NITheCS mini-school
Modelling optical spectra
28 August 2024

Towan Nöthling

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

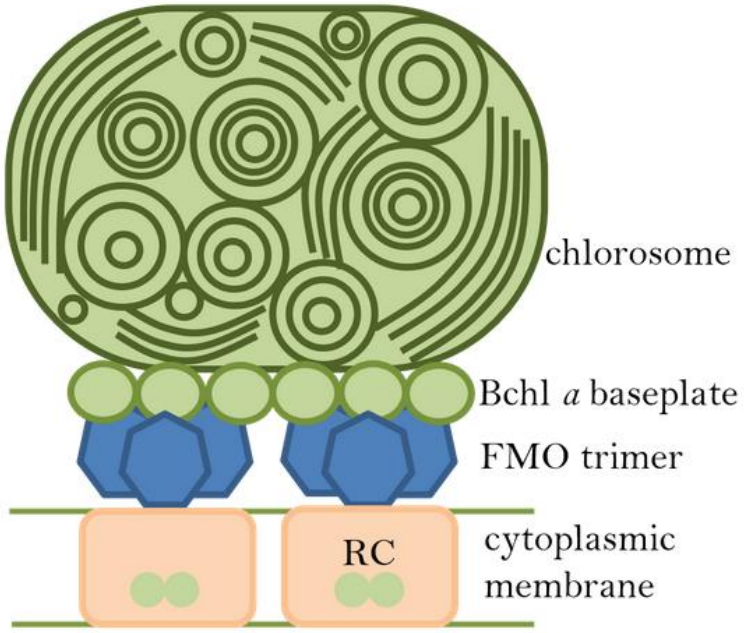
Photo credit: https://www.flickr.com/photos/ingridt/5551456055

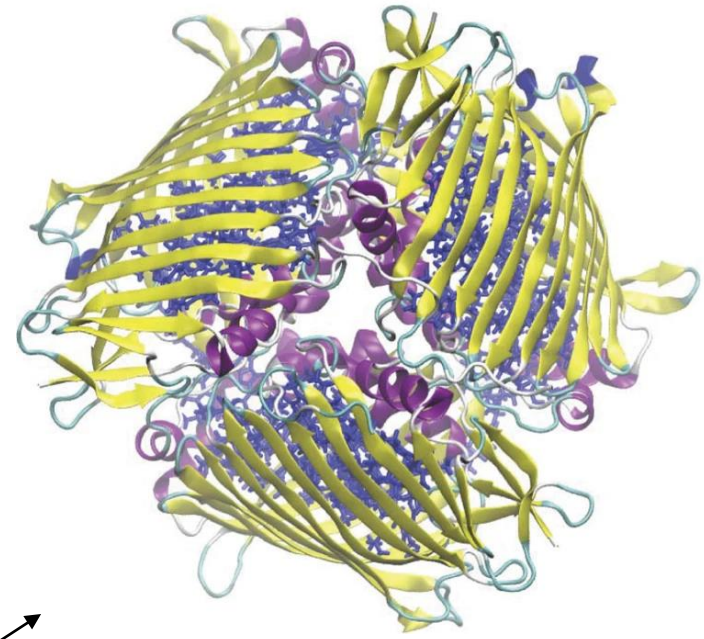

End of route
You are here

Aerial view

1. Excitation transfer dynamics is important for spectroscopy (especially nonlinear spectroscopy)
   - Förster energy transfer for incoherent hopping
   - The correlation function and spectral density characterise how the environment facilitates energy transfer
   - Redfield transfer for exciton relaxation
2. Nonlinear spectroscopy relates to the nonlinear response function
   - Third-order response
   - Pump-probe spectroscopy
   - Two-dimensional electronic spectroscopy
3. Calculate absorption spectra (very quick tutorial)

FMO complex





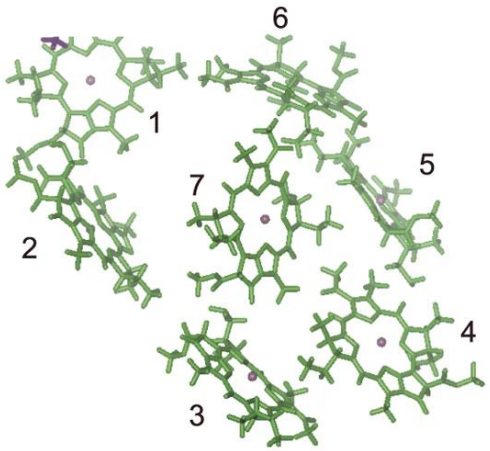
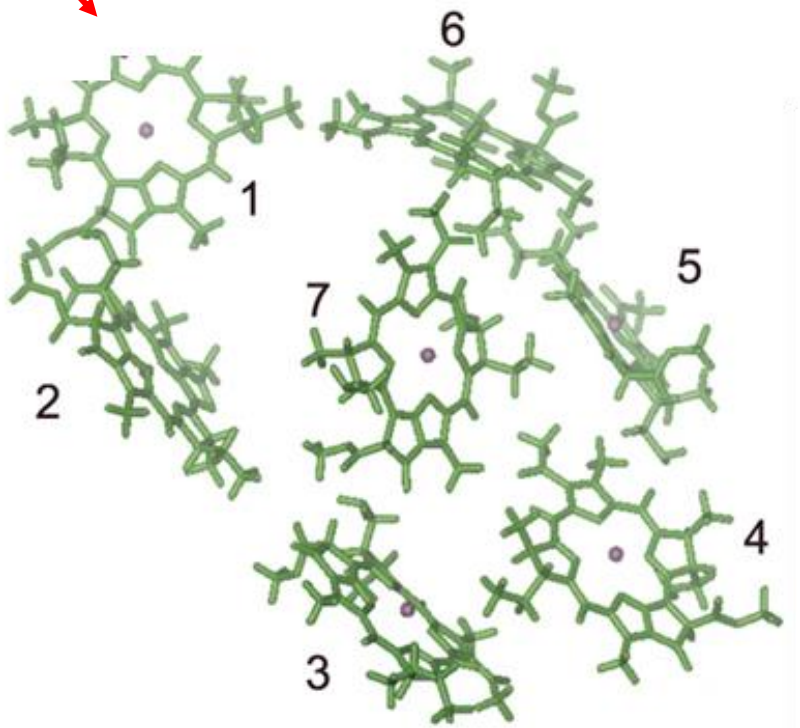


Figure credit: Jia, X., Mei, Y., Zhang, J. *et al*. *Sci Rep* **5**, 17096 (2015). CC BY 4.0

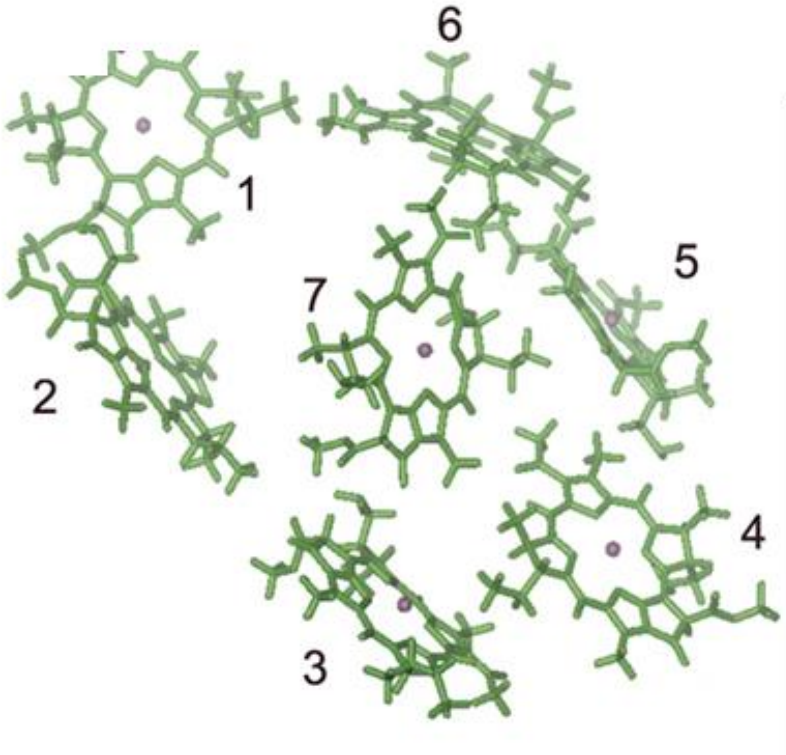
Energy transfer

in

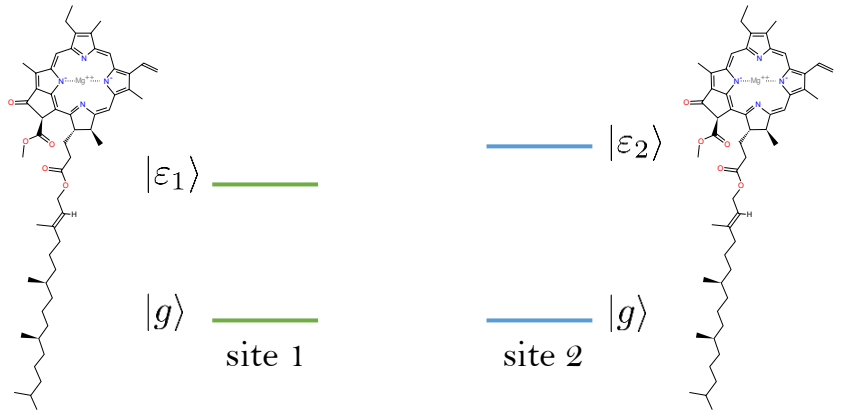


out

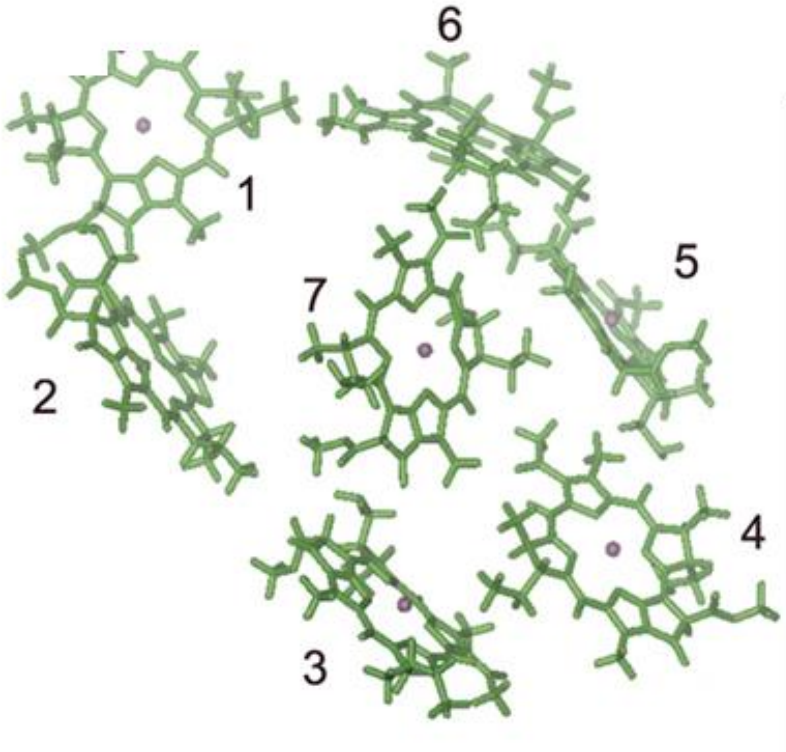
Energy transfer



$$\hat{H}_{\mathrm{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$

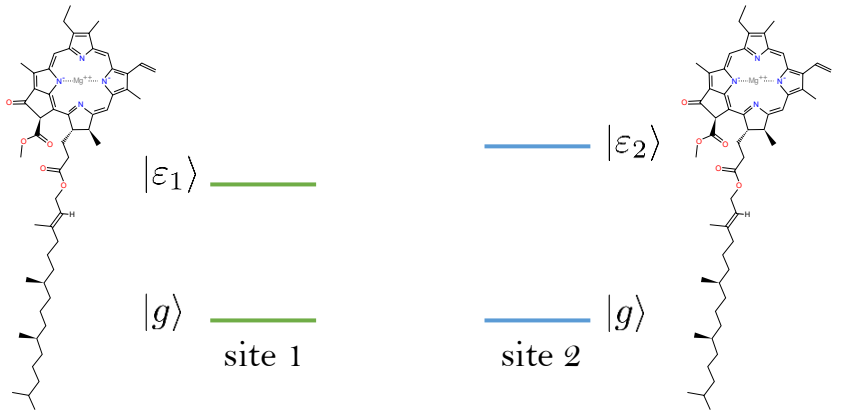


Förster theory

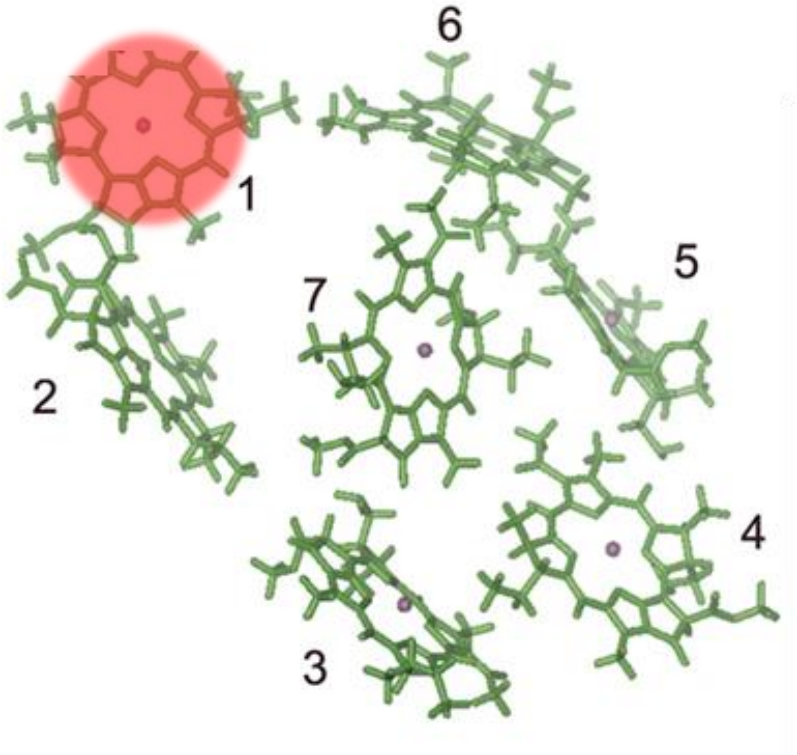


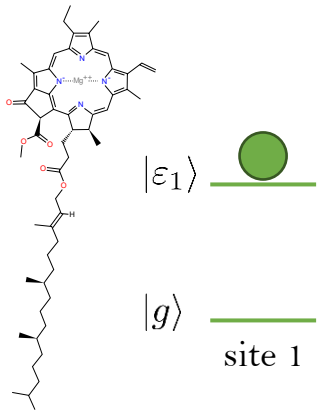
$$\hat{H}_{\mathrm{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$

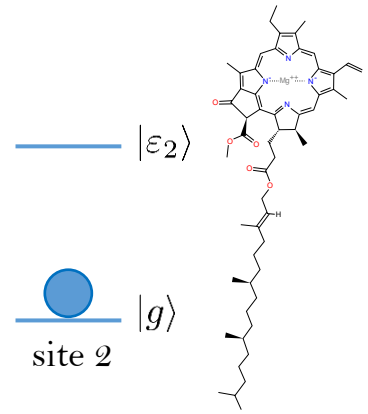
small



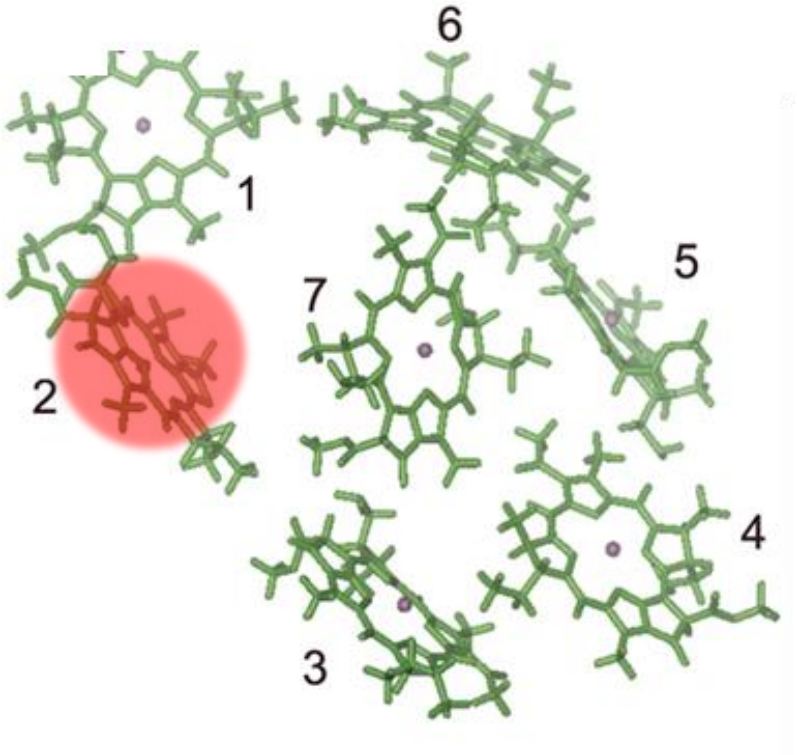
Förster theory

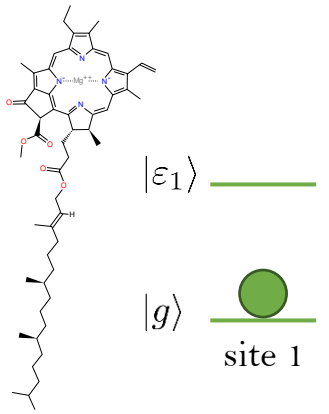


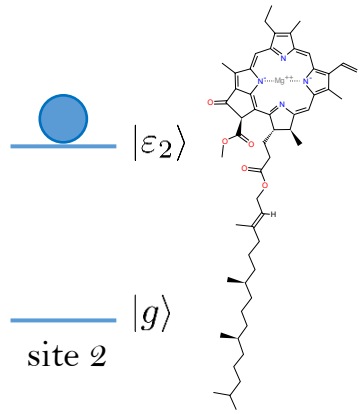




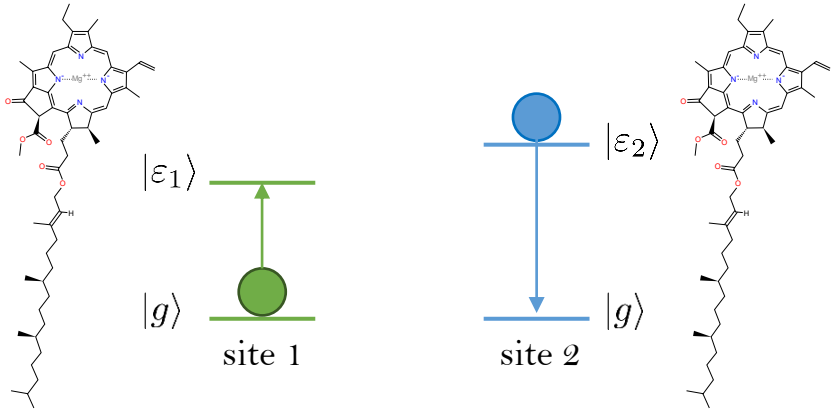
Förster theory



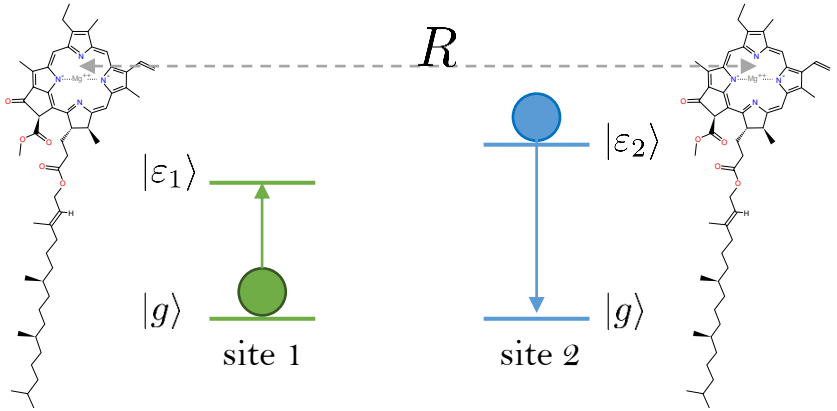




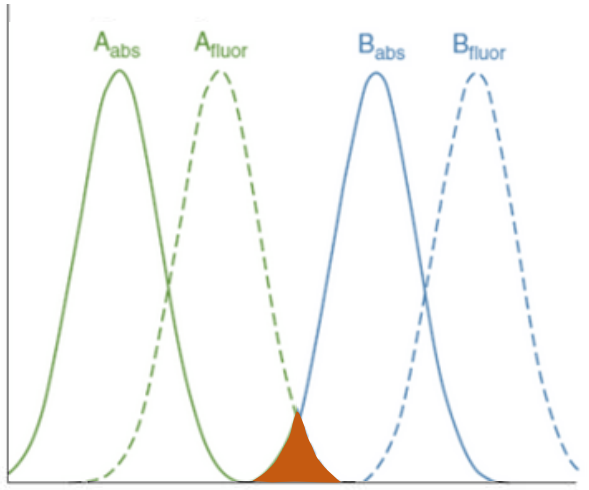
Förster theory



Förster theory

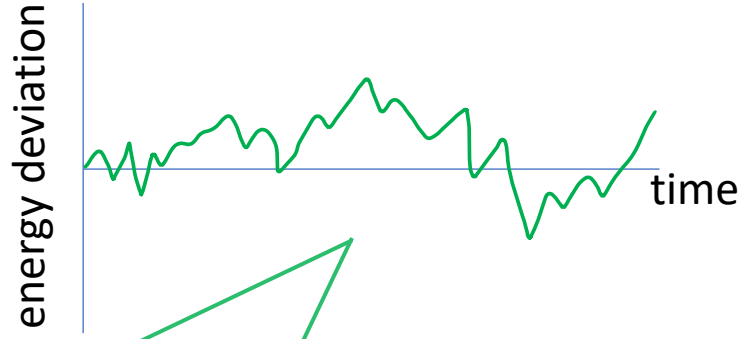


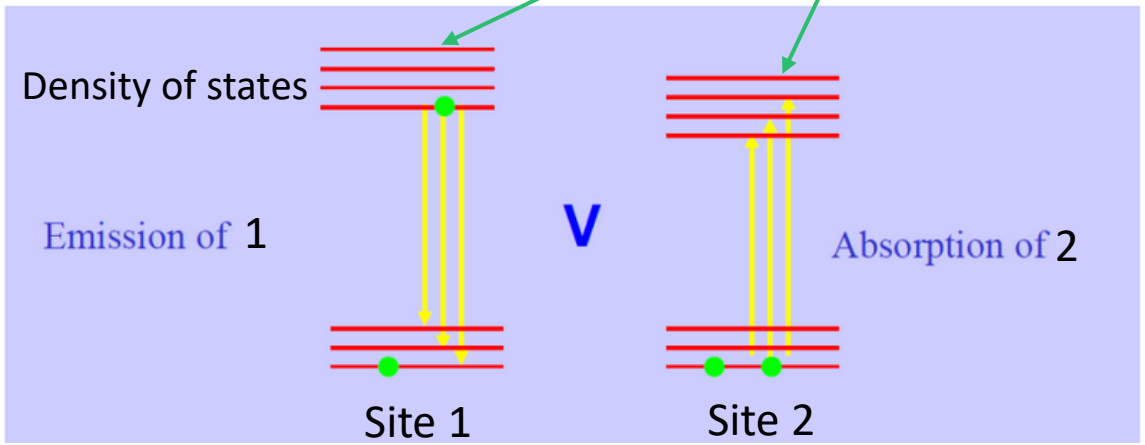
$$k_{1\leftarrow 2} \propto \left(\frac{R_0}{R}\right)^6$$



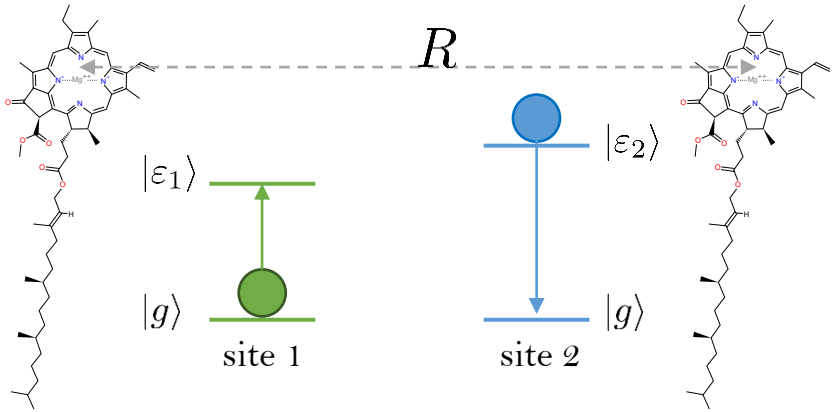
Förster theory

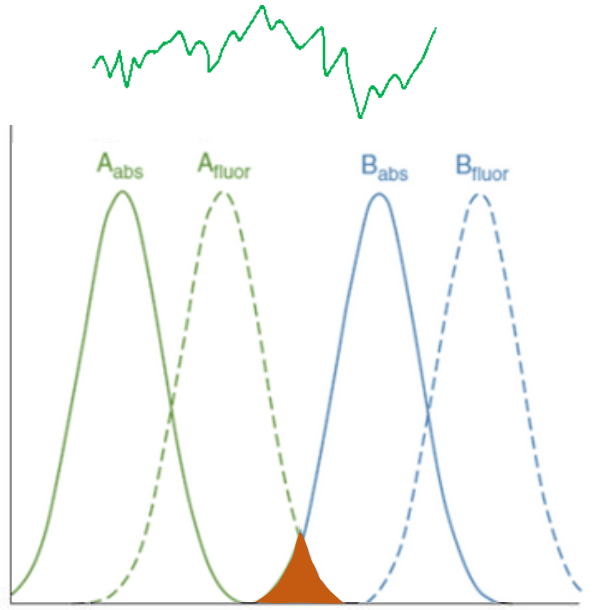
$$\langle \xi_n(t)\xi_n(t') \rangle \quad = \quad C_n(t-t')$$





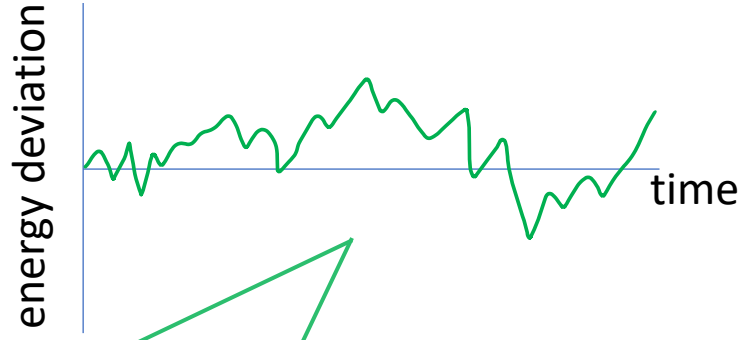
$$C_n(\omega) = \int_{-\infty}^{\infty} C_n(t) e^{i\omega t} dt$$

