Photochemical Experiments

Molecular Photochemistry

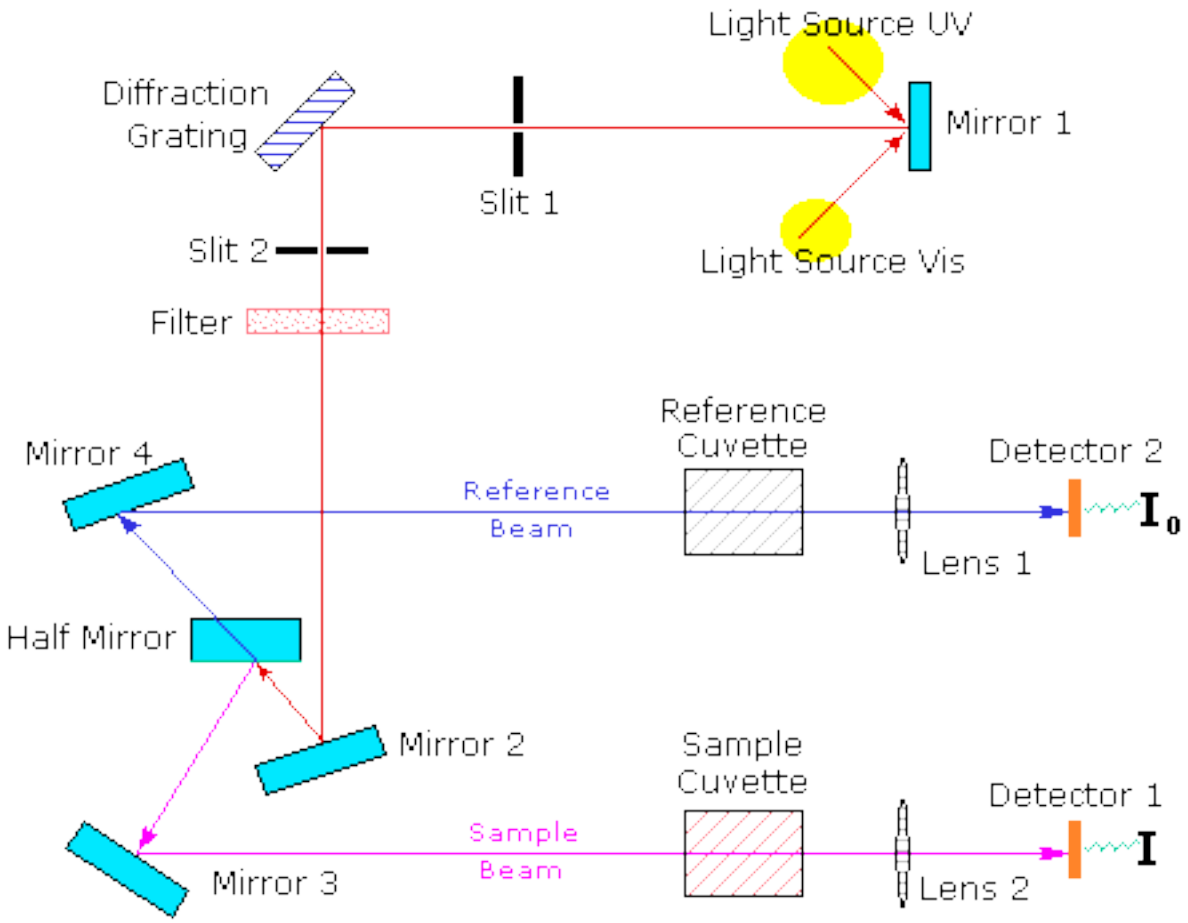
CHEM 4801

Information from Electronic Spectra

Photochemical Experiments

Ultraviolet-Visible Spectroscopy

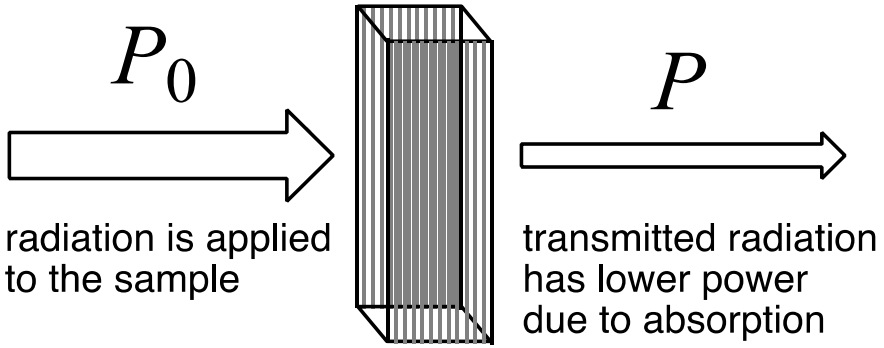
An ***ultraviolet-visible (UV-vis) spectrometer*** is used to measure the response of a sample to ultraviolet or visible light. The instrument is designed to cancel fluctuations in the light source or electronics.



https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/UV-Vis/uvspec.htm

Absorption Spectra

An ***absorption spectrum*** depicts ***absorbance (A)*** or ***molar absorption coefficient (ε)*** of the sample as a function of wavelength (λ) or frequency (ν).

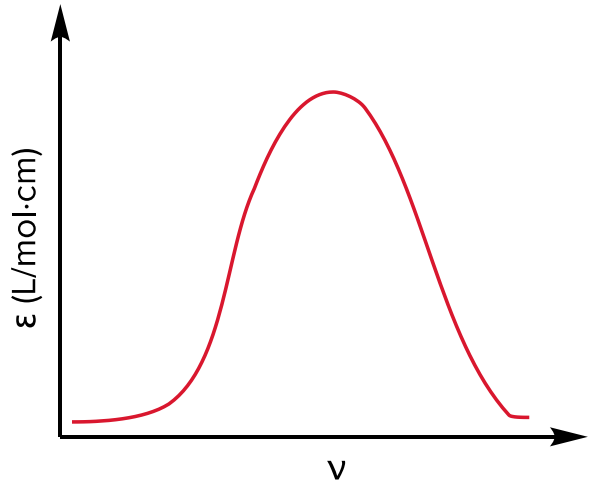


$$A = \log_{10}\left(\frac{P_0}{P}\right)$$

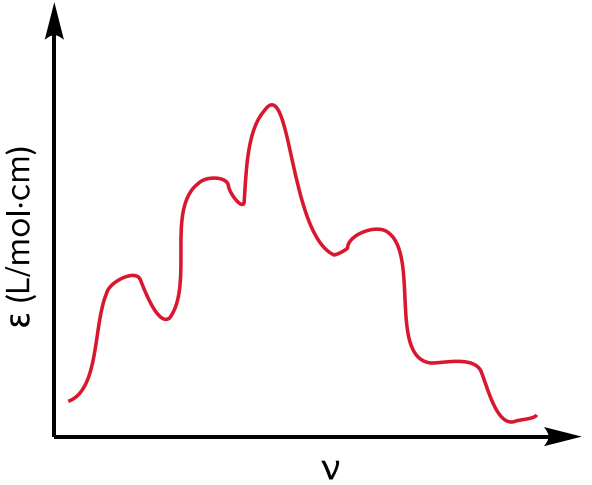
- P_0: Incident radiant power
- P: Transmitted radiant power

Electronic spectra are solvent dependent. Vibrational structure may be visible in spectra taken in nonpolar solvents.

Polar solvent



Nonpolar solvent

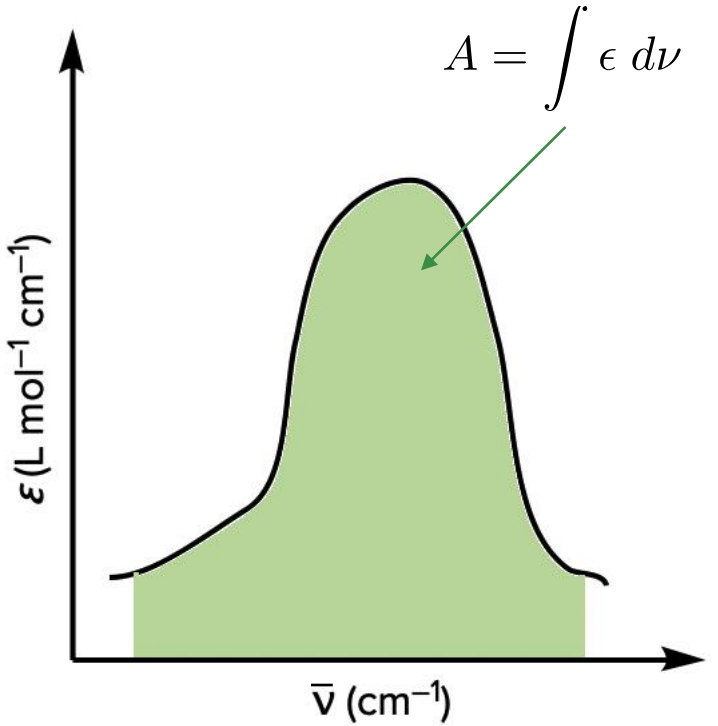


Oscillator Strength and Radiative Lifetime

We have seen previously that absorption features can be used to determine oscillator strengths *f*; they can also be used to calculate radiative lifetimes τ_0 for the corresponding excited states.

