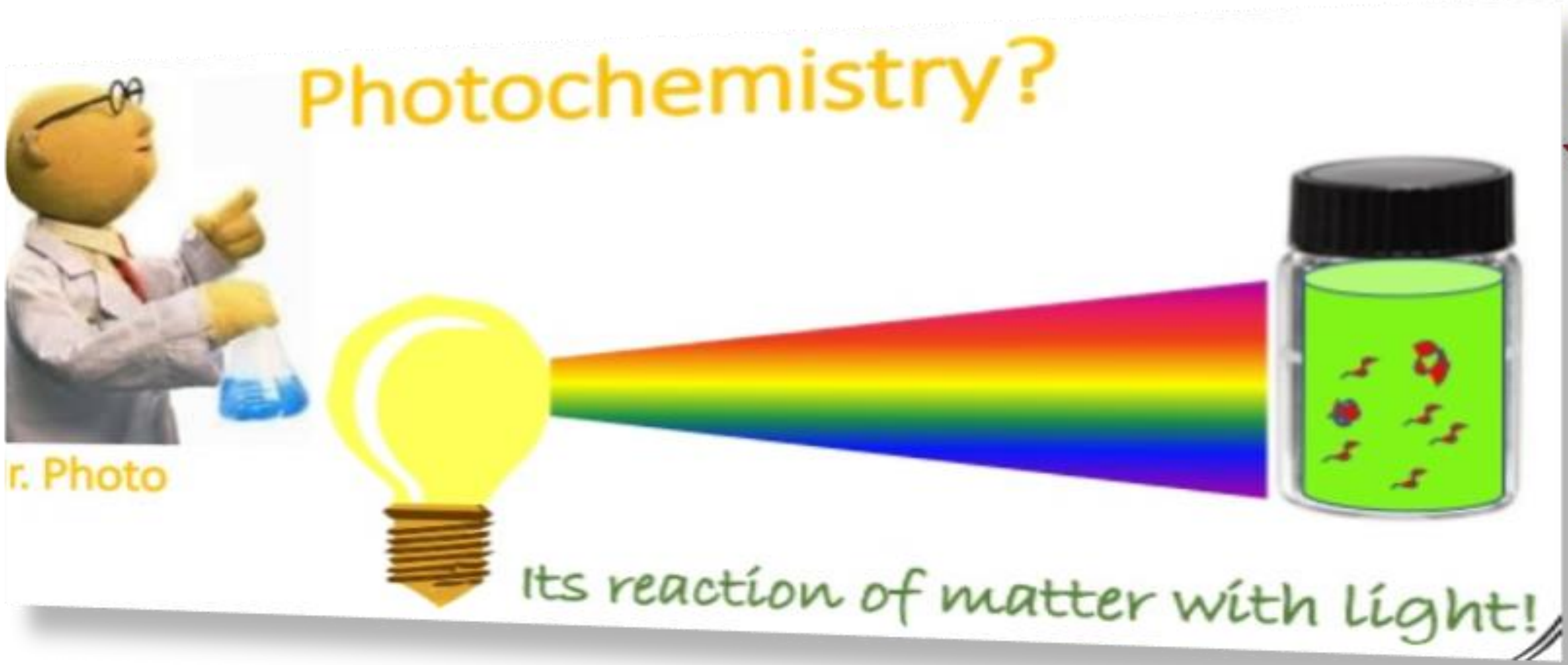
PHOTOCHEMISTRY



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Paper-II: Physical Chemistry

Unit- IVth

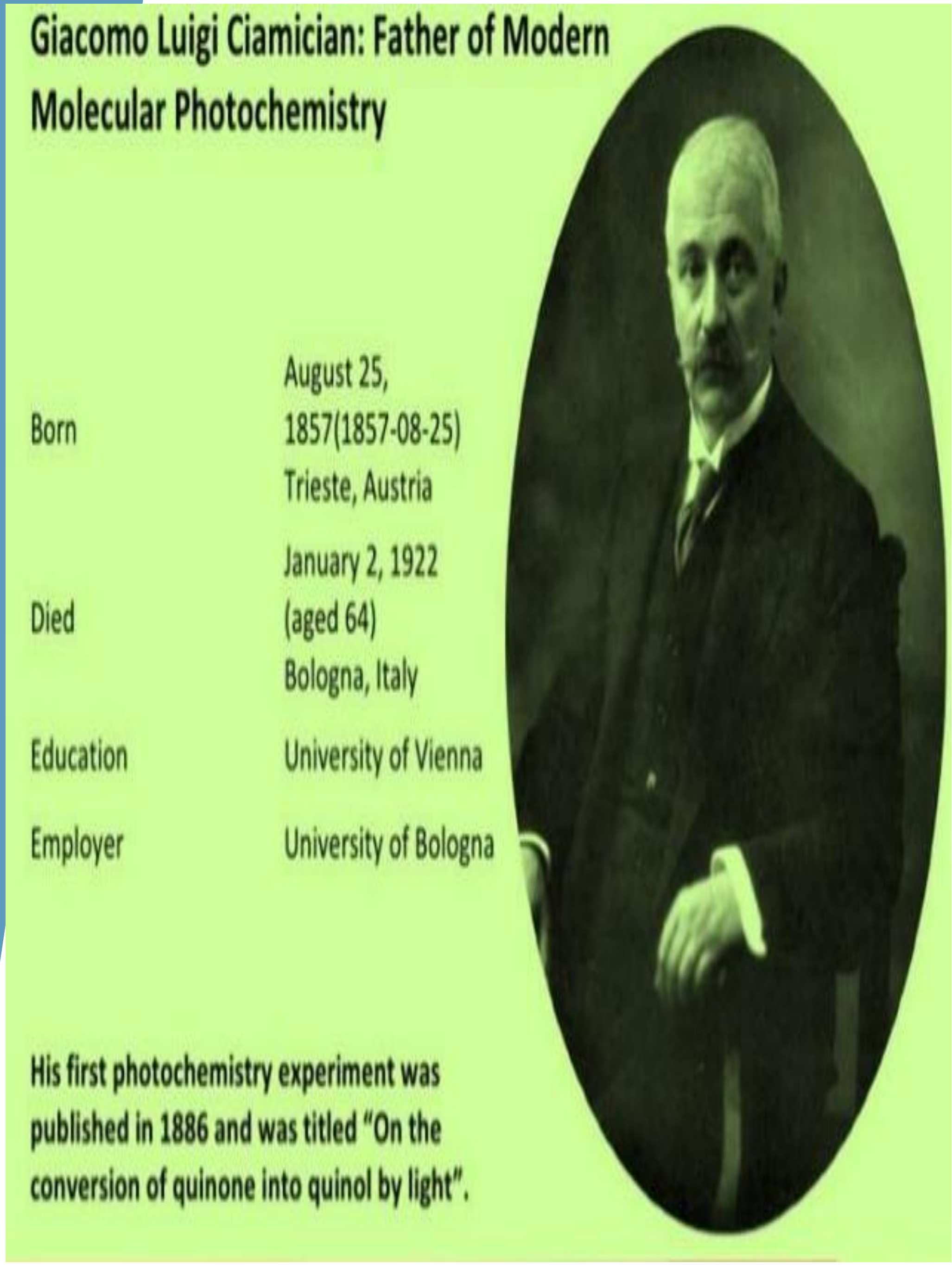
A] Photochemistry

B] Ramam Spectroscopy

Photochemistry

Agenda

- **Introduction**
- **Lambert’s law**
- **Beer’s law**
- **Law of photochemistry**
- **Quantum Yield or quantum efficiency**
- **Jablonski diagram**
- **Fluorescence**
- **Phosphoresce**
- **Chemiluminescence**
- **Photosensitization**



Giacomo Luigi Ciamician: Father of Modern Molecular Photochemistry

Born	August 25, 1857(1857-08-25) Trieste, Austria
Died	January 2, 1922 (aged 64) Bologna, Italy
Education	University of Vienna
Employer	University of Bologna

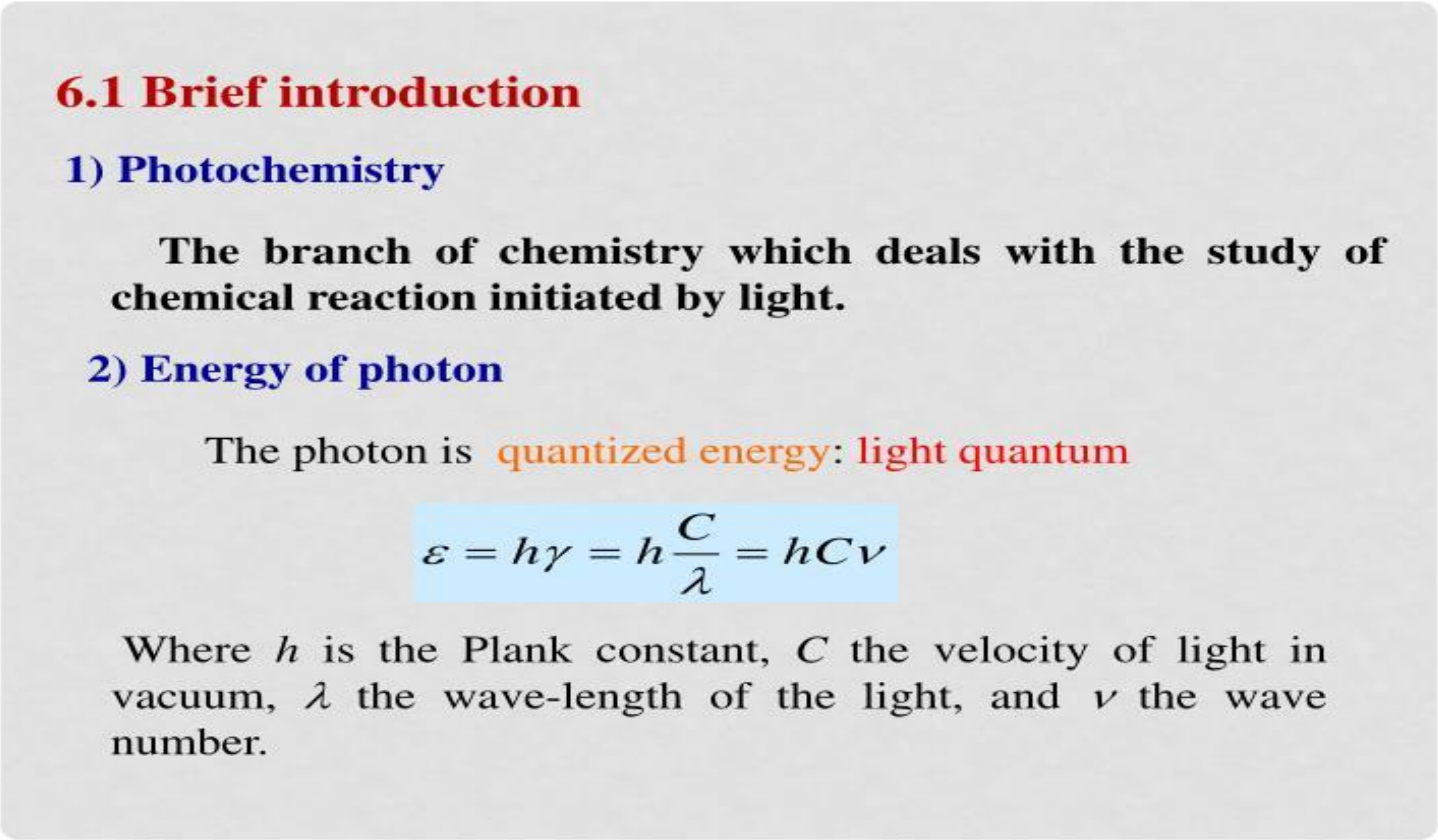
His first photochemistry experiment was published in 1886 and was titled "On the conversion of quinone into quinol by light".

Introduction

Defination: the study of interaction with matter resulting into a physical change or into a chemical reaction whose rates and mechanisms are studied after initiation by the radiant energy is called as photochemistry.

- The reaction which take place by absorbing of light by the reacting substance are called as photochemical reaction
- In photochemical reactions, importance radiations are visible and ultraviolent region from (8000Ao - 2000Ao) 800 nm-200nm

Introduction



6.1 Brief introduction

1) Photochemistry

The branch of chemistry which deals with the study of chemical reaction initiated by light.

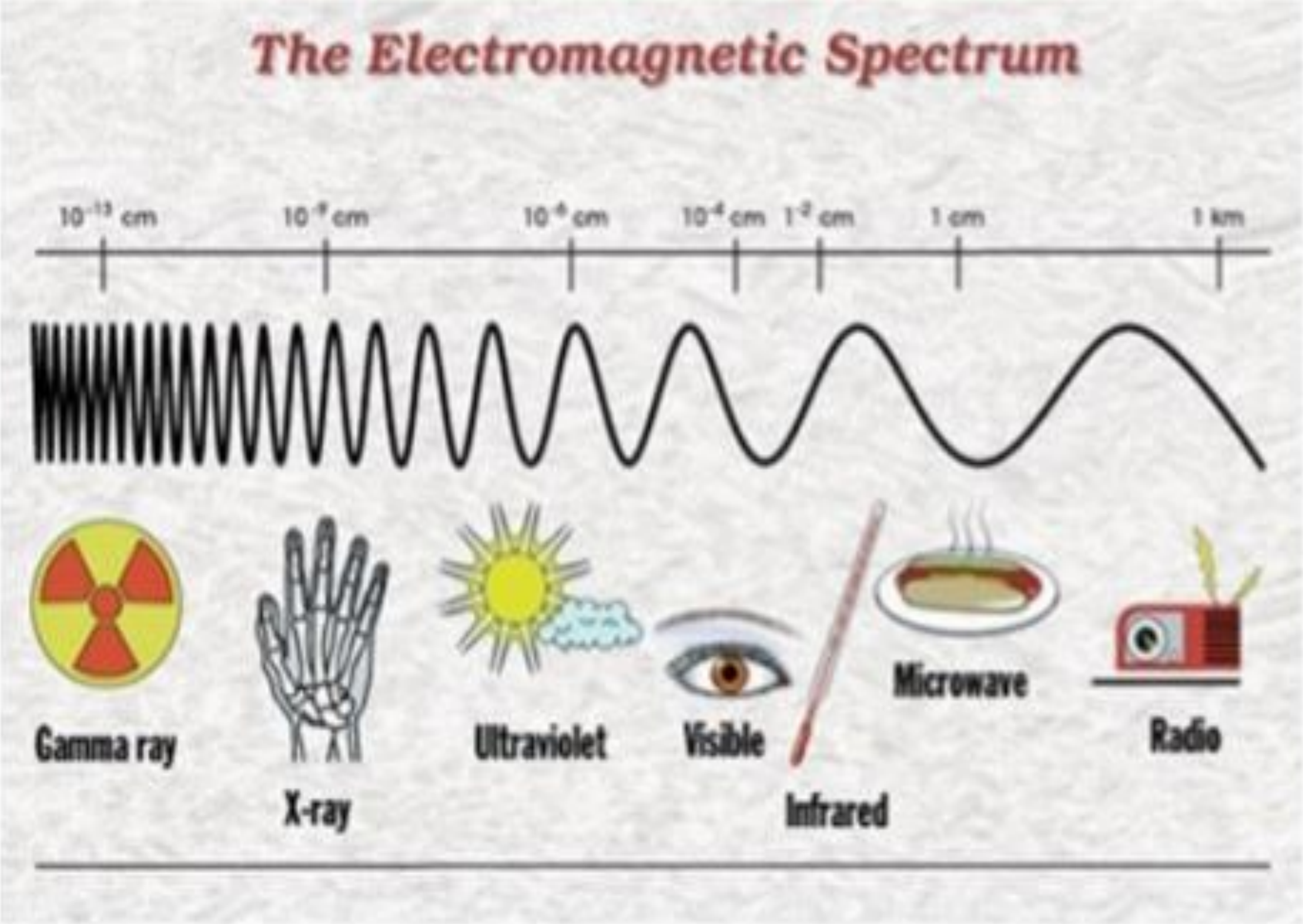
2) Energy of photon

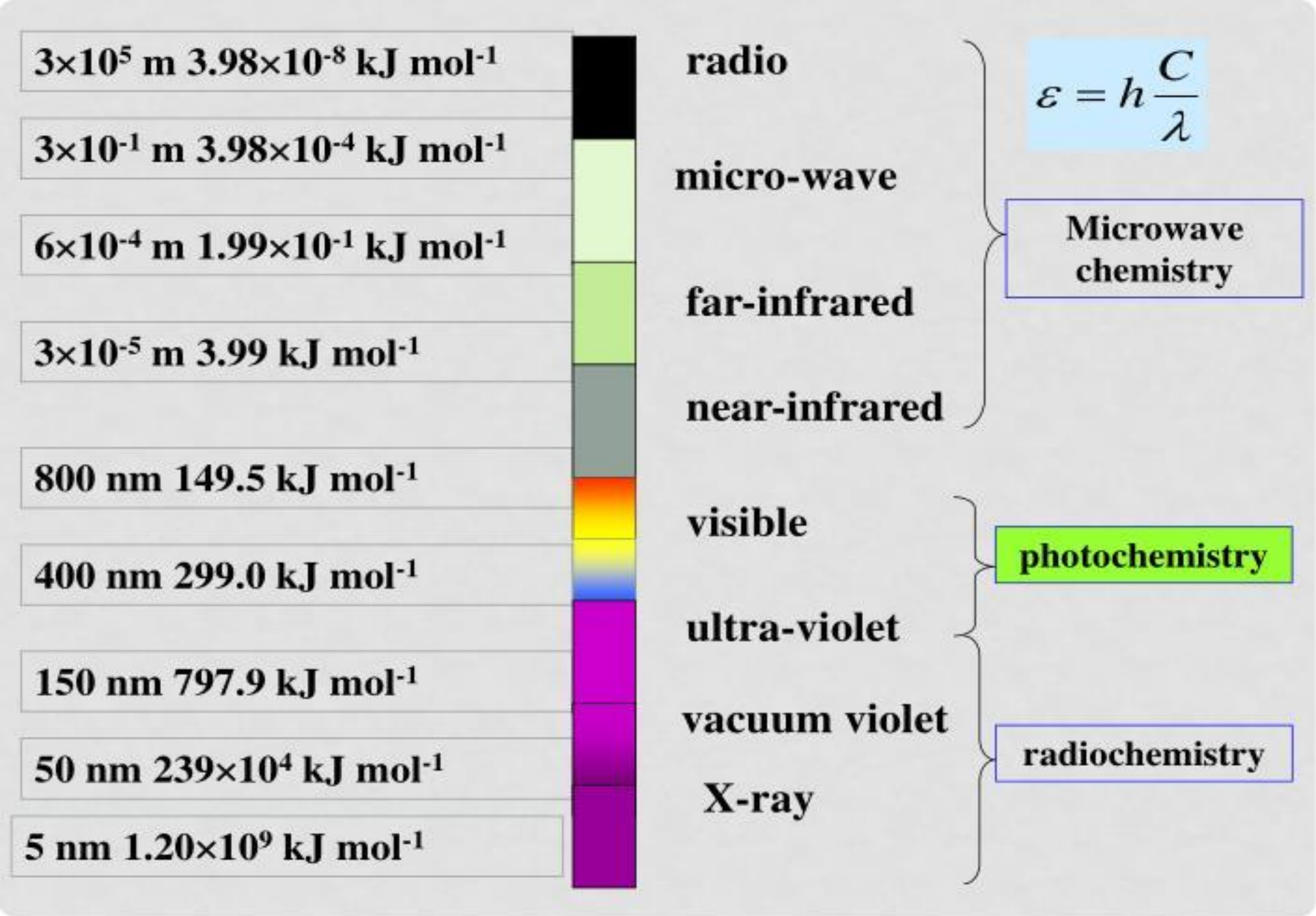
The photon is quantized energy: light quantum

$$\varepsilon = h\gamma = h\frac{C}{\lambda} = hC\nu$$

Where h is the Plank constant, C the velocity of light in vacuum, λ the wave-length of the light, and ν the wave number.

(Light) Electromagnetic spectrum important for photochemistry:





3×10^{5} m 3.98×10^{-8} kJ mol^{-1}

3×10^{-1} m 3.98×10^{-4} kJ mol^{-1}

6×10^{-4} m 1.99×10^{-1} kJ mol^{-1}

3×10^{-5} m 3.99 kJ mol^{-1}

800 nm 149.5 kJ mol^{-1}

400 nm 299.0 kJ mol^{-1}

150 nm 797.9 kJ mol^{-1}

50 nm 239×10^{4} kJ mol^{-1}

5 nm 1.20×10^{9} kJ mol^{-1}

radio

micro-wave

far-infrared

near-infrared

visible

ultra-violet

vacuum violet

X-ray

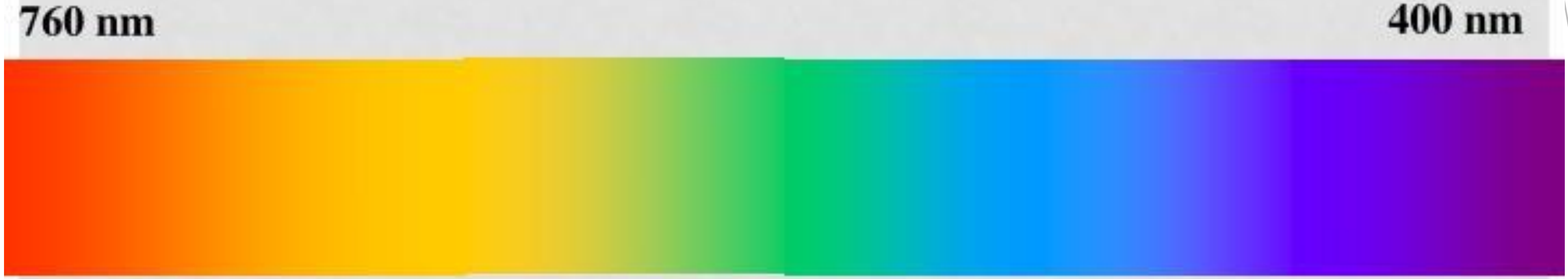
$$\varepsilon = h\frac{C}{\lambda}$$

Microwave chemistry

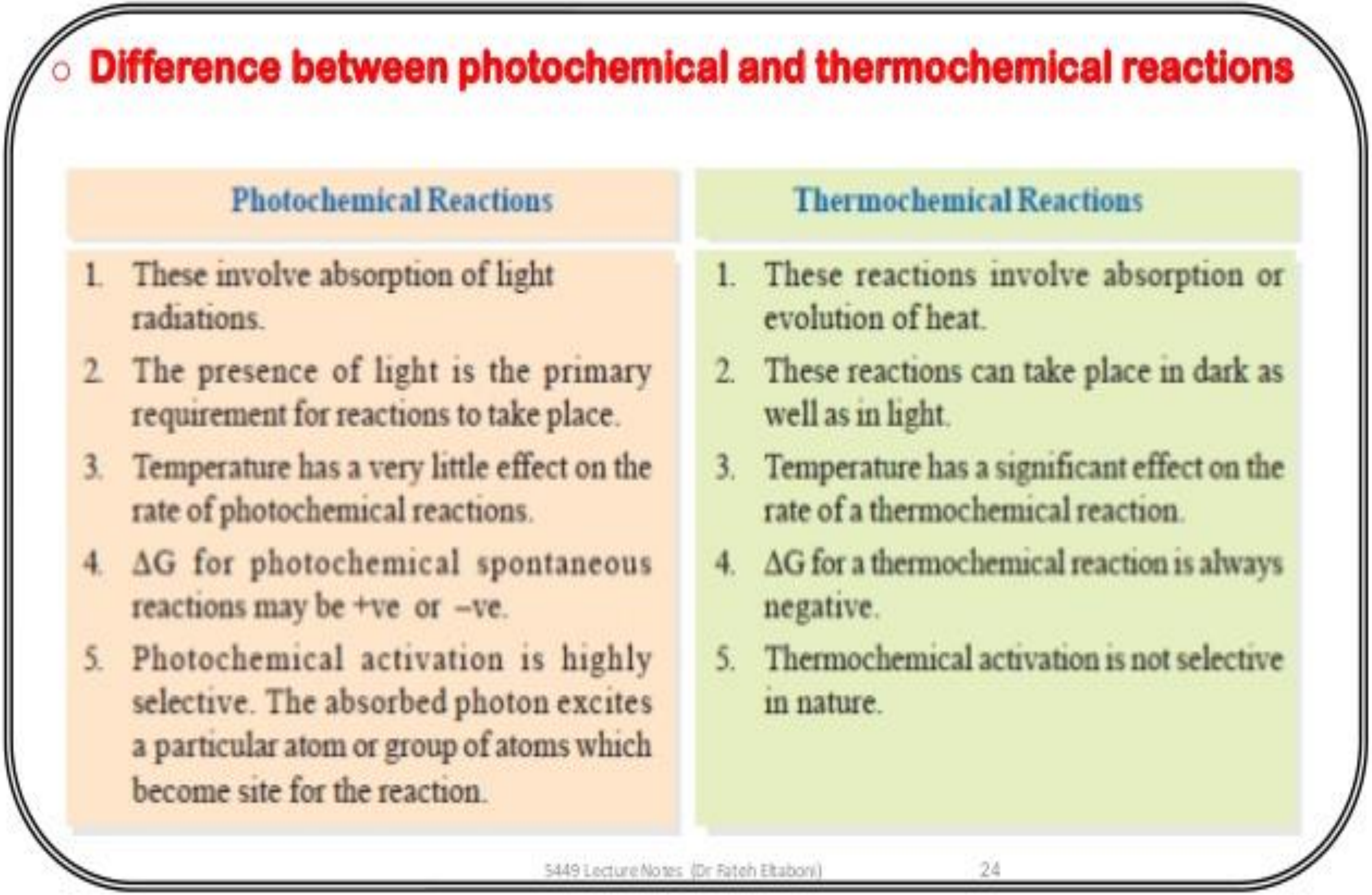
photochemistry

radiochemistry

3) Spectrum of visible light

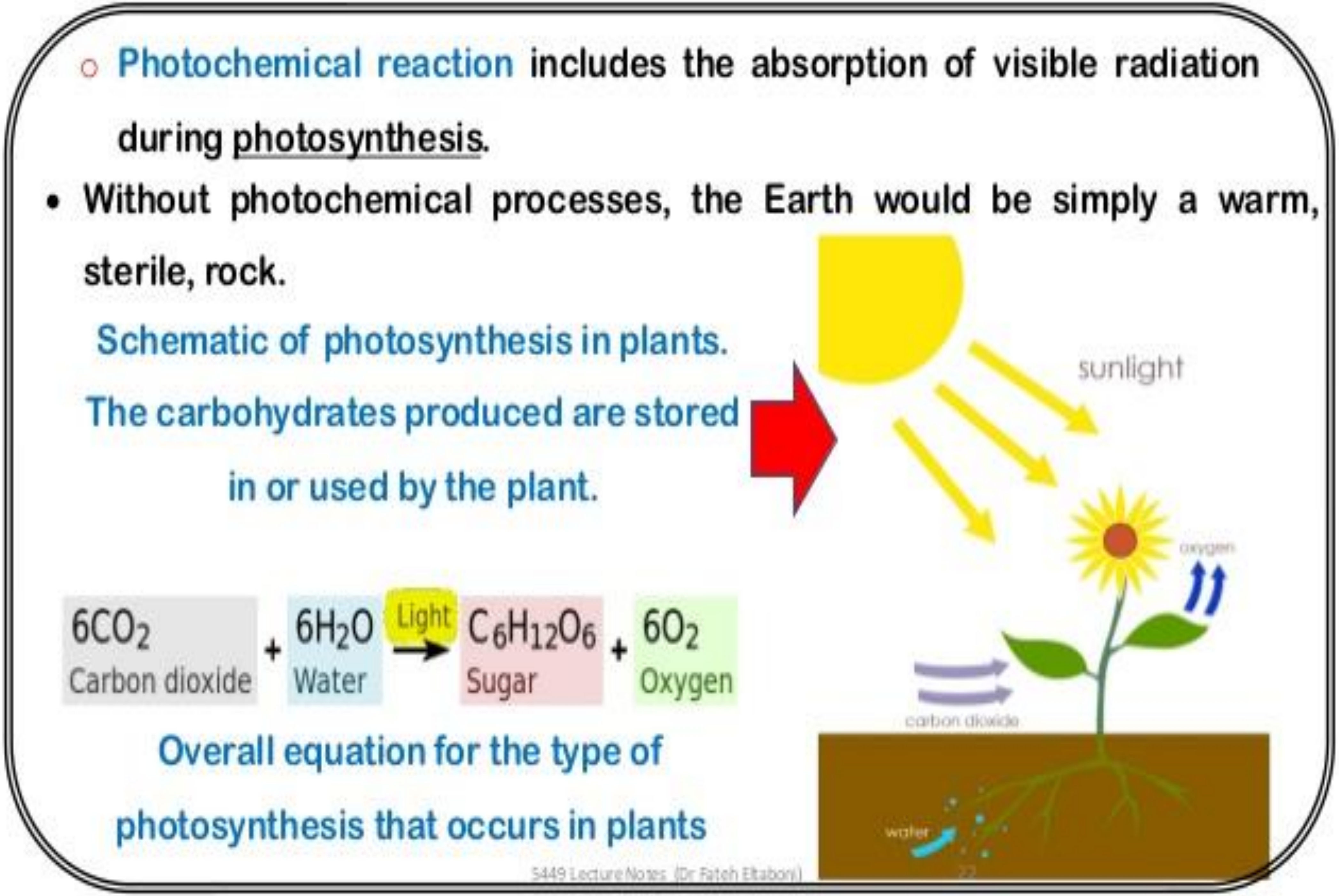


760-630 nm	630-600 nm	600-570 nm	570-500 nm	500-450 nm	450-430 nm	430-400 nm
red	orange	yellow	green	blue	indigo	violet



○ Difference between photochemical and thermochemical reactions

Photochemical Reactions	Thermochemical Reactions
1. These involve absorption of light radiations.	1. These reactions involve absorption or evolution of heat.
2. The presence of light is the primary requirement for reactions to take place.	2. These reactions can take place in dark as well as in light.
3. Temperature has a very little effect on the rate of photochemical reactions.	3. Temperature has a significant effect on the rate of a thermochemical reaction.
4. ΔG for photochemical spontaneous reactions may be +ve or –ve.	4. ΔG for a thermochemical reaction is always negative.
5. Photochemical activation is highly selective. The absorbed photon excites a particular atom or group of atoms which become site for the reaction.	5. Thermochemical activation is not selective in nature.



- ○ **Photochemical reaction** includes the absorption of visible radiation during photosynthesis.

- Without photochemical processes, the Earth would be simply a warm, sterile, rock.

Schematic of photosynthesis in plants. The carbohydrates produced are stored in or used by the plant.

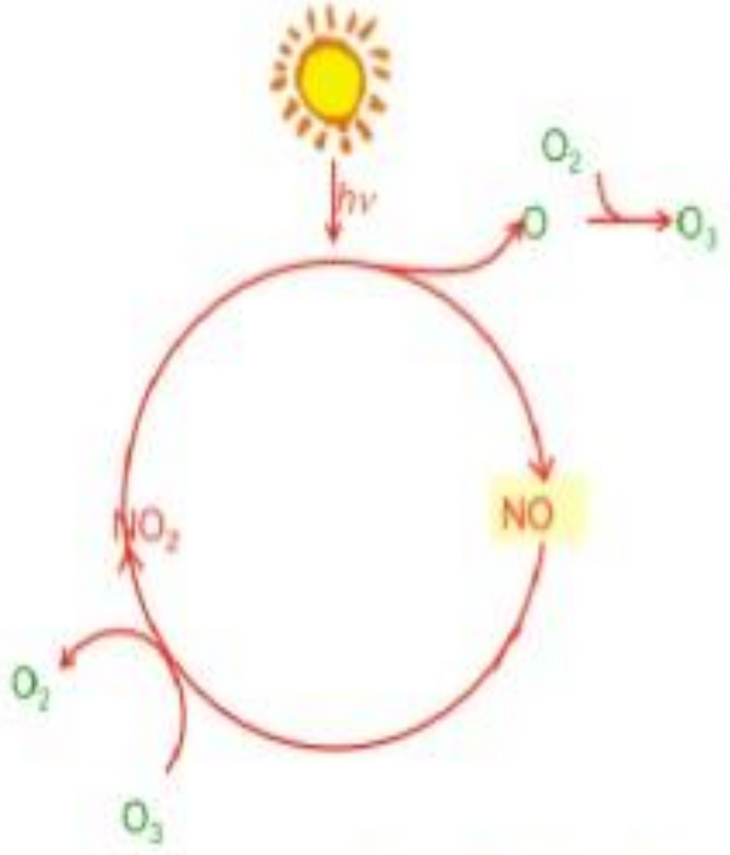
$$\underset{\text{Carbon dioxide}}{6CO_2} + \underset{\text{Water}}{6H_2O} \xrightarrow{\text{Light}} \underset{\text{Sugar}}{C_6H_{12}O_6} + \underset{\text{Oxygen}}{6O_2}$$

Overall equation for the type of photosynthesis that occurs in plants

- **Photochemical reaction**:
- Its a reaction which takes place by absorption of the visible and ultraviolet radiations (200-800 nm)

- Photochemical reaction

leads to the <u>heating of the atmosphere during the daytime</u> by absorption of ultraviolet radiation.



- Mechanism of photochemical reactions occurring during atmospheric: <u>Photochemical change occurs only by absorption of photons</u>.

- **Photochemistry:**
- **Its the branch of chemistry which deals with the study of photochemical reactions.**

  - **Demonstration of a Photochemical reaction**

$$H_2 + Cl_2 \xrightarrow{\text{dark}} \text{No reaction}$$

$$H_2 + Cl_2 \xrightarrow{\text{light}} 2HCl$$

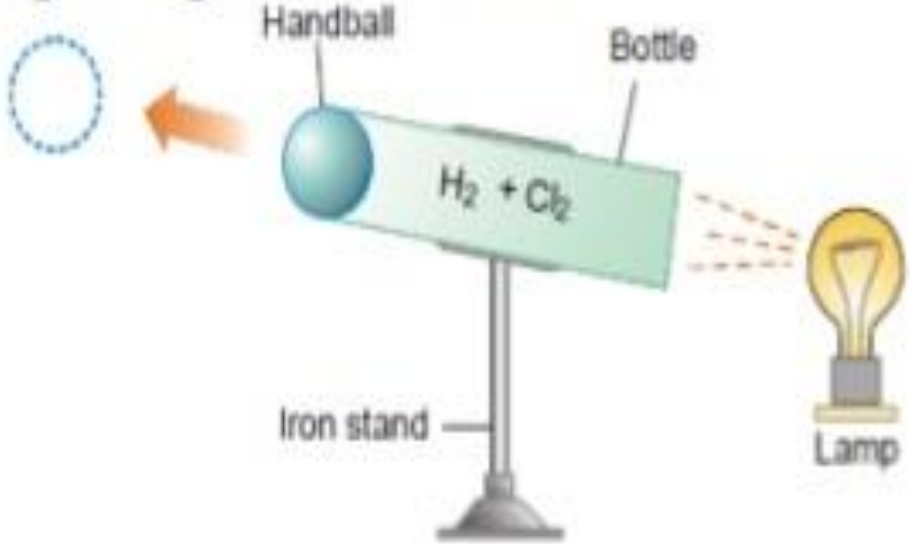
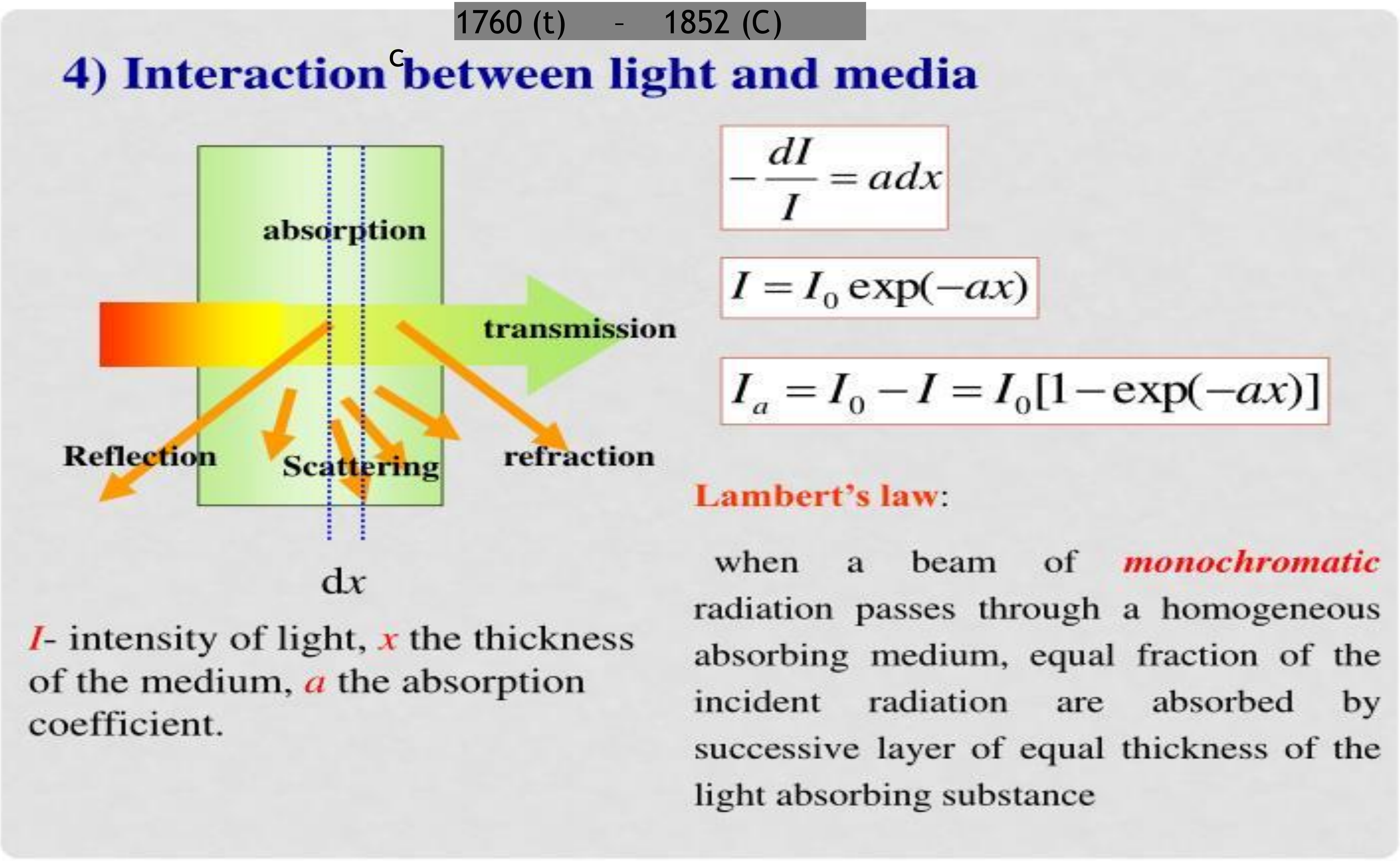


Figure 30.1
The 'HCl-cannon' experiment.

Lambert-beer's law

1760 (t) – 1852 (C)



4) Interaction between light and media

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

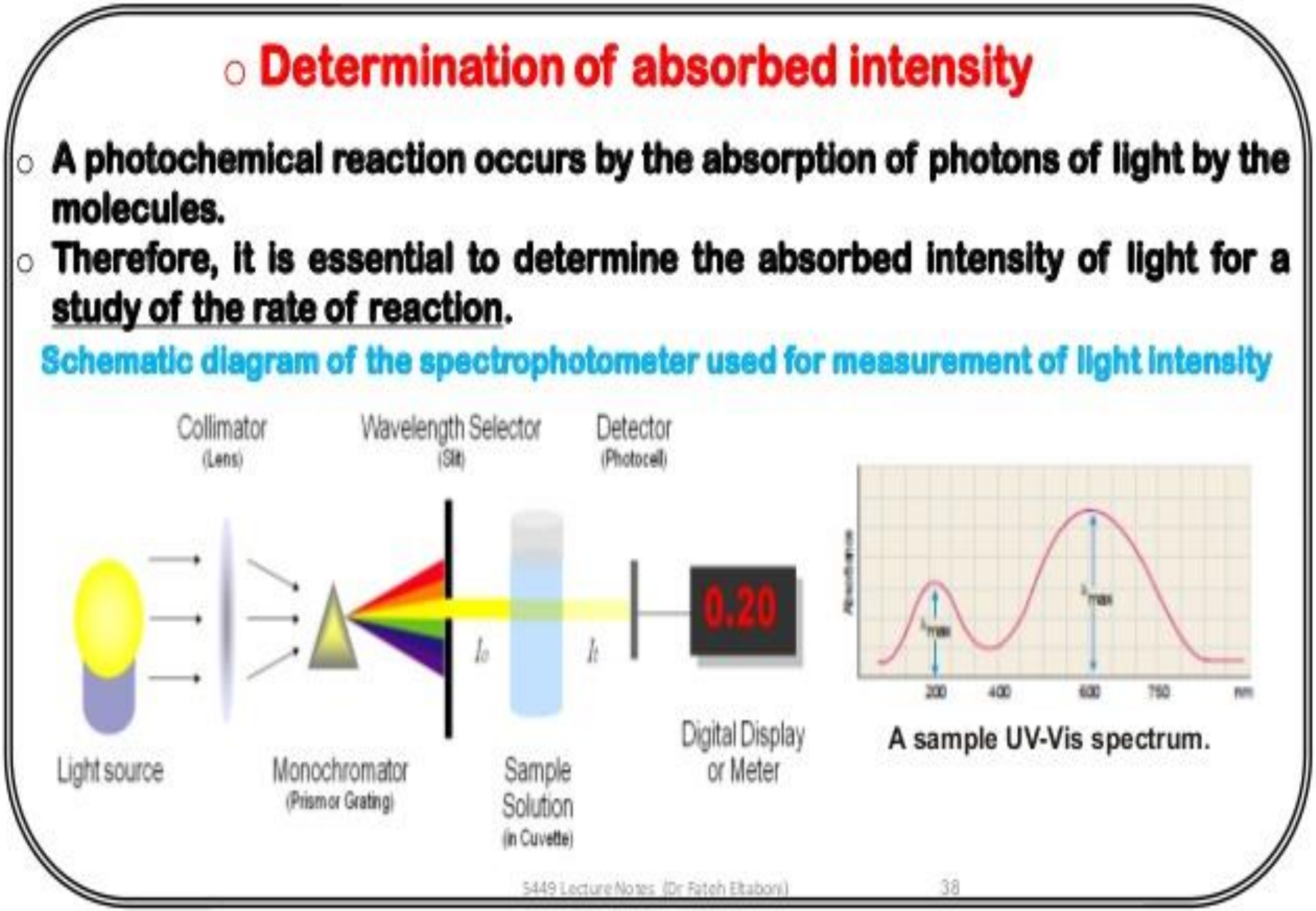
$$I = I_0 \exp(-ax)$$

$$I_a = I_0 - I = I_0[1 - \exp(-ax)]$$

I- intensity of light, *x* the thickness of the medium, *a* the absorption coefficient.

Lambert's law:

when a beam of ***monochromatic*** radiation passes through a homogeneous absorbing medium, equal fraction of the incident radiation are absorbed by successive layer of equal thickness of the light absorbing substance



○ Determination of absorbed intensity

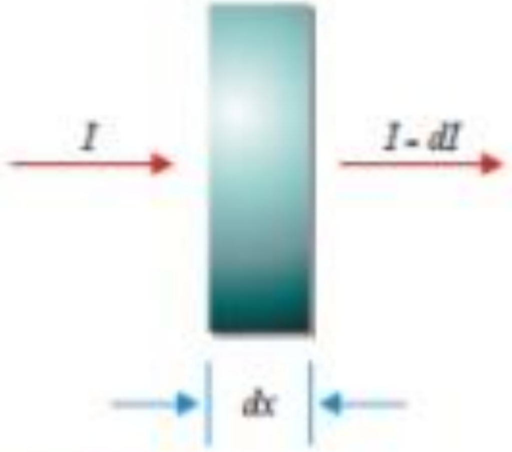
- ○ A photochemical reaction occurs by the absorption of photons of light by the molecules.
- ○ Therefore, it is essential to determine the absorbed intensity of light for a study of the rate of reaction.

Schematic diagram of the spectrophotometer used for measurement of light intensity

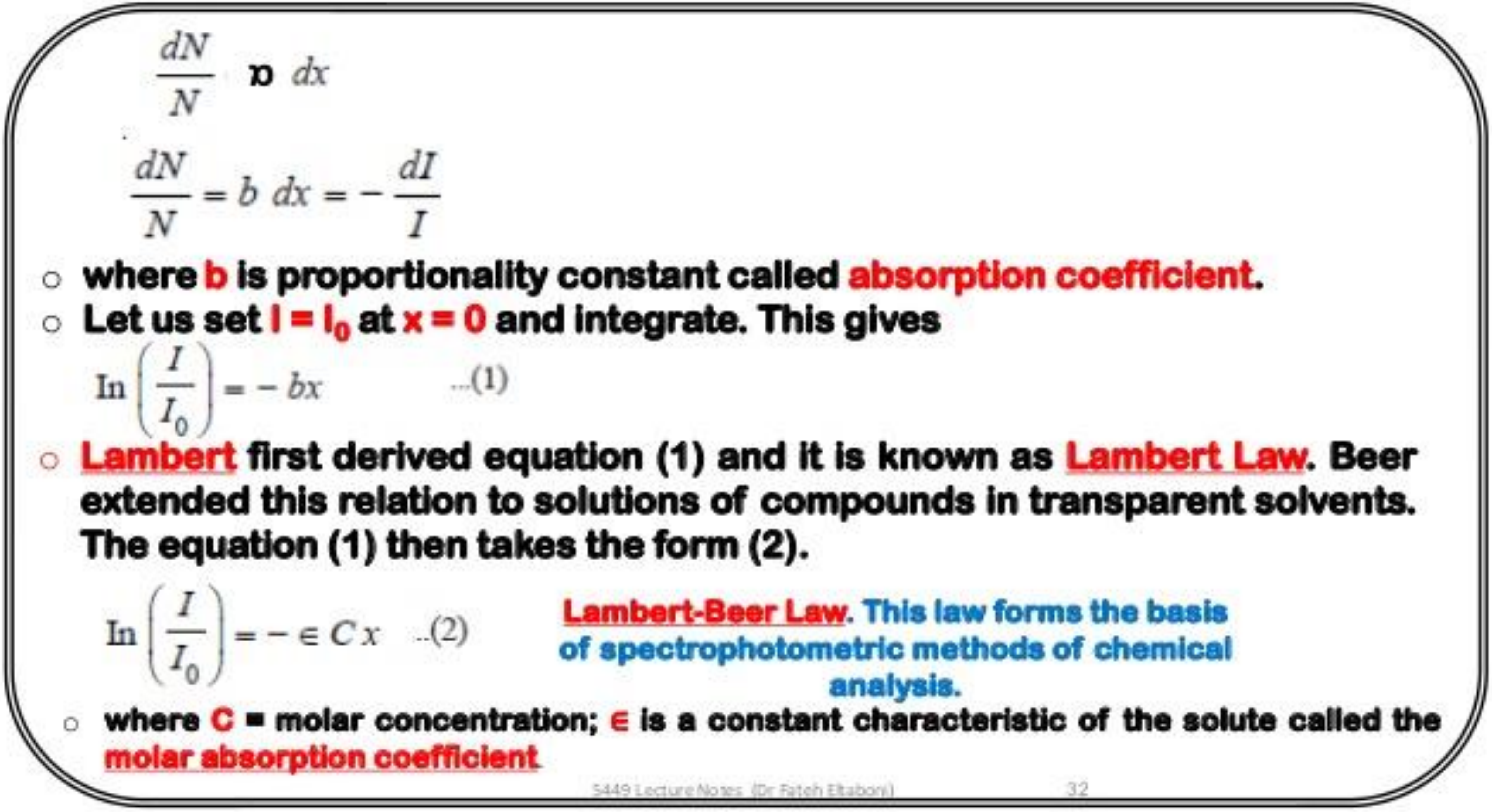
A sample UV-Vis spectrum.

○ Light absorption

- ○ When light is passed through a medium, a part of it is absorbed. This absorbed portion of light which causes photochemical reactions.
- ○ Let a beam of monochromatic light pass through a thickness dx of the medium. The intensity of radiation reduces from I to I-dI.
- ○ **The intensity** of radiation can be defined as the number of photons that pass across a unit area in unit time.
- ○ Let us denote the number of incident photons by N and the number absorbed in thickness dx by dN.
- ○ The fraction of photons absorbed is then dN/N which is proportional to thickness dx. That is,



■ **Figure 30.2**
As a beam of intensity I passes through a medium of thickness dx, the intensity of the beam is reduced to $I - dI$.



$$\frac{dN}{N} \propto dx$$

$$\frac{dN}{N} = b\ dx = -\frac{dI}{I}$$

- where b is proportionality constant called absorption coefficient.
- Let us set $I = I_0$ at $x = 0$ and integrate. This gives

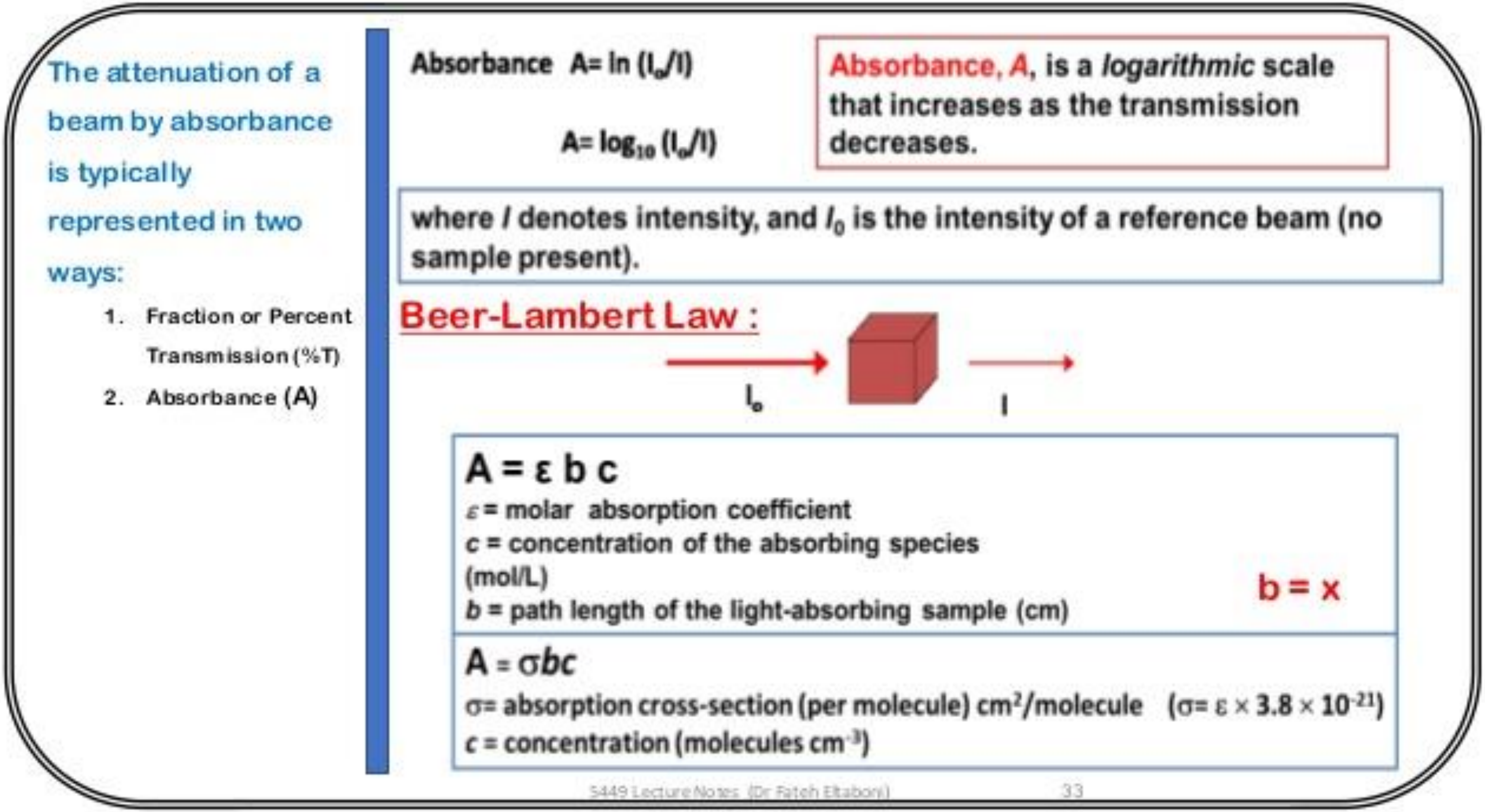
$$\ln\left(\frac{I}{I_0}\right) = -bx \qquad ...(1)$$

- Lambert first derived equation (1) and it is known as Lambert Law. Beer extended this relation to solutions of compounds in transparent solvents. The equation (1) then takes the form (2).

$$\ln\left(\frac{I}{I_0}\right) = -\in C\,x \qquad ..(2)$$

Lambert-Beer Law. This law forms the basis of spectrophotometric methods of chemical analysis.

- where C = molar concentration; $\in$ is a constant characteristic of the solute called the molar absorption coefficient



The attenuation of a beam by absorbance is typically represented in two ways:

1. Fraction or Percent Transmission (%T)
2. Absorbance (A)

Absorbance $A = \ln(I_o/I)$

$A = \log_{10}(I_o/I)$

Absorbance, *A*, is a *logarithmic* scale that increases as the transmission decreases.

where *I* denotes intensity, and I_0 is the intensity of a reference beam (no sample present).

Beer-Lambert Law :

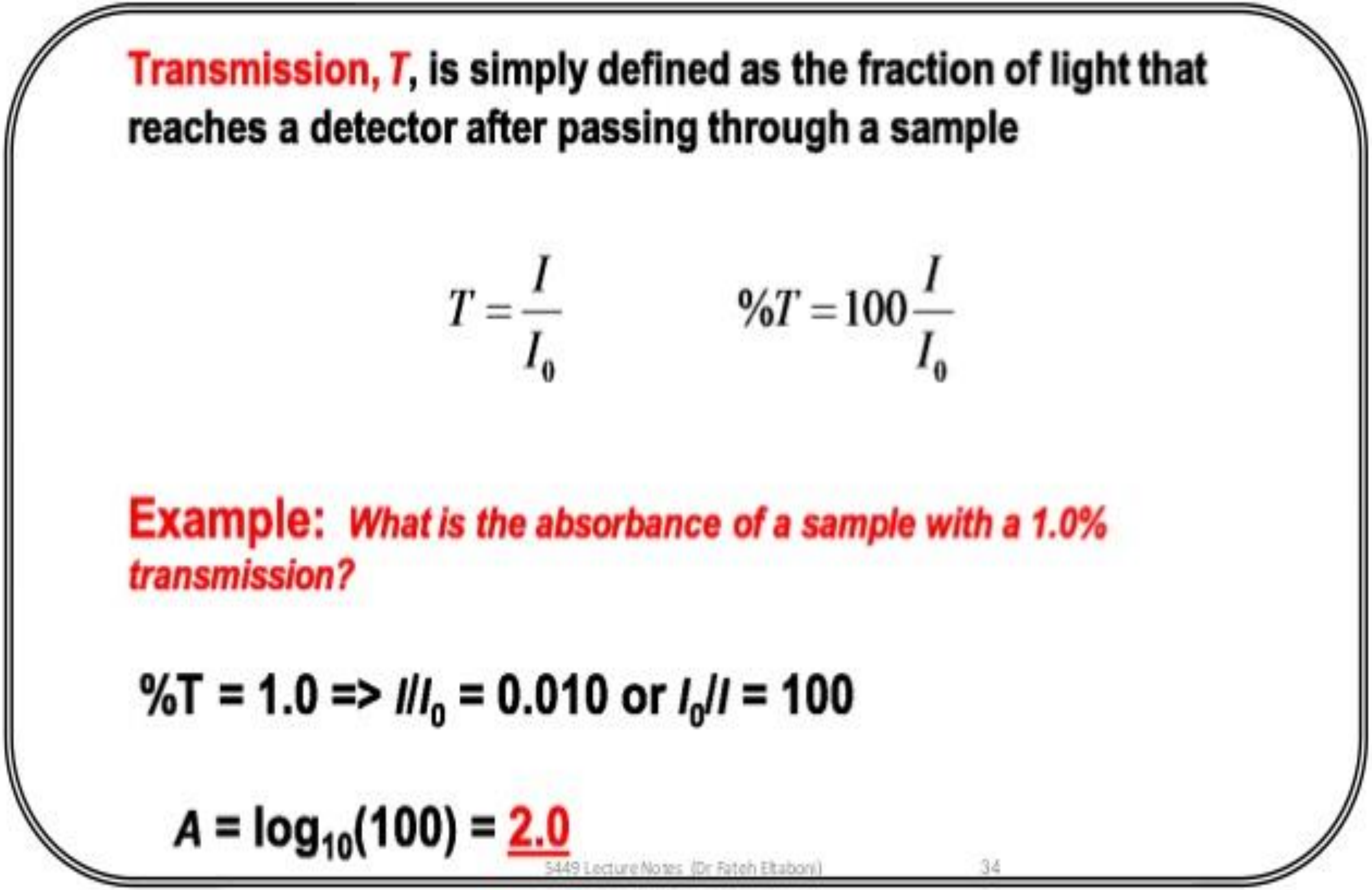
$A = \varepsilon\, b\, c$

ε = molar absorption coefficient
c = concentration of the absorbing species (mol/L)
b = path length of the light-absorbing sample (cm)

b = x

$A = \sigma b c$

σ= absorption cross-section (per molecule) cm^2/molecule ($\sigma = \varepsilon \times 3.8 \times 10^{-21}$)
c = concentration (molecules cm^{-3})



Transmission, *T*, is simply defined as the fraction of light that reaches a detector after passing through a sample

$$T = \frac{I}{I_0} \qquad \%T = 100\frac{I}{I_0}$$

Example: ***What is the absorbance of a sample with a 1.0% transmission?***

$\%T = 1.0 \Rightarrow I/I_0 = 0.010$ or $I_0/I = 100$

$A = \log_{10}(100) = \underline{2.0}$

Example:

The percentage transmittance of an aqueous solution of disodium fumarate at 250 nm is 19.2% for 5×10^{-4} mol/L solution in 1 cm cell.

(a) Calculate the absorbance A and molar absorption coefficient ε.

(b) what will be The percentage transmittance of a 1.75×10^{-5} mol/L soultion in 10 cm

(a) $A = \log (I_o/I) \qquad = \log (100/19.2) = 0.717$

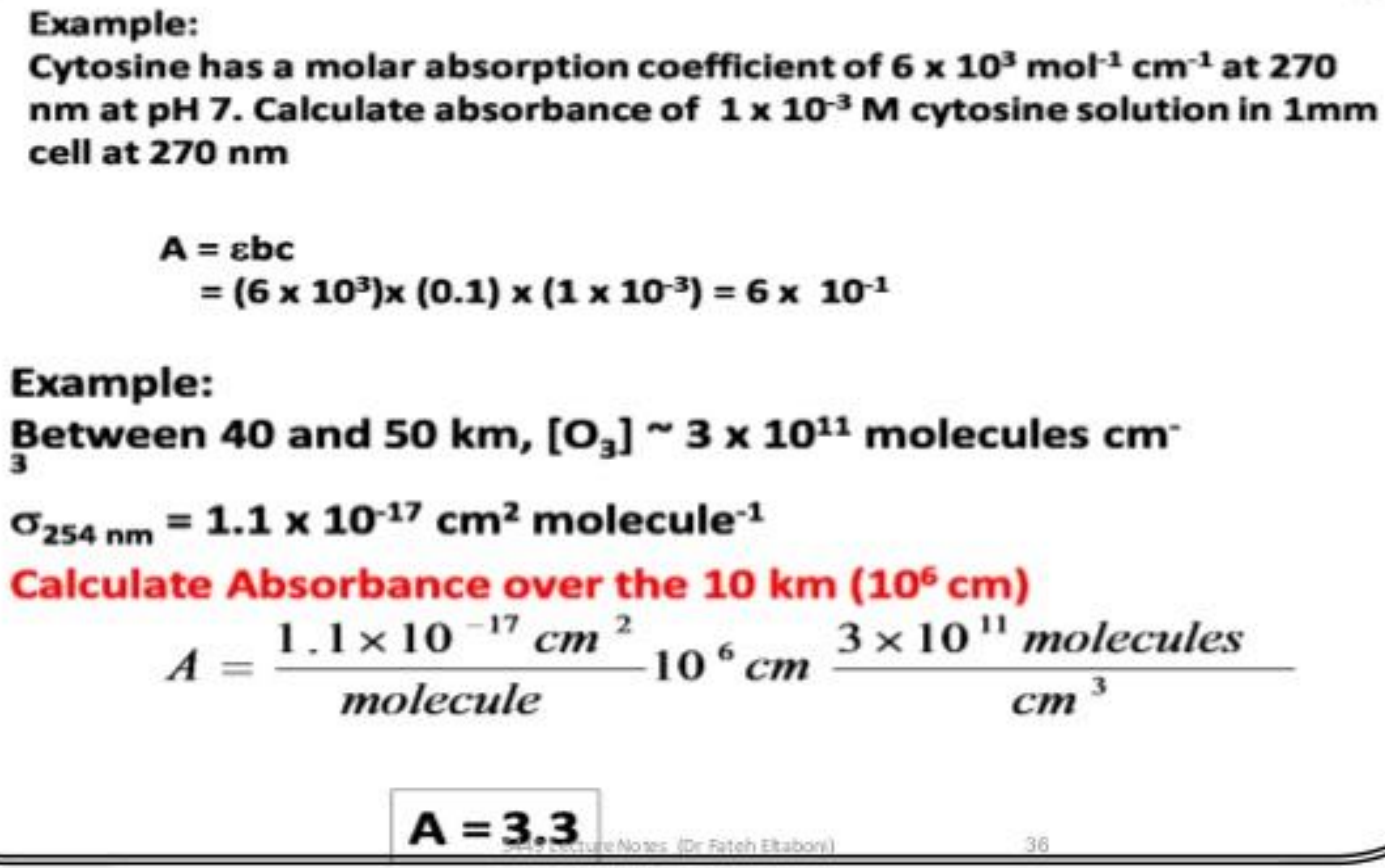
$\varepsilon = A/bc = 0.717/ 1\text{ cm} \times 5\times10^{-4}\text{ mol/L} = 1.43\times10^{3}\text{ L/ mol. cm}$

(b) $\log (I_o/I) = A\, b\, \varepsilon$

$\log (I_o/I) = (1.43\times10^{3}\text{ L/ mol. cm})\,(10\text{ cm})\,(1.75\times10^{-5}\text{ mol/L}) = 0.251$

$(I_o/I) = 1.782$

$\%T = 100\frac{I}{I_o} \qquad 100\, I/I_o = 56.1\ \%$



Example:

Cytosine has a molar absorption coefficient of 6×10^{3} mol^{-1} cm^{-1} at 270 nm at pH 7. Calculate absorbance of 1×10^{-3} M cytosine solution in 1mm cell at 270 nm

$$A = \varepsilon bc$$
$$= (6 \times 10^{3}) \times (0.1) \times (1 \times 10^{-3}) = 6 \times 10^{-1}$$

Example:

Between 40 and 50 km, $[O_3]$ ~ 3×10^{11} molecules cm^{-3}

$\sigma_{254\,nm} = 1.1 \times 10^{-17}$ cm^{2} $molecule^{-1}$

Calculate Absorbance over the 10 km (10^{6} cm)

$$A = \frac{1.1 \times 10^{-17}\ cm^{2}}{molecule} 10^{6}\ cm\ \frac{3 \times 10^{11}\ molecules}{cm^{3}}$$

$$\boxed{A = 3.3}$$

6.2 Photochemistry

(1) The first law of photochemistry:

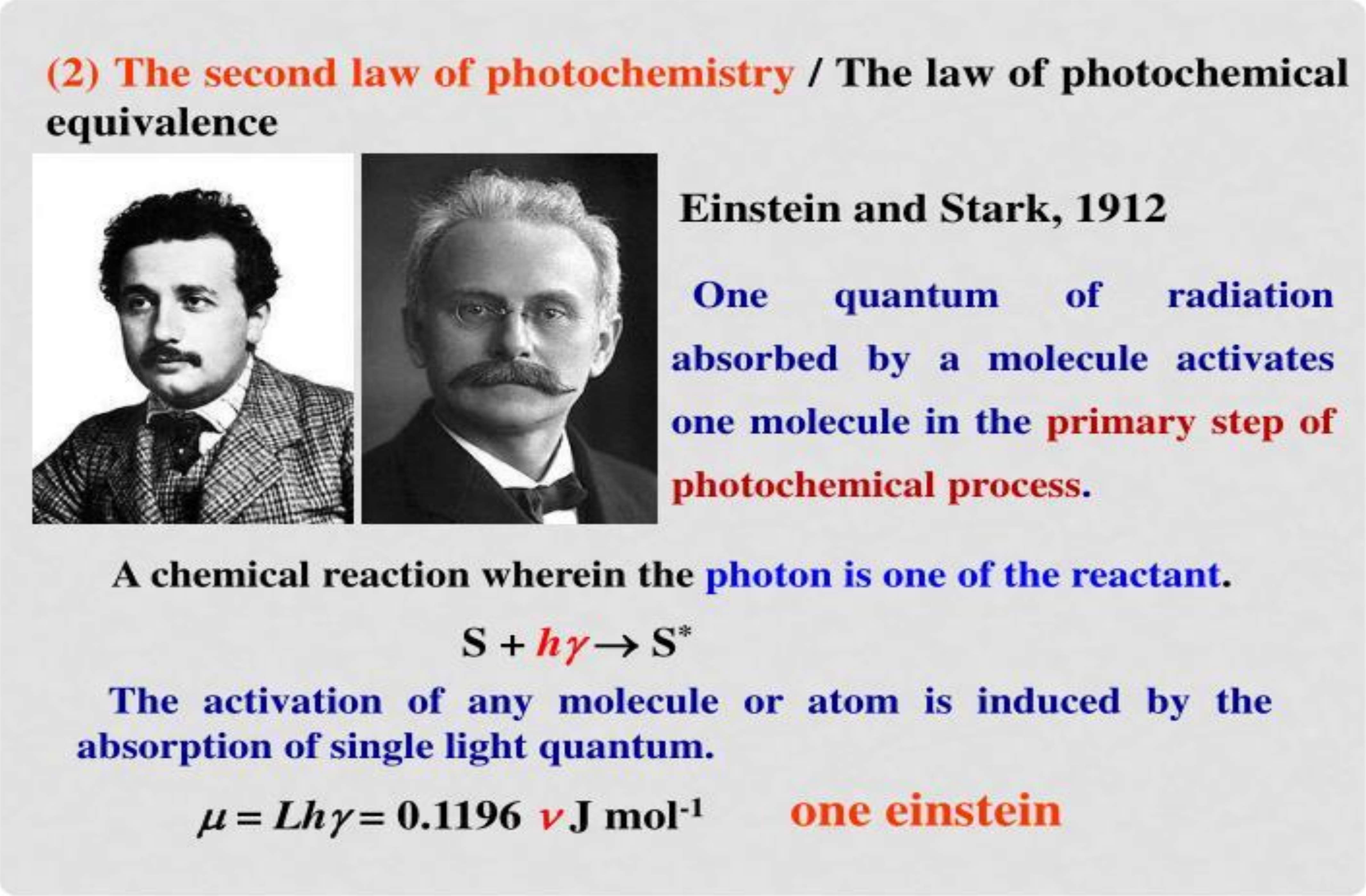
Grotthuss and Draper, 1818: → Theoretically

and confirmed by **draper experimentally in 1839**

light must be absorbed by a chemical substance in order to initiate a photochemical reaction.


Theodor v. Grotthuss


John William Draper (1811-1882) SI neg. #52,757



(2) The second law of photochemistry / The law of photochemical equivalence

Einstein and Stark, 1912

One quantum of radiation absorbed by a molecule activates one molecule in the primary step of photochemical process.

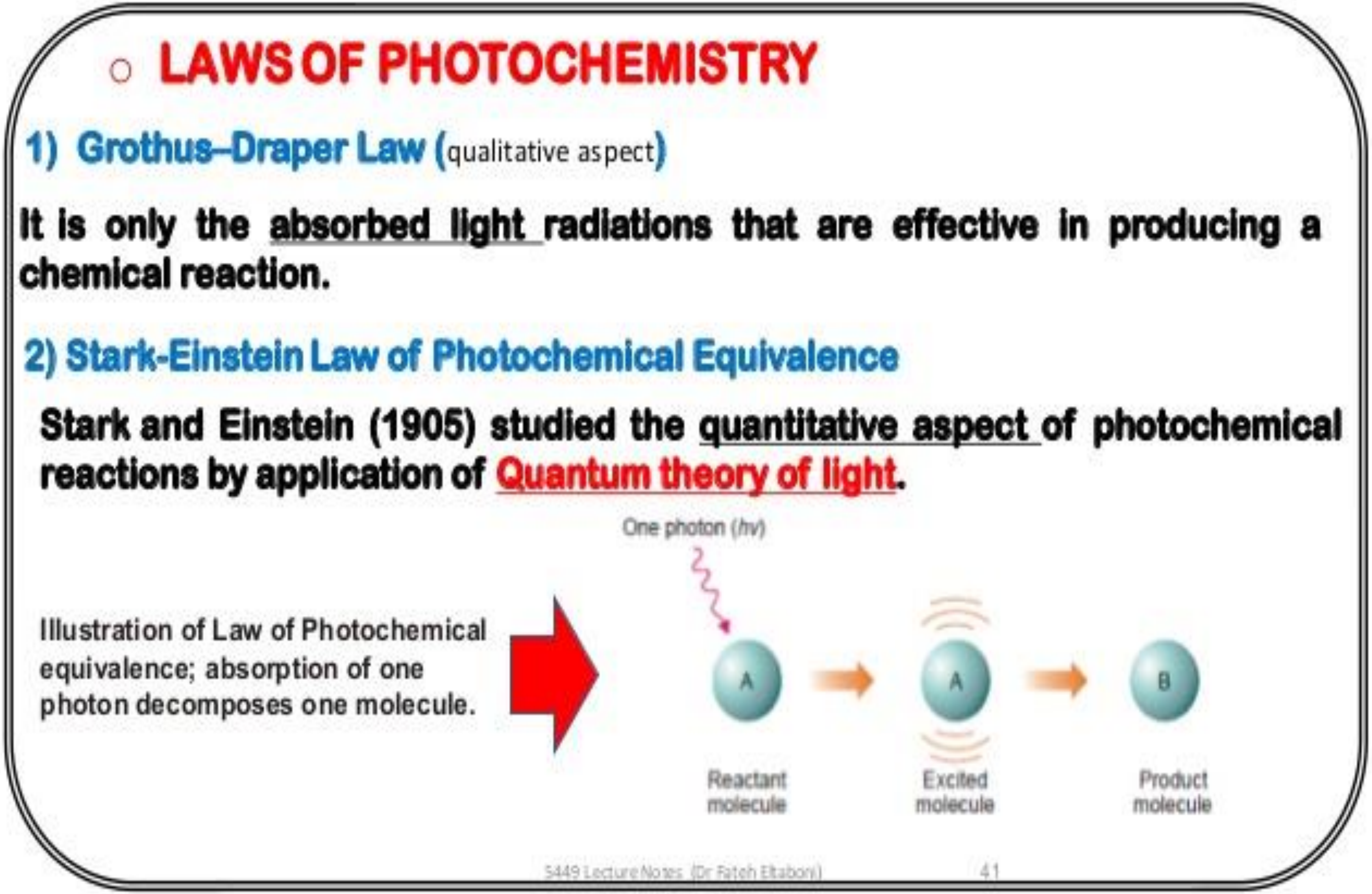
A chemical reaction wherein the photon is one of the reactant.

$$S + h\gamma \rightarrow S^*$$

The activation of any molecule or atom is induced by the absorption of single light quantum.

$$\mu = Lh\gamma = 0.1196\ \nu\ \mathrm{J\ mol^{-1}}$$

one einstein



○ LAWS OF PHOTOCHEMISTRY

1) Grothus–Draper Law (qualitative aspect)

It is only the absorbed light radiations that are effective in producing a chemical reaction.

2) Stark-Einstein Law of Photochemical Equivalence

Stark and Einstein (1905) studied the quantitative aspect of photochemical reactions by application of Quantum theory of light.

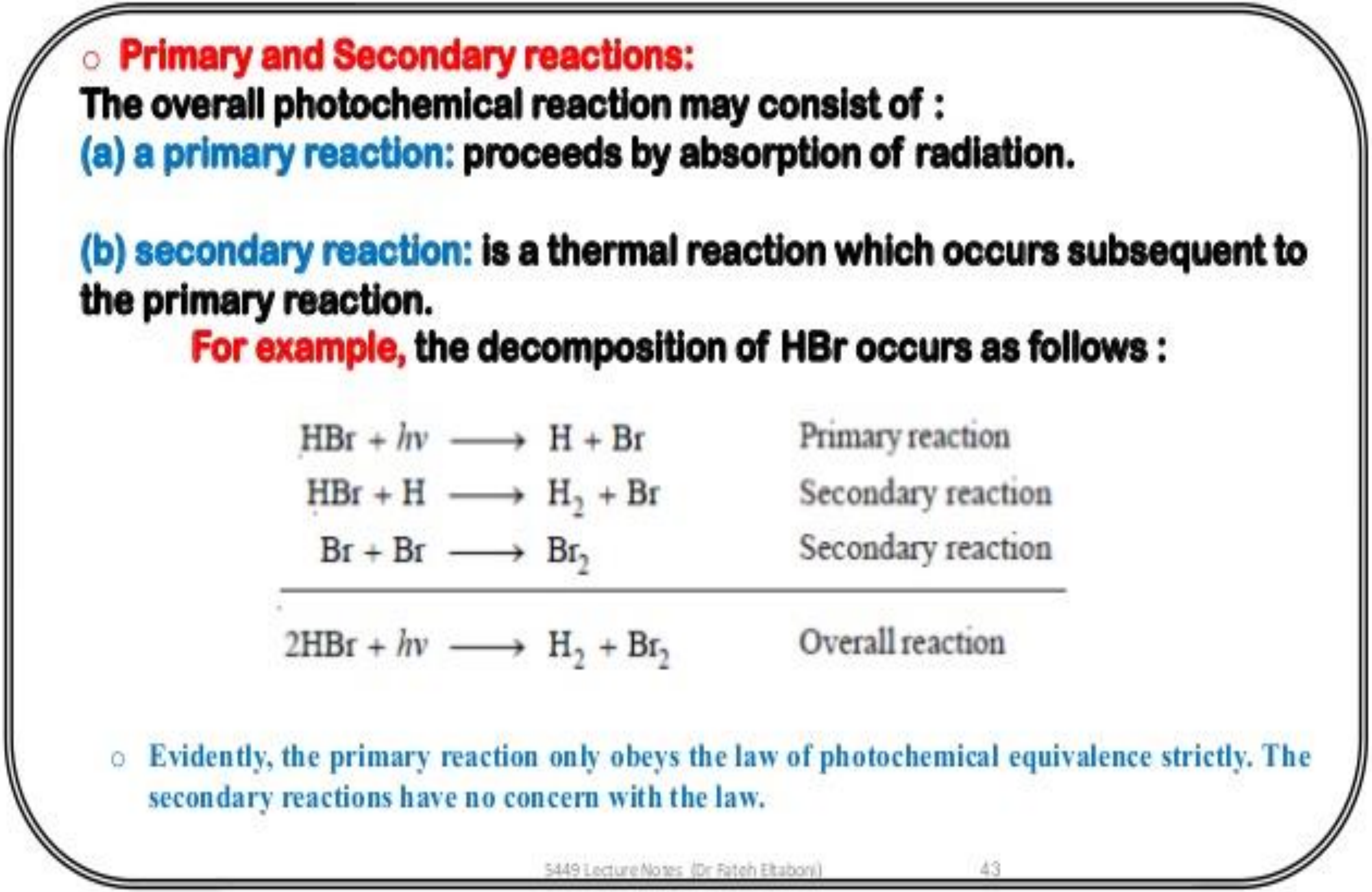
Illustration of Law of Photochemical equivalence; absorption of one photon decomposes one molecule.

- **In a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products.**

$$\begin{array}{lrcl} & A + h\nu & \longrightarrow & A^{*} \\ & A^{*} & \longrightarrow & B \\ \hline \text{overall} & A + h\nu & \longrightarrow & B \end{array}$$

- **In practice, we use molar quantities. That is, one mole of A absorbs one mole of photons or <u>one einstein</u> of energy, E. The value of E can be calculated by using the expression given below:**

$$E = \frac{2.859}{\lambda} \times 10^{5} \ \text{kcal mol}^{-1}$$



○ Primary and Secondary reactions:

The overall photochemical reaction may consist of :

(a) a primary reaction: proceeds by absorption of radiation.

(b) secondary reaction: is a thermal reaction which occurs subsequent to the primary reaction.

For example, the decomposition of HBr occurs as follows :

$HBr + h\nu \longrightarrow H + Br$ Primary reaction

$HBr + H \longrightarrow H_2 + Br$ Secondary reaction

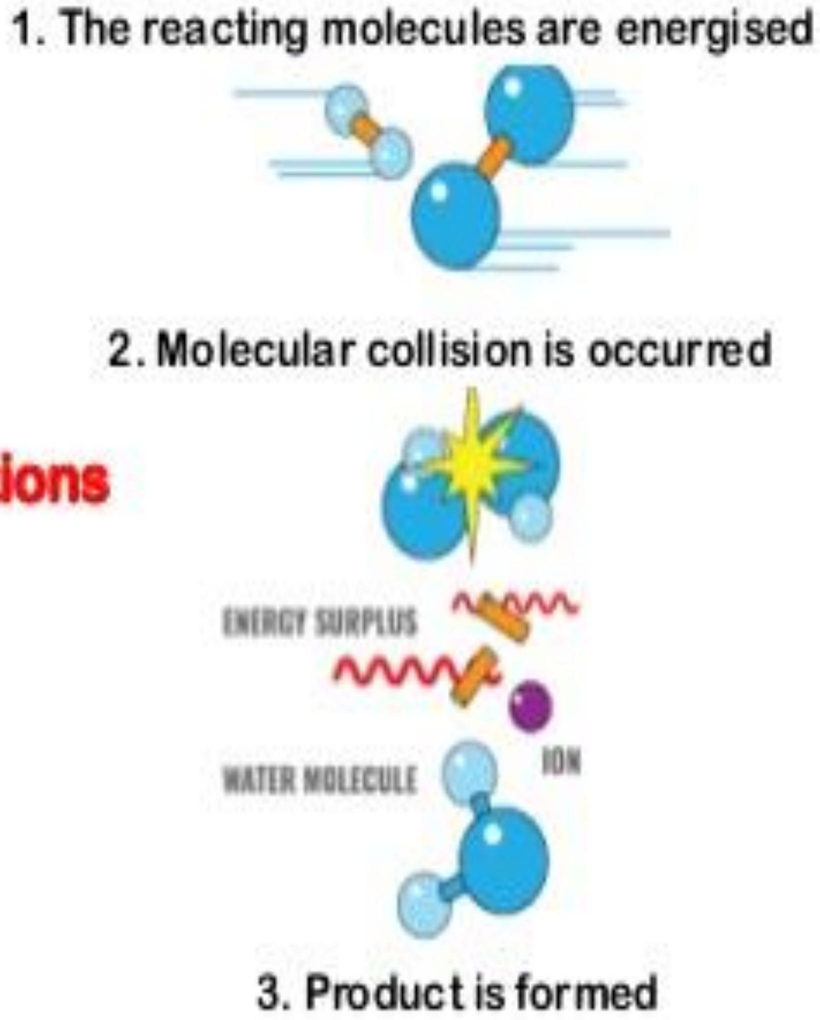
$Br + Br \longrightarrow Br_2$ Secondary reaction

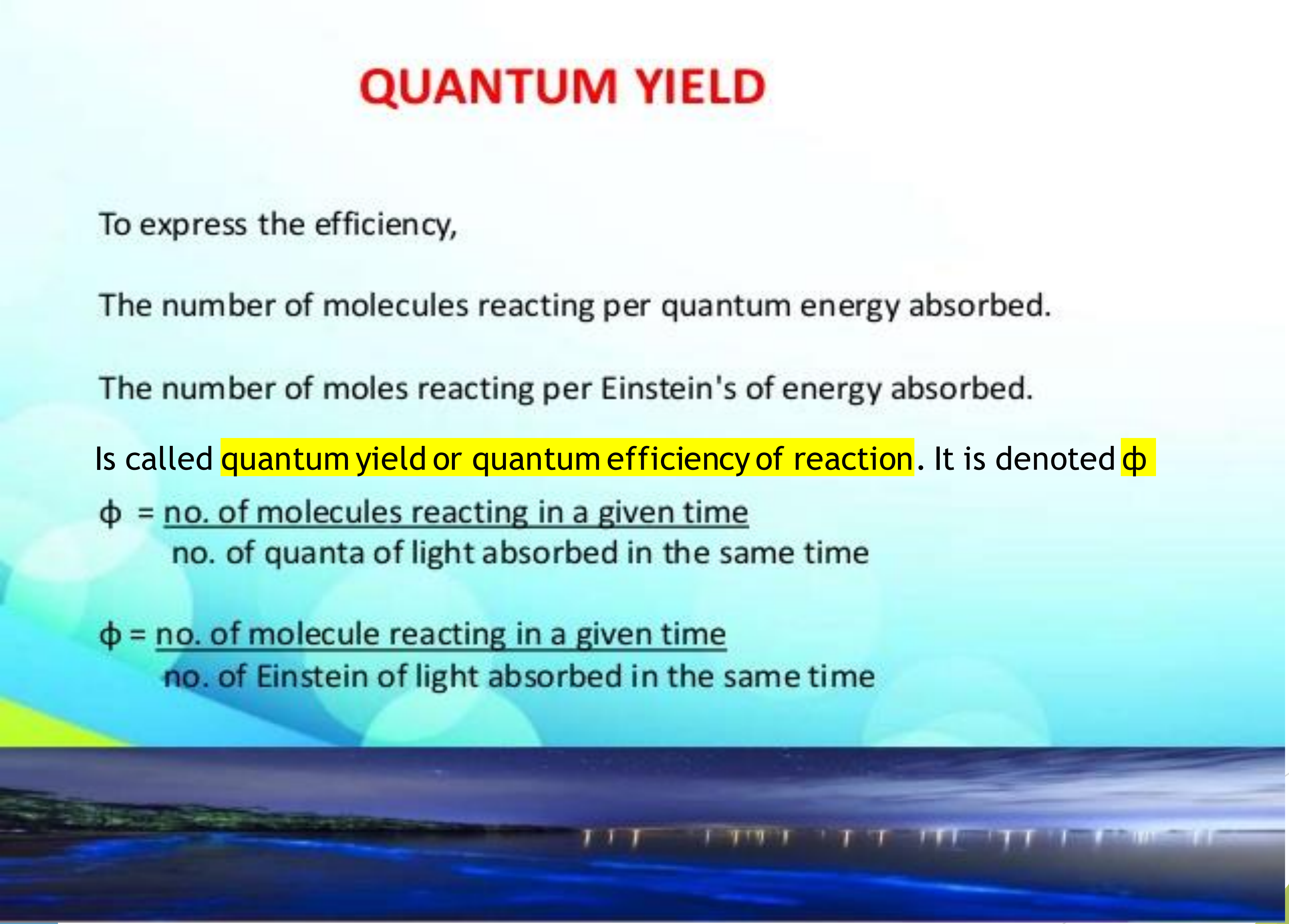
$2HBr + h\nu \longrightarrow H_2 + Br_2$ Overall reaction

- Evidently, the primary reaction only obeys the law of photochemical equivalence strictly. The secondary reactions have no concern with the law.

- ○ **Ordinary reaction (**thermal or dark reaction**):**
- ○ Its occurs by absorption of heat energy from outside in absence of light.

Steps of Ordinary reactions





QUANTUM YIELD

To express the efficiency,

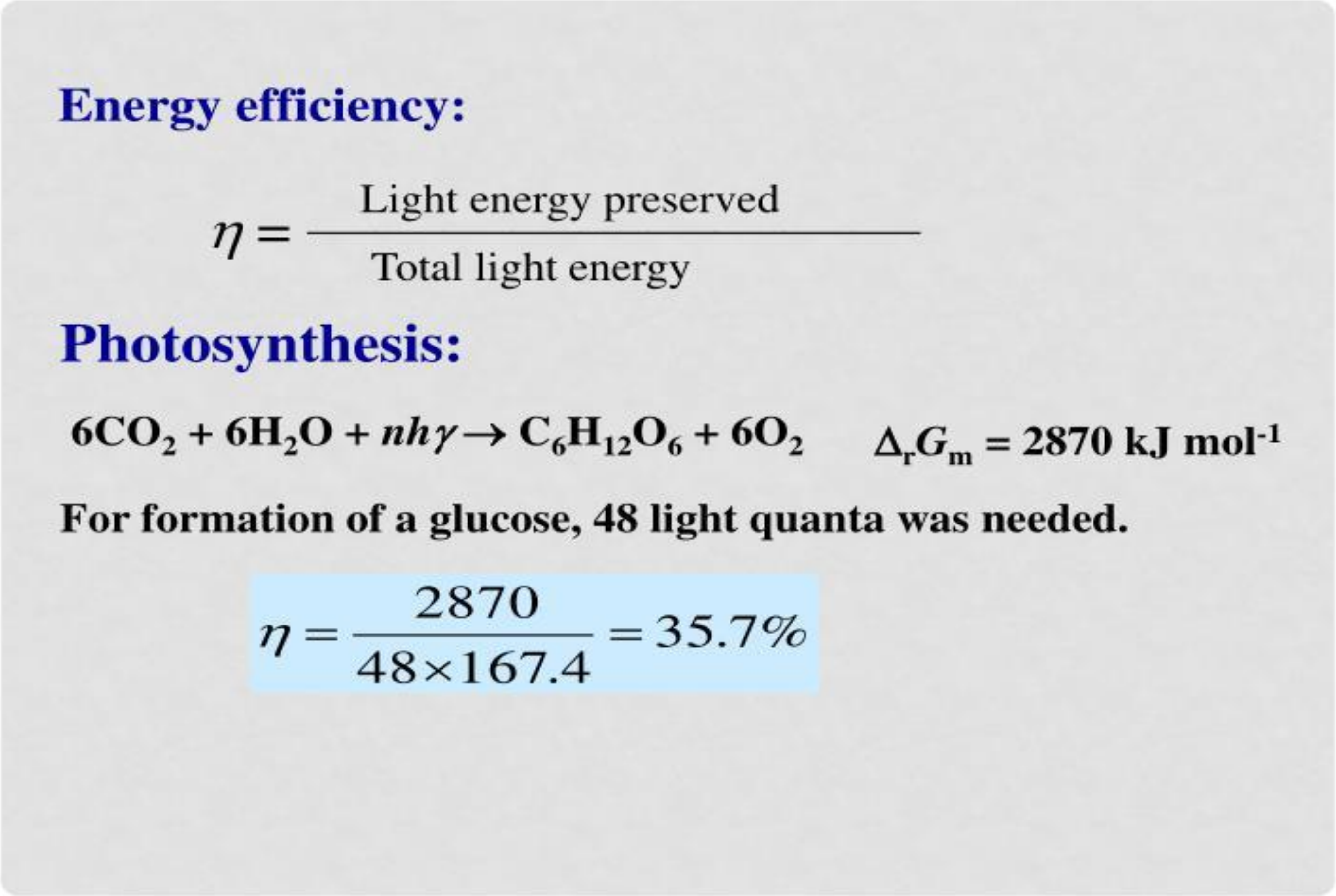
The number of molecules reacting per quantum energy absorbed.

The number of moles reacting per Einstein's of energy absorbed.

Is called quantum yield or quantum efficiency of reaction. It is denoted ϕ

$$\phi = \frac{\text{no. of molecules reacting in a given time}}{\text{no. of quanta of light absorbed in the same time}}$$

$$\phi = \frac{\text{no. of molecule reacting in a given time}}{\text{no. of Einstein of light absorbed in the same time}}$$



Energy efficiency:

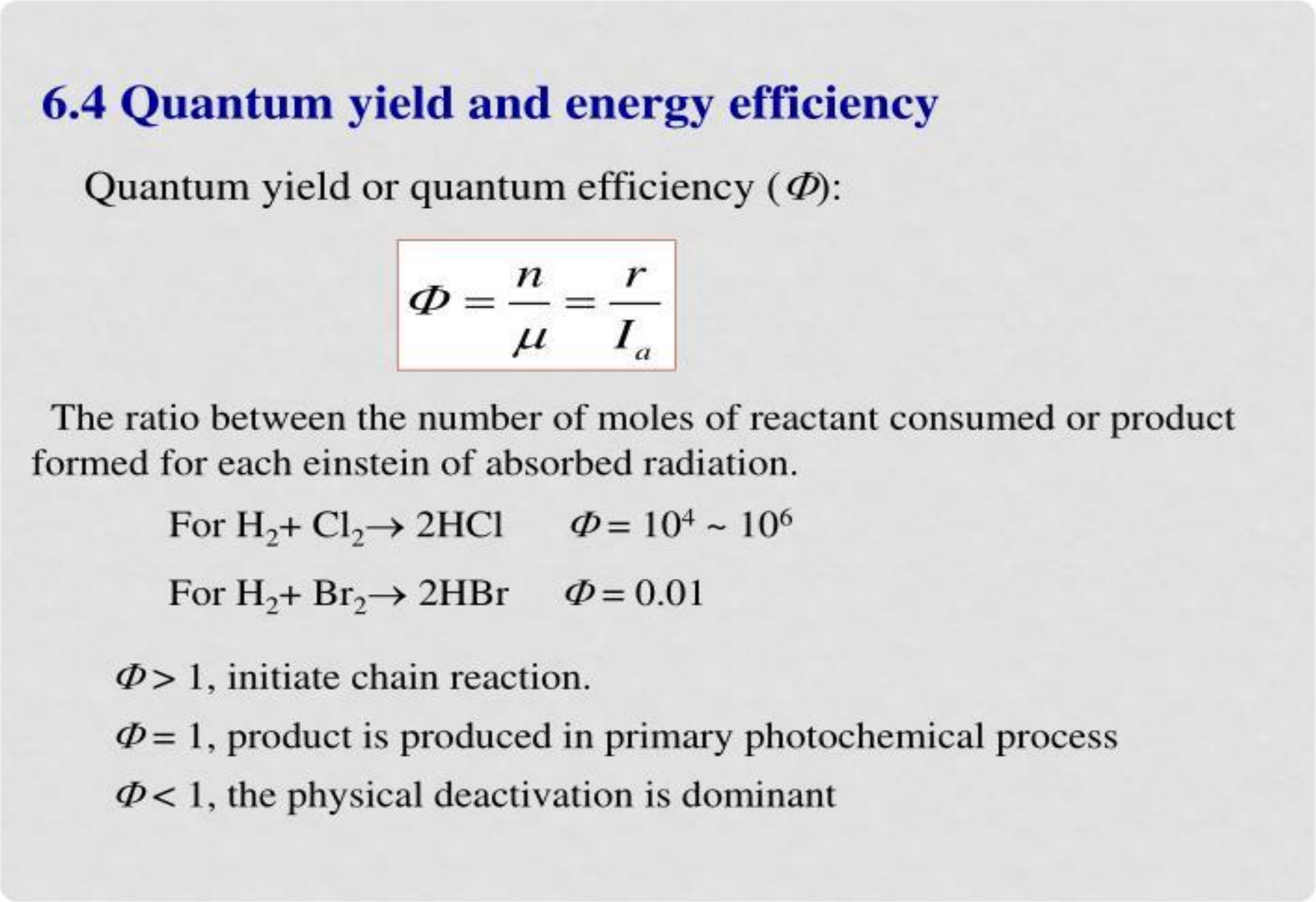
$$\eta = \frac{\text{Light energy preserved}}{\text{Total light energy}}$$

Photosynthesis:

$$6CO_2 + 6H_2O + nh\gamma \rightarrow C_6H_{12}O_6 + 6O_2 \qquad \Delta_r G_m = 2870\ \text{kJ mol}^{-1}$$

For formation of a glucose, 48 light quanta was needed.

$$\eta = \frac{2870}{48 \times 167.4} = 35.7\%$$



6.4 Quantum yield and energy efficiency

Quantum yield or quantum efficiency (Φ):

$$\boxed{\Phi = \frac{n}{\mu} = \frac{r}{I_a}}$$

The ratio between the number of moles of reactant consumed or product formed for each einstein of absorbed radiation.

For $H_2 + Cl_2 \rightarrow 2HCl$ $\quad \Phi = 10^4 \sim 10^6$

For $H_2 + Br_2 \rightarrow 2HBr$ $\quad \Phi = 0.01$

$\Phi > 1$, initiate chain reaction.

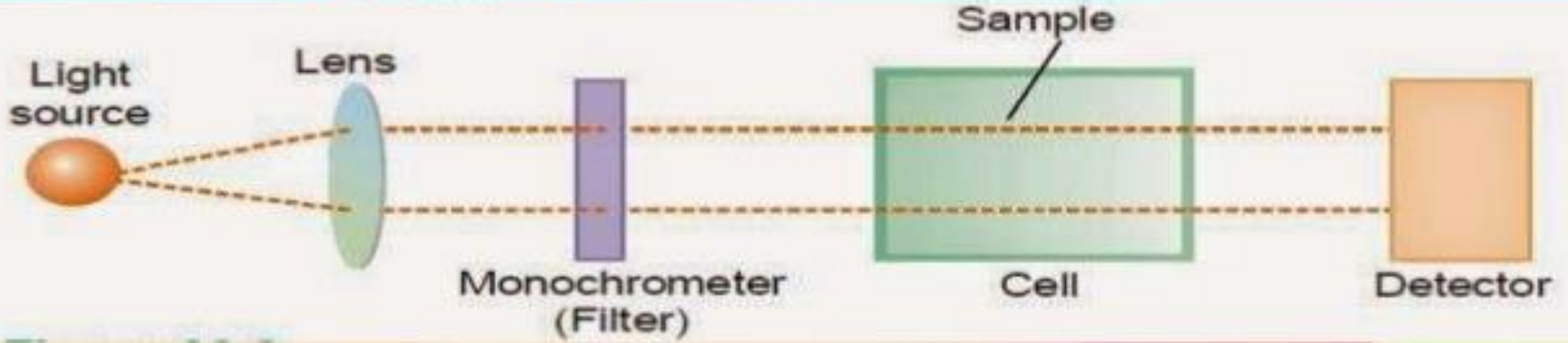
$\Phi = 1$, product is produced in primary photochemical process

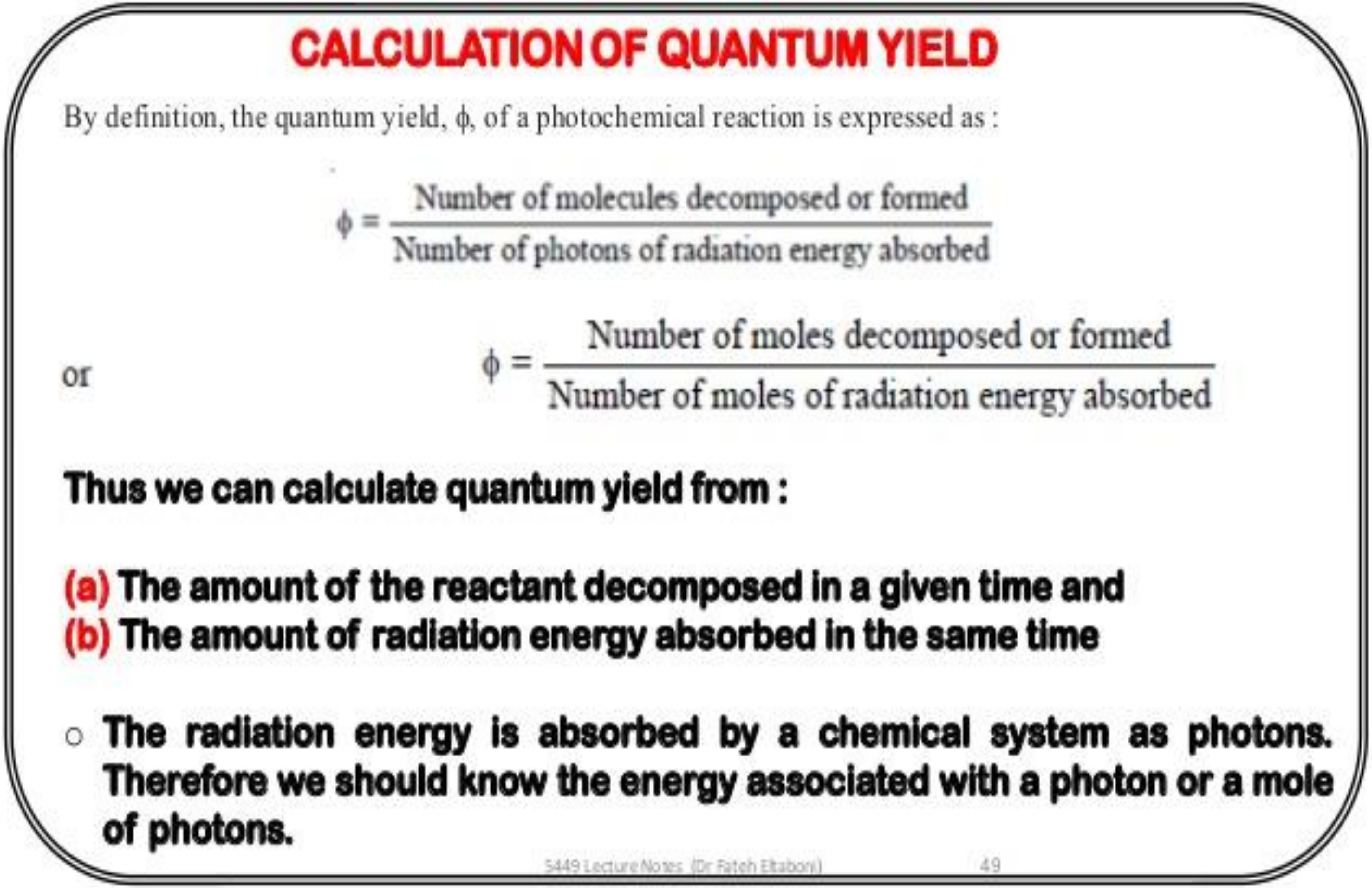
$\Phi < 1$, the physical deactivation is dominant

Experimental Determination of Quantum Yield

1. Determination of number of moles reacted.
2. Determination of number of Einstein's absorbed.
3.

Source of light
Monochromator
Reaction cell
Detector





CALCULATION OF QUANTUM YIELD

By definition, the quantum yield, ϕ, of a photochemical reaction is expressed as :

$$\phi = \frac{\text{Number of molecules decomposed or formed}}{\text{Number of photons of radiation energy absorbed}}$$

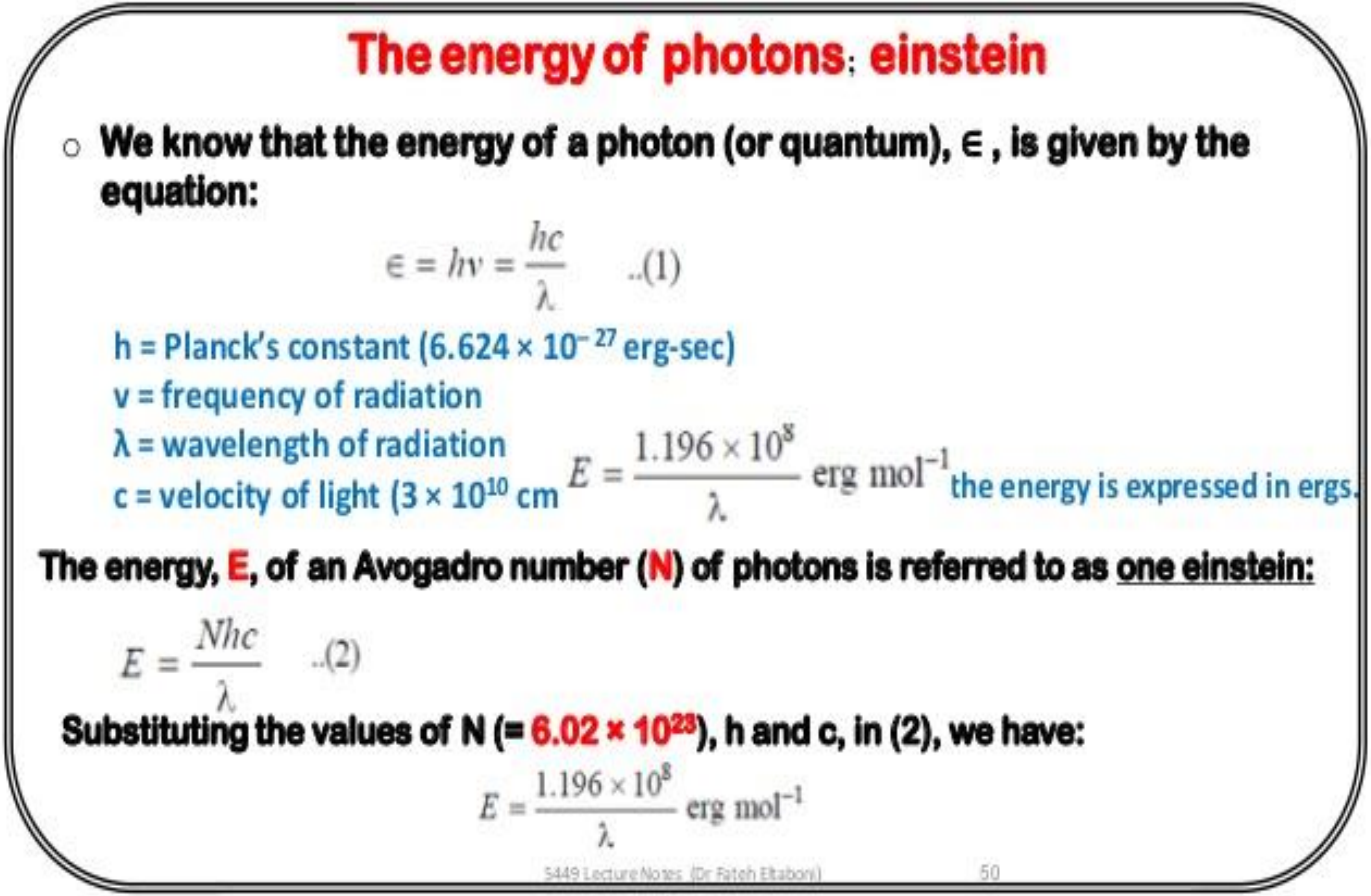
or

$$\phi = \frac{\text{Number of moles decomposed or formed}}{\text{Number of moles of radiation energy absorbed}}$$

Thus we can calculate quantum yield from :

(a) The amount of the reactant decomposed in a given time and
(b) The amount of radiation energy absorbed in the same time

- **The radiation energy is absorbed by a chemical system as photons. Therefore we should know the energy associated with a photon or a mole of photons.**



The energy of photons: einstein

- **We know that the energy of a photon (or quantum), ∈ , is given by the equation:**

$$\epsilon = h\nu = \frac{hc}{\lambda} \quad ..(1)$$

h = Planck's constant (6.624 × 10^{-27} erg-sec)
v = frequency of radiation
λ = wavelength of radiation
c = velocity of light (3 × 10^{10} cm

$$E = \frac{1.196 \times 10^{8}}{\lambda} \text{ erg mol}^{-1}$$

the energy is expressed in ergs.

The energy, E, of an Avogadro number (N) of photons is referred to as <u>one einstein:</u>

$$E = \frac{Nhc}{\lambda} \quad ..(2)$$

Substituting the values of N (= 6.02 × 10^{23}), h and c, in (2), we have:

$$E = \frac{1.196 \times 10^{8}}{\lambda} \text{ erg mol}^{-1}$$

If λ is expressed in Å units ($1 Å = 10^{-8}$ cm),

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}^{-1} \qquad ...(3)$$

Since 1 cal = 4.184×10^7 erg, energy in calories would be:

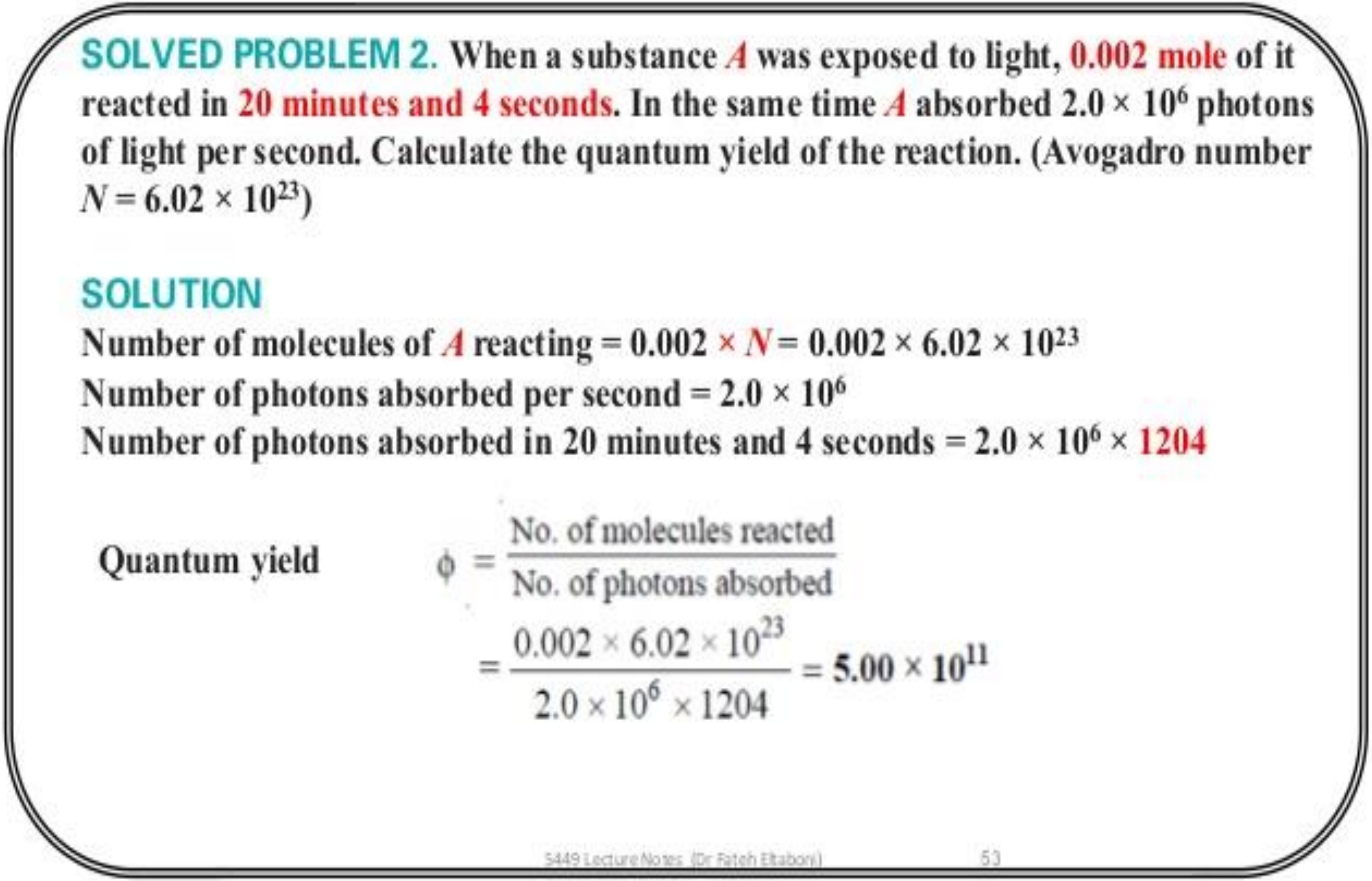
$$E = \frac{1.196 \times 10^{16}}{\lambda \times 4.184 \times 10^7} \qquad ..(4)$$

$$= \frac{2.859}{\lambda} \times 10^8 \text{ cal mol}^{-1}$$

$$E = \frac{2.859}{\lambda} \times 10^5 \text{ kcal mol}^{-1} \qquad ...(5)$$

Electron-volt (eV) is another commonly used energy unit, $1 \text{ eV} = 1.6 \times 10^{-19}$ J.

- **It is evident from (3) that the numerical value of einstein varies inversely as the wavelength of radiation.**
- **The higher the wavelength, the smaller will be the energy per einstein.**



SOLVED PROBLEM 2. When a substance *A* was exposed to light, 0.002 mole of it reacted in 20 minutes and 4 seconds. In the same time *A* absorbed 2.0×10^6 photons of light per second. Calculate the quantum yield of the reaction. (Avogadro number $N = 6.02 \times 10^{23}$)

SOLUTION

Number of molecules of *A* reacting $= 0.002 \times N = 0.002 \times 6.02 \times 10^{23}$

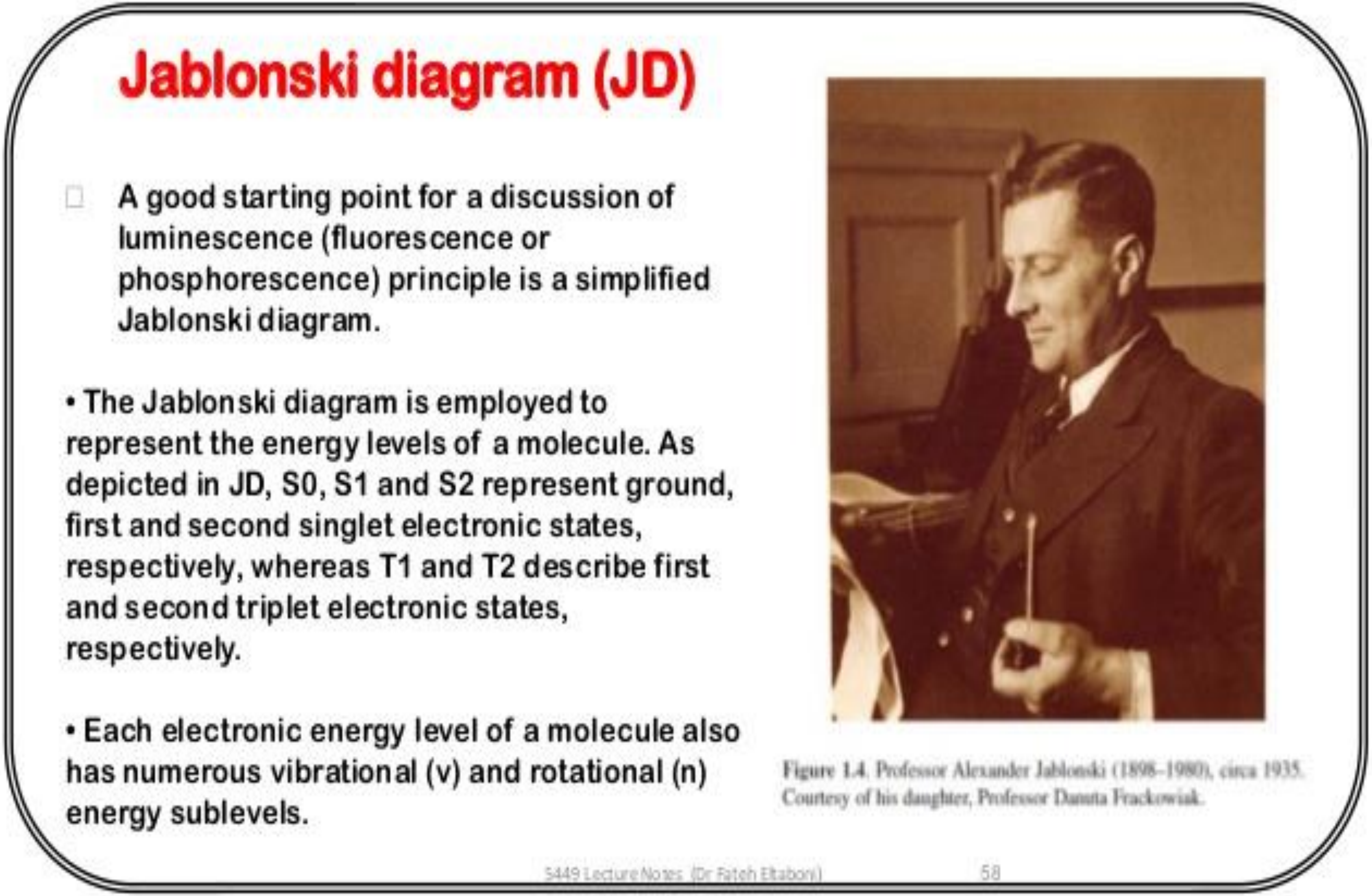
Number of photons absorbed per second $= 2.0 \times 10^6$

Number of photons absorbed in 20 minutes and 4 seconds $= 2.0 \times 10^6 \times 1204$

Quantum yield

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$$

$$= \frac{0.002 \times 6.02 \times 10^{23}}{2.0 \times 10^6 \times 1204} = \mathbf{5.00 \times 10^{11}}$$



Jablonski diagram (JD)

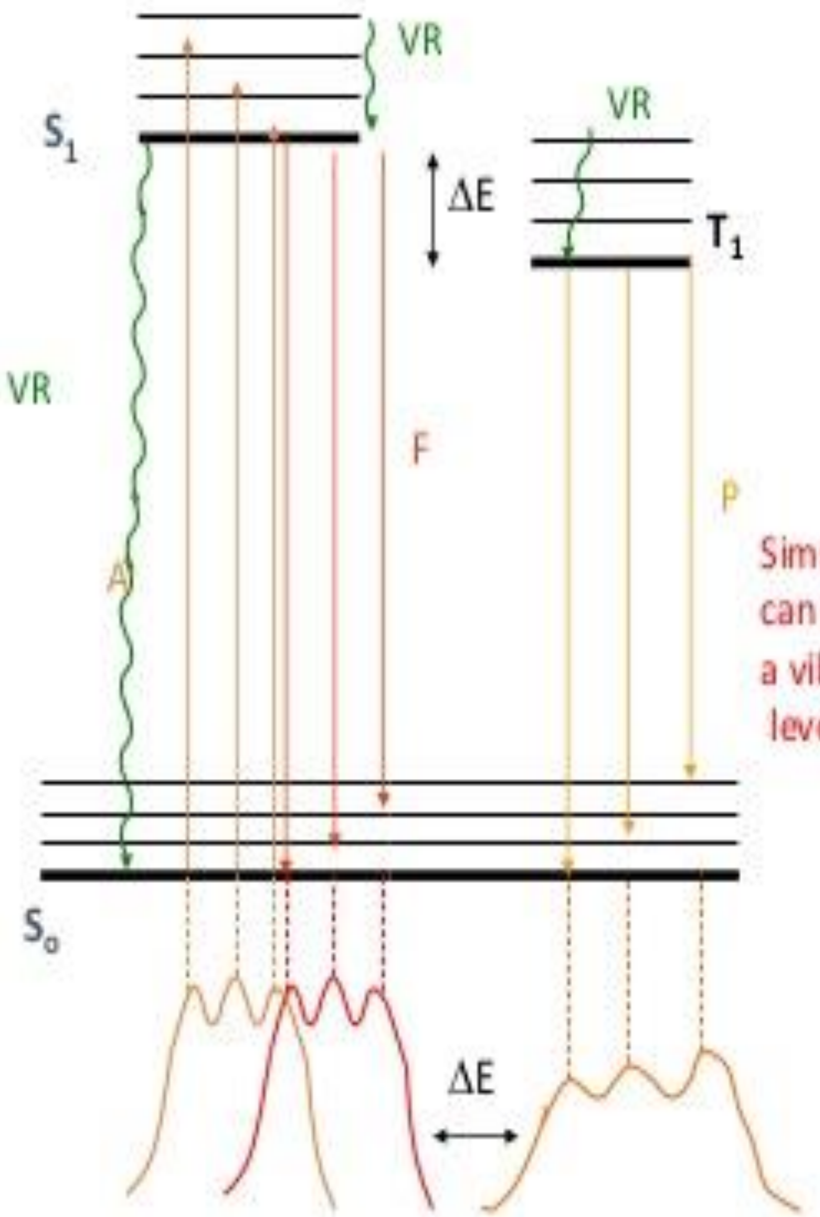
- A good starting point for a discussion of luminescence (fluorescence or phosphorescence) principle is a simplified Jablonski diagram.

- The Jablonski diagram is employed to represent the energy levels of a molecule. As depicted in JD, S0, S1 and S2 represent ground, first and second singlet electronic states, respectively, whereas T1 and T2 describe first and second triplet electronic states, respectively.

- Each electronic energy level of a molecule also has numerous vibrational (v) and rotational (n) energy sublevels.

Figure 1.4. Professor Alexander Jablonski (1898–1980), circa 1935. Courtesy of his daughter, Professor Danuta Frackowiak.

Relationship between fluorescence, phosphorescence and absorption spectra

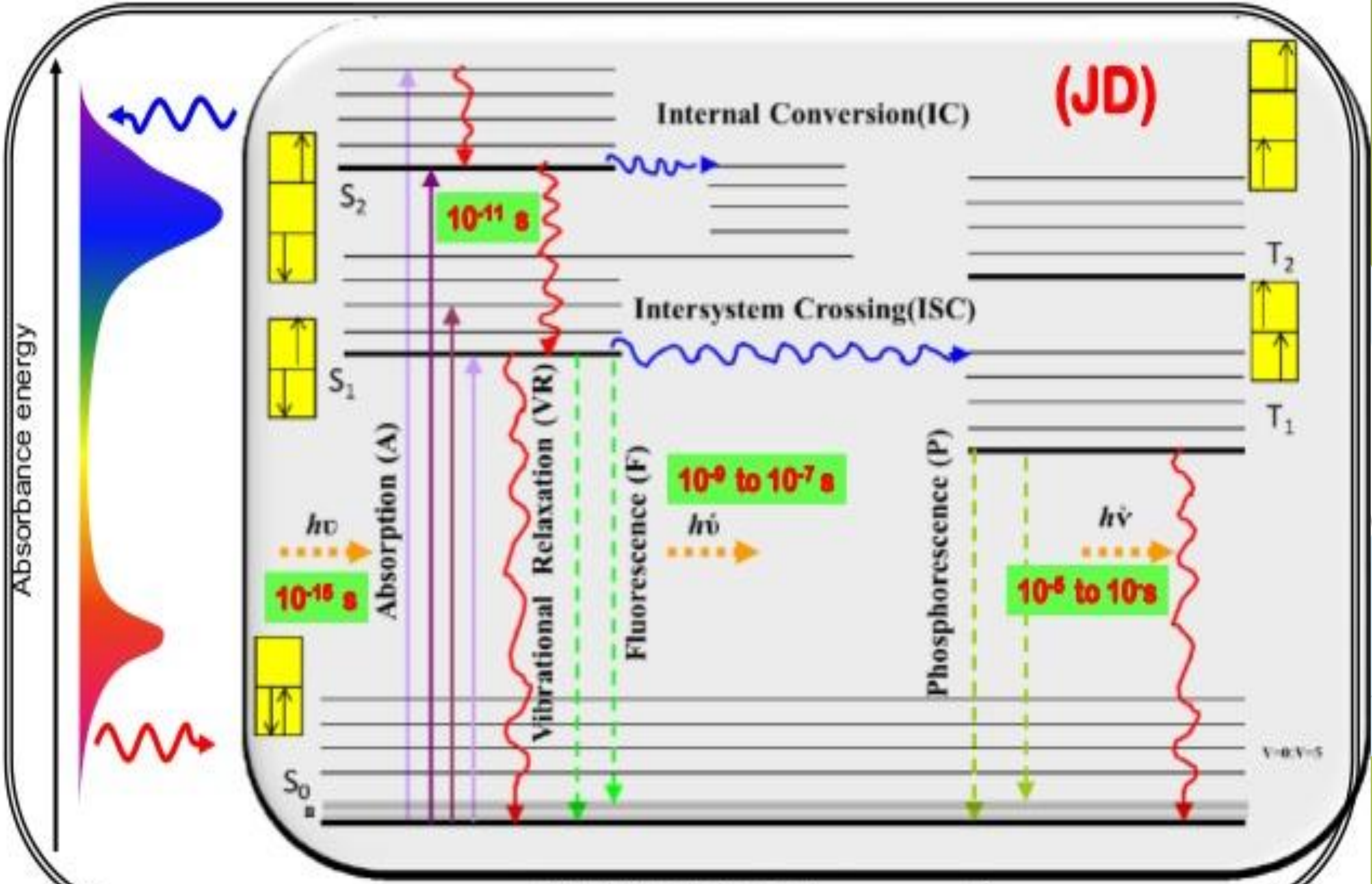


- have vibrational fine structure in absorption and in emission

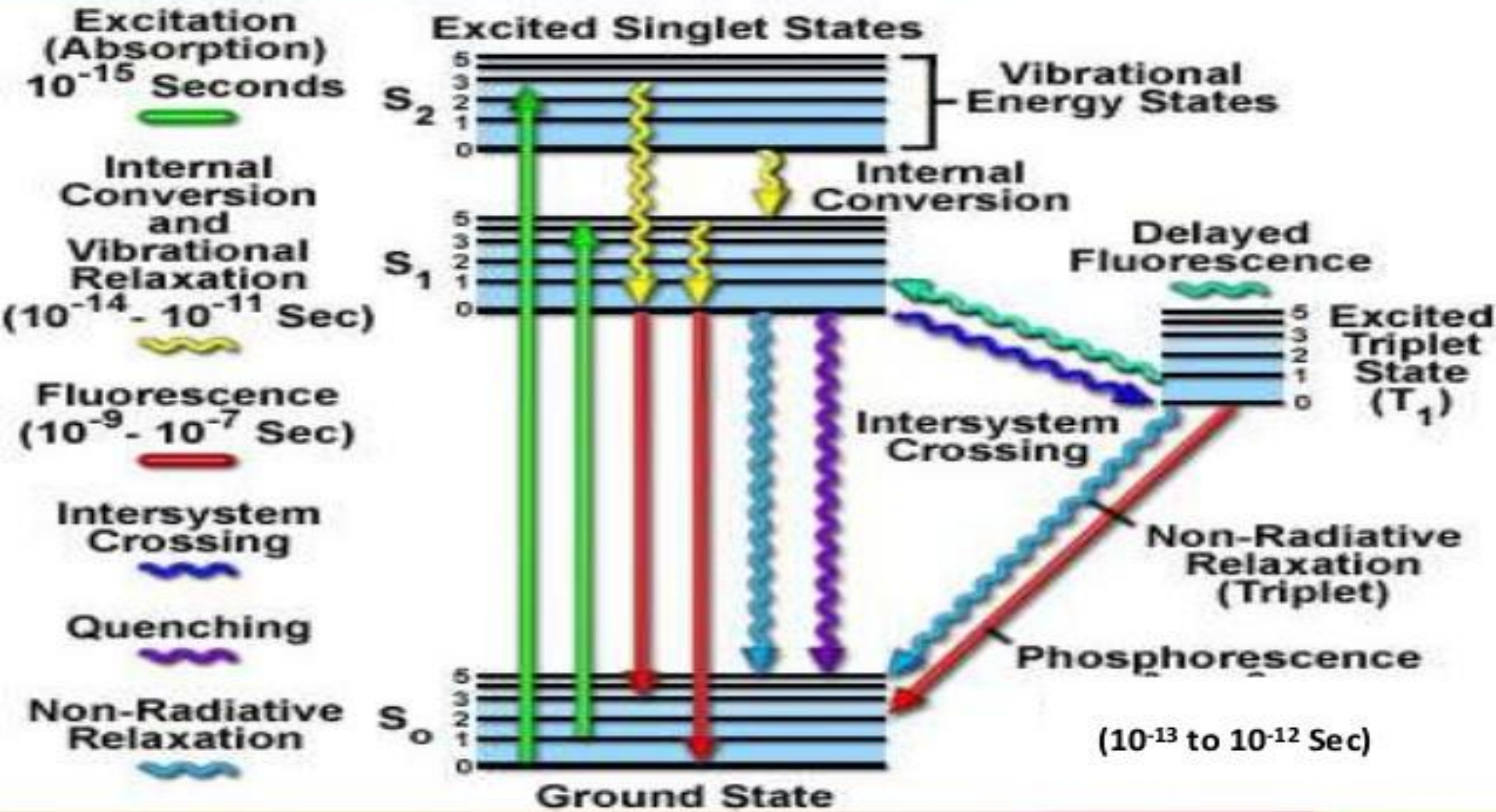
molecule relaxes back from the S_1 state to a vibrationally excited level of the ground state S_o.

Similarly, a molecule can relax back to a vibrationally excited level of S_o from T_1.

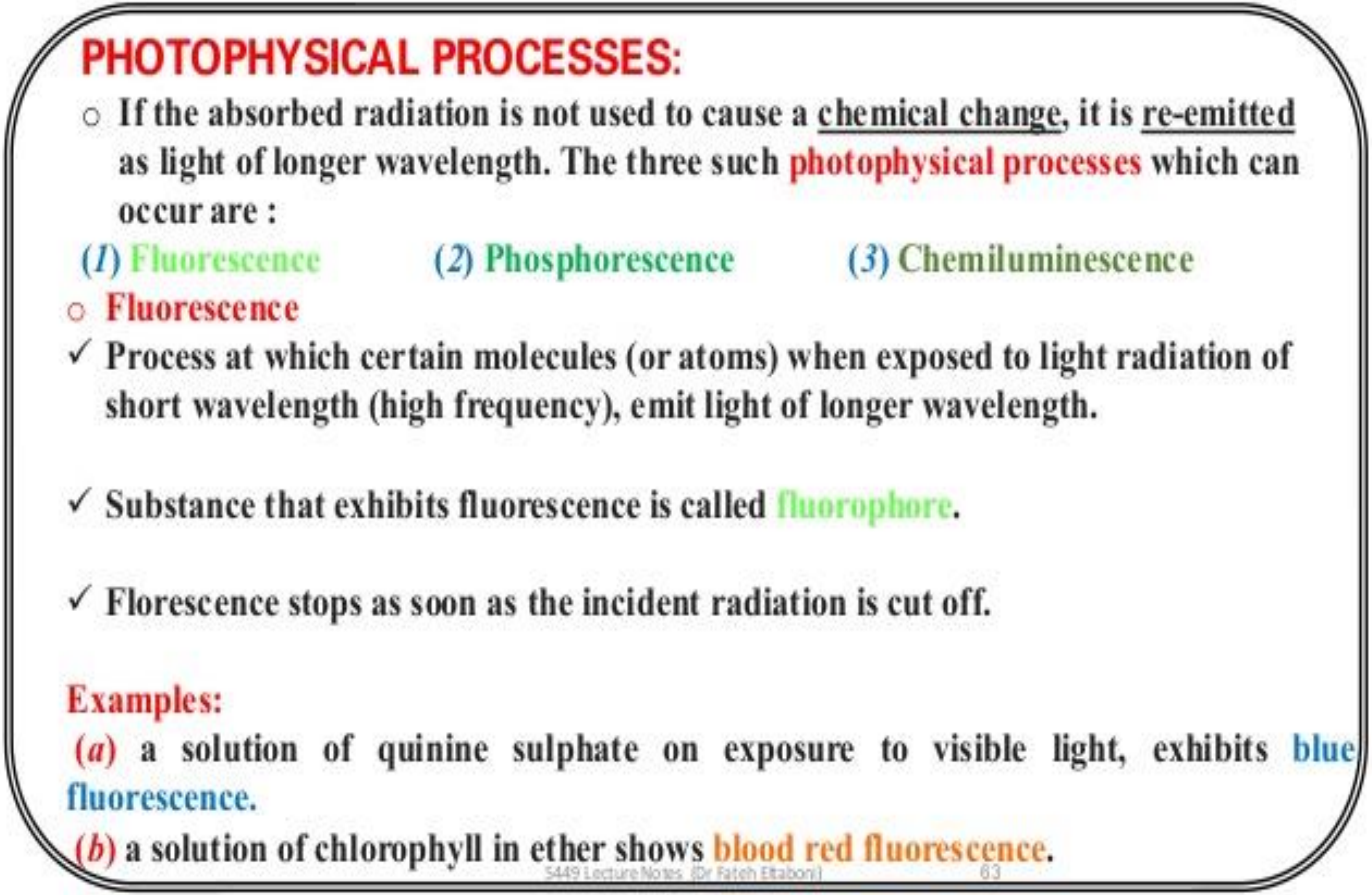
-spectrum: intensity of luminescence *vs* wavelength


(JD)
Absorbance energy
Internal Conversion(IC)
Intersystem Crossing(ISC)
S_2
S_1
S_0
T_2
T_1
10^{-11} s
10^{-15} s
10^{-9} to 10^{-7} s
10^{-5} to 10^{1}s
Absorption (A)
Vibrational Relaxation (VR)
Fluorescence (F)
Phosphorescence (P)
hυ
hύ
hν̀
V=0:V=5

Joblonski Diagram



(10^{-13} to 10^{-12} Sec)



PHOTOPHYSICAL PROCESSES:

- ○ If the absorbed radiation is not used to cause a chemical change, it is re-emitted as light of longer wavelength. The three such **photophysical processes** which can occur are :

(*1*) **Fluorescence** (*2*) **Phosphorescence** (*3*) **Chemiluminescence**

- ○ **Fluorescence**

- ✓ Process at which certain molecules (or atoms) when exposed to light radiation of short wavelength (high frequency), emit light of longer wavelength.

- ✓ Substance that exhibits fluorescence is called **fluorophore**.

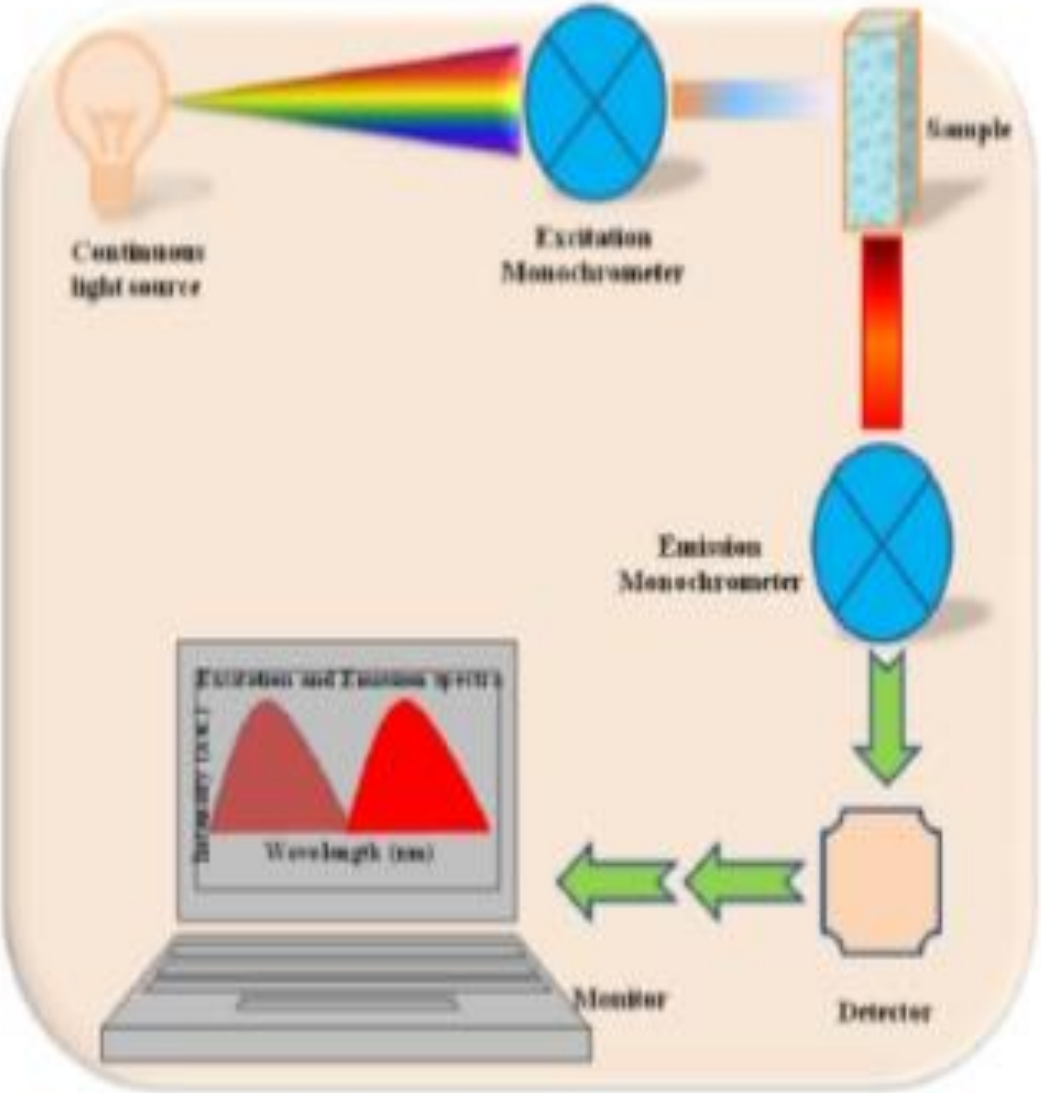
- ✓ Florescence stops as soon as the incident radiation is cut off.

Examples:

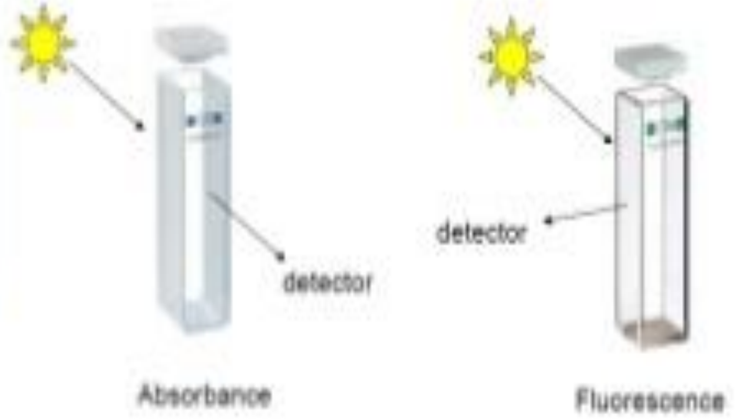
(*a*) a solution of quinine sulphate on exposure to visible light, exhibits **blue fluorescence.**

(*b*) a solution of chlorophyll in ether shows **blood red fluorescence**.

SPECTROFLUOROMETER:

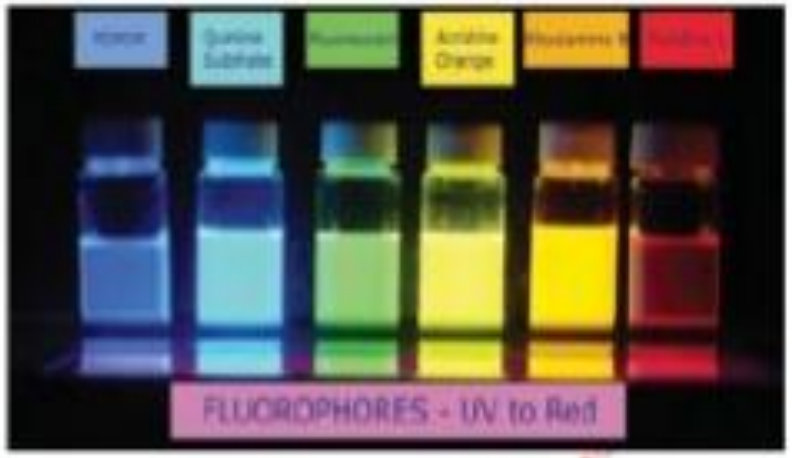


Fluorescence *versus* Absorbance



○ Fluorescence depends on:

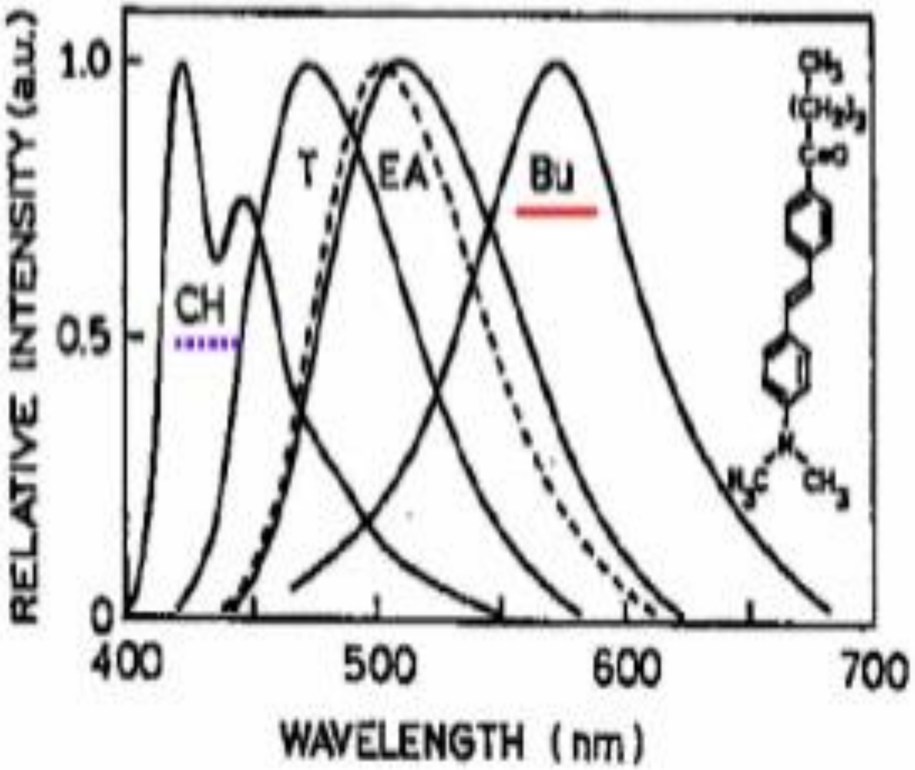
1. pH
2. Solvent
3. Temperature
4. Salts
5. Concentration

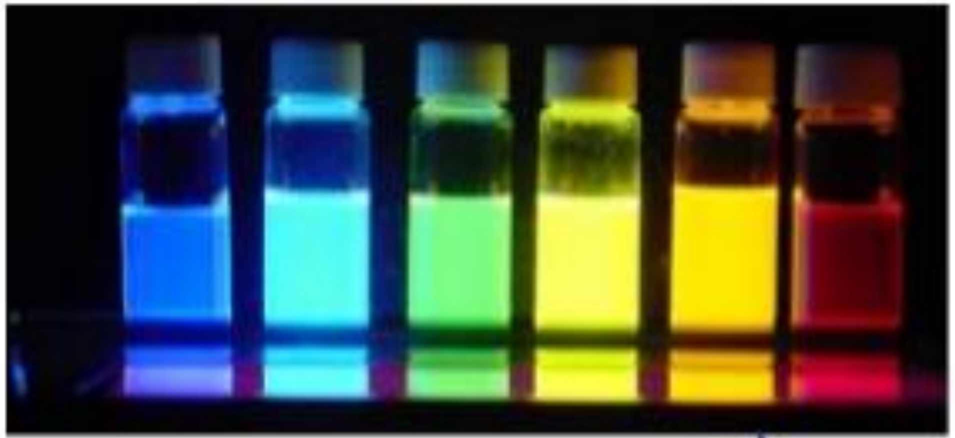


Fluorescence

The light absorbed may be remitted almost instantaneously in one or more steps this phenomenon is known as fluorescence.

Demonstration of a Solvent Sensitive Fluorophore





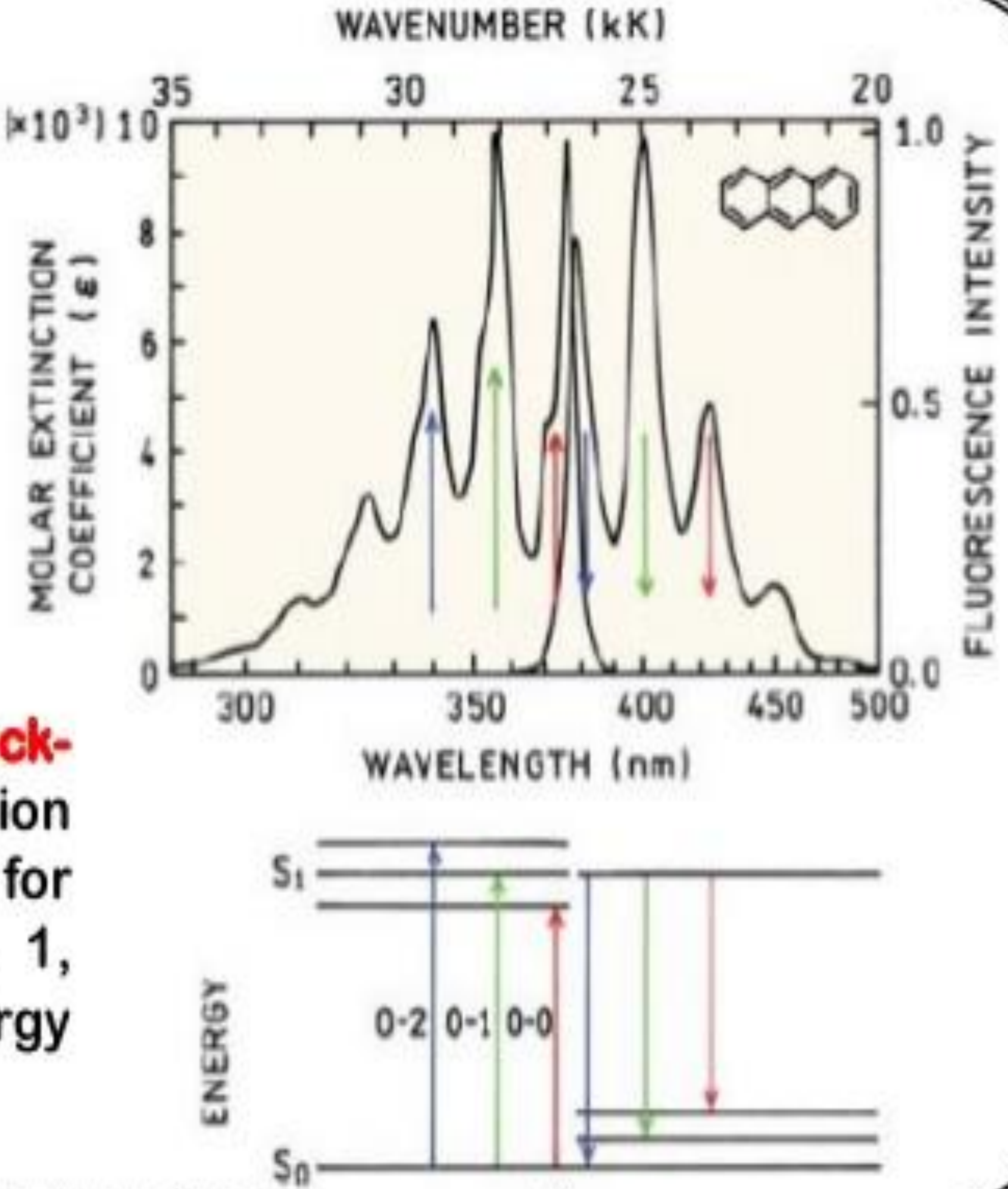
Solvent Polarity

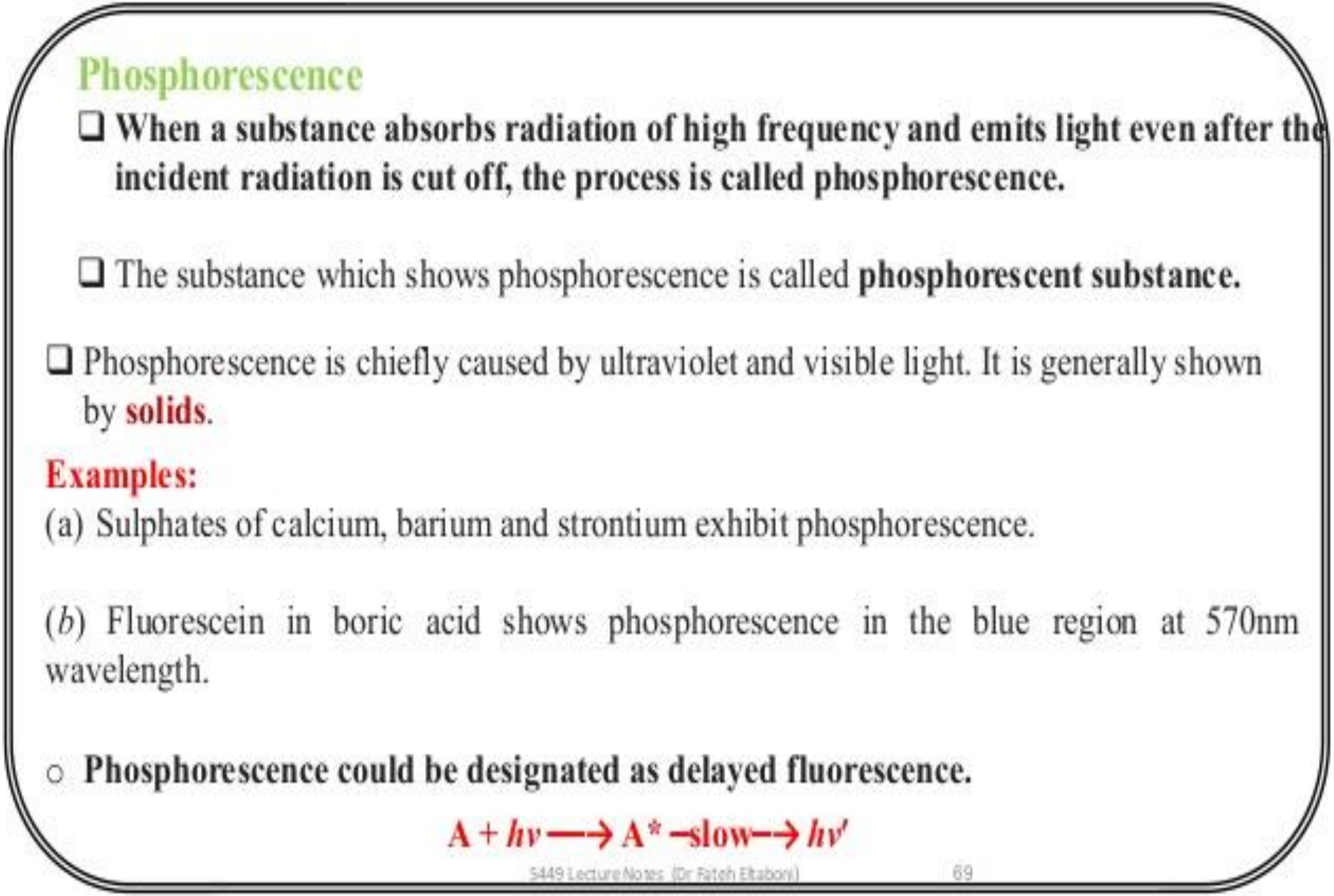
Corrected fluorescence emission spectra of DOS in cyclohexane(CH), toluene (T), ethylacetate(EA) and butanol(Bu). The dashed line shows the emission of DOS from DPPC vesicles

- Phosphorescence and ISC are spin-forbidden transitions. In contrast, fluorescence and IC are spin-allowed transitions.

"Stokes" shift
Absorption vs Emission

- **Mirror-image rule and Franck-Condon factors.** The absorption and emission spectra are for anthracene. The numbers 0, 1, and 2 refer to vibrational energy levels.





Phosphorescence

- **When a substance absorbs radiation of high frequency and emits light even after the incident radiation is cut off, the process is called phosphorescence.**

- The substance which shows phosphorescence is called **phosphorescent substance.**

- Phosphorescence is chiefly caused by ultraviolet and visible light. It is generally shown by **solids**.

Examples:

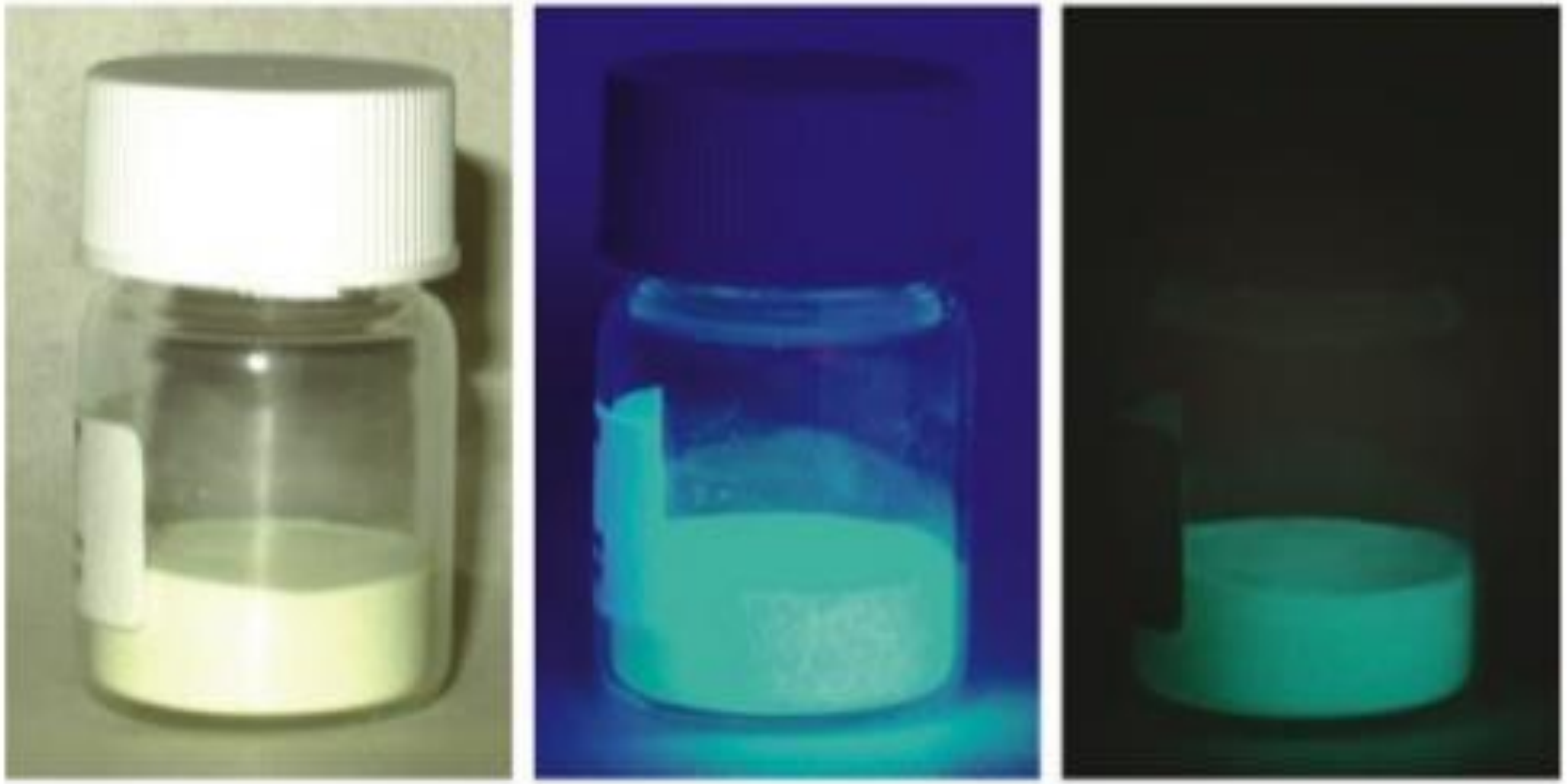
(a) Sulphates of calcium, barium and strontium exhibit phosphorescence.

(*b*) Fluorescein in boric acid shows phosphorescence in the blue region at 570nm wavelength.

- **Phosphorescence could be designated as delayed fluorescence.**

$$A + h\nu \longrightarrow A^* \xrightarrow{\text{slow}} h\nu'$$

Phosphorescent powder under:



visible light, ultraviolet light, darkness

Phosphorescence

The emission in fluorescence ceases with the removal of source of light, this phenomenon is know as phosphorescence.

How much luminescence is observed depends on efficiency of the various processes shown in the Jablonski Diagram.

- which compete with one another to deactivate the excited state

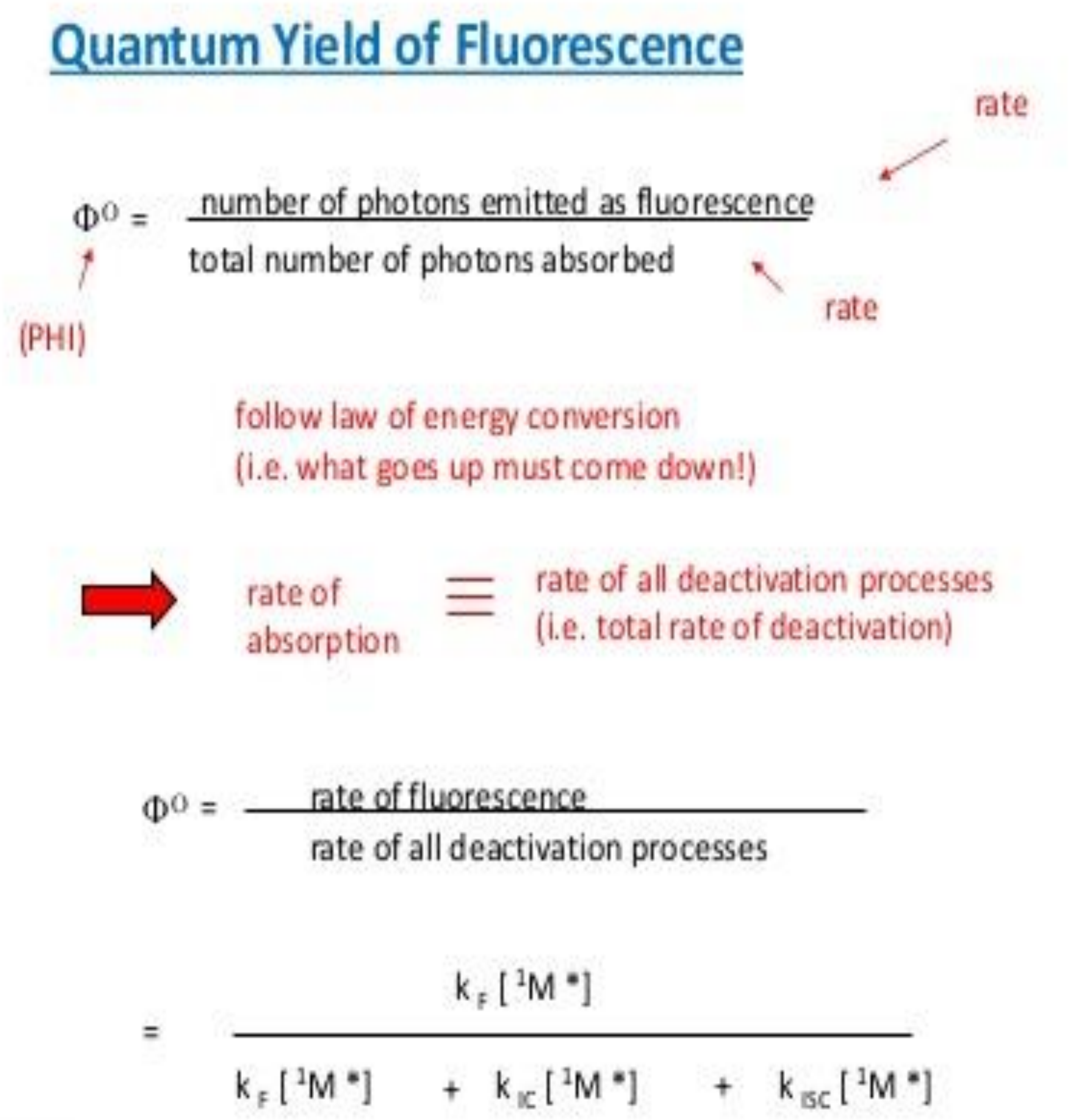
Consider fluorescence:

-amount of fluorescence observed is dependent on relative rates of the following unimolecular processes:

Consider a molecule, M

	process	rate
$^1M \xrightarrow{h\upsilon} {}^1M^*$	absorption	I_a
$^1M^* \xrightarrow{k_F} {}^1M + h\upsilon$	fluorescence	$k_F[{}^1M^*]$
$^1M^* \xrightarrow{k_{IC}} {}^1M$	internal conversion	$k_{IC}[{}^1M^*]$
$^1M^* \xrightarrow{k_{ISC}} {}^3M^*$	intersystem crossing	$k_{ISC}[{}^1M^*]$

(* denotes electronically excited)



Quantum Yield of Fluorescence

rate

$$\Phi^{O} = \frac{\text{number of photons emitted as fluorescence}}{\text{total number of photons absorbed}}$$

rate

(PHI)

follow law of energy conversion
(i.e. what goes up must come down!)

➡ rate of absorption $\equiv$ rate of all deactivation processes
(i.e. total rate of deactivation)

$$\Phi^{O} = \frac{\text{rate of fluorescence}}{\text{rate of all deactivation processes}}$$

$$= \frac{k_F\,[^1M^*]}{k_F\,[^1M^*] \quad + \quad k_{IC}\,[^1M^*] \quad + \quad k_{ISC}\,[^1M^*]}$$

$$= \frac{k_F \cancel{[^1M^*]}}{(k_F + k_{IC} + k_{ISC}) \cancel{[^1M^*]}}$$

$$\Phi^o = \frac{k_F}{k_F + k_{IC} + k_{ISC}}$$

since $k_{nr} = k_{IC} + k_{ISC}$

rate of non-radiative deactivation

then

$$\boxed{\Phi^o = \frac{k_F}{k_F + k_{nr}}}$$

Now, since k = rate of all deactivation processes for the excited state

then $\boxed{\tau_o = \frac{1}{k} = \frac{1}{k_F + k_{nr}}}$ $\boxed{= \frac{k_F}{k_F + k_{nr}} \times \frac{1}{k_F} = \frac{\Phi^o}{k_F}}$

Example: **In water, the fluorescence quantum yield and observed fluorescence lifetime of tryptophan are $\phi^o = 0.20$ and $\tau_0 = 2.6$ ns, respectively. The fluorescence rate constant k_f is?**

Solution: $\tau_o = \frac{\Phi^o}{k_F}$ So, $k_F = \frac{\Phi^o}{\tau_o} = \frac{0.20}{2.6 \times 10^{-9}\ s} = 7.7 \times 10^{7}\ s^{-1}$

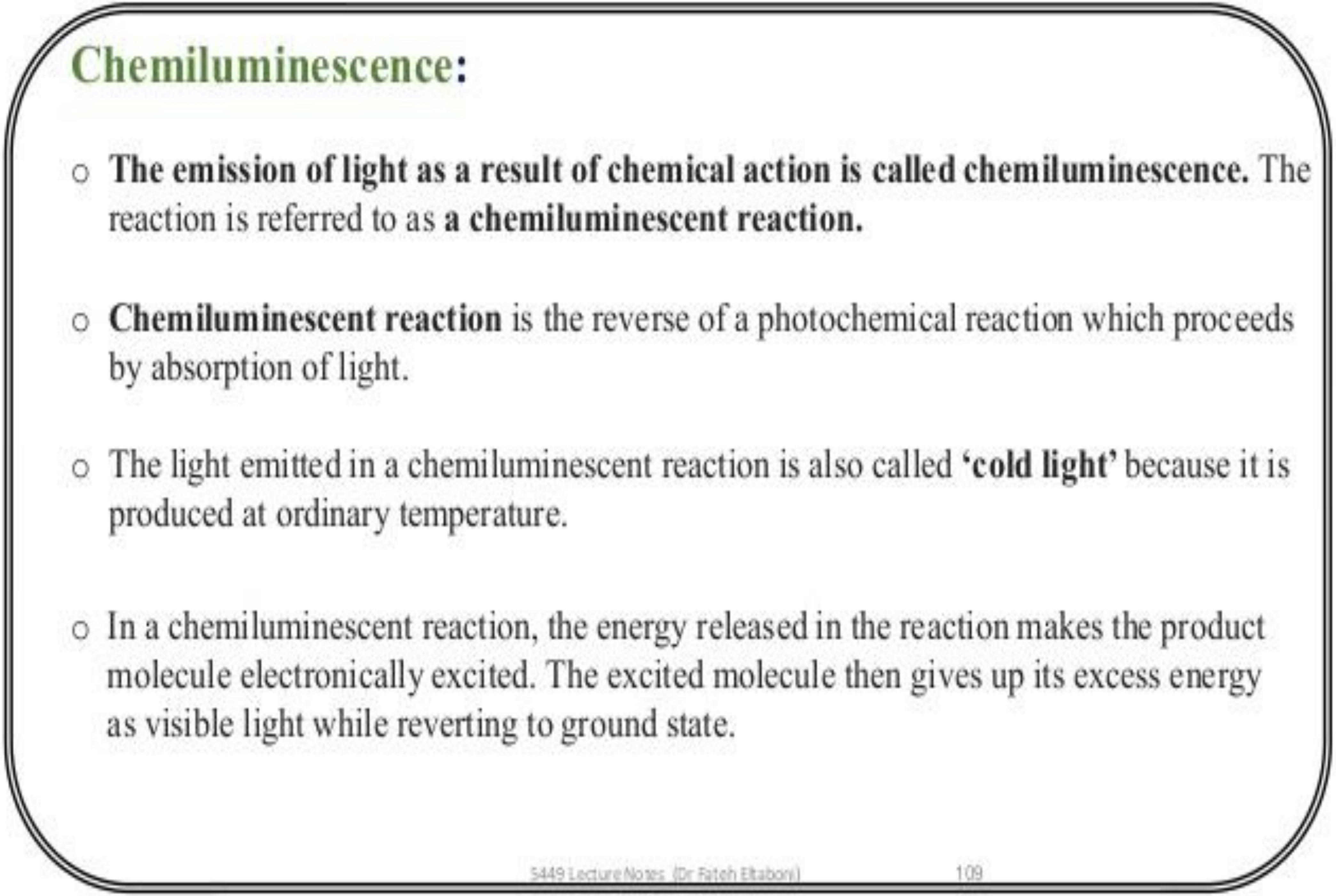
What does a lifetime mean?

Physically it corresponds (due to the exponential nature of the decay) to the time taken for $[\,^1M^*]$ to decay from $[\,^1M^*]_o$

This is a *Relaxation Process* $\longrightarrow$ to $1/e\ [\,^1M^*]_o$

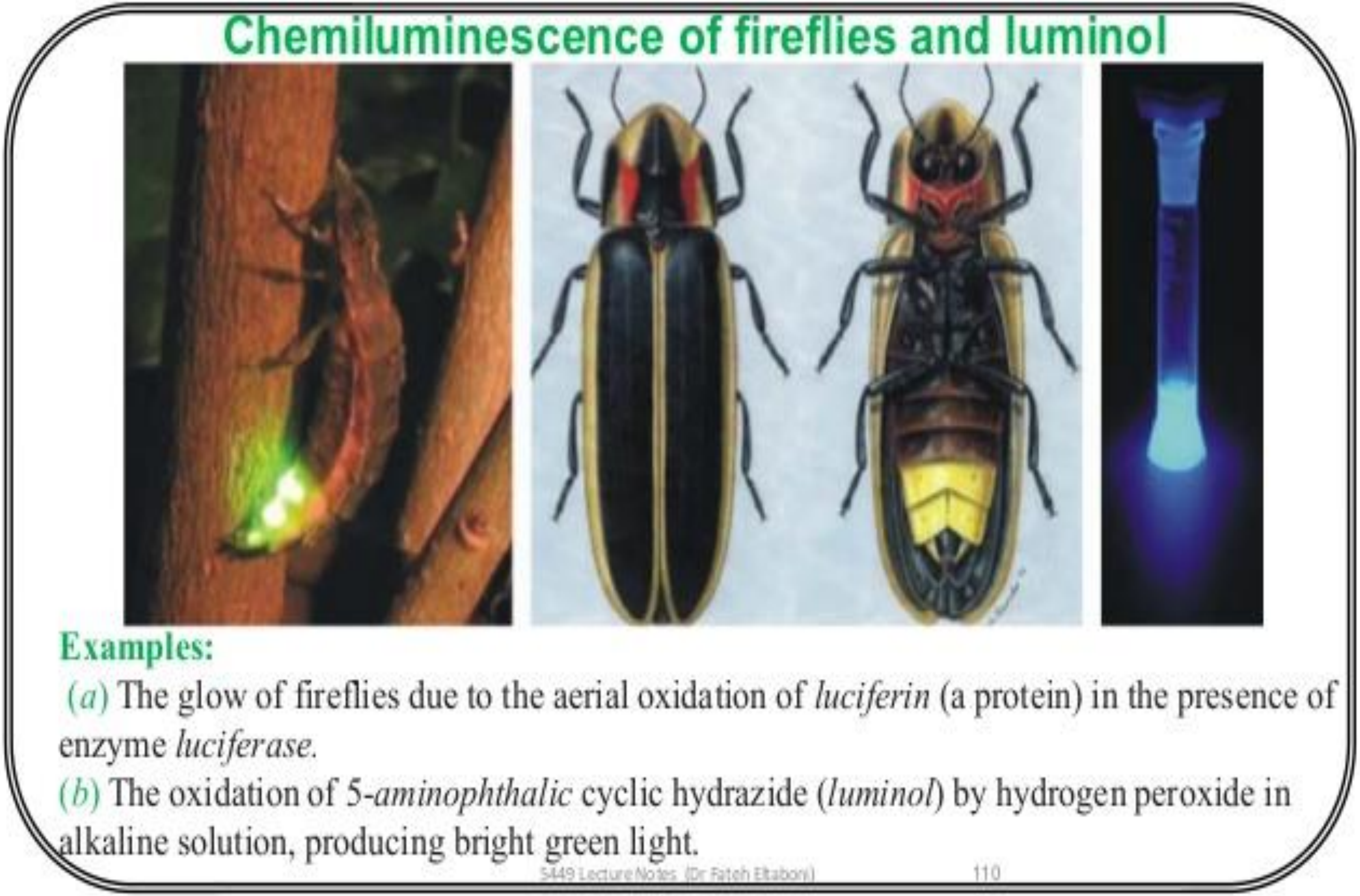
$^1M^*$ population relaxes back to the ground state

lifetime $\equiv \tau_o \equiv$ relaxation time



Chemiluminescence:

- **The emission of light as a result of chemical action is called chemiluminescence.** The reaction is referred to as **a chemiluminescent reaction.**
- **Chemiluminescent reaction** is the reverse of a photochemical reaction which proceeds by absorption of light.
- The light emitted in a chemiluminescent reaction is also called **'cold light'** because it is produced at ordinary temperature.
- In a chemiluminescent reaction, the energy released in the reaction makes the product molecule electronically excited. The excited molecule then gives up its excess energy as visible light while reverting to ground state.



Chemiluminescence of fireflies and luminol

Examples:

(*a*) The glow of fireflies due to the aerial oxidation of *luciferin* (a protein) in the presence of enzyme *luciferase.*

(*b*) The oxidation of 5-*aminophthalic* cyclic hydrazide (*luminol*) by hydrogen peroxide in alkaline solution, producing bright green light.

Chemiluminescence

- The emission of light in chemical reaction at ordinary temperature is called chemiluminescence.
- It is just the reverse of photochemical reaction.

Bioluminescence

- Production and emission of light by living organism is called bioluminescence.
- Bios – Living   and Lumen – Light.
- Is a naturally occurring form of chemiluminescence where energy id released by a chemical reaction in the form of light emission.


Thank
you