Light emission

Thermal radiation, luminescence laser

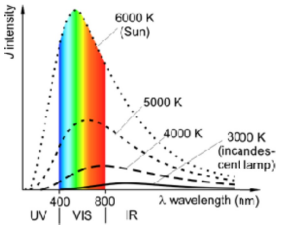
Miklós Kellermayer

Sources of light emission

1. Thermal (black body) radiation

Mechanism: thermal motion of atoms, molecules

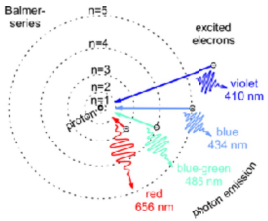
Source of light energy: internal energy of the system



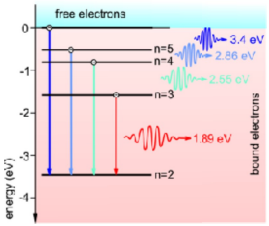
... what is a "black body"...?

2. Luminescence

Mechanism: emission of excited-state energy



Source of light energy: energy of excited state



A black body absorbs all the light falling on it

Objects not only emit radiation but absorb it as well.

Ratio of spectral emissive power (M) and absorptivity (α) is constant (Kirchoff's law):

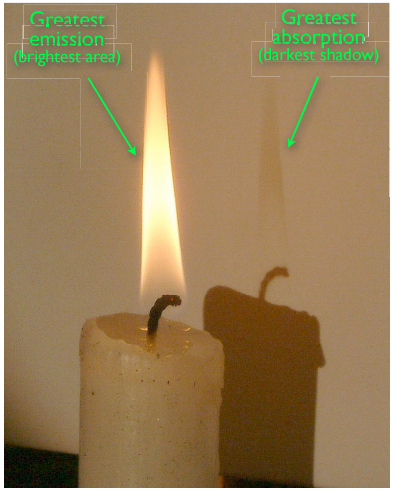
Gustav Robert **Kirchoff** (1824-1887)

$$\frac{M_{\lambda i}}{\alpha_{\lambda i}} = \frac{M_{\lambda j}}{\alpha_{\lambda j}}$$

For a black body (BB):

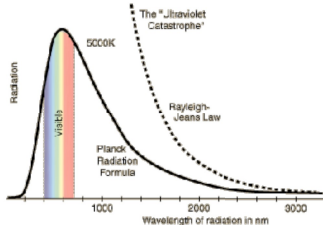
$$\alpha_{\lambda BB} = 1$$

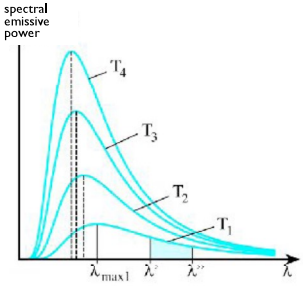
- That is, the black body absorbs all light that it is exposed to (nothing is reflected).
- The black body is an ideal object for investigating temperature-dependent emission.



Black-body radiation

Properties and inferences





Stefan-Boltzmann law:

$$M_{BB}(T) = \sigma T^4$$

M_{BB} = emissive power, area under emission spectrum.

Wien's displacement law:

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

Planck's law of radiation:

$$E = hf$$

h = Planck's constant (6.626×10^{-34} Js).

Meaning: energy is absorbed and emitted in discrete packets (***quanta***).

Jozef Stefan (1835-1893)

Ludwig Eduard **Boltzmann** (1844-1906)

Wilhelm **Wien** (1864-1928)

Max Karl Ernst Ludwig **Planck** (1858-1947)

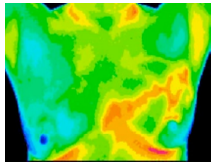
Applications of thermal radiation

Thermography, infradiagnostics

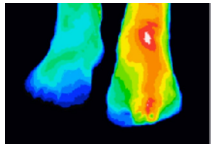
"Seeing through" a non-absorbing layer

Airport thermography

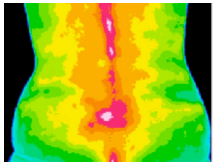
Detection of febrile condition, prevention of epidemics



Breast carcinoma



Inflammation



Chronic musculoskeletal stress (pain)

