

Welcome to

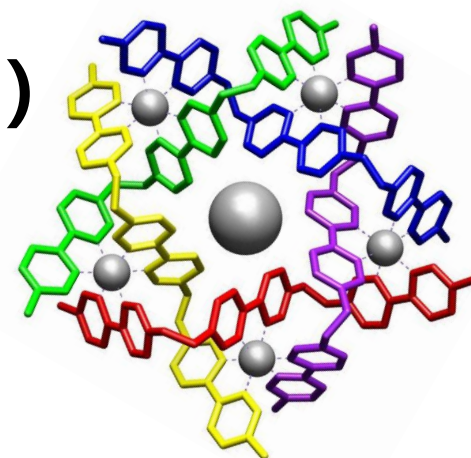
Photochemistry and Photophysics

Presented by Zhang Xiujuan (张秀娟)

Email: xjzhang@suda.edu.cn

Office: 910-601B

苏州大学纳米科技学院



- **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**

- **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.**

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

□ 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

- 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:

Class 2

Deactivation of excited states (Radiationless transitions, Radiative transitions)

- **Deactivation of excited states**
- **Jablonski Diagrams**
- **Radiationless transitions**
 - Vibrational relaxation (Vr)**
 - Internal conversion (IC)**
 - Intersystem crossing (ISC)**
- **Radiative transitions**
 - Fluorescence**
 - Delayed fluorescence**
 - Phosphorescence**

- Electronically-excited states of molecules are endowed with excess energy due to their formation by photon absorption. These excited states are short-lived, losing their excess energy within a very short period of time through a variety of deactivation processes and returning to a ground-state configuration.
- If the excited molecule returns to its original ground state then the dissipative process is a physical process, but if a new molecular species is formed then the dissipative process is accompanied by chemical change.

Physical deactivation of excited states

分子内过程

Intramolecular processes

分子间过程

Intermolecular processes

Vibrational
relaxation

振动弛豫

Energy
transfer

能量转移

Electron
transfer

电子转移

Radiative transitions

辐射跃迁

Fluorescence

荧光

Delayed
fluorescence

延迟荧光

Phosphorescence

磷光

Radiationless transitions

非辐射跃迁

Internal
conversion

内转换

Intersystem
crossing

系间穿越

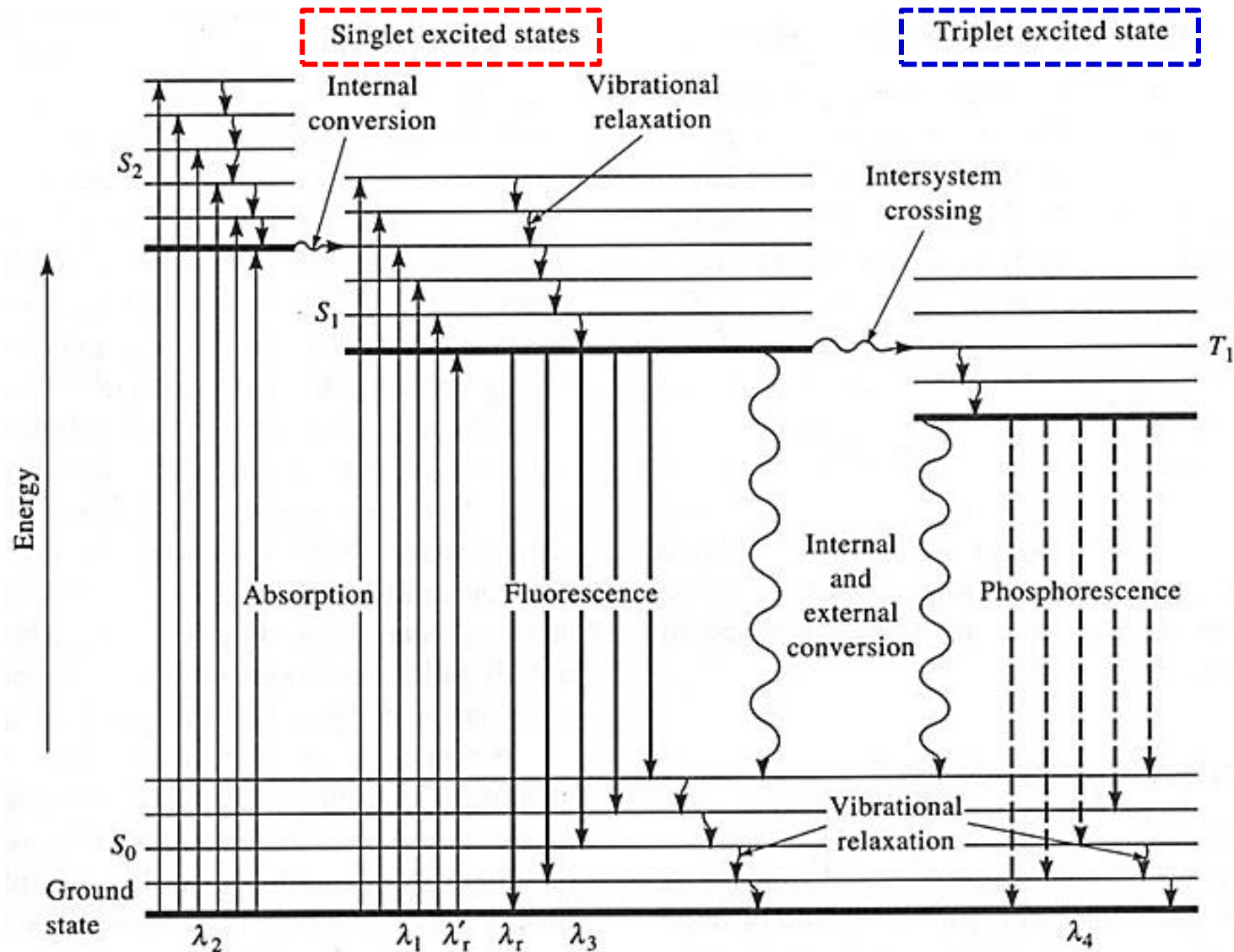
Vibrational
relaxation

振动弛豫

✓ **Radiative transitions**, which involve the emission of electromagnetic radiation as the excited molecule relaxes to the ground state. Fluorescence and phosphorescence are known collectively as luminescence.

✓ **Radiationless transitions**, where no emission of electromagnetic radiation accompanies the deactivation process.

- **Vibrational relaxation**, where molecules having excess vibrational energy undergo rapid collision with one another and with solvent molecules to produce molecules in the lowest vibrational level of a particular electronic energy level.
- **Energy transfer**, where the electronically-excited state of one molecule (the donor) is deactivated to a lower electronic state by transferring energy to another molecule (the acceptor), which is itself promoted to a higher electronic state. The acceptor is known as a quencher and the donor is known as a sensitiser.
- **Electron transfer**, considered as a photophysical process, involves a photoexcited donor molecule interacting with a ground-state acceptor molecule. An ion pair is formed, which may undergo back electron transfer, resulting in quenching of the excited donor.



