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van der Post, S.T.

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Spectroscopy

2.1 Light-Matter Interaction

Many phenomena in nature can be readily described by oscillations. An oscillation is the natural response of a system that is pushed out of a stable equilibrium by a stimulus. On the molecular scale, the displacement of atoms will lead to molecular vibrations. Although an idealized situation, the harmonic oscillator is the natural starting point for any treatise of oscillatory behavior. We will start with classical systems, since these provide a more intuitive picture that can still be related to molecular vibrations. Since transitions are not explained by classical theory, we eventually provide a (concise) quantum description as well. Along the way, the relation of the theory to physical systems is highlighted.

2.1.1 The Harmonic Oscillator

The classical harmonic oscillator (CHO) is a system in which a mass $m$ experiences a linear restoring force in case it is displaced from its equilibrium position $x_0$ in the vibrational coordinate $x$. The common example is a mass-spring system with spring force constant $k$. In the analog to a molecular vibration, the mass corresponds to the reduced mass of the total system of an atom that is covalently bonded (the spring) to the rest of the molecule. The equation of motion (EOM) of the CHO including damping and driving terms is given by,

$$m\ddot{x} + 2\gamma m\dot{x} + kx = V(t)$$  \hspace{1cm} (2.1)

where $k$ is the linear force constant, $\gamma$ the damping coefficient and $V(t)$ the driving force. In the absence of any damping or a driving force, the fundamental frequency of the oscillator is given by $\omega_0 = \sqrt{k/m}$.

Coupling of the oscillator to its environment leads to damping. Without the driving force, the general solution to the EOM of the damped oscillator is given by,

$$x(t) = A \cos(\Omega t + \phi) e^{-\gamma t}, \hspace{1cm} \Omega = \sqrt{\frac{k}{m} - \gamma^2}$$  \hspace{1cm} (2.2)
Figure 2.1. The power spectrum of the susceptibility and the associated absorption coefficient calculated for a resonance at 2500 cm\(^{-1}\) with the damping factor \(\gamma = 40\) cm\(^{-1}\).

where the integration constants \(A\) (amplitude) and \(\phi\) (phase) follow from the boundary conditions. Damping thus has two consequences: The fundamental frequency of the mode is shifted and the vibration decays with a time constant \(\gamma\). The stronger the coupling of the oscillator to its environment is, the larger the damping constant \(\gamma\) and the faster the decay will be.

In order to be able to study molecular vibrations by vibrational spectroscopy, they need to couple to light, that is, to electromagnetic field oscillations. We therefore consider the driving force to be an oscillating electric field with frequency \(\omega_d\) and amplitude \(E_0\) interacting with charges positioned on the oscillating masses (ie. the atoms in a molecule),

\[
V(t) = qE(t) = qE_0 \cos(\omega_d t) \tag{2.3}
\]

The solutions to the EOM Eq. (2.1) are then given by,

\[
x(t) = \frac{qE_0 |\chi(\omega_d)|}{m} \cos(\omega_d t + \text{arg}(\chi(\omega_d))) \tag{2.4}
\]

where \(\chi(\omega_d)\) denotes the linear susceptibility,

\[
\chi(\omega_d) = \frac{1}{\omega_0^2 - \omega_d^2 + 2i\gamma\omega_d} \tag{2.5}
\]

The susceptibility can be regarded as a measure of how easily the oscillator responds to the driving stimulus. The power spectrum \(|\chi(\omega_d)|^2\) is shown in Fig. 2.1. The largest amplitude is naturally at the resonance frequency \(\omega_0\). The spectrum has a Lorentzian lineshape with far extending shoulders, indicating that a small but nonzero cross section exists to drive the oscillator with a frequency \(\omega_d\) far away from the resonance frequency \(\omega_0\). If the driving
field is exactly resonant with the oscillator, the phase shift of the response is 
\[ \arg(\chi(\omega_0)) = 90^\circ. \]

The susceptibility also constitutes the ability of the medium to polarize in response to the driving electric field. This relation can be written as,

\[ \vec{P} = \varepsilon_0 \chi^{(1)}(\omega) \vec{E} \]  

(2.6)

The superscript (1) in the susceptibility anticipates to the introduction of additional (non-linear) terms to the polarization later in this chapter. Other microscopic effects like the polarizability of electronic wave functions also contribute to the macroscopic polarization. An electromagnetic oscillation as driving force thus induces an oscillating polarization, which re-emits an electromagnetic field.