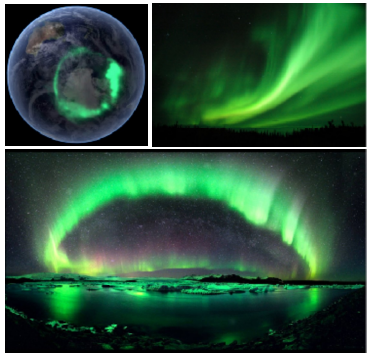
Emission by luminescence: everywhere

Photoluminescence

Luminescence everywhere

Radioluminescence

Display lights



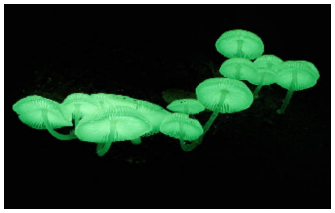
Aurora borrealis

Luminescence everywhere

Bioluminescence

Jellyfish

Phytoplankton

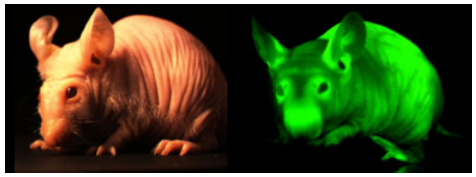


Fungi

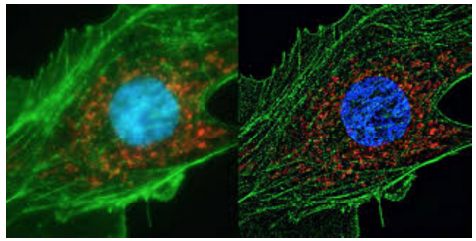
Firefly (luciferin-luciferase reaction)

Luminescence everywhere

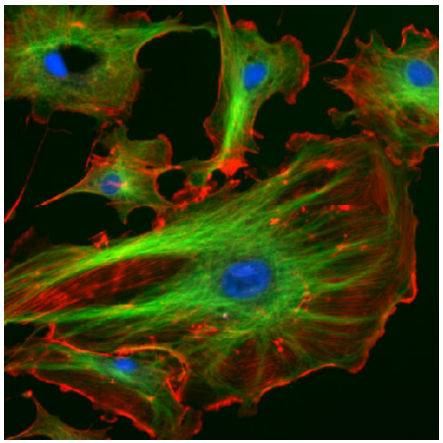
Fluorescence



GFP-mouse (green nude mouse)



Superresolution microscopy (Nobel-prize 2014)



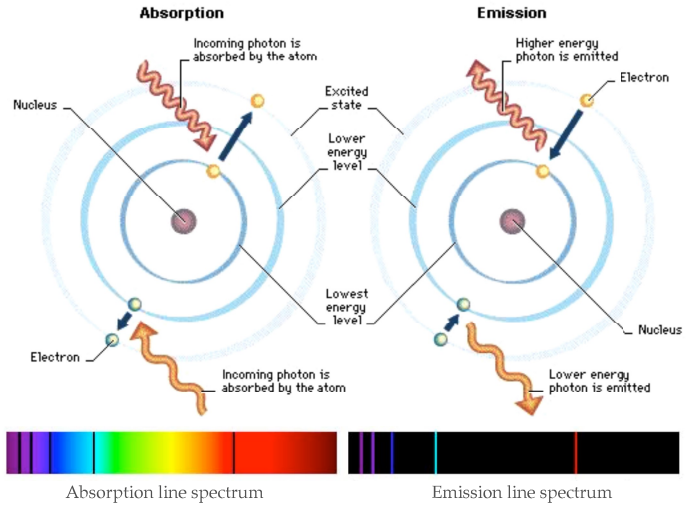
Epifluorescence microscopy (cytoskeletal system)

Types of luminescence

(a) Excitation Mode	Luminescence Type
absorption of radiation (UV/VIS)	photoluminescence
chemical reaction	chemiluminescence, bioluminescence
thermally activated ion recombination	thermoluminescence
injection of charge	electroluminescence
high energy particles or radiation	radioluminescence
friction	triboluminescence
sound waves	sonoluminescence

(b) Excited State (Assuming Singlet State)	Luminescence Type
first excited singlet state	fluorescence, delayed fluorescence
lowest triplet state	phosphorescence

Emission by an excited atom



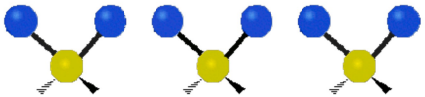
Absorption line spectrum

Emission line spectrum

Emission by an excited **molecule** is more complex...

...because its **energy levels** are complex.

Molecule: atoms connected by covalent bonds
Simplest case: diatomic molecule (e.g., hydrogen)



Asymmetric stretching *Symmetric stretching* *Scissoring*

Molecules **vibrate** and **rotate:**

Vibration: periodic motion ***along*** the axis of the covalent bond
Rotation: periodic motion ***around*** the axis of the covalent bond

Energy of a molecule: Born-Oppenheimer - approximation:

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

- Types of energies are independent (not coupled)
- Energy states are non-continuous (discrete)
- Transition between states involves packets (quanta) of energy
- Scale of transition energies between different states are different