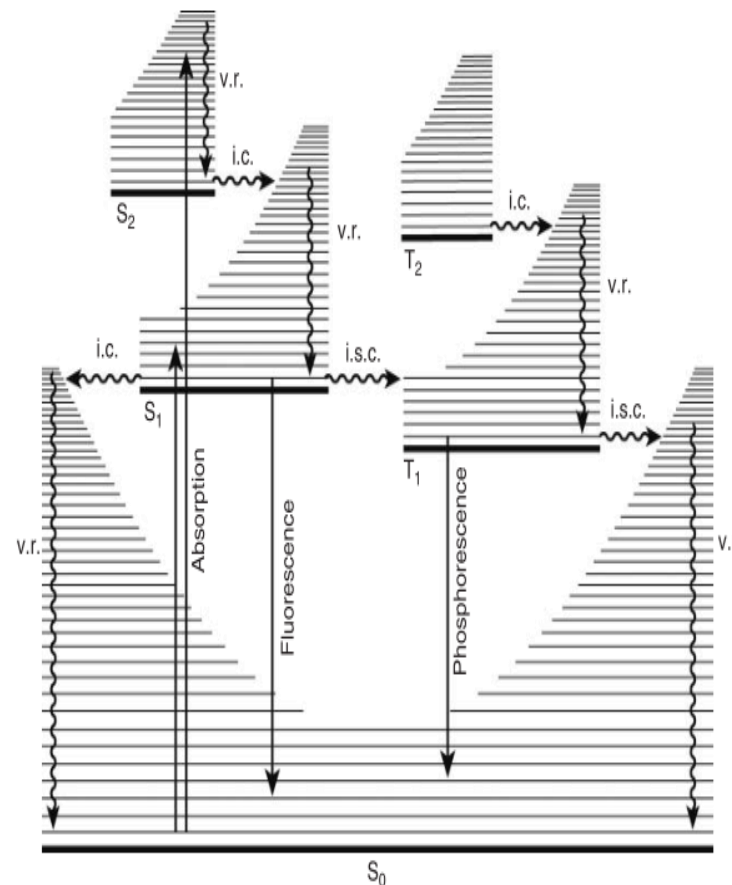
(分子激发和失活的雅布隆斯基图)

The Jablonski diagram shows:

- **The electronic states of the molecule and their relative energies.** Singlet electronic states are denoted by S_0 , S_1 , S_2 , etc. and triplet electronic states as T_1 , T_2 , etc.
- **Vibrational levels associated with each state** are denoted as $v = 0$, $v = 1$, $v = 2$, etc. in order of increasing energy.
- **Radiative transitions** are drawn as **straight arrows** and **radiationless transitions** as **wavy arrows**.
- If an electronically-excited state is formed as a ‘ vibrationally-hot ’ excited molecule (with $v > 0$) then it will undergo **vibrational relaxation** within that electronic energy level until it reaches the $v = 0$ level. The vibrational relaxation within each electronically excited state is drawn as a **vertical wavy arrow**.
- **Radiationless transitions** (internal conversion and intersystem crossing) between electronic states are isoenergetic processes and are drawn as wavy arrows from the $v = 0$ level of the initial state to a ‘ vibrationally - hot ’ ($v > 0$) level of the final state.

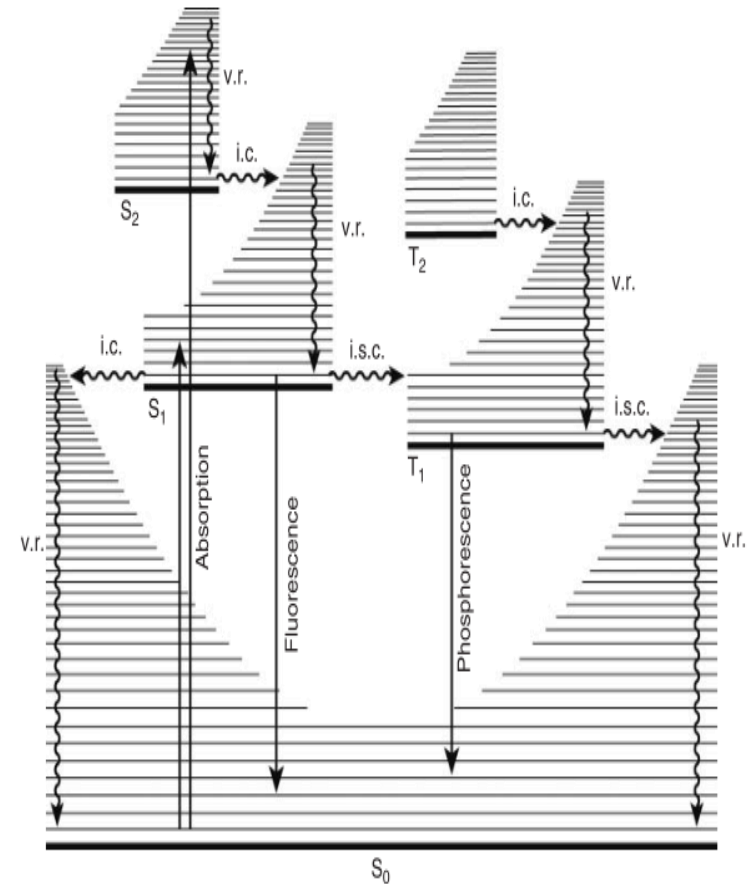
Changes in energy

- ◆ The energy difference between the ground and the lowest excited state **is usually much higher** than the energy difference between two successive excited states.
- ◆ Because of the Franck–Condon principle and excited state distortion **light absorption usually generates the excited state in a high vibrational level.**
- ◆ For the same reason, **light emission generates the ground state in a high vibrational level.**



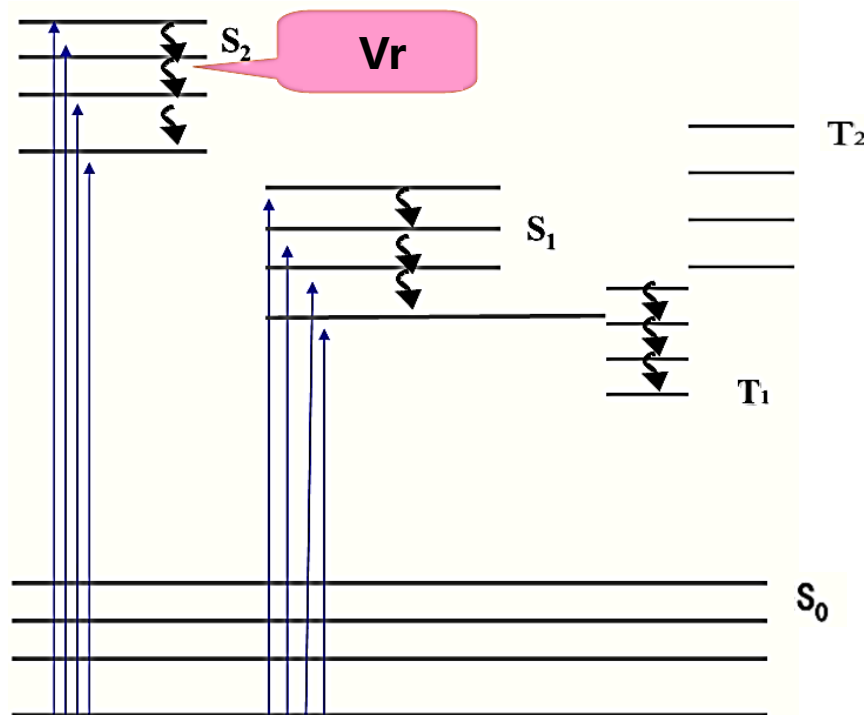
The process take place in time

- ◆ As pointed out when discussing the Franck–Condon principle, **light absorption takes place in a very short time scale compared with the time scale of nuclear movements.**
- ◆ **The deactivation processes compete with each other** and the relative magnitudes of the rate constants determine the contribution made by a particular pathway



