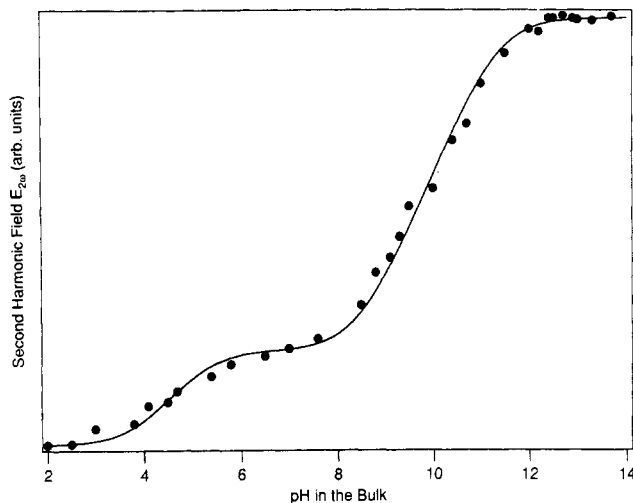


Figure 5. Second harmonic electric field (in arbitrary units) from the $\text{SiO}_2/\text{H}_2\text{O}$ interface as a function of pH in the bulk solution. The dots are experimental points, while the solid line is the theoretical fit with constant capacitance model. The percentage of site I, $\phi = 20\%$ with $\text{p}K_a(1) = 4.5$; the percentage of site II, $1 - \phi = 80\%$ with $\text{p}K_a(2) = 8.5$.

the SH signal on the bulk electrolyte concentration. At a given bulk pH we would expect that the number of SiO^- moieties would increase as electrolyte concentration increases due to the increased Debye screening. Since we inferred that $\alpha^{(2)}$ for SiO^- is greater than SiOH from the higher SH signal at high pH, we would predict that the SH signal should increase as electrolyte increases. However, we found that the SH signal decreased as the electrolyte concentration increased. We were troubled further by the results of the temperature dependence of the SH signal. At high pH (>12.5), where all ($>99.9\%$) of the silanols are ionized, we would predict that the SH signal should stay the same or decrease as the temperature was raised, depending on the sign of the enthalpy change for the acid-base reaction. We find that the SH signal increases with temperature at high pH, contrary to expectations. From the electrolyte and temperature results we concluded that the SH signal could not be due simply to the populations of the SiO^- and SiOH forms. It turns out that the SH is generated not only by a second-order process that depends on the populations and nonlinear polarizabilities $\alpha^{(2)}$ of all of the interfacial species, $\alpha_{\text{H}_2\text{O}}^{(2)}$, $\alpha_{\text{SiO}^-}^{(2)}$, $\alpha_{\text{SiOH}}^{(2)}$, but also by a third-order process arising from the very large electric field E_0 arising from the charged silica interface (SiO^-),

$$E_{2\omega} \sim P_{2\omega}^{(3)} = \chi^{(3)} E_0 E_\omega E_\omega \quad (6)$$

The field E_0 extends into the bulk solution and polarizes the water molecules, both by a third-order nonlinear polarizability $\chi^{(3)}$ and by the alignment of water molecules that breaks the bulk inversion symmetry. Depending on the electrolyte concentration, the field E_0 extends from tens to hundreds of angstroms into the bulk region. The total second harmonic signal is given by

$$E_{2\omega} \propto P_{2\omega} = \chi^{(2)} E_\omega E_\omega + \chi^{(3)} \Phi(0) E_\omega E_\omega \quad (7)$$

where $\Phi(0)$ is the electrostatic potential at the interface and results from the integration of the third-order polarization $P_{2\omega}^{(3)}$ from the bulk to the surface. It was

found that including the water polarization contribution, which dominates the SH signal at alkaline pH values, yields quantitative agreement with the electrolyte and temperature dependent results. Briefly the SH signal decreases with increasing electrolyte concentration due to the more rapid decay of the electric field (increased Debye shielding) with distance from the interface. Thus, fewer water molecules experience the polarizing electric field and the SH decreases. The increase in SH with higher temperature is due to the decrease in the dielectric constant, which increases the distance over which the electrostatic field extends. Fitting of the SH signal vs bulk pH with the polarization model yielded two silanol sites, one having a $\text{p}K_a$ of 4.5 occupying 20% of the sites and the other occupying 80% of the sites having a $\text{p}K_a$ of 8.5. One of the promising results of this study is that SHG can be used to measure the surface electrostatic potential at charged liquid interfaces.

