Objectives:

1. Define the individual Fresnel correction factors for interfacial SFG and SHG.
2. Define Lorentz local field correction factors for SHG and SFG microscopy.
3. Introduce the problem of refractive index uncertainty.
4. Review differences in the literature and describe the evidence supporting the Fresnel factors used.
5. Integrate the Fresnel factors into the larger vectorized tensor architecture for polarization analysis in linear and nonlinear optics.

Garth J. Simpson
Fresnel factors for the incident light

Incident light, p-polarization

We’ll work through the Fresnel factor for the X-polarized incident field first.

The first contribution incorporates the amplitude transmission coefficient for traversing the 13 interface, $t_{13}$.

The next contribution arises from reflection at the 32 interface, $r_{32}$. Note the sign change in the X-polarized field upon reflection and the phase shift $e^{-i\beta}$ resulting from traversing the thin film.

The infinite series can be arranged as a power series, with the final correction given by $L_{XX}^{\omega}$.

Garth J. Simpson
The other two incident correction factors are generated similarly.

\[ L_{XX}^{\omega_0} = \frac{t_{p13}^{\omega_0}}{1 - r_{p32}^{\omega_0}r_{p31}^{\omega_0}e^{-i2\beta^{\omega_0}}} \left( 1 - r_{p32}^{\omega_0}e^{-i\beta^{\omega_0}} \right) \]

\[ L_{YY}^{\omega_0} = \frac{t_{s13}^{\omega_0}}{1 - r_{s32}^{\omega_0}r_{s31}^{\omega_0}e^{-i2\beta^{\omega_0}}} \left( 1 + r_{s32}^{\omega_0}e^{-i\beta^{\omega_0}} \right) \]

\[ L_{ZZ}^{\omega_0} = \frac{t_{p13}^{\omega_0}}{1 - r_{p32}^{\omega_0}r_{p31}^{\omega_0}e^{-i2\beta^{\omega_0}}} \left( 1 + r_{p32}^{\omega_0}e^{-i\beta^{\omega_0}} \right) \]

In the thin film limit, the phase term \( e^{-i\beta} \) can be approximated as 1.

The two sets of Fresnel factors for the incident light are then given by the following matrices.

The two are identical for SHG, but can differ for SFG.

Garth J. Simpson
Fresnel factors for the NLO Source

\[ e_{X}^{\omega_{\text{sum}}} = P_{X}^{\omega_{\text{sum}}} \begin{cases} t_{p31}^{\omega_{\text{sum}}} [1 + r_{p31}^{\omega_{\text{sum}}} r_{p32}^{\omega_{\text{sum}}} e^{-i2\beta^{\omega_{\text{sum}}}} + \left(r_{p31}^{\omega_{\text{sum}}} r_{p32}^{\omega_{\text{sum}}} e^{-i2\beta^{\omega_{\text{sum}}}}\right)^2 + \cdots] \\ -r_{p32}^{\omega_{\text{sum}}} t_{p31}^{\omega_{\text{sum}}} e^{-i\beta^{\omega_{\text{sum}}}} [1 + r_{p31}^{\omega_{\text{sum}}} r_{p32}^{\omega_{\text{sum}}} e^{-i2\beta^{\omega_{\text{sum}}}} + \left(r_{p31}^{\omega_{\text{sum}}} r_{p32}^{\omega_{\text{sum}}} e^{-i2\beta^{\omega_{\text{sum}}}}\right)^2 + \cdots] \end{cases} \]

**NOTE:** With this definition of the Fresnel factor, the internal angle \( \theta \) within the NLO layer must be used for the SFG/SHG output, and not the angle in the ambient or substrate!

\[
L_{\omega} = \begin{bmatrix} L_{XX}^{\omega_{\text{sum}}} & 0 & 0 \\ 0 & L_{YY}^{\omega_{\text{sum}}} & 0 \\ 0 & 0 & L_{ZZ}^{\omega_{\text{sum}}} \end{bmatrix}
\]

\[
\mathbf{L}^{\omega_{\text{sum}}} \otimes \mathbf{L}^{\omega_{1}} \otimes \mathbf{L}^{\omega_{2}}
\]

\[ \bar{\chi}_{C,\text{eff}} = \mathbf{L} \cdot \bar{\chi}_{C} \]

\[ \bar{e}_{\omega_{\text{sum}}} = \mathbf{E} \cdot \bar{\chi}_{J} = \mathbf{E} \cdot \mathbf{J} \cdot \mathbf{L} \cdot \bar{\chi}_{C} \]

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But what do we use for the optical constants?

COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in Physical Review B. Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

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

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A recent paper by Eisert et al. [Phys. Rev. B 58, 10860 (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.
1. \( n_{ir}, n_{vis}, \) and \( n_{sfg} \) within the interfacial layer are typically difficult to independently determine: (3 unknowns).

