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COMMENTS

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Comment on ''Molecular orientation determined by second-harmonic generation: Self-assembled monolayers''

Dipankar Roy*
Department of Physics, Clarkson University, Potsdam, New York 13699-5820

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A recent paper by Eisert *et al.* [Phys. Rev. B **58**, 10 860 (1998)] describes a second-harmonic generation (SHG) technique for probing molecular orientation in self-assembled monolayers (SAMs). Their results have raised some questions about the frequently used description of the optical properties of thin films. In their paper, the SAM film is considered anisotropic for SHG, but is assumed to be isotropic in terms of its linear optical response. It is likely that these different treatments of the same system have contributed to the unusual perspectives developed in the above paper. The purpose of this communication is to attempt a clarification of these observations. Here, a phenomenological model is outlined that treats linear and nonlinear optics of the interface in a single framework and can be used to analyze SHG from SAMs. It is also shown that, depending on the experimental system, conventional SHG measurements of phase and intensity may not be enough to determine the orientation of SAMs.

Eisert *et al.* have demonstrated how the unique surface sensitivity of second-harmonic generation (SHG) can be utilized to study interfaces of Au and self-assembled monolayers (SAMs).[1] Their results, however, lead to a number of apparently surprising implications. Their analysis of the Fresnel factors, initially presented in a three-phase model, relies eventually on a two-phase model to achieve agreement between the results of SHG and those of linear optical methods. The authors consider this finding unexpected in view of the success of three-phase models in linear surface optics. Moreover, the implications of the local field factors are relatively unclear. It was also possible to explain the SHG data collected in ethanol simply by replacing the requirement of phase information with the incorporation of a readjusted higher refractive index in the Fresnel factors. This observation is also unexpected in view of the strong governing role of phase factors in SHG.[2]

It is likely that these apparently unexpected implications of the SHG results are related to certain qualitative features of the model used by Eisert *et al.* to interpret their data. Their model, based on previously used simple formulations, focuses primarily on the nonlinear response of the interface and treats the linear effects only qualitatively. For instance, the nonlinear effects in the SAM film are used to probe its anisotropy (orientation), but its linear refractive index is assumed to be isotropic. While such assumptions are found to hold for certain systems (depending on the fundamental frequency for SHG), they may not hold as well in the case of SAMs.[3] This, in particular, is a relevant issue—considering the wide range of linear optical methods that are sensitive to and used to measure anisotropies in SAMs.[4–6]

To note the importance of the linear optical parameters in surface SHG, consider the net surface polarization (up to its second-order term): $\mathbf{P}=\mathbf{P}^{(1)}+\mathbf{P}^{(2)}$. For a fundamental electric field $\mathbf{E}(\omega)$ at the location of the polarization sheet, we have $P_i^{(1)}(\omega)=\Sigma_j\chi_{ij}^{(1)}E_j(\omega)$ and $P_i^{(2)}(2\omega)=\Sigma_{jk}\chi_{ijk}^{(2)}E_j(\omega)E_k(\omega)$. Here, $\chi_{ij}^{(1)}$ and $\chi_{ijk}^{(2)}$ are the (total) linear and nonlinear surface susceptibilities, respectively; ω is the incident photon frequency. The linear refractive index $\tilde{n}_{ij}$ of a surface layer of thickness d has the form $(\tilde{n}_{ij})^2=\delta_{ij}+4\pi(\chi_{ij}^{(1)}/d)$. Since $\mathbf{P}^{(1)}$ and $\mathbf{P}^{(2)}$ are coupled, all adsorbate effects experienced by $\chi_{ijk}^{(2)}$ are also experienced by $\tilde{n}_{ij}$ and hence by the Fresnel factors.[7] Thus, the linear and nonlinear optical parameters of the SAM interface should be treated identically in the working equations used to analyze the SHG data. Such a formalism can be developed in two steps. In the first step, a proper correspondence should be established between the interpretations of the two-phase (used in SHG) and three-phase (used in linear optics) models. In the second step, the relevant effects of the SAM film (such as its spatial anisotropy) should be included in both the linear refractive indices and the nonlinear susceptibility elements of the interface.

