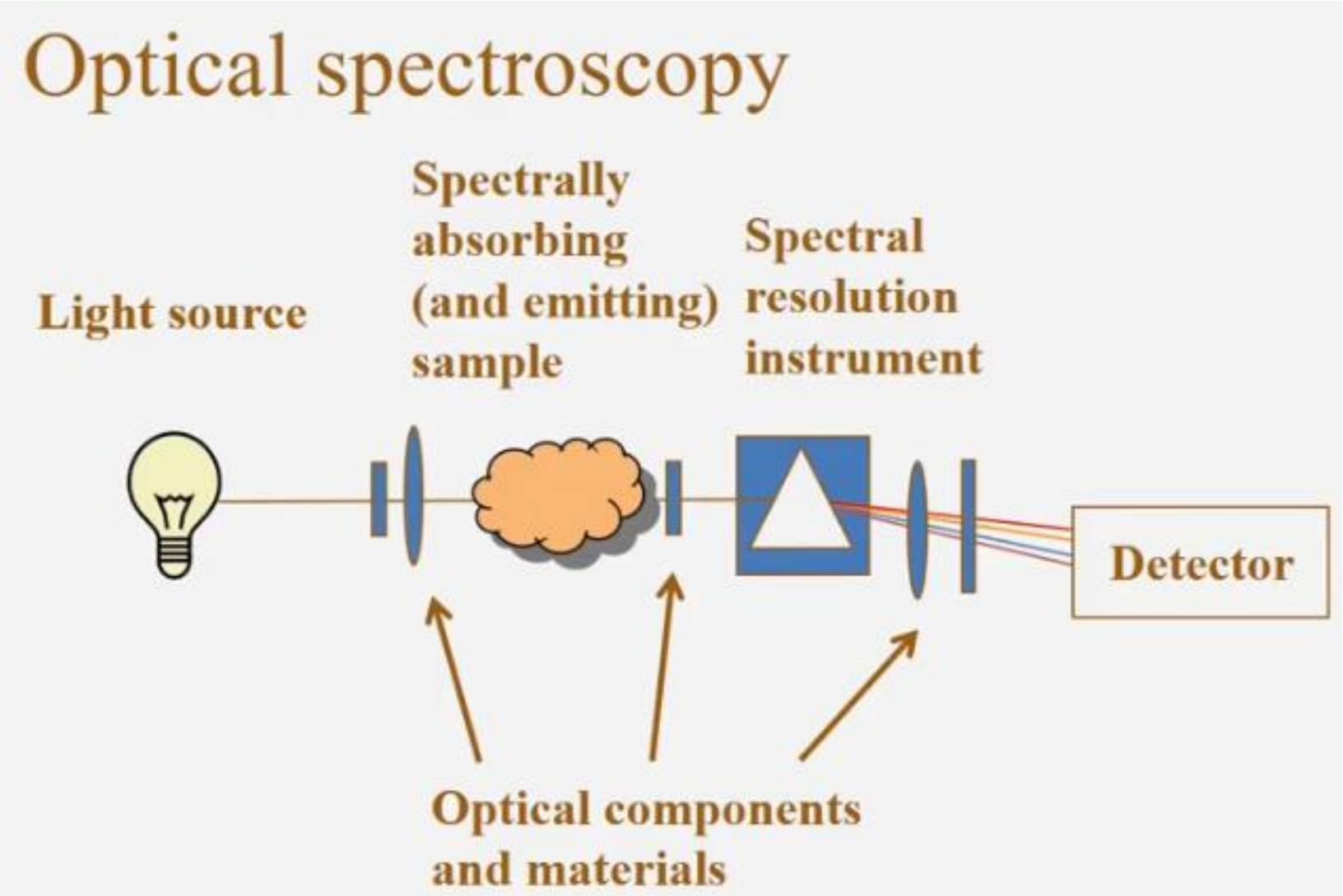
Optical Spectroscopy

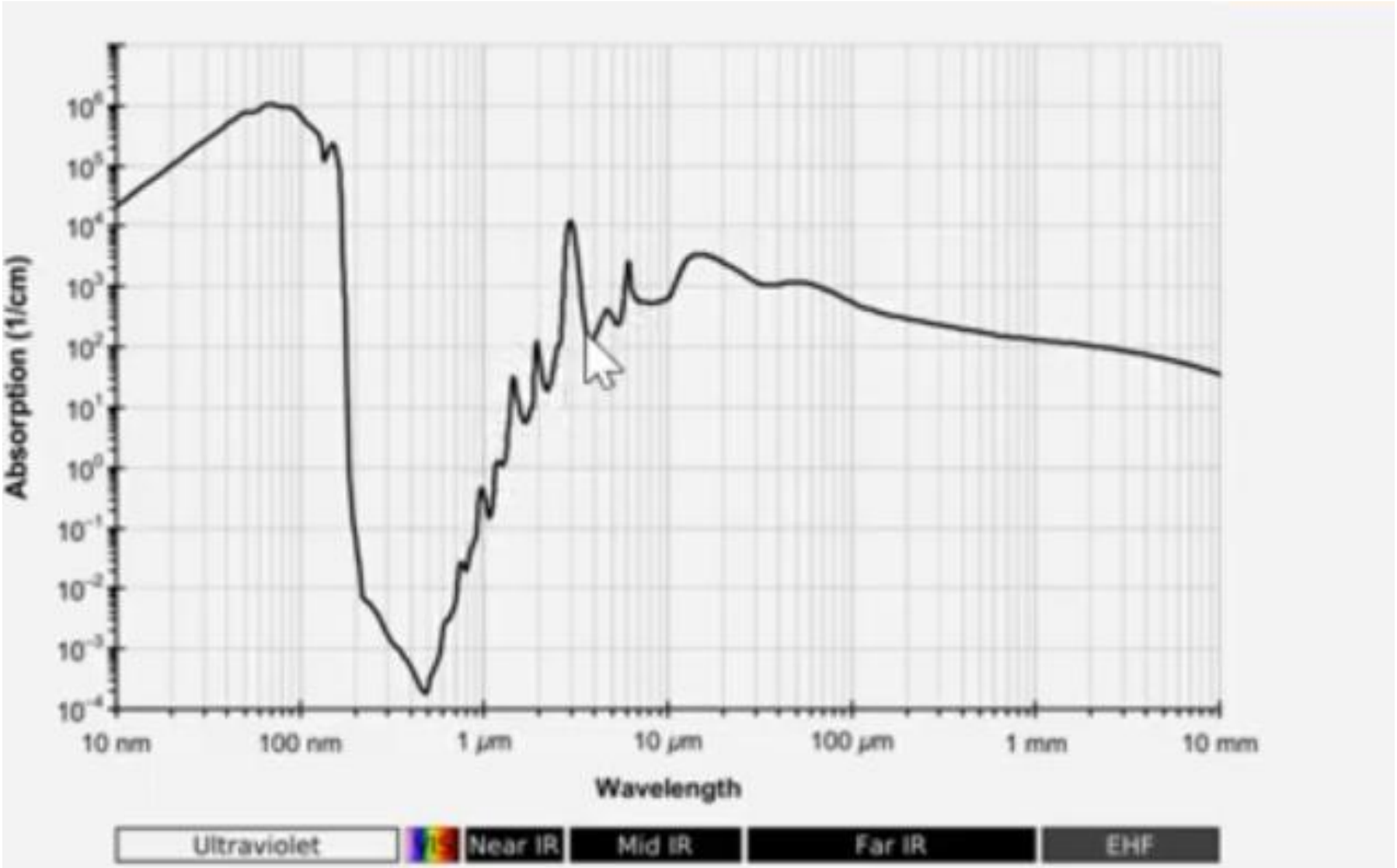
Virginia Lorenz, Kai Wen Teng, Alexey Bezryadin

PHYS 403

What is optical spectroscopy

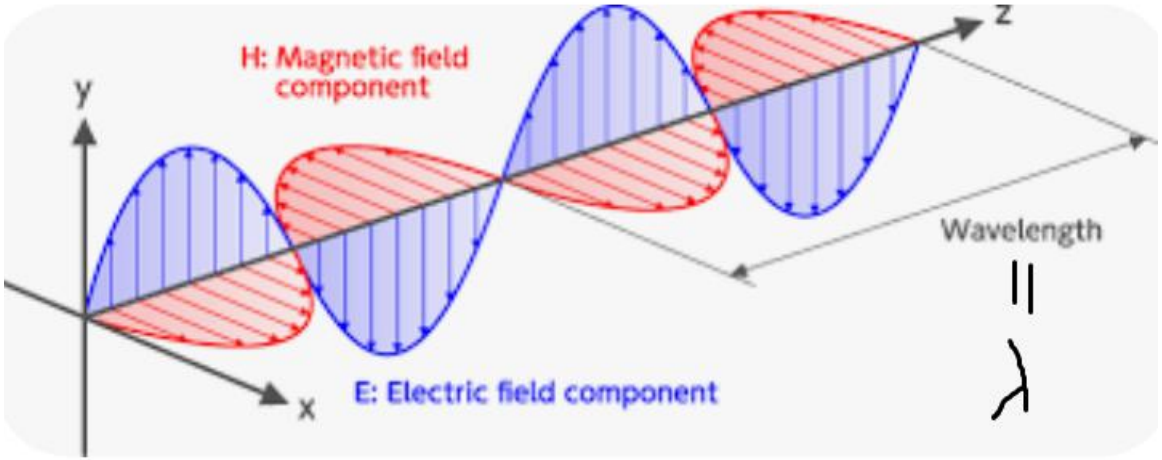


Example



The visible and UV spectra of liquid water

What is light: wave and photon



Main formulas:

1. Wave formula: frequency*wavelength=speed of light; $c = f\lambda$
2. Planck's formula: energy of one quantum (photon) $E = hf$

Here h is Planck's constant

3. Light is a transverse wave.
4. The direction of the electric field is called "polarization direction"
5. Photons (particles of light) carry spin (angular momentum), which equals $\hbar$, which is the "reduced Planck's constant".

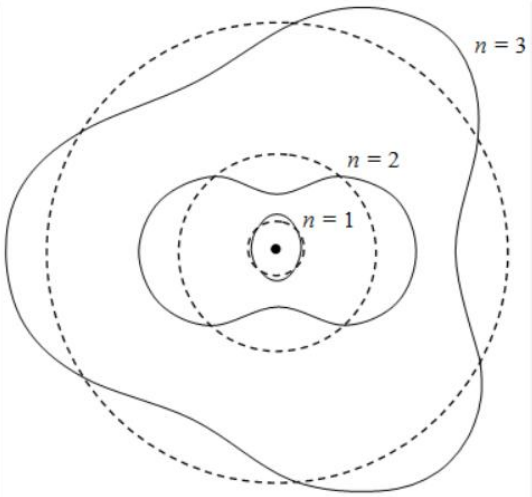
De Broglie standing wave – electronic orbitals

Each stable closed orbit must have a length equal to the wavelength multiplied by an integer.

The Stationary States of the Hydrogen Atom

- The de Broglie wavelength for a particle *has* to be $\lambda = h/p = h/mv$. Thus the standing-wave condition for a de Broglie wave is $2\pi r = n\frac{h}{mv}$
- This condition $v = \frac{nh}{2\pi mr} \qquad n = 1, 2, 3, \ldots$ is true only if the electron's speed is
- The electron cannot have just any speed, only the discrete values given by this equation.

$$L = rp = mvr = n\frac{h}{2\pi} = n\hbar$$



The calculation shows
How the angular momentum
Is quantized.

Key idea: a photon can be absorbed by the atom, in which case the electron transitions to a higher orbit.

How to calculate De Broglie standing wave – solve the Schrodinger equation

Application of the Schrödinger Equation to the Hydrogen Atom

- Potential energy of the electron-proton system is electrostatic (no magnetic effects in the beginning):

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

- Rewrite the three-dimensional time-independent Schrödinger Equation.

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right]=E-V(r)$$

Energy bands in molecules and solids

Band structure of Solids

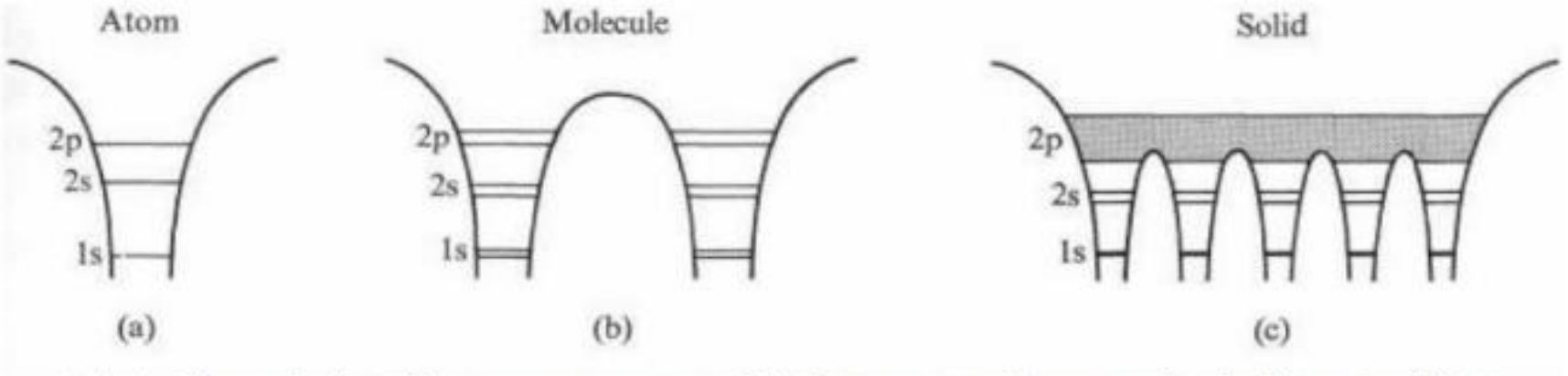


Fig.1 The evolution of the energy spectrum of Li from an atom (a), to a molecule (b), to a solid (c).

