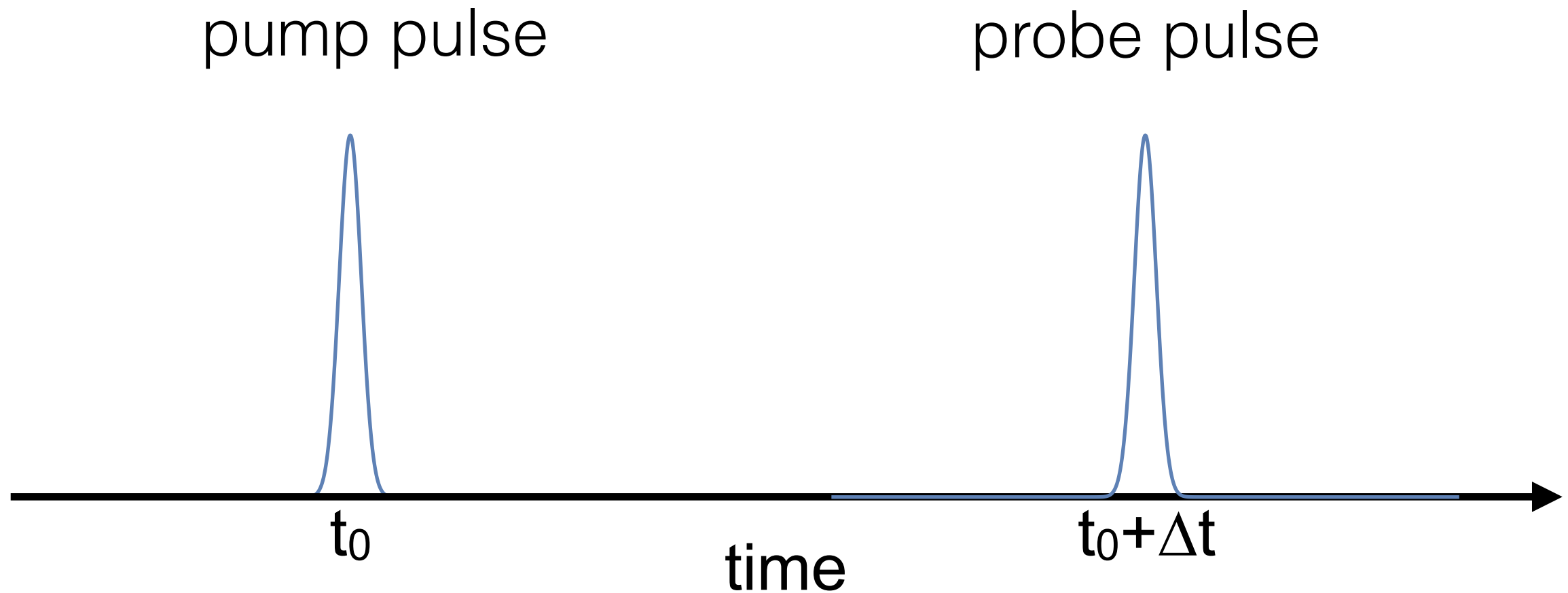


Rates from transient spectroscopy

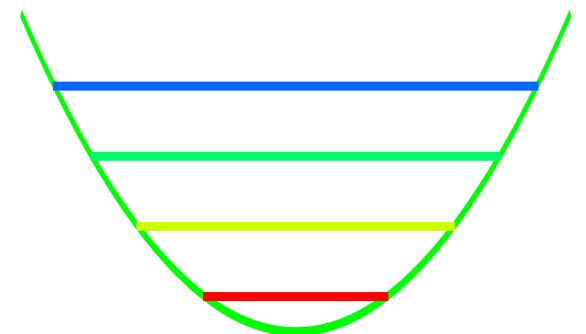
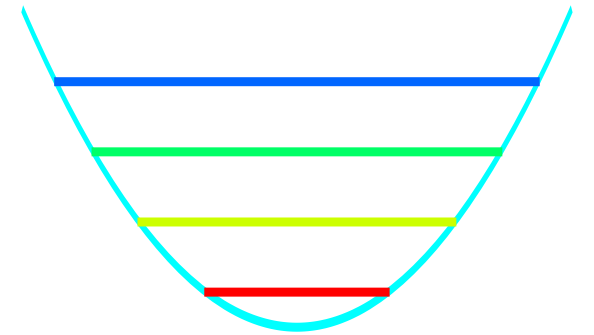
linear pump-probe spectroscopy



Rates from transient spectroscopy

some issues (out of many)

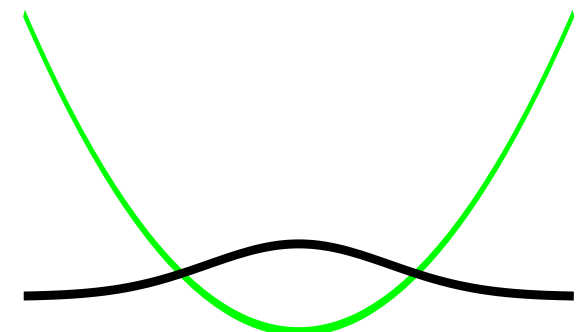
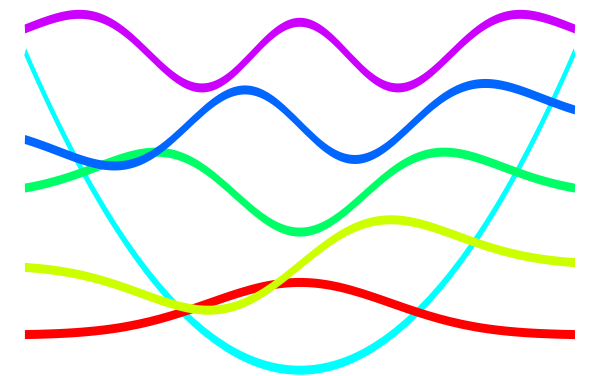
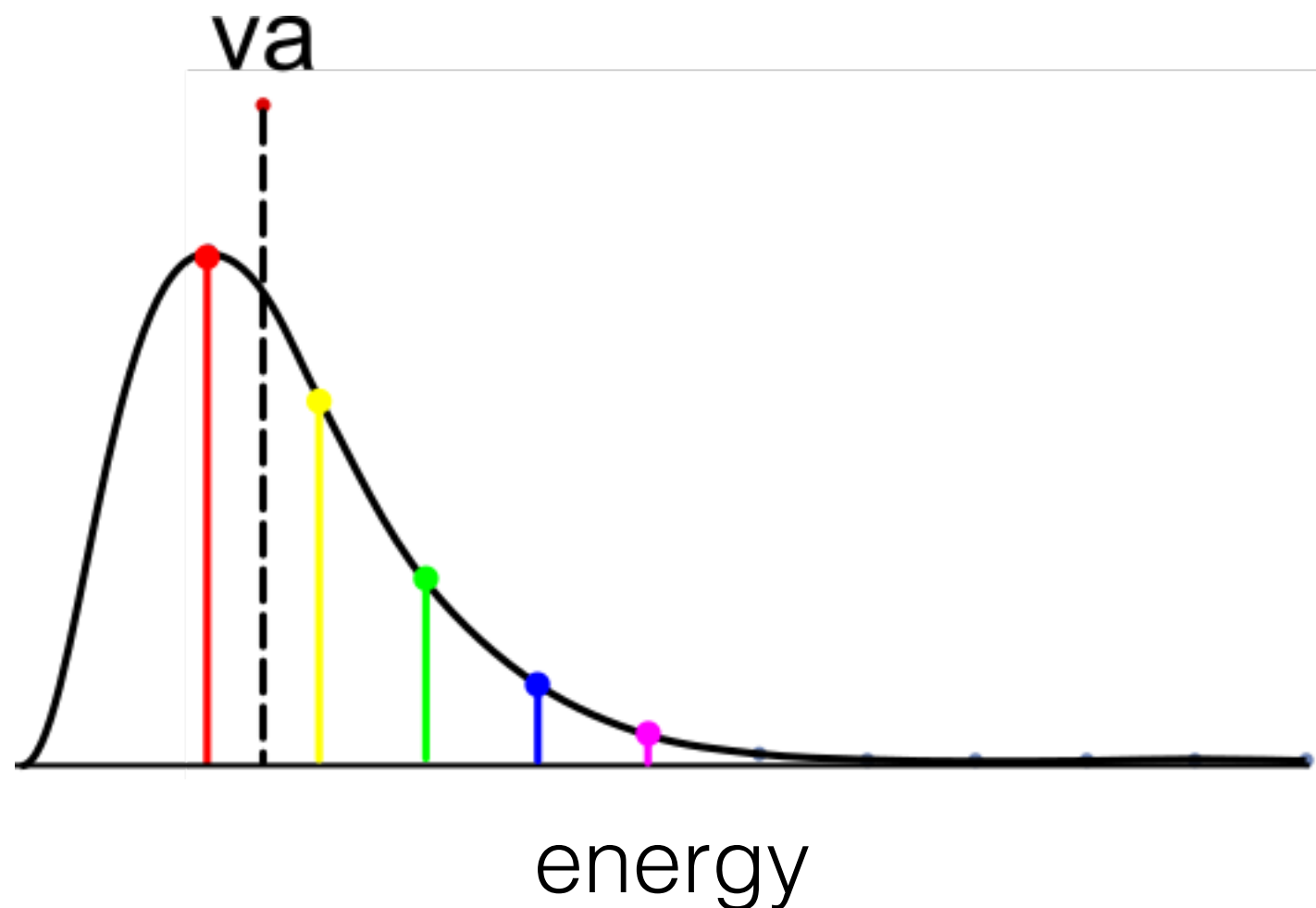
fs pump pulses have large bandwidth



Rates from transient spectroscopy

some issues (out of many)

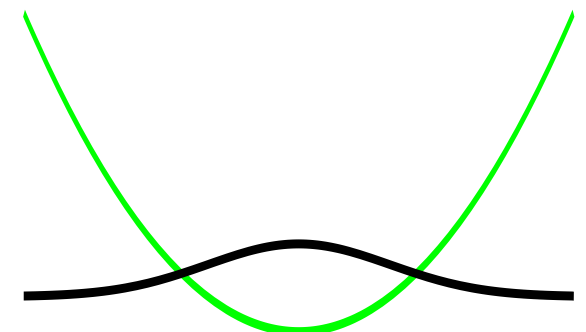
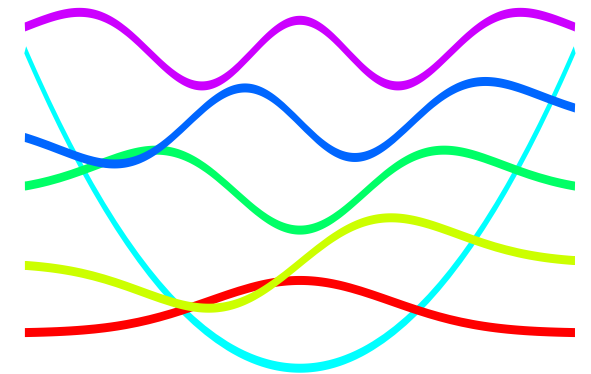
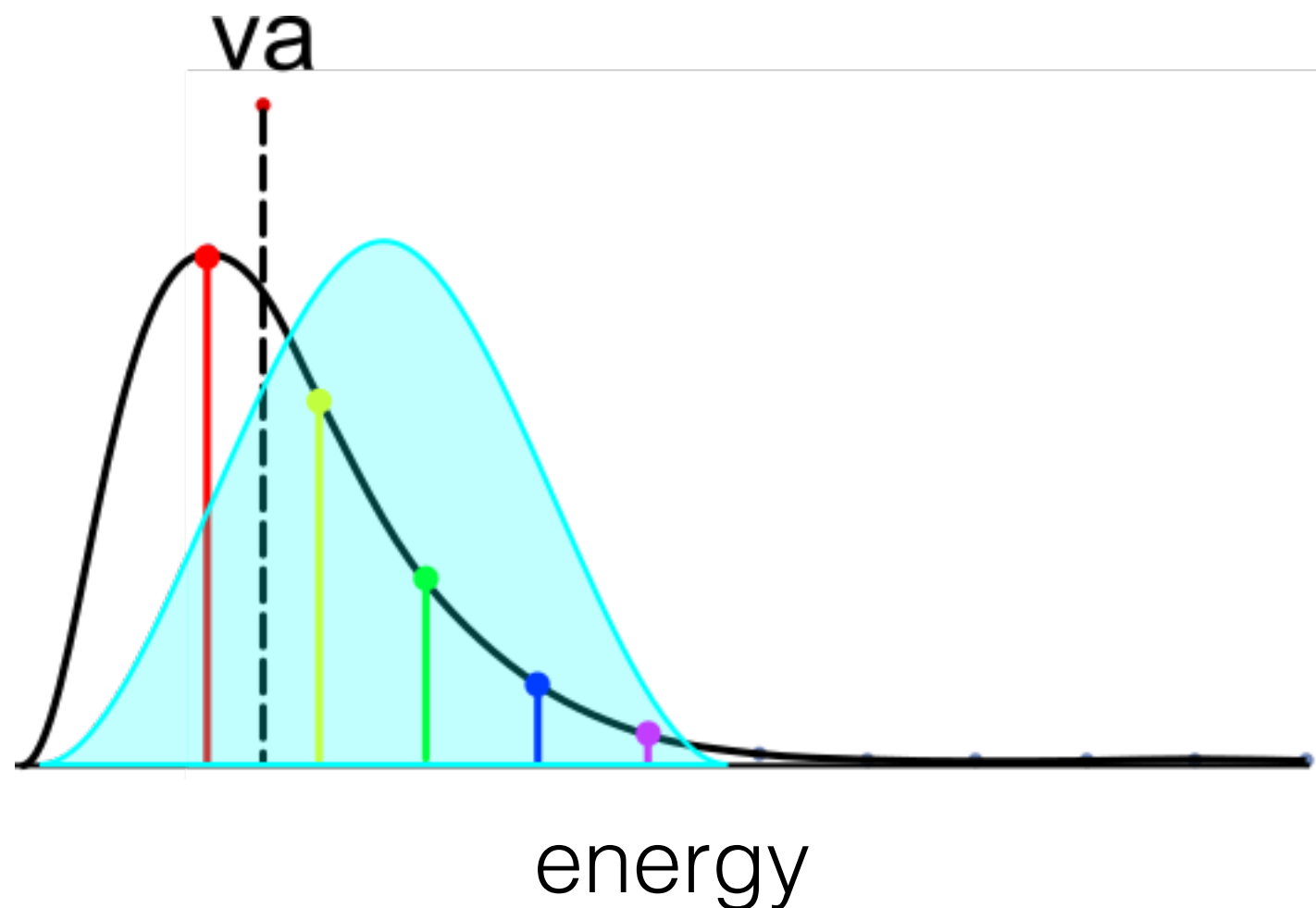
fs pump pulses have large bandwidth



