

Absorption and Emission in Molecular Spectroscopy

Electronic Transitions

Ground state (S_0) \rightarrow Excited states (S_1, S_2, \dots)

$$\Delta E = E_{\text{excited}} - E_{\text{ground}} = h\nu$$

Allowed transitions follow selection rules

Vibrational Modes

Molecular vibrations (stretching, bending)

IR absorption region

Fine structure in spectra

Characteristic frequencies for bonds

Selection Rules

Allowed: $\Delta l = \pm 1$ (dipole transitions)

Spin: $\Delta S = 0$ (singlet-singlet)

Symmetry: Determines intensity

Forbidden: Weak but observable

Stokes Shift

$$\lambda_{\text{emission}} > \lambda_{\text{excitation}}$$

Energy loss to vibrations

Typically 20-100 nm shift

Enables fluorescence detection

Quantum Yield (Φ)

$\Phi = \text{photons emitted} / \text{photons absorbed}$

Range: 0-1 (0-100%)

High $\Phi \rightarrow$ bright fluorophores

GFP: $\Phi \approx 0.79$

Detailed Explanations with Diagrams

1. Vibrational Modes

Molecules are not rigid structures but vibrate continuously at characteristic frequencies. These vibrations can be classified into different modes based on the atomic motion patterns.

Types of Vibrational Modes:

- **Symmetric Stretching:** Bonds extend and contract in phase
- **Asymmetric Stretching:** Bonds extend and contract out of phase
- **Bending (Scissoring):** Bond angles change periodically
- **Rocking, Wagging, Twisting:** More complex molecular deformations

Energy Levels:

Vibrational energy is quantized according to:

$$E_v = h\nu (v + 1/2)$$

where $v = 0, 1, 2, \dots$ is the vibrational quantum number

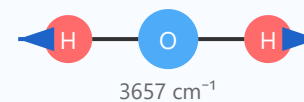
Example: Water (H_2O) has three vibrational modes:

- Symmetric stretch: $\sim 3657\text{ cm}^{-1}$
- Asymmetric stretch: $\sim 3756\text{ cm}^{-1}$
- Bending: $\sim 1595\text{ cm}^{-1}$

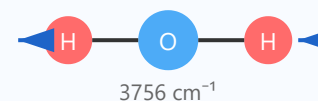
These frequencies are in the infrared region and are unique molecular fingerprints.

Vibrational Modes of H_2O

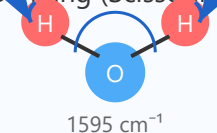
Symmetric Stretch



Asymmetric Stretch



Bending (Scissoring)



2. Selection Rules

Selection rules determine which electronic transitions are allowed or forbidden based on quantum mechanical principles. These rules govern the intensity and probability of spectroscopic transitions.

Key Selection Rules:

- **Orbital Angular Momentum ($\Delta l = \pm 1$):** For atomic transitions, the orbital quantum number must change by exactly one unit. This corresponds to electric dipole transitions.
- **Spin Selection Rule ($\Delta S = 0$):** The total spin must not change during the transition. This means singlet-to-singlet or triplet-to-triplet transitions are allowed, but singlet-to-triplet are forbidden.
- **Laporte Rule (Parity):** Transitions must involve a change in parity ($g \leftrightarrow u$ for centrosymmetric molecules).

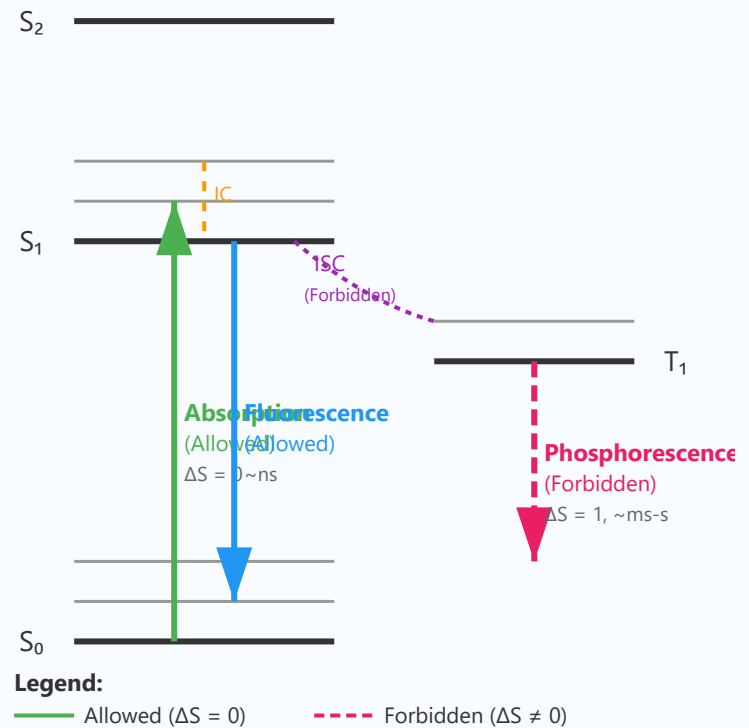
Forbidden Transitions:

"Forbidden" transitions can still occur but with much lower probability due to:

- Spin-orbit coupling (allows $S_0 \rightarrow T_1$ transitions)
- Vibronic coupling (mixing of electronic and vibrational states)
- Magnetic dipole or electric quadrupole mechanisms

Example: In fluorescence, the $S_1 \rightarrow S_0$ transition is spin-allowed ($\Delta S = 0$) and typically occurs in nanoseconds. In contrast, phosphorescence ($T_1 \rightarrow S_0$) is spin-forbidden ($\Delta S = 1$) and occurs over milliseconds to seconds, making it much weaker.

