

Photochemistry and Photophysics

2022/9/6

1. 期中考试，期末考试
2. 少数化学，光催化有机合成，主讲光物理
3. 10%(提问) 30%(期中) 60%(期末)
4. ground state – excited state
5. refraction (折射) transmission (透射) reflection (反射) incidence (入射)
6. normal (法线)
7. 臭氧可吸收高能紫外线，小于 300 nm。
8. 400(B) -500(G)-700(R) nm visible range
9. HOMO-LUMO (Highest occupied molecule orbitals – Lowest occupied molecule orbitals)
10. 名词解释：

Photochemistry and photophysics are process experienced by molecule that accept the light irradiation. Namely, photochemistry is chemistry process while photophysics is physical process.

11. electronically-excited state

Electronically-excited state FUNSOM
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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 process of light absorption

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

O（氧） 是成对出现，不是单个电子激发

- 12.名词解释

Electronically-excited state

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

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Electronic ground state: The steady state of the electron, which allows the atom to be at the lowest energy level and the electron moves in the orbital closest to the nucleus.

Electronically excited state: The state of electron that excited by external energy along with the energy absorption and the movements of electron from ground state to different higher energy orbitals.

13. Laws:

Light absorption principles

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**.

$$M + \text{light} \rightarrow M^*$$

- 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.

G-D: only the light which is absorbed by a system can bring about a photochemistry change.

II

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.

单量子过程 except the laser.

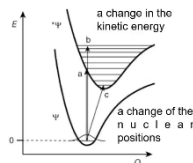
III. Nuclear no change

3. Franck-Condon Principle

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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.



IV. 分光光度原理: concentration and thickness determine the absorbance.

4. Lambert-Beer law

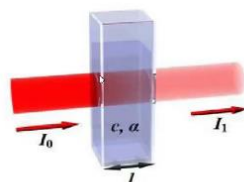
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4. Lambert-Beer law

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- 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.



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

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.

14. selection rules for light absorption.

Selection rules for light absorption

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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

Spin Multiplicity (自旋多重度)

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The spin quantum number of the electron is $\pm 1/2$, the net spin S is the sum of all the spin quantum numbers,

Spin Multiplicity is defined as: $2S+1$

Singlet state: When the spins of a pair of electrons are opposite, the net spin S is 0, and $2S+1=1$.
Its energy level is not affected by the external magnetic field to produce fission, is diamagnetic species, most of the organic molecules are resistant to magnetic. They have a singlet ground state.



Spin-forbidden transitions: transitions between states of different multiplicities are forbidden.

symmetry-forbidden transitions: a transition can be forbidden for symmetry reasons (departure 背离 from perfect symmetry such as vibronic coupling 电子振动耦合).

单线态 (singlet state): 所有配对电子的自旋(1/2)呈反平行的状态。净自旋 $S=1/2-1/2=0$ 三线态 (triplet state): 所有配对电子的自旋(1/2)呈同向平行的状态。Double

state: 单电子净自旋 $S=1/2+1/2=1$, 磁量子数 $M=2S+1$. (自旋多重度)。

Spin Multiplicity

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Triplet state: When the spins of a pair of electrons are the same, the net spin S is 1, $2S+1 = 3$, which is. Triplet states are more common in the excited states of luminescent dyes. Species with triplet ground states are relatively rare, except for oxygen, there are some diradical molecules with triplet ground states.

11

Double state: If there is an unpaired electron with a net spin of $1/2$, $2S+1 = 2$. The most typical example of a double state is an organic single radical.

1

O: triplet state. The singlet state of $[O]$ is harmful to the cells