Optical methods in chemistry
or
Photon tools for chemical sciences

Session 4:

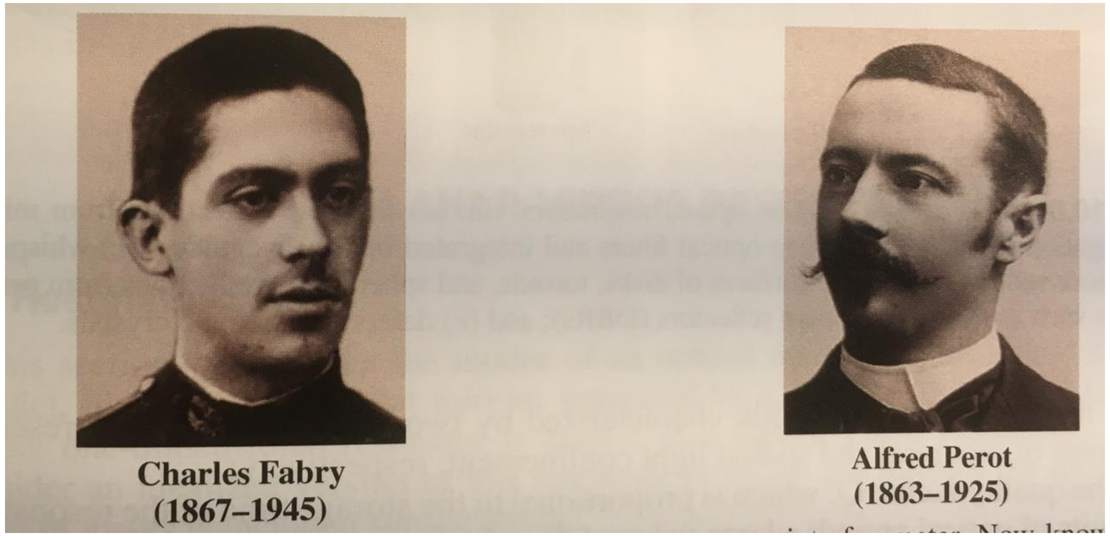
Course layout – contents overview and general structure

- Introduction and ray optics
- Wave optics
- Beams
- From cavities to lasers
- More lasers and optical tweezers
- From diffraction and Fourier optics
- Microscopy
- Spectroscopy
- Electromagnetic optics
- Absorption, dispersion, and non-linear optics
- Ultrafast lasers
- Introduction to x-rays
- X-ray diffraction and spectroscopy
- Summary

Todays learning goal:

Understanding cavities and the principles of lasers

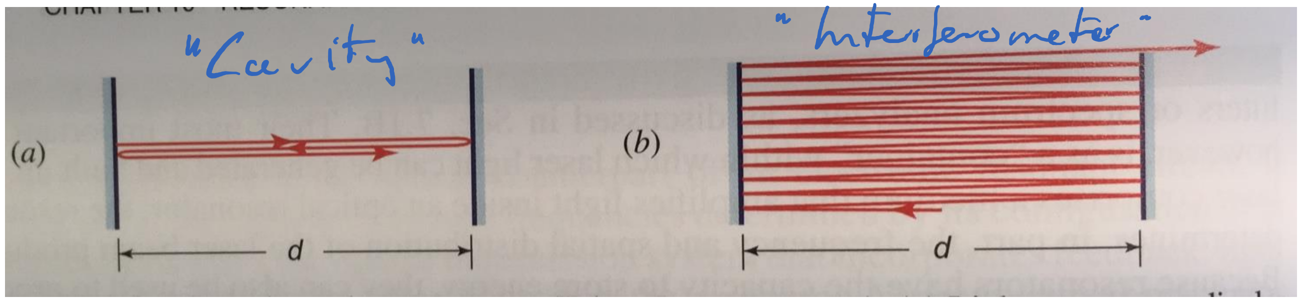
Optical resonantors (“cavities”)


Charles Fabry (1867–1945)
Alfred Perot (1863–1925)

Fabry – Perot Interferometer / Resonator

Fabry-Perot Resonator

Idea: Trap light between highly reflective mirrors



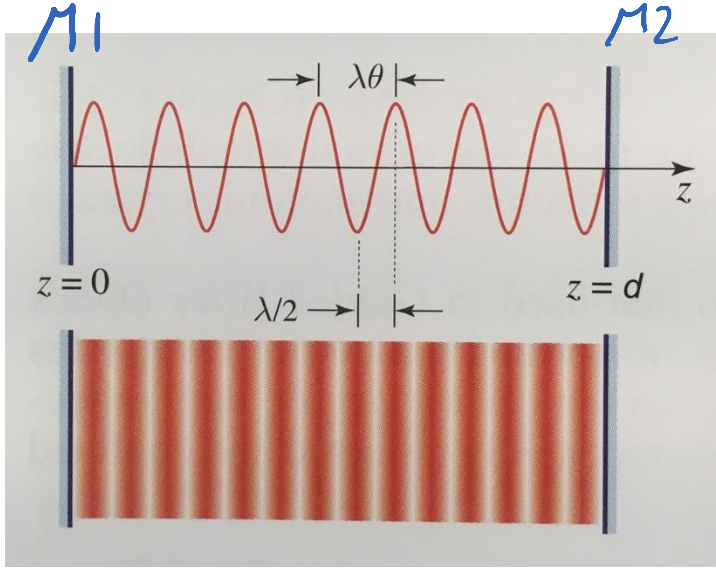
Idea

→ Send light back/forth

→ "trap" light in that manner

→ interference condition → standing wave

Standing waves represent resonator modes



Standing wave if "fits" → constructive interference condition

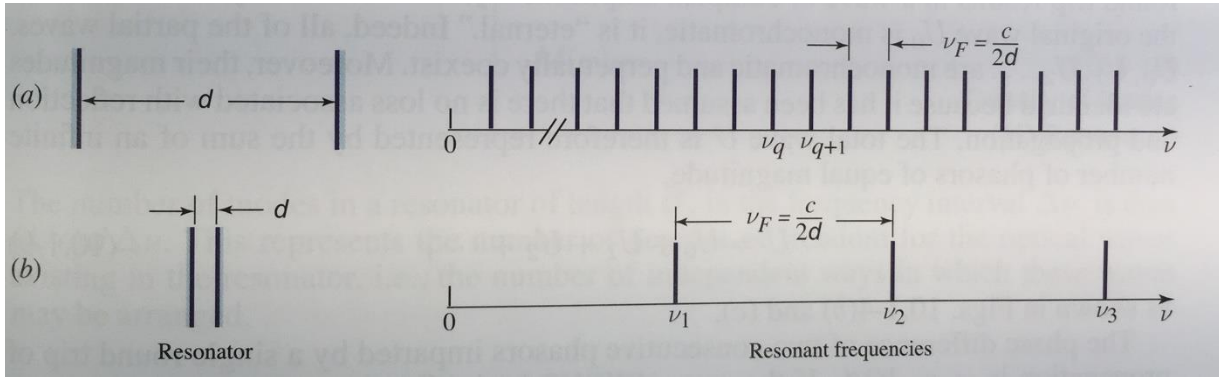
$$\hookrightarrow n\lambda = 2d \quad / \text{ or } \; n \cdot \frac{\lambda}{2} = d$$