To determine radiative lifetime for the excited state corresponding to an absorption feature at ν_{max} cm^{-1},

$$\tau_0 = \frac{3.5 \times 10^8}{\bar{\nu}^2 \epsilon_{max} \bar{\nu}_{fwhm}}$$

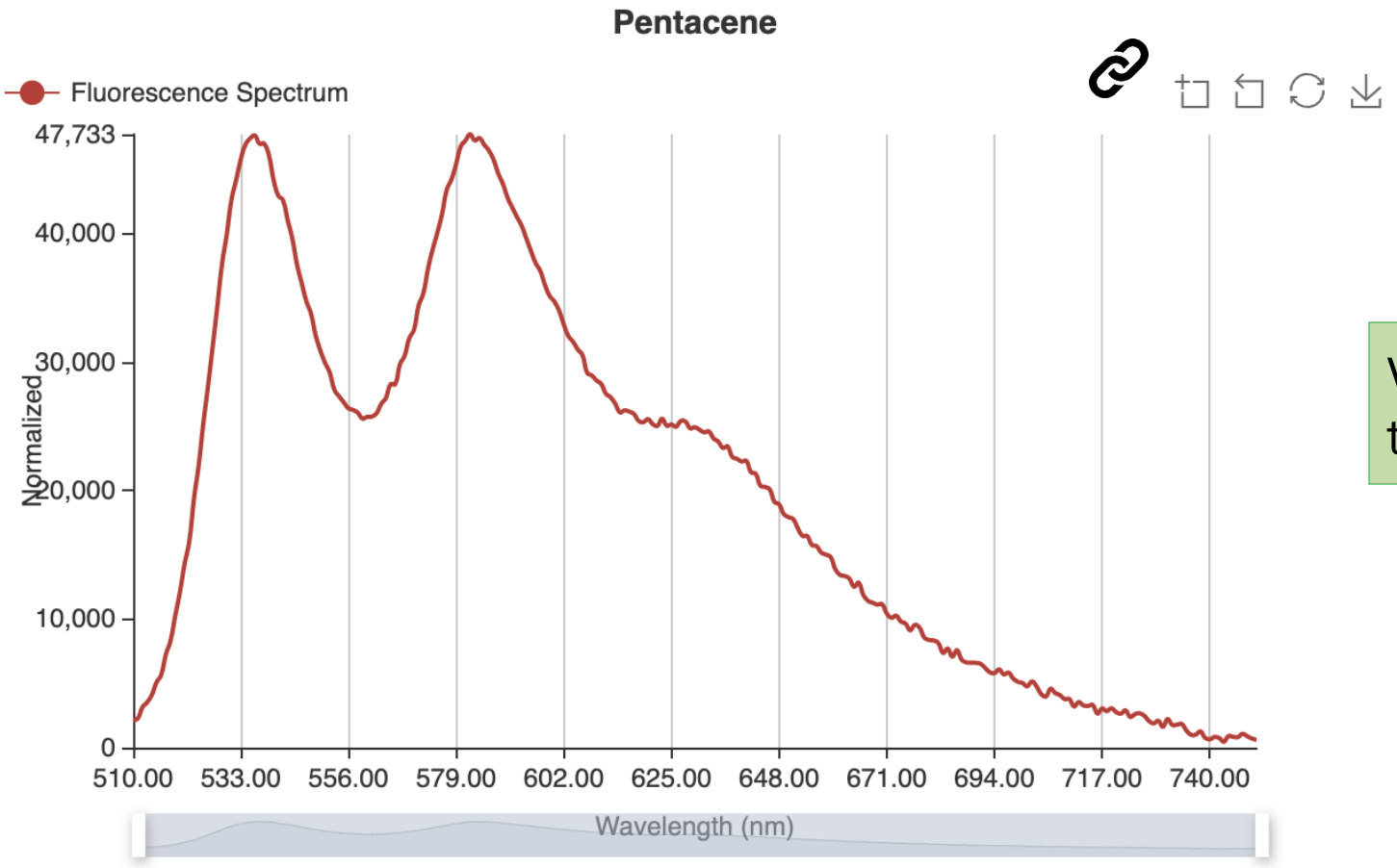


$$f_{mn} = (4.319 \times 10^{-9} \text{ mol L}^{-1} \text{ cm}^2) A$$

$$f_{mn} \approx (6.784 \times 10^{-9} \text{ mol L}^{-1} \text{ cm}^2) \epsilon_{max} \bar{\nu}_{fwhm}$$

Emission Spectra

An ***emission spectrum*** depicts the normalized intensity of emitted light as a function of wavelength (λ) or frequency (ν). The wavelength of excitation is not terribly important (*Kasha's rule*).



Also called:

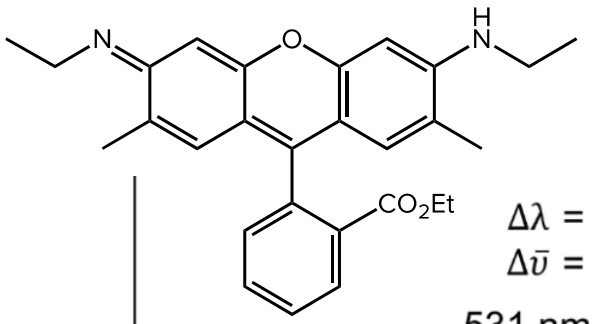
- Photoluminescence (PL) spectra
- Fluorescence spectra
- Phosphorescence spectra

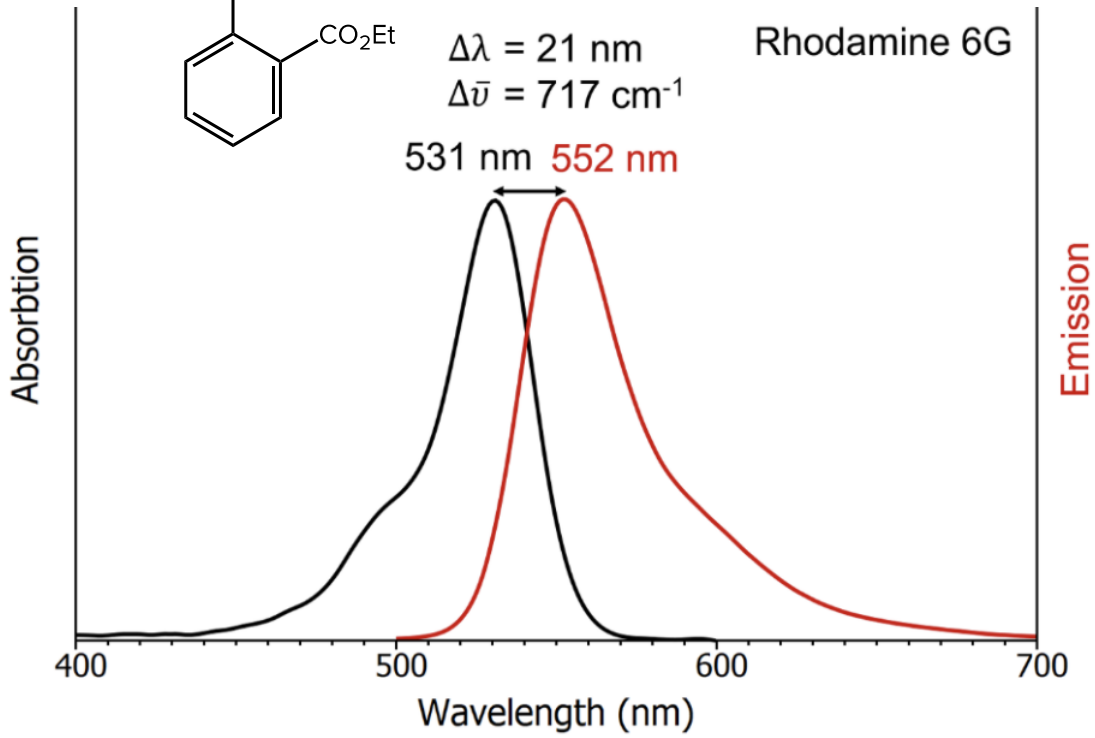
Vibrational structure in emission spectra typically reflect the *ground* state.

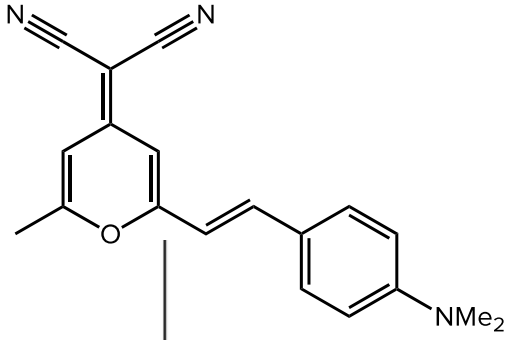
PhotochemCAD. https://photochemcad.com/compound-detail.php?name=Pentacene

