

Photochemistry

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Unit 1 – Photochemistry: Light-Matter Interactions

1.1 Nature of light and electromagnetic spectrum

Light exhibits a dual nature: it behaves as both a wave and a particle. This duality is the foundation of photochemistry, explaining everything from interference patterns to the photoelectric effect. Understanding how light carries and delivers energy to molecules is essential before diving into any photochemical process.

The electromagnetic spectrum stretches from low-energy radio waves to high-energy gamma rays, but photochemistry focuses primarily on the narrow visible band (380–750 nm) and nearby UV region. These wavelengths carry enough energy to excite electrons in molecules, driving reactions like photosynthesis, vision, and photocatalysis.

Electromagnetic Radiation and Light

Wave-particle duality of light

Light doesn't fit neatly into one category. Sometimes it behaves like a wave, sometimes like a stream of particles. Both descriptions are correct, and you need both to fully explain how light interacts with matter.

Wave behavior shows up in phenomena you can observe directly:

- Interference — in the double-slit experiment, light passing through two narrow slits creates alternating bright and dark bands on a screen, just as overlapping water waves reinforce or cancel each other
- Diffraction — light bends around obstacles or spreads after passing through a narrow opening
- Refraction — light changes speed and direction when moving between media (e.g., air to glass), which is why a straw looks bent in water

Particle behavior appears when light interacts with matter at the quantum level:

- Photoelectric effect — light striking a metal surface ejects electrons, but only if the light's frequency exceeds a threshold. Increasing intensity (brightness) alone won't work if the frequency is too low. This was the observation Einstein explained by proposing that light comes in discrete energy packets called photons.
- Compton scattering — X-ray photons collide with electrons and lose energy, shifting to longer wavelengths, exactly as you'd expect from a particle collision.

Each photon carries a specific amount of energy given by:

$$E = h\nu$$

where h is Planck's constant (6.626×10^{-34} J·s) and ν is the frequency of the light.

Historical progression: Classical physics treated light purely as a wave, described by Maxwell's electromagnetic equations (1860s). Planck introduced energy quantization in 1900 to explain blackbody radiation, and Einstein extended this in 1905 by proposing that light itself is quantized into photons. Together, these ideas launched quantum theory.

Regions of the electromagnetic spectrum

The electromagnetic spectrum is a continuum of radiation organized by wavelength (or equivalently, frequency and energy). Here are the major regions, from lowest to highest energy:

Region	Wavelength	Photon Energy	Common Uses
Radio waves	> 1 m	< 1.24 μeV	AM/FM radio, telecommunications
Microwaves	1 m – 1 mm	1.24 μeV – 1.24 meV	Cooking, radar
Infrared	1 mm – 750 nm	1.24 meV – 1.65 eV	Thermal imaging, IR spectroscopy
Visible light	750 nm – 380 nm	1.65 eV – 3.26 eV	Vision, photochemistry
Ultraviolet	380 nm – 10 nm	3.26 eV – 124 eV	Sterilization, sunburns
X-rays	10 nm – 0.01 nm	124 eV – 124 keV	Medical imaging, crystallography
Gamma rays	< 0.01 nm	> 124 keV	Radioactive decay, cancer treatment

For photochemistry, the visible and UV regions matter most. These photons have enough energy (roughly 1.5–6 eV) to promote electrons into higher-energy molecular orbitals, which is the first step in any photochemical reaction.

Wavelength, frequency, and energy relationships

Three equations tie together the key properties of light. They're worth knowing cold.

1. Speed of light equation: $c = \lambda \nu$

This says the speed of light ($c = 3.00 \times 10^8$ m/s in vacuum) equals wavelength times frequency. Since c is constant, wavelength and frequency are inversely related: longer wavelength means lower frequency, and vice versa.

1. Photon energy: $E = h\nu$

Energy is directly proportional to frequency. Higher frequency means more energy per photon.

1. Combining the two: $E = \frac{hc}{\lambda}$

Substituting $\nu = \frac{c}{\lambda}$ into the energy equation gives you energy in terms of wavelength. Energy is inversely proportional to wavelength: shorter wavelengths pack more energy.

Quick summary of relationships:

- Wavelength $\uparrow \rightarrow$ Frequency $\downarrow \rightarrow$ Energy $\downarrow$ (radio waves: long wavelength, low energy)
- Wavelength $\downarrow \rightarrow$ Frequency $\uparrow \rightarrow$ Energy $\uparrow$ (gamma rays: short wavelength, high energy)

Example calculation: What's the energy of a green photon at 520 nm?

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(3.00 \times 10^8)}{520 \times 10^{-9}} = 3.82 \times 10^{-19} \text{ J} \approx 2.39 \text{ eV}$$

That 2.39 eV is enough to trigger electronic transitions in many organic chromophores.

Visible light in photochemistry

The visible spectrum (380–750 nm) is a small slice of the electromagnetic spectrum, but it's where most photochemistry happens. The approximate color breakdown:

- Violet: 380–450 nm
- Blue: 450–495 nm
- Green: 495–570 nm
- Yellow: 570–590 nm
- Orange: 590–620 nm
- Red: 620–750 nm

When a molecule absorbs a visible photon, the energy promotes an electron from a lower-energy orbital to a higher one. This is called an electronic transition, and it occurs in the part of the molecule known as the chromophore (the light-absorbing group).

Several major processes depend on visible-light absorption:

- Photosynthesis — Chlorophyll absorbs strongly in the red (~680 nm) and blue (~430 nm) regions, which is why plants appear green (they reflect green light). The absorbed energy drives the conversion of CO_2 and H_2O into glucose.
- Vision — The protein rhodopsin in your retinal cells contains a chromophore called retinal. When retinal absorbs a photon, it undergoes photoisomerization (a light-driven shape change from cis to trans), triggering a nerve signal to the brain.
- Photocatalysis — Materials like titanium dioxide (TiO_2) absorb light and generate reactive species on their surfaces, useful for breaking down pollutants or splitting water.
- Photovoltaics — Solar cells absorb visible photons to generate electrical current. Solar radiation peaks in the visible range, which is why this region is so important for energy applications.

Analytical techniques also rely on visible light. UV-Vis spectroscopy measures which wavelengths a sample absorbs, revealing information about electronic structure and concentration. Fluorescence spectroscopy detects light that molecules re-emit after absorbing photons, useful for identifying and quantifying specific compounds.

1.2 Light-matter interactions: absorption, emission, and scattering

Light-Matter Interactions: Fundamental Processes

Light-matter interactions form the basis of photochemistry. Every photochemical process begins when light encounters a molecule, and the outcome depends on whether that light is absorbed, emitted, or scattered. Understanding these three processes is essential for interpreting spectroscopic data and designing photochemical reactions.

When molecules absorb light, electrons are promoted to higher energy states. These transitions follow quantum mechanical selection rules and can lead to several outcomes: fluorescence, phosphorescence, non-radiative decay, or photochemical reaction.

Absorption vs. Emission vs. Scattering

Absorption occurs when matter takes in photon energy, causing an electron to jump to a higher energy state. This only happens when the photon's energy matches the energy gap between two electronic states. Absorption decreases the intensity of transmitted light, which is the basis of UV-visible spectroscopy.

Emission is the reverse: an excited electron returns to a lower energy level and releases a photon. There are two types:

- Spontaneous emission occurs without any external trigger. Fluorescence is a common example.
- Stimulated emission occurs when an incoming photon prompts an excited molecule to emit a second, identical photon. This is the principle behind lasers.

Scattering involves a change in the direction of light upon interacting with matter. Unlike absorption, the molecule doesn't retain the photon's energy.

- Elastic scattering (Rayleigh): the scattered photon keeps its original wavelength. This is why the sky appears blue, since shorter wavelengths scatter more strongly.
- Inelastic scattering (Raman): the scattered photon gains or loses energy, shifting its wavelength. Raman spectroscopy exploits this effect to probe molecular vibrations.

Electronic Transitions in Light Interactions

Electronic transitions occur when electrons move between quantized energy levels in atoms or molecules. Quantum mechanical selection rules determine which transitions are "allowed" (high probability) and which are "forbidden" (low probability, but not necessarily zero).

During absorption, an electron jumps from the ground state to an excited state by absorbing a photon of the correct energy. The Franck-Condon principle governs which vibrational level the electron lands in: transitions are most probable when the vibrational wavefunctions of the initial and final states have maximum overlap. Because nuclei are much heavier than electrons, the nuclear geometry doesn't change during the electronic transition (a vertical transition on a potential energy diagram).

During emission, the excited electron drops back to the ground state and releases a photon whose energy equals the energy difference between the two states involved.

The common types of electronic transitions, ordered from highest to lowest energy:

- $\sigma \rightarrow \sigma^*$: requires high-energy UV light. Found in saturated molecules like alkanes, which is why they're transparent in the near-UV and visible range.
- $n \rightarrow \sigma^*$: moderate-energy UV transitions. Seen in molecules with lone pairs on heteroatoms, such as alcohols and amines.
- $\pi \rightarrow \pi^*$: lower energy, often in the near-UV or visible region. Characteristic of conjugated systems like dienes and aromatic rings. These are typically strong, allowed transitions.
- $n \rightarrow \pi^*$: also lower energy, but these transitions are symmetry-forbidden, making them weaker (lower molar absorptivity). Common in carbonyl compounds like ketones and aldehydes.

Photoluminescence and Efficiency Factors

Principles of Fluorescence and Phosphorescence

Fluorescence is a rapid emission process, typically occurring on the nanosecond timescale. The transition occurs between states of the same spin multiplicity (usually $S_1 \rightarrow S_0$, singlet-to-singlet). Before emission, the molecule undergoes vibrational relaxation within the excited state, losing some energy as heat. This means the emitted photon always has less energy (longer wavelength) than the absorbed photon. The difference in wavelength between absorption and emission maxima is called the Stokes shift.

Phosphorescence is a much slower process, lasting from milliseconds to even hours. Here's why it's slow:

1. The molecule absorbs light and reaches an excited singlet state (S_1).
2. Intersystem crossing (ISC) occurs: the electron's spin flips, converting the molecule to a triplet state (T_1). This spin-forbidden process is facilitated by spin-orbit coupling, which is stronger in molecules containing heavy atoms.
3. The molecule emits from $T_1 \rightarrow S_0$. Because this transition involves a change in spin multiplicity, it's formally forbidden, which is what makes it so slow.
4. Phosphorescence exhibits a larger Stokes shift than fluorescence because the triplet state is lower in energy than the corresponding singlet.

The Jablonski diagram is the standard way to visualize all of these processes. It maps out the singlet and triplet electronic states as horizontal lines, with arrows showing absorption (upward), fluorescence (downward from S_1), phosphorescence (downward from T_1), and wavy arrows for non-radiative processes like internal conversion and intersystem crossing.

Efficiency Factors in Light-Matter Interactions

Not every absorbed photon leads to emission. Several factors determine how efficiently a molecule converts absorbed light into emitted light or photochemical products.

Absorption cross-section (σ) quantifies how likely a molecule is to absorb a photon at a given wavelength. A larger cross-section means higher absorption probability. It depends on both the molecular structure and the wavelength of incident light.

Quantum yield (Φ) is the ratio of photons emitted to photons absorbed:

$$\Phi = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

A quantum yield of 1.0 means every absorbed photon produces an emitted photon. In practice, competing non-radiative pathways (internal conversion, intersystem crossing, collisional quenching) reduce the quantum yield below 1.

Factors that affect emission efficiency:

- Molecular rigidity reduces non-radiative decay. Rigid molecules like rhodamine dyes have high quantum yields because they can't easily dissipate energy through bond rotations.
- Solvent and temperature matter because collisions with solvent molecules and increased thermal motion both promote non-radiative relaxation.
- Quenchers are species that deactivate excited states through energy transfer or electron transfer, reducing emission intensity.

- Concentration can cause self-quenching at high levels, where emitted photons are reabsorbed by neighboring molecules.

Oscillator strength (f) is a dimensionless quantity that indicates the probability of an electronic transition. Higher values correspond to stronger, more probable transitions. Allowed transitions like $\pi \rightarrow \pi^*$ have oscillator strengths near 1, while forbidden transitions like $n \rightarrow \pi^*$ have values closer to 0.01 or lower.

The Beer-Lambert Law connects absorption measurements to molecular concentration:

$$A = \epsilon bc$$

- A = absorbance (dimensionless)
- ϵ = molar absorptivity ($\text{L mol}^{-1}\text{cm}^{-1}$), a measure of how strongly a substance absorbs at a given wavelength
- b = path length through the sample (cm)
- c = molar concentration (mol L^{-1})

This law assumes dilute solutions and monochromatic light. At high concentrations, deviations occur due to molecular interactions and scattering effects.

1.3 Historical development of photochemistry

Photochemistry's journey spans centuries, from ancient observations of light-induced phenomena to modern quantum theory. Early milestones include Priestley's experiments on plant growth and air quality, while the 19th century saw groundbreaking discoveries like ultraviolet light and photosynthesis.

The 20th century revolutionized photochemistry with quantum theory and advanced techniques. Einstein's photoelectric effect explanation and the development of flash photolysis opened new doors. Today, photochemistry plays a crucial role in medicine and solar energy conversion.

Historical Development of Photochemistry

Milestones in photochemistry development

- Ancient observations of light-induced phenomena shaped early understanding of photochemistry revealed fading of dyes and tanning of skin
- 18th century scientific investigations advanced understanding Joseph Priestley experimented on plant growth and air quality relationship
- 19th century laid foundation for modern photochemistry Johann Wilhelm Ritter discovered ultraviolet light Julius Robert Mayer identified photosynthesis process
- Early 20th century quantum theory revolutionized photochemistry Einstein explained photoelectric effect Stark-Einstein law developed quantifying light absorption
- Mid-20th century advanced spectroscopic techniques emerged Ronald Norrish and George Porter invented flash photolysis enabling study of short-lived intermediates
- Late 20th century to present expanded applications and interdisciplinary research photodynamic therapy in medicine developed solar energy conversion technologies advanced (perovskite solar cells)

Contributions of notable photochemists

- Theodor Grotthuss proposed first law of photochemistry in 1817 recognized light absorption necessity for photochemical reactions
- John William Draper independently formulated first law of photochemistry in 1842 conducted experiments on chemical effects of light on various substances (silver halides)
- Giacomo Ciamician pioneered organic photochemistry envisioned solar energy potential for sustainable chemical processes conducted systematic studies of photochemical reactions in organic compounds (benzophenone photoreduction)

Significance of Grotthuss-Draper law

- Law states only absorbed light produces photochemical change establishes fundamental requirement for photochemical reactions
- Emphasizes light absorption importance in photochemical processes provides basis for understanding selectivity of photochemical reactions
- Influences design of photochemical experiments and applications guides development of photocatalysts and photosensitizers (titanium dioxide)

Impact of quantum mechanics

- Quantization of energy explains discrete energy levels in atoms and molecules provides framework for understanding electronic transitions (Bohr model)
- Wave-particle duality of light reconciles wave and particle nature in photochemical processes explains phenomena like photoelectric effect
- Schrödinger equation allows calculation of molecular orbitals and energy states enables prediction of allowed electronic transitions
- Franck-Condon principle explains intensity of vibronic transitions in spectroscopy helps interpret absorption and emission spectra
- Jablonski diagram visualizes electronic states and transitions in photochemical processes aids understanding of fluorescence and phosphorescence
- Spin selection rules govern probability of transitions between different spin states explain forbidden and allowed transitions
- Quantum yield concept quantifies efficiency of photochemical reactions helps optimize reaction conditions and photocatalyst design
- Molecular orbital theory provides basis for understanding bonding and reactivity in excited states predicts photochemical reaction pathways

1.4 Applications and importance of photochemistry

Photochemistry plays a crucial role in nature and technology. From powering photosynthesis to enabling vision, natural processes harness light's energy. Meanwhile, scientists apply photochemical principles to develop materials, convert energy, and address environmental challenges.

Sustainable technologies and synthesis benefit greatly from photochemistry. Solar cells and photocatalysis drive clean energy production, while photochemical reactions enable efficient, environmentally-friendly

synthesis of complex compounds. These applications showcase photochemistry's potential to shape a greener future.

Natural Processes and Applications of Photochemistry

Photochemistry in natural processes

- Photosynthesis drives plant growth through light-dependent reactions
- Chlorophyll excitation absorbs light energy
- Electron transfer chain generates chemical energy
- ATP and NADPH production fuels carbon fixation
- Vision enables light perception in animals
- Rhodopsin photoisomerization triggers visual cascade
- Retinal conformational changes amplify signal
- Signal transduction in photoreceptor cells converts light to neural impulses
- Vitamin D synthesis maintains bone health
- UV-induced conversion of 7-dehydrocholesterol to previtamin D3 occurs in skin
- DNA damage and repair protects genetic integrity
- UV-induced formation of pyrimidine dimers distorts DNA structure
- Photolyase-mediated DNA repair reverses UV damage

Applications across scientific fields

- Materials science enhances product capabilities
- Photopolymerization enables rapid 3D printing (dental resins)
- Photochromic materials create adaptive smart windows (sunglasses)
- Photoresists facilitate precise semiconductor manufacturing (computer chips)
- Energy conversion harnesses solar power
- Photovoltaic cells generate electricity from sunlight (rooftop solar panels)
- Artificial photosynthesis mimics natural light-harvesting processes
- Photocatalytic water splitting produces clean hydrogen fuel
- Environmental chemistry addresses pollution
- Photodegradation breaks down organic pollutants (pesticides)
- Atmospheric chemistry studies ozone depletion mechanisms
- Water purification using UV light inactivates pathogens

Sustainable Technologies and Synthesis

Importance for sustainable technologies

- Solar cells convert sunlight to electricity
- Dye-sensitized solar cells offer low-cost alternatives (Grätzel cells)
- Perovskite solar cells achieve high efficiencies
- Organic photovoltaics enable flexible, lightweight panels
- Photocatalysis drives chemical transformations
- Water splitting produces clean hydrogen fuel
- CO₂ reduction converts greenhouse gas to valuable chemicals (methanol)
- Self-cleaning surfaces use light-activated titanium dioxide coatings
- Energy storage systems capture solar energy
- Photochemical energy storage mimics natural photosynthesis
- Solar fuels production creates storable energy carriers (hydrogen)
- Green chemistry reduces environmental impact
- Photochemical reactions replace energy-intensive thermal processes
- Reduced energy consumption and waste generation improve sustainability

Use in synthesis of compounds

- Photocycloaddition reactions form new rings
- [2+2] cycloadditions create four-membered rings (cyclobutanes)
- [4+4] cycloadditions yield eight-membered rings (cyclooctadienes)
- Photoisomerization alters molecular geometry
- Cis-trans isomerization of alkenes changes shape (retinal in vision)
- Azobenzene-based molecular switches enable responsive materials
- Photoredox catalysis facilitates challenging transformations
- C-C bond formation reactions build complex molecules
- Functionalization of aromatic compounds adds versatility
- Photoinduced electron transfer (PET) reactions enable unique chemistry
- Synthesis of complex natural products becomes more accessible
- Generation of reactive intermediates opens new reaction pathways
- Photochemical protection and deprotection strategies
- Orthogonal protection in multi-step synthesis increases efficiency

- Photopolymerization creates advanced materials
- Synthesis of crosslinked polymers improves material properties
- Preparation of hydrogels and biomaterials enables medical applications (contact lenses)

Unit 2 – Quantum Mechanics in Photochemistry

2.1 Basic principles of quantum mechanics

Fundamental Concepts of Quantum Mechanics

Quantum mechanics describes how matter and energy behave at the atomic and molecular scale. It replaced classical physics for these systems because classical models couldn't explain key experimental results, like the photoelectric effect or atomic emission spectra. For photochemistry, quantum mechanics is essential: it tells you why molecules absorb specific wavelengths of light, how excited states form, and what drives photochemical reactions.

Two foundational ideas run through everything here: energy is quantized (it comes in discrete packets, not continuous amounts), and particles behave as both waves and particles depending on how you observe them. The Schrödinger equation ties these ideas together mathematically.

Wave-Particle Duality of Matter

Wave-particle duality means that light and matter can exhibit both wave-like and particle-like properties, depending on the experiment. A beam of electrons, for example, produces an interference pattern in a double-slit experiment (wave behavior), yet those same electrons hit a detector at discrete points (particle behavior). This has been demonstrated not just for electrons but even for large molecules like buckminsterfullerene (C_{60}).

The de Broglie relation connects a particle's momentum to its wavelength:

$$\lambda = \frac{h}{p}$$

where h is Planck's constant (6.626×10^{-34} J·s) and p is the particle's momentum. For macroscopic objects, λ is negligibly small, which is why you don't see wave behavior in everyday life. But for electrons and other light particles, the wavelength is significant and directly affects how they interact with matter.

This duality is what forced physicists to abandon purely classical descriptions. The photoelectric effect, for instance, can only be explained by treating light as discrete photons (particles), while diffraction and interference require a wave description.

Heisenberg Uncertainty Principle

The uncertainty principle sets a fundamental limit on how precisely you can simultaneously know certain pairs of properties. For position and momentum:

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$

where $\hbar = h/2\pi$. This isn't about measurement error or imperfect instruments. It's a built-in feature of quantum systems. The more precisely you pin down a particle's position, the less precisely you can know its momentum, and vice versa.

There's also an energy-time form:

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

This version matters a lot in photochemistry. A short-lived excited state (small Δt) has a large uncertainty in energy (large ΔE), which directly broadens spectral lines. So when you see a broad absorption or emission peak, part of that width comes from the uncertainty principle limiting how well-defined the energy of a transient state can be.

The uncertainty principle also explains why we describe electrons in orbitals (probability clouds) rather than fixed orbits. You simply can't assign an electron a precise trajectory.

Quantum Mechanical Systems and Energy

Applications of the Schrödinger Equation

The time-independent Schrödinger equation is the central equation for finding the allowed energy states of a quantum system:

$$\hat{H}\Psi = E\Psi$$

Here, $\hat{H}$ is the Hamiltonian operator (which encodes the total energy of the system), Ψ is the wavefunction, and E is the energy of that state. Solving this equation for a given system gives you both the allowed energies and the corresponding wavefunctions.

Particle in a box is the simplest model and a good starting point. Imagine a particle confined to a one-dimensional box of length L with infinitely high walls. Solving the Schrödinger equation with the boundary condition that $\Psi = 0$ at the walls gives:

- Energy levels: $E_n = \frac{n^2 h^2}{8mL^2}$, where $n = 1, 2, 3, \dots$

- Wavefunctions: $\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$

Notice that n can only be a positive integer, so energy is automatically quantized. The number of nodes (zero-crossings) in the wavefunction increases with n , and higher n means higher energy.

The quantum harmonic oscillator models molecular vibrations. A diatomic molecule's bond stretching, near equilibrium, behaves approximately like a harmonic oscillator with energy levels:

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega$$

The $\frac{1}{2} \hbar \omega$ term is the zero-point energy, meaning a molecule always retains some vibrational energy even at absolute zero. This has real consequences for photochemistry, since it affects the baseline energy from which electronic transitions occur.

For any wavefunction, the probability density $|\Psi|^2$ tells you the likelihood of finding the particle at a given location. This is how quantum mechanics replaces the classical idea of a definite trajectory with a probability distribution.

Quantization of Energy

Quantum mechanics explains why atoms and molecules have discrete energy levels rather than a continuous range. This is what produces the sharp lines in atomic emission spectra and the structured bands in molecular spectra.

Atomic orbitals are described by four quantum numbers:

- n (principal): determines the energy level and size of the orbital
- l (angular momentum): determines the orbital shape ($l = 0$ is s, $l = 1$ is p, $l = 2$ is d, $l = 3$ is f)

- m_l (magnetic): determines the orbital's orientation in space
- m_s (spin): specifies the electron's spin ($+\frac{1}{2}$ or $-\frac{1}{2}$)

Molecular orbitals form when atomic orbitals on different atoms combine. The LCAO (linear combination of atomic orbitals) approach produces bonding orbitals (lower energy, electron density between nuclei) and antibonding orbitals (higher energy, node between nuclei). The energy gap between these orbitals determines what wavelengths of light a molecule can absorb.

Spectroscopic transitions occur when a photon's energy matches the gap between two allowed energy levels. Not all transitions are equally probable; selection rules, derived from quantum mechanical considerations of symmetry and angular momentum, dictate which transitions are allowed and which are forbidden. For example, in atomic spectra the rule $\Delta l = \pm 1$ governs which orbital transitions can occur.

These electronic transitions are at the heart of photochemistry. When a molecule absorbs a photon and moves to an excited electronic state, the resulting energy can drive chemical reactions. Photosynthesis and the chemistry of vision both depend on specific electronic excitations that quantum mechanics predicts and explains.

2.2 Atomic and molecular orbitals

Atomic and Molecular Orbitals

Atomic and molecular orbitals describe where electrons are most likely found, first around individual atoms and then within molecules. In photochemistry, these orbitals matter because light absorption and emission involve electrons moving between them. This section covers the quantum mechanical description of atomic orbitals, how they combine into molecular orbitals via LCAO theory, and how to read molecular orbital diagrams to predict bond strength and magnetic behavior.

Atomic Orbitals

Atomic and Molecular Orbital Properties

An atomic orbital is a mathematical function that describes the probability of finding an electron in a region of space around a single atom. Each orbital is fully specified by four quantum numbers:

- n (principal): determines the energy level and overall size of the orbital ($n = 1, 2, 3, \dots$)
- l (angular momentum): determines the orbital shape ($l = 0$ for s, $l = 1$ for p, $l = 2$ for d, $l = 3$ for f)
- m_l (magnetic): determines the orbital's orientation in space ($m_l = -l, \dots, 0, \dots, +l$)
- m_s (spin): specifies the electron's intrinsic spin ($+\frac{1}{2}$ or $-\frac{1}{2}$)

A molecular orbital extends over an entire molecule rather than a single atom. Molecular orbitals form when atomic orbitals on neighboring atoms combine, producing three possible types:

- Bonding orbitals concentrate electron density between nuclei, stabilizing the molecule.
- Antibonding orbitals (marked with an asterisk, e.g., σ^*) place a node between nuclei, destabilizing the molecule.
- Non-bonding orbitals remain localized on one atom and don't significantly affect bond strength.

Types of Atomic Orbitals

Each orbital type has a characteristic shape, a set number of orientations per energy level, and a specific count of angular nodes (equal to l):

- s orbitals ($l = 0$): spherical, one orbital per energy level, zero angular nodes. Examples: 1s, 2s, 3s. Each higher n adds a radial node, but the overall shape stays spherical.
- p orbitals ($l = 1$): dumbbell-shaped, three orientations per level (p_x, p_y, p_z), one angular node each. These first appear at $n = 2$.
- d orbitals ($l = 2$): mostly cloverleaf-shaped (with one "doughnut-plus-lobes" exception, d_{z^2}), five orientations per level, two angular nodes. First appear at $n = 3$.
- f orbitals ($l = 3$): more complex multi-lobed shapes, seven orientations per level, three angular nodes. First appear at $n = 4$.

For photochemistry, the shapes and symmetry labels of these orbitals directly determine which electronic transitions are allowed when a molecule absorbs light.

Molecular Orbitals

Formation of Molecular Orbitals

Molecular orbitals are constructed using the Linear Combination of Atomic Orbitals (LCAO) method. The idea: take the wave functions of atomic orbitals on two (or more) atoms and add or subtract them to produce new wave functions that span the molecule.

1. Identify atomic orbitals of similar energy and compatible symmetry on neighboring atoms. Orbitals must belong to the same symmetry representation to combine effectively.
2. Add the wave functions (constructive interference). The resulting bonding orbital has increased electron density between the nuclei and sits lower in energy than the original atomic orbitals.
3. Subtract the wave functions (destructive interference). The resulting antibonding orbital has a node between the nuclei and sits higher in energy than the original atomic orbitals.

Two important symmetry types arise from how the orbitals overlap:

- σ bonds: head-on overlap along the internuclear axis (e.g., two s orbitals, or two p_z orbitals pointing at each other). Cylindrically symmetric about the bond axis.
- π bonds: side-on overlap above and below (or in front of and behind) the internuclear axis (e.g., p_x with p_x). These have a nodal plane containing the bond axis.

Each bonding combination produces a corresponding antibonding counterpart (σ^* , π^*). In photochemistry, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are among the most common excitations triggered by UV-visible light.

Molecular Orbital Diagrams

An MO diagram is a visual map of the molecular orbital energy levels, showing which orbitals electrons occupy. Here's how to build and read one for a homonuclear diatomic:

1. Draw the atomic orbital energy levels for each atom on the left and right sides of the diagram.

2. Connect atomic orbitals of matching symmetry to the molecular orbitals they form in the center column. Place bonding orbitals below and antibonding orbitals above the parent atomic orbital energies.
3. Fill electrons from lowest energy up, following the Aufbau principle, Pauli exclusion (max two electrons per orbital, opposite spins), and Hund's rule (maximize unpaired spins in degenerate orbitals).

Energy level ordering has a subtlety worth knowing. For O_2 , F_2 , and Ne_2 , the expected ordering holds: $\sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}^*$. But for Li_2 through N_2 , s-p mixing pushes the σ_{2p} orbital above the π_{2p} orbitals. Forgetting this switch is a common mistake.

Bond order quantifies bond strength:

$$\text{Bond order} = \frac{(\text{bonding electrons}) - (\text{antibonding electrons})}{2}$$

- N_2 : 10 electrons total, 8 bonding, 2 antibonding $\rightarrow$ bond order = 3 (triple bond, very strong).
- O_2 : 12 electrons total, 8 bonding, 4 antibonding $\rightarrow$ bond order = 2 (double bond).
- A bond order of 0 means the molecule won't form (e.g., He_2).

Higher bond order corresponds to shorter, stronger bonds.

