Experimental photochemistry and its practical problems

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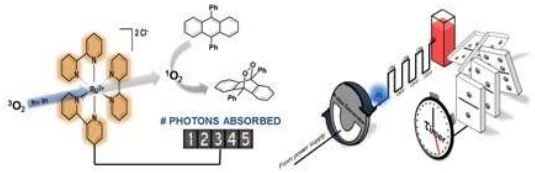

Light sources

2

- The energy of the photons emitted by the light source should be suitable for exciting the studies molecules.
- Photolysis from the view of the light source:
  - The sample is illuminated continuously with an intense light source, the photon flux is constant. The photoreaction is monitored through the offline or online determination of reactant and/or product concentrations. The concentration of the reactive excited states is very low and constant.
  - Excitation with short, high energy pulses (*flash photolysis*). It is used if very reactive excited molecules or radicals formed from the need to be prepared in high initial concentration.

Light sources

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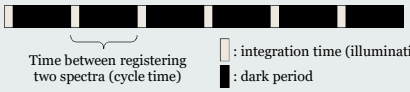
- Light sources from the point of view of photolysis:
  - Continuously emitting (***laser***, *diode array spectrophotometer*),
  - Pulsed (flash photolysis, ***laser***, *diode array spectrophotometer*).



Time between registering two spectra (cycle time)

: integration time (illumination)

: dark period

Light sources

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- Based on the energy distribution of emitted photons:
  - Monochromatic,
    - *Lasers*: typical light sources of very narrow band width,
    - *Fluorescent light sources „filled" with low pressure metals*: radiation containing a few lines, mostly emitting at the resonance line of the filling metal. E.g. low pressure mercury vapor lamps emit at 253.7 nm
  - Polychromatic – monochromator or filter might be needed.
    - *Light sources filled with high pressure mercury vapor, halogens, noble gases (Xe) or their mixtures.*
    - *Solar simulator*: the spectral distribution resembles that of the sunlight reaching the surface of Earth. Suitable for studying processes induced by natural sunlight. Extremely large power is common (up to 1000 W).

Diode array spectrophotometer: close to a solar simulator.

Light sources

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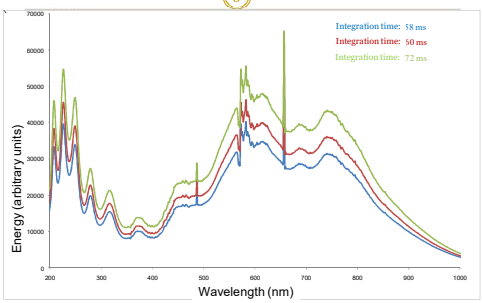

Actinometers

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- The quantitative description of a photoreactions assumes exact knowledge of the number of photons entering the reactor in unit time.
- Physical or chemical actinometers are needed:
  - Chemical actinometer: A photoreactant with known Φ, the extent of reaction is measurable easily and rapidly.
  - Physical actinometer: light energy measuring devices.
    - Michelson-Martin actinometer: the sensor is black bimetal, whose distortion moves a quartz filament.
    - Linke-Feussner actinometer

Chemical actinometers

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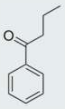
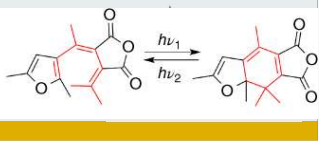
- For continuous lamps:
  - Tris-oxalato-ferrate(III), $[Fe(C_2O_4)_3]^{3-}$
  - Uranyl oxalate, $[UO_2(C_2O_4)]$
  - Reinecke salt, $[Cr(NH_3)_2(SCN)_4]^-$
  - A lot of organic molecules (butirophenon, piperylene).



- Pulsed lasers:
  - Hexacyano-ferrate(II)
  - Organic molecules (e.g.



