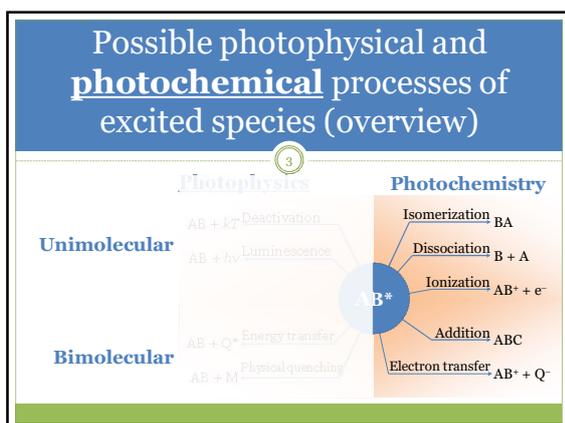


### Photochemical reactions of excited species

2

- **Excited species** formed after absorbing a photon:
  - have electron configuration and energies different from the ground states,
  - the spatial coordinates of their nuclei are unchanged (Franck–Condon transitions).
- The **excited state with the lowest energy**:
  - may have a spin multiplicity that is identical to or different from that of the ground state,
  - has a different configuration of nuclei than the ground state.
- Both the Franck–Condon state and the „thexi” molecule are much more reactive than the ground state.



### I. Photoisomerization

4

- The simplest unimolecular photochemical reactions
- The composition and oxidation state of the reactant does not change, the structure does.
- Characteristic of transition metal complexes
- The interconversion of isomers is much faster through the excited state, so photoisomerization is an important tool both in structural studies and kinetics.
- Classification based on the site of structural change:
  - Only on the central atom – **spin isomerization**,
  - Only on the ligand(s) – **photoisomerization and tautomerization reaction of coordinated ligands**,
  - On the bond between the central atom and the ligand – **photo-induced geometrical, optical and bond isomerization**.

### I. Photoisomerization

#### I/1. Photoinduced spin isomerization

5

- Fe(II) complexes often change the number of unpaired electrons in response to a change in  $T$  or  $p$ .
- The low spin  $\rightleftharpoons$  high spin transition may be induced by light, and the high spin isomer may be trapped at low  $T$ : „light-induced excited spin-state trapping”
- Equilibrium process:  $^1[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2 \rightleftharpoons ^5[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ 
  - Order of energy:  $^1A_{1g} < ^5T_{2g} < ^3T_{1g} < ^3T_{2g} < ^5E_g < ^1T_{1g} < ^1T_{2g}$
  - Singlet excited state. Short lifetime.
  - Returning to the ground state by internal conversion (IC).
  - Intersystem crossing (ISC) to a triplet excited state, then another ISC to low spin, ground state singlet or high spin quintet.
  - $V_m(^5T_{2g}) > V_m(^1A_{1g})$ , measurable both in liquid and crystal.

### I. Photoisomerization

#### I/2. Photoisomerization reactions of coordinated ligands

6

- Photoexcitation of complexes yields an excited state in which the electron distribution on the ligands is different.
- Two types of excitations:
  - Charge transfer (CT)
  - Intraligand (IL)
- The  $[\text{MX}(\text{trans-stpy})_2] \rightarrow [\text{MX}(\text{trans-stpy})(\text{cis-stpy})]$  **photoisomerization** occurs with a number of different central atoms ( $M = \text{Ru(II)}, \text{W(o)}, \text{Re(I)}$ ).
  - The ratio of isomers in a photostationary state depends sensitively on the wavelength of the exciting light.
- **Phototautomerization: ditionatho complexes**
  - The cis-trans isomerization of the azomethine group involves proton relocation and localization of a  $\pi$  bond in the ligand.