Magnetic properties follow directly from the diagram:

- Paramagnetic: the molecule has unpaired electrons and is attracted to a magnetic field. O_2 is paramagnetic because its two highest-energy electrons occupy separate degenerate π_{2p}^* orbitals with parallel spins.
- Diamagnetic: all electrons are paired, and the molecule is weakly repelled by a magnetic field. N_2 is diamagnetic.

The fact that MO theory correctly predicts O_2 's paramagnetism, while Lewis structures do not, is one of the strongest arguments for the MO approach. For photochemistry specifically, knowing which orbitals are occupied and which are empty tells you exactly which electronic transitions are possible when a photon arrives.

2.3 Electronic configurations and energy levels

Electronic Configuration Principles

Electronic configurations describe how electrons occupy orbitals in atoms and molecules. In photochemistry, these configurations matter because they determine which electronic transitions are possible when a molecule absorbs light, and that directly controls photochemical reactivity.

Electronic configurations of atoms and ions

Electrons fill orbitals according to three foundational rules:

- Aufbau principle: Electrons occupy the lowest-energy orbitals first. The filling order is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p. The reason 4s fills before 3d is that interelectron repulsion and shielding effects make 4s slightly lower in energy for neutral atoms of that row.
- Hund's rule: When filling orbitals of equal energy (degenerate orbitals), electrons occupy them singly with parallel spins before any pairing occurs. This maximizes total spin angular momentum and minimizes electron-electron repulsion.

- Pauli exclusion principle: No two electrons in an atom can share the same set of four quantum numbers (n, l, m_l, m_s). In practice, this means each orbital holds at most two electrons, and they must have opposite spins.

Notation shortcuts: Orbital diagrams use boxes with arrows ($\uparrow \downarrow$) to show individual electrons. Shorthand notation uses the noble gas core plus valence electrons. For example, sodium is written as $[\text{Ne}]3s^1$ rather than writing out $1s^2 2s^2 2p^6 3s^1$.

Ground state vs excited state configurations

The ground state is the lowest-energy arrangement of electrons, following all three rules above. An excited state results when one or more electrons absorb energy and move to a higher-energy orbital, violating the Aufbau filling order.

Take beryllium as an example. Its ground state configuration is $1s^2 2s^2$. If one of the 2s electrons absorbs a photon and jumps to the 2p orbital, the excited state becomes $1s^2 2s^1 2p^1$. This distinction between ground and excited states is central to photochemistry because photon absorption is what creates excited states, and excited-state molecules have fundamentally different reactivity than ground-state ones.

Valence electrons (those in the outermost shell) are the ones that participate in bonding and are most commonly involved in electronic transitions. Core electrons sit much closer to the nucleus and are tightly bound, so they rarely participate in photochemical processes.

In molecules, molecular orbital (MO) theory extends these ideas. Atomic orbitals on adjacent atoms combine to form bonding orbitals (lower energy, stabilizing) and antibonding orbitals (higher energy, destabilizing). In H_2 , for instance, two 1s orbitals combine into one σ bonding orbital and one σ^* antibonding orbital. Photochemical excitation often promotes an electron from a bonding or nonbonding orbital into an antibonding orbital.

Energy levels and electronic transitions

Energy levels in atoms and molecules are quantized, meaning electrons can only exist in discrete energy states described by quantum numbers. Transitions between these levels involve absorbing or emitting photons whose energy matches the gap: $\Delta E = h\nu$.

Not all transitions are equally probable. Selection rules determine which transitions are "allowed" (strong absorption) versus "forbidden" (weak or absent):

- The orbital angular momentum quantum number must change by one: $\Delta l = \pm 1$
- The magnetic quantum number can change by: $\Delta m_l = 0, \pm 1$
- For multi-electron atoms, additional rules apply to total spin ($\Delta S = 0$ for spin-allowed transitions)

Spectroscopic term symbols like $^2S_{1/2}$ or $^2P_{3/2}$ compactly encode the total spin multiplicity, orbital angular momentum, and total angular momentum of an electronic state. The format is $^{2S+1}L_J$, where S is total spin, L is total orbital angular momentum (labeled S, P, D, F...), and J is the total angular momentum quantum number.

The Franck-Condon principle is especially relevant in molecular photochemistry. It states that electronic transitions happen so fast that the nuclei don't move during the transition. The probability of a particular vibronic transition depends on the overlap between the vibrational wavefunctions of the initial and final electronic states. Transitions with greater wavefunction overlap produce stronger absorption bands.

Relative energies of electronic configurations

Several factors determine the energy ordering of electronic states:

- Principal quantum number (n) sets the main energy level. Higher n means higher energy and greater average distance from the nucleus.
- Angular momentum quantum number (l) splits each shell into subshells. Within the same n , energy generally increases as l increases ($s < p < d < f$) in multi-electron atoms due to differences in penetration and shielding.
- Effective nuclear charge (Z_{eff}): Inner electrons shield outer electrons from the full nuclear charge. Electrons in orbitals that penetrate closer to the nucleus (s orbitals, for example) experience higher Z_{eff} and are more tightly bound.
- Electron-electron repulsion: Hund's rule reflects the fact that electrons in singly occupied orbitals with parallel spins have lower repulsion energy than paired electrons. This exchange energy stabilization is why half-filled and fully filled subshells are particularly stable.
- Spin-orbit coupling: The interaction between an electron's spin and its orbital angular momentum splits energy levels into fine structure components. The classic example is the sodium D line, where the 2P state splits into $^2P_{1/2}$ and $^2P_{3/2}$, producing two closely spaced yellow emission lines.

For molecules, correlation diagrams track how atomic orbital energies evolve into molecular orbital energies as atoms approach each other. These diagrams are useful for predicting the electronic structure of diatomic molecules and understanding which MOs are occupied in ground and excited states. Hybridization models (like sp^3 in methane) offer a complementary, localized picture of bonding geometry, though MO theory provides the more complete framework for understanding photochemical transitions.

Unit 3 – Electronic Transitions and Selection Rules

3.1 Types of electronic transitions

Electronic Transitions in Photochemistry

Electronic transitions describe how electrons in molecules move between energy levels when they absorb light. The type of transition that occurs determines everything from how strongly a molecule absorbs to what kind of photochemistry it can do. Two key selection rules govern which transitions are likely, and the rest of this guide builds on that foundation.

Selection rules for electronic transitions

Selection rules predict whether a given electronic transition is "allowed" (high probability, strong absorption) or "forbidden" (low probability, weak absorption). Two rules matter most here:

Spin selection rule: Transitions are allowed only between states of the same spin multiplicity. A singlet-to-singlet transition is allowed; a singlet-to-triplet transition is forbidden. This rule arises because the photon itself carries no spin angular momentum to flip an electron's spin.

Laporte (parity) selection rule: In centrosymmetric molecules (those with an inversion center, like octahedral complexes), transitions are allowed only between orbitals of different parity ($g \rightarrow u$ or $u \rightarrow g$). Transitions between orbitals of the same parity ($g \rightarrow g$, such as d-d transitions) are forbidden.

- Allowed transitions have high molar absorptivities and produce strong bands in absorption spectra (e.g., $\pi \rightarrow \pi^*$ transitions in organic chromophores).
- Forbidden transitions still occur, just with much lower intensity (e.g., singlet-to-triplet absorption, or d-d transitions in octahedral complexes). "Forbidden" in spectroscopy doesn't mean impossible; it means the probability is greatly reduced.

Singlet-singlet vs. singlet-triplet transitions

Singlet-singlet ($S_0 \rightarrow S_1$): - Spin-allowed, so these transitions are fast and intense. - Absorption happens on a femtosecond timescale, and the resulting excited state typically has a nanosecond-scale lifetime. - These transitions dominate UV-Vis absorption spectra.

Singlet-triplet ($S_0 \rightarrow T_1$): - Spin-forbidden, so direct absorption is extremely weak. You rarely see this transition in a normal absorption spectrum. - Triplet states are instead populated indirectly through intersystem crossing (ISC), where a molecule in S_1 crosses over to T_1 . - Triplet excited states are long-lived (microseconds to seconds) because the return trip ($T_1 \rightarrow S_0$, phosphorescence) is also spin-forbidden.

Spin-orbit coupling is the main mechanism that relaxes the spin selection rule and makes ISC possible. It mixes singlet and triplet character, and it scales with atomic number. That's why molecules containing heavy atoms like bromine or iodine show much more efficient ISC and stronger phosphorescence. This is called the heavy atom effect.

Characteristics of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions

These are the two most important transition types in organic photochemistry.

$n \rightarrow \pi^*$ transitions promote a non-bonding (lone pair) electron into an antibonding π^* orbital. - Found in molecules with heteroatoms carrying lone pairs: carbonyls (C=O), imines (C=N), azo groups (N=N). - Typically low energy (long wavelength) but weak intensity, with molar absorptivities often below $\epsilon \approx 100 \text{ L mol}^{-1}\text{cm}^{-1}$. They appear as shoulder peaks or broad, low bands. - The weakness comes from poor spatial overlap between the non-bonding orbital (in the molecular plane) and the π^* orbital (above/below the plane). - Show a characteristic blue shift (hypsochromic shift) in polar solvents, because polar solvents stabilize the ground-state lone pair through hydrogen bonding more than they stabilize the excited state.

$\pi \rightarrow \pi^*$ transitions promote a bonding π electron into an antibonding π^* orbital. - Found in conjugated systems: aromatics, polyenes, enones. - Higher energy (shorter wavelength) than $n \rightarrow \pi^*$ in the same molecule, but much stronger intensity, often with $\epsilon > 10,000 \text{ L mol}^{-1}\text{cm}^{-1}$. They produce sharp, well-defined peaks. - Show a slight red shift in polar solvents (the excited state is more polarizable), but the solvent sensitivity is much less dramatic than for $n \rightarrow \pi^*$.

Quick comparison:

Property	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
Intensity (ϵ)	Weak (10–100)	Strong (1,000–100,000+)
Energy (same chromophore)	Lower	Higher
Solvent shift in polar solvents	Blue shift	Slight red shift
Orbital overlap	Poor	Good

Electronic transitions in inorganic complexes

Inorganic complexes show a richer variety of transitions because metals bring d (and sometimes f) orbitals into play.

d-d transitions involve electron promotion between crystal-field-split d orbitals. In octahedral complexes, these are Laporte-forbidden (both the initial and final orbitals have g symmetry), so they are weak ($\epsilon \approx 1\text{--}50$). They are, however, responsible for the characteristic colors of many transition metal compounds. Copper(II) sulfate's blue color, for example, comes from a d-d transition.

Charge transfer (CT) transitions move electron density between the metal and its ligands. Because they are both spin- and Laporte-allowed, they tend to be very intense ($\epsilon > 1,000$).

- MLCT (metal-to-ligand charge transfer): An electron moves from a metal d orbital to a ligand π^* orbital. Classic example: $[\text{Ru}(\text{bpy})_3]^{2+}$, whose strong visible absorption and long-lived excited state make it a workhorse in photocatalysis.
- LMCT (ligand-to-metal charge transfer): An electron moves from a ligand orbital to an empty metal d orbital. The deep purple of permanganate (MnO_4^-) is an LMCT transition.

Intraligand transitions are $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions localized on the ligand itself. They behave much like the same transitions in free organic molecules.

f-f transitions occur in lanthanide and actinide complexes. These are both Laporte-forbidden and often spin-forbidden, making them extremely weak. The sharp, narrow emission lines of europium and terbium complexes used in luminescent materials come from f-f transitions.

Vibronic coupling is worth noting: molecular vibrations temporarily break the perfect symmetry of a centrosymmetric complex, partially relaxing the Laporte rule. This is why d-d transitions are weak but not completely absent. Without vibronic coupling, octahedral complexes would be nearly transparent in the visible range.

3.2 Selection rules and transition probabilities

Electronic Transitions: Selection Rules and Probabilities

Selection rules for electronic transitions

Selection rules tell you which electronic transitions can actually happen (and show up in a spectrum) versus which ones are formally forbidden. They come from conservation laws and symmetry requirements in quantum mechanics.

Spin selection rule: The total spin quantum number must be conserved, so $\Delta S = 0$. This prohibits transitions between states of different spin multiplicity. A singlet-to-triplet transition, for example, is spin-forbidden. In practice, spin-orbit coupling can partially relax this rule, especially in molecules containing heavy atoms.

Laporte (parity) selection rule: In centrosymmetric molecules, transitions must involve a change in parity. Only $g \rightarrow u$ or $u \rightarrow g$ transitions are allowed. Transitions between states of the same parity ($g \rightarrow g$ or $u \rightarrow u$) are forbidden. This is discussed in more detail below.

Orbital angular momentum selection rule: For atoms, the orbital angular momentum quantum number must change by exactly one: $\Delta L = \pm 1$. This is why an $s \rightarrow p$ transition is allowed but an $s \rightarrow d$ transition is not.

Total angular momentum selection rule: The total angular momentum quantum number follows $\Delta J = 0, \pm 1$, with the added restriction that $J = 0 \rightarrow J = 0$ is forbidden.

A transition is formally "allowed" only when it satisfies all applicable selection rules simultaneously. Violating even one rule reduces the transition probability, often by orders of magnitude.

Calculation of transition dipole moments

The transition dipole moment is the central quantity that connects selection rules to measurable absorption intensities. It captures how effectively the molecule's charge distribution is reorganized during a transition.

The transition dipole moment between an initial state ψ_i and a final state ψ_f is defined as:

$$\mu_{if} = \int \psi_f^* \hat{\mu} \psi_i d\tau$$

where $\hat{\mu}$ is the electric dipole moment operator. If this integral evaluates to zero, the transition is dipole-forbidden. If it's nonzero, the transition is dipole-allowed.

Transition probability is proportional to the square of the transition dipole moment:

$$P_{if} \propto |\mu_{if}|^2$$

This is why selection rules matter so concretely: they determine whether μ_{if} is zero or nonzero, and therefore whether the transition has any measurable intensity.

Oscillator strength provides a dimensionless measure of transition intensity, connecting the quantum mechanical result to a classical oscillator framework:

$$f = \frac{4\pi m_e \nu}{3e^2 \hbar} |\mu_{if}|^2$$

Fully allowed transitions typically have f values near 1, while forbidden transitions can have f values of 10^{-3} or smaller.

Franck-Condon factors account for the overlap between vibrational wavefunctions of the initial and final electronic states. Even if the electronic part of μ_{if} is nonzero, the vibrational overlap modulates the intensity of each vibronic band within the transition. This is why electronic absorption bands often show vibrational fine structure, with some vibronic peaks stronger than others depending on the geometry change between the two electronic states.

Laporte rule in centrosymmetric molecules

The Laporte rule applies specifically to molecules with an inversion center (centrosymmetric molecules, such as octahedral complexes). It states that transitions between states of the same parity are forbidden:

Laporte rule: Only $g \rightarrow u$ and $u \rightarrow g$ transitions are allowed. Transitions $g \rightarrow g$ and $u \rightarrow u$ are forbidden.

This has direct consequences for transition metal chemistry. In octahedral complexes, all d orbitals have gerade (g) symmetry, so d-d transitions are Laporte-forbidden. This is why d-d absorption bands are characteristically weak, with molar absorptivities (ϵ) typically in the range of $1\text{--}100 \text{ M}^{-1}\text{cm}^{-1}$. By contrast, charge-transfer transitions (which are parity-allowed) often have ϵ values of $10^3\text{--}10^4 \text{ M}^{-1}\text{cm}^{-1}$ or higher.

Despite being formally forbidden, d-d transitions do occur. Several mechanisms partially break the Laporte rule:

- Vibronic coupling: Asymmetric vibrations temporarily distort the molecular geometry, removing the inversion center for brief moments. This is the most common mechanism and is why octahedral transition metal complexes are colored at all.
- Static distortions: Structural effects like the Jahn-Teller distortion permanently remove the inversion center, making the Laporte rule no longer strictly applicable.
- Spin-orbit coupling: This mixes states of different parity, partially relaxing the rule. The effect is stronger for heavier atoms (the heavy atom effect).

Factors affecting transition intensity

Several factors combine to determine how intense a spectral band actually appears:

Electronic factors: - Transition dipole moment magnitude: Larger $|\mu_{if}|^2$ values produce stronger absorptions. The $\pi \rightarrow \pi^*$ transition, for instance, is typically much more intense than $n \rightarrow \pi^*$ because the orbital overlap contributing to the transition dipole moment is greater for $\pi \rightarrow \pi^*$. - Selection rule compliance: Transitions that obey all selection rules are orders of magnitude more intense than forbidden ones. A spin-allowed, Laporte-allowed charge-transfer band will dwarf a spin-forbidden d-d band. - Franck-Condon overlap: The vibrational wavefunction overlap distributes intensity across vibronic sub-bands and determines which vibronic peak is strongest.

Environmental factors: - Solvent effects: The solvent can shift transition energies and alter intensities through changes in molecular geometry or stabilization of excited states. This phenomenon is called solvatochromism. - Temperature: Higher temperatures populate higher vibrational levels of the ground state, giving rise to "hot bands" and altering the apparent intensity distribution.

Measurement factors: - Concentration and path length determine the observed absorbance through the Beer-Lambert law: $A = \epsilon c l$. These affect the measured signal but not the intrinsic transition probability. - Spectral bandwidth of the instrument affects peak shape and resolution but does not change the integrated absorption intensity.

The key distinction to keep straight: transition dipole moments, oscillator strengths, and selection rules govern the intrinsic probability of a transition. Concentration, path length, and instrumental settings affect what you measure but not the underlying physics.

3.3 Franck-Condon principle

3.3 Franck-Condon Principle

The Franck-Condon principle explains why certain vibronic transitions in a molecule are strong while others are weak. It connects the speed of electronic transitions to the resulting vibrational structure in absorption and emission spectra, making it essential for interpreting UV-Vis spectroscopic data.

Fundamentals of the Franck-Condon Principle

Franck-Condon principle in electronic transitions

The core idea rests on the Born-Oppenheimer approximation: electrons move so much faster than nuclei that, during an electronic transition ($\sim 10^{-15}$ s), the nuclei essentially don't move. Because the nuclear positions and momenta stay frozen, the transition is drawn as a straight vertical line on a potential energy diagram. That's why these are called vertical transitions.

But which vibrational level does the molecule land in after the transition? That depends on the Franck-Condon factor, which is the square of the overlap integral between the vibrational wavefunction of the initial state and the vibrational wavefunction of the final state:

$$\text{FC factor} = |\langle \chi_{v'} | \chi_{v''} \rangle|^2$$

The larger the overlap, the more probable (and more intense) that particular vibronic transition will be. The pattern of Franck-Condon factors across all accessible vibrational levels is what shapes the intensity envelope you see in a UV-Vis spectrum.

Vibrational structure of spectra

A vibronic transition involves a simultaneous change in both electronic and vibrational quantum numbers. In a spectrum, these appear as a series of peaks called a vibrational progression, where each peak corresponds to a transition ending in a different vibrational level.

How the intensity is distributed across that progression depends on how much the equilibrium geometry changes between the two electronic states:

- Small geometry change: The best overlap is between $v = 0$ in the ground state and $v' = 0$ in the excited state. The 0-0 transition dominates, and the progression is short.
- Large geometry change: The $v = 0$ wavefunction of the ground state overlaps best with higher vibrational levels in the excited state. The 0-0 transition is weak, and the progression extends over many peaks.

The Huang-Rhys factor (S) quantifies this displacement between the two potential energy curves. A larger S means a bigger geometry change and a longer vibrational progression. The most probable transition lands near vibrational level $v' \approx S$.

Emission spectra typically originate from the lowest vibrational level of the excited state ($v' = 0$), following Kasha's rule. The resulting emission progression is often an approximate mirror image of the absorption spectrum, reflected about the 0-0 transition. Deviations from this mirror-image relationship occur when the excited-state potential energy surface has a significantly different shape than the ground state.

Advanced Concepts and Applications

Vertical transitions and Franck-Condon principle

Because the transition is vertical, the molecule arrives in the excited electronic state with its nuclei still in the ground-state equilibrium geometry. If the excited state has a different equilibrium bond length, the molecule is now in a non-equilibrium nuclear configuration and carries excess vibrational energy.

What happens next follows a predictable sequence:

1. The vertical transition populates a distribution of vibrational levels in the excited state, weighted by Franck-Condon factors.
2. Vibrational relaxation rapidly dissipates excess vibrational energy (typically on a 10^{-12} s timescale), funneling population down to $v' = 0$.
3. Emission then occurs vertically from $v' = 0$, landing on various vibrational levels of the ground state.
4. The ground state undergoes its own vibrational relaxation back to $v = 0$.

The energy lost to vibrational relaxation in both states means the emitted photon has less energy than the absorbed photon. This energy gap between the absorption maximum and the emission maximum is the Stokes shift. A larger geometry change between states produces a larger Stokes shift.

Factors in vibronic transition intensity

Several factors beyond the basic Franck-Condon overlap influence what you actually observe in a vibronic spectrum:

- **Equilibrium geometry changes:** As discussed, the magnitude and direction of bond length or angle changes between states control the breadth and peak position of the vibrational progression.
- **Symmetry considerations:** Molecular symmetry imposes selection rules on which vibronic transitions are allowed. In benzene, for example, the $S_0 \rightarrow S_1$ electronic transition is symmetry-forbidden but gains intensity through vibronic coupling with certain vibrational modes.
- **Temperature effects:** At higher temperatures, excited vibrational levels of the ground state become thermally populated. Transitions originating from these levels ($v > 0$) produce hot bands on the low-energy side of the absorption spectrum.
- **Solvent interactions:** The solvent stabilizes different electronic states to different extents, shifting and reshaping the potential energy surfaces. This leads to solvatochromism, where absorption and emission maxima shift with solvent polarity.
- **Vibronic coupling:** Interaction between electronic and vibrational motions can cause a formally forbidden electronic transition to "borrow" intensity from a nearby allowed transition. This is why some symmetry-forbidden transitions still appear in spectra, though with reduced intensity.
- **Duschinsky rotation:** The normal modes of vibration can mix (rotate in normal-mode space) between the ground and excited states. This complicates the Franck-Condon analysis because you can no longer treat each mode independently; multidimensional overlap integrals become necessary.

Unit 4 – Absorption and Emission Spectroscopy

4.1 Beer-Lambert law and absorption spectroscopy

Beer-Lambert Law and Absorption Spectroscopy

The Beer-Lambert law connects how much light a sample absorbs to the sample's concentration and the distance light travels through it. This relationship is the foundation of quantitative absorption spectroscopy, letting you figure out how much of a substance is present just by measuring how light passes through a solution.

Beer-Lambert Law Components

The core equation is:

$$A = \epsilon bc$$

Each variable has a specific physical meaning:

- A (Absorbance) — a dimensionless number that measures how much light the sample absorbs. Higher A means more light absorbed.
- ϵ (Molar attenuation coefficient) — a constant that describes how strongly a substance absorbs light at a particular wavelength. Units are $\text{L mol}^{-1}\text{cm}^{-1}$. Every compound has its own ϵ value at each wavelength, so this acts like a fingerprint for absorption strength.
- b (Path length) — the distance light travels through the sample, usually set by the width of the cuvette. Measured in cm (typically 1 cm for standard cuvettes).
- c (Concentration) — the molar concentration of the absorbing species in solution, in mol L^{-1} .

Two other quantities show up constantly alongside this equation:

- I_0 — the intensity of light entering the sample (incident light)
- I — the intensity of light that makes it through the sample (transmitted light)
- Transmittance (T) — the fraction of light that passes through: $T = I/I_0$. A value of 1 means all light passes through; 0 means none does.

Absorbance, Transmittance, and Concentration

Absorbance and transmittance are related logarithmically:

$$A = -\log_{10}(T)$$

This means that as absorbance increases linearly, transmittance drops exponentially. For example, $A = 1$ corresponds to $T = 0.1$ (only 10% of light transmitted), while $A = 2$ corresponds to $T = 0.01$ (only 1%).

When the Beer-Lambert law holds, absorbance is directly proportional to concentration. Double the concentration, double the absorbance. But this linear relationship breaks down at high concentrations (roughly above $A \approx 1.0$). Common causes of deviation include:

- Molecular interactions at high concentrations (solute molecules start affecting each other's absorption behavior)
- Stray light reaching the detector without passing through the sample
- Polychromatic radiation — if the monochromator isn't selecting a narrow enough wavelength band, the law's assumption of monochromatic light is violated

Concentration Calculations with Beer-Lambert Law

To find an unknown concentration from an absorbance measurement, rearrange the equation:

$$c = \frac{A}{\epsilon b}$$

Here's the step-by-step process:

1. Choose the wavelength where your analyte absorbs most strongly (its λ_{max}). This maximizes sensitivity.
2. Look up or determine ϵ for your substance at that wavelength.
3. Measure the path length b of your cuvette (usually 1 cm).
4. Record the absorbance A using a spectrophotometer, after blanking against a reference.
5. Plug values into $c = A/(\epsilon b)$ and solve.

For reliable results, keep A in the range of roughly 0.1 to 1.0. Below 0.1, noise dominates. Above 1.0, deviations from linearity become significant. If your reading falls outside this range, dilute (or concentrate) and re-measure.

Always check that your units are consistent: ϵ in $\text{L mol}^{-1}\text{cm}^{-1}$, b in cm, and C in mol L^{-1} .

Absorption Spectroscopy Setup

A typical UV-Vis spectrophotometer has four main components arranged in sequence:

1. Light source — a tungsten-halogen lamp covers the visible range (~350–800 nm), while a deuterium lamp covers the UV range (~190–350 nm). Many instruments switch between the two automatically.
2. Monochromator — isolates a narrow band of wavelengths from the source. This is what lets you select a specific wavelength for measurement.
3. Sample holder (cuvette) — holds the solution in the light path. Glass cuvettes work for visible wavelengths; quartz cuvettes are needed for UV work because glass absorbs UV light.
4. Detector — measures the intensity of transmitted light. Common types include photomultiplier tubes (very sensitive) and photodiode arrays (can measure many wavelengths simultaneously).

To collect good data:

- Prepare a blank (solvent only, no analyte) and use it to zero the instrument. This corrects for absorption by the solvent and cuvette.
- Handle cuvettes by the frosted sides only; fingerprints on the optical faces scatter light and introduce error.
- For quantitative work with unknowns, build a calibration curve by measuring absorbance for several standards of known concentration. Plot A vs. C , confirm linearity, then read your unknown's

concentration from the curve.

- Control temperature if your analyte's absorption is temperature-sensitive.
- Watch for interferences from other species in the sample that absorb at the same wavelength.

4.2 Fluorescence and phosphorescence spectroscopy

Photoluminescence Processes

Fluorescence and phosphorescence are the two main ways molecules emit light after absorbing it. They differ in which excited state the emission comes from, and that difference controls how fast and how intensely the light is released. The Jablonski diagram ties all of these transitions together into a single energy-level picture, making it the central framework for this topic.

Fluorescence vs. Phosphorescence

Fluorescence is emission from a singlet excited state ($S_1 \rightarrow S_0$). Because the electron doesn't need to flip its spin, this is a spin-allowed transition ($\Delta S = 0$). That makes it fast: fluorescence lifetimes are typically on the order of nanoseconds, and the emission is relatively intense. Common fluorophores include organic dyes like fluorescein and rhodamine, as well as fluorescent proteins like GFP.

Phosphorescence is emission from a triplet excited state ($T_1 \rightarrow S_0$). This requires a spin flip, making it a spin-forbidden transition ($\Delta S \neq 0$). Forbidden doesn't mean impossible; it just means the probability is low. The result is much slower emission, ranging from milliseconds to seconds or even longer, and lower intensity. Glow-in-the-dark materials are the classic everyday example.

The bridge between the two is intersystem crossing (ISC), a non-radiative transition from S_1 to T_1 that involves a spin flip. ISC is what makes phosphorescence possible in the first place. Two factors that enhance ISC:

- Heavy atom effect: Heavy atoms (like bromine or iodine) in or near the molecule increase spin-orbit coupling, which makes the spin flip more probable.
- Spin-orbit coupling: The interaction between an electron's spin and its orbital motion. Stronger spin-orbit coupling relaxes the spin selection rule, boosting ISC rates.

Electronic Transitions in the Jablonski Diagram

The Jablonski diagram is an energy-level map showing every major pathway a molecule can take after absorbing a photon. Here's how to read it from top to bottom:

1.

Absorption ($S_0 \rightarrow S_1$ or S_2): A UV-visible photon promotes an electron from the ground state to a higher singlet excited state. This is extremely fast ($\sim 10^{-15}$ s).

2.

Vibrational relaxation: Within any electronic state, the molecule quickly sheds excess vibrational energy as heat to the surroundings, dropping to the lowest vibrational level of that state ($\sim 10^{-12}$ s).

3.

Internal conversion (IC): A non-radiative transition between electronic states of the same spin multiplicity (e.g., $S_2 \rightarrow S_1$). Combined with vibrational relaxation, this is why emission almost always originates from S_1 regardless of which state was initially excited (this is Kasha's rule).

4.

Fluorescence: Radiative decay from S_1 to S_0 , emitting a photon. The emitted photon has lower energy (longer wavelength) than the absorbed photon because energy was lost in steps 2 and 3. This wavelength difference is the Stokes shift.

5.

Intersystem crossing (ISC): Non-radiative $S_1 \rightarrow T_1$ transition involving a spin flip. T_1 sits lower in energy than S_1 because of exchange interaction (unpaired electrons in the triplet state experience less electron-electron repulsion).

6.

Phosphorescence: Radiative decay from T_1 to S_0 . Because it's spin-forbidden, the rate constant is small and the emission is long-lived.

The key takeaway: absorption is fast, non-radiative relaxation funnels everything to S_1 , and from there the molecule either fluoresces, undergoes ISC to T_1 and phosphoresces, or loses energy non-radiatively.

