

Resonant Second Harmonic Generation Studies of *p*-Nitrophenol Adsorption at Condensed-Phase Interfaces

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A comprehensive analysis of adsorption strength, average molecular orientation, and absolute molecular direction for *p*-nitrophenol at solid-air, solid-liquid, and liquid-air interfaces is obtained from the near-resonant optical second harmonic generation (SHG) from the interface. Perturbation theory calculations of the molecular nonlinear polarizability tensor elements using π -electron wave functions are used to identify the dominant tensor elements. The near-resonant SHG from a monolayer of *p*-nitrophenol is shown to require the use of two molecular nonlinear polarizability tensor elements in the equations relating the experimentally measured SHG to the average molecular orientation in the monolayer and therefore cannot be correctly described with the usual assumption of the complete dominance of a single molecular nonlinear polarizability tensor element. The average molecular orientation within the adsorbed monolayer is then obtained from the polarization dependence of the surface SHG and is described by the orientation parameter, $D = \langle \cos^3 \theta \rangle / \langle \cos \theta \rangle$, where θ is the angle between the molecular symmetry axis and the surface normal. A more realistic description of the molecular orientation is obtained by allowing for a partial Gaussian distribution in the angle θ . Additional measurements of the phase of the surface SHG are used in conjunction with the theoretical calculations of the molecular nonlinear polarizability to ascertain the direction of the transition dipole moment relative to the surface.

Introduction

Optical second harmonic generation (SHG) has been employed extensively at a wide variety of interfaces as a surface probe because of its demonstrated submonolayer sensitivity, rapid optical response time, and ability to easily discriminate between surface species and species in the adjacent bulk media.¹⁻⁵ Surface SHG experiments have been used to study dyes, surfactants, and a variety of other small organic molecules at both solid and liquid surfaces.⁶⁻²⁵ For systems where the SHG from the interface is dominated by the molecular contributions to the surface non-

linear susceptibility, the relative surface coverage and average orientation of molecules adsorbed to the interface can be measured. The strength of adsorption is obtained through the optically measured adsorption isotherm, and the average molecular orientation is determined through the analysis of the polarization and phase dependence of the surface second harmonic response.

Previous investigations of molecular orientation at condensed-phase interfaces via SHG have relied upon the assumption of the complete dominance of a single molecular nonlinear polarizability tensor element (known as the "uniaxial approximation") to correctly model the observed nonlinear response.^{5,16,23} In this paper a system is presented for which this approximation is no longer valid, therefore requiring a more rigorous theoretical analysis. It will be unequivocally shown that for the near-resonant SHG studies of *p*-nitrophenol adsorption at solid-air, solid-liquid, and liquid-air interfaces, a second molecular nonlinear polarizability tensor element must be included in the analysis in order to properly describe the SHG from the interface. The incorporation of this second tensor element is a simple extension of the theory presented previously for uniaxial systems and remains fully compatible with those works. The inclusion of more than one molecular nonlinear polarizability tensor element in the analysis of the SHG data is an important addition to the methodology in that it allows for the development of new applications which may not permit the selection of probe molecules with simple uniaxial behavior, as has been shown in previous SHG studies of large dye molecules.^{25,26}

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In this paper, the complete methodology is presented for obtaining the adsorption strength, average molecular orientation, and absolute molecular direction with the SHG from the interface. As shown previously,²⁵ molecular nonlinear polarizability calculations employing Pople-Pariser-Parr (PPP) π -electron wave functions can be used to determine which molecular nonlinear polarizability tensor elements will dominate the surface SHG. In addition, approximate calculations of the monolayer dielectric constants are performed at the fundamental and second harmonic wavelengths through a Kramers-Kronig analysis of the UV-vis absorption spectrum in order to circumvent the errors incurred by the assumption of these values. The average molecular orientation within the adsorbed monolayer is then obtained from the polarization dependence of the surface SHG and is described by an orientation parameter $D = \langle \cos^3 \theta \rangle / \langle \cos \theta \rangle$,²⁷ where θ is the angle between the molecular symmetry axis and the surface normal. A more realistic description of the average orientation is obtained by using partial Gaussian functions to model the possible distribution of orientations within the monolayer. Finally, the analysis of the molecular orientation is completed through the comparison of the experimentally measured phase of the surface SHG with the calculated signs of the molecular nonlinear polarizability tensor elements in order to determine the absolute direction (e.g., NO₂ up or down) of the molecules at the interface.