We showed in Eq. (2.4) that at resonance the polarization field is 90° out of phase with the driving field. The re-emitted field is therefore 180° out of phase with the driving field and both will destructively interfere. This is a way of picturing absorption. The complex index of refraction is related to the susceptibility by,

\[ \hat{n}(\omega) = n(\omega) + i\kappa(\omega) = \sqrt{1 + \chi(\omega)} \]  

(2.7)

The imaginary part of the refractive index \( \kappa(\omega) \) is the extinction coefficient, which is directly related to the absorption coefficient \( \alpha(\omega) \) by,

\[ \alpha(\omega) = \frac{2\kappa(\omega)\omega}{c} \]  

(2.8)

Fig. 2.1 shows the frequency dependence of the absorption coefficient for a resonance at 2500 cm\(^{-1}\). From Eq. (2.4) it is clear that \( \chi(\omega) \) has a lorentzian shape of which the width is determined by the damping factor \( \gamma \). This shape is quite well maintained in the absorption coefficient and explains why the lorentzian lineshape is frequently encountered in nature.

### 2.1.2 Non-Linear Systems

A purely harmonic oscillator is an approximation that is rarely encountered in nature. For most systems, a large displacement from the equilibrium position results in a restoring force that is not linear in the displacement anymore. A commonly used example is that of an atom covalently bound to another atom. In this situation, a large displacement will eventually lead to dissociation of the atoms. The potential of such a system can be modeled by the Morse-potential,

\[ V_m(x) = V_0(e^{-2\beta x} - 2e^{\beta x}) \]  

(2.9)

where \( V_0 \) is the binding energy and \( \beta \) a parameter that defines the width of the potential. The solutions to the equations of motion in the Morse-potential without damping or driving are written for small displacements as [13],

\[ x(t) = \frac{1}{\beta} \ln \left( 1 - C_1 \cos(\omega_0 t) - C_2 \sin(\omega_0 t) \right) \]  

(2.10)
where \( C_1 \) and \( C_2 \) are constants following from the boundary conditions and \( \omega_0 \) is the fundamental frequency in the harmonic limit. This solution to the EOM clearly shows very nontrivial oscillatory behavior. A power expansion of the natural logarithm yields,

\[
x(t) = \frac{C_1}{\beta} \left( \cos(\omega_0 t) + \sin(\omega_0 t) \right) - \frac{C_1^2 - C_2^2}{4\beta} \left( 1 - \cos(2\omega_0 t) \right) + \frac{C_1 C_2}{2\beta} \sin(2\omega_0 t) + O(3) \tag{2.11}
\]

where the quadratic second order terms were rewritten. As can be seen, the oscillations in the Morse-potential contain frequencies of higher order than the fundamental frequency \( \omega_0 \).

In analogy to the Morse potential, in certain dielectric media the induced polarization does not depend linearly on the driving electromagnetic field. As a result, the electromagnetic field that is radiated by the induced polarization will contain higher order frequencies similar to what we saw above. Typically, the polarization is written as a function of the driving field \( \vec{E}(t) \) in Eq. (2.6) can be expanded to encompass these higher orders as,

\[
\vec{P}(\omega) = \varepsilon_0 \left( \chi^{(1)} \vec{E}(\omega) + \chi^{(2)} \vec{E}^2(\omega) + \chi^{(3)} \vec{E}^3(\omega) + \cdots \right) \tag{2.14}
\]

where \( \chi^{(i)} \) is the \( i \)-th order susceptibility. Since the susceptibility may be different for the various polarization directions, the \( \chi^{(i)} \) are tensors. The values of the susceptibilities depend on the properties of the dielectric medium and the higher order susceptibilities are in general very small. Therefore very large electric fields are needed to induce a non-linear polarization. Lasers can provide such large electric fields.