Polarization of Water Molecules at an Air/Charged Monolayer Interface: Measurement of Interface Potential

The silica/water results suggest that if we had a charged monolayer at the air/water interface that had a smaller second-order nonlinearity, then we should be able to observe the polarization of the bulk water manifested in the $\chi^{(3)}$ term and thus be able to obtain the interface electrostatic potential. Indeed it was found that the third-order contribution ($\chi^{(3)}$) is a major part of the SH signal from the negatively charged monolayer, *n*-docosyl potassium sulfonate, $\text{CH}_3(\text{CH}_2)_{21}\text{SO}_3^- \cdots \text{K}^+$, and from the positively charged monolayer *n*-docosyltrimethylammonium bromide $\text{CH}_3(\text{CH}_2)_{21}\text{N}^+(\text{CH}_3)_3 \cdots \text{Br}^-$ at air/water interfaces.³³ The interface electric potential was determined to extend from -50 mV to -265 mV for the negatively charged monolayer $\text{CH}_3(\text{CH}_2)_{21}\text{SO}_3^-$ and from $+50$ mV to $+265$ mV for the positively charged monolayer $\text{CH}_3(\text{CH}_2)_{21}\text{N}^+(\text{CH}_3)_3$ depending on monolayer charge density and bulk electrolyte concentration.

Dynamics of Molecular Adsorption to an Air/Water Interface

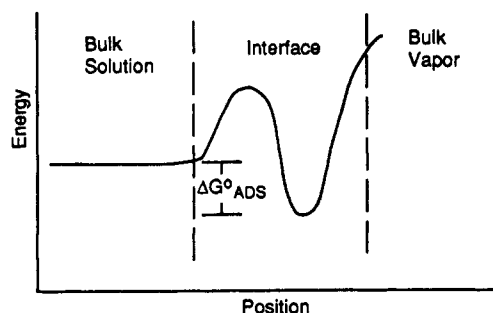
How long does it take a solute molecule in the bulk to diffuse to the interface, and in point of fact is the adsorption kinetics governed by diffusion? One way to investigate such dynamic processes at an air/liquid interface is to use a liquid jet. One of the useful aspects of a liquid jet is that the formation of the air/liquid interface immediately after the moving liquid exits the nozzle is probably not the equilibrium air/liquid interface. The population and structure of the initially formed air/liquid interface is determined by the interactions of the liquid molecules with the nozzle material and the liquid motions involved in forming the jet. The equilibrium air/liquid jet interface properties take time to develop. Measurements of the SH signal at various distances from the jet nozzle combined with knowledge of the jet velocity yield the time-dependent change in the air/liquid interface. Using an aqueous nitrophenol solution flowing through a glass nozzle to generate the liquid jet, the kinetics of

⁽³³⁾ Zhao, X.; Ong, S.; Eisenthal, K. B. *Chem. Phys. Lett.* 1993, 202, 513.

adsorption of nitrophenol to the air/solution jet interface was obtained.³⁴ It was determined that a time-



dependent Langmuir model yielded an excellent fit to the data. The adsorption rate constant is $4.4 \pm 0.2 \times 10^4 \text{ s}^{-1}$, and for desorption the rate constant is $6 \pm 2 \text{ s}^{-1}$. The adsorption free energy calculated from the kinetic data was found to be the same as that obtained from an equilibrium measurement of the static air/aqueous nitrophenol solution. This agreement supports the validity of the kinetic model since the free energy must be the same whether measured by a dynamic method that yields the forward and backward rate constants or by an equilibrium constant measurement that can only yield the ratio of the rate constants. With respect to the question of whether the kinetics was diffusion controlled, the answer is no. The rate constants were found to be time independent and considerably slower than that predicted by a diffusion process. Although all the dynamics up to the vicinity of the interface must surely be diffusive, it was suggested that an adsorption activation barrier of a few kilocalories/mole governed the adsorption kinetics.



Photoisomerization Dynamics

The liquid-phase kinetics of a unimolecular reaction such as an excited-state structural change can be described in many cases in terms of the barrier separating the reactant and product states, and the frictional force exerted by the solvent as the molecule moves on the reaction potential surface. Experimental and theoretical studies of photoisomerization in bulk solution have active areas of research that seek to understand the role of the solvent in so-called "simple" unimolecular reactions.³⁵ It is natural to extend these studies to liquid interfaces to determine how the unique features of the interface asymmetry affect the barrier to chemical reactions and the friction opposing barrier crossing.