Scaling of transition energies:

$$E_e \overset{\sim 100x}{>} E_v \overset{\sim 100x}{>} E_r$$

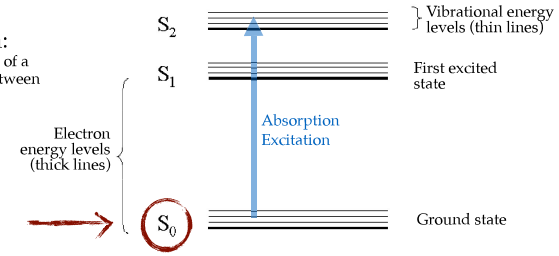
$\sim 3 \times 10^{-19}$ J (~2 eV) > $\sim 3 \times 10^{-21}$ J > $\sim 3 \times 10^{-23}$ J

(Rule of thumb: ultraviolet > visible > infrared)

Representation of energy states

Alexander Jabłoński
(1898-1980)

Jabłoński diagram:
illustrates the electronic states of a molecule and the transitions between them (with arrows)



What is this "S" (singlet) state?

Spin states - Pauli's principle

Wolfgang Pauli
(1900-1958)

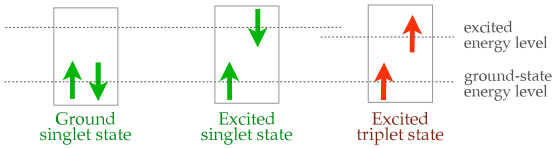
- Each quantum state can be occupied by a single electron.
- Within an atom there cannot be two electrons for which all four quantum numbers are identical.

fully occupied subshell: spin pairing (opposite-spin electrons pair)

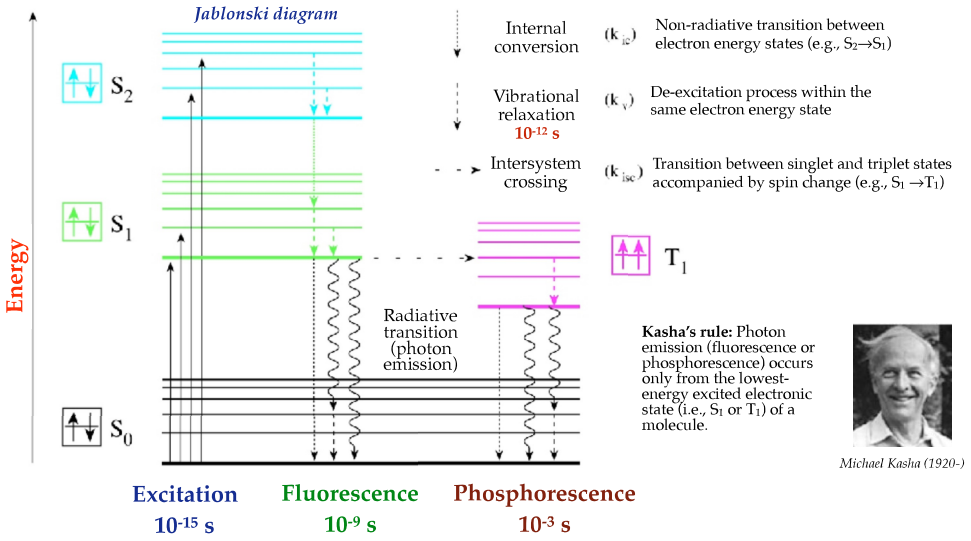
Singlet and ***triplet*** states: number of orientations of magnetic moment associated with net spin state (in magnetic field) = 2S+1 = 1 (*singlet*) or 3 (*triplet*). (S = net spin, e.g., in fully occupied subshell (+1/2)+(-1/2) = 0)

S: singlet state: paired electrons with opposite spins, net spin (S) = 0, *number of orientations (2S+1) = 1.*

T: triplet state: there are identical spin-state electrons in the molecule, net spin = 1 (e.g., (+1/2)+(+1/2) = 1), *number of orientations (2S+1 = 2+1) = 3.*



Processes and timescales of luminescence

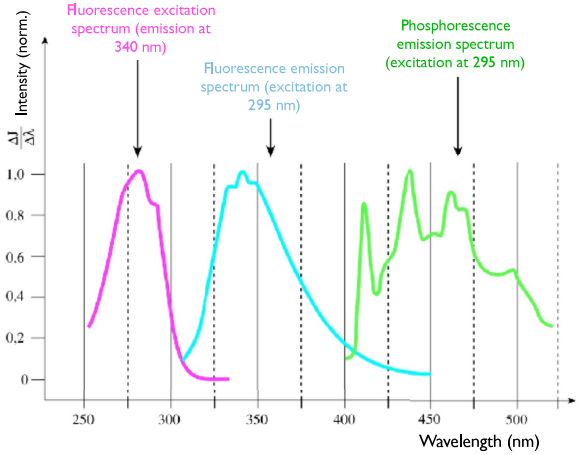


Kasha's rule: Photon emission (fluorescence or phosphorescence) occurs only from the lowest-energy excited electronic state (i.e., S_1 or T_1) of a molecule.

