The cool state of water: Infrared insights into ice
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3 Spectroscopic techniques

The previous chapter outlined the theoretical framework of this research. We will now proceed to explore the versatile toolbox of spectroscopy, focusing on the techniques used in the experimental chapters of this thesis.

3.1 Absorption spectrum

Light with intensity $I_0$ travelling through an absorbing medium will leave the medium with a lower intensity $I$ (Fig. 3.1). For an electric field travelling through a medium of thickness $l$, the transmission can be calculated using Eq. (2.11):

$$\frac{I(\omega)}{I_0(\omega)} = \frac{|E(\omega)e^{ik(\omega)}l|^2}{|E(\omega)|^2} = e^{-2\text{Im}(n(\omega))\omega l/c}.$$ (3.1)

The absorption $\alpha$ is the natural logarithm of the transmission, i.e.

$$\alpha(\omega) \equiv -\ln \left( \frac{I(\omega)}{I_0(\omega)} \right) = \frac{2\omega l}{c} \text{Im}(n(\omega)) = \frac{\omega l}{c} \frac{\text{Im}(\chi(\omega))}{\text{Re}(n(\omega))},$$ (3.2)

where we made use of Eq. (2.12) in the last equality. Recording the attenuation of light as a function of frequency yields a linear absorption spectrum. Previously in this thesis (Fig. 1.6) we encountered the absorption spectra of ice and liquid water in the stretching region. The imaginary part of the electrical susceptibility determines the extent of the light absorption. This is a result of a cascade of effects, as we will see in the following: An electric field $E$ induces a polarization $P$, which in turn serves as a radiation source of an electric field $E_{\text{rad}}$. The field is radiated with a 90° phase delay with respect to the polarization,\textsuperscript{[23,26]} i.e.

$$E_{\text{rad}}(\omega) \propto iP(\omega).$$ (3.3)

![Figure 3.1: Absorbance of a beam of light with initial intensity $I_0$ as it travels through a sample of thickness $l$.](image)
This radiated field interferes with the original field $E$. The light transmission becomes

$$\frac{I(\omega)}{I_0(\omega)} = \frac{|E(\omega) + E_{\text{rad}}(\omega)|^2}{|E(\omega)|^2}$$

$$= \frac{|E(\omega)|^2 + 2 \text{Re}(E^*(\omega) E_{\text{rad}}(\omega)) + |E_{\text{rad}}(\omega)|^2}{|E(\omega)|^2}$$

$$\approx 1 + \frac{2 \text{Re}(E^*(\omega) E_{\text{rad}}(\omega))}{|E(\omega)|^2},$$

(3.4)

where we assumed in the last line the radiated field to be much smaller than the incoming field, i.e. $E_{\text{rad}} \ll E$. Using a Taylor expansion of the natural logarithm of the transmission gives the absorption

$$\alpha(\omega) \equiv -\ln \left(\frac{I(\omega)}{I_0(\omega)} \right) \approx -\frac{2 \text{Re}(E^*(\omega) E_{\text{rad}}(\omega))}{|E(\omega)|^2}.$$  

(3.5)

Employing Eq. (3.3) we arrive at

$$\alpha(\omega) \propto \frac{2 \text{Im}(E^*(\omega) P(\omega))}{|E(\omega)|^2},$$  

(3.6)

which agrees with our observation of Eq. (3.2) that the absorption scales proportionally with the imaginary part of $\chi$.

At relatively low field intensities, the higher-order polarizations are very small and the extinction process is dominated by the first-order polarization $P^{(1)} = \epsilon_0 \chi^{(1)} E$. The absorption is then independent of the light intensity [Eq. (3.6)]. For a medium containing a concentration $C$ of absorbers with cross section $\sigma$, the decrease in intensity scales linearly with its magnitude according to

$$\frac{dI(\omega)}{dx} = -C \sigma_{wv}(\omega) I(\omega).$$

(3.7)

Integrating this differential equation over a length $l$ yields the Bouguer–Lambert–Beer law

$$\frac{I(\omega)}{I_0(\omega)} = e^{-C l \sigma_{wv}(\omega)}.$$  

(3.8)

Hence the light attenuates exponentially with distance, similar to Eq. (3.1). The absorption $\alpha$ depends linearly on all parameters, i.e.

$$\alpha(\omega) \equiv -\ln \left(\frac{I(\omega)}{I_0(\omega)} \right) = C l \sigma_{wv}(\omega).$$  

(3.9)

Combining the above equation with Eq. (3.2), we obtain a relation between the molecular cross section and the material properties:

$$\sigma_{wv}(\omega) = \frac{1}{C} \frac{\omega}{c} \frac{\text{Im}(\chi(\omega))}{\text{Re}(n(\omega))},$$

(3.10)
3.2 Spectroscopic techniques

3.2 Pump–probe spectroscopy

Dynamical information of molecular processes can be obtained with pump–probe experiments (Fig. 3.2). This technique uses two laser pulses separated in time. An intense pump pulse brings the system in a non-equilibrium state. This state relaxes in time as described in the previous chapter. The evolution is monitored by probing the sample with another weak time-delayed pulse: the probe pulse. The time delay between the pump and probe pulse can be varied. The absorption of the probe pulse is monitored in the presence and absence of a pump pulse.

