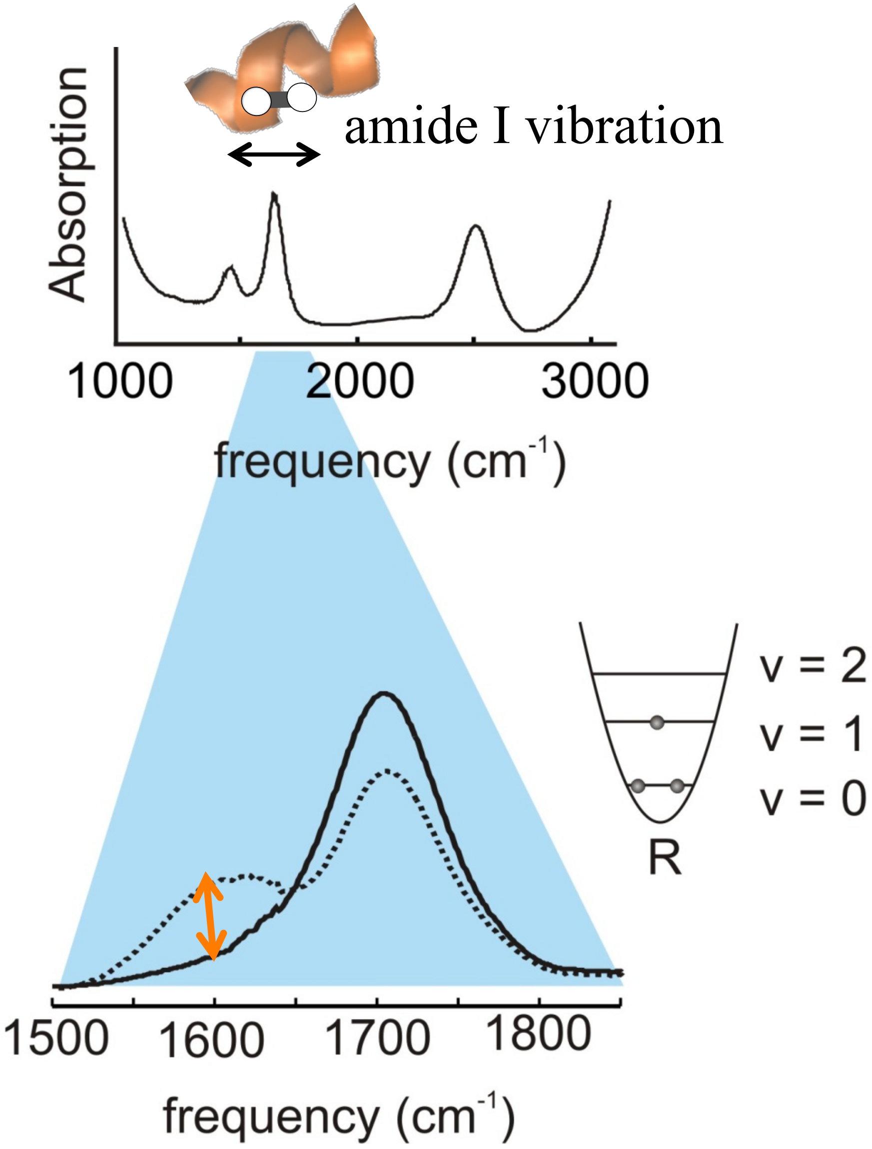
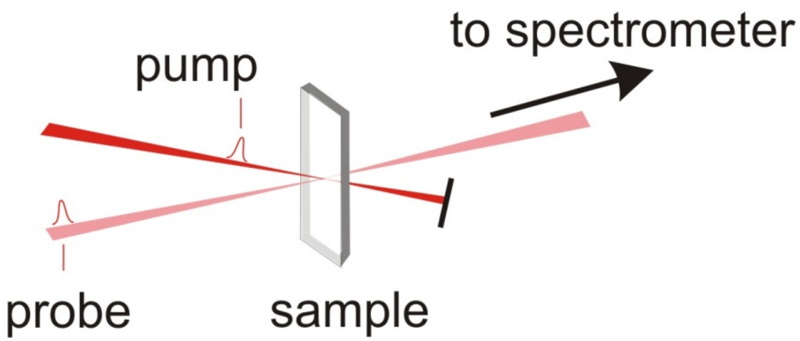
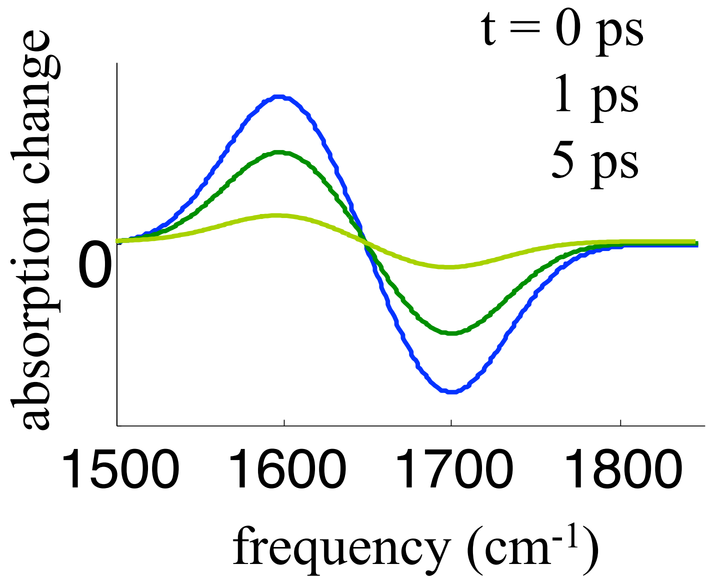
Pump-probe spectroscopy