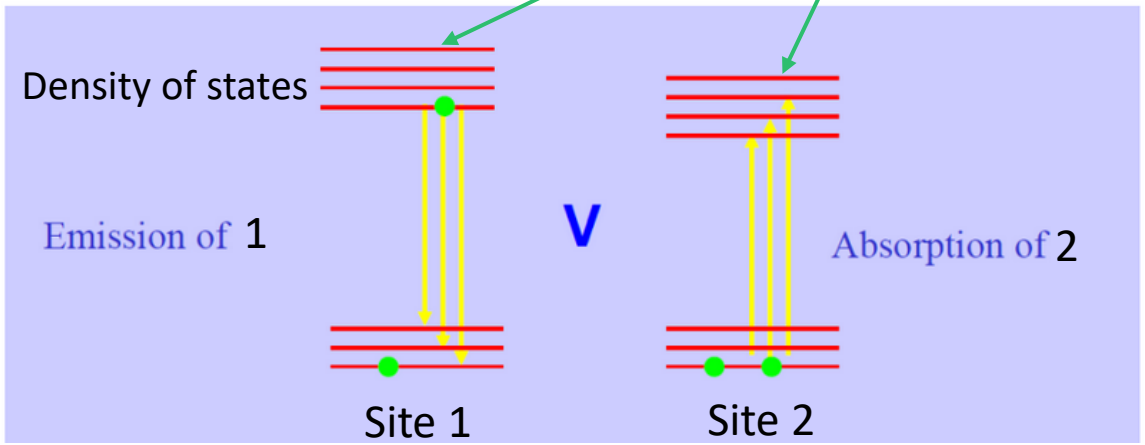


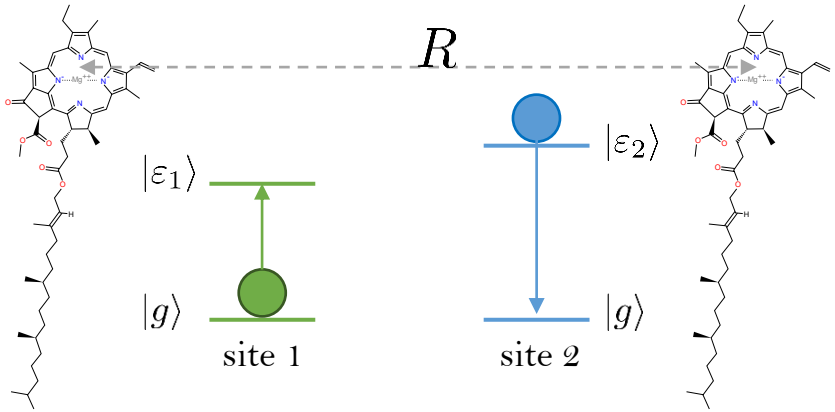


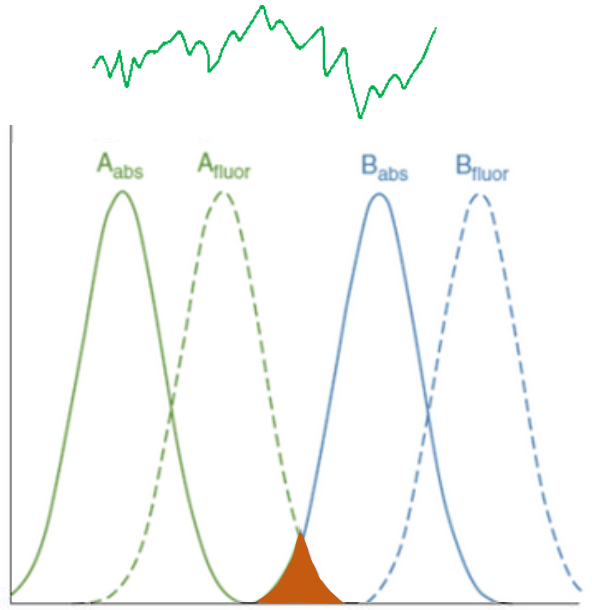
Förster theory

$$\langle \xi_n(t)\xi_n(t') \rangle \quad = \quad C_n(t-t')$$







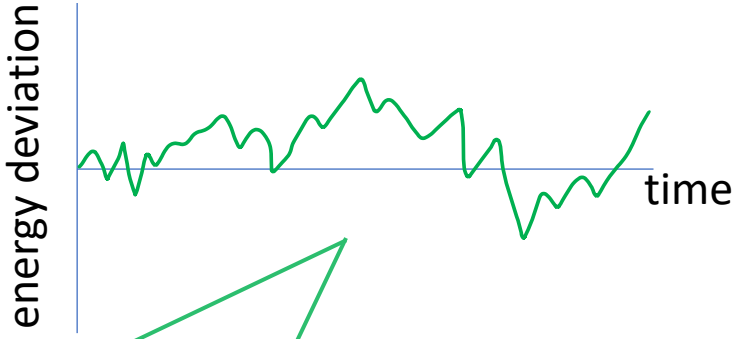


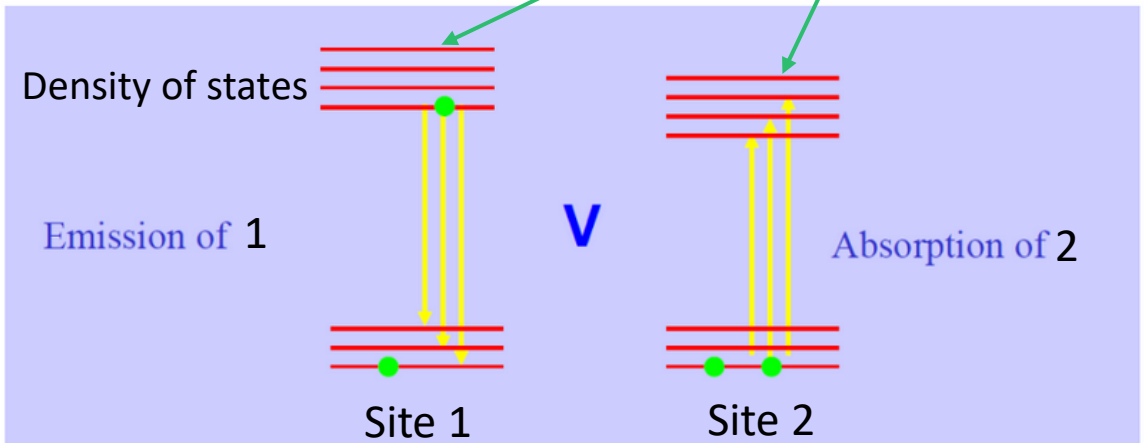
$$C_n(\omega) = \int_{-\infty}^{\infty} C_n(t) e^{i\omega t} dt = C'_n(\omega) + C''_n(\omega)$$

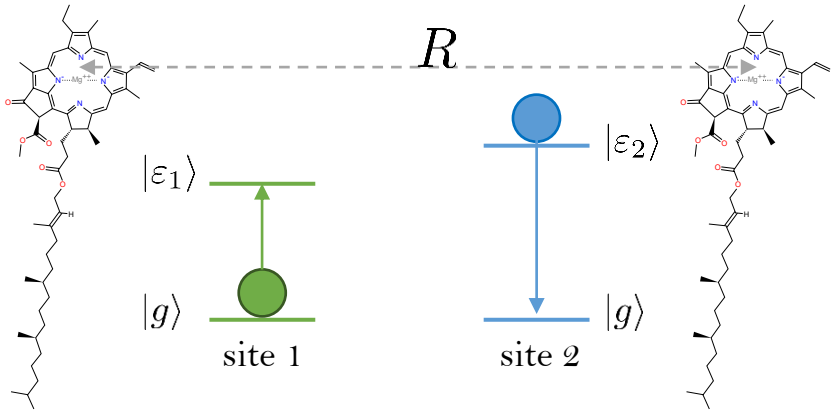
even odd

Förster theory

$$\langle \xi_n(t)\xi_n(t') \rangle = C_n(t-t')$$





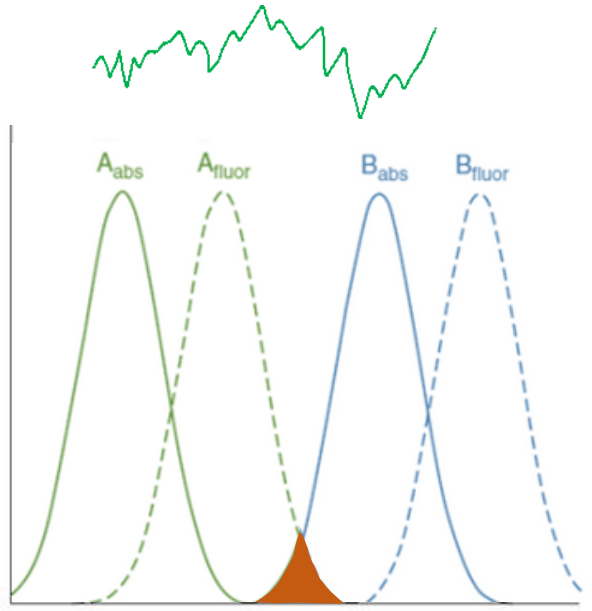


$$C_n(\omega) = \int_{-\infty}^{\infty} C_n(t) e^{i\omega t} dt = C_n'(\omega) + C_n''(\omega)$$

even

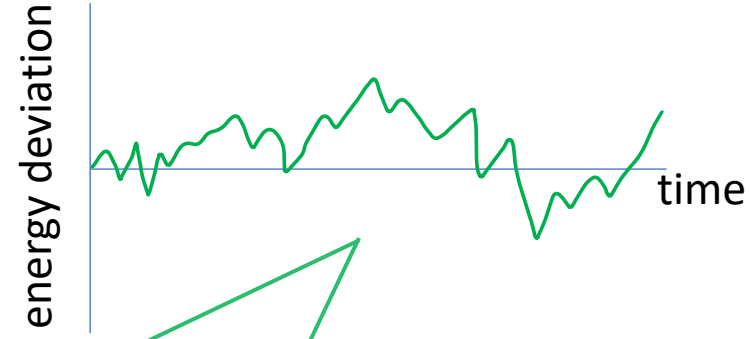
odd

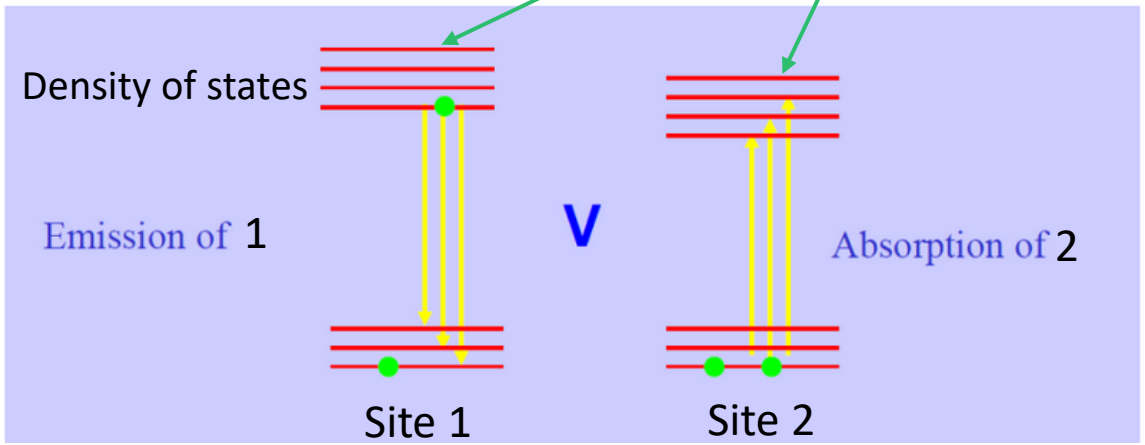
- Density of states
- Coupling strength to each state

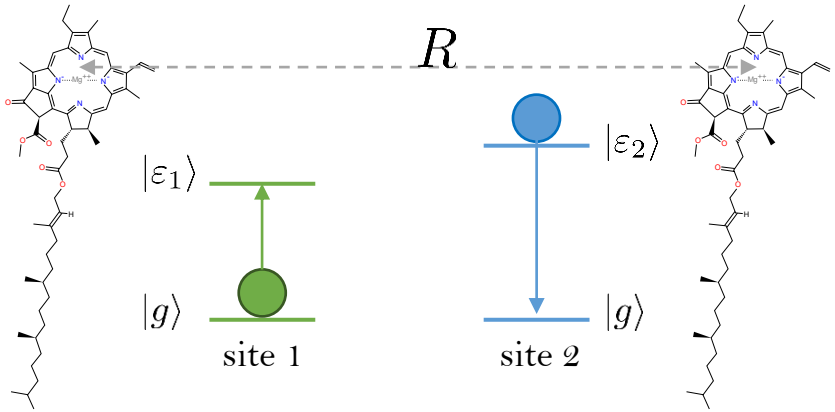


Förster theory

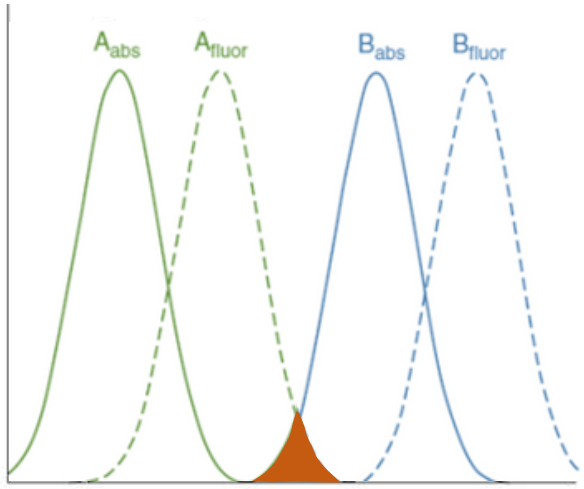
$$\langle \xi_n(t)\xi_n(t') \rangle = C_n(t-t')$$







$$k_{1\leftarrow 2} \propto \left(\frac{R_0}{R}\right)^6$$



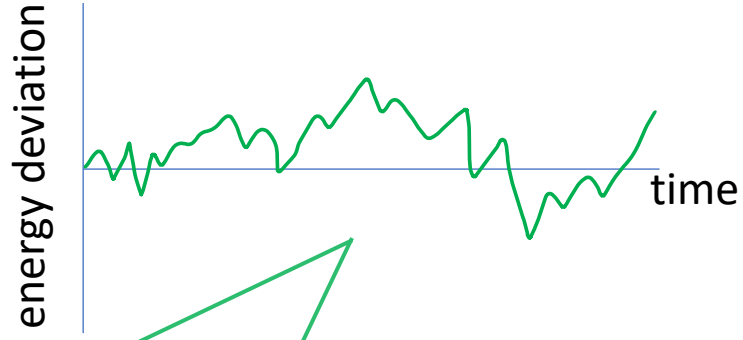
$$C_n(\omega) = \int_{-\infty}^{\infty} C_n(t) e^{i\omega t} dt = C_n'(\omega) + C_n''(\omega)$$

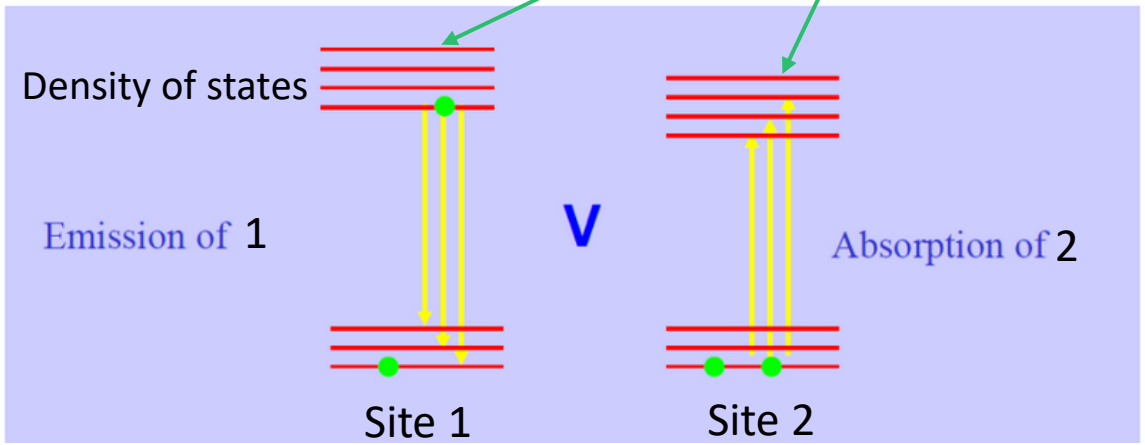
even odd

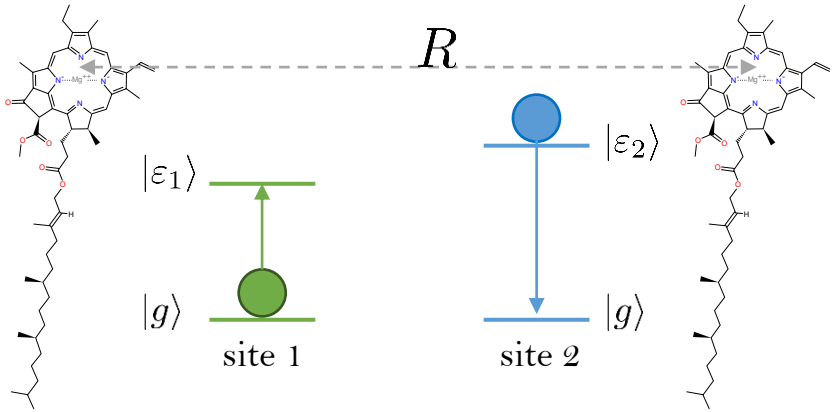
$$C_n(\omega) = \left(1 + \coth\left(\frac{\omega}{2k_B T}\right)\right) C''(\omega)$$

Förster theory

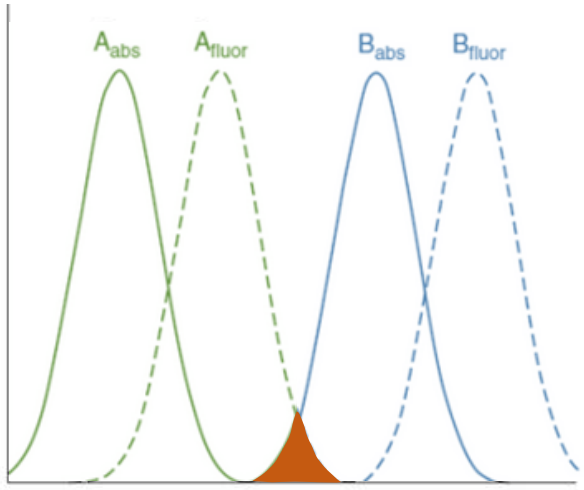
$$\langle \xi_n(t)\xi_n(t') \rangle = C_n(t-t')$$







$$k_{1\leftarrow 2} \propto \left(\frac{R_0}{R}\right)^6$$



$$C_n(\omega) = \int_{-\infty}^{\infty} C_n(t) e^{i\omega t} dt = C_n'(\omega) + C_n''(\omega)$$

even odd

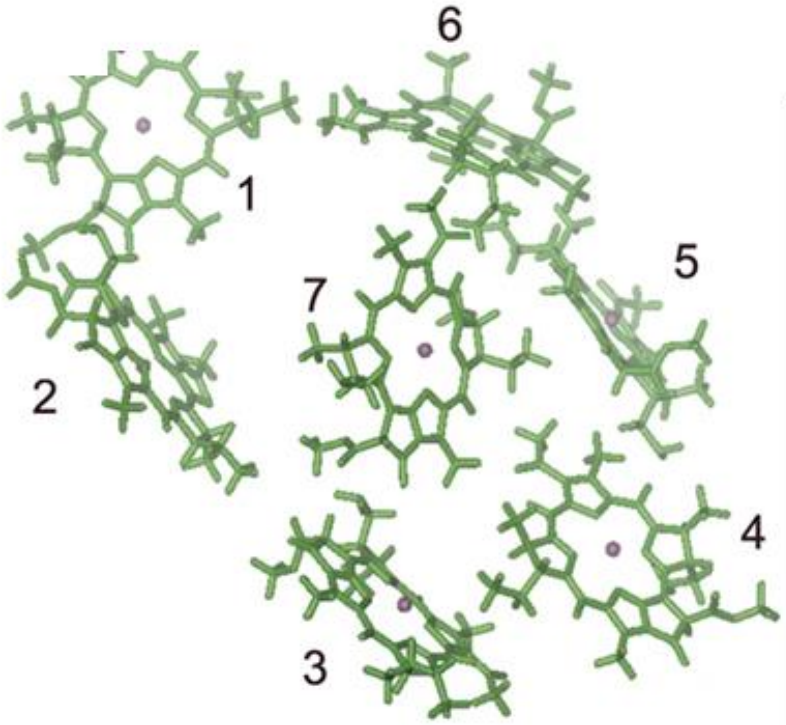
Model

Overdamped harmonic oscillator

$$C_n(\omega) = \left(1 + \coth\left(\frac{\omega}{2k_B T}\right)\right) C''(\omega)$$

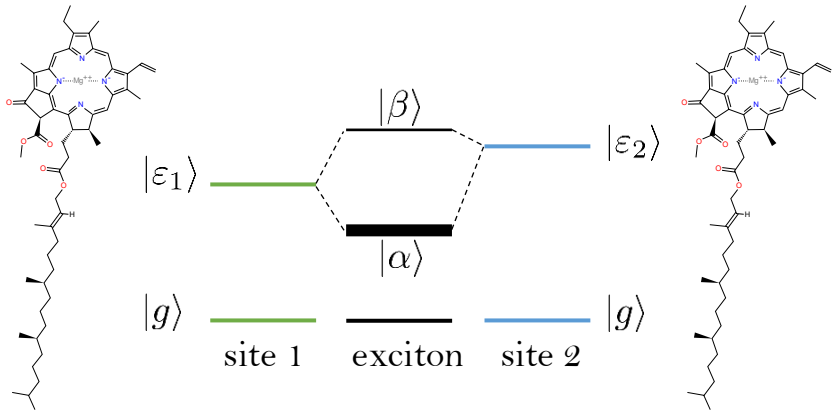
$$C''(\omega) = 2\lambda_0 \frac{\gamma_0 \omega}{\omega^2 + \gamma_0^2}$$

Redfield theory

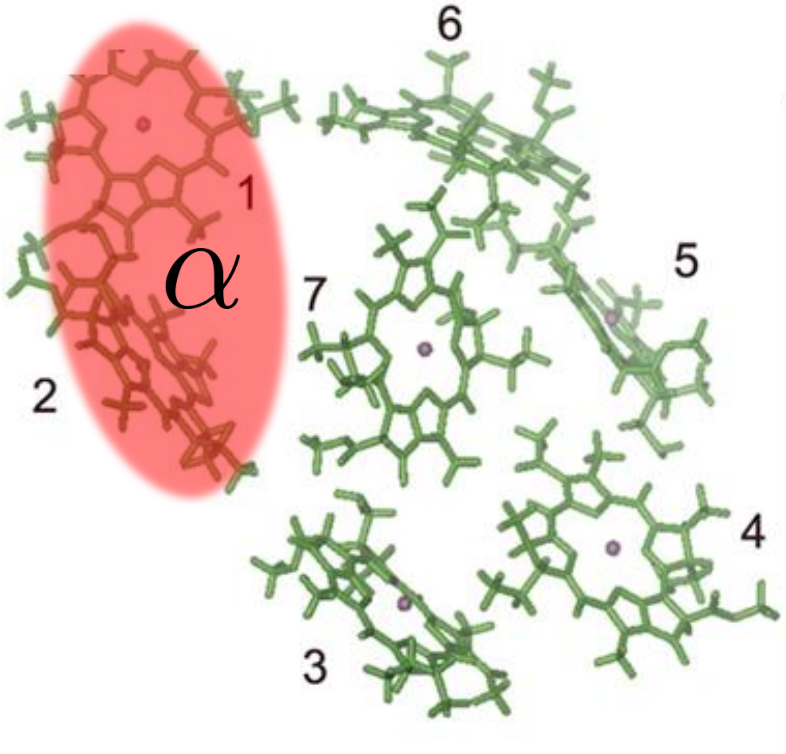


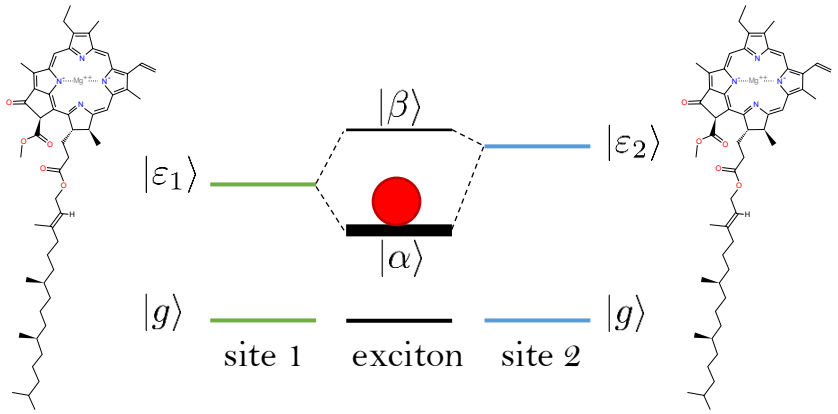
NOT small

$$\hat{H}_{\mathrm{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$

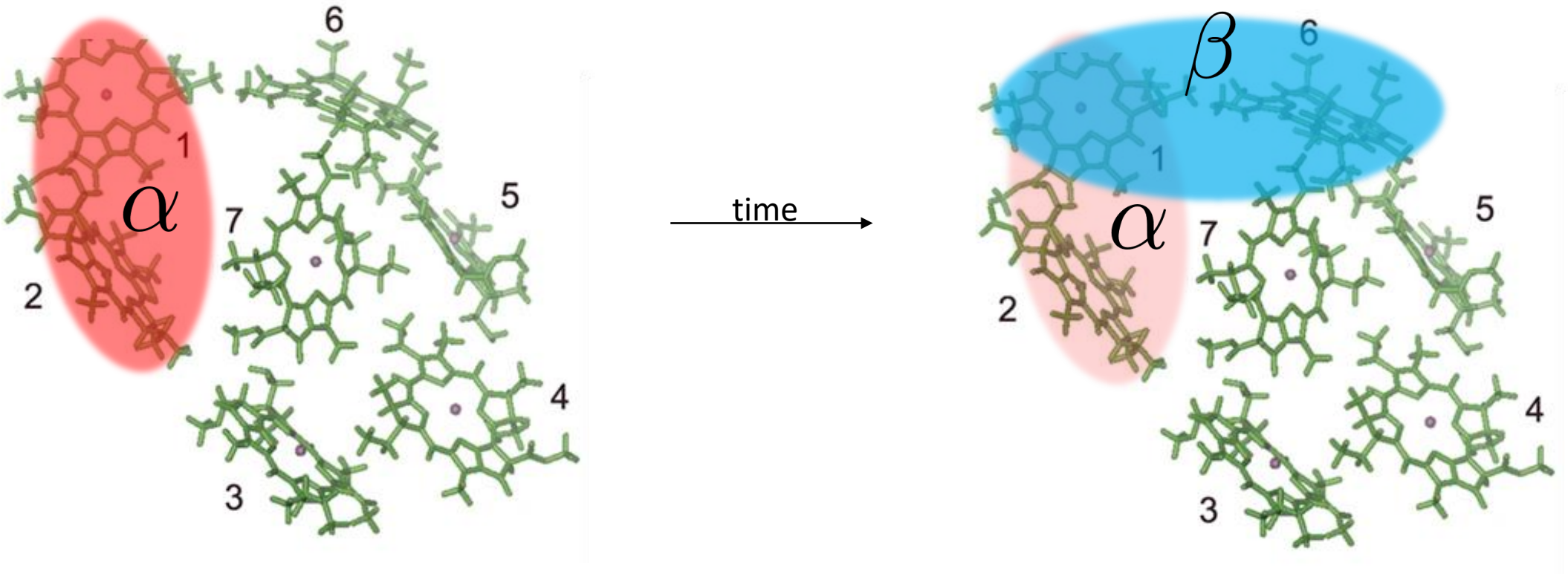


Redfield theory



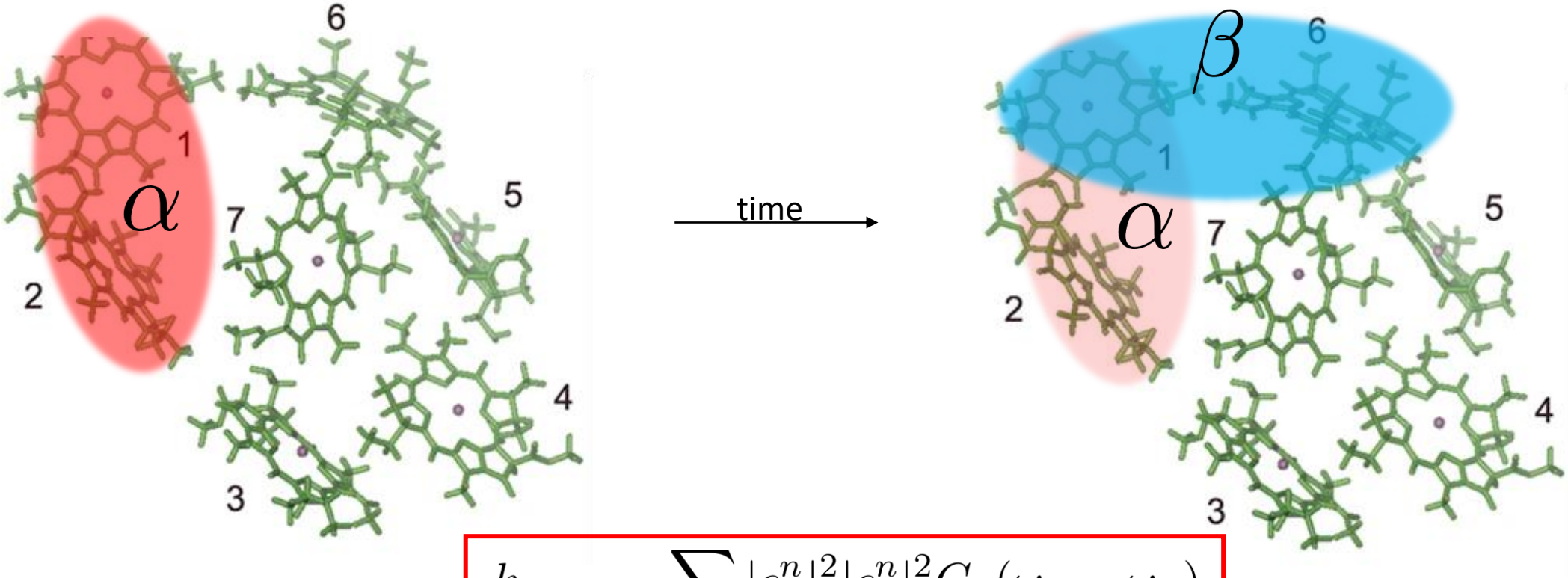


Redfield theory



$$\frac{\partial}{\partial t}\rho_S(t)$$

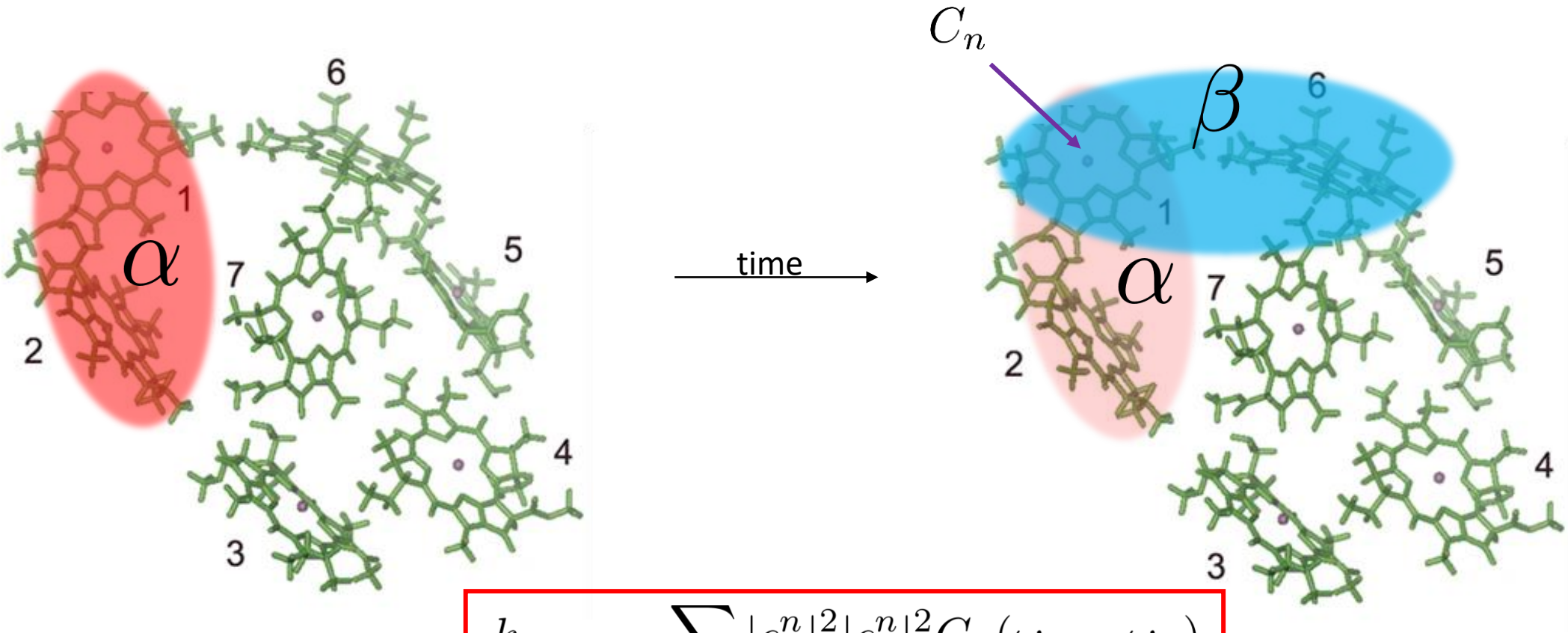
Redfield theory



$$k_{\beta\leftarrow\alpha} = \sum_n |c_\alpha^n|^2 |c_\beta^n|^2 C_n(\omega_\beta - \omega_\alpha)$$

