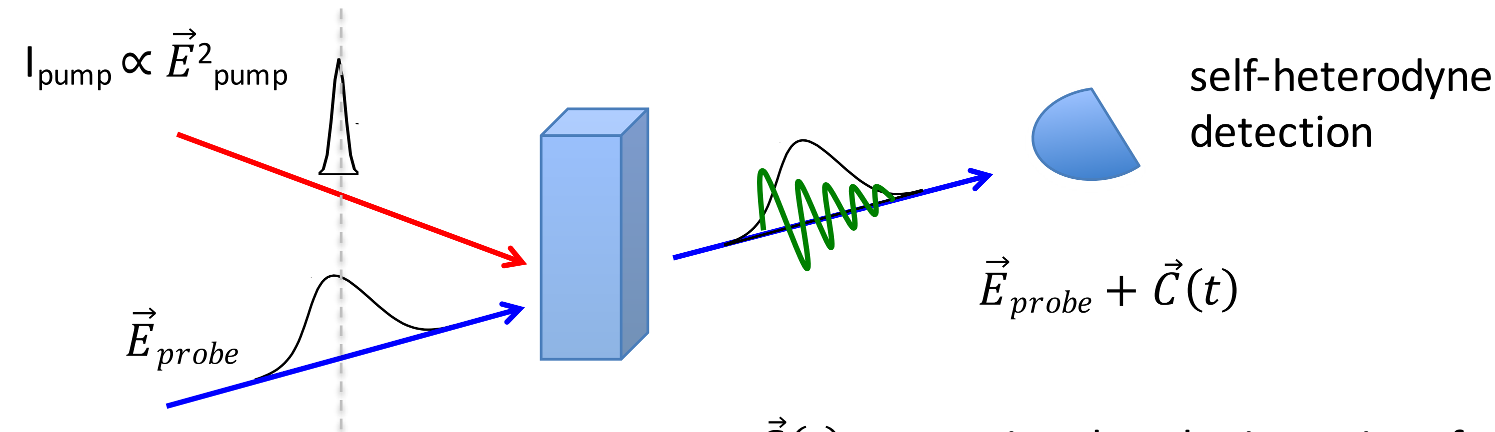
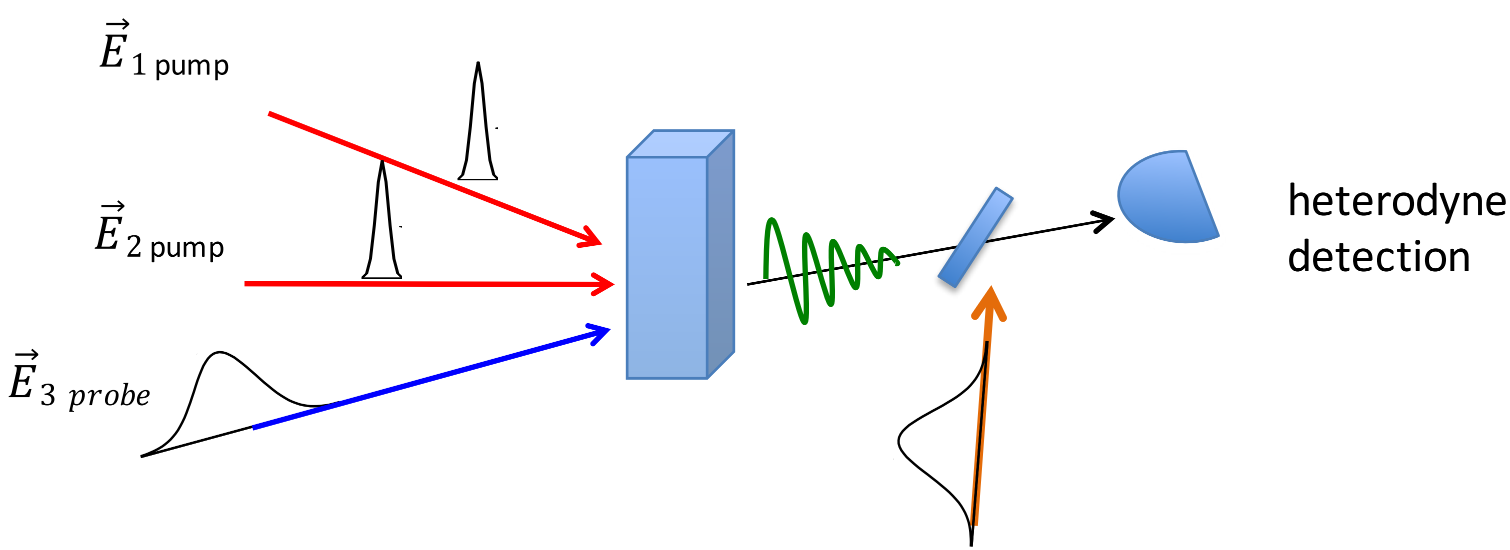
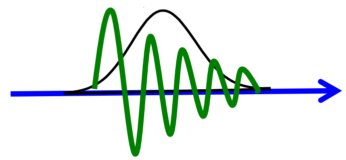
Heterodyne detection of a weak signal:



