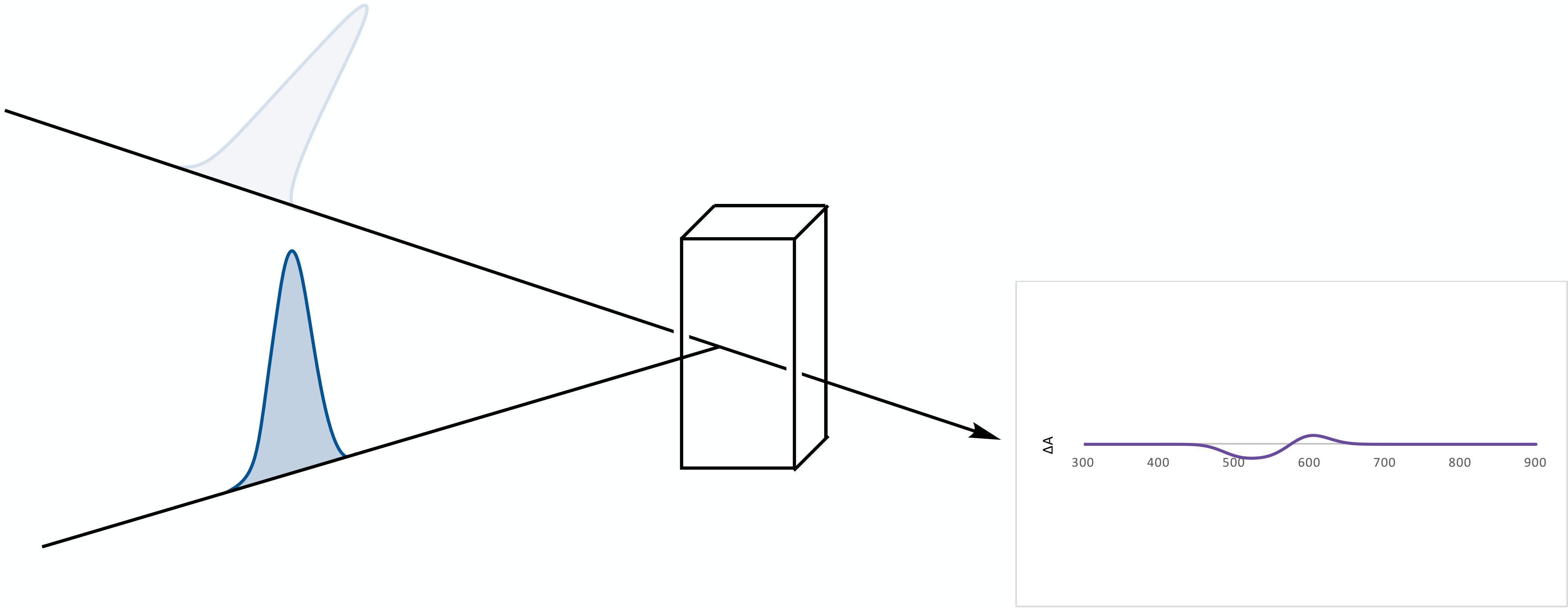
Ultrafast Spectroscopic Methods:

Fundamental Principles and Applications in Photocatalysis

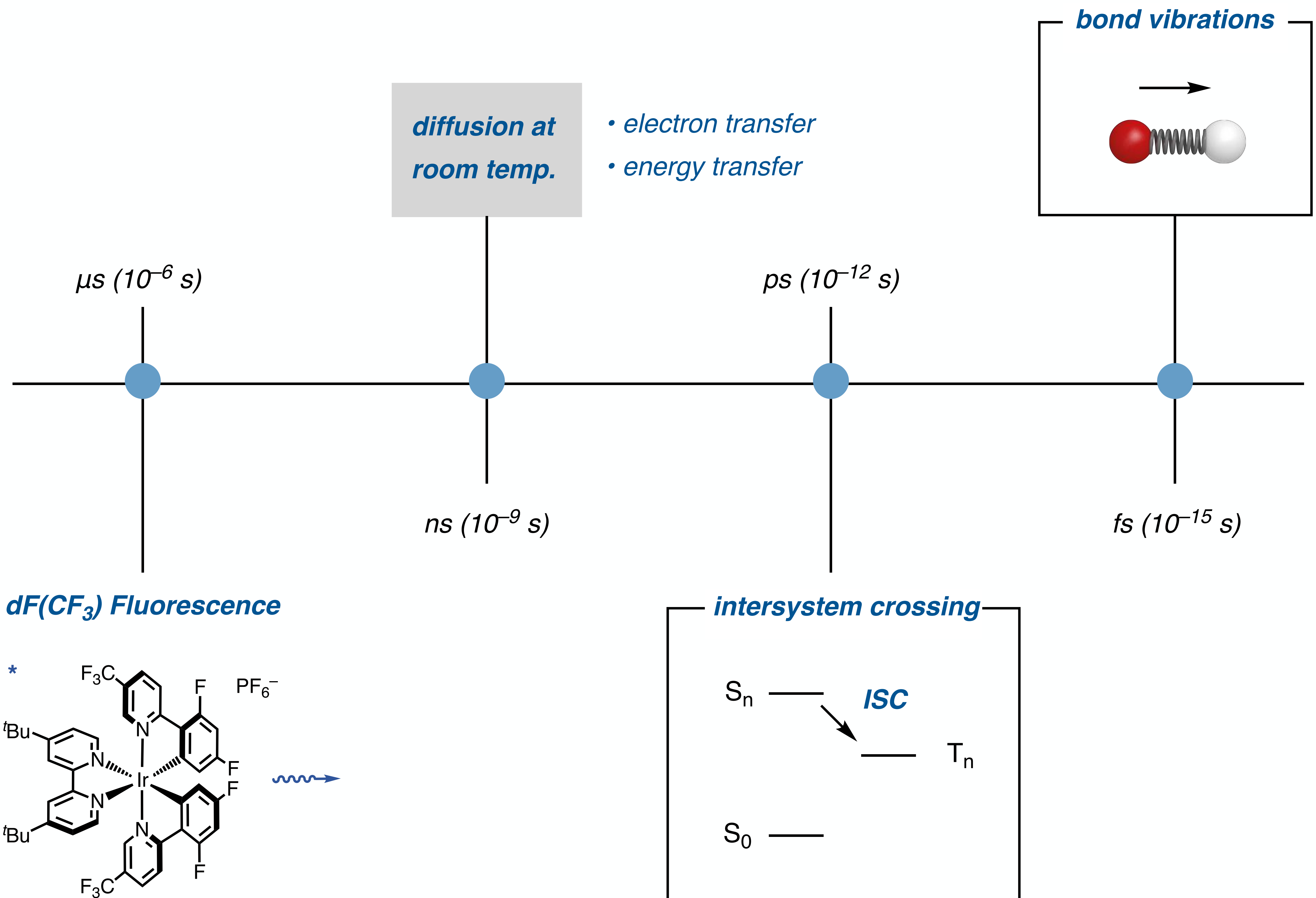


Nick Till

MacMillan Group Meeting

May 25, 2018

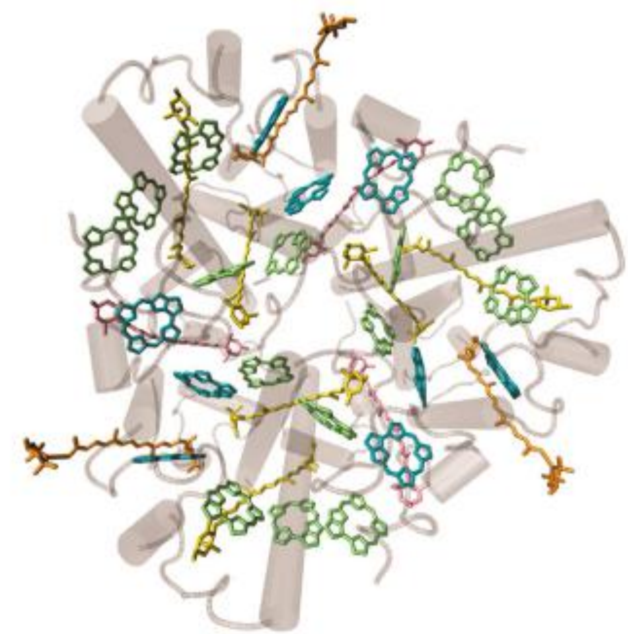
Timescales of Molecular Events



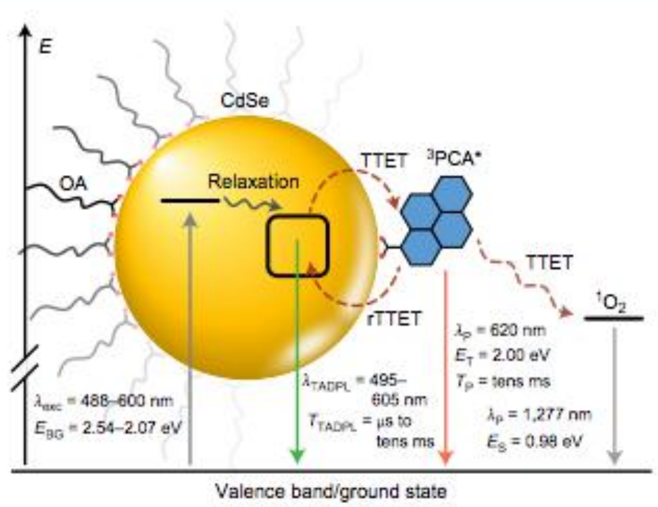
Molecular Systems Studied with Ultrafast Spectroscopy

short timescale processes

- Energy transfer (***EnT***)
- Electron transfer (***ET***)
- Photoluminescence (***PL***)
- Internal conversion (***IC***)
- Intersystem crossing (***ISC***)
- Proton transfer
- Bond isomerization

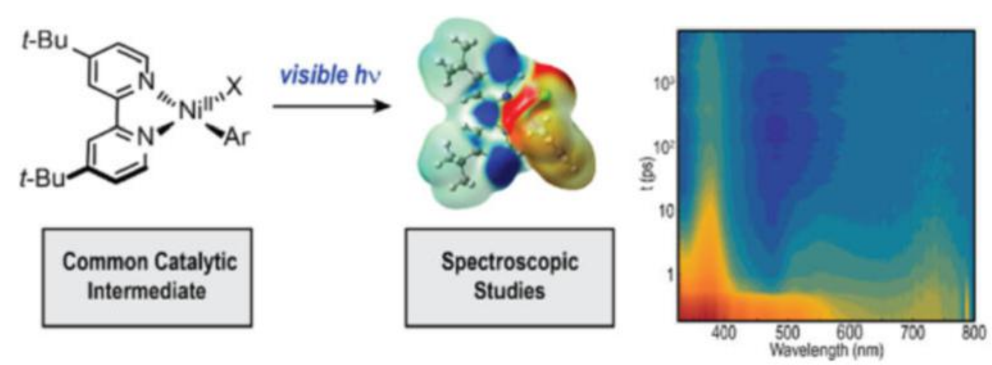


photosynthetic light-harvesting complexes



materials science

excited-state organometallic chemistry



Shields, B. J.; Kudisch, B.; Scholes, G. D.; Doyle, A. G. *J. Am. Chem. Soc.* **2018**, *140*, 3035–3039.
Mirkovic, T.; Ostroumov, E. E.; Anna, J. M.; van Grondelle, R.; Govindjee; Scholes, G. D. *Chem. Rev.* **2017**, *117*, 249–293.
Mongin, C.; Moroz, P.; Zamkov, M.; Castellano, F. N. *Nature Chemistry* **2018**, *10*, 225–230.

Outline for the Presentation

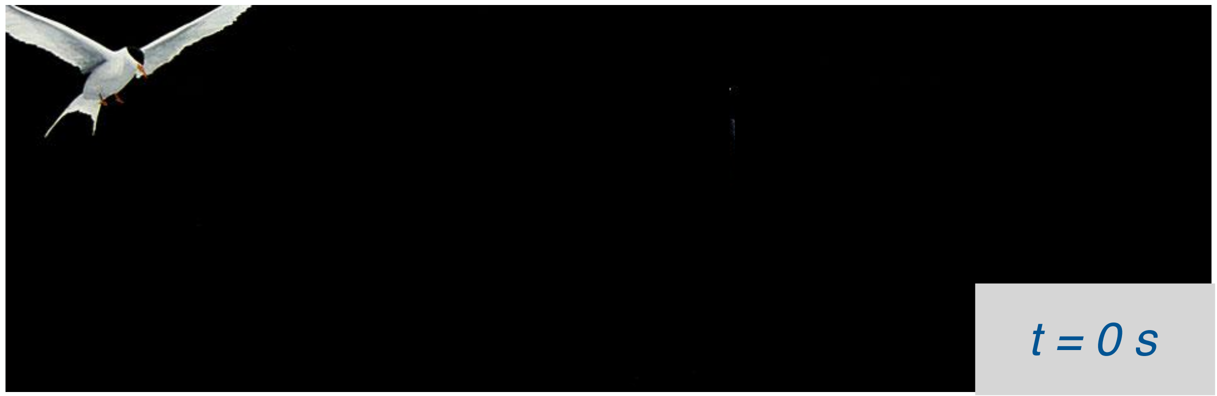
- ***Basics of Transient Absorption Spectroscopy***
  - *physicsl basis for observed spectral changes*
  - *experimental setup*
  - *data analysis*

- ***Case Study 1: Excited State Dynamics in a Photocatalytic Polymerizaiton***
  - *original hypothesis and revised mechanism*

- ***Case Study 2: Observation of an Ultrafast Energy Transfer Event***
  - *Intro to TCSPC (time-correlated single photon counting)*
  - *excited-state lifetime measurements and TEAS measurements reveal EnT event*

- ***Case Study 3: Excited-State Conformational Changes in Cu^{I} Complexes***
  - *physical basis for time-resolved fluorescence spectroscopy*
  - *experimental apparatus for ultrafast fluorescence measurements*

