Optical spectroscopy

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Optical spectroscopy

Outline

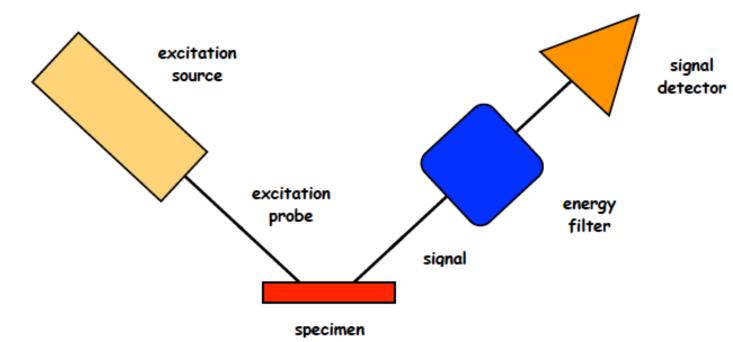
- 1. Introduction
- 2. Excitation sources
- 3. Dispersive elements
- 4. Photodetectors
- 5. Special spectroscopy methods:
 - 1. Raman spectroscopy
 - 2. Cathodoluminescence
- 6. Applications

Optical and other spectroscopy techniques

Goals of optical spectroscopy:

- Characterize the electronic energy levels of a system by exciting electrons and observing the energy of emitted light
- Excitation can be done by light (photo-luminescence, **PL**) or by electrons (cathodoluminescence, **CL**)
- In some systems, optical absorption is measured (photoluminescence excitation spectroscopy, PLE, absorption spectroscopy, or spectrophotometry/FTIR)

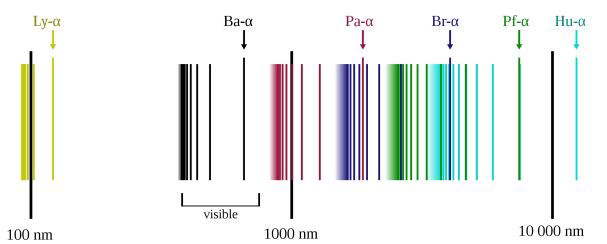
- Other related techniques:
 - Raman spectroscopy (inelastic scattering of photons)
 - EDS (emission of X-ray photons, excitation by electrons)
 - AES (emission of electrons, excitation by UV/X-ray photons)
 - **EELS** (energy loss of scattered electrons)

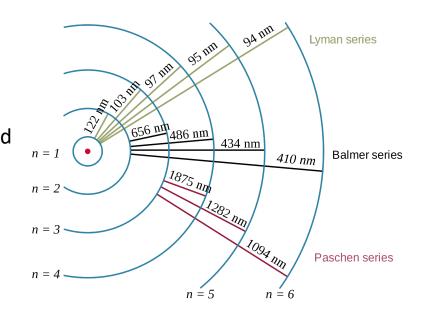


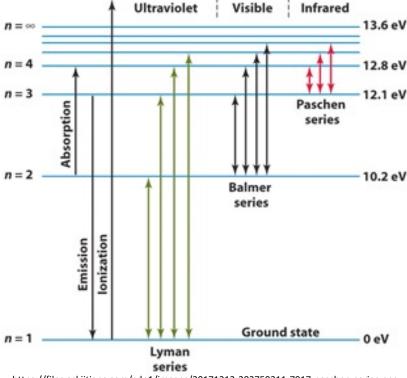
https://en.wikipedia.org/wiki/Hydrogen spectral series

Example: The Hydrogen atom

- The electron in the Hydrogen atom can occupy any of many energy levels, from its ground state (n=1, defined here at E=0 eV), to a free electron (ionized atom), at n=∞ and E=13.6 eV.
- Excitation by an electron (e.g. in a discharge tube) or a photon of sufficient energy can excite the electron to any level, from which it will fall to a lower level (event. to the ground state) by the emission of a photon.
- The photon energy corresponds to the energy difference between the levels, and can thus be in the UV, visible, or IR range.
- The excitation energy should be sufficiently high! E.g. to see the full Lyman series, we need to excite with deep UV (E>13.6 eV or λ <90 nm). The emitted photon energy will be between 10.2 and 13.6 eV. The Balmer series will show a photon energy between 1.9 and 3.4 eV (excitation E>3.4 eV, λ <360 nm), etc.



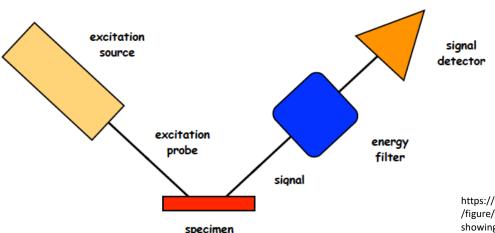




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Energy range

- Important classification: according to wavelength (energy) range
- The electronic energy levels of the system determine the wavelength of emitted light:
 - Near UV range (100< λ <400 nm): E = 3-12 eV (electronic levels in atoms, insulators)
 - Visible near-IR range ($400 < \lambda < 1500 \text{ nm}$): E = 0.8-3 eV (electronic levels in semiconductors)
 - IR range (1.5< λ <10 µm): E = 0.1-0.8 eV (vibration/rotation levels in molecules, dopants and subbands in semiconductors)
- The energy range determines the type of excitation source and detector to be used



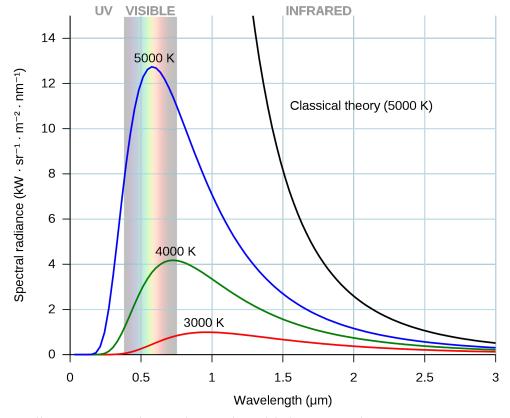
Photon energy (eV) 10⁻¹ 1000 100 Frequency (Hz) Wavelength 100 μm 10 μm 1 μm :100 nm 10 nm 1 nm

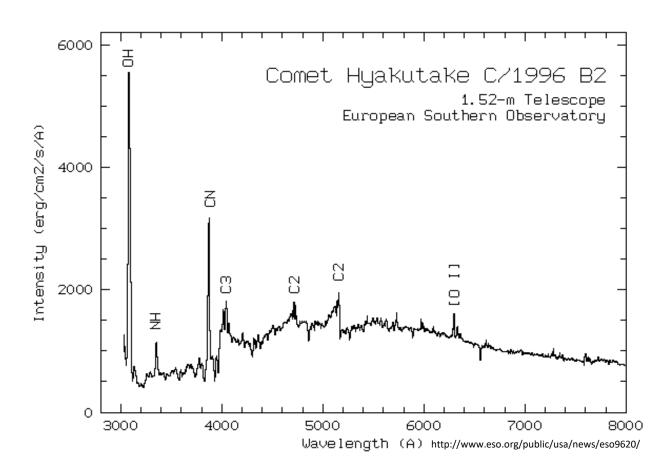
https://www.researchgate.net/profile/Roland_Macana/publication/326705984 /figure/fig2/AS:669064661831684@1536528854132/Electromagnetic-spectrum-showing-the-energy-of-one-photon-the-frequency-and-wavelength.ppm

Typical applications of optical spectroscopy(1)

In astronomy:

- Blackbody radiation allows to measure the temperature of stars, their velocity (Doppler shift) and distance.
- Absorption lines allow to identify elements and molecules in the atmosphere of stars and planets.
- Reflected light spectra can show the composition of comets.