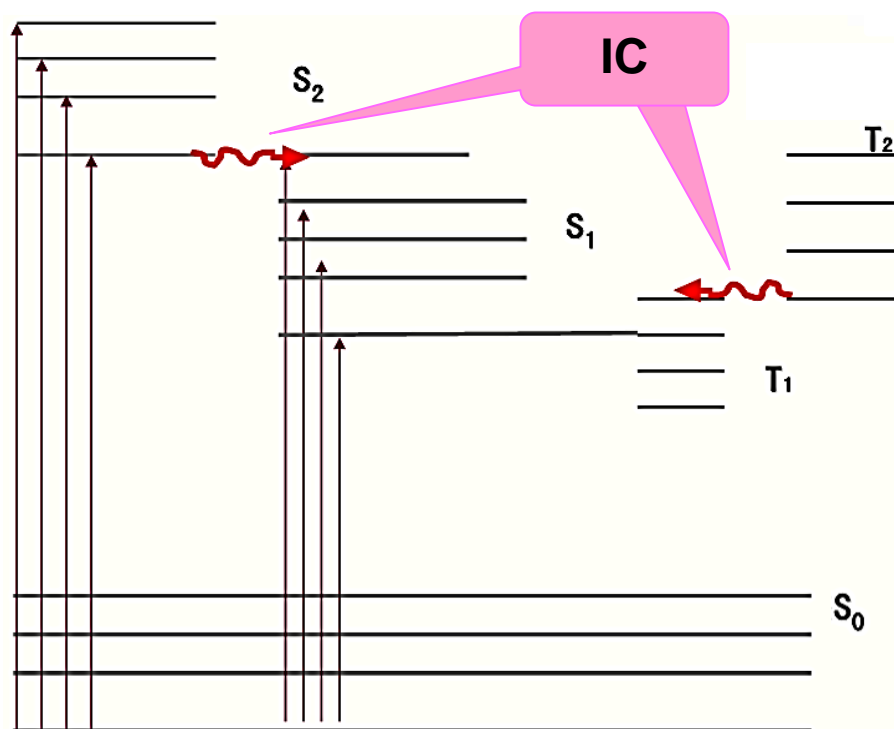
- **Radiationless transitions occur between isoenergetic vibrational levels of different electronic states.**
- **As there is no change in the total energy of the system, no photon is emitted and the process is represented by a horizontal wavy line in the Jablonski diagram, although they are usually indicated by downward wavy arrows.**
- **Radiationless transitions are essentially irreversible processes** because they are associated with an entropy increase (higher density of vibrational levels in the lower energy excited state) and because the vibrational relaxation within the lower excited state is very fast.

Vibrational relaxation (振动弛豫)

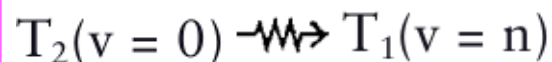
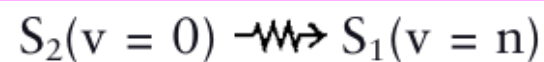


An electronically-excited species is usually associated with an excess of vibrational energy in addition to its electronic energy, unless it is formed by a transition between the zero-point vibrational levels ($v = 0$) of the ground state and the excited state ($0 \sim 0$ transition). **Vibrational relaxation involves transitions between a vibrationally-excited state ($v > 0$) and the $v = 0$ state within a given electronic state when excited molecules collide with other species such as solvent molecules, for example $S_2 (v=3) \sim S_2 (v=0)$.**

- Vibrational relaxation (non-radiative process): the energy deposited by the photon into the electron is given away to other vibrational modes as *kinetic energy*.
- **This kinetic energy may stay within the same molecule, or it may be transferred to other molecules around the excited molecule during collisions of the excited molecule with the surrounding molecules (solvent)**



Examples:



Typical timescales are of the order of 10^{-14} - 10^{-11} s (internal conversion between excited states) and 10^{-9} - 10^{-7} s (internal conversion between S_1 and S_0).

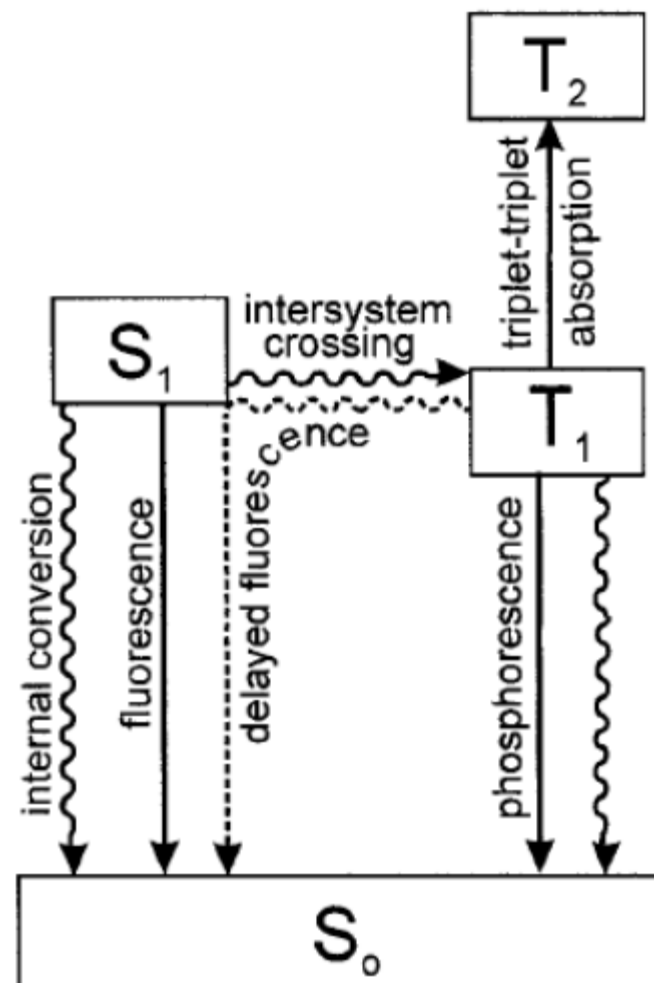
Internal conversion involves intramolecular radiationless transitions between vibronic states of the same total energy (isoenergetic states) and the same multiplicity.

Relaxation from an upper excited electronic state such as S_2 , S_3 , etc. **to a lower electronic excited state with the same energy and multiplicity** takes place rapidly by the radiationless process of internal conversion.

