Molecular orientation at biological interfaces: Water and lipids studied through surface-specific vibrational spectroscopy
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2.1 Nonlinear polarization

The data presented in this thesis are obtained, for the largest part, by means of spectroscopic techniques. Spectroscopy is the practice of characterising matter by looking at its interaction with light. Being electromagnetic radiation itself, light is affected by the electronic and magnetic properties of the molecules and atoms that it encounters. Given that the electronic forces and interactions are many orders of magnitude larger than the magnetic ones, we will deduce the theoretical description of spectroscopy to the coupling of the electric fields of light and matter.

This chapter is largely based on the excellent tutorial overviews of Lambert [63] and Miranda [26]. The discussion is limited to the electric dipole approximation, not considering quadrupole and higher contributions, and ignoring interactions between the dipoles of molecules. For an advanced and thorough description, refer to textbooks by Boyd [64] and Shen [65] which provide the quantum mechanical background necessary for a more complete understanding of the principles of SFG.

Let us consider the interaction of a molecule with a light source through the oscillating electric field $E$.\(^a\) The molecule’s electron cloud will follow the oscillation, inducing an electric polarization $\mu$ proportional to the electric field:

$$\mu = \alpha E$$ \hspace{1cm} (2.1)

where the proportionality constant $\alpha$ is the polarizability of the molecule. For a large number of molecules in a condensed state, the individual molecular polarizabilities can be summed up to find the macroscopic polarizability. This material property is called the susceptibility $\chi$ and determines the bulk polarization $P$ induced by an electric field:

$$P = \epsilon_0 \chi E$$ \hspace{1cm} (2.2)

where $\epsilon_0$ is the permittivity of free space. For the intense, coherent fields of high-power pulsed laser light, however, equation 2.1 and 2.2 break down. On the molecular level, the electron cloud cannot follow the oscillation any more, introducing anharmonicity in its response. Macroscopically, this anharmonicity manifests itself as a nonlinearity of the susceptibility $\chi$. We may express this nonlinearity by writing $\chi$ as a sum of components, $\chi = \chi^{(1)} + \chi^{(2)} + \chi^{(3)} + \ldots$.

\(^a\)Throughout this chapter, bold typeface indicates a vector quantity with both magnitude and direction.
Here $\chi^{(1)}$, the first-order susceptibility, expresses the linear relation between $P$ and $E$. The second-order nonlinear susceptibility $\chi^{(2)}$ expresses the quadratic relation between $P$ and $E$, the third-order nonlinear susceptibility $\chi^{(3)}$ the cubic relation between $P$ and $E$, etcetera, where the nonlinear terms are much smaller than the linear one. Equation 2.2 now becomes

$$P = \epsilon_0 \left( \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right)$$  \hspace{1cm} (2.3)$$

The two-photon processes SHG and SFG originate from the second-order nonlinear susceptibility $\chi^{(2)}$. We can demonstrate this by explicitly stating the time dependence of $E$,

$$E = E_1 \cos \omega t$$  \hspace{1cm} (2.4)$$

Considering only the polarization due to second-order effects $P^{(2)}$, we obtain

$$P^{(2)} = \epsilon_0 \chi^{(2)} (E_1 \cos \omega t)^2 = \frac{1}{2} \epsilon_0 \chi^{(2)} E_1^2 (1 + \cos 2\omega t)$$  \hspace{1cm} (2.5)$$

This demonstrates that through $\chi^{(2)}$, an electric field of frequency $\omega$ may cause a polarization that oscillates at a frequency $2\omega$.

To explore the origins of SFG, we need to consider an electric field consisting of two different frequencies $\omega_1$ and $\omega_2$:

$$E = E_1 \cos \omega_1 t + E_2 \cos \omega_2 t$$  \hspace{1cm} (2.6)$$

Producing the second-order polarization

$$P^{(2)} = \epsilon_0 \chi^{(2)} (E_1 \cos \omega_1 t + E_2 \cos \omega_2 t)^2$$

$$= \epsilon_0 \chi^{(2)} (E_1^2 \cos^2 \omega_1 t + E_2^2 \cos^2 \omega_2 t$$

$$+ E_1 E_2 \cos(\omega_1 + \omega_2) t + E_1 E_2 \cos(\omega_1 - \omega_2) t)$$

$$= \frac{1}{2} \epsilon_0 \chi^{(2)} (E_1^2 + E_2^2 + E_1^2 \cos 2\omega_1 t + E_2^2 \cos 2\omega_2 t$$

$$+ 2E_1 E_2 \cos(\omega_1 + \omega_2) t + 2E_1 E_2 \cos(\omega_1 - \omega_2) t)$$  \hspace{1cm} (2.7)$$