Experimental Considerations

p-Nitrophenol (NO₂C₆H₄OH) was obtained from Fluka Chemical Corp. and was purified by recrystallization prior to use. Optically flat fused silica windows obtained from ESCO were used as the solid substrates. The windows were cleaned before use as described previously.²⁵ Surface SHG experiments were performed at fused silica-air, fused silica-water, fused silica-chloroform, and water-air interfaces. For the fused silica-air experiments, the p-nitrophenol monolayer was formed by dipping the substrate into dilute ethanolic solution. The surface concentration of p-nitrophenol could be varied by changing the dipping solution concentration. An absorption spectrum of a full adsorbed monolayer was obtained with an HP 8452A diode array spectrometer and is shown in Figure 1. The absorption maximum at 320 nm suggests that a resonant SHG response will be observed at 640 nm. Comparison of this absorption spectrum to that of a dilute solution leads to an estimated surface coverage of 4×10^{14} molecules cm⁻². The surface coverage of p-nitrophenol at the other interfaces was controlled by its solution concentration (all aqueous solutions were made from Millipore-filtered water and adjusted to a pH of 2.0; chloroform was obtained from Burdick and Jackson and was used as received). All of the SHG results reported here have been corrected for the small contributions of the background SHG from the bare interface; however, this correction was always within the noise of the measurement at surface coverages greater than ~40% of a monolayer. All molecular orientation measurements were performed on monolayers with a surface coverage of ~80% of a full monolayer.

The experimental apparatus employed here is similar to that described previously.^{26,28} The silica substrate was used as the entrance window of a Teflon cell that could be filled with the appropriate liquid for the liquid-solid experiments. Pulses of light (10-ns pulse width, 10-Hz repetition rate) at 610 nm were focused through the window at an incident angle of 45° (corresponding to an incident angle of approximately 30° on the back surface) onto the monolayer with a typical surface energy density of 300 mJ cm⁻². For the liquid-air experiments, the beam was directed downward onto the surface at an angle of 45° with the reflected SHG being collected. The polarization of the

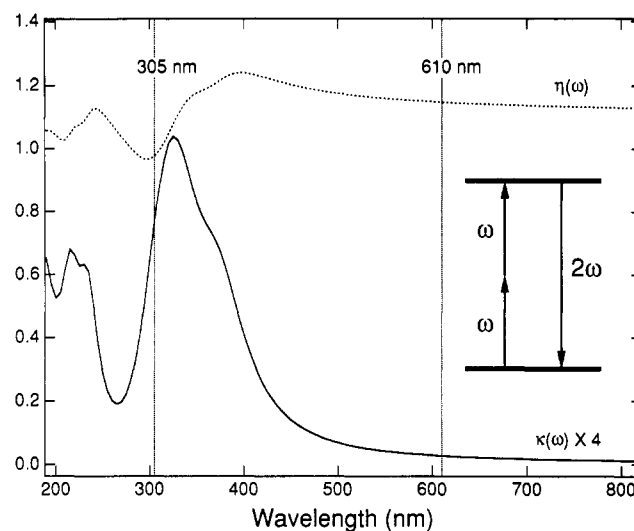


Figure 1. Optical absorption spectrum for a monolayer of p-nitrophenol adsorbed to a fused silica surface. The spectrum is plotted as the imaginary component of the dielectric constant, $\kappa \times 4$ (—). The absorption maximum at 320 nm corresponds to an absorbance of 1×10^{-2} . SHG is observed with incident laser light at 610 nm due to the resonance at the second harmonic wavelength of 305 nm (see diagram). Also plotted is the real component of the dielectric constant, η (- - -), as calculated by a Kramers-Kronig analysis of the absorption spectrum. The dielectric constant is given by $(\eta + i\kappa)^2$.

incident fundamental beam was varied continuously from 0° (p-polarized) to 90° (s-polarized) by a broad-band $\lambda/2$ plate/polarizer combination. The reflected second harmonic light from the monolayer was collected and sent through a second polarizer set to pass either s-polarized or p-polarized light from the surface. Appropriate UV-passing filters removed the reflected fundamental light, and a 0.175-m monochromator was used to verify the SHG wavelength. The SHG was detected with a cooled PMT, the output of which was averaged with a boxcar averager. No fluorescence from two-photon absorption was observed at the surface energy densities employed.

Absolute phase measurements were made with an interference technique utilizing a piece of z-cut quartz as described previously by Kemnitz et al.⁹ In the interference experiments, the fundamental beam was polarized at 45° and the s-polarized SHG was collected. In order to obtain the phase of the surface SHG relative to the input electric field, it was necessary to calibrate the interference pattern with a standard for which the phase of the SHG is known. This was accomplished by replacing the sample with a second piece of z-cut quartz of known absolute orientation and repeating the aforementioned interference experiment with the same polarizations. The z-cut quartz standard was aligned so that its positive x-axis was antiparallel to the laboratory x-axis. All phase measurements reported here are for molecules at the air-water interface. The results of the phase measurements are accurate to within $\pm 10^\circ$.

Results and Discussion

The complete methodology involved in the analysis of molecular monolayers with SHG incorporates several steps. First, prior to undertaking the adsorption and orientation investigation, it is necessary to understand the nonlinear response of the molecules to be studied. This involves the theoretical calculation of the second-order molecular nonlinear polarizability tensor, β , and results in the determination of the approximate magnitudes and signs of the various β tensor elements as a function of input photon energy. This information is fundamental to the determination of both the average molecular orientation and the absolute molecular direction. Once the molecular nonlinear response is understood, the monolayer is prepared and the SHG measurements can then be performed. In

