Water Interacting with interfaces, ions and itself

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2 Spectroscopy

Until about 1800, visible light was considered to be the only form of radiation. It took nearly the whole 19th century for scientists to realize the existence of different forms of radiation, the near infrared to be discovered first (William Herschel experiment), followed by the ultraviolet (Johann Ritter experiment). Soon after, Maxwell formulated his description of the properties of electromagnetic (EM) radiation. With the discovery of different forms of radiation a world of applications opened up. The electromagnetic spectrum we know now, forms a continuum of radiation, of which the wavelength spreads over many orders of magnitude (see figure 2.1).

In the early 19th century people realized that it is possible to match radiation of a certain frequency to obtain or enhance certain effects in matter. This realization gave birth to quantum mechanics and spectroscopy, the field that investigates the properties of matter with the use of EM radiation.

We now realize that life exists thanks to light-matter interactions. The light emitted by the sun is absorbed by plants and used in chemical reactions that are crucial for their existence. Not all of the EM radiation, however is beneficial. A big part of the high energy radiation (X-rays and gamma-rays) is highly destructive for live tissues. Interestingly, the same type of interactions with the molecules present in the Earth’s atmosphere protects us against this radiation.

Different parts of the electromagnetic spectrum are named differently, partially because they were discovered over the course of many years and were believed to be separate types of radiation, and partially because they interact

![Figure 2.1. Electromagnetic spectrum and molecular processes associated with the mid-infrared region.](image-url)
with different degrees of freedom. The part of the spectrum characterized with the longest wavelengths ($\lambda \approx \text{m}$), called ‘radio waves’ is used for instance in radio astronomy or in medicine in magnetic resonance imaging (MRI). The most energetic waves with the shortest wavelengths ($\lambda < 10^{-8} \text{ m}$) are x-rays and gamma rays and are used in medicine and sensing applications.

In this thesis we have used only a small fraction of the EM spectrum in the near- and mid-infrared (mid-IR) region (see figure 2.1). We have used wavelengths ranging from 800 nm to about 6000 nm. The near infrared part ($\sim$800 nm - 2100 nm) has been used in frequency mixing processes (see section 2.6) in order to generate light in the mid-IR region ($\sim$2800 nm - 6000 nm). The mid-IR part of the spectrum is associated mainly with intramolecular vibrations (motions of atoms forming molecules) and librations (hindered rotations of the molecular moieties).

## 2.1 Harmonic Oscillator

“Physics is that subset of human experience which can be reduced to coupled harmonic oscillators”

Michael Peskin

Following classical mechanics the periodic harmonic motion of an object is described by Newton’s second law of motion:

$$ F(t) = m \frac{d^2x}{dt^2} = -kx, \quad (2.1) $$

where $F$ is the force acting on an object with mass $m$ that is displaced from its equilibrium by a distance $x$. The constant $k$ is called the force constant. A solution of the above equation is:

$$ x = \sin(\omega t), \quad (2.2) $$
where $\omega$ is the frequency of the oscillation defined as:

$$\omega = \sqrt{\frac{k}{m}}.$$  \hfill (2.3)

The motion of an object is periodic, repeating itself in a sinusoidal manner with a constant amplitude. The frequency of the oscillation is dependent only on the objects mass $m$ and the force constant $k$. In the classical picture, the energy of a system is defined in terms of its position and momentum, which implies that the time evolution of the system can be predicted with any given accuracy:

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2.$$  \hfill (2.4)

The above description of an oscillator is in many ways simplified. The largest simplification lies in the linear dependence between the displacement ($x$) and the force ($F$). In reality no motion is truly harmonic and the forces acting on the system contain higher order terms. In spite of its simplicity, however, the harmonic oscillator can be successfully applied to many complex systems exhibiting small amplitude periodic motions. In figure 2.2 we show the harmonic oscillator in the form of a spring/mass system and in analogy an OH stretch vibration of the water molecule.

### 2.2 Quantum harmonic oscillator

The quantum world is known to us for about a century now, since Bohr’s postulate that the electrons have quantized energy levels and their first experimental observation by Stern and Gerlach. Once the size of an object becomes comparable to the atomic scale we enter the so-called quantum realm. Quantum particles possess quantized energy states and can behave both as classical particles as well as waves (wave-particle duality). In analogy to classical mechanics we describe the motion of a particle as a quantum mechanical harmonic oscillator [22]. Let us consider the same example of a mass $m$ connected by a spring with force constant $k$ to an infinitely massive object. The energy of the system is given by the Hamiltonian:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2,$$  \hfill (2.5)

where $\hat{p}$ and $\hat{x}$ are the momentum and position operators. The first term describes the kinetic energy of the system (with $\hat{p} = -i\hbar \frac{\partial}{\partial x}$), whereas the second term represents the potential energy.

