Molar absorption rate coefficient

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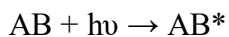
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The **molar absorption rate coefficient** is a measure of how fast a chemical species absorbs light at a given wavelength. It is an intrinsic property of the chemical species, also a measure of the rate of the electronic transition. The larger the molar absorption rate coefficient, the faster the electronic transition. The prime objective of writing this paper is to outline a formula for the calculation of the molar absorption rate coefficient.

Possible energy pathways following photon absorption:

$$AB + h\upsilon \rightarrow AB^*$$

$AB^* \rightarrow AB^+ + e^-$	Photoionization
$AB^* \rightarrow A + B$	Photodissociation
$AB^* \rightarrow AB + h\upsilon$	Fluorescence
$AB^* + M \rightarrow AB + M^*$	Quenching
$AB^* + C \rightarrow A + BC$	Chemical reaction

Johann Heinrich Lambert was a Swiss polymath who made important contributions to the subjects of mathematics, physics, philosophy, astronomy and map projections.

Lambert's Law: If temperature, composition, and other factors including wavelength are kept constant, then the rate of absorption of intensity of incident monochromatic radiation with

distance on passage through a homogenous absorbing substance, $-\dfrac{dI}{dx}$, where dI is the change in intensity and x the distance, is directly proportional to the intensity of incident monochromatic radiation traversing the slab, namely, that

$$-\frac{dI}{dx} = k\,I$$

The constant of proportionality, k, appearing in the above equation is called the absorption coefficient, and this is a characteristic of the absorbing substance and a measurement of how strong a chemical species absorbs light at a given wavelength. Further, the negative sign signifies that the intensity of incident monochromatic radiation traversing the slab decreases with distance.

$$-\frac{dI}{dt} = k\,I\,\frac{dx}{dt}$$

In optics, the refractive index or index of refraction of a substance is a dimensionless number that describes how fast light travels through the substance. The refractive index of a substance (η) is equal to the speed of light (c) divided by the velocity of light through the substance (v):

$$\eta = \frac{c}{v}$$

$$v = \frac{dx}{dt} = \frac{c}{\eta}$$

$$-\frac{dI}{dt} = k\,I\,\frac{c}{\eta}$$

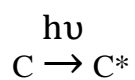**Molar absorption coefficient** is defined as:

$$\varepsilon = \frac{k}{C}$$

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where C is the concentration of the absorbing chemical species.

$$-\frac{dI}{dt} = \frac{\varepsilon\,Ic}{\eta} \times C$$

$$\text{Light absorption rate} \propto \frac{I}{\eta} \times C$$

For Photoexcitation process:

$$C \xrightarrow{h\upsilon} C^*$$

$$\text{Rate} = \frac{dC^*}{dt} = I_a \times \varphi_{\text{excitation}}$$

where $\varphi_{\text{excitation}} = \dfrac{\text{number of molecules excited}}{\text{number of photons absorbed}} = \dfrac{n^*}{n_a}$
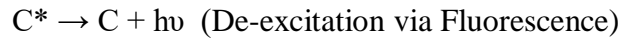
$$\frac{-dI/dt}{dC^*/dt} = \frac{\varepsilon\,Ic}{\eta} \times \frac{C}{I_a\varphi_{\text{excitation}}}$$

Absorbed intensity of incident monochromatic radiation is defined as:

$$I_a = I\,(1 - T)$$

where T is the transmittance.

$$-\frac{dI}{dC^*} = \frac{\varepsilon c}{\eta} \times \frac{C}{(1-T)\varphi_{excitation}}$$

$$C^* \rightarrow C + h\upsilon \quad \text{(De-excitation via Fluorescence)}$$

$$\text{Rate} = -\frac{dC^*}{dt} = k_2\,C^*$$

where k_2 is the rate constant.

The **Degree of de-excitation** (α_d) is the fraction of excited molecules de-excited via Fluorescence.

$$\alpha_d = \frac{\text{number of excited molecules de-excited via Fluorescence}}{\text{number of excited molecules}} = \frac{n_d}{n^*}$$

$$\varphi_{excitation} = \frac{n^*}{n_a} = \frac{n_d}{\alpha_d n_a}$$

Fluorescence quantum yield:

$$\varphi_F = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} = \frac{n_e}{n_a}$$

$$\frac{\varphi_{excitation}}{\varphi_F} = \frac{n_d}{\alpha_d n_e}$$

$$\boldsymbol{\alpha}_d \times \frac{\varphi_{\text{excitation}}}{\varphi_F} = \frac{\text{number of excited molecules de}-\text{excited via Fluorescence}}{\text{number of photons emitted}}$$

$$\boldsymbol{\alpha}_d \times \frac{\varphi_{\text{excitation}}}{\varphi_F} = \frac{-\dfrac{dC^*}{dt}}{\text{Fluorescence intensity}} = \frac{k_2 C^*}{I_F}$$

$$\varphi_{\text{excitation}} = \frac{k_2 C^*}{I_F} \times \frac{\varphi_F}{\alpha_d} = \frac{k_2 C^*}{I_a} \times \frac{1}{\alpha_d} = \frac{k_2 C^*}{I(1-T)} \times \frac{1}{\alpha_d}$$

$$-\frac{dI}{dC^*} = \frac{\varepsilon c}{\eta} \times \frac{C}{(1-T)\varphi_{\text{excitation}}}$$

$$-\frac{dI}{dC^*} = \frac{\varepsilon c}{\eta} \times \frac{\alpha_d \, I \, C}{k_2 C^*}$$

