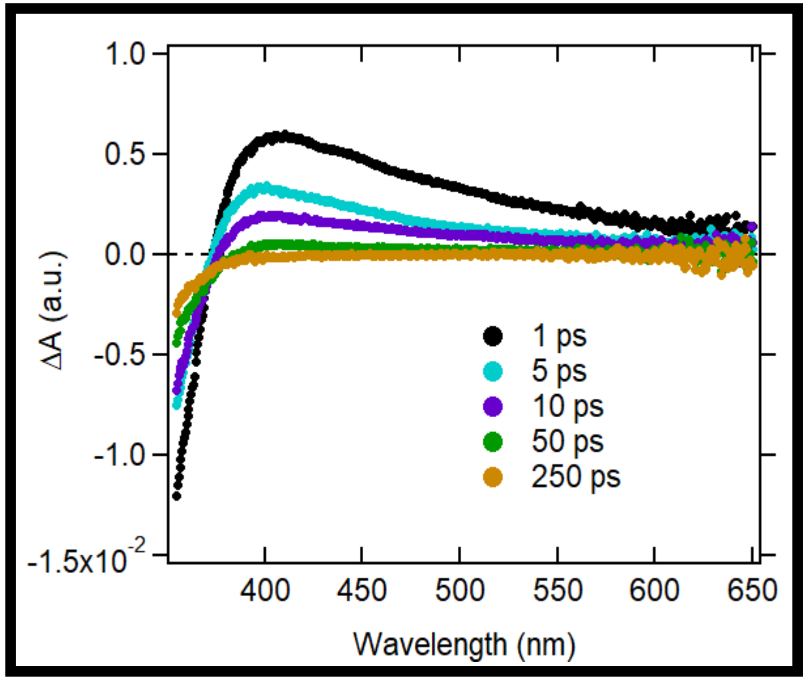
Research in the Kudisch Lab: Introduction to photochemical and photophysical dynamics and kinetics