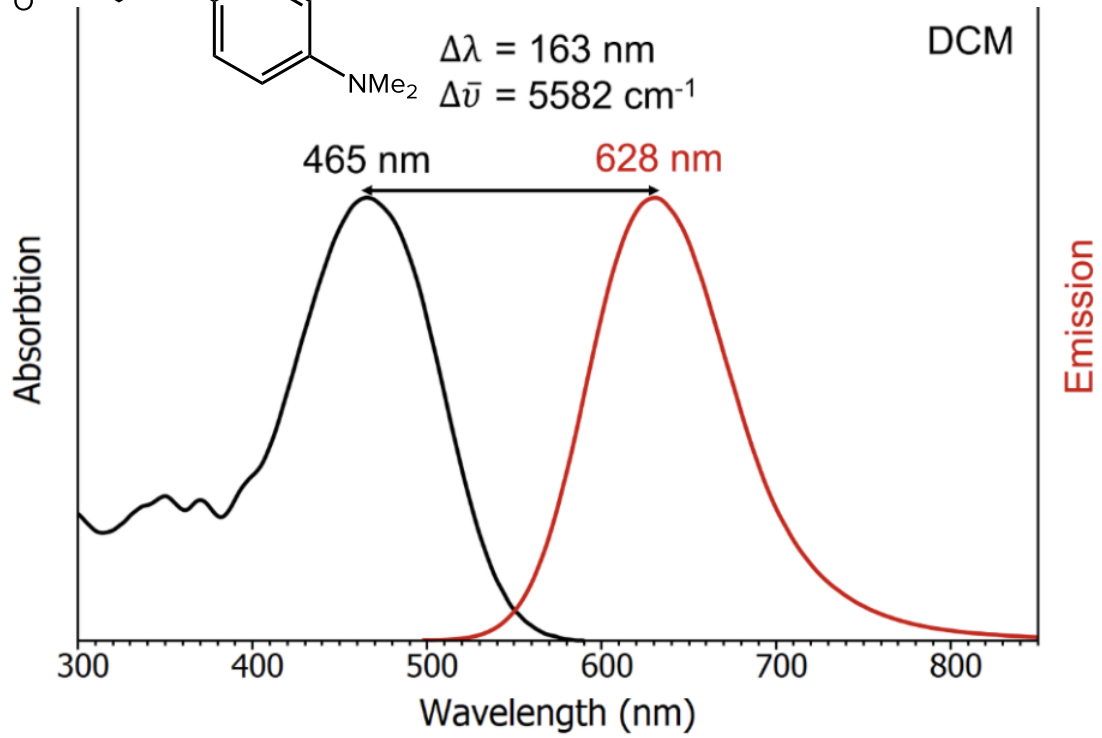
Combining Absorption and Emission

A difference in maxima between absorption and emission spectra (***Stokes shift***) points to structural differences in the ground and excited states (recall Franck-Condon). Stokes shift is solvent dependent.



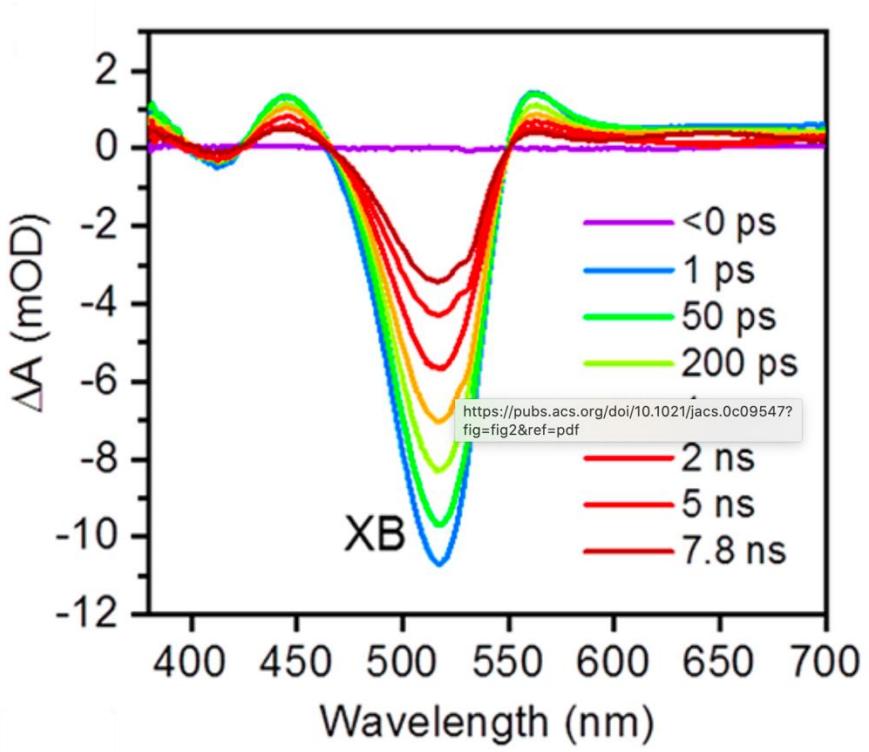




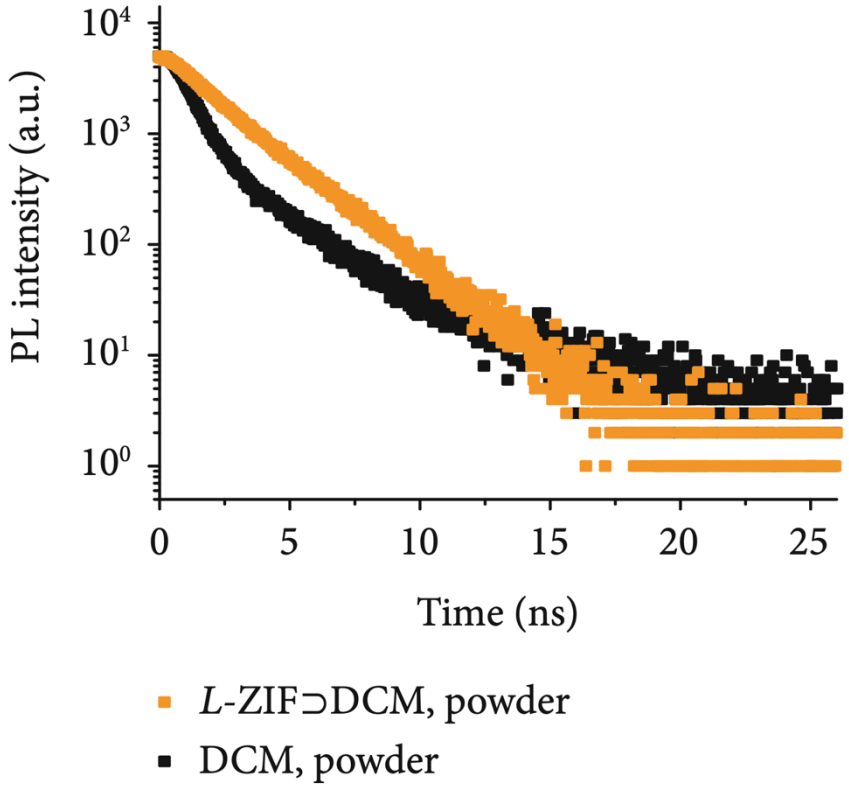


Time-resolved Spectroscopy

Measuring the time dependence of absorption or emission gives a ***time-resolved*** spectrum. Femtosecond resolution is now routine (10^{-15} s); attosecond resolution is state of the art (10^{-18} s).



Full spectra at various time points



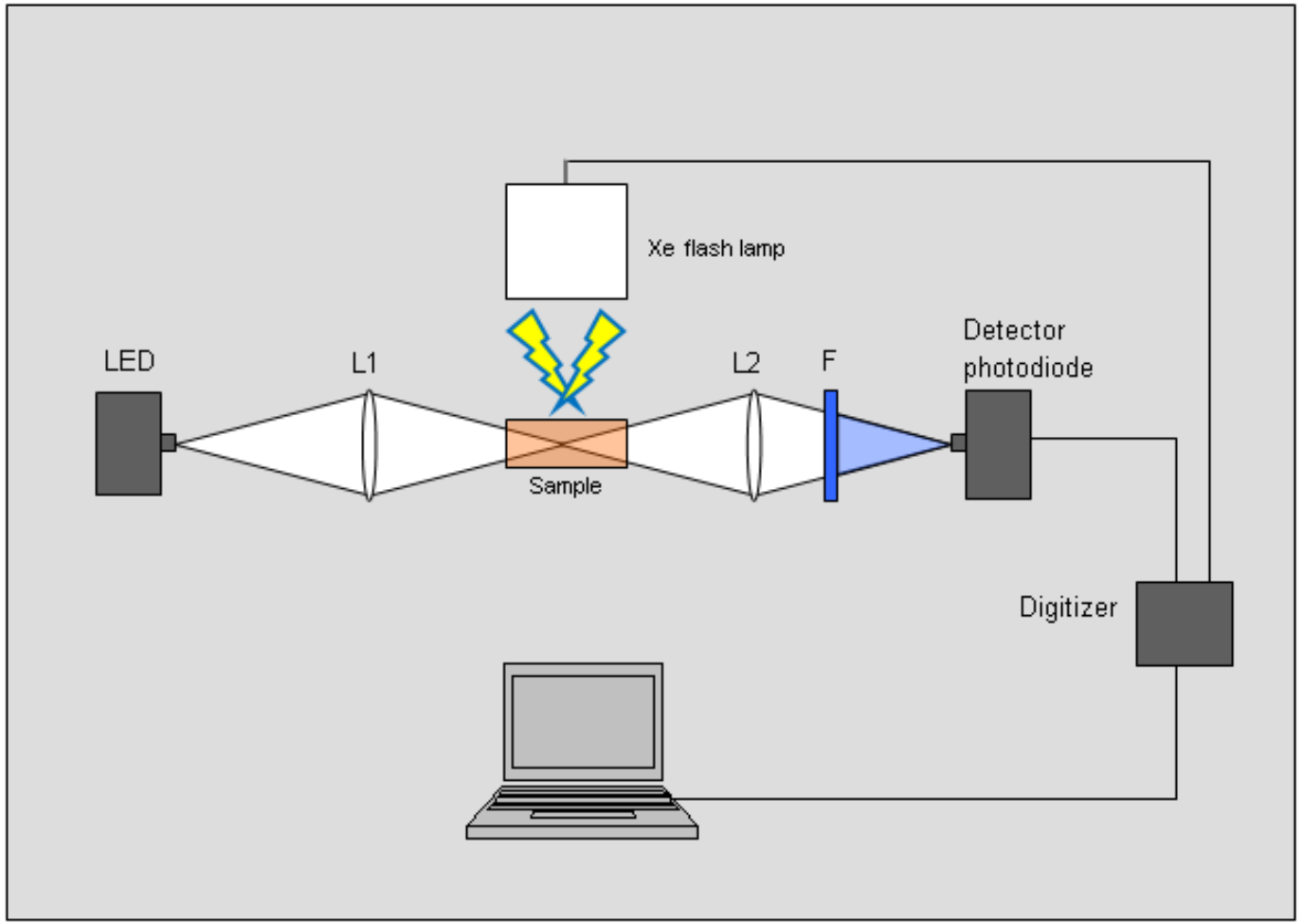
Decay at a single wavelength (ε_{max} or I_{max})