Because the difference in energy of these upper excited states is relatively small, there is a high probability of the $v=0$ level of, say, S_2 being very close in energy to a high vibrational level of S_1 , allowing rapid energy transfer between the two electronic levels to occur.

Because of the rapid rate of internal conversion between excited states, other radiative and nonradiative transitions do not generally occur from upper electronically-excited states as they are unable to compete with internal conversion.

- Intersystem crossing is a non-radiative transition between two isoenergetic vibrational levels belonging to electronic states of different multiplicities.
- For example, an excited molecule in the 0 vibrational level of the S_1 state can move to the isoenergetic vibrational level ($v > 0$) of the T_1 triplet state. Then vibrational relaxation brings it into the lowest vibrational ($v = 0$) level of T_1 .
- For some molecule (phosphorus) **intersystem crossing** may be fast enough (10^{-7} – 10^{-9} s) to **compete** with other pathways of de-excitation from S_1 (fluorescence and internal conversion $S_1 \rightarrow S_0$).



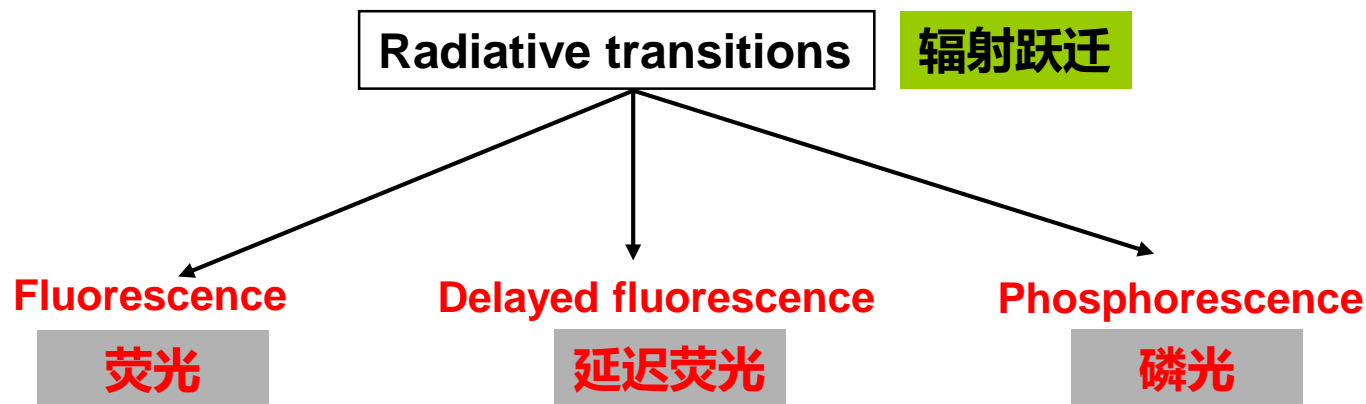
Crossing between states of different multiplicity is in principle forbidden, but for some molecules spin–orbit coupling can be large enough to make it possible!

The probability of intersystem crossing depends on the singlet and triplet states involved.

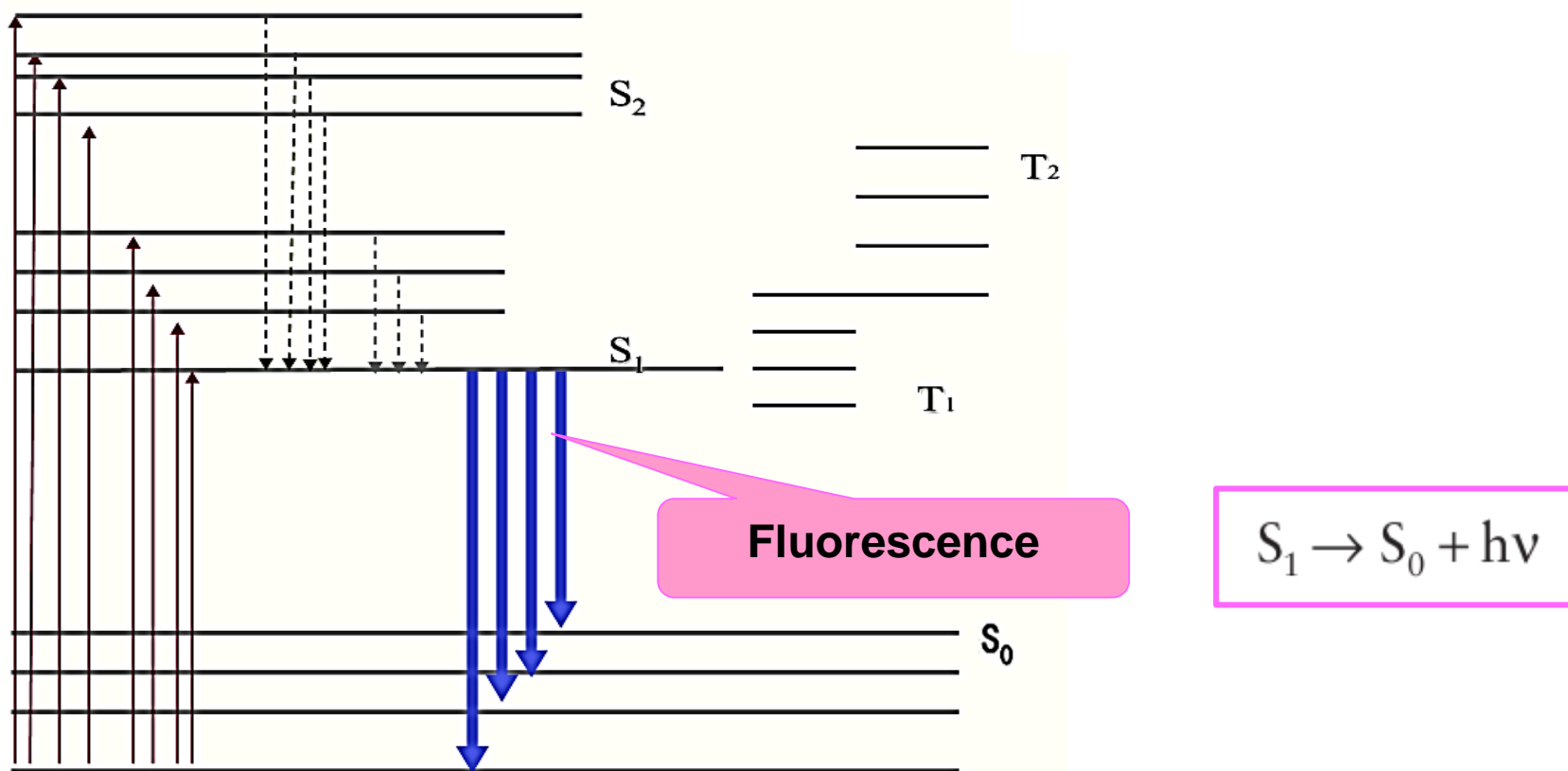
- ① If the electronic transition $S_0 \rightarrow S_1$ is $n \rightarrow \pi^*$ type, intersystem crossing is **often efficient**.
- ② The presence of **heavy atoms** increases spin–orbit coupling and thus favors intersystem crossing.

