UvA-DARE (Digital Academic Repository)

Dynamics of water interacting with biomolecules

Groot, C.C.M.

Link to publication

Citation for published version (APA):
Groot, C. C. M. (2017). *Dynamics of water interacting with biomolecules*. [Thesis, externally prepared, Universiteit van Amsterdam].

2 VIBRATIONAL SPECTROSCOPY

2.1 VIBRATIONS AND THE HARMONIC OSCILLATOR

The simplest vibration is the harmonic oscillator. Imagine a mass suspended by a spring (fig. 2.1A). If it is displaced slightly from its equilibrium position along the spring direction, it experiences a restoring force $F = -kx$. Newton's balance of forces states

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

which has the solution

$$x(t) = x_1 \cos(\sqrt{k/m}t) \qquad (2.2)$$

This means that the mass oscillates harmonically around its equilibrium position with a frequency $\omega_0 = \sqrt{k/m}$.

A polyatomic molecule can be represented by a series of masses connected by springs (fig. 2.1B), where the masses are the nuclei and the springs the forces between them (these internuclear forces depend on the electronic structure of the molecule). Since in this case the movement of a single mass will cause motion of the others, Newton's balance of forces in terms of mass displacement is more complex. Despite this complexity, the vibrations of a polyatomic molecule can be described as a sum of independent harmonic oscillators, provided all restoring forces are harmonic[52,53]. These harmonic oscillations are called normal modes. A normal mode involves the synchronous movement of several nuclei; the vibrations are delocalized. In this case, the mass is replaced by the effective mass, which is usually a complicated function of the individual nuclear masses. The number of normal modes of a molecule is always equal to the number of vibrational degrees of freedom, which is 3N-6 for a nonlinear molecule with N nuclei and 3N-5 for linear molecules.
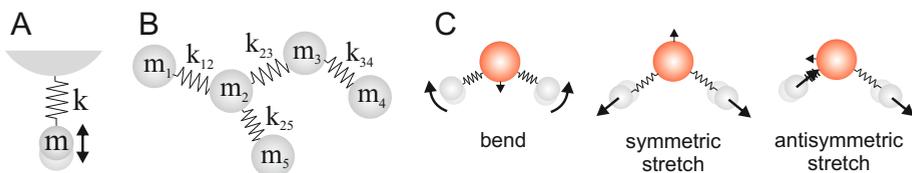

FIGURE 2.1. (A) Example of a harmonic oscillator: a mass suspended by a spring. (B) Representation of a polyatomic molecule as a series of masses - the nuclei - connected by springs. The spring constants depend on the electronic structure of the molecule. (C) The normal modes of a water molecule.

The normal modes of a water molecule are shown in fig. 2.1C; these are the bend, the symmetric stretch and the antisymmetric stretch vibration. The normal modes of water are not pure normal modes in the sense that the oscillations are independent. Instead the different vibrations are coupled. This originates from the restoring forces for nuclear displacement, which are not linear in x; the vibrations are anharmonic. This is, in fact, the case for all molecules, but as for water, a set of *coupled* harmonic oscillations can often still accurately describe the vibrational motion of the molecule.

2.2   THE QUANTUM HARMONIC OSCILLATOR

To describe oscillations on the molecular level, it is necessary to treat the molecule quantum mechanically. Since we saw in the previous section that vibrations can be described by a set of coupled harmonic oscillations, we again consider the simple case of a harmonic oscillator. The Hamiltonian of a quantum harmonic oscillator is given by

$$\hat{H}_0 = \frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}k\hat{x}^2 \qquad (2.3)$$

where the first term is the kinetic energy and the second term the potential energy corresponding to a linear force $\vec{F} = -k\hat{\vec{x}}$. The energy levels of the oscillator can be found by solving the time-independent Schrödinger equation

$$\hat{H}_0\psi = E\psi \qquad (2.4)$$

and are

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega_0 \qquad\qquad v = 0, 1, 2... \qquad (2.5)$$

with v the vibrational quantum number and $\omega_0 = \sqrt{k/m}$ the vibrational frequency. The energy is quantized, and we can speak of zeroth, first, second and higher vibrational states, which are evenly spaced by an energy separation of $\hbar\omega_0$ (fig. 2.2A). A transition from one vibrational state to another can be induced by interacting with light, which can be described by solving the time-dependent Schrödinger equation

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad (2.6)$$

in the presence of light. We can consider the light as a time-dependent perturbation of the original Hamiltonian $\hat{H}_0$, so that the Hamiltonian is defined as

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t) \qquad (2.7)$$

Since light is an electromagnetic wave, it interacts with the charges of the system, and $\hat{V}(t)$ is a function of the electric field of the light, $\vec{E}(t)$, and the electric
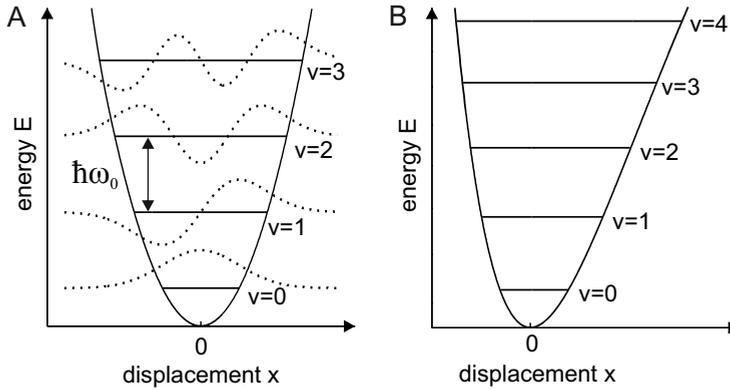
FIGURE 2.2. (A) The energy levels of a harmonic oscillator, which are evenly spaced with a separation of $\hbar\omega_0$, and the corresponding eigenstates ψ. (B) The energy levels of a Morse oscillator, which decrease in separation with increasing quantum number.