The non-linear terms in Eq. (2.14) give rise to a large variety of responses. Consider the driving field to be a superposition of two electromagnetic waves with different frequencies \( \omega_i \) \( (i = 1, 2) \),

\[
\vec{E}(\vec{x}, t) = \vec{E}_1 e^{i(\vec{k}_1 \cdot \vec{x} - \omega_1 t)} + \vec{E}_2 e^{i(\vec{k}_2 \cdot \vec{x} - \omega_2 t)} + c.c. \tag{2.15}
\]

where \( \vec{k}_i = \vec{n}(\omega_i) \omega_i / c \) is the wave vector in a medium with refractive index \( \vec{n} \) for frequency \( \omega_i \) and the \( c.c. \) denote the complex conjugate terms. It is quite straightforward to calculate the second order \( (\chi^{(2)}) \) non-linear response of the
polarization for a dispersion-free medium,

\[ \vec{E}^2_\text{(x, t)} = |\vec{E}_1|^2 e^{i(2\vec{k}_1 \cdot \vec{x} - 2\omega_1 t)} + \text{c.c.} \quad (SHG) \]  
\[ |\vec{E}_2|^2 e^{i(2\vec{k}_2 \cdot \vec{x} - 2\omega_2 t)} + \text{c.c.} \quad (SHG) \]  
\[ 2\vec{E}_1 \cdot \vec{E}_2 e^{i((\vec{k}_1 + \vec{k}_2) \cdot \vec{x} - (\omega_1 + \omega_2) t)} + \text{c.c.} \quad (SFG) \]  
\[ 2\vec{E}_1 \cdot \vec{E}_2 e^{i((\vec{k}_1 - \vec{k}_2) \cdot \vec{x} - (\omega_1 - \omega_2) t)} + \text{c.c.} \quad (DFG) \]  
\[ 2(|\vec{E}_1|^2 + |\vec{E}_2|^2) \quad (OR) \]

A medium driven by the electromagnetic field described above thus emits light at frequencies that are completely different from the fundamental frequencies of the driving fields. The process leading to the production of light at the doubled frequencies \(2\omega_1\) and \(2\omega_2\) is called second harmonic generation (SHG), at \(\omega_1 + \omega_2\) sum frequency generation (SFG), to light at \(\omega_1 - \omega_2\) difference frequency generation (DFG) and to a static field called the optical rectification (OR). The non-linear susceptibility of a material can thus be used to convert light to different frequencies.

The non-linear response generates an oscillating polarization that emits light at the new frequency at every point in the medium along the propagation direction of the incident light. However, in general the phase-velocity of the re-emitted light will be unequal to that of the incident light. Light that was emitted at one point will then have a different phase than the light emitted further along the propagation direction. Over distances larger than the coherence length the light destructively interferes. Only under a detailed balancing of the refractive indices at different frequencies, the phase velocities of the light components are matched such that constructive interference is achieved. For instance for the process of SFG (\(\omega_3 = \omega_1 + \omega_2\) optimal conversion is achieved if:

\[ \vec{k}_1 + \vec{k}_2 = \vec{k}_3 \rightarrow \vec{n}(\omega_1)\omega_1 + \vec{n}(\omega_2)\omega_2 = \vec{n}(\omega_3)\omega_3 \]  

(2.17)

This requirement is called the phase matching condition. Similar conditions can be written for the SHG and DFG responses. A birefringent medium has different refractive indices in different directions of the crystal structure that can be used for phase-matching. In the simplest case of an uniaxial crystal, the refractive index is identical in two spatial directions and different in a third. This third axis is called the optic axis. \(\beta\)-Barium borate (BBO), frequently used in the experiments describe in this thesis, is uniaxial. Light incident on such a crystal will experience different refractive indices for different polarization directions only if the propagation direction is not coinciding with the optic axis. The effective refractive indices can be tuned by rotating the crystal around an axis different from the optic axis. This method of angle-tuning is used to chose a geometry in which the phase matching condition is met for the desired frequencies and light conversion process.
2.1.3 Quantum Mechanical Systems