Rates from transient spectroscopy

some issues (out of many)

fs pump pulses have large bandwidth

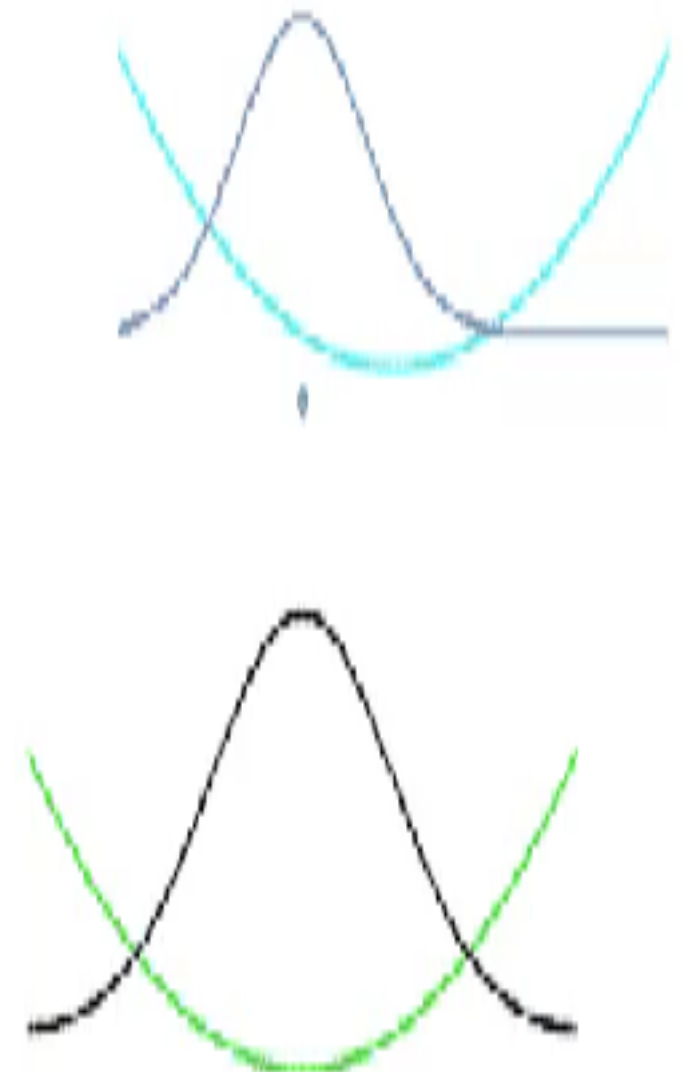
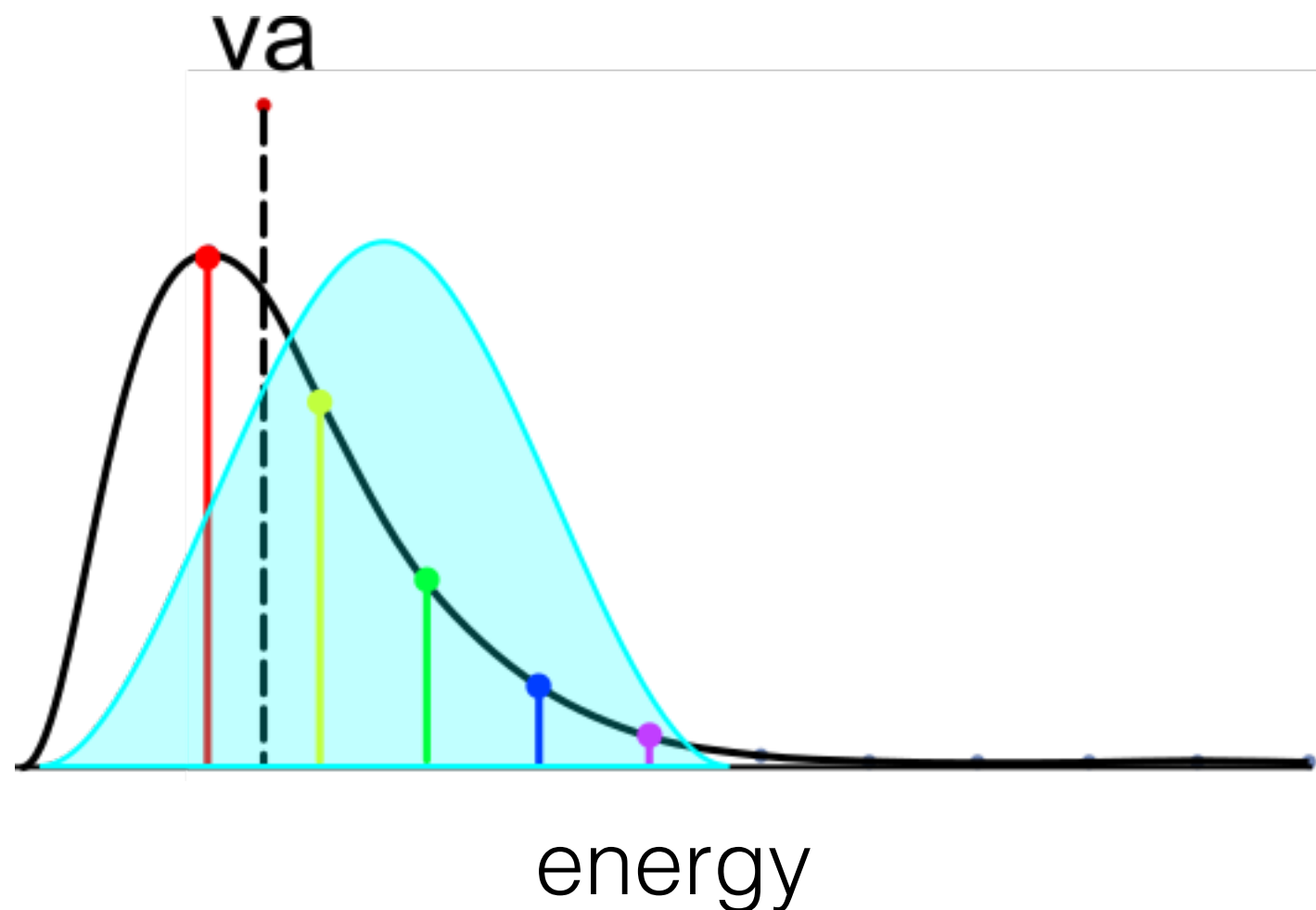


Rates from transient spectroscopy

some issues (out of many)

fs pump pulses have large bandwidth

coherent vibrations in ground and excited state



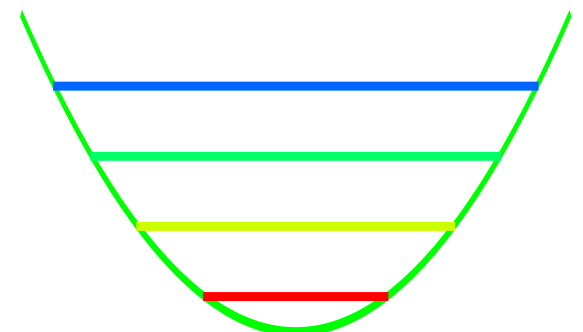
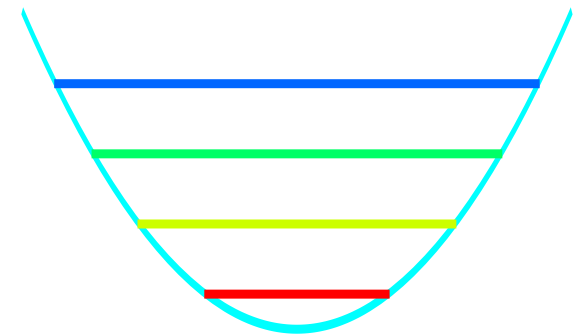
Rates from transient spectroscopy

some issues (out of many)

fs pump pulses have large bandwidth

coherent vibrations in ground and excited state

stimulated emission limits population transfer



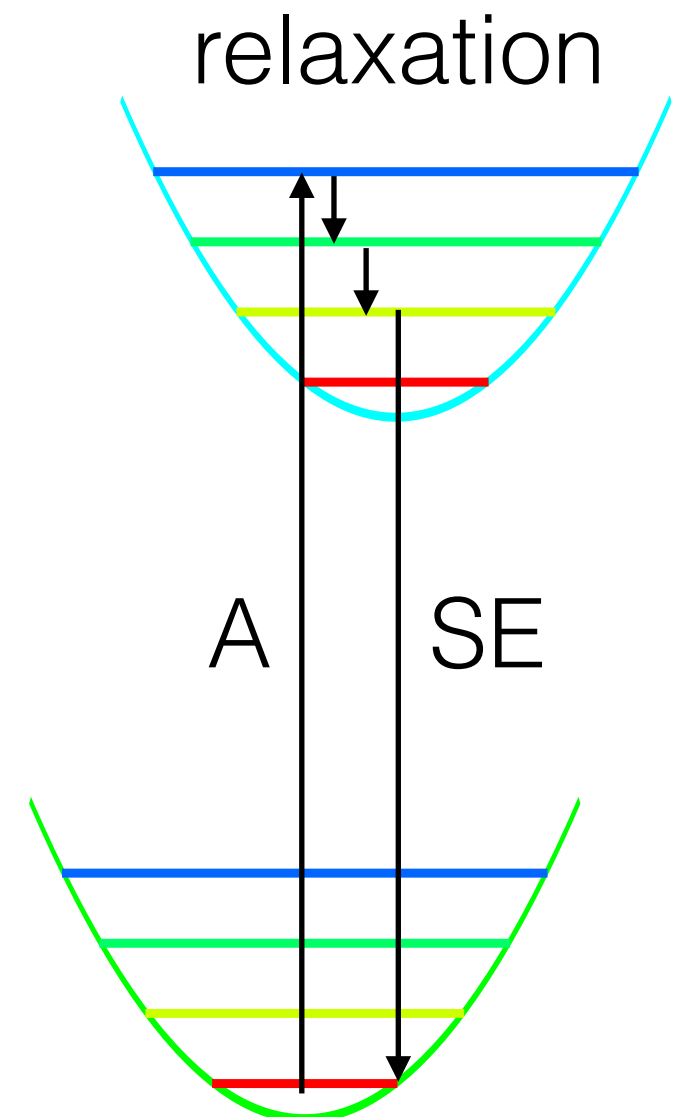
Rates from transient spectroscopy

some issues (out of many)

fs pump pulses have large bandwidth

coherent vibrations in ground and excited state

stimulated emission limits population transfer



Rates from transient spectroscopy

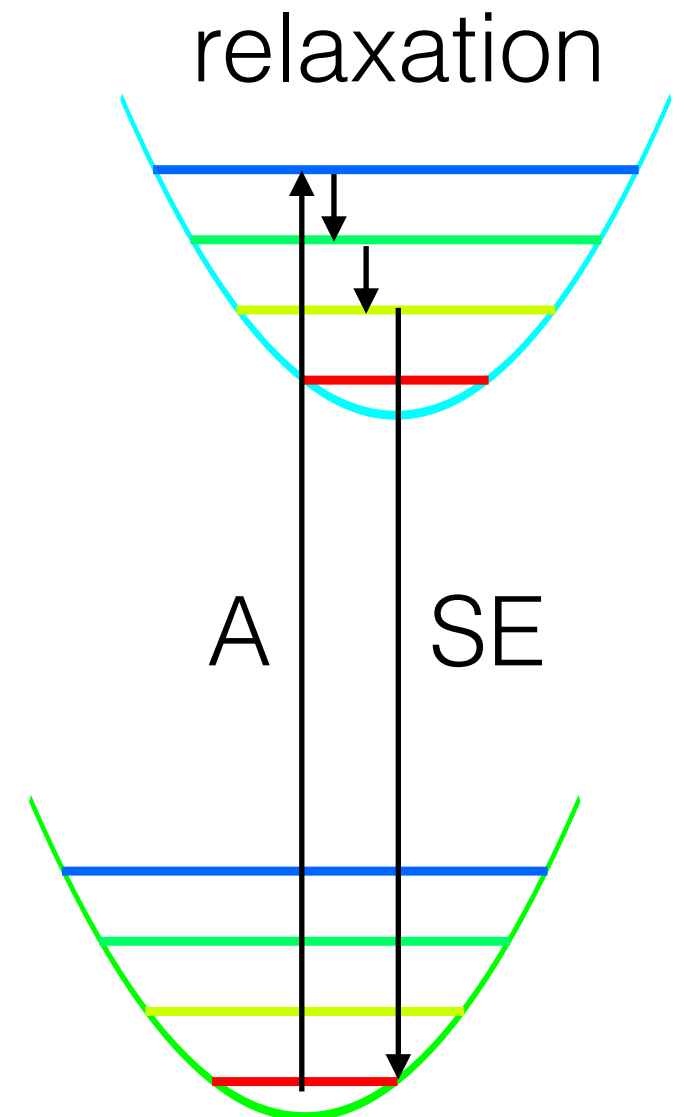
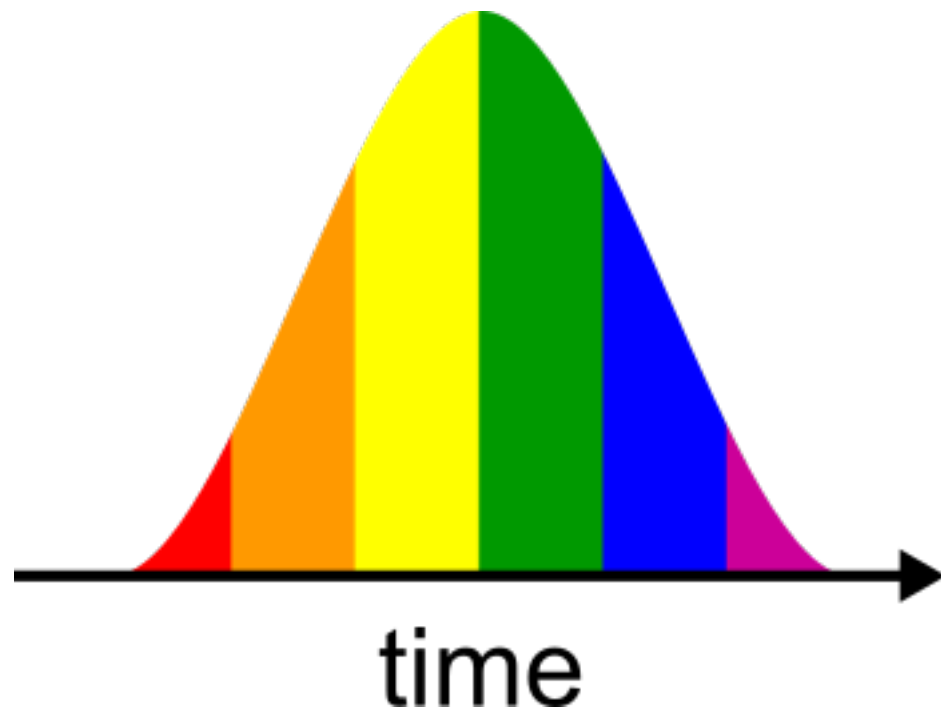
some issues (out of many)

fs pump pulses have large bandwidth

coherent vibrations in ground and excited state

stimulated emission limits population transfer

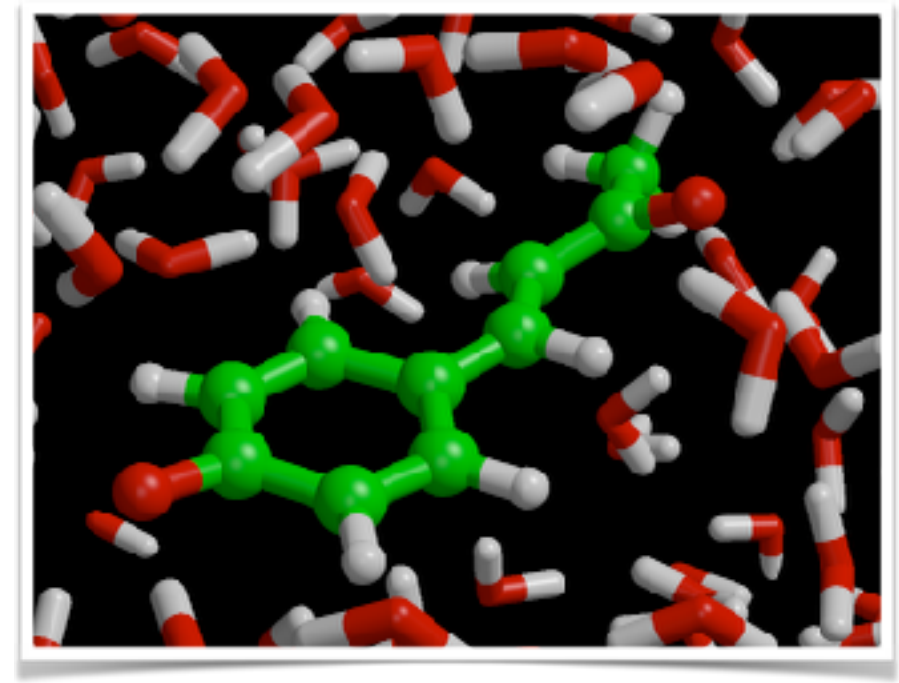
chirped pulses



Time-resolved spectroscopy

linear pump-probe spectroscopy

idealised example: PCK in water

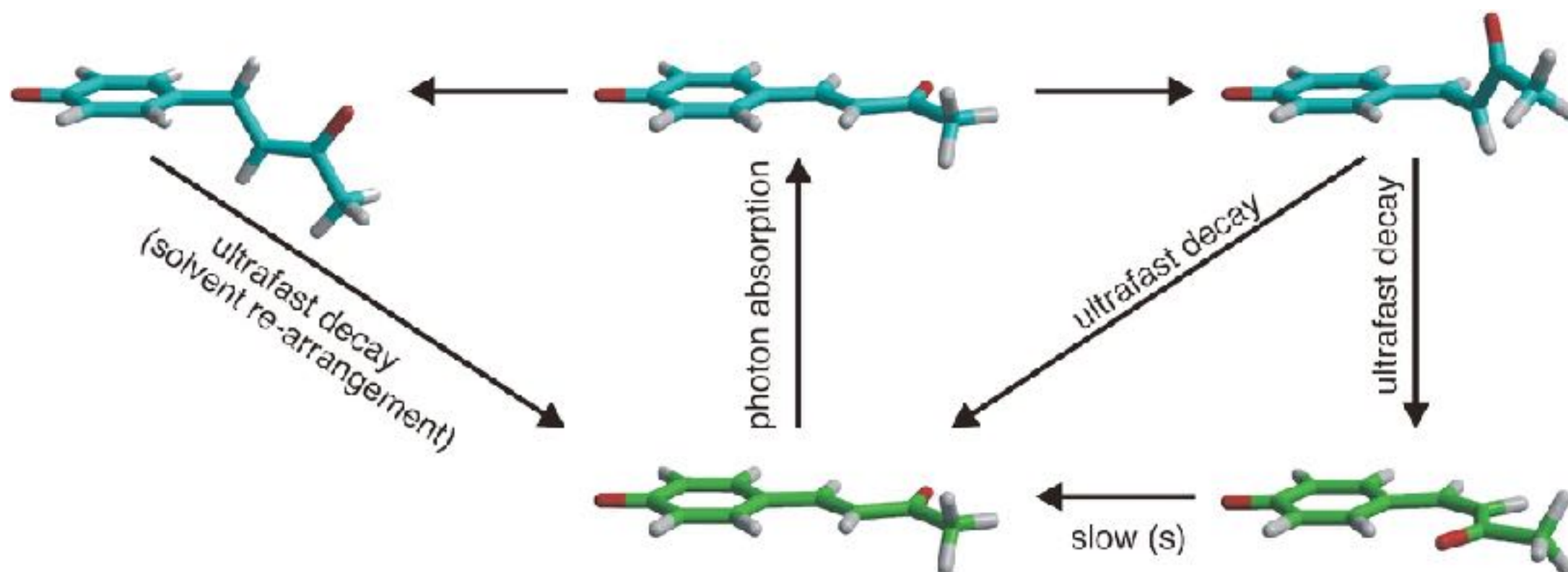
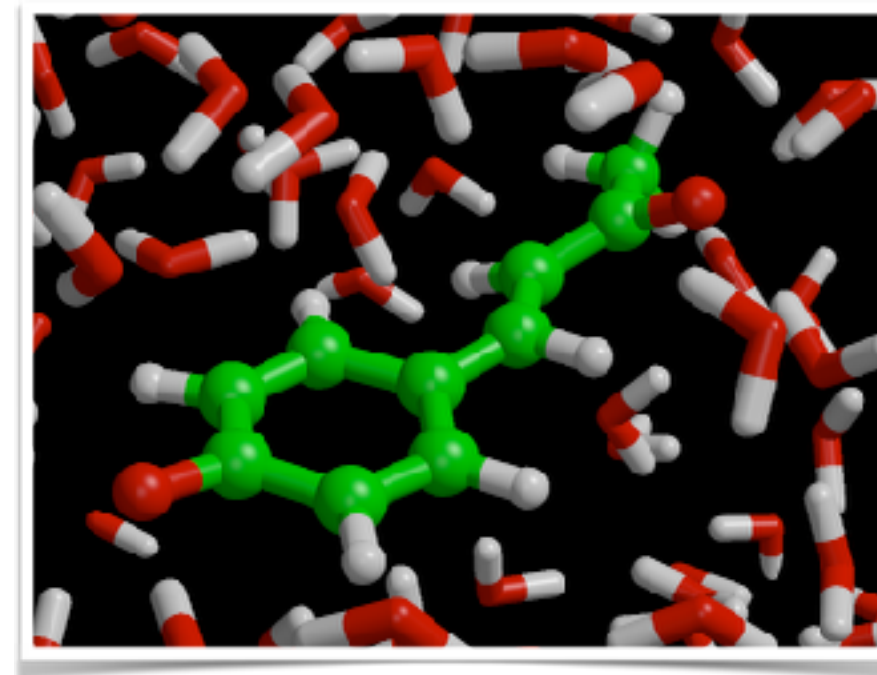


Time-resolved spectroscopy

linear pump-probe spectroscopy

idealised example: PCK in water

we assume our simulations are correct ;-)



CASSCF(6,6)/3-21G//SPCE

CASSCF(8,8)/6-31G*//SPCE

CASSCF(12,11)/cc-pVTZ//EFP

JACS 131 (2009) 13581

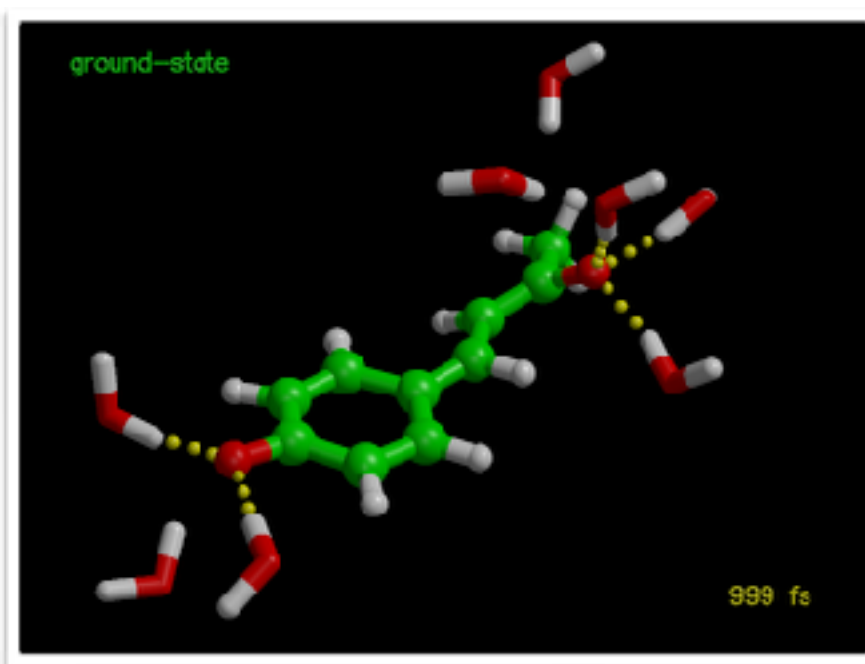
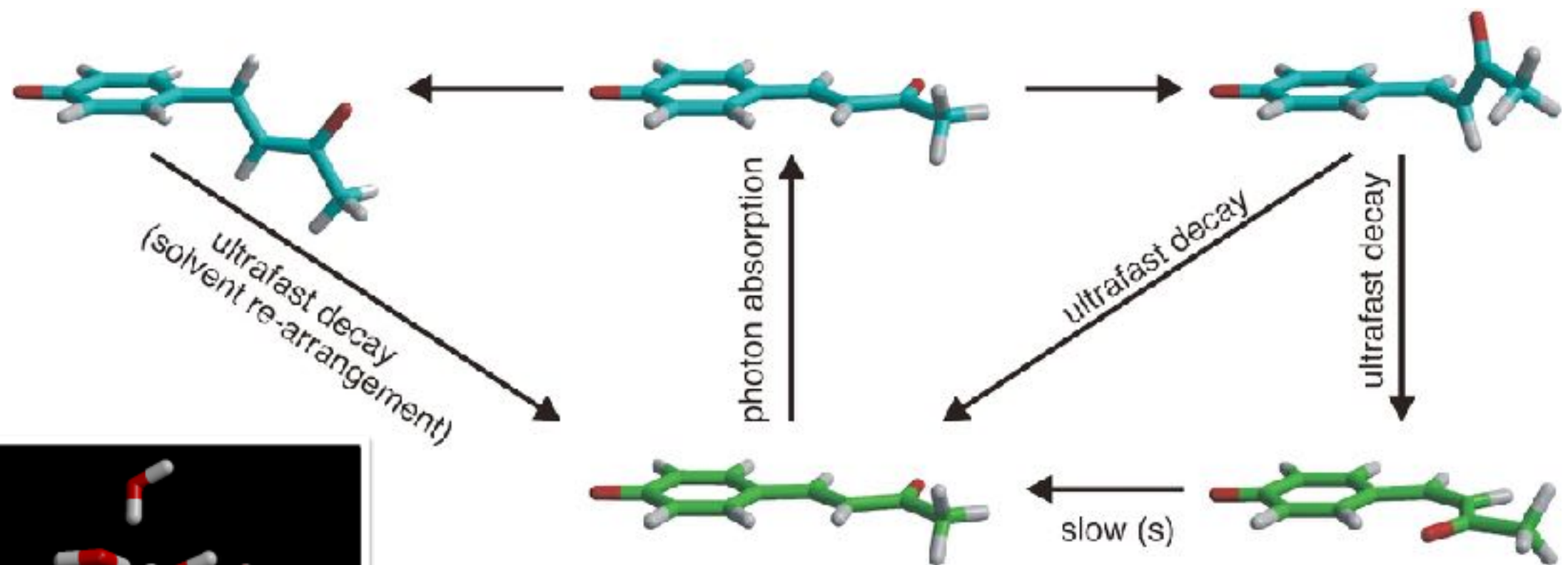
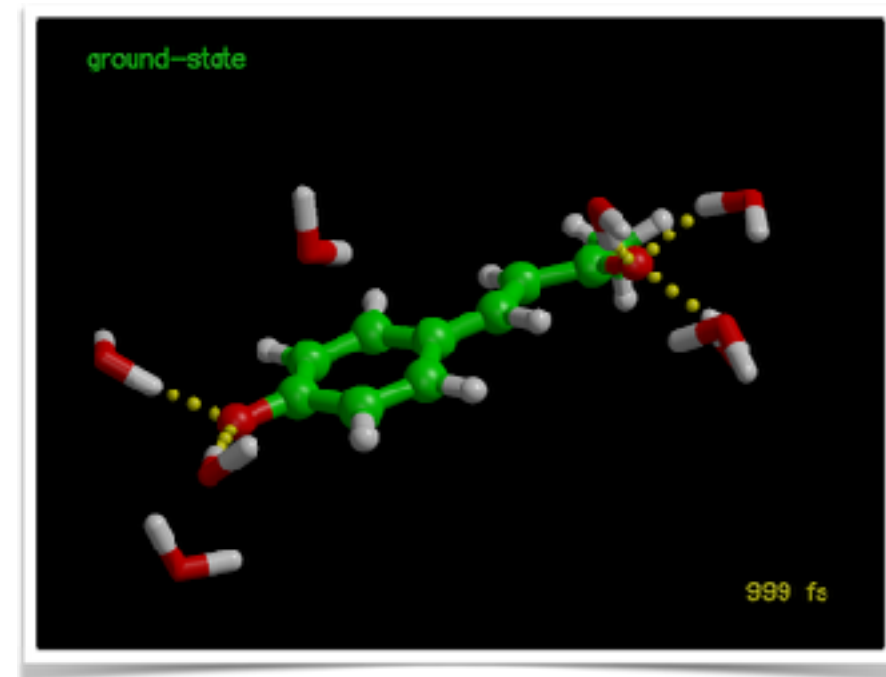
Phys. Chem. Chem. Phys. 14 (2012) 7912

Time-resolved spectroscopy

linear pump-probe spectroscopy

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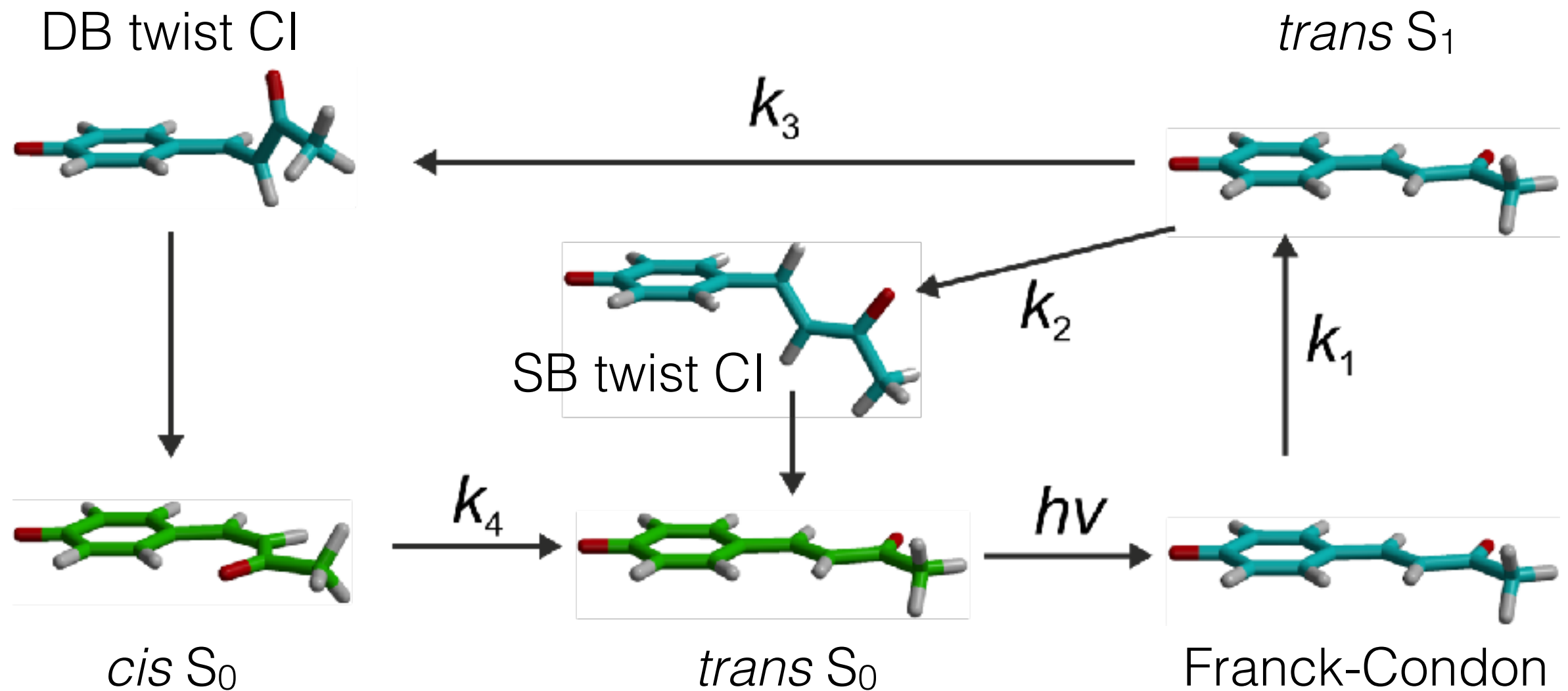
JACS 131 (2009) 13581

Phys. Chem. Chem. Phys. 14 (2012): 7912

Species Associated Spectra

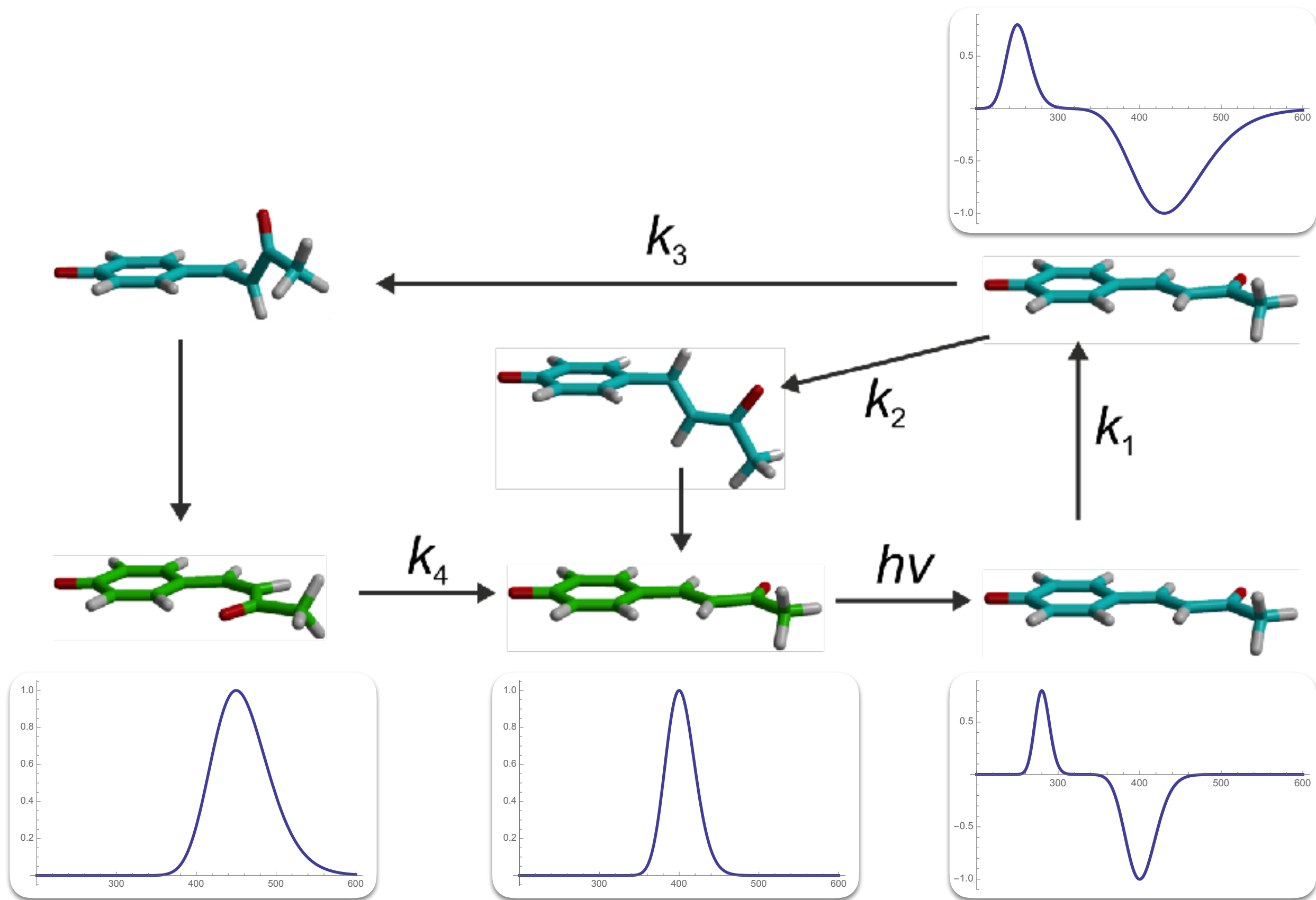
different orientation of scheme

horizontal excitation ;-)



Species Associated Spectra

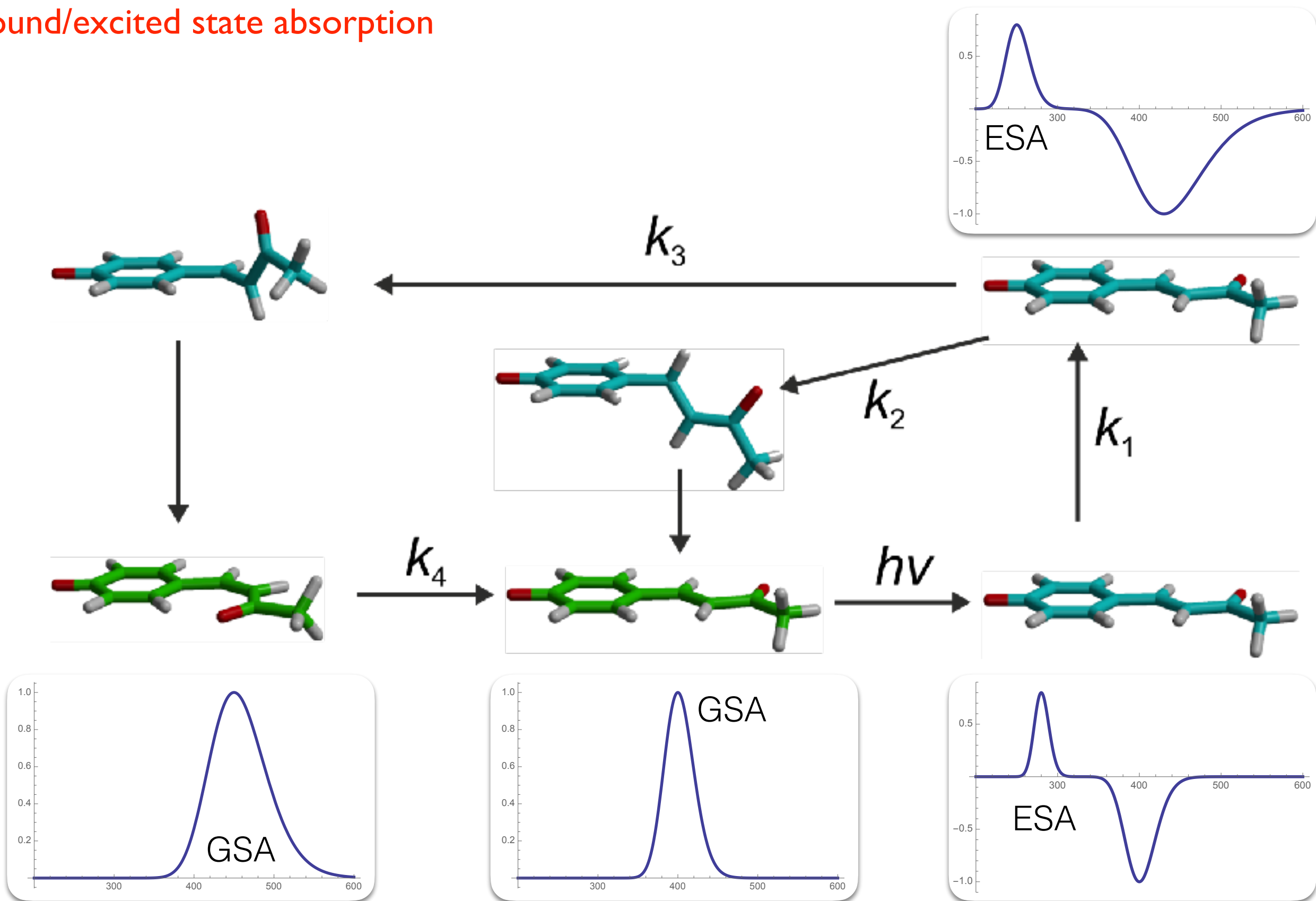
intermediates are species with own spectrum:



Species Associated Spectra

intermediates are species with own spectrum:

ground/excited state absorption

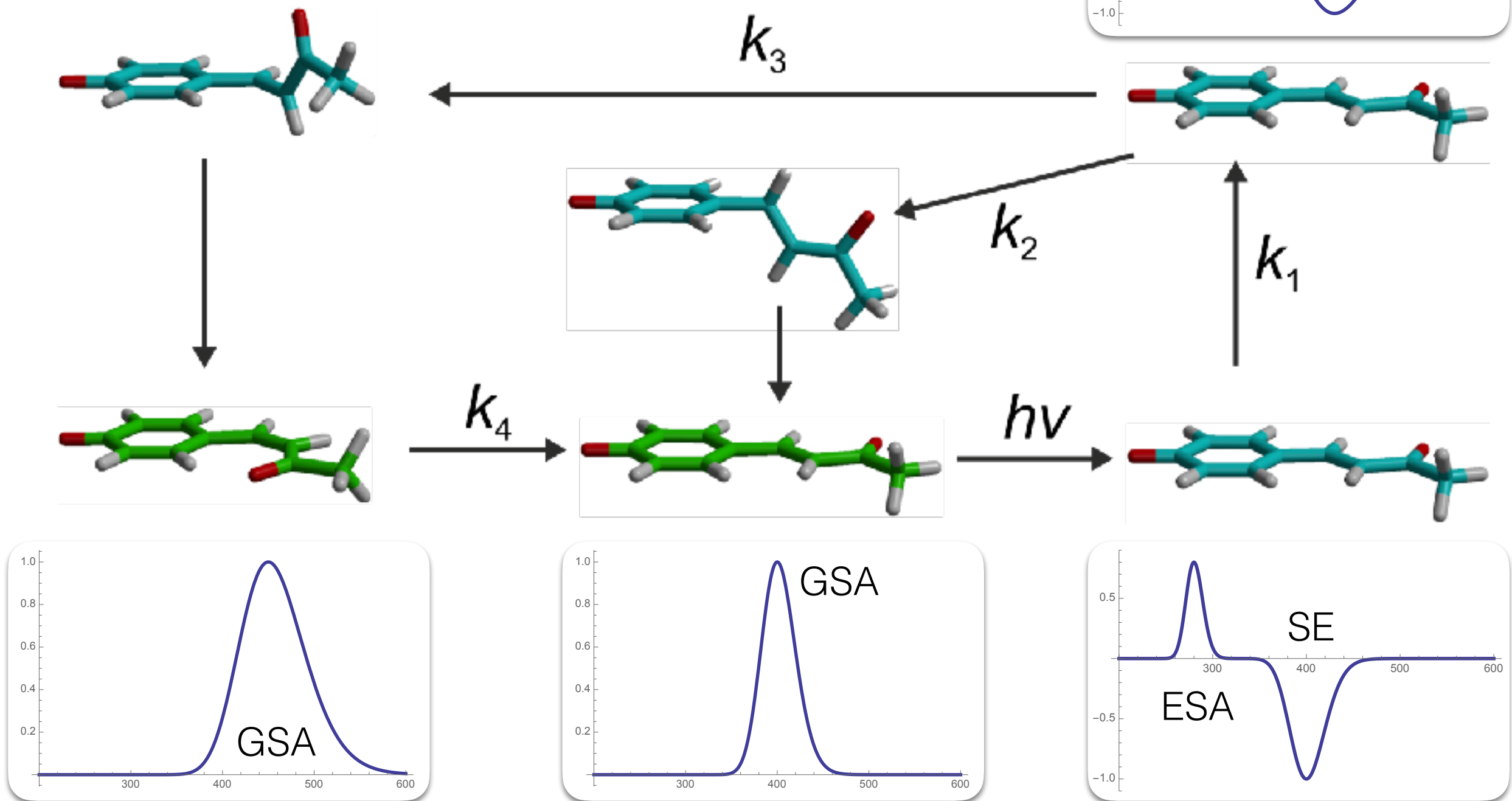


Species Associated Spectra

intermediates are species with own spectrum:

ground/excited state absorption

stimulated emission



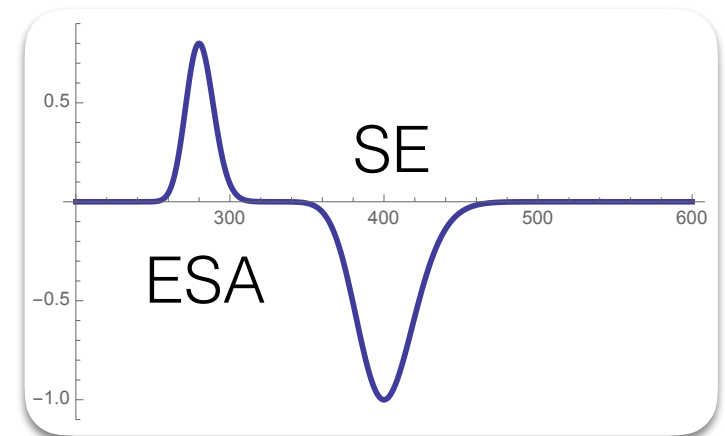
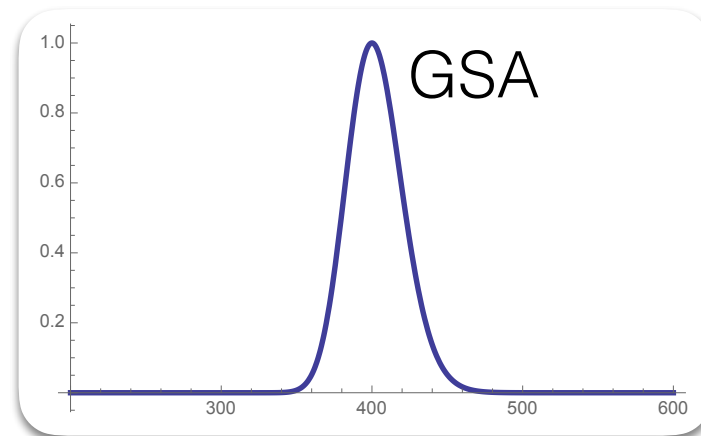
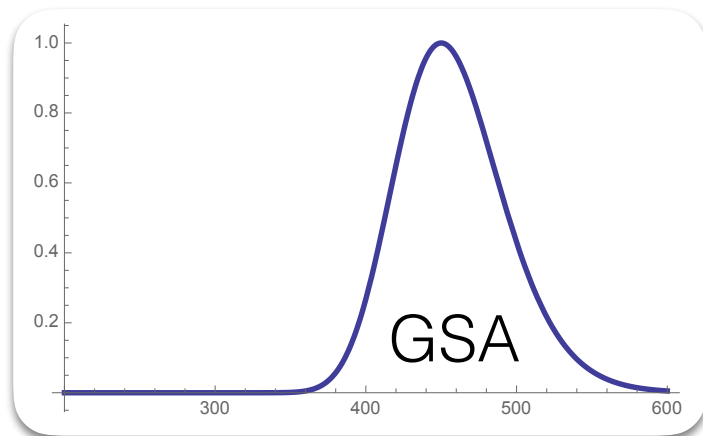
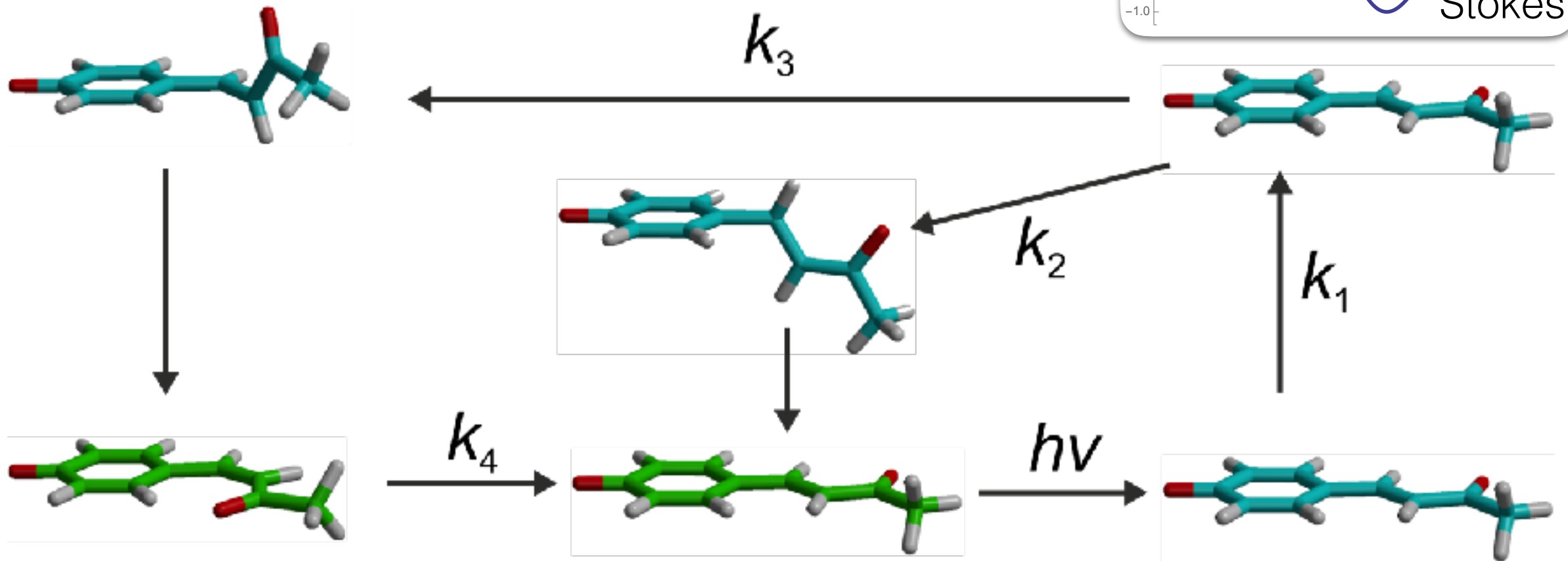
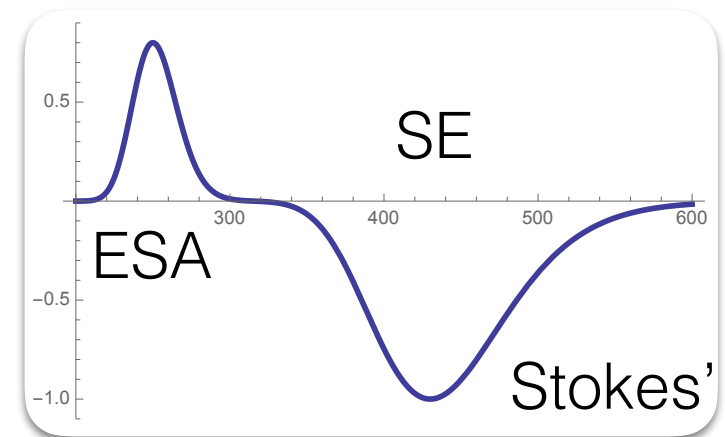
Species Associated Spectra

intermediates are species with own spectrum:

ground/excited state absorption

stimulated emission

Stokes' shift



Spectral evolution

kinetic model

$$S(\lambda, t) = \sum_i c_i(t) s_i(\lambda)$$

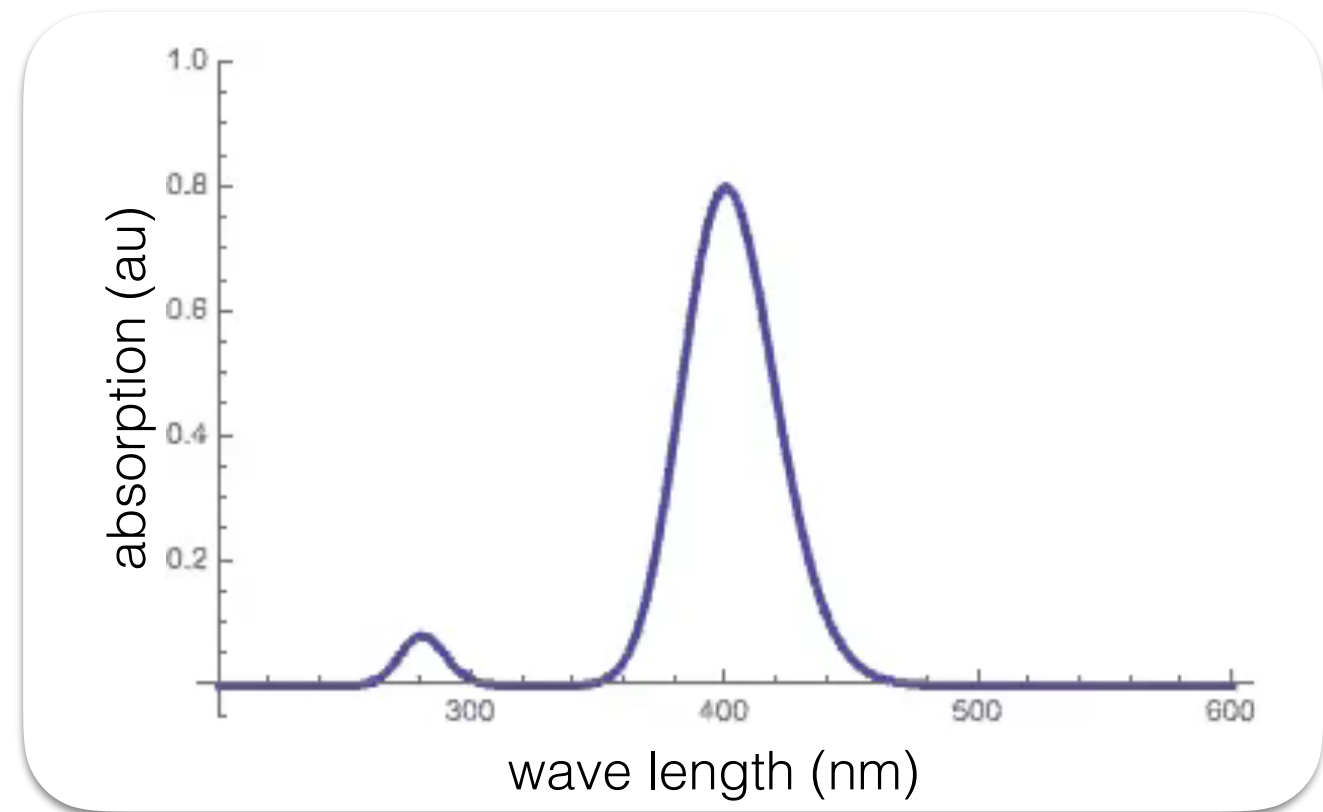
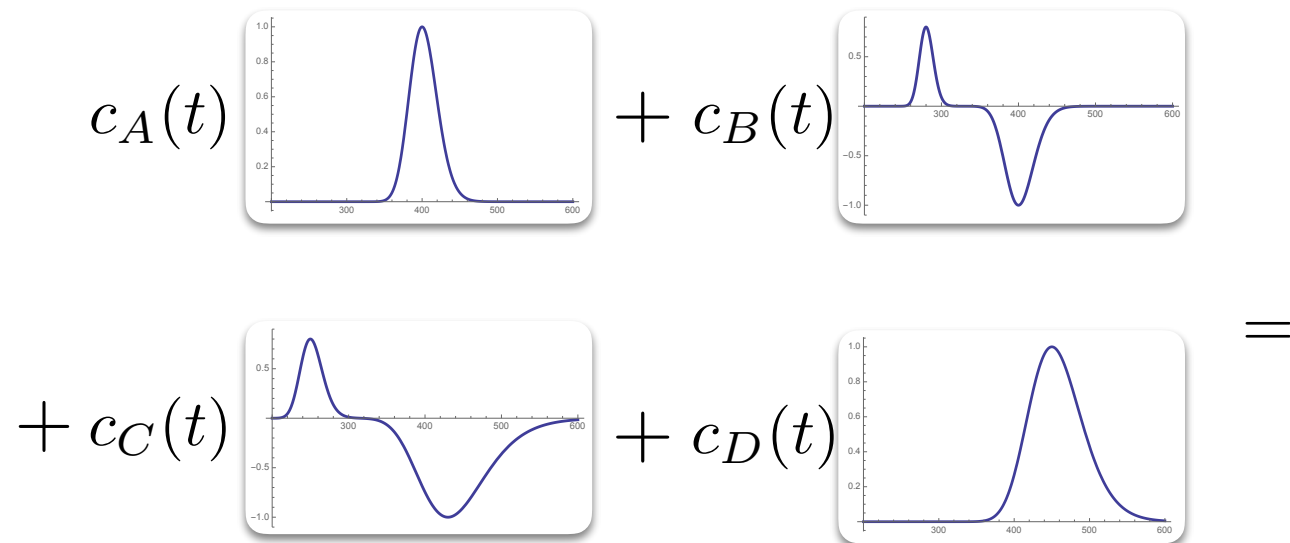
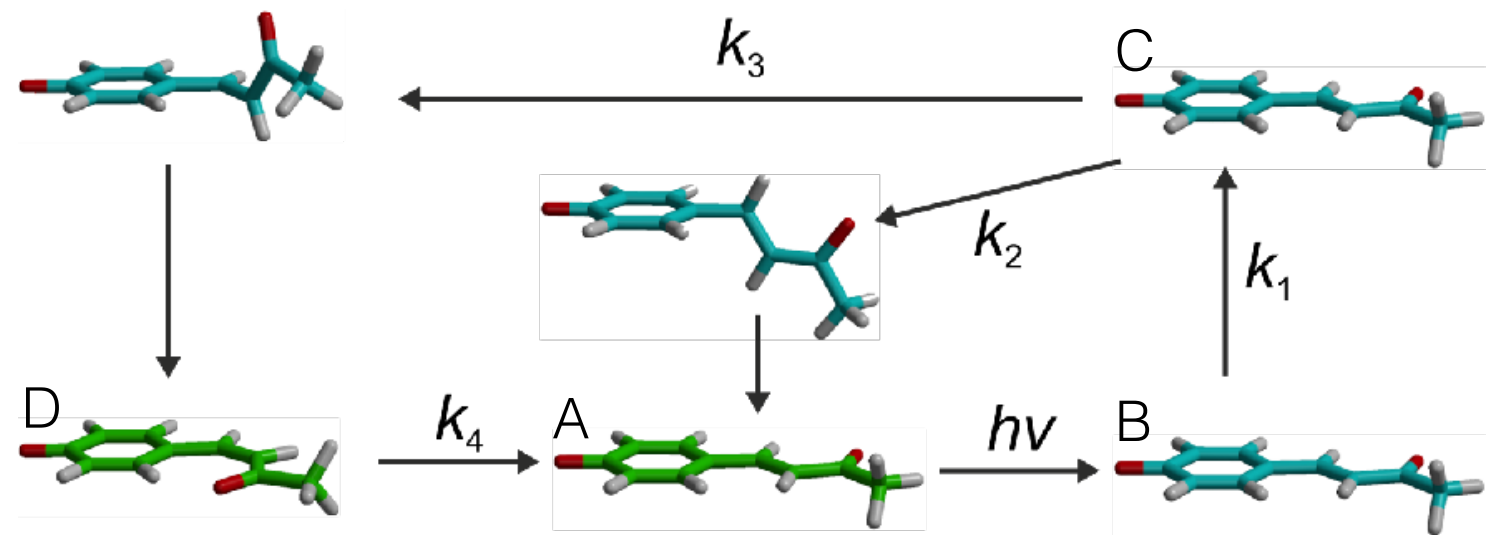
not for fs coherent dynamics!

congested

difficult to interpret

limited population transfer with fs pulses

ground state absorption dominates

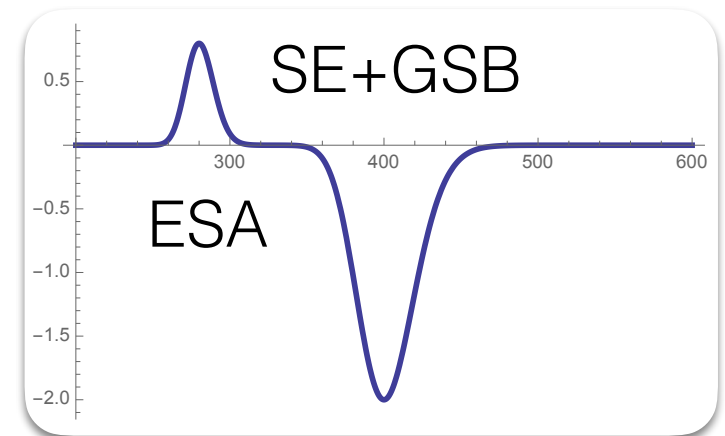
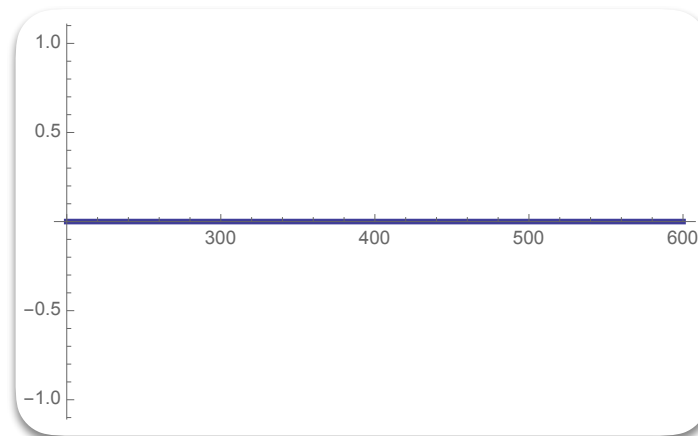
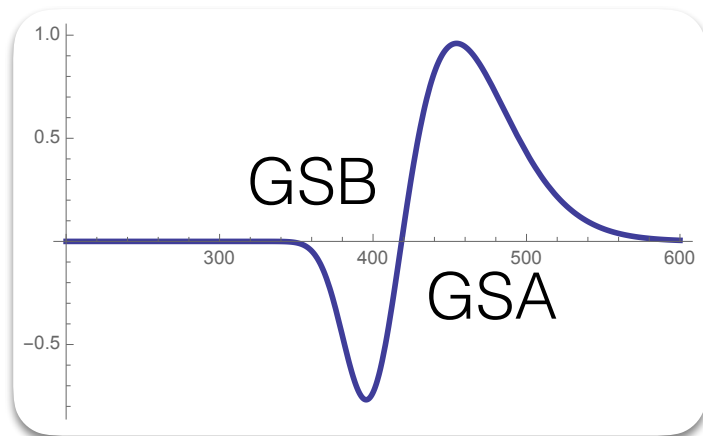
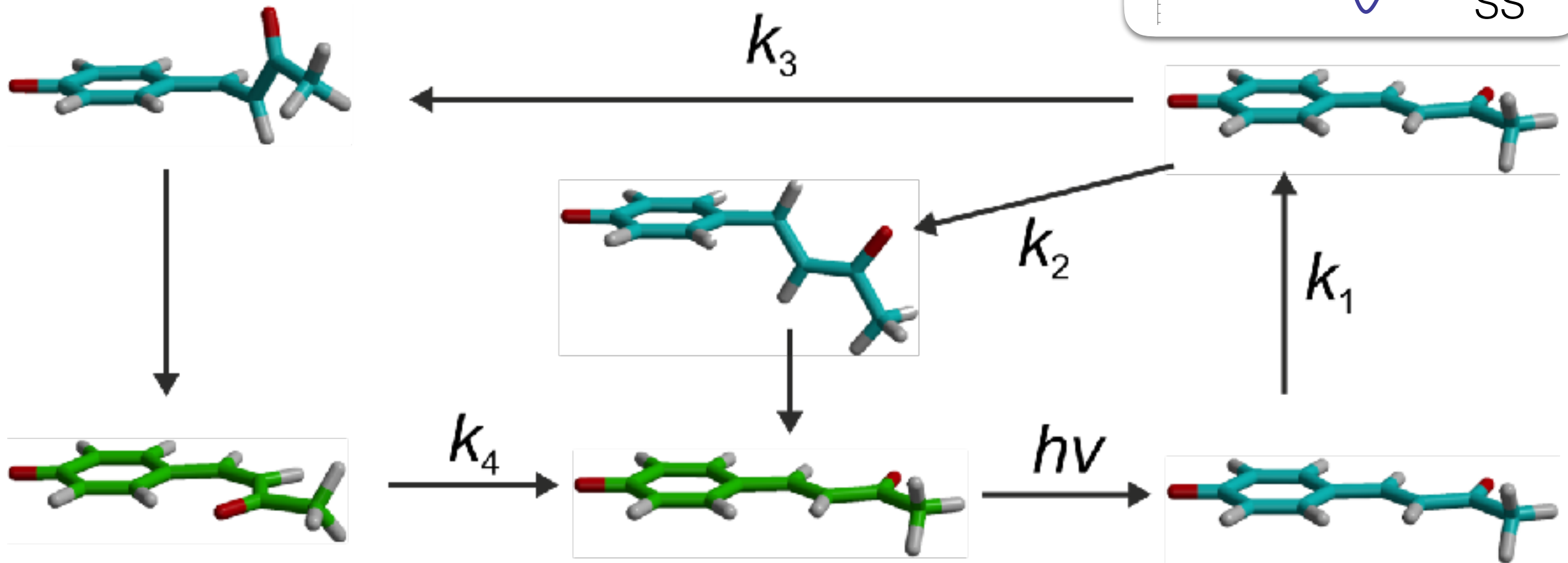
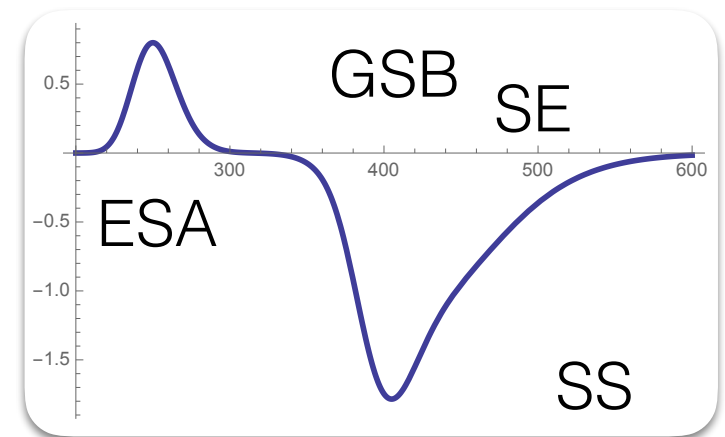