Chemical actinometers

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- Tris-oxalato-ferrate(III), $[Fe(C_2O_4)_3]^{3-}$; 254-500 nm
  - $[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow {}^*[Fe(C_2O_4)_3]^{3-}$
  - ${}^*[Fe(C_2O_4)_3]^{3-} \rightarrow [Fe(C_2O_4)_2]^{2-} + C_2O_4^{\cdot-}$
  - $[Fe(C_2O_4)_3]^{3-} + C_2O_4^{\cdot-} \rightarrow [Fe(C_2O_4)_3]^{2-} + C_2O_4^{2-}$
  - $[Fe(C_2O_4)_3]^{2-} \rightarrow [Fe(C_2O_4)_2]^{2-} + 2\ CO_2$
  - The absorption of the Fe(II) complex is negligible compared to the Fe(III) complex.
  - The concentration of Fe(II) is measured through complexation by 1,10-phenanthroline by spectrophotometry.
  - The quantum yield of Fe(II) formation is known at several different wavelengths, $\Phi \approx 1$.

Chemical actinometers

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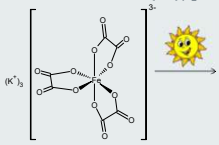
- Tris-oxalato-ferrate(III), $[Fe(C_2O_4)_3]^{3-}$; 254-500 nm



$Fe^{2+} + 4\ C_2O_4^{2-} + 2\ CO_2$

Fe(II) + 3 o-phenanthroline

Chemical actinometers

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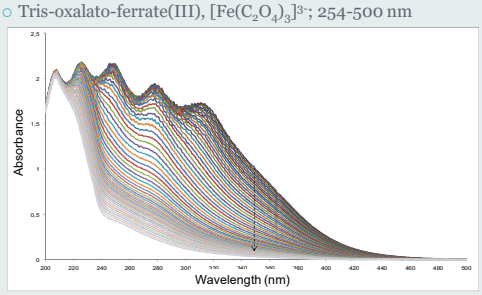
- Tris-oxalato-ferrate(III), $[Fe(C_2O_4)_3]^{3-}$; 254-500 nm



Chemical actinometers

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- Uranyl oxalate, $[UO_2(C_2O_4)]$; 200-450 nm
  - Products of the photodecomposition of the oxalate ion: CO_2, CO and HCOOH.
  - U(VI) is reduced to U(IV).
  - For the oxalate decomposition: $\Phi = 0.48\text{-}0.61$.
  - Toxic and radioactive.

Chemical actinometers

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- Reinecke salt, $[Cr(NH_3)_2(SCN)_4]^-$; 310-750 nm
  - $[Cr(NH_3)_2(SCN)_4]^- + H_2O + h\nu \rightarrow [Cr(NH_3)_2(SCN)_3(H_2O)] + SCN^-$
  - $[Cr(NH_3)_2(SCN)_3(H_2O)] + H_2O \rightleftharpoons [Cr(NH_3)_2(SCN)_2(H_2O)_2] + SCN^-$
  - For the formation of SCN^- $\Phi = 0.27\text{-}0.31$

Spectrophotometers

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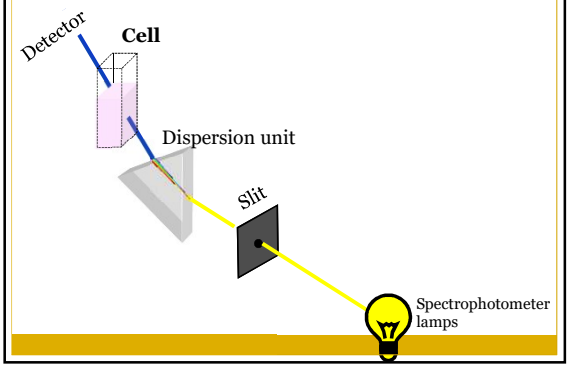
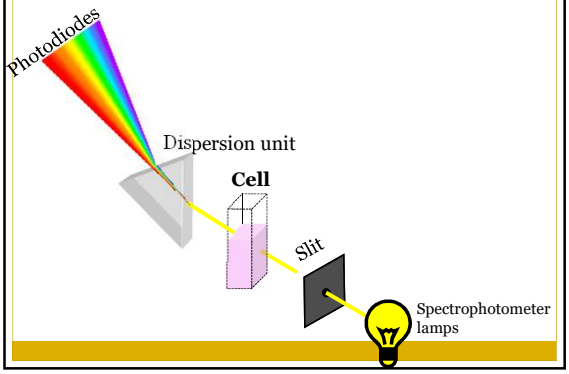
- Starting point of photochemical investigations: registration of the absorption spectrum.
- Absorption spectra are often used in monitoring processes (spectrophotometric detection).
- Classification of spectrophotometers:
  - Singe beam – typically diode array
  - Double beam – Scanning
    - Photocell, photoelectron-multiplier tube (PMT) or photodiode.

