

# Polarization of water molecules at a charged interface: second harmonic studies of the silica/water interface

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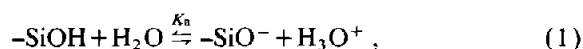
Surface second harmonic generation was used to probe the silica/water interface. At pH values where the silica surface is charged, we found that the water molecules near the interface are polarized by the interfacial electric field and are responsible for the observed second harmonic light. Two types of silanol sites having  $pK_a$  values of 4.5 and 8.5 were inferred from the data. A promising result of the studies was the development of a new method for obtaining electric potentials at charged liquid interfaces.

## 1. Introduction

Despite the importance and widespread interest in liquid/solid interfaces it remains a difficult task to experimentally probe these interfaces with conventional spectroscopic methods [1]. With the emergence of the nonlinear technique of second harmonic generation a new method is now available to selectively probe the interface region [2,3]. This method should prove to be of particular importance in probing buried interfaces, such as the liquid/solid interface. In this paper we wish to report the use of second harmonic generation to study the fused silica/water interface. We chose the fused silica/electrolyte because of the wide spread interest in and importance of silica/liquid interfaces. In particular we were interested in extending our studies of acid-base reactions at the air/water interface [4,5] to other liquid interfaces. In this case it is the silica/water interface where the acidic moieties are silanol ( $-\text{SiOH}$ ) groups, which terminate the silica surface. By measuring the second harmonic signal as a function of the solution pH we hoped to obtain new information on the charges, the potential, and the acid-base equilibrium constants of the various silanol sites.

It is well known that the silica surface becomes negatively charged in neutral or basic aqueous so-

lutions [6]. The surface silanols ionize progressively to produce the negatively charged  $-\text{SiO}^-$  groups as the solution pH is increased. A number of different studies including NMR [7-9], IR [10], and potentiometry [11-13], have indicated that there are at least two types of silanol groups at the aqueous solution/silica suspension interface. The acid-base equilibria for the various types of silanol sites at the silica interface are of the form



where  $K_a$  is the equilibrium constant for a given type of site. Using the technique of second harmonic generation we hope to determine the  $K_a$  values at the aqueous solution/fused silica (quartz) interface. All previous studies have been carried out on aqueous suspensions of silica, often referred to as gel, fumed and precipitated, i.e. not on planar silica interfaces [6]. The general approach we will use to obtain the  $pK_a$  values of the surface silanols is the same as we used previously for acid-base equilibria of alkylphenols and alkyilanilines at the air/aqueous interface [4]. In this approach we obtained from SH measurements the ratio of the charged and uncharged densities at the interface. Combining the interface charge density with an electrical double layer model, such as that of Gouy-Chapman, we obtained the surface potential. From the surface potential and the bulk pH we could calculate the interface pH. The

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$pK_a$  is then readily found, being equal to the sum of the surface pH and the logarithm of the basic to acid interface densities. The experiments to be described therefore involve the measurement of the SH signal as the change in bulk pH changes the interface  $-\text{SiOH}/-\text{SiO}^-$  populations. A similar approach has been independently developed to determine the  $pK_a$  of hemicyanine dye molecules embedded in a negatively charged stearic acid monolayer at the air/water interface [14].

## 2. Experimental

The experimental setup, described previously [15], consists of a synchronously pumped picosecond dye laser and a single photon counting detection system. The sample cell is made of teflon, or stainless steel for temperature experiments, and tightly covered with an Esco  $60^\circ$  equilateral fused silica prism. The incoming polarized laser beam at 600 nm was incident on the fused silica prism/liquid interface at  $67^\circ$  from the interface normal. The reflected SH light was detected at 300 nm.

The fused silica prism was cleaned thoroughly with methanol, sodium hydroxide solution and mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  and rinsed with distilled water and doubly distilled water before use. Fisher standard HCl and NaOH solutions were used to adjust pH of aqueous solution prepared from doubly distilled water and NaCl for controlling the electrolyte concentration. NaCl was heated up to  $600^\circ\text{C}$  for more than 6 h before use. The pH of electrolyte solutions was measured with a Corning pH meter.