in frequency

$$\nu_n = n \cdot \frac{c}{2d} \quad \text{with } \nu = \frac{c}{\lambda}$$

Properties of the Fabry Perot Resonator

→ in frequency space



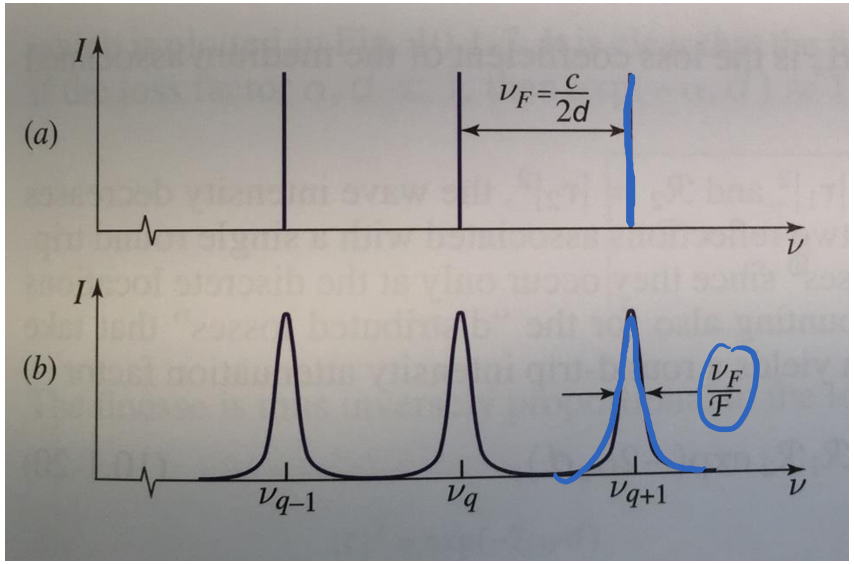
narrower resonator → broader spacing!

Frequency spacing $\nu_F = \frac{c}{2d}$ → free spectral range

↳ In wavelength: roundtrip distance at resonance must be an integer of the wavelength $2d = n\lambda_n$

$n = 1, 2, 3, \ldots$

Ideal vs real resonator – real is with losses



For a cavity with losses (→ a real cavity) the ideal δ-like behavior is altered

↳ add spectral width

$$\delta_\nu = \frac{\nu_F}{F}$$

F – "finesse" of the cavity

$F \sim \frac{\pi}{\tau}$ and τ – Transmission

Losses increasing → Finesse decreasing

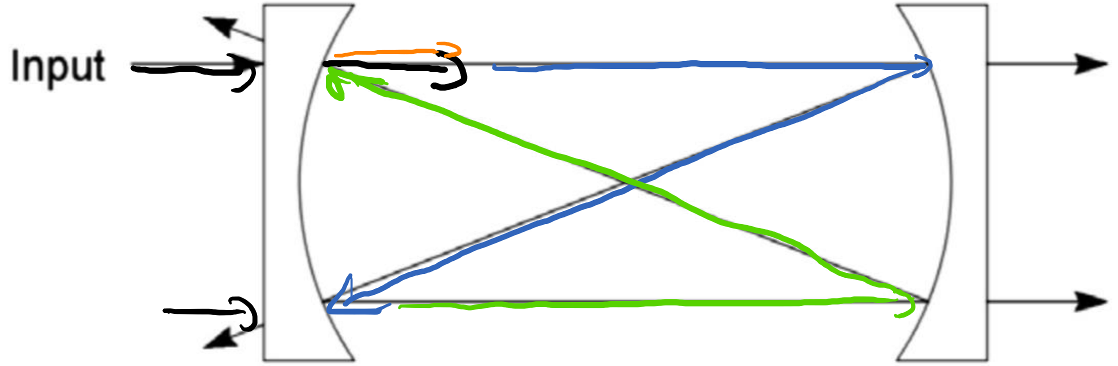
→ $\delta\nu$ increasing

Quality factor $Q \approx \frac{\text{stored energy}}{\text{energy loss/cycle}}$

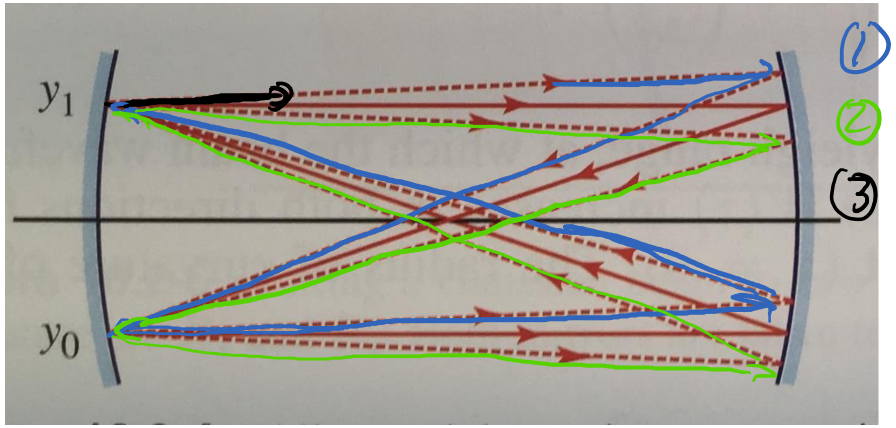
$Q \approx \frac{\nu_0}{\nu_F} F$ $\quad \nu_0$ – optimal frequency