Flash Photolysis

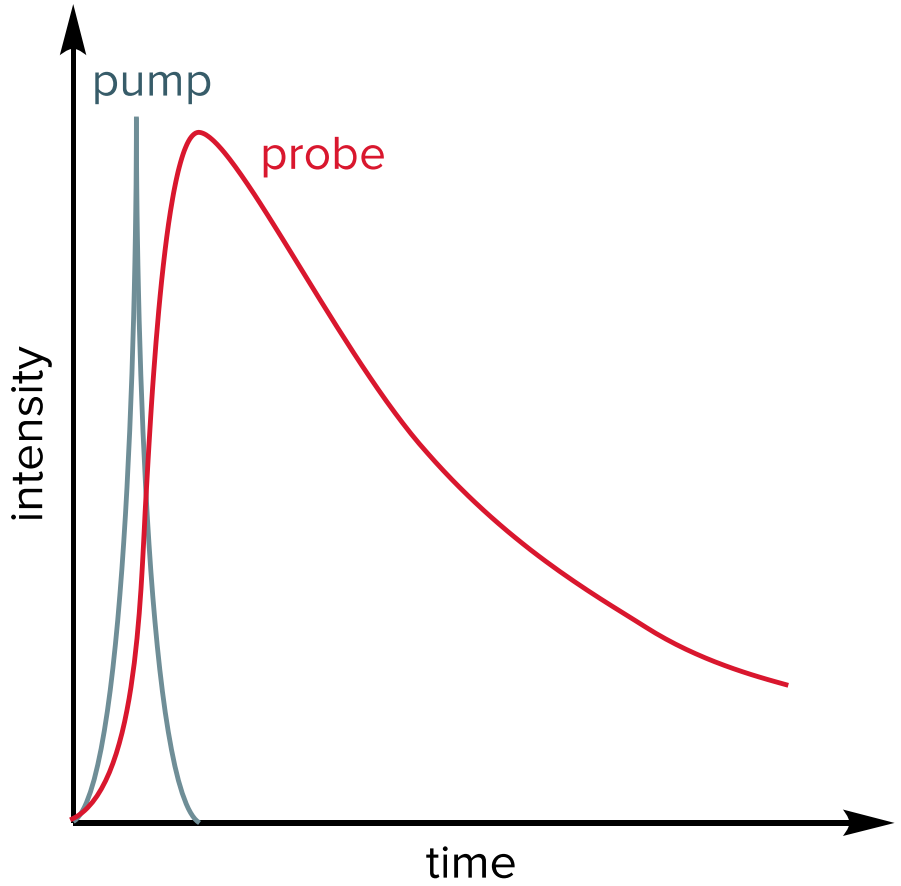
Photochemical Experiments

Rapid Excitation and Analysis

The technique of ***flash photolysis*** is based on extremely rapid and intense excitation followed by spectroscopic analysis.

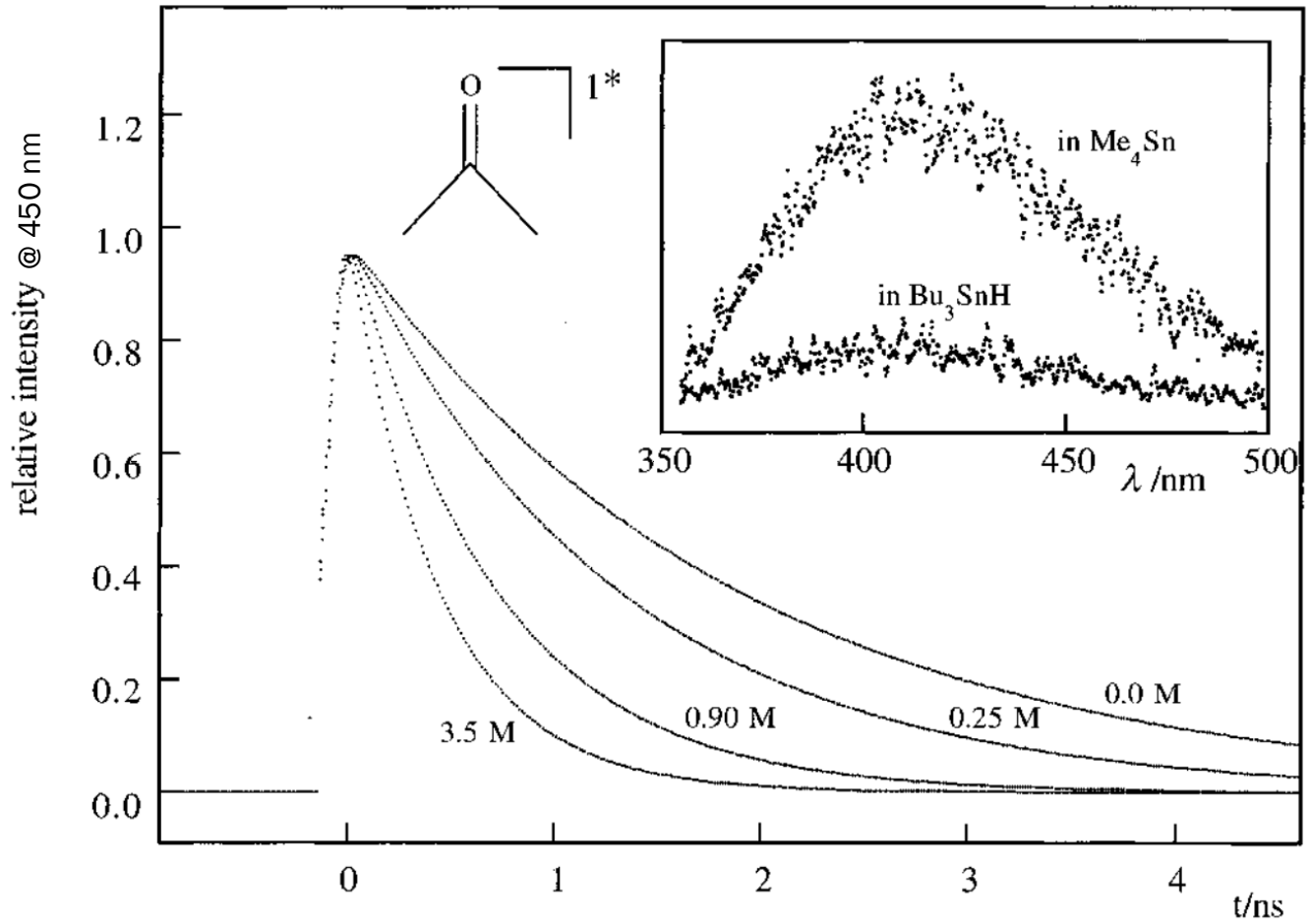


- Excited-state lifetime τ
- Beware multiple decay processes…



Excited-state Lifetime and Rate Constant

Flash photolysis is used to measure lifetimes in quenching studies (e.g. as an alternative to steady-state emission) and rate constants of photochemical reactions.



Quenching of acetone fluorescence via hydrogen transfer from $HSnBu_3$

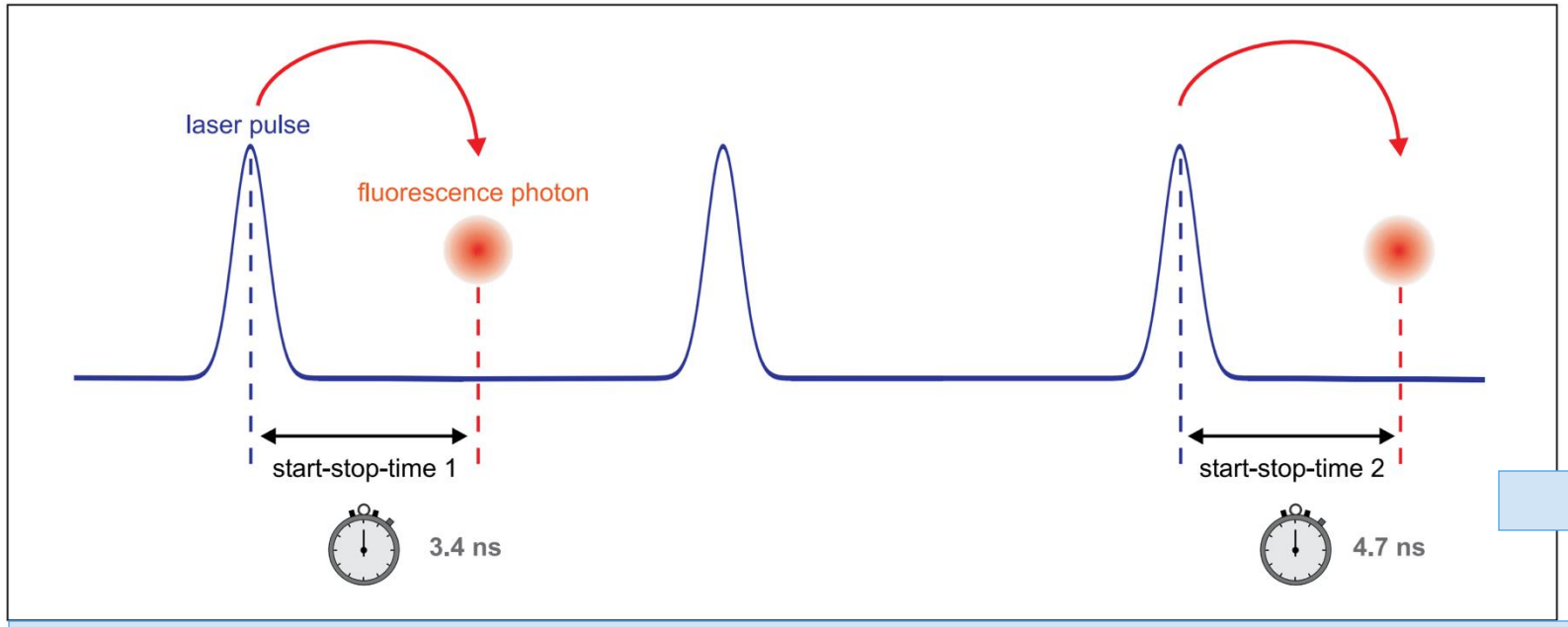
J. Am. Chem. Soc. **1996**, *118*, 2275.