## 3. Results

The variation of the second harmonic electric field  $E_{2\omega}$  with bulk pH is shown in fig. 1. The increase in  $E_{2\omega}$  starts at about pH 4 and is followed by a plateau and then a second rise at about pH 8 with a final plateau above pH 12. This behavior is characteristic of the titration of a diprotic acid, which in this case suggests the presence of two silanol sites. The increase in the second harmonic field,  $E_{2\omega}$ , with pH indicates that the nonlinear susceptibility of the interface is greater when the silanol groups are ionized. If we ex-

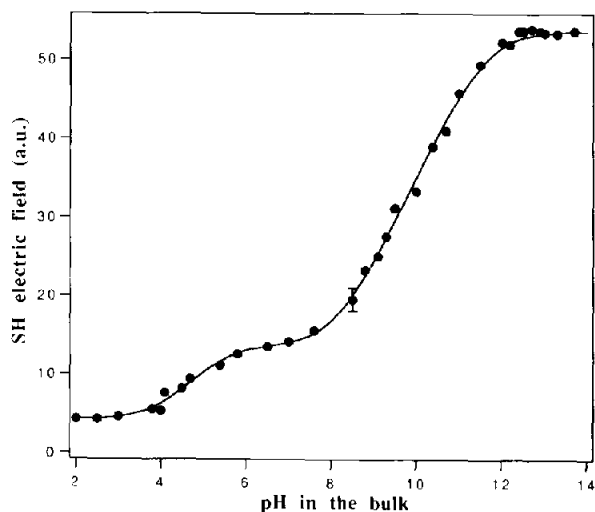


Fig. 1. SH electric field (in arbitrary unit) as a function of pH in the bulk solution. The dots are experimental points, while the solid line is the theoretical fit with constant capacitance model. The percentage of site I,  $\phi = 19\%$  with  $pK_a(1) = 4.5$ ; the percentage of site II,  $1 - \phi = 81\%$  with  $pK_a(2) = 8.5$ .

press the second harmonic field  $E_{2\omega}$  in terms of the nonlinear susceptibility  $\chi^{(2)}$ , which we then write in terms of the surface densities  $n$  and the nonlinear polarizabilities  $\alpha^{(2)}$ , we obtain

$$E_{2\omega} \propto P_{2\omega}^{(2)} = \chi^{(2)} E_{\omega} E_{\omega} \\ = (n_{\text{SiOH}} \alpha_{\text{SiOH}}^{(2)} + n_{\text{SiO}^-} \alpha_{\text{SiO}^-}^{(2)}) E_{\omega} E_{\omega}, \quad (2)$$

where the two different sites are implicit in  $n$  and  $\alpha^{(2)}$ ,  $P_{2\omega}$  is the nonlinear polarization and  $E_{\omega}$  is the incident optical field. In terms of the nonlinear polarizabilities of the ionized and neutral silanols, the results shown in fig. 1 suggest that  $\alpha_{\text{SiO}^-} \gg \alpha_{\text{SiOH}}$ . It should be noted that we know of no other experimental or theoretical studies that could be used to check this inference.

### 3.1. Dependence of second harmonic generation on electrolyte concentration

Prompted by the need to test the validity of the model (2), which we have used to explain the change in the SH signal with solution pH, we investigated the effect of solution electrolyte concentration and temperature on the SH signal. The effect of increas-

ing the electrolyte concentration at a fixed pH, should be to increase  $n_{\text{SiO}^-}$  due to the increased Debye screening. Indeed it is known from studies on silica gels that the density of negatively charged sites, i.e.  $-\text{SiO}^-$  groups, increases with increasing electrolyte concentration [16,17]. Since the interpretation of our SH results in terms of the model given by eq. (2) indicates that  $\alpha_{\text{SiO}^-} \gg \alpha_{\text{SiOH}}$ , we would predict therefore that the SH signal would increase with electrolyte concentration. However, we found the opposite result, namely that the SH signal decreases with increasing electrolyte concentration. Fig. 2 shows the results carried out at two different pH values.

