Two-dimensional coherent Fourier transformed spectroscopy

Summary of the method

- analysis of a third order response
  - correlates absorption and emission
  - correlation is mediated by excited state dynamics

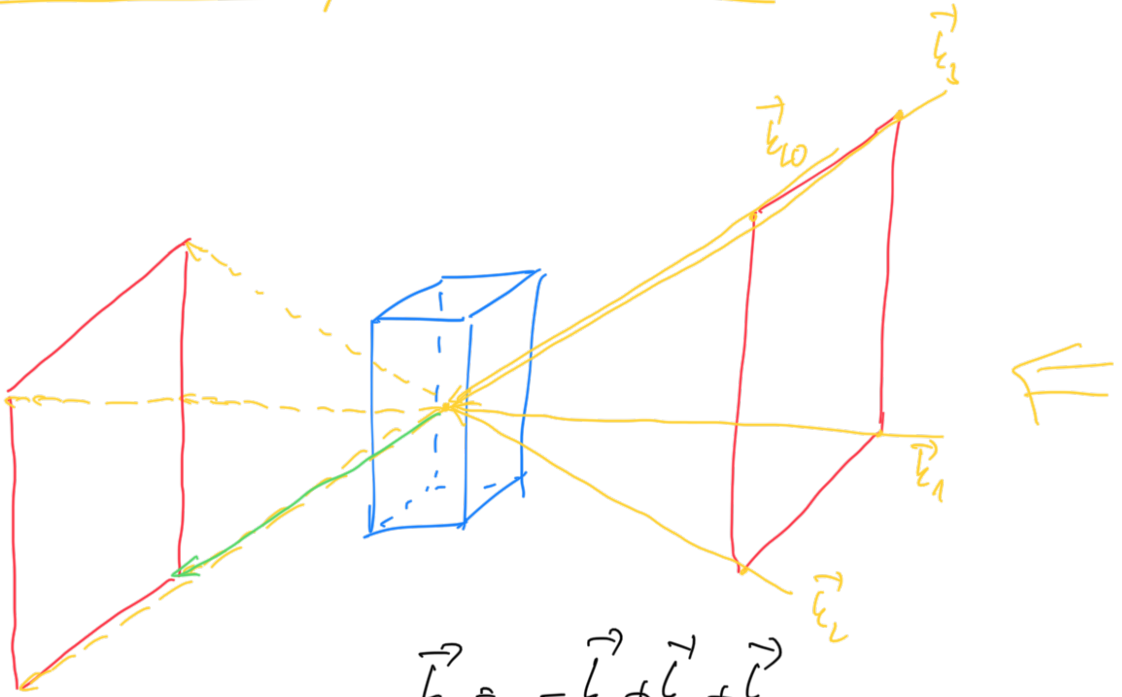
⇒ we can observe excited state dynamics

Notes:

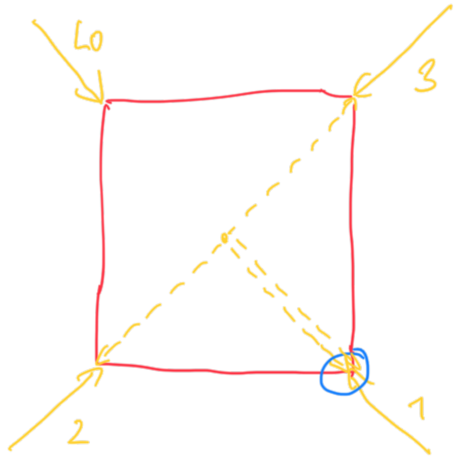
- there is a „static" groundstate signal
- emission has a generalized meaning
  - different components
    - ~ SE
    - ~ ESA
    - ~ GSB

    } differ by phase

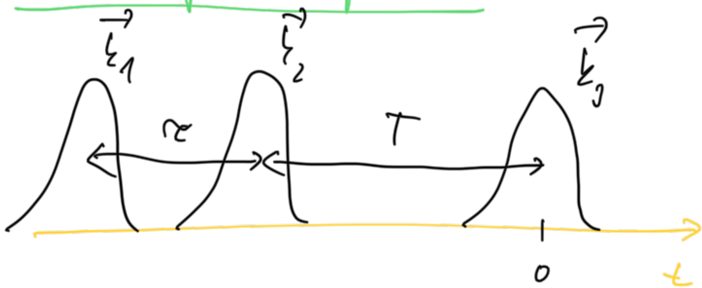
How is the 2D spectrum measured?