dipole moment of the system $\vec{\mu}$. (For the moment we ignore higher order electric moments, and magnetic interactions as well, because these are much weaker than the interaction with the electric dipole moment.) The electric dipole moment depends on the positions $\vec{\hat{x}}$ of all charges q in the system:

$$\vec{\hat{\mu}} = \sum_n q_n \vec{\hat{x}}_n \tag{2.8}$$

We can consider the light as a simple oscillating electric field if we assume that the wavelength of the light is much larger than the size of the system, such that we can ignore the spatial variation of the field. This is quite reasonable for infrared light ($\lambda \sim 10^{-6}$m) interacting with molecular vibrations (bond lengths $\sim 10^{-10}$m). Then the perturbation is defined as

$$\hat{V}(t) = -\vec{\hat{\mu}} \cdot \vec{E}(t) = -\vec{\hat{\mu}} \cdot \vec{E}_0 \cos(\omega t) \tag{2.9}$$

The time-dependent Schrödinger equation (eq. 2.6) can be solved by separation of variables:

$$\Psi(\hat{x}, t) = \psi(\hat{x})e^{-iEt/\hbar} \tag{2.10}$$

where ψ is the solution to the time-*in*dependent Schrödinger equation (eq. 2.4). The general solution to the time-dependent Schrödinger equation is thus given by

$$\Psi(\hat{x}, t) = \sum_n c_v(t)\psi_v(\hat{x})e^{-iE_v t/\hbar} \tag{2.11}$$

which means that the system can be described at all times as a superposition of the different vibrational states ψ_v with a phase term and a time-dependent amplitude $c_v(t)$. We can calculate the time-dependent amplitudes by solving the Schrödinger equation with the perturbed Hamiltonian. From the calculation

it follows that the transition rate from a negligibly perturbed state ψ_a to state ψ_b is given to first order approximation by [54]

$$R_{a\to b} \cong \frac{d}{dt}|c_b|^2 = \frac{\pi}{2\hbar^2}|\langle\psi_b|\,\vec{\hat{\mu}}\cdot\vec{E}_0\,|\psi_a\rangle\,|^2 \int \delta(\omega \pm \omega_{ab})d\omega \qquad (2.12)$$

This equation is known as Fermi's golden rule. We can rewrite it as

$$R_{a\to b} \cong \frac{\pi E_0^2}{2\hbar^2}\cos^2\theta|\mu_{ab}|^2 \int \delta(\omega \pm \omega_{ab})d\omega \qquad (2.13)$$

where θ is the angle between the polarization direction of the light $\vec{E}_0$ and the electric dipole moment $\vec{\hat{\mu}}$, and $\mu_{ab} = \langle\psi_b|\,\hat{\mu}\,|\psi_a\rangle$ is the so-called transition dipole moment. Since we are interested in vibrations around an equilibrium position $\hat{x}_0$, we write the electric dipole moment as a Taylor expansion around $\hat{x}_0$:

$$\hat{\mu} = \hat{\mu}_0 + \frac{d\hat{\mu}}{dx}(\hat{x} - \hat{x}_0) + ... + \frac{1}{n!}\frac{d^n\hat{\mu}}{dx^n}(\hat{x} - \hat{x}_0)^n \qquad (2.14)$$

Combining this expression up to first order with Fermi's golden rule finally gives

$$R_{a\to b} \cong \frac{\pi E_0^2}{2\hbar^2}\cos^2\theta\left(\frac{d\mu}{dx}\right)^2 |\langle\psi_b|\,\hat{x}\,|\psi_a\rangle\,|^2 \int \delta(\omega \pm \omega_{ab})d\omega \qquad (2.15)$$

This equation has a few important implications:

- $R_{a\to b} \propto \int \delta(\omega \pm \omega_{ab})d\omega$: The frequency of the light, ω, has to match the frequency of the transition, $\omega_{ab} = (E_b - E_a)/\hbar$, for the transition to take place (this is basically energy conservation). For vibrational transitions, the required light is in the infrared range.

- $R_{a\to b} \propto |\frac{d\mu}{dx}|^2$: Light can only interact with vibrations that cause a change in dipole moment; these vibrations are said to be infrared active. Homonuclear diatomic molecules, for instance, are not infrared active, because a change in relative position of the nuclei does not change the net dipole moment.

- $R_{a\to b} \propto \cos^2\theta$: Light interacts most strongly with the system when it is polarized along the direction of the dipole moment. This forms the basis of polarization-resolved pump-probe spectroscopy (see section 2.6).

- $R_{a\to b} \propto |\langle\psi_b|\,\hat{x}\,|\psi_a\rangle|^2$: For a harmonic oscillator, it can be shown that $\langle\psi_b|\,\hat{x}\,|\psi_a\rangle$ is always zero unless $b = a \pm 1$, which means that transitions are only allowed between consecutive states [54]. For anharmonic oscillators this rule is lifted, though generally the transition rate is much lower for transitions involving two or more quanta.

- $R_{a\to b} = R_{b\to a}$: A transition from state ψ_a to ψ_b is just as likely as the reverse process. An upward transition corresponds to absorption: the matter absorbs energy $\hbar\omega_{ab}$ from the light. A downward transition corresponds to stimulated emission: the light gains energy $\hbar\omega_{ab}$.[a] (See fig. 2.3.)