The process of excitation by the pump pulse and subsequent detection by the probe pulse is a three-field interaction process with two interactions of the pump field $E_{pu}$ and one interaction with the probe field $E_{pr}$. The interaction is described by the third-order susceptibility $\chi^{(3)}$, which yields a third-order polarization $P^{(3)}$. Interference between the radiated field generated by $P^{(3)}$ and the probe field $E_{pr}$ leads to the following third-order absorption [cf. Eq. (3.6)]:

$$\alpha^{(3)}(\omega) \propto \frac{2 \text{Im}(E_{pr}^*(\omega) P^{(3)}(\omega))}{|E_{pr}(\omega)|^2}.$$  \hspace{1cm} (3.11)

We will proceed with a phenomenological description of pump–probe spectroscopy, yielding good understanding of the experiments in Chapter 4 & 5.

The absorption of the probe pulse in absence of the pump pulse $\alpha_0$ is given by

$$\alpha_0(\omega) = n \sigma_{10}(\omega),$$  \hspace{1cm} (3.12)

where $n = C l$ is the amount of absorbers per unit surface. The pump pulse will excite molecules from the ground state to the $v = 1$ state. Consequently, there will be less molecules in the ground state, such that the absorption of the probe pulse at the fundamental frequency will be smaller. On the other hand, the first excited state is populated after excitation by the pump pulse. In addition, stimulated emission from this excited state contributes equally to the absorption
decrease. These two contributions lead to a bleaching of the absorption at the fundamental frequency. Furthermore, the molecules in the first excited state can be promoted to the \( v = 2 \) state. This causes an increase in absorption at the \( v = 1 \rightarrow 2 \) transition frequency and is called induced absorption. The \( v = 1 \rightarrow 2 \) transition has in general a lower frequency than the \( v = 0 \rightarrow 1 \) transition owing to the anharmonicity of the vibrational potential. The bleaching and induced absorption signals give rise to the following expression for the absorption:

\[
\alpha(\omega) = (n - 2n_1) \sigma_{10}(\omega) + n_1 \sigma_{21}(\omega),
\]

(3.13)

where \( n_1 \) denotes the concentration of excitations.

The difference between the pumped and unpumped spectra is called the transient absorption \( \Delta \alpha \):

\[
\Delta \alpha(\omega) = \alpha(\omega) - \alpha_0(\omega) = -2n_1 \sigma_{10}(\omega) + n_1 \sigma_{21}(\omega) \quad \text{bleaching} + \text{induced absorption}.
\]

(3.14)

Although two signals are contributing to the bleaching signal and only one to the induced absorption, they roughly have the same intensity as \( 2\sigma_{10} = \sigma_{21} \) in the harmonic oscillator approximation (see Section 2.3.2). Transient absorption spectra can be obtained by blocking every second pump pulse and subtracting the absorption spectrum of the probe pulse in the absence of the pump pulse from the absorption spectrum in the presence of the pump pulse. Alternatively, one can modulate the interference of two identical pump pulses in a Mach–Zehnder and perform a Fourier transformation of the absorption of the probe pulse. The latter yields the additional information of which spectral component of the pump pulse is responsible for the transient absorption and is called two-dimensional (2D) pump–probe spectroscopy.

The transient absorption is independent of the intensity of the probe pulse but the transient absorption does dependent on the intensity of the pump pulse. The pump intensity and the spot area of the pump beam \( A_{\text{pu}} \) determine the amount of pump-excited vibrations per surface \( n_1 \) by the Bouguer–Lambert–Beer law [Eq. (3.8)]. The number of photons in the pump pulse is given by \( N_{\text{pu}} = \int d\omega N_{\text{pu}}(\omega) \). Taking into account both the bandwidth of the molecular transition and the spectral width of the pump pulse we get

\[
n_1 = \frac{1}{A_{\text{pu}}} \int d\omega \left[ 1 - e^{-Cl \sigma_{10}(\omega)} \right] N_{\text{pu}}(\omega),
\]

(3.15)

where \( A_{\text{pu}} \) is the spot area of the pump beam. For a sample with little absorption, we have \( e^{-Cl \sigma_{10}(\omega)} \approx 1 - Cl \sigma_{10}(\omega) \). Combining Eqs. (3.14) and (3.15) we find the transient absorption to scale approximately with the cross section squared for a sample with little absorption. In case the sample has a very high optical density and the pump pulse depletes, the transient absorption will scale linearly with the cross section.