The set of energies and corresponding eigenstates are obtained by solving the time-independent Schrödinger equation:

$$\hat{H} |\phi(x)\rangle = E |\phi(x)\rangle.$$  \hfill (2.6)

The solution of this equation yields a set of eigenstates of the form:

$$|\phi_n(r)\rangle = \sqrt{\frac{1}{2^n n!}} \left(\frac{m \omega_0}{\pi \hbar}\right)^{1/4} \exp \left(-\frac{m \omega_0 r^2}{2 \hbar}\right) H_n \left(\sqrt{\frac{m \omega_0}{\hbar}} r\right),$$  \hfill (2.7)
Figure 2.3. Energy level scheme for quantum harmonic oscillator. ϕ_n are the eigenstates of the corresponding energy states E_n. The energy levels are spaced equally with the spacing equal to ℏω_0.

where n=0,1,2,... and the functions H_n(r) represent the so-called Hermite polynomials. When squared (|ϕ(x)|^2), this function describes the probability of a particle to be at a distance x. The energy of each state is given by:

\[ E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right), \]  \hspace{1cm} (2.8)

where ω_0 is the resonance frequency of the oscillating particle. In figure 2.3 we show the eigenstates φ_n(r) at corresponding eigenvalues E_n for n = 0, 1, 2 and 3.

So far we have considered the isolated case of a system in equilibrium, showing no interactions with its surroundings. The experimental determination of the state of the system and its properties, however, often involves the interaction with an electromagnetic field. The presence of the electromagnetic field will perturb the energetic state of the system and may promote it to an energetically higher state (i.e. E_n→E_{n+1}). Such inter-state transitions can be described by adding a time-dependent perturbation to the Hamiltonian [21, 141]:

\[ \hat{H} | \Phi(r, t) \rangle = i \hbar \frac{\partial}{\partial t} | \Phi(r, t) \rangle, \]  \hspace{1cm} (2.9)

where \( \hat{H}(t) \) is now the time dependent total energy of the system including the energy of the unperturbed system \( \hat{H}_0 \) and the time-dependent perturbing term \( \hat{V}(t) \):

\[ \hat{H}(t) = \hat{H}_0 + \hat{V}(t). \]  \hspace{1cm} (2.10)

In case the perturbing force originates from electromagnetic radiation \( \hat{V}(t) \) is defined as:

\[ \hat{V}(t) = \frac{1}{2} \vec{\mu} \cdot \vec{E}_0 (e^{i\omega t} + e^{-i\omega t}), \]  \hspace{1cm} (2.11)

where \( \vec{\mu} \) is the transition dipole moment operator, \( \vec{E}_0 \) is the amplitude of the electric field oscillating with frequency \( \omega \). Solving the time-dependent
Schrödinger equation to first order in the perturbation yields the probability of the particle going from its initial state \(a\) to state \(b\):

\[
P_{a\rightarrow b} = \frac{2\pi t}{\hbar^2} \int |\langle \Phi_b | \hat{V} | \Phi_a \rangle|^2 \delta(\omega \pm \omega_{ab})d\omega,
\]  

(2.12)

where \(\delta(\omega \pm \omega_{ab})\) is a delta function that ensures that the resonant condition is fulfilled. The transition between two states can only occur if the driving field has a frequency \(\omega\) that is equal to the energy difference between the two states expressed in \(\omega_{ab}\). Equation 2.12 is known as Fermi’s golden rule.

According to equation 2.12 the transition probability \(P_{a\rightarrow b}\) is proportional to the time \(t\) over which the interaction takes place. Differentiating the formula over time \(\frac{\partial P_{a\rightarrow b}}{\partial t}\) we obtain the transition rate \(\Gamma_{a\rightarrow b}\). We further substitute the perturbing term \(\hat{V}\) according to equation 2.11 and obtain:

\[
\Gamma_{a\rightarrow b} = \frac{\pi}{2\hbar^2} \int E_0^2 \cos^2 \theta \langle \Phi_b | \hat{\mu} | \Phi_a \rangle^2 \delta(\omega \pm \omega_{ab})d\omega.
\]

(2.13)

The dipole operator \(\hat{\mu}\) depends on the electronic structure of the molecule and may refer to any type of transition (vibrational, translational, etc.). In this thesis we are interested in the molecular vibrations, thus it is more appropriate to express \(\hat{\mu}\) in terms of a vibrational coordinate \(x\) (particles displacement axis):

\[
\vec{\mu} = \vec{\mu}_0 + \hat{x} \frac{\partial \vec{\mu}}{\partial x}.
\]

(2.14)

We substitute expression 2.14 into equation 2.13 and arrive at:

\[
\Gamma_{a\rightarrow b} = \frac{\pi}{2\hbar^2} \int E_0^2 \cos^2 \theta \left( \frac{\partial \vec{\mu}}{\partial x} \right)^2 \langle \Phi_b | \hat{x} | \Phi_a \rangle^2 \delta(\omega \pm \omega_{ab})d\omega.
\]

(2.15)

The above formula carries important consequences for vibrational spectroscopy:

- The delta function involves both the sum and the difference of the molecules resonant frequency and the driving frequency. Since the states \(a\) and \(b\) can be situated differently with respect to each other (either \(E_a > E_b\) or \(E_b > E_a\)) the transition represents either absorption or stimulated emission. As the transition dipole moment is the same, the probability of the two processes to occur is the same.

