

Adsorption of thiocyanate ions to the dodecanol/water interface characterized by UV second harmonic generation

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Recent experimental and theoretical results have firmly established the existence of enhanced concentrations of selected ions at the air/water interface. Ion adsorption to aqueous interfaces involving complex organic molecules is relevant to biology in connection with the familiar but incompletely understood Hofmeister effects. Here, we describe resonant UV second harmonic generation (SHG) studies of the strongly chaotropic thiocyanate ion adsorbed to the interface formed by water and a monolayer of dodecanol, wherein the Gibbs free energy of adsorption was determined to be -6.7 ± 1.1 and -6.3 ± 1.8 kJ/mol for sodium and potassium thiocyanate, respectively, coincident with the value determined for thiocyanate at the air/water interface. Interestingly, near 4 M and higher concentrations, the resonant SHG signal increases discontinuously, indicating a structural change in the interfacial region.

buried interface | Langmuir model | nonlinear optics | self-assembled monolayer | surface spectroscopy

The Hofmeister series, first described in 1888 in terms of salt-dependent effects on the aqueous solubility of proteins (1), appears in fields ranging from biochemistry to colloid chemistry (2–4). More than a century after Hofmeister's work, there is still no comprehensive molecular explanation for these macroscopic ion-selective effects, despite numerous published studies and models. Interfacial effects are currently believed to be the predominant source of the Hofmeister phenomena (3–5), and recent studies have confirmed that long-range solvation effects play a minimal role, as the water hydrogen bonding structure is generally not significantly affected beyond the first hydration shell of aqueous monovalent ions (6–8).

The interfacial affinities of various anions for a protein-like/water interface have been shown to follow a Hofmeister series in studies by Chen et al. using vibrational sum frequency spectroscopy (VSFS) (9), demonstrating that stronger interfacial affinities correlate with “salting-in” of proteins. Using surface tension measurements, Pegram and Record have found similar results for the air-water interface (10, 11). Collins has proposed the “law of matching water affinities” to explain Hofmeister effects, which utilizes ion hydration strength to explain ion-specific interactions (12). Jungwirth et al. have recently performed a number of simulations investigating the relation between the Hofmeister series and specific-ion interactions with various model and chemical interfaces (13–19). In one of these studies, ions at opposite ends of the Hofmeister anion series, fluoride and iodide, exhibit two different mechanisms of adsorption to a model macromolecule (16). The weakly hydrated iodide ions preferentially adsorb to hydrophobic surfaces, while the strongly hydrated fluoride ions adsorb via an electrostatic interaction to regions of positive charge. Using x-ray photoelectron spectroscopy (XPS), Krisch et al. found the iodide surface concentration enhancement at the air/liquid interface of a butanol and water mixture to be less than that of a pure aqueous solution (20).

It is clearly of interest to establish the affinities of such simple ions for the chemical moieties that exist at aqueous interfaces with proteins and other biologically relevant complex molecules, such as fatty acids, polyglycerides, and lipids. Herein we describe our investigations of selective adsorption of the thiocyanate anion, positioned at the extreme of the Hofmeister “structure breaker” anion series, to a long-chain alcohol/water interface. The presence of thiocyanate ions at the interface comprising a monolayer of dodecanol with water is probed by means of charge-transfer-to-solvent (CTTS) resonant SHG, and the Gibbs free energy of surface adsorption is determined using a Langmuir adsorption model. The effect of cation identity is also assessed by comparing adsorption from sodium thiocyanate (NaSCN) and potassium thiocyanate (KSCN) solutions. Interfacial adsorption of thiocyanate has been the focus of many recent experimental studies, and we compare our results to those recently obtained for the air/water (21–23) and macromolecule/water (9) interfaces.

SHG and the Langmuir Adsorption Model. SHG spectroscopy of CTTS bands has recently been used to determine the affinity of several anions [thiocyanate (21), azide (24), iodide (25, 26), ferrocyanide (27), and hydroxide (28)] for the air/water interface. In these and the current experiments, the fundamental beam in the visible region of the spectrum is two-photon resonant with the CTTS band located in the deep UV, providing a direct probe for selected anions. Since SHG is a second-order nonlinear optical technique, under the dipole approximation SHG is only generated when the system does not exhibit centro-symmetric symmetry and is therefore interface specific for the dodecanol/water system. For this reason, it is a useful technique for probing the interface of complex molecules with water.