First we discuss the formulation of the appropriate three-phase model. Each nonzero element $\chi_{ijk}^{(2)}$ of the total nonlinear susceptibility in the present case has the form[1,7]

$$\chi_{ijk}^{(2)}=\chi_{2;ijk}^{(2)}+\chi_{3;ijk}^{(2)}+\chi_{I;ijk}^{(2)}, \tag{1}$$

where $\chi_{u;ijk}^{(2)}$ denotes the susceptibility of the uth phase in Fig. 3 of Ref. 1 [$u=1$ (isotropic environment), 2 (anisotropic film), and 3 (isotropic substrate)]; $\chi^{(2)}_{I;ijk}$ corresponds to the interactions at the (2-3) interface. A two-phase model has been traditionally used to describe Eq. (1).[8] On the other hand, the linear effects are commonly treated with a three-phase model.[5,6,9] For surface SHG, it is necessary to combine the essential features of these two- and three-phase models in one description (otherwise, as noted by Eisert *et al.* in Ref. 1, the task of choosing the right Fresnel factors becomes nontrivial). For submonolayer adsorption of monatomic species, it is convenient to use a modified two-phase model for SHG that also incorporates certain elements of a three-phase model to describe the linear effects.[7,10,11] A three-phase model is more appropriate for a SAM where the sheet of superimposed nonlinear polarizations is chosen within the surface film. While making the transition from the traditional two-layer description of Eq. (1), one must also account for all the additional complications of the three-layer case. These include interference effects within the film, as well as the effect of film thickness d on the phase of SHG.

Sipe's three-phase model for linear surface optics provides the basis for the considerations of these effects.[12] Considering the beam coordinates and Fig. 3 from Ref. 1, and locating $z=0$ at the (1-2) interface, one can place the polarization sheet describing $\chi^{(2)}_{ijk}$ at $-z_a$ below the (1-2) plane (z_a corresponds to the position of the center of the molecular unit representing the predominant nonlinear polarizability). Applying Sipe's formulation to this system, it is possible to write the following general expression for the SHG intensities $I^{\gamma p}_{\mathrm{SHG}}$ in the γ (input)–p (output) polarization configuration[12,13]:

$$\sqrt{I^{\gamma p}_{\mathrm{SHG}}}=|f_0||F_z(2\omega)P^{(2)\gamma}_z-F_x(2\omega)P^{(2)\gamma}_x|, \tag{2}$$

where $f_0=[4\pi i\bar{\omega}n_1(2\omega)]\sqrt{c/2\pi}$. Denoting the frequencies as ω_μ [$\mu=1$ (fundamental, $\omega_1=\omega$) or 2 (SHG, $\omega_2=2\omega$)], we write $\bar{\omega}_\mu=(\omega_\mu/c)$; c is the velocity of light in vacuum. The superscript γ implies p or s polarization, and provides the value of the angle that describes the polarization; $\gamma=0$ for p polarization and $\gamma=\pi/2$ for s polarization. For a uniaxial surface film, $P^{(2)p}_z=\chi^{(2)}_{zxx}(E^p_x)^2+\chi^{(2)}_{zzz}(E^p_z)^2$; $P^{(2)p}_x=2\chi^{(2)}_{xxz}E^p_xE^p_z$; $P^{(2)s}_z=2\chi^{(2)}_{zyy}(E^s_y)^2$; $P^{(2)s}_x=0$. The fundamental field components E^γ_i in the sample are related to the incident laser field E_L as

$$E^\gamma_i(\omega)=G_i(\gamma)F_i(\omega)E_L(\omega). \tag{3}$$

Here, $G_x=G_z=\cos\gamma$; $G_y=\sin\gamma$. For molecules such as those studied by Eisert *et al.*, $\chi^{(2)}_{zxx}=\chi^{(2)}_{zyy}\equiv\chi^{(2)}_{xxz}$.[14,15] One can express $\chi^{(2)}_{zxx}$ and $\chi^{(2)}_{zzz}$, in terms of the molecular tilt angle θ by using Eq. (5) of Ref. 14. The Fresnel factors for the present case are expressed as

