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# ORGANIC PHOTOCHEMISTRY I



## A few good textbooks:

- Modern Molecular Photochemistry, N. J. **Turro**, University Science Books, California (Mill-Valley), 1991.  
(the next Turro is coming [and coming, and coming.....])
- Essentials of Molecular Photochemistry, A. **Gilbert**, J. **Baggott**, Blackwell Scientific Publications, London, 1991.
- Organic Photochemistry: A Comprehensive Approach, W. A. **Horspool**, D. **Armesto**, Ellis Horwood, PTR Prentice Hall. New York, 1992.
- Synthetic Organic Photochemistry, A. **Griesbeck**, J. **Mattay**, CRC Press, Marcel Dekker,, New York, 2006.
- Photochemical Reactions as Key Steps in Organic Synthesis, N. **Hoffmann**, *Chem. Rev.* **2008**, *108*, 1052. **A copy is distributed during the course.**

# Introductory Remarks

## Why is photochemistry important (really very very important!)

- The energy problem (biological / technical):

Photosynthesis: Production of biomass, photonic efficiency of photosynthesis:

<http://photoscience.la.asu.edu/photosyn/education/photointro.html>

<http://faculty.clintoncc.suny.edu/faculty/Michael.Gregory/files/Bio%20101/Bio%20101%20Lectures/Photosynthesis/photosyn.htm>

<http://www.photosynthesisresearch.org/>

Energy equivalents of photosynthesis

Worldwide consumption of energy via coal or natural gas

Application of renewable energy sources:

Photovoltaics, Photo(Solar)thermal processes, Solar chemistry

- Information registration and storage (biological / technical)

Process of vision – cis/trans-isomerization

Photographic processes – silver halide technique

Holographic data storage, spectral hole burning

- Chemical Processes:

One ground state – two relevant excited states – rule

Electronic and spin isomers / states

Potential for organic synthesis – Triplication of reaction channels



Primary production of biomass: approx.  $172 \cdot 10^9$  tons/year

### Energy calculation:

Earth (Area  $0,51 \cdot 10^{15} \text{ m}^2$ ):

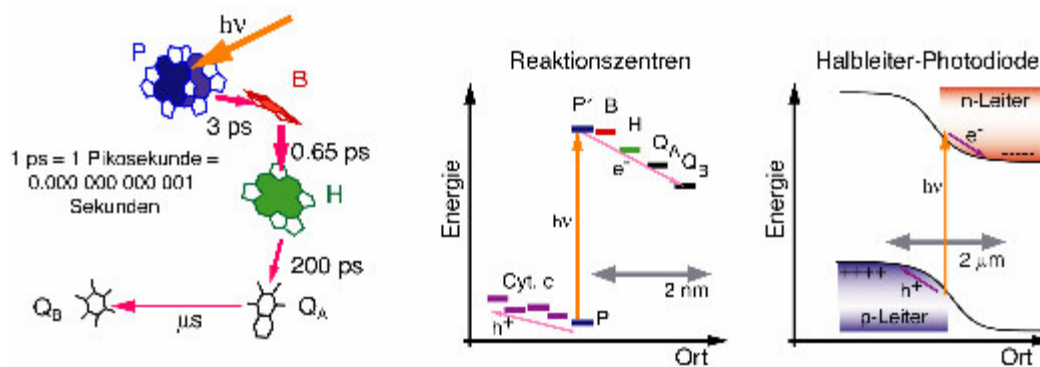
$80 \cdot 10^{15} \text{ g a}^{-1}$  (100 %),

Oceans (Area  $0,36 \cdot 10^{15} \text{ m}^2$ ):

$28 \cdot 10^{15} \text{ g a}^{-1}$  (35,4 %),

Surface (Area  $0,15 \cdot 10^{15} \text{ m}^2$ ):