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$$\beta_{ijk} + \beta_{ikj} = \frac{-e^3}{4\hbar^2} \sum_{n,n'=g}^N (r_{gn'}^j r_{n'n}^i r_{ng}^k + r_{gn'}^k r_{n'n}^i r_{ng}^j) \left(\frac{1}{(\omega_{n'n} - 2\omega + i\Gamma_{n'n})} \left(\frac{1}{(\omega_{ng} + \omega - i\Gamma_{ng})} - \frac{1}{(\omega_{n'g} - \omega + i\Gamma_{n'g})} \right) \pm \frac{1}{(\omega_{n'n} - 2\omega - i\Gamma_{n'n})} \left(\frac{1}{(\omega_{ng} + \omega + i\Gamma_{ng})} - \frac{1}{(\omega_{n'g} - \omega - i\Gamma_{n'g})} \right) \right) + (r_{gn'}^j r_{n'n}^k r_{ng}^i + r_{gn'}^k r_{n'n}^j r_{ng}^i) \left(\frac{1}{(\omega_{n'g} - \omega + i\Gamma_{n'g})(\omega_{ng} - 2\omega + i\Gamma_{ng})} \pm \frac{1}{(\omega_{n'g} - \omega - i\Gamma_{n'g})(\omega_{ng} - 2\omega - i\Gamma_{ng})} \right) + (r_{gn'}^i r_{n'n}^j r_{ng}^k + r_{gn'}^i r_{n'n}^k r_{ng}^j) \left(\frac{1}{(\omega_{ng} + \omega - i\Gamma_{ng})(\omega_{n'g} + 2\omega - i\Gamma_{n'g})} \pm \frac{1}{(\omega_{ng} + \omega + i\Gamma_{ng})(\omega_{n'g} + 2\omega + i\Gamma_{n'g})} \right) \quad (1)$$

order to evaluate the average molecular orientation from the surface SHG, it is necessary both to verify the presence of the molecules in the interfacial region and to demonstrate the dominance of the molecular contribution to the observed SHG signal. Such a determination involves the construction of an adsorption isotherm by varying the solution concentration of the molecules under investigation while monitoring the magnitude of the SHG. Next, polarization-dependent measurements of the surface SHG are performed, with the results being fit to theoretical equations in order to determine the macroscopic surface nonlinear susceptibility, $\chi^{(2)}$. The relative magnitudes of the nonzero β tensor elements, and subsequently the orientation parameter, D , are then calculated from the theoretical relationships between $\chi^{(2)}$ and β . Finally, the absolute molecular direction is obtained by measurement of the phase of the surface SHG followed by comparison of this phase to that calculated for a given molecular direction in the molecular nonlinear polarizability results.

A. Molecular Nonlinear Polarizability Calculation. In order to obtain average molecular orientation and absolute molecular direction information from the polarization dependence and phase measurements of the near-resonant surface SHG, knowledge of the complex second harmonic response of an isolated molecule is required. The sign and magnitude of this molecular SHG response are described by β . In the majority of previous SHG orientation studies, the complete dominance of a single molecular nonlinear polarizability tensor element, β_{zzz} (for molecules like *p*-nitrophenol), has been assumed. As stated above, this approximation is found to be invalid for the near-resonant SHG studies of *p*-nitrophenol. This fact will be demonstrated both through the theoretical calculation of the elements of β and through their experimental measurement. Using perturbation theory, the components of β can be expressed in terms of the molecular energies and wave functions as shown in eq 1,²⁹ where β_{ijk} is the tensor element referenced to the molecular coordinate axes i , j , and k , ω is the incident laser frequency, $h\omega_{ng}$ is the energy difference between excited state n and the ground state, Γ_{ng} is the lifetime (approximately the dephasing time) of excited state n , and r_{ng}^i is the transition dipole matrix element between states n and g along the molecular i -axis. Excited-state lifetimes (Γ_{nn}) and population feeding terms have been neglected in this equation. Where the plus/minus notation occurs, the plus signs are used to obtain the in-phase (real) component of β and the minus signs are used to obtain the 90° out of phase (imaginary) component.

For most aromatic molecules, it is reasonable to assume that the π -electronic structure is the sole contributor to

β in the UV-vis region of the electromagnetic spectrum. For these molecules, a Pople-Pariser-Parr (PPP) π -electron calculation^{30,31} can be used to obtain the energies and wave functions for the molecule.^{25,32} Using these results, the principle β tensor elements for *p*-nitrophenol have been calculated and are plotted in Figure 2. For *p*-nitrophenol, in the domain of an electronic resonance, the tensor element β_{zzz} is theoretically found to dominate the second harmonic response, with the tensor element β_{zxx} having the next most important contribution. The third possible nonzero tensor element, $\beta_{xxx} = \beta_{zzx}$, is found to be about an order of magnitude smaller than β_{zzz} . Both the real and imaginary components of β_{zzz} and β_{zxx} are plotted as a function of input photon energy in the figure. For this calculation the values of Γ_{ng} , $\Gamma_{n'g}$, and $\Gamma_{n'n}$ were all set to 2000 cm⁻¹, the experimentally determined half-width at half-maximum for the first electronic absorption of *p*-nitrophenol.

