

Photoluminescence

Physical principle

- Photoluminescence occurs for the **radiative recombination** of an excited electron. In a certain way, it is the inverse process of optical absorption.
- Huge **technological interest** (solid state lasers, displays, ...) and important tool for the **characterization of materials and semiconductor devices**.
- Based on the excitation source, we speak about thermo-, cathodo-, photo- or electroluminescence. Also ions or X-rays can be used.

We can use photoluminescence to characterize the electronic structure of materials

Physical principle, molecular case

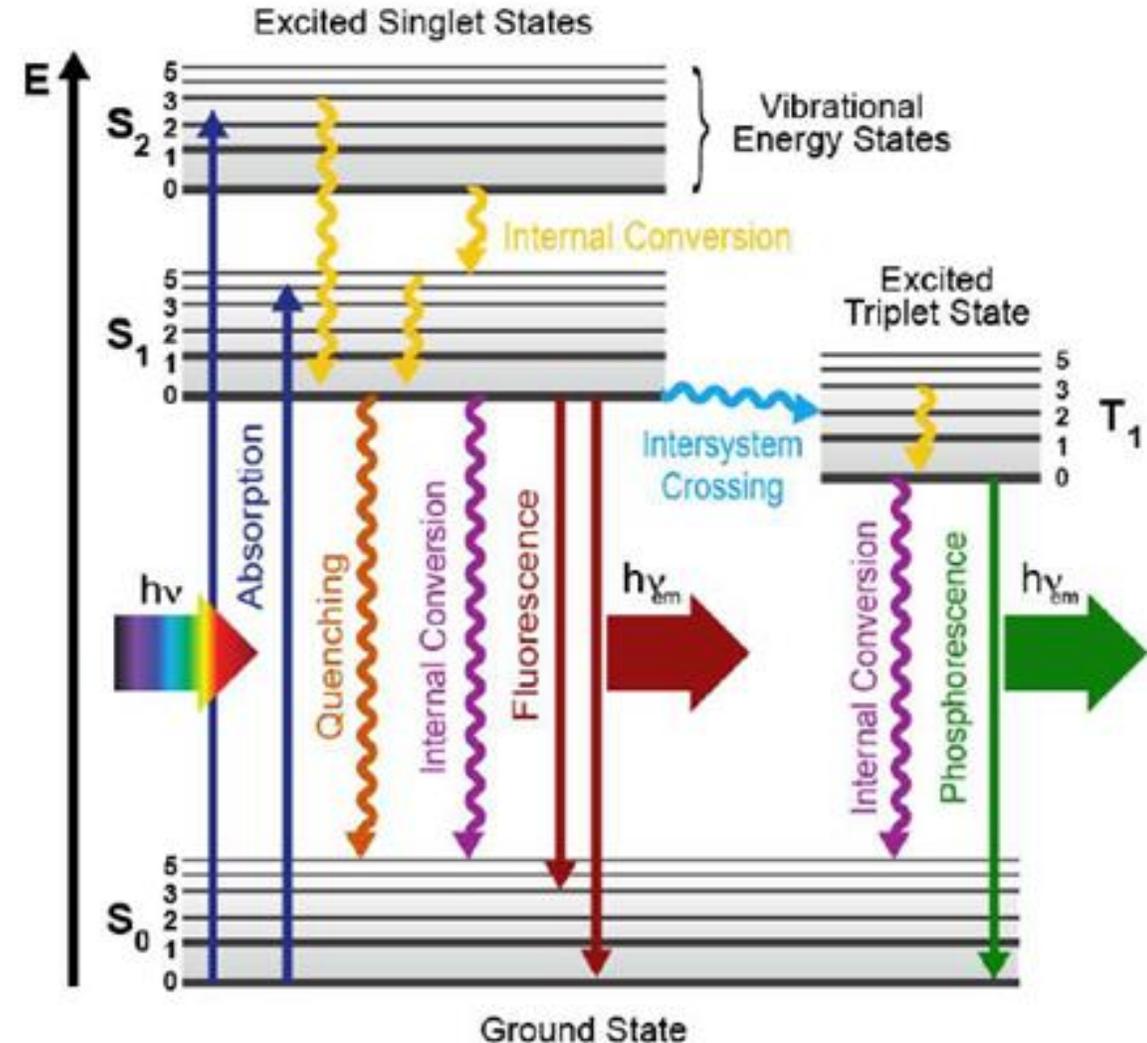
By stimulating the sample with a photon of sufficient energy ($> E_{\text{gap}}$), we promote an electron into an excited state ($\tau_{\text{abs}} \sim \text{fs}$).

The electron relaxes by internal conversion (non radiative, $\tau_{\text{NR}} \sim 10 \text{ fs} - 10 \text{ ps}$) to reach the excited state with minimum energy (Kasha rule).

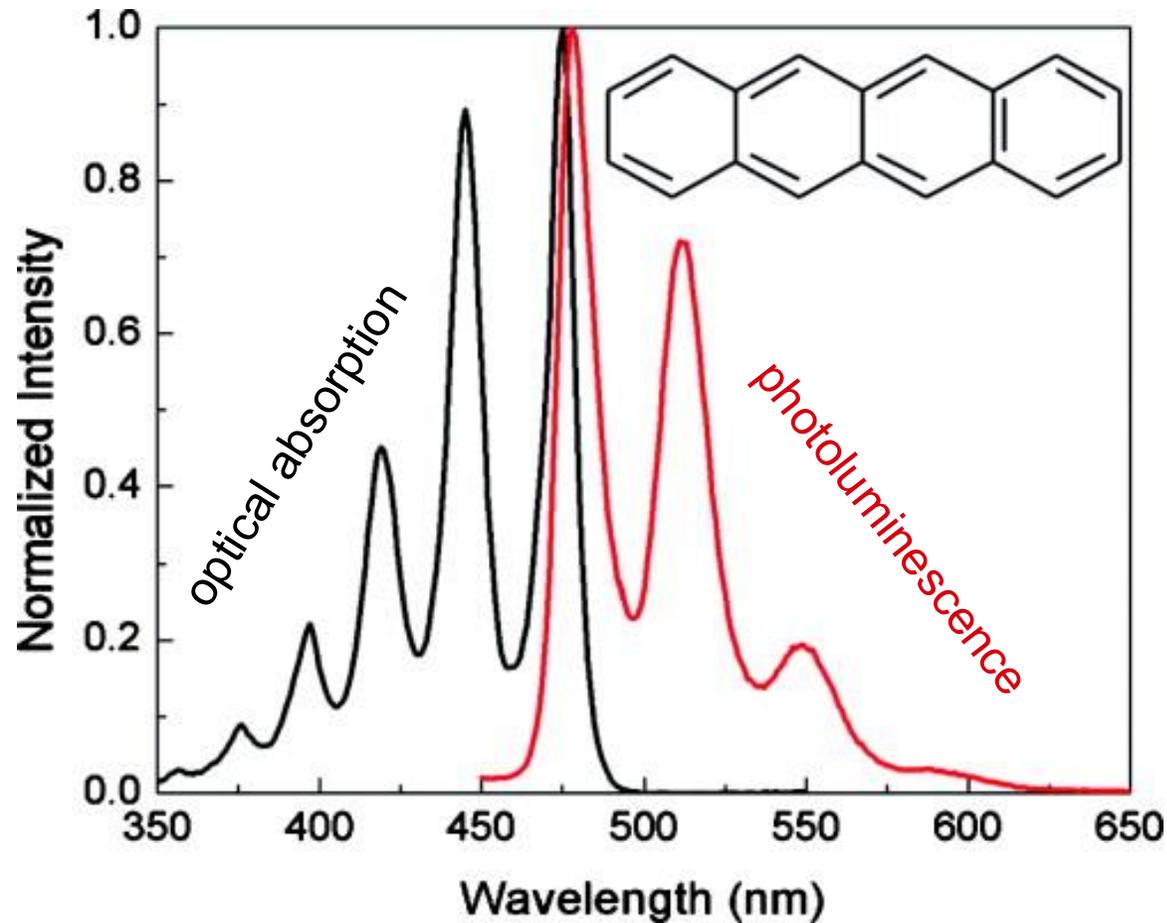
From there the electron can:

1. Keep relaxing non radiatively (energy dissipated as heat);
2. Decay to the ground state by emitting a photon (**luminescence**);
3. Reach an excited triplet state via *inter-system crossing* (ISC).

Jablonski diagram



Photoluminescence spectra



Tetracene molecule in solution

Photons emitted via luminescence generally have different energy compared to the absorbed photons, because electrons tend to relax non-radiatively to the least energetic excited state: **Stokes shift**.