The SHG intensity can be written

$$I_{SHG} = |\chi_{system}^{(2)}|^2 I_{fundamental}^2 \quad [1]$$

where the system response, $\chi_{system}^{(2)}$, can be partitioned into contributions due to the solvent, in this case the dodecanol/water interface, and contributions due to the solute:

$$\chi_{system}^{(2)} = \chi_{solvent}^{(2)} + \chi_{solute}^{(2)} \quad [2]$$

The dodecanol/water response is nonresonant, and therefore will be a purely real quantity. In the case of CTTS SHG, the solute response is the product of the number of surface anions in the laser focus, N_S , and the orientationally averaged hyperpolarizability,

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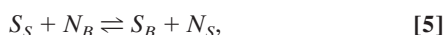
$$\chi_{\text{solute}}^{(2)} = N_S \langle \beta \rangle_{\text{orientation}} \quad [3]$$

The application of a Langmuir adsorption model to SHG of ions at an interface has been described in detail previously (24, 26) and is only described briefly here. Since the system response is proportional to the number of anions at the interface, a Langmuir model may be used to determine the affinity of the anions for the interface. The system response can be parameterized as

$$\chi_{\text{system}}^{(2)} = |A + (B + iC)N_S|^2 \quad [4]$$

Here, A represents the nonresonant solvent response and B and C represent the real and imaginary components of the solute response.

A Langmuir model is applied here by dividing the solution into bulk and surface domains for which an equilibrium equation can be written describing the exchange of surface and bulk species,



where S is one solvent molecule and X_B and X_S reside in the bulk and surface partitions, respectively. In this formulation it is assumed that the solvent and solute exchange in a 1:1 ratio. This model also presumes that all interfacial adsorption sites are equivalent and always occupied by either a solvent or solute molecule, implying two things in the dodecanol/water case. First, the model is only valid up to one monolayer of surface adsorption by the ion. Second, interactions between neighboring adsorption sites must be negligible.

Manipulation of the Langmuir model provides the following expression for the number of surface ions in terms of the bulk concentrations of the solvent and solute:

$$N_S = \frac{N_S^{\text{max}}[N_B]}{[N_B] + [S_B] \exp[\Delta G_{\text{ads}}/RT]} \quad [6]$$

Here, $N_S^{\text{max}} = S_S + N_S$ and represents the total number of surface sites, and ΔG_{ads} is the Gibbs free energy of solute adsorption to the interface. Inserting [6] into [4] and allowing the B and C parameters of [4] to include N_S^{max} provides the equation used to fit the data. The data are fit such that at different wavelengths the parameters A , B , and C are independent, while ΔG_{ads} is fit to all of the wavelengths simultaneously.

Dodecanol/Water Structure. The intrinsic structure of the long-chain alcohol/water interface is well-understood. The surface area of a 1-dodecanol molecule on the water surface is $\approx 20 \text{ \AA}^2$ (29, 30). X-ray studies have confirmed that the alcohol chains stand nearly vertically on the water surface (31, 32). Hence, the OH terminus of dodecanol is able to form hydrogen bonds with water or to contribute to the hydration shell of an adsorbed anion. VSFS has been used to determine that *gauche* defects of the aliphatic chain are very rare below the 2D phase transition temperature ($T_m(2D)$), which for 1-dodecanol is $39.1 \text{ }^\circ\text{C}$ (30, 33, 34).

$T_m(2D)$ of dodecanol on pure water and on a 20% by weight solution of KBr agreed within error (29). This implies that any bromide ions at the interface, which have been predicted to preferentially adsorb to the air/water interface (35, 36), do not penetrate into the dodecanol layer. Similarly, VSFS of the CH region of another macromolecule, poly-(*N*-isopropylacrylamide) (PNIPAM), on D_2O was the same for pure water and numerous 1 M salt solutions, including NaSCN (9). Since VSFS is sensitive to number density and orientational changes, both the concentration and orientation were invariant to salt addition. Therefore, it is assumed that interfacial adsorption of thiocyanate at the dodecanol/water interface does not disrupt the concentration or orientation of the dodecanol monolayer.