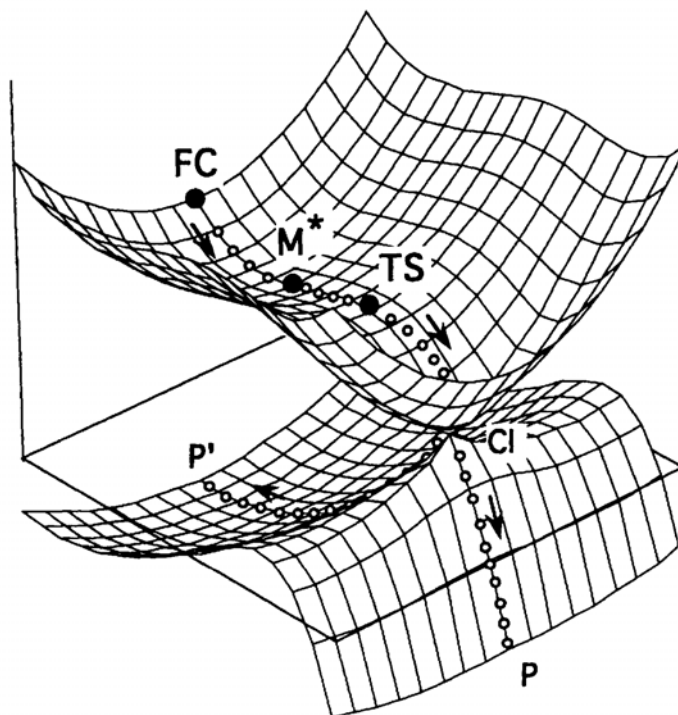
$52 \cdot 10^{15} \text{ g a}^{-1}$  (64,6 %)



• Chemical Processes

Way to *thermodynamically impossible* pathways via a detour using electronically excited states – reaction potential energy surfaces

Compare ground-state (thermal, catalyzed or non catalyzed) with excited state reactions



**Figure 1** Model conically intersecting potential energy surfaces plotted along the branching space ( $x_1, x_2$ ). The arrows indicate the direction of the minimum energy path connecting the FC point to the photoproducts **P** and **P'**. **M\*** is the excited state intermediate and **TS** is a transition state connecting **M\*** to the conical intersection (**CI**)

## Photochemical Principles and Laws

### 1. Photochemical Law

Grotthuss-Draper law / „absorption criteria“

Energy relation, Planck-constant, Planck equation:  $E = h \nu$

⇒ Maximum accessible energies and comparison with bond dissociation energies

Compare energies with different scales (nm, eV,  $\text{cm}^{-1}$ ).

Bond dissociation energies of single and multiple bonds

**Kasha-rule** ( $S_1$ -Fluorescence)

Fluorescence and phosphorescence as emission pathways (luminescence general)

Definition of singlet and triplet states

“radiative and non-radiative decay“

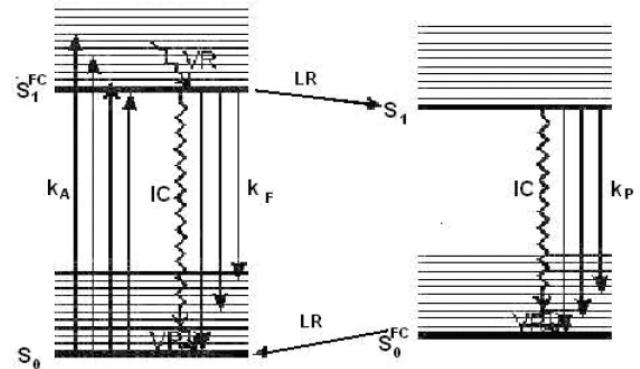
**Kasha- and Vavilov-rules** (photophysical rules)

Physical basis of these rules and laws

What are the chemical consequences of these rules?

HOMO/LUMO-description of electronic excitation and ISC process

Definition of  $S_0$ ,  $S_1$  and  $T_1$ -states.



Photophysical processes:

- Absorption
- Intersystem-Crossing
- Vibrational relaxation
- Internal Conversion

Emission: general luminescence

What kinds of luminescence effects are known?