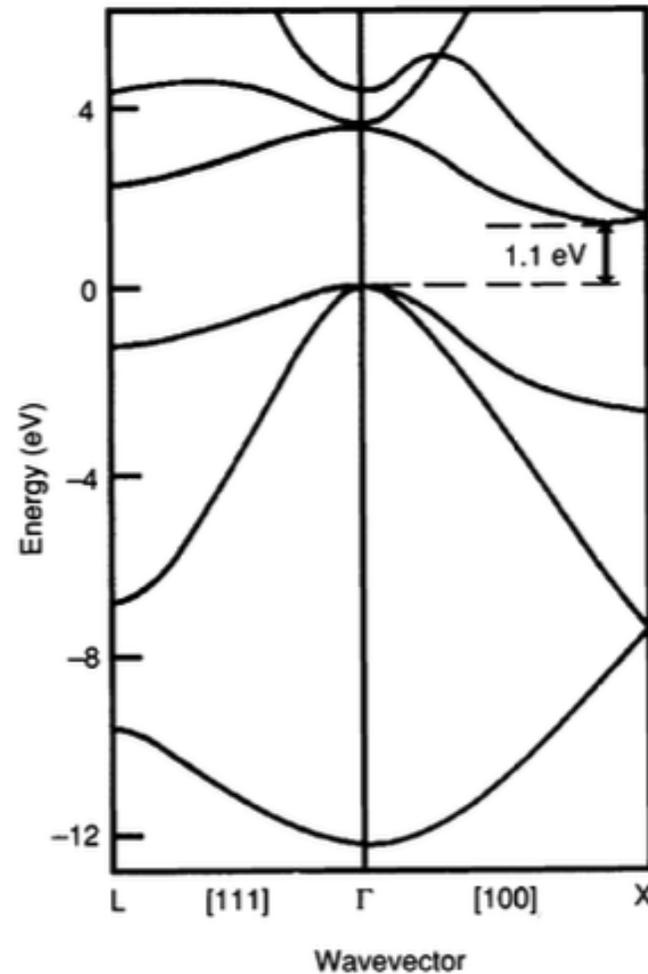
$$E = hc/\lambda$$
$$E[\text{eV}] \sim 1240/\lambda[\text{nm}]$$

Photoluminescence in solids

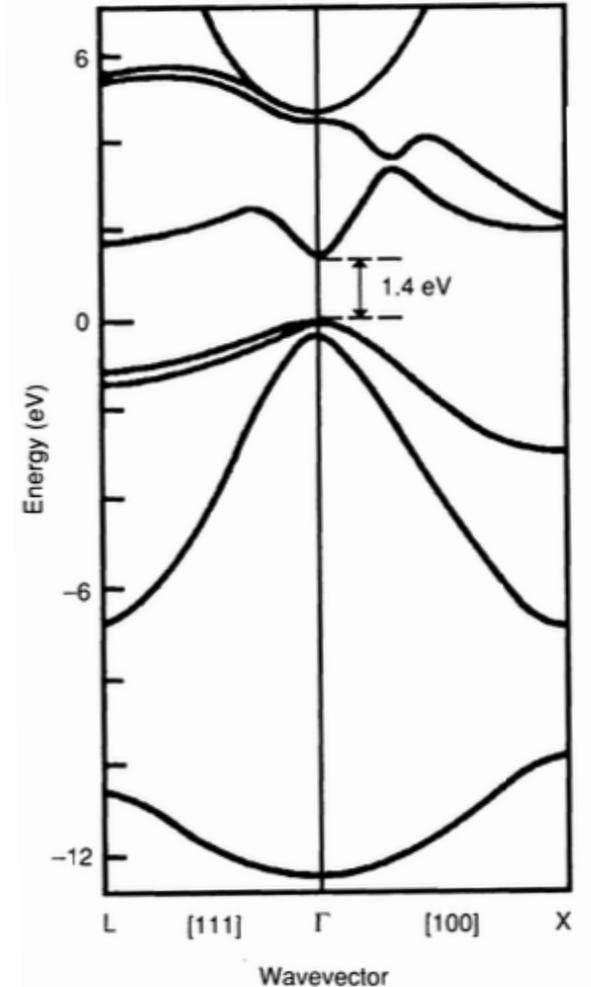
When atoms are arranged in a crystal, the discrete energy levels split into many separate levels forming continuous energy bands.

Optical excitation can promote electrons from the valence band into the conduction band, from which the system can decay radiatively through luminescence.

Luminescence spectra provide insights into the electronic structure.



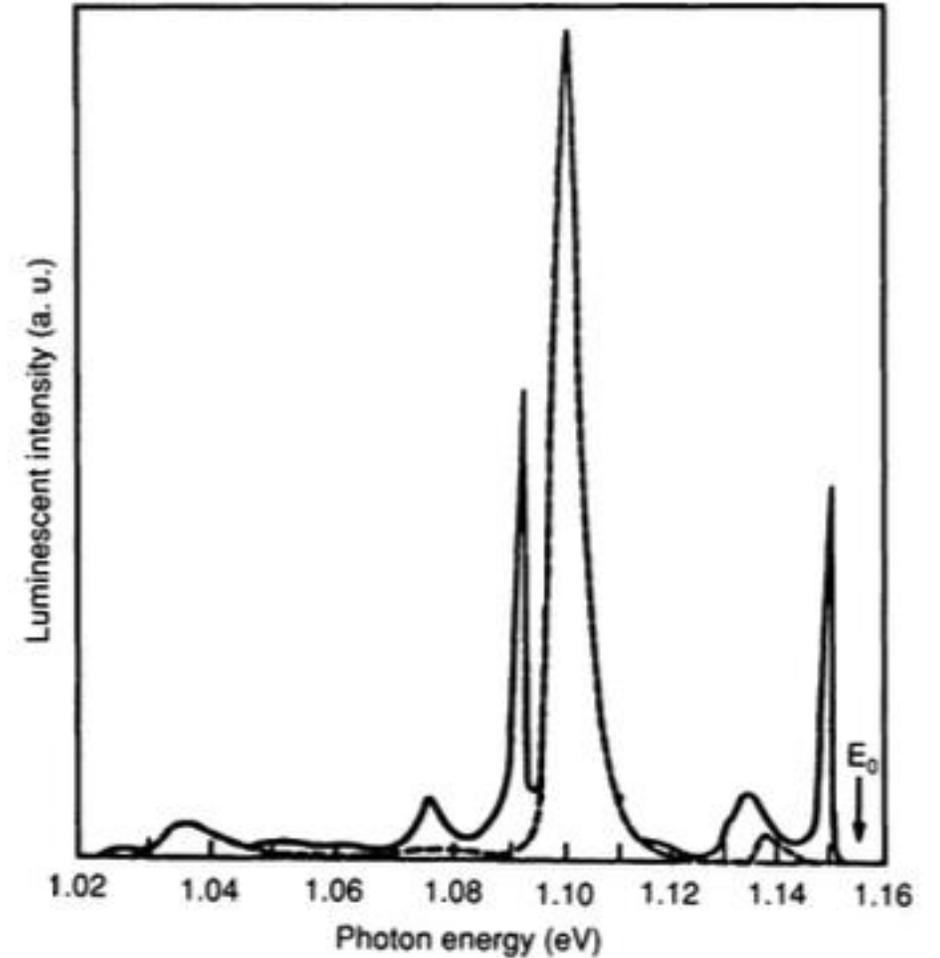
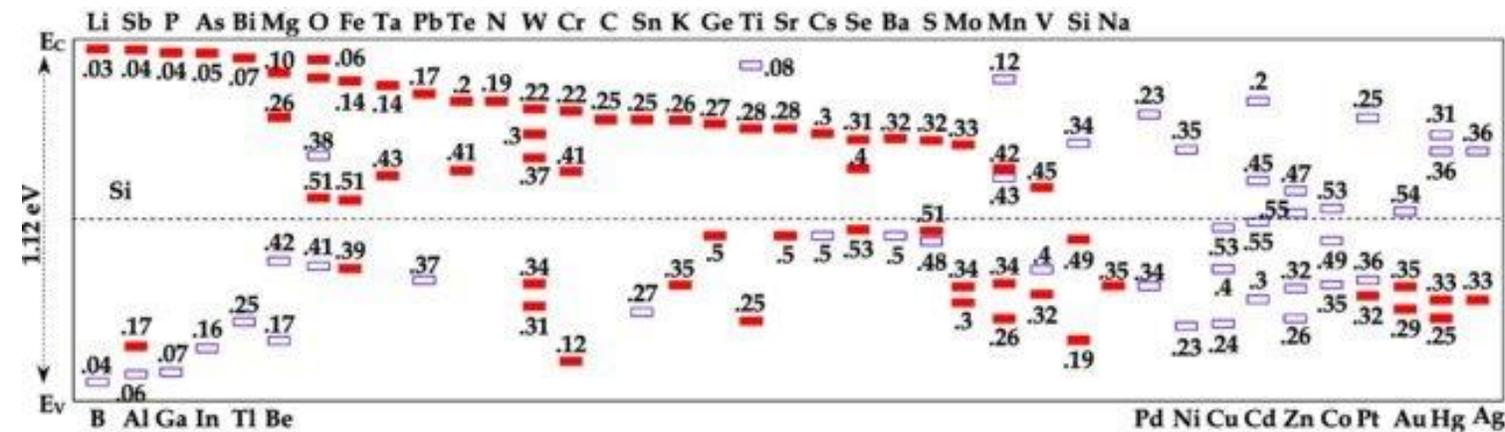
Silicon



GaAs

Photoluminescence from impurities

If impurities are added (on purpose or not) into the crystal structure, the crystalline potential is locally modified, and new electronic states may become accessible inside the band gap (lower ΔE).



- Low impurity concentration
- $8 \times 10^{-16} \text{ cm}^{-3}$ As atoms

Photoluminescence from impurities

Impurities (0.1-1% in weight) cause the different colors in gem stones.

For example:

- **Ruby** is Al_2O_3 (corundum) matrix with Cr^{3+} ions.
- **Emerald** is $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ (beryl) with Cr^{3+} or V^{3+} .
- **Acquamarine** is beryl with Fe^{2+} .
- ...



Elements of an experimental setup

Signal generator – perturbation

- Photons (laser).

Sample – signal emission

- Luminescence, radiative recombination.