2. For measurements at surfaces and interfaces, the interfaces will generally exhibit birefringence: (6 unknowns).

\[
\begin{align*}
n_{ir}^x &= n_{ir}^y, n_{ir}^z \\
n_{vis}^x &= n_{vis}^y, n_{vis}^z \\
n_{sum}^x &= n_{sum}^y, n_{sum}^z
\end{align*}
\]

3. In spectroscopic measurements, the frequencies exhibiting resonance-enhancement will be complex-valued optical constants: (typically 8 and up to 12 unknowns).

\[
\begin{align*}
n_{ir}' &= n_{ir}'^x, n_{ir}'^z, k_{ir}' = k_{ir}'^y, k_{ir}'^z \\
n_{vis}' &= n_{vis}'^x, n_{vis}'^z, k_{vis}' = k_{vis}'^y, k_{vis}'^z \\
n_{sum}' &= n_{sum}'^x, n_{sum}'^z, k_{sum}' = k_{sum}'^y, k_{sum}'^z
\end{align*}
\]

\[n = n' + ik\]
A path forward: Assume that the effective interfacial refractive index is simply given by the numerical average of the subphase and superphase.

Justification:
1. This strategy has worked splendidly for linear ellipsometry measurements of rough surfaces for decades.
2. We are averaging over many molecules in many environments, spanning subphase-like to superphase-like.
3. Should hold for dilute films with minimal inter-chromophore coupling.
4. It seems to work well experimentally, even for monolayer films of coupled chromophores!
For vib. SFG from a uniaxial achiral film with $C_{\infty v}$ symmetry:

\[ \chi_{ppp}, \chi_{pss}, \chi_{sps}, \chi_{ssp} \Rightarrow \chi_{zxx}, \chi_{zzz}, \chi_{xxz} \]

\[ \beta^{(2)}, f(\theta, \psi) \]

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\[ \beta^{(2)}, f(\theta, \psi) \]

In general, each of these tensor elements will be complex-valued, doubling the total number of observables possible.

Garth J. Simpson
In SHG, fewer parameters are available (C\(_\infty v\) symmetry, achiral):

\(\chi_{ppp}, \chi_{pss}, \chi_{ssp} \Rightarrow \chi_{zxx}, \chi_{zzz}, \chi_{xxz}\)

\(\beta^{(2)}, f(\theta, \psi)\)

In a chiral film with C\(_\infty\) symmetry:

\(\chi_{ppp}, \chi_{pps}, \chi_{psp}, \chi_{spp}, \chi_{ssp} \Rightarrow \chi_{zxx}, \chi_{zzz}, \chi_{xxz}, \chi_{yzx}\)

\(\beta^{(2)}, f(\theta, \psi)\)

Two additional measured parameters emerge, both of which depend only on a single tensor element.

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Instead of measuring intensity, measure the complete polarization state of the exiting beam.

The following relationship is dictated by symmetry:

\[ \chi_{XYZ} = -\chi_{YXZ} \]

\[ \frac{\chi_{XYZ}}{\chi_{YXZ}} = -1 + 0i \]

From the measured values of \( \chi_{PSP} \) and \( \chi_{PPS} \), can we find a set of optical constants that recovers this required symmetry condition?

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**Table 2. Comparison of Measured and Predicted Interfacial Optical Constants for FITC–BSA**

<table>
<thead>
<tr>
<th>optical constants</th>
<th>measured by NONE</th>
<th>predicted from case 2(^a)</th>
<th>predicted from case 1(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{2\omega} )</td>
<td>1.387 (± 0.005)</td>
<td>1.3982</td>
<td>1.365–1.655</td>
</tr>
<tr>
<td>( k_{2\omega} )</td>
<td>0.0000i (± 0.0009i)</td>
<td>0</td>
<td>0.0004i–0.002i</td>
</tr>
</tbody>
</table>

\(^a\) From eq 10. \(^b\) From refs 34 and 35 combined with Kramers–Kronig transformation of the visible absorbance spectrum.
Outcomes:

1. Fresnel factors correct for differences between the detected fields and those experienced and produced within the immediate environment surrounding the molecules.

2. Ray-tracing was used to generate Fresnel factors, which agree well for the incident beam with those constructed based on the solution to the wave equation in the thin film limit.

3. Caution – the internal angles from within the thin film should be used for the nonlinear field and external angles for the linear fields when using the ray-tracing expressions.

4. The Fresnel factors can be systematically incorporated into the linear algebra framework through matrix multiplication by $L = L \otimes L \otimes L$.

5. In principle, uncertainties in the local optical constants can complicate polarization analysis in thin films. In practice, the effective medium approximation appears to allow the use of the average optical constants of the adjacent media.

Garth J. Simpson