Lecture 39 — Fluorescence, Phosphorescence & Photochemistry
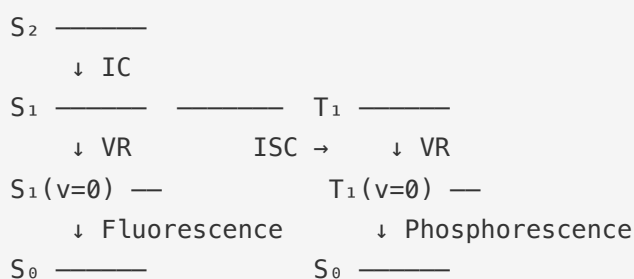
Reading: Engel 4th ed., Chapter 14 (Sections 14.5–14.8)

Learning Objectives

- Describe the Jablonski diagram and the processes following photon absorption
- Distinguish between fluorescence and phosphorescence
- Explain internal conversion, intersystem crossing, and vibrational relaxation
- Define quantum yield and fluorescence lifetime
- Describe applications: lasers, fluorescent probes, photodynamic therapy, solar cells

1. The Jablonski Diagram

After absorbing a photon, a molecule can relax via several pathways:

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S₂ ———————
    ↓ IC
S₁ ———————    ———————   T₁ ———————
    ↓ VR          ISC →     ↓ VR
S₁(v=0) —              T₁(v=0) —
    ↓ Fluorescence        ↓ Phosphorescence
S₀ ———————            S₀ ———————
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Process	Abbreviation	Timescale	ΔS
Absorption	Abs	10^{-15} s	0
Vibrational relaxation	VR	10^{-12}–10^{-10} s	0
Internal conversion	IC	10^{-12}–10^{-9} s	0
Fluorescence	F	10^{-9}–10^{-7} s	0
Intersystem crossing	ISC	10^{-8}–10^{-3} s	±1

Process	Abbreviation	Timescale	ΔS
Phosphorescence	P	10^{-3}–10^2 s	±1

2. Fluorescence

Characteristics

- **Spin-allowed**: $S_1 \rightarrow S_0$ ($\Delta S = 0$)
- **Fast**: lifetime $\tau_f \sim 10^{-9}$–10^{-7} s (nanoseconds)
- **Stokes shift**: fluorescence is always at **longer wavelength** (lower energy) than absorption because of vibrational relaxation in S_1

Kasha's Rule

> Fluorescence (and phosphorescence) occurs from the **lowest excited state** of a given multiplicity, regardless of which state was initially excited.

This is because internal conversion and vibrational relaxation are faster than emission.

Mirror Image Rule

The fluorescence spectrum is often approximately the mirror image of the $S_0 \rightarrow S_1$ absorption band, shifted to longer wavelength. This arises because:

- Absorption: $v'' = 0 \rightarrow v' = 0, 1, 2, \ldots$ (vibrational progression in S_1)
- Fluorescence: $v' = 0 \rightarrow v'' = 0, 1, 2, \ldots$ (vibrational progression in S_0)

> [!NOTE] **Concept Check 39.1** Fluorescence is almost always observed at a longer wavelength than the corresponding absorption. What is this phenomenon called, and what physical process (occurring immediately after absorption) is responsible for it?

3. Phosphorescence

Characteristics

- **Spin-forbidden**: $T_1 \to S_0$ ($\Delta S = -1$)
- **Slow**: lifetime $\tau_p \sim 10^{-3}$–10^2 s (milliseconds to seconds)
- **Lower energy** than fluorescence: $T_1 < S_1$ (exchange stabilization)
- Requires **intersystem crossing** ($S_1 \to T_1$), enhanced by spin-orbit coupling

Heavy Atom Effect

Heavy atoms (Br, I, transition metals) increase spin-orbit coupling, which:

- Enhances ISC ($S_1 \to T_1$)
- Increases phosphorescence intensity
- Decreases fluorescence (competing pathway)

> [!NOTE] **Concept Check 39.2** How does the "heavy atom effect" influence the competition between fluorescence and phosphorescence? Which process is enhanced by the presence of a heavy atom like Iodine?