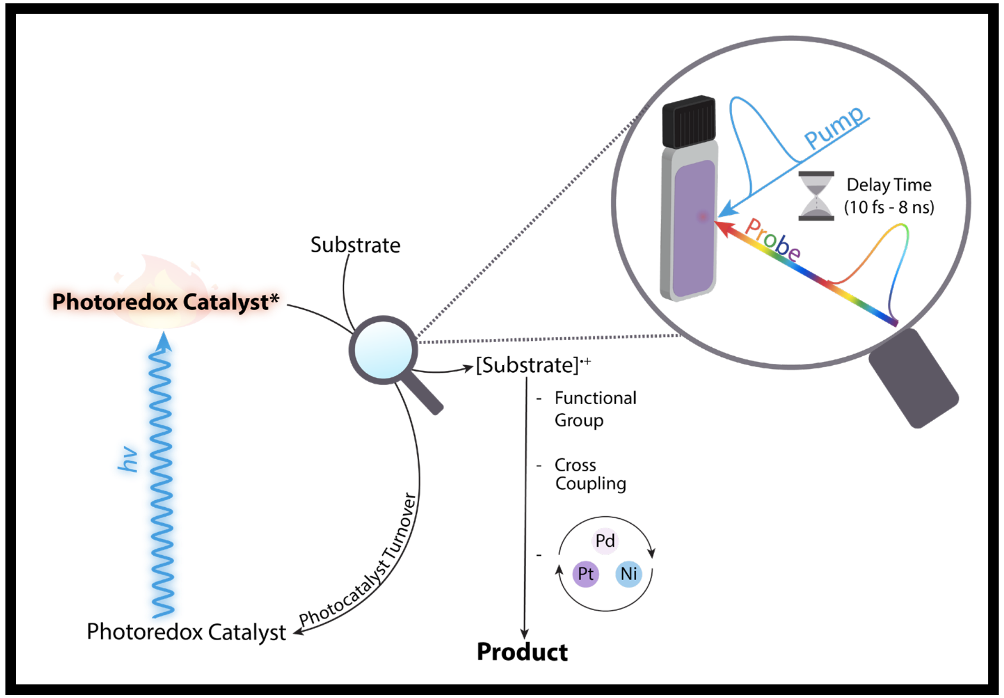
Bryan Kudisch

Assistant Professor

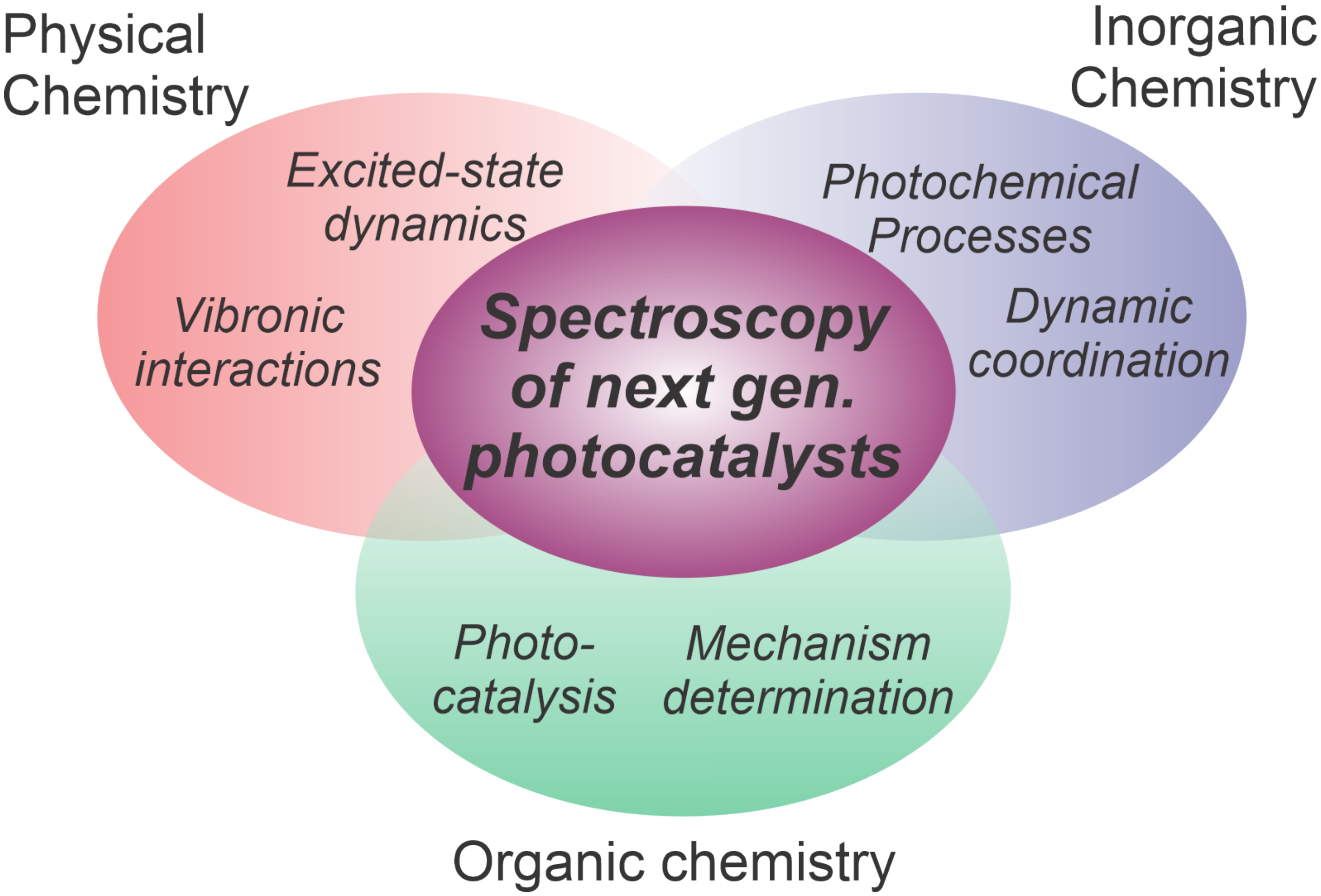
Department of Chemistry & Biochemistry

Florida State University

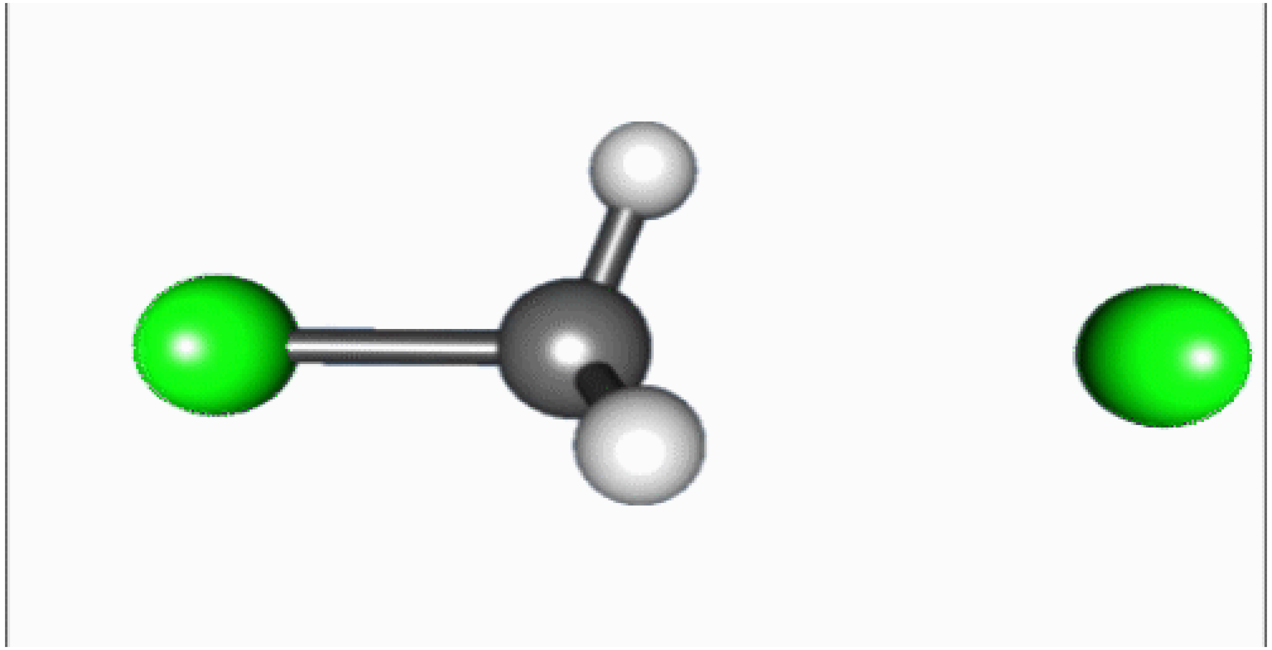
Photochemistry Café, July 16th, 2024



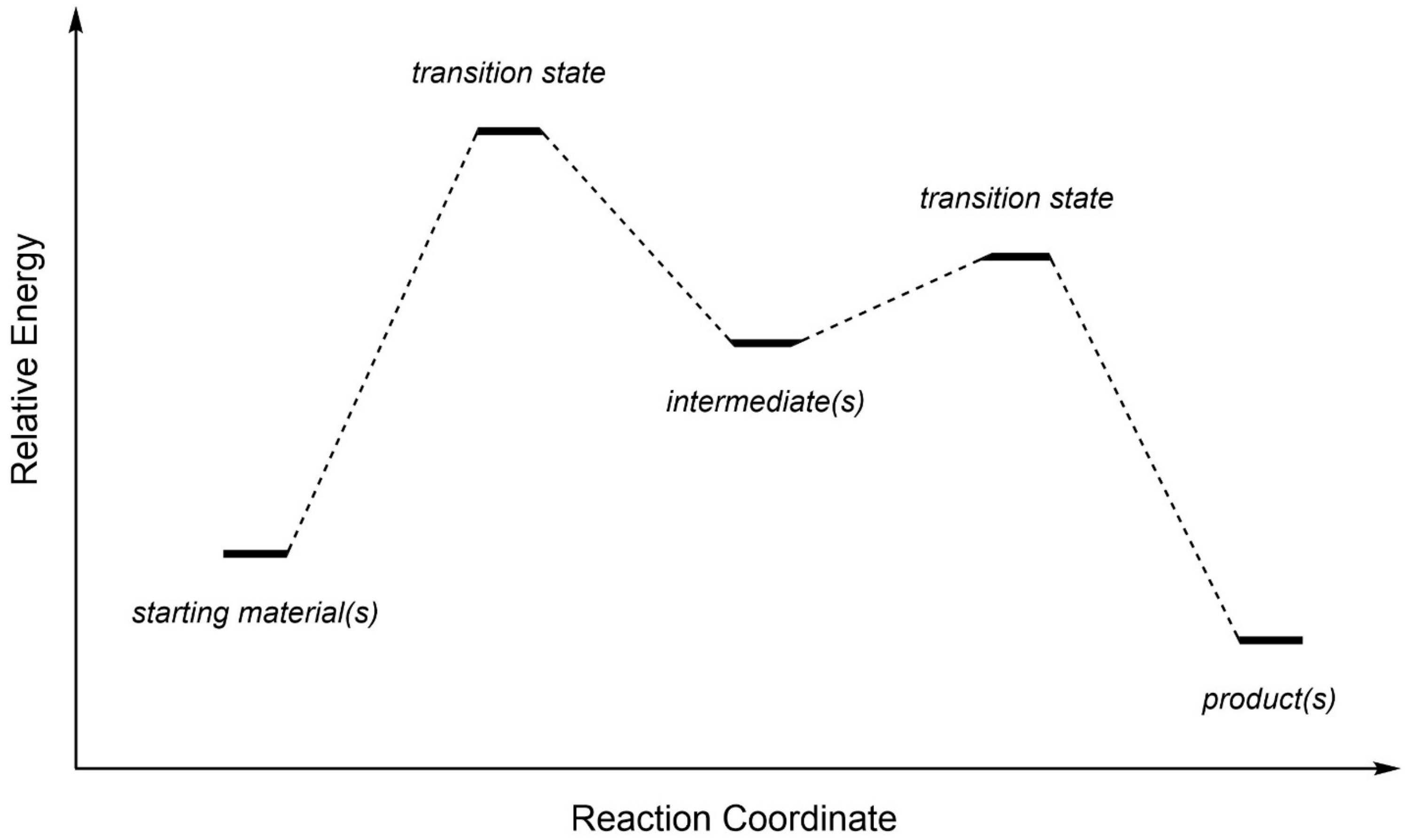
At the intersection of physical, organic, and inorganic chemistry



How do you think about chemical reactions *as they are happening?*



Relevant vocabulary in chemical dynamics



Reaction coordinate

- An abstract one-dimensional coordinate that represents progress along a reaction pathway
  - A roadmap of relevant transition states, intermediates, and their energies

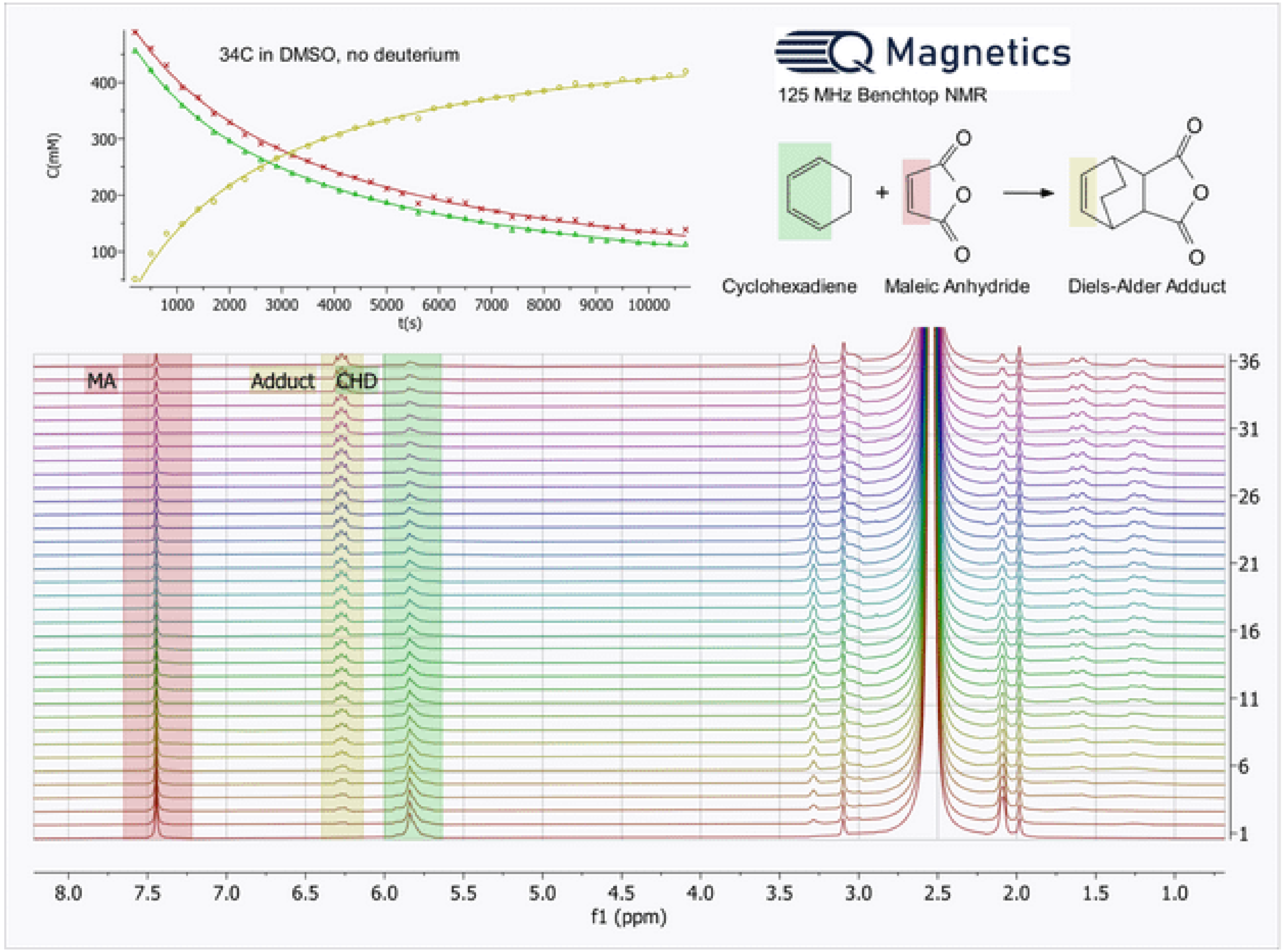
Transition state

- The lowest energy configuration needed to convert between two species
  - On a lineararized reaction coordinate, the highest energy configuration between two species

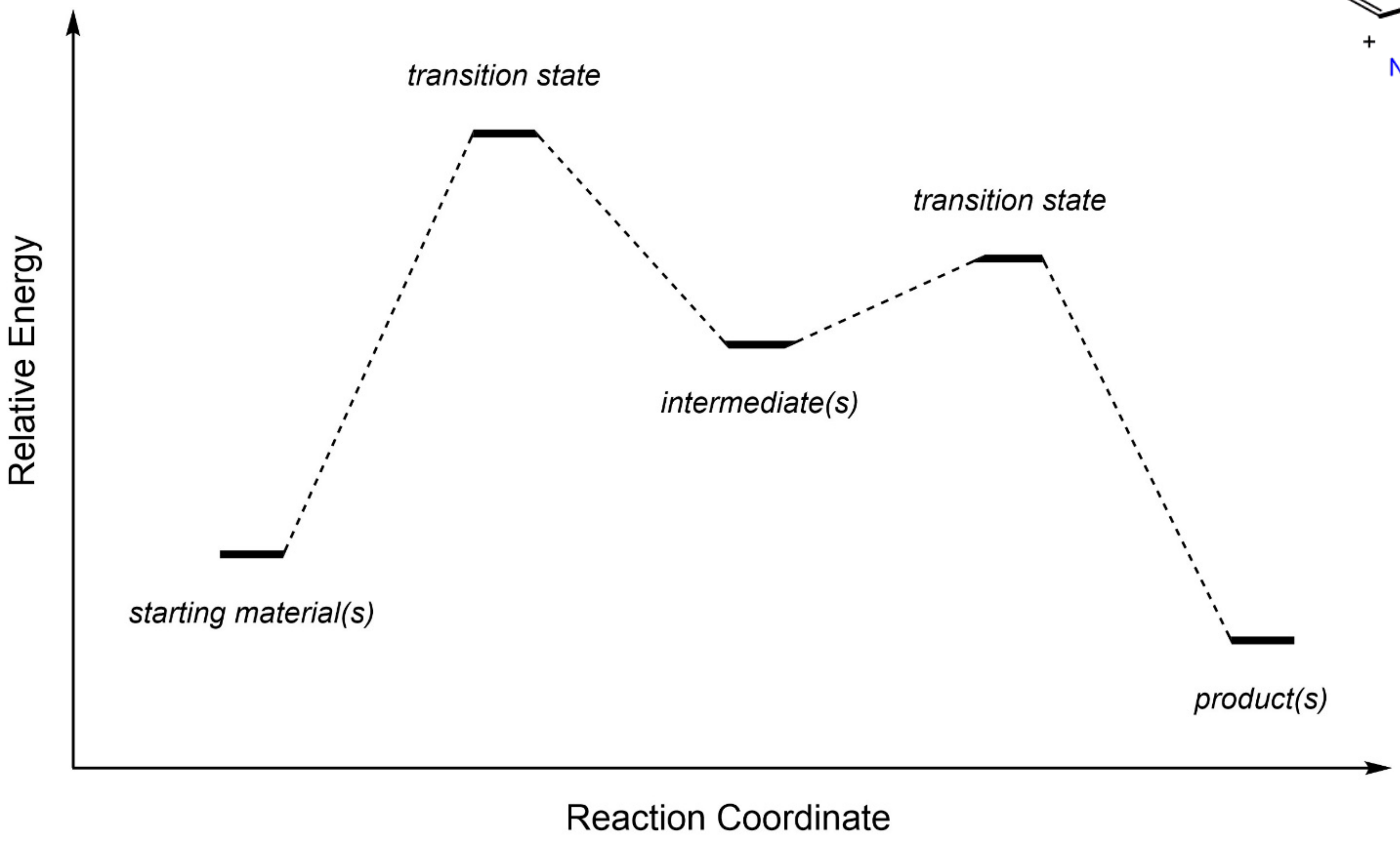
Intermediate

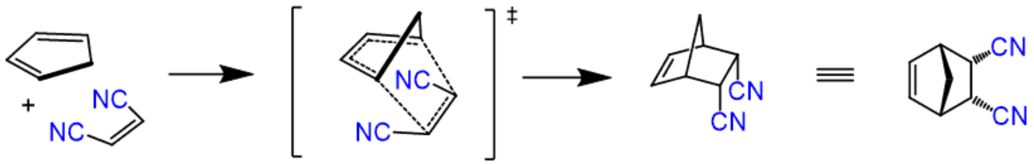
- A relatively high-energy species that exists as a local minimum on a reaction coordinate

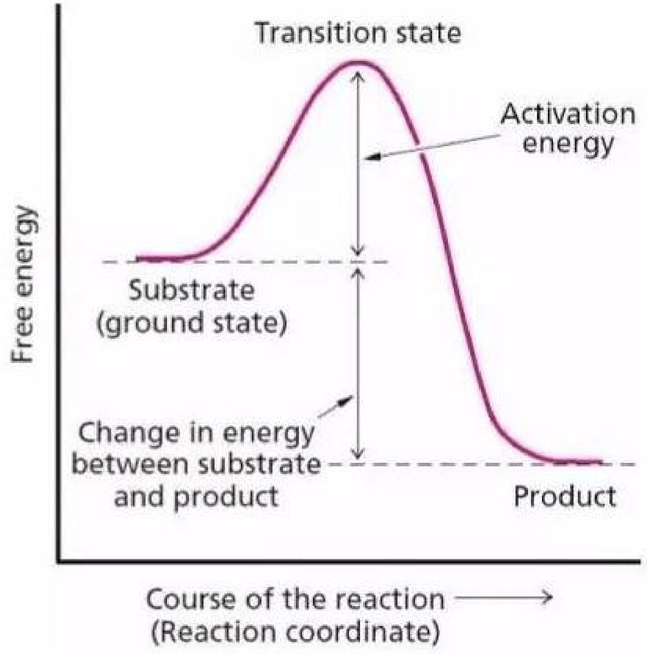
Great, awesome, cool—now show me a reaction *happening*



What about all of that fun stuff in between?