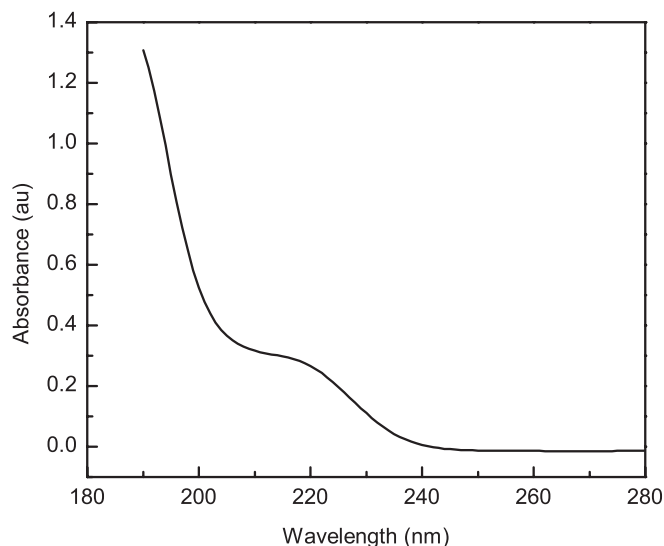


Fig. 1. UV absorption spectrum of aqueous sodium thiocyanate.

Results and Discussion

The bulk aqueous CTTS absorption spectrum of NaSCN is presented in Fig. 1. The SHG spectrum at the dodecanol/water interface is likely shifted from that of the bulk aqueous solution due to the different environment presented by the interfacial region, as observed for other anions at the air/water interface (37).

The SHG intensities of NaSCN and KSCN at the dodecanol/water interface are plotted in Fig. 2 for a series of wavelengths as a function of bulk concentration. The SHG intensity is normalized such that it is unity for the dodecanol/water interface with no dissolved salt. The nonresonant signal due to the intrinsic dodecanol/water interface is approximately four times greater than that of neat water. The SHG intensity clearly increases with anion concentration, indicating that thiocyanate is present at the water/dodecanol interface, since the structure of the dodecanol monolayer has been shown to remain invariant upon salt addi-

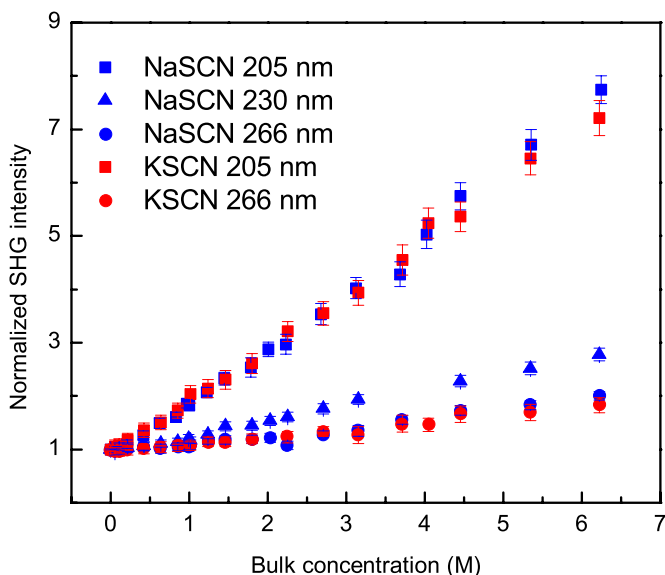


Fig. 2. SHG response for NaSCN and KSCN solutions plotted as a function of bulk concentration. The wavelengths 205 nm, 230 nm, and 266 nm represent resonant, weakly-resonant, and nonresonant responses, respectively. The error bars are one standard deviation.