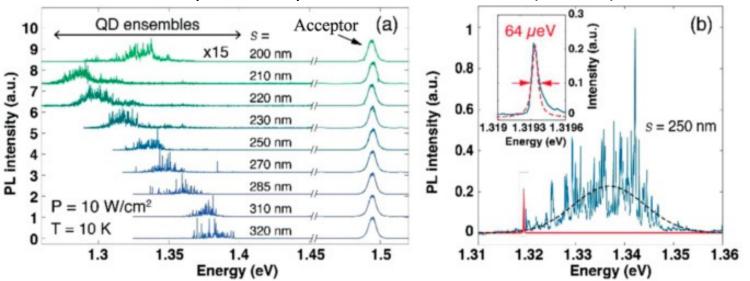


Typical applications of optical spectroscopy(2)

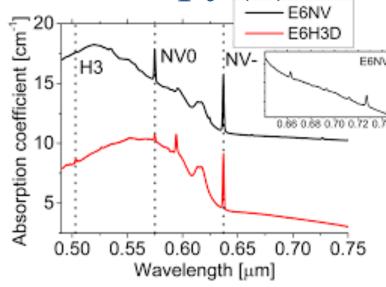
In semiconductor research:

- Measurement of energy gap in compound semiconductors.
- Measurement of light emission of LEDs and laser diodes.
- Study of impurities and and defects in semiconductors.
- Physics research of semiconductor nanostructures: Quantum dots, nanowires, layered 2D semiconductors, graphene, nanotubes,...

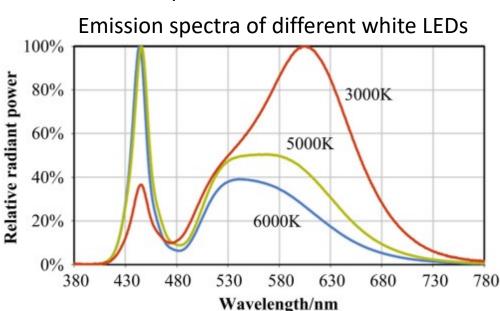




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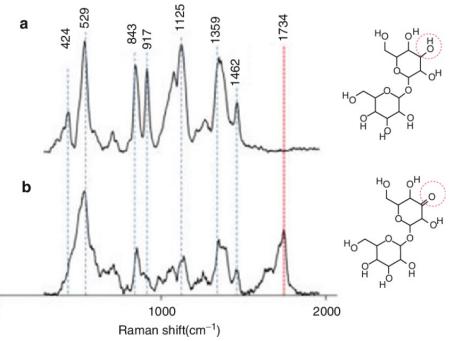
Emission spectra of NV centers in diamond

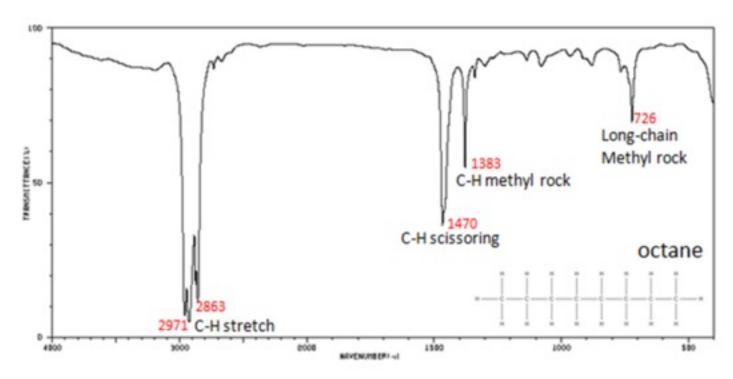


Typical applications of optical spectroscopy(3)

In (bio)chemistry:

- Identification of elements by atomic emission spectroscopy (AES).
- Identification of molecules by UV-VIS-IR absorption spectroscopy.
- Characterization of chemical reactions by ultrafast spectroscopy.
- Investigation of chemical bonds by Raman spectroscopy.





Typical applications of optical spectroscopy(4)

In police work:

• Quick automatic identification of drugs, explosives and other substances by UV-VIS-IR absorption spectroscopy or VIS Raman spectroscopy.





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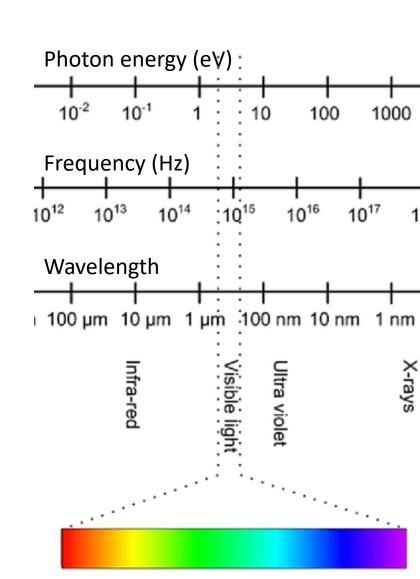
Optical spectroscopy: Energy vs. Wavelength

- Most optical spectroscopy is done with dispersive optics: prisms, gratings, etc.
- The link between energy and wavelength: $E=h\nu$ and $\nu=c/\lambda$, or: $E(eV)=hc/e\lambda=1.24/\lambda(\mu m)$
- Typical photon energy in the visible range: $\lambda \approx 500$ nm, E ≈ 2.5 eV
- Resolution depends on the derivative of the dispersion: $\Delta E = \Delta \lambda \cdot dE/d\lambda = -1.24 \cdot \Delta \lambda/\lambda^2$
- It's much more precise to measure optical wavelength than photon energy!
 - Example: In the visible range (e.g. $\lambda \approx 500$ nm) we can easily measure $\Delta \lambda = 5$ pm, equivalent to $\Delta E = 25$ μeV . It's difficult to find a photon detector with similar energy resolution!
- Particle (e.g. electron) and X-ray spectroscopy is usually done with energy-dispersive instruments or direct energy-sensitive detectors (Si or Ge diodes etc.). It's possible to measure energies of 1-10 keV with a precision of 1-2 eV.
- Thermal effects (phonons): At room temperature E = 26meV, which can cause spread in detected energy. It might be useful to cool the sample! Detectors might need cooling too.
- In Raman and IR spectroscopy, it is customary to use energy units called Wavenumber: $\sigma=1/\lambda$ (unit=cm⁻¹). So for $\lambda=500$ nm, $\sigma=20,000$ cm⁻¹; at $\lambda=5\mu$ m, $\sigma=2,000$ cm⁻¹.
- The unit conversion is: $E(eV)=(100hc/e)\cdot\sigma=1.24\cdot10^{-4}\cdot\sigma$.

Optical spectroscopy: Energy vs. Wavelength

• Table of unit conversions:

	Wavelength	Wavenumber	Frequency	Photon energy
Symbol $\lambda[nm]$		σ [cm^{-1}]	ν [<i>Hz</i> ,]	$E_p[eV]$
sion	λ	$10^7/\lambda$	$3\cdot 10^{17}/\lambda$	1224/λ
conver	10 ⁷ /σ	σ	$3 \cdot 10^{10} \cdot \sigma$	$1.22 \cdot 10^{-4} \sigma$
Factor of conversion	$3 \cdot 10^{17} / v$	3.33 · 10 ¹¹ v	ν	$4.1 \cdot 10^{-15} v$
Facto	$1224/E_p$	$8197 \cdot E_p$	$2.44 \cdot 10^{14} E_p$	E_p
Ŋ	200	$5 \cdot 10^4$	$1.5\cdot10^{15}$	6.12
Examples	500	$2 \cdot 10^4$	$6 \cdot 10^{14}$	2.45
மி	1000	104	$3 \cdot 10^{14}$	1.224