- The term \(\left( \frac{\partial \vec{\mu}}{\partial x} \right)\) indicates that the vibrational transition can only be observed (= is infrared active) if the vibration changes the dipole moment of the oscillator.

- It follows from equation 2.15 that the transition dipole moment \(\vec{\mu}_{ab}\) is:

\[
\vec{\mu}_{ab} = \left( \frac{\partial \vec{\mu}_{el.}}{\partial x} \right) \langle \Phi_b | \hat{x} | \Phi_a \rangle,
\]

(2.16)

where \(\partial \vec{\mu}_{el.}\) (Born-Oppenheimer approximation) reflects the dependence of the electronic dipole moment on the vibrational coordinate. It can be
shown that for the harmonic oscillator $\langle \Phi_b \mid \hat{x} \mid \Phi_a \rangle$ has the following properties [141, 22]:

$$\langle \Phi_b | \hat{x} | \Phi_a \rangle = \begin{cases} 
0 & \text{if } b \neq a \pm 1 \\
\frac{1}{\alpha} \sqrt{\frac{a+1}{2}} & \text{if } b = a+1 \\
\frac{1}{\alpha} \sqrt{\frac{a}{2}} & \text{if } b = a - 1
\end{cases} \quad (2.17)$$

where $\alpha$ is a constant for a harmonic oscillator and equals ($\alpha = \sqrt{\hbar/m\omega}$).

- The first property tells us that the transition can only occur between consecutive levels.
- It further follows that for a transition from the ground state ($a=0$) to the first excited state ($b=1$), $\langle \Phi_b | \hat{x} | \Phi_a \rangle = \sqrt{\hbar/2m\omega}$, whereas for a transition from the first excited state ($a=1$) to the second excited state ($b=2$) $\langle \Phi_b | \hat{x} | \Phi_a \rangle = \sqrt{\hbar/m\omega}$. This means that for a harmonic oscillator the transition dipole moment of the $1 \rightarrow 2$ transition is $\sqrt{2}$ times larger than the transition dipole moment of the $0 \rightarrow 1$ transition.

$$\frac{\mu_{12}}{\mu_{01}} = \sqrt{2}. \quad (2.18)$$

### 2.3 Quantum Anharmonic Oscillator

If we assume that the resonance condition is fulfilled, meaning that $\delta(\omega \pm \omega_{ab}) = 1$, the transition rate becomes:

$$\Gamma_{a \rightarrow b} = \frac{\pi}{2\hbar^2} E_0^2 \cos^2 \theta \left( \frac{\partial \mu}{\partial x} \right)^2 |\langle \Phi_b | \hat{x} | \Phi_a \rangle|^2. \quad (2.19)$$
2.4 Spectroscopy

We can express the transition rate in terms of the intensity of light using the following relation:

\[ E_0^2 = \frac{2I(\omega_{ab})}{n\epsilon_0}, \]  

(2.20)

where \( n \) is the refractive index, \( c \) is the speed of light and \( \epsilon_0 \) is the vacuum electric permittivity. Replacing the position operator \( \hat{x} \) with the dipole moment operator \( \hat{\mu} \) and using the property that the average value of \( \cos^2 \theta = 1/3 \) we obtain:

\[ \Gamma_{a \rightarrow b} = \frac{\pi \mu^2}{3\hbar^2 n\epsilon_0} I(\omega_{ab}). \]  

(2.21)

The proportionality term between the transition rate and the intensity of light is called the absorption cross section:

\[ \sigma_{ab} = \frac{\pi \mu^2}{n\hbar^2 \epsilon_0}. \]  

(2.22)

We will see later that the absorption of the sample (or the absorption change measured in pump-probe experiment) is directly proportional to the absorption cross section \( \sigma_{ab} \).

As mentioned before a harmonic oscillator is a great simplification of reality. The motion of a particle does not depend linearly on the forces acting on it. When the restoring force is nonlinear, the energy levels can be written as:

\[ E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right) \left[ 1 - A_1(n + \frac{1}{2}) + A_2(n + \frac{1}{2})^2 + \ldots \right], \]  

(2.23)

where \( A_n \) are \( n \)-th order anharmonicity constants. In figure 2.4 we show a comparison of a harmonic (black) and an anharmonic (blue) potential for a particle moving along coordinate \( x \). In the anharmonic potential the energy levels are not spaced equally anymore and the selection rules of the harmonic oscillator (equation 2.17) no longer apply.