\(^{2}\)It follows from Eq. (2.79) that \( \sigma_{10} = \sigma_{01} \).
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Polarization-resolved pump–probe The pump pulse excites preferentially molecules with their transition dipole moments aligned parallel to the pump polarization. As a consequence the distribution of excited molecules is anisotropic after excitation by the pump pulse. Hence, the transient absorption of the probe pulse depends on its relative polarization compared to the pump pulse. One can measure the transient absorption of the probe pulse twice, once with its polarization parallel to the pump pulse ($\Delta \alpha_\parallel$) and once with its polarization perpendicular to the pump pulse ($\Delta \alpha_\perp$). In an isotropic medium, the transient absorption initially is three times larger for the parallel polarization with respect to the perpendicular polarization. Depolarization by molecular reorientation and energy transfer could reduce this difference over time until eventually an isotropic distribution of excited molecules is reached. In that case $\Delta \alpha_\parallel$ decays faster, and the transient absorption of the probe pulse with the polarization perpendicular to the pump pulse $\Delta \alpha_\perp$ decays slower. An isotropic signal $\Delta \alpha_{\text{iso}}$ that is free of depolarization processes can be constructed in the following way:

$$\Delta \alpha_{\text{iso}}(\omega,t) = \frac{\Delta \alpha_\parallel(\omega,t) + 2\Delta \alpha_\perp(\omega,t)}{3}.$$ (3.16)

Information about the depolarization dynamics can be obtained by monitoring the difference between the parallel and perpendicular transient absorption changes. Normalized by the isotropic signal, this yields the anisotropy $R$, which depends exclusively on the depolarization dynamics:

$$R(\omega,t) = \frac{\Delta \alpha_\parallel(\omega,t) - \Delta \alpha_\perp(\omega,t)}{3\Delta \alpha_{\text{iso}}(\omega,t)} = \frac{\Delta \alpha_\parallel(\omega,t) - \Delta \alpha_\perp(\omega,t)}{\Delta \alpha_\parallel(\omega,t) + 2\Delta \alpha_\perp(\omega,t)}.$$ (3.17)

For a sample with an isotropic distribution of dipoles, it can be shown that the anisotropy is proportional to

$$R(t) = \frac{2}{5} \langle P_2(\hat{\mu}(0) \cdot \hat{\mu}(t)) \rangle$$
$$= \frac{3}{5} \langle \cos^2(\theta(t)) \rangle - \frac{1}{5},$$ (3.18)

where $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial, $\hat{\mu}(0) \cdot \hat{\mu}(t) = \cos(\theta(t))$ is the correlation of the direction of the transition dipole moment between times 0 and $t$, and $\langle .. \rangle$ denotes the average over all molecules. As $0 \leq \cos^2 \leq 1$ we find from Eq. (3.18) that $-1/5 \leq R(t) \leq 2/5$. At $t = 0$, the correlation function is unity and the anisotropy equals 2/5.

3.3 Sum-frequency generation

Specific information about the molecular configuration at an interface can be obtained from sum-frequency generation (SFG) experiments (Fig. 3.3). We have already seen in Section 2.1 that in a non-linear medium the frequencies of two electromagnetic waves can mix. This requires strong fields. For a visible and
Figure 3.3: Schematic of a SFG experiment. At the interface (where the symmetry is broken), two pulses with different frequencies combine and generate a pulse at the sum frequency.

Infrared light source, with frequencies $\omega_{\text{VIS}}$ and $\omega_{\text{IR}}$, respectively, light can be produced at the sum of these frequencies, i.e.

$$\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}}.$$  \hspace{1cm} (3.19)

The positive frequency part of the second-order polarization $P^{(2)}$ can be written in vector component form as follows:

$$P^{(2)}_{\alpha}(\omega_{\text{SF}}) = \epsilon_0 \chi^{(2)}_{\alpha\beta\gamma}(\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}}) E_\beta(\omega_{\text{IR}}) E_\gamma(\omega_{\text{VIS}}),$$ \hspace{1cm} (3.20)

where the Einstein summation notation is used over repeated Greek indices. [43] $E(\omega_{\text{VIS}})$ and $E(\omega_{\text{IR}})$ are the electric field amplitudes of the visible and the infrared beams, respectively. The intensity of the emitted SF light is proportional to the absolute magnitude squared of the second-order polarization $P^{(2)}$, i.e.

$$I^{(2)}_{\alpha}(\omega_{\text{SF}}) \propto \left| \chi^{(2)}_{\alpha\beta\gamma}(\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}}) E_\beta(\omega_{\text{IR}}) E_\gamma(\omega_{\text{VIS}}) \right|^2.$$ \hspace{1cm} (3.21)