As seen in Figure 2, a resonance is observed at half the energy of the first excited state, which is at approximately 4.3 eV (287 nm). The exact position of this resonance varies with the condensed-phase environment of the molecule (for example, as shown in Figure 1 for a monolayer at the silica-air interface, the absorbance maximum

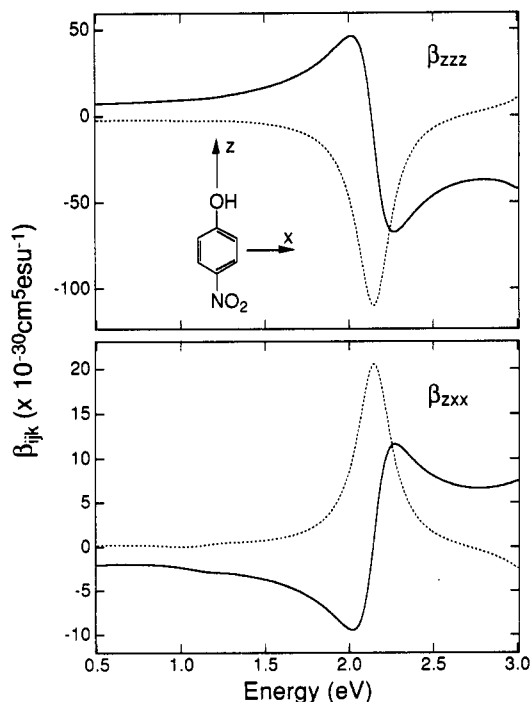


Figure 2. π -electron molecular nonlinear polarizability calculation for *p*-nitrophenol. The tensor elements β_{zzz} and β_{zxx} were found to be the dominant elements (with β_{zxx} approximately an order of magnitude smaller than β_{zzz}) and are defined with respect to the molecular axes depicted in the figure. Both real (—) and imaginary (---) components are shown for β_{zzz} and β_{zxx} .

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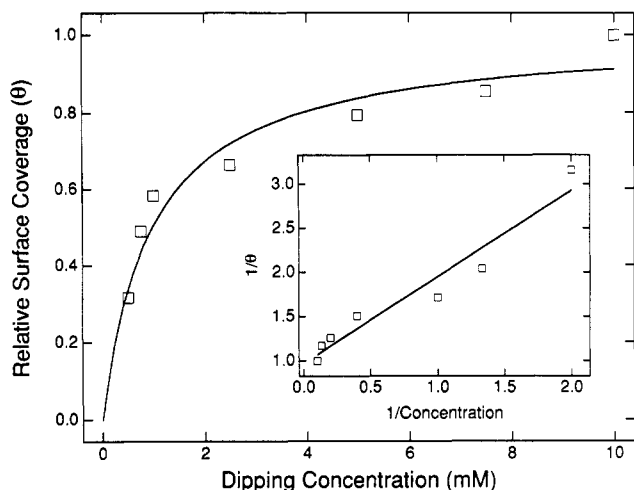


Figure 3. Relative surface coverage of *p*-nitrophenol on fused silica as determined from the resonant surface SHG. The data are plotted as a function of dipping concentration in ethanol. The inset shows the fit of the data to a Langmuir adsorption isotherm with an adsorption coefficient K_{ads} of 1100 M^{-1} .

occurs at 320 nm). The dominance of the β_{zzz} element arises from the fact that the electronic transition to the first excited state involves both a large transition dipole (r_{ng}) and a large change in the permanent dipole moment, both of which occur in the z -direction. The nonzero contribution of β_{zzz} is due to the presence of a higher energy transition at 5.5 eV which possesses a large x -transition dipole as well as a large x -transition dipole to the first excited state ($r_{n'n}$), thus leading to a large contribution from the term $r_{gn}^x r_{n'n}^x r_{ng}^z$ in eq 1. As will be demonstrated below, the inclusion of β_{zzz} and β_{zzx} is necessary in order to properly describe the near-resonant SHG from these molecules. However, due to the uncertainties in theoretical calculations of this type, the exact magnitudes of the two tensor elements will not be taken from the nonlinear polarizability calculation, but instead can be determined experimentally from the polarization dependence of the SHG signal. The experimental determination of the relative importance of β_{zzz} and β_{zzx} will also allow for the confirmation of their theoretically calculated relative phases. In addition, the signs of the tensor elements obtained from nonlinear polarizability calculations will be required in the determination of the absolute molecular orientation from the surface SHG phase measurements. This use of the nonlinear polarizability calculations is discussed in detail in section D.

B. Adsorption Isotherm Measurements. Once the molecular nonlinear response is understood, initial SHG measurements are then undertaken to determine the extent to which the molecular nonlinear response contributes to the surface SHG, the relative surface coverage of the molecules being probed, and the strength of adsorption to the interface. The dominance of the molecular response in the surface SHG can be readily verified by simply noting dramatic changes in the SHG intensity as a function of surface coverage of the molecules of interest; this dominance virtually eliminates the errors caused by background SHG from the interface. In addition, if a molecule's orientation is found to remain constant over a wide range of surface coverages (as is the case for *p*-nitrophenol at the surfaces reported here), this same information can be used to determine the relative surface coverage of the adsorbed molecules.^{6,11} For example, the relative surface coverage of *p*-nitrophenol adsorbed onto a silica surface as a function of dipping solution concentration is shown in Figure 3. This con-

centration dependence can be fit with a Langmuir adsorption isotherm (see inset graph) and yields an adsorption coefficient, K_{ads} , of $1100 \pm 200 \text{ M}^{-1}$.