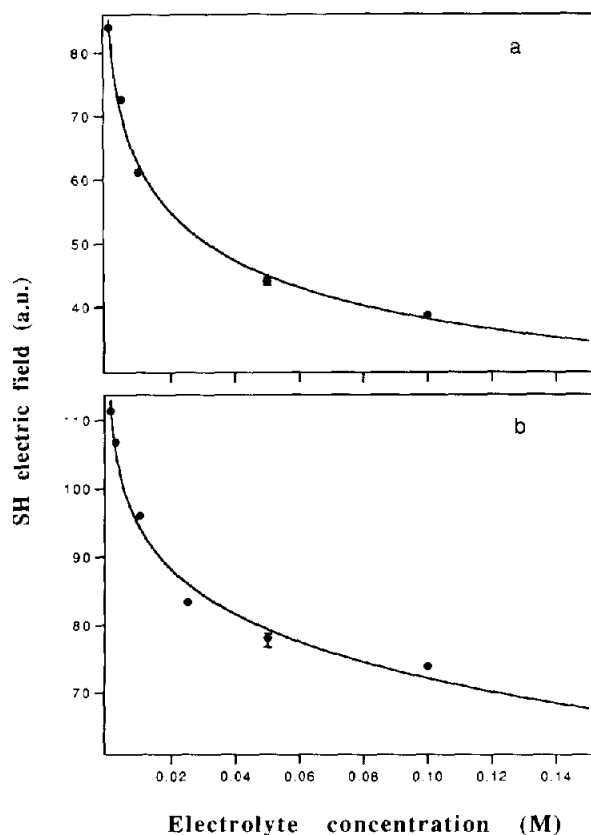


Fig. 2. SH electric field as a function of total electrolyte concentration for pH 5.8 (a) and pH 10 (b), respectively. The dots are experimental points, the solid lines the theoretical fits to eqs. (8) and (19).  $D=40.6$  and  $\sigma_{\text{max}}=0.87 \times 10^{14} \text{ cm}^{-2}$ .

### 3.2. Temperature dependence of second harmonic signal

Before proceeding to a discussion of the electrolyte result we consider the effect of temperature on the SH signal. If with increasing temperature the equilibrium shifts toward the product side ( $-\text{SiO}^-$  and  $\text{H}_3\text{O}^+$ ), i.e. the equilibrium constant  $K_a$  increases, then the second harmonic signal should also increase. This follows since we have observed that the nonlinear susceptibility regardless of model, increases as the surface is converted to the ionized silanol groups  $-\text{SiO}^-$ . If however with increasing temperature the equilibrium moves toward the reactant side, the neutral silanol (the enthalpy change being exothermic), then the SH signal should decrease. Since we do not know if the acid-base reaction is endothermic or exothermic we cannot predict how the SH signal will change with temperature based on the preceding considerations. However, if we adjust the solution pH to a value greater than 12.5, then effectively all ( $> 99.9\%$ ) of the silanols will be in the ionized  $-\text{SiO}^-$  form. Thus the SH signal could not further increase with temperature; it would either stay the same or decrease depending on the sign of the enthalpy change. In fig. 3 we see that the signal increases with temperature at a solution pH of 12.7, contrary to predictions based on the model (2). We thus infer from the electrolyte and temperature experiments, that the origin of the SH signal cannot be

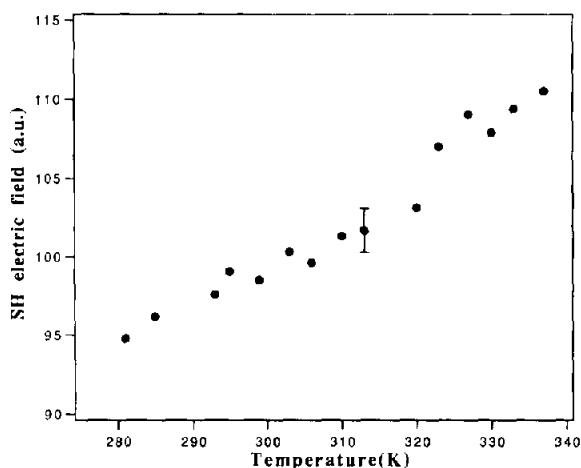


Fig. 3. SH electric field as a function of temperature at pH 12.7 and 0.5 M electrolyte concentration.

simply described in terms of the second-order nonlinear polarization  $P_{2\omega}^{(2)}$  given in eq. (2).

### 3.3. Polarization of water molecules by the charged interface

What then can account for the very large increase (factor of  $10^2$ ) observed in the SH signal as the pH of the solution is increased? A key point to be considered is that in going from low to high pH the interface is transformed from a neutral surface to a highly charged one. The electric field at the interface can achieve values in excess of  $10^6$  V/cm for a surface density of  $10^{14}$  charges ( $-\text{SiO}^-$ ) per  $\text{cm}^2$ . At such a large electric field the SH signal can be generated by a third-order process, in addition to the second-order process given by eq. (2). The third-order process involves the action of three electric fields on the material. For the oxide/water interface one of the fields is the static electric field due to the charged interface. The second harmonic field  $E_{2\omega}$  due to this third-order process is given by [18–23]