2.4 Linear light-matter interaction

Light-matter interactions can be measured in various ways. One of these is by measuring the attenuation of light that passes through the sample. The frequency dependent intensity of the outcoming light defines the absorption spectrum of the sample. The linear absorption spectrum carries information on the spectral position of various resonances and their line shape. Let us consider a sample with thickness \( L \) (see figure 2.5) and a concentration of absorbers \( C \). The intensity of the incident beam is denoted as \( I_0(\omega) \) and the intensity of the transmitted light is denoted as \( I(\omega) \). The light intensity change induced by the sample is proportional to the concentration of absorbers \( C \), the absorption cross section of the absorbing molecules \( \sigma(\omega) \), and the intensity of the incoming beam:

\[ dI(\omega) = -\sigma(\omega)CI_0(\omega)dL. \]  

(2.24)
The solution of this differential equation is:

$$\ln(I(\omega)) = -\sigma(\omega)CL + \ln(I_0(\omega)) .$$ (2.25)

Now we can calculate the difference between the light intensity before the sample and the transmitted intensity:

$$\ln(I(\omega)) - \ln(I_0(\omega)) = -\sigma(\omega)CL ,$$ (2.26)

and arrive at the expression for the transmission of the sample:

$$T(\omega) = \frac{I(\omega)}{I_0(\omega)} = \exp ( -\sigma(\omega)CL ) .$$ (2.27)

The absorbance is defined as:

$$\alpha(\omega) = \sigma(\omega)CL .$$ (2.28)

Equation 2.27 is known as Lambert-Beer’s law and relates a macroscopic, measurable property - the absorption of light with the microscopic properties of the absorbing molecules.

## 2.5 Nonlinear light-matter interaction

### 2.5.1 Pump-probe experiment

Linear absorption spectroscopy as described in section 2.4 provides information about a system in equilibrium, meaning that the interactions between the molecules and light do not lead to a (significant) change in the population distribution. In order to access the vibrational (population) relaxation properties of the system it is necessary to first bring the system to a non-equilibrium state and then probe its recovery (see figure 2.6). We can achieve this by using a high intensity laser beam that perturbs the population distribution. We first induce vibrational population changes (excite some of the molecules to their first
2.5 Spectroscopy

Figure 2.6. Schematic representation of the pump-probe experiment (A). IR pump and probe beams are overlapped in time and space in the sample. Pump beam excites a subset of molecules to their excited state (B). Pump induced absorption changes are monitored with the weaker probe pulse.

excited state) and then we probe the population dynamics with a weak probe beam (which is too weak to significantly change the population distribution by itself). The absorbance of the probe light is given by:

\[ \alpha_0(\omega) = \sigma_{01}(\omega)n \, , \]  

(2.29)

where \( n \) is the amount of absorbers per unit surface \( (n = CL) \). The pump induced absorption changes in the sample comprise of:

- ground state bleach - molecules promoted to the first vibrationally excited state will no longer absorb at the fundamental \( \omega_{01} \) frequency,
- stimulated emission - molecules in the excited state are stimulated back to the ground state emitting photons at the fundamental frequency,
- induced absorption - molecules in the excited state will absorb light at the frequency matching the transition to the second excited state \( \omega_{12} \). We can thus describe the modified absorption as:

\[ \alpha(\omega) = \sigma_{01}(\omega)(n - 2N_1) + \sigma_{12}(\omega)N_1 \, , \]  

(2.30)

where \( N_1 \) denotes concentration of the excited molecules. We can represent the absorption changes as:

\[ \Delta\alpha(\omega) = (-2\sigma_{01}(\omega) + \sigma_{12}(\omega))N_1 \, . \]  

(2.31)

The measured pump induced transient absorption spectrum consists of a negative contribution called the bleach signal and a positive contribution called the induced absorption (figure 2.7 B).

Combining equations 2.18 and 2.22 we see that the cross section for the transition \( 1 \rightarrow 2 \) is two times bigger that for \( 0 \rightarrow 1 \). Since for the harmonic oscillator \( 0 \rightarrow 1 \) and \( 1 \rightarrow 2 \) transitions have the same frequency and the absorption change for the two transition is the same we would not be able to perform any pump-probe experiments. However for the anharmonic oscillator the \( 0 \rightarrow 1 \) and \( 1 \rightarrow 2 \) transition frequencies are different, and thus we observe a bleaching and an induced absorption at different frequencies.
Figure 2.7. Schematic representation of the pump probe signal. Panel A: The dashed line represents the absorption band of the sample. Dotted line indicates the pump beam spectrum. Solid line shows pump-induced changes in the absorption spectrum. Panel B shows differential pump-probe spectrum characterized with the negative contribution at $\omega_{01}$ and positive contribution at $\omega_{12}$.

The pump induced changes in the population distribution are transient. After a certain time the excited molecules will relax back to the ground state. The transient absorption changes in the presence of the relaxation is given by:

$$\Delta \alpha(\omega) = (-2\sigma_{01}(\omega) + \sigma_{12}(\omega))N_1(t=0)\exp(-kt),$$

where $k$ is the relaxation rate. Rather than the relaxation rate we often use a vibrational lifetime (defined as $T_1 = 1/k$) as a measure of how long a molecule stays in the excited state.