tion (9, 29). The two-photon resonance with the CTTS band at 205 nm provides a significant signal enhancement relative to the weakly resonant signal at 230 nm and nonresonant signal at 266 nm. The signal enhancement, defined here as $(I_{SHG}^{205}-1)/(I_{SHG}^{266}-1)$, fluctuates at low concentrations, but >1 M the enhancement factor is 7.9 ± 1.2 . The NaSCN and KSCN data are remarkably similar, despite effects due to the different cations. For each wavelength nearly all common concentration data points lie within their relative errors, as previously found for ions at the air/water interface (26). The only significant exception occurs at concentrations >4 M (henceforth concentrations ≥ 4 M will be referred to as high concentration), where the SHG intensity for NaSCN is greater than that of KSCN for both on- and off-resonant wavelengths.

At 266 nm, the SHG intensity increases with concentration despite being far from any expected resonance. Similar behavior for nonresonant SHG of sodium halide salts has been attributed to a thickening of the interfacial layer (defined as the region exhibiting broken inversion symmetry) with increasing concentration (38). However, this assumes that both the ions and their solvation shells are symmetric, and therefore do not contribute to the SHG signal. The hydration shell of thiocyanate will not be symmetric as the ion itself is asymmetric. Moreover, molecular dynamics simulations have shown that thiocyanate is not expected to be well hydrated at the air/water interface (21), and this may also be the case at the alcohol/water interface. Therefore, the nonresonant increase in SHG signal with increasing thiocyanate concentration originates from the local alteration of the interfacial hydrogen bonding structure by thiocyanate as well as from any change in interfacial thickness.

Inspection of the data for both NaSCN and KSCN reveals that there is a salient kink in the SHG intensity at high concentrations (see Fig. 3). The SHG intensity at high concentrations is greater than extrapolation of the lower concentration data would predict based on the Langmuir adsorption model. Therefore, the Langmuir fits shown in Fig. 3 only include the data at concentrations below the onset of this kink. The fit parameters are shown in Table 1; the errors are one standard deviation.

The Langmuir fit parameters for the entire concentration range are also included in Table 1 for NaSCN. Comparing the relative errors of the fit parameters of the truncated and full data sets, especially parameter C for 205 nm, indicates that including the high concentration SHG intensity in the Langmuir fit is not appropriate. The Langmuir fit of the entire concentration range of KSCN does not converge, serving as further evidence of the divergence from Langmuir conditions at high concentrations.

The Gibbs free energy of adsorption of the thiocyanate ion to the surface was found to be -6.7 ± 1.1 kJ/mol for NaSCN and -6.3 ± 1.8 kJ/mol for KSCN using the truncated data sets. Interestingly, despite different interfacial structures, the thiocyanate affinity at the dodecanol/water interface is within experimental error of that determined for NaSCN at the air/water interface, -7.5 ± 0.1 kJ/mol (21). Adsorption of thiocyanate to the air/water interface was previously found by directly probing thiocyanate via VSFS, but no thermodynamic data were reported (22, 23).

Whether the agreement between the air/water and dodecanol/water interfaces is coincidental or the adsorption mechanism is relatively unchanged between the two interfaces remains an interesting question. Weakly hydrated ions have been shown to adsorb to air/water and hydrophobic/water interfaces by both experiment (10, 11, 39, 40) and theory (14, 16, 41), presumably due to hydrophobic effects, resulting in minimal disruption of the strong hydrogen bonding interactions of water. However, since the structure of the surfactant is unchanged by the presence of ions in similar systems (9, 29) and the dodecanol layer is part of the hydrogen bond network at the interface, the energetic preference of ions for the interface due to hydrophobic exclusion