$$\frac{d}{dt} P_\beta = \sum_\alpha k_{\beta\leftarrow\alpha} P_\alpha$$

Redfield theory

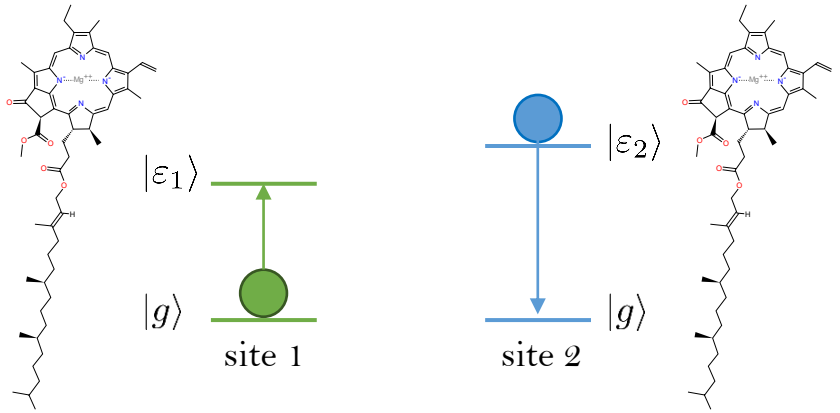


$$k_{\beta\leftarrow\alpha} = \sum_n |c_\alpha^n|^2 |c_\beta^n|^2 C_n(\omega_\beta - \omega_\alpha)$$

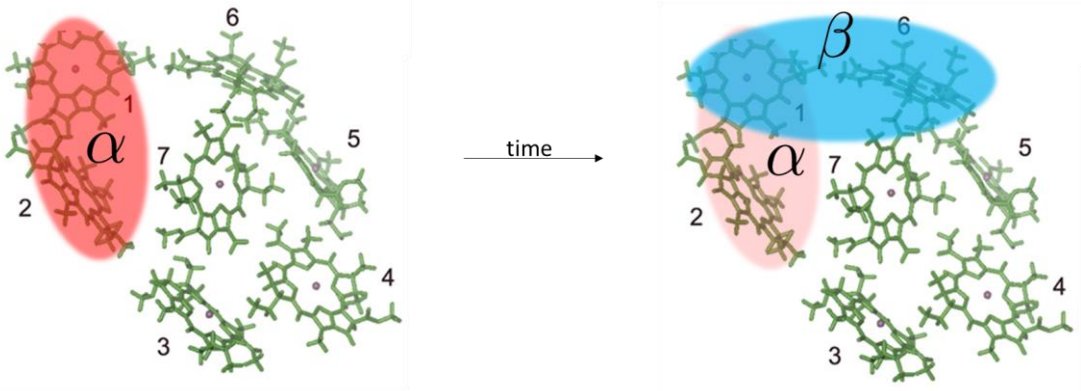
$$\frac{d}{dt} P_\beta = \sum_\alpha k_{\beta\leftarrow\alpha} P_\alpha$$

Summary

Förster theory



Redfield theory



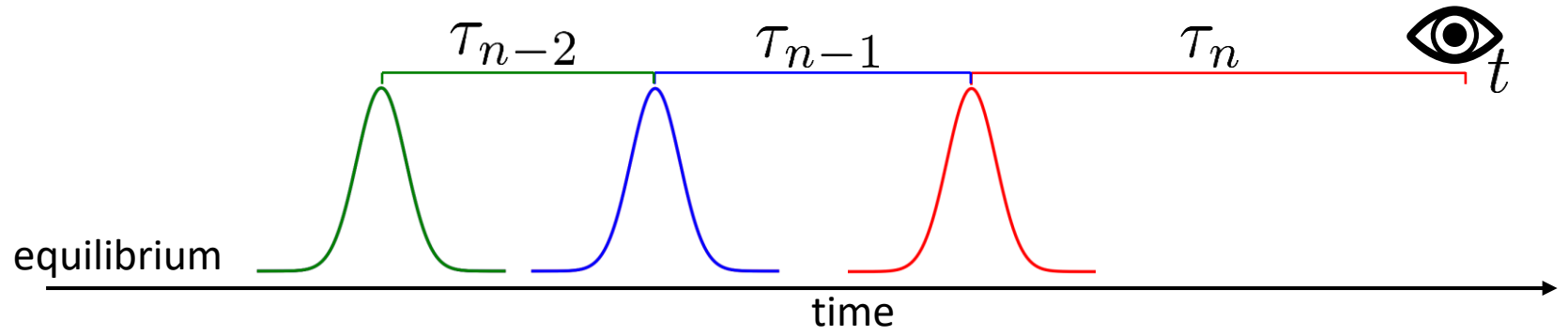
$$\frac{\partial}{\partial t}\rho_S(t)$$

$$\frac{d}{dt}P_\beta = \sum_\alpha k_{\beta\leftarrow\alpha}P_\alpha$$

$$k_{\beta\leftarrow\alpha} = \sum_n |c_\alpha^n|^2 |c_\beta^n|^2 C_n(\omega_\beta - \omega_\alpha)$$

Nonlinear response

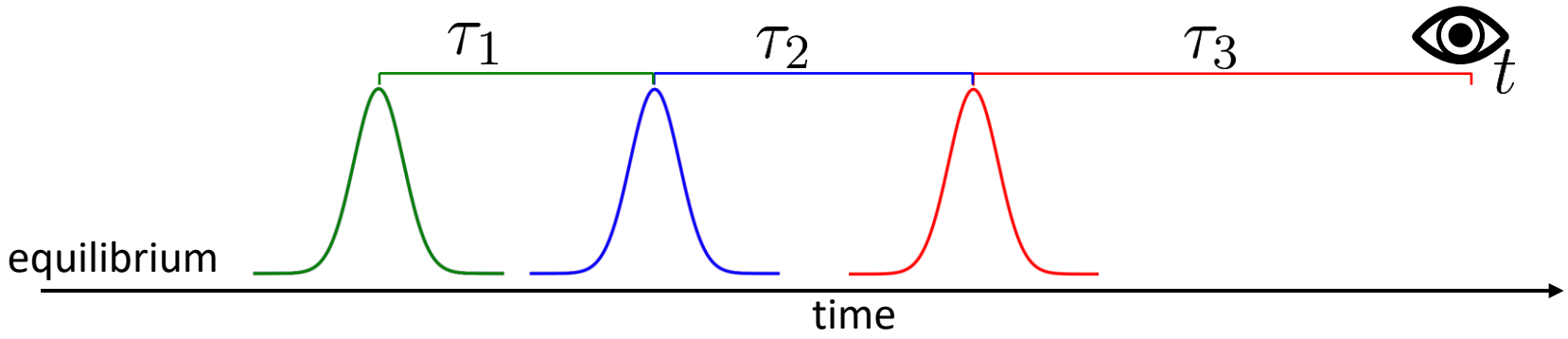
$$P^{(n)}(t) = \int_0^\infty d\tau_n \int_0^\infty d\tau_{n-1} \ldots \int_0^\infty d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) E(t-\tau_n) E(t-\tau_n-\tau_{n-1}) \ldots E(t-\tau_n-\tau_{n-1}-\ldots-\tau_1)$$



$$\mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) = i^n \mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(\tau_n)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_{n-1})\mathcal{V}\ldots\mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]$$

Third-order response

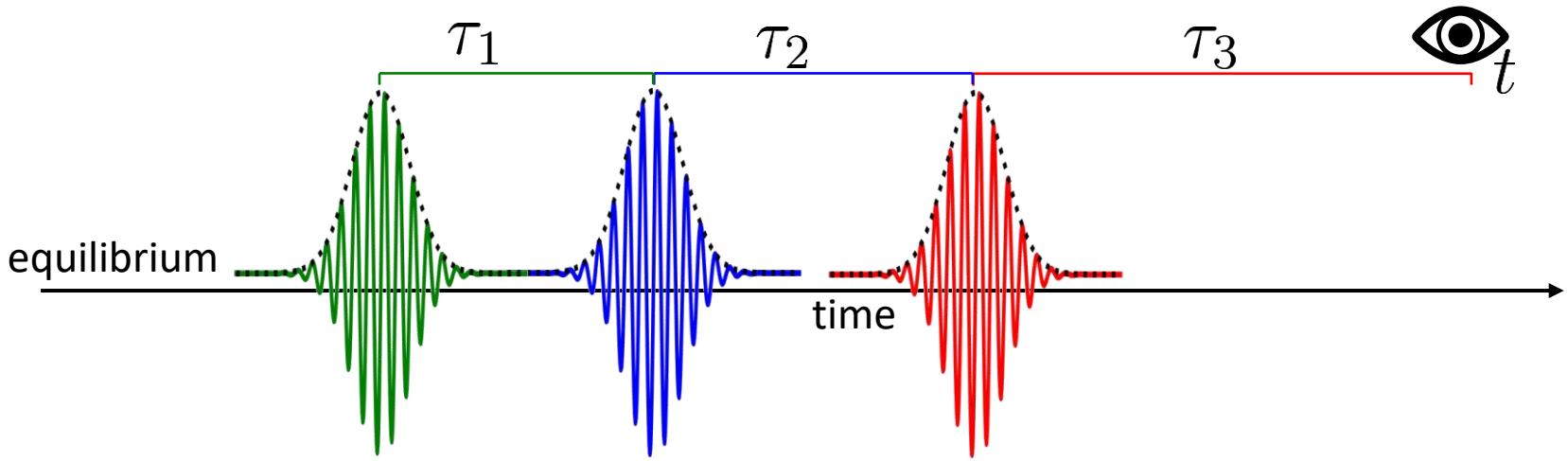
$$P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \mathcal{R}^{(3)}(\tau_3, \tau_2, \tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) E(t-\tau_3-\tau_2-\tau_1)$$



$$\mathcal{R}^{(3)}(\tau_3, \tau_2, \tau_1) = i^n \mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(\tau_3)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_2)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]$$

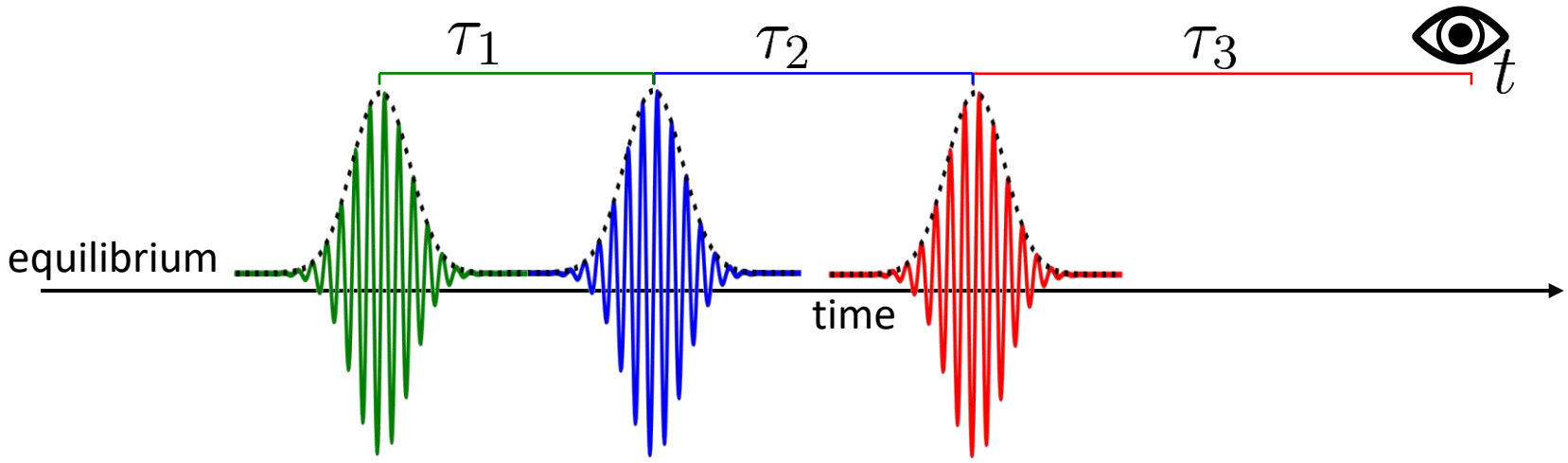
Third-order response

$$P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \mathcal{R}^{(3)}(\tau_3, \tau_2, \tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) E(t-\tau_3-\tau_2-\tau_1)$$



Third-order response

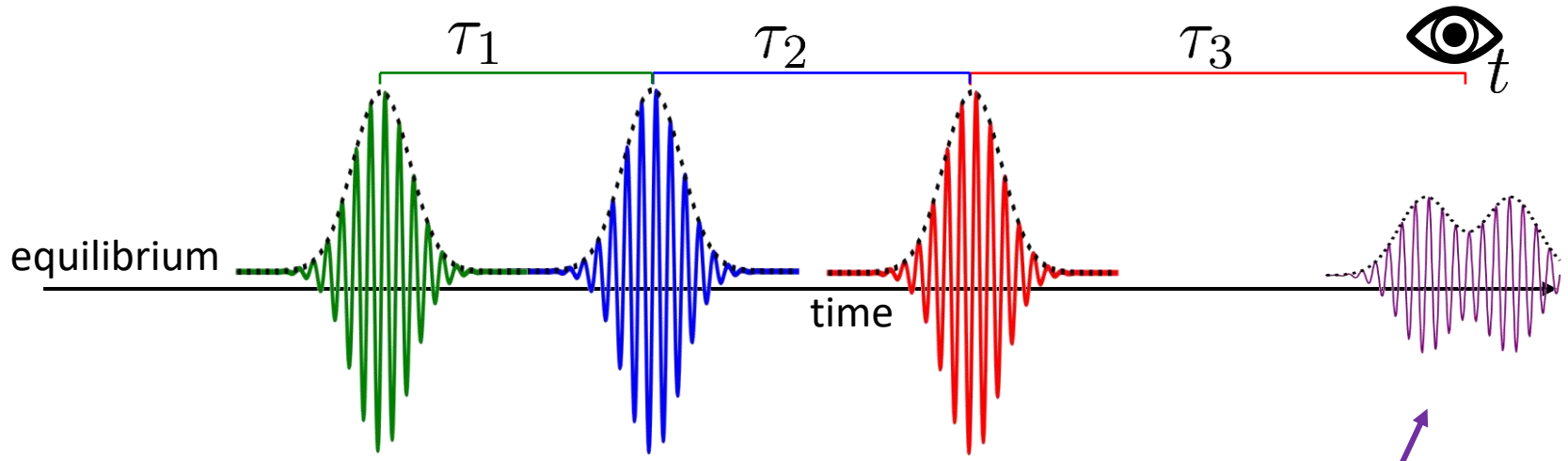
$$P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \mathcal{R}^{(3)}(\tau_3, \tau_2, \tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) E(t-\tau_3-\tau_2-\tau_1)$$



$$\boldsymbol{E}_2(t) = \hat{\boldsymbol{e}}\mathcal{E}(r,t)e^{i\boldsymbol{k}_2\cdot r - i\omega_2 t} + \text{c.c.}$$

Third-order response

$$P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) E(t-\tau_3-\tau_2-\tau_1)$$

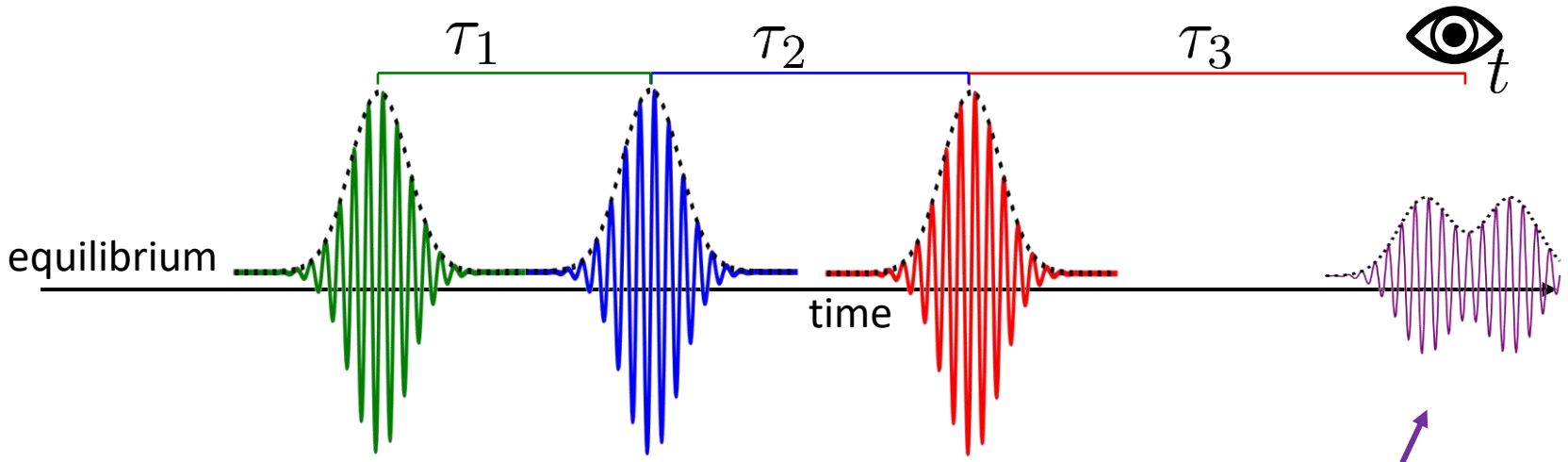


$$\boldsymbol{E}_s(t) = \mathcal{E}_s(r,t) e^{i\boldsymbol{k}_s \cdot r - i\omega_s t} + \text{c.c.}$$

$$\boldsymbol{k}_s = \sum_{n=1}^{3} \pm \boldsymbol{k}_n \quad \omega_s = \sum_{n=1}^{3} \pm \omega_n$$

Third-order response

$$P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) E(t-\tau_3-\tau_2-\tau_1)$$



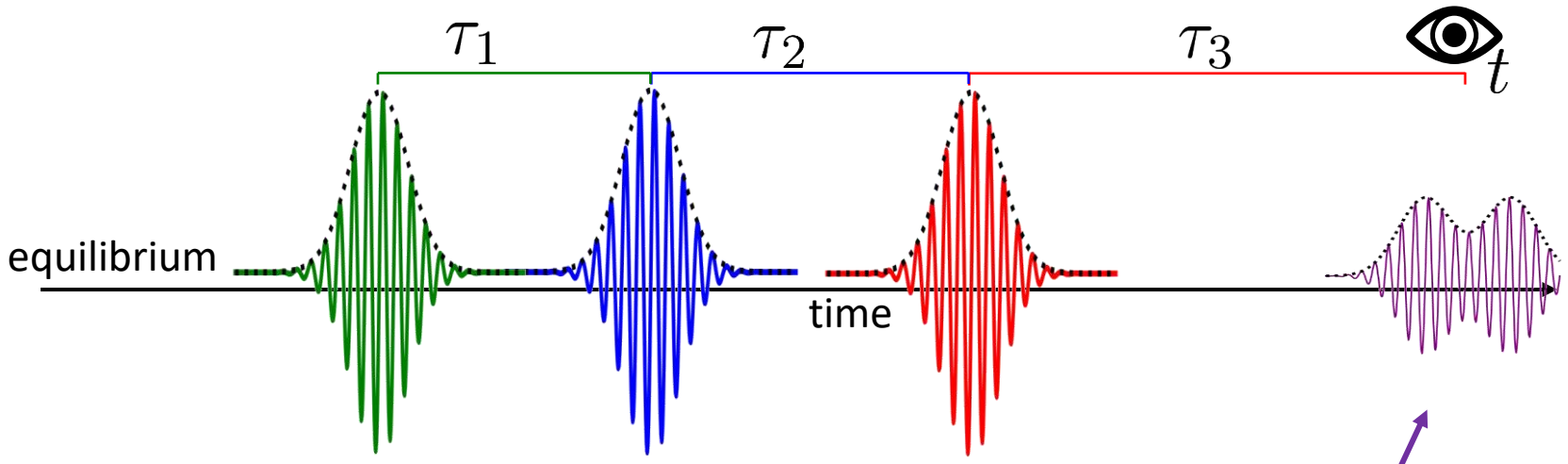
$$\mathcal{E}_s(r,t) \approx i\mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1)$$

$$\boldsymbol{E}_s(t) = \mathcal{E}_s(r,t)e^{i\boldsymbol{k}_s\cdot r - i\omega_s t} + \text{c.c.}$$

$$\boldsymbol{k}_s = \sum_{n=1}^{3} \pm \boldsymbol{k}_n \quad \omega_s = \sum_{n=1}^{3} \pm \omega_n$$

Third-order response

$$P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \mathcal{R}^{(3)}(\tau_3, \tau_2, \tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) E(t-\tau_3-\tau_2-\tau_1)$$

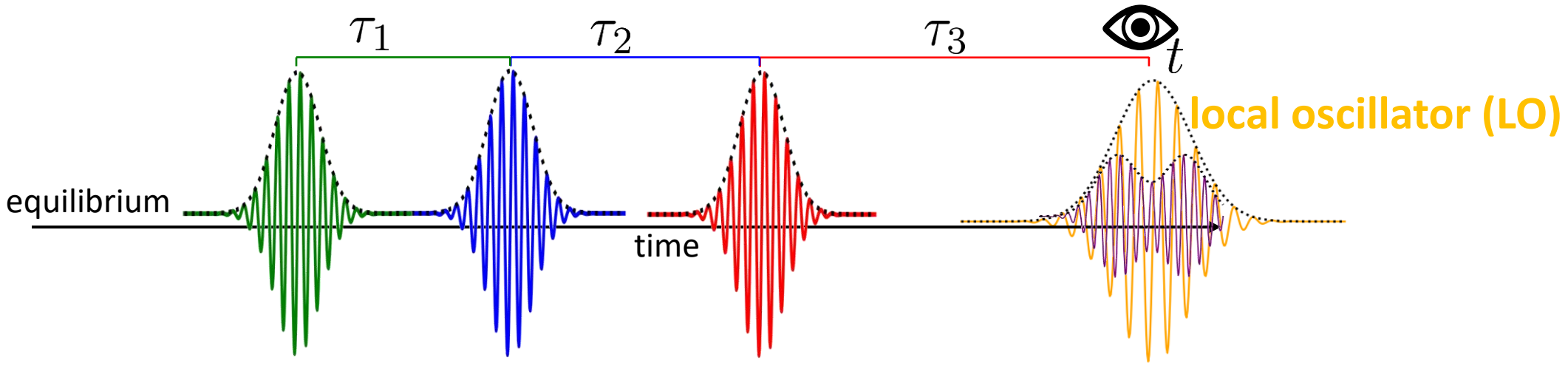


Measure?

$$\boldsymbol{E}_s(t) = \mathcal{E}_s(r,t) e^{i\boldsymbol{k}_s \cdot r - i\omega_s t} + \text{c.c.}$$

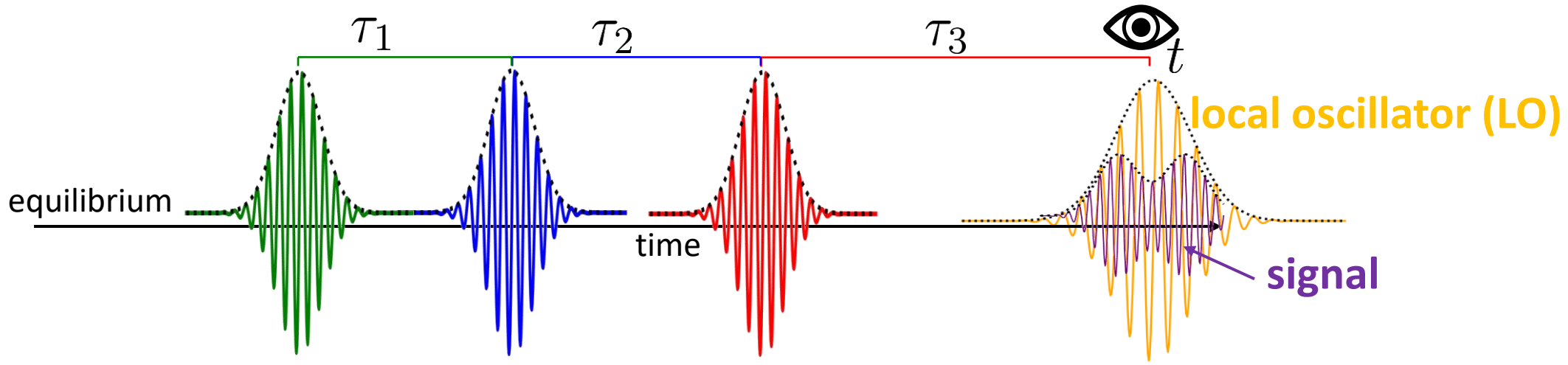
Heterodyne detection

$$P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) E(t-\tau_3-\tau_2-\tau_1)$$



Heterodyne detection

$$P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) E(t-\tau_3-\tau_2-\tau_1)$$