SFG is a powerful tool to study surface behaviour, because this process is bulk forbidden for an isotropic material. This is easily understood by the following argument. In a centrosymmetric material all directions are identical and the physical response of the material is independent of the axis system. This also applies for the second-order susceptibility under a parity inversion $\Pi$ in the three spatial coordinates:

$$\Pi_{\alpha\alpha'}\Pi_{\beta\beta'}\Pi_{\gamma\gamma'}\chi_{\alpha'\beta'\gamma'}^{(2)}(\text{centrosymmetry}).$$ \hspace{1cm} (3.22)

In Cartesian coordinates the parity operator is represented by the matrix

$$\Pi = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$ \hspace{1cm} (3.23)
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Figure 3.4: The $p$- and $s$-polarizations of an electric field with an angle of incidence $\theta_i$. The $p$-polarization is parallel to the plane of incidence and can be decomposed into both a perpendicular as well as a parallel component to the interface. The $s$-polarization is perpendicular to the plane of incidence and lays entirely parallel to the interface.

or in index notation $\Pi_{\alpha\beta} = -\delta_{\alpha\beta}$. Applying this on Eq. (3.22) gives $\chi^{(2)} = -\chi^{(2)}$, which can only be true if and only if $\chi^{(2)} = 0$. A direct consequence is that for centrosymmetric materials SF light can only be generated at positions with broken symmetry, i.e. at interfaces.

In general, the second-order susceptibility $\chi^{(2)}$ is a third-order tensor with 27 components. Symmetry considerations, however, reduce the number of non-zero components greatly according to Neumann’s principle.$^4$ An achiral rotationally isotropic interface is rotation symmetric in the axis perpendicular to the surface and mirror symmetric in the interfacial plane. Therefore, the second-order susceptibility $\chi^{(2)}$ has only four independent non-zero elements.$^{[46,47]}$ These can be deduced by different polarization combinations of the SF, VIS, and IR fields. The polarization of these electric fields can be split up in two components, one parallel and one perpendicular to the plane of incidence, which are denoted by $p$ and $s$, respectively.$^4$ The polarization combinations are denoted like $ssp$ where the polarizations are listed in order of decreasing frequency (SF, VIS, and IR). $s$-polarized light is polarized entirely parallel to the surface, whereas $p$-polarized light has both a parallel as well as a perpendicular component. This is illustrated in Fig. 3.4. Hence, the $ppp$-polarization combination probes a combination of the four non-zero $\chi^{(2)}$ components. The effective second-order susceptibility $\chi^{(2)}_{\text{eff}}$ for a given polarization combination of the SF, VIS, and IR

$^4$Neumann’s principle states that all symmetries of a system are possessed by every physical property of that system.$^{[45]}

$^p$ stands for parallel, and $s$ stands for senkrecht (German for perpendicular).
beams has the following dependence on the $\chi^{(2)}$ components:

$$\chi^{(2)}_{\text{eff}, ss \rightarrow sp} \propto \chi^{(2)}_{\text{11} \perp}$$

$$\chi^{(2)}_{\text{eff}, sp \rightarrow ss} \propto \chi^{(2)}_{\text{11} \perp}$$

$$\chi^{(2)}_{\text{eff}, ps \rightarrow sp} \propto \chi^{(2)}_{\text{11} \perp}$$

$$\chi^{(2)}_{\text{eff}, pp \rightarrow pp} \propto \chi^{(2)}_{\text{11} \perp}$$

where we omitted the Fresnel and angular factors in the last line. These local field factors correct for the influence of the interfacial reflection and the projection in the separate components. The Fresnel and angular factors depend on the optical constants and the angles of incidence.

The second-order susceptibility $\chi^{(2)}$ reveals information about the surface structure, because it is the macroscopical average over the molecular hyperpolarizabilities $\beta$,

$$\chi^{(2)}_{\alpha \beta \gamma} = \frac{N_s}{\epsilon_0} \langle R_{\alpha i} R_{\beta j} R_{\gamma k} \beta_{ijk} \rangle,$$

where $N_s$ is the number of surface molecules, $R_{\alpha i}$ are rotation matrices using all three Euler angles to project the molecule coordinate system (Roman indices) on the surface plane coordinate system (Greek indices), and $\langle \ldots \rangle$ denotes the ensemble average.

