Optical methods in chemistry
or
Photon tools for chemical sciences

Session 5:

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:

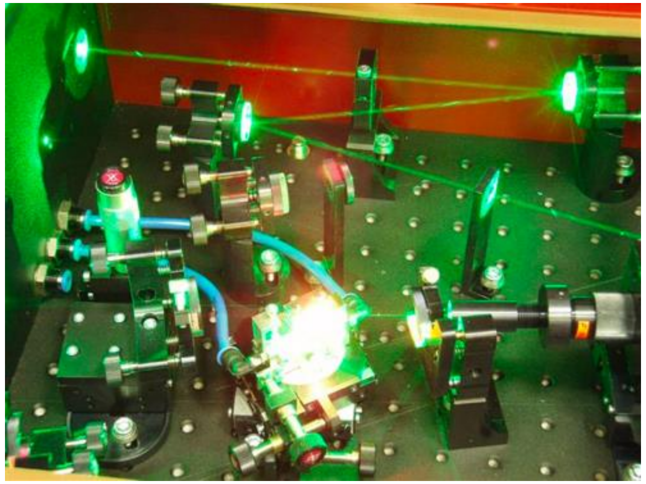
Understand wide variety of lasing transitions

Appreciate particle character of light

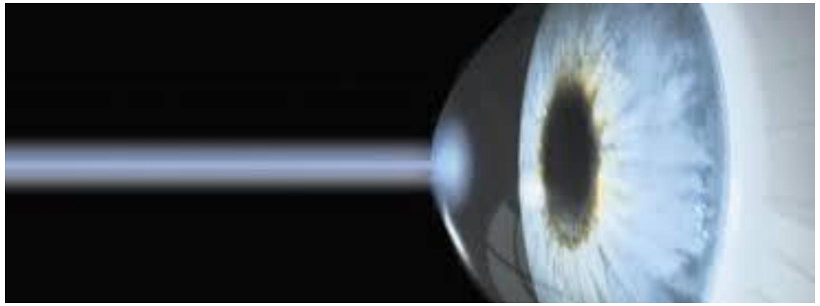
Have fun with optical tweezers

Most likely you will encounter lasers in your career

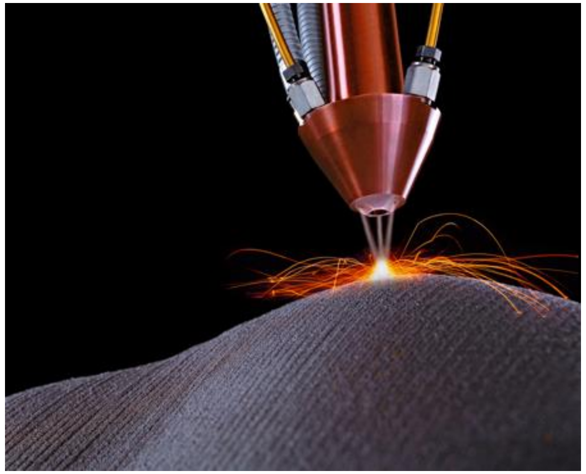
Research



Medical applications



Manufacturing



Navigation

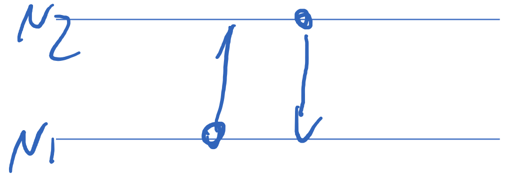
Communications

Recap: 2, 3, 4 level systems

high flux

⇒ medium becomes transparent!

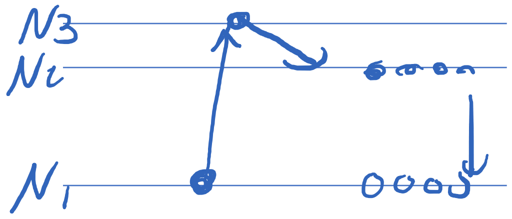
2 level system



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

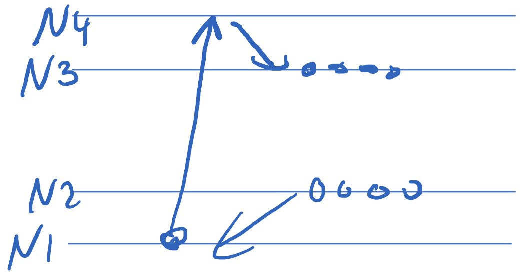
⇔ stimulated emission and absorption are in balance

3 level system



metastable } lasing line → N_2 populated over time → inversion

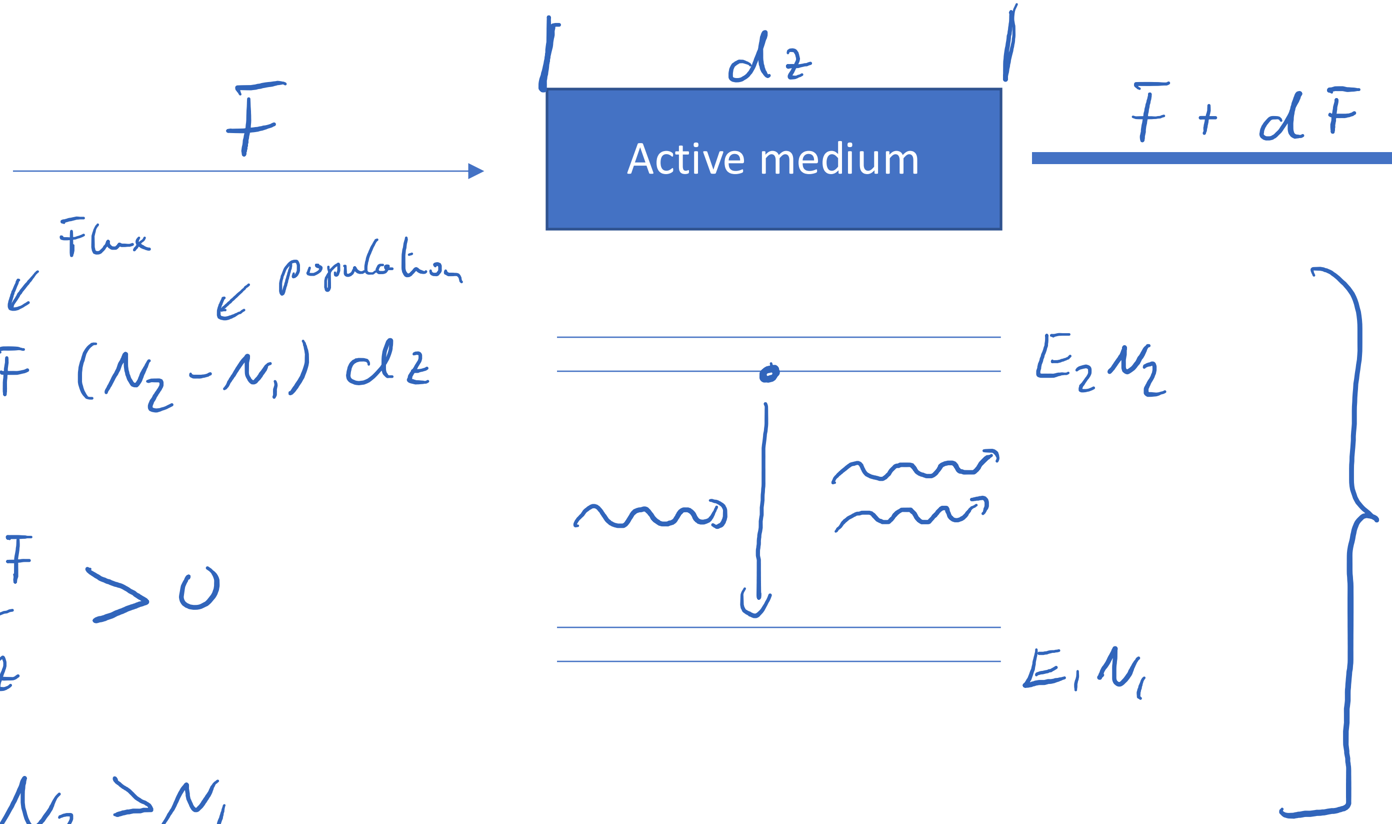
4 level system



long lifetime
always empty } lasing line

Recap: Fundamental concept of laser

F – flux



trans. prob. ↓ Flux ↙ population ↙

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

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

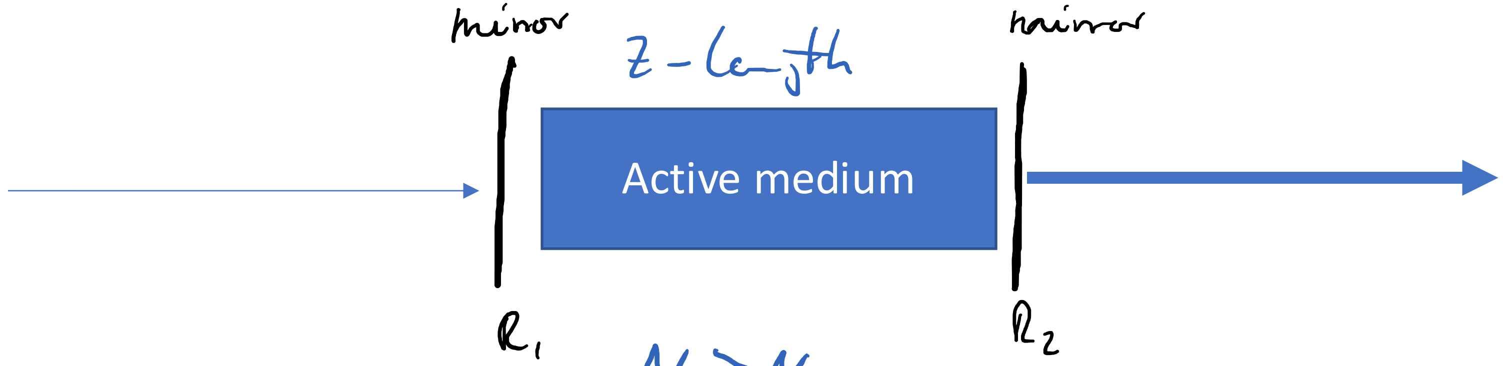
$\Rightarrow N_2 > N_1$

$\Rightarrow$ need population inversion!

