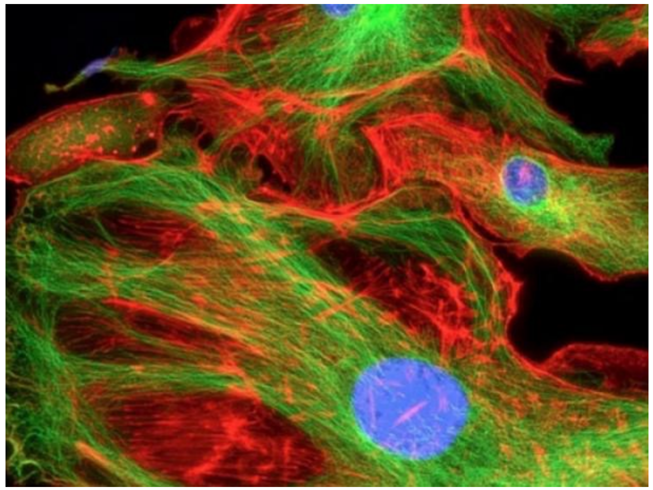
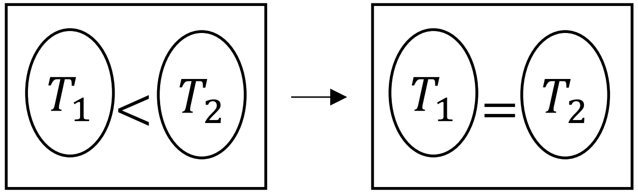
Mechanisms of light emission

Laws of thermal radiation and Luminescence

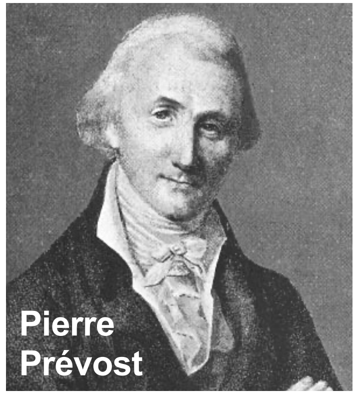


Zsolt Mártonfalvi

Thermal radiation



The temperature of the two bodies will become equal with time even in vacuum!
(no convection or conduction between them)



Consequently:
All bodies emit radiation independently of the temperature of their surroundings. (*Prévost, 1791*)
The emitted radiation is always **electromagnetic radiation**.

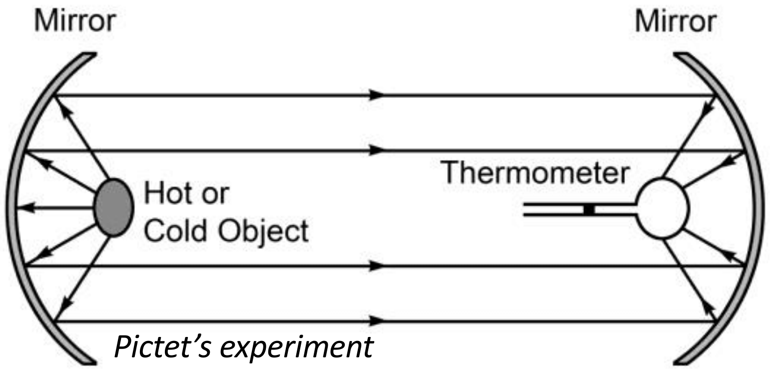
Quantitative description of thermal radiation:

- **Radiant emittance** (M)

$$M = \frac{\Delta P}{\Delta A} = \left[\frac{W}{m^2}\right]$$

- **Absorption coefficient** (α)

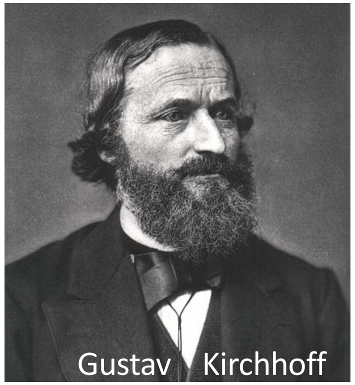
$$\alpha = \frac{J_{absorbed\ by\ the\ surface}}{J_{recived\ by\ the\ surface}} \quad (0 \leq \alpha \leq 1)$$



Pictet's experiment

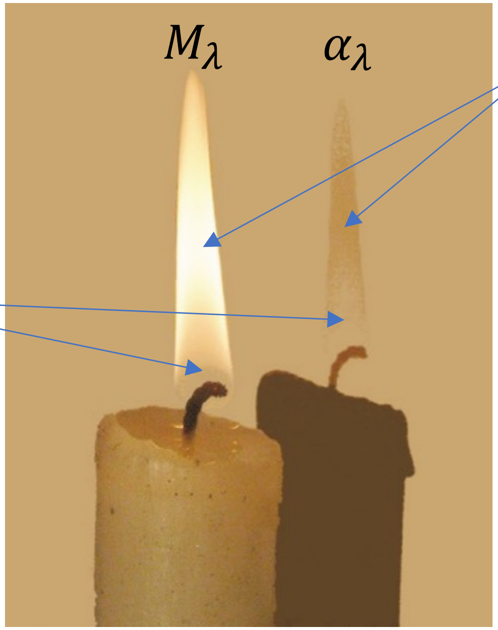
M and α strongly depend on the absolute temperature of the body!

Kirchhoff's law



Bodies that emit more also absorb more. The ratio between radiant emittance and absorption coefficient is constant within a narrow range of wavelength (λ):

$$\frac{M_{\lambda\ body1}}{\alpha_{\lambda\ body1}} = \frac{M_{\lambda\ body2}}{\alpha_{\lambda\ body2}} = constant$$



Stronger emission, more absorption

Weaker emission, less absorption

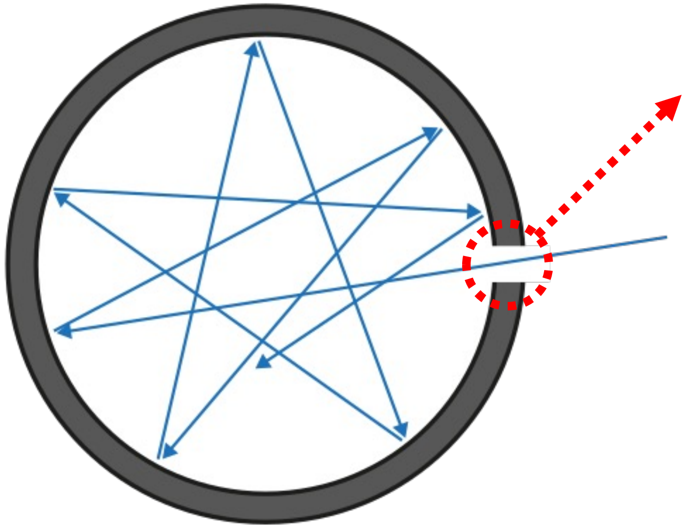
The ideal black body

A theoretical body that is used as a model in the description of thermal radiation.
It absorbs all radiation that falls on it:

$$\alpha_{black\ body} = 1$$

thus, we can calculate any real body's radiant emittance if we know its absorption coefficient ($\alpha_{\lambda i}$):

$$M_{\lambda i} = \alpha_{\lambda i} M_{\lambda\ black\ body}$$



The hole on a dark cavity approximates an ideal black body

The radiant emittance of a black body depends strongly on the absolute temperature!

Stefan's law:

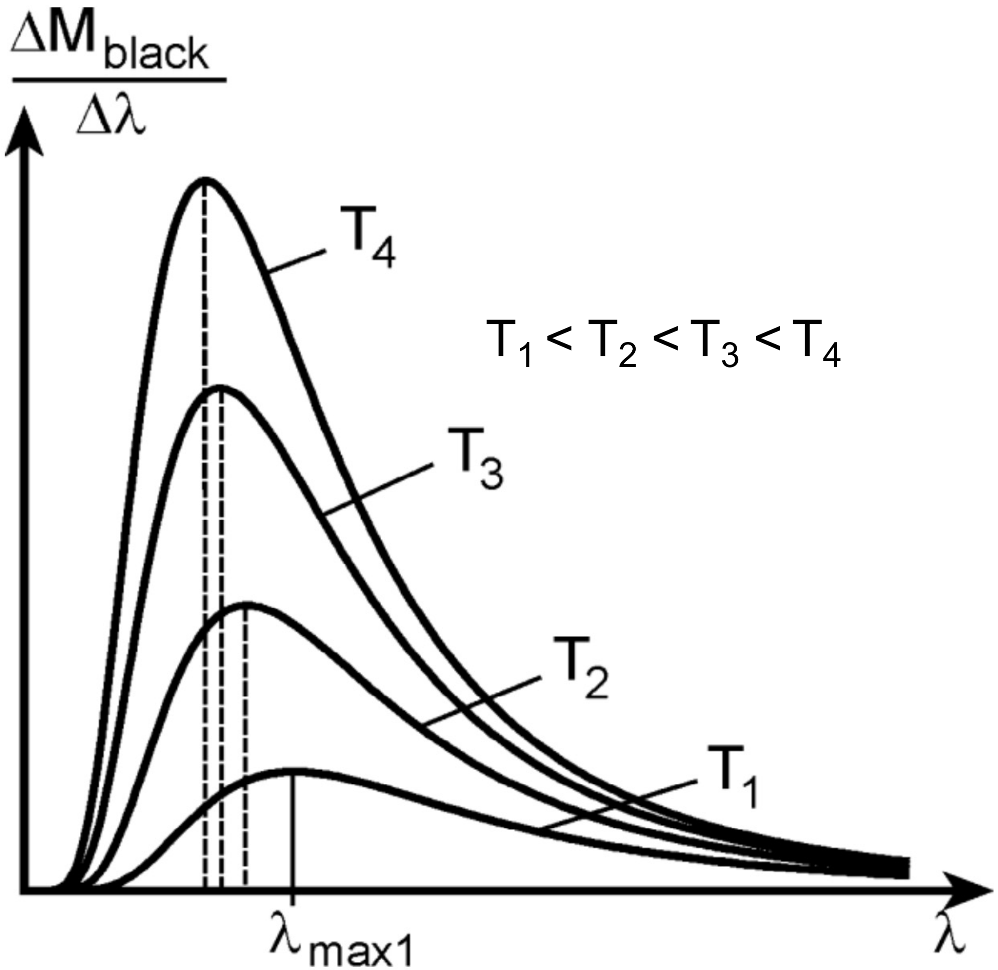
$$M = \sigma T^4$$

$$\sigma = 5.67 \cdot 10^{-8} \frac{W}{m^2 K^4}$$

Jozef Stefan

The ideal black body

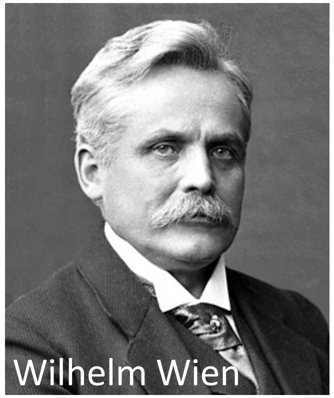
The emission spectrum of the black body is **continuous**.



Wien's displacement law:

$$\lambda_{max}T = constant$$

constant = 0.0029 m · K



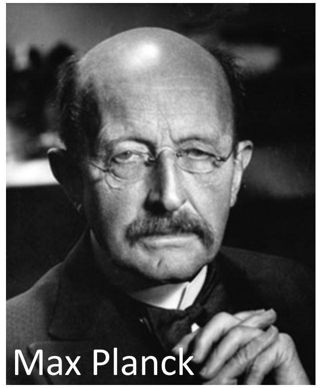
Max Planck's radiation law:

The radiation energy of a black body is emitted in discrete integer multiples of a fundamental "package", the quantum.

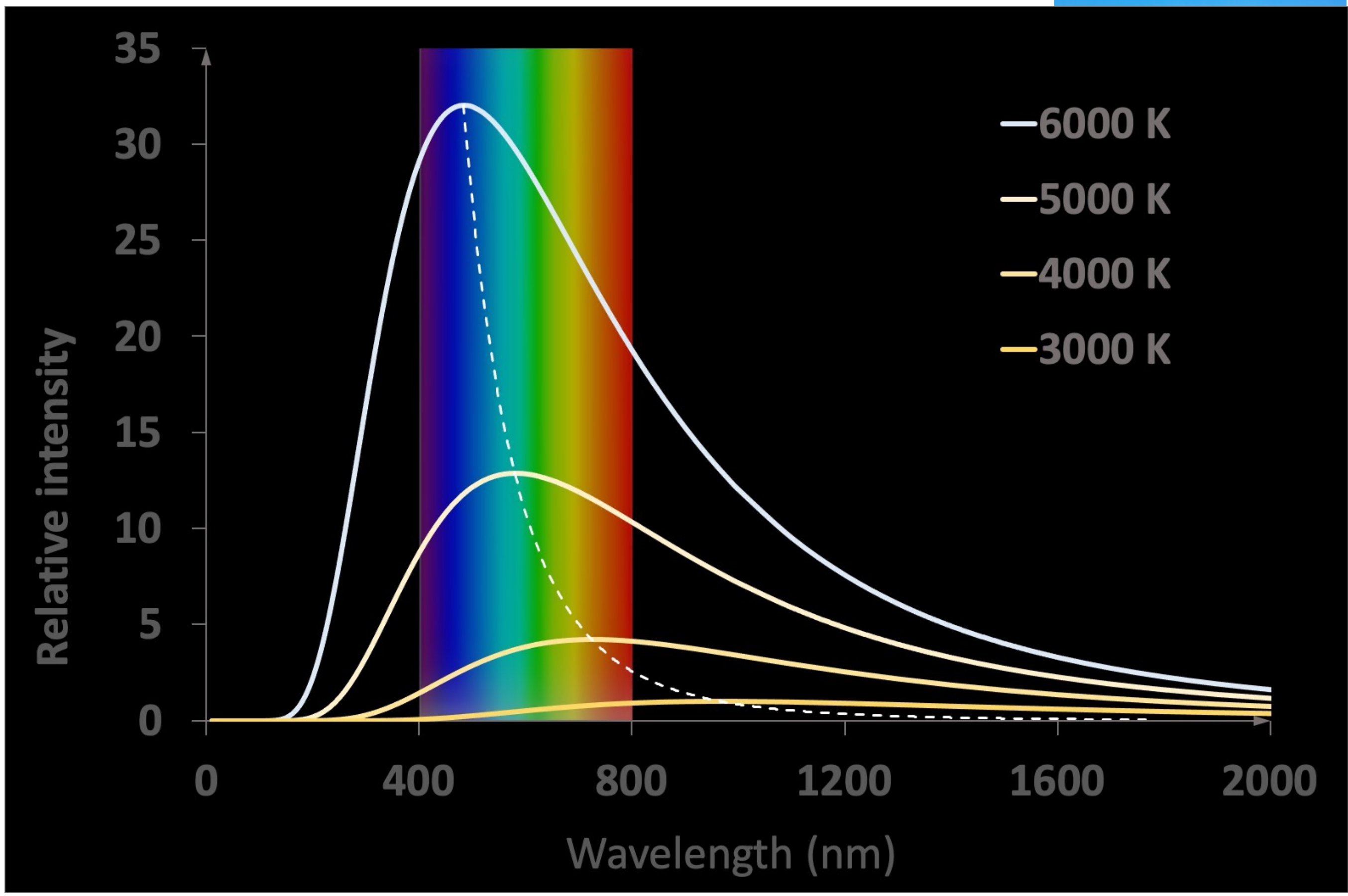
$$E = hf$$

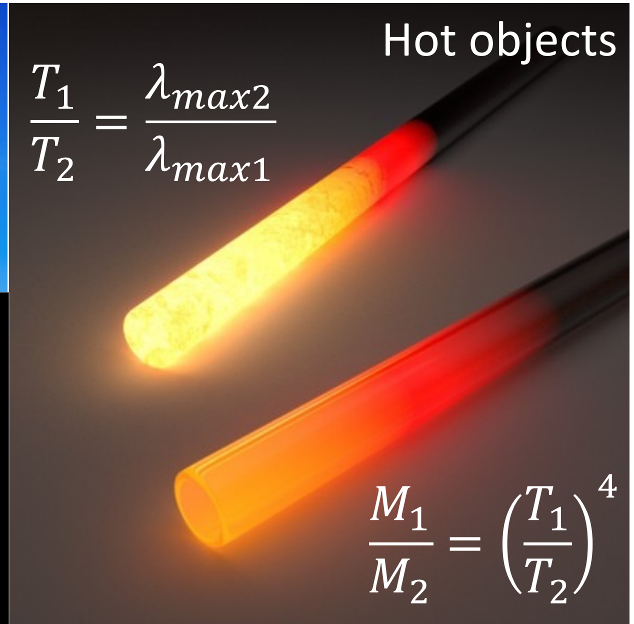
$h = 6.63 \cdot 10^{-34}$ J · s

$$M_{(f)} = \frac{2\pi hf^3}{c^2} \cdot \frac{1}{e^{\left(\frac{hf}{k_B T}\right)} - 1}$$