**Molecular reorientation**

We have shown in section 2.2 that if the pump beam is polarized linearly the excitation probability is a $\cos^2(\theta)$ distribution (equation 2.13), where $\theta$ is the angle between the pump beam polarization and the vibrational coordinate. After the excitation we thus have an anisotropic distribution of vibrationally excited molecules (see figure 2.8 A). If we use a linearly polarized probe beam we can separately detect the induced absorption changes that are parallel $\Delta \alpha_{\parallel}$ and perpendicular $\Delta \alpha_{\perp}$ to the pump light polarization (figure 2.8 B).

It is immediately obvious that the rate with which the amplitudes of $\Delta \alpha_{\parallel}$ and $\Delta \alpha_{\perp}$ change is related to the orientational motion of the probed molecules. Initially excited molecule will contribute at early delays predominantly to the parallel component of the pump-probe signal $\Delta \alpha_{\parallel}$. In time the molecule will reorient and contribute more and more to the perpendicular signal. The ratio between the two signals changes continuously in time and eventually the two signals will become the same and the excited molecules will acquire an orientationally isotropic distribution. The normalized difference between the two signals, $\Delta \alpha_{\parallel}$ and $\Delta \alpha_{\perp}$ is called the anisotropy parameter $R(t)$:

$$R(t) = \frac{\Delta \alpha_{\parallel} - \Delta \alpha_{\perp}}{\Delta \alpha_{\parallel} + 2\Delta \alpha_{\perp}},$$

where $\Delta \alpha_{\parallel} + 2\Delta \alpha_{\perp}$ represents the isotropic signal. The orientational motion of the oscillator is expressed by the rate at which the relative magnitudes of
the parallel $\Delta \alpha_\parallel$ and perpendicular $\Delta \alpha_\perp$ absorption components change. The temporal window over which we can determine the anisotropy parameter is thus limited by the vibrational lifetime of the oscillator.

Depending on the system and the local environment of the probed oscillator its orientational motion can be a complicated function. In the simplest case the anisotropy decay due to orientational diffusion is described with a monoexponential function:

$$R(t) = \exp (-t/\tau_{or}),$$  \hspace{2cm} (2.34)

where $\tau_{or}$ is the reorientation time.

**Vibrational Resonant Energy Transfer**

The ratio between the measured parallel $\Delta \alpha_\parallel$ and perpendicular $\Delta \alpha_\perp$ absorption changes may change not only due to orientational diffusion of the molecules, but also due to resonant vibrational energy transfer between oscillators oriented in different directions. Vibrational resonant energy transfer (VRET) results from the dipole-dipole interactions between the excited donor molecule and an unexcited acceptor molecule. The formulation of this molecular dipole-dipole coupling was developed by Förster and originally used to describe the transfer of an electronic excitation between fluorescent dye molecules.

In general the rate of energy transfer - $k_F$ (Förster rate) is [48, 112, 132]:

$$k_{F,ab} \propto \frac{|\vec{\mu}_a|^2 |\vec{\mu}_b|^2 k_{ab}^2}{|\vec{R}_{ab}|^6} \int d\nu \sigma_a(\nu) \sigma_b(\nu),$$  \hspace{2cm} (2.35)
where $\vec{\mu}_a$ and $\vec{\mu}_b$ are the vibrational transition dipole moments of the emitting and receiving molecules, $\kappa_{ab}$ is a geometrical factor taking into account the mutual orientation of the coupled oscillators and $R_{ab}$ is the distance between the two molecules. The integral reflects the spectral overlap between the emission and absorption spectra of the donor and acceptor, respectively.

For the energy transfer between the same type of oscillators the emission and absorption spectra are similar. If we further assume that the orientation between the dipoles is independent on the distance $R_{ab}$ between them, for a given donor/acceptor pair, we can express the Förster transfer rate as:

$$k_j = \frac{1}{T_1} \left( \frac{r_0}{r_j} \right)^6,$$

(2.36)

where $T_1$ is the intrinsic lifetime of the excitation in the absence of the energy transfer and $r_0$ is the so-called Förster radius, which defines the distance at which the rates of relaxation and resonant energy transfer are equal (i.e. the distance for which there is a probability of 50% that energy transfer occurs within the lifetime).