Spherical Resonator → ray optics

Note: spherical resonator more stable than planar resonator



} intuitive with ray optics

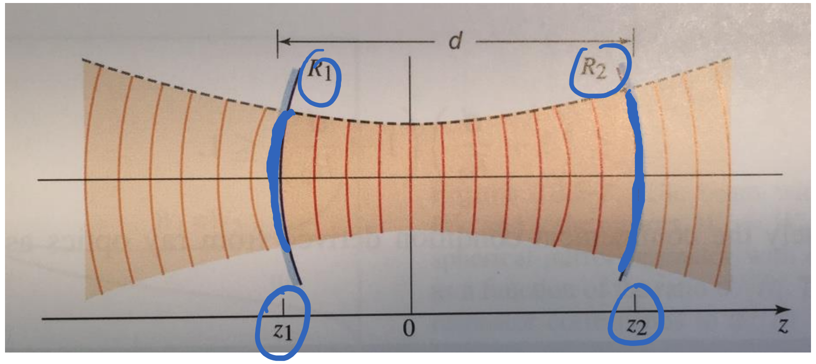


→ after two round trip same paths

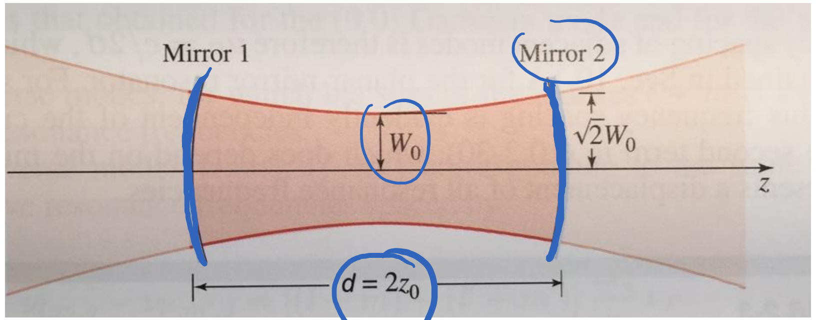
→ paraxial beams

Gaussian Beam Resonator

→ spherical resonator matches Gaussian beam

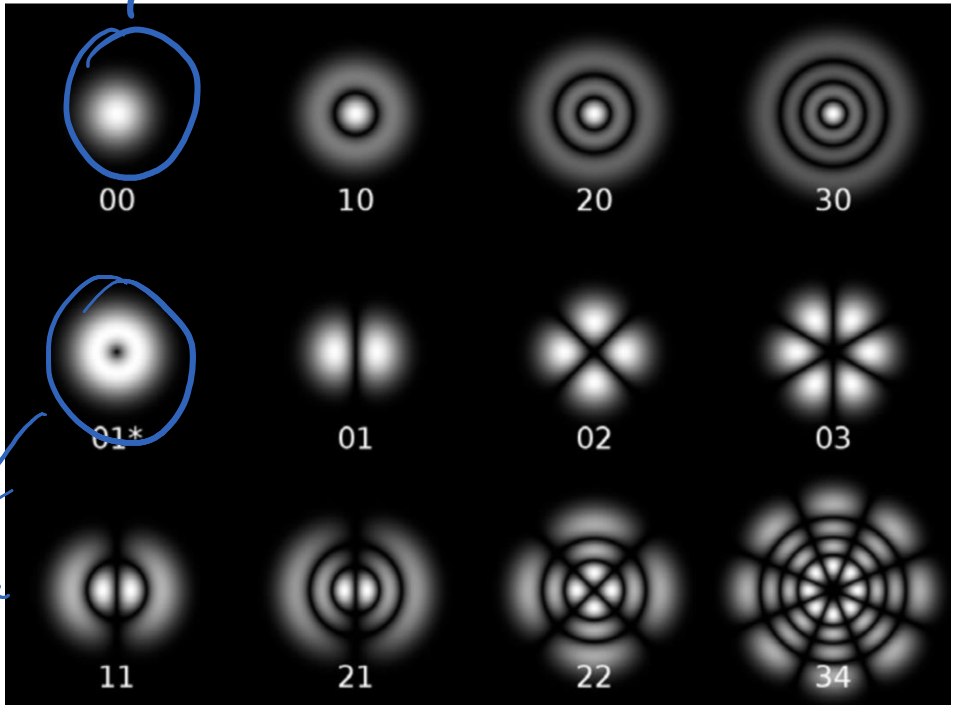


match of curvature & wavefront



most common

Laguerre-Gaussian modes

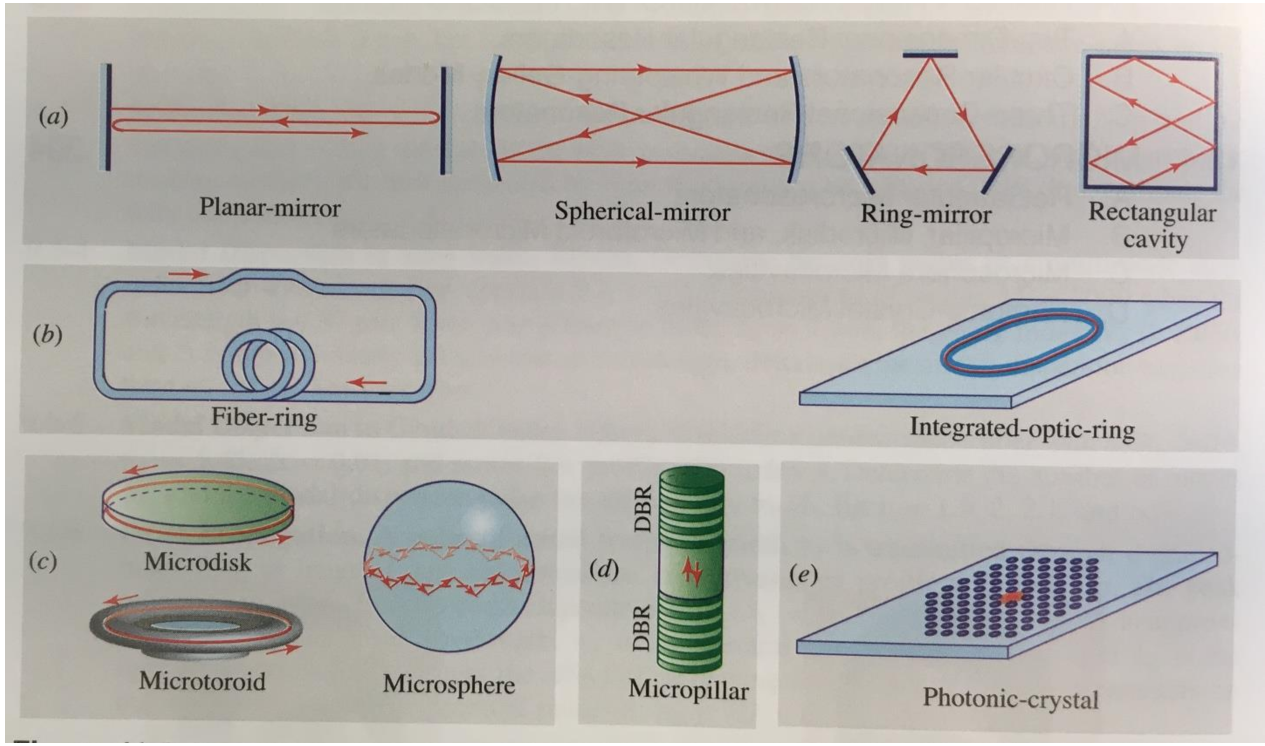


Donut mode

↳ very stable cavity

The Gaussian beam is a mode of the spherical resonator!

Note: There are many other possible cavity configurations!



Application Note: Cavity Ring Down Spectroscopy

- Absorption spectroscopy guided by Beer-Lambert-Law

Extinction $E_\lambda = \log \frac{I_0}{I} = \varepsilon_\lambda \, c_i \, l$ (extinction factor ε_λ, concentration c_i, length l)

- What do to for samples with weak absorption / weak transitions?

Max l

$$I = I_0 \exp[-\alpha \, l]$$ (α small, l max)

in time: $l = c \, t_e$

$$= I_0 \exp[-\alpha \, c \, t_e]$$

- Solution: Use a cavity!

→ measure decay time instead → "ring down"

→ light in cavity → Σn of round trips

Homework Reading: Cavity Ring Down Spectroscopy

- Idea: Instead of measuring absorption measure decay time

FARADAY
RESEARCH ARTICLE

Cavity ring-down spectroscopy

Martyn D. Wheeler, Stuart M. Newman, Andrew J. Orr-Ewing† and Michael N. R. Ashfold
School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS

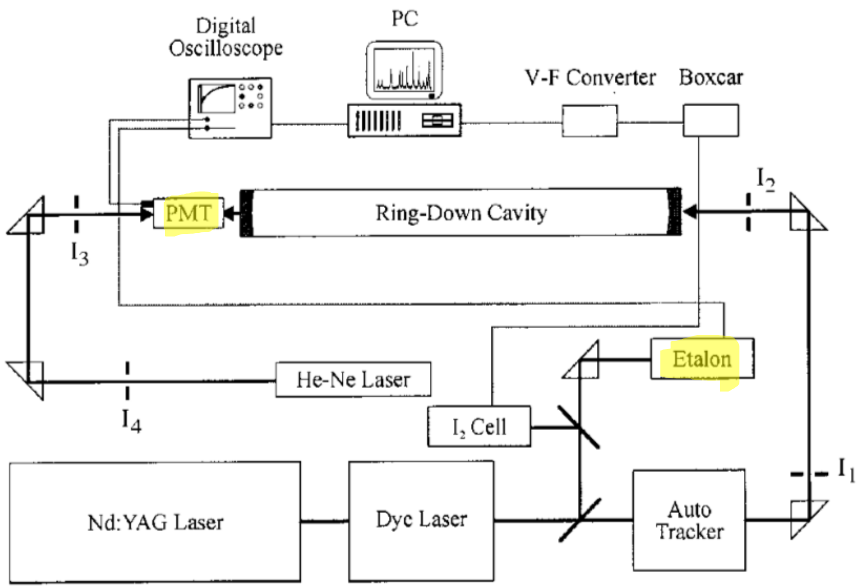


Fig. 2 Schematic diagram of the CRD apparatus at Bristol. Abbreviations in the figure are: photomultiplier tube (PMT), voltage-to-frequency converter (V–F) and irises (I) used to assist cavity alignment. The iodine cell and etalon provide accurate calibration of the laser wavelength.