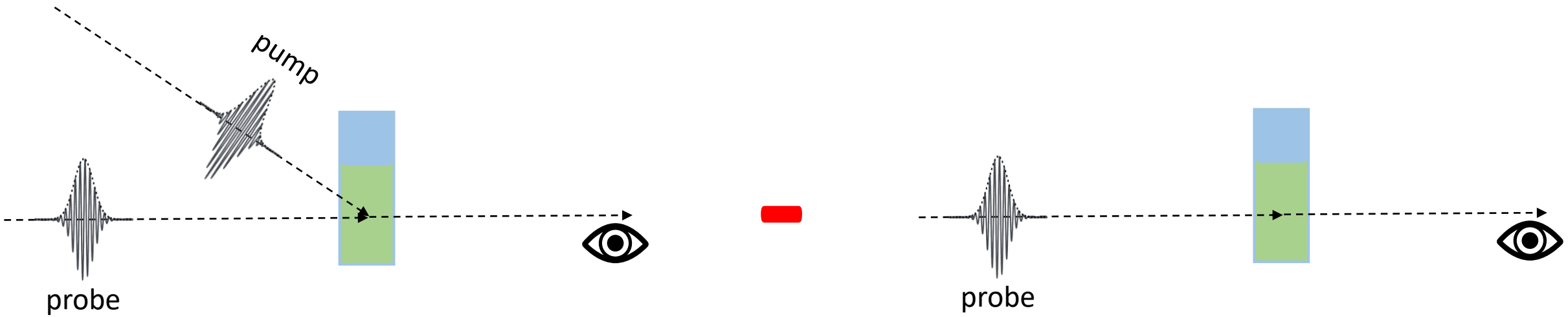


$$I_{\text{det}} = |E_S + E_{\text{LO}}|^2 = |E_s|^2 + |E_{\text{LO}}|^2 + 2\text{Re}|E_S E_{\text{LO}}^*|$$

small known

Pump-probe spectroscopy

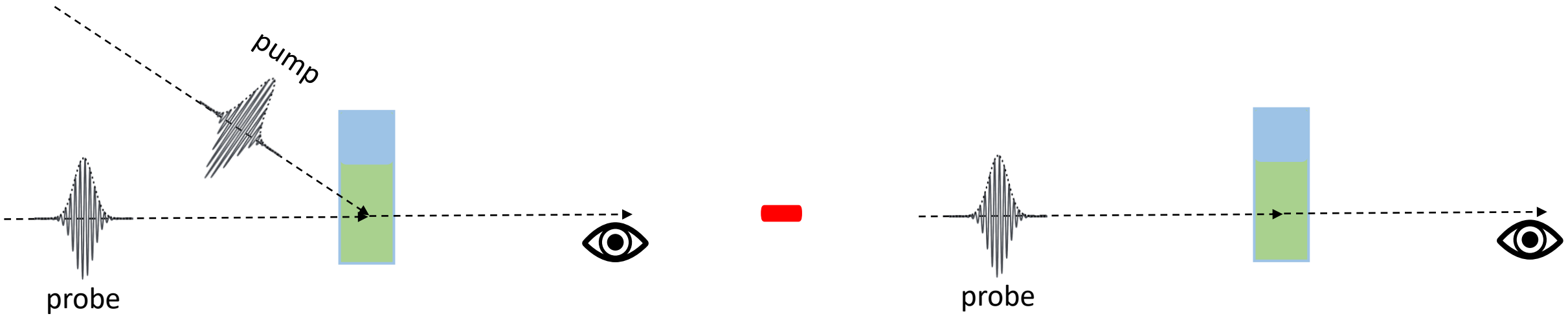
$$\Delta\mathrm{Abs} = \mathrm{Abs}_{\mathrm{pump\ on}} - \mathrm{Abs}_{\mathrm{pump\ off}}$$



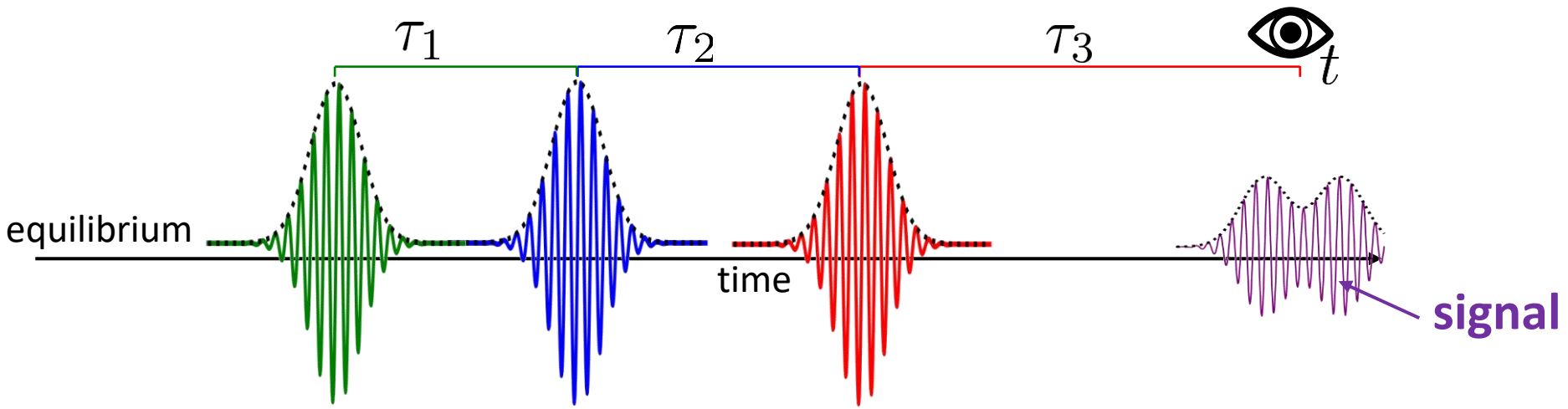
Pump-probe spectroscopy

$$\Delta \mathrm{Abs} = \mathrm{Abs}_{\mathrm{pump\ on}} - \mathrm{Abs}_{\mathrm{pump\ off}}$$

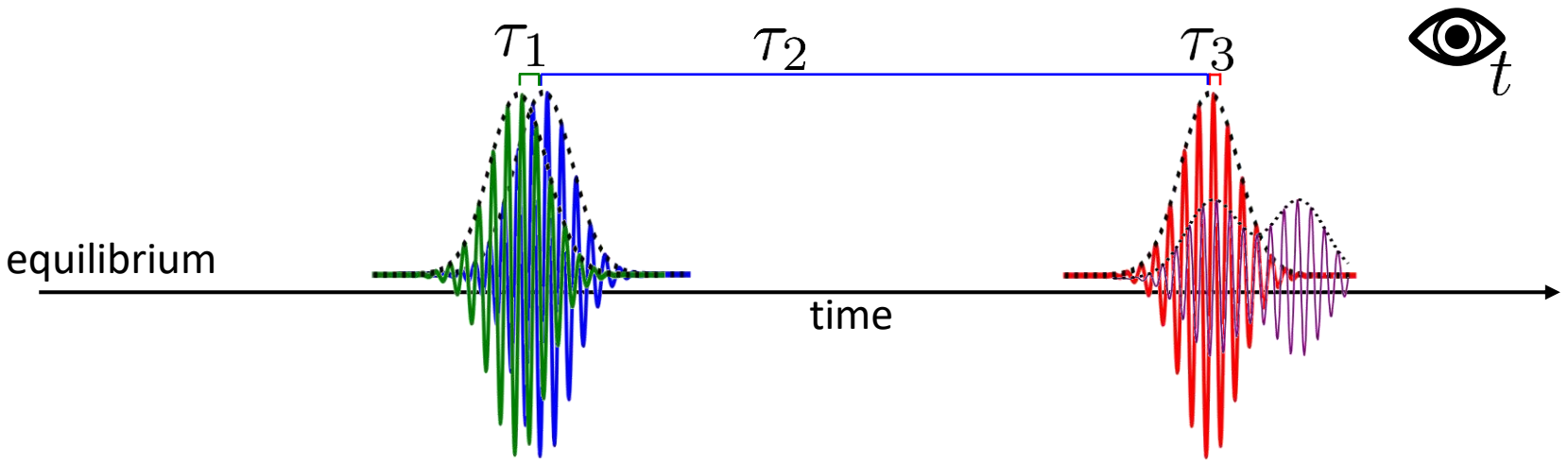
$$\Delta \mathrm{I} = \mathrm{I}_{\mathrm{pump\ on}} - \mathrm{I}_{\mathrm{pump\ off}}$$



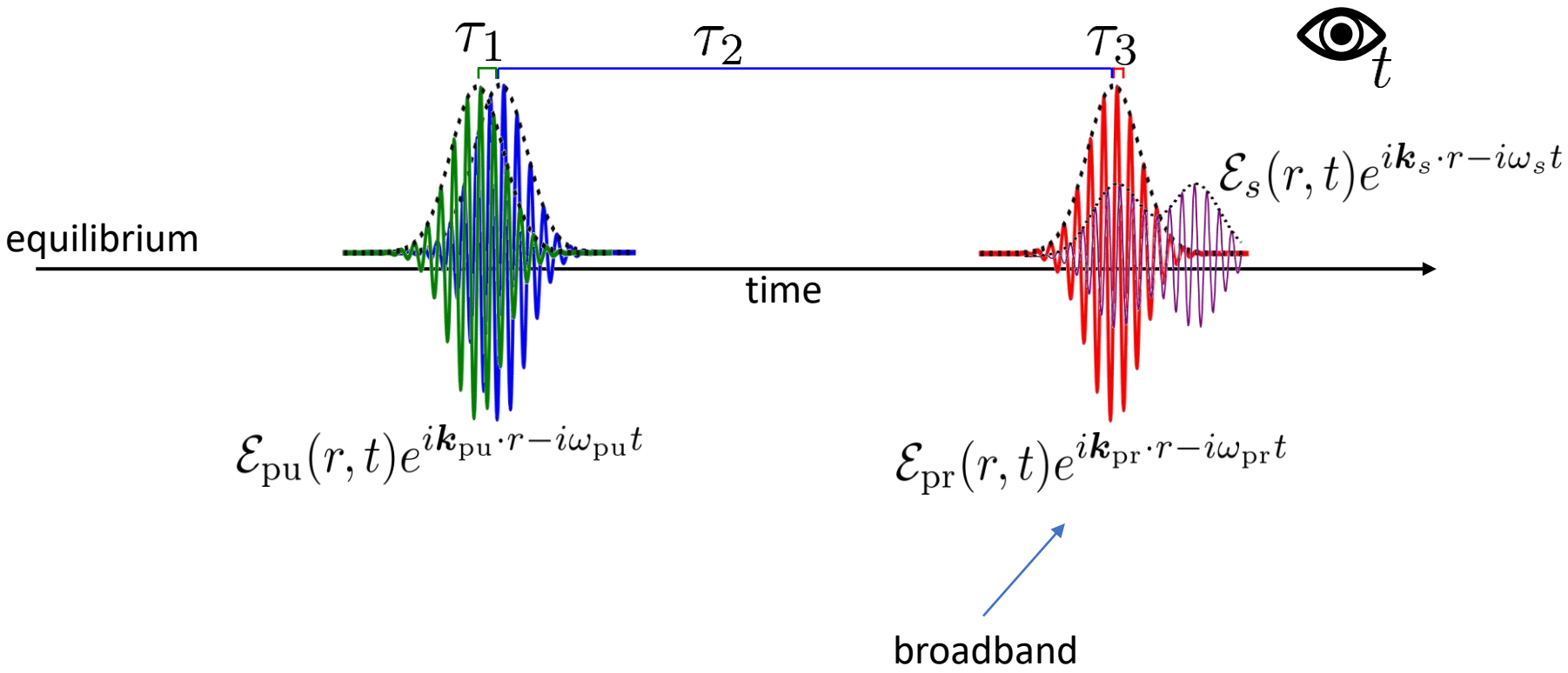
Pump-probe spectroscopy



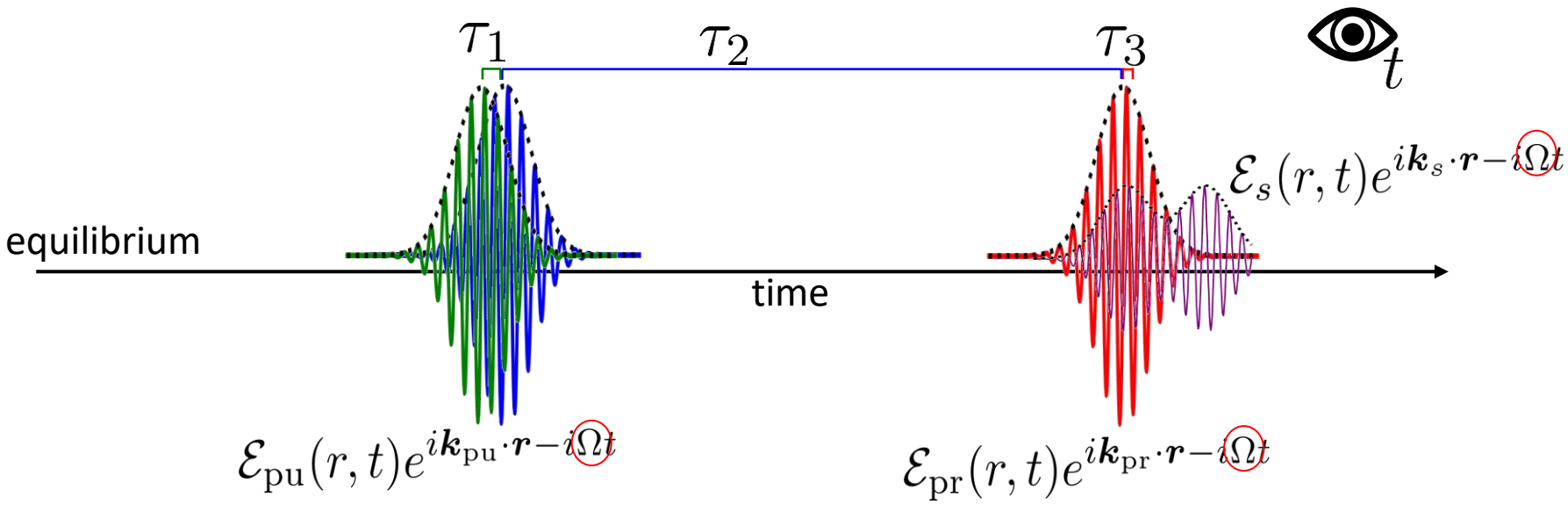
Pump-probe spectroscopy



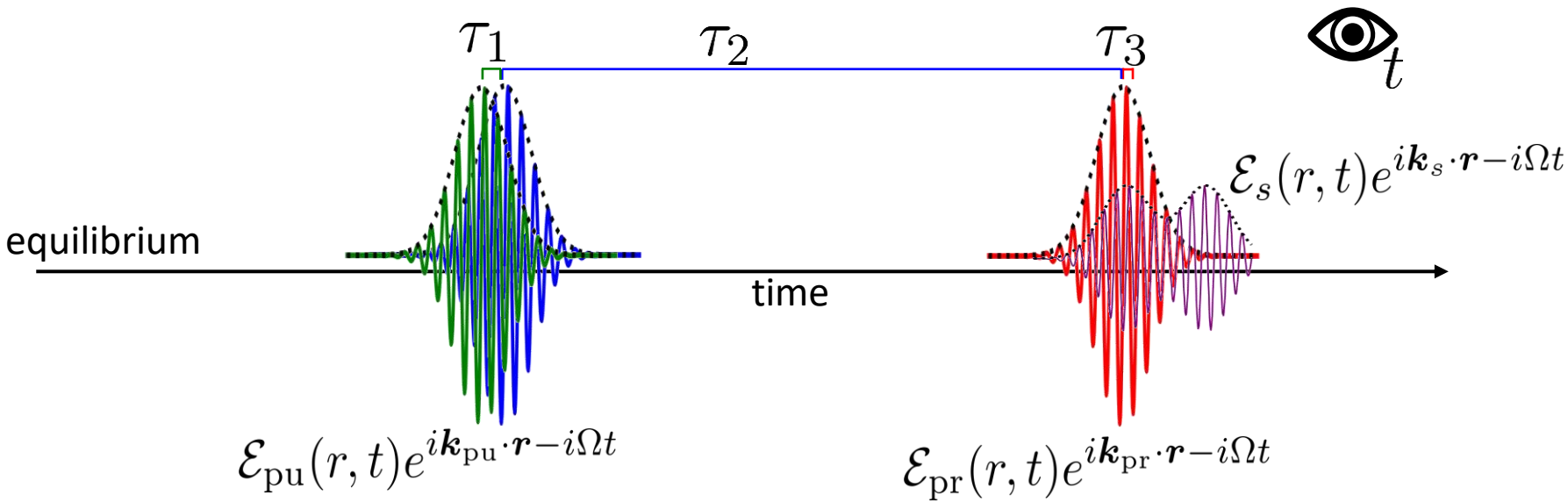
Pump-probe spectroscopy

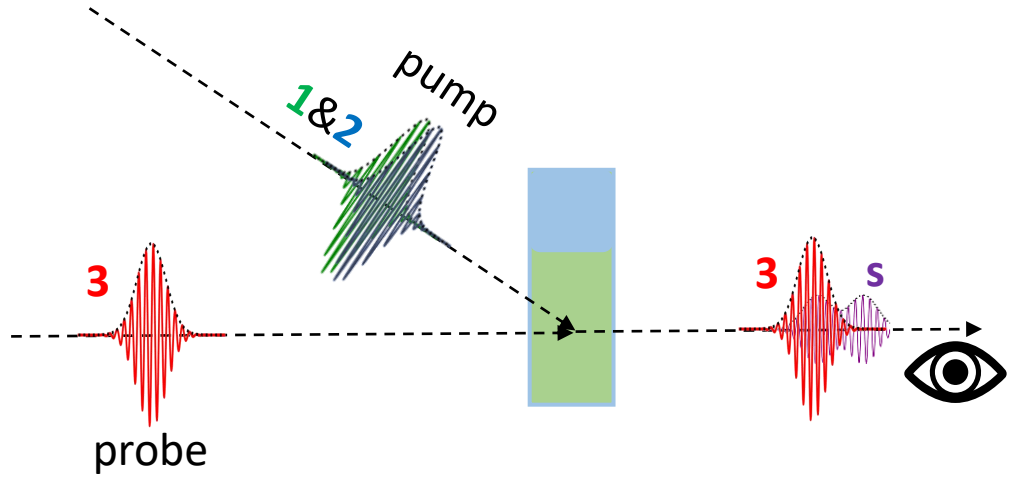


Pump-probe spectroscopy



Pump-probe spectroscopy

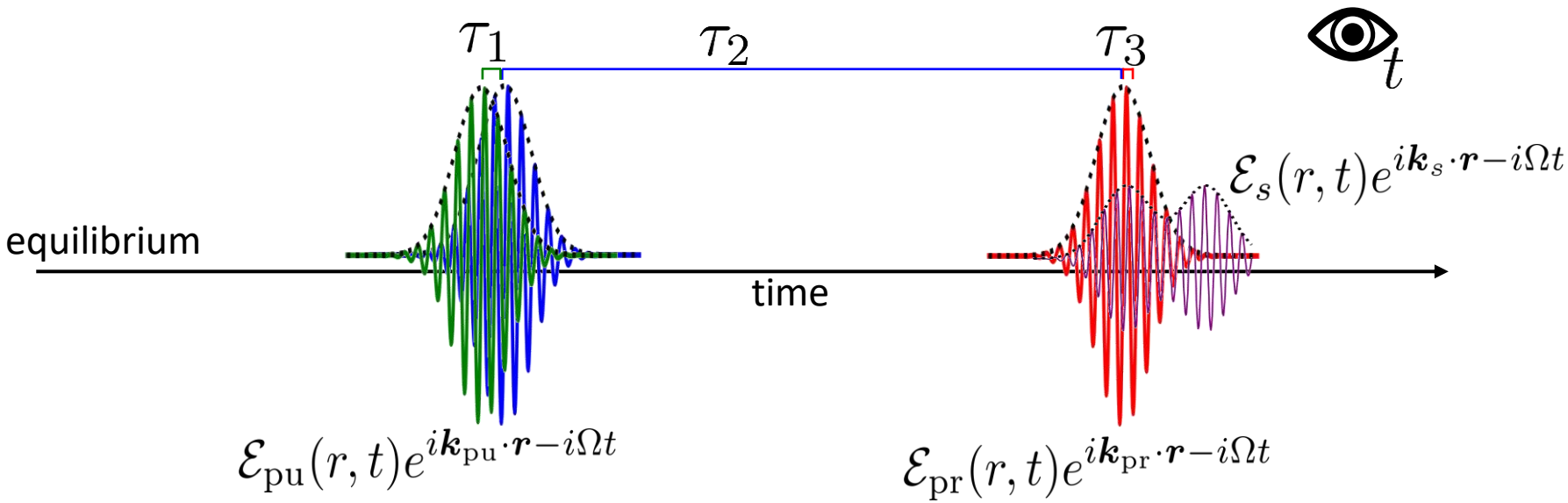


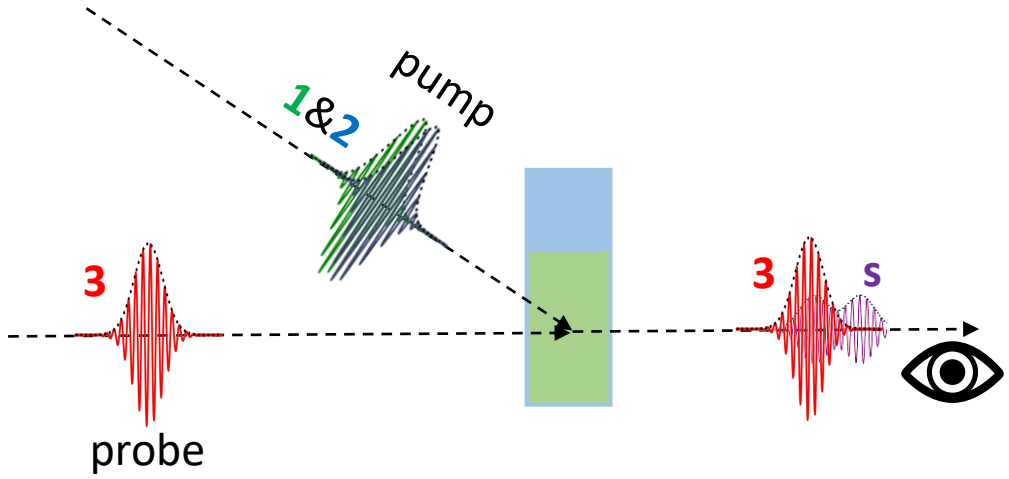


$$\boldsymbol{k}_s = -\boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pr} \qquad \omega_s = -\omega_{\rm pu} + \omega_{\rm pu} + \omega_{\rm pr}$$

$$\boldsymbol{k}_s = \boldsymbol{k}_{\rm pu} - \boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pr} \qquad \omega_s = \omega_{\rm pu} - \omega_{\rm pu} + \omega_{\rm pr}$$

Pump-probe spectroscopy

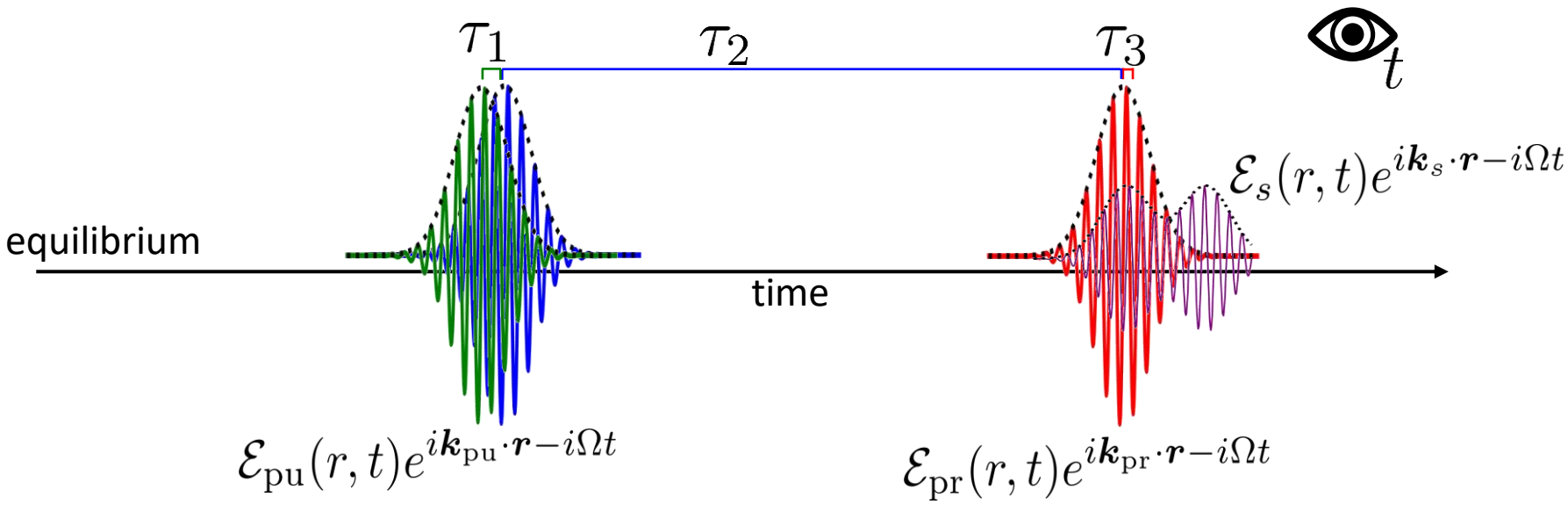


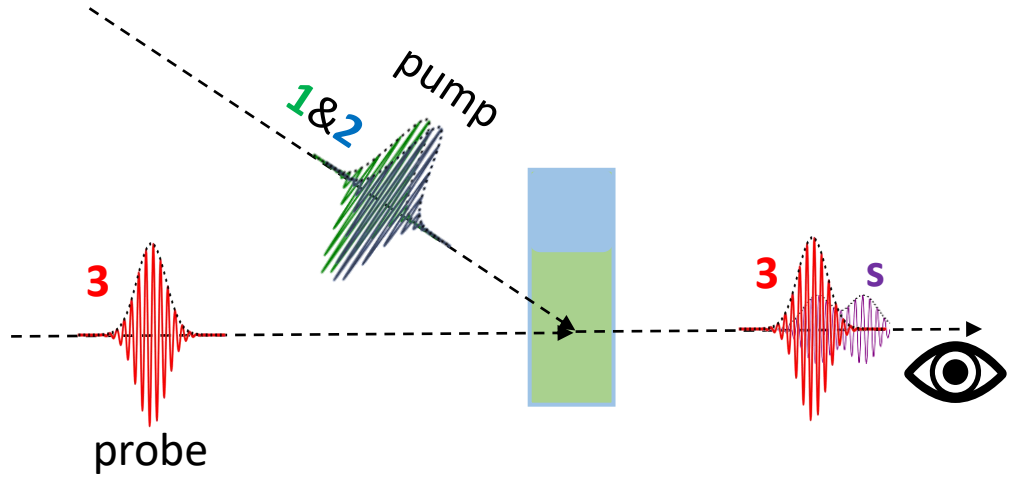


$$\boldsymbol{k}_s = -\boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pr} \qquad \omega_s = -\omega_{\rm pu} + \omega_{\rm pu} + \omega_{\rm pr}$$
$$\boldsymbol{k}_s = -\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$$

$$\boldsymbol{k}_s = \boldsymbol{k}_{\rm pu} - \boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pr} \qquad \omega_s = \omega_{\rm pu} - \omega_{\rm pu} + \omega_{\rm pr}$$
$$\boldsymbol{k}_s = \boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$$

Pump-probe spectroscopy





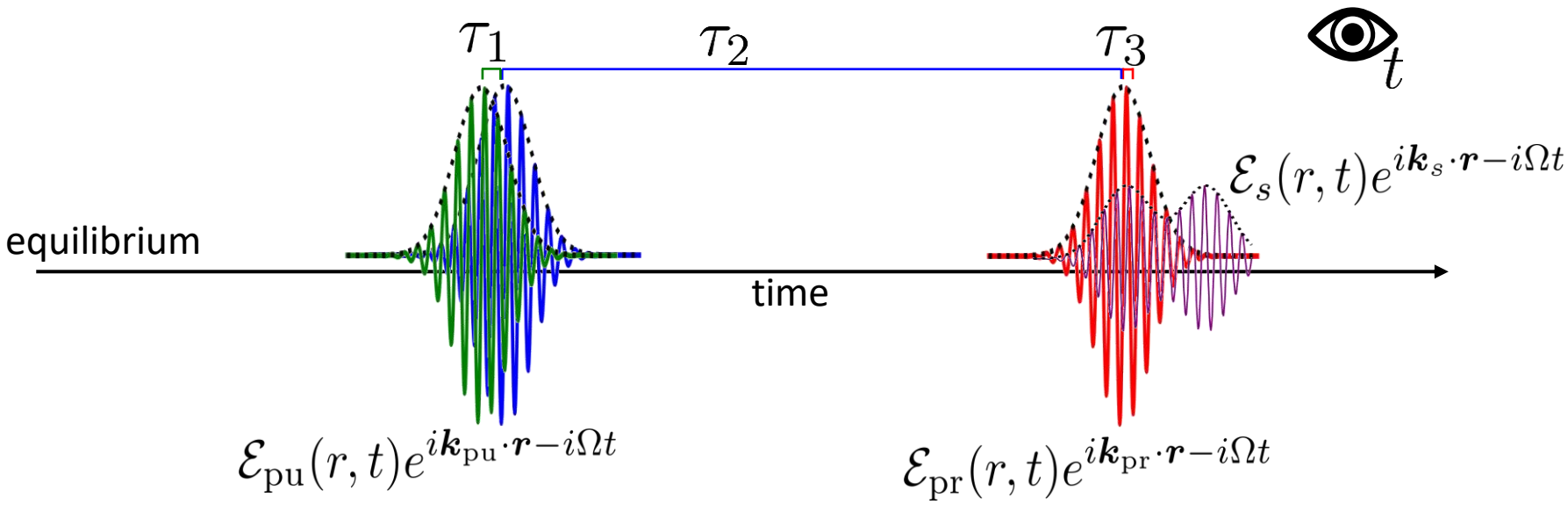
$$\boldsymbol{k}_s = -\boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pr} \qquad \omega_s = -\omega_{\rm pu} + \omega_{\rm pu} + \omega_{\rm pr}$$