The resonant and hence dominant part of the hyperpolarizability $\beta$ is given by

$$\beta_{ijk} = \frac{1}{2\hbar} \sum_w M_{ij} A_k \omega_w - \omega_{\text{IR}} - i\Gamma_w / 2,$$

where the sum is taken over all resonances $w$ with their corresponding resonance frequencies $\omega_{w}$ and decay rates $\Gamma_w$ [cf. Eq. (2.81)]. $M$ and $A$ are the Raman and IR transition moments, respectively, and are given by

$$M_{ij} = \frac{1}{\hbar} \sum_s \frac{\langle v | \hat{\mu}_i | s \rangle \langle s | \hat{\mu}_j | w \rangle}{\omega_{\text{SF}} - \omega_{sv}} - \frac{\langle v | \hat{\mu}_j | s \rangle \langle s | \hat{\mu}_i | w \rangle}{\omega_{\text{VIS}} + \omega_{sv}}$$

$$A_k = \langle w | \hat{\mu}_k | v \rangle \approx \frac{\partial \mu_k}{\partial q}(w | \hat{q} | v).$$

Here $s$ can be any state of the system and the wave functions are taken to be real. For the approximation of the Raman transition moment $M$ we employed the condition $\omega_{\text{SF}} + \omega_{sv} \gg \omega_{\text{SF}} - \omega_{sv}$ and for the approximation of the IR transition moment $A$ we employed Eq. (2.76).

An important note is that the squares of the absolute values of $M$ and $A$ are directly proportional to the Raman and IR cross sections, respectively. Therefore, from Eq. (3.26) it follows that SFG needs the vibration to be both Raman and IR active, i.e. $M$ and $A$ are both non-zero. This can also be inferred from the energy diagram shown in Fig. 3.5.
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\[ \omega_{\text{IR}} |v \rangle + \omega_{\text{VIS}} |w \rangle = \omega_{\text{IR}} |v \rangle + \omega_{\text{VIS}} |w \rangle \]

**Figure 3.5:** Diagrammatic representation of an SFG process, which can be regarded as a combination of an IR transition in combination with an anti-Stokes Raman scattering process.

**Spectral resolution and normalization** Sum-frequency generation can be used to study the vibrations of molecules at an interface. As the vibrational resonances make the SFG signal species specific, varying the infrared frequency creates a vibrational spectrum. For this purpose a visible beam with a fixed and narrow wavelength is often used in combination with an infrared beam that has a broad spectrum covering the vibrational resonances to be studied. The bandwidth of the visible light defines the maximal spectral resolution. The spectral shape is determined by the effective second-order susceptibility \( \chi_{\text{eff}}^{(2)} \), which includes all angular and Fresnel factors. Taking into account the spectral width of the VIS beam, the SF intensity can be written as

\[
I_{\alpha}(\omega_{\text{SF}}) \propto \left| \chi_{\text{eff},\alpha\beta\gamma}(\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}}) E_{\beta}(\omega_{\text{IR}}) \ast E_{\gamma}(\omega_{\text{VIS}}) \right|^2 , \tag{3.28}
\]

where \( \ast \) denotes the convolution operator.

In order to divide out the spectral envelope of the IR light, the SF spectrum is often normalized with respect to a reference SF signal acquired from a material with a non-resonant and therefore non-dispersive second-order susceptibility. For this purpose often crystalline quartz is employed. For a certain polarization combination, the normalized SF intensity is given by

\[
\frac{I_{\text{sample}}}{I_{\text{reference}}}(\omega_{\text{SF}}) \propto \left| \chi^{(2)}_{\text{eff},\alpha\beta\gamma}(\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}}) \ast E(\omega_{\text{VIS}}) \right|^2 . \tag{3.29}
\]

**Hyperpolarizabilities for molecular groups with \( C_{nv} \) symmetry** The strength of the \( \chi^{(2)} \) response depends on the underlying hyperpolarizabilities \( \beta \). The \( \chi_{\alpha'\beta'\gamma'}^{(2)} \) tensor elements are directly connected to the hyperpolarizability tensor elements \( \beta_{\alpha'\beta'\gamma'} \) through transformation of the Euler angles [Eq. (3.25)]. The most general relations are given in Hirose et al. They simplify considerably when we calculate the relations for molecular groups with symmetry \( C_{nv} \), on a rotational-isotropic interface. When we follow the convention of the molecular axes system given in Fig. 3.6, many hyperpolarizability elements are zero. For a rotational-isotropic interface with a random dis-

\[ \text{The Schönflies symmetry notation } C_{nv} \text{ stands for an } n \text{-fold rotational axis with } n \text{ vertical mirror planes containing the axis of rotation.} \]
For the symmetric stretching ($v_1$) and bending ($v_2$) modes the dipole moment changes in the $c$-direction, hence only hyperpolarizability elements with the last subindex $c$ are active, i.e., $\beta_{aac}$, $\beta_{bcc}$ and $\beta_{ccc}$. Similarly, for the antisymmetric stretching modes ($v_3$) the dipole moment changes in the $a$- or $b$-direction. Hence only hyperpolarizability elements with the third index equal to $a$ or $b$ contribute, i.e., $\beta_{aca}$, $\beta_{bcb}$, $\beta_{caa}$, and $\beta_{cbb}$.