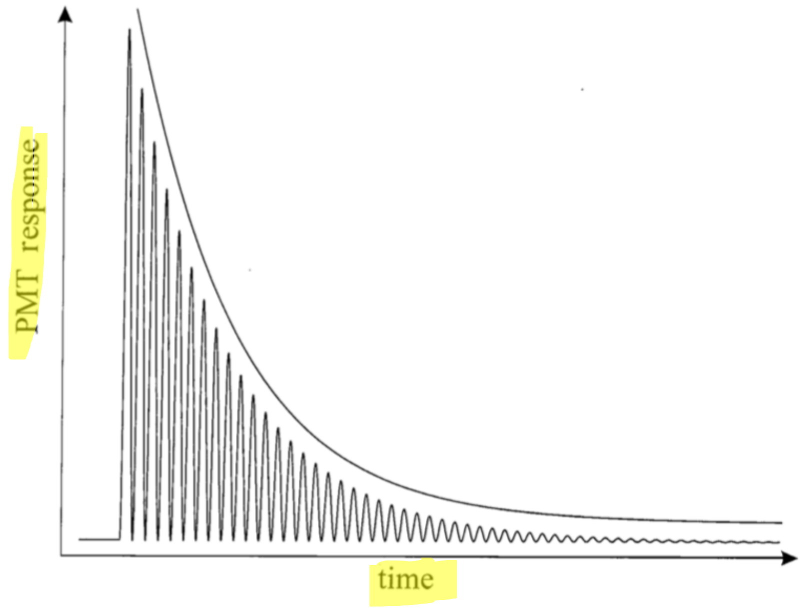


Fig. 3 Schematic diagram of the expected response of the photomultiplier tube to a train of laser pulses leaking through one cavity end mirror after successive cavity round trips. Also shown is the exponential envelope arising from smoothing of the pulse train by the time response of the experimental detection apparatus.

Example spectra

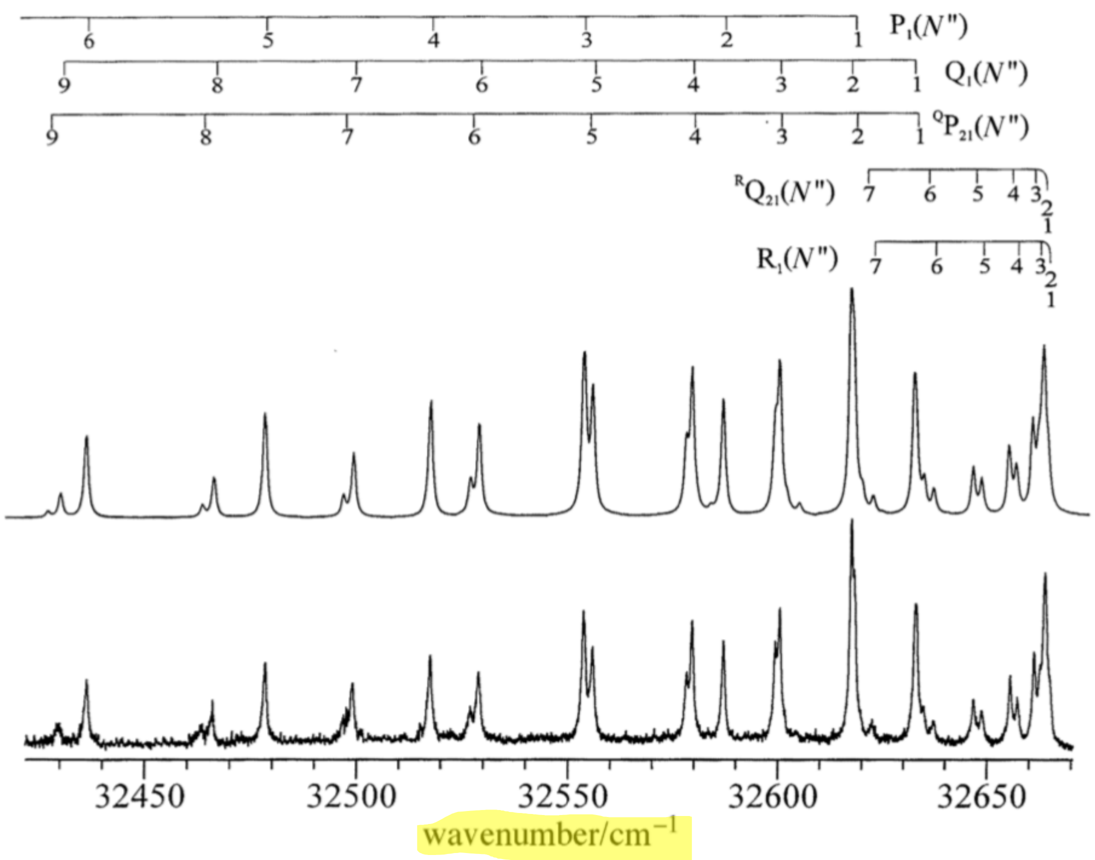
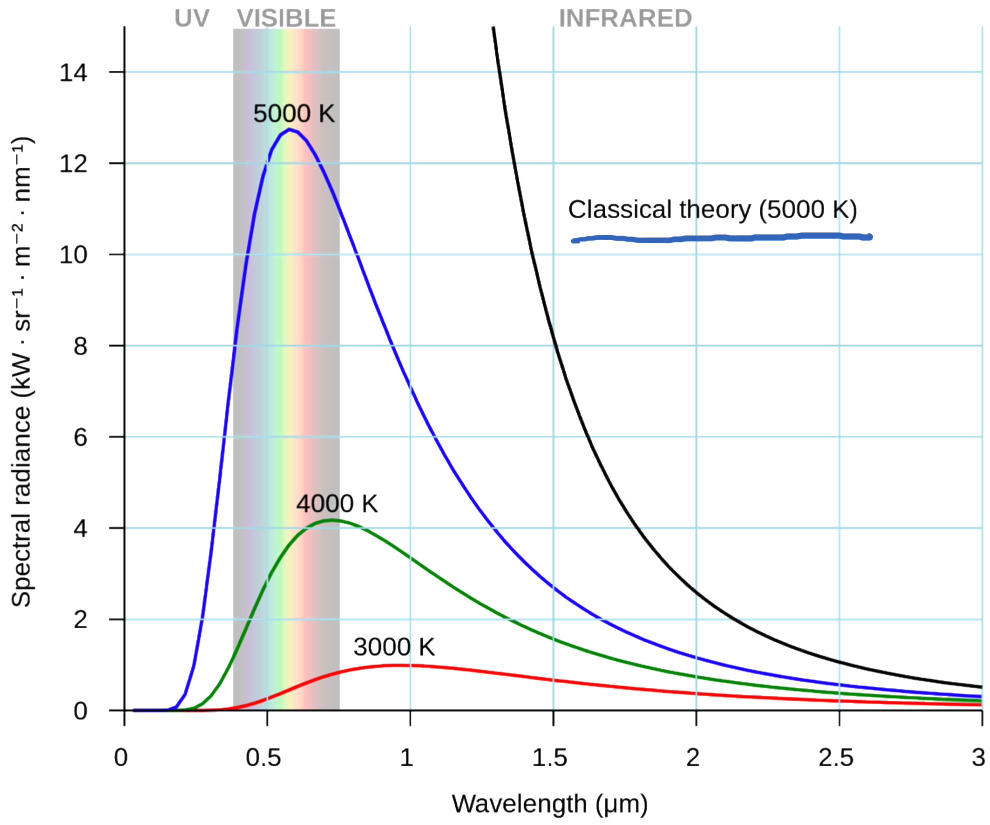


Fig. 8 CRD spectrum (bottom) and simulation (top) of the A $^2\Sigma^+$–X $^2\Pi$ (1, 0) band of SH. The combs above the spectra indicate rotational line assignments. The simulation includes a Lorentzian component to the rotational linewidths of 1 cm^{-1} because of lifetime broadening.

Think about resolution!

And now, towards lasers

Black body radiation: Energy is quantized



- Stefan Boltzmann Law

Radiance $L \sim T^4$

- Wiens displacement law

max moves with Wiens constant

$\lambda_{max} \rightarrow b/T$

- Plancks law (Nobel prize 1918)

$$B \simeq \frac{2h\nu^3}{c^2} \frac{1}{\exp\left[\frac{h\nu}{kT}\right] - 1}$$

spectral radiance

⇒ h → energy is quantized!