$$\vec{k}_s = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$$

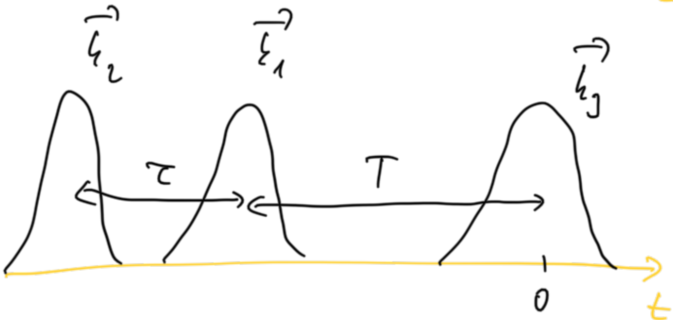


Order of the pulses



$\Rightarrow$ Rephasing signal/spectrum

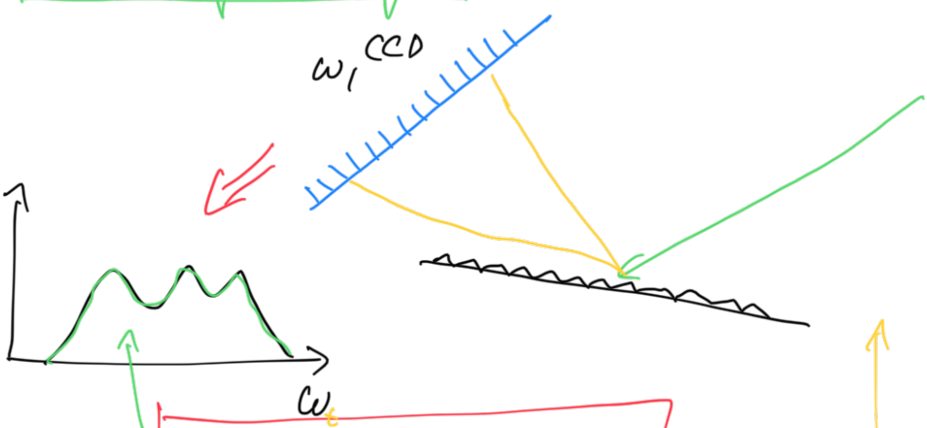
$\sigma_R(\omega_t, T, \tau)$



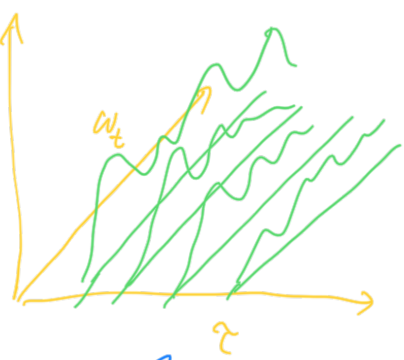
$\Rightarrow$ Non-rephasing signal/spectrum

$\sigma_{NR}(\omega_t, T, \tau)$

Detection of the signal



$$\boxed{\mathrm{Re}\left[\sigma_{R/NR}(\omega_t, T, \tau)\, e^{i\phi}\right]}$$



$\Uparrow$

Fourier transform

Two problems to solve

1) How to measure complex signal?
2) How to fix the phase?