Michael Kasha (1920-)

Characterization of luminescence

Luminescence spectra



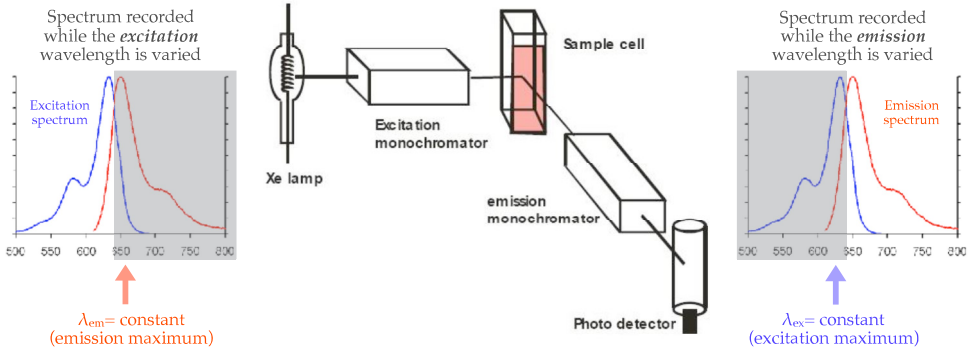
- Band spectra
- Fluorescence excitation and emission spectra are symmetric
- Stokes shift

George Stokes
(1819-1903)

Fluorescent dyes: "fluorophores"
By the specific attachment fluorophores, non-fluorescent molecules may also be studied (fluorescent labeling)

Measurement of luminescence

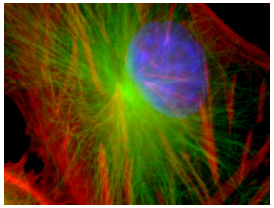
Luminescence spectrometer
("Steady-state" spectrofluorometer)

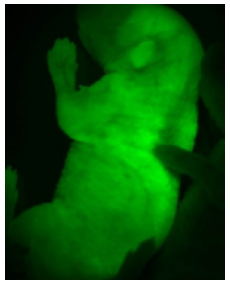
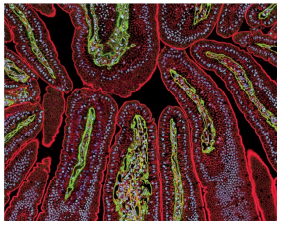


Biomedical applications of fluorescence

A few examples:

- DNA sequencing (chain termination method)
- DNA detection (EtBr)
- DNA microarray
- Immunofluorescence
- Förster resonance energy transfer (FRET)
- Fluorescence recovery after photoleaching (FRAP)
- Fluorescent protein conjugation technologies
- Quantum dots
- **Fluorescence-activated cell sorting (FACS)**
- **Fluorescence microscopy**
- etc...

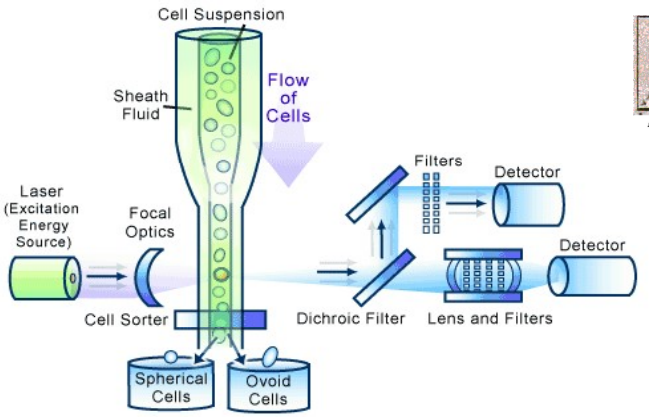


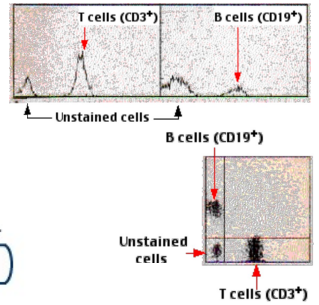
Fluorescence activated cell sorter (FACS)

Flow cytometry

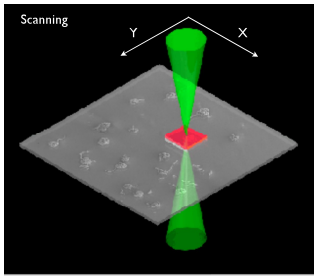
- A cell suspension, fluorescently labeled by using specific antibodies, is analyzed cell by cell
- Numerous parameters are measured simultaneously (fluorescence intensity at several wavelengths, small- and large-angle scatter)
- Statistical analysis
- If needed, cells can be separated according to their fluorescence