---

[a]In addition to these light-driven processes the system can "spontaneously" decay to a
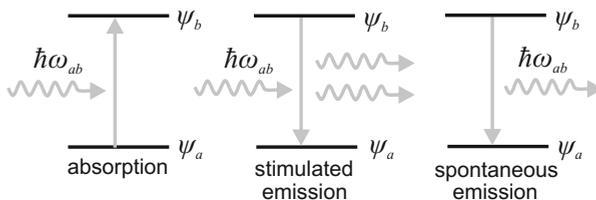
FIGURE 2.3. Illustration of absorption, stimulated emission and spontaneous emission for a two-level system. Photons are indicated as wiggly arrows and have energy $\hbar\omega_{ab}$, corresponding to the energy difference between the two states. The rate of absorption equals the rate of stimulated emission, while the rate of spontaneous emission is directly related to these by a factor of $\frac{\hbar\omega_{ab}^3}{\pi^2 c^3}$ as a consequence of energy conservation[55].

ANHARMONICITY   Most molecular vibrations have some degree of anharmonicity. At high vibrational excitations, the harmonic approximation always breaks down because the molecular bond can dissociate. In this case the restoring force is no longer linear with the displacement $\hat{x}$, and the potential energy is no longer quadratic (recall that $V_0 = \frac{1}{2}k\hat{x}^2$ for the harmonic oscillator), but converges to a constant value for large distances $\hat{x}$. A potential accounting for this behavior is the Morse potential[55]

$$V_0 = D(1 - e^{-a\hat{x}})^2 \tag{2.16}$$

where D and a are the depth and curvature of the potential, respectively. The energy levels of the Morse oscillator can be found by solving the time-dependent Schrödinger equation, and are given by

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega_0 - \left(v + \frac{1}{2}\right)^2 \frac{\hbar^2\omega_0^2}{4D} \tag{2.17}$$

with $\omega_0 = a\sqrt{2D/m}$. The energy levels are spaced closer together with increasing vibrational quantum number v (see fig. 2.2B). This is generally the case for anharmonic vibrations. Aside from the Morse potential, many other potentials have been put forward to describe the energy landscape of molecular vibrations. Lippincott and Schroeder, for instance, developed an emperical potential for water and other hydrogen-bonding materials that explicitly takes into account the anharmonicity arising from hydrogen-bond formation[56].

Besides these modifications of the potential, which are referred to as mechanical anharmonicity, vibrational transitions can be modified by a nonlinear dependence of the electric dipole moment on the position $\hat{x}$: this is referred to as electrical anharmonicity. In this case quadratic and higher order terms in eq. 2.14 significantly contribute to the transition rate, enabling $\Delta v > 1$ transitions.

---

lower energy state by spontaneous emission. This process happens even in the absence of external light, because the electromagnetic field is never truly zero due to the zero-point energy of vacuum.
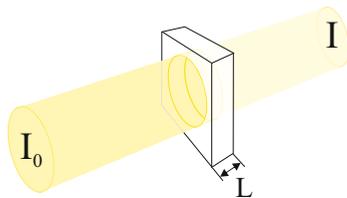
FIGURE 2.4. In linear spectroscopy, one measures the attenuation of a beam of light as it travels through a piece of material.

2.3   LINEAR SPECTROSCOPY

In linear spectroscopy, one generally measures the attenuation of a beam of light as it travels through a piece of material (fig. 2.4). Here the light has a moderate intensity, such that it excites only a very small fraction of the molecules. In this case the macroscopic response of the material is linear with the electric field of the light. This section describes how the linear spectrum is determined by the microscopic light-matter interaction described earlier.

2.3.1   ABSORPTION CROSS SECTION

At room temperature and moderate light intensities, most molecules are in the ground vibrational state, so we only observe the process of absorption. Suppose we start out with a beam of light with intensity

$$I_0 = \frac{c\epsilon_0}{2} E_0^2 \tag{2.18}$$

which is the intensity (radiated power per unit area) for a beam with an electric field of $\vec{E}_0 \cos(\omega t)$, with c the speed of light, and ϵ_0 the permittivity of vacuum. Assuming ω matches the frequency of the first vibrational transition ω_{01}, a single molecule absorbs photons with energy $\hbar\omega_{01}$ from the beam at a rate of

$$R_{0\rightarrow1} \cong \frac{\pi I}{3c\epsilon_0\hbar^2}|\mu_{01}|^2 \tag{2.19}$$

This equation follows from eq. 2.13, under the assumption that the medium is isotropic, such that $\cos^2\theta = \frac{1}{3}$. Now suppose we have a material with C molecules per volume, then the intensity reduction after traveling through a tiny slab dL of this material is

$$dI = -\hbar\omega_{01}\frac{\pi I}{3c\epsilon_0\hbar^2}|\mu_{01}|^2 \cdot C \cdot dL \tag{2.20}$$

$$= -\sigma_{01} \cdot I \cdot C \cdot dL \qquad\qquad \sigma_{01} = \frac{\pi\omega_{01}}{3c\epsilon_0\hbar}|\mu_{01}|^2 \tag{2.21}$$

The quantity σ_{01} is called the absorption cross section; it can be interpreted as the optical area of the molecule (note that this is not the same as the actual
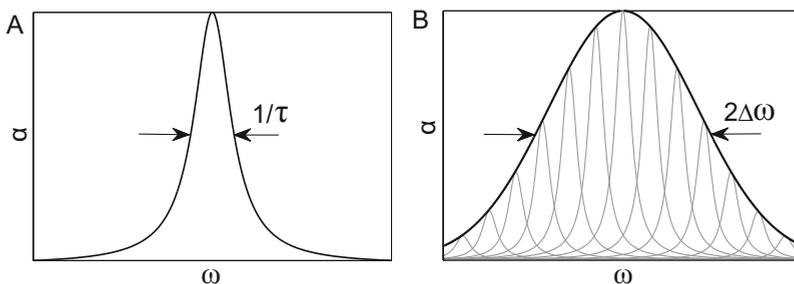
FIGURE 2.5. (A) Lorentzian or homogeneous lineshape, (B) Gaussian or inhomogeneous lineshape with underlying homogeneous lines.

