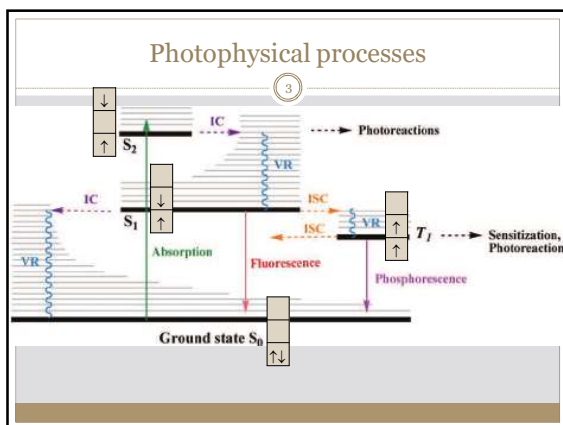


Characterization of photophysical processes

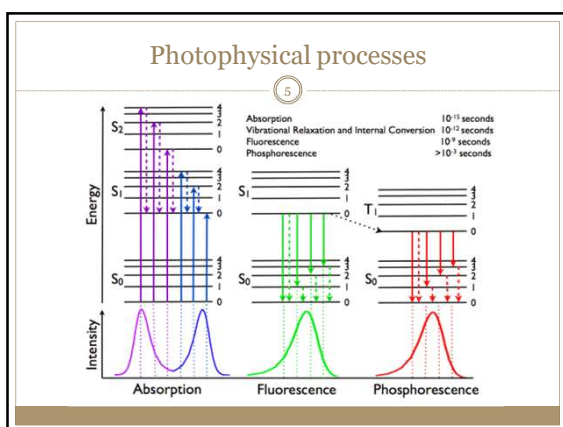
Photophysical processes

- **Photophysical processes:**
 - during which, after light absorption, the reactive molecule is formed, and/or
 - disappears without chemical change.
- **What to measure:**
 - absorption spectrum of the ground state molecule,
 - absorption and emission spectrum of the excited molecule,
 - lifetime of the excited molecule ($= 1/k_1$),
 - quenching, sensitization and photochemical experiments.



Photophysical processes

- **Photon absorption**
- **Non-radiative photophysical processes:**
 - Internal Conversion (IC)
 - InterSystem Crossing (ISC)
 - Vibrational relaxation (VR)
- **Photon emission, luminescence:**
 - **Fluorescence:** the initial and final states are of the same spin multiplicity
 - **Phosphorescence:** the initial and final states are of different spin multiplicity



Possible photophysical and photochemical processes of excited molecules (overview)

Unimolecular

- Photophysics:**
 - Deactivation: $AB + kT$
 - Luminescence: $AB + h\nu$
- Photochemistry:**
 - Izomerisation: BA
 - Dissociation: $B + A$
 - Ionisation: $AB^+ + e^-$

Bimolecular

- Photophysics:**
 - Energy transfer: $AB + Q^*$
 - Physical quenching: $AB + M$
- Photochemistry:**
 - Addition: ABC
 - Electron transfer: $AB^+ + Q^-$

I. Non-radiative photophysical processes

7

- An excited molecule can get rid of its excess energy without radiation (= light emission):
 - Vibrational relaxation:** Generally, the excited electron state molecule does not have an equilibrium geometry, so the vibration quantum number $v \neq 0$. In equilibrium, $v = 0$.
 - The process is very fast in condensed phase ($10^{-13} - 10^{-11}$ s) because of the interaction between the excited particle and the surrounding molecules.
 - The $v = 0$ particle is in thermal equilibrium with its surroundings.
 - In the liquid phase, the new solvate shell develops during vibrational relaxation.
 - „Thexi“ molecule:** an excited electron state molecule in thermal equilibrium with its surroundings. It has a well-defined energy, entropy, free energy, structure and chemical properties.

I. Non-radiative photophysical processes

8

- Two possible unimolecular photophysical transformations of the thexi molecule:
 - Internal Conversion (IC):** ${}^n A_j \xrightarrow{k_{IC}} {}^n A_i$ (the spin state does not change)
 - The process is spin-allowed, so it is very fast ($k_{IC} > 10^9 \text{ s}^{-1}$)
 - The electron excitation energy is converted into vibrational energy
 - A high vibration quantum level of a lower energy electron state is formed.