$\vec{C}(t)$ proportional to the intensity of the pump but quadratic detector makes the signal dependent to the square of the pump intensity!

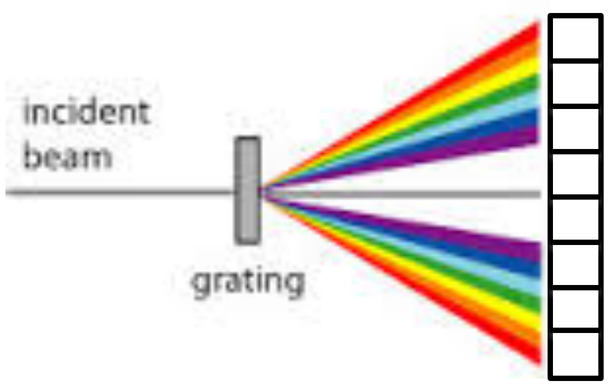




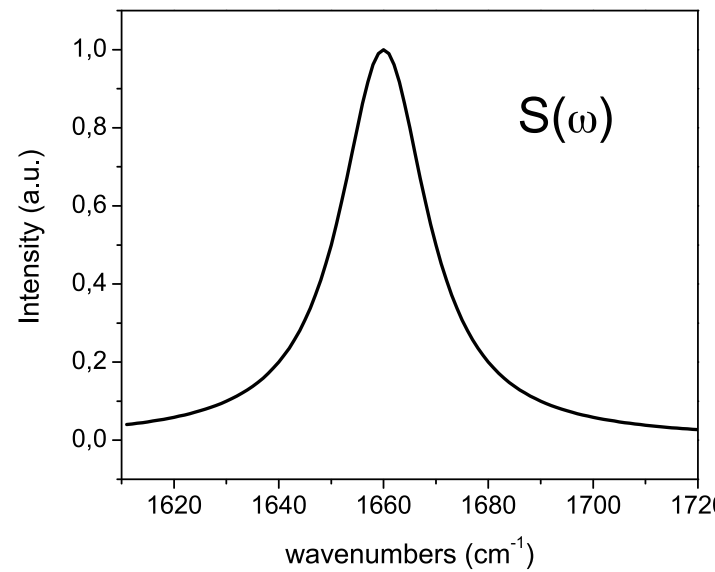
$\vec{C}(t)$ The Signal

$$C(t) = < \mu(t)\mu(0) >$$

Correlation function of transition dipole moment (electronic dipole, vibration…)



MONOCHROMATOR
Intrinsic Fourier Transformation



$$S(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt e^{i\omega t} < \mu(t)\mu(0) >$$

NB: <…> = average on all possible n states of the system at thermal equilibrium.

Statistics and Spectroscopy

$$C(t) = < A(t)A(0) >$$

a generic observable A fluctuates stochastically over time

In solution: there is no way to deterministically preview energy and position of all particles at each istant.

The **correlation function** describes for how long fluctuations of A remains correlated.

Classical definitions:

$$< A >= \int dAAP(A)$$

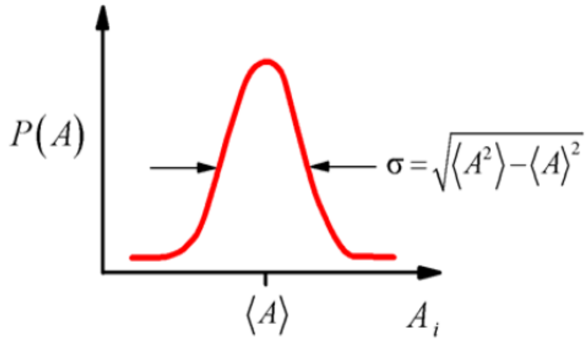
Expectation value

$$P(A) = \frac{g_i e^{\frac{-E_i}{KT}}}{\sum_i^n g_i e^{\frac{-E_i}{KT}}}$$

Boltzmannn distribution at temperature T_{room} over *n* micro-states

$$< A^2 >= \int dAA^2 P(A)$$

Mean square



Root mean square
STANDARD DEVIATION

Variance $\sigma^2 =< A^2 > -< A >^2$

Covariance $C_{AB} =< AB >-< A >< B >$

$$C_{AA'}(t) = < A(t) A(0) >-< A(t) >< A(0) > =$$

$$= (< A(0)^2 > -< A(0) >^2) e^{-i\omega t}$$

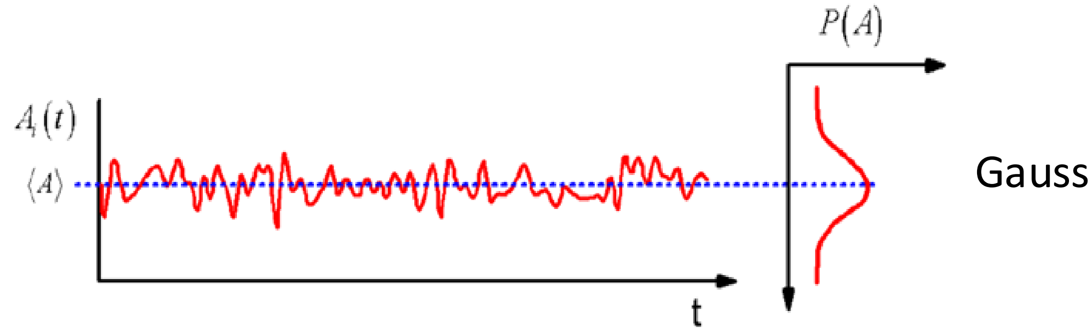
$$A(t) = A(0) e^{-i\omega t}$$

QM definition:

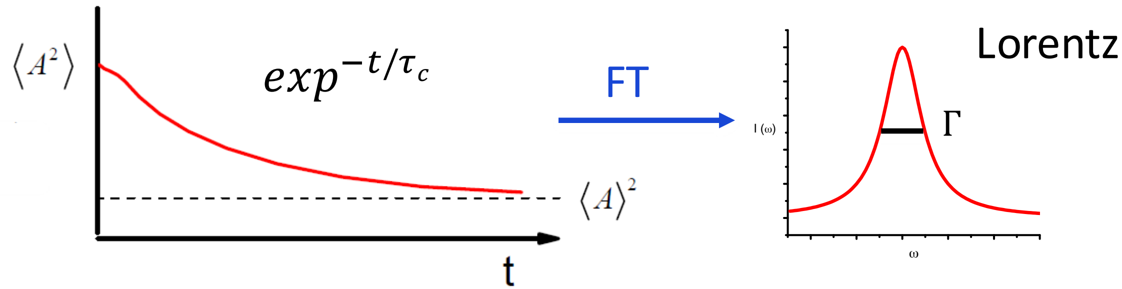
$$C_{AA'}(t) = \sum_n p_n \langle n | A(t') A(t) | n \rangle$$

$$|\psi >= \sum_n a_n | n >$$

Uncorrelated fluctuations



Correlated fluctuations



Homogeneous and Inhomogeneous BROADENING

HOMOGENEOUS: very fast dynamic processes mix up oscillator frequencies within the EM perturbation.

IN-HOMOGENEOUS: the EM field probes a static distribution of slightly different oscillator frequencies.

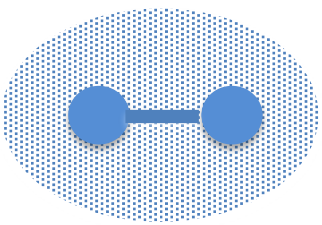
natural broadening

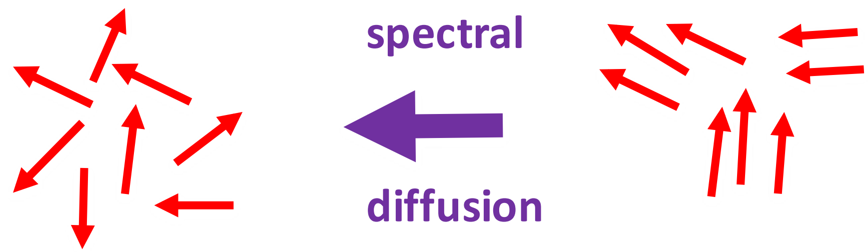
random distribution

static distribution

HOMOGENEOUS

INHOMOGENEOUS





You cannot simultaneous defines position and energy of all electrons involved in the dipole transition Heisenberg uncertainty