$$F_z(\omega_\mu)=\frac{a^p_\mu S^{p+}_\mu k^p_{1x}(\omega_\mu)}{n^p_2(\omega_\mu)N^p_\mu l^p_\mu}, \tag{4}$$

$$F_x(\omega_\mu)=\frac{a^p_\mu S^{p-}_\mu k^p_{2z}(\omega_\mu)}{n^p_2(\omega_\mu)N^p_\mu l^p_\mu}, \tag{5}$$

$$F_y(\omega_\mu)=(-\omega_\mu a^s_\mu S^{s-}_\mu)/(N^s_\mu l^s_\mu), \tag{6}$$

$$S^{\gamma\pm}_\mu=1\pm r^\gamma_{23}(\omega_\mu)b^\gamma_\mu, \tag{7}$$

$$N^\gamma_\mu=1-r^\gamma_{21}(\omega_\mu)r^\gamma_{23}(\omega_\mu)g^{(\gamma)}_\mu, \tag{8}$$

where $k^\gamma_{1x}(\omega_\mu)=\bar{\omega}_\mu n_1(\omega_\mu)\sin\alpha_1$ and $k^\gamma_{2z}(\omega_\mu)=\bar{\omega}_\mu n^\gamma_2(\omega_\mu)\cos\alpha^\gamma_2(\omega_\mu)$. The angle $\alpha^\gamma_u(\omega_\mu)$ characterizes the propagation of the γ-polarized fundamental ($\mu=1$) or the SH ($\mu=2$) beam in medium u;$n^\gamma_u(\omega_\mu)$ is the linear refractive index of the uth phase for γ-polarized photons at the frequency ω_μ, and $\mathbf{k}^\gamma_u(\omega_\mu)$ is the corresponding wave vector. For an isotropic medium, $n^p_u=n^s_u$ and $\alpha^p_u(\omega_\mu)=\alpha^s_u(\omega_\mu)$. We also define $a^\gamma_\mu=\exp[-ik^\gamma_{2z}(\omega_\mu)z_a]$; $b^\gamma_\mu=\exp[2ik^\gamma_{2z}(\omega_\mu)(d+z_a)]$; $g^\gamma_\mu=\exp[2ik^\gamma_{2z}(\omega_\mu)d]$; $l^p_1=[\bar{\omega}/t^p_{12}(\omega)]$; $l^p_2=[k^p_{2z}(2\omega)/t^p_{21}(2\omega)]$; $l^s_\mu=[\bar{\omega}_\mu/t^s_{12}(\omega_\mu)]$; r^γ_{uv} and t^γ_{uv} are the standard reflection and transmission coefficients for the u-v interface with γ-polarized photons.[12] In the limit $d\rightarrow 0$, I_{SHG} in Eq. (2) does not vanish, and still contains the signature $[n^\gamma_2(\omega_\mu)]$ of the adsorbate. Furthermore, unlike the earlier three-phase models of SHG,[15] all the nonzero susceptibility terms in the present case have the form of Eq. (1). Also note that Eqs. (4)–(8) are considerably simplified as a^γ_μ, b^γ_μ, and g^γ_μ approach unity in the limit of a thin (but finite) film where d is small compared to both $[\mathrm{Re}\,k^\gamma_{2z}(\omega_\mu)]^{-1}$ and $[2\,\mathrm{Im}\,k^\gamma_{2z}(\omega_\mu)]^{-1}$. Equations (1)–(8) describe the SHG from an isotropic film on a substrate that is also active in SHG. These expressions provide a framework that can include both linear and nonlinear optical effects of the SAM interface. In the absence of strong linear optical absorption at the ω_μ frequencies, it might be possible to obtain reasonable results by assuming unique (isotropic) values for $n^\gamma_\mu(\omega_\mu)$ and $\alpha^\gamma_2(\omega_\mu)$. In such a case, the above three-layer description for an isotropic adsorbate can be assumed to describe SHG from SAMs. In the presence of absorption, this assumption breaks down, and it becomes necessary to consider the appropriate components of $n^\gamma_\mu(\omega_\mu)$ and $\alpha^\gamma_2(\omega_\mu)$.