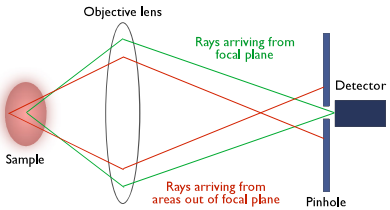
Cytometry statistics

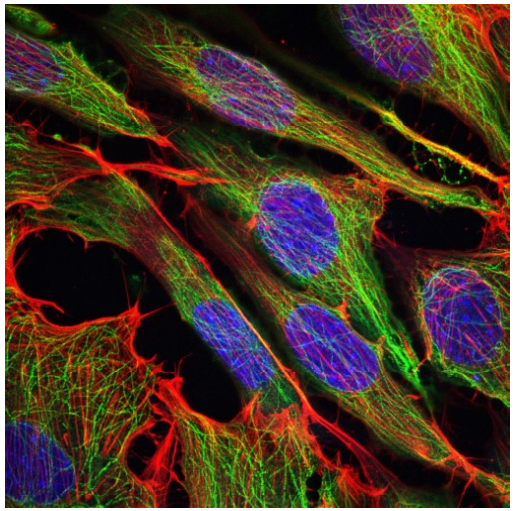


Laser scanning confocal microscopy



"Confocal principle"

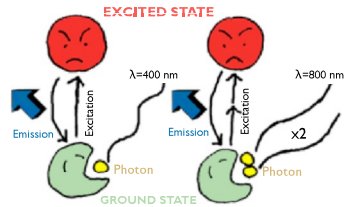


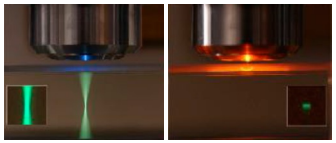


Green: microtubules; Red: actin; Blue: nuclei

Multiphoton microscopy

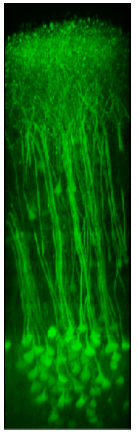
- Energy of two (or more) photons are added during excitation
- Excitation (hence emission) only in the focal point (limited photodamage)
- Excitation with long wavelength (near-IR), short (fs) light pulses
- Large (up to 2 mm) penetration due to long wavelength



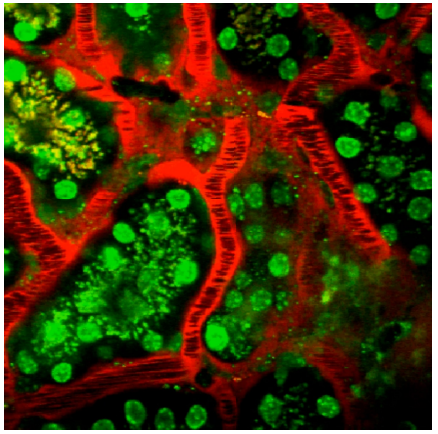


Single-photon fluorescence

Two-photon fluorescence



Cortical pyramidal cells



Green: proximal kidney tubules; Red: albumin (plasma)

Super-resolution microscopy

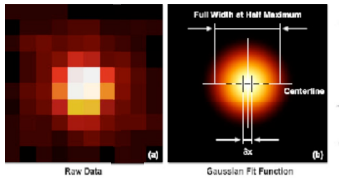
Chemistry Nobel-prize, 2014

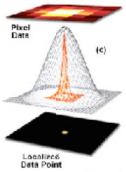
Resolution problem is converted into position-determination problem

Resolution problem (Abbé)

$$d \doteq \frac{0.61\lambda}{n \sin\alpha}$$

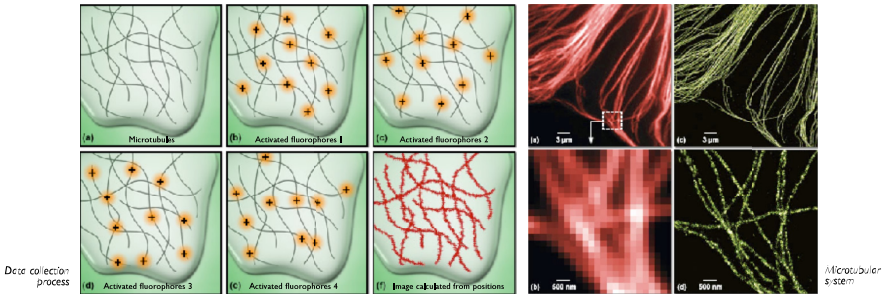
Position determination problem (precision depends on photon count)