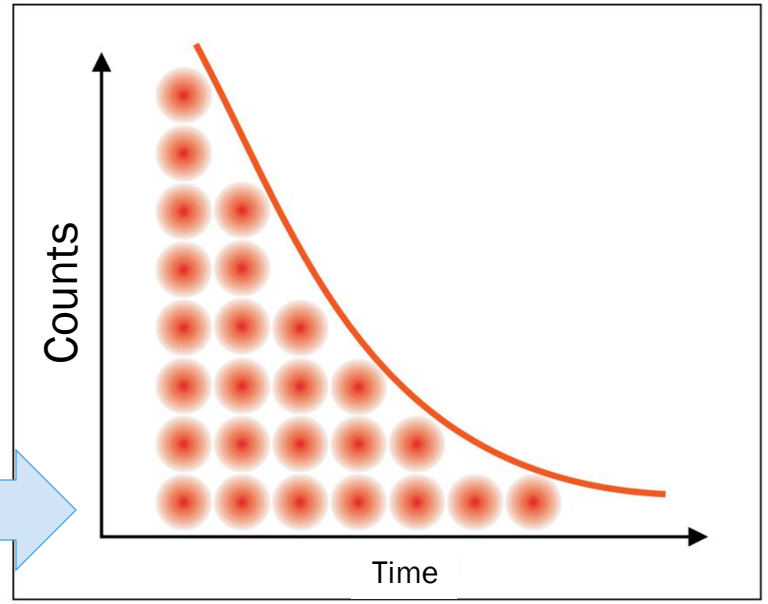
Time-correlated Single-photon Counting (TCSPC) Experiments

Photochemical Experiments

TCSPC: The Racing Photons

In a ***time-correlated single photon counting (TCSPC)*** experiment, time delay between excitation and emission is measured and the resulting data is a histogram of times to emission.

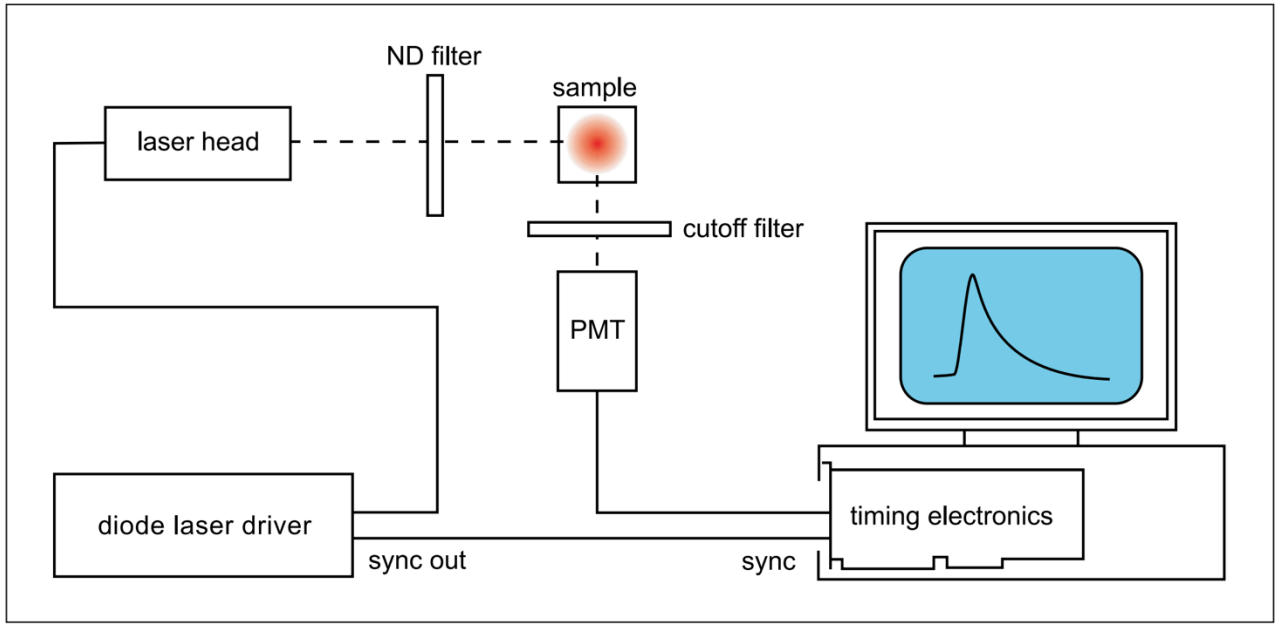


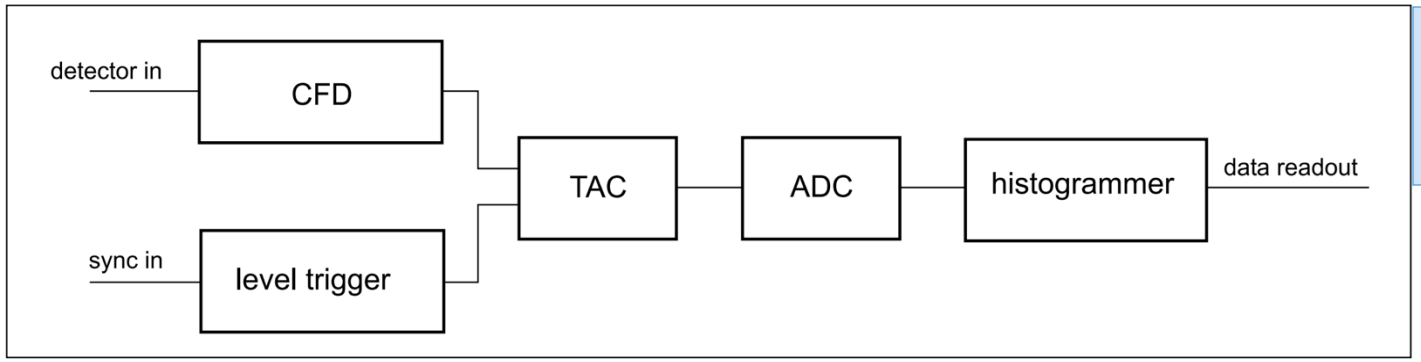


Minimizing emission of photons in a wrong “later” cycle is important. To achieve this, <5% of cycles typically display emission.

Design of a TCSPC Instrument

Timing electronics, often including a voltage ramp and analog-to-digital converter, ensure precise measurement of the time to emission.