I. Non-radiative photophysical processes

9

- Two possible unimolecular photophysical transformations of the thexi molecule:
 - InterSystem Crossing (ISC):** ${}^n A_j \xrightarrow{k_{ISC}} {}^m A_i$, where $n = m \pm 2$
 - The transition is spin-forbidden
 - Much slower process (it is mainly characteristic of molecules composed of atoms with small atomic numbers)
 - The rate is mainly determined by the spin coupling
 - For molecules containing heavy atoms and aromatic compounds can be relatively fast and highly effective ($\phi_{ISC} \approx 1$)
 - If the energies of ${}^m A_i$ and ${}^n A_j$ in $v = 0$ are similar, then the reverse process happens and the two states will be in equilibrium.

II. Radiative photophysical processes

10

- Kasha studied the luminescence of organic molecules in detail. The 1S_1 state fluoresces, the 3T_1 phosphoresces.
- New (higher-resolution) spectroscopic studies revealed further radiations** (for coordination compounds, azulene).
 - Kasha's rule:** photon emission (fluorescence or phosphorescence) occurs in appreciable yield only from the lowest excited state of a given multiplicity.
 - Demas-Crosby rule:** In the absence of chemical reactions from higher-energy excited states, the emission of an unoccupied d-orbital complex occurs from the lowest energy excited or from an equivalent Boltzmann state.
- In liquid phase, the formation of the thexi state is much faster than the emission, so luminescence usually occurs from the vibration level of $v = 0$ (Vavilov rule).**

II. Radiative photophysical processes

Fluorescence

11

- Gaseous atoms or simple molecules:**
 - At low pressure (where the collision probability is low), E_{em} is the same as the E_{ex} (resonance fluorescence).
 - Best known:

*Na(${}^2P_{1/2}$)	$\xrightarrow{489.6 \text{ nm}}$	Na(2S)	}	doublet resonance
*Na(${}^2P_{3/2}$)	$\xrightarrow{489.0 \text{ nm}}$	Na(2S)		
 - *Hg(1P_1) $\xrightarrow{253.7 \text{ nm}}$ Hg(1S_0) Mercury vapor lamp
- Multi-atomic molecules, complexes:**
 - The E_{em} is less than the E_{ex} .
 - The two spectra are generally mirror symmetrical.
 - *Cr(III)-complexes: ${}^4T_2 \rightarrow {}^4A_2$
 - If the ligand field is strong, the **Franc-Condon overlap** is small, so the **Stokes shift** is large.

II. Radiative photophysical processes

Fluorescence

Compound	Absorption band max. (cm ⁻¹)	Emission max. (cm ⁻¹)	Stokes shift (cm ⁻¹)
[Cr(H ₂ O) ₆] ³⁺			4170
[CrF ₆ (H ₂ O) ₃]			3920
Ruby			3600
Beryl			3300
CrBr ₃			2800
CrCl ₃	13900	11300	2600
(NH ₄) ₂ [CrF ₆]			2240

↑ Increasing ligand field strength

- Multi-atomic molecules, complexes:**
 - The E_{em} is less than the E_{ex} .
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II. Radiative photophysical processes

Fluorescence and phosphorescence

13

- Many Cr(III) complexes are known to show both.
- The efficiency of the two types of emissions depends on the energy difference between the excited states 4T_2 and 2E .
- [Cr(urea)₆]³⁺: its luminescence spectrum shows temperature dependence:
 - At room temperature, both can be detected, and the lifetimes of the two types of luminescences are the same.
 - At lower temperatures, fluorescence disappears.
 - The fluorescent quartet excited state from lower energy doublet excited state can be reached by thermal activation.
 - The name of this mechanism is *E-type delayed fluorescence*.