Factors and Applications

Factors Affecting Fluorescence Intensity

Quantum yield is the single most important measure of fluorescence efficiency. It's defined as the fraction of absorbed photons that result in emitted photons:

$$\Phi_F = \frac{k_F}{k_F + k_{nr}}$$

where k_F is the radiative (fluorescence) rate constant and k_{nr} is the sum of all non-radiative rate constants (internal conversion, ISC, quenching). A quantum yield of 1.0 means every absorbed photon produces a fluorescence photon. Fluorescein in basic solution has $\Phi_F \approx 0.95$, which is why it's such a popular reference standard.

Concentration and optical factors also control the observed signal:

- Fluorophore concentration directly affects signal strength, but only in the dilute regime. At high concentrations, the inner filter effect (reabsorption of emitted light) distorts the signal.
- The molar absorption coefficient (ϵ) determines how efficiently the fluorophore captures excitation light.
- Path length and excitation source intensity set how many photons are available to be absorbed.

Quenching mechanisms reduce fluorescence by opening up competing non-radiative pathways:

- Collisional (dynamic) quenching: The excited fluorophore collides with a quencher molecule (molecular oxygen is the most common culprit), transferring energy non-radiatively. Described quantitatively by the Stern-Volmer equation: $\frac{F_0}{F} = 1 + K_{SV}[Q]$, where $[Q]$ is quencher concentration.
- Static quenching: The quencher forms a non-fluorescent ground-state complex with the fluorophore before excitation even occurs.
- Self-quenching: At very high fluorophore concentrations, molecules quench each other through energy transfer or reabsorption.

Environmental factors:

- Higher temperature increases molecular collisions, promoting collisional quenching and reducing intensity.
- pH can protonate or deprotonate functional groups on the fluorophore, dramatically shifting its electronic structure. Fluorescein, for example, is strongly fluorescent at high pH but nearly non-fluorescent under acidic conditions.
- Solvent polarity affects the energy gap between ground and excited states, shifting emission wavelengths and sometimes altering quantum yield.

Structural factors:

- Molecular rigidity enhances quantum yield by reducing non-radiative vibrational losses. BODIPY dyes are a good example: their rigid core gives them high Φ_F values.
- Heavy atoms in the molecular structure (or in the solvent) promote ISC, which drains population from S_1 and reduces fluorescence while enhancing phosphorescence.

Applications of Luminescence Spectroscopy

Luminescence spectroscopy is one of the most sensitive analytical techniques available, often detecting analytes at nanomolar or even picomolar concentrations. Here are the major application areas:

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Biochemistry and molecular biology: Förster resonance energy transfer (FRET) measures distances between two fluorophores in the 1–10 nm range, making it a powerful tool for studying protein conformational changes and molecular interactions. Fluorescent nucleotide labels enable DNA sequencing, and fluorescence microscopy (confocal, super-resolution) is standard for cellular imaging.

•

Medical diagnostics: Fluorescence imaging can highlight tumor tissue during surgery by using targeted fluorescent probes that accumulate in cancer cells. Immunoassays that use fluorescent labels detect biomarkers for disease at very low concentrations.

•

Environmental analysis: Fluorescence detects organic pollutants like polycyclic aromatic hydrocarbons (PAHs) in water at trace levels. Dissolved organic matter in natural waters has a characteristic fluorescence signature useful for monitoring water quality.

•

Forensic science: Alternate light sources excite bodily fluids (blood, saliva, semen) that fluoresce or can be treated with fluorescent reagents. Security inks in currency and documents use phosphorescent or fluorescent compounds for authentication.

•

Materials science: Photoluminescence spectroscopy characterizes semiconductor band gaps and defect states. Organic light-emitting diodes (OLEDs) rely on both fluorescent and phosphorescent emitters to convert electrical energy into light efficiently.

•

Analytical chemistry and sensors: Fluorescent probes detect specific ions (e.g., Ca^{2+} indicators like Fura-2) or respond to pH changes. Quantitative fluorescence spectrophotometry exploits the linear

relationship between intensity and concentration in dilute solutions.

-

Food and agriculture: Fluorescence monitors food freshness (e.g., detecting spoilage-related compounds) and screens for pesticide residues on produce.

4.3 Time-resolved spectroscopy techniques

Time-resolved spectroscopy reveals the dynamic world of molecules in action. By measuring spectral changes over time, we can witness ultra-fast reactions, energy transfers, and structural shifts happening in real-time.

From pulsed lasers to sensitive detectors, this technique uses cutting-edge tools to capture fleeting molecular moments. Applications range from tracking protein folding to studying photosynthesis, offering insights into the fundamental processes that drive life and technology.

Time-Resolved Spectroscopy Techniques

Principles of time-resolved spectroscopy

- Measures spectral changes over time revealing dynamic molecular processes
- Excitation methods
 - Pulsed laser excitation initiates reactions with short light pulses
 - Flash photolysis uses intense light flashes to trigger photochemical reactions
- Detection methods
 - Time-correlated single-photon counting (TCSPC) records individual photon arrival times
 - Streak camera captures light intensity vs time with high temporal resolution
- Time scales span femtosecond to millisecond range allowing study of ultra-fast to slow processes
- Key parameters
 - Temporal resolution determines shortest measurable time interval
 - Spectral resolution defines ability to distinguish closely spaced wavelengths
- Data collection yields time-dependent absorption or emission spectra tracking molecular changes
- Signal processing employs deconvolution techniques to extract true signal from instrument response

Instrumentation for fluorescence spectroscopy

- Light source uses pulsed laser or LED to generate short excitation pulses
- Sample chamber features temperature control and holds cuvette or flow cell
- Monochromator selects specific wavelengths for excitation or emission
- Detector
 - Photomultiplier tube (PMT) amplifies weak light signals
 - Microchannel plate (MCP) offers higher sensitivity and faster response

- Electronics
- Constant fraction discriminator (CFD) improves timing accuracy
- Time-to-amplitude converter (TAC) measures time intervals between events
- Data acquisition system employs multichannel analyzer (MCA) to build histogram of photon arrival times
- Optical components include mirrors, lenses, and polarizers for anisotropy measurements

Applications in molecular dynamics

- Excited state lifetimes measured through fluorescence decay reveal molecular relaxation processes
- Energy transfer processes like Förster resonance energy transfer (FRET) probe molecular distances
- Conformational changes tracked in protein folding dynamics illuminate structural transitions
- Reaction kinetics monitored by observing transient species formation and decay
- Photochemical processes such as isomerization reactions studied in real-time
- Solvation dynamics investigated through time-dependent Stokes shift measurements
- Charge transfer reactions examined in photosynthesis and artificial light-harvesting systems

Interpretation of spectral data

- Decay curve analysis uses exponential fitting to determine fluorescence lifetimes
- Global analysis techniques fit multiple wavelengths simultaneously for complex systems
- Kinetic models extract rate constants from time-dependent spectral changes
- Time-resolved emission spectra (TRES) reveal spectral evolution over time
- Anisotropy decay measurements yield rotational correlation times related to molecular size and shape
- Deconvolution removes instrument response function (IRF) to obtain true signal
- Error analysis calculates confidence intervals and examines residuals to assess fit quality

4.4 Interpretation of spectral data

Absorption and Emission Spectra

Absorption and emission spectra reveal how molecules interact with light. Every spectrum contains peaks, intensities, and band shapes that encode information about molecular structure, electronic transitions, and the local environment around a molecule. Learning to read these features is what turns raw spectral data into useful chemical insight.

Key Features of Spectra

Absorption spectra show which wavelengths of light a molecule absorbs. The peak positions tell you the energy of electronic transitions, the intensities reflect how probable those transitions are, and the band shapes (narrow or broad) hint at the molecule's environment and vibrational structure.

Emission spectra show the light a molecule releases after excitation. Two key observations here:

- Stokes shift: Emitted light appears at longer wavelengths (lower energy) than the absorbed light. This happens because the excited molecule loses some energy to vibrational relaxation before emitting a photon.
- Anti-Stokes emission: Less commonly, emitted light appears at shorter wavelengths. This occurs when the molecule was already in a vibrationally excited ground state before absorbing light.

Emission also splits into two categories based on the spin state involved:

- Fluorescence is rapid emission (nanosecond timescale) from a singlet excited state ($S_1 \rightarrow S_0$).
- Phosphorescence is much slower (microseconds to seconds) because it involves a spin-forbidden triplet-to-singlet transition ($T_1 \rightarrow S_0$).

Mirror image relationship. Absorption and fluorescence spectra of the same molecule often look like mirror images of each other. This arises from the Franck-Condon principle: the vibrational level spacing in the ground and excited electronic states is similar, so the pattern of vibronic transitions is roughly symmetric.

Beer-Lambert Law for Concentration

The Beer-Lambert law is the foundation of quantitative spectroscopy:

$$A = \epsilon bc$$

- A = absorbance (unitless)
- ϵ = molar absorption coefficient ($\text{L mol}^{-1}\text{cm}^{-1}$), a measure of how strongly the molecule absorbs at that wavelength
- b = path length through the sample (cm)
- C = molar concentration (mol L^{-1})

Because A is directly proportional to C , you can build a calibration curve by measuring absorbance for several known concentrations, then use it to find the concentration of an unknown sample.

Limitations. The linear relationship breaks down at high concentrations (roughly above 0.01 M). At that point, solute-solute interactions, aggregation, and increased light scattering cause deviations. Stray light reaching the detector and instrumental limitations can also cause non-linearity.

Insights from Spectral Bands

Each spectral band carries several layers of information:

Band position reflects the energy gap of the electronic transition. Factors that shift band position include:

- Conjugation: Extending a conjugated π -system lowers the energy gap, shifting absorption to longer wavelengths. For example, butadiene absorbs near 217 nm while hexatriene absorbs near 258 nm.
- Solvent polarity: Polar solvents stabilize charge-transfer excited states differently than nonpolar ones, shifting peak positions.

Band shape is governed by vibrational and rotational fine structure. Two types of broadening obscure that fine structure:

- Homogeneous broadening affects all molecules equally (e.g., collisional broadening at higher temperatures).

- Inhomogeneous broadening arises because different molecules experience slightly different local environments (e.g., in a disordered solid or mixed solvent).

Spectral shifts have specific names you should know:

- Bathochromic shift (red shift): absorption moves to longer wavelengths / lower energy
- Hypsochromic shift (blue shift): absorption moves to shorter wavelengths / higher energy

Intensity changes also have standard terminology:

- Hyperchromic effect: increase in absorption intensity, indicating a higher transition probability
- Hypochromic effect: decrease in absorption intensity (classic example: DNA base stacking reduces UV absorption compared to free nucleotides)

Applications in Chemical Analysis

Spectral data feeds into a wide range of practical analyses:

- Qualitative analysis: Identifying functional groups and molecular structure. For instance, a carbonyl stretch appears near 1700 cm^{-1} in IR spectroscopy, serving as a diagnostic marker.
- Quantitative analysis: Determining concentration of active ingredients in pharmaceuticals or assessing sample purity using Beer-Lambert calibration curves.
- Kinetics: Monitoring how absorbance changes over time tracks reaction progress. Enzyme kinetics studies, for example, often follow substrate disappearance or product formation at a characteristic wavelength.
- Thermodynamics: Measuring how spectra change with concentration or temperature lets you derive equilibrium constants and binding affinities (e.g., protein-ligand interactions via fluorescence quenching).
- Environmental monitoring: Detecting pollutants like heavy metals in water (via atomic absorption) or quantifying organic contaminants.
- Biomedical applications: HPLC with UV detection for drug analysis, and fluorescence microscopy for imaging specific biomolecules in cells.

Unit 5 – Excited State Dynamics in Photochemistry

5.1 Excited state formation and relaxation pathways

Excited states form when molecules absorb energy, leading to electrons jumping to higher energy levels. This can happen through light absorption, chemical reactions, electrical excitation, heat, or mechanical forces. Understanding these processes is crucial for photochemistry.

Once excited, molecules have various ways to relax back to their ground state. These include radiative processes like fluorescence and phosphorescence, and non-radiative processes like internal conversion. Factors like molecular structure and environment influence these relaxation pathways.

Excited State Formation

Excited state formation processes

- Photon absorption transitions molecules from ground to excited state upon light absorption (UV-Vis spectrum)
- Chemical reactions release energy exothermically transferring to reactants (chemiluminescence)
- Electrical excitation promotes electrons in conducting materials via applied electric field (electroluminescence)
- Thermal excitation induces vibrational and rotational excitation through heat absorption (blackbody radiation)
- Mechanical excitation generates excited states through physical forces (sonoluminescence, triboluminescence)

Excited State Relaxation Pathways

Excited state relaxation pathways

- Internal conversion non-radiatively transitions between electronic states with same spin multiplicity ($S_2 \rightarrow S_1$)
- Intersystem crossing non-radiatively transitions between states of different spin multiplicity ($S_1 \rightarrow T_1$)
- Fluorescence radiatively transitions between states of same spin multiplicity emitting photons ($S_1 \rightarrow S_0$)
- Phosphorescence radiatively transitions from triplet to singlet state with longer lifetime ($T_1 \rightarrow S_0$)
- Vibrational relaxation dissipates energy through molecular vibrations to surrounding medium
- Energy transfer excites nearby acceptor molecules through dipole-dipole interactions (FRET)

Radiative vs non-radiative relaxation

- Radiative processes emit photons during excited state decay (fluorescence, phosphorescence)

- Non-radiative processes release energy without photon emission (internal conversion, intersystem crossing)
- Quantum yield measures radiative vs non-radiative efficiency as ratio of emitted to absorbed photons

Factors in excited state kinetics

- Molecular structure affects relaxation rates through conjugation, aromaticity, heavy atom effect
- Environmental factors influence decay processes via solvent polarity, viscosity, temperature
- Concentration impacts relaxation through self-quenching and excimer formation at high concentrations
- Energy gap law correlates non-radiative decay rate with energy difference between states
- Franck-Condon principle determines transition probability based on vibrational wavefunction overlap
- Selection rules govern allowed transitions based on spin and symmetry considerations
- Competing processes like photochemical reactions or impurity quenching affect observed kinetics

5.2 Jablonski diagram and state transitions

The Jablonski diagram is a visual tool that maps out energy levels and transitions in molecules. It shows ground states, excited states, and the various ways molecules can absorb, emit, or transfer energy through processes like fluorescence and phosphorescence.

Understanding these energy pathways is crucial for grasping photophysical processes. From absorption to emission, the Jablonski diagram helps predict how molecules will behave when exposed to light, which is essential for applications in spectroscopy, photochemistry, and beyond.

Understanding the Jablonski Diagram

Components of Jablonski diagram

- Jablonski diagram structure depicts energy levels on vertical axis and spin multiplicity on horizontal axis
- Energy states include ground state (S_0), excited singlet states (S_1 , S_2) and excited triplet states (T_1 , T_2)
- Vibrational levels within each electronic state shown as closely spaced horizontal lines
- Radiative transitions represented by straight arrows indicate emission of photons
- Non-radiative transitions depicted by wavy arrows show energy dissipation without photon emission

Electronic states and transitions

- Singlet states (S) feature paired electron spins in orbitals (S_0 , S_1 , S_2)
- Triplet states (T) have unpaired electron spins in separate orbitals (T_1 , T_2)
- Transitions between states include: 1. Absorption: ground to excited state jump 2. Internal conversion: relaxation between states of same multiplicity 3. Intersystem crossing: transition between states of different multiplicity 4. Fluorescence: excited singlet to ground state emission 5. Phosphorescence: excited triplet to ground state emission

Photophysical Processes

Processes in photophysics

- Absorption occurs when molecule gains energy from incident photon, transitioning from ground to excited state in femtoseconds
- Fluorescence involves radiative transition from excited singlet to ground state, emitting photon with typical nanosecond lifetime
- Phosphorescence consists of radiative transition from excited triplet to ground state, emitting photon with longer lifetime (milliseconds to seconds)
- Intersystem crossing entails non-radiative transition between states of different multiplicity, usually from excited singlet to triplet state, involving spin flip of an electron

Applications of Jablonski diagram

- Stokes shift measures difference between absorption and emission wavelengths, caused by vibrational relaxation and solvent effects
- Quantum yield calculates ratio of emitted to absorbed photons, affected by competing non-radiative processes
- Fluorescence quenching decreases fluorescence intensity due to external factors (collisions with other molecules, energy transfer)
- Energy transfer processes include Förster resonance energy transfer (FRET) and Dexter electron transfer
- Photochemical reactions initiate from excited states, leading to isomerization, dissociation, or other chemical changes (photosynthesis, vision)
- Predicting dominant relaxation pathways based on molecular structure and environment considers spin-orbit coupling, energy gaps, and selection rules

5.3 Excited state lifetime and quantum yield

Excited State Dynamics

Excited state dynamics govern how long molecules remain in an excited electronic state and how efficiently they convert absorbed light into useful outcomes. These two measurable quantities, the excited state lifetime and the quantum yield, are central to predicting reaction efficiency, designing fluorescent sensors, and optimizing photocatalysts.

Excited State Lifetime: Significance

The excited state lifetime (τ) is the average time a molecule spends in an excited state before returning to the ground state. It's typically on the order of nanoseconds (10^{-9} s) for fluorescent states or microseconds to seconds for phosphorescent (triplet) states.

Why does τ matter so much? It sets the window during which any excited-state process can occur. A molecule can only undergo energy transfer, electron transfer, or a photochemical reaction while it's still excited. If the lifetime is too short, the molecule relaxes before anything useful happens.

Several factors shorten or lengthen τ :

- Molecular structure: Rigid, planar molecules (like pyrene) tend to have longer lifetimes because they have fewer vibrational modes that drain energy.
- Solvent environment: Polar solvents can stabilize or destabilize excited states, shifting the balance between decay pathways.
- Temperature: Higher temperatures generally increase non-radiative decay rates, shortening the lifetime.
- Quenchers: Dissolved oxygen is a common triplet-state quencher. Its presence can dramatically reduce τ by opening additional non-radiative channels.

Calculating Excited State Lifetime

The lifetime depends on the total rate at which the excited state depopulates. If k_r is the radiative decay rate constant and k_{nr} is the sum of all non-radiative decay rate constants, then:

$$\tau = \frac{1}{k_r + k_{nr}}$$

The key radiative pathways are fluorescence (singlet $\rightarrow$ singlet) and phosphorescence (triplet $\rightarrow$ singlet). Non-radiative pathways include internal conversion (same spin multiplicity, energy lost as heat) and intersystem crossing (spin flip from singlet to triplet or vice versa).

A few things to notice about this equation:

- When k_{nr} is small compared to k_r , the molecule decays mostly by emitting light, and τ approaches $1/k_r$. This limiting value is called the natural radiative lifetime (τ_0).
- When k_{nr} dominates, the lifetime shortens and emission becomes weak.
- Adding any new decay channel (a quencher, for instance) increases the denominator and reduces τ .

Experimentally, τ is measured using time-resolved spectroscopy. A short laser pulse excites the sample, and you monitor the emission intensity as it decays. The decay curve typically follows $I(t) = I_0 e^{-t/\tau}$, and fitting this exponential gives τ directly.

Quantum Yield: Concept

The quantum yield (Φ) quantifies how efficiently absorbed photons produce a specific outcome. The general definition is:

$$\Phi = \frac{\text{number of events of interest}}{\text{number of photons absorbed}}$$

The "event" depends on what you're measuring. For fluorescence quantum yield, it's photons emitted. For a photochemical reaction quantum yield, it's molecules of product formed (or reactant consumed).

Φ ranges from 0 to 1 for most processes. A fluorescence quantum yield of 0.90 means 90% of absorbed photons result in fluorescence emission. Values above 1 are possible for chain reactions where one absorbed photon triggers multiple product-forming steps.

The fluorescence quantum yield connects directly to the rate constants:

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

This tells you something useful: $\Phi_f = k_r \cdot \tau$. So a molecule with a long lifetime and a large radiative rate constant will be a bright emitter.

Factors that affect Φ mirror those that affect τ :

- Molecular rigidity reduces non-radiative losses (BODIPY dyes are bright partly because of their rigid core).
- Heavy atoms enhance intersystem crossing, lowering Φ_f but potentially increasing phosphorescence yield.
- Quenchers and energy transfer acceptors (e.g., FRET pairs) open competing pathways that reduce the quantum yield of the initially excited species.

Determining Quantum Yield Experimentally

Two common approaches are used to measure Φ :

Comparative method (for emission quantum yield):

1. Choose a reference fluorophore with a well-known quantum yield (e.g., rhodamine 6G in ethanol, $\Phi_f = 0.95$).
2. Prepare solutions of the reference and your sample with matched absorbance at the excitation wavelength (typically $A < 0.05$ to avoid inner filter effects).
3. Record emission spectra of both under identical instrument conditions.
4. Calculate Φ using:

$$\Phi_{\text{sample}} = \Phi_{\text{ref}} \times \frac{F_{\text{sample}}}{F_{\text{ref}}} \times \frac{n_{\text{sample}}^2}{n_{\text{ref}}^2}$$

where F is the integrated emission intensity and n is the solvent refractive index.

Chemical actinometry (for reaction quantum yield):

1. Use a chemical actinometer (e.g., potassium ferrioxalate) to measure the photon flux entering your sample.
2. Irradiate the reaction mixture and measure the amount of product formed (or reactant consumed) over a known time.
3. Apply the formula:

$$\Phi_{\text{rxn}} = \frac{\text{moles of product formed}}{\text{moles of photons absorbed}}$$

For accurate results, ensure the sample absorbs essentially all incident light at the excitation wavelength, correct for any inner filter effects if concentrations are high, and keep conversions low enough that product absorption doesn't distort the measurement.

These measurements have direct practical applications: evaluating photocatalyst performance (e.g., TiO_2 for water splitting), optimizing photopolymerization conditions, and screening fluorescent probes for bioimaging.

Unit 6 – Radiative and Non–Radiative Transitions

6.1 Radiative decay processes

Radiative Decay Processes

Radiative decay is what happens when an excited molecule releases its extra energy by emitting a photon. The two main types, fluorescence and phosphorescence, differ in which excited state the photon comes from and how long the process takes. These processes underpin technologies from biological imaging to LED lighting, so understanding the mechanisms and the factors that control emission rates is essential.

Process of Fluorescence

Fluorescence is the emission of light from an excited singlet state (S_1). Because the transition from S_1 back to the ground state S_0 is spin-allowed, it happens fast, typically on the order of nanoseconds (10^{-9} s).

A Jablonski diagram is the standard way to visualize what's going on. The sequence looks like this:

1. A photon is absorbed, promoting the molecule from S_0 to a higher vibrational level of S_1 (or S_2 , etc.).
2. The molecule undergoes vibrational relaxation, quickly losing energy to surrounding molecules and settling into the lowest vibrational level of S_1 .
3. From there, the molecule emits a photon and drops back to some vibrational level of S_0 .

Because energy is lost during vibrational relaxation, the emitted photon always has less energy (longer wavelength) than the absorbed photon. The difference in wavelength between the absorption maximum and the emission maximum is called the Stokes shift.

Two quantities you need to know for characterizing fluorescence:

- Quantum yield (Φ_f): the ratio of photons emitted to photons absorbed. A quantum yield of 1.0 means every absorbed photon leads to an emitted photon; real fluorophores are always less than that because non-radiative pathways compete.
- Fluorescence lifetime (τ_f): the average time a molecule spends in S_1 before emitting. It's defined as the inverse of the total decay rate constant.

One more pattern worth remembering: the mirror image rule. The emission spectrum of many molecules is roughly a mirror image of the absorption spectrum. This happens because the spacing of vibrational levels in S_0 and S_1 is often similar, so the same set of vibronic transitions appears in both spectra, just reversed in energy order.

Mechanism of Phosphorescence vs. Fluorescence

Phosphorescence is emission from an excited triplet state (T_1). The transition $T_1 \rightarrow S_0$ is spin-forbidden, which is why phosphorescence is much slower than fluorescence, with lifetimes ranging from microseconds to seconds (or even longer).

To reach T_1 , the molecule first has to undergo intersystem crossing (ISC), a non-radiative transition from S_1 to T_1 . ISC requires a spin flip, which is normally unlikely. However, spin-orbit coupling can mix singlet and triplet character, making ISC much more efficient. Heavy atoms (like bromine, iodine, or transition metals) dramatically enhance spin-orbit coupling, which is why heavy-atom-containing molecules are often strong phosphors.

Because T_1 sits lower in energy than S_1 , phosphorescence photons are lower in energy (longer wavelength) than fluorescence photons from the same molecule.

Here's a quick comparison:

Property	Fluorescence	Phosphorescence
Emitting state	S_1 (singlet)	T_1 (triplet)
Spin character of transition	Allowed	Forbidden
Typical lifetime	$10^{-9} - 10^{-7}$ s	$10^{-6} - 10^0$ s
Quantum yield	Generally higher	Generally lower
Stokes shift	Smaller	Larger
Typical conditions	Room temperature, solution	Often requires low temperature or rigid matrix

Phosphorescence is often quenched at room temperature because the long-lived triplet state gives non-radiative processes (collisions, oxygen quenching) plenty of time to drain the energy. Rigid environments like frozen glasses or polymer matrices suppress molecular motion and protect the triplet state, which is why phosphorescence experiments are frequently run at 77 K.

Factors Influencing Radiative Decay Rates

Several interconnected factors determine how fast (and how efficiently) a molecule emits.

Einstein coefficients provide the fundamental framework. The spontaneous emission coefficient A_{21} gives the rate at which an excited molecule emits a photon on its own, while B_{12} and B_{21} describe stimulated absorption and emission rates, respectively. A larger A_{21} means a shorter radiative lifetime. For a two-level system, the radiative lifetime is simply $\tau_{rad} = 1/A_{21}$.

Oscillator strength (f) quantifies how strongly a transition couples to the electromagnetic field. Transitions with large oscillator strength have large A_{21} values and therefore short radiative lifetimes. Fully allowed transitions typically have f values near 1; forbidden transitions have f values orders of magnitude smaller.

The Franck-Condon principle adds another layer. Transition probability depends on the overlap integral between the vibrational wavefunctions of the initial and final electronic states. Good overlap means a more probable (and therefore faster) transition. This is why the shape of emission spectra, and even the overall emission rate, depends on the geometry change between ground and excited states.

Environmental and structural factors also matter:

- Solvent polarity can shift energy levels and change the emission wavelength and rate. Polar solvents stabilize charge-transfer excited states, often causing red-shifted emission.
- Viscosity and rigidity reduce molecular motion, suppressing non-radiative decay and increasing the observed quantum yield.
- Temperature affects the competition between radiative and non-radiative pathways. Lower temperatures generally favor emission.

- Conjugation length influences the energy gap and oscillator strength. Extended conjugation typically red-shifts emission and can increase the radiative rate.
- Heavy atoms enhance spin-orbit coupling, boosting ISC and phosphorescence at the expense of fluorescence.

Keep in mind that the observed decay rate is the sum of radiative and non-radiative rate constants. Even if the radiative rate is large, a molecule won't fluoresce efficiently if non-radiative pathways (internal conversion, vibrational relaxation, energy transfer) are faster.

Applications of Radiative Decay Principles

These emission processes show up across a wide range of technologies:

- Fluorescence microscopy uses fluorescent labels to image specific structures inside cells with high spatial resolution. Techniques like confocal and super-resolution microscopy rely on carefully chosen fluorophores with known quantum yields and lifetimes.
- Fluorescent probes and sensors detect local conditions such as pH, metal ion concentrations (Ca^{2+} , Zn^{2+}), or oxygen levels. The probe's emission intensity or wavelength shifts in response to the analyte.
- Photodynamic therapy (PDT) uses photosensitizer molecules that undergo ISC to populate long-lived triplet states. These triplet states transfer energy to molecular oxygen, generating reactive singlet oxygen ($^1\text{O}_2$) that destroys cancer cells.
- LEDs and OLEDs convert electrical energy into light through electroluminescence. Phosphorescent emitters (often iridium or platinum complexes) are used in OLEDs because they can harvest both singlet and triplet excitons, pushing internal quantum efficiency toward 100%.
- Phosphorescent materials in glow-in-the-dark products (safety signs, watch dials) store energy in triplet states and release it slowly after the excitation source is removed.
- Laser technology relies on stimulated emission from a population-inverted medium. The Einstein B coefficients govern the stimulated emission rate, and the gain medium's radiative properties determine the laser wavelength and efficiency.
- Analytical fluorescence techniques such as fluorescence spectroscopy, fluorescence lifetime imaging (FLIM), and Förster resonance energy transfer (FRET) measurements are standard tools for studying molecular structure, dynamics, and interactions.

6.2 Non-radiative decay mechanisms

Non-Radiative Decay Mechanisms in Photochemistry

Non-radiative decay mechanisms govern how excited molecules lose energy without emitting a photon. In photochemistry, these pathways often compete directly with fluorescence and phosphorescence, so understanding them is key to predicting quantum yields, designing efficient photosensitizers, and controlling excited-state reactivity.

This section covers the three main non-radiative channels (vibrational relaxation, collisional quenching, and energy transfer) and the structural and environmental factors that determine how fast each one operates.

Vibrational relaxation in decay

Vibrational relaxation is the process by which an excited molecule sheds excess vibrational energy while staying on the same electronic state. After a molecule absorbs a photon, it typically lands in a high vibrational level of the excited state. Vibrational relaxation brings it down to the lowest vibrational level of that state, which is the starting point for everything else (fluorescence, intersystem crossing, further non-radiative decay).

The mechanism works through collisions with surrounding solvent or gas-phase molecules. Each collision converts a small amount of vibrational energy into translational or rotational energy of the collision partner. Because these collisions happen extremely frequently in condensed phases, vibrational relaxation is fast, typically on the picosecond (10^{-12} s) timescale. That's orders of magnitude faster than fluorescence (nanoseconds) or phosphorescence (microseconds to seconds).