But... how?

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

Recap: Fundamental concept of laser oscillator:

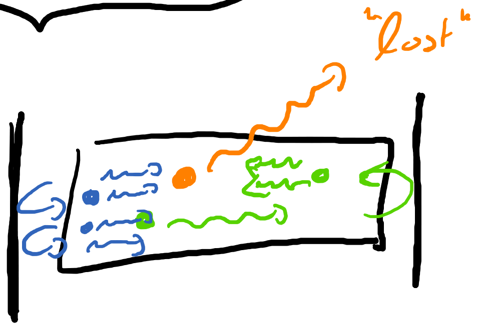


$N_2 > N_1$ "inversion"

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

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

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



exponential growth of output on axis!

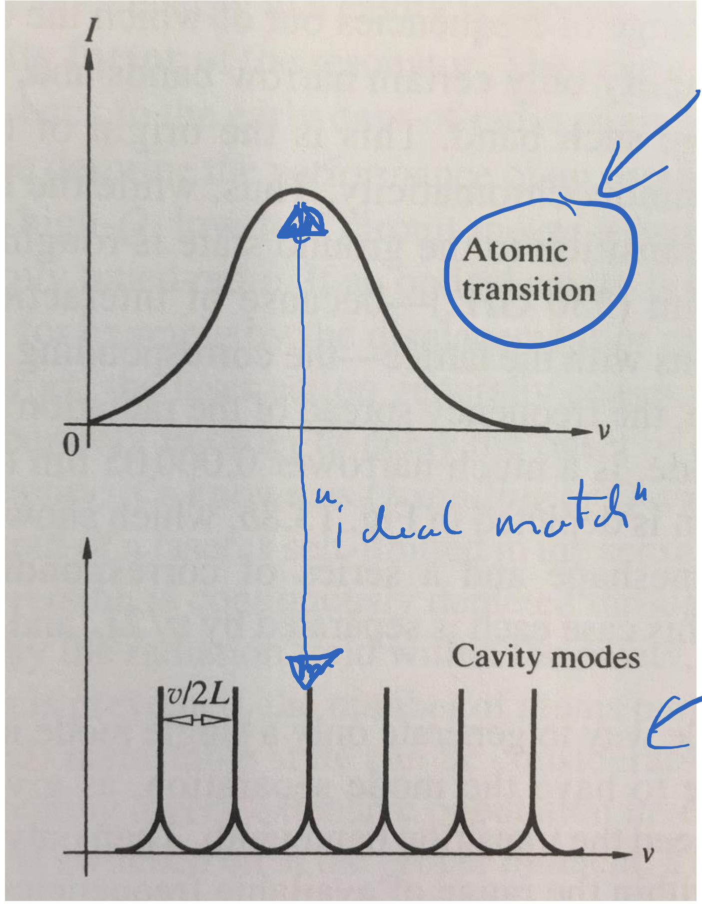
Note: The gain must always be higher than the losses! $\rightarrow$ add mirror reflectivities

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

Lasing condition

Recap: Lasers and laser cavities

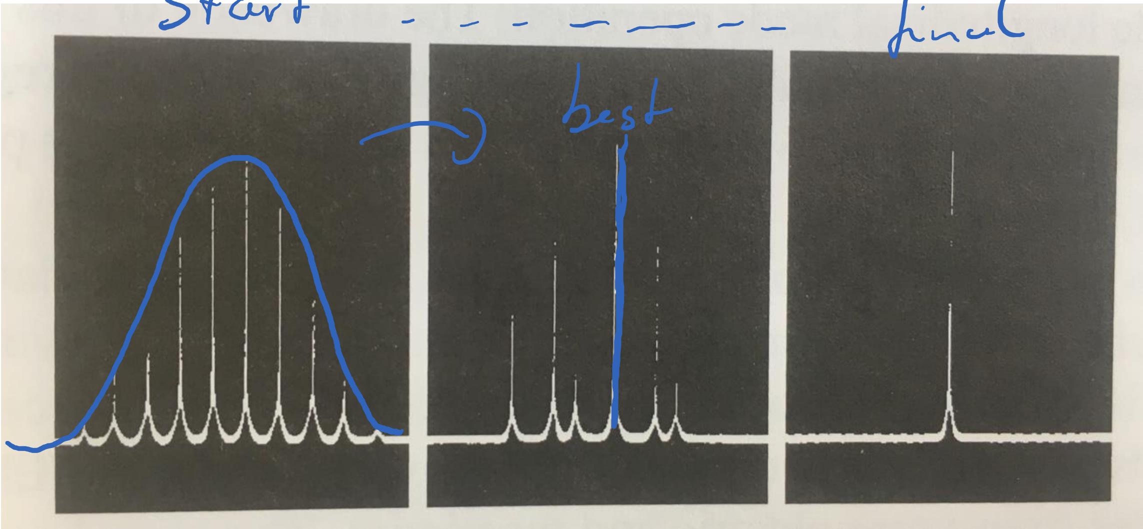
Atomic lines vs cavity modes



broadened by lifetime, Doppler, etc

cavity only supports selected modes

Mode selection

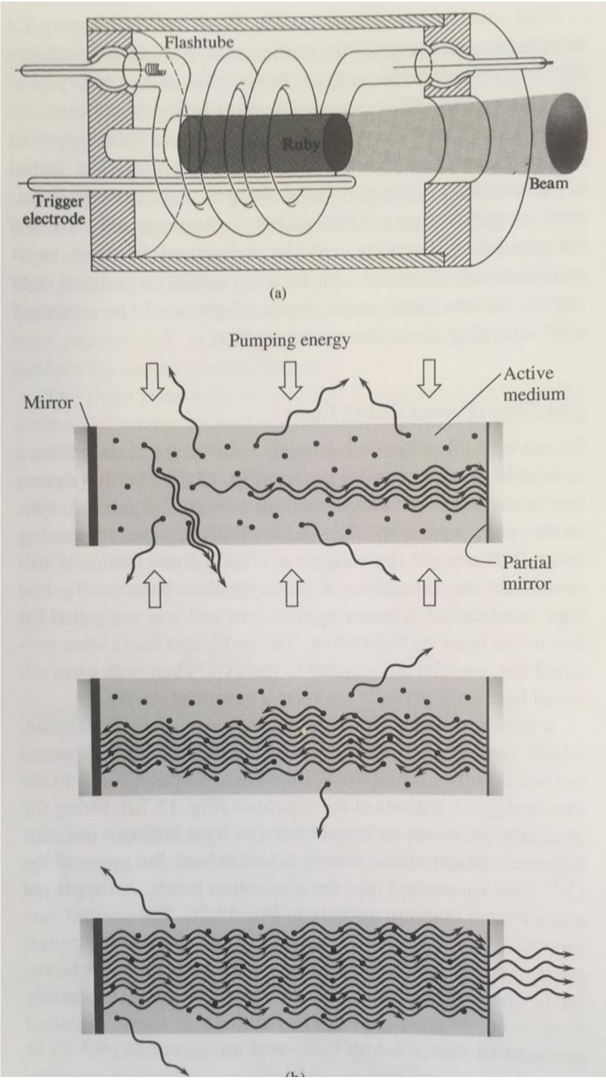


Convolution cavity & atomic lines

Only strongest mode survives!

Cavity important part of laser

The Ruby laser



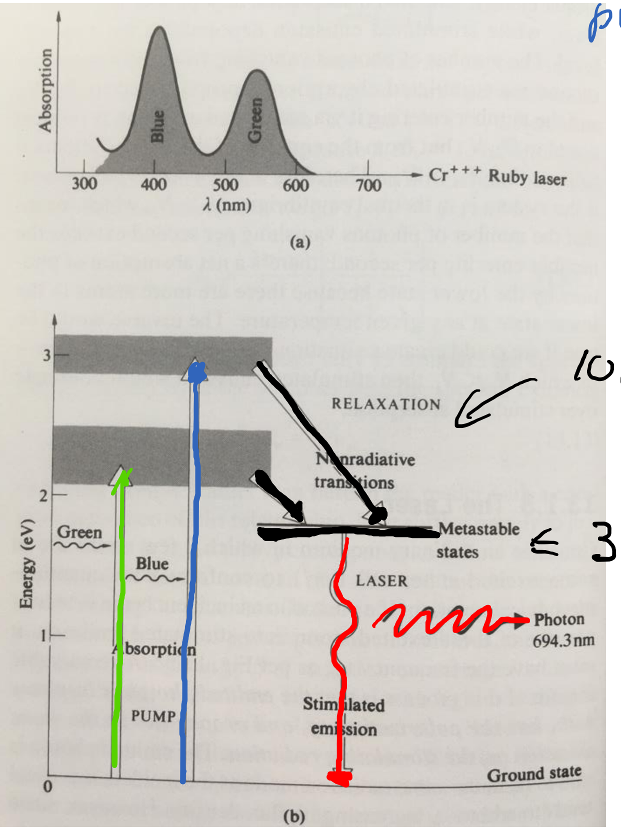
1st laser

Al_2O_3 crystal with Cr_2O_3 active sites

0.05% Cr_2O_3 - Ruby

- Surfaces polished & mirrored
- Cavity is/contains active medium
- discharge lamp as pump