The energy spectrum gradually changes as atoms are assembled to form the solid

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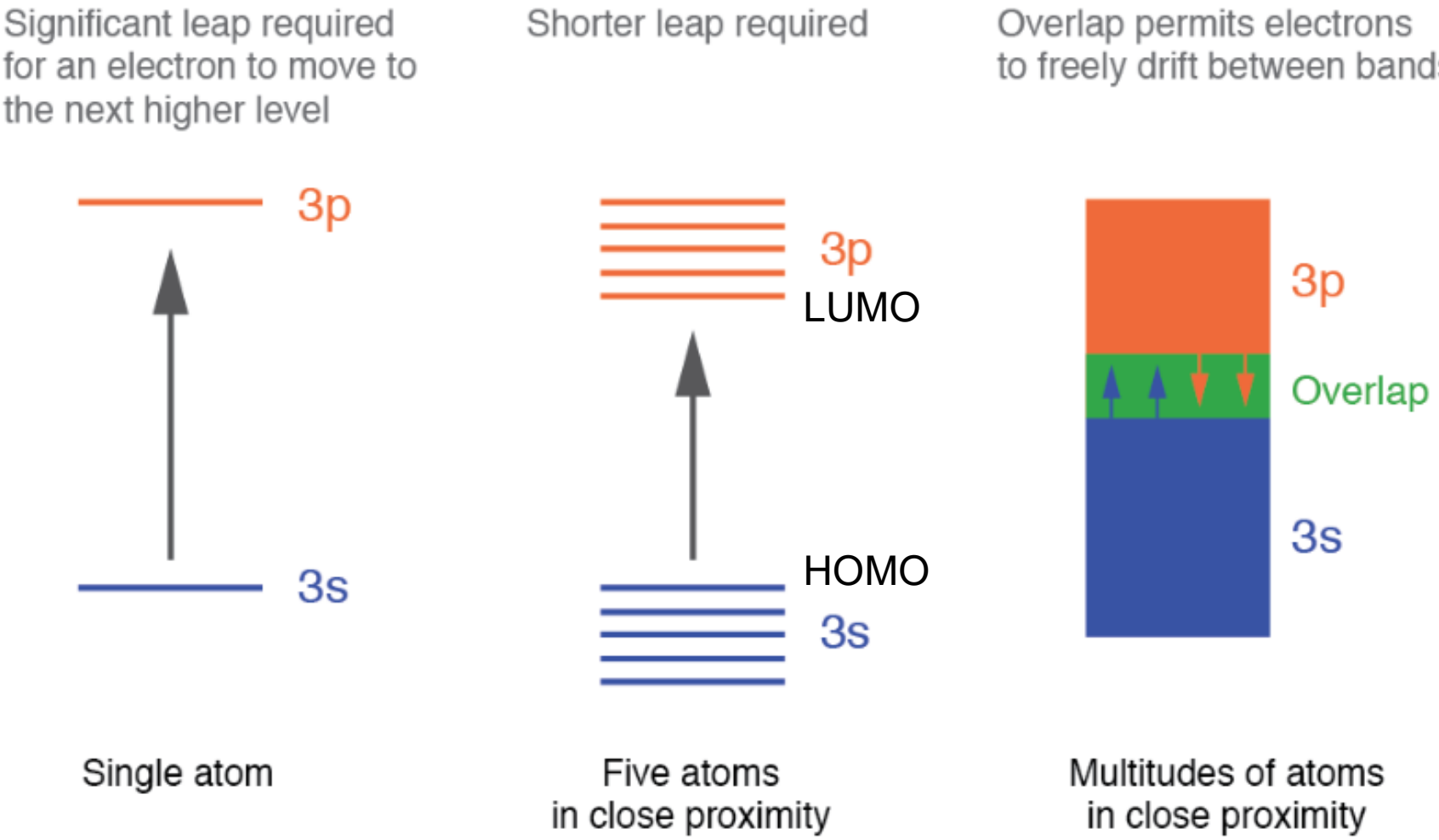
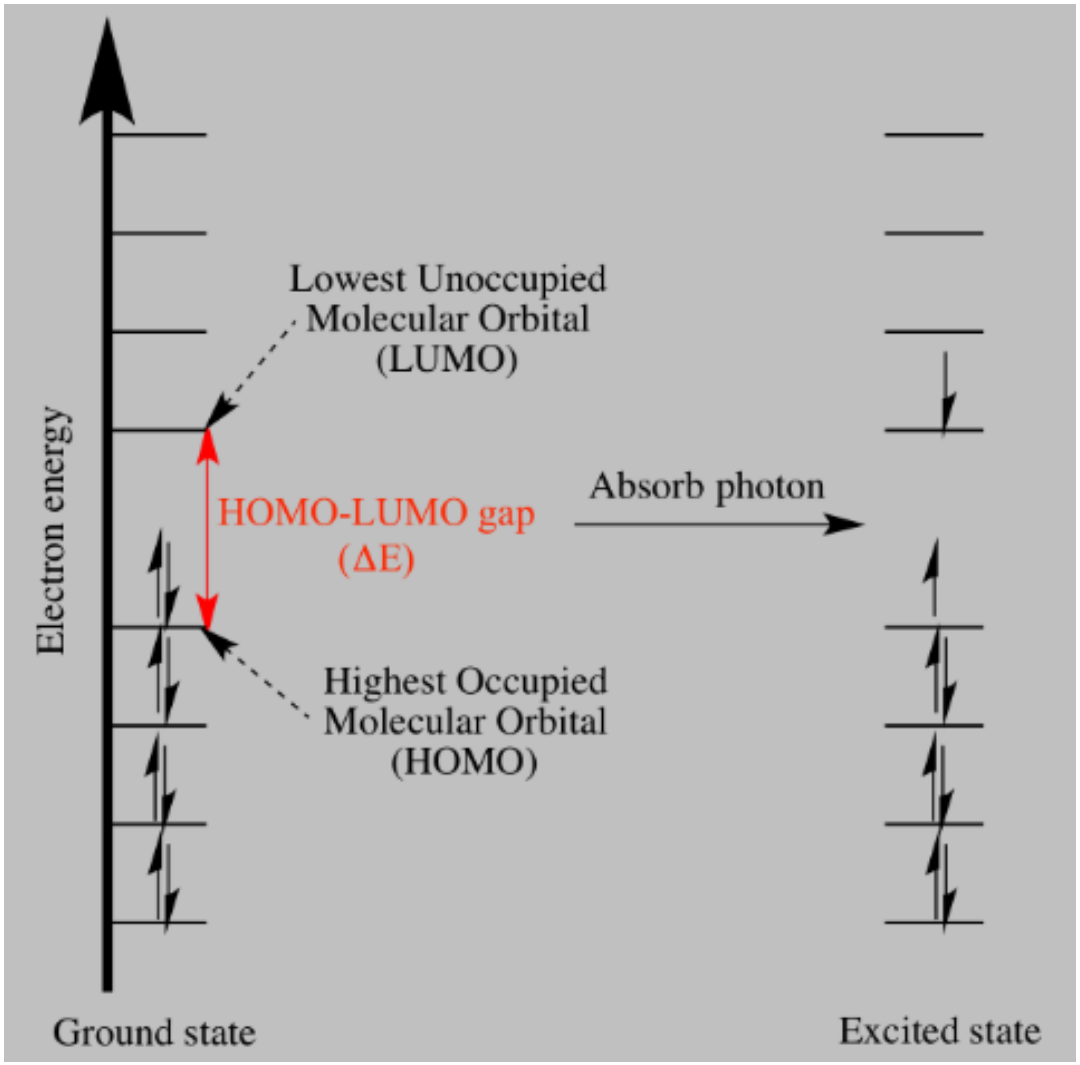
Energy bands in molecules and solids

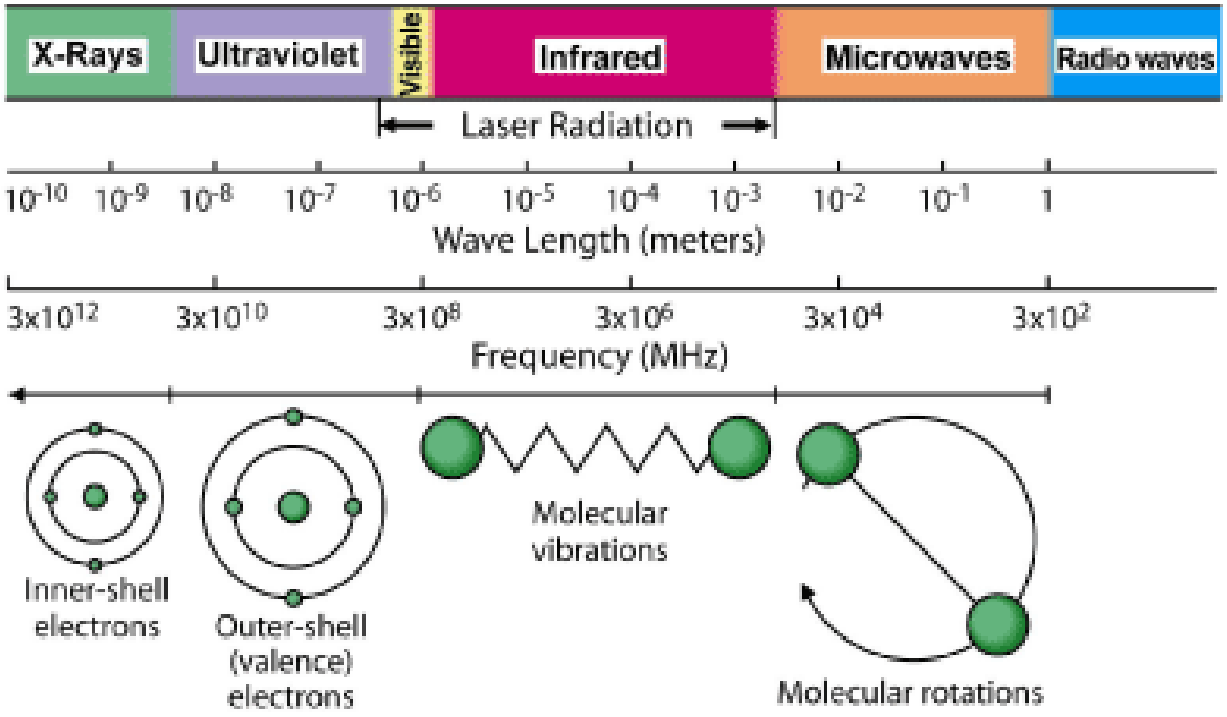


Energy bands in molecules and solids



Each arrow epresent an electron. Each electron has internal angular momentum, called “spin” which can be either +1/2 (up) or -1/2 (down).

Electromagnetic Spectrum of atoms and molecules

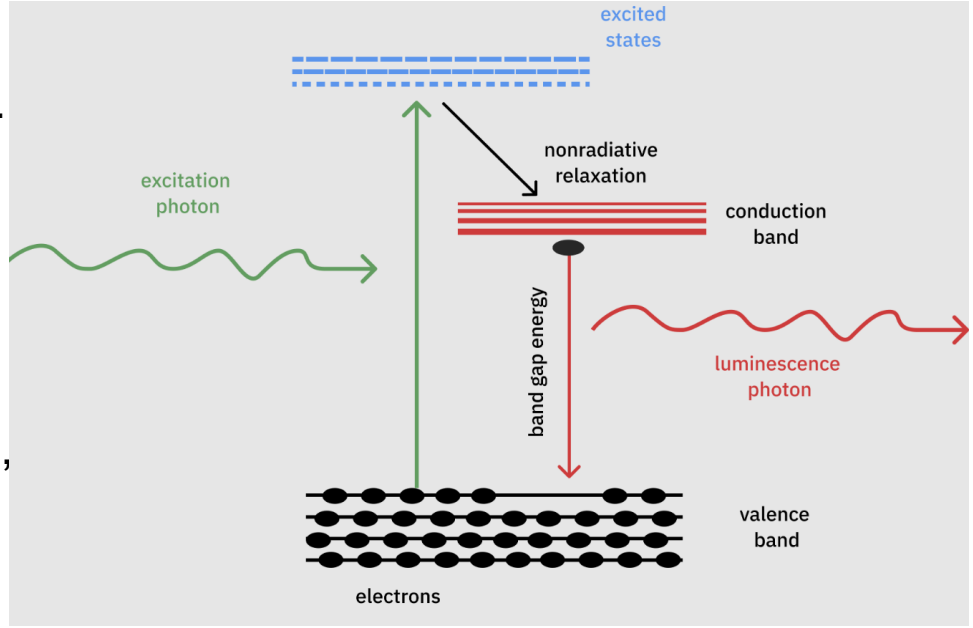


From http://de.cem.com

https://www.olympus-lifescience.com/en/microscope-resource/primer/techniques/fluorescence/fluorescenceintro/

Luminescence and Photoluminescence

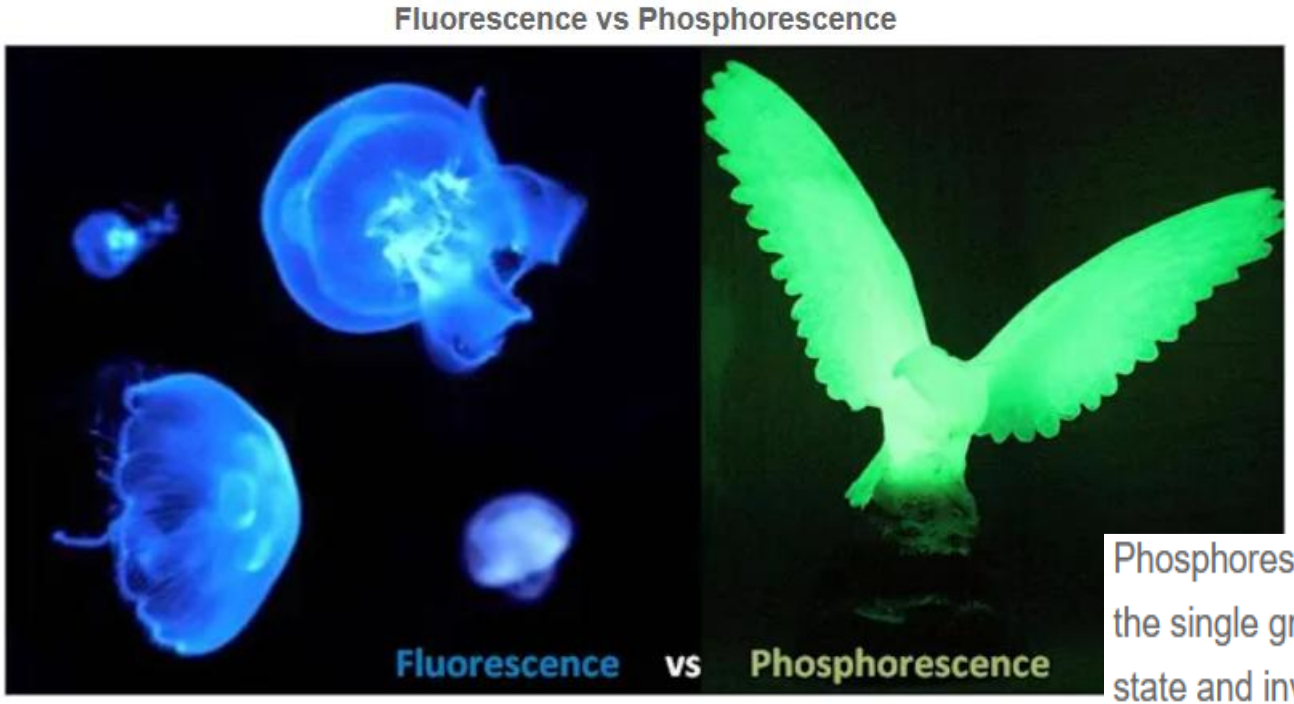
Luminescence is the emission of light produced by methods other than heat. Luminescence is caused by the movement of electrons from higher energy states to lower energy states. There are many different types of luminescence including bioluminescence, chemiluminescence, phosphorescence, and fluorescence.



Fluorescent solutions under UV light. Absorbed photons are rapidly re-emitted under longer electromagnetic wavelengths.

Photoluminescence (abbreviated as **PL**) is light emission from any form of matter after the absorption of photons (electromagnetic radiation).