Why this matters for photochemistry:

- It ensures that emission almost always originates from the lowest vibrational level of the excited electronic state (this is the physical basis of Kasha's rule)
- It facilitates internal conversion by funneling population toward regions of strong vibronic coupling between electronic states
- It contributes to thermal equilibration, meaning the excess photon energy ultimately appears as heat in the surroundings

Concrete examples include heat dissipation in photosynthetic light-harvesting complexes, where vibrational relaxation channels energy toward the reaction center, and CO₂ laser systems, where vibrational relaxation rates among different modes control population inversion.

Collisional quenching of excited states

Collisional (dynamic) quenching occurs when an excited molecule encounters another species, the quencher, and transfers its excitation energy during the collision. The excited molecule returns to the ground state without emitting a photon, and the quencher carries away the energy, often as vibrational or translational motion.

The energy conversion during quenching frequently involves an electronic-to-vibrational (E-to-V) pathway: the electronic excitation of the donor is converted into vibrational excitation of the quencher. Common quenchers include:

- Molecular oxygen (O₂): a highly efficient quencher in both solution and gas phase because its triplet ground state readily accepts energy from excited triplet states
- Paramagnetic species such as transition metal ions (e.g., Cu²⁺, Ni²⁺), which promote spin-forbidden relaxation through spin-orbit coupling

Quenching kinetics are described by the Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{SV}[Q]$$

where I_0 is the fluorescence intensity without quencher, I is the intensity with quencher at concentration $[Q]$, and K_{SV} is the Stern-Volmer constant. A plot of I_0/I versus $[Q]$ gives a straight line with slope K_{SV} . For purely dynamic quenching, $K_{SV} = k_q\tau_0$, where k_q is the bimolecular quenching rate constant and τ_0 is the unquenched lifetime.

Practical applications rely directly on this relationship:

- Oxygen sensors measure fluorescence quenching to determine O₂ concentration
- Photodynamic therapy exploits energy transfer from a photosensitizer's triplet state to O₂, generating cytotoxic singlet oxygen (¹O₂)
- Fluorescence-based molecular probes use quenching to detect specific analytes in biological or environmental samples

Energy transfer between molecules

Energy transfer is a non-radiative process in which excitation energy moves from a donor molecule to an acceptor molecule without the emission and reabsorption of a photon. Two distinct mechanisms dominate, and they operate over very different distance ranges.

1. Förster Resonance Energy Transfer (FRET)

FRET operates through a long-range dipole-dipole interaction between the donor's transition dipole and the acceptor's transition dipole. No physical contact or orbital overlap is required. The rate of FRET depends on:

- Spectral overlap between the donor emission spectrum and the acceptor absorption spectrum
- Distance: the rate scales as r^{-6} , where r is the donor-acceptor separation

The characteristic distance at which FRET efficiency is 50% is called the Förster radius (R_0), typically 1–10 nm. This steep distance dependence makes FRET a powerful "molecular ruler" in biophysics.

2. Dexter Energy Transfer

Dexter transfer is a short-range electron exchange mechanism that requires direct orbital overlap between donor and acceptor (typically < 1 nm separation). The rate falls off exponentially with distance. Unlike FRET, Dexter transfer can mediate triplet-triplet energy transfer, because the exchange of spin-correlated electrons conserves overall spin.

Triplet-triplet energy transfer via the Dexter mechanism is central to photosensitization, where a sensitizer absorbs light, undergoes intersystem crossing to its triplet state, and then transfers that triplet energy to a substrate that could not be excited directly.

Key consequences and applications of energy transfer:

- Sensitization: indirect excitation of molecules that don't absorb at the irradiation wavelength
- Upconversion: combining two lower-energy excitations (e.g., two triplets) to produce a higher-energy singlet state via triplet-triplet annihilation
- Photocatalysis: initiating reactions on substrates through energy transfer from a photocatalyst
- Technology: FRET underpins biosensor design; Dexter transfer is exploited in OLEDs to harvest triplet excitons and in artificial photosynthesis to shuttle energy across molecular assemblies

Factors in non-radiative decay

Several molecular and environmental factors control how fast non-radiative decay competes with emission. The overall quantum yield of emission ties these together:

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

where k_r is the radiative rate constant and k_{nr} is the sum of all non-radiative rate constants. Anything that increases k_{nr} lowers the quantum yield.

Energy gap and Franck-Condon factors. The energy gap law states that non-radiative decay rates increase as the energy gap between two electronic states decreases. This is because a smaller gap means fewer vibrational quanta are needed to bridge it, improving the Franck-Condon factor (the overlap integral between vibrational wavefunctions of the two states). A large gap with poor vibrational overlap suppresses internal conversion.

Molecular rigidity. Flexible molecules have more low-frequency vibrational modes that can accept electronic energy, so they tend to have higher k_{nr} . Rigid molecules like anthracene restrict these motions and consequently show strong fluorescence. Compare this to a flexible aliphatic chain like hexane, which dissipates excitation energy rapidly through torsional and bending modes.

Temperature. Higher temperatures populate higher vibrational levels and increase collision frequency, both of which generally raise k_{nr} . Some non-radiative processes have a true activation energy barrier (e.g., conformational changes that open a decay channel), making them strongly temperature-dependent. Temperature-dependent phosphorescence quenching is a classic example.

Solvent interactions. Solvent polarity can stabilize or destabilize excited states relative to the ground state, shifting the energy gap and thereby changing non-radiative rates. Solvent viscosity matters too: high viscosity restricts molecular motion, reducing collisional quenching and conformational relaxation, which tends to lower k_{nr} .

Heavy atom effect. Heavy atoms (either within the molecule or in the solvent, e.g., brominated solvents) enhance spin-orbit coupling, which increases the rate of intersystem crossing ($S_1 \rightarrow T_1$). This is a non-radiative transition between states of different spin multiplicity. The heavy atom effect is widely exploited in phosphorescent emitter design and photosensitizer development.

Marcus theory. For non-radiative processes that involve electron transfer (e.g., photoinduced charge separation), Marcus theory provides the rate expression. The rate depends on the reorganization energy (λ), which accounts for nuclear rearrangement of the molecule and solvent, and the driving force (ΔG^0). A key prediction is the "inverted region": when $-\Delta G^0 > \lambda$, the rate actually decreases with increasing driving force, a counterintuitive result confirmed experimentally.

6.3 Internal conversion and intersystem crossing

Excited state deactivation processes are crucial in photochemistry. Internal conversion and intersystem crossing allow molecules to release energy without emitting light, influencing everything from photosynthesis to OLEDs.

Various factors affect these processes, including energy gaps, molecular structure, and environment. Understanding deactivation mechanisms is key for applications in fields like photodynamic therapy, atmospheric chemistry, and materials science.

Excited State Deactivation Processes

Internal conversion in excited states

- Internal conversion (IC) facilitates non-radiative transitions between electronic states with same spin multiplicity occurs between higher excited states or from lowest excited state to ground state
- IC rapidly converts electronic energy to vibrational energy on femtosecond to picosecond timescale competes with fluorescence

- Energy conservation during IC dissipates excess energy as heat to surrounding molecules (solvent molecules)
- Franck-Condon principle governs IC probability depends on overlap of vibrational wavefunctions (potential energy surfaces)

Intersystem crossing in photochemistry

- Intersystem crossing (ISC) enables non-radiative transitions between electronic states of different spin multiplicity usually from singlet to triplet state or vice versa
- ISC populates triplet states leads to phosphorescence and triplet-state reactivity (photosensitization)
- Spin-orbit coupling mechanism allows ISC to occur by mixing spin and orbital angular momentum
- ISC generally occurs slower than internal conversion typically on nanosecond to microsecond timescale

Factors affecting deactivation rates

- Energy gap law dictates smaller energy gaps between states lead to faster non-radiative transitions
- Vibronic coupling strength increases rate of internal conversion
- Heavy atom effect enhances spin-orbit coupling increasing ISC rate (iodine, bromine)
- Molecular structure influences deactivation rates:
 - Rigid structures often have slower IC rates
 - Flexible structures facilitate faster IC (aromatic hydrocarbons)
- Higher temperatures increase rates of both IC and ISC
- Solvent polarity and viscosity influence deactivation rates (polar solvents)
- Excited state geometry affects energy gaps and transition rates through conformational changes

Applications of deactivation processes

- Photosynthesis utilizes: 1. IC in light-harvesting complexes to funnel energy 2. ISC in reaction centers to generate long-lived charge-separated states
- Photodynamic therapy employs ISC in photosensitizers to produce reactive oxygen species (singlet oxygen)
- Organic light-emitting diodes (OLEDs) use ISC to harvest both singlet and triplet excitons for improved efficiency
- Photochromic materials control color-changing mechanisms through IC and ISC (sunglasses, smart windows)
- Atmospheric chemistry involves IC and ISC in ozone formation and depletion processes
- DNA photodamage occurs through ISC in thymine dimers formation under UV exposure
- Fluorescence quenching uses IC and ISC as mechanisms for reducing fluorescence intensity in sensors (molecular beacons)

Unit 7 – Fluorescence and Phosphorescence

7.1 Principles of fluorescence and phosphorescence

Luminescence is a fascinating light emission process triggered by various stimuli. It encompasses photoluminescence, where materials absorb and re-emit light. Understanding the Jablonski diagram is key to grasping the electronic states and transitions involved in this phenomenon.

Fluorescence and phosphorescence are two main types of luminescence, differing in their emission speeds and electron spin changes. Various factors affect luminescence efficiency, including molecular structure, environmental conditions, and quenching processes. These principles are crucial for applications in chemistry and materials science.

Fundamentals of Luminescence

Principles of luminescence phenomena

- Luminescence emits light from electronically excited states triggered by various stimuli
- Photoluminescence absorbs photons to induce luminescence common in fluorescent materials
- Jablonski diagram visually represents electronic states and transitions crucial for understanding luminescence
- Excitation process absorbs photons promoting electrons to higher energy states ($S_0 \rightarrow S_1$ or S_2)
- Relaxation process returns excited electrons to ground state emitting photons as radiative decay ($S_1 \rightarrow S_0$)
- Stokes shift measures difference between excitation and emission wavelengths due to energy loss in excited state (typically 20-50 nm)

Fluorescence vs phosphorescence mechanisms

- Fluorescence involves singlet-singlet transitions emitting rapidly within nanoseconds without changing electron spin
- Phosphorescence utilizes triplet-singlet transitions emitting slower over milliseconds to hours changing electron spin
- Intersystem crossing transitions between singlet and triplet states enabling phosphorescence process
- Fluorescence occurs in many organic dyes (fluorescein) while phosphorescence in glow-in-the-dark materials (zinc sulfide)

Electronic transitions in luminescence

- Ground state (S_0) represents lowest energy state where electrons reside at room temperature
- Excited singlet states (S_1 , S_2) feature electrons with opposite spins higher energy than S_0
- Excited triplet state (T_1) contains electrons with parallel spins lower energy than S_1

- Fluorescence transitions emit photons from $S_1 \rightarrow S_0$ producing characteristic emission spectra
- Phosphorescence transitions release photons from $T_1 \rightarrow S_0$ resulting in longer-wavelength emission
- Vibrational relaxation causes non-radiative transitions within a state dissipating excess energy as heat

Factors Affecting Luminescence

Efficiency factors in luminescence

- Quantum yield measures ratio of emitted to absorbed photons indicating luminescence efficiency (0-1 scale)
- Fluorescence lifetime averages time molecule spends in excited state before emission (1-10 ns typical)
- Environmental factors impact luminescence:
 - Temperature affects non-radiative decay rates generally decreasing intensity at higher temperatures
 - Solvent polarity influences Stokes shift with polar solvents causing larger shifts
- Molecular structure plays role in luminescence properties:
 - Rigidity reduces non-radiative decay enhancing quantum yield (fluorescein vs fluorescein derivatives)
 - Conjugation affects absorption and emission wavelengths shifting to longer wavelengths with increased conjugation
- Quenching processes decrease luminescence intensity:
 1. Collisional quenching transfers energy to surrounding molecules (oxygen quenching fluorescence)
 2. Static quenching forms non-fluorescent complexes (heavy metal ions quenching organic fluorophores)
- Heavy atom effect enhances intersystem crossing promoting phosphorescence (iodine in thyroid hormones)
- Oxygen efficiently quenches phosphorescence limiting its observation in solution
- Concentration effects lead to self-quenching at high concentrations due to energy transfer between molecules
- Energy transfer processes allow excitation energy to move between molecules:
 - Förster resonance energy transfer (FRET) operates over longer distances (1-10 nm)
 - Dexter electron transfer requires closer contact between molecules (<1 nm)

7.2 Stokes shift and mirror image rule

Fluorescence Spectroscopy Principles

Fluorescence spectroscopy relies on the energy difference between absorbed and emitted photons. The Stokes shift quantifies this difference, while the mirror image rule describes the symmetry between absorption and emission spectra. Together, these concepts are essential for interpreting fluorescence data and designing sensitive detection methods.

Stokes Shift in Fluorescence Spectroscopy

The Stokes shift is the difference in energy (or equivalently, wavelength/wavenumber) between the absorption maximum and the emission maximum of a fluorophore. Emitted photons are always lower in energy than absorbed photons, so the emission spectrum is red-shifted relative to absorption.

Why does this matter practically? The Stokes shift allows you to separate excitation light from emission light using optical filters. A larger shift makes this separation easier, which directly improves detection sensitivity.

The energy "lost" between absorption and emission comes from several relaxation processes:

- Vibrational relaxation — After absorbing a photon, the molecule lands in a vibrationally excited level of the excited electronic state. It quickly sheds that excess vibrational energy as heat to the surrounding medium (typically on a picosecond timescale), relaxing to the lowest vibrational level of S_1 .
- Internal conversion — Non-radiative transfer of energy between electronic states of the same spin multiplicity (e.g., $S_2 \rightarrow S_1$) further dissipates energy before emission occurs.
- Solvent reorganization — Solvent molecules reorient around the new charge distribution of the excited state, stabilizing it and lowering its energy. This is especially significant in polar solvents when the fluorophore has a large excited-state dipole moment.

All three processes reduce the energy available for the emitted photon, producing the observed red shift.

Mirror Image Rule for Spectra

For many organic fluorophores (rhodamine, fluorescein, anthracene), the emission spectrum is an approximate mirror image of the absorption spectrum when plotted on a wavenumber scale. The axis of symmetry falls near the 0–0 transition, where no vibrational quanta are gained or lost.

This symmetry arises because the Franck-Condon principle governs both absorption and emission. During absorption, vertical transitions from the $v = 0$ level of S_0 populate various vibrational levels of S_1 , with intensities determined by the overlap of vibrational wavefunctions. During emission, the process reverses: transitions from $v' = 0$ of S_1 populate vibrational levels of S_0 with a similar pattern of Franck-Condon factors. If the potential energy surfaces of S_0 and S_1 have similar shapes (similar vibrational frequencies and spacing), the vibronic progressions in absorption and emission will be mirror images of each other.

The mirror image rule breaks down when:

- Excited-state reactions change the molecular structure before emission occurs (e.g., excited-state proton transfer, tautomerization).
- Excimer or exciplex formation creates a new emissive species with a different potential energy surface than the initially excited monomer.
- The geometry of S_1 differs substantially from S_0 , altering vibrational frequencies enough to distort the symmetry.

Factors Affecting Stokes Shift

Several molecular and environmental factors determine the magnitude of the Stokes shift:

Solvent polarity. If the fluorophore's dipole moment changes significantly upon excitation, polar solvents will stabilize the excited state through reorientation. Greater solvent polarity leads to greater stabilization and a larger Stokes shift. The Lippert-Mataga equation formalizes this relationship, connecting the Stokes

shift to the solvent's orientation polarizability and the change in dipole moment.

Conformational relaxation. Some molecules undergo structural changes in the excited state, such as twisting or bending. These geometry changes lower the energy of S_1 relative to the Franck-Condon state, increasing the Stokes shift. Rigid molecules like anthracene and perylene have small Stokes shifts because their geometry barely changes upon excitation.

Electronic structure. Electron-donating or electron-withdrawing substituents modify the charge distribution in the excited state. Intramolecular charge transfer (ICT) states, common in push-pull fluorophores, often exhibit large Stokes shifts because the excited-state dipole moment is much larger than the ground-state dipole.

Energy transfer. Förster resonance energy transfer (FRET) from a donor to an acceptor produces emission at the acceptor's wavelength, which can appear as an apparent Stokes shift much larger than either molecule alone would show.

Interpretation of Fluorescence Spectra

Reading a fluorescence spectrum involves both qualitative and quantitative analysis.

Calculating the Stokes shift. Express both maxima in wavenumber units and take the difference:

$$\Delta\bar{\nu} = \bar{\nu}_{abs} - \bar{\nu}_{em}$$

For example, if absorption peaks at $25,000\text{ cm}^{-1}$ and emission at $22,000\text{ cm}^{-1}$, the Stokes shift is $3,000\text{ cm}^{-1}$. Using wavenumbers rather than wavelengths gives a value directly proportional to energy.

What the shift tells you:

- A large Stokes shift (e.g., PRODAN, $\sim 5,000\text{ cm}^{-1}$ in polar solvents) indicates significant excited-state relaxation, often involving charge transfer and solvent reorganization.
- A small Stokes shift (e.g., perylene, $\sim 500\text{ cm}^{-1}$) suggests the molecule's geometry and electronic distribution change very little upon excitation.

Spectral overlap. The region where absorption and emission spectra overlap matters because it enables self-absorption and self-quenching. At high fluorophore concentrations, emitted photons can be reabsorbed by neighboring molecules, distorting the emission spectrum and reducing apparent quantum yield.

Environmental sensitivity. Solvatochromic fluorophores like ANS shift their emission wavelength depending on solvent polarity or binding environment. Tracking these shifts lets you probe local polarity in membranes, protein binding sites, or other microenvironments. Similarly, pH-sensitive dyes like acridine orange shift spectra upon protonation or deprotonation.

Time-resolved measurements. Collecting emission spectra at different delay times after excitation reveals how the spectrum evolves as solvent relaxation and conformational changes proceed. Early-time spectra appear blue-shifted, while later spectra are red-shifted, directly mapping the dynamics of excited-state relaxation.

7.3 Fluorescence quenching mechanisms

Fluorescence Quenching Mechanisms

Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. These mechanisms matter because they form the basis of fluorescence-based sensors, allow you to probe molecular environments, and help you study interactions between molecules at the nanoscale.

There are several distinct quenching pathways, and telling them apart is a core skill in photochemistry. The Stern-Volmer equation ties most of this together quantitatively, so you'll want to be comfortable with it.

Mechanisms of Fluorescence Quenching

Dynamic (collisional) quenching happens when a quencher molecule physically collides with a fluorophore while it's in the excited state. The collision provides a non-radiative pathway for the fluorophore to return to the ground state, so fewer photons get emitted. Dissolved oxygen is a classic dynamic quencher, which is why many fluorescence experiments require degassed solvents.

Static quenching works differently. Here, the quencher binds to the fluorophore in the ground state, forming a non-fluorescent complex before excitation even occurs. This removes fluorophores from the emitting population entirely. Heavy metal ions like Cu^{2+} or Hg^{2+} often quench this way.

Self-quenching occurs at high fluorophore concentrations. Excited fluorophores transfer energy to nearby ground-state copies of themselves, and the energy gets dissipated non-radiatively. Fluorescein at high concentrations is a textbook example. This is why simply adding more dye doesn't always give you a brighter signal.

Resonance energy transfer (RET) involves non-radiative energy transfer from an excited donor to a nearby acceptor molecule. The efficiency depends on spectral overlap between the donor's emission and the acceptor's absorption, and it falls off steeply with distance (proportional to $1/r^6$). FRET (Förster resonance energy transfer) pairs are widely used to measure molecular distances in the 1–10 nm range.

Photoinduced electron transfer (PET) occurs when the excited fluorophore either donates or accepts an electron from the quencher, producing a charge-separated state instead of emitting a photon. Crown ether sensors that detect metal ions often exploit PET: the electron transfer is "switched off" when the metal binds, restoring fluorescence.

Dynamic vs. Static Quenching

These two mechanisms are the most commonly tested distinction, and they differ in several experimentally measurable ways.

Dynamic quenching: - Diffusion-controlled, so it increases with temperature and decreases with solvent viscosity (faster diffusion = more collisions) - Reduces both fluorescence intensity and fluorescence lifetime, because the excited state is being depopulated faster - Fully reversible since no permanent complex forms - Stern-Volmer plot (F_0/F vs. $[Q]$) gives a straight line

Static quenching: - Temperature-independent, or efficiency actually decreases with rising temperature (heat destabilizes the ground-state complex) - Does not change the fluorescence lifetime of the remaining uncomplexed fluorophores, since those molecules behave normally once excited - May be reversible or irreversible depending on binding strength - Stern-Volmer plot can also appear linear, which is why lifetime measurements are essential for distinguishing the two

Key distinction: If you measure both intensity and lifetime, dynamic quenching reduces both proportionally ($F_0/F = \tau_0/\tau$), while static quenching reduces intensity but leaves lifetime unchanged.

The Stern-Volmer Equation

The central quantitative relationship for quenching studies is:

$$F_0/F = 1 + K_{SV}[Q]$$

where: - F_0 = fluorescence intensity without quencher - F = fluorescence intensity with quencher - K_{SV} = Stern-Volmer quenching constant - $[Q]$ = quencher concentration

For dynamic quenching specifically, $K_{SV} = k_q \tau_0$, where k_q is the bimolecular quenching rate constant and τ_0 is the unquenched fluorescence lifetime. This means you can extract k_q if you know τ_0 .

How to use a Stern-Volmer plot:

1. Measure fluorescence intensity at several quencher concentrations.
2. Plot F_0/F on the y-axis against $[Q]$ on the x-axis.
3. A linear plot indicates a single quenching mechanism. The slope equals K_{SV} .
4. Upward curvature (positive deviation) suggests both static and dynamic quenching are occurring simultaneously.
5. Repeat at different temperatures: if K_{SV} increases with temperature, the mechanism is dynamic; if it decreases, it's static.

Common applications: - Determining quenching mechanism through temperature-dependence studies - Calculating bimolecular quenching rate constants - Estimating fluorophore accessibility in proteins or membranes (e.g., how buried a tryptophan residue is) - Designing fluorescence-based sensors for metal ions, oxygen, or biomolecules

Effects of Quenching on Fluorescence Observables

Fluorescence intensity decreases with increasing quencher concentration following the Stern-Volmer relationship. A linear plot points to a single mechanism, while upward curvature suggests combined static and dynamic quenching are both at work.

Fluorescence lifetime is the most diagnostic observable: - In dynamic quenching, lifetime decreases because the excited state gains an additional deactivation pathway. - In static quenching, lifetime stays constant because the complexed molecules never reach the excited state in the first place; the uncomplexed fluorophores that do emit behave normally. - Time-resolved fluorescence measurements are therefore the most reliable way to distinguish the two mechanisms.

Quantum yield drops in both quenching types, proportionally to the intensity decrease. This follows directly from the definition of quantum yield as the ratio of emitted to absorbed photons.

Emission spectrum shape is generally preserved in dynamic quenching, since the emitting species is the same fluorophore. In static quenching, the ground-state complex can sometimes absorb at slightly different wavelengths, and if the complex has any residual emission, you may see a spectral shift (red or blue). But typically, the spectral shape of the uncomplexed fluorophore emission remains unchanged.

7.4 Applications of fluorescence and phosphorescence

Fluorescence and phosphorescence have revolutionized scientific analysis and everyday applications. From detecting pollutants to enhancing medical diagnostics, these light-emitting phenomena offer powerful tools for visualization and measurement across diverse fields.

Fluorescent probes and microscopy techniques enable researchers to peer into cellular processes with unprecedented detail. Meanwhile, phosphorescent materials find use in everything from lighting to anti-counterfeiting, showcasing the broad impact of these photochemical principles.

Fluorescence and Phosphorescence Applications

Applications of fluorescence and phosphorescence

- Analytical chemistry
- Fluorescence spectroscopy quantifies analytes by measuring light emission intensity
- Phosphorescence-based oxygen sensing detects O₂ levels through quenching effects
- Biochemistry and molecular biology
- Fluorescence-based protein assays measure protein concentration and interactions
- DNA sequencing using fluorescent dyes enables high-throughput genetic analysis
- Environmental science
- Detection of pollutants in water and air using fluorescent tracers (polycyclic aromatic hydrocarbons)
- Monitoring of oil spills using fluorescence identifies contamination extent and type
- Forensic science
- Fingerprint detection using fluorescent powders enhances latent print visibility
- Analysis of bodily fluids using UV light reveals otherwise invisible evidence (semen, saliva)
- Medical diagnostics
- Fluorescence-based immunoassays detect specific antigens or antibodies in clinical samples
- Photodynamic therapy for cancer treatment uses light-activated drugs to target tumors
- Materials science
- Fluorescent pigments in paints and coatings enhance visibility and aesthetics
- Phosphorescent materials for glow-in-the-dark products provide long-lasting luminescence (exit signs)

Fluorescent probes in analysis

- Fluorescent probes
- Small molecules emit light upon binding to specific targets revealing molecular interactions
- Calcium indicators (Fura-2), pH-sensitive dyes (BCECF) monitor intracellular conditions
- Fluorescent labels
- Molecules covalently attached to biomolecules of interest track cellular processes
- Fluorescein, rhodamine, Alexa Fluor dyes offer diverse spectral properties
- Applications in protein studies

- Fluorescence resonance energy transfer (FRET) measures protein-protein interactions and conformational changes
- Protein localization using fluorescent fusion proteins reveals subcellular distribution
- Nucleic acid analysis
- Fluorescence in situ hybridization (FISH) maps chromosomal locations of specific DNA sequences
- Real-time PCR using fluorescent probes quantifies gene expression levels
- Enzyme activity assays
- Fluorogenic substrates measure enzyme kinetics by producing fluorescent products
- Membrane studies
- Fluorescent lipid analogs investigate membrane dynamics and lipid rafts

Principles of fluorescence microscopy

- Basic principles
- Excitation of fluorophores with specific wavelengths triggers light emission
- Collection of emitted light using appropriate filters isolates desired signals
- Types of fluorescence microscopy
- Widefield fluorescence microscopy provides broad sample illumination
- Confocal microscopy improves resolution and enables 3D imaging through optical sectioning
- Two-photon microscopy allows deep tissue imaging with reduced phototoxicity
- Sample preparation techniques
- Immunofluorescence staining labels specific proteins with fluorescent antibodies
- Live-cell imaging using fluorescent proteins tracks dynamic cellular processes
- Applications in cell biology
- Visualization of subcellular structures and organelles reveals cellular architecture
- Tracking of protein dynamics and interactions elucidates cellular signaling pathways
- Study of cell division and differentiation uncovers developmental processes
- Advanced techniques
- Super-resolution microscopy (STORM, PALM) breaks diffraction limit for nanoscale imaging
- Fluorescence lifetime imaging microscopy (FLIM) measures fluorophore environment and interactions

Role of phosphorescence in materials

- Phosphorescent materials
- Long-lived excited states result from forbidden transitions extending emission duration
- Transition metal complexes, lanthanide compounds exhibit strong phosphorescence

- Applications in lighting
- Phosphors for fluorescent lamps and LEDs convert UV or blue light to visible spectrum
- Glow-in-the-dark safety signs and emergency lighting provide visibility without power
- Organic light-emitting diodes (OLEDs)
- Phosphorescent emitters improve efficiency by harvesting triplet excitons
- Display technologies and solid-state lighting benefit from OLED advancements
- Optical storage
- Phosphorescent materials enable data storage and retrieval through persistent luminescence
- Sensors and detectors
- Oxygen sensors utilize phosphorescence quenching to measure O₂ concentrations
- Temperature-sensitive phosphors enable non-contact thermal imaging
- Photocatalysis
- Phosphorescent materials act as photocatalysts for solar energy conversion and water splitting
- Anti-counterfeiting measures
- Phosphorescent inks and dyes create security features for currency and official documents

Unit 8 – Energy Transfer and Quenching in Photochem

8.1 Collisional quenching and Stern-Volmer relationship

Collisional Quenching

Process of collisional quenching

Collisional (or dynamic) quenching happens when a molecule in its excited state bumps into another molecule, called a quencher, and returns to the ground state without emitting a photon. The fluorophore isn't chemically changed in the process. For example, dissolved oxygen can quench tryptophan fluorescence this way.

The underlying mechanism typically involves either energy transfer from the excited fluorophore to the quencher, or electron transfer between them. Either way, the excited state is deactivated before fluorescence can occur.

Several factors control how effective collisional quenching is:

- Temperature: Higher temperature means faster diffusion, so molecules collide more often and quenching increases.
- Viscosity: A more viscous solvent (like glycerol compared to water) slows diffusion and reduces the collision rate, making quenching less efficient.
- Diffusion rates: Both the fluorophore and quencher need to encounter each other during the excited-state lifetime. Larger or slower-diffusing molecules quench less effectively.

The observable result is a decrease in both fluorescence intensity and excited-state lifetime. That lifetime point is critical for distinguishing dynamic quenching from static quenching later on.

Common quenchers include molecular oxygen (O_2), halogens and halide ions (I^- , Br^-), amines, and acrylamide. Each has different selectivity, which makes them useful probes. For instance, iodide is charged and can only quench surface-exposed fluorophores in a protein, while oxygen is small and nonpolar enough to penetrate into hydrophobic regions.

Stern-Volmer relationship in quenching

The Stern-Volmer equation provides a quantitative link between quencher concentration and the reduction in fluorescence:

$$F_0/F = 1 + K_{SV}[Q]$$

Here, F_0 is the fluorescence intensity without quencher, F is the intensity at quencher concentration $[Q]$, and K_{SV} is the Stern-Volmer quenching constant. A larger K_{SV} means the fluorophore is more easily quenched.

If you plot F_0/F on the y-axis against $[Q]$ on the x-axis, purely dynamic quenching gives a straight line with slope K_{SV} and y-intercept of 1.