Scanning spectrophotometer



Diode array spectrophotometer



Photochemical measurements in diode array spectrophotometers

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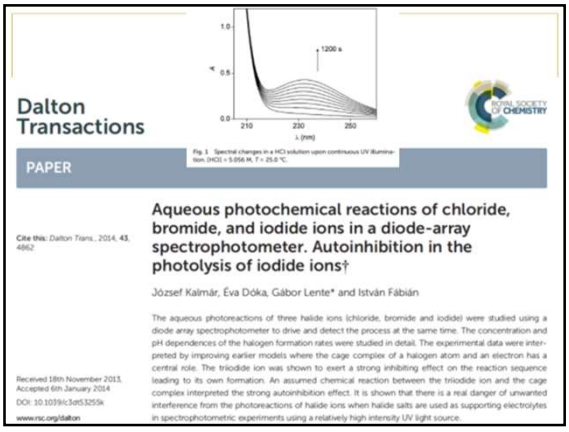
- Polychromatic light is the driving force
- Relatively low light intensity
- Excited states cannot be detected
- The stoichiometric photoreaction is readily monitored
- Solution homogeneity must be maintained
- Light: a „reactant” whose amount can be changed with limitations



Spectrofluorimeters

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- Excitation with light of selected wavelength.
- The light emitted by the sample is measured in a wavelength range that is selected independently of the excitation.
- Excitation and detection are perpendicular.
- Usually two monochromators:
  - Excitation
  - Detection
- If the excitation wavelength is varied, luminescence surfaces can be obtained.

Spectrofluorimeters

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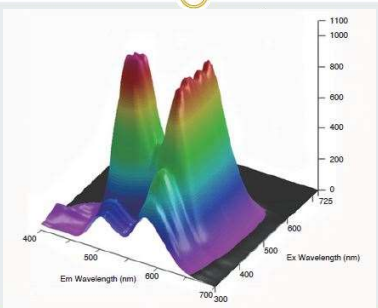

Lasers

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- Fundamental role in photochemical investigations.
- Solid lasers:
  - Ruby laser
  - Nd-YAG (yttrium aluminum- garnet): the most common today
  - Ti-sapphire laser
- Liquid lasers:
  - Dye lasers: solution of compound with intense luminescence
- Gas lasers:
  - CO_2, He, Ne
  - Excimer lasers: XeCl, KrF, ArF

Flash photolysis

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- Two light sources:
  - Exciting: only in pulsed operation.
  - Detecting: both pulsed and continuous operations possible.
- Originally a flash lamp was used, the introduction of lasers was a major development.
- Laser pulses are typically a few ns long and provide about 100 mJ of energy (power: about 100 MW).
  - Development: shorter path length, larger energy.
  - The pulse length is of fundamental importance, as it set the limit for the fastest reaction that can be studied reliably.

Flash photolysis

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- Detector: typically PMT, best time resolution is 20-30 ps. Both emission and absorbance measurements possible.
- Man applications:
  - Photophysical measurements (fluorescence or phosphorescence life time).
  - Photochemistry: generally, monitoring of reactive intermediates with absorbance measurements.

