

Welcome to

Photochemistry and Photophysics

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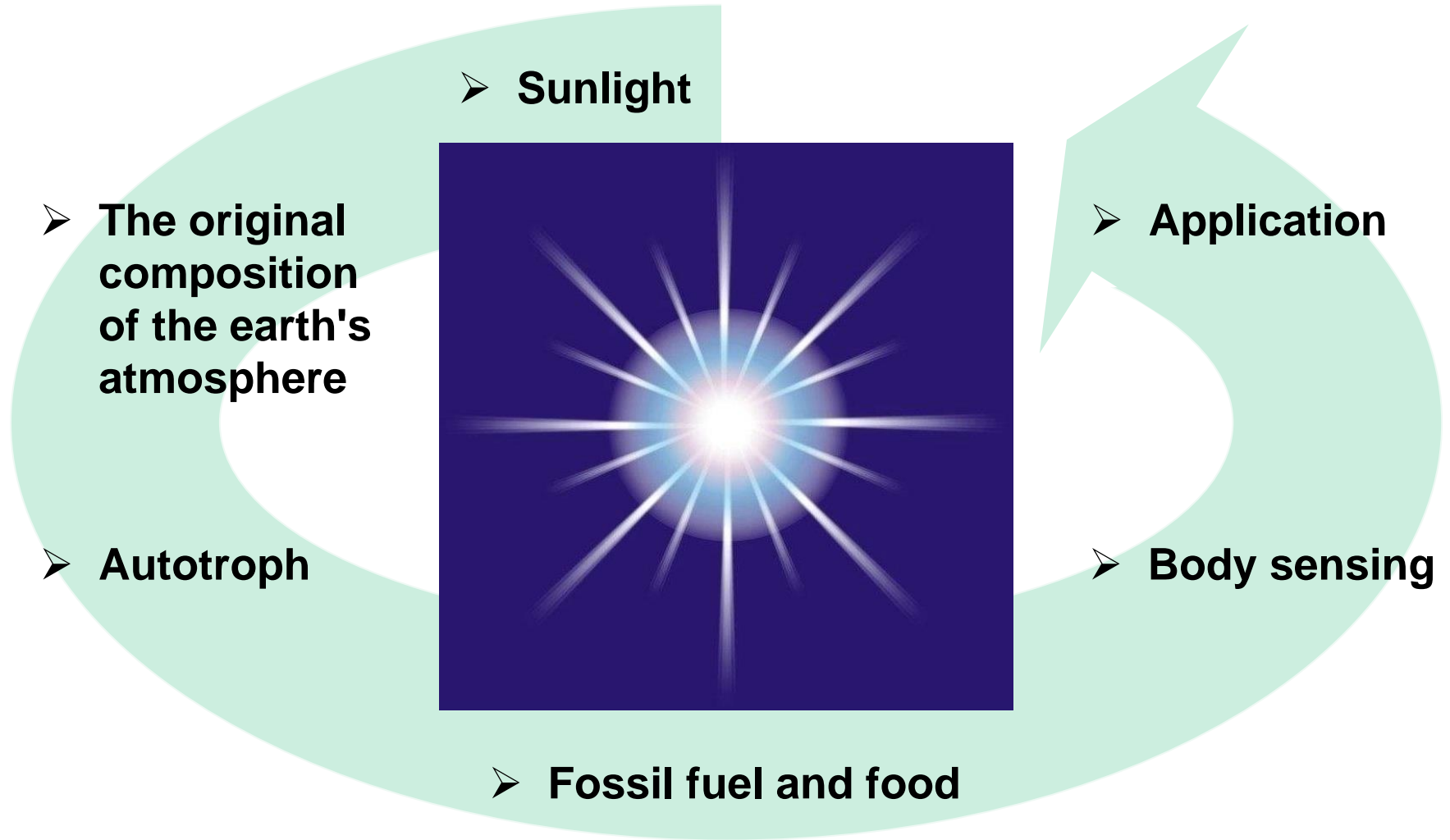
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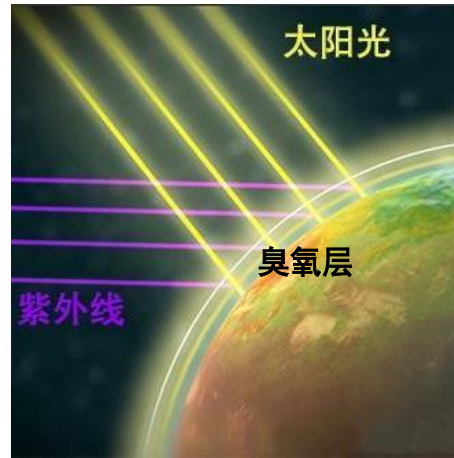
苏州大学纳米科技学院