Up to now we considered classical systems as these already provide an intuitive picture of the dependence of absorption on driving fields etc. However, oscillations on a molecular level should be treated quantum mechanically. A bound quantum oscillator possesses eigenstates $|\phi_n\rangle$ ($n=1,2,\ldots$) of which the energies $E_n$ are the eigenvalues that follow from the Schrödinger equation,

$$\hat{H}_0 |\phi_n\rangle = E_n |\phi_n\rangle,$$

where $\hat{H}_0$ is the unperturbed hamiltonian of the harmonic oscillator. The first and second term in $\hat{H}_0$ describe the kinetic and potential energy, respectively. $\hat{p}$ and $\hat{x}$ are the momentum and position operators. The eigenvalues that follow from this equation are,

$$E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right)$$

with $\omega_0 = \sqrt{k/m}$ the fundamental frequency of the classical oscillator we derived above.

A perturbation of the system, for example by interaction with an external electromagnetic field, may induce a transition from one energy state to another. Such a process is described by the time-dependent Schrödinger equation,

$$i \hbar \frac{d}{dt} |\phi\rangle = \hat{H} |\phi\rangle \quad (2.20)$$

where $\hat{H} = \hat{H}_0 + \hat{V}_{int}(t)$ is the perturbed hamiltonian. The interaction can be described as,

$$\hat{V}_{int}(t) = \frac{1}{2} \vec{\mu} \cdot \vec{E}_0(e^{i\omega dt} + e^{-i\omega dt}) \quad (2.21)$$

where $\vec{\mu}$ is the dipole moment operator. $\vec{\mu}$ reflects the distribution of charges $q_i$ in a molecule and is a function of the position operators $\vec{x}_i$:

$$\vec{\mu} = \sum_i q_i \vec{x}_i \quad (2.22)$$

$V_{int}(t)$ is defined here in perfect analogy to the driving force that we defined in Eq. (2.3) for the classical oscillator, with the cosine written in its complex notation. From Eq. (2.20) the rate $W_{i\rightarrow j}$ at which a transition occurs from state $|\phi_i\rangle$ to another state $|\phi_j\rangle$ can be derived, This is known known as Fermi’s Golden Rule, which is written to first order in the perturbation as,

$$W_{i\rightarrow j} = \frac{2\pi}{\hbar^2} |\langle \phi_j | \hat{V}_{int}(t) |\phi_i\rangle|^2 \delta(\omega_{ij} \pm \omega_d)$$

$$= \frac{\pi E_0^2}{2\hbar^2} \cos^2(\theta) |\langle \phi_j | \vec{\mu} |\phi_i\rangle|^2 \delta(\omega_{ij} \pm \omega_d) \quad (2.23)$$

given that state $|\phi_i\rangle$ is sufficiently populated. The delta functions assure that only transitions occur at the transition frequency $\omega_{ij} = (E_i - E_j)/\hbar$. The $\pm$ sign
in the delta function indicates that not only transitions from a low energy state to a high energy state can happen. The transition from a high energy state to a low energy state is allowed as well and is referred to as stimulated emission. Both transitions have the same probability. The excitation probability is proportional to $\cos^2(\theta)$, where $\theta$ is the angle between the polarization of the driving field and the dipole moment operator. This property is used in polarization resolved pump-probe experiments, where a linearly polarized light pulse excites a subset of oscillators that have their transition dipole moment preferentially aligned parallel to the polarization direction.