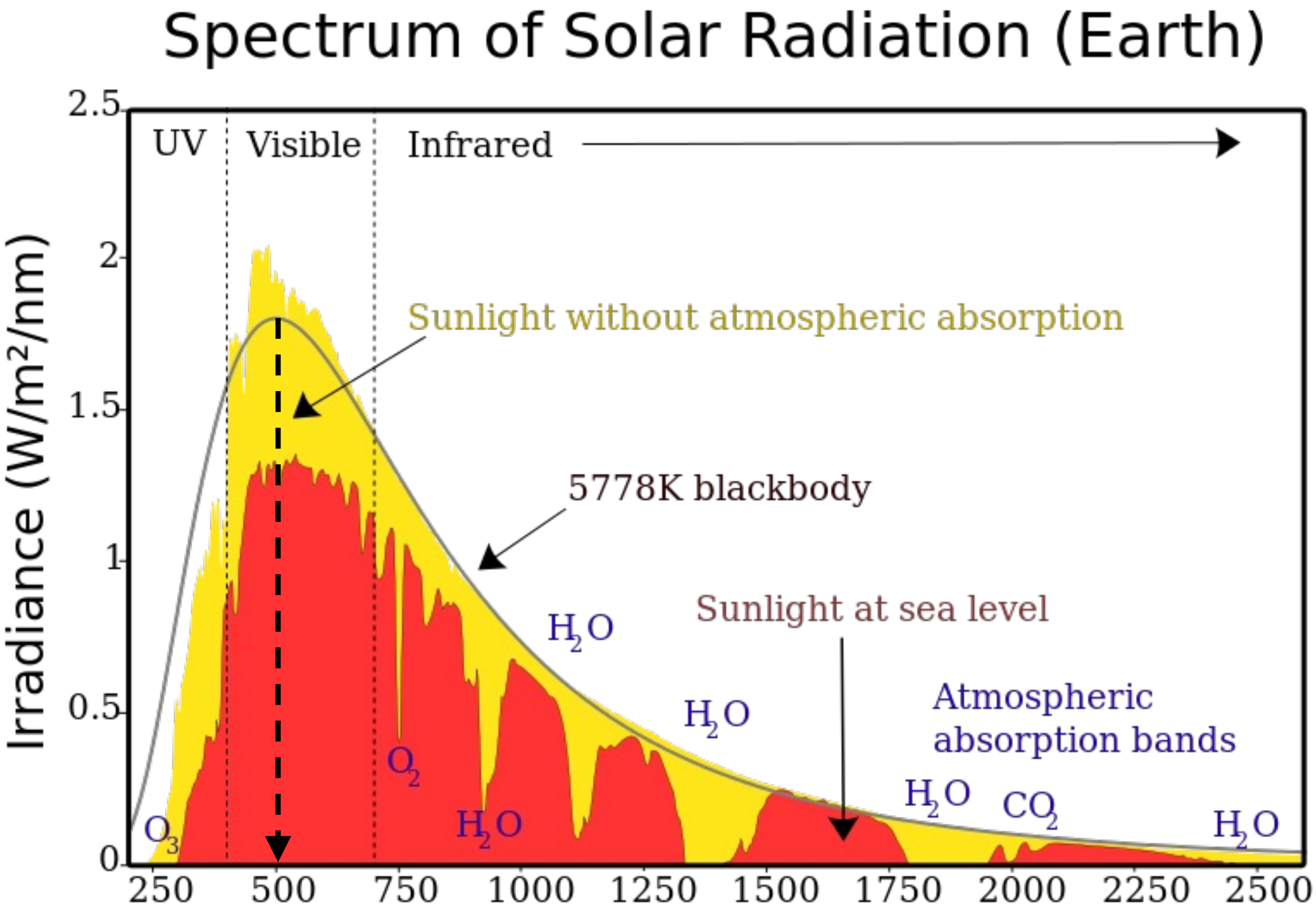


Light sources based on thermal radiation





Sun light



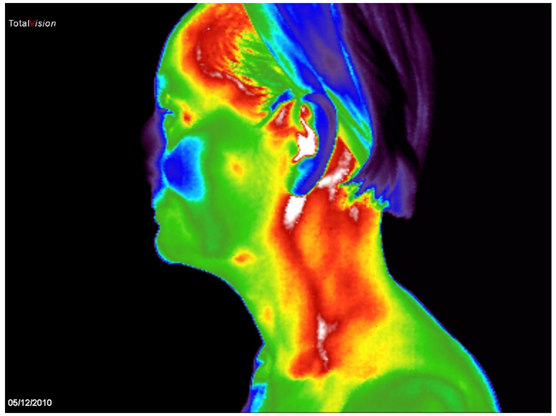
$\lambda_{max} \approx 500\ nm$

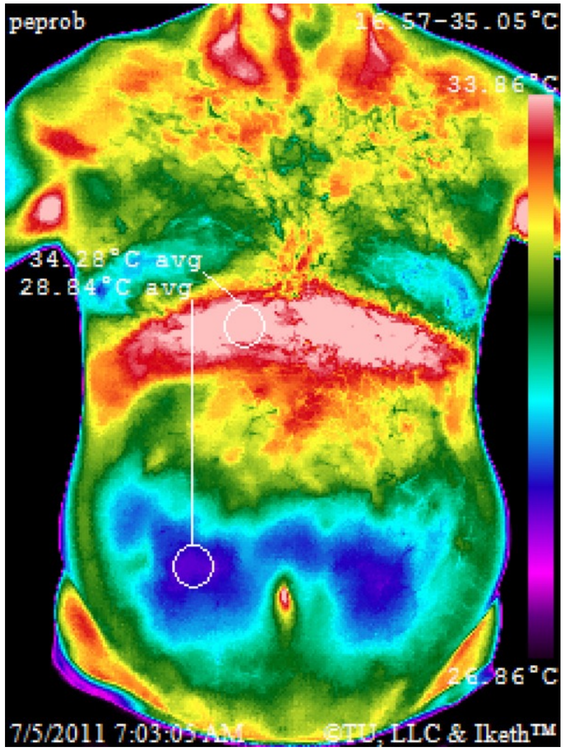
Medical applications

Telethermography

Measures the radiant emittance of thermal radiation of the human body.
Human body: $\lambda_{max} \approx 10\ \mu m$ (infrared)
$\alpha \approx 0.95$ (95% of ideal black body)

Radiant emittance strongly depends on temperature!





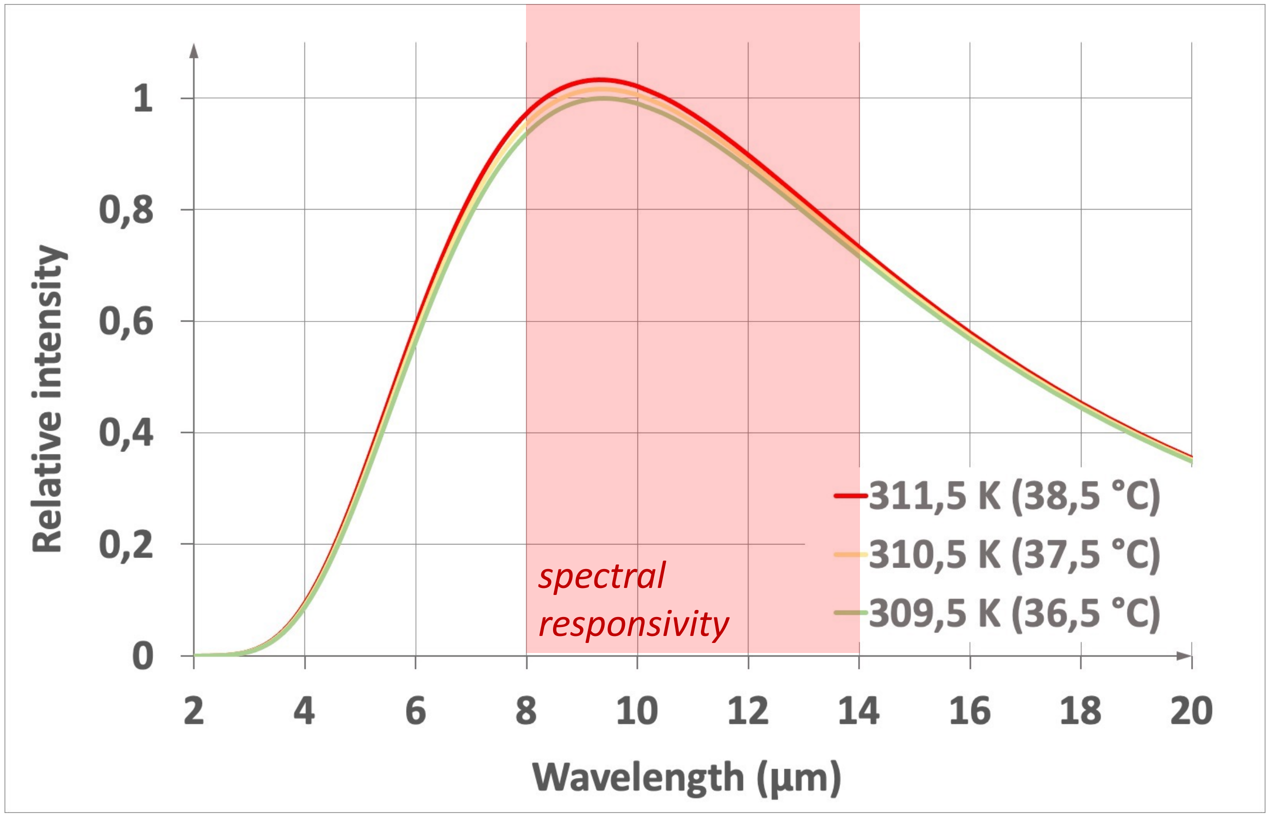
Medical IR scanner

Diagnosis of inflammations, cancer, circulatory defects that cause the change in local temperature.

Medical applications

Non-contact thermometry

Typically measures the total radiant intensity between 8-14 μm *(spectral responsivity).*
1 °C of temperature difference will increase the radiante emittance by ~1.5% !



Luminescence

Spontaneous emission of a photon due to the relaxation of an excited electron.