Conclusions:

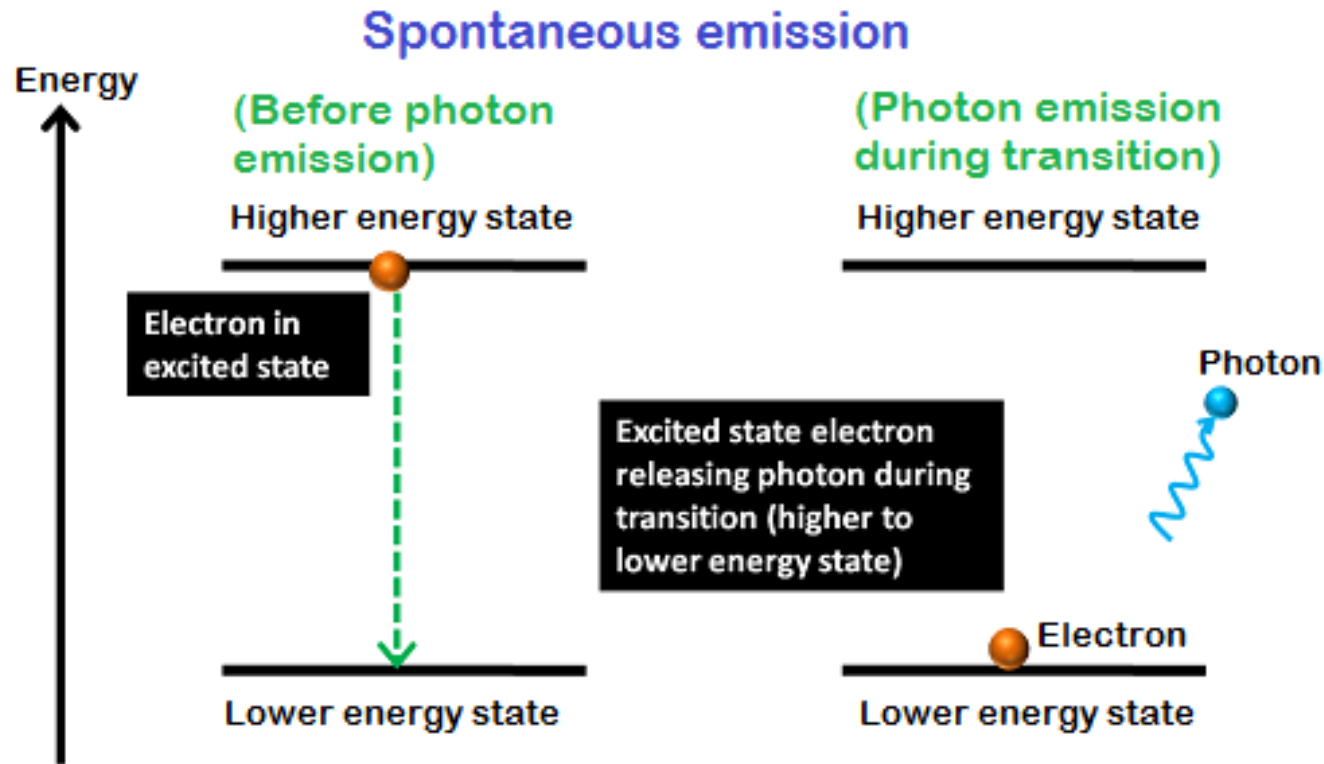
- ✓ Internal conversion within each excited state manifold of any given multiplicity (e.g., $S_n \rightsquigarrow S_1$ and $T_n \rightsquigarrow T_1$) is exceedingly fast (usually in the picosecond region);
- ✓ Intersystem crossing between the lowest excited states of any multiplicity (e.g., $S_1 \rightsquigarrow T_1$) may be fast to moderately fast (subnanosecond to nanosecond region);
- ✓ Radiationless deactivations from the lowest excited states of any multiplicity to the ground state are much slower (microseconds to nanoseconds for $S_1 \rightsquigarrow S_0$ and seconds to milliseconds for $T_1 \rightsquigarrow S_0$).



- ✓ According to the spin selection rule, radiative transitions could be classified as fluorescence, delayed fluorescence and phosphorescence.
- ✓ As the spin selection rule plays an important role, it is customary to call:
 - ✓ Fluorescence a spin-allowed emission (e.g., $S_1 \rightarrow S_0$).
 - ✓ Phosphorescence a spin-forbidden emission (e.g., $T_1 \rightarrow S_0$).



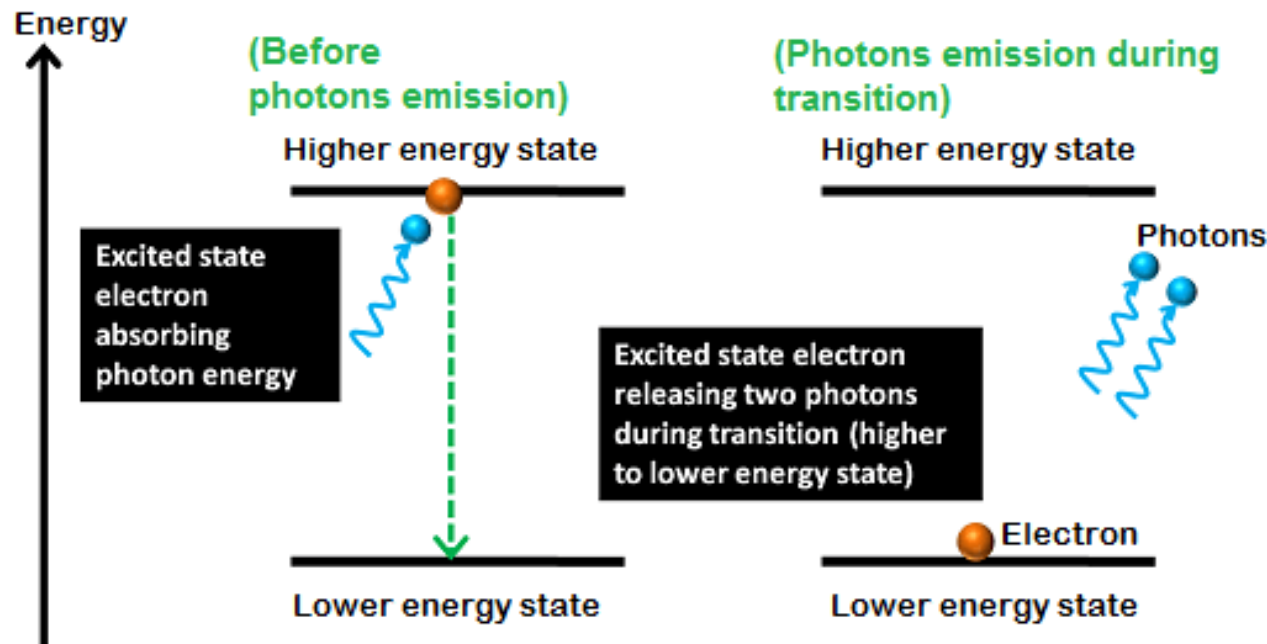
- Fluorescence involves a radiative transition (photon emission) between states of the same multiplicity (spin-allowed), usually from the lowest vibrational level of the lowest excited singlet state, S_1 ($v=0$).
- Typical timescales for fluorescence emission are of the order of 10^{-12} – 10^{-6} s.