Jablonski Diagram



3. Stokes Shift

The Stokes shift is the difference between the wavelength positions of the absorption and emission maxima. This phenomenon is named after Irish physicist George Gabriel Stokes who first observed it in 1852.

Physical Origin:

- **Vibrational Relaxation:** After photon absorption to S_1 , the molecule rapidly relaxes to the lowest vibrational level of S_1 through non-radiative processes (~ps timescale)
- **Energy Dissipation:** This energy is converted to heat in the surrounding medium
- **Lower Energy Emission:** Fluorescence occurs from this relaxed state, resulting in longer wavelength (lower energy) emission
- **Solvent Reorganization:** Excited state has different charge distribution, causing solvent molecules to reorient

Magnitude:

$$\text{Stokes Shift} = \lambda_{\text{em}} - \lambda_{\text{abs}}$$

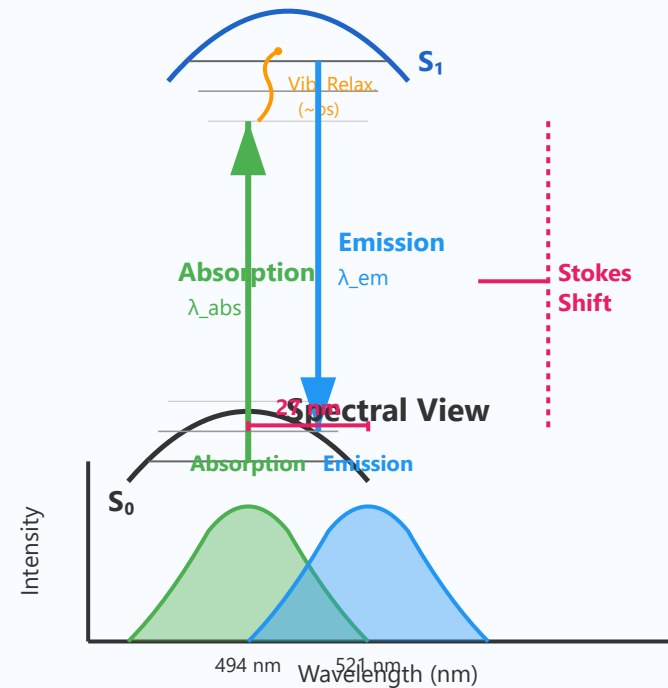
Typical values: 20-100 nm for organic fluorophores

Practical Importance:

- Enables spectral separation of excitation and emission
- Reduces self-absorption and inner filter effects
- Allows efficient fluorescence detection with minimal scattered light interference
- Critical for fluorescence microscopy and sensing applications

Example: Fluorescein has an absorption maximum at 494 nm and emission maximum at 521 nm, giving a Stokes shift of 27 nm. This shift allows use of dichroic mirrors to separate excitation and emission light in fluorescence microscopy.

Stokes Shift Visualization



4. Quantum Yield (Φ)

Quantum yield is the efficiency of the fluorescence process, representing the ratio of photons emitted to photons absorbed. It is a crucial parameter for characterizing fluorophores and determining their practical utility.

Definition:

$$\Phi = \frac{\text{(Number of photons emitted)}}{\text{(Number of photons absorbed)}}$$

Rate Constant Perspective:

Quantum yield can also be expressed in terms of rate constants:

$$\Phi = \frac{k_r}{k_r + k_{nr}}$$

where k_r is the radiative rate constant and k_{nr} is the sum of all non-radiative rate constants

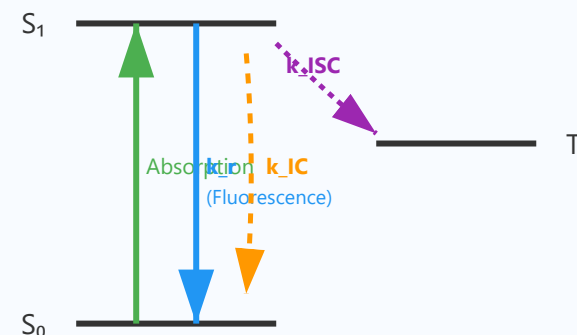
Non-radiative Deactivation Pathways:

- **Internal Conversion (IC):** $S_1 \rightarrow S_0$ without radiation
- **Intersystem Crossing (ISC):** $S_1 \rightarrow T_1$ (spin forbidden)
- **Collisional Quenching:** Energy transfer to other molecules
- **Photochemical Reactions:** Chemical bond breaking or formation

Factors Affecting Quantum Yield:

- Molecular rigidity (rigid molecules have higher Φ)
- Heavy atom effects (increase ISC, decrease Φ)

Quantum Yield Competition



Quantum Yield Formula

$$\Phi = \frac{k_r}{k_r + k_{IC} + k_{ISC} + \dots}$$

Examples of Different Quantum Yields

Fluorescein
 $\Phi = 0.92$

Very Bright
 $k_r \gg k_{nr}$

Tryptophan
 $\Phi = 0.14$

Moderate
 $k_r \approx k_{nr}$

Azulene
 $\Phi \approx 0$

Non-fluor.
 $k_r \ll k_{nr}$

- Temperature (higher T increases non-radiative decay)
- Solvent polarity and viscosity
- pH for molecules with ionizable groups

Examples of Quantum Yields:

- **Fluorescein (pH 9):** $\Phi \approx 0.92$ (very bright)
- **GFP:** $\Phi \approx 0.79$ (excellent for bioimaging)
- **Tryptophan:** $\Phi \approx 0.14$ (moderate)
- **Benzene:** $\Phi \approx 0.05$ (weak fluorophore)
- **Azulene:** $\Phi \approx 0.00001$ (essentially non-fluorescent)

High quantum yield fluorophores are preferred for imaging and sensing applications.