Photoelectric effect

(side note) → quantized electromagnetic field

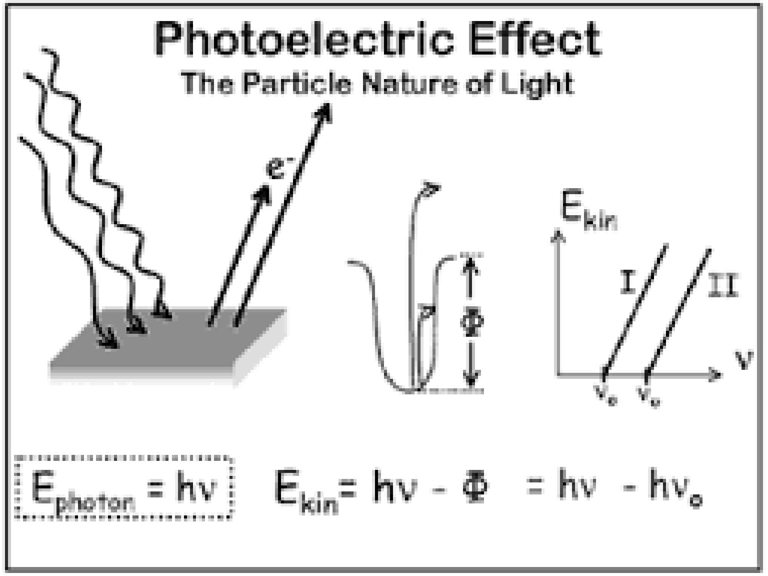
- Einstein Nobel prize 1921
- Light has particle nature

Electrons from metal surface

$E_{kin} = h\nu - \phi$

↑ "photon energy" ← ↑ discrete energy

↑ metal / element specific effect



UC Berkeley's Digital Chem1A

⇒ Light behaves as particles with discrete energy called "Photons"

Bohr model and Rydberg atoms

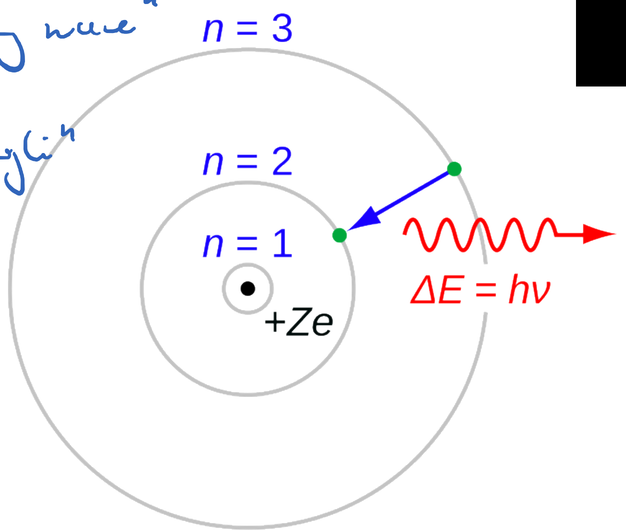
- Bohr model: semiclassical approach
- Nobel prize 1922
- Dense nucleus with surrounding electrons
- Discrete energy states
- A lot of shortcomings but works

- Rydberg atom:
- excited states in Bohr model
- Principle quantum numbers n
- Transition under emission / absorption of photon
- Balmer series of hydrogen

$n\lambda = 2\pi r$ "standing wave"

$n\lambda = \frac{h}{mv}$ "de Broglie"

$\frac{nh}{mv} = 2\pi r$



Balmer series

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

R_H – Rydberg constant

Fermis Golden Rule (from perturbation theory)

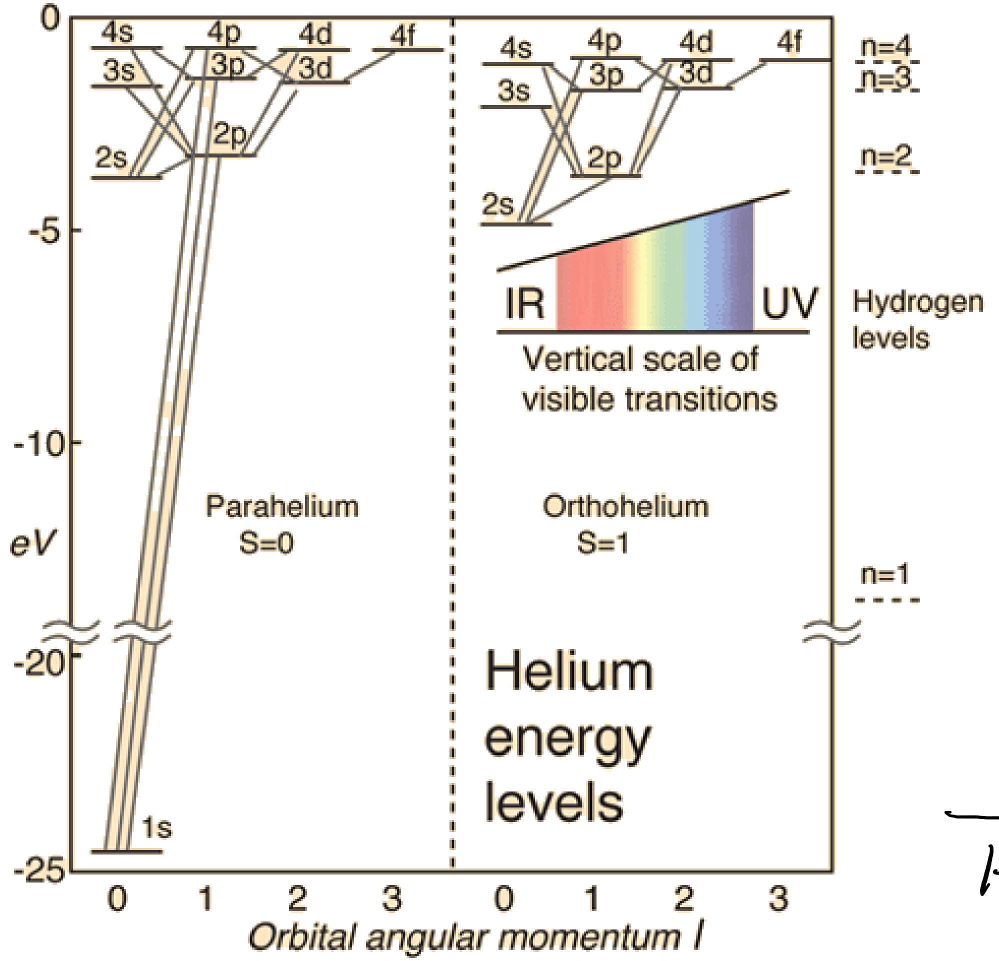
- Full quantum mechanical description of the atom (not here)
- Fermi Golden Rule describes transition probability between levels
- Including selection rules

Transition rates

$$\Gamma_{if} = \frac{2\pi}{\hbar} \underbrace{|\langle f | H' | i \rangle|^2}_{\text{transition matrix element}} \underbrace{\rho(E_f)}_{\text{density of final states}}$$

hand waving argument: Transition propability depends on orbital overlap and energy + selection rules

Absorption, energy level diagram



s-p dipole allowed $\Delta l = 1$

s-s, s-d } dipole forbidden

selection rule $\Delta l = 1$

Note photon has $l = 1$

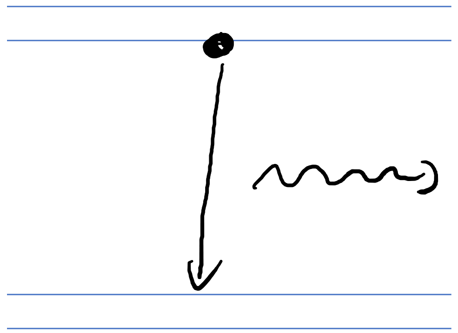
How to populate 2s level?

