Photochemistry I

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http://photochemistry.epfl.ch/PC.html
PHOTOCHEMISTRY I

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1. Basic principles
**Photochemistry (light-induced chemistry)**

Chemistry: forming or breaking of chemical bonds and charge transfer within or between molecules.

Photochemical reactions are processes during which the energy required for their activation ($\Delta U^\ddagger$) or their development ($\Delta G_r$) is provided by an electromagnetic radiation.

Activation energies of the order of $\Delta U^\ddagger = 100 \text{ kJ} \cdot \text{mol}^{-1}$ and bond energies of the order of $\Delta G = 200-400 \text{ kJ} \cdot \text{mol}^{-1}$ imply absorption of photons that should individually carry an equivalent amount of energy.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\Delta H$ [kJ mol$^{-1}$]</th>
<th>$\lambda$ [nm]</th>
<th>Bond</th>
<th>$\Delta H$ [kJ mol$^{-1}$]</th>
<th>$\lambda$ [nm]</th>
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<tr>
<td>H–H</td>
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<td>274</td>
<td>N–N</td>
<td>160</td>
<td>748</td>
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<tr>
<td>C–H</td>
<td>413</td>
<td>290</td>
<td>N=N</td>
<td>631</td>
<td>190</td>
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<tr>
<td>N–H</td>
<td>393</td>
<td>304</td>
<td>N≡N</td>
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<td>127</td>
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<td>403</td>
<td>N–O</td>
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<tr>
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<td>240</td>
<td>C–S</td>
<td>259</td>
<td>461</td>
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</table>
Types of photochemical reactions

a) $\Delta G_r < 0$ (exergonic reaction, spontaneous)
   Light enable for overcoming the activation barrier or to lower it by acting as a catalyst. Such reactions are called "photocatalytic"

Example: $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$

b) $\Delta G_r > 0$ (endergonic, non spontaneous)
   Energy required by the reaction is brought by light. Light energy is (partially) converted into chemical energy.

Example:
Natural photosynthesis

$$\text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{hv}} \text{chloroplasts} \quad \frac{1}{6} \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 \quad \Delta G = 496 \text{ kJ} \cdot \text{mol}^{-1}$$

Functions associated with light

$$\text{A} \xrightarrow{\text{hv}} \text{B} \ (\pm \Delta G)$$

a) **Light as a reactant**
   - synthesis of B
   - reaction inhibition (photo-stabilization of A)

b) **Light as an energy vector**
   - endergonic formation of B
   - energy storage

c) **Light as information vector**
   - optical absorption profile (photography, information storage)
   - charge density profile (xerography)
   - 3D material profile (photolithography)
Fundamental laws of photochemistry

**Grotthuss-Draper law** (1812, 1842)
*Light must be absorbed by a chemical substance in order for a photochemical reaction to take place.*

**Stark-Einstein law** (1908-1913)
Also known as the "photo-equivalence law"
*For each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction.*

\[
\Delta G_{\text{molecule}} = N_A \cdot h \nu = N_A \cdot \frac{hc}{\lambda}
\]

1 *Einstein* = 1 mol of photons = \(N_A\) photons
**1.2 Laws of light absorption**

**Phenomenological (macroscopic) law of absorption**

\[
I_T = I_0 - I_A - I_R
\]

**Transmittance** \( T = \frac{I_T}{I_0} \)

**Reflectance** \( R = \frac{I_R}{I_0} \)

**Absorbance** \( A = -\log\left(\frac{I_T}{I_0}\right) = -\log T \)

\[A = -\log\left(\frac{I_T}{I_0}\right) = -\log T = \varepsilon \cdot c \cdot l\]

**Lambert’s law**

\[
I(x) = I_0 \cdot \exp(-\alpha x)
\]

\[
\ln\left(\frac{I(x)}{I_0}\right) = -\alpha x \quad \ln\left(\frac{I_T}{I_0}\right) = -\alpha l
\]

\[\alpha = \text{absorption constant \, [cm}^{-1}\text{]}\]

Link with the medium’s complex refractive index:

\[\tilde{n} = n - i\kappa \quad [-] \quad \kappa = \text{absorption coefficient \, [-]}\]

\[\alpha = \frac{4\pi \cdot \kappa}{\lambda_0}\]