area). Solving the differential equation 2.21 leads to the following expression

$$\frac{I}{I_0} = e^{-\sigma_{01} \cdot C \cdot L} \tag{2.22}$$

This equation is known as the Lambert-Beer law. It relates the macroscopic transmission I/I_0, which can be measured experimentally, to the molecular property σ_{01}. In linear spectroscopy, one usually quantifies the macroscopic absorbance, defined as

$$\alpha = \ln\left(\frac{I}{I_0}\right) = \sigma_{01} \cdot C \cdot L \tag{2.23}$$

This is a convenient measure because it is linear with all the relevant parameters.

2.3.2 ABSORPTION LINESHAPE

So far we described vibrational transitions with a single frequency, which implies that the absorption spectrum of a single resonance is infinitely narrow. However, this is not the case in reality. The absorption lineshape cannot be infinitely narrow due to the energy-time uncertainty principle:

$$\Delta E \Delta t \gtrsim \hbar \tag{2.24}$$

which means that the energy of a state cannot be determined exactly when the state exists for a finite time. The lifetime of a state is limited by the rate of spontaneous emission. It can be deduced by Fourier transformation[57] that the spectral lineshape of a state with lifetime τ has the following form:

$$\alpha(\omega) \propto \frac{\Delta \omega}{2\pi} \frac{1}{(\omega - \omega_{01})^2 + (\Delta \omega/2)^2} \tag{2.25}$$

with $\Delta \omega = 1/\tau$. This spectral lineshape is called a Lorentzian lineshape and is shown in fig. 2.5A.

Many vibrational lines are actually much broader than the Lorentzian linewidth dictated by the vibrational lifetime. The OD stretch vibration in isotopically diluted water, for example, has a lifetime of 1.7 picoseconds, which corresponds to a linewidth of $\sim$3 cm^{-1}, but the actual spectrum is more than fifty times broader. Line-broadening processes that affect all molecules equally are called homogeneous. In the case of water, the broadening is mostly due to the pushing and pulling of the water molecules at each other: local differences in hydrogen bond strength lead to different potential energy surfaces for each OD stretch vibration, and hence to different vibrational frequencies. Broadening of this type, which originates from differences in local environment, is called inhomogeneous. In most cases the center frequency of the individual Lorentzian lineshapes is statistically distributed and the overall lineshape is Gaussian (fig. 2.5B).

Due to the dynamical nature of the hydrogen-bond network of water, the vibrational frequency of a water molecule is modulated continuously, and the spectral lineshape reflects the time-averaged frequency distribution. In general, if the frequency modulations are very small or very fast ($\Delta\omega \cdot \tau_c \ll 1$, see section 2.5.1), the average observed linewidth becomes narrower than the actual frequency distribution. This phenomenon is called motional narrowing, and is responsible for a slight narrowing of the lineshape of the water stretch vibration[58]. Additional mechanisms contribute to the lineshape of the water stretch vibration as well, such as the fact that the transition dipole moment increases strongly with increasing hydrogen-bond strength (non-Condon effect)[59]. Since the frequency of the water stretch vibration depends on the hydrogen-bond strength, with strongly hydrogen-bonded water molecules absorbing at lower frequencies, this effect leads to a relative enhancement of the absorption at lower stretch frequencies.

2.4   Pump-probe spectroscopy

In vibrational pump-probe spectroscopy, vibrations are excited with an intense light pulse, the pump. These vibrations are monitored by measuring the absorption of a second, weaker probe pulse (fig. 2.6). In contrast to linear spectroscopy, which gives a time-averaged picture, pump-probe spectroscopy is sensitive to vibrational dynamics: the pump pulse perturbs the system from equilibrium,
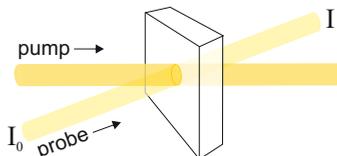

Figure 2.6. In pump-probe spectroscopy, an intense pump pulse excites vibrations in the sample, which are subsequently monitored by measuring the absorption of a second weaker probe pulse.
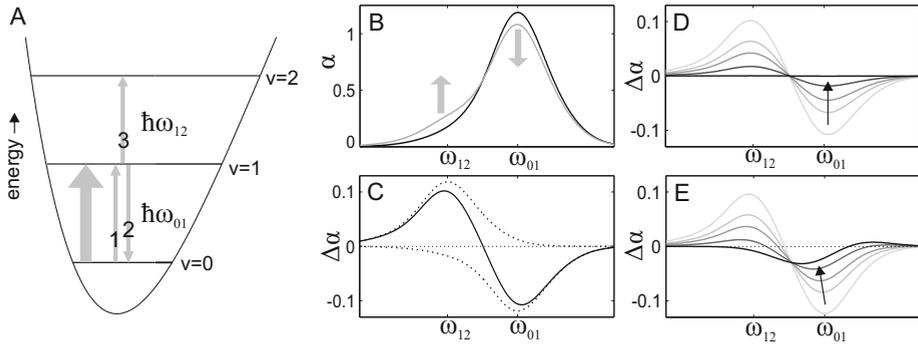
FIGURE 2.7. Illustration of pump-probe spectroscopy, with spectra that are chosen to resemble those of the OD stretch vibration of HDO molecules. (A) Energy level description: the pump (big arrow) excites vibrations from the ground state to the first excited state, which are then monitored by the probe (small arrows). (B) Probe absorption spectrum: excitation by the pump lowers the absorption around ω_{01} and increases the absorption around ω_{12}. (C) Probe differential absorption spectrum, with the positive σ_{12} and negative σ_{01} contributions shown in dotted lines. (D) Probe differential absorption spectrum at different pump-probe delay times. (E) Probe differential absorption spectrum at different pump-probe delay times, with a contribution from sample heating.

and the relaxation of the excited vibrations back to the ground state is measured with the probe pulse. As we will see later on, pump-probe spectroscopy can supply information on molecular fluctuations, coupling and reorientation dynamics.