Pump-probe spectroscopy

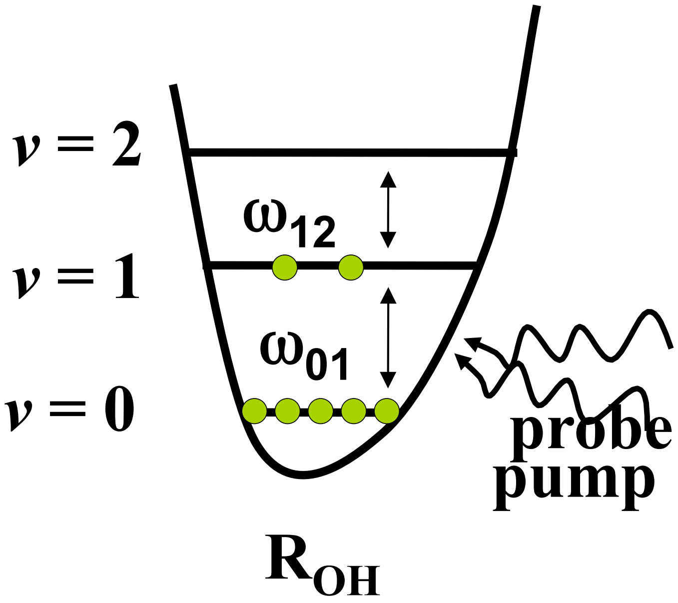




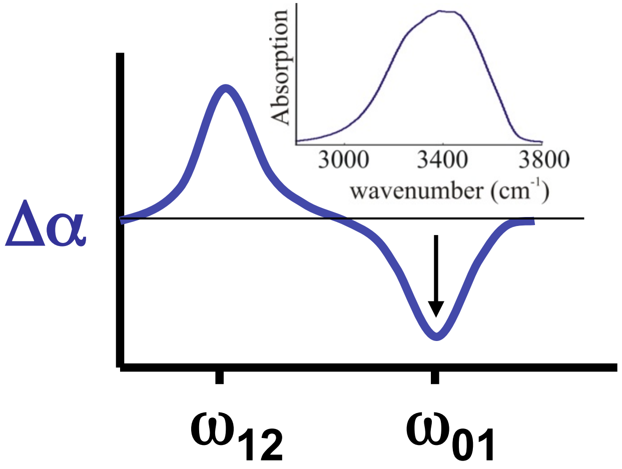


Pump-probe: principle

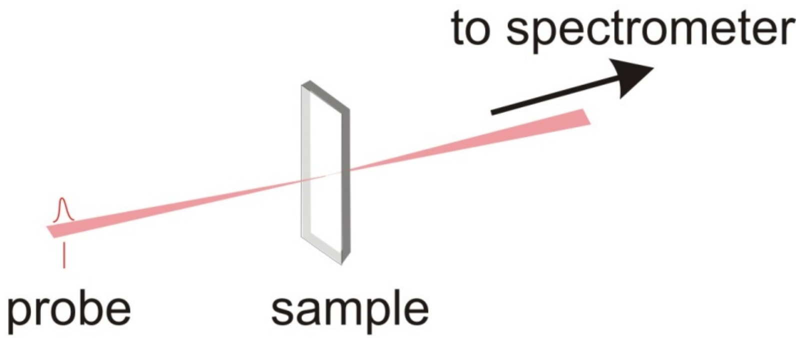
Energy levels

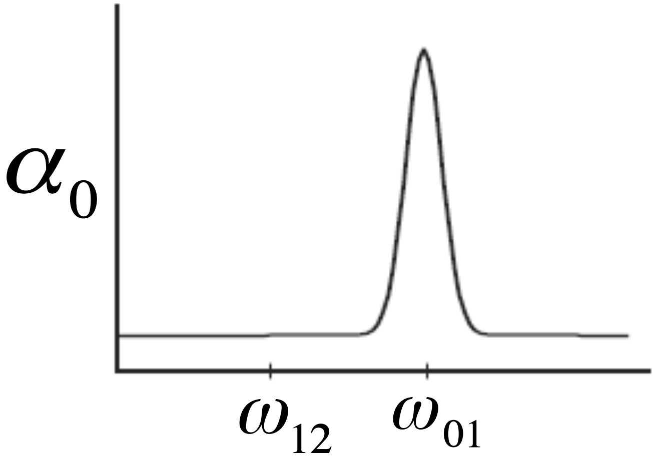


Transient spectrum

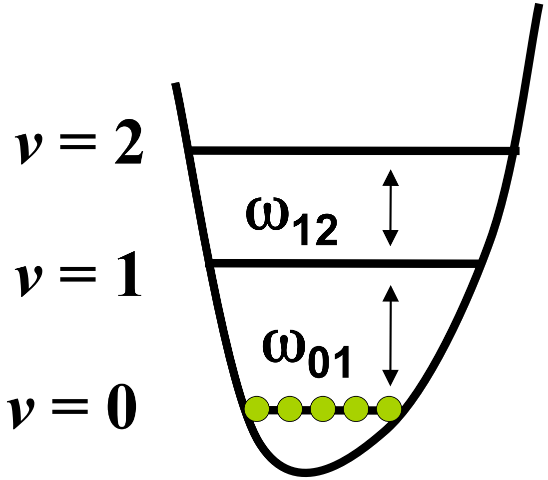


Pump-probe spectroscopy

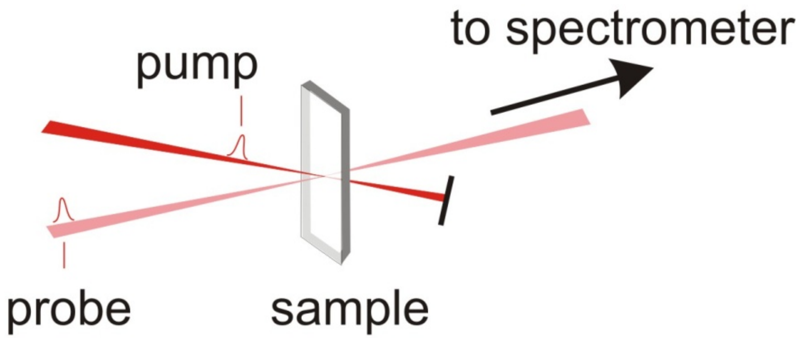


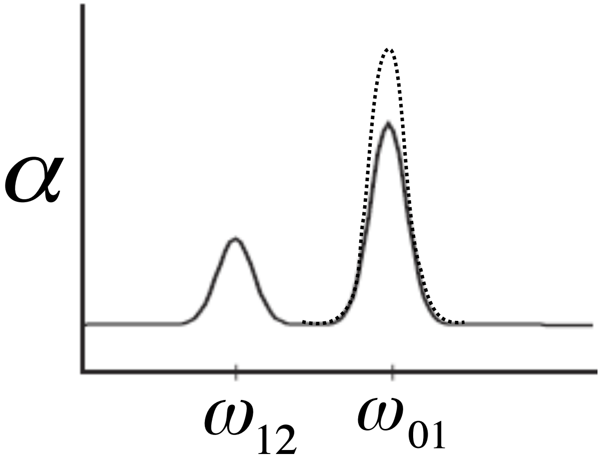


$$\alpha_0 = \sigma_{01}(\omega) n$$



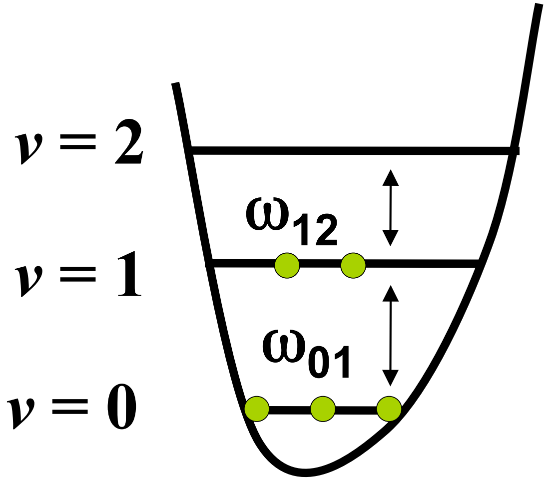
Pump-probe spectroscopy



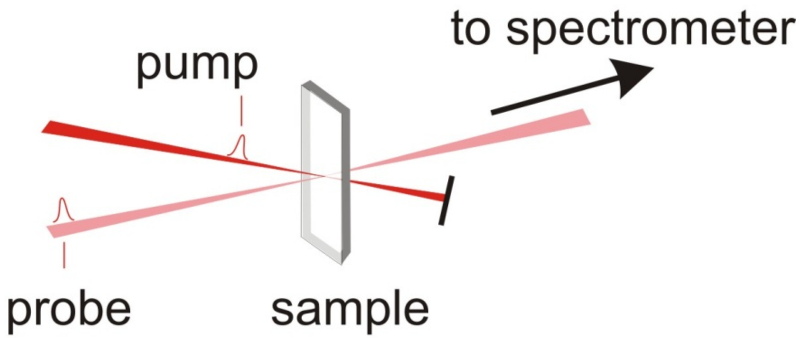


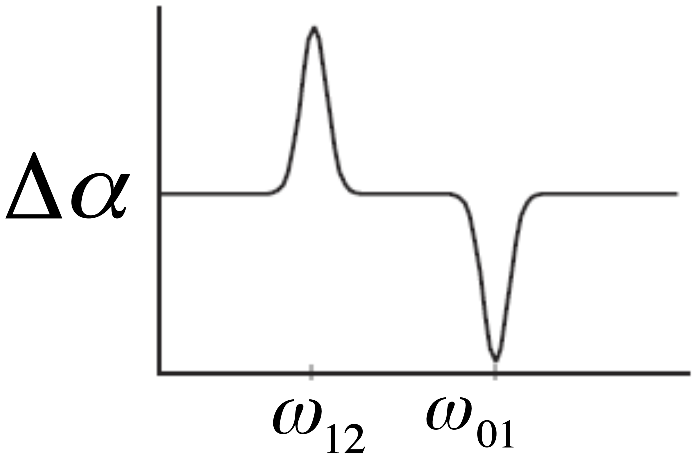
$$\alpha = \sigma_{01}(\omega)(n - 2N_1) + \sigma_{12}(\omega) N_1$$

$$\alpha_0 = \sigma_{01}(\omega) n$$

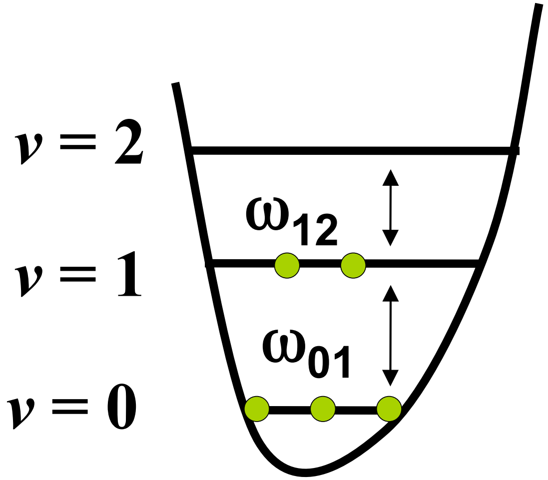


Pump-probe spectroscopy





$$\Delta\alpha = -2N_1\sigma_{01}(\omega) + \sigma_{12}(\omega)N_1$$



Pump-probe spectroscopy

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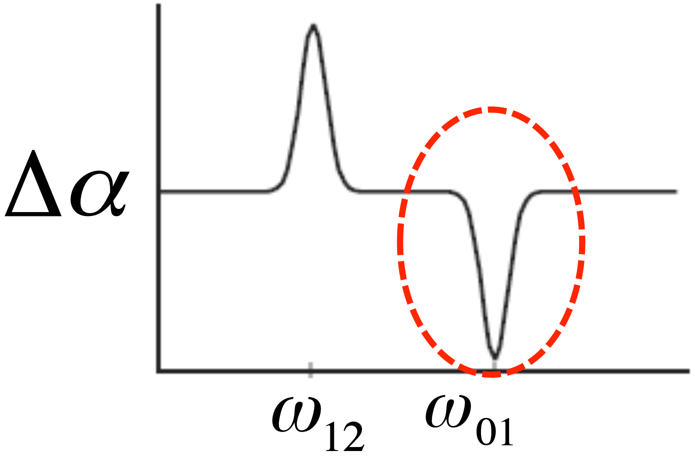
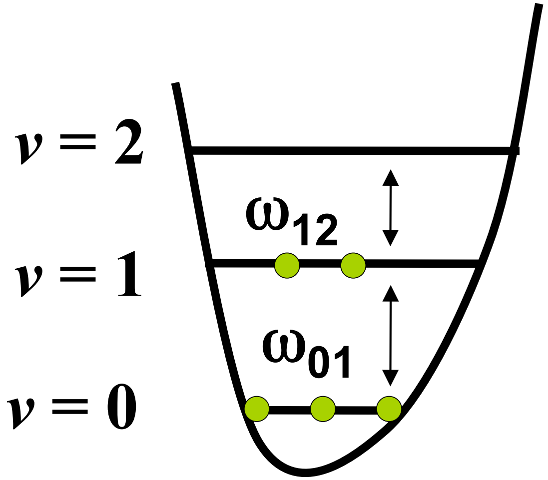


Bleach has two contributions

- Ground state depletion
- Stimulated emission



Pump-probe spectroscopy

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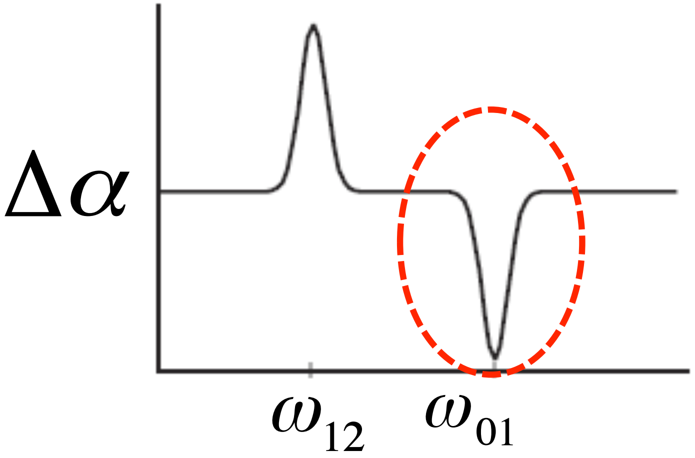

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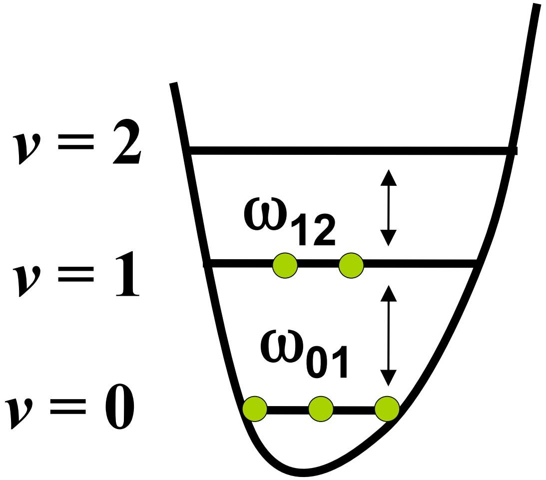

Pump-probe spectroscopy

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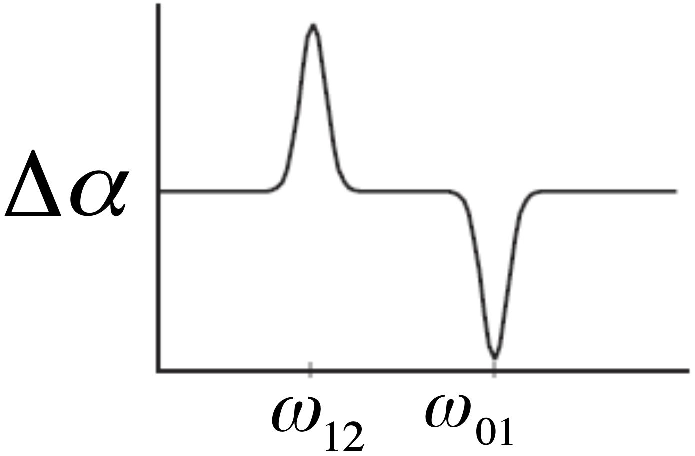
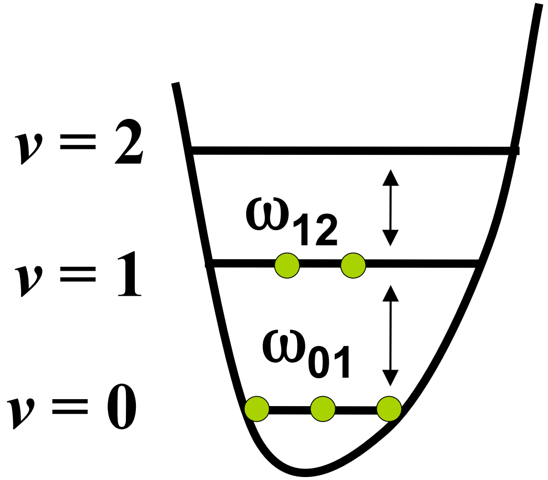


For a perferct harmonic oscillator

$$\sigma_{12}(\omega) = 2\sigma_{01}(\omega)$$

No pump-probe signal!



Pump-probe spectroscopy

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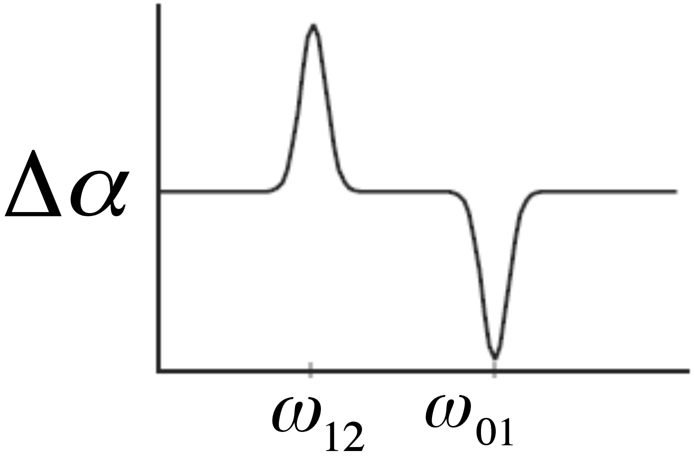


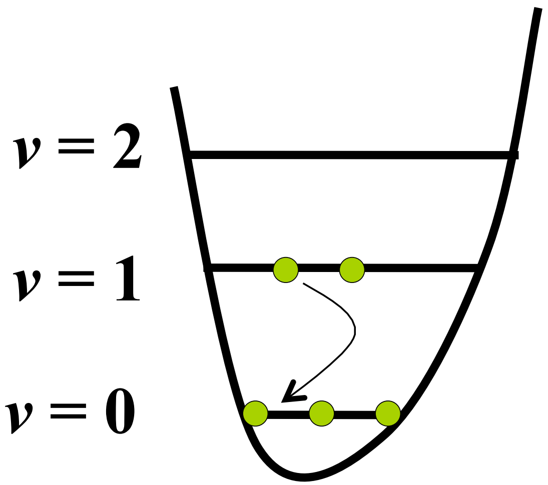
Galileo

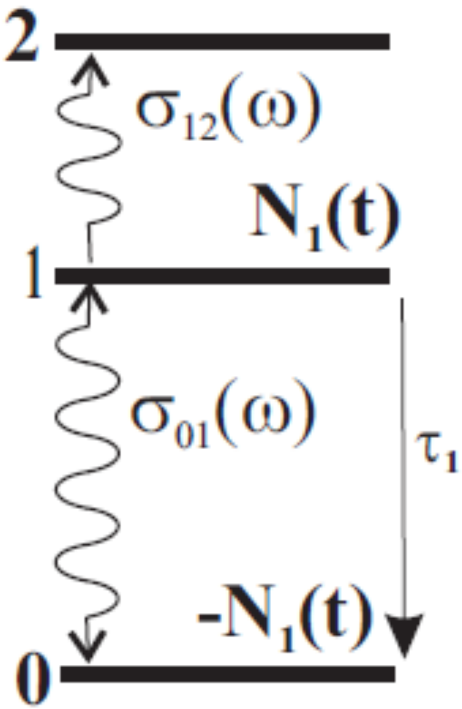
Anharmonicity is required for a pump-probe signal