Your detection time is so long that you are not able anymore to distinguish differences among your oscillators

There are well distinguished groups of oscillators in your sample

natural broadening present even for a single oscillator

homogeneous and inhomogeneous broadening present for an ensemble of oscillators

Homogeneous broadening effects:

$$\Gamma_{tot} = \frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*} + \frac{1}{T_{or}}$$

Intra-molecular processes:
POPULATION TIME

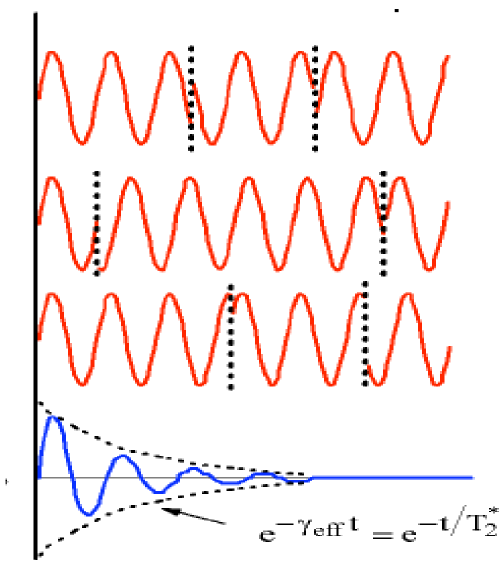
$$\frac{1}{T_1} = \frac{1}{T_{rad}} + \frac{1}{T_{NR}}$$

Radiative processes gives a homogeneous broadening because there is a correlation.

Non radiative thermal effects give the spectral diffusion .

Inter-molecular processes:
PURE DEPHASING

Due to collisions or different attractive/repulsive potentials of their own environment, oscillators change phase.



Dipole reorientation:

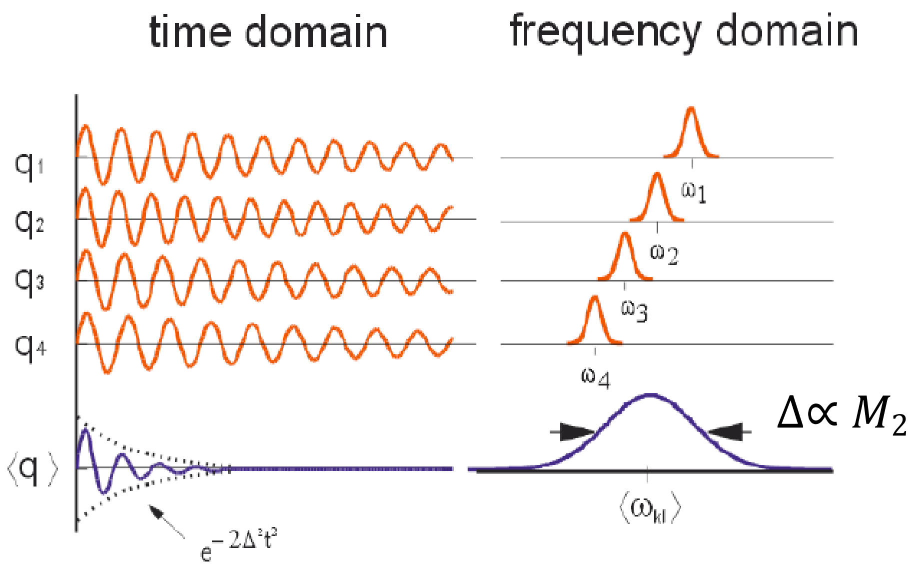
Dipoles are first alligned to the EM field then randomly change direction.

Static inhomogeneous broadening:

Several oscillator frequencies

sum

Damped oscillation



Second order moment of the gaussian function related to standard dev.

$$C(t) =< \mu(t)\mu(0) >= exp^{-t/\tau_c} \cdot exp^{-2\Delta^2 t^2}$$

$$\frac{1}{\tau_c} = \frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*} + \frac{1}{T_{or}}$$