Class 1

Light, Light Absorption, ground state , excited state

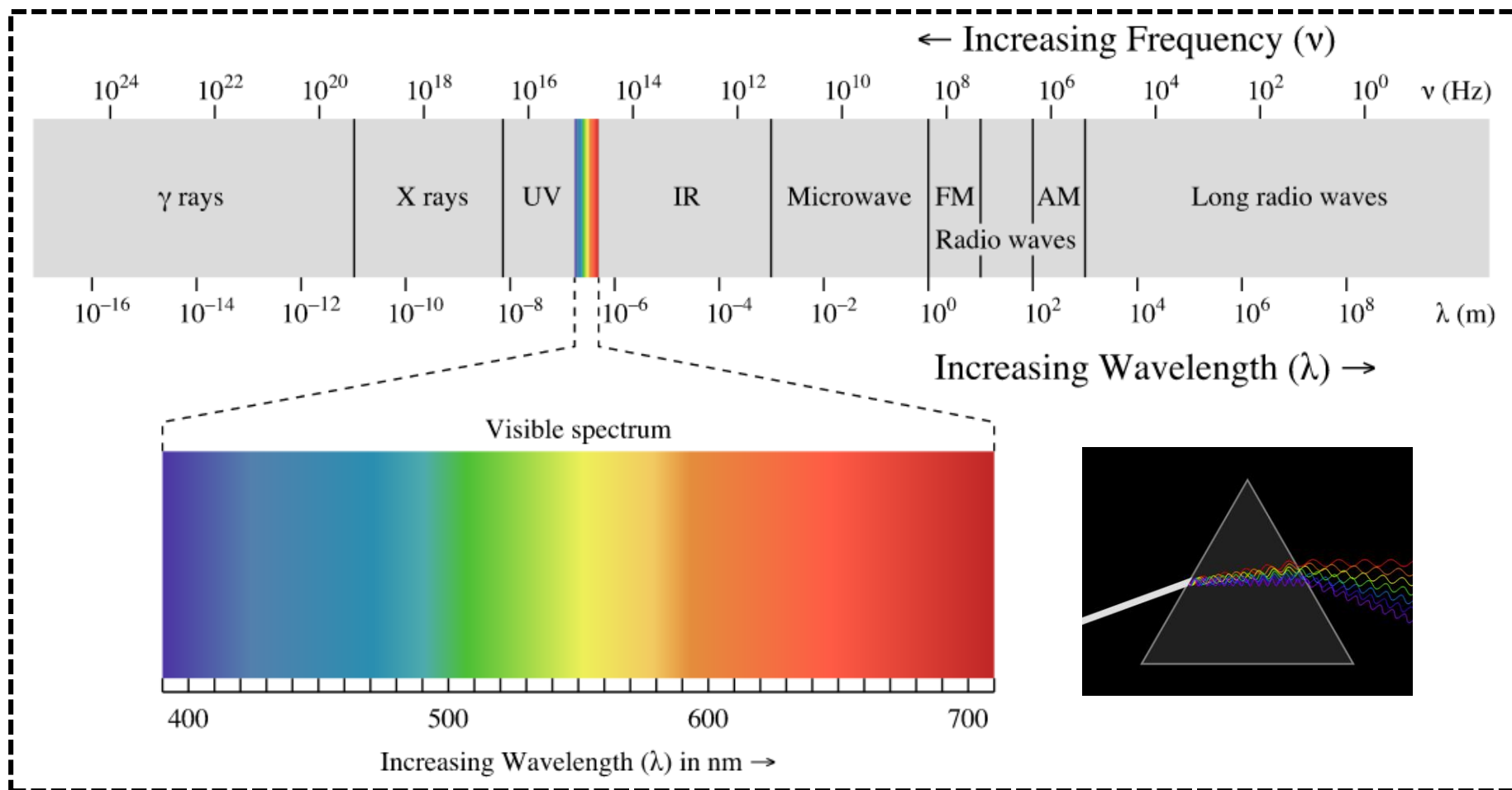
- **Photochemistry and photophysics in nature**
- **The nature of light**
- **Light absorption**
- **Electronically-excited state**
- **Fundamental principles relating to light absorption**
- **Selection rules for light absorption**
- **Absorption spectrum**





□ The interactions with photons in the natural world are important.

The nature of light



□ Light is **electromagnetic radiation** within a certain portion of the electromagnetic spectrum.

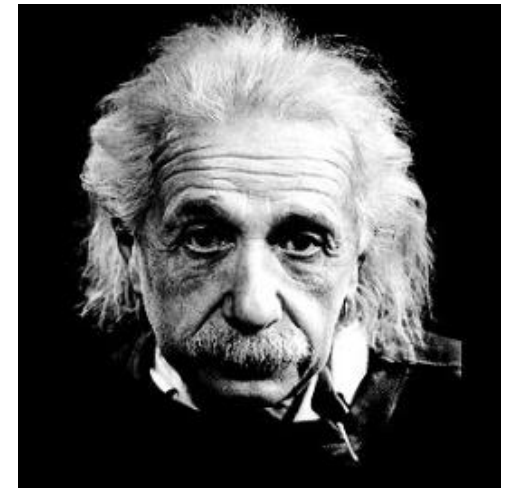
The nature of light



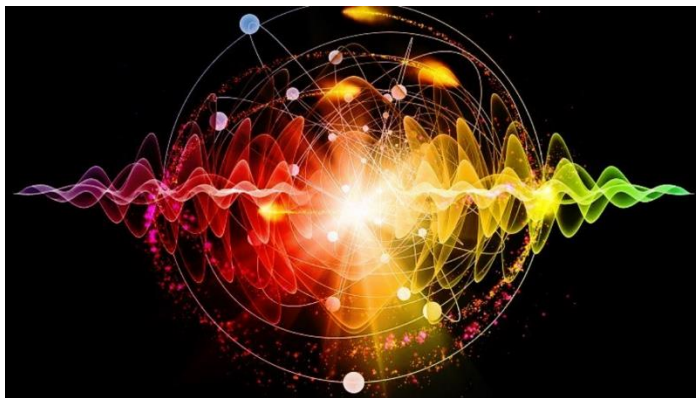
Huygens
Wave theory



Newton
Corpuscular theory



Einstein
Quantum theory



□ The nature of light:
Wave-Particle Dualism

- **In the wave model**, the characteristics of electromagnetic radiation are wavelength λ , frequency ν and velocity c :

$$\lambda\nu = c$$

The values of λ and ν are in a range, c is a constant ($c = 2.998 \times 10^8$ m/s, in vacuum).

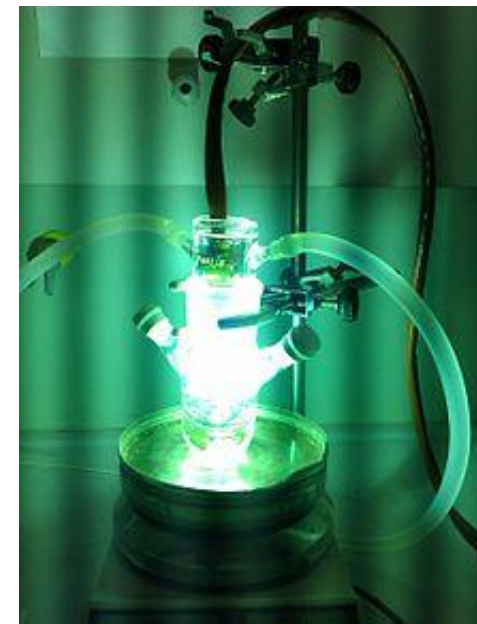
- **In the quantum model**, a beam of radiation is considered a series of photons or quanta. Each photon has its specific energy E , and the relation with frequency ν is:

$$E = h\nu$$

h is a constant, $h = 6.63 \times 10^{-34}$ J·s

Definition of photochemistry and photophysics

- ❑ Photophysics and photochemistry both deal with the impact of energy in the form of photons on materials.
- ❑ **Photochemistry** focuses on the chemistry involved as a material is impacted by photons. **Photophysics** deals with physical changes that result from the impact of photons.
- ❑ Generally, this term is used to describe a chemical or physical reaction caused by absorption of **ultraviolet** (wavelength from 100 to 400 nm), **visible light** (400–750 nm) or **infrared radiation** (750–2500 nm).