Now we discuss how one can incorporate a phenomenological description of the anisotropy of a SAM in the framework of Eqs. (2)–(8). We consider uniaxial films, as studied in Ref. 1. For such films, $\tilde{n}_{2;ij}$ is diagonalized so that $\tilde{n}_{2;xx}=\tilde{n}_{2;yy}=\tilde{n}_{2\parallel}$, and $\tilde{n}_{2;zz}=\tilde{n}_{2\perp}$.[6] The symbols $\parallel$ and $\perp$ denote directions parallel and perpendicular to the interface, respectively. Note that a Fresnel factor in Eq. (12) of Ref. 1 follows from Eq. (5) of Ref. 15 via the application of the ordinary Snell's law. For the anisotropic film, however, p-polarized photons do not obey the usual form of Snell's law. For the present case, denoting all anisotropic quantities with a tilde, we write the generalized Snell's law as[16] $n_1(\omega_\mu)\sin\alpha_1=\tilde{n}^p_2(\omega_\mu)\sin\tilde{\alpha}^p_2=n_3(\omega_\mu)\sin\alpha_3$ (for p polarization) and $n_1(\omega_\mu)\sin\alpha_1=\tilde{n}^s_2(\omega_\mu)\sin\alpha^s_2=n_3(\omega_\mu)\sin\alpha_3$ (for s polarization). The refractive indices for p and s polarizations are given as[16,17]

$$\frac{1}{[\tilde{n}^p_2(\omega_\mu)]^2}=\frac{\sin^2\tilde{\alpha}^p_2(\omega_\mu)}{[\tilde{n}^p_{2\perp}(\omega_\mu)]^2}+\frac{1-\sin^2\tilde{\alpha}^p_2(\omega_\mu)}{[\tilde{n}^p_{2\parallel}(\omega_\mu)]^2} \tag{9}$$

and $\tilde{n}_2^s(\omega_\mu)=\tilde{n}_{2\parallel}(\omega_\mu)$, respectively. Combining Eq. (9) with the generalized Snell's law, one can express the *p* refractive index of the film as

$$\tilde{n}_2^p(\omega_\mu)=\tilde{n}_{2\parallel}(\omega_\mu)[1+\tilde{G}_\mu]^{1/2}, \tag{10}$$

where $\tilde{G}_\mu=n_1^2(\omega_\mu)\sin^2\alpha_1[\tilde{n}_{2\parallel}^{-2}(\omega_\mu)-\tilde{n}_{2\perp}^{-2}(\omega_\mu)]$. The unknown angle α_3 in the isotropic substrate is obtained as $\alpha_3=\sin^{-1}\{[n_1(\omega_\mu)/n_3(\omega_\mu)]\sin\alpha_1\}$. The *x* components of the wave vectors have the same forms in the anisotropic and isotropic cases. By using Eq. (10) in the generalized Snell's law, we obtain the *z* components of $\mathbf{k}_2^\gamma$ in the form $\tilde{k}_{2z}^\gamma(\omega_\mu)=\overline{\omega}_\mu\tilde{\xi}_\mu^\gamma$, where

$$\tilde{\xi}_\mu^p=\frac{\tilde{n}_{2\parallel}(\omega_\mu)}{\tilde{n}_{2\perp}(\omega_\mu)}[\tilde{n}_{2\perp}^2(\omega_\mu)-n_1^2(\omega_\mu)\sin^2\alpha_1]^{1/2}, \tag{11}$$

$$\tilde{\xi}_\mu^s=[\tilde{n}_{2\parallel}^2(\omega_\mu)-n_1^2(\omega_\mu)\sin^2\alpha_1]^{1/2}. \tag{12}$$

Equations (10)–(12) provide the basis for treating the linear optical effects that interfere with SHG from the anisotropic film. To our knowledge, this treatment of an anisotropic layer has not been incorporated in any detailed calculations of surface SHG.