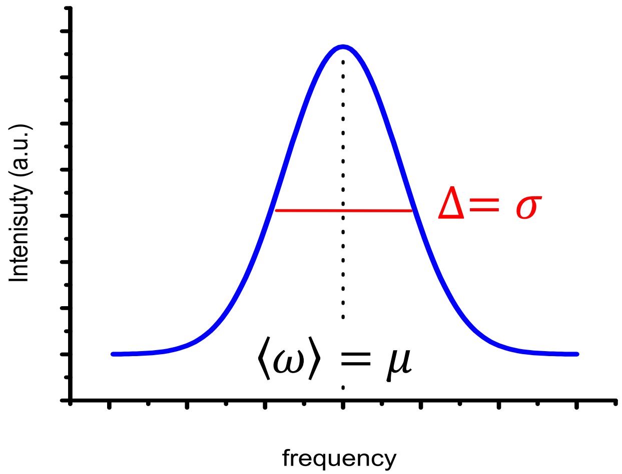
Convolution of several lorentzian bands

SIMOULTANEOUS CONTRIBUTIONS PRESENT!!!

Homogeneous and inhomogeneous broadening are the two limit cases of the KUBO model!

KUBO MODEL: Δ and τ_c

Δ:



Central limit theorem for a normal distribution:

$$\omega(t) = <\omega> + \delta\omega(t)$$

$$\langle \delta\omega(t) \rangle = 0$$

$$\Delta = \langle \delta\omega(t)^2 \rangle^{1/2} \quad \text{FWHM}$$

Intensity of fluctuations: all posiible value of frequencies that oscillator can explore

$$y = \frac{A}{\sigma} \cdot exp^{-2\frac{(x-\mu)^2}{\sigma^2}} \qquad \Delta = x - \mu$$

τ_c:

$$\mu(t) = \mu(0)e^{-i\omega t}$$

$$\frac{\partial\mu}{\partial t} = -i\omega\mu(t)$$

$$\mu(t) = \mu(0)exp\left[-i\int_0^t \omega(\tau)\partial\tau\right] = \mu(0)exp\left[-i <\omega> t - i\int_0^t \delta\omega(\tau)\partial\tau\right]$$

$$\mu(t) = \mu(0) exp\left[-i\int_0^t \omega(\tau)\partial\tau\right] = \mu(0) exp\left[-i <\omega> t - i\int_0^t \delta\omega(\tau)\partial\tau\right]$$

$$C_{\mu\mu} = \langle\mu(t)\mu(0)\rangle = |\mu(0)|^2 \cdot e^{-i<\omega>t} \cdot \underbrace{\left\langle e^{-i\int_0^t \delta\omega(\tau)d\tau}\right\rangle}_{F(t)}$$

Average on exp functions

$F(t) =$

$$= exp\left[-i\int_0^t d\tau < \delta\omega(\tau') > + \frac{i^2}{2!}\int_0^t d\tau' \int_0^{\tau'} d\tau'' \underline{< \delta\omega(\tau'')\delta\omega(\tau') >} + \cdots\right]$$

Cumulant expansion

Time interval 0 - τ

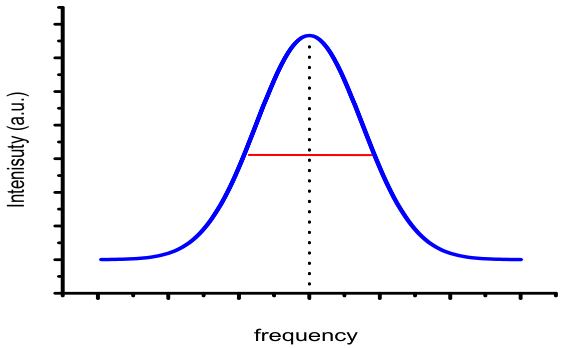
$$F(t) = exp\left[-\frac{1}{2}\int_0^t d\tau' \int_0^{\tau'} d\tau < \underbrace{\delta\omega(\tau)\delta\omega(0)}_{C_{\delta\omega}(t)} >\right]$$

damping of oscillations

$$C_{\mu\mu} \propto C_{\delta\omega\delta\omega}$$

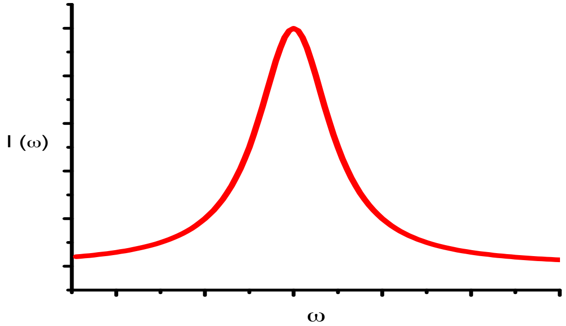
$$C_{\delta\omega\delta\omega} = A^2 e^{-t/\tau_C}$$