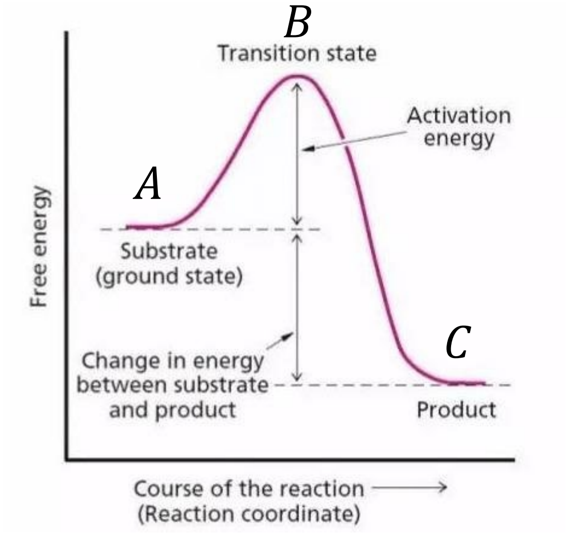






Transition states live for ~10 fs, or 10^{-14} s

The inverted kinetics problem



$$A \xrightarrow{k_{AB}} B \xrightarrow{k_{BC}} C$$

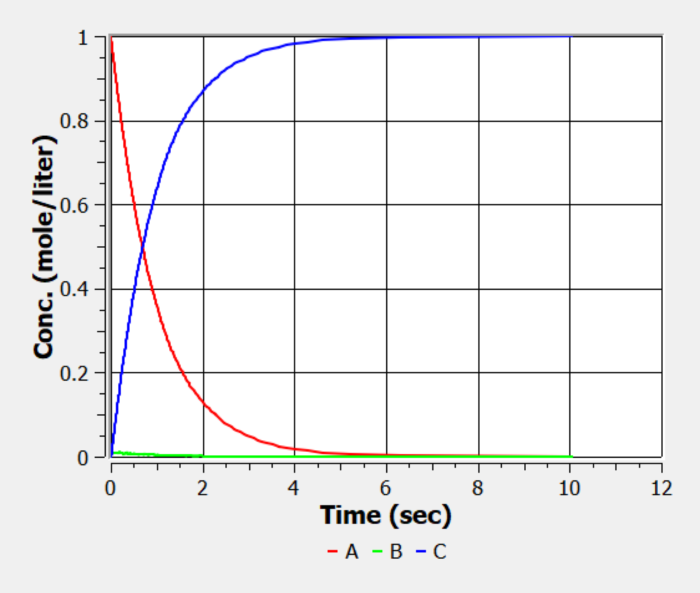
$$dA/dt = -k_{AB}[A]$$
$$dB/dt = k_{AB}[A] - k_{BC}[B]$$
$$dC/dt = k_{BC}[B]$$

In the “transition state” situation, this corresponds to

$$k_{BC} \gg k_{AB}$$

A simulation with fake numbers, this is with $k_{BC} = 100k_{AB}$

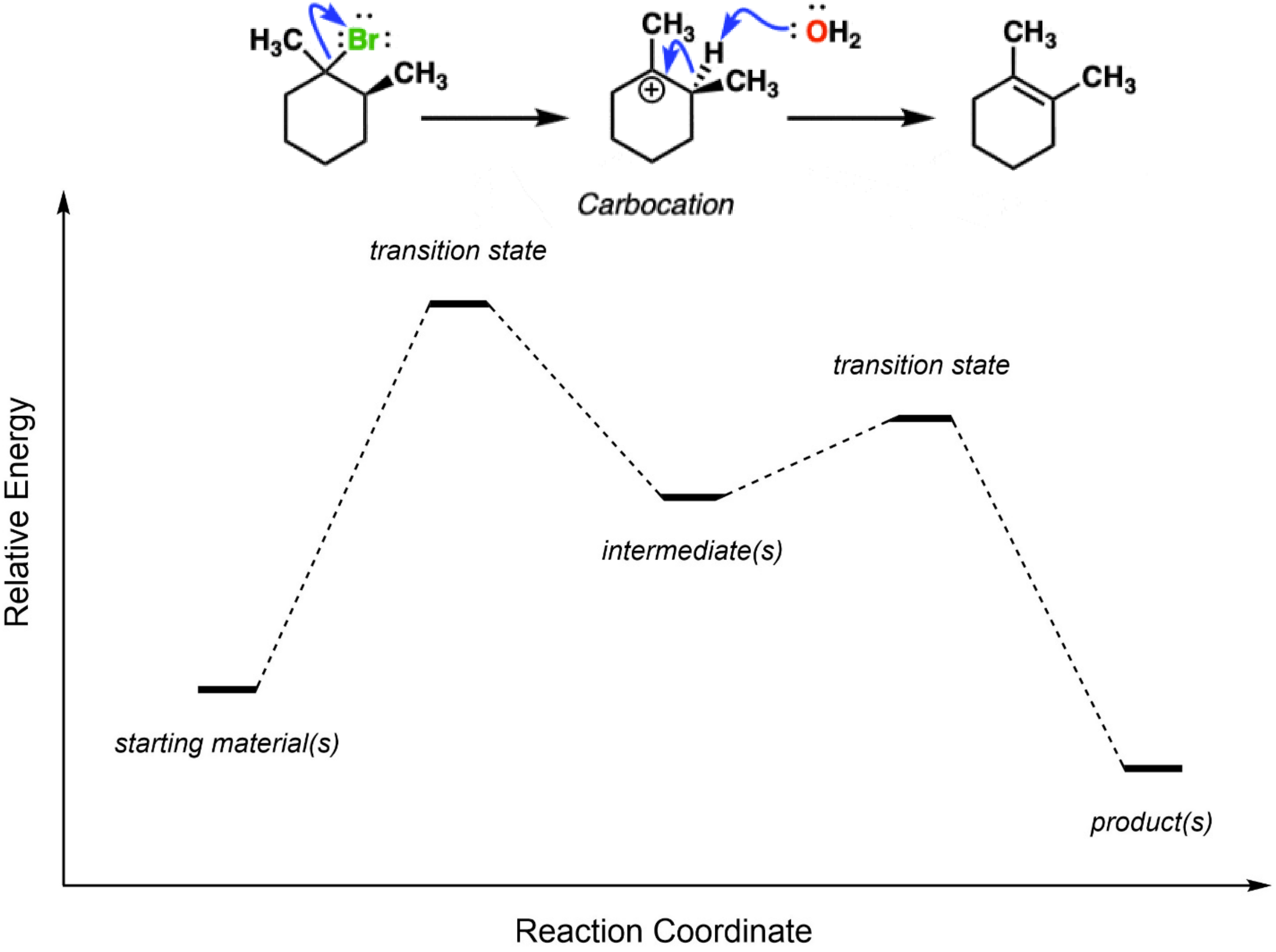
KINETISCOPE
a stochastic kinetics simulator



You never see a significant “buildup” of B, if it’s being consumed faster than it’s being formed.

→**Inverted kinetics**

A pervasive (but more addressable) problem for intermediates



$$k_{A \to INT} = A' exp(-\frac{\Delta G'^{\ddagger}}{k_B T})$$

$$k_{INT \to B} = A'' exp(-\frac{\Delta G''^{\ddagger}}{k_B T})$$

So, what about for the diagram on the left?

It would still have inverted kinetics, since the free energy barrier for the second step is smaller than the first

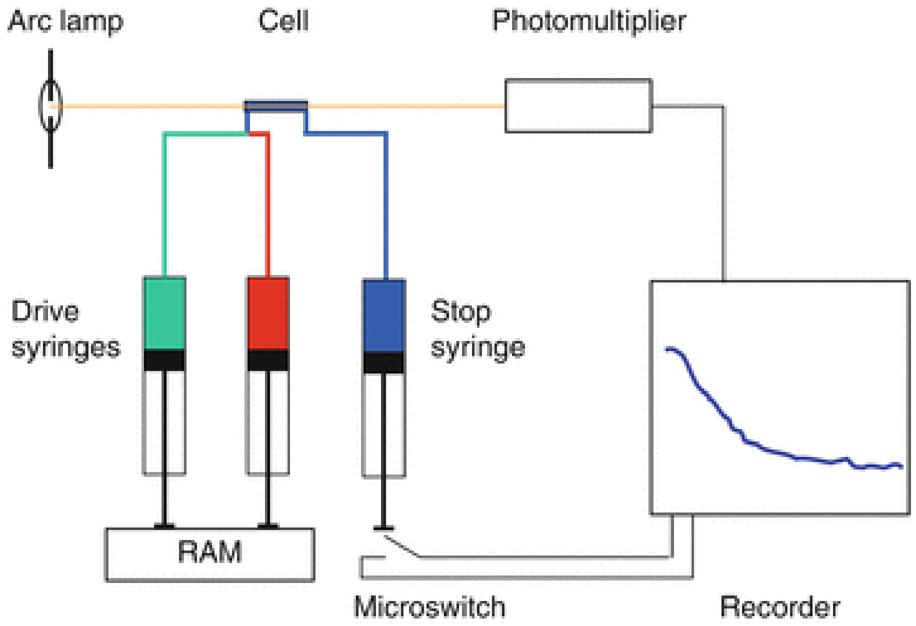
- At least, though, this gives hope that some reactions do have intermediates that “build up” and thus have reactions you can see

Experimental tricks to see reaction intermediates/elementary steps

$$A + B \rightarrow I \rightarrow C$$

If we can mix A and B faster than they form I or C, then we track the reaction kinetics

Stopped-flow apparatus



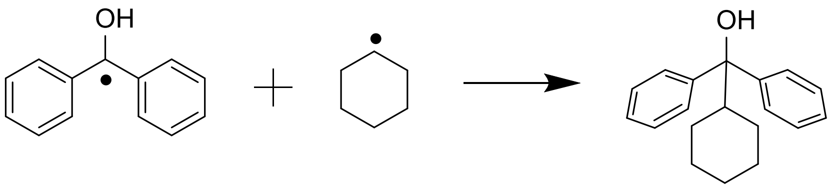
Requirements:

- Reaction needs to be initiated by mixing
  - Many reactions fall under this category, **most bimolecular** reactions, pH jump experiments, etc.
- Reactants/intermediates/products need to have **distinct spectroscopic signatures** that can be read out “fast”
  - UV-Vis, fluorescence, IR spectra

Limitations:

- Reaction has to be **slower than the time it takes to mix**, typically ∼40 ms
  - Lots, lots of reactions take place on timescales shorter than this

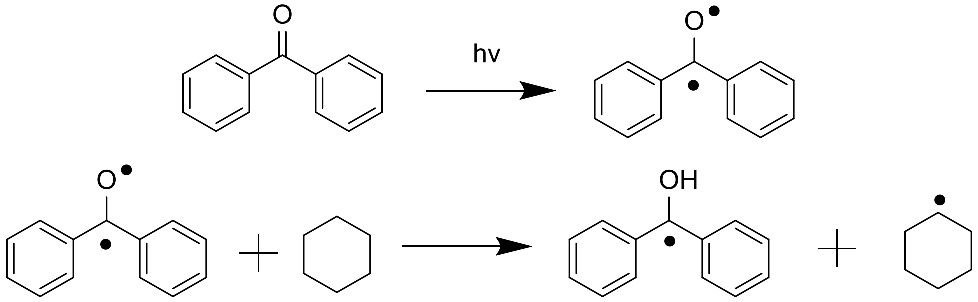
Chemical kinetics on faster timescales: nanosecond flash photolysis



Let’s say I want to know the rate of this reaction.

