INSTRUMENTATION IN RAMAN SPECTROSCOPY: ELEMENTARY THEORY

UNIVERSITÉ DE LORRAINE

J.Dubessy, M.C. Caumon

GeoRessources (Nancy, France)

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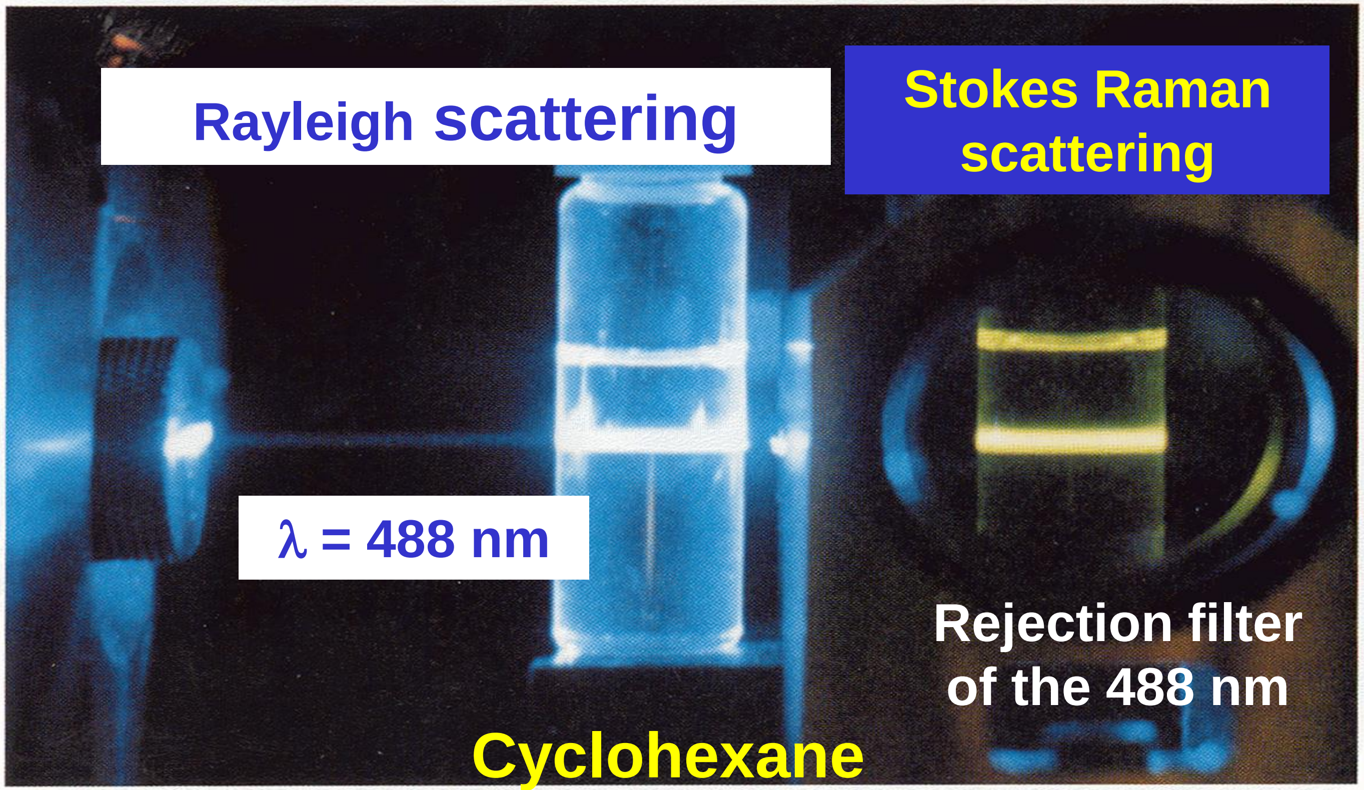
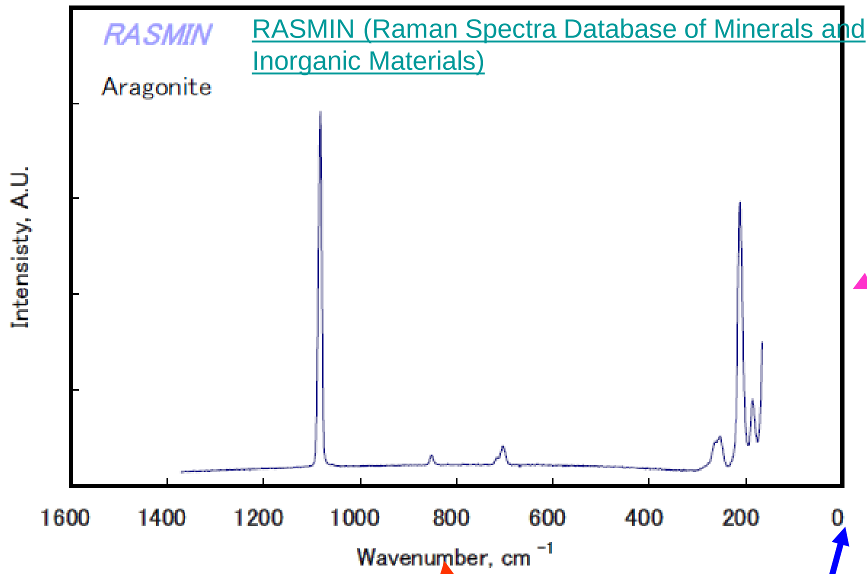


GEORAMAN-XXII-2016 School joint to the
VIIIth International Siberian Early Career GeoScientists Conference

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 + Raman microprobes + laser rejection by filters: highly luminous systems**
- **Highly simplified « portable » systems: Earth surface, Mars surface (EXOMARS mission, Supercam system)**

Where is the information in a Raman spectrum ?

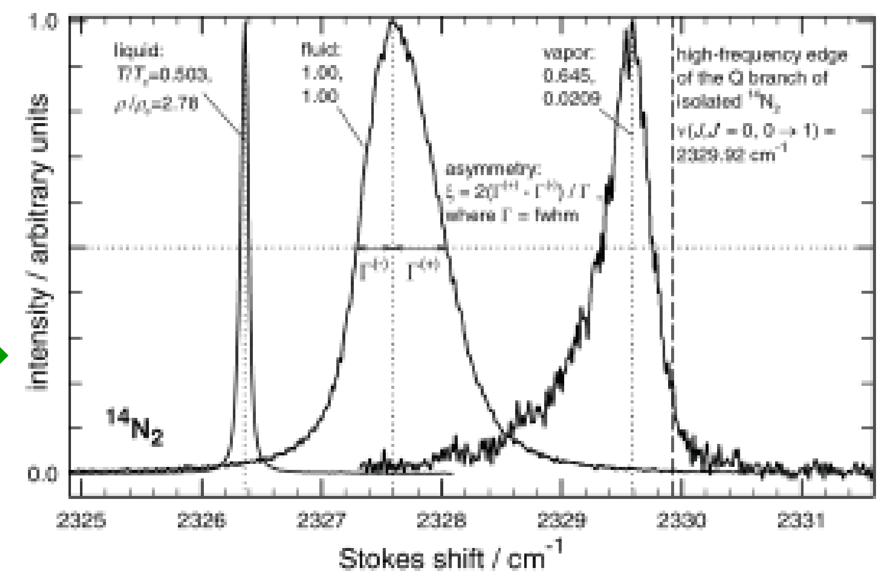


Raman line intensities, function of:

- **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

Consequences on the variation of the efficiency of components

Precision of 1 cm^{-1} ⇔ to 6.3×10^{-3} nm = **6.3×10^{-2} Å precision in λ** for **λ_0 = 250 nm**

Precision of 1 cm^{-1} ⇔ 6.1×10^{-2} nm = **0.61 Å precision in λ** for **λ_0 = 785 nm**

Raman line intensities: orders of magnitude estimated by radiometric calculations

Number of excitation photons

Differential Raman scattering cross section

Number of Raman photons

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

Excited area of the sample

Solid angle of collection

Number of molecules in the excited volume

Raman line intensities: orders of magnitude estimated by radiometric calculations

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

$N_{\bar{\nu}_0}(1s) = W_{\bar{\nu}_0} / \left[E_{1photon}(\lambda_0)\right]$ $\qquad W_{\bar{\nu}_0} = 0.01\,\text{Watt} = 0.01\,\text{J.s}^{-1}$

$E_{1photon}(\lambda_0) = h(c/\lambda_0) \approx 6.62\times10^{-34}\left(3\times10^{8}/(0.5\times10^{-6})\right) \approx 4\times10^{-19}\,J$ $\qquad N_{\bar{\nu}_0}(1s) = 2\times10^{16}$ photons

$\left(\frac{d\sigma}{d\Omega}\right) \approx 10^{-35}$ to $10^{-33}\,\text{m}^2.\text{sr}^{-1}$ $\qquad \Delta\Omega = 1\,\text{sr}$ $\qquad N_m = \rho AL \Rightarrow N_m/A = \rho L$

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

$$N_{\bar{\nu}_0-\bar{\nu}_R} = 2\times10^{16}\times\left(10^{-35}\text{ to }10^{-33}\right)\times3\times10^{28}\times10^{-2} = 6\times10^{7}\text{ to }10^{9}$$