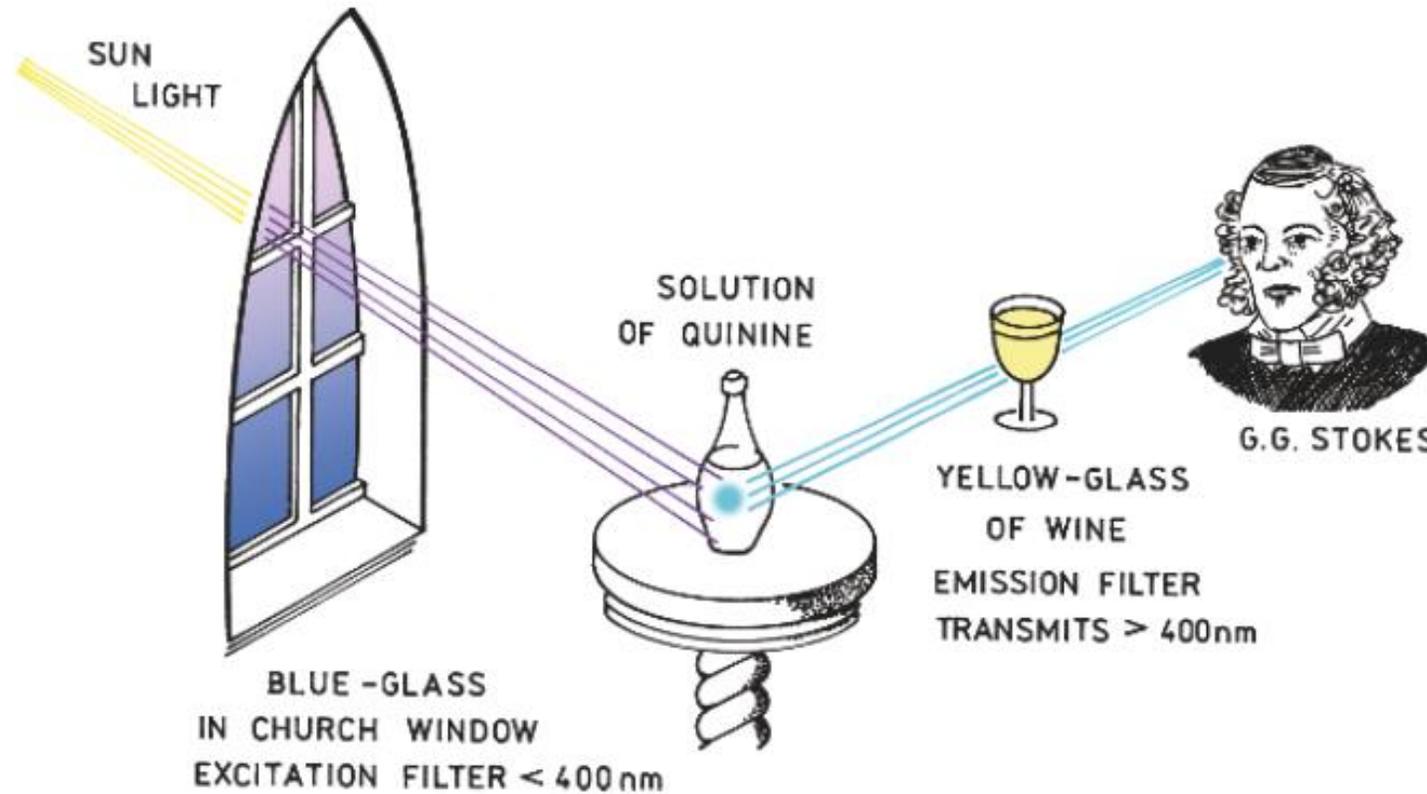
Transducer + signal processor

- The emission spectrum is dispersed in wavelength (energy).

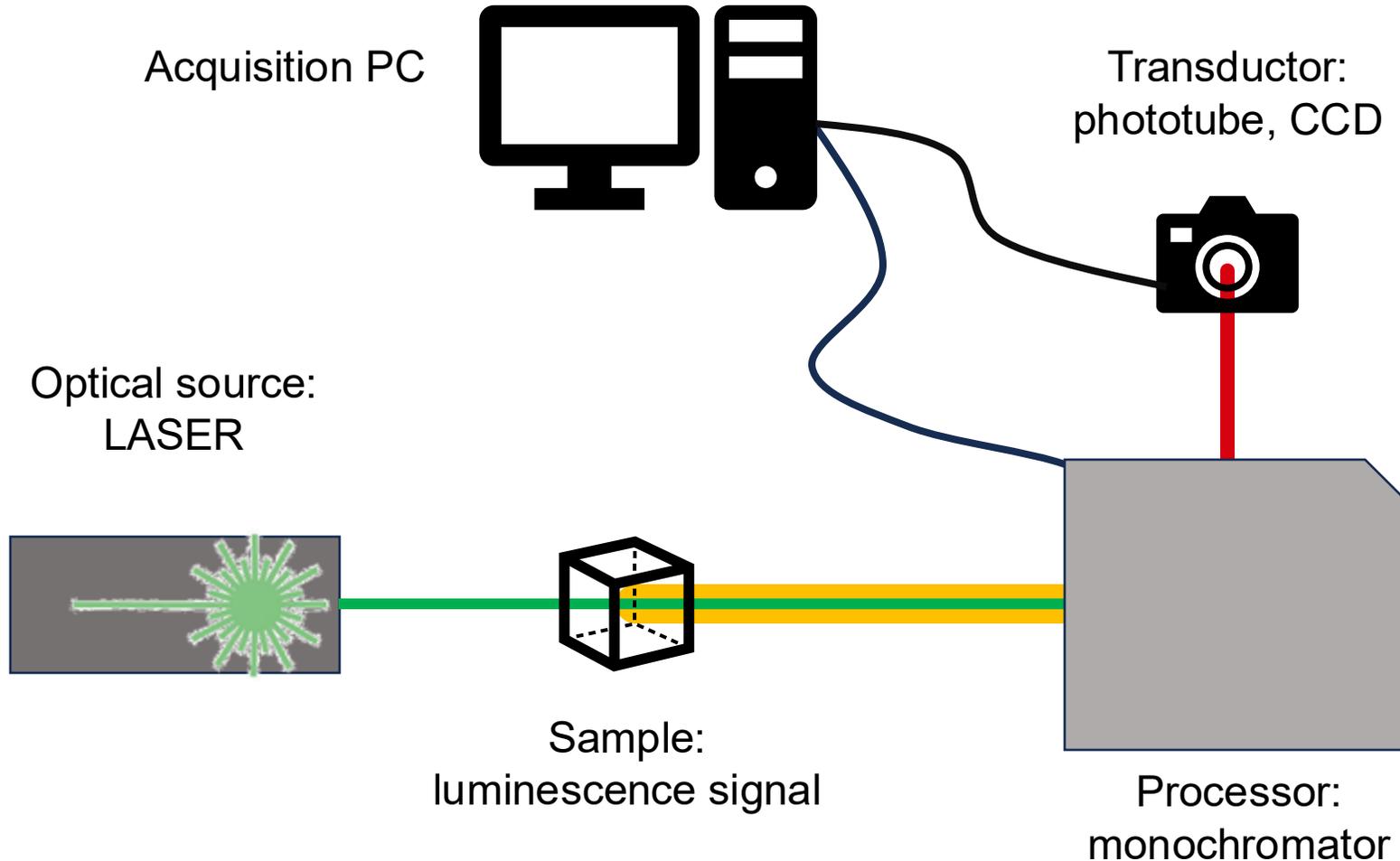
Reading device (output transducer)

- Photons are converted to electrical signals by means of photomultiplier tubes, photodiodes, or CCDs.

Photoluminescence apparatus (1850s)



Photoluminescence apparatus (now)



Useful additions:

- Focusing lenses
- Filters (interferential, low-pass,...)
- Amplifier

Lasers

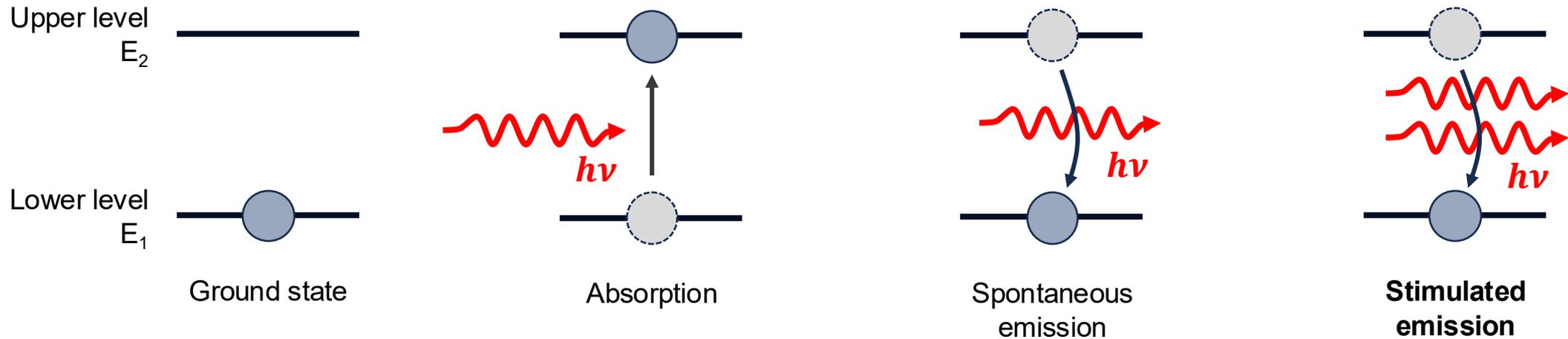
Why do we need lasers?