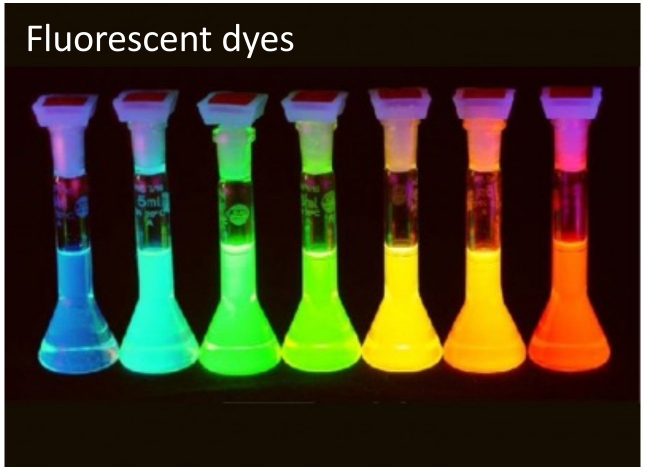
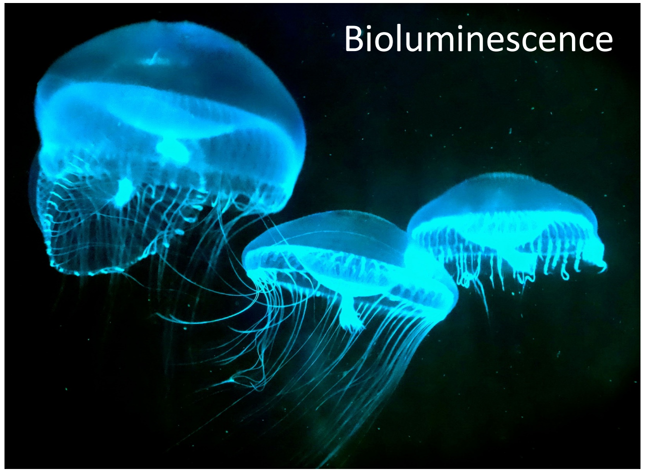
Phases of luminescence:

- Absorption of external energy
- Excitation
- Emission of energy in the form of electromagnetic radiation

Types of luminescence

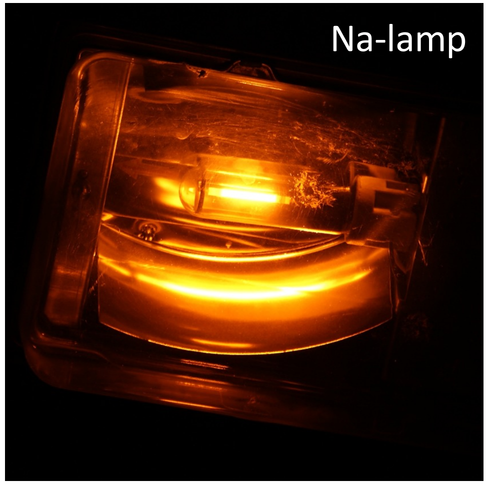
Type of excitation	Name	Example
Light	Photoluminescence	Fluorescent lamp
Electric	Electroluminescence	Na-lamp
Radioactive	Radioluminescence	NaI (Tl) (scintillator)
Mechanical	Triboluminescence	(Percussion, friction)
Biochemical	Bioluminescence	firefly
Thermal	Thermoluminescence	$CaSO_4$ (Dy) (dosimeter)

Type of relaxation	Name	Example
$S_1 - S_0$ (fast)	Fluorescence	Fluorescein
$T_1 - S_0$ (slow)	Phosphorescence	Phosphorous


Fluorescent dyes

Bioluminescence

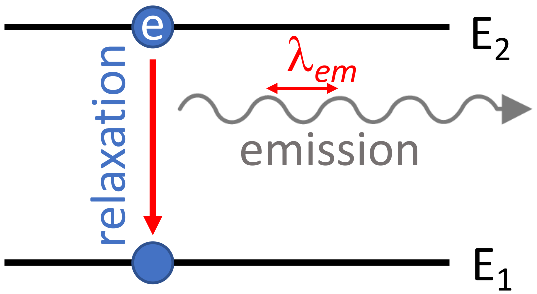
LED

Phosphorescent dial

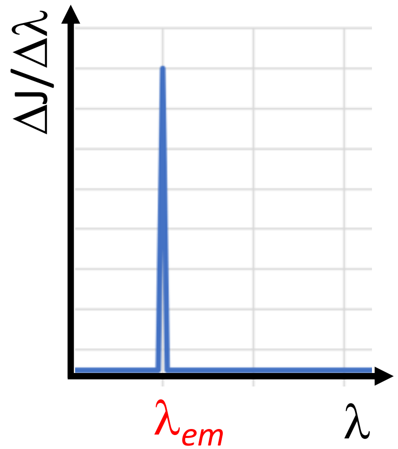
Radioluminescence - scintillation

Na-lamp

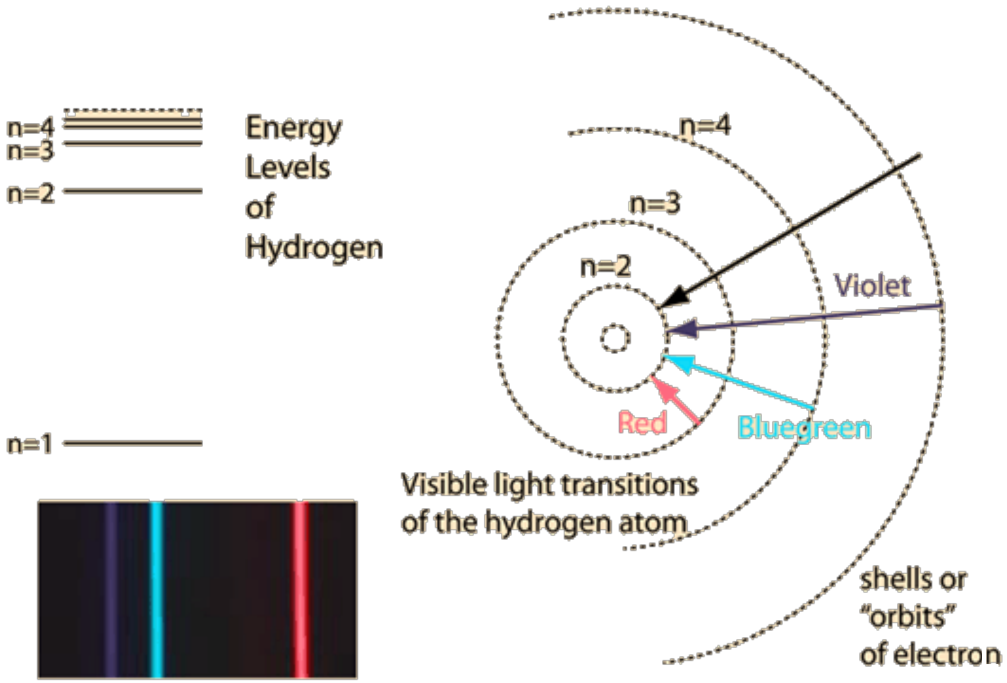
Luminescence of atoms

Luminescence emission of atoms has a **line spectrum.**

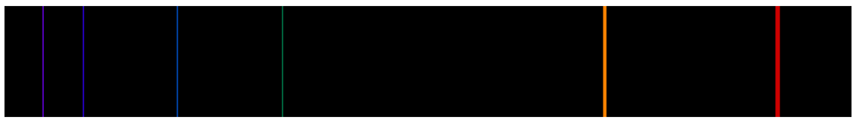


$$E_{photon} = E_2 - E_1 = hf = h\frac{c}{\lambda_{em}}$$



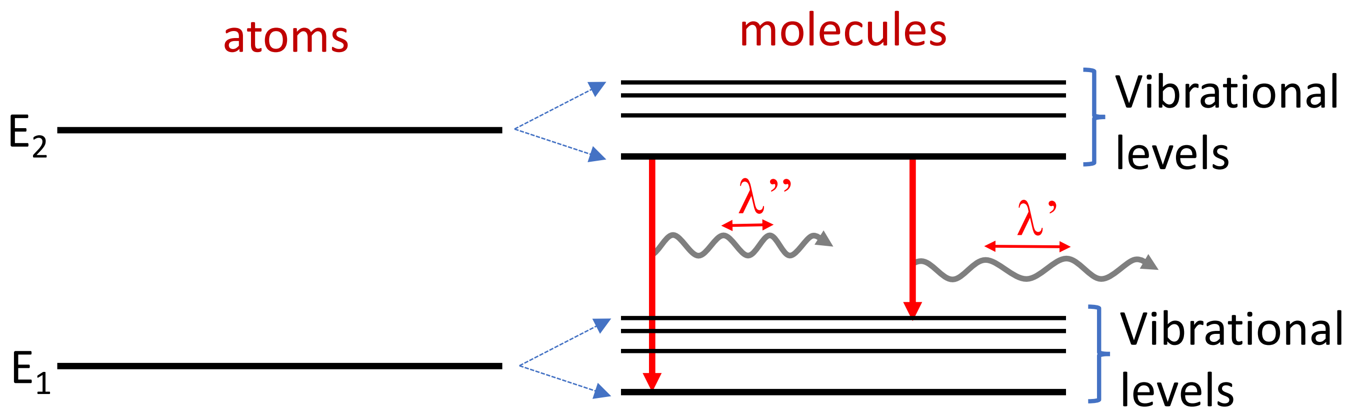


Flame test



Luminescence of molecules

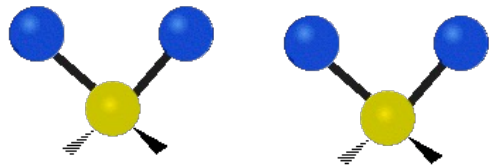
Discrete energy levels split into **vibrational levels**.