These relations can be simplified when both the SF and VIS beams are off-resonance. In that case the Kleinman’s conjecture holds and the first two subindices of the hyperpolarizability are approximately symmetric on interchange [cf. Eq. (3.27)]:

$$\beta_{ijk} \approx \beta_{jik}$$  (3.31)
Under Kleinman’s conjecture the relations simplify to
\[
\chi_{111}^{(2)} = \frac{N_s}{4\epsilon_0} \left[ (2\beta_{ccc} + \beta_{aac} + \beta_{bbc} - 2\beta_{aca} - 2\beta_{bcb})(\cos(\theta)) - (2\beta_{ccc} - \beta_{aac} - \beta_{bbc} - 2\beta_{aca} - 2\beta_{bcb})(\cos^3(\theta)) \right]
\]
\[
\chi_{1,1,1}^{(2)} = \chi_{111}^{(2)} = \frac{N_s}{4\epsilon_0} \left[ (2\beta_{ccc} - \beta_{aac} - \beta_{bbc})(\cos(\theta)) - (2\beta_{ccc} - \beta_{aac} - \beta_{bbc} - 2\beta_{aca} - 2\beta_{bcb})(\cos^3(\theta)) \right]
\]
\[
\chi_{111}^{(2)} = \frac{N_s}{2\epsilon_0} \left[ (\beta_{aac} + \beta_{bbc} + 2\beta_{aca} + 2\beta_{bcb})(\cos(\theta)) + (2\beta_{ccc} - \beta_{aac} - \beta_{bbc} - 2\beta_{aca} - 2\beta_{bcb})(\cos^3(\theta)) \right].
\]

Furthermore, for the point groups \(C_{\infty v}, C_{3v}, C_{4v}\), and \(C_{6v}\), the hyperpolarizability tensor is symmetric in \(a\) and \(b\), i.e. \(\beta_{aac} = \beta_{bbc}\) and \(\beta_{aca} = \beta_{bcb}\). For the \(C_{2v}\) group \(\beta_{bcb} = 0\).\(^{[48]}\)

The non-vanishing tensor elements for certain molecular groups with \(C_{nv}\) symmetry are given in Table I. The hyperpolarizabilities are normalized to the \(\beta_{ccc}\) element of the corresponding mode. The hyperpolarizabilities of the \(\text{H}_2\text{O}\) \(v_2\) bending mode are one order of magnitude smaller than the hyperpolarizabilities of the \(\text{H}_2\text{O}\) \(v_1\) stretching mode.\(^{[60]}\) CH modes in an alkane chain have an opposite dipole moment derivative with respect to an OH mode,\(^{[61,62]}\) yielding an opposite sign in the hyperpolarizabilities.\(^{[63]}\) However, care has to be taken as the dipole moment derivative of a CH mode strongly depends on the residual group and sometimes even changes its sign.\(^{[64]}\) The factor of 2 in \(\beta_{\text{CH}_3}\) should be applied in case the two antisymmetric stretch vibrations of the methylene group are degenerate.\(^{[48]}\) For the \(\text{CH}_2\) group, the term \(2\beta_{ccc} - \beta_{aac} - \beta_{bbc}\) vanishes at the standard bond angle 109.5°.\(^{[65]}\) For the water molecule the bond angle is 105° and \(2\beta_{ccc} - \beta_{aac} - \beta_{bbc}\) is very small.\(^{[66]}\) The CH, CH, and CH\(_3\) hyperpolarizability elements have the following relative magnitudes: \(\beta_{\text{ccc}}^{\text{CH}} = 4.4\beta_{\text{ccc}}^{\text{CH}_2}\) and \(\beta_{\text{ccc}}^{\text{CH}} = 20\beta_{\text{ccc}}^{\text{CH}_2}\).\(^{[48]}\)

Water molecules do not always possess \(C_{2v}\) symmetry because of hydrogen bonding. As the hydrogen bonds of a single water molecule may be different in strength/length, the two stretch modes \((v_1\) and \(v_3)\) can decouple and become local modes, as is the case for HDO. In that case the water molecule no longer possesses \(C_{2v}\) symmetry, but \(C_{1v}\) symmetry. When the localization is strong as for HDO, \(C_{\infty v}\) symmetry may be assumed for the single OH/OD branches. The stretch vibration of the free OH bond for \(\text{H}_2\text{O}\) molecules at the air–water interface is weakly coupled to the stretch vibration of the other OH bond,\(^{[73]}\) so strictly it neither possesses \(C_{\infty v}\) nor \(C_{2v}\) symmetry. However, it can be well described with \(C_{\infty v}\) symmetry.\(^{[66]}\)

The orientation of molecules or molecular groups can be determined by comparing the relative strengths of the \(\chi^{(2)}\) elements, which can be probed using different polarization combinations of the SF, VIS, and IR beams [see Eq. (3.24)]. A precise analysis of the SFG spectra requires the Fresnel factors.
and the experimental angles of incidence of the incoming VIS and IR beams. As a guideline for the identification of the vibrational modes and the orientation of the molecules, we can formulate rules of thumb following Wang et al. The polarization dependencies are as follows for the CH$_3$ stretching modes:

(a) The $v_1$ mode is stronger in the ssp-polarization combination than in the ppp-, sps-, or pss-polarization combinations.