Photochemical immersion well reactor (50 mL) with a mercury-vapor lamp.

Definition of photochemistry and photophysics

The chemical and physical processes experienced by molecules that absorb ultraviolet or visible light.

--C. H. Wells

Photochemistry studies the chemical behavior and physical processes of molecules in the excited states of electrons.

--N. J. Turro



Carl W. Scheele

◆ The first artificial photochemical reaction



Theodor von Grotthuss



John w. Draper

◆ Grotthuss – Draper law



**Johannes Stark
Albert Einstein**

◆ Stark – Einstein law

Development of photochemistry and photophysics

◆ The first artificial photochemical reaction

Carl W. Scheele

1777

◆ Grotthuss – Draper law

1817

Theodor von Grotthuss

John w. Draper

1841

1908-1913

Johannes Stark
Albert Einstein

◆ Stark – Einstein law

◆ Application of molecular orbital theory

1930- 1950

◆ The concept of excited state reactivity

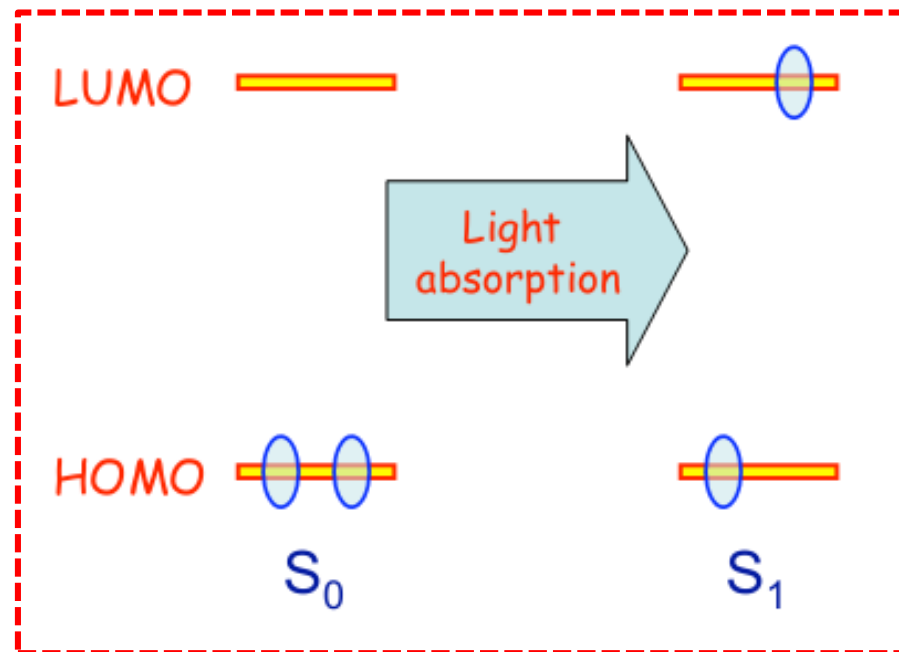
1960

◆ Supramolecular chemistry

1990



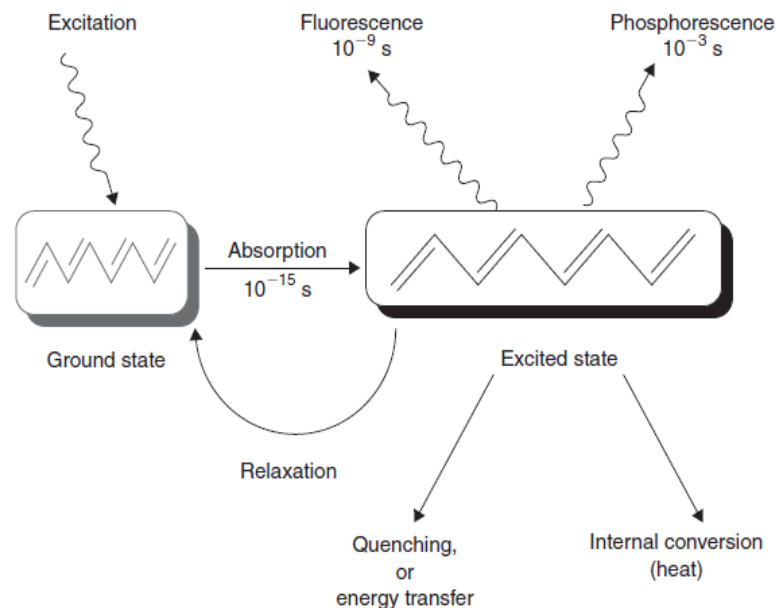
- The absorption of light is a prerequisite for it to be able to cause **chemical change**.
- This can be viewed as another expression of the laws of **energy conservation**.
- Most molecules have all their electrons paired in their ground states, and the simplest (but not the only) effect of light absorption is the **promotion of an electron from the HOMO to the LUMO**.
- Molecular oxygen and stable (or persistent) free radicals are exceptions of molecules that **have unpaired electrons in their ground states**.



A standard abbreviation:

$$\text{Light absorption} = h\nu$$

- Light is composed of particles known as **photons**, each of which has the **energy of Planck's quantum**: hc/λ ; where h is Planck's constant, c is velocity of light, and λ is the wavelength of the radiation.
- Light has **dualistic properties** of both waves and particles.
- Ejection of electrons from an atom as a result of light bombardment is due to the **particle behavior**.
- The observed light diffraction at gratings is attributed to the **wave properties**.



The different processes related to light interactions with molecules.

According to the quantum theory, light is also quantised. The absorption or emission of light occurs by the transfer of energy as photons. These photons have both wavelike and particle-like properties and each photon has a specific energy, E , given by

Planck's law:

$$E = h\nu$$

where h is Planck's constant ($6.63 \times 10^{-34} \text{ Js}$) and ν is the frequency of oscillation of the photon in units of s^{-1} or Hertz (Hz).

➤ **The term ' $h\nu$ '** is used in equations for photophysical and photochemical processes to **represent a photon**.