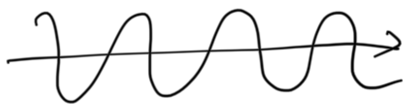
Detection of the complex signal

- why complex? : we want to add σ_R and σ_{NR}

- σ_R, σ_{NR} as a function of τ

$$\sigma_R(\omega, T, \tau) \approx e^{i\omega_{vg}\tau}$$

$$\mathrm{Re}\, e^{i\omega_{vg}\tau} = \cos \omega_{vg}\tau$$

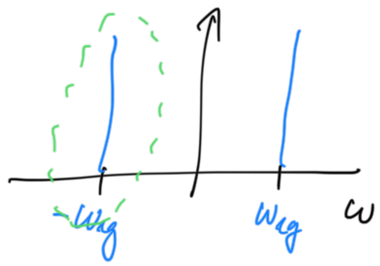


How can we get $e^{i\omega_{vg}\tau}$ from $\cos\omega_{vg}\tau$?

$$\boxed{\cos \omega_{vg}\tau = \frac{1}{2}\left(e^{i\omega_{vg}\tau} + e^{-i\omega_{vg}\tau}\right)}$$

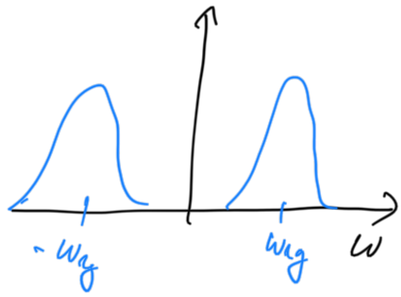
real signal

FT $\Longrightarrow$



Real signal

$\Longrightarrow$

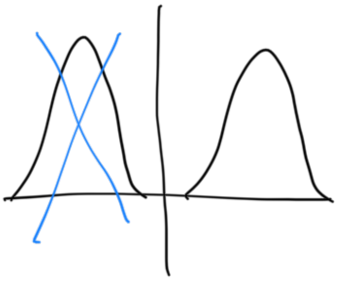


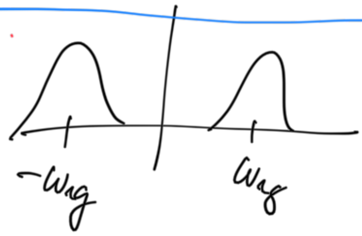
Experimental data processing procedure

$$\mathrm{Re}\,\sigma_R(\omega,T,\tau)e^{i\phi} \xrightarrow{FT} FT\left[\mathrm{Re}\,\sigma_R(\omega,T,\tau)e^{i\phi}\right](\omega_\tau)$$

remove $e^{-i\omega_{eg}\tau}$

$\longrightarrow$





FT^{-1}

$$\longrightarrow \sigma_R(\omega,T,\tau)e^{i\phi}$$ $\Leftarrow$ complex rephasing signal

The same procedure with NR !

$\Downarrow$ we preserve $e^{-i\omega_{eg}\tau}$ (remove $e^{i\omega_{eg}\tau}$)

2D Fourier transformed spectrum !

$$\sigma_m(\omega,T,\omega_\tau) = \int_0^\infty d\tau\, \sigma_R(\omega,T,\tau)e^{i\phi}e^{-i\omega_\tau\tau}$$

$$+ \int_0^\infty d\tau\, \sigma_{NR}(\omega,T,\tau)e^{i\phi}e^{i\omega_\tau\tau}$$

$$= e^{i\phi}\int_{-\infty}^{\infty} d\tau \left[\Theta(\tau)\sigma_R(\omega,T,\tau) + \Theta(-\tau)\sigma_{NR}(\omega,T,|\tau|)\right]e^{-i\omega_\tau\tau}$$

$$\Theta(\tau=0) = \frac{1}{2}$$

Fixing the phase ϕ

How does $\delta(\omega, T, \omega_\tau)$ and pump-probe signals compare?