(b) The $v_3$ mode is weaker in the ssp- than in the ppp-polarization combination. For both polarization combinations the $v_3$ mode is maximal for the magic tilt angle $\theta = \arccos(1/\sqrt{3}) \approx 54.7^\circ$.

(c) In the sps- and pss-polarization combinations, the $v_3$ mode is largest and the $v_1$ mode is smallest for small tilt angles $\theta$.

(d) In the ssp-polarization combination the $v_1$ and $v_3$ modes have opposite signs and negatively interfere whereas they have equal signs in the ppp-polarization combination.

For the stretching modes of H$_2$O and CH$_2$, the following dependencies hold:

(e) The $v_1$ mode is stronger in the ssp-polarization combination than in the ppp-polarization combination.

(f) The $v_3$ mode is weaker in the ssp-polarization combination than in the ppp-polarization combination.

(g) In the sps- and the pss-polarization combinations, the $v_3$ mode is much stronger than the $v_1$ mode. The $v_3$ mode is largest for small tilt angles $\theta$ in both polarization combinations.

(h) No $v_1$ strength in the sps- and the pss-polarization in case of CH$_2$ and only very little strength in case of H$_2$O.
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(i) In the ssp-polarization combination the \( v_1 \) and \( v_3 \) modes have opposite signs and negatively interfere, whereas they have equal signs in the ppp-polarization combination.

For the stretching vibrations of OH and CH groups and of OH\(^-\), the polarization dependencies are:

(j) Strongest in the ssp-polarization combination for large tilt angles \( \theta \).

(k) Strongest in the ppp-polarization combination for small tilt angles \( \theta \).

(l) The sps- and pss-polarization combinations are largest for the magic tilt angle \( \theta \approx 54.7^\circ \).

Similar we have for the H\(_2\)O bending mode (\( v_2 \)):

(m) Stronger in the ssp- than in the ppp-polarization combination.

(n) The mode is largest for the magic tilt angle \( \theta \approx 54.7^\circ \) in the sps- and pss-polarization combinations.

(o) The mode is much weaker in the sps- and pss-polarization combinations than in the ssp- and ppp-polarization combinations for small tilt angles \( \theta \).

3.3.1 Real and imaginary part of \( \chi^{(2)} \)

Omitting the tensorial indices, the frequency dependence of a resonant \( \chi^{(2)} \) response of a single molecular transition \( v \to w \) is given by [Eq. (3.26)]

\[
\chi^{(2)} \propto \frac{1}{\omega_{uv} - \omega_{IR} - i\Gamma_w/2}.
\]

The response can be separated into a real and imaginary part, viz.

\[
\frac{1}{\omega_{uv} - \omega_{IR} - i\Gamma_w/2} = \frac{\omega_{uv} - \omega_{IR}}{(\omega_{uv} - \omega_{IR})^2 + \Gamma_w^2/4} + i \frac{\Gamma_w/2}{(\omega_{uv} - \omega_{IR})^2 + \Gamma_w^2/4}.
\]

The real and imaginary parts of \( \chi^{(2)} \) for a single resonance are plotted in Fig. 3.7. Re \( \chi^{(2)} \) is an odd function in \( (\omega_{uv} - \omega_{IR}) \), whereas Im \( \chi^{(2)} \) is an even function in \( (\omega_{uv} - \omega_{IR}) \). This is in agreement with the Kramers–Kronig relations [Eq. (2.7)]. Im \( \chi^{(2)} \) can be interpreted as a surface absorption spectrum and the maximal response strength is found on resonance, i.e. when \( \omega_{IR} = \omega_{uv} \). Unlike a linear absorption spectrum, Im \( \chi^{(2)} \) can be positive or negative. The sign of Im \( \chi^{(2)} \) reflects the polar orientation of the transition dipole moment derivative revealing the molecular orientation. In a conventional SFG experiment one measures the squared magnitude \( |\chi^{(2)}|^2 \). For a single resonance, \( |\chi^{(2)}|^2 \) has the same spectral shape as Im \( \chi^{(2)} \), but the information of the polar orientation is lost by squaring. In case of multiple interfering resonances or the presence of a non-resonant background, the spectral shapes of \( |\chi^{(2)}|^2 \) and Im \( \chi^{(2)} \) are different and the spectral shape of Im \( \chi^{(2)} \) can only be retrieved by spectral fitting. However, the
uniqueness of the fit is not ensured, especially when $\chi^{(2)}$ comprises a continuum of resonances like the OH stretches of hydrogen-bonded water.\cite{74,75} These problems can be circumvented by employing an experimental configuration in which the SF signal from the sample interferes with the SF signal generated at a local oscillator. This technique yields the phase of $\chi^{(2)}$ directly and is called phase-resolved SFG. We will discuss the theoretical and experimental approach of this technique in detail in Chapter 6.