In a strictly phenomenological approach, one can obtain a set of working equations from Eqs. (2)–(8) by replacing the isotropic reflection and transmission coefficients by their respective anisotropic counterparts. In this approach, Eqs. (4)–(8) are utilized (preferably in the thin film limit), where the isotropic quantities $n_1(\omega_\mu)$, $n_3(\omega_\mu)$, and $k_{1x}^\gamma(\omega_\mu)$ are retained, and the anisotropic Fresnel factors $\tilde{F}_i(\omega_\mu)$ are used in place of the isotropic factors $F_i(\omega_\mu)$. To evaluate the Fresnel factors, one uses the replacements $n_2^\gamma(\omega_\mu)\rightarrow\tilde{n}_2^\gamma(\omega_\mu)$, $\alpha_2^p(\omega_\mu)\rightarrow\tilde{\alpha}_2^p(\omega_\mu)$, $k_2^\gamma(\omega_\mu)\rightarrow\tilde{k}_2^\gamma(\omega_\mu)=\overline{\omega}_\mu\tilde{n}_2^\gamma(\omega_\mu)\cos\tilde{\alpha}_2^\gamma(\omega_\mu)$, $r_{uv}^p\rightarrow\tilde{r}_{uv}^p$, and $t_{uv}^p\rightarrow\tilde{t}_{uv}^p$ in Eqs. (4)–(8). Following previously published calculations,[16–19] the reflection and transmission coefficients for *p* polarization can be expressed as follows:

$$\tilde{r}_{21}^p(\omega_\mu)=\frac{\tilde{A}_1^p(\omega_\mu)-\tilde{A}_2^p(\omega_\mu)}{\tilde{A}_1^p(\omega_\mu)+\tilde{A}_2^p(\omega_\mu)}, \tag{13}$$

$$\tilde{A}_1^p(\omega_\mu)=n_1(\omega_\mu)[\tilde{n}_{2\perp}^2(\omega_\mu)-n_1^2(\omega_\mu)\sin^2\alpha_1]^{1/2}, \tag{14}$$

$$\tilde{A}_2^p(\omega_\mu)=\tilde{n}_{2\parallel}(\omega_\mu)\tilde{n}_{2\perp}(\omega_\mu)\cos\alpha_1, \tag{15}$$

$$\tilde{r}_{23}^p(\omega_\mu)=\frac{\tilde{B}_1^p(\omega_\mu)-\tilde{B}_2^p(\omega_\mu)}{\tilde{B}_1^p(\omega_\mu)+\tilde{B}_2^p(\omega_\mu)}, \tag{16}$$

$$\tilde{B}_1^p(\omega_\mu)=n_3(\omega_\mu)[\tilde{A}_1^p(\omega_\mu)/n_1(\omega_\mu)], \tag{17}$$

$$\tilde{B}_2^p(\omega_\mu)=(\cos\alpha_3/\cos\alpha_1)\tilde{A}_2^p(\omega_\mu), \tag{18}$$

$$\tilde{t}_{12}^p(\omega_\mu)=\frac{2n_1(\omega_\mu)\cos\alpha_1\tilde{D}_\mu^p}{\tilde{n}_{2\perp}(\omega_\mu)[\tilde{A}_1^p(\omega_\mu)+\tilde{A}_2^p(\omega_\mu)]}, \tag{19}$$

$$\tilde{D}_\mu^p=[n_1^2(\omega_\mu)\tilde{J}_\mu+\tilde{n}_{2\perp}^4(\omega_\mu)]^{1/2}, \tag{20}$$