- Expect it to be fast, since it’s a radical reaction
- So, we have to **make the reactants** faster than two radicals couple together!

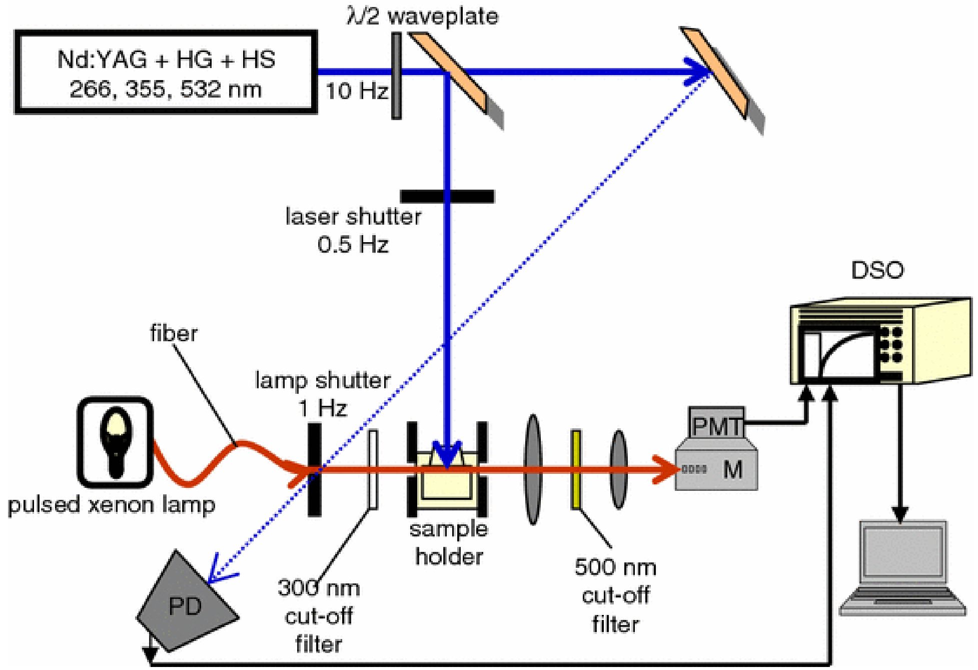
The trick is to use **a pulse of light** that rapidly generates the reactants



As long as these two steps are faster than the one of interest, this is kinetically possibly

Requirements:

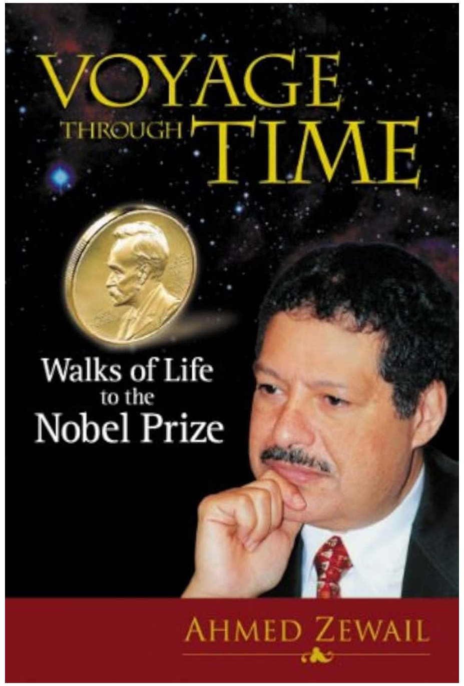
- Pulsed laser source (~5 ns pulses are typical)
  - Can generate up to mM concentrations of excited-states
- Fast detection electronics
  - Typically 10s of nanosecond (10^{-9} s)
- Detectable intermediates/products



Pushing the limits: femtosecond and faster chemical dynamics

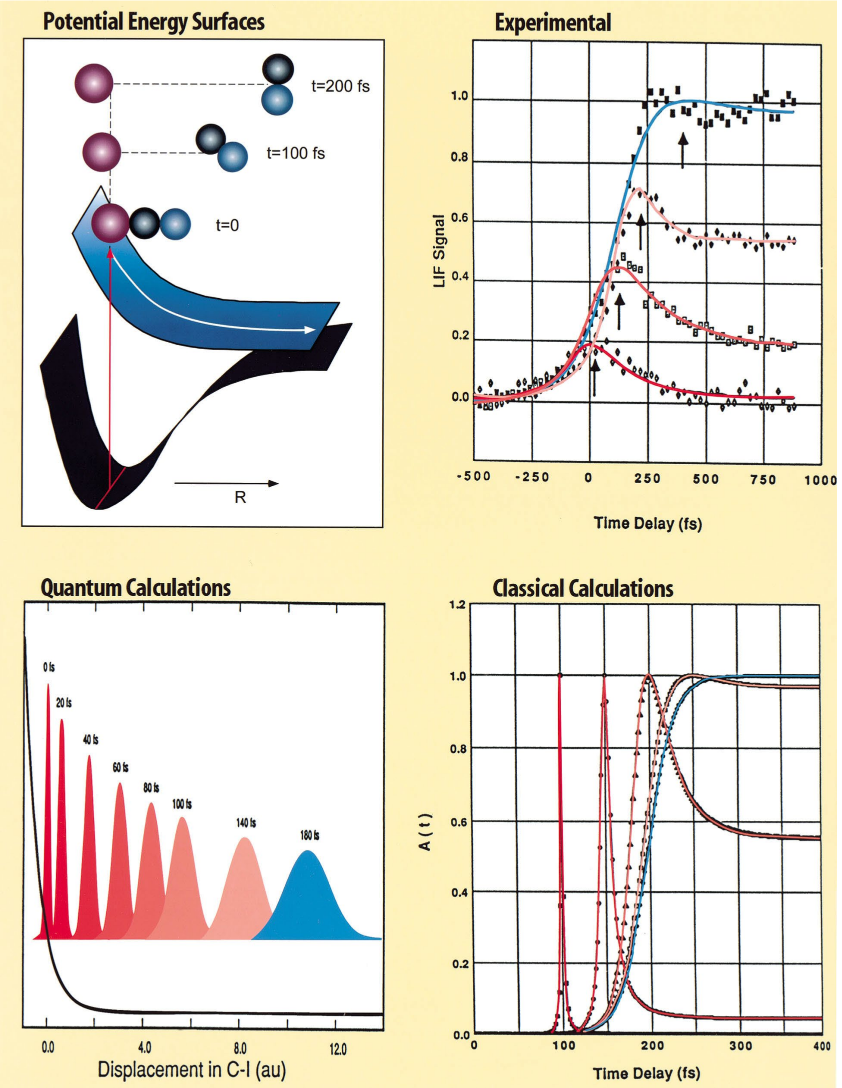
Chemical processes within one molecule and between molecules can take place on extremely fast timescales

- Experimentally, we can push fast enough in time resolution to actually catch the transition state of some classes of reactions

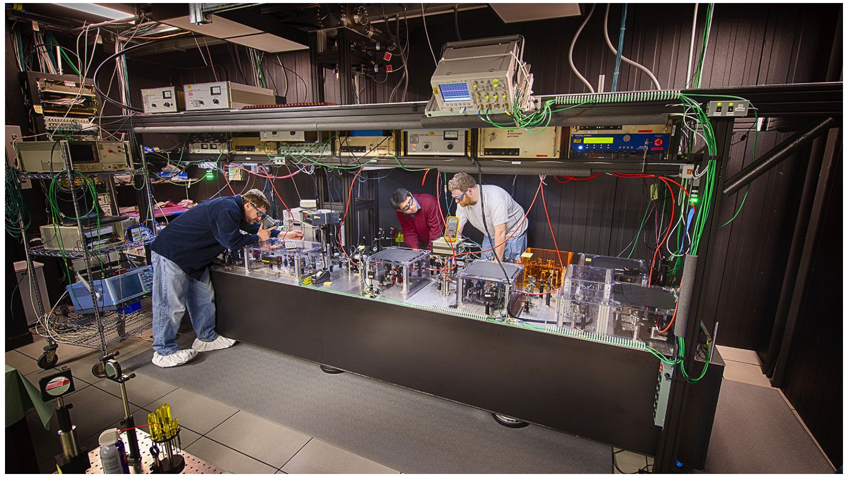


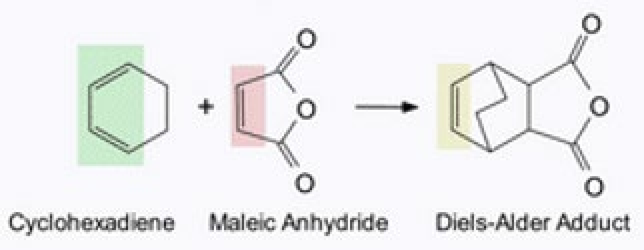
Ahmed Zewail

- Nobel prize in 1999
- "For his studies of the transition states of chemical reactions using femtosecond spectroscopy"



The faster we go, the more “physics-y” you get—can we get back?