Applications of this relationship include:

- Quenching efficiency: Using acrylamide to quench tryptophan residues in proteins tells you how exposed those residues are to solvent.
- Accessibility studies: Charged quenchers like iodide only reach surface-exposed fluorophores, so comparing K_{SV} values for different quenchers reveals which fluorophores sit on the protein surface versus buried inside.
- Conformational changes: If a protein unfolds, previously buried tryptophans become exposed, and K_{SV} increases. This makes Stern-Volmer analysis a useful probe of protein structure.
- Membrane permeability: Measuring how efficiently oxygen quenches a probe embedded in a lipid bilayer reports on how easily small molecules penetrate the membrane.

Stern-Volmer Analysis

Analysis of Stern-Volmer plots

The shape of a Stern-Volmer plot tells you what type of quenching is occurring:

1. Dynamic (collisional) quenching produces a linear plot. The quencher deactivates the excited state through diffusion-controlled encounters.
2. Static quenching arises when the quencher forms a non-fluorescent ground-state complex with the fluorophore. This also reduces intensity, but the plot curves upward at higher $[Q]$. When both dynamic and static quenching operate simultaneously, you also see upward curvature.

Two experimental tests distinguish dynamic from static quenching:

- Temperature dependence: For dynamic quenching, raising the temperature increases diffusion, so K_{SV} goes up. For static quenching, heat destabilizes the ground-state complex, so K_{SV} goes down.
- Lifetime measurements: This is the most definitive test. In dynamic quenching, the excited-state lifetime decreases with added quencher, so $\tau_0/\tau = F_0/F$. In static quenching, only complexed fluorophores are removed from the emitting population; the uncomplexed ones still have their normal lifetime, so $\tau_0/\tau = 1$ regardless of $[Q]$.

Applications of the Stern-Volmer equation

The Stern-Volmer constant connects directly to the bimolecular quenching rate constant k_q through the unquenched lifetime τ_0 :

$$K_{SV} = k_q \tau_0$$

This is useful because k_q is the more fundamental quantity. It tells you how fast quenching occurs per molar concentration of quencher, independent of the fluorophore's intrinsic lifetime. You can rearrange to find it:

$$k_q = K_{SV}/\tau_0$$

For diffusion-controlled quenching in water, k_q is typically around $10^{10} \text{ M}^{-1}\text{s}^{-1}$. Values significantly below this suggest steric shielding or limited accessibility.

You can also rearrange the basic equation to solve for unknown quencher concentration if K_{SV} is known:

$$[Q] = (F_0/F - 1)/K_{SV}$$

For systems where only a fraction of fluorophores are accessible to the quencher (common in proteins with multiple tryptophans), the modified Stern-Volmer equation applies:

$$F_0/(F_0 - F) = 1/(f_a K_{SV}[Q]) + 1/f_a$$

Here f_a is the fraction of accessible fluorophores. Plotting $F_0/(F_0 - F)$ versus $1/[Q]$ gives a straight line with y-intercept $1/f_a$ and slope $1/(f_a K_{SV})$.

Finally, when quenching shows slight upward curvature that can't be fully explained by a static complex, a sphere-of-action model is sometimes used:

$$F_0/F = (1 + K_{SV}[Q])\exp(V[Q])$$

The term V represents the volume around the fluorophore within which any quencher molecule present at the moment of excitation causes immediate quenching. This accounts for quencher molecules that happen to be adjacent to the fluorophore without forming a true ground-state complex.

8.2 Förster resonance energy transfer (FRET)

Principles and Mechanisms of FRET

Förster resonance energy transfer (FRET) is a non-radiative process in which an excited donor fluorophore transfers energy to a nearby acceptor fluorophore through long-range dipole-dipole coupling. Because the transfer efficiency drops off with the sixth power of distance, FRET acts as a molecular ruler sensitive to changes on the 1–10 nm scale. That distance dependence is what makes it so widely used for probing protein interactions, conformational changes, and biosensor design.

Principles of FRET

The donor fluorophore absorbs a photon and reaches an excited state. Instead of emitting a photon, it transfers that energy to an acceptor fluorophore in the ground state through dipole-dipole coupling. No photon is emitted or absorbed during the transfer itself.

For FRET to occur, two spectral conditions must be met:

- The emission spectrum of the donor must overlap with the absorption spectrum of the acceptor. A classic example is the fluorescein (donor) and rhodamine (acceptor) pair.
- The degree of this overlap is quantified by the spectral overlap integral, $J(\lambda)$.

The Förster distance (R_0) is the characteristic donor-acceptor separation at which FRET efficiency equals 50%. Typical R_0 values fall in the 2–6 nm range, depending on the fluorophore pair and local environment.

Factors Influencing FRET Efficiency

FRET efficiency is not controlled by distance alone. Five variables matter:

- Donor-acceptor distance (R): Efficiency falls off as R^{-6} , so even small increases in separation beyond R_0 cause a steep drop. The practical working range is roughly 1–10 nm.
- Spectral overlap integral (J): A larger overlap between donor emission and acceptor absorption means more efficient transfer. The GFP-to-RFP pair, for instance, has moderate overlap that makes it useful for live-cell work.
- Quantum yield of the donor (Q_D): A higher donor quantum yield means the excited state is longer-lived and more likely to transfer energy before decaying by other pathways. Quantum dots are popular donors partly for this reason.

- Orientation factor (κ^2): This describes the relative alignment of the donor and acceptor transition dipole moments. It can range from 0 (perpendicular dipoles, no transfer) to 4 (head-to-tail, collinear). For freely rotating fluorophores in solution, the isotropic average $\kappa^2 = 2/3$ is commonly assumed.
- Refractive index of the medium (n): The strength of dipole-dipole coupling depends on the local dielectric environment. Transfer in water ($n \approx 1.33$) differs from transfer inside a lipid bilayer ($n \approx 1.45$).

Calculation of FRET Parameters

FRET efficiency relates the actual donor-acceptor distance R to the Förster distance R_0 :

$$E = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6}$$

When $R = R_0$, $E = 0.50$. When $R \ll R_0$, E approaches 1. When $R \gg R_0$, E drops toward 0.

Förster radius is calculated from the photophysical properties of the donor-acceptor pair and the medium:

$$R_0 = 0.211 [\kappa^2 n^{-4} Q_D J(\lambda)]^{1/6}$$

where R_0 is in nanometers when $J(\lambda)$ is in units of $M^{-1}cm^{-1}nm^4$.

Spectral overlap integral captures how well the donor emission and acceptor absorption match across wavelength:

$$J(\lambda) = \int F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda$$

Here $F_D(\lambda)$ is the area-normalized donor emission spectrum (dimensionless when integrated to unity) and $\epsilon_A(\lambda)$ is the acceptor molar extinction coefficient. The λ^4 weighting means that overlap at longer wavelengths contributes disproportionately.

Applications of FRET in Biomolecules

FRET's sensitivity to nanometer-scale distances makes it a go-to tool across molecular biology and drug discovery.

- Protein-protein interactions: FRET can detect and quantify binding events by labeling two suspected partners with a donor-acceptor pair. If they bind, the fluorophores come within FRET range and efficiency increases. This approach has been used to study insulin receptor-substrate interactions and measure binding affinities.
- Conformational changes: Placing the donor and acceptor at two sites on the same protein lets you monitor folding, unfolding, or allosteric transitions. Calmodulin, for example, undergoes a large structural rearrangement upon calcium binding that produces a clear FRET signal change.
- Nucleic acid structure: DNA and RNA hairpin formation, hybridization assays, and helicase activity can all be tracked by FRET between labels on complementary strands or different positions along a single strand.
- Membrane dynamics: Labeling lipids or membrane proteins with FRET pairs reveals information about lipid-protein interactions and membrane fusion. SNARE-mediated vesicle fusion is a well-studied example.
- Biosensors: Engineered FRET-based sensors report on intracellular ion concentrations (calcium sensors like Cameleon) or enzyme activity by changing conformation in response to a specific analyte.

- Single-molecule FRET (smFRET): By observing one molecule at a time, smFRET reveals heterogeneity that bulk measurements average out. It has been used to watch ribosome translation dynamics and capture transient intermediate states in real time.
- Drug discovery: High-throughput FRET assays screen for compounds that disrupt or stabilize protein-protein interactions, a strategy used in anticancer drug development.
- Live-cell imaging: Genetically encoded FRET pairs (e.g., CFP/YFP) allow real-time visualization of protein localization, trafficking, and signaling inside living cells, including neurons.

8.3 Dexter electron transfer

Dexter Electron Transfer Mechanism and Characteristics

Dexter electron transfer is a mechanism where two molecules physically exchange electrons when their orbitals overlap. Because it requires such close contact, it only works at very short distances (1–2 nm), which sets it apart from Förster Resonance Energy Transfer (FRET). Understanding Dexter transfer is essential for explaining triplet-triplet energy transfer, designing photocatalysts, and engineering solid-state lighting devices.

Mechanism of Dexter electron transfer

In Dexter transfer, the donor and acceptor molecules simultaneously swap electrons. The donor's excited electron moves to the acceptor, while an electron from the acceptor moves back to the donor, all in a single concerted step. This is fundamentally different from FRET, which transfers energy through dipole-dipole coupling without any electron exchange.

For this simultaneous swap to happen, the molecular orbitals of the donor and acceptor must physically overlap. That's why the two molecules need to be essentially in contact or separated by no more than about 1–2 nm.

Dexter vs. FRET at a glance: - Dexter: direct electron exchange, requires orbital overlap, effective range ~1–2 nm, rate decays exponentially with distance - FRET: dipole-dipole energy transfer, no physical contact needed, effective range up to ~10 nm, rate follows $1/r^6$ distance dependence

At very short donor-acceptor separations, Dexter transfer can outcompete FRET and become the dominant energy transfer pathway.

Orbital overlap and spin conservation

Orbital overlap is the gating requirement for Dexter transfer. Without sufficient overlap of the donor and acceptor wavefunctions, the electron exchange simply can't occur. Since wavefunction amplitude drops off exponentially as you move away from a molecule, even small increases in separation cause large drops in transfer probability.

A distinctive feature of Dexter transfer is that total spin is conserved during the exchange. Both electrons move simultaneously, so the overall spin state of the donor-acceptor pair doesn't change. This has a major practical consequence: Dexter transfer can mediate triplet-triplet energy transfer, where a triplet-excited donor transfers its energy to produce a triplet-excited acceptor. FRET, by contrast, is spin-forbidden for triplet-triplet transfer because it relies on dipole-dipole coupling (which requires spin-allowed transitions). This makes Dexter the primary mechanism behind phosphorescence sensitization and triplet-based photochemistry.

Distance dependence of Dexter transfer

The rate constant for Dexter transfer follows an exponential decay with distance:

$$k_{ET} \propto e^{-\beta R}$$

where R is the donor-acceptor separation and β is the attenuation factor, which describes how quickly the rate falls off. A larger β means the transfer rate drops more steeply with distance. The value of β depends on the medium between donor and acceptor; through-vacuum or through-space transfer has a large β , while conjugated molecular bridges can lower it significantly.

Because of this exponential dependence, the transfer rate becomes negligible beyond about 1–2 nm. In practice, Dexter transfer dominates in systems where molecules are packed tightly together, such as solid-state films, concentrated solutions, or rigid molecular assemblies.

Examples of Dexter-dominated systems

- Triplet-triplet annihilation (TTA) upconversion: Two triplet-excited molecules undergo Dexter-mediated energy transfer, combining their energy to produce a higher-energy singlet excited state. This converts low-energy photons into higher-energy ones and has applications in photovoltaics and bioimaging.
- Photocatalysis: Dexter transfer facilitates electron exchange between a photocatalyst and a substrate molecule. This is central to reactions in organic synthesis and photocatalytic water splitting.
- Phosphorescent OLEDs: In solid-state lighting, Dexter transfer moves triplet excitons between host and guest molecules in the emissive layer, enabling efficient phosphorescent emission.
- Photosynthetic reaction centers: Bacterial photosynthesis relies on short-range electron transfer steps between closely spaced cofactors, where Dexter-type exchange plays a role.
- Molecular wires and bridges: Conjugated molecular bridges can extend the effective range of Dexter transfer by lowering β , enabling electron exchange over distances that would otherwise be too large for through-space transfer.

8.4 Marcus theory of electron transfer

Fundamentals of Marcus Theory

Marcus theory provides a quantitative framework for predicting the rates of electron transfer reactions. Developed by Rudolph Marcus in the 1950s (earning him the 1992 Nobel Prize in Chemistry), it connects thermodynamics and kinetics by showing how both the energy released in a reaction and the structural rearrangements required to accommodate that transfer jointly determine how fast the transfer occurs. This framework applies broadly, from simple inorganic redox couples to the charge-separation steps in photosynthesis.

Key Concepts

Reorganization energy (λ) is the energy the system would need to rearrange all nuclear coordinates from the reactant geometry to the product geometry without actually transferring the electron. It has two components:

- Inner-sphere (λ_i): Changes in bond lengths and angles within the donor and acceptor molecules themselves. For example, when Fe^{2+} loses an electron to become Fe^{3+} , the metal-ligand bonds shorten.

- Outer-sphere (λ_o): Reorientation of surrounding solvent molecules in response to the new charge distribution. In polar solvents like water, this component is often dominant.

Driving force (ΔG°) is the standard Gibbs free energy change for the electron transfer. A negative ΔG° means the reaction is exergonic (thermodynamically favorable). The more negative ΔG° is, the more energy is released.

Activation energy ($\Delta G^\ddagger$) is the energy barrier the system must overcome for the transfer to occur. Marcus theory's central achievement is providing an exact relationship between $\Delta G^\ddagger$, λ , and ΔG° .

Potential Energy Surfaces

Marcus theory models the reactant and product states as two parabolic potential energy surfaces plotted against a generalized nuclear coordinate (sometimes called the reaction coordinate). This coordinate captures all the structural changes: bond lengths, bond angles, and solvent positions.

The parabolas have equal curvature (the harmonic oscillator approximation), and they're offset both horizontally (different equilibrium geometries) and vertically (by ΔG°). The point where the two parabolas intersect is the transition state. At this geometry, the electron can transfer because the reactant and product states have the same energy, satisfying the Franck-Condon principle (nuclei don't move during the instantaneous electron hop).

The height of the intersection point above the reactant minimum gives $\Delta G^\ddagger$. Changing either λ or ΔG° shifts the parabolas relative to each other, raising or lowering this intersection.

Mathematical Framework and Applications

The Marcus Equation

The central result of the theory is:

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda}$$

This expression for the activation barrier feeds directly into the rate constant through transition-state-like kinetics:

$$k_{ET} = A \exp \left[-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_B T} \right]$$

where:

- k_{ET} is the electron transfer rate constant
- A is the pre-exponential factor, determined primarily by the electronic coupling H_{DA} between donor and acceptor (stronger orbital overlap means larger A)
- k_B is the Boltzmann constant
- T is the absolute temperature

How to read the equation: The numerator $(\lambda + \Delta G^\circ)^2$ controls the barrier height. Because ΔG° is negative for exergonic reactions, increasing the magnitude of ΔG° first decreases the numerator (lowering the barrier) and then, once $|\Delta G^\circ|$ exceeds λ , increases it again. This produces three distinct regimes:

1. Normal region ($|\Delta G^\circ| < \lambda$): Making the reaction more exergonic lowers the barrier and speeds up the rate. This matches everyday chemical intuition.

2. Activationless point ($-\Delta G^\circ = \lambda$): The barrier vanishes ($\Delta G^\ddagger = 0$), and the rate reaches its maximum. The two parabolas intersect exactly at the reactant minimum.
3. Inverted region ($|\Delta G^\circ| > \lambda$): Making the reaction even more exergonic now raises the barrier and slows down the rate. This counterintuitive prediction was the most controversial aspect of Marcus theory and took decades to confirm experimentally.

The inverted region is the signature prediction of Marcus theory. It means that a reaction can become "too favorable" for its own good: the product parabola drops so far below the reactant parabola that their intersection point climbs back up.

Applications

Chemical systems: - Self-exchange reactions like $\text{Fe}^{2+}/\text{Fe}^{3+}$ are the simplest test cases because $\Delta G^\circ = 0$, so the barrier depends only on λ . - The Creutz-Taube ion (a mixed-valence ruthenium dimer) provided early evidence for strong electronic coupling and delocalized electron transfer.

Biological systems: - In photosynthetic reaction centers, the initial charge separation after chlorophyll excitation is extremely fast (picoseconds) because $-\Delta G^\circ$ is tuned close to λ , placing the system near the activationless point. Subsequent back-electron-transfer (charge recombination) is much slower because it falls in the inverted region, which is exactly what the organism needs to preserve the separated charges. - In the mitochondrial electron transport chain, each step involves a modest driving force and relatively small reorganization energies, keeping transfer rates fast and efficient.

Key factors that modulate k_{ET} : - Donor-acceptor distance: The electronic coupling H_{DA} decays exponentially with distance, roughly as $H_{DA} \propto e^{-\beta r}$, where β depends on the intervening medium (about $1.0\text{--}1.4 \text{ \AA}^{-1}$ through protein, higher through vacuum). - Solvent polarity: Higher dielectric constant solvents increase λ_o , which shifts the activationless point to larger $|\Delta G^\circ|$ values and changes which regime the reaction falls in. - Temperature: Higher T increases the rate in the normal region (classical barrier crossing) but the effect is more complex in the inverted region, where nuclear tunneling can become significant.

Experimental techniques: - Transient absorption spectroscopy tracks the appearance and decay of radical ion intermediates on femtosecond-to-nanosecond timescales, directly measuring k_{ET} . - Electrochemical methods (cyclic voltammetry, chronoamperometry) probe redox potentials and heterogeneous electron transfer rates at electrode surfaces, providing ΔG° and rate data in a single experiment.

Unit 9 – Photochemical Kinetics and Quantum Yields

9.1 Rate laws for photochemical reactions

Fundamentals of Photochemical Rate Laws

Photochemical rate laws describe how fast reactions proceed when driven by light absorption rather than heat. They differ from thermal rate laws in a few important ways: the energy source is photons instead of molecular collisions, the temperature dependence is weaker, and light intensity becomes a key variable. Mastering these rate laws lets you predict reaction speeds, calculate quantum yields, and understand how changing conditions will shift outcomes.

Rate Laws for Photochemical Reactions

The core challenge in photochemical kinetics is that light absorption creates short-lived excited states and reactive intermediates. You rarely observe these directly, so you need a systematic way to connect them to measurable product formation rates.

The steady-state approximation is the main tool here. It assumes that the concentration of each reactive intermediate stays roughly constant over time because its rate of formation equals its rate of consumption. This isn't literally true at the very start of a reaction, but it holds well once the intermediates reach their (low) steady-state concentrations.

Deriving a photochemical rate law follows these steps:

1. Write out every elementary step in the mechanism (photon absorption, excited-state decay, quenching, product-forming steps, etc.)
2. Identify the reactive intermediates (excited states, radicals, etc.)
3. Apply the steady-state approximation to each intermediate: set $\frac{d[\text{intermediate}]}{dt} = 0$
4. Solve the resulting algebraic equations for the intermediate concentrations
5. Substitute those expressions into the rate equation for product formation

The result is a rate law written entirely in terms of measurable quantities: ground-state reactant concentrations, light intensity, and rate constants for each elementary step.

Quantum yield (Φ) often appears in the final rate law. It's defined as the number of molecules reacted (or product molecules formed) per photon absorbed. A quantum yield of 1 means every absorbed photon leads to one reaction event. Values above 1 are possible in chain reactions; values below 1 indicate competing deactivation pathways.

Factors in Photochemical Reaction Rates

Several variables control how fast a photochemical reaction proceeds:

- Light intensity (I_0): The reaction rate is directly proportional to the rate of photon absorption. More photons in means more excited-state molecules formed per unit time.

- **Reactant concentration:** Higher concentration increases light absorption according to the Beer-Lambert law ($A = \epsilon \ell C$, where ϵ is the molar absorptivity, ℓ is the path length, and C is the concentration). However, at very high concentrations, the solution can become optically thick, meaning nearly all light is absorbed in a thin front layer and the relationship between concentration and overall rate becomes nonlinear.
- **Temperature:** Unlike thermal reactions, photochemical rates are often only weakly temperature-dependent. Temperature mainly affects non-radiative decay rates and diffusion-controlled steps (like quenching), which can shift the quantum yield slightly.
- **Solvent:** The solvent influences excited-state lifetimes through viscosity, polarity, and specific interactions. A polar solvent may stabilize a charge-transfer excited state, for example, altering which decay pathway dominates.
- **Photosensitizers and quenchers:** A photosensitizer absorbs light and transfers energy to the reactant, effectively increasing the rate. A quencher deactivates the excited state before it can react, decreasing the rate.

Application and Analysis of Photochemical Rate Laws

Thermal vs. Photochemical Rate Laws

Understanding the contrasts between thermal and photochemical kinetics helps you recognize when standard assumptions (like Arrhenius behavior) do and don't apply.

Feature	Thermal	Photochemical
Initiation	Molecular collisions supply energy	Photon absorption creates excited state
Energy input	Must overcome activation energy barrier	Electronic excitation to specific state
Temperature dependence	Strong (Arrhenius: $k = Ae^{-E_a/RT}$)	Weak; mainly affects secondary steps
Reaction order	Typically integer	Can be fractional due to light-absorption terms
Rate-determining step	Slowest elementary step	Often photon absorption rate or excited-state decay

A key practical difference: for thermal reactions, raising the temperature is the main way to speed things up. For photochemical reactions, increasing light intensity or improving quantum yield matters far more.

Working with Photochemical Rate Laws

The general form of a photochemical rate law is:

$$\text{Rate} = k[A]^a[B]^bI_0^c$$

Here k is the rate constant, $[A]$ and $[B]$ are reactant concentrations, I_0 is the incident light intensity, and the exponents a , b , and c are determined experimentally. Notice that I_0 appears explicitly, which never happens in a purely thermal rate law.

Calculating reaction rates: Plug known concentrations and light intensity into the experimentally determined rate law. You can also rearrange to solve for an unknown parameter if the rate has been measured.

Determining quantum yield: Measure both the reaction rate and the rate of photon absorption (I_{abs}), then apply:

$$\Phi = \frac{\text{Rate of reaction}}{I_{\text{abs}}}$$

For example, if a reaction produces 2.0×10^{-6} mol of product per second and the solution absorbs 5.0×10^{-6} einstein per second (one einstein = one mole of photons), then $\Phi = 0.40$. That tells you 40% of absorbed photons lead to product.

Predicting rate changes: The rate law lets you quantify how changes propagate. If the rate law is first-order in I_0 and you double the lamp intensity, the rate doubles. If it's half-order in $[A]$, doubling the concentration increases the rate by a factor of $\sqrt{2} \approx 1.41$. Always check the exponents before making predictions.

9.2 Quantum yield determination and interpretation

Quantum Yield Fundamentals

Quantum yield tells you how efficiently absorbed light drives a photochemical process. If a molecule absorbs a photon, does something useful happen, or does the energy get wasted? Quantum yield puts a number on that question, making it one of the most important metrics in photochemistry for comparing reactions, diagnosing mechanisms, and optimizing real systems.

Quantum yield definition and significance

The quantum yield (Φ) is defined as the ratio of the number of molecules undergoing a specific process to the number of photons absorbed:

$$\Phi = \frac{\text{Number of molecules undergoing the process}}{\text{Number of photons absorbed}}$$

"The process" here could be a chemical reaction, fluorescence emission, intersystem crossing, or any other fate of the excited state. Each process gets its own quantum yield, and for a given molecule the quantum yields of all possible processes should sum to 1.

Φ is dimensionless and directly connects product formation (or emission intensity) to light input. That makes it the standard way to compare photochemical efficiencies across different reactions, catalysts, or conditions.

Quantum yield calculations

Determining Φ experimentally requires two independent measurements: how much chemistry happened, and how many photons were absorbed.

Step-by-step procedure:

1. Quantify the chemical change. Measure the concentration change of reactant consumed or product formed over a known irradiation time (UV-Vis spectroscopy, chromatography, etc.).
2. Quantify absorbed photons. This is the trickier part. Two main approaches: - Chemical actinometry uses a reference reaction with a well-known quantum yield (e.g., potassium ferrioxalate actinometer, $\Phi \approx 1.24$ at 254 nm) to convert observed chemical change into photon flux. - Physical radiometry uses a calibrated photodetector to measure incident light intensity directly; you then correct for the fraction actually absorbed by the sample using its absorbance.
3. Apply the quantum yield formula. Convert both quantities to the same units (typically moles) and divide.

Common pitfalls to watch for:

- Non-uniform illumination. If parts of the solution receive more light than others, local reaction rates vary and your averaged Φ becomes unreliable. Stirring and thin-path-length cells help.
- Secondary reactions. Products that absorb at the irradiation wavelength or react further with starting material will distort the apparent Φ . Measuring initial rates (short irradiation times, low conversion) minimizes this.
- Inner filter effects. At high optical densities, not all of the solution is uniformly illuminated. Keeping absorbance below about 0.3 at the irradiation wavelength, or using correction factors, addresses this.

Interpretation of quantum yield values

The value of Φ carries direct mechanistic information:

- $\Phi = 1$ means every absorbed photon produces one event of interest. This is perfect one-to-one efficiency.
- $\Phi < 1$ (the most common case) means competing deactivation pathways are draining excited-state population. These include fluorescence, phosphorescence, internal conversion, and intersystem crossing. A low Φ doesn't necessarily mean a "bad" reaction; it means you need to account for where the energy goes.
- $\Phi > 1$ signals that a single photon-absorption event triggers multiple product-forming steps. The classic example is a radical chain reaction: one photon generates a radical that propagates through many substrate molecules before terminating. Some photopolymerizations and HBr formation from H_2 and Br_2 show Φ values well above 1 (sometimes 10^4 or higher for chain processes).

For simple, non-chain photoreactions, Φ is bounded between 0 and 1. Whenever you see $\Phi > 1$, think chain mechanism.

Comparing Φ values across conditions (different solvents, temperatures, wavelengths) is one of the best ways to probe what controls a photochemical reaction's efficiency.

Factors affecting quantum yield

Several categories of factors can raise or lower Φ :

Competing excited-state processes

Every deactivation pathway that doesn't lead to the desired chemistry reduces Φ . The main competitors are fluorescence, phosphorescence, internal conversion (vibrational relaxation back to S_0), and intersystem crossing ($S_1 \rightarrow T_1$). The quantum yields of all pathways from a given excited state must sum to 1, so enhancing one pathway necessarily suppresses others.

Energy transfer

Mechanisms like Förster resonance energy transfer (FRET) and Dexter exchange transfer can redirect excitation energy to a nearby acceptor molecule. Whether this helps or hurts Φ depends on whether the acceptor undergoes the desired reaction. In photosensitization, energy transfer is deliberately used to increase the effective quantum yield of a reaction that the original absorber wouldn't undergo efficiently on its own.

Environmental conditions

- Temperature: Higher temperatures generally increase rates of thermally activated steps (like bond-breaking from a triplet state) but also accelerate non-radiative decay, so the net effect on Φ depends on the system.

- Solvent polarity: Polar solvents stabilize charge-transfer excited states, shifting energetics and lifetimes. For example, acetone's $n \rightarrow \pi^*$ state behaves differently in hexane versus water.
- pH: Protonation or deprotonation changes the chromophore's electronic structure. Phenol and phenolate have different absorption spectra and different excited-state reactivities, so Φ can shift dramatically across a few pH units.

Molecular structure

- Extended conjugation (e.g., anthracene vs. naphthalene) tends to lengthen excited-state lifetimes, giving more time for productive chemistry.
- Electron-donating or electron-withdrawing substituents modify orbital energies and excited-state character (e.g., nitrobenzene undergoes efficient intersystem crossing due to the nitro group, lowering its fluorescence Φ).
- Rigid molecular frameworks reduce non-radiative decay, generally increasing Φ .

Concentration effects

- Self-quenching: At high concentrations, an excited molecule can transfer energy to a ground-state neighbor non-productively, lowering Φ . Fluorescein solutions show this clearly above ~1 mM.
- Aggregation: Molecular aggregates can either enhance or diminish Φ . J-aggregates (head-to-tail stacking) tend to have high fluorescence quantum yields, while H-aggregates (face-to-face stacking) are often quenched.

Light intensity and wavelength

- Very high photon fluxes can populate excited states faster than they decay, leading to multiphoton processes or saturation effects that lower the apparent single-photon Φ .
- Wavelength matters because different electronic transitions have different excited-state characters. Chlorophyll a and chlorophyll b absorb at different wavelengths and feed energy into the photosynthetic reaction center with slightly different efficiencies, though Kasha's rule means that for most molecules, Φ is independent of excitation wavelength within the same electronic band.

9.3 Steady-state and time-resolved kinetics

Kinetic Techniques in Photochemistry

Photochemical reactions involve short-lived intermediates that are difficult to detect with conventional methods. Steady-state and time-resolved kinetic techniques offer complementary ways to study these reactions: steady-state methods give you the big picture of overall rates, while time-resolved methods let you watch individual molecular events unfold in real time.

Steady-State vs. Time-Resolved Kinetics

These two approaches differ in timescale, light source, and the kind of information they provide.

Steady-state kinetics measures overall reaction rates by assuming that intermediate concentrations remain roughly constant over the observation period (seconds to hours). You illuminate the sample continuously and track how reactants or products change over relatively long timescales.

Time-resolved kinetics directly observes transient species and intermediates by monitoring concentration changes on very short timescales (femtoseconds to milliseconds). Instead of continuous illumination, you hit the sample with a short pulse of light and then watch what happens.

Steady-state methods tell you how fast a reaction goes overall. Time-resolved methods tell you what happens along the way by capturing each intermediate step.

The choice between them depends on your question. If you need a rate law or a quantum yield, steady-state is often sufficient. If you need to identify a triplet state or a radical intermediate, you'll need time-resolved techniques.