**(imaginary part of the refractive index)**

**Beer-Lambert Law**

\[A = -\log\left(\frac{I_T}{I_0}\right) = -\log T = \varepsilon \cdot c \cdot l \quad [-]\]

\[c \text{, molar concentration \, [mol} \cdot \text{L}^{-1}\text{]}\]

\[l \text{, optical pathlength \, [cm]}\]

\[\varepsilon \text{, molar decadic extinction coefficient}\]

**Example:** \( c = 10^{-3} \text{ M}, \varepsilon = 10^4 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}\)

\[\Rightarrow T = 0.01, \quad A = 2 \Rightarrow 99\% \text{ of the light is absorbed within the first 2 mm of the solution}\]

**Superimposition of absorbing systems**

Transmittance is multiplicative:

\[T_{\text{tot}} = \prod_i T_i\]

Absorbance is additive:

\[A_{\text{tot}} = \sum_i A_i\]

August Beer

(1825-1863)
Justification of Beer-Lambert law

**Initial assumptions**
- individual molecules totally block light within a characteristic cross-section $\sigma$
- monochromatic light
- molecules do not cast any shadow on each other (only conceivable if the concentration $c$ is very low)

Absorptance of a solution volume $S \cdot dx$ containing $n$ molecules:

$$-\frac{dI}{I(x)} = \frac{I(x+dx) - I(x)}{I(x)} = \frac{n \cdot \sigma}{S} = \frac{c \cdot S \cdot N_A \cdot dx \cdot \sigma}{S} = c \cdot \sigma \cdot N_A \cdot dx$$

$$-\frac{1}{I(x)} \frac{dI}{dx} = c \cdot \sigma \cdot N_A \Rightarrow \ln \frac{I}{I_0} = c \cdot \sigma \cdot l \cdot N_A$$

By defining: $\varepsilon = \sigma \cdot N_A \cdot \log(e) = \frac{\sigma \cdot N_A}{2.303}$ \Rightarrow $-\log \frac{I}{I_0} = A = \varepsilon \cdot c \cdot l$

Absorption by non-continuous media

Absorption and reflexion by a specular (mirror-like) surface

$I_0 = I_R + I_A + I_T$

$R_s = I_R / I_0$ specular reflectance

**Fresnel law**

$$R_s = \frac{I_R}{I_0} = \frac{(n-1)^2 + n^2 \cdot \kappa^2}{(n+1)^2 + n^2 \cdot \kappa^2}$$

at $\varphi = 0$

Augustin Fresnel (1788-1827)
Absorption by a scattering medium

Diffuse reflectance \( I_0 = I_{Rd} + I_A + I_T \)

Schuster-Kubelka-Munk theory

\[
\begin{align*}
\text{Phenomenological extinction constants:} \\
k \ [cm^{-1}] \text{ absorption} & \quad k_{x=0} = -\frac{1}{dx} \cdot \ln \frac{dl}{I_0} \\
s \ [cm^{-1}] \text{ scattering} & \quad s_{k=0} = -\frac{1}{dx} \cdot \ln \frac{dl}{I_0}
\end{align*}
\]

Kubelka and Kubelka-Munk equations

Kubelka's hyperbolic solutions

\[
\begin{align*}
R &= \frac{1 - R_s (a - b \cdot \coth (b \cdot 2s \cdot l))}{a + b \cdot \coth (b \cdot 2s \cdot l) - R_s} \\
T &= \frac{b}{a \cdot \sinh (b \cdot 2s \cdot l) + b \cdot \cosh (b \cdot 2s \cdot l)}
\end{align*}
\]

with: \( R_s = \) background reflectance

\[
\begin{align*}
a &= 1 + \frac{k}{s} \\
b &= \sqrt{a^2 - 1}
\end{align*}
\]

Kubelka-Munk simplified solution

\[
I \to \infty \quad \Rightarrow \quad F(R_s) = \frac{k}{s} = \frac{(1 - R_s)^2}{2R_s}
\]

Absorber homogeneously dispersed in a scattering medium (powder)

\[
k \ [cm^{-1}] = \ln(10) \cdot \varepsilon \ [mol^{-1} \ L \ cm^{-1}] \cdot c \ [mol \ L^{-1}]
\]

\[
F(R_s) = \frac{(1 - R_s)^2}{2R_s} = \varepsilon \cdot c \cdot \frac{\ln(10)}{s}
\]
Integrating sphere for diffuse reflectance spectroscopy

A. Diffuse reflectance

Specular light trap

Specular white plate

B. Total reflectance