The **Degree of excitation** (α^*) is the fraction of molecules excited via photon absorption.

$$\boldsymbol{\alpha}^* = \frac{\text{number of molecules excited via Photon absorption}}{\text{number of absorbing molecules}} = \frac{C^*}{C}$$

$$-\frac{dI}{dC^*} = \frac{\varepsilon c}{\eta} \times \frac{\alpha_d \, I}{k_2 \boldsymbol{\alpha}^*}$$

The equation $-\dfrac{dC^*}{dt} = k_2 \, C^*$ typically follows **first order kinetics**.

$$d\ln C^* = -k_2 dt$$

On integration within the limits of C_0^* to C^* for concentration of excited molecules and 0 to t for time we get,

$$\int_{C_0^*}^{C^*} d\ln C^* = -k_2 \int_0^t dt$$

From this it follows that:

$$\ln \left(\frac{C^*}{C_0^*}\right) = -k_2 t$$
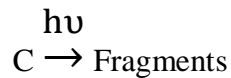
If $C^* = \dfrac{1}{e} C_0^*$:

$$t = \Gamma$$

$$k_2 = \frac{1}{\Gamma}$$

$\Gamma \rightarrow$ is the time at which the concentration of excited molecules has reduced to $\dfrac{1}{e}$ of the original value.

$$-\frac{dI}{dC^*} = \frac{\varepsilon c}{\eta} \times \frac{\alpha_d I \Gamma}{\alpha^*}$$

Note:

$$C \xrightarrow{h\upsilon} \text{Fragments}$$

Quantum yield for Photodissociation process:

$$\varphi = \frac{\text{number of molecules dissociated}}{\text{number of photons absorbed}}$$

$$\frac{\varphi}{\varphi_{\text{excitation}}} = \frac{\text{number of molecules dissociated}}{\text{number of molecules excited}} = \varkappa$$

- where $\varkappa$ is the transmission coefficient (the fraction of excited molecules dissociated into fragments without undergoing the process of **de-excitation**)

August Beer was a German physicist, chemist, and mathematician of Jewish descent.

$$-\frac{dI}{dt} = \frac{\varepsilon\, Ic}{\eta} \times C$$

$$\frac{-dI/dt}{I} = \frac{\varepsilon c}{\eta} \times C$$

$$\left.\frac{-dI/dt}{I}\right\} = k_r$$

where k_r, called the light absorption rate coefficient, is a measurement of how fast a chemical species absorbs light at a given wavelength.

$$k_r = \frac{\varepsilon c}{\eta} \times C$$

Molar absorption rate coefficient is defined as:

$$\boxed{K_M = \frac{k_r}{C}}$$

where C is the concentration of the absorbing chemical species.

$$K_M = \frac{\varepsilon c}{\eta}$$

$$\frac{K_M}{\varepsilon} = \frac{c}{\eta}$$

Since η is always less than c. Therefore:

$$\boxed{K_M \text{ is} > \text{than } \varepsilon}$$

which means: rate of absorption is always greater than the strength of absorption.

One Einstein = $N_A\, h\upsilon$

One Einstein = $6.02214076 \times 10^{23}\ \mathrm{mol^{-1}} \times \dfrac{hc}{\lambda}$

One Einstein = $6.02214076 \times 10^{23} \times 6.625 \times 10^{-34} \times 3 \times 10^{8} \times \dfrac{1}{\lambda}$

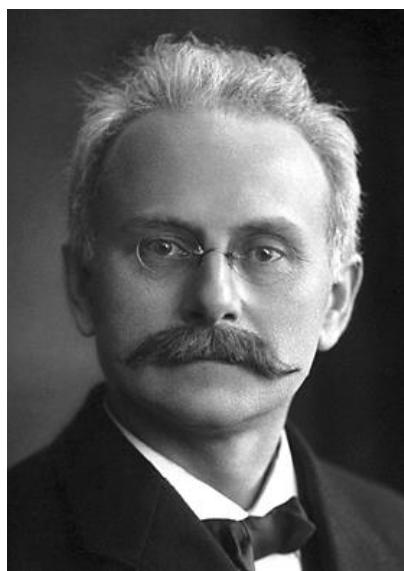One Einstein = $119.690047605 \times 10^{-3}\ \mathrm{J\text{-}m/mol} \times \dfrac{1}{\lambda}$

John William Draper was an English-born American scientist, philosopher, physician, chemist, historian and photographer. He is credited with producing the first clear photograph of a female face and the first detailed photograph of the moon in 1840.

Freiherr Christian Johann Dietrich Theodor von Grotthuss was a Lithuanian chemist of German descent known for establishing the first theory of electrolysis in 1806 and formulating the first law of photochemistry in 1817.

Johannes Stark was a German physicist who was awarded the Nobel Prize in Physics in 1919 "for his discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields". This phenomenon is known as the Stark effect.

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