- Monochromaticity
- Intensity
- Coherence
- Collimated beams



Lasers: stimulated emission

Theory by Einstein, 1916



$$h\nu = E_2 - E_1$$

$$\frac{\partial N_2(t)}{\partial t} = -\frac{\partial N_1(t)}{\partial t}$$

$$\frac{\partial N_2(t)}{\partial t} = B_{12}\rho(\nu)N_1(t)$$

$$\frac{\partial N_2(t)}{\partial t} = -A_{21}N_2(t)$$

$$\frac{\partial N_2(t)}{\partial t} = -B_{21}\rho(\nu)N_2(t)$$

$$B_{12} = B_{21}$$

The net rate of emission is:

$$-\frac{\partial N_2(t)}{\partial t} = A_{21}N_2(t) + B_{21}\rho(\nu)(N_2(t) - N_1(t))$$

For lasing to occur: $N_2 > N_1$ – **population inversion!**

N_i is the number of atoms in level i

A_{ij}, B_{ij} are proportionality constants

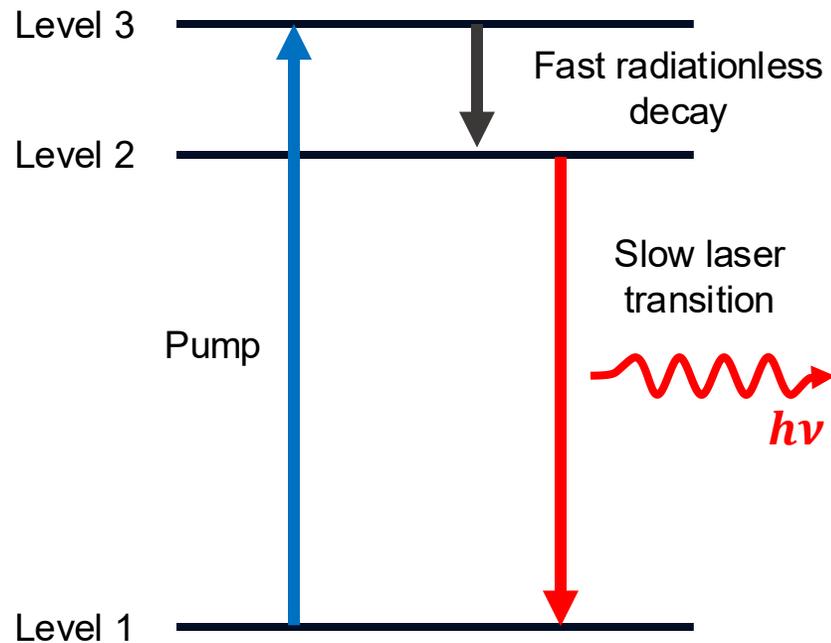
$\rho(\nu)$ is the radiation density at frequency ν

Population inversion

Population inversion is required for light amplification in lasers.

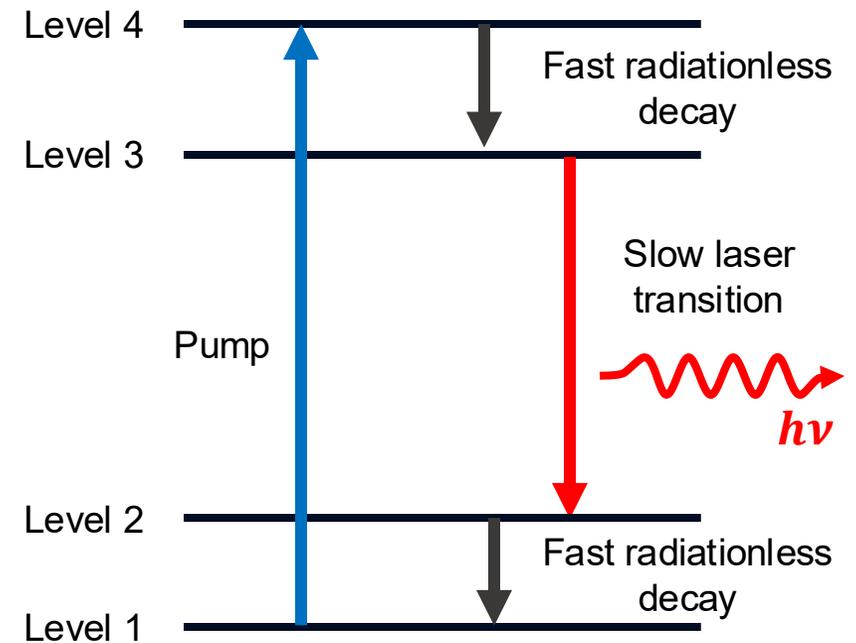
Two energy levels are not enough: at best $N_1 = N_2$, which means optical transparency but no gain.

Three-level system



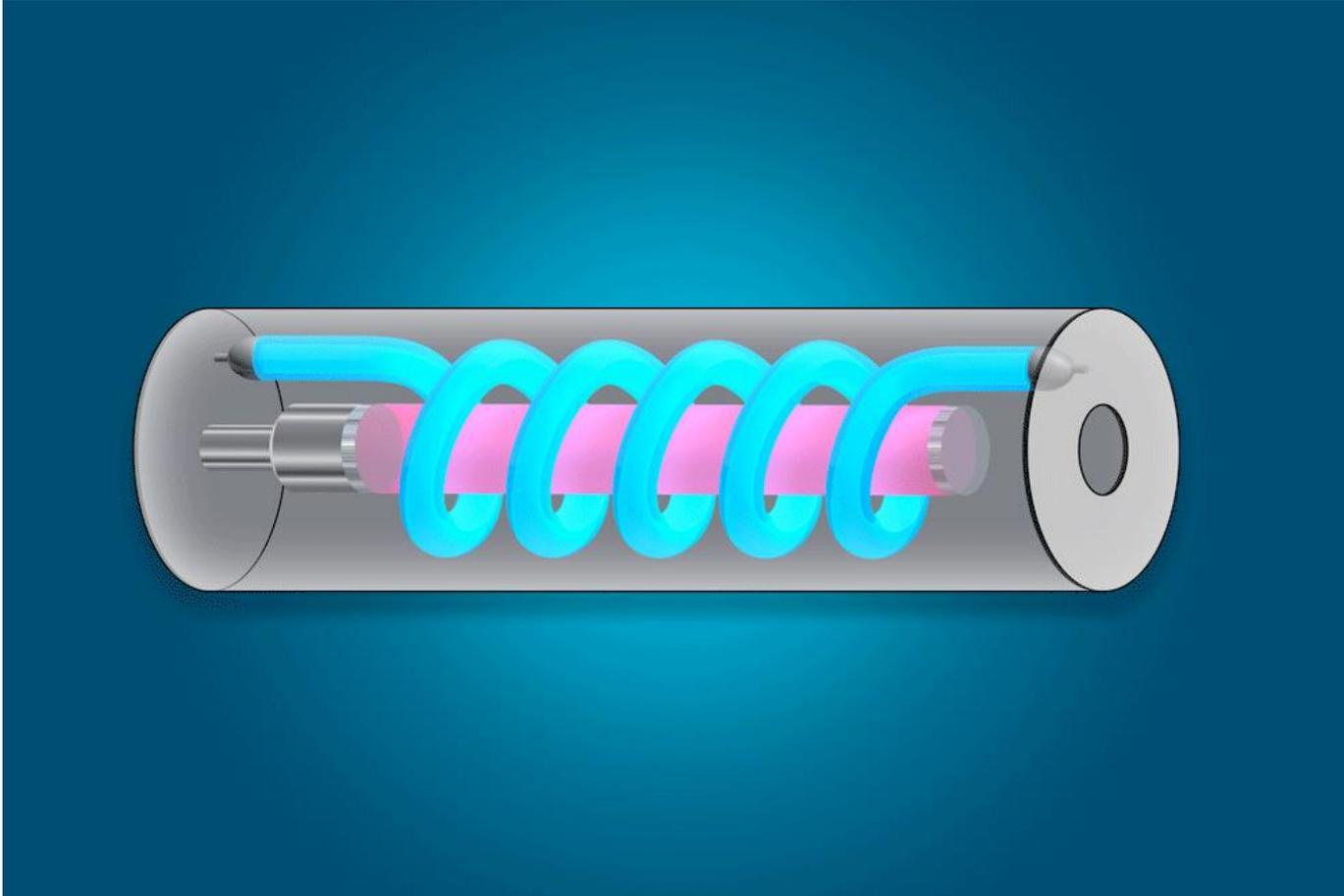
At least half of the atoms must be in level 2 to have $N_2 > N_1$
Inefficient, although it was the first working laser (ruby).

Four-level system



Level 3 is quickly populated, and level 2 is quickly depleted:
easier to achieve $N_3 > N_2$, more efficient!

A basic laser



Gain medium

The material that is excited and accumulates energy.

