Polarization of water molecules at a charged interface. Second harmonic studies of charged monolayers at the air/water interface

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The second harmonic generation from charged monolayers at air/water interfaces is shown to be linearly related to the interface electric potential. This dependence is due to the polarization of water molecules in the electrostatic field of the charged monolayer. The observed linear dependence of the second harmonic field on the interface electric potential serves as the basis of a proposed method for obtaining the interface potential, which it should be noted is a nonintrusive optical method. The work presented here also indicates that the Gouy–Chapman model is valid at the air/water charged interface up to at least a 1 M total electrolyte concentration.

1. Introduction

The second harmonic signal from neutral molecules located between centrosymmetric bulk media can usually be expressed in terms of a second-order nonlinear polarization,

$$P^{(2)}=\chi^{(2)}E_\omega E_\omega\,, \tag{1}$$

where $\chi^{(2)}$ is the second-order nonlinear susceptibility of the interface, and E_ω is the incident optical field at frequency ω [1]. When the interface is charged however the static electric field due to the charge can induce a third-order nonlinear polarization $P^{(3)}$. This can be an additional source for second harmonic generation [1–4]. The nonlinear polarization $P^{(3)}$ has both an electronic part and an orientational part due to the field-induced alignment of bulk molecules [5,6]. The second harmonic field $E_{2\omega}$, generated by the third-order polarization $P^{(3)}_{2\omega}$ can be expressed as [2–6],

$$E_{2\omega}\propto P^{(3)}_{2\omega}=\chi^{(3)}E_0E_\omega E_\omega\,, \tag{2}$$

where $\chi^{(3)}$ is the third-order nonlinear susceptibility of the solution and E_0 is the static field due to the surface charges. We have found this third-order process to be important at silica/water interfaces [7]. In fact the polarization of the bulk water molecules by the negatively charged $-SiO^-$ groups at the silica/water interface was found to be the dominant mechanism for generating the second harmonic signal. Support for these inferences was based on the quantitative agreement between the dependence of the SH (second harmonic) signal on bulk pH, electrolyte concentration and temperature, and the predictions of the third-order polarization model. It should be noted that in the early years of SH research there were pioneering studies on SHG (second harmonic generation) from bulk liquids where the SH signal was induced by externally applied static electric fields [6]. In addition there has been important work using SHG to study electrode surfaces [8–12].

In this Letter, we focus our attention on charged monolayers at air/water interfaces. Among the questions we will address are the following ones. Is the electric field-induced third-order polarization mechanism important? Is the value of $\chi^{(3)}$ dependent only on the bulk liquid and consequently the same for different water interfaces such as the silica/water interface and positively and negatively charged air/water interfaces? Is the measurement of the second

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harmonic signal of a charged interface a general method for obtaining the electric potential $\Phi(0)$ of an interface, independent of any interface electrostatic model? The two systems we have investigated are KCl aqueous solutions covered with either an insoluble monolayer of *n*-docosyl trimethylammonium bromide, CH_3-$(CH_2)_{21}N(CH_3)_3Br$, ($C_{22}NBr$), or an insoluble monolayer *n*-docosyl sulfonate potassium, CH_3-$(CH_2)_{21}$-SO_3K, ($C_{22}SK$). At the air/water interface $C_{22}NBr$ and $C_{22}SK$ ionize completely to form positively and negatively charged monolayers, respectively. The results obtained from these studies on the positively and negatively charged air/water and the silica/water interfaces demonstrate that SHG can be used to measure the interface electric potential $\Phi(0)$, and thus provides a new way to study electric phenomena at the interfaces of non-conducting materials [#1].

2. The origin of the second harmonic signal

The interaction of an electromagnetic field E_ω with a material can be described by the polarization P induced in the material. For the charged interface the polarization $P_{2\omega}$ responsible for the SH light field can be expressed in terms of the second-order $\chi^{(2)}$ and third-order $\chi^{(3)}$ susceptibilities,

$$P_{2\omega}=\chi^{(2)}E_\omega E_\omega+\chi^{(3)}E_\omega E_\omega E_0 \, . \tag{3}$$