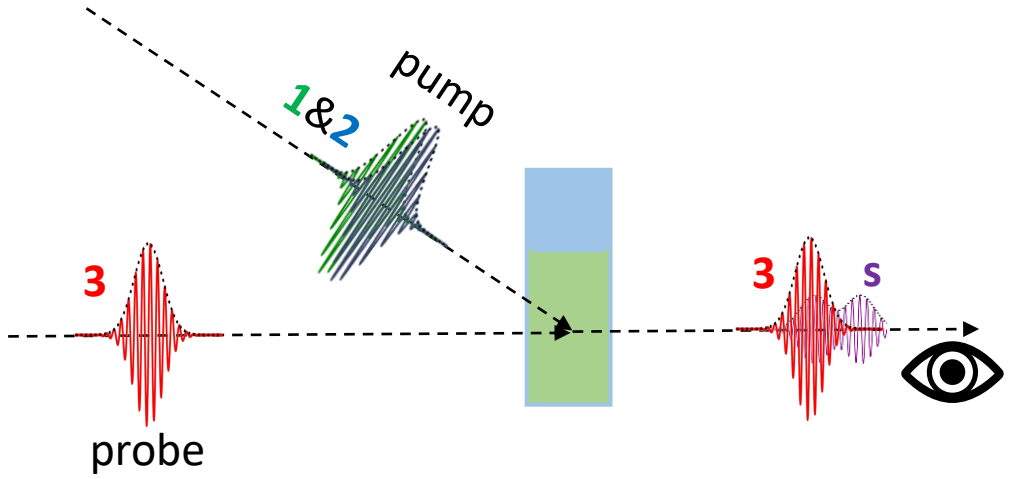
$$\boldsymbol{k}_s = -\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$$

$$\boldsymbol{k}_s = \boldsymbol{k}_{\rm pu} - \boldsymbol{k}_{\rm pu} + \boldsymbol{k}_{\rm pr} \qquad \omega_s = \omega_{\rm pu} - \omega_{\rm pu} + \omega_{\rm pr}$$

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

Pump-probe spectroscopy





$$\Delta \mathrm{I}_{\mathrm{pp}} = \mathrm{I}_{\mathrm{pu\ on}} - \mathrm{I}_{\mathrm{pu\ off}}$$

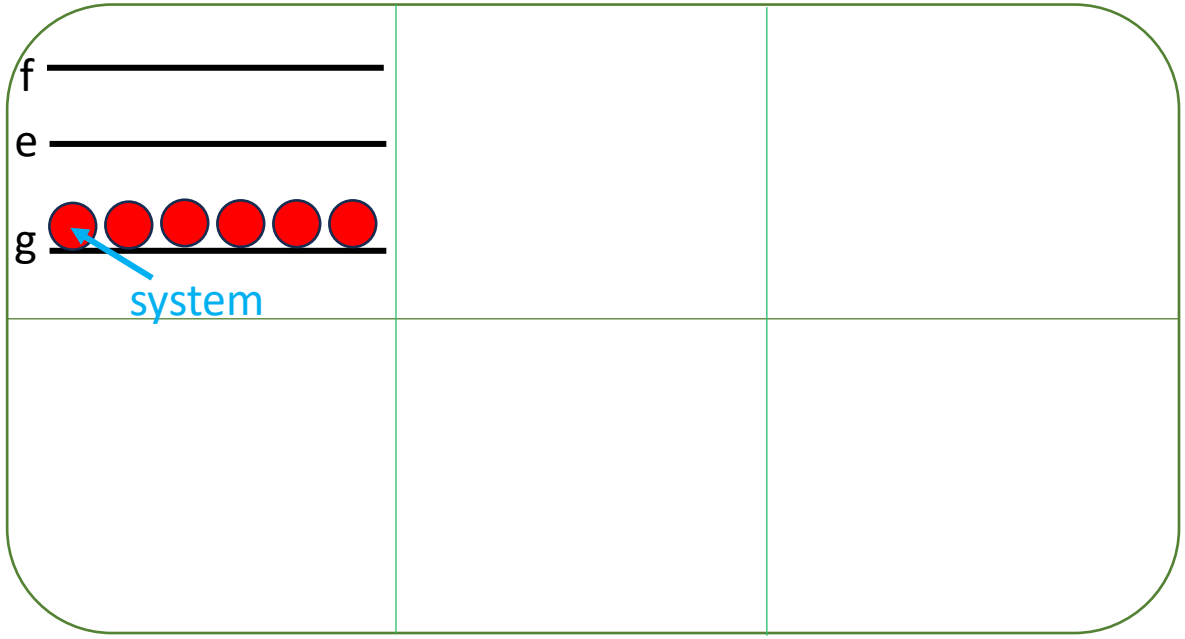
$$= |E_s|^2 + |E_{\mathrm{pr}}|^2 + 2\mathrm{Re}|E_S E_{\mathrm{pr}}^*| - |E_{\mathrm{pr}}|^2$$

$$\approx 2\mathrm{Re}|E_s E_{\mathrm{pr}}^*|$$

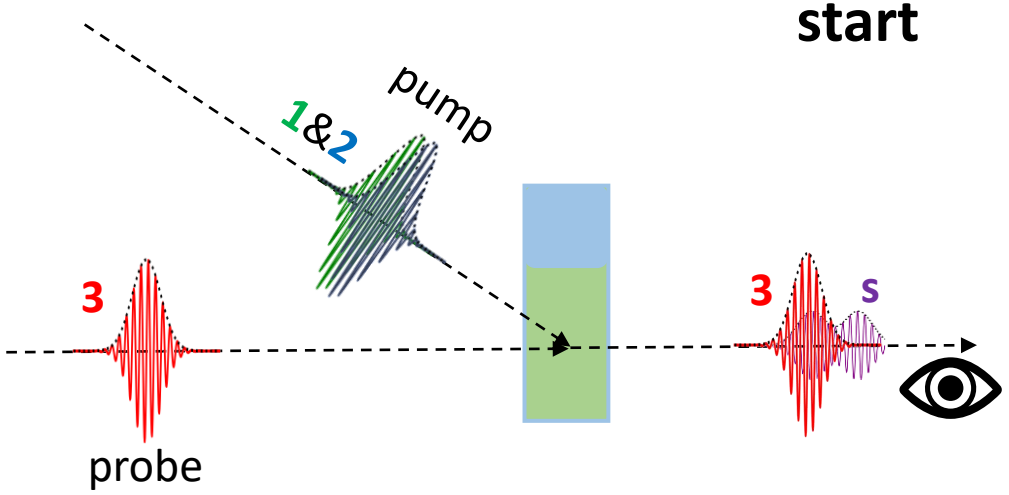
$$= 2\mathrm{Re}\left(\mathcal{E}_s \mathcal{E}_{\mathrm{pr}} e^{i(\phi_s - \phi_{\mathrm{pr}})}\right)$$

Pump-probe spectroscopy

with pump

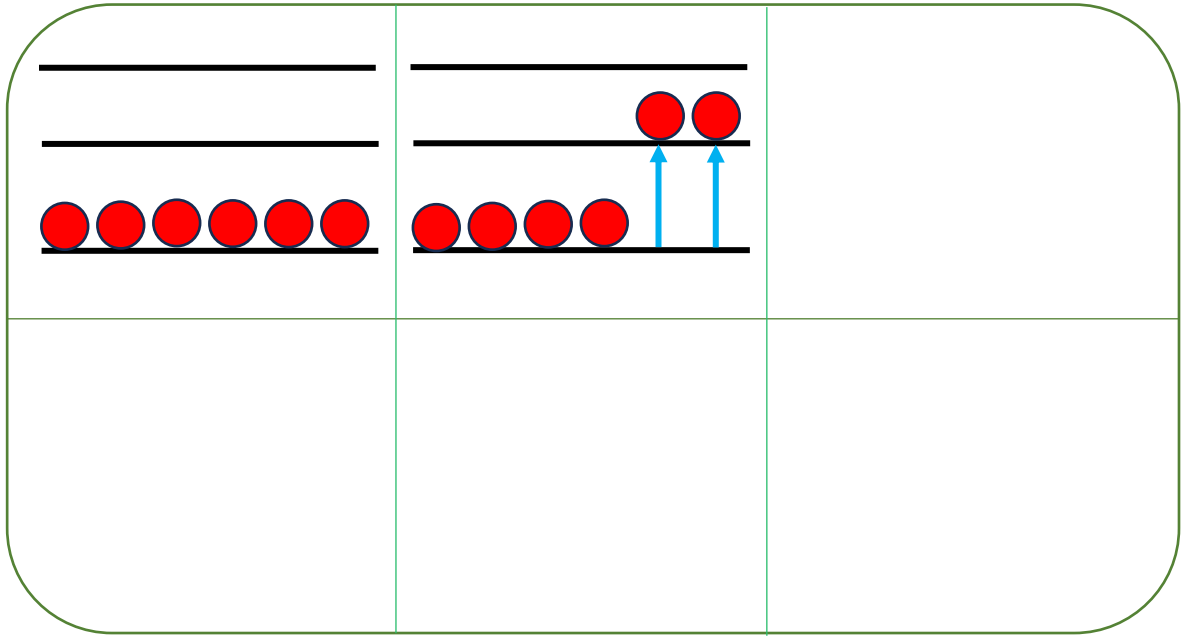


start pump probe

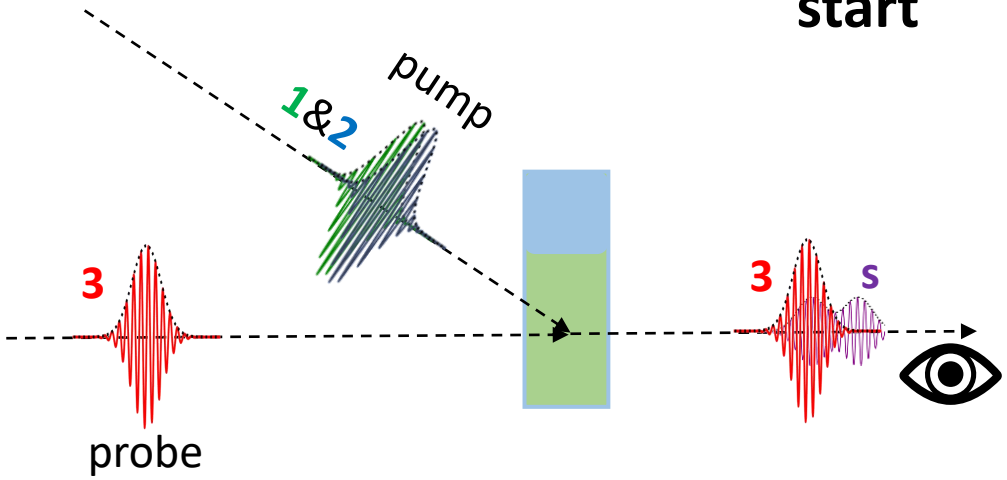


Pump-probe spectroscopy

with pump

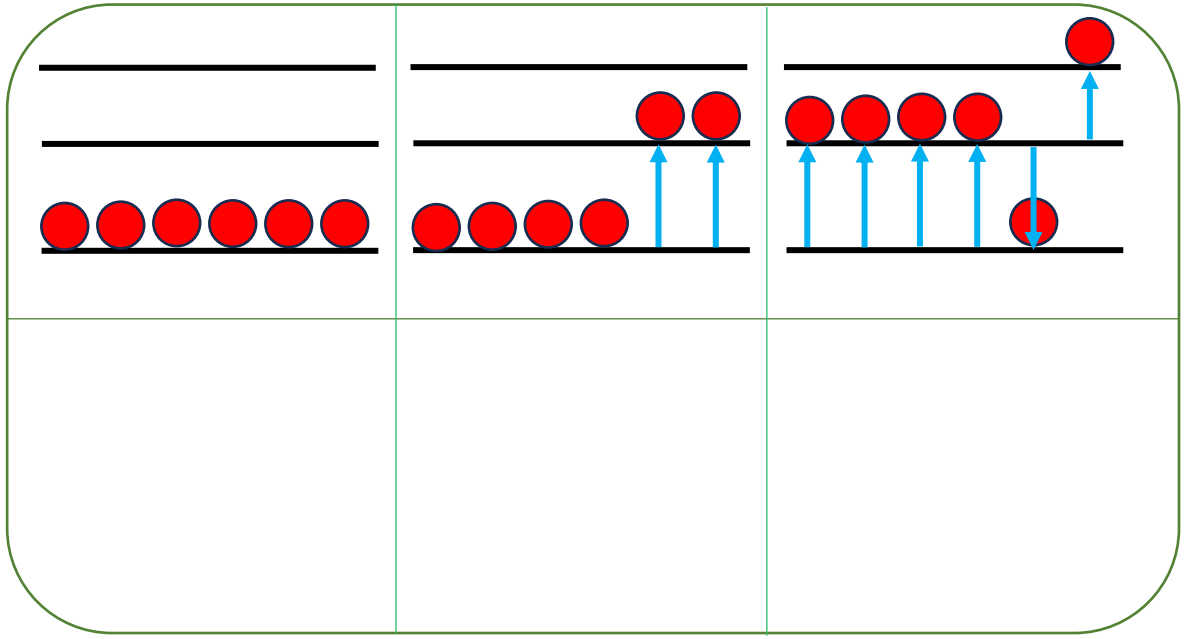


start pump probe

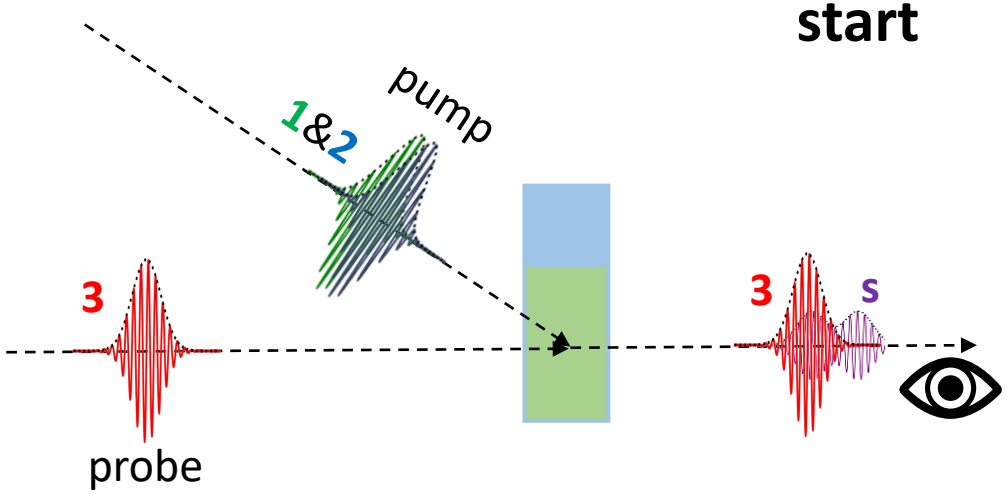


Pump-probe spectroscopy

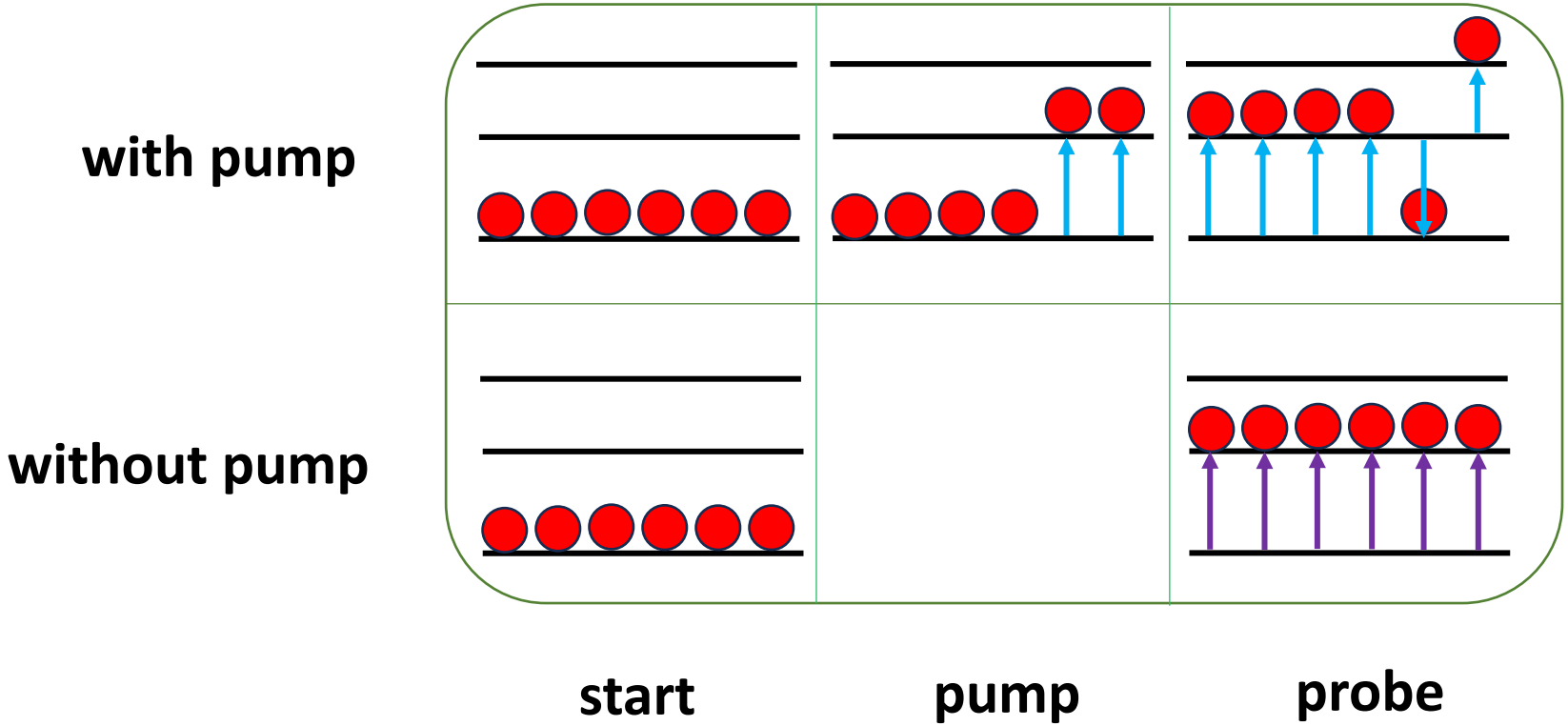
with pump

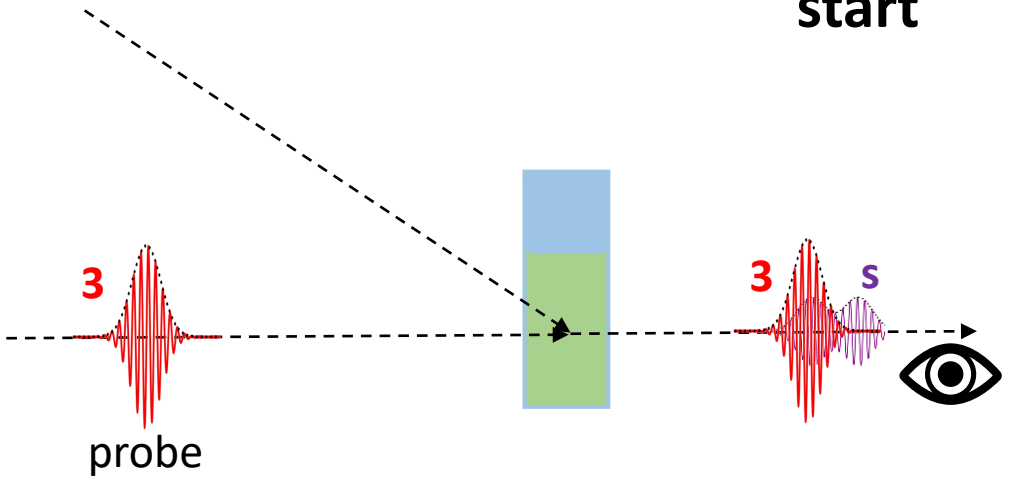


start pump probe

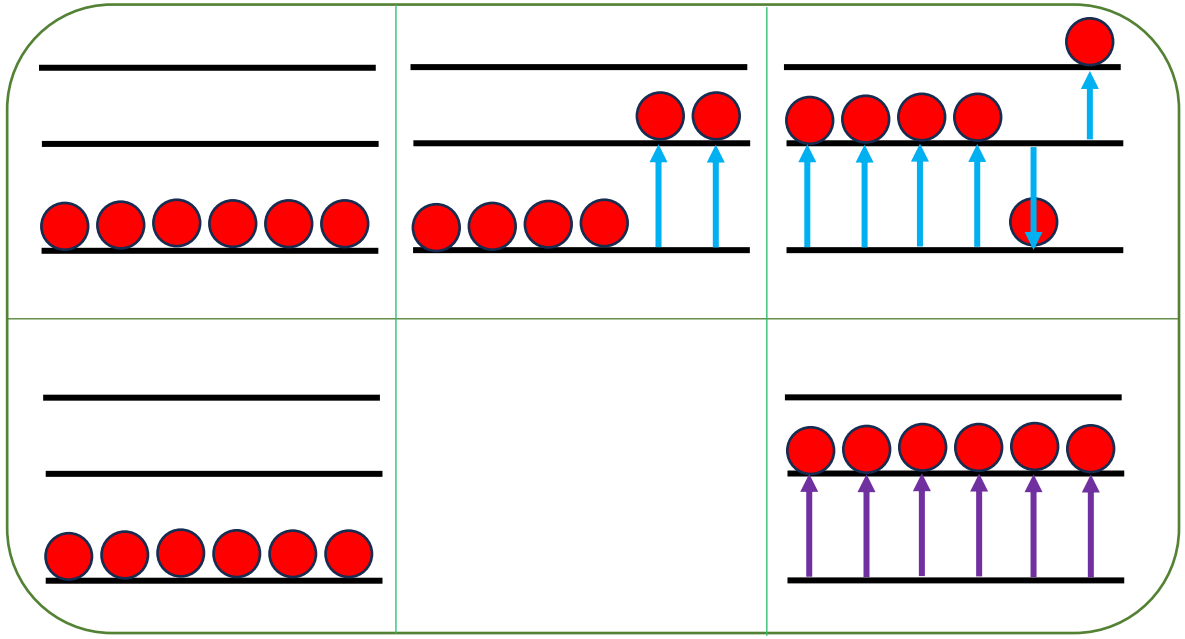


Pump-probe spectroscopy

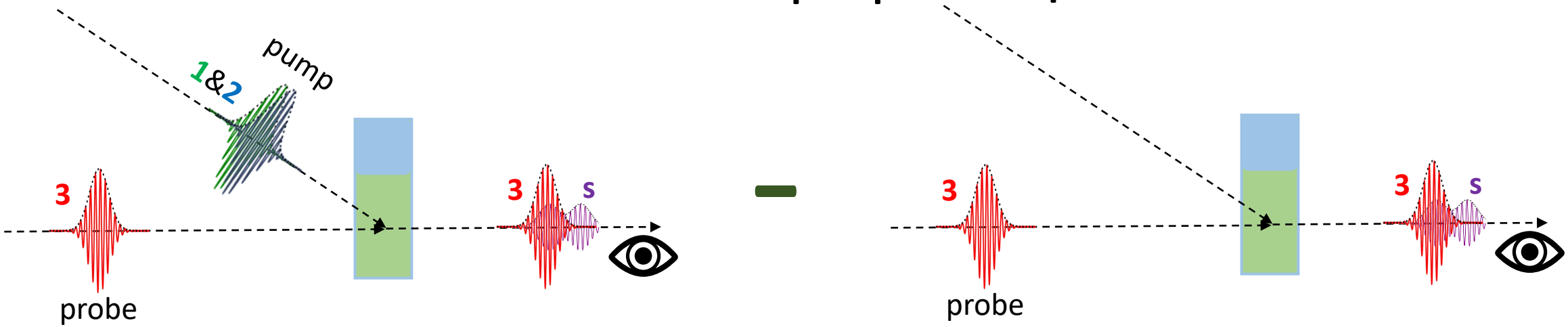




Pump-probe spectroscopy



start pump probe

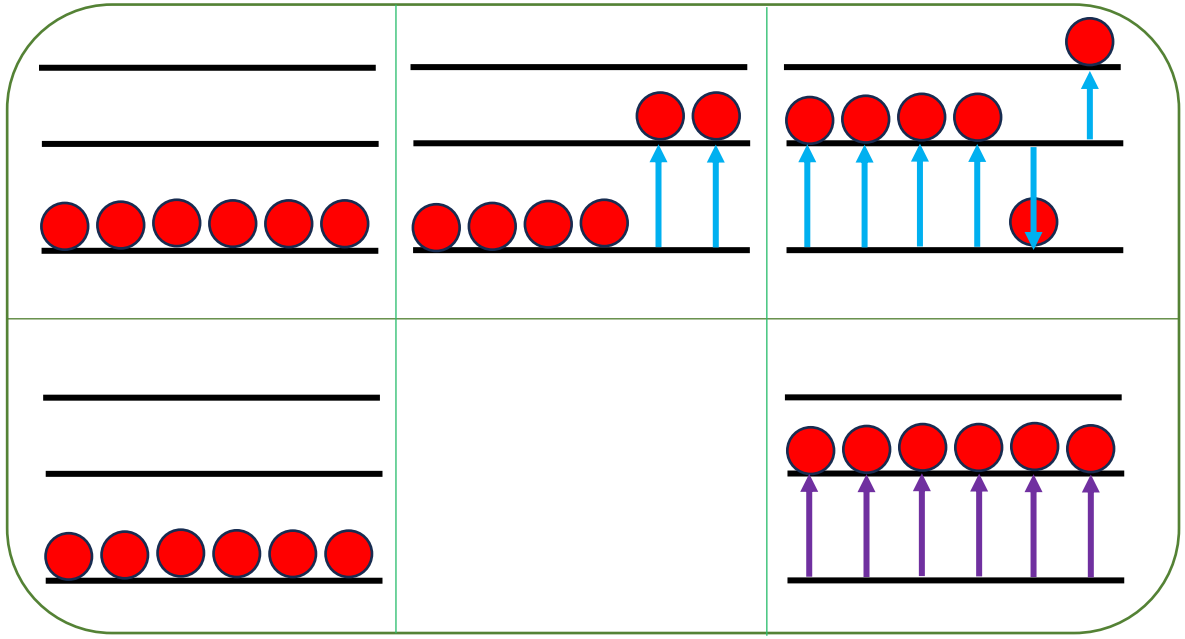


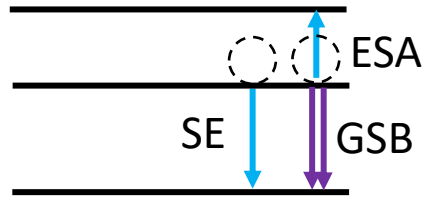
Pump-probe spectroscopy

with pump

−

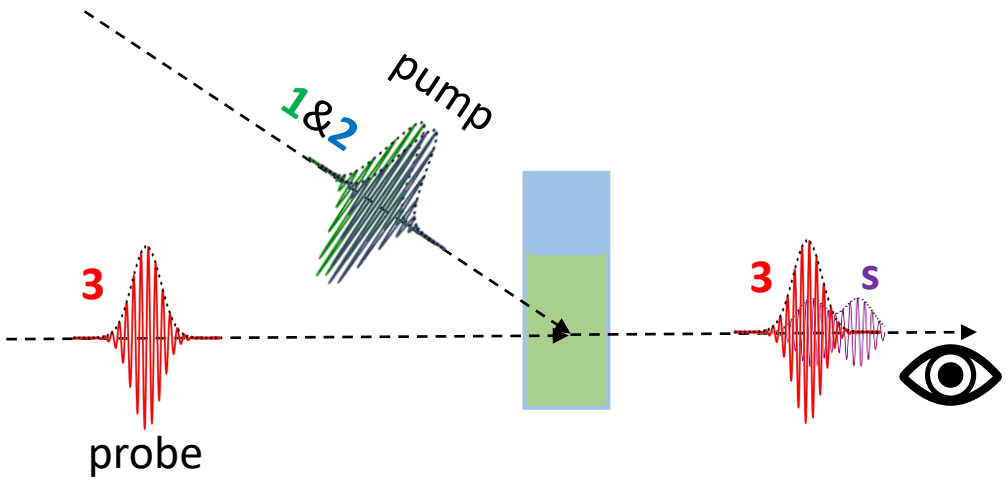
without pump



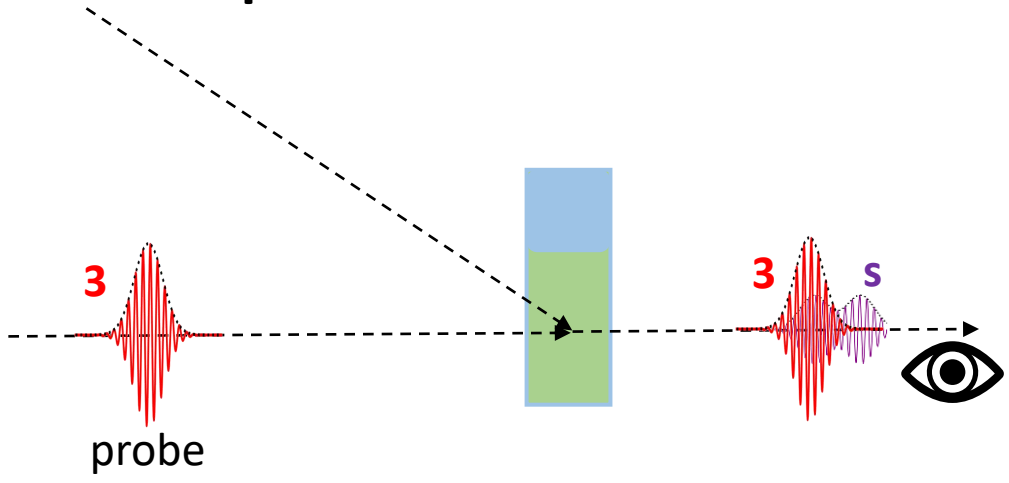


GSB –ground state bleaching
SE – stimulated emission
ESA – excited state absorption