© B. Dwir IPHYS EPFL 2024 Optical spectroscopy: Experimental setup – micro-PL

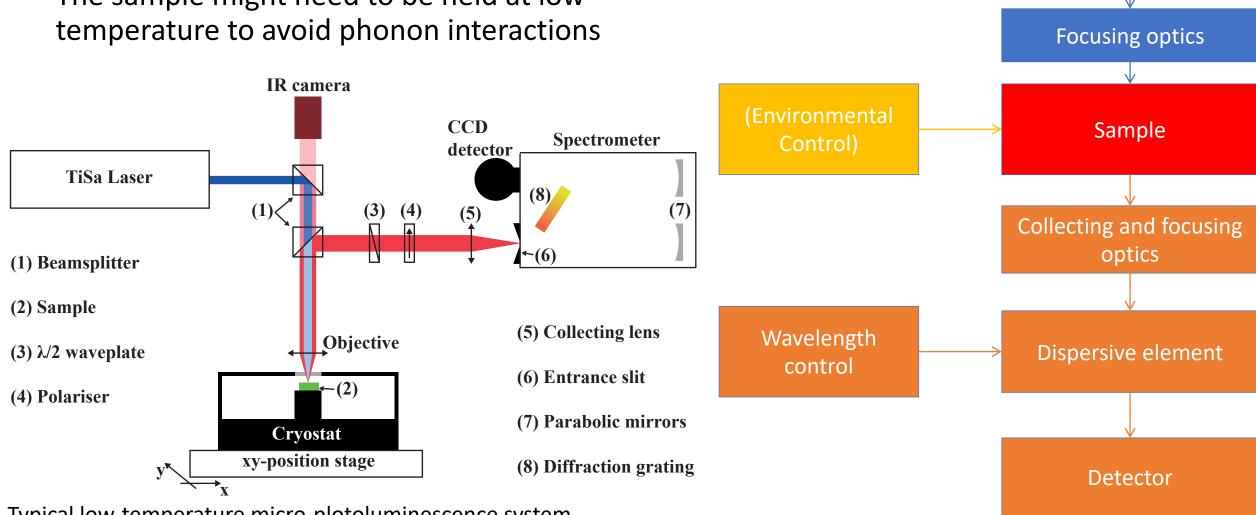
(Wavelength

Control)

Excitation source

(e.g. laser)

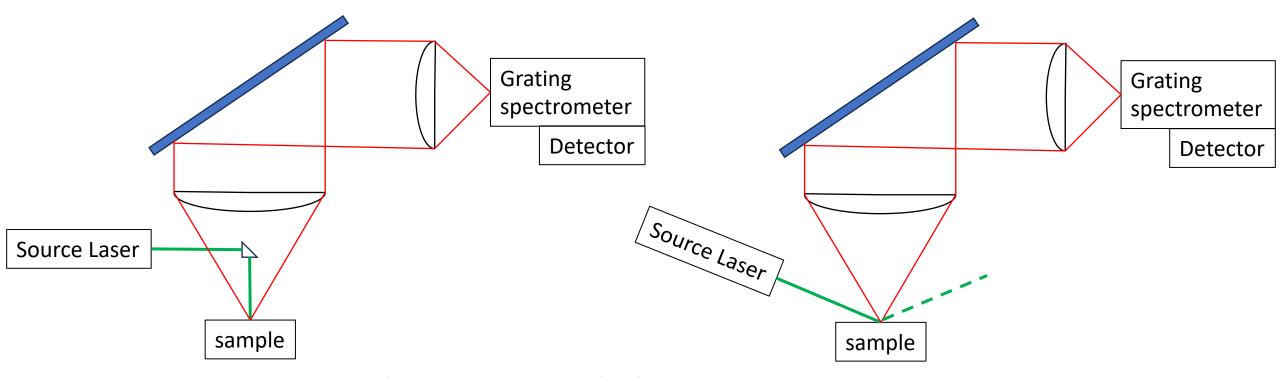
- In many systems there is an external excitation source. Its energy can sometimes be tuned
- The sample might need to be held at low



Typical low-temperature micro-plotoluminescence system

Optical spectroscopy: Experimental setup – PL

- In some cases large-area and room-temperature PL is enough, leading to a simplified system.
- The laser source might be inclined to avoid reflections into the spectrometer

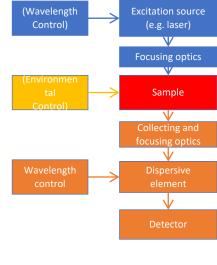


Typical room-temperature plotoluminescence systems

Excitation sources

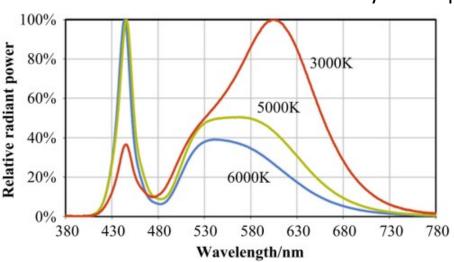
- In most systems there is an external excitation source. Its energy must be higher than that of the studied transitions!
- Typical exceptions: characterization of light sources (LEDs, lasers), discharge or flame spectroscopy, astronomy.
- The excitation source can be broadband (white light or discharge lamp) or monochromatic (broad source plus filter / monochromator, laser).
- Comparison of excitation sources:

Source type:	Broadband	Broadband + Filter	Broadband + Monochromator	LED	Laser
Advantages:	CheaperHigh light output	CheaperSelectable wavelength	 Monochromatic light at any wavelength 	CheaperHigh power at a narrow wavelength band	High intensity monochromatic lightSome tuning is possible
Disadvantages:	No wavelength selectionSource energy is spread over band	Power loss in filterFilter is usually broadband	ExpensiveVery low light output per unit wavelength	- No tuning	ExpensiveTuning range is sometimes limited



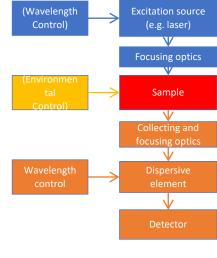
Broadband sources

- Three main types of broadband sources:
 - Thermal filament (e.g. Halogen-tungsten)
 - Gas discharge at high pressure
 - White LED (recent types can emit high power)
- Typical image and spectra of broadband light sources:
 - Halogen spectrum is blackbody (very smooth, but low in UV)
 - High-pressure discharge lamps have many broad peaks that form a quasi-continuous spectrum
 - White LED has a moderately wide spectrum



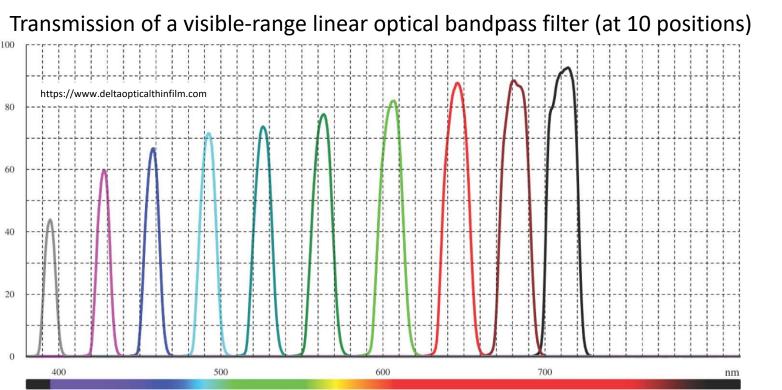


Halogen and Discharge lamps (Hg, Xe) - 100 W Hg at 0,5 m [mW m² nm³] -100 W Halogen - 30 W D, 75 W Xe -75 W Xe OFR



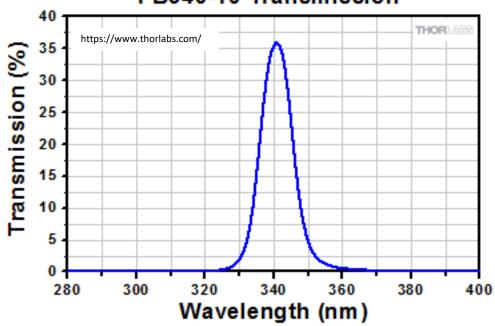
Broadband source + filters

- To obtain a narrower bandwidth, the light from a broadband sources is filtered by a bandpass optical filter of fixed or variable wavelength
- Typical bandwidth: 10-20 nm at WL=400-700 nm
- Typical power at 340 nm, distance 25cm, filter D= 25mm, BW=10 nm:
 - Halogen lamp: 0.014 mW
 - Hg lamp: 1.4 mW