The transition rate in Eq. (2.23) is quadratically proportional to the transition dipole moment $\mu_{i,j}$,

$$\mu_{i,j} = \langle \phi_j | \hat{\mu} | \phi_i \rangle$$  \hspace{1cm} (2.24)

In Eq. (2.22) the dipole moment operator $\hat{\mu}$ was defined in terms of an ordinary Cartesian coordinate system. In considering vibrational transitions, it makes more sense to define $\hat{\mu}$ in terms of the normal coordinates of vibrations $Q_i$. All molecules with $N$ atoms have $3N - 6$ of such normal coordinates ($3N - 5$ in case the molecule is linear). Expanding $\hat{\mu}$ in all $Q_i$ for small displacements from the equilibrium positions $Q_i = 0$ yields,

$$\hat{\mu} = \mu_0 + \sum_i \left( \frac{\partial \hat{\mu}}{\partial Q_i} \right)_0 Q_i + \frac{1}{2} \sum_i \sum_j \left( \frac{\partial^2 \hat{\mu}}{\partial Q_i \partial Q_j} \right)_0 Q_i Q_j + O(3)$$  \hspace{1cm} (2.25)

where $\mu_0$ is the dipole moment of the molecule in equilibrium position. For the water molecule, the normal modes correspond to the bending mode, symmetric OH stretch mode and asymmetric OH stretch mode. The transition dipole moment $\mu_{\nu_0 \nu_0'}$ for transitions in the (symmetric) OH stretch coordinate is thus given by,

$$\mu_{\nu_0 \nu_0'} = \left( \frac{d \hat{\mu}}{d Q_{\text{OH}}} \right)_0 \langle \nu_0' | Q_{\text{OH}} | \nu_0 \rangle + \frac{1}{2} \left( \frac{d^2 \hat{\mu}}{d Q_{\text{OH}}^2} \right)_0 \langle \nu_0' | Q_{\text{OH}}^2 | \nu_0 \rangle + O(3)$$  \hspace{1cm} (2.26)

where the expansion is around the equilibrium position $Q_{\text{OH}} = 0$ and $\nu_{\text{OH}}$ denotes the energy level of the mode. A vibrational transition thus requires a change of the dipole moment in the corresponding vibrational coordinate.

Two approximations are often made. First, the second and higher derivatives in Eq. (2.26) are assumed to be zero (no electrical anharmonicity), and secondly the wave functions $|\nu_{\text{OH}}\rangle$ are those of the harmonic oscillator (no mechanical anharmonicity, i.e. no anharmonic potential). Under this double harmonic approximation, only transitions between adjacent states can occur, since all other matrix elements are zero,

$$\langle \nu_0' | Q_{\text{OH}} | \nu_{\text{OH}} \rangle = \begin{cases} 1 & \text{if } \nu_0' = \nu_{\text{OH}} \pm 1 \\ 0 & \text{if } \nu_0' \neq \nu_{\text{OH}} \pm 1 \end{cases}$$  \hspace{1cm} (2.27)
This means that transitions directly from the ground state $|\nu_{OH} = 0\rangle$ to an overtone state $|\nu_{OH} \geq 2\rangle$ are forbidden. The formation of a hydrogen-bond makes the OH stretch vibration in liquid water quite anharmonic. Lippincott and Schroeder developed a potential based on empirical data that describes the energy levels of the OH stretch vibration and is given by [14],

$$V_{LS}(r, R_{OO}) = D_{Ia} \left(1 - e^{-n_{Ia}(r-r_0)^2/2r}\right) + D_{Ib} \left(1 - e^{-n_{Ib}(R_{OO}-r-r_0)^2/2(R_{OO}-r)}\right)$$

(2.28)

where $r$ is the oxygen-proton distance and $R_{OO}$ is the oxygen-oxygen distance between the hydrogen-bonding water molecules. $D_{Ia} = 38750$ cm$^{-1}$ is the binding energy of the OH covalent bond, $N_{Ia} = 9.8$ Å$^{-1}$ is the parameter defining the OH stretch vibrational frequency and $r_0 = 0.97$ Å is the gas phase OH bond length. $D_{Ib}$ and $n_{Ib}$ are obtained from comparison of the model to empirical values [14]. The potential is shown in Fig. 2.2 for an oxygen-oxygen distance $R_{OO} = 2.81$ Å, which is the average distance in liquid water at room temperature. The wave functions were calculated using a Numerov integration scheme. From these wave functions, it can be shown that transitions with $\Delta \nu_{OH} > 1$ have a non-zero transition dipole moment and hence are allowed.