Taking Snapshots of Ultrafast Molecular Dynamics



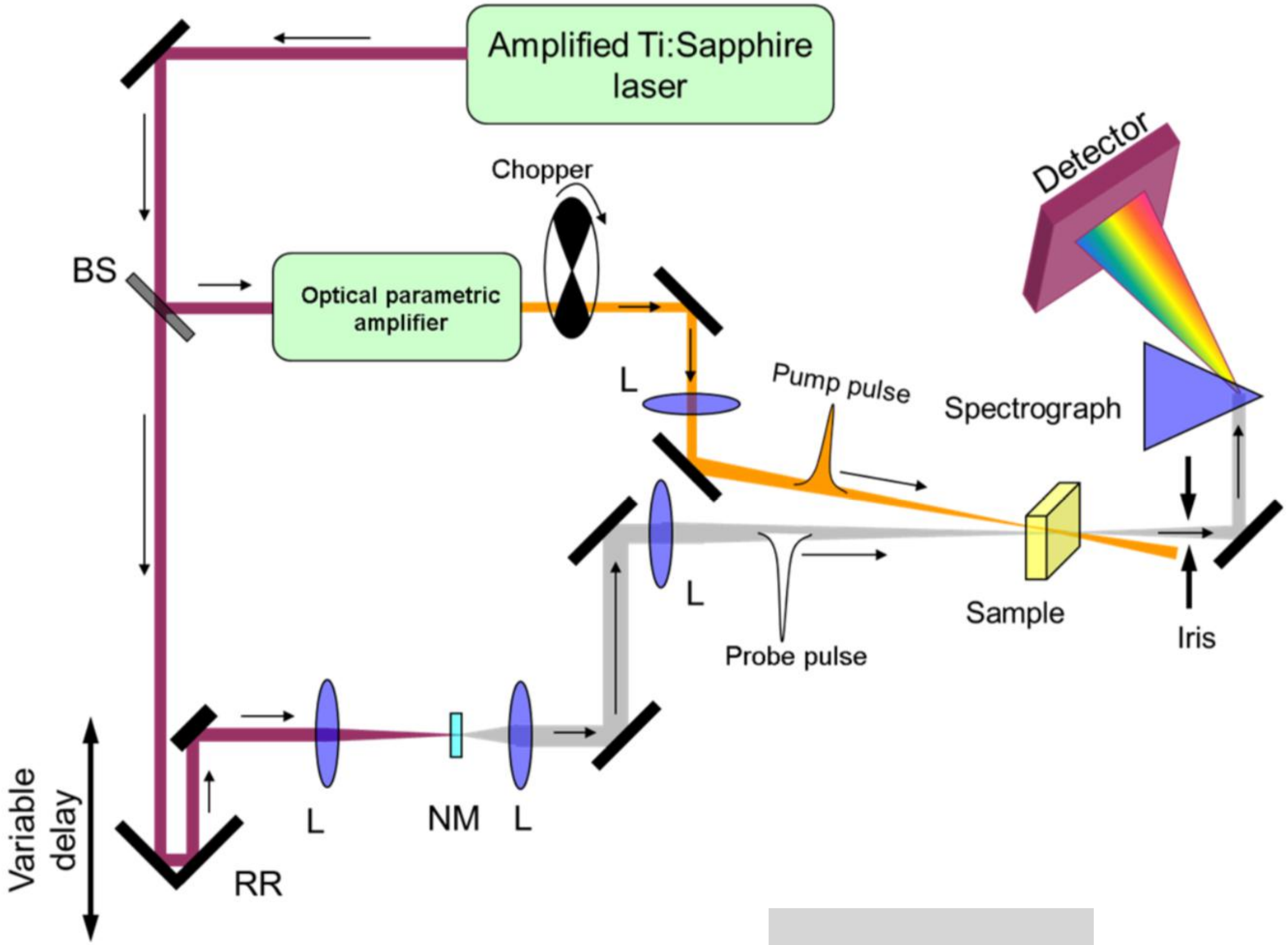
flight can be reconstructred from multiple snapshots of the process taken at different delays

processed data

detector requirements

- *fast shutter speed (short laser pulse)*
- *short delays*

Experimental Setup and Hardware



Crucial Features

- *spatial and temporal overlap of pump/probe*
- *short pulse duration*
- *short pulse delay (ps-µs timescale)*
- *stable, broad spectrum probe*

pump

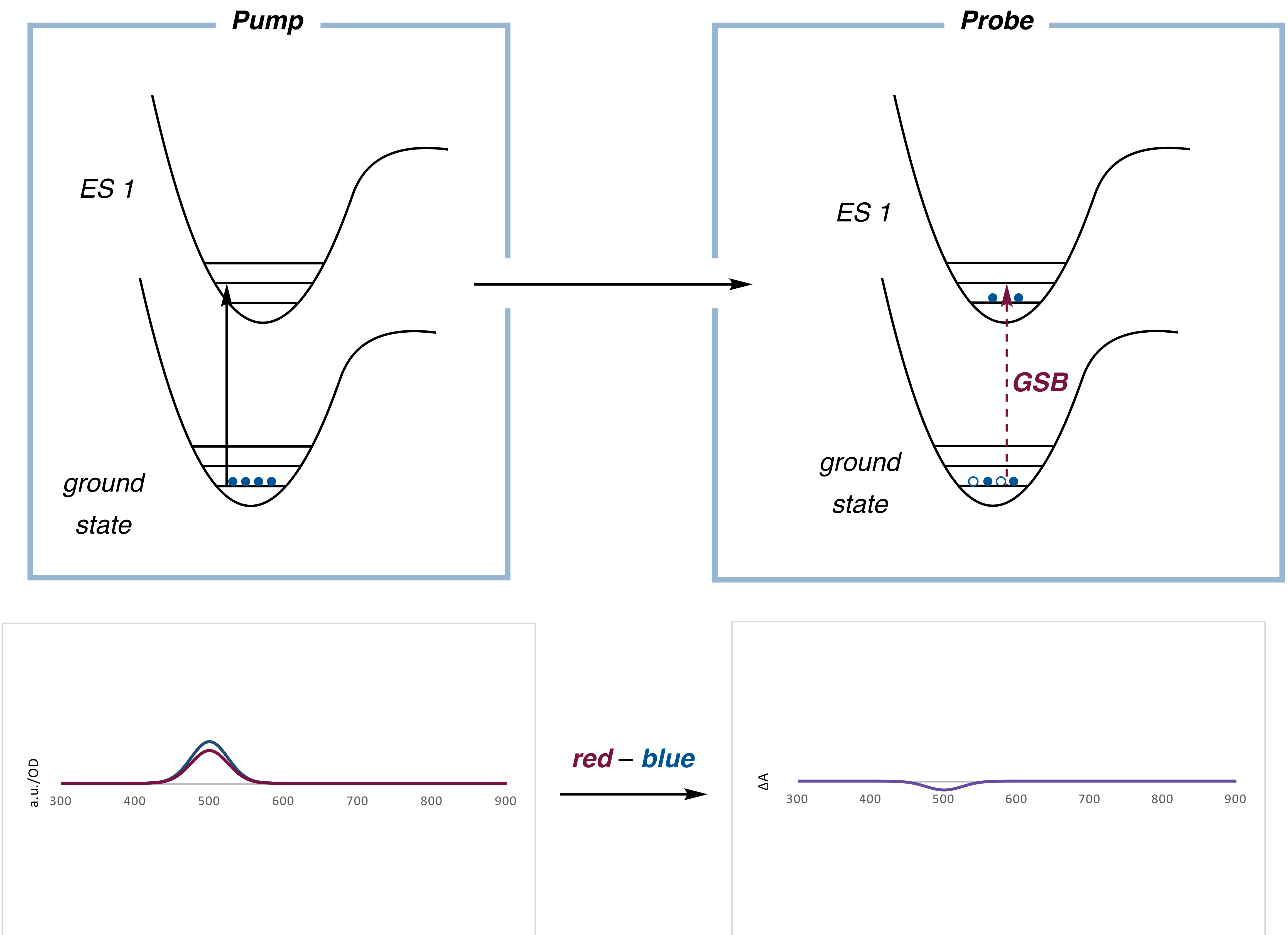
visible light

probe

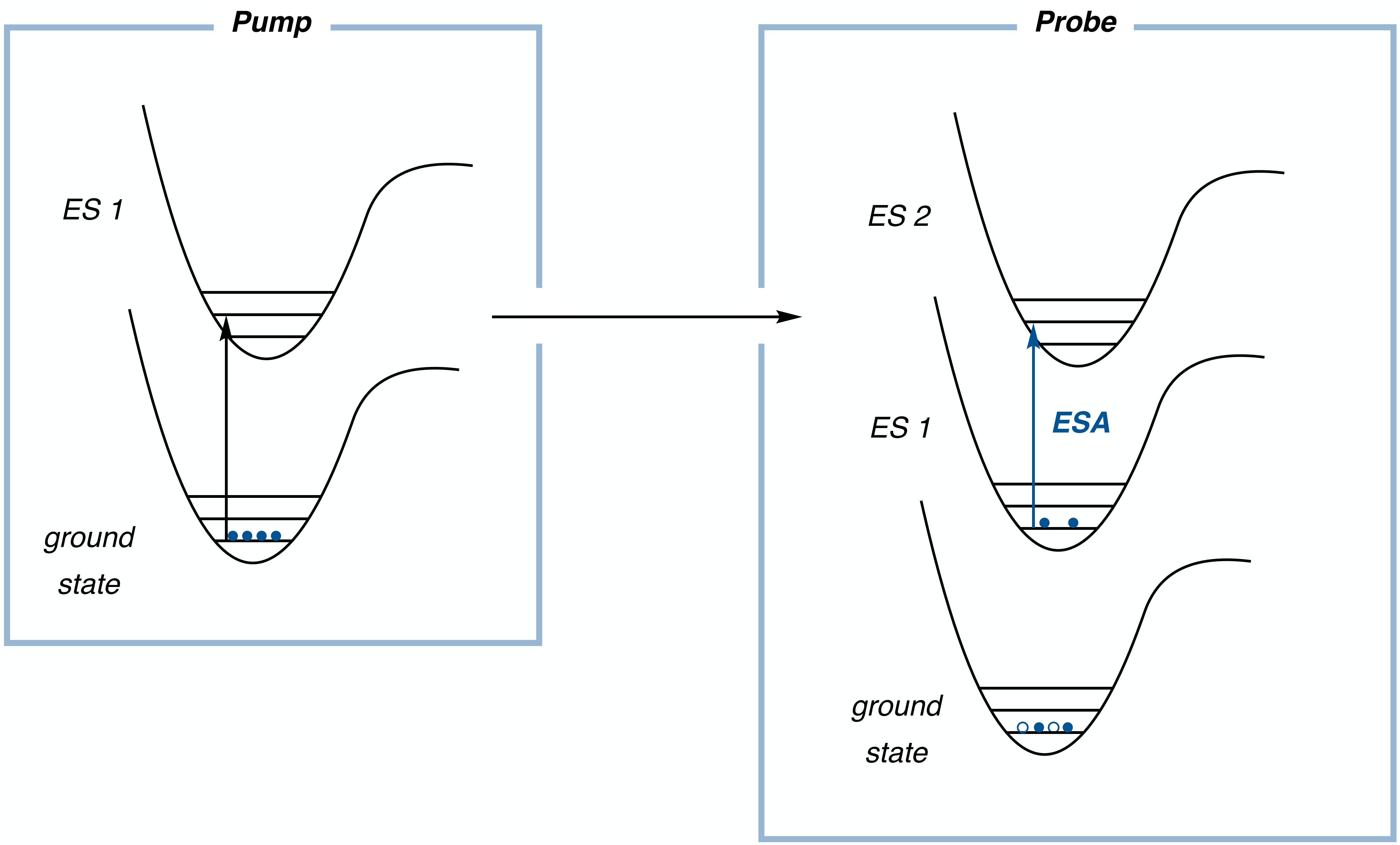
- *white light*
- *broadband IR*
- *XAS (X-ray Absorption)*
- *NMR*

website of Mikas Vengris http://web.vu.lt/ff/m.vengris/

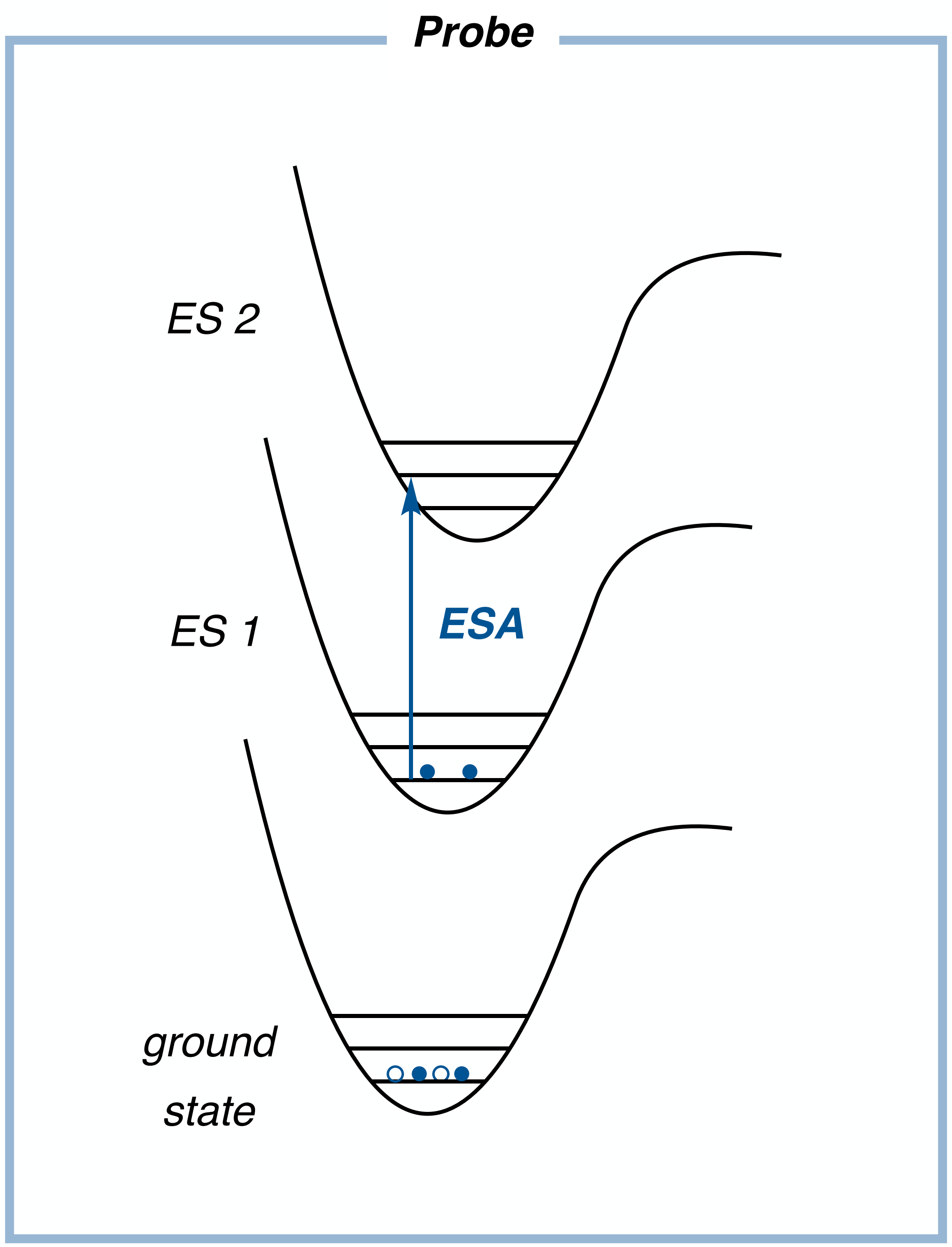
Origin of the Ground State Bleach (GSB) Feature