FB340-10 Transmission

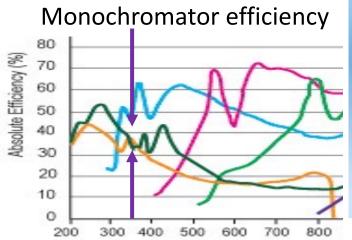




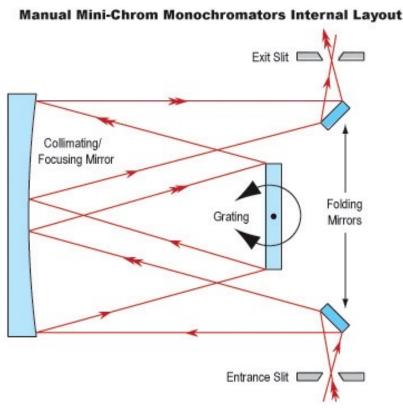
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Broadband source + monochromator

- To obtain a very narrow and variable bandwidth, the light from a broadband sources is filtered by a simple grating monochromator (see below)
- The bandwidth and transmission are determined by the monochromator slit width: a simple 7.4 cm monochromator has a dispersion of 5.3 nm/mm, so a slit of 1 mm width will have a spectral width of 5.3 nm. Light intensity is also proportional to the slit width...
- Typical power at 340 nm, distance 25cm:
 - Halogen lamp: 70 nW
 - Hg lamp: 7 μW

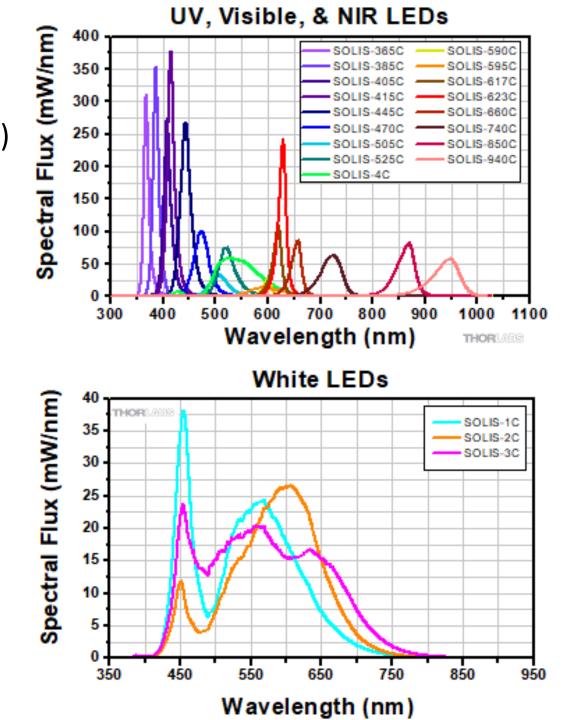






LED sources

- New LED sources can emit at one wavelength band ("colored LEDs") or broadband ("White LEDs"):
- "White" LED has higher UV emission than a halogen lamp
- The UV source at 365 nm has a bandwidth of 10 nm and emits a power of 3W – more than any broadband source.



(Wavelength

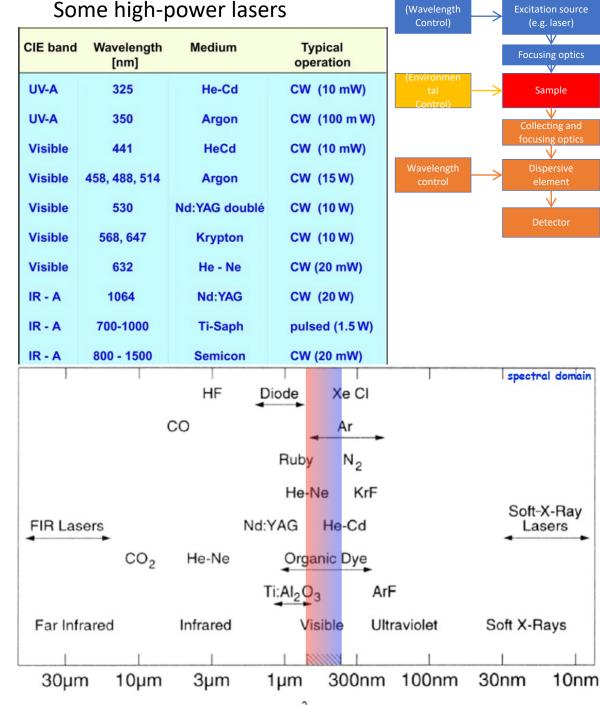
Control)

Excitation source

Sample

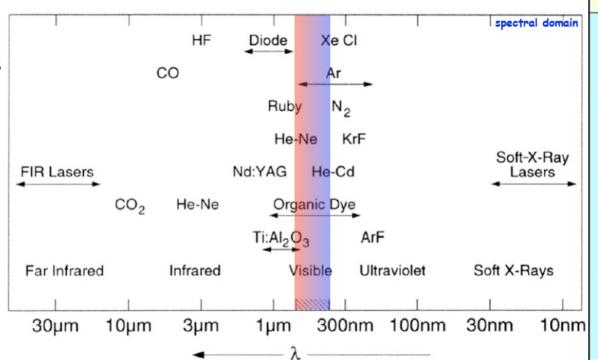
Laser sources

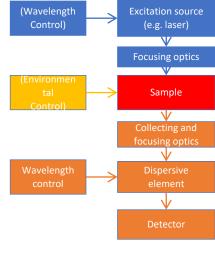
- Laser sources have several advantages:
 - Monochromatic light (<< 1 nm): all the energy is concentrated in one wavelength
 - Parallel beam of small diameter (mm): easy to focus
- The main disadvantage: limited or no tunability.
- Main types of lasers:
 - Gas lasers (HeNe, Ar, CO₂, ...)
 - Organic dye lasers* (less used now)
 - Excimer lasers (ArF, KrF, ...)
 - Solid crystal lasers (Ti:Saphire*, Nd:Yag, ...)
 - Diode lasers
 - Fiber lasers
 - Free-electron lasers (huge, very expensive!)



Main laser sources used in spectroscopy

- Laser sources for spectroscopy usually have power of 1 mW 1W, tunability is a plus
- Fixed-wavelength types, for simple applications:
 - HeNe (628 nm)
 - Fixed-wavelength diode lasers (wavelength can be chosen)
 - Nd:Yag and Doubled Nd:Yag (DPSS) (1062 and 532 nm)
- For UV excitation, high-power pulses:
 - Excimer lasers (ArF, KrF, ...)
- Tunable lasers:
 - Ti:Saphire
 - Some diode lasers



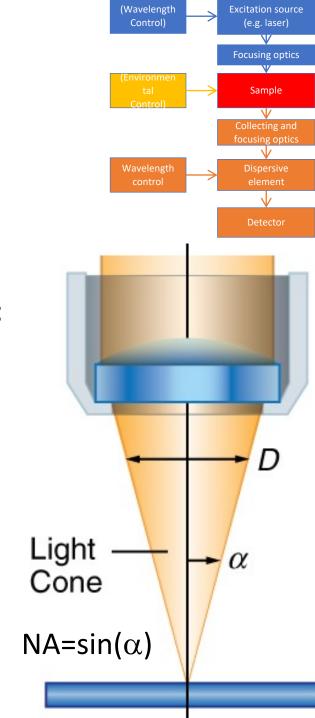


Some high-power lasers

	CIE band Wavelength [nm]		Medium	Typical operation				
	UV-A	325	He-Cd	CW (10 mW)				
	UV-A	350	Argon	CW (100 mW)				
	Visible	441	HeCd	CW (10 mW)				
	Visible	458, 488, 514	Argon	CW (15 W)				
	Visible	530	Nd:YAG doublé	CW (10 W)				
	Visible	568, 647	Krypton	CW (10 W)				
	Visible	632	He - Ne	CW (20 mW)				
	IR - A	1064	Nd:YAG	CW (20 W)				
	IR - A	700-1000	Ti-Saph	pulsed (1.5 W)				
1	IR - A	800 - 1500	Semicon	CW (20 mW)				