For example, for a molecule R in its ground state which absorbs a photon to produce an electronically-excited molecule, R^* , we may write the process as:



Each photon oscillates with wavelength λ , where $\lambda = c/\nu$ and where c is the speed of light. Thus:

$$E = h\nu = hc/\lambda$$

This equation demonstrates the important properties relating to the energy of photons:

- **The energy of a photon is proportional to its frequency and inversely proportional to its wavelength**

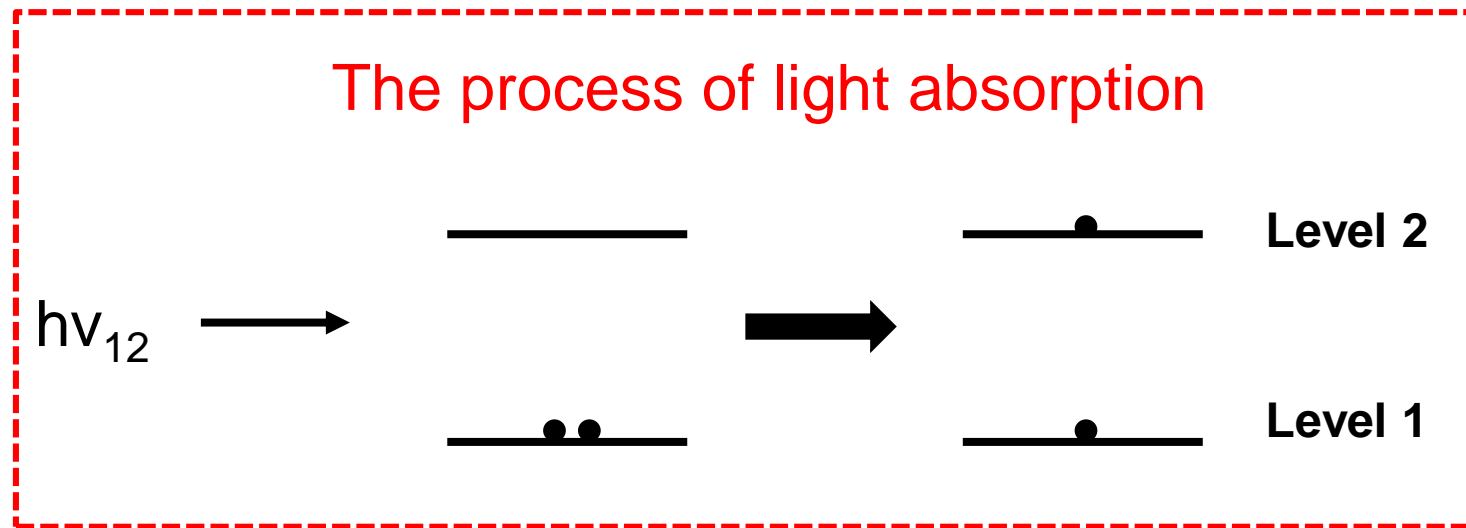
Table. Properties of visible and ultraviolet light

Colour	λ/nm	$\nu/10^{14}\text{ Hz}$	$\bar{\nu}/10^4\text{ cm}^{-1}$	$E/\text{kJ mol}^{-1}$
red	700	4.3	1.4	170
orange	620	4.8	1.6	193
yellow	580	5.2	1.7	206
green	530	5.7	1.9	226
blue	470	6.4	2.1	254
violet	420	7.1	2.4	285
ultraviolet	<300	>10.0	>3.3	>400

- The **production of the electronically-excited state by photon absorption** is the feature that characterises photochemistry and separates it from other branches of chemistry.

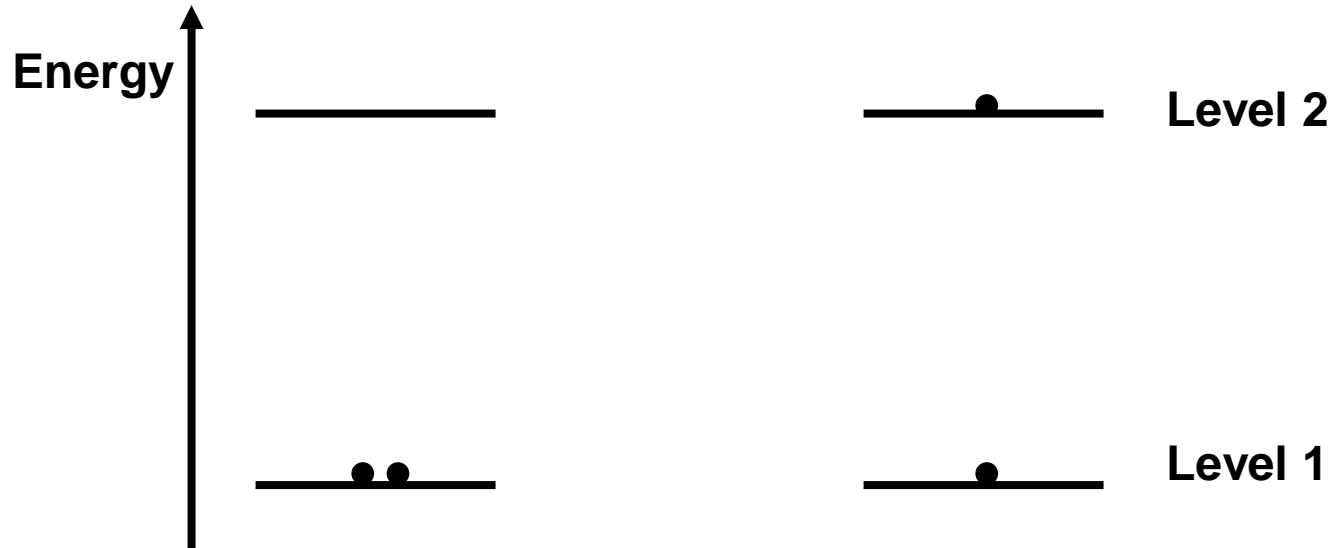
Electronically-excited state

In absorption of light, a photon having energy equal to the energy difference between two electronic states can use its energy to move an electron from the lower energy level to the upper one, producing **an electronically-excited state**:



- ❑ The photon is completely destroyed in the process, its energy becoming part of the total energy of the absorbing species.

Electronically-excited state



Lowest energy electronic
Configuration
(**Electronic ground state**)

Higher energy electronic
Configuration
(**Electronically excited state**)

Quantised energy levels in matter, where an electron (●) may be found in either of the two energy levels shown.



□ Electronic ground state

- Under normal conditions, the atom is at **the lowest energy level**, and the electron moves in the orbital closest to the nucleus. A stationary state called the ground state. This is the steady state of the electron.