Applications of Steady-State Methods

The steady-state approximation simplifies complex mechanisms by setting the rate of formation of each intermediate equal to its rate of consumption. This eliminates intermediate concentrations from the rate law, giving you an expression in terms of reactant and product concentrations only.

Several standard analyses rely on this framework:

- Rate law and order determination: You classify reactions as zero-order, first-order, or second-order by fitting concentration-vs.-time data to integrated rate equations. For example, a first-order decay gives a linear plot of $\ln[A]$ vs. time.
- Stern-Volmer analysis quantifies how a quencher reduces fluorescence intensity or lifetime:

$$\frac{F_0}{F} = 1 + K_{SV}[Q]$$

Here F_0 is the fluorescence without quencher, F is the fluorescence with quencher at concentration $[Q]$, and K_{SV} is the Stern-Volmer constant. A linear plot of F_0/F vs. $[Q]$ indicates a single quenching mechanism (dynamic or static). Upward curvature suggests both mechanisms operate simultaneously.

- Michaelis-Menten kinetics applies when photochemical reactions involve enzyme-catalyzed steps:

$$v = \frac{V_{max}[S]}{K_m + [S]}$$

The Lineweaver-Burk plot linearizes this by taking the reciprocal:

$$\frac{1}{v} = \frac{K_m}{V_{max}} \cdot \frac{1}{[S]} + \frac{1}{V_{max}}$$

This makes it easier to extract K_m and V_{max} from experimental data, though non-linear fitting of the original equation is generally more accurate.

Time-Resolved Techniques for Intermediates

These methods all follow the same basic logic: excite the sample with a short pulse, then probe what happens afterward. They differ in timescale, detection method, and the kind of intermediate they're best suited to observe.

- Flash photolysis uses an intense light pulse to generate intermediates, then monitors their absorption spectra as they evolve (nanosecond to millisecond timescales). This was the original time-resolved photochemistry technique, developed by Norrish and Porter.
- Pump-probe (transient absorption) spectroscopy uses two ultrashort laser pulses. The pump pulse excites the sample, and the probe pulse arrives at a controlled delay time to measure absorbance changes. By varying the delay, you build up a picture of how the absorption spectrum evolves. This can reach femtosecond resolution, making it possible to track excited-state dynamics and very short-lived intermediates.
- Time-correlated single photon counting (TCSPC) measures fluorescence lifetimes with picosecond to nanosecond resolution. After pulsed excitation, you detect individual emitted photons and build a histogram of arrival times. The decay profile gives you the excited-state lifetime directly.

- Laser-induced fluorescence (LIF) selectively excites a species and detects its fluorescence with high sensitivity. It's particularly useful for detecting low-concentration intermediates in gas-phase photochemistry and reaction dynamics studies.

Kinetic Data Analysis

Once you've collected kinetic data, you need to extract meaningful parameters. Here's how the main analysis tools work:

Fitting rate constants: For simple first- or second-order kinetics, linear regression on the appropriate transformed plot (e.g., $\ln[A]$ vs. t for first-order) works well. For complex multi-exponential decays, non-linear least-squares fitting is necessary.

Arrhenius analysis extracts the activation energy E_a from the temperature dependence of the rate constant:

$$k = Ae^{-E_a/RT}$$

Plotting $\ln k$ vs. $1/T$ gives a straight line with slope $-E_a/R$. The pre-exponential factor A relates to the frequency of reactive collisions or attempts.

Eyring analysis uses transition state theory to connect the rate constant to thermodynamic activation parameters:

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT}$$

This separates the activation free energy into enthalpic ($\Delta H^\ddagger$) and entropic ($\Delta S^\ddagger$) contributions, giving you deeper mechanistic insight than the Arrhenius equation alone.

Global analysis is essential for time-resolved spectroscopic data where multiple intermediates have overlapping spectra. Instead of fitting each wavelength independently, you fit all wavelengths simultaneously, constraining them to share the same set of rate constants. This resolves the spectra and lifetimes of individual species that would be impossible to separate otherwise.

Kinetic isotope effects (KIEs) compare rate constants for reactions involving isotopically substituted substrates (e.g., H vs. D). A primary KIE (typically $k_H/k_D = 2-7$) indicates that bond breaking at the isotopically labeled position occurs in the rate-determining step. Secondary KIEs are smaller and reflect changes in hybridization or bonding environment.

Unit 10 – Photochemical Reactions: Types and Processes

10.1 Photoisomerization reactions

Photoisomerization Mechanisms and Processes

Photoisomerization is the process by which light absorption causes a molecule to change its geometric shape without altering its chemical formula. This seemingly simple transformation drives critical biological functions (like human vision) and enables technologies ranging from smart windows to light-activated drug delivery.

Understanding photoisomerization requires working through excited-state chemistry, potential energy surfaces, and the rules governing how electrons rearrange during ring-opening and ring-closing reactions.

Mechanisms of Light-Induced Isomerization

Cis-trans (E/Z) isomerization is the most common type. Here's how it works:

1. A molecule absorbs a photon and is promoted to an electronically excited state.
2. In the excited state, the energy barrier to rotation around a double bond drops significantly (the π bond character weakens).
3. The molecule rotates around what was a rigid double bond in the ground state.
4. Upon relaxation back to the ground state, the molecule can land in either the cis or trans configuration.

Stilbene (1,2-diphenylethylene) is the textbook example: UV light converts trans-stilbene to cis-stilbene and vice versa.

Electrocyclic reactions are the other major mechanism. These involve cyclic rearrangement of π electrons, where a ring opens or closes in response to light. The Woodward-Hoffmann rules dictate whether the process is conrotatory (bond ends rotate the same direction) or disrotatory (opposite directions), depending on the number of π electrons and whether the reaction is photochemical or thermal. For example, under photochemical conditions, the ring closure of 1,3-butadiene to cyclobutene proceeds by a conrotatory pathway, which is the opposite of what happens thermally.

Quantum yield (Φ) measures how efficient a photoisomerization reaction is:

$$\Phi = \frac{\text{number of molecules isomerized}}{\text{number of photons absorbed}}$$

Values range from 0 (no isomerization) to 1 (every absorbed photon produces an isomerized molecule). For reference, the trans-to-cis photoisomerization of stilbene has $\Phi \approx 0.35$ in solution, while retinal isomerization in the eye achieves a remarkably high $\Phi \approx 0.67$.

Role of Excited States in Photoisomerization

Both singlet and triplet excited states can participate in photoisomerization, and they often lead to different product distributions. The excited-state potential energy surface has a very different shape from the ground state, which is why reactions that are impossible thermally can proceed readily with light.

Conical intersections are points where two potential energy surfaces (typically S_1 and S_0) become degenerate in energy. At these geometries, the molecule can undergo ultrafast non-radiative decay from the excited state to the ground state. This is not a slow, gradual process; passage through a conical intersection happens on the femtosecond timescale. Retinal isomerization in rhodopsin (the first step of vision) proceeds through a conical intersection, completing the 11-cis to all-trans conversion in roughly 200 fs.

The Franck-Condon principle governs the initial excitation step. Because electronic transitions occur much faster than nuclear motion, the molecule is promoted to the excited state vertically, meaning the nuclear geometry stays essentially frozen during absorption. The molecule then relaxes on the excited-state surface toward geometries that may favor isomerization.

Applications and Compound-Specific Behavior

Applications of Photoisomerization

Molecular switches exploit the reversible structural change between two isomers to toggle a molecular property on and off. Each isomer has distinct physical or chemical characteristics (shape, polarity, absorption spectrum), so switching between them with light can control functions like ion transport through a membrane or triggered drug release from a nanocarrier.

Photochromic materials change color upon light exposure because photoisomerization shifts their absorption spectrum. Transition lenses in eyeglasses are a familiar example. Smart windows use similar chemistry to modulate light transmission, and some data storage concepts encode information as the isomeric state of photochromic molecules.

Biological systems rely heavily on photoisomerization:

- Vision: Absorption of a photon by 11-cis-retinal in rhodopsin triggers isomerization to all-trans-retinal, initiating the signal cascade that produces sight.
- Plant responses: Phytochrome proteins undergo photoisomerization between P_r (red-absorbing) and P_{fr} (far-red-absorbing) forms to regulate germination, flowering, and shade avoidance.
- Optogenetics: Engineered light-sensitive proteins containing photoisomerizable chromophores allow researchers to activate or silence specific neurons with light.

Photoisomerization of Compound Classes

Stilbenes undergo cis-trans isomerization around their central $C = C$ double bond upon UV irradiation. Cis-stilbene can also undergo a secondary reaction: photocyclization to form dihydrophenanthrene, which can then be oxidized to phenanthrene. This makes stilbene photochemistry richer than a simple two-state switch. Resveratrol, a naturally occurring stilbene found in grapes, also exhibits photoisomerization between its trans and cis forms.

Azobenzenes isomerize around an $N = N$ double bond. Several features distinguish them from stilbenes:

- They can be switched with visible light (not just UV), since the $n \rightarrow \pi^*$ transition of the trans form falls in the visible range.
- Photoisomerization is generally faster than in stilbenes.
- The cis form can thermally revert to the more stable trans form without light, with half-lives ranging from milliseconds to days depending on substituents.

Azo dyes are the most common industrial application of this chemistry.

Diarylethenes operate by an electrocyclic mechanism: UV light drives ring closure of the open form, and visible light reopens the ring. Their key advantages are high thermal stability (both isomers are stable indefinitely in the dark) and excellent fatigue resistance (they can be cycled thousands of times without degradation). These properties make them strong candidates for optical memory devices and rewritable data storage.

Factors affecting isomerization behavior cut across all compound classes:

- Substituents tune the absorption wavelength and can raise or lower energy barriers, directly affecting quantum yield. Electron-donating or electron-withdrawing groups shift λ_{max} and alter excited-state lifetimes.
- Solvent polarity influences reaction rates because the two isomers often have different dipole moments. A polar solvent can stabilize one isomer over the other, shifting the photostationary state.
- Steric hindrance around the isomerizable bond can either impede rotation (lowering Φ) or destabilize one isomer, favoring conversion to the other.

10.2 Photodissociation and bond cleavage

Photodissociation Fundamentals

Photodissociation is the process of breaking chemical bonds using light energy. It's one of the most direct photochemical reactions you'll encounter: a molecule absorbs a photon, and if that photon carries enough energy, a bond breaks. The products you get depend on how the bond breaks and which bond is targeted, both of which you can predict and control.

Bond dissociation energy in photodissociation

Bond dissociation energy (BDE) is the minimum energy required to break a specific chemical bond, measured in kJ/mol or kcal/mol. It's the threshold your photon needs to clear.

The core relationship is straightforward:

$$E = h\nu \geq \text{BDE}$$

The photon energy ($E = h\nu$) must meet or exceed the BDE for cleavage to occur. If it doesn't, the molecule may reach an excited state but won't dissociate along that bond.

A few things determine BDE values:

- Bond order: Triple bonds have higher BDEs than double bonds, which are higher than single bonds. For example, the C $\equiv$ C bond in acetylene has a BDE of ~839 kJ/mol, while a C–C single bond in ethane is ~376 kJ/mol.
- Atomic properties: Larger atoms form weaker bonds (C–I is weaker than C–F), and electronegativity differences affect bond strength.
- Molecular context: The same bond type can have different BDEs depending on the surrounding structure. The O–H bond in water (~497 kJ/mol) differs from O–H in methanol (~436 kJ/mol).

This is why BDE is so useful in practice: if you know the BDE of each bond in a molecule, you can choose a wavelength that selectively breaks one bond while leaving others intact.

Homolytic vs heterolytic bond cleavage

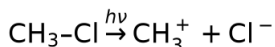
Once a bond breaks, the two bonding electrons have to go somewhere. How they're distributed defines the type of cleavage and the products you get.

Homolytic cleavage splits the electron pair evenly. Each fragment keeps one electron, producing two radicals:



Radicals are highly reactive species with unpaired electrons. This pathway dominates in the gas phase and in nonpolar solvents, where there's nothing to stabilize charged species.

Heterolytic cleavage gives both electrons to one fragment, producing a cation and an anion:



This pathway is favored when:

- The bond is already polar (uneven electron sharing in the ground state)
- The solvent is polar enough to stabilize the resulting ions
- The molecular structure can delocalize or stabilize the charge on one or both fragments

Quick rule of thumb: Gas phase or nonpolar solvent → expect homolytic cleavage. Polar solvent with a polar bond → heterolytic cleavage becomes more likely.

Photodissociation Processes and Factors

Excited states and dissociative pathways

Absorbing a photon doesn't automatically break a bond. The molecule first reaches an electronically excited state, and what happens next depends on the shape of the potential energy surface (PES) for that state.

The Franck-Condon principle governs the initial excitation: because nuclei are much heavier than electrons, the electronic transition happens so fast that the nuclei don't move during absorption. The molecule lands on the excited-state PES at whatever geometry it had in the ground state.

From there, three main dissociative pathways are possible:

1. Direct dissociation — The excited state itself is repulsive (its PES has no energy minimum). The bond stretches immediately and breaks. This is the fastest pathway, often completing in tens of femtoseconds.
2. Predissociation — The molecule is initially excited to a bound state (one with an energy minimum), but that state crosses a repulsive state at some geometry. The molecule can "leak" onto the repulsive surface and dissociate. This is slower than direct dissociation because it depends on the coupling between the two states.
3. Internal conversion followed by dissociation — The molecule relaxes non-radiatively to a lower electronic state (or a vibrationally hot ground state) that has enough energy to break a bond. This is the slowest of the three and competes most directly with other relaxation pathways like fluorescence.

All three pathways operate on ultrafast timescales (femtoseconds to picoseconds) and compete with radiative decay, intersystem crossing, and other deactivation processes.

Factors in photodissociation selectivity

Several variables determine which bonds break, how efficiently, and what products form.

Wavelength is your primary tool for selectivity. Different chromophores in a molecule absorb at different wavelengths, so tuning your light source lets you excite one part of the molecule while leaving the rest alone. This only works if the absorption bands are reasonably well separated.

Light intensity matters in two regimes. At normal intensities, photodissociation is a one-photon process and scales linearly with intensity. At very high intensities (e.g., focused laser pulses), multiphoton dissociation becomes possible, where a molecule absorbs two or more photons sequentially or simultaneously to reach higher-energy dissociative states.

Molecular structure influences dissociation in several ways:

- Weak bonds (low BDE) break preferentially
- Good leaving groups stabilize the departing fragment
- Steric strain can lower the effective barrier to dissociation
- Conjugation or resonance can either stabilize the excited state (slowing dissociation) or stabilize the products (promoting it)

Environmental factors also play a role. In solution, the solvent cage effect can trap radical pairs together, promoting recombination and lowering the apparent dissociation yield. Temperature affects the rate of thermally activated predissociation pathways.

Quantum yield (Φ) quantifies how efficient the overall process is: it's the number of bonds broken per photon absorbed. A quantum yield of 1.0 means every absorbed photon leads to dissociation. Values below 1.0 indicate that competing processes (fluorescence, internal conversion without dissociation, cage recombination) are siphoning away some of the excited-state population.

10.3 Pericyclic reactions and Woodward-Hoffmann rules

Pericyclic reactions reshape molecules through concerted electron movements, creating new bonds without intermediates. These reactions follow strict rules based on orbital symmetry, leading to predictable and stereospecific outcomes in cycloadditions, sigmatropic shifts, and electrocyclic processes.

Woodward-Hoffmann rules guide chemists in predicting allowed reactions and product stereochemistry. By considering orbital symmetry and electron count, we can determine if a reaction will proceed thermally or photochemically, opening up diverse synthetic possibilities.

Pericyclic Reactions Fundamentals

Characteristics of pericyclic reactions

- Pericyclic reactions involve concerted electron redistribution through cyclic orbital arrays without intermediates
- Stereospecific outcomes result from orbital symmetry-governed processes
- Cycloadditions form two new σ bonds (Diels-Alder reaction, [2+2] cycloaddition)
- Sigmatropic rearrangements migrate σ bonds across π systems (Cope rearrangement, Claisen rearrangement)

- Electrocyclic reactions interconvert π and σ bonds (ring opening/closing of cyclobutene)

Application of Woodward-Hoffmann rules

- Conservation of orbital symmetry predicts allowed and forbidden reactions
- Thermal reactions: $[4n+2]$ electrons allowed conrotatory, $[4n]$ electrons allowed disrotatory
- Photochemical reactions: $[4n+2]$ electrons allowed disrotatory, $[4n]$ electrons allowed conrotatory
- Determine reaction feasibility and product stereochemistry
- Guide electrocyclic ring closures and cycloaddition reactions

Orbital Symmetry and Reaction Mechanisms

Orbital factors in pericyclic mechanisms

- Orbital symmetry elements classify symmetric and antisymmetric orbitals
- Frontier Molecular Orbitals (HOMO and LUMO) drive pericyclic reactions
- Correlation diagrams visualize orbital energy changes and identify symmetry-allowed pathways
- Suprafacial and antarafacial interactions determine orbital phase matching
- Symmetry-allowed processes differentiated from symmetry-forbidden reactions

Photochemical vs thermal pericyclic pathways

- Thermal reactions use ground state reactants (thermal $[4+2]$ cycloaddition, 6π electrocyclization)
- Photochemical reactions involve excited state reactants (photochemical $[2+2]$ cycloaddition, 4π electrocyclization)
- Thermal reactions limited by activation energy barriers, photochemical reactions overcome barriers through excitation
- Thermal reactions often yield thermodynamically favored products, photochemical reactions access higher energy intermediates
- Regioselectivity in cycloadditions and stereoselectivity in electrocyclic reactions influenced by reaction conditions
- Complementary thermal and photochemical pathways enable diverse synthetic route design

10.4 Photorearrangements and photocycloadditions

Photorearrangements and excited state reactivity are key players in photochemistry. These processes involve complex molecular transformations triggered by light, leading to unique products and reaction pathways not accessible through thermal chemistry.

Understanding these mechanisms is crucial for harnessing the power of light in organic synthesis and materials science. From di- π -methane rearrangements to photocycloadditions, these reactions offer tools for creating complex structures and novel materials with exciting applications.

Photorearrangements

Mechanisms of common photorearrangements

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Di- π -methane rearrangement involves 1,2-acyl shift followed by 1,2-alkyl shift results in ring contraction or expansion with stereochemistry typically retained (cyclopropylacetone to bicyclo[3.1.0]hexanone)

-

Oxa-di- π -methane rearrangement proceeds through biradical intermediates leads to formation of cyclopropanone derivatives in oxygen-containing compounds (benzophenone to phenylcyclopropyl ketone)

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Norrish Type I reaction cleaves α -carbon-carbon bond in ketones forms acyl-alkyl radical pair leads to decarbonylation or recombination products (acetophenone to benzaldehyde and methane)

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Norrish Type II reaction involves intramolecular hydrogen abstraction in γ -hydrogen containing ketones forms 1,4-biradical intermediate results in cyclobutanol formation or fragmentation (2-pentanone to acetone and ethylene)

Principles of photocycloaddition reactions

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[2+2] Photocycloaddition reacts two π -bonds forms four-membered rings follows Woodward-Hoffmann rules for photochemical reactions (ethylene to cyclobutane)

-

[4+4] Photocycloaddition reacts two conjugated dienes forms eight-membered rings less common than [2+2] cycloadditions (1,3-butadiene to cyclooctadiene)

-

Applications in organic synthesis enable stereospecific formation of cyclic compounds access strained ring systems used in natural product synthesis (artemisinin)

-

Applications in materials science include photopolymerization reactions self-healing materials photoswitchable molecules (azobenzene derivatives)

Excited State Reactivity and Orbital Symmetry

Factors in photochemical reactions

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Excited state reactivity

- Singlet vs triplet excited states determine reaction pathways and product distribution
- Energy transfer processes enable sensitized reactions (triplet sensitizers)

- Intersystem crossing influences excited state lifetime and reactivity (heavy atom effect)
-

Orbital symmetry considerations

- Frontier molecular orbital theory predicts allowed and forbidden reactions
- Correlation diagrams visualize orbital interactions during reaction progress
- Conservation of orbital symmetry in pericyclic reactions governs stereochemical outcomes (conrotatory vs disrotatory)
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Conformational effects

- Molecular geometry in excited states impacts reaction pathways and product distribution
- Steric and electronic factors affect conformational preferences influence regioselectivity and stereoselectivity

Applications of photochemical reactions

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Synthetic utility

- Access complex molecular structures enables synthesis of natural products (vitamin D)
- Stereospecific and regioselective transformations allow precise control over product formation
- Formation of strained ring systems provides unique building blocks for further synthesis (cubane)
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Limitations

- Scale-up challenges due to light penetration issues require specialized reactor designs
- Potential side reactions include photooxidation and radical-induced polymerization
- Substrate-specific reactivity may limit general applicability
-

Applications in organic synthesis

- Total synthesis of natural products utilizes photochemical key steps (paclitaxel)
- Preparation of pharmaceutical intermediates employs photochemical transformations
- Construction of polycyclic frameworks achieves complex molecular architectures (dodecahedrane)
-

Applications in materials science

- Photopolymerization for 3D printing enables rapid prototyping and manufacturing
- Development of photochromic materials creates smart windows and adaptive lenses

- Design of molecular machines and switches forms basis for nanoscale devices (rotaxanes)

Unit 11 – Photosensitization and Photocatalysis

11.1 Principles of photosensitization

Photosensitization is a powerful process that harnesses light energy to trigger chemical changes. It's like having a middleman that absorbs light and passes the energy to another molecule, kickstarting reactions without direct light absorption.

This mechanism is crucial in various fields, from solar cells to cancer treatment. Understanding energy transfer types and applications helps us tap into this phenomenon, making it a key player in photochemistry and beyond.

Fundamentals of Photosensitization

Principles of photosensitization

- Photosensitization transfers energy from light-absorbing molecule to another initiates photochemical changes in target molecule without direct absorption (sunscreens, photodynamic therapy)
- Absorption of light by photosensitizer excites to higher energy state then transfers energy to target molecule triggers chemical changes (chlorophyll in photosynthesis, dye-sensitized solar cells)
- Photosensitizer returns to ground state after energy transfer can be reused for multiple cycles enhances overall efficiency of process (photocatalysts in water treatment)

Energy transfer in photosensitization

- Excitation of photosensitizer absorbs photons transitions from ground state to excited singlet state (chlorophyll absorbing red and blue light)
- Intersystem crossing converts excited singlet state to longer-lived triplet state increases efficiency of energy transfer (Rose Bengal for singlet oxygen generation)
- Förster resonance energy transfer (FRET) occurs through long-range dipole-dipole interactions without molecular collision (fluorescent protein pairs in microscopy)
- Dexter electron transfer requires short-range orbital overlap between molecules involves exchange of electrons (triplet-triplet energy transfer in photochemical upconversion)
- Target molecule relaxation leads to chemical reactions or emission of light as phosphorescence or delayed fluorescence (glow-in-the-dark materials)

Photosensitization Mechanisms and Applications

Type I vs Type II mechanisms

- Type I involves direct interaction between excited photosensitizer and substrate through electron or hydrogen transfer forms radical species (riboflavin-mediated degradation of amino acids)
- Type II transfers energy from excited photosensitizer to ground state oxygen generates highly reactive singlet oxygen oxidizes nearby molecules (methylene blue for water disinfection)

- Type I often dominates in oxygen-poor environments while Type II prevails in oxygen-rich conditions affects choice of photosensitizer for specific applications

Applications of photosensitizers

- Organic dyes like methylene blue and Rose Bengal used in antimicrobial applications and photooxidation reactions (food preservation, wastewater treatment)
- Porphyrins and phthalocyanines employed in photodynamic therapy for cancer treatment and solar energy conversion (tumor targeting, artificial photosynthesis)
- Transition metal complexes such as ruthenium polypyridyl complexes utilized in dye-sensitized solar cells and photocatalysis (Grätzel cells, CO₂ reduction)
- Semiconductor nanoparticles like titanium dioxide (TiO₂) applied in water purification and self-cleaning surfaces (air purifiers, self-sterilizing coatings)
- Natural photosensitizers including chlorophyll and riboflavin found in light-harvesting during photosynthesis and food preservation (plant growth, milk sterilization)

11.2 Singlet oxygen generation and reactions

Singlet Oxygen: Formation and Applications

Singlet oxygen is an excited electronic state of molecular oxygen that forms primarily through photosensitization. Because it's far more reactive than ground-state (triplet) oxygen, it opens up reaction pathways that would otherwise be inaccessible. Understanding how singlet oxygen is generated and how it reacts is central to fields ranging from organic synthesis to cancer therapy.

Formation of singlet oxygen

Ground-state molecular oxygen is unusual: it's a triplet ($^3\Sigma_g^-$), with two unpaired electrons. Singlet oxygen has those electrons paired, and it comes in two excited states:

- $^1\Delta_g$: The lower-energy singlet state, sitting 94 kJ/mol above the ground state. This is the one that matters for almost all photochemistry because it lives long enough to do useful chemistry.
- $^1\Sigma_g^+$: A higher-energy singlet state (157 kJ/mol above ground state) that relaxes to $^1\Delta_g$ extremely rapidly, so it rarely participates in reactions directly.

How it forms:

- Photosensitization is the most common and controllable method (covered in detail below).
- Chemical generation uses reagents like H_2O_2 with $NaOCl$, or thermal decomposition of endoperoxides.
- Microwave discharge through O_2 gas can also produce singlet oxygen, though this is mainly a lab technique.

Detection and lifetime:

Singlet oxygen ($^1\Delta_g$) emits characteristic IR phosphorescence at 1270 nm, which is the primary way to detect and quantify it. Its lifetime depends heavily on the solvent: roughly 2–4 μ s in water, but up to ~50 μ s in deuterated solvents like D_2O , and even longer in non-hydroxylic solvents like carbon tetrachloride (~30 ms). This solvent dependence matters because it directly affects how much time singlet oxygen has to

encounter and react with a substrate.

Quenching removes singlet oxygen before it can react:

- Physical quenching: The singlet oxygen transfers its energy to a quencher (e.g., carotenoids, DABCO) and returns to the ground state without any chemical change.
- Chemical quenching: The singlet oxygen actually reacts with the substrate, consuming it in the process.

Generation through photosensitization

Photosensitization is the workhorse method for generating singlet oxygen because it gives you control over when and where it forms.

The mechanism proceeds in three steps:

1. The photosensitizer absorbs a photon and reaches its excited singlet state (S_1).
2. The sensitizer undergoes intersystem crossing (ISC) to its longer-lived triplet state (T_1).
3. The triplet sensitizer transfers energy to ground-state O_2 ($^3\Sigma_g^-$), producing $^1\Delta_g$ singlet oxygen and regenerating the ground-state sensitizer.

This is a Type II photosensitization process. The sensitizer acts as a catalyst: it's not consumed, so one molecule can generate many equivalents of singlet oxygen.

What makes a good photosensitizer?

- High ISC quantum yield (Φ_{ISC}): You need efficient conversion to the triplet state.
- Triplet energy ≥ 94 kJ/mol: The sensitizer's T_1 must have enough energy to excite O_2 .
- Photostability: The sensitizer shouldn't degrade under irradiation.
- Strong visible-light absorption: Especially important for biological applications where UV would cause tissue damage.

Common photosensitizers:

- Organic dyes: Rose Bengal ($\Phi_\Delta \approx 0.75$ in methanol) and Methylene Blue are classic choices with high singlet oxygen quantum yields.
- Porphyrins and phthalocyanines: Widely used in photodynamic therapy because of their strong absorption in the red/near-IR region.
- Transition metal complexes: $Ru(bpy)_3^{2+}$ and related complexes, valued for their tunability and photostability.

Factors affecting efficiency:

- Oxygen concentration: Higher dissolved O_2 means more frequent collisions with the triplet sensitizer, increasing the rate of energy transfer.
- Solvent: Polar solvents can stabilize or destabilize the sensitizer's triplet state. Heavy-atom solvents (e.g., those containing bromine) can enhance ISC.
- Light intensity and wavelength: Must match the sensitizer's absorption spectrum.

Reactivity in organic reactions

Singlet oxygen is an electrophile. It preferentially reacts with electron-rich substrates like alkenes, dienes, sulfides, and phenols. Three major reaction types dominate:

[4+2] Cycloaddition (Diels-Alder type)

Singlet oxygen acts as a dienophile, reacting with conjugated dienes to form endoperoxides. This reaction requires a cis-diene conformation (s-cis). A classic example is the reaction with 1,3-cyclohexadiene.

[2+2] Cycloaddition

Electron-rich alkenes (especially those with electron-donating groups like enol ethers) react with singlet oxygen to form 1,2-dioxetanes. These four-membered ring peroxides are often thermally unstable and can decompose with light emission, which is the basis of some chemiluminescence systems.

Ene Reaction

Alkenes bearing allylic hydrogens undergo the ene reaction, producing allylic hydroperoxides with a shift of the double bond. The selectivity follows the "cis effect": hydrogen abstraction preferentially occurs from the same face as the approaching singlet oxygen. Substitution patterns and steric accessibility of allylic hydrogens govern regioselectivity.

Mechanistic considerations:

Whether these reactions proceed through concerted or stepwise pathways is still debated for some cases. Proposed intermediates include perepoxides (a three-membered ring intermediate) and zwitterionic species. The [4+2] cycloaddition is generally considered concerted and stereospecific, retaining the stereochemistry of the diene. The ene reaction shows suprafacial selectivity.

Selectivity factors:

- Electron density at the double bond (more substituted alkenes react faster)
- Steric accessibility
- Solvent polarity (can influence the balance between concerted and stepwise pathways)

Applications in synthesis vs therapy

Synthetic applications

Singlet oxygen enables transformations that are difficult to achieve by other means:

- Natural product synthesis: The antimalarial drug artemisinin involves a singlet oxygen ene reaction as a key step. Ascaridole, a naturally occurring endoperoxide, is synthesized via [4+2] cycloaddition of singlet oxygen with α -terpinene.
- Pharmaceutical intermediates: Used in the preparation of oxygenated steroids and prostaglandin precursors, where selective C-H or C=C oxidation is needed.
- Fine chemicals: Production of fragrances and flavor compounds through controlled oxidation.