"Stochastic" data collection, single fluorophores

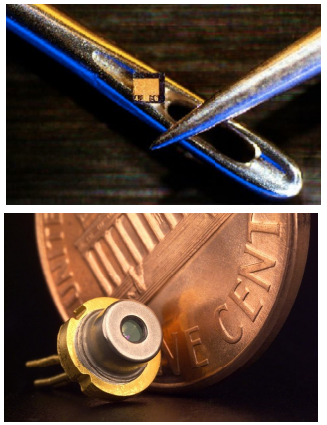
STORM ("stochastic optical reconstruction microscopy"); PALM ("photoactivated localization microscopy")



Laser:

"Light Amplification by Stimulated Emission of Radiation"

Luminescent light source based on light amplification.

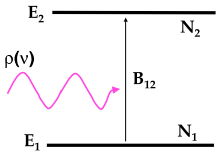


5 mW diode laser
few mms

Terawatt NOVA laser - Lawrence Livermore Laboratories
Size of a football field

Principles of laser I. Stimulated emission

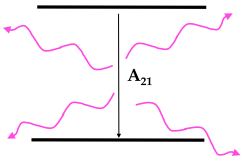
1. Absorption



Frequency of transition:
$n_{12}=N_1B_{12}\rho(\nu)$

$\Delta E= E_2-E_1=h\nu$
energy quantum is absorbed.

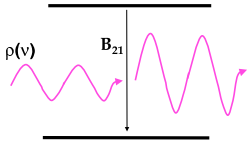
2. Spontaneous emission



Frequency of transition:
$n_{21}=N_2A_{21}$

E_2-E_1 photons
travel independently in all directions.

3. Stimulated emission



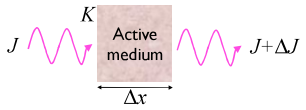
Frequency of transition:
$n_{21}=N_2B_{21}\rho(\nu)$

In the presence of exernal field.
Field energy is increased.
Phase, direction and frequency of emitted and external photons are identical.

Explanation: two-state atomic or molecular system.
E_1, E_2 : energy levels, $E_2>E_1$
$\rho(\nu)$: spectral energy density of external field.
N_1, N_2 : number of atoms or molecules on the given energy level.
B_{12}, A_{21}, B_{21}: transition probabilities (Einstein coefficients), $B_{12} = B_{21}$

Principles of laser II. Population inversion

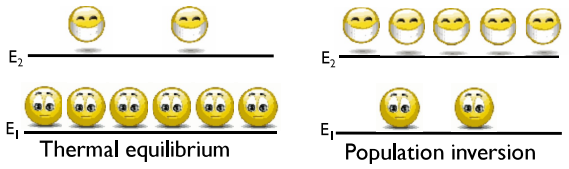
Light amplification depends on the relative population of energy levels.



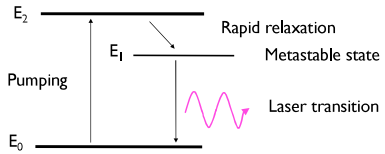
$$\Delta J=JK(N_2-N_1)\Delta x$$

J = intensity
K = constant
x = distance travelled within medium
N_1, N_2 = number of atoms on the E level

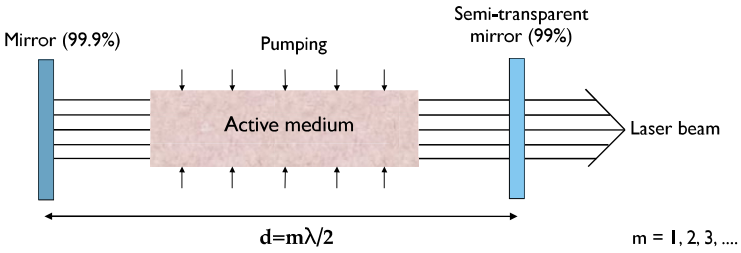
N.B.: If ΔJ is positive, more light exits the medium, than has entered!



- Population inversion only in multiple-state systems!
- Pumping: electrical, optical, chemical energy



Principles of laser III. Optical resonance



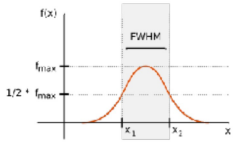
Resonator:

- two parallel (or concave) mirrors
- part of the exiting light is coupled back into the medium
- positive feedback -> self-excitation -> resonance

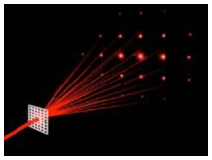
- Optical switch in the resonator: Q-switch, pulsed mode

Properties of laser light

1. **Small divergence**
   Parallel (collimated) beam
2. **Large power**
   In continuous (CW) mode, tens, hundreds of W (e.g., CO_2 laser)
   In Q-switched mode, momentary power is enormous (GW)
   Because of small divergence, large spatial power density.
3. **Small spectral bandwidth**
   "Monochromaticity"
   Large spectral energy density