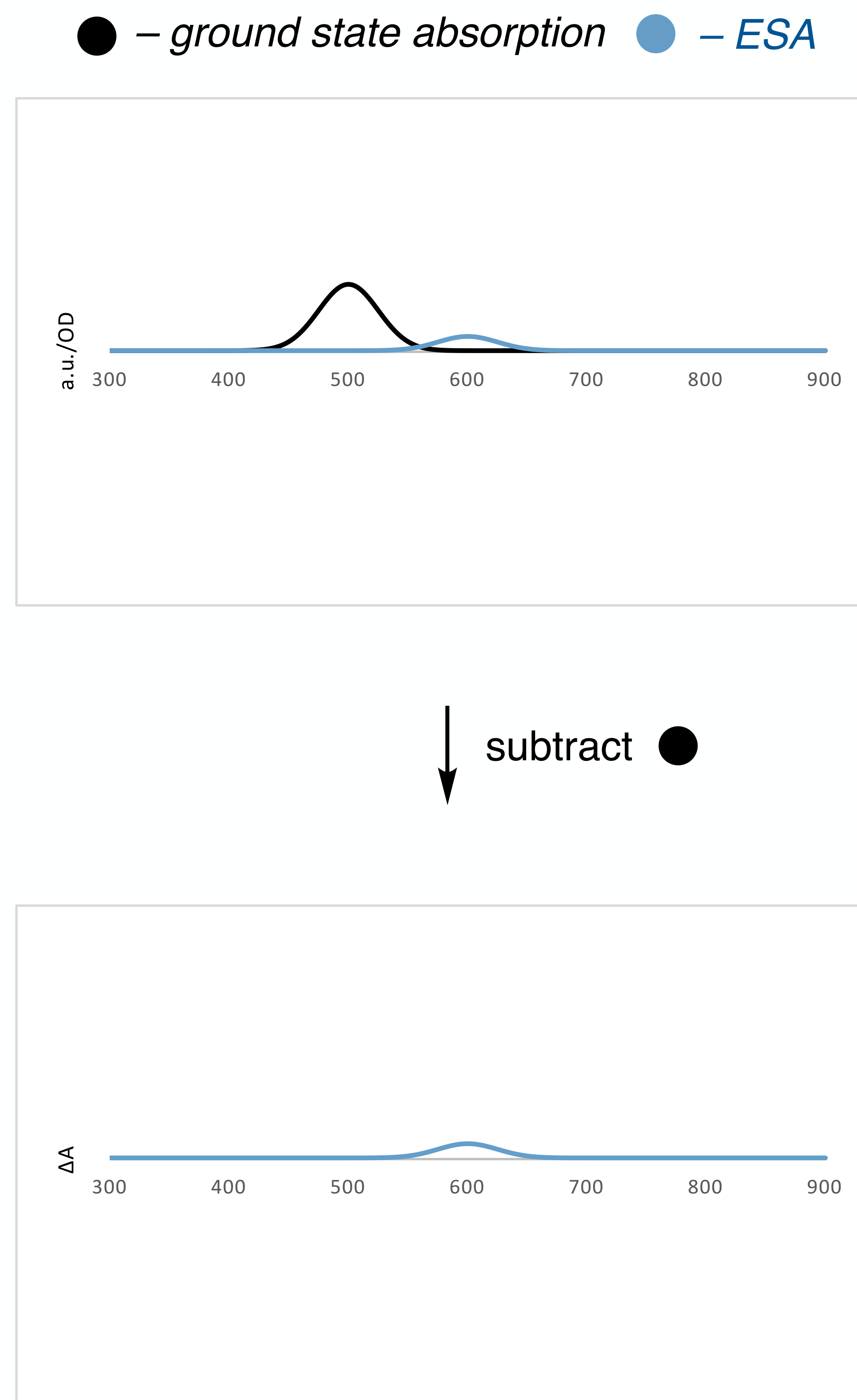


Origin of the Excited State Absorption (ESA) Feature



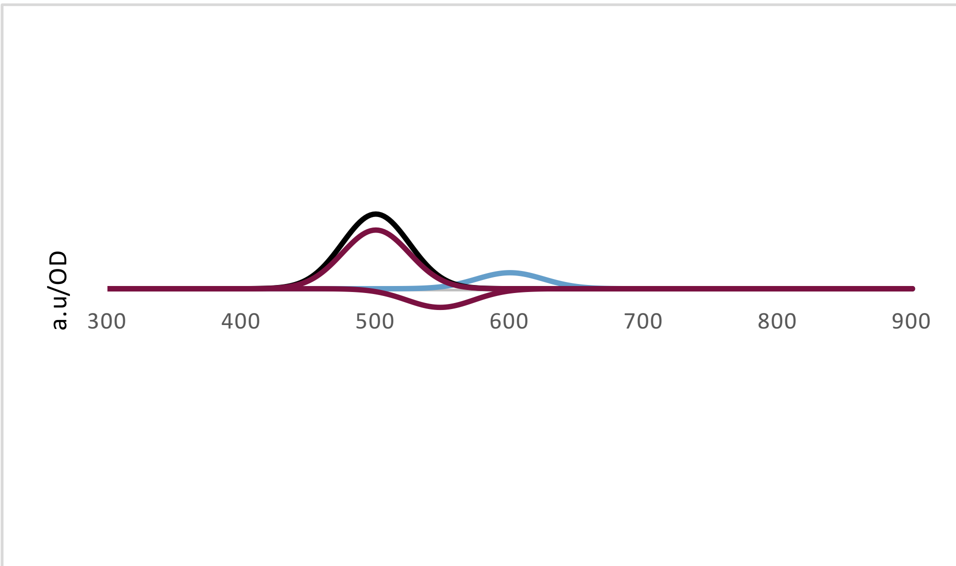
Origin of the Excited State Absorption (ESA) Feature

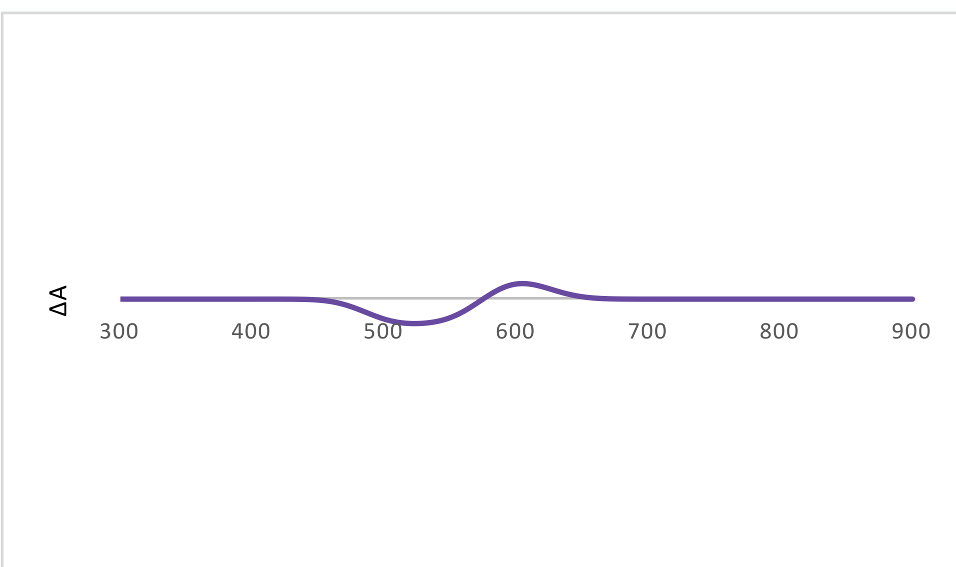


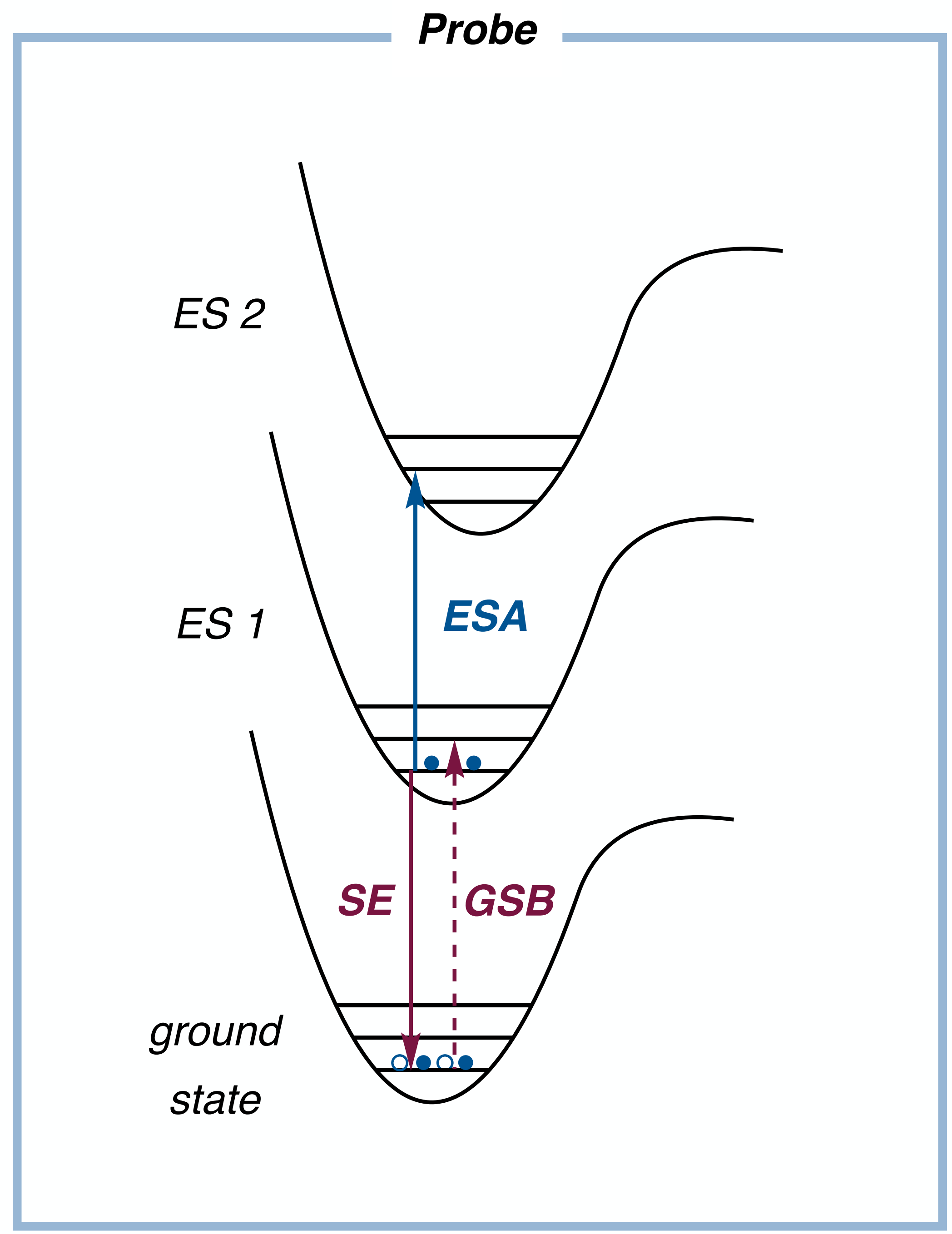


Excited State Absorption - *positive signal in ΔA spectrum*

Overview of Commonly Observed ΔA Features



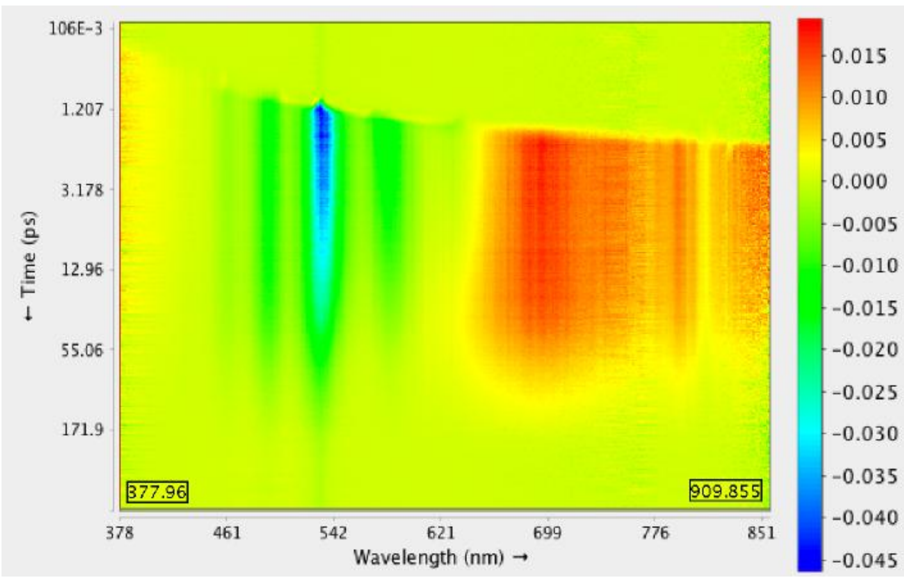




***GSB** and **SE** features often overlap in wavelength - can be hard to distinguish within negative feature*

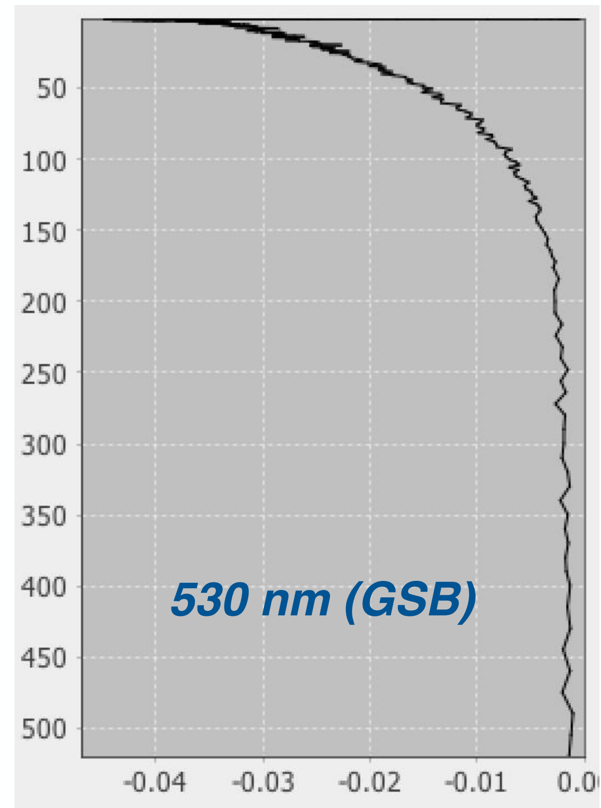
Representation and Handling of 3-Dimensional Data

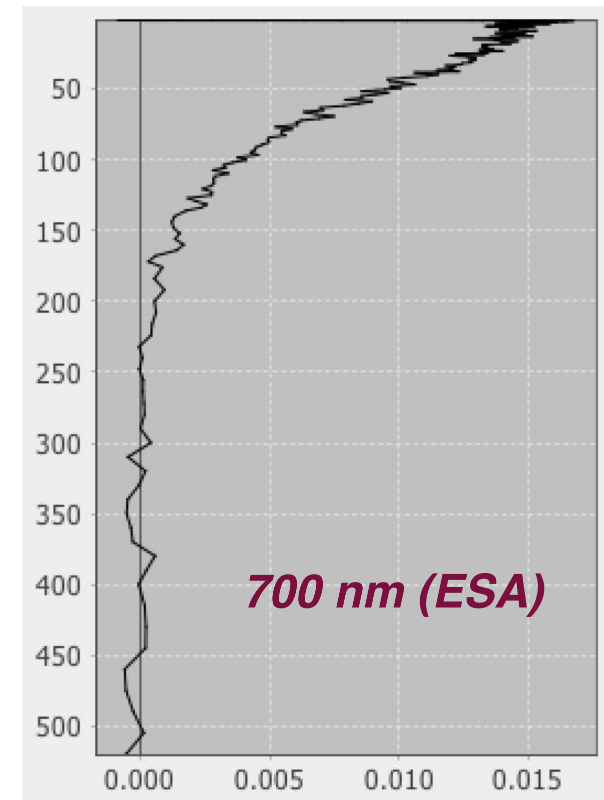
contour plot/heat map



single-wavelength analysis

t (ps)