Photodynamic therapy (PDT)

PDT uses singlet oxygen to destroy diseased cells, and it works in two stages:

1. A photosensitizer is administered and allowed to accumulate preferentially in target tissue (e.g., a tumor). This selectivity arises from differences in uptake and retention between diseased and healthy

cells.

2. The target area is irradiated with light at the sensitizer's absorption wavelength. The resulting singlet oxygen damages cellular components (membranes, proteins, DNA), triggering cell death.

PDT's major advantage is dual selectivity: you control where the sensitizer goes and where you shine the light. It's minimally invasive compared to surgery and avoids the systemic toxicity of chemotherapy.

Clinical PDT applications:

- Cancer treatment: approved for skin cancers, esophageal cancer, and certain lung cancers
- Dermatology: actinic keratoses, acne, psoriasis
- Antimicrobial PDT: an emerging approach against drug-resistant bacteria

Environmental and industrial applications:

- Water treatment: Singlet oxygen generated by sunlight-absorbing dissolved organic matter contributes to natural water purification. Engineered systems use immobilized photosensitizers for treating contaminated water.
- Air purification: Removal of volatile organic compounds (VOCs) through singlet-oxygen-mediated oxidation.
- Industrial processes: Polymer surface modification, controlled degradation of waste polymers, and bleaching in the paper and textile industries.

11.3 Photocatalysis mechanisms and applications

Photocatalysis harnesses light to speed up chemical reactions using special catalysts. It's a powerful tool that creates electron-hole pairs, driving redox reactions at the catalyst surface. Different types of photocatalysts, from semiconductors to metal-based ones, offer unique advantages.

Photocatalysis comes in two flavors: heterogeneous and homogeneous. It's widely used in environmental cleanup, from water purification to air cleaning. While it offers eco-friendly benefits, challenges like low efficiency and scaling issues remain. Future research aims to overcome these hurdles.

Fundamentals of Photocatalysis

Principles of photocatalysis

- Photocatalysis accelerates chemical reactions using light and a light-absorbing catalyst
- Light absorption by photocatalyst generates electron-hole pairs
- Charge carriers separate and migrate to catalyst surface
- Redox reactions occur at catalyst surface driving chemical transformations
- Bandgap energy determines light absorption range (UV, visible, infrared)
- Conduction and valence bands facilitate electron movement and hole formation
- Quantum efficiency measures photocatalytic performance comparing reacted molecules to absorbed photons

Types of photocatalysts

- Semiconductor photocatalysts utilize bandgap for charge separation (TiO₂, ZnO, CdS)
- Metal-based photocatalysts exploit plasmonic effects (Au, Ag, Pt nanoparticles)
- Organic photocatalysts employ dye-sensitization or organic semiconductors
- Composite photocatalysts combine materials for enhanced performance (metal-semiconductor, semiconductor-semiconductor)
- Photocatalytic activity influenced by bandgap energy, surface area, particle size, crystal structure, and recombination rate

Heterogeneous vs homogeneous photocatalysis

- Heterogeneous photocatalysis uses solid catalyst separate from reactants 1. Light absorption 2. Charge separation 3. Surface reactions 4. Adsorption-desorption processes
- Surface defects and trap states affect heterogeneous reactions
- Homogeneous photocatalysis occurs with catalyst and reactants in same phase 1. Photoexcitation of catalyst molecules 2. Energy or electron transfer to substrates 3. Regeneration of catalyst
- Heterogeneous and homogeneous differ in reaction environment, charge transfer, and catalyst recovery

Applications in environmental remediation

- Water purification degrades organic pollutants (pesticides, pharmaceuticals) and disinfects pathogens (bacteria, viruses)
- Air purification removes VOCs (benzene, formaldehyde) and reduces NO_x emissions
- Soil decontamination treats contaminated sites (oil spills, heavy metals)
- Organic synthesis enables selective oxidation reactions and C-C bond formation
- Photocatalytic water splitting produces hydrogen for clean energy
- CO₂ reduction creates value-added chemicals (methanol, formic acid)
- Energy applications include solar cells and artificial photosynthesis systems

Advantages and limitations of photocatalysis

- Advantages include environmentally friendly operation, room temperature reactions, complete pollutant mineralization, and solar light utilization
- Limitations involve low quantum efficiency, limited light penetration in turbid solutions, catalyst deactivation, and scaling challenges
- Future directions focus on improving visible light activity, enhancing charge separation, developing novel reactor designs, and scaling up for industrial use

Unit 12 – Photosynthesis and Vision in Nature

12.1 Light-harvesting complexes and energy transfer in photosynthesis

Light-harvesting complexes are nature's solar panels, capturing sunlight for photosynthesis. These protein-pigment structures in thylakoid membranes use various pigments to absorb light across a wide spectrum, funneling energy to reaction centers.

Energy transfer in these complexes is a marvel of efficiency. Through Förster resonance energy transfer, excitation energy hops between pigments, guided by their precise arrangement. This process happens in picoseconds, potentially enhanced by quantum effects.

Light-Harvesting Complexes in Photosynthesis

Structure of light-harvesting complexes

- Light-harvesting complexes (LHCs) function as protein-pigment complexes embedded in thylakoid membranes
- Antenna complexes contain multiple pigment molecules (chlorophylls, carotenoids) arranged in specific spatial orientations
- LHCs increase light absorption efficiency expanding the spectrum of light captured (400-700 nm)
- Pigments funnel excitation energy to reaction centers enhancing photosynthetic performance

Energy transfer to reaction centers

- Excitation energy transfer (EET) occurs via Förster resonance energy transfer (FRET) mechanism
- Energy transfer steps: 1. Light absorption by antenna pigments 2. Rapid transfer between pigments within LHCs 3. Directional transfer towards reaction centers
- Transfer efficiency affected by pigment distance, spectral overlap, and transition dipole orientation
- Quantum coherence potentially enhances energy transfer speed and efficiency in photosynthetic systems

Role of pigments in photosynthesis

- Photosynthetic pigments capture light energy and funnel it to reaction centers
- Types: chlorophylls (a, b, c, d), carotenoids (β -carotene, xanthophylls), phycobilins (cyanobacteria, red algae)
- Absorption spectra complementary to reflected light determine effective wavelengths for photosynthesis
- Energy funneling occurs through downhill energy transfer from higher to lower energy pigments
- Special pair chlorophylls in reaction centers receive energy from antenna pigments

Spatial organization for energy transfer

- Pigments in LHCs arranged at precise distances and orientations optimizing energy transfer efficiency
- Excitonic coupling between closely spaced pigments affects energy transfer rates and pathways
- Antenna size and geometry influence overall light-harvesting efficiency adapting to different light conditions (shade, full sun)
- Pigment organization facilitates rapid and efficient energy transfer to reaction centers (picosecond timescale)

12.2 Photosynthetic reaction centers and electron transport

Photosynthetic reaction centers are the powerhouses of light-driven energy conversion in plants. These specialized complexes contain chlorophyll molecules that absorb light and initiate electron transfer, along with accessory pigments and electron acceptors that form an efficient electron transport chain.

The process of charge separation in reaction centers is lightning-fast. When light excites electrons in the special pair, they quickly transfer to acceptors, creating a charge-separated state. This initiates a cascade of electron transfers that ultimately powers the production of ATP and NADPH for plant growth.

Photosynthetic Reaction Centers

Components of photosynthetic reaction centers

- Special pair of chlorophyll molecules absorb light energy and initiate electron transfer as primary electron donor (P680 in PSII, P700 in PSI)
- Accessory pigments enhance light absorption and funnel energy to special pair (carotenoids, phycobilins)
- Primary electron acceptor receives electron from excited special pair (pheophytin in PSII, A0 chlorophyll in PSI)
- Secondary electron acceptors form electron transport chain (quinones, iron-sulfur clusters)
- Protein scaffold holds components in optimal arrangement for efficient electron transfer
- Redox-active cofactors facilitate electron transfer between components (plastoquinone, plastocyanin)

Charge separation in reaction centers

- Light absorption by special pair excites electrons to higher energy state
- Excited electrons transfer from special pair to primary acceptor within picoseconds
- Charge-separated state forms with positive special pair and negative primary acceptor
- Rapid electron transfer through acceptors prevents charge recombination
- Final electron acceptor reduces (QB in PSII, ferredoxin in PSI)
- Oxidized special pair regains electron from donor (water in PSII, plastocyanin in PSI)

Electron Transport and Energy Conversion

Electron transport chain in energy conversion

- Sequential redox reactions transfer electrons from higher to lower redox potential
- Proton pumping across thylakoid membrane creates electrochemical gradient
- ATP synthesis occurs via ATP synthase using proton gradient energy
- NADP⁺ reduction to NADPH by ferredoxin-NADP⁺ reductase
- Cyclic electron flow around PSI produces additional ATP without NADPH

Photosystem I vs photosystem II

- PSII initiates electron transport, oxidizes water to produce oxygen, reduces plastoquinone
- PSI receives electrons from PSII via cytochrome b6f complex, reduces ferredoxin
- Light absorption spectra: PSII maximum at 680 nm, PSI maximum at 700 nm
- Electron flow: PSII to PSI (linear transport), PSI only (cyclic transport)
- Final electron acceptors: PSII (plastoquinone), PSI (ferredoxin)
- PSII contains P680 reaction center, PSI contains P700 reaction center
- PSII involved in water oxidation, PSI involved in NADP⁺ reduction

12.3 Photochemistry of vision: retinal isomerization and signal transduction

Vision's photochemistry is a marvel of nature, transforming light into neural signals. Rhodopsin, the key player, undergoes rapid changes when hit by photons, kicking off a cascade of events in our eyes.

This process shares similarities with photosynthesis, but is fine-tuned for speed and sensitivity. Both convert light energy, but vision's lightning-fast reactions and high efficiency make it uniquely suited for our visual world.

Photochemistry of Vision

Structure and function of rhodopsin

- Rhodopsin structure combines protein opsin with chromophore 11-cis-retinal
- Located in rod cells of retina acts as light-sensitive receptor protein
- Light absorption triggers conformational changes initiates visual transduction cascade
- Opsin provides protein scaffold for retinal binding and signal propagation
- 11-cis-retinal absorbs light efficiently in visible spectrum (peak ~500 nm)

Retinal isomerization in vision

- Light absorption causes 11-cis-retinal to all-trans-retinal isomerization within femtoseconds

- Isomerization transfers energy from chromophore to opsin protein
- Conformational changes in rhodopsin lead to activation of G-protein transducin
- Process initiates visual signal transduction pathway
- Quantum yield of isomerization ~ 0.65 ensures efficient light detection
- Photoisomerization occurs through conical intersection mechanism

Signal transduction in visual process

- Activated rhodopsin (metarhodopsin II) triggers transducin activation 1. Transducin stimulates cGMP phosphodiesterase 2. cGMP hydrolyzed to GMP closing cGMP-gated ion channels 3. Rod cell membrane hyperpolarizes 4. Neurotransmitter release at synaptic terminal altered
- Signal amplification occurs throughout cascade (one photon can activate ~ 100 transducin molecules)
- Process sensitivity allows detection of single photons
- Adaptation mechanisms regulate sensitivity in varying light conditions

Vision vs photosynthesis photochemistry

- Similarities involve light absorption by specialized pigments (rhodopsin, chlorophyll) triggering isomerization reactions
- Both convert light energy to chemical signals or energy (ATP, NADPH)
- Differences include primary pigments cellular location (animal vs plant cells) end products (neural signals vs chemical energy)
- Vision operates on faster timescales (femtoseconds) compared to photosynthesis (picoseconds to nanoseconds)
- Quantum efficiency higher in vision ($\sim 65\%$) than photosynthesis ($\sim 30\%$ for PSII)
- Vision optimized for sensitivity photosynthesis for energy production

Unit 13 – Atmospheric Photochemistry in Environment

13.1 Stratospheric ozone chemistry

Stratospheric Ozone Chemistry

The stratospheric ozone layer absorbs most of the Sun's harmful ultraviolet radiation before it reaches Earth's surface. Understanding how ozone forms, how it gets destroyed, and what humans have done about it connects core photochemistry concepts to one of the biggest environmental success stories in modern science.

Ozone formation in stratosphere

The Chapman cycle describes the natural formation and destruction of ozone in the stratosphere through four key reactions. Two build ozone up, and two break it down.

Formation (two steps):

1.

UV photons split molecular oxygen into two oxygen atoms: $- O_2 + h\nu \rightarrow O + O$ - This requires short-wavelength UV light ($\lambda < 240$ nm), which is only available high in the stratosphere.

2.

Each oxygen atom then combines with another O_2 to form ozone: $- O + O_2 + M \rightarrow O_3 + M$ - M is a third body (usually N_2 or O_2) that carries away excess energy. Without it, the newly formed O_3 would just fly apart.

Destruction (two steps):

1.

Ozone absorbs UV and breaks apart: $- O_3 + h\nu \rightarrow O_2 + O$

2.

Atomic oxygen reacts with ozone: $- O + O_3 \rightarrow 2O_2$

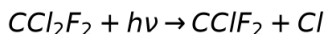
The net result of the full cycle is a steady-state balance: ozone is constantly being created and destroyed, maintaining a roughly stable concentration. Solar UV radiation drives the entire process, and the ozone produced absorbs UVB (280–315 nm) and UVC (100–280 nm), preventing most of it from reaching the surface.

One thing the Chapman cycle alone doesn't explain: it predicts more ozone than we actually observe. That discrepancy is what led scientists to discover catalytic destruction cycles involving species like Cl , Br , NO_x , and HO_x .

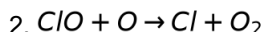
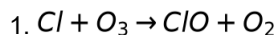
CFCs and ozone depletion

Chlorofluorocarbons (CFCs) are synthetic compounds containing chlorine, fluorine, and carbon. They were widely used as refrigerants, aerosol propellants, and foam-blowing agents because they're chemically stable and non-toxic at ground level. That very stability is the problem: CFCs don't break down in the troposphere, so they drift intact into the stratosphere over decades (atmospheric lifetimes of 50–100+ years).

Once in the stratosphere, UV radiation photolyzes CFCs and releases free chlorine atoms. For example:



The freed chlorine then catalyzes ozone destruction through a two-step cycle:



Notice that Cl is regenerated in step 2. This is what makes it a catalytic cycle: a single chlorine atom can destroy roughly 100,000 ozone molecules before it's finally removed (typically by reacting with methane or nitrogen dioxide to form reservoir species like HCl or $ClONO_2$).

Other ozone-depleting substances (ODS) work through similar catalytic mechanisms:

- Halons (used in fire extinguishers) release bromine, which is 40–100 times more effective at destroying ozone per atom than chlorine
- Carbon tetrachloride (CCl_4 , used in solvents)
- Methyl chloroform (CH_3CCl_3 , used in industrial cleaning)

Effects of ozone depletion

When the ozone layer thins, more UV radiation reaches Earth's surface. The consequences span ecosystems, agriculture, and human health.

Environmental effects:

- Damage to phytoplankton, which form the base of marine food chains. Even modest UV increases reduce their productivity, with ripple effects through ocean ecosystems.
- Reduced crop yields in UV-sensitive species like soybeans, wheat, and rice
- Accelerated degradation of materials such as plastics, paints, and rubber

Human health impacts:

- Higher rates of skin cancer, including melanoma, basal cell carcinoma, and squamous cell carcinoma. A sustained 1% decrease in ozone corresponds to roughly a 2% increase in skin cancer incidence.
- Increased risk of cataracts and other eye damage
- Suppression of the immune system, making people more vulnerable to infectious diseases

Polar ozone holes are the most dramatic manifestation of depletion. The Antarctic ozone hole forms each spring (September–November) because polar stratospheric clouds (PSCs) that form during the extremely cold polar winter provide surfaces for heterogeneous reactions. These reactions convert reservoir species (HCl , $ClONO_2$) back into reactive chlorine, which destroys ozone rapidly when sunlight returns in spring. The Arctic experiences similar but less severe depletion because its stratosphere doesn't get quite as cold.

Effectiveness of ozone agreements

The Montreal Protocol (1987) committed nations to phasing out production and consumption of ozone-depleting substances. It has been ratified by 198 countries, making it the first universally ratified UN treaty.

Successive amendments strengthened the original agreement:

1. London Amendment (1990) — expanded the list of controlled substances and created a financial mechanism to help developing countries comply
2. Copenhagen Amendment (1992) — accelerated phase-out schedules for CFCs and halons
3. Montreal Amendment (1997) — established a licensing system to control international trade in ODS
4. Beijing Amendment (1999) — added bromochloromethane to the controlled list
5. Kigali Amendment (2016) — targeted HFCs, which aren't ozone-depleting but are potent greenhouse gases used as CFC replacements

The results have been substantial:

- 98% reduction in global CFC production and consumption since 1986
- Atmospheric concentrations of most ODS are measurably declining
- The ozone layer is projected to recover to 1980 levels by approximately 2050–2070, depending on latitude

Challenges remain. HCFCs (transitional replacements for CFCs) are still being phased out. Illegal production of banned substances like CFC-11 was detected as recently as 2018, highlighting the need for continued monitoring. And HFCs, while ozone-safe, have global warming potentials thousands of times greater than CO_2 , which is why the Kigali Amendment was added.

The Montreal Protocol is widely considered the most successful international environmental agreement ever enacted, and it serves as a reference point for how global cooperation can address atmospheric threats.

13.2 Tropospheric photochemistry and air pollution

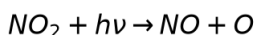
Tropospheric Photochemistry and Air Pollution

Tropospheric ozone forms through complex reactions involving sunlight, nitrogen oxides, and volatile organic compounds. Unlike stratospheric ozone (which shields us from UV), tropospheric ozone is a harmful pollutant that damages lungs, crops, and materials. Understanding how it forms is the key to figuring out how to reduce it.

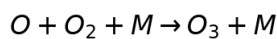
Primary Reactions in Ozone Formation

Ozone production in the troposphere starts with the photostationary state, a cycle involving NO , NO_2 , and O_3 that, on its own, produces no net ozone. VOCs then disrupt this cycle and tip the balance toward ozone accumulation.

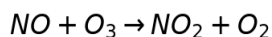
Step 1: Photolysis of nitrogen dioxide. UV-A and violet light (wavelengths < 420 nm) break apart NO_2 :



Step 2: Ozone formation. The oxygen atom reacts almost immediately with O_2 . A third body M (typically N_2 or O_2) absorbs excess energy and stabilizes the product:

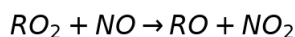


Step 3: Ozone destruction by NO. NO reacts with the ozone just formed, regenerating NO_2 :



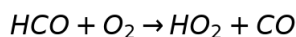
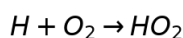
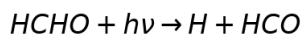
If only these three reactions operated, ozone would be created and destroyed at roughly equal rates, so no net ozone would build up. This is the photostationary state.

How VOCs break the cycle. VOCs react with hydroxyl radicals (OH) in the atmosphere to produce peroxy radicals (RO_2 and HO_2). These radicals convert NO to NO_2 without consuming ozone:



That extra NO_2 feeds back into Step 1, generating more ozone while the ozone-destroying Step 3 is bypassed. This is why VOCs are so important: they shift the cycle toward net ozone production.

Formaldehyde as a radical source. Photolysis of $HCHO$ is one important pathway for generating HO_2 radicals:



Each molecule of formaldehyde can produce two HO_2 radicals, making it a significant contributor to the radical pool that drives ozone formation.

Role of NOx and VOCs

NOx ($NO + NO_2$) comes primarily from combustion: vehicle engines, power plants, and industrial boilers. It acts as the catalyst in the ozone-forming cycle described above.

VOCs come from both anthropogenic sources (vehicle exhaust, industrial solvents, fuel evaporation) and biogenic sources (isoprene and terpenes emitted by trees). VOCs react with OH radicals to form the peroxy radicals that amplify ozone production.

The NOx-to-VOC ratio determines which chemical regime controls ozone levels in a given area:

- VOC-limited (NOx-saturated) regime: Common in dense urban centers. There's plenty of NOx but not enough VOCs to generate radicals. Reducing VOC emissions is more effective at lowering ozone here. Counterintuitively, reducing NOx alone can actually increase ozone in this regime because excess NO that was scavenging ozone (Step 3) is removed.
- NOx-limited regime: Common in suburban and rural areas downwind of cities. VOCs are abundant (often from biogenic sources), but NOx is the bottleneck. Reducing NOx emissions is the most effective strategy here.

Getting this distinction right matters enormously for policy. Applying the wrong control strategy can be ineffective or even counterproductive.

Peroxyacetyl nitrate (PAN) forms as a secondary pollutant from the reaction of VOC-derived radicals with NO_2 . PAN is thermally unstable, so it decomposes at higher temperatures, releasing NO_2 far downwind of the original emission source. This makes PAN an important reservoir species that transports reactive

nitrogen over long distances and can cause ozone formation in remote areas.

Effects of Tropospheric Pollution

Human health. Ground-level ozone is a powerful oxidant that irritates airways. Short-term exposure causes coughing, wheezing, and chest tightness, and it aggravates asthma. Long-term exposure is linked to increased susceptibility to respiratory infections and premature mortality. The WHO estimates that outdoor air pollution contributes to millions of premature deaths annually.

Vegetation. Ozone enters leaves through stomata and damages cells, reducing photosynthesis. Visible symptoms include stippling and chlorosis on leaf surfaces. Crop yield losses are significant: studies estimate global yield reductions of 7–12% for wheat and 6–16% for soybeans due to ozone exposure. Over time, chronic ozone stress alters ecosystem composition by favoring ozone-tolerant species over sensitive ones.

Materials. Ozone accelerates degradation of many materials. Limestone and marble on buildings erode faster. Copper and bronze surfaces corrode (the green patina on copper statues is partly driven by atmospheric oxidants). Rubber loses elasticity and cracks, and textiles and dyes fade more rapidly.

Strategies for Ozone Reduction

Emissions control targets the precursors directly:

- Tightening vehicle emission standards and mandating catalytic converters to reduce both *NO_x* and VOC tailpipe emissions
- Adopting low-*NO_x* burner technology in power plants
- Regulating industrial VOC emissions through vapor recovery systems and solvent substitution

Urban planning reduces emissions at the source:

- Expanding public transit systems (e.g., bus rapid transit) to cut vehicle miles traveled
- Establishing low-emission zones that restrict high-polluting vehicles in city centers
- Increasing urban green spaces, though with care since some tree species (e.g., oaks, poplars) emit significant biogenic VOCs

Alternative energy addresses the root cause by transitioning electricity generation to renewables (solar, wind) and promoting electric vehicles, which eliminate tailpipe *NO_x* and VOC emissions entirely.

Air quality monitoring networks provide real-time ozone and precursor data. These enable health advisories on high-ozone days and supply the data needed to evaluate whether control strategies are working.

International cooperation is necessary because ozone precursors travel across borders. The Convention on Long-Range Transboundary Air Pollution (CLRTAP) in Europe is one example of a framework for coordinated emission reductions.

Public education helps people understand air quality indices and take protective action on high-pollution days. It also encourages behaviors that reduce emissions, such as carpooling, reducing idling, and choosing low-VOC consumer products.

13.3 Photodegradation of pollutants and water treatment

Photocatalysis and Advanced Oxidation Processes

Principles of photocatalysis

Photocatalysis uses light energy to drive chemical reactions on the surface of a semiconductor, generating highly reactive species that break down pollutants in water. The core idea is straightforward: a semiconductor absorbs photons and produces reactive radicals that oxidize contaminants into harmless (or less harmful) products.

Here's how the process works, step by step:

1. Light absorption — A photon with energy equal to or greater than the semiconductor's band gap strikes the catalyst. For TiO_2 (anatase), that band gap is about 3.2 eV, corresponding to UV light ($\lambda < 387 \text{ nm}$).
2. Electron-hole pair generation — The absorbed photon excites an electron from the valence band to the conduction band, leaving behind a positively charged "hole" (h^+) in the valence band.
3. Charge carrier migration — The electron (e^-) and hole migrate to the catalyst surface. If they recombine before reaching the surface, no useful chemistry happens, which is why minimizing recombination is a major design goal.
4. Surface redox reactions — At the surface, holes oxidize water or hydroxide ions to form hydroxyl radicals ($\text{OH}^\bullet$), while electrons reduce dissolved oxygen to form superoxide radicals ($\text{O}_2^{\bullet -}$). These reactive oxygen species (ROS) then attack pollutant molecules.

Two degradation pathways operate simultaneously:

- Direct oxidation — Holes at the catalyst surface directly oxidize adsorbed pollutant molecules.
- Indirect oxidation — Hydroxyl radicals generated in solution diffuse and react with pollutants that aren't directly adsorbed on the surface. This pathway often dominates because $\text{OH}^\bullet$ is an extremely powerful, non-selective oxidant.

Key applications in water treatment:

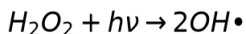
- Organic dye removal — Decolorizes textile wastewater by breaking down chromophores. Methylene blue is a common model pollutant in research because its degradation is easy to track spectrophotometrically.
- Pharmaceutical waste — Breaks down drug residues like ibuprofen and diclofenac that pass through conventional treatment plants largely intact.
- Pesticide detoxification — Degrades persistent compounds like atrazine in agricultural runoff.
- Disinfection — Inactivates waterborne pathogens such as E. coli through oxidative damage to cell membranes.

Mechanisms of advanced oxidation processes

Advanced oxidation processes (AOPs) are defined by their ability to generate hydroxyl radicals ($\text{OH}^\bullet$) in sufficient quantities to mineralize organic pollutants, ideally converting them all the way to CO_2 and H_2O . Two of the most studied AOPs in photochemistry are the $\text{UV}/\text{H}_2\text{O}_2$ and UV/TiO_2 systems.

$\text{UV}/\text{H}_2\text{O}_2$ system

This system relies on the photolysis of hydrogen peroxide by UV light:

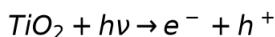


Each photon that cleaves an H_2O_2 molecule produces two hydroxyl radicals. These radicals then initiate chain reactions, abstracting hydrogen atoms from organic pollutants and generating carbon-centered radicals that react further with dissolved oxygen. The process continues until the pollutant is mineralized or converted to smaller, biodegradable fragments.

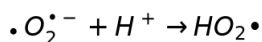
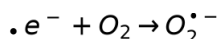
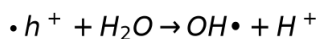
A practical advantage of this system is its simplicity: no solid catalyst to recover. However, it requires continuous dosing of H_2O_2 , and excess peroxide can actually scavenge $OH^\bullet$ radicals, reducing efficiency.

UV/ TiO_2 system

Here, the semiconductor itself generates the reactive species upon UV irradiation:



The photogenerated holes and electrons then produce multiple types of ROS:



The combination of $OH^\bullet$, $O_2^{\bullet -}$, and $HO_2^\bullet$ gives this system versatility against a wide range of pollutants. The main challenge is electron-hole recombination, which wastes absorbed photon energy and lowers quantum efficiency.

Comparing the two systems:

Factor	UV/ H_2O_2	UV/ TiO_2
Radical source	Homolytic cleavage of H_2O_2	Semiconductor charge separation
Phase	Homogeneous (all in solution)	Heterogeneous (solid catalyst + solution)
Post-treatment	No catalyst recovery needed	Catalyst must be separated or immobilized
Reagent cost	Ongoing H_2O_2 consumption	Catalyst is reusable but degrades over time
Turbid water tolerance	Better (no light-catalyst interaction needed)	Worse (particles scatter light, block catalyst)

The best choice depends on the specific pollutant, water matrix, and scale of treatment.

Photocatalytic Materials and Reactor Design

Comparison of photocatalytic materials

Not all photocatalysts are created equal. The choice of material determines what wavelengths of light you can use, how efficiently charge carriers are generated, and how stable the system is over time.

Common photocatalytic materials:

- TiO_2 — The most widely studied photocatalyst. Anatase phase is generally more active than rutile due to its slightly higher band gap (3.2 eV vs. 3.0 eV) and lower recombination rate. Mixed-phase materials like Degussa P25 (roughly 80% anatase, 20% rutile) often outperform either pure phase because the phase junction helps separate charge carriers.
- ZnO — Similar band gap to TiO_2 and sometimes shows higher activity for certain pollutants. Offers good surface area as nanoparticles. The drawback is photocorrosion: ZnO can dissolve under prolonged UV irradiation in acidic conditions.
- WO_3 and other metal oxides — Narrower band gaps (~ 2.7 eV for WO_3) allow absorption of visible light, but the conduction band position is often too positive to reduce O_2 to $O_2^{\bullet-}$, limiting ROS generation.
- Doped and composite materials — Strategies like nitrogen doping of TiO_2 or coupling TiO_2 with $g-C_3N_4$ extend light absorption into the visible range and improve charge separation. This is one of the most active areas of current research.

Four factors that control photocatalyst efficiency:

1. Band gap energy — Determines the minimum photon energy (and maximum wavelength) that can activate the catalyst. A smaller band gap captures more of the solar spectrum but may reduce the oxidizing power of the holes.
2. Surface area and porosity — Higher surface area means more active sites for pollutant adsorption and radical generation. Mesoporous and nanostructured catalysts excel here.
3. Crystallinity and defects — Well-crystallized materials have fewer bulk defects that trap and recombine charge carriers. However, controlled surface defects can sometimes improve adsorption.
4. Charge carrier recombination rate — The single biggest efficiency killer. If electrons and holes recombine before reaching the surface, the absorbed photon energy is wasted as heat. Heterojunctions, co-catalysts, and morphology engineering all aim to suppress recombination.