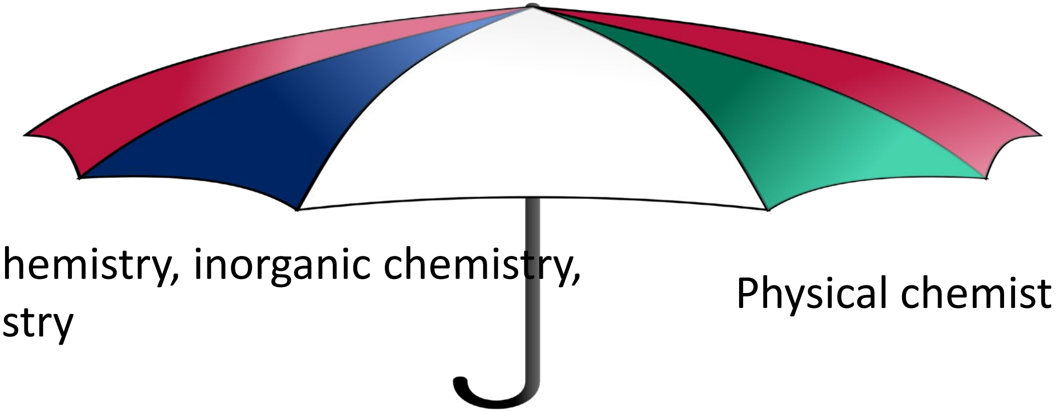




I-CN

Also, the techniques seem to be much more specialized…

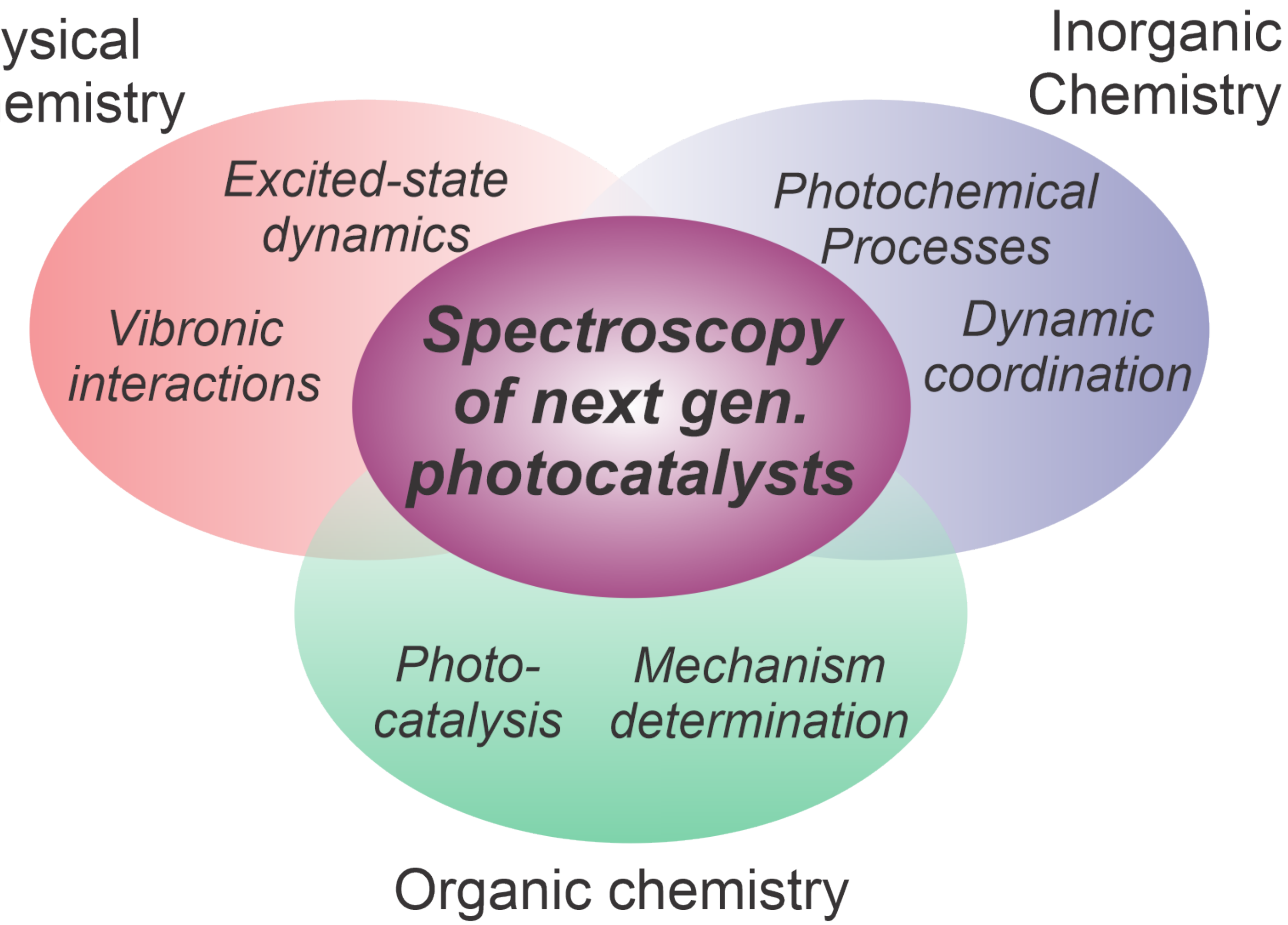
- Pulsed laser sources can cost as much as a Lamborghini
  - Utilizing femtosecond lasers to their fullest potential requires extensive training in linear and nonlinear optics, electronics, and programming



Organic chemistry, inorganic chemistry, biochemistry

Physical chemistry

At the intersection of physical, organic, and inorganic chemistry



Physical Chemistry

Inorganic Chemistry

Excited-state dynamics

Vibronic interactions

Photochemical Processes

Dynamic coordination

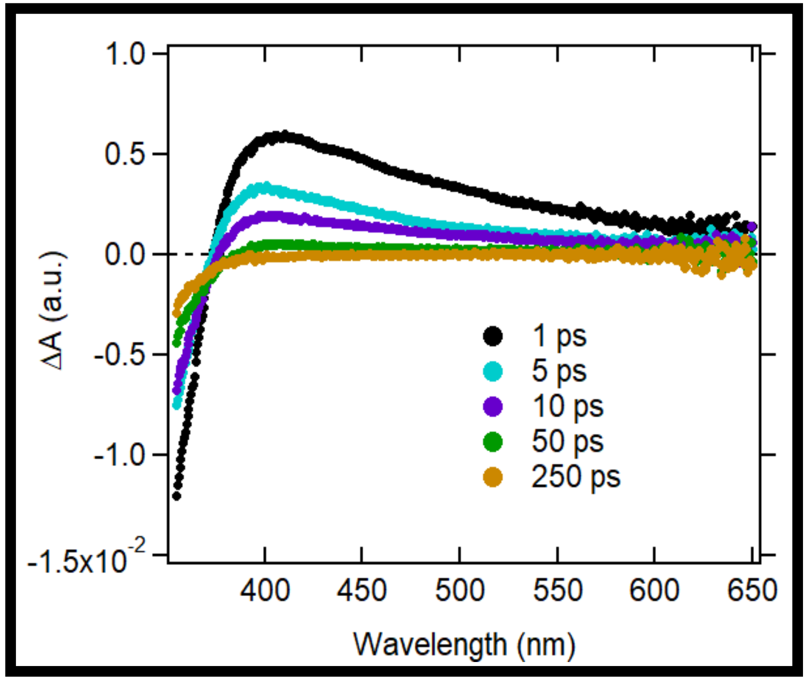
Spectroscopy of next gen. photocatalysts

Photo-catalysis

Mechanism determination

Organic chemistry

Ultrafast Spectroscopy Uncovers the Mechanistic Underpinnings of Next-Generation Photocatalysts



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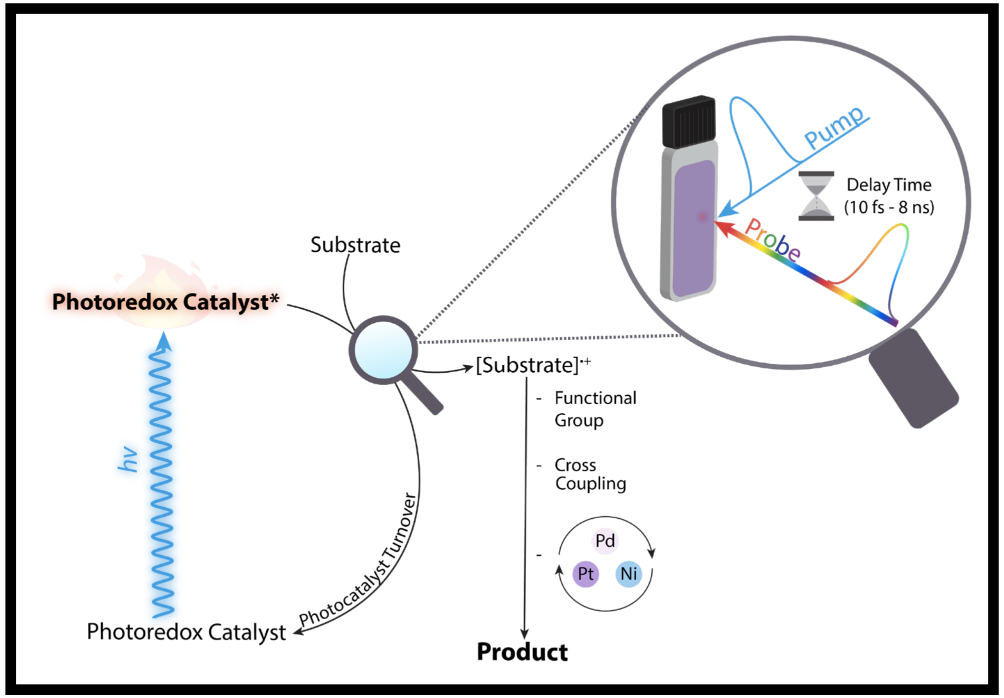
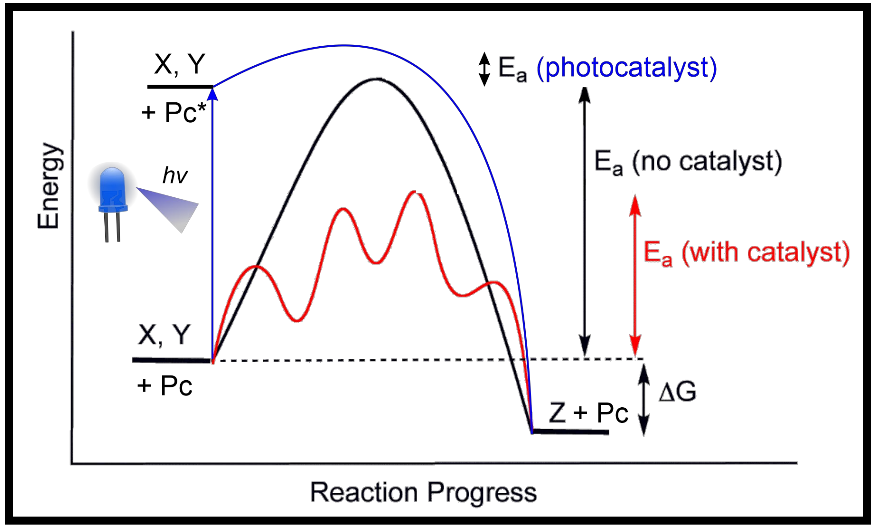
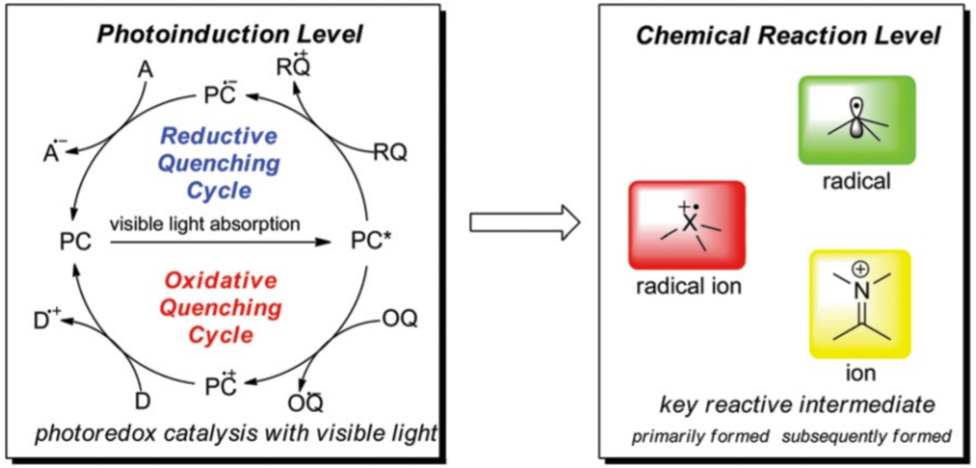
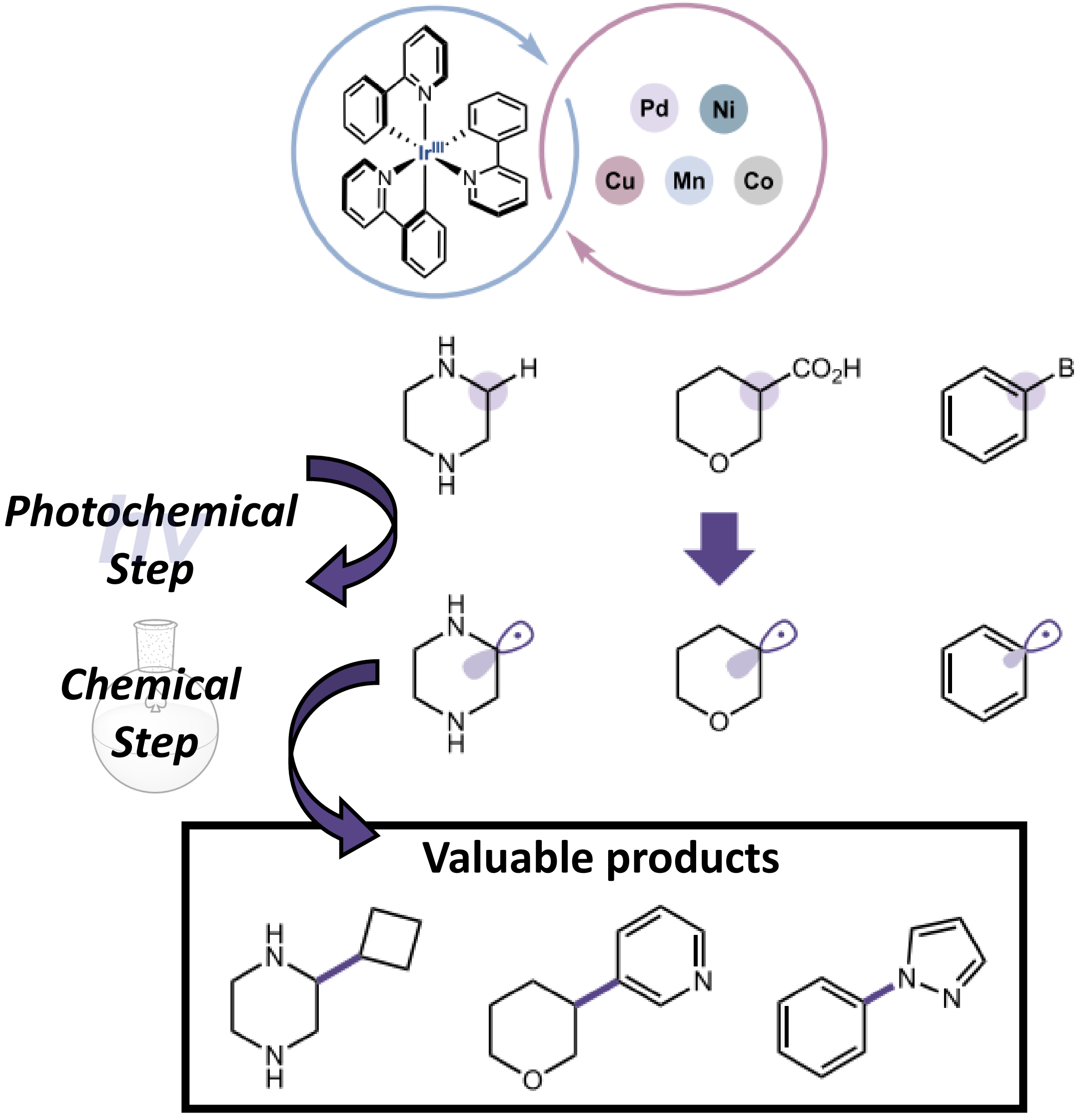