Vibrational relaxation and its effects

Vibrational relaxation

Molecules relax to the ground state

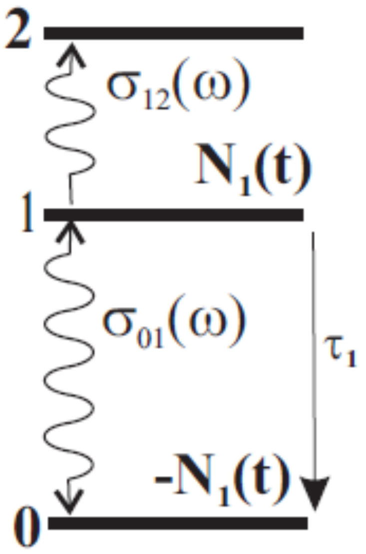


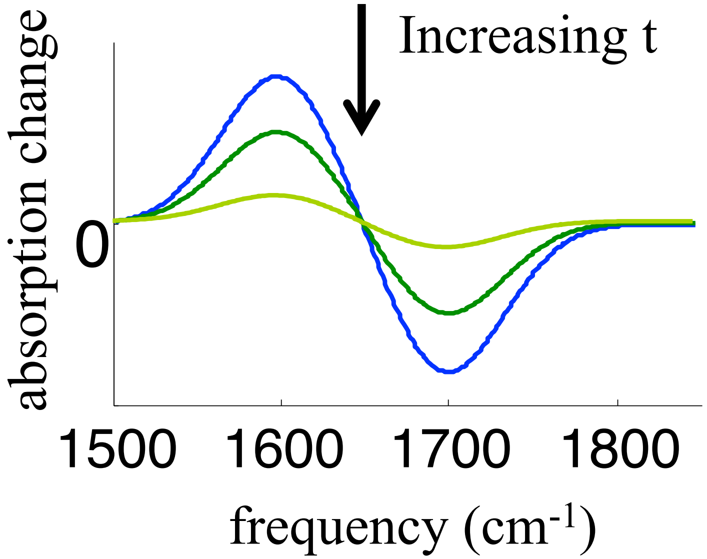


$$\Delta\alpha(\omega,t) = \left[-2\sigma_{01}(\omega) + \sigma_{12}(\omega)\right]N_1(t)$$

Vibrational relaxation

Molecules relax to the ground state





$$\Delta\alpha(\omega,t) = \left[-2\sigma_{01}(\omega) + \sigma_{12}(\omega)\right]N_1(t)$$

Vibrational relaxation

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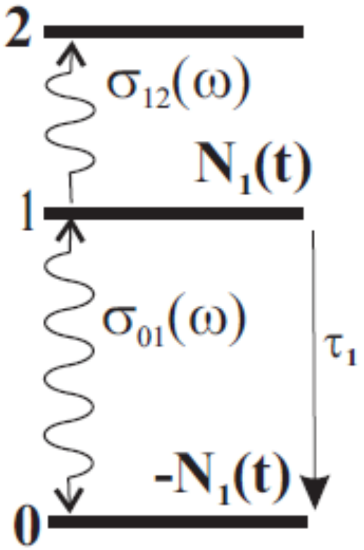
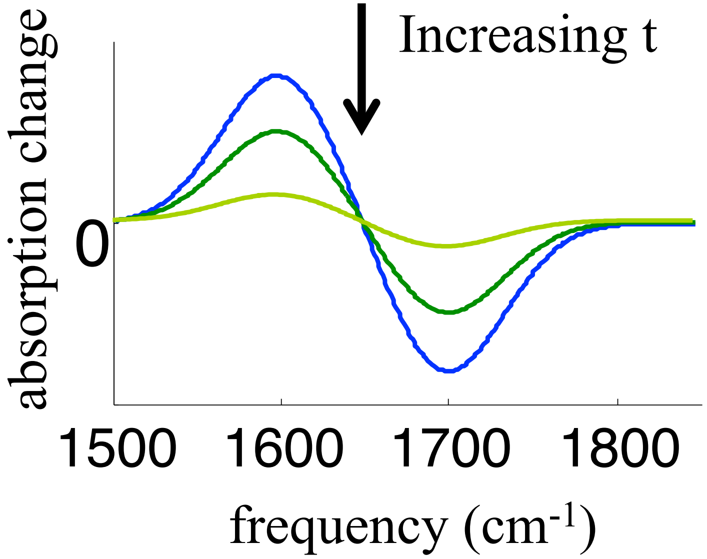
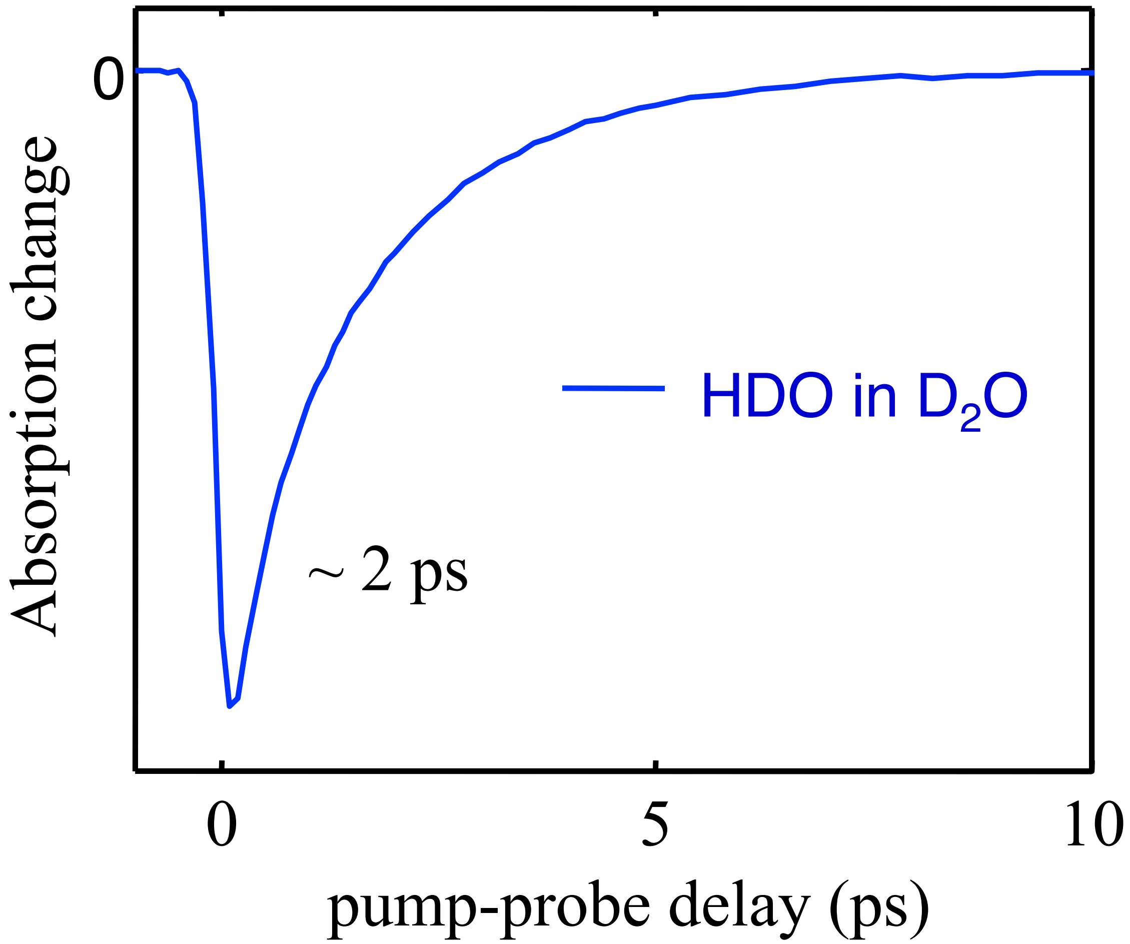


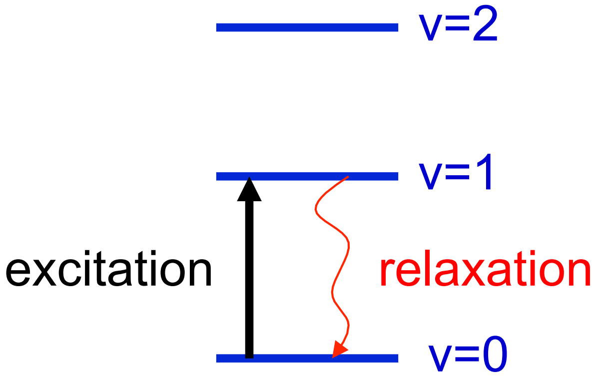


$$\Delta\alpha(\omega,t) = \left[-2\sigma_{01}(\omega)+\sigma_{12}(\omega)\right]N_1(0)e^{-t/\tau_1}$$

Simplest case: exponential relaxation

Delay time scan (shows vibrational relaxation)





Exponential relaxation

When do we get exponential relaxation (or decay)?
What does it mean microscopically?

Spontaneous emission rate (Einstein theory, Wigner-Weisskopf)

$$1/\tau_1 = \frac{\omega_{01}^3 \left|\mu_{01}\right|^2}{3\pi\varepsilon_0 \hbar c^3}$$

Electronic transitions → ~nanosecond
Vibrational transitions → microsecond-millisecond

Exponential relaxation

When do we get exponential relaxation (or decay)?
What does it mean microscopically?

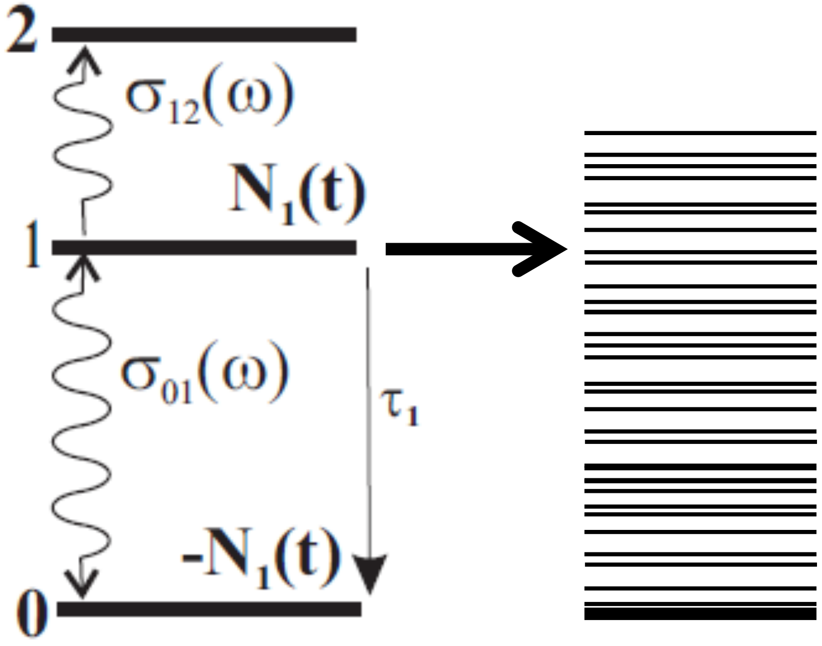
<u>Radiative decay</u>
Vibrational transitions → microsecond-millisecond

<u>Non-radiative decay rate</u>
Vibrational transitions → picosecond

In the condensed phase vibrational excitations decay non-radiatively on a picosecond timescale.