Pump-probe spectroscopy is a form of nonlinear spectroscopy. This means that the system is perturbed from equilibrium, and as a consequence its response is no longer linear with the total electric field (pump+probe) of the light. A full description of the pump-probe signal therefore requires nonlinear response theory[60,61]. Here we limit ourselves to a mathematically simpler description that nonetheless captures the main observed features and refer the interested reader to the books by Hamm and Zanni[60] and Mukamel[61].

The absorbance of a piece of material is given by

$$\alpha_0(\omega) = \sigma_{01}(\omega)N_0 \tag{2.26}$$

where N_0 is the amount of molecules per area ($N_0 = CL$, see eq. 2.23). In case an intense pump pulse excites vibrations from the ground state to the first vibrational state, the absorbance changes due to three processes (fig. 2.7):

1. Ground state depletion: since there are less molecules in the ground state, less light is absorbed at the fundamental frequency ω_{01}.
2. Stimulated emission from the first excited state: light is emitted at the fundamental frequency ω_{01}.
3. Excited state absorption: molecules in the first excited state can be further excited to the second vibrational state, absorbing light at frequency ω_{12}.

The resulting absorbance is given by

$$\alpha(\omega, t) = \sigma_{01}(\omega)\Big(N_0 - 2N_1(t)\Big) + \sigma_{12}(\omega)N_1(t) \tag{2.27}$$

where $N_1(t)$ is the amount of excited molecules per area. The processes of ground state absorption and stimulated emission lower the absorbance equally, since the rates of absorption and stimulated emission are the same (eq. 2.15), hence the factor 2 in the above equation. By comparing the probe spectrum with and without pump excitation, we can calculate the differential absorbance

$$\Delta\alpha(\omega, t) = \alpha(\omega, t) - \alpha_0(\omega, t) \tag{2.28}$$
$$= -2\sigma_{01}(\omega)N_1(t) + \sigma_{12}(\omega)N_1(t) \tag{2.29}$$
$$= \big(-2\sigma_{01}(\omega) + \sigma_{12}(\omega)\big)N_1(t) \tag{2.30}$$

For a harmonic oscillator, the frequencies of the first and second vibrational transition overlap, and $\sigma_{12} = 2\sigma_{01}$. As a consequence, the pump-probe signal of a harmonic oscillator is zero. Luckily for spectroscopists, molecular vibrations are anharmonic. Usually, ω_{12} is lower than ω_{01}, and the differential absorbance is thus nonzero (fig. 2.7C).

Note that the differential absorbance is a function of the time delay between pump and probe pulses, since the excited vibrations relax back to the ground state (fig. 2.7 D). For this reason the differential absorbance is often referred to as the transient absorption spectrum. In the simplest case, the vibrational relaxation can be described by

$$N_1(t) = N_1(0)e^{-t/T_1} \tag{2.31}$$

where T_1 is the lifetime of the vibration. In general, a vibration relaxes by transferring energy to its environment, exciting lower-energy vibrations of the same molecule or surrounding molecules in the process[62]. The lifetime of a vibration therefore strongly depends on the coupling to its immediate surroundings. The lifetime can provide structural information: In chapter 5, for example, we will show that the vibrational response of OD stretch vibrations of water can be distinguished from the OD stretch vibrations of sugars using their difference in spectrum and vibrational lifetime. Ultimately, the energy of excited vibrations is transferred into heat. This can create an additional contribution to the transient spectrum, because the cross section of a vibration usually depends on temperature. The contribution due to sample heating has the shape of a thermal difference spectrum (fig. 2.7E), i.e. the difference between the absorption spectrum at room temperature and the absorption spectrum at an elevated temperature.

2.5 Frequency-resolved pump-probe spectroscopy: 2DIR

In vibrational pump-probe spectroscopy, it is often useful to pump and probe at different frequencies, such that the vibrational response of a system can be
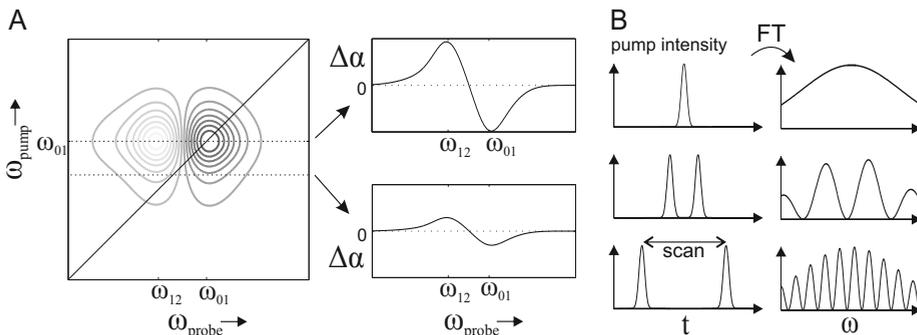
FIGURE 2.8. Two-dimensional infrared spectroscopy (2DIR). (A) Illustration of a 2DIR spectrum. Each horizontal slice of the 2D spectrum corresponds to the spectral response after excitation at a specific frequency ω_{pump}. (B) The 2D spectrum can be recorded by exciting with two broadband pump pulses with variable time delay between them. Scanning this time delay corresponds to a sinusoidal modulation of the pump pulse in the frequency domain. The 2D spectrum then can be obtained by Fourier transformation of the transient probe spectrum (recorded as usual) with respect to the scanned pump time delay.

probed after a subset of vibrations is excited. By scanning the frequency of a spectrally narrow pump pulse and recording transient spectra with a broadband probe pulse, we can construct a transient two-dimensional infrared (2DIR) spectrum, where each horizontal slice of the spectrum corresponds to the spectral response following excitation at a specific frequency (fig. 2.8A).