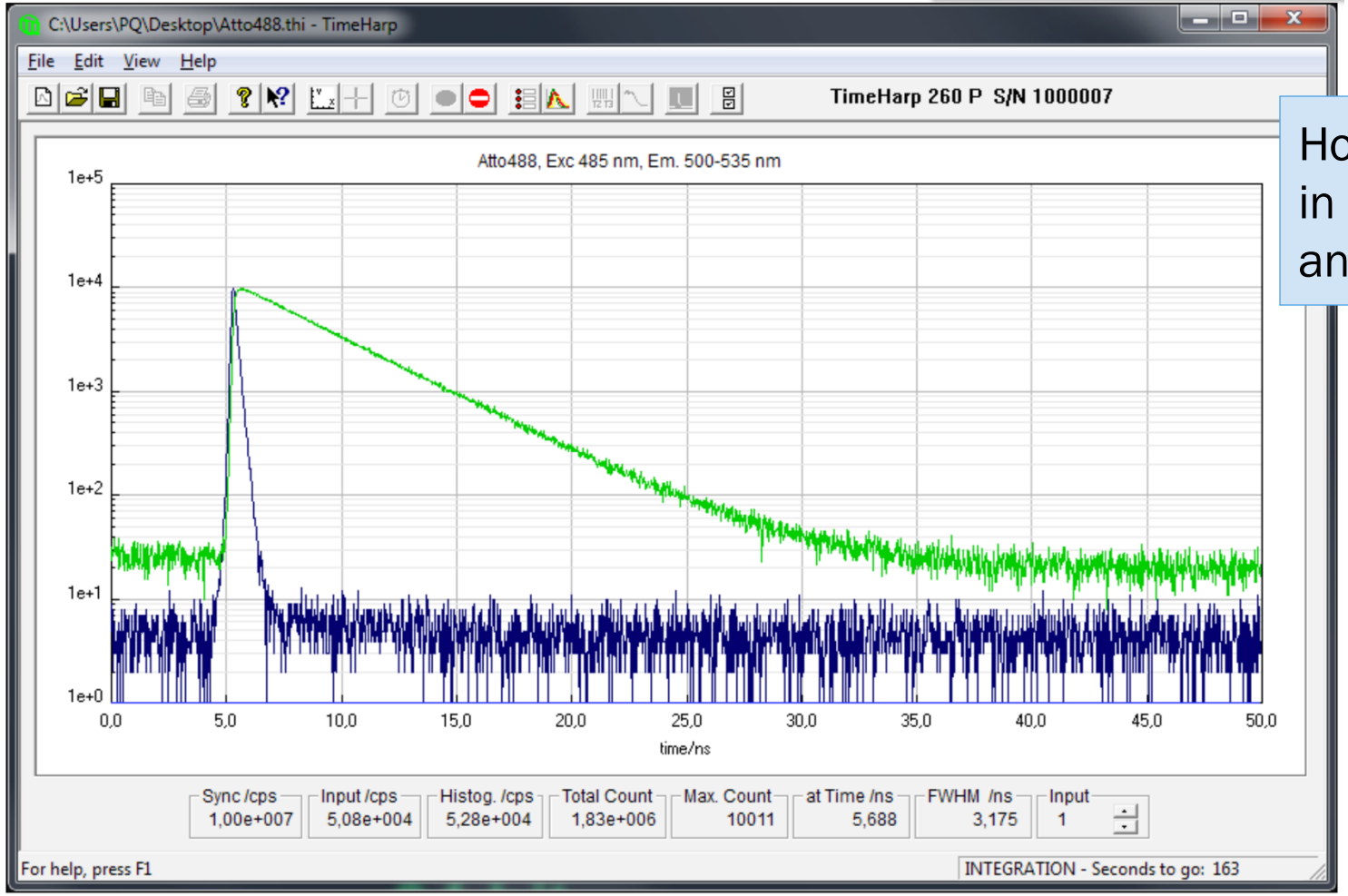




Constant-fraction discriminator and level trigger ensure precise measurement of times.

Data Analysis: Fluorescence τ and k

Fluorescence lifetime can be calculated by fitting the histogram to an exponential decay function: $N(t) = e^{-t/\tau}$.



How does a single excited molecule in any given cycle “know” to exhibit an exponential decay profile?

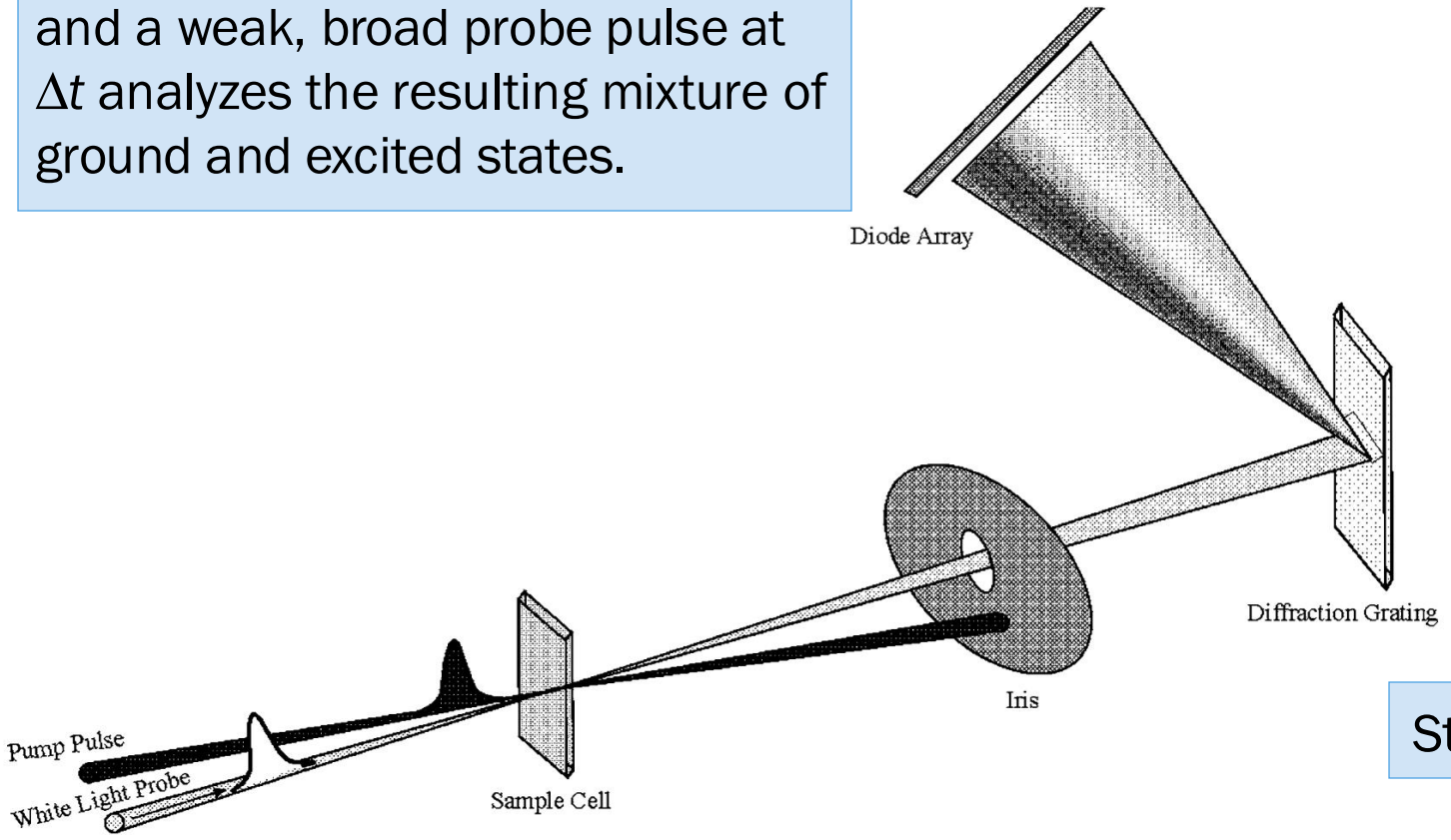
Transient Absorption Spectroscopy

Photochemical Experiments

Excited States Have Spectra…

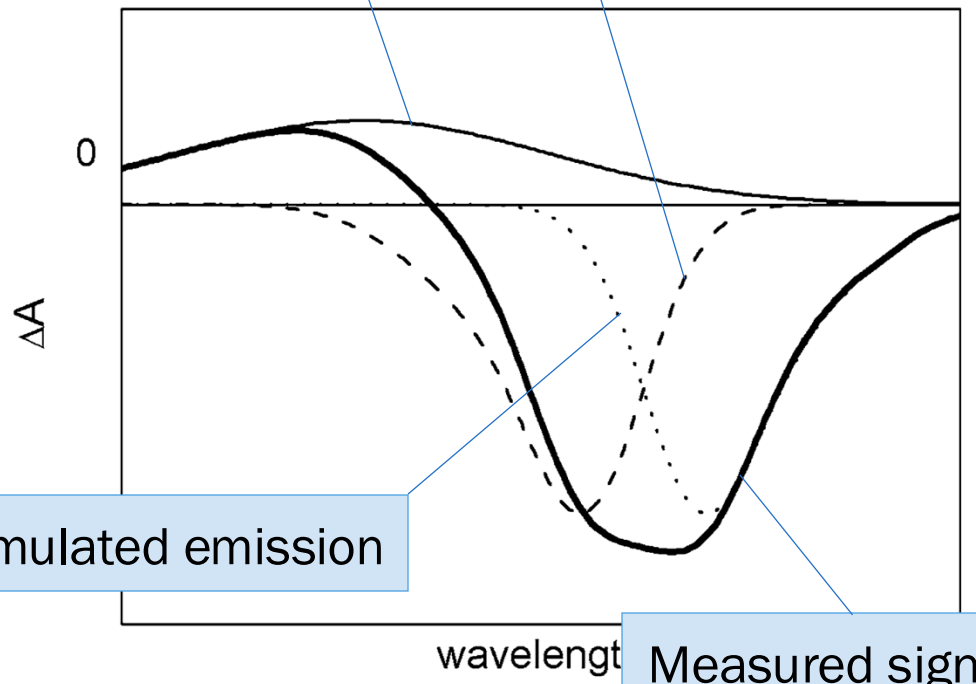
Excited states are capable of absorbing light themselves to reach higher excited states. The absorption spectrum of an excited state is called a ***transient absorption spectrum***.

A pump pulse excites the sample and a weak, broad probe pulse at Δt analyzes the resulting mixture of ground and excited states.