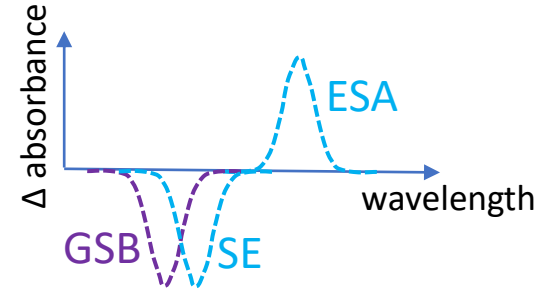
start **pump** **probe**



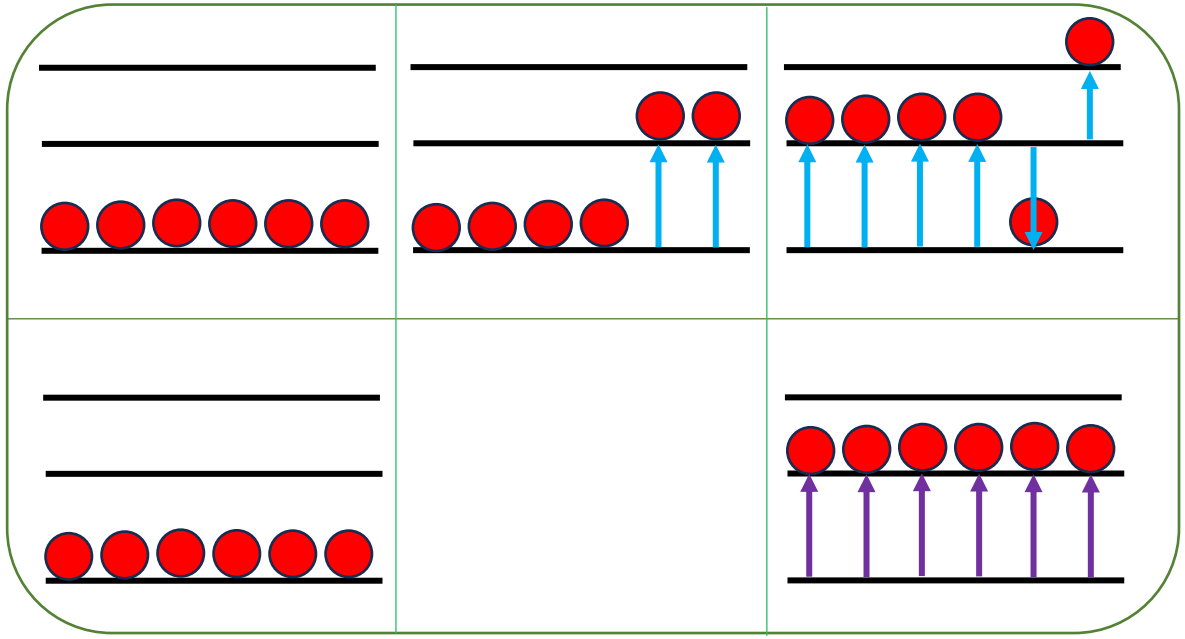
−

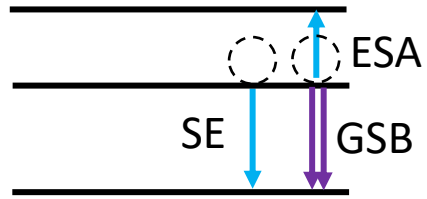


Pump-probe spectroscopy



with pump

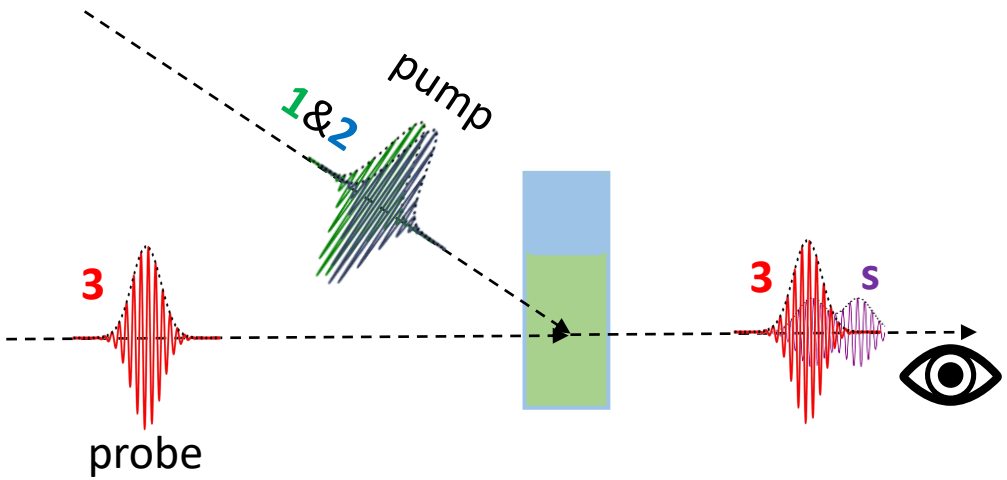


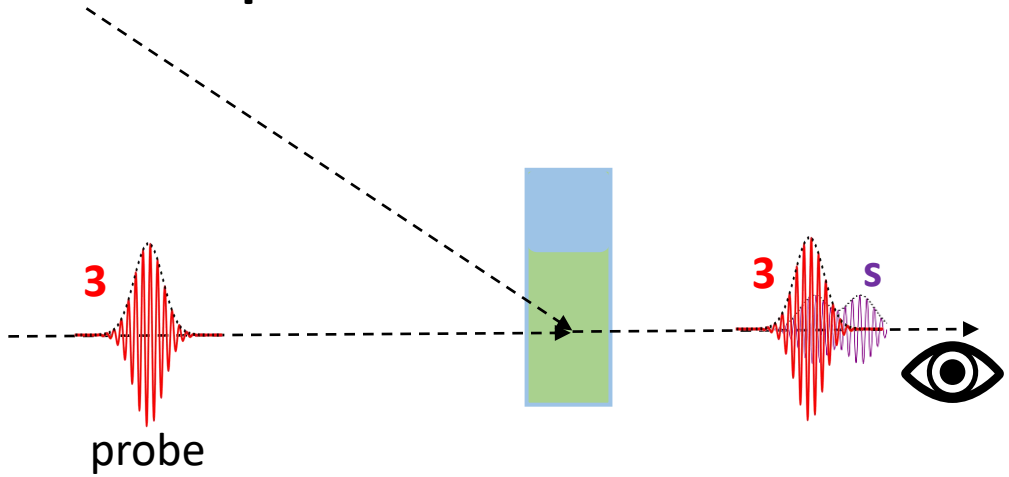


without pump

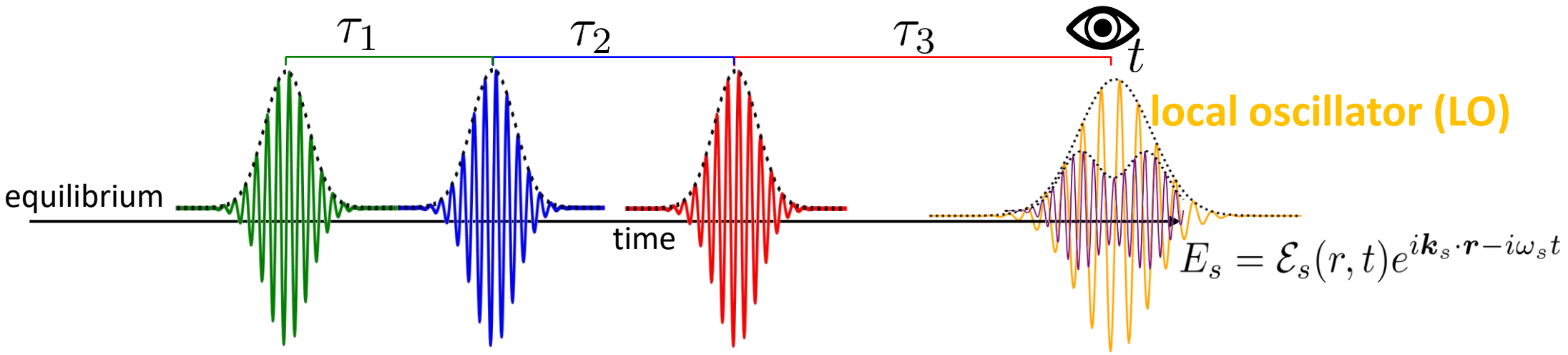
GSB –ground state bleaching
SE – stimulated emission
ESA – excited state absorption

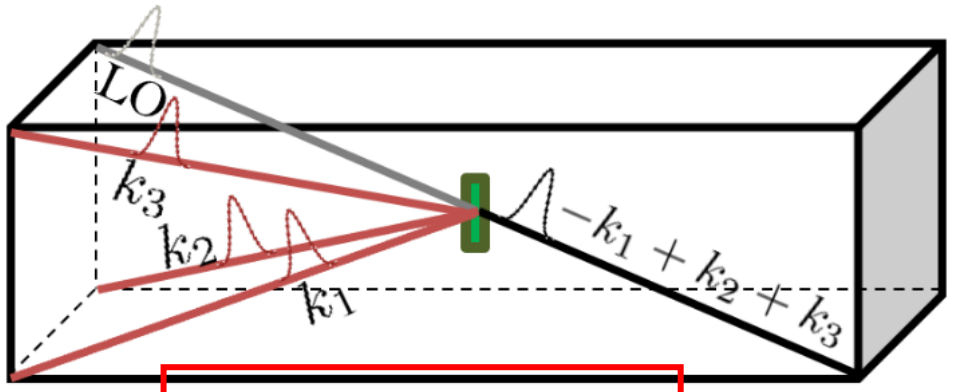
start **pump** **probe**





2D electronic spectroscopy

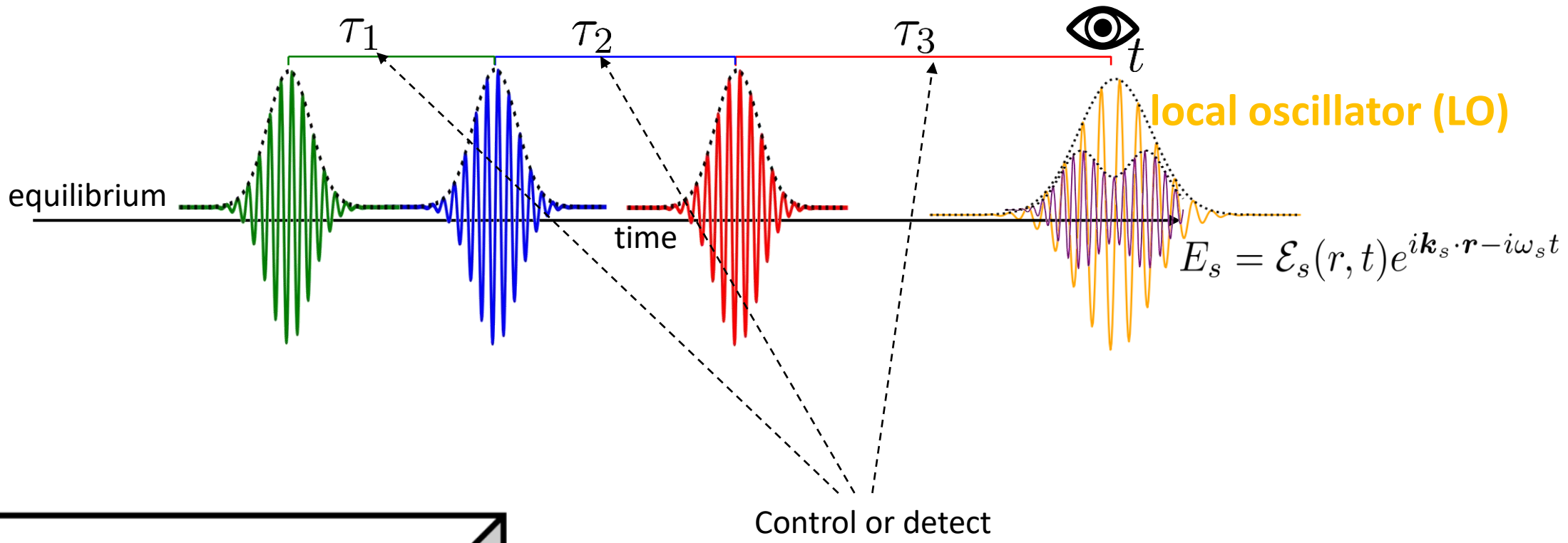


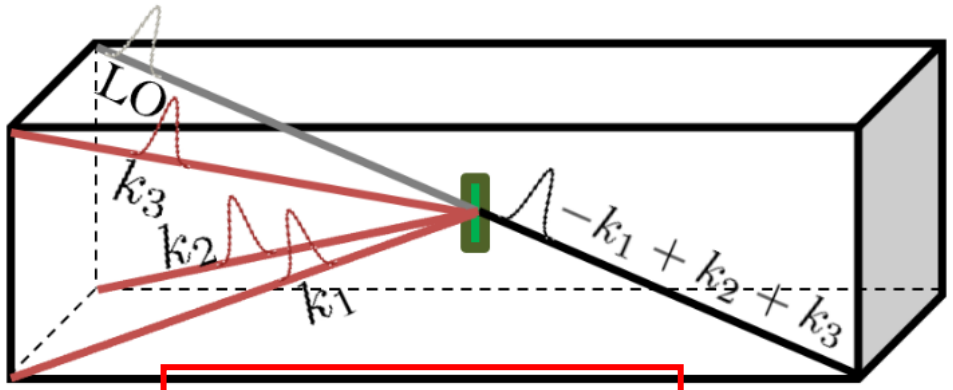


$$\boldsymbol{k}_s = -\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$$

$$\omega_s = -\omega_1 + \omega_2 + \omega_3$$

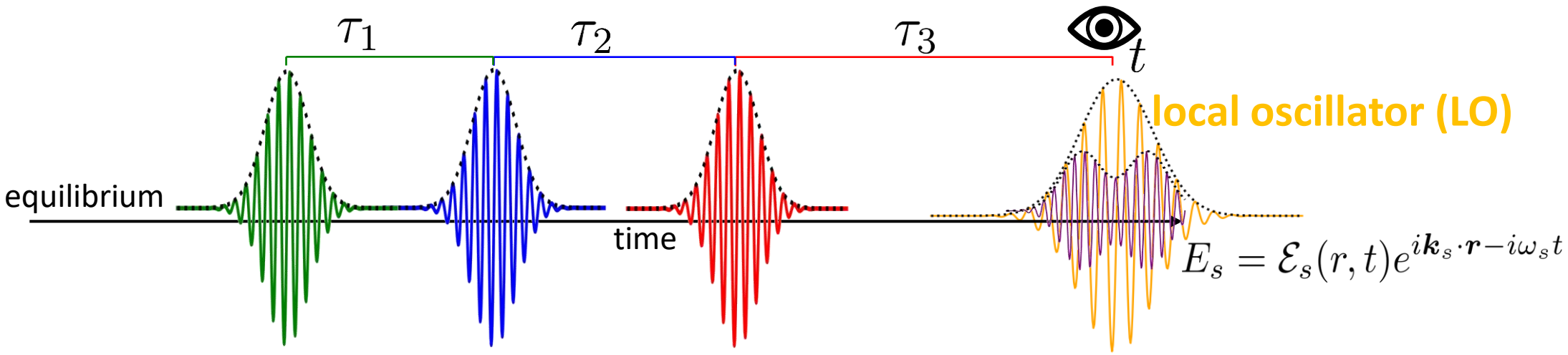
2D electronic spectroscopy





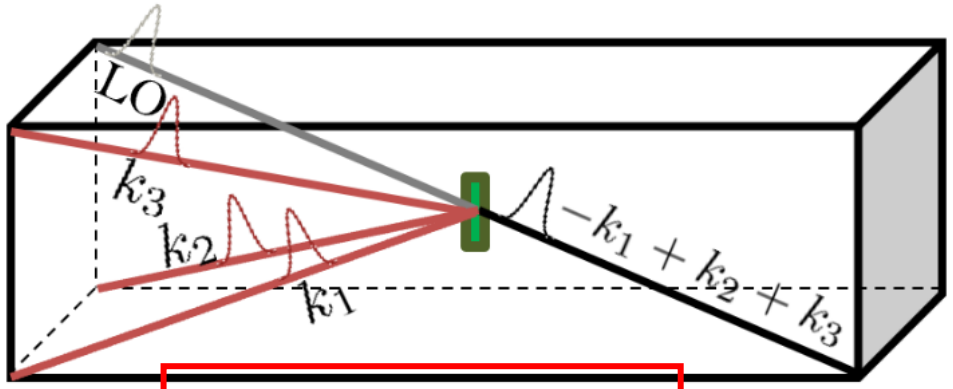
$$\boldsymbol{k}_s = -\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$$
$$\omega_s = -\omega_1 + \omega_2 + \omega_3$$

2D electronic spectroscopy



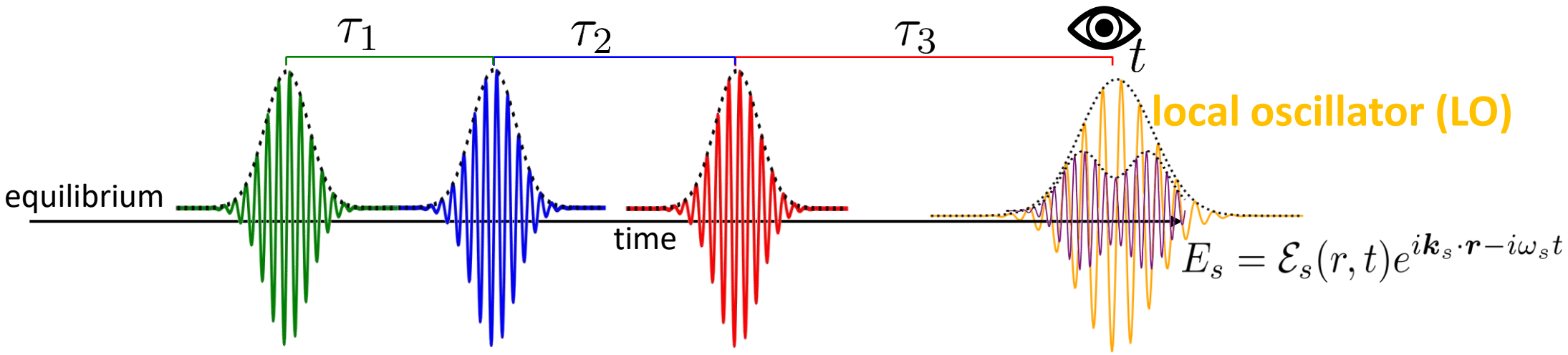
$$\mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1) = i^n \mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(\tau_3)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_2)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]$$

$$\mathcal{E}_s(r,t) \approx i\mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1)$$



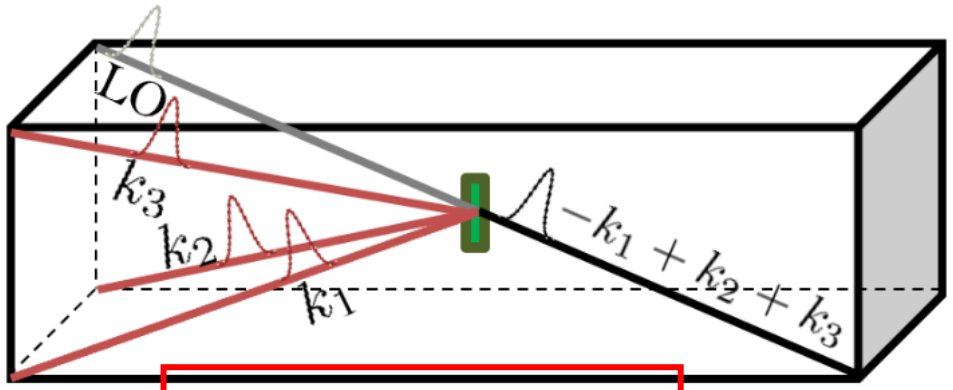
$$\boldsymbol{k}_s = -\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$$
$$\omega_s = -\omega_1 + \omega_2 + \omega_3$$

2D electronic spectroscopy



$$\mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1) = i^n \mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(\tau_3)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_2)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]$$

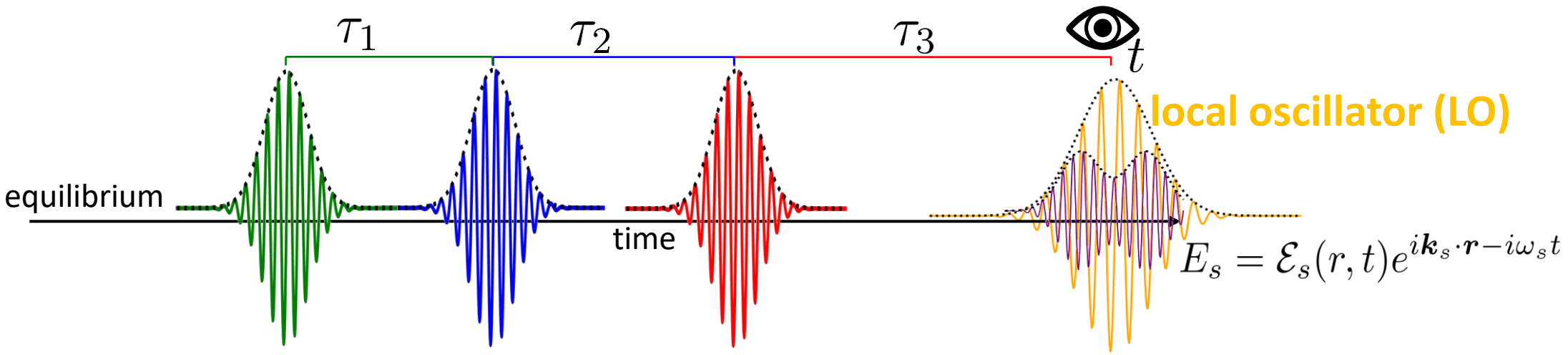
$e^{i\omega_{\alpha\beta}t}$ $\qquad$ $e^{-i\omega_{\alpha\beta}t}$



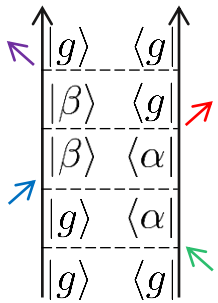
$$\boldsymbol{k}_s = -\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$$
$$\omega_s = -\omega_1 + \omega_2 + \omega_3$$

$$\mathcal{R}^{(3)}_{\mathrm{rephasing}} = R_{2g} + R_{3g} - R^*_{1f}$$

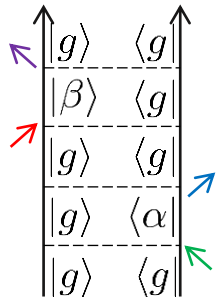
2D electronic spectroscopy



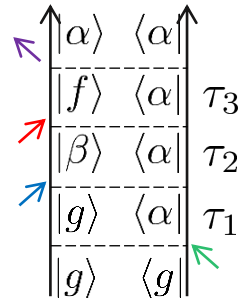
$$\mathcal{R}^{(3)}_{\text{rephasing}} = R_{2g} + R_{3g} - R^*_{1f}$$