Energy source

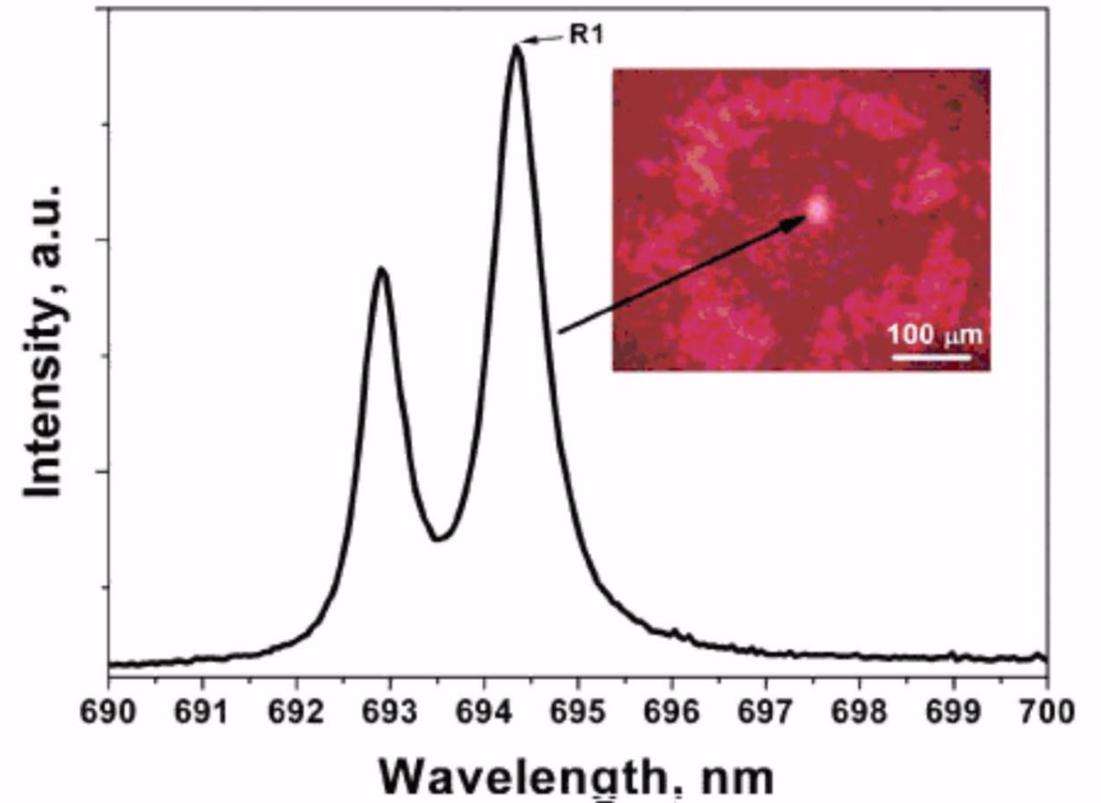
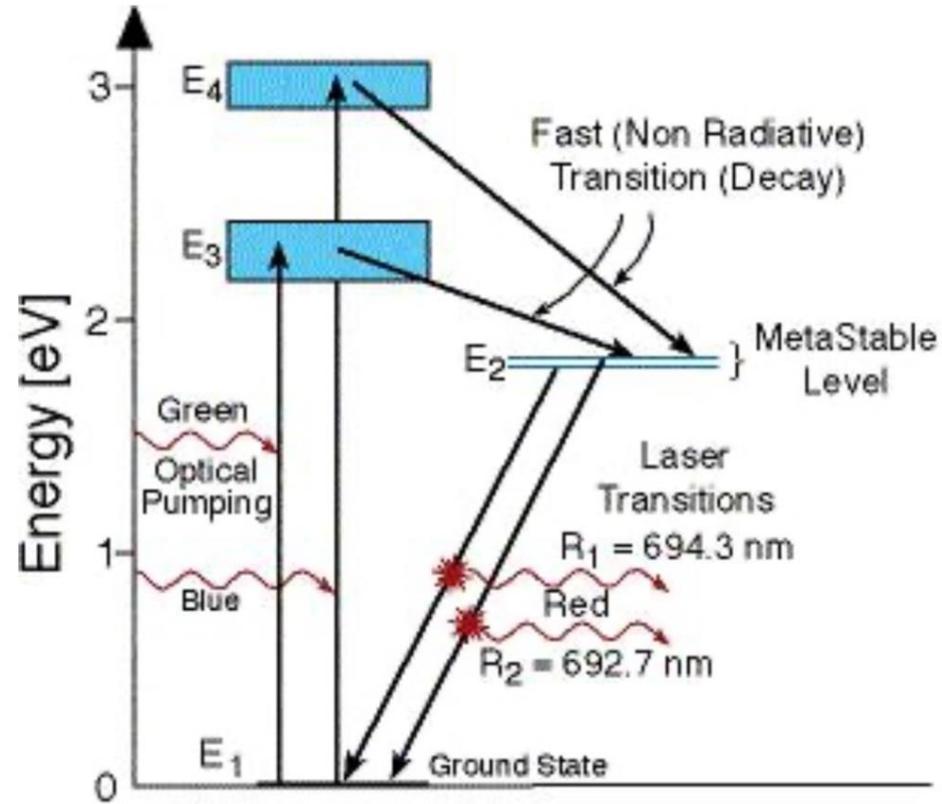
The pump used to create population inversion. Can be optical, electrical, etc.

Optical resonator (cavity)

The gain medium is between two parallel mirrors, one partially transmitting.

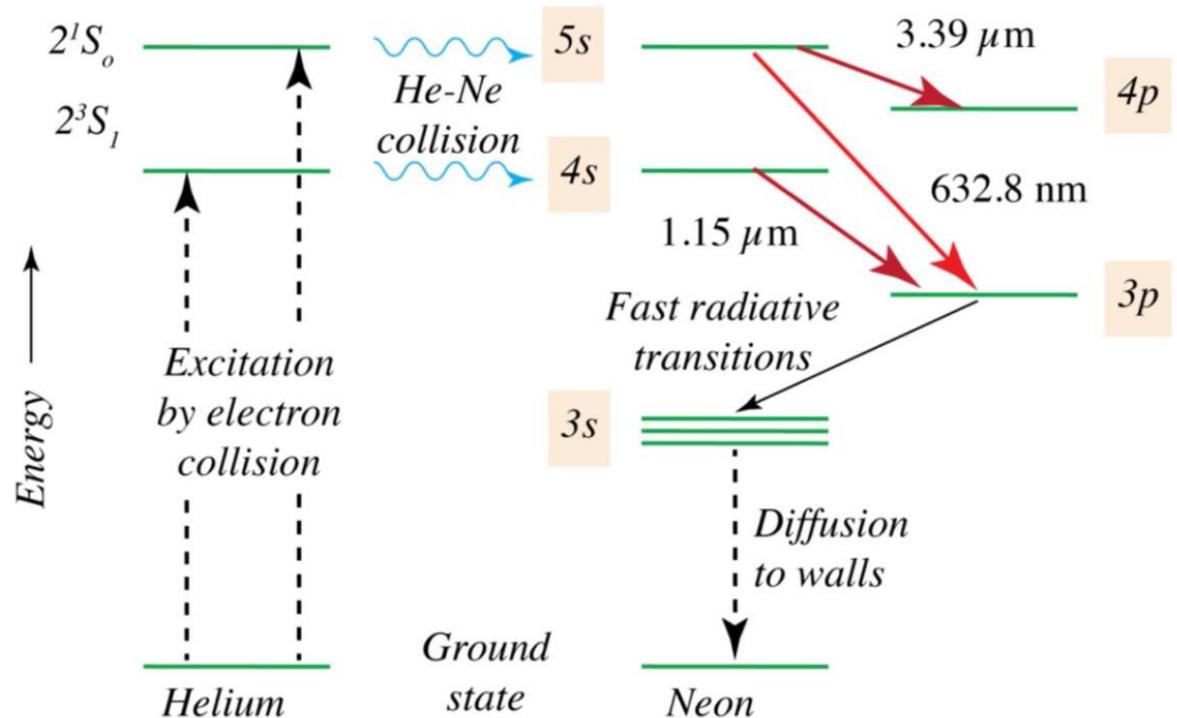
When the gain is higher than the loss inside the cavity lasing occurs.

Ruby laser

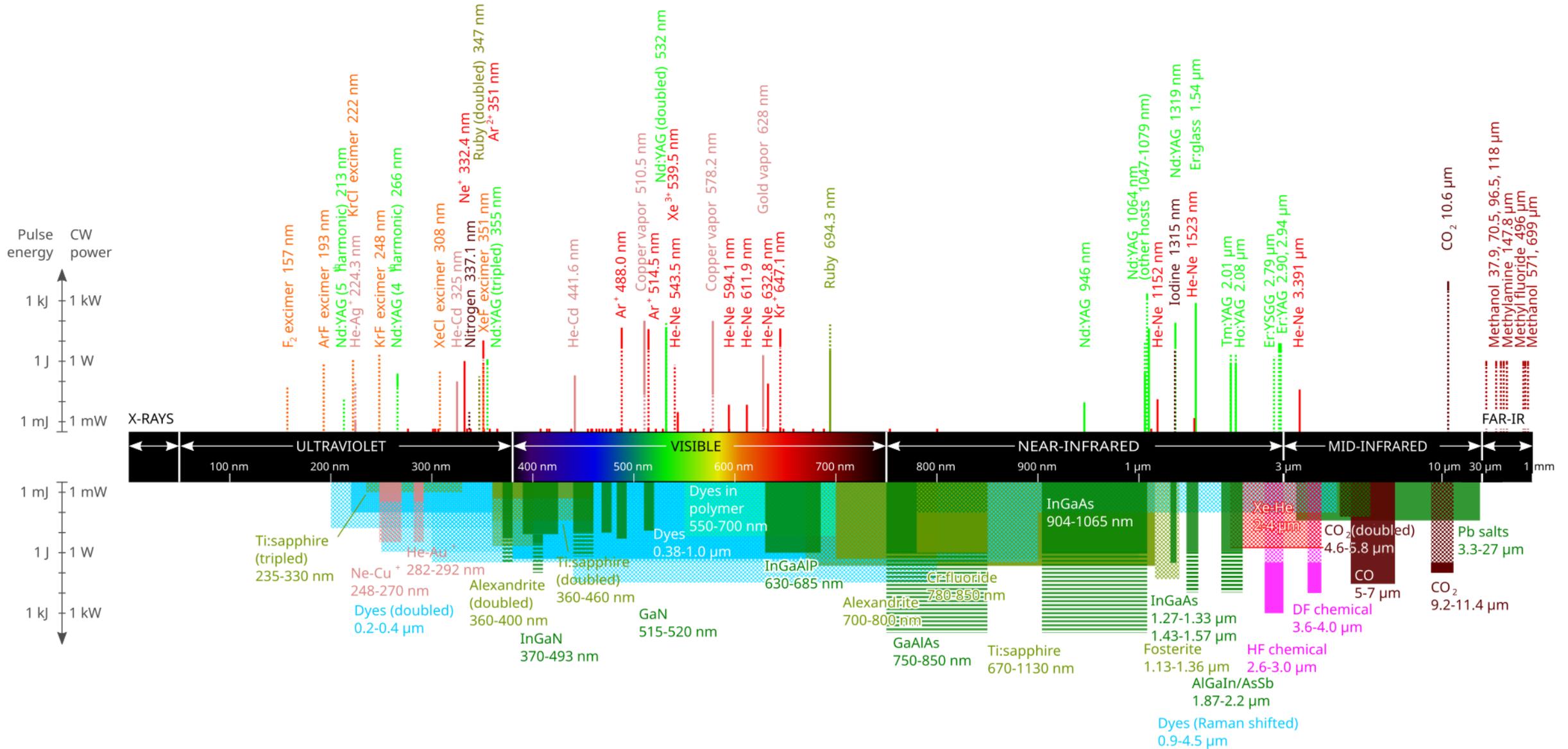


Helium-neon laser

- An **electric discharge** in the gas excites He atoms via electron collision. The excited states decay into the 2^1S_0 and 2^3S_1 levels – with a very long lifetime (up to 8000s).
- By chance, Ne has excited 5s e 4s levels within few meV from the metastable He states. Therefore, for collision He can deexcite by promoting Ne atoms into 5s and 4s states, with 4p and 3p states that remain empty.
- **Population inversion forms between the s and p states in Ne.**
- Amplification by stimulated emission is achieved between one s and one p state, if the cavity is properly tuned.
- The commonly used laser transition is the visible one at 632.8 nm.