where $\tilde{J}_\mu=\sin^2\alpha_1[\tilde{n}_{2\parallel}^2(\omega_\mu)-\tilde{n}_{2\perp}^2(\omega_\mu)]$. The above expressions indicate how the linear optical properties of the anisotropic interface govern the results of surface SHG with *p*-polarized photons. For *s*-polarized input, $\tilde{r}_{uv}^s$ and $\tilde{t}_{uv}^s$ [appearing in $F_y(\omega)$ of Eq. (6)] follow the usual formulation for an isotropic system. Following previously reported calculations, these parameters can be expressed as.[12,18,19]

$$\tilde{r}_{21}^s(\omega_\mu)=\frac{\tilde{\xi}_\mu^s-n_1(\omega_\mu)\cos\alpha_1}{\tilde{\xi}_\mu^s+n_1(\omega_\mu)\cos\alpha_1}, \tag{21}$$

$$\tilde{r}_{23}^s=\frac{\tilde{\xi}_\mu^s-n_3(\omega_\mu)\cos\alpha_3}{\tilde{\xi}_\mu^s+n_3(\omega_\mu)\cos\alpha_3}, \tag{22}$$

$$\tilde{t}_{12}^s(\omega_\mu)=\frac{2n_1(\omega_\mu)\cos\alpha_1}{n_1(\omega_\mu)\cos\alpha_1+\tilde{\xi}_\mu^s}, \tag{23}$$

$$\tilde{t}_{21}^\gamma(\omega_\mu)=\frac{1-[\tilde{r}_{12}^\gamma(\omega_\mu)]^2}{\tilde{t}_{12}^\gamma(\omega_\mu)}, \tag{24}$$

$$\tilde{t}_{23}^s(\omega_\mu)=\frac{2\tilde{\xi}_\mu^s}{n_3(\omega_\mu)\cos\alpha_3+\tilde{\xi}_\mu^s}, \tag{25}$$

where $\tilde{\alpha}_2^s\equiv\alpha_2^s$ (isotropic), and Eq. (24) holds for both *p* and *s* polarizations. The above description accounts for certain optical features of a SAM interface that were excluded from the previously reported analysis.[1]

The model of surface SHG based on Eqs. (1)–(25) suggests a possible explanation for the apparently surprising observations reported in Ref. 1. This model also provides a suitable framework for combining linear and nonlinear optical experiments involving SAMs. Note that, due to the relatively large number of unknown parameters in Eqs. (2)–(25), it is difficult to measure molecular orientation using SHG. The SHG signal $\sqrt{I_{\mathrm{SHG}}^{\gamma p}}$ in Eq. (2) is related to the molecular tilt angle θ, via the angle-dependent nonlinear susceptibility elements.[14] The consideration of anisotropic Fresnel factors introduces the additional unknown factors, $\mathrm{Re}\,\tilde{n}_{2\parallel}(\omega_\mu)$, $\mathrm{Re}\,\tilde{n}_{2\perp}(\omega_\mu)$, $\mathrm{Im}\,\tilde{n}_{2\parallel}(\omega_\mu)$, and $\mathrm{Im}\,\tilde{n}_{2\perp}(\omega_\mu)$. For a ''thick'' film, two more unknowns, d and z_a, appear through the quantities $\tilde{a}_\mu^\gamma$, $\tilde{b}_\mu^\gamma$, and $\tilde{g}_\mu^\gamma$. All these parameters must be determined to evaluate Eqs. (2)–(8), which, in turn, can allow for a proper calculation of $\langle\theta\rangle$ in terms of the measured $\sqrt{I_{\mathrm{SHG}}^{\gamma p}}$ (the angular bracket implies an average over the distribution of tilt angles). Usually, this is not possible with conventional SHG (phase and intensity) measurements alone. The situation is further complicated when the probe molecular unit in the surface film absorbs light at the fundamental and/or the SH wavelength. In this case, both real and imaginary parts of $\tilde{n}_{2\parallel}$ and $\tilde{n}_{2\perp}$ become θ dependent.[5] Depending on the absorption frequency, a combination of several linear optical techniques might be necessary to evaluate these refractive indices (and the film thickness). Detailed discussion of these linear techniques for probing anisotropic films is available in the literature.[5,6,16–22] Here, we briefly mention certain aspects of such measurements that are relevant in the context of SHG experiments.

