

Lecture 12. Fundamentals of Photochemistry: The Interaction of Light and Matter

Goal of the lecture: To understand the fundamental principles of photochemistry, including how light interacts with atoms and molecules, the mechanisms of photoexcitation and photochemical reactions, and the importance of light-induced processes in chemistry, biology, and technology.

Brief lecture notes: Photochemistry is the branch of chemistry that studies chemical reactions initiated by the absorption of light. Unlike thermochemical reactions, which are driven by heat, photochemical reactions occur when molecules absorb **photons** — quanta of electromagnetic radiation — leading to electronic excitation.

The energy of light can be expressed using **Planck's equation**:

$$E = h\nu = \frac{hc}{\lambda}$$

where

E = energy of the photon (J),

h = Planck's constant (6.626×10^{-34} J·s),

ν = frequency (s^{-1}),

c = speed of light (3×10^8 m/s),

λ = wavelength (m).

When a molecule absorbs light energy, it transitions from its **ground state** to an **excited state**, often resulting in chemical or physical changes.

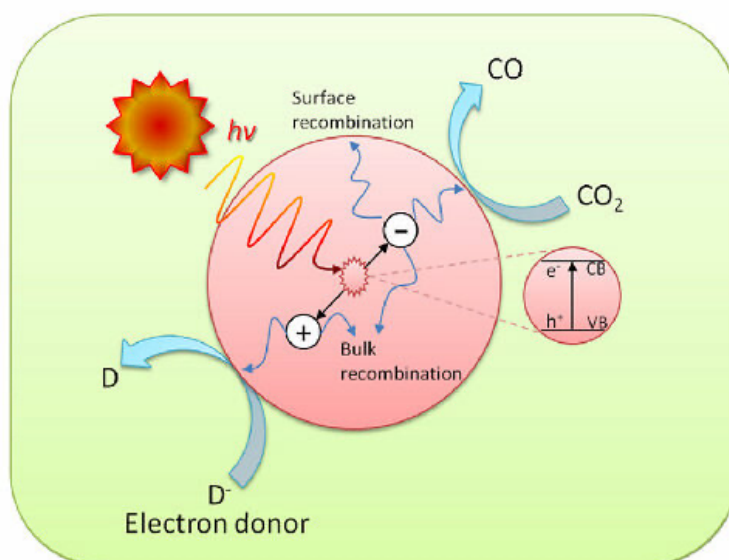


Figure 1 – Schematic diagram of electronic excitation

The absorbed photon promotes an electron to a higher energy level, creating an excited molecule with new chemical reactivity.

1. Fundamental Laws of Photochemistry

Photochemical processes obey two main laws:

1. **Grotthuss–Draper Law (First Law of Photochemistry):**
Only light that is absorbed by a substance can produce a photochemical change.
2. **Einstein's Law of Photochemical Equivalence (Second Law):**
Each absorbed photon excites one molecule, initiating one primary reaction.
The energy absorbed is related to **one quantum per molecule**:

$$E = Nh\nu$$

where N is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$).

Thus, one mole of photons corresponds to **one einstein** of energy.

2. Processes Following Light Absorption

When a molecule absorbs a photon, several competing processes can occur:

- **Internal conversion (IC):** Energy is lost as heat without emission of light.
- **Fluorescence:** Emission of light when the molecule returns from an excited singlet state to the ground state.
- **Phosphorescence:** Emission of light from a triplet excited state; occurs more slowly than fluorescence.
- **Photochemical reaction:** The excited molecule undergoes bond breaking, rearrangement, or reaction with another molecule.

These processes are illustrated by the **Jablonski diagram**, which shows the electronic states and transitions between them.

3. Quantum Yield (Φ)

The **quantum yield** of a photochemical process is the number of molecules reacting or produced per photon absorbed:

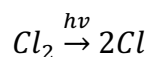
$$\phi = \frac{\text{Number of molecules reacted}}{\text{Number of photons absorbed}}$$

If $\Phi > 1$, the reaction involves **chain propagation**, where one photon initiates multiple reaction events.

4. Types of Photochemical Reactions

1. Photodissociation: Breaking of chemical bonds upon light absorption.

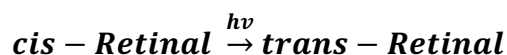
Example:



This reaction is the first step in **free radical chain reactions** such as chlorination of methane.

2. Photoisomerization: Conversion of molecules into isomers.

Example: **cis–trans isomerization** of stilbene or retinal in vision:



3. Photooxidation and Photoreduction: Electron transfer processes induced by light, important in photosynthesis and photochemical catalysis.

4. Photosensitization: A molecule called a **sensitizer** absorbs light and transfers its energy to another molecule, initiating its reaction.

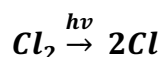
Example: In photosynthesis, chlorophyll acts as a sensitizer absorbing sunlight and initiating CO₂ fixation.

5. Photochemical Chain Reactions

Many photochemical processes involve **chain mechanisms** consisting of three stages:

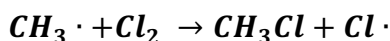
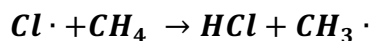
1. Initiation: Light absorption produces reactive species (free radicals).

Example:



2. Propagation: Radicals react with molecules, forming products and regenerating radicals.

Example:



3. Termination: Radicals combine to form stable products.

Example:

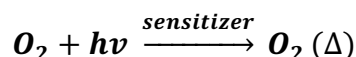


Such chain reactions explain high quantum yields and are key to understanding polymerization, combustion, and atmospheric reactions.

6. Photosensitized and Photocatalytic Reactions

In **photosensitized reactions**, a light-absorbing species transfers its energy to another molecule that cannot directly absorb the same light.

Example:



In **photocatalysis**, light activates a catalyst (e.g., TiO₂) that promotes redox reactions — such as water splitting or degradation of organic pollutants.

Table 1 – Differences between Thermal and Photochemical Reactions

Feature	Thermal Reaction	Photochemical Reaction
Source of energy	Heat	Light (photons)
Temperature dependence	High temperature required	Often occurs at room temperature
Initiation	By molecular collisions	By photon absorption
Reaction pathway	Ground-state molecules	Excited-state molecules
Examples	Combustion, hydrolysis	Photosynthesis, halogenation of alkanes

Questions for self-control:

1. What is photochemistry, and how does it differ from thermochemistry?
2. State the Grotthuss–Draper and Einstein laws of photochemistry.
3. What processes can occur when a molecule absorbs a photon?
4. Write an example of a photochemical chain reaction.
5. Explain the role of chlorophyll as a photosensitizer in photosynthesis.

Literature:

1. Atkins, P., de Paula, J. *Atkins' Physical Chemistry*, 11th Edition, Oxford University Press, 2018.
2. Moran, M.J. *Fundamentals of Engineering Thermodynamics*, 9th Edition, Wiley, p.156.
3. House, J.E. *Fundamentals of Quantum Chemistry*, 2nd Edition, Academic Press, 2004.
4. Hammes-Schiffer, S. et al. *Physical Chemistry for the Biological Sciences*, University Science Books, 2009.
5. Zhdanov, V.P. *Elementary Physicochemical Processes on Solid Surfaces*, Springer, 1991.