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## Spectroscopy and modeling of aqueous interfaces

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**Summary.** — The development of deep-UV second-harmonic generation spectroscopy (SHG) for measuring the strong charge transfer to solvent (CTTS) transitions characteristic of all stable aqueous anions has provided a powerful new probe of water interfaces. By employing suitable models, quantitative thermodynamic results have been obtained for a number of fundamental electrolytes, which are generally in good agreement with theoretical calculations. Details of the experiments and models are described and salient results supporting a novel mechanism for the selective adsorption of ions to the air/water interface are reviewed.

The progress made towards understanding the nature of liquid/vapor interfaces of aqueous systems over the past decade has been remarkable. Recent articles describe the advent of new experiments and theoretical advances that have drastically revised the classical textbook view that ions are repelled from interface formed by water and any lower dielectric medium [1-7]. While this field remains a highly controversial one, the accumulated data for aqueous electrolytes unambiguously establishes the presence of selected simple anions in the outermost few layers of liquid density. Theoretical models

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have interpreted these new data in terms of new mechanisms wherein the strong solvent (water) interaction energy compensates the unfavorable electrostatics of moving a charge towards the low dielectric medium, and revealing an unforeseen entropic force, *viz.* the suppression of capillary waves [5]. This chapter is not intended to comprise a thorough review of the field, but rather focuses on the advances made by our own group at Berkeley. However, refs. [1-7] and references therein will provide a reasonable guide to the recent literature.

Nonlinear optical spectroscopy experiments performed at Berkeley not only establish the presence of ions at the air/water interface, but also yield numerical values for the Gibbs free energy of adsorption, which can be directly compared with results from simulations. In order to extract such numerical results from the experiments, a suitable model must be employed. In this chapter, we consider the nature and application of a series of simple Langmuir adsorption models, describing how to use such models as a diagnostic of the mechanism of adsorption of these ions into the interface. We highlight the important distinction between *surface* (*viz.* outermost liquid layer) and *interface*, and do not use these terms interchangeably.

## 1. – SHG as a surface probe

Second-harmonic generation (SHG) is a second-order nonlinear process that transfers the energy of two photons into a single photon of twice the energy, the result of the nonlinear polarization of a medium induced by an electric driving field. Under a sufficiently strong driving field, the dipole polarization of a medium can be expressed as a perturbation of the usual linear response of a medium [8,9]

$$(1) \quad \begin{aligned} \vec{P} &= \vec{\chi}^{(1)} \cdot \vec{E} + \vec{\chi}^{(2)} : \vec{E}\vec{E} + \vec{\chi}^{(3)} \vec{E}\vec{E}\vec{E} + \dots \\ &\equiv \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} + \dots, \end{aligned}$$

wherein the induced polarization of a given order of perturbation is described by the macroscopic susceptibility tensor ( $\chi$ ), a material constant of the system. The  $n$ th-order nonlinear polarization of the medium can engender frequencies that are the sums of  $n$  (positive and negative) frequency components of the driving field. In the case of a single, monochromatic driving field, the total second-order polarization the medium is described by

$$(2) \quad \vec{P}^{(2)} = \vec{\chi}(\Omega = \omega - \omega) : \vec{E}(\omega)\vec{E}(-\omega) + \vec{\chi}(\Omega = \omega + \omega) : \vec{E}(\omega)\vec{E}(\omega),$$

where the notation  $\chi(\Omega = \omega \pm \omega)$  indicates that the susceptibility tensor is specifically defined for the polarization of the system oscillating at frequency  $\Omega$  due to the combination of frequencies  $\omega \pm \omega$ . Thus, the allowed second-order polarization frequencies for a monochromatic driving field of frequency  $\omega$  are  $\Omega = 0$  (optical rectification) and  $\Omega = 2\omega$  (second harmonic).

The utility of SHG as a surface probe lies in its forbidden nature within centrosymmetric media, under the dipole approximation. The susceptibility tensor is a direct reflection of the properties of the material and obeys the same symmetry that the material itself possesses. In the case of a centrosymmetric material, this indicates that the tensor must be invariant over any rotation and inversion. Applying inversion symmetry to the system (in the dipole approximation) then reveals that a second-order polarization, like any other even-ordered dipolar process, is forbidden in a centrosymmetric medium.

$$\begin{aligned}
 (3) \quad P_i^{(2)} &= \chi_{ijk}^{(2)} E_j E_k, \\
 P_{-i}^{(2)} &= \chi_{-i-j-k}^{(2)} E_{-j} E_{-k}, \\
 \chi_{ijk}^{(2)} &= \chi_{-i-j-k}^{(2)}, \quad \text{by symmetry} \\
 -P_i^{(2)} &= \chi_{ijk}^{(2)} (-E_j) (-E_k) = \chi_{ijk}^{(2)} E_j E_k, \\
 -P_i^{(2)} &= P_i^{(2)} = 0, \\
 \therefore \chi_{ijk}^{(2)} &= 0.
 \end{aligned}$$

At the air/water interface, this symmetry is necessarily broken, and the second-order response is then entirely due to the properties of the boundary region where the symmetry remains broken. This is selective to a very natural definition of the air/water interface: the region for which the symmetry of the system is no longer centrosymmetric. For a rotationally isotropic surface, such as the air/water interface, the susceptibility components of the interface are reduced by symmetry to seven components of which only three are independent [8, 9]:

$$\begin{aligned}
 (4) \quad \chi_{xxz}^{(2)} &= \chi_{zxx}^{(2)} = \chi_{yzy}^{(2)} = \chi_{yyz}^{(2)}, \\
 \chi_{zxx}^{(2)} &= \chi_{xyy}^{(2)}, \\
 \chi_{zzz}^{(2)}.
 \end{aligned}$$

Here the normal of the interface is taken to be in the  $\hat{z}$ -direction.

The macroscopic susceptibility of the system is the sum of the responses of its component oscillators (*i.e.* molecular induced dipole oscillations), and can be decomposed into the sum of the individual responses as

$$(5) \quad \vec{\chi}^{(2)} = \sum_J N_J \left\langle \vec{\beta}_J \right\rangle_{\text{Orientation}} \equiv \sum_J N_J \beta_{J,\text{eff}},$$

where  $\vec{\beta}_J$  is the molecular second-order susceptibility (hyperpolarizability) of species  $J$ . The second-order hyperpolarizability tensor is defined in the reference frame of the molecules themselves, the average over orientation reflecting the transformation from the molecular frame to the lab frame. The molecular susceptibility tensor is subject to the same symmetry requirements (*i.e.* selection-rules) as the macroscopic susceptibility

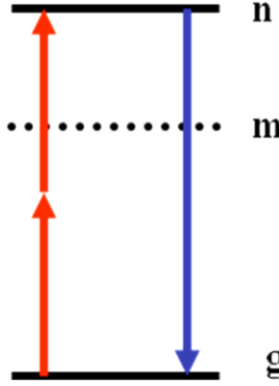


Fig. 1. – Schematic representation of two photon resonance between the ground (g) and excited (n) states for second harmonic described in eq. (6). Two photons of frequency  $\omega$  (red) are converted to a single photon of energy  $2\omega$  (blue).

tensor. The hyperpolarizability tensor can be derived from third-order time-dependent perturbation theory as a sum-over states expression, and for SHG:

$$(6) \quad \beta_{ijk}(2\omega = \omega + \omega) \propto \sum_{mn} \frac{\mu_{gn}^i (\mu_{nm}^j \mu_{mg}^k + \mu_{nm}^k \mu_{mg}^j)}{(2\omega - \omega_{ng} + i\gamma_{ng})(\omega - \omega_{mg} + i\gamma_{mg})} \\ + \frac{\mu_{mg}^i (\mu_{gn}^j \mu_{nm}^k + \mu_{gn}^k \mu_{nm}^j)}{(2\omega + \omega_{mg} + i\gamma_{mg})(\omega + \omega_{ng} + i\gamma_{ng})} \\ - \frac{\mu_{nm}^i (\mu_{mg}^j \mu_{gn}^k + \mu_{mg}^k \mu_{gn}^j)}{(\omega + \omega_{ng} + i\gamma_{ng})(\omega + \omega_{mg} + i\gamma_{mg})}$$

Here  $\mu_{gn}$  is the dipole transition moment between states  $n$  and  $g$ .  $\gamma$  is a damping parameter, usually interpreted as the dipole dephasing time [8]. It is clear that the first and second term can be under either one- or two- photon resonance (as the complex driving field includes both positive and negative frequency contributions), while the third term can only contribute to one-photon resonance (fig. 1). This forms the basis of species selectivity in surface second harmonic via the observation of resonance enhancement.

Second-order spectroscopy of the liquid water surface models the dipolar response of the interface as an oscillating polarization sheet of thickness much smaller than a wavelength, and the radiated second harmonic of this sheet in the reflected direction is given by [8, 9]

$$(7) \quad I_{2\omega} = \frac{8\pi^3 (2\omega)^2 \sin^2(\theta)}{c^3 \sqrt{\varepsilon_{2\omega}^\alpha \varepsilon_\omega^\alpha \varepsilon_\omega^\alpha}} \left| \gamma(2\omega) : \overset{\leftrightarrow}{\chi}_{\text{eff}}^{(2)} : \gamma(\omega) \gamma(\omega) \right|^2 I_\omega^2.$$

Here  $I_\Omega$  is the intensity of the incident field ( $\Omega = \omega$ ) or reflected second harmonic

( $\Omega = 2\omega$ ),  $\theta$  is the angle of the reflected second harmonic with respect to the surface normal and  $\varepsilon_{\Omega}^{\alpha}$  is the dielectric constant for frequency  $\Omega$  of the medium ( $\alpha$ ) of incidence (e.g. air). The susceptibility  $\overset{\leftrightarrow}{\chi}_{\text{eff}}^{(2)}$  is an effective susceptibility which we assume to be entirely due to the surface sheet, and  $\gamma(\Omega) = \overset{\leftrightarrow}{L}(\Omega) \cdot \hat{e}(\Omega)$  is the tensor product of the Fresnel factor and the polarization vector for frequency  $\Omega$ . The Fresnel factor effectively accounts for the fact that the oscillators in the polarization sheet experience an electric field strength that is altered in the dielectric medium of the sheet itself, due to the electric fields transmission across the sheet/air dielectric boundary. In our studies, ([8,9] and references therein), the Fresnel factors are neglected and the experimental configuration is unchanged throughout an experiment. In this case the above expression can simply be reduced to

$$(8) \quad I_{2\omega} \propto \left| \chi_{\text{eff}}^{(2)} \right|^2 I_{\omega}^2.$$

For a two-component system of water and a resonant solute, substitution of eq. (5) with rearrangement gives

$$(9) \quad \frac{I_{2\omega}}{I_{\omega}^2} \propto \left| N_{\text{water}} \beta_{\text{water}}^{\text{eff}} + N_{\text{solute}} \beta_{\text{solute}}^{\text{eff}} \right|^2.$$

which is the spectroscopic basis for the determination of the surface concentration of solute with respect to changing bulk composition used in published SHG studies of electrolyte interface affinities [8-19]. For the wavelengths in our studies, water is considered to be entirely non-resonant, while the solute may be in resonance. As such, the solute hyperpolarizability is complex-valued relative to the real response of water, and taking the modulus of (the complex-valued) eq. (9) gives the functional form of the second-harmonic response of the air/electrolyte solution interface [9]:

$$(10) \quad \begin{aligned} \frac{I_{2\omega}}{I_{\omega}^2} &\propto \left( N_{\text{water}} \beta_{\text{water}}^{\text{eff}} + N_{\text{solute}} \text{Re}[\beta_{\text{solute}}^{\text{eff}}] \right)^2 + \left( N_{\text{solute}} \text{Im}[\beta_{\text{solute}}^{\text{eff}}] \right)^2 \\ &= (AN_{\text{water}} + BN_{\text{solute}})^2 + (CN_{\text{solute}})^2. \end{aligned}$$

Here the effective molecular susceptibilities are assumed to be constants of the system.

## 2. – Langmuir models for interfacial adsorption

**2.1. The 1:1 exchange model.** – In previous similar studies, the adsorption of ions to the interface has been described by an adapted Langmuir model (hereafter exchange model) whereby the anion competes with water molecules for surface sites [1-3,12-19]. It models the effective equilibrium:



$$(12) \quad K_{\text{ads}} = \frac{[SX^-][W]}{[SW][X^-]} = \frac{[SX^-][W]}{([S_{\text{max}}] - [SX^-])[X^-]},$$

where  $S$  is one of  $S_{\max}$  surface sites (all occupied by water molecules in the neat water interface).  $W$  refers to water and  $X^-$  is a surface active anion of interest. The usual Langmuir adsorption assumptions of non-interacting adsorbates and conservation of surface sites apply. It deserves to be mentioned that the standard states for the bulk and surface species are considered to be identical: 55.5 M for bulk water and surface water, 1 M for bulk and surface solute. This defines  $S_{\max}$  to be 55.5 M. Rearrangement of eq. (12) provides the number of surface anions in terms of the bulk concentrations of water and anion:

$$(13) \quad [SX^-] = [S_{\max}] \frac{[X^-]}{([W]K_{\text{ads}}^{-1} + [X^-])}.$$

When substituted into eq. (10), we resolve a functional form of the expected intensity of second harmonic as a function of bulk concentration of water and anion,

$$(14) \quad \frac{I_{2\omega}}{I_{\omega}^2} = \left( A + B' \frac{[X^-]}{([W]K_{\text{ads}}^{-1} + [X^-])} \right)^2 + \left( C' \frac{[X^-]}{([W]K_{\text{ads}}^{-1} + [X^-])} \right)^2.$$

The fit of the SHG intensity as a function of bulk solute concentration and four unknown parameters allows for the determination of  $K_{\text{ads}}$ . Although the application of this model has been very successful in a variety of previous studies, the adapted model contains one explicit and one implicit assumption over the usual Langmuir assumptions: an explicit assumption of a 1:1 exchange of anion and water, and the implicit assumption that the cation is irrelevant in describing the processes.

**2.2. The effects of water exchange in the exchange model.** – Considering first the nature of water exchange begs the question of how many water molecules *would* be displaced in the interface if an ion partitioned there. There are several possible ways to approach this problem. Using partial molar volumes as a rough guide [20], it is clear that in bulk solution even atomic anions effectively rival or exceed the volumetric dimensions of a water molecule (table I). For adsorption to a surface that is two-dimensional on the scale of an individual molecule, we expect that the replacement of water would scale roughly as the 2/3 power of its volume. Other parameters, such as ionic radii or effective hydrated radii, might also help make some useful approximations, but fundamentally the exchange model always demands that we choose a number before we examine the system in this fashion.

Fortunately, the consequences of choosing a particular number of waters to displace is appreciable only if the concentration of water can change appreciably over a Langmuir isotherm. Choosing zero (requiring empty surface sites for neat water) is tantamount to holding the concentration of water fixed, albeit now the value of  $S_{\max}$  is not pre-defined. In some early works [12-15], the concentration of water was assumed to be constant at its pure value in the application of the Langmuir isotherm. While appropriate for low concentration studies, such as those performed in the Jones-Ray concentration

TABLE I. – *Partial molar volumes of selected anions and cations from ref. [20].*

Species	Partial molar volume (ml/mol)	Volume relative to water
H <sub>2</sub> O	18	1.00
H <sup>+</sup>	−5.4	−0.30
Na <sup>+</sup>	−7.4	−0.41
K <sup>+</sup>	3.4	0.19
F <sup>−</sup>	3.3	0.18
Cl <sup>−</sup>	23.7	1.32
Br <sup>−</sup>	30.2	1.68
I <sup>−</sup>	41.4	2.30
NO <sub>3</sub> <sup>−</sup>	34.8	1.93

regime [1, 2, 12], the water concentration in concentrated electrolyte solutions can deviate strongly from its pure value. For example, measurements of sodium nitrate solution densities demonstrate a linear trend that effectively conserves the number of species in a given volume (water + anion + cation = 55 M), leading to a 20% decrease in water concentration in the case of 5.5 M sodium nitrate [21]. The effect of excluding the decreased concentration of water as a function of increased solute concentration is to make the adsorption process appear more favorable than the model implies by a ratio of

$$(15) \quad \frac{K^{(\text{actual})}([X_B])}{K^{(\text{observed})}} = \frac{[W_B([X_B])]}{[W_B]^\theta},$$

at any given bulk concentration. This suggests that the fitting process would attribute the concentration of surface solute at high concentrations to a more favorable thermodynamic process by discounting the effect of the reduction of bulk water molecules competing for surface sites. The SHG/Langmuir fit is nonlinear in  $K_{\text{ads}}$  and the bias is dependent on the concentration that the Langmuir expression is evaluated at (fit to) such that no general correction factor can be applied to results interpreted under the constant water concentration approximation. However, the bias is monotonic in bulk solute concentration and an upper limit can be determined by taking at the highest concentration measured. Assuming a 20% decrease in water concentration, this upper limit amounts to a relatively modest  $\sim 0.5 \text{ kJ}\cdot\text{mol}^{-1}$  negative shift in the observed value from the model value.

It is easy to demonstrate that the equilibrium constants for the other 1: $n$  water replacements relate by

$$(16) \quad {}^{1:n}K_{\text{ads}} = {}^{1:1}K_{\text{ads}} \frac{[W]^{n-1}}{([S_{\text{max}}] - [SX])^{n-1}}.$$

While the bias would clearly be more pronounced if more than one water molecule is



chosen to be displaced, for low concentrations of solute (wherein the constant water concentration approximation is valid) *and* somewhat weak adsorption of the solute, these values are roughly indistinguishable. If the concentration of water is made to vary significantly, it is conceivable that the relative displacement of water could be deduced by applying the various fits for each order of replacement.

If different integer replacements (or rational fraction) exchanges are then assumed, the expression for the surface solute concentration dependence on bulk concentration dependence remains analytical, albeit more complicated:

$$\begin{aligned}
 (17) \quad 1:1[SX] &= \frac{[S_{\max}][X]}{[W]K_{\text{ads}}^{-1} + [X]} \\
 1:2[SX] &= 2[S_{\max}] + \frac{[W]^2 - [W]\sqrt{[W]^2 + 4K_{\text{ads}}[S_{\max}][X]}}{2K_{\text{ads}}[X]} \\
 1:3[SX] &= [S_{\max}] \\
 &+ [W]^2 \sqrt[3]{\frac{2}{27K_{\text{ads}}^2[S_{\max}][X]^2 + 3\sqrt{3}K_{\text{ads}}^3[X]^3(4[W]^3 + 27K_{\text{ads}}^2[S_{\max}]^2[X])}} \\
 &- [W]^3 \sqrt[3]{\frac{9K_{\text{ads}}^2[S_{\max}][X]^2 + \sqrt{3}K_{\text{ads}}^3[X]^3(4[W]^3 + 27K_{\text{ads}}^2[S_{\max}]^2[X])}{18K_{\text{ads}}^3[X]^3}}
 \end{aligned}$$

Along with the added complexity, notion of an integer replacement of water in the interface is non-intuitive. Due to the limited resolution of our SHG studies, this effect is not explored herein.

Of course, the volume of the interface is finite, and, in principle, SHG probes the entirety of this region provided there is some asymmetry induced on the electronic transitions we probe [1-22]. The argument above is then somewhat pedantic when one considers that a surface site in a finite volume interface is a fictitious concept. From here forward, we treat the interface as a finite volume, consistent with both the natural notion of a continuous transition between the bulk phases and the effective probe region of second-order spectroscopies. In this sense we make a complete distinction between the *surface* (*viz.* outermost layer of liquid density) and the *interface*.

**2.3. An alternative approach.** – If the interface volume was treated ideally, one would simply define a partition coefficient for the adsorption of ions into the interface

$$(18) \quad K_{\text{ads}} = \frac{[X_{(\sigma)}]}{[X_{(aq)}]},$$

where  $[X_{(\sigma)}]$  is the concentration of the adsorbate in the surface region ( $\sigma$ ). However, the system is not ideal, and if there is a significant population of solute in the inter-

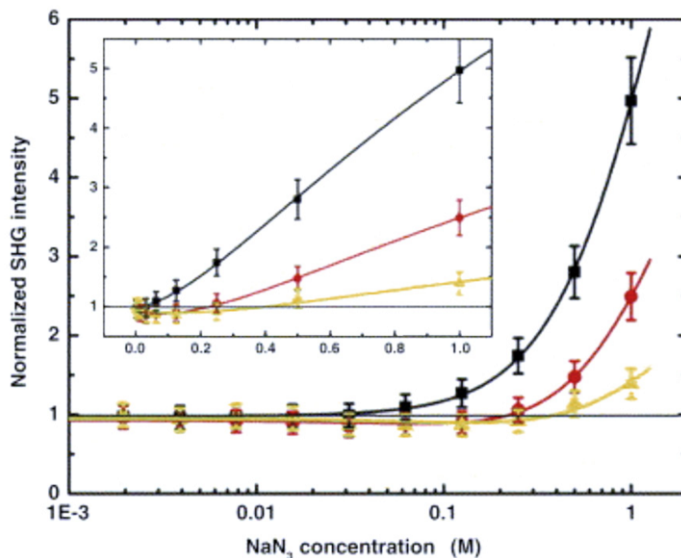


Fig. 2. – The second-harmonic signal profile of aqueous  $\text{NaN}_3$  as determined by resonant SHG at (largest to smallest) 200 nm, 225 nm, and 250 nm. At high bulk concentrations (inset) the surface begins to saturate, as is evidenced by the sub-second-order dependence of SHG on concentration.

face, the surface species will eventually crowd each other due to the restricted volume available. This is reflected in previous SHG studies of strongly adsorbing anions through the saturation of signal observed at high concentrations (fig. 2) [12-16]. Allowing the volume of the interface *available* to adsorbates be a function of the size and number of the interfacial molecules, we adopt

$$(19) \quad [X_{(\sigma)}]_{\text{eff}} = \frac{N_{X_{(\sigma)}}}{V_{\text{Int}} - \sum_J b_J N_{J_{(\sigma)}}}.$$

Here  $N_{J_{(\sigma)}}$  is the number of the interfacial species  $J_{(\sigma)}$  with an empirical effective exclusion volume of  $b_J$ , and  $V_{\text{Int}}$  is the actual volume of the interface region. This expression has its analogy in the Van der Waals expression for a real gas [23], where the  $b$  coefficient reflects a Van der Waals gas molecule's exclusion volume. Borrowing further from ideal gas theory we will assume that only solutes exclude volume, allowing water to effectively act as a non-interacting background (ideal) gas. As is usual when dealing with non-ideal systems, we can always include the effect of water through the application of an activity coefficient if necessary. Rewriting this expression for a single species and multiplying the interface volume to both numerator and denominator, we find that we recover the usual form of the Langmuir adsorption isotherm:

$$(20) \quad K_{\text{ads}} = \frac{[X_{(\sigma)}]_{\text{eff}}}{[X_{(aq)}]} = \frac{[X_{(\sigma)}]}{(1 - b_{X_{(\sigma)}}[X_{(\sigma)}])[X_{(aq)}]},$$

$$(21) \quad [X_{(\sigma)}] = \frac{[X_{(aq)}]K_{\text{ads}}}{1 + b_{X_{(\sigma)}}K_{\text{ads}}[X_{(aq)}]} \\ = \frac{b_{X_{(\sigma)}}^{-1}[X_{(aq)}]}{b_{X_{(\sigma)}}^{-1}K_{\text{ads}}^{-1} + [X_{(aq)}]} \\ = \frac{[S_{\text{max}}][X_{(aq)}]}{[S_{\text{max}}]K_{\text{ads}}^{-1} + [X_{(aq)}]}.$$

This approach avoids the issue of considering water replacement altogether by allowing such effects to be characterized by the effective exclusion volume and/or activity coefficient. Comparison with eq. (13) demonstrates that the exchange model and this model are equivalent when the same assumptions are applied; in this case the exchange ratio is 1:1, and surface water is assumed to have the same concentration as bulk water in its standard state:

$$(22) \quad \frac{[S_{\text{max}}][X_{(aq)}]}{[S_{\text{max}}]K_{\text{ads}}^{-1} + [X_{(aq)}]} \cong \frac{[S_{\text{max}}][X^-]}{([W]K_{\text{ads}}^{-1} + [X^-])}.$$

In this regard we have validated applying the exchange model to a volume, recognizing that we are not making any more assumptions than were already present in the usual exchange model.

To explicitly account for a true *competitive* equilibrium of water and solute, one would also model the adsorption of water to the interface. The argument set out above leads to

$$(23) \quad [X_{(\sigma)}] = \frac{K_{\text{ads}}[X_{(aq)}]}{1 + b_W K_{W_{(\sigma)}}[W_{(aq)}] + K_{\text{ads}}b_X[X_{(aq)}]} \\ = \frac{[X_{(\sigma)\text{max}}][X_{(aq)}]}{K_{\text{ads}}^{-1}[X_{(\sigma)\text{max}}](1 + b_W K_{W_{(\sigma)}})[W_{(aq)}] + [X_{(aq)}]},$$

where  $K_{W_{(\sigma)}}$  is the effective adsorption of water to the interface, and presumably would model the density of water in the interfacial volume (that an adsorbate can partition to) at zero solute concentration. This expression is equivalent to the usual Langmuir isotherm for *competitive* adsorption to surface sites [24]. Unfortunately, this expression also directly couples the desired  $K_{\text{ads}}$  to unknown parameters;

$$(24) \quad [X_{(\sigma)}] = \frac{[X_{(\sigma)\text{max}}][X_{(aq)}]}{\gamma[W_{(aq)}] + [X_{(aq)}]},$$

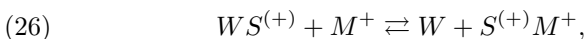
where

$$(25) \quad \gamma = K_{\text{ads}}^{-1}[X_{(\sigma)\text{max}}](1 + b_W K_{W_{(\sigma)}});$$

and cannot be used to fit the SHG response.

Thus, by judicious application of Ockham's razor, we retain the 1:1 exchange model for its simplicity in use, the ability to compare with other like-modeled systems, and its success in previously modeling the concentration dependence of the SHG signal. However, we recognize that the energies it describes for the adsorption process are only relevant when compared to equivalently modeled systems and, at minimum, discounts some of the water desorption free energy that would be present for >1:1 replacements.

*2.4. Langmuir adsorption modeling including cations.* – While this discussion has focused thus far on the nature of water desorption in the interface region, and consideration of the Langmuir adsorption model against a volume, another concern is the issue of the cations in the interface. By the electroneutrality condition, if an anion adsorbs to the interface region a cation must also be absorbed, although the microscopic partitioning depth with respect to the Gibb's dividing surface is likely be unique to each [25-29]. In related SHG studies previously mentioned, this is generally disregarded, as the model takes no account of cations and the signal observed is only resonant with the anion. However, those studies that do explicitly consider cation dependence suggest a relatively weak effect [12, 19]. Nonetheless, in order for an anion to adsorb into the interface, the process must not only have sufficient free energy for the anion to do so, but it must have also enough in excess to bring a cation into this vicinity such that electroneutrality is maintained. Uneven partitioning may mean that the necessary excess energy is negligible, but this effect is still easily captured for a 1:1 electrolyte under a slight revision to the exchange model:



$$(27) \quad K_{\text{ads}}^{+} = \frac{[S^{(+)}M^{+}][W]}{[S^{(+)}W][M^{+}]} = \frac{[S^{(+)}M^{+}][W]}{([S_{\text{max}}] - [S^{(+)}M^{+}])[M^{+}]}.$$

Here we have allowed the surface sites of the cation to be distinct from those of the anion, to reflect that for preferential anion adsorption the cations partition into a deeper region of the interface than that of the anion [22, 26, 27, 29-32]. The restriction of electroneutrality for a 1:1 electrolyte gives,

$$(28) \quad [S^{(-)}X^{-}] = [S^{(+)}M^{+}],$$

and the overall adsorption constant is then

$$(29) \quad K_{\text{U}} = K_{\text{ads}}^{+}K_{\text{ads}}^{-} = \frac{[S^{(-)}X^{-}]^2[W]^2}{\left([S_{\text{max}}^{(-)}] - [S^{(-)}M^{-}]\right)\left([S_{\text{max}}^{(+)}] - [S^{(-)}X^{-}]\right)[X^{-]}^2} \\ = \frac{[S^{(+)}X^{-}][W]^2}{\left([S_{\text{max}}^{-}] - [S^{(-)}X^{-}]\right)^2[X^{-]}^2}.$$

Here we have assumed, as in the 1:1 exchange model, that the maximum number of surface sites for both species are equal (to the concentration of water in the neat interface). Consideration of same-site competition merely leads to a factor of two in the difference in the denominator. The net result is isomorphic to that of simple anion adsorption by 1:1 exchange, only now the total energy of adsorption is recognized to be divided between both the cation and anion (but not necessarily evenly). In this model, the cation and anion are still free to independently explore their respective interfacial volumes, but electroneutrality is conserved explicitly. While this conclusion is not necessarily new or striking, it forms the basis for considering the co-adsorption of cation and anion to a single surface site:

$$(30) \quad K_B = \frac{[M^+SX^-][W]}{([S_{\max}] - [M^+SX^-])[X^-][M^+]} = \frac{[M^+SX^-][W]}{([S_{\max}] - [M^+SX^-])[X^-]^2}.$$

In this expression, the translational partition functions of the two surface species are coupled as the ions are “bonded” to the same surface site, and is reflective of ion-pairing in the interface. The fundamental difference is that now the observed surface concentration will be identifiably second order in bulk concentration. This can act as a distinguishing characteristic between two possible mechanisms for bringing anions to the interface, one in which the anion has an intrinsic propensity for the interface, and the other where charge neutralization by its paired cation helps it overcome the usual electrostatic costs associated with such partitioning.

**2.5. SHG/Langmuir fitting procedures.** – Fits of the SHG/Langmuir expressions (eq. (14) and related) were performed using the nonlinear curve fitting tool of Origin 7.03 (Origin Labs). The fitting tool utilizes the Levenberg-Marquardt regression algorithm and the fits were performed with sample weighting of the inverse variance of the measurements. Reported errors by this algorithm are based on the weighted variance of the data points and their dependence on the parameters for which the error relates, and were scaled by  $\chi^2/\text{DoF}$ . The default optimization parameters of the tool were used. For unimolecular fits, all fitting parameters were set to +1 for initial conditions, while bimolecular fits used a  $\Delta G$  value of either  $-20000$  or  $-40000$  to avoid a local minimum in the fitting process that clearly did not replicate the data.

### 3. – Applications

The models and fitting procedures described herein and employed in the references studies have been used to interpret SHG measurements of electrolyte solutions, specifically seeking to extract reliable numerical values for the thermodynamic quantities that govern ion adsorption (Gibbs Free Energy) that can be directly compared with results from calculations. Both the experimental and theoretical studies were usually performed on high (molar) concentration solutions, and generally good agreement was found for

these systems [1-3]. However, quite different results were obtained for dilute (millimolar) solutions. For example, molar solutions of potassium iodide and potassium ferrocyanide exhibit “normal” ion adsorption behavior, *viz.* adsorption free energy changes of  $-1$  kJ/mol, whereas much higher values are found for millimolar concentrations [2, 14]. This is reminiscent of the controversial “Jones-Ray experiments” of the 1930s, wherein 13 salts were found to exhibit negative surface tension increments (and thus positive ion adsorption) at sub-millimolar concentrations, while exhibiting maxima at  $\sim 1$  millimolar before becoming positive and behaving normally ( $\sim$  proportional to salt concentration) in the molar region. We have analyzed these Jones-Ray data with the simple adsorption models described herein, showing them to exhibit free energy changes that are  $\sim 10\times$  larger than our “usual” molar concentration values [2, 6].

Another study, made at molar concentrations, revealed strikingly different behavior for the adsorption of the ostensibly similar  $\text{NaNO}_3$  and  $\text{NaNO}_2$  salts [17, 18]. While *nitrate* exhibited “normal” behavior, following the independent adsorption model used for all systems we have studied in the molar region, sodium *nitrite* yielded very different SHG data that could not be fit with that model, but instead fit well to a correlated ion pair adsorption model, with a much higher free energy change. Sodium nitrite thus resembles the Jones-Ray salts described above.

Finally, temperature-dependent SHG experiments on sodium thiocyanate solutions in the molar region enabled the separate determination of the enthalpy and entropy components of the adsorption free energy change [5]. In contrast to most expectations, both quantities turned out to be negative and of comparable magnitude, indicating that the observed strong adsorption of the thiocyanate anion is driven by enthalpy, despite the strong unfavorable electrostatic repulsion accompanying movement of a charge from the bulk solution to the surface. Calculations (from Geissler and Schaffer) showed that the favorable enthalpy resulted from the displacement of weakly interacting water molecules from both the ion hydration shell and from the outermost liquid layers back into the strongly interacting bulk liquid. The unfavorable entropy change was shown to result from suppression of the amplitude of capillary waves as the ion moved into the interface, overcoming the favorable, but much smaller, orientational entropy change accompanying the formation of a solvent cavity at the interface versus in the bulk. Future experiments and calculations will continue to explore the generality of these results, but the modeling from the Geissler group indicates that this indeed reflects a general behavior of weakly hydrated simple ions [5, 33, 34].

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