The $\chi^{(2)}$ contribution is electric field independent and arises chiefly from the molecules at the interface whereas the $\chi^{(3)}$ contribution can arise from both the interface and bulk species. Since the static electric field extends into the bulk solution it is expected that the $\chi^{(3)}$ contribution to the second harmonic signal is dominated by the large number of bulk water molecules. Although the bulk counter-ions can contribute through their third-order electronic polarizability, we found from studies of the silica/water interface that the second harmonic signal was the same for Li^+ and Na^+ counter-ions. This indicates that at least for these counter-ions their contribution to $\chi^{(3)}$ can be neglected. The magnitude of the third-order nonlinear polarization, which we refer to as the $\chi^{(3)}$ contribution, is thus determined by the electronic nonlinear polarizability $\alpha^{(3)}$ of water, the degree of alignment of water molecules by the static field E_0, and the magnitude of the field E_0. In the absence of a static field the water molecules beyond the first few layers would be randomly oriented [14]. They would consequently not contribute to the SH signal via the electric dipole part of the $\chi^{(2)}$ term. However, in the presence of charged molecules at the interface the centro-symmetry experienced by the bulk water molecules is broken. The alignment of the water molecules by the static field enables them to contribute to the nonlinear polarization $P^{(3)}_{2\omega}$ and the generation of second harmonic light.

Because the static field extends into the bulk solution all bulk water molecules that are subject to this field can contribute to $P^{(3)}_{2\omega}$. Their contribution is obtained by integrating $P^{(3)}_{2\omega}$ from the interface at $z=0$ to $z=\infty$, i.e. well into the bulk liquid, where the electric field has decayed to zero. Thus,

$$P^{(3)}_{2\omega}=\chi^{(3)}E_\omega E_\omega \int_0^\infty E_0 \, dz \, . \tag{4}$$

Assuming that $\chi^{(3)}$ does not vary with z, which essentially means that any variation in the density of water from the vicinity of the liquid interface into the bulk solution can be neglected, and using the relation between the electric field $E_0(z)$ and the electric potential $\Phi(z)$, we obtain

$$\begin{aligned} P^{(3)}_{2\omega} &= -\chi^{(3)}E_\omega E_\omega[\Phi(\infty)-\Phi(0)] \\ &= \chi^{(3)}E_\omega E_\omega \Phi(0) \, , \end{aligned} \tag{5}$$

where $\Phi(0)$ is the potential at the interface and $\Phi(\infty)$, the potential well into the bulk solution is set equal to zero. The total second harmonic signal due to the second- and third-order polarizations is given by

$$E_{2\omega}\propto P_{2\omega}=\chi^{(2)}E_\omega E_\omega+\chi^{(3)}\Phi(0)E_\omega E_\omega \, . \tag{6}$$

The linear relationship between the measured SH field $E_{2\omega}$ and the interface potential $\Phi(0)$,

$$E_{2\omega}=[A+B\Phi(0)]E_\omega E_\omega \, , \tag{7}$$

provides a new and direct method for measuring interface electric potentials. The quantity A contains the $\chi^{(2)}$ and B the $\chi^{(3)}$ contributions to $E_{2\omega}$. In sec-

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[#1] For a discussion of electrical phenomena at interfaces, see ref. [13].

tions 3 and 4 of this Letter we will test the validity of eq. (7) by determining whether the variation of $E_{2\omega}$ with electrolyte concentration and surface charge density obeys this equation. In addition we will determine the relative importance of the A and $B\Phi(0)$ terms for negatively and positively charged monolayers.

3. Experimental

n-$C_{22}NBr$ was synthesized from n-$C_{22}Br$ and trimethylamine. n-$C_{22}SK$ was synthesized from the $KMnO_4$ oxidation of $C_{22}SH$. All samples were purified by recrystallization at least five times before use. The spreading solvent, chloroform is HPLC grade. All water used was double distilled from $KMnO_4$. KCl was heated up to 600°C for purification. Monolayers were prepared with a 0.1 mM spreading solution at the aqueous solution surface.

The SHG experiment, which has been described before consists of an Ar^+ sync-pumped and cavity-dumped dye laser at 600 nm [15]. The signal passing through a monochromator is detected by a PMT and recorded by a single-photon counting system. The SH signal from monolayer was normalized to that from the neat air/water.

