

Optical methods in chemistry  
or  
Photon tools for chemical sciences

# 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
- Summary

# Ray optics and basic optical components

# Postulate of ray optics

- Light travels in form of rays
  - Rays are emitted by a light source and can be observed when they reach an optical detector
- An optical medium is characterized by a quantity  $n \geq 1$  called refractive index with
  - $n = c_0/c$  and  $c$  = speed of light
  - Time for traveling a distance  $d$  takes:
    - $nd$  is called the optical path length
- In an inhomogeneous medium the refractive index  $n(r)$  depends on  $r(x,y,z)$ 
  - Optical path length expressed as integral:
  - Time to travel from A to B is proportional to the optical path length

## Fermat's principle

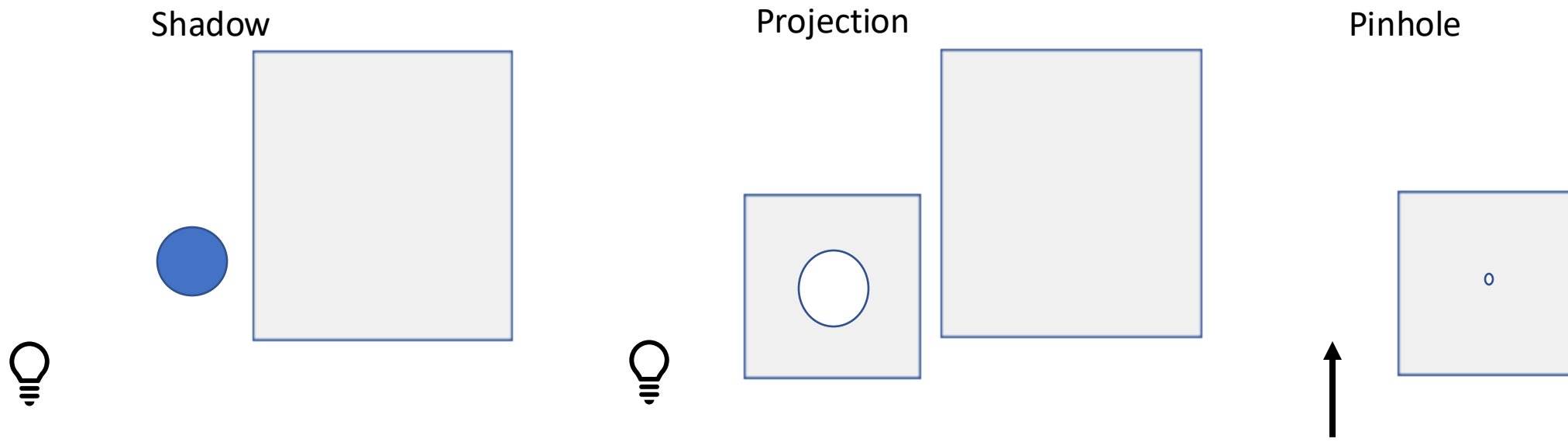
Optical rays traveling between two points A and B follow a path such that the time of travel (that is optical path length) between the two points is at an extremum (usually minimum)

In other words: Light travels along the path of least time

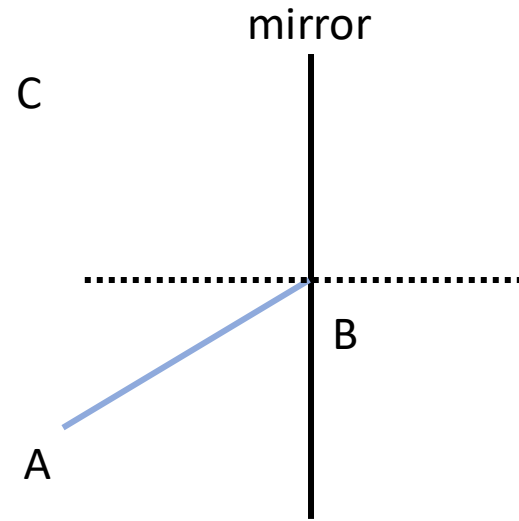
In homogenous media this results in Hero's principle

Hero's principle: The path of minimal time is also the path of minimal distance.

Or in other words: Light travels in straight lines. Lets try it, draw an image of



## Reflection from a mirror



The reflection lays in the plane of incidence.

The angle of the reflection

the angle of incidence

## Snell's law – reflection and refraction at the boundary of two media

At the boundary of two media with  $n_1$  and  $n_2$  the incident ray is split in two beams:  
a *reflected* and a *refracted* beam

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

Snell's law

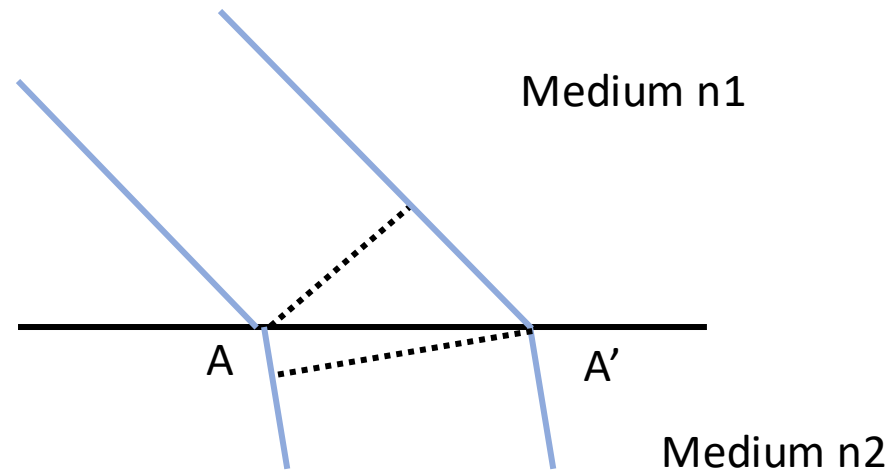
or

$$\frac{n_1}{n_2} = \frac{\sin \theta_2}{\sin \theta_1}$$

Important note: the proportion of the reflected and refracted light beams are *not* described by Ray optics



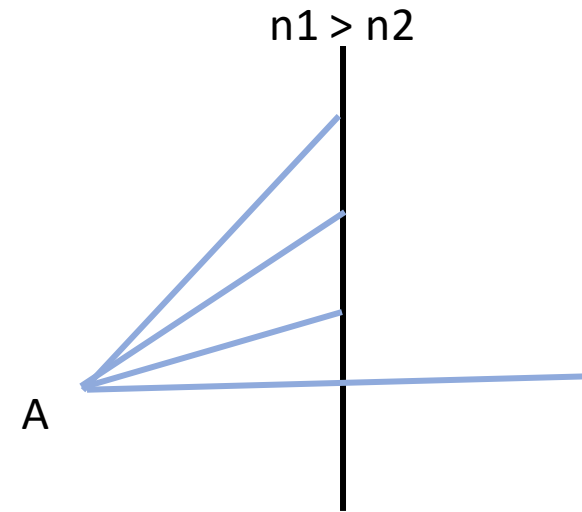
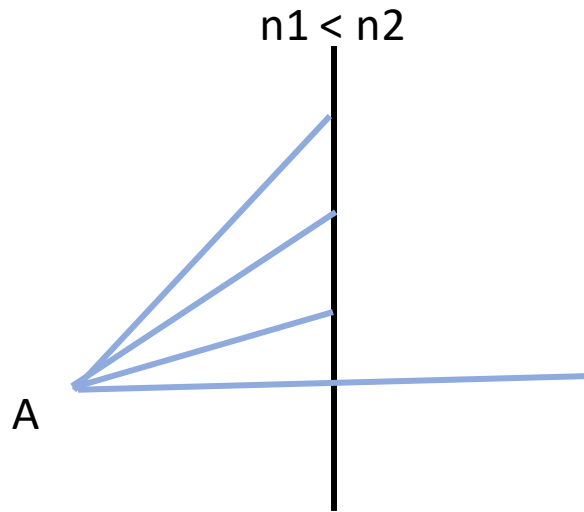
## Snell's law based on what we have learned so far



- Same time means same distance travelled,  $t = \text{const}$
- From geometry:  $\sin$
- Relation:
- Results in Snell's law

# Optical boundaries

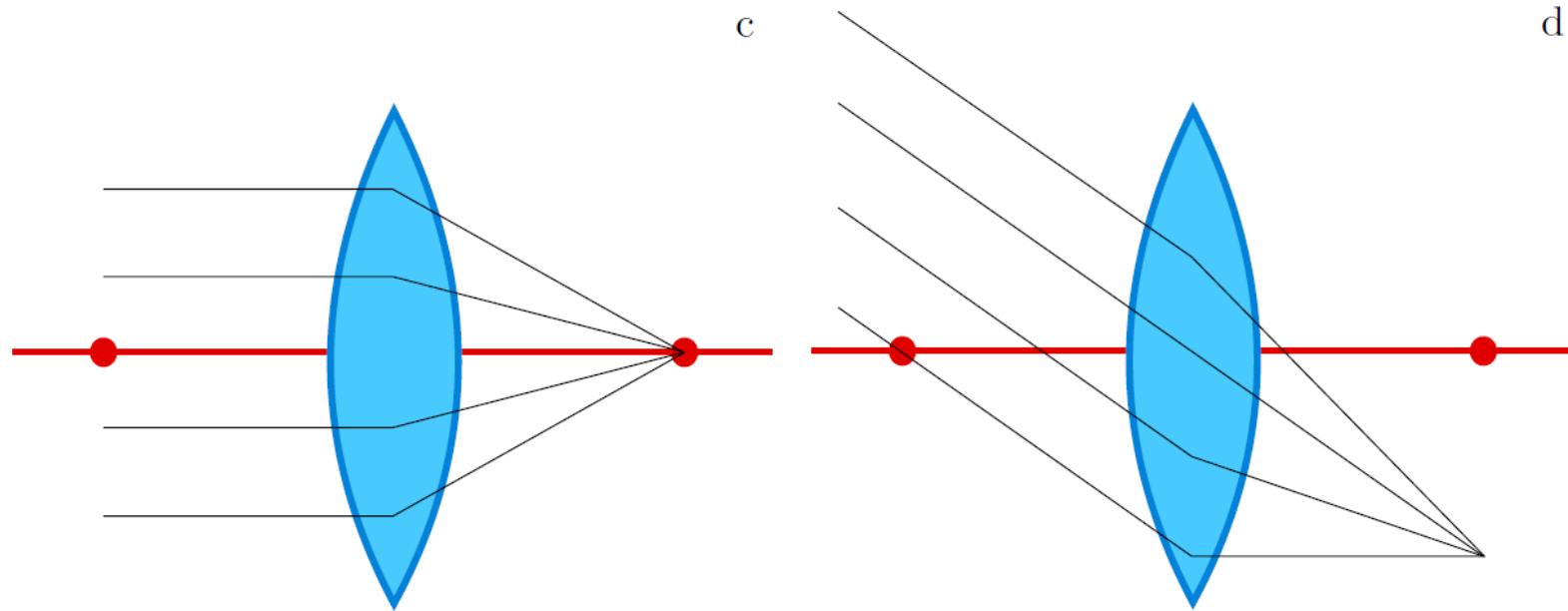
- External refraction  $n_1 < n_2$  – refracted ray bends away
- Internal refraction  $n_1 > n_2$  – refracted light bends towards boundary



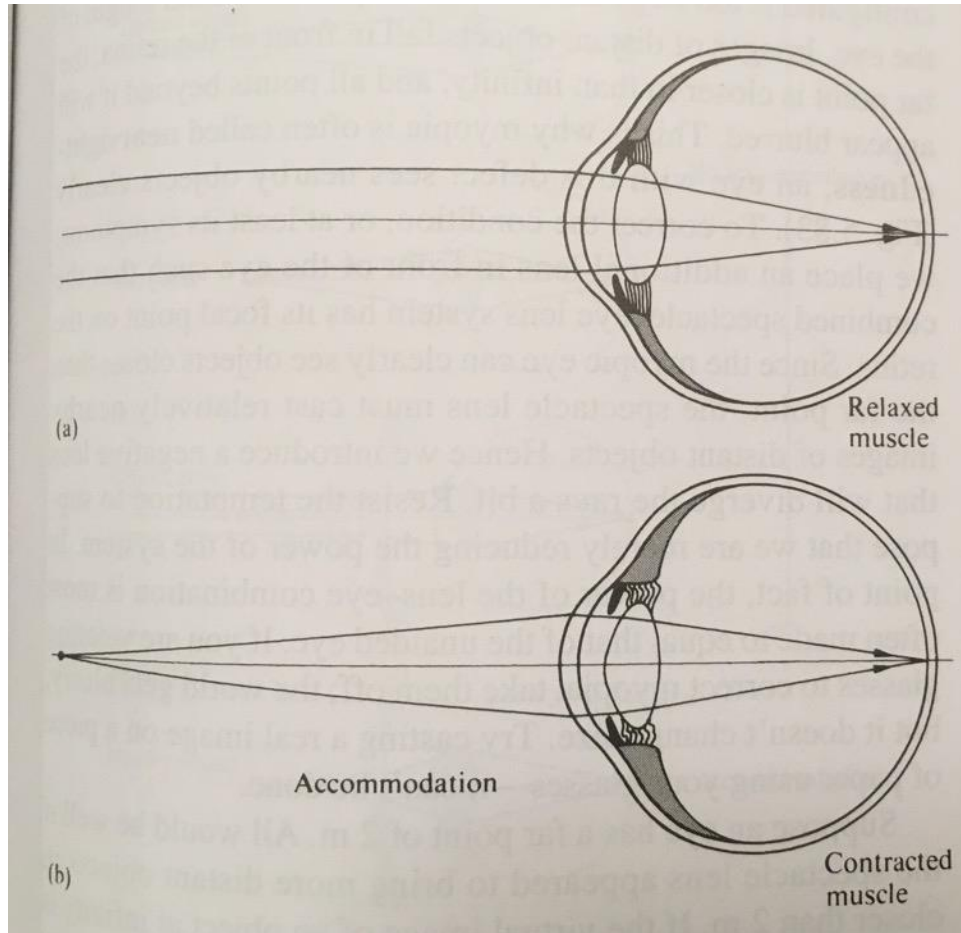
- Total internal reflection
- Use for optical fibers



# Recall: Focusing properties of a lens (ray optics)



## Reminder: Our eye as an optical system

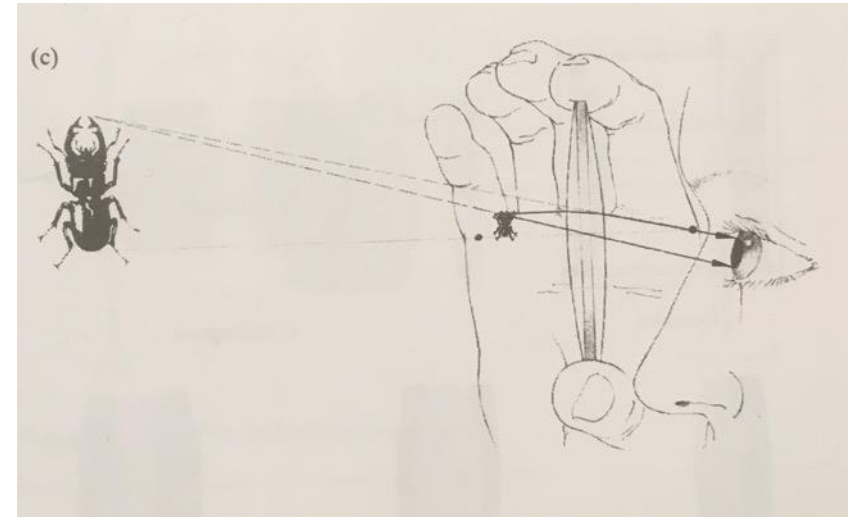
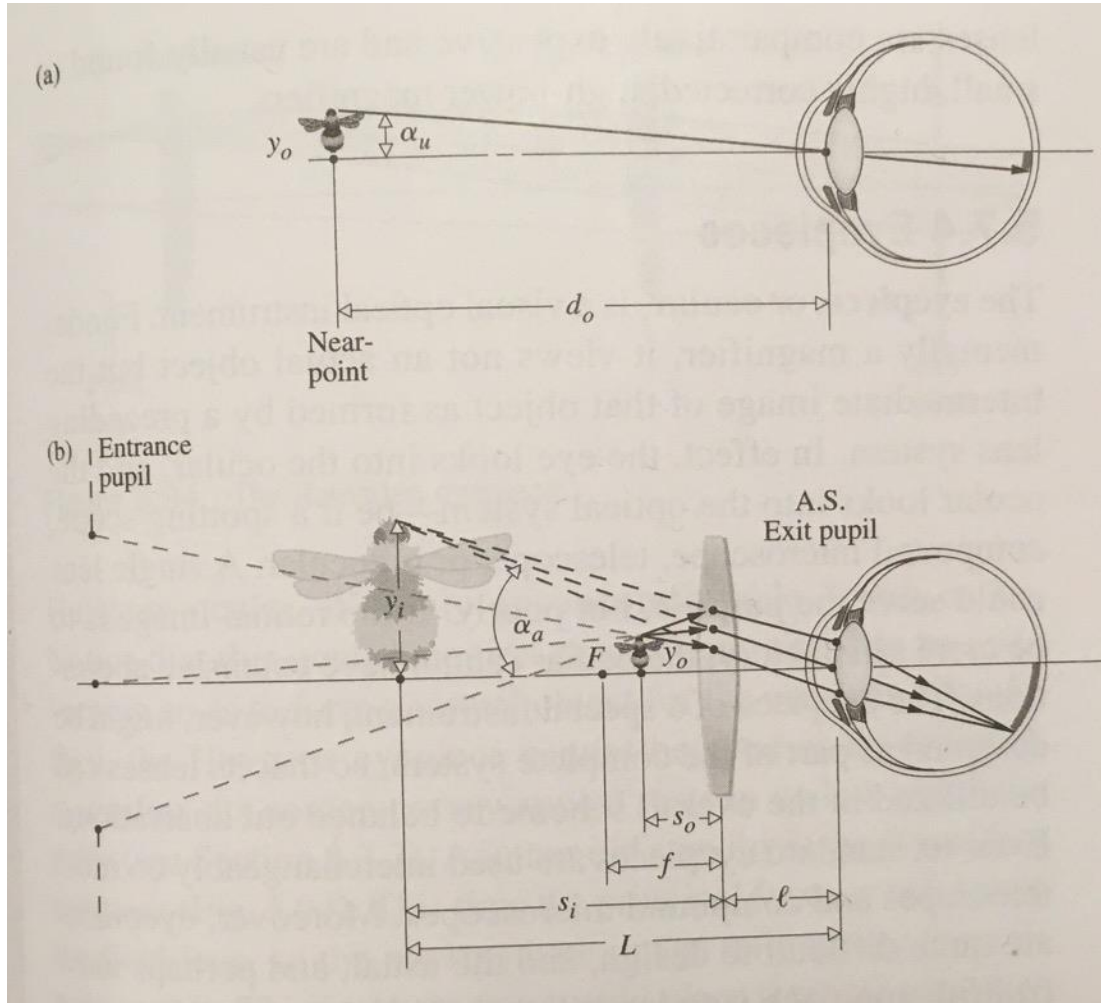


This makes laser radiation so dangerous to eye: parallel beams give perfect focus

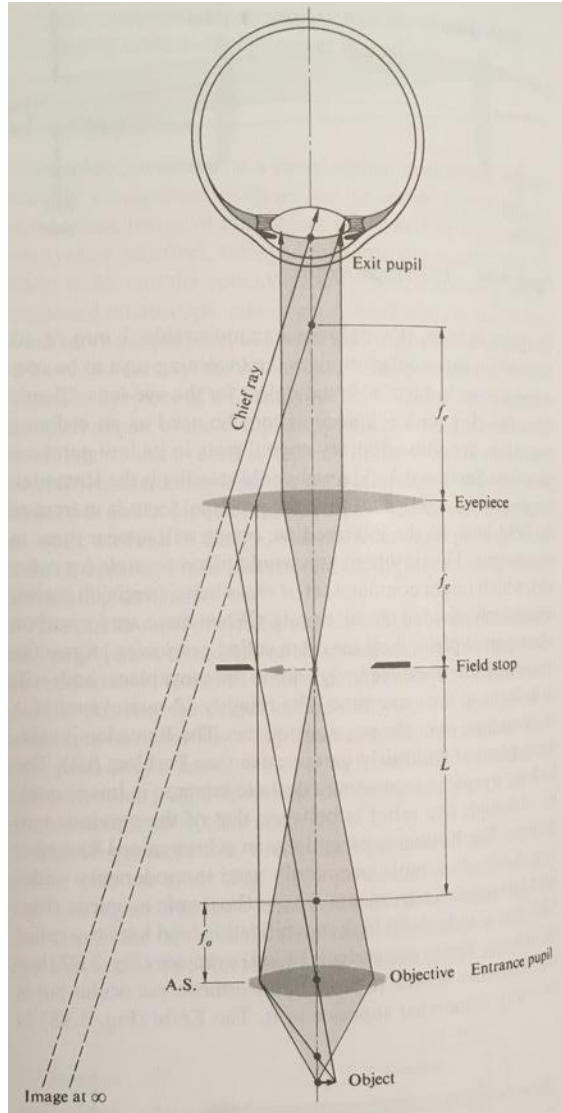
When designing optical systems (microscopes) need to consider eye as optical element.

Nowadays eye is typically replaced by camera which is also an imaging system.

# Magnifying glass: a simple optical element



# The microscope – a classical view



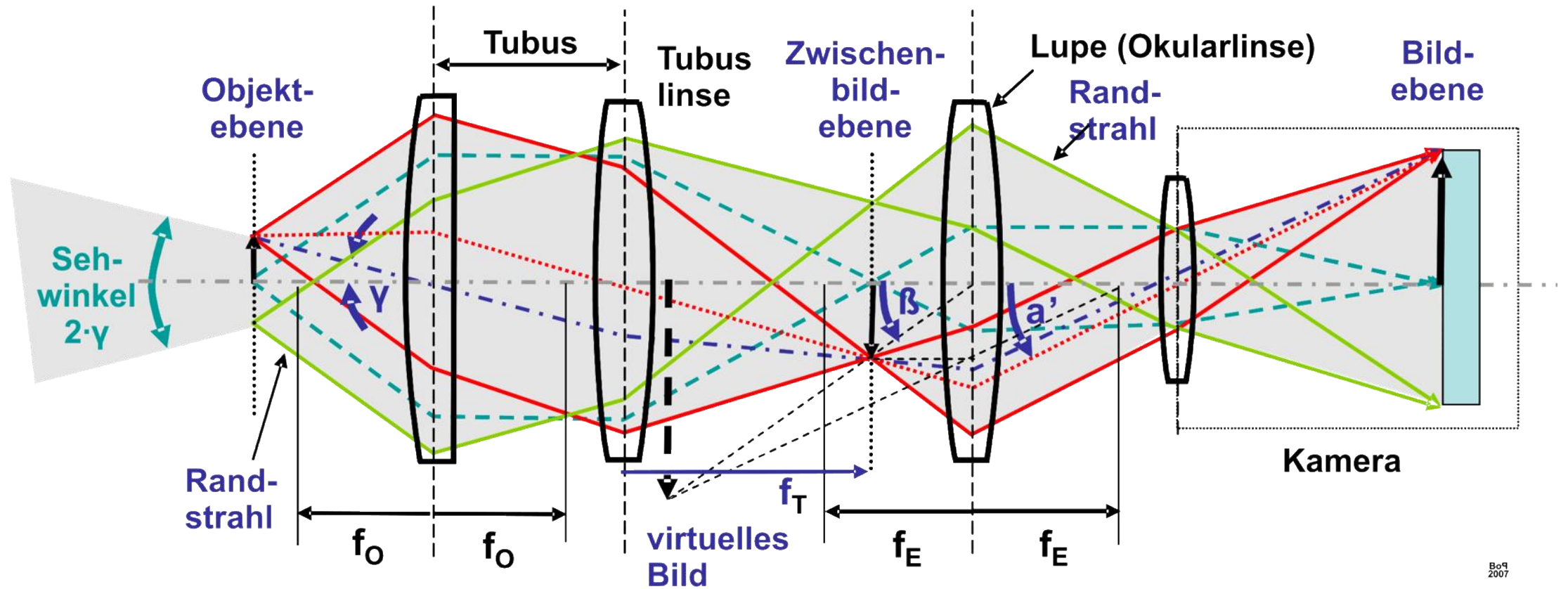
Principle:

Objective forms intermediate image

Eyepiece looks at and magnifies intermediate image

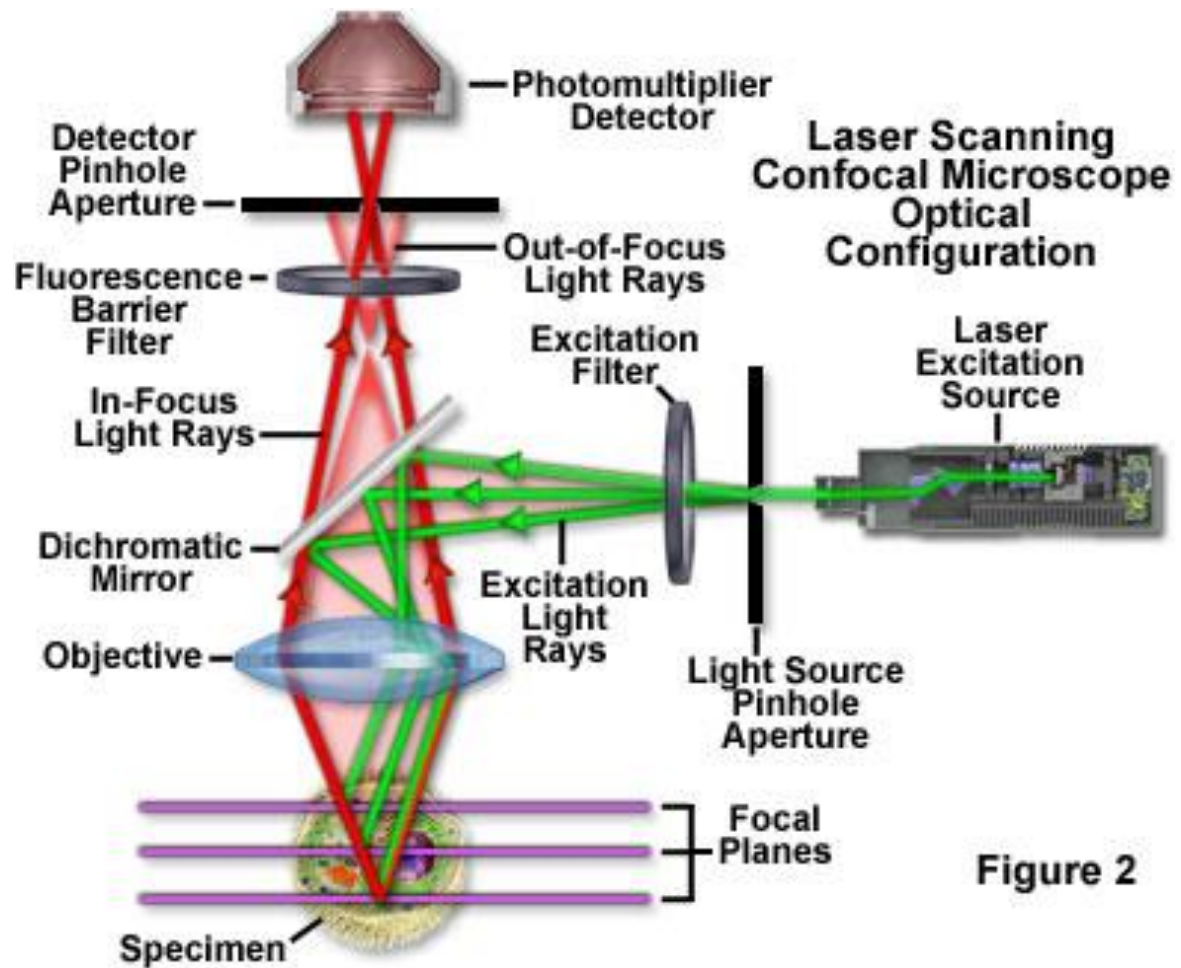
Magnification:

More extensive and more realistic schematic:





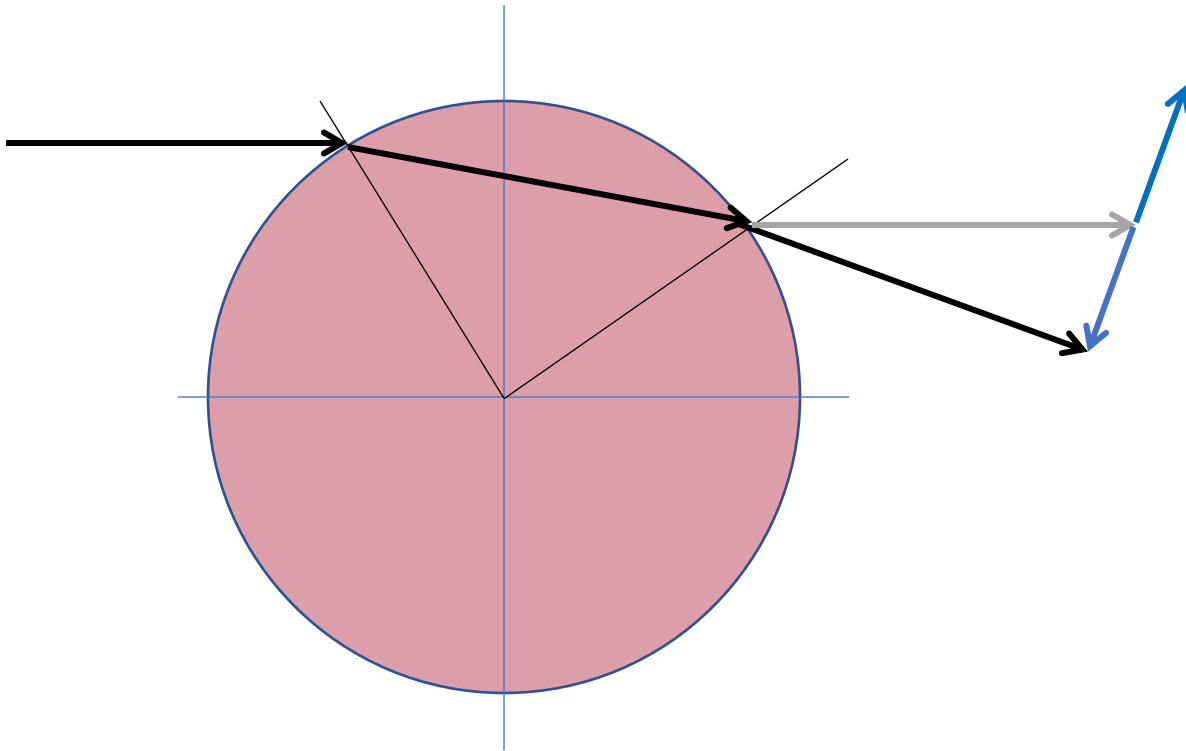
# Microscope variations: Confocal microscope



## Light going through a lens:

- Ray optics
- Momentum vectors

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



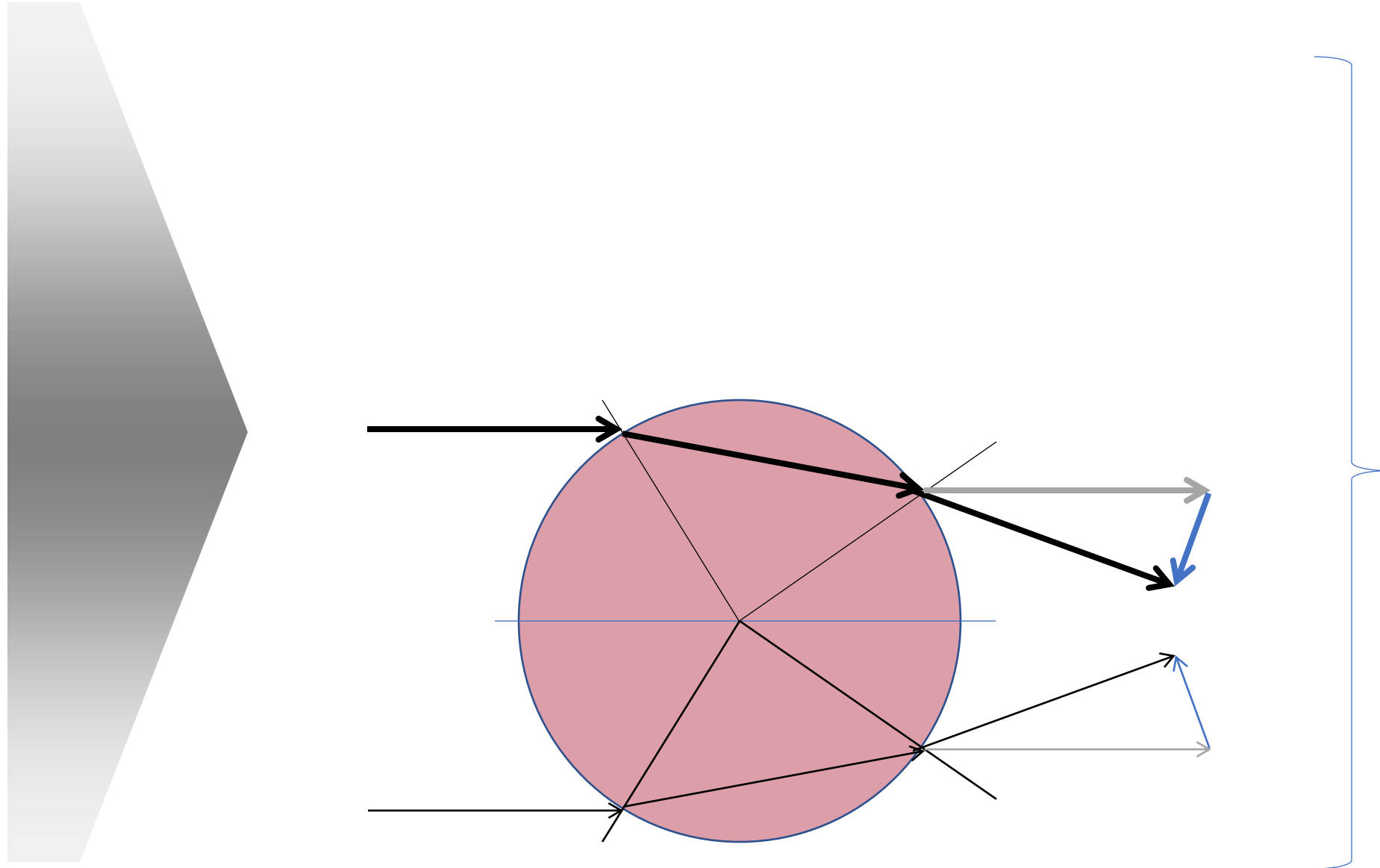
Some boundary conditions:

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

Process:

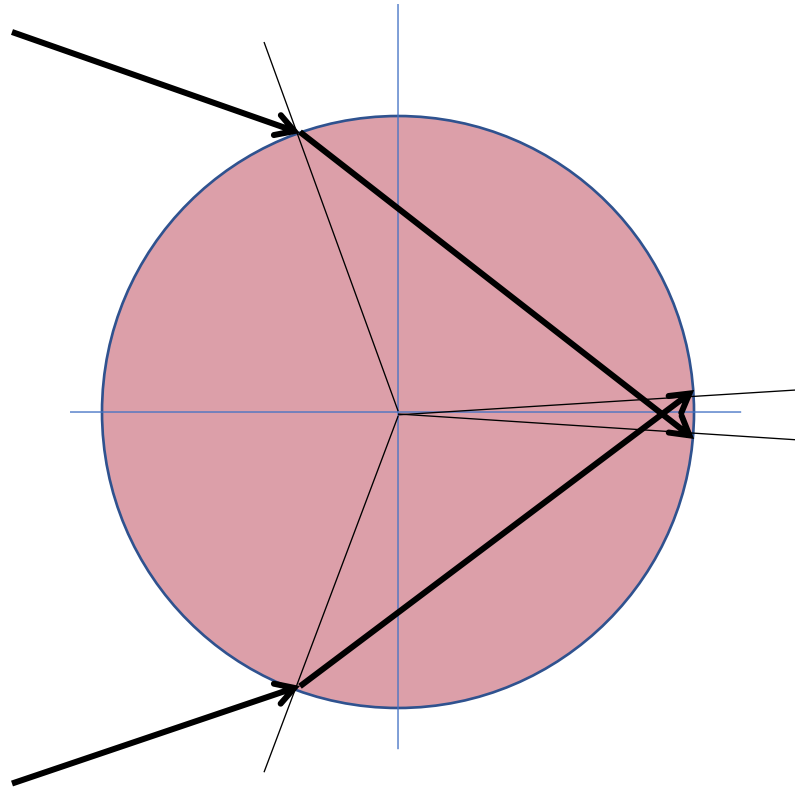
- Rays are refracted, leading to momentum change
- Action equals reaction, sphere is pushed .....wards
- With equal illumination there is.....

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

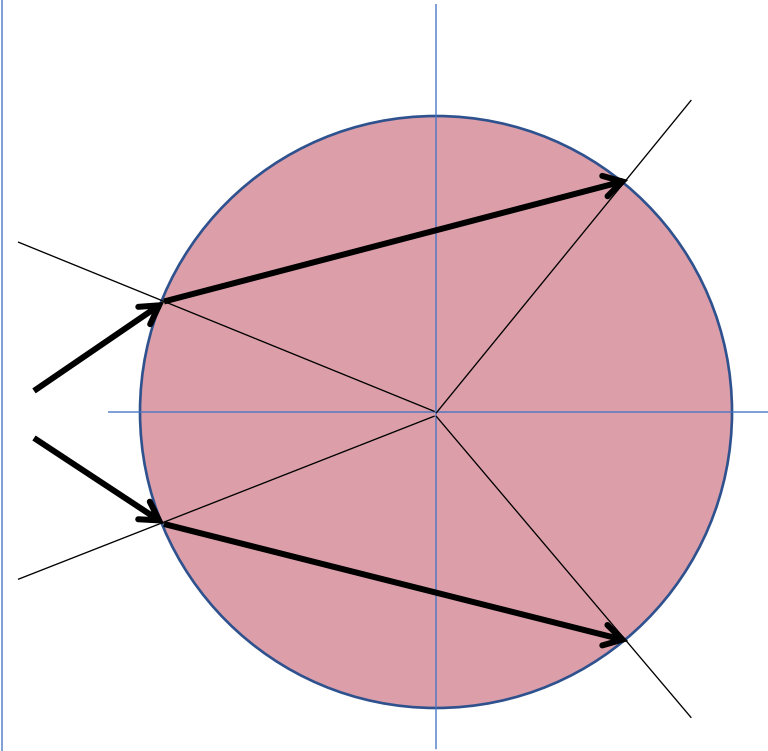


# Now before and after focus

Particle before to focus



Particle behind to focus



# Waves, wavefronts, interference and diffraction

## Postulate of wave optics

- Light propagates in the form of waves, in vacuum light travels with  $c_0$ .
- An homogenous transparent medium is characterized by a single constant, the refractive index  $n \geq 1$ . In the medium light travels with reduced speed  $c = c_0/n$ .
- An optical wave is described by a wave function  $u(r,t)$  at position  $r$  and time  $t$ .

## Wave function

The wave function satisfies the (partial) differential equation

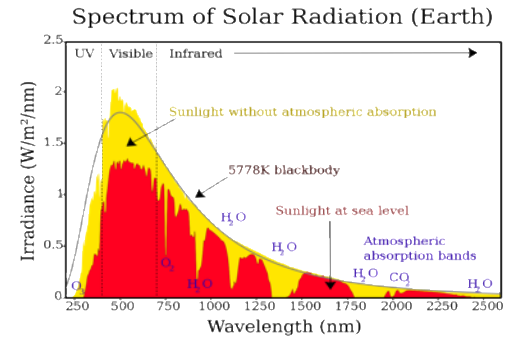
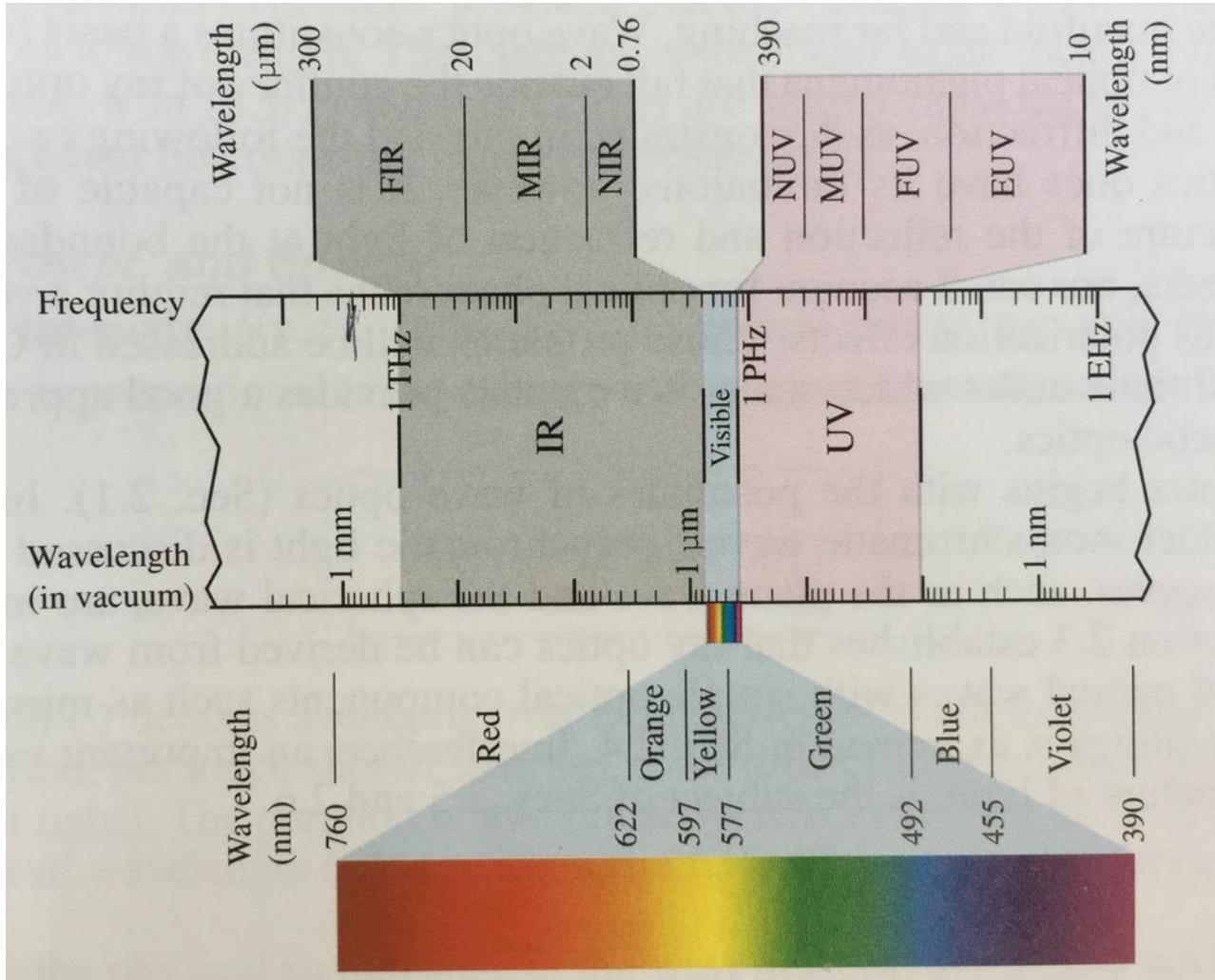
\_\_\_\_\_ Laplace operator in cartesian coordinates

The principle of superposition applies, i.e., if  $u_1$  and  $u_2$  are optical waves then

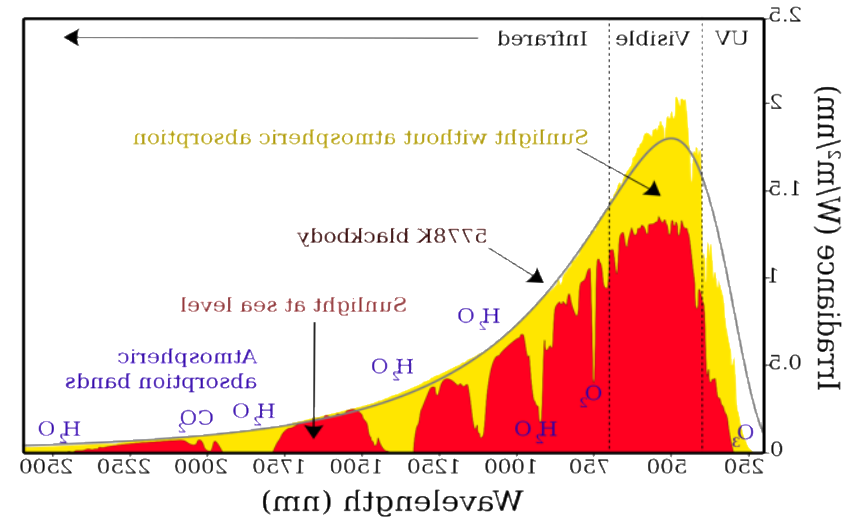
Also represents an optical wave



# Optical frequencies and wavelengths



Spectrum of Solar Radiation (Earth)



Source: wikipedia

## Optical intensity, power, energy

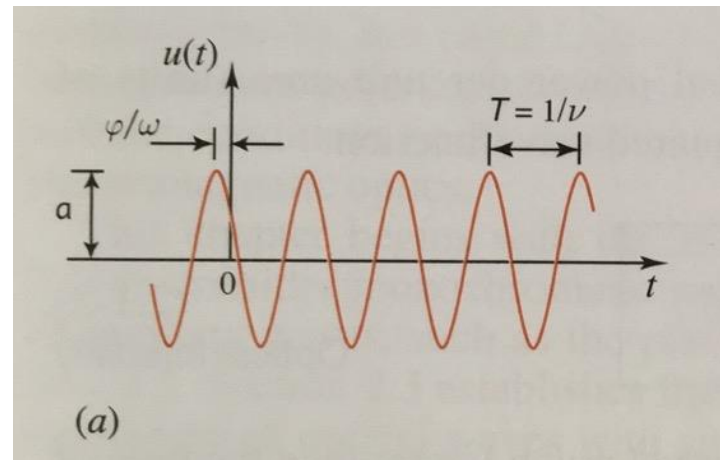
- The optical intensity  $I(r,t)$  is the optical power per unit area.
  - The unit is Watts/cm<sup>2</sup>
  - average of the squared wave function.
  