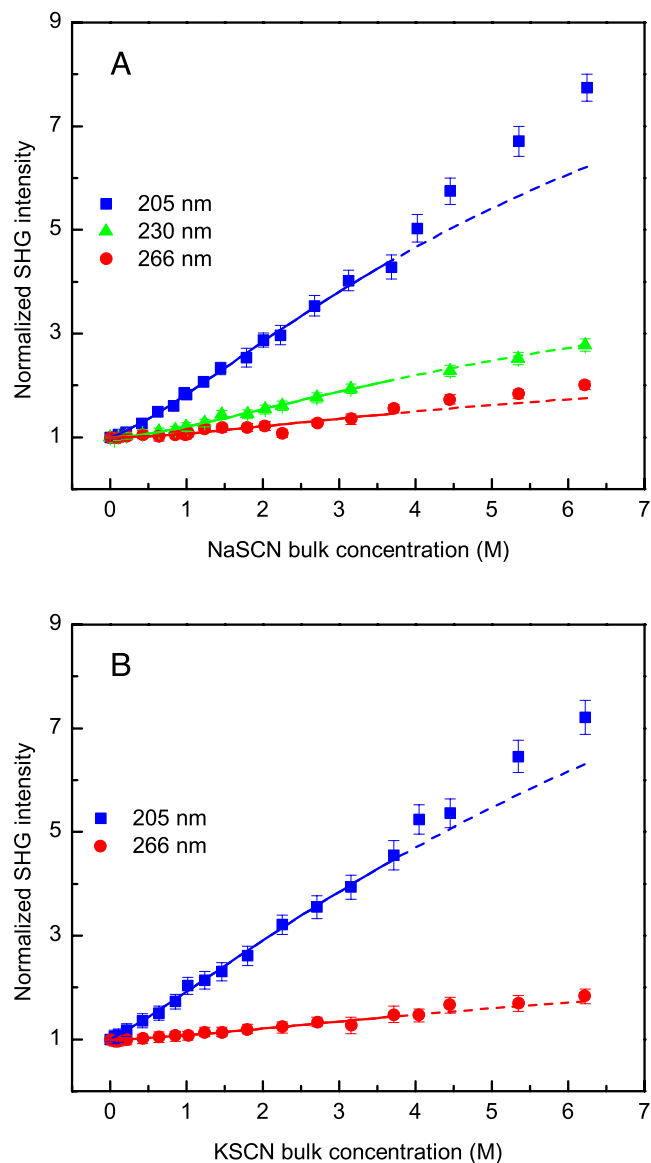


Fig. 3. SHG response for NaSCN (A) and KSCN (B) solutions and the corresponding Langmuir fits. The fits only include concentrations <4 M. The high concentration data are shown and the Langmuir fits are continued as dotted lines to illustrate the divergence from the fits of the high concentration data. The error bars are one standard deviation.

may be less than at the air/water interface. This difference could be counteracted by the relative image charge repulsions of thiocyanate at the air/water interface and the dodecanol/water interface. The image charge repulsion at the dodecanol/water interface is weaker since the dielectric constant of dodecanol is greater than that of air.

The presence of ions at the air/alcohol/water interface was previously investigated by XPS (20). In that study the photoelectron kinetic energy was varied to probe different depths of a 1-butanol and water solution deliquesced on a potassium iodide crystal. The authors conclude that the surface-enhanced concentration previously observed at the air/water interface (42) is suppressed at the air/butanol/water interface, as evidenced by a flattening of the ratio of iodide to potassium as a function of escape depth. This would appear to be in contrast with the results presented here, albeit with a different anion. However, the nature of the two interfaces makes direct comparisons difficult.

Table 1. Langmuir fit parameters*

	wavelength (nm)	B	C	ΔG_{ads} (kJ/mol)
NaSCN all data	205	3.2 ± 1.5	2.1 ± 1.8	-4.5 ± 0.9
	230	1.0 ± 0.5	1.6 ± 0.4	
	266	0.1 ± 0.2	1.9 ± 0.3	
NaSCN molarity < 4	205	1.0 ± 0.8	2.6 ± 0.3	-6.7 ± 1.1
	230	0.1 ± 0.2	1.8 ± 0.3	
	266	0.0 ± 0.2	1.2 ± 0.3	
KSCN [†] molarity < 4	205	1.7 ± 1.7	1.8 ± 1.4	-6.3 ± 1.8
	266	0.1 ± 0.2	1.1 ± 0.4	

*Parameter A is equal to one within 1% error in all cases.

[†]Fit of the full KSCN concentration range does not converge.