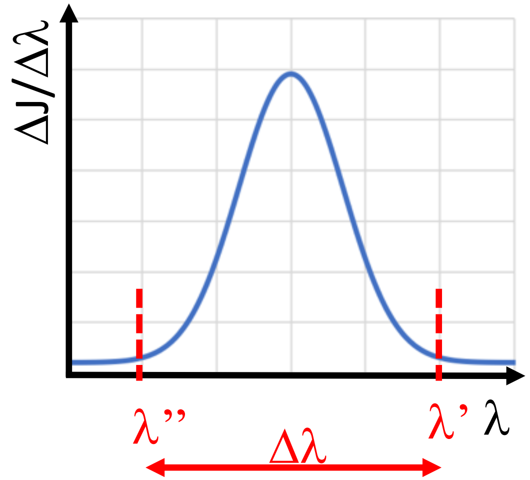
The energy of a molecule is the sum of its electronic-, vibrational, and rotational transition energies. :

$$E_{total} = E_e + E_v + E_r$$

Molecular vibrations:
(2 examples)

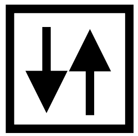


Luminescence of molecules has **band spectrum**

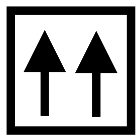


Spin states of excited electrons

Singlet state (S)
Sum of spin quantum numbers is S = 0 (+1/2, -1/2)



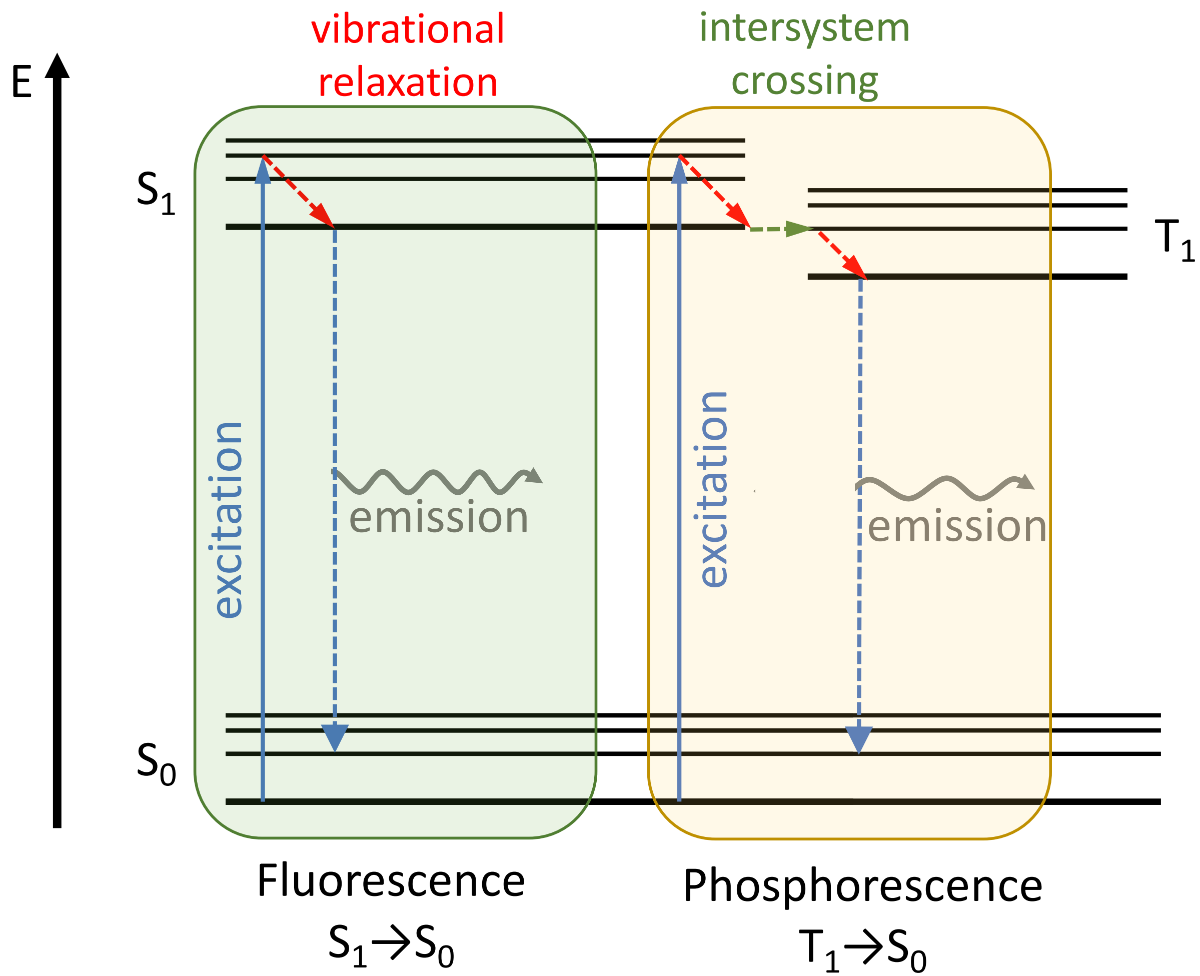
Triplet state (T)
Sum of spin quantum numbers is S = 1 (+1/2, +1/2)

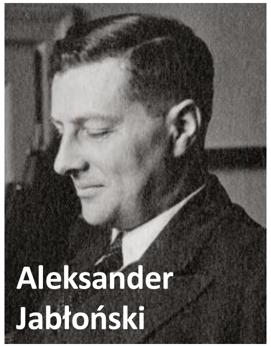


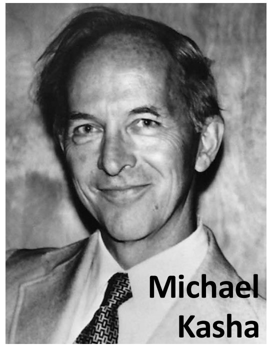
Magnetic moment of spin state: $2S + 1$

Luminescence emission of molecules

Jabłoński diagram



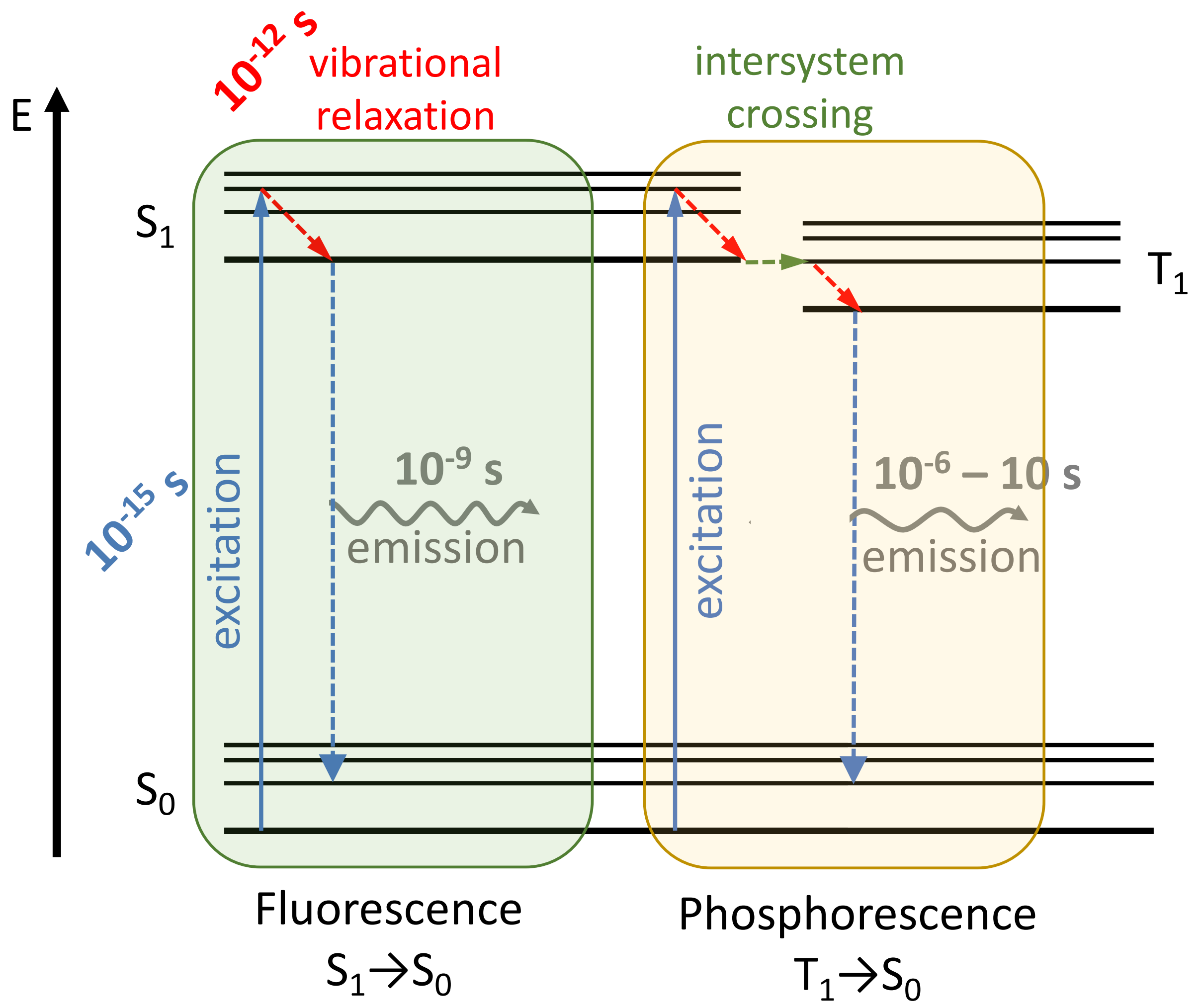




Kasha's rule: The excited molecule first reaches the lowest vibrational level of S_1 and photon emission occurs always from this state to any vibrational level of the ground (S_0) state.