- photolumineszenz (light induced – e.g. fluorescence lamp)
- thermolumineszenz (heat induced – e.g. match)
- triboluminescence (induced by rubbing – e.g. polymer foil)
- chemoluminescence (induced by chemical reaction – e.g. peroxide decomposition or a firefly\*)
- sonoluminescence (induced by sound – see “bubble fusion”)

\* part of a huge chapter: **bioluminescence**

## 2. Photochemical Law

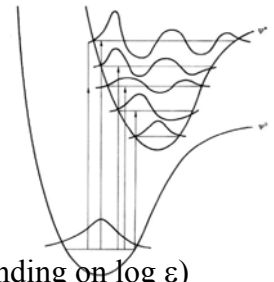
Stark-Einstein (1912) / Quanta criteria

„Absorption is a one quanta process“ (exceptions in laser photochemistry)

**Absorption:** Lambert-Beer-law:  $A = \log I_0/I = \epsilon \times c \times l$

A typical electronic absorption spectrum:

Allowed, partially allowed, forbidden and strongly forbidden transitions (depending on  $\log \epsilon$ )



### Jablonski term diagrams

(a) simple:  $S_0$ ,  $S_1$  and  $T_1$ -terms and transitions.

Straight arrows: radiating transitions

wavy arrows: non-radiating or radiationless transitions

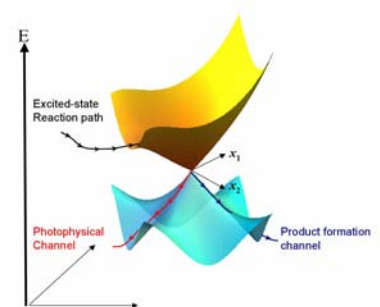
(b) more complex: when vibrations are taken into account:

Intersystem-Crossing (ISC) radiationless and isoenergetic

Vibrational Relaxation (VR) radiationless

Internal Conversion (IC) radiationless and isoenergetic

Two-dimensional cut through the  $(3n-5)$  /  $(3n-6)$ -dimensional potential energy hyper surface



Cartoon of a "classic" double cone conical intersection, showing the excited state reaction path and two ground state reaction paths.

- diabatic (non-adiabatic) processes (with „transfer“)  $A^* \rightarrow B \rightarrow C$  (often)

- adiabatic processes (without „transfer“)<sup>1</sup>  $A^* \rightarrow B^* \rightarrow C^* \rightarrow C$  (less often)

Kinetics of photophysical processes:

Relative size of fluorescence and phosphorescence decay rate constants:

$k_F$ :  $10^9 - 10^7 \text{ sec}^{-1}$ ,  $k_P$ :  $10^4 - 10^{-2} \text{ sec}^{-1}$

**Natural lifetimes of an excited state:**

$$I = I_0 e^{-k(0)t}$$

$$\tau_0 = 1 / k(0) = 1.5 / \nu_{\max}^2 f$$

examples for  $f = 1$  ( $S_0 \rightarrow S_1$ )  $\tau_0$  approx. 1ns, for  $f = 10^{-9}$  ( $S_0 \rightarrow T_1$ )  $\tau_0$  ca. 3 sec

**Quantum yields** for a photochemical or photophysical process:

$\Phi$  = Number of transformed molecules / number of excited states (= absorbed photons)

For „transformed molecules“:  $0 > \Phi > 10^4-10^5$  / for photophysical processes:  $\Phi = 1.00$

Photophysical relevant processes: ISC / IC / VR / phosphorescence and fluorescence

<sup>1</sup> (from Greek ἀ-δι-βαίνειν, not-through-to pass)

$$\tau_{T1} = 1 / (k_P + k_{ISC(T1-S0)})$$

$$\Phi_P = \tau_{S1} k_{ISC(S1-T1)} k_P / (k_P + k_{ISC(T1-S0)})$$

$$\Phi_{T1} = \tau_{S1} k_{ISC(S1-T1)}$$

$$\Phi_P = \tau_{S1} k_{ISC(S1-T1)} \tau_{T1} k_P$$

$$\Phi_{ISC(T1-S0)} = \Phi_{T1} k_{ISC(T1-S0)} / (k_P + k_{ISC(T1-S0)})$$

Primary processes:

$$\Sigma (\Phi_F + \Phi_{IC} + \Phi_{ISC(T1-S0)} + \Phi_P) = 1.00$$

	<u>dezi</u>	<u>zenti</u>	<u>milli</u>	<u>micro</u>	<u>nano</u>	<u>pico</u>	<u>femto</u>	<u>atto</u>	<u>zepto</u>	<u>yokto</u>
symbol	d	c	m	$\mu$	n	p	f	a	z	y
factor	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-6}$	$10^{-9}$	$10^{-12}$	$10^{-15}$	$10^{-18}$	$10^{-21}$	$10^{-24}$