Although there have been only a few studies of photoisomerization dynamics at interfaces, the results have been markedly different from those for their bulk solution counterparts.^{36,37} The first photoisomerization study at a liquid interface was on the dye molecule

3,3'-diethyloxadicyanone iodide (DODCI) at the air/water interface.²³ It was found that the cis-trans isomerization on the lowest excited singlet surface of DODCI is considerably faster at the interface (220 ps) than in bulk aqueous solution (520 ps). Whether the reaction potential surface is significantly different at the interface and thus effects a faster barrier crossing or the anticipated lower friction at the interface is predominant is not clear. A result that points to friction being the key factor was the observation that the reaction at the interface became faster when methanol was added to the solution and adsorbed to the interface whereas the rate becomes slower in the bulk with increasing methanol concentration.³⁹ The decrease in rate in the bulk could be attributed to the lower polarity of methanol, which results in an increase in barrier height, and not to an increase in viscosity since the viscosity at high methanol concentrations is less than the viscosity of neat water. If the lower polarity of the interface also results in an increased reaction barrier, then we conclude that it is the lower friction at the interface that is responsible for the faster isomerization rate.

Molecular Rotation at an Air/Water Interface

The investigation of rotational motions at liquid interfaces has been limited generally to fluorescent probes covalently attached to insoluble long-chain amphiphiles.^{40a} As a result the rotational motions are hindered by the bonding of the probe to the amphiphile and do not yield the "free" rotational motions of the fluorescent probe. The reason for tying the probe to an insoluble monolayer is based on the need to avoid the dominating fluorescence that would result from the probe bulk population. It has been possible in some cases where the fluorescent probe adsorption to the interface was very large to use a sufficiently small bulk population so that the bulk fluorescence could be neglected.^{40b} Unfortunately this is not the usual case.

It is possible, however, to selectively study the rotational motions of interface molecules using SHG even when there is a large population of the molecules of interest in the bulk solution. The method was first applied to Rhodamine 6G at the air/water interface.⁴¹ A picosecond pump pulse was used to perturb the equilibrium orientational distribution by photoselective excitation (Figure 6). The time-dependent change due to the rotational motions of the ground and excited Rhodamine 6G molecules moving toward their respective equilibrium orientations, as well as the decay of the photoexcited molecules, was observed by measurement of the SH signal from a probe pulse that was time delayed with respect to the pump pulse. The measured SH kinetics was attributed to rotational motions based on the observed polarization dependence of the kinetics. By controlling the polarization of the incident probe pulse and using an analyzer to select a given polarization of the SH light generated at the interface, the kinetics of different susceptibility elements $\chi_{ijk}^{(2)}$ were deter-

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(35) For a review, see: Waldeck, D. *Chem. Rev.* 1991, 91, 415.

(36) Meech, S. R.; Yoshihara, K. *Chem. Phys. Lett.* 1990, 174, 423-7.

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(38) This reference was deleted on revision.

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(40) (a) Anfinrud, P. A.; Hart, D. E.; Struve, W. S. *J. Phys. Chem.* 1988, 92, 4067. (b) Wirth, M. J.; Burbage, J. D. *J. Phys. Chem.* 1992, 96, 9022.

(41) Castro, A.; Sitzmann, E. V.; Zhang, D.; Eisenthal, K. B. *J. Phys. Chem.* 1991, 95, 6752.

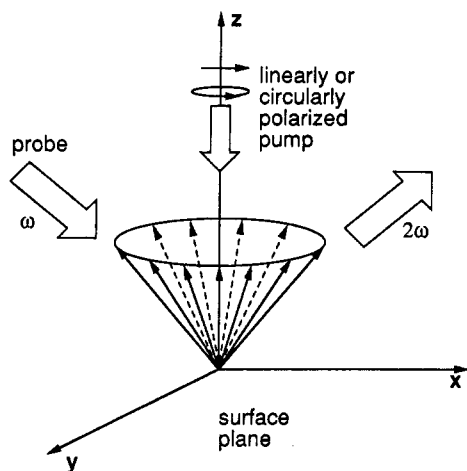


Figure 6. Schematic experimental setup. The arrows represent the molecular transition dipoles arranged to a common origin. The linearly or circularly polarized pump disturbs the equilibrium orientational distribution at the interface. The relaxation of the perturbed distribution is monitored by observing the SH signal (2ω) generated by a time-delayed probe (ω).

