

March 30, 2005

➤ Apologies for website errors!

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Spectroscopy: Molecular Luminescence Spectrometry

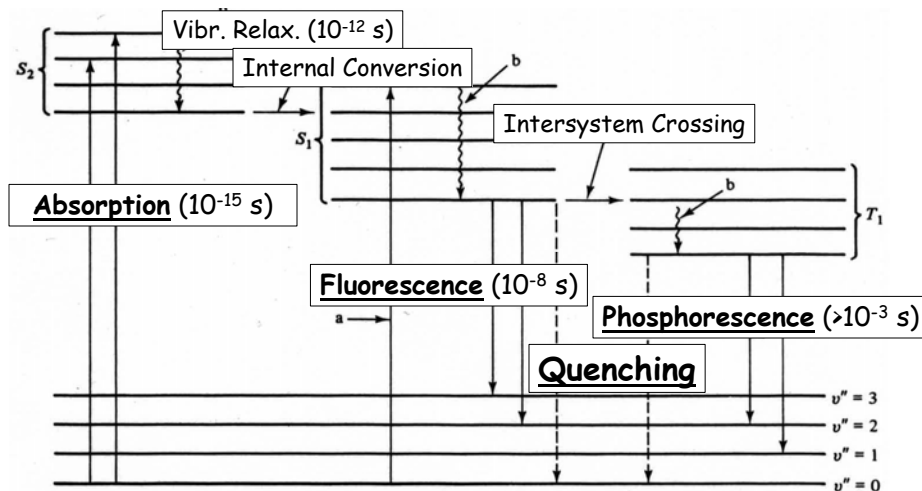
Chem 221
Instrumental Analysis
Spring 2005

Overview

- We will be concerned with:
 - Photon-excited emission
 - Decay from singlet state
 - *Fluorescence*
- Electronic Transitions (molecular)
 - UV/Vis
- Very low detection limits
 - ppb and below

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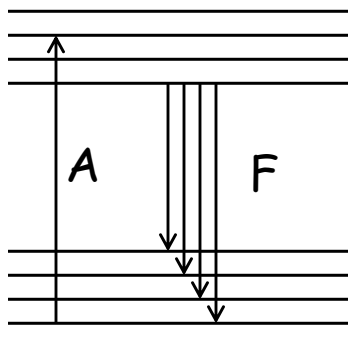
Remember Jablonski!



Fluorescence Spectrum

- **Excitation** at a single wavelength (λ_{ex})

- **Emission** at a range of wavelengths (longer λ)



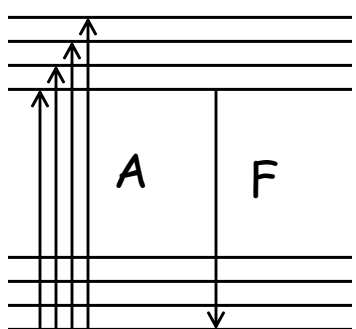
See vibrational structure of ground state

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Excitation Spectrum

- **Excitation** at a range of wavelengths

- **Emission** at a specific wavelength (λ_{em})



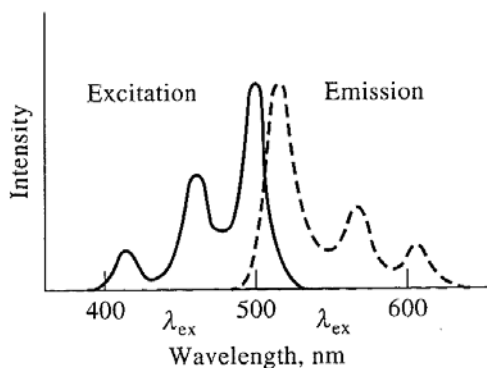
See vibrational structure of excited state

- **Excitation spectrum should mimic absorption spectrum** (assuming vibrational relaxation is complete)

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Emission/Excitation Spectra

- **Excitation spectrum** like absorption spectrum
- **Emission (fluorescence) spectrum** at lower energy (longer wavelength)



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Fluorescence Quantum Efficiency

Not all molecules *fluoresce* - **Why?**

➤ Reflected in Quantum Efficiency (Φ):

$$\Phi = k_f / (k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d)$$

fraction of excited molecules that fluoresce

rate constants for deactivation processes (lowest excited singlet state)

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Deactivation Rate Constants

- k_i - intersystem crossing
 - k_{ec} - external conversion
 - k_{ic} - internal conversion
- } mostly affected by *environment*
- k_{pd} - predissociation
 - k_d - dissociation
 - k_f - fluorescence
- } mostly affected by *structure*

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Factors Affecting Fluorescence Intensity

➤ Absorption Transitions

$\sigma \rightarrow \sigma^*$: too energetic (bonds break - k_d big)
(limits absorption to $\lambda > \sim 250\text{nm}$)

$n \rightarrow \pi^*$: low molar absorptivity (ϵ)
= long π^* lifetime ($10^{-5} - 10^{-7}$ s)
(more chance for non-fluor deactivation)

$\pi \rightarrow \pi^*$: high molar absorptivity (ϵ)
= short π^* lifetime ($10^{-7} - 10^{-9}$ s)
(greatest k_f)

Also: smaller k_i (less singlet/triplet overlap)

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More FAFI: Molecular Structure

- **Low energy $\pi \rightarrow \pi^*$ transitions preferred**
 - aromatic functional groups
 - highly-conjugated double-bond structures
 - fused-ring structures
- **Substitution Effects**
 - *Heavy atom substitution*: increases k_i
 - ✓ Example: halogen substitution on Benzene
 - Substitutions that decrease energy of $n \rightarrow \pi^*$
 - ✓ Heterocyclic rings (not fused)
 - ✓ COOH or C=O on aromatic rings
- **Rigid Structures preferred**
 - likely due to decreased k_{ic}

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Still More FAFI: Environment Effects

- **Solvent**
 - \uparrow viscosity, $\downarrow k_{ec}$
 - heavy atom effect (solutes and solvent)
- **Temperature**
 - \uparrow temp, $\uparrow k_{ec}$
- **pH**
 - affects electronic structure of acidic or basic substituents
- **Dissolved Oxygen**
 - paramagnetic - $\uparrow k_i$

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