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

where  $\chi^{(3)}$  is the third-order nonlinear susceptibility and  $E_0$  is the static electric field in the interfacial region. The electrostatic field extends into the bulk solution interacting with the water molecules and the counterions. The  $\chi^{(3)}$  contribution to the SH signal is chiefly due to the water molecules. Although the counterions can contribute through their third-order electronic hyperpolarizability our experimental results are the same for different counterions, e.g.  $\text{Li}^+$  versus  $\text{Na}^+$ , indicating that the contribution of the counterion to  $\chi^{(3)}$  is negligible. The magnitude of  $\chi^{(3)}$ , due to the bulk water molecules, can have two distinct origins. One is the contribution of the third-order electronic nonlinear polarizability  $\alpha^{(3)}$  of a water molecule. The other contribution is due to the alignment of water molecules by the static electric field  $E_0$  due to the charged interface. The water molecules in this region, specifically those water molecules not in contact with the oxide interface, would be randomly oriented and would not contribute via the second-order term  $\chi^{(2)}$ , to the SH signal. However in the presence of an electric field due to the charged interface the centrosymmetry experienced by the bulk water molecules is broken. The align-

ment of the water molecules by the static field  $E_0$  contributes to the SH signal as expressed in the nonlinear polarization term  $P_{2\omega}^{(3)}$  in eq. (3). If we express the third-order nonlinear susceptibility  $\chi^{(3)}$  in terms of the molecular properties of water, for the case where the static orienting interaction  $\mu E_0$  is less than the thermal energy  $kT$  we obtain [22,23]

$$P_{2\omega}^{(3)} = \chi^{(3)} E_0 E_\omega E_\omega \\ = n_{\text{H}_2\text{O}} \left( \alpha_{\text{H}_2\text{O}}^{(3)} + \frac{\mu \alpha_{\text{H}_2\text{O}}^{(2)}}{bkT} \right) E_0 E_\omega E_\omega, \quad (4)$$

where  $n_{\text{H}_2\text{O}}$  is the density of water (molecules/ $\text{cm}^3$ ),  $\alpha_{\text{H}_2\text{O}}^{(3)}$  is the third-order electronic polarizability of water,  $\mu$  is the permanent dipole moment of water,  $\alpha_{\text{H}_2\text{O}}^{(2)}$  is the second-order electronic polarizability of water and  $b$  is a constant determined by the particular susceptibility element under consideration.

Since all of the water molecules that are subject to the static field  $E_0$ , which extends into the bulk solution will contribute to  $E_{2\omega}$ , we include their contribution by integrating from the interface at  $z=0$  to  $z=\infty$ . Thus

$$P_{2\omega}^{(3)} = \chi^{(3)} E_\omega E_\omega \int_0^\infty E_0(z) dz, \quad (5)$$

where we have assumed that the density of water molecules does not change significantly from the vicinity of the silica/aqueous solution interface to the solution far from the interface. The relation between the electric field  $F_0(z)$  and the potential  $\Phi(z)$  yields

$$P_{2\omega}^{(3)} = -\chi^{(3)} E_\omega E_\omega [\Phi(\infty) - \Phi(0)] \\ = \chi^{(3)} E_\omega E_\omega \Phi(0), \quad (6)$$

where the potential at infinity, i.e. far into the bulk, is set equal to zero. Although important work has been carried out on the electric-field-induced second harmonic generation by application of an external field across a bulk water sample [22], there is little experimental evidence of the orientation and alignment of water molecules at a charged interface. There is no work to our knowledge on charged oxide/aqueous interfaces. There is however evidence from IR intensity studies of a metal (Pt) electrode/water interface that the water molecules change their orientation from one that is parallel to the metal surface at the point of zero charge (pzc) to one where the

water molecules "stand up", with the oxygen end toward the metal, as the potential goes in the positive direction [24].

To account for the second harmonic signal over the pH range extending from low pH where the silanols are in their neutral form, to the high pH-SiO<sup>-</sup> region, we must include a  $\chi^{(2)}$  as well as a  $\chi^{(3)}$  contribution. This follows from our observation of a SH signal at low pH values (pH < 3) where the silica surface is neutral ( $E_0=0$ ) and the third-order polarization  $P_{2\omega}^{(3)}$  does not contribute. The expression for  $E_{2\omega}$  is thus written as

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

where  $\chi^{(3)}$  is given by eq. (4) and  $\chi^{(2)}$  contains contributions from the silanols and the electric field independent contribution of interfacial water molecules.