- **The spontaneous transition from an excited state to a lower energy state or ground state is called spontaneous radiation.**
- The electrons in the excited state do not stay for a long period because the lifetime of electrons in the higher energy state or excited state is very small, of the order of 10^{-8} sec. Hence, after a short period, they fall back to the ground state by releasing energy in the form of photons or light.

Stimulated emission (受激辐射)

Stimulated emission



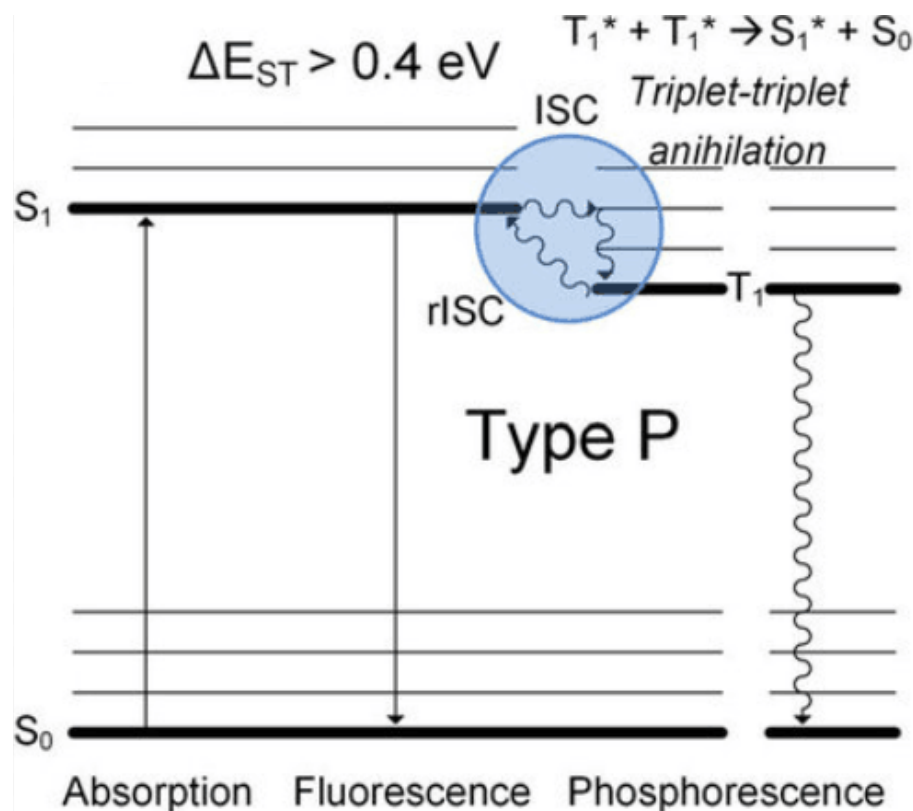
- The incident photon stimulates or forces the excited electron to emit a photon and fall into a lower state or ground state. In this process, the excited electron releases an additional photon of same energy (same frequency, same phase, and in the same direction) while falling into the lower energy state.
- Such a process can be observed only under very specific conditions and constitutes the basis for laser operation

Delayed fluorescence originates from the radiative transition of S_1 state regenerated from the first excited triplet (T_1). The lifetime of the singlet is generally 10^{-8} seconds, and the longest is 10^{-6} seconds, but it is sometimes observed that the singlet has a lifetime of 10^{-3} seconds. This long lifetime of fluorescence is called delayed fluorescence.

These emissions of delayed fluorescence can arise by several mechanisms that

- ✓ triplet–triplet annihilation (‘P-type’ delayed fluorescence).
- ✓ the thermally activated intramolecular processes (‘E-type’ delayed fluorescence).

Delayed fluorescence (TTA)

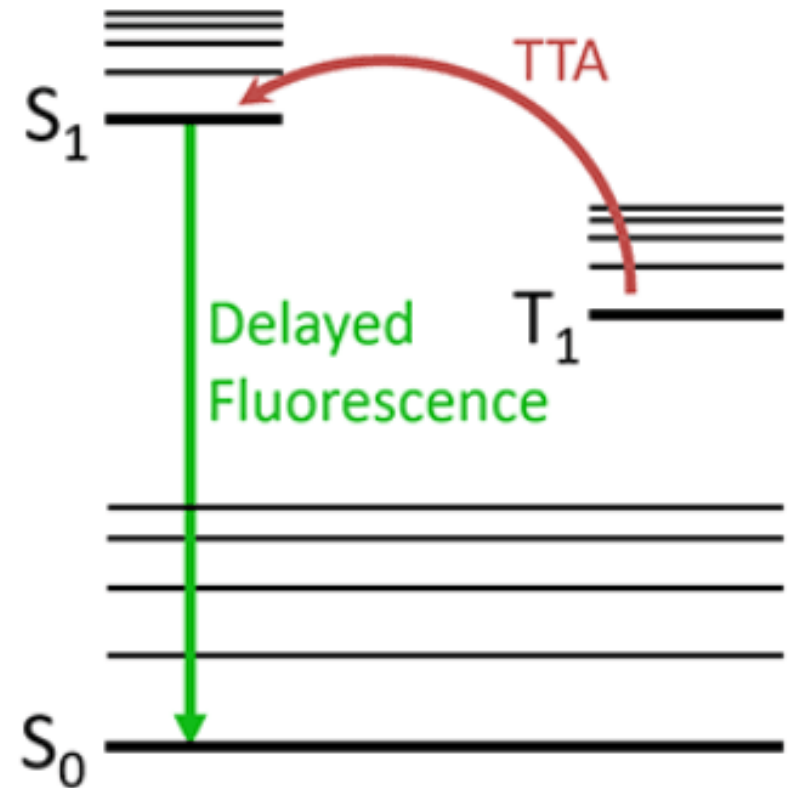


- The P-type delayed fluorescence is derived from the process of quenching two triplet states to generate a single state (TTA).