II. Radiative photophysical processes

Phosphorescence

14

- Phosphorescence of inorganic compounds can be grouped according to the characteristics of the emission spectra and the characteristics of the luminescent states:
 - Narrow band
 - Broad band
 - Fine structure
 - Ligand phosphorescence
- Kasha's rule** and the **Demas-Crosby rule** is valid, so
 - the phosphorescent state is often of the same atomic configuration as the ground state,
 - the electron configuration of the two particles differs only in the number of unpaired electrons.

II. Radiative photophysical processes

Phosphorescence

15

- Narrow-band phosphorescence
 - The atomic configurations (*i.e.* the equilibrium atomic distances) of the excited state and the ground state are very similar.
- Broad-band phosphorescence
 - It usually involves a large Stokes shift.
 - Excludes fine-structure phosphorescence
- Fine-structure phosphorescence
 - Excludes broad-band phosphorescence
- Ligand phosphorescence
 - It can be assigned to the ligand, not to the central metal ion.
 - It would work without metal ion, the presence of the metal only modifies it.

III. Intramolecular energy transfer

16

- Energy transfer within a molecule is observed if it contains at least 2 separate **chromophore (C)** groups or metals separated by multiple atoms.
- Following excitation of one of the chromophore groups in the molecule, the energy migrates to the other **lumiphore (L)** group.
- Conditions for energy transfer:
 - The energy of the L group should be less than or equal to the energy of the C group (*i.e.* the energy transfer is exothermic or weakly endothermic).
 - The spin multiplicities of the excited states of the two groups are correlated. The essence of **electron spin correlation** is the net spin quantum numbers of the before- and after-E-transfer molecule. These are determined by the spin quantum numbers of the C and L groups. Possible values are:
 - $|{}^*S_C + S_L|$, $|{}^*S_C + S_L - 1|$, ... $|{}^*S_C - S_L|$, and
 - $|S_C + {}^*S_L|$, $|S_C + {}^*S_L - 1|$, ... $|S_C - {}^*S_L|$.
 - The transfer of energy is only likely if the two sequences of spin quantum numbers have at least one common element.

III. Intramolecular energy transfer

17

- [NC-Ru(bpy)₂-NC-Cr(CN)₅]²⁻ complex in DMF solvent:
 - Luminescence characteristic of 2E state of ${}^3Cr(III)$ can be measured between 750 and 900 nm.
 - The smallest energy band of the excitation spectrum is almost identical to the spectrum of the [Ru(bpy)₂(CN)₂] complex.

IV. Bimolecular photophysical processes

18

- The excited molecule is returned to its ground state, while another molecule interacting with it becomes excited:
 - at least one of its electrons jumps to a higher energy molecular orbital,
 - or the molecule becomes vibrationally excited.
- The energy transfer
 - mainly happens as a result of collision, but
 - can also be performed so that the distance between the donor and the acceptor molecule is approx. 10-times the collision distance.

- Collision energy transfer
- Long distance or resonance energy transfer
- Formation of excimers and exciplexes

IV. Bimolecular photophysical processes
 A. Collision energy transfer

19

- Only effective if
 - the collision of the reactants occurs with a high frequency and
 - the product is formed in an adiabatic process, *i.e.* the energy surfaces of the reactants and the products intersect and are interconnected through the transition state.
 - The molecules involved in the process must also meet the **energy condition** in addition to the **electron spin correlation** (*i.e.* the process leads to a smaller or to a slightly higher energy state).
- In the case of atoms and small molecules, both the **electron spins**, the **orbital momentums** and the **parities** must correlate.
- For polyatomic molecules with low symmetry, only the **electron spin correlation counts**.