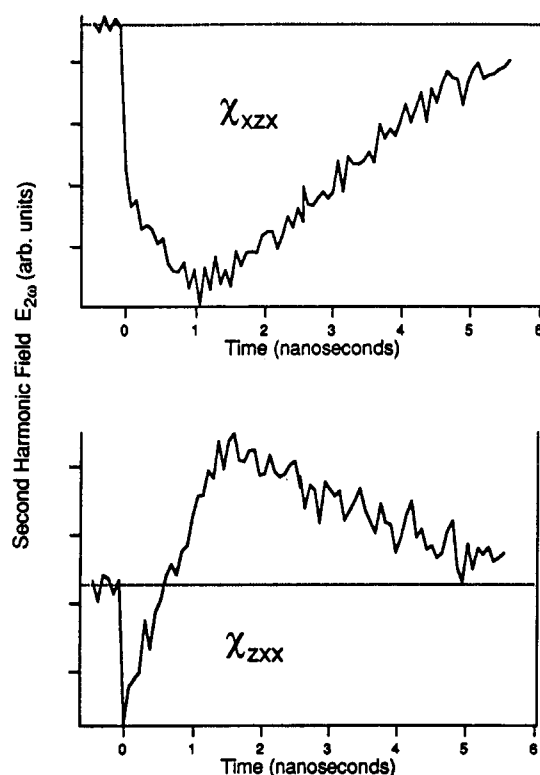


Figure 7. $\chi_{xzx}^{(2)}$ and $\chi_{zxx}^{(2)}$ components of the second harmonic signal from the surface of a $20\ \mu\text{M}$ Rhodamine 6G aqueous solution versus probe delay time.

mined. They were found to differ as anticipated for orientation relaxation kinetics (Figure 7). At the low concentrations used there was no change in the kinetics on doubling the concentration, indicating that the dynamics is not due to intermolecular energy transfer. The time scale of the rotations is in the range of several hundred picoseconds, which appears to be slower than the 200 ps in bulk water.⁴² However, different orientational moments are being probed by SH than in fluorescence.

A model of the interface motion is needed to extract the rotational constants. Unlike the bulk solution, the

rotation of the interface molecules is determined not only by the collision-induced time-varying torques but also by the asymmetric force field at the interface that favors certain molecular orientations. The molecular motions can be thought of as rotational diffusion in an external force field.

In addition to the "apparently" slower time scale for rotations, it was inferred from the SH measurements that the equilibrium orientation of the photoexcited molecules is different from that of the ground-state molecules possibly due to the change in dipole moment and charge distribution. In addition, the rotational motions were attributed to out-of-plane molecular motions, chiefly, i.e., motions perpendicular to the interface plane, on the basis of the observation that the kinetics was the same whether the pump pulse propagating normal to the interface was linearly polarized or circularly polarized. The linearly polarized pump light should induce an anisotropy in the plane of the interface whereas circularly polarized pump light would not. The absence of any observed difference indicates that the relaxation of this in-plane anisotropy was faster than the picosecond time resolution or that the effect of the anisotropy on the nonlinear susceptibility elements measured was small. Further experiments on rotations at interfaces will hopefully clarify these effects and in general provide information about the orientational force field at an interface and the friction at interfaces and its connection with a hydrodynamic description of molecular motions in this unique region of the liquid.

Summary

What I have tried to do in these few pages is to kindle further interest and activity in the study of the equilibrium and dynamic processes at liquid interfaces, in part by demonstrating the power of second harmonic and sum frequency spectroscopy to probe these ubiquitous and often elusive regions of matter. From the studies outlined in this Account we see that we can gain new fundamental information on the orientation of molecules, their energetics of adsorption, the changes in chemical equilibria at interfaces, and the effects of hydrogen bonding and solvation on the vibrational spectrum, as well as hydrogen bonding and solvation effects on the structure and unexpected phase transition of molecules at interfaces. When there are charged species at the interface, the resulting polarization of bulk water molecules can be investigated using these methods. The time-dependent phenomena including the kinetics of adsorption and desorption, the rotation of molecules in the anisotropic field of an interface, and the photochemistry of an excited-state isomerization can also be studied by SHG and SFG techniques. Besides the desire of scientists to probe the fundamental laws that govern the interesting world of interfaces, there is keen interest due to their important role in environmental, medical, and technology issues. These include the effects of pollutants on the abundant life processes that occur at the air/water interfaces of oceans, lakes, and rivers, as well as the impact of these air/water interfaces on the earth's weather and atmospheric chemistry. Similarly the aqueous/solid interface is crucial to our understanding the multitude of natural phenomena that occur in the soil as well as the

(42) Berndt, K.; Durr, H.; Palme, D. *Opt. Commun.* 1982, 42, 419.

development of new knowledge necessary to deal with the massive effects of pollution in our soils and ground waters. In my view the investigation of interfaces is in its earliest stages of development and, with the application of modern spectroscopic methods and theoretical modeling, great advances can be anticipated not only

in the fundamental science but in its application to important world problems.

My special thanks has to go to the members of my group and collaborators for venturing into this exciting area starting with our first efforts in 1986. My special thanks to Dr. J. Gutow for his comments and assistance.