The 2DIR spectrum is often obtained by exciting the sample with two broadband pump pulses instead of a narrowband pump pulse. In this case different subsets of vibrations can be excited by varying the time delay between the two pump pulses, which creates a sinusoidally modulated pump spectrum with varying period (fig. 2.8B). The 2D spectrum can then be calculated by Fourier transformation: the transient probe spectrum determines the probe axis, and its modulation by the pump pulse pair after Fourier transformation yields the pump axis.

2.5.1   2D LINESHAPE

We already noted that the frequency of a vibrational mode is continuously modulated due to the mutual pushing and pulling of molecules (section 2.3.2). While the linear lineshape reflects the time-averaged frequency distribution, the 2DIR lineshape is sensitive to the frequency fluctuations. An inhomogeneous vibrational mode gives rise to a 2DIR spectrum that is elongated along the diagonal, as the excitation frequency corresponds to a particular subset of the vibrations that will show their maximum response at the same frequency. At later delays, however, the character and thus the resonance frequency of the excited subset changes (due to the molecular dynamics). The average resonance
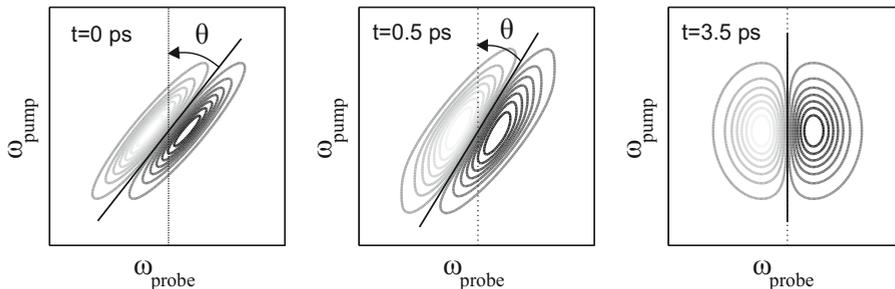
FIGURE 2.9. Illustration of a 2DIR spectrum of an inhomogeneous vibrational mode at different pump-probe delay times. The 2DIR spectrum is initially elongated along the diagonal, but acquires a more spherical shape with increasing delay time. The decay of the nodal line slope, $\sin\theta$, is a measure for the frequency-frequency correlation function.

frequency of each subset of excited vibrations tends more towards the overall average and the spectrum will acquire a more spherical shape. This phenomenon is spectral diffusion resulting from structural dynamics, and is illustrated in figure 2.9.

For a vibrational mode with overlapping peaks due to the $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions, inhomogeneity results in a tilt of the nodal line between the two responses. The nodal line slope as a function of time is a measure for the spectral diffusion as expressed in the frequency-frequency correlation function (FFCF)[63]:

$$C_1(t) = \langle \delta\omega_{01}(\tau)\delta\omega_{01}(0) \rangle \qquad (2.32)$$

where $\delta\omega_{01}$ is the instantaneous fluctuation away from the mean vibrational frequency ω_{01}, and $\langle ... \rangle$ denotes the ensemble average. The decay of the FFCF can often be described emperically by

$$C_1(t) = \Delta\omega^2 e^{-\tau/\tau_c} \qquad (2.33)$$

where $\Delta\omega$ is the fluctuation amplitude and τ_c the characteristic timescale of the frequency fluctuations. The latter is a direct measure of how fast surrounding molecules move around the excited vibrational mode. Aside from the nodal line slope method, several other methods exist to obtain the frequency-frequency correlation function from the 2DIR spectrum[63–65].

2.5.2   Cross peaks

Perhaps the most prominent feature of a 2DIR spectrum is the presence of cross peaks. Cross peaks appear off the diagonal (fig. 2.10A) and indicate that exciting a certain vibrational mode affects the vibration of another mode. Hence, cross peaks supply information on molecular coupling. The coupling in turn provides information on molecular structure, since the interaction between vibrations depends on their relative orientation and distance. We can distinguish between two types of vibrational coupling:
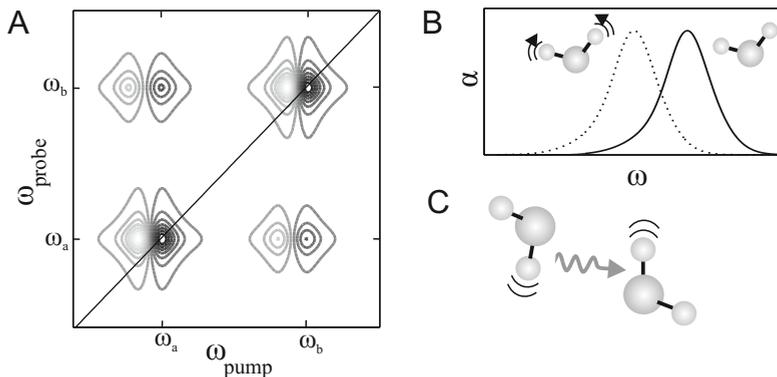
FIGURE 2.10. (A) Illustration of a 2DIR spectrum of two coupled vibrational modes with different center frequencies ω_a and ω_b. Cross peaks appear off the diagonal. (B) Illustration of anharmonic coupling for water: the spectrum of the OH stretch vibration is redshifted if the bending vibration is excited. (C) Illustration of energy transfer: the vibrational excitation transfers from one vibration to the other via the coupling of their transition dipole moments.