### 3.3.2 Sum-frequency scattering

Sum-frequency signals can also be generated from non-planar interfaces. This method is used to probe the surface structure of dispersed particles with sum-frequency scattering experiments. In these experiments the IR and VIS beams are overlapped in a solution with dispersed particles and the SF signal is generated all around the particle’s surface. Because of the phase difference at the detection point between the polarization components generated at different parts of the surface, the SF photons interfere and generate a scattering pattern (Fig. 3.8). The scattering pattern is depending on the polarization configuration, the particle size and shape, surface structure, and the experimental geometry.\cite{76–79} The intensity of the SF light from particle $n$ is proportional to the modulus squared of the effective particle susceptibility tensor $\chi_{\text{eff},n}^{(2)}$, i.e.\cite{82,83}

$$I_{\alpha,n}(\omega_{\text{SF}},\theta) \propto |\chi_{\text{eff},\alpha\beta\gamma,n}^{(2)}(\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}},\theta) E_\beta(\omega_{\text{IR}}) * E_\gamma(\omega_{\text{VIS}})|^2, \quad (3.34)$$

\footnote{In literature the effective particle susceptibility tensor is often denoted by $\Gamma_n^{(2)}$.\cite{80–82}}
3.3 Spectroscopic techniques

Figure 3.8: Schematic of a sum-frequency scattering experiment. A sum-frequency signal is generated at the surface of a particle (where \( \chi^{(2)} \neq 0 \)). Interference of the signals generated at different parts gives rise to a scattering pattern.

where \( \theta \) is the scattering angle. The total SF intensity is the incoherent sum of the SF intensities that are generated on the individual particles \( n \),\(^{[79]} \) i.e.

\[
I_\alpha(\omega_{SF}, \theta) = \sum_n I_{\alpha,n}(\omega_{SF}, \theta)
\]

\[
\propto \sum_n |\chi^{(2)}_{\text{eff}, \alpha\beta\gamma,n}(\omega_{SF} = \omega_{IR} + \omega_{VIS}, \theta) E_\beta(\omega_{IR}) * E_\gamma(\omega_{VIS})|^2.
\] (3.35)

In case the particles are homogeneous and all have the same effective particle susceptibility tensor, i.e. \( \chi^{(2)}_{\text{eff}, n} = \chi^{(2)}_{\text{eff}} \), the expression of the total SF intensity becomes equivalent to the previous obtained result for planar SFG [Eq. (3.28)]:

\[
I_\alpha(\omega_{SF}, \theta) \propto |\chi^{(2)}_{\text{eff}, \alpha\beta\gamma}(\omega_{SF} = \omega_{IR} + \omega_{VIS}, \theta) E_\beta(\omega_{IR}) * E_\gamma(\omega_{VIS})|^2.
\] (3.36)

It is illustrative to examine the scattering pattern in the extreme case of particles with an infinitely small radius and collinear IR and VIS beams. Then a polarization is only created at a single point. Like an oscillating dipole, there is no emission in the forward direction and the scattered light will have the maximal intensity at an angle \( \theta \) of 90°.\(^{[31]} \) For particles with a finite radius and an arbitrary angle between the IR and VIS beams, non-linear Mie theory can be applied to calculate the scattering pattern.\(^{[76]} \) The calculated scattering pattern for water droplets in air is given in Fig. 3.9.

The SF scattering signal increases with increasing particle size. For a spherical particle with radius \( r \), the volume scales \( \propto r^3 \). For small particles with \( r < c/\omega_{SF} \), the scattering cross section scales \( \propto r^6 \).\(^{[76]} \) Therefore, the SF scattering intensity of an emulsion with fixed volume fractions follows an \( r^3 \) dependence in the limit of small particles.
Figure 3.9: Computations of the SF scattering patterns for water droplets with in air as function of the particle radius and the scattering angle in the ppp-polarization combination. Every scattering pattern has been normalized to its respective peak value. The non-collinear scattering setup consists of source waves with a VIS wavelength of 800 nm and an IR wavelength of 2708 nm (3693 cm$^{-1}$) under a relative angle of 15°. Adapted with permission from de Beer and Roke.\cite{[76]}