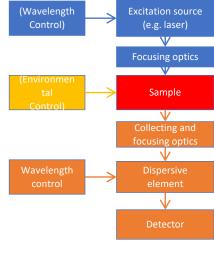
Focusing optics

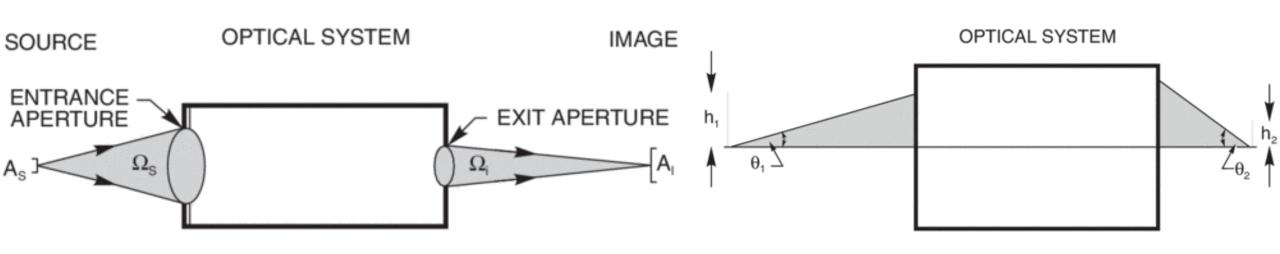
- The focusing optics brings the light from the source to the sample, covering the required area: from cm² (liquid absorption) to μ m² (micro-photoluminescence, μ PL)
- In many systems, the light intensity is controlled by attenuators
- In some cases, the light polarization is also controlled
- In the case of large areas, illumination homogeneity can be important; sometimes a "white" diffuser is needed.
- When focusing on small areas, microscope objectives are used to obtain a diffraction-limited spot ($D=1.22\lambda/NA$)
- Optical fibers can also be used to bring the excitation light to the sample. They have the advantage of small size and flexibility (e.g. in moving systems)
- In rare cases, an elliptical excitation spot is needed; the optics should then include a cylindrical lens.



Size considerations – optical etendue

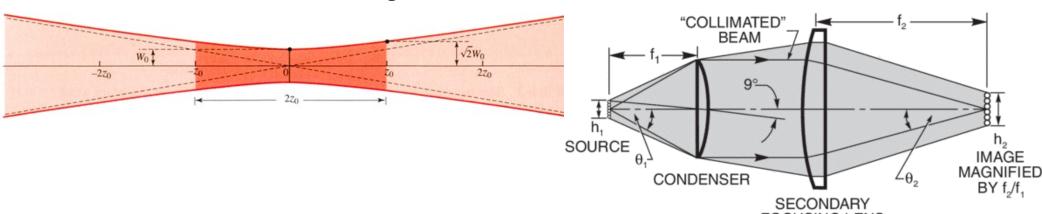
- The source size and emission angle form an optical **invariant** called the **optical etendue**. In air, it is the product of the source area and the solid angle of the emitted light: $G=A_S\Omega_S$.
- In a system with axial symmetry (as most optical systems are), we can use a 1D version: $G=h_S\theta_S$.
- In practice, this means that we need to match the value of G between source and image, otherwise we lose part of the intensity.

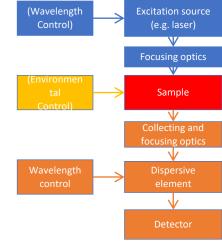


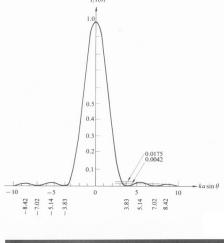


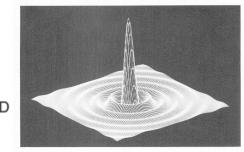
Size considerations – optical etendue

- Example of the use of the optical etendue:
 - Most lasers emit a TEM00 mode, which is a Gaussian beam; it has the property that: $G = W_0 \theta_0 = \lambda/\pi \approx 2 \cdot 10^{-7} m$.
 - The diffraction limit of a lens gives: $h_S=\frac{0.61\lambda}{NA}$, so: $G=h_S\theta_S\cong h_SNA=0.61\lambda\approx 3.6\cdot 10^{-7}m$.
 - Comparing these equations, we see how it's easy to focus a laser beam to a diffraction-limited spot without much loss.
- Another example:
 - A halogen or discharge lamp with a size of 2 mm and emission angle of 1 rad, will have: $G = r\theta \approx 1 \cdot 10^{-3} m$. Since a focusing lens can not have a much bigger angle than 1 rad, we can't focus this light to a smaller spot than the lamp's size, unless we limit the size with an iris and lose light.



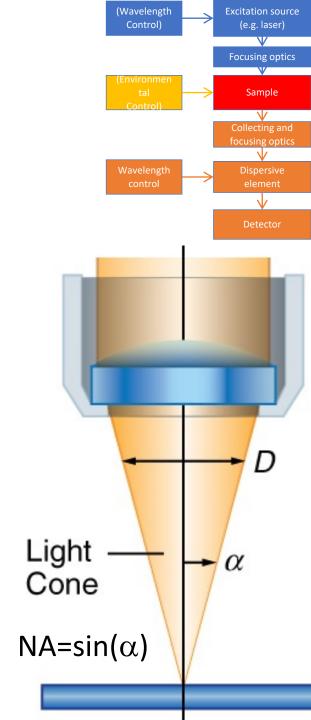






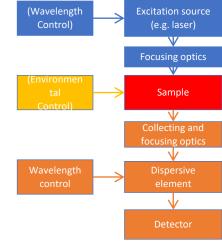
Collecting optics

- The collecting optics brings the light from the sample to the dispersive element, covering the required area: from cm² (liquid absorption) to μ m² (micro-photoluminescence, μ PL)
- When collecting from a small area (in μ PL systems), microscope objectives with high numerical aperture are used to collect the maximum light. The same optics is then used for excitation and collection. Semi-transparent mirrors are used to direct the incoming and outgoing beams.
- In many cases, especially when the same lens is used, filters are needed to remove the (much stronger) reflected excitation light from the dispersive element entrance.
- In some cases, the light polarization is also controlled, and can also be used to distinguish between the reflected excitation and the signal.
- Optical fibers can also be used, sometimes a single fiber can send the
 excitation light and bring back the PL light. They have the advantages
 of very compact size and flexibility, but the disadvantage of a small
 optical etendue. Fiber luminescence can sometimes be a problem.