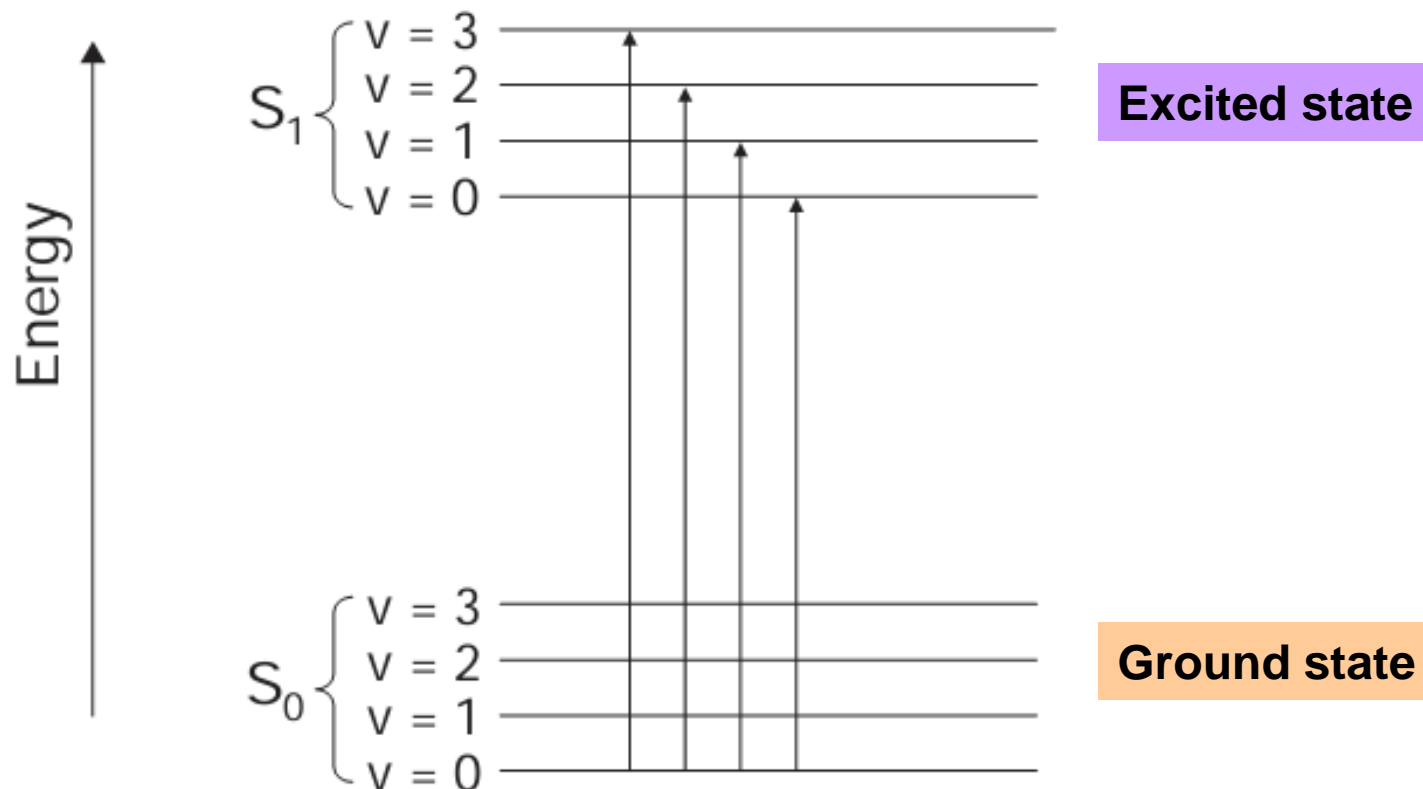
At absolute zero, all particles are in the lowest possible state of energy, that is, all particles are in the ground state.

□ Electronically excited state

- When ground state atoms are **excited by external energy** (such as thermal energy, light energy, etc.), their outer electrons absorb certain energy and jump to different energy states (such energy states are called excited states). Therefore, **atoms may have different excited states**.

All photochemical reactions are chemical reactions that occur when molecules are elevated to excited states

Electronically-excited state



Schematic diagram of the electronic ground state and the first excited electronic state, with their associated quantised vibrational energy levels, for an inorganic molecule. The vertical arrows show vibronic transitions due to the absorption of photons.

Fundamental principles relating to light absorption are the basis for understanding photochemical transformations:

1. **The Grotthuss- Draper Law**
2. **The Stark- Einstein Law**
3. **The Franck–Condon Principle**
4. **Lambert-Beer law**

1. Grotthuss-Draper law

(光化学第一定律)

The Grotthuss–Draper law (also called the Principle of Photochemical Activation) states that **only that light which is absorbed by a system can bring about a photochemical change.**



- Materials such as dyes and phosphors must be able to absorb "light" at optical frequencies. This law provides a basis for fluorescence and phosphorescence. The law was first proposed in 1817 by Theodor Grotthuss and in 1842, independently, by John William Draper.

2. Stark–Einstein law

(光化学第二定律)

The Stark-Einstein law is named after German-born physicists Johannes Stark and Albert Einstein, who independently formulated the law between 1908 and 1913. It is also known as the photochemical equivalence law or photo-equivalence law.

In essence it says that every photon that is absorbed will cause a (primary) chemical or physical reaction.

- ❑ The photochemical equivalence law applies to the part of a light-induced reaction that is referred to as the primary process.

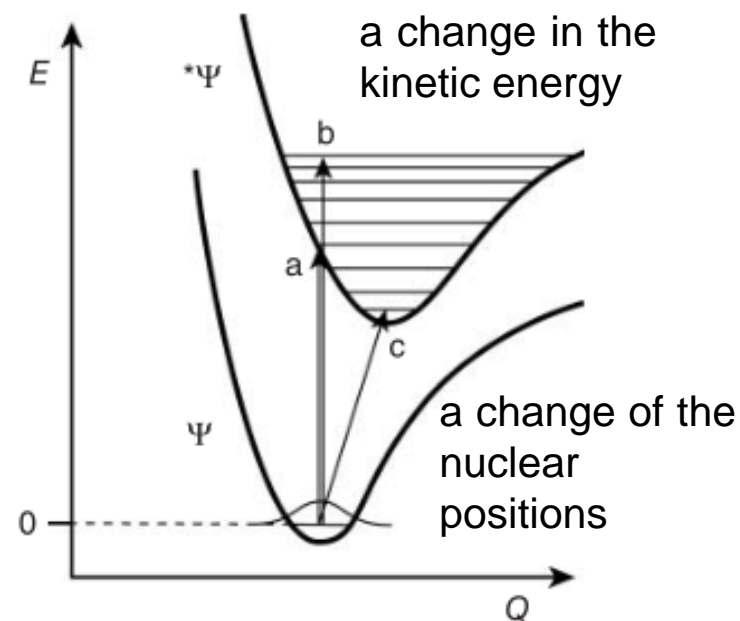
2. Stark–Einstein law

- The Stark-Einstein law states that the primary act of light absorption by a molecule is a one-quantum process.
- For each photon absorbed only one molecule is excited. This law is obeyed in the vast majority of cases.
- Exceptions occur when very intense light sources such as lasers are used for irradiation of a sample. In these cases, concurrent or sequential absorption of two or more photons may occur.