The linear refractive indices and the thickness of the film can be measured using (uv-visible) reflectance spectroscopy[23] and/or ellipsometry.[18] The linear reflectivity of the interface probed in such experiments has the form[12,18]

$$\tilde{R}^{\gamma}_{123}(\omega_{\mu}) = \frac{\tilde{r}^{\gamma}_{12}(\omega_{\mu}) + \tilde{r}^{\gamma}_{23}(\omega_{\mu}) g^{\gamma}_{\mu}}{1 - \tilde{r}^{\gamma}_{12}(\omega_{\mu}) \tilde{r}^{\gamma}_{23}(\omega_{\mu}) g^{\gamma}_{\mu}}. \tag{26}$$

To evaluate the unknown parameters of this expression, multiple angle (α_1) measurements are necessary for each frequency. The quantity $n_{2\parallel}$ can be determined with a set of measurements using *s*-polarized light. In addition, $n_1(\omega_{\mu})$ can be utilized as a known variable by employing different sample environments (in nitrogen and inert aqueous electrolytes, for example).[20] The analysis is considerably simplified in the absence of absorption, where the real parts of both $n_{2\parallel}$ and $n_{2\perp}$ can be replaced by the real bulk refractive index of the film. In the presence of absorption, a formalism for simultaneous measurements of refractive index and molecular tilt angle is available in the literature of infrared reflection absorption spectroscopy (IRRAS).[5,6] This formalism can be extended to the uv-visible linear reflectance measurements. In the latter case, often the linear dipole moment of the probe molecular unit can be derived from a predominant transition of a dipole along the molecular axis.[21] For a uniaxial sample, exhibiting such a linear transition at the frequency ω_{μ}, one assumes $\mathrm{Im}\,\tilde{n}_{2\parallel}(\omega_{\mu}) = (3/2)\mathrm{Im}\,n_b(\omega_{\mu})\langle\sin^2\theta\rangle$, and $\mathrm{Im}\,\tilde{n}_{2\perp}(\omega_{\mu}) = 3\,\mathrm{Im}\,n_b(\omega_{\mu})\langle\cos^2\theta\rangle$, where n_b is the bulk isotropic refractive index of the film material.[5,6] The real refractive indices of the anisotropic film also depend on θ. As shown by Parikh and Allara, $\mathrm{Re}\,\tilde{n}_{2\parallel}$ and $\mathrm{Re}\,\tilde{n}_{2\perp}$ can be obtained in terms of the imaginary refractive indices by using an approximate Kramers-Kronig transformation.[5] Thus, in the linear optical techniques, the information about θ follows directly from the refractive index measurements. Linear electroreflectance spectroscopy can be used to probe dipole transitions in the uv-visible range.[21,22] The molecular tilt angle can also be determined by combining the results of these linear measurements with the SHG results, in the framework of Eqs. (2)–(25). Due to the relatively complex nature of data analysis in such a case, the final result should be checked with independent (and more direct) measurements such as IRRAS.[6]

In view of the above discussion, it is unlikely that the conventional SHG technique will serve on its own as an efficient, routine method for measuring molecular orientation of SAMs. Moreover, the actual potential of the SHG technique may remain underutilized in experiments that are focused strictly on developing SHG as a self-sufficient method of measuring molecular orientation. The potential of SHG for SAM studies lies in the unique surface selectivity of this technique, as well as in its instantaneous response to changes in the electronic properties of the interface. The molecular tilt angle and the linear refractive indices can be measured conveniently by using the linear techniques described by previous authors.[5,6,16–19] Subsequently, by using this information in the framework of phase-sensitive SHG experiments, it should be possible to obtain a detailed picture of electronic interactions at the SAM interface.

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*Electronic address: samoy@clarkson.edu

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