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4. Quantum Yield and Lifetimes

Fluorescence Quantum Yield

$\Phi_f = \frac{\text{photons emitted}}{\text{photons absorbed}} = \frac{k_f}{k_f + k_{IC} + k_{ISC}}$

where k_f, k_{IC}, and k_{ISC} are rate constants for fluorescence, internal conversion, and intersystem crossing.

Fluorescence Lifetime

$\tau_f = \frac{1}{k_f + k_{IC} + k_{ISC}}$

Quenching

Fluorescence quenching reduces Φ_f via additional deactivation pathways:

Stern-Volmer equation:

$$\frac{\Phi_f^0}{\Phi_f} = 1 + K_{SV}[Q]$$

where $[Q]$ is the quencher concentration and $K_{SV} = k_q \tau_0$ is the Stern-Volmer constant.

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5. Applications

Lasers (Light Amplification by Stimulated Emission of Radiation)

Requirements:

1. **Population inversion**: more molecules in excited state than ground state
2. **Stimulated emission**: incoming photon triggers emission of identical photon
3. **Optical cavity**: mirrors to amplify the signal

FRET (Förster Resonance Energy Transfer)

Non-radiative energy transfer between a donor and acceptor chromophore:

$$E_{\text{FRET}} = \frac{1}{1 + (r/R_0)^6}$$

where R_0 is the Förster radius (~2–8 nm). Used as a "molecular ruler" in biochemistry.

Photodynamic Therapy

- Photosensitizer absorbs light → ISC → triplet state
- Triplet transfers energy to molecular oxygen: $^3O_2 \rightarrow\, ^1O_2$ (singlet oxygen)
- Singlet oxygen destroys tumor cells

Photovoltaics

The photovoltaic effect converts light to electrical energy through:

1. Photon absorption creates electron–hole pair
2. Charge separation at a junction
3. Electrons flow through external circuit

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6. Summary of Photophysical Processes

Process	Radiative?	ΔS	Timescale	Energy change
Absorption	Yes	0	fs	↑
Fluorescence	Yes	0	ns	↓
Phosphorescence	Yes	$\neq 0$	ms–s	↓
IC	No	0	ps–ns	↓
ISC	No	$\neq 0$	ns–ms	↓
VR	No	0	ps	↓

Key Equations Summary

Equation	Expression
Quantum yield	$\Phi_f = k_f/(k_f + k_{IC} + k_{ISC})$
Lifetime	$\tau = 1/(k_f + k_{IC} + k_{ISC})$
Stern-Volmer	$\Phi_f^0/\Phi_f = 1 + K_{SV}[Q]$
FRET efficiency	$E = 1/[1 + (r/R_0)^6]$
Stokes shift	$\Delta\tilde{\nu} = \tilde{\nu}_{abs} - \tilde{\nu}_{em} > 0$

Recent Literature Spotlight

"Highly Efficient Organic Light-Emitting Diodes from Delayed Fluorescence" *H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi*, Nature, **2012**, 492, 234–238. DOI

This landmark paper introduced thermally activated delayed fluorescence (TADF) as a mechanism for achieving nearly 100% internal quantum efficiency in organic LEDs without heavy metals. By engineering a small singlet-triplet energy gap (ΔE_{ST}) through twisted donor-acceptor molecular design, the authors enabled reverse intersystem crossing ($T_1 \rightarrow S_1$) — directly exploiting the singlet/triplet state energetics and spin selection rules covered in this lecture.

Practice Problems

1. **Jablonski diagram.** A molecule has $k_f = 10^8$ s⁻¹, $k_{IC} = 10^7$ s⁻¹, $k_{ISC} = 5 \times 10^7$ s⁻¹. Calculate (a) the fluorescence lifetime, (b) the fluorescence quantum yield, and (c) the phosphorescence yield (assuming all ISC leads to phosphorescence).

2. **Stern-Volmer.** A fluorescent probe has $\tau_0 = 5$ ns. Adding a quencher at 0.01 M reduces the fluorescence intensity by 30%. Calculate K_{SV} and k_q.

3. **Heavy atom effect.** Explain why naphthalene shows strong fluorescence but weak phosphorescence, while 1-bromonaphthalene shows weak fluorescence but strong phosphorescence.

Next week: Computational Chemistry, NMR Spectroscopy & Course Review