3. Franck–Condon Principle

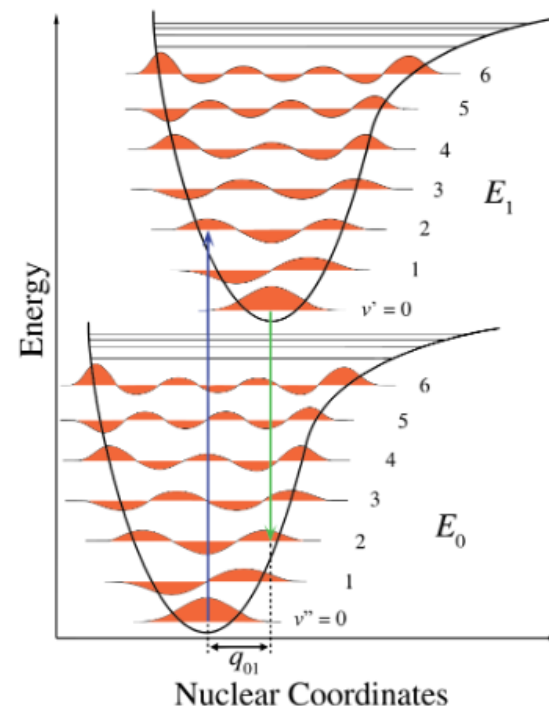
The **Franck–Condon Principle** states that when a molecule is undergoing an electronic transition, **the nuclear configuration of the molecule experiences no significant change.**

- ◆ no change in nuclear position or nuclear kinetic energy occurs during the transition.
- ◆ the electronic transition takes place faster than the nuclei can respond.



3. Franck–Condon Principle

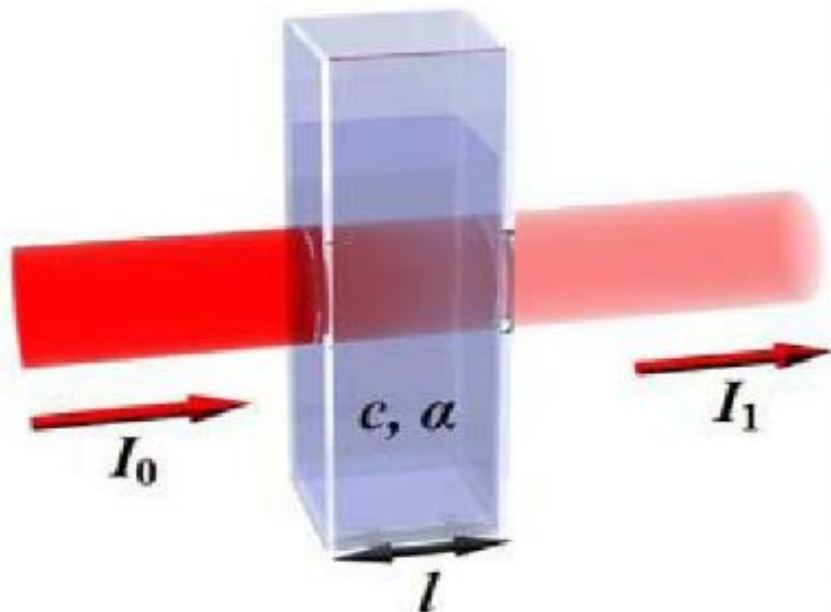
- ◆ Classically, the Franck–Condon principle is the approximation that **an electronic transition is most likely to occur without changes** in the positions of the nuclei in the molecular entity and its environment.
- ◆ Expressed in quantum mechanical terms, the Franck–Condon principle states that **the most probable transitions between electronic states occur when the wave function of the initial vibrational state most closely resembles** the wave function of the final vibrational state.



4. Lambert-Beer law

- Lambert-Beer law is **the basic law of spectrophotometry**, which describes the relationship between the intensity of light absorption of a certain wavelength and the concentration of the light-absorbing substance and the thickness of the liquid layer.
- **Physical significance:** When a beam of parallel monochromatic light passes vertically through a uniform unscattered light-absorbing substance, its **absorbance (A) is proportional to the concentration (c) of the light-absorbing substance and the thickness (l) of the absorption layer**, while the transmittance (T) is inversely proportional to c and l .

4. Lambert-Beer law



$$A = \lg \frac{I_0}{I_t} = \lg \frac{1}{T} = \varepsilon \cdot l \cdot c$$

A: Absorbance
T: Transmittance
 ε : Absorption coefficient
 l : Thickness of absorption layer
 c : Concentration of light-absorbing substance

The Beer–Lambert law relates the attenuation of light to the properties of the material through which the light is travelling.

There are two major selection rules for absorption transitions:

1. Spin-forbidden transitions. Transitions between states of different multiplicities are forbidden, i.e. singlet–singlet and triplet–triplet transitions are allowed, but singlet–triplet and triplet–singlet transitions are forbidden. However, there is always a weak interaction between the wavefunctions of different multiplicities via spin–orbit coupling.