This expression shows all contributions of the second-order nonlinear susceptibility $\chi^{(2)}$ to the polarization. There are two constant terms, two SHG terms corresponding to the two doubled original frequencies, the sum-frequency (SF) term, and a difference-frequency (DF) term. In an SFG experiment, all of these contributions will be present. However, since we are specifically detecting the SF signal, in practice they do not influence the measurement. In the following discussion we will therefore only elaborate on the SF term. Omitting the explicit time dependence again, we may express the SF component of the polarizability as

$$P_{SF}^{(2)} = \epsilon_0 \chi^{(2)} E_1 E_2$$  \hspace{1cm} (2.8)$$
In the context of this thesis, $\mathbf{E}_1$ and $\mathbf{E}_2$ are the fields originating from a visible and IR pulsed laser source, $\mathbf{E}_{\text{VIS}}$ and $\mathbf{E}_{\text{IR}}$. The vector quantities $\mathbf{P}_{\text{SF}}^{(2)}$, $\mathbf{E}_{\text{VIS}}$ and $\mathbf{E}_{\text{IR}}$ can all have components in each of the three dimensions. Therefore, in Cartesian coordinates $\chi^{(2)}$ is a third-rank tensor with 27 elements. The $y$-component of $\mathbf{P}_{\text{SF}}^{(2)}$ originating from the $y$-component of $\mathbf{E}_{\text{VIS}}$ and the $z$-component of $\mathbf{E}_{\text{IR}}$, for example, is given by

$$P_{y,\text{SF}}^{(2)} = \epsilon_0 \chi^{(2)}_{yyz} E_{y,\text{VIS}} E_{z,\text{IR}}$$

(2.9)

The full description of $\mathbf{P}_{\text{SF}}^{(2)}$, including all possible vector components, is given by summing over all three dimensions:

$$\mathbf{P}_{\text{SF}}^{(2)} = \sum_{i=x,y,z} \mathbf{P}_{i,\text{SF}}^{(2)} = \epsilon_0 \sum_{i=x,y,z} \sum_{j=x,y,z} \sum_{k=x,y,z} \chi^{(2)}_{ijk} E_{j,\text{VIS}} E_{k,\text{IR}}$$

(2.10)

Since $\chi^{(2)}_{ijk}$ describes the physical response of the material to radiation, its properties should be independent of the axis system. Redefining all axes by reversing their sign should also reverse the sign of $\chi^{(2)}_{ijk}$ describing the physical material properties, i.e.,

$$\chi^{(2)}_{ijk} = -\chi^{(2)}_{-i-j-k}$$

(2.11)

However, in a centrosymmetric medium all directions are equivalent. Reversing the axis system in this environment does not change anything about the description of the system, including $\chi^{(2)}_{ijk}$:

$$\chi^{(2)}_{ijk} = \chi^{(2)}_{-i-j-k}$$

(2.12)

The apparent contradiction between equations 2.11 and 2.12 indicates that $\chi^{(2)}_{ijk}$ can only be zero in a centrosymmetric medium. Thus, an SFG signal can only be generated when this symmetry is broken. This typically occurs at an interface between two bulk media, where the medium is isotropic in the planar surface formed by the $x$ and $y$-axes, but the not along the $z$-axis. Such a medium is said to have $C_\infty$ symmetry. All systems studied in this thesis fall within this category.

Intuitively, although incompletely, the requirement of symmetry breaking can be understood in terms of the molecular hyperpolarizabilities canceling out on the microscopic scale.

## 2.2 The Electric Field at an Interface

We have established that laser light can induce an SF oscillation in the macroscopic polarization of a material, providing it is not centrosymmetric. Equation

\[ \text{b} \] The same reasoning can be applied to any odd-order tensor quantity, implying that $\chi^{(4)}_{ijk}$, $\chi^{(6)}_{ijk}$, etcetera are also zero in a centrosymmetric medium.
2.8 shows how this polarization follows from the local electric fields. However, we still need to derive how the magnitude of this field follows from the incident laser light.