Luminescence emission of molecules

Jabłoński diagram



Lifetimes (τ)

Excitation:
femtosecond (10^{-15} s)

Vibrational relaxation:
picosecond (10^{-12} s)

Fluorescence emission:
nanosecond (10^{-9} s)

Phosphorescence emission:
microsecond to seconds
(10^{-6} – 10 s)

Luminescence emission of molecules

Quantum yield (Q_F):

$$Q_F = \frac{k_f}{k_f + k_{nr}} = \frac{number\ of\ photons\ emitted}{number\ of\ photons\ absorbed}$$

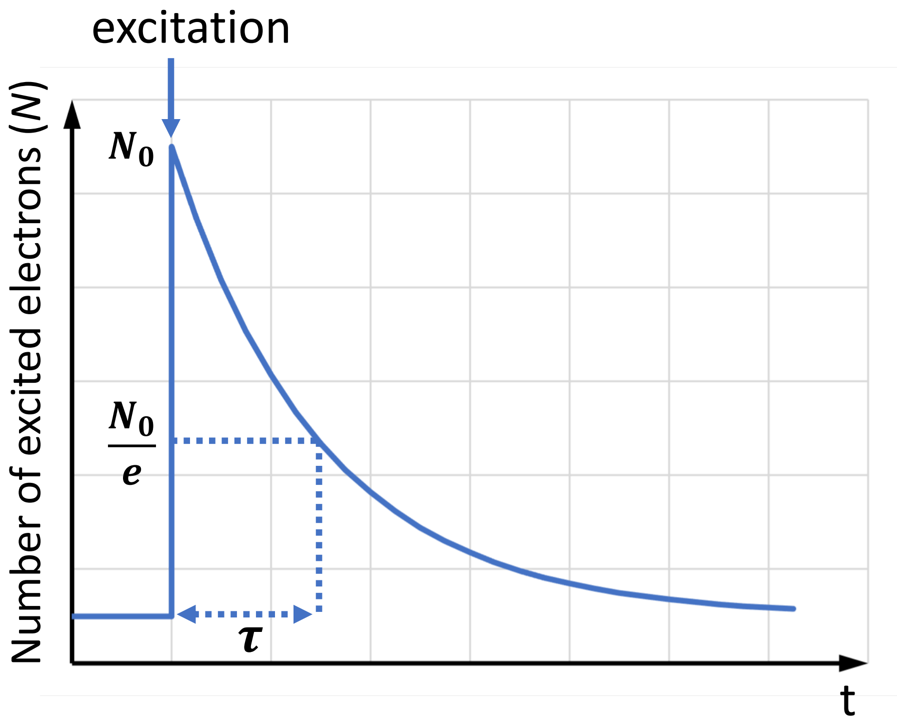
Lifetime (τ):

$$N = N_0 \cdot e^{-\frac{t}{\tau}}$$

$$\tau = \frac{1}{k_f + k_{nr}}$$

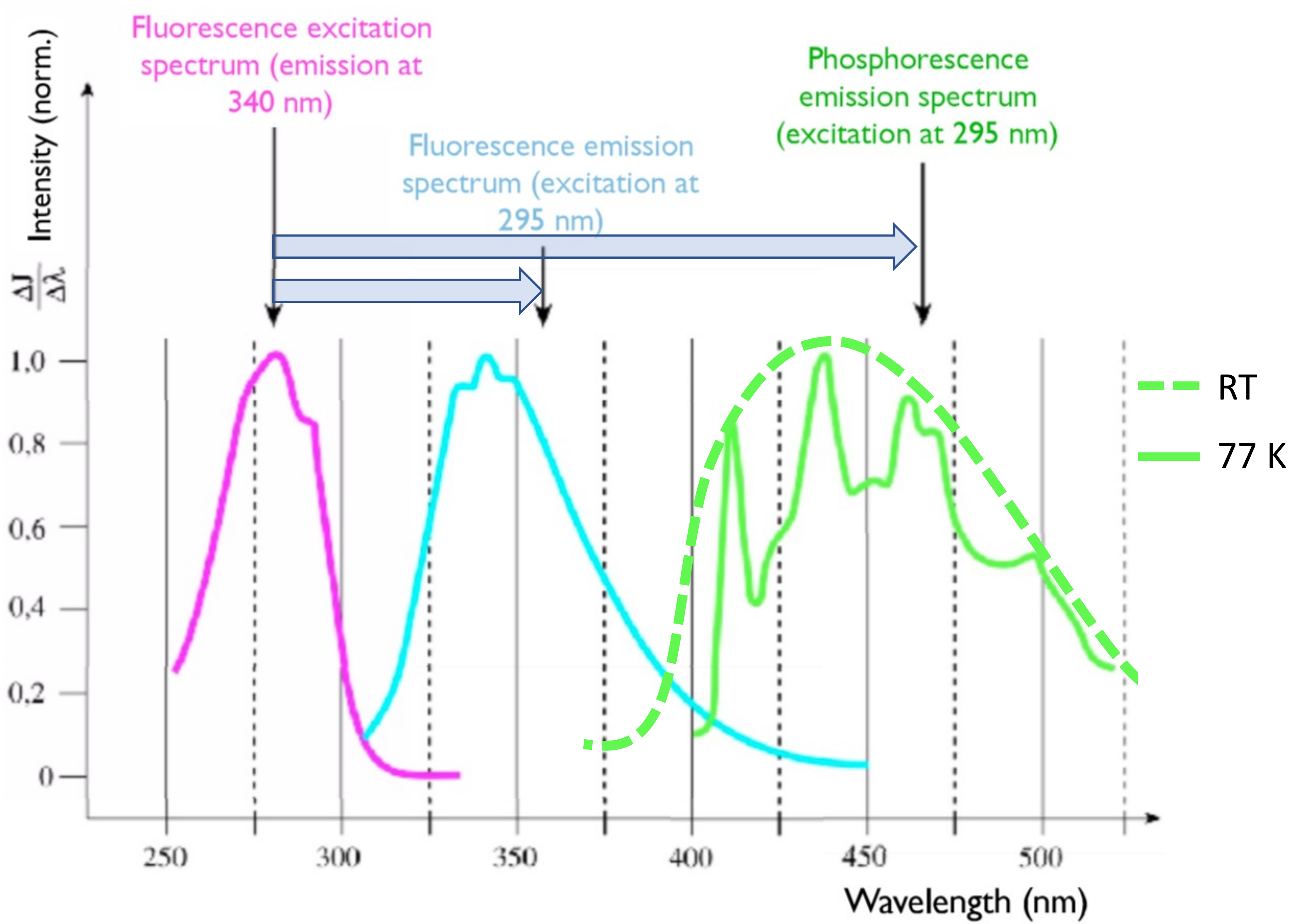
k_f: Rate of photon producing transitions