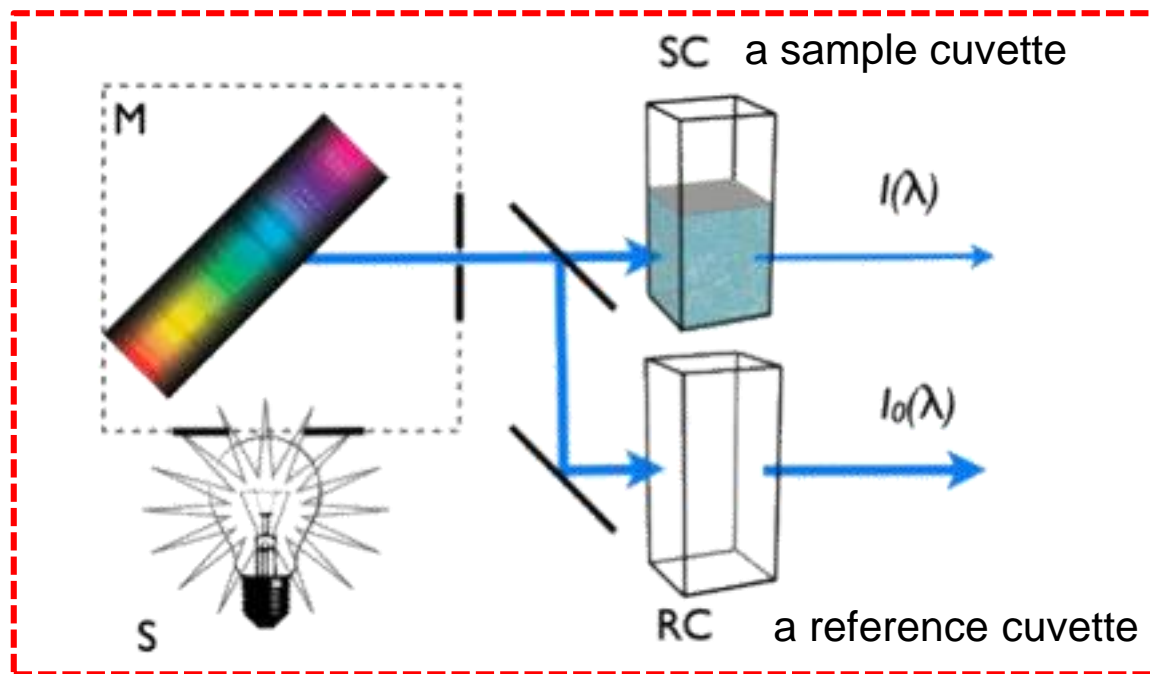
自旋禁阻跃迁

2. Symmetry-forbidden transitions. A transition can be forbidden for symmetry reasons. It is important to note that a symmetry-forbidden transition can nevertheless be observed because the molecular vibrations cause some departure from perfect symmetry (vibronic coupling).

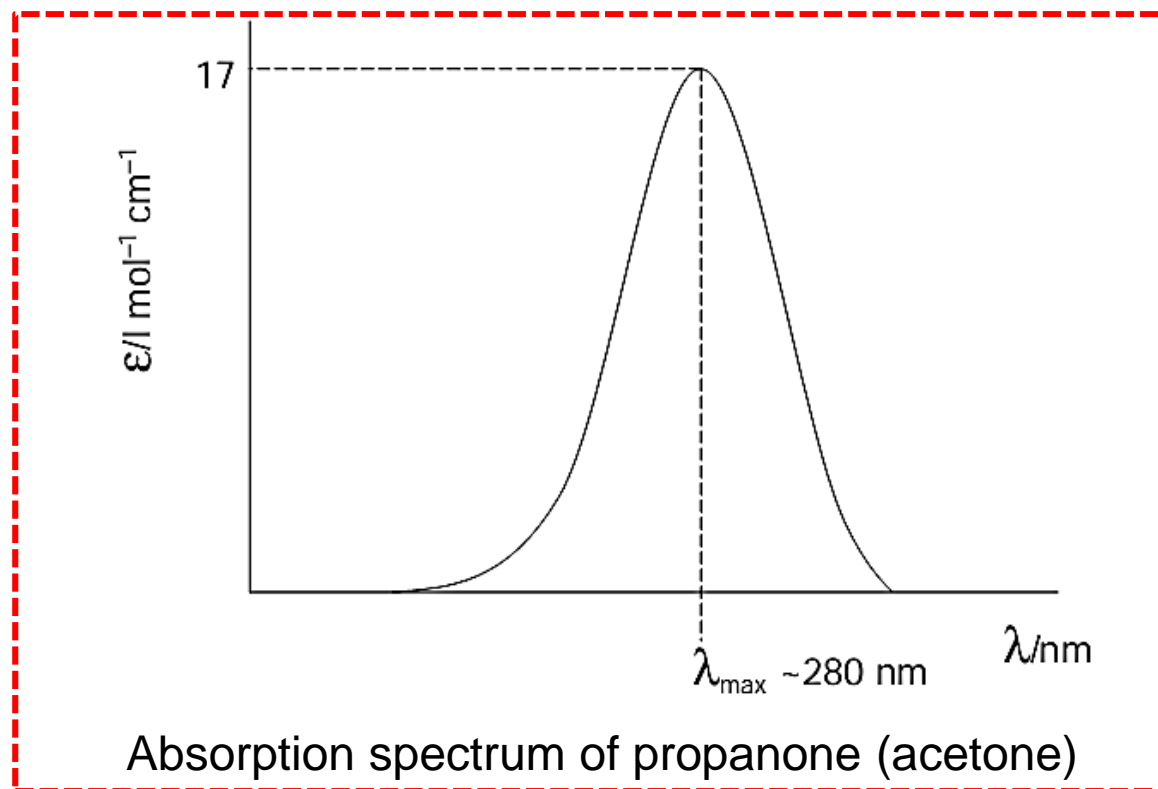
对称禁阻跃迁



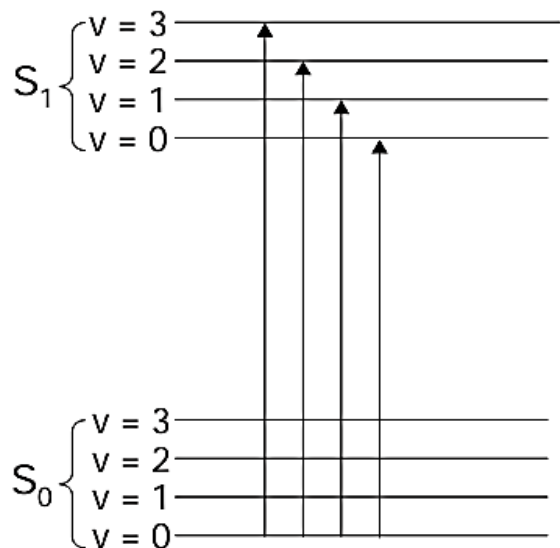
The measurement of an absorption spectrum is based on **the Lambert-Beer law**, and shows the ability of the investigated sample to absorb light at different wavelengths.