The dispersive element

- The dispersive element is the most important part of the system. It allows to distinguish between different photon energies (wavelengths)
- The type of dispersive element to be used depends on the needs:
 - Resolvance or resolution (distinguish between close wavelengths)
 - In some cases (e.g. Raman spectroscopy), the rejection ratio is very important
 - Wavelength range of operation
 - Throughput (or efficiency, or losses): the transmission of the element
 - Speed and ease of use
- We look here at several types of dispersive elements:
 - The diffraction grating (the most common)
 - The FTIR spectrometer (also very popular)
 - The refractive prism
 - The Fabri-Perot interferometer



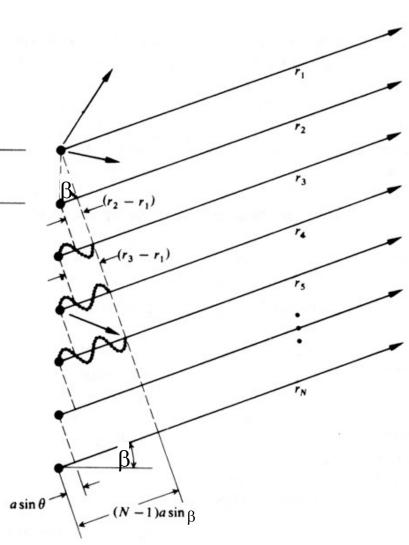
The diffraction grating spectrometer

- The diffraction grating spectrometer is the most widely used in physics research and industry.
- It combines high resolution, wide spectral range, moderately high efficiency, and simple use.
- Its operation is based on the wavelength dispersion properties of the diffraction grating.



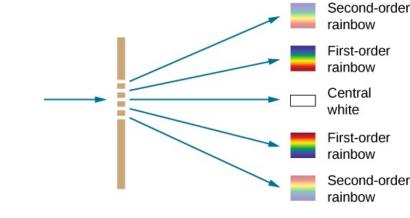
The diffraction grating – physics (1)

- A transmission grating is a regular array of N slits, with a periodicity a, illuminated by a plane wave. Each slit can be modeled as a source, emitting a field: $E_j=E_0e^{i({\bf k}\cdot{\bf r}-\omega t)}$, $E_0=E_{in}/N$, or an intensity: $I_0=I_{in}/N^2$
- The waves emitted at an angle β have an increasing phase lag, each successive wave has an extra phase: $\Delta \varphi = k \cdot \Delta r = ka \sin \beta = \frac{2\pi a}{\lambda} \sin \beta$, so wave no. j has a phase : $\Delta \varphi_j = (j-1)\Delta \varphi$ relative to the first wave.
- The sum of all fields gives a total intensity: $I = \left| \sum_{j=1}^{N} E_0 e^{i\varphi_j} \right|^2 = I_0 \left| \sum_{j=1}^{N} e^{i\Delta\varphi(j-1)} \right|^2 = I_0 \left| \frac{1-e^{i\Delta\varphi N}}{1-e^{i\Delta\varphi}} \right|^2 = I_0 \left| \frac{e^{i\Delta\varphi N/2}(e^{-i\Delta\varphi N/2}-e^{i\Delta\varphi N/2})}{e^{i\Delta\varphi/2}(e^{-i\Delta\varphi/2}-e^{i\Delta\varphi/2})} \right|^2 = I_0 \left| \frac{-2i\sin\Delta\varphi N/2}{-2i\sin\Delta\varphi/2} \right|^2 = I_0 \left| \frac{\sin^2\Delta\varphi N/2}{\sin^2\Delta\varphi/2} \right|.$



The diffraction grating – physics (2)

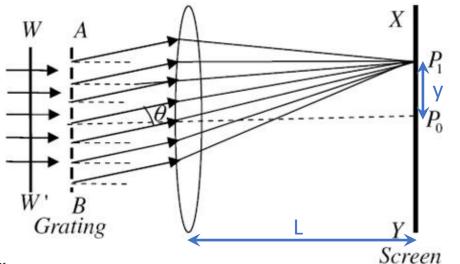
- The total intensity is: $I = I_0 \frac{\sin^2 \Delta \varphi N/2}{\sin^2 \Delta \varphi/2}$. Let's analyze this expression:
 - The big peaks correspond to: $\sin^2 \Delta \varphi/2 = 0$, or: $\Delta \varphi_{\text{max}} = 2m\pi$. m=...,-2,-1,0,1,2,... is the **diffraction order**. The intensity is: $I=N^2I_0=I_{\text{in}}$.
 - The minima (I=0) correspond to: $\sin^2 \Delta \varphi N/2 = 0$, or: $\Delta \varphi_{min} = 2m'\pi/N$.
 - The small peaks correspond to: $\sin^2\Delta\varphi N/2=1$, or: $\Delta\phi_{\text{max'}}$ = $(2m'+1)\pi/N$.

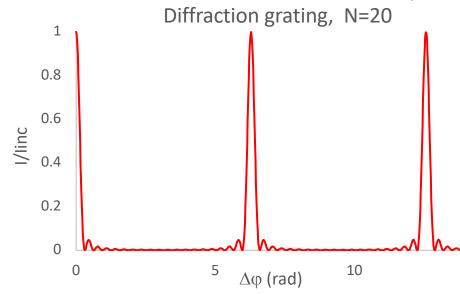


• The emerging waves are parallel, so a lens (or curved mirror) is needed to focus them on a screen. If its focal length is L, the focused point on the screen will correspond to: $y \approx L\beta$.

• In a typical grating, N = 10^5 ; the function $\sin^2 \Delta \varphi N/2$ is extremely narrow! The first zero corresponds to: $\Delta \varphi_0$ =

 $2\pi/N \approx 10^{-4}$.





The diffraction grating – physics

• If the arriving wave has an angle α , there is an extra phase between the successive emitted waves, due to the path difference before the grating:

$$\Delta \varphi_{AC} = -rac{2\pi a}{\lambda} \sin lpha$$
 , which adds to the phase difference acquired after the grating: $\Delta \varphi_{BD} = rac{2\pi a}{\lambda} \sin eta$.

- Total phase difference is then: $\Delta \varphi = \frac{2\pi a}{\lambda} (\sin \beta \sin \alpha)$.
- The condition for a maximum: $\Delta \phi_{\text{max}} = 2m\pi$ gives now: $\sin \beta \sin \alpha = \frac{m\lambda}{a}$.
- The intensity of the peaks is the same: $I = N^2 I_0 = I_{in}$.
- The condition for minima: $\Delta \phi_{\min} = 2m'\pi/N$ gives now: $\sin \beta \sin \alpha = \frac{m'\lambda}{aN} = \frac{m'\lambda}{I_{\min}}$ (L_r = total grating size).
- The transmission grating has two drawbacks:
 - Loss of light by the opaque regions (25-50%).
 - The transmitted intensity is divided between the diffraction orders.



Second-order

rainbow

Central white

First-order

rainbow

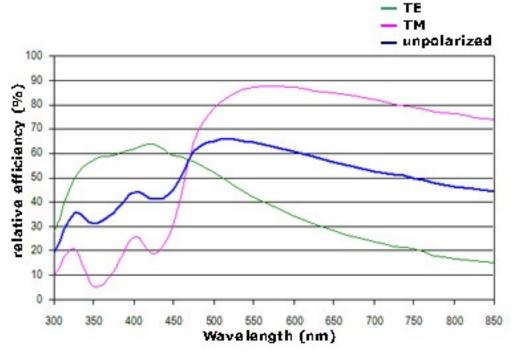
rainbow

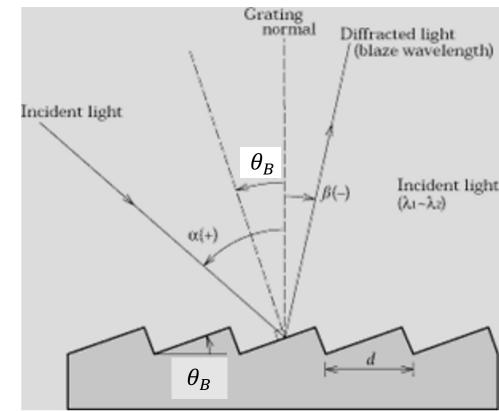
First-order rainbow

The diffraction grating – physics (4)

- It is more efficient to use a grating of mirrors (**reflective grating**). It allows to choose the mirror angle θ_B .
- The condition for the maxima is the same: $\sin \beta \sin \alpha = \frac{m\lambda}{a}$.
- Choosing the angle allows to maximize the reflected intensity in a specific diffraction order, by satisfying the reflection condition: $\alpha-\beta=2\theta_B$ as well ("blazing"). This gives: $2\sin\theta_B\cos(\alpha-\theta_B)=\frac{m\lambda_{max}}{a}$, so λ_{max} is determined by system geometry (α , θ_B). The optimized "blazed" wavelength can reach >80% efficiency; for other

wavelengths, the intensity is lower.