![Figure 2.1. Generation of the SFG signal at an interface.](image)

In equation 2.7 we found the origin of the SF component. For a visible and IR source of frequencies $\omega_{\text{VIS}}$ and $\omega_{\text{IR}}$, the frequency of the resulting SFG signal will be

$$\omega_{\text{SF}} = \omega_{\text{VIS}} + \omega_{\text{IR}}$$

(2.13)

The angle at which the SFG signal is generated is defined by the angles of incidence of the visible and IR laser beams through the conservation of momentum:

$$n_{\text{SF}}k_{\text{SF}} \sin \theta_{\text{SF}} = n_{\text{VIS}}k_{\text{VIS}} \sin \theta_{\text{VIS}} + n_{\text{IR}}k_{\text{IR}} \sin \theta_{\text{IR}}$$

(2.14)

where all angles are given relative to the surface normal as indicated in figure 2.1, $n$ is the refractive index of the propagation medium and $k = \omega/c$, with $c$ the speed of light. Note that two SFG signals are generated at the interface: one reflected from it, and one propagating into the bulk. In this thesis, only the reflected signal is detected, because it is more easily accessible than the signal disappearing into the sample. The relative sizes of the two signals scale with the reflection coefficients discussed later this chapter. Generally, we will only consider the reflection signal to avoid unnecessary complication.

The direction of the oscillation of the incident visible and IR beams, i.e. their polarization, can be split into two components. The component parallel to the plane of incidence is called $p$-polarized (from parallel), while the one
perpendicular to it is called \( s \)-polarized (from \( senkrecht \), German for perpendicular). The orientation of a \( p \)-polarized incident beam of magnitude \( E_p^I \) and the orientation of an \( s \)-polarized incident beam of magnitude \( E_s^I \) are demonstrated in figures 2.2 and 2.3, respectively. Because in a typical optical setup the beams are reflected into a complex path, the \( p/s \) convention relative to the beam is much more practical than the use of a fixed axis system. To calculate the SFG response from the interface, however, we need to be able to express the electric fields in terms of their Cartesian coordinates. From figure 2.2 and 2.3 we may deduce the following relation:

\[
E_x^I = E_x^I \hat{x} = -E_p^I \cos \theta \hat{x} \\
E_y^I = E_y^I \hat{y} = E_s^I \hat{y} \\
E_z^I = E_z^I \hat{z} = E_p^I \sin \theta \hat{z} \tag{2.15}
\]

To find the SFG polarization from equation 2.10, it is not the incident fields that we need, but rather the interfacial electric fields. These are the sum of the incident and the reflected field. The latter is found by multiplying the incident field by the Fresnel amplitude coefficients for reflection; \( r_p \) for \( p \)-polarized light, and \( r_s \) for \( s \)-polarized light:
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Figure 2.3. \( p \)-polarized light at an interface. The interfacial electric field contains only a \( y \)-component.

\[
\begin{align*}
E_x &= E_x^I + E_x^R = E_x^I + r_p E_x^I = -(E_p^I \cos \theta_I + r_p E_p^I \cos \theta_I) \\
&= -E_p^I \cos \theta_I (1 + r_p) \equiv -K_x E_p^I \\
E_y &= E_y^I + E_y^R = E_y^I + r_s E_y^I = E_y^I + r_s E_s^I = E_y^I (1 + r_s) \equiv K_y E_s^I \\
E_z &= E_z^I + E_z^R = E_z^I + r_p E_z^I = E_p^I \sin \theta_I + r_p E_p^I \sin \theta_I \equiv K_z E_p^I
\end{align*}
\]

where in the last step we defined the Fresnel \( K \)-factors to simplify the notation.

We can now describe the magnitude of the interfacial field as a function of the incident fields.

\[
E = E_x^I + E_y^R + E_z^I = E_x^I + r_p E_x^I = -(E_p^I \cos \theta_I + r_p E_p^I \cos \theta_I)
\]

\[
= -E_p^I \cos \theta_I (1 + r_p) \equiv -K_x E_p^I
\]

\[
E = E_x^I + E_y^I + E_z^I = E_x^I + r_s E_x^I = E_p^I \sin \theta_I + r_p E_p^I \sin \theta_I \equiv K_z E_p^I
\]

\[
E = E_x^I + E_y^I + E_z^I = E_p^I \sin \theta_I (1 + r_p)
\]