In addition, the mechanical anharmonicity leads to a difference in the transition frequencies $\omega_{01}$ and $\omega_{12}$. This difference is fundamental to vibrational pump-probe spectroscopy, in which a vibrational mode is excited and the resulting absorption changes (transient absorption) are subsequently probed. The excitation leads to an induced absorption at $\omega_{12}$, reduced absorption due to stimulated emission at $\omega_{01}$ and an equal reduced absorption at $\omega_{01}$ due to the depleted ground state. For the harmonic oscillator, the transition $\nu = 1 \rightarrow 2$ has twice the cross section as the $\nu = 0 \rightarrow 1$ transition. Since in addition all $\omega_{ij}$ are identical for $j = i \pm 1$ in the harmonic potential, the total absorption change is zero. The anharmonic potential leads to different $\omega_{01}$ and $\omega_{12}$ frequencies and therefore a non-zero transient absorption spectrum.

If the electrical harmonic approximation is also abandoned, higher orders in Eq. (2.26) can also contribute to the overtone transition dipole moment $\nu_{OH} = 0 \rightarrow 2$. In case the partial charges on the atoms of the molecule are independent on the distance, $\mu_{\nu_{OH}\nu'_{OH}}$ varies linearly with the extension of the covalent bond for small displacements in the $Q_{OH}$ coordinate. If this is not the case, $d^2\hat{\mu}/dQ_{OH}^2$ is non-zero and the second term in Eq. (2.26) will have a contribution to $\mu_{0,2}$ given that the matrix element $\langle 2 | Q_{OH}^2 | 0 \rangle$ is not vanishing. This last condition is true for both the harmonic and the Lippincott-Schroeder potential.

Finally, in analogy to overtones, combination modes like the $\text{H}_2\text{O}$-bend/OH-stretch mode in water are only allowed if both oscillations are anharmonically coupled. In such a case, the second order cross term between the vibrational coordinates of both modes in Eq. (2.25) is not vanishing,

$$\frac{1}{2} \left(\frac{d^2\hat{\mu}}{dQ_{OH}^2 dQ_{\text{bend}}}\right) \langle \nu'_{OH}, \nu'_{\text{bend}} | Q_{OH} Q_{\text{bend}} | \nu_{OH}, \nu_{\text{bend}} \rangle$$

(2.29)
Figure 2.2. The Lippincott-Schroeder potential for an oxygen-oxygen distance of $R_{OO} = 2.81 \text{Å}$. The wave functions of the first four states were calculated using a Numerov integration scheme. Due to the anharmonicity of the potential, non-zero transition dipole moments exist between the ground state and the $|\nu_{OH} = 2\rangle$ overtone state.

### 2.2 Line Broadening and Spectral Diffusion

In section 2.1.1 we found that the absorption coefficient of a single, damped oscillator has a lorentzian dependence on frequency, the width of the lineshape being determined by the damping parameter $\gamma$. $\gamma$ was found to be related to the vibrational lifetime of the oscillator. The vibrational lifetime of the OD stretch vibration of HDO molecules in water is 1.8 ps, implying a homogeneous linewidth of $\gamma \approx 6 \text{ cm}^{-1}$. Clearly, the linear absorption spectrum of the OD stretch vibration is much broader than that. A number of processes in water lead to additional line-broadening that results in the observed broad absorption spectrum. The line-broadening of a single oscillator is called homogeneous line-broadening. Inhomogeneous line-broadening occurs if the absorption spectrum of a collection of oscillators shows a broadening additional to the homogeneous linewidth.