broad absorption
↳ absorbs energy from flash light pumping



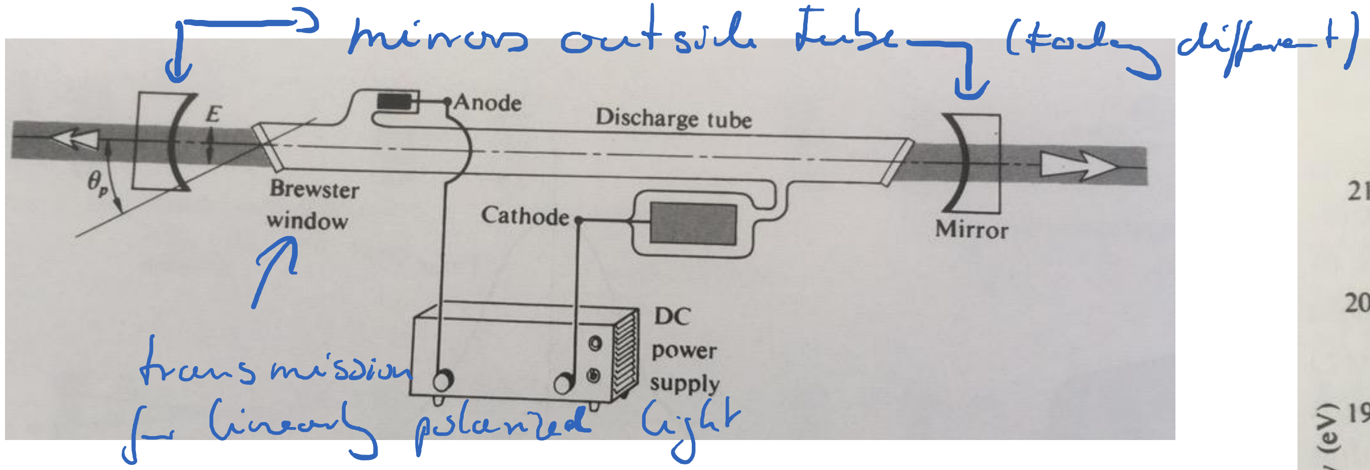
100 nsec

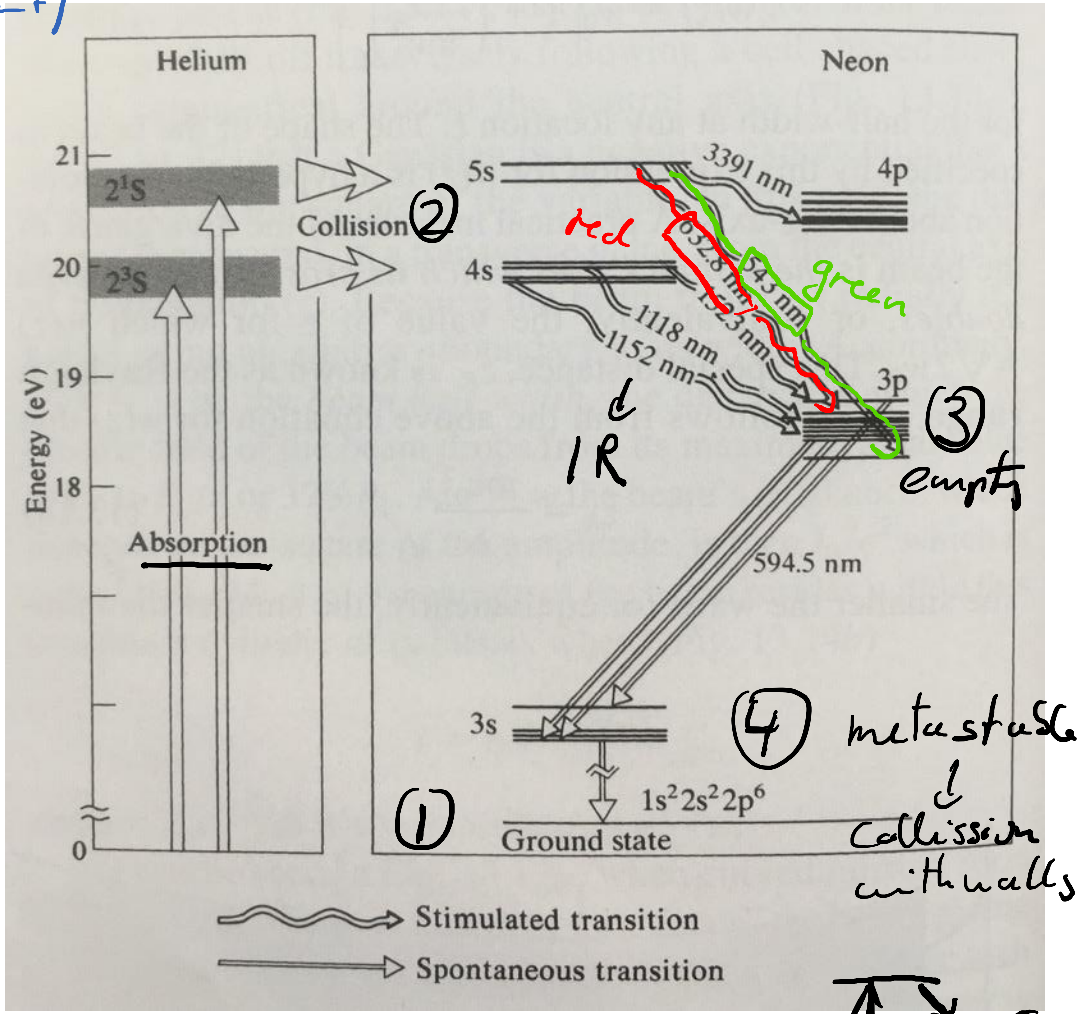
3 msec

Today up to 100J

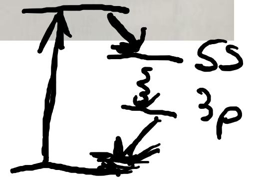
For fun https://www.youtube.com/watch?v=yV09p5LY7GA

The Helium Neon Laser - HeNe → continuous wave (cw) laser





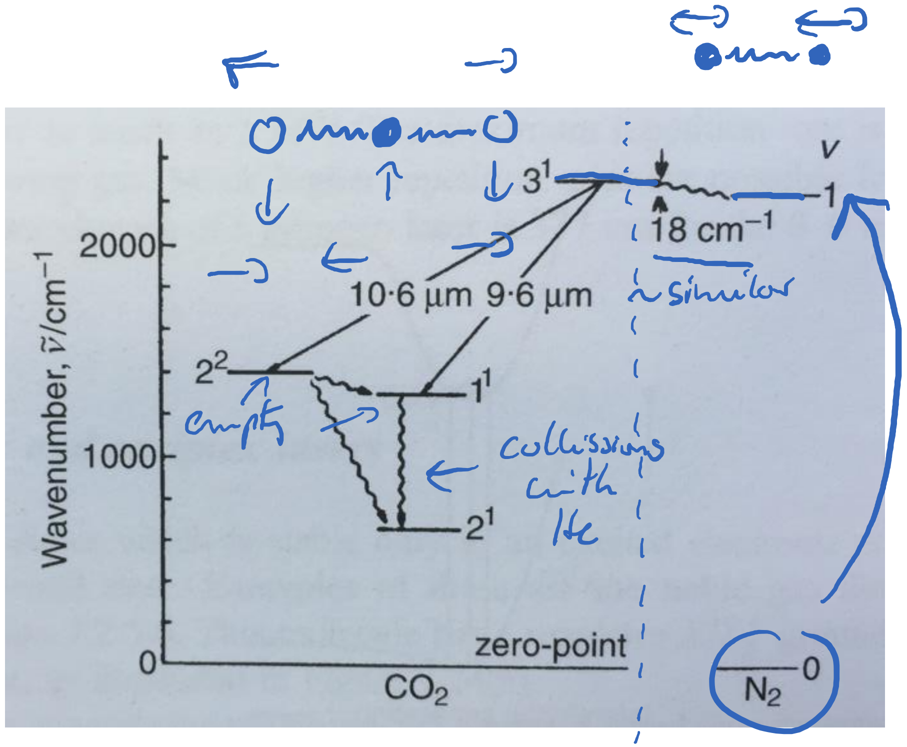
- ~0.8 Torr He
  0.1 Torr Ne
- pump with electrical discharge
  He relaxes to 2S states
  no allowed further relaxation
- collisional energy transfer to Ne
  matching in energy with 5s/4s
- 3p virtually always empty ⟺ always/easily inverted



Selected laser examples: Molecular gas laser

- Example: CO_2 laser → efficiency 20%, 2W power levels
- Output in the mid-IR region
- High-power cw laser
- Machining and medical applications

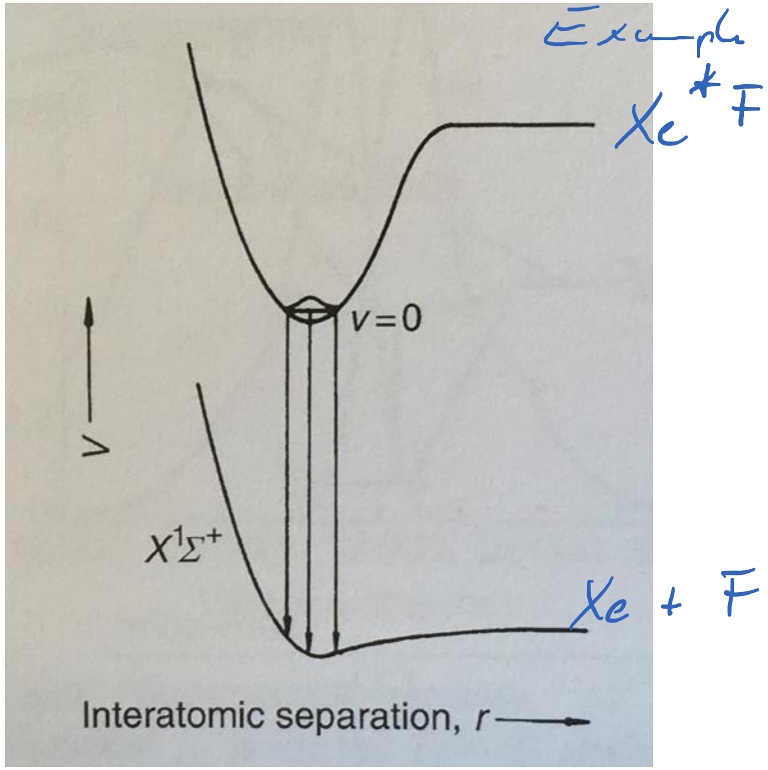
- CO_2 – N_2 – He gas mix pumped with discharge
- N_2 → $v=1$ vibrational level is metastable
- N_2 – CO_2 energy transfer
- Lasing to 2^2, 1^1 levels