Reactor designs:

Reactor Type	Advantage	Limitation
Slurry reactor	Maximum catalyst-pollutant contact; easy to scale catalyst loading	Requires post-treatment separation (filtration or centrifugation)
Immobilized catalyst	No separation step needed; continuous flow operation	Reduced mass transfer; lower surface area exposed to solution
Thin film reactor	High surface-area-to-volume ratio; efficient light utilization	Catalyst film can degrade or detach over time
Optical fiber reactor	Delivers light deep into opaque or turbid solutions	Complex fabrication; limited catalyst loading per fiber

Reactor performance ultimately depends on how well you manage light distribution, mass transfer, catalyst loading, and residence time. A reactor with poor light penetration will have a "dead zone" where no photocatalysis occurs, no matter how good the catalyst is.

Challenges in large-scale implementation

Moving photocatalytic water treatment from the lab bench to a real treatment plant is one of the biggest hurdles in this field. The challenges fall into several categories.

Technical challenges:

- Lab-scale results often use idealized conditions (pure water spiked with a single pollutant, high catalyst loading, intense UV lamps). Real wastewater contains mixtures of pollutants, dissolved ions, and natural organic matter that compete for reactive species and foul catalyst surfaces.
- Catalyst deactivation over time requires regeneration strategies (thermal treatment, UV cleaning) that add complexity.
- Uniform light distribution becomes much harder in large reactors. Light intensity drops exponentially with distance from the source (Beer-Lambert law), so thick water layers receive almost no photons at their center.

Economic considerations:

- Capital costs include reactor construction, UV lamp arrays or solar concentrators, and catalyst synthesis.
- Operating costs are driven by energy consumption (UV lamps are energy-intensive), catalyst replacement, and H_2O_2 dosing for AOP systems.
- Photocatalysis must compete with established methods like activated carbon adsorption, ozonation, and chlorination, which are cheaper per volume treated for many common pollutants.

Environmental concerns:

- Incomplete mineralization can produce transformation byproducts that are sometimes more toxic than the parent compound. Monitoring byproduct formation is essential.
- Spent catalyst nanoparticles (especially those containing heavy metals from doping) require proper disposal to avoid secondary contamination.
- Life cycle assessment should account for the energy and materials used to manufacture catalysts and UV systems, not just the treatment step itself.

Where the field is heading:

- Developing visible-light-active and solar-driven photocatalysts to reduce dependence on UV lamps and lower energy costs.
- Improving catalyst durability so materials can be reused through hundreds of treatment cycles without significant activity loss.
- Hybrid systems that combine photocatalysis with membrane filtration, biological treatment, or electrochemistry to handle complex real-world wastewater more effectively.
- Pilot-scale demonstrations that bridge the gap between promising lab results and practical deployment.

Unit 14 – Photochemistry: Materials Applications

14.1 Photoresists and lithography

Photoresists and Lithography Fundamentals

Photolithography uses light to transfer geometric patterns onto a substrate, forming the backbone of modern microfabrication. Every microchip, sensor, and display screen you interact with was built through repeated cycles of this process. The photochemistry at its core determines how small, how precise, and how reliable those patterns can be.

Principles of photolithography

The photolithography process follows a strict sequence. Each step builds on the last, so errors early on cascade through the entire pattern transfer.

1. Substrate preparation — the surface is cleaned and primed to ensure uniform coating
2. Photoresist application — a thin film of light-sensitive polymer is spin-coated onto the substrate
3. Soft baking — gentle heating drives off excess solvent and improves adhesion to the substrate
4. Mask alignment — a photomask containing the desired pattern is precisely positioned over the coated substrate
5. UV exposure — light passes through the mask and selectively changes the solubility of the photoresist wherever it strikes
6. Development — a chemical developer dissolves away the more soluble regions, revealing the pattern
7. Hard baking — higher-temperature heating stabilizes the remaining photoresist so it can withstand subsequent processing
8. Etching or deposition — the exposed substrate areas are chemically etched or have material deposited onto them
9. Photoresist removal (stripping) — the remaining resist is dissolved away, leaving only the patterned substrate

Four key components make this work:

- Light source — typically emitting UV wavelengths, since shorter wavelengths allow finer features
- Photomask — a patterned template (usually chrome on glass) that selectively blocks or transmits light
- Photoresist — the light-sensitive polymer whose solubility changes upon exposure
- Substrate — the base material (often a silicon wafer) that receives the final pattern

Photolithography shows up across many industries: integrated circuit production, MEMS fabrication (tiny sensors and actuators), microfluidic lab-on-a-chip devices, and flat panel display manufacturing.

Composition of photoresists

Photoresists fall into two categories based on how they respond to light. The distinction matters because it determines which areas get removed during development.

Positive photoresists become more soluble where exposed to light. The exposed regions wash away in developer, so the pattern on the substrate matches the dark areas of the mask. They contain three main components:

- Base resin (novolac) — a phenolic polymer that provides the structural film
- Photoactive compound (diazonaphthoquinone, or DNQ) — this is the molecule that undergoes a photochemical change, switching from dissolution-inhibiting to dissolution-promoting upon UV absorption
- Solvent (e.g., PGMEA) — allows the resist to be applied as a uniform thin film by spin-coating

Positive resists are favored when you need high resolution and tight process control, which is why they dominate in semiconductor manufacturing.

Negative photoresists become less soluble where exposed to light. The exposed regions harden and remain after development, so the pattern on the substrate matches the clear areas of the mask. Their composition differs accordingly:

- Base polymer (epoxy-based, such as SU-8, or polyisoprene) — forms the film that will crosslink upon exposure
- Photoinitiator — absorbs UV light and generates reactive species (typically free radicals or acids) that trigger crosslinking
- Solvent — enables thin film formation during coating

Negative resists offer better adhesion to substrates and higher chemical resistance, making them well-suited for applications where the patterned resist itself must survive harsh processing, such as electroplating molds or microfluidic channel walls. Their trade-off is lower resolution compared to positive resists, because swelling during development can distort fine features.

Photochemical reactions in patterning

The chemistry that happens during UV exposure is what makes the entire process work. The reactions differ fundamentally between the two resist types.

In positive photoresists, the key reaction is the photodecomposition of DNQ:

1. DNQ absorbs a UV photon and loses a molecule of N_2 gas (a Wolff rearrangement occurs)
2. The resulting carbene intermediate reacts with trace water to form a carboxylic acid (indenecarboxylic acid)
3. This carboxylic acid is polar and readily dissolves in the alkaline developer solution
4. Unexposed DNQ remains hydrophobic and acts as a dissolution inhibitor, protecting those regions from the developer

In negative photoresists, the reaction is a light-initiated polymerization:

1. The photoinitiator absorbs UV light and fragments, generating free radicals (or, in chemically amplified resists, a photoacid)

2. These radicals initiate chain reactions that crosslink neighboring polymer chains into a dense network
3. The crosslinked network is insoluble in the organic developer solvent
4. Unexposed regions remain un-crosslinked and dissolve away during development

Quantum yield (Φ) measures how efficiently these photochemical reactions proceed: it's the number of reaction events per photon absorbed. A higher quantum yield means the resist is more sensitive, requiring less exposure energy and shorter exposure times. This directly affects manufacturing throughput.

Advanced Lithography Concepts

Resolution limits in lithography

The smallest feature you can print is governed by the Rayleigh criterion:

$$R = k_1 \frac{\lambda}{NA}$$

- R = minimum resolvable feature size
- λ = wavelength of the exposure light
- NA = numerical aperture of the projection lens (describes how much light the lens can collect and focus)
- k_1 = a process-dependent factor (accounts for resist chemistry, mask optimization, and imaging tricks; theoretically bounded at 0.25 on the low end)

The equation tells you there are three levers for shrinking features: use a shorter wavelength, increase the numerical aperture, or reduce k_1 through process engineering.

Challenges at small scales:

- Diffraction blurs pattern edges, making it harder to define sharp features
- Depth of focus shrinks as resolution improves, restricting how thick the resist layer can be and how flat the substrate must be
- Proximity effects cause nearby features to influence each other's exposure dose
- Line edge roughness (LER) introduces random variations in feature dimensions that become significant when features are only tens of nanometers wide

Techniques that push beyond traditional limits:

- Extreme ultraviolet (EUV) lithography — uses a 13.5 nm wavelength (compared to 193 nm for conventional deep-UV), dramatically improving resolution. This is the current leading-edge technology for sub-7 nm semiconductor nodes.
- Electron beam (e-beam) lithography — writes patterns directly with a focused electron beam, achieving extremely fine resolution without a mask. It's slow, so it's mainly used for mask making and research rather than mass production.
- Nanoimprint lithography — mechanically presses a mold into the resist to create patterns, bypassing optical diffraction limits entirely.
- Multi-patterning — combines multiple exposure and etch steps to create features smaller than a single exposure could achieve.

Emerging approaches are also under active development:

- Directed self-assembly (DSA) guides block copolymers to spontaneously form regular nanoscale patterns, using the thermodynamic tendency of the two polymer blocks to phase-separate
- Plasmonic lithography exploits near-field optical effects at metal nanostructures to confine light below the diffraction limit

14.2 Photopolymerization reactions and applications

Photopolymerization is a light-triggered process that forms polymers using photoinitiators, monomers, and light sources. It offers rapid curing, precise control, and versatility, making it valuable for various applications like 3D printing and coatings.

Compared to thermal polymerization, photopolymerization is faster and allows for selective curing. It's used in diverse fields, from creating dental composites to fabricating microelectronics, showcasing its wide-ranging impact in modern materials science.

Fundamentals of Photopolymerization

Principles of photopolymerization reactions

- Light-initiated polymerization process involves absorption of photons by photoinitiators triggering generation of reactive species (free radicals or ions)
- Chain reaction mechanism progresses through initiation forming active centers, propagation growing polymer chains, termination ceasing chain growth
- Types include free radical photopolymerization utilizing radical species and cationic photopolymerization using cationic intermediates
- Quantum yield measures efficiency as ratio of polymerized molecules to absorbed photons indicating reaction effectiveness
- Kinetics depend on light intensity affecting initiation rate while monomer concentration influences overall polymerization rate

Components in photopolymerization systems

- Photoinitiators classified as Type I (unimolecular) or Type II (bimolecular) with examples (benzoin ethers, benzophenones, thioxanones) absorb light matching source spectrum
- Monomers commonly used include acrylates, methacrylates, vinyl ethers, and epoxides providing diverse material properties
- Oligomers act as pre-polymers enhancing final material characteristics (flexibility, strength)
- Additives like photosensitizers extend spectral sensitivity while oxygen scavengers prevent inhibition improving cure efficiency
- Light sources range from UV lamps to LED systems and lasers for specific applications offering varied curing options

Applications and Comparisons

Photopolymerization vs thermal polymerization

- Advantages of photopolymerization include rapid curing at ambient temperatures, precise spatial and temporal control, energy efficiency, and solvent-free formulations
- Limitations encompass depth of cure restrictions due to light absorption, oxygen inhibition in some systems, higher initial equipment costs, and potential incomplete conversion in thick samples
- Comparison reveals photopolymerization generally faster, less affected by ambient temperatures, allows patterning and selective curing enhancing versatility

Applications of photopolymers

- 3D printing utilizes photopolymers in: 1. Stereolithography (SLA) building objects layer by layer 2. Digital Light Processing (DLP) curing entire layers at once 3. Continuous Liquid Interface Production (CLIP) enabling faster prints
- Coatings benefit from UV-curable formulations in wood finishes, automotive clear coats, and protective layers for electronics providing durable surfaces
- Adhesives employ photopolymers in dental composites, optical lens bonding, and pressure-sensitive applications offering quick and strong bonds
- Additional uses include photoresists in microelectronics fabrication, holographic recording materials, and hydrogels for biomedical applications expanding material versatility

14.3 Principles of photovoltaic devices

Photovoltaic energy conversion turns light into electricity using semiconductors. This process involves photon absorption, electron excitation, and charge separation. Key factors include band gap energy, quantum efficiency, and voltage-current characteristics.

Solar cells have a layered structure with contacts and semiconductor layers. They work by absorbing photons, separating charges at the p-n junction, and collecting them for power generation. Different materials offer unique properties and challenges in efficiency and stability.

Fundamentals of Photovoltaic Energy Conversion

Principles of photovoltaic conversion

- Photovoltaic effect transforms light directly into electricity in semiconductor materials (silicon)
- Energy conversion process involves photon absorption exciting electrons generating charge carriers separated by internal electric field
- Band gap energy determines minimum energy needed for electron excitation varies by material (1.1 eV for silicon)
- Quantum efficiency measures ratio of generated electrons to incident photons indicates device performance
- Open-circuit voltage represents maximum voltage produced by cell under illumination without current flow

- Short-circuit current signifies maximum current produced by cell when voltage across device is zero

Structure and function of solar cells

- Basic solar cell structure consists of front contact (transparent conductor), n-type and p-type semiconductor layers forming p-n junction, and back contact
- Photon absorption occurs mainly in active layer depends on material thickness and absorption coefficient
- Charge separation takes place at p-n junction due to built-in electric field
- Electron-hole pair generation creates excited electrons in conduction band and holes in valence band
- Charge collection drives electrons to n-type layer and holes to p-type layer
- External circuit allows current flow generating electrical power for use

Advanced Concepts and Challenges in Photovoltaic Devices

Properties of photovoltaic materials

- Silicon exists in crystalline and amorphous forms offers mature technology moderate efficiency high stability indirect band gap
- Perovskites provide high absorption coefficient tunable band gap solution-processability rapid efficiency improvements face stability challenges
- Organic semiconductors offer flexibility lightweight properties low-cost production solution-processability lower efficiency shorter lifespan compared to inorganic materials

Challenges in photovoltaic efficiency

- Efficiency challenges include thermalization losses transmission losses recombination losses limit overall device performance
- Efficiency improvement strategies involve:
 1. Multi-junction cells
 2. Tandem architectures
 3. Light trapping techniques
 4. Quantum dot sensitization
- Stability challenges encompass environmental degradation photo-induced degradation thermal stress affect long-term performance
- Stability improvement strategies include encapsulation techniques interface engineering compositional optimization
- Cost reduction approaches utilize thin-film technologies roll-to-roll processing alternative abundant materials
- Emerging concepts explore hot carrier cells intermediate band solar cells up-conversion and down-conversion techniques push efficiency limits

14.4 Emerging photochemical materials and technologies

Photochemical materials are revolutionizing technology with color-changing properties and light-triggered functions. From smart windows to molecular machines, these materials offer exciting possibilities in data storage, drug delivery, and catalysis. Their ability to respond to light opens up new avenues for controlling matter at the nanoscale.

Upconversion, plasmonic nanostructures, and emerging technologies are pushing the boundaries of photochemistry. These advancements enable deeper tissue imaging, improved solar cells, and more efficient light harvesting. While challenges remain, the future of photochemical materials looks bright, promising innovations in energy, healthcare, and beyond.

Advanced Photochemical Materials

Developments in photochromic materials

- Photochromic materials change color reversibly upon light exposure through photoisomerization or ring-opening/closing reactions (spiropyrans, diarylethenes)
- Photoswitchable materials alter properties reversibly with light stimuli including azobenzenes, diarylethenes, and spiropyrans
- Smart windows regulate light transmission and heat flow in buildings
- Optical data storage increases data density using photochromic molecules
- Molecular machines perform mechanical work at nanoscale triggered by light
- Responsive drug delivery systems release medication at specific sites when activated by light
- Multi-stimuli responsive materials combine light sensitivity with other triggers (pH, temperature)
- Near-infrared (NIR) activated photoswitches allow deeper tissue penetration for biomedical applications
- Photoswitchable catalysts control chemical reactions with light, enabling spatiotemporal control

Principles of upconversion

- Upconversion converts lower-energy photons to higher-energy photons
- Triplet-triplet annihilation (TTA) involves energy transfer between excited molecules
- Energy transfer upconversion (ETU) uses sequential absorption in lanthanide ions
- Lanthanide-doped nanoparticles (NaYF₄:Yb,Er) exhibit efficient upconversion
- Organic dye-based systems use triplet-triplet annihilation for upconversion
- Deep tissue imaging benefits from NIR excitation and visible emission
- Photodynamic therapy activates photosensitizers in deeper tissues
- Multiplexed imaging allows simultaneous detection of multiple targets
- Solar cell efficiency improves by converting sub-bandgap photons
- Tandem solar cells utilize upconversion to harvest broader spectrum

Emerging Technologies and Future Prospects

Plasmonic nanostructures for photochemistry

- Surface plasmon resonance (SPR) occurs at metal-dielectric interfaces
- Localized surface plasmon resonance (LSPR) arises in metal nanoparticles
- Metal nanoparticles (gold, silver) exhibit strong plasmonic effects
- Core-shell structures tune plasmonic properties (Au@SiO₂)
- Nanorod arrays provide directional plasmonic enhancement
- Near-field enhancement amplifies local electromagnetic fields
- Hot electron injection transfers energy from plasmons to molecules
- Plasmon-induced resonance energy transfer (PIRET) couples plasmonic and molecular states
- Photocatalysis benefits from enhanced light absorption and charge separation
- Solar-to-fuel conversion improves efficiency through plasmonic effects
- Plasmonic photovoltaics increase light absorption in thin-film solar cells
- Broadband light absorption extends spectral range of light harvesting
- Increased absorption cross-section enhances light capture efficiency
- Directional light scattering improves light trapping in devices

Challenges in photochemical materials

- Stability and durability limit long-term performance of photochemical materials
- Scalability of nanomaterial synthesis hinders large-scale production
- Efficiency of light-to-energy conversion remains suboptimal for many applications
- Integration with existing technologies requires compatibility and cost-effectiveness
- Artificial photosynthesis mimics natural processes for solar fuel production
- Quantum dot-based devices offer tunable optoelectronic properties
- Perovskite materials show promise for high-efficiency solar cells and LEDs
- Smart responsive materials enable wearable sensors and displays
- Multifunctional photochemical materials combine multiple properties (sensing, actuation)
- Bio-inspired light-harvesting systems mimic natural photosynthetic complexes
- Photon upconversion for solar energy storage extends usable spectrum
- Photochemical water splitting produces clean hydrogen fuel
- Single-molecule photochemistry reveals fundamental reaction mechanisms
- Ultrafast spectroscopy probes femtosecond-scale reaction dynamics

- Photochemical 3D printing enables complex structure fabrication with light
- Light-controlled drug release and activation improves therapeutic efficacy and reduces side effects

Unit 15 – Photodynamic Therapy and Optogenetics

15.1 Principles of photodynamic therapy

Photodynamic therapy (PDT) is a cutting-edge treatment that uses light, photosensitizers, and oxygen to zap diseases. It's like a targeted light show in your body, creating reactive oxygen species that destroy harmful cells while minimizing damage to healthy ones.

PDT is a triple threat, combining special light-absorbing molecules, carefully chosen light sources, and oxygen to pack a powerful punch. It's being used to fight cancer, clear up skin issues, and even tackle eye problems. Talk about a versatile player in the medical field!

Fundamentals of Photodynamic Therapy

Principles of photodynamic therapy

- Photodynamic therapy (PDT) leverages light-activated treatment modality combining photosensitizers, light, and oxygen generates reactive oxygen species (ROS) for therapeutic effects
- Key components of PDT work synergistically photosensitizer absorbs light energy, transfers to oxygen, produces ROS leading to cellular damage and death
- Mechanism of action involves photosensitizer activation through light absorption initiates energy transfer to oxygen molecules creating ROS induces oxidative stress and cellular destruction
- Applications in disease treatment span various fields including cancer therapy (skin, head and neck, lung cancers), dermatological conditions (acne, psoriasis), ophthalmological disorders (age-related macular degeneration), and antimicrobial applications (dental infections, wound infections)

Components of photodynamic process

- Photosensitizers function as light-absorbing molecules ideal characteristics include high absorption in therapeutic window (600-800 nm), low dark toxicity, selective accumulation in target tissue (porphyrins, chlorins, phthalocyanines)
- Light sources encompass lasers, light-emitting diodes (LEDs), and broad-spectrum lamps wavelength selection matched to photosensitizer absorption considers tissue penetration depth delivery methods include surface illumination, interstitial fibers, and endoscopic delivery
- Oxygen plays crucial role in ROS generation facilitates Type I (electron transfer) and Type II (energy transfer, singlet oxygen production) photochemical reactions emphasizes importance of tissue oxygenation for PDT efficacy

Photodynamic therapy vs conventional treatments

- Advantages of PDT include minimally invasive approach, targeted treatment reduces systemic side effects, repeatability without cumulative toxicity, potential for outpatient treatment, improved cosmetic outcomes in dermatological applications
- Limitations of PDT involve light penetration depth restrictions, post-treatment photosensitivity period, limited efficacy in hypoxic environments, need for specialized equipment and expertise, cost

considerations

- Comparison to conventional treatments: 1. Surgery: PDT less invasive with better cosmetic outcomes, surgery more comprehensive for tumor removal 2. Chemotherapy: PDT provides localized treatment with fewer systemic side effects, chemotherapy offers systemic treatment with broader applicability 3. Radiotherapy: PDT has no cumulative dose limit and is repeatable, radiotherapy effective for deeper tumors but limited by total dose

Mechanisms of photodynamic cell death

- ROS-induced damage triggers lipid peroxidation, protein oxidation, DNA damage disrupting cellular structures and functions
- Cell death pathways activated by PDT: 1. Apoptosis involves mitochondrial damage, cytochrome c release, caspase activation leading to programmed cell death 2. Necrosis results from severe cellular damage causing membrane rupture and inflammatory response 3. Autophagy initiated as cellular stress response activates lysosomal degradation pathways
- Vascular effects of PDT include endothelial cell damage, vessel constriction and shutdown induces tumor hypoxia and nutrient deprivation
- Immune system activation occurs through damage-associated molecular pattern (DAMP) release recruits neutrophils and macrophages stimulates adaptive immune response
- Molecular targets affected by PDT include Bcl-2 family proteins, NF- κ B pathway, p53 activation modulating cell survival and death signaling
- Resistance mechanisms to PDT involve antioxidant upregulation, efflux pump expression, hypoxia-inducible factor (HIF) activation potentially reducing treatment efficacy

15.2 Photosensitizers and their biological applications

Photosensitizers are light-activated compounds crucial in photodynamic therapy. They come in organic and inorganic forms, each with unique properties. The ideal photosensitizer absorbs light efficiently, produces reactive oxygen species, and selectively accumulates in target tissues.

Photosensitizers have diverse biological applications, from cancer treatment to antimicrobial therapy. Targeted delivery strategies, like nanocarriers and antibody conjugation, enhance their effectiveness. These methods improve biodistribution and cellular uptake, maximizing therapeutic potential while minimizing side effects.

Types and Properties of Photosensitizers

Types of photosensitizers

- Organic photosensitizers encompass porphyrins, chlorins, and phthalocyanines with cyclic tetrapyrrole structures absorb visible light efficiently
- Inorganic photosensitizers include transition metal complexes (ruthenium, iridium) and quantum dots (CdSe, ZnS) exhibit tunable optical properties
- Chemical properties govern photosensitizer effectiveness involving light absorption characteristics (extinction coefficients), triplet state quantum yield (efficiency of intersystem crossing), photostability (resistance to photobleaching), and solubility in biological media (lipophilicity, hydrophilicity)

Ideal photosensitizer characteristics

- High absorption coefficient in therapeutic window (600-900 nm) maximizes tissue penetration and light activation
- Efficient intersystem crossing to triplet state enhances production of reactive oxygen species
- Long triplet state lifetime increases probability of energy transfer to oxygen
- High singlet oxygen quantum yield boosts photodynamic effect
- Low dark toxicity minimizes side effects in absence of light activation
- Selective accumulation in target tissues improves therapeutic index
- Rapid clearance from normal tissues reduces systemic toxicity
- Amphiphilic nature facilitates cellular uptake and localization

Biological Applications and Delivery Strategies

Biological applications of photosensitizers

- Cancer treatment utilizes photosensitizers for tumor cell destruction through oxidative stress, vascular shutdown leading to ischemia, and immune system stimulation enhancing antitumor response
- Antimicrobial therapy employs photodynamic inactivation of bacteria disrupting cell membranes and treating localized infections (dental, skin)
- Ophthalmology applications include age-related macular degeneration treatment targeting abnormal blood vessels
- Dermatology uses photosensitizers for acne treatment reducing inflammation and psoriasis management controlling keratinocyte proliferation

Targeted delivery of photosensitizers

- Nanocarrier-based delivery systems (liposomes, polymeric nanoparticles, dendrimers) improve biodistribution and cellular uptake
- Active targeting approaches use antibody conjugation or peptide-mediated targeting for enhanced selectivity
- Stimuli-responsive delivery systems (pH-sensitive, enzyme-activated prodrugs) enable controlled release at target sites
- Photochemical internalization facilitates light-induced endosomal escape improving intracellular delivery
- Combination with other treatment modalities (chemotherapy, immunotherapy) synergizes therapeutic effects

15.3 Optogenetics: light-controlled cellular processes

Optogenetics is a game-changing technique that lets scientists control cells with light. By combining genetics and optics, researchers can switch specific cellular activities on and off with incredible precision, opening new doors in neuroscience and beyond.

This powerful tool relies on light-sensitive proteins called opsins. When engineered into target cells, these proteins act like tiny switches, allowing researchers to manipulate cellular processes in real-time and study complex biological systems with unprecedented detail.

Understanding Optogenetics

Definition and significance of optogenetics

- Combines genetic and optical methods to control specific cellular activities with light
- Enables precise temporal and spatial control of cellular processes allowing non-invasive manipulation of biological systems
- Provides real-time observation of cellular responses
- Offers higher specificity than pharmacological approaches
- Allows reversible and repeatable activation/inhibition of target cells
- Facilitates study of complex neural circuits and behaviors (memory formation, decision-making)

Principles of light-sensitive proteins

- Microbial opsins include bacteriorhodopsin, halorhodopsin, channelrhodopsin
- Animal opsins encompass rhodopsin, melanopsin
- Transmembrane proteins contain light-sensitive retinal chromophore
- Undergo conformational changes upon light absorption
- Excitatory opsins (channelrhodopsin-2) function as light-gated cation channels depolarizing neurons
- Inhibitory opsins (halorhodopsin) act as light-driven ion pumps hyperpolarizing neurons
- Different opsins respond to specific wavelengths enabling multiplexed control of cellular populations

Genetic engineering for optogenetics

- Viral vector delivery utilizes adeno-associated virus (AAV) or lentivirus
- Transgenic animal models employ Cre-lox recombination system and tissue-specific promoters
- In vitro transfection methods include lipofection and electroporation
- CRISPR-Cas9 gene editing allows precise insertion of opsin genes into target loci
- Promoter selection enables cell type-specific or activity-dependent expression

Applications in scientific research

- Neuroscience: maps neural circuits, studies behavior and cognition, investigates neurological disorders (Parkinson's, epilepsy)
- Cell biology: controls gene expression, manipulates intracellular signaling pathways, studies cell migration and development
- Cardiac optogenetics examines heart function and arrhythmias

- Optogenetic control of immune cells investigates immune responses
- Plant optogenetics studies photosynthesis and growth responses
- Therapeutic potential explores treating neurological disorders and vision restoration in retinal degeneration

Ethics and limitations of optogenetics

- Ethical concerns include animal welfare, potential human enhancement, and privacy issues with brain-computer interfaces
- Technical limitations involve light delivery to deep brain structures and potential immune responses to viral vectors
- Biological limitations encompass potential off-target effects and altered gene expression due to opsin overexpression
- Translational challenges include safety concerns for human applications and scalability for clinical use
- Ongoing development of red-shifted opsins aims to achieve deeper tissue penetration
- Creation of bi-stable opsins seeks to enable prolonged activation/inhibition

15.4 Photoactivatable drugs and caged compounds

Photoactivatable drugs and caged compounds revolutionize targeted drug delivery. These initially inactive molecules become pharmacologically active when exposed to light, offering precise spatial and temporal control. This innovative approach reduces side effects and improves therapeutic outcomes.

The design of light-activated drugs involves careful consideration of photochemical properties and synthesis techniques. By attaching photolabile groups to active molecules, researchers can create drugs that respond to specific wavelengths of light, opening up exciting possibilities in various medical fields.

Understanding Photoactivatable Drugs and Caged Compounds

Photoactivatable drugs and caged compounds

- Photoactivatable drugs become pharmacologically active when exposed to light, initially inactive
- Caged compounds are biologically active molecules temporarily inactivated by photolabile protecting groups
- Spatial and temporal control in targeted drug delivery reduces systemic side effects and improves therapeutic index

Design principles of light-activated drugs

- Consider photochemical properties, absorption wavelength, quantum yield, and stability
- Synthesize by attaching photolabile groups (o-nitrobenzyl, coumarin, azobenzene) to active molecules
- Utilize photocleavage, photoisomerization, and energy transfer mechanisms
- Optimize structure-activity relationships for enhanced photochemical properties

Advantages of spatiotemporal drug release

- Precise localization in specific tissues minimizes off-target effects
- On-demand activation allows pulsed or sustained release patterns
- Fine-tune drug concentration through light intensity and duration
- Non-invasive activation via external light sources or fiber optics
- Some systems offer reversibility for drug deactivation
- Synergizes with molecular targeting or nanocarrier approaches

Applications in biology and medicine

- Neuroscience: study neurotransmitter dynamics and map neural circuits
- Cancer therapy: photodynamic therapy and targeted chemotherapy activation
- Ophthalmology: controlled drug delivery for retinal diseases
- Cardiology: localized vasodilation and anti-arrhythmic drug release
- Gene therapy: light-activated expression systems and photocontrolled CRISPR-Cas9
- Drug delivery: photosensitive liposomes and light-responsive hydrogels
- Tissue engineering: control growth factors and pattern cell adhesion molecules
- Pain management: localize analgesic activation
- Antimicrobial: trigger antibiotic release and photodynamic therapy