1) usually different sign convention

$$R\,\delta(\omega, T, \omega_\tau) \approx - \text{pump-probe}$$

SE positive

stimulated emission (SE) is negative

2) Some prefactors such as $\frac{\omega}{n(\omega)}$ ⟵ can be removed

3) $$\mathrm{Re}\; \delta(\omega, T, \tau = 0) \approx - \text{pump-probe}$$

FT of ω_τ

sum of R and NR pathway at $\tau = 0$

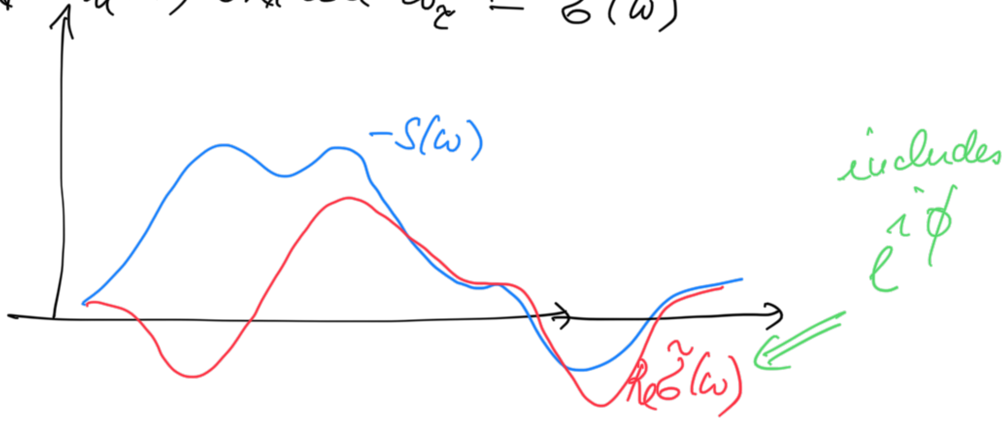
$$\boxed{- \text{pump-probe}} = \mathrm{Re}\; \delta(\omega, T, \tau=0) = \mathrm{Re} \int_{-\infty}^{\infty} \frac{d\omega_\tau}{2\pi}\, \delta(\omega, T, \omega_\tau)\, e^{i\omega_\tau \tau}\Big|_{\tau=0}$$

$$\boxed{= \mathrm{Re} \int_{-\infty}^{\infty} \frac{d\omega_\tau}{2\pi}\, \delta(\omega, T, \omega_\tau)}$$

1) we measure $\underline{\delta_m = e^{i\phi} \delta(\omega)}$

2) we measure pump-probe $= \underline{S(\omega)}$ at certain value of T

3) we integrate $\sigma_m(\omega)$ over all ω_τ $= \tilde{\sigma}(\omega)$



For certain value of ϕ we get an agreement!

$$\boxed{\sigma(\omega, T, \omega_\tau) = e^{-i\phi}\,\sigma_m(\omega, T, \omega_\tau)}$$

after <u>PHASING PROCEDURE</u>

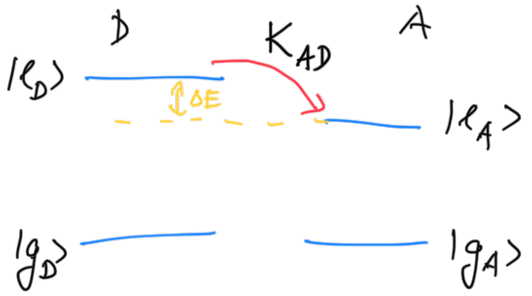
$\rightarrow$ $\mathrm{Re}\,\sigma(\omega_t, T, \omega_\tau)$ ... has a good interpretation as an absorption-emission plot

This spectrum has an <u>imaginary part</u>

- no good interpretation
- represents an additional information

2D spectrum of a dimer with energy transfer

donor – acceptor



- dephasing
- energy transfer

Collective states:

$$|G\rangle = |g_D\rangle|g_A\rangle$$
$$|A\rangle = |g_D\rangle|e_A\rangle$$
$$|D\rangle = |e_D\rangle|g_A\rangle$$
$$|f\rangle = |e_D\rangle|e_A\rangle$$

Description of excited state evolution:

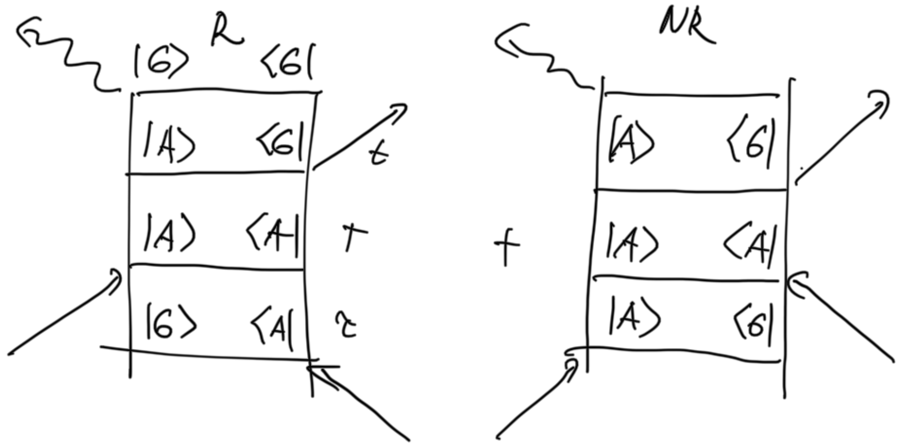
$\mathcal{U}_{AAAA}(T)$; $\mathcal{U}_{DDDD}(T)$ ← element of the evolution superoperator

$\mathcal{U}_{AADD}(T)$; $\mathcal{U}_{ADAD}(T)$ ← evolution of coherence

⇑ energy transfer from $|D\rangle \to |A\rangle$

Liouville pathways of a dimer

SE_A

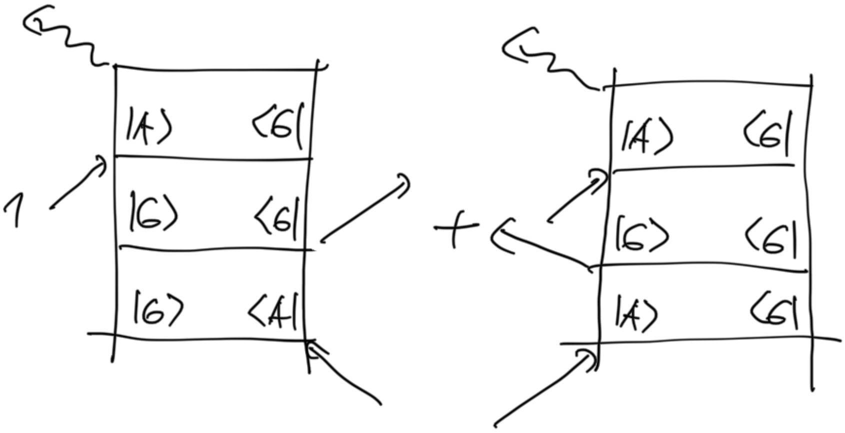


$$\langle d_A^4 \rangle_\Omega \cdot G_{AG}(\omega_t)\, \mathcal{U}_{AAAA}(T)\, \underbrace{\mathrm{Re}\, G_{AG}(\omega_\tau)}_{\text{absorption on } |A\rangle}$$

$$\mathcal{U}_{AAAA}(T) = 1$$

GSB_A

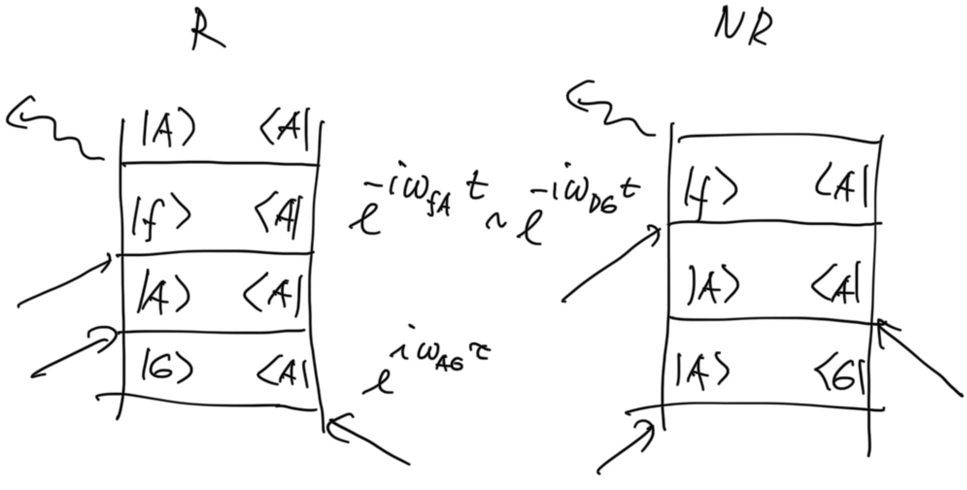
$\mathcal{U}_{GGGG}(T) = 1$



$$\langle d_A^4 \rangle\, G_{AG}(\omega_t)\, \mathcal{U}_{GGGG}(T)\, \mathrm{Re}\, G_{AG}(\omega_\tau)$$