We then arrive at the full expression for the SF polarization (omitting the summation operators):

\[
P_{i,\text{SF}}^{(2)} = \epsilon_0 \chi_{ijk}^{(2)} i K_j E_{p/s, \text{VIS}}^I \mathbf{k} K_k E_p^I
\]
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2.3 Emission of the SFG signal

Up to now, we have described the SF polarization generated at the interface. The next step is to show how this polarization gives rise to the emission of radiation at this frequency. The relation between radiation and the SFG field is given by the nonlinear Fresnel coefficients, or $L$-factors:

$$\mathbf{E}_{i,\text{SF}} = L_i \mathbf{P}_{i,\text{SF}}^{(2)}$$

(2.19)

The $L$-factors are based on conservation of momentum (phase-matching) conditions between the waves, and continuity of the electric fields across the interface [66]. For a reflection geometry, they are given by

$$L_x^R = \frac{-i\omega_{\text{SF}}}{c\epsilon_0} \frac{\cos \theta_{\text{SF}}^T}{n_T \cos \theta_{\text{SF}}^I + n_I \cos \theta_{\text{SF}}^T}$$  
$$L_y^R = \frac{i\omega_{\text{SF}}}{c\epsilon_0} \frac{1}{n_I \cos \theta_{\text{SF}}^I + n_T \cos \theta_{\text{SF}}^T}$$  
$$L_z^R = \frac{i\omega_{\text{SF}}}{c\epsilon_0} \frac{(n_T/n_{\text{layer}})^2 \sin \theta_{\text{SF}}^T}{n_I \cos \theta_{\text{SF}}^I + n_T \cos \theta_{\text{SF}}^T}$$  

(2.20)

Here, the angles $\theta_{\text{SF}}^I$ and $\theta_{\text{SF}}^T$ are the angles of the emitted SFG field in the incidence and transmission medium, respectively, while $n_I$ and $n_T$ are the refractive indices in these media. $n_{\text{layer}}$ is the refractive index of the interface, which may be different from those of the two bulk materials bordering it, and can be hard to define. Combining equation 2.18 and 2.19, we can now fully describe the SFG signal generated at an interface based on the angles of incidence and field magnitudes of the visible and IR beam, the refractive indices of the sample, and the second-order nonresonant susceptibility $\chi^{(2)}$. Note that both the $K$ and the $L$-factors are also defined by these properties. The intensity of the SFG signal scales with the square of its field strength. The complete description of the $p$ and $s$ components of the intensity of the emitted SFG radiation then becomes
### 2.4 Spectral analysis of the SFG signal

In the previous sections, we have derived how the SFG signal originates from two overlapping beams at an interface, and how its magnitude depends on the setup geometry and material properties. In this thesis, SFG is used as a means to obtain information about the molecular structure at surfaces. To quantify this information, the spectra are fitted with a model that describes the material properties underlying the response. Although many factors contribute to the SFG signal, as is described in 2.21, the only variable that is strongly frequency dependent, and therefore defines the shape of the spectrum, is the second-order susceptibility \( \chi^{(2)} \). The resonances, which are used to identify the chemical structure of the sample, are contained within \( \chi^{(2)} \). Spectral analysis can therefore be reduced to the fitting of \( \chi^{(2)} \) with a physically meaningful mathematical expression, describing the resonant vibrational modes of the sample. Additionally, to obtain a good fit a frequency-independent nonresonant background signal is needed. This background is generally assumed to originate from electronic transitions. These transitions have a high energy but are spectrally remote, resulting in a low intensity, flat signal in the SFG spectral region. It is common to split the nonresonant contribution into a nonresonant amplitude \( A_{nr} \) and phase \( e^{i\phi_{nr}} \), where \( \phi_{nr} \) accounts for the phase difference of the nonresonant and resonant oscillations:

\[
I_{p,\text{SF}} \propto |\mathbf{E}_{x,\text{SF}}|^2 + |\mathbf{E}_{z,\text{SF}}|^2 \\
\propto |L_x \mathbf{P}_{x,\text{SF}}^{(2)}|^2 + |L_z \mathbf{P}_{z,\text{SF}}^{(2)}|^2 \\
\propto \left| \epsilon_0 L_x \sum_{j} \sum_{k} \chi_{xjk}^{(2)} K_{j} E_{p,\text{VIS}}^I K_k E_{p,\text{IR}}^I + \epsilon_0 L_z \sum_{j} \sum_{k} \chi_{zjk}^{(2)} K_{j} E_{p,\text{VIS}}^I K_k E_{p,\text{IR}}^I \right|^2 \tag{2.21}
\]