Thermodynamic information cannot be obtained from adsorption isotherms of monolayers prepared with the dipping procedure. However, isotherms involving spontaneous adsorption at liquid–solid and liquid–air interfaces can be used to obtain values for the free energy of adsorption.¹¹ The ΔG° values are obtained from K_{ads} exactly as described by Castro et al., with the requisite substitution of the appropriate solvent molarity.¹¹ For example, using resonant SHG, it was observed that *p*-nitrophenol adsorbs spontaneously to the fused silica surface from chloroform solution with a K_{ads} of $70 \pm 20 \text{ M}^{-1}$, corresponding to a ΔG° of $-17 \pm 1 \text{ kJ M}^{-1}$. This value compares favorably with the strength of a hydrogen bond (20 kJ M^{-1}) and thus suggest that the *p*-nitrophenol OH group is hydrogen-bonded to the open OH sites on the fused silica. *p*-Nitrophenol is also found to adsorb to the water–air interface.¹⁰ The K_{ads} for this system was measured to be 40 M^{-1} , which corresponds to a ΔG° of -19 kJ M^{-1} . As in the case of *p*-nitrophenol on fused silica, this result also suggests that the formation of hydrogen bonds is important in the adsorption process. In contrast, no surface SHG was observed for *p*-nitrophenol at the fused silica–water interface from aqueous solution of pH 2.0. This result is most likely due to the preferential adsorption of water to the surface.

C. Average Molecular Orientation Calculation. The SHG from the surface can be described as a group of individual molecules collectively responding to an incident laser light field to create an induced nonlinear optical response. As discussed in section A, the nonlinear behavior of an individual molecule is described by the molecular nonlinear polarizability tensor, β . The summation of the elements of β over all molecules, while simultaneously taking into account the orientation of each molecule, then gives the macroscopic surface nonlinear susceptibility tensor, $\chi^{(2)}$, for the interface. It is this nonlinear susceptibility tensor which is probed in the SHG experiment. The mathematical equation which describes this process of relating the nonlinear response of a group of molecules to the experimentally measured nonlinear susceptibility is given by eq 2, where the summation over all of the

$$\chi_{IJK} = N_s \sum \langle F_{IJKijk}(\phi, \theta, \alpha) \rangle \beta_{ijk} \quad (2)$$

molecules on the surface has been reduced to simply multiplying the average of the molecular orientation distribution function, $\langle F_{IJKijk}(\phi, \theta, \alpha) \rangle$, by the surface concentration, N_s , and β . The molecular angles ϕ , θ , and α are defined relative to the space-fixed coordinates as presented previously.²⁵ The remaining summation is over the molecular coordinates i , j , and k .

As stated above, the SHG from a monolayer of molecules is described by the nonlinear susceptibility, $\chi^{(2)}$, which relates the intensity of the surface SHG signal, $I(2\omega)$, to the square of the incident laser intensity, $I(\omega)$.¹ If one assumes that the molecules at the interface are randomly oriented in terms of rotation around the surface normal, $\chi^{(2)}$ has only three unique elements: χ_{xxz} , χ_{zxx} , and χ_{zzz} . The intensity of the s-polarized and p-polarized SHG signal can then be directly related to these elements:²⁶

$$I_s(2\omega) \propto |a_1 \chi_{XXX} \sin 2\gamma|^2 I(\omega)^2 \quad (3)$$

$$I_p(2\omega) \propto |(a_2 \chi_{XXZ} + a_3 \chi_{ZXX} + a_4 \chi_{ZZZ}) \cos^2 \gamma + a_5 \chi_{ZXX} \sin^2 \gamma|^2 I(\omega)^2 \quad (4)$$

where γ is the polarization angle of the incident light ($\gamma = 0^\circ$ for p-polarized light and $\gamma = 90^\circ$ for s-polarized light) and the a_i terms describe the electric fields in the monolayer, and thus include the dielectric constants of the monolayer at frequencies ω and 2ω .^{33,34} These dielectric constants are determined separately through a Kramers-Kronig analysis of the optical absorption spectrum.²⁵ The calculated real and imaginary components of the dielectric constant for *p*-nitrophenol on fused silica are shown in Figure 1. From this calculation, the approximate dielectric constants for the monolayer are found to be 1.3 for $\epsilon_M(\omega)$ at 600 nm and 1.0 for $\epsilon_M(2\omega)$ at 300 nm. These values are approximate since the thickness of the monolayer is required for the calculation and has been estimated at 1 nm.²⁵