Other laser types



Pulsed lasers

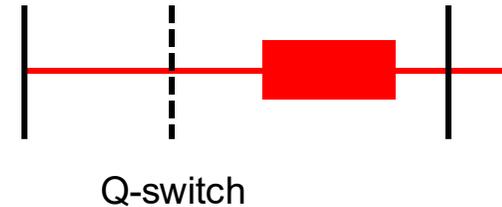
Instead of a continuous beam (CW), for time-resolved spectroscopies we need pulsed lasers

Q-switching

The energy is stored in the cavity by keeping the medium in the excited state, when saturated the Q-switch is opened and the energy is quickly released into a giant pulse.

High peak intensity, low repetition rate (10 Hz – few kHz), duration >1 ns.

Used for tattoo removal, laser cutting, material processing.



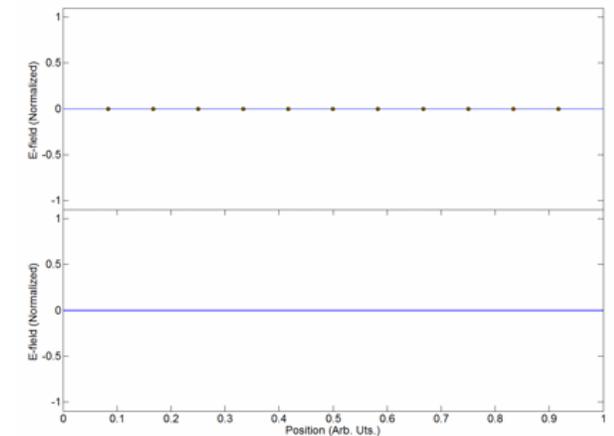
Mode locking

Light bouncing inside the cavity interacts with itself with constructive and destructive interference. If the cavity is tuned to synchronize the phases of different longitudinal modes, they interfere constructively at regular intervals.

Allowed modes are those for which $L = q \lambda/2$

Train of pulses at consistent intervals ($\Delta t = 2L/c$) and very short duration.

High peak intensity, high repetition rate (several MHz), duration down to few fs.



Pulsed lasers

Mode locking: How many modes are supported?

Let's consider a 30 cm cavity, and calculate the frequency spacing between consecutive modes:

$$L = q \frac{\lambda}{2} = q \frac{c}{2\nu},$$

$$\nu = q \frac{c}{2L},$$

$$\nu' = (q + 1) \frac{c}{2L},$$

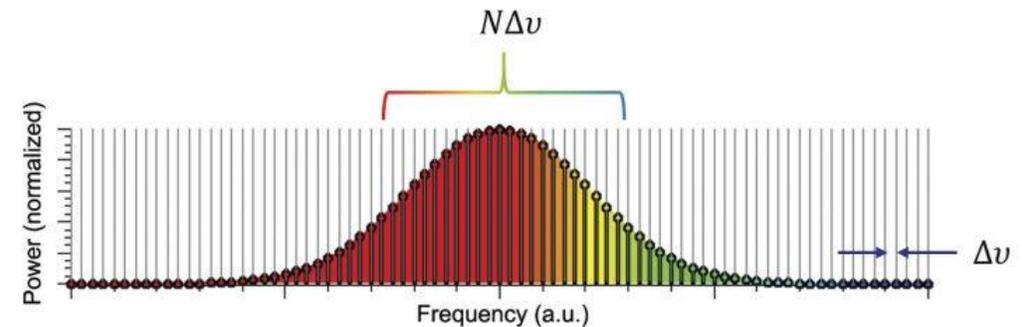
$$\Delta\nu = \frac{c}{2L} = \frac{3 \times 10^8 \text{ m/s}}{2 \times 0.3 \text{ m}} = 0.5 \text{ GHz}$$

The number of supported modes depend on the gain medium bandwidth:

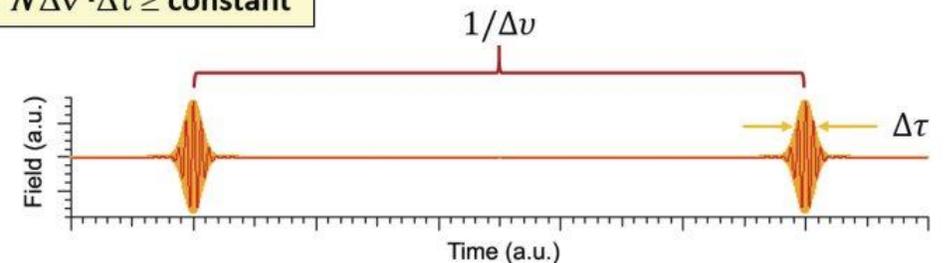
HeNe: 633 nm central wavelength with 0.002 nm width
⇒ 1.5 GHz ⇒ 3 modes supported

Ti:sapphire: 800 nm central wavelength with 300 nm width
⇒ 128 THz ⇒ 250,000 modes supported!

Ti:sapphire will produce shorter pulses!



$$N\Delta\nu \cdot \Delta\tau \geq \text{constant}$$



High Harmonic Generation

We can use nonlinear optics to generate higher harmonics of the fundamental wavelength.

Nonlinear crystals are those in which \mathbf{P} (polarization density) responds non-linearly to the application of an electric field, \mathbf{E} . Sizable effects with high intensity \mathbf{E} ($>10^8$ V/m): pulsed lasers!

$$\mathbf{P}(t) = \varepsilon_0 (\chi^{(1)}\mathbf{E}(t) + \chi^{(2)}\mathbf{E}^2(t) + \chi^{(3)}\mathbf{E}^3(t) + \dots) \quad \mathbf{P}^{\text{NL}} = \varepsilon_0\chi^{(2)}\mathbf{E}^2(t)$$

If we have an electric field with two components:

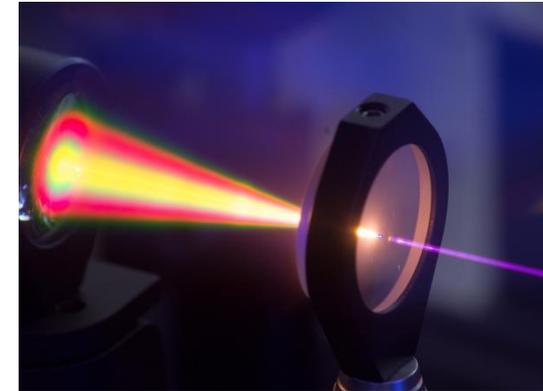
$$\mathbf{E}(t) = E_1 \cos(\omega_1 t) + E_2 \cos(\omega_2 t) \quad \mathbf{E}(t) = \frac{1}{2}E_1 e^{-i\omega_1 t} + \frac{1}{2}E_2 e^{-i\omega_2 t} + \text{c.c.}$$

We obtain:

$$\begin{aligned} \mathbf{P}^{\text{NL}} &= \varepsilon_0\chi^{(2)}\mathbf{E}^2(t) \\ &= \frac{\varepsilon_0}{4}\chi^{(2)} [E_1^2 e^{-i2\omega_1 t} + E_2^2 e^{-i2\omega_2 t} + 2E_1 E_2 e^{-i(\omega_1 + \omega_2)t} + 2E_1 E_2^* e^{-i(\omega_1 - \omega_2)t} + (|E_1|^2 + |E_2|^2) e^0 + \text{c.c.}] \end{aligned}$$

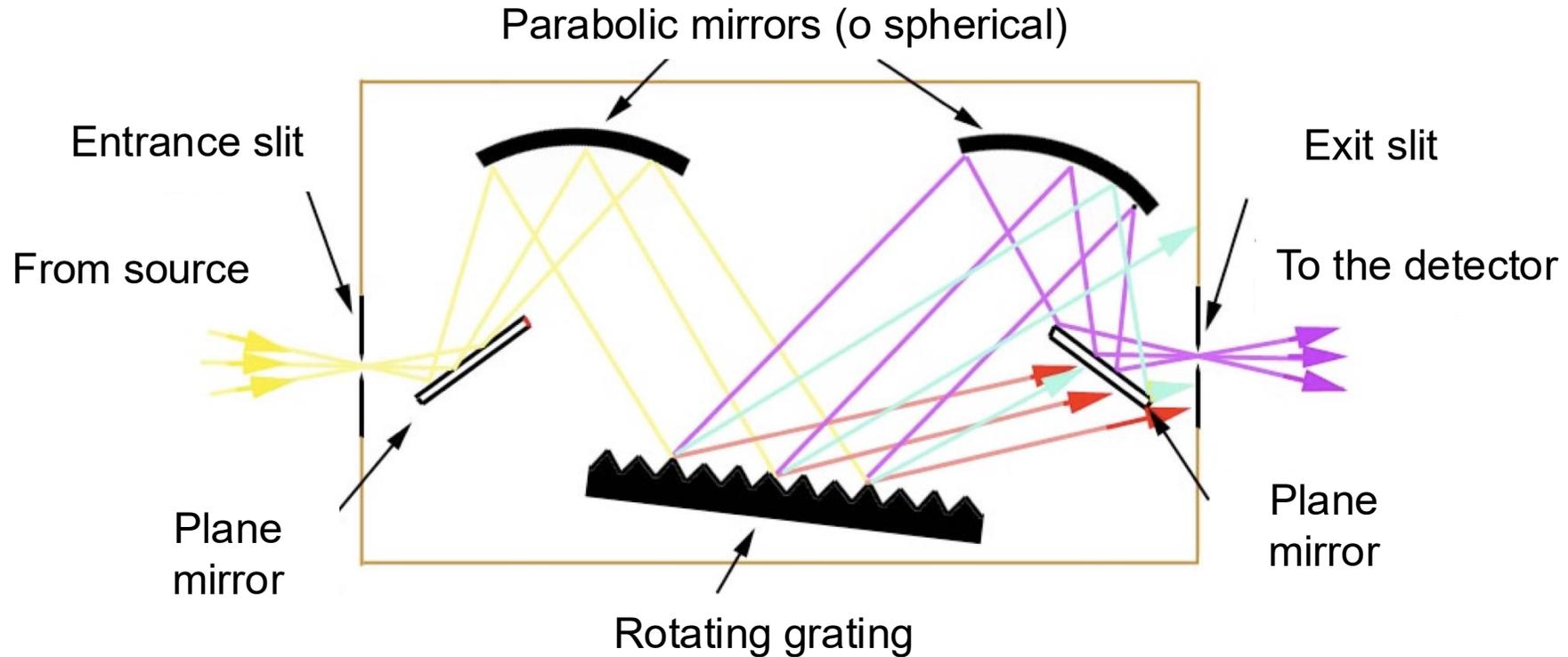
We obtain radiation with different frequencies: $2\omega_1$, $2\omega_2$, $\omega_1 + \omega_2$, $\omega_1 - \omega_2$