Species Associated *Difference Spectra*

intermediates are species with own difference spectrum

subtract 'normal' absorption spectrum

$$\Delta s_i(\lambda) = s_i(\lambda) - S(\lambda, t < t_{\text{pump}})$$



Species Associated *Difference Spectra*

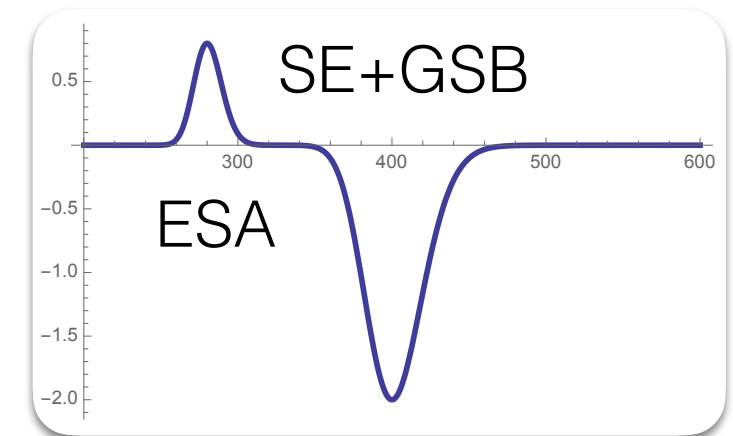
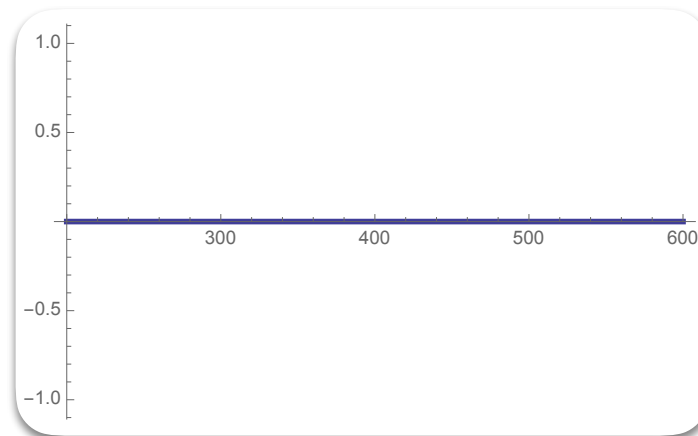
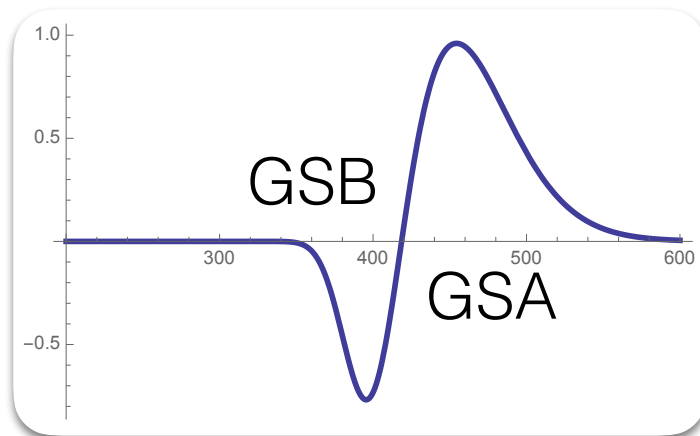
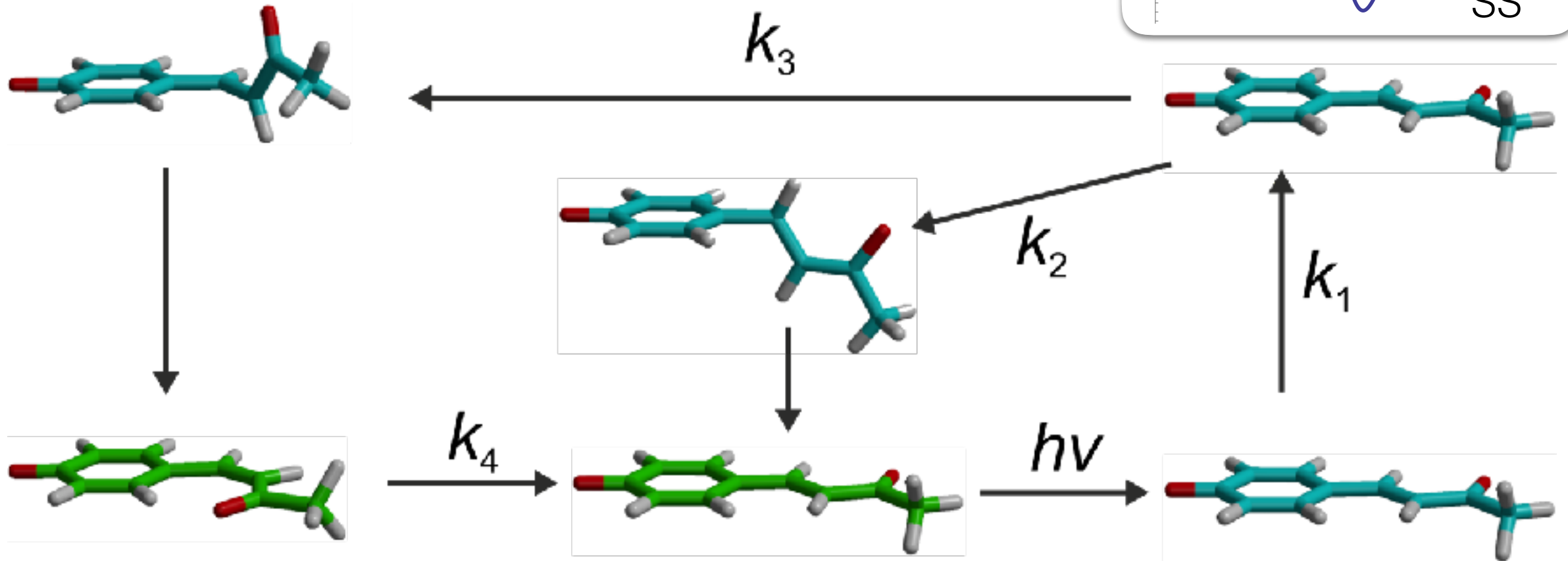
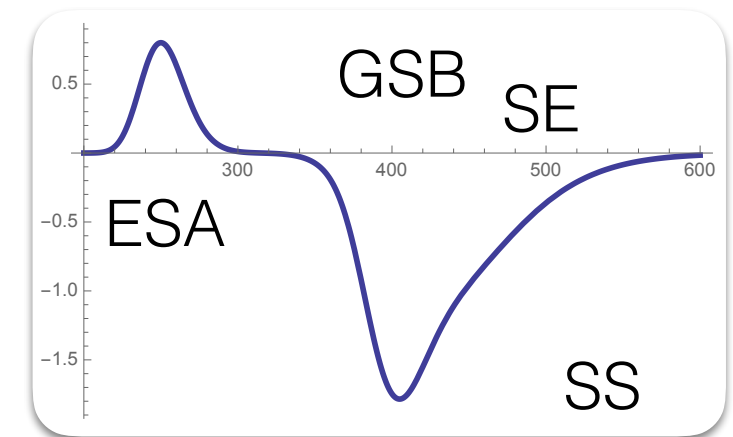
intermediates are species with own difference spectrum

ground/excited state absorption

stimulated emission

Stokes' shift

ground state bleach



Spectral evolution

kinetic model

$$\Delta S(\lambda, t) = \sum_i c_i(t) \Delta s_i(\lambda)$$

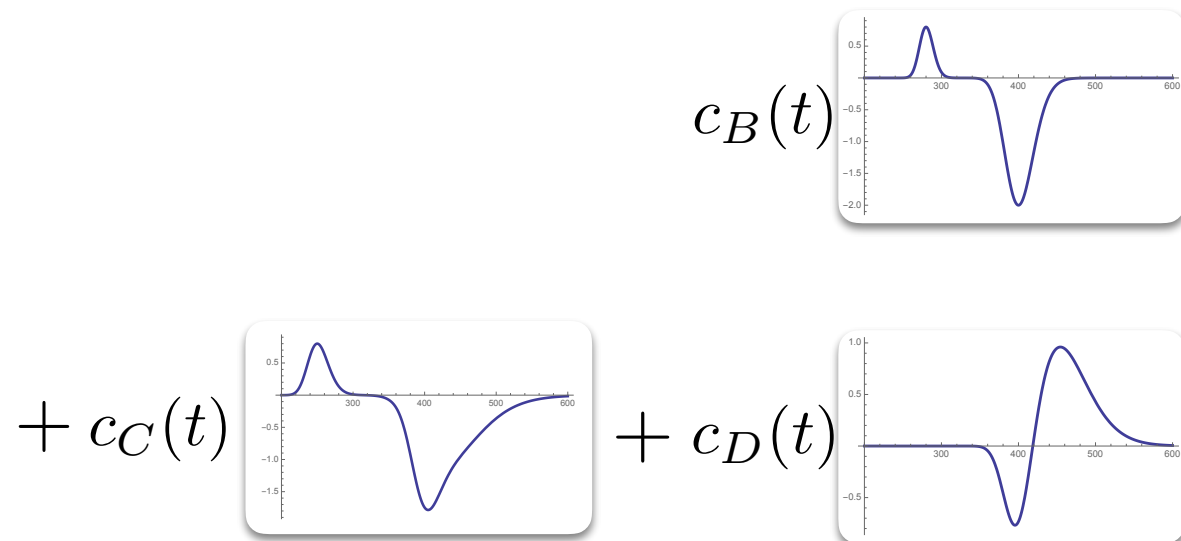
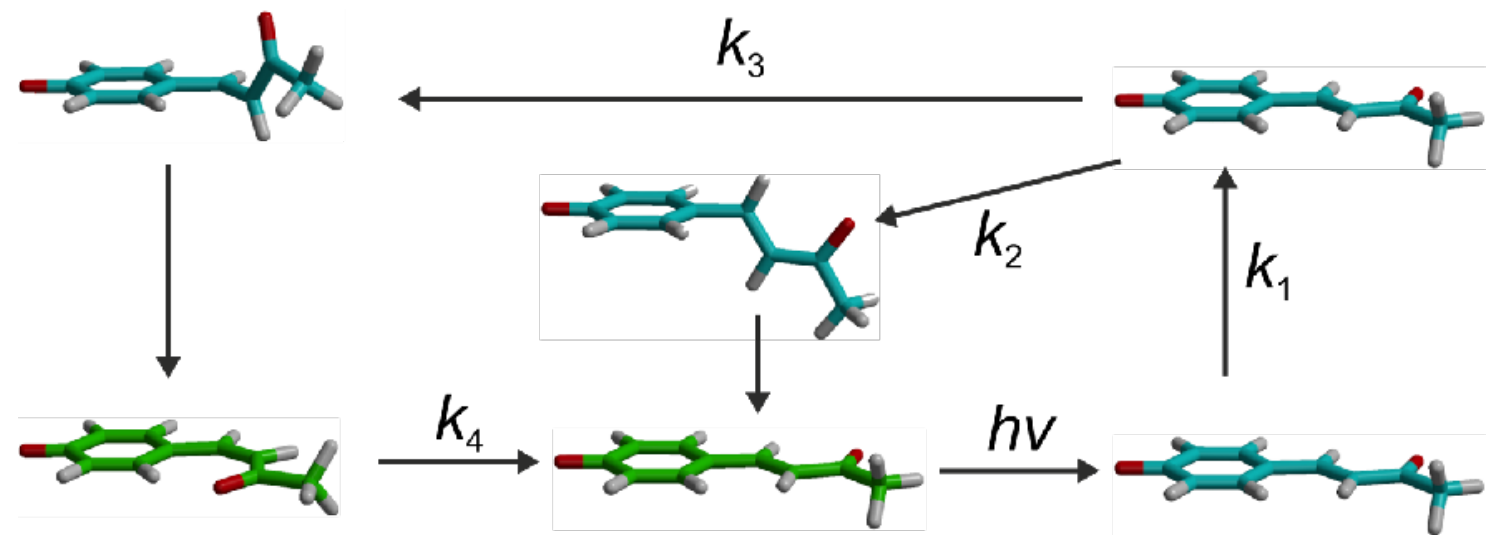
not for fs coherent dynamics!

