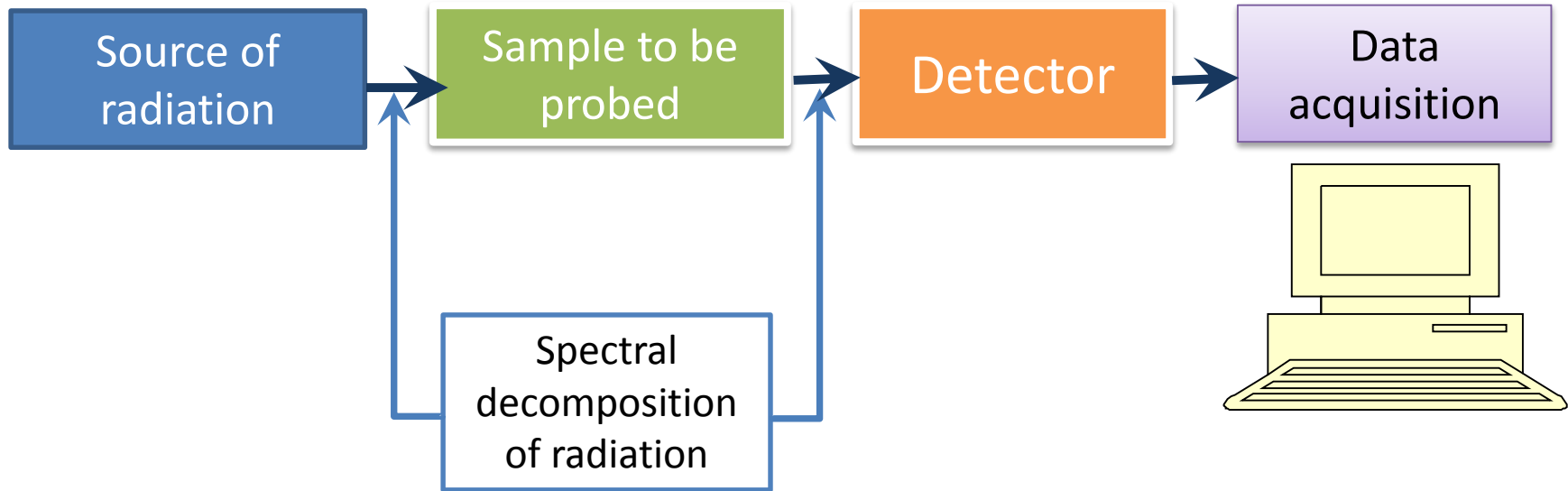


Basics of experimental spectroscopy

1. Light sources, detectors
2. Dispersing elements
3. Spectrometers
4. Introduction to laser radiation

General scheme of an experimental set-up



- **X-ray** spectroscopy
- **UV/Vis** Spectroscopy
- **Infrared** spectroscopy
- **Microwave** spectroscopy

Beer-Lambert Law

$$\ln \frac{I_0}{I_x} = \tau = \alpha l$$

$$\alpha = \sigma N$$

I_x : transmitted intensity

I_0 : incoming intensity

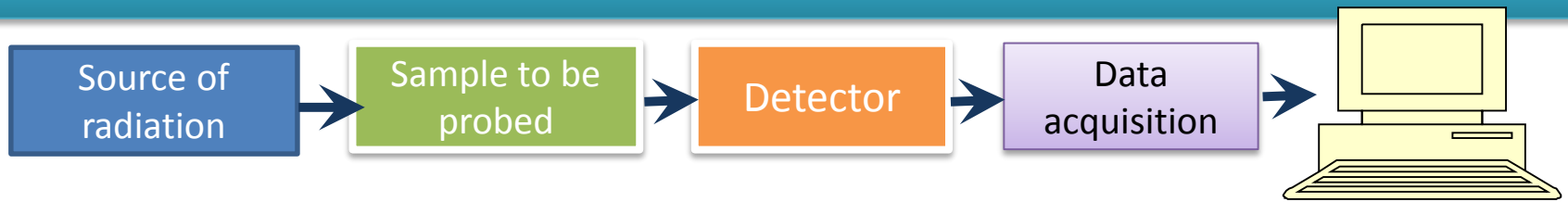
τ : optical depth; or optical density "OD"

α : absorption coefficient [cm^{-1}]

σ : absorption cross section [cm^2] of a molecule
(molecule specific, **wavelength dependent**)

N : density of molecules [cm^{-3}]

Break down of the Beer-Lambert Law



Beer-Lamberts Law

$$\ln \frac{I_0}{I_x} = \tau = \alpha l$$

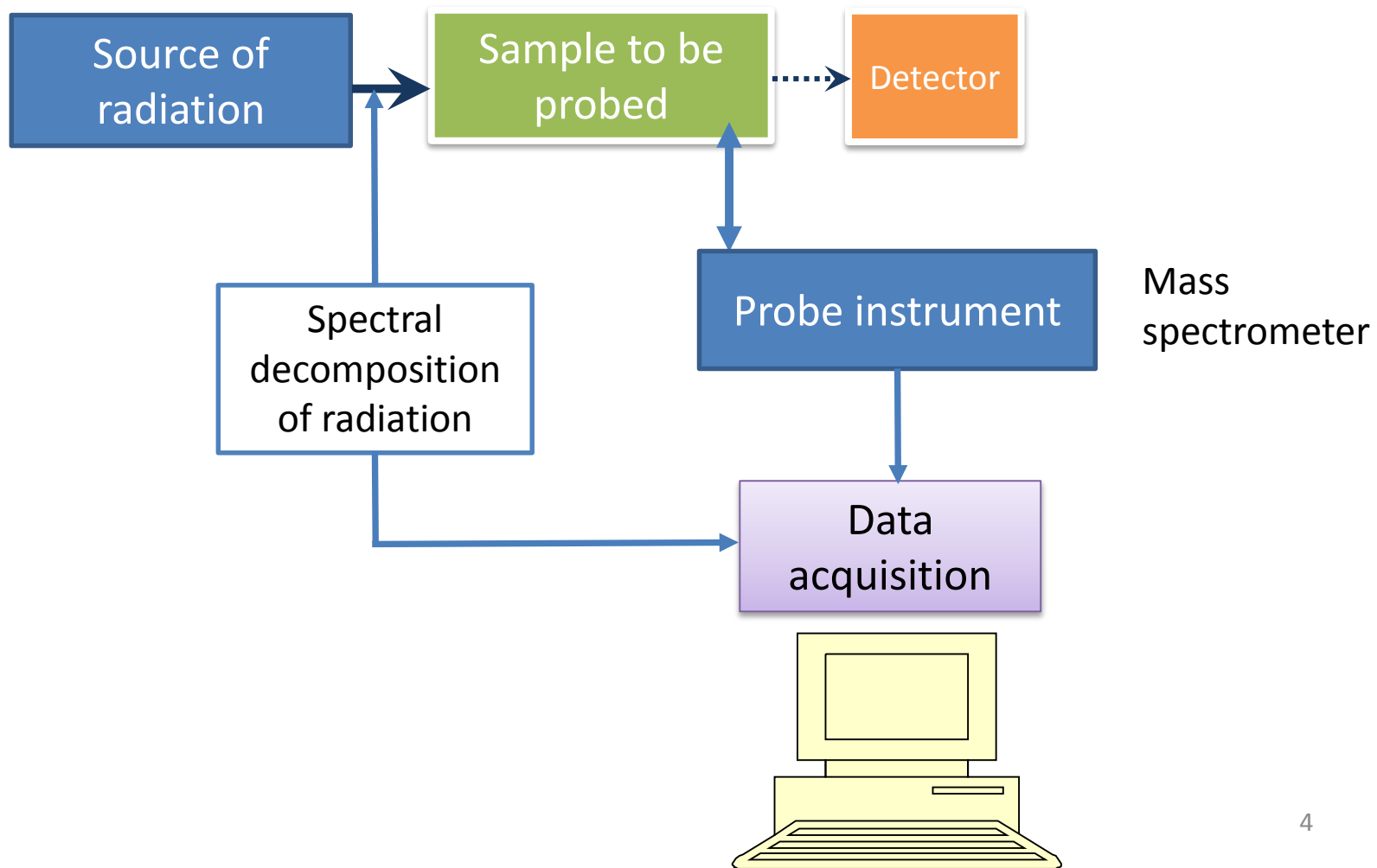
$$\alpha = \sigma N$$

Six conditions that need to be fulfilled in order for Beer-Lambert law to be valid.

1. The attenuators (molecules...) must act independently of each other.
2. The attenuating **medium must be homogeneous** in the interaction volume.
3. The attenuating medium **must not scatter** the radiation
4. The **incident radiation must consist of parallel rays**, each traversing the same length in the absorbing medium.
5. The **incident radiation should preferably be monochromatic**, or have at least a width that is narrower than that of the attenuating transition. **Otherwise a spectrometer as detector is needed** instead of a photodiode which has not a selective wavelength dependence.
6. **The incident flux must not influence the atoms or molecules**; it should only act as a non-invasive probe of the species under study. In particular, this implies that the light should not cause **optical saturation** or **optical pumping**, since such effects **will deplete the lower level** and possibly give rise to stimulated emission. In UV spectroscopy, photolysis is a problem.

If any of these conditions are not fulfilled, there will be deviations from Beer-Lambert law.

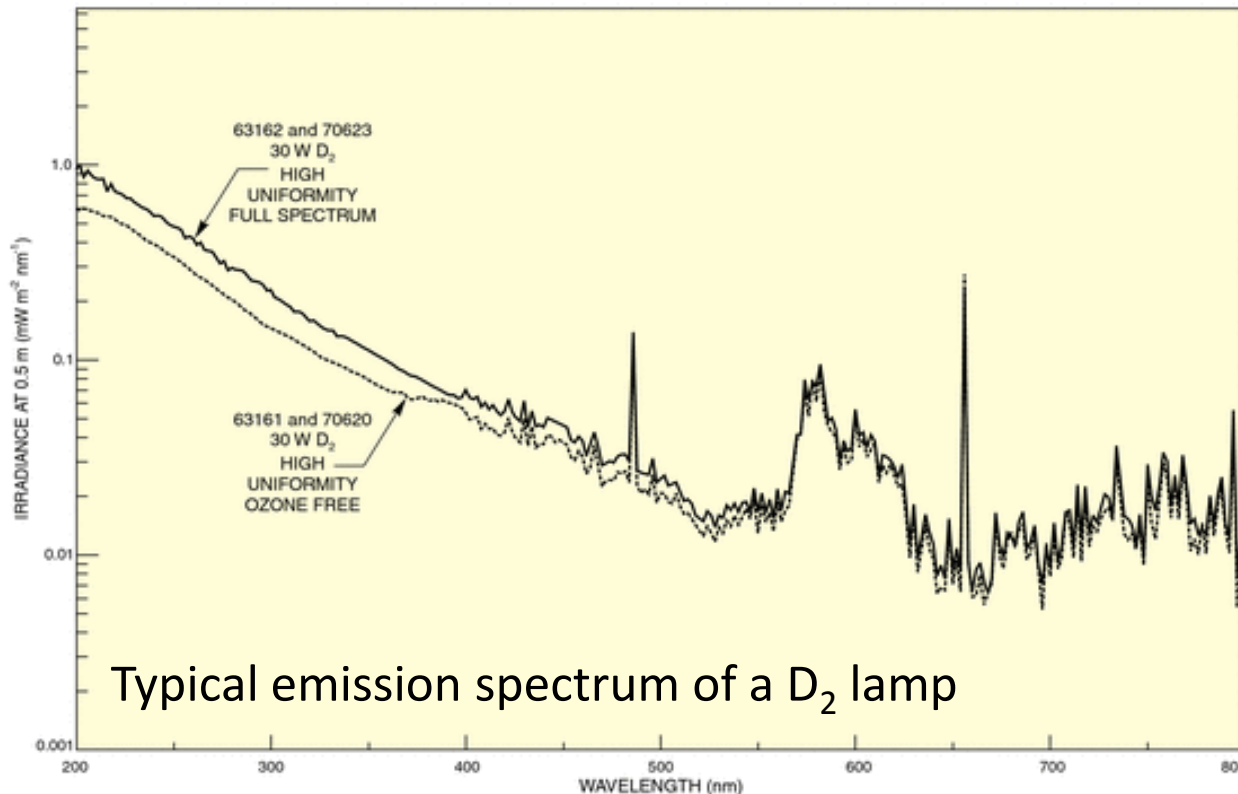
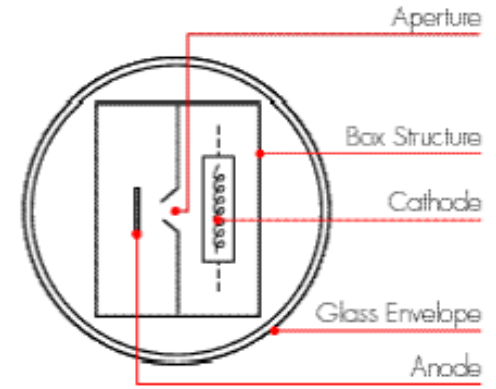
Action spectroscopy in the laboratory



Light Sources, example: deuterium lamp

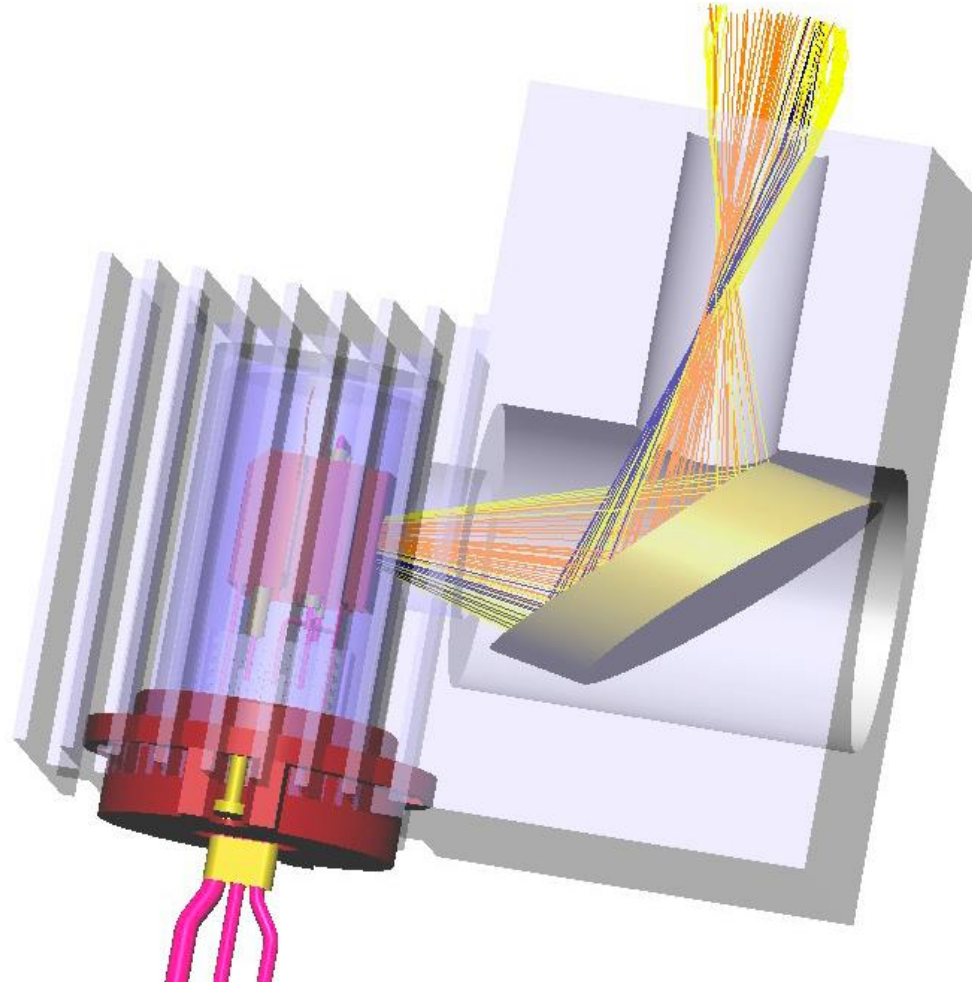
A discharge arc is formed between the anode and the cathode (« Arc lamp »)

- The arc excites the molecular deuterium which in turn emits radiation
- The emission spectrum is strongly dependent on the pressure inside the lamp



Light Sources, example: deuterium lamp

- Such a discharge lamp emits radiation in all directions (isotropic light source)
- In a typical experiment, the light has thus to be re-focalized using lenses or concave mirrors



- Microwave and TeraHertz radiation sources
 - *Lecture Arnaud Cuisset*

Spectral decomposition of radiation

For any spectroscopic study, it is necessary decompose **white light** (i.e. containing « all » or many wavelengths) coming out of a lamp > **chromatic dispersion**

➤ Basically we can distinguish 3 dispersing elements to be treated in this lecture :

- The triangular prism
- The diffraction grating
- Interferometer

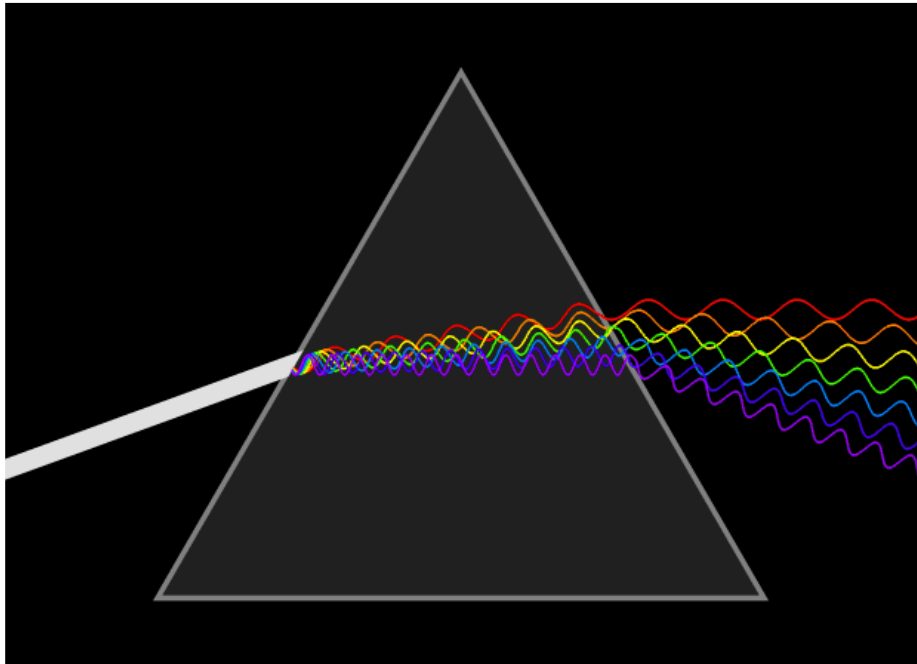
➤ The **spectral resolution** $\Delta\lambda$ [m] is the capacity of a dispersing element to separate two neighboring wavelength

- The spectral resolution can also be expressed in terms of frequency $\Delta\nu$ [Hz] or wave numbers $\Delta\tilde{\nu}$ [m⁻¹]

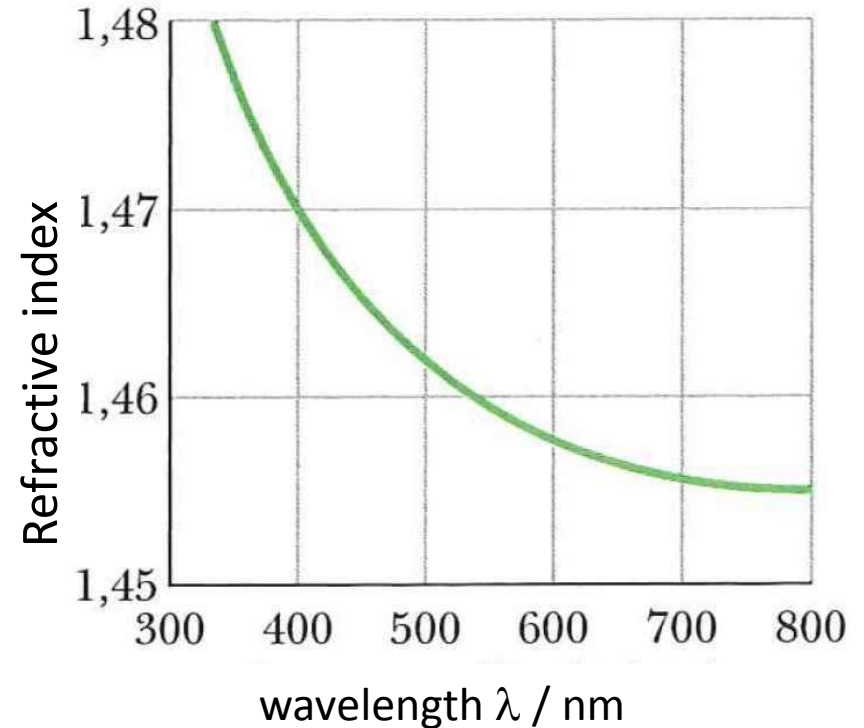
➤ One must distinguish the spectral resolution (with units of m, Hz or m⁻¹) from the **dimensionless resolving power** R of the dispersing element:

$$R = \frac{\lambda}{\Delta\lambda} = \frac{\nu}{\Delta\nu} = \frac{\tilde{\nu}}{\Delta\tilde{\nu}}$$

The triangular prism



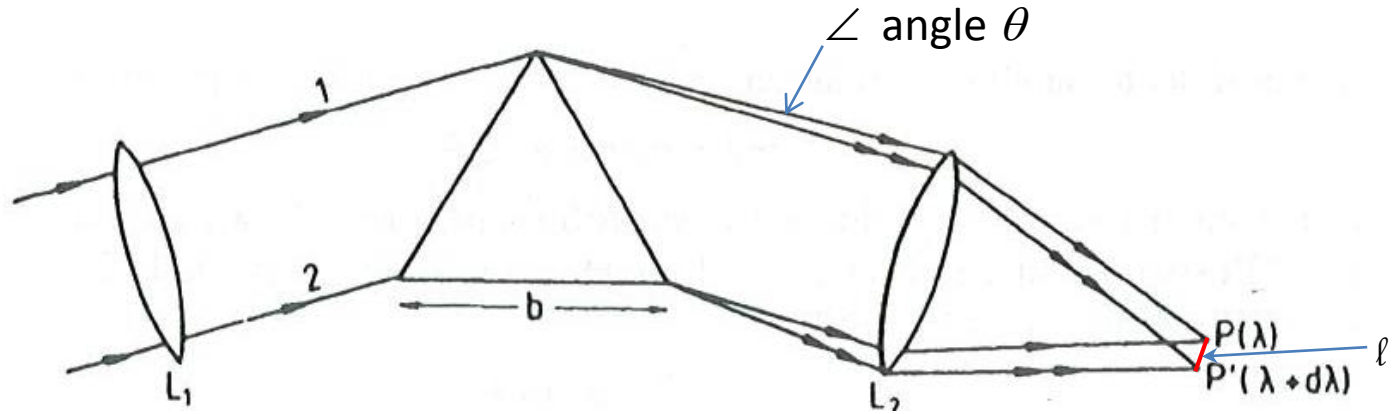
Refractive index of fused quartz as a function of the wavelength



- **Remember:** A light wave propagates in a medium at the speed $v = c / n \leq c$ with n : refractive index (1 for the vacuum).
- n changes with wavelength
- The partial derivative quotient $dn/d\lambda$ changes also with the wavelength !

The triangular prism as dispersing element

$$R = b \frac{dn}{d\lambda}$$



- b : base length of the prism
- $R \propto \mathbf{dn/d\lambda}$; $dn/d\lambda$ is highest close to wavelengths where the radiation is absorbed by the material :
 - borosilicate glass: absorption @ $\lambda < 360$ nm
 - quartz: absorption @ $\lambda < 185$ nm (above 185 nm, n is thus decreasing, see above)
- Angle θ gives the angular dispersion of the prism: $\mathbf{d\theta / d\lambda}$
- Separation in space l between P and P' defines the **linear dispersion** of the prism : $\mathbf{dl / d\lambda}$

❖ Since $\mathbf{dn/d\lambda}$, R (and by consequence $\mathbf{dl / d\lambda}$) depend all on λ : **a prism spectrum is not linear in the abscissa. That is the main reason why prisms are no longer used in spectrometers**

❖ However, prisms are very often used in optical setups integrating polychromatic lasers (i.e. containing several λ 's), in order to **separate spatially the spectral lines**

The diffraction grating as dispersing element

- **Most used dispersive element**
- Series of parallel lines engraved on a hard material (glass or metal)
- The lines are very tight, the spacing d is of the order of μm
- The grating is covered by a **reflective material**, thus it also acts as a mirror. **The reflection of the material is also a function of the wavelength.**
- The surface can be **flat or concave**

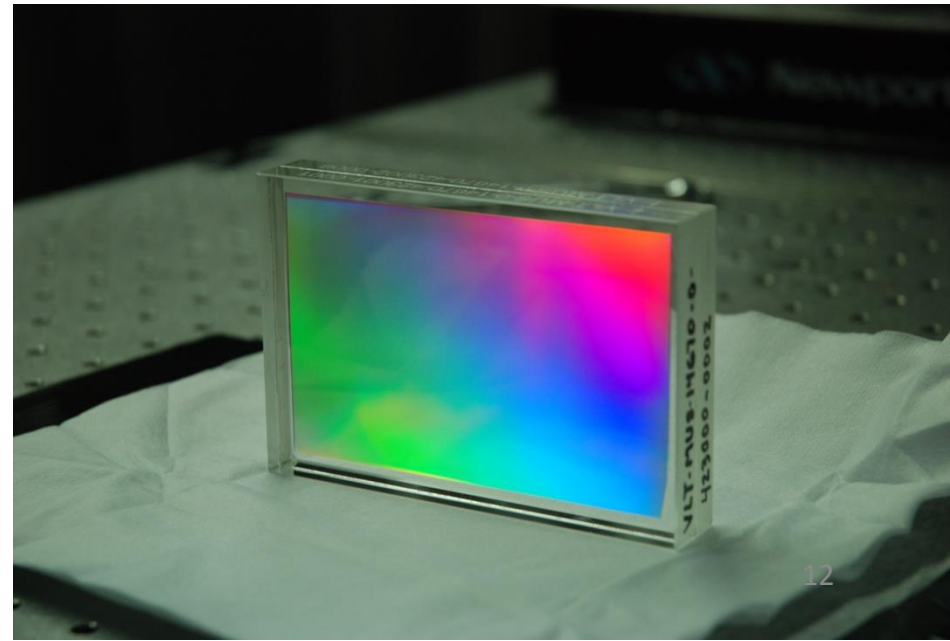
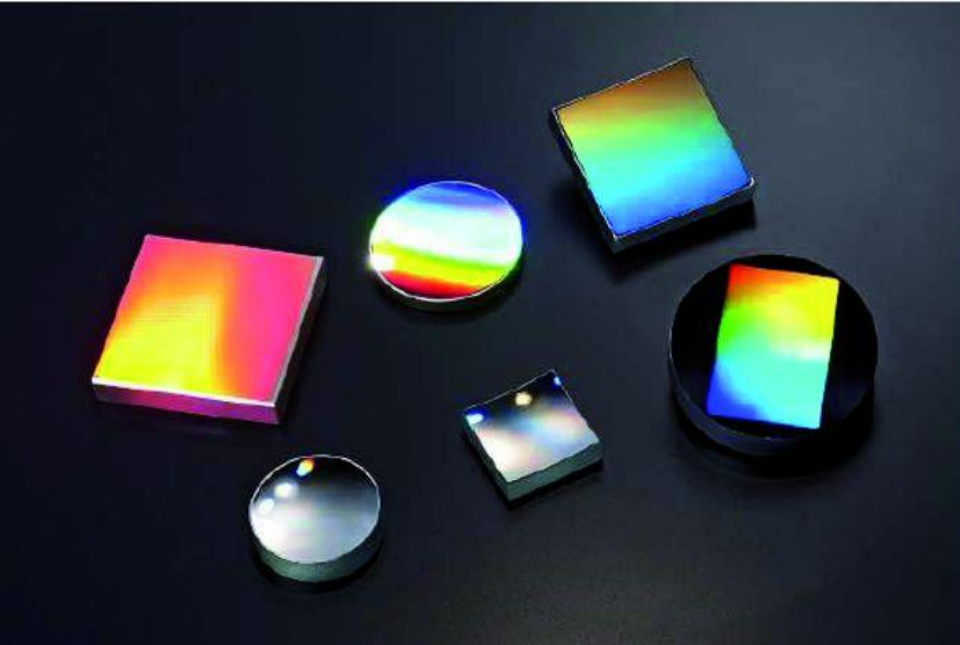
• General equation for the diffraction by a grating :

$$m \lambda = d (\sin i + \sin \theta)$$

eq. 1

- i : angle of incidence relative to the normal of the surface
 - θ : angle of diffraction relative to the normal of the surface
 - λ : wavelength of the radiation
 - m : diffraction order : 0, 1, 2, 3
 - d : spacing between two lines of the grating
 - $1/d$: number of lines per mm (or per other unit of length). $1/d$ is also called the “grating constant” C_r
- No that $\lambda \propto (\sin) \theta$: Red light is thus diffracted at larger angles than blue light

The diffraction grating as dispersing element



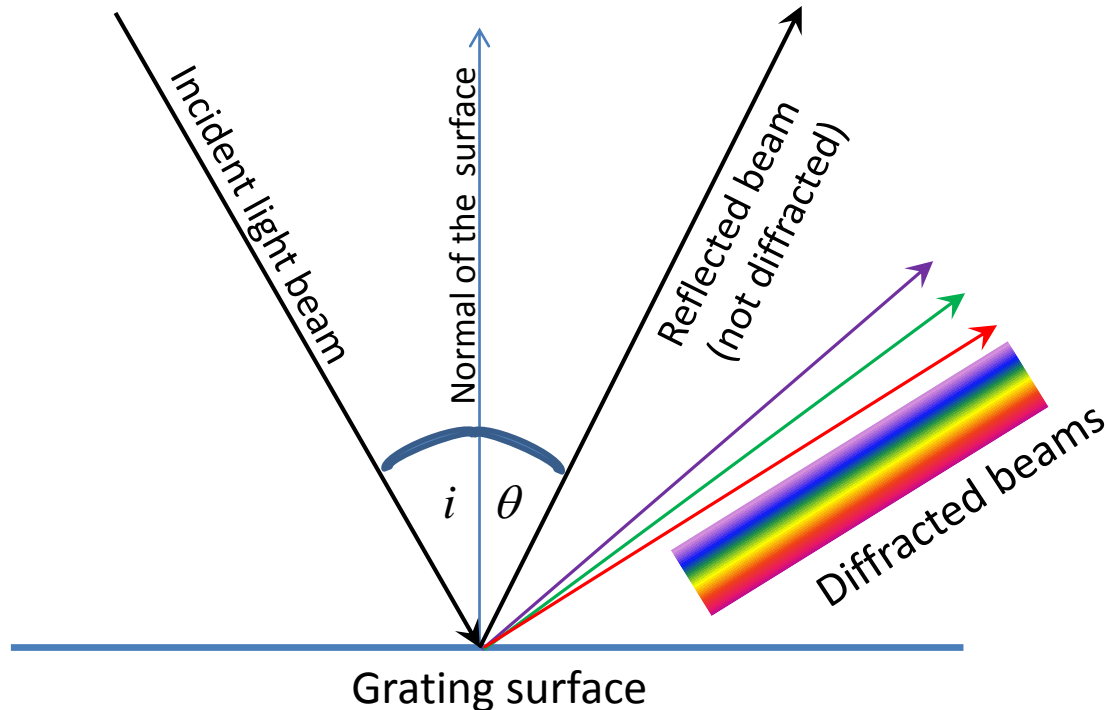
The diffraction grating as dispersing element

$$m \lambda = d (\sin i + \sin \theta)$$

eq. 1

Special case 1 of eq. 1 :

- $i = -\theta$: no diffraction \rightarrow $m = 0$; **zero order of the grating**: it acts like a mirror for $m=0$.
- **The main fraction of the incoming photons ($\sim 90\%$) are just reflected in the zeroth order.**
The exact percentage of the amount of light reflected depends largely on the material that the grating is covered with (and the associated wavelength).
- *In the laboratory the zeroth order serves to align any optical setup including a diffraction grating (using for example a monochromatic laser).*



The diffraction grating as dispersing element

$$m \lambda = d (\sin i + \sin \theta)$$

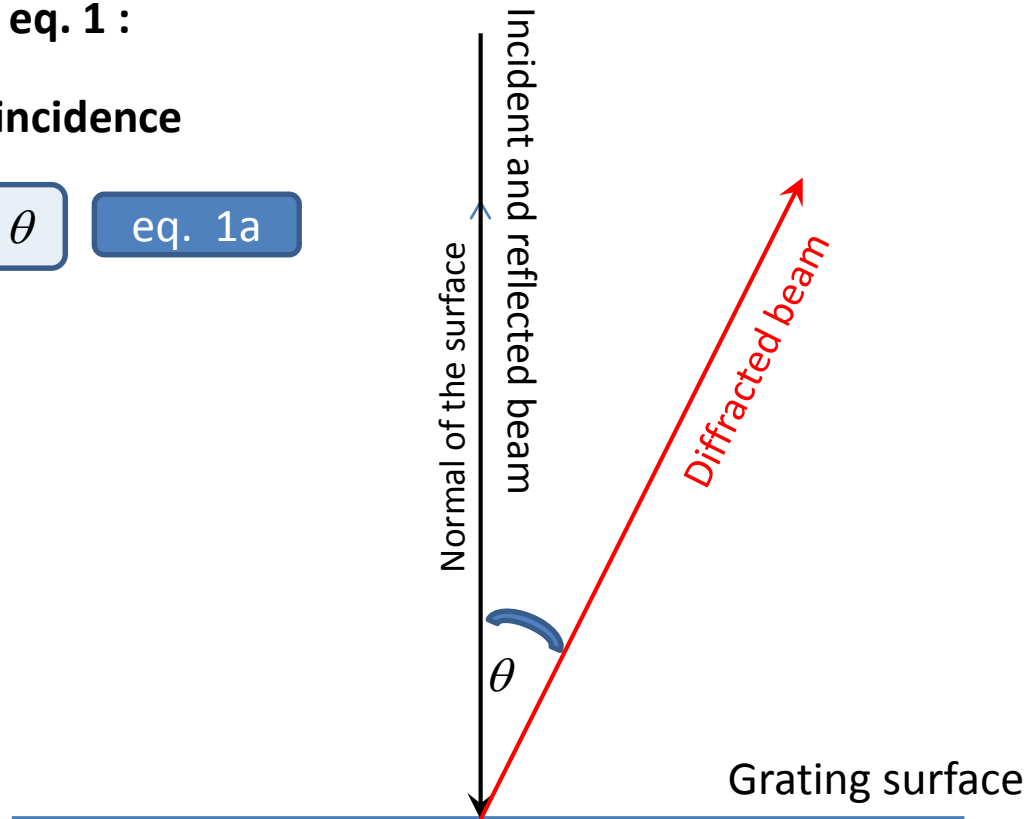
eq. 1

Special case 2 of eq. 1 :

- $i = 0$: **normal incidence**

→ $m \lambda = d \sin \theta$

eq. 1a



- Very common: >> **normal incidence (« NIM ») monochromators**
- In reality, there is small angle (for example 10°) between the incident and the reflected light beam, in order to separate both correctly.

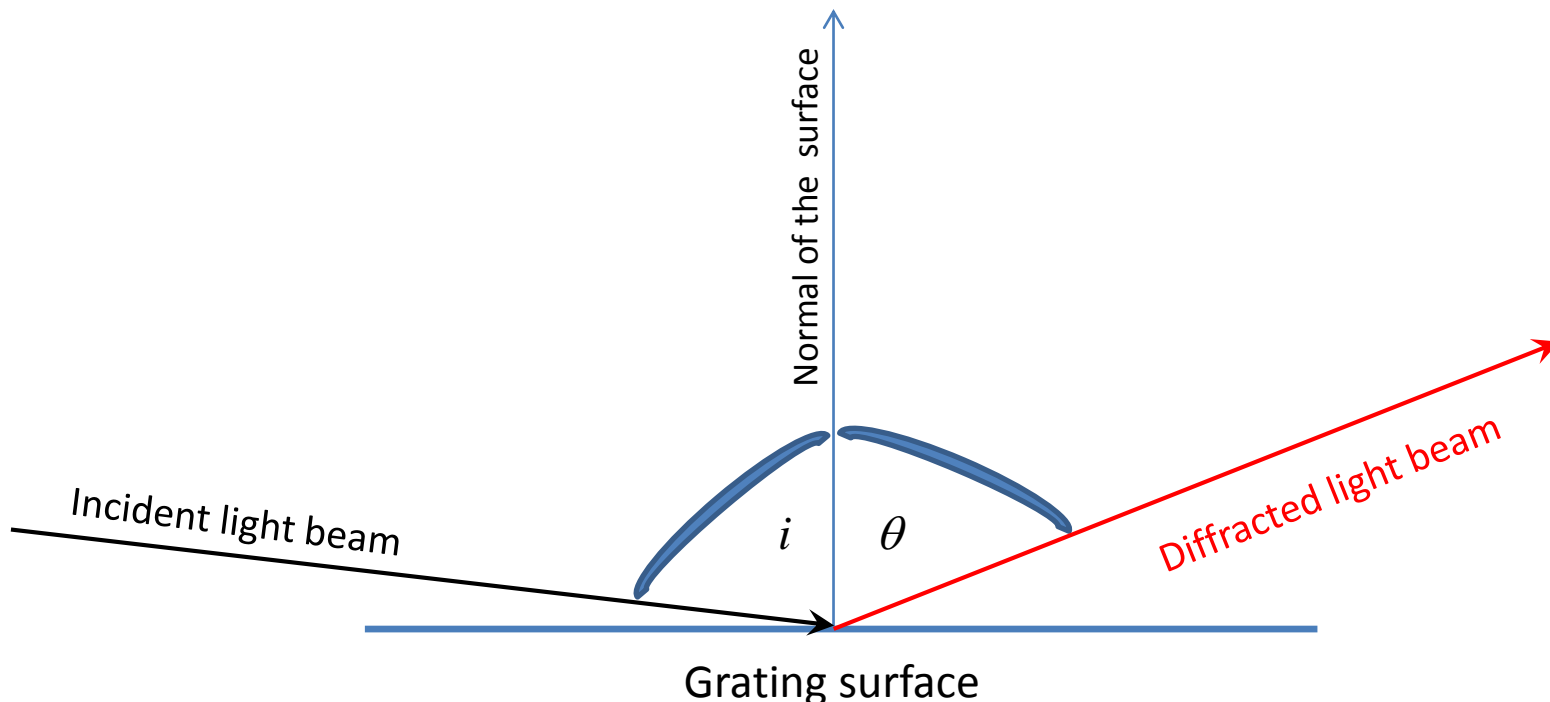
The diffraction grating as dispersing element

$$m \lambda = d (\sin i + \sin \theta)$$

eq. 1

Special case 3 of eq. 1 :

- i close to -90° : **grazing incidence**
- Limits penetration of photons into the material of the grating
- **Used in the vacuum ultraviolet** and in the **X-ray domain** (where few reflecting materials exist)
- Can be an alternative if geometry of the experiment doesn't permit normal incidence



Parameters of the diffraction grating

- **Angular (chromatic) dispersion $D_\theta = d\theta/d\lambda$ of a grating**

$$D_\theta = \frac{d\theta}{d\lambda} = \frac{m}{d \cos \theta}$$

eq. 2

Distinguish:

d : differential

d : spacing between the lines of the grating

Angular dispersion is a characteristic parameter of the grating alone !

- **Resolving power**

$$R = mN$$

eq. 3

- m : order of diffraction [dimensionless]
- N : **total number** of lines [dimensionless]

- R therefore depends only on m and N . **N depends on the constant of the grating C_r** ($= 1 / d$) i.e. the **number of lines per millimeter and the size of the grating**

- *concerning the size: in reality this is the **surface illuminated by the incident beam**.*

- That is why it is necessary to illuminate the surface of the grating as much as possible in order to maximize R .*

- According to eq. 3 one can also work in the higher orders m to increase R . **But** : the spectral domains of different adjacent orders can be superimposed which makes the analysis of the spectrum difficult.

- **CAUTION:** Do not confuse the resolving power R of the grating (eq. 3) with that of the entire spectrometer which depend on other parameters as well (see below).

Parameters of the diffraction grating

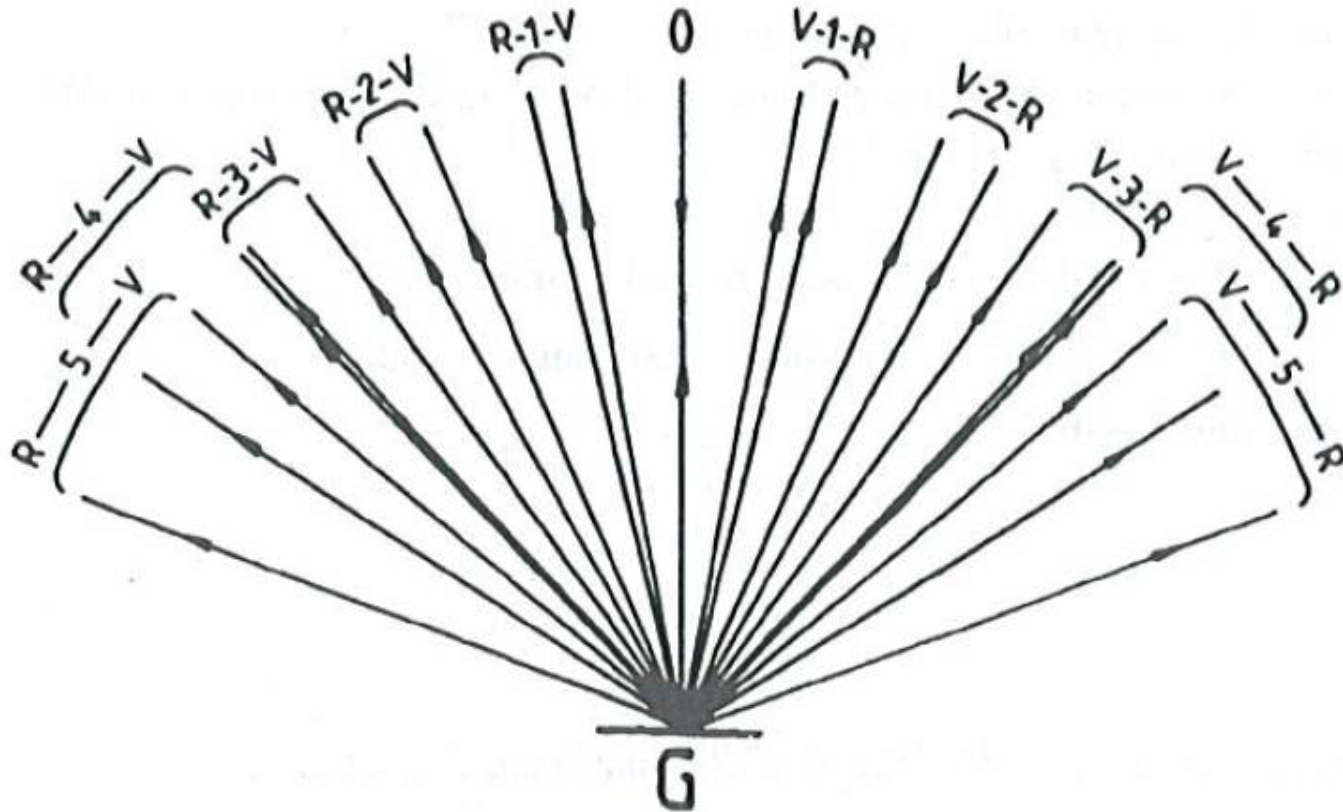


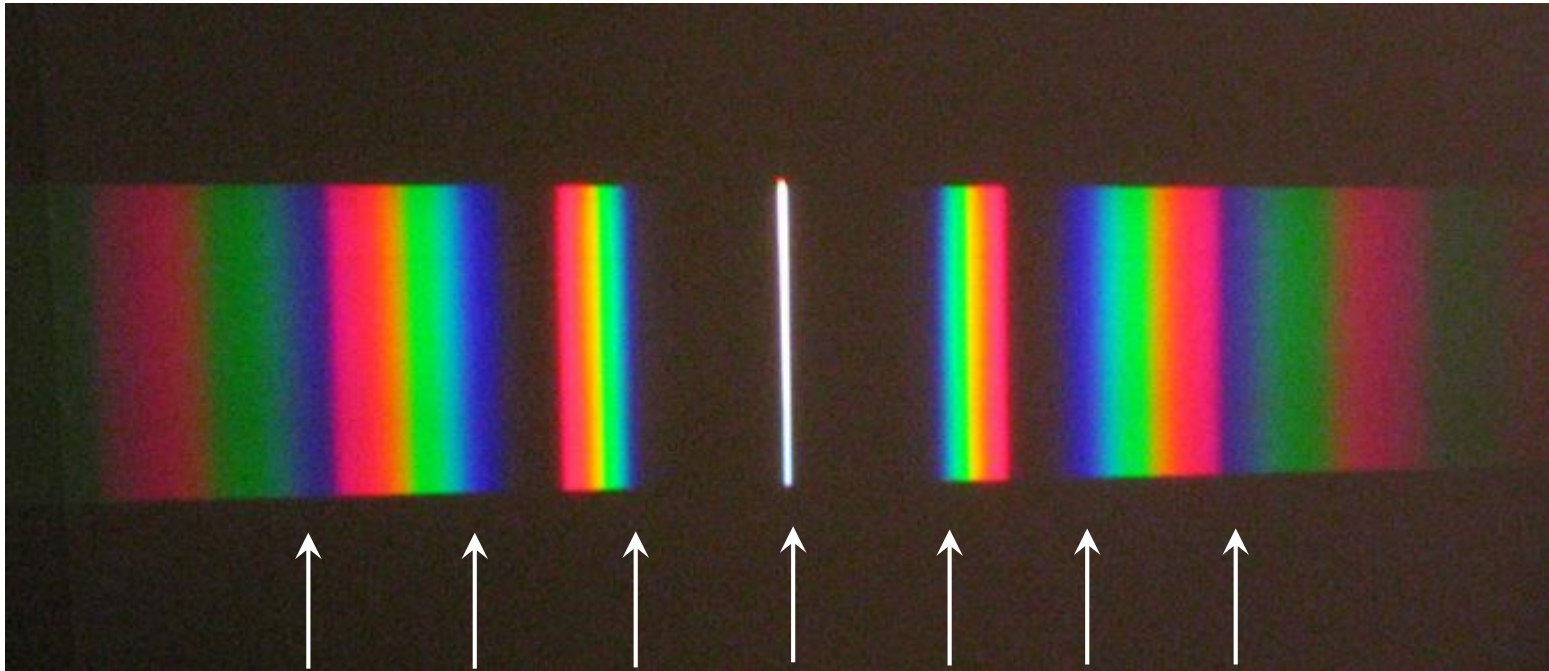
Fig. 3 — *Différents ordres de diffraction à partir d'un réseau plan G, fonctionnant en réflexion.*

• Note :

1. that there are also negative orders.
2. that higher orders diffract "more"

Figure taken from J.M. Hollas: « Modern spectroscopy ». V= Violet, R = red.

Parameters of the diffraction grating



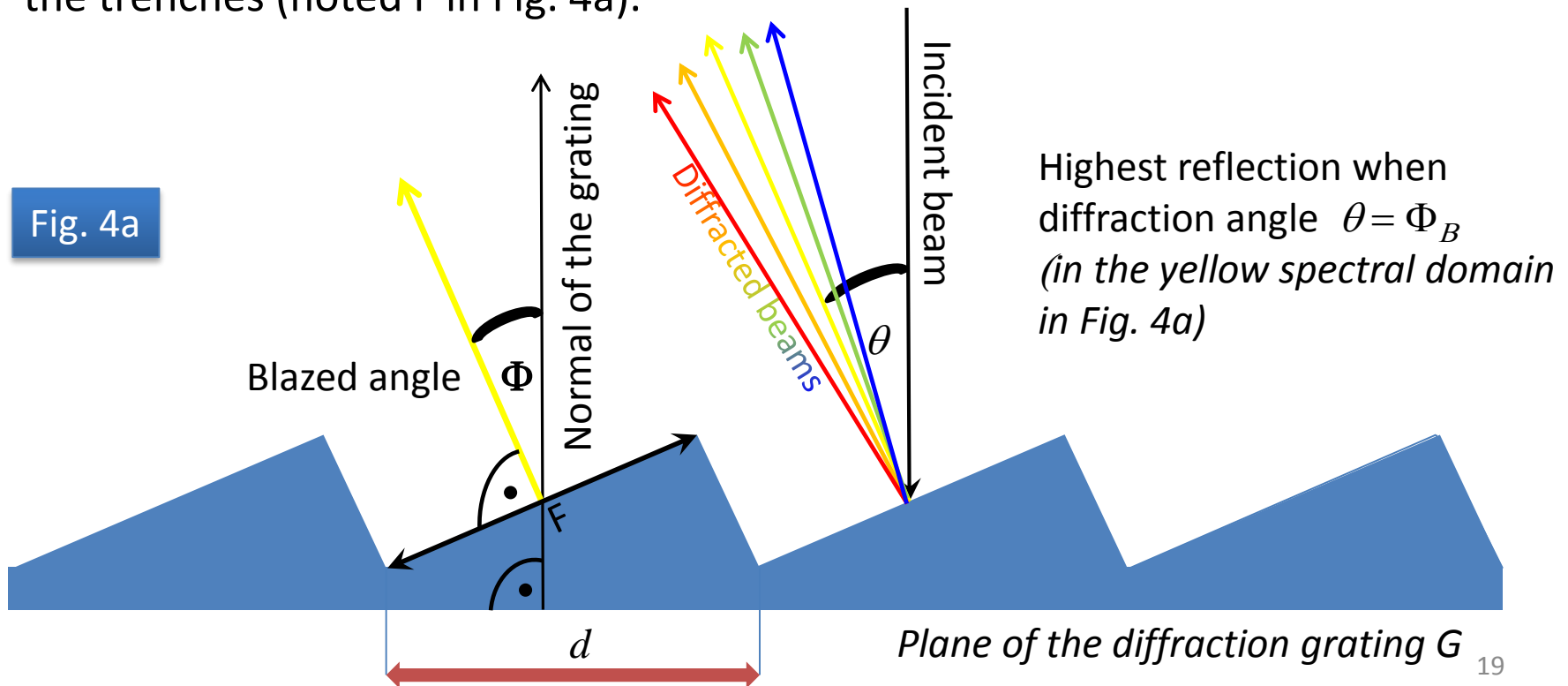
Grating Order m : 3 2 1 0 -1 -2 -3

- Note :

1. that there are also negative orders.
2. that higher orders diffract “more”

Parameters of the diffraction grating: Blazed angle Φ_B

- The intensity in order 0 is the highest
- The **distribution of diffracted intensities in the different orders depends on the profile of the graved lines**. Lines are engraved with diamond precision tools, the normal profile is that of a V.
- When the trenches have a **short flank and a long flank** (cf. Fig. 4a), the **reflection is highest when the beam leaves at the angle Φ_B called blaze angle**, which is formed by the normal of the grating and the normal of the long side of the trenches (noted F in Fig. 4a).



Blazed angle Φ_B \rightarrow Blazed wavelength λ_B

• To blaze a grating is the main way to make it **efficient in a particular order and in a given spectral domain** (yellow in Fig. 4), otherwise the incident radiation intensity would be distributed among too many orders.

• The wavelength that is diffracted at the blazed angle Φ_B is called the **blaze wavelength λ_B** (In fig. 4a it is situated in the yellow). For incoming radiation at the normal ($i = 0$) they are related by:

$$m \lambda_B = 2 d \sin \Phi_B$$

Éq. 4

Blazed grating: Littrow configuration

- The Littrow configuration is a special geometry of a blazed grating:
 - ❖ The incident beam arrives at the blaze angle, so perpendicular to F. The most intense diffracted light is thus in the same direction as the incident beam.
 - ❖ This configuration is exploited **when the reflection grating is part of a laser cavity**, as for example in tunable dye lasers and external cavity tunable diode lasers (ECDL).

Φ_B : blaze angle

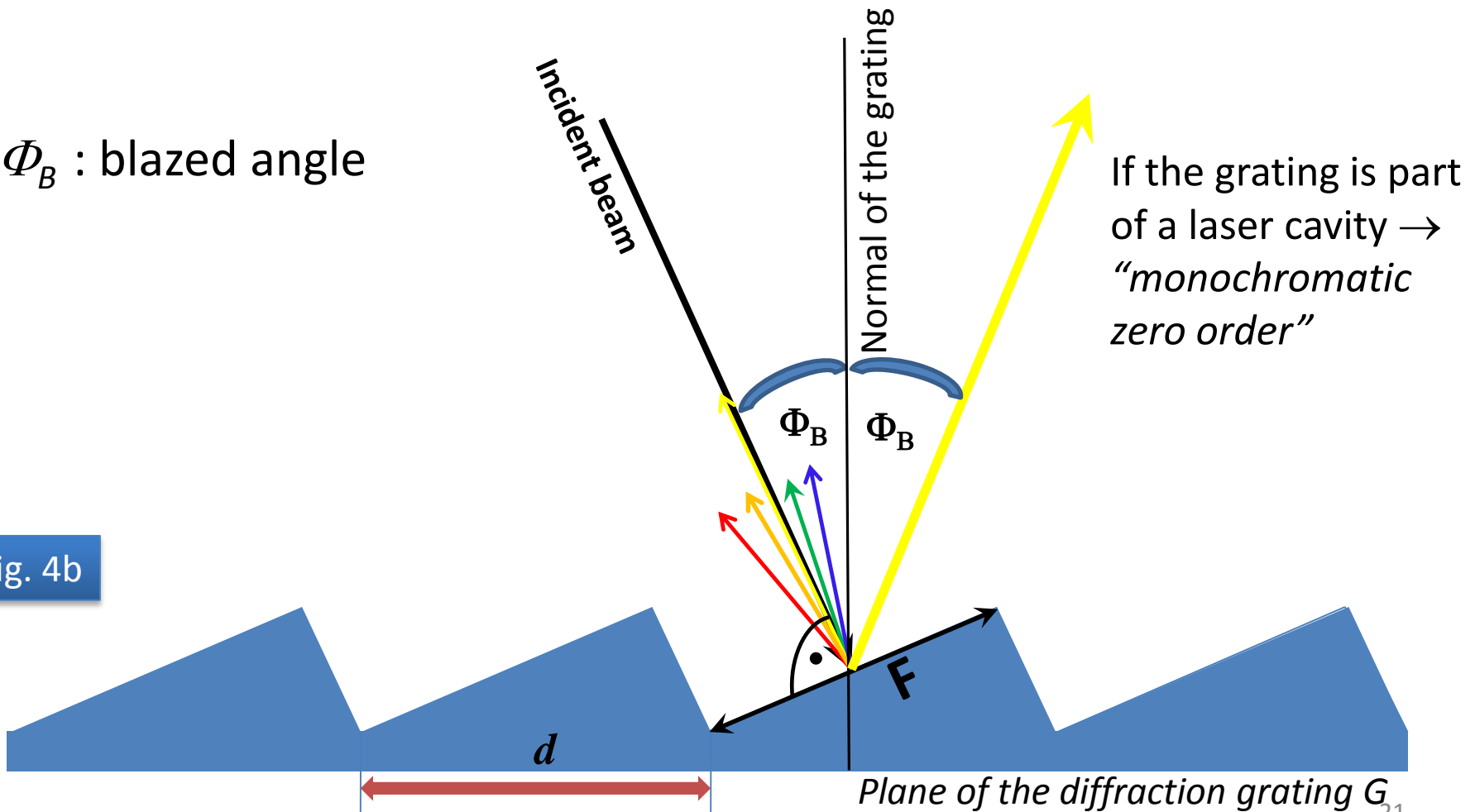


Fig. 4b

Littrow configuration in external cavity diode lasers (ECDL)

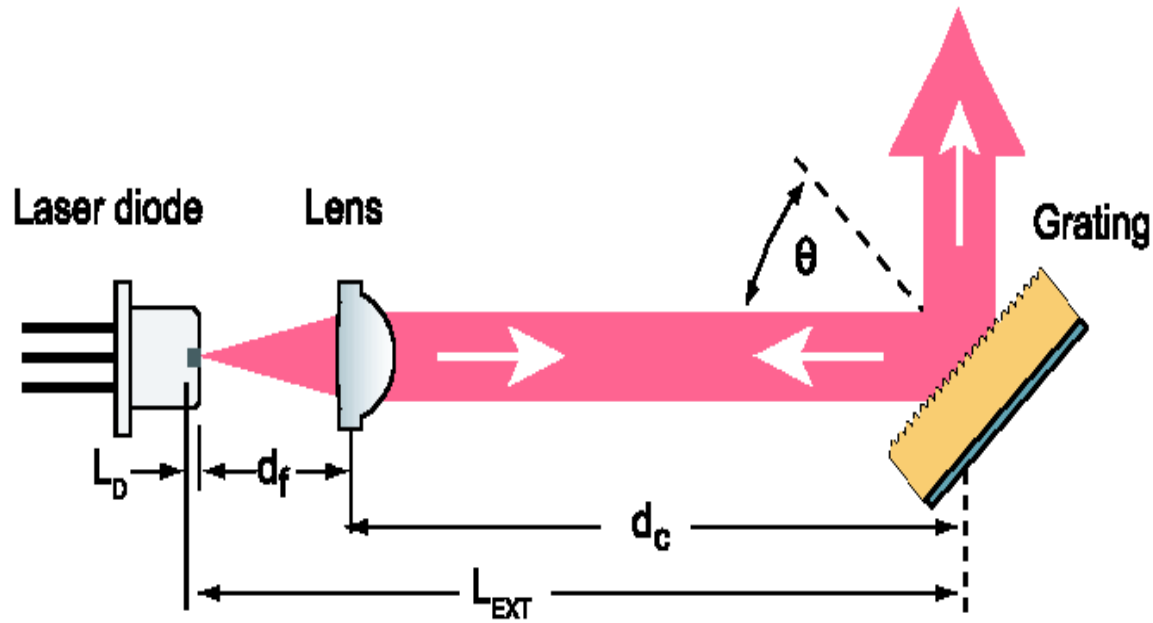


Fig. 1. (Color online) Schematic of a Littrow configuration ECDL

Spectrometers

A diffraction grating is always integrated in an optical setup, for example in spectrometers

- **Among the different type of spectrometers we can distinguish, for example :**
 1. The **Monochromator** focuses light of a particular wavelength to a an exit slit
 2. The **Spectrograph** detects a 2D graph to measure a spectrum
- 3. The **Interferometers** (*don't use a diffraction grating...*)
 - ❖ Fabry-Perot interferometer (one beam interferometer)
 - ❖ Michelson interferometer (double beam interferometer)

Monochromators and spectrographs

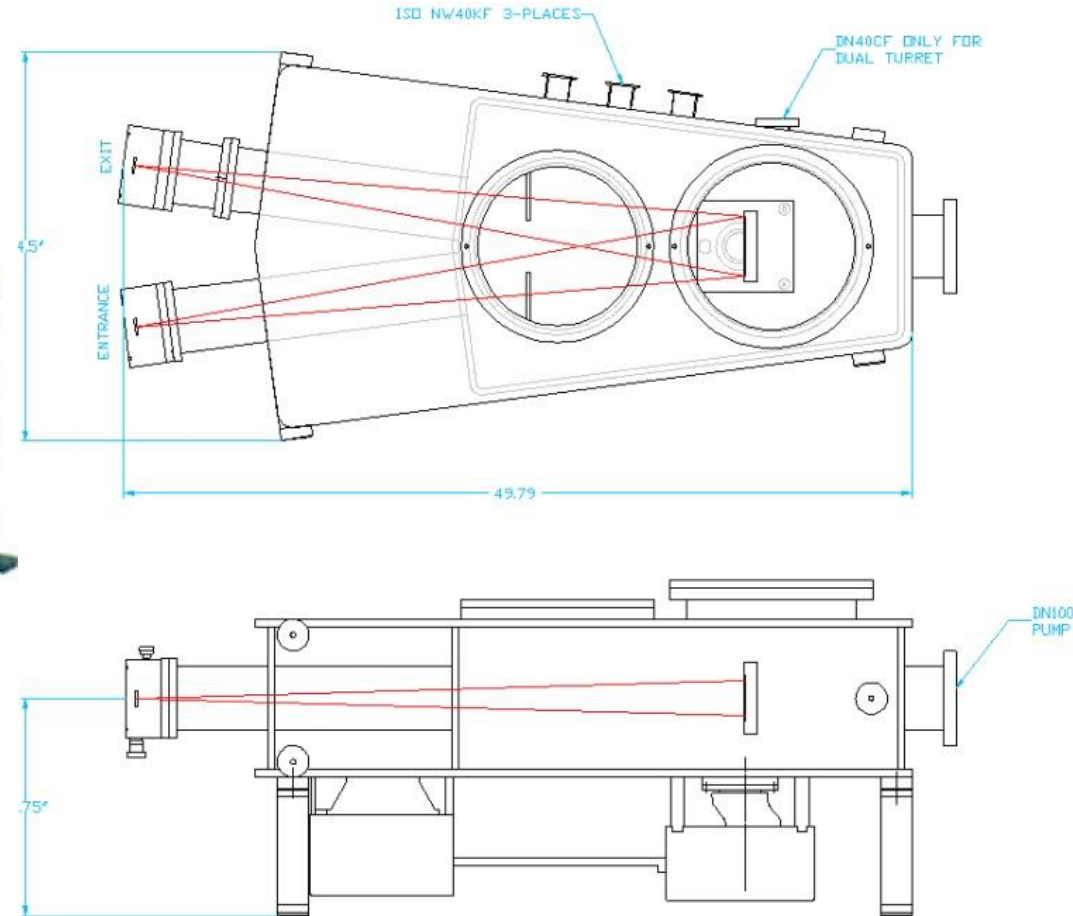
❖ The monochromator :

- disperses the light and
- **focuses a monochromatic beam** (hence its name) **on the exit slit**.
 - **Concave grating** must be used to achieve the focusing (or spherical mirrors in combination with planar grating).
 - The grating **must move circularly during a wavelength scan** and (especially for high resolution) also **laterally**. Stepper motors or (for more precision) piezo-electric actuators are used.

❖ The spectrograph :

- does not focus the diffracted light.
- A planar grating is sufficient.
- As a result, different wavelengths arrive at different places and a two-dimensional detector must be used (A "graph" is detected hence the name).
 - **CCD cameras, diode arrays are used**. This type of detectors are sometimes referred to as the "Optical Multichannel Analyzers" (OMA).
 - Formerly (until the 1980s...) **photographic plates** have been used.
- Naturally, the design of the spectrograph is simpler because the optical elements do not move. For this reason, space probes exploring the solar system or Earth satellites often prefer a spectrograph.

Monochromators and spectrographs



- McPherson model 225 normal incidence monochromator (NIM; 15° in reality...),
- 1m focal length

Concave grating and Rowland circle

- Concave gratings combine diffraction and focusing
- For **maximum spectral resolution**, the object (**entrance slit**) and image (**exit slit**) must be on the **Rowland circle whose diameter is and the radius of the spherical surface of the grating**
- Generally, in such a monochromator, one must turn and reposition the grating during a scan. Two motors are therefore necessary.
- **Below 200 nm (vacuum-UV) and in the infrared the monochromator must be evacuated from ambient air.**

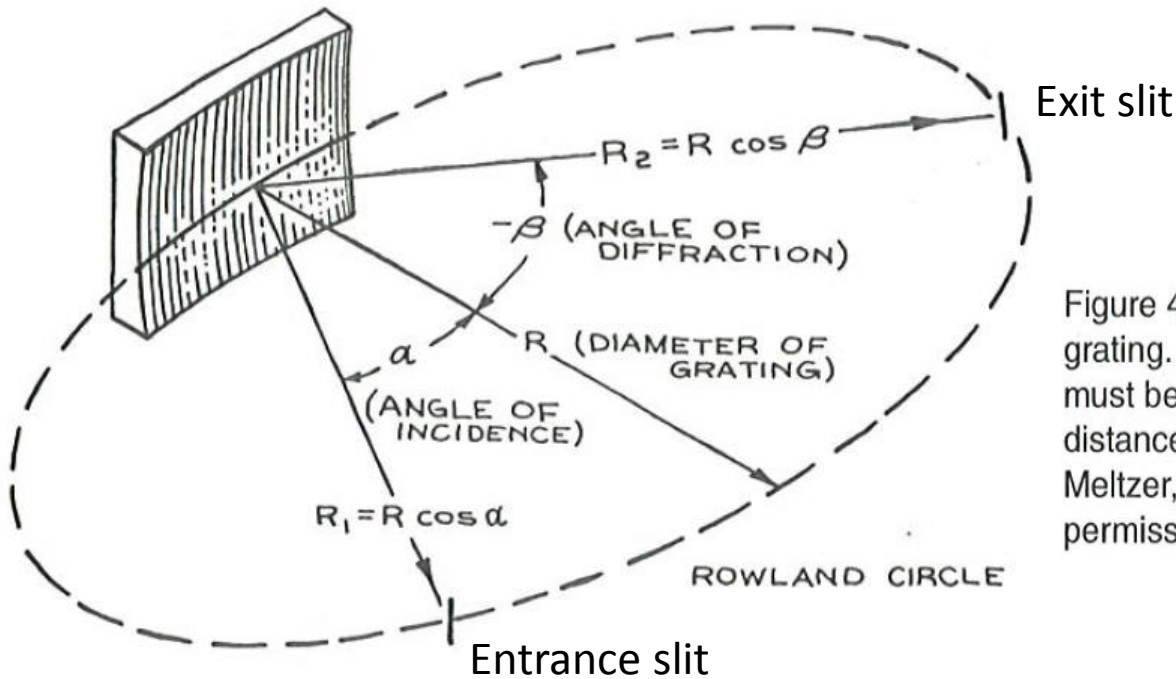


Figure 4.145 Rowland circle of a concave diffraction grating. For maximum resolution, both object and image must be on the Rowland circle. R = object (entrance slit) distance: R_2 = image (exit slit) distance. (From R. J. Meltzer, "Spectrographs and Monochromators" by permission of Academic Press.)

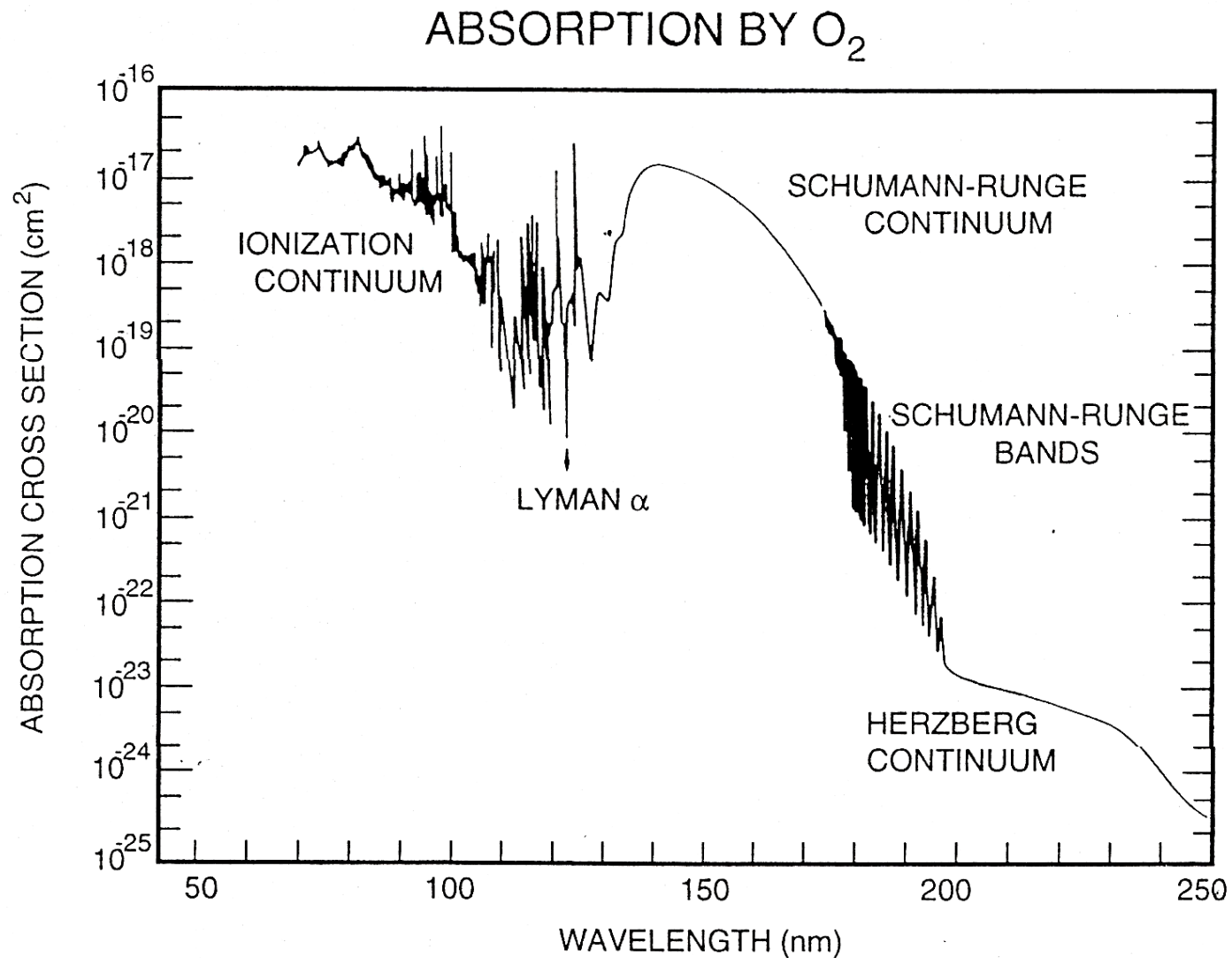


Figure 8.12 Absorption cross section as a function of wavelength for molecular oxygen. After Brasseur and Solomon (1986). Reprinted by permission of Kluwer Academic Publishers.

Czerny-Turner and Ebert-Fastie configuration of a (UV/Vis/IR) monochromator

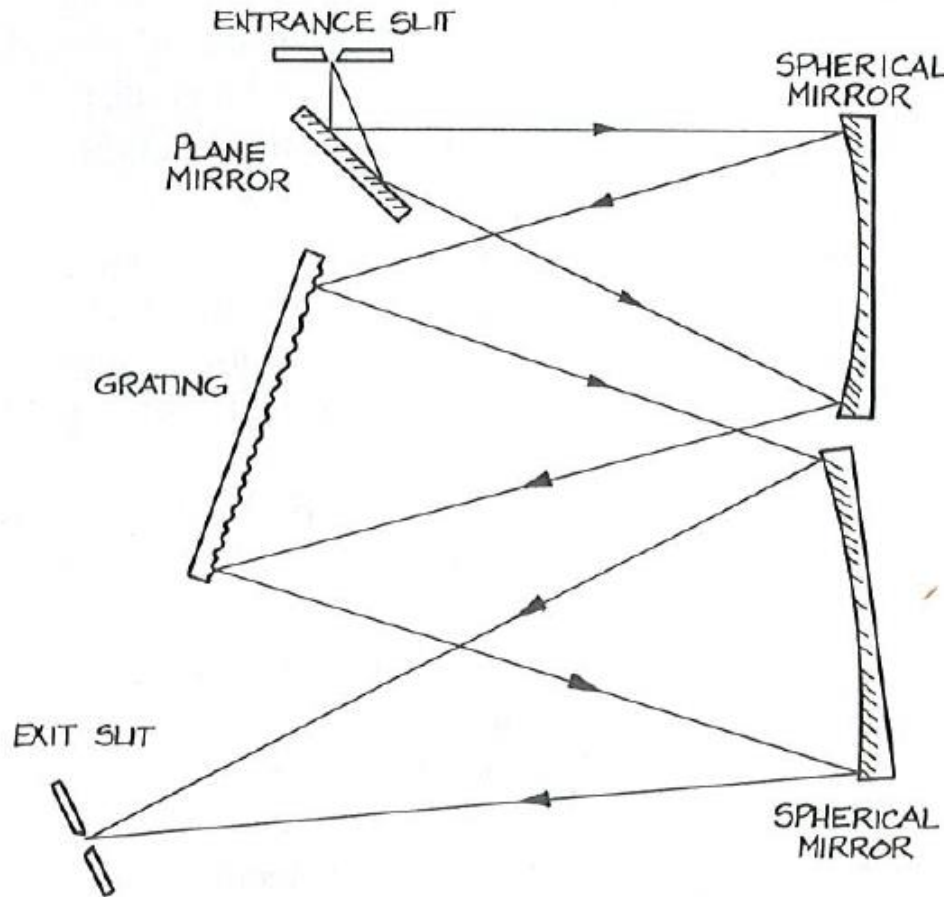


Figure 4.144 Arrangement of a Czerny-Turner grating monochromator.

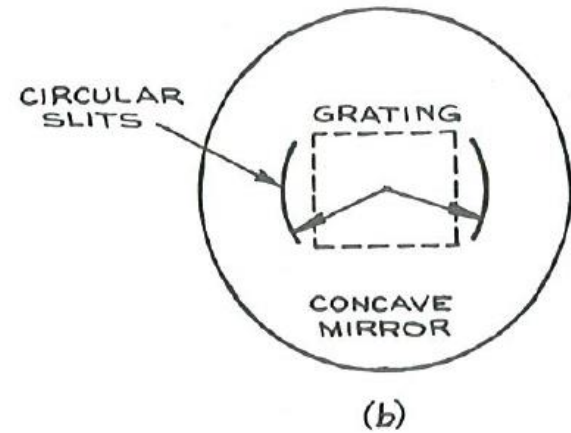
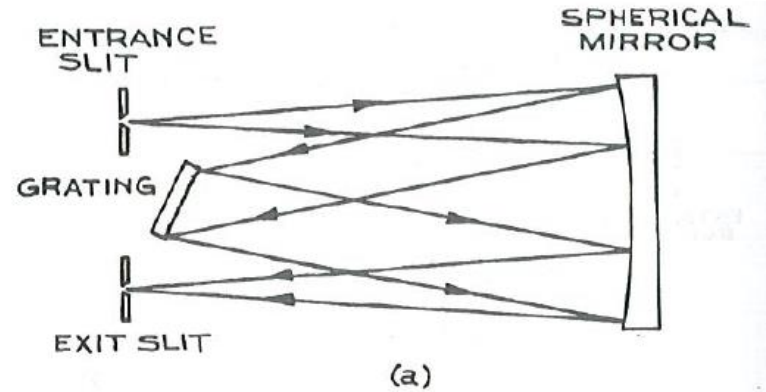
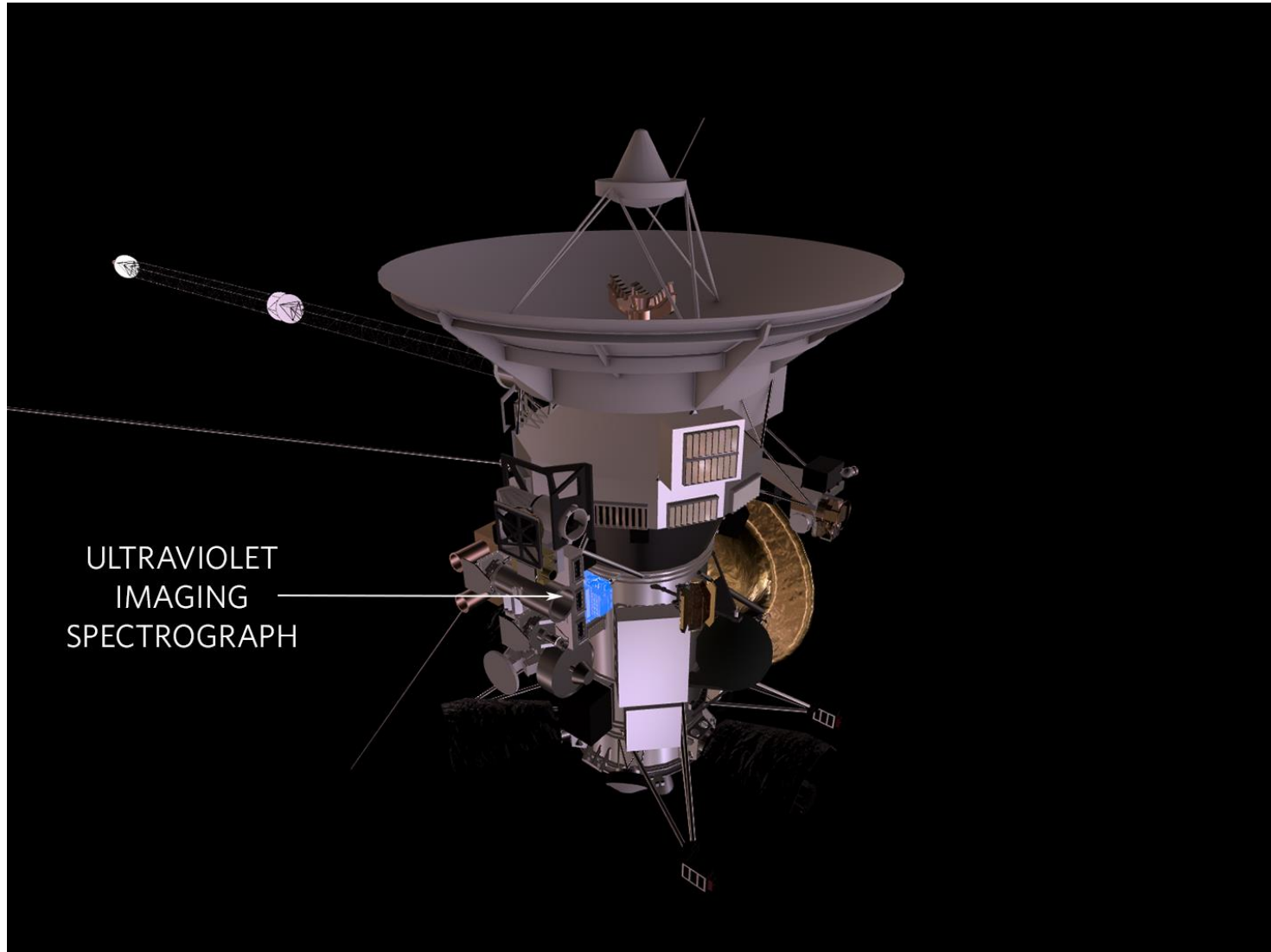
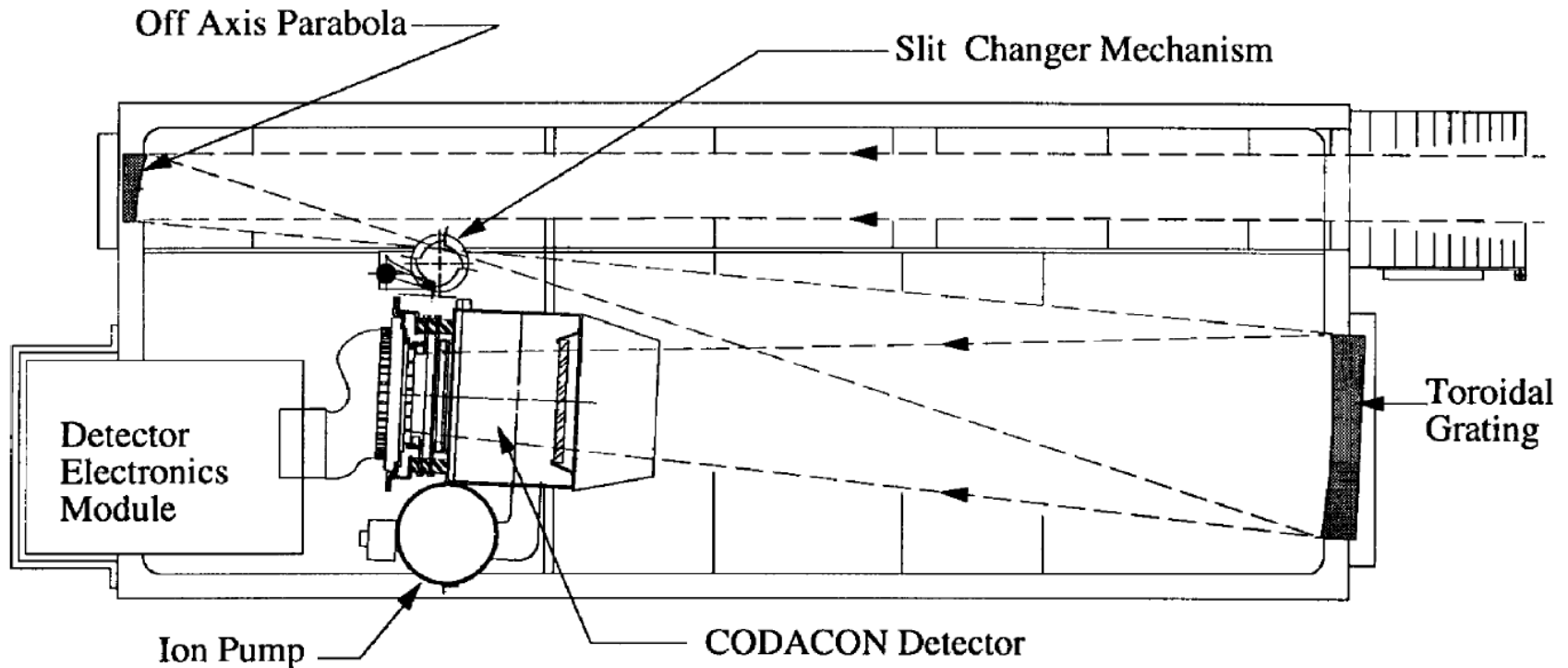


Figure 4.143 (a) Ebert-Fastie monochromator; (b) curved entrance and exit slit configuration for use with the above.

Ultraviolet Imaging Spectrograph (UVIS) on board Cassini (2015-2017)



Ultraviolet Imaging Spectrograph (UVIS) on board Cassini (2005-2017)



- Mass = 14.46 kg
- Peak Operating Power = 11.83 W
- Peak Data Rate = 32.096 kilobits/sec
- Dimensions (approx.) = 48 cm x 30 cm x 23 cm
- Spectral rang 55.8 to 190 nanometers (vacuum-UV)

Esposito et al., Space Science Reviews 115: 299–361, 2004

Science objectives: molecules, aerosols, clouds; neutrals in the Saturn magnetosphere, D/H ratio for Titan and Saturn; icy satellite surface properties; structure and evolution of Saturn's rings.



Benzene @Titan, measured in the Vacuum-UV by the Cassini space probe

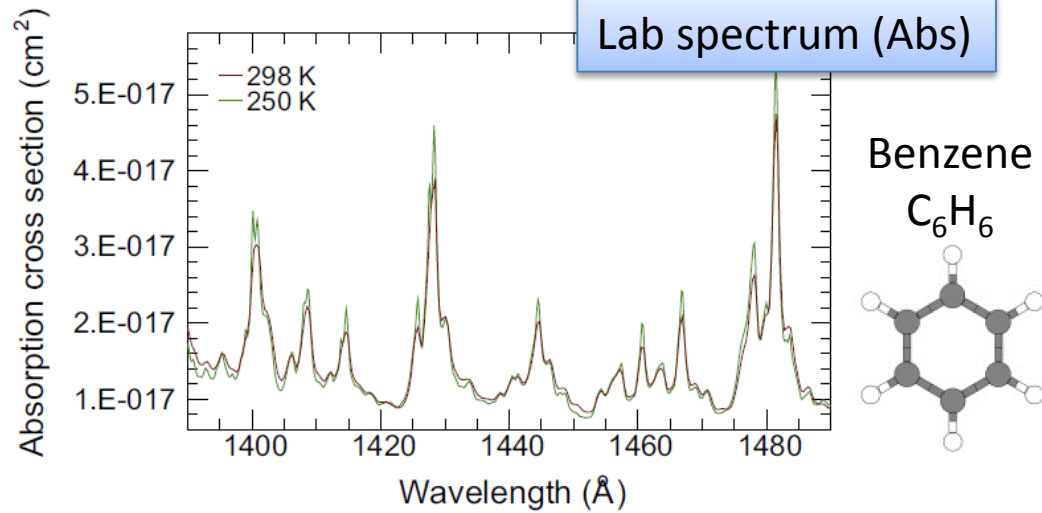


Fig. 3. Benzene absorption cross section measured at two different temperatures, 298 K and 250 K, in the range 1390–1490 \AA .

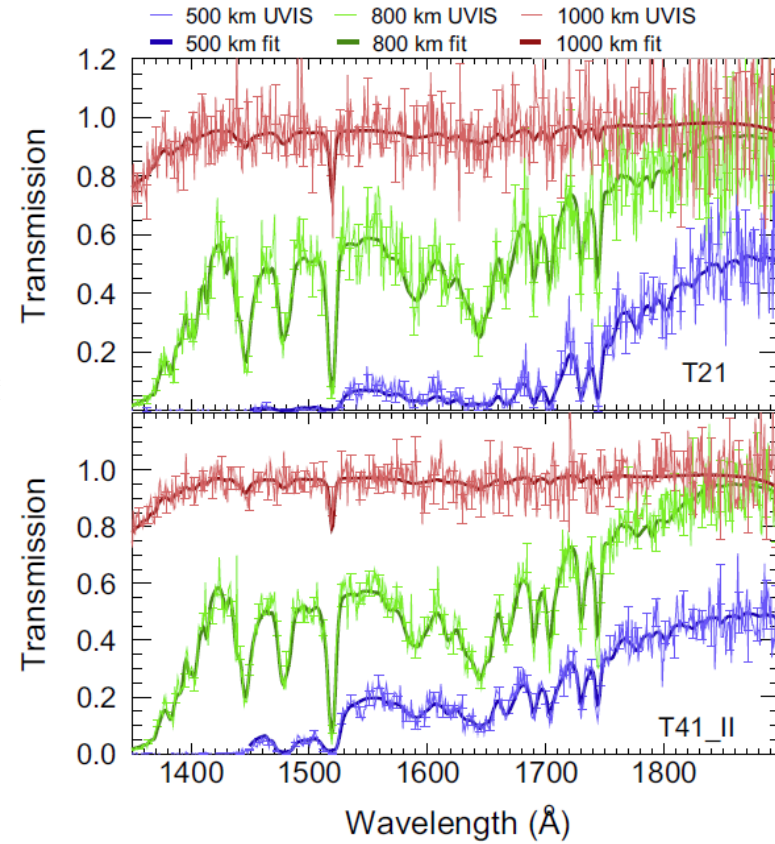
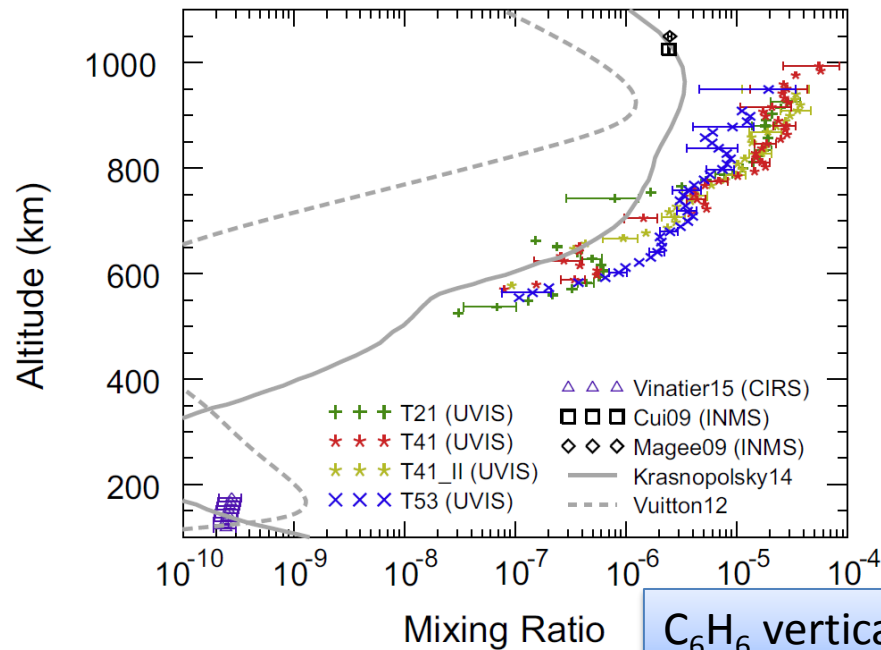


Fig. 5. Measured transmission (light, thin lines) and modeled transmission (thick lines) at 500 km, 800 km, and 1000 km, from flybys T21 and T41_II. Only $\pm 1\sigma$ uncertainty bars are shown for clarity.



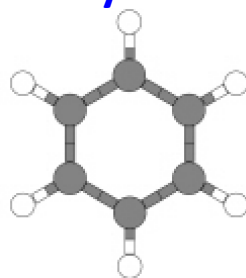
Space spectrum (UVIS transmission @diff. altitudes)

F.J. Capalbo et al., *Icarus* (2016), 95-109.

On Benzene in the Circumstellar Envelopes

J. Cernicharo, A. M. Heras, A. G. G. M. Tielens, J. R. Pardo, F. Herpin, M. Guélin, and L. B. F. M. Waters,

Infrared Space Observatory's (ISO) Discovery of C₄H₂, C₆H₂, and Benzene in CRL 618, Astrophys. J. 546, L123–L126 (2001);



ISO space telescope : 1995-1998

Critical analysis (H. Müller, Cologne Database of Molecular Spectroscopy (CDMS), Univ. Cologne; <https://www.astro.uni-koeln.de/cdms>) :

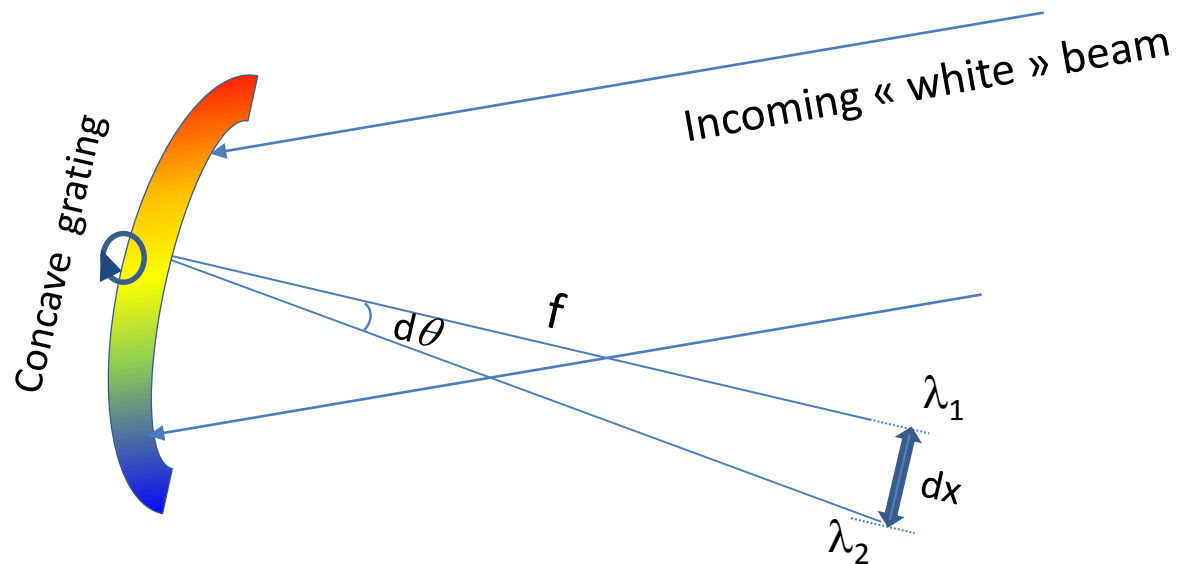
Report on the **detection of the ν_4 band of benzene with an origin at 674.0 cm^{-1} (or $14.84 \text{ }\mu\text{m}$)** employing mid-infrared spectroscopy. The band is clearly observed, but not particularly strong. **Unfortunately, possible rotational substructure**, including that from hot-band, may be present, but is **near the noise limit** as pointed out by the authors. The derived abundances seem plausible. Moreover, the **PAH hypothesis**, which most astronomers accept with little caution, if any, **requires the presence of benzene in such environments**, as probably do the recently reported rather secure detections of C₆₀ and C₇₀. Finally, **there does not seem to be any alternative assignment for this feature**. Overall, one can probably view the detection of benzene as, at least, **fairly secure, but a small degree of caution may be useful**.

Monochromator

- Remember: Angular dispersion D_θ is a parameter of the grating alone. If the grating is integrated in the monochromator we have to introduce a new parameter: the linear dispersion D_x
- Angular dispersion $D_\theta = dn/d\theta$ produces a linear displacement dx of the diffracted beam at a point at some distance of the grating. \rightarrow Spatial separation dx in to λ_1 and λ_2 .
- Linear dispersion

$$D_x = \frac{dx}{d\lambda}$$

eq. 5



- f is the focal length of the monochromator. We can write easily :
 $\tan d\theta = dx / f \Leftrightarrow dx = f \times \tan d\theta \approx f \times d\theta$ (approx. $\tan d\theta \approx d\theta$);
If we multiply with $1/d\lambda$ follows:

$$\frac{dx}{d\lambda} = f \times \frac{d\theta}{d\lambda}$$

\Leftrightarrow

$$D_x = f \times D_\theta$$

eq. 6

Linear dispersion of a monochromator

- Formally, linear dispersion D_x is dimensionless (length / length)
- In practice it is still given with dimensions, for example [mm/nm] or [mm/Å] (or the opposite! → pay attention to the units...)
- We can link easily the **linear dispersion to the grating constant C_r ($=1/d$) and the focal length f** of the monochromator :

$D_x = f \times D_\theta$ eq 6 ; with eq 2 (see above) we find:

$$\Rightarrow D_x = \frac{f \times m}{d \cos \theta} \quad \text{or} \quad D_x = \frac{f \times m \times C_r}{\cos \theta}$$

With $\sin^2 \theta + \cos^2 \theta = 1$, $m = 1$, the incident angle $i = 0$ (NIM), and eq 1 ($m\lambda = d \sin \theta$) :

$$D_x = \frac{f \times C_r}{\sqrt{1 - (C_r \times \lambda)^2}}$$

eq. 7

**With this equation
one can easily
calculate D_x !**

(only valid for order $m=1$)

- **$D_x \propto f$**
- For m and C_r constant, we can work with more or less “big” monochromators to realize the desired linear dispersion D_x .
- For this reason, small and large monochromators exist (for example **$f = 50$ cm (“laboratory bench”)**, but also **$f = 10$ m for high-resolution spectroscopy.**
- Note: **the focal length f is the radius of the concave grating**, so the “size” of a monochromator is predefined by the choice of the grating (machined with a given curvature).

Slits in the monochromator

Spectral resolution of the monochromator

$$\Delta\lambda = \frac{\sqrt{2} \times S}{D_x}$$

eq. 8

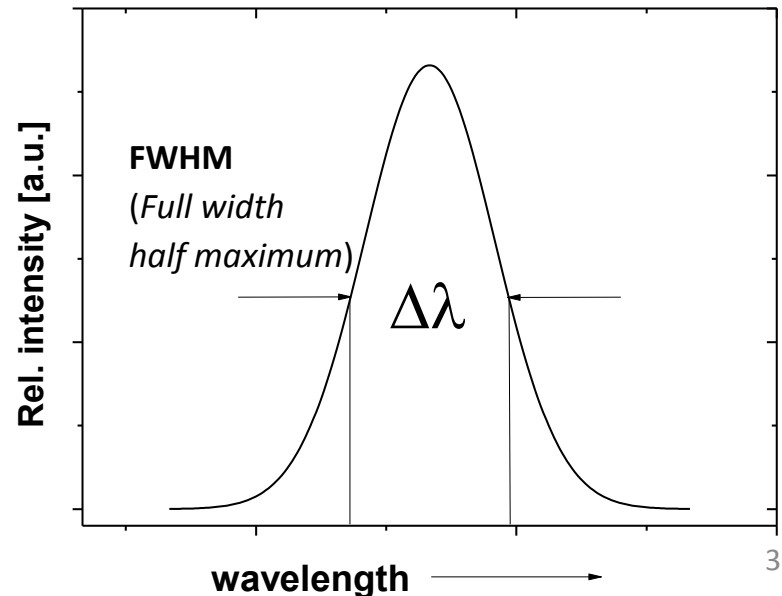
• With the linear dispersion D_x available, one can easily calculate the spectral resolution $\Delta\lambda$ of the monochromator ; with S: real width of the exit slit

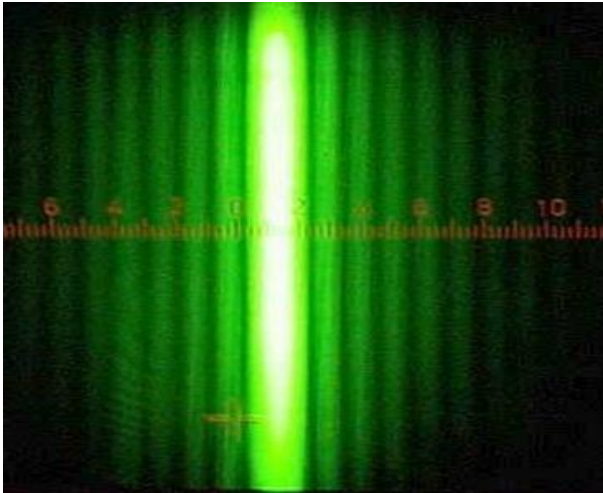
If the widths of the exit slit S_{Exit}^2 and entrance slit S_{Ent}^2 are different $\Delta\lambda$ is calculated by eq. 9:

$$\Delta\lambda = \frac{\sqrt{S_{Exit}^2 + S_{Ent}^2}}{D_x}$$

eq. 9

- The observed spectral profile of a line produced by a **slit of finite width** is actually a Gaussian (if the “molecular line width” is $< \Delta\lambda$).
- If $\Delta\lambda$ is limited by the monochromator, it is equal to the FWHM of the Gaussian profile

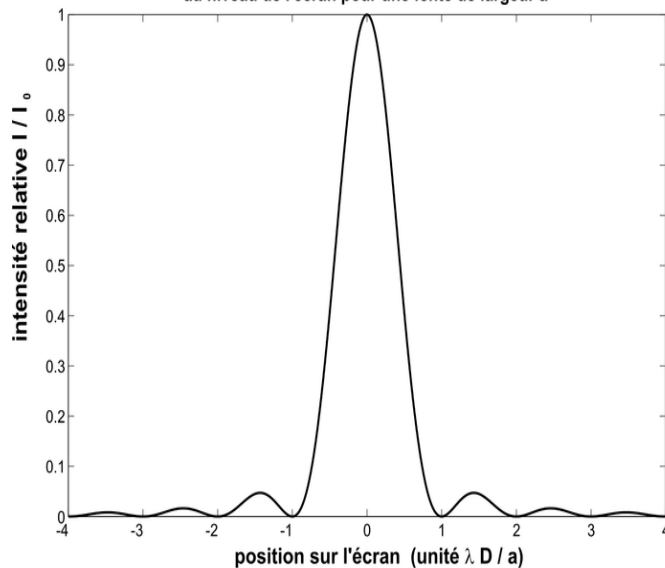




- Diffraction of a monochromatic laser beam ($\lambda = 532 \text{ nm}$) by a slit
- **Only if wavelength $\lambda \sim S$**
- In practice, **when measuring a spectrum**, the width S of the exit slit in a monochromator **is rarely below $10 \mu\text{m}$** (*no photons left....*)



Variation relative de l'intensité
au niveau de l'écran pour une fente de largeur a



- But: The observation of diffraction fringes created by a rectangular slit (when almost entirely closed) serves to **align a monochromator** (or more generally any optical assembly) using a monochromatic laser beam.

- **Diffraction by a slit:**
- Intensity I on a screen with distance D from slit:

$$I(x) = I_0 \cdot \text{sinc}^2 \left(\frac{\pi a}{\lambda D} \cdot x \right) \quad \text{with} \quad \text{sinc}(x) = \frac{\sin(x)}{x}$$

- a : slit width
- λ : wavelength
- period $P = \lambda D/a$



Monochromator, spectrographs - résumé

The **spectral resolution** $\Delta\lambda$ of a spectrometer using a diffraction grating for light dispersion depends on several parameters:

1. The **angular dispersion** D_θ (eq.2) which is a property of the diffraction grating alone. It defines the angular separation of two wavelengths λ_1 and λ_2 by this grating. It is determined by the grating constant C_r which is the number of lines *per millimeter* (reciprocal to distance between lines; $C_r = 1/d$)
2. The **resolving power R of the diffraction grating** is $R = mN$ (eq.3) with N being the total number of lines of the grating illuminated by the incoming beam of the light source).

Points 1 and 2 are physically related since N depends also on C_r .

3. The **focal length f** of the monochromator leads to the **linear dispersion** D_x at the exit slit such as $D_x = f \times D_\theta$;
4. **The user chooses** the (exit) **slit width S** of the monochromator **according to the desired spectral resolution** (eqs. 8,9). S, calculated from D_x , also determines the number of photons that go through it. For many applications, it takes a certain number of photons for them to work... There is thus a natural lower limit of S for each application.

Points 3 and 4 are physically independent

A few, last remarks

- For any scientific application (laboratory or satellite) it is necessary to have a good idea which spectral resolution is actually needed for the study to be undertaken....
 - Sometimes one tries to close the slits in order to find some fine structure and this does not affect the spectrum....
 - This is because the observed line width is simply natural, determined by a physical phenomenon such as the lifetime of the excited state populated by the absorption of radiation.
 - *In the UV, a molecule can photodissociate and thus the life time of an excited state can be strongly reduced (absorption will be broadened...)*
 - In addition, if there are many (broadened) lines close in position they can be all superimposed. This is called "spectral congestion".

Introduction to laser radiation

Laser light sources are now **indispensable tools** for basic research in chemistry, physics, biology, and **especially in spectroscopy**. For more than 50 years now, researchers have used these monochromatic sources of **high intensity (brilliance), monochromaticity, very low divergence and phase coherence**.

Laser technology is constantly advancing. Different methodologies exist today to make **them tunable in wavelength** (for example by integrated gratings in the cavity) and their **handling has becomes more and more user-friendly**

Apart from their scientific applications in fundamental scientific research, lasers are used intensively for **industrial applications**. These applications naturally concern the field of work of a physicist in industry...

Industrial fields of application include:

- Processing, transformation and machining of materials
- Medicinal therapy and medical devices
- Analytical applications in chemistry and biology (laser desorption MS for example)
- Communication technology
- Printing and Entertainment

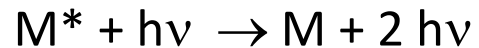
Introduction to laser radiation

- **Laser = Light amplification by Stimulated Emission of Radiation**
 - If the radiation concerned is in the spectral range of the microwave, we speak of a "Maser" (= Microwave amplification by Stimulated Emission of Radiation)
 - The first device was an ammonia Maser introduced in 1953 (Charles H. Townes, James P. Gordon, and H. J. Zeiger at Columbia University). It is the "the ancestor" of the laser (term created later)
 - Maser also exist naturally, emitted from astrophysical objects (OH, H₂O).
 -
 -
- Since then lasers have had a huge impact in science and industry, in the infrared, visible and ultraviolet range. Even outside these ranges (Far-infrared , extreme UV ...) lasers are available today.

Introduction to laser radiation : **stimulated emission**

- Light emission can be spontaneous or stimulated (= induced)
- The laser radiation is entirely emitted by the **stimulated emission** process, unlike more conventional radiation sources (black body, discharge lamps, etc ...).

Stimulated emission :

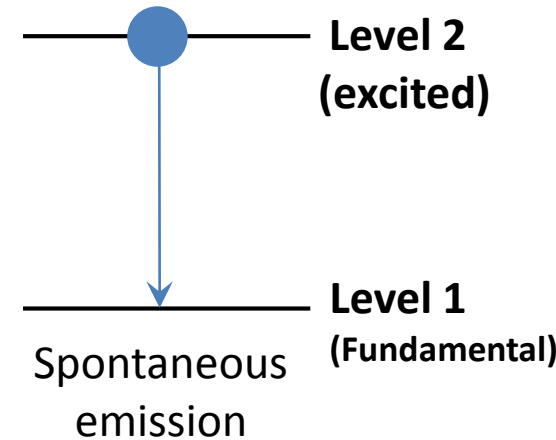
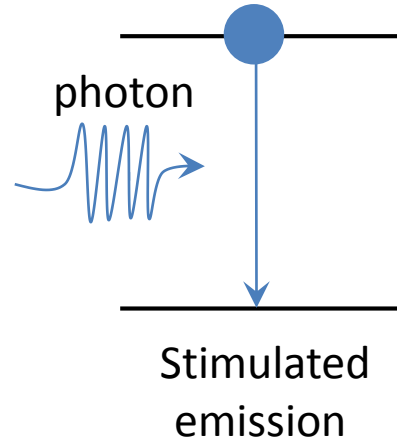
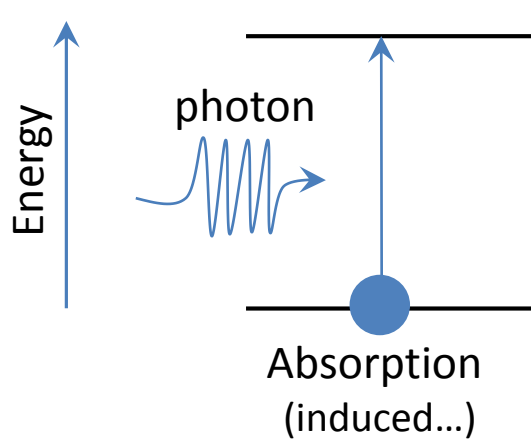


eq. 10

- The **two photons produced are of the same frequency**, the stimulated emission therefore requires an incoming photon whose frequency (energy) corresponds to a resonant transition between two states of the molecule, high and low in energy.
- In a two-level system n and m , if stimulated emission should predominate over (induced) absorption ($M + h\nu \rightarrow M^*$) one must have a **population inversion**, that is to say **more molecules must be in the higher state 2 than in the lower state 1**.
- Note: absorption is always “induced” or “stimulated” (by a photon)

Introduction to laser radiation : stimulated emission

Energy diagram of a molecule (or atom)



Probability of absorption

$$\frac{dN_2}{dt} = N_1 \times B_{12} \times \rho(\nu)$$

Probability of

stimulated emission

$$\frac{dN_2}{dt} = -N_2 \times B_{21} \times \rho(\nu)$$

Probability of

spontaneous emission

$$\frac{dN_2}{dt} = -N_2 \times A_{21}$$

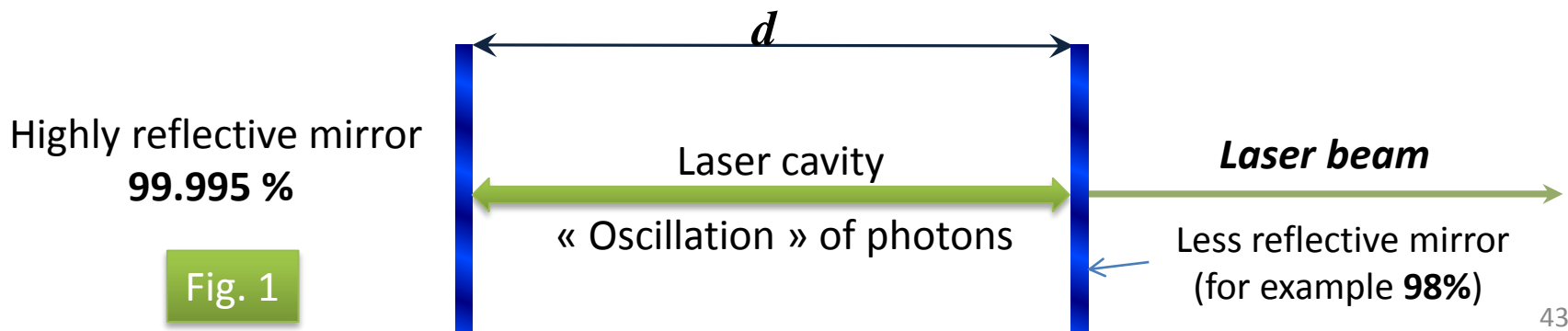
- N_1, N_2 : **number of molecules** in respective level
- $\rho(\tilde{\nu})$: spectral radiance
- B_{12} : Einstein coefficient of absorption

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

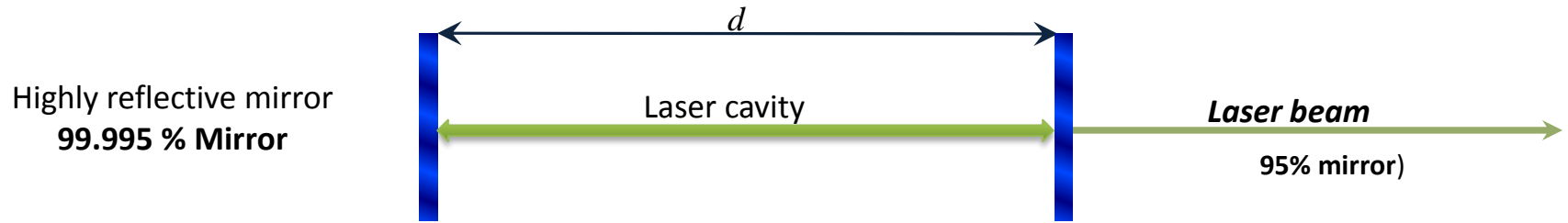
$$A_{21} = \frac{8\pi\nu^3}{c^3} \times B_{12}$$

Laser terminology

- "**Population inversion**": $N_2 > N_1$; (N: #molecules; 2,1 higher, lower energy level)
- The process to achieve population inversion is called "**pumping**"
- A physico-chemical system in which population inversion is created is called "**active medium**" (sometimes called "active system"). **The active medium acts as an amplifier of the radiation** it receives, because for each photon that enters, two photons are produced.
- If the active medium is placed between two highly reflective mirrors we speak about a "**Resonator**".
- If one of the mirrors is a little less reflective, a fraction of the radiation escapes as laser radiation. The region between the two mirrors is then called the "**laser cavity**". Fig. 1 shows a simplified scheme. **The separation of the mirrors must be an integer multiple of the half-wavelength of the radiation ($d = n \times \lambda/2$)** which requires an extremely precise alignment of the cavity.



Resonance frequencies of a laser



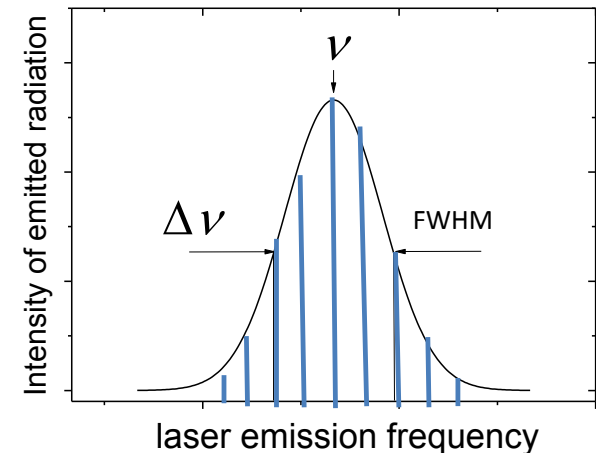
- As a consequence of the $d = n \times \lambda/2$ condition we can define the **resonance frequencies ν of the laser cavity**

$$\nu = n c / 2d$$

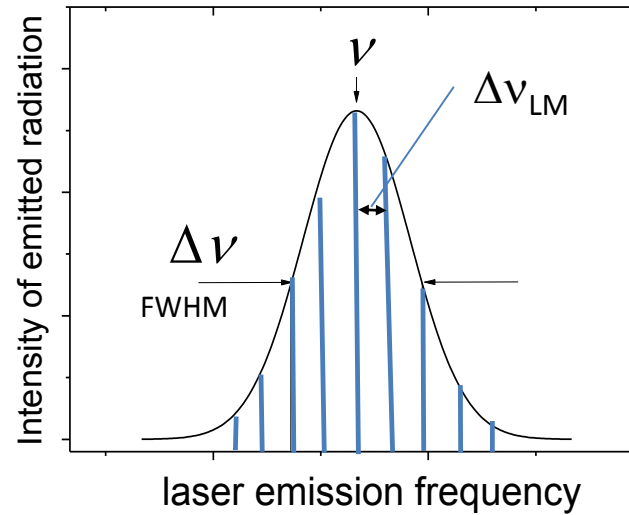
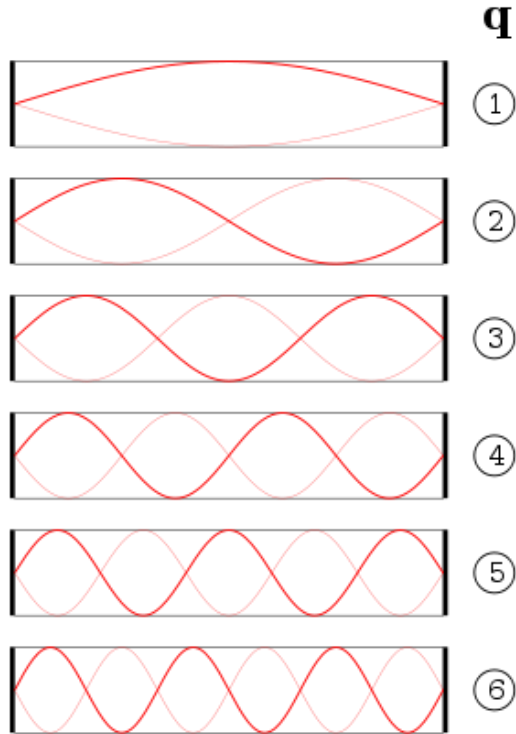
eq. 11

- Eq. 11 gives a comb of possible frequencies of the radiation to be emitted by the laser cavity. Theoretically, there is an infinite number n of resonance frequencies (since n is any integer).
- But:** the emitted frequencies ν are naturally fixed by an optical transition between the two levels of involved active medium, with its associated spectral width $\Delta\nu$! :

Optical transition with frequency ν and spectral width (or finesse) $\Delta\nu$, including comb of frequencies called **longitudinal modes of the laser**.



Longitudinal modes of a laser



- Equation 11 ($\nu = n c / 2 d$) defines the longitudinal modes of the cavity.

They are equidistant and their separation is given by :

$$\Delta \nu_{LM} = c / 2 d$$

eq. 11b

Doppler width and longitudinal modes (LM) of a laser

Example: If the active medium is a gas (and in the absence of collisions, therefore low pressure), the spectral width $\Delta\nu$ of a rovibrational emission line is given by the **Doppler width**:

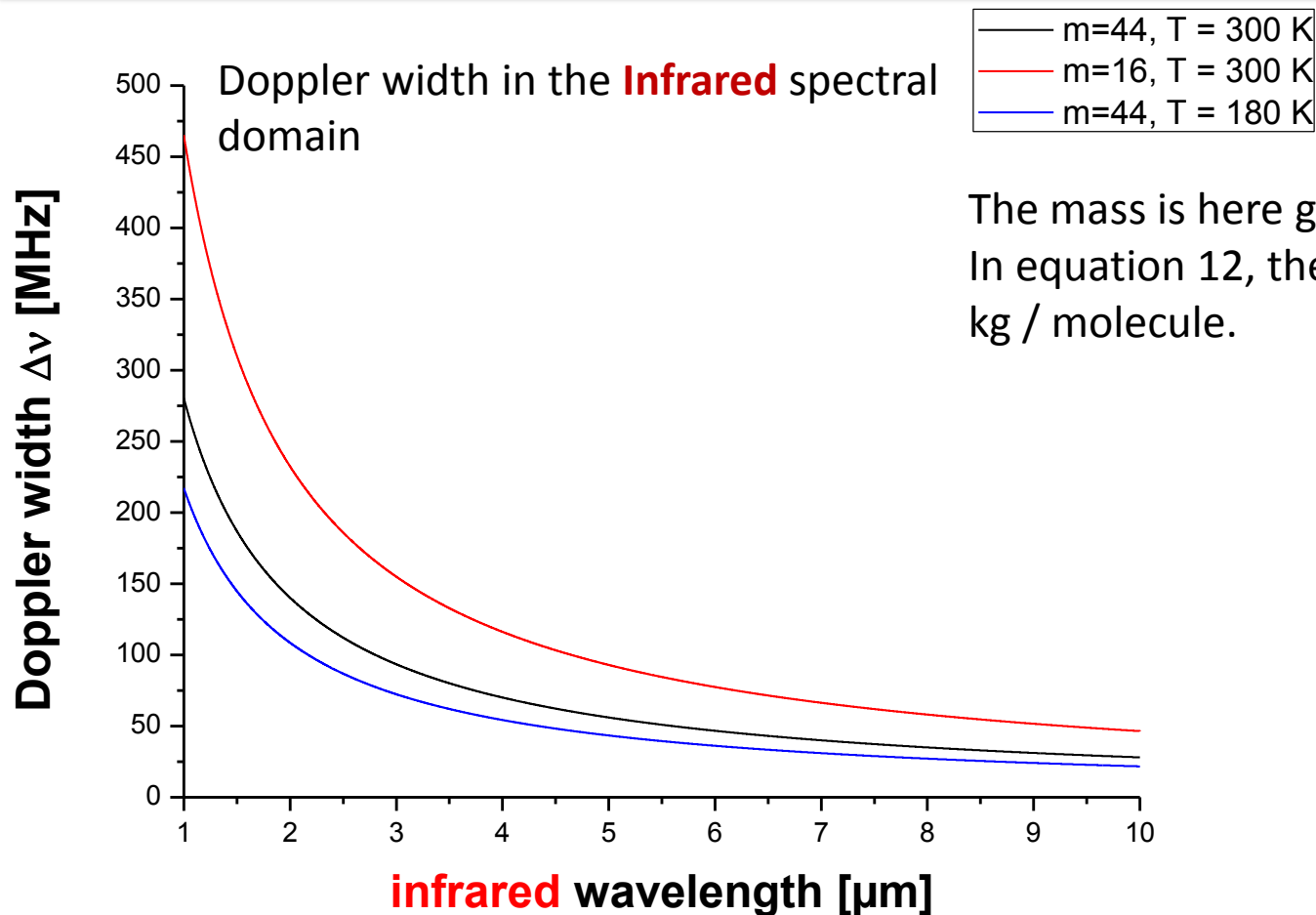
$$\Delta\nu = \frac{\nu}{c} \sqrt{\frac{2 kT \ln 2}{m}}$$

eq. 12

m : molecular mass (in a.m.u.); ν : frequency of the transition
 k : Boltzmann constant; c : light speed in vacuum

- ❖ The optical doppler width is linked to the random movement of molecules in a sample of diluted gas
- ❖ **the Doppler spectral profile is a Gaussian profile** (whereas if the optical transition is **lifetime limited** the spectral profile will be a **Lorentzian profile**)

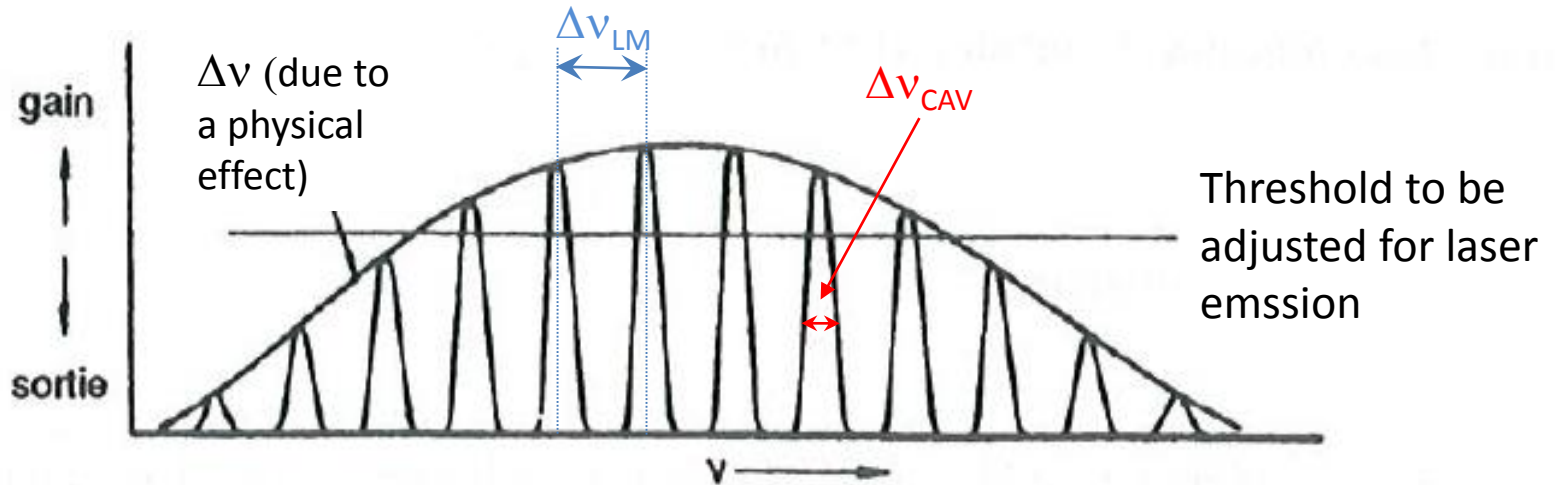
Doppler width and longitudinal modes (LM) of a laser



- Example: equation 11b gives for a cavity of length $d = 50 \text{ cm}$ a separation of the longitudinal modes of $\Delta\nu_{\text{LM}} = 300 \text{ MHz}$ (or in wave number: $\Delta\nu = 10^{-2} \text{ cm}^{-1}$ (this is small !))
- This is of the same order of magnitude than the Doppler width: as a consequence, in the IR one works with small cavities ($\Delta\nu_{\text{LM}} \uparrow$) of a few centimeters in order to have only one laser mode for the spectroscopic study of Doppler limited lines.

Spectral width of laser emission lines

- Illustration of longitudinal modes contained in an optical transition width given width due to a physical effect (for example Doppler in a diluted gas)



- ❖ Note: The LM modes have themselves Gaussian profiles ... why is that ??
- ❖ This is linked to the « **cavity finesse** » since the cavity length d possess also some uncertainty associated to the surface roughness Δd . Both mirrors of the cavity must therefore be well polished ... Δd should be a small fraction of the emission wavelength.
- ❖ We can thus define the cavity finesse as:

$$\Delta\nu_{\text{CAV}} = c / 2 \Delta d$$

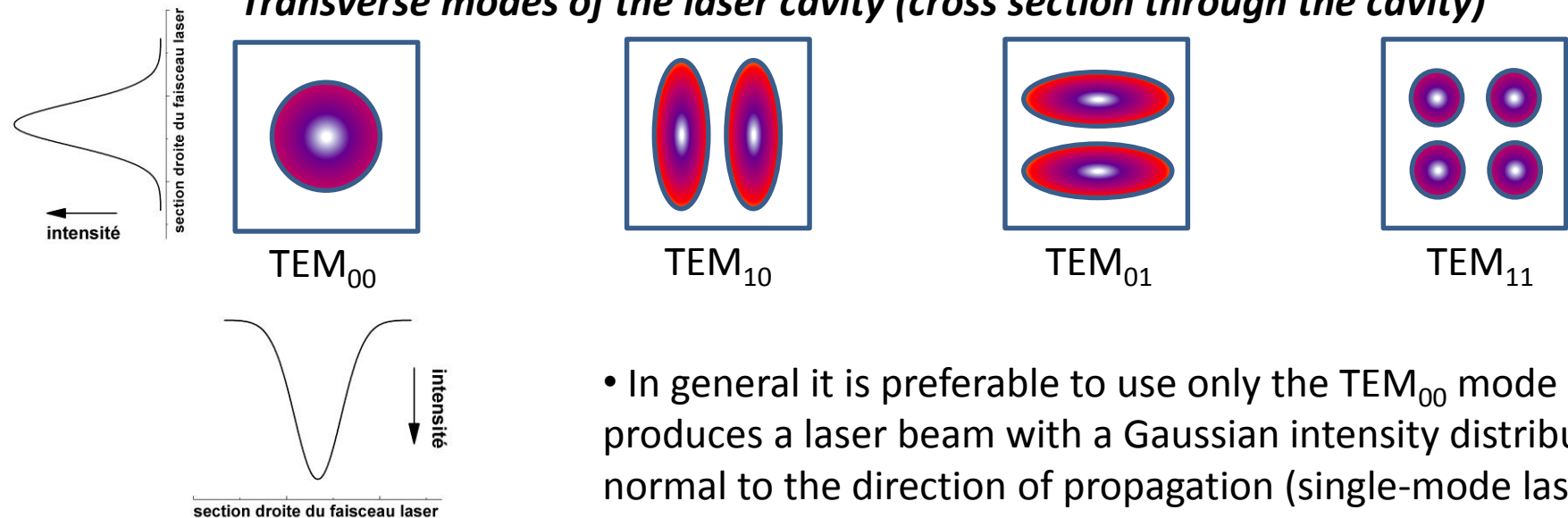
eq. 11c

- Generally, a laser operates in a **multi-mode** way. But for many applications (high resolution spectroscopy, but not only) it is preferable to have a **single (LM) mode laser**.
- We have seen that in order to obtain a single-mode laser, it can be sufficient to reduce the length of the cavity so that only one axial mode is in the spectral width of the transition used in the laser. ($\Delta\nu = c / 2d$) The frequency separation of the modes increases as d decreases.
- **"Mode-hopping" can be a problem:** Single-mode laser diodes can, while a measurement is being made, change from one mode to the next mode and therefore the emission wavelength is changing. This obviously distorts the measurement... In a diode laser, mode hopping may be related to poor temperature and current regulation of the diode.

Transversal modes of lasers

- The laser **cavity** can **resonate in various ways** during the laser process. It can be considered as a box of square section and has modes of oscillations.
- There are two types of modes: the longitudinal modes (or axial, along the direction of propagation of the laser) and the **transversal modes** which are **normal to the direction of radiation propagation**).
- The transverse modes are noted $TEM_{m,l}$. (TEM = transversal electrical and magnetic). **m and l are integers** which correspond to the numbers of **nodal planes of the oscillation, respectively vertical and horizontal**.

Transverse modes of the laser cavity (cross section through the cavity)



- In general it is preferable to use only the TEM_{00} mode which produces a laser beam with a Gaussian intensity distribution normal to the direction of propagation (single-mode laser)

- Optical cavities, like those used in lasers, are used intensively today for **intra-cavity spectroscopy**
- General aim: to **enhance significantly the optical path length** from a base length of, for example 30 cm to **a few km**.
- **Everything depicted above also applies to high finesse optical cavities used for absorption spectroscopy** (i.e. the cavity is itself an absorption cell)
- To tackle the problem of **mode hopping** (important for high resolution spectroscopy and many other applications...) the cavity must be stabilized. For this purpose numerous techniques exist.

The four remarkable properties of laser radiation

- 1. Directionality.** The laser beam that emerges from the cavity exit mirror is highly parallel, which is **a consequence of the strict alignment conditions of the mirrors of the cavity**. The divergence of the beam is very small (but strongly depends on the type of laser...). In a gas laser, it is typically a few milli-radians.
- 2. Monochromatism.** The "degree of monochromaticity" is in principle determined by the spectral width of the optical transition of the physicochemical system used in the active medium (gas, liquid, solid.....) but not only. As we have seen, the ultimate finesse of laser emission is determined by the quality of the cavity $\Delta\nu_{CAV} = n c / 2 \Delta d$ governed by the precise alignment of the mirrors (and eventually other optical elements) and the quality of the mirrors.

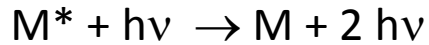
The four remarkable properties of laser radiation

- 3. Brightness (or brilliance).** It is defined as the **power** emitted
1. per unit area of the source (the part of the output mirror that actually emits)
 2. per unit of solid angle (the divergence) and
 3. per wavelength interval .

The unit of brightness is therefore $[\text{W}\cdot\text{cm}^{-2}\cdot\text{sr}^{-1}\cdot\text{nm}^{-1}]$.

The brightness is extremely high compared to conventional light sources. The main reason for this is the solid angle of emission that is very small compared to conventional sources. **The brightness is in this sense a consequence of the directionality**, but also the very high number of photons coming out of the cavity. Brightness, and not power alone, is a relevant quantity for many applications.

- 4. Phase Coherence.** Conventional sources of light are incoherent: it means that the electromagnetic waves associated with two photons of the same wavelength are (in general) not in phase. The phase coherence of laser persists for a relatively long time and extends over a relatively large distance (depending on the laser type).



eq. 10

Stimulated emission

- This equation gives the impression that a photon is created “ex nihilo” because it does not include the pumping process. In reality, it is necessary to provide a lot of energy in order to create more molecules of M in its excited state than in the ground state in a given sample.
- The efficiency of the overall process is low in general, of the order of a **few%**. Only **semiconductor lasers** ("diode lasers") achieve efficiencies of the order of **30%**.
- This means that only a few percent of the electrical energy consumed is actually converted into photons. The powerful lasers used in physical chemistry studies, for example, are therefore large consumers of electrical energy in general.

Laser pumping and inversion of population

- So far we have considered a two-level system. But in reality, in such a system, the laser process does not work ... Why ? There are **two reasons**.

1) At thermal equilibrium, the population of both states is given by the law of Maxwell Boltzmann (MB):

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \times e^{-\frac{\Delta E}{kT}}$$

g: degeneracy factor of the respective energy levels

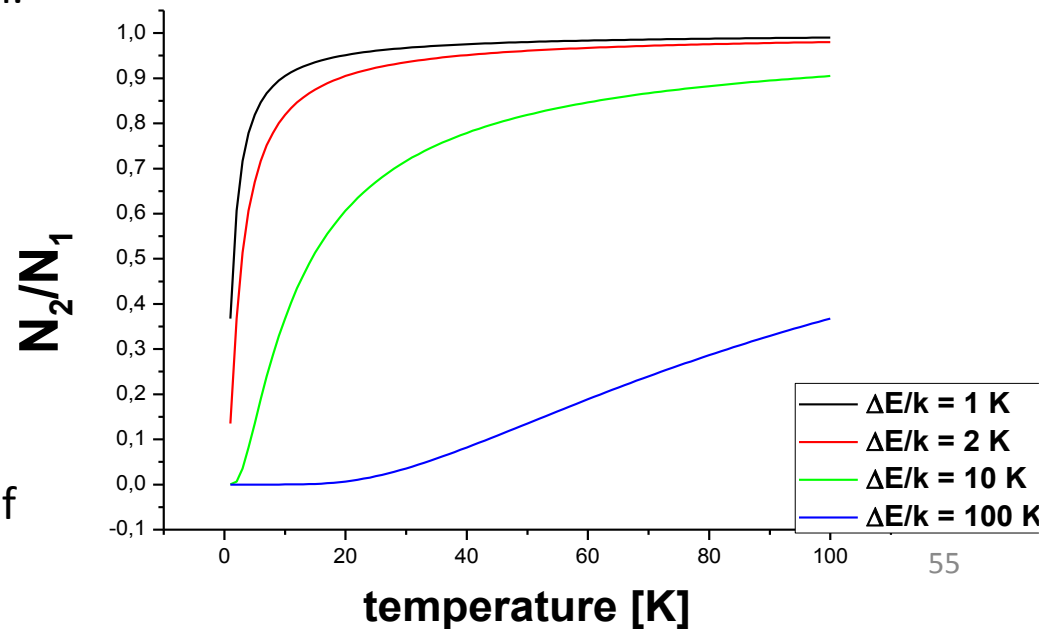
ΔE : energy difference between the two levels.

k: Boltzmann constant [J.K⁻¹]

T: absolute temperature [K]

Figure: Relative population between the two states according to the law of Maxwell Boltzmann (MB):

- If ΔE is of the vibrational or electronic type, the population in the excited this level is extremely low at room temperature.
- The equation shows that "thermal pumping" is not enough to achieve population inversion in a 2-level system.



2) There is **another physical effect that prevents population inversion**: it is related to the probability of stimulated emission and absorption expressed by the respective **Einstein coefficients B_{21} and B_{12} which are equal** for given transition. This in principle, the two processes occurs with **the same probability** when the same photon $\Delta E = h\nu$ than is emitted is used for optical pumping.

- A population inversion can thus not be physically achieved in a two-level system.
- Fortunately, in reality, there are much more than two levels in atoms and molecules ...

- To achieve a population inversion we need a multi-level system:

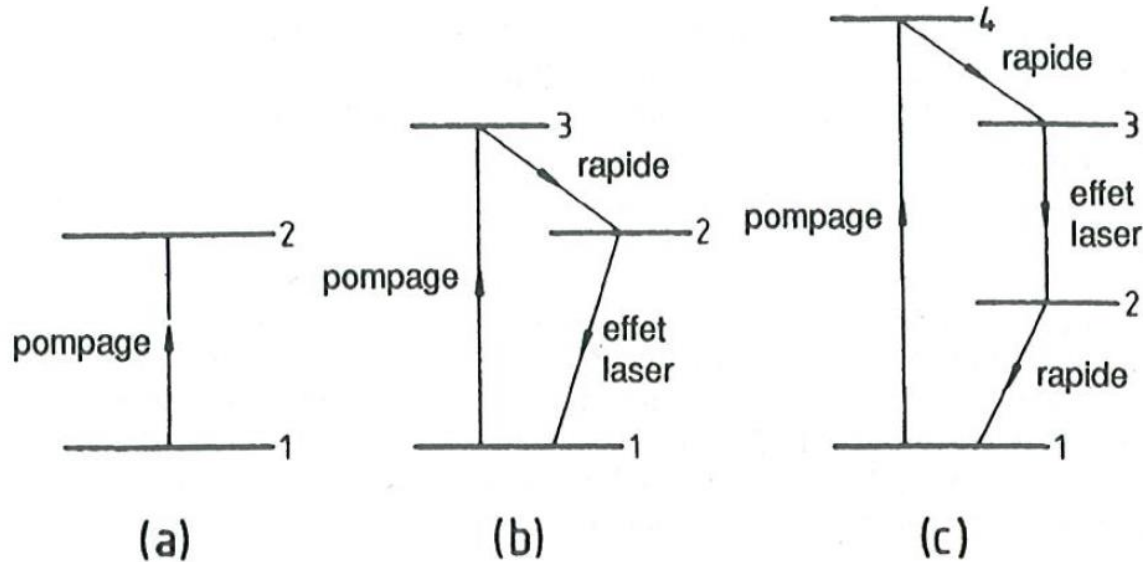


Fig. 9.2 — Systèmes laser à (a) deux, (b) trois et (c) quatre niveaux.

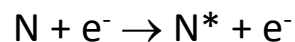
- Population inversion is difficult not only **difficult to obtain but also difficult to maintain**. For many laser systems there is no pumping method that can **maintain a population inversion in a continuously**. In this case, the inversion can be realized by a pump source that delivers pulses of very short duration (for ex. nanoseconds) and high energy which leads *in fine* to a pulsed laser.
- There are therefore **two types of lasers: pulsed & continuous wave** (the latter are called "cw" lasers).

- There are two pumping methods : **optical** and **electrical**.
- Optical pumping** involves a transfer of energy from a high intensity light source to the active medium. It **is mainly used for solid and liquid lasers**. For example, rare gas flash lamps can be used. Organic dye lasers are often pumped by another laser.
 - The repetition rate of the laser ("rep rate") and the pulse duration are usually the same as those of the pump source.
- Electrical pumping** is mainly used for **gas lasers and semiconductor lasers**. In a gas laser, an electric discharge is realized in the active medium where using high voltage electrodes supplied by a so called "Thyratron" (a high voltage condensator).
 - Free electrons are produced in the discharge** which with the gaseous molecules (or atoms) promoting them to their excited state . This is the pumping process.
 - In a gas laser, often **several gases are mixed** in addition to the gas M being the molecule that actually "lases". Another gas X can be excited by electrons to X* and subsequently transfer its energy to M, by collision.

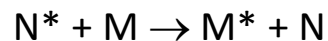
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Electrical pumping (simplified):

1 Electronic excitation



2 Collisional energy transfer



3 Laser emission :

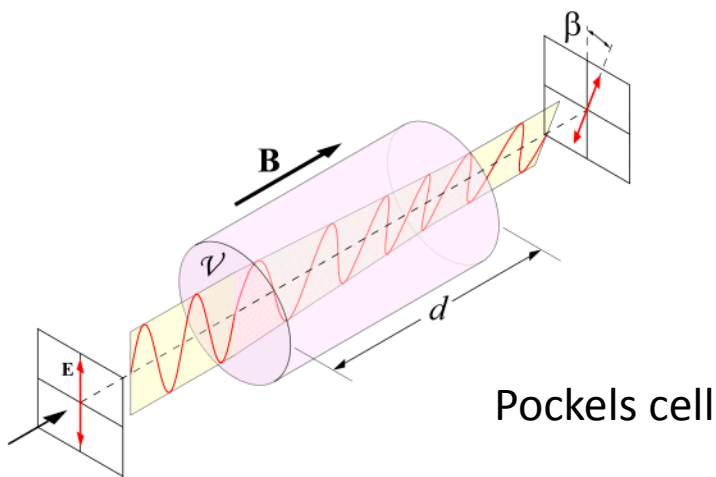


Ideally, the **N* state should be long-lived** in order to allow the collision (before its radiative decay or dissociation).

- **Remote sensing : LIDAR** (« light detection and ranging), **analysis of back-scattered light, pulsed or chopped laser**
 - Aerosol LIDAR (multi-spectral)
 - LIDAR for molecular absorption (« λ_{off} and λ_{on} »)
- **In-situ observations in the Earth Atmosphere (ground, research plane)**
 - Small radicals by Laser induced fluorescence (LiF)
 - Lasers in combination with **High finesse optical cavities**
 - ❖ Cavity ring down spectroscopy (CRDS)
 - ❖ Cavity Enhanced Absorption Spectroscopy (CEAS), with lasers or incoherent radiation)
- **Lab studies of molecular physical chemistry** (including molecules of atmospheric interest...)
 - Pulsed lasers are used to study all kind of phenomena as a function of time...
 - ❖ Gas kinetics (μs , ms or more), in **flow tubes or atm. process chambers**
 - ❖ Elementary photoreactions (ns)
 - ❖ **Intra-molecular dynamics** : Tautomerisation, isomerisation (moving of atoms in a molecule ns); Folding of proteins (ns-ps) (molecular biology); transfer of electrons after photoexcitation (ns-ps). (photosynthesis!); redistribution of energy among the vibrational modes of a molecule after excitation, observation of vibrations in the molecule (ps-fs)
- **As typical gas laser pulse is of ns duration.** For even shorter pulses (ps , fs), intra-cavity techniques are used, for example "**Q-switching**" or "**mode locking**".

Production of very short pulses using intra-cavity techniques

- **Q-switching (makes ns pulses from YAG lasers for example)**
 - Technique that can trigger (and therefore pulse) a laser beam.
Q denotes the quality of the laser cavity $Q = \nu / \Delta\nu$
 - The technique consists in **placing an element in the cavity which reduces the quality Q** during a time Δt . Different optical elements can be used
 - **Mirror or rotating prism**, wheel with holes ("chopper wheel"). The radiation is prevented from being reflected by the two mirrors during Δt and thus the **population of the high level of the laser transition increases**. At the end of Δt , an intense laser pulse of very short duration is emitted.
 - **Electro-optic material** with fast electronics (a Pockels cell changes the polarization plane, for example). Has the same effect than rotating mirrors but faster → allows to obtain pulses of ns duration .



■ Mode locking (ps, fs pulses).

- This **technique is applicable only in multi-mode operation of a laser** and involves many longitudinal modes of the cavity, but with a particular condition on the amplitude and the phase (Normally, amplitudes and phases of the laser modes are random).
- The radiation in the cavity is modulated by a frequency $f = c / 2d$ by an **acousto-optic modulator (AOM)** (d : length of the cavity). f : frequency of the cavity for $n = 1$. It follows that only the modes with nodes near the ends of the cavity leave the laser

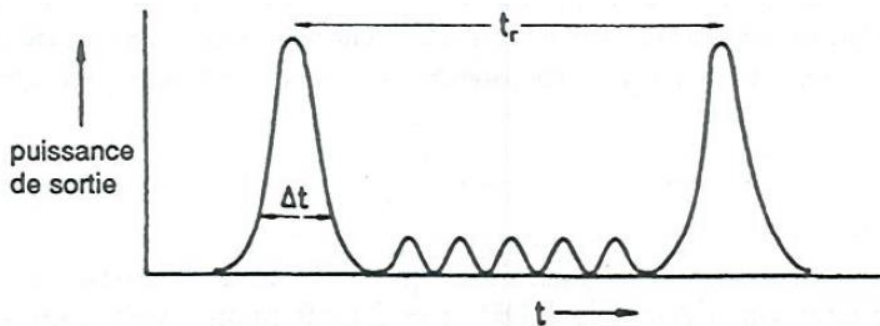


Fig. 9.5 — *Suppression, par blocage de modes, de cinq des sept modes axiaux de la cavité.*

An **acousto-optic modulator (AOM)**, also called a **Bragg cell**, uses the **acousto-optic effect** to diffract and shift the frequency of light using sound waves (usually at radio-frequency).

Faster than tiltable mirrors and more practical than pockels cells.

- Today, few scientists will build their laser themselves, unless the developers... (but the situation was different only 20 years ago)
- On the other hand, understanding the inside of a laser is absolutely necessary for its use in order:
 - to apprehend his performances,
 - to know what we can be done and what not (better than trial and error...),
 - to understand what arises from artifact and what is a real property of the physicochemical system under study,
 - to be able to align it,
 - to understand the health and safety problems related to the use of lasers (not treated in this lecture)
 - especially those related to intense radiation (but also high voltage and corrosive gases for excimer lasers).
 - each laser type presents particular dangers (most dangerous intense NIR..)
- Different type of lasers :
 - Gas laser : Excimer laser, HeNe
 - Liquid laser: dyes
 - Solid laser
 - Doped crystals (for example Nd:YAG)
 - Semiconductor laser ("laser diodes")

● FIN