There will be corresponding SE_D, GSB_D signals

ESA_A



$$e^{-i\omega_{fA} t} \sim e^{-i\omega_{DG} t}$$

$$e^{i\omega_{AG}\tau}$$

$$- \underbrace{\langle d_{fA}^2 d_A^2 \rangle}_{\approx d_D^2} G_{fA}(\omega_t)\, \mathcal{U}_{AAAA}(T)\, \mathrm{Re}\, G_{AG}(\omega_\tau)$$

What is d_{fA} and $G_{fA}(\omega_t)$?

Transition $|A\rangle \longrightarrow |f\rangle$ is $|e_A\rangle|g_D\rangle \longrightarrow |e_A\rangle|e_D\rangle$

$$\Rightarrow |g_D\rangle \rightarrow |e_D\rangle$$

Therefore:

$$d_{fA} \equiv d_D$$

$$\langle d_{fA}^2 d_A^2 \rangle_\Omega \equiv \langle d_D^2 d_A^2 \rangle_\Omega$$

Similarly $G_{fA}(\omega_t) \equiv G_{e_D g_D}(\omega_t) \equiv G_{DG}(\omega_t)$

ESA$_A$ $\Rightarrow$

$$- \langle d_D^2 d_A^2 \rangle\, \underline{G_{DG}(\omega_t)}\, \underline{\mathcal{U}_{AAAA}(T)}\, \mathrm{Re}\, \underline{G_{AG}(\omega_\tau)}$$

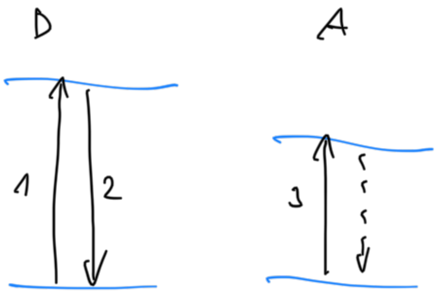
ESA$_D$ $\Rightarrow$

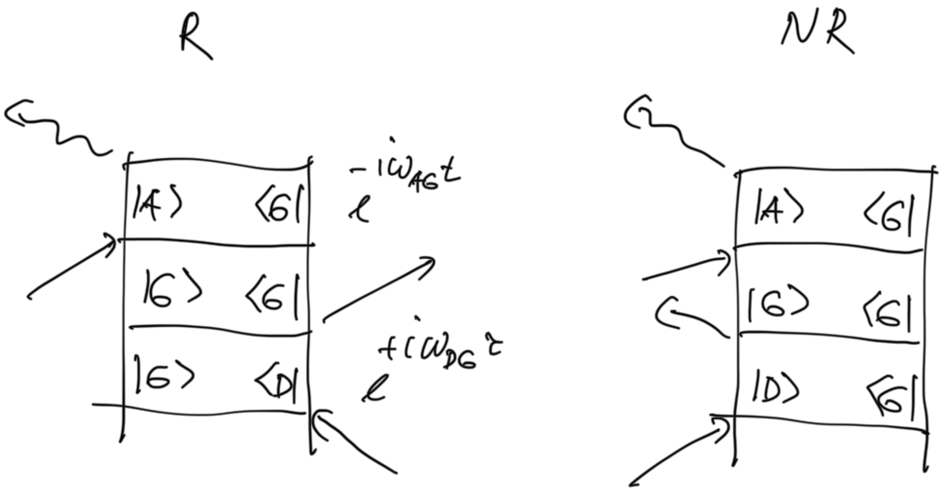
$$- \langle d_A^2 d_D^2 \rangle\, G_{AG}(\omega_t)\, \underline{\mathcal{U}_{DDDD}(T)}\, \mathrm{Re}\, G_{DG}(\omega_\tau)$$