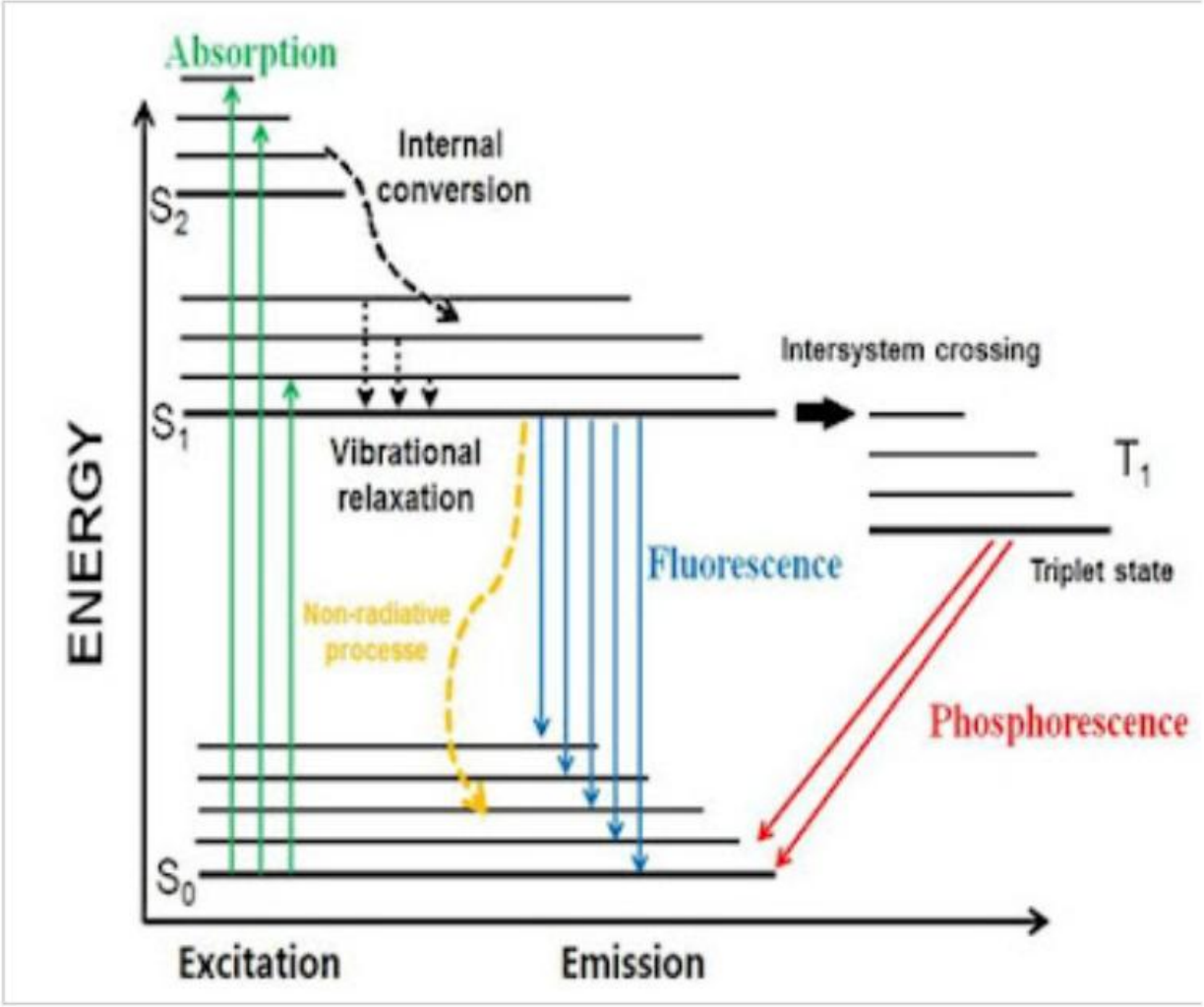
Group-21.png (3419×2266)



Phosphorescence involves the transition from the single ground energy state to excited triplet state and involving a change of spin state

Fluorescence is a two-stage chemical process involving absorption of shorter-wavelength light by a chemical fluorophore such as a protein or carotenoid (excitation), followed by the release of some of the absorbed energy as longer-wavelength light (emission).

Fluorescence and Phosphorescence

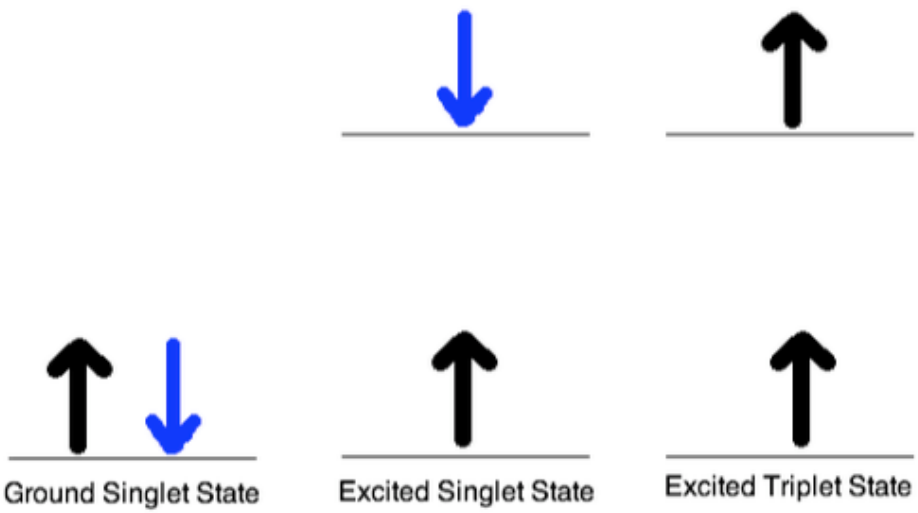


Mechanism of fluorescence and phosphorescence emission.

Singlet states and triplet states

In spectroscopy and quantum chemistry, the **multiplicity** of an energy level is defined as $2S+1$, where S is the total spin angular momentum.[1][2][3] States with multiplicity 1, 2, 3, 4, 5 are respectively called singlets, doublets, triplets, quartets and quintets.[2]

In the ground state of an atom or molecule, the unpaired electrons usually all have parallel spin. In this case the multiplicity is also equal to the number of unpaired electrons plus one.[4]



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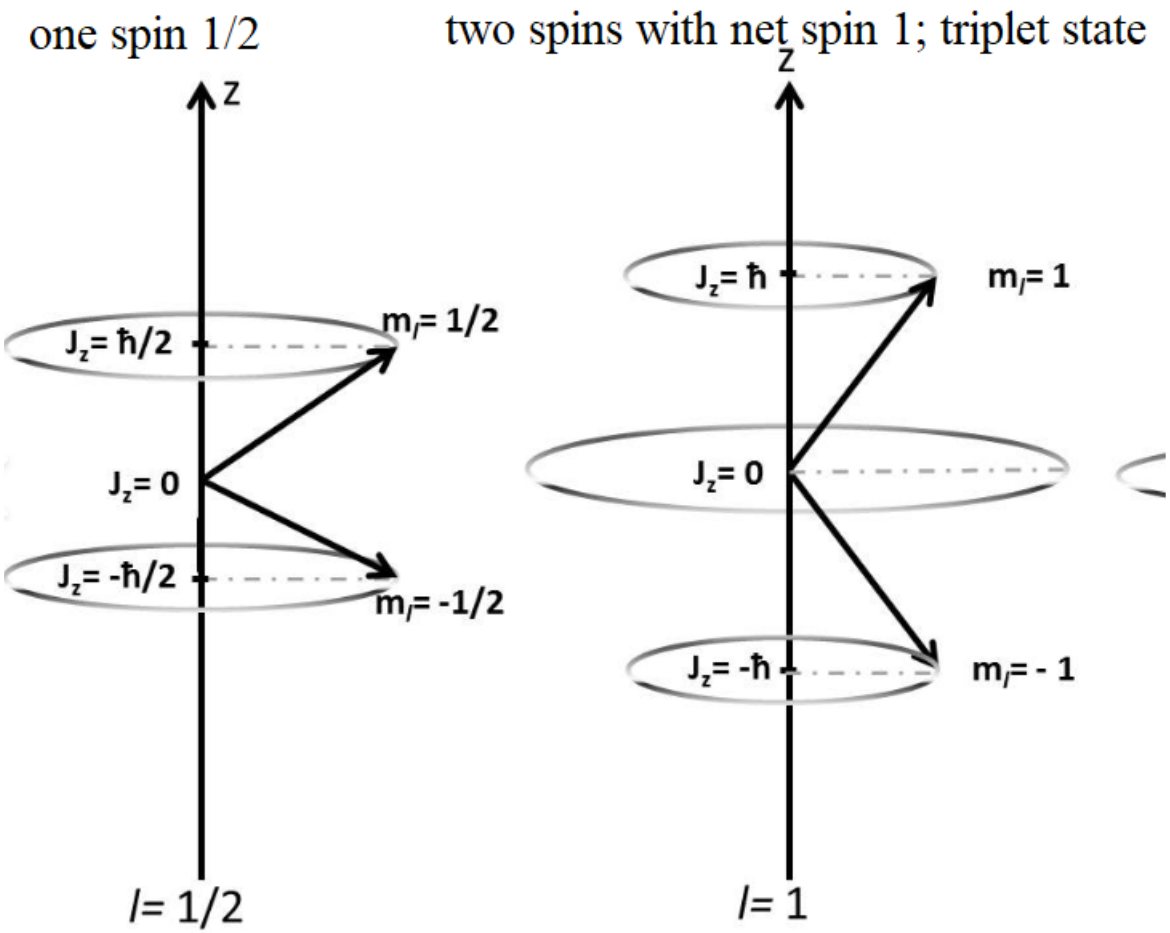
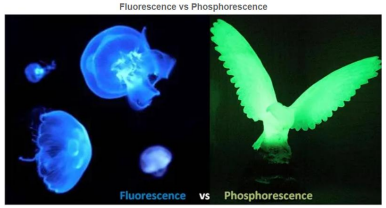


Singlet state has a total zero angular momentum, so it is not shown on the picture. Such state can only have value of its projection: zero. Therefore, it is called “singlet”.

Fluorescence vs Phosphorescence

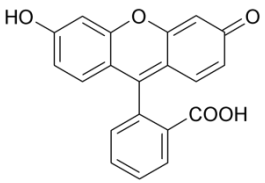


The emitted photon (light) has lower energy than the absorbed photon and emission occurs at a longer wavelength than the incident light	The emitted photon (light) has lower energy than the absorbed photon and emission occurs at a longer wavelength than fluorescence
In fluorescent materials, gives an **'an immediate flash or afterglow'** on excitation	Phosphorescent materials appears to **'glow in the dark',** because of slow emission of light over time.
Examples of Fluorescence: Gemstones fluoresce, including gypsum, talc. Jelly fish, chlorophyll extract, vitamins etc	**Examples of Phosphorescence**: Glow of clock dial or toys or in bulbs after switching off the light in the room. The glow remains for some minutes or even hours in a dark room Phosphorescent materials in sign board illuminate during night.

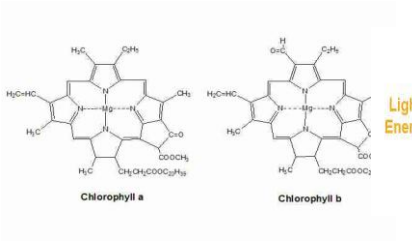
Types of Fluorescent Molecules

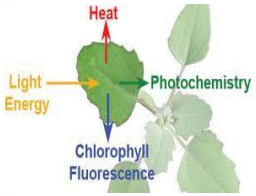
Synthetic Organic:

Fluorescein



Naturally Occuring:

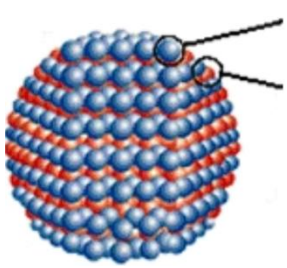


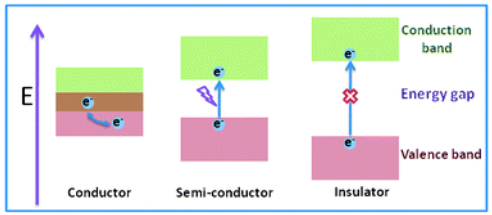


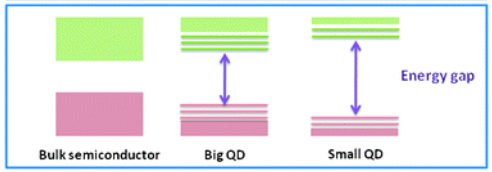
Fluorescent Proteins:

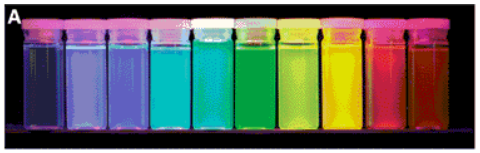
Green Fluorescent Protein

Semiconductor Nanocrystal:









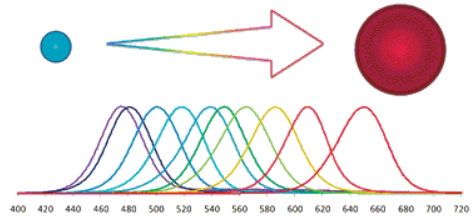
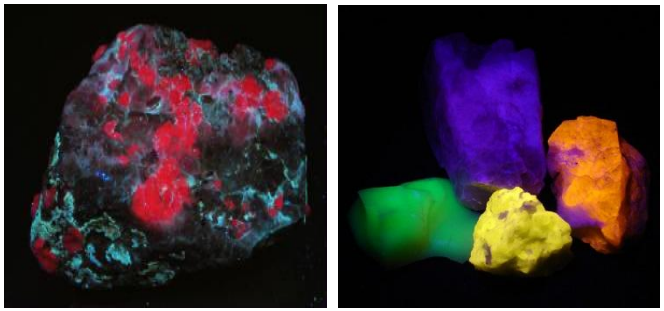


Image from Zrazhevskiy et al. 2010

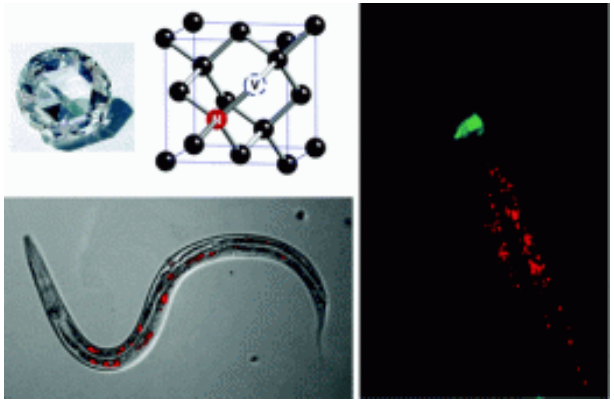
Crystals:



Ruby and assorted minerals

From mineralman.net

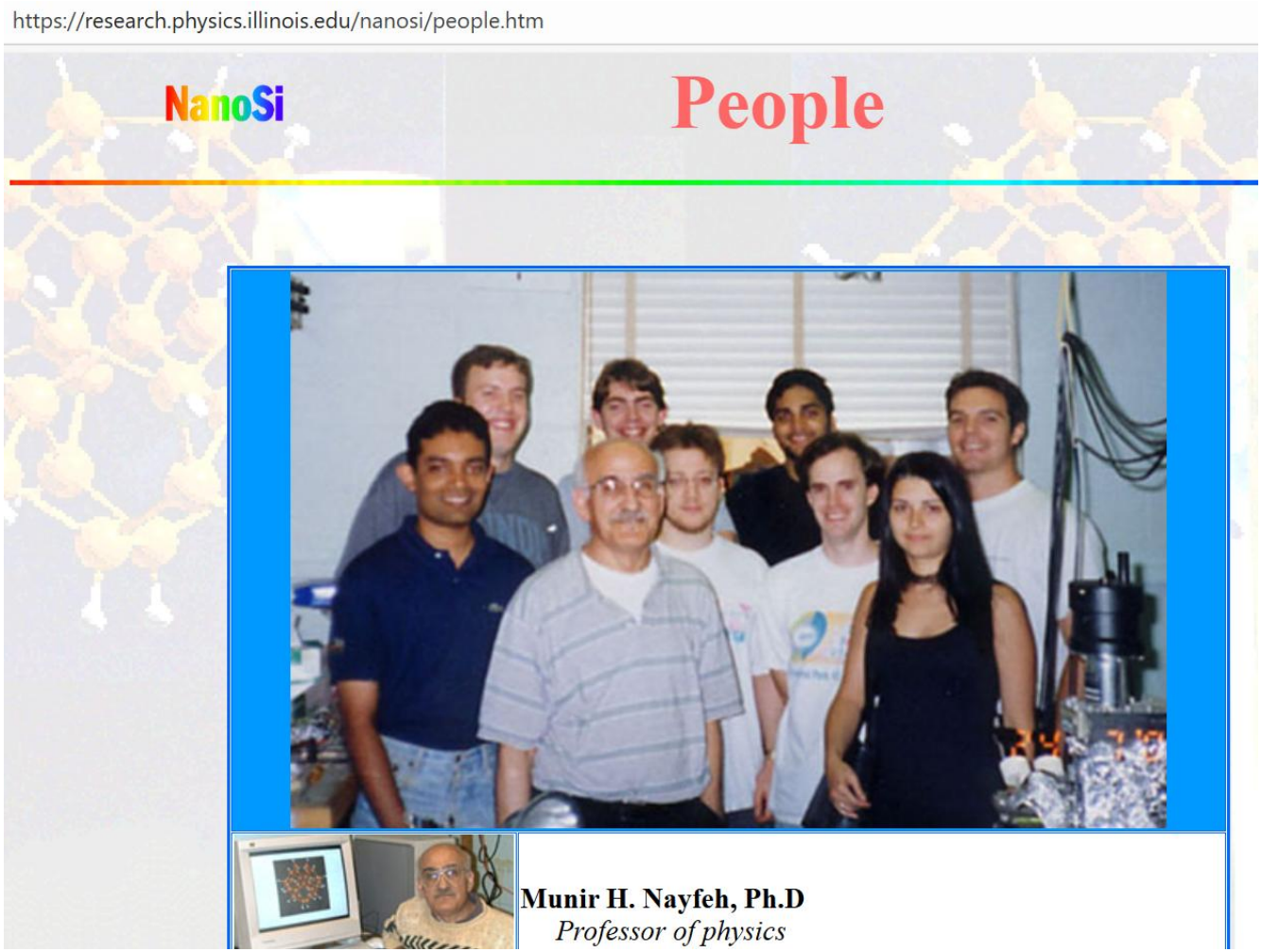
Fluorescent Nanodiamonds



Nano Lett., 2010, 10 (9), pp 3692-3699. DOI: 10.1021/nl1021909

Fluorescent Si nanostructures at Illinois

Prof. Munir Nayfeh



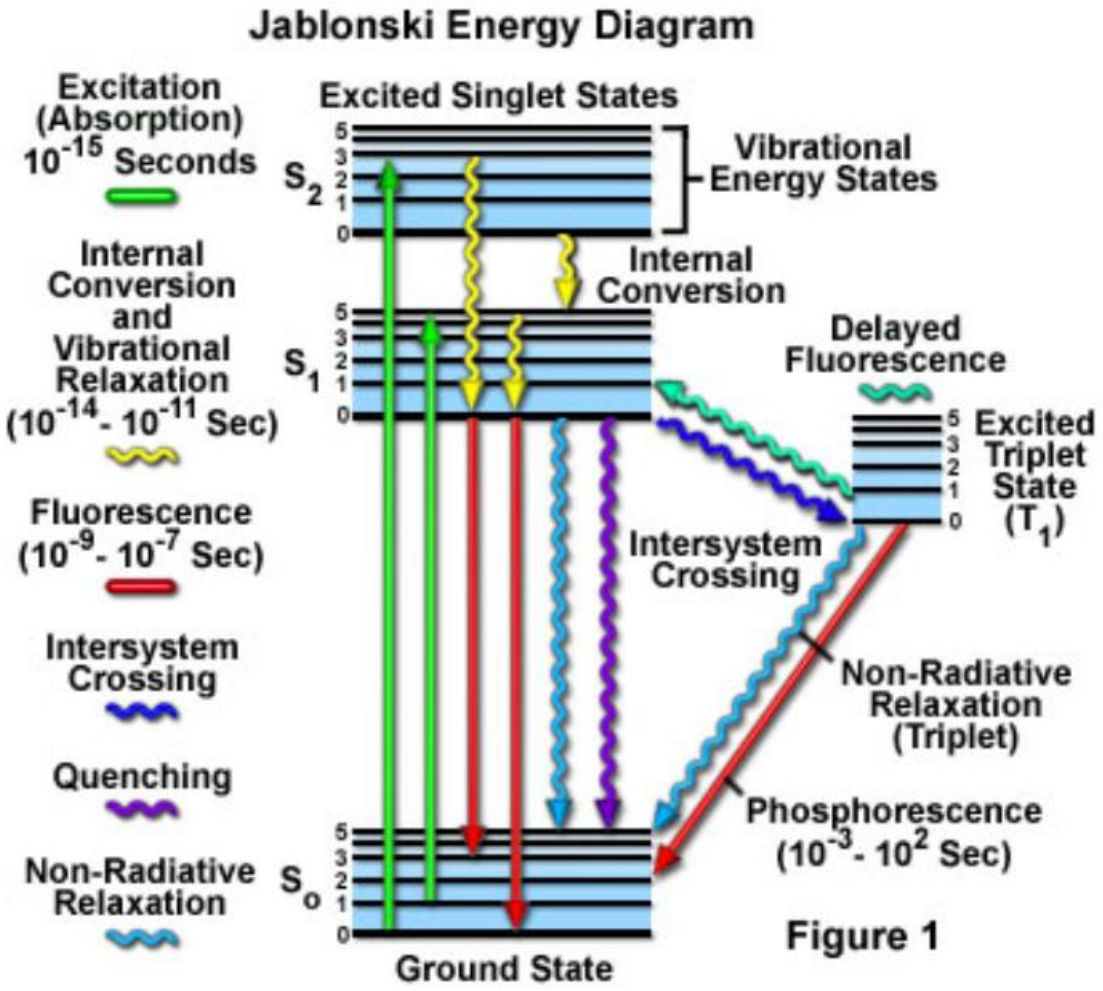
Munir H Nayfeh | Physics | Illinois

Perrin-Jablonski energy diagram

illustrates the electronic states of a molecule and the transitions between them

Alexander Jabłoński

1898-1980



ground electronic singlet state

Diagram by Ulai Noomnarm in Photosynth Res. 2009 Aug-Sep;101(2-3):181-94.

Key Components of a Jablonski Diagram

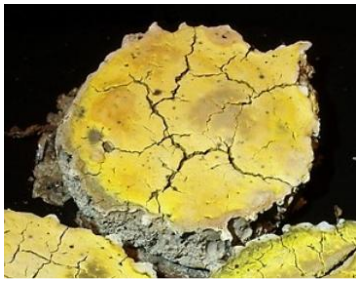
1. **Electronic States**:
   - **Ground state (S_0)**: The lowest energy singlet state.
   - **Excited singlet states (S_1, S_2, ...)**: Higher energy states with paired electron spins.
   - **Triplet states (T_1, T_2, ...)**: Excited states with unpaired electron spins (important for phosphorescence).
2. **Transitions**:
   - **Absorption**: Vertical upward arrows from S_0 to S_1 or higher states, caused by photon absorption.
   - **Fluorescence**: Vertical downward arrows from S_1 to S_0, representing radiative decay (emission of a photon).
   - **Phosphorescence**: Downward arrows from T_1 to S_0, typically slower than fluorescence due to spin-forbidden nature.
   - **Intersystem Crossing (ISC)**: Diagonal arrows from singlet to triplet states (e.g., $S_1 \rightarrow T_1$), a non-radiative spin-flip process.
   - **Internal Conversion (IC)**: Non-radiative transitions between electronic states of the same spin multiplicity (e.g., $S_2 \rightarrow S_1$).
   - **Vibrational Relaxation**: Rapid non-radiative decay within the same electronic state to the lowest vibrational level.

The Bolognian Stone

http://www.isbc.unibo.it/Files/10_SE_BoStone.htm

The Bologna Stone was discovered in 1603, at the base of a dead volcano near Bologna. When treated with heat, and exposed to sunlight, it would glow for hours—sometimes days. It took 400 years to figure out why.
In 1603, Vincenzo Cascariolo was digging in the volcanic rock near Bologna, Italy. The man was a shoemaker by trade, but he hoped to get rich by alchemy. When he found a milky-white stone he decided to take some samples back to his workshop. There, he most likely heated a sample of the stone, possibly in a special oven that let him control the exposure of the material to both the source of heat (coals or flames) and the oxygen in the air. The process is called “calcination.” Cascariolo failed to come up with the Philosopher’s Stone, but he can’t be faulted for thinking he did. After all, after the treatment, if exposed to sunlight or flames this particular stone glowed in the dark for hours.

Marc Antonio Cellio (1680) representing the light emission of heated barite



https://www.flickr.com/photos/28617364@N04/sets/72157635506831648/
Here’s someone who made “Bologna stone pies,” by adding, among other things, copper chloride to barium sulfate and baked the result.

It took scientists a long time to figure out what it was that made baryte glow the way it did. Over four centuries after its discovery, scientists took a lab to samples of the Bologna Stone. What they found was an impurity in the baryte. Copper ions, denuded of two electrons each, were sprinkled through the baryte. When exposed to light, they would absorb energy, and then slowly emit it over multiple days.
https://gizmodo.com/the-bologna-stone-was-a-glowing-mystery-for-400-years-1724589932

It is now a long time since the cobbler of Bologna, in Italy, astonished and amused his friends with a peculiar substance since known as *Bologna phosphorus*, *Bologna stone*, or *Solar phosphorus*, which shines brightly in the dark after having been placed in the sunlight for some time. This substance is sulphuret of barium. The cobbler prepared it by heating red-hot with charcoal a piece of *sulphate of baryta*, or *Barytine*, (Fig. 1,) a stone which he

Fig. 1.

picked up in the secondary strata of the Monte Paterno, where he found it in lumps of considerable weight.* The German chemist, Marggraf, used to prepare solar phosphorus by powdering down the stone, and making it into thin cakes, with a mixture of flour and water, before submitting it to calcination. This "Bologna phosphorus" was the first substance known to become phosphorescent after insolation, and, consequently, it has been submitted to many and varied experiments. It is best obtained by the calcination of pulverized sulphate of baryta, made into a firm paste with common gum. It should be preserved in a bottle which closes hermetically with a glass stopper.

It will be easily understood what is meant by the term *Phosphorescence*, when we remind our readers that phosphorus, which shines so curiously in the dark, and which enters into the composition of our common lucifer matches, is the most remarkable of all phosphorescent bodies. The word "phosphorus," which signifies a substance that bears or emits a light, has frequently been applied to various other substances besides the non-metallic element termed *phosphorus* in chemistry, on account of the property these substances possess likewise of shining in the dark.

1870.

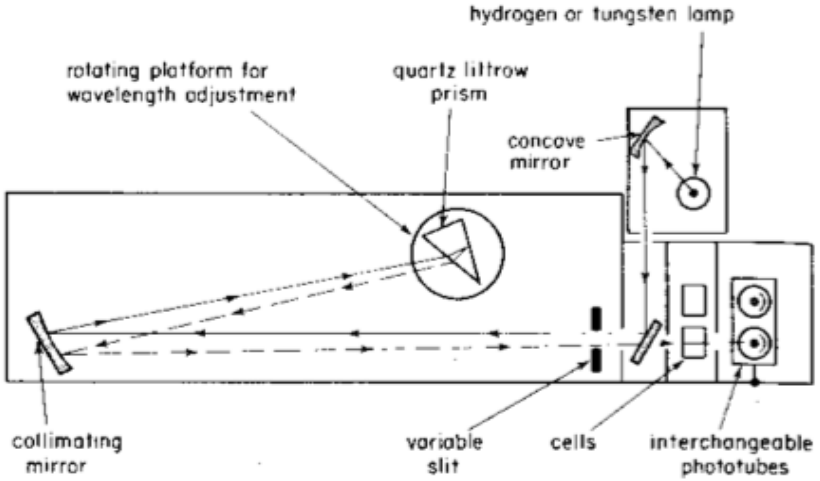
T. L. PHIPSON, PH.D., F.C.S.

First mention of lifetimes?