### I. Photoisomerization

#### I/3. Photochemical rearrangement of geometrical isomers

7

- The symmetry of the complex changes of photon absorption, but the composition, the identity and the number ( $n$ ) of ligands in the coordination sphere does not.
  - cis-trans* isomerization:  $MA_2B_2$  (square planar) és  $MA_4B_2$  ( $O_h$ )
  - mer-fac* isomerization:  $MA_3B_3$
- $cis-[PtCl_2(PEt_3)_2] \rightleftharpoons trans-[PtCl_2(PEt_3)_2]$ 
  - In a photostationary state, the ratio of isomers depends on the polarity of the solvent (*cis* in polar, *trans* in non-polar).
  - The reaction proceeds through a triplet t<sub>1</sub>g state
  - Dissociative and „twisting” mechanisms
- $mer-[IrCl_3(PEt_3)_3] \rightarrow fac-[IrCl_3(PEt_3)_3]$ 
  - Dissociative mechanism

### I. Photoisomerization

#### I/4. Photoinduced optical isomerization

8

- Complexes of  $O_h$  symmetry containing bidentate ligands.
- The  $\phi$  of the photoisomerization of D and L enantiomers is the same.
- Photoresolution: a racemic mixtures is exposed to circularly polar light. In a photostationary state, the molar fraction of the isomer with the more intense absorption is higher.
- Only efficient for a high dissymmetry factor ( $g$ ):  $g = (\epsilon_{A,\lambda} - \epsilon_{A,\lambda'}) / \epsilon_{N,\lambda}$
- The mechanism of isomerization depends on the ligand:
  - „Twisting” mechanism:
  - Dissociative mechanism:

### I. Photoisomerization

#### I/5. Photoinduced bond isomerization

9

- In multidentate ligands, different donor atoms often have different donor strengths. In these cases, excitation by a photon may lead to a change in the coordination of the ligand.

Reakció	$\phi$	$\lambda_{exc}$ (nm)
$[Co(NH_3)_5(NO_2)]^{2+} \rightarrow [Co(NH_3)_5(ONO)]^{2+}$	0.13	254
	0.11	313
$[Co(NH_3)_5(SCN)]^{2+} \rightarrow [Co(NH_3)_5(NCS)]^{2+}$	0.15	333
	0.012	470
$[Co(NH_3)_5(O_2CH)]^{2+} \rightarrow [Co(NH_3)_5(CO_2H)]^{2+}$		254

- The structure of the chromophore (perhaps its symmetry and the structure of the ligand) changes.
- Significance of preparative chemistry: kinetically inert, but less stable isomers can be synthesized.

### II. Photodissociation

10

- Simplest case: homolytic bond cleavage in a diatomic molecule.
- If the excited state is more stable, the molecule luminesces, and bond breakage only occurs if it collides with another molecule with suitably high energy. The dissociation can only be proved by observing the atoms (optical or MS).
- UV-Vs Absorption spectra of diatomic molecules in the gas phase:
  - Continuous: the energy of the excited state of the molecule decreases monotonically with a decrease in internuclear distance ( $F_2$ , HI).
  - Rotational and vibrational fine structure: there is an energy minimum in the excited state. This is continuous beyond the convergence limit.

### II. Photodissociation

#### II/1. Optical dissociation

11

- Occurs if a molecule is excited by a photon whose energy is large than the **convergence limit**:  $E_{exc} > E_{conv}$
- The energy of the photon is much larger than the actual dissociation energy of the molecule:  $E_{exc} > E_{diss}$

$F_2$	400–200nm	$\rightarrow 2F$
$Cl_2$	440–250nm	$\rightarrow 2Cl$
$Br_2$	510.8–300nm	$\rightarrow 2Br$

- Weak absorption is observed even in the 818–645 nm region due to the spin-forbidden  ${}^1\Sigma_g^+ \rightarrow {}^3\Pi(I_u)$  transition. Bromine atoms are formed from the  $A {}^3\Pi(I_u)$  state.
- The next transition appears in the 640–511 region ( ${}^1\Sigma_g^+ \rightarrow {}^3\Pi(O_u^+)$ ). From this, ground state Br and metastable  ${}^2P_{1/2}$  are formed.
- Convergence limit: 510.8 nm. A continuous band up to 300 nm.

### II. Photodissociation

#### II/2. Preliminary dissociation

12

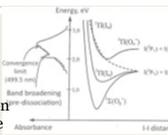
- Molecules composed of two heavy atoms or more than two atoms may undergo photodissociation in the gas phase even when  $E_{exc} < E_{konv}$ . (Interpretation: transition between two excited states of the molecule.)
- Band broadening and overlap can be observed in the part of the absorption spectra where rotational and vibrational fine structure is present.
  - Reason: the otherwise narrow bands broaden because the transition between the two states greatly decreases the life time of the given vibrational state that the uncertainty in wavelength due to the Heisenberg uncertainty principle increases:
 
$$\Delta\lambda = \lambda^2 / (2\pi c \tau_0)$$
  - If the life time of an excited state decreases from  $10^{-8}$  s to  $10^{-13}$  s, the original band width ( $5 \cdot 10^{-9}$  nm) increases to 0.5 nm.