$\tau_C >> \Delta$: For long correlaction time of fluctuations, each family of oscillator does not correlate anyhow with some other one and a static distribution of frequencies is observed.



$$F(t) = \exp(-\Delta^2 t^2/2)$$

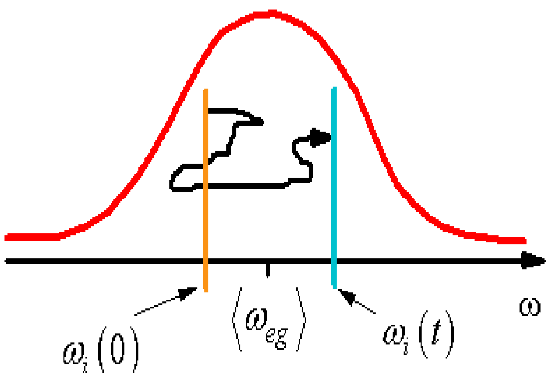
$\tau_C << \Delta$: For short correlaction time, oscillators explore rapidly all possible frequencies around the central mean value, so rapidly that the band appears even narrower than the real frequency distribution probability: "*motional narrowing*"



$$F(t) = \exp(-t/T_2)$$

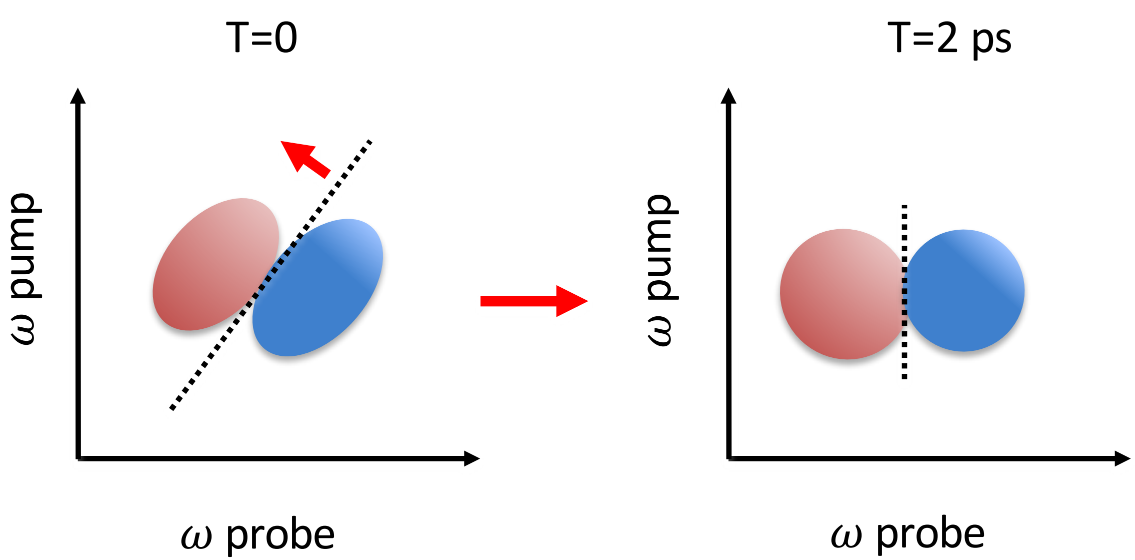
Generally, the real case is an intermediate case where SPECTRAL DIFFUSION is observed!!!

The spectral diffusion



What you really have is a Voigt profile
(weighted sum of a lorentzian and a gaussian profile)
And you are not able to disentangle on linear spectra
Homo- inhomo geneous contributions!

Expanding on a second dimension…



- A signal tilted along the diagonal is inhomogeneously broaden.
- Its antidiagonal bandwidth is a measure of the homogeneous width.
- The tilt can evolve toward the vertical in the presence of dynamic processes: final homogeneous distribution.

Moments in statistics:

$$M_1 = \int_{-\infty}^{\infty} \delta\omega \, f(\omega) \, d\omega = \sum_i \delta\omega \, p_\omega$$

mean value

$$M_2 = \int_{-\infty}^{\infty} \delta\omega^2 \, f(\omega) \, d\omega = \sum_i \delta\omega^2 \, p_\omega$$

variance (fwhm)

$$M_3 = \int_{-\infty}^{\infty} \delta\omega^3 \, f(\omega) \, d\omega = \sum_i \delta\omega^3 \, p_\omega$$

simmetry of the band

fluctuations $\delta\omega$ are equally probable around the mean value: $M_3 = 0$