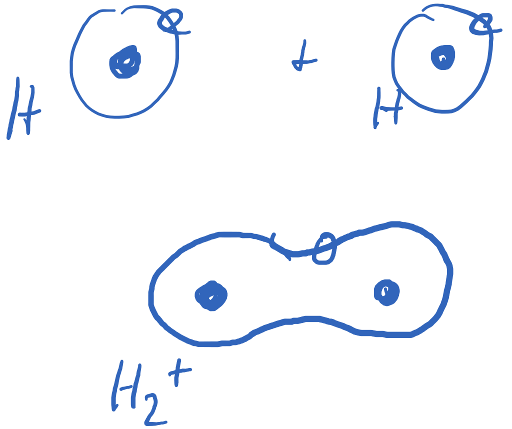
Lasing from vibrational excitation levels

Selected laser examples: Excimer laser

- Excimer – ”excited dimer”
- Important for output in UV spectral region
- UV processing, medical applications
- Pulsed, high output



Prologue: Remember H_2^+ molecule



→ effective bonding through delocalization

Similar Ar_2^+ etc → quasi covalent bond

Excimer: stable only in excited state

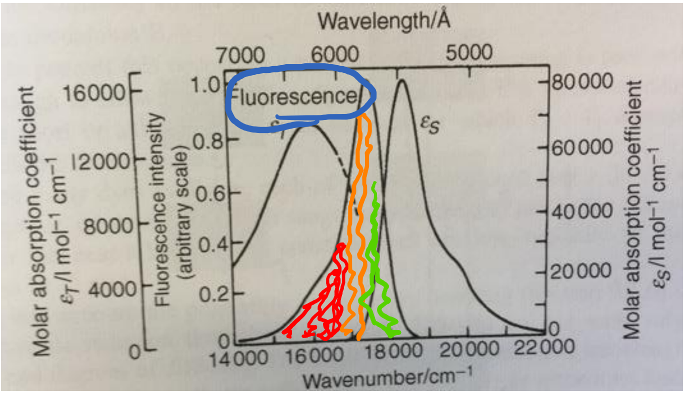
↳ population inversion through formation of short lived molecules

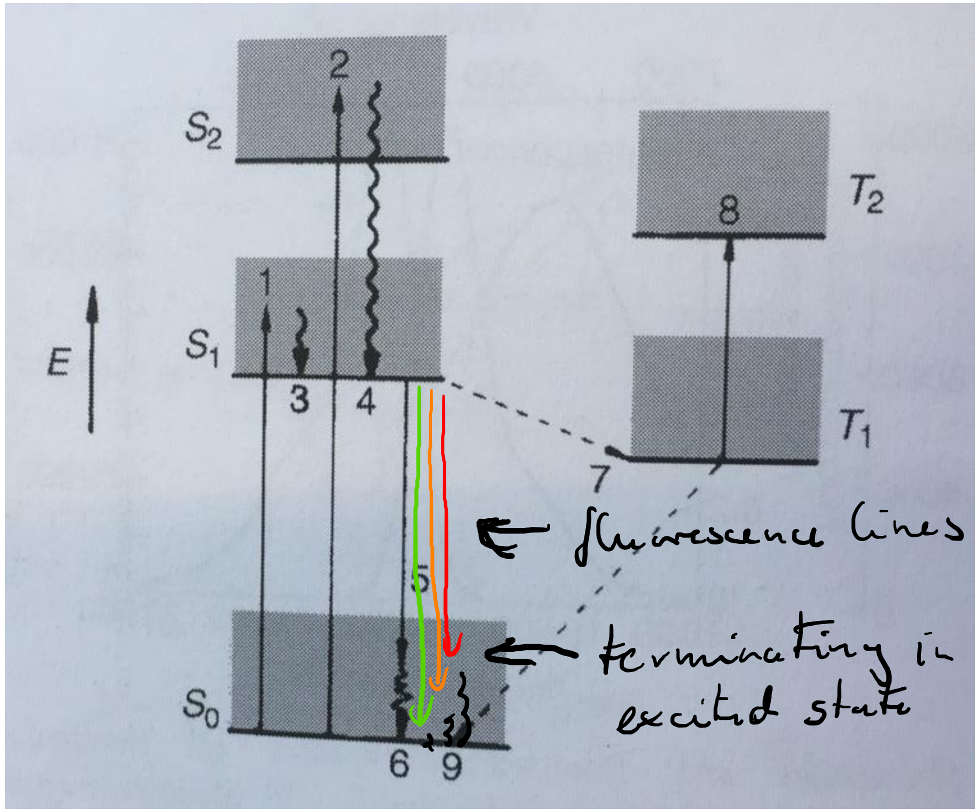
~ two level system but not by pumping but by creating (new) excimer molecule

↳ Noble gas – halide lasers in UV

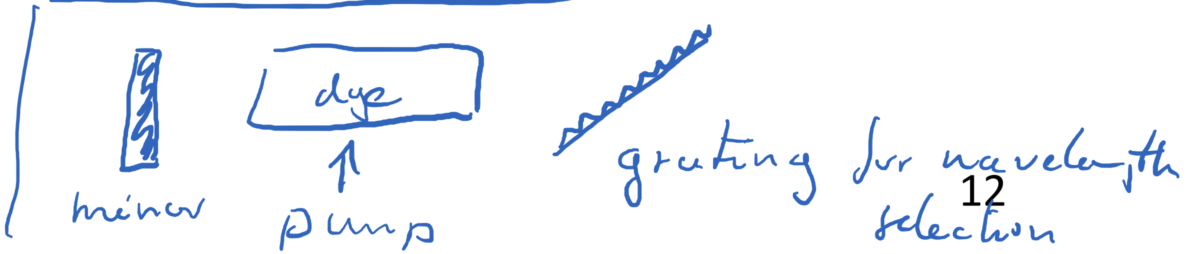
Selected laser examples: Dye laser

- Tunable over large wavelength regime
- Organic dyes in solution
- High maintenance, mostly replaced by solid state lasers





- use broad molecular bands for lasing
- excitation into S_2, S_1 states, relaxation
- lasing into S_0 excited state
- wavelength selection through cavity tuning



Selected laser examples: Semiconductor laser

- Based on solid state devices
- Light emitted at junction of two semiconductors
- Transitions between bands
- Compact, integrate able, …

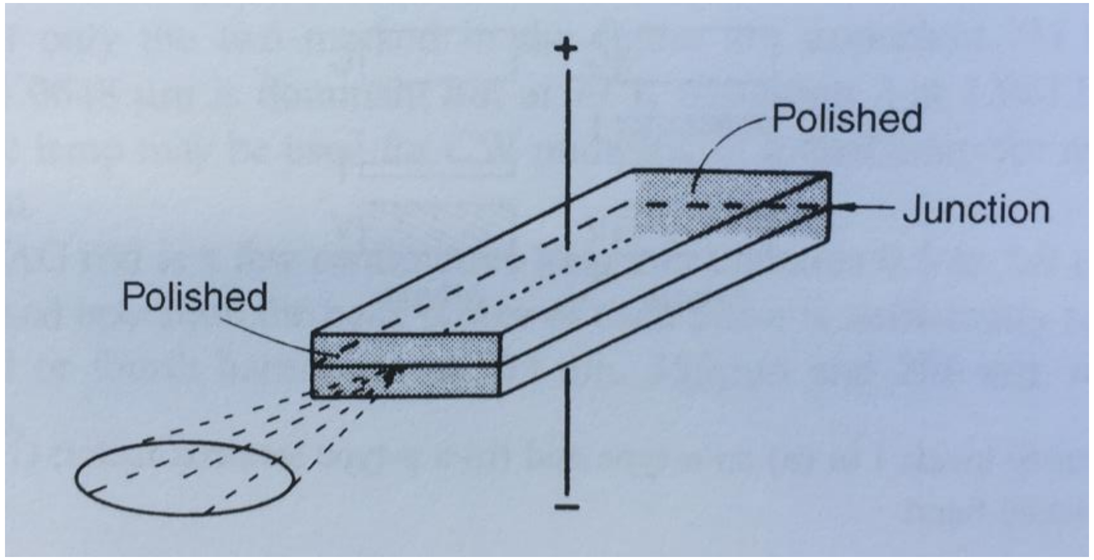
→ similar to LED

→ charge recombination at p-n-junction

→ couple out light

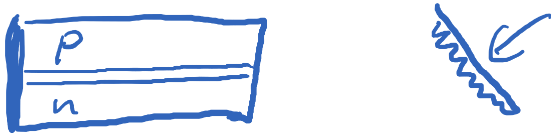
→ cheap & broad

couple with external cavity



Cheap & efficient (≈30%)

mirror



grating for wavelength selection

⇒ now spectral width depends on cavity

Selected laser examples: Nd:YAG

- Neodym doped Yttrium-Aluminium-Granate
- Nd3+ ions in glass matrix
- Solid state laser
- Main line 1064 nm
- Work horse laser in many laboratories

→ remember Ruby Laser

→ Nd^{3+} ions in solid matrix

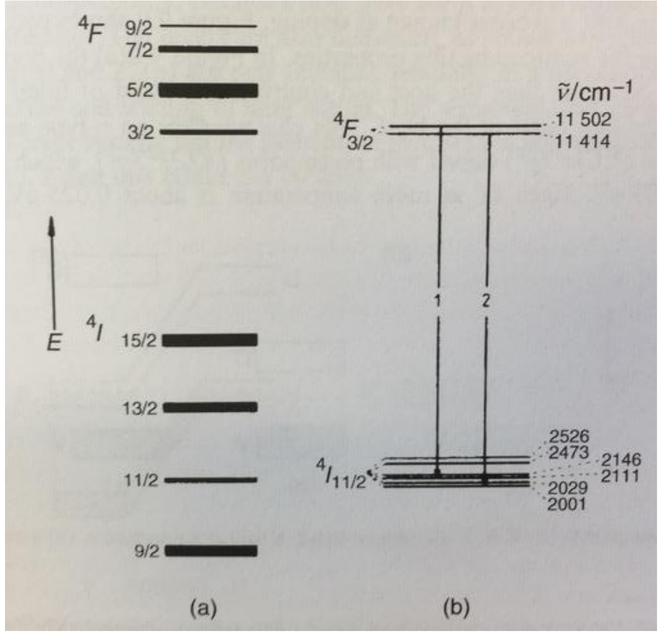
→ in free Nd^{3+} ions, $F_{3/2} \to I_{11/2}$ transition forbidden

but in matrix allowed (crystal field splitting)