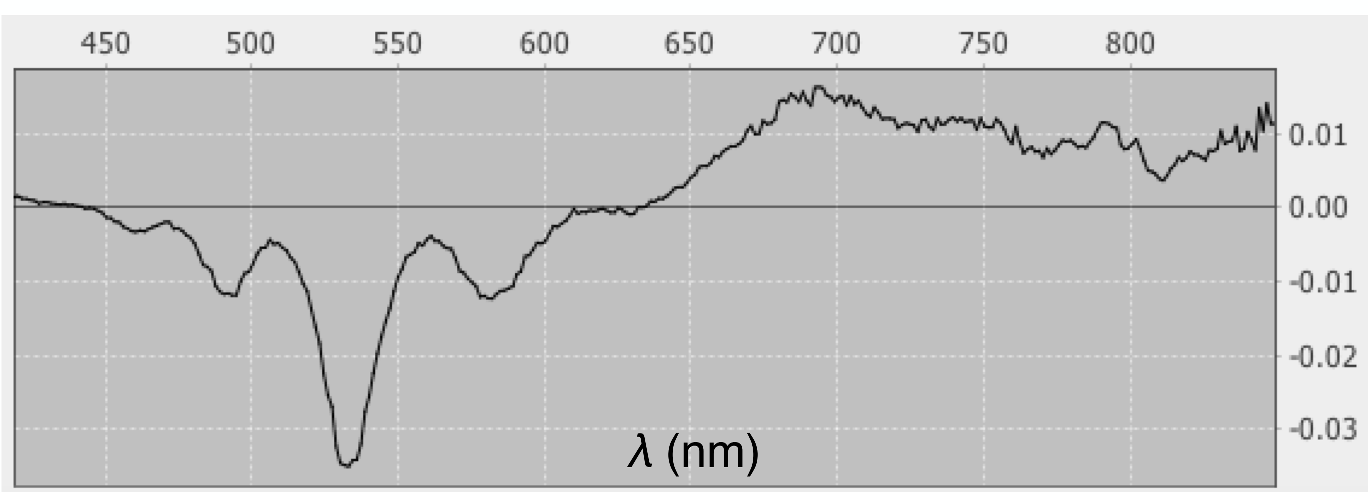




ΔA

ΔA

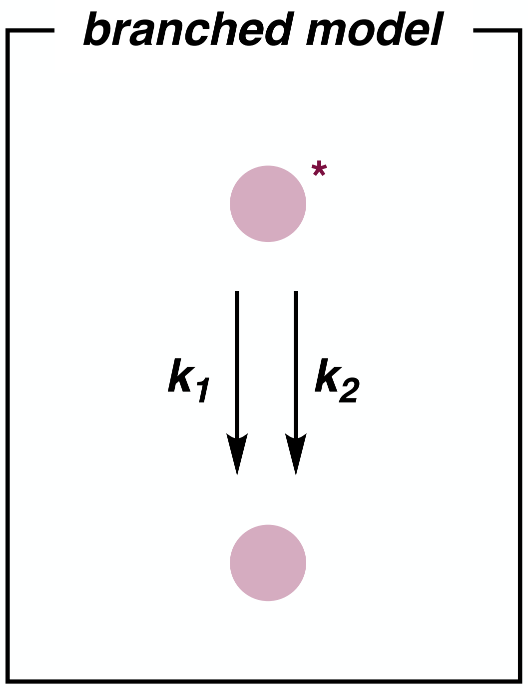
single-timepoint analysis

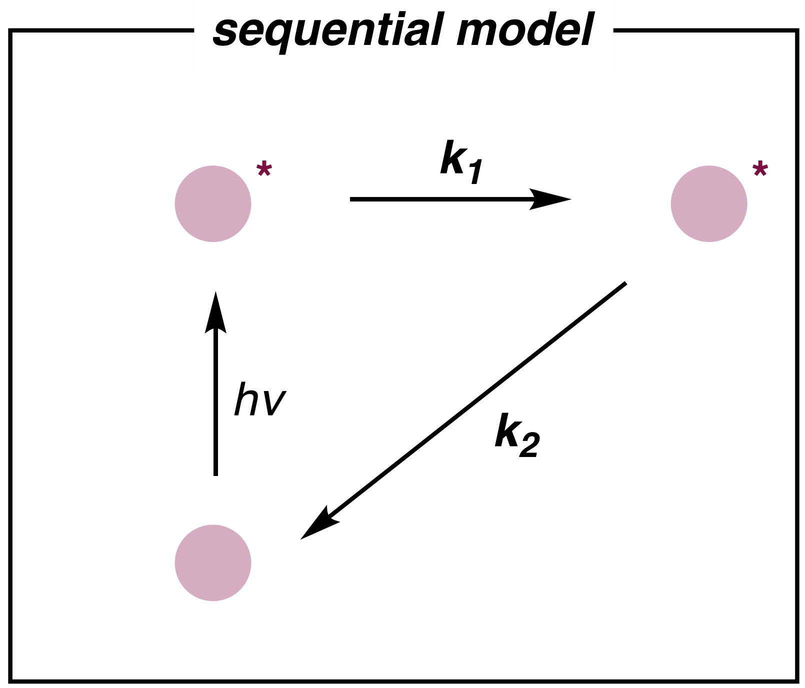


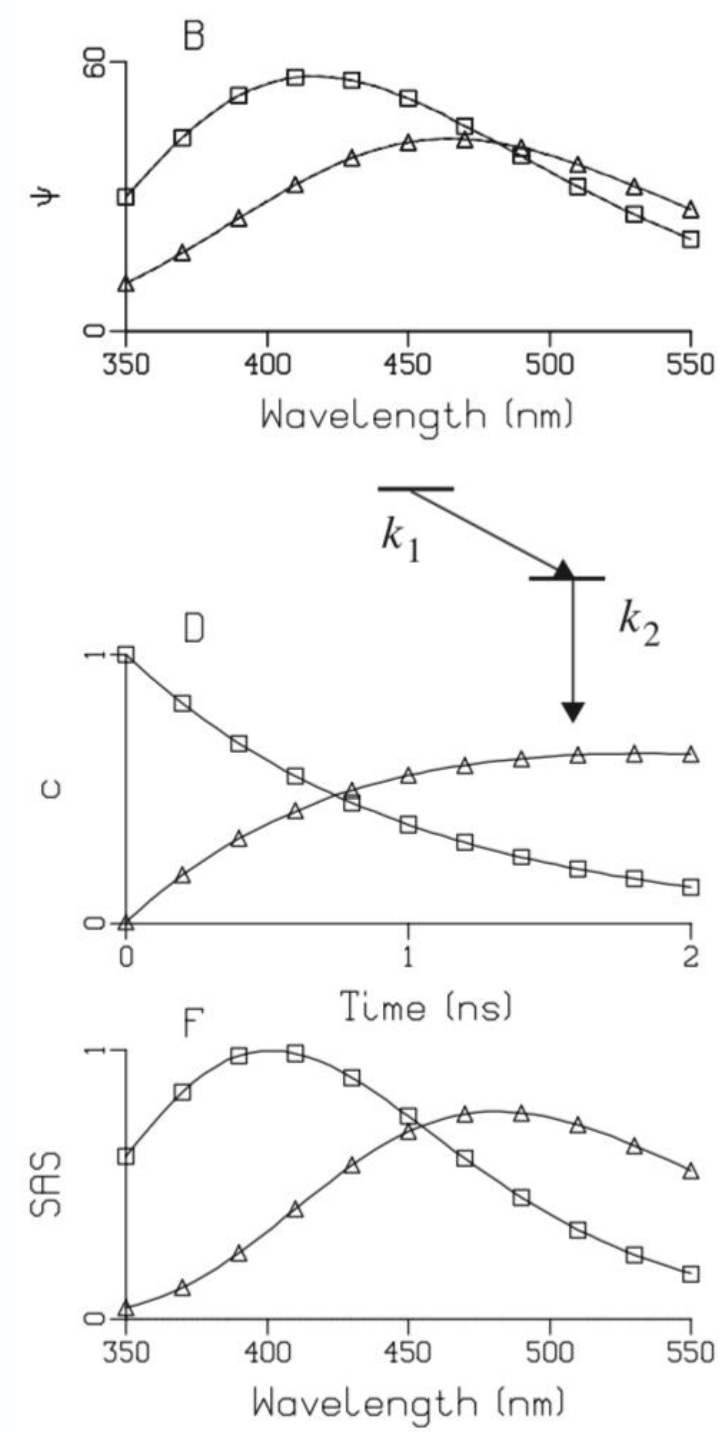
ΔA

- multiple ways to visualize data
- multiple single-timepoint traces may be most common

Kinetic Models for Excited State Decay







choice of model precedes fitting process:

some intuition or physical knowledge required

- more complicated combinations of these simple models can be invoked
- beware of overfitting: complex models can fit data well, but be unphysical

van Stokkum, I. H. M.; Larsen, D. S.; van Grondelle, R. *Biochimica et Biophysica Acta (BBA) - Bioenergetics* **2004**, *1657*, 82–104.

Outline for the Presentation

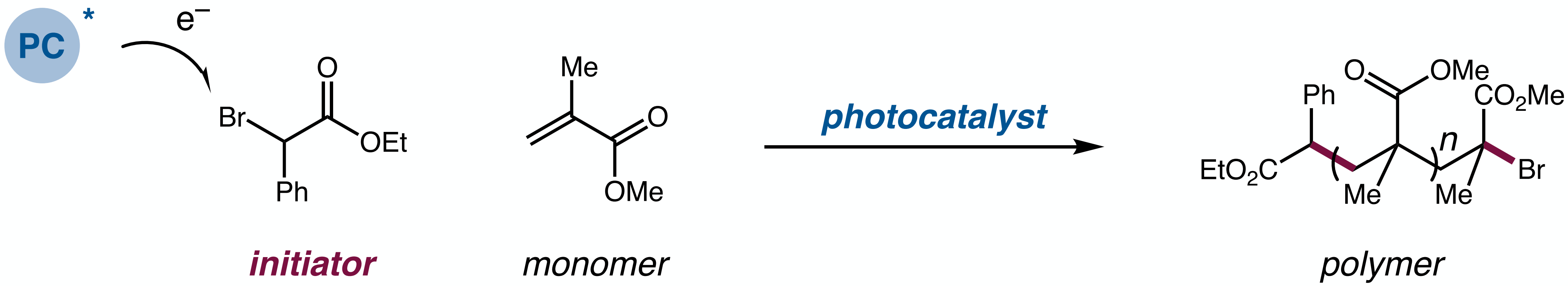
- ***Basics of Transient Absorption Spectroscopy***
  - *physicsl basis for observed spectral changes*
  - *experimental setup*
  - *data analysis*

- ***Case Study 1: Excited State Dynamics in a Photocatalytic Polymerizaiton***
  - *original hypothesis and revised mechanism*

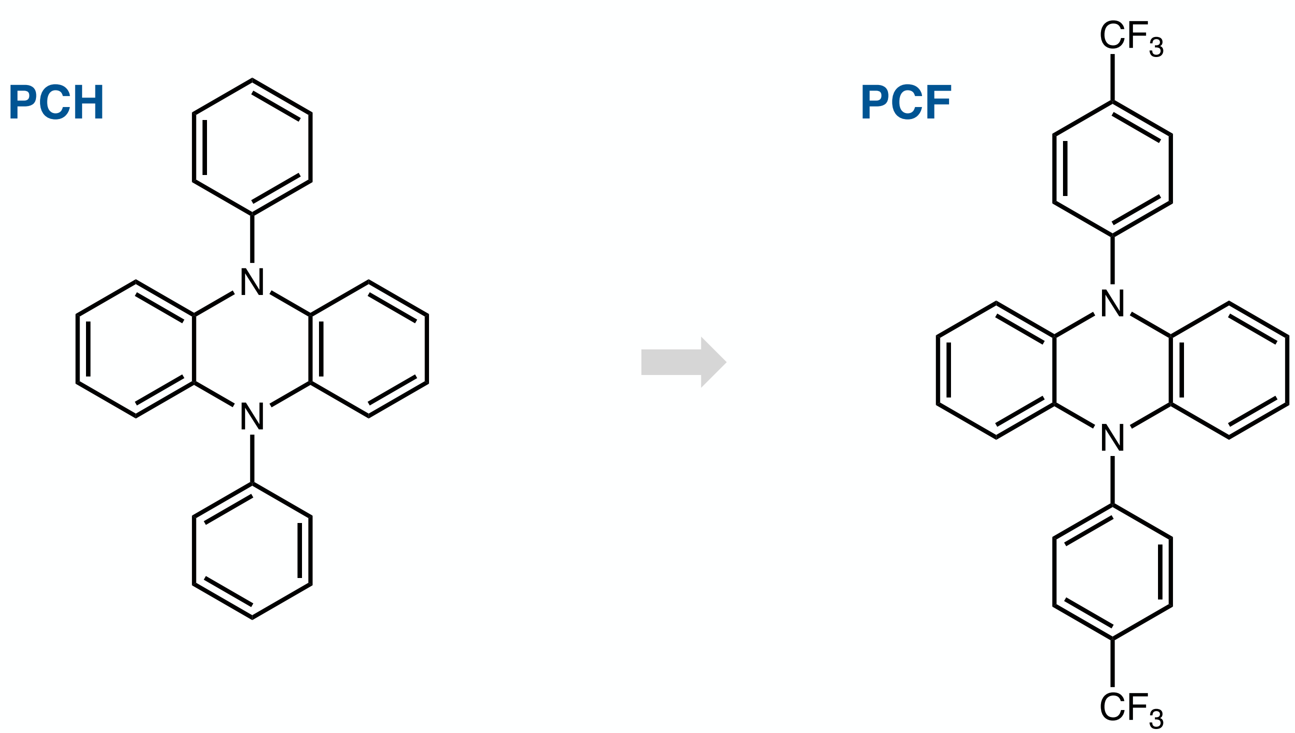
- ***Case Study 2: Observation of an Ultrafast Energy Transfer Event***
  - *Intro to TCSPC (time-correlated single photon counting)*
  - *excited-state lifetime measurements and TEAS measurements reveal EnT event*

- ***Case Study 3: Excited-State Conformational Changes in Cu^{I} Complexes***
  - *physical basis for time-resolved fluorescence spectroscopy*
  - *experimental apparatus for ultrafast fluorescence measurements*

Atom-Transfer Radical Polymerization with an Organic Photocatalyst



photocatalyst



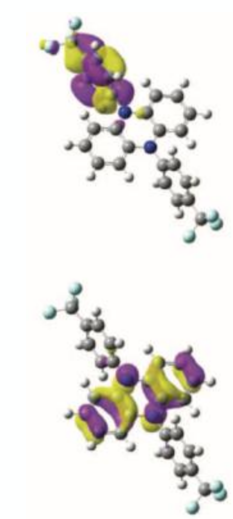
Đ = 1.55

I* = 74.5%

superior dispersity (**Đ** = 1.17)

high initiation efficiency (**I*** = 69.5%)

PCF



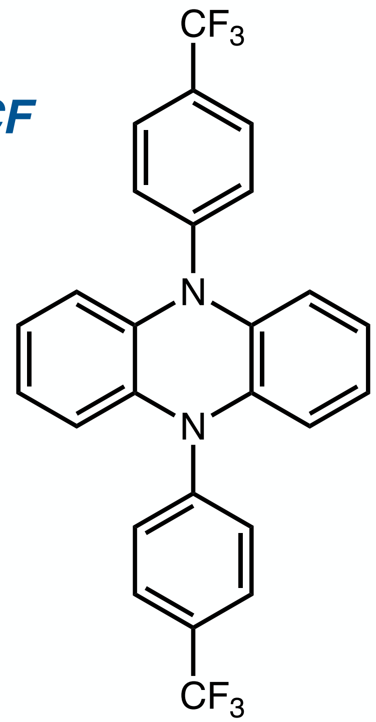
long-lived, charge separated T_1 state

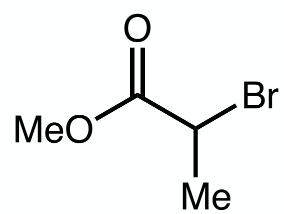
superior dispersity

Theriot, J. C.; Lim, C.-H.; Yang, H.; Ryan, M. D.; Musgrave, C. B.; Miyake, G. M. *Science* **2016**, *352*, 1082–1086.

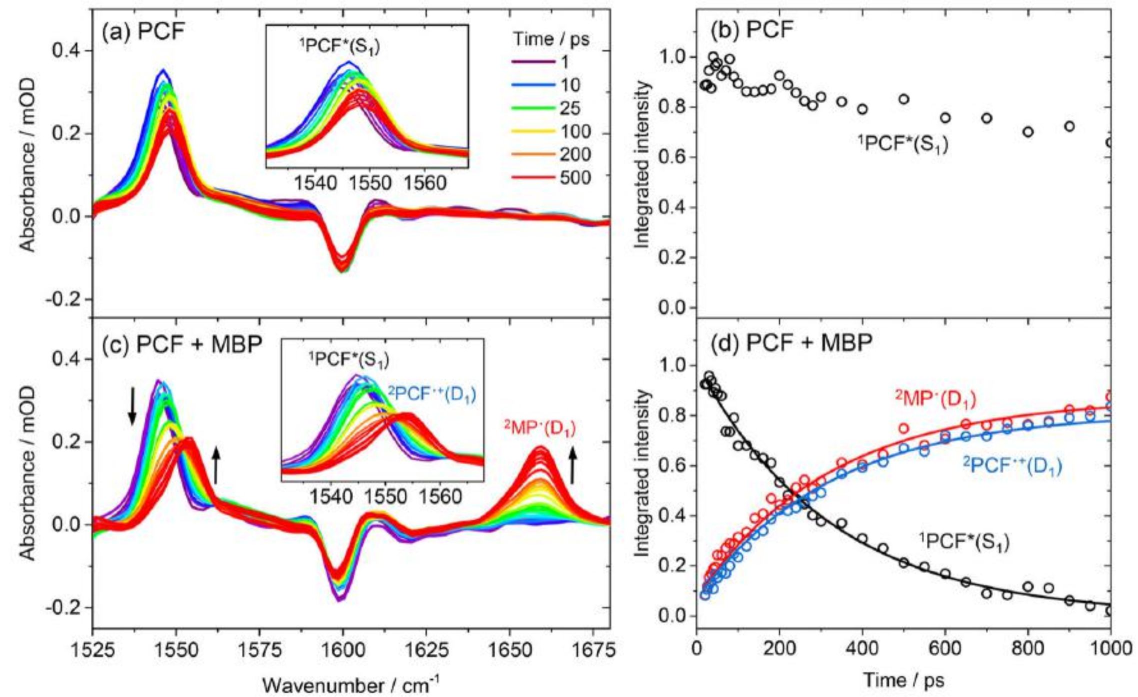
Bimolecular Excited-State Dynamics of PCF by TVAS and TEAS

PCF





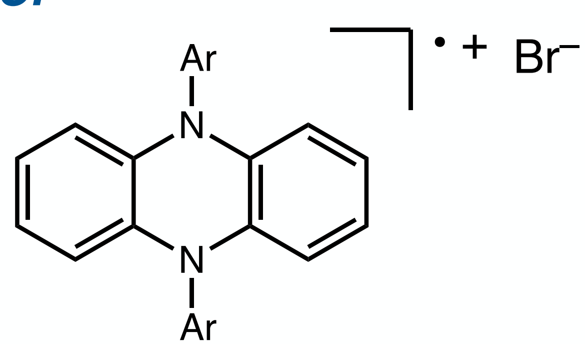
MBP

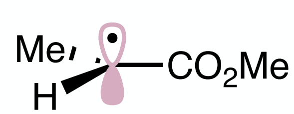


triplet sensitizers do not quench ***PCF****

PCF* does not access T_n manifold by TVAS

PCF•+



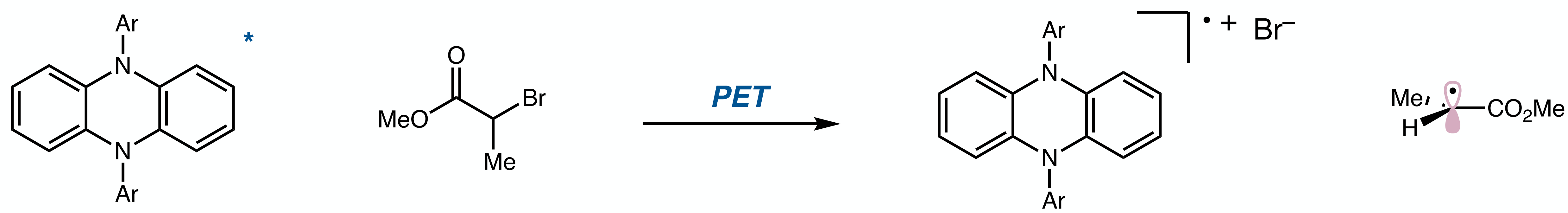


MP•

MP•** is generated by SET from S_1 state of **PCF*

Koyama, D.; Dale, H. J. A.; Orr-Ewing, A. J. *J. Am. Chem. Soc.* **2018**, *140*, 1285–1293.

Excited State Electron Transfer Rates for PCF and PCH



PCF (Ar = 4-(CF_3)-phenyl)

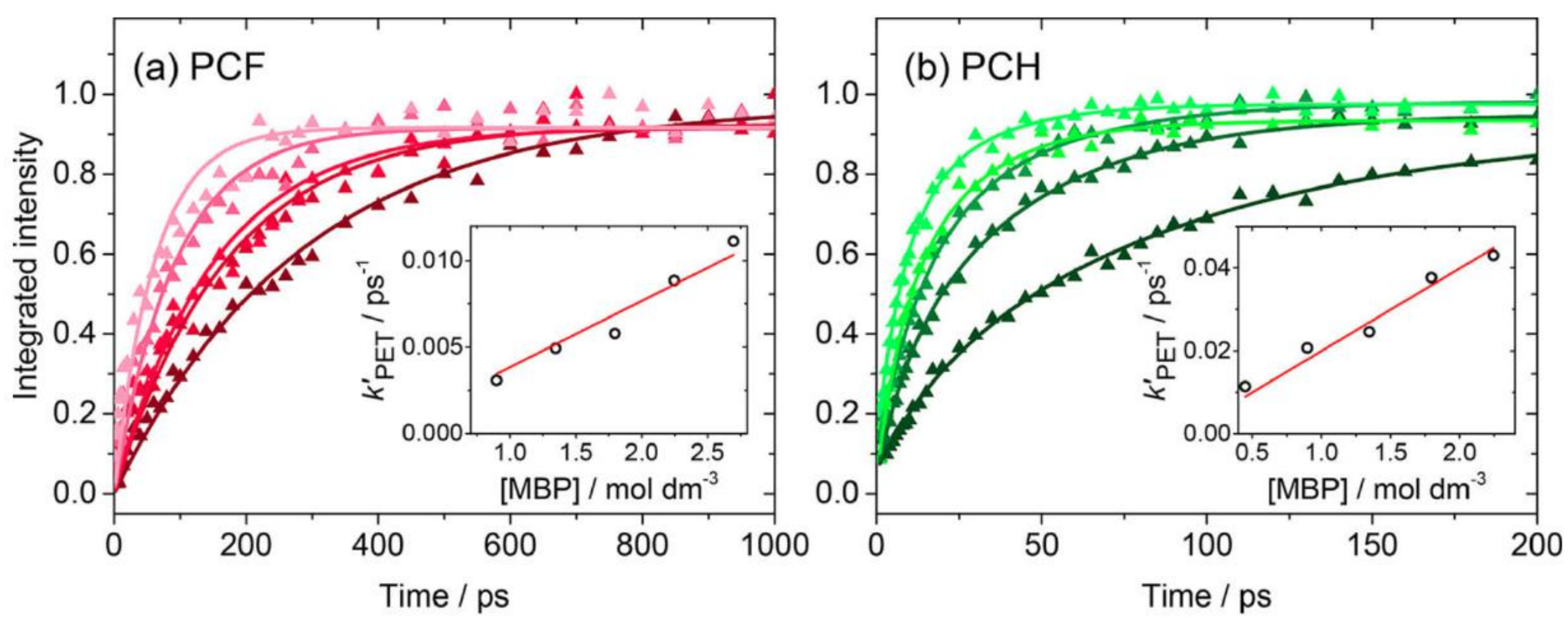
MBP

PCH/F•+

MP•

PCH (Ar = phenyl)

plots of 1/τ v.s. [**MBP**] reveals ***k_{PET}*** values for **PCF** and **PCH**



PC	***k_{PET}*** (s^{-1} M^{-1})
PCF	$3.9 \pm 0.2 \times 10^{9}$
PCH	$3.6 \pm 0.2 \times 10^{10}$

- biexponential fit of the ***PET*** kinetics for ***PCH*** reveals static ***PET*** (within 7-17 ps) to ***MBP***

Koyama, D.; Dale, H. J. A.; Orr-Ewing, A. J. *J. Am. Chem. Soc.* **2018**, *140*, 1285–1293.

Outline for the Presentation

- ***Basics of Transient Absorption Spectroscopy***
  - *physicsl basis for observed spectral changes*
  - *experimental setup*
  - *data analysis*

- ***Case Study 1: Excited State Dynamics in a Photocatalytic Polymerizaiton***
  - *original hypothesis and revised mechanism*

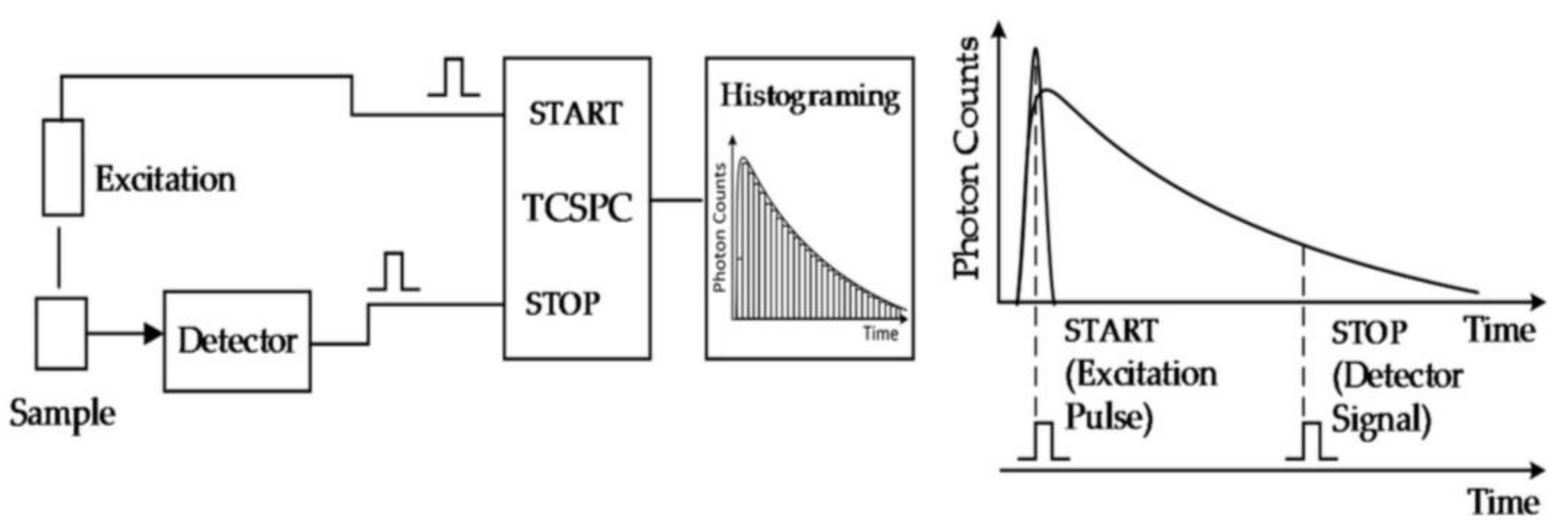
- ***Case Study 2: Observation of an Ultrafast Energy Transfer Event***
  - *Intro to TCSPC (time-correlated single photon counting)*
  - *excited-state lifetime measurements and TEAS measurements reveal EnT event*

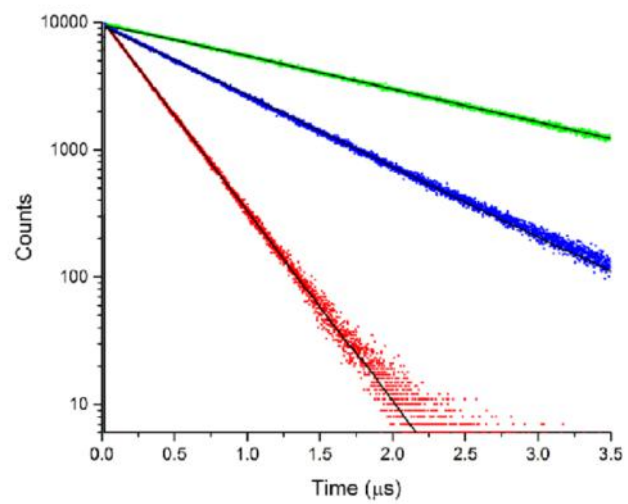
- ***Case Study 3: Excited-State Conformational Changes in Cu^{I} Complexes***
  - *physical basis for time-resolved fluorescence spectroscopy*
  - *experimental apparatus for ultrafast fluorescence measurements*

Time-Correlated Single Photon Counting (TCSPC)

- Method of choice for determining excited state lifetimes of ***luminescent*** molecules with lifetimes as low as 10 ns
- Requires 1-6 hours per experiment, depending on phosphorescence intensity

Experimental Setup

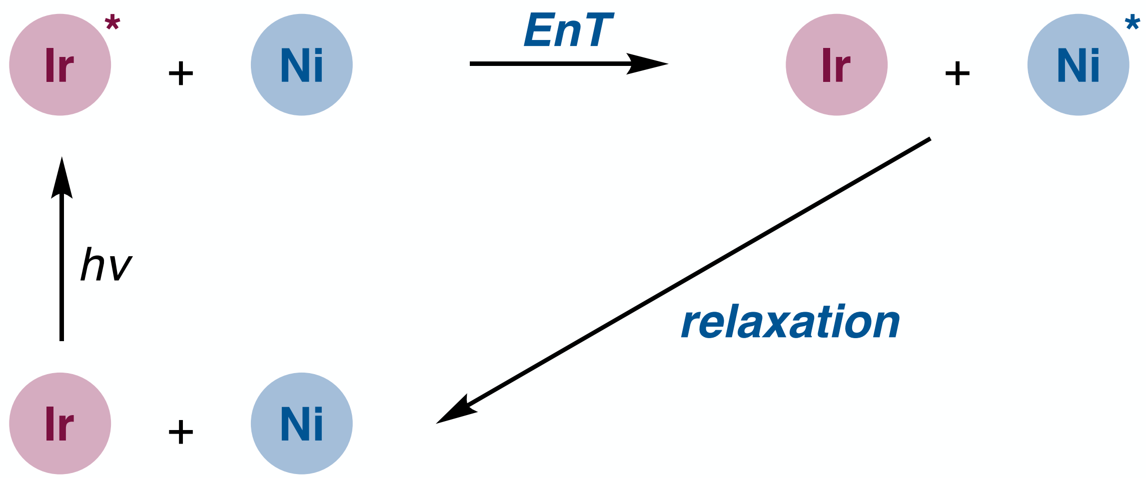




counts v. time (log scale)

Wei, L.; Yan, W.; Ho, D. *Sensors* **2017**, *17*, 2800.