Curves of $I_p(2\omega)$ and $I_s(2\omega)$ as a function of γ for a monolayer of *p*-nitrophenol adsorbed at the silica-air interface are shown in Figure 4. From this data, the magnitudes of the various $\chi^{(2)}$ elements are then obtained via eqs 3 and 4. Once the elements of $\chi^{(2)}$ have been determined, they can be related to the elements of β by the molecular orientation distribution function, given in eq 2. The orientation distribution function can be reduced to a function of θ alone (the angle between the surface normal and the molecular *z*-axis) by making the usual assumptions that the molecules are oriented randomly about the surface azimuth (ϕ) and in rotation about the molecular *z*-axis (α), thus greatly simplifying the orientation analysis. The assumption of a random distribution in α is reasonable for a small molecule like *p*-nitrophenol. Alternatively, a fixed value for α could have been assumed, as has been done previously for large dye molecules.^{17,25-27} As shown in section A, for molecules with C_{2v} symmetry there are three independent nonzero molecular tensor elements, β_{zzz} , β_{zxx} , and $\beta_{xxx} = \beta_{xxx}$. These tensor elements can be shown to relate to the experimentally determined χ 's through the manipulation of eq 2 (with the aforementioned assumptions) to yield

$$\frac{\beta_{zxx} - \beta_{xxx}}{\beta_{zxx} + \beta_{xxx}} = 2 \frac{\chi_{ZXX} - \chi_{XXX}}{\chi_{ZZZ} + 2\chi_{XXZ}} \quad (5)$$

Far from resonance, Kleinmann symmetry dictates that $\beta_{zxx} = \beta_{xxx}$ and $\chi_{ZXX} = \chi_{XXX}$; hence, both sides of eq 5 are zero. Likewise, for molecules which can be assumed to be uniaxial in β_{zzz} , the assumption that $\beta_{zxx} = \beta_{xxx} = 0$ is made, and again, $\chi_{ZXX} = \chi_{XXX}$. However, as resonance is approached Kleinmann symmetry is no longer valid, as is the case in the *p*-nitrophenol experiments presented here. From the molecular nonlinear polarizability calculations, it is apparent that $\beta_{zzz} > \beta_{zxx} \gg \beta_{xxx}$, and therefore eq 5 can further be reduced to

$$\frac{\beta_{zxx}}{\beta_{zzz}} = 2 \frac{\chi_{ZXX} - \chi_{XXX}}{\chi_{ZZZ} + 2\chi_{XXZ}} \quad (6)$$

which is valid for all near-resonant SHG experiments in which the molecular nonlinear response can be described by the two tensor elements β_{zzz} and β_{zxx} while still remaining valid for all molecules which can be assumed

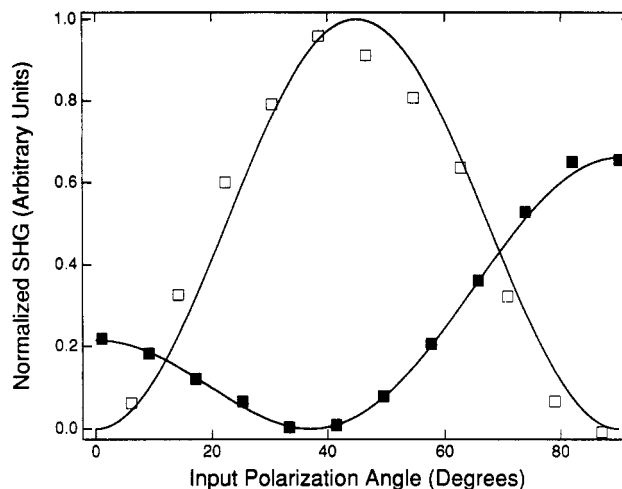


Figure 4. Polarization dependence of the resonant SHG from a *p*-nitrophenol monolayer on fused silica. The p-polarized (filled squares) and s-polarized (open squares) SHG from the monolayer are plotted as a function of input polarization, where 0° corresponds to p-polarized fundamental light and 90° to s-polarized fundamental light. The solid lines are the fits to eqs 3 and 4 used to determine the values of χ_{ZXX} , χ_{XXX} , and χ_{ZZZ} for the surface SHG.

to be uniaxial in β_{zzz} for both resonant and nonresonant experiments. Thus, eq 6 remains fully compatible with all previous works of this type while allowing for the expansion of the theory to include the possibility of a nonzero contribution from β_{zxx} .

The experimental values of χ_{XXZ} and χ_{ZXX} for *p*-nitrophenol at the fused silica-air interface demonstrate that β_{zzz} cannot be the only contributing β tensor element as $\chi_{XXZ}/\chi_{ZXX} = 1.7$ (when the monolayer dielectric constants calculated above are used). Previous researchers who have assumed β_{zzz} to be the only contributing tensor element were required to make further assumptions in the assignment of the monolayer dielectric constants in order to meet the requirement that $\chi_{XXZ} = \chi_{ZXX}$.¹⁶ In our experiments on *p*-nitrophenol adsorbed at the fused silica-air interface this would require $\epsilon_M(2\omega)/\epsilon_M(\omega) = 1.3$, a value which is significantly different from the value of 0.77 calculated from the Kramers-Kronig analysis (see Figure 1). Therefore, the assumption of a single dominant β tensor element must be eliminated as a viable approximation in these experiments. Using the SHG results in Figure 4, the ratio for the two dominant β elements, β_{zxx}/β_{zzz} , is found to be -0.31 . Note that the two elements are observed to be 180° out of phase, as is predicted in the molecular nonlinear polarizability calculations. The experiments at the chloroform-silica and water-air interfaces also yielded negative values for β_{zxx}/β_{zzz} and were slightly different from -0.31 , presumably due to the shifting of the electronic resonance in the different solvents.