k_{nr}: Rate of non-radiative transitions



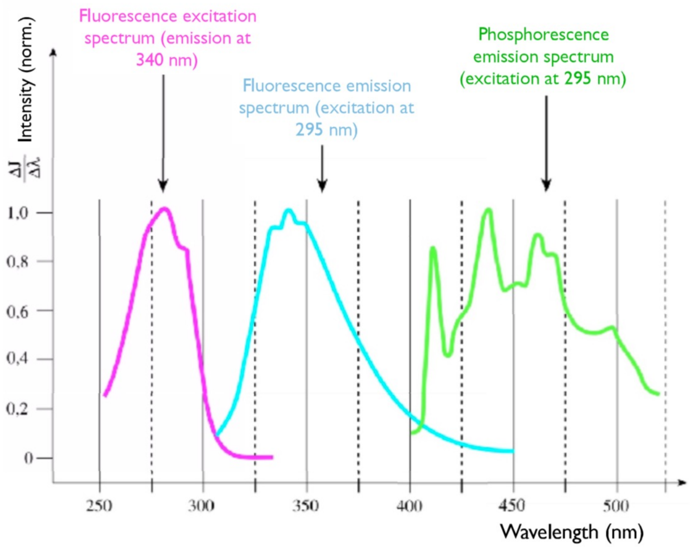
Stokes shift

The shift between the emission and excitation spectra



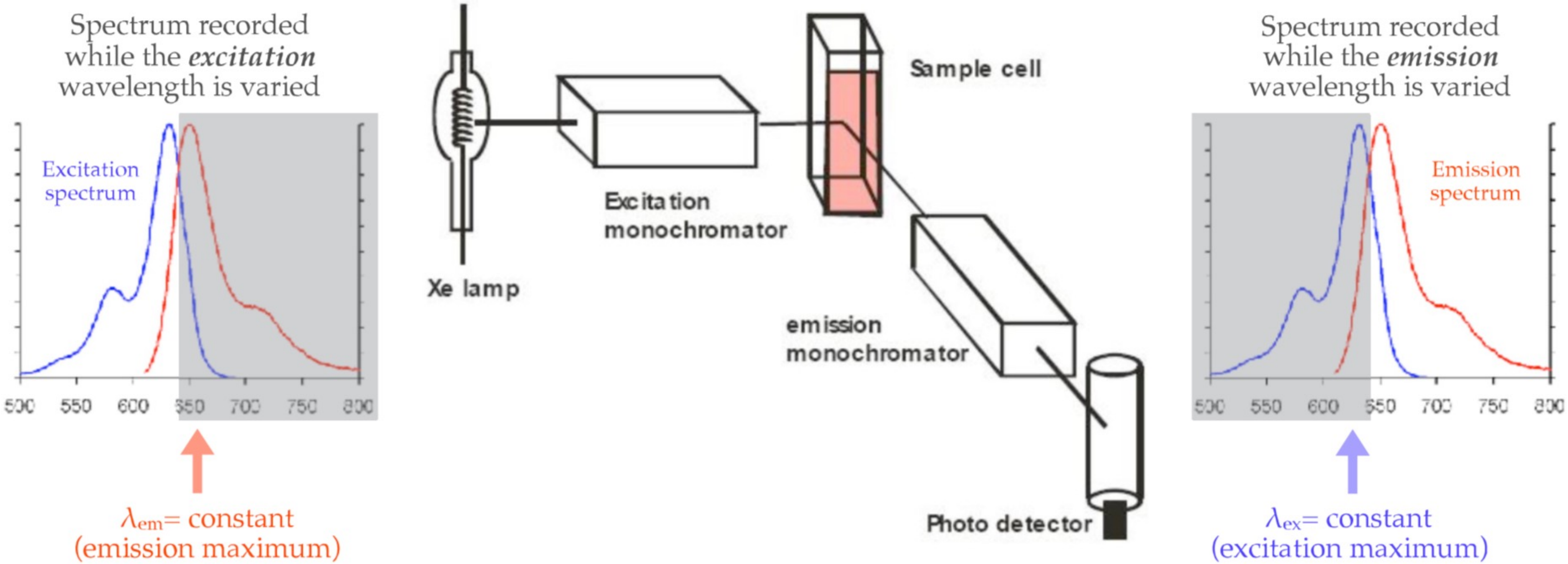
Comparing emission processes

	Fluorescence	Phosphorescence
Relaxation	From singlet state $S_1 \rightarrow S_0$	From triplet state $T_1 \rightarrow S_0$
Lifetime	Nanoseconds	From microseconds up to seconds
Stokes shift	Smaller	Larger (because T_1 is at lower energy than S_1)



Measurement of luminescence

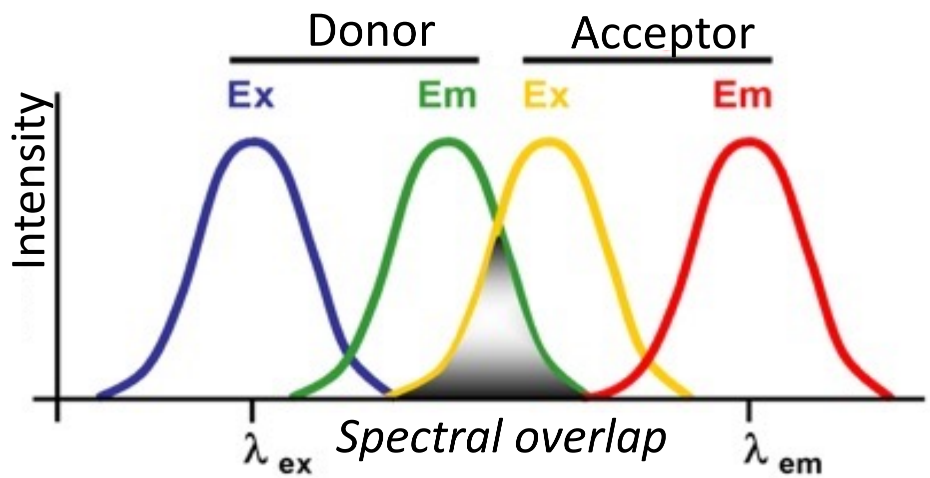
Luminescence spectrofluorimeter



Applications - FRET

Förster **R**esonance **E**nergy **T**ransfer

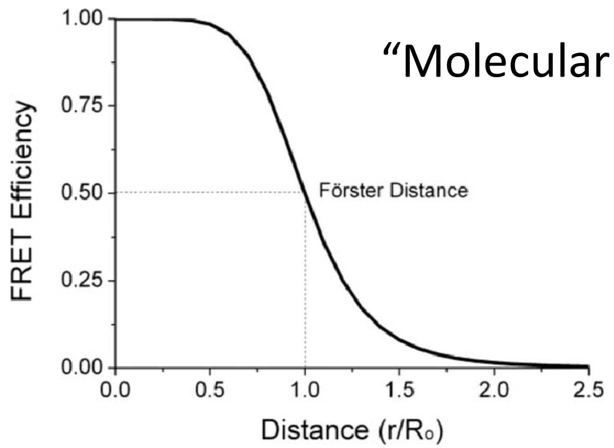
Energy transfers from donor without emission to acceptor in diploe-diploe interactions. Requires spectral overlap between donor emission and acceptor absorption.



FRET efficiency or quantum yield (E):

$$E = \frac{1}{1 + (r/r_0)^6}$$

r_0: *Förster distance*

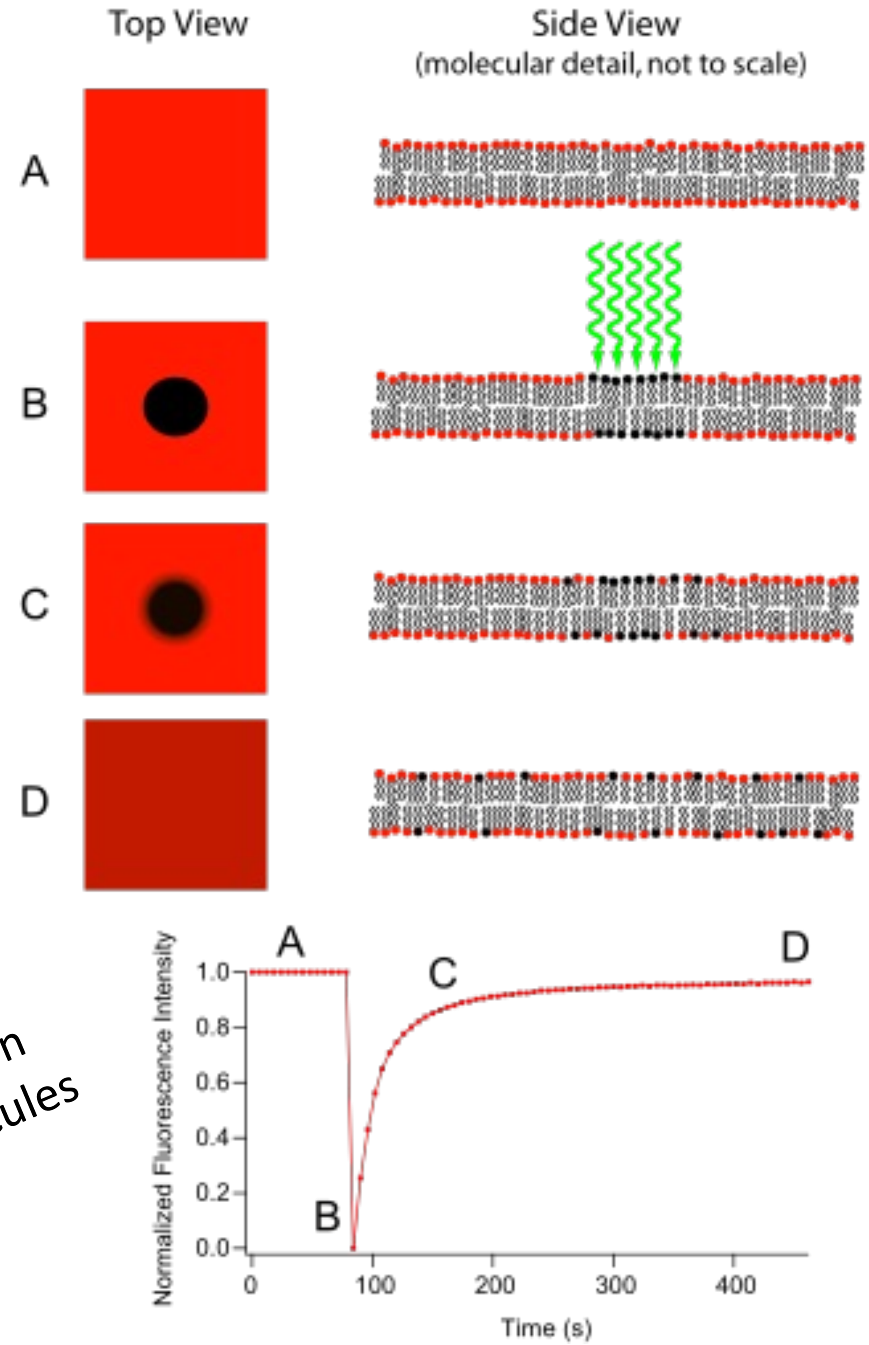


"Molecular ruler"