Energy Transfer Between Transition Metal Centers

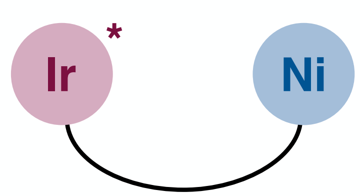


inverted kinetics

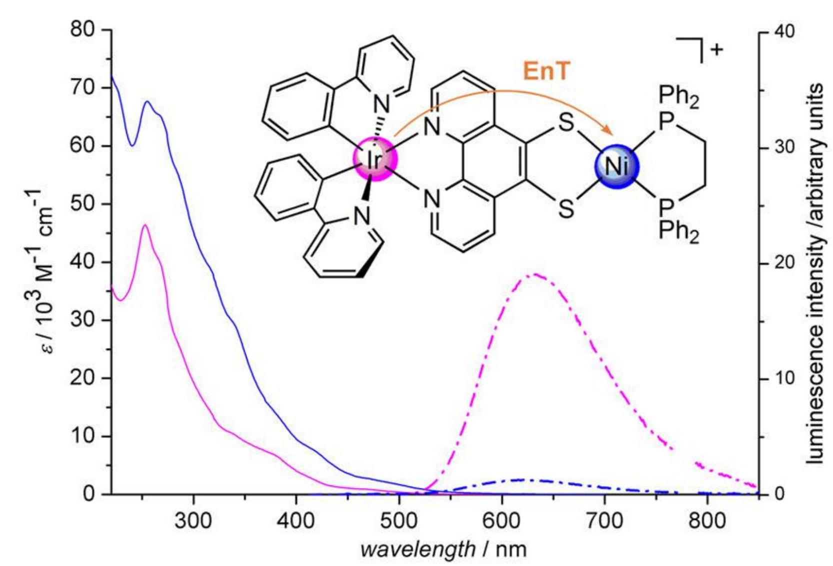
$k_{relax} >> k_{enT}$

Ni* *cannot be observed*

if $k_{relax} > 10^9\ s^{-1}$, we cannot observe the build up of Ni* since k_{EnT} is diffusion-limited

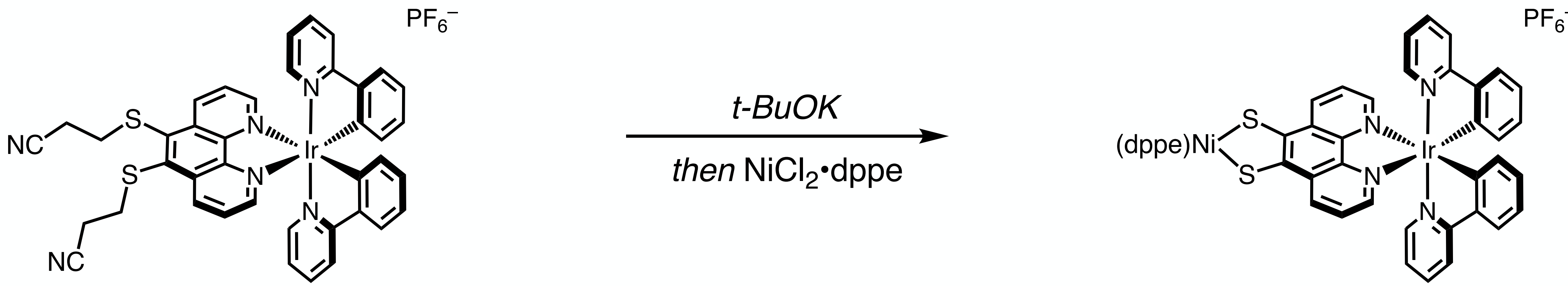


k_{EnT} *no longer diffusion-limited*



Schallenberg, D.; Neubauer, A.; Erdmann, E.; Tänzler, M.; Villinger, A.; Lochbrunner, S.; Seidel, W. W. *Inorg. Chem.* **2014**, *53*, 8859–8873.

Observation of Partial Quenching of Excited-State Iridium



Φ_{PL} = 0.17 (±0.02)

τ = 640 ns (±60 ns)

anomalous lowered ***photoluminescence***
with unchanged ***lifetime*** *(τ)*

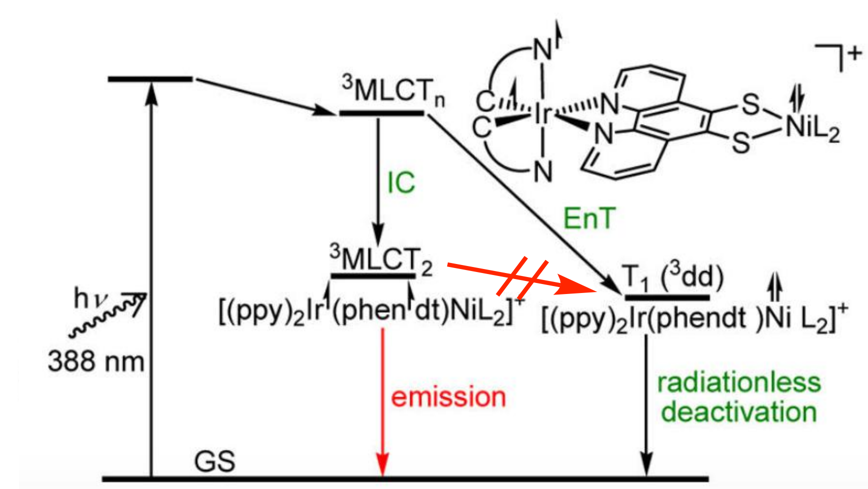
Φ_{PL} = 0.011 (±0.002)

τ = 650 ns (±70 ns)

- excited state reduction of Ni ruled out by electro- and spectroelectrochemical experiments

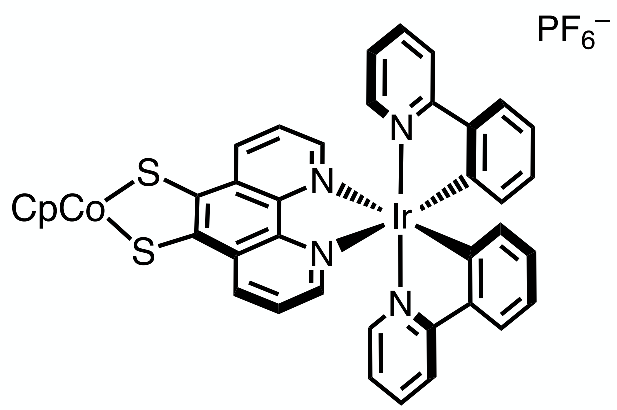
proposed mechanism

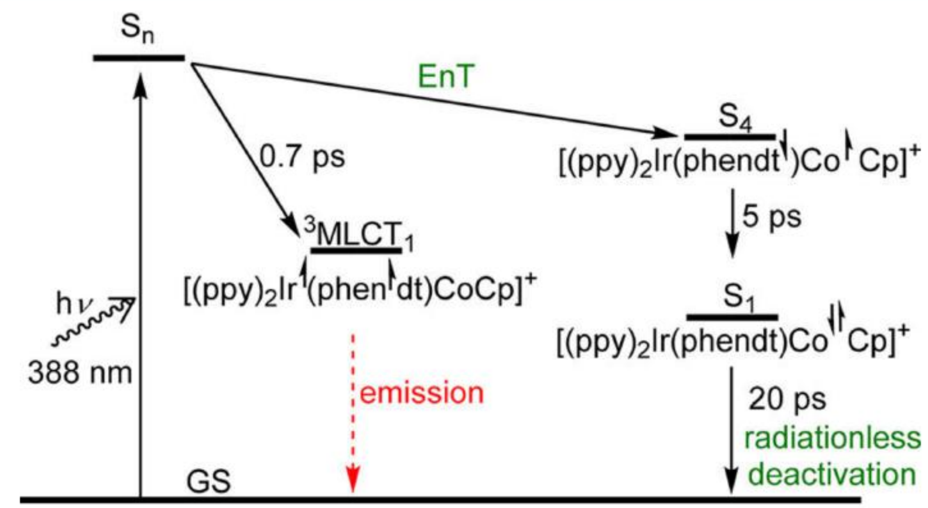
- ***EnT*** quenches excited state
- ***EnT*** must compete with IC
- requires ***EnT*** to be on ps timescale

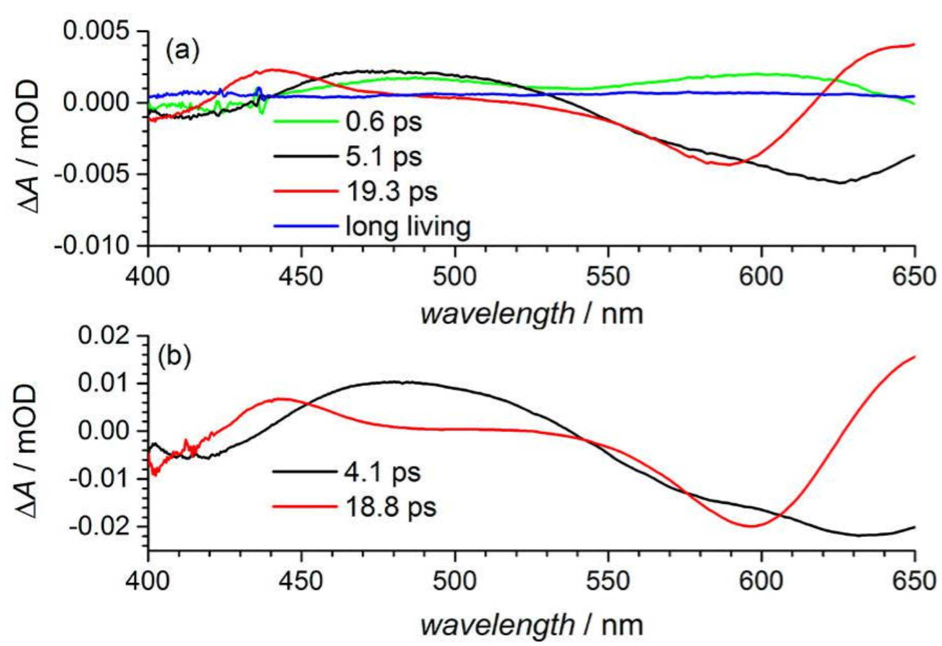


Schallenberg, D.; Neubauer, A.; Erdmann, E.; Tänzler, M.; Villinger, A.; Lochbrunner, S.; Seidel, W. W. *Inorg. Chem.* **2014**, *53*, 8859–8873.

Observation of Ultrafast EnT from Ir(ppy)$_2$(phen) to CoCp



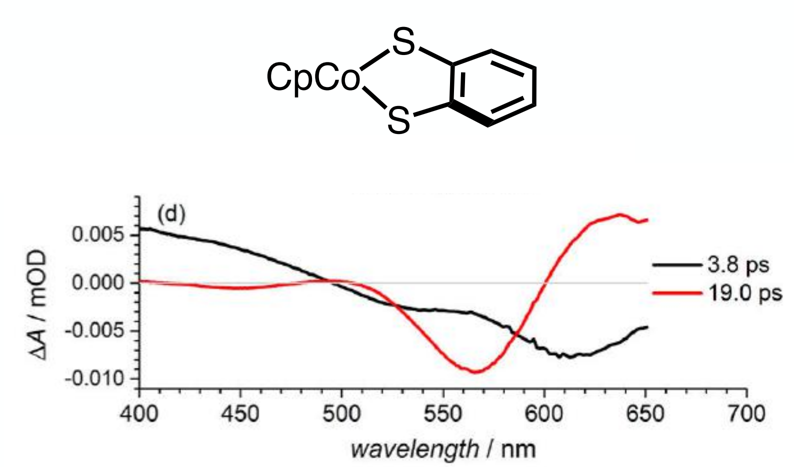




388 nm excitation
(iridium-selective)

590 nm excitation
(cobalt-selective)

dynamics of isolated Co center



- excited state dynamics of Ir-Co complex mirrors that of isolated Co center: implies Ir–Co ***EnT***

Erdmann, E.; Lütgens, M.; Lochbrunner, S.; Seidel, W. W. *Inorg. Chem.* **2018**, *57*, 4849–4863.

Outline for the Presentation

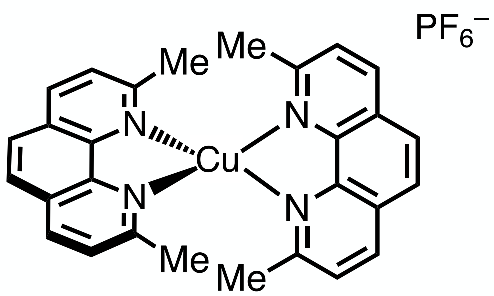
- ***Basics of Transient Absorption Spectroscopy***
  - *physicsl basis for observed spectral changes*
  - *experimental setup*
  - *data analysis*

- ***Case Study 1: Excited State Dynamics in a Photocatalytic Polymerizaiton***
  - *original hypothesis and revised mechanism*

- ***Case Study 2: Observation of an Ultrafast Energy Transfer Event***
  - *Intro to TCSPC (time-correlated single photon counting)*
  - *excited-state lifetime measurements and TEAS measurements reveal EnT event*

- ***Case Study 3: Excited-State Conformational Changes in Cu^{I} Complexes***
  - *physical basis for time-resolved fluorescence spectroscopy*
  - *experimental apparatus for ultrafast fluorescence measurements*

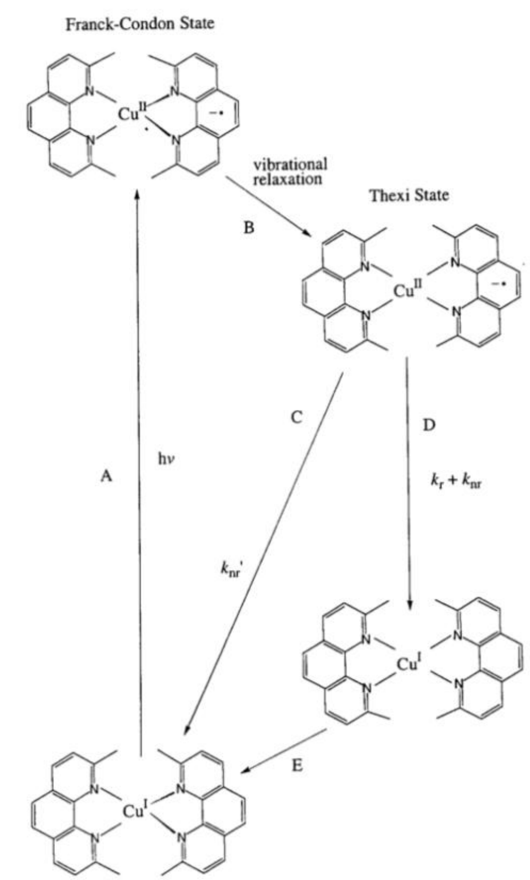
Photophysics of Excited-State Cu^{I}(phen) Complexes



$Cu^{I}(dmphen)_2PF_6$

- large Stokes shift
- excited-state lifetime modulated by phenanthroline substituents

photophysical model



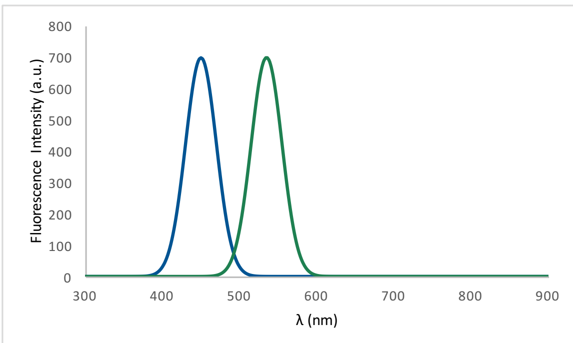
Compound	λ_{abs} (nm) (ε)[b]	λ_{PL} (nm)[c]	Φ_{PL}^{d} $\times 10^4$	τ (ns)[c]	ΔG_{es}^{f} (eV)	$E_{1/2}^{g}$	E_{y7}^{*h}
$Cu(phen)_2(PF_6)$	458 (6880)	–	–	<10	–	0.19	–
$Cu(dmp)_2(PF_6)$	454 (7950)	740	2.3	85	2.04	0.64	−1.4
$Cu(dpp)_2(PF_6)$	448 (3440)	715	9.7	250	1.99	0.58	−1.4
$Cu(bcp)_2(PF_6)$	478 (13 200)	765	1.5	70	1.98	0.58	−1.4

- *excited state is characterized as MLCT, and quenched by ET and EnT mechanisms*
- *structurally related Cu^{I} complexes have been implicated in photocatalytic transformations*

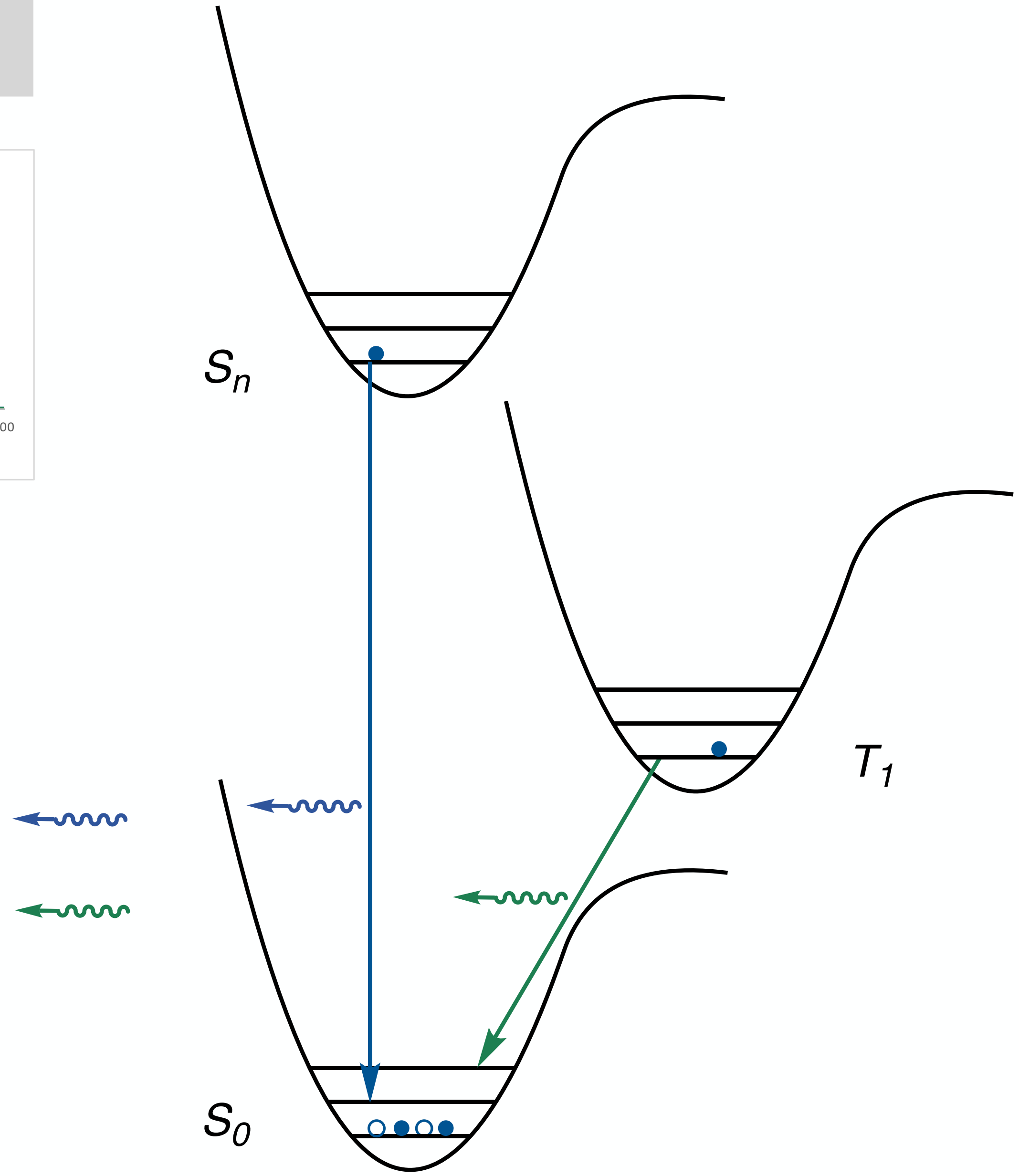
Ruthkosky, M.; Kelly, C. A.; Castellano, F. N.; Meyer, G. J. *Coordination Chemistry Reviews* **1998**, *171*, 309–322.
Scaltrito, D. V.; Thompson, D. W.; O'Callaghan, J. A.; Meyer, G. J. *Coordination Chemistry Reviews* **2000**, *208*, 243–266.

Molecular Basis for Time-Resolved Fluorescence Spectroscopy

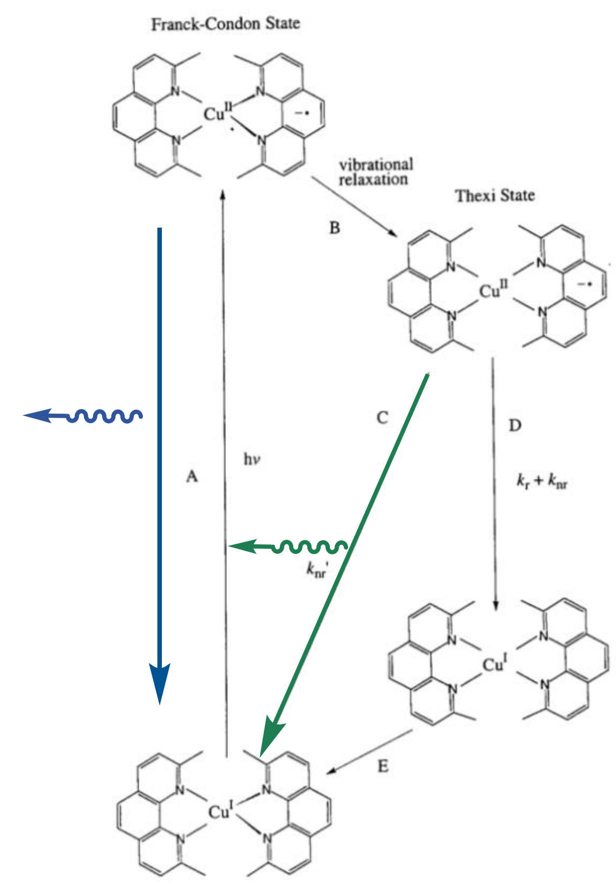
fluorescence spectrum



fluorescence detector

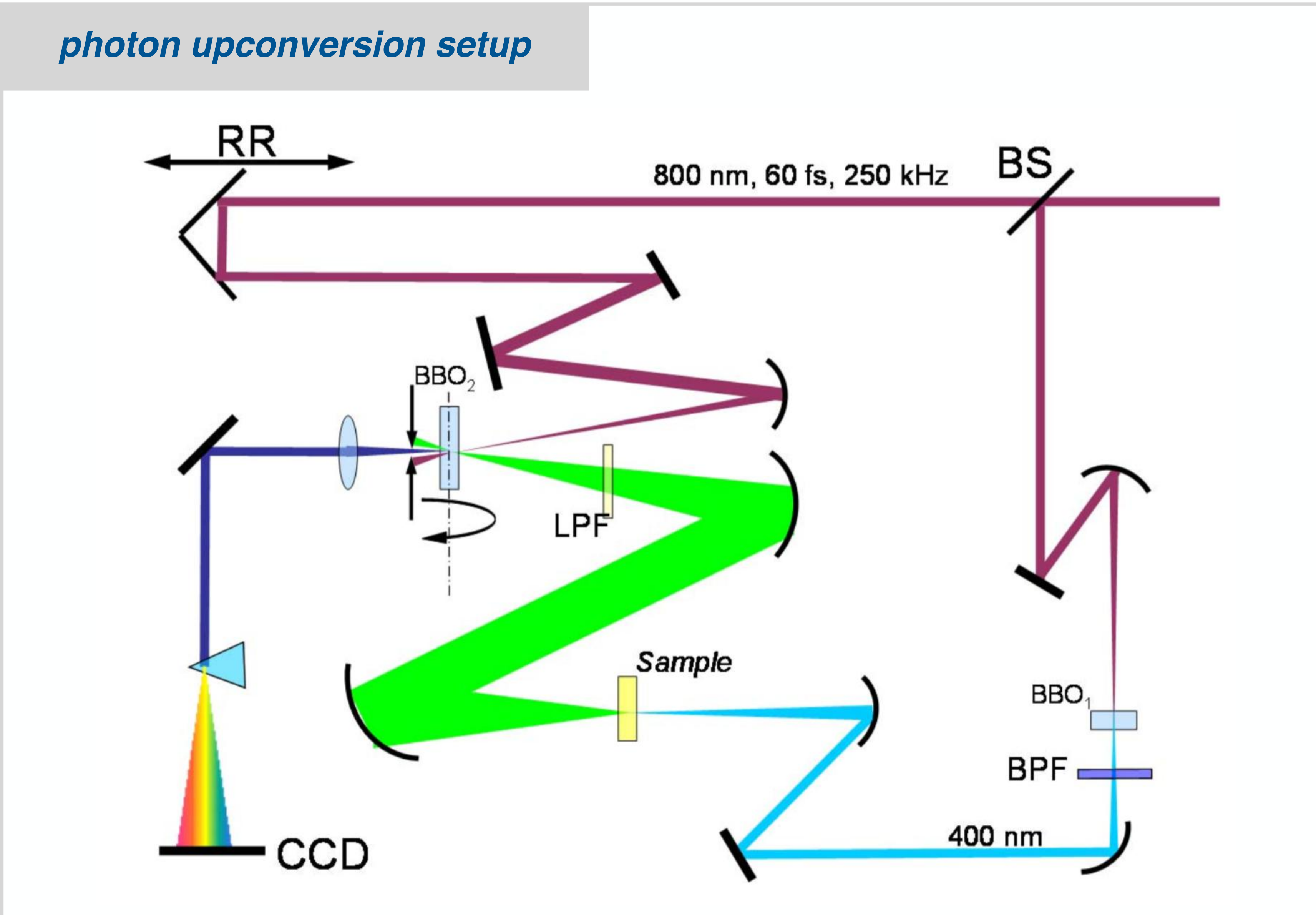


photophysical model



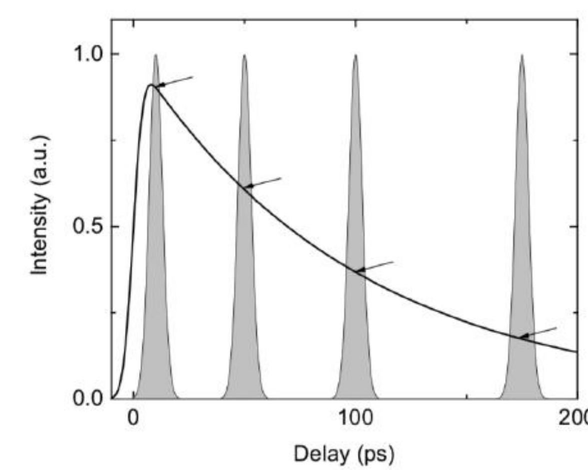
- *time resolution of detector technology does not permit this approach to measuring fast dynamics*
- *two solutions are often implemented: an optical Kerr shutter, and* ***photon upconversion***

Experimental Setup for Time Resolved Fluorescence via Upconversion



gate pulse + ***fluorescence***

must overlap



gate pulse takes slices

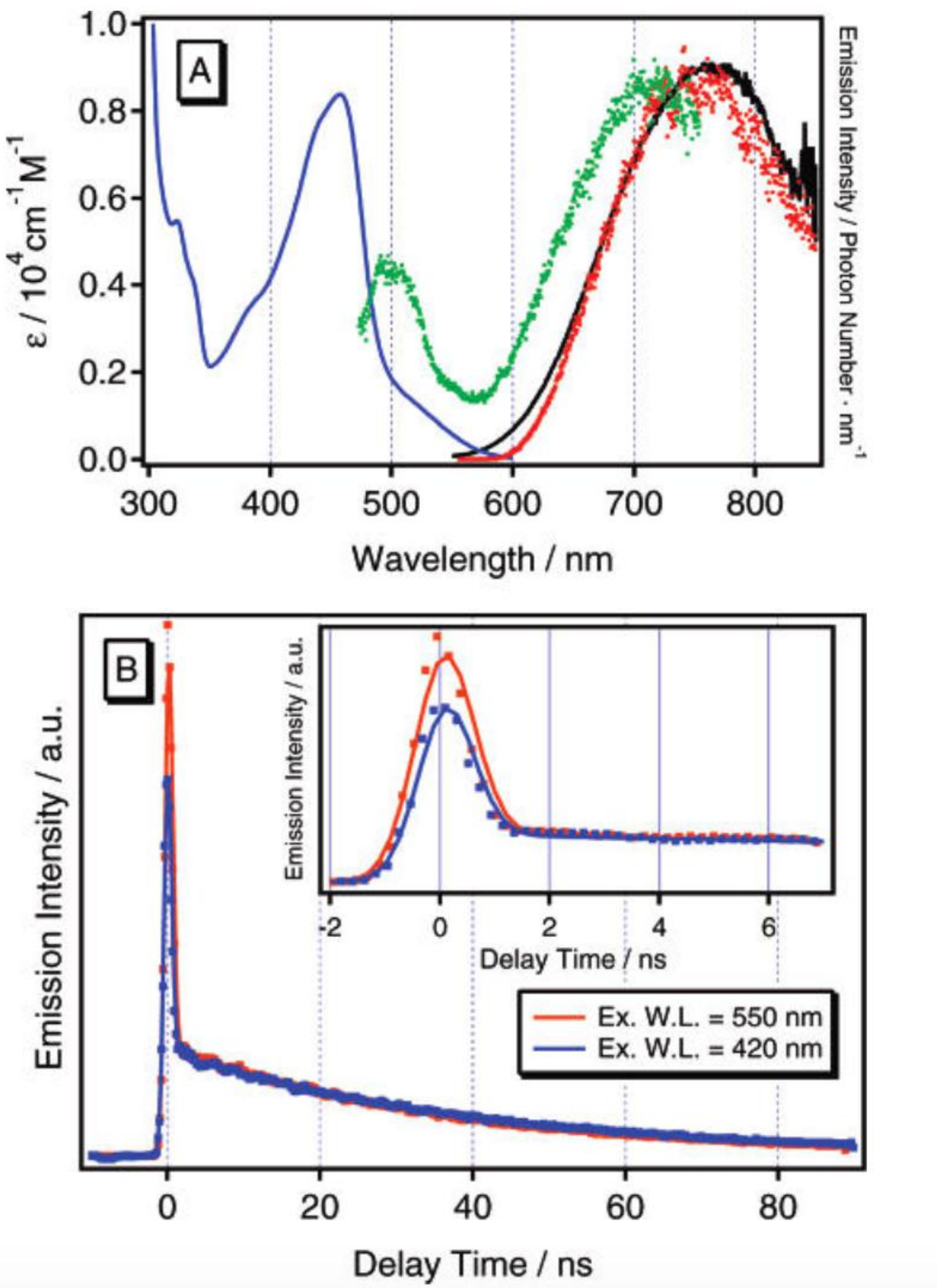
out of ***fluorescence*** signal

$$I_{upconv}(t) \sim I_{gate}(t) \times I_{fluorescence}(t)$$

$$\frac{1}{\lambda_{recorded}} = \frac{1}{\lambda_{fluorescence}} + \frac{1}{\lambda_{gate}}$$