$$\mathcal{U}_{DDDD}(T) = e^{-K_{AD} T}$$

Groundstate mixed terms

GSB_{AD}



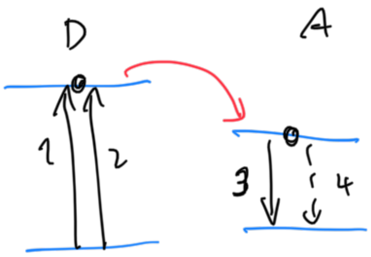


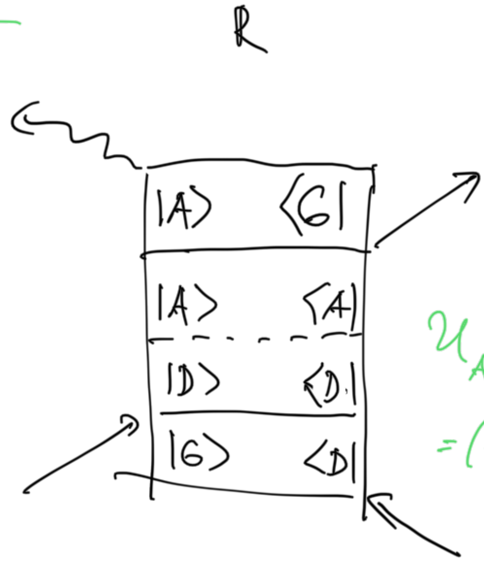
$$GSB_{AD} = \langle d_D^2 d_A^2 \rangle_\Omega \, G_{AG}(\omega_t)\, \mathcal{U}_{GGGG}(T)\, \mathrm{Re}\, G_{DG}(\omega_\tau)$$

$$GSB_{DA} = \langle d_D^2 d_A^2 \rangle_\Omega \, G_{DG}(\omega_t)\, \mathcal{U}_{GGGG}(T)\, \mathrm{Re}\, G_{AG}(\omega_\tau)$$

$$\mathcal{U}_{GGGG}(T) = 1$$

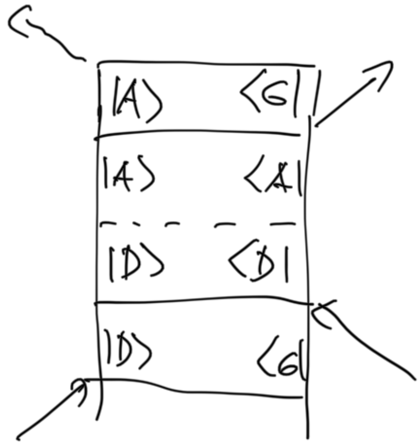
Excitation transfer terms

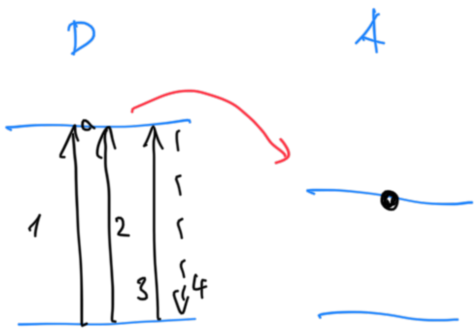


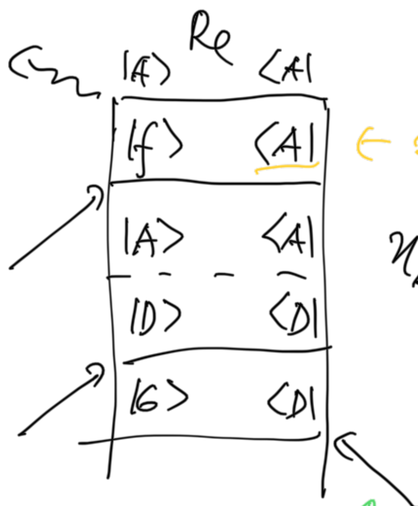


$$\mathcal{U}_{AADD}(T) = (1 - e^{-k_{AD} T})$$

$$SE_{AD} \sim \langle d_D^2 d_A^2 \rangle\, G_{AG}(\omega_t) \times \mathcal{U}_{AADD}(T)\, \mathrm{Re}\, G_{DG}(\omega_\tau)$$