Figures of merit of a Raman spectrometer

- excitation source: high power and stable monochromatic source

3-5 orders of magnitude

$$N_{\bar{\nu}_0-\bar{\nu}_R} = 10^{7} \text{ to } 10^{10}$$

6-9 orders of magnitude

$$N_{\bar{\nu}_0,Rayleigh} = 10^{11} \text{ to } 10^{13}$$

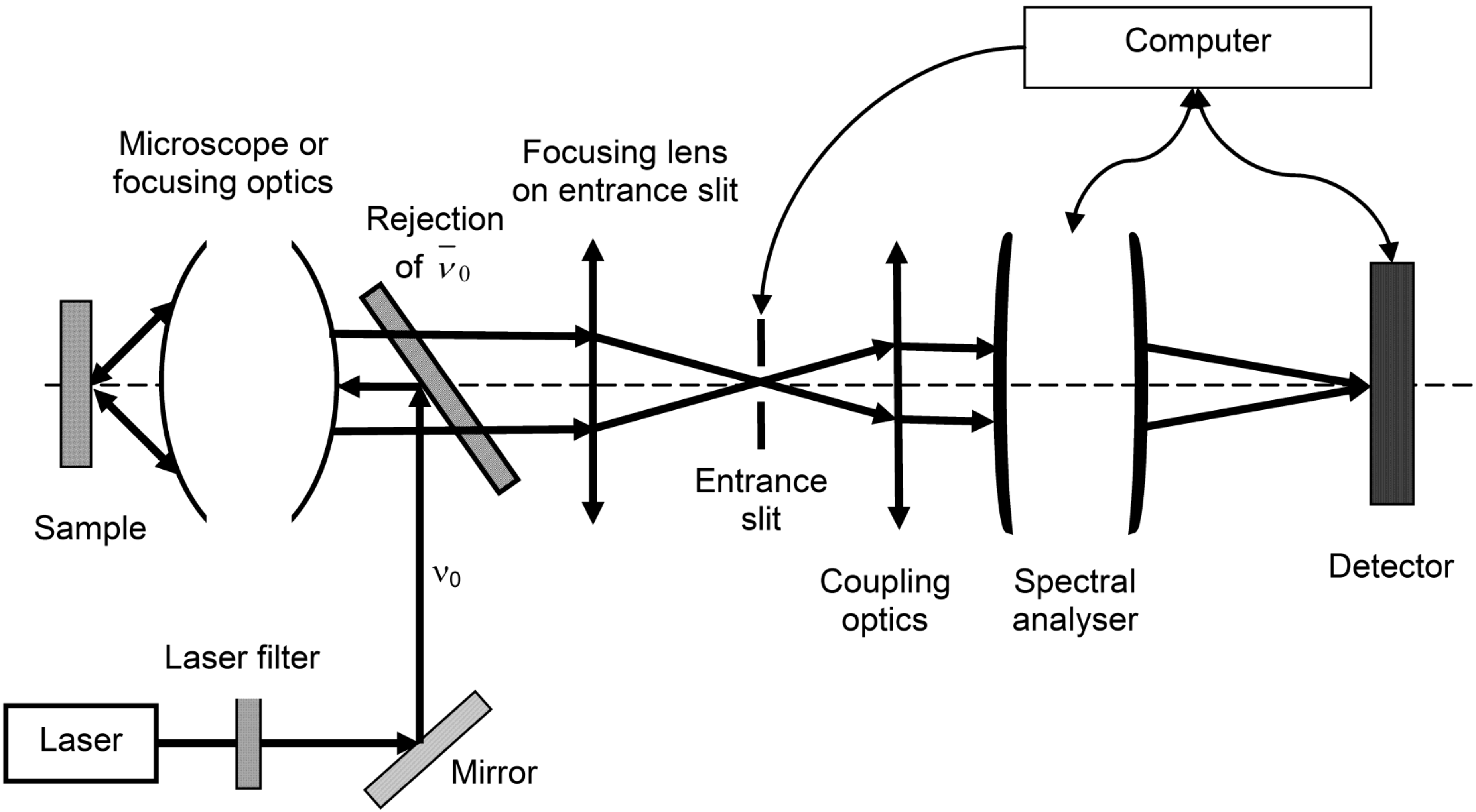
$$N_{\bar{\nu}_0,reflection} = 10^{12} \text{ to } 10^{15}$$

- high rejection of the excitation wavelength

- high transmission of the dispersive system and high spectral resolution

- high efficiency detector: high sensitivity, high dynamics

The different elements of a Raman (micro)-spectrometer



The excitation sources

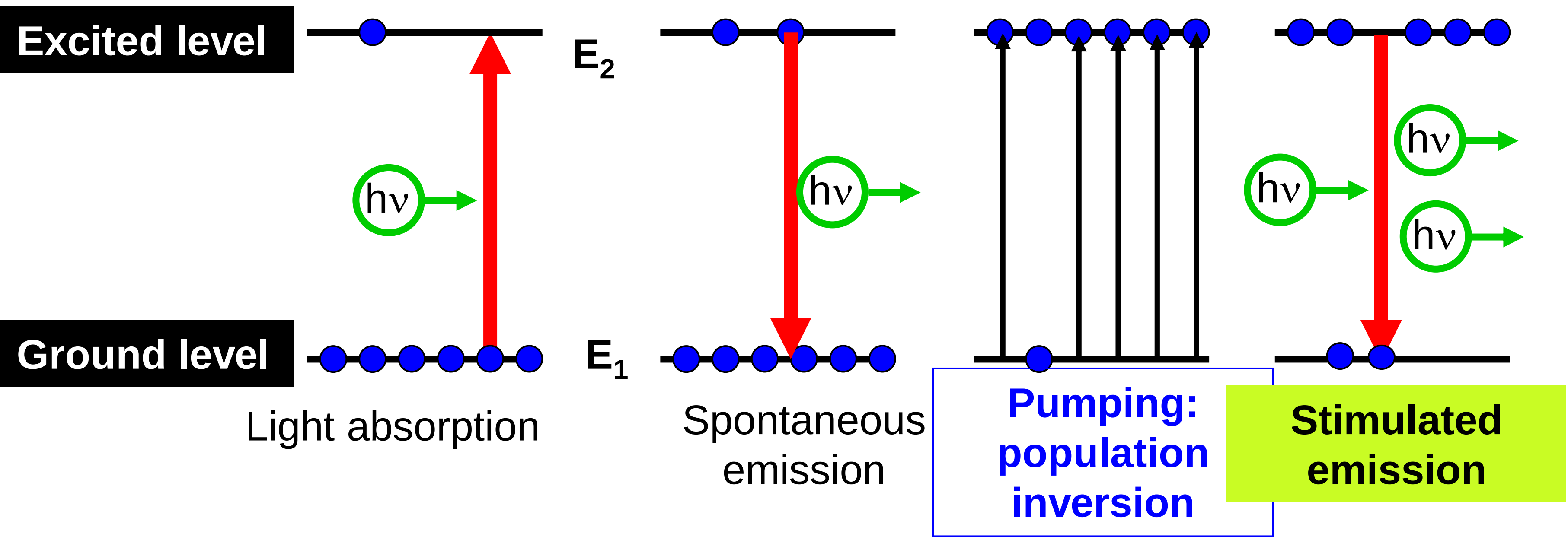
1928	1960	1963	1969	2000	2005
Sun, Hg lamp	Townes suggests the use of lasers	First laser use (Porto-Weber)	Ar^+, Kr^+	Nd-Yag 532 nm	Laser diodes
		1964 (He-Ne) on Cary spectrometer			

End of high power (1W-10W) Ar^+ / Kr^+ lasers soon ?

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)



Different materials: Gases, solids (crystals, glasses, semi-conductors), liquids
Different pumping systems.

Wavelength of lasers and laser choice

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

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

Nd-YAG$^+$: 256; 365; 532; 1064;

solid: 660; diode laser : 785

UV **V I S I B L E** **NIR**

OPSL(InGaAS): 458; 488; 514; 532; 552; 561; 568; 588; 594 nm

FIBER LASERS: 488; 515 nm

The choice of the excitation source

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

Figures of merit of laser beam

1.Frequency stability

2.Spectral width (kHZ to Ghz (8 Ghz for 488 nm Ar+ without etalon). 3 GHz = 0.1 cm^{-1}.

3. Output polarization: linear > 100/1

4. Power stability: <0.2 %

5. The quality factor, M^2:describe the deviation of the laser beam from a theoretical Hermite-Gaussian beam**. M^2<1.1**

Rejection of λ_0 and Raman lines separation

Two types of Raman spectrometers

1) FFT spectrometer: excitation in the NIR

2) Dispersive spectrometer: excitation in the UV or visible

- **either by a double (50 cm^{-1}/λ_0) or triple spectrometer (5 cm^{-1}/λ_0)**
- **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 (30-100 cm^{-1}) $/\lambda_0$**
- **edge filter: high band pass filters (30-100 cm^{-1}) $/\lambda_0$**

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 : geometrical lines separation

• **Gratings work either in transmission or in reflection**

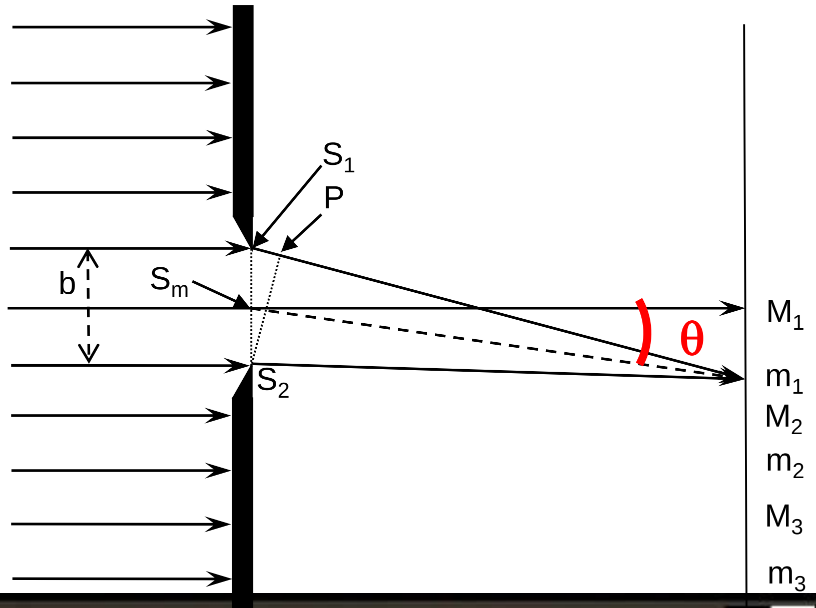
• **Transmission gratings are made of parallel elongated domains which transmit the light and opaque domains: thus they can be considered as arrangement of parallel slits corresponding to the transmission zones**

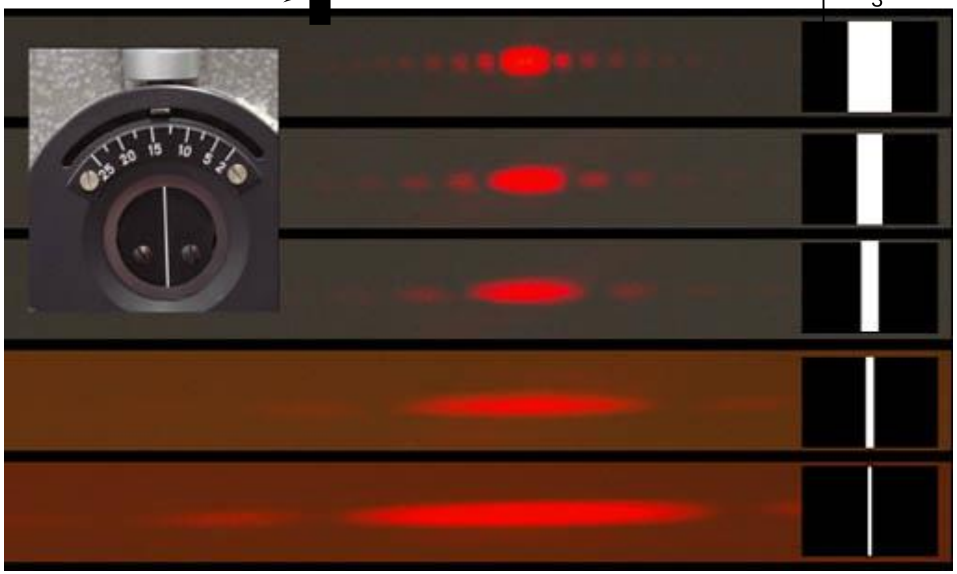
• **Reflection gratings are an assembly of elongated mirrors acting as slits; the grooves are the opaque parts.**

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

1 SLIT – N SLITS

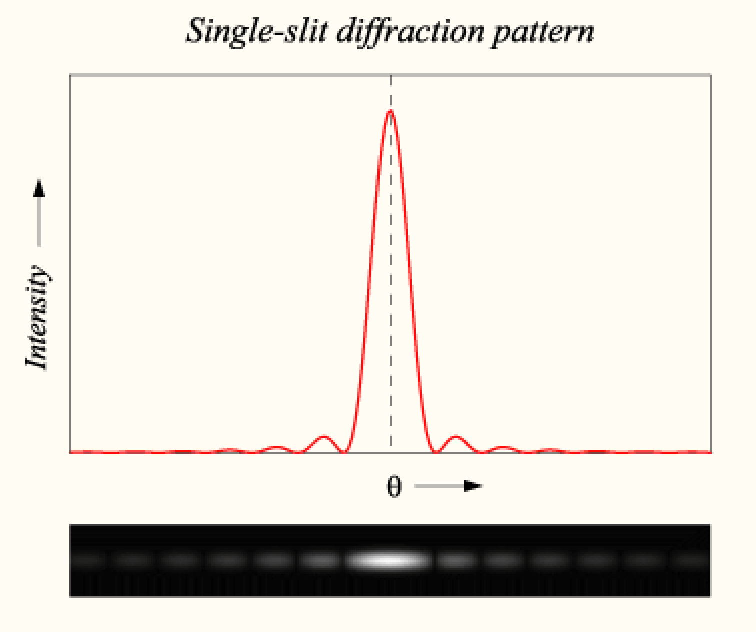
GRATING THEORY: 1 single slit (Fraunhoffer slit)



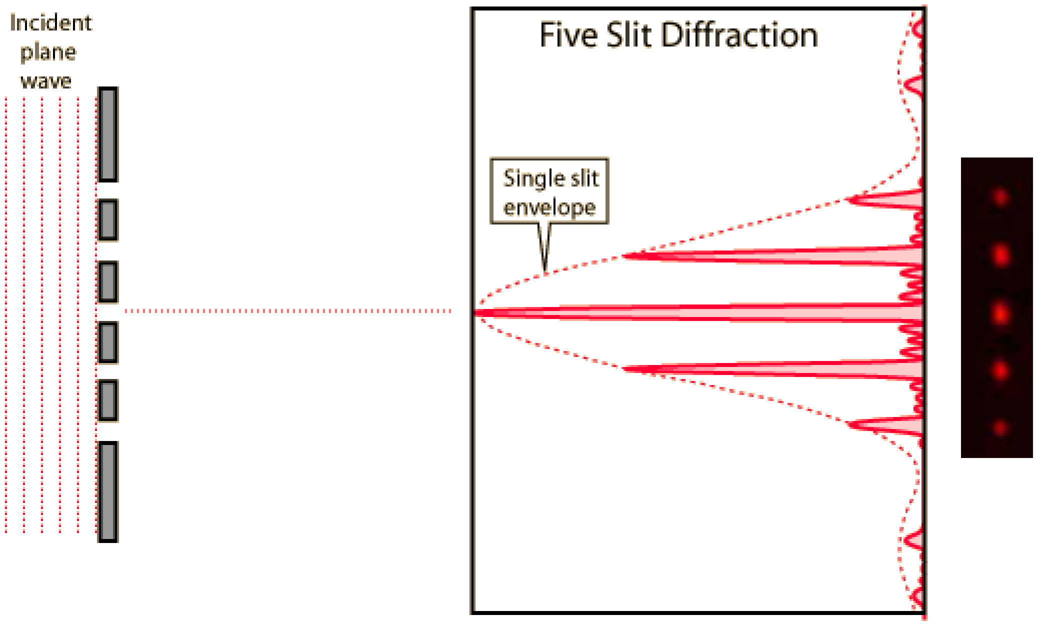


$$I = I_0 \times \left(\frac{\sin\beta}{\beta} \right)^2$$

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



GRATING THEORY: N slits



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

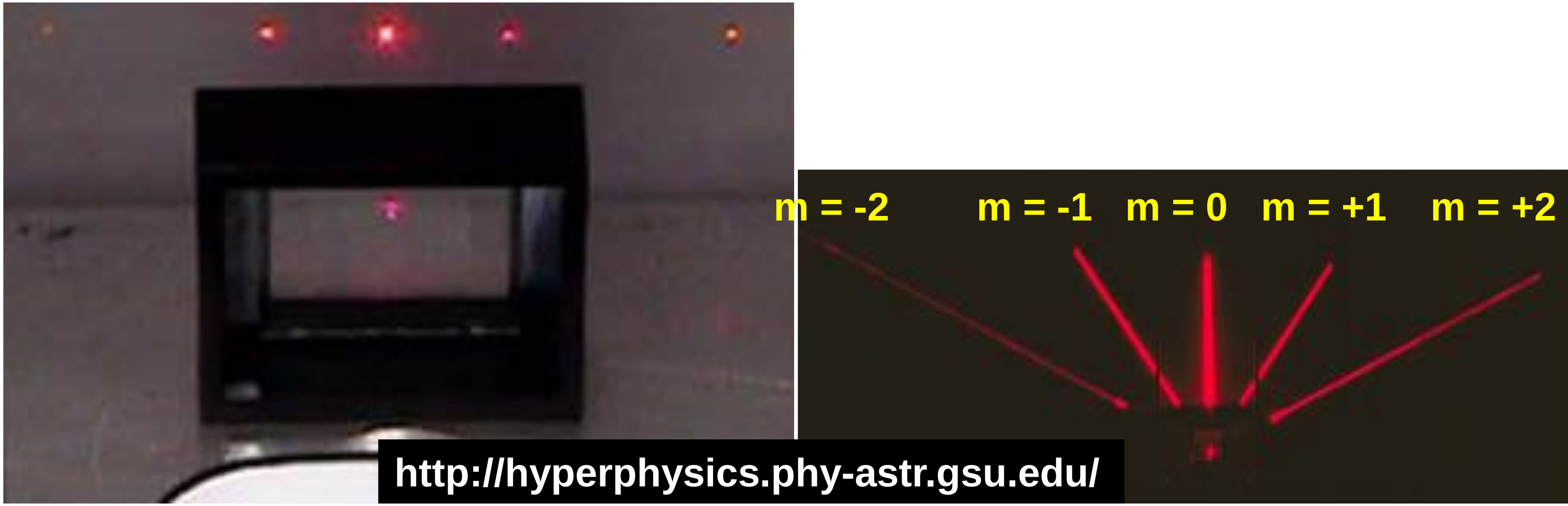
Single slit term enveloppe

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: grating equation



$$\frac{(\sin N\gamma)^2}{(\sin\gamma)^2}\ \text{maximum for}\ \gamma = m\times\pi = \frac{\pi\times d\times\sin\theta}{\lambda}$$

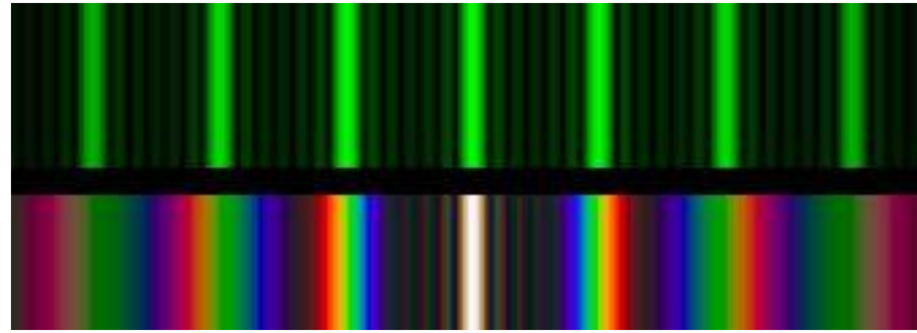
$$\boxed{d\times\sin\theta = m\times\lambda = 0,\ \lambda,\ 2\lambda,\ 3\lambda,\ldots m\lambda}$$

GRATING THEORY: monochromatic/polychromatic

http://h2physics.org

Monochromatic diffraction

Polychromatic diffraction



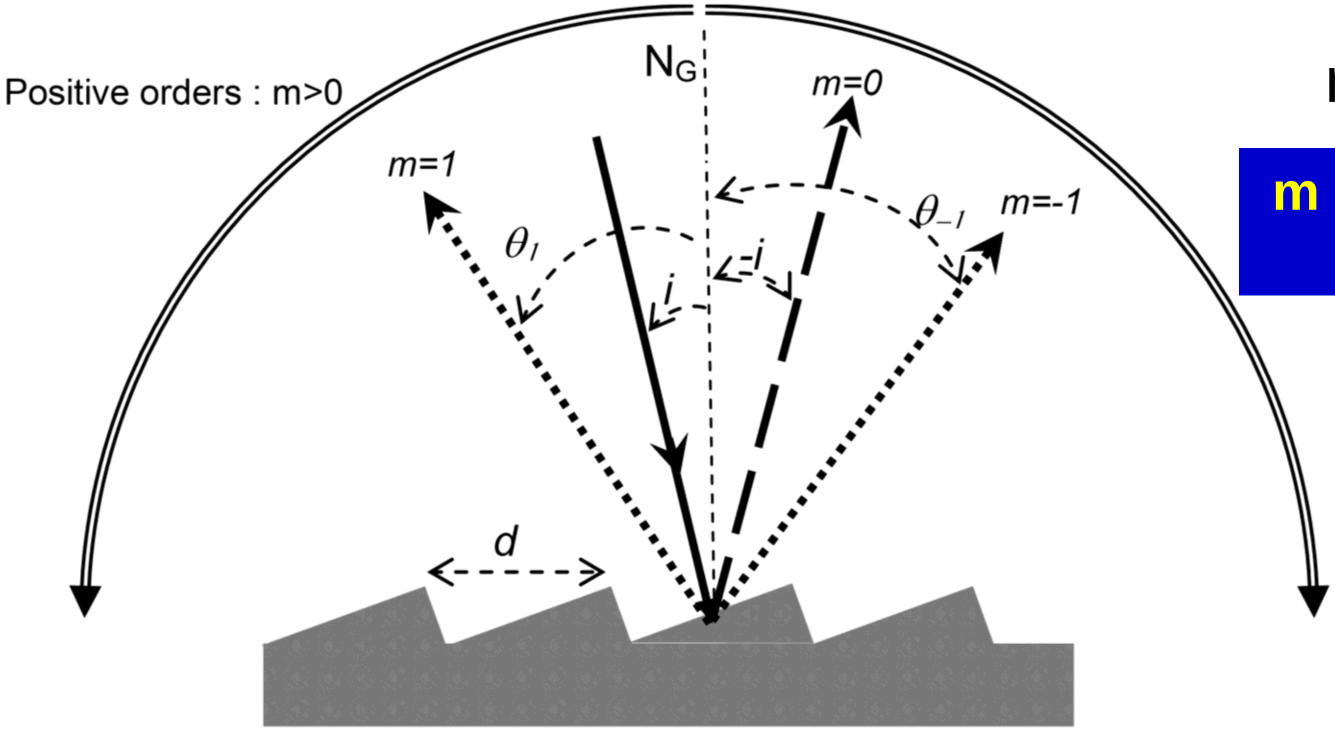
m =0

Mirror, specular reflection

λ_{laser} = 514.535 nm Raman spectrum; m=1;

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

m = 1 for Czerny-Turner spectrometers

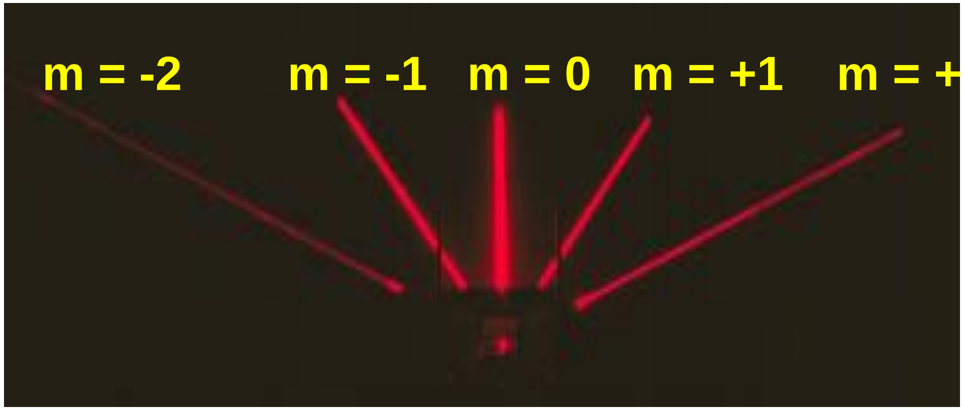
Groove density /mm
G = 1/d = 150-3000 to 6000 (VPHG)

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

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

at constant m and G, diffraction angle increases with wavelength.

GRATING THEORY: angular dispersion



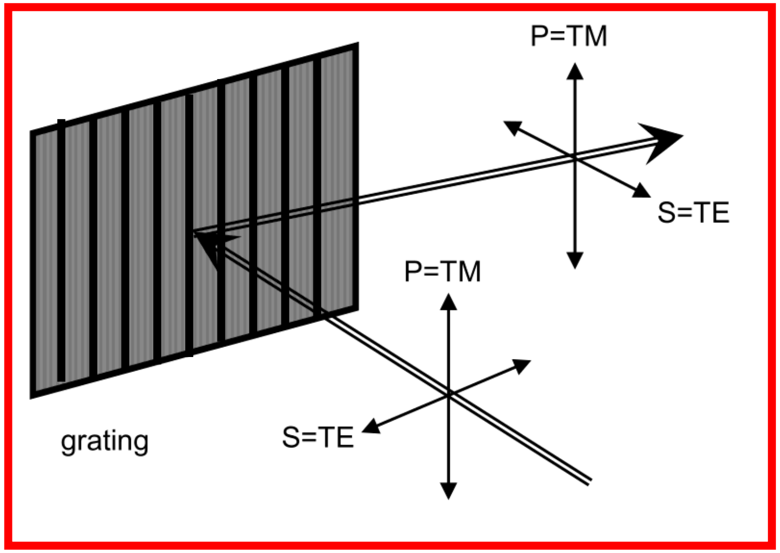
$$l \times (\sin i + \sin\theta) = m\lambda \quad \text{and} \quad AD \equiv \frac{d\theta}{d\lambda}$$

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

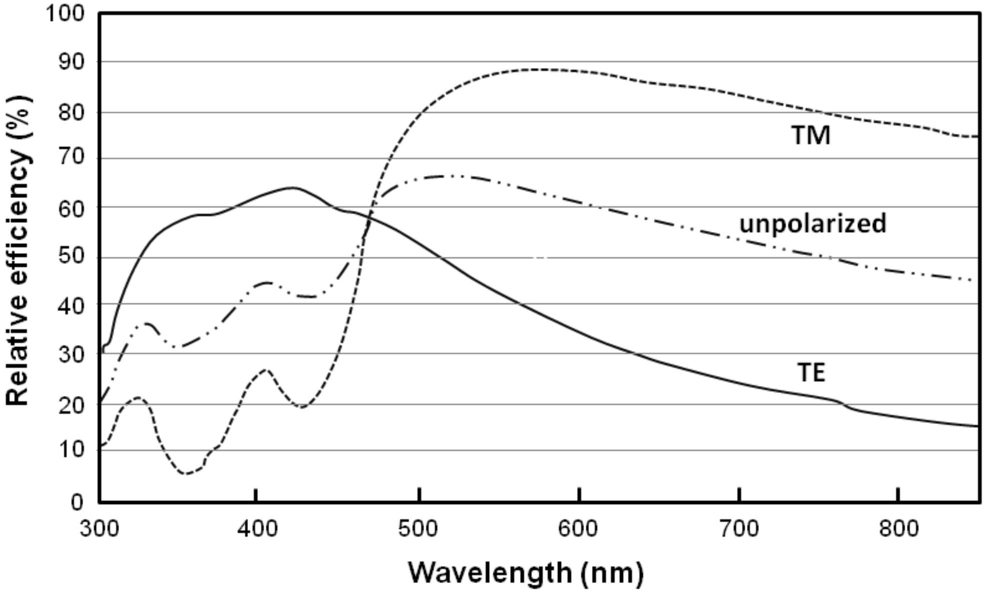
AD : proportional to m and G

AD increases for higher Stokes wavenumber

GRATING THEORY: line intensity



The polarization state of the incident radiation

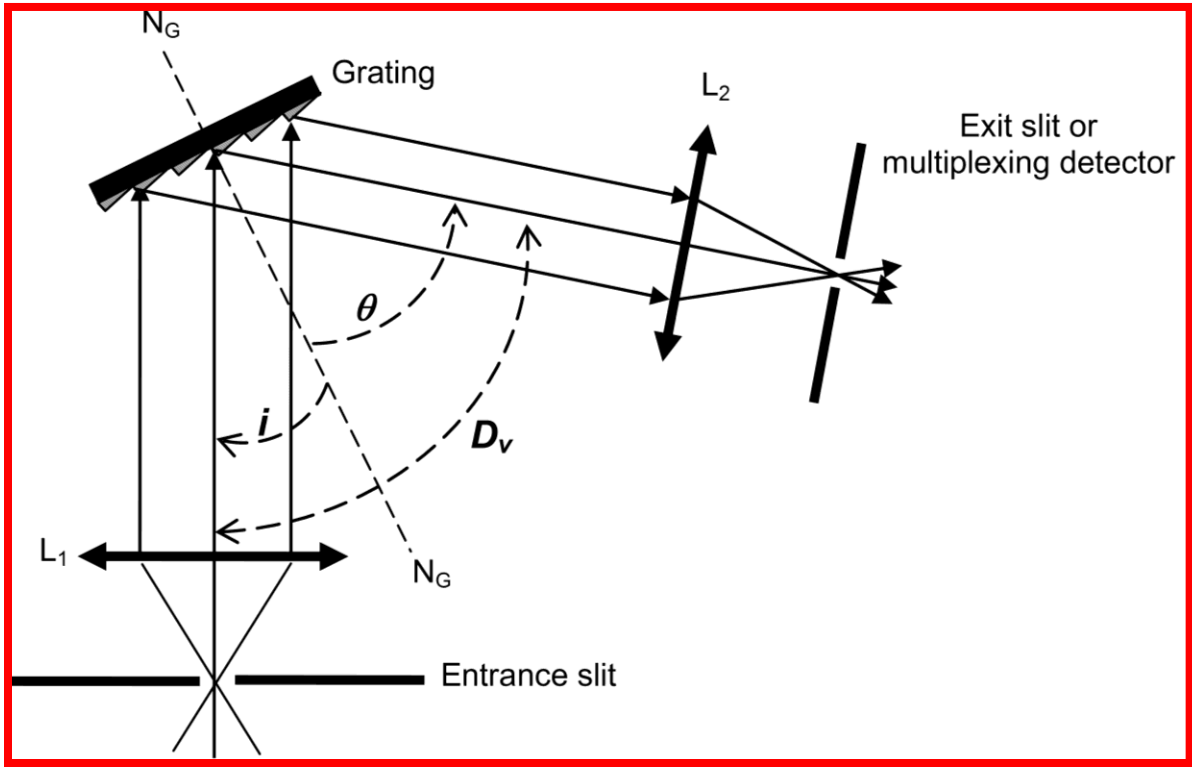


Efficiency curves are function of wavelength
Relative = Diffracted(λ)/Reflected(λ)
by mirror with same coating

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

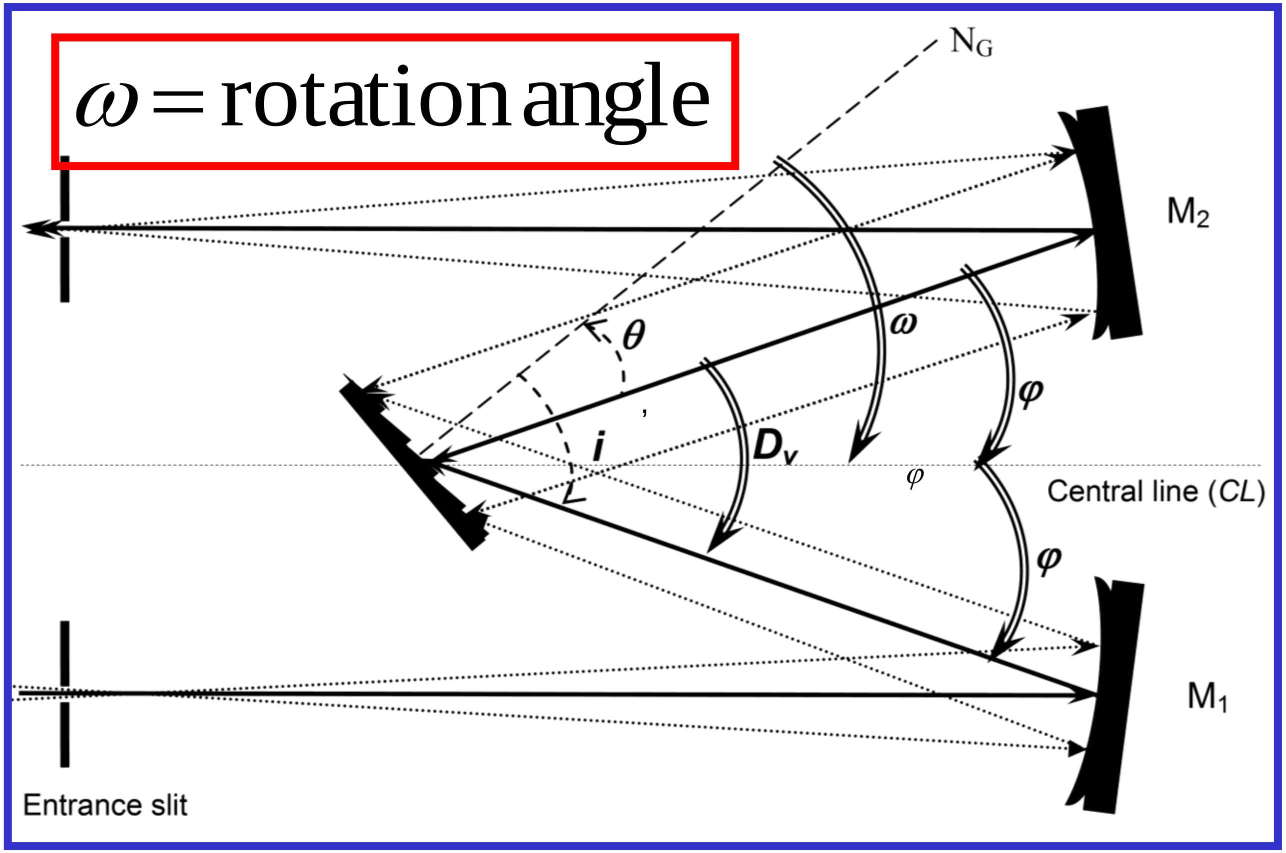
$$D_v = \theta - i$$

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

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

CZERNY-TURNER SPECTROMETER:rotating grating

$\omega = \text{rotation angle}$



Angular relationships

$\varphi = D_v / 2$

$2\varphi = i - \theta$

$\theta = \omega - \phi$

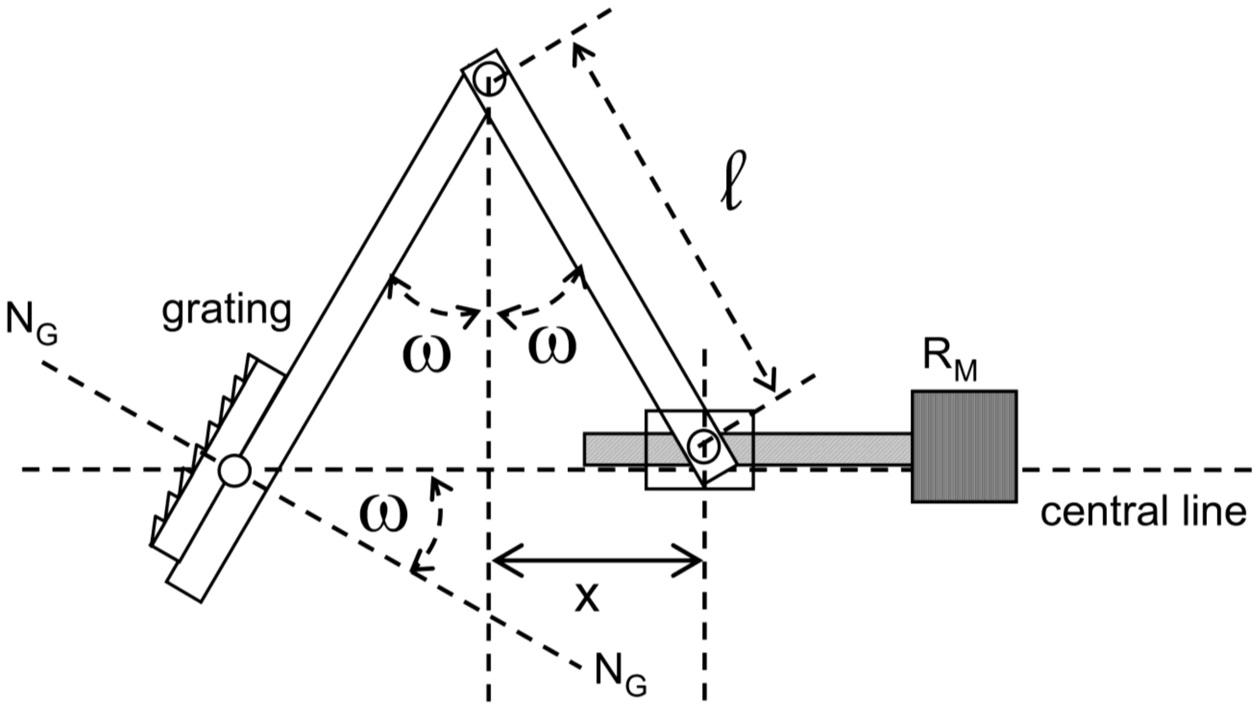
$i = \varphi + \omega$

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

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

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

CZERNY-TURNER SPECTROMETER: sine bar



$$\sin\omega = x/l$$

$$\Delta(\sin\omega) = \Delta x/l$$

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

$$\Delta\lambda = 2\times(\Delta x/l)\times\frac{\cos\varphi}{Gm}$$

DETECTORS

1928 | 1940 | 1950 | 1964-1967 | 1978 | 1986 | 2016

Eyes, photographic plate

Photomultiplier tube

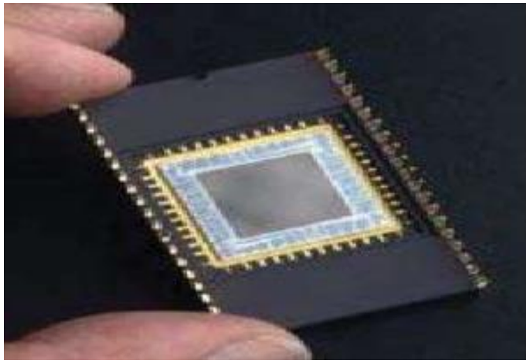
Image Intensifier Vidicon Camera

Intensified Photodiode Array

CCD / EMCCD CMOS-SPAD

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) or smaller in size

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

200-1100 nm

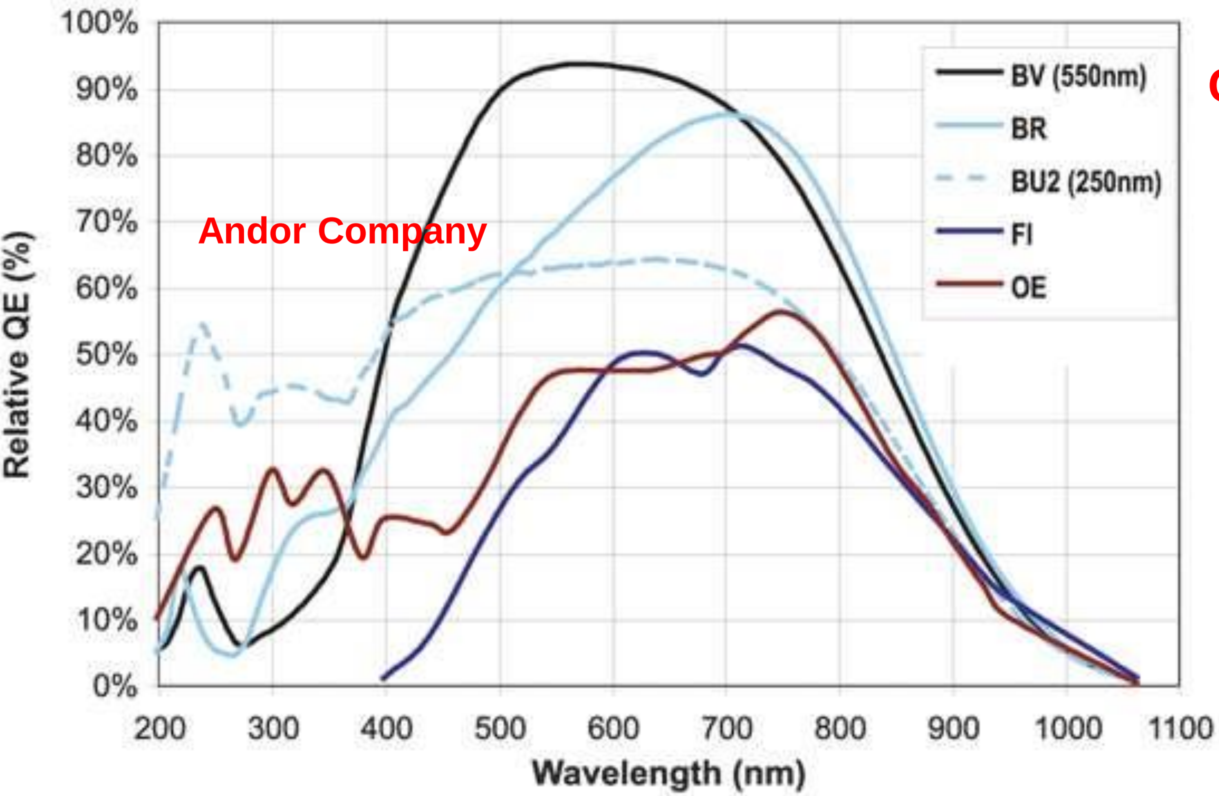
Front or back illuminated: consequences on quantum efficiency.
UV or non-UV coated

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

EMCCD: Electron Multiplying CCD. No read-out noise limitation. Used for very weak signals from spectra with quasi neal background (no fluorescence). Rare in Earth sciences materials ! Raman imaging with short integration time.

CCD: figures of merit

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



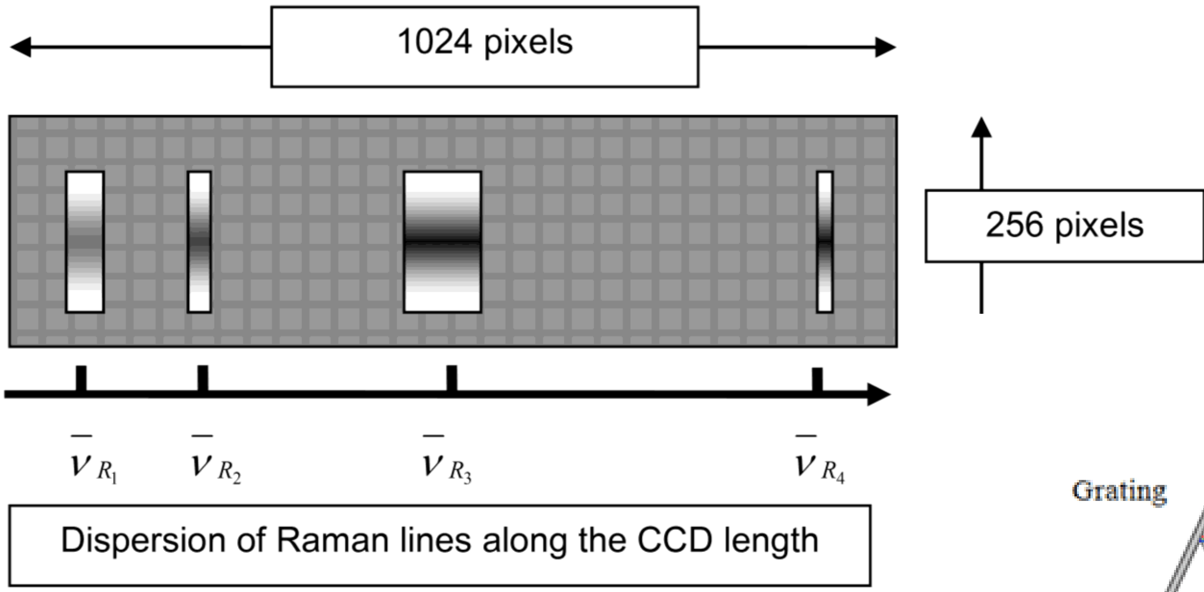
Criterion choice as a function of the excitation source: visible, UV, red

highest Q_E,

low dark current,

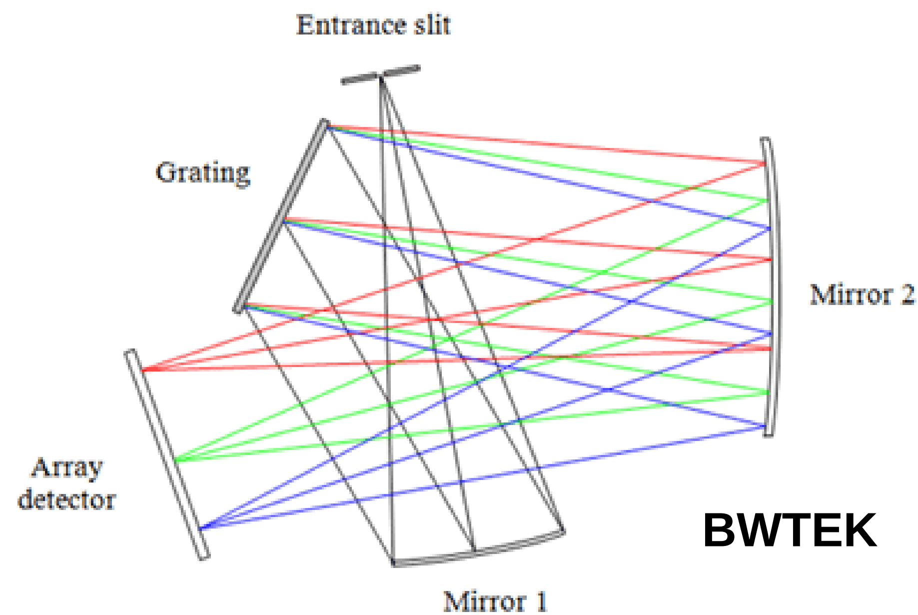
low read-out

CCD: intensity and wavenumber coding



Intensity: vertical binning of pixels

BWTEK

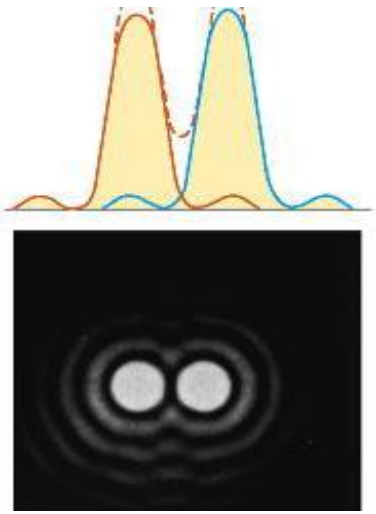


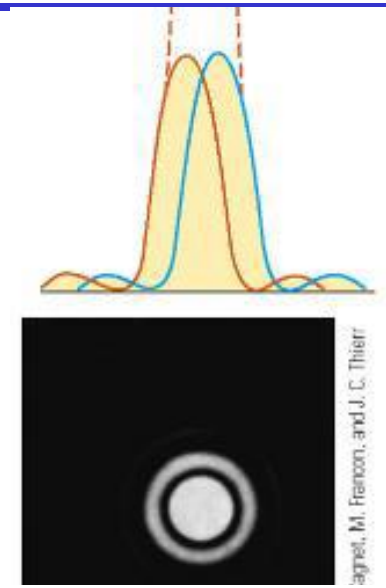
BWTEK

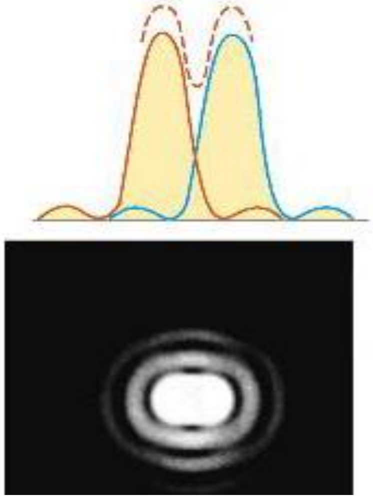
Linear dispersion for the different radiations: deduced from the angular dispersion produced by the grating => $\overline{\nu} = f(LD)$

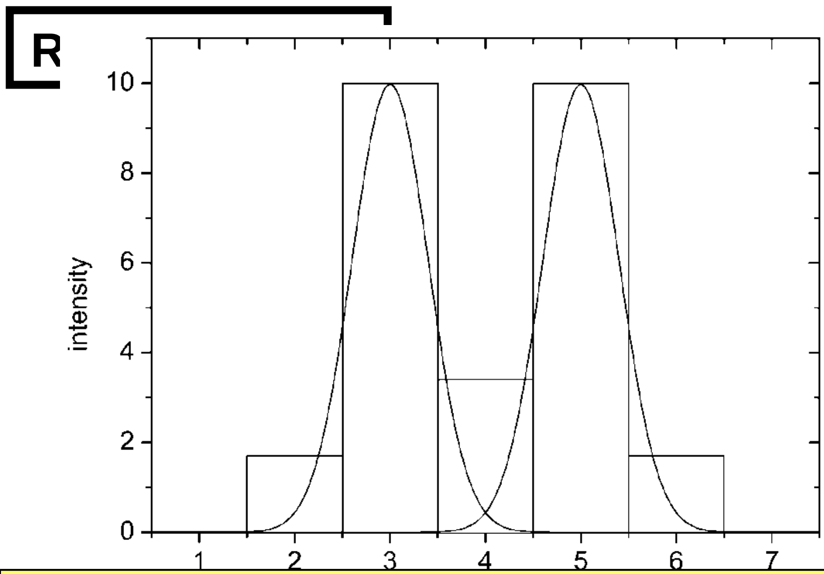
CCD: pixel limiting resolution

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









Unresolved lines

Just resolved line: Rayleigh criterion:

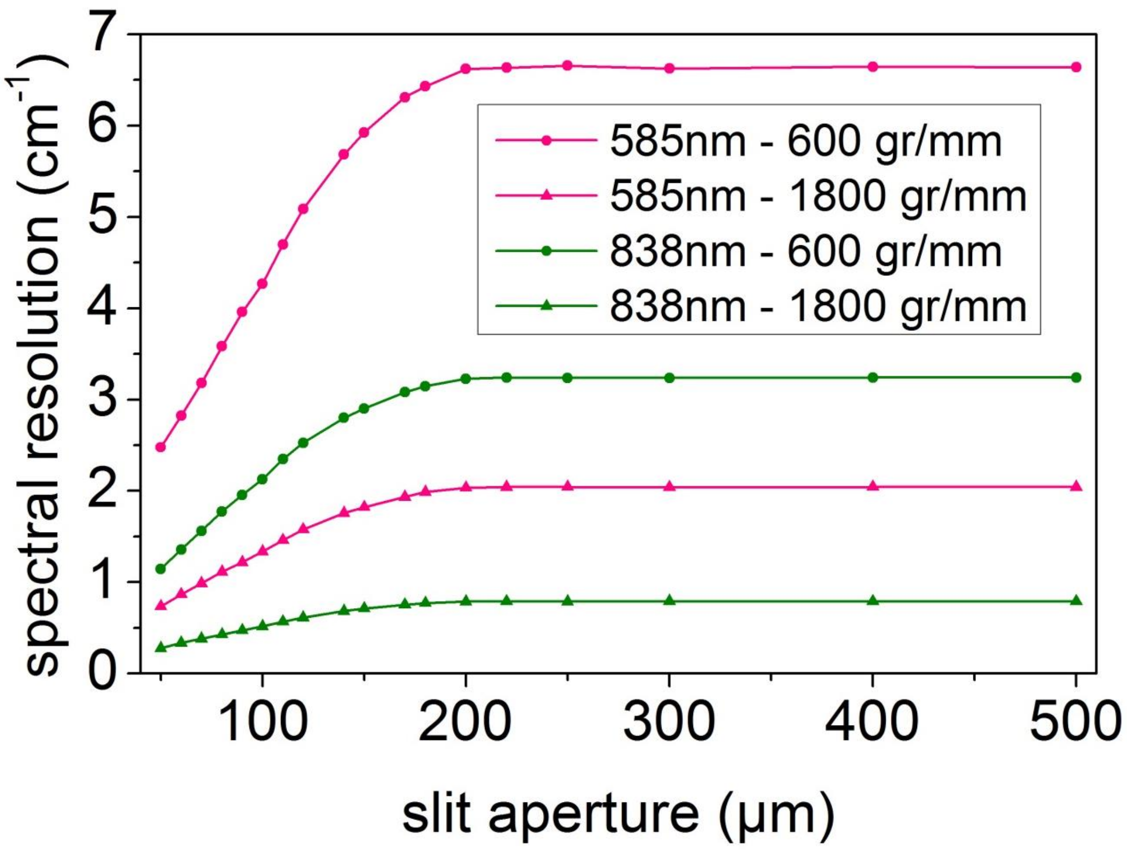
Limiting resolution of the spectrometer including the detector

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

Spectral resolution of a Raman spectromer

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

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



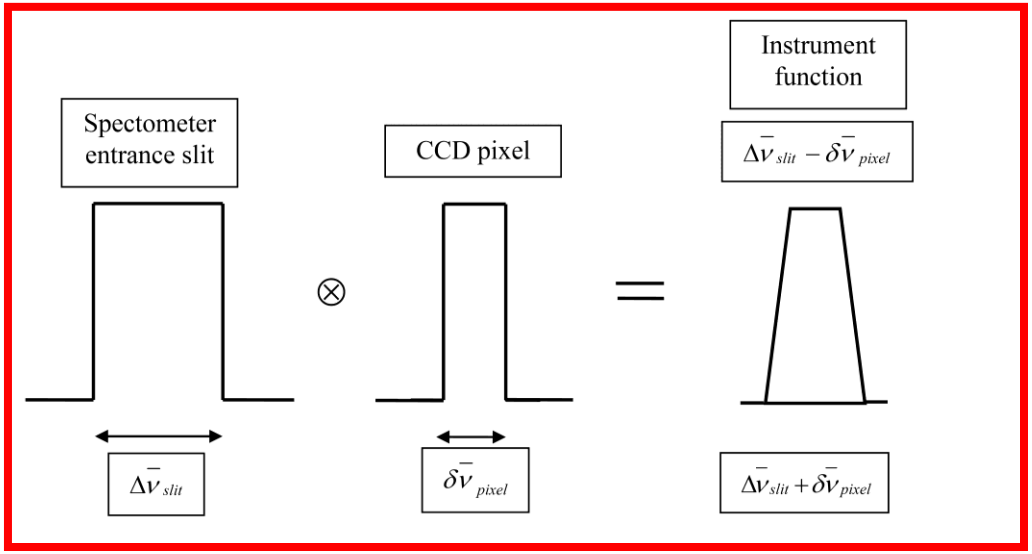
Procedure:

1. **Spectrum of atomic emission line**
2. **Profile fitting**
3. **Measurement of FWHM**

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 function **Apparatus**



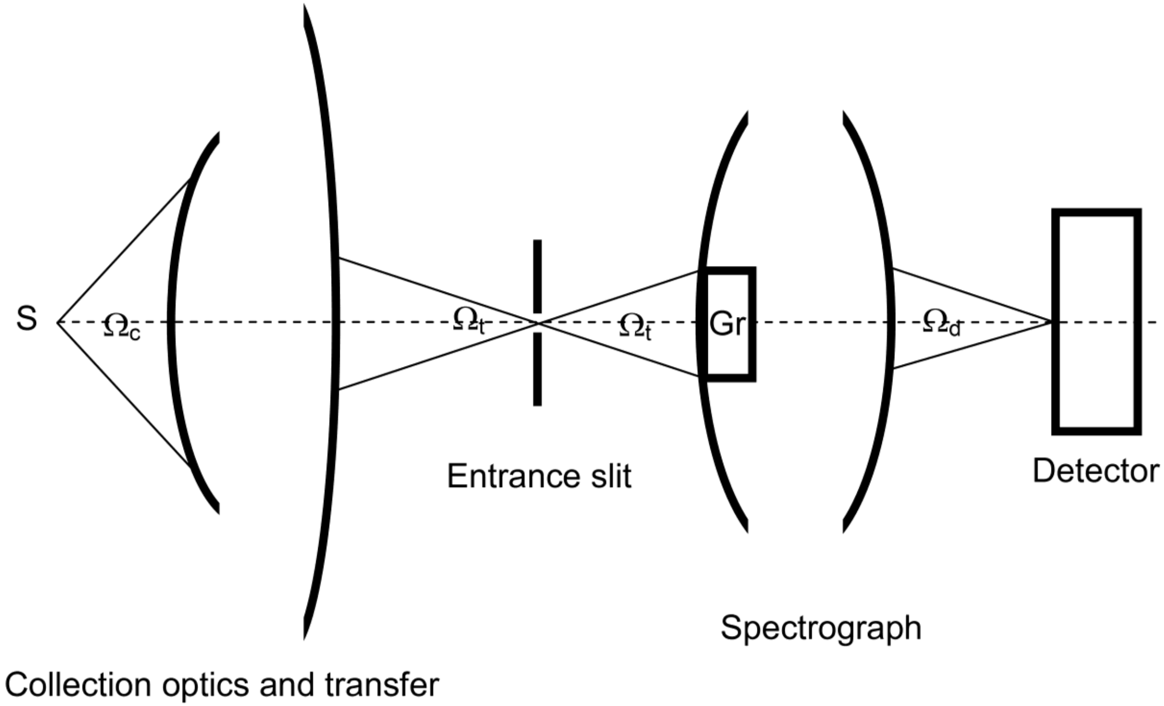
Modification of the band profile by the instrument.

Lorentzian => Gaussian, mixtures

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

Instrumental resolution < 1/5 FWHM of natural profile

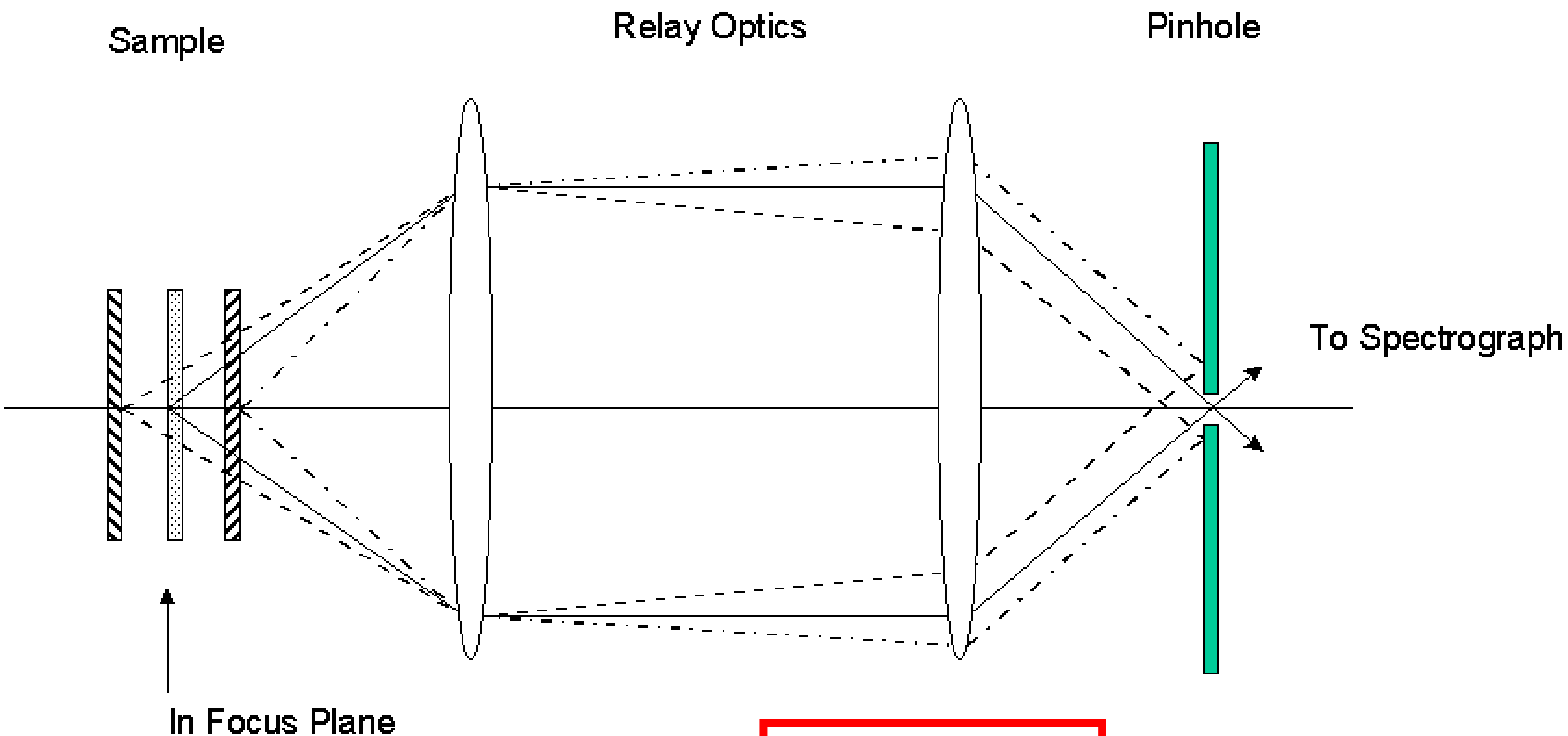
Coupling sampling system with spectrometer



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 should be constant

Spatial resolution of confocal Raman spectrometers



Axial resolution

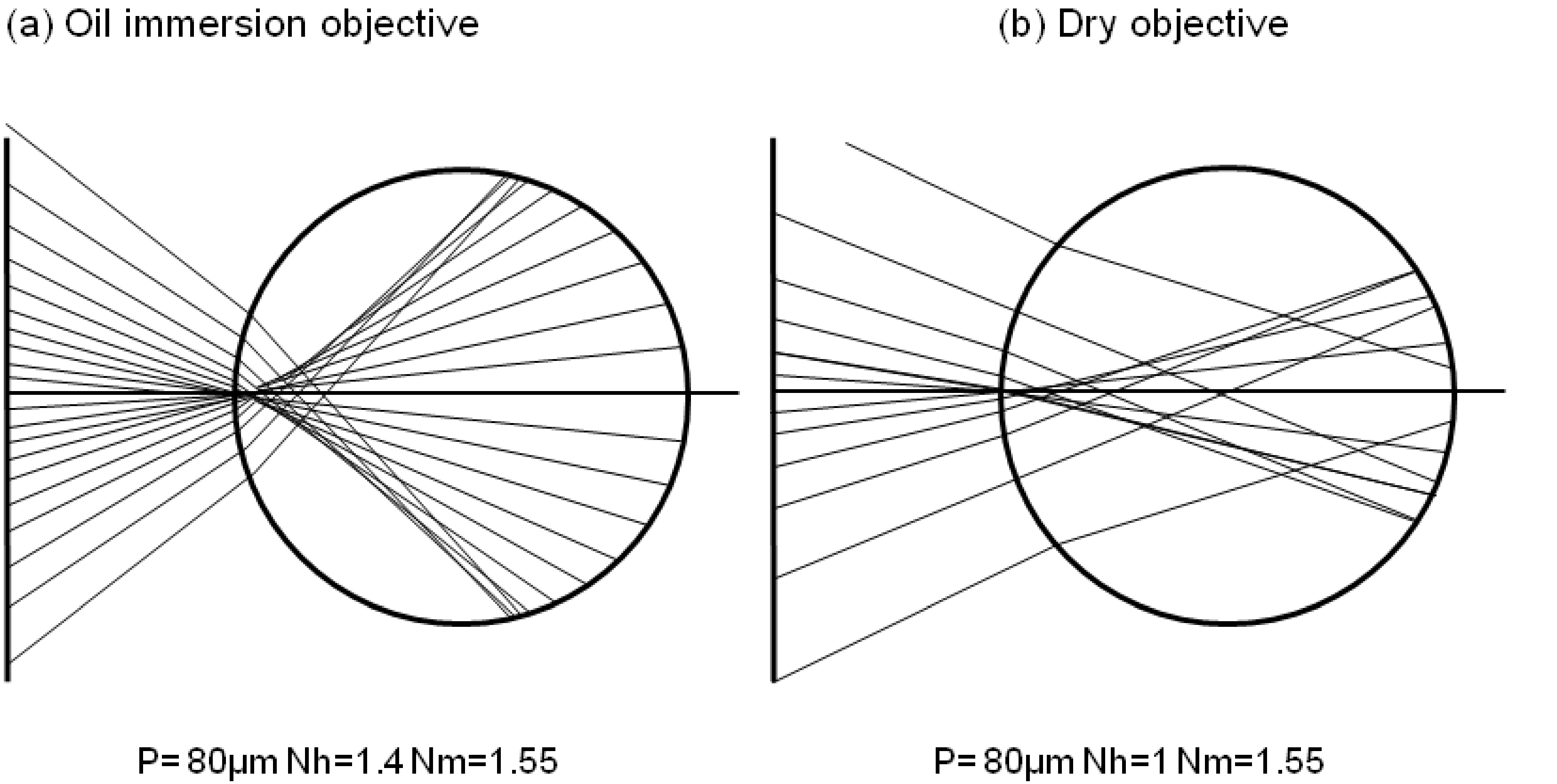
$$\delta z = \frac{1.4\lambda}{(N.A.)^2}$$

Lateral resolution

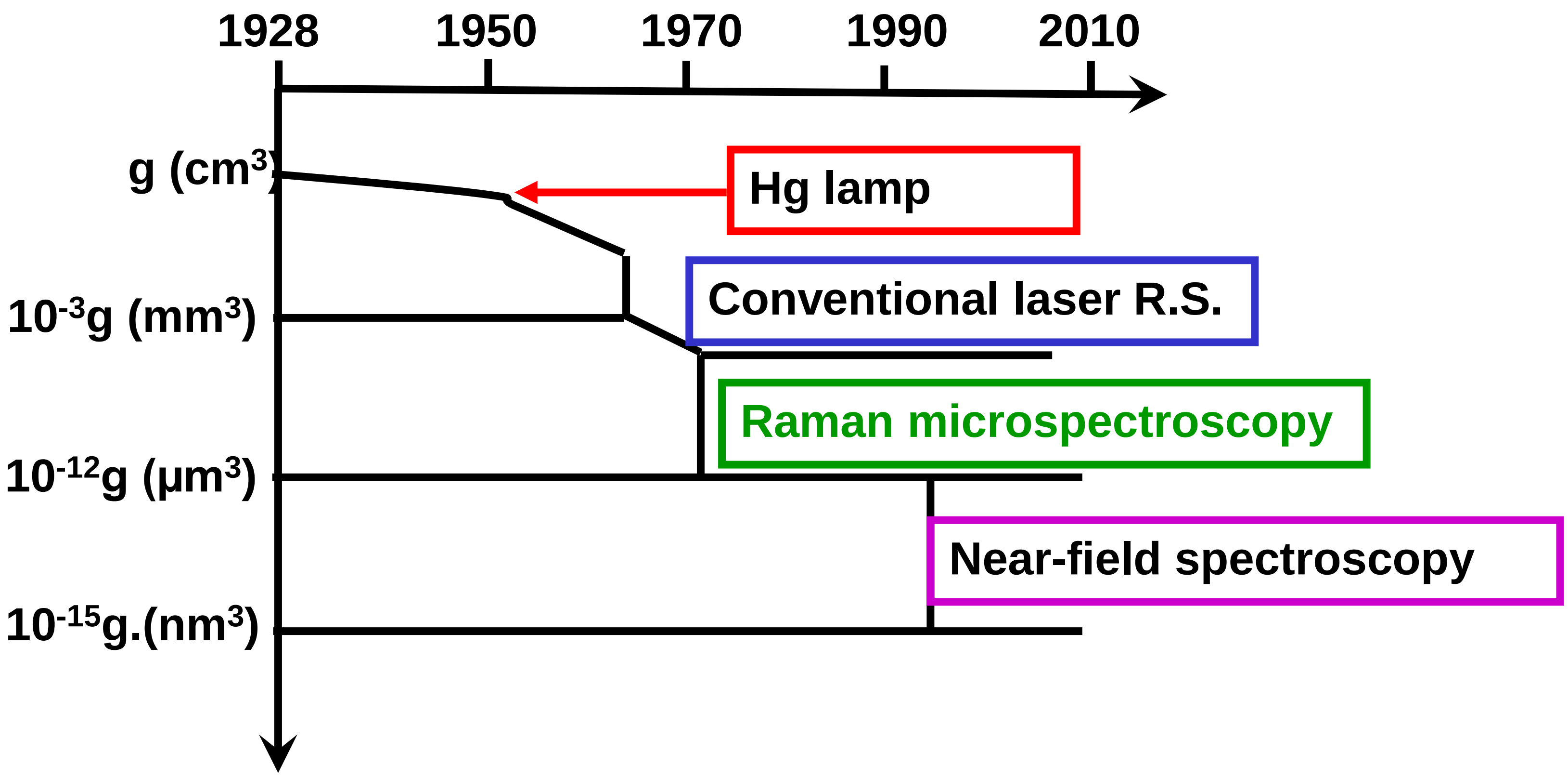
$$\delta xy = 0.46\lambda/(N.A.)$$

Degradation of spatial resolution by refraction

Use of immersion objective



RAMAN SAMPLING VOLUME

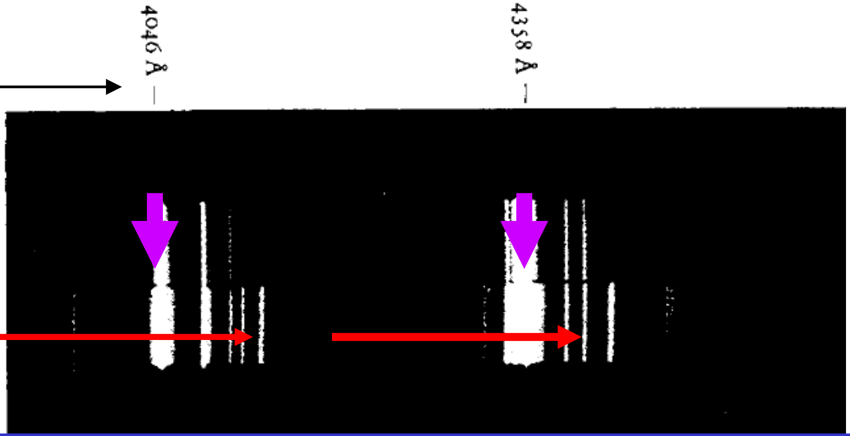


From Delhaye and Dhamelincourt

1928: First Raman experiment

Hg excitation lines

Raman lines



2016 :Highly simplified « portable » systems:
Earth surface, Art objects,
Mars surface (EXOMARS mission, Supercam system)