Triplet-triplet annihilation (TTA) (三重态-三重态湮没)

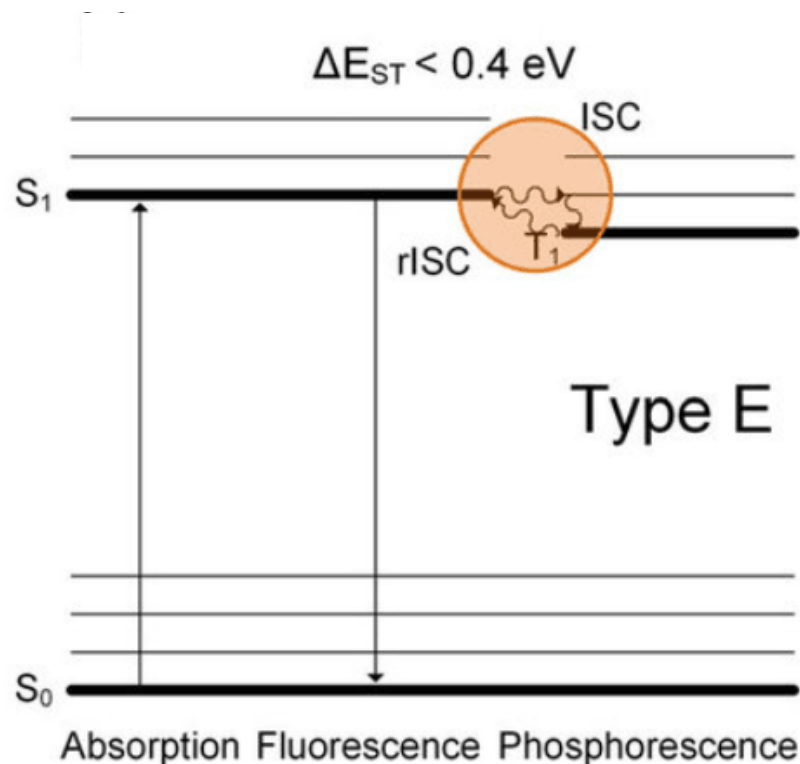
- ✓ TTA is an energy transfer mechanism between **two molecules** in their triplet state.
- ✓ It is related to the Dexter energy transfer mechanism.
- ✓ $T_1^* + T_1^* \rightarrow S_1^* + S_0$ It is a process known as photon upconversion.

Triplet-Triplet Annihilation (TTA) (P-type Delayed Fluorescence)



Thermally activated delayed fluorescence

(TADF)

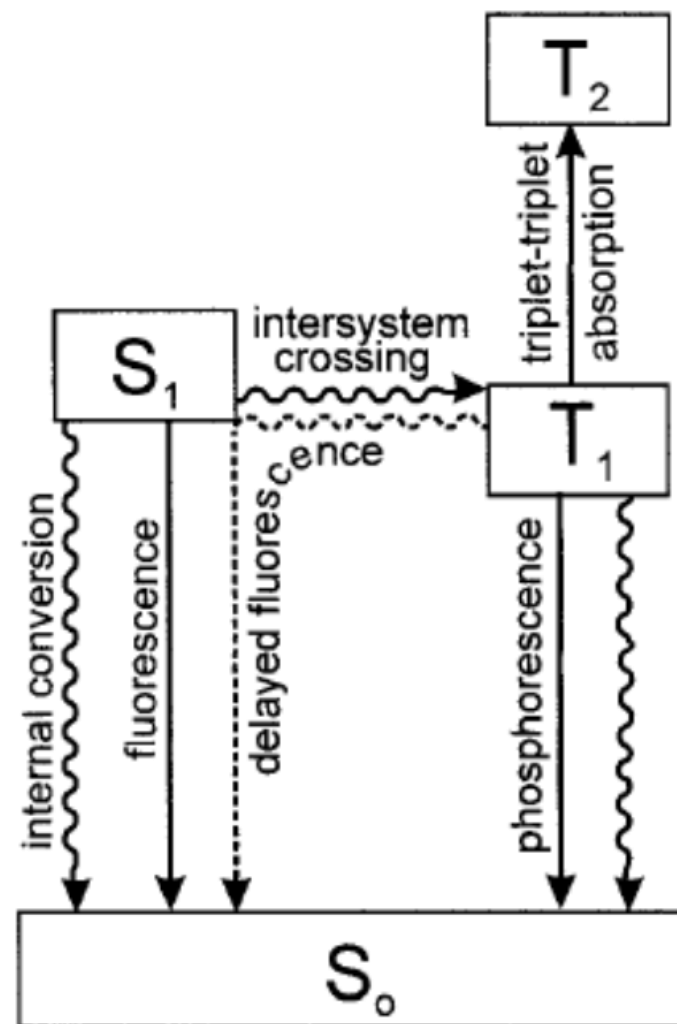


- The E-type delayed fluorescence refers to that when the energy of the triple excited state is close to that of the single excited state, the triple excited state can pass through the thermal activation reverse system to the single excited state, also known as thermal activation delayed fluorescence (TADF)

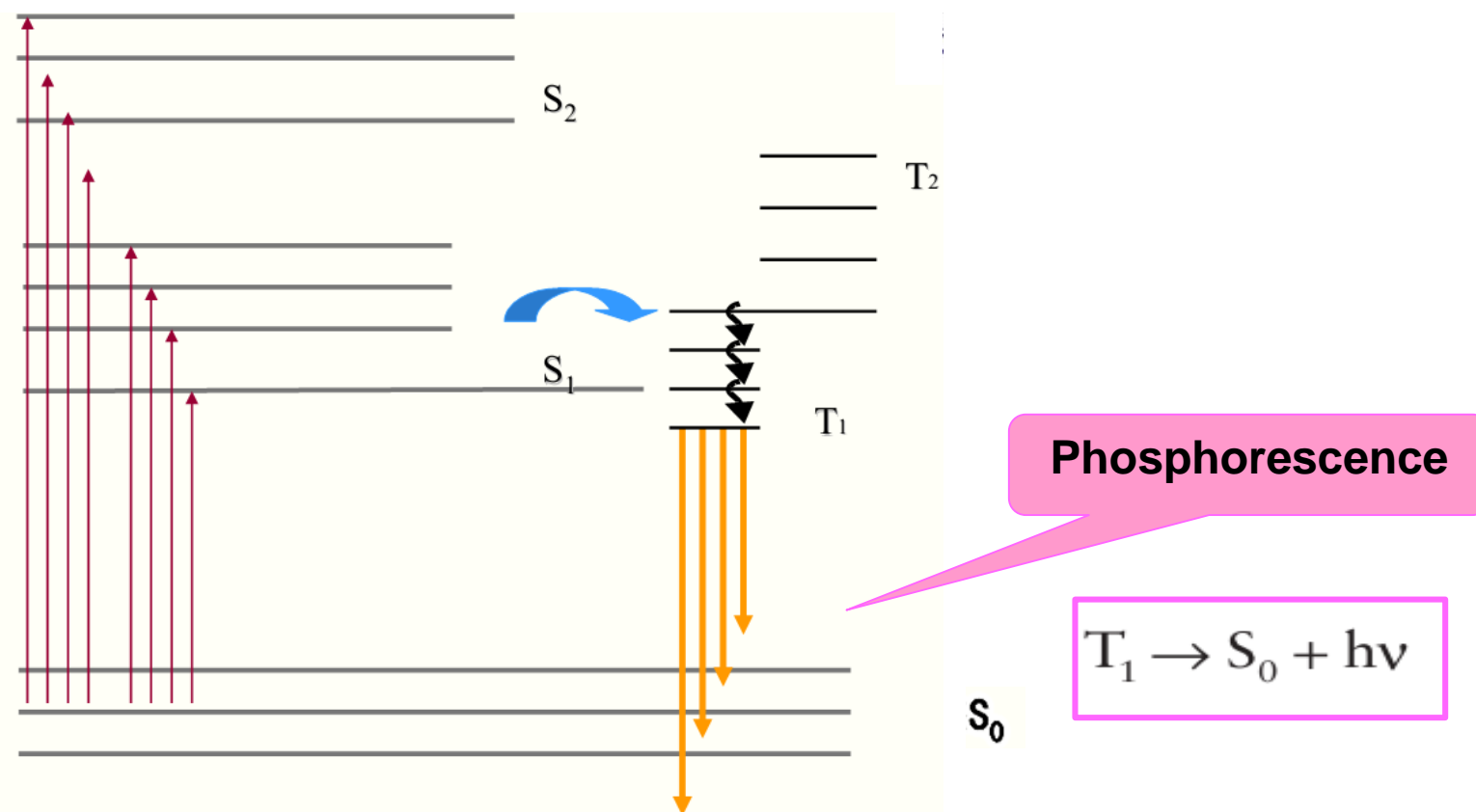


(TADF)