Arbitrary frequencies with combination of crystals: optical parametric amplification (OPA).



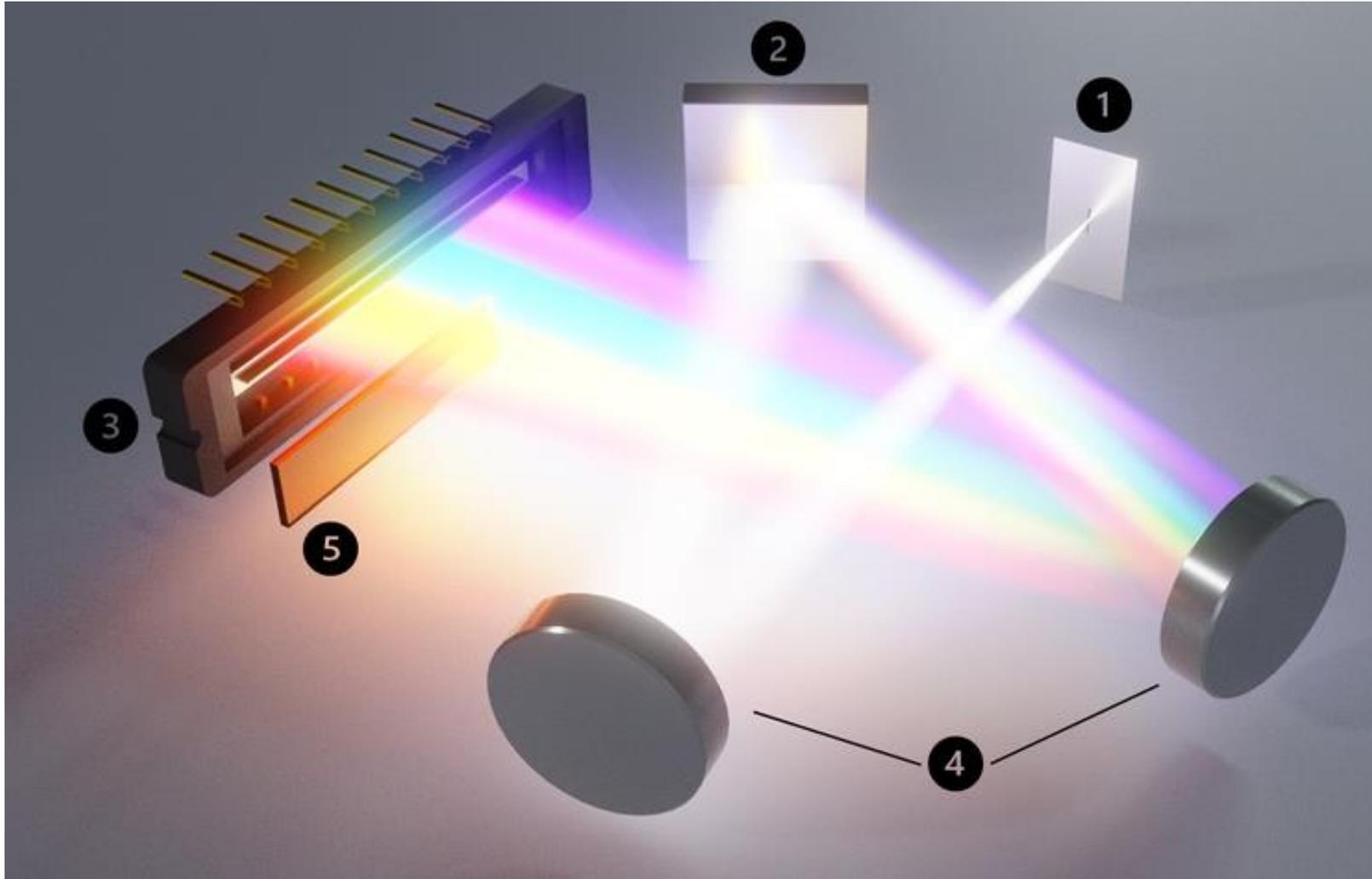
Monochromator

We must be able to select photons in a λ to $\lambda + \Delta\lambda$ interval in our emission spectra.



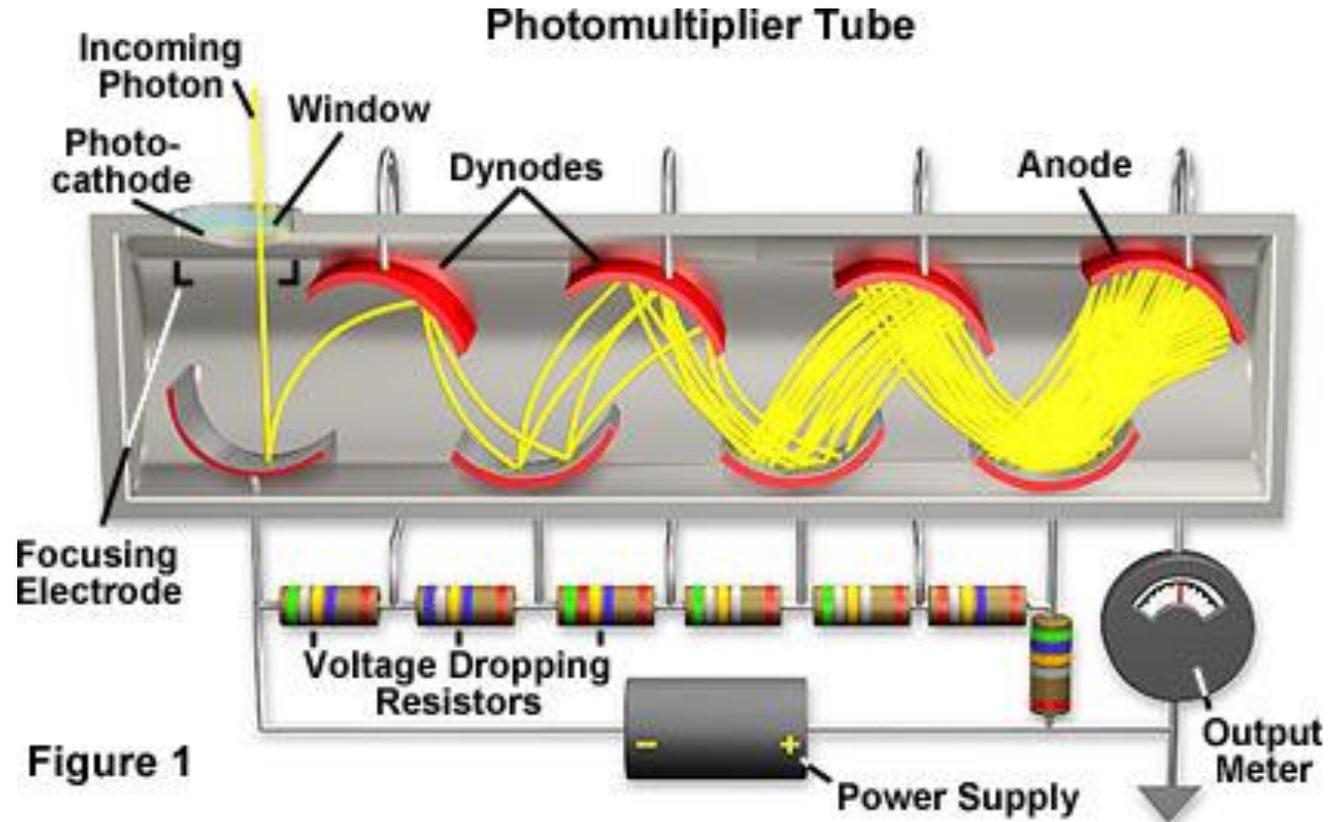
Light emitted from the sample is focused on the entrance slits to achieve a “point source”.