Exponential relaxation

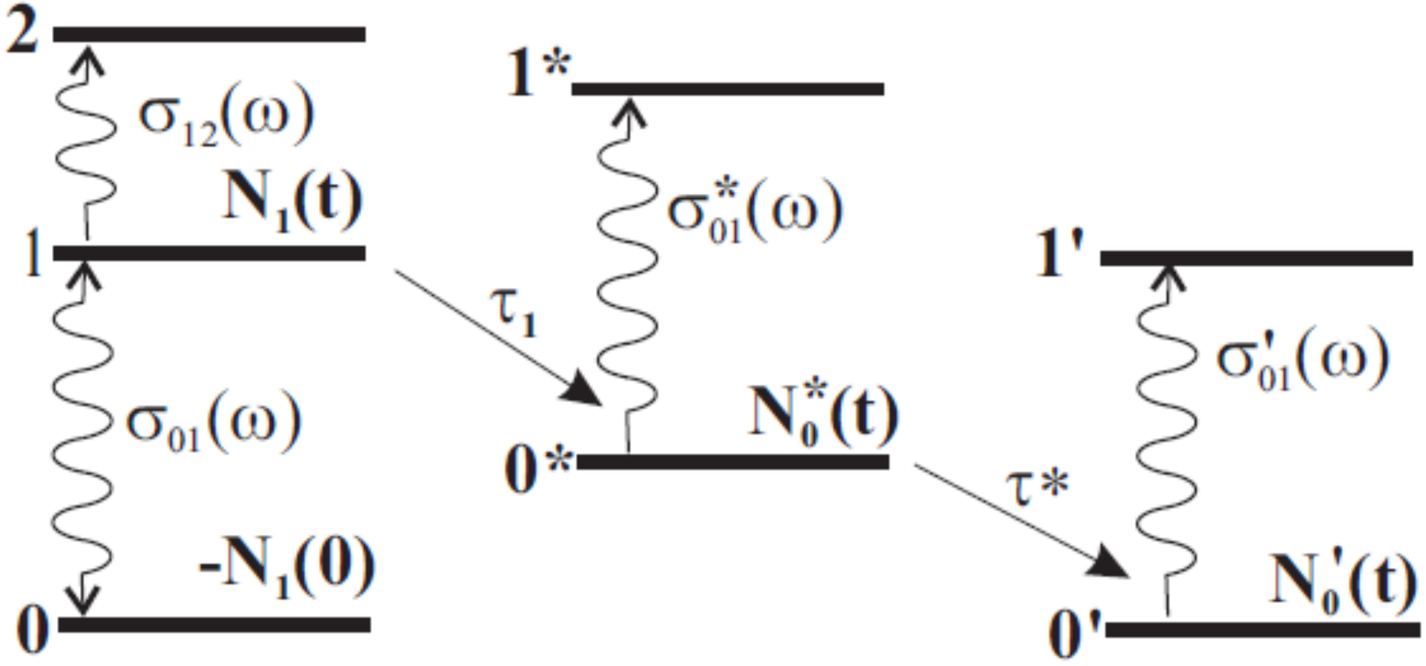
Many closely lying states that are nearly resonant



low-frequency vibrations,
intermolecular modes, etc.

Relaxation mechanisms

E.g. relaxation of OD stretching vibration of HDO in H2O



Relaxation mechanisms

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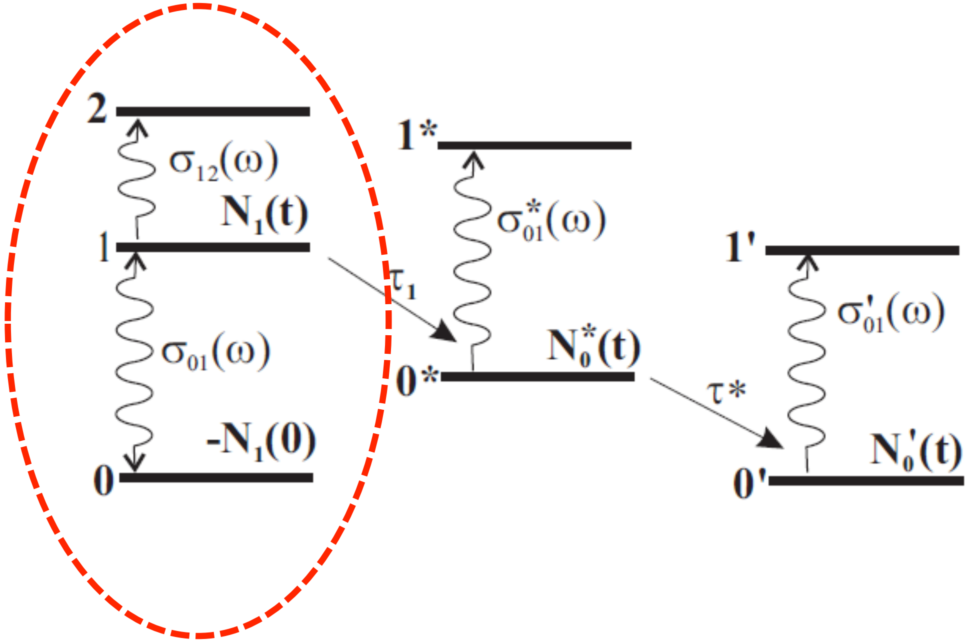
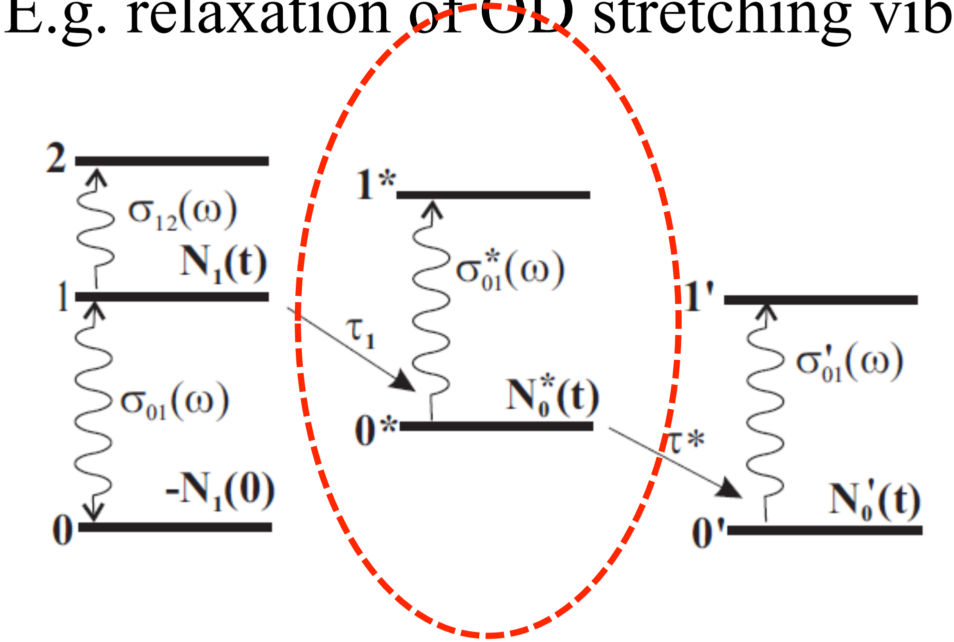


Vibrational anharmonicity

Relaxation mechanisms

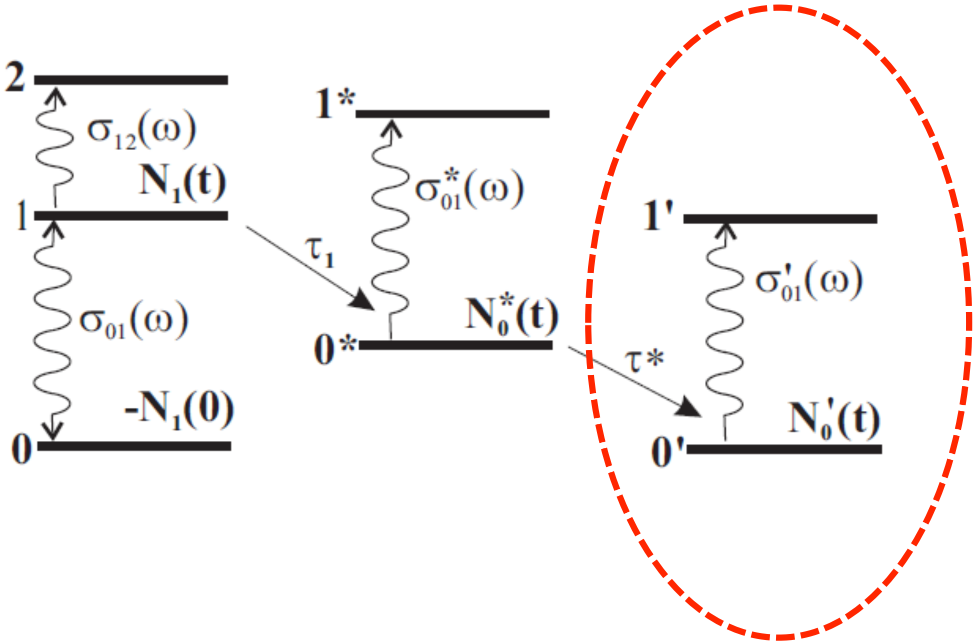
E.g. relaxation of OD stretching vibration of HDO in H2O



Low-frequency mode excited (anharmonic shift)