- The optical power (in units of Watts) flowing into an area  $A$  normal to the direction of propagation is the integrated intensity
  
- The optical energy (in units of Joules) in a given time interval is the integral of the optical power over the time interval

## Simple example: Monochromatic wave

- For a monochromatic wave the, the wave function reduces to

With:

- The amplitude and phase are generally position dependent
- Representation of a monochromatic wave



## Simple example: Monochromatic wave but as complex wave function

- A monochromatic wave can be explained by complex wave function

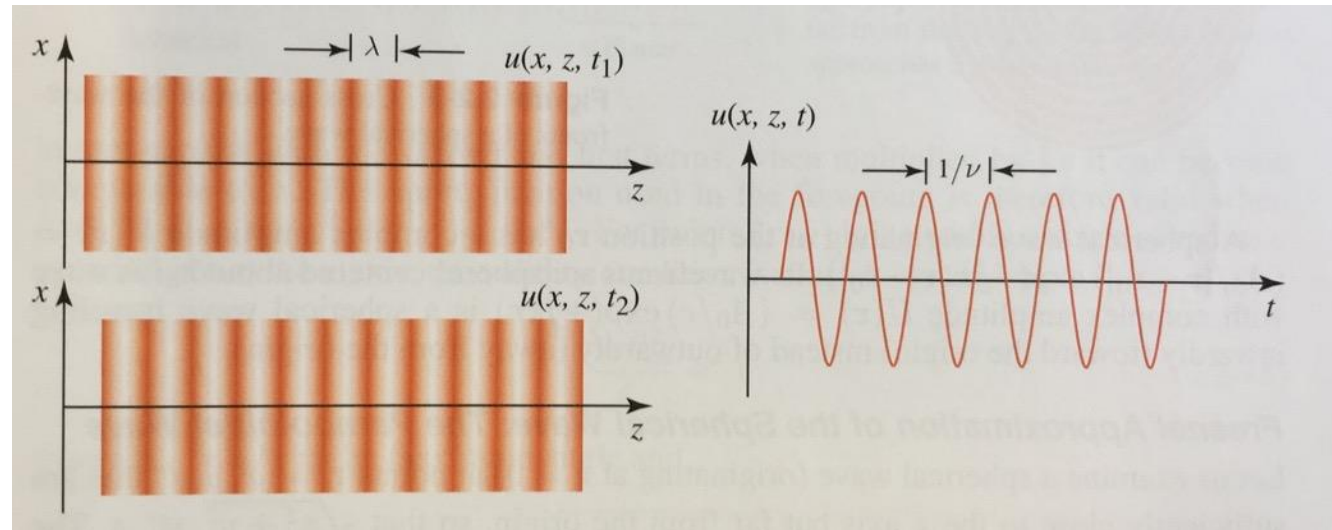
- This general description satisfies the

Helmholtz equation:

With wavenumber  $k =$

- Note intensity:
  - Monochromatic wave intensity is (complex amplitude)<sup>2</sup>
  - Intensity does not vary in time
- Note: Wavefronts are surfaces of equal phase

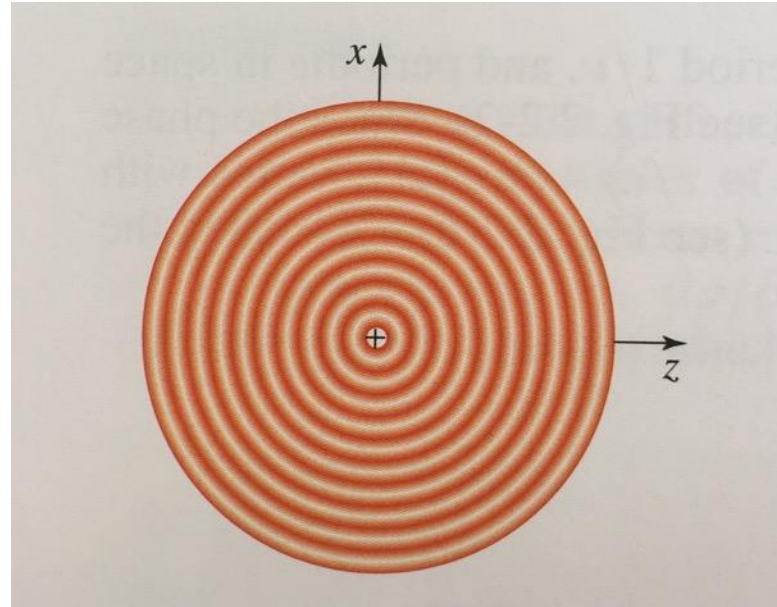
## Special case: plane wave



Plane waves: wavefronts are parallel planes perpendicular to  $\mathbf{k}$  and separated by  $\lambda$

For graphical animations visit [https://en.wikipedia.org/wiki/Sinusoidal\\_plane\\_wave](https://en.wikipedia.org/wiki/Sinusoidal_plane_wave)

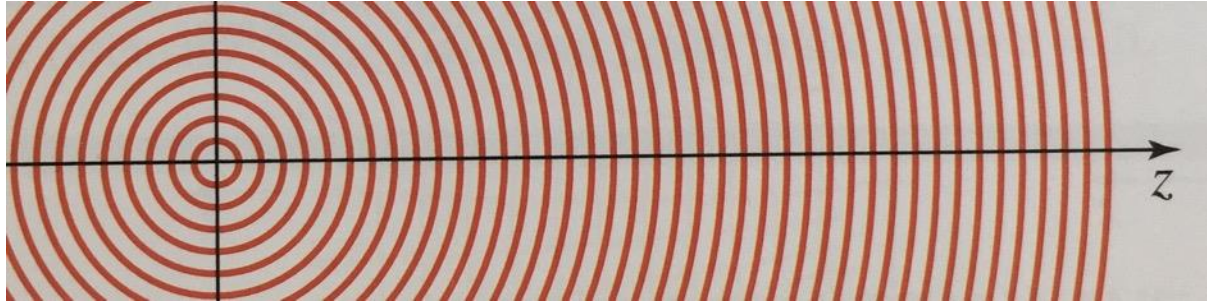
## Special case: spherical wave



Spherical waves: wavefronts are concentric spheres separated by  $\lambda=2\pi/k$

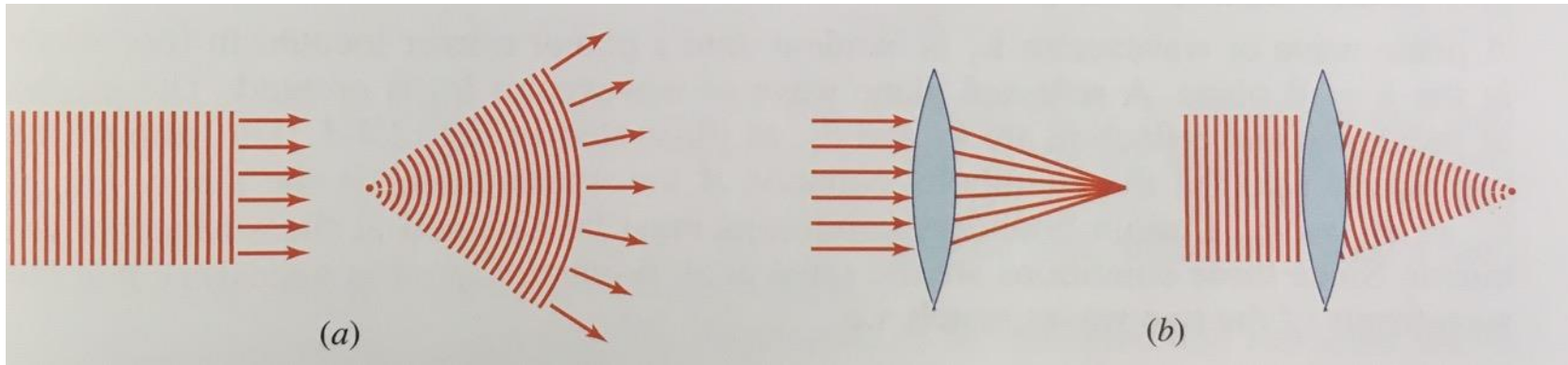
For graphical animations visit [https://en.wikipedia.org/wiki/Wave\\_equation#Spherical\\_waves](https://en.wikipedia.org/wiki/Wave_equation#Spherical_waves)

## Special case: Fresnel approximation



- Spherical wave close to z-axis but far away from origin

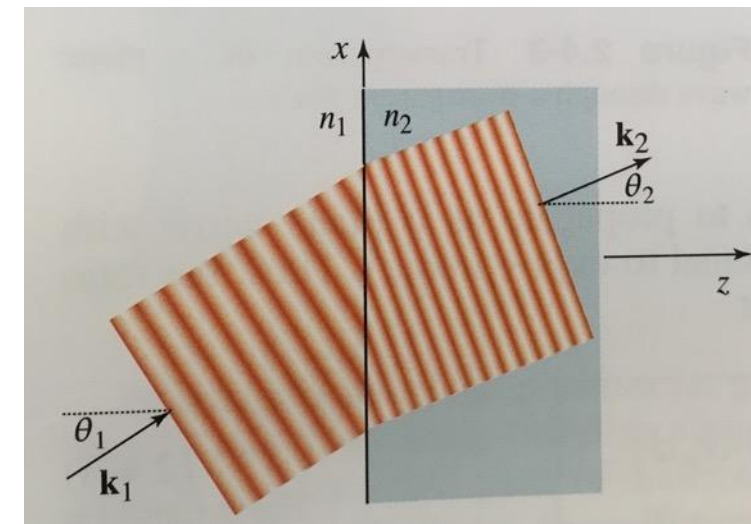
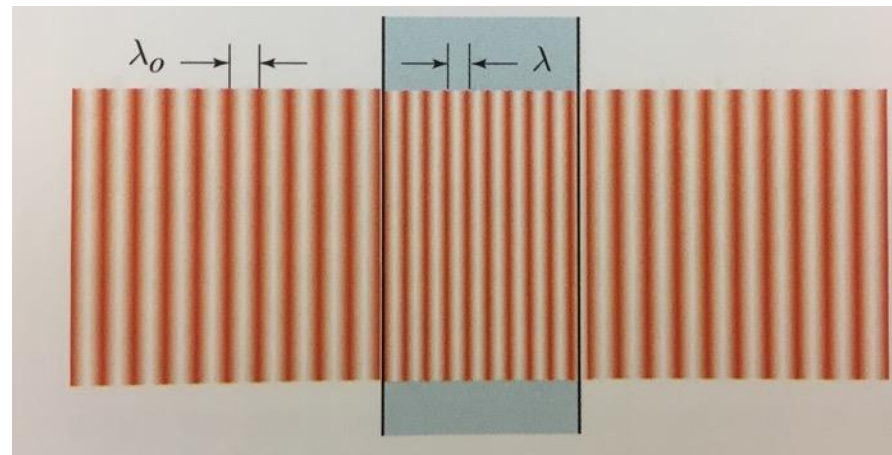
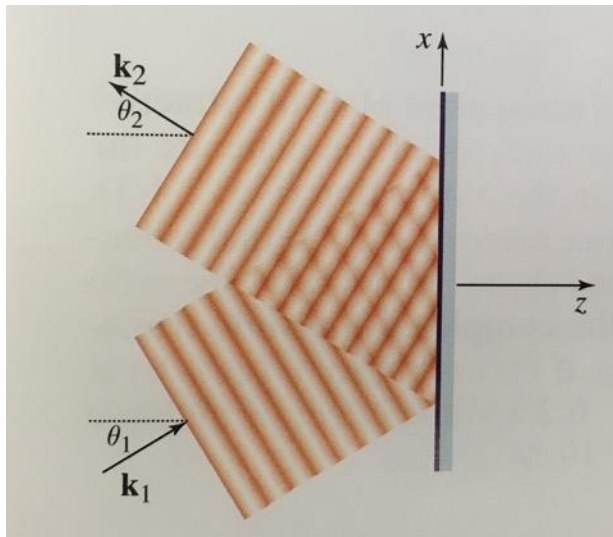
# From ray to wave optics



What happens after focal point?



# Wave optics and simple optical components



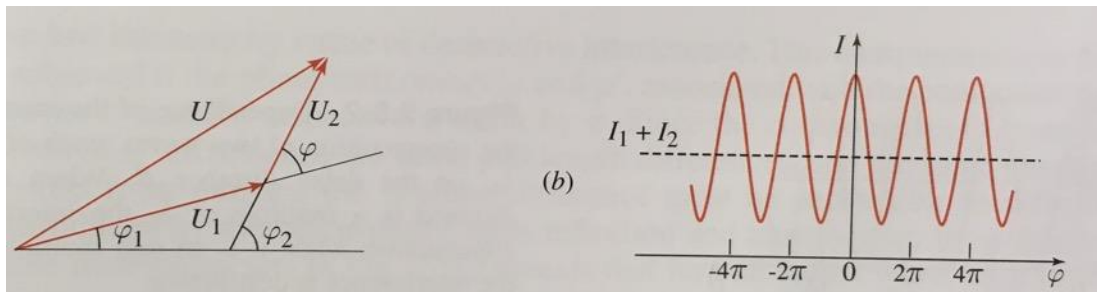
## Interference of two waves

When two monochromatic waves with complex amplitudes  $U_1$  and  $U_2$  are superimposed, the result is a monochromatic wave of the same frequency that has a complex amplitude

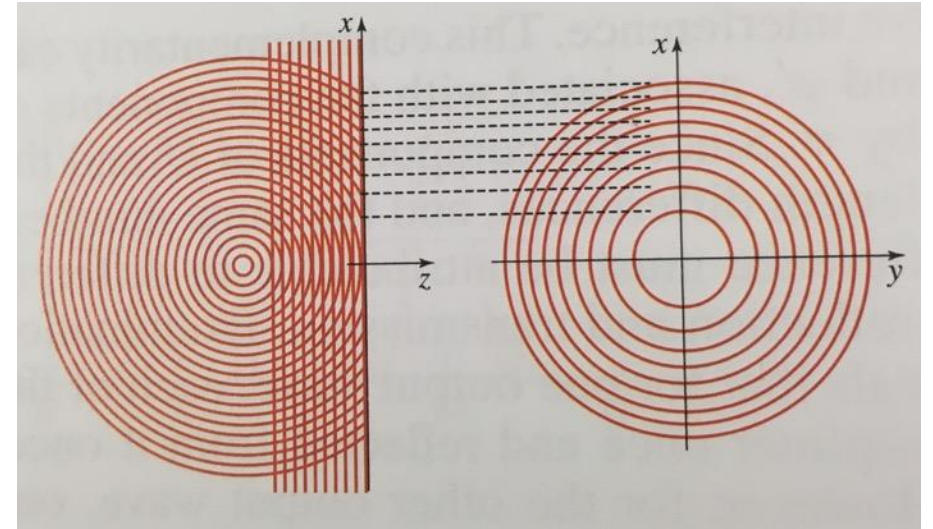
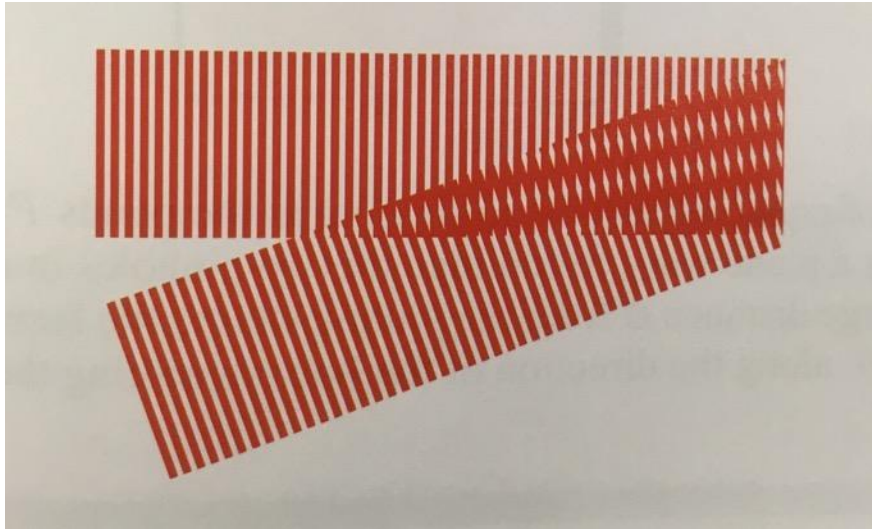
$$U(r) = U_1(r) + U_2(r)$$

The intensity of the resulting wave is:

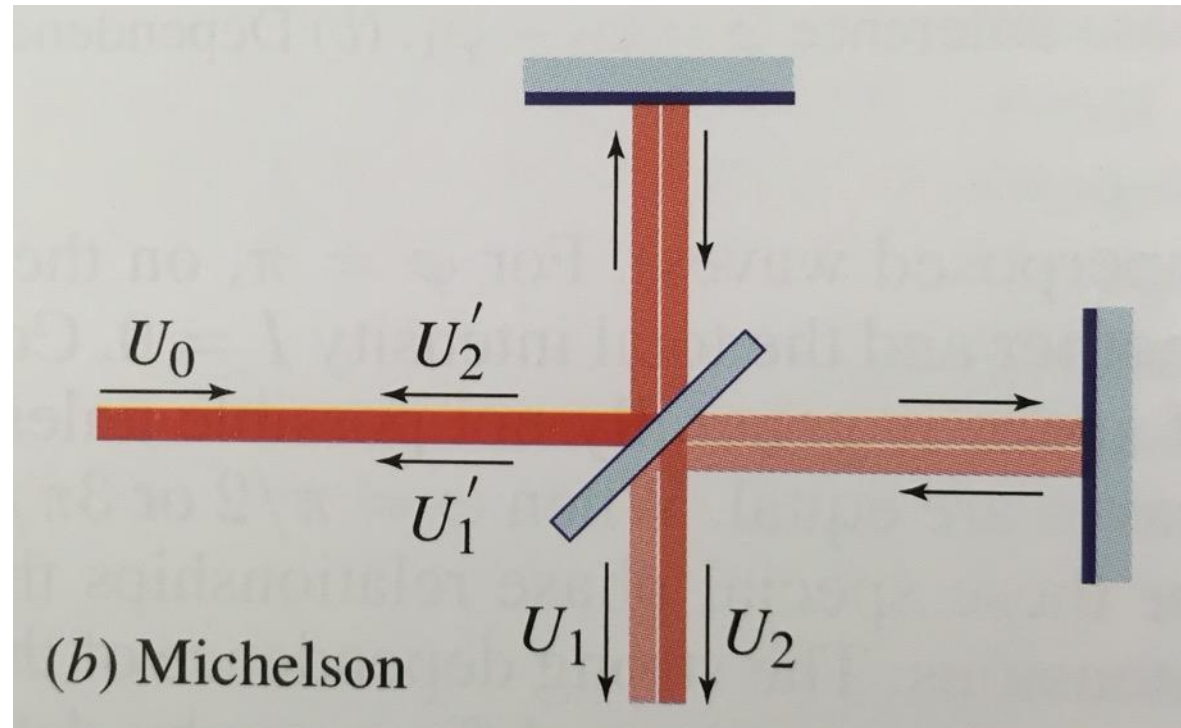
Resulting in the interference equation:



# Interference: Some examples



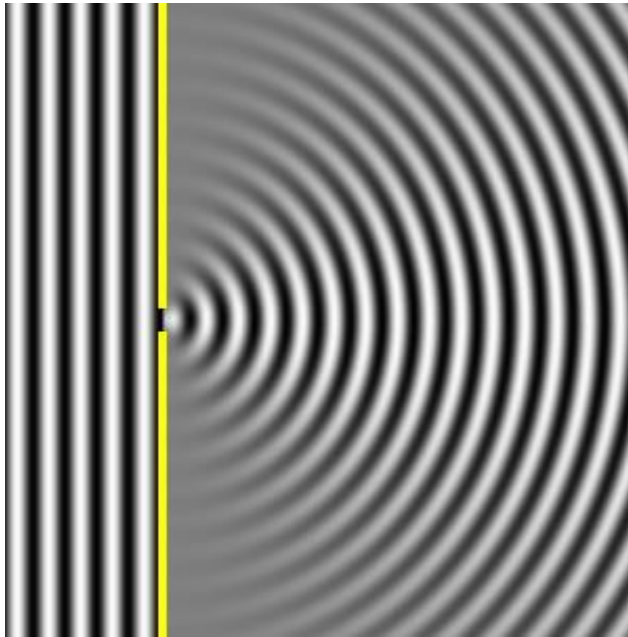
## Interferometer, example Michelson



Nice demonstration: <https://www.youtube.com/watch?v=j-u3IEgcTiQ>

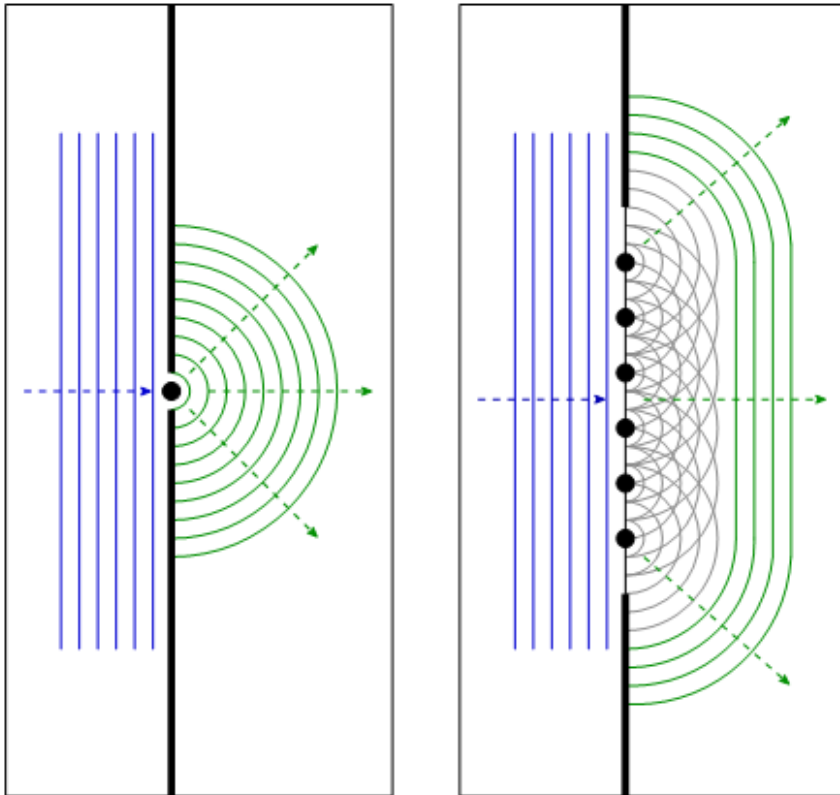
# The Huygens-Fresnel Principle

- Hugen: every point a wave (a luminous disturbance) reaches becomes a source of a spherical wave; the sum of these secondary waves determines the form of the wave at any subsequent time.
- Huygens-Fresnel: every unobstructed point of a wavefront serves as a source of spherical secondary wavelets. The amplitude of the wave beyond is the superposition of all these wavelets. (includes amplitude and relative phase)

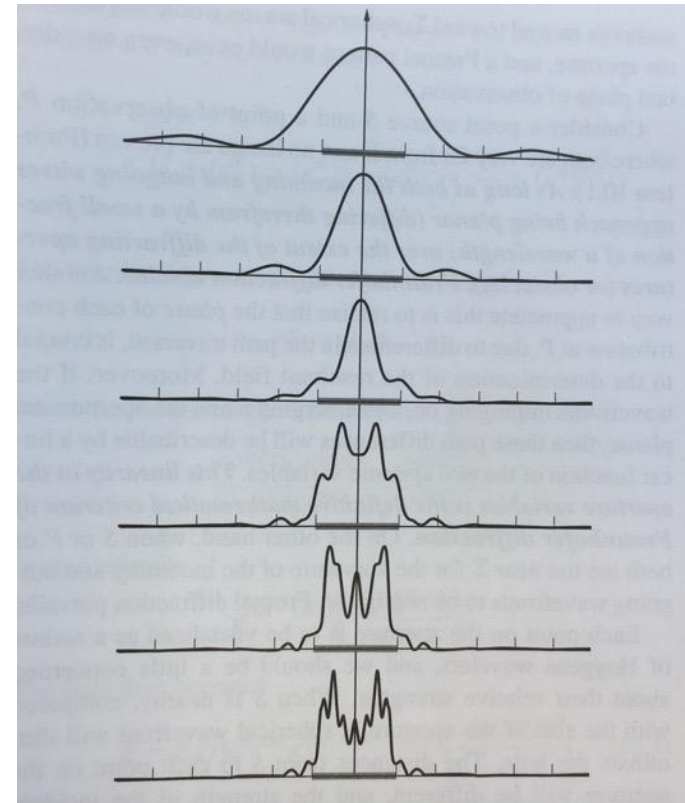


# Wavefronts behind slit

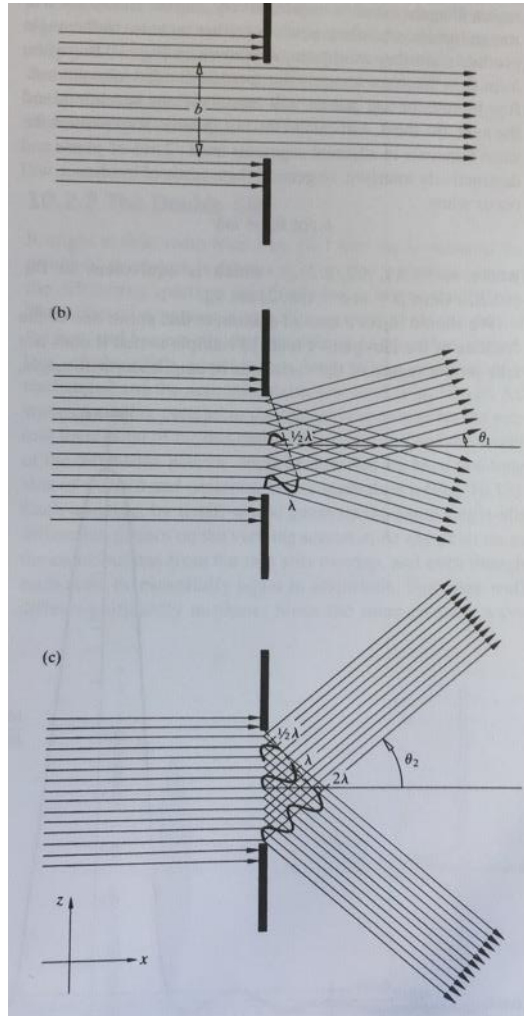
Small vs. real slit



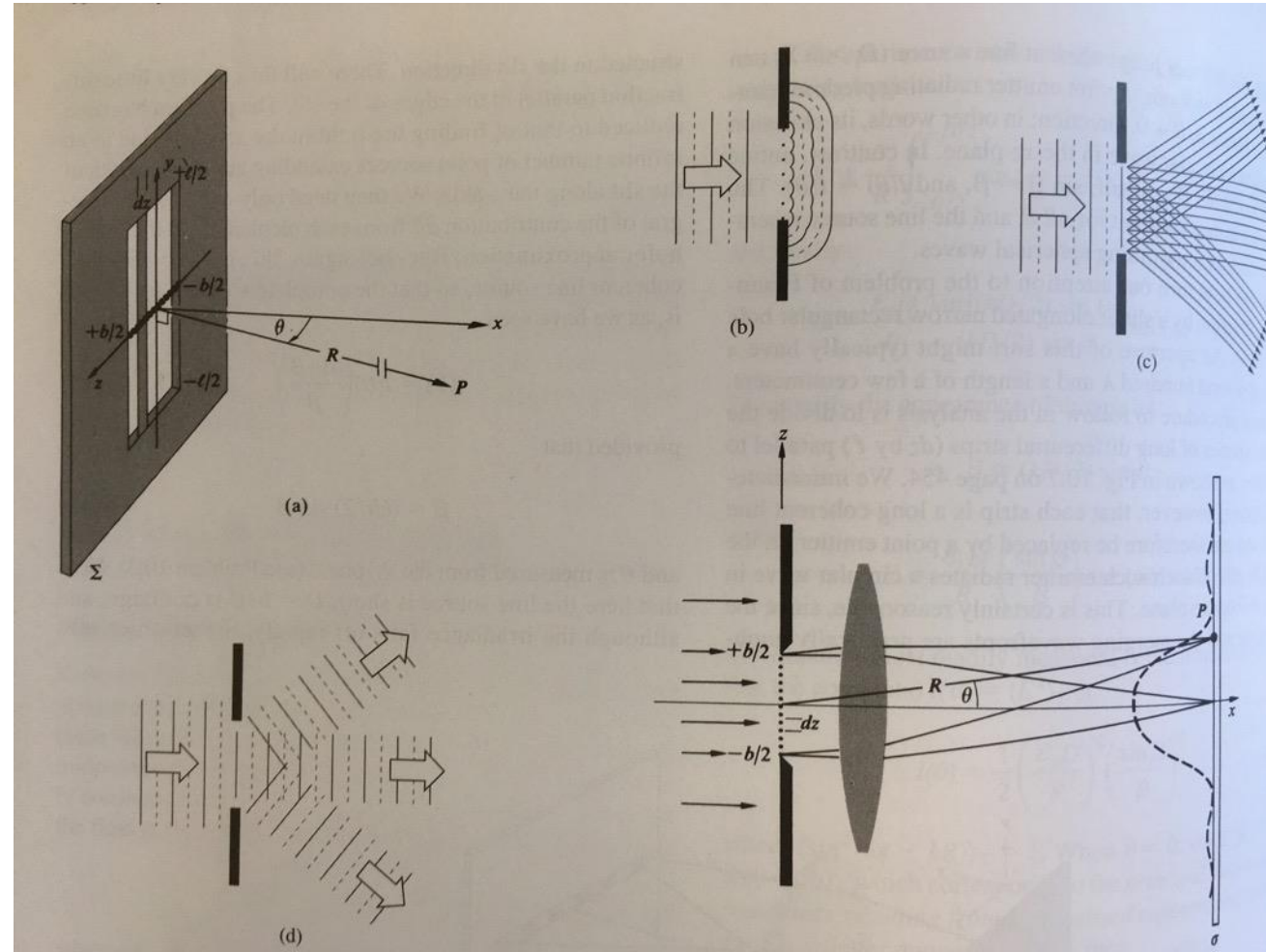
Fresnel and Fraunhofer regime



# Different views on Fraunhofer Diffraction ( $R \gg D$ ) for single slit

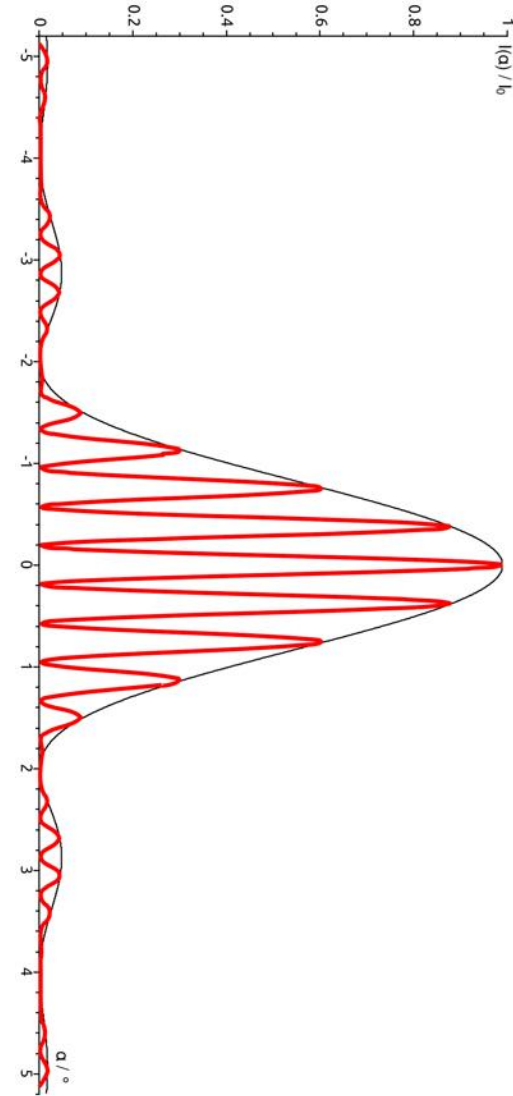
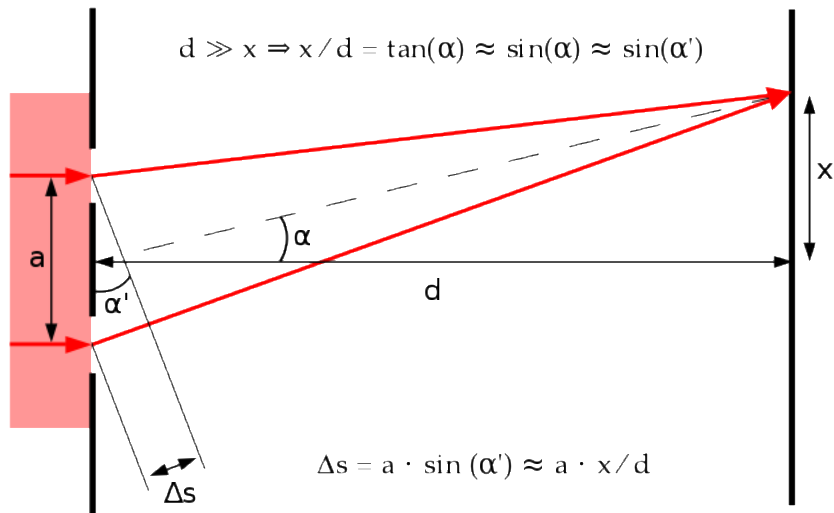


# Different views on Fraunhofer Diffraction ( $R \gg D$ ) for single slit



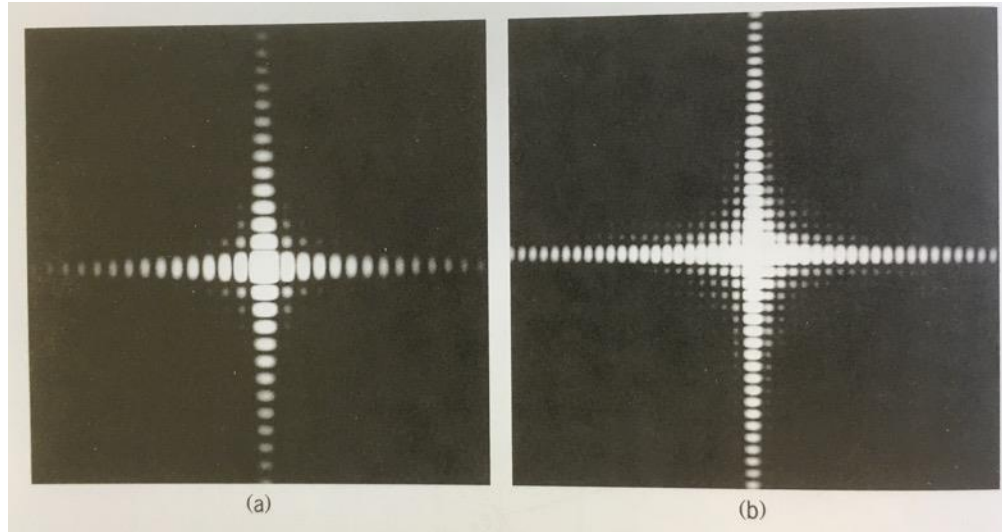


# Now the double slit

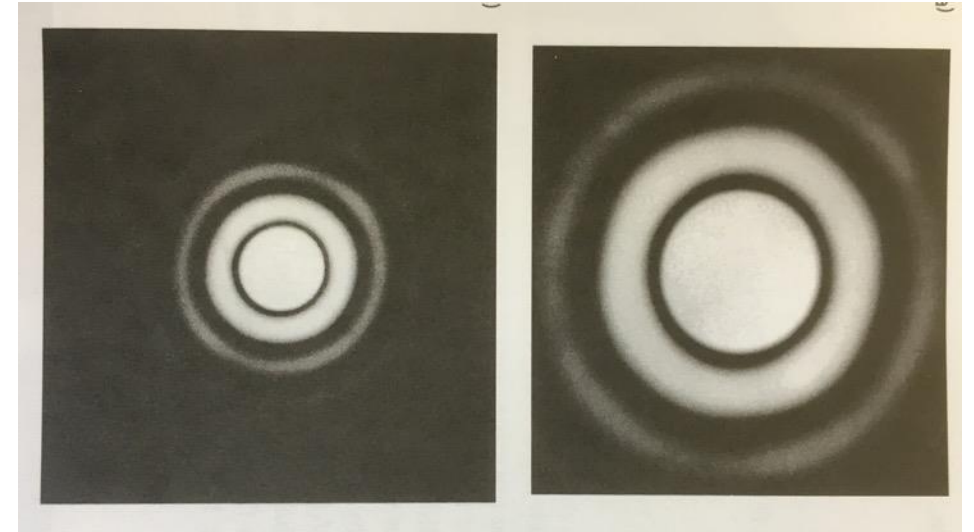


# Diffraction pattern of 2D objects – 2 examples

Square aperture



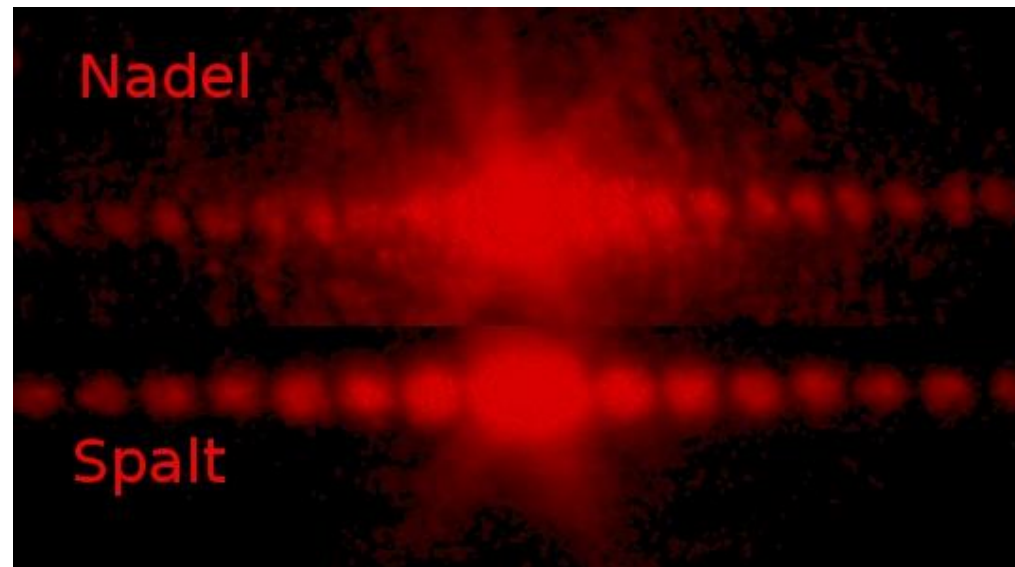
Round aperture



## Note: Babinet's principle

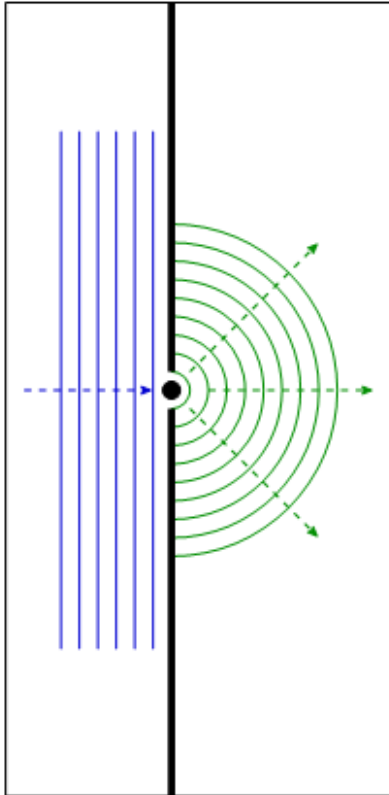
The diffraction pattern of an opaque body is identical to the one of a hole of the same size and shape except in the forward direction.

Example:

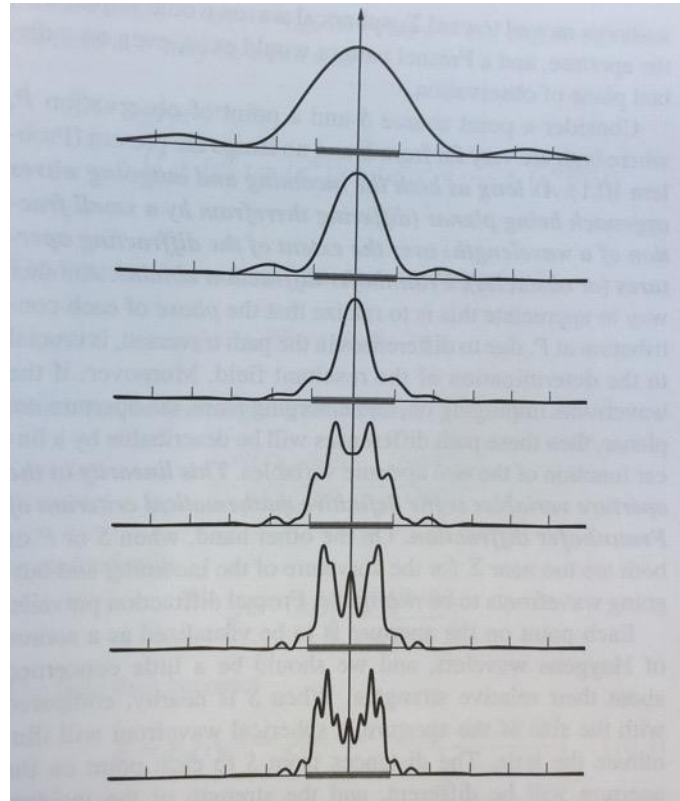


# Resolution limit of a classical optical apparatus: Remember Huygens Fresnel principle, diffraction at a slit, Airy rings

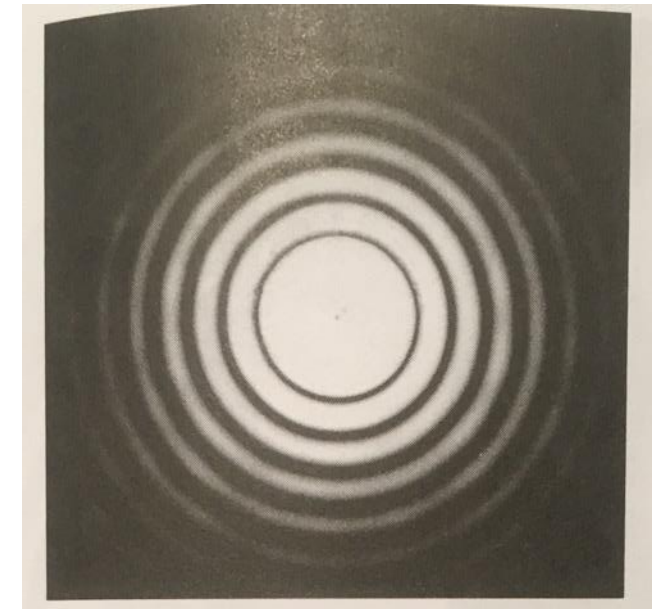
Diffraction at slit / aperture



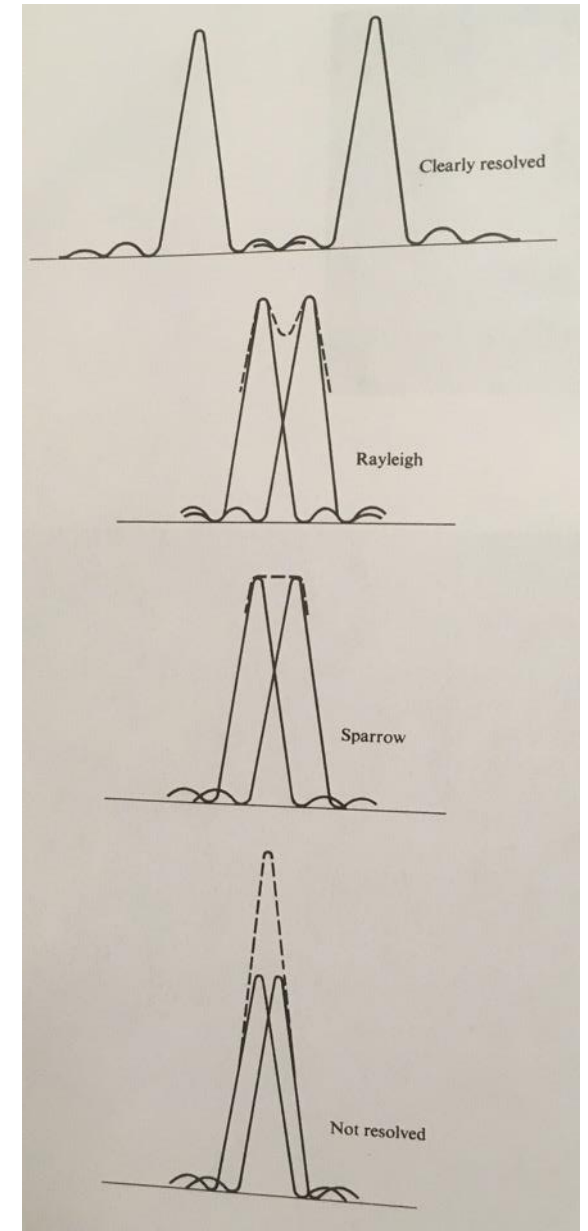
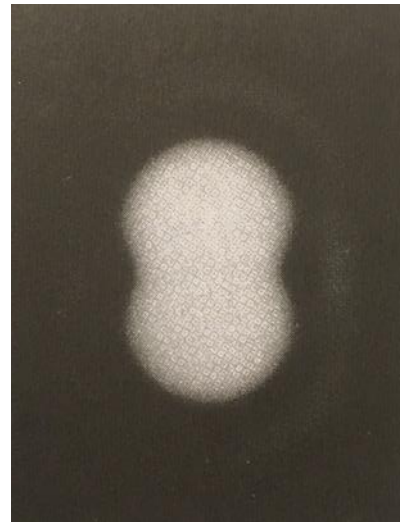
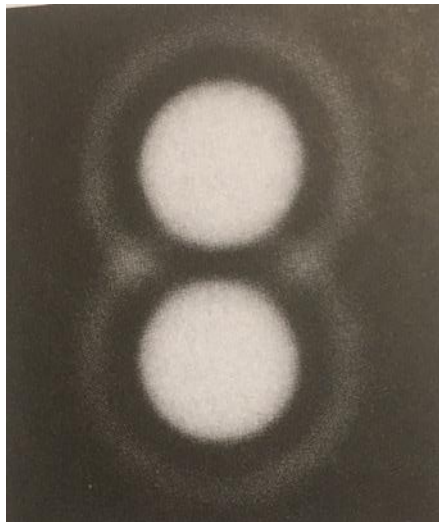
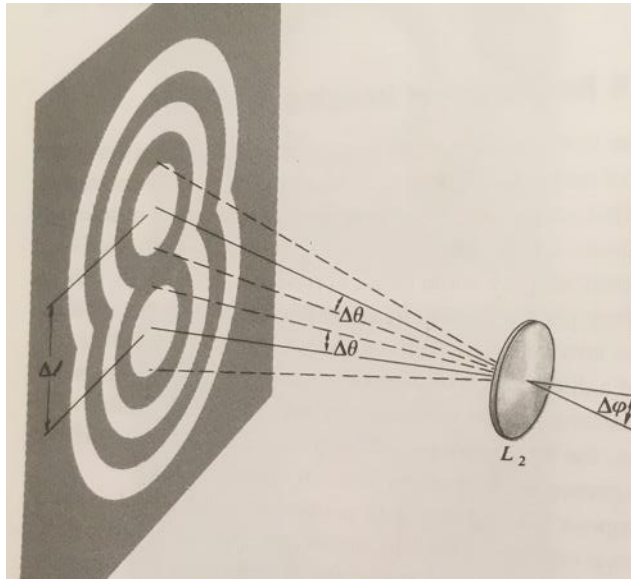
Fresnel and Fraunhofer regime



Airy rings of circular aperture



# Resolution limit of a classical optical apparatus



# Beam optics

## Gaussian beam III

- $U(\mathbf{r})$  is called a Gaussian beam

$$U(\mathbf{r}) = A_0 \frac{W_0}{W(z)} \exp\left[-\frac{\rho^2}{W^2(z)}\right] \exp\left[-jkz - jk\frac{\rho^2}{2R(z)} + j\zeta(z)\right]$$

- With the following parameters

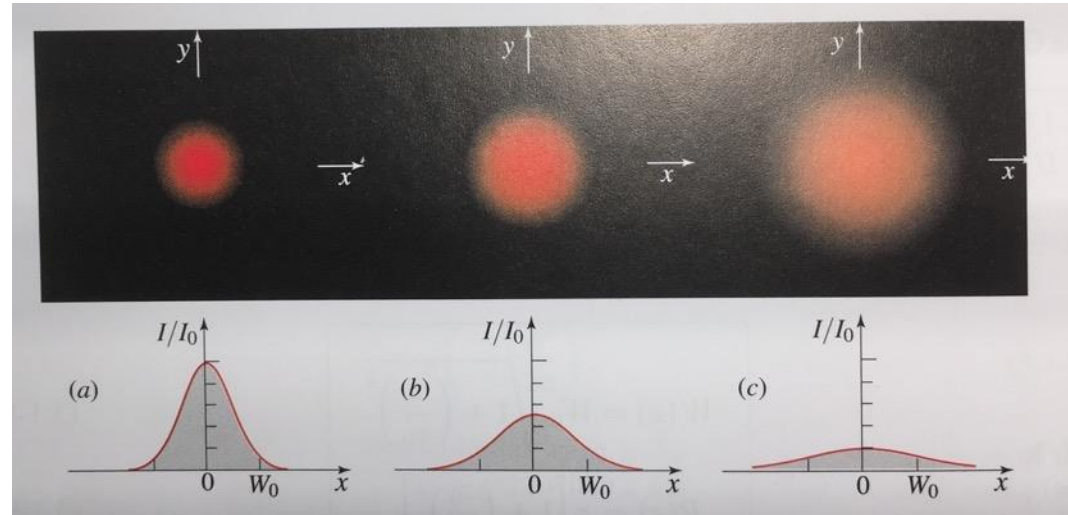
$$W(z) = W_0 \sqrt{1 + \left(\frac{z}{z_0}\right)^2}$$

$$R(z) = z \left[1 + \left(\frac{z_0}{z}\right)^2\right]$$

$$\zeta(z) = \tan^{-1} \frac{z}{z_0}$$

$$W_0 = \sqrt{\frac{\lambda z_0}{\pi}}$$

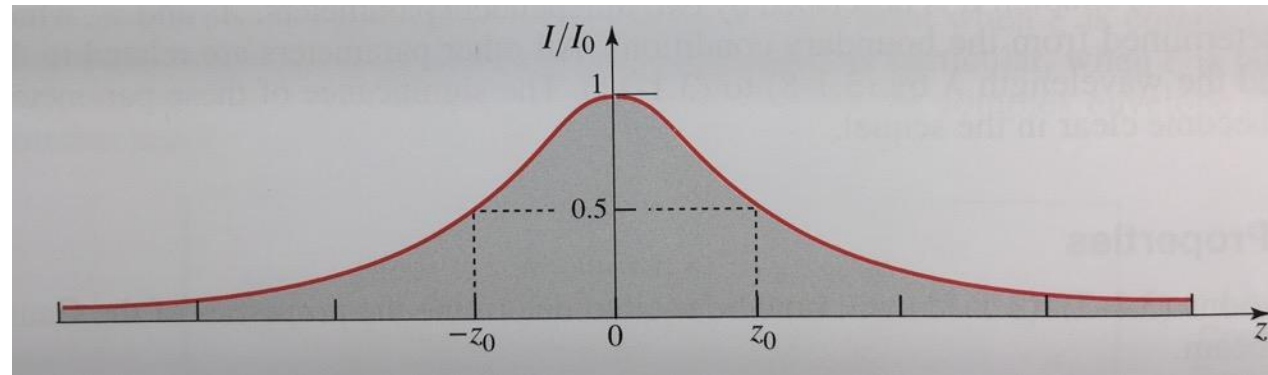
Parameter: Intensity as function of radial distance



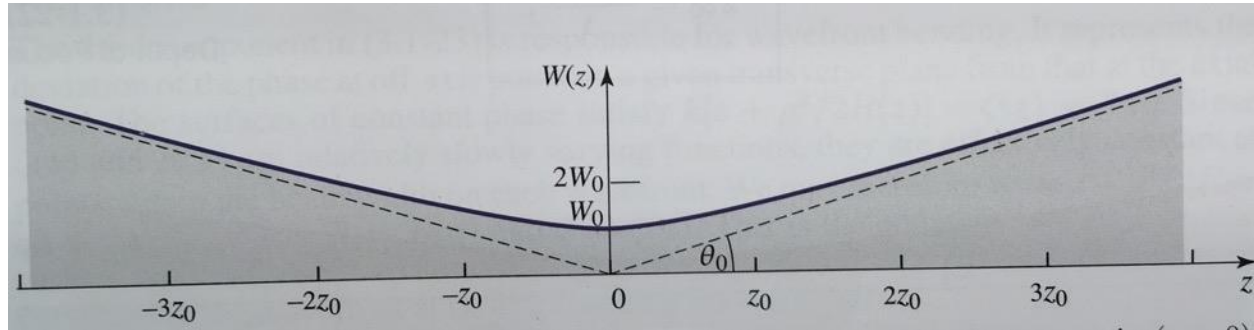
Once a Gaussian – always a Gaussian!



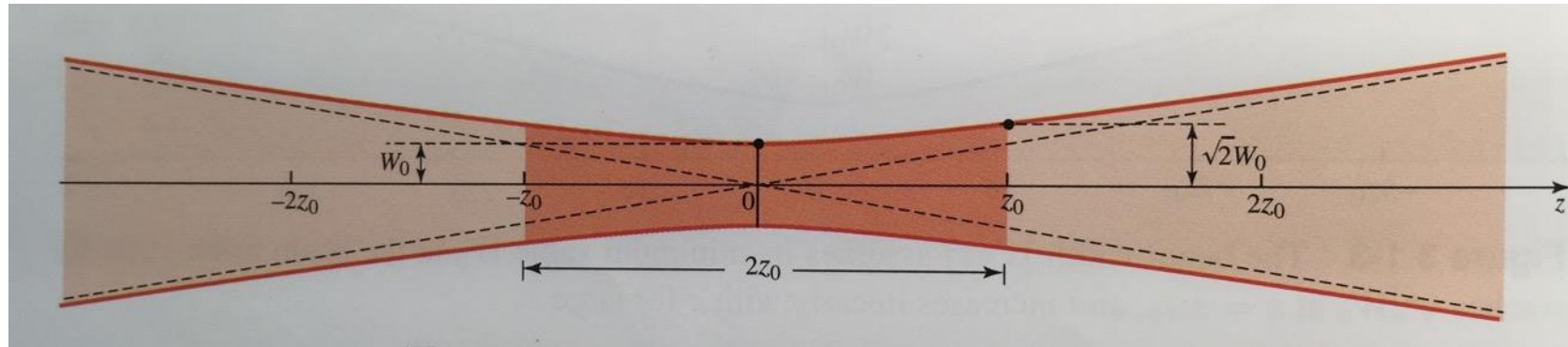
Parameter: Intensity on beam axis



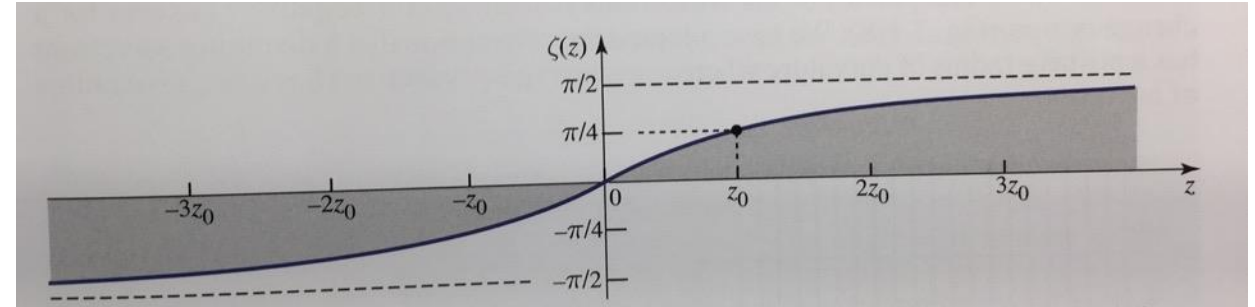
Parameter: Beam waist



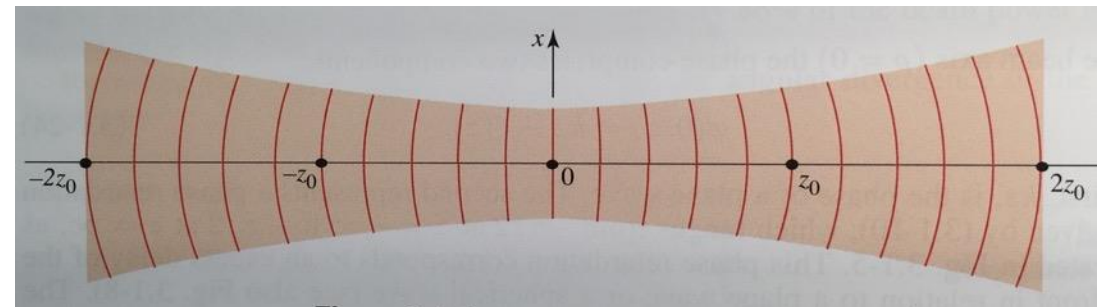
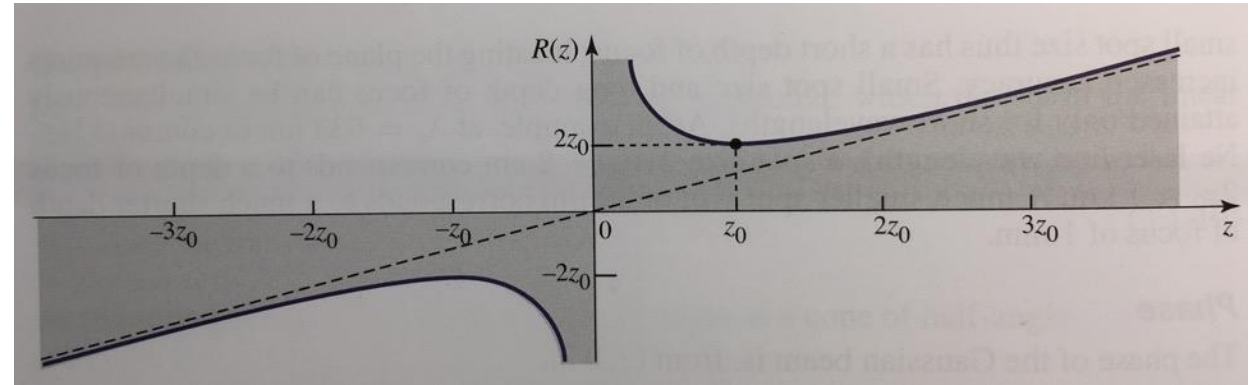
Parameter: Depth of focus



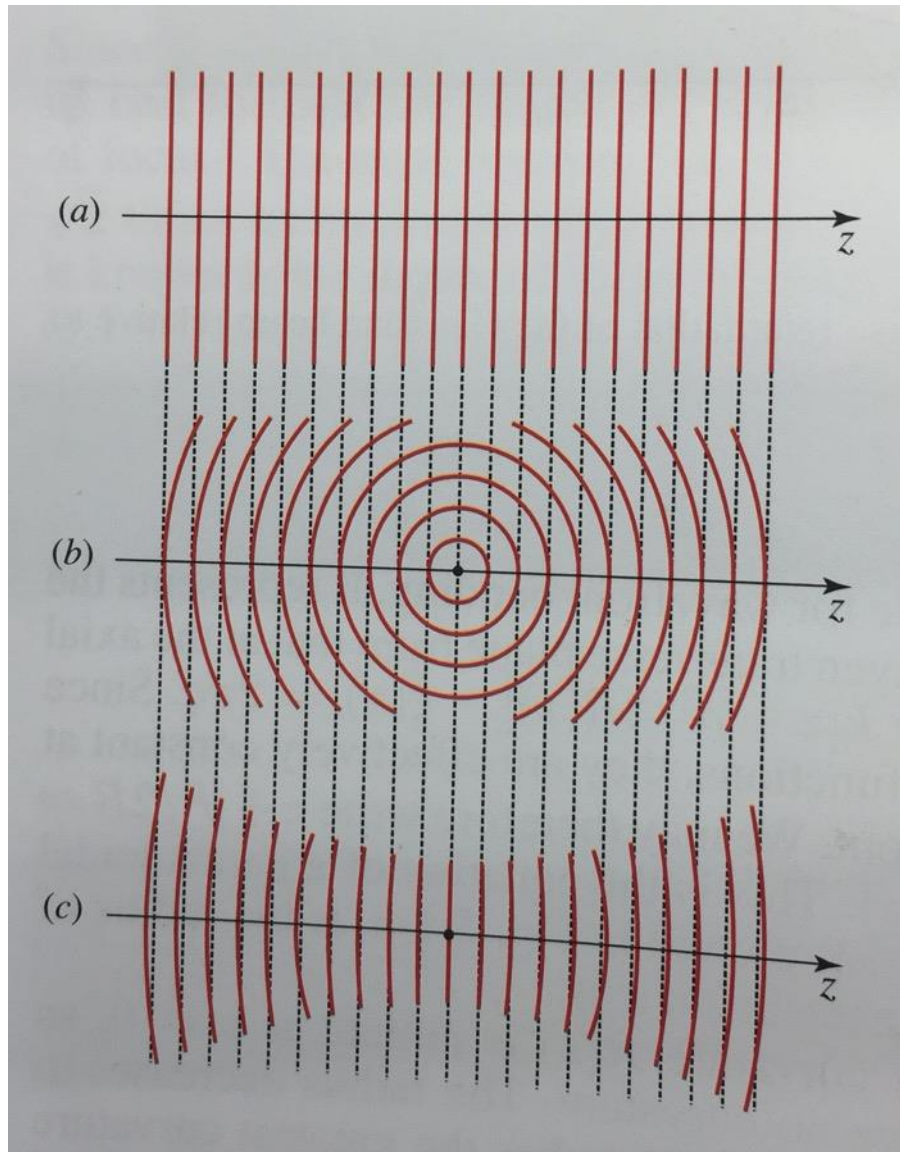
# Parameter: Phase



# Parameter: Curvature of wavefront

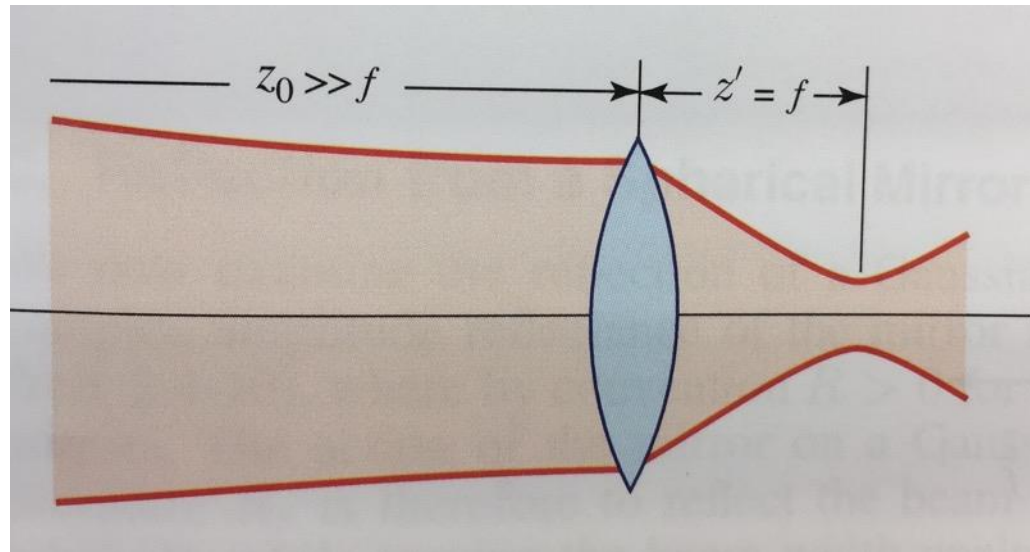


# Comparison: plane wave, spherical wave, Gaussian beam

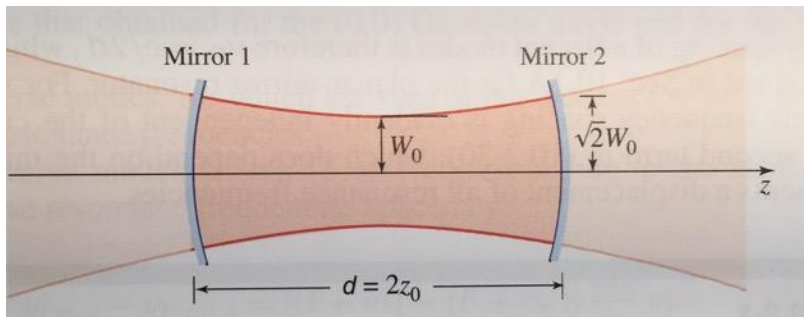
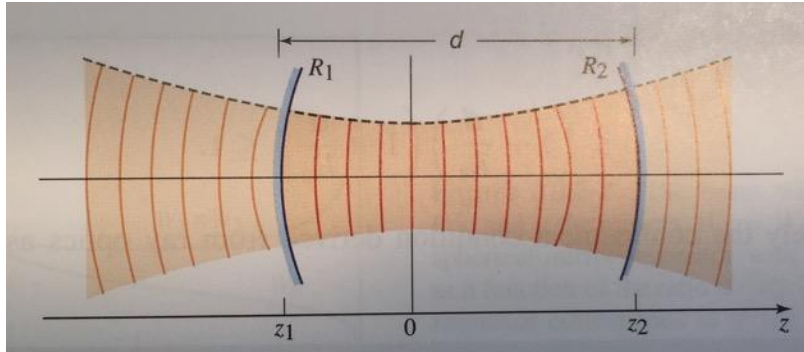


## Some statements to remember

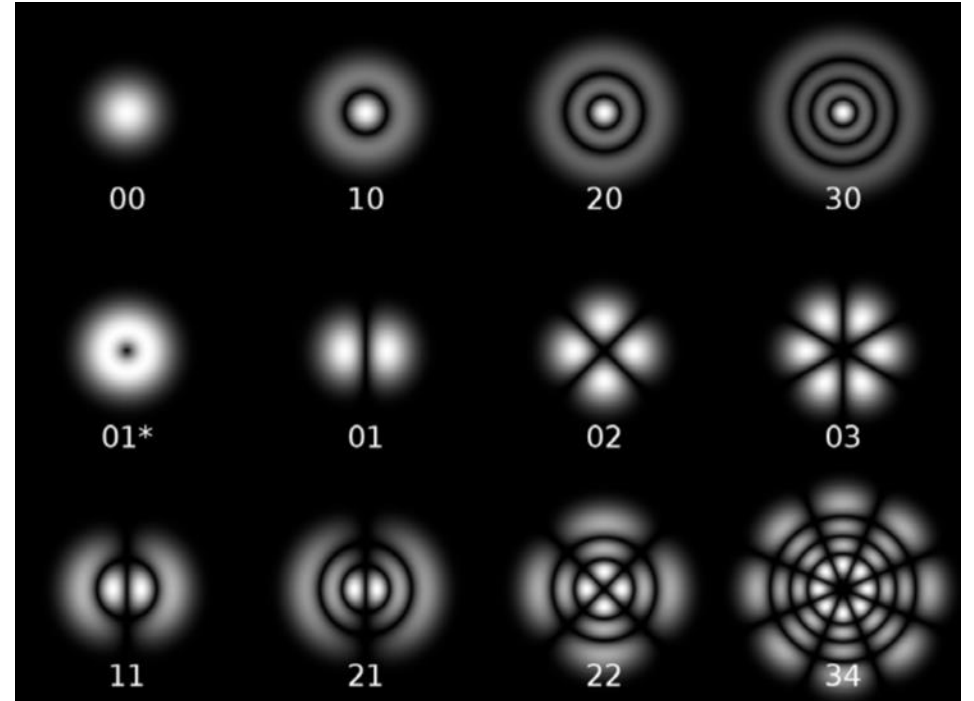
- A Gaussian beam transmitted through a circularly symmetric optical component remains a Gaussian beam
- Such optical components reshape the beam, i.e., its waist and curvature
- Focusing a collimated Gaussian beam:



# Gaussian Beam Resonator



## Laguerre-Gaussian modes

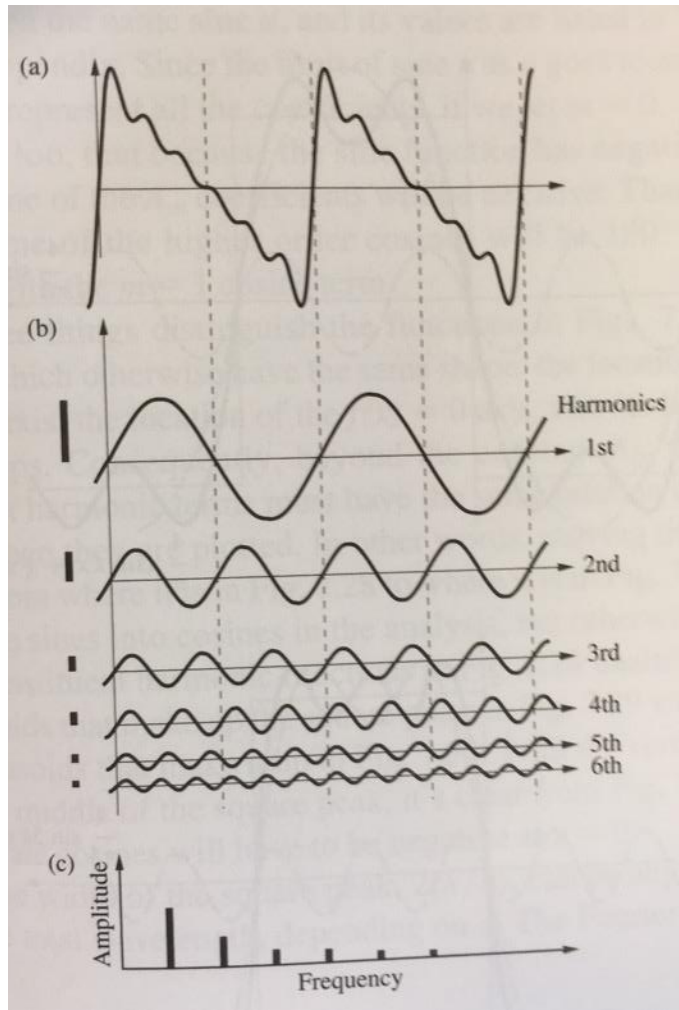






# Fourier transforms and Fourier optics

# Principle idea



## Mathematical description

- The principle idea of the Fourier analysis / transformation is that any function can be represented by an (infinite) series of harmonic functions.
- The Fourier transform decomposes a function into its constituent frequencies.

Thus we can write

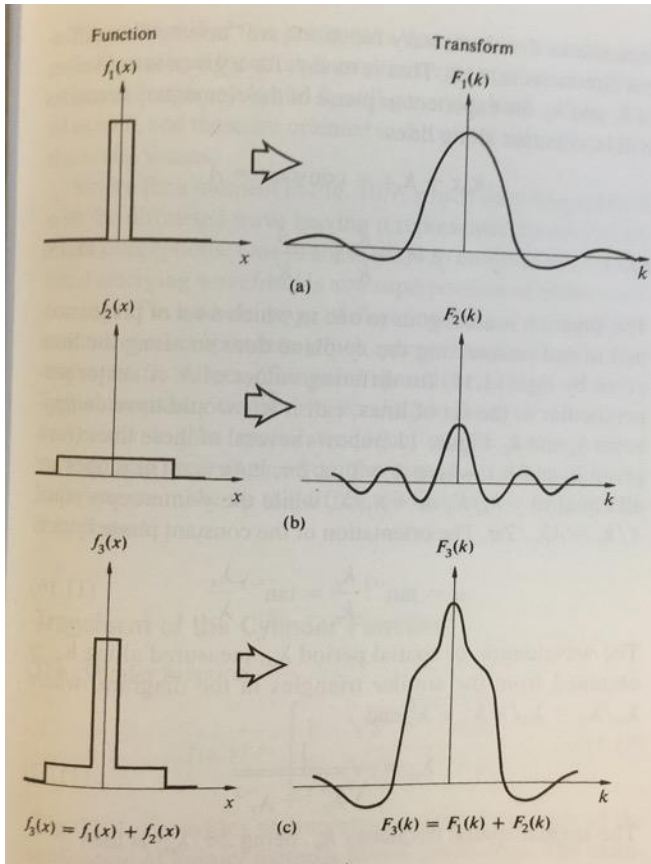
$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(k) e^{-ikx} dk$$

provided that

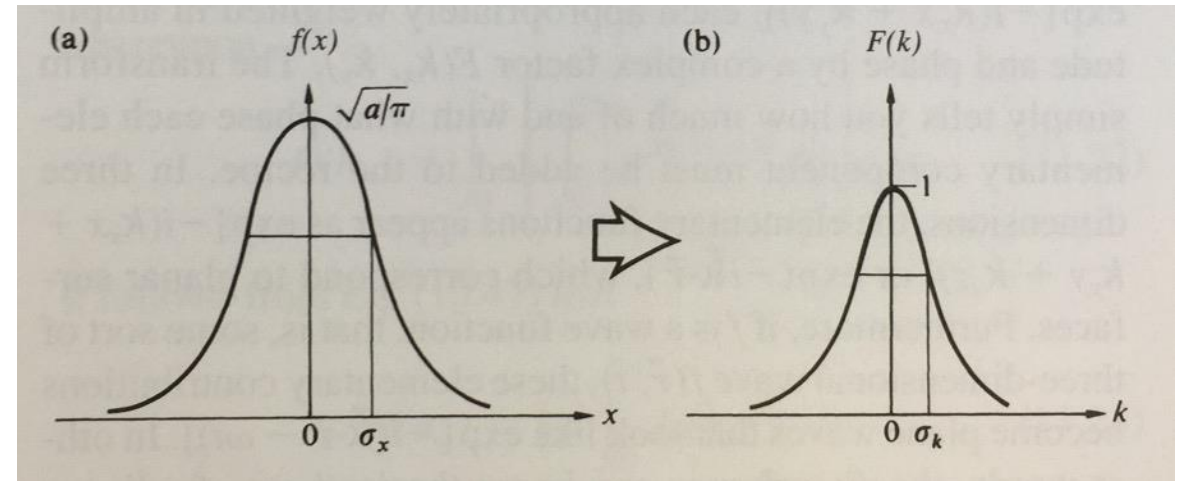
$$F(k) = \int_{-\infty}^{+\infty} f(x) e^{ikx} dx$$

# Examples

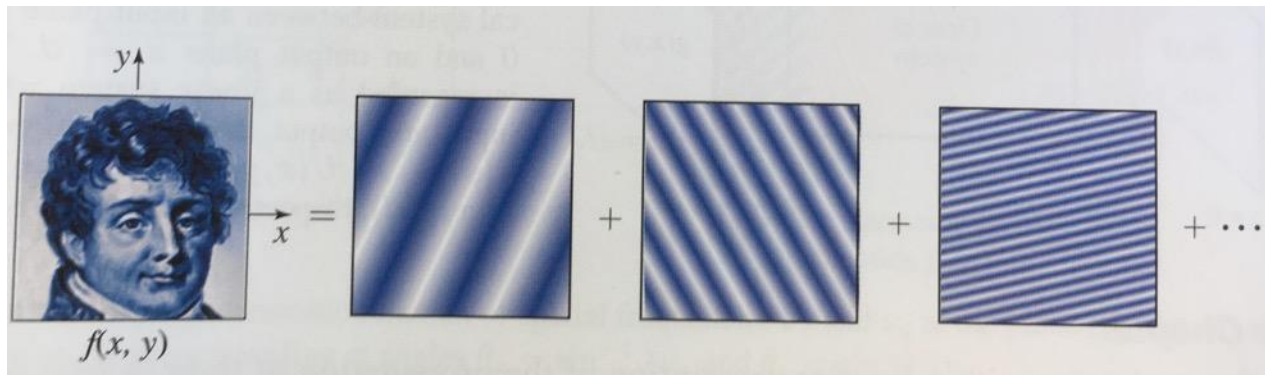
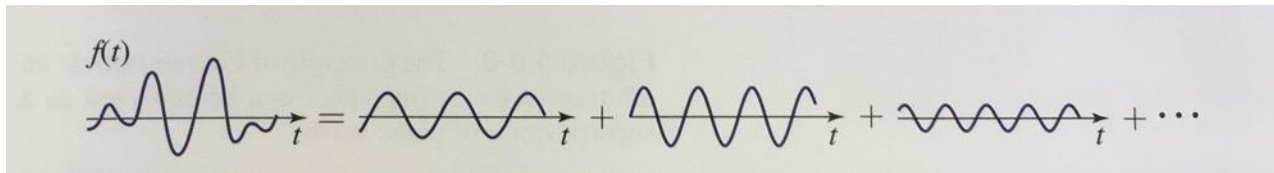
## Squares and composite



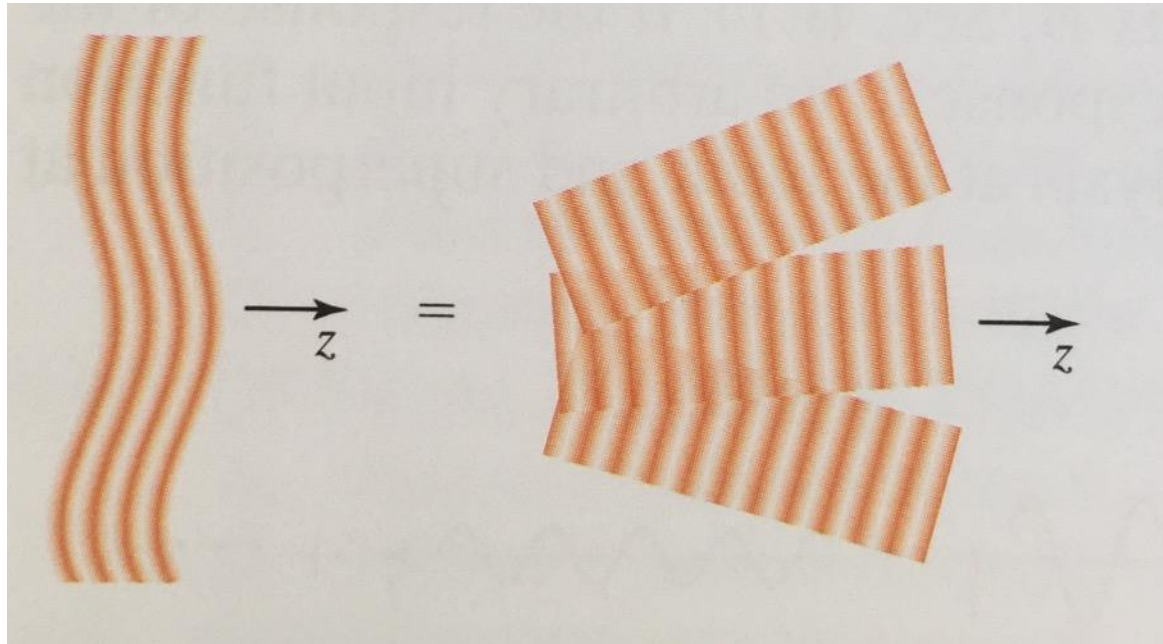
## Gauss function



# Expansion 2D



Principle of Fourier Optics: Any wavefront can be analyzed as superposition of plane waves

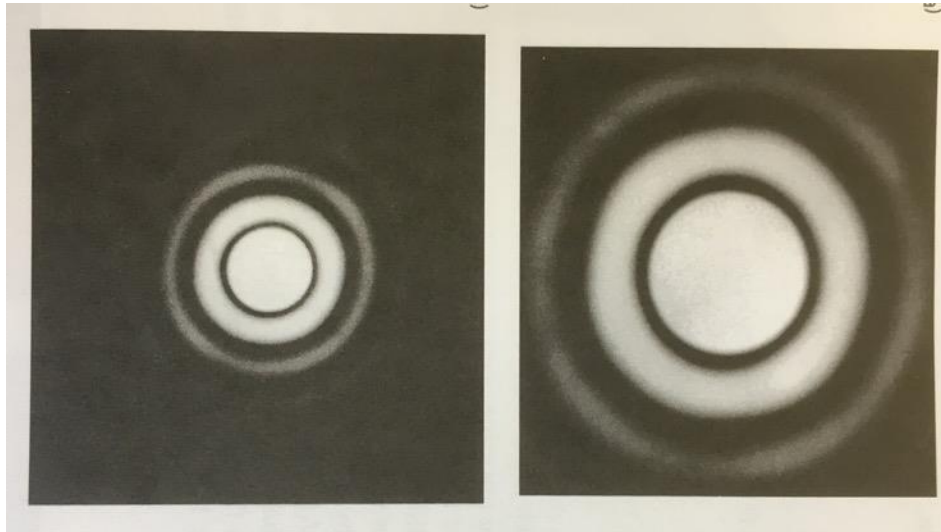


# Implications

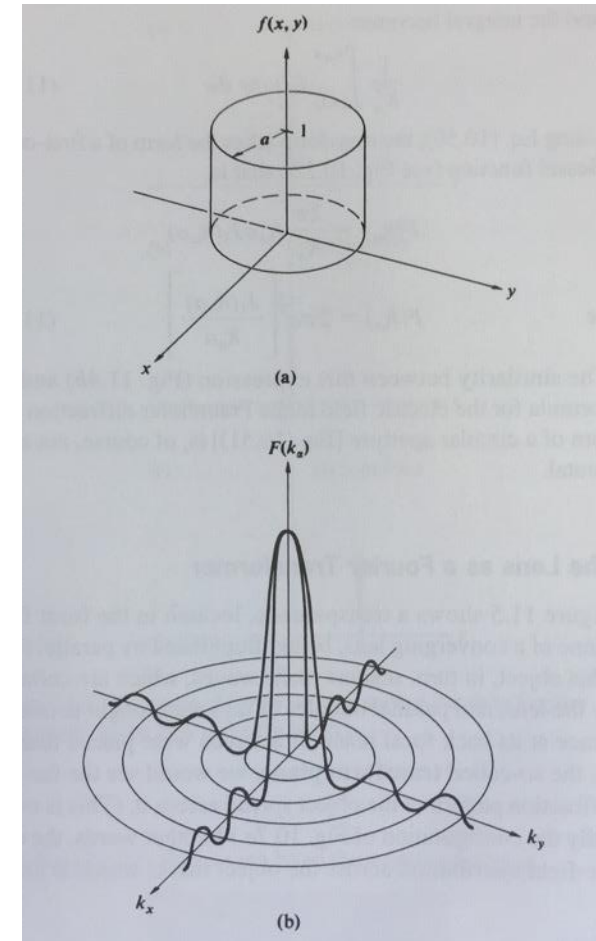


# Fourier transform of round aperture and airy pattern

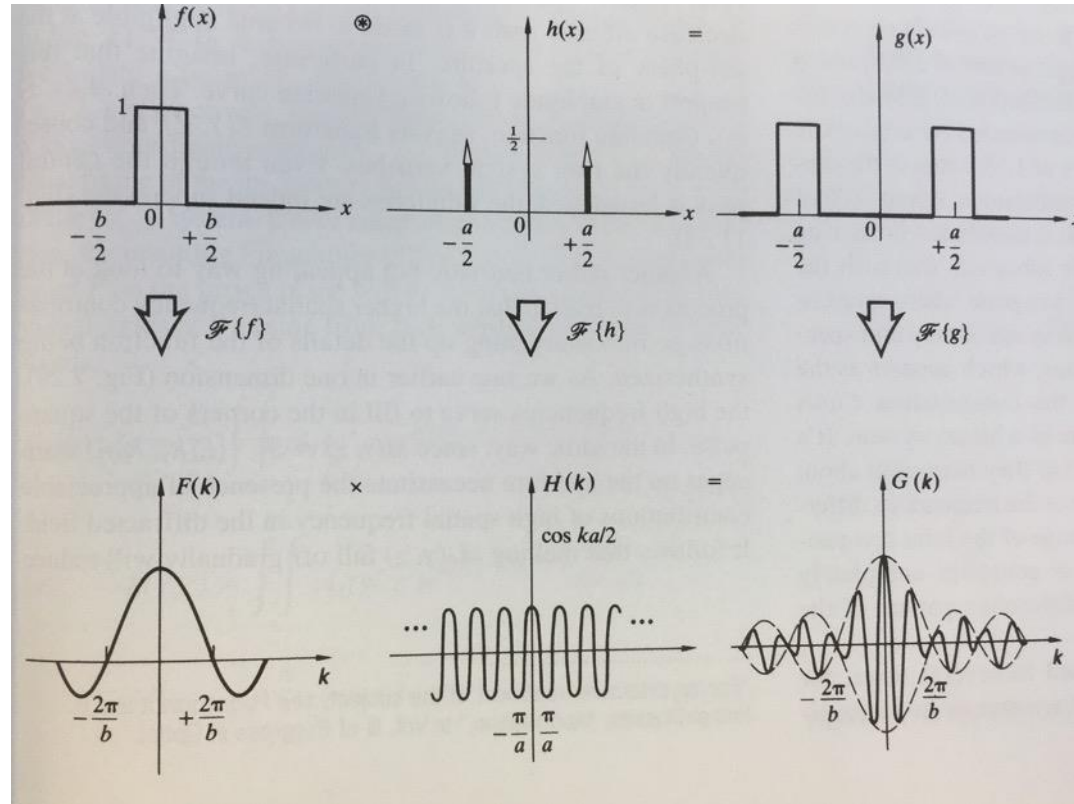
Experiment: Diffraction pattern of circular aperture, Airy pattern



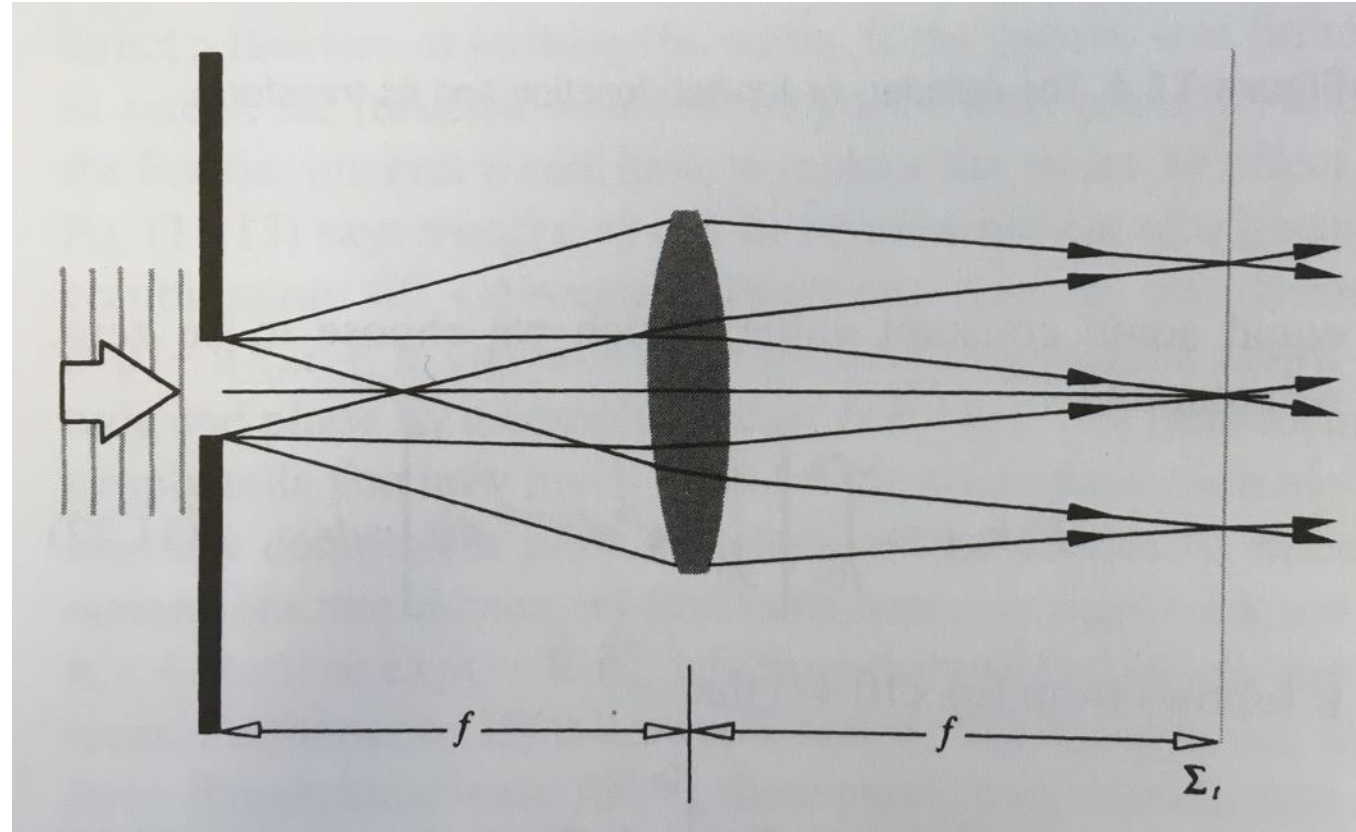
Theory: Fourier transform of cylinder or “top-hat” function



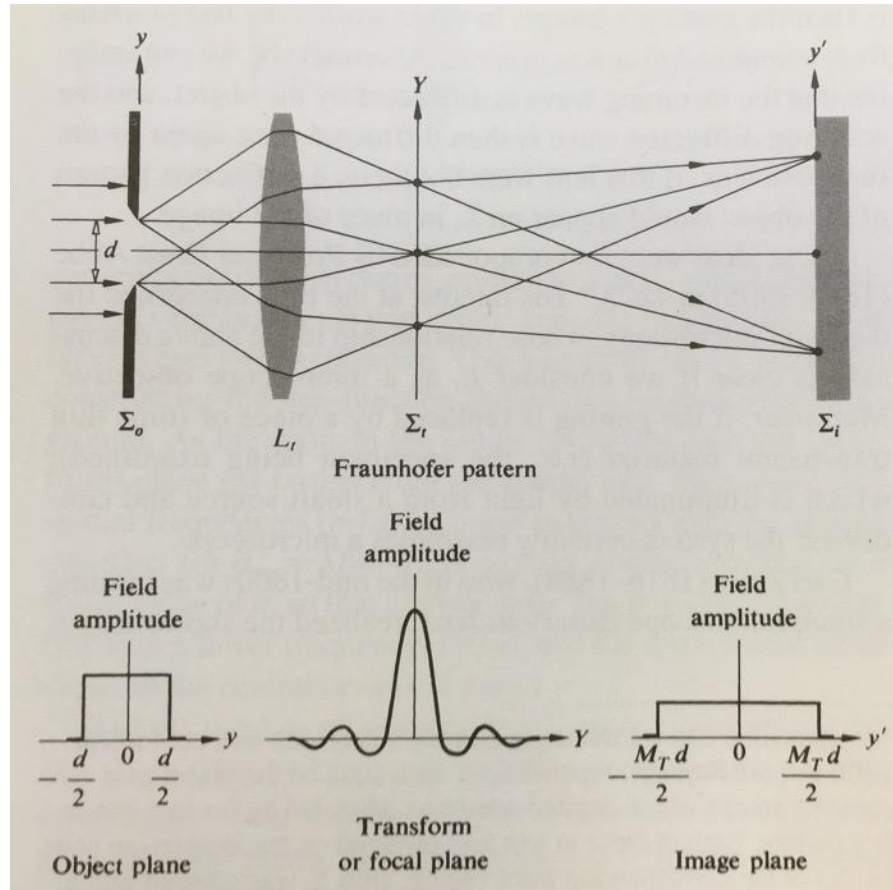
# Diffraction as Fourier transform:



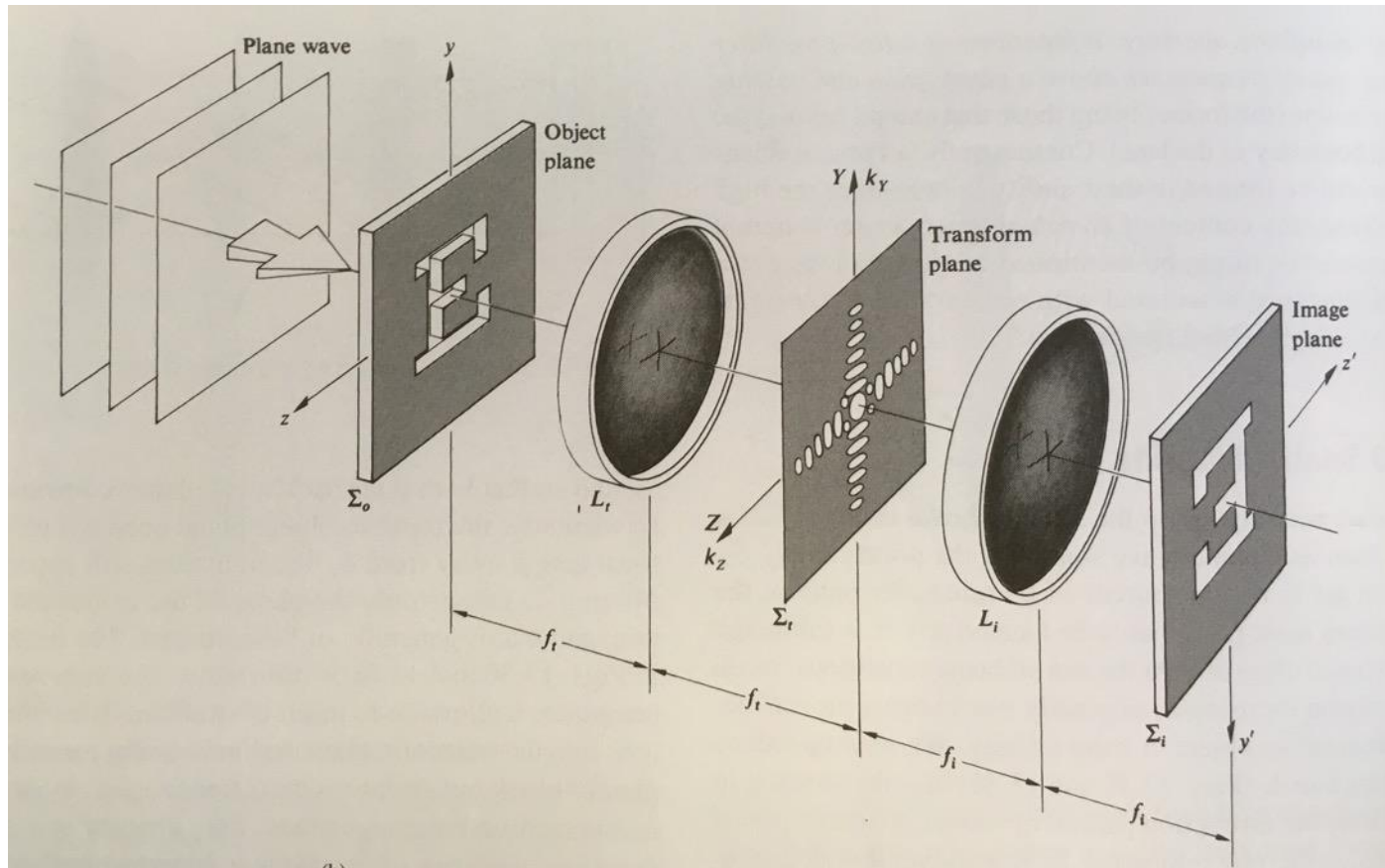
# Lens as Fourier transformer



# Abe image formation



# 4f imaging setup



# Phase contrast microscopy

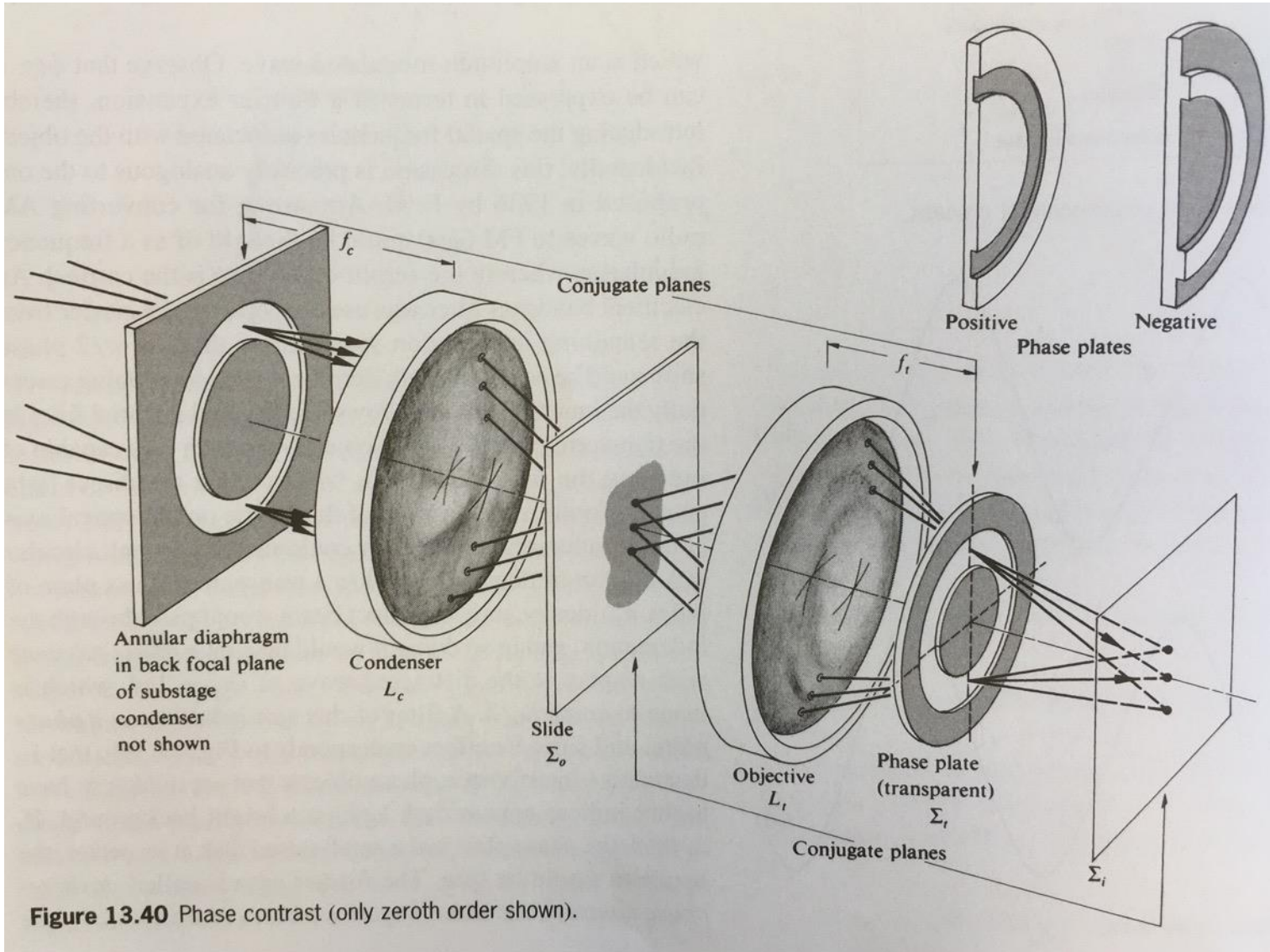


Figure 13.40 Phase contrast (only zeroth order shown).

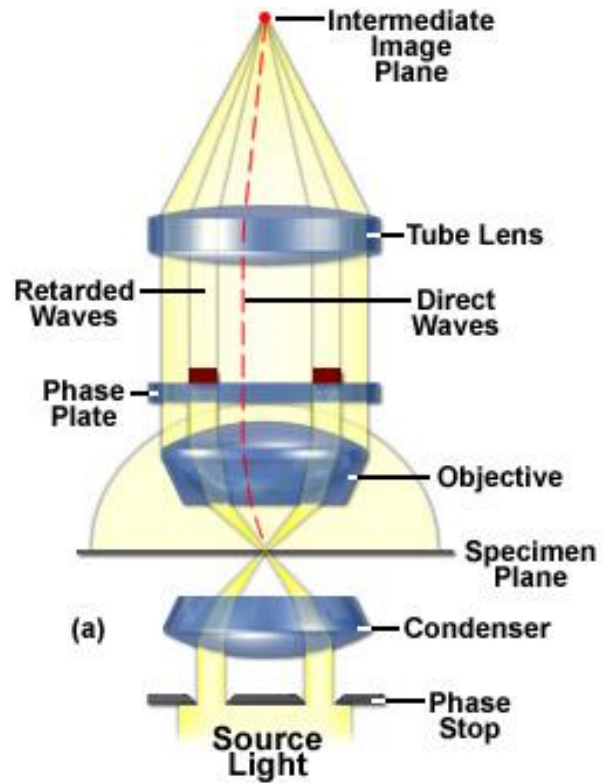


Photo from the Nobel Foundation archive.

Frits Zernike

Prize share: 1/1

# Phase contrast microscopy



Phase Contrast Optical Train and Condenser Components

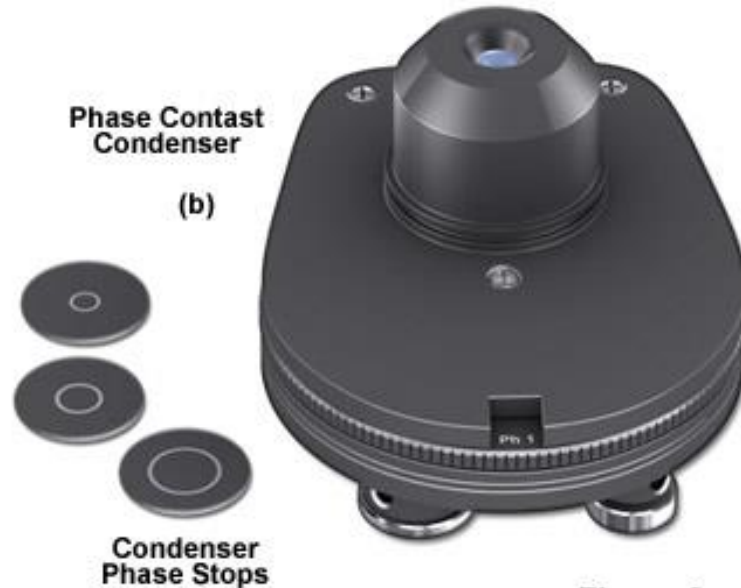


Figure 3

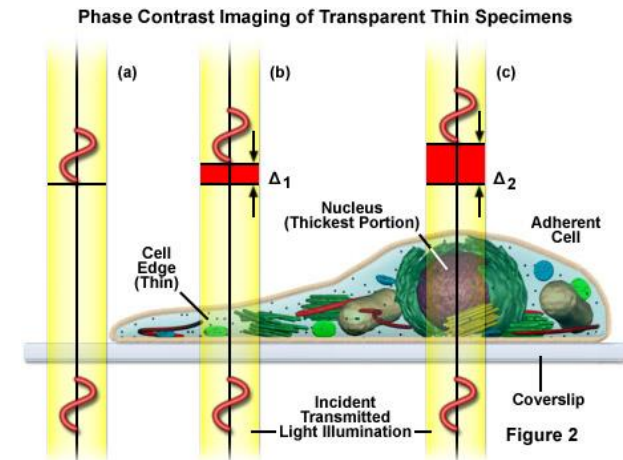
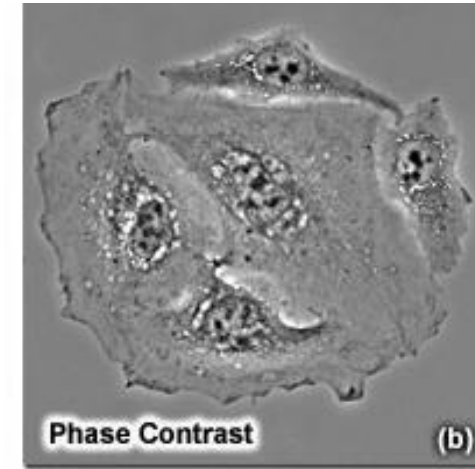
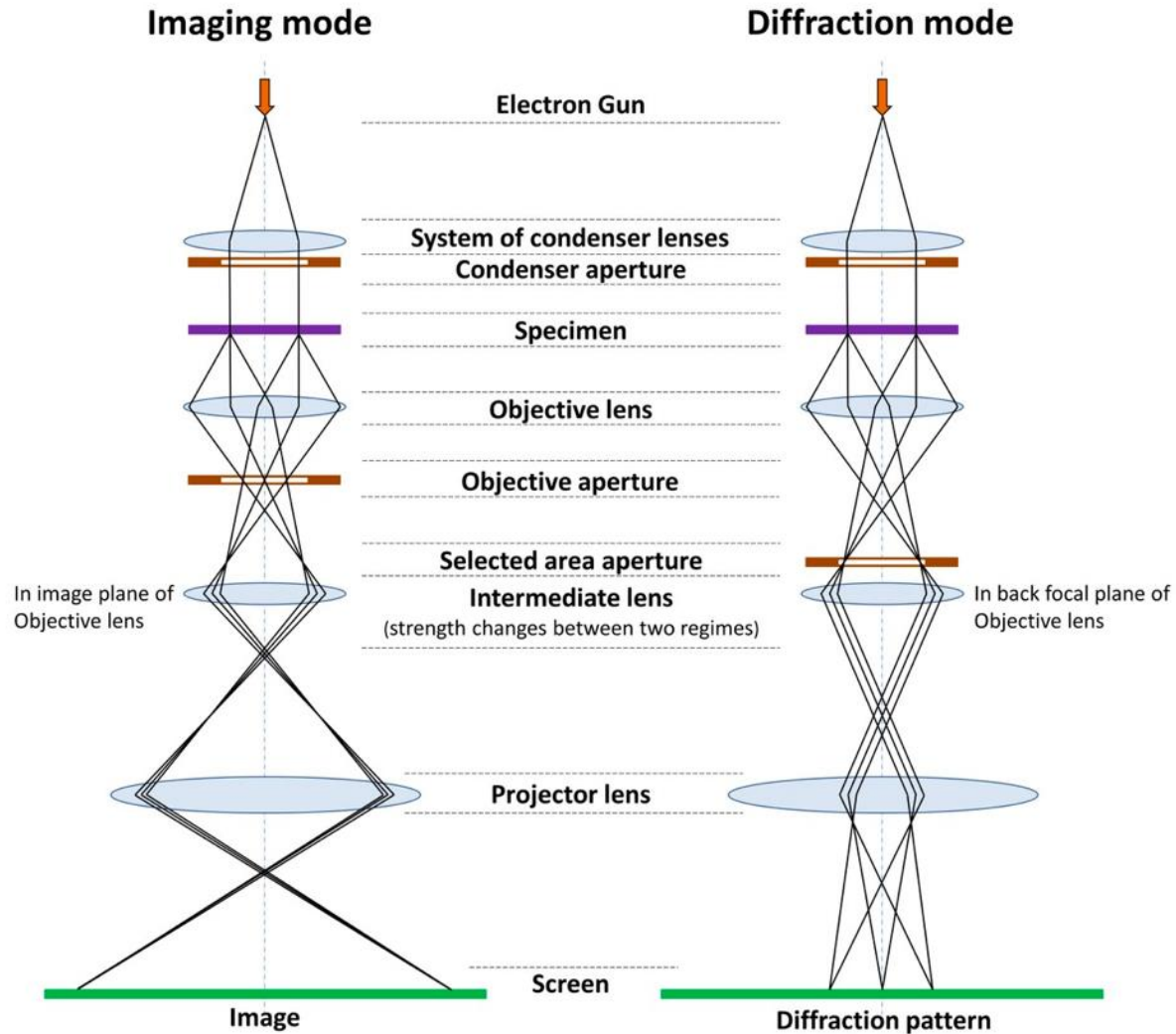


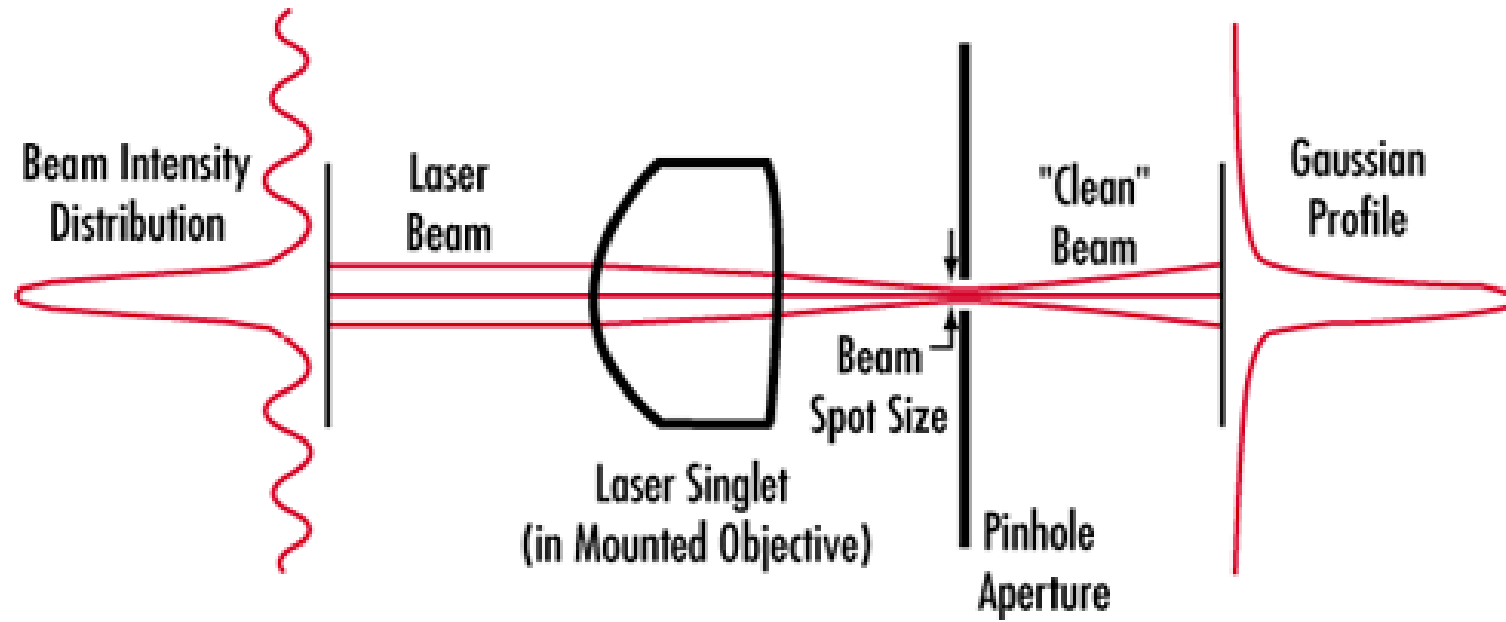
Figure 2

# Note: Electron microscopy





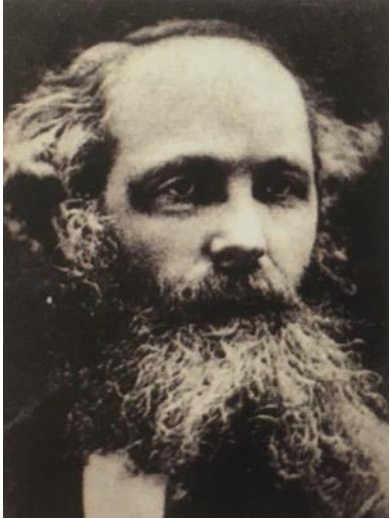
## Note on optical tricks: How to make a Gaussian beam or “Spatial Filtering”



<https://www.edmundoptics.com/resources/application-notes/lasers/understanding-spatial-filters/>

# Light as electromagnetic waves

# Welcome to EM description of light!



James Maxwell  
1831 - 1879

$$\begin{aligned}\nabla \times \mathcal{H} &= \epsilon_0 \frac{\partial \mathcal{E}}{\partial t} \\ \nabla \times \mathcal{E} &= -\mu_0 \frac{\partial \mathcal{H}}{\partial t} \\ \nabla \cdot \mathcal{E} &= 0 \\ \nabla \cdot \mathcal{H} &= 0,\end{aligned}$$

Familiar wave equation:

## Maxwell equation in medium

$$\nabla \times \mathcal{H} = \frac{\partial \mathcal{D}}{\partial t}$$

$$\nabla \times \mathcal{E} = -\frac{\partial \mathcal{B}}{\partial t}$$

$$\nabla \cdot \mathcal{D} = 0$$

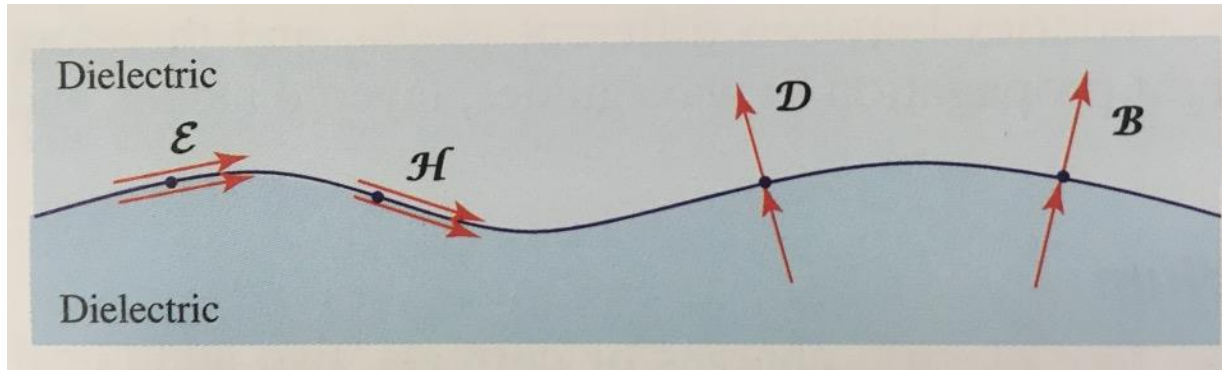
$$\nabla \cdot \mathcal{B} = 0.$$

$$\mathcal{D} = \epsilon_0 \mathcal{E} + \mathcal{P}$$

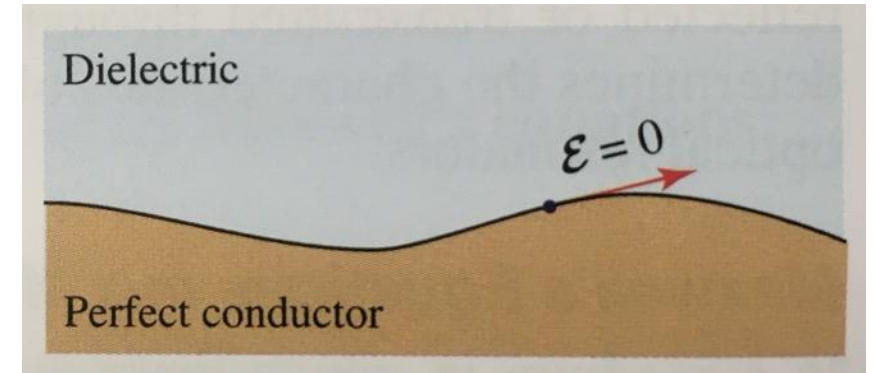
$$\mathcal{B} = \mu_0 \mathcal{H} + \mu_0 \mathcal{M}.$$

# Boundary conditions at interfaces

Two dielectric media

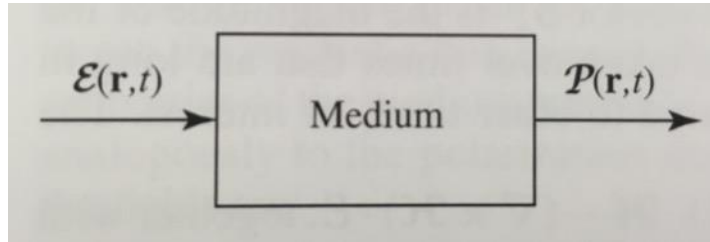


Dielectric and conducting media



# Electromagnetic waves in dielectric media

General



But stick with linear, nondispersive, homogenous, and isotropic media right now:

$$\mathcal{P} = \epsilon_0 \chi \mathcal{E},$$

This leads to the following Maxwell and wave equations wave equations

$$\begin{aligned}\nabla \times \mathcal{H} &= \epsilon \frac{\partial \mathcal{E}}{\partial t} \\ \nabla \times \mathcal{E} &= -\mu \frac{\partial \mathcal{H}}{\partial t} \\ \nabla \cdot \mathcal{E} &= 0 \\ \nabla \cdot \mathcal{H} &= 0.\end{aligned}$$

# Complex refractive index

General:

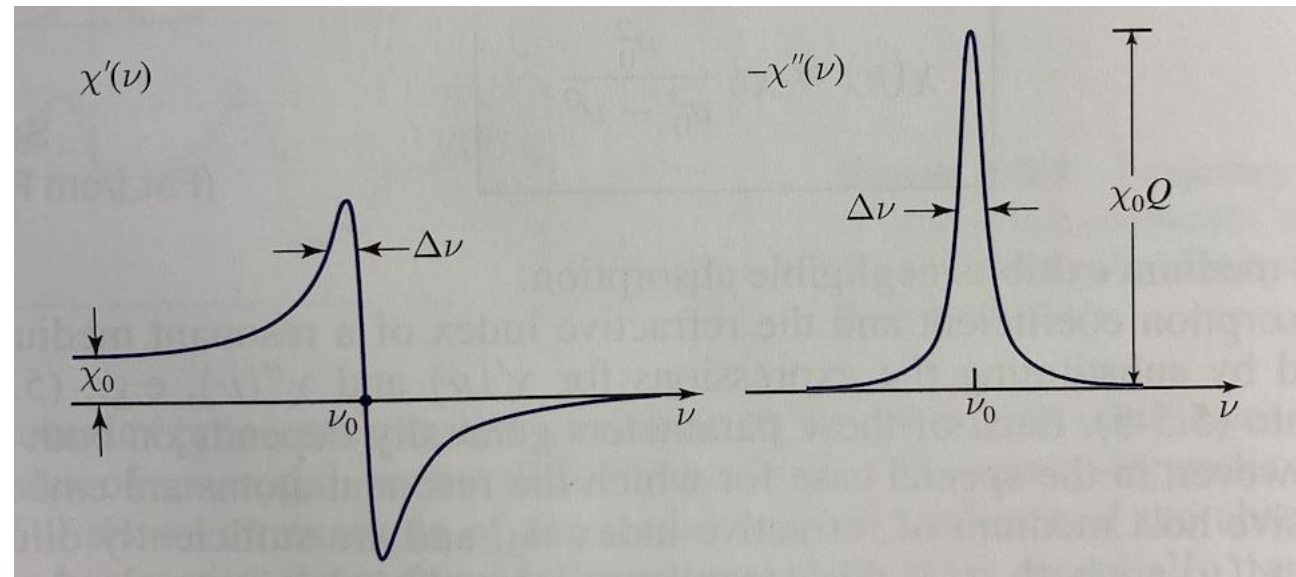
$$n - j\frac{1}{2} \frac{\alpha}{k_0} = \sqrt{\epsilon/\epsilon_0} = \sqrt{1 + \chi' + j\chi''}.$$

Weakly absorbing media:

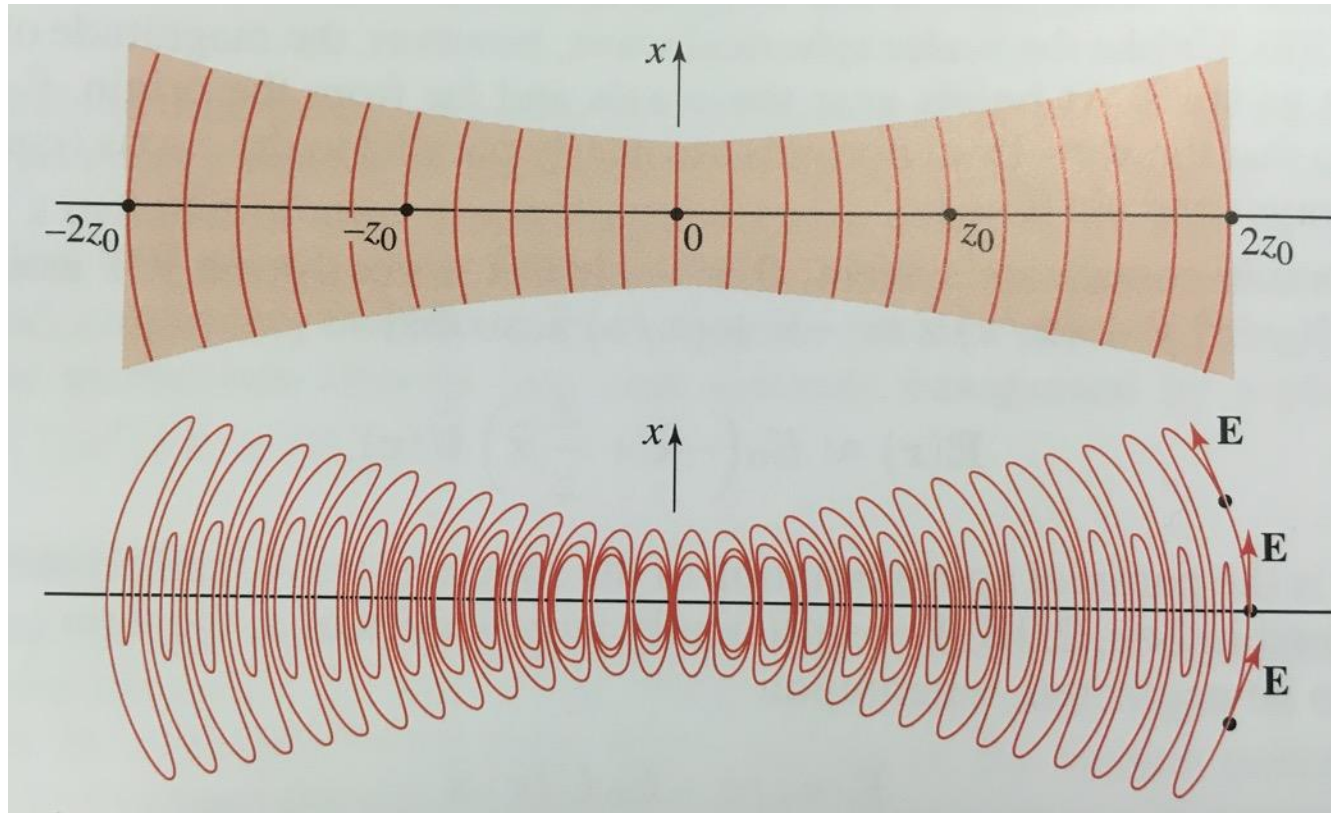
$$n \approx \sqrt{1 + \chi'}$$
$$\alpha \approx -\frac{k_0}{n} \chi''.$$



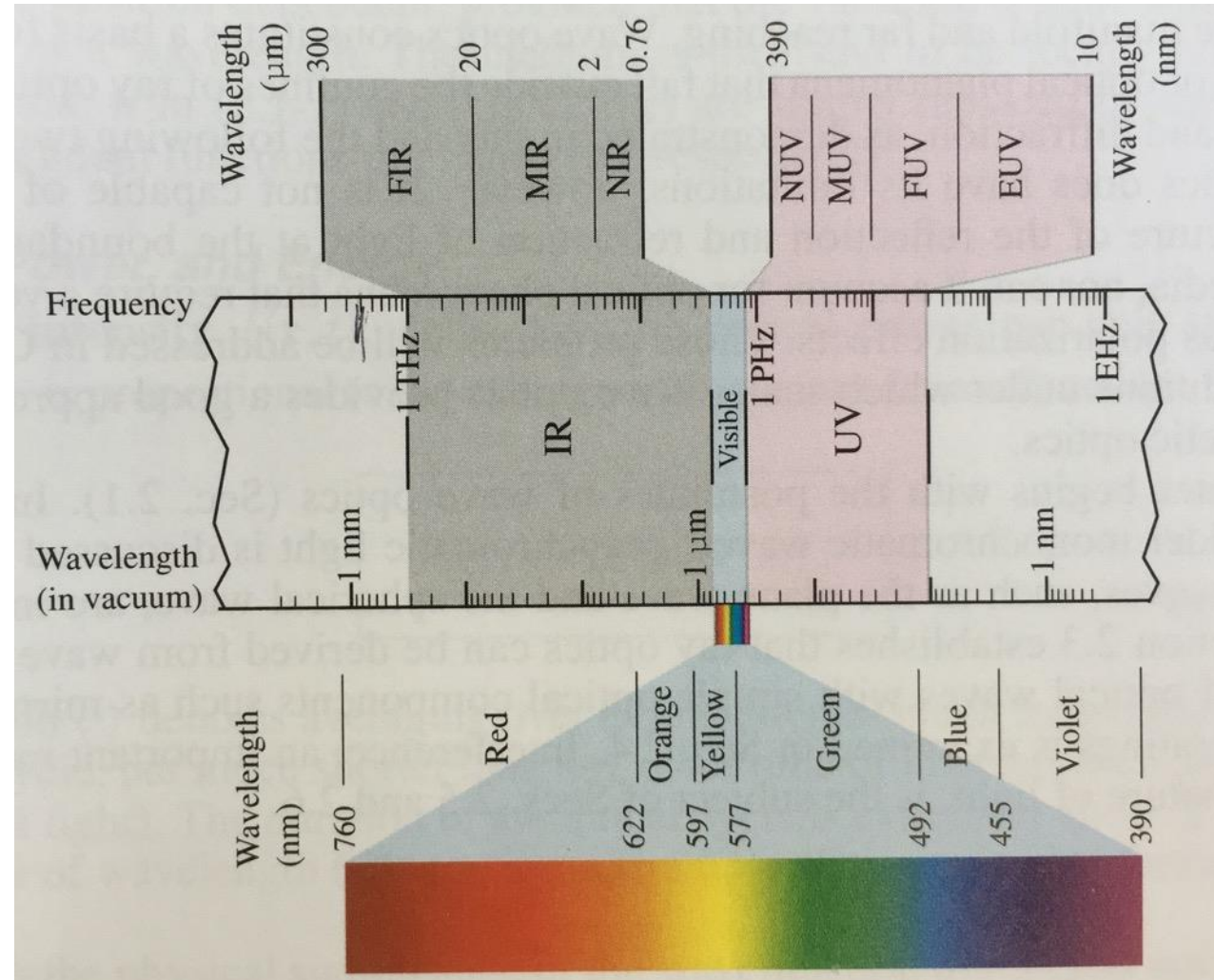
## Resonances and refractive index



# A note on wavefronts



# Characteristic fingerprints of a molecule: rotational, vibrational, electronic transitions



# Spectroscopy – different approaches

# The “classic approach” to spectroscopy

Version 1

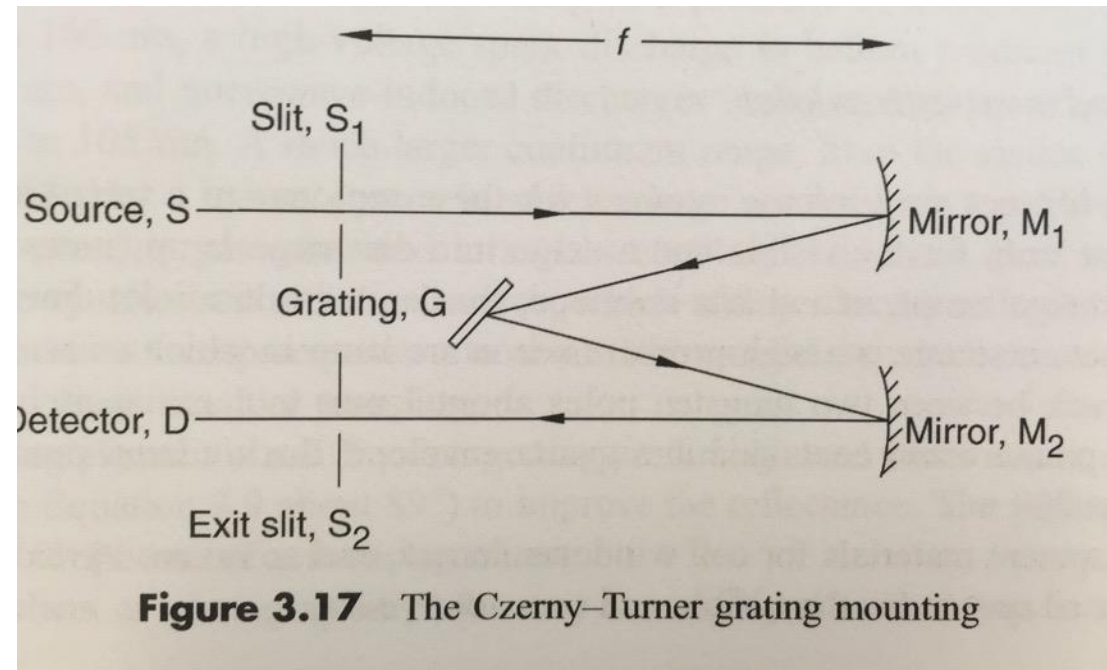
Version 2

# Grating spectrometer

Common use in (far) infrared spectroscopy not restricted to this regime

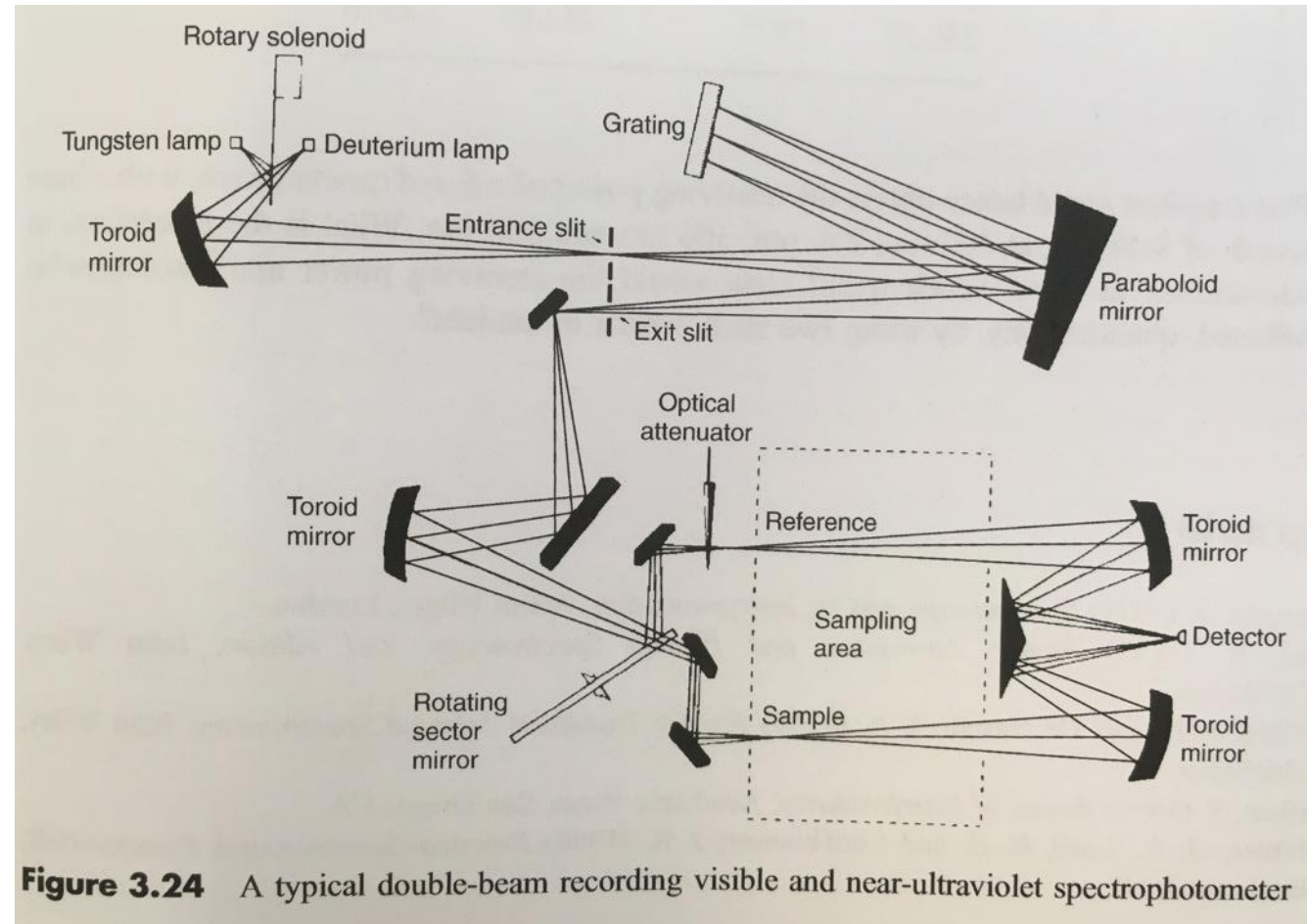
Note strong absorption of water, work in “dry conditions”

Excitation source can be mercury discharge lamp

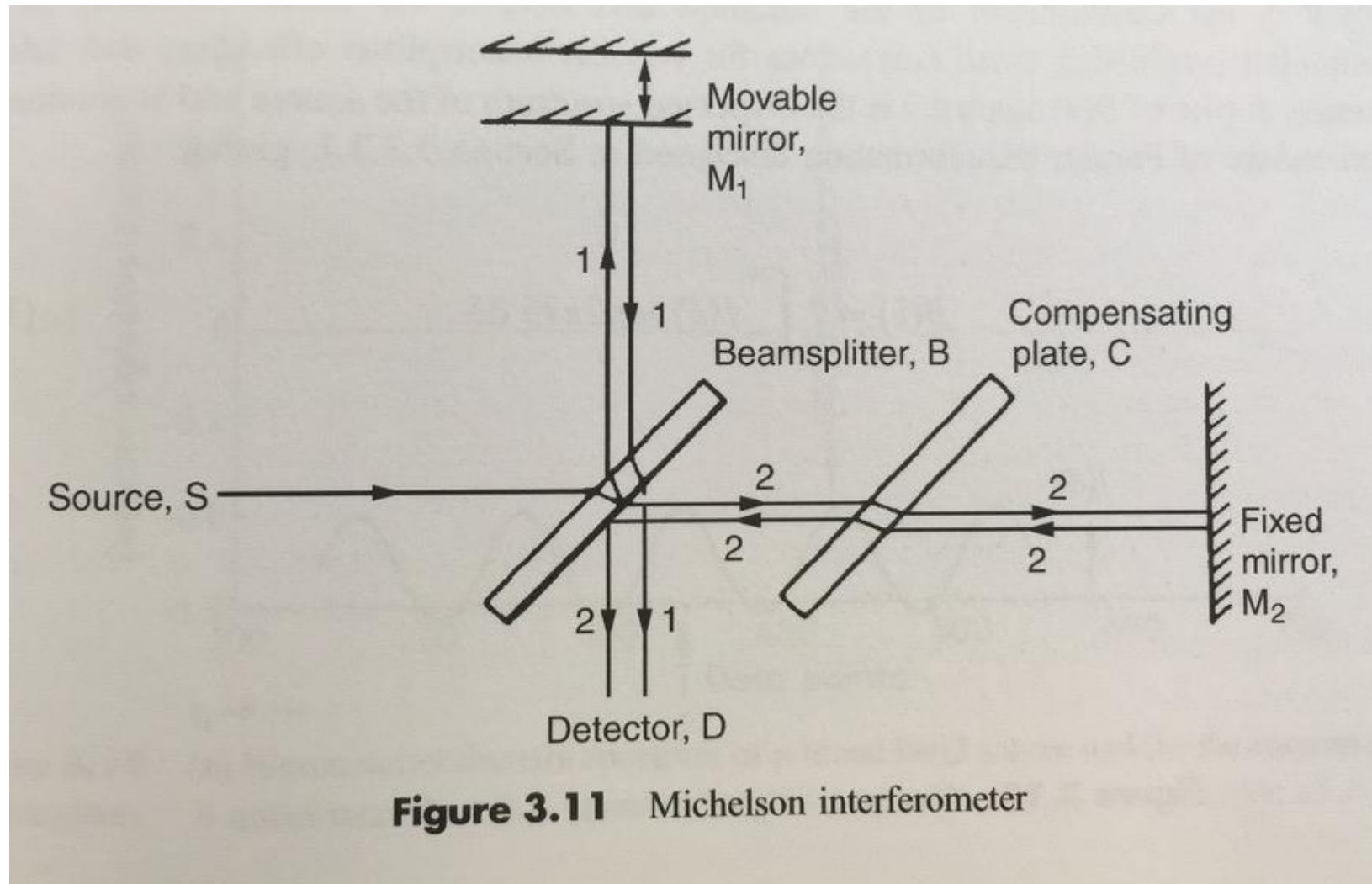


# Spectrophotometer

Depending on excitation source from IR to visible to near-uv

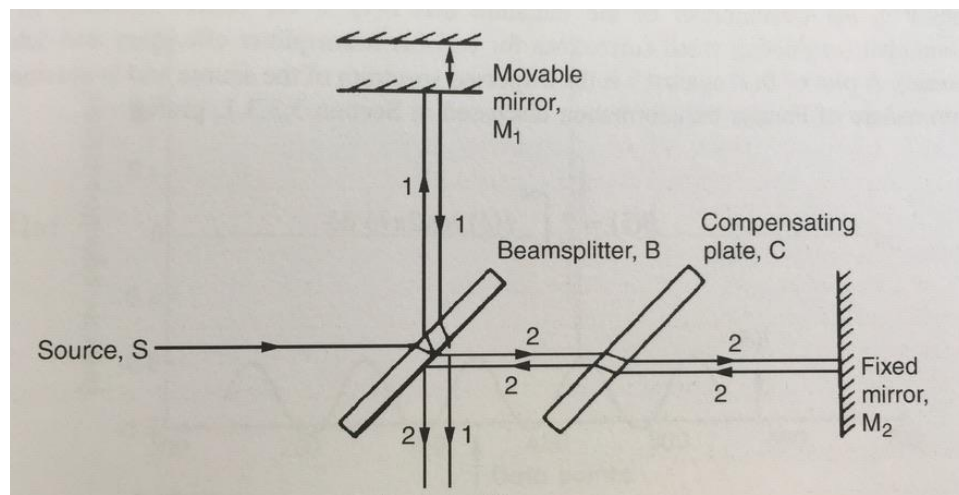


## Basics of Michelson interferometer (mono)



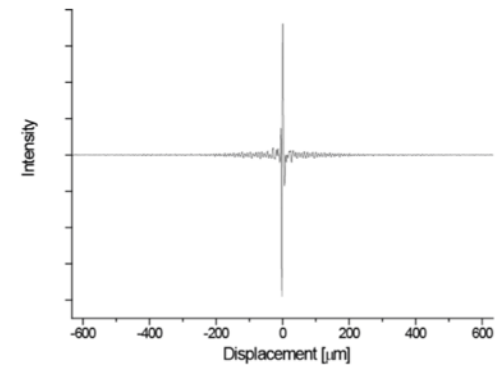


# Measuring an interferogram

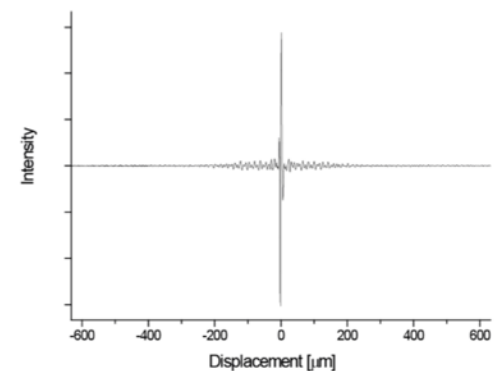
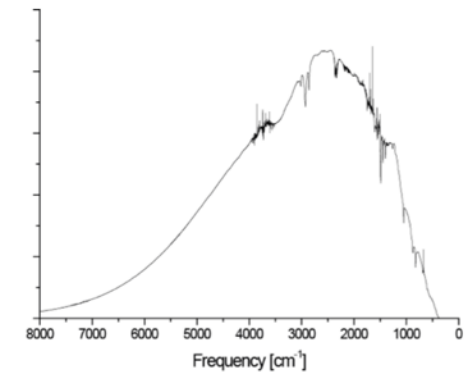


Sample

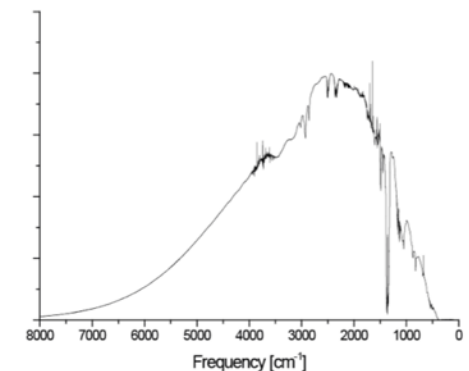
Detector



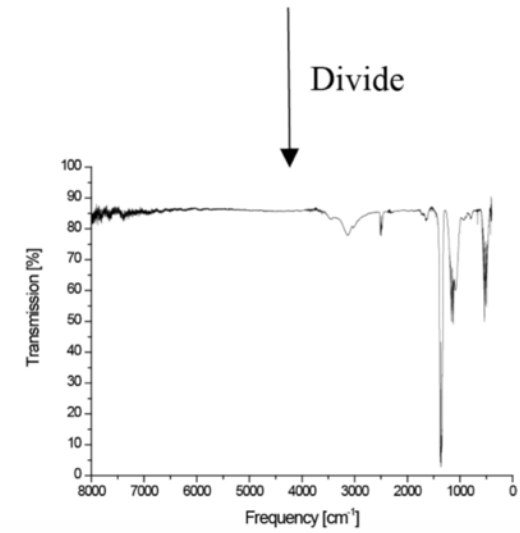
Empty Cell  
FT



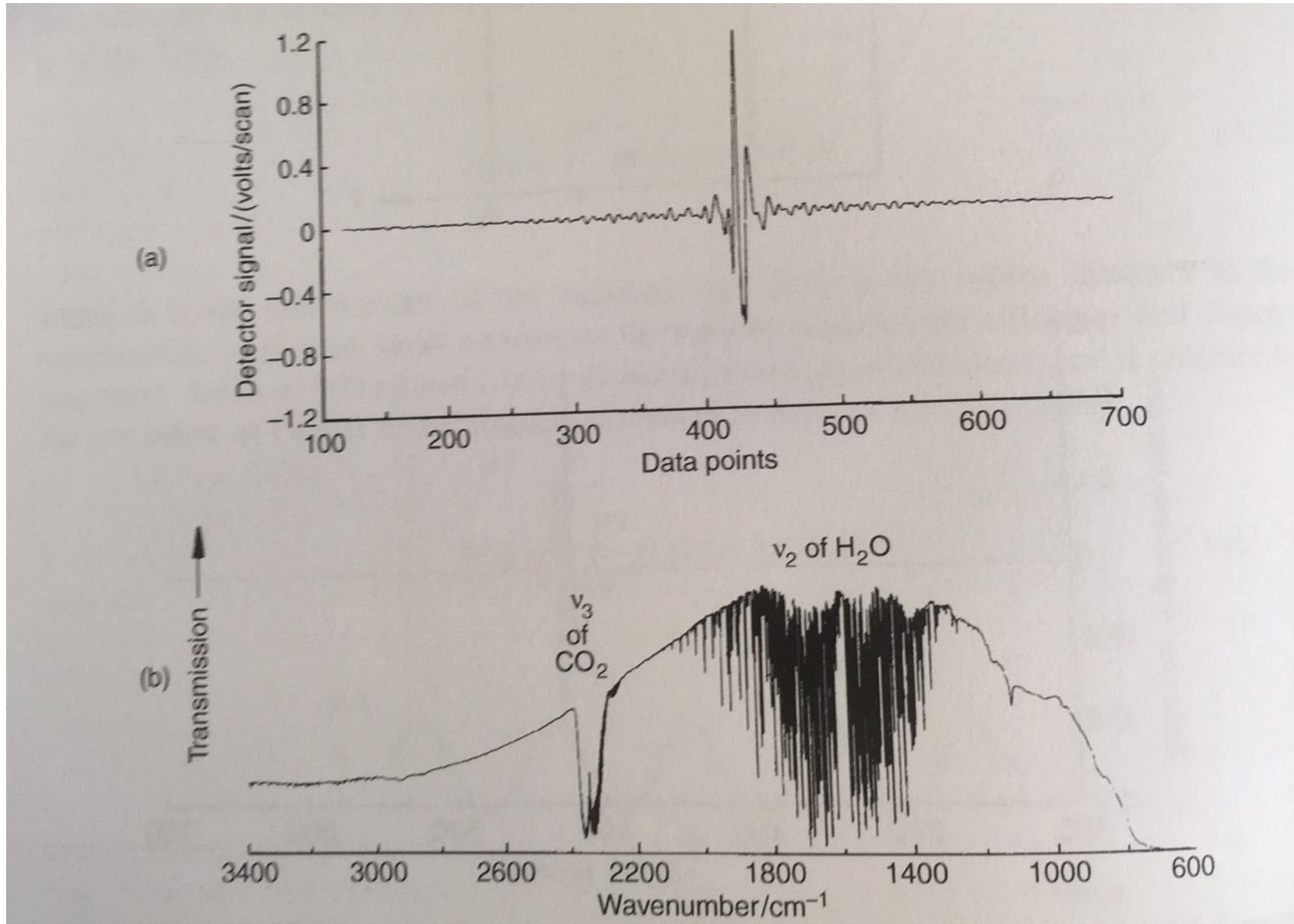
Filled Cell  
FT



Divide



# Example: Interferogram and spectrum of air



# Fourier spectroscopy

- Advantages
  - Higher overall transmission through interferometer compared to spectrometer
  - Multiplexing through use of all frequencies
  - Faster acquisition times and better signal to noise ratio
  - Higher accuracy for measuring mirror travel
- Limitations
  - Typically restricted to IR measurements
  - Accuracy determined by mirror travel distance
- Video by Brooker company for modern apparatus

<https://www.facebook.com/bruker.corp/videos/o.712956095479376/10152856330318129/?type=2&theater>

# Raman spectroscopy (short introduction)

Raman process: Inelastic scattering of light

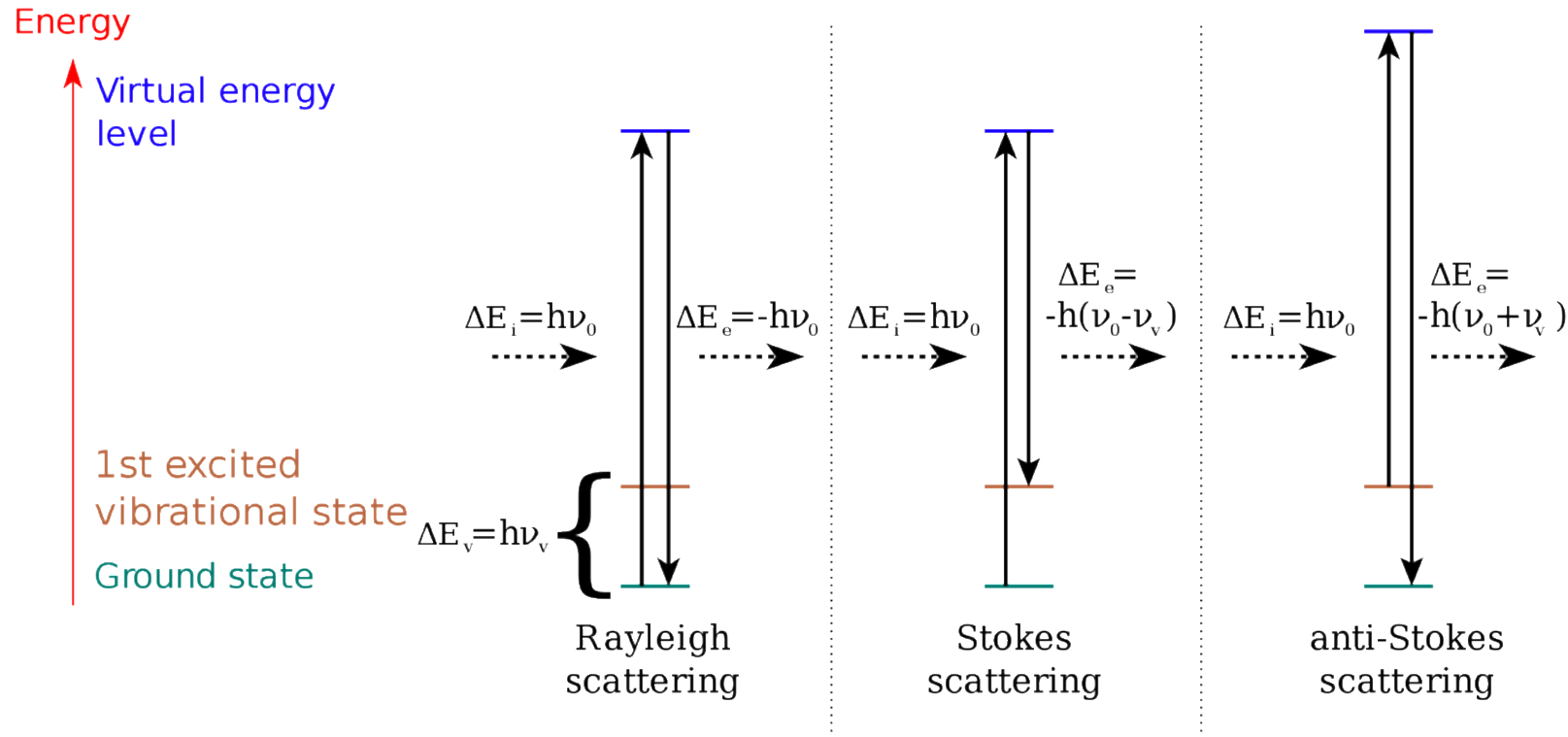
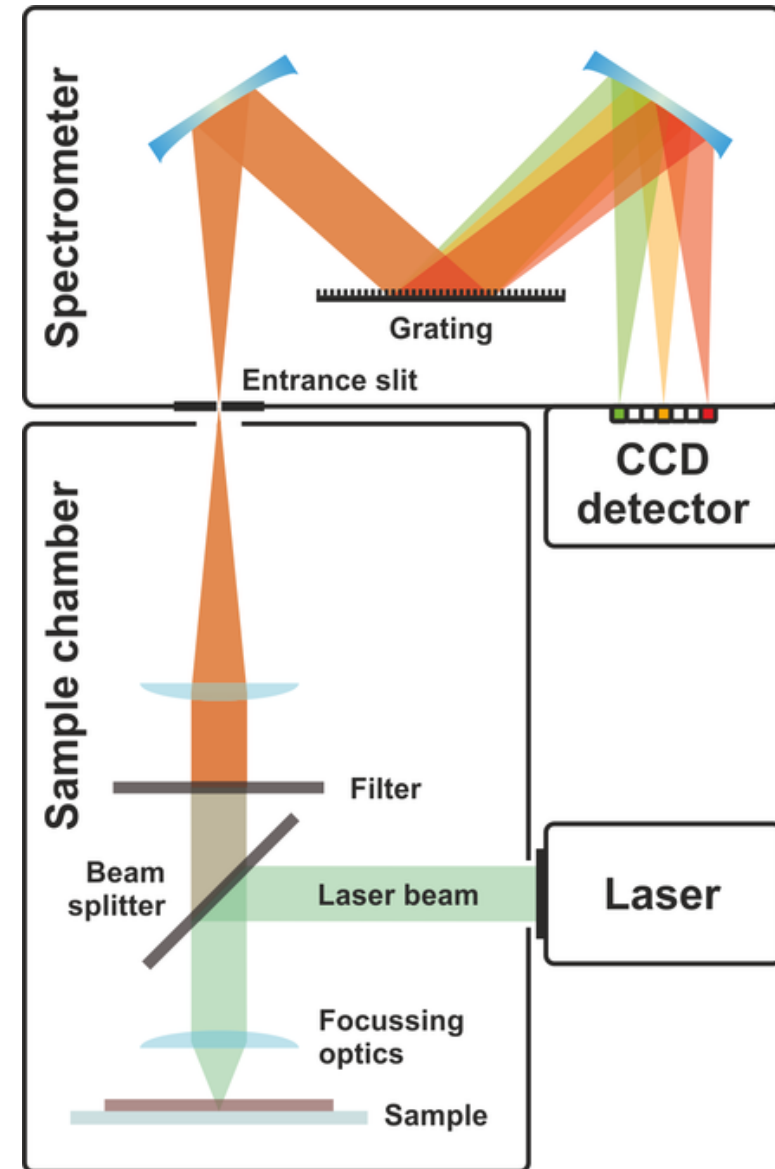
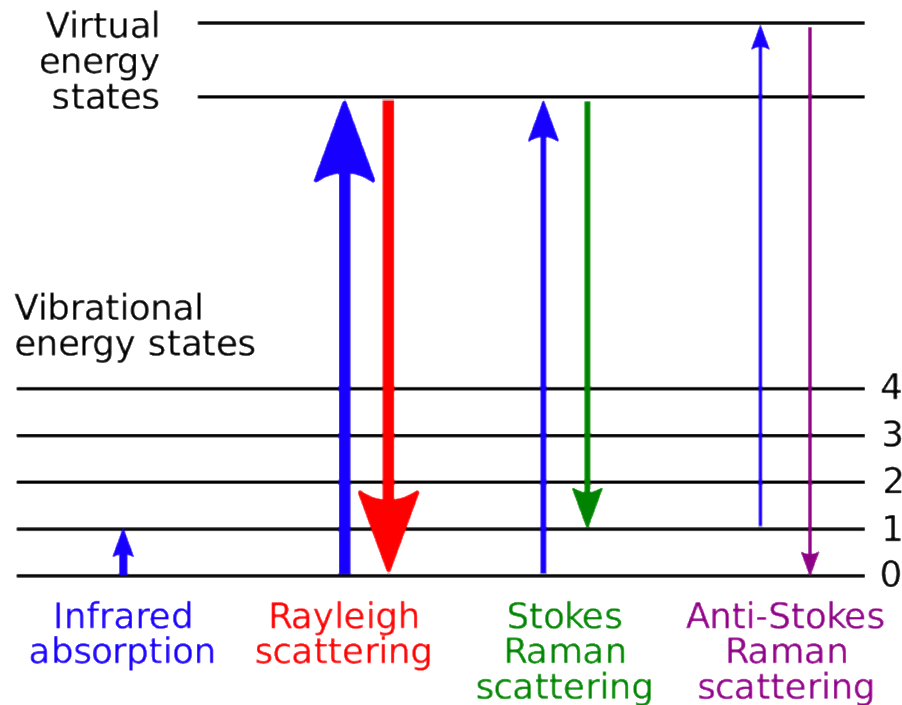


Photo from the Nobel Foundation archive.  
Sir Chandrasekhara Venkata Raman

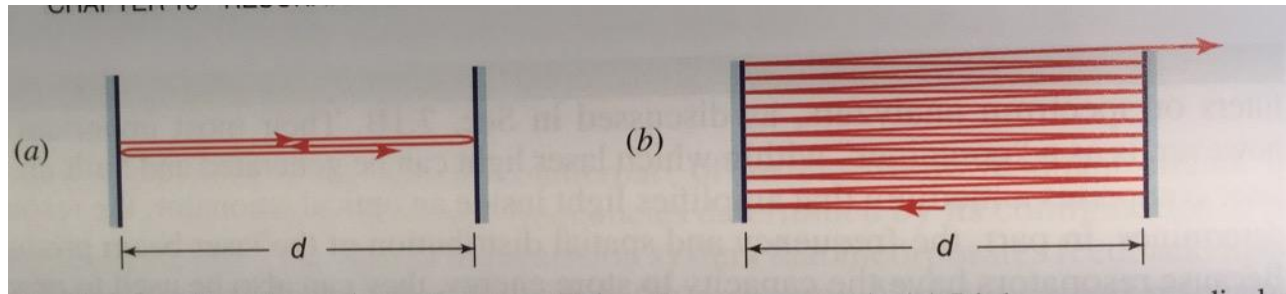
# Raman spectroscopy



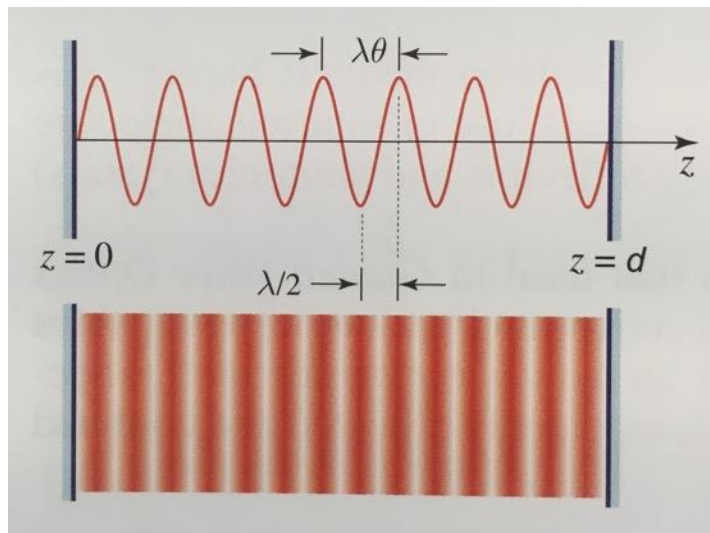
# Optical resonators, cavities

# Fabry-Perot Resonator

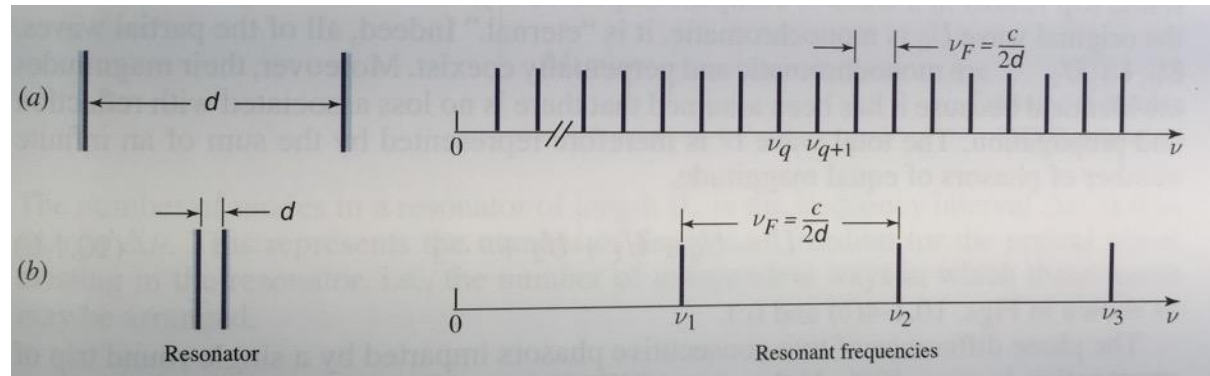
Idea: Trap light between highly reflective mirrors



Standing waves represent resonator modes

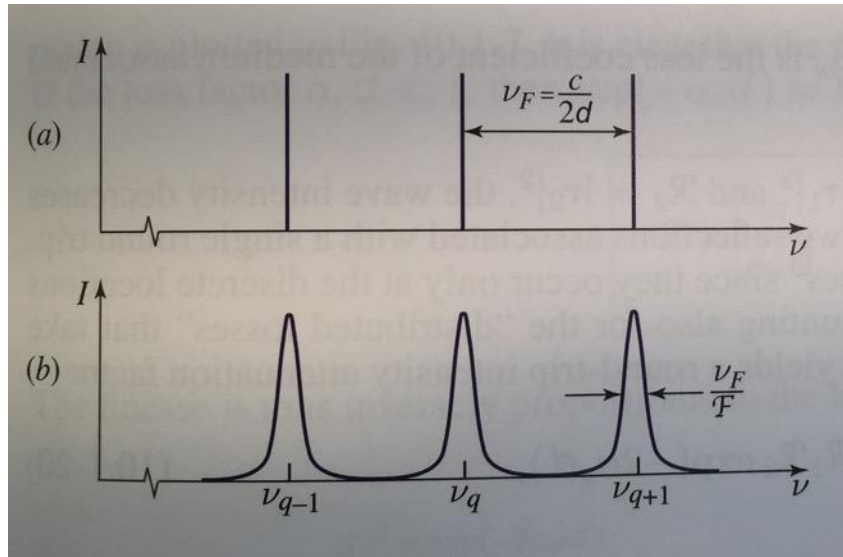


# Properties of the Fabry Perot Resonator

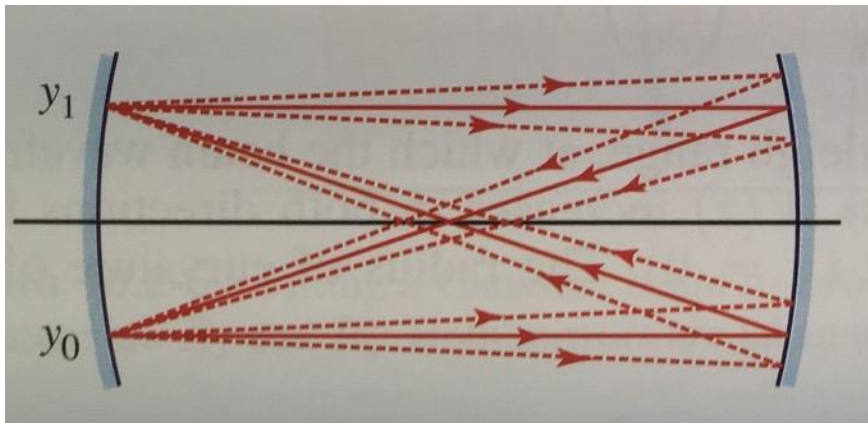
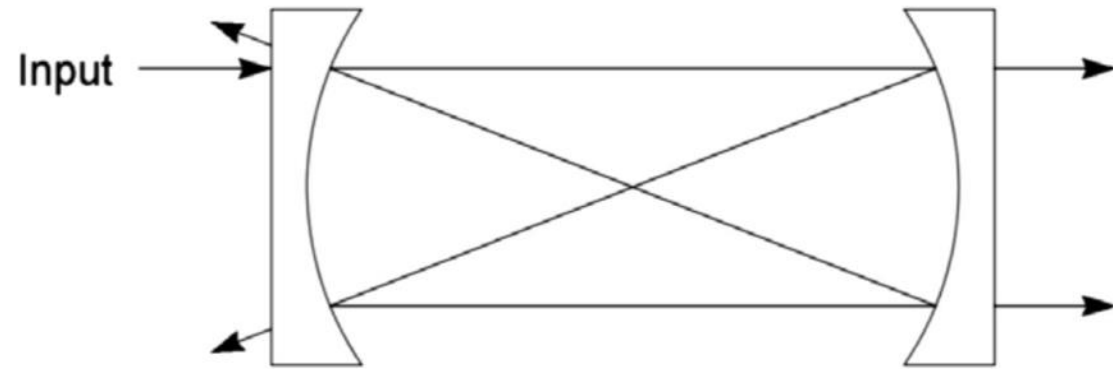




# Ideal vs real resonator – real is with losses

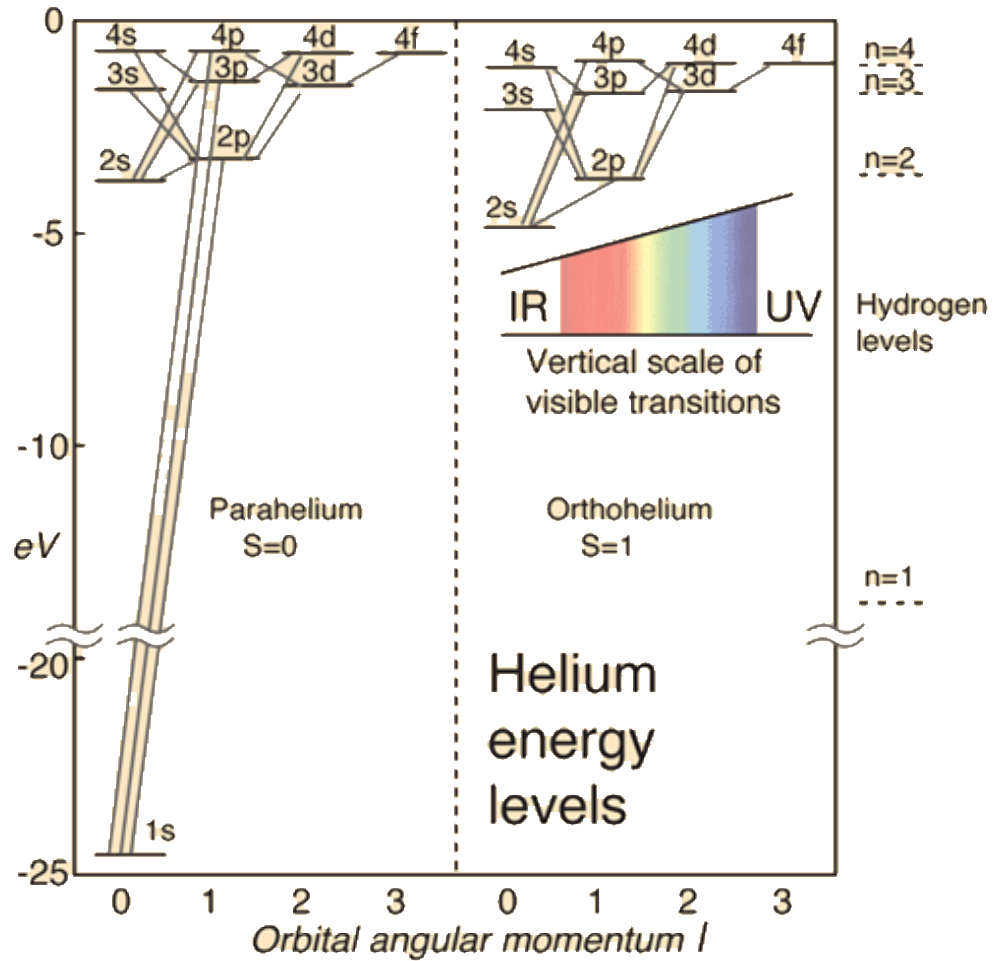


# Spherical Resonator



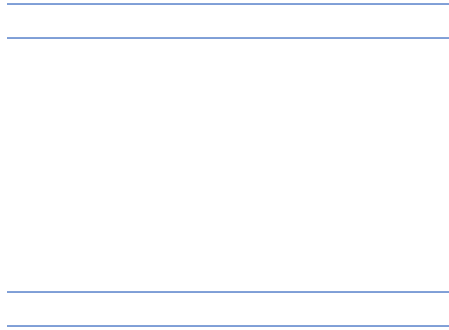
# Lasers

# Absorption, energy level diagram

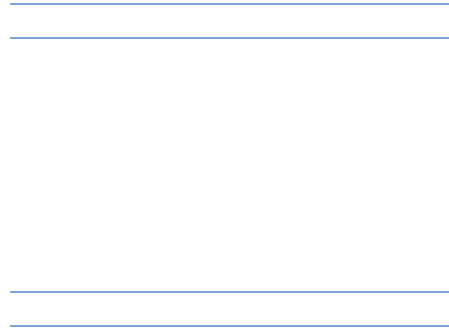


# Absorption, emission, stimulated emission - overview

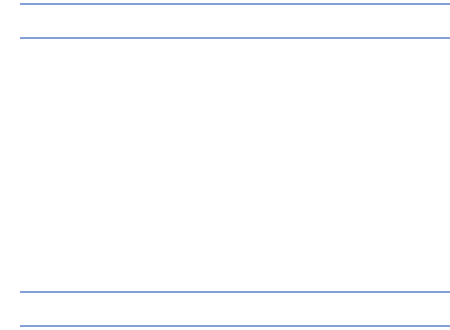
Spontaneous  
emission



Stimulated  
Emission



(Stimulated)  
absorption



# Fundamental concept of laser



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

## 2, 3, 4 level systems

2 level system

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---

3 level system

---

---

---

4 level system

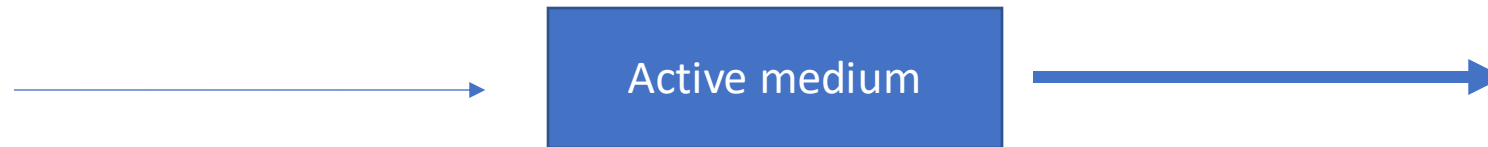
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## Fundamental concept of laser laser oscillator:

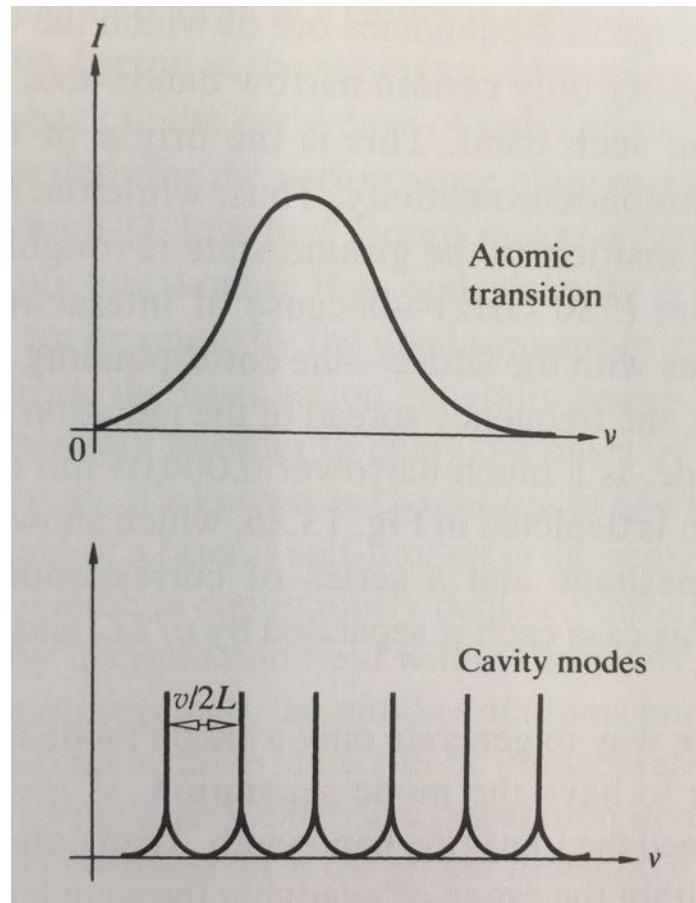


Note: The gain must always be higher than the losses!

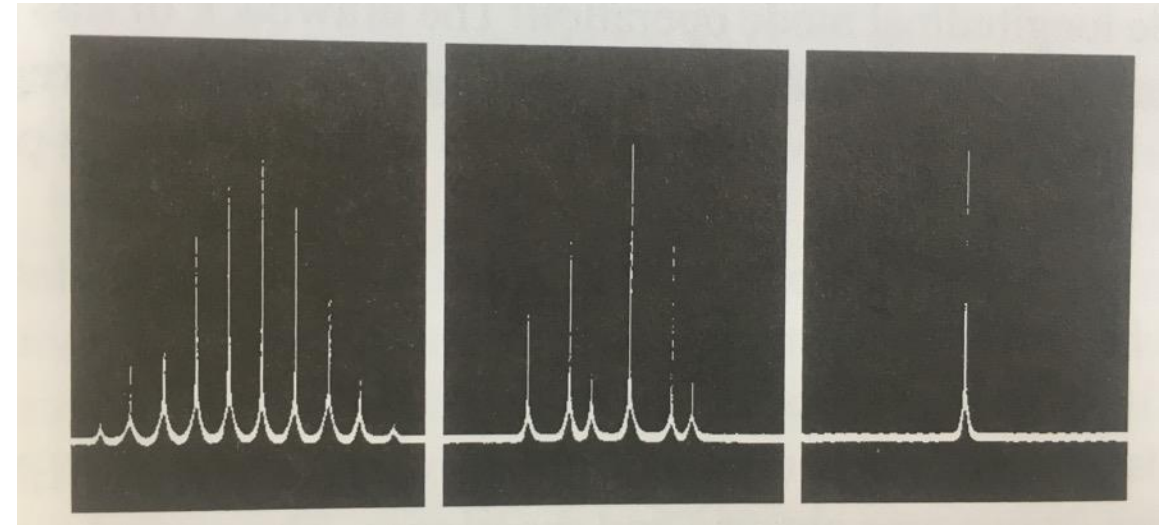


# Lasers and laser cavities

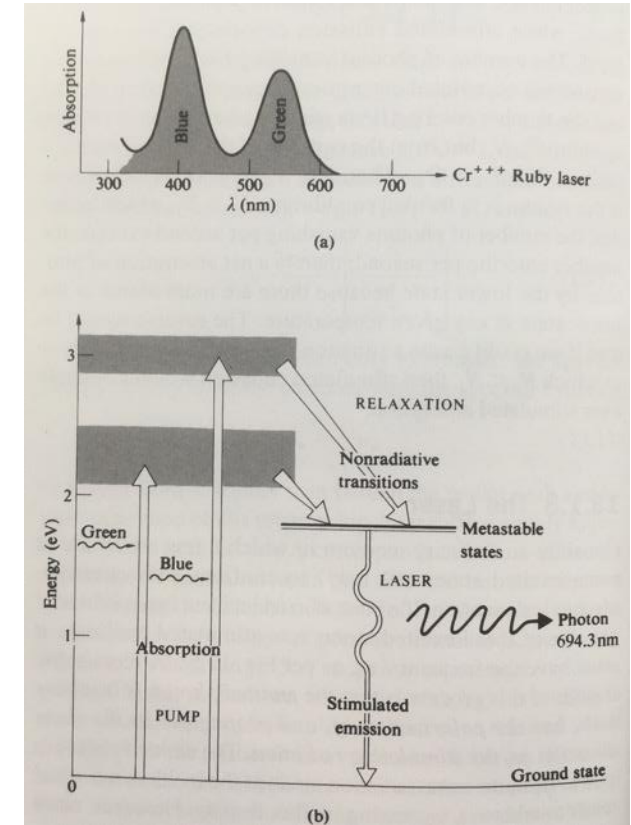
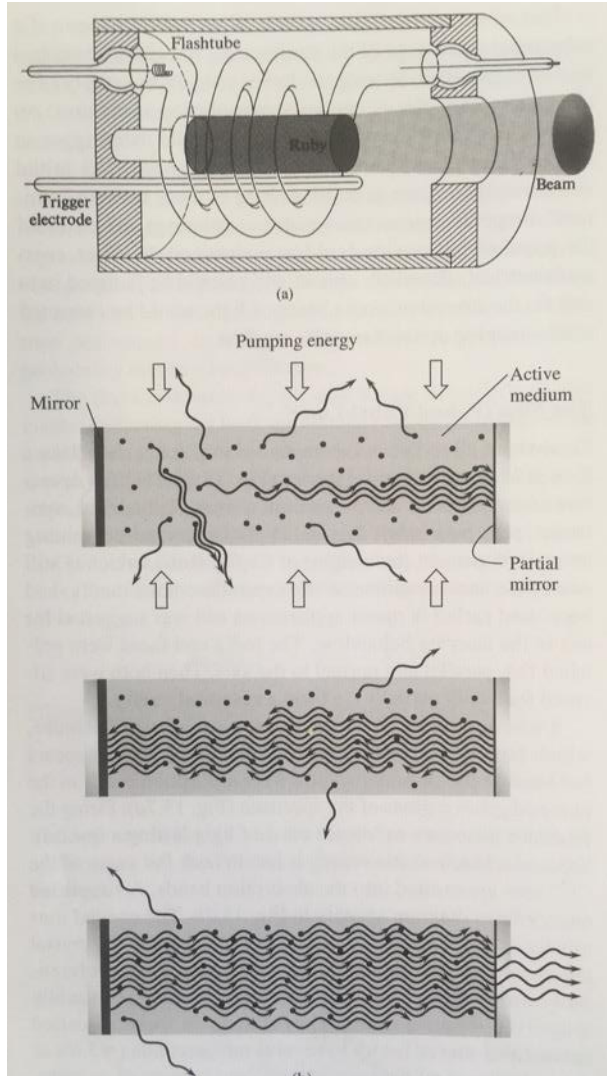
## Atomic lines vs cavity modes



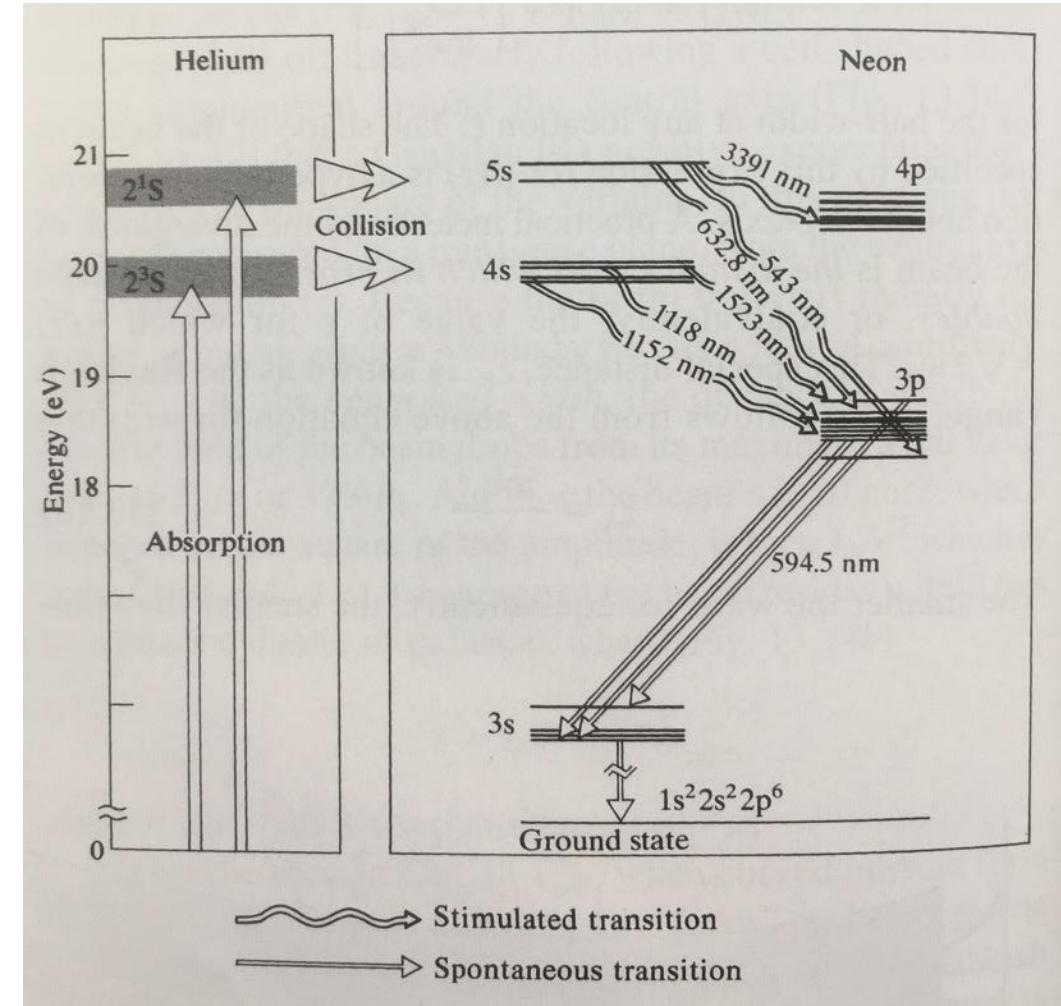
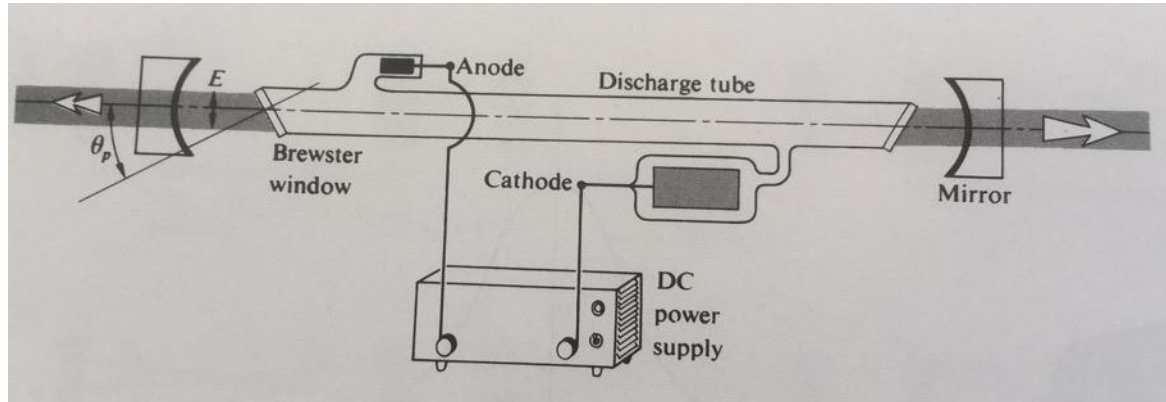
## Mode selection



# The Ruby laser

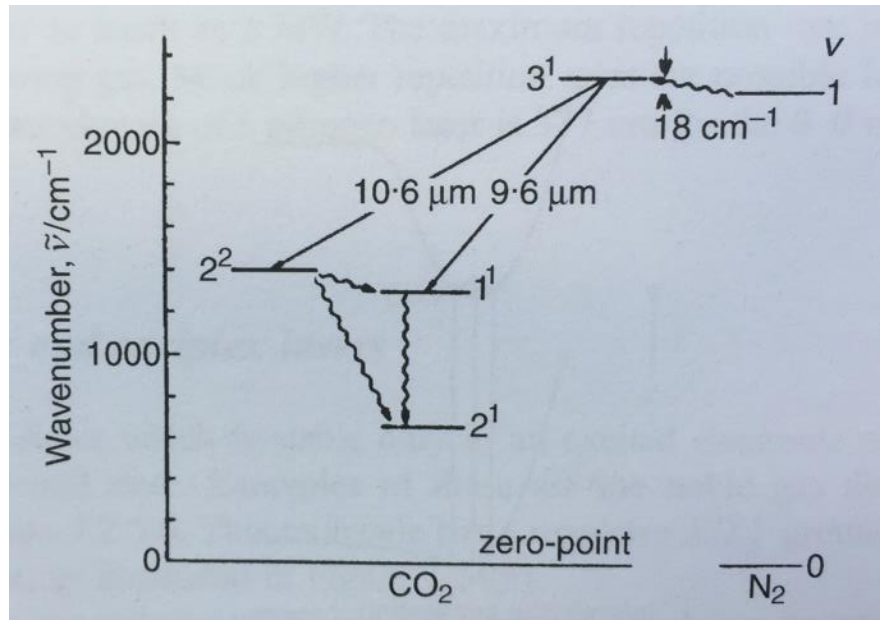


# The Helium Neon Laser - HeNe



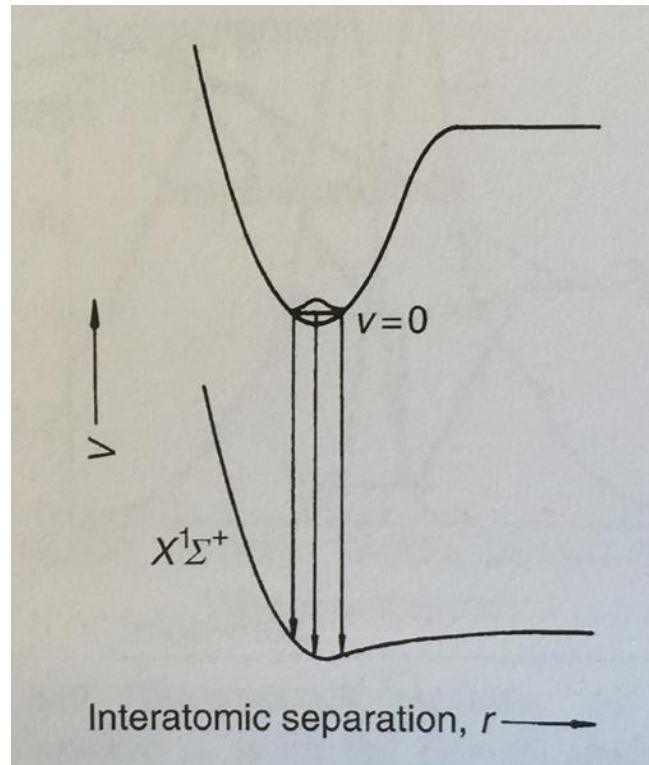
## Selected laser examples: Molecular gas laser

- Example: CO<sub>2</sub> laser
- Output in the mid-IR region
- High-power cw laser
- Machining and medical applications



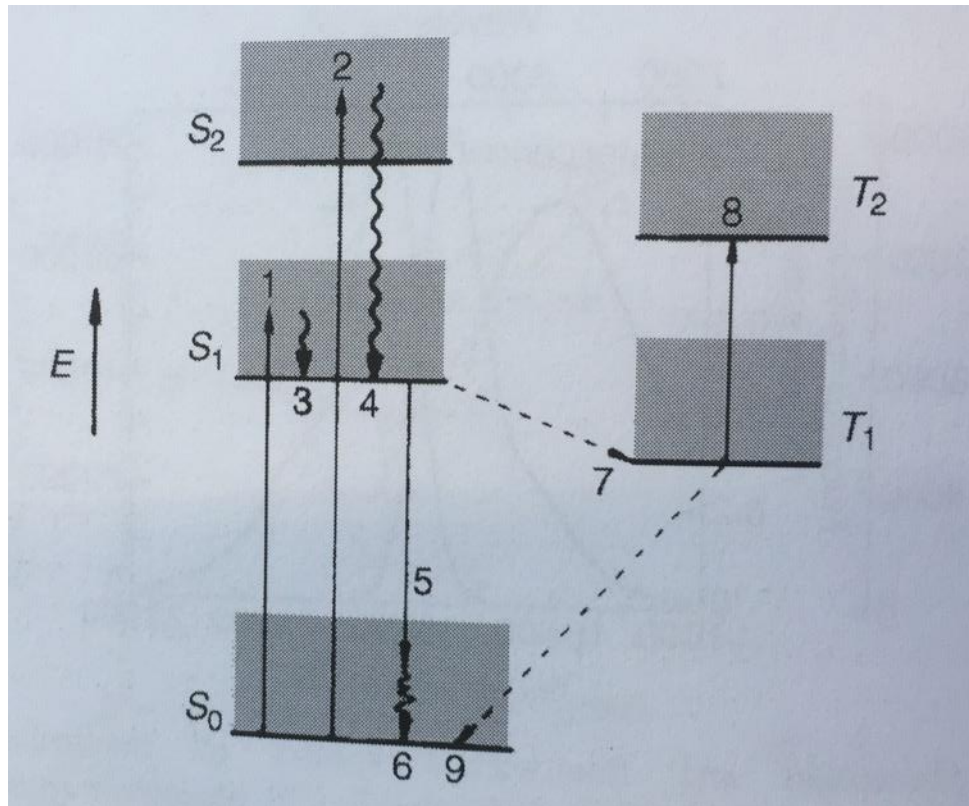
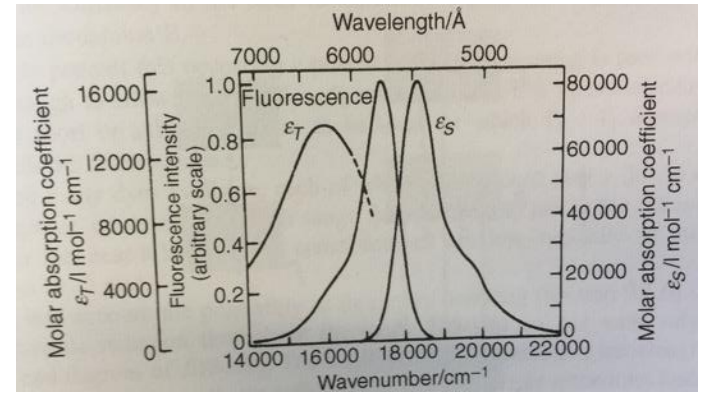
## Selected laser examples: Excimer laser

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



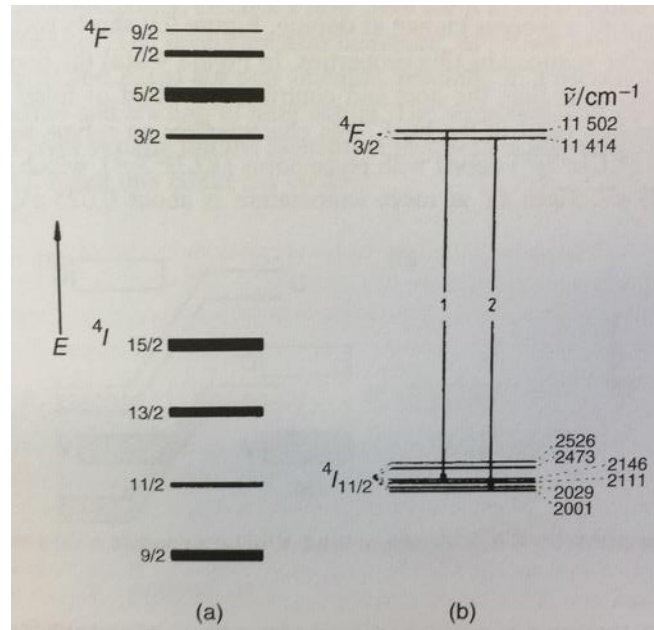
## Selected laser examples: Dye laser

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



## Selected laser examples: Nd:YAG

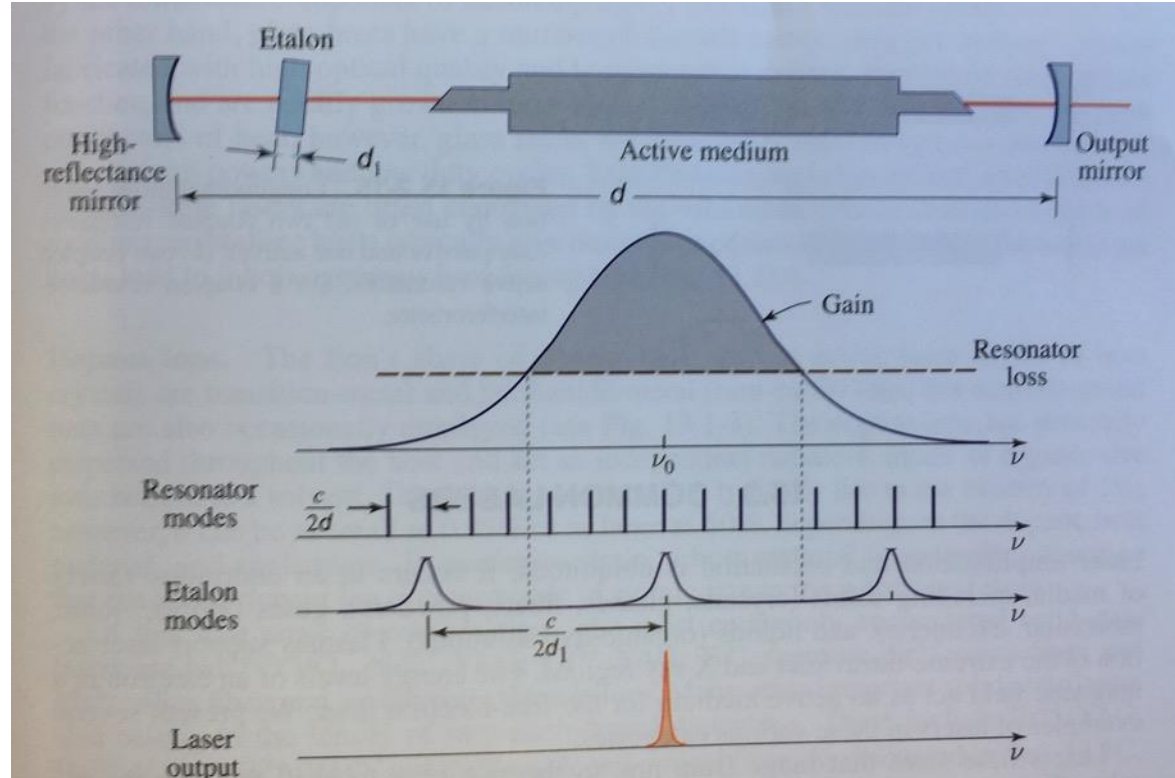
- Neodym doped Yttrium-Aluminium-Granate
- Nd<sup>3+</sup> ions in glass matrix
- Solid state laser
- Main line 1064 nm
- Work horse laser in many laboratories





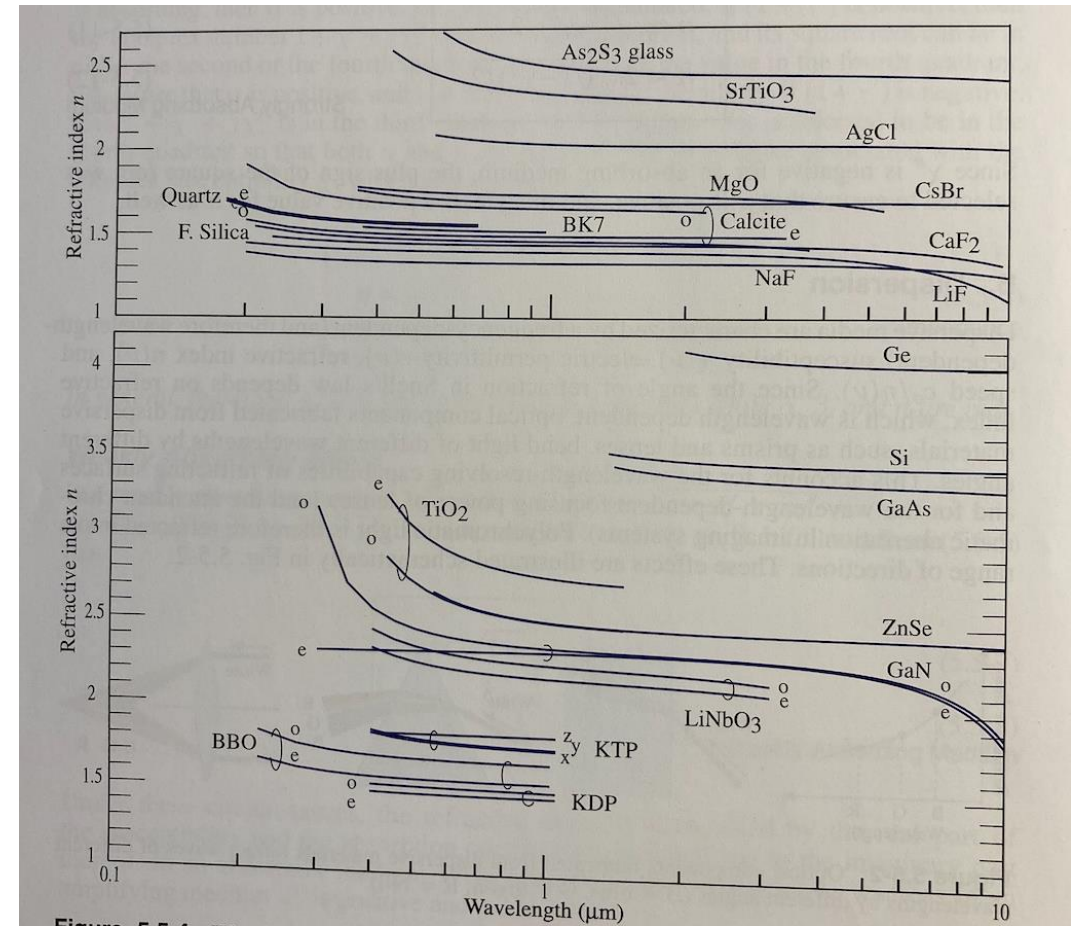
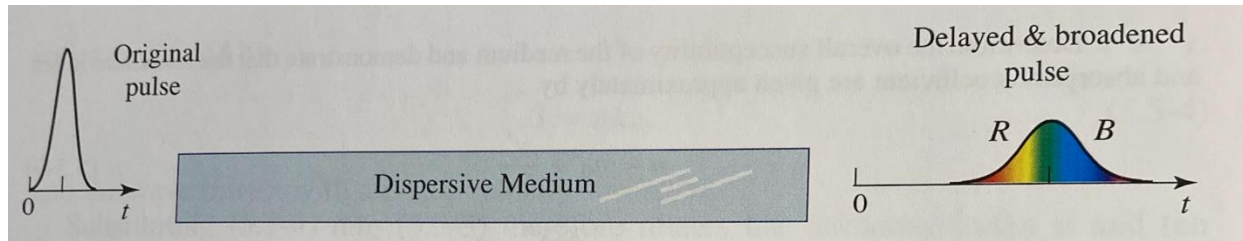


# Better approach: Mode selection with intracavity etalon

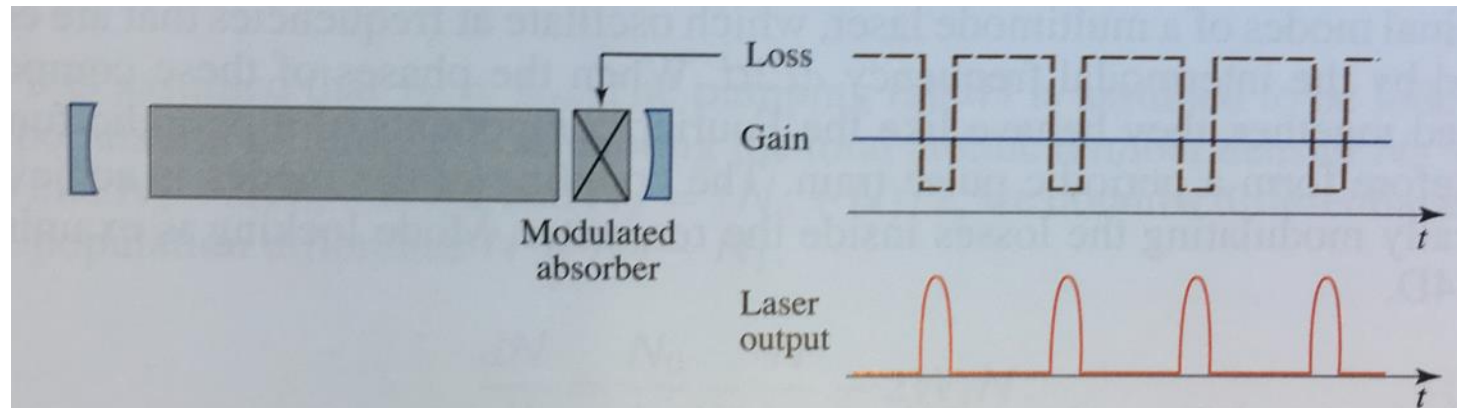


# Pulsed and Ultrafast Lasers

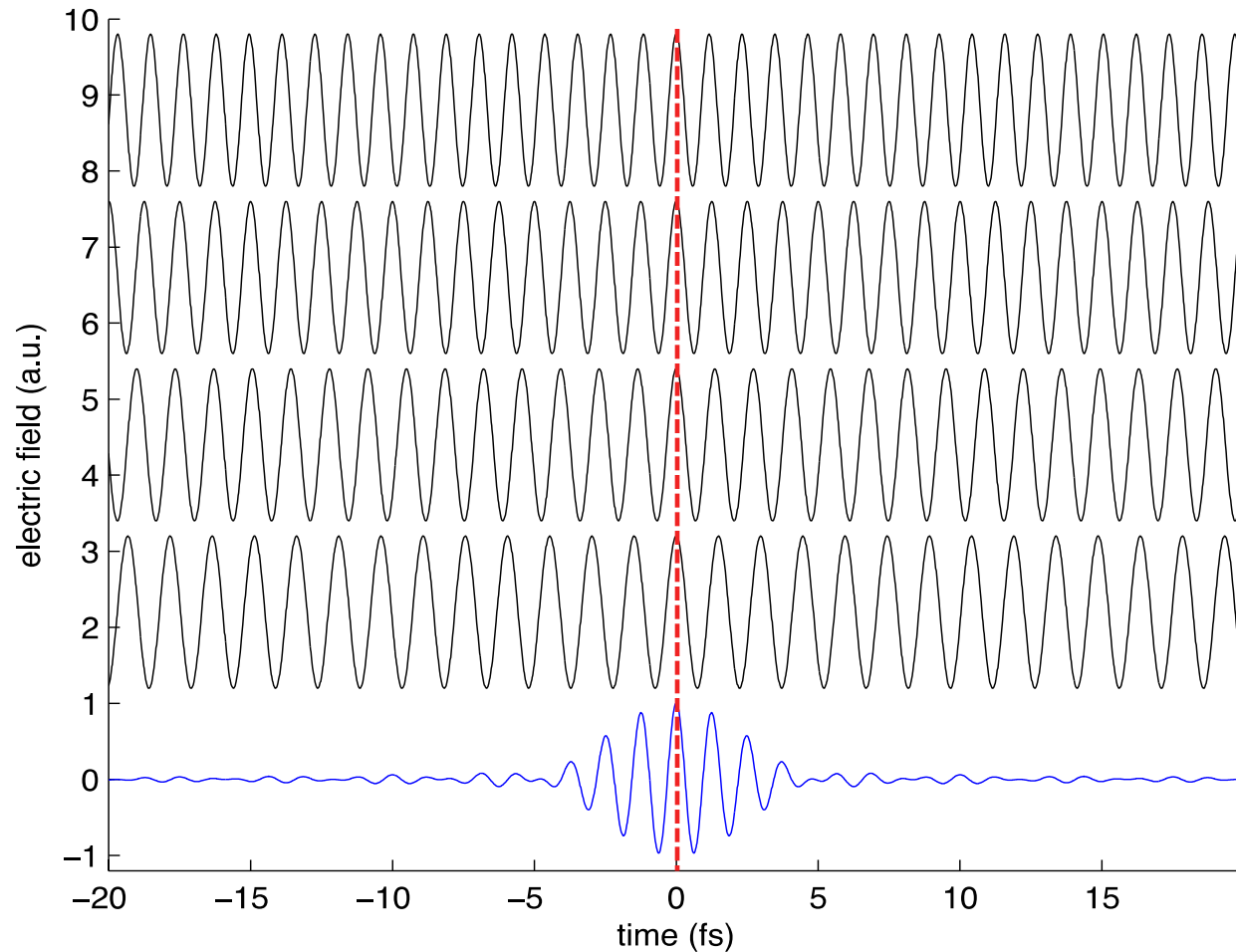
# A short pulse in a dispersive medium



# Pulsed lasers: Q-switching

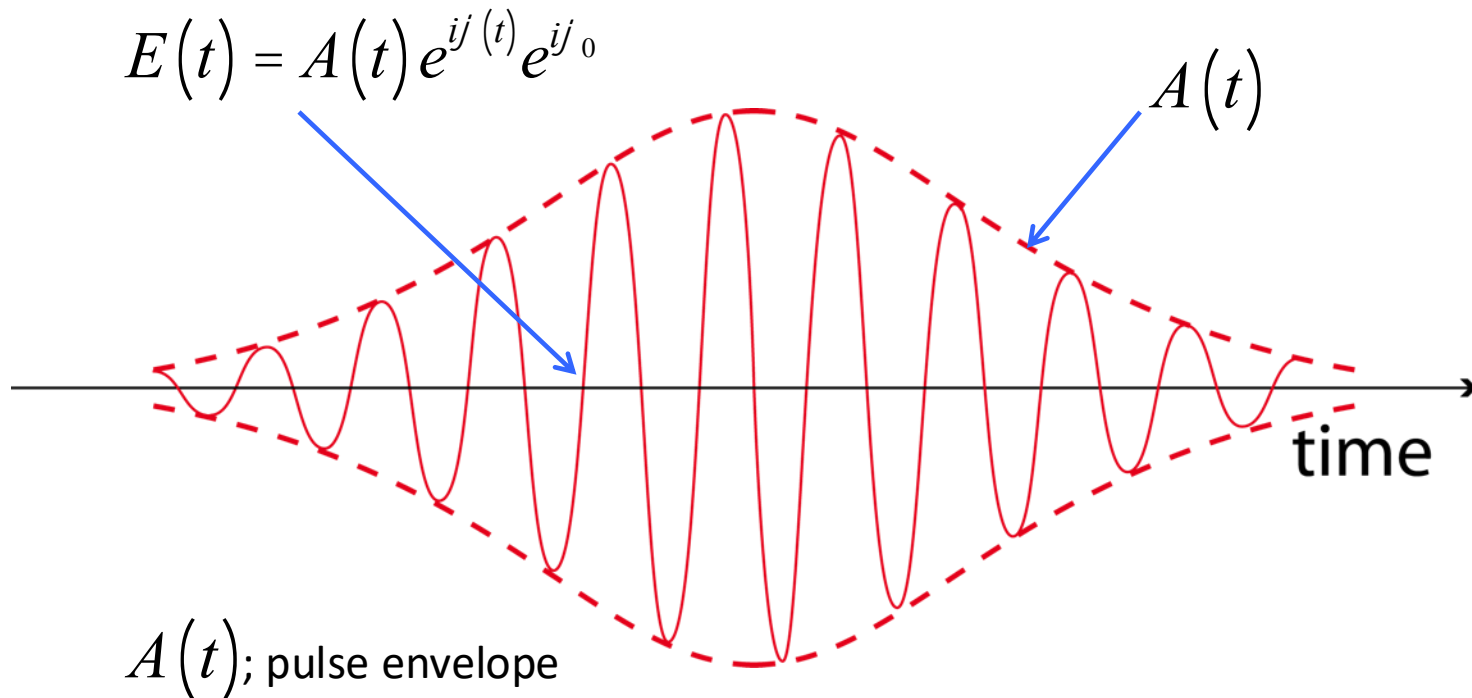


Short pulse needs many frequencies: Shortest pulse is Fourier transform limited pulse (aka bandwidth limited pulse)



## Note: Mathematical description of optical pulse

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$A(t)$ ; pulse envelope

$j(t)$ ; time dependent phase of electric field

$\omega(t) = -\frac{dj(t)}{dt}$ ; instantaneous frequency

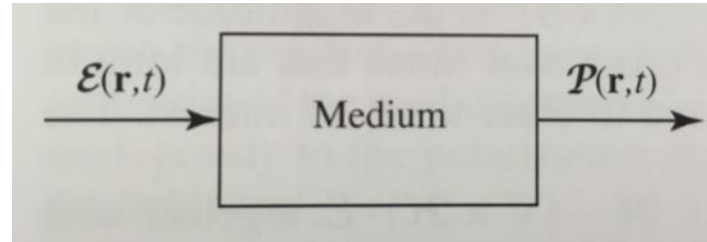
$j_0$ ; absolute phase (typically neglected for multi-cycle pulses)

# Back to formal description of light as EM wave



James Maxwell  
1831 - 1879

$$\begin{aligned}\nabla \times \mathcal{H} &= \epsilon_0 \frac{\partial \mathcal{E}}{\partial t} \\ \nabla \times \mathcal{E} &= -\mu_0 \frac{\partial \mathcal{H}}{\partial t} \\ \nabla \cdot \mathcal{E} &= 0 \\ \nabla \cdot \mathcal{H} &= 0,\end{aligned}$$



But stick with linear, nondispersive, homogenous, and isotropic media right now:

$$\mathcal{P} = \epsilon_0 \chi \mathcal{E},$$

$$\begin{aligned}\nabla \times \mathcal{H} &= \epsilon \frac{\partial \mathcal{E}}{\partial t} \\ \nabla \times \mathcal{E} &= -\mu \frac{\partial \mathcal{H}}{\partial t} \\ \nabla \cdot \mathcal{E} &= 0 \\ \nabla \cdot \mathcal{H} &= 0.\end{aligned}$$

## Generalization of susceptibility $\chi$ (still linear)

- Inhomogeneous media
- Anisotropic media
- Dispersive media

General:

Interpretation: Dynamic relationship between  $E$  and  $P$

- $E$  induces bound electrons in material to oscillate
- Time-dependent Polarization density  $P(t)$
- Time-delay between  $E(t)$  and  $P(t)$

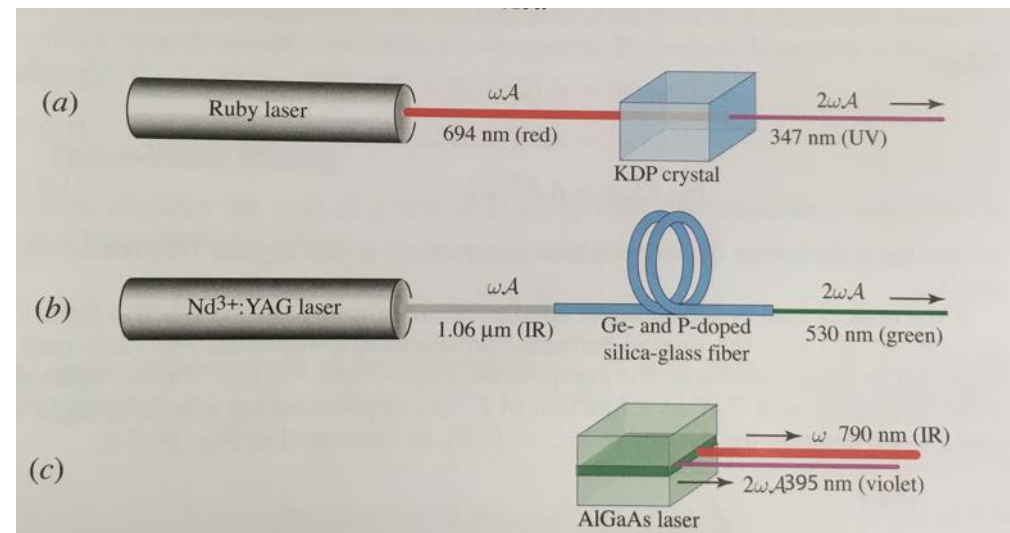


# Non-linear optical media

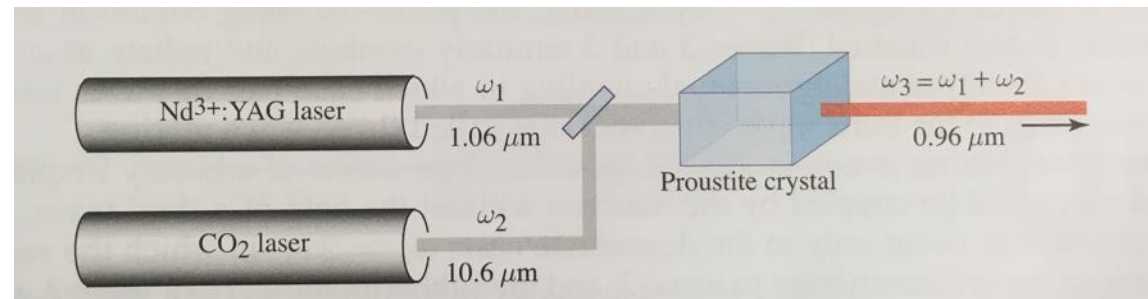
Handwaving:

- Linear: restoring force of light induced fields linear (“Hookes law applies”)
- Non-linear: Light induced fields comparable to inter-atomic fields in crystal (“no more linear forces”)
- (Note: fields still weak compared to intra-atomic fields – that is a later topic)

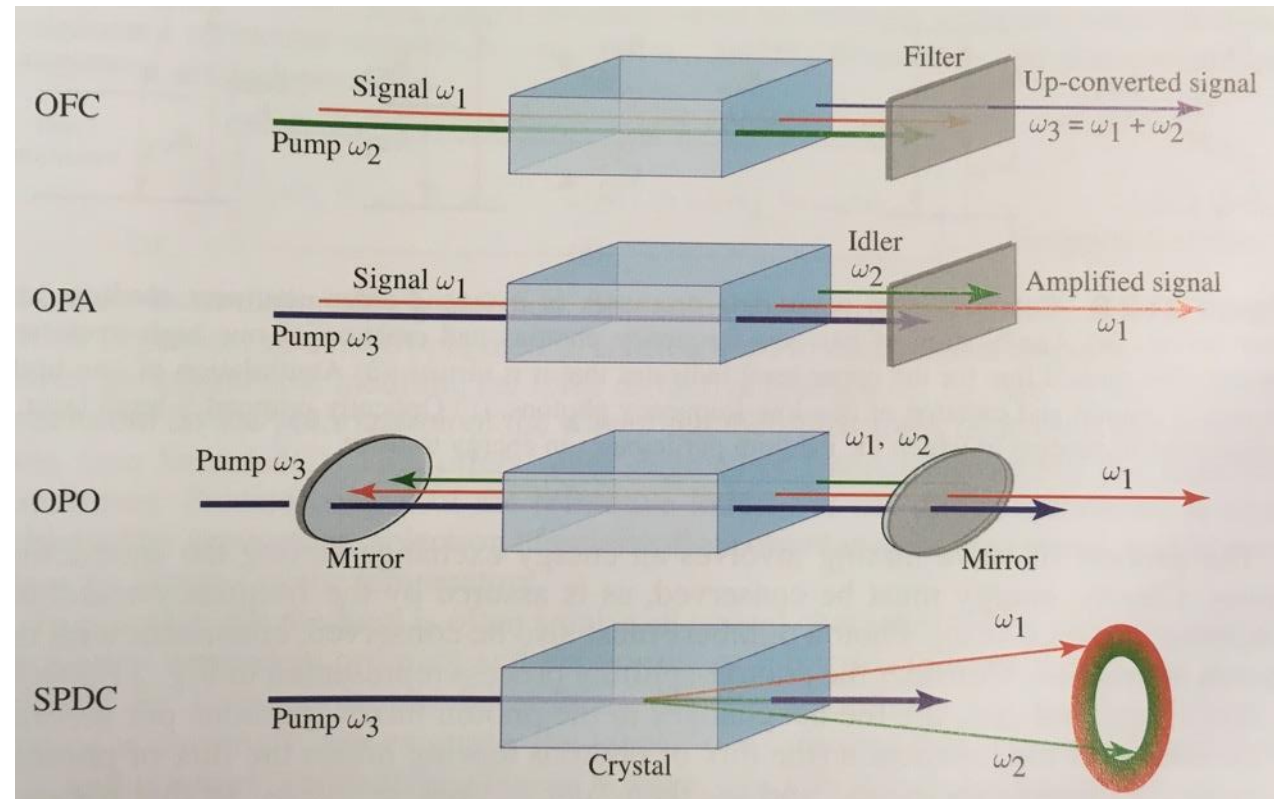
## Second order non-linear optics example: Second harmonic generation



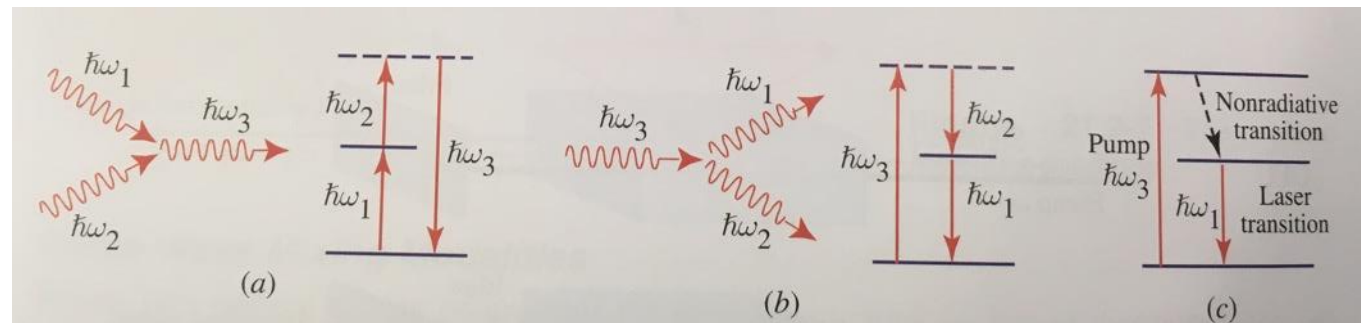
## Second order non-linear optics example: Sum frequency generation



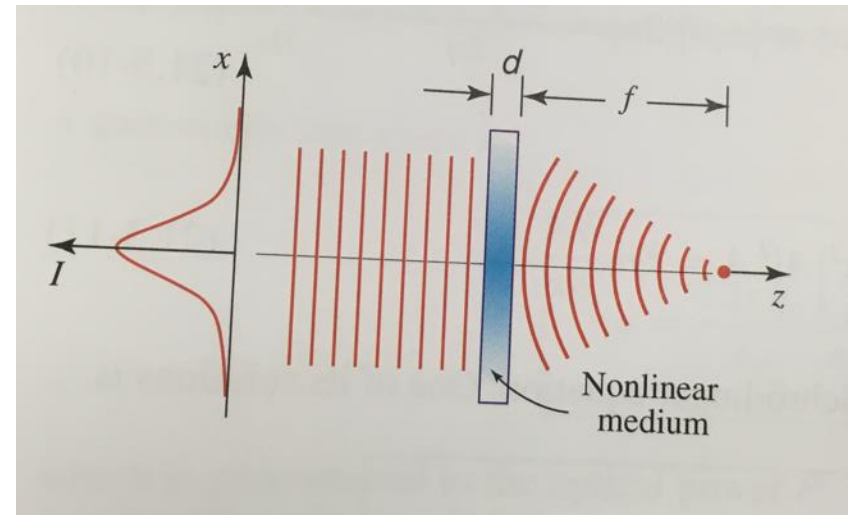
## Second order non-linear optics example: Optical parametric devices



# Second order non-linear optics example: Description as photon interaction process

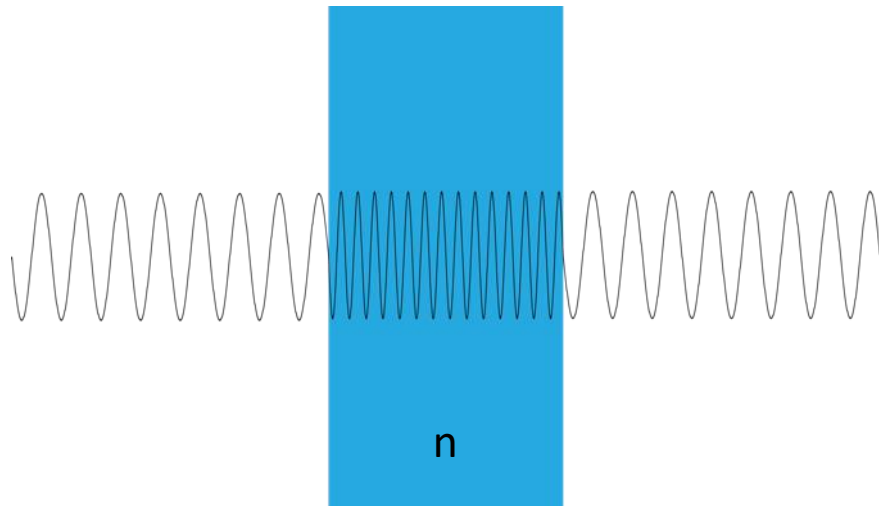


## Third order non-linear optics example: Optical Kerr Effect and Self-Focusing

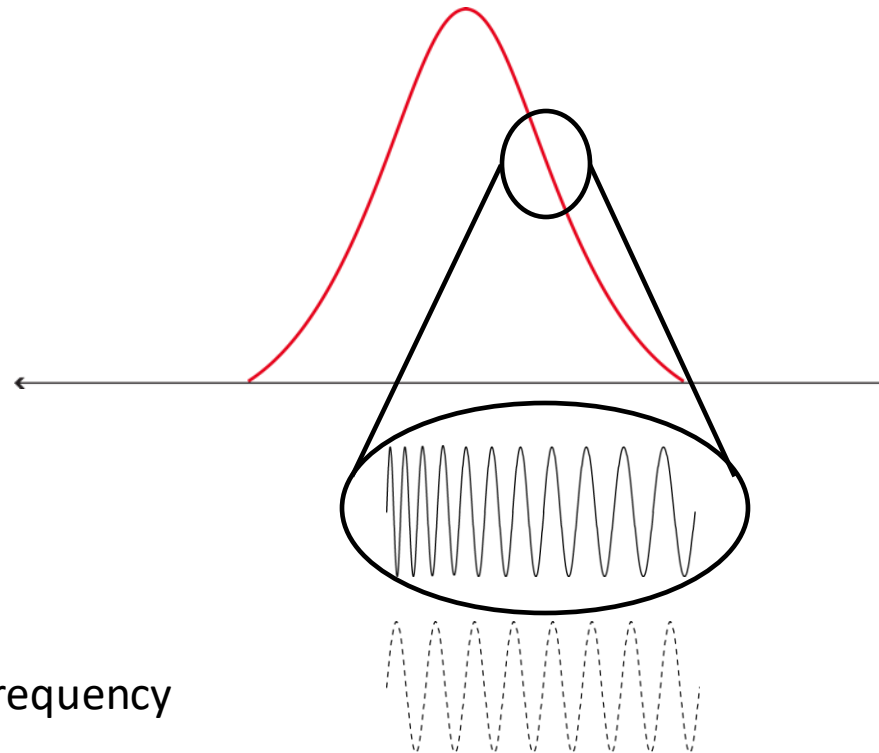


# Third order non-linear optics example: Self-phase modulation

normal refractive index



time-dependent refractive index

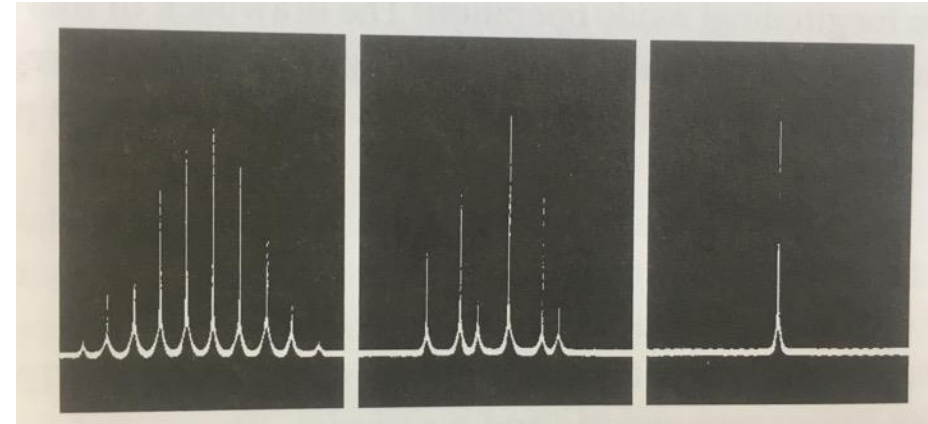
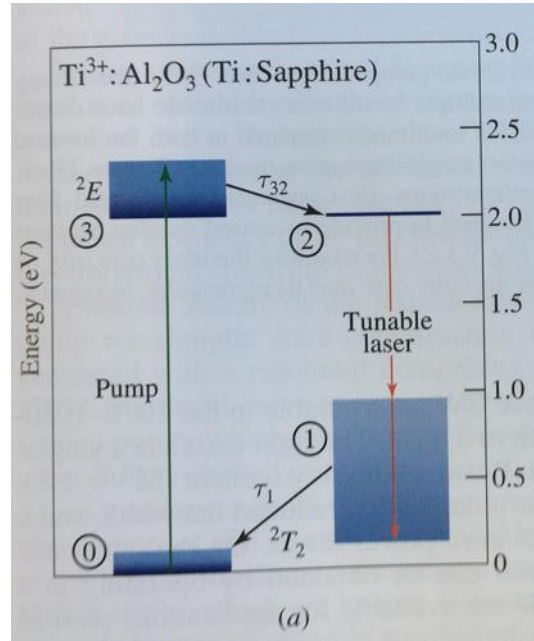


$$\omega(t) = -\frac{dj(t)}{dt} ; \text{instantaneous frequency}$$

- Conceptually – consider a plane monochromatic wave
- Time-dependent index leads to time-dependent frequency
- New frequency components are generated

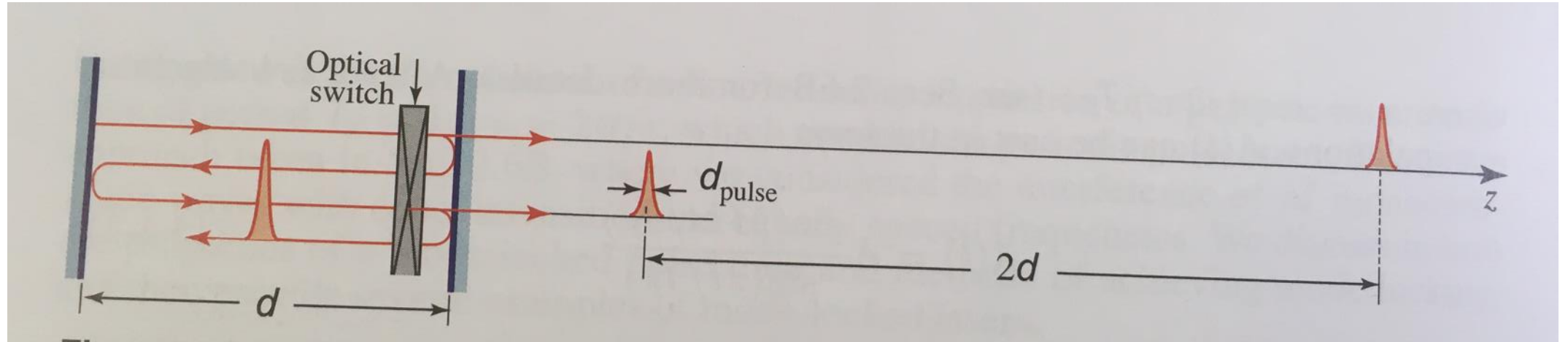
Back to lasers. Remember the problem?

Short pulses and cavities – how do they go together?



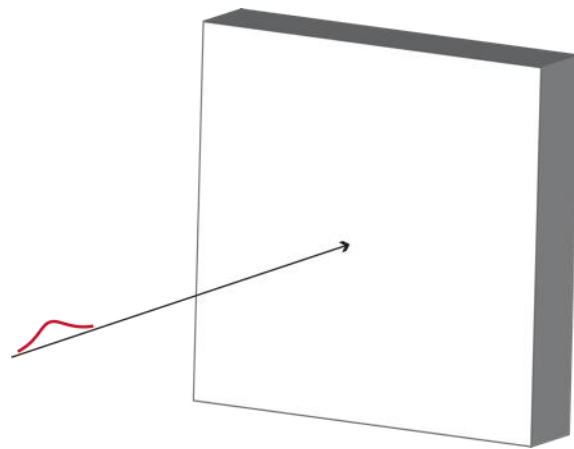
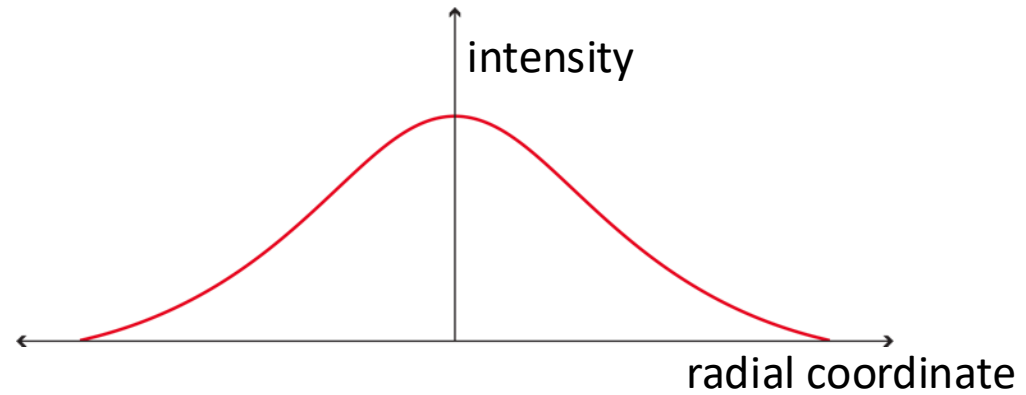


# Mode locking

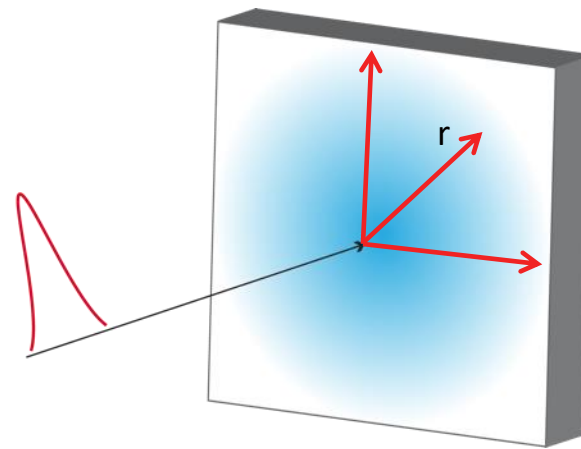


# Kerr lens from non-linear refractive index

spatial profile:

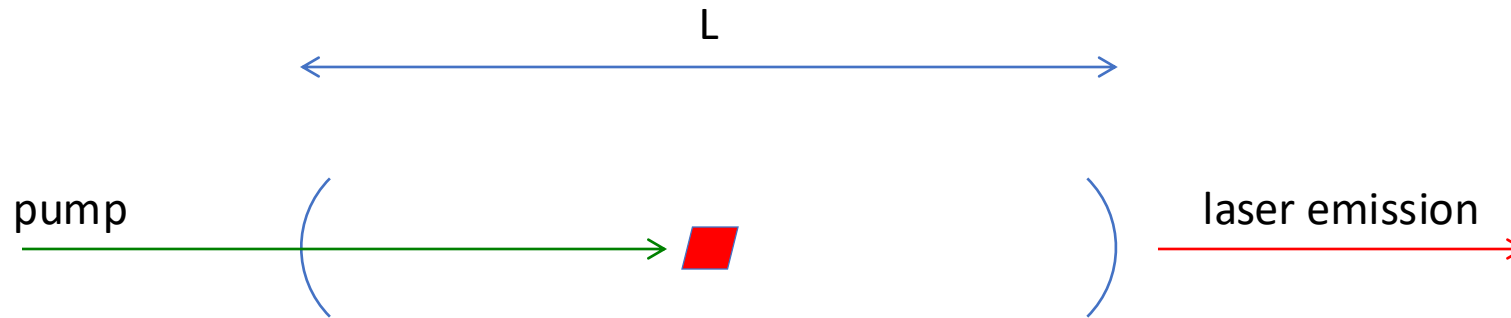


material behaves transparent



material behaves as a lens

## Resonant laser cavity

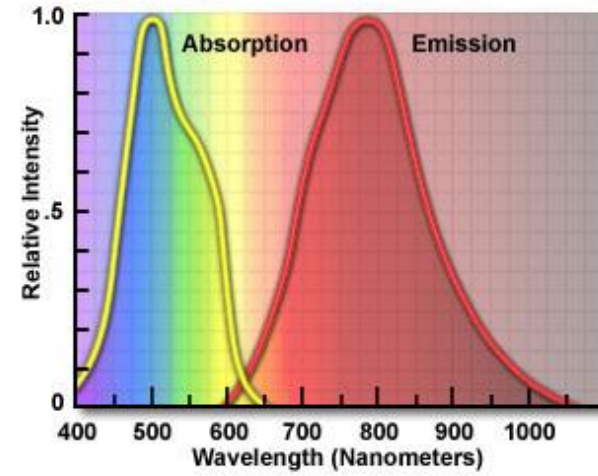
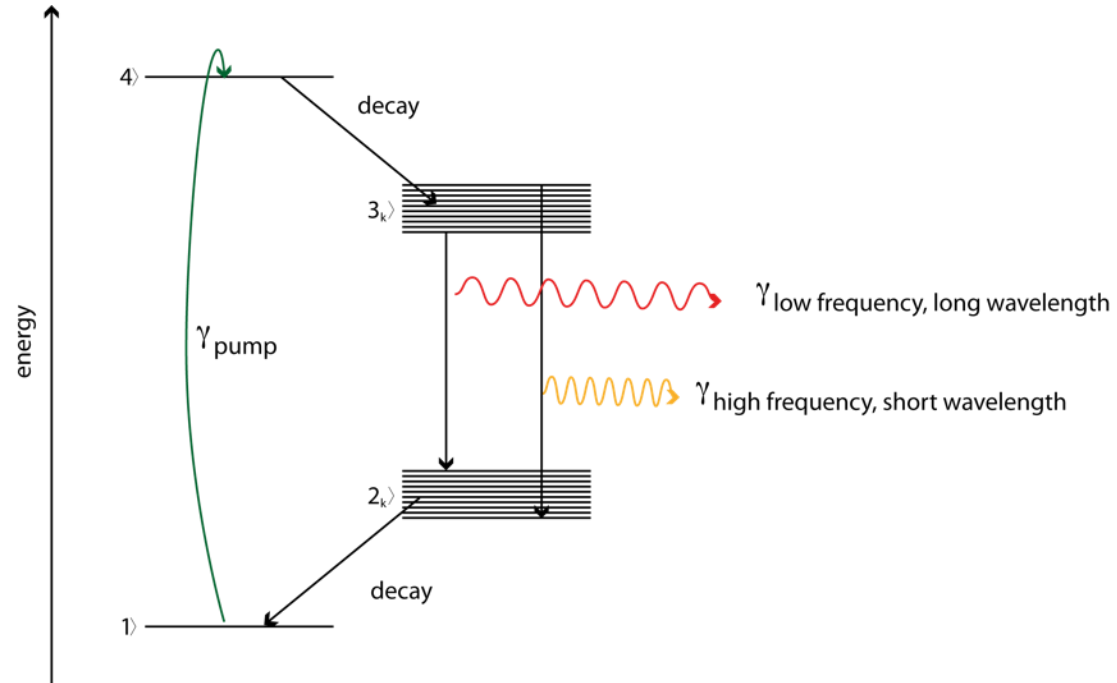


Resonant modes have nodes at cavity end mirrors

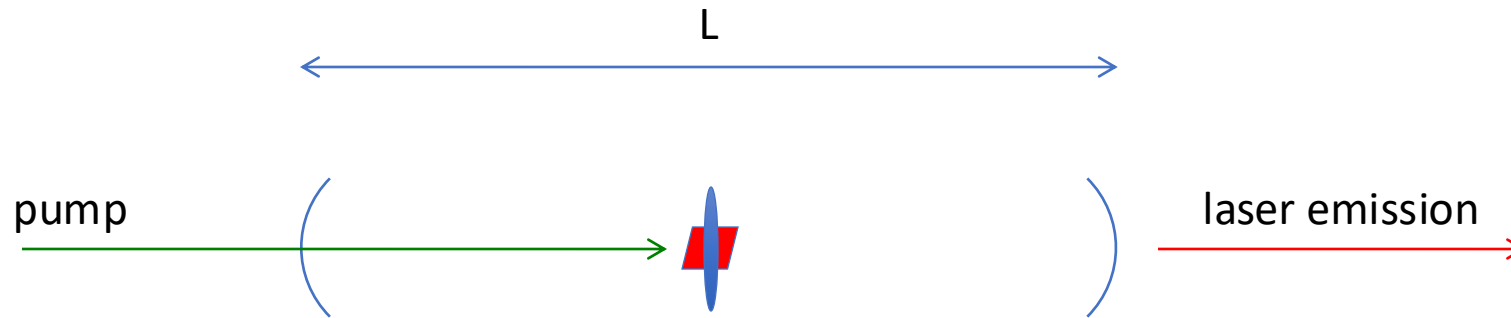
Resonant wavelengths and possible frequency modes given by:

$$l_n = \frac{2L}{n} \quad \nu_n = n \frac{c}{2L}$$

# TiSapphire gain medium



# Self mode locking

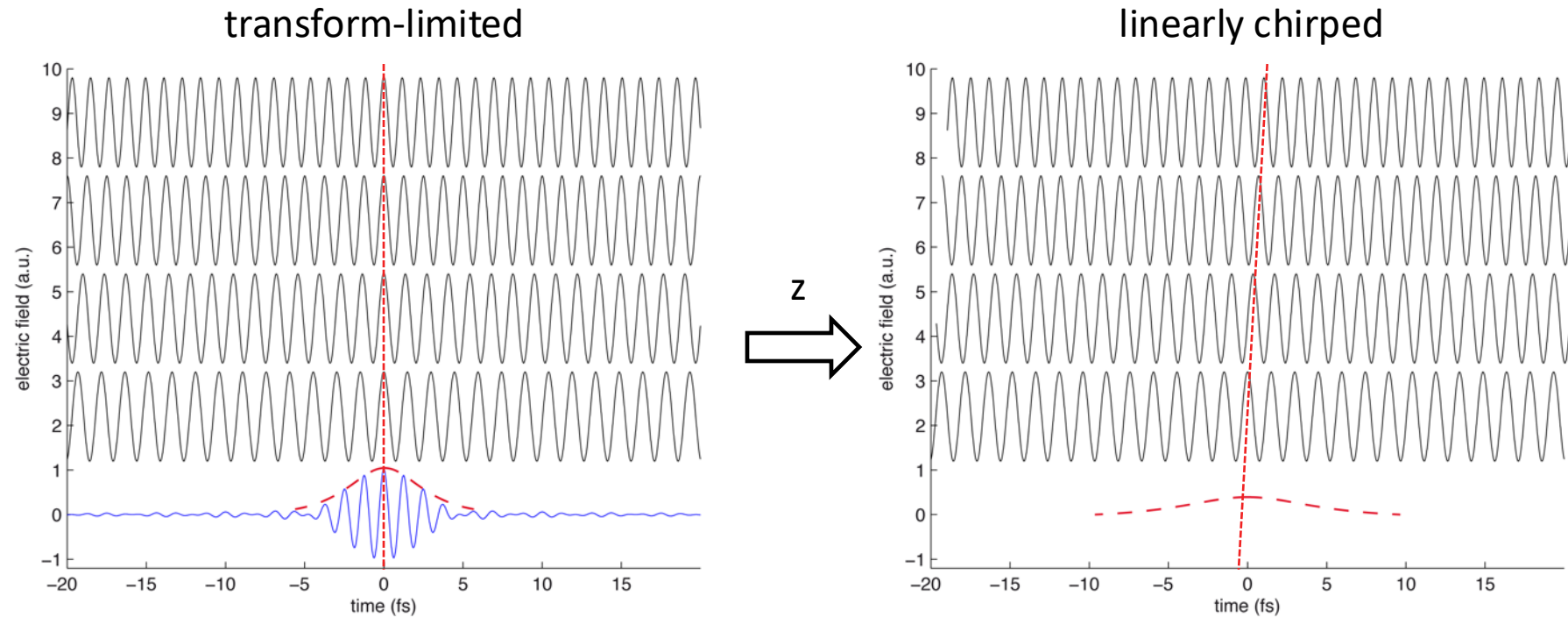


- Kerr Lens Effect, due to nonlinear index of refraction
- At high intensities, the gain crystal acts like a lens
- Cavity tuned so that is most efficient with the crystal behaving as a lens
- Many modes lase and automatically arrange phases for pulsed high-intensity operation
- Intra-cavity dispersion tuned to support pulsed operation
- nJ pulse energies as short as 4 fs FWHM
- Output ~100MHz repetition rate pulse train

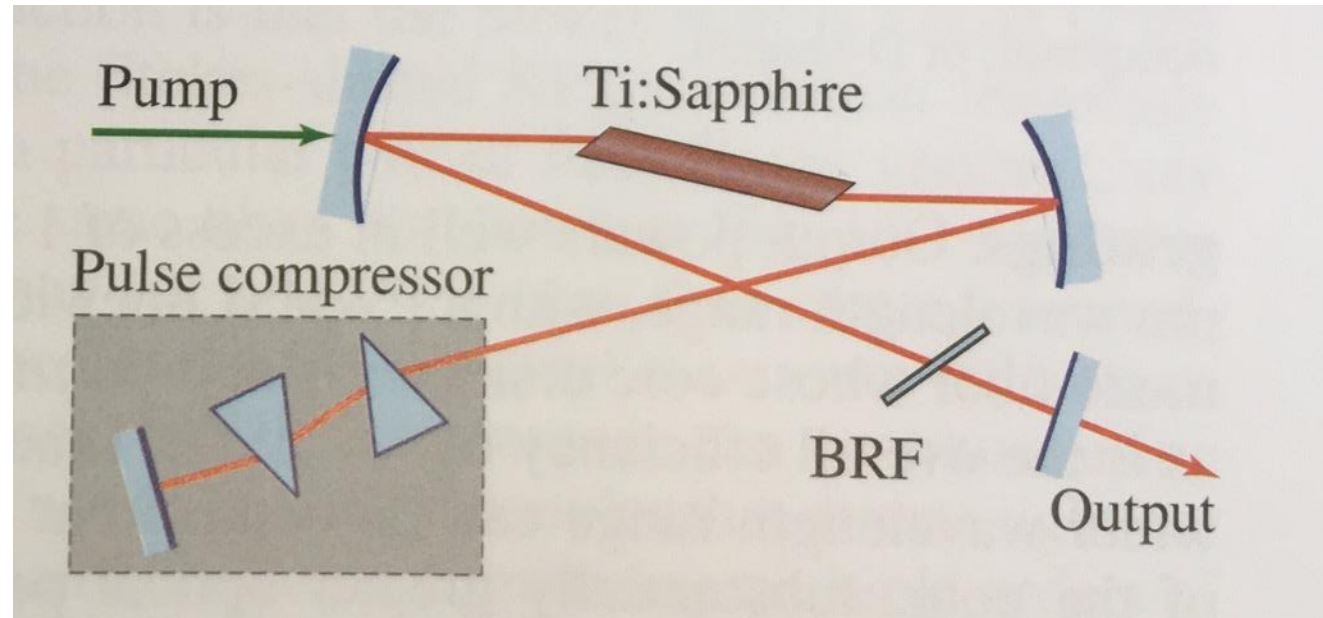
$$U_{rep-rate} = \frac{\pi c \theta}{2L \theta}$$

# A note on “chirp”

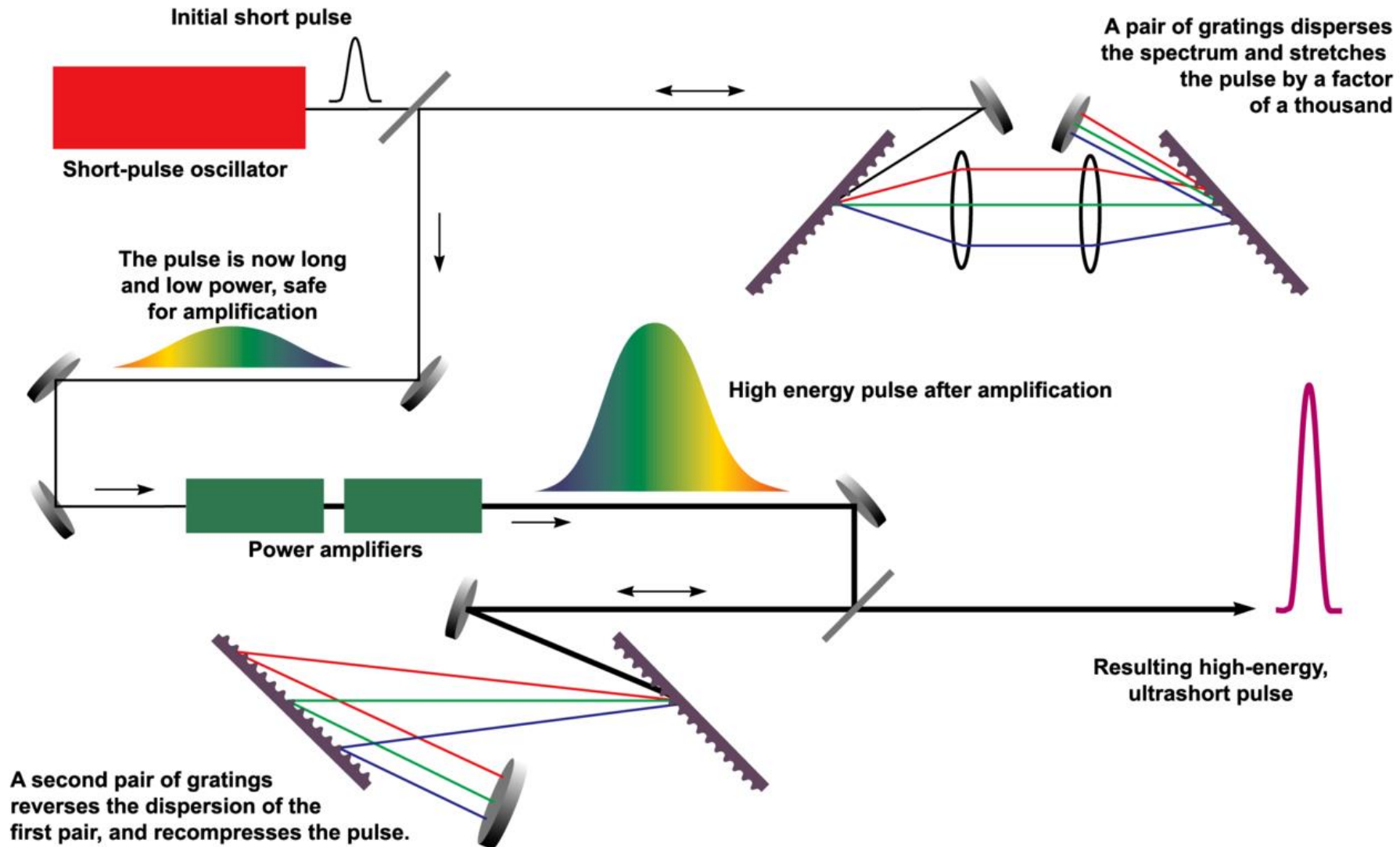
Initially transform limited pulse becomes chirped upon propagation, ( $k_2 \neq 0, \gamma = 0$ )



# Ti:Sapphire oscillator setup



# Chirped pulse amplification

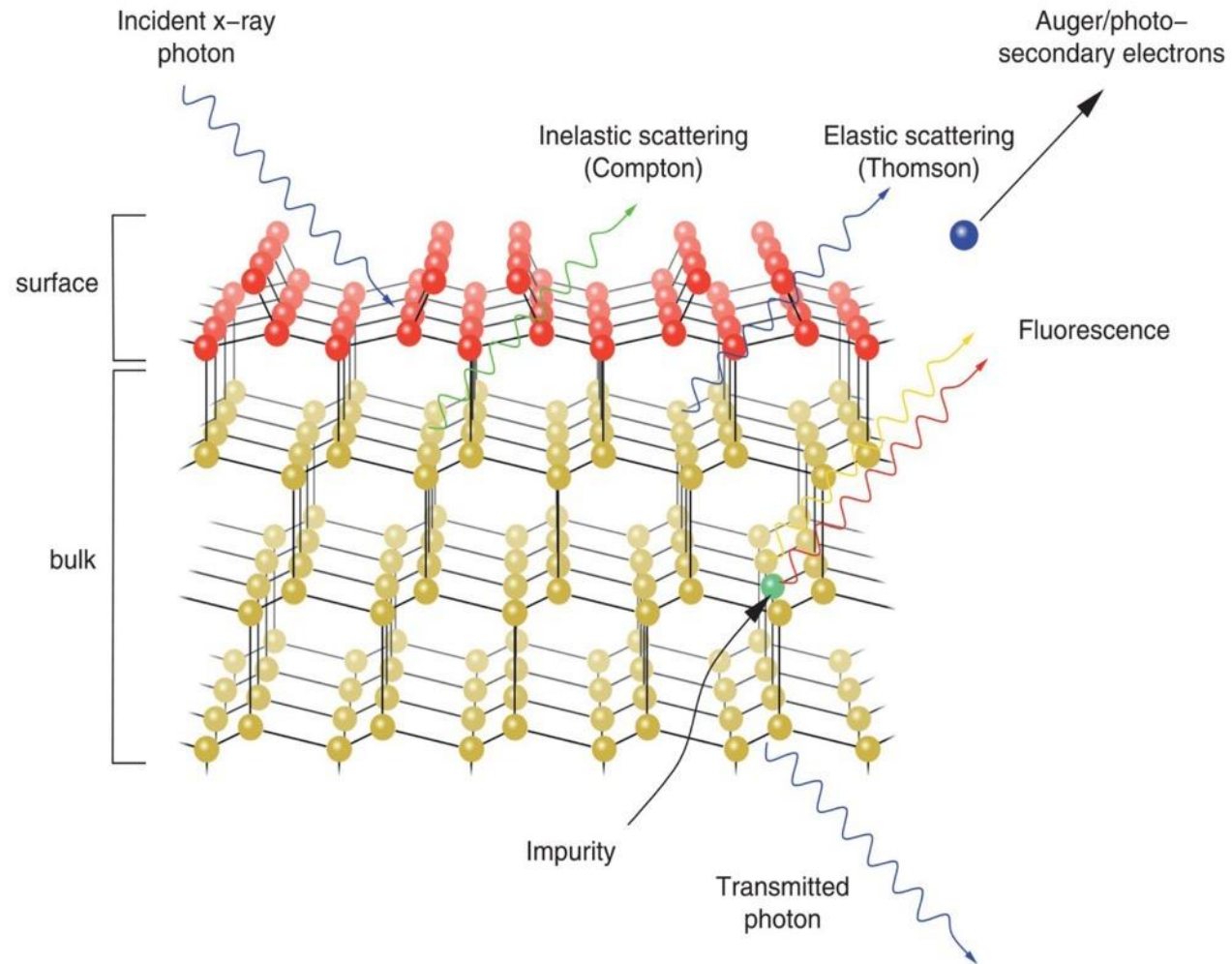




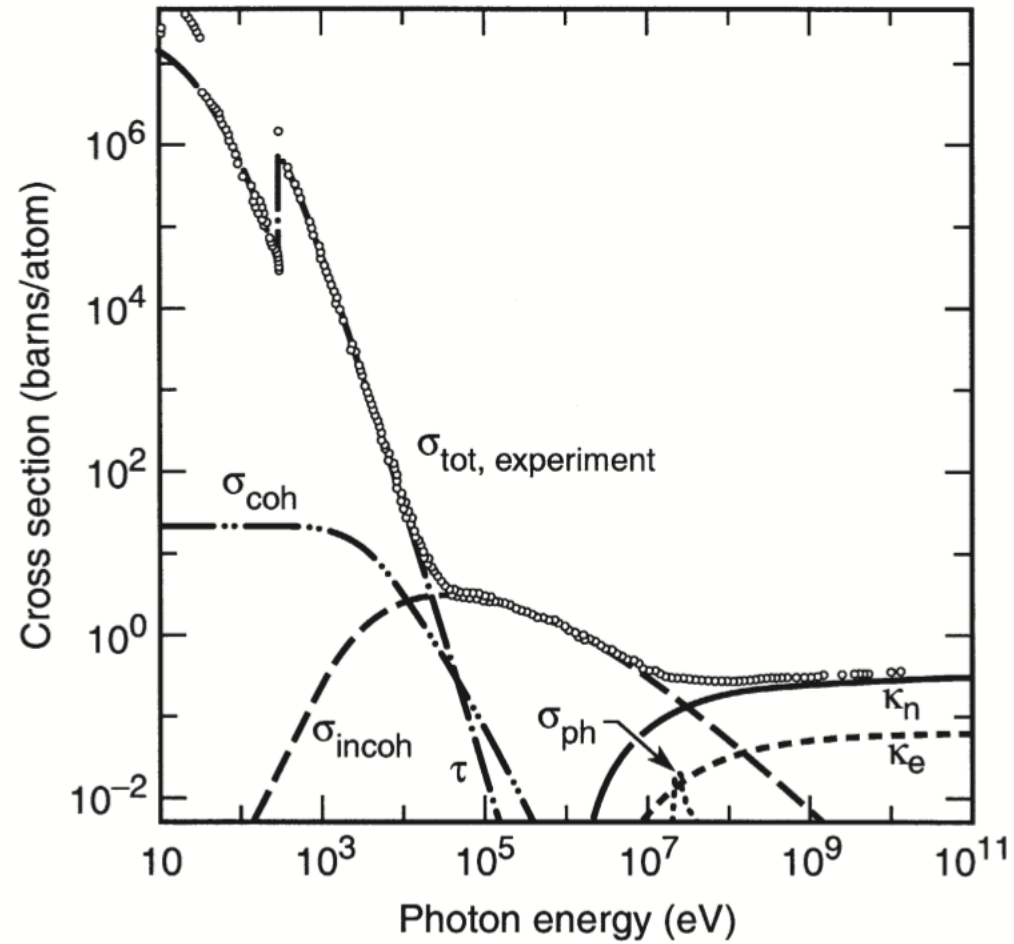
X-rays

# X-ray interactions with matter

# X-ray interactions with matter

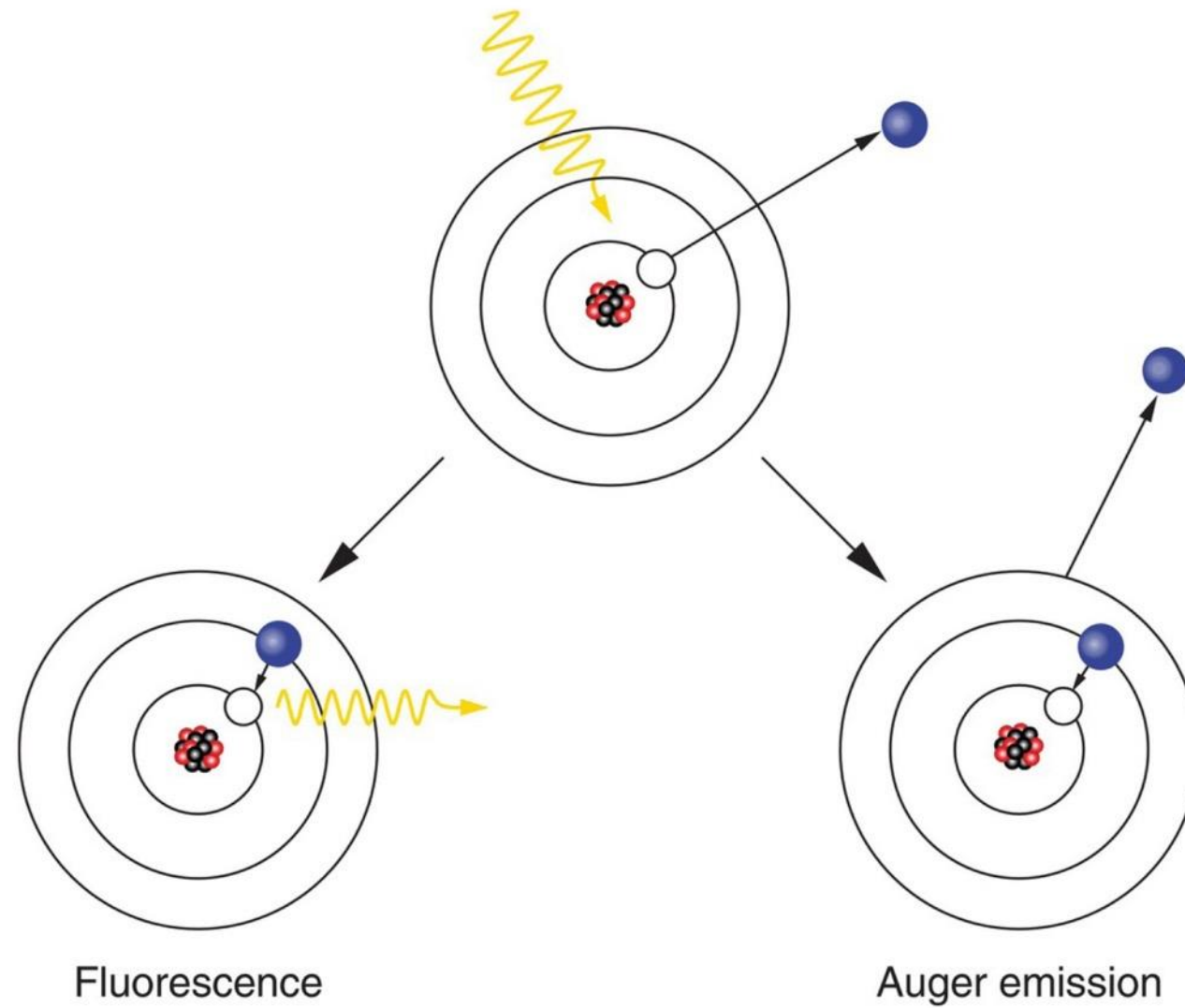


# X-ray cross sections

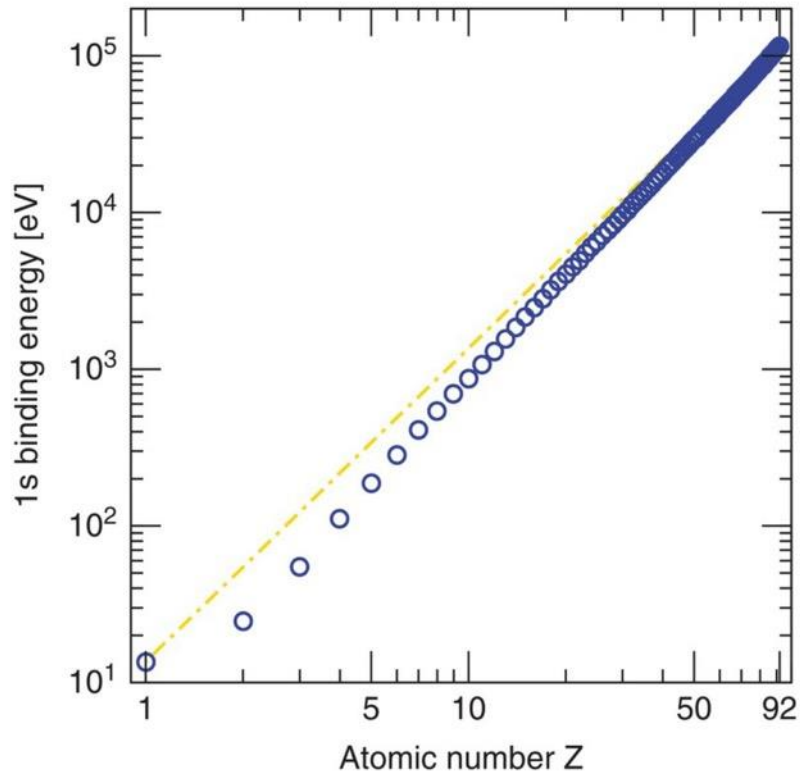


*Fig. 3-1. Total photon cross section  $\sigma_{tot}$  in carbon, as a*

# Photoionization / absorption



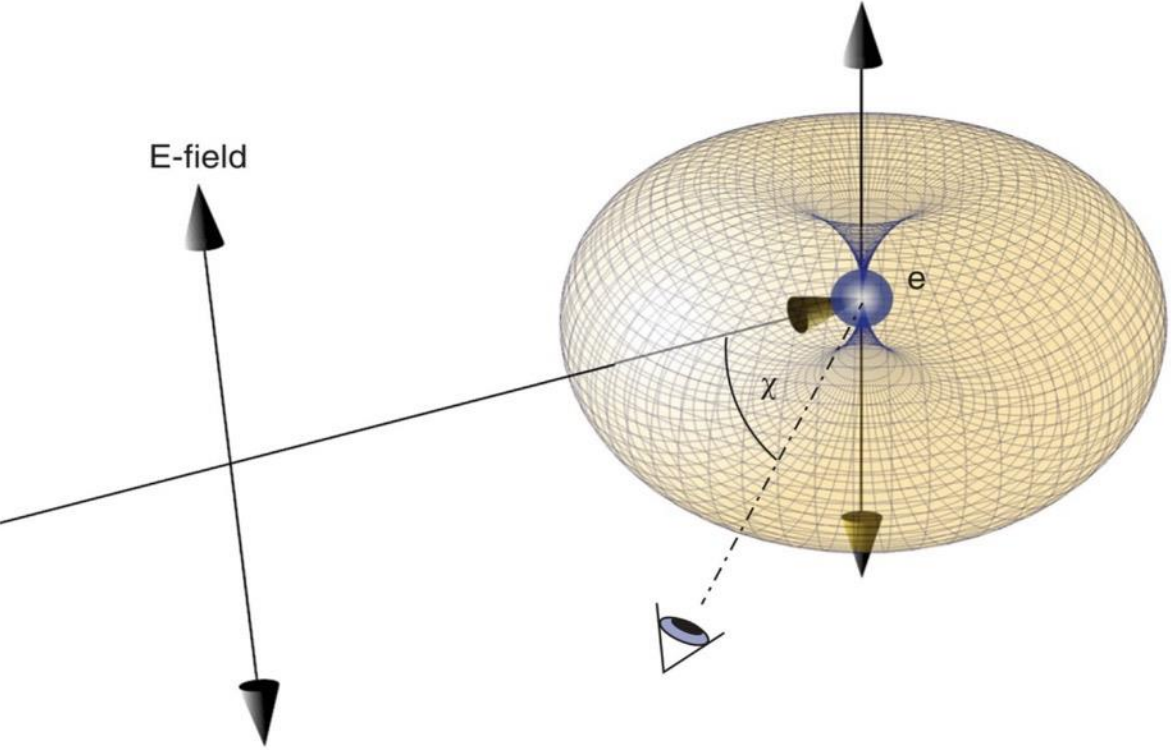
# Ionization energies of elements



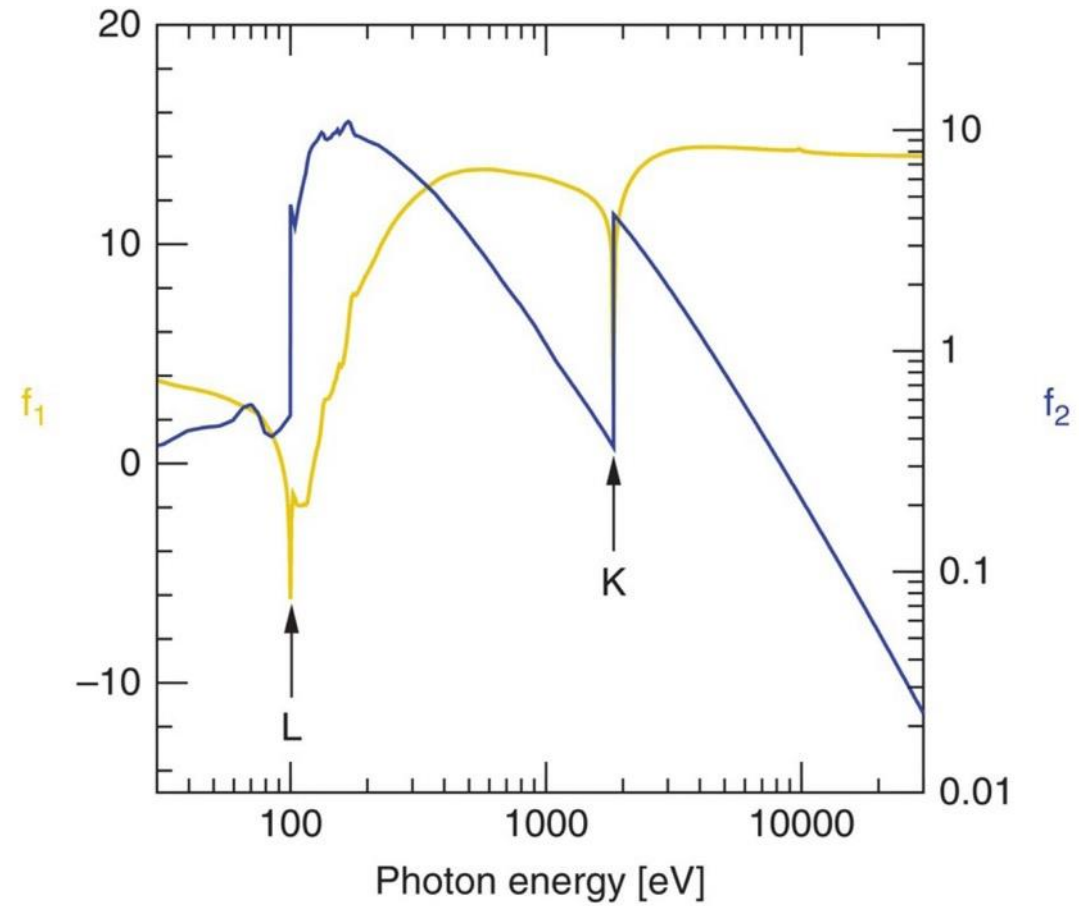
*Table I-1. Electron binding energies, in electron volts, for the elements in their natural forms.*

Element	K 1s	L <sub>1</sub> 2s	L <sub>2</sub> 2p <sub>1/2</sub>	L <sub>3</sub> 2p <sub>3/2</sub>	M <sub>1</sub> 3s	M <sub>2</sub> 3p <sub>1/2</sub>	M <sub>3</sub> 3p <sub>3/2</sub>	M <sub>4</sub> 3d <sub>3/2</sub>	M <sub>5</sub> 3d <sub>5/2</sub>	N <sub>1</sub> 4s	N <sub>2</sub> 4p <sub>1/2</sub>
1 H	13.6										
2 He	24.6*										
3 Li	54.7*										
4 Be	111.5*										
5 B	188*										
6 C	284.2*										
7 N	409.9*	37.3*									
8 O	543.1*	41.6*									
9 F	696.7*										
10 Ne	870.2*	48.5*	21.7*	21.6*							
11 Na	1070.8†	63.5†	30.65	30.81							
12 Mg	1303.0†	88.7	49.78	49.50							
13 Al	1559.6	117.8	72.95	72.55							
14 Si	1839	149.7*b	99.82	99.42							
15 P	2145.5	189*	136*	135*							
16 S	2472	230.9	163.6*	162.5*							
17 Cl	2822.4	270*	202*	200*							
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*				
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*				
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†				
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*				
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†				

# Thomson scattering

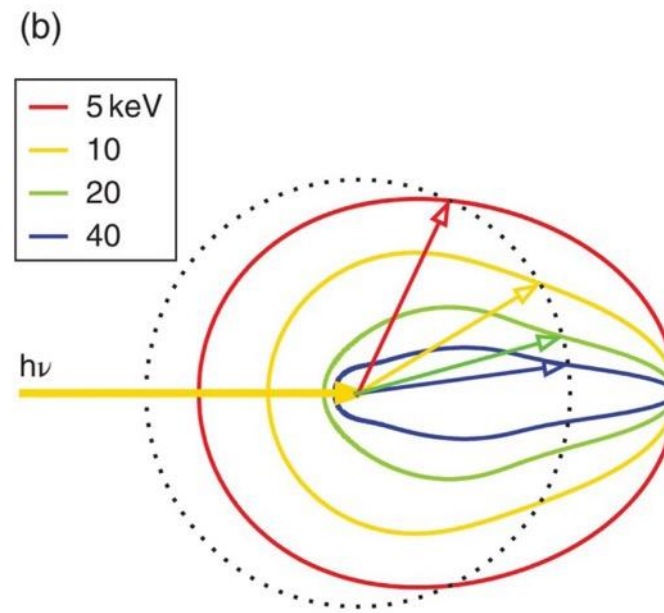
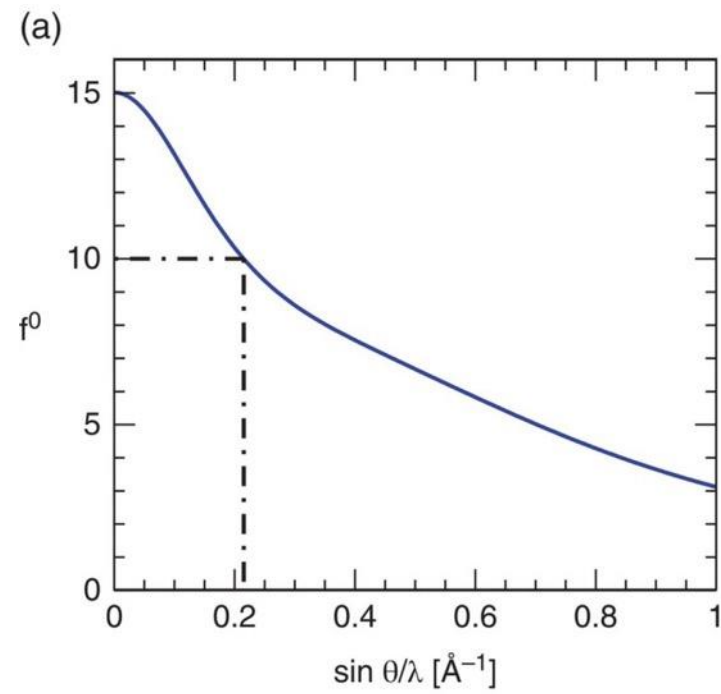


# Atomic scattering factors and refractive index



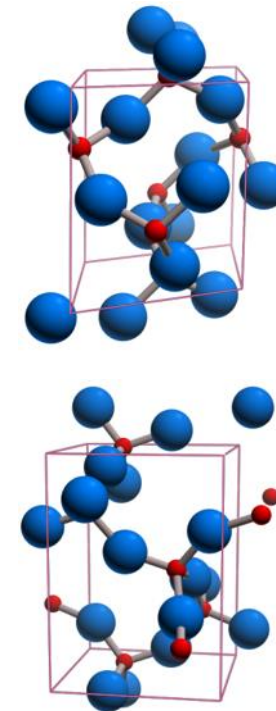
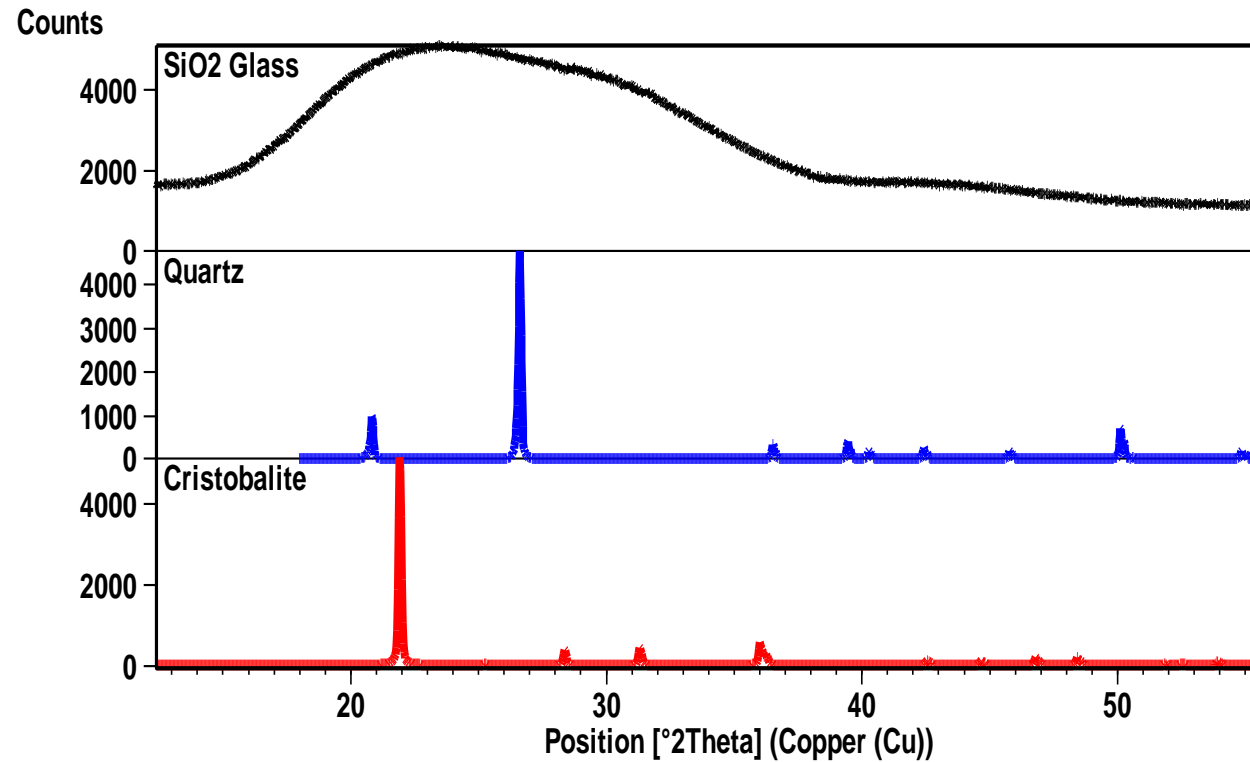


# Now full cross section / atomic scattering factors

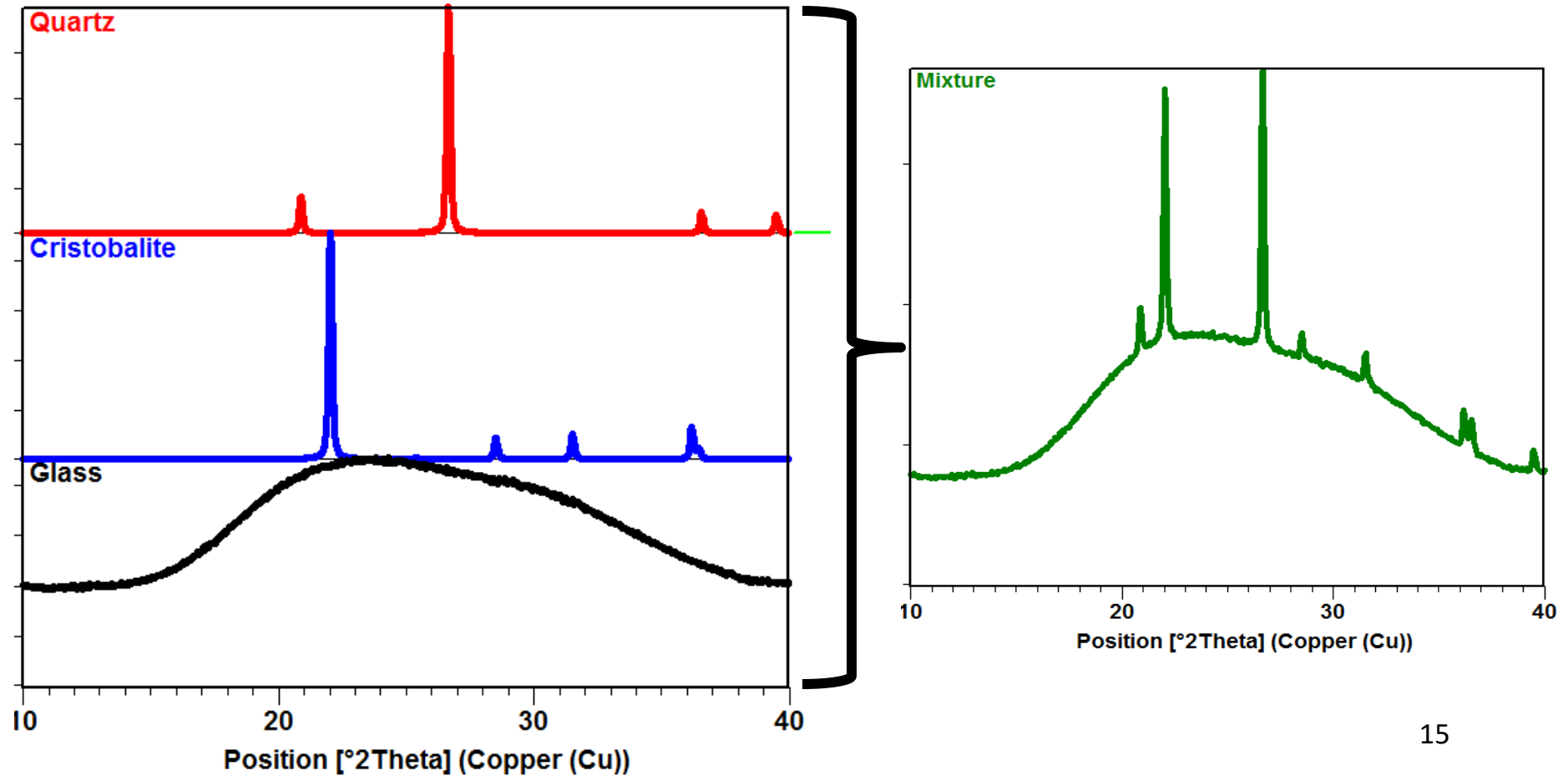


# Diffraction by a crystal

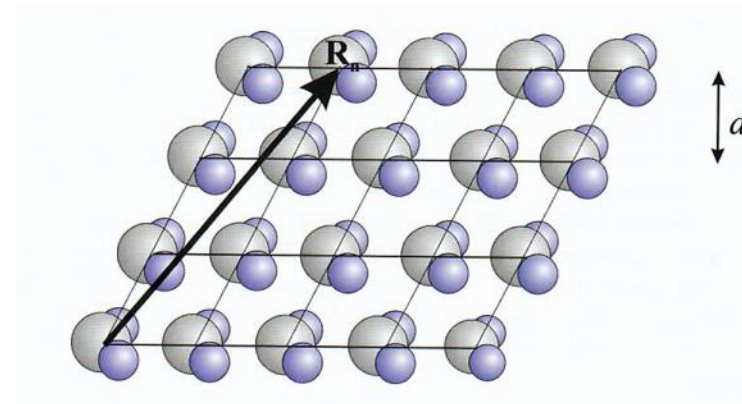
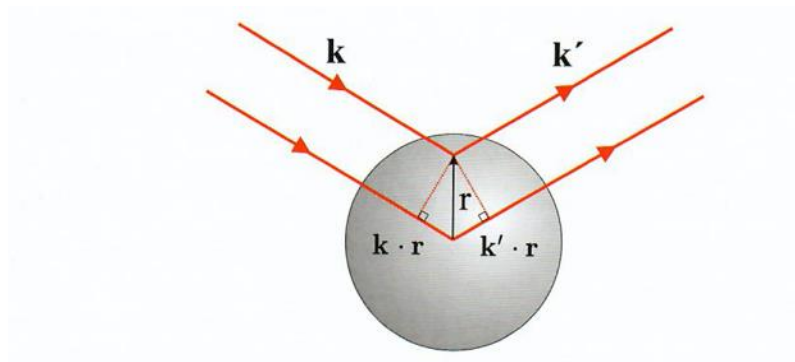
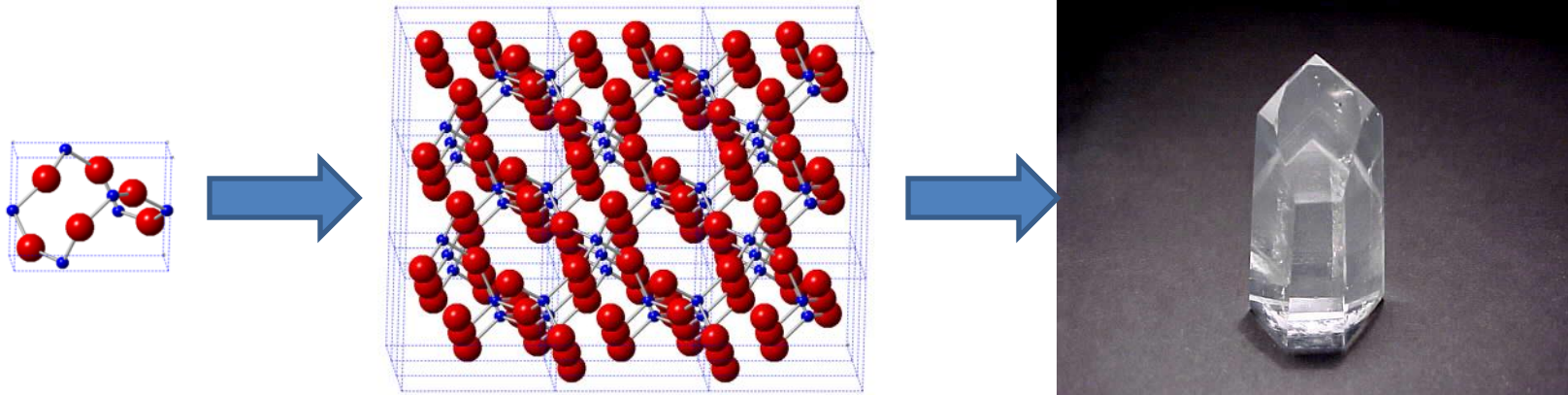
# Characteristic signals from different – chemically identical – samples



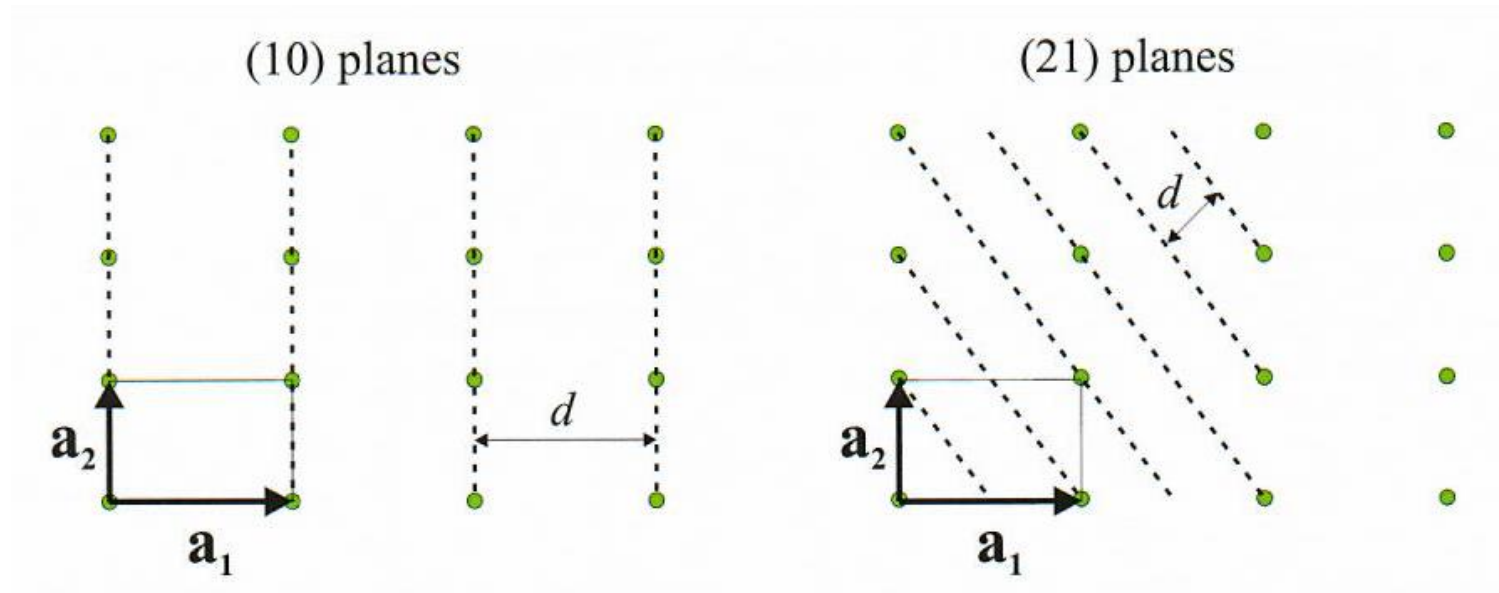
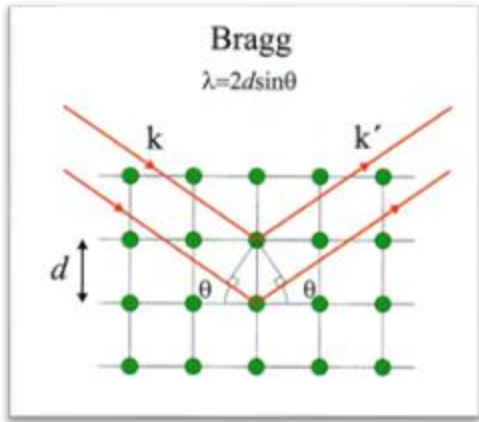
The diffraction pattern of a mixture is a simple sum from each component phase



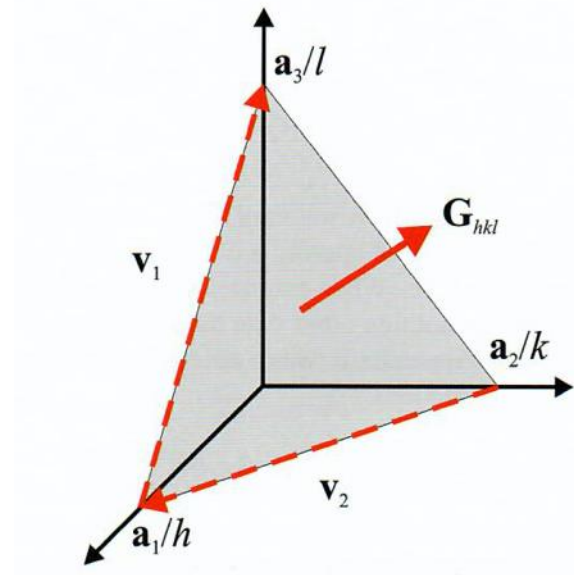
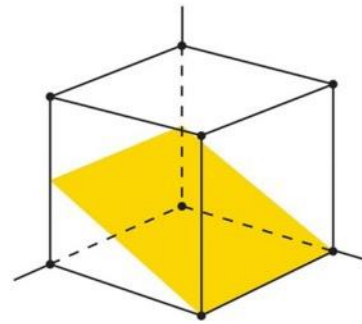
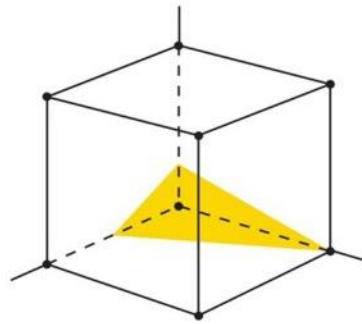
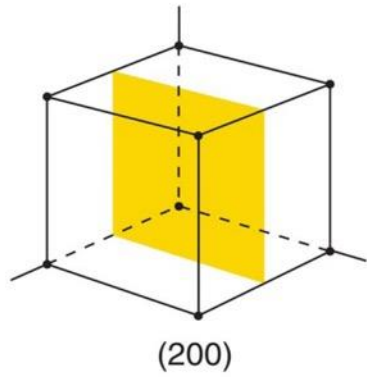
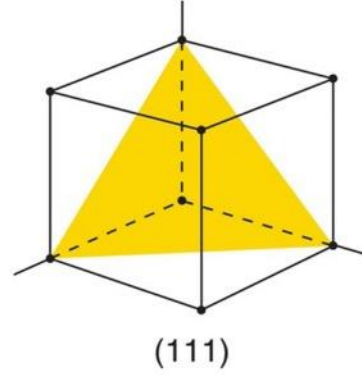
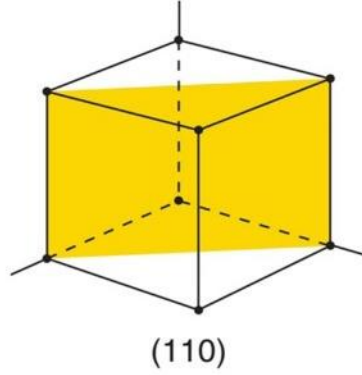
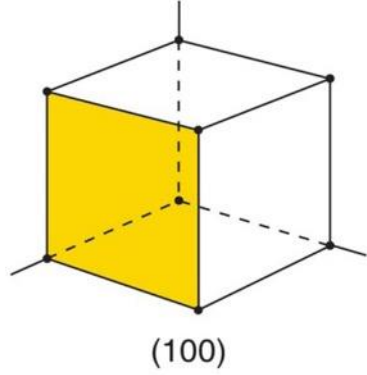
Crystalline materials are characterized by the long-range order



# Lattice planes



# Miller indices



# Bragg scattering

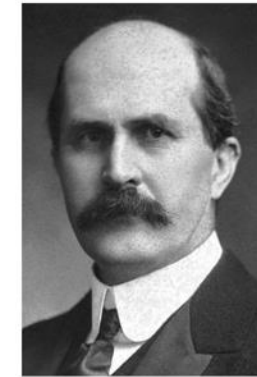
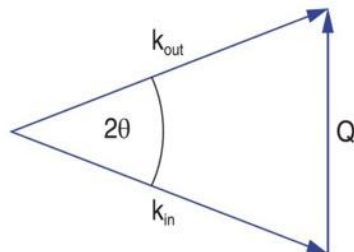
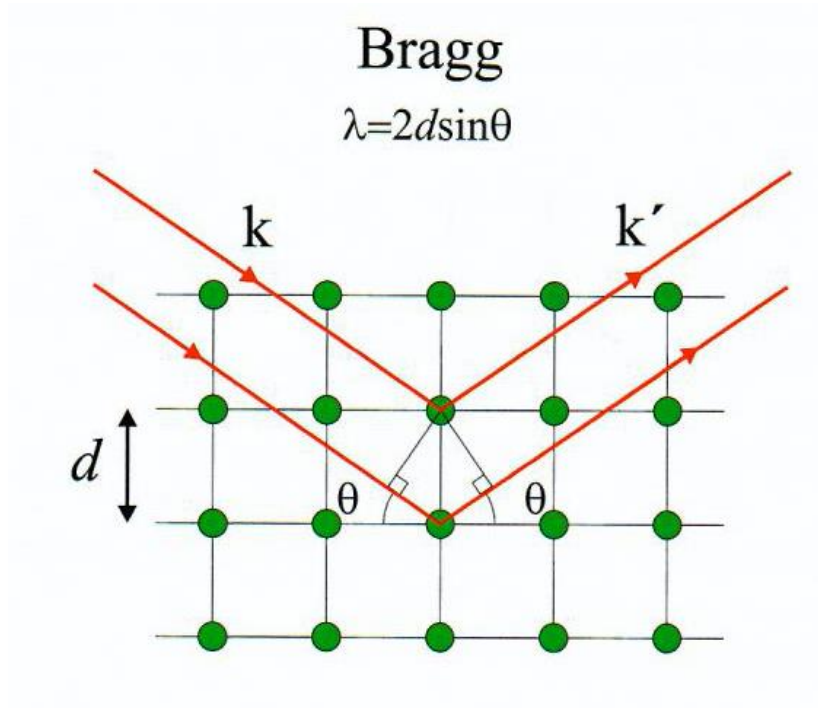


Photo from the Nobel Foundation archive.  
**Sir William Henry Bragg**  
Prize share: 1/2

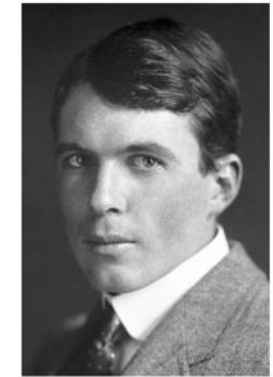
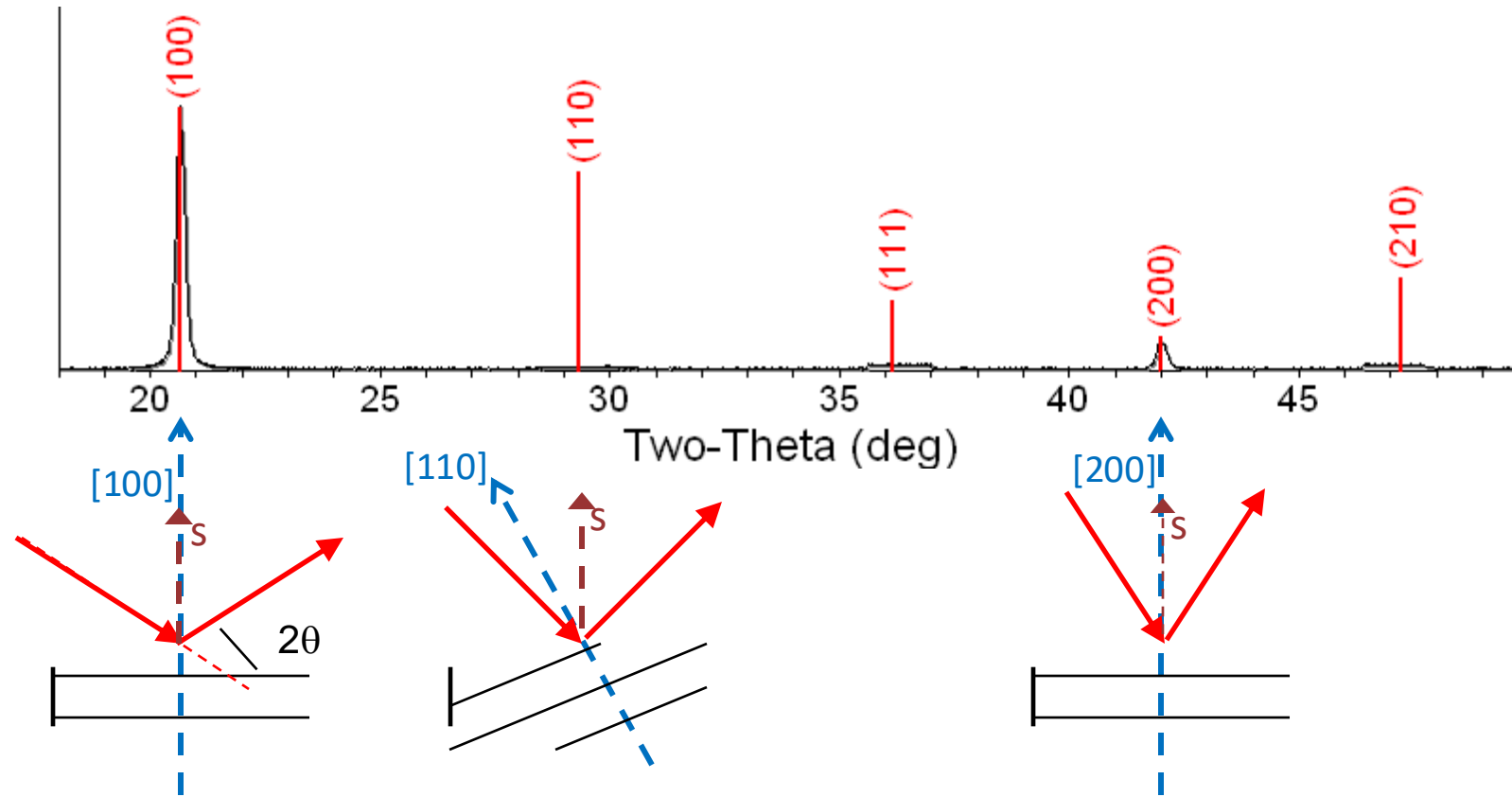


Photo from the Nobel Foundation archive.  
**William Lawrence Bragg**  
Prize share: 1/2

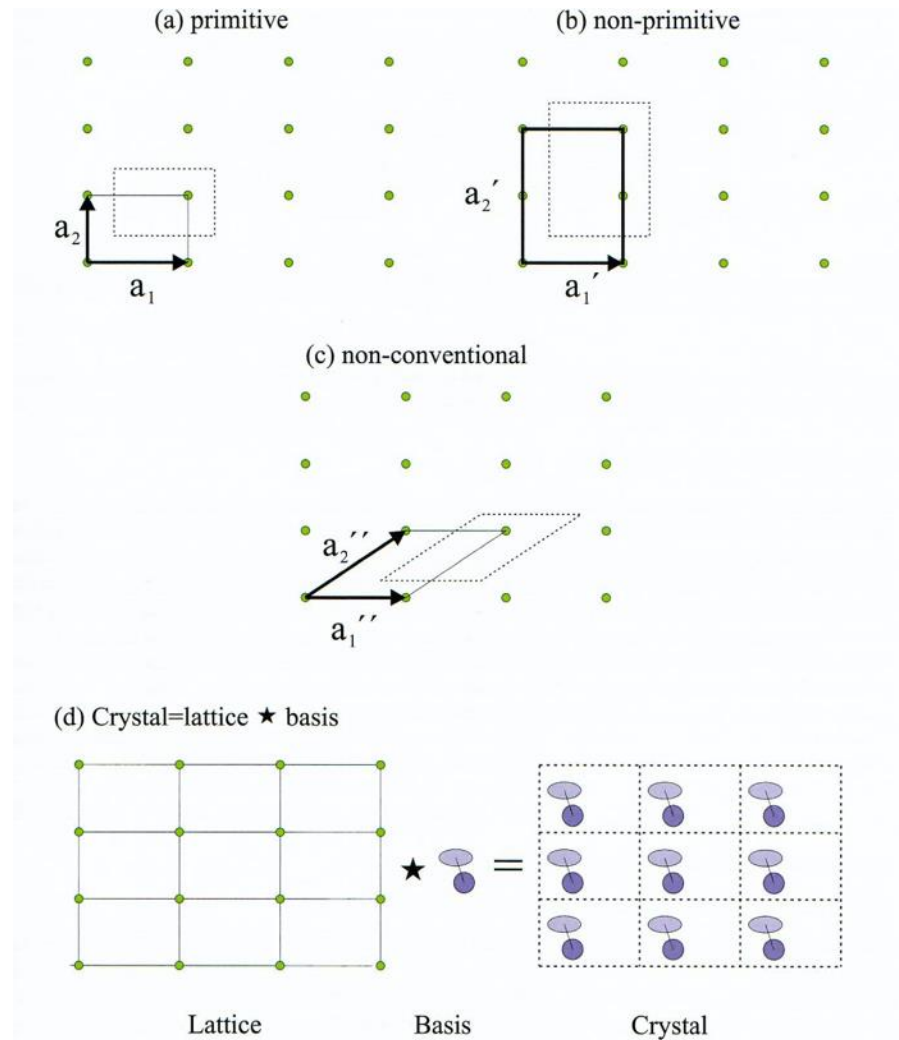


A single crystal (typically) produces one family of Bragg peaks for fixed geometry and  $\lambda$



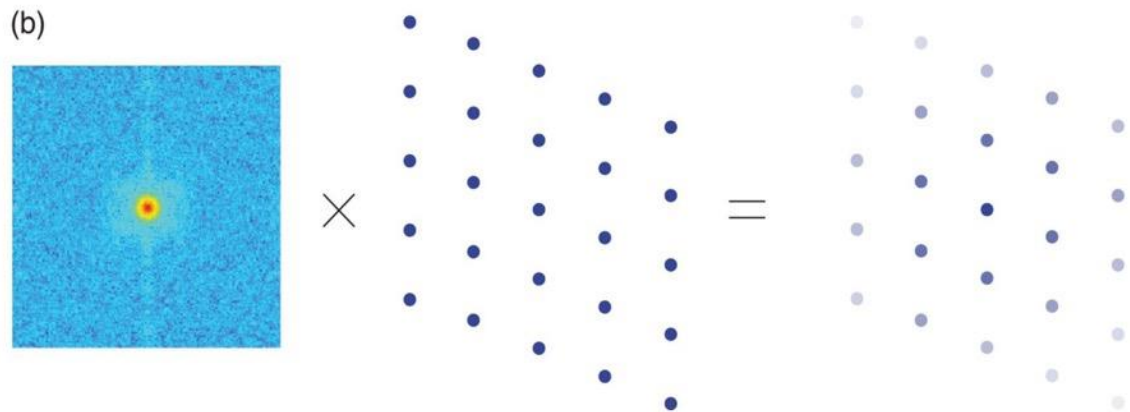
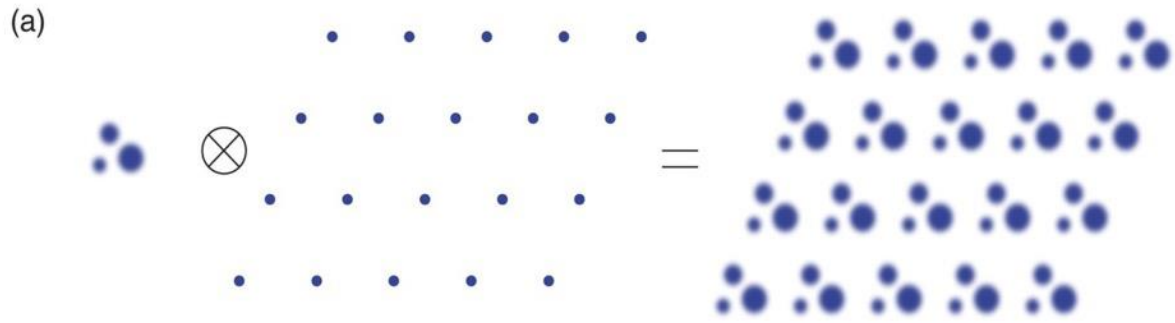
Why care about x-ray diffraction of crystals?

# A crystal is defined by its lattice and basis

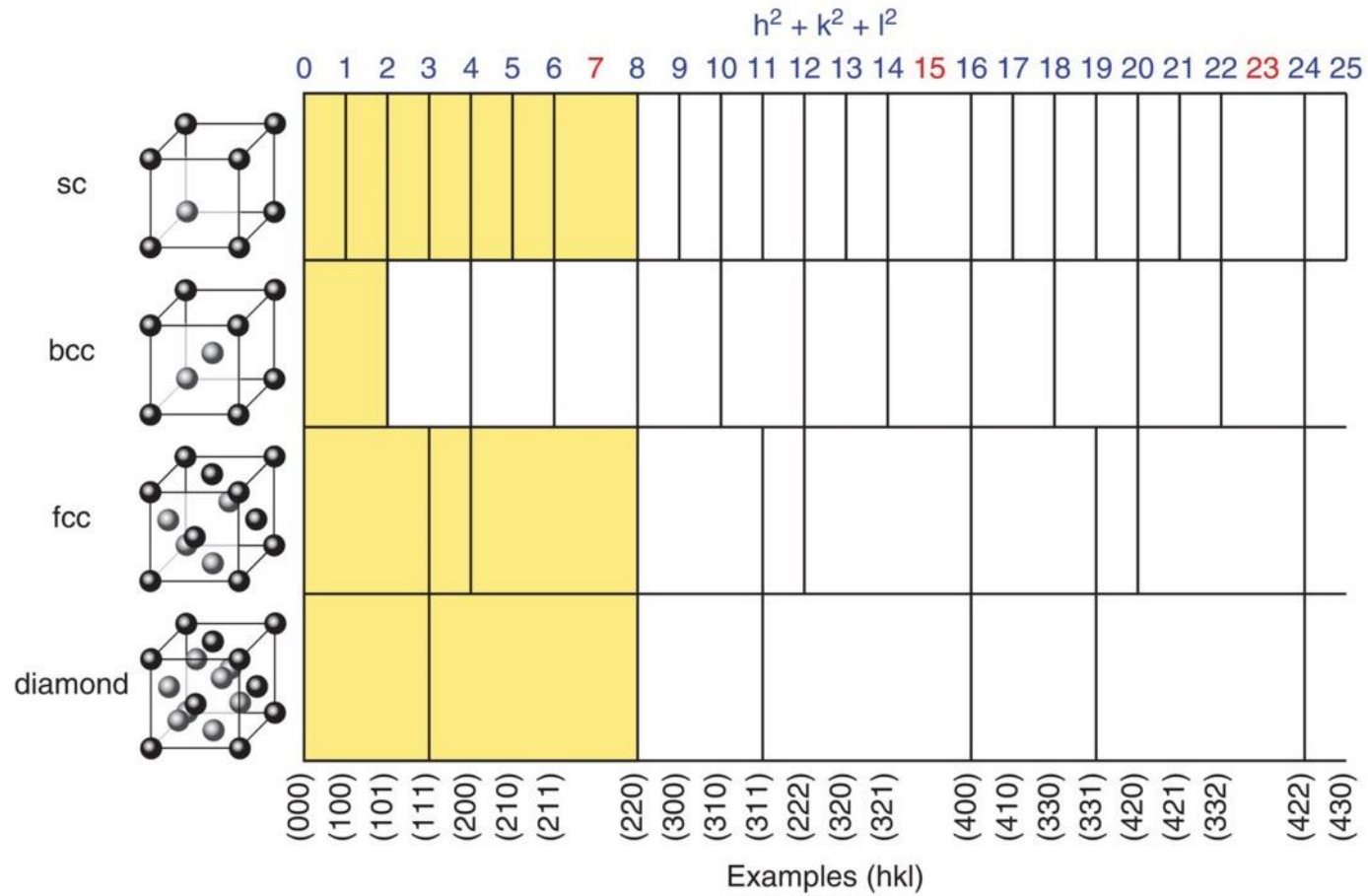


# Why and how does it work?

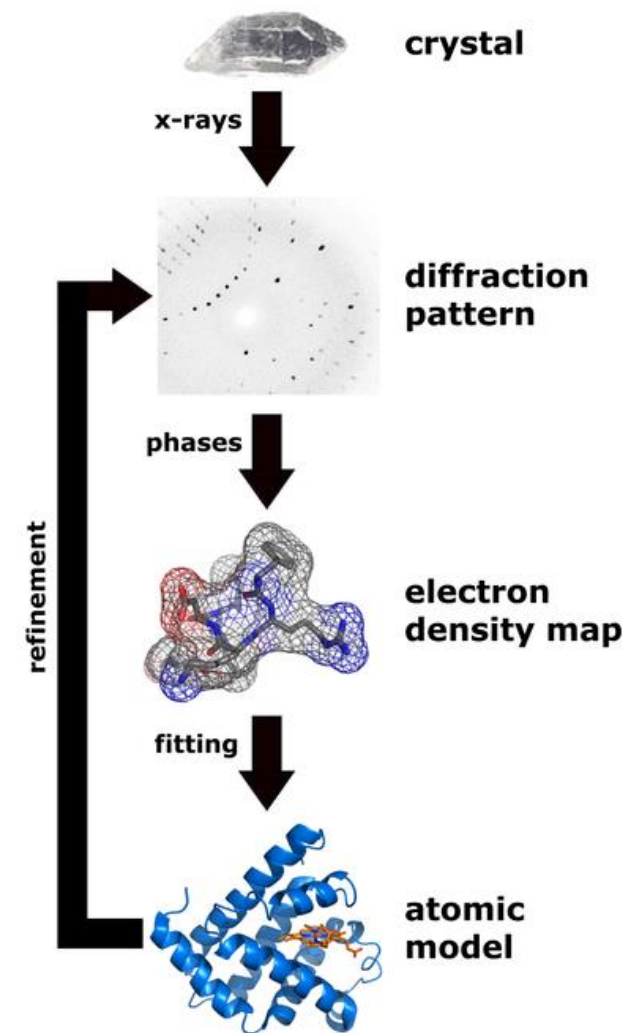
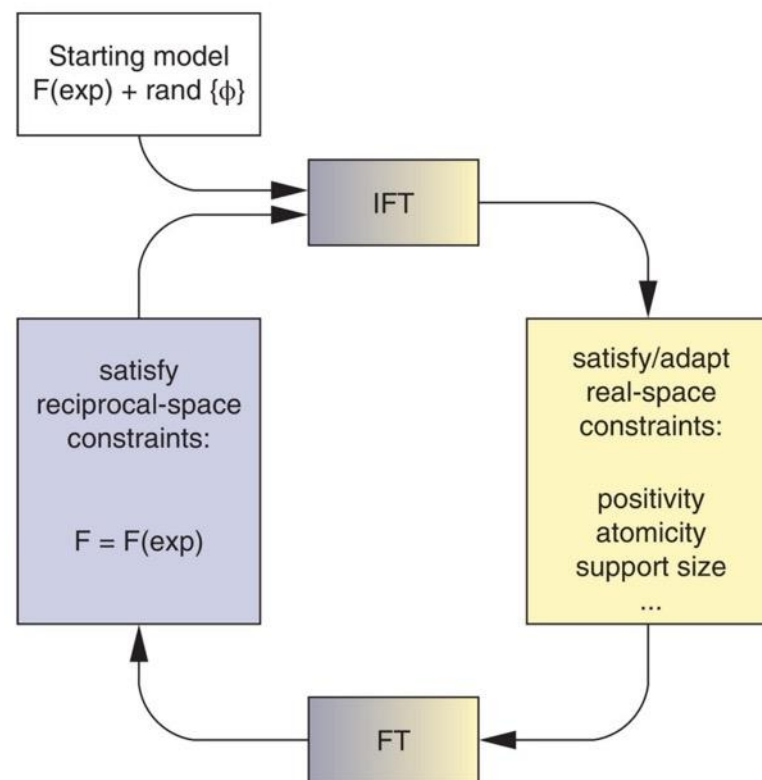
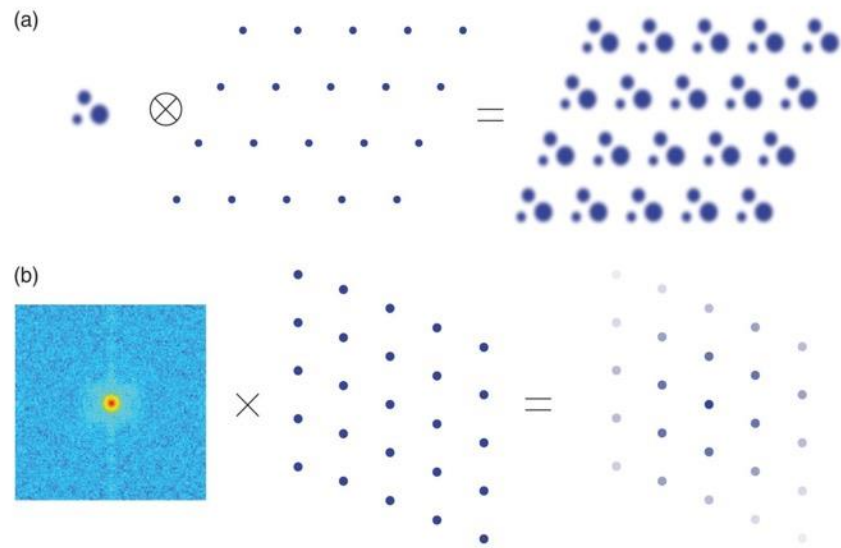
Remember last week:



# Allowed and forbidden reflections

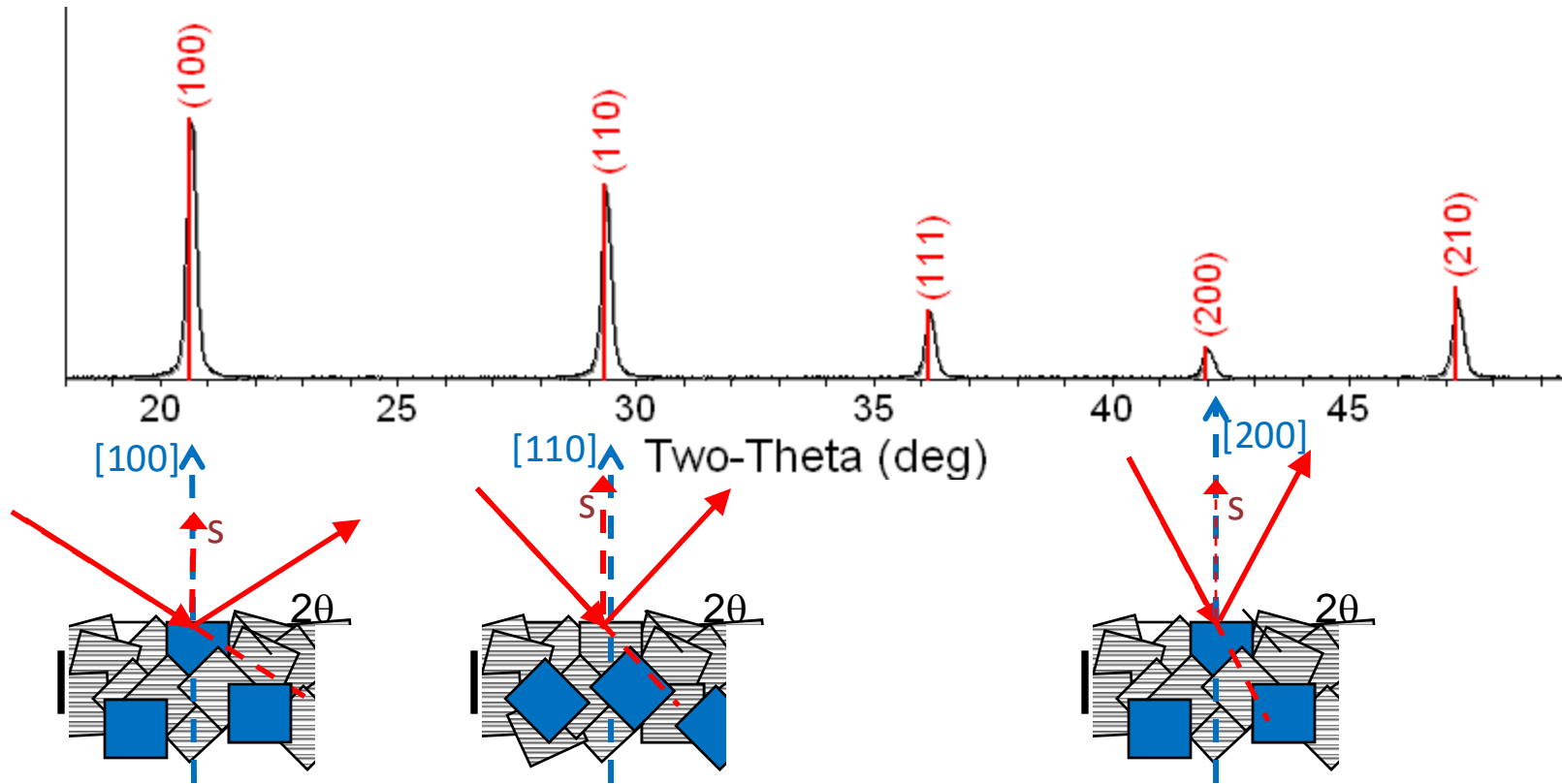


# Solving a crystal structure



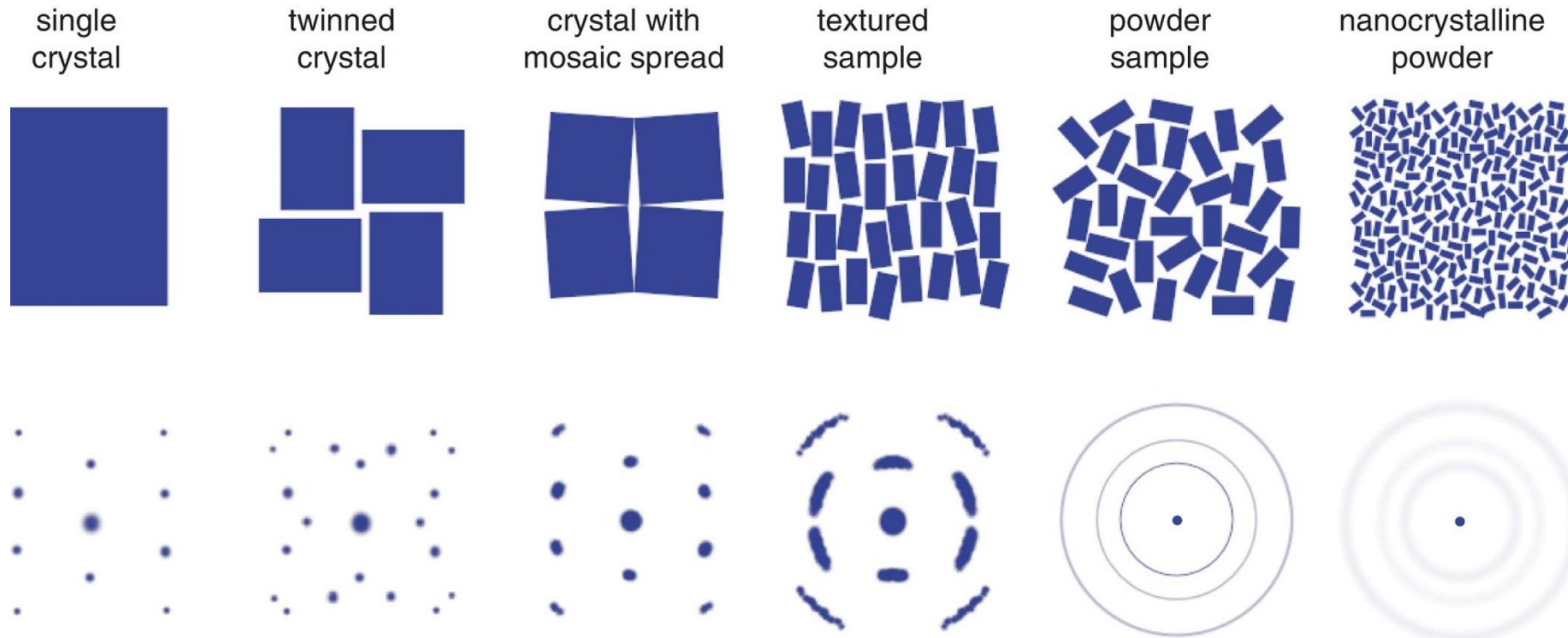
# Powder diffraction

# Diffraction of a polycrystalline sample

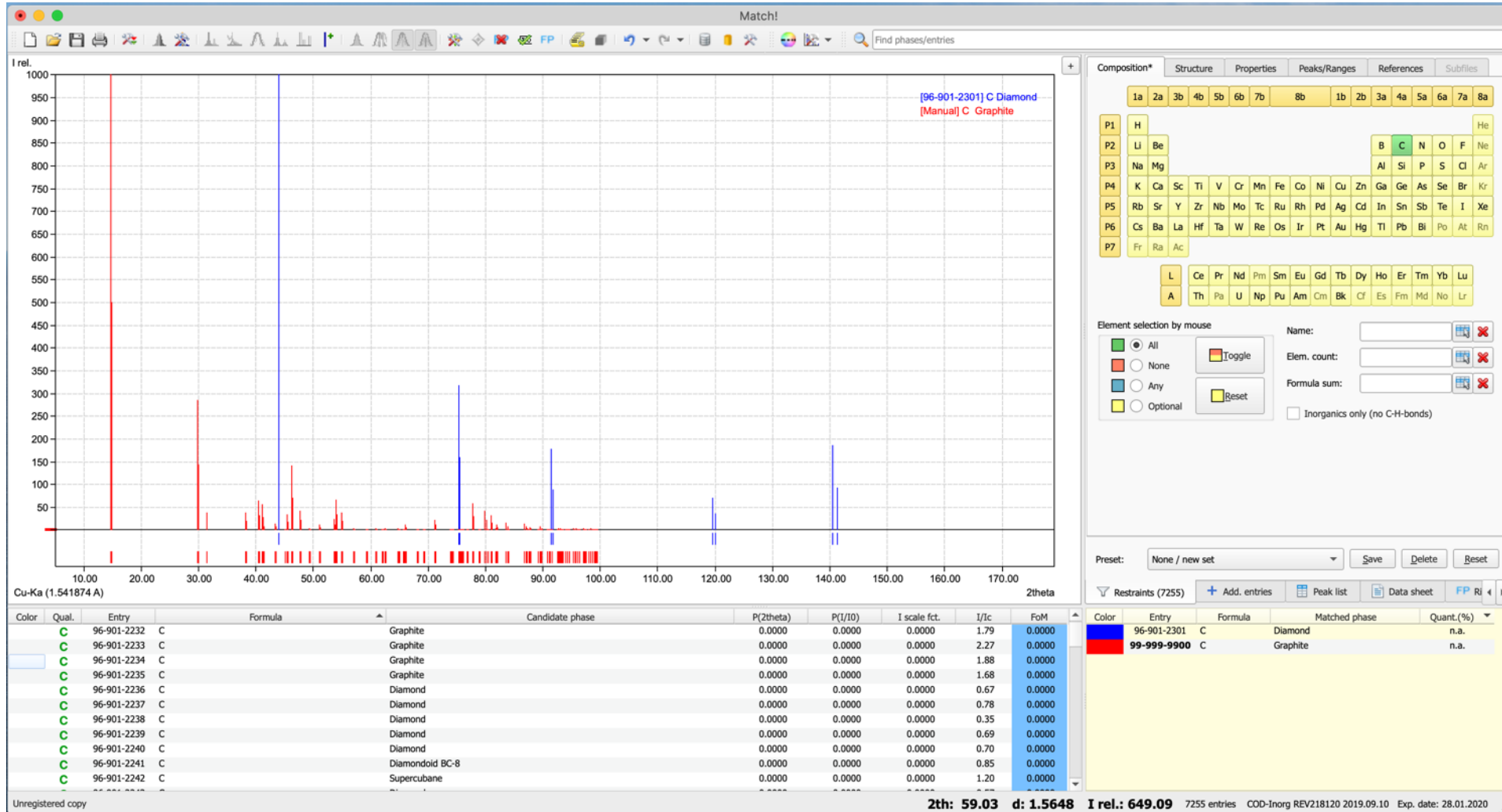




# Diffraction signal of different sample types

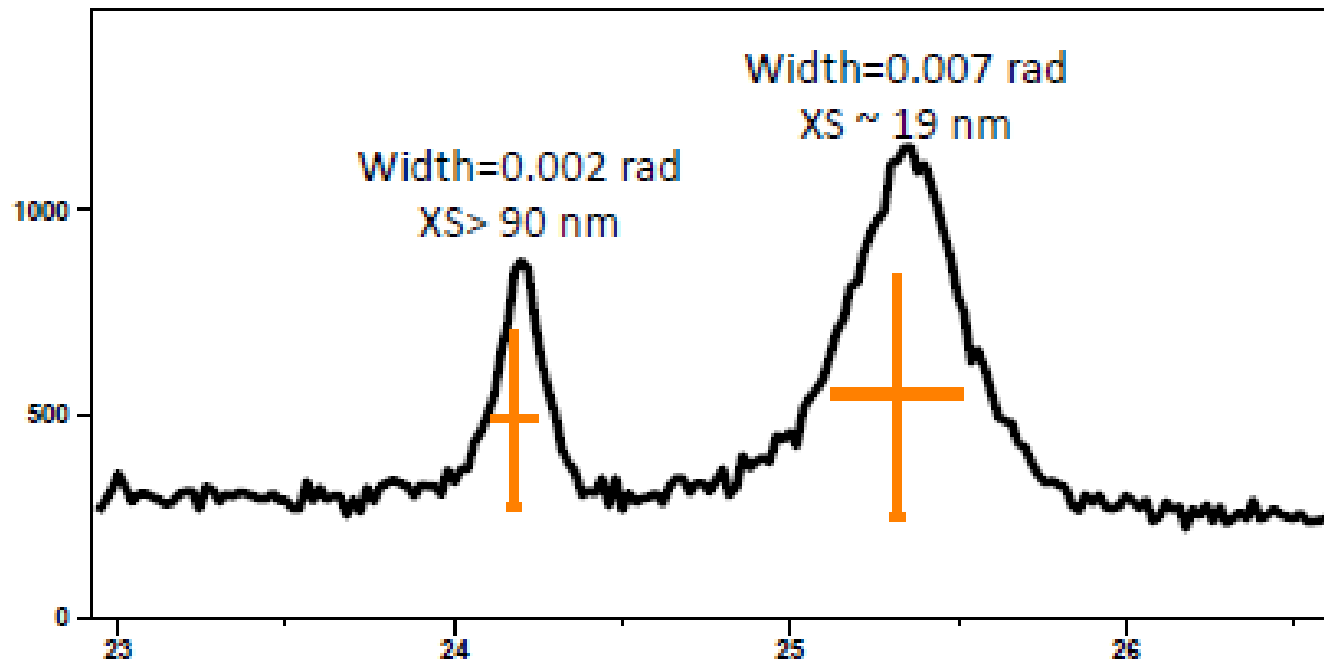


# Powder diffraction data bases for elemental analysis

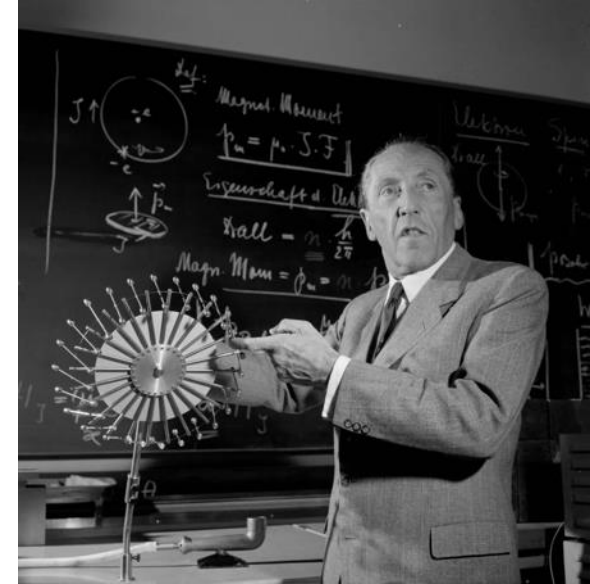


# Debye-Scherrer Formula

The diffraction peak width may contain microstructural information



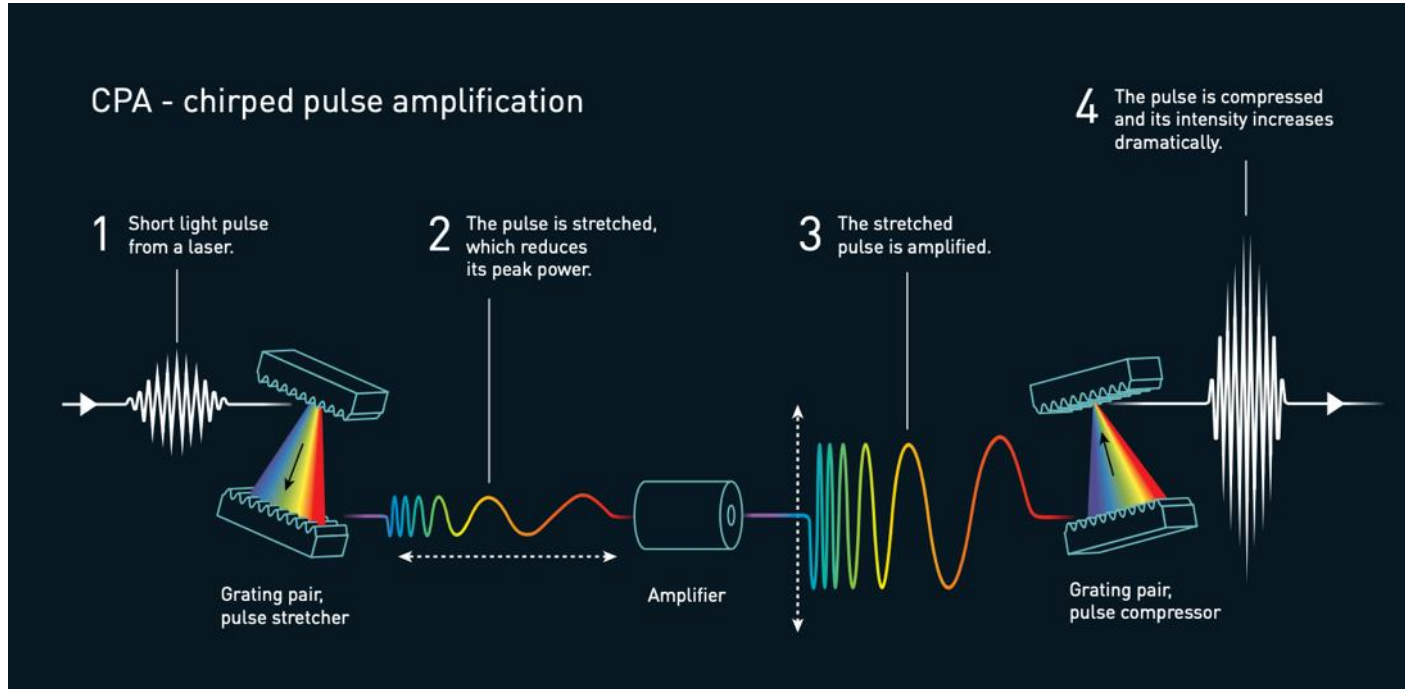
$$\text{Size} = \frac{K\lambda}{\text{Width} \cdot \cos \theta}$$



Paul Scherrer  
Swiss Physicist (1890-1969)

Things you may want to remember

# Back to start



## The Nobel Prize in Physics 2018



Ill. Niklas Elmehed. © Nobel Media  
**Arthur Ashkin**  
Prize share: 1/2



© Nobel Media AB. Photo: A. Mahmoud  
**Gérard Mourou**  
Prize share: 1/4

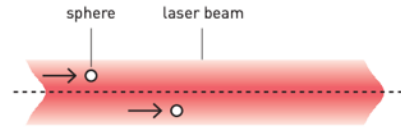


© Nobel Media AB. Photo: A. Mahmoud  
**Donna Strickland**  
Prize share: 1/4

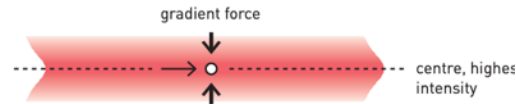
The inventions being honoured this year have revolutionised laser physics. Extremely small objects and incredibly fast processes now appear in a new light. Not only physics, but also chemistry, biology and medicine have gained precision instruments for use in basic research and practical applications. 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.

## Also in physics

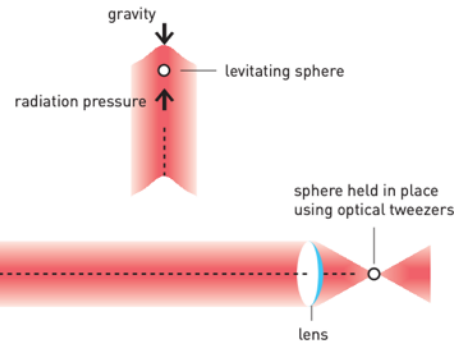
1 Small transparent spheres are set in motion when they are illuminated with laser light. Their speed corresponds to Ashkin's theoretical estimation, demonstrating that it really is radiation pressure pushing them.



2 One unexpected effect was the gradient force that pushes the spheres towards the centre of the beam, where the light is most intense. This is because the intensity of the beam decreases outwards and the sum of all the forces pushing the spheres sends them towards its centre.



3 Ashkin makes the spheres levitate by pointing the laser beam upwards. The radiation pressure counteracts gravity.

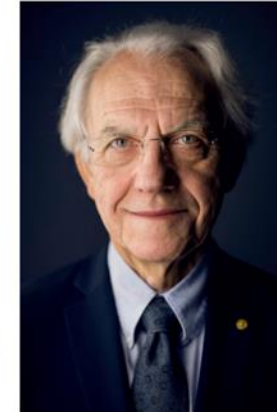


4 The laser beam is focused with a lens. The light captures particles and even live bacteria and cells in these optical tweezers.

## The Nobel Prize in Physics 2018



Ill. Niklas Elmehed. © Nobel Media  
**Arthur Ashkin**  
Prize share: 1/2



© Nobel Media AB. Photo: A. Mahmoud  
**Gérard Mourou**  
Prize share: 1/4



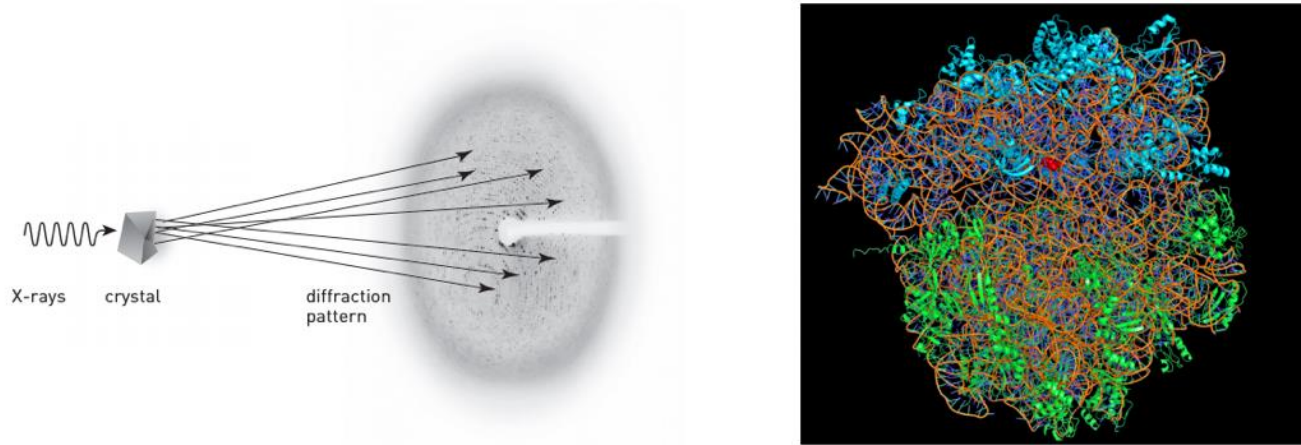
© Nobel Media AB. Photo: A. Mahmoud  
**Donna Strickland**  
Prize share: 1/4

Optical tweezers:

<https://www.youtube.com/watch?v=ju6wENPtXu8>

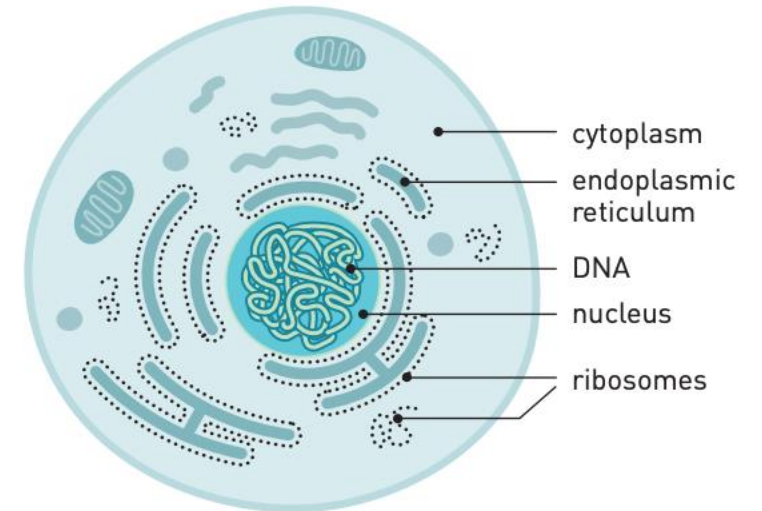
The inventions being honoured this year have revolutionised laser physics. Extremely small objects and incredibly fast processes now appear in a new light. Not only physics, but also chemistry, biology and medicine have gained precision instruments for use in basic research and practical applications. 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.

## Recent examples of applications of light to chemistry



**Figure 4. X-ray crystallography.** The researchers create X-rays using synchrotrons, circular tunnels where electrons are accelerated to nearly the speed of light. When the rays hit the ribosome crystal they scatter, making millions of dots on a CCD detector. By analyzing this pattern, researchers can determine the position of each atom in the ribosome. Special software is used to visualize the ribosome (picture to the right).

*At the beginning of the twentieth century, the chemical foundations for life were a mystery. Today we know how many of the most important processes function, all the way down to the atomic level. The 2009 Nobel Prize in Chemistry is awarded for the detailed mapping of the ribosome – the cell's own protein factory. The ribosome translates the passive DNA information into form and function.*



## Recent examples of applications of light to chemistry

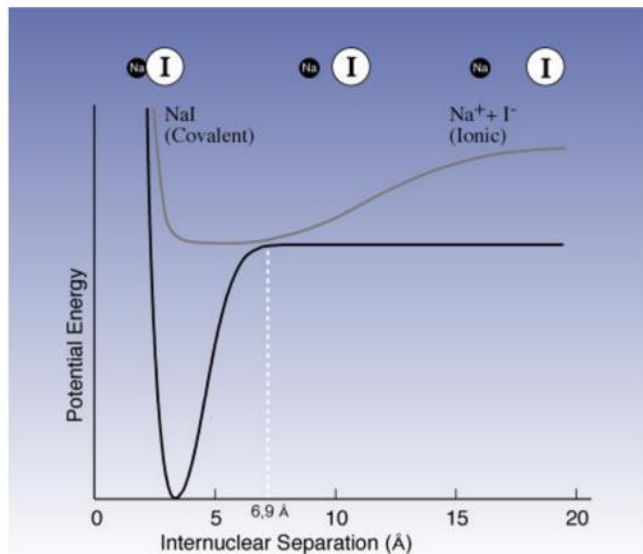


Fig. 1a) Potential energy curves showing the energies of ground state (bottom curve with deep minimum) and excited state (top curve) for NaI as function of the distance between the nuclei.

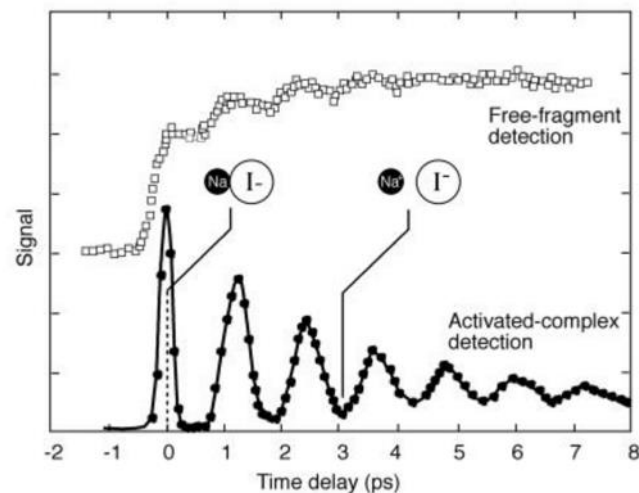


Fig. 1b) Experimental observations of coherent vibrations (so-called wave-packet motion) in femtosecond-excited NaI, on one hand manifested in terms of amount of activated complex [Na-I]\* at covalent (short) distance, on the other



Photo from the Nobel Foundation archive.

Ahmed H. Zewail

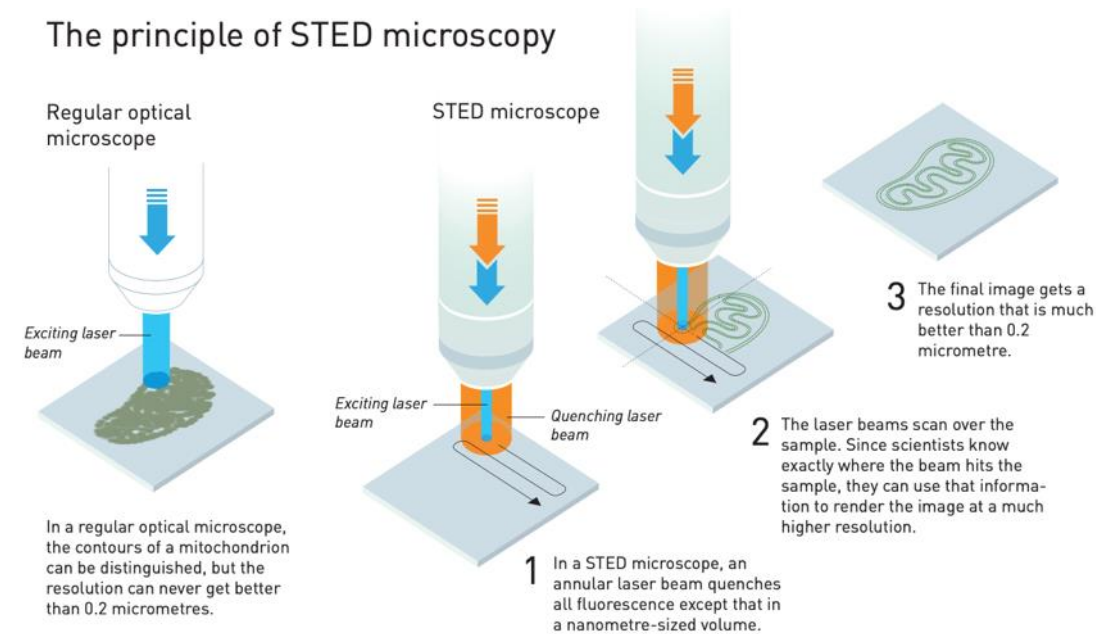
Prize share: 1/1

This year's Nobel Laureate, Professor Ahmed Zewail, is rewarded for his pioneering investigations of chemical reactions on the time-scale they really occur. This is the same timescale on which the atoms in the molecules vibrate, namely femtoseconds (1 fs = 10<sup>-15</sup> seconds). Only recently have developments in laser technology enabled us to study such rapid processes, using ultra-short laser flashes. Professor Zewail's contributions have brought about a revolution in chemistry, with consequences for many other fields of science, since this type of investigation allows us to understand and predict important processes.



*Last comment: Remember session 1?*

Recent examples of applications of light to chemistry



© Nobel Media AB, Photo: A. Mahmoud  
Eric Betzig  
Prize share: 1/3



© Nobel Media AB, Photo: A. Mahmoud  
Stefan W. Hell  
Prize share: 1/3



© Nobel Media AB, Photo: A. Mahmoud  
William E. Moerner  
Prize share: 1/3

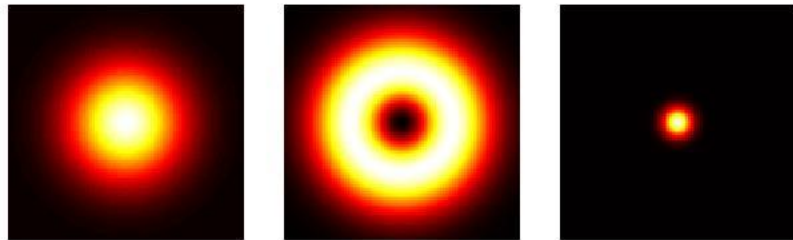
*Eric Betzig, Stefan W. Hell and William E. Moerner are awarded the Nobel Prize in Chemistry 2014 for having bypassed a presumed scientific limitation stipulating that an optical microscope can never yield a resolution better than 0.2 micrometres. Using the fluorescence of molecules, scientists can now monitor the interplay between individual molecules inside cells; they can observe disease-related proteins aggregate and they can track cell division at the nanolevel.*

# Stefan Hell: Stimulated Emission Depletion Microscope (STED)

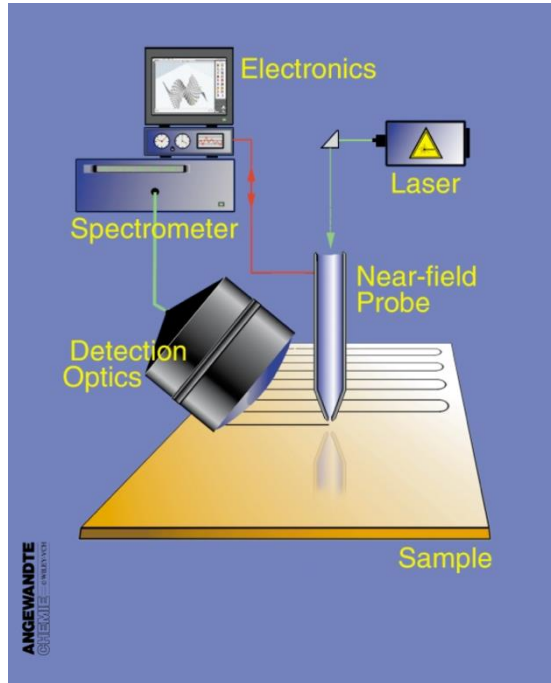
- Based on Fluorescence Microscope
- Based on Laser Scanning Microscope

But with Important additional concepts:

Remember Gaussian, Bessel beams, focal spots



# SNOM – Scanning Near Field Optical Microscope



Zenobi and Deckert, *Angew. Chemie Review*, 2000

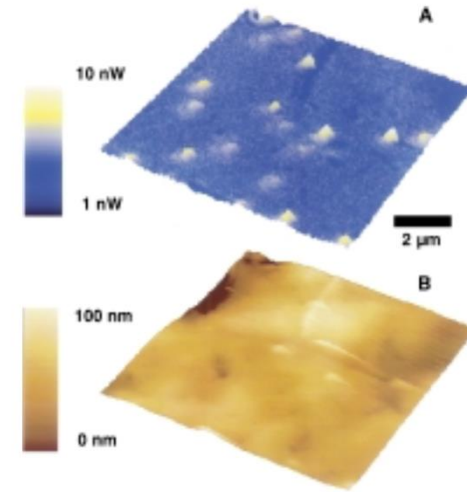
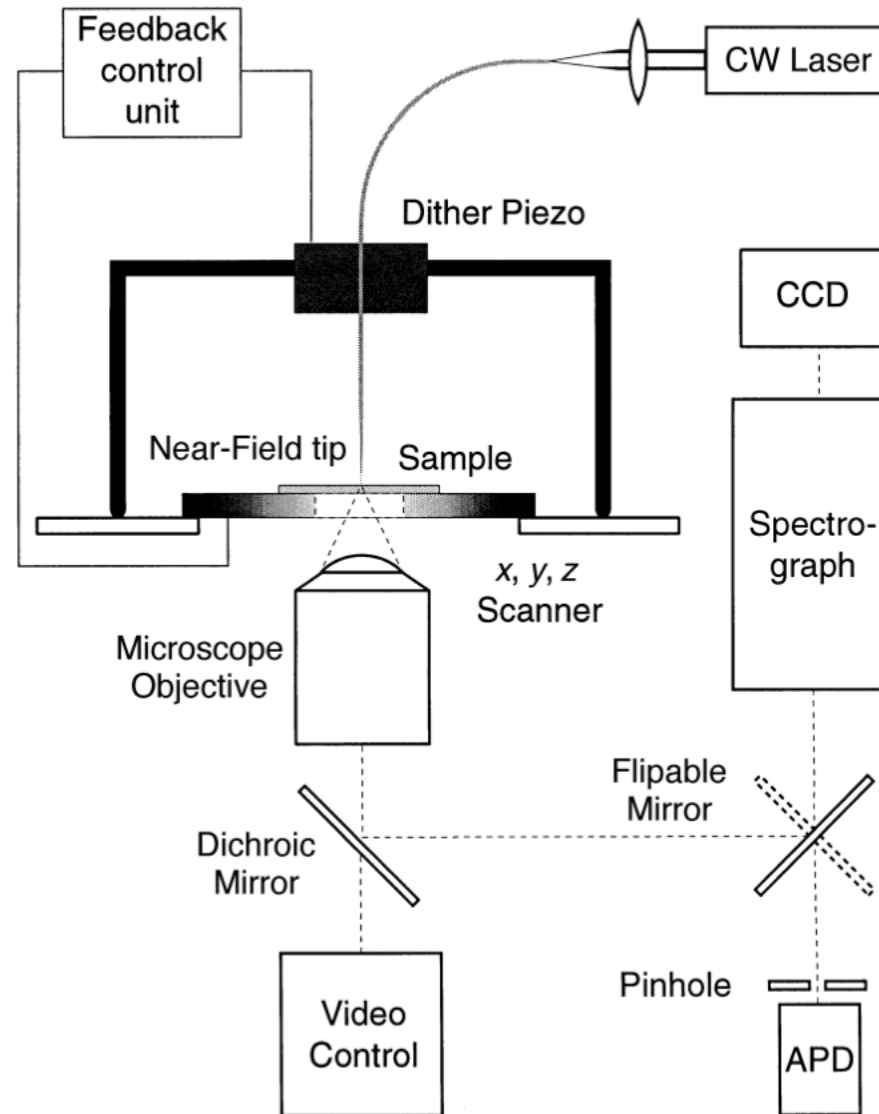


Figure 4. A) SNOM/fluorescence image and B) topographic image of a  $10 \times 10 \mu\text{m}$  area of a PVB film containing fluorescent microspheres. The spheres had a diameter of 288 nm. The fluorescence was excited with the 488 nm line of an Ar-ion laser.