The probability that the excited molecules remain excited at time $t = \tau$ is:

$$\rho(\tau) = \sum_{j=1}^{N_{OD}} \exp \left( -k_j \tau \right),$$

(2.37)

where $N_{OD}$ ($N_{OD}=2N_{D_2O}$) is the number of accepting oscillators and $k_j$ is the rate constant for energy transfer. The probability to find an accepting molecule at a distance $r_j$ and $r_j + dr_j$ is equal to the contents of the spherical shell normalized to the total volume of the sample $V$:

$$\eta(r) = \frac{4\pi r_j^2 dr_j}{V}, \quad \text{where} \quad V = \frac{4\pi R^3}{3},$$

(2.38)

and $R$ is the radius of the sphere. Substituting equation 2.36 in equation 2.37...
and integrating over all possible acceptors we arrive at:

\[ \rho(t) = \left\{ \frac{4\pi}{V} \int_0^R e^{r_0^6/T_1 r^6} r^2 dr \right\}^{N_{OD}}. \]  

(2.39)

Performing the integration, we obtain:

\[ \rho(\tau) = \left\{ \exp\left(\frac{-r_0^6}{T_1 r^6}\right) + \sqrt{\frac{\pi r_0^6}{T_1 R}} \text{Erf} \left(\sqrt{\frac{\pi r_0^6}{T_1 R}}\right) \right\}^{N_{OD}}. \]

We can express the concentration of the sample as the number of molecules in the volume \( C_{OD} = \frac{3N_{OD}}{4\pi R^3 N_A} \) (expressed in \([\text{mol/Å}^3]\)), where \( N_A \) is Avogadro’s number. Using this expression we can eliminate \( R \). Performing the power expansion in terms of \( 1/N_{OD} \) we arrive at:

\[ \rho(\tau) = \left\{ 1 - \frac{4 \pi^{3/2} C_{OD} N_A}{3} \sqrt{\frac{r_0^6}{T_1}} \left(\frac{1}{N_{OD}}\right) + \alpha \left(\frac{1}{N_{OD}}\right)^2 \right\}^{N_{OD}}. \]  

(2.40)

The number of accepting molecules is in most cases very large so the term containing \((1/N_{OD})^2\) becomes small and can be neglected. We then obtain:

\[ \rho(t) = \exp\left(-\frac{4 \pi^{3/2} C_{OD} N_A \sqrt{r_0^6}}{3 \sqrt{T_1}}\right). \]  

(2.41)

The above expression describes resonant vibrational energy transfer for molecules in the bulk. If we assume that after transfer the excitation becomes isotropic the anisotropy will be proportional to the excitation survival probability (equation 2.41):

\[ R(t) = \rho(t) \propto \exp\left(-\frac{4 \pi^{3/2} C_{OD} N_A \sqrt{r_0^6}}{3 \sqrt{T_1}}\right). \]  

(2.42)

The two processes - orientational diffusion (equation 2.34) and vibrational energy transfer (equation 2.41) occur at the same time. The anisotropy decay in the presence of both effects is expressed as:

\[ R(t) = \exp\left(-\frac{t}{\tau_{or}} - \frac{4 \pi^{3/2} C_{OD} N_A \sqrt{r_0^6}}{3 \sqrt{T_1}}\right). \]  

(2.43)

### 2.6 Frequency Mixing

A common way of describing nonlinear light-matter interactions is by writing the light induced polarization as a sum of different contributions \( P^{(n)}(t) \):

\[ P(t) = P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + \ldots, \]  

(2.44)
that differ in their order dependence $n$ on the light electric field:

$$P(t) = \epsilon_0 \left( \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \ldots \right),$$

(2.45)

where $\chi^{(n)}$ represents the $n$-th order susceptibility. We assume here that the polarization at time $t$ depends only on the instantaneous value of the electric field strength. This implies that the medium is lossless and dispersionless. This description becomes handy when describing mixing of fields oscillating with different frequencies.

**SECOND-ORDER NONLINEAR PROCESSES**

Let us consider the case where two electromagnetic field overlap in space and time in a material with a non-zero $\chi^{(2)}$. The two electromagnetic fields are characterized with their frequencies $\omega_1$ and $\omega_2$:

$$E(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + \text{c.c.}.$$  

(2.46)

In this case the second-order non-linear polarization ($P^{(2)}$) of the material is given by:

$$P^{(2)} = \chi^{(2)} E^2$$

$$= \chi^{(2)} \left( E_1 e^{-i\omega_1 t} + E_1^* e^{i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_2^* e^{i\omega_2 t} \right)^2$$

$$= \chi^{(2)} \left\{ 2(|E_1|^2 + |E_2|^2) + \right. \right.$$  

$$\left. E_1^2 e^{-i2\omega_1 t} + E_2^2 e^{-i2\omega_2 t} + \text{c.c.} \right. \right.$$  

$$\left. + \left( \text{OR} \right) \right.$$  

$$2E_1 E_2 e^{-i(\omega_1 + \omega_2) t} + \text{c.c.} \right. \right.$$  

$$\left. + \left( \text{SFG} \right) \right.$$  

$$2E_1 E_2^* e^{-i(\omega_1 - \omega_2) t} + \text{c.c.} \right. \right.$$  

$$\left. \right\} (DFG),$$

where the asterisk symbol indicates a complex conjugate.