→ decay from other levels

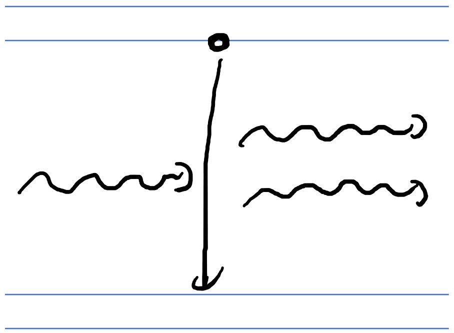
→ electron impact ionization

Absorption, emission, stimulated emission - overview

Spontaneous emission

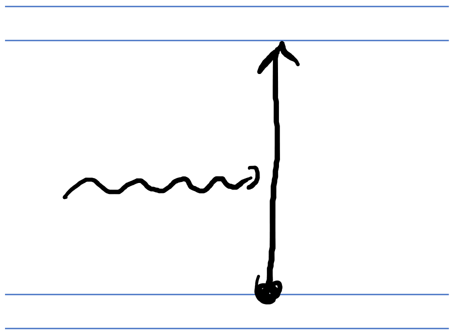


Stimulated Emission



stimulated photon is exact copy of incoming photon with respect to energy, direction, polarization, etc

(Stimulated) absorption



Remember

Population of any level follows Boltzmann distribution

$N_1 = N_0 \cdot \exp[-E_1/k_B T]$

E_1 → energy of level

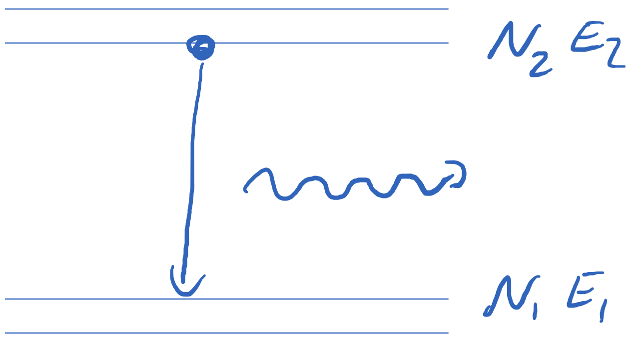
↓

the higher the energy the lower the population

Which processes are equivalent? Stimulated emission & absorption!

Spontaneous emission

Spontaneous emission



Energy difference is emitted as photon

$E_2 - E_1 = h\nu$ energy of emitted photon

Describe with Einstein coefficients

"transition is proportional to population"

$$\frac{dN_2}{dt} = -A N_2$$

A - Einstein coefficient

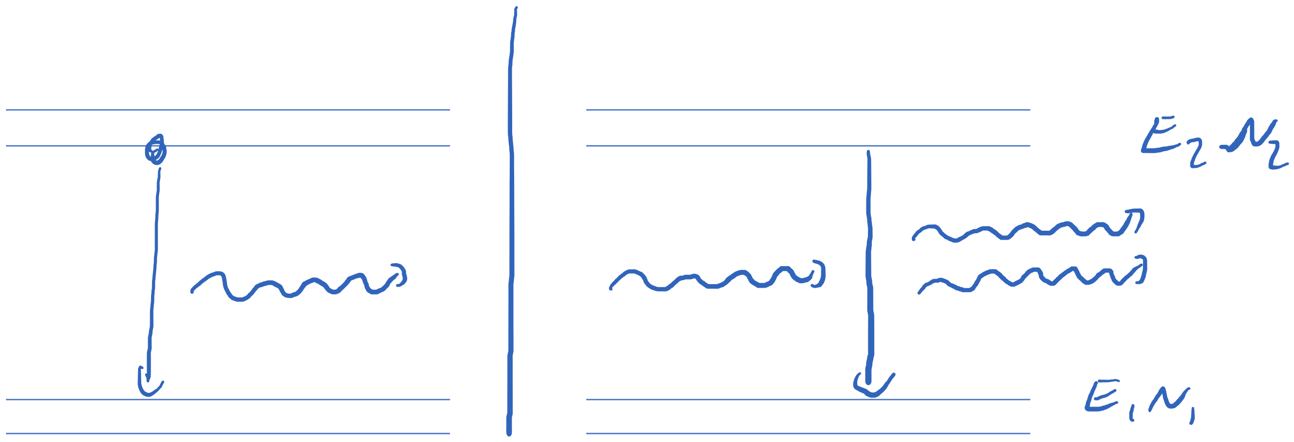
Stimulated emission

One photon with hv simulates another transition

The second photon is identical in direction, frequency, phase and polarization

Spontaneous emission

Stimulated Emission



$$\frac{dN_2}{dt} = w_{21} N_2$$

w_{21} – stimulated transmission propability

w_{21} – stimulated transition propability

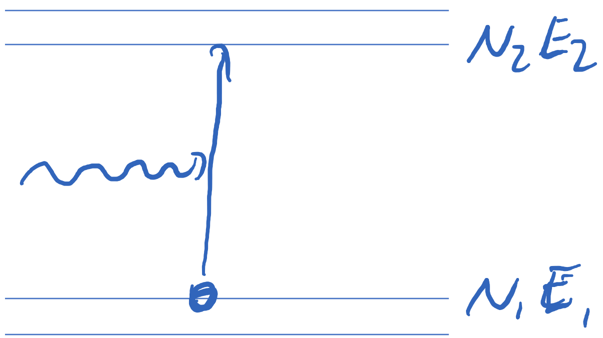
w_{21} – depends on intensity of incoming light → flux

$$w_{21} = \sigma_{12} F = B_{21} \rho_\omega$$

σ_{12} ↑ transition propability; F ↑ flux; B_{21} ↑ Einstein coefficient; ρ_ω ↑ energy density

Absorption

(Stimulated)
Absorption



- The photon stimulates from lower to higher state

$$\frac{dN_1}{dt} = -w_{12} N_1$$

similar $w_{12} = \sigma_{12} F = B_{12} S_\omega$

Einstein showed $\sigma_{12} = \sigma_{21}$

$\Rightarrow$ electron within atom in ground state is equally propable of going up as one in excited state of going down

Atoms (systems) in thermal balance

In thermal balance the lower population is always higher than that of the upper population