→ pumped with flash lamp (diodes today)

→ powerful, short-pulse (nsec) laser

→ harmonic generation possible



General

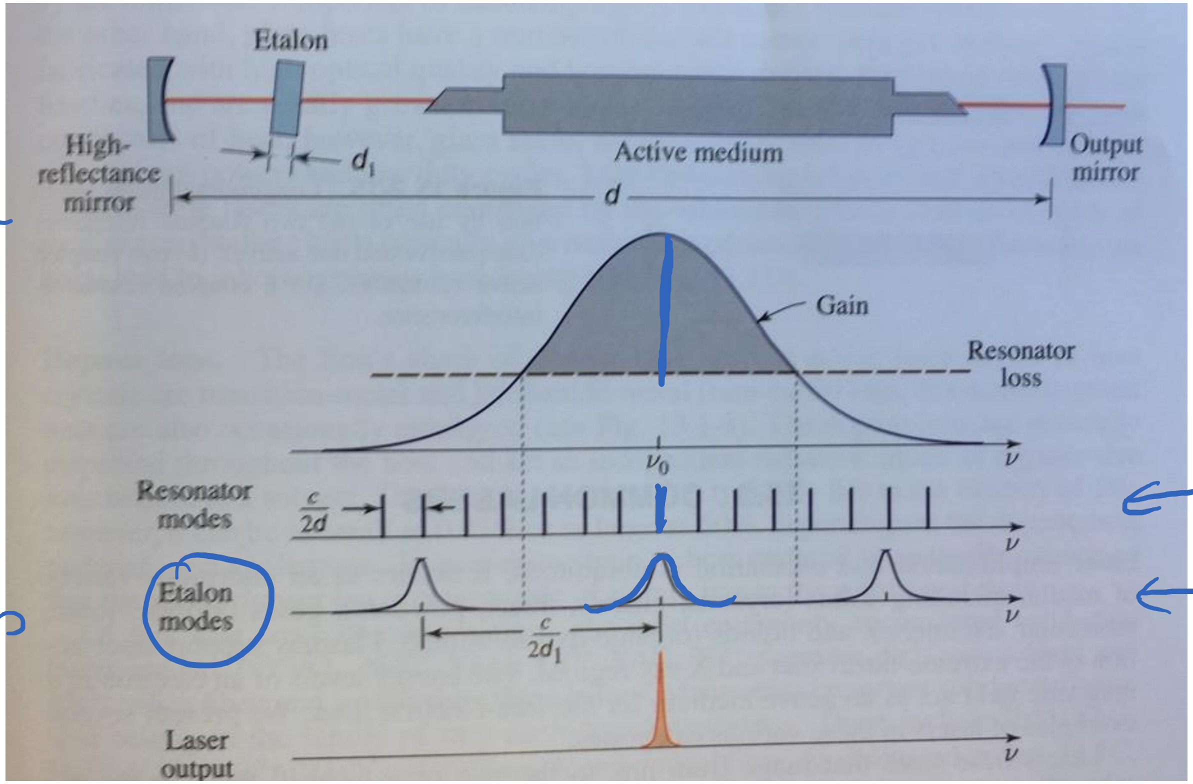
~~Better~~ approach: Mode selection with intracavity etalon

Remember:

free spectral range

$\nu_n \sim n \, c/2d$

→ broader for shorter resonators



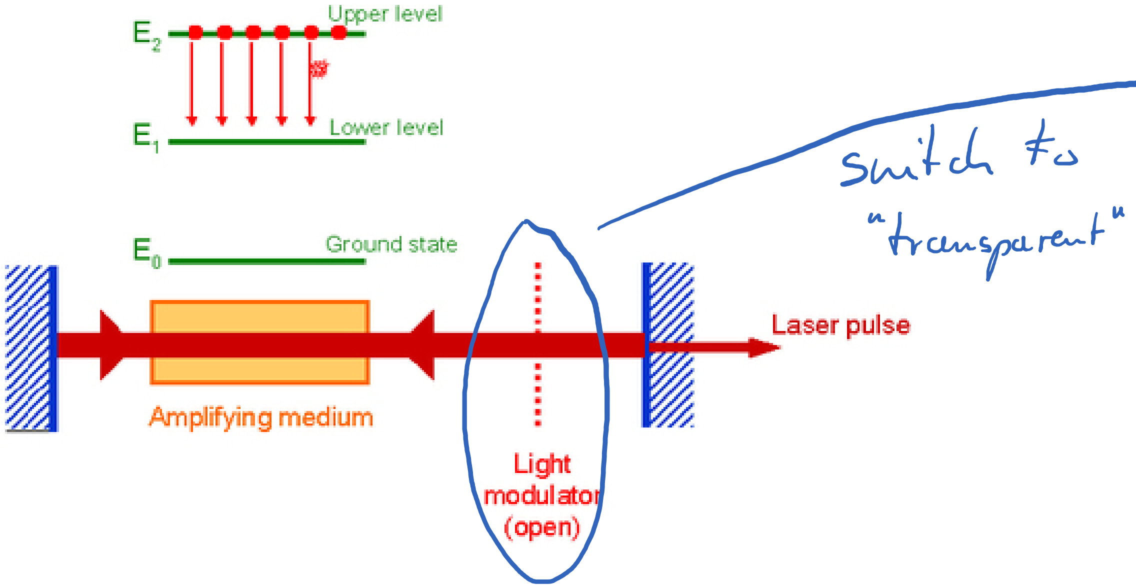
← long resonator

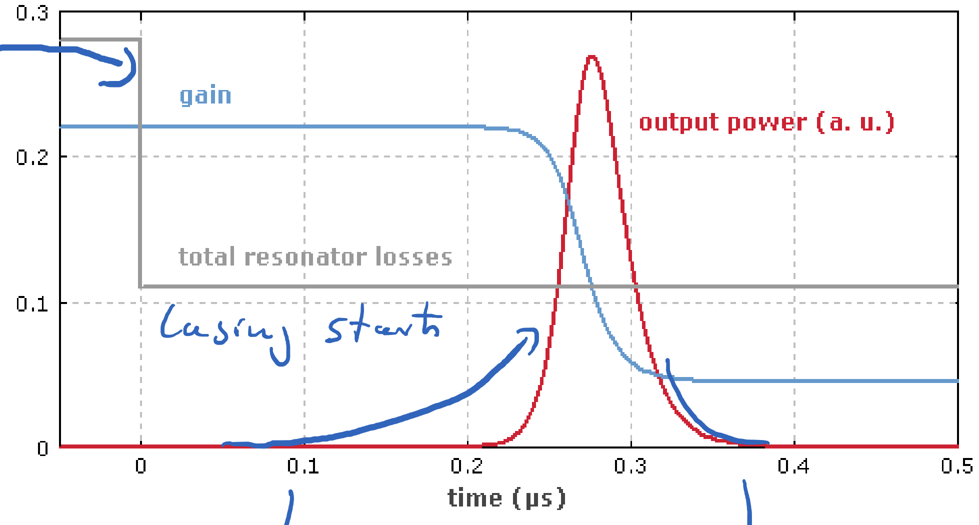
← Etalon modes

→ alternatively: optical coatings, gratings, prisms, ...

Q Switching

→ how to control lasing process
or how to achieve strong inversion } ⇒ suppress lasing with electro-optical switch





exponentially building laser pulse

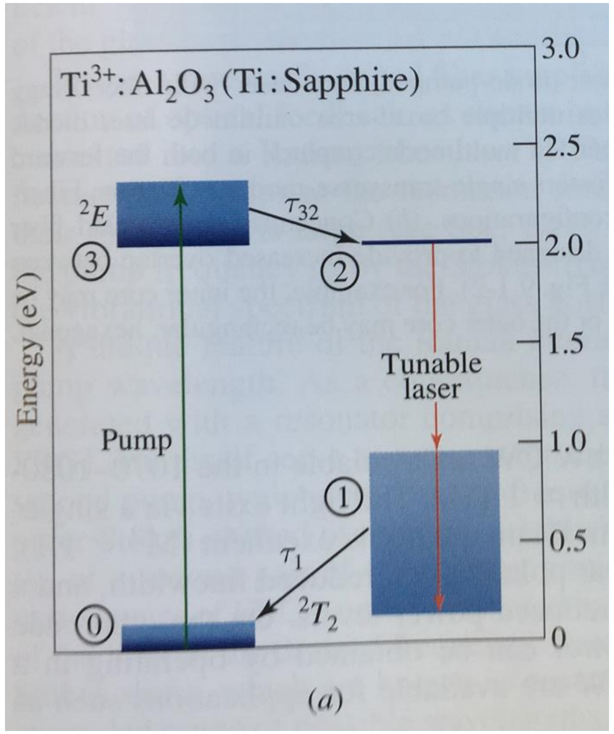
all depleted

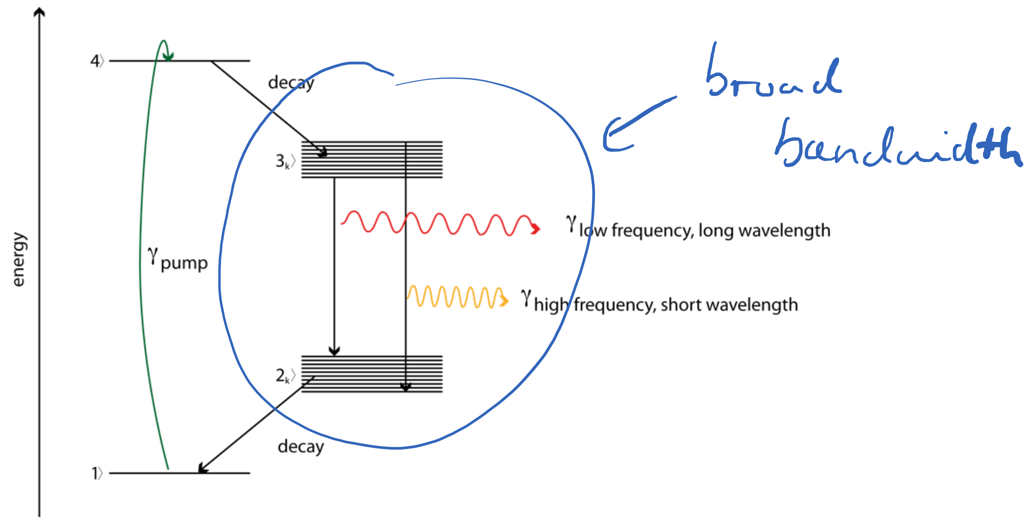
See video at: https://www.rp-photonics.com/q_switching.html