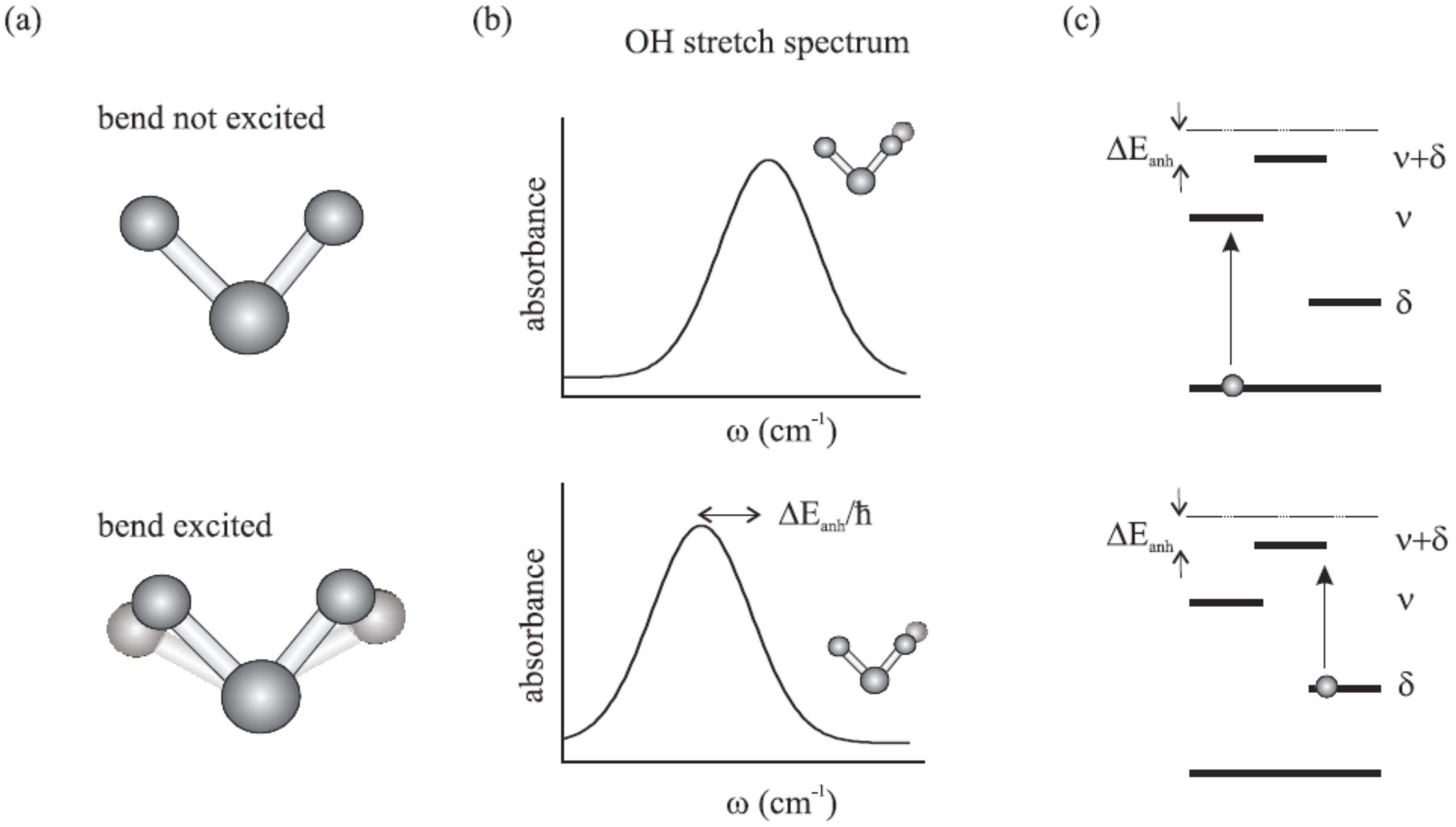
Relaxation mechanisms

E.g. relaxation of OD stretching vibration of HDO in H2O



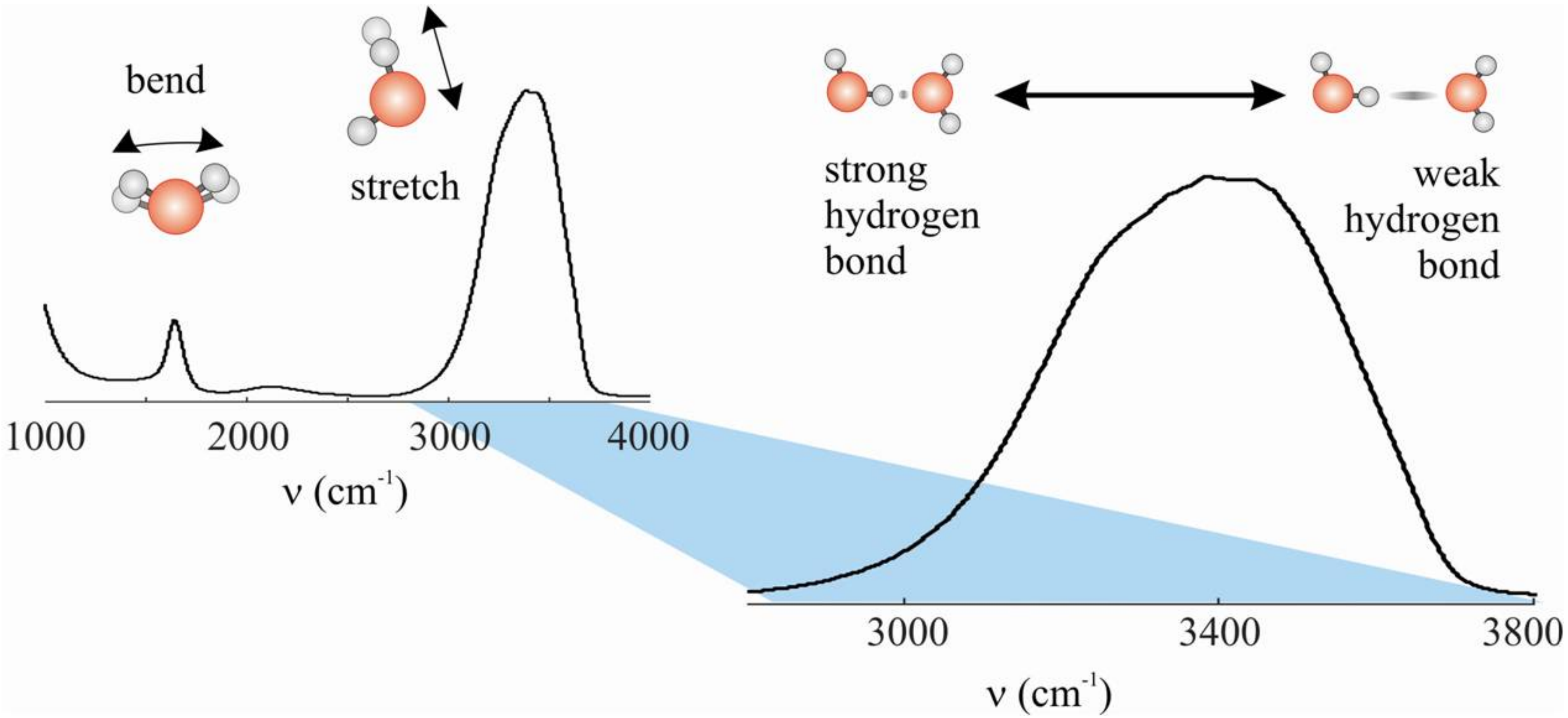
Sample heating

Anharmonic vibrational couplings

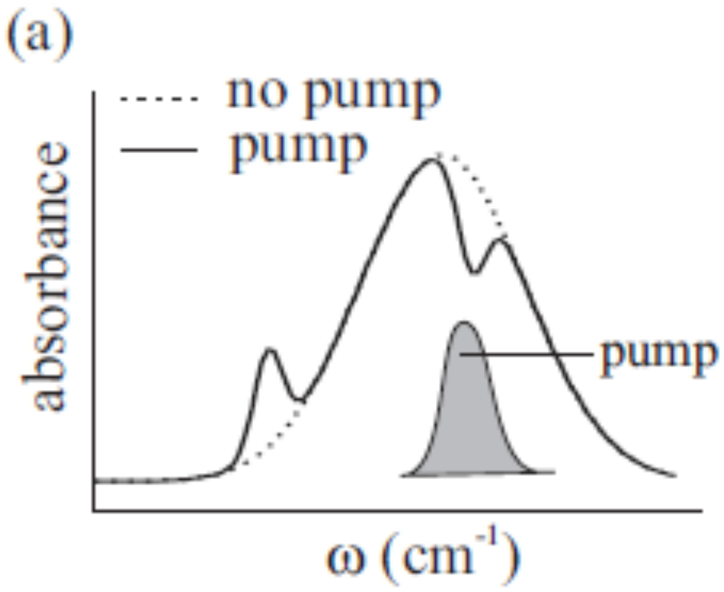


Inhomogeneous broadening and spectral diffusion

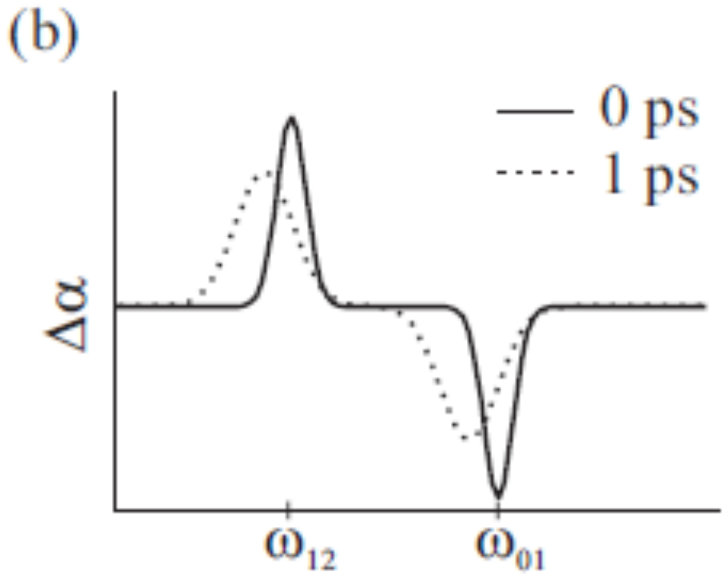
Inhomogeneous broadening



Probing spectral diffusion



Spectral hole

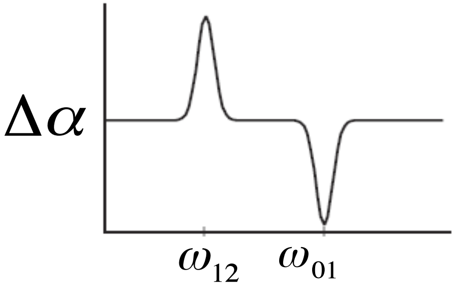


Spectral hole in transient spectrum

Spectral hole broadens due to spectral diffusion

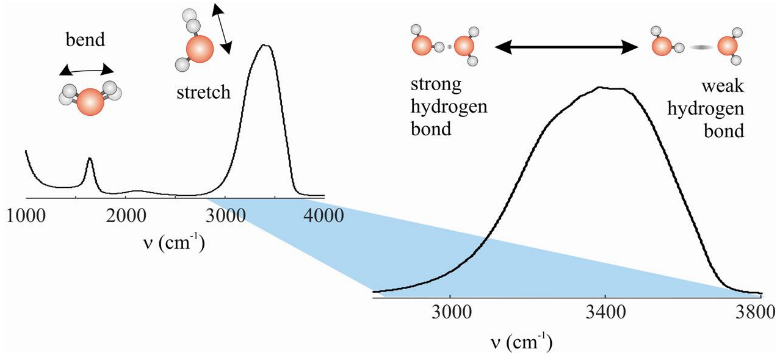
Summary ‘Pump-probe spectroscopy’

- Origin of the vibrational pump-probe signal → anharmonicity



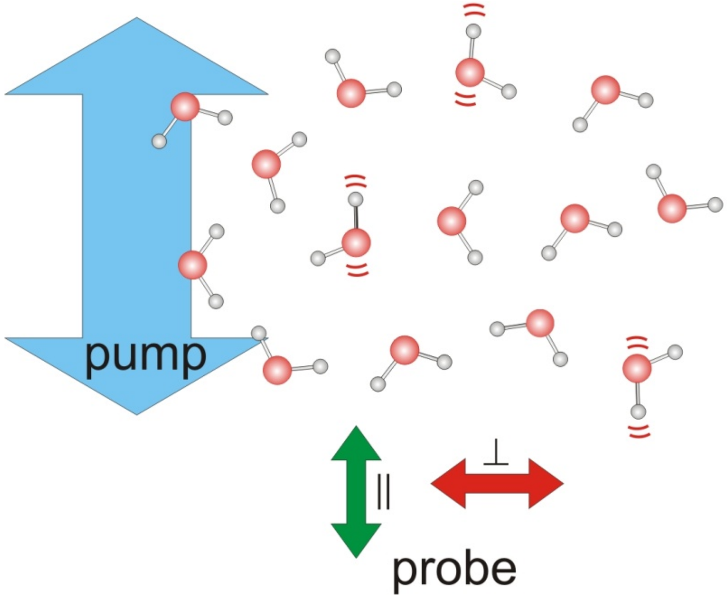
- Vibrational relaxation

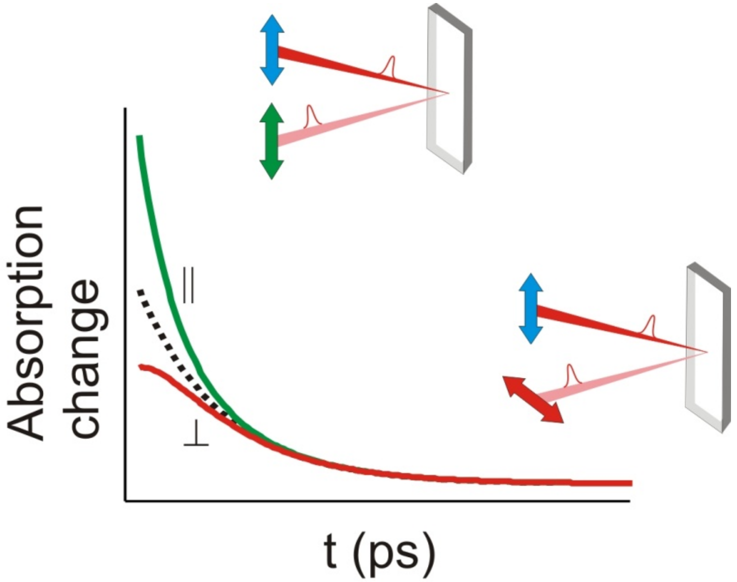
- Spectral diffusion



Polarization properties of the pump-probe signal

Polarization

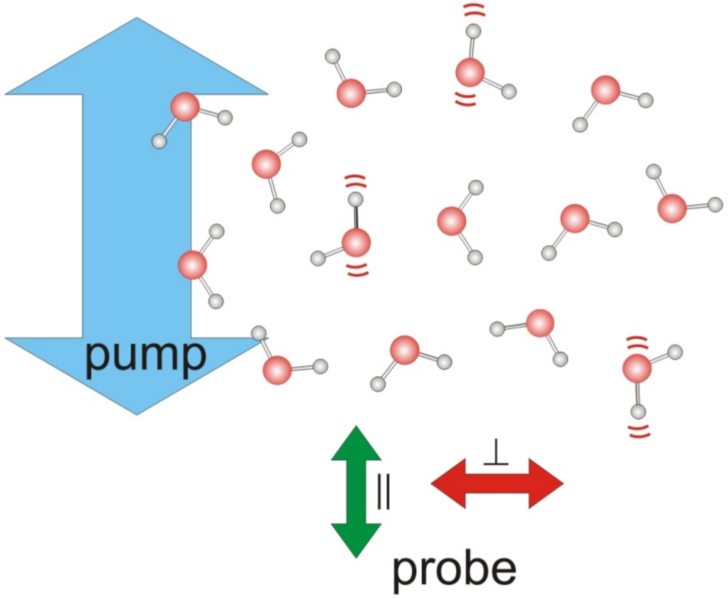


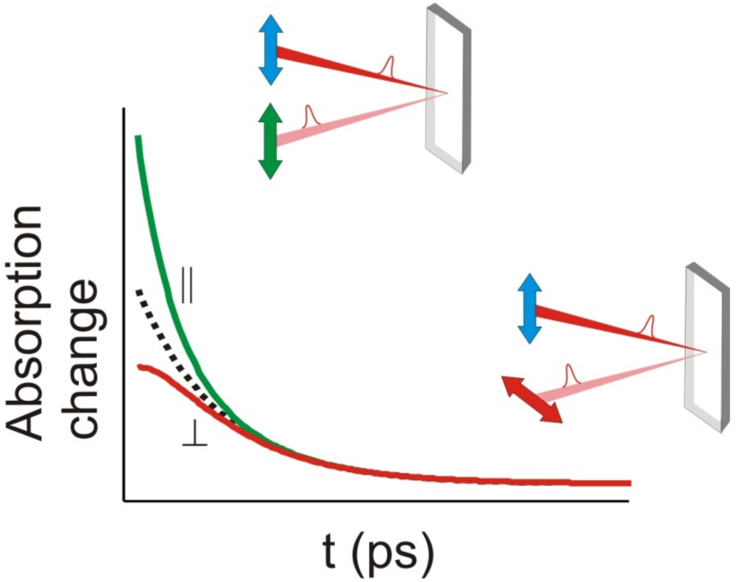


To study vibrational relaxation we need the isotropic signal:

- which depends only on the concentration of excited molecules
- which is not affected by orientational motion

Polarization

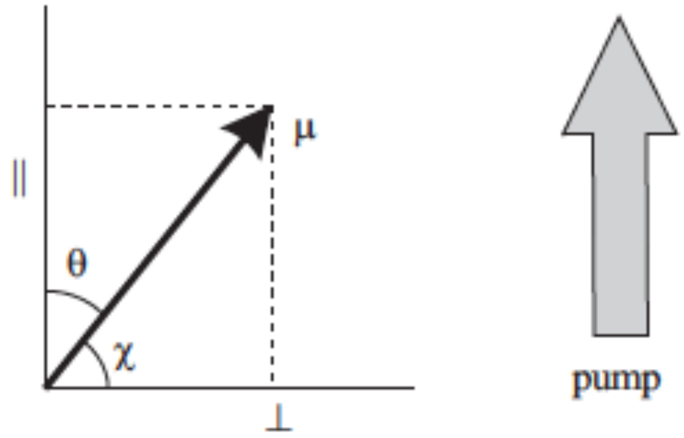




$$\Delta\alpha_{iso} \neq \frac{\Delta\alpha_{\parallel} + \Delta\alpha_{\perp}}{2}$$

Polarization

In two dimensions

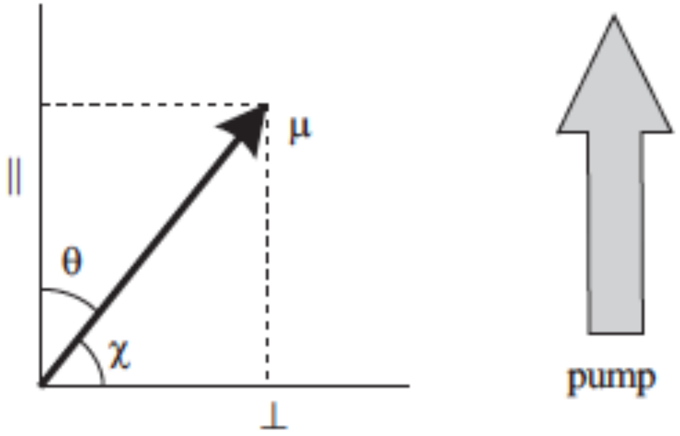


Contribution of an excited vibration to the parallel and perpendicular signal:

$$
\begin{aligned}
\Delta\alpha_{||} &\propto \cos^2\theta, \\
\Delta\alpha_{\perp} &\propto \cos^2\chi
\end{aligned}
$$

Polarization

In two dimensions



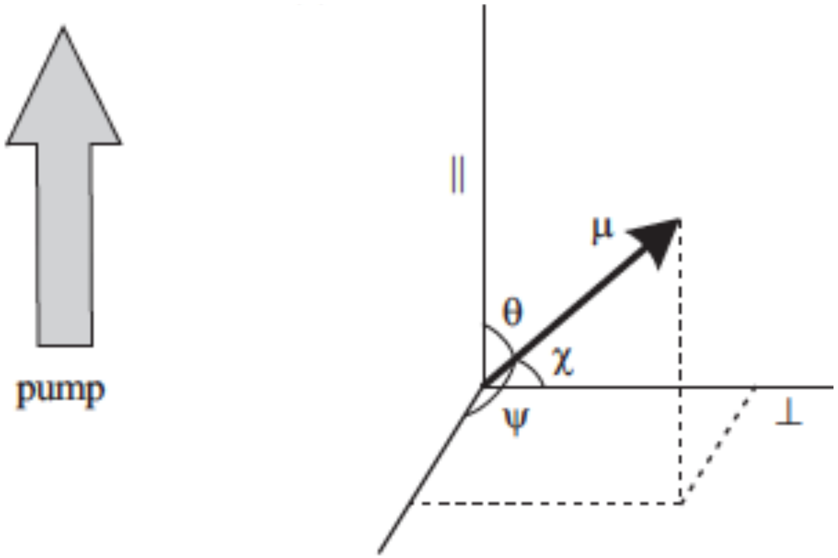
The following quantity is independent of orientation

$$\Delta\alpha_{\|} + \Delta\alpha_{\perp} \propto \cos^2\theta + \cos^2\chi$$

In two dimensions this would be the isotropic signal

Polarization

In three dimensions

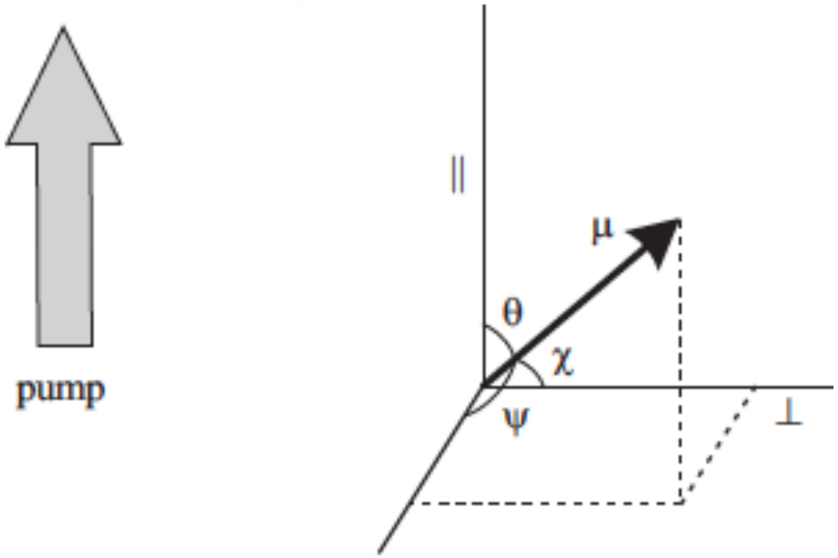


Independent of the orientation of an excited dipole

$$\cos^2\theta + \cos^2\chi + \cos^2\psi$$

Polarization

In three dimensions



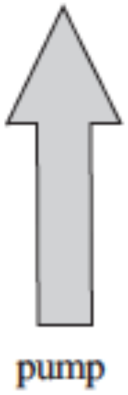
However in a macroscopic measurement one probes the average over all molecules

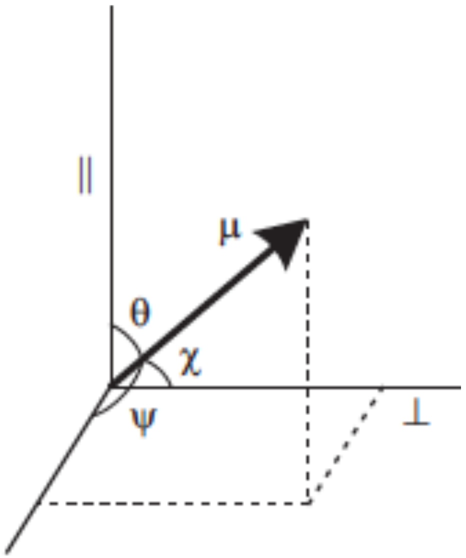
$$\left\langle \cos^2\theta \right\rangle + \left\langle \cos^2\chi \right\rangle + \left\langle \cos^2\psi \right\rangle$$

Polarization

In three dimensions

$$\left\langle \cos^2 \chi \right\rangle = \left\langle \cos^2 \psi \right\rangle$$





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In three dimensions

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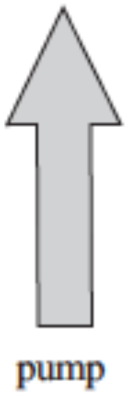
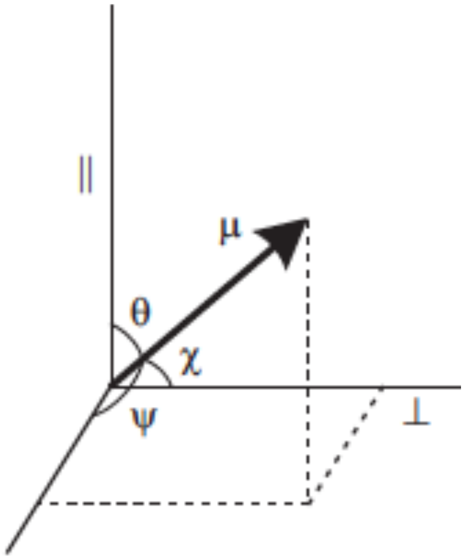




The quantity independent of orientation is

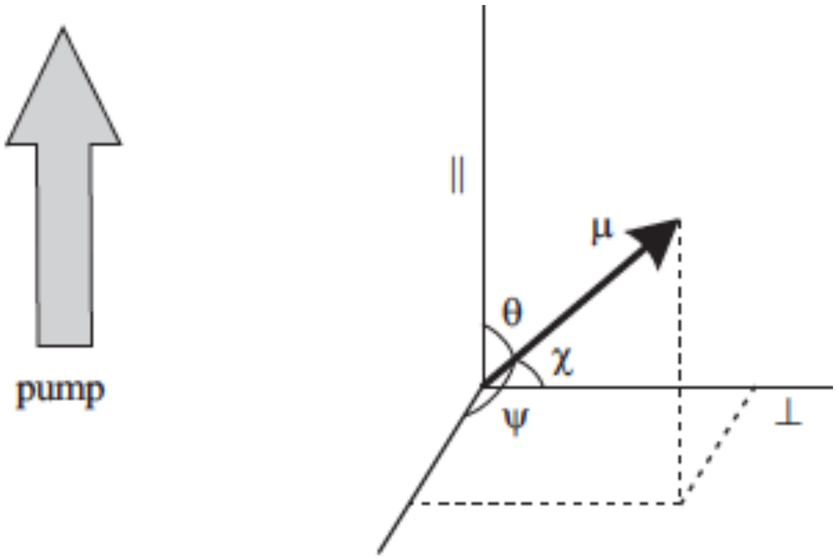
$$\Delta\alpha_{iso} = \frac{\Delta\alpha_{\parallel} + 2\Delta\alpha_{\perp}}{3} = \left\langle \cos^2 \theta \right\rangle + 2\left\langle \cos^2 \chi \right\rangle$$