## II. Photodissociation

### II/2. Preliminary dissociation

13

- photolysis of  $I_2$ :  $I_2 \longrightarrow 2I$ 
  - ✦ Ground state:  $^1\Sigma_g^+$
  - ✦  $E_{\text{diss}} = 1,542 \text{ eV}$
  - ✦ Absorption spectrum:  $^1\Sigma_g^+ \rightarrow ^3\Pi(I_u)$  transition in the 930-830 nm region with fine structure
  - ✦ 840-499 nm: system of bands with fine structure attributable to the  $^1\Sigma_g^+ \rightarrow ^3\Pi(O_u^+)$  transition on a structureless, wide absorption band. From this, a ground state and an excited state I forms ( $^2P_{3/2}$  and  $^2P_{1/2}$ ) if  $E_{\text{exc}} > E_{\text{conv}}$ . At lower energies, only ground state I forms with preliminary dissociation as a result of the spin-changing  $^3\Pi(O_u^+) \rightarrow ^3\Pi(I_u)$  transition, or phosphorescence occurs.
  - ✦ The **convergence limit** is 499.5 nm, the spectrum is continuous from this point. The dissociation yields ground state I atoms ( $^2P_{3/2}$ ).



## II. Photodissociation

### II/3. Induced preliminary dissociation

14

- The probability of the transition causing pre-dissociation is sometimes very low: only luminescence occurs in these cases.
- External factor may weaken the selection rules:
  - **Collision induced pre-dissociation:**
    - ✦ The fine structure of the absorption spectrum becomes murky.
    - ✦ Can be increased by increasing the pressure.
    - ✦ The photon absorption does not follow Beer's law, the apparent absorbance increases steeper.
    - ✦ The luminescence intensity of  $I_2$  decreases, the yield of I increases.
  - **External electric or magnetic field:**
    - ✦ A strong magnetic field quenches the luminescence of  $I_2$  entirely and increases the efficiency of dissociation.  $\Delta J = 0$  does not apply.

## II. Photodissociation

### II/4. Photodissociation with heterolytic bond breaking

15

- Three kinds of excited states from the photon absorption of a coordination compound:
  - **Intraligand (IL) excitation,**
  - **charge transfer (CT) excited state:** the residence probability of electrons changes around both M and L.
    - ✦ These are often the precursors of redox reactions.
  - **Ligand Field (LF) or d-d excited state:** complexes of M with incomplete d subshell
    - ✦ Ligand exchange reaction typically occur from this state.
      - Associative mechanism: the species formed in the primary photochemical process has a coordination number of  $n+1$
      - Dissociative mechanism = heterolytic photodissociation
- $[NiX_2(PMe_3)_3] \rightarrow trans-[NiX_2(PMe_3)_2] + PMe_3$

## III. Photosubstitution

16

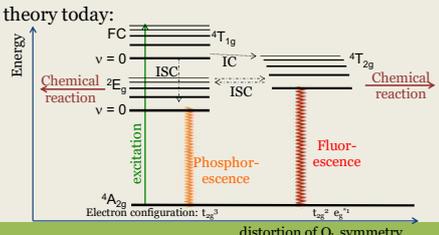
- \*De-activation of coordination compounds through reaction:
  - **Changing in the coordination environment (from LF states)**
  - **Redox reaction (from CT excited state)**
  - **Change only in the structure or composition of a ligand (from L-L states)**
  - **Reality is often more complicated because**
    - ✦ Different bands in the absorption spectra often overlap,
    - ✦ Excited states may interconvert by IC and ISC,
    - ✦ The final products of the overall reaction may be very different from the primary products formed from the excited state species.
- **LMCT excitation of  $[Co(NH_3)_n]^{3+}$  complexes:**  $\Phi_{\text{ligand exchange}} \approx \Phi_{\text{redox reaction}}$  (although  $[Co(NH_3)_n]^{2+}$  and L- form in primary processes)