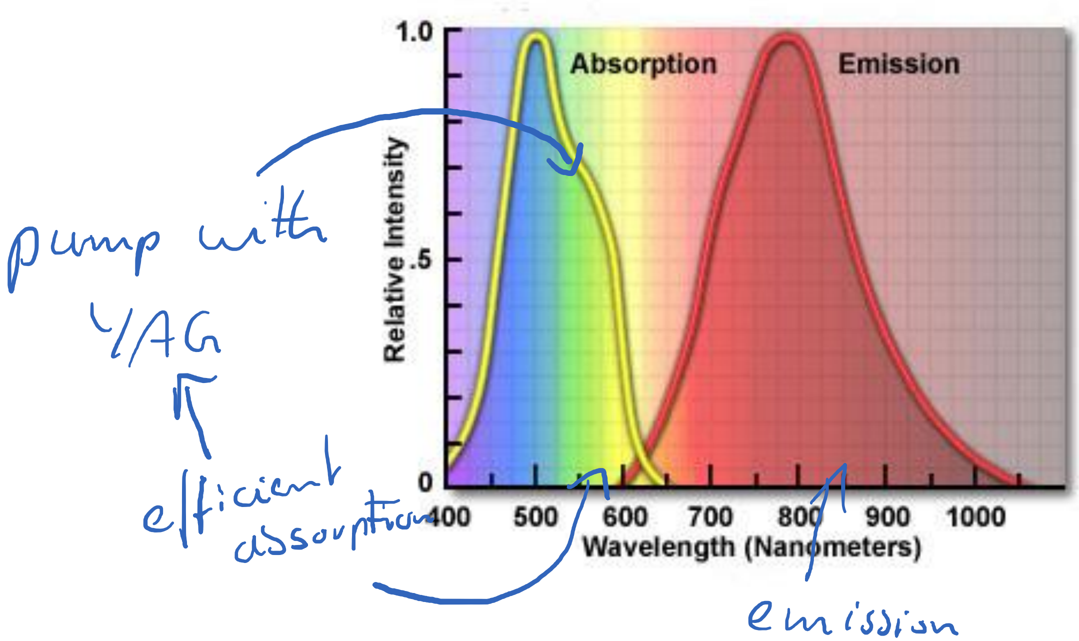
Important laser: TiSa

more later, but here for completeness

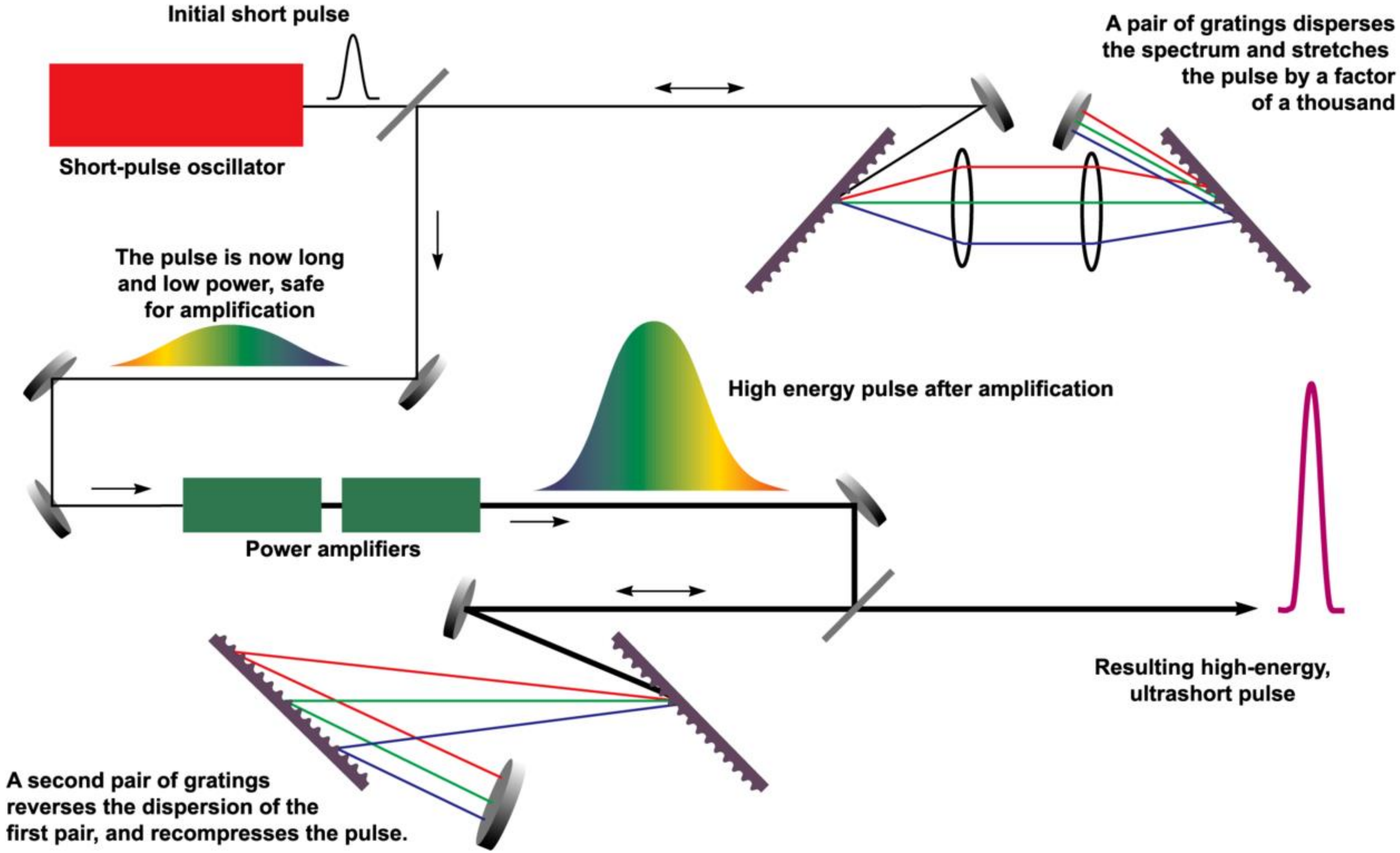
- Ti^{3+} ions in Al_2O_3 (Saphire)
- Tunable, broad bandwidth
- Can provide ultrashort pulses
- Workhorse laser for ultrafast sciences