Applications - FRAP

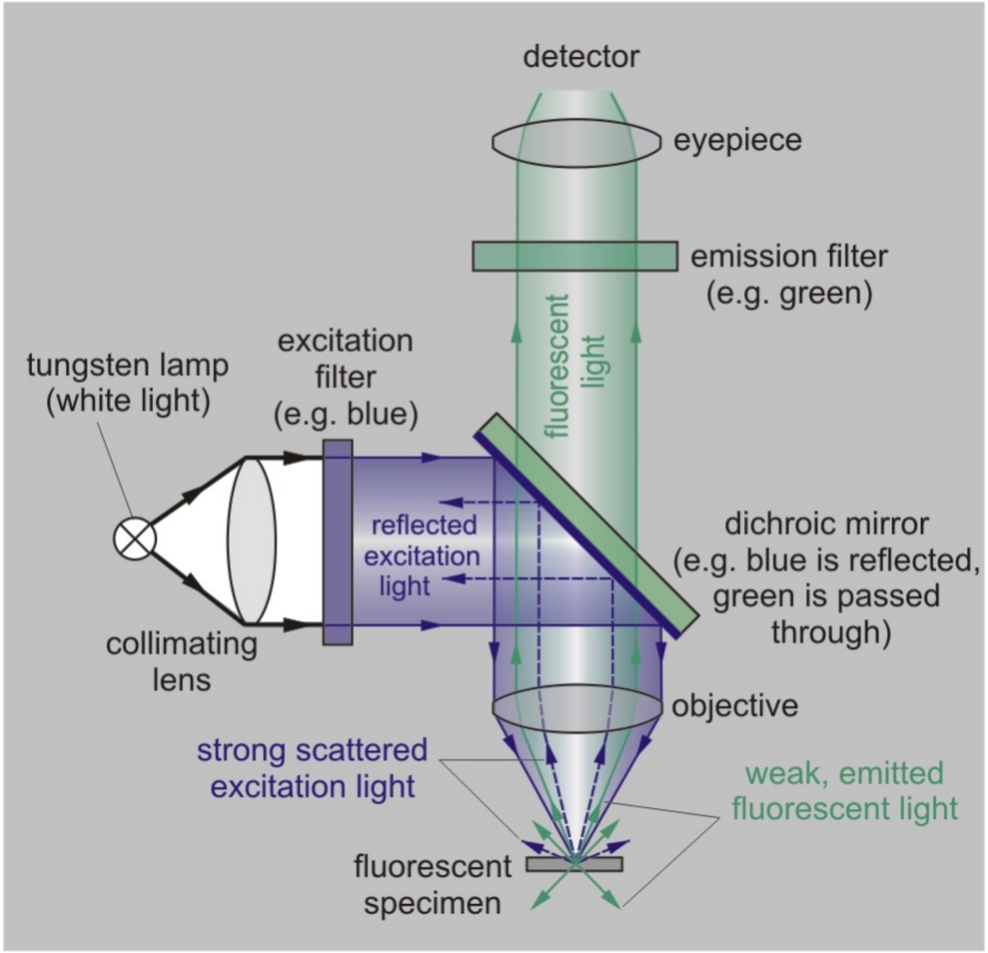
Fluorescence **R**ecovery **A**fter **P**hotobleaching

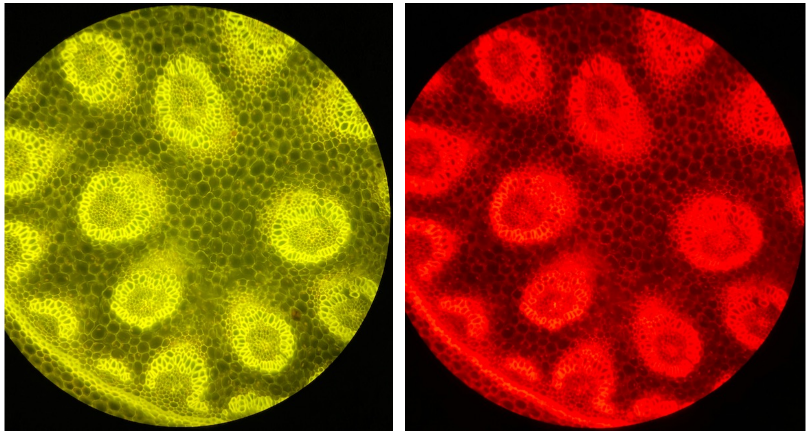
Photobleaching: The permanent loss of fluorescence due to photochemical reactions.

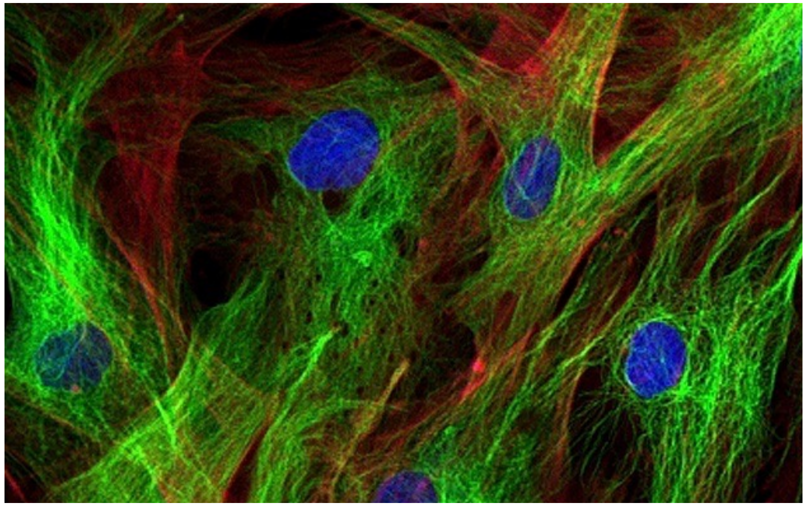


Lateral diffusion of lipid molecules

Fluorescence microscope

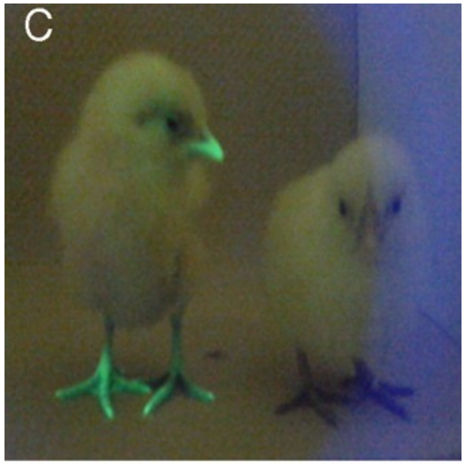




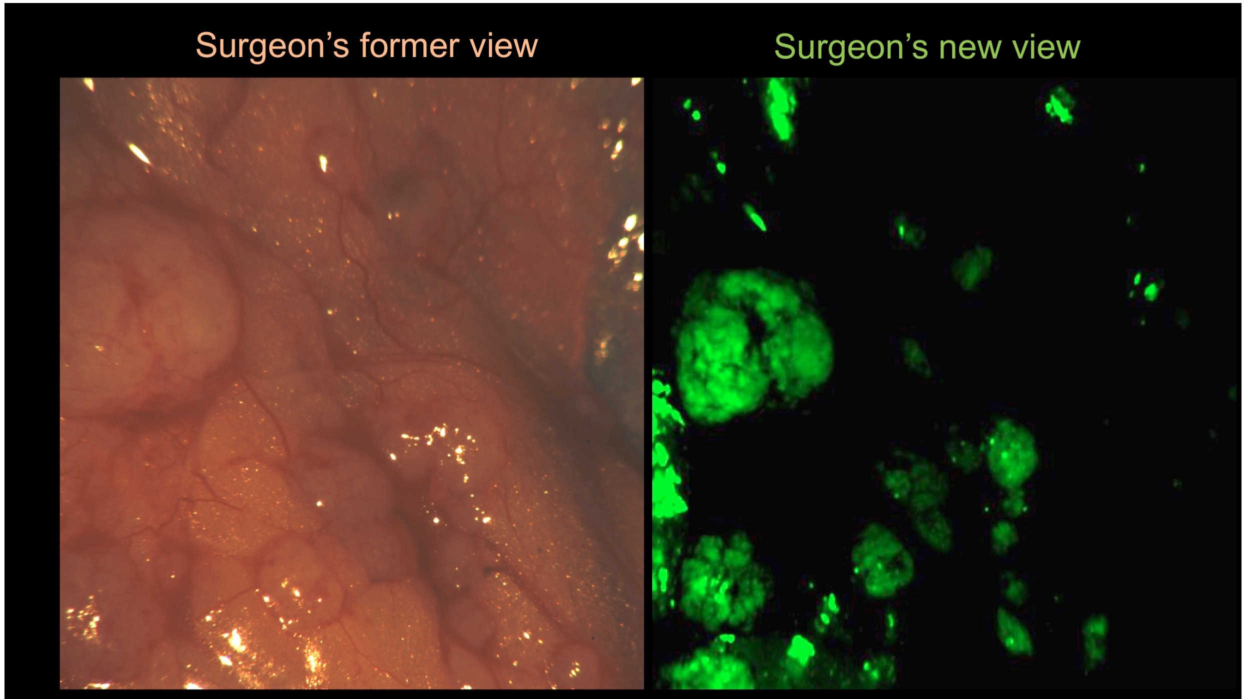


Biomedical applications

Fluorescent transgenic animals



Fluorescence guided surgery



View of localized region in peritoneal cavity of an ovarian cancer patient as seen with the naked eye (left) or with the aid of a tumor-targeted fluorescence dye (right).