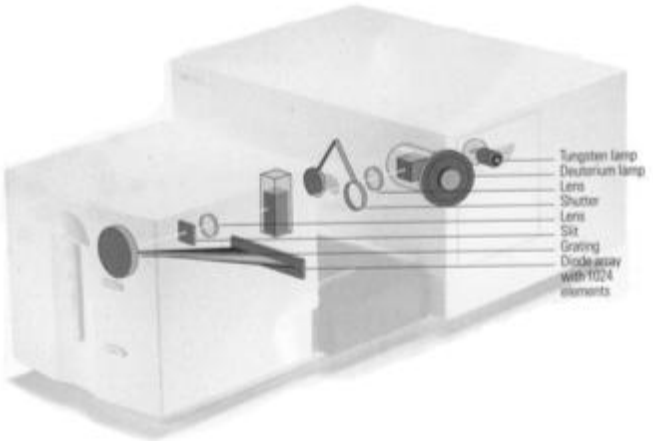
"The Bologna stone, when placed in the sun attracts the rays, and retains them so long as to give light a considerable time after it is removed into the dark. "
Goethe "The Sorrows of Werter"

Steady State Measurements: Absorbance

One of the very first commercially available instruments that measures absorbance was the Beckman DU spectrophotometer



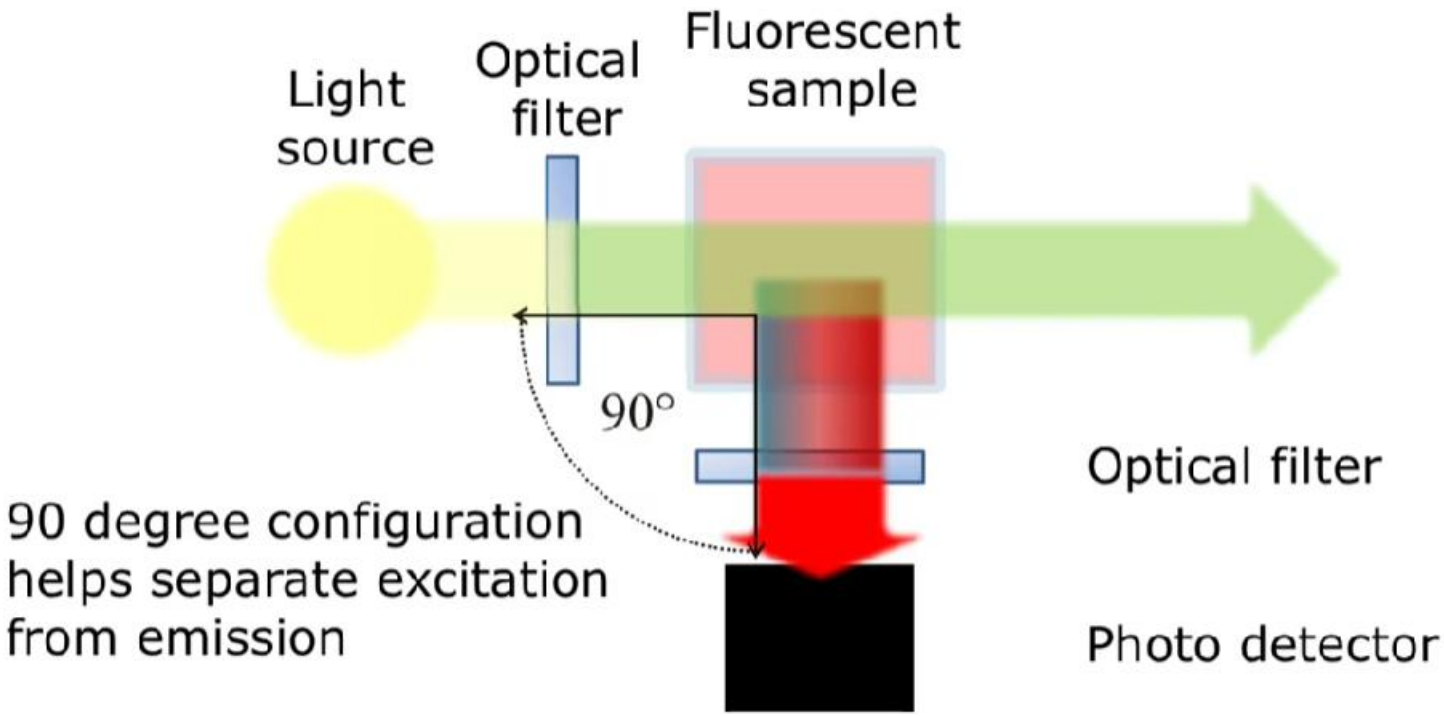
Machines nowadays that utilize diffraction grating and diode array detector can acquire an absorbance spectra in less than 10 seconds.



Fluorescence spectroscopy

Schematic view of instrument

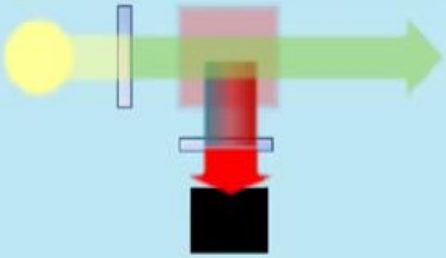
Ibsen photonics



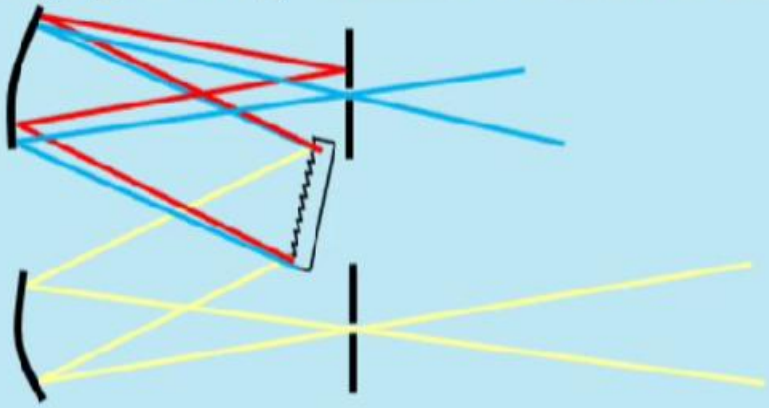
Fluorescence spectroscopy

Optical emission-side

Ibsen photonics

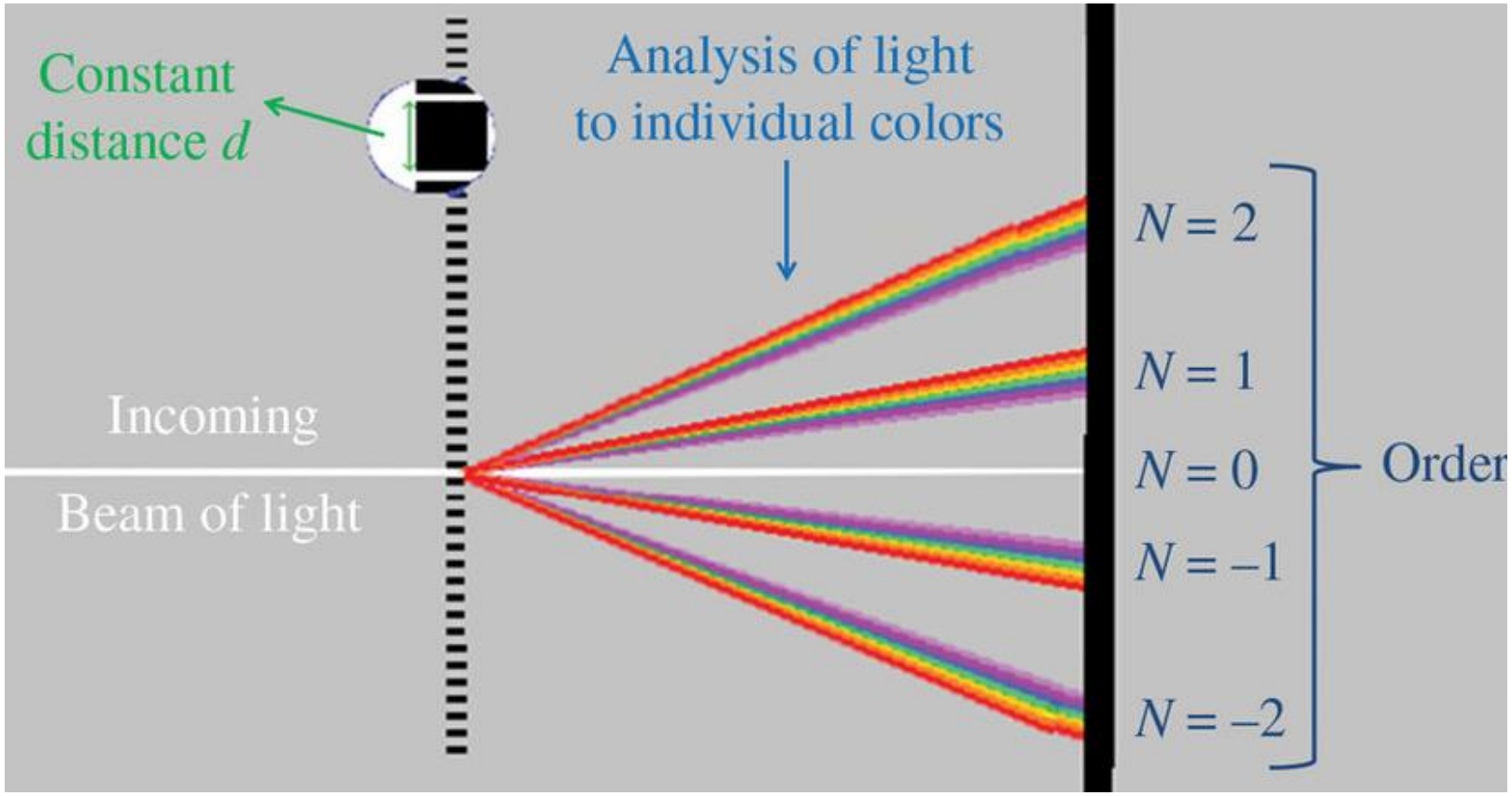


- Scanning grating mono-chromator



- Fixed optical bandpass filter
- Scanning linear variable bandpass filter
- Diode array spectrometer

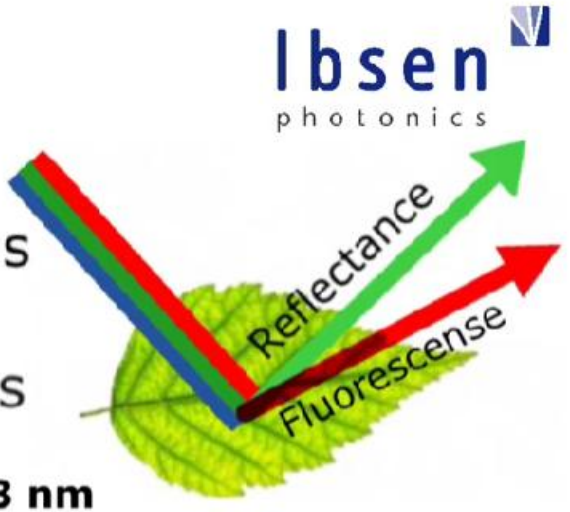
Diffraction grating

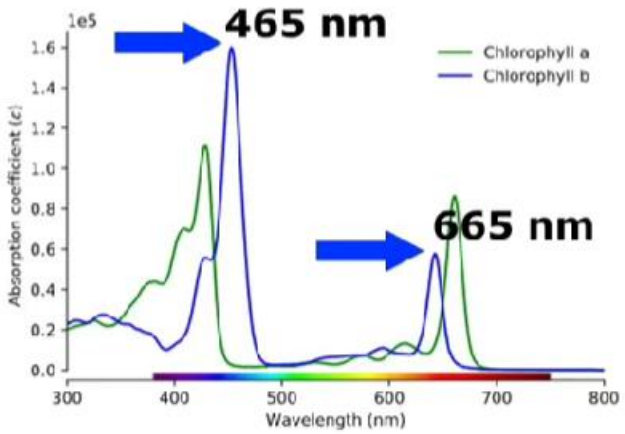


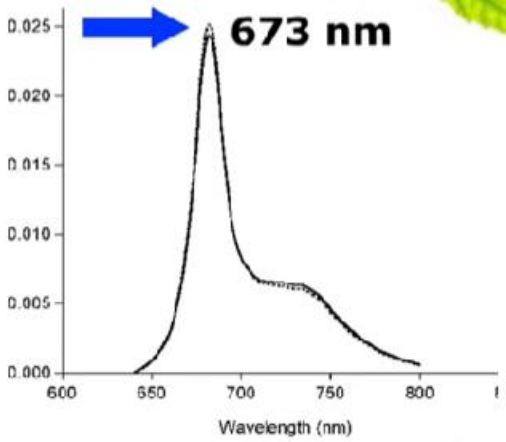
Fluorescence spectroscopy

Natural fluorophores

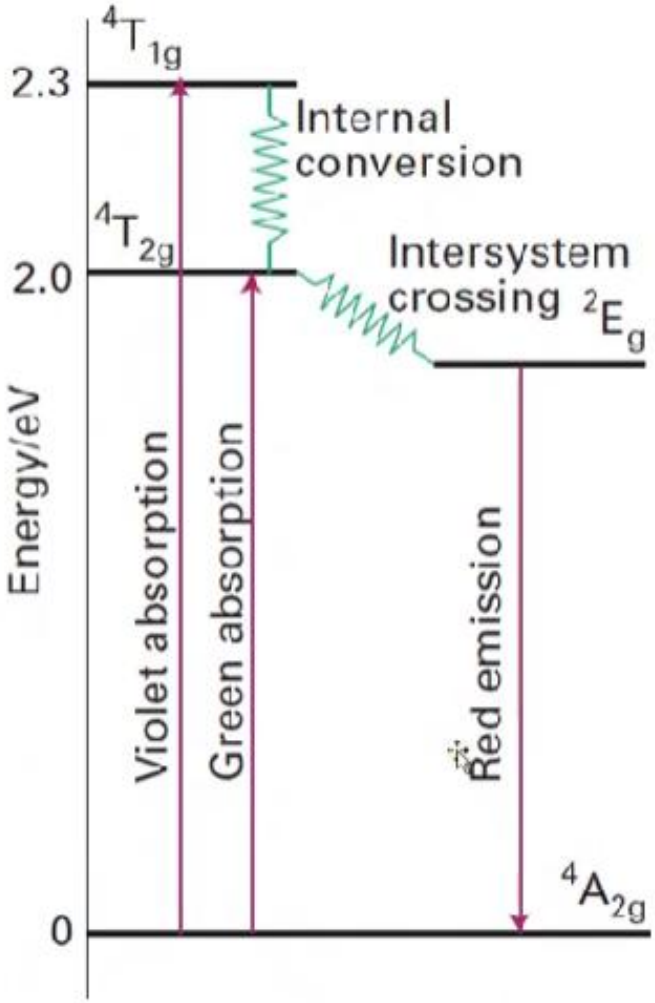
- Chlorophyll (a and b)
  - Absorbs red and blue wavelengths
  - Reflects green
  - Fluoresces in the red wavelengths



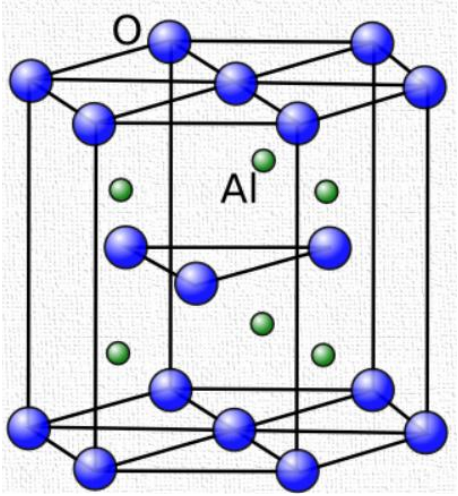


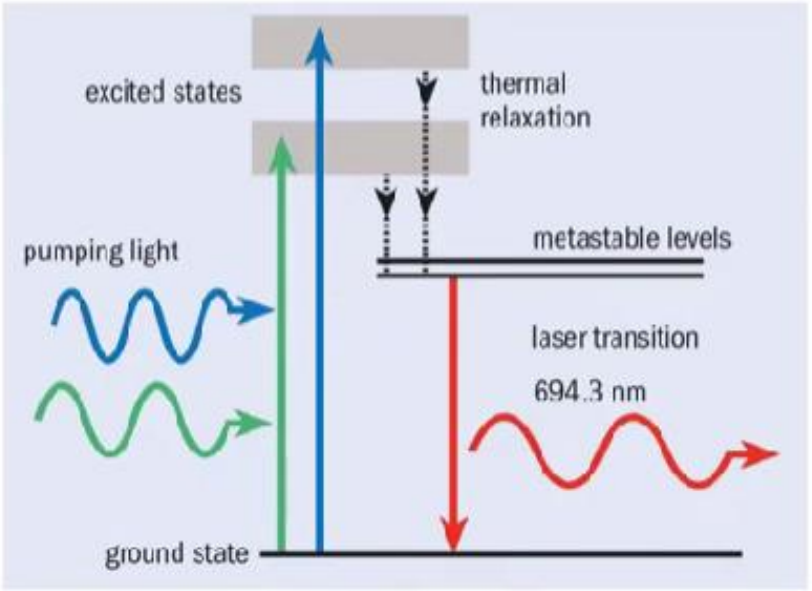


Fluorescence in ruby (some Al is substituted with Cr)



Ruby (Al_2O_3:Cr)





Absorption and luminescence of Cr^{3+} in ruby.

Fluorescence in ruby (some Al is substituted with Cr)

Fluorescence measurement in **ruby doped with chromium (Cr^{3+})** involves studying the light emitted by Cr^{3+} ions embedded in the aluminum oxide (Al_2O_3) crystal lattice of ruby when they are optically excited. Here's a breakdown of how this process works:

1. Electronic Structure of Cr^{3+} in Ruby

- Cr^{3+} ions replace Al^{3+} in the crystal lattice.
- The Cr^{3+} ion has a **$3d^3$** electron configuration.
- In the crystal field of Al_2O_3, the d-orbitals split into energy levels due to the **octahedral crystal field**.
- The relevant energy levels are:
  - **Ground state**: $^4A_2$
  - **Excited states**: ^2E and $^4T_2$

2. Optical Excitation

- A **green or blue laser** (typically around 400–550 nm) excites electrons from the ground state $^4A_2$ to higher energy states like $^4T_2$.
- These excited states quickly relax non-radiatively to the lower excited state ^2E.

3. Fluorescence Emission

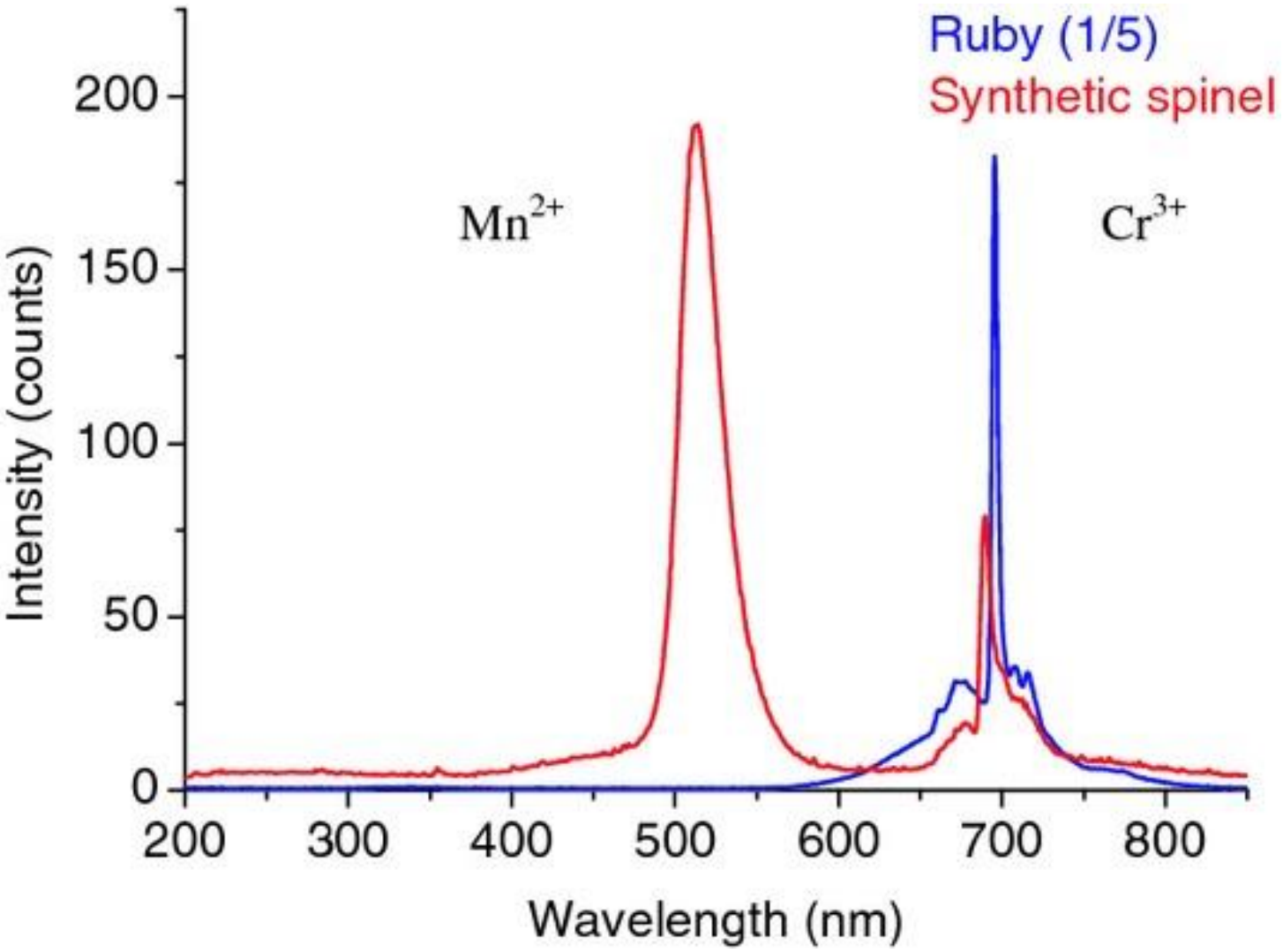
- The $^2E \rightarrow {}^4A_2$ transition is **spin-forbidden** but **partially allowed** due to spin-orbit coupling and crystal field effects.
- This transition results in **red fluorescence**, typically around **694 nm**.
- This is the same transition used in **ruby lasers**.

Fluorescence in ruby
(some Al is substituted with Cr)

Term Symbol Components: $^4A_2$

1. **Superscript "4"**:
   - This indicates the **spin multiplicity**, calculated as $2S + 1$, where **S** is the total spin quantum number.
   - So, $^4A_2$ means **S = 3/2**, a **quartet state** with four spin orientations.
2. **Letter "A"**:
   - This refers to the **type of symmetry** of the electronic state under the crystal field:
     - **A**: Non-degenerate (symmetric under rotation).
     - **E**: Doubly degenerate.
     - **T**: Triply degenerate.
3. **Subscript "2"**:
   - This distinguishes between different **non-degenerate states** with similar symmetry.
   - In the **octahedral (O_h)** or **trigonal (C_{3v})** point groups (common in crystals like ruby), the subscript "2" indicates how the state transforms under certain symmetry operations:
     - **"1"** usually means symmetric under all operations.
     - **"2"** means antisymmetric under certain operations (like rotation or reflection).

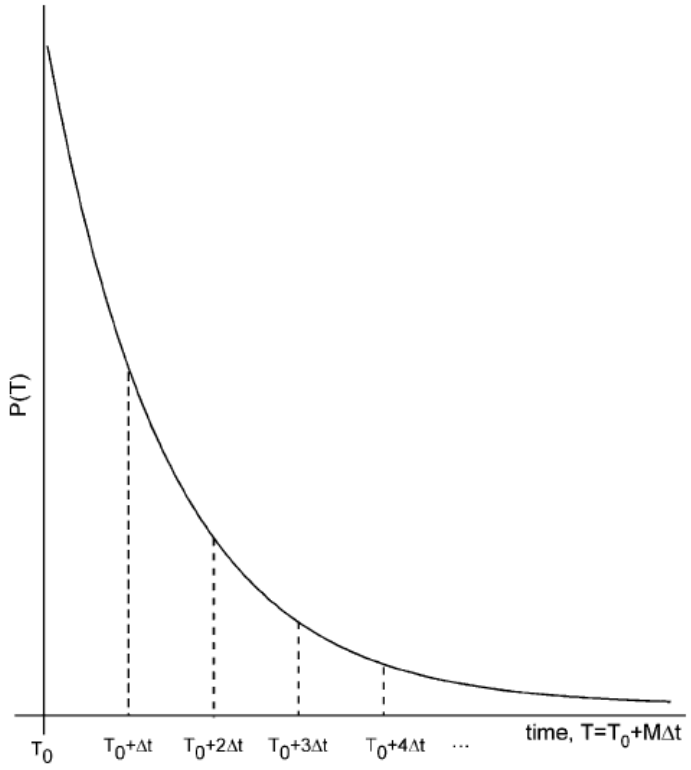
Fluorescence in ruby
(some Al is substituted with Cr)



Time-Dependent Fluorescence: Fluorescence Lifetime

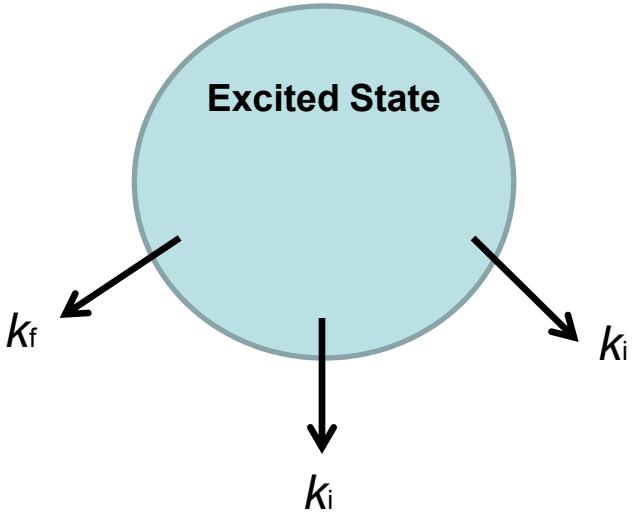
Fluorescence Lifetime: The average amount of time a molecule stays in excited state

Probability of being in the excited state



k_f = rate constant for leaving excited state while emitting a photon

k_i = rate constant for leaving excited state through other means (ie. Dynamic quenching, Energy Transfer, etc)



Fluorescence Lifetime: $\frac{1}{\tau} = \sum_i k_i$

Diagram by Robert Clegg in Photosynth Res. 2009 Aug-Sep;101(2-3):181-94.

Lifetime is sensitive to other decaying pathways present!

Lambert law

A common and practical expression of the Beer–Lambert law relates the optical attenuation of a physical material containing a single attenuating species of uniform concentration to the optical path length through the sample and absorptivity of the species. This expression is:

$$A = \varepsilon \ell c$$

Where

- A is the absorbance
- ε is the molar attenuation coefficient or absorptivity of the attenuating species
- ℓ is the optical path length
- c is the concentration of the attenuating species

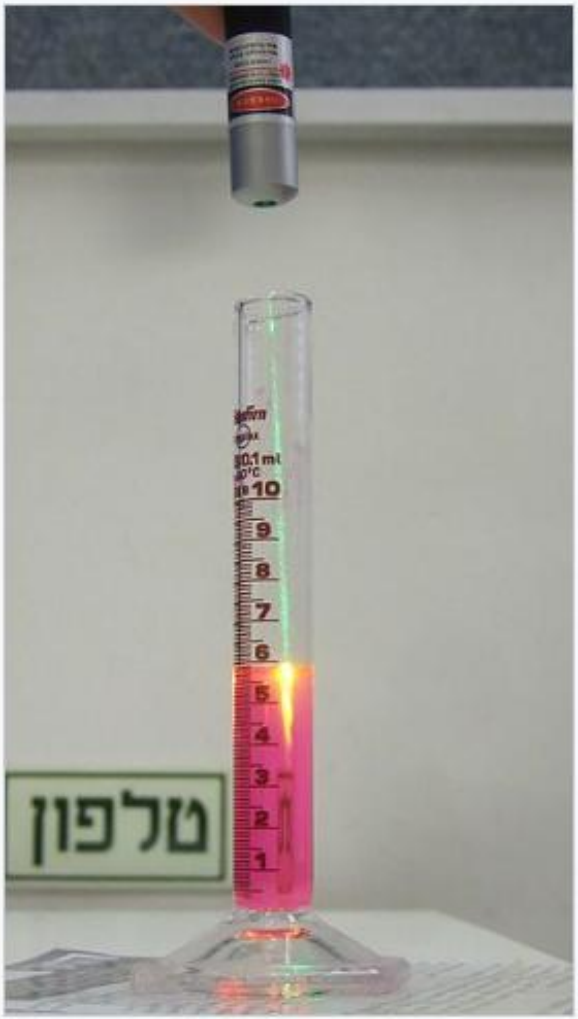
Absorbance is defined as "the logarithm of the ratio of incident to transmitted radiant power through a sample

Lambert law

History [edit]

The law was discovered by Pierre Bouguer before 1729, while looking at red wine, during a brief vacation in Alentejo, Portugal.[1] It is often attributed to Johann Heinrich Lambert, who cited Bouguer's *Essai d'optique sur la gradation de la lumière* (Claude Jombert, Paris, 1729) – and even quoted from it – in his *Photometria* in 1760.[2] Lambert's law stated that the loss of light intensity when it propagates in a medium is directly proportional to intensity and path length. Much later, the German scientist August Beer discovered another attenuation relation in 1852. Beer's law stated that the transmittance of a solution remains constant if the product of concentration and path length stays constant.[3] The modern derivation of the Beer–Lambert law combines the two laws and correlates the absorbance, which is the negative decadic logarithm of the transmittance, to both the concentrations of the attenuating species and the thickness of the material sample.[4] The first modern formulation was given possibly by Robert Luther and Andreas Nikolopulos in 1913.[5]

Lambert law



A demonstration of the Beer–Lambert law: a beam of green laser light passes through a solution of Rhodamine 6B. The beam's radiant power becomes weaker as it passes through solution.

Dr. Brand in 1674-5 attempted to distil human urine and in this way discovered phosphorus.

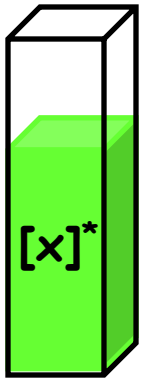
Phosphorus (Greek phosphoros was the ancient name for the planet Venus) was discovered by German alchemist Hennig Brand in 1669 through a preparation from urine. Working in Hamburg, Brand attempted to distill salts by evaporating urine, and in the process produced a white material that glowed in the dark and burned brilliantly.

Misnomer: Phosphorescence of phosphorous is due to slow oxidation

Painting by Joseph Wright of Derby (18thcentury) representing the discovery of the "phosphorescence" of the phosphorus extracted from urine by Hennig Brand in 1669

Measuring the Depletion of the excited state

$$\left[\#x^*\right] = \left[\#x_o^*\right] e^{-(k_F + k_t)t}$$

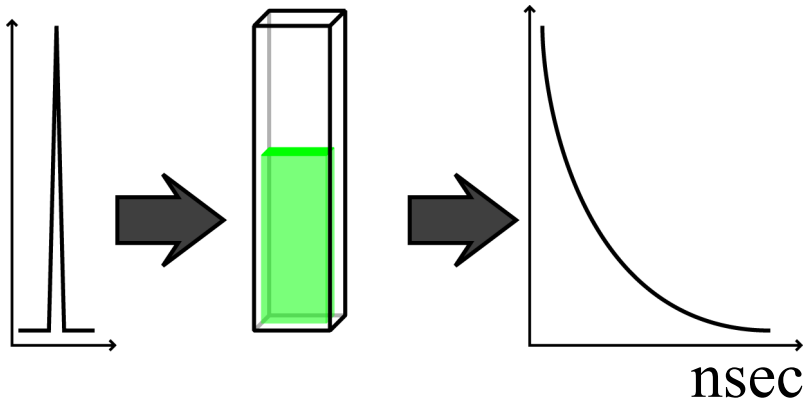


$\left[\#x^*\right](k_F)$ = Intensity that you measure

K_F is rate constant of fluorescence

Intensity measured is proportional to the # of molecules in the excited state!

Measuring Lifetime: Time Domain



What do you need?

-Collect signal fast enough

-Fitting

Measuring Lifetime: Setup

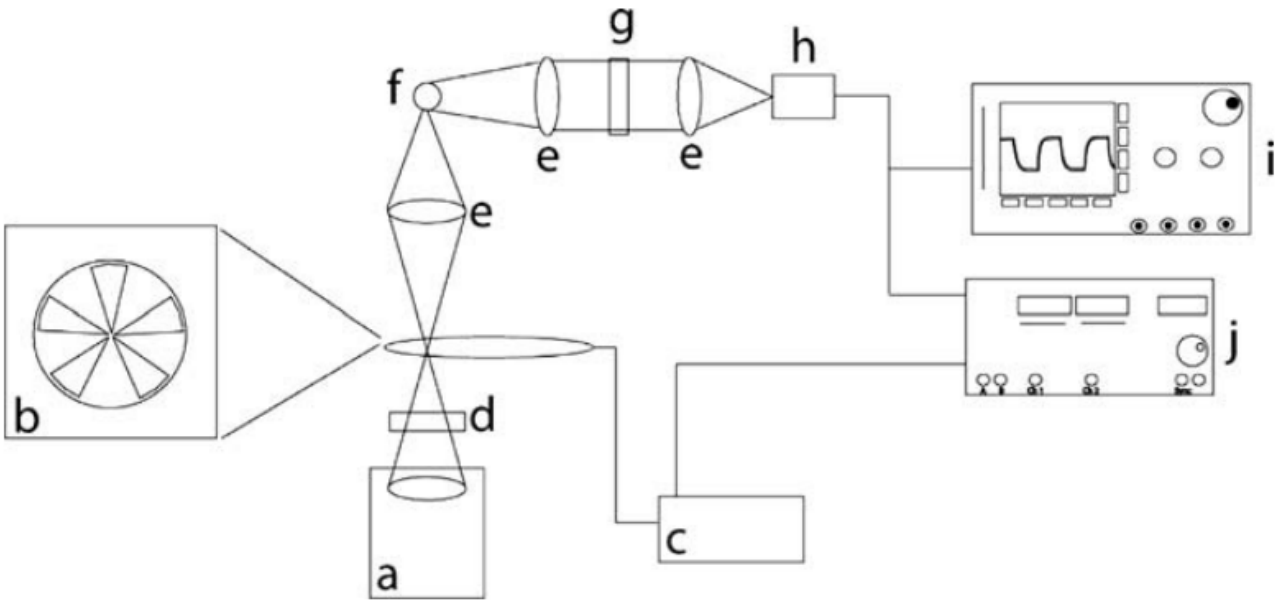
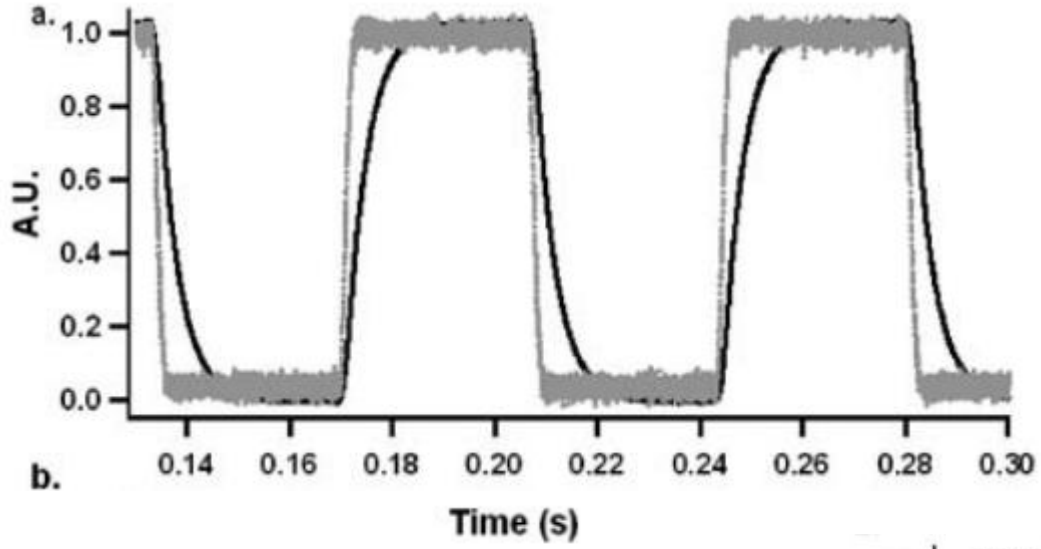
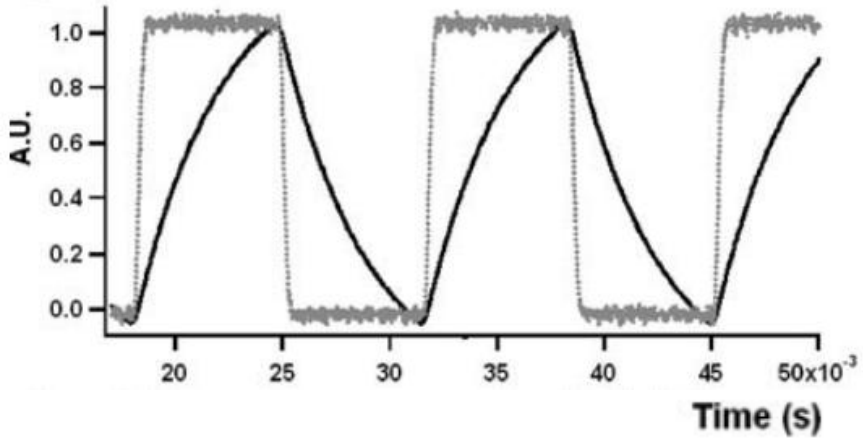


Fig. 1 A block diagram of Setup 1. Light from a Xe-Hg arc lamp (a) is directed through a 390-nm excitation filter (d) and focused onto the ruby or rhodamine sample (f) with a lens (e). The excitation light is modulated with a beam chopper (b) and a variable-speed chopper controller (c). The fluorescence light from the sample is passed through a 600-nm emission filter (g) and onto the detector (h). Data from the detector may be collected using an oscilloscope (i) or lock-in amplifier (j)

Measuring Lifetime: Measured signals

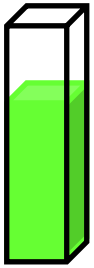




Square wave modulation of rhodamine and ruby with a chopper. For **a**) and **b**), ruby in solid lines (black) and rhodamine in dotted lines (grey) **a**) 13.6 Hz, **b**) 74 Hz. **c**) comparison of ruby modulation at 13.6 (solid black) and 120 Hz (dotted grey).

Measuring Lifetime: Frequency Domain

$$E(t) = E_o + E_\omega cos\left(\omega_E t + \varphi_E\right)$$



$$F(t) = F_o + F_\omega cos\left(\omega_E t + \varphi_E - \varphi\right)$$

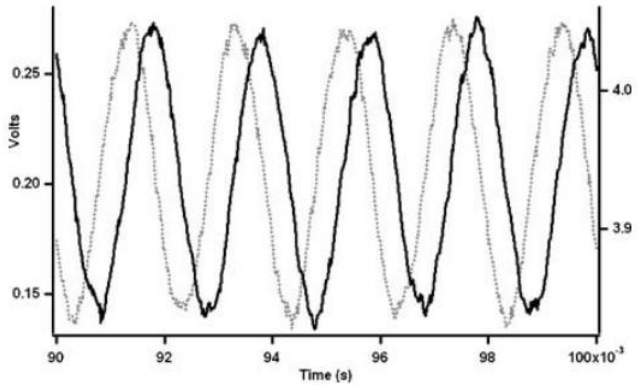
For a simple sine wave excitation of the form

$$E(t) = E_0 + 2E_1 \cos(\omega t) = E_0 + E_1(e^{i\omega t} + e^{-i\omega t}), \qquad (3)$$

and for a single relaxing fluorescence component, the fluorescence response reduces to

$$\begin{aligned} F(t) &= F_0 + F_1(\omega)\cos(\omega t + \phi) \\ &= Q\int_0^t (E_0 + 2E_1\cos(\omega t))Ae^{-(t-t')/\tau}dt' \\ &= Q\left[E_0 A\tau + E_1\left(\frac{2A\tau}{\sqrt{1+(\omega t)^2}}\cos(\omega\tau + \tan^{-1}(\omega\tau))\right)\right] \\ &= QA\tau[E_0 + 2ME_1\cos(\omega\tau + \phi)] \qquad (4) \end{aligned}$$

$$\phi = \tan^{-1}(\omega\tau) \qquad M = \frac{F_1(\omega)/F_0}{E_1/E_0} = \frac{1}{\sqrt{1+(\omega\tau)^2}}$$



Rhodamine (dotted grey) and ruby (solid black) emission driven by sine wave modulation at 500 Hz. Left vertical axis is for rhodamine signal, right axis is for ruby. The input and output frequencies are the same

J Fluoresc (2006) 16:793–807
DOI 10.1007/s10895-006-0123-7

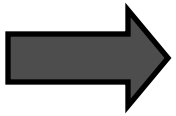
ORIGINAL PAPER

Ruby Crystal for Demonstrating Time- and Frequency-Domain Methods of Fluorescence Lifetime Measurements

Danielle E. Chandler · Zigurts K. Majumdar · Gregor J. Heiss · Robert M. Clegg

Samples Described by Multiple Lifetimes

$$I(t) = \sum_i a_i e^{-t/\tau_i}$$



Some Examples:
- -ECFP (Enhanced Cyan Fluorescent Protein (FP)), FPs
- -Ruby Rhodamine Mixture
- -Crystals

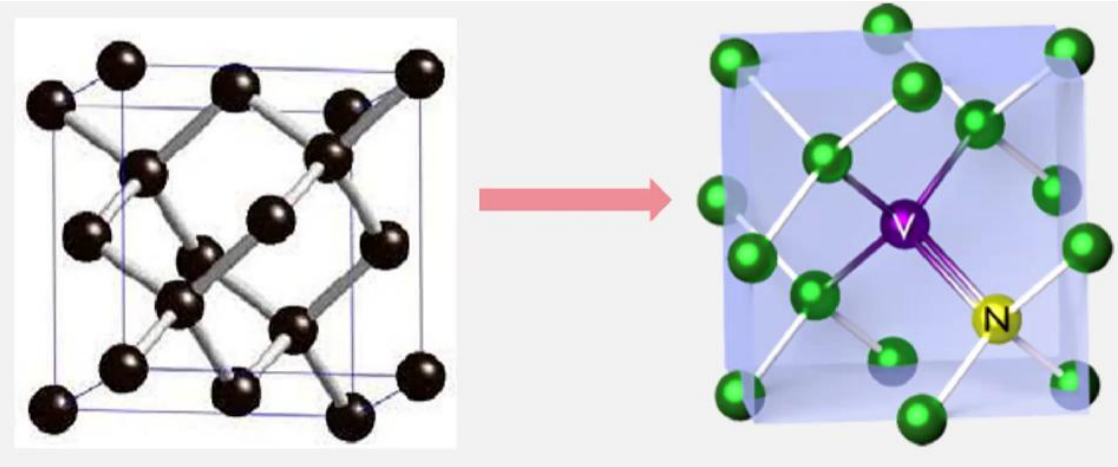
$$F(t) = E_o \sum_i a_i \tau_i + E_\omega \sum_i \frac{a_i \tau_i}{\sqrt{1+(\omega_E \tau_i)^2}} \cos(\omega_E t - (\varphi_i - \varphi_E))$$

You still can only measure one (M, φ)

$$\frac{F(t)}{F_o} = 1 + \frac{E_\omega}{E_o} \sum_i \frac{\alpha_i}{\sqrt{1+(\omega_E \tau_i)^2}} \cos(\omega_E t - (\varphi_i - \varphi_E))$$

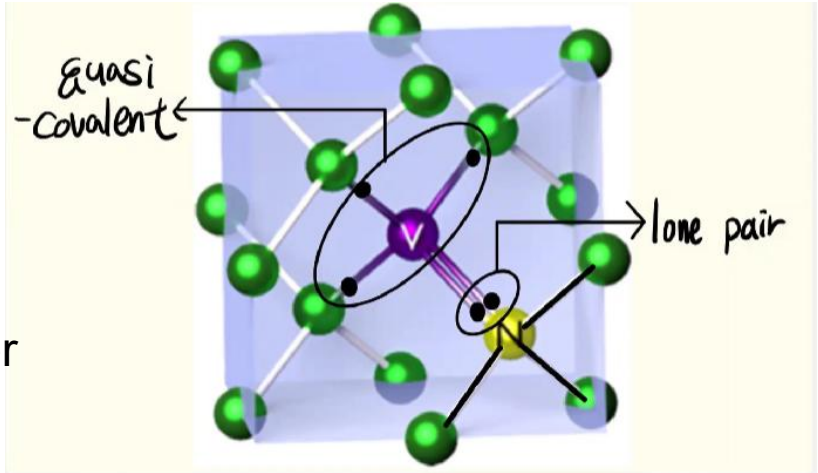
$$\frac{F(t)}{F_o} = 1 + \frac{E_\omega}{E_o} M \cos(\omega_E t - (\varphi_i - \varphi))$$

Optical spectroscopy applications:
Color centers or NV centers in diamond



Diamond, carbon atoms

Diamond+ vacancy (V) + nitrogen (N)