The interaction of the two electromagnetic waves leads to polarizations at frequencies that are different from the two driving light fields. These polarizations will generate light beams at the corresponding frequencies. We thus distinguish difference frequency generation (DFG) that leads to a new frequency component at $\omega_3 = \omega_1 - \omega_2$, sum frequency generation (SFG) at a frequency that is the sum of the two original frequencies, $\omega_3 = \omega_1 + \omega_2$, and second harmonic generation (SHG), a process that generates fields at frequencies $\omega_3 = 2\omega_1$ and $\omega_3 = 2\omega_2$.

One of the most commonly used frequency conversion processes is difference frequency generation (DFG). It is commonly used in two steps: first - to generate intense near-infrared photons (1.1 - 2.2 $\mu$m) and second - to use the two near infrared photons to generate photons in the mid-infrared range 3 - 8 $\mu$m. This light can be used to study the properties of molecular vibrations.

**PHASE MATCHING**

The second-order nonlinear susceptibility of a material is usually very small. Nevertheless the generated new field may still have a significant intensity if
the two input electric fields are very strong, as often is the case for ultrashort laser pulses. Another frequency conversion efficiency limiting factor is the phase mismatch between the fields generated at different positions in the material. The time and position varying electric field is expressed by:

\[ E(x,t) = \exp(i(kx - \omega t)) , \quad (2.48) \]

where the wave vector \( k \) is defined as \( k(\omega) = \frac{n(\omega)\omega}{c} \), where \( c \) is the speed of light. The polarization induced by two incident fields at position \( x \) and time \( t \) is given by:

\[ P^{(2)}(x,t) = E_1 E_2^* \exp(i((k_1 - k_2)x - \omega_3 t)) . \quad (2.49) \]

In a material with normal dispersion, in which the refractive index increases with frequency, the new \( \omega_3 \) field generated at position \( x \) will travel through the material at a different speed than the two original fields (\( \omega_1 \) and \( \omega_2 \)). After the input fields travelled a distance \( \Delta x \), the newly generated \( \omega_3 \) field (at \( x + \Delta x \)) will have a different phase than the \( \omega_3 \) field generated at position \( x \). After a certain length (the so-called coherence length) this phase mismatch leads to a destructive interference which significantly lowers the intensity of the \( \omega_3 \) light exiting from the nonlinear material.

To take full advantage of a nonlinear frequency conversion process we need to match the \( k_3 \) phase with \( (k_1 - k_2) \).

\[ k_3 = k_1 - k_2 , \quad (2.50) \]

or using the relation \( k(\omega) = \frac{n(\omega)\omega}{c} ; \)

\[ n_3\omega_3 = n_1\omega_1 - n_2\omega_2 . \quad (2.51) \]

A commonly used method to ensure phase matching is by using a birefringent material. A birefringent material possesses two axes that exhibit different refractive indices for light of different (orthogonal) polarizations: \( n_e \) along the optical axis and \( n_o \) in the other two directions. By rotating the crystal over an axis perpendicular to the optical axis we can change the refractive index (between \( n_e \) and \( n_o \)) for the light polarized in the plane perpendicular to the rotation axis. By using different polarizations for the light fields at \( \omega_1 \), \( \omega_2 \) and \( \omega_3 \) we can thus vary their specific refractive indices. This method allows us to significantly extend the coherence length in the material and enhance the frequency conversion.

### 2.6.1 Time-resolved sum-frequency generation

One of the frequency mixing processes described in section 2.5 forms a base for an important spectroscopic technique called surface sum frequency generation (SFG). This technique relies on an important property which is that the second order nonlinear susceptibility is zero in centrosymmetric media. The second order polarization is given by:

\[ P^{(2)} = \chi^{(2)}E^2 . \quad (2.52) \]
In a centrosymmetric medium both the polarization and the electric field have the same magnitude when their direction is inverted. In other words \( E^2 = (-E)^2 \), and \( P^{(2)}(E) = -P^{(2)}(-E) \), which can only be fulfilled if \( \chi^{(2)} = 0 \). This means that molecules with a center of inversion do not have a non-zero second-order nonlinear susceptibility and thus do not generate an SFG signal. Even for media consisting of molecules that are non-centrosymmetric the second-order nonlinear susceptibility is zero if their arrangement is fully isotropic like in liquids or glasses.

The zero second order nonlinear susceptibility of the isotropic, bulk phase can be advantageous, as it makes the SFG process extremely selective and specific for only a few molecular layers at the surface at which the symmetry is broken.

The only conditions for obtaining an SFG signal from the surface is that the two beams can access the surface of the sample and that the generated SFG beam can escape the surface. Once the beams are overlapped in space and time SFG signal is generated. The intensity of the SFG signal is given by:

\[
I_{\text{SFG}}(\omega_3) \propto |\chi^{(2)}|^2 I_1(\omega_1) I_2(\omega_2) .
\]  

To relate the macroscopic quantity which is the nonlinear susceptibility to the molecular scale properties of the system an approximation of weakly interacting absorbers is made:

\[
\chi^{(2)} = N_S \langle \alpha^{(2)} \rangle_{\text{or.}},
\]

where \( N_S \) is the number of molecules per centimeter square (surface density of molecules) and \( \langle \alpha^{(2)} \rangle \) is the averaged (over all possible orientations) second order nonlinear polarizability of the interfacial molecules.