## III. Photosubstitution

### III/1. Characterization of the reactive excited state

17

- A lot of data for Cr(III) complexes, interpreting them was very important for the development of the field.
- Main question: **doublet or quartet** photoactive state?
- The best theory today:



## III. Photosubstitution

### III/2. Mechanism

18

- The ground state has  $O_h$  symmetry, the excited state (quartet) is often different (e.g. tetragonal,  $D_{4h}$ ).
- Two limiting cases of the mechanism:
  - **Dissociative:** the first step is the heterolytic cleavage of the M-L bond in the excited species,  $n$  decreases:
    - ✦  $[ML_nX]^* \rightarrow [ML_n] + X$
  - **Associative:** the first step is the coordination of a solvent molecule (S) to the excited complex,  $n$  increases:
    - ✦  $[ML_n]^* + S \rightarrow [ML_nS]$
- The two mechanisms can be distinguished by measuring the volume of activation (pressure dependence of kinetics).
- The coordination properties of the solvent influence the type and rate of the reaction:
  - **In a weakly coordinating solvent, the dissociative path is likely.**

## III. Photosubstitution

## III/3. Rules

19

- **Adamson's rules:** observations on photochemical and thermal reactions of 6-coordinated Cr(III) complexes:
  1. It is the axis bearing the ligand with lowest ligand field that turns labile during excitation and the  $\phi$  of the substitution reaction will roughly be the same as the  $\phi$  of the complex of  $O_h$  symmetry with the same ligand field as the average ligand field of the complex studied.
  2. If there are two different ligands on the axis that turns labile, the one with stronger ligand field is activated. (A variation of the *trans* rule of coordination chemistry.)
- Complex with M of  $d^3$  and  $d^6$  configuration (which are usually inert, e.g. Co(III), Rh(III)) follow similar rules.

## III. Photosubstitution

## III/4. Ligand exchange reaction of Cr(III) complexes

20

- Inert Cr(III) complexes:

- Thermal reaction:  $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} + \text{X}^-$
- Photochemical rxn:  $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} + \text{X}^-$

X	$\phi_x$	$\phi_{\text{NH}_3}$
F	0.004	0.43
Cl	0.007	0.37
Br	0.01	0.36
NCS	0.025	0.47
CN	< 0.0005	0.33

- **Demonstration of Adamson's rules:** Cl<sup>-</sup> has a lower ligand field than NH<sub>3</sub>, so the NH<sub>3</sub>-Cr(III)-Cl axis turns labile in the excited state. As the ligand with the stronger field is activated favorably (2nd rule), the substitution of NH<sub>3</sub> is more likely, so the four remaining NH<sub>3</sub> will be in a single plane.

## III. Photosubstitution

III/5. Ligand exchange reactions of  $d^6$  complexes

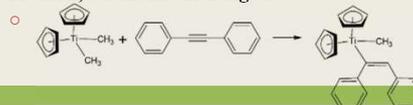
21

- Fe(II), Co(III), Ru(II), Rh(III) and Ir(III) complexes.
  - Ammin complexes of Co(III) are photoinert,  $\phi \approx 10^{-3}$ .  $\phi$  increases greatly as the wavelength of the photons decreases, so substitution is more likely to occur from a higher vibrational state of the excited species than the hexi state.
    - ✦  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} + \text{Cl}^-$
    - ✦ The thermal activation energy of the process is  $101 \pm 4$  kJ/mol, which is very close to the limiting excitation energy of the photochemical reaction ( $109 \pm 13$  kJ/mol).
  - Ammin complexes of Rh(III) and Ir(III) are more photoactive,  $\phi \approx 10^{-1}$ . Ligand substitution occurs from the hexi state.
  - The hexacyano complex of Fe(II) has a large  $\phi$ , but it depend on pH strongly, so the protonation of CN<sup>-</sup> must play a role.