 IV. Bimolecular photophysical processes
 A. Collision energy transfer

20

- The **electron spin correlation** for collisions:
 - The spin quantum number of # formed from the reactants:
 - ✦ $|S_A + S_B|, |S_A + S_B - 1|, \dots, |S_A - S_B|$.
 - The spin quantum number of # formed from the products (C,D):
 - ✦ $|S_C + S_D|, |S_C + S_D - 1|, \dots, |S_C - S_D|$.
 - The two series must have at least one common element! *For example, a singlet and a triplet reactant as well as two singlet products do not have a common spin-multiplicity activated complex, so the reaction does not take place.*

Spin states for reactants (A and B)	Spin state for the # (C,D)
singlet + singlet ($S_A = S_B = 0$)	singlet ($S_T = 0$)
singlet + doublet ($S_A = 0, S_B = 1/2$)	doublet ($S_T = 1/2$)
singlet + triplet ($S_A = 0, S_B = 1$)	triplet ($S_T = 1$)
doublet + doublet ($S_A = S_B = 1/2$)	singlet, triplet ($S_T = 0, 1$)
doublet + triplet ($S_A = 1/2, S_B = 1$)	doublet, kvartet ($S_T = 1/2, 3/2$)
triplet + triplet ($S_A = S_B = 1$)	singlet, triplet, kvintet ($S_T = 0, 1, 2$)

 IV. Bimolecular photophysical processes
 A. Collision energy transfer

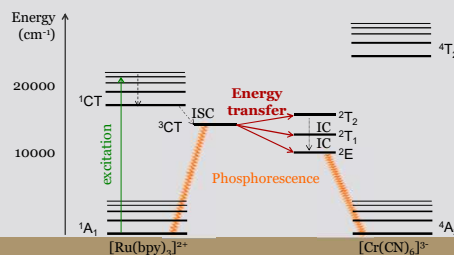
21

- Adiabatic reactions tend to be highly effective, and are
 - fast if $\Delta E = E_{\nu_A} - E_{\nu_D}$ is negative (exothermic process: the rate of the reaction is determined by diffusion),
 - slow if ΔE is positive (endothermic process: the rate of the reaction is determined by the ΔE activation energy).
- Non-adiabatic processes are much slower or have very low efficiency.
- **Efficient energy transfer** occurs only when the kinetic energy released during the collision is small, *i.e.* the energy levels of the corresponding states of the donor and acceptor molecules are almost the same, and
- the $\nu = 0$ vibration levels quickly develop within the excited electron state.

 IV. Bimolecular photophysical processes
 A. Collision energy transfer

22

- **Quenching** (for Ru(III))
- **Sensitization** (for Cr(III))


 IV. Bimolecular photophysical processes
 B. Resonance energy transfer

23

- It is relatively rare in inorganic photochemical systems.
- There is a need for overlap between the luminescence spectrum of the donor molecule (D) and the absorption spectrum of the acceptor molecule (A).
- If there is a large overlap and ϵ_A is also large enough, energy can be transmitted at a distance of more than 4 nm (40 Å).
- In the 1940s, Förster studied the process in detail. His model is still considered valid today.

 IV. Bimolecular photophysical processes
 C. Formation of excimers and exciplexes

24

- In principle, the interaction of an excited and a ground-state molecule can result in two molecular products:
 - if the two components are the same in the ground state, then an **excimer** (excited dimer) is formed,
 - if the two components are different in the ground state, then an **exciplex** (excited complex) forms.
- Both can go through the same deactivation processes as conventional excited states:
 - Radiative or non-radiative
 - IC, ISC or chemical reaction.

IV. Bimolecular photophysical processes
C. Formation of excimers and exciplexes

25

- Excimers and exciplexes can only be created under certain conditions:
 - the lifetime of the excited component is relatively long,
 - complex formation is thermodynamically favored (exothermic, because entropy usually decreases when the transition complex (T) is formed).
- More common in organic photochemistry.
- Designation of exciplexes formed with excited transition metal complexes: **TMCE** (Transition Metal Complex Exciplex)
 - inner sphere exciplexes,
 - outer sphere exciplexes.

Kinetics of photophysical processes

26

Photophysics **Photochemistry**

Unimolecular

- AB + kT Deactivation
- AB + hv Luminescence

Bimolecular

- AB + Q* Energy transfer
- AB + M Physical quenching

Photochemistry reactions:

- Isomerisation BA
- Dissociation B + A
- Ionisation AB* + e⁻
- Addition ABC
- Electron transfer AB* + Q⁻

Kinetics of photophysical processes

27

Diagram illustrating the energy levels and transitions in a photophysical process. The ground state is S₀. Absorption leads to the S₂ state, which undergoes internal conversion (IC) to S₁. From S₁, fluorescence (k_F) returns to S₀, or intersystem crossing (ISC) leads to the T₁ state. From T₁, phosphorescence (k_P) returns to S₀, or ISC leads back to S₁. Other transitions include vibrational relaxation (VR) and photoreactions from S₂ and T₁.