\[
I_{s,\text{SF}} \propto |\mathbf{E}_{y,\text{SF}}|^2 \\
\propto |L_y \mathbf{P}_{y,\text{SF}}^{(2)}|^2 \\
\propto \left| \epsilon_0 L_y \sum_{j} \sum_{k} \chi_{yjk}^{(2)} K_{j} E_{s,\text{VIS}}^I K_k E_{s,\text{IR}}^I \right|^2
\]
\[ E_{SF} \propto \chi^{(2)} V, E_{IR} \]
\[ \propto \left( \chi^{(2)}_{nr} + \chi^{(2)}_{r} \right) V, E_{IR} \]
\[ \propto \left( A_{nr} e^{i\phi_{nr}} + \chi^{(2)}_{r} \right) V, E_{IR} \]  

(2.22)

Resonances that are driven by an external force, in our case the oscillating electric field of the IR laser, can be described by a Lorentzian function. The resonant part of \( \chi^{(2)} \) can therefore be fitted as a sum of these Lorentzians, one for each resonance. The full fitting expression then becomes:

\[ \chi^{(2)} = A_{nr} e^{i\phi_{nr}} + \sum_{n} \frac{A_{n}}{\omega_{n} - \omega_{IR} - i\Gamma_{n}} \]  

(2.23)

where \( A_{n} \), \( \omega_{n} \), and \( \omega_{IR} \) are the amplitude of resonance \( n \), the center frequency of resonance \( n \), and the frequency of the IR excitation beam. \( \Gamma_{n} \) gives the vibrational lifetime of resonance \( n \), which defines the linewidth of the spectral feature. Equation 2.23 clearly shows that the maximum field strength is found on a resonance, where \( \omega_{IR} = \omega_{n} \), limited in intensity by the vibrational lifetime \( \Gamma_{n} \). \( A_{n} \) can be positive or negative, depending on the orientation of the molecular bond that gives rise to the vibrational resonance. When recording an SFG intensity spectrum, \( I_{SF} \propto |E_{SF}|^{2} \) and the absolute orientational information is lost in squaring of the field. In fitting however, the sign assigned to \( A_{n} \) is relevant to the interference of the resonances. Often, the sign is known from literature, or the molecular orientation at the interface is known. Another option is retrieval of the sign through maximum entropy method (MEM), a useful but not always successful computational method [67]. Phase-sensitive SFG spectroscopy is a more powerful, but experimentally challenging technique that is able to measure the molecular orientation directly through interference with a reference signal. Chapter 5 will discuss the theoretical and experimental approach of this technique in detail.

The resonant second-order nonlinear susceptibility, \( \chi^{(2)}_{r} \), is a complex quantity. The most common way to plot it is to take its squared magnitude, since this is proportional to the SFG signal intensity. To look into the spectral properties of \( \chi^{(2)}_{r} \) in more detail, it can be separated into a real and imaginary part. For a single resonance \( n \) we obtain:

\[ \chi^{(2)}_{r,n} = \frac{A_{n}}{\omega_{n} - \omega_{IR} - i\Gamma} \]
\[ = \frac{A_{n}(\omega_{n} - \omega_{IR} + i\Gamma)}{(\omega_{n} - \omega_{IR})^{2} + \Gamma^{2}} \]  

(2.24)

Equation 2.24 shows that for the imaginary part of the second-order nonresonant susceptibility, \( \text{Im}(\chi^{(2)}) \), the frequency dependence is contained only in...
Figure 2.4. The fitted SFG intensity spectrum (black) along with the real (grey dashed) and imaginary (grey dotted) parts of the fit.

the denominator. This implies that its shape closely resembles that of the resonances contained within the unsquared χ(2). This is demonstrated in figure 2.4, where the fitted SFG intensity spectrum of the lipid monolayer described in section 1.3 is plotted. Additionally, the Re(χ(2)) and Im(χ(2)) obtained from the fit are displayed. The intensity, fitted by the modeled |χ(2)|^2, contains clear spectral features, but only of positive amplitude. Re(χ(2)) is distorted and difficult to interpret due to its intricate frequency dependence. Im(χ(2)) contains roughly the same spectral features as the intensity spectrum, with the added advantage of displaying the absolute (positive or negative) amplitude of the resonances. For this reason, whenever possible it is informative to look at the Im(χ(2)) when analysing an SFG spectrum.