↳ Boltzmann distribution

$$N_i = N_0 \exp\left[-E_i / k_B T\right]$$

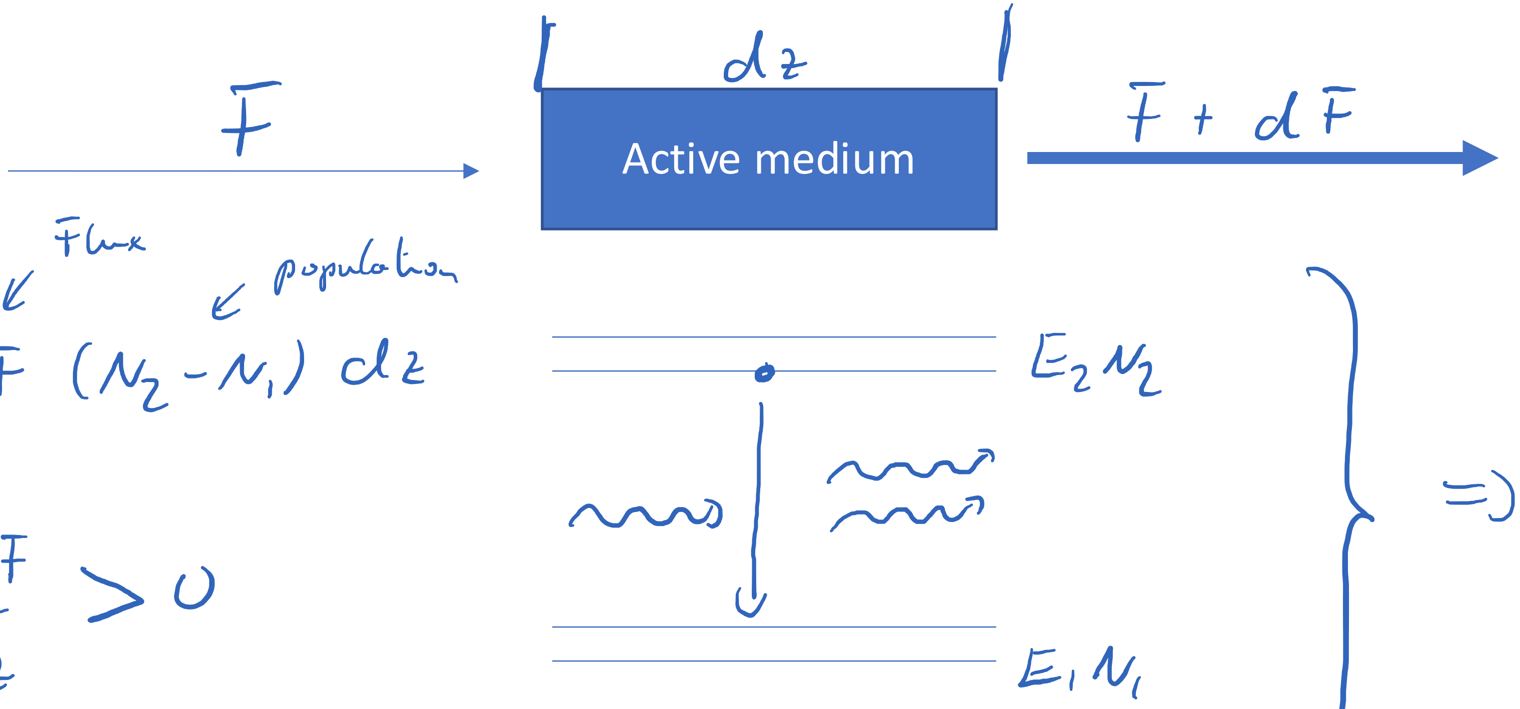
↳ higher energy levels are less populated

$$\frac{N_2}{N_1} = \exp\left[-\frac{(E_2 - E_1)}{k_B T}\right] = \exp\left[-\Delta E / kT\right]$$

$\Rightarrow N_2 < N_1 \Rightarrow$ absorption dominates in thermal equilibrium (in 2 level system)

Fundamental concept of laser

F – flux



trans. prob. ↓ Flux ↙ population ↙

$$dF = \sigma_{21} \, F \, (N_2 - N_1) \, dz$$

gain $\frac{dF}{dz} > 0$

$\Rightarrow N_2 > N_1$

$\Rightarrow$ need population inversion!

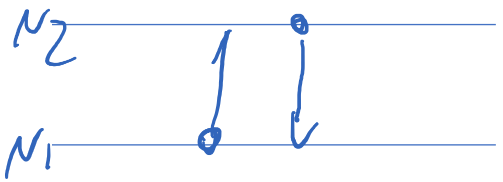
But... how?

Note: The gain must always be higher than the losses!

2, 3, 4 level systems

high flux

2 level system

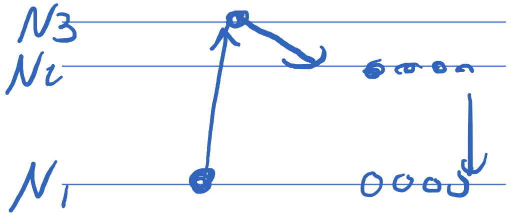


population inversion not possible even with highest flux $N_2 = N_1$

⇔ stimulated emission and absorption are in balance

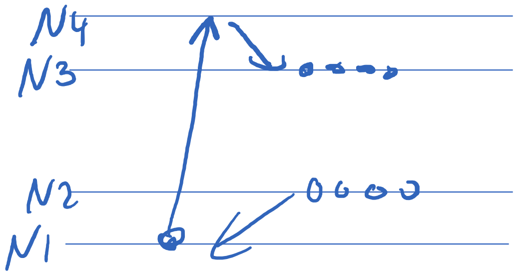
high flux ⇗ medium becomes transparent!

3 level system



metastable } lasing line → N_2 populated over time → inversion

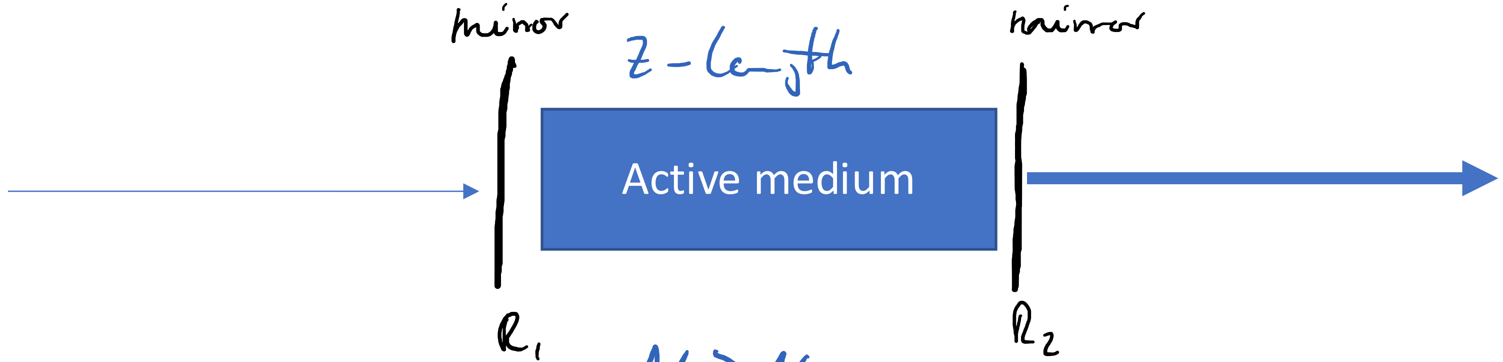
4 level system



long lifetime } lasing line

always empty

Fundamental concept of laser oscillator:

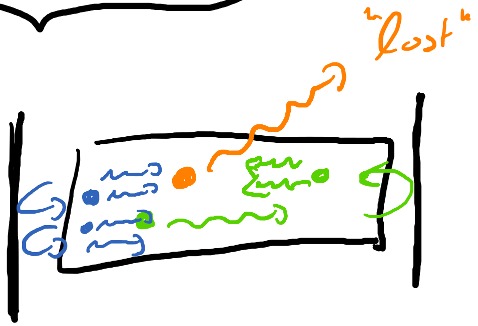


$N_2 > N_1$ "inversion"

$\frac{dF}{dz} > 0$ "gain"