For the determination of the average molecular orientation, a second relationship can be derived from eq 2, which provides a value for the orientation parameter, D , directly from the measured $\chi^{(2)}$ values:²⁷

$$D = \frac{\langle \cos^3 \theta \rangle}{\langle \cos \theta \rangle} = \frac{\chi_{ZZZ} - \chi_{ZXX} + \chi_{XXX}}{\chi_{ZZZ} + 3\chi_{XXZ} - \chi_{ZXX}} \quad (7)$$

where θ is the angle between the molecular *z*-axis and the surface normal. All of the assumptions used in the derivation of eq 6 were also used to obtain eq 7. As for eq 6, eq 7 is valid for all molecules in which β_{zxx} and β_{zzz} can be assumed to be the only nonzero tensor elements and remains valid for all molecules which are uniaxial in β_{zzz} . For *p*-nitrophenol at the silica-air interface, D is

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(34) Mizrahi, V.; Sipe, J. E. *J. Opt. Soc. Am.* 1988, **B5**, 660.

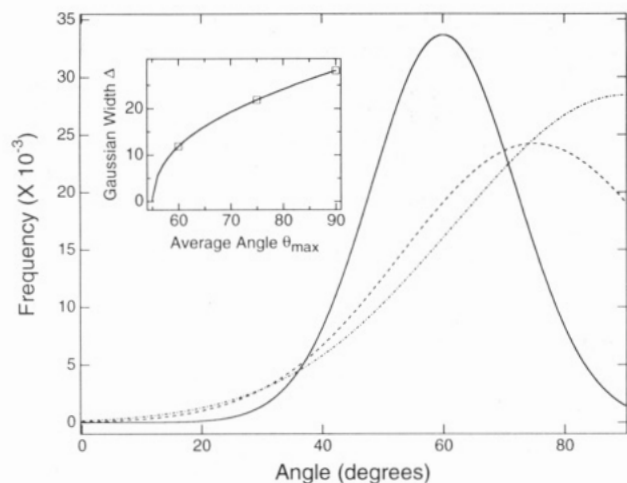


Figure 5. Three possible partial Gaussian distributions that fit the observed orientation parameter $D = 0.33$ for *p*-nitrophenol at the silica-air interface with θ_{\max} of 60° (—), 75° (---), and 90° (---). The insert plots the Gaussian width, Δ , required as a function of the most probable molecular angle.

measured to be 0.33 ± 0.07 . The results are similar for *p*-nitrophenol at the water-air and chloroform-silica interfaces, yielding $D = 0.26$ and $D = 0.27$, respectively. The experimentally determined values for D demonstrate that there is a preferential orientation of molecules in the monolayer since D would be equal to $2/3$ if the *p*-nitrophenol molecules in the monolayer were distributed evenly, with angle θ ranging between 0° and 90° .

If all of the *p*-nitrophenol molecules were aligned on the surface with exactly the same orientation, a D of 0.33 would correspond to an angle θ of 55° . This value is comparable to that reported previously for similar aromatic molecules.⁸ A more realistic view of molecular orientation in the monolayer can be obtained by allowing for a distribution in the angle θ . This distribution can be modeled as a partial Gaussian function of width Δ about an angle θ_{\max} . The term "partial Gaussian" refers to the fact that the distribution is not necessarily symmetric about θ_{\max} , but is truncated at 0° and 90° (see Figure 5 for example). The angle θ_{\max} corresponds to the most probable value of θ for a given molecule in the monolayer, and the parameter Δ corresponds to the normal Gaussian width. In the case of *p*-nitrophenol at the silica-air interface, the experimentally determined orientation parameter can be fit by these partial Gaussian distributions having θ_{\max} angles ranging between 55° and 90° and corresponding widths ranging from 0° to 28° , respectively. The orientation parameter could not be fit with any θ_{\max} less than 55° . Some representative partial Gaussian distributions which give a D value of 0.33 are shown in Figure 5. The inset in Figure 5 gives the variation of Δ as a function of θ_{\max} when $D = 0.33$.