The parameters of homogeneous broadening are difficult to obtain due to inhomogeneous broadening and spectral diffusion. Coupling of the vibrational modes of a single water molecule to the environment by hydrogen-bonds causes the resonance frequencies to be shifted. A stronger hydrogen-bond for example induces a larger red-shift on the OH stretch transition frequency $\omega_{01}$. Water exists of an inhomogeneous mixture of oscillators that donate hydrogen-bonds of different strengths, resulting in a distribution of lorentzian lineshapes. This is referred to as inhomogeneous line broadening. Finally, the total cross section $\sigma_c(\omega_{01})$ of a single oscillator depends on its hydrogen-bond strength and thus on its resonance frequency $\omega_{01}$. Such a dependence is called a Non-Condon effect [15].

In the following we set up a simple model to demonstrate the static effects
of an excitation of the inhomogeneously broadened OD stretch absorption band
by a narrow-band pump pulse. To this end, we assume that the lineshape of
a single oscillator with resonance frequency $\omega_{01}$ is lorentzian with a FWHM of
$40 \text{ cm}^{-1}$ and denote this by $L(\omega; \omega_{01})$. Let $G_{OD}(\omega)$ be the distribution function
of OD oscillators, normalized such that,

$$\int d\omega G_{OD}(\omega) = 1 \quad (2.30)$$

The absorption spectrum $S_{OD}(\omega)$ is then given by the convolution of the homo-
genous lineshape and the inhomogeneous broadening,

$$S_{OD}(\omega) = \int d\omega_{01} G_{OD}(\omega_{01}) \sigma_c(\omega_{01}) L(\omega; \omega_{01}) \quad (2.31)$$

The number density $n_{OD}(\omega)$ of excited OD oscillators with resonance frequency
$\omega_{01}$ after excitation by a pump with spectral shape $P(\omega)$ is proportional to,

$$n_{OD}(\omega_{01}) = G_{OD}(\omega_{01}) \sigma_c(\omega_{01}) \int \omega P(\omega) L(\omega; \omega_{01}) \quad (2.32)$$

The spectrum of the excited oscillators finally reads,

$$S_e = \int d\omega_{01} n_{OD}(\omega_{01}) \sigma_c(\omega_{01}) L(\omega; \omega_{01}) \quad (2.33)$$

For simplicity we assume that the hydrogen-bond distributions of the OD
stretch and OH stretch oscillators multiplied by the cross sections follow the
linear spectra of isotopically diluted OD in H$_2$O. Fig. 2.3 shows the evaluation of $n_{OD}(\omega)$ and $n_{OH}(\omega)$ under these conditions. Although the excitation spectrum was positioned far off resonance of the OH-stretch band, still one third of the excited oscillators are OH oscillators. This effect can be assigned to the far extending lorentzian shoulders of the homogeneous lineshapes. For similar reasons, the frequency maximum of the OD stretch oscillators is red-shifted compared to the excitation band. These results depend on the choice of the homogeneous linewidth: broader lines enhances these effects. If the linewidth is broader for red-absorbing (strongly hydrogen-bonded) oscillators, the relative number of excited OH oscillators will be still larger.

As a result of dynamic processes, the number density $n_{OD}(\omega)$ of excited oscillators will eventually be redistributed according to the static distribution function $G_{OD}(\omega)$. The time-evolution to this randomized state is called spectral diffusion and three molecular processes can be identified that contribute to this. First, librational motions can result in a very fast change of hydrogen-bond strength and thus $\omega_{01}$ on a timescale of 100 fs. Secondly, translational motions lead to a structural reorganization that has the same effect on a timescale of 1 ps. Finally, excitation energy may transfer in a resonant way from an excited oscillators to an accepting mode nearby in a process called Förster transfer. Since the accepting mode can have a slightly different resonance frequency, this process also leads to spectral diffusion. The timescale of this process in pure liquid water is 50 fs but becomes slower for isotopically diluted systems, since this process is strongly dependent on the distance between the donating and (resonant) accepting mode.