Excited-state absorption

Ground-state bleach



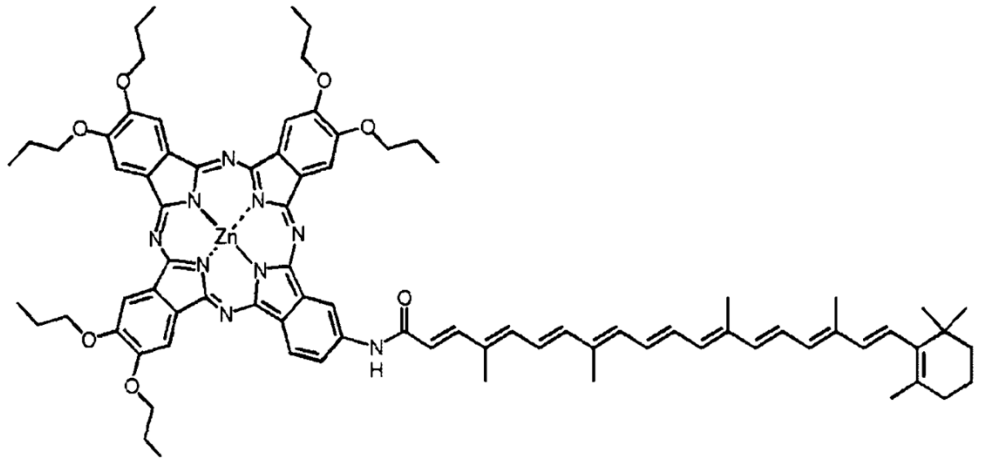
Stimulated emission

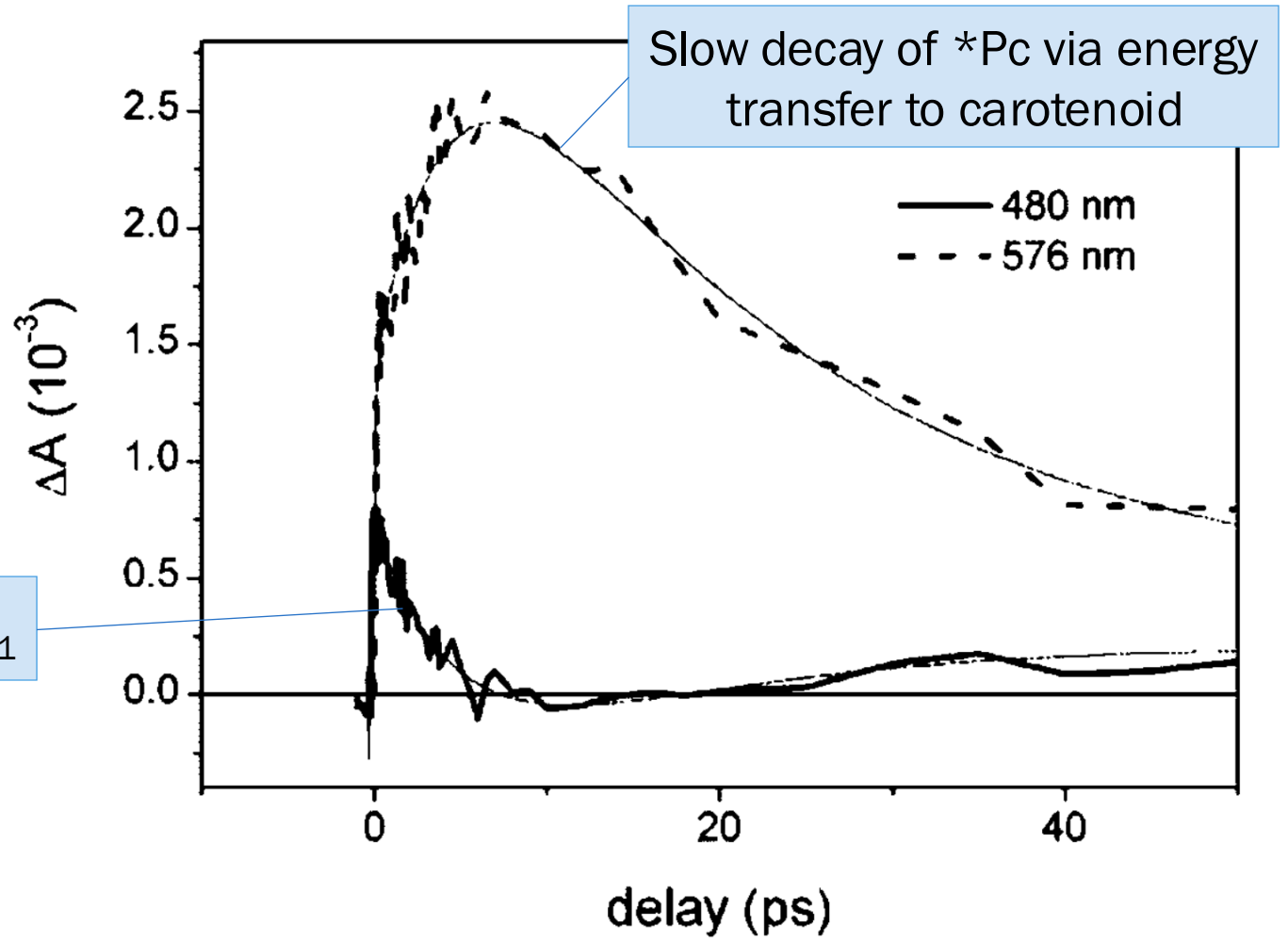
Measured signal

Photosynth. Res. **2009**, *101*, 105.

Time-resolved TAS

Time-resolved TAS provides information about the dynamics of the excited state.





Rapid decay of carotenoid S_1

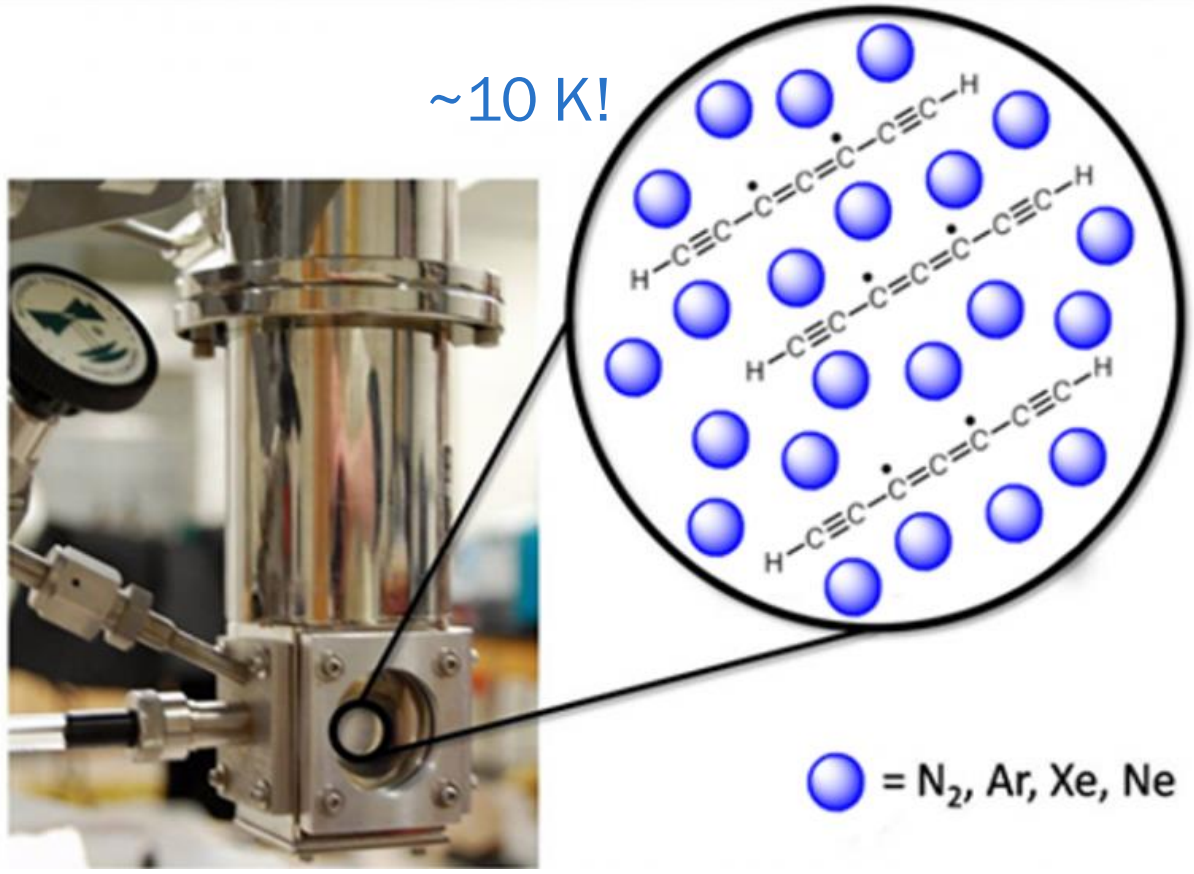
Photosynth. Res. **2009**, *101*, 105.

Low-temperature Matrix Studies

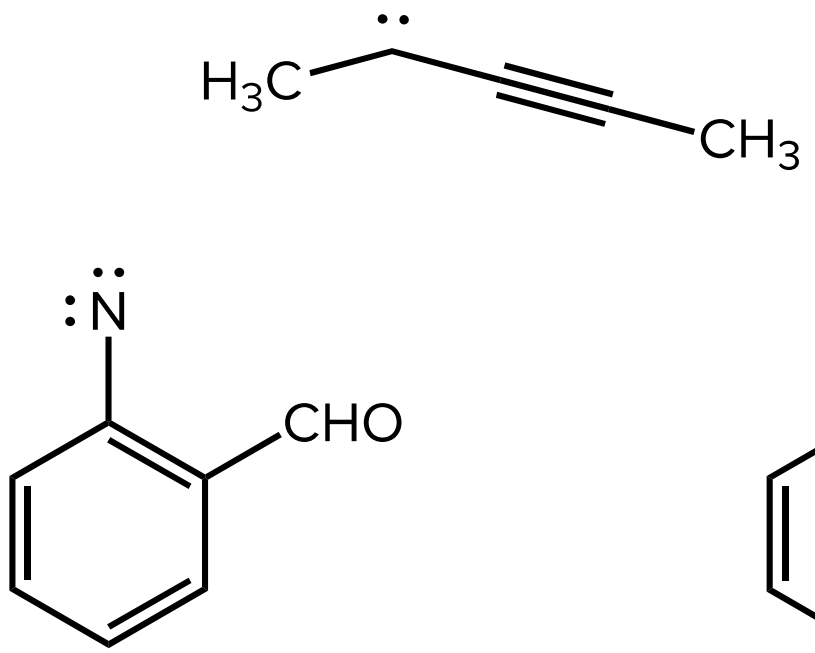
Photochemical Experiments

Matrix Isolation

Freezing a dilute sample at very low temperatures in an inert matrix enables study of unstable molecules and minimizes collisional energy dissipation.