4. Results and discussion

4.1. *Effects of electrolyte and charge density on SH signal*

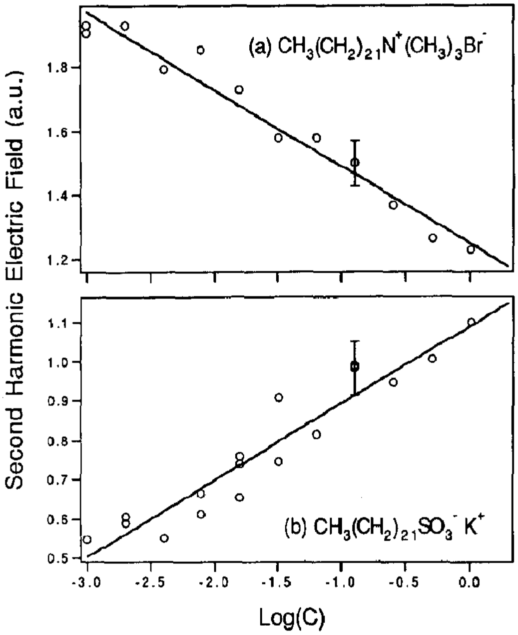

Fig. 1. Second harmonic electric field versus log C, C=total bulk electrolyte concentration (mol/ℓ) for (a) the positively charged monolayer of CH_3-$(CH_2)_{21}N(CH_3)_3Br$, ($C_{22}NBr$), and (b) the negatively charged monolayer of CH_3-$(CH_2)_{21}$-SO_3K, ($C_{22}SK$) at the air/water interfaces.

We have measured the dependence of the second harmonic field $E_{2\omega}$ on the KCl bulk electrolyte concentration for positively and negatively charged monolayers at an interface coverage of 50 Å^2/charge. In complementary experiments the dependence of $E_{2\omega}$ on the area/charge at a fixed electrolyte concentration of 1 mM were performed. In figs. 1a and 1b the s-polarized component of the second harmonic field, i.e. perpendicular to the plane of incidence (YZ) and thus parallel to the interface (X), is shown in a semilog plot as a function of bulk electrolyte concentration. The only susceptibility components that can generate X polarized second harmonic light are $\chi^{(2)}_{xzx}$ and $\chi^{(3)}_{xzxz}$, where the last subscript on $\chi^{(3)}$ gives the direction of the static field E_0. The strong dependence of $E_{2\omega,x}$ on the bulk electrolyte concentration indicates the importance of the $P^{(3)}_{2\omega}$ term since the $\chi^{(2)}_{xzx}$ term has no significant dependence on electrolyte concentration. To fit eq. (7) to the measured second field $E_{2\omega}$ it is necessary at this point to have an explicit expression for the interface potential $\Phi(0)$ in terms of electrolyte concentration and interface charge density σ, where $\sigma=1/A$ and A=area per charged molecule. Fortunately there is a model of the interface potential, namely the Guoy–Chapman model, which has been shown to be applicable at the air/water interface under the same conditions as that of our experiment [16]. For a 1:1 electrolyte the interface potential is given by

$$\Phi(0)=\frac{2kT}{ze}\sinh^{-1}\left(\sigma\sqrt{\frac{\pi}{2\epsilon kTC}}\right), \qquad (8)$$

where C is the total bulk electrolyte concentration and z is the sign of the charged monolayer. The fits of eq. (7) to the second harmonic measurements as a function of the bulk electrolyte concentration at a fixed surface charge density are shown in figs. 1a and 1b. The dependence of $E_{2\omega}$ on electrolyte concentration is contained in the interface potential, eq. (7), and not in the constants A and B. The good fit of the experimental data to eq. (7) supports the model used to describe the origin of the second harmonic signal. It may be noted that the linear dependence of $E_{2\omega}$ on $\log C$, as seen in figs. 1a and 1b, reflects precisely the logarithmic dependence of a $\sinh^{-1}$ function under our experimental conditions. In figs. 2a and 2b we see that the complementary experiments of $E_{2\omega}$ versus the surface charge density σ, at a fixed electrolyte concentration of 1 mM, are also in agreement with the model expressed in eq. (7).

The response of the second harmonic signal to electrolyte concentration and surface charge density can be understood in terms of the third-order polarization. As the electrolyte concentration decreases the Debye–Hückel screening length becomes larger resulting in more bulk molecules interacting with the static field E_0 and thus contributing to the third-order polarization. Similarly as the surface charge density σ increases the electric field increases in magnitude. The increase in E_0 increases both the third-order electronic contribution and the orientational contribution to $\chi^{(3)}$. Both the decrease in bulk electrolyte and the increase in charge density results in a larger third-order polarization. The net effect of this on the generated second harmonic field $E_{2\omega}$, according to the model contained in eq. (7), depends on the sign of the monolayer. As seen in eq. (8), the sign of the interface potential $\Phi(0)$ is opposite for positively and negatively charged monolayers. This in turn means that the effect of the third-order polarization term $B\Phi(0)$ on the second harmonic field $E_{2\omega}$, is predicted to be opposite for positively and negatively charged monolayers. Considering the positively charged monolayer, for which the sign of $\Phi(0)$ is positive, we conclude from fig. 1a, which shows a decrease of $E_{2\omega}$ with increasing electrolyte concentration and from fig. 2a, which shows an increase of $E_{2\omega}$ with increasing charge density σ, that the sign (or phase) of the constants A and B are the same. For the negatively charged monolayer the dependence of electrolyte and charge density on the second harmonic signal as shown in figs. 1b and 2b are opposite to the positive monolayer. A physical model consistent with these observations is the following one. For the positive monolayer, the effect of A and $B\Phi(0)$ having the same sign is to enhance $E_{2\omega}$ as the magnitude and interaction length of the static field E_0 increases. The electric field E_0 of the positive monolayer preferentially aligns the water molecule with its dipole moment directed toward the bulk, i.e. protons down and oxygen up. If the preferred alignment of the water molecules due to forces at the interface other than that of E_0 favor the same water dipole orientation, then the predicted result would be an increase in the second harmonic signal as the length of interaction increases (lower electrolyte concentration) and as the field E_0 increases (increase in positive charge density). From earlier experiments on the alignment (absolute orientation) of water molecules at the air/neat water interface it was concluded that the preferred orientation of water is the dipole moment pointing toward the bulk water [17]. This earlier finding is in accord therefore with the observations on the positively charged monolayer interface. For the negatively charged monolayer the field E_0 would preferentially align the water

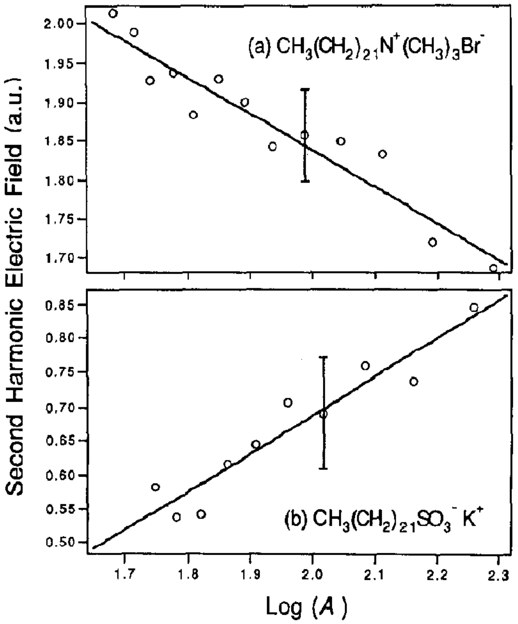

Fig. 2. Second harmonic electric field versus log A, A=inverse charge density (area Å^2/charge) at a fixed electrolyte concentration of 1 mM for (a) the positively charged monolayer of CH_3-$(CH_2)_{21}N(CH_3)_3Br$, ($C_{22}NBr$), and (b) the negatively charged monolayer of CH_3-$(CH_2)_{21}$-SO_3K, ($C_{22}SK$) at the air/water interfaces.

dipoles with the protons pointing up toward the interface. This field-induced alignment opposes the alignment in the absence of interface charges. The partial cancellation due to these opposing forces results in a reduction of the second harmonic signal as the electrolyte concentration decreases and the negative charge density increases.

We therefore conclude on the basis of the electrolyte concentration and charge density studies of the negatively and positively charged interface that the contribution of the nonlinear polarization $P_{2\omega}^{(3)}$ is essential to any description of the SH signal originating from these interfaces.

4.2. *Symmetry test of the polarization model*

A further quantitative test of the third-order polarization model derives from the relationship between the various elements of the B (effective $\chi^{(3)}$) tensor. It has been shown for weak to intermediate electric field strengths,

$$\frac{\mu E_0}{kT} < 1 , \tag{9}$$

where μ is the permanent molecular dipole moment, that

$$B_{zzzz} = 2B_{xzxz} + B_{zxxz} . \tag{10}$$

The last index is the E_0 field direction [5]. Thus the determination of the different elements of B is a further test of whether the third-order field-induced polarization of the water molecules contributes to the SH signal. We see from table 1 that the relation of B elements given by eq. (10) is satisfied.

The values of A_{xzx} and B_{xzxz} can be obtained from the measured dependence of $E_{2\omega}$ on electrolyte concentration as well as from the dependence of $E_{2\omega}$ on surface charge density. The values obtained in these two ways are summarized in table 2. The values of B_{xzxz} obtained from the electrolyte and charge density experiments are in good agreement. It should be noted that the second harmonic signal and hence the signal to noise for the negatively charged monolayer

Table 1

Values of different elements of $B(\chi^{(3)})$: comparison of experimental results with theoretical prediction. Upper part: For positively charged monolayer of CH_3-$(CH_2)_{21}N(CH_3)_3Br$, ($C_{22}NBr$) at air/water interface. Lower part: For silica/water interface

B_{xzxz} ($\times 10^{-3}$)	B_{zxxz} ($\times 10^{-3}$)	B_{zzzz} ($\times 10^{-3}$)	$2B_{xzxz}+B_{zxxz}$ ($\times 10^{-3}$)
1.2±0.2	1.2±0.2	4±1	3.6±0.6
1.3±0.4	1.3±0.4	4.1±0.4	3.9±0.4

Table 2

Values of A ($\chi^{(2)}$) and B ($\chi^{(3)}$) (eq. (7)) for charged monolayers at air/water interfaces, the silica/water interface, and the air/neat water interface

	A_{xzx}	A_{zxx}	B_{xzxz} ($\times 10^{3}$)	B_{zxxz} ($\times 10^{3}$)
$C_{22}NBr$ [a]	0.89±0.14	0.40±0.15	1.2±0.2	1.2±0.2
$C_{22}NBr$ [b]	0.96±0.17		1.2±0.2	
ave. ($C_{22}NBr$)	0.93±0.17		1.2±0.2	
$C_{22}SK$ [a]	1.36±0.14		1.0±0.2	
$C_{22}SK$ [b]	1.72±0.17		1.4±0.2	
ave. ($C_{22}SK$)	1.54±0.17		1.2±0.2	
silica/water	0.3±0.05	0.30±0.05	1.3±0.4	1.3±0.4
air/neat water	1.0±0.04	0.38±0.04	0.96 [c]	0.96 [c]

[a] From $E_{2\omega}$ versus log C plot, C = total bulk electrolyte concentration.

[b] From $E_{2\omega}$ versus log A plot, A = inverse charge density (area/charge).

[c] B value for water in the bulk calculated using literature values [6,18], presented as the ratio of $\chi^{(3)}$ of water to $\chi^{(2)}$ of air/water interface.

is not as good as for the positively charged monolayer because the A and $B\Phi(0)$ partially cancel each other for the negative monolayer. Nonetheless it is clear that the B values for the negatively charged and positively charged monolayers are equal with an average value of 1200±200. The A values for the negatively and positively charged monolayers are close to $A=1$, which is the value for the neat air/water interface. This indicates that most of the effective $\chi^{(2)}$, i.e. the A value, is due to water. The deviation from 1.0 is due to the contribution of the negative (SO_3^-) and positive ($N^+(CH_3)_3$) head groups to the effective $\chi^{(2)}$ value. Because the A values for the monolayers are of the same order of magnitude as the neat air/water interface we can use the $A\approx1$ value and the $B\approx1200$ value to estimate the ratio of the second- to the third-order polarizabilities of water. We can then check if this ratio is consistent with published data. We note that A or the effective $\chi^{(2)}$ is related to $\alpha^{(2)}$ by $\chi^{(2)}=N_s\langle\alpha^{(2)}\rangle$ and B, or the effective $\chi^{(3)}$, is related to $\alpha^{(3)}$ by $\chi^{(3)}=N_0\times(\langle\alpha^{(3)}\rangle+\mu\langle\alpha^{(2)}\rangle/bkT)$, where b is a constant depending on the element measured, N_s and N_0 are the density of water at interface and in the bulk, respectively [5]. Using $N_s\approx10^{15}$ water molecule/cm^2 and $N_0=3.35\times10^{22}$ molecule/cm^3 the ratio of $\alpha^{(2)}$ to $\alpha^{(3)}$ is 10^4–10^5. This is in agreement with literature values [6].

4.3. Measurement of surface electrostatic potential by SHG

An important part of any description of a charged interface is the interface potential. It is a major factor in determining the interface population of ions and thereby controlling equilibria involving charged species such as acid–base reactions, electron transfer reactions, and interface pH. In the following discussion, we will show how the electric potential can be obtained using SHG, independent of an electrostatic model of the charged interface. The relation between the second harmonic field and the interface potential is expressed in eq. (7). If the values of the constants A and B, which respectively contain the $\chi^{(2)}$ and $\chi^{(3)}$ susceptibilities, are known then a measurement of the SH signal will yield the electric potential of the interface. We have found that the values of B for the ammonium monolayer ($C_{22}NBr$), which is a positively charged surfactant, and for the sulfonate monolayer ($C_{22}SK$), which is a negatively charged surfactant, are the same. In other words, it is the water that determines the $\chi^{(3)}$ and thus the value of B. In fact our finding that the value of B at the silica/water interface is the same as at air/water interfaces, indicates that B depends only on the bulk liquid. The values for B_{xzxz} and B_{zxxz} at the silica/water interface are 1300±400 [#2], which is in agreement with the 1200±200 value for both the positively and negatively charged air/water interfaces. The remaining issue in order to obtain the interface potential from eq. (7) is the value of the A constant, i.e. the effective $\chi^{(2)}$ of the interface. If we could determine the value of A for the interface at a given surfactant density and electrolyte concentration, then we could directly obtain the interface potential from a measurement of the SH signal. Although we are not able to evaluate A independent of an electrical double layer model at this time we can show that having once obtained A, for example from an electrical double layer model we can use it under conditions where the model is no longer applicable. This was done for the silica/water interface where A was obtained at an electrolyte concentration for which the Gouy–Chapman model is applicable. Eq. (7) was then used for the interface at higher concentrations where the Gouy–Chapman model fails. We found that the interface potential versus pH using eq. (7) agreed with the results fitted to the appropriate model of the electrical double layer at a high electrolyte concentration, namely the constant capacitance model [19–21] as shown in fig. 3. For the air/water interface we can also evaluate the electric potential from measurements of the SH signal since it turns out that the value of A for the charged interfaces is close to that of neat water. This means that the $\chi^{(2)}$ for water is greater than the $\chi^{(2)}$ values for the surfactants. This result follows from the much greater surface density of water than that of the surfactants and the small value of the surfactant second-order nonlinear polarizabilities. We find that the ratio of the A_{xzx} element to the A_{zxx} element for the positively charged $C_{22}NBr$ air/water interface is 2.5, which is in agree-

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[#2] In a previous paper [7], B_{xzxz} and B_{zxxz} were mistakenly indicated to be different. The correct data are presented in table 1 of this Letter.

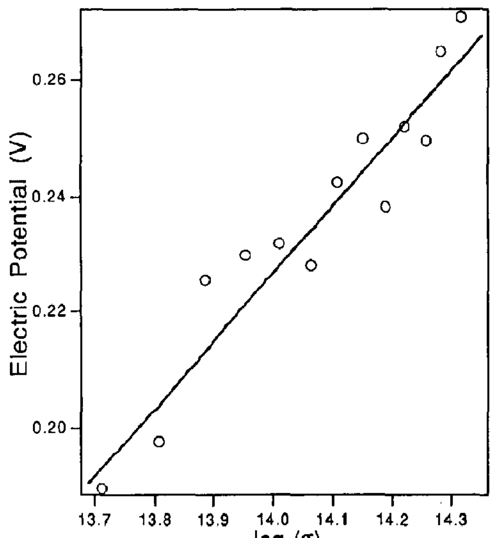

Fig. 3. Surface potential measurements at the silica(quartz)/H_2O interface by SHG versus pH in the bulk solution at 0.5 M electrolyte concentration. (+) Calculated using constant capacitance model; (○) model independent calculation from SH data with single reference point.