Photoredox catalysis: entryway into modern radical organic chemistry

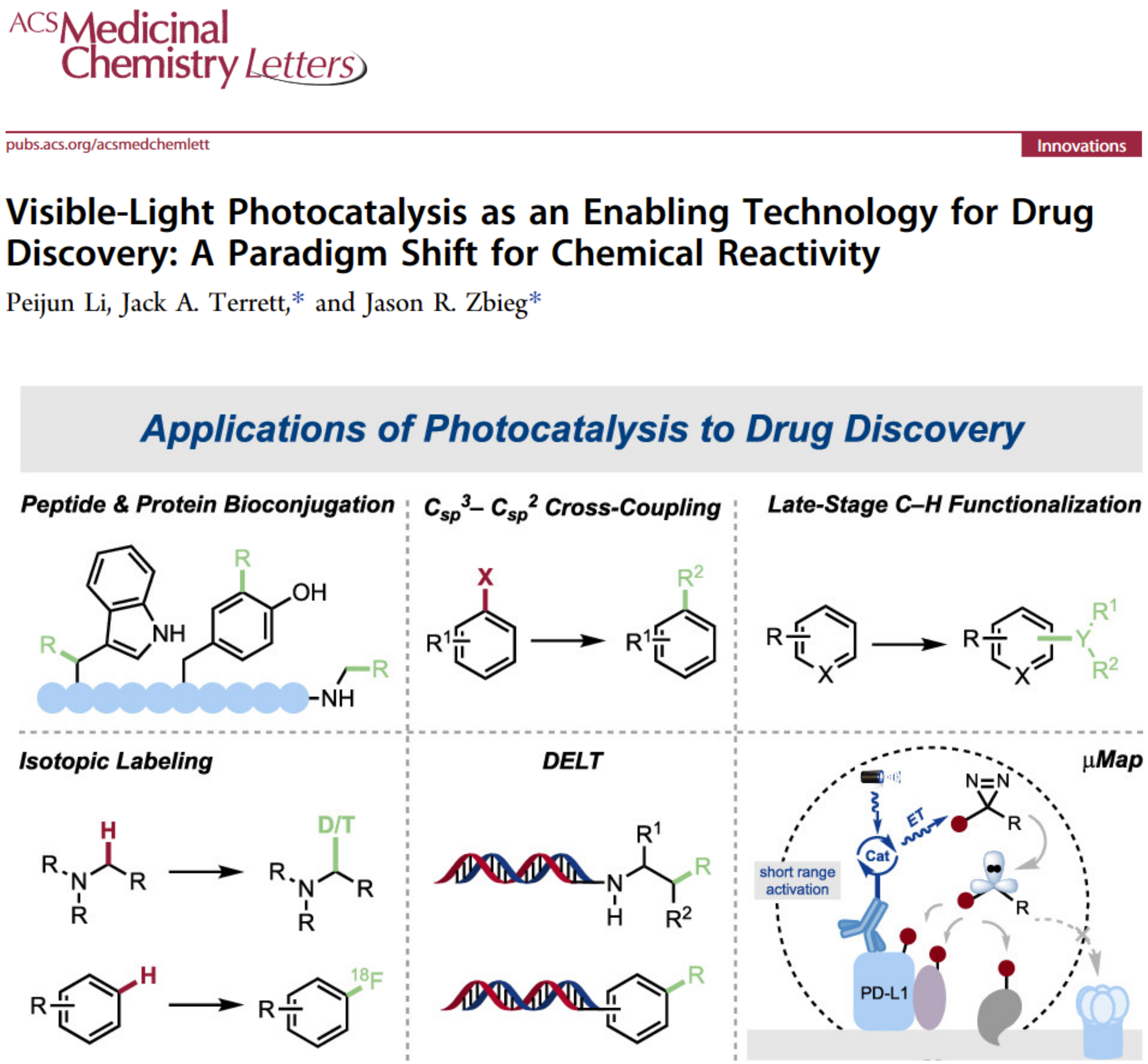




Utilize light to generate high energy, reactive intermediates



Photoredox in medicinal chemistry

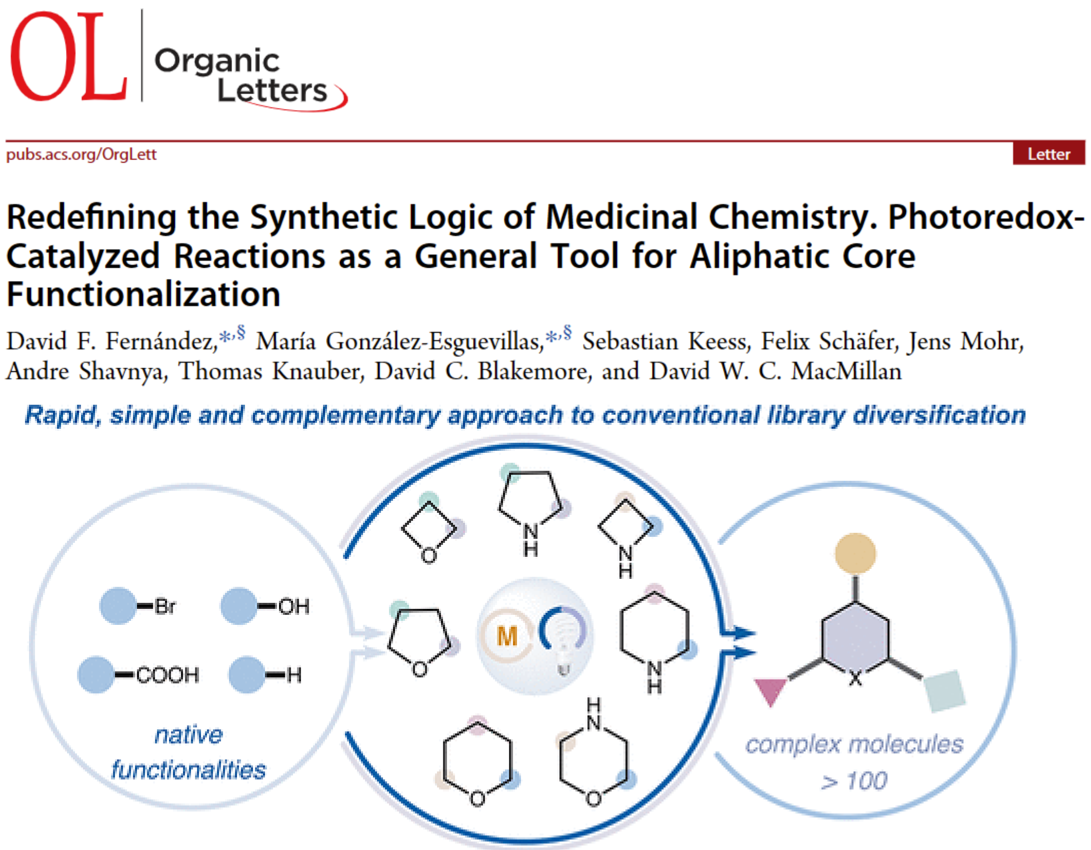


ACS Medicinal Chemistry Letters

pubs.acs.org/acsmedchemlett Innovations

Visible-Light Photocatalysis as an Enabling Technology for Drug Discovery: A Paradigm Shift for Chemical Reactivity

Peijun Li, Jack A. Terrett,* and Jason R. Zbieg*



OL Organic Letters

pubs.acs.org/OrgLett Letter

Redefining the Synthetic Logic of Medicinal Chemistry. Photoredox-Catalyzed Reactions as a General Tool for Aliphatic Core Functionalization