- ✓ **Reverse intersystem crossing** $T_1 \rightarrow S_1$ can occur when the energy difference between S_1 and T_1 is small and when the **lifetime of T_1 is long enough**.
- ✓ Results an emission with **the same spectral distribution** as **normal fluorescence** but with a **much longer decay time constant** because the molecules stay in the triplet state before emitting from S_1 .
- ✓ This delayed fluorescence emission is **thermally activated**; consequently, its efficiency increases with increasing temperature.



Phosphorescence (磷光)



- ◆ Phosphorescence is a spin-forbidden radiative transition between state of different multiplicity, usually from the lowest vibrational level of the lowest excited triplet state, T_1 ($v = 0$).
- ◆ Typical timescales for phosphorescence emission are of the order of 10^{-3} – 10^2 s.

- At **low temperatures** and/or in a rigid medium, phosphorescence can be observed.
- The **lifetime** of the triplet state may, under these conditions, be **long enough** to observe phosphorescence on a timescale up to seconds, even minutes or more
- The **phosphorescence spectrum** is located at wavelengths **higher** than the **fluorescence spectrum** because the energy of the lowest vibrational level of the triplet state T_1 is lower than that of the singlet state S_1 .

Conclusions:

- ✓ The radiation transition of molecular excited state is the process of inactivating from high-energy state to low-energy state by releasing photons, which is the inverse process of light absorption;
- ✓ There is a close relationship between radiation transition and light absorption. Absorption and radiation follow the same selection rules.
- ✓ Both the radiation transition and the absorption of photons follow the Franck-Condon principle

较高激发态

$A + h\nu \rightarrow **A$

$**A \xrightarrow{k_r} A + h\nu'$

$**A \xrightarrow{k_p} B$

$**A \xrightarrow{k_{nr}} A + \text{heat}$

$**A \xrightarrow{k_{isc}} *A$

$*A \xrightarrow{k_r'} A + h\nu''$

$*A \xrightarrow{k_p'} C$

$*A \xrightarrow{k_{nr}'} A + \text{heat}$

- ◆ The three unimolecular processes (**radiative deactivation**, k_r ; **nonradiative deactivation**, k_{nr} ; and **chemical reaction**, k_p) described earlier compete for deactivation of any excited state of a molecule.
- ◆ Therefore, their individual specific rates and the kinetics of their competition in each excited state are of utmost importance in determining the actual behavior of the excited molecule.

Summary of Jablonski Diagrams

Relaxation Process	Details
Vibrational relaxation	Involves transitions between a vibrationally-excited state and the $v = 0$ state within a given electronic state when excited molecules collide with other species such as solvent molecules, e.g. $S_2(v = 3) \xrightarrow{\text{W}} S_2(v = 0)$. The excess vibrational energy is dissipated as heat.
Internal conversion	Involves radiationless transitions between vibronic states of the same total energy (isoenergetic states) and the same multiplicity. Internal conversion between excited states, e.g. $S_2 \xrightarrow{\text{W}} S_1$ is much faster than internal conversion between S_1 and S_0 .
Intersystem crossing	Intramolecular spin-forbidden radiationless transitions between isoenergetic states of different multiplicity, e.g. $S_1 \xrightarrow{\text{W}} T_1$.
Fluorescence	Photon emission. Fluorescence involves a radiative transition between states of the same multiplicity (spin allowed), usually from the lowest vibrational level of the lowest excited singlet state, S_1 . $S_1(v = 0) \rightarrow S_0 + h\nu$
Phosphorescence	Photon emission. Phosphorescence involves a spin-forbidden radiative transition between states of different multiplicity, usually from the lowest vibrational level of the lowest excited triplet state, T_1 . $T_1(v = 0) \rightarrow S_0 + h\nu$



Characteristic times:

absorption: 10^{-15}s

vibrational relaxation: $10^{-12}\text{-}10^{-10}\text{s}$

internal conversion: $10^{-11}\text{-}10^{-9}\text{s}$

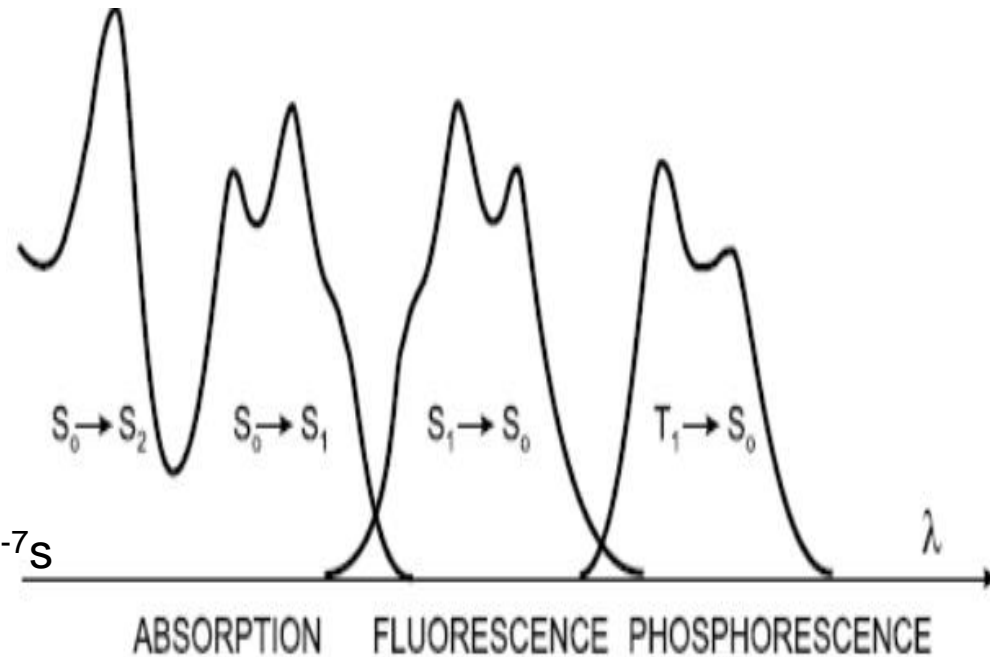
intersystem crossing: $10^{-10}\text{-}10^{-8}\text{s}$

lifetime of the excited states: $10^{-10}\text{-}10^{-7}\text{s}$

(fluorescence)

lifetime of the excited states: 10^{-6}s

(phosphorescence)



Thanks