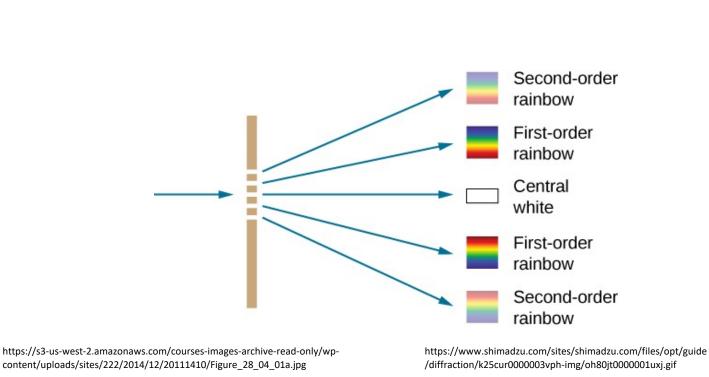


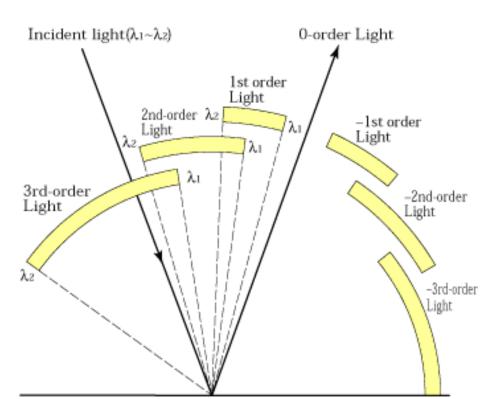


https://www.horiba.com/uk/scientific/products/diffraction-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/for-industrial-applications/holographic-plane-gratings/holographic-pl

The diffraction grating – physics (5)

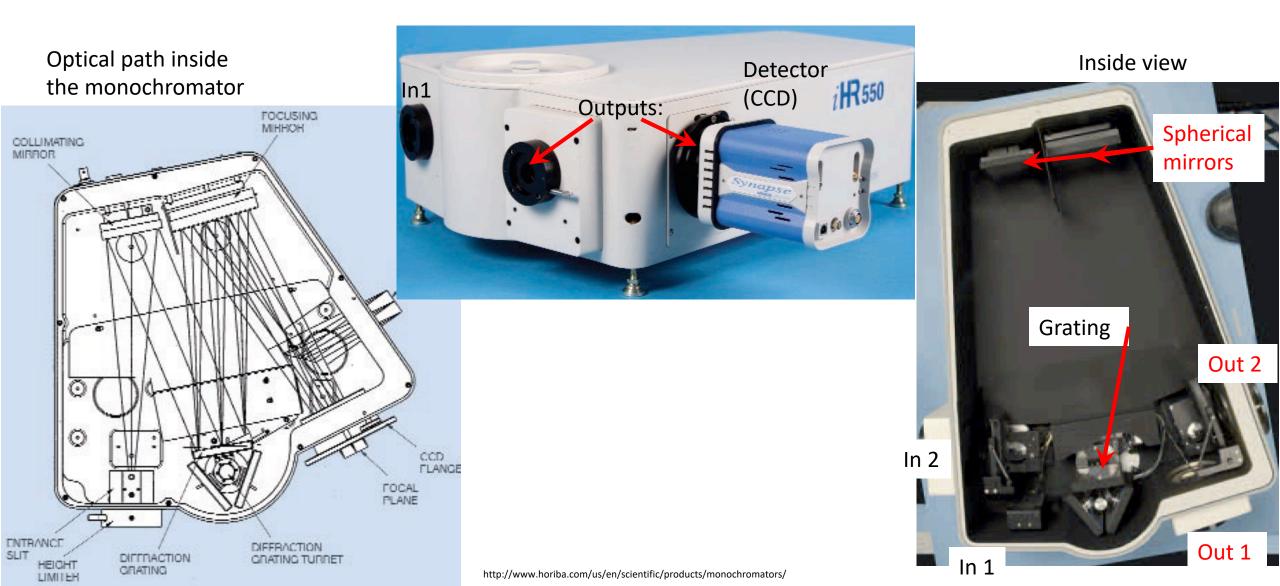
- Let's suppose that wavelengths λ_1 of an order m and λ_2 of an order m+1 are diffracted into the same angle β . The grating equation gives: $\sin \beta \sin \alpha = \frac{m\lambda_1}{\alpha} = \frac{(m+1)\lambda_2}{\alpha}$, or: $m\lambda_1 = (m+1)\lambda_2$.
- The difference is: $\Delta \lambda = \lambda_1 \lambda_2 = \frac{\lambda_2}{m} = \frac{\lambda_1}{m+1}$.
- The result: there is an overlap between half the first order and the second order, a third of the second order and the third order, etc.





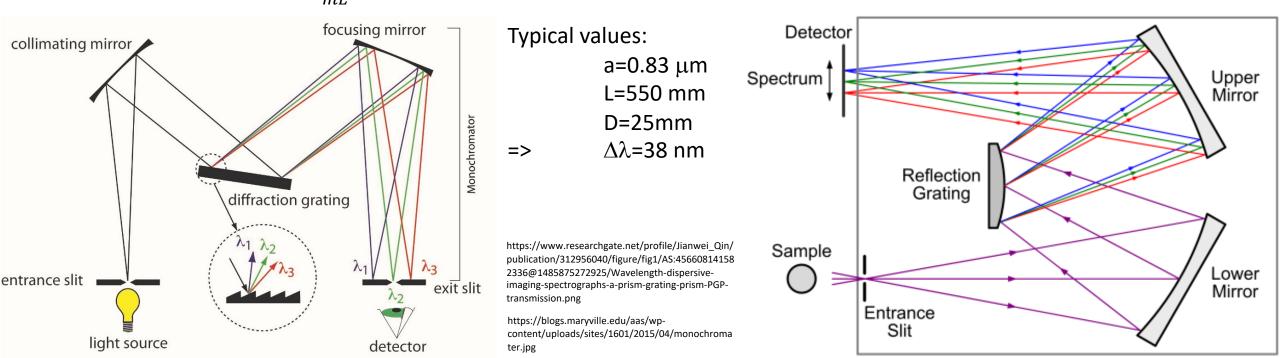
The grating monochromator/spectrograph

• A typical grating spectrometer is composed of two spherical mirrors and a grating:



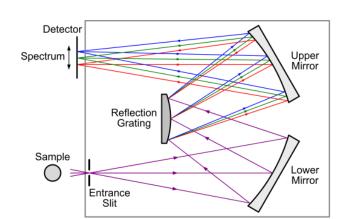
Using the grating monochromator

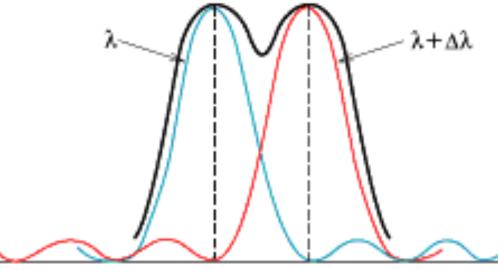
- As a filter, using a broadband light source at the input to obtain a (low efficiency) source of monochromatic light.
- To measure the spectrum of the sample emission. There are two modes of operation:
 - Spectrometer: A narrow output slit selects the output wavelength, then a single detector measures the intensity. To obtain the full spectrum, we turn the grating according to: $\sin \beta \sin \alpha = \frac{m\lambda}{a}$.
 - Spectrograph: A camera or detector array at the output measures simultaneously a full or partial spectrum. The position of the spectrum peak on the detector is determined by: $\sin\frac{y}{L} \sin\alpha = \frac{m\lambda}{a}$. If the detector size is D, the measured spectral range is: $\Delta\lambda \approx \frac{aD}{mL}$. For a larger spectral range, several spectra should be measured by turning the grating.