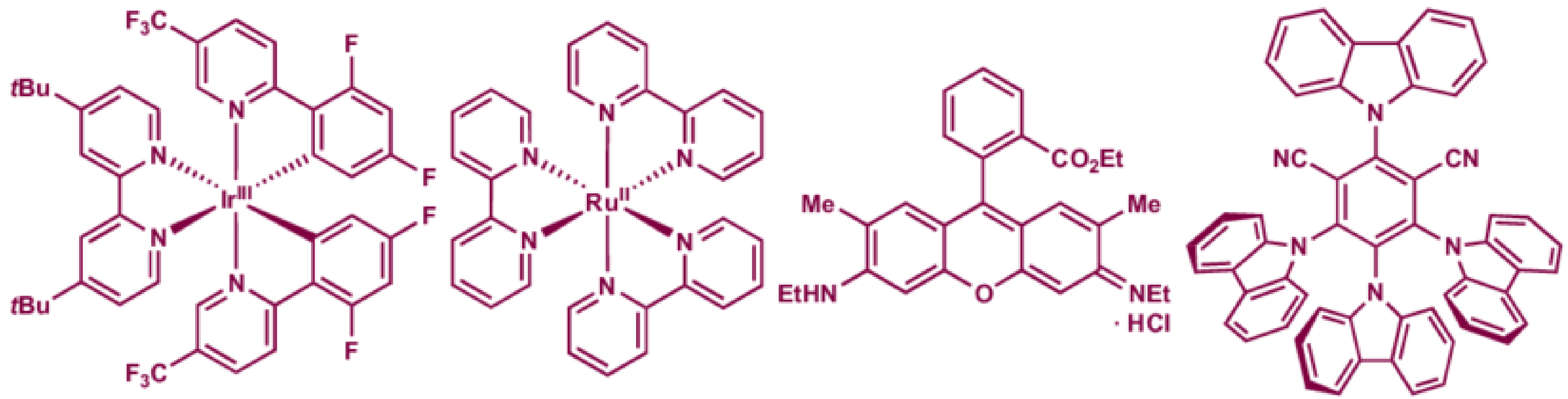
David F. Fernández,*,§ María González-Esguevillas,*,§ Sebastian Keess, Felix Schäfer, Jens Mohr, Andre Shavnya, Thomas Knauber, David C. Blakemore, and David W. C. MacMillan

MERCK Genentech

abbvie Pfizer

The classic, workhorse photoredox catalysts

Visible Light Photoredox Catalysts

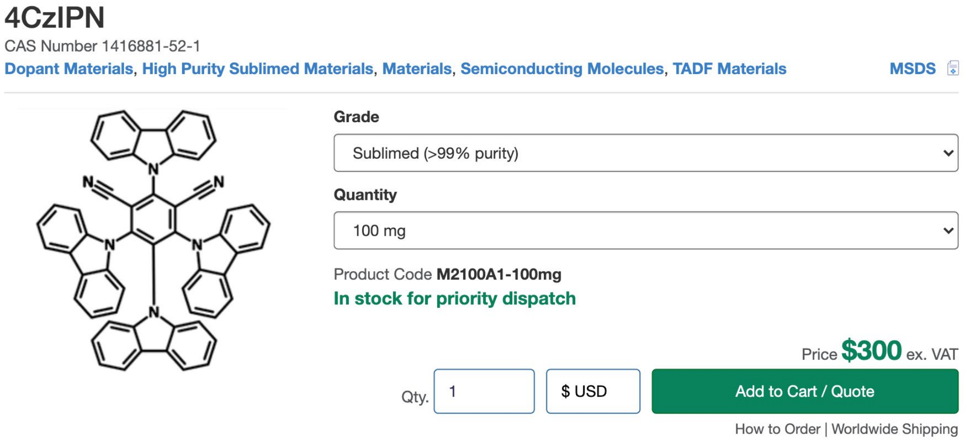


$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]^+$ $[Ru(bpy)_3]^{2+}$ Rhodamine 6G 4CzIPN

1-3 steps to make from commercially available precursors

Air stable

Some incorporate "rare earth" metals like Ir, Ru, and Os



4CzIPN

CAS Number 1416881-52-1

Dopant Materials, High Purity Sublimed Materials, Materials, Semiconducting Molecules, TADF Materials MSDS

Grade: Sublimed (>99% purity)

Quantity: 100 mg

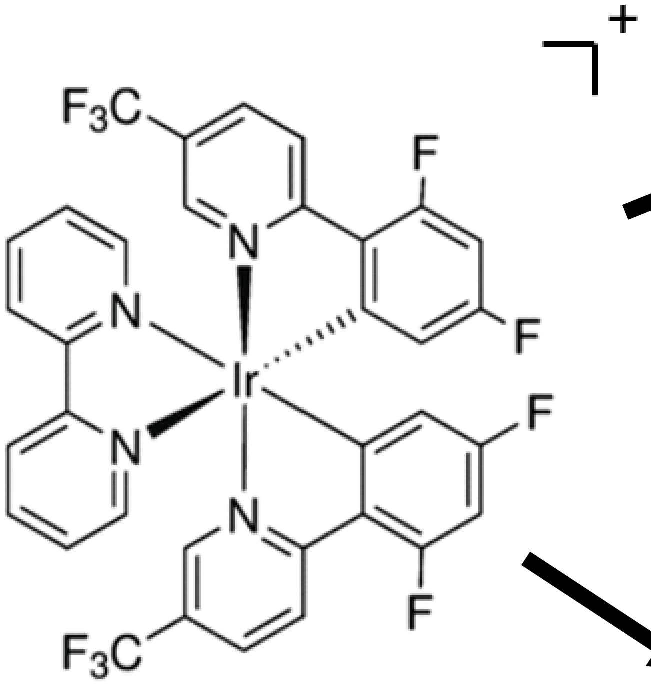
Product Code **M2100A1-100mg**

In stock for priority dispatch

Price $300 ex. VAT

Qty. 1

The underlying inorganic and physical chemistry



MLCT excited state

Highly redox-active/reactive excited-state

Long-lived excited state (>10 ns)

Resistant to decomposition in photochemical conditions

Desirable properties of next-gen photocatalysts

-More reactive

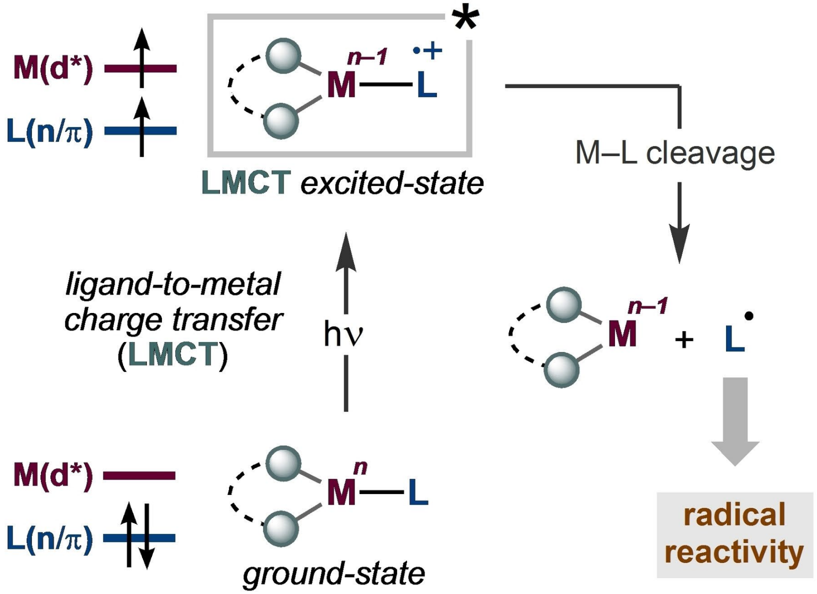
-More selective

-High photonic efficiency

-Improved cost efficiency

-More biocompatible

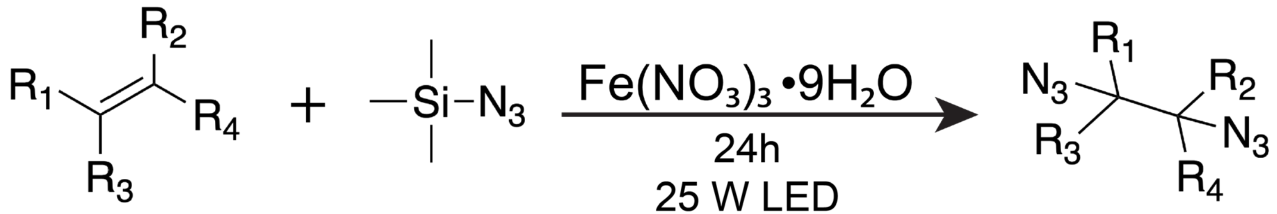
Ligand-to-metal charge transfer (LMCT) photoredox



Juliá, F. *ChemCatChem.* **2022**

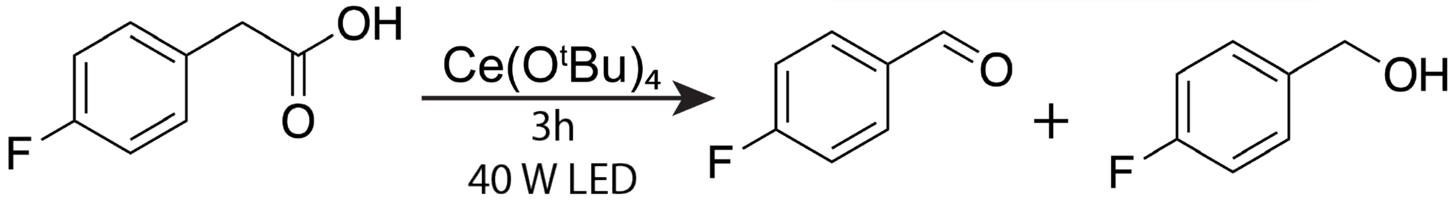
A clear impetus for mechanistic inquiry

Generating ligand radicals through bond rupture is not the predominant decay pathway, so what is?