## IV. Photoaddition and photoinserion

22

- **Photoaddition:** a new ligand bonds to M,  $n$  increases.
  - square planar M with  $d^8$  electron configuration
  - especially for hard, tetradentate ligands, e.g. OEP, Mb, Hb + Ni(II)
  - $[\text{Ni}(\text{OEP})] + 2 \text{ py} \rightarrow \text{trans-}[\text{Ni}(\text{OEP})(\text{py})_2]$
  - $\text{trans-}[\text{Cr}(\text{en})_2\text{F}_2]^+ + \text{H}_2\text{O}^+ \rightarrow [\text{Cr}(\text{en})(\text{enH})(\text{H}_2\text{O})\text{F}_2]$ 
    - ✦ The pK of the coordinated ligand increases in the excited state
- **Photoinserion:** insertion of one or more atoms between M and L,  $n$  remains unchanged.



## IV. Photoaddition and photoinserion

23

Complex	Excitation	Ligand	pK	pK*
$[\text{Ru}(\text{bpy})_2(\text{MChpy})]^+$	MLCT	4-carboxyl-4'-methyl-bpy	3.0	4.85
$[\text{Ru}(\text{bpy})_2(\text{DCbpy})]$	MLCT	4,4'-dicarboxyl-bpy	1.8	3.7
$[\text{Ru}(\text{bpy})_2(\text{CN})_2]$	MLCT	CN <sup>-</sup>	1.2	4.3
$[\text{Ir}(\text{bpy})_3(\text{OH})]^{2+}$	IL + MLCT	2,2'-bipyridyl	3.0	3.5
$[\text{Cr}(\text{DCbpy})_3]^{3+}$	LF	4,4'-dicarboxyl-bpy		pK = pK*

## V. Photoredox reactions

24

- A sort of charge separation at first, then the separated unlike charges recombine spontaneously providing energy than can be used in various ways.
  - Important research in utilizing solar energy,
  - or in the physical and chemical processes in the atmosphere
  - and in photobiology (use of solar energy by living organisms).
- By molecularity:
  - Unimolecular:
    - ✦ Electron relocation within the molecule (bi- or multinuclear complexes), ionization ( $e_{\text{sol}}^-$  formation), homolytic bond cleavage
  - Bimolecular:
    - ✦ Electron exchange in the outer sphere, oxidative or reductive addition.

**V. Photoredox reactions**  
**V/1. Intramolecular electron transfer**

25

- The complex contains two different central atoms connected by a bridging ligand.
- In the mechanism study of photoinduced redox reaction, significant factors are: systematic control of...
  - redox potentials of the reactant and product,
  - distance between electron donor and acceptor.
- The bridging ligand often has important role.
- $[(S_2)ClRu^{III}(L)Ru^{II}Cl(bpy)_2]^{3+} \rightarrow [(S_2)ClRu^{II}(L)Ru^{III}Cl(bpy)_2]^{3+}$ 
  - IVCT (= InterValence Charge Transfer) often leads to the dissociation of the complex:
    - $[(NH_3)_5Co^{III}(NC)Ru^{II}(CN)_6]^- \rightarrow [Ru^{III}(CN)_6]^{3-} + Co^{2+} + 5 NH_3$

**V. Photoredox reactions**  
**V/2. Photoionization, formation of photoelectrons**

26

- Well known in **gas phase**.
  - $NO \rightarrow NO^+ + e^- < 134 \text{ nm}$
  - $O_2(^1\Delta_g) \rightarrow O_2^+ + e^- 103 \text{ nm}$
  - $O_2^+ + N_2 \rightarrow NO^+ + NO$  (NO<sup>+</sup> production in the atmosphere)
- The photon energy necessary for the photoionization of diatomic molecules is much larger than for photodissociation.
- In solution**,  $e^-_{solv}$  often forms from anions. E.g.:
  - $I^- \rightarrow I + e^-_{solv} 280-300 \text{ nm}$
- Similarly,  $e^-_{solv}$  may be formed even from metal ions, e.g.: Co(II), Fe(II), V(II), Eu(II), Cr(II)
- The  $\Phi$  of the formation of hydrated electrons from  $[Fe(CN)_6]^{4-}$  depends very sensitively on wavelength (0,9 at 229 nm).
- $e^-_{solv}$  takes part in numerous secondary reactions.