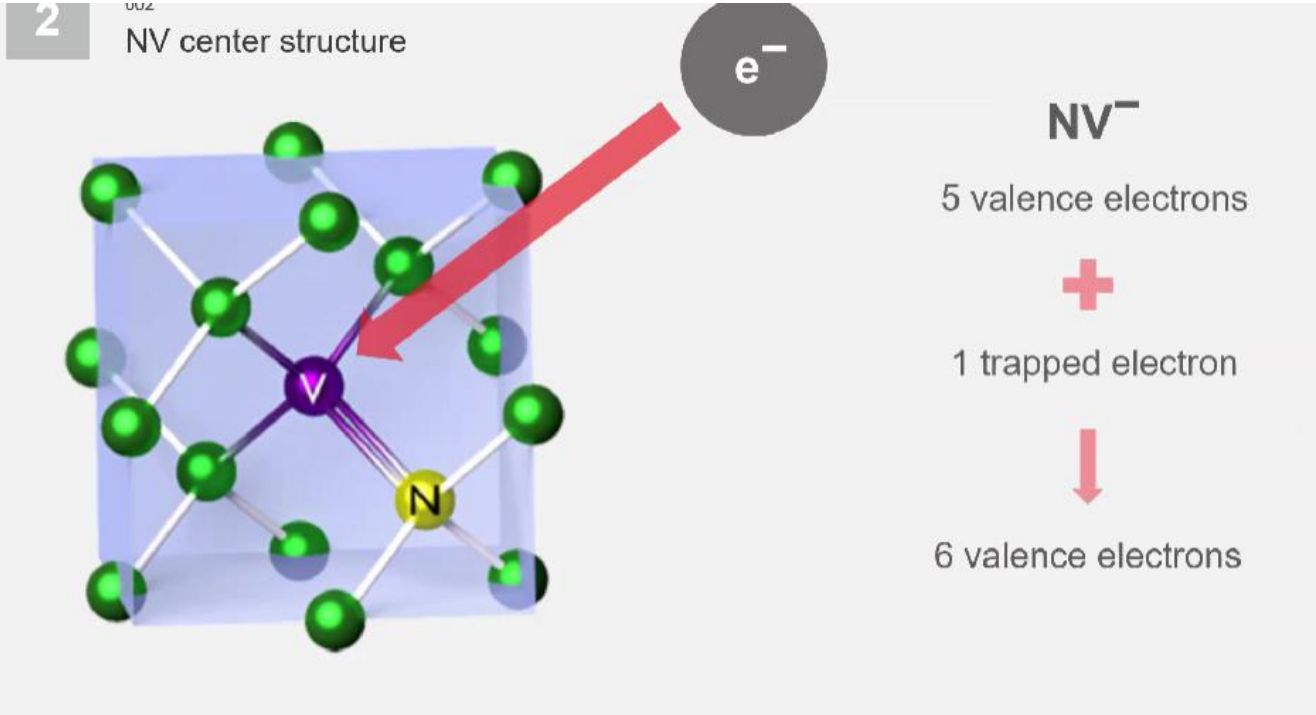


There are 5 electrons localized on the NV center

Color center: Nitrogen vacancy center in diamond

https://www.youtube.com/watch?v=hwePZkk2L2I

Optical spectroscopy: negatively charged NV centers in diamond

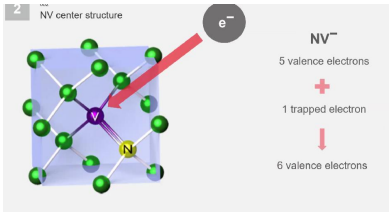


This negatively charged NV center can be used as a magnetic field sensor
Using optical spectroscopy

Color center: Nitrogen vacancy center in diamond

https://www.youtube.com/watch?v=hwePZkk2L2I

Optical spectroscopy: negatively charged NV centers in diamond



- **Ground State ($^3A_2$):**
  - This is a *spin triplet state* with spin quantum number $S = 1$.
  - It has three sublevels: $m_s = 0, \pm 1$, which are split by zero-field splitting (~2.87 GHz).
  - This state is stable and used for sensing and spin manipulation.

- **Photoluminescence:**
  - The spin-dependent fluorescence makes it possible to read out spin states optically.
  - The $m_s = 0$ state fluoresces more brightly than $m_s = \pm 1$, enabling spin state discrimination.

- **Applications:**
  - The NV^- center's spin triplet ground state allows for *optically detected magnetic resonance (ODMR)*.
  - It's used in magnetometry, and nanoscale sensing.

Negatively charged NV centers in diamond

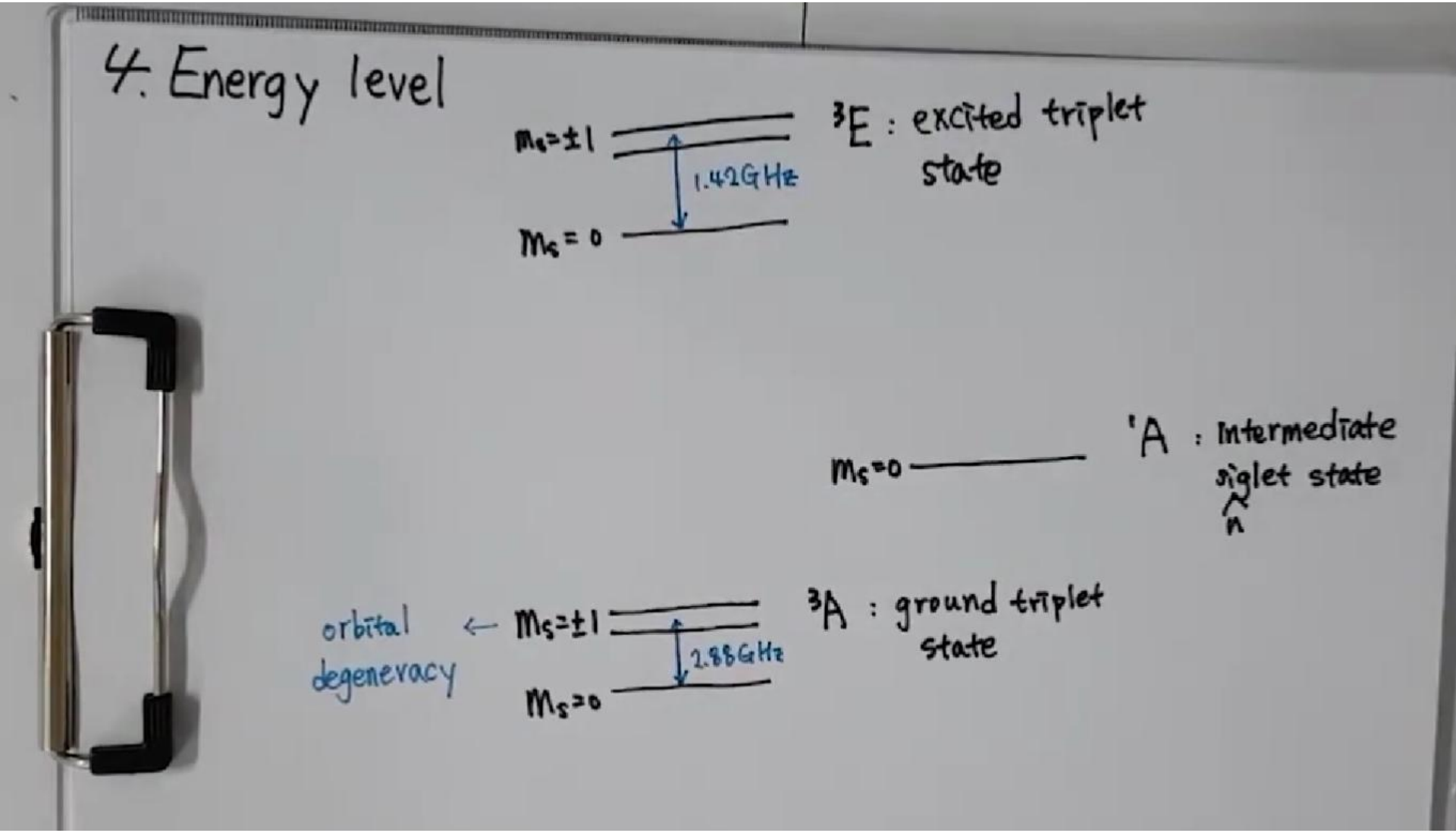
🧪 Electron Configuration (6 Electrons)

The six electrons fill the orbitals in this order:

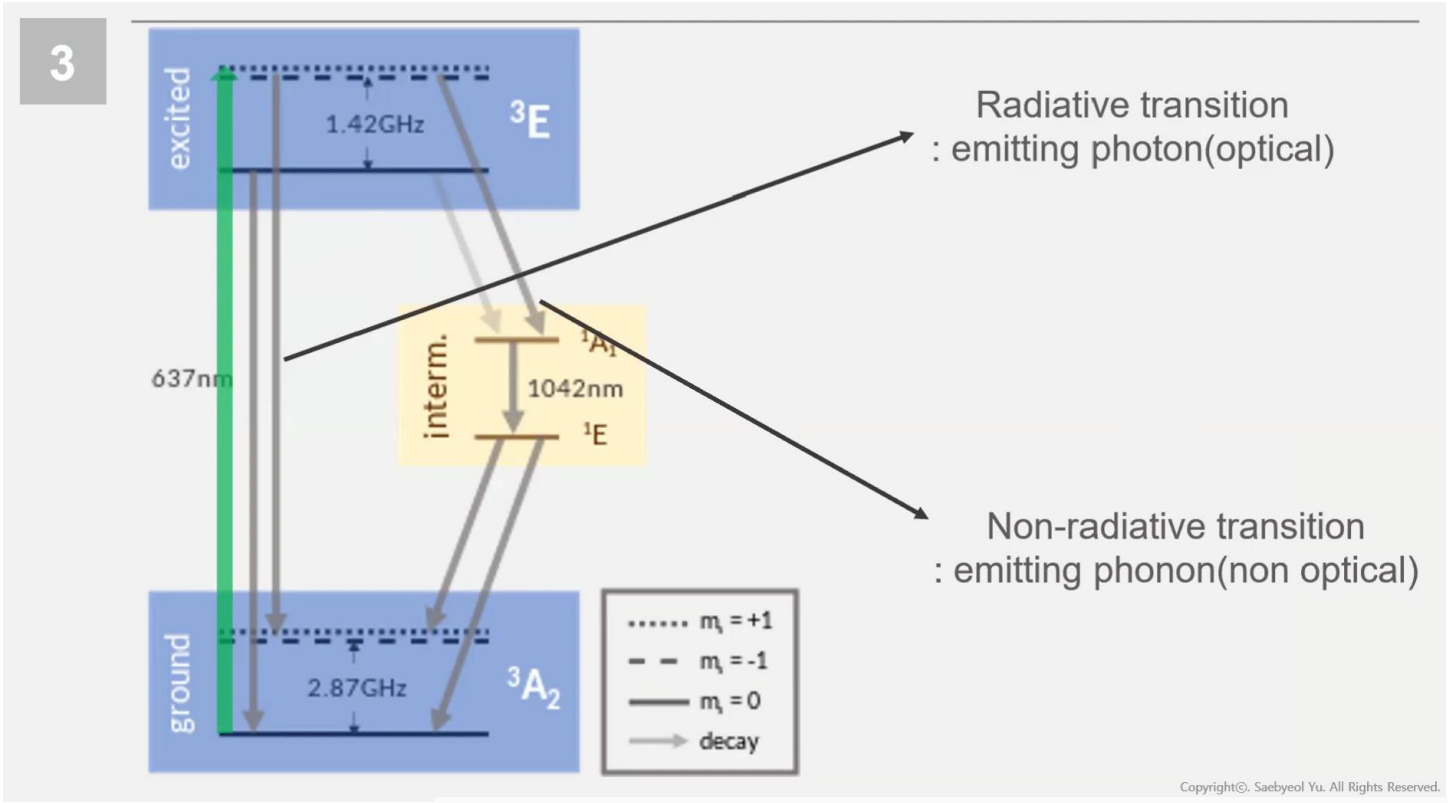
Orbital	Occupancy	Notes
a_1	2 electrons (↑↓)	Fully filled
a_1'	2 electrons (↑↓)	Fully filled
e_x, e_y	2 electrons (↑ ↑)	One in each, parallel spins

- The **e orbitals** are half-filled with **parallel spins**, giving rise to a **spin triplet (S = 1)** ground state.
- This configuration corresponds to the **$^3A_2$ ground state**.

Energy structure of the (NV-) center



NV center optical spectroscopy



2. Spin Selection Rules

- **Optical transitions are spin-conserving**:
  - Allowed transitions: $m_s = 0 \leftrightarrow m_s = 0$ and $m_s = \pm 1 \leftrightarrow m_s = \pm 1$
  - These transitions are **dipole-allowed** and dominate the fluorescence process.
- **Intersystem crossing (ISC)** to singlet states is **spin-selective**:
  - $m_s = \pm 1$ states preferentially decay non-radiatively via ISC to singlet states, leading to reduced fluorescence.
  - $m_s = 0$ state decays radiatively, producing stronger fluorescence.

This spin-dependent fluorescence is the basis for **optical spin readout**.

NV center optical spectroscopy

Color center: Nitrogen vacancy center in diamond

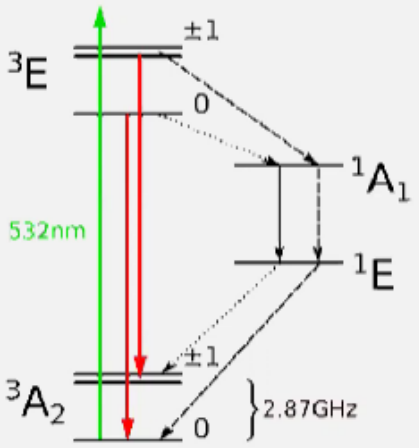
https://www.youtube.com/watch?v=hwePZkk2L2I

3

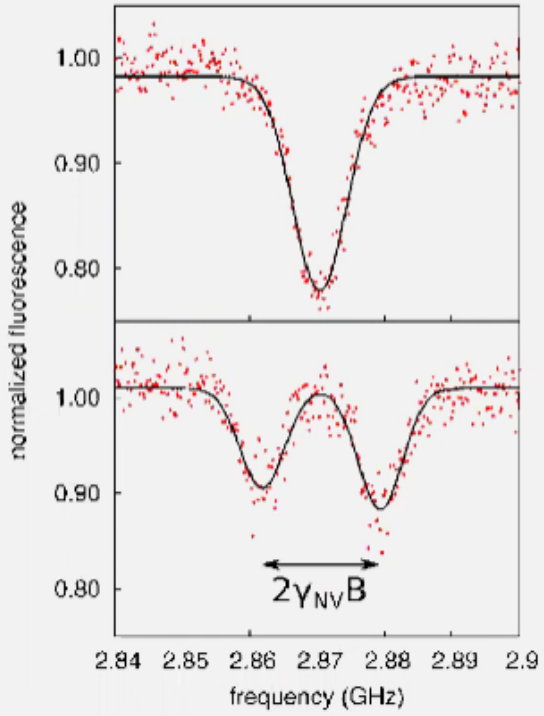
003

NV^- center energy state

a)

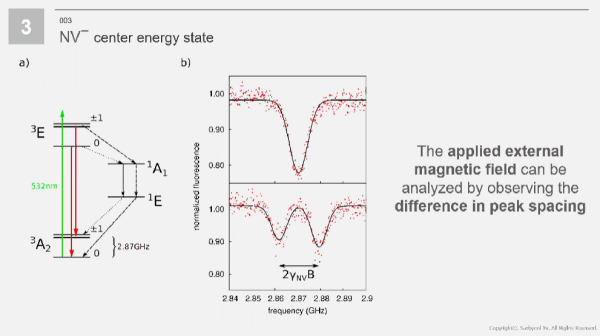


b)



The **applied external magnetic field** can be analyzed by observing the **difference in peak spacing**

NV center optical spectroscopy



Fluorescence from **NV centers in diamond** is typically measured using a technique called **confocal microscopy**, combined with **optical excitation and photon counting**. Here's how the process works step by step:

1. Optical Excitation

- A **laser**, usually at **532 nm (green)**, is focused onto the NV center.
- This excites electrons from the ground triplet state ($^3A_2$) to the excited triplet state (^3E).

2. Fluorescence Emission

- The NV center emits **red fluorescence** (typically in the 637–800 nm range) as it relaxes back to the ground state.
- The intensity of this fluorescence depends on the spin state:
  - **Bright** for $m_s = 0$
  - **Dimmer** for $m_s = \pm 1$ due to non-radiative decay via singlet states.