Langmuir **1998,** *14,* 1472−1477

Molecules at Liquid and Solid Surfaces

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Received July 3, 1997. In Final Form: September 16, 1997

The discovery of structural phase transitions in a series of alkanenitriles, acetonitrile (CH_3CN), propionitrile (CH_3CH_2CN), nonadecanitrile [$CD_3(CH_2)_{19}CN$], but not butyronitrile ($CH_3CH_2CH_2CN$), at the air/water is described. Using sum frequency spectroscopy, the phase transition is manifested by an abrupt change in the orientation and an abrupt change in the vibrational frequency of the CN head group of the interface nitrile molecules. The competition between the distance dependent nitrile−nitrile dipolar interactions and the hydrogen bonding and solvation of the CN moieties is used to describe the phase transitions. A new application of second harmonic and sum frequency generation to study the interfaces of centrosymmetric microscopic particles is presented. Examples of this new use to the adsorption of molecules to a polystyrene microsphere/aqueous interface and the polarization of bulk water molecules by a charged microsphere of polystyrene sulfate are discussed.

Brian Bent

It remains difficult for me to comprehend and accept the reality that it is almost one year since Brian Bent died. I know that all of us continue to feel pain when we think of him and recall his smiling face, and his wonderful enthusiasm for science and for life. To the Columbia Chemistry Department Brian was not only seen as an extremely talented scientist and as a gifted teacher but also,of great importance to us, a person who truly cared about the well being of his students and his colleagues. The healing process is very slow. I believe that this symposium is a helpful and good thing to do, and I commend Professor Somorjai for organizing it. We all would agree that it is time to remember and enjoy the many good things that were part of Brian's life. Among them was Brian's love of science, and thus it is fitting that we celebrate in this symposium his life in science, and especially his love for surface science.

Introduction

In this paper we wish to describe two studies carried out in our laboratory on liquid and solid interfaces. One is the use of sum frequency generation (SFG), to probe recently discovered structural phase transitions in alkyl nitriles at air/aqueous solution interfaces. The series of nitriles, acetonitrile (CH_3CN), propionitrile (CH_3CH_2CN), butyronitrile ($CH_3CH_2CH_2CN$), and the water insoluble nonadecanitrile $CD_3(CH_2)_{19}CN$ provide insight into the role of hydrogen bonding, solvation, dipole−dipole interactions, and packing density on the observed phase transitions. The second topic deals with a recent discovery in our laboratory that makes it possible to selectively probe the surfaces of liquid and solid microscopic particles by second harmonic and sum frequency spectroscopy.

A. Alkyl Nitriles at Air/Water Interfaces

As we know there has been some excellent work on the use of SFG to study equilibrium properties such as the orientation and spectra of vibrational chromophores at interfaces[1−5] as well as dynamical studies of vibrational relaxation[6,7] at interfaces. In contrast to these investigations that focused on a single chromophore in a molecule of interest, we were motivated to use SFG to probe more than one chromophore on the same molecule. The idea was to probe different parts of an interface by observing the different chromophores of a given molecule. In particular we wanted to study flexible molecules and to monitor the changes in the mutual orientation and interactions of the two different chromophores as the composition and conditions at the interface were altered. With this in mind we selected CD_3CN at the air/water interface as a test case to establish whether we could measure the orientations of the CD_3 and CN chromophores in separate experiments and obtain the correct result that they had the same orientations.

The SFG experiments[8] used a picosecond laser beam at 532 nm and a picosecond tunable IR beam in the spectral region of 2000−2500 cm^{-1}. This infrared energy region includes the CD_3 (methyl) symmetric stretch and the CN vibrations of the nitriles. The two beams were incident at 70° to the interface normal and were in a counterpropagating geometry. Both the IR and visible beams were polarized parallel to each other and at 45° relative to the interface normal. The detected signal was s polarized. The experiments were carried out at a sufficiently low power that the SFG spectra and orientations of the CD_3 and CN chromophores were found to be independent of the input powers of the visible and IR beams.

It was found in SFG experiments at the IR wavelength corresponding to the CD_3 vibration, and in separate experiments carried out at the IR wavelength of the CN vibration, that the inferred orientations of the CD_3 and CN chromophores were the same. The molecular orien-

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(1) Dick, B.; Gierulski, A.; Marowsky, G.; Reider, G. A. *Appl. Phys.* **1985**, *B38*, 107.

(2) Hirose, C.; Akamatsu, N.; Domen, K. *Appl. Spectrosc.* **1992**, *46*, 1051.

(3) Stanners, C. D.; Du, Q.; Chin, R. P.; Cremer, P.; Somorjai, G.; Shen, Y. R. *Chem. Phys. Lett.* **1995**, *232*, 407.

(4) Messmer, M. C.; Conboy, J. C.; Richmond, G. L. *J. Am. Chem. Soc.* **1995**, *117*, 8039.

(5) Guyot-Sionnest, P.; Hunt, J. H.; Shen, Y. R. *Phys. Rev. Lett.* **1987**, *59*, 1597.

(6) Harris, A. L.; Rothberg, L. *J. Chem. Phys.* **1991**, *94*, 2449.

(7) Chabal, Y. J.; Dumas, B.; Guyot-Sionnest, P.; Higashi, G. S. *Surf. Sci.* **1991**, *242*, 524.

(8) Zhang, D.; Gutow, J. H.; Eisenthal, K. B.; Heinz, T. F. *J. Chem. Phys.* **1993**, *98*, 5099.

S0743-7463(97)00717-8 CCC: $15.00

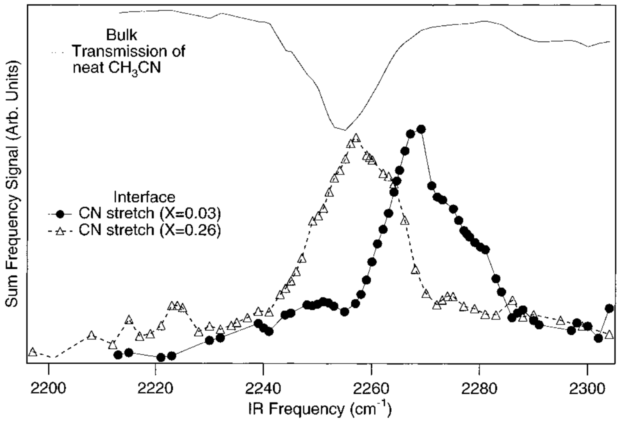

Figure 1. Solid line of the top trace is the transmission spectrum of neat bulk CH_3CN at the CN vibrational frequency using the same IR pulses as were used in the SFG experiment. The two bottom traces are the SFG spectra of the CN vibration at the air/aqueous nitrile interface at acetonitrile bulk mole fractions of $X = 0.03$ and 0.26.

tations were obtained by an analysis of the polarization measurements using a phenomenological method.[1-5] Although these results demonstrated that we could reliably obtain orientational information of different chromophores on the same molecule, we did obtain an unexpected result. It was that at low CD_3CN bulk mole fractions (<0.07), the tilt angle of the CD_3CN symmetry axis was 40 ± 4° to the interface normal, whereas at higher mole fractions the tilt was 70 ± 4°, i.e. closer to being parallel with the interface. A marked difference in the CN spectrum was also observed at low and higher CD_3CN concentrations (Figure 1). Below a mole fraction of 0.07, the CN frequency at the interface was blue shifted with respect to the CN frequency in neat bulk CD_3CN by 13 cm^{-1}. This was not surprising based on bulk solution studies[9,10] of nitriles that showed that the CN group is hydrogen bonded and solvated in protic liquids, such as water, with a concomitant blue shift in the CN frequency. The surprise was that above a mole fraction of 0.07 the CN interface frequency red shifted to within 1 cm^{-1} of its value in bulk neat acetonitrile. This finding indicated that the CN group was not hydrogen bonded and solvated by the water molecules at the higher acetonitrile concentrations. We thus see that there is a dramatic change in interfacial structure in going from low to higher acetonitrile concentrations. A plot of the CN frequency shift and molecular tilt angle as a function of the bulk CD_3CN mole fraction is given in Figure 2. The abrupt change in the orientation of CD_3CN and the abrupt change in the CN vibrational frequency at a particular concentration of bulk CD_3CN, which corresponds to a particular density of interfacial CD_3CN, shows that a structural phase transition has occurred at the air/solution interface. Raman measurements of the CN vibrational frequency in the bulk aqueous soution showed no discontinuity as the bulk acetonitrile concentration was varied but rather showed a smooth change from the fully hydrogen bonded and solvated CN group to the non-hydrogen-bonded CN in the neat bulk CD_3CN liquid. Furthermore we found no abrupt changes or discontinuity in the surface tension, or its slope, as a function of bulk acetonitrile concentration. At a bulk concentration of $X_{CD_3CN} = 0.07$, which is where the phase transition occurs, the surface tension measurements indicate that a monolayer of CD_3CN has formed.

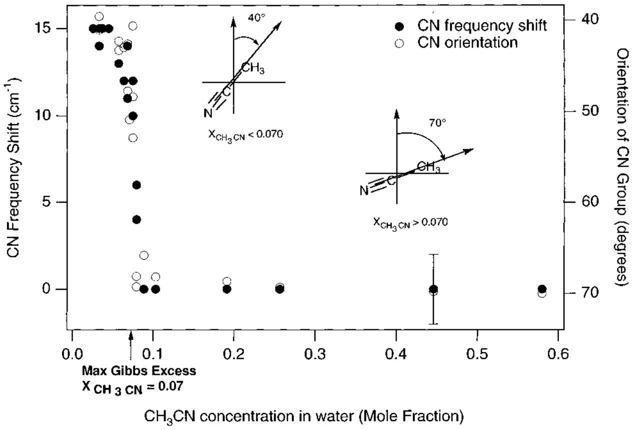

Figure 2. On the left axis sum frequency measurements of the CN vibrational frequency shifts of acetonitrile (CH_3CN) at the air/aqueous interface with respect to the CN vibrational frequency in neat bulk acetonitrile. On the right axis the molecular angle of CH_3CN obtained from measurements of the polarization of the sum frequency light. The abscissa is the mole fraction of acetonitrile in the bulk aqueous solution.

The acetonitrile interface density, expressed as area per molecule, is estimated using the surface tension method to be 24 Å^2/acetonitrile molecule at a bulk mole fraction of $X_{CD_3CN} = 0.07$.

We have developed the following physical model to describe the phase transition. At low surface densities the interfacial acetonitrile molecules are hydrogen bonded and solvated by neighboring water molecules, which result in an equilibrium molecular tilt angle of 40° for CD_3CN and a blue-shifted CN vibrational frequency. As the nitrile interface density increases, the neighboring water molecules that solvate the nitriles and screen the nitrile–nitrile dipole interactions are reduced in number. When the nitrile density is in the vicinity of a monolayer, the strong dipole interactions among the nitriles becomes sufficient to drive the nitrile orientations from the higher energy more upright tilt of 40° toward the energetically more favorable head to tail dipole configuration of 70°. In this flatter orientational structure the CN chromophore is no longer hydrogen bonded or solvated by water molecules and thus produces the abrupt red shift in the CN frequency. This unexpected structural phase transition involving small mutually soluble molecules (CD_3CN and H_2O) is the first such case to our knowledge of such a phase transition. It would be surprising if there were not many other examples of such interface structural phase transitions involving small molecules.

By extending this SFG study to include other members of the *n*-alkanenitrile series, we have obtained some insight into the effect of the alkyl part of the nitrile on the structural phase transition first observed for acetonitrile. SFG experiments[11] on the next member of the series, propionitrile (CH_3CH_2CN), indicated that an interface structural phase transition occurs at a bulk concentration $X_{PCN} = 0.011$, which from surface tension measurements corresponds to the maximum in the propionitrile interface density (Figure 3). The phase transition density occurs at 26 Å^2/molecule, with a spectral shift of 3 cm^{-1} and a change in CN orientation of 10 ± 4°. These changes in orientation and spectra are not as large as was observed for acetonitrile. The propionitrile remains blue shifted by 10 cm^{-1} with respect to the CN frequency in neat propionitrile, which indicates that there is still some

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(9) Fawcett, W. R.; Liu, G.; Kessler, T. *J. Phys. Chem.* **1993**, *97*, 9293.

(10) Ben-Amotz, D.; Lee, M. R.; Cho, S. Y.; List, D. J. *J. Chem. Phys.* **1992**, *96*, 8781.

(11) Zhang, D.; Gutow, J. H.; Eisenthal, K. B. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 539.

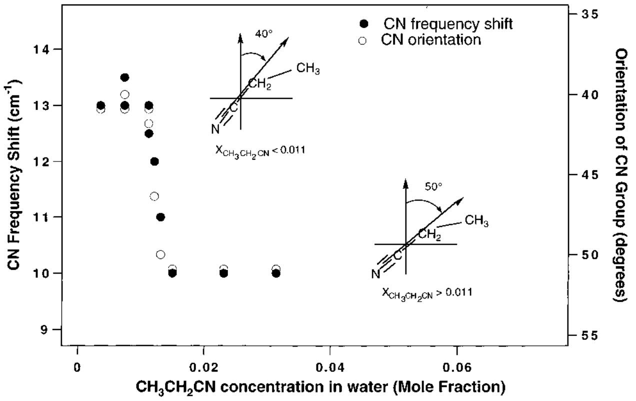

Figure 3. On the left axis sum frequency measurements of the CN vibrational frequency shifts of propionitrile (CH_3CH_2-CN) at the air/aqueous interface with respect to the CN vibrational frequency in neat bulk propionitrile . On the right axis the angle of the CN group obtained from measurements of the polarization of the sum frequency light. The abscissa is the mole fraction of propionitrile in the bulk aqueous solution.

hydrogen bonding and solvation by water on the high density side of the phase transition.

The results for butyronitrile at the air/water interface do not show a structural phase transition. At both the lower and higher butyronitrile concentrations the CN frequency remains shifted by about 13 cm^{-1} from its bulk neat liquid value. Similarly there is only a small change (~3°) in the CN orientation at the lowest vs the highest butyronitrile concentrations. It should be noted that at the lowest densities a CN orientation of 40° was found for all of the nitriles: acetonitrile, propionitrile, and butyronitrile at their respective air/solution interfaces. Similarly the CN frequencies are shifted by 13 cm^{-1} with respect to their bulk neat liquid values, for all of the nitriles at their lowest concentrations. We thus see that at sufficiently low concentrations it is the CN chromophore interactions with the water molecules that determine its orientation, irrespective of the attached alkyl groups. However as the interface densities are increased, the importance of the nitrile−nitrile interactions increases and the effects of the different sizes and conformations of the attached hydrocarbon group result in changes in the orientations and spectra of the CN chromophore. The different interfacial behavior for the three nitrile interfaces is attributed to the differences in the interfacial packing density that can be achieved for the various nitriles at the air/water interface. From surface tension measurements we find that the maximum interface density, expressed as area per molecule, is 32 Å^2 for butyronitrile, 26 Å^2 for propionitrile, and 24 Å^2 for acetonitrile. The lower surface density for butyronitrile is due not only to its larger excluded volume but most importantly to its small maximum bulk solubility, which in terms of mole fraction is $X_{\max} = 0.0085$. Efforts to increase the butyronitrile interface concentration by spreading it with a volatile solvent directly onto the water surface were not successful because the butyronitrile coalesced on the surface to form lenses. The maximum bulk solubility of propionitrile is $X_{\max} = 0.032$, and for acetonitrile $X_{\max} \rightarrow 1$ because acetonitrile and water are totally miscible at room temperature. We thus propose that when the maximum density of a nitrile at the air/solution interface cannot reach a sufficiently high value, as with butyronitrile, the nitrile−nitrile dipolar interactions do not reach a value sufficient to overcome the hydrogen bonding and solvation interactions of the CN moiety with neighboring water molecules. As a consequence, the change in the balance of intermolecular interactions, as the nitrile−nitrile separations become smaller, is not sufficient to cause a structural phase transition.

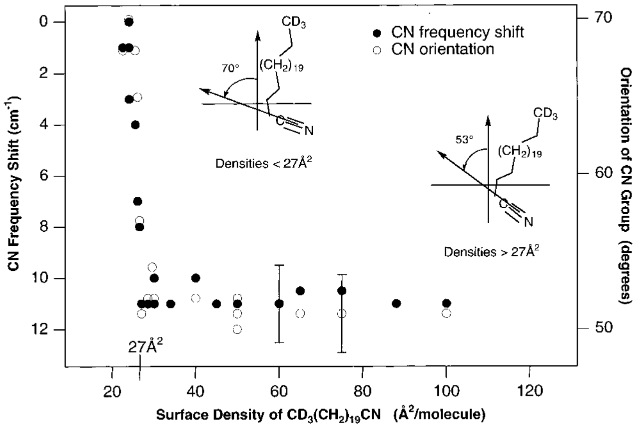

Figure 4. On the left axis sum frequency measurements of the CN vibrational frequency shifts of nonadecanitrile CD_3-$(CH_2)_{19}CN$ at the air/aqueous interface with respect to the CN vibrational frequency in neat bulk nonadecanitrile. On the right axis the molecular angle of the CN group obtained from measurements of the polarization of the sum frequency light. The abscissa is the $CD_3(CH_2)_{19}CN$ surface density.

We obtain a better understanding of the different interfacial behavior of these nitriles by considering SFG studies[12] from our laboratory on the insoluble long chain alkanenitrile, $CD_3(CH_2)_{19}CN$, at the air/aqueous interface. We observed a heretofore unknown structural phase transition in the orientation of the CN head group and alkyl chain of the $CD_3(CH_2)_{19}CN$ at an interface density in excess of 27 Å^2/molecule, or equivalently a density of 3.7×10^{14} molecules/cm^2 (Figure 4). The phase transition discovered for the long chain nitrile was of the same type as the phase transition observed for the short chain nitriles. At densities below 27 Å^2/molecule the CN head group of $CD_3(CH_2)_{19}CN$ is oriented at 53° to the interface normal and the CN vibrational frequency is blue shifted by 11 cm^{-1} with respect to its value in bulk solid $CD_3(CH_2)_{19}CN$. As with the shorter chain nitriles the blue shift of the long chain nitrile indicates that the CN group is hydrogen bonded and solvated by surrounding water molecules at the air/aqueous interface.

The density of 27 Å^2/molecule is the terminus point in the surface pressure vs density (area per molecule) phase diagram for $CD_3(CH_2)_{19}CN$ that separates the inhomogeneous gas plus liquid coexistence region from the homogeneous liquid phase region. Throughout the coexistence region the interface consists of liquid phase regions, where the nitrile density is exactly 27Å^2/molecule, and gas phase regions of very low nitrile density, which separate the liquid phase regions. At higher densities, i.e., slightly less than 27 Å^2, the nitrile separation decreases and we observe the new phase transition. The phase transition is characterized by a red shift in the CN frequency to the value corresponding to the non-hydrogen-bonded, non-water-solvated, bulk solid $CD_3(CH_2)_{19}CN$ value (Figure 4). At this same density the orientation of the CN head group changes from the more upright 53° orientation to a flatter 70° orientation. This is precisely what we observed for the phase transitions of the small chain nitriles. For $CD_3(CH_2)_{19}CN$ we also observe at a density slightly above 27 Å^2/molecule a discontinuous change in the orientation of the terminal CD_3 group of the alkyl chain to a more upright position.

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[12] Zhang, D.; Gutow, J. H.; Eisenthal, K. B. *J. Phys. Chem.* **1994**, *98*, 13729.

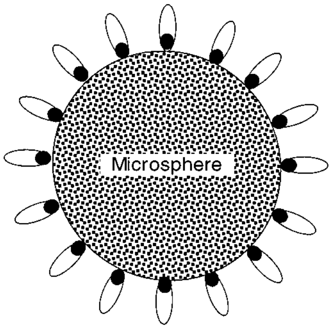
We have used these density dependent findings for the long chain nitrile to propose that a minimum density of 27Å^2/molecule is necessary to raise the nitrile−nitrile dipole−dipole interactions to a value sufficient to induce a reorientation of the CN head groups and thus produce a structural phase transition. If we now apply this proposal to the small chain nitriles, we see that both acetonitrile and propionitrile can achieve the minimum interface density of 27 Å^2/molecule necessary to trigger the phase transition. For acetonitrile the interface density of 24 Å^2/molecule and for propionitrile the interface density of 26 Å^2/molecule satisfy the requirement of a density above 27 Å^2/molecule. Unlike these two smaller nitriles, we find that butyronitrile can only achieve a maximum surface density of 32 Å^2/molecule and, thus, is predicted to not undergo a phase transition, consistent with our observations. We thus see for all of the nitriles, short as well as long chain, that it is the change in the balance of hydrogen bonding and solvation of the CN moiety by neighboring water molecules, in competition with the density dependent dipole interactions among the nitrile head groups, which triggers the phase transition when the nitrile density achieves some value in excess of 27 Å^2/molecule.

B. Interfaces of Microscopic Structures

In the past decade the interface selectivity of second harmonic and sum frequency generation has led to the development of second harmonic generation SHG and SFG as powerful methods to study the properties of a wide range of interfaces. The origin of their interface selectivity is the fact that SHG and SFG are electric dipole forbidden in centrosymmetric bulk media. Because the interface is noncentrosymmetric, strong SHG and SFG signals can be generated by molecules there, whereas molecules in centrosymmetric bulk media cannot. It is for this reason that we can detect a small interface molecular population in the presence of an overwhelmingly larger bulk population.

On examining the connection between symmetry and the allowedness or forbiddeness of SHG and SFG, we can uncover important new possibilities. The first step is to recognize that symmetry is a length dependent concept. For example if we consider a molecule such as *p*-nitroaniline, $NO_2-C_6H_4-NH_2$, we see that it is noncentrosymmetric on the molecular scale but that a single crystal of *p*-nitroaniline packs in its unit cell in such a way that the crystal is centrosymmetric. Similarly a water molecule is noncentrosymmetric, but liquid water is centrosymmetric on average. In a similar way it can be shown that although SHG and SFG are often described as being electric dipole forbidden in centrosymmetric systems, this conclusion is true only if the system is centrosymmetric on length scales much less than the coherence length of the process. This condition is not satisfied for micrometer size centrosymmetric particles because this size range is comparable to the coherence length of the process. The coherence length depends on the wavelength of the light used and the refractive indices at these wavelengths. Because the particle size and coherence length are of the same order, it follows that the induced second-order polarizations from “opposite” positions on the surface of the micrometer size particle do not cancel, as they would for smaller centrosymmetric structures (Chart 1).

Chart 1[a]



[a] Although the particle is centrosymmetric, the contribution of the oppositely oriented adsorbates, located on opposite sides of the microsphere, do not cancel, and a strong second harmonic and sum frequency signal can be generated.

We have recently carried out experiments that demonstrate the validity of this analysis.[13] Among the microscopic centrosymmetric particles that we have so far studied are molecules adsorbed to the surface of polymer beads (polystyrene and poly(styrene sulfate)), charged polymer bead (poly(styrene sulfate))/aqueous surfaces, oil droplet/water interfaces in emulsions, vesicles, and liposomes, clay particles, and semiconductor colloids. The sizes of the microstructures so far studied are in the range of 0.05 μm to several micrometers radii.

In this paper we will give two examples of the application of SHG to the investigation of microscopic surfaces. One demonstrates how the method can be used to measure the population of molecules adsorbed from the bulk solution to the interface of 1 μm polystyrene beads immersed in water. In addition the free energy of adsorption, which is the driving force for the adsorption, is also determined. The system consisted of an organic molecule, malachite green, as the interface adsorbing species. The laser system was an 82 MHz femtosecond Ti:sapphire laser that generated 100 fs pulses at 850 nm. A modified Langmuir model,[14] which included the decrease in bulk concentration due to surface adsorption, provided an excellent fit to the dependence of the second harmonic signal on the bulk concentration of the adsorbing species (Figure 5). Because of this excellent fit obtained from the SHG measurements, a free energy of adsorption of $\Delta G° = -12.2$ kcal/mol and a maximum number of malachite green adsorption sites, $N_{max} = 1.0 \times 10^6$ per polymer bead. It is worth noting that by this SHG method we obtain the absolute number of molecules/cm^3 adsorbed to the surfaces of the microscopic structures. To our knowledge this is the only method that can provide this information in situ. This is in contrast to such other methods that require the removal of the supernatant liquid for analysis, with the assumption that this removal of the supernatant liquid does not affect the population of molecules adsorbed to the particle’s surface. This SHG approach to obtain the $\Delta G°$ of adsorption and the absolute adsorbate concentration is equally applicable to other microscopic particles, e.g., oil droplets in an oil/water emulsion where it is of course not possible to separate any supernatant liquid for analysis.

The SHG signal from an interface is most commonly due to the second-order nonlinearity of the molecules adsorbed to the interface. However a SHG signal can also be generated by a higher order process when there are charges at an interface. The charges at the interface, which are charge balanced by the presence of counterions in the surrounding bulk solution, generate a static electric

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(13) Wang, H.; Yan, E. C. Y.; Borguet, E.; Eisenthal, K. B. *Chem. Phys. Lett.* **1996**, *259*, 15.

(14) Wang, H.; Yan, E. C. Y.; Liu, Y.; Eisenthal, K. B. Molecules at Microscopic Liquid and Solid Surfaces. Submitted to *J. Phys. Chem.* for publication.

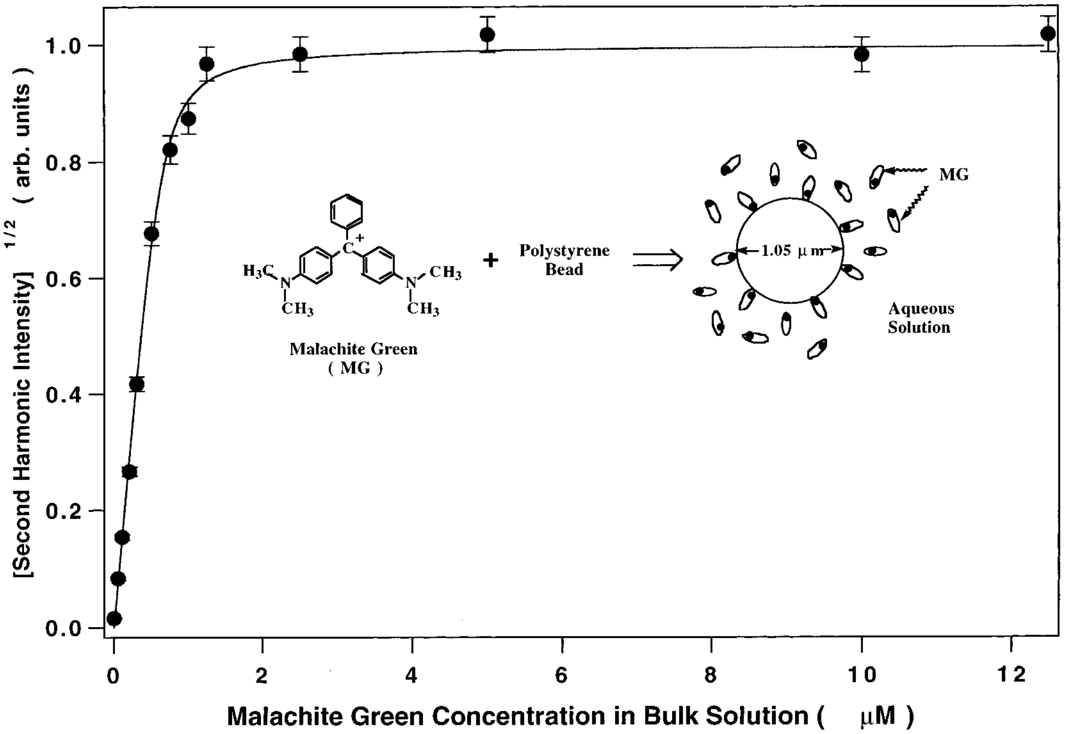

Figure 5. The square root of the second harmonic intensity vs the bulk concentration of malachite green in aqueous solution. The adsorption free energy $\Delta G° = -12.2 \pm 0.3$ kcal/mol and maximum number of malachite green sites, $N_{\max} = 1.0 \times 10^6$ on a single polystyrene bead. Density of beads is 8.25×10^8 cm^{-3}; bead diameter is 1.05 μm. Solid line is fit to modified Langmuir model.

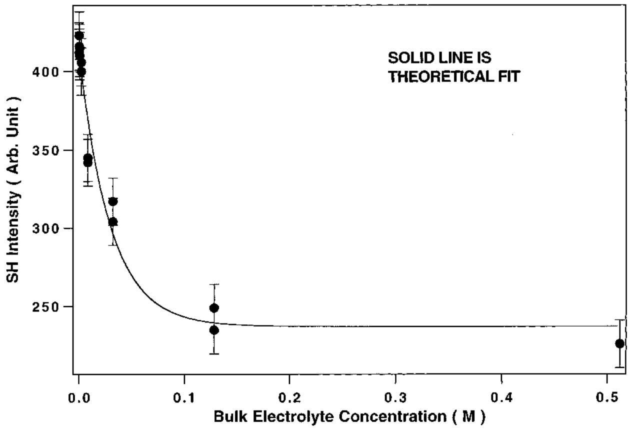

Figure 6. Second harmonic electric field = [SH intensity]$^{1/2}$ as a function of ionic strength for a bulk aqueous solution of 1.05 μm diameter charged poly(styrene sulfate) microspheres. Solid line is the theoretical fit of the SHG, arising from polarization of bulk water by sulfate charges on polystyrene microspheres, using the Gouy−Chapman model of the interface electrostatic potential, eq 1.

field in the bulk solution. This electric field polarizes the solvent molecules, destroys the local centrosymmetry in the bulk solution, and is responsible for a third-order contribution that generates an SHG signal. It should be noted that the total system remains centrosymmetric because the electric field on one side of the microscopic particle is balanced by an equal magnitude, oppositely directed static electric field due to the charges on the opposite side of the microscopic particle. The dependence of the electrostatic potential, responsible for the SHG, on surface charge density, temperature, and bulk electrolyte concentration is found to be in agreement with a Poisson−Boltzmann description of the electrostatics as contained in the Gouy−Chapman equation for the surface potential. In our previous work on charges at air/water[15] and solid silica/water[16] interfaces, we have shown that the SH signal is proportional to the interface potential $\Phi(0)$ expressed in the Gouy−Chapman model as

$$\Phi(0) = \frac{2kT}{e}\sinh^{-1}\left[\sigma_0\left(\frac{\pi}{2C\epsilon kT}\right)\right] \qquad (1)$$

where σ_0 is the interface charge density, e is the electronic charge, ϵ is the bulk dielectric constant, and C is the bulk electrolyte concentration. In Figure 6 the dependence of the measured SH electric field on bulk electrolyte concentration for an aqueous solution of 1 μm polystyrene sulfate spheres are shown. The solid line is the theoretical fit to the SH intensity, which is dependent on the electrolyte concentration as given in the Gouy−Chapman expression, eq 1. The observed decrease in the SH intensity as the electrolyte concentration is increased is due to the increased screening of the surface sulfate groups. This reduction in the penetration of the electric field into the bulk water reduces the polarization of the bulk water molecules and thereby results in a smaller third-order contribution to the SH signal. We have had similar success in describing the SH signal arising from surfactant charges at the surface of microscopic oil droplets in water emulsions. Using this second harmonic method, we have succeeded in determining the value of the electrostatic potential at the polystyrene sulfate microscopic surface. This new method for determining interface potentials of microparticles is being pursued and will be discussed further in a later publication.

Summary

In the first part of this paper we have described the discovery of a structural phase transition in the orientation

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[15] Zhao, X. L.; Ong, S. W.; Eisenthal, K. B. *Chem. Phys. Lett.* **1993**, *202*, 513.

[16] Ong, S. W.; Zhao, X. L.; Eisenthal, K. B. *Chem. Phys. Lett.* **1992**, *191*, 327.

of acetonitrile (CH_3CN), propionitrile (CH_3CH_2CN), and nonadecanitrile [$CD_3(CH_2)_{19}CN$] at their respective air/aqueous−nitrile solution interfaces. The abrupt change in the orientation and abrupt change in the vibrational frequency of the CN head group as the nitrile interface density is varied signal the phase transitions. The hydrogen bonding and solvation of the CN group by neighboring water molecules compete with the increasing CN−CN dipolar interactions as the nitrile surface density increases. At some nitrile density the dipole−dipole interactions win out and the orientation of the CN head group abruptly changes from a more upright to a flatter orientation. The absence of a phase transition for butyronitrile ($CH_3CH_2CH_2CN$) at its air/aqueous interface is attributed to the fact that butyronitrile is unable to achieve the surface density necessary to trigger the phase transition.

The last part of this paper described a new application of SHG and SFG to the study of the interfaces of centrosymmetric microscopic (∼1 μm) particles. Although the microparticles and the total system are centrosymmetric, it is shown that SHG and SFG are electric dipole allowed, contrary to what is commonly described for these second-order processes. Examples of the application of SHG to the adsorption of organic molecules to a polystyrene microsphere/aqueous interface and the generation of SHG due to a charged microsphere of polystyrene sulfate in aqueous solution were presented. This latter application offers promise as a new method for measuring the interface potential by a noninvasive spectroscopic method.

Acknowledgment. The author thanks the Division of Chemical Science of the Department of Energy for their support and the National Science Foundation for their equipment support.

LA9707179