https://mcmahon.chem.wisc.edu/research/



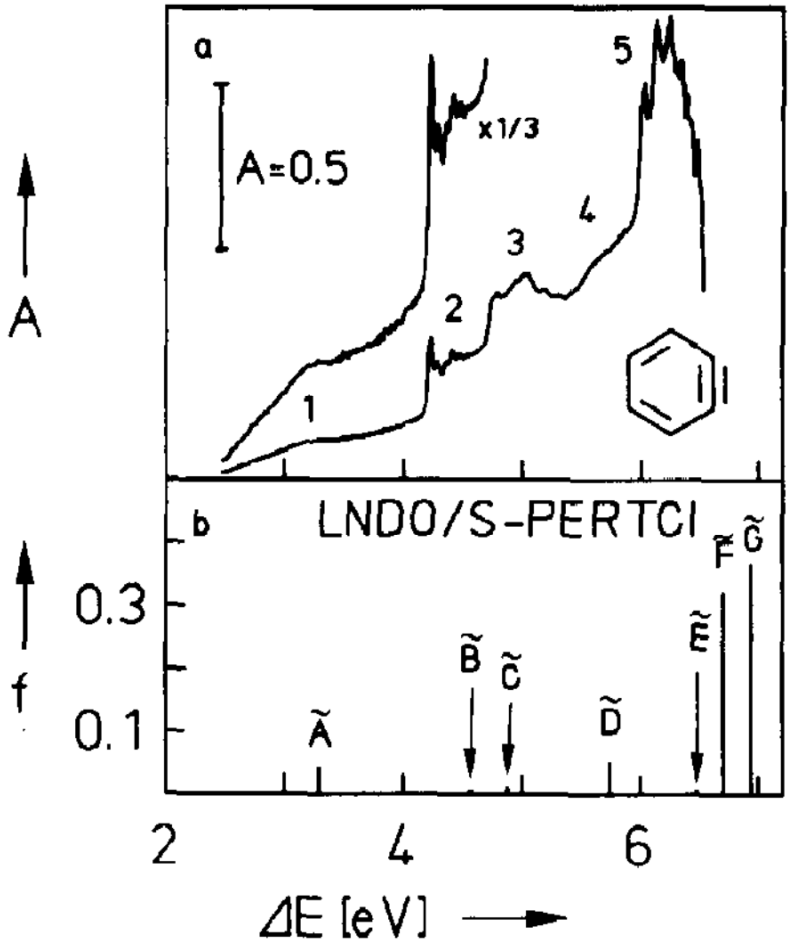
Chem. Phys. Lett. **1988**, *147*, 192.

Matrix Isolation

Unlike solution-phase spectra, UV-vis spectra of matrix-isolated molecules often display sharp peaks.

Measured absorption spectrum at 15 K

Calculated oscillator strengths



Chem. Phys. Lett. **1988**, *147*, 192.

Actinometry for Quantum Yields

Photochemical Experiments

How Do We Count Photons?

Counting photons is generally very inefficient, especially for “odd” irradiation geometries. Even if the efficiency response of an instrument is known, it can vary by manufacturer, by place, or by day!

Physical detectors

Hamamatsu PMT

Vishay photodiode

Senba infrared thermopiles

Chemical Actinometry

A ***chemical actinometer*** is a photochemical process whose quantum yield is very precisely known. Actinometry is used to quantify photons for measurement of quantum yields of other processes.

Potassium ferrioxalate actinometer

$$[Fe(C_2O_4)_3]^{3-}(aq) + Fe^{3+}(aq) \longrightarrow [Fe(C_2O_4)]^{+}(aq) + [Fe(C_2O_4)_2]^{-}(aq)$$

$$[Fe(C_2O_4)]^{+}(aq) + h\nu \longrightarrow Fe^{2+}(aq) + C_2O_4^{-}(aq)$$

Precisely known Φ

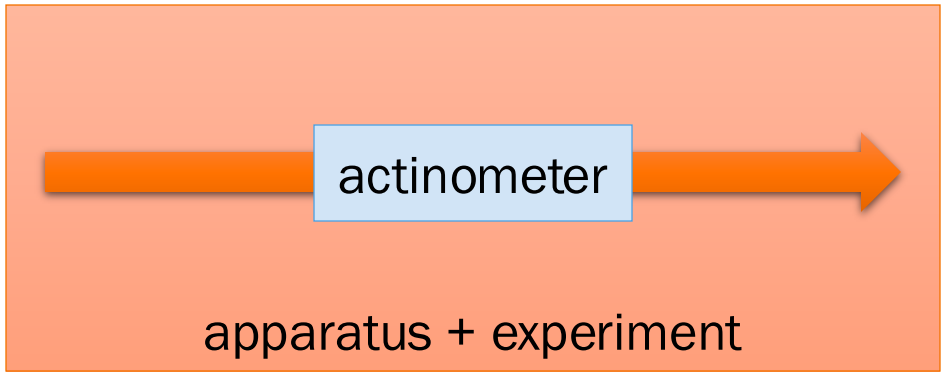
$$[Fe(C_2O_4)]^{+}(aq) + C_2O_4^{-}(aq) \longrightarrow Fe^{2+}(aq) + C_2O_4^{2-}(aq) + 2\,CO_2(g)$$

$$Fe^{2+} + 3\,phen \longrightarrow [Fe(phen)_3]^{2+}$$

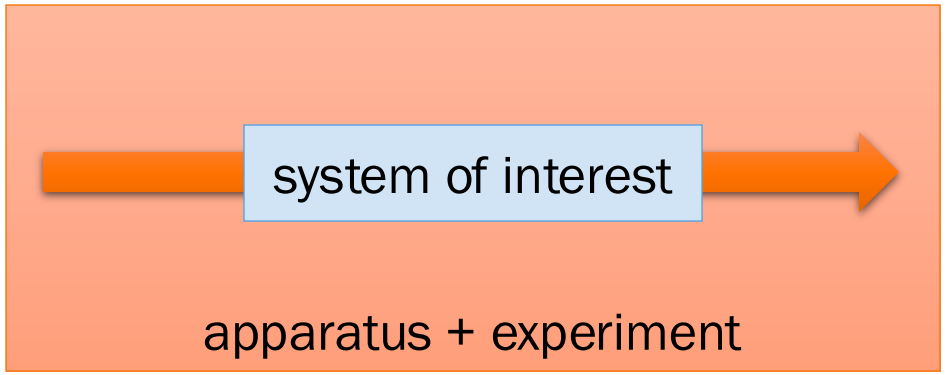
Precisely known ε

Chemical Actinometry

The actinometer is “inserted” into an experiment to measure the “concentration” of photons involved. Then, the experiment is run with the system of interest and product yield (or other outcome) is measured.



N photons

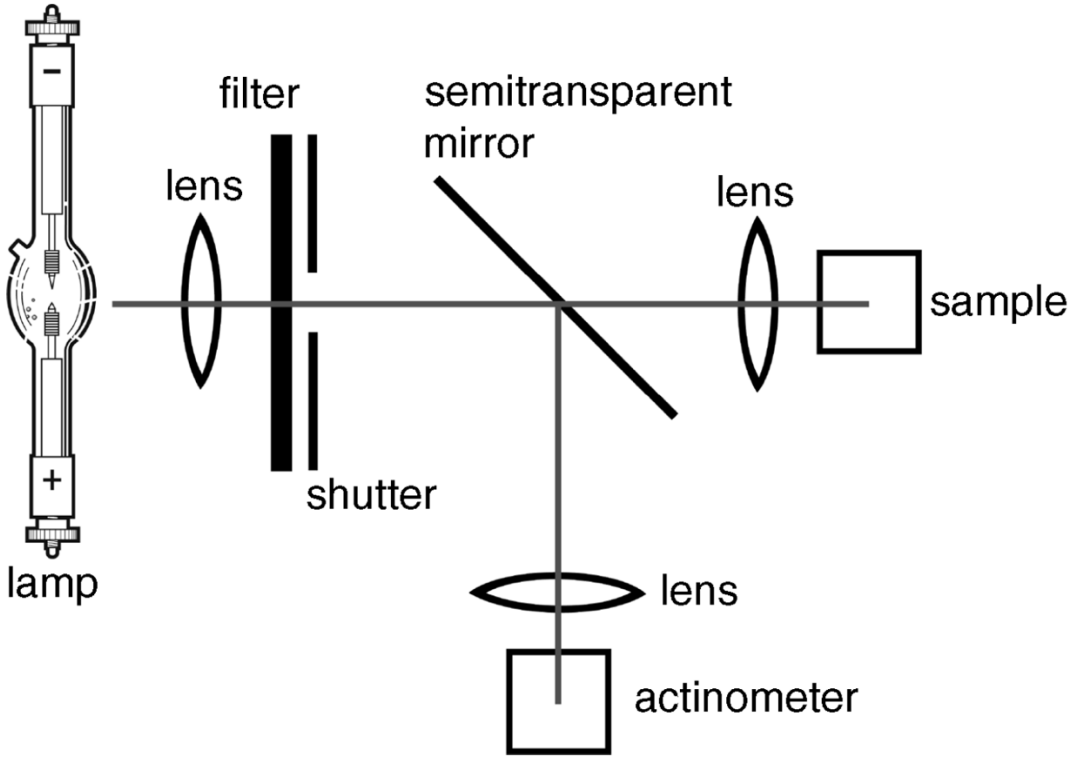


N photons

Chemical Actinometry

Split-beam or “merry-go-round” setups may be used to measure the actinometer and sample at the same time.

Split-beam apparatus



Merry-go-round apparatus