website of Mikas Vengris http://web.vu.lt/ff/m.vengris/

Steady-State and Time-Resolved Emission Spectra of $Cu^{I}(dmphen)_2PF_6$

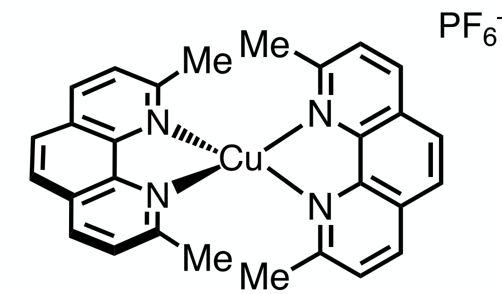


● ***steady-state absorption***

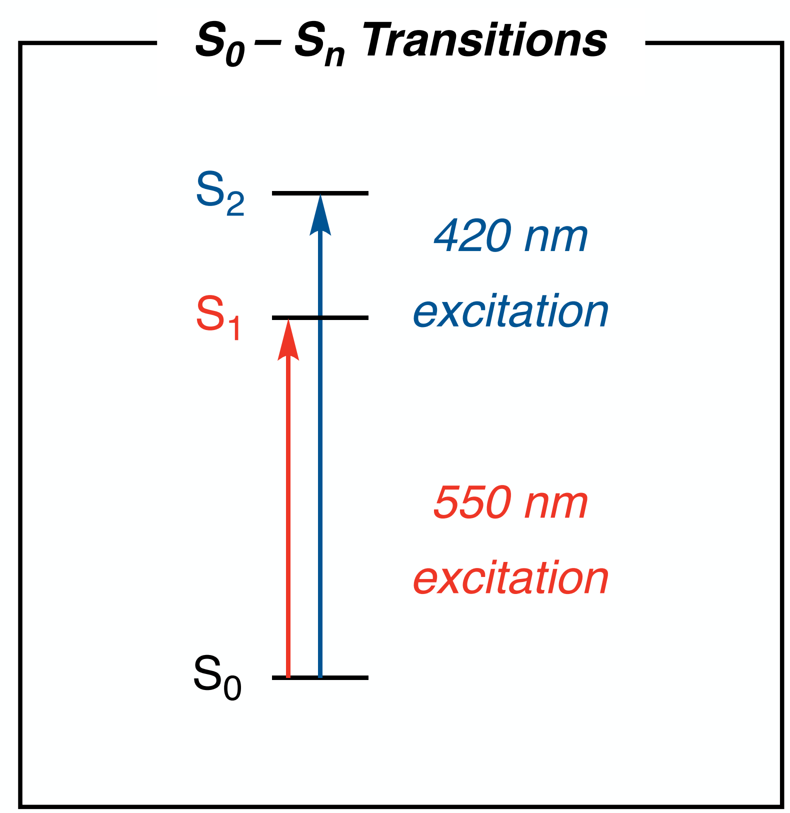
● ***sub 50 fs fluorescence***

● ***sub 100 ns fluorescence***

● ***steady-state fluorescence***



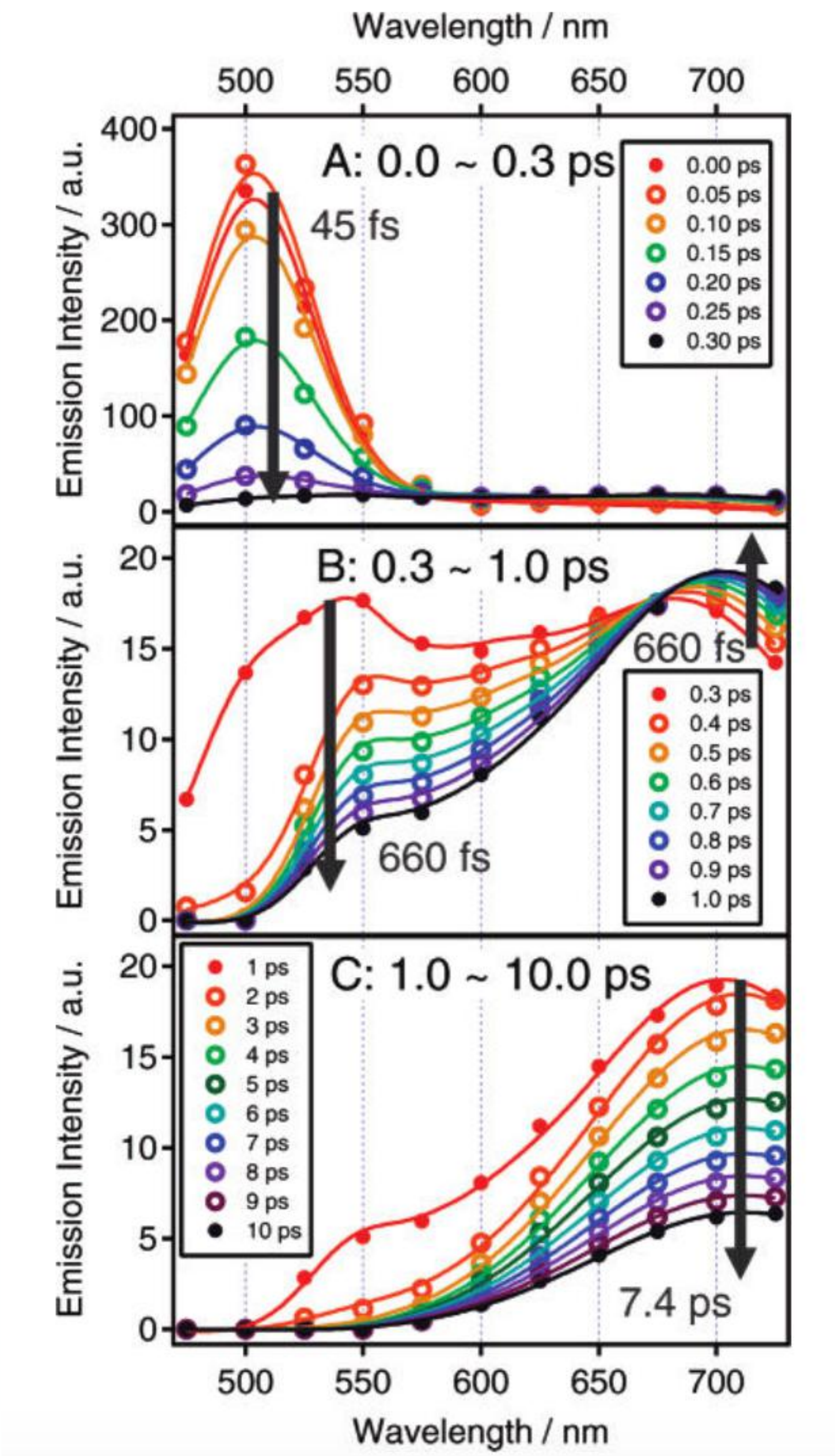
$Cu^{I}(dmphen)_2PF_6$



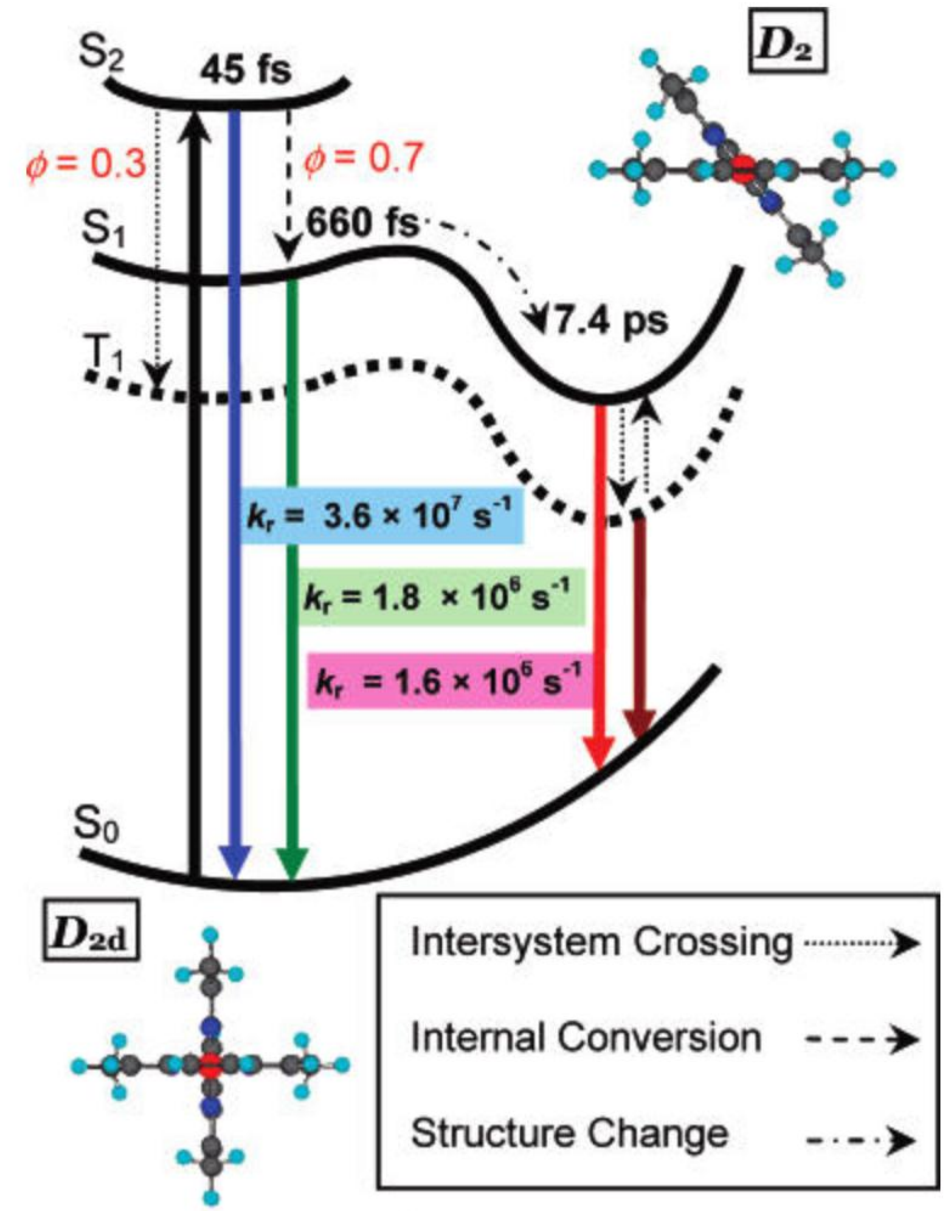
■ ***lower*** *oscillator strength at* ***550 nm****, but higher fluorescence intensity:* ***branching kinetics?***

Iwamura, M.; Takeuchi, S.; Tahara, T. *J. Am. Chem. Soc.* **2007**, *129*, 5248–5256.

Excited-State Dynamics of $Cu^I(dmphen)_2PF_6$ by Fluorescence Upconversion



fitting



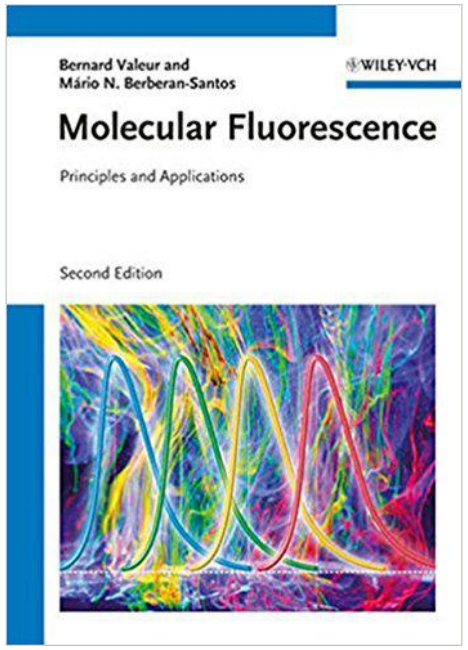
- ***branching*** *model fits fluorescence decay kinetics and reveals long-lived* ***flattened S_1*** *state*

Iwamura, M.; Takeuchi, S.; Tahara, T. *J. Am. Chem. Soc.* **2007**, *129*, 5248–5256.

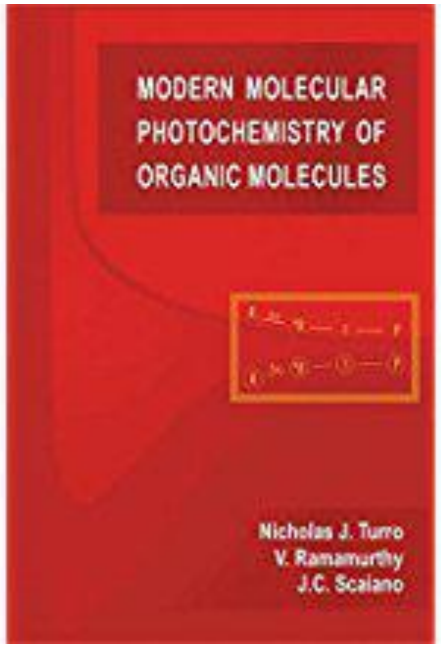
Useful References and Reviews on Ultrafast Measurements

- more on $Cu^{I}(phen)_2$ excited-state rearrangements: *Acc. Chem. Res.* **2015**, *48*, 782–791.
- good primer on TEAS, and time-resolved fluorescence spectroscopies: http://web.vu.lt/ff/m.vengris/
- review on fitting data from ultrafast measurements:
  Biochimica et Biophysica Acta (BBA) - Bioenergetics **2004**, *1657*, 82–104.

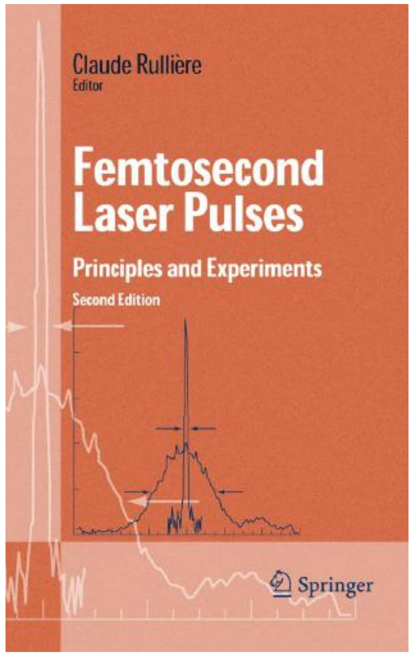
textbooks



tripletes and fluorescence



everything photophysics



ultrafast laser pulses