#### 3.4. Comparison of water polarization model with SH results

Let us consider now whether the electrolyte and temperature dependences of the SH signal as contained in eq. (7) are in accord with the SH experimental results. As discussed earlier we have found that the  $\chi^{(2)}$  dependence on electrolyte concentration does not account for our experimental findings. If the third-order mechanism is dominating at intermediate and high pH values, where the charged surface is present, then the dependence of  $E_{2\omega}$  on electrolyte is contained in the surface potential  $\Phi(0)$ . There is no dependence of  $\chi^{(3)}$  on electrolyte as can be seen from eq. (4). If we use the Gouy-Chapman model for the charged interface, which is reasonable at moderate electrolyte concentrations (< 0.1 M) [25-28], then the SH field  $E_{2\omega}$ , which is proportional to the surface potential, is given by

$$E_{2\omega} \propto P_{2\omega} = \chi^{(2)} E_{\omega} E_{\omega} + \chi^{(3)} \frac{2kT}{e} \sinh^{-1} \left( \sigma_0 \sqrt{\frac{\pi}{2C\epsilon kT}} \right) E_{\omega} E_{\omega}, \quad (8)$$

where  $e$  is the electronic charge,  $\sinh^{-1}$  is the inverse hyperbolic sine,  $\sigma_0$  is the surface charge density,  $\epsilon$  is the bulk dielectric constant and  $C$  is the total bulk electrolyte concentration. Indeed we see that eq. (8) predicts that  $E_{2\omega}$  should decrease with increasing

electrolyte concentration, in agreement with our experimental results. As shown in fig. 2 the fitting of the SH data to eq. (7) yields good agreement with experiment. The fitting treats the  $\chi^{(2)}$  contribution as a static field independent constant term and the potential  $\Phi(0)$  is obtained from the Gouy-Chapman model. The fitting of both sets of data, one at pH 5.8 and the other at pH 10, used three parameters.  $\chi^{(3)}$ , and the maximum surface charge density  $\sigma_{\max}$  are common to both sets of data, as they should be, and the value of  $\chi^{(2)}$  is fitted for a given pH. Furthermore, we note that the contribution of the  $\chi^{(2)}$  term to the SH field  $E_{2\omega}$  is small compared with the  $E_{2\omega}$  value at high pH, and thus is not important to the fitting in the intermediate and high pH regions. At low pH ( $\approx 2$ ) we note that there is no contribution from the  $\chi^{(3)}$  term. Based on the success of fitting the electrolyte dependent SH data using the  $\chi^{(3)}$  term we would like to offer a physical picture of this mechanism. We view the underlying physical origin of the decrease in SH signal with increasing electrolyte concentration to be the effect of the electrolyte on the length of the electrical double layer. As the electrolyte concentration increases, the Debye shielding of the charged diffuse layer of counterions causes a more rapid decay of the electric field with distance from the interface. Fewer water molecules therefore experience a strong orienting electric field and the resulting nonlinear polarization  $P_{2\omega}$ , which generates  $E_{2\omega}$ , is diminished.

Let us now consider whether the SH temperature dependent data can also be fitted to the  $\chi^{(3)}$  mechanism, recalling that the  $\chi^{(2)}$  mechanism was unable to do so. In testing the  $\chi^{(2)}$  model, the temperature dependent data were obtained at a high pH (12.7), so that the silica surface was fully ionized. At this pH an electrolyte concentration of 0.5 M was used. This relatively high electrolyte concentration reduces the counterion density in the diffuse layer to the point where the Gouy-Chapman model for the interface potential is no longer appropriate [25-28]. The counterions are compressed into a layer that is more reasonably described by a constant capacitance model [25-28], consisting of a layer of negative SiO<sup>-</sup> charges, separated from a layer of the positive Na<sup>+</sup> counterions by a distance  $L$ . For this model the potential drop across the double layer is given by

$$\Phi(0) = \frac{4\pi\sigma_0 L}{\epsilon}, \quad (9)$$

where  $\epsilon$  is the dielectric constant and  $\sigma_0$  is the  $-\text{SiO}^-$  interface charge density. If we insert eq. (9) into eq. (7), using the expression for  $\chi^{(3)}$  given in eq. (4), we obtain

$$E_{2\omega} \propto P_{2\omega} = \chi^{(2)} E_{\omega} E_{\omega} + n_{\text{H}_2\text{O}} \left( \alpha_{\text{H}_2\text{O}}^{(3)} + \frac{\mu\alpha_{\text{H}_2\text{O}}^{(2)}}{bkT} \right) \frac{4\pi\sigma_0 L}{\epsilon} E_{\omega} E_{\omega}. \quad (10)$$

The temperature dependence of the SH field  $E_{2\omega}$  appears explicitly in the second term on the rhs and implicitly in the dielectric constant also appearing on the rhs. Since we have found that the  $\chi^{(2)}$  term does not account for the observed SH temperature dependence, and since the  $\chi^{(3)}$  term is the largest at the high pH of 12.7, we treat the  $\chi^{(2)}$  term as temperature independent. From temperature measurements at pH 2, where only the  $\chi^{(2)}$  term contributes to  $E_{2\omega}$ , we found that  $\chi^{(2)}$  is temperature independent. To get a qualitative feel of how the SH field,  $E_{2\omega}$ , should depend on temperature according to the model of eq. (10), let us assume that the dielectric constant of the water in the double layer region, i.e. between the negatively charged silica and the layer of positive counterions, has the same temperature dependence as water far from the interface. The dielectric constant would then vary almost linearly with  $1/T$  [29]. From this it follows using eq. (10) that  $E_{2\omega}$  would increase almost linearly with  $T$ , which is in agreement with the data shown in fig. 3.

To carry out the fitting to eq. (10) we first subtract the contribution of the  $\chi^{(2)}$  term. In our electrolyte studies, we found that the  $\chi^{(2)}$  contribution is the same, within our precision, at low, intermediate and high pH values. If we multiply both sides of eq. (10) by the dielectric constant we obtain a simple  $1/T$  temperature dependence on the rhs,

$$\epsilon \{ E_{2\omega}(\text{pH } 12.7) - E_{2\omega}(\text{pH } 2) \} = A + B/T. \quad (11)$$

The fitting is shown in fig. 4. On the basis of the very good agreement of the fitting of the temperature and electrolyte results using eq. (10), we conclude that the nonlinear polarization of the water molecules in

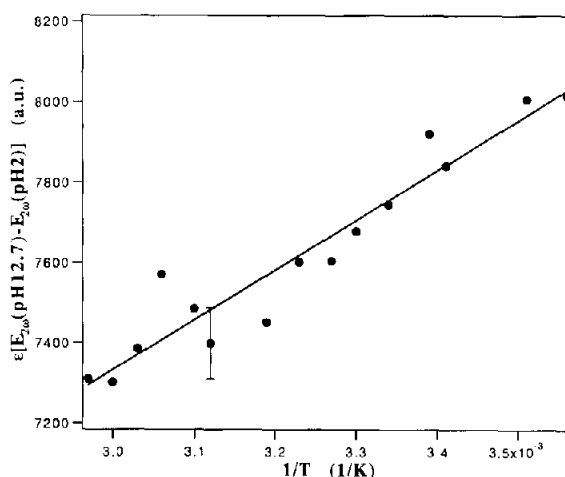


Fig. 4.  $\epsilon \{ E_{2\omega}(\text{pH } 12.7) - E_{2\omega}(\text{pH } 2) \}$  versus  $1/T$ . The dots are experimental points and the solid line the theoretical fit to eq. (11).

Table 1  
 $\chi^{(3)}$  elements (normalized) at pH 13 and 0.1 M electrolyte concentration. Comparison with prediction that  $\chi_{zzz}^{(3)} = 2\chi_{xzx}^{(3)} + \chi_{zxx}^{(3)}$

$\chi_{xzx}^{(3)}$	$\chi_{zxx}^{(3)}$	$\chi_{zzz}^{(3)}$	$2\chi_{xzx}^{(3)} + \chi_{zxx}^{(3)}$
1.00	0.76	2.56	2.76

the electrical double layer accounts quantitatively for the second harmonic signal.

As a further test of the validity of the water polarization mechanism we measured the various  $\chi^{(3)}$  elements to determine if they were in accord with the known symmetry requirement imposed by the presence of a static electric field. If the nonlinear susceptibility elements that we are measuring are indeed the  $\chi^{(3)}$  elements then they are related as follows [23],

$$\chi_{zzz}^{(3)} = 2\chi_{xzx}^{(3)} + \chi_{zxx}^{(3)}. \quad (12)$$

By carrying out measurements at pH 13 and 0.1 M electrolyte concentration we further diminish the relative contribution of  $\chi^{(2)}$  to the SH signal. To further reduce the small  $\chi^{(2)}$  term we subtract from the observed  $E_{2\omega}$  at pH 13 the observed value of  $E_{2\omega}$  at pH 2, where only the  $\chi^{(2)}$  term contributes. The results shown in table 1 demonstrate that the required relationship given by eq. (8) is obeyed. The deviation is 8%.

We conclude from the foregoing results and discussion that the SH signal from the charged silica/aqueous interface is due chiefly to the nonlinear polarization of the bulk water molecules in the electrical double layer region.