- Anharmonic coupling:
  Excitation of one vibrational mode alters the potential, and therefore the vibrational energy levels, of another vibrational mode (fig. 2.10B). This is the case when the two vibrations are part of the same molecule and affect each other through chemical bonds, i.e. mechanically, or when the two vibrations are coupled electrically by the interaction between their transition dipole moments. The effect of anharmonic coupling is present immediately after excitation of the vibration.

- Coupling by energy transfer:
  Coupling between the transition dipole moments of vibrational modes can also lead to transfer of the vibrational excitation of one vibrational mode to another (fig. 2.10C). Energy transfer shows up in the 2DIR spectrum as a rising cross peak, where the rise is defined by the rate of transfer. This process is usually referred to as vibrational resonant energy transfer, or Förster transfer, after Theodor Förster. The rate of Förster energy transfer is given by[66,67]

$$K_F \propto \frac{|\vec{\mu}_a|^2 |\vec{\mu}_b|^2 \kappa_{ab}^2}{|\vec{R}_{ab}|^6} \int \sigma_a(\omega)\sigma_b(\omega)d\omega \qquad (2.34)$$

where $\vec{\mu}_a$ and $\vec{\mu}_b$ are the transition dipole moments of the coupled vibrations, R_{ab} is their mutual distance, κ_{ab} is a geometrical factor, and σ is the absorption cross section. The rate of Förster transfer depends on the distance between the two coupled vibrations, the magnitude of their transition dipole moments, and their spectral overlap.

Aside from vibrational coupling, cross peaks can arise from structural dynamics, which is usually slower. This is for example the case when molecules can exist in two different hydrogen-bonded configurations that give rise to different vibrational frequencies. During the time between pump and probe pulses, the molecules can be converted from one configuration to the other, which results in cross peaks that rise with the average structural conversion time. This phenomenon is much like the spectral diffusion resulting from structural dynamics described earlier, except that the vibrational frequency distribution is bimodal in this case, instead of continuous.

2.6   POLARIZATION-RESOLVED   PUMP-PROBE   SPECTROSCOPY

We showed that light interacts most strongly with vibrations that have their transition dipole moment aligned with the polarization direction of the light (eq. 2.15):

$$R_{a \to b} \propto \cos^2 \theta \qquad (2.35)$$

where θ is the angle between the transition dipole moment of the vibration and the polarization direction of the light. This property can be exploited to measure molecular reorientation dynamics.

Suppose we start out with a collection of randomly oriented molecules (fig. 2.11A). A linearly polarized pump pulse creates the following normalized directional distribution of excited vibrations

$$p(\theta, \phi, t_0) = \frac{3}{4\pi} \cos^2 \theta \qquad (2.36)$$

If we probe the resulting absorption change with probe pulses that are polarized either parallel or perpendicular to the probe polarization, the parallel absorption change is initially higher, since more vibrations were excited in the parallel direction. With the angle definitions as shown in fig. 2.11B, the parallel and perpendicular transient absorption signals are given by:

$$\Delta\alpha_\parallel = 3\sigma_1 N_1 \int_0^{2\pi} \int_0^{\pi} p(\theta, \phi, t) \cos^2 \theta \sin \theta d\theta d\phi \qquad (2.37)$$

$$\Delta\alpha_\perp = 3\sigma_1 N_1 \int_0^{2\pi} \int_0^{\pi} p(\theta, \phi, t) \sin^2 \theta \sin^2 \phi \sin \theta d\theta d\phi \qquad (2.38)$$

where σ_1 is the average isotropic cross section. Substituting $p(\theta, \phi, t_0)$ as defined by eq. 2.36, and integrating over all coordinates yields:

$$\Delta\alpha_\parallel(t_0) = \frac{9}{5}\sigma_1 N_1 \qquad (2.39)$$

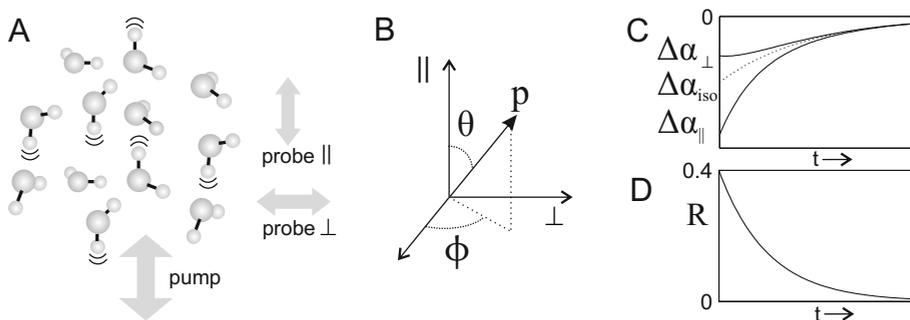$$\Delta\alpha_\perp(t_0) = \frac{3}{5}\sigma_1 N_1 \qquad (2.40)$$

Figure 2.11. Polarization-resolved pump-probe spectroscopy. (A) A linearly polarized pump pulse creates an anisotropic distribution of excited vibrations, which is measured with probe pulses in parallel and perpendicular polarization configuration. (B) Angle definitions for the distribution of excited vibrations p, as mentioned in the text. (C) The transient absorption for parallel and perpendicular probe polarizations, and the isotropic signal. (D) The anisotropic signal.