The direction of propagation of the SFG signal (see figure 2.10) is determined by the phase-matching relation:

\[
\omega_1 \sin \theta_1 + \omega_2 \sin \theta_2 = \omega_3 \sin \theta_3.
\]

The intensity of the SFG signal depends on the square of the surface density of the molecules \( N_S \). One of the consequences of this dependence is that the measured SFG signal gives direct information on the propensity of molecules to reside at the interface. The nonlinear susceptibility, \( \chi^{(2)} \) is frequency dependent. \( \chi^{(2)} \) becomes large when one of the frequencies involved is close to a (vibrational) resonance. Hence, by scanning the infrared beam one can obtain a vibrational spectrum of the interfacial molecules, in analogy to obtaining vibrational spectra from a linear absorption experiment. SFG can thus be used to investigate the local structure and other properties that are encoded in the vibrational spectrum of interfacial molecules.

Similarly to infrared pump-probe experiments, SFG spectroscopy can be extended to access the vibrational dynamics of interfacial molecules. Analogously we can perturb the system by exciting a vibrational transition of the molecule and monitor its relaxation with the SFG process. Figure 2.10 B shows the concept of an IR pump - SFG probe experiment. IR-pump SFG-probe spectroscopy allows us to resolve vibrational relaxation rates of interfacial molecules, vibrational couplings between interfacial molecules as well as between the interfacial
2.6 Spectroscopy

Figure 2.10. Schematic representation of the time-resolved SFG experiment. Panel A shows experimental TR-SFG realisation. In panel B we show the TR-SFG concept in terms of the energy level scheme and timing between different pulses.

and bulk phases (as discussed in chapter 10), or the orientational mobility of for instance water molecules at the water-air interface [66].

It should be noted here that in contrast to IR pump-probe spectroscopy described in the previous chapter, the $1\rightarrow2$ induced SFG component is very small in the IR-pump SFG-probe signal. The magnitude of the induced SFG signal is proportional to $\Delta N^2$ (where $N$ is the ground state population), whereas the SFG bleach signal is proportional to $2N\Delta N$. Taking into account that the $1\rightarrow2$ transition cross section is two times the cross section of the $0\rightarrow1$ transition, the ratio between the bleach and the induced absorption signals is thus $N/\Delta N$. With a typical population change $\Delta N$ of a few percent, the induced SFG signal is not observed.

2.6.2 TWO-DIMENSIONAL TR-SFG

To get more insight into molecular interactions at interfaces one can extend the time-resolved SFG experiments to a two-dimensional scheme. 2D spectroscopy generally refers to the fact that the measured signals can be presented in the form of contour plots as a function of two frequencies - a pump frequency and a probe frequency. This technique reveals the couplings between molecules absorbing at different frequencies. In the TR-SFG experiment described in the previous section the pump pulse and the infrared probe pulse of the SFG process have the same spectral width and central frequency. These pulses thus excite and probe the same molecular vibration.

In the 2D case we scan a spectrally narrow pump across the vibrational resonance thus exciting only specific sub-ensembles of molecules, whereas with a broadband infrared probe pulse we probe all molecules. This approach is sometimes called a spectral hole burning experiment. That means that we generate a hole in the spectrum by exciting only a very narrow distribution (with respect to the whole absorption band) of molecules. In time these molecules, due
to intra- and intermolecular interactions, may change their resonant frequency and induce a reduction of the SFG signal in a spectral region different from the excitation spectral window. Using the 2D approach we can follow these spectral fluctuations in time. At time delay \( \tau = 0 \) ps only molecules that are directly excited will give a response and thus the detected signal will lie along the diagonal on the 2D plot as shown in figure 2.11, panel B. On the other hand if the system is fully homogeneous, the same SFG response is measured across the whole resonance (figure 2.11 A) irrespectively of the excitation frequency. In most cases a molecular system exhibits mixed behavior and is neither fully homogeneous nor fully inhomogeneous. For dynamic systems like the water-air interface (studied in chapter 10) the occurrence of spectral diffusion leads to a complete loss of the frequency-frequency correlation between the excitation and detection. The rate of spectral randomization can be quantified by measuring the time-dependent slope of the 2D SFG response.

The two-dimensional approach to vibrational spectroscopy may provide additional molecular scale information about the coupling between molecules or parts of molecules absorbing at different frequencies. If two vibrational modes are coupled, the excitation of one of the modes will cause an appearance of signal at frequencies corresponding to the other mode. Such couplings manifest themselves in a 2D spectrum in the form of cross-peaks (see figure 2.11 B).

Figure 2.11. Representation of the 2D spectra in A - homogeneous limit and B - inhomogeneous limit.