Using a distribution function

Distribution of excited molecules

$$N(\vartheta,\varphi,t) = g(\vartheta,\varphi,t)N_1$$

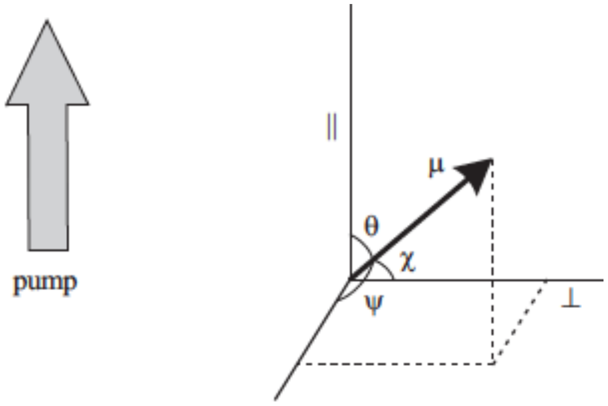
Total number of excited molecules



Properties

- Normalization

$$\int g(\theta, \phi, t)\, d\Omega = 1$$



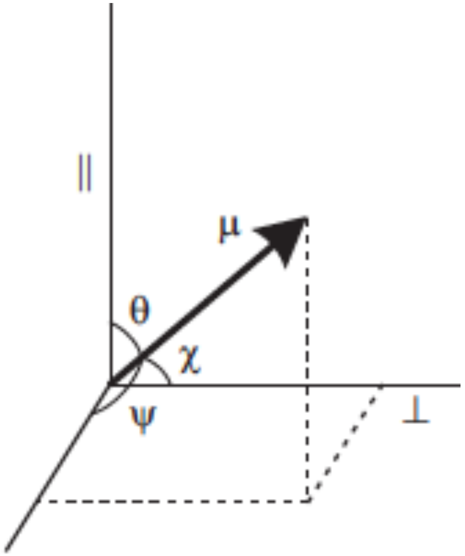
- At zero delay

$$g(\theta, \phi, 0) = \frac{3}{4\pi} \cos^2 \theta.$$

- Tends to an isotropic distribution for long delays

$$\lim_{t \to \infty} g(\theta, \phi, t) = \frac{1}{4\pi}$$

Signals



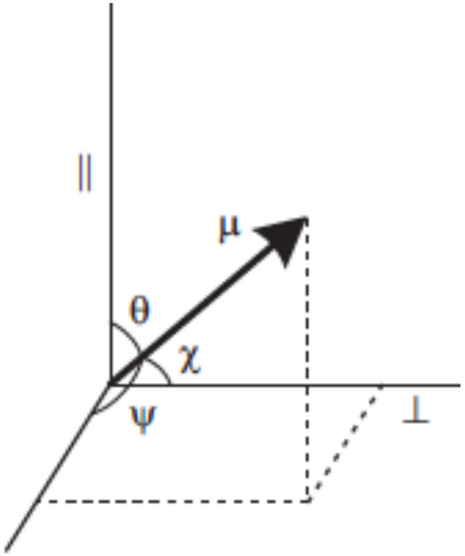
$$\Delta\alpha_{||}(t) = 3\sigma_{12}N_1 \int g(\theta,\phi,t)\cos^2\theta\, d\Omega,$$

$$\Delta\alpha_{\perp}(t) = 3\sigma_{12}N_1 \int g(\theta,\phi,t)\sin^2\theta\,\sin^2\phi\, d\Omega,$$

Signals

$$\cos^2\chi = (\vec{\mu}(\theta,\phi)\cdot\hat{y})^2$$

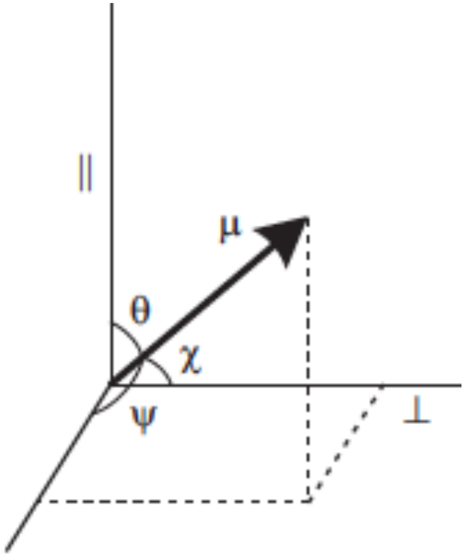
$$= \sin^2\theta\sin^2\phi$$



$$\begin{aligned}\Delta\alpha_{||}(t) &= 3\sigma_{12}N_1\int g(\theta,\phi,t)\cos^2\theta\,d\Omega,\\ \Delta\alpha_{\perp}(t) &= 3\sigma_{12}N_1\int g(\theta,\phi,t)\boxed{\sin^2\theta\sin^2\phi}\,d\Omega,\end{aligned}$$

Signals

Cross section is defined as isotropic average = 1/3 of maximum value



$$\begin{aligned} \Delta\alpha_{||}(t) &= 3\sigma_{12} N_1 \int g(\theta, \phi, t) \cos^2\theta \, d\Omega, \\ \Delta\alpha_{\perp}(t) &= 3\sigma_{12} N_1 \int g(\theta, \phi, t) \sin^2\theta \sin^2\phi \, d\Omega, \end{aligned}$$

Signals

$$\begin{aligned}\Delta\alpha_{||}(t) &= 3\sigma_{12}N_1\int g(\theta,\phi,t)\cos^2\theta\,d\Omega,\\ \Delta\alpha_{\perp}(t) &= 3\sigma_{12}N_1\int g(\theta,\phi,t)\sin^2\theta\sin^2\phi\,d\Omega,\end{aligned}$$

$$\Delta\alpha_{iso}=\frac{1}{3}(\Delta\alpha_{||}+2\Delta\alpha_{\perp})$$

$$\Delta\alpha_{iso}=\sigma_{12}N_1\int g(\theta,\varphi,t)\left[\cos^2\theta+2\sin^2\theta\sin^2\varphi\right]d\Omega$$

Signals

$$\Delta\alpha_{iso} = \sigma_{12} N_1 \int g(\theta,\varphi,t)\left[\cos^2\theta + 2\sin^2\theta\sin^2\varphi\right] d\Omega$$

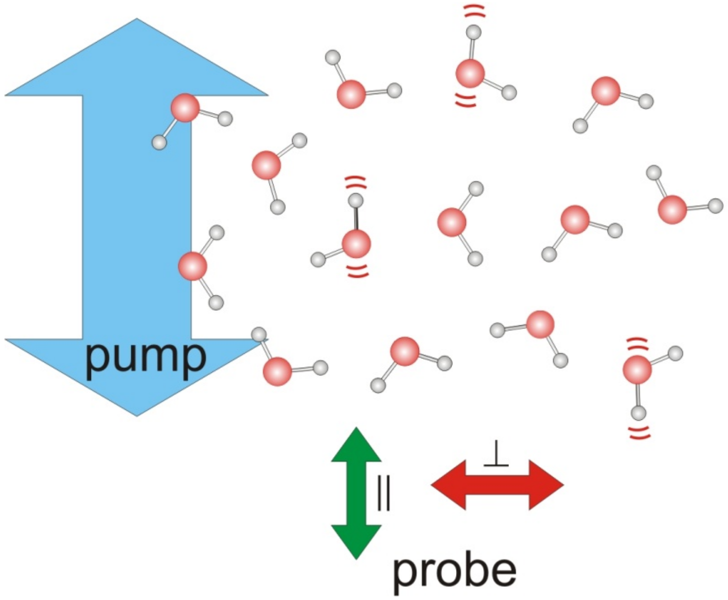
Isotropic sample

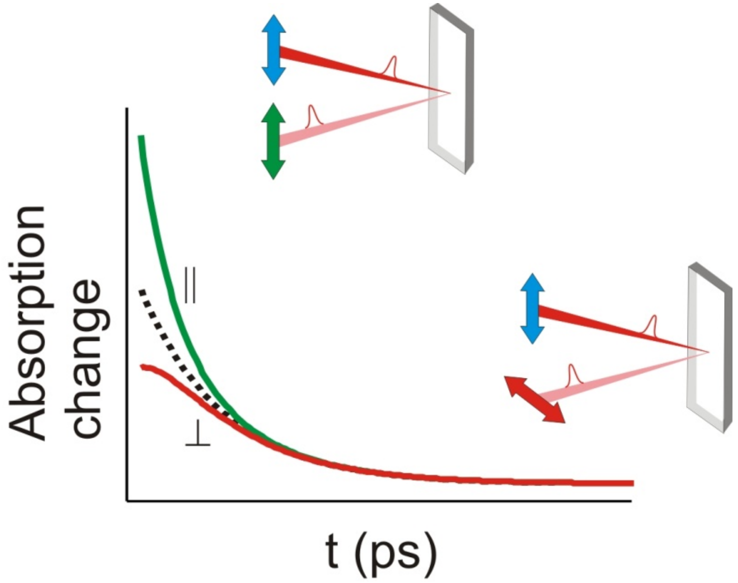
$$g(\vartheta,\varphi,t) = g(\vartheta,t)$$

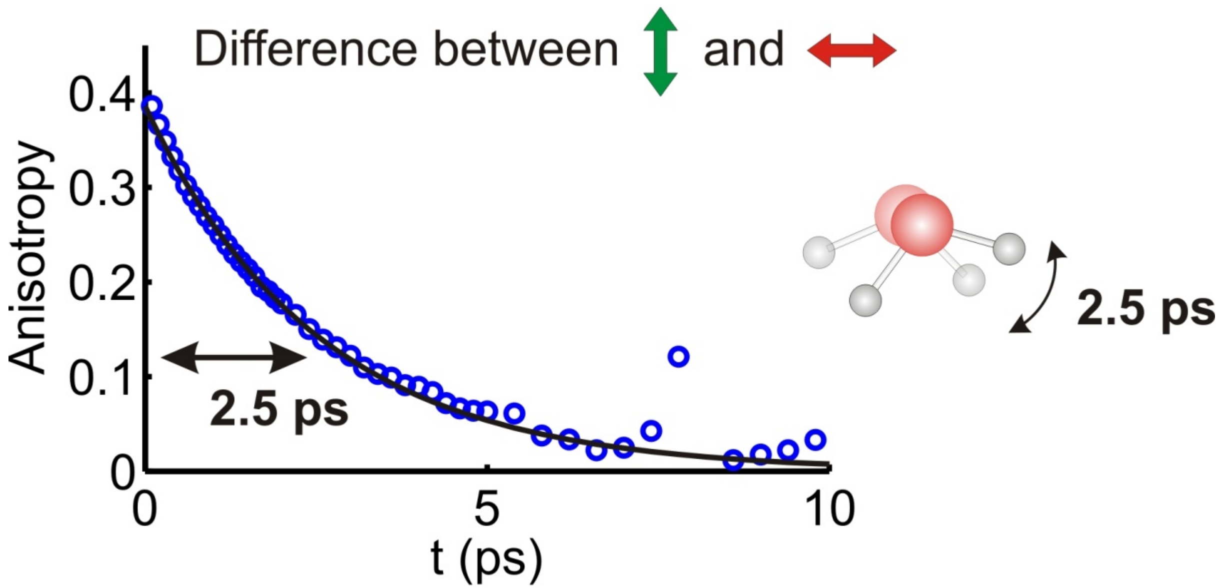
$$\Delta\alpha_{iso} = \sigma_{12} N_1$$

Indeed the isotropic signal depends only on the total number of excited molecules!

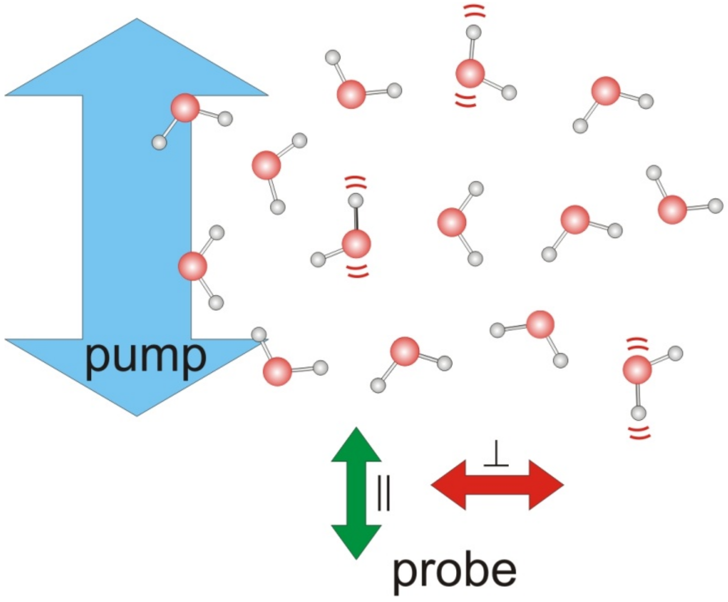
Anisotropy: molecular motion

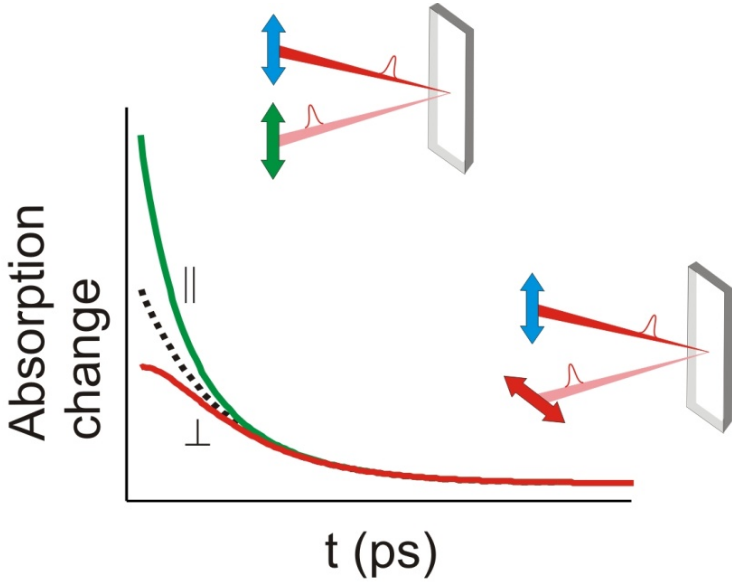






Anisotropy: molecular motion





$$R(t) = \frac{\Delta\alpha_{\parallel} - \Delta\alpha_{\perp}}{3\Delta\alpha_{iso}}$$

What microscopic quantity does the anisotropy represent?