Performance of the grating spectrometer/spectrograph

- The angle of the peaks: $\sin \beta \sin \alpha \approx \sin \frac{y}{L} \sin \alpha = \frac{m\lambda}{a}$ (y≈L β is the position of the peak on the detector).
- The **dispersion** (difference in peak position for a given wavelength change) is: $\frac{d\lambda}{dy} \approx \frac{a}{m} \frac{d}{dy} \sin \frac{y}{L} = \frac{a \cos \beta}{mL}$.
- The **resolution** is given by the Rayleigh criterion to distinguishing between two wavelengths: the coincidence of the peak of a wavelength λ_1 with the zero of a wavelength $\lambda_2 = \lambda_1 + \Delta \lambda$, for the same grating angle.
- The corresponding angles are given by: $\sin\beta = \frac{m\lambda_1}{a} = \frac{m\nu\lambda_2}{Na}$; the wavelength difference is : $\Delta\lambda = \lambda_2 \frac{m'-mN}{mN}$. The **resolution** corresponds to: m'-mN=1, giving: $\frac{\Delta\lambda}{\lambda} = \frac{1}{mN}$. The **resolvance** is: $R \equiv \frac{\lambda}{\Delta\lambda} = mN$.
- Typical values: a=0.83 μ m (1200 l/mm), L=55cm, N=91200, β =28°; for the 1st order: $\frac{d\lambda}{dy} \cong 1.35 \ nm/mm$, $\frac{\Delta\lambda}{\lambda} \cong 1.1 \cdot 10^{-5}$. A typical element of a CCD detector (13 μ m) corresponds to $\Delta\lambda$ =17 pm, and the Rayleigh resolution is 11 pm at λ =1 μ m. The resolvance is: R=N=91200.
- The spectral range is 38 nm for a 2000 pixel (25.4 mm) CCD.





Summary of grating spectrometer properties

Advantages:

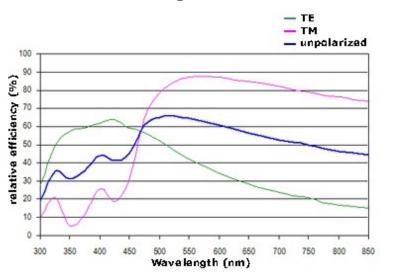
- High resolvance
- Large spectral range
- Weak dependence of resolution on wavelength

• Disadvantages:

- High resolution instruments are large, expensive
- Medium efficiency, wavelength and polarization-dependent

Main applications:

• "Workhorse" spectrometer in most physics laboratories, when high resolution and large spectral range are needed







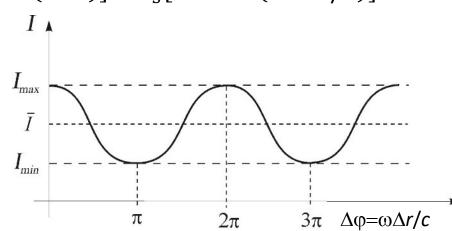
The FTIR spectrometer

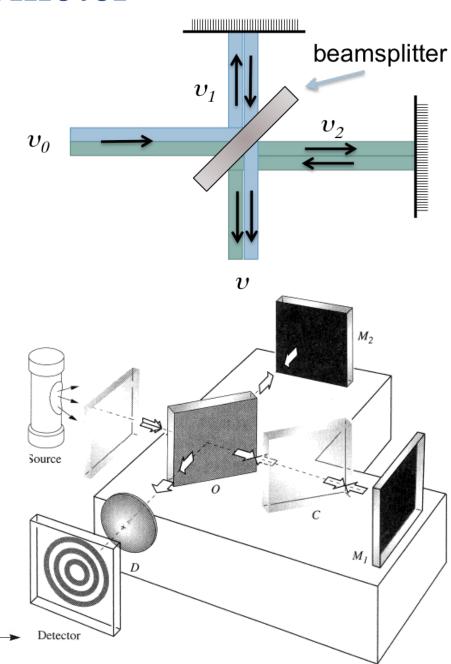
- The Fourier-Transform IR (FTIR) spectrometer is widely used in (bio-)chemistry research and industry, where it is used to measure the absorption spectra of molecules.
- It combines moderately high resolution, wide spectral range (usually 1-10 μ m), high efficiency, and simple (automatic) use.
- Its operation is based on light interference in the Michelson interferometer.



The Michelson interferometer

- The Michelson interferometer (1885) is composed of a 50% beamsplitter and two mirrors. Light coming from v_0 is split into the two equal beams $(v_1 \text{ and } v_2)$, that are reflected back and redirected by the beamsplitter in the direction v towards a detector, where they interfere.
- If the initial beam is described by: $E_S=E_0\cos(kx-\omega t)$, then the detector receives the sum: $E_d=E_1+E_2=\frac{E_0}{\sqrt{2}}[\cos(kx_1-\omega t)+\cos(kx_2-\omega t)]=\sqrt{2}E_0\cos(kx_a-2\omega t)\cos(k\Delta x/2)$, where: x_a =(x_1 + x_2)/2 , and: Δx = x_1 - x_2 is the **optical path difference** (OPD)
- The detector measures the intensity: $I_d \propto \langle E_d^2 \rangle_T = 2E_0^2 \langle \cos^2(kx_a 2\omega t) \rangle_T \cos^2(k\Delta x/2) = I_s[1 + \cos(k\Delta x)] = I_s[1 + \cos(2\pi\Delta x/\lambda)] = I_s[1 + \cos(2\pi\Delta x/\lambda)].$
- $\sigma = \frac{1}{\lambda}$ is the *spatial frequency*, usually measured in cm⁻¹ (1 μ m = 10⁴ cm⁻¹)





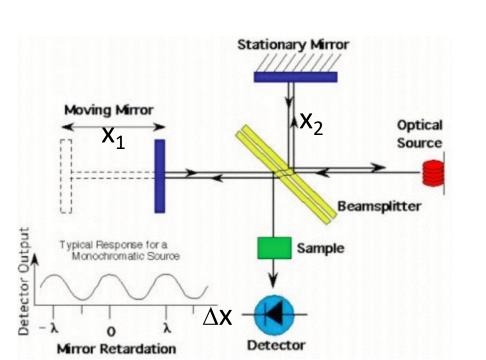
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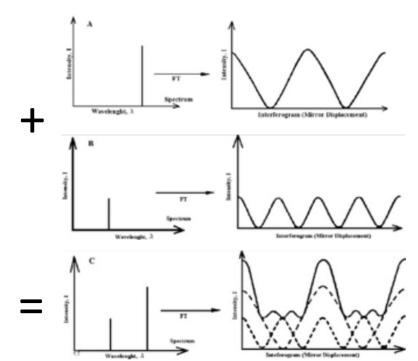
The Michelson interferometer can produce a spectrum

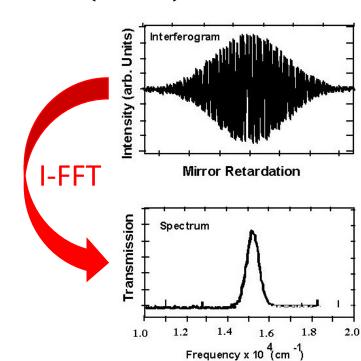
- We build an interferometer with one fixed and one moving mirror. The detected intensity varies with the moving mirror's position $x:I_d=I_s[1+cos(2\pi\sigma\Delta x)]$.
- If the source contains two frequencies, the intensity will be their sum:

$$I_d(\Delta