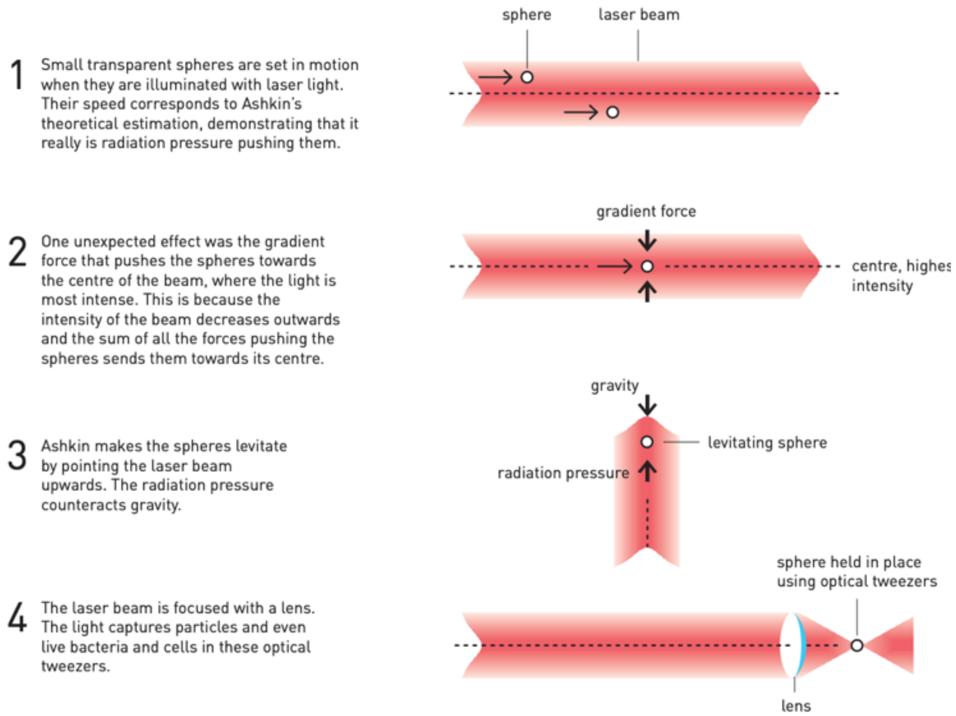


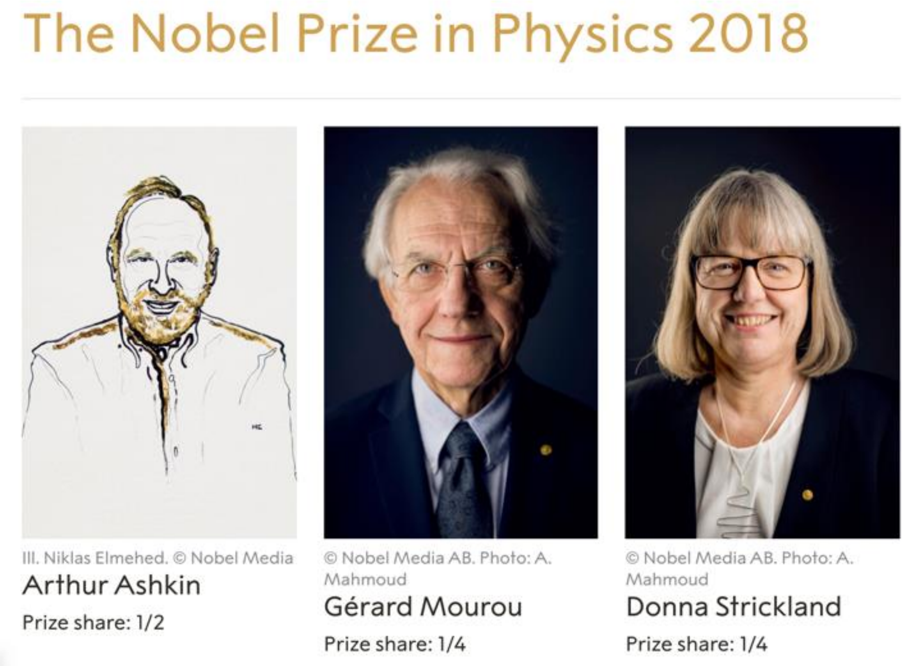
Chirped pulse amplification



Optical tweezers

Back to Session 1





Optical tweezers:
https://www.youtube.com/watch?v=ju6wENPtXu8

The inventions being honoured this year have revolutionised laser physics. Extremely small objects and incredibly fast processes now appear in a new light. Not only physics, but also chemistry, biology and medicine have gained precision instruments for use in basic research and practical applications. Arthur Ashkin invented optical tweezers that grab particles, atoms and molecules with their laser beam fingers. Viruses, bacteria and other living cells can be held too, and examined and manipulated without being damaged. Ashkin's optical tweezers have created entirely new opportunities for observing and controlling the machinery of life. Gérard Mourou and Donna Strickland paved the way towards the shortest and most intense laser pulses created by mankind. The technique they developed has opened up new areas of research and led to broad industrial and medical applications; for example, millions of eye operations are performed every year with the sharpest of laser beams.

Remember some basic properties of the photon

- Photon: Massless particle with

- Energy $E = h\nu = \hbar\omega$

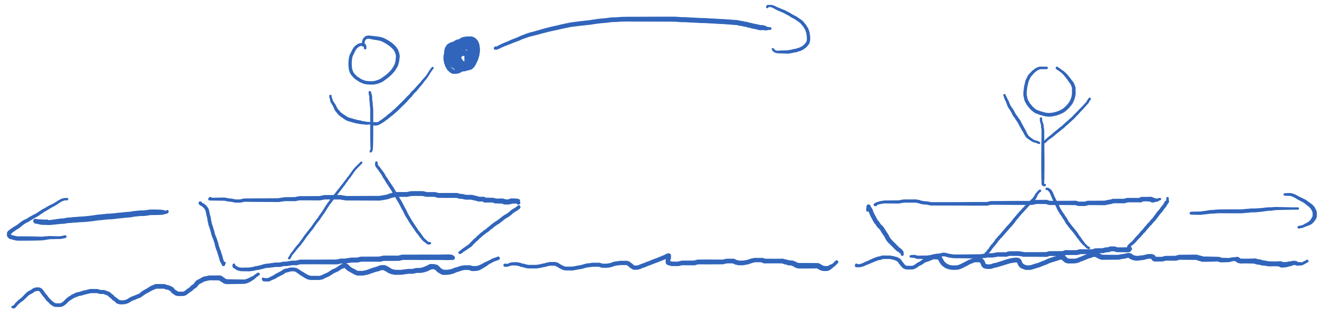
- Momentum $\vec{p} = \hbar\vec{k}$ $\quad |\vec{k}| = \frac{h\nu}{c} = \frac{h}{\lambda}$

From classical physics we know that action = reaction. That is Newtons third law.

First law: In an inertial frame of reference, an object either remains at rest or continues to move at a constant velocity, unless acted upon by a force.

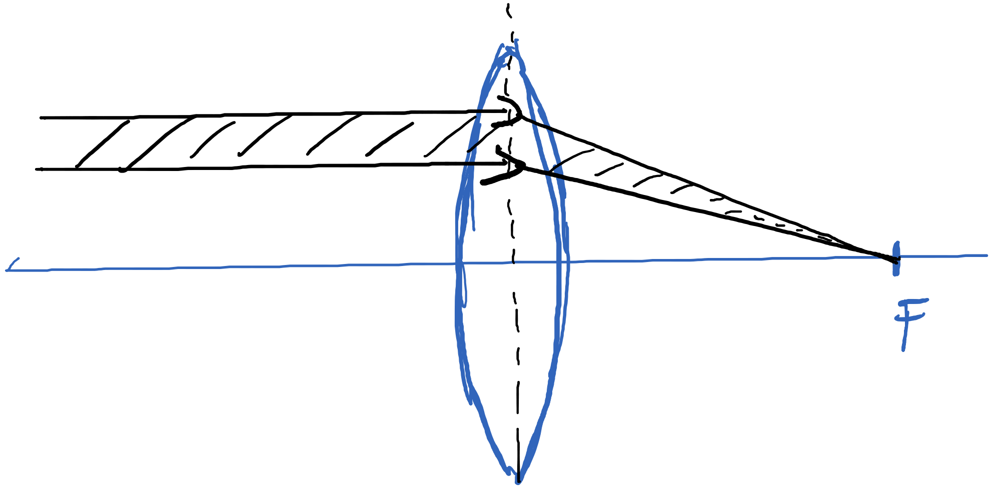
Second law: In an inertial frame of reference, the vector sum of the forces **F** on an object is equal to the mass *m* of that object multiplied by the acceleration **a** of the object: $\mathbf{F} = m\mathbf{a}$.,

Third law: When one body exerts a force on a second body, the second body simultaneously exerts a force equal in magnitude and opposite in direction on the first body.

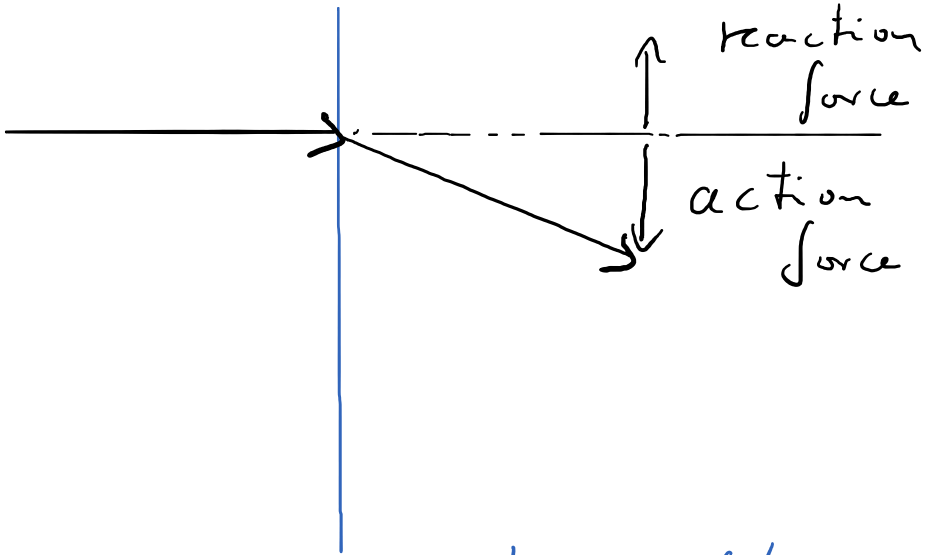


Light going through a lens:

- Ray optics



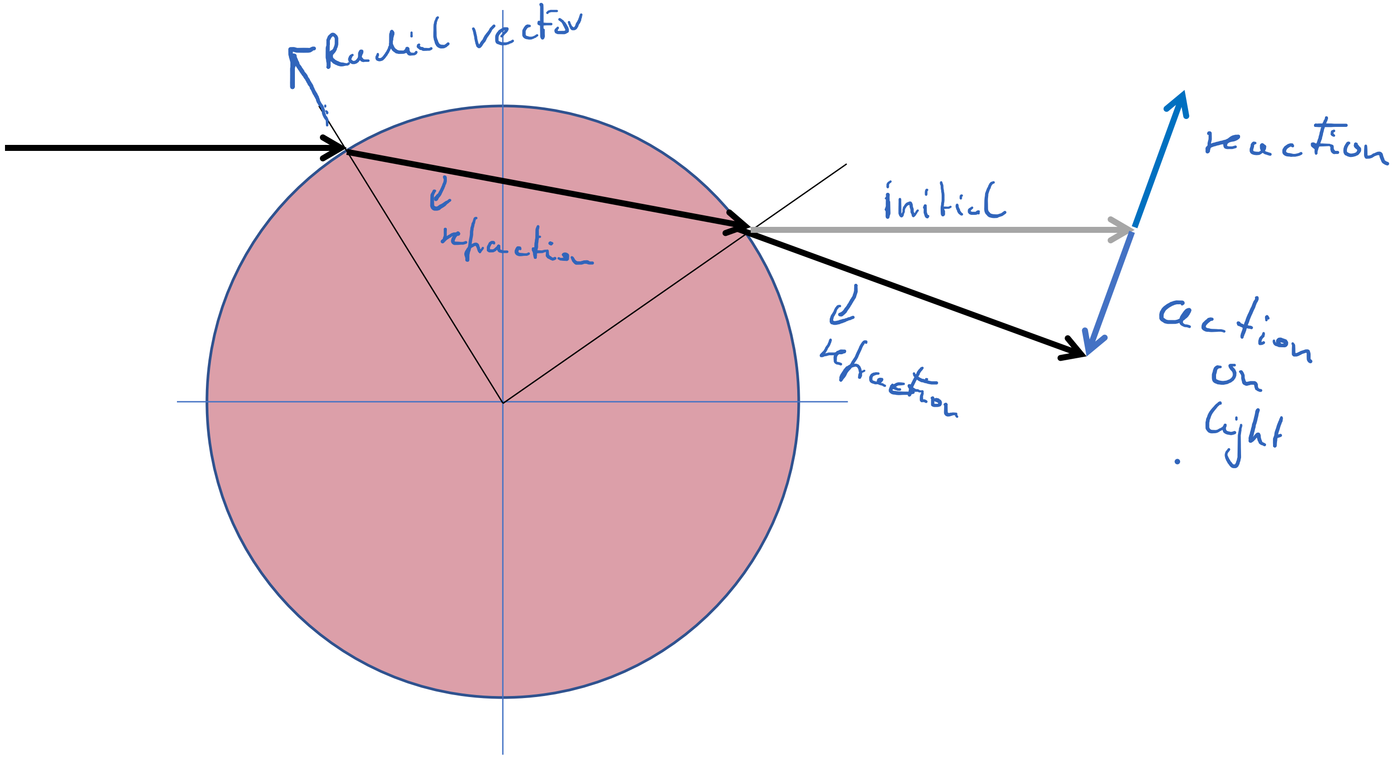
- Momentum vectors



→ there is a net force under current conditions

→ here: lens moves up

Now: Not a lens but a small particle in a (homogenous) light field



Some boundary conditions:

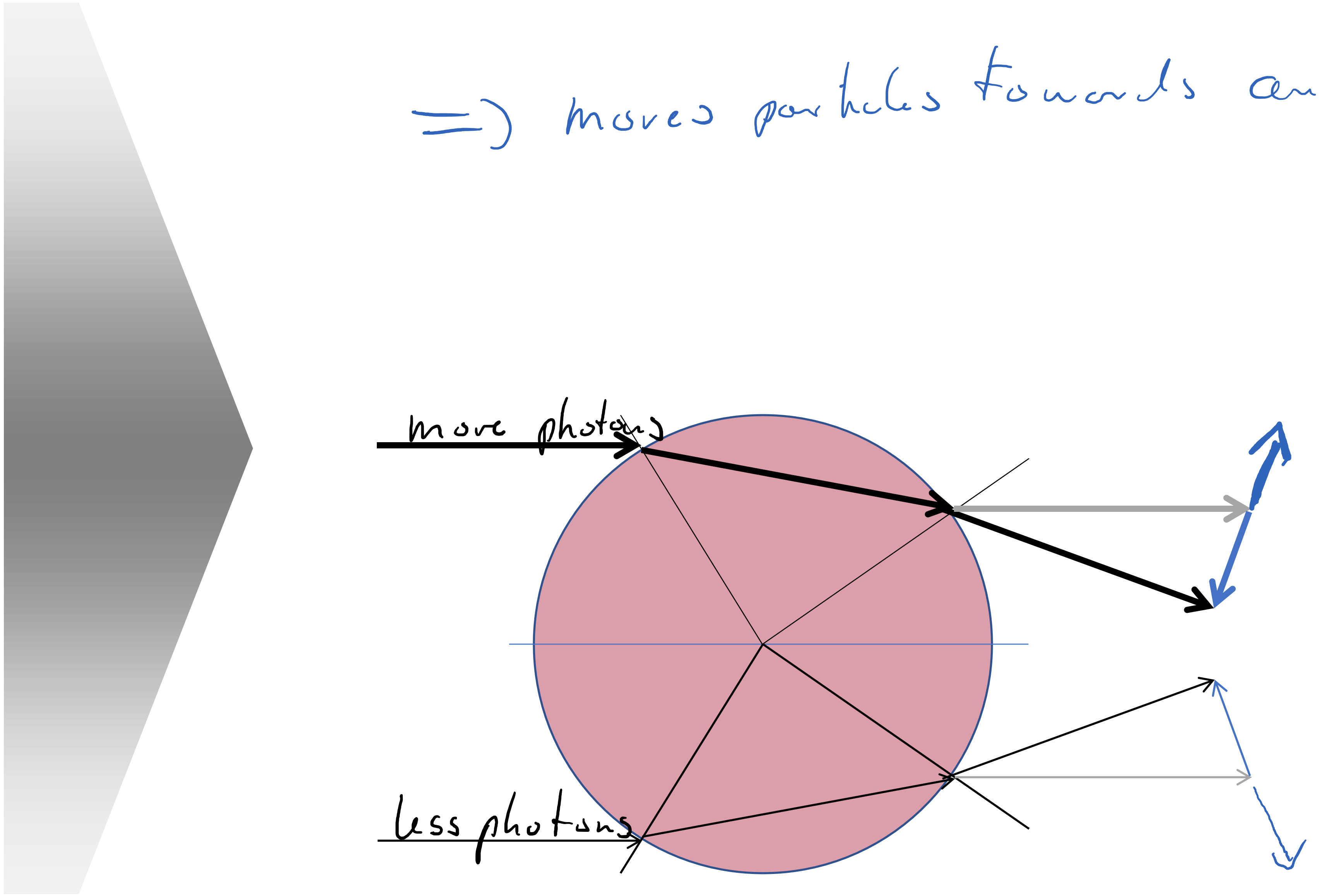
- Optically thicker sample in optically thinner medium
- Transparent sample, i.e., negligible scattering and reflection compared to transmission

Process:

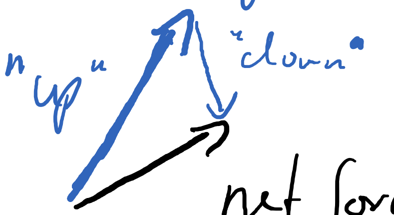
- Rays are refracted, leading to momentum change
- Action equals reaction, sphere is pushed ……up……wards
- With equal illumination there is……∅ up/down movement

But we learned: Laser beam has a Gaussian beam profile. More intense in center!

⇒ moves particles towards center!



Force diagram



net force towards center

⇓

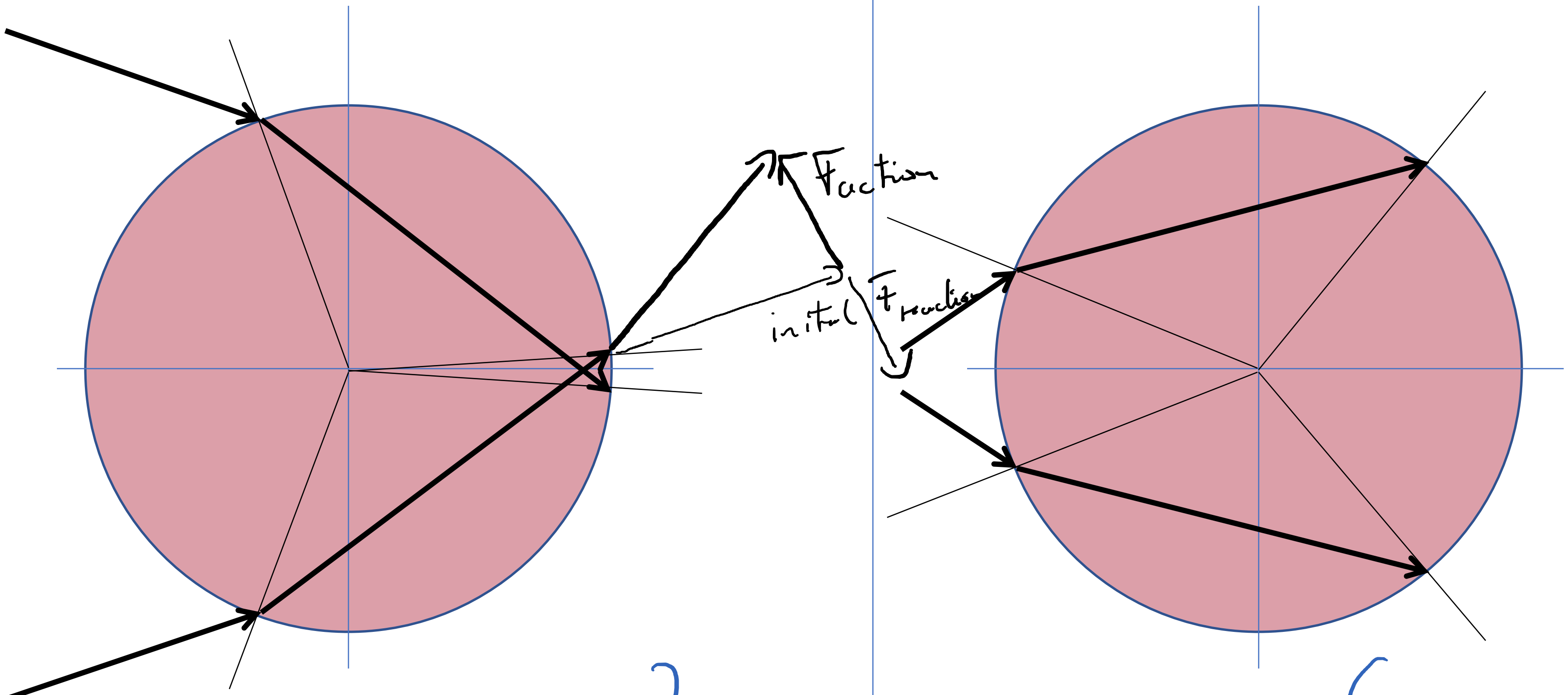
intensity distribution yields effective force towards center

Now before and after focus

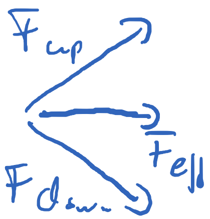
→ particles are trapped!

Particle before to focus

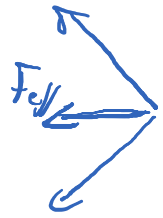
Particle behind to focus



force diagram



⇒ effective force towards the focus!



For transparent particles much larger than wavelength we can use ray optics and momentum transfer considerations.

And it works nicely:

https://www.youtube.com/watch?v=BPN90U4yzBc

Catching and moving in liquids

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

Note → extension to em fields

⇒ alignment and control of molecules (samples with D<λ)

The end.