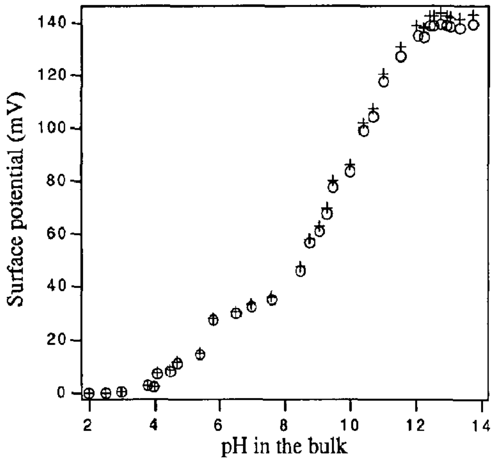

Fig. 4. Surface potential as a function of surface charge density (number of charges/cm^2) for the positively charged monolayer of CH_3-$(CH_2)_{21}N(CH_3)_3Br$, ($C_{22}NBr$) by (○) SHG measurements and (——) SH/SHG calculation with the Gouy–Chapman model of the charged interface.

ment with the value of 2.3 found at the air/neat water interface. This result supports the idea that the water component is the most important contributor to the value of A. Further support for this result is seen in a comparison of the A_{zxx} values for the silica/water interface, the $C_{22}NBr$ air/water interface and the air/neat water interface. In arbitrary units, the value is 0.30 ± 0.05 for silica/water, 0.40 ± 0.15 for $C_{22}NBr$ air/water, and 0.38 ± 0.04 for the air/neat water interface. We therefore see that no large error is made in using the A_{zxx} value of the air/neat water interface for these other water interfaces.

A further illustration that SHG can be used to obtain the surface electric potential $\Phi(0)$ is seen in the dependence of the SH signal on the surface charge density of $C_{22}NBr$ at the air/water interface. Using the value of A for the neat water interface and the B value we have obtained for bulk water, we can directly use eq. (7) to plot $\Phi(0)$ versus surface charge density. This is then compared with the calculation of $\Phi(0)$ as a function of surface charge density using the Gouy–Chapman model at an electrolyte concentration where the Gouy–Chapman has been shown to be valid. The results presented in fig. 4 show that the agreement is excellent. We thus conclude that SHG is a new method for obtaining the electric potential $\Phi(0)$ at a nonconducting material interface, independent of any electrostatic model of the interface. The proviso, which we have emphasized in our discussion of eq. (7), is that the A value must be determined in some way. For monolayers with head groups such as in the positively charged trimethyl ammonium ($N^+(CH_3)_3$), the negatively charged sulfonate (SO_3^-), and the silica/water interface we found that the A value of the air/neat water interface can be used.

5. Conclusions

The polarization of bulk and interface water molecules by charged monolayers at air/water interfaces and the charged silica/water interface, is shown to be a major contributor to the second harmonic signal generated when a laser beam is incident on these interfaces. This third-order ($\chi^{(3)}$) contribution to the second harmonic field is found to be proportional to the electric potential at the charged interface and serves as the basis for a proposed method to measure the electric potential of an interface. The conditions under which this optical method can be used to obtain the interface potential independent of any electrostatic model of the interface are discussed. Using SHG the interface electric potential were determined to be in the range of −50 to −265 mV for the negatively charged monolayer CH_3-$(CH_2)_{21}$-SO_3K, and from +50 mV to +265 mV for the positively charged monolayer CH_3-$(CH_2)_{21}N(CH_3)Br$, depending on the monolayer charge density at the air/water interface and the bulk electrolyte concentration. At the silica/water interface, the interface electric potential varied from zero to −160 mV, depending on pH, bulk electrolyte concentration and temperature. A comparison of the observed dependence of the second harmonic signal on electrolyte concentration and surface charge density with the predictions of the Gouy–Chapman model of a charged interface demonstrate the validity of the Gouy–Chapman model for these monolayer charged air/water interfaces up to at least a 1 M bulk electrolyte concentration.

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