Monochromator



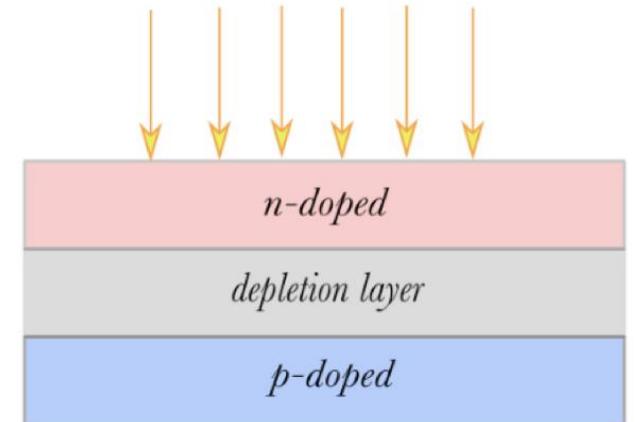
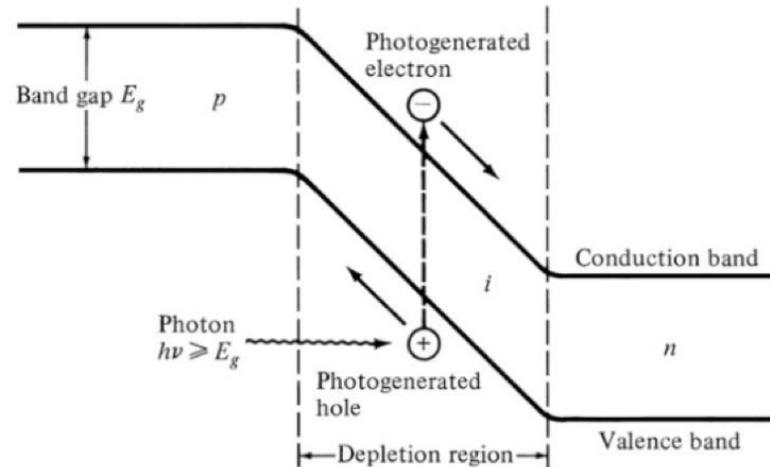
1. Entrance slit
2. Diffraction grating
3. Detector (CCD)
4. Focusing optics
5. Filter for higher orders

Detector: photomultiplier tube



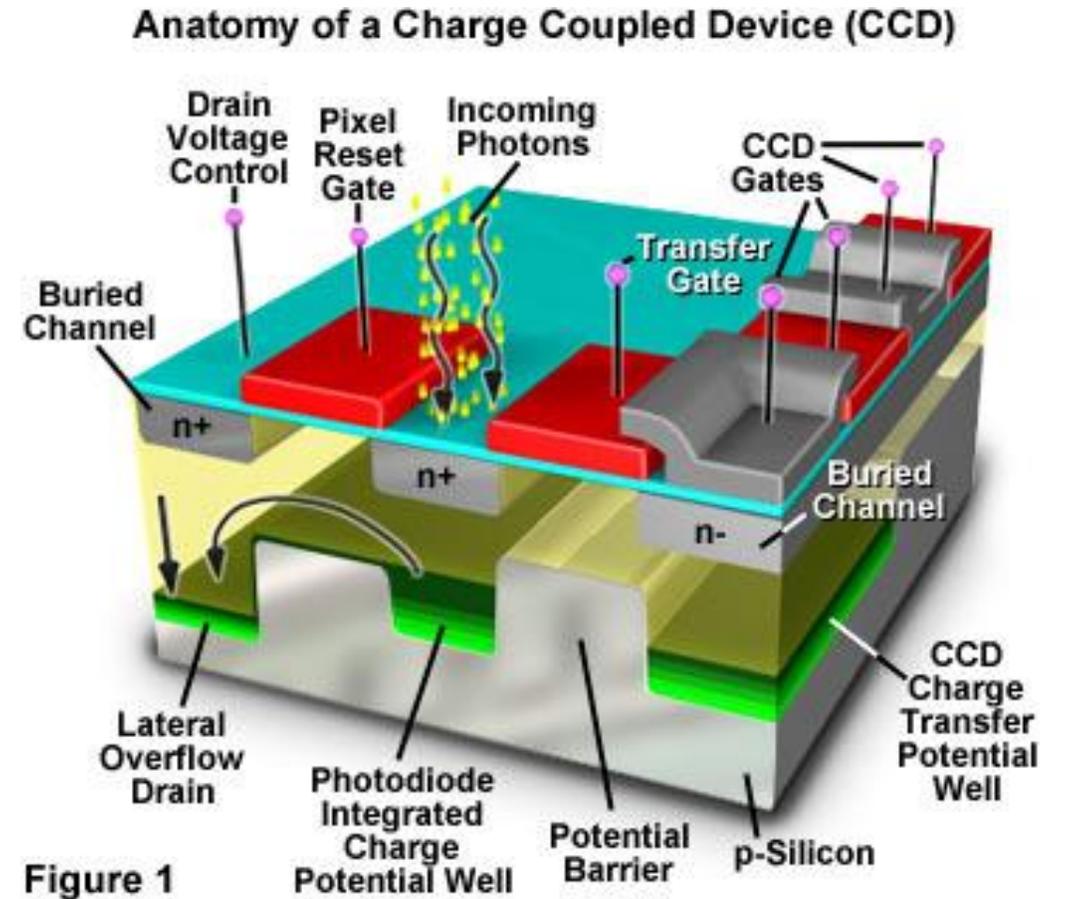
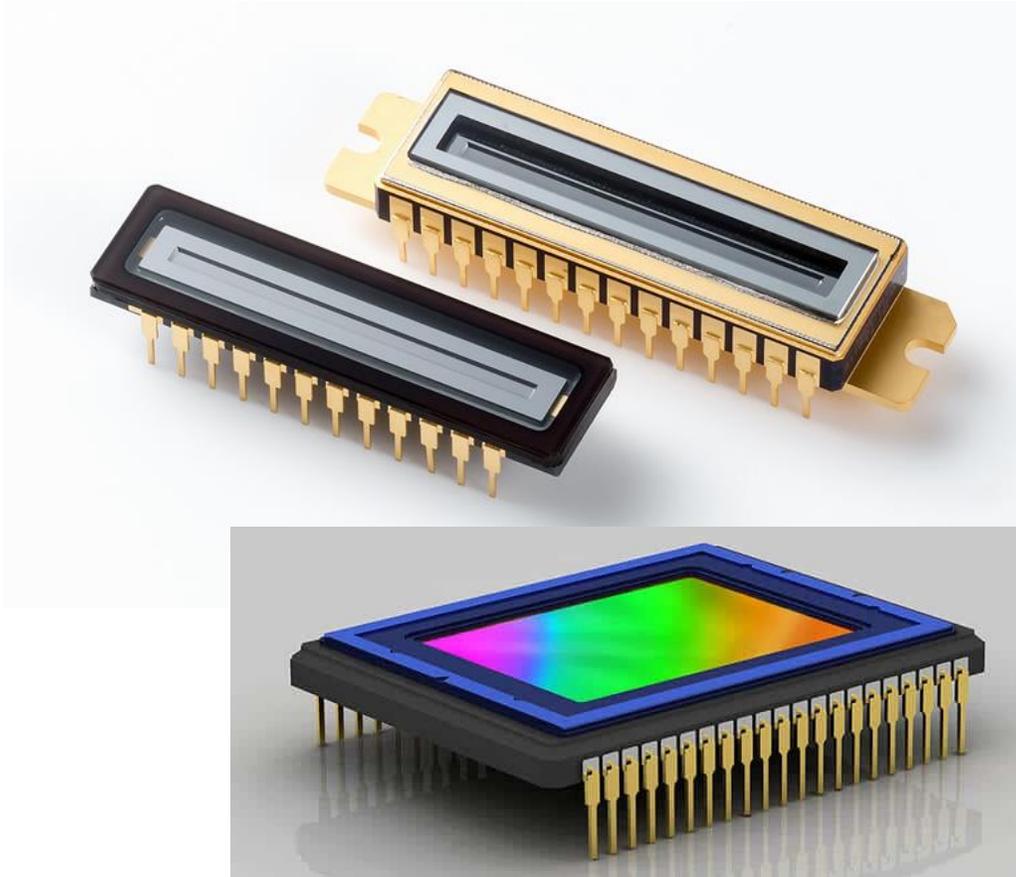
Photons impinging on the photosensitive material inside the phototube cause electron emission (photoelectric effect). The electrons are then accelerated to a chain of dynodes and multiplied exponentially, achieving a measurable electric current on the anode.

Detector: photodiode



When photons with energy above the band gap impinge on a p - n junction, an exciton is generated. Electron and hole can be separated due to the potential drop present across the junction, thus generating a measurable current.

Detector: CCD



Absorption of a photon in the sensitive area of a CCD cause a charge build-up. After a set integration period, accumulated charges are transferred to an electrode by a proper modulation of the voltages applied to the different transfer gates.

Characterization of the spectrometer

Activity #1

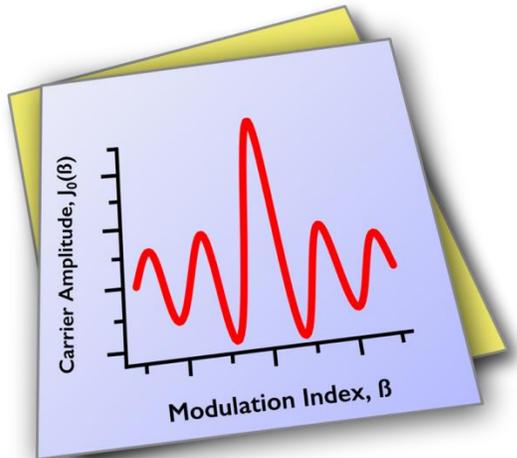
- Measurement of the spectral resolution as a function of the slit widths.
- Spectra of known radiation sources (blackbody, discharge lamps,...) to verify calibration and accuracy of the setup.
- Determination of the instrument response function (monochromator + detector).

Software

Acquired spectra will be text files, that can be handled with different software for data analysis.

Option 1

Igor Pro 9 – annual coursework license
www.wavemetrics.com/downloads/current
practical GUI, scripting capability, adopted
by numerous laboratories worldwide.



Option 2

Python

Multiple existing editors, open source,
many packages for data treatment and
analysis, very large community, ...