D. Absolute Molecular Orientation Measurements. Although the average molecular orientation angle can be obtained directly from the polarization dependence of the surface SHG, a complete description of the molecular orientation in the monolayer can only be obtained by performing further SHG measurements in order to deduce the absolute direction of the molecular orientation on the surface. As described previously, these experiments entail the measurement of the phase of the χ_{XXZ} surface susceptibility tensor element through an interference method with a second SHG source.⁹ Upon comparison of the measured phase of this tensor element with that expected from the molecular nonlinear polarizability calculation, the absolute orientation with respect

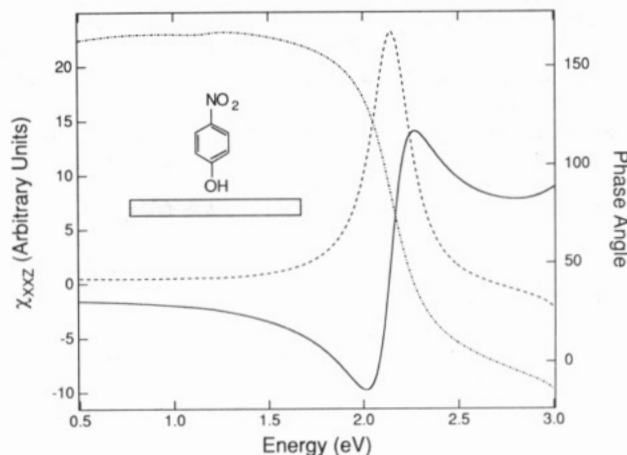


Figure 6. The real (—) and imaginary (---) components and the expected phase (---) of the χ_{XXZ} surface nonlinear susceptibility element as a function of fundamental photon energy. These curves are obtained through eq 2 from the results of Figure 2 and the measured orientation of *p*-nitrophenol. The calculation shown here is for the case where the NO_2 group points up (out of the water-air interface).

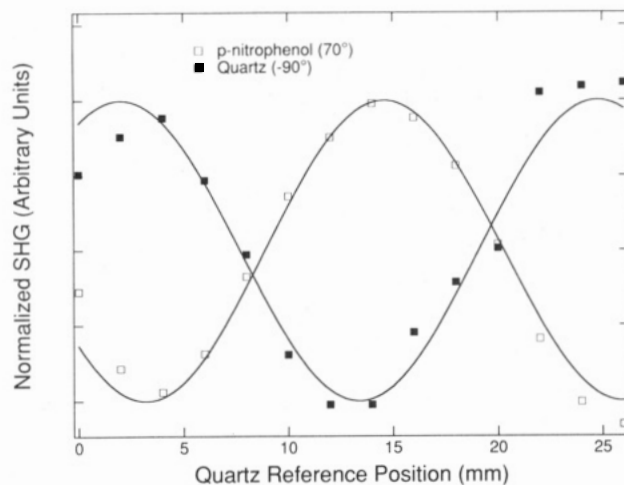


Figure 7. Interference measurements of the phase of the resonant SHG signal at 610 nm used to determine the absolute orientation of the *p*-nitrophenol at the air-water interface. The filled squares are from the *z*-cut quartz standard and correspond to a phase of 270° relative to the fundamental electric fields. The open squares are from the *p*-nitrophenol monolayer and exhibit a phase of 70° , thus indicating that the NO_2 group points up, out of the water (see Figure 6).

to the surface (which in the case of *p*-nitrophenol at the air-water interface means NO_2 up or down) can be ascertained.

The expected phase of χ_{XXZ} can be calculated from the molecular nonlinear susceptibility by eq 2. The results of this calculation for the case where the molecule has its nitro group up are plotted in Figure 6. As seen in the figure, the phase of χ_{XXZ} is calculated to be 180° below resonance, 90° on resonance, and 0° above resonance. In contrast, if the molecule were oriented with its nitro group down, the phase of χ_{XXZ} would range between 0° and -180° with a value of -90° on resonance. For the *p*-nitrophenol molecule at the air-water interface, the phase of χ_{XXZ} was found to be $70^\circ \pm 10^\circ$ at 610 nm, as is shown in Figure 7. This result suggests that the nitro group is up (i.e., pointing out of the water), a result which is consistent with previous nonresonant SHG studies.⁹

Summary and Conclusions

In summary, the complete methodology for determining

adsorption strength, average molecular orientation, and absolute molecular direction in interfacial regions has been presented along with the results of its application to the adsorption of *p*-nitrophenol at a variety of interfaces. While maintaining complete compatibility with previous works of this type, this methodology allows for the extension of the SHG experiments to systems which require the inclusion of two molecular nonlinear polarizability elements, β_{zzx} and β_{zzz} , in the description of the SHG from the interface. It has been demonstrated that, without the inclusion of a nonzero β_{zzx} element for near-resonant SHG experiments on *p*-nitrophenol, the dielectric constants for the monolayer must be adjusted to values significantly different from those calculated with a Kramers-Kronig analysis of the UV-vis absorption spectrum of the monolayer in order to meet the requirement that $\chi_{xxz} = \chi_{zxx}$. Further improvements in the methodology have been obtained by allowing for a distribution of angles θ within the monolayer, thus providing for a more realistic de-

scription of order within the monolayer as measured through the experimentally determined orientation parameter, $D = \langle \cos^3 \theta \rangle / \langle \cos \theta \rangle$. This distribution of molecular orientations has been modeled with a partial Gaussian function of width Δ and maximum θ_{\max} . Finally, measurements of the phase of the near-resonant surface SHG can be compared to the phase expected from the molecular nonlinear polarizability calculations to determine the absolute orientation of the molecules adsorbed at the interface. The methodology developed in this paper can be extended to other molecules and interfaces and is currently being used in our laboratory to study adsorption and orientation at the interface between two immiscible electrolyte solutions (ITIES).

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