4. **Often polarized**
5. **Possibility of extremely short pulses**
   ps, fs
6. **Coherence**
   phase identity, interference tendency; temporal coherence (phase identity of photons emitted at different times); spatial coherence (phase identity across beam diameter). *Application:* holography, optical coherence tomography



Types of lasers

Based on active medium:

1. Solid state lasers
Metal doping in crystals or glasses; Ruby, Nd-YAG, Ti-sapphire
Red-infrared spectral range; CW, Q-switched mode, large power

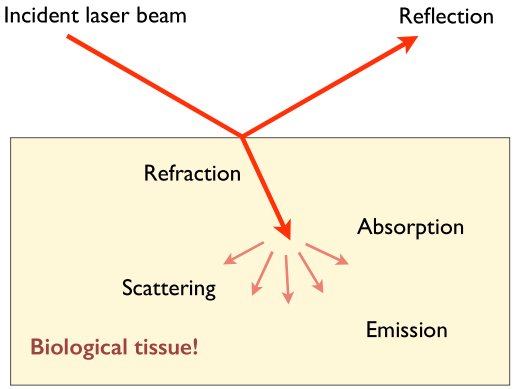
2. Gas lasers
Best known: *He-Ne laser* (10 He/Ne). Small energy, wide use
CO_2 laser: CO_2-N_2-He mixture; λ~10 μm; Huge power (100 W)

3. Dye lasers
Dilute solution of organic dyes (e.g., rhodamine, coumarine); Pumped by another laser.
Large power (Q-switched mode); Tunable

4. Semiconductor (diode) lasers
On the boundary of p- and n-type doped semiconductors.
No need for resonator mirrors (total internal reflection)
Red, IR spectral range. Huge CW power (up to 100W)
Beam characteristics are not very good. Wide use because of small size.

Today: laser lines (wavelengths) are available from X-rays to infrared light!

Biomedical applications of lasers



Laser properties to consider:

- Steerability (small divergence, surgeries)
- Power (surgical applications)
- Monochromaticity (tissue absorbance)
- Coherence (interference, image formation)

The effects depend not only on the properties of the laser, but also on those of the biological tissue: absorbance, transmittivity, light-induced reactions.

Biomedical applications of lasers

Surgical disciplines: "laser knife", coagulation, blood-less surgery. Tumor removal, tattoo removal. CO_2 and Nd:YAG lasers, holmium laser lithotripsy (urology).

Dentistry: caries absorbs preferentially.

Photodynamic tumor therapy: laser acivation of photosensitive chemicals preferentially taken up by the tumor.

Dermatology: wide-spread uses (tattoo removal, naevus removal, etc.)

Opthalmology: Retina lesions, photocoagulation, glaucoma, photorefractive keratektomy (PRK).

Dermatological applications

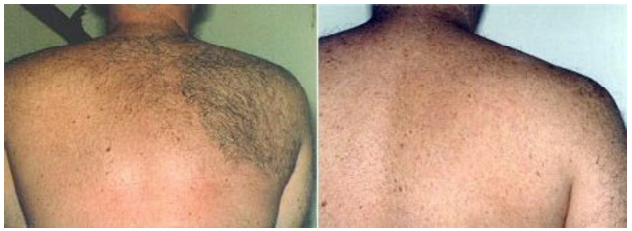
Hair removal

Phototricholysis, photoepilation

Mechanism: selective photothermolysis, selective absorption by chromophores

Employed chromophores:

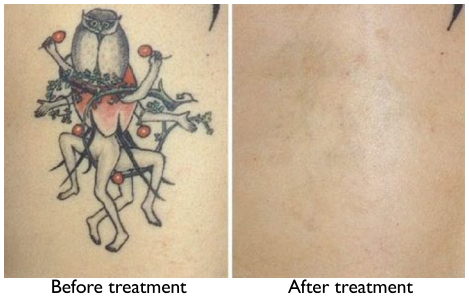
1. Carbon (exogenous, carbon or graphite-containing creams)
2. Hemoglobin (endogenous)
3. Melanin (endogenous)