#### 4. Measurements of the surface silanol $pK_a$ values

From eq. (1) we write the equilibrium constant for a given type of site as

$$K_a = \frac{[-\text{SiO}^-][\text{H}_3\text{O}^+]_s}{[-\text{SiOH}]}, \quad (13)$$

where  $[\text{H}_3\text{O}^+]_s$  is the surface hydronium ion concentration. Its value at the interface is related to its bulk value by the potential difference between the surface and bulk. It is

$$[\text{H}_3\text{O}^+]_s = [\text{H}_3\text{O}^+]_b \exp[-e\Phi(0)/kT], \quad (14)$$

where  $\Phi(0)$  is the potential at the surface. We are now in a position to determine the  $pK_a$  of surface silanols using eq. (7). At the relatively high electrolyte concentration (0.5 M) we have found, as discussed earlier in the temperature dependent studies, that the constant capacitance model provides a good description of the double layer potential. We therefore substitute the potential given by eq. (9) into the expression for  $E_{2\omega}$  given in eq. (7) and obtain

$$E_{2\omega} \propto P_{2\omega} = \chi^{(2)} E_\omega E_\omega + \chi^{(3)} \frac{4\pi\sigma_0 L}{\epsilon} E_\omega E_\omega. \quad (15)$$

Defining  $f$  as the fraction of the maximum surface charge, we obtain the relation

$$\sigma_0 = f\sigma_{\max}, \quad (16)$$

where  $\sigma_{\max}$  is the surface charge at high pH ( $\geq 12.5$ ). Substituting into eq. (15), we obtain

$$E_{2\omega} = E_{2\omega}(\text{pH } 2) + A_0 f, \quad (17)$$

where  $E_{2\omega}$  is the measured SH field at the solution pH,  $A_0$  is a constant and the  $E_{2\omega}(\text{pH } 2)$  approximates the small  $\chi^{(2)}$  term contribution. The fraction  $f$  is obtained from the SH measurements,

$$f = \frac{E_{2\omega} - E_{2\omega}(\text{pH } 2)}{E_{2\omega}(\text{pH } 13) - E_{2\omega}(\text{pH } 2)}. \quad (18)$$

The parameters that enter into the fitting of eq. (17) to the  $E_{2\omega}$  versus pH data shown in fig. 1 are the silanol equilibrium constant for the two sites and the value of  $A_0$ . As seen in fig. 1 we obtain a good fit to the data with a  $pK_a$  value of 4.5 for 19% of the silanols and a  $pK_a$  of 8.5 for the remaining 81% of the silanols.

We would like to compare the SH results obtained for a planar silica/aqueous interface with work carried out on silica gel suspensions in aqueous solutions. The only work to our knowledge is a potentiometric titration study of the exchange of sodium ions and protons bound to the interface in a silica gel suspension [11–13]. Although NMR work subsequently showed that there is no strong site binding of sodium ions to the negatively charged surface silanol groups [30] the results of the potentiometric titration work can still be used to estimate gel surface  $pK_a$  values. What is necessary is to omit the sodium ion concentration from the equations used in the referenced work and to interpret the sodium ion exchange free energy term as the interface electrostatic free energy. It was assumed in the potentiometric study that the exchange free energy increases linearly with the fraction of sites occupied by sodium ions [13]. This fraction would equal the fraction of surface sites that are charged if we recognize that the sodium ions are not specifically adsorbed [30]. The remarkable intuitive assumption that the free energy increases linearly with the fraction of charged sites [13] can be shown to be equivalent to a constant capacitance model for the electrical double layer. This result is reasonable at the high electrolyte concentration (1 M NaCl) of their experiments. To obtain good agreement with experiment they found that two silanol sites are required. The values that they obtained are  $pK_a$  5.5 for 15% of the silanols, and  $pK_a$  9.0 for the remaining 85% of the silanol sites [13]. These numbers are in qualitative agreement with  $pK_a$  values of 4.5 for 19% and  $pK_a$  8.5 for 81% that we obtained from our SH experiments. A possible origin of the observed disparity could be the dependence of the charge densities obtained from potentiometric titration data on the accuracy of the chosen specific silanol area of the solid. In any case, these results suggest that there are two principal silanol sites and that the properties of the silanols on the silica gel interface and the planar fused silica (quartz) inter-

face are qualitatively similar. The origin of the two silanol group sites is not known. One possibility is that one site has a silanol hydrogen bonded to a neighboring silanol and for the other site a silanol that is hydrogen bonded to water.

### 5. Direct measurement of surface potential by SHG

Knowledge of the surface potential is an essential part of any microscopic description of a charged interface. An example of this was encountered in the forgoing treatment of interface  $pK_a$  values. Despite its importance, there is presently no method available to directly measure the oxide/aqueous potential since the oxide is an insulator. The current approach to investigate oxide/aqueous interface potentials is the measurement of the zeta-potential by electrokinetic methods such as electrophoresis [31]. In this latter method the velocity of the charged particle is measured in an applied electrical field, which can then be related to a double layer potential (zeta potential) at some distance from the charged surface. The difficulty with this approach is the ambiguity in locating this distance from the charged surface [31,32]. The zeta potential is the potential at the shear plane, which is the boundary separating the mobile liquid phase and the particle. Since the macroscopic solid particle can have a layer of immobilized water molecules adhering to it, the location of the shear plane within the double layer is uncertain. The zeta potential is therefore primarily useful as a qualitative estimate of the potential in the vicinity of the solid surface, sometimes ascribed to the beginning of the Stern layer [31,32].