**V. Photoredox reactions**  
**V/3. Photoredox rearrangement in the inner sphere**

27

- A lot of highly significant rearrangement reaction are known from organic compounds. This is less common in inorganic chemistry. E.g.:
  - $[(CO)_4Fe^0(BrHC=CBrH)] \rightarrow [(CO)_4Fe^{II}Br(HC=CBrH)]$
  - $[(PPh_3)_2Pt^0(N\equiv C-C\equiv C-N)] \rightarrow [(PPh_3)_2Pt^{II}(CN)(C\equiv C-N)]$ 
    - The photoactivity of the Pt<sup>0</sup> complexes can be favorably used for synthesizing new ligands on a preparative scale

**V. Photoredox reactions**  
**V/4. Reactions with homolytic bond breaking**

28

- MLCT excitation of a paramagnetic transition metal complex that is not the most stable for the given stoichiometry may lead to a homolytic cleavage of the coordinative M-L bond:
  - $[Mo(CN)_6]^{3-} \rightarrow [Mo(CN)_5]^{3-} + CN\cdot$
  - $[CuCl_4]^{2-} \rightarrow [CuCl_3]^{2-} + Cl\cdot$
  - $Cl\cdot + Cl\cdot \rightarrow Cl_2\cdot$
- The tetrachloro complex of Fe(III) does not release a chlorine atom in the first step, but a hydroxyl radical (OH·) as the photoactive species is  $[Fe(OH)_xCl_{4-x}]^-$  rather than  $[FeCl_4]^-$ .

**V. Photoredox reactions**  
**V/5. Electron transfer with outer sphere mechanism**

29

- Both the **oxidation and reduction potentials** of excited species are higher than the ground state species:
  - The excited molecule has at least one electron with a larger energy than usual, so it is a better reducing agent.
  - It has a vacant orbital at lower energy, so it is a better oxidizing agent.
- The excited state can be quenched by both a Lewis base or Lewis acid.
- Electron acceptors or donors can induce efficient electron transfer on the lifetime of the excited state is longer than 0,1 ns. So photoredox reactions are rare or very inefficient in systems displaying fluorescence.

LUMO

HOMO

LUMO

HOMO

$A \xrightarrow{h\nu} A^*$

$A^* + D \rightarrow A + D^*$

$D \xrightarrow{h\nu} D^*$

$D^* + A \rightarrow D + A^*$

**V. Photoredox reactions**  
**V/5. Electron transfer with outer sphere mechanism**

30

- Kinetic scheme for photoinduced electron transfer in the presence of an electron acceptor quenching agent (A):

$D + A \xrightleftharpoons[k_{-d}]{k_d} D \dots A$

$D + A \xrightleftharpoons[k_{-d}]{k_d} D \dots A$

Diffusion

Electron transfer in the excited state

Electron transfer in the ground state

Product formation

**V. Photoredox reactions**

**V/5. Electron transfer with outer sphere mechanism**

31

- $\text{Ru}(\text{bpy})_3^{2+}$  has very favorable photophysical and redox properties:
  - Very stable in the ground state.
  - The oxidation and reduction potentials of the excited state are very large and almost equal.
  - The excited state show phosphorescence, forms with  $\phi \approx 1$ , its lifetime exceeds 1  $\mu\text{s}$ .

**V. Photoredox reactions**

**V/6. Photoredox reaction of ion pairs**

32

- Makes it possible to study (weak) interactions characteristic of the outer coordination sphere.
- Ion pairs = adducts held together by electrostatic interactions only.
- **Fuoss equation:**

$$K_{\text{ip}} = \frac{4\pi N_A d^3}{3000} \exp\left(-\frac{z_+ z_- e^2}{\epsilon_s d \left(1 + \sqrt{\frac{8\pi N_A e^2 d^2}{1000 \epsilon_s RT}}\right) RT}\right)$$
  - $K_{\text{ip}}$ : equilibrium constant of ion pair formation
  - $d$ : the sum of the two ionic radii
  - $\epsilon_s$ : static permittivity of the solvent
- The ion pair is a photoactive species on its own, but it cannot be isolated.
- Its excitation can be IPCT, anion-only or cation only.

**V. Photoredox reactions**

**V/7. Photoredox reactions of coordinated ligands**

33

- Only for complexes that have intense absorptions caused by Ligand-ligand transitions and M is not active in redox chemistry (e.g.  $\text{Zn}^{2+}$ ).
- Typically complexes of unsaturated multidentate macrocyclic ligands (e.g. porphyrin, phthalocyanin)