Anisotropy

$$\begin{aligned}
\Delta\alpha_{||}(t) &= 3\sigma_{12}N_1 \int g(\theta,\phi,t)\cos^2\theta\, d\Omega, \\
\Delta\alpha_{\perp}(t) &= 3\sigma_{12}N_1 \int g(\theta,\phi,t)\sin^2\theta\sin^2\phi\, d\Omega,
\end{aligned}$$

$$R(t) = \frac{\Delta\alpha_{||} - \Delta\alpha_{\perp}}{3\Delta\alpha_{iso}} \qquad \Delta\alpha_{iso} = \sigma_{12}N_1$$

$$R(t) = \int g(\theta,\varphi,t)\left[\cos^2\theta - \sin^2\theta\sin^2\varphi\right]d\Omega$$

Anisotropy

$$\Delta\alpha_{||}(t) = 3\sigma_{12}N_1\int g(\theta,\phi,t)\cos^2\theta\, d\Omega,$$

$$\Delta\alpha_{\perp}(t) = 3\sigma_{12}N_1\int g(\theta,\phi,t)\sin^2\theta\sin^2\phi\, d\Omega,$$

Indeed:
The anisotropy reflects the time-dependent distribution of excited molecules!

$$R(t) = \int g(\theta,\varphi,t)\left[\cos^2\theta - \sin^2\theta\sin^2\varphi\right]d\Omega$$

Anisotropy

- Expression is difficult to interpret
- Let’s rewrite in terms of properties of the individual molecules

$$R(t) = \int g(\theta,\varphi,t)\left[\cos^2\theta - \sin^2\theta\sin^2\varphi\right]d\Omega$$

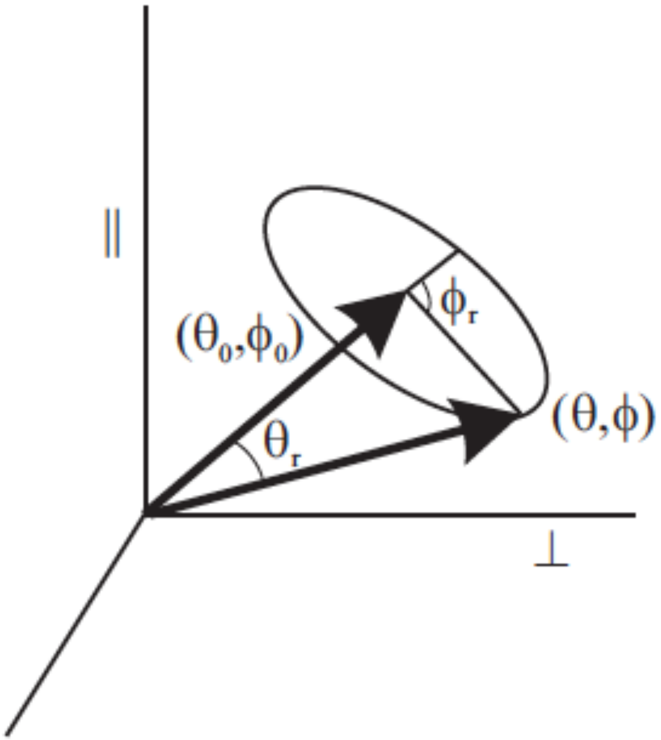
Anisotropy

$$g(\theta,\varphi,t) = \int p(\theta,\varphi,t \mid \theta_0,\varphi_0,0)g(\theta_0,\varphi_0,0)\, d\Omega_0$$

$$p(\theta,\varphi,t \mid \theta_0,\varphi_0,0)\, d\Omega =$$

- Probability that a molecule with orientation (θ_0,ϕ_0) at t=0 has diffused to (θ,ϕ) at t=0

- Green's function for the rotational diffusion equation



Anisotropy

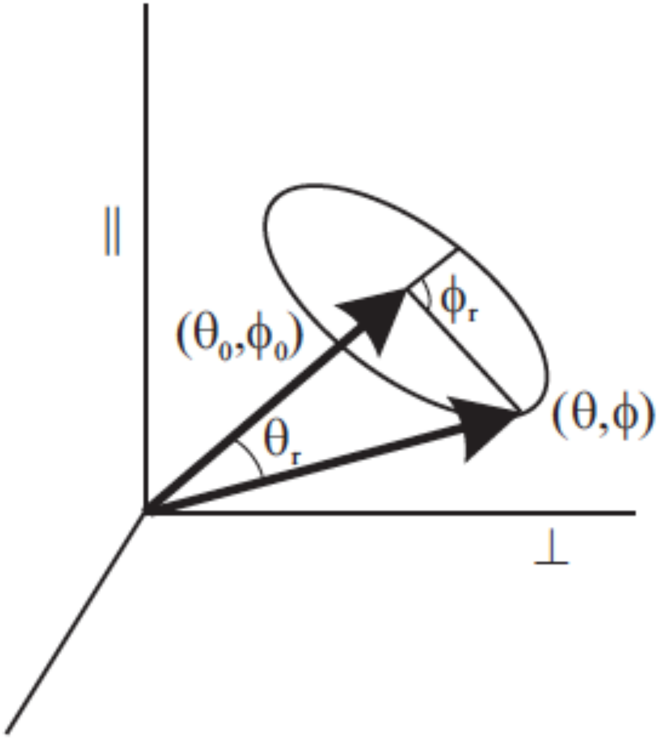
$$g(\theta,\varphi,t) = \int p(\theta,\varphi,t \mid \theta_0,\varphi_0,0)\, g(\theta_0,\varphi_0,0)\, d\Omega_0$$

$$g(\theta,\varphi,t) = \int p(\theta,\varphi,t \mid \theta_0,\varphi_0,0)\, \frac{3}{4\pi}\cos^2\theta_0\, d\Omega_0$$

Anisotropy

$$R(t) = \int g(\theta,\varphi,t)\left[\cos^2\theta - \sin^2\theta\sin^2\varphi\right]d\Omega$$

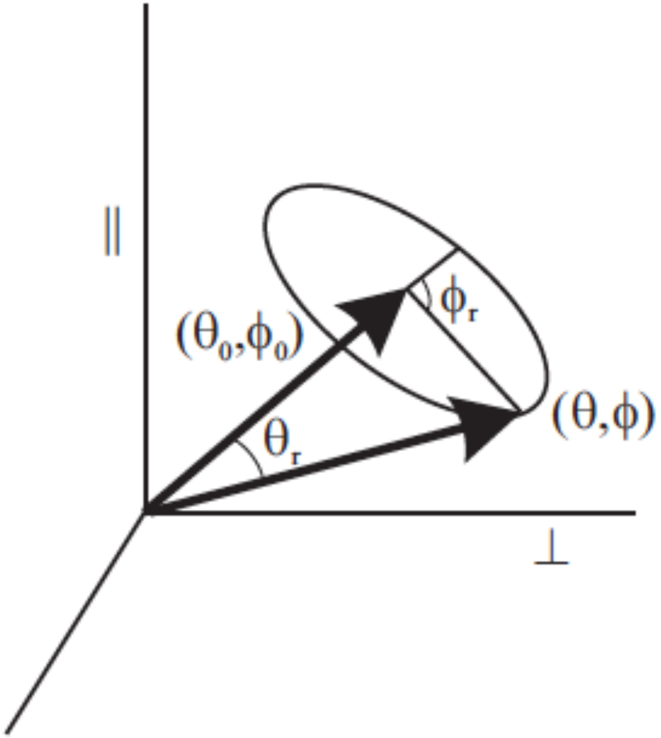
$$R(t) = \int\int p(\theta,\varphi,t \mid \theta_0,\varphi_0,0)\frac{3\cos^2\theta_0}{4\pi}[\cos^2\theta - \sin^2\theta\sin^2\varphi]d\Omega d\Omega_0$$



Anisotropy

$$R(t) = \int\int p(\theta,\varphi,t \mid \theta_0,\varphi_0,0)\frac{3\cos^2\theta_0}{4\pi}[\cos^2\theta - \sin^2\theta\sin^2\varphi]d\Omega d\Omega_0$$

Change integration variables to (θ_0,ϕ_0) and (θ_r,ϕ_r)



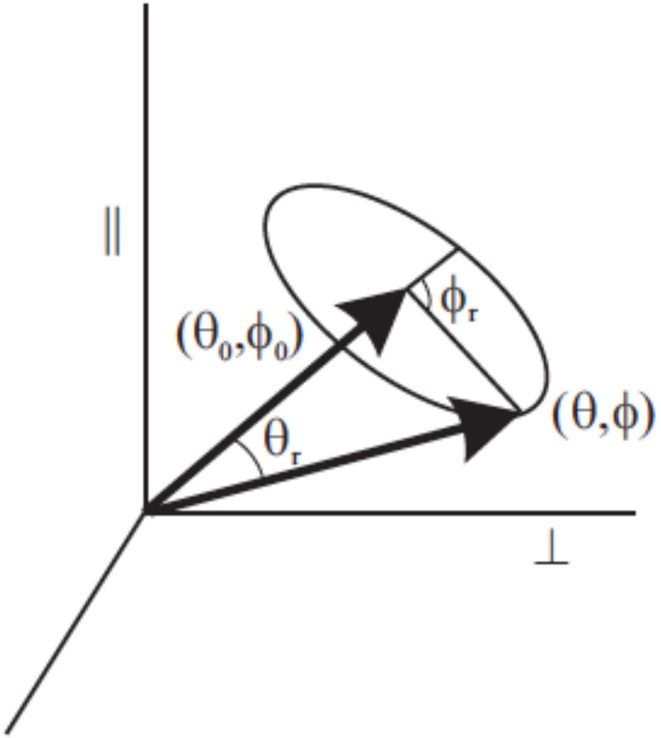
Anisotropy

$$R(t) = \int\int p(\theta,\varphi,t \mid \theta_0,\varphi_0,0)\frac{3\cos^2\theta_0}{4\pi}[\cos^2\theta - \sin^2\theta\sin^2\varphi]d\Omega d\Omega_0$$

- Change integration variables to (θ_0,ϕ_0) and (θ_r,ϕ_r)
- Do a lot of algebra

- Finally this gives

$$\begin{aligned} R(t) &= \frac{2}{5}\langle P_2(\cos\theta_r)\rangle, \\ &= \frac{2}{5}\langle P_2(\vec{\mu}(0)\cdot\vec{\mu}(t))\rangle, \\ &= \frac{2}{5}\langle(3\cos^2\theta_r - 1)/2\rangle \end{aligned}$$



Anisotropy

$$\begin{aligned} R(t) &= \frac{2}{5}\langle P_2(\cos\theta_r)\rangle, \\ &= \frac{2}{5}\langle P_2(\vec{\mu}(0)\cdot\vec{\mu}(t))\rangle, \\ &= \frac{2}{5}\langle(3\cos^2\theta_r - 1)/2\rangle \end{aligned}$$

Jump/diffusion angle θ_r

The anisotropy is the average over all molecules of the following function of θ_r

$$\frac{2}{5}\cdot\frac{3\cos^2\theta_r - 1}{2}$$

Simple applications

- Isotropic diffusion (check)

- Delocalization in a plane

- Energy transfer over an angle θ_t

$$R(t) = \frac{2}{5}\left\langle \frac{3\cos^2\theta_r(t) - 1}{2} \right\rangle$$

Summary ‘Polarization properties’

- Moving from the lab frame to a molecular frame

- Isotropic signal

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

- Anisotropy

$$R(t) = \frac{2}{5}\left\langle \frac{3\cos^2\theta_r(t) - 1}{2} \right\rangle$$