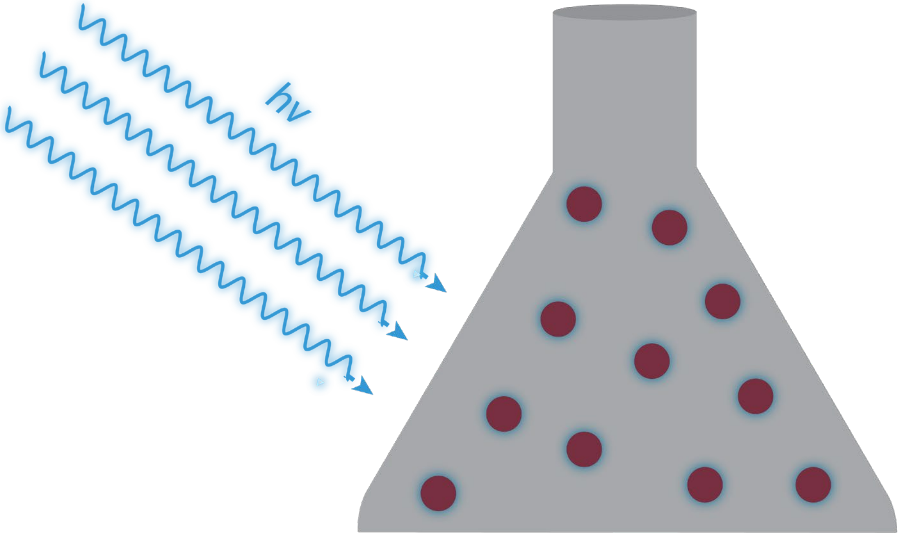


Reaction Yield 86%
Bian, K. *et al. Nat. Commun.* 2022

$QY \approx 10^{-5}$



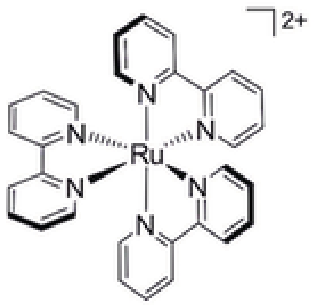
Reaction Yield > 99%
Shirase, S. *et al. J. Am. Chem. Soc.* 2020

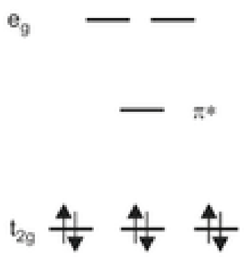


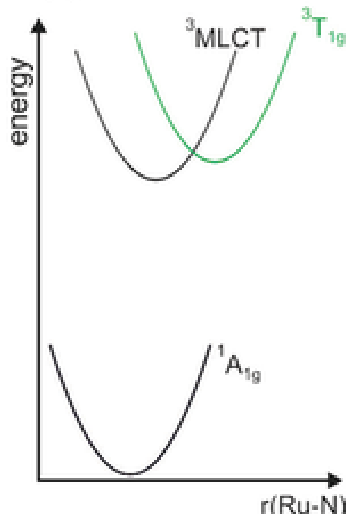
Photochemical Quantum Yield (QY) = Number of Productive Reactions ● / Number of Photons Absorbed ●

$$= \frac{k_{productive}}{k_{productive} + \Sigma k_{nonproductive}}$$

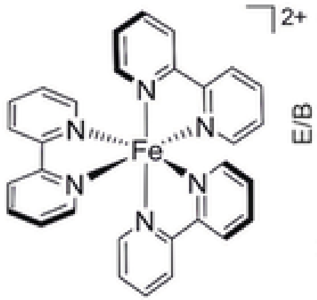
Classically, Fe and other 1st row metals are supposed to be bad photocatalysts!

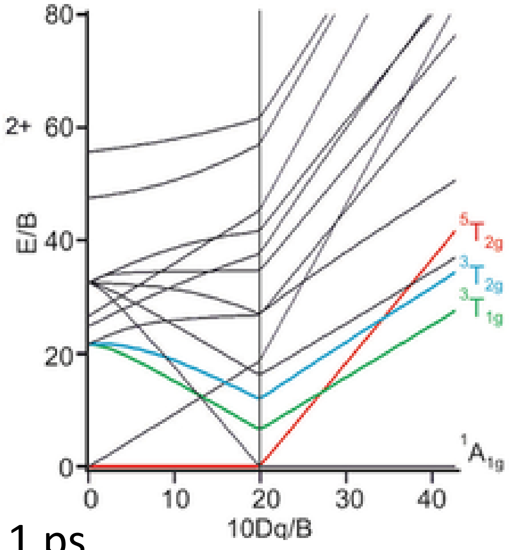


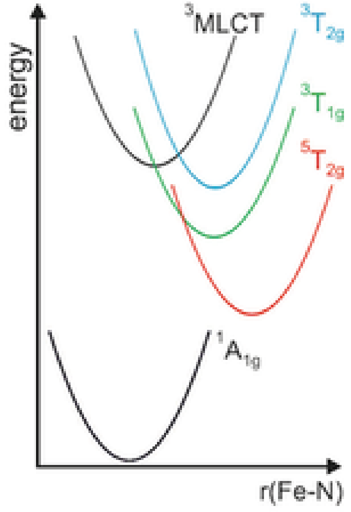




MLCT lifetime: 930 ns

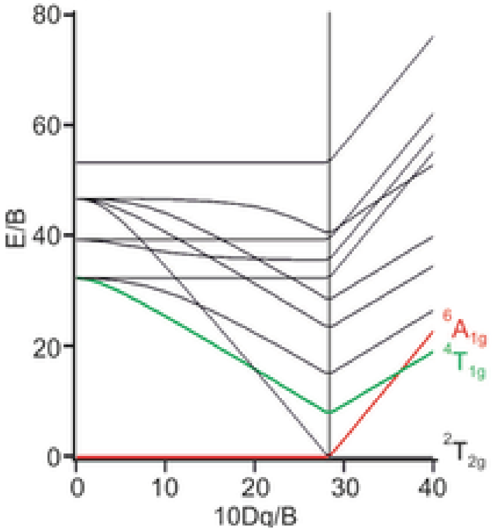


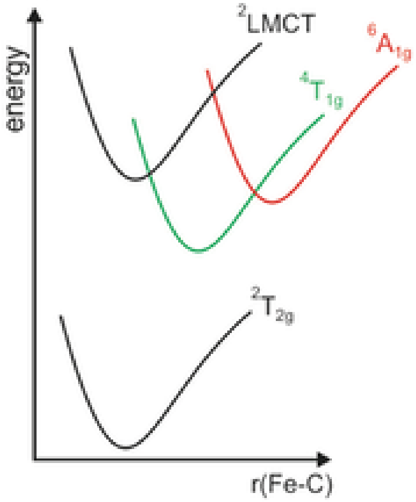


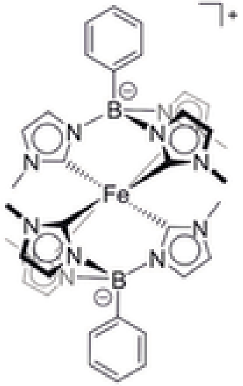


MLCT lifetime: < 1 ps

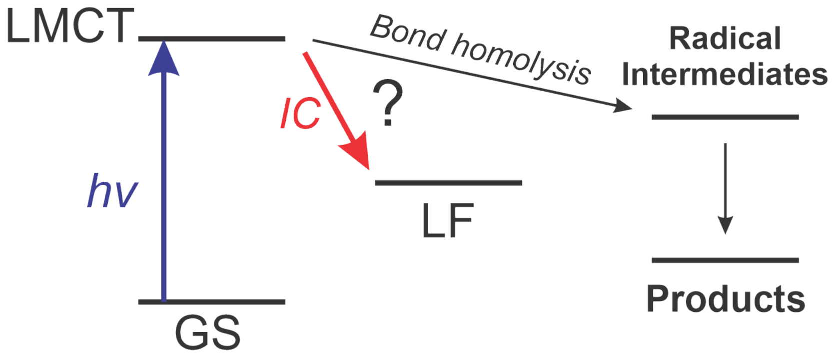
A whole field emerged trying to deal with Fe LF deactivation







Ag(II) d^9, Cu(II) d^9, and Fe(III) d^5 all have partially filled d-orbitals!

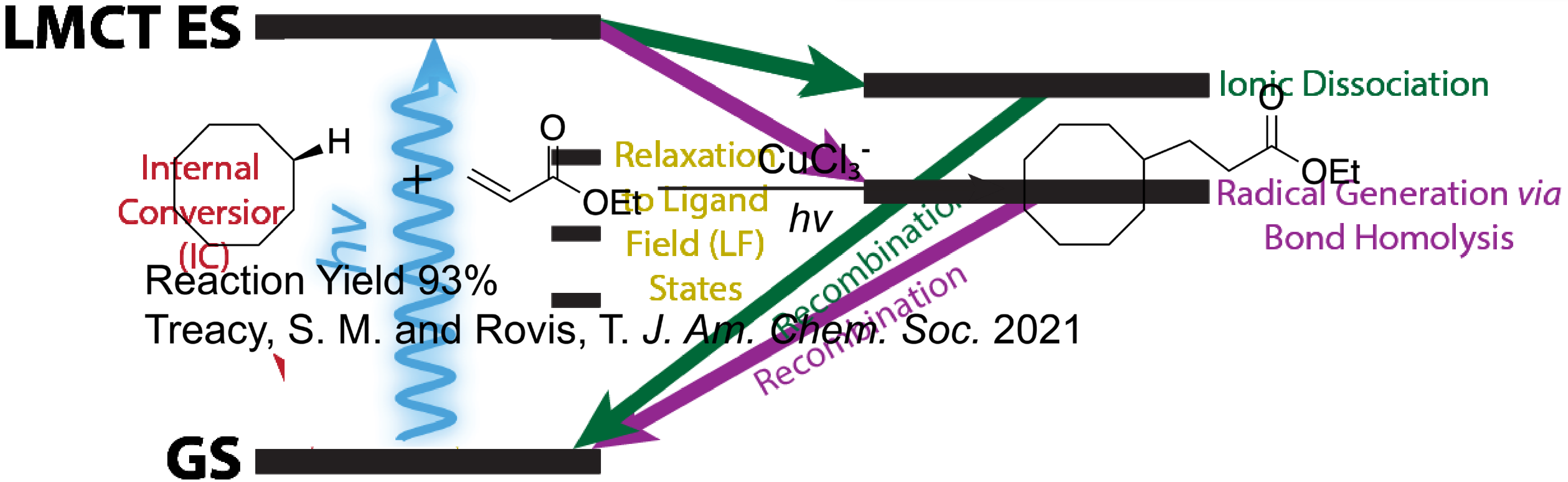


Wenger, O. *Chem. Eur. J.* **2019**

Competing Decay Pathways

Ultrafast Processes: 10^{-15}-10^{-12} s
(fs to ps)

$$QY = \frac{k_{productive}}{k_{productive} + \Sigma k_{nonproductive}}$$



Reaction Yield 93%

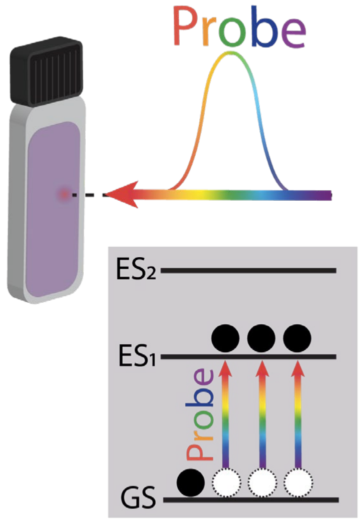
Treacy, S. M. and Rovis, T. *J. Am. Chem. Soc.* 2021

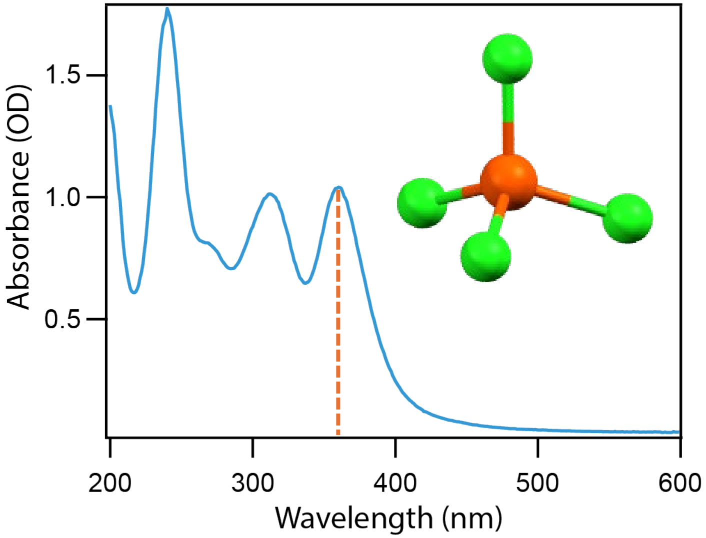
Metal Chlorides

- Demonstrated utility
- Generation of Cl•
- Inexpensive
- Understand photoinduced dynamics

Intro to ultrafast transient absorption (TA)

Steady State Absorption Spectroscopy (UV-Vis)





LMCT Band 365 nm

Ultrafast Transient Absorption Spectroscopy (fs-TA)