In contrast to the electrokinetic approach we see from eq. (7) that the SH electric field  $E_{2\omega}$  is directly proportional to the surface potential  $\Phi(0)$ . The  $\chi^{(2)}$  contribution to  $E_{2\omega}$  as given in eq. (7) can be determined by measuring the SH field when the static field  $E_0$  is zero, i.e. when the surface is uncharged. To highlight this we rewrite eq. (7) as

$$E_{2\omega} - E_{2\omega}(\text{uncharged}) = D\Phi(0), \quad (19)$$

where  $D$  is a constant for the given solvent, which in our studies is water. We therefore see that we can make absolute measurements of the potential at a water interface. However, one reference point is

needed, i.e. the value of the SH signal for a known surface potential  $\Phi(0)$ . Since we do not know  $\Phi(0)$  from direct measurements we decided to use as our one reference point the value of  $\Phi(0)$  calculated from SH measurements at low electrolyte concentrations using the Gouy–Chapman model. Under low electrolyte conditions there is good evidence that the Gouy–Chapman model is valid [25–28]. We can then use this result to obtain an absolute value of the constant  $D$  in eq. (19). To check whether the choice of this reference point yields a model independent method as opposed to its being restricted to conditions where the Gouy–Chapman model is applicable, we chose to examine SH data at a high electrolyte concentration (0.5 M). Under these conditions, the Gouy–Chapman model is not applicable. Rather than simply making a comparison at 0.5 M electrolyte concentration and some single pH, we calculated  $\Phi(0)$  for all of the pH values at 0.5 M electrolyte for which we had SH results (see fig. 1).

The calculated potentials were then compared with the potentials obtained from fitting of the experimental SH data, but where a model of the potential was needed to make the fitting. As we noted in our discussion of fig. 1 the fitting using the constant capacitance model yielded excellent results. We now compare these fitted results with the model independent calculation of  $\Phi(0)$  using eq. (19). The potentials obtained by these two approaches are shown in fig. 5. The excellent agreement indicates that we can obtain the surface potential directly from a measurement of the SH signals without requiring any model for the electrical double layer. In fact having obtained  $D$  appearing in eq. (19) we can apply this approach to any charged water interface upon correcting for the change in Fresnel factors relative to the silica/water standard interface.

### 6. Conclusions

We have discovered that the second harmonic signal at a charged silica/aqueous interface is due chiefly to the electric field induced polarization and orientation of water molecules in the electrical double layer region of the interface. We have been able to obtain an excellent fit of the second harmonic signal as a function of solution pH by using a two site model of



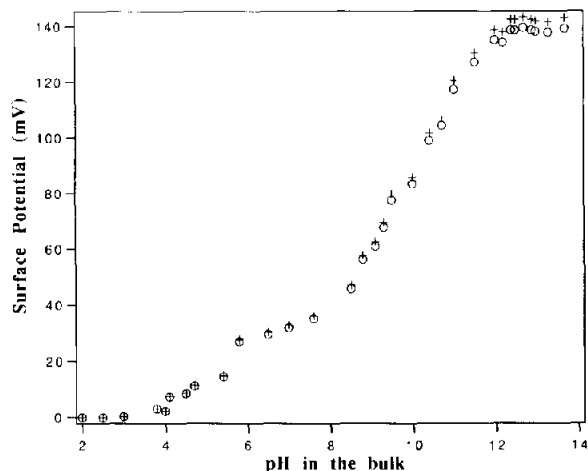


Fig. 5. Surface potential measured by SHG versus pH in the bulk solution for 0.5 M. (+) calculated using constant capacitance model; (O) model independent calculation from SH data with single reference point.

the silica/aqueous interface. One of the silanol sites was found to have a  $pK_a$  of 4.5 and to occupy 19% of the sites. The other silanol site has a  $pK_a$  of 8.5 and occupied the remaining 81% of the sites. It was found that for 0.5 M total electrolyte concentration the maximum interface potential is 140 mV at high pH values ( $> 12.5$ ). At lower ionic strength, the maximum surface potential is larger. An important aspect of this study was the demonstration that second harmonic generation can be used to measure the surface potential of charged liquid interfaces, independent of any model of the surface potential.

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