The air/solution interface comprising butanol and water is characterized by a non-uniform layer of loosely packed butanol, whereas the air/solution interface comprising dodecanol and water is a rigid monolayer. Furthermore, the manner in which the interface is probed is quite different for XPS and SHG. In XPS, the depth into the solution that is probed is determined by the photoelectron kinetic energy, while SHG probes regions characterized by broken inversion symmetry. Moreover, XPS measures relative concentrations, and our work reports Gibbs free energies of adsorption. The concentration and the Gibbs free energy are related in our model through the number of surface adsorption sites, which will vary depending on the system.

Another study of a macromolecule/water interface investigated thiocyanate at the PNIPAM/water interface with VSFS (9). Their work used a different formulation of the Langmuir model, but analysis of their data with the formulation used here yields a ΔG_{ads} of approximately -18 kJ/mol. The stronger adsorption to the PNIPAM/water interface is likely due to the presence of strongly polar amide moieties at the interface.

The fractional surface coverage of thiocyanate ions can be calculated from the Gibbs free energy by dividing Eq. [6] by N_S^{max} . The surface coverage versus bulk concentration is plotted in Fig. 4. As the bulk concentration of thiocyanate ions is

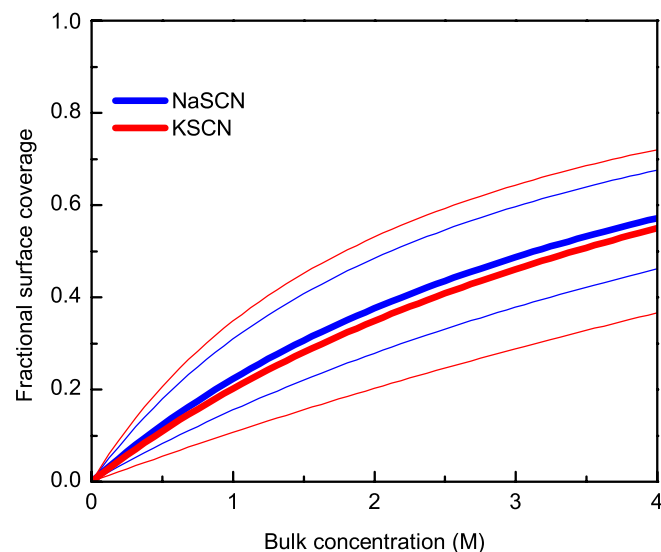


Fig. 4. Predicted fractional surface coverage of NaSCN and KSCN as a function of bulk concentration (bold lines). The narrow lines represent the error, one standard deviation.

increased, the surface concentration eventually becomes large enough that ion-ion interactions cannot be neglected. The breakdown of the Langmuir model for this system occurs when the thiocyanate surface coverage is approximately half of the number of surface sites. At this bulk concentration the ratio of all ions (including both anions and cations) to water molecules is $\approx 1:6$. Not only will there be repulsion between surface anions, but ion pairing of the cation and anion will also occur. It is therefore not surprising that the Langmuir model breaks down in this regime, but it is striking that the transition from Langmuir to non-Langmuir conditions appears to be so sharp. This is indicative of a structural change at the interface. Although the nature of the structural change is not clear from this work, it could be a change in the interfacial water structure, a second thiocyanate adsorption site in the interfacial layer, or a disruption of the dodecanol monolayer structure.

In most of the previous surface sensitive spectroscopic studies of thiocyanate, concentrations >4 M have not been investigated (9, 21, 22). However, Viswanath et al. (23) included concentrations up to 5 M in their direct VSFS study of thiocyanate at the air/water interface, finding that the oscillator strength, indicative of the surface anion density, leveled off at and >3 M concentrations. Further study of this interesting interfacial structural change is of considerable interest.

Conclusions

The prevailing explanation for the Hofmeister series invokes specific ion interactions at the macromolecule/water interface (5, 9, 12–19). To experimentally assess more complex issues, such as protein solubility and enzyme inhibition the interactions of ions with specific and relevant chemical moieties must be understood. Here, we report the study of anion adsorption to the interface formed by a monolayer of a long-chain alcohol and water, using resonant CTTS SHG of the strongly chaotropic thiocyanate ion. A Langmuir analysis shows that thiocyanate exhibits an enhanced interfacial concentration relative to that of the bulk. Cation identity has a minimal effect on the affinity of thiocyanate for the interface, since the surface affinities of thiocyanate for NaSCN and KSCN solutions were identical within error. These results are relevant to water/lipid interfaces, for example, since thiocyanate would now be expected to preferentially adsorb to OH rich cell walls. However, such interfaces are obviously more complex than an alcohol monolayer, and a more thorough understanding is clearly necessary. At high concentrations the increase in SHG signal with concentration is discontinuously greater than predicted by extrapolating lower concentrations, indicating an apparent change in the interfacial structure. High concentration analysis may be more relevant to physiological systems, since ions often have large apparent concentrations due to confinement by other structures.

Understanding the general mechanisms of surface adsorption involves a balance of competing forces, including hydrophobic exclusion effects, image charge repulsion, and direct interactions between the ion and the adsorbent. Varying the identity of both the ion and the liquid-liquid interface in future SHG studies can provide further insight on these interactions.

Materials and Methods

Experimental Design. The laser system has been described in detail previously (26). Briefly, a home-built Ti:sapphire oscillator seeds a regenerative amplifier (Spectra-Physics Spitfire). The amplified pulses pump an OPA (Quantronix TOPAS) generating the visible light used as the fundamental beam (1 kHz, 2 μ J, ≈ 100 fs) for SHG generation. A motorized variable neutral density filter is used to modulate the fundamental beam power during the course of the experiment. A beam splitter is used to direct $<10\%$ of the fundamental beam intensity to a photodiode as a relative measure of the power applied to the sample surface. The remaining fundamental light is focused on the sample surface with a 10 cm lens at 60° relative to the surface normal with p -polarization. For an isotropic surface with the plane of incidence defined as

the xz-plane, the symmetry of the system dictates that the only non-zero $\chi^{(2)}$ elements accessed by p-polarized incident light are $\chi_{zzz}^{(2)}$, $\chi_{zxx}^{(2)}$, and $\chi_{xzx}^{(2)} = \chi_{xxz}^{(2)}$. Therefore, all generated SHG is p-polarized. The SHG light is collimated by a 10 cm fused-Si lens and separated from the fundamental beam through the use of three dichroic mirrors and a monochromator (PI Acton, Spectra Pro SP-2155) before being collected by a solar-blind PMT (Hamamatsu, R7154PHA).

The modulated power of each pulse of the fundamental beam, R , is measured by the photodiode and binned into groups of $R^2 \pm \Delta$. The average number of photons, \bar{k} , collected per laser pulse is much less than one, and the PMT is used as a photon counter. The number of laser pulses where zero photons are detected, $N_{pulses}^{k=0}$, is counted, and assuming Poisson statistics for the distribution of photons detected in a given shot, the expectation value for the number of photons in a given fundamental power bin, $R^2 \pm \Delta$, can be evaluated as

$$\langle k \rangle = - \ln \left[\frac{N_{pulses}^{k=0}}{N_{pulses}^{total}} \right]_{R^2 \pm \Delta} \quad [7]$$

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Since SHG is a second-order process, plotting this value versus R^2 provides a linear relationship. The slope of the resulting line, determined by a variance-weighted least-squares fit, is taken as the system response, proportional to $|\chi_{system}^{(2)}|^2$. This also provides an inherent confirmation that the SHG signal exhibits the correct second-order power dependence.

Sample Preparation. All glassware was cleaned using Nochromix dissolved in concentrated sulfuric acid and rinsed with 18.2 M Ω water (Millipore MilliQ). Solutions were made with 18.2 M Ω water, NaSCN (Sigma-Aldrich, >99.99% metals basis), and KSCN (Sigma-Aldrich, >99.0%), which were used without further purification. An alcohol monolayer was prepared on the solution surface by floating a 1-dodecanol (Sigma-Aldrich, 98%) crystal on the solution surface, as described by Casson et al. (33). All samples were prepared and measured at room temperature.

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