Further photophysical relevant processes:

$$\tau_{S1} = 1 / (k_F + k_{IC} + k_{ISC(S1-T1)})$$

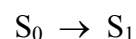
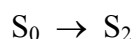
$$\Phi_F = k_F / (k_F + k_{IC} + k_{ISC(S1-T1)}) = \tau_{S1} k_F$$

$$\Phi_{IC} = k_{IC} / (k_F + k_{IC} + k_{ISC(S1-T1)}) = \tau_{S1} k_{IC}$$

$$\Phi_{T1} = k_{ISC(S1-T1)} / (k_F + k_{IC} + k_{ISC(S1-T1)}) = \tau_{S1} k_{ISC(S1-T1)}$$

$$\tau_{T1} = 1 / (k_P + k_{ISC(T1-S0)})$$

**Lowest and second lowest excited singlet states (please insert energies and state configurations!):**



Benzene

Naphthalene

Acetone

Benzophenone

**Quantum yields and lifetimes (*please insert quantum yields and lifetimes!*):**

	$\Phi_F$	$\tau_{S1}$	$\Phi_P$	$\tau_{T1}$	$\Phi_{S1T1}$
Benzene					
Naphthalene					
Acetone					
Benzophenone					

**Spectroscopic methods:**

- absorption spectroscopy (Lambert-Beer law)
- emission spectroscopy (static: fluorescence and phosphorescence)
- time-resolved absorption and emission spectroscopy (ns, ps, down to fs – spectroscopy)

msec =  $10^{-3}$  sec;  $\mu$ sec =  $10^{-6}$  sec; nsec =  $10^{-9}$  sec; psec =  $10^{-12}$  sec; fsec =  $10^{-15}$  sec;

Excitation and detection principles, Stock shift, e-decay,  $T_1$ - $T_2$ -absorption,  $S_0$ - $T_1$ -absorption;

Relevant electronic excited states in aromatic and carbonyl photochemistry:

$^1n\pi^*$ ,  $^3n\pi^*$ ,  $^1\pi\pi^*$ ,  $^3\pi\pi^*$  - states

MO-Scheme for a carbonyl compound with low lying  $n_{C=O}$ -orbital;

Energetic spacing of  $^1n\pi^*$  and  $^1\pi\pi^*$  or  $^3n\pi^*$ , and  $^3\pi\pi^*$  - states.

- differences between  $^1n\pi^*$  and  $^3n\pi^*$  - states: approx. 5-8 kcal / Mol (little structure dependence)
- differences between  $^1\pi\pi^*$  and  $^3\pi\pi^*$  - states: approx. 10-35 kcal / Mol (strong structure dependence)

Photochemistry of electronically excited  $n\pi^*$ -carbonyls:

Prominent example benzophenone:

3 ways: hydrogen transfer (in general: group transfer, i.e. H, D,  $SiR_3$ ,  $SnR_3$  etc.) energy or electron / proton transfer

H-transfer and coupled electron / proton transfer result in the same product (s)!

Organic Photochemistry Photochemical Process [Gurdeep.R.Chatwal, Reaction Mechanism and Reagents in Organic Chemistry , Himalaya Publications, 2005, p 932]Â The activated molecule returns to the ground state by dissipating its energy through the non-radiative and radiative transition process. Photoreactions of Carbonyl Compounds; Enes, Dienes & Arens [Gurdeep.R.Chatwal, Reaction Mechanism and Reagents in Organic Chemistry, Himalaya Publications, 2005, p 959-961]