Kinetics of photophysical processes

28

- Consecutive first-order processes:
 - $\frac{d[S_2]}{dt} = -k_{IC1} \cdot [S_2]$
 - $[S_2] = [S_2]_0 \cdot e^{-k_{IC1}t}$
 - $\frac{d[S_1]}{dt} = k_{IC1} \cdot [S_2] - (k_{ISC} + k_F + k_{IC2})[S_1]$
 - $[S_1] = \frac{[S_2]_0 k_{IC1}}{k_{IC1} - k_{IC2} - k_{ISC} - k_F} \cdot (e^{-(k_{IC2} + k_{ISC} + k_F)t} - e^{-k_{IC1}t}) \approx [S_2]_0 \cdot e^{-(k_{IC2} + k_{ISC} + k_F)t}$
 - $\frac{d[T_1]}{dt} = k_{ISC}[S_1] - k_P[T_1]$
 - $[T_1] = a_1 e^{-(k_{IC2} + k_{ISC} + k_F)t} + a_2 e^{-k_{IC1}t} - a_3 e^{-k_P t}$

Diagram illustrating the energy levels and transitions in a photophysical process, similar to slide 27.

Kinetics of fluorescence

29

- Rate of fluorescence (intensity): $\frac{dF}{dt} = k_F \cdot [S_1]$
- Number of emitted F photons: $F(\infty) = k_F \int_0^\infty [S_1] dt = \frac{k_F k_{IC1} [S_2]_0}{k_{IC1} - k_{IC2} - k_{ISC} - k_F} \int_0^\infty (e^{-(k_{IC2} + k_{ISC} + k_F)t} - e^{-k_{IC1}t}) dt = \frac{k_F [S_2]_0}{k_{IC2} + k_{ISC} + k_F}$
- Quantum yield of fluorescence: $\Phi_F = \frac{F(\infty)}{[S_2]_0} = \frac{k_F}{k_{IC2} + k_{ISC} + k_F}$

Diagram illustrating the energy levels and transitions in a photophysical process, similar to slide 27.

Kinetics of phosphorescence

30

- Rate of phosphorescence (intensity): $\frac{dP}{dt} = k_P \cdot [T_1]$
- Number of emitted P photons: $P(\infty) = k_P \int_0^\infty [T_1] dt = \dots = \frac{k_{ISC} [S_2]_0}{k_{IC2} + k_{ISC} + k_F}$
- Quantum yield of phosphorescence: $\Phi_P = \frac{P(\infty)}{[S_2]_0} = \frac{k_{ISC}}{k_{IC2} + k_{ISC} + k_F}$

Diagram illustrating the energy levels and transitions in a photophysical process, similar to slide 27.

Static quenching

31

- The quenching agent (Q) forms an adduct (DQ) with the luminescent molecule (D). DQ is not luminescent.
- The quenching agent reduces the concentration of the luminescent D molecule.
- **Steps of the mechanism:**
 - $D + Q \rightleftharpoons DQ$ (fast pre-equilibrium)
 - $D + h\nu_a \rightarrow D^*$
 - $D^* \rightarrow D + h\nu_e$
- Quantum yields do not change, but the number of absorbed photons (due to the decrease in concentration) does.

Dynamic quenching

32

- The quenching agent (Q) reacts with the excited state (D^*) of the luminescent molecule in a non-radiative process.
- The quenching agent is a new way for D^* to lose energy.
- **Steps of the mechanism :**
 - $D + h\nu_a \rightarrow D^*$
 - $D^* \rightarrow D + h\nu_e$
 - $D^* + Q \rightarrow D + \dots$ (non-excited states)
- Quantum yield(s) decreases with increasing concentration of the quenching agent.