Flash photolysis

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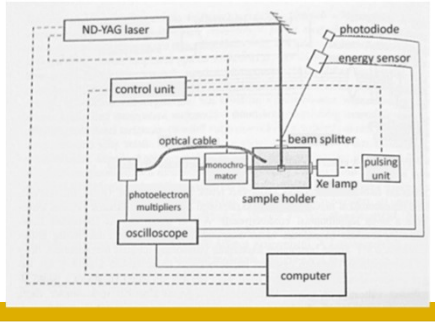

Flash photolysis

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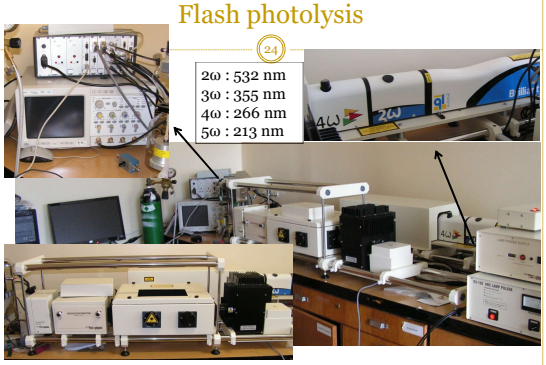

Applied Photophysics LKS.60 laser flash photolysis instrument

Flash photolysis

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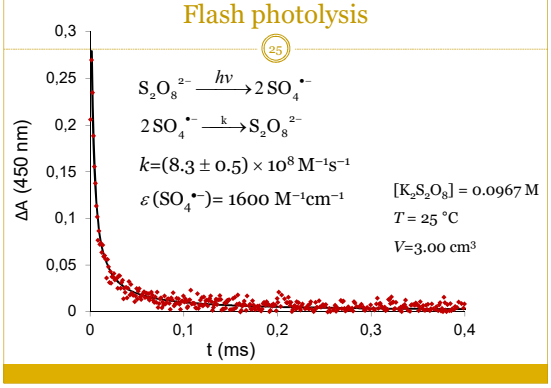
$S_2O_8^{2-} \xrightarrow{h\nu} 2\,SO_4^{\bullet-}$

$2\,SO_4^{\bullet-} \xrightarrow{k} S_2O_8^{2-}$

$k=(8.3 \pm 0.5) \times 10^8\ M^{-1}s^{-1}$

$\varepsilon(SO_4^{\bullet-})= 1600\ M^{-1}cm^{-1}$

$[K_2S_2O_8]$ = 0.0967 M
T = 25 °C
V=3.00 cm³



Flash photolysis

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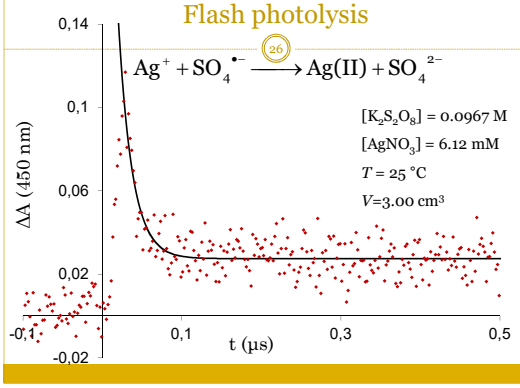
$Ag^+ + SO_4^{\bullet-} \longrightarrow Ag(II) + SO_4^{2-}$

$[K_2S_2O_8]$ = 0.0967 M
$[AgNO_3]$ = 6.12 mM
T = 25 °C
V=3.00 cm³



Flash photolysis

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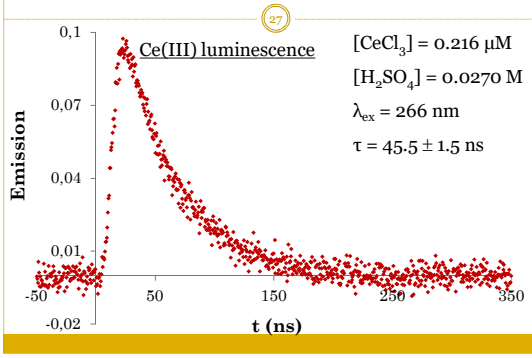
Ce(III) luminescence

$[CeCl_3]$ = 0.216 µM
$[H_2SO_4]$ = 0.0270 M
λ_{ex} = 266 nm
$\tau = 45.5 \pm 1.5$ ns



Quantitative description of photochemical reactions

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- The rate of the primary photochemical process is directly proportional to the number of absorbed photons in unit time
- This can be calculated from the molar absorbances and the intensity of the incident light beam
- Any other (non-photochemical) reaction in the networks is described by normal thermal kinetics

Quantitative description of photochemical reactions

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- Number of adsorbed photon in unit time for mono-chromatic light (N):

$$N = \frac{\lambda E_L}{hc}\left(1-10^{-A}\right)$$

- Polychromatic light:

$$N = \int \frac{\lambda \cdot E_L(\lambda)}{hc}\cdot\left(1-10^{-A(\lambda)}\right)d\lambda$$

- Polychromatic light + inert absorbing species (inner filter effect):

$$N = \int \frac{c_{abs}\cdot\varepsilon_{abs}}{\sum c_i\cdot\varepsilon_i}\cdot\frac{\lambda \cdot E_L(\lambda)}{hc}\cdot\left(1-10^{-A(\lambda)}\right)d\lambda$$

ferrioxalate actinometry

Quantitative description of photochemical reactions

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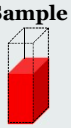
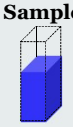
- Inner filter effect:

Sample 1



$Abs_1 = 1$
Passes: 10%
Absorbed: **90%**

Sample 2



$Abs_2 = 1$
Passes: 10%
Absorbed: **90%**

Sample 1 & 2

$Abs_{1\&2} = 2$
Passes: 1%
Absorbed: **99%**
= **49.5%** + **49.5%**

Quantitative description of photochemical reactions

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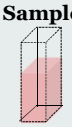
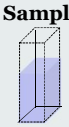
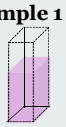
- Inner filter effect:

Sample 1	Sample 2	Sample 1 & 2
		
Abs_1 = 0.01 Passes: 97.7% Absorbed: 2.8%	Abs_2 = 0.01 Passes: 97.7% Absorbed: 2.8%	$Abs_{1\&2}$ = 0.02 Passes: 95.5% Absorbed: 4.5% = 2.25% + 2.25%

Quantitative description of photochemical reactions

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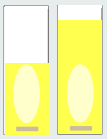
- The sample volume outside the illuminated space significantly influences the number of absorbed photons in unit volume.
- Volume dependence of photoreactions: $\left(\frac{V_1}{V_2}\right)^n = \frac{v_2}{v_1}$



Quantitative description of photochemical reactions

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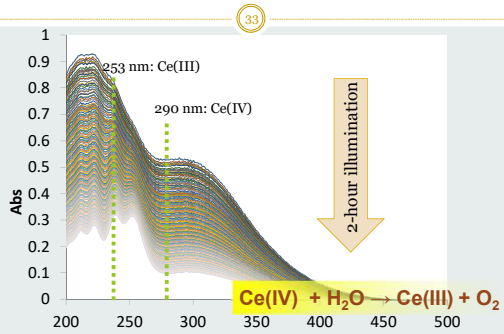

Quantitative description of photochemical reactions

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- Photochemical decay of Ce(IV):

$$N = \int \frac{c_{abs} \cdot \varepsilon_{abs}}{\sum c_i \cdot \varepsilon_i} \cdot \frac{\lambda \cdot E_L(\lambda)}{hc} \cdot \left(1 - 10^{-A(\lambda)}\right) d\lambda$$

$$-\frac{dc_{Ce(IV)}}{dt} = \int \frac{\Phi_{P,\lambda} \Phi}{V} \left(1 - 10^{-A_\lambda}\right) \frac{A_{Ce(IV),\lambda}}{A_\lambda} d\lambda$$