It follows that the parallel signal is three times larger than the perpendicular signal. With increasing delay time between pump and probe pulses this difference will become smaller, because the excited molecules will reorient. This randomizes the directional distribution of excited vibrations until it becomes completely isotropic, at which stage the parallel and perpendicular signals are equal (fig. 2.11C). Another process that leads to directional randomization is vibrational Förster transfer, because transfer of a vibrational excitation from one vibration to another can lead to a change of the direction of the transition dipole moment of the excited vibration.

A consequence of the above described depolarization (due to molecular reorientation or Förster energy transfer) is that the transient absorption signal does not simply decay with the vibrational lifetime. It is therefore convenient to define the isotropic signal

$$\Delta\alpha_{iso} = \frac{1}{3}\left(\Delta\alpha_\parallel + 2\Delta\alpha_\perp\right) \tag{2.41}$$

which decays with the vibrational lifetime and is independent of orientational dynamics, provided the sample itself is isotropic.[b]

In addition to the isotropic signal, we can construct the anisotropic signal

$$R = \frac{\Delta\alpha_\parallel - \Delta\alpha_\perp}{\Delta\alpha_\parallel + 2\Delta\alpha_\perp} \tag{2.46}$$

which is the difference between the two absorption signals, normalized by the rate of vibrational relaxation (note the similarity between the denominator of

---

[b]The fact that the isotropic signal depends only on the vibrational lifetime can be shown by returning to the expressions of eq. 2.37 and 2.38, which combined with eq. 2.41 yield

$$\Delta\alpha_{iso} = \sigma_1 N_1 \int_0^{2\pi} \int_0^\pi p(\theta, \phi, t)\left(\cos^2\theta + 2\sin^2\theta\sin^2\phi\right)\sin\theta d\theta d\phi \tag{2.42}$$

above equation and the isotropic signal), which makes it independent of the vibrational lifetime. It can be shown that the anisotropy is directly proportional to the second order orientational correlation function of the direction of an excited vibration[68,69]:

$$R(t) = \frac{2}{5}\big\langle P_2(\cos\theta_r(t))\big\rangle \tag{2.47}$$

where $\theta_r(t)$ is the rotation of the transition dipole moment of the excited vibration as a function of time and $P_2 = \frac{1}{2}(3x^2 - 1)$ is the second order Legendre polynomial. Note that $R(0) = \frac{2}{5}$, which follows directly from the initial values of the parallel and perpendicular signals given in eq. 2.39 and 2.40, which in turn are a direct consequence of the $\cos^2\theta$ dependence of the excitation. Using eq. 2.47, which connects the macroscopic observable R with the molecular orientational dynamics, we can calculate the anisotropy decay for different events.

REORIENTATION   In the simplest case, the molecules reorient diffusively in all directions. The distribution of excited vibrations is then described by:

$$\frac{\partial p_\theta(\theta, t)}{\partial t} = D_\theta \nabla^2 p_\theta(\theta, t) \tag{2.48}$$

with D_θ the orientational diffusion constant, ∇^2 the Laplacian operator and p_θ the distribution of excited vibrations for an isotropic sample (which is independent of the angle ϕ). The solution to the above diffusion equation is a sum of exponentially decaying Legendre polynomials P_l:

$$p_\theta(\theta, t) = \sum_{l \geq 0} c_l P_l(\cos\theta) e^{-D_\theta l(l+1)t} \tag{2.49}$$

where c_l are coefficients that are determined by the initial distribution $p_\theta(\theta, 0)$. Since the anisotropy is related to the second order Legendre polynomial, it follows from above equation that the anisotropy decay due to orientational diffusion is given by

$$R(t) = \frac{2}{5} e^{-t/\tau_{reor}} \tag{2.50}$$

with $\tau_{reor} = \frac{1}{6D_\theta}$.

    In some systems, molecules can only reorient diffusively within a limited cone angle θ_c. As a consequence, the anisotropy decays with τ_{reor} to a value of

$$R = \big(\frac{1}{2}\cos\theta_c(1 + \cos\theta_c)\big)^2 \tag{2.51}$$

For an isotropic sample, the distribution p does not depend on ϕ, in which case

$$\Delta\alpha_{iso} = \sigma_1 N_1 \int_0^{2\pi} \int_0^\pi \frac{p_\theta(\theta, t)}{2\pi}\big(\cos^2\theta + 2\sin^2\theta\sin^2\phi\big)\sin\theta\, d\theta\, d\phi \tag{2.43}$$

$$= \sigma_1 N_1 \int_0^\pi p_\theta(\theta, t)\big(\cos^2\theta + \sin^2\theta\big)\sin\theta\, d\theta \tag{2.44}$$

$$= \sigma_1 N_1 \tag{2.45}$$

In the above calculation we have used the fact that p and p_θ are normalized distributions.

FÖRSTER TRANSFER   Transfer of the vibrational energy over an angle θ_t leads to a decay of the anisotropy to a value of

$$R = \frac{1}{5} \left(3 \cos^2 \theta_t - 1 \right) \tag{2.52}$$

If the energy transfer occurs between two vibrations with different frequencies, we can deduce the relative angle between their transition dipole moments from the anisotropy value of the corresponding cross peak in the 2DIR spectrum. In general, the anisotropy of cross peaks often differs from that of the diagonal peaks, in which case we can enhance the visibility of the cross peaks by constructing the polarization-difference signal:

$$\Delta \alpha_{diff} = \Delta \alpha_{\perp} \left(\frac{\Delta \alpha_{\parallel,max}}{\Delta \alpha_{\perp,max}} \right) - \Delta \alpha_{\parallel} \tag{2.53}$$

The above equation relies on the fact that $\Delta \alpha$ usually reaches its maximum along the diagonal. At the maximum $\Delta \alpha_{diff} = 0$, and thus the diagonal peaks are eliminated.