$dF = \sigma_{21} F (N_2 - N_1) dz$

$\rightsquigarrow$ gain $\sim \exp[\sigma_{21}(N_2 - N_1) z]$



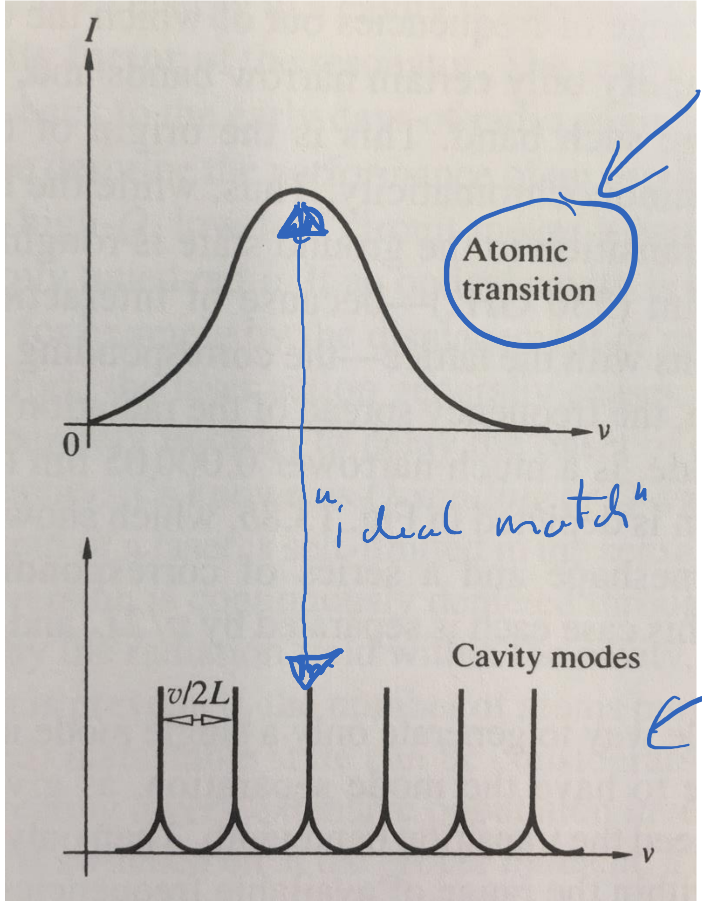
exponential growth of output on axis!

Note: The gain must always be higher than the losses! → add mirror reflectivities

$R_1 R_2 \exp[\sigma_{21} (N_2 - N_1) \ell] > 1$ Lasing condition

Lasers and laser cavities

Atomic lines vs cavity modes

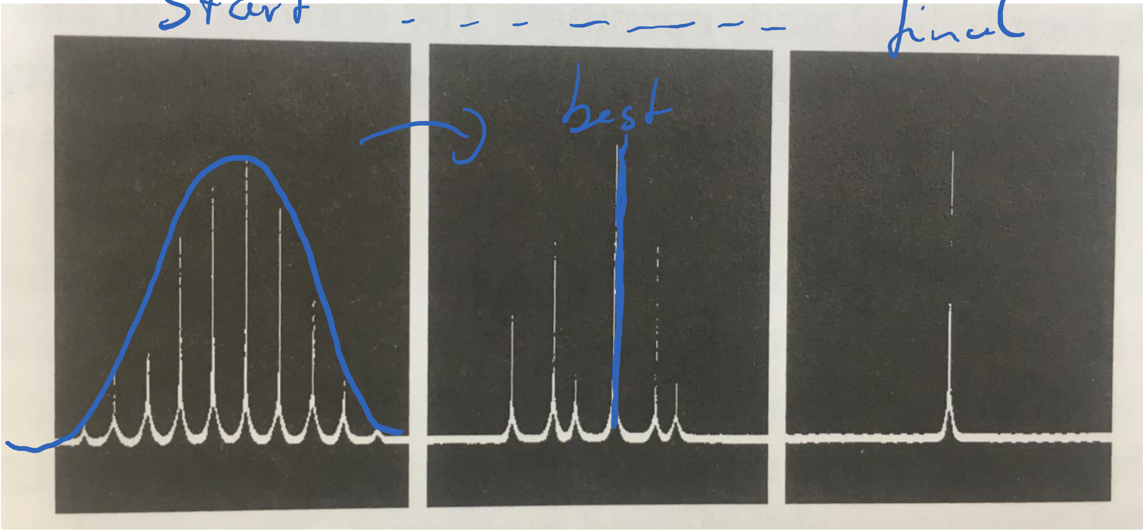


broadened by lifetime, Doppler, etc

cavity only supports selected modes

Mode selection

Start - - - - - - - - - final

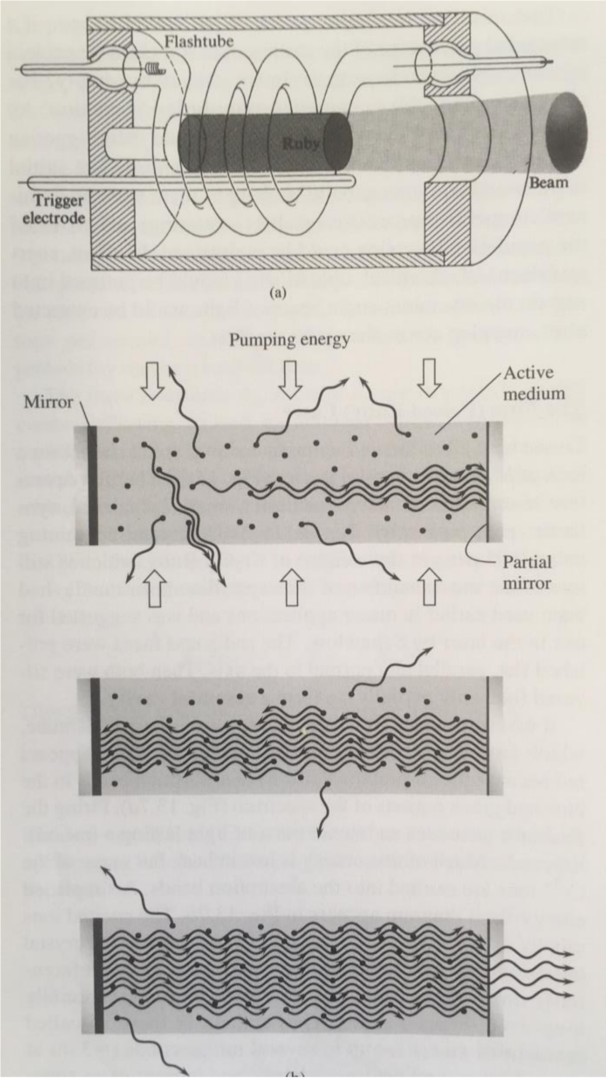


Convolution cavity & atomic lines

Only strongest mode survives!

Cavity important part of laser

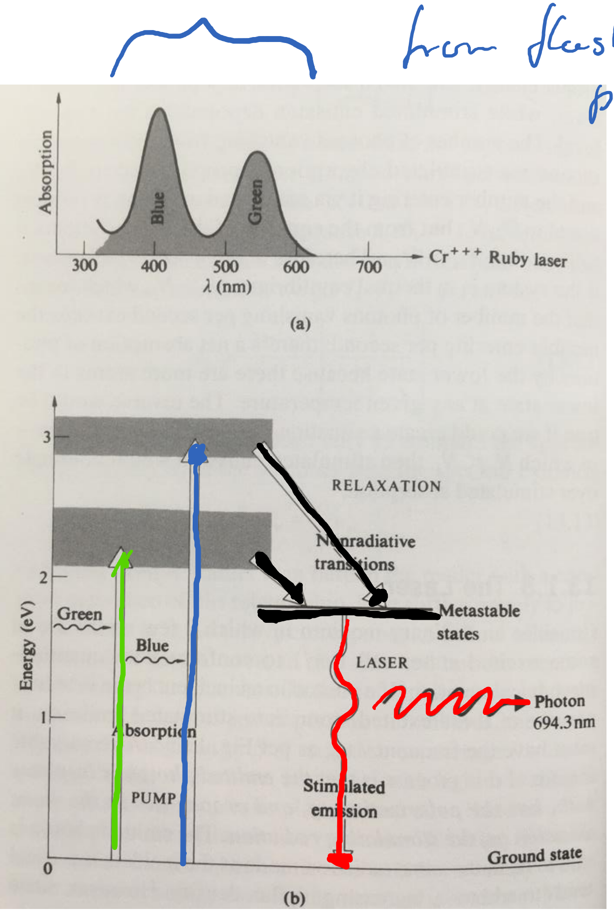
The Ruby laser



1st laser

Al_2O_3 crystal
with Cr_2O_3
active sites

broad absorption
↳ absorbs energy
from flash light
pumping



For fun https://www.youtube.com/watch?v=yV09p5LY7GA

The end.

Fabry Perot Interferometer

Na D line: