INSTRUMENTATION IN RAMAN SPECTROSCOPY: ELEMENTARY THEORY AND PRACTICE

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EMU-CNRS International School: Applications of Raman Spectroscopy to Earth Sciences and cultural Heritage : 14-16th of june 2012

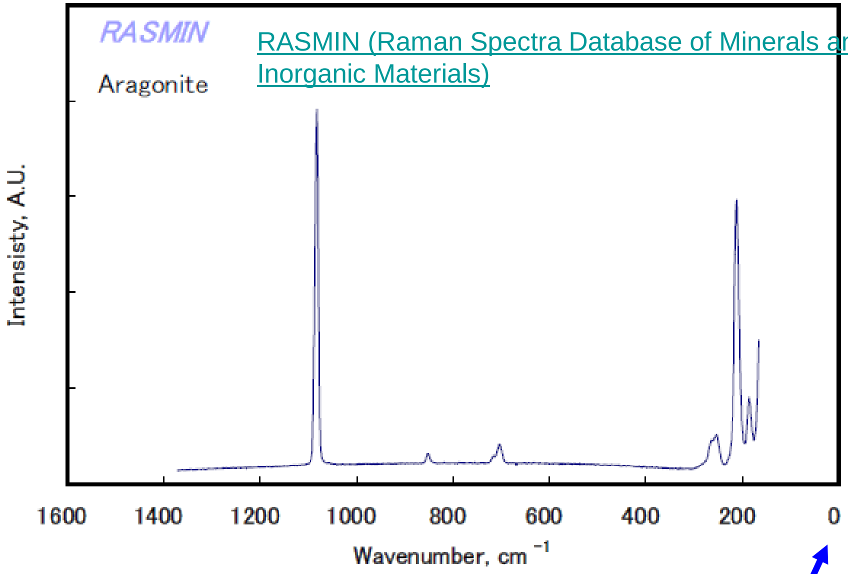
OUTLINE

- Raman instruments, elementary theory: J.Dubessy
- Calibration: M.C. Caumon
- From the laboratory to the field: F. Rull
- Coupling with other techniques: S. Sharma

Raman instruments, elementary theory

- Initially, Raman a physics curiosity: low intensity signals
- The lasers and electronic detection (PM): crystals, gases, liquid studies in physical-chemistry-crystallography laboratories
- Raman microprobes: 1975-1978: Rosasco (USGS) and Delhaye-Dhamelincourt (LASIR, Lille, France) + instrument company.
- CCD detectors in Raman microprobes + laser rejection by filters

Where is the information in a Raman spectrum ?

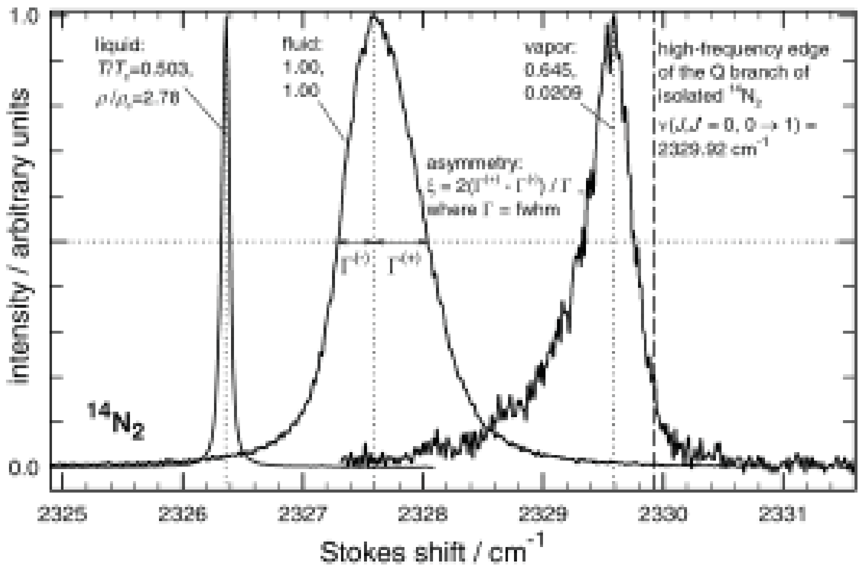


Raman line **intensities**, function of:

- Intrinsic polarisation of the line
- Polarisation conditions of the excitation and signal collection
- Concentration
- Raman scattering cross-section
- Molecular interactions….

Raman shift: in relative wavenumbers with respect to the excitation radiation

Raman line **shift, width and shape**



Musso et al. (2004) Critical line shape behavior of fluid nitrogen. Pure Applied Chem, 76, 147-155

Raman shift: in relative wavenumbers with respect to the excitation radiation

λ_0 wavelength of the excitation radiation => absolute wavenumber: $\overline{\nu_0} = 1/\lambda_0$

1 µm ⇔ 10000 cm^{-1}; 0.5 µm = 500 nm ⇔ 20000 cm^{-1}

$\overline{\nu_{R,j}}$ Raman wavenumber => absolute wavenumber for a stokes Raman line: $\overline{\nu_{R,j}^{abs}} = \overline{\nu_0} - \overline{\nu_{R,j}}$

$$\lambda_{R,j} = 1/\overline{\nu_{R,j}^{abs}} = 1/\left(\overline{\nu_0} - \overline{\nu_{R,j}}\right)$$

wavelength of the Raman line

Raman shift in wavelength: $\Delta\lambda_{R,j} = \lambda_{R,j} - \lambda_0$

Raman shift: in relative wavenumbers with respect to the excitation radiation

Stokes Raman shift (4000 cm^{-1}) in wavelength:

λ_0 (nm)	$\overline{\nu_0}$ (cm^{-1})	$\overline{\nu^{abs}_{R,j\max}}$ (cm^{-1})	$\lambda_{R,\max}$ (nm)	$\Delta\lambda_{R,\max}$ (nm)
250	40000	36000	277.7	27.7
400	25000	21000	476.2	76.2
500	20000	16000	625.0	125.0
660	15151	11151	896.7	236.7
785	12739	8739	1144.3	359.3
1064	9398	5398	1852.5	788.5

The Raman spectrum is scattered over a larger spectral interval range in wavelength for red excitations than for green or UV excitation lines

A precision of 1 cm^{-1} ⇔ to 6.3×10^{-3} nm = 6.2×10^{-2} Å for the 250 nm excitation

A precision of 1 cm^{-1} ⇔ 6.1×10^{-2} nm = 0.61 Å for the 785 nm excitation

Raman line intensities: orders of magnitude estimated by radiometric calculations

$$N_{\bar{\upsilon}_0-\bar{\upsilon}_R} = \frac{N_{\bar{\upsilon}_0}}{A}\left(\frac{d\sigma}{d\Omega}\right)(\Delta\Omega)(N_m)$$

- $N_{\bar{\upsilon}_0-\bar{\upsilon}_R}$: Number of Raman photons
- $N_{\bar{\upsilon}_0}$: Number of excitation photons
- A: Excited area of the sample
- $\frac{d\sigma}{d\Omega}$: Differential Raman scattering cross section
- $\Delta\Omega$: Solid angle of collection
- N_m: Number of molecules in the excited volume

Raman line intensities: orders of magnitude estimated by radiometric calculations

$$N_{\overline{\upsilon}_0-\overline{\upsilon}_R} = \frac{N_{\overline{\upsilon}_0}}{A}\left(\frac{d\sigma}{d\Omega}\right)(\Delta\Omega)(N_m)$$

$$N_{\overline{\nu}_0}(1s) = W_{\overline{\nu}_0} / \left[E_{1\,photon}(\lambda_0)\right] \qquad W_{\overline{\nu}_0} = 0.1\,\text{Watt} = 0.1\,\text{J.s}^{-1}$$

$$E_{1\,photon}(\lambda_0) = h(c/\lambda_0) \approx 6.62\times10^{-34}\left(3\times10^{8}/0.5\times10^{-7}\right) \approx 4\times10^{-18}\,J$$

$$N_{\overline{\nu}_0}(1s) = 4\times10^{17}\ \text{photons}$$

$$\left(\frac{d\sigma}{d\Omega}\right) \approx 10^{-35}\ \text{to}\ 10^{-33}\ \text{m}^2.\text{sr}^{-1}$$

$$\Delta\Omega = 1\,\text{sr}$$

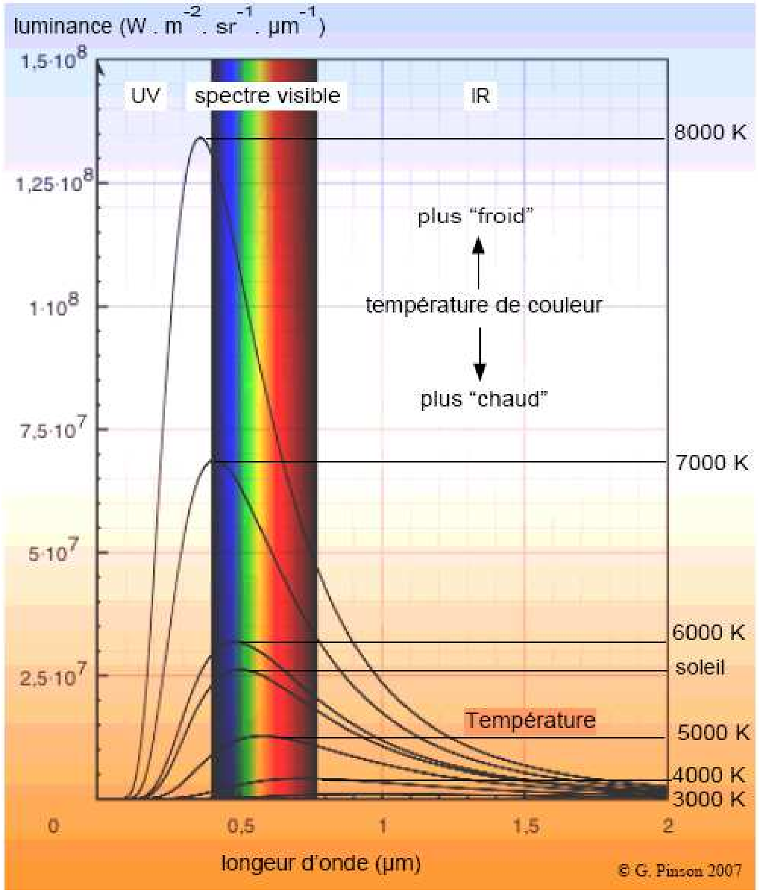
$$N_m = \rho A L \;\Rightarrow\; N_m/A = \rho L$$

$$\rho = \frac{10^3}{0.02/\left(6.02\times10^{23}\right)} \approx 3\times10^{28}\ \text{molecules.m}^{-3} \qquad L = 0.01\ \text{m}$$

$$N_{\overline{\nu}_0-\overline{\nu}_R} = 4\times10^{17}\times\left(10^{-35}\ \text{to}\ 10^{-33}\right)\times3\times10^{28}\times10^{-2} = 10^{9}\ \text{to}\ 10^{11}$$

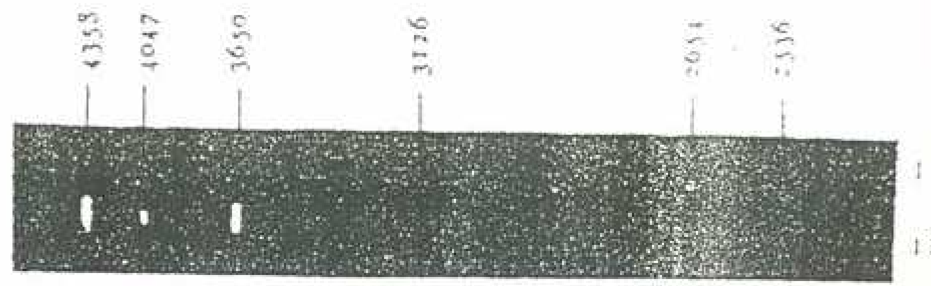
Raman line intensities: orders of magnitude estimated by radiometric calculations

Monochromatic luminance of the light of the sun at 0.5 µm wavelength with 1 cm^{-1} line width



0.02 à 2 Raman photons s^{-1} !

a narrow band photographic filter to create monochromatic light (violet), and a filter (yellow-green) to block violet monochromatic light

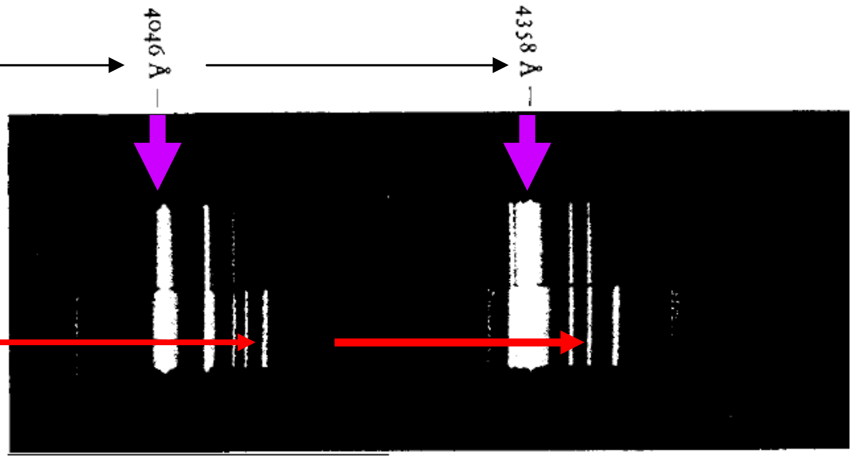


I. Das Spektrum des zerstreuten Lichtes.

First Raman experiment

Hg excitation lines

Raman lines



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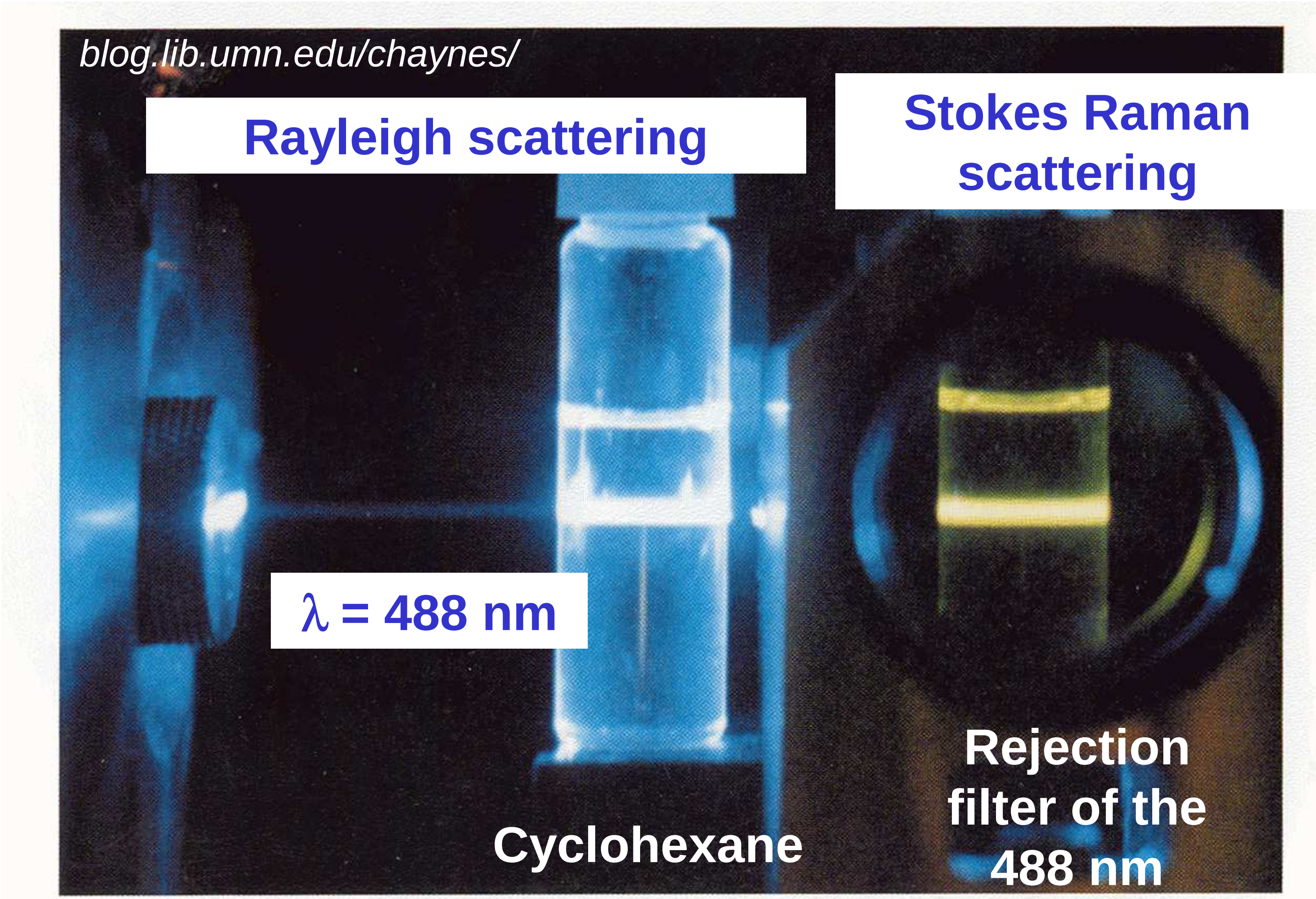
Raman experiment and eyes !



Figures of merit of a Raman spectrometer

- **excitation source: high power and stable monochromatic source**

$$N_{\overline{\nu_0}-\overline{\nu_R}} = 10^{7} \text{ to } 10^{11}$$

$$N_{\overline{\nu_0},Rayleigh} = 10^{12} \text{ to } 10^{13}$$

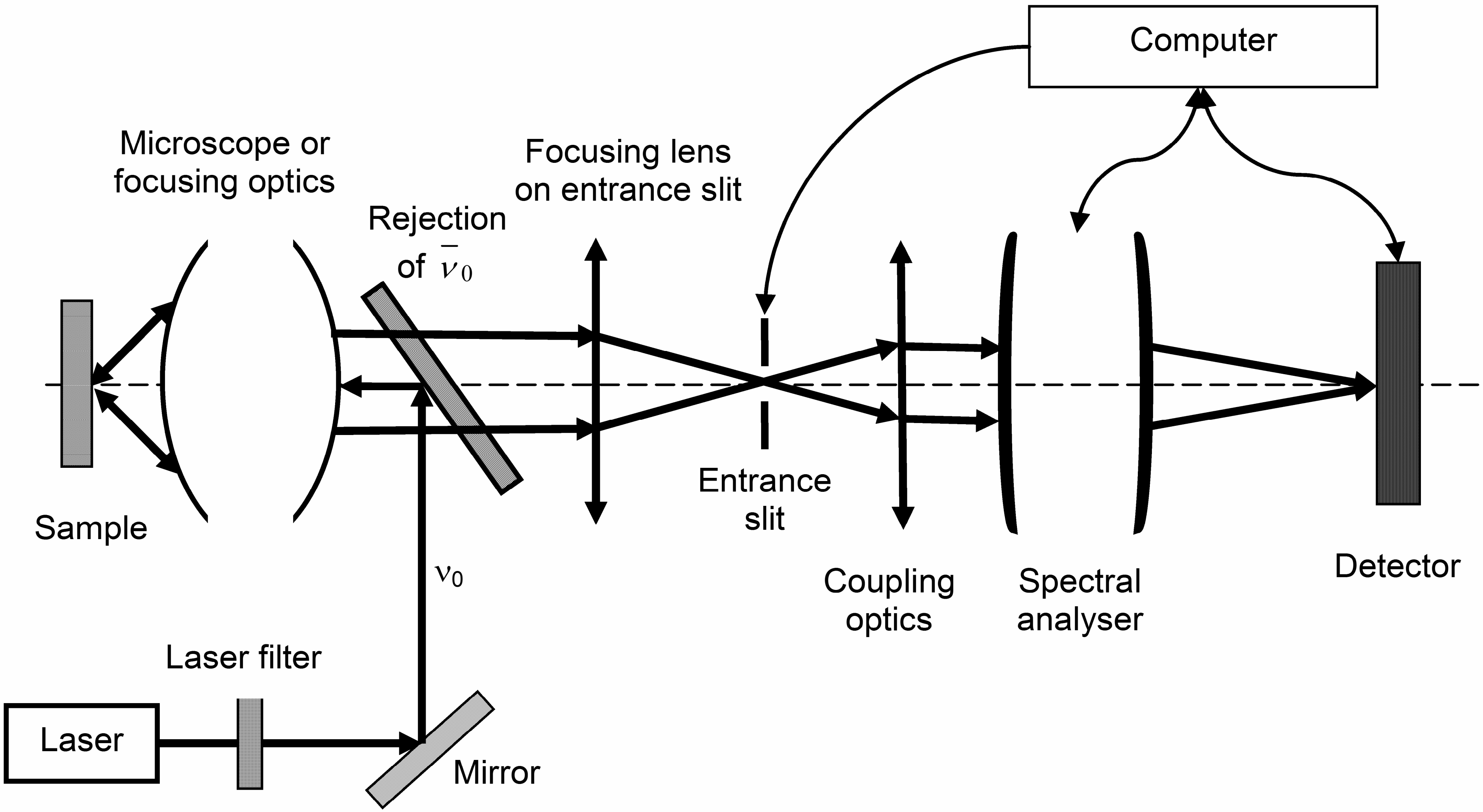
$$N_{\overline{\nu_0},reflection} = 10^{15} \text{ to } 10^{17}$$

- **high rejection of the excitation wavelength**

- **high transmission of the dispersive system and high spectral resolution**

- **high efficiency detector**

The different elements constitutive of a Raman (micro)-spectrometer



The excitation sources

1928	1960	1963	1969	2000	2005
Sun, Hg lamp	Townes suggests the use of lasers	First laser use (Porto-Weber)	Ar^+, Kr^+	Nd-Yag 532 nm	Laser diodes

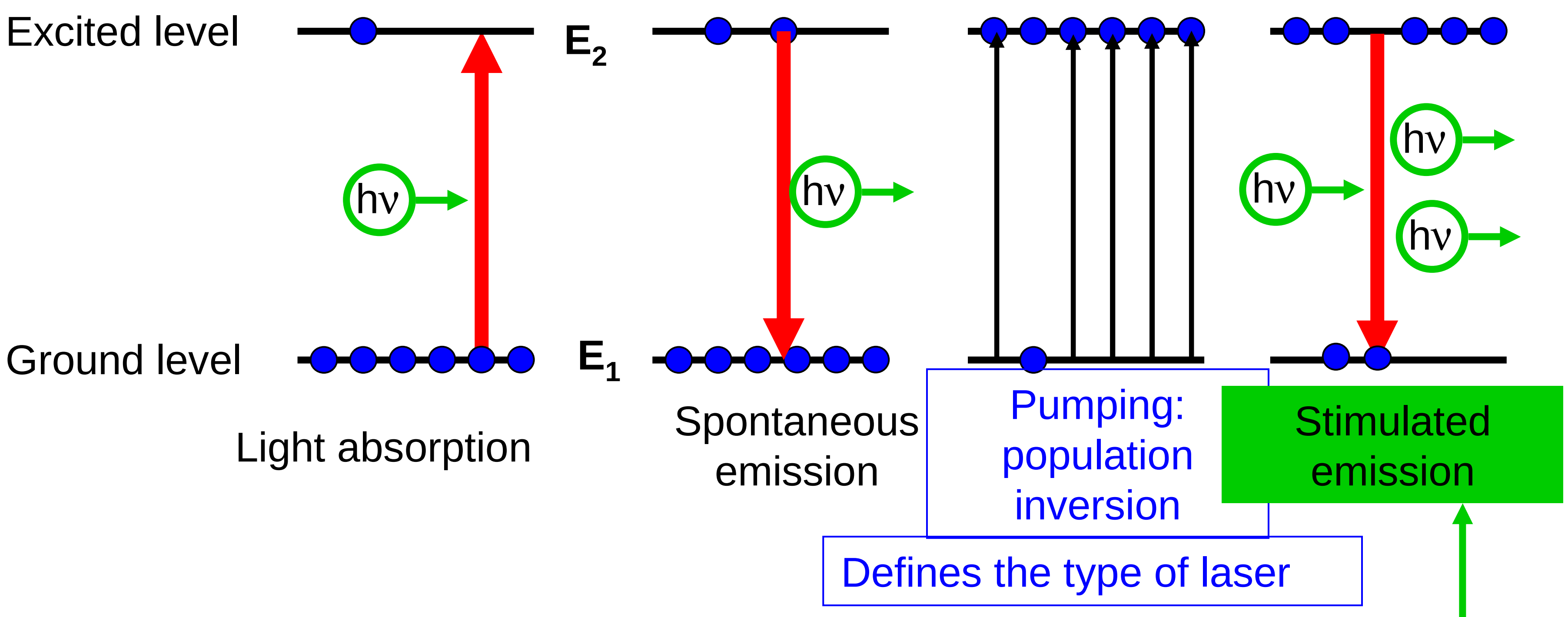
1964 (He-Ne) on Cary spectrometer

End of Ar^+ / Kr^+ lasers in 2013-2015 ?

The excitation source: lasers

Laser = Light amplification by stimulated emission of radiation: 1957-1960

Charles Hard Townes, Arthur Leonard Schawlaw (Bell labs); Gordon Gould (Columbia University); Theodore H. Maiman (Hugue Research lab)



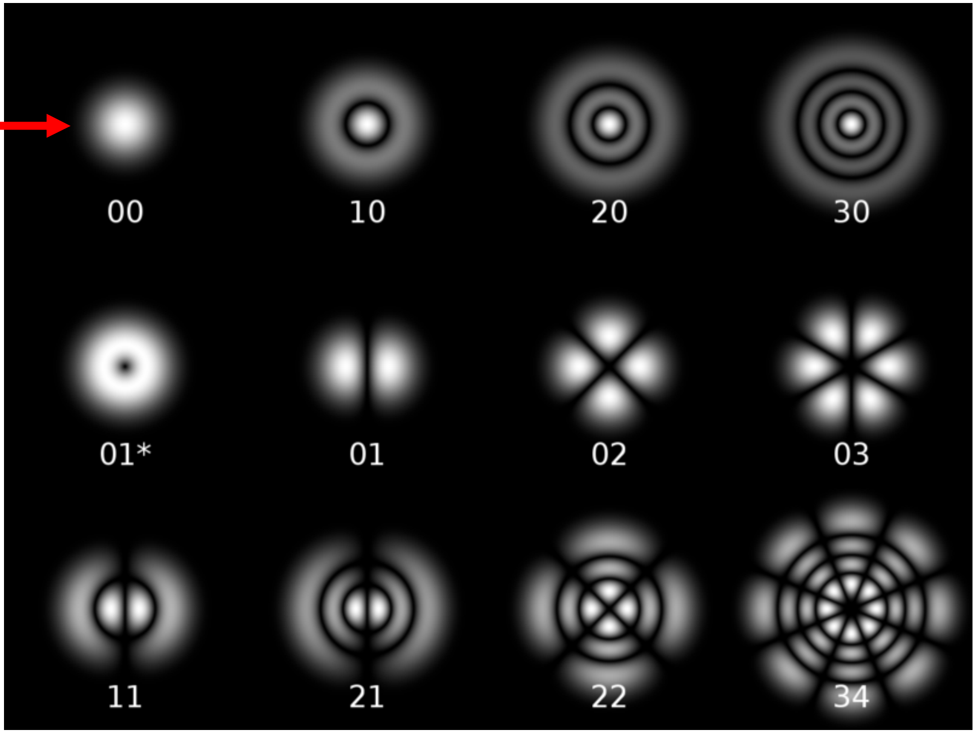
+ optical resonator to promote stimulated emission rather than spontaneous emission with two mirrors (1 highly reflective at the rear and another partially reflective near 99% at the head)

The excitation source: lasers
Transverse modes

Resonator modes can be divided into two types: longitudinal modes, which differ in frequency from each other; and transverse modes, which may differ in both frequency and the intensity pattern of the light.

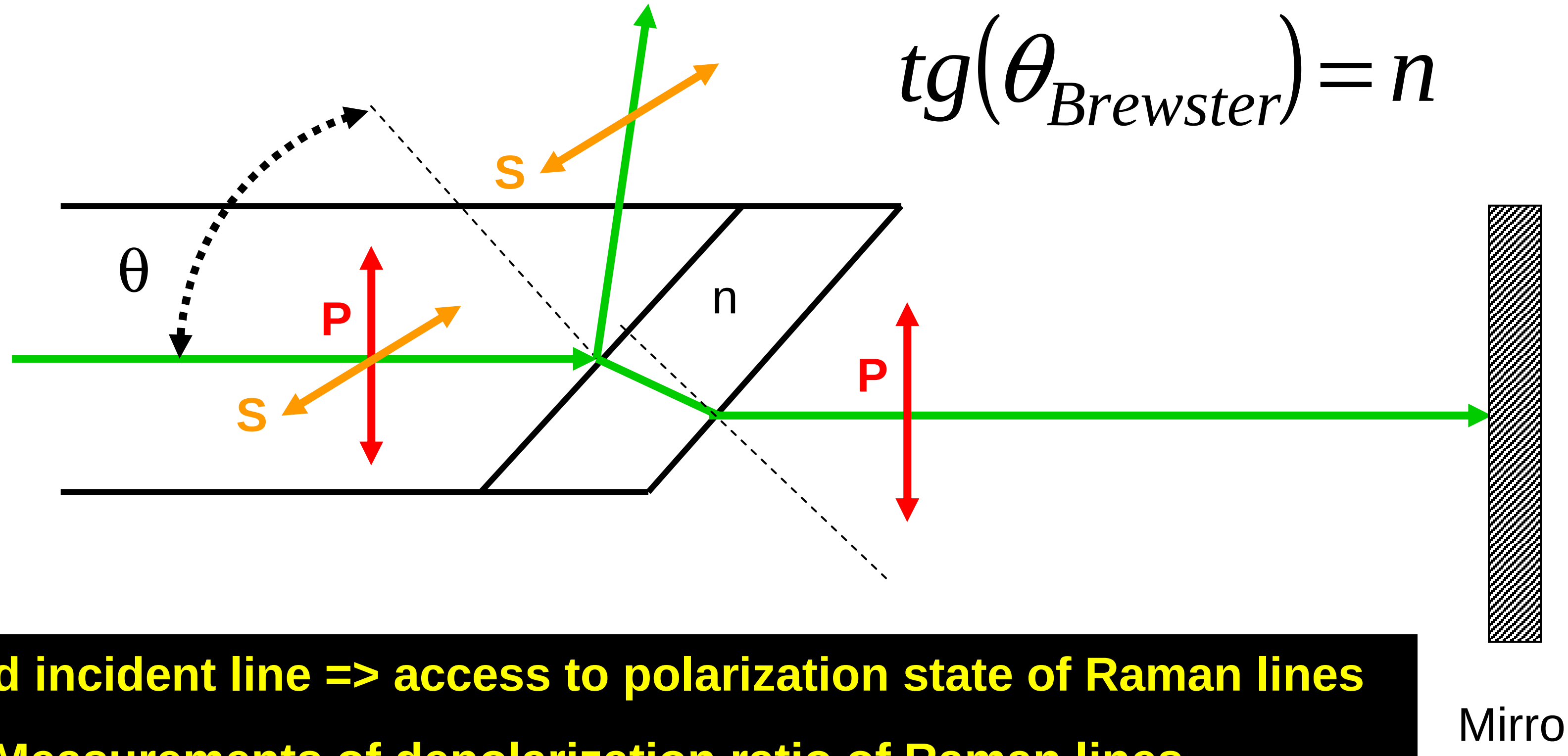
Only TEM_{00} mode is used in Raman spectroscopy and microRaman spectroscopy

Gaussian beam profile



Polarization of the laser beam

At the Brewster incidence angle, the windows transmit all light polarized parallel to the incident plane (P). Light polarized perpendicular to the incidence plane (S) is reflected out the cavity.



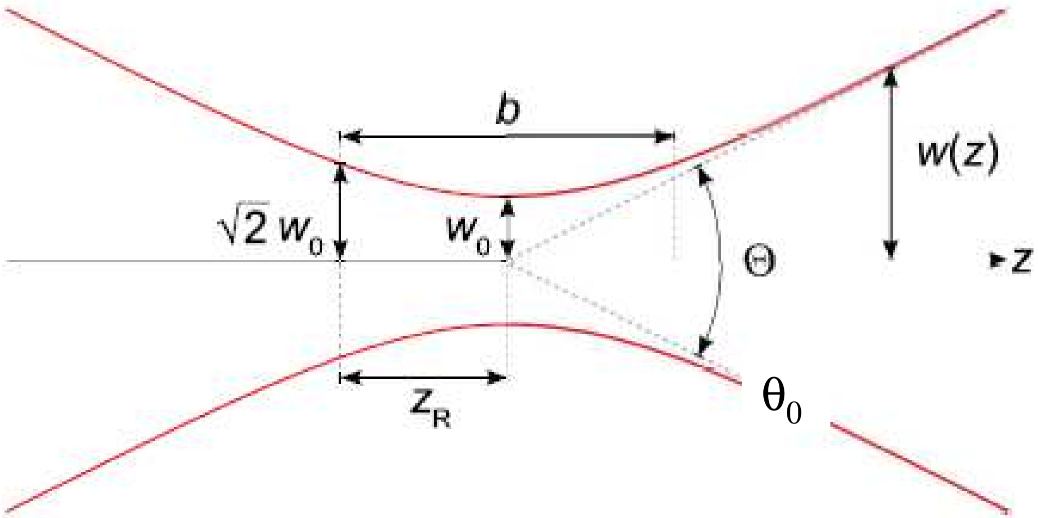
$$tg(\theta_{Brewster}) = n$$

Polarized incident line => access to polarization state of Raman lines

Measurements of depolarization ratio of Raman lines

Consequences of the light transmission of gratings

Divergence of the laser beam: Figure of Merit M^2



Perfect Hermite Gaussian laser beam

The quality factor, M^2
(called the "M-squared" factor), is defined to describe the deviation of the laser beam from a theoretical Hermite-Gaussian beam.

$$M^2 = \frac{w_{0,R} \times \theta_{0,R}}{w_0 \times \theta_0}$$

For CW lasers and helium neon lasers, $1.1<M^2<1.3$ less than 1.1;

For diode lasers $1.1<M^2<1.7$

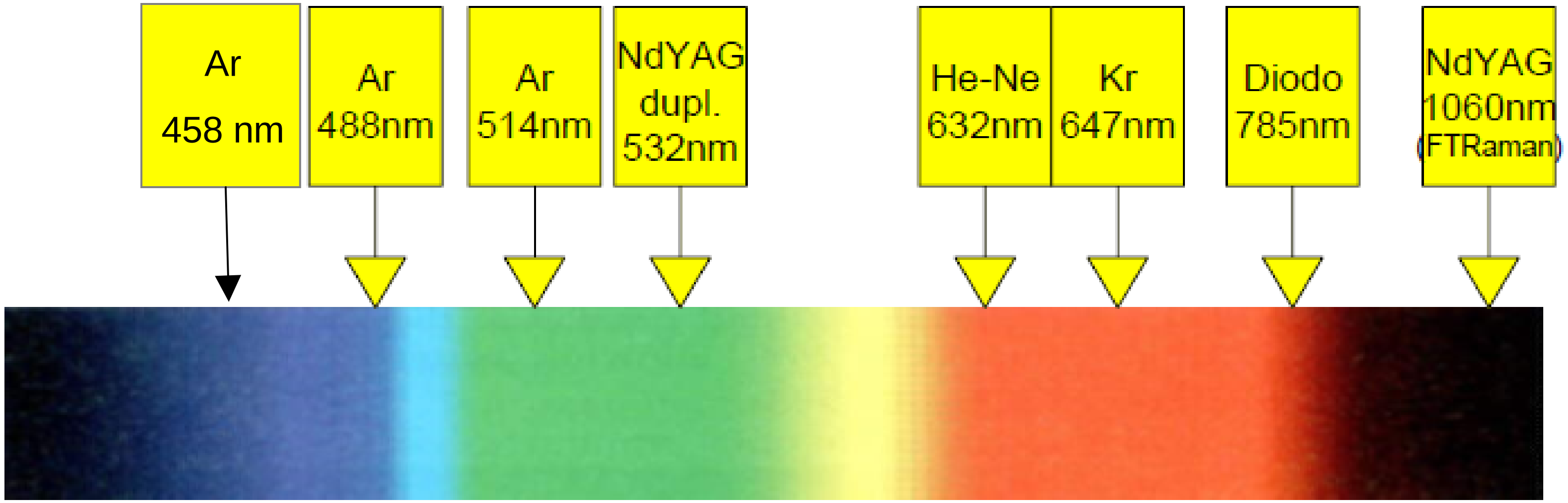
Wavelength of lasers and laser choice

Ar^+: 351.1; 364; **457.9; 488; 514.5**

$Nd\text{-}YAG^+$: 256; 365; **532; 1064;**

Kr^+: 350.7; 406.7; 413.1; 530.9; **647.1**; 676.4

Laser diodes: 405; **635; 660; 785**



The choice of the excitation source

- luminescence of the usual samples;
- Consequences on optics, gratings, detector

Rejection of λ_0

- **either by a double or triple spectrometer**

- **either by a rejection filter with DO = 6**

$$\log\left(\frac{I_{transmitted}}{I_{0,incident}}\right) = -DO = -6$$

- **super-Notch filter: well centred on λ_0 30 cm^{-1}**

- **edge filter: high band pass filters.**

Rejection of λ_0 and Raman lines separation

1785 **1928** **1953** **1972**

Gratings Hairs !

prisms

ruled precision gratings

holographic gratings

Diffraction based

Refraction based:

$n = f(\lambda)$

Cary: double additive Czerny-Turner spectrometer

GRATINGS to separate the different radiations

• Gratings work either in transmission or in reflection

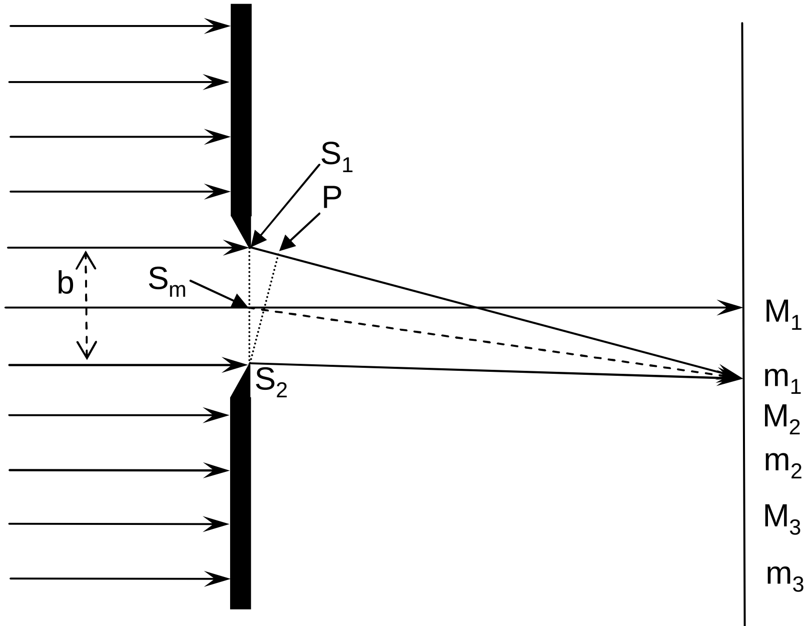
• Transmission gratings are made of parallel elongated domains which transmit the light and opaque domains: thus they can be considered as arrangement of parallel slits corresponding to the transmission zones

• Reflection gratings are an assembly of elongated mirrors acting as slits; the grooves are the opaque parts.

PHYSICS MODELS: ARRANGEMENT OF MANY PARALLEL EQUIDISTANT SLITS WITH THE SAME WIDTH

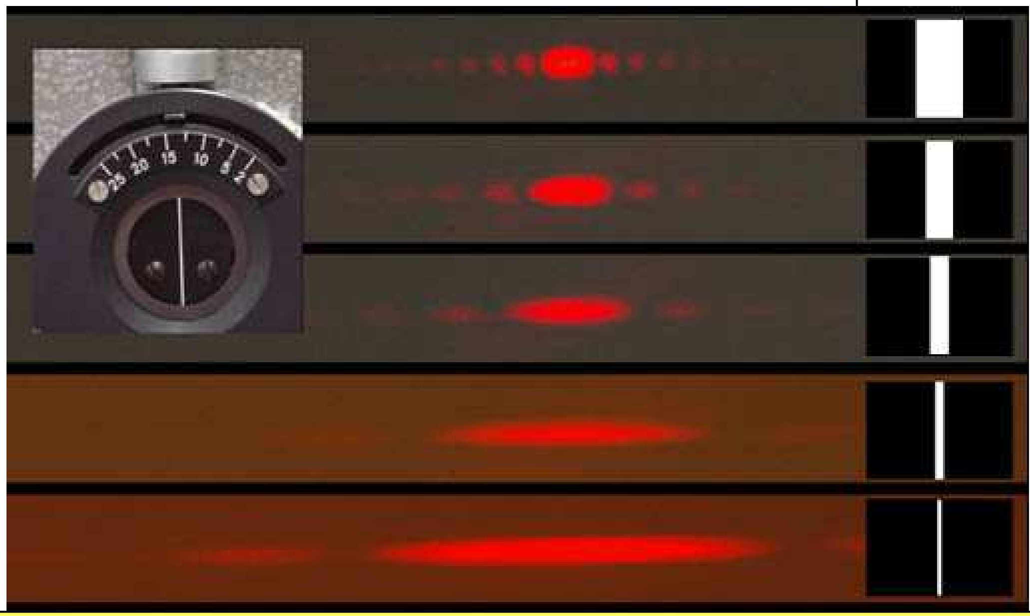
1 SLIT - 2 SLITS – N SLITS

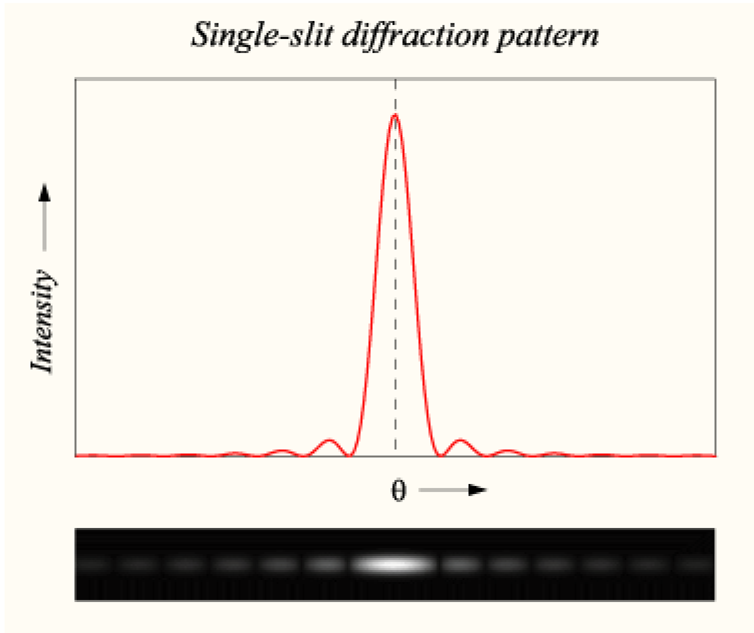
GRATING THEORY: 1 single slit: Fraunhoffer slit



$$I = I_0 \times \left(\frac{\sin \beta}{\beta} \right)^2$$

$$\beta = \frac{\pi \times b \times \sin \theta}{\lambda}$$

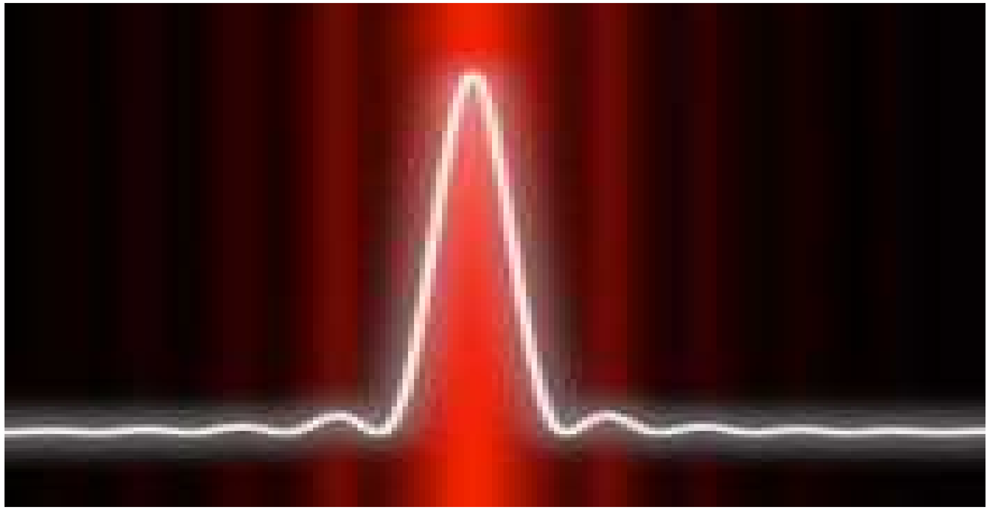




GRATING THEORY: 1 single slit

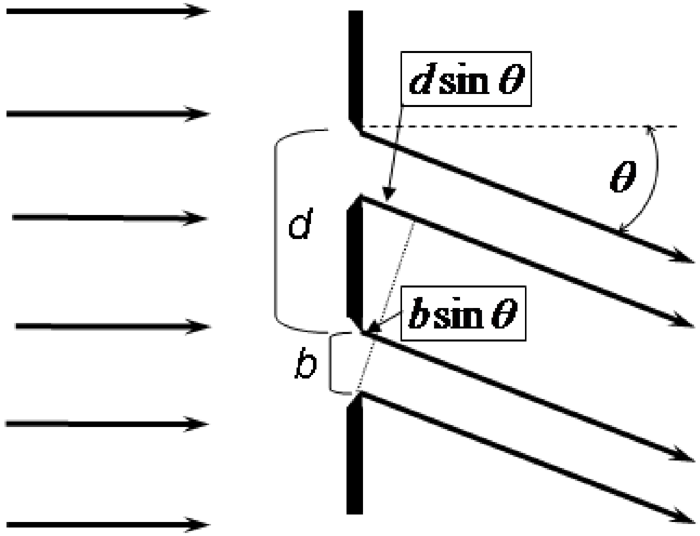
$$I = I_0 \times \left(\frac{\sin \beta}{\beta} \right)^2$$

$$\beta = \frac{\pi \times b \times \sin \theta}{\lambda}$$



- Symmetric distribution of maxima and minima
- Secondary maxima for $\beta = (2k+1)\frac{\pi}{2} = \frac{\pi b \sin \theta}{\lambda} \Rightarrow \sin \theta_{max} = \frac{(2k+1)\lambda}{2b}$
- Secondary minima for $\beta = (2k+1)\pi = \frac{\pi b \sin \theta}{\lambda} \Rightarrow \sin \theta_{min} = \frac{(2k+1)\lambda}{b}$
- Width of central max ≈ 2 (λ/b) θ→ 0 if b is large with respect to λ: point source
- if (λ/b) ≈1, then at k=0, $\theta_{min} \approx \pi/2$ => large central maxima

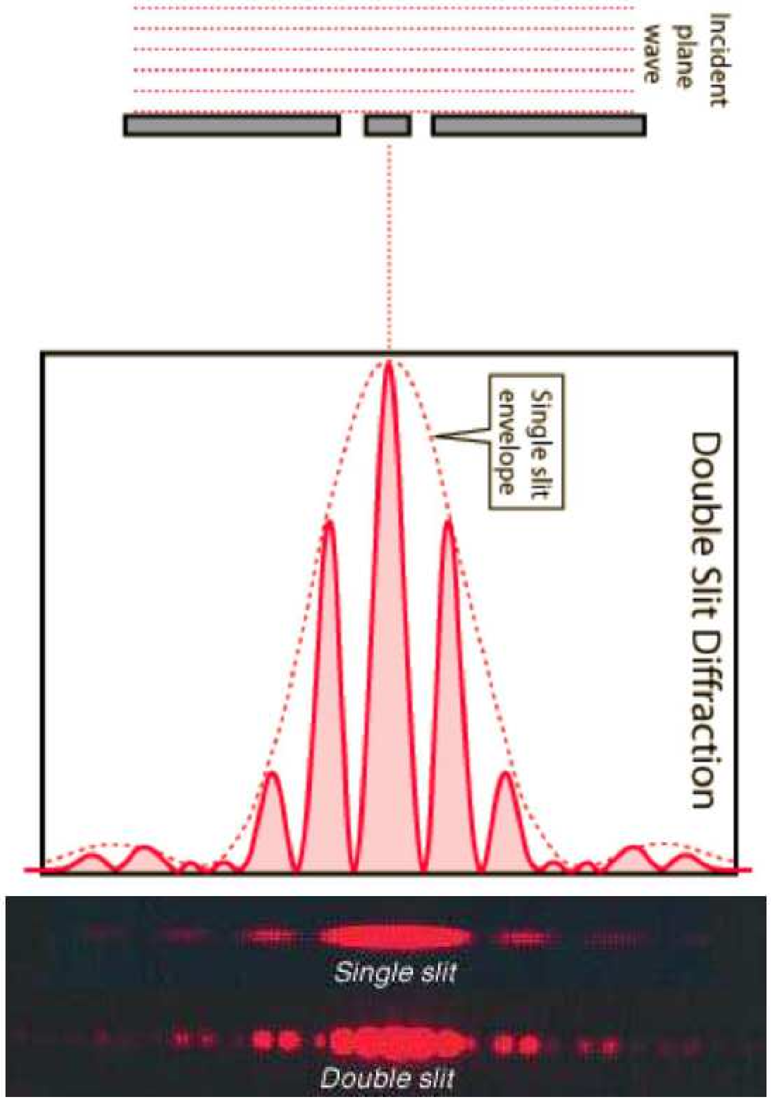
GRATING THEORY: 2 single slits



Single slit term enveloppe

$$I = 2I_0 \times \left(\frac{\sin^2\beta}{\beta^2}\right) \times \cos^2\gamma$$

$$\gamma = (\pi/\lambda) d \sin\theta$$



GRATING THEORY: 2 single slits

$$\beta = \frac{\pi b \sin\theta}{\lambda}$$

Single slit term enveloppe

Represents the interferences resulting from two beams of equal intensity

$$I = 2I_0 \times \left(\frac{\sin^2\beta}{\beta^2}\right) \times \cos^2\gamma$$

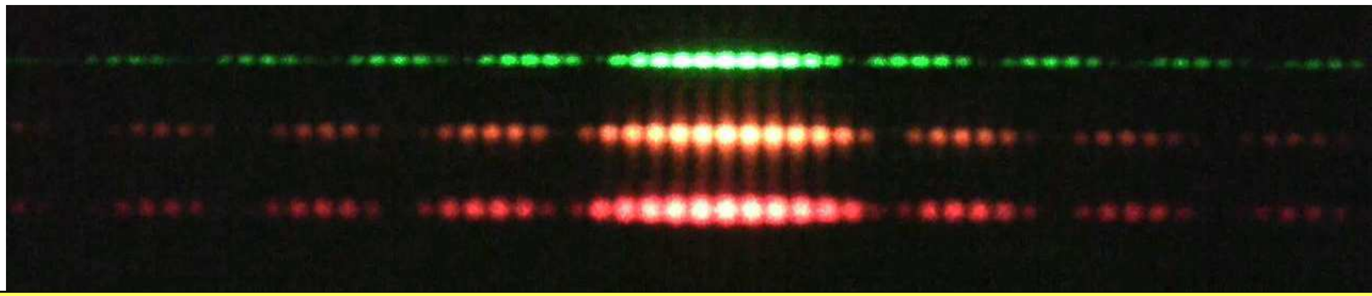
$$\gamma = (\pi/\lambda) d \sin\theta$$

When the slits are narrow, the positions of the maxima are determined mainly by $\cos^2\gamma$

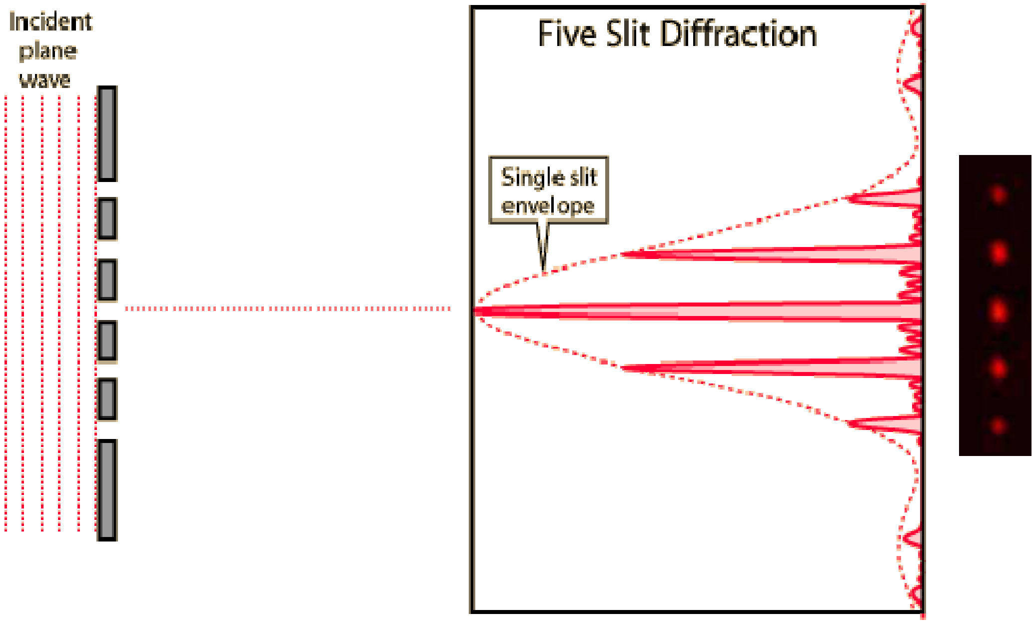
Maxima occur for $\cos^2\gamma = 1$

$$\gamma = (\pi/\lambda) d \sin\theta = 0, \pi, 2\pi, 3\pi, \ldots$$

$$d \sin\theta = 0, \lambda, 2\lambda, 3\lambda, \ldots m\lambda$$



GRATING THEORY: N single slits



$$\beta = \frac{\pi b \sin\theta}{\lambda}$$

Single slit term enveloppe

Represents the interferences resulting from N beams of equal intensity arising from N slits

$$I = 2I_0 \times \left(\frac{\sin^2\beta}{\beta^2}\right) \times \frac{(\sin N\gamma)^2}{(\sin\gamma)^2}$$

$$\gamma = \frac{\pi \times d \times \sin\theta}{\lambda}$$

GRATING THEORY: N single slits

$$I = 2I_0 \times \left(\frac{\sin^2 \beta}{\beta^2} \right) \times \frac{(\sin N\gamma)^2}{(\sin \gamma)^2}$$

$$\gamma = \frac{\pi \times d \times \sin \theta}{\lambda}$$

$$\frac{(\sin N\gamma)}{(N \sin \gamma)} \rightarrow \pm 1 \text{ when } \gamma \rightarrow m\pi$$

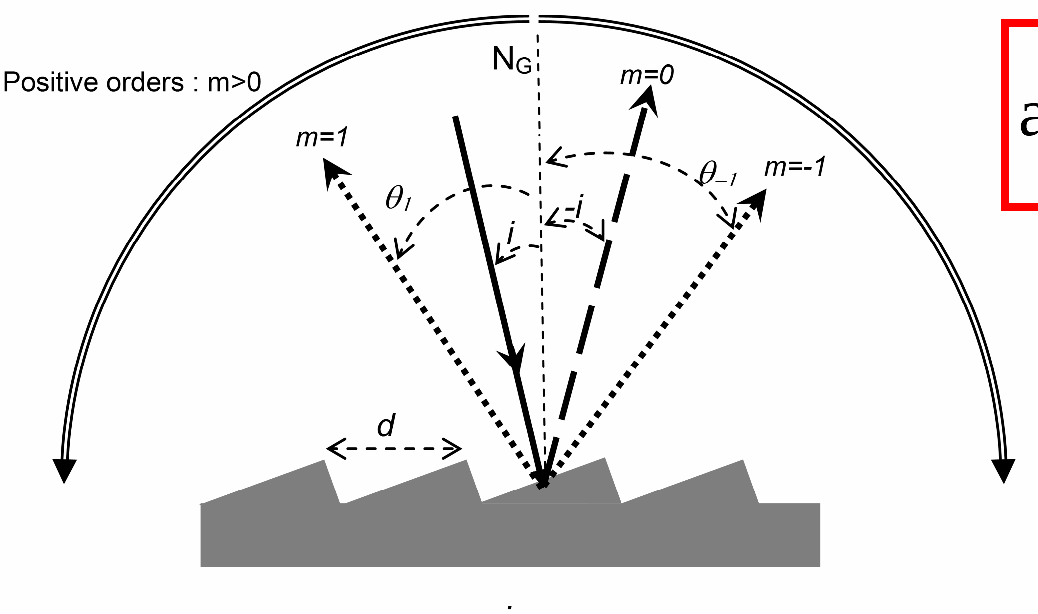
Maximum value

$$d \times \sin \theta = m \times \lambda = 0, \lambda, 2\lambda, 3\lambda, \ldots m\lambda$$

GRATING THEORY: grating equation

$$d \times (\sin i + \sin \theta) = m \times \lambda = 0, \lambda, 2\lambda, 3\lambda, \ldots m\lambda$$

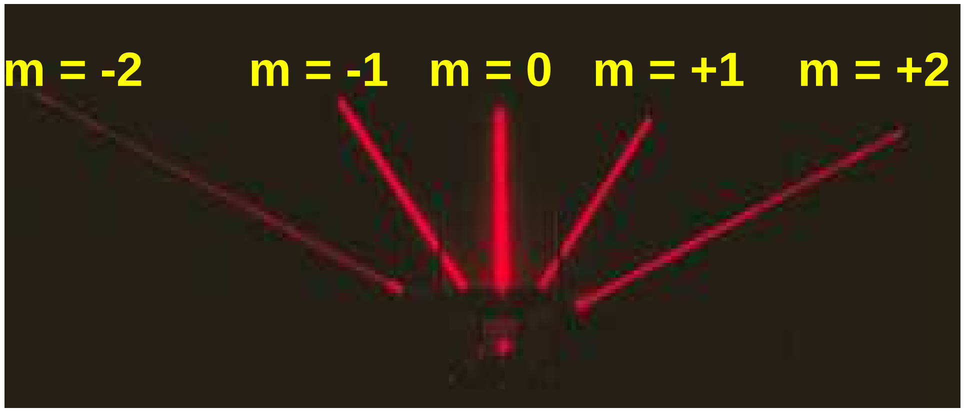
m : diffraction order



$$\text{as } |\sin i + \sin \theta| \leq 2, \quad |m| \frac{\lambda}{\mathrm{d}} \leq 2$$

$m = 0 \Rightarrow$ Mirror, specular reflection

GRATING THEORY: grating equation

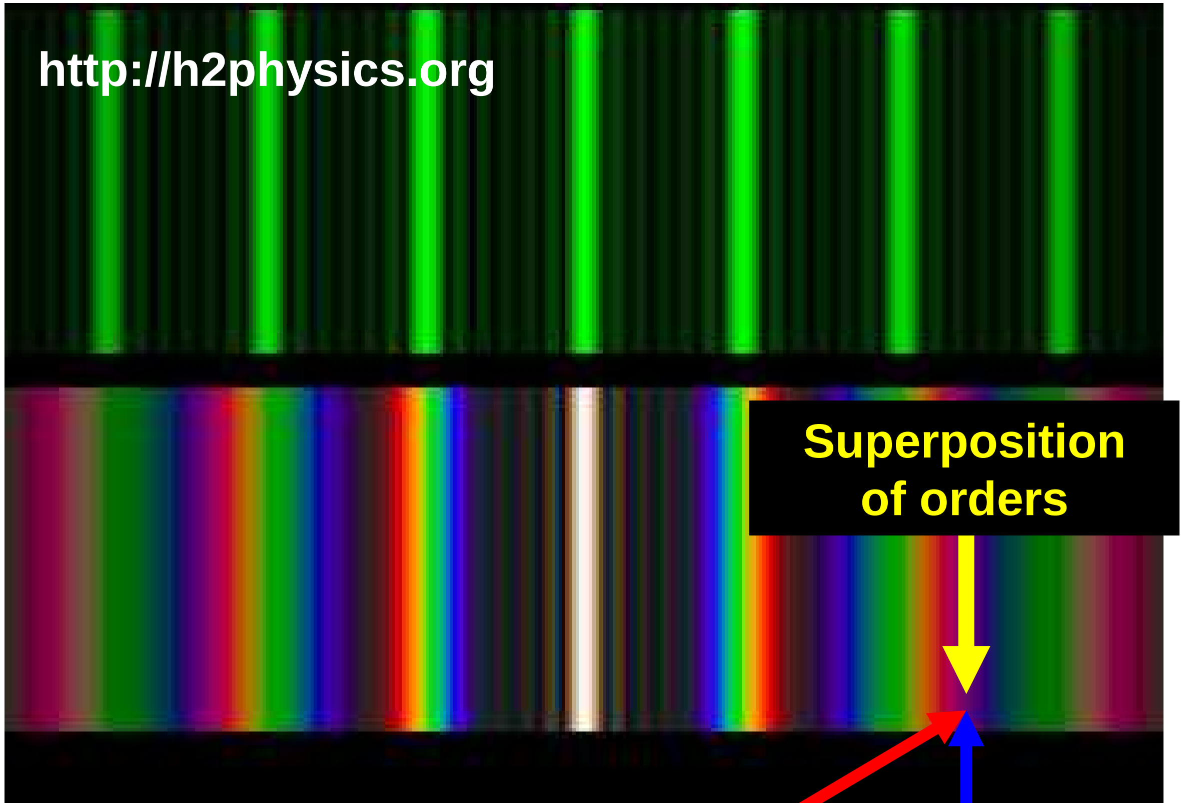


http://hyperphysics.phy-astr.gsu.edu/

GRATING DIFFRACTION

Monochromatic diffraction

Polychromatic diffraction



$$d \times \sin\theta_1 = m_1 \times \lambda_1$$

$$d \times \sin\theta_2 = m_2 \times \lambda_2$$

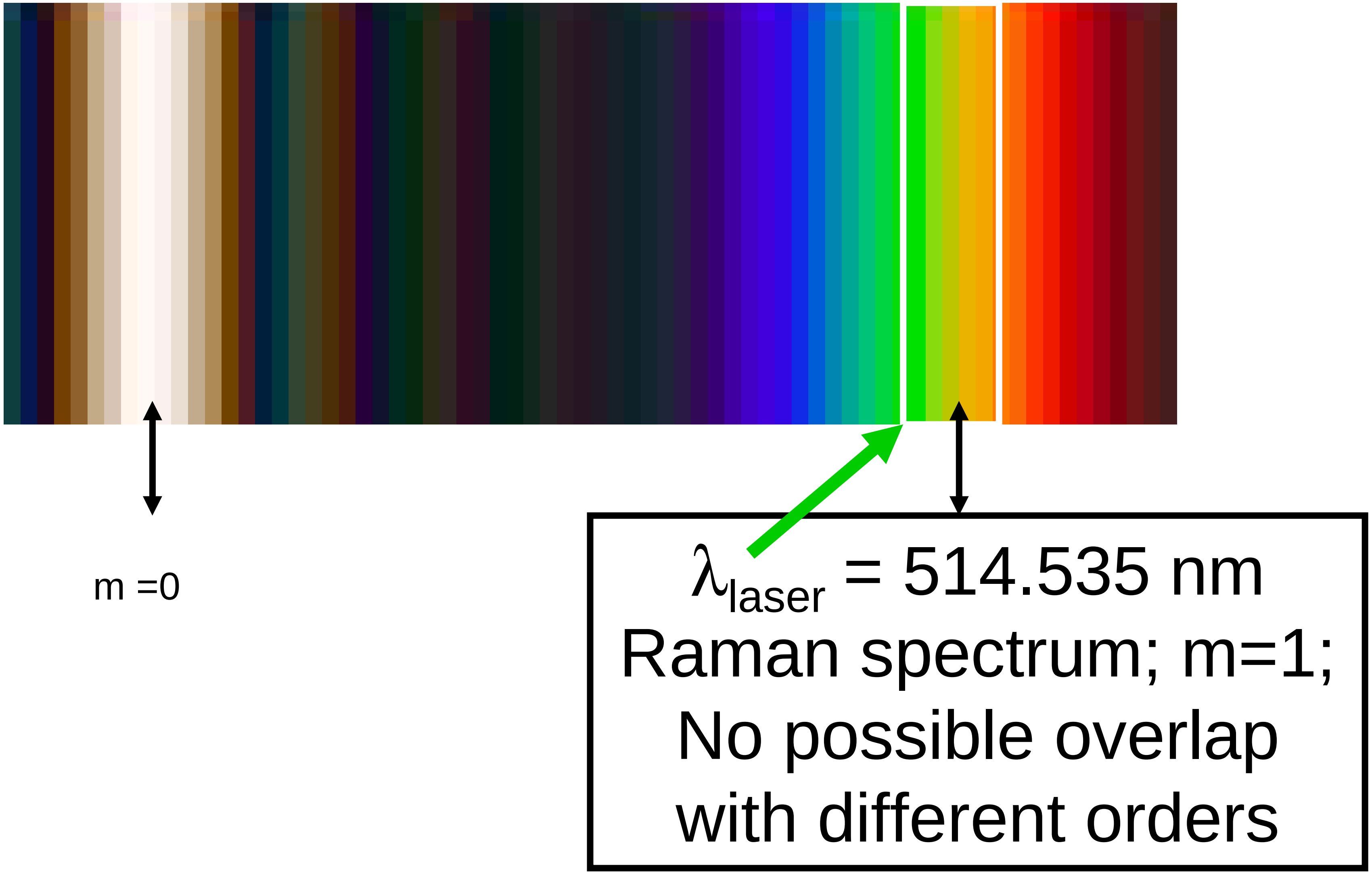
$$\theta_1 = \theta_2 \Leftrightarrow m_1\lambda_1 = m_2\lambda_2$$

Red: 600 nm

$$m_1 = 2; m_2 = 3 \Rightarrow \lambda_1 = \frac{3}{2}\lambda_2$$

bleu: 400 nm

GRATING DIFFRACTION and Raman spectrum



GRATING DIFFRACTION and grooves density

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

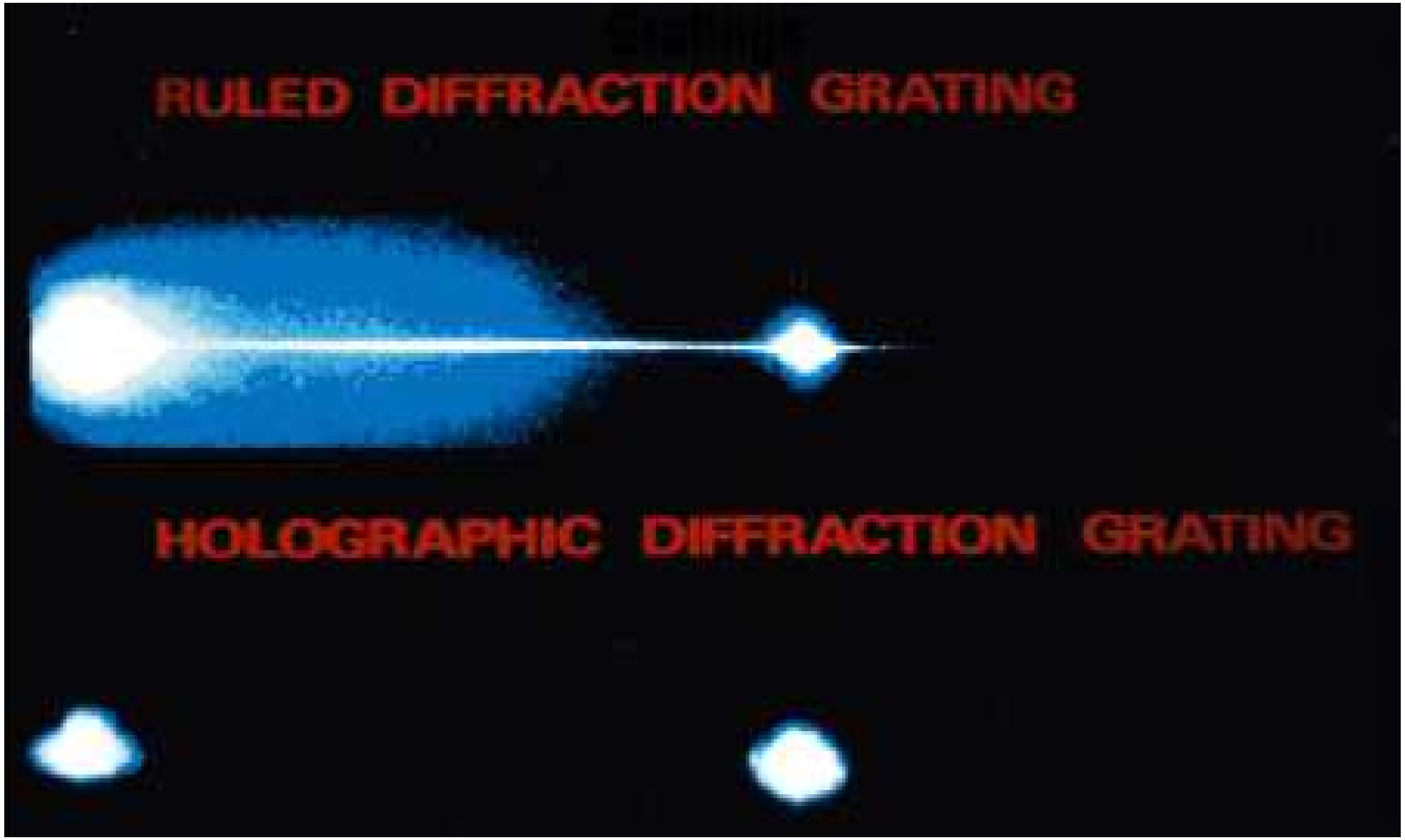
$$\text{groove density} : G = \frac{1}{d} = \text{number of grooves/mm}$$

$$\text{G} = 150 - 3000 - 6000 (\text{VPHG})$$

$$\sin i + \sin \theta = G \times m \times \lambda$$

at constant m and wavelength, diffraction angle is proportional to groove density

RULED GRATING
and HOLOGRAPHIC GRATING



GRATING DIFFRACTION and Raman spectrum
Angular dispersion versus wavelength

Dispersion on the screen of the different wavelengths for a given diffraction order results in different angular dispersion

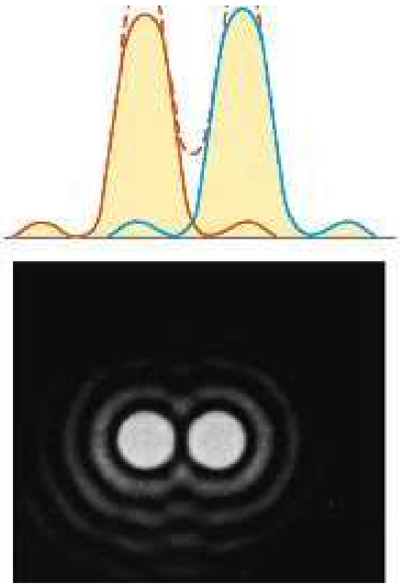
$$d \times (\sin i + \sin \theta) = m\lambda \text{ and } AD \equiv \frac{d\lambda}{d\theta}$$

$$(d \cos \theta) d\theta = m \frac{d\lambda}{d\theta} \Rightarrow AD = \frac{m}{d \cos \theta} = \frac{Gm}{\cos \theta}$$

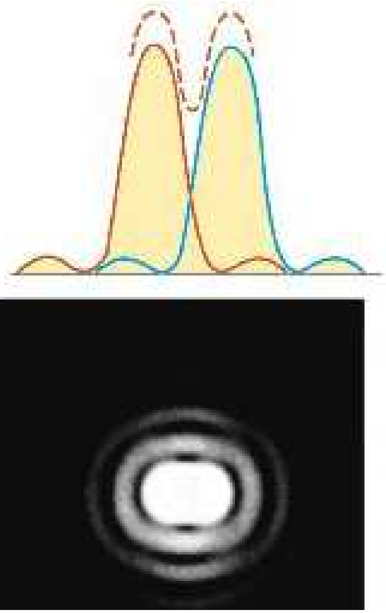
AD : proportional to m and G

GRATING DIFFRACTION and Chromatic resolving power

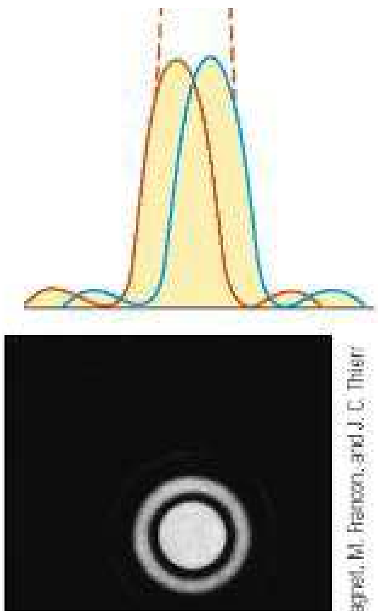
$$R = \frac{\lambda}{\Delta\lambda} = mN$$



Resolved lines



Just resolved line: Rayleigh criterion
The first **diffraction minimum** of the image of one source point **coincides** with the **maximum** of another.



Unresolved lines

GRATING DIFFRACTION and Chromatic resolving power

$$\left.\begin{aligned} R &= \frac{\lambda}{\Delta\lambda} = mN \\ N &= \frac{L_g}{d} \end{aligned}\right\} \Rightarrow R = m\frac{L_g}{d} \text{ and } d \times (\sin i + \sin\theta) = m\lambda$$

$$\text{best}\left(\frac{\lambda}{\Delta\lambda}\right) = \frac{2L_g}{\lambda}$$

The spectral resolution is proportional to the length of the grating (perpendiculary to the grooves)

GRATING DIFFRACTION and Resolution in wavenumber scale

Wave-vector $k = 2\pi/\lambda \qquad \lambda/\Delta\lambda = k/\Delta k = mN$

$$k = 2\pi\overline{\upsilon} \Rightarrow \Delta k = 2\pi \times \overline{\Delta\upsilon} \Rightarrow \overline{\Delta\upsilon} = \frac{\overline{\upsilon}}{mN} = \frac{1}{\lambda mN}$$

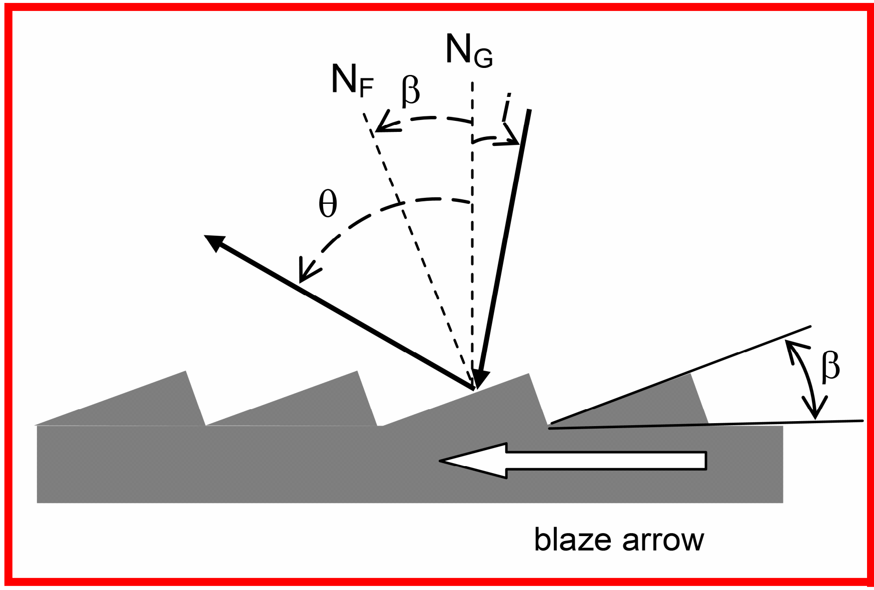
At the first order, if $d \approx \lambda, d = \alpha \times \lambda$

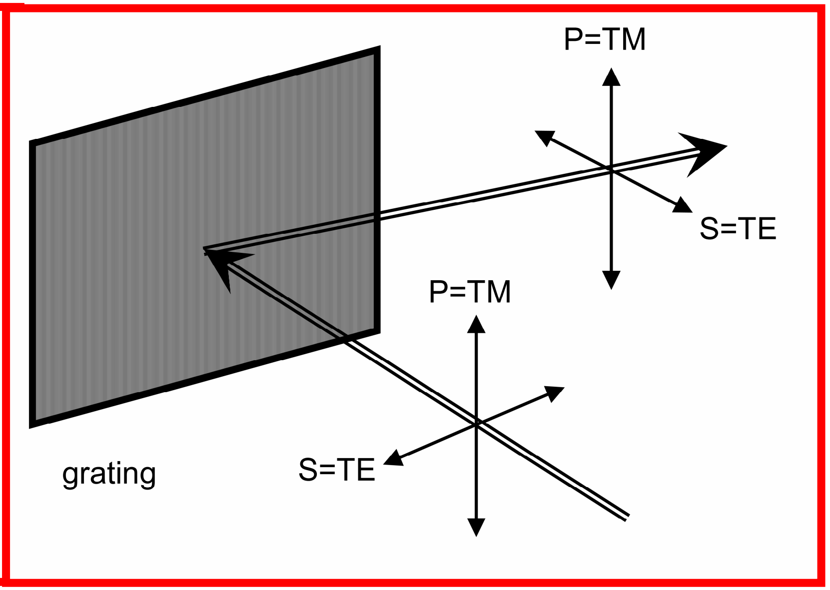
$$\Delta\overline{\nu_{\min}} = \frac{\alpha}{d \times N} = \frac{\alpha}{L_g}$$

$$\lambda = 0.5\,\mu\text{m}$$
$$L_g = 10\,\text{cm}$$

$$\Rightarrow \Delta\nu_{\min} = \frac{1}{10} = 0.1\,\text{cm}^{-1}$$

GRATING DIFFRACTION and line intensity





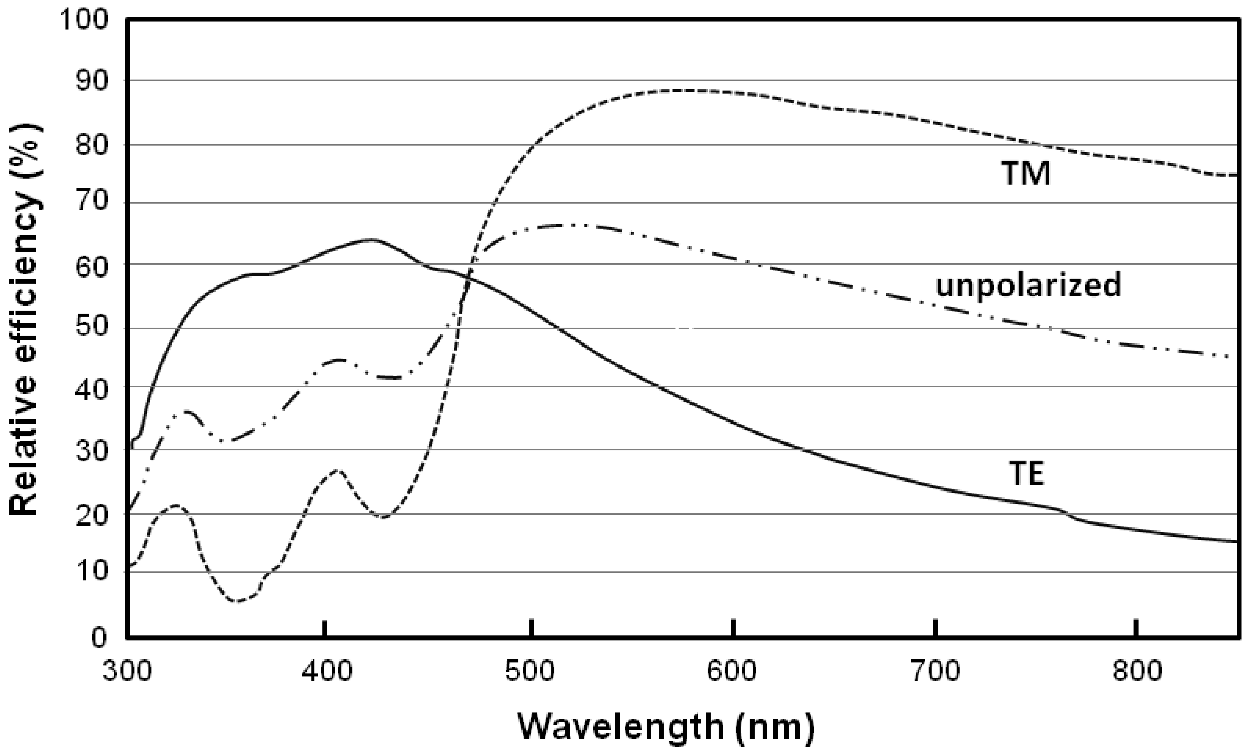
The incident angle vs the blaze angle

The polarization state of the incident radiation

Efficiency curves are function of wavelength: 1) Absolute = Incident(λ)/Diffracted(λ)

2) Relative = Diffracted(λ)/Reflected(λ) by mirror with same coating

GRATING DIFFRACTION and line intensity



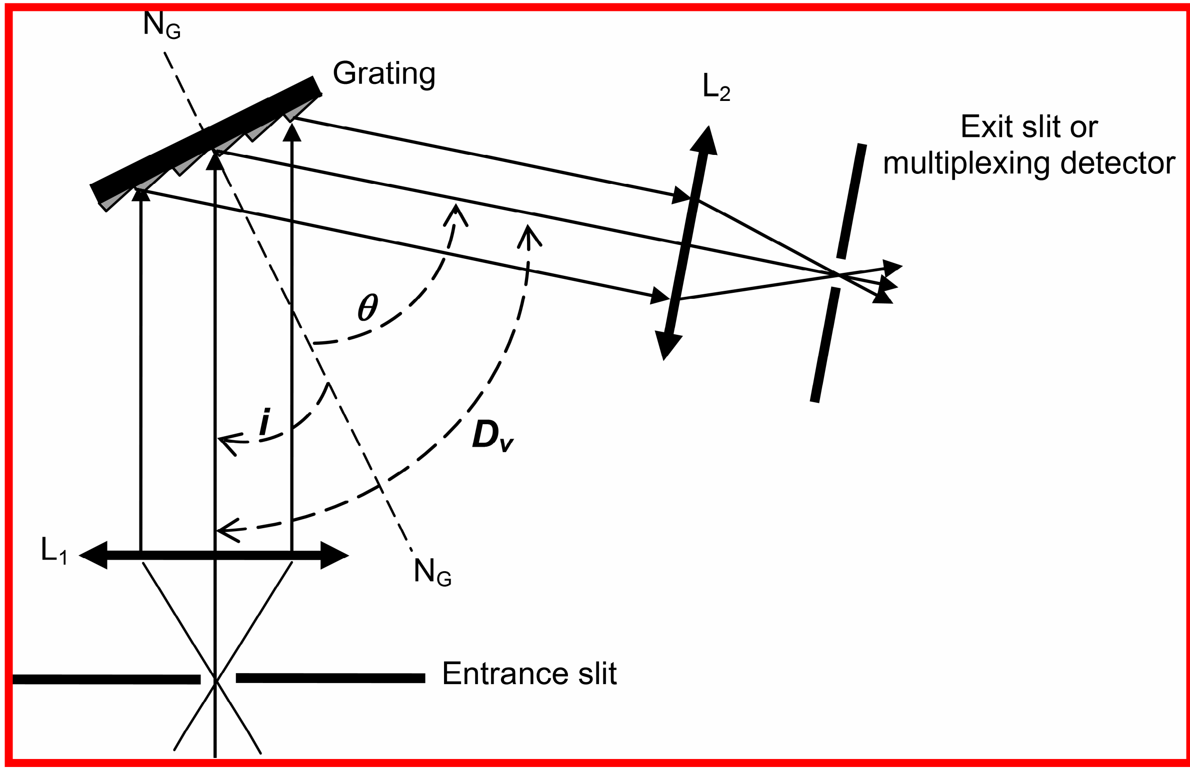
Blaze angle, maximum efficiency

Grating efficiency depends on

Wavelength, polarization in incident light, incidence angle, diffraction order, groove profile and coating material.

Selection of the grating from the exciting radiation wavelength

CZERNY-TURNER SPECTROMETER: Basic principles



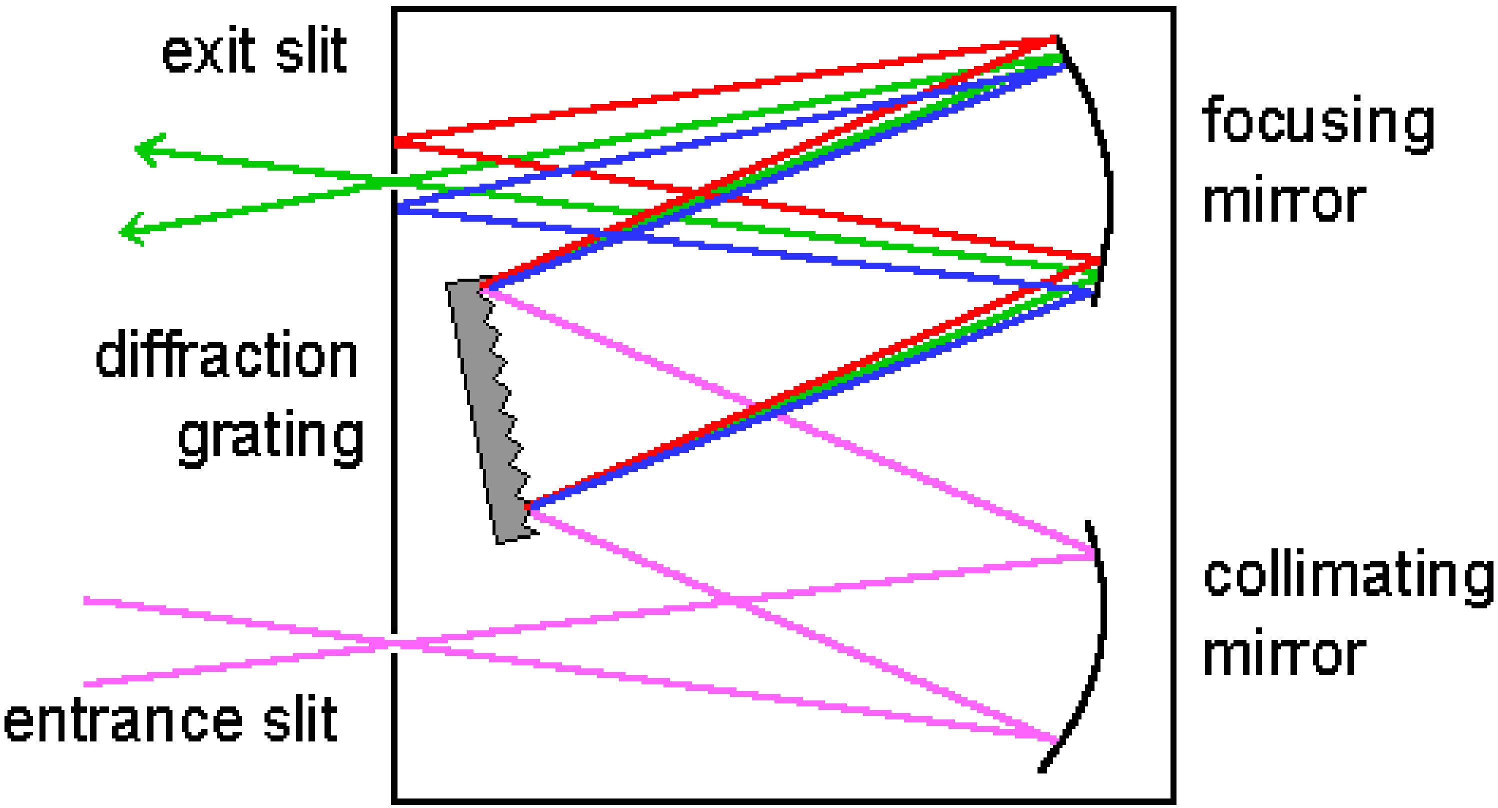
Sources and detectors are in a fixed position: Dv = deviation angle

$$D_v = \theta - i$$

$$\sin i + \sin\theta = G \times m \times \lambda$$

$$2\times\sin\left(\frac{i+\theta}{2}\right)\times\cos\left(\frac{\theta-i}{2}\right) = 2\times\sin\left(\frac{i+\theta}{2}\right)\times\cos\left(\frac{D_v}{2}\right) = G\times m\times\lambda$$

CZERNY-TURNER SPECTROMETER:
Actual optical design



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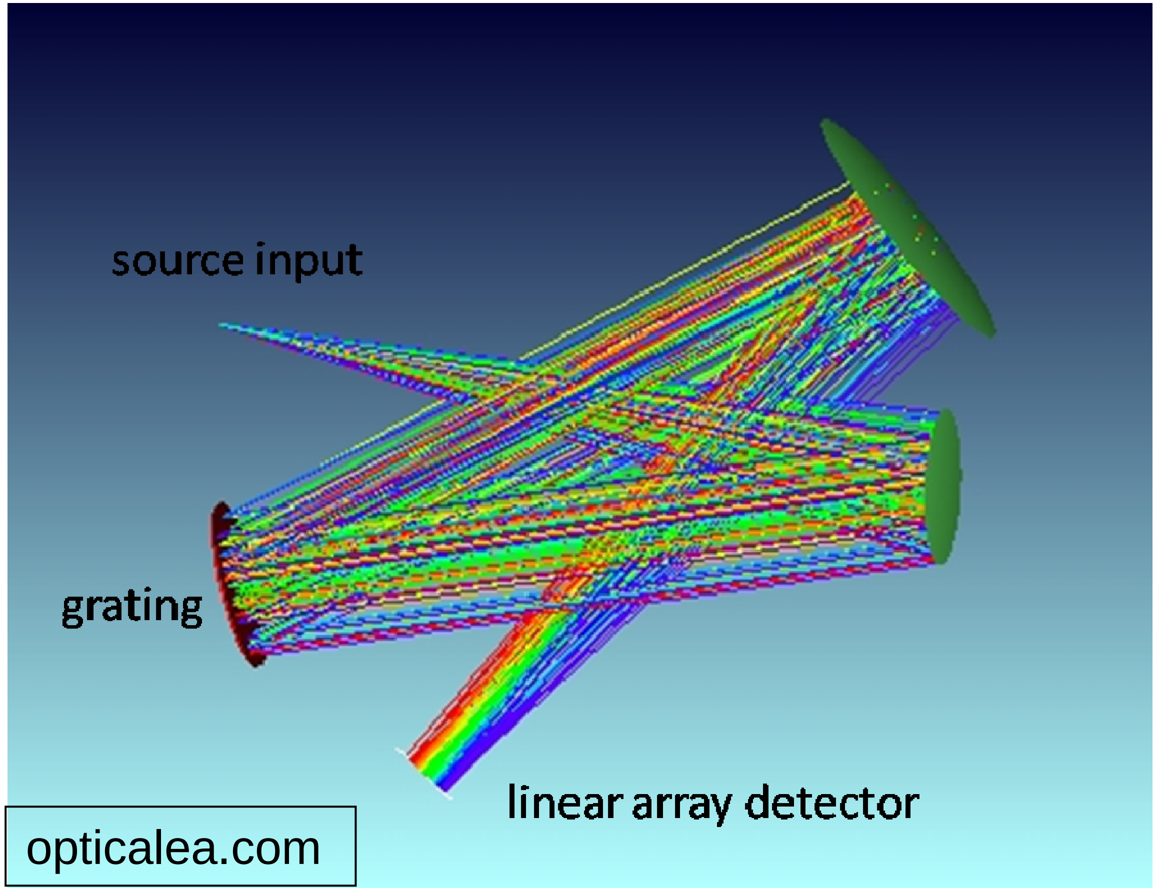
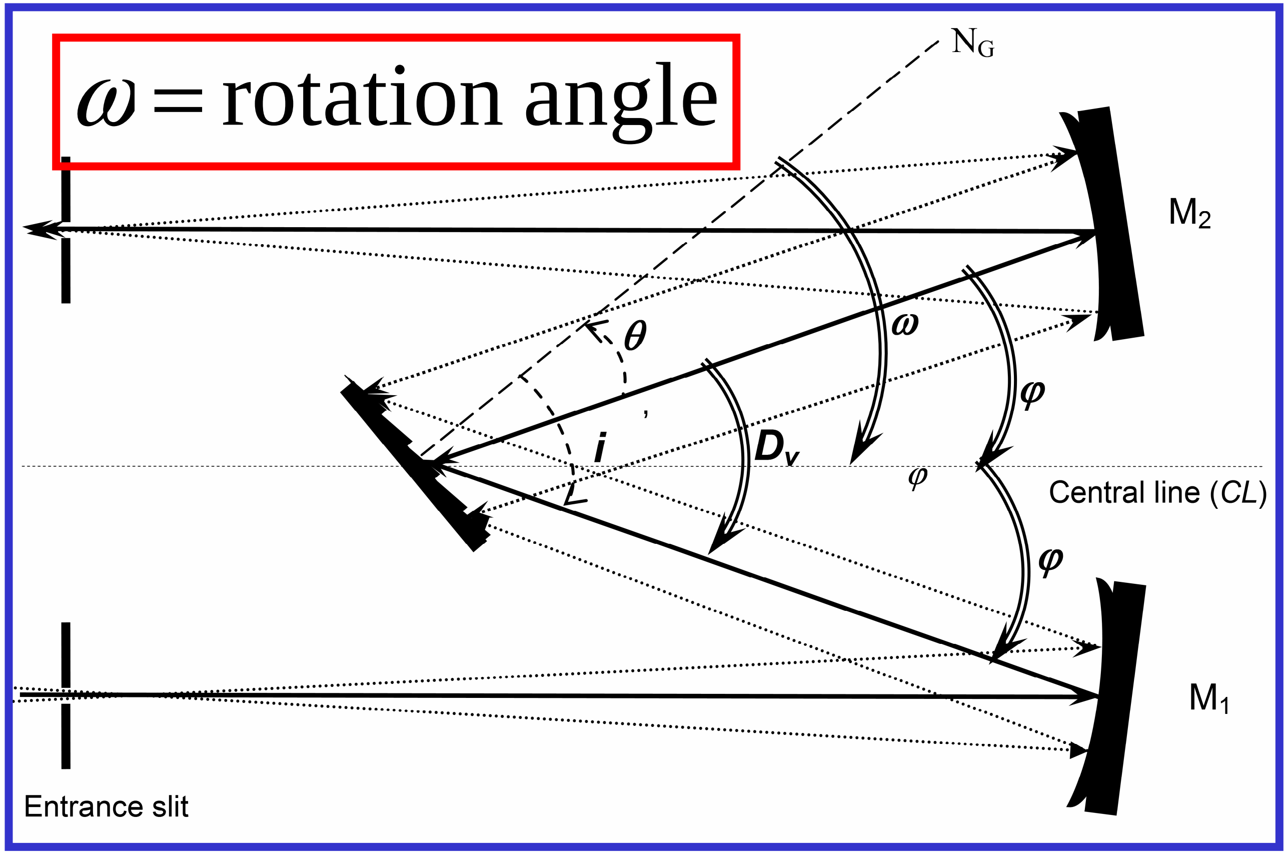
CZERNY-TURNER SPECTROGRAPH:
Actual optical design

Crossed Czerny Turner Spectrometer



Spectrometer
Image Plane

CZERNY-TURNER SPECTROGRAPH: Actual optical design



Angular relationships

$$\varphi = D_v / 2$$

$$2\varphi = i - \theta$$

$$\theta = \omega - \phi$$

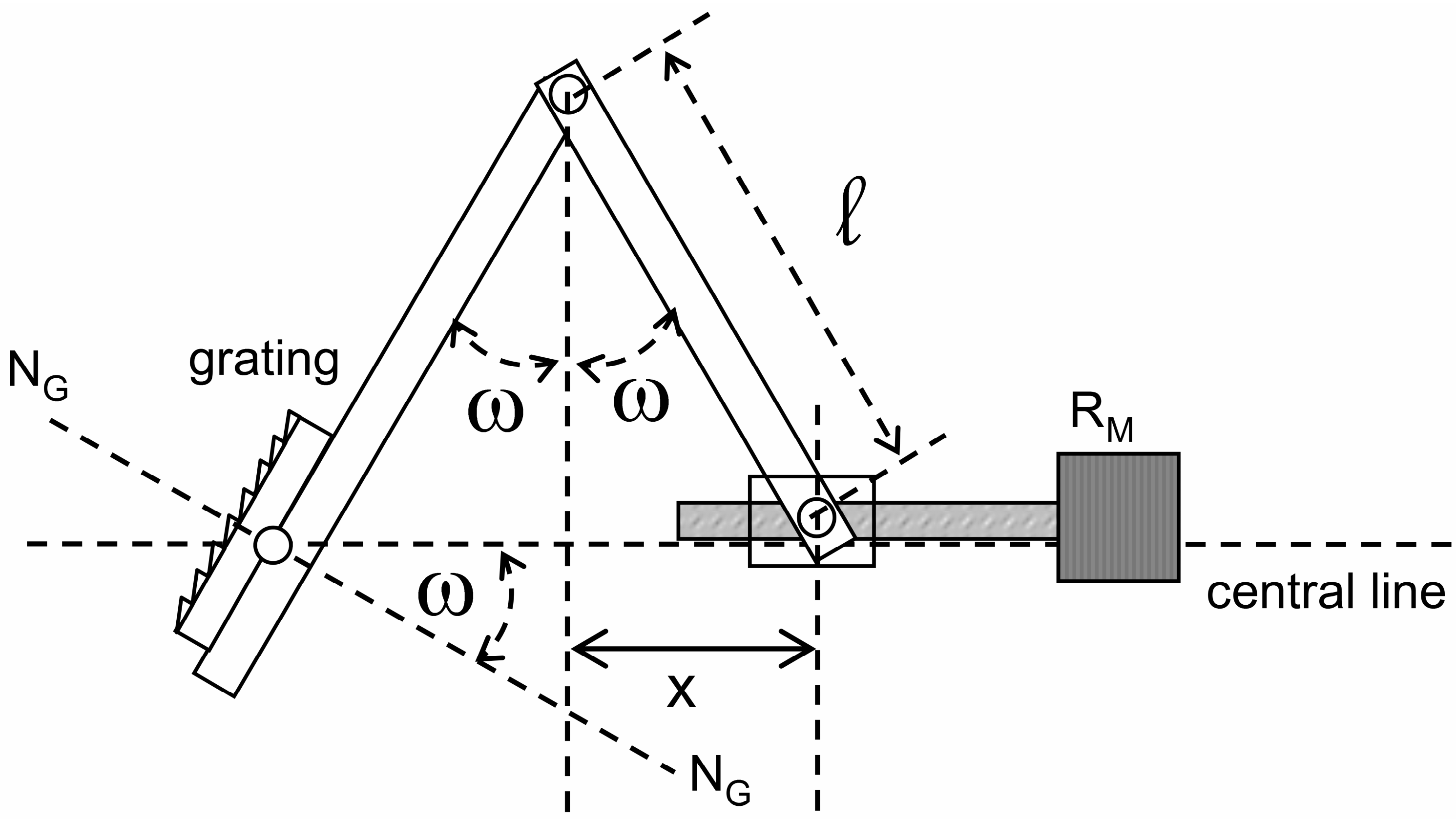
$$i = \varphi + \omega$$

$$(i + \theta)/2 = \omega$$

$$(i - \theta)/2 = \varphi$$

$$2 \times \sin\omega \times \cos\varphi = G \times m \times \lambda$$

CZERNY-TURNER SPECTROGRAPH: Sine bar for grating rotation



DETECTORS

1928	1940	1950	1964-1967	1978	1986	2012

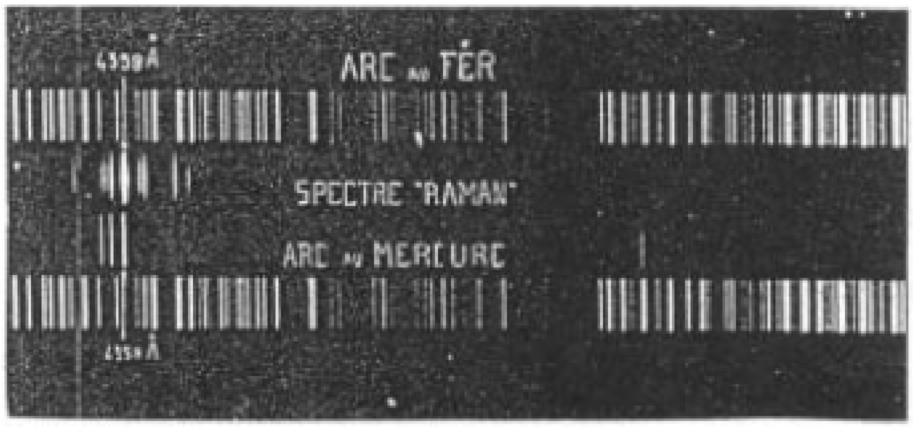
Eyes, photographic plate

Photomultiplier tube

Image Intensifier Vidicon Camera

Intensified Photodiode Array

CCD

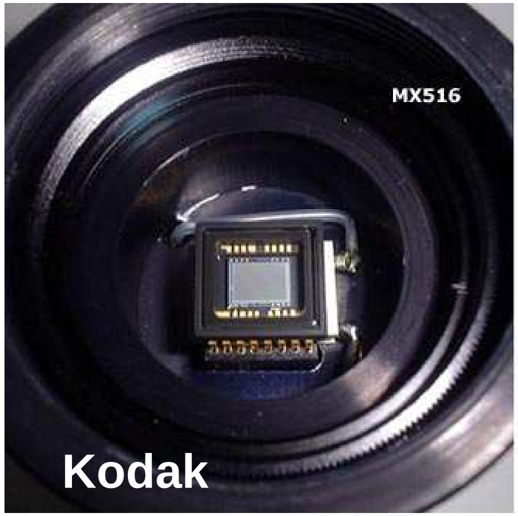


CCD DETECTORS

Invented in 1969 at AT&T Bell Labs by Willard Boyle and George E. Smith
Nobel Prize of Physics in 2009

2D Array of individual « detectors » = pixels

1024 x 256 pixels (26 µm x 26 µm)



Formation of an electron/hole pair in p-dopped silicon layer if E(photon) > Si band gap

200-1100 nm

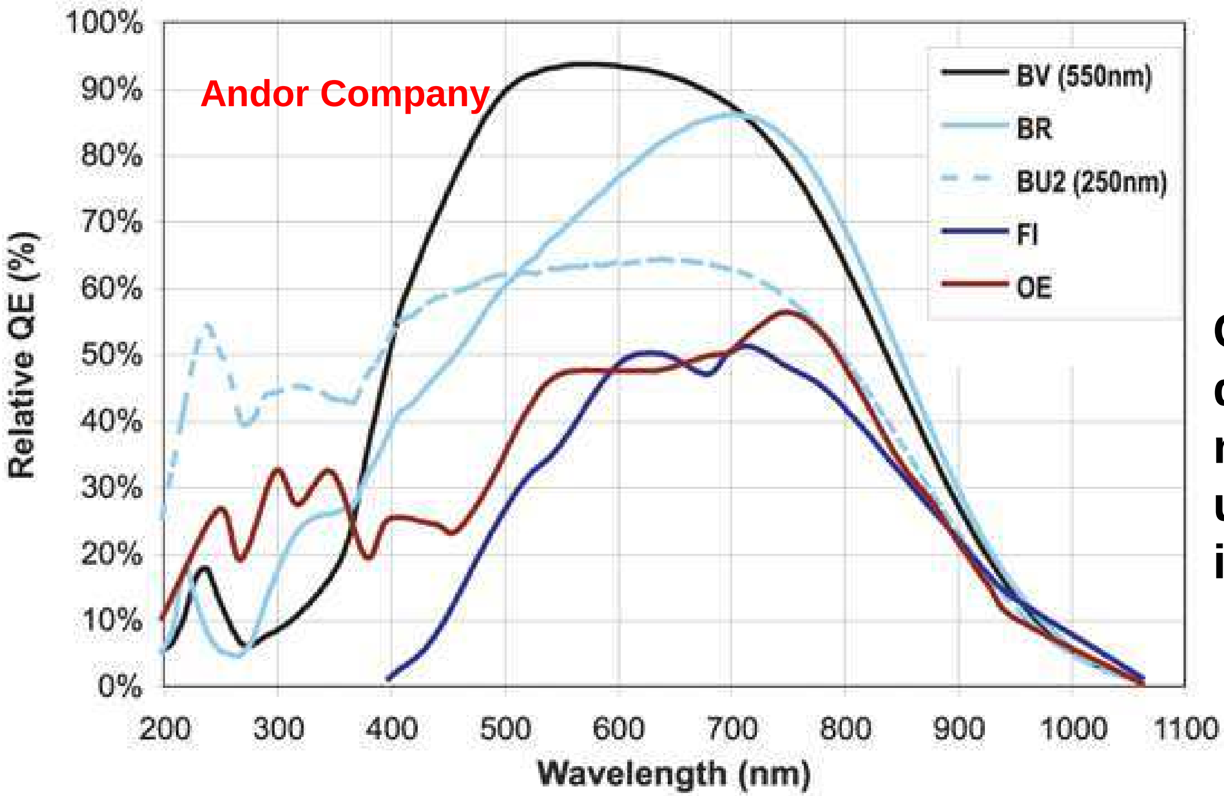
Front or back illuminated: consequences on quantum efficiency

Electrons are stored in a potential well characterized by is Full Well Capacity and read-out by an electrode

Cooled at -90 °C (Pelletier effect) or -130°C (liquid N_2) to eliminate thermal noise

CCD Detectors:
quantum efficiency curves

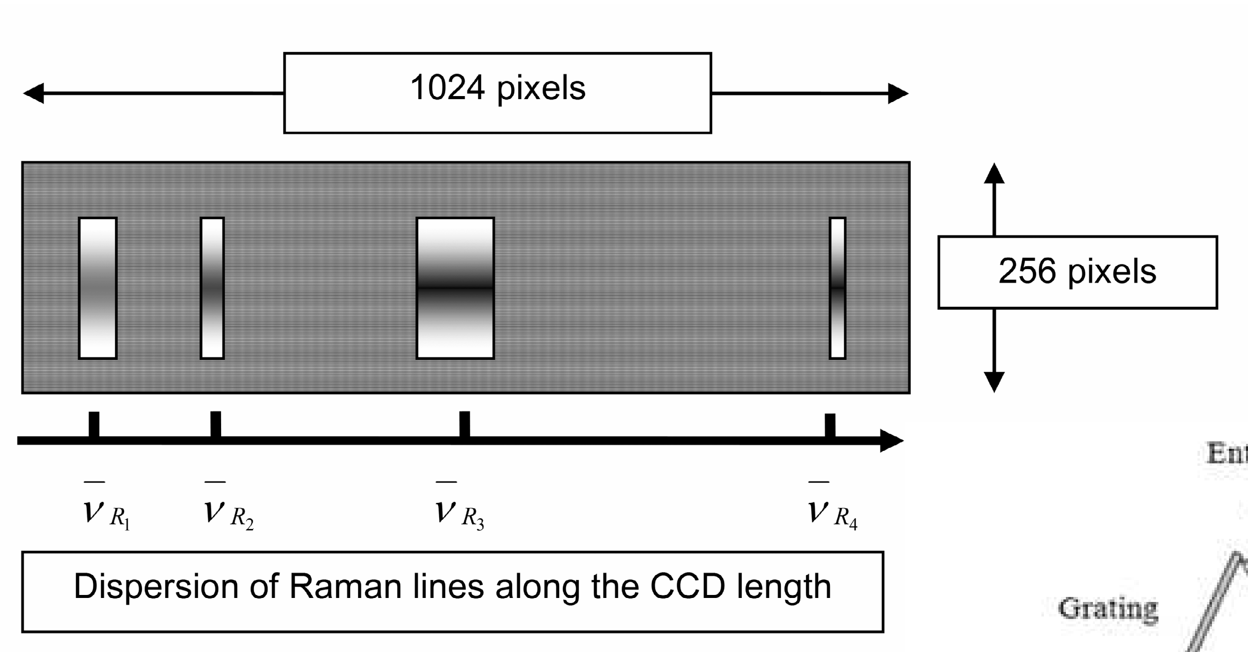
Quantum efficiency $Q_E(\lambda)$ **= number of electrons generated per incident photon**



To choose as a function of the excitation source

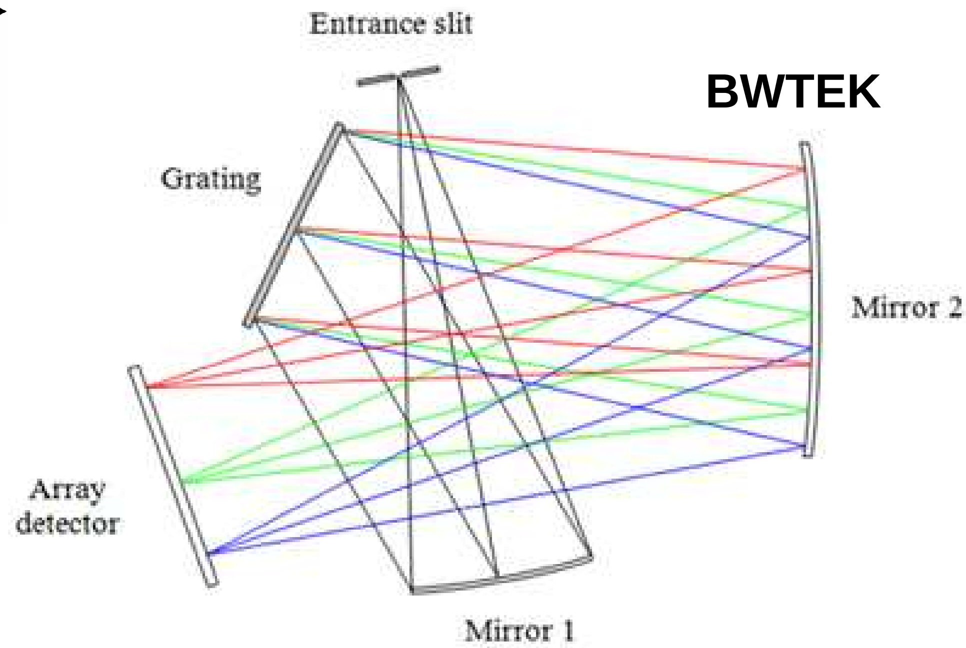
CCD detectors: high Q_E, low dark current, low read-out noise => great input in the use of Raman spectroscopy, in Earth sciences.

CCD : intensity and wavenumber coding



Intensity: vertical binning of pixels

BWTEK



Linear dispersion of the different radiations: deduced from the angular dispersion produced by the grating

CCD : wavenumber coding

Average wavelength dispersion or Reciprocal Linear Dispersion

$$RLD \equiv \frac{d\lambda}{dx}$$

***RLD* is linked to *AD* by** $\frac{d\lambda}{dx} = \frac{d\lambda}{d\omega} \times \frac{d\omega}{dx}$ $\quad RLD = AD \times \frac{d\omega}{dx}$

Where ω is the rotation angle of the grating

For a spectrometer with a *focal distance f* $\quad dx = f \times d\omega$

For a Czerny-Turner spectrograph

$$2 \times \sin\left(\frac{i+\theta}{2}\right) \times \cos\left(\frac{\theta - i}{2}\right) = 2 \times \sin\left(\frac{i+\theta}{2}\right) \times \cos\left(\frac{D_v}{2}\right) = G \times m \times \lambda$$

$$\frac{d\lambda}{dx} = \frac{2d}{f \times m} \times \cos\omega \times \cos\varphi = \frac{2\cos\omega \times \cos\varphi}{G \times f \times m}$$

CCD : wavenumber coding

$$\frac{d\lambda}{dx} = \frac{2d}{f \times m} \times \cos\omega \times \cos\varphi = \frac{2\cos\omega \times \cos\varphi}{G \times f \times m}$$

Numerical application: small ω angle (cos ω =1); f = 800 mm; grooves d = 0.5 µm;

1st order diffraction; ϕ = 30 °

$$\frac{d\lambda}{dx} = \frac{2 \times 0.5 \times \cos(30°)}{800} = 1.08 \times 10^{-3} \mu m.mm^{-1}$$

In wavenumber scale

$$\frac{d\bar{\nu}}{dx} = \frac{d\bar{\nu}}{d\lambda} \times \frac{d\lambda}{dx}$$

As $\bar{\nu} = 1/\lambda$ $\quad \frac{d\bar{\nu}}{d\lambda} = -\frac{1}{\lambda^2} = -\bar{\nu}^{-2} \Rightarrow \frac{d\bar{\nu}}{dx} = -\bar{\nu}^{-2} \times \frac{d\lambda}{dx}$

At 1000 cm^{-1} Raman shift / 514.5 nm $\quad \overline{\nu_{laser}} = 19435 cm^{-1} \Rightarrow \bar{\nu}_{1000cm-1} = 18435 cm^{-1}$

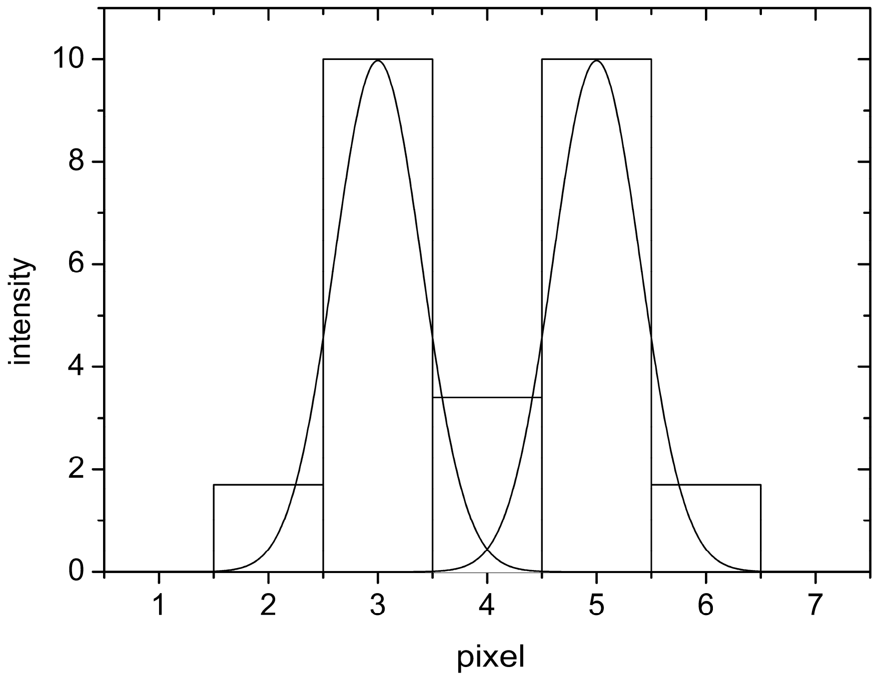
$$\frac{\Delta\nu}{\Delta x} = 367 cm^{-1} / cm \Rightarrow \approx 880\ cm^{-1} \text{coverage of CCD}$$

CCD : wavenumber coding

$$\frac{\Delta\nu}{\Delta x} = 367\mathrm{cm}^{-1}/\mathrm{cm}$$

1 pixel 26 µm = 2.6 10^{-3} cm

1 pixel 26 µm corresponds to 0.95 cm^{-1} /pixel = pixel size resolution



Limiting resolution of the spectrometer including the detector

$$\Delta\bar{\nu}_{spectrometer} = \delta\bar{\nu}_{pixel} \times 3 = \left(\frac{\Delta\bar{\nu}}{\Delta x}\right) \times \delta w_{CCD} \times 3$$

Spectral resolution

$$SR_{\lambda} = \sqrt{(\Delta\lambda_{slit})^2 + (\Delta\lambda_{spectrometer})^2}$$

$$SR_{\bar{\nu}} = \sqrt{(\Delta\bar{\nu}_{slit})^2 + (\Delta\bar{\nu}_{spectrometer})^2}$$

$$\Delta\bar{\nu}_{slit} = \gamma \times l \times \frac{d\bar{\nu}}{dx}$$

γ : magnifying power of the spectomer

$$\gamma = \frac{\cos(i)}{\cos(\theta)} \times \frac{L_A}{L_B}; \frac{L_A}{L_B} = 1 \text{ and } \gamma \approx 1$$

l = slit width

Thus , for the same numerical application

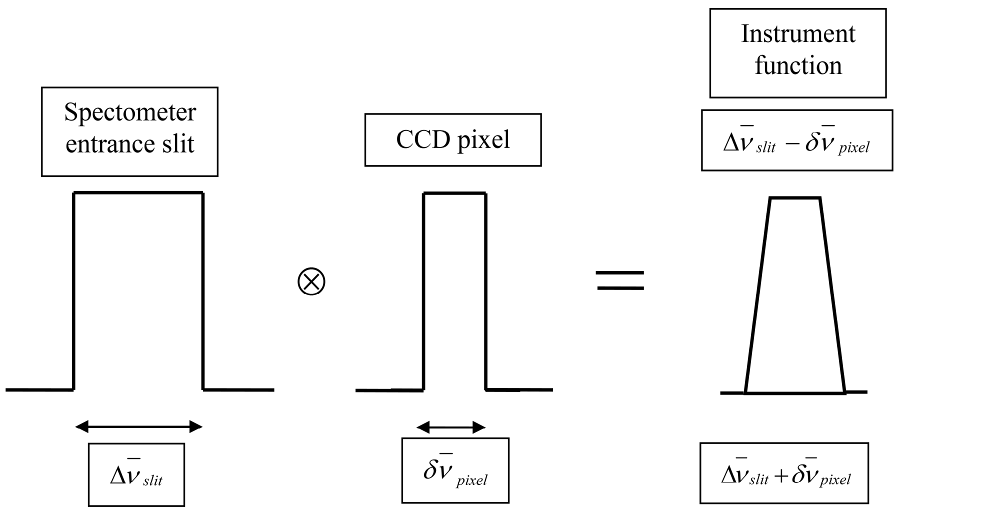
$$\frac{d\bar{\nu}}{dx} = 367\,\text{cm}^{-1}/\text{cm},\ l = 100\ \mu\text{m} \qquad \Delta\bar{\nu}_{slit} = 3.67\ \text{cm}^{-1}$$

$$SR_{\bar{\nu}} = 4.74\ \text{cm}^{-1}$$

Band Shape

$$F(\bar{\nu}) = \int_0^x L(\bar{\nu}) \times A(\bar{\nu}, \bar{\nu}_0) \times d\bar{\nu} = L(\bar{\nu}) \otimes A(\bar{\nu}, \bar{\nu}_0)$$

Source **Apparatus function**



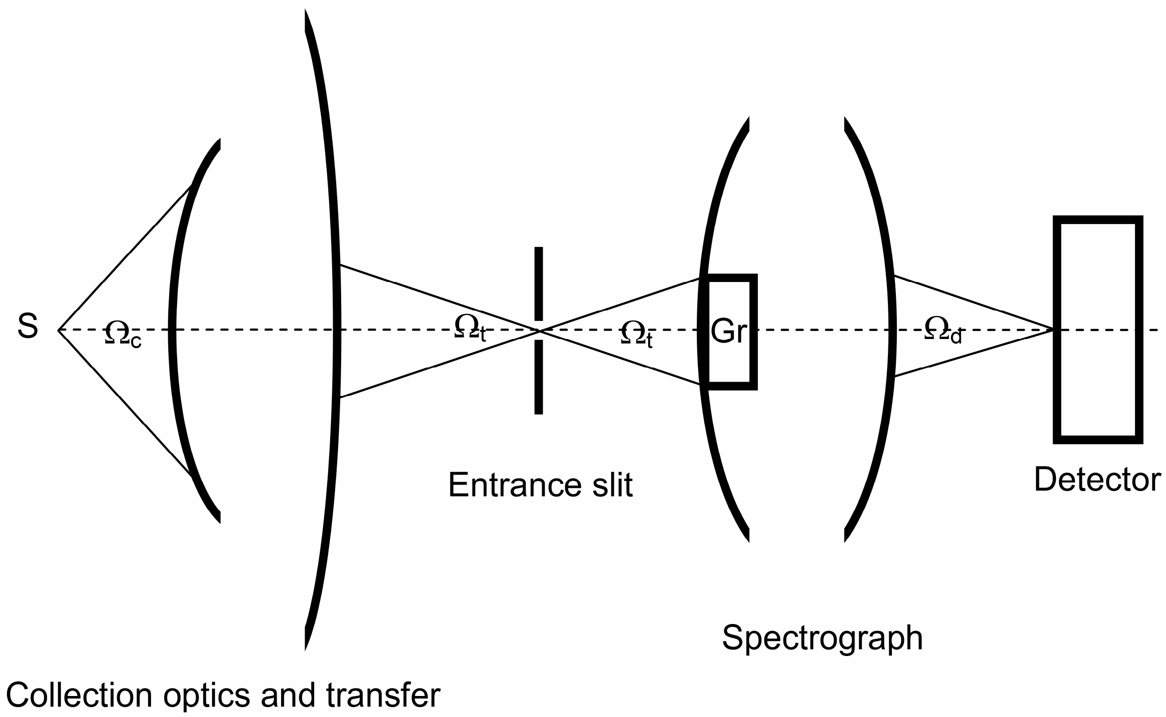
Modification of the band profile by the instrument.

Lorentzian => Gaussian, mixtures

Condition of no modification of the band profile and no enlargement:

Instrumental resolution < 1/5 FWHM of natural profile

Coupling sampling system with spectrometer



Optimum coupling conditions: constant flux of photons transported from the sample to the detector without any loss (except those resulting from absorption): Etendue or throughput is constant

Radiometric calculations

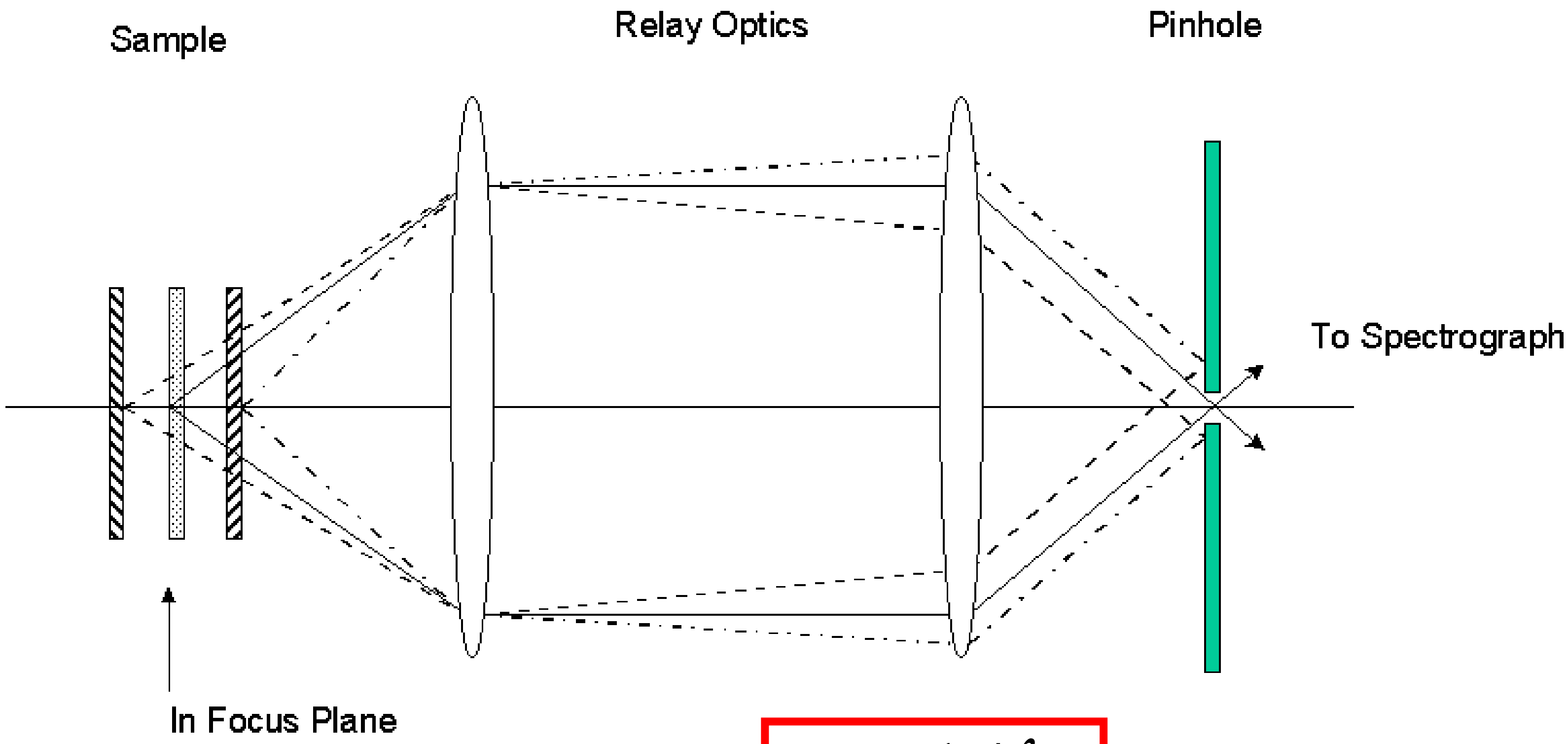
Calculation of number of Raman photons from the source

Calculation of number of Raman photons collected by the sampling system (lens, microscope objective)

from the value of transmission of each optical element ($T = I/I_0$),

from the value of the QE of the detector, the number of photo-electrons can be calculated.

Spatial resolution of confocal Raman microspectrometers



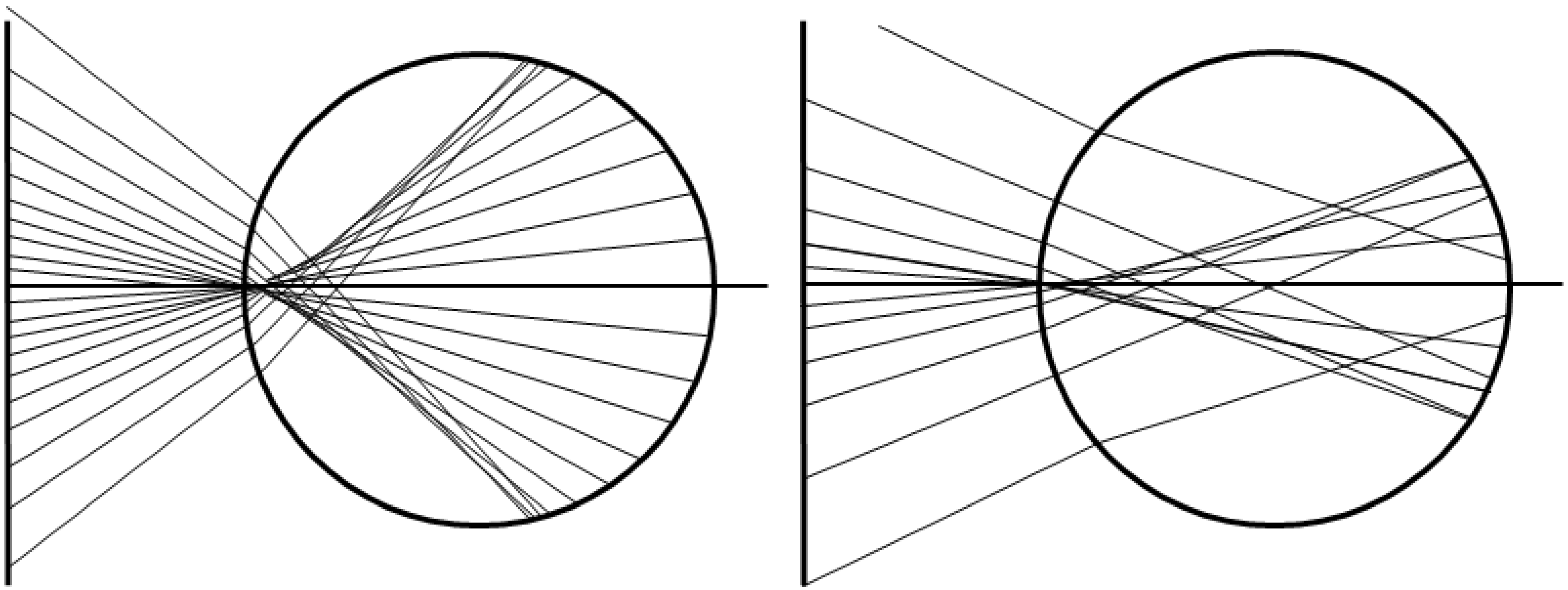
Axial resolution $\delta z = \dfrac{1.4\lambda}{(N.A.)^2}$

Lateral resolution $\delta xy = 0.46\lambda / (N.A.)$

Degradation of spatial resolution by refraction

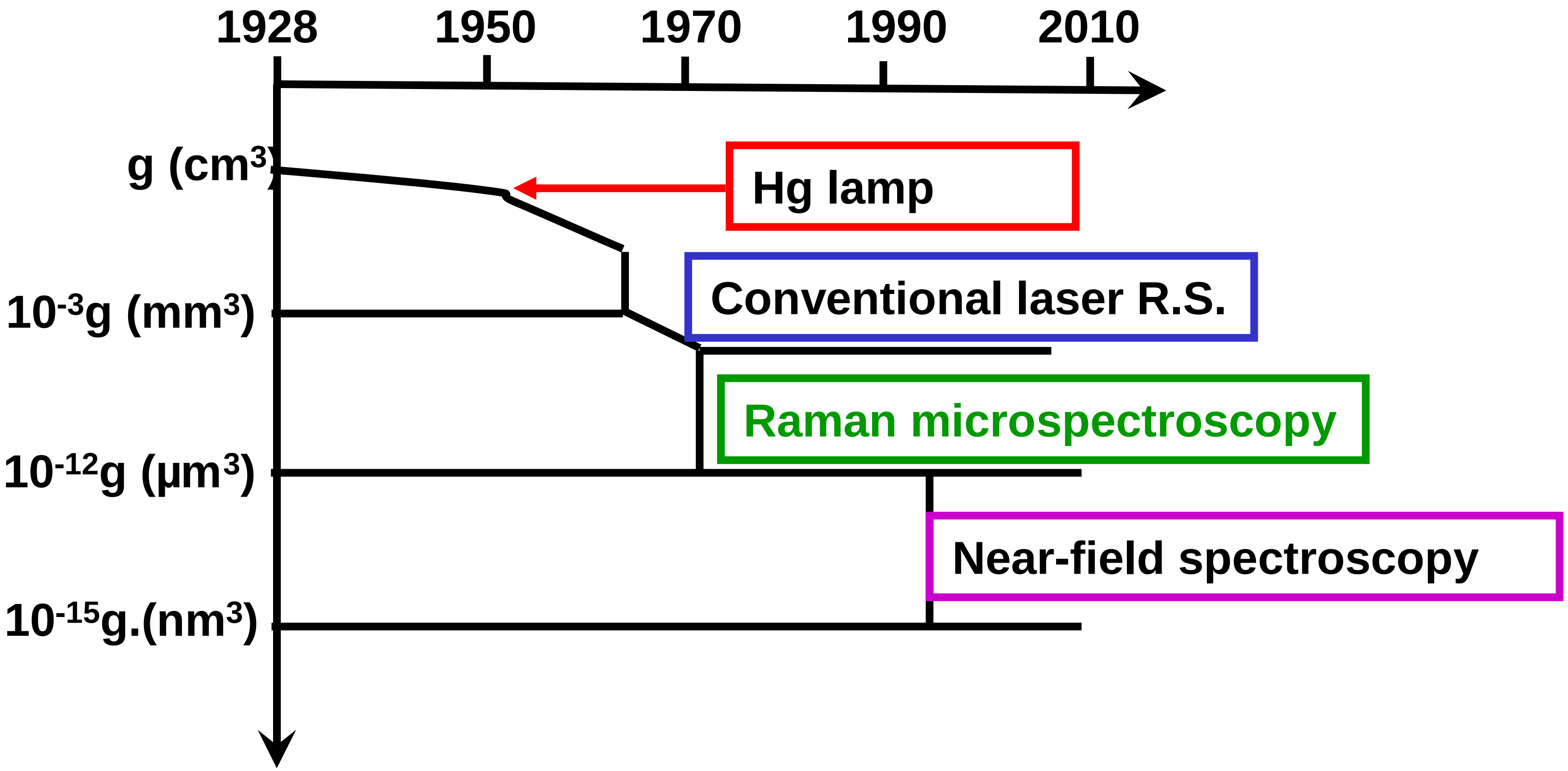
Use of immersion objective

(a) Oil immersion objective (b) Dry objective



P= 80µm Nh=1.4 Nm=1.55 P= 80µm Nh=1 Nm=1.55

RAMAN SAMPLING VOLUME



From Delhaye and Dhamelincourt