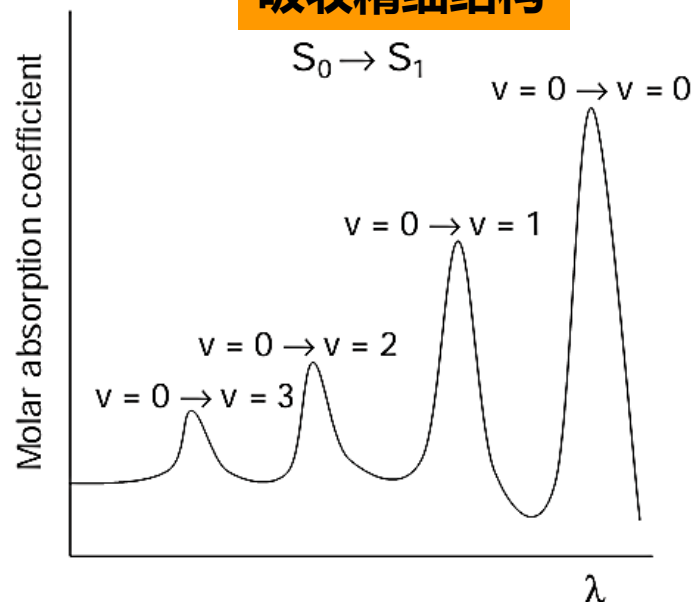
As light absorption occurs almost always from the lowest vibrational level of the electronic ground state, the absorption spectrum characterizes the energetic structures of the electronic excited states of an aromatic molecule.



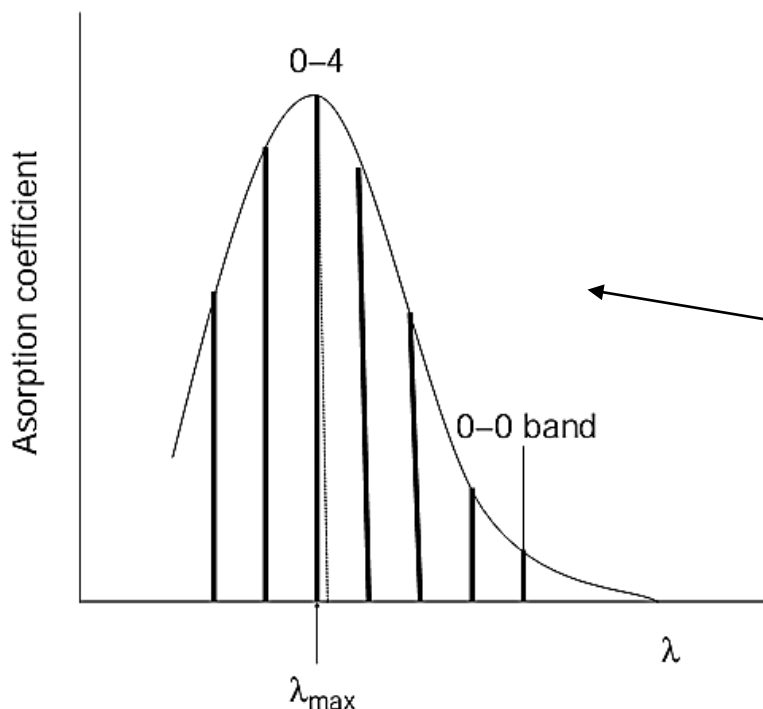
- ❑ For a given substance, the molar absorption coefficient ϵ varies with the wavelength of the light used.
- ❑ A plot of ϵ (or $\log \epsilon$) against wavelength (or wavenumber) is called the absorption spectrum of the substance.



吸收精细结构



- The UV-visible spectrum of a **very dilute solution of anthracene in benzene**, which clearly shows small fingers superimposed on a broader band (or envelope). These fingers are called **the vibrational fine structure** and we can see that each finger corresponds to a transition from the $v = 0$ of the ground electronic state to the $v = 0, 1, 2, 3$, etc. vibrational level of the excited electronic state.
- The absorption spectra of **rigid hydrocarbons in nonpolar solvents** may show **vibrational fine structure**

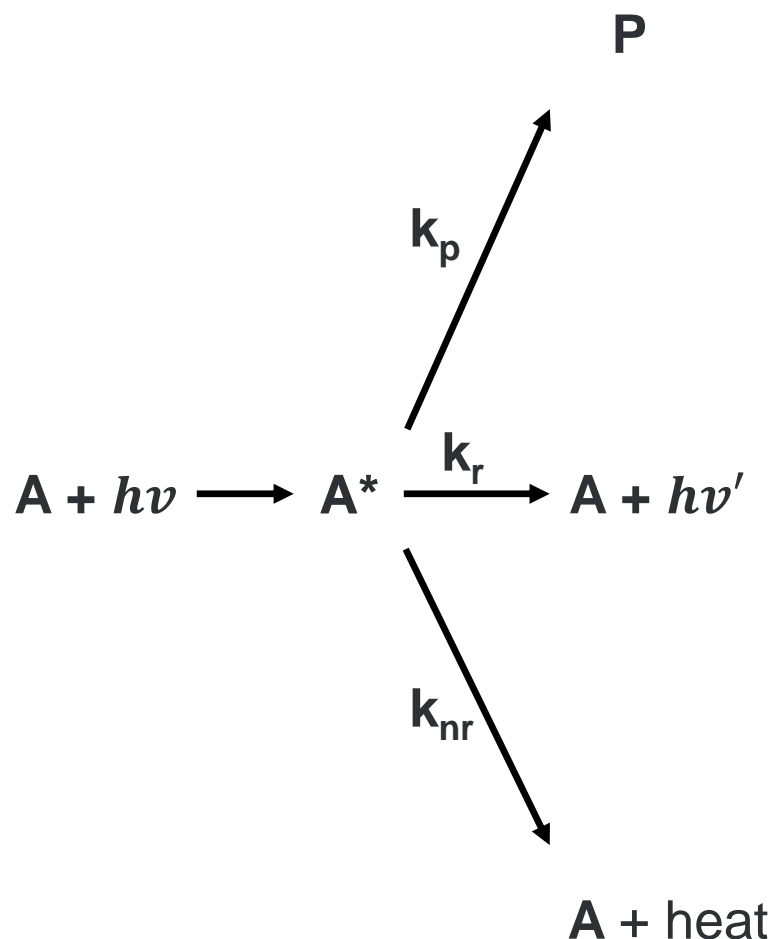


宽且无精细结构的吸收

Broad, featureless absorption spectrum of the solution of an organic compound.

- Absorption spectra of other organic molecules in solution tend to be broad, featureless bands with little or no vibrational structure. This is due to the **very large number of vibrational levels in organic molecules** and to **blurring of any fine structure** due to interaction between organic molecules and solvent molecules.

Deactivation electronically-excited state



Photoreaction (chemical reaction)

- Sometimes electronic excitation can result in chemical changes, such as the fading of dyes, photosynthesis in plants, suntans, or even degradation of molecules.

Luminescence (radiative deactivation)

- resulting in emission of light (luminescence) or conversion of the excess energy into heat, whereby the original ground state is reformed.

Degradation to heat (nonradiative deactivation)

Thanks