$\leftarrow \approx |D\rangle \langle G|$

$$\mathcal{U}_{AADD}(T) = \left(1 - e^{-K_{AD} T}\right)$$

$$ESA_{AD} \sim -\langle d_D^4 \rangle_\Omega\, G_{DG}(\omega_t)\, \mathcal{U}_{AADD}(T)\, \mathrm{Re}\, G_{DG}(\omega_\tau)$$

minus sign

$$+ NR$$

Sum of the described pathways gives the total 2D spectrum!

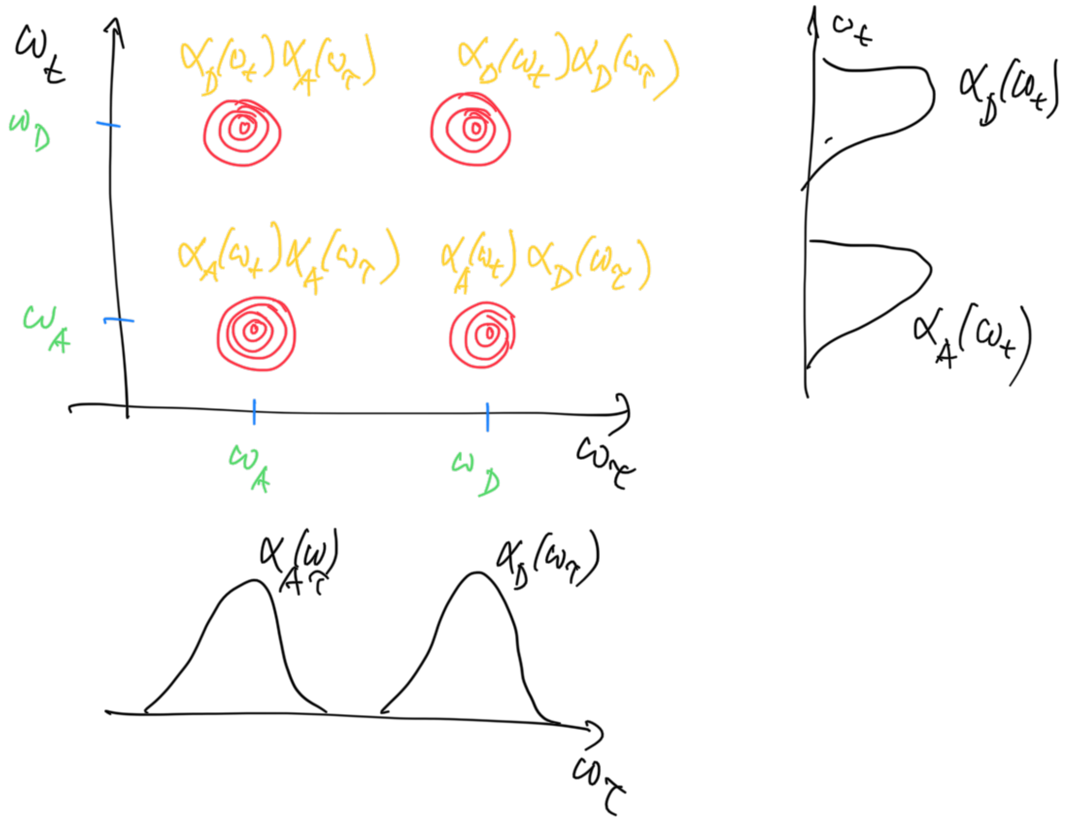
Placing the signals

centered around ω_A

$$\mathrm{Re}\, G_{AG}(\omega) \rightarrow \alpha_A(\omega) = \tilde{\alpha}_A(\omega - \omega_A) \approx \tilde{\alpha}(\omega - \omega_A)$$

$$\mathrm{Re}\, G_{DG}(\omega) \rightarrow \alpha_D(\omega) = \tilde{\alpha}_D(\omega - \omega_D)$$

all possible lineshapes and positions



Spectrum of the D–A dimer