SE

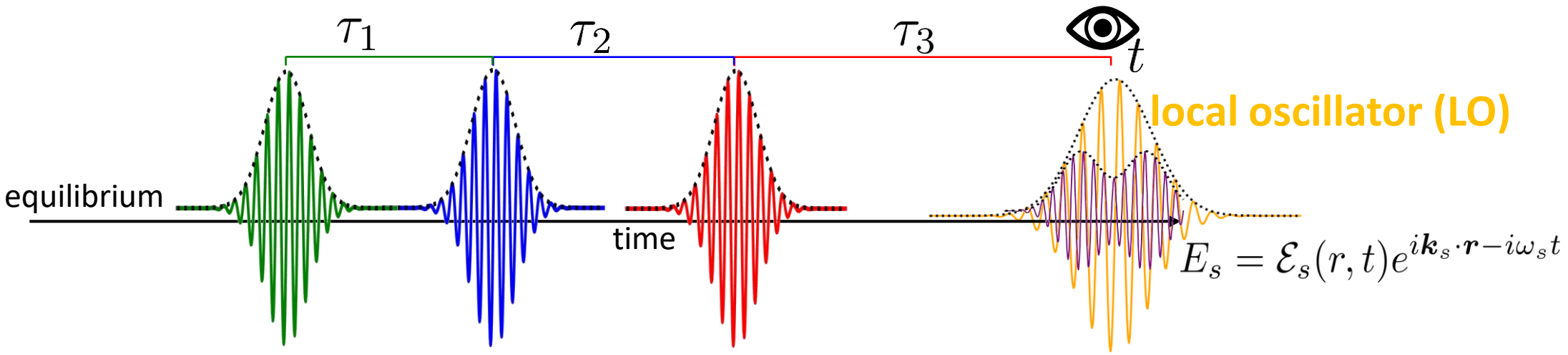


GSB

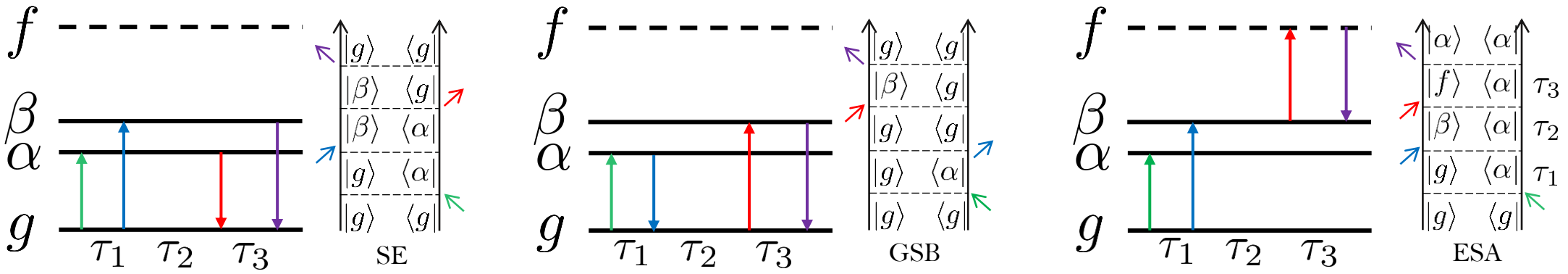


ESA

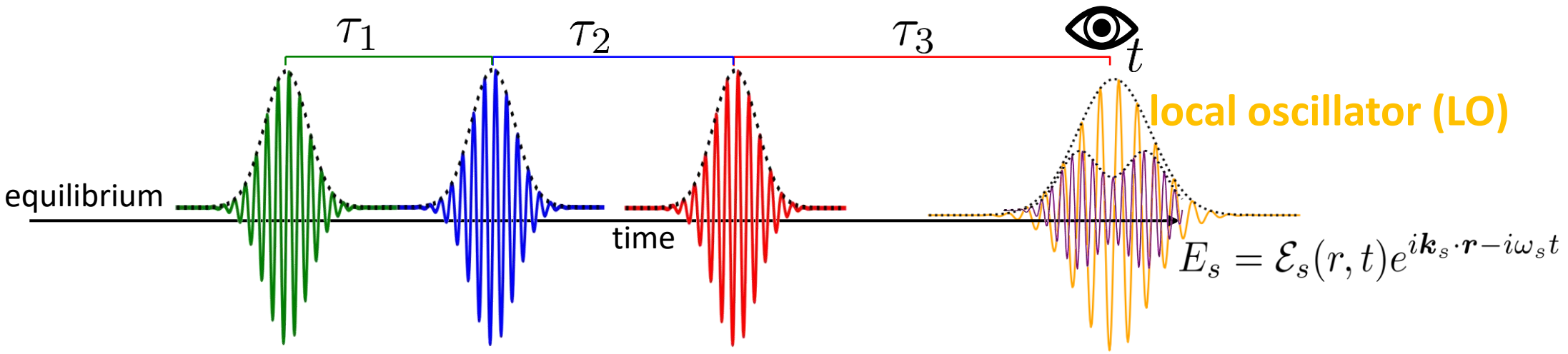
2D electronic spectroscopy

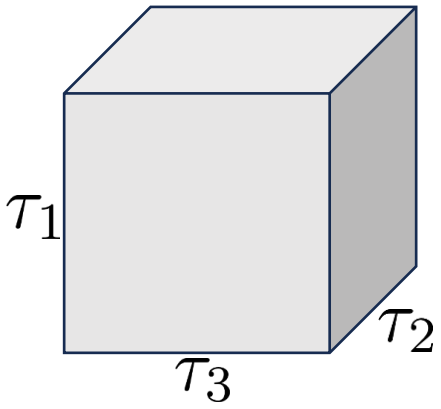


$$\mathcal{R}^{(3)}_{\text{rephasing}} = R_{2g} + R_{3g} - R^*_{1f}$$

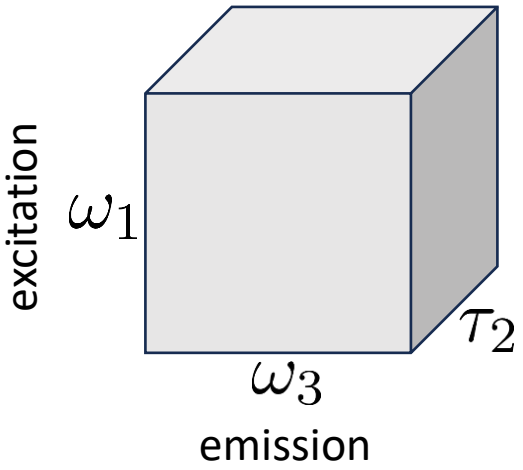


2D electronic spectroscopy

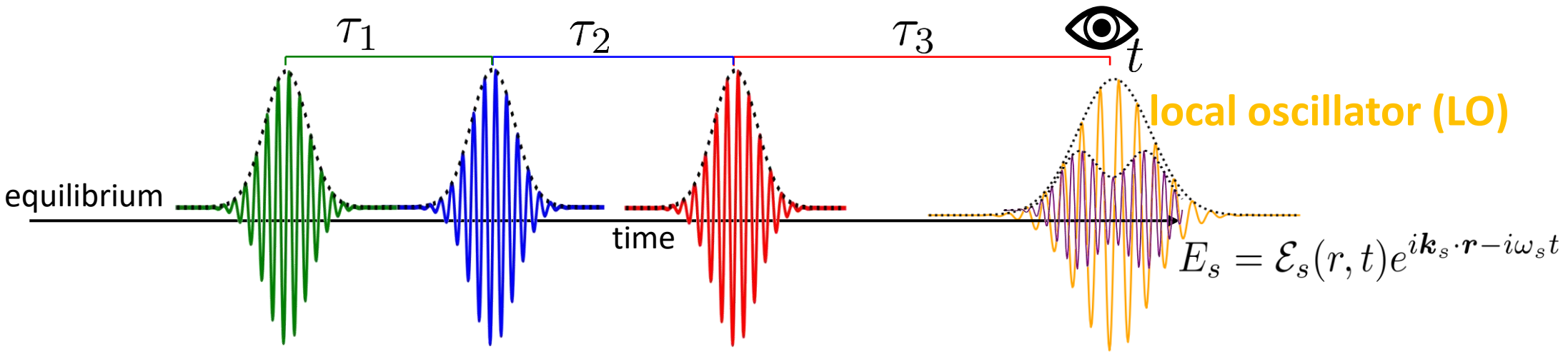


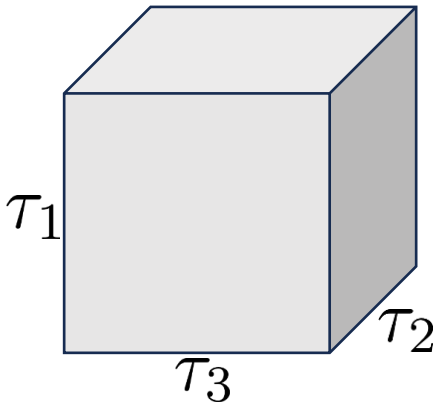


FT over τ_1 and τ_3

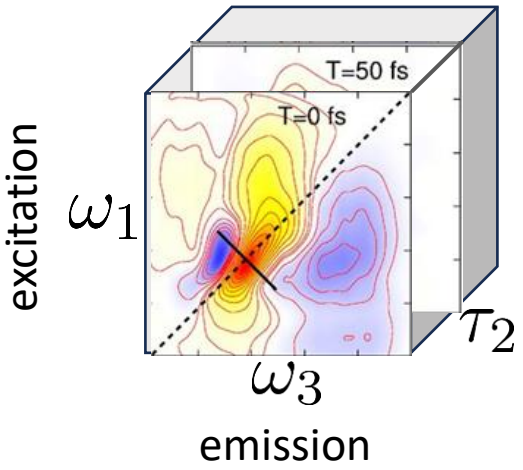


2D electronic spectroscopy

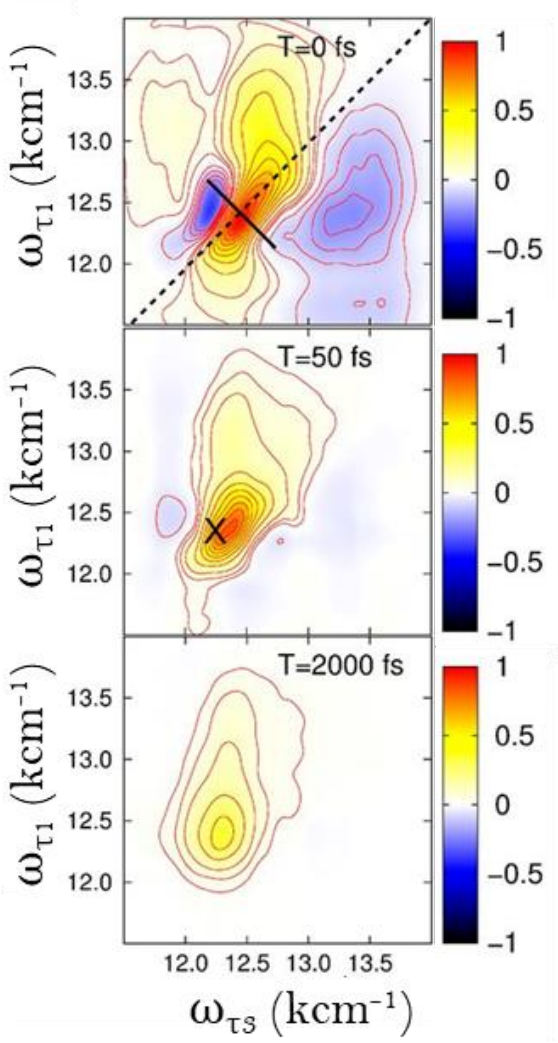


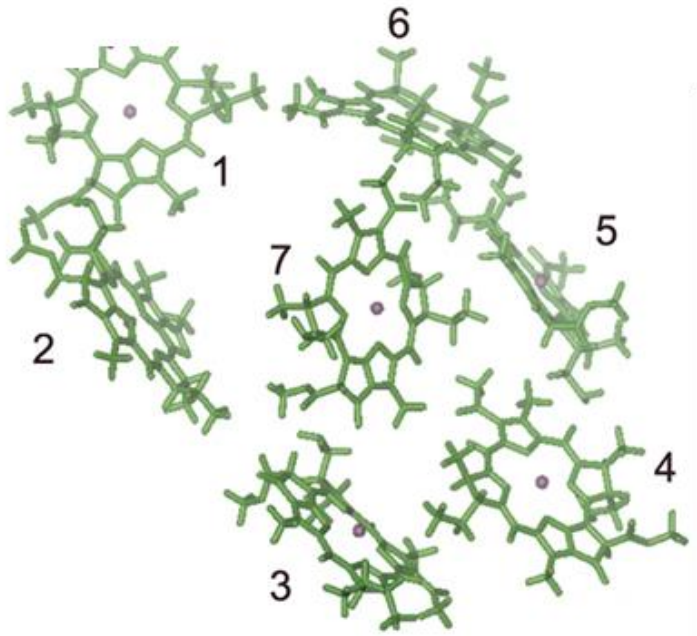


FT over τ_1 and τ_3



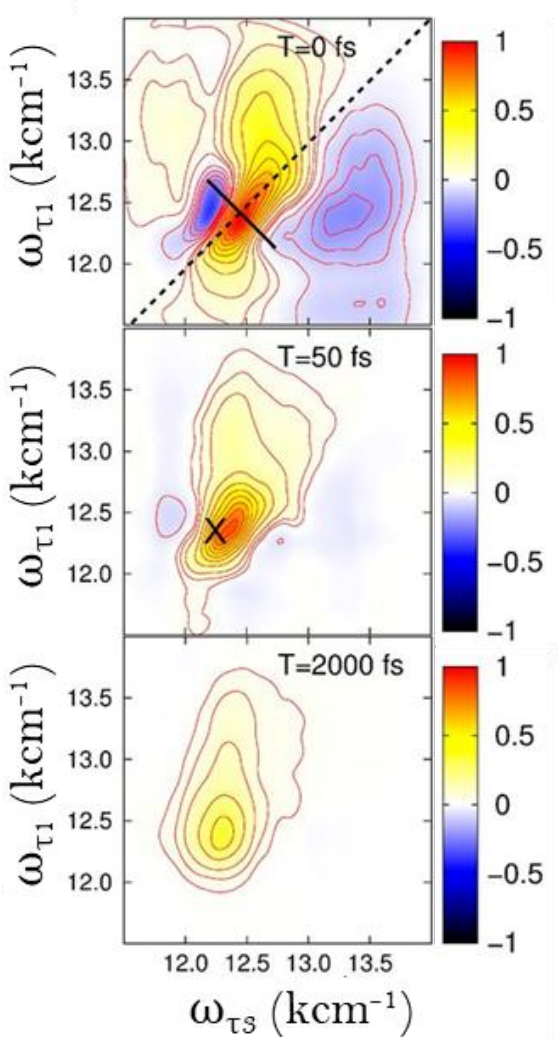
2D electronic spectroscopy

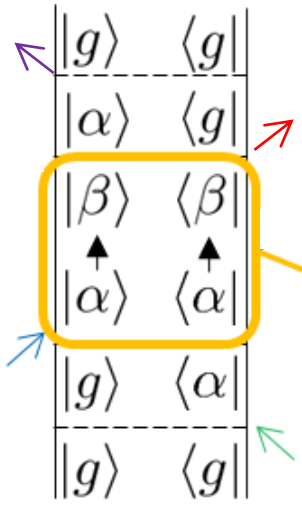




Duan *et al.* 2017. Proc. Natl. Acad. Sci. U.S.A., 114(32)

2D electronic spectroscopy





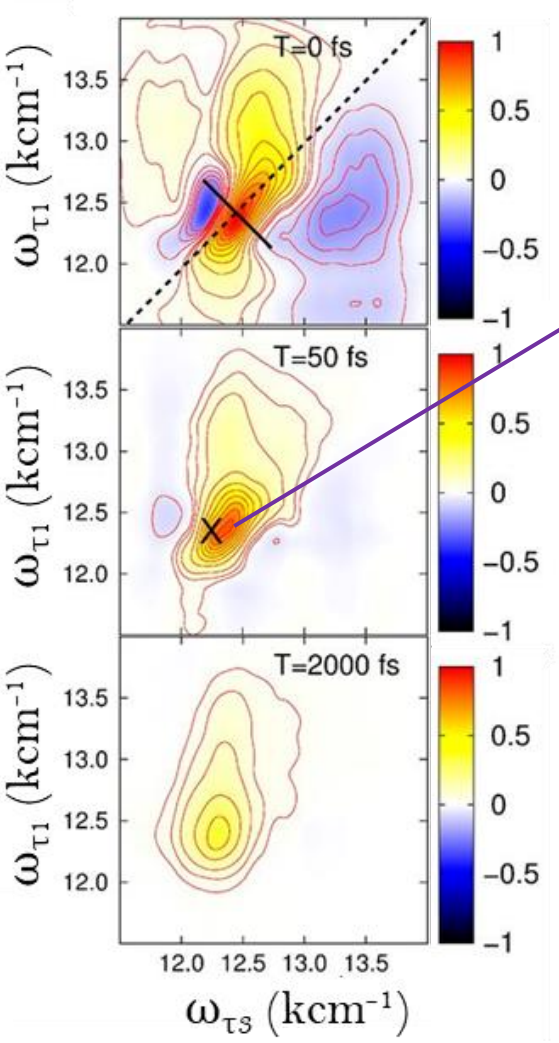
SE

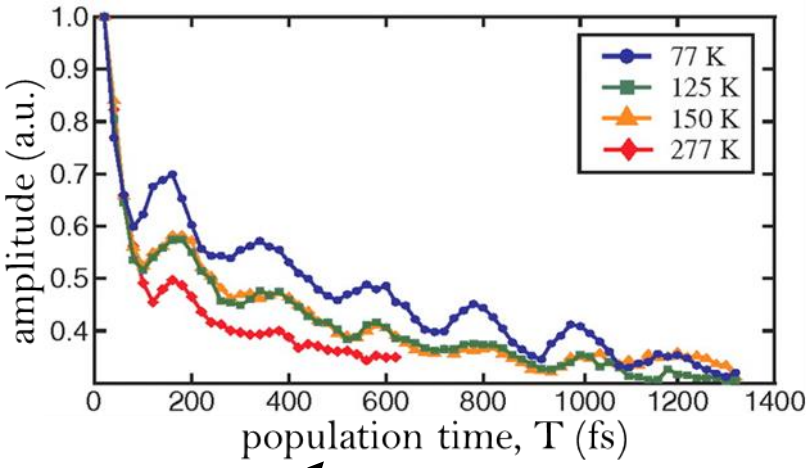
$$k_{\beta\leftarrow\alpha} = \sum_n |c_\alpha^n|^2 |c_\beta^n|^2 C_n(\omega_\beta - \omega_\alpha)$$

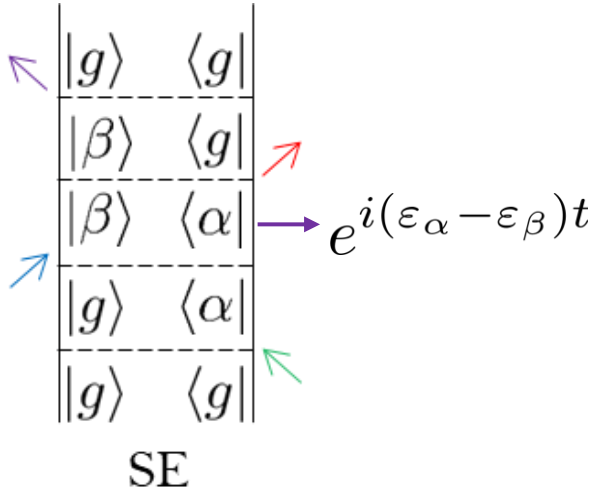
$$\frac{d}{dt} P_\beta = \sum_\alpha k_{\beta\leftarrow\alpha} P_\alpha$$

Duan *et al.* 2017. Proc. Natl. Acad. Sci. U.S.A., 114(32)

2D electronic spectroscopy



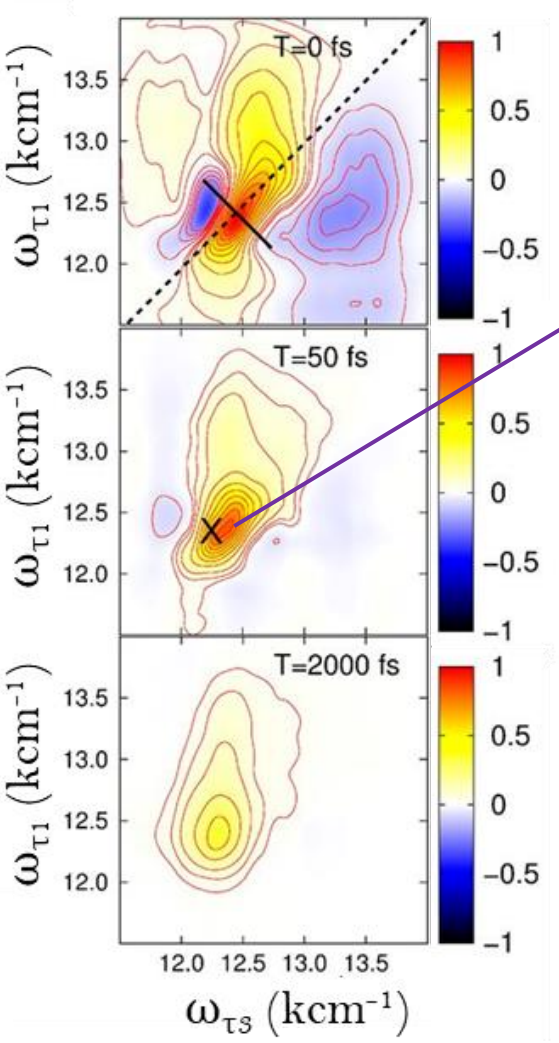




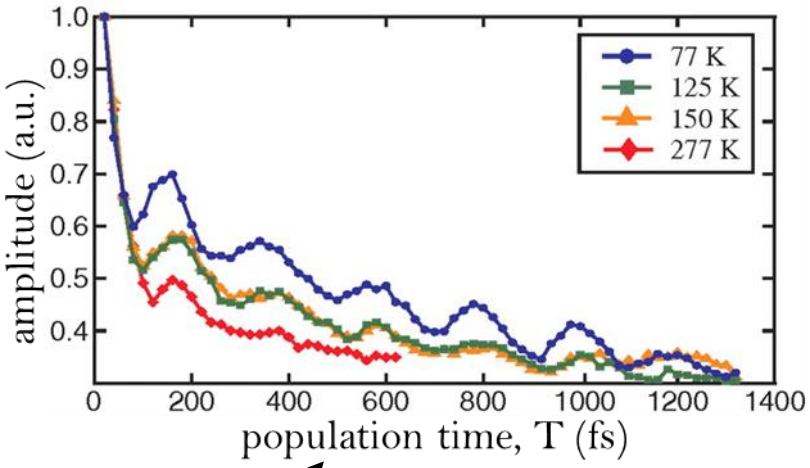
Panitchayangkoon *et al.* 2010. Proc. Natl. Acad. Sci. U.S.A., 107(29)

Duan *et al.* 2017. Proc. Natl. Acad. Sci. U.S.A., 114(32)

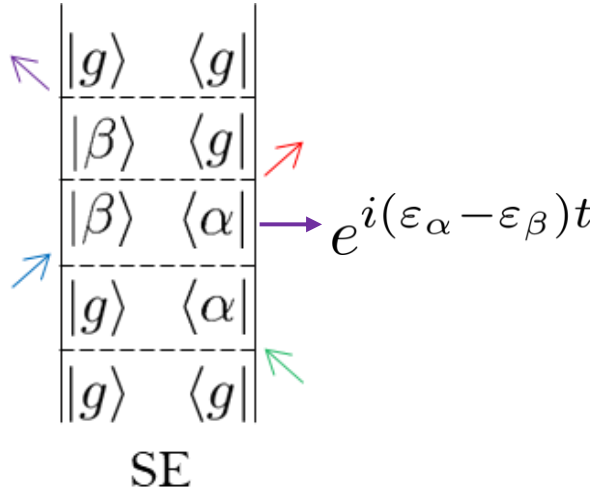
2D electronic spectroscopy

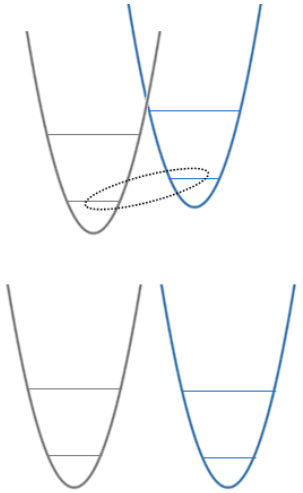


Duan *et al.* 2017. Proc. Natl. Acad. Sci. U.S.A., 114(32)



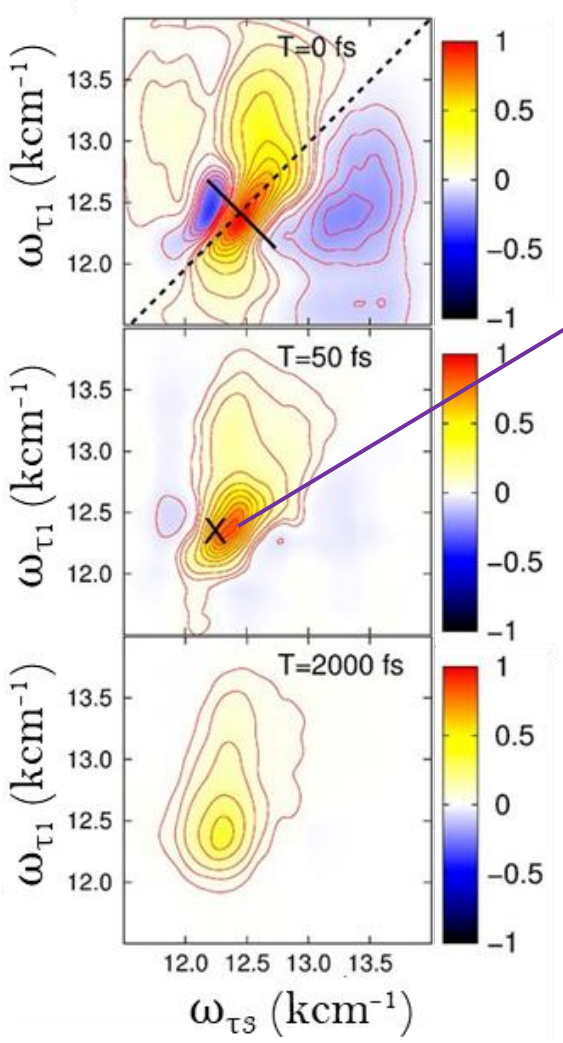
Panitchayangkoon *et al.* 2010. Proc. Natl. Acad. Sci. U.S.A., 107(29)



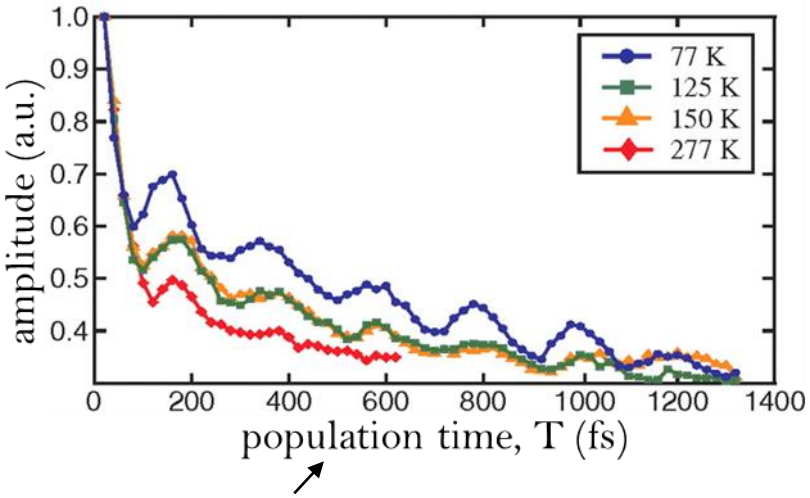


electronic

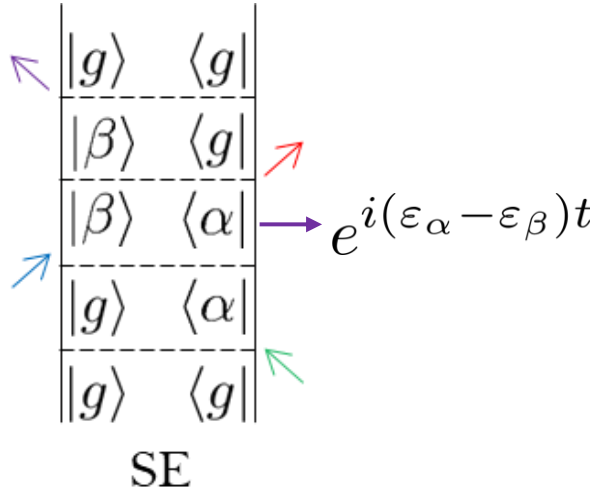
2D electronic spectroscopy

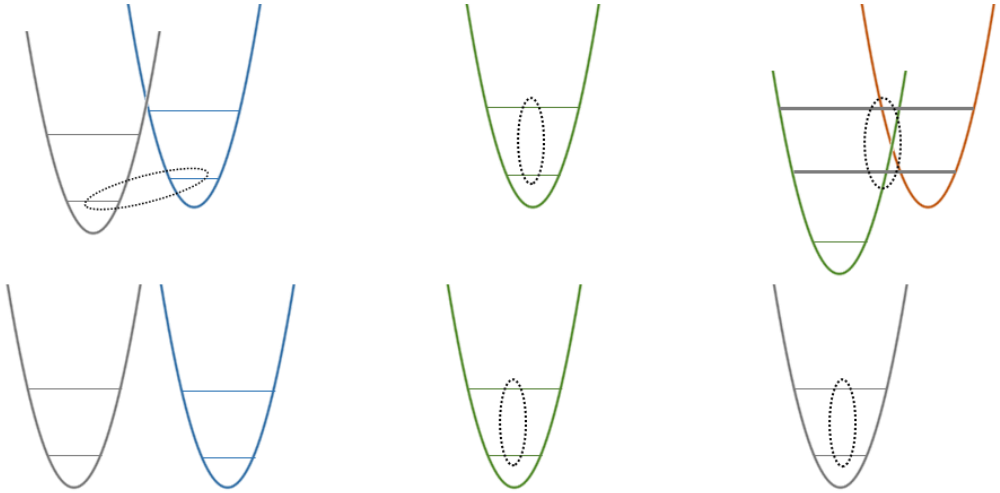


Duan *et al.* 2017. Proc. Natl. Acad. Sci. U.S.A., 114(32)



Panitchayangkoon *et al.* 2010. Proc. Natl. Acad. Sci. U.S.A., 107(29)





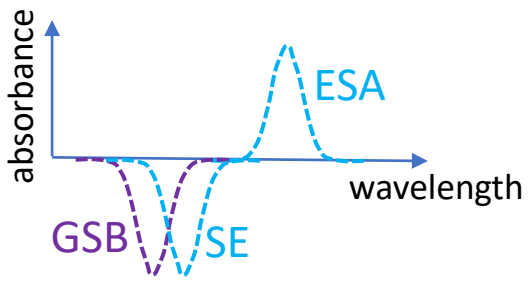
Summary

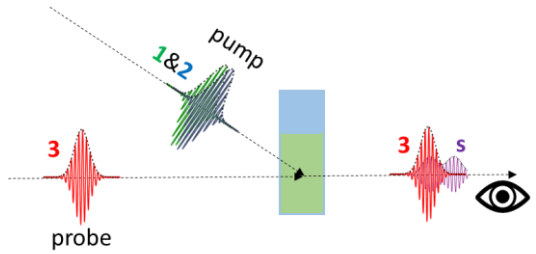
$$\mathcal{R}^{(3)}(\tau_3,\tau_2,\tau_1) = i^n \mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(\tau_3)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_2)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]$$

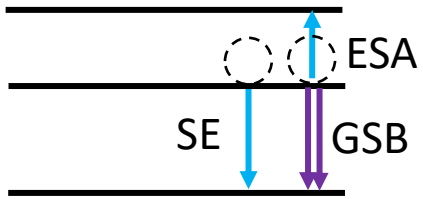
$$\boldsymbol{E}_s(t) = \mathcal{E}_s(r,t)e^{i\boldsymbol{k}_s\cdot r - i\omega_s t} + \mathrm{c.c.}$$

$$\boldsymbol{k}_s = \sum_{n=1}^{3} \pm \boldsymbol{k}_n \quad \omega_s = \sum_{n=1}^{3} \pm \omega_n$$

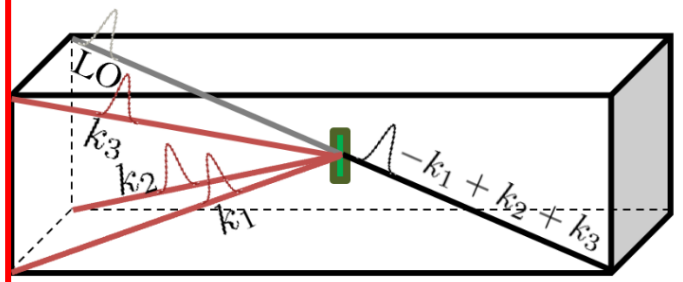
$$I_{\mathrm{det}} = |E_S + E_{\mathrm{LO}}|^2 = |E_s|^2 + |E_{\mathrm{LO}}|^2 + 2\mathrm{Re}|E_S E_{\mathrm{LO}}^*|$$



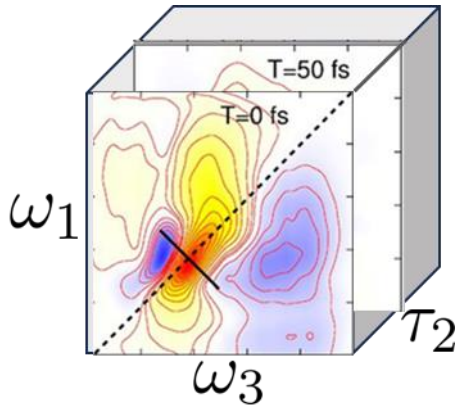




GSB –ground state bleaching
SE – stimulated emission
ESA – excited state absorption



excitation



emission

Absorption spectroscopy tutorial

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[\mathrm{Re} \int_{0}^{\infty} dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]$$

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \sum_{i=1}^{7} |\mu_{i0}|^2 \mathrm{Re} \int_{0}^{\infty} d\tau\, e^{-i(\omega-\omega_{i0})\tau - g_{ii}(\tau) - \frac{\Gamma_i}{2}\tau}$$

Absorption spectroscopy tutorial

site basis

matrix
diagonalization

exciton basis

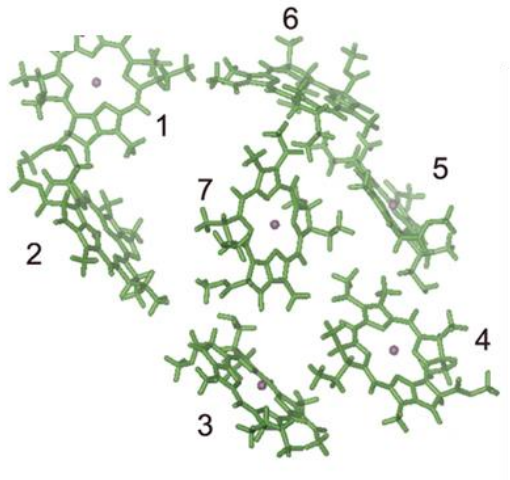
$$\mathrm{S^A}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[\mathrm{Re} \int_0^{\infty} dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]$$

$$\mathrm{S^A}(\omega) \propto \sum_{i=1}^{7} |\mu_{i0}|^2 \mathrm{Re} \int_0^{\infty} d\tau\, e^{-i(\omega-\omega_{i0})\tau - g_{ii}(\tau) - \frac{\Gamma_i}{2}\tau}$$

Absorption spectroscopy tutorial

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[\mathrm{Re} \int_{0}^{\infty} dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]$$

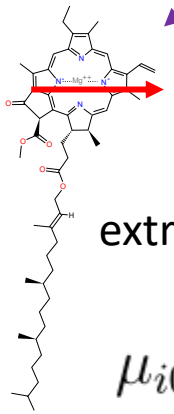
$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \sum_{i=1}^{7} |\mu_{i0}|^2 \mathrm{Re} \int_{0}^{\infty} d\tau\, e^{-i(\omega-\omega_{i0})\tau - g_{ii}(\tau) - \frac{\Gamma_i}{2}\tau}$$



Absorption spectroscopy tutorial

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[\mathrm{Re} \int_{0}^{\infty} dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]$$

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \sum_{i=1}^{7} |\mu_{i0}|^2 \mathrm{Re} \int_{0}^{\infty} d\tau\, e^{-i(\omega-\omega_{i0})\tau - g_{ii}(\tau) - \frac{\Gamma_i}{2}\tau}$$



extract from Protein Data Bank

$$\mu_{i0} = \sum_{n} c_i^n \mu_{n0}$$

Absorption spectroscopy tutorial

$$\mathrm{S^A}(\omega) \propto \omega \sum_{m=1}^{N}\sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[\mathrm{Re}\int_0^{\infty} dt\, e^{i\omega t}\mathrm{I}_{mn}^{\mathrm{A}}(t)\right]$$

$$\mathrm{S^A}(\omega) \propto \sum_{i=1}^{7} |\mu_{i0}|^2 \mathrm{Re}\int_0^{\infty} d\tau\, e^{-i(\omega-\omega_{i0})\tau - g_{ii}(\tau) - \frac{\Gamma_i}{2}\tau}$$

exciton energy

Absorption spectroscopy tutorial

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[\mathrm{Re} \int_{0}^{\infty} dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]$$

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \sum_{i=1}^{7} |\mu_{i0}|^2 \mathrm{Re} \int_{0}^{\infty} d\tau\, e^{-i(\omega-\omega_{i0})\tau - g_{ii}(\tau) - \frac{\Gamma_i}{2}\tau}$$

lineshape function

$$g_{ii}(t) = \frac{1}{\pi} \int_{0}^{\infty} d\omega \frac{C_i''(\omega)}{\omega^2} \left[\coth\left(\frac{\hbar\omega}{2k_B T}\right) (1 - \cos(\omega t)) + i\,(\sin(\omega t) - \omega t) \right]$$

example: overdamped harmonic oscillator

$$C''(\omega) = 2\lambda_0 \frac{\gamma_0 \omega}{\omega^2 + \gamma_0^2}$$

$$C_i''(\omega) = \sum_n |c_i^n|^2 C_n''(\omega)$$

Absorption spectroscopy tutorial

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[\mathrm{Re} \int_{0}^{\infty} dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]$$

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \sum_{i=1}^{7} |\mu_{i0}|^2 \mathrm{Re} \int_{0}^{\infty} d\tau\, e^{-i(\omega-\omega_{i0})\tau - g_{ii}(\tau) - \frac{\Gamma_i}{2}\tau}$$

$$\Gamma_i = \sum_j k_{ji}$$

$$k_{\beta \leftarrow \alpha} = \sum_n |c_\alpha^n|^2 |c_\beta^n|^2 C_n(\omega_\beta - \omega_\alpha) \qquad \text{with} \qquad C_n(\omega) = \left(1 + \coth\left(\frac{\omega}{2k_B T}\right)\right) C''(\omega)$$

Absorption spectroscopy tutorial

PLEASE SEE JUPYTER NOTEBOOK ON NITheCS WEBSITS

```python
# -*- coding: utf-8 -*-
"""
In this script, the absorption spectrum of the Fenna-Matthews-Olson complex
is calculated in order to illustrate spectral calculations. This script
is for educational purposes only. It likely contains errors and is not
optimised for speed. Author: JA Nothling.
"""

import numpy as np
from scipy.interpolate import UnivariateSpline
from matplotlib import pyplot as plt

Kb = 0.695034800 #Boltzman constant
SUBTRACTED_OMEGA_CONSTANT = 12300 #This will be subtracted from the frequency axis to have calculations centered around zero.

FMO_Hamiltonian = np.array(
    [[ 1.241e+04, -8.770e+01,  5.500e+00, -5.900e+00,  6.700e+00, -1.370e+01, -9.900e+00],
     [-8.770e+01,  1.253e+04,  3.080e+01,  8.200e+00,  7.000e-01, 1.180e+01,  4.300e+00],
     [ 5.500e+00,  3.080e+01,  1.221e+04, -5.350e+01, -2.200e+00, -9.600e+00,  6.000e+00],
     [-5.900e+00,  8.200e+00, -5.350e+01,  1.232e+04, -7.070e+01, -1.700e+01, -6.330e+01],
     [ 6.700e+00,  7.000e-01, -2.200e+00, -7.070e+01,  1.248e+04, 8.110e+01, -1.300e+00],
     [-1.370e+01,  1.180e+01, -9.600e+00, -1.700e+01,  8.110e+01, 1.263e+04,  3.970e+01],
     [-9.900e+00,  4.300e+00,  6.000e+00, -6.330e+01, -1.300e+00, 3.970e+01,  1.244e+04]]) #See Adolphs and Renger, Biophys. J. vol 91. 2006.

FMO_dipole_moments = np.array([[-3.93434131,  1.95662989,  3.06472803],
                               [-4.6837954 ,  0.31322633, -2.58146275],
                               [-1.19976106,  0.84516501, -5.1523072 ],
                               [-4.28031747,  1.37988325,  2.91115176],
                               [-4.01985586, -1.03314672, -3.38723585],
                               [-0.52956811, -2.31553655,  4.80185882],
                               [-2.58031356,  2.77208469,  3.78913294]]) #Nb - Nd direction in PDB structure 3eni.pdb.


def get_overdamped_spectral_density(omega, reorganization_en, gamma): #Calculates an overdamped harmonic oscillator spectral density
    overdamped_Cw = 2*reorganization_en*omega*gamma/(omega**2 + gamma**2)
    return overdamped_Cw

def get_g(time, omega, spectral_density, temperature): #Calculates the lineshape function g
    g = np.zeros(time.size, dtype=complex)
    for ii, t in enumerate(time):
        g_integrand = 1/(2*np.pi*omega**2)*spectral_density\
                                  *(1/np.tanh(omega/(2*Kb*temperature))\
                                  *(np.cos(omega*t) - 1)\
                                  - 1j*(np.sin(omega*t) - omega*t))
        g_real = -UnivariateSpline(omega, np.real(g_integrand), s=0)\
                                .antiderivative()(omega[-1])
        g_imag = -UnivariateSpline(omega, np.imag(g_integrand), s=0)\
                                .antiderivative()(omega[-1])
```

Absorption spectroscopy tutorial

PLEASE SEE JUPYTER NOTEBOOK ON NITheCS WEBSITS

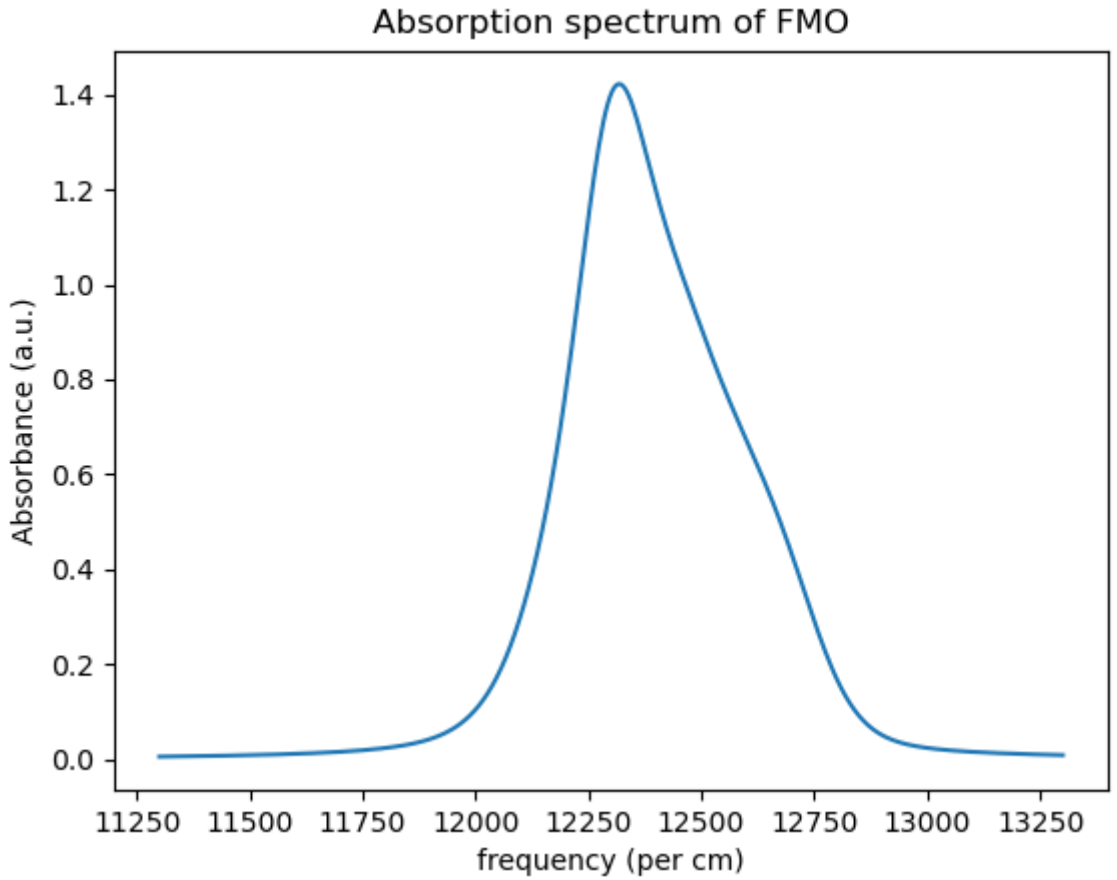
```
                                .antiderivative()(omega[-1])
            g[ii] = g_real + 1j*g_imag
        return g

    def calculate_Redf_rates_matrix(exciton_energies, transformation_matrix,\
                                    reorganization_en, gamma, temperature): #Calculates the Redfield rate matrix
        beta = 1/(Kb*temperature)
        rates_matrix = np.zeros((exciton_energies.size, exciton_energies.size))
        for ii in range(exciton_energies.size): #over exciton states
            for jj in range(exciton_energies.size): #over exciton states
                if ii != jj:
                    ex_energy_diff = exciton_energies[ii] - exciton_energies[jj]
                    for nn in range(exciton_energies.size): #over sites
                        rates_matrix[ii,jj] += transformation_matrix[nn, ii]**2\
                                               *transformation_matrix[nn, jj]**2\
                                               *(1 + 1/np.tanh(0.5*(ex_energy_diff)\
                                               *beta))\
                                               *get_overdamped_spectral_density(\
                                                   ex_energy_diff,\
                                                   reorganization_en, gamma)

        return rates_matrix

    time = np.linspace(0,0.3,2001) #Array of time for trapz function
    omegas = np.linspace(-1000,1000,400) #Range of Frequency
    temperature = 300
    reorganization_energy = 40
    gamma = 40

    specdens = get_overdamped_spectral_density(omegas, reorganization_energy, gamma)
    g = get_g(time, omegas, specdens, temperature)
    exciton_energies, transformation_matrix = np.linalg.eigh(FMO_Hamiltonian)

    g_transformation_factor = np.sum(transformation_matrix**4, axis=0) #sum over the states
    exciton_dipole_moments = transformation_matrix.T @ FMO_dipole_moments

    Redfield_rates = calculate_Redf_rates_matrix(exciton_energies,\
                                                 transformation_matrix,\
                                                 reorganization_energy, gamma,\
                                                 temperature)
    Redfield_population_decay = np.sum(Redfield_rates, axis=0)/2

    spectrum = np.zeros(omegas.size)
    for oo in range(omegas.size):
        spec = 0
        for ii in range(7):
            spec += np.dot(exciton_dipole_moments[ii], exciton_dipole_moments[ii])\
                        *np.real(np.trapz(np.exp(-1j*(omegas[oo] \
```

Absorption spectroscopy tutorial

PLEASE SEE JUPYTER NOTEBOOK ON NITheCS WEBSITS

```
    return rates_matrix

time = np.linspace(0,0.3,2001) #Array of time for trapz function
omegas = np.linspace(-1000,1000,400) #Range of Frequency
temperature = 300
reorganization_energy = 40
gamma = 40

specdens = get_overdamped_spectral_density(omegas, reorganization_energy, gamma)
g = get_g(time, omegas, specdens, temperature)
exciton_energies, transformation_matrix = np.linalg.eigh(FMO_Hamiltonian)

g_transformation_factor = np.sum(transformation_matrix**4, axis=0) #sum over the states
exciton_dipole_moments = transformation_matrix.T @ FMO_dipole_moments

Redfield_rates = calculate_Redf_rates_matrix(exciton_energies,\
                                             transformation_matrix,\
                                             reorganization_energy, gamma,\
                                             temperature)
Redfield_population_decay = np.sum(Redfield_rates, axis=0)/2

spectrum = np.zeros(omegas.size)
for oo in range(omegas.size):
    spec = 0
    for ii in range(7):
        spec += np.dot(exciton_dipole_moments[ii], exciton_dipole_moments[ii])\
                        *np.real(np.trapz(np.exp(-1j*(omegas[oo] \
                        + SUBTRACTED_OMEGA_CONSTANT \
                        - exciton_energies[ii])*time\
                        - g_transformation_factor[ii]*g
                        - Redfield_population_decay[ii]*time), x=time))
    spectrum[oo] = spec

plt.plot(omegas + SUBTRACTED_OMEGA_CONSTANT, spectrum)
plt.title('Absorption spectrum of FMO')
plt.xlabel('frequency (per cm)')
plt.ylabel('Absorbance (a.u.)')
plt.show()
```

Absorption spectroscopy tutorial



Resources

nature › nature reviews methods primers › primers › article

Primer | Published: 09 November 2023

Two-dimensional electronic spectroscopy

Elisa Fresch, Franco V. A. Camargo, Qijie Shen, Caitlin C. Bellora, Tõnu Pullerits, Gregory S. Engel, Giulio Cerullo & Elisabetta Collini

Nature Reviews Methods Primers **3**, Article number: 84 (2023) | Cite this article

BBA - Bioenergetics 1860 (2019) 271–285

Contents lists available at ScienceDirect

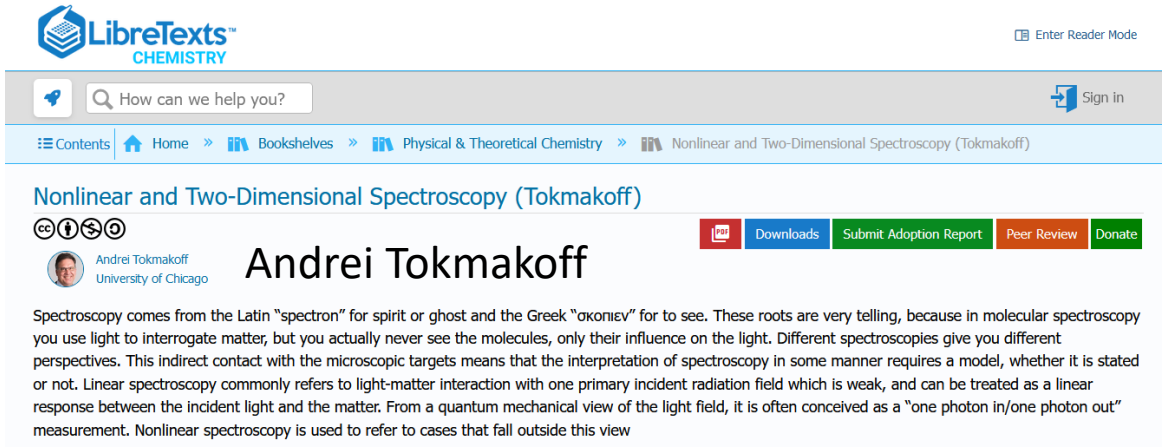
BBA - Bioenergetics

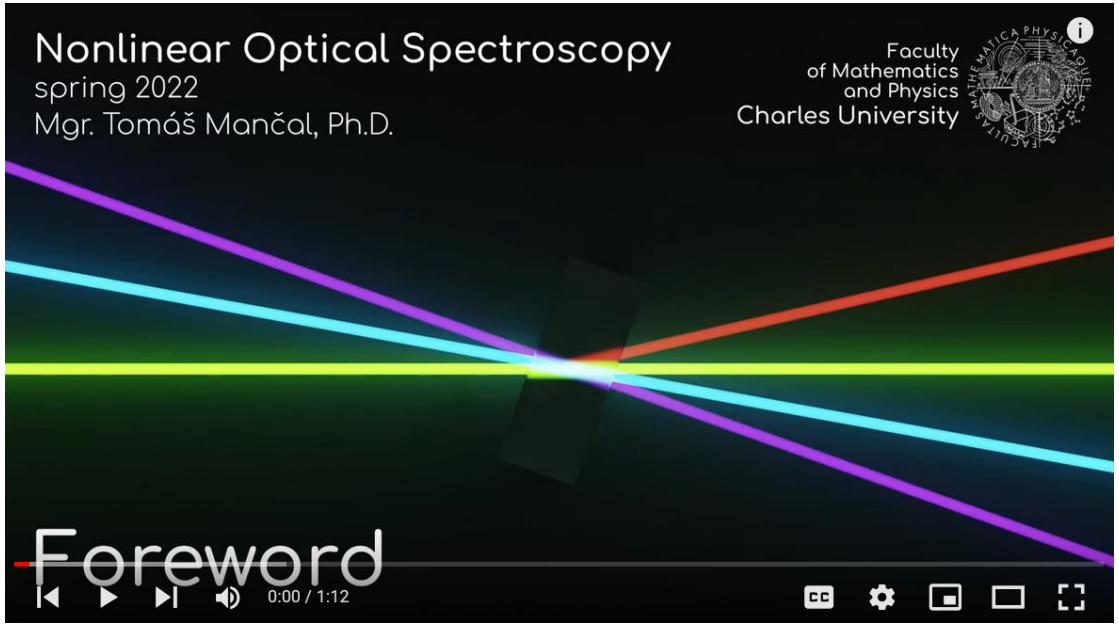
journal homepage: www.elsevier.com/locate/bbabio

Two-dimensional spectroscopy for non-specialists

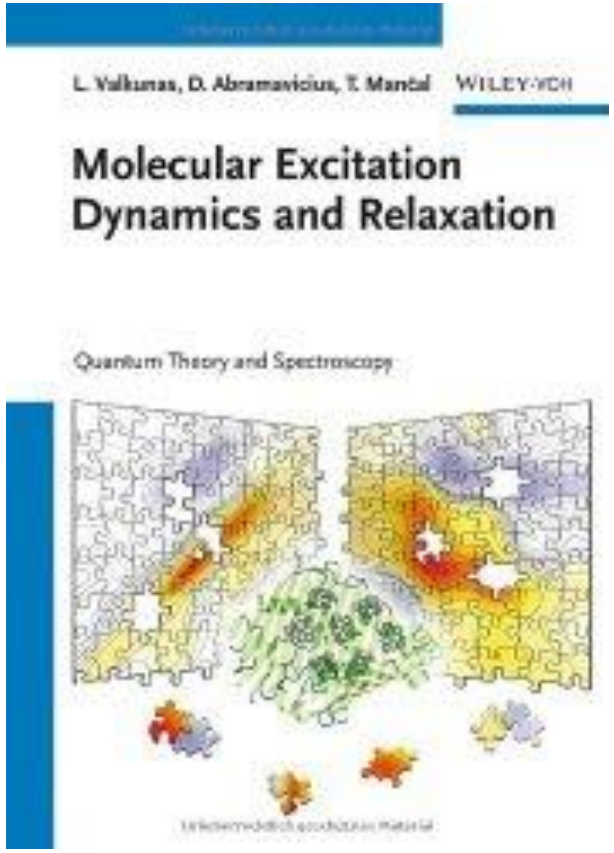
Andrius Gelzinis[a,b], Ramūnas Augulis[b], Vytautas Butkus[a], Bruno Robert[c], Leonas Valkunas[a,b,*]

Resources

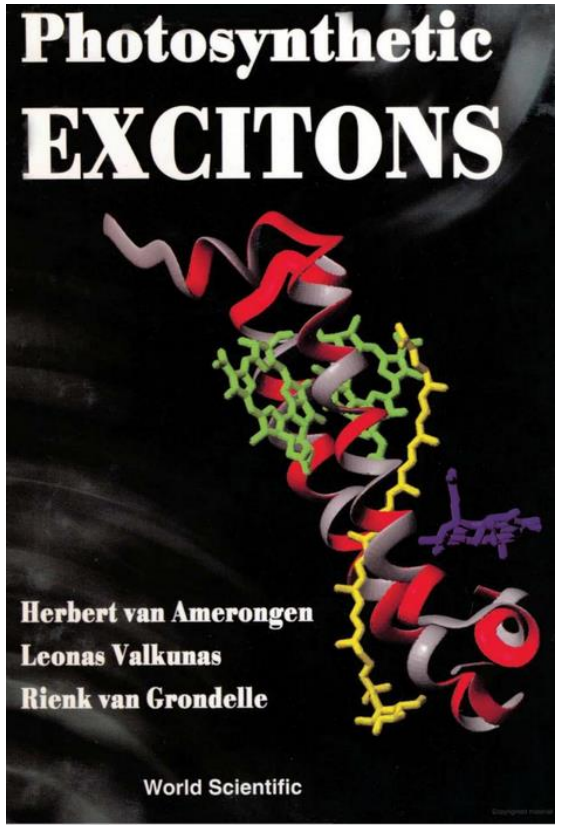


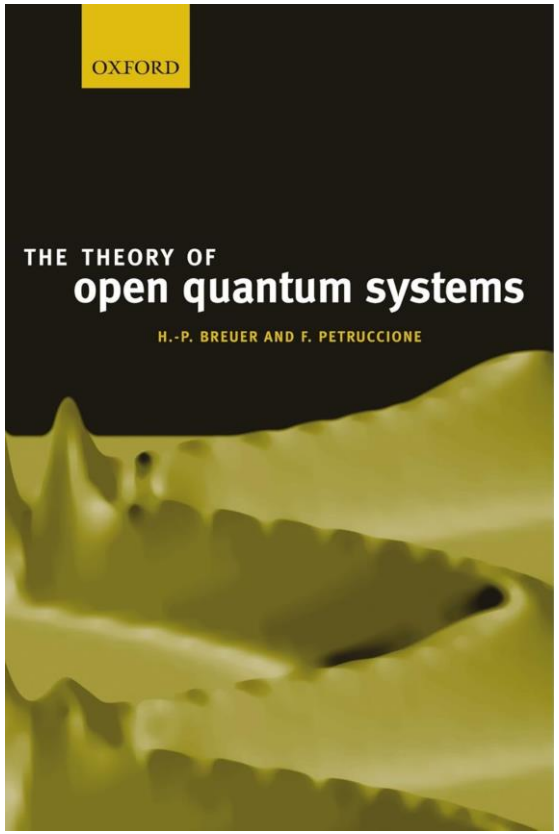


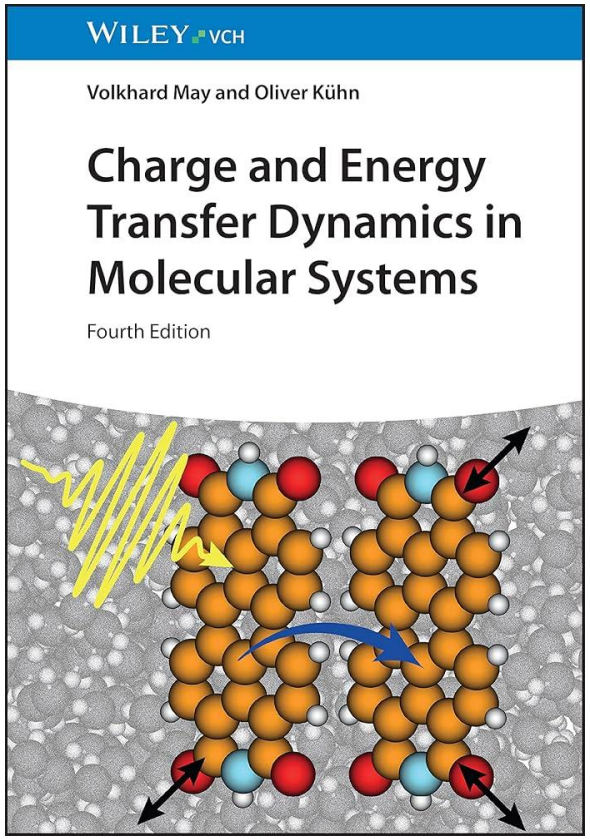
Tomáš Mančal, Charles University, Prague. On YT



Resources


Photosynthetic
EXCITONS
Herbert van Amerongen
Leonas Valkunas
Rienk van Grondelle
World Scientific


OXFORD
THE THEORY OF
open quantum systems
H.-P. BREUER AND F. PETRUCCIONE


WILEY VCH
Volkhard May and Oliver Kühn
Charge and Energy Transfer Dynamics in Molecular Systems
Fourth Edition