features only differences

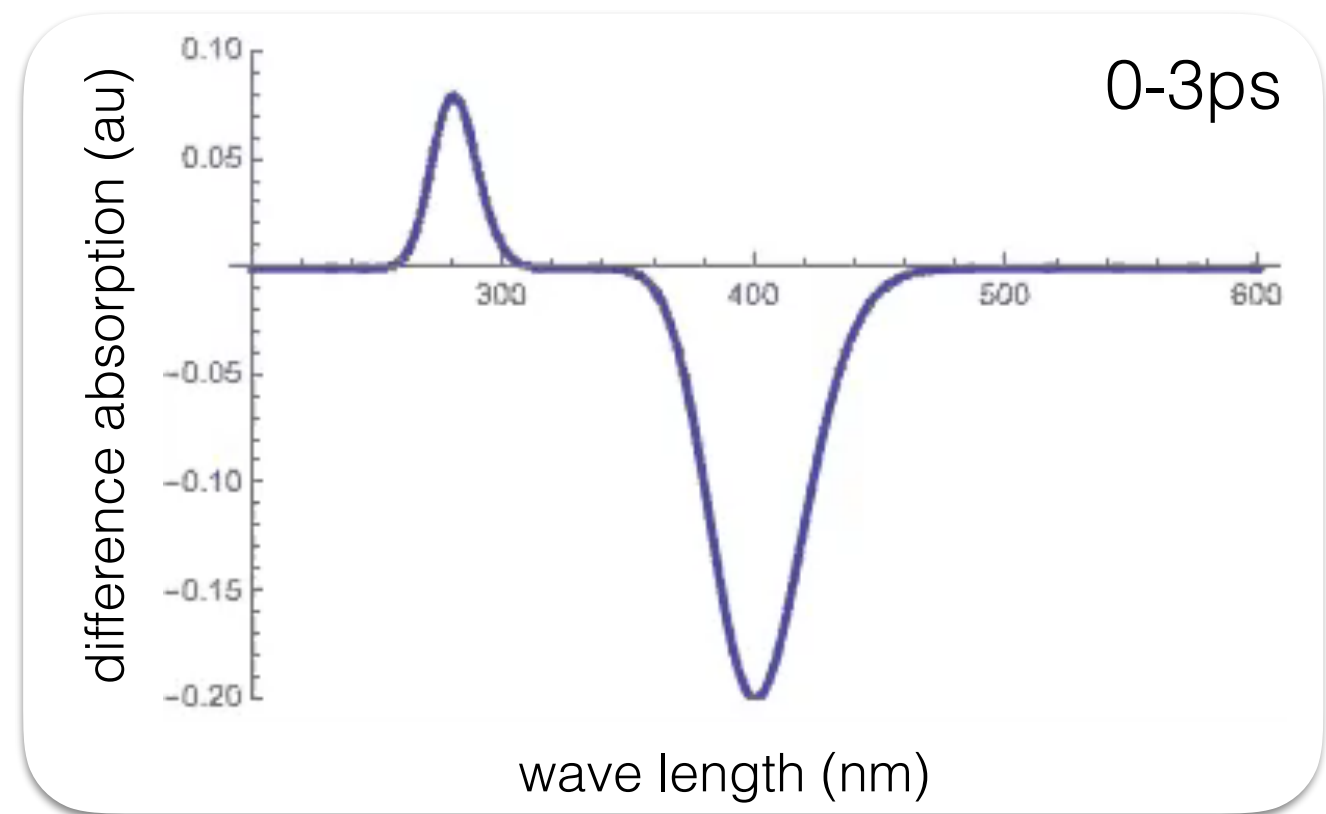
easier to interpret

no effect of limited population transfer with fs pulses

ground state absorption cancels



=



Spectral evolution

kinetic model

$$\Delta S(\lambda, t) = \sum_i c_i(t) \Delta s_i(\lambda)$$

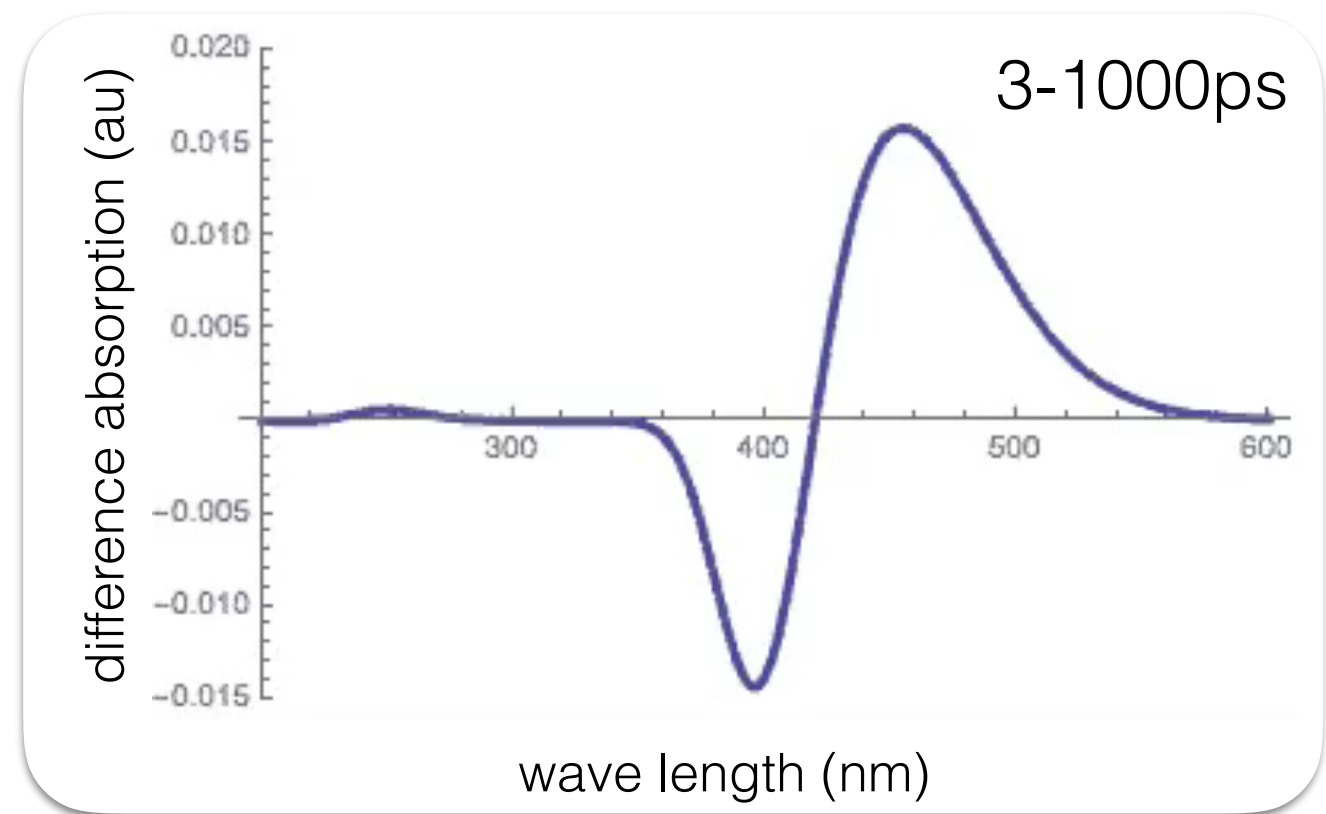
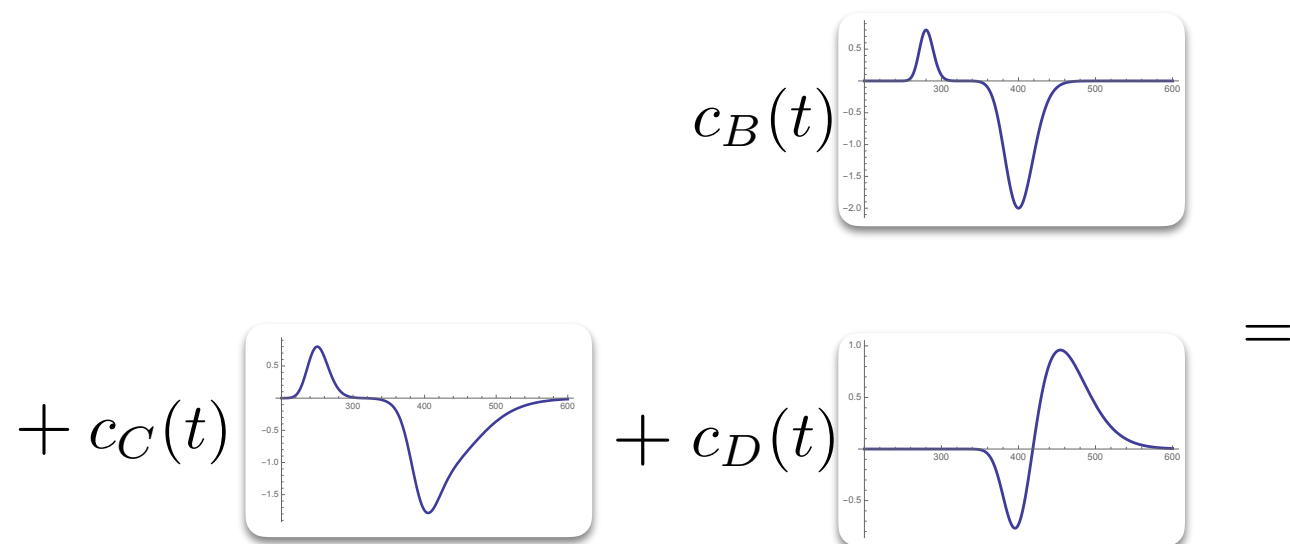
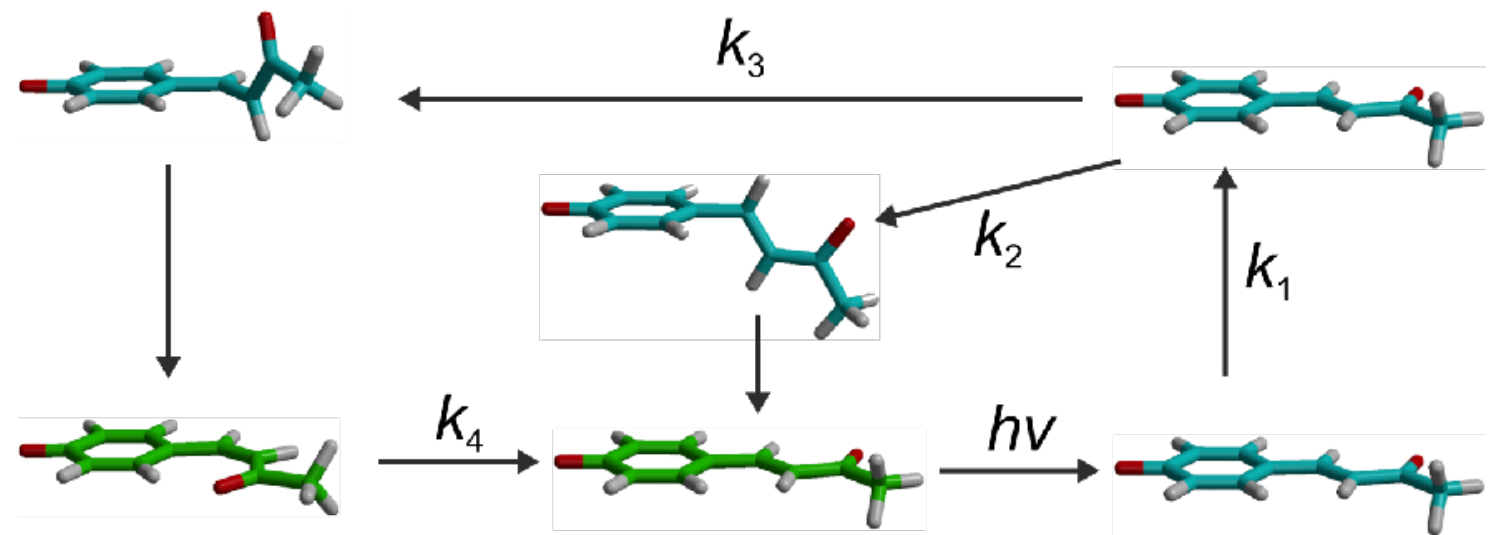
not for fs coherent dynamics!

features only differences

easier to interpret

no effect of limited population transfer with fs pulses

ground state absorption cancels



Time-resolved spectroscopy

measure difference spectra

design kinetic model

trial & error

singular value decomposition

spectra decomposition

basis differences spectra (SADS)

time-dependent populations

$$\Delta S(\lambda, t) = \sum_i c_i(t) \Delta s_i(\lambda)$$

obtain c and Δs from a fit to the data

and know everything!!

no need for theory/computation ;-)