Before treatment After treatment

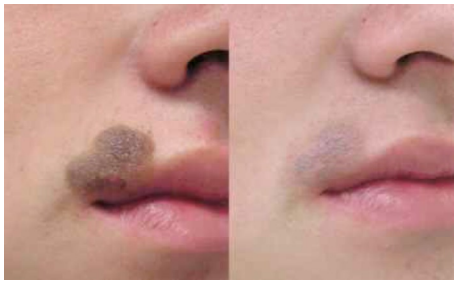
Dermatological applications

Tattoo removal



Before treatment After treatment

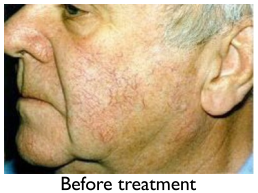
Naevus removal



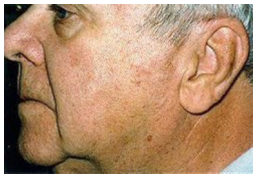
Before treatment After treatment

Dermatological applications

Removal of superficial blood vessels



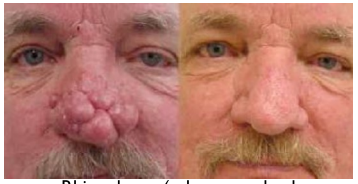
Before treatment



After treatment

Resurfacing

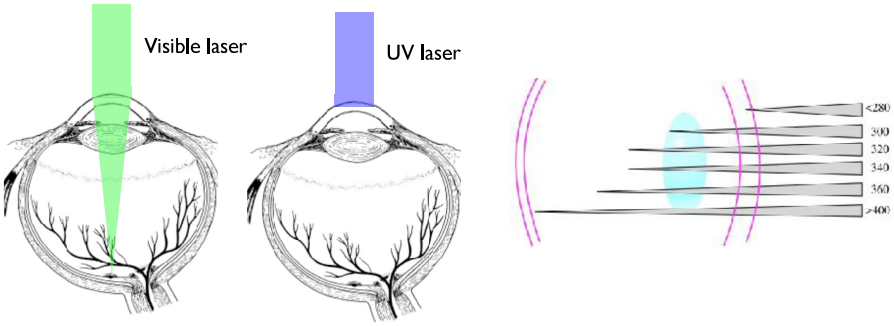
Wrinkle removal



Rhinophyma (sebaceous gland hypertrophy, fibrosis)

Ophthalmologic applications:
Considerations

Transmittivity of optical media is wavelength-dependent

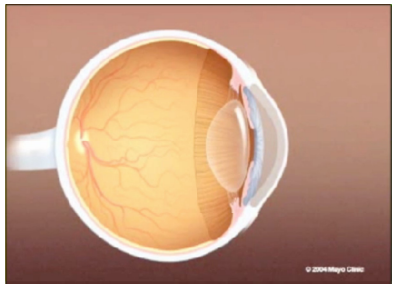


Ophthalmologic applications
LASIK

"Laser-assisted In Situ Keratomileusis"
One type of refractive laser eye surgery

History:
Jose Barraquer, 1970: construction of a microkeratome, with which he was able to cut lines and lobes in the cornea with laser (keratomileusis).
Lucio Buratto (Italian) and Ioannis Pallikaris (Greek), 1990: combination of keratomileusis photorefractive keratectomy.
Thomas and Tobias Neuhann (Germany), 1991: automated microkeratome.

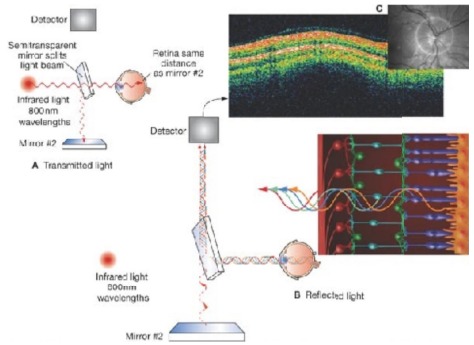
Steps:
1. Removal of contact lens (7-10 days prior to treatment)
2. Scanning the topography of the cornea with low-power laser.
3. Cutting and lifting a layer of the cornea with femtosecond laser.
4. Removal of material from the corneal stroma (few tens of microns). Excimer laser (193 nm).

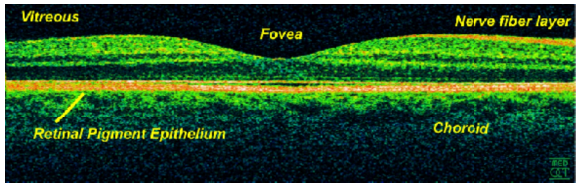


Ophthalmologic applications
Optical Coherence Tomography (OCT)

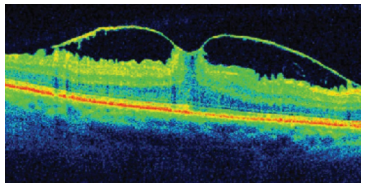
- Non-invasive
- Contrast-agent free
- Near microscopic resolution

Principles: light rays reflected in deeper tissue layers can be separated from scatter by using *interferometry*. The spatial position of the reflecting layers can be determined. The structure of the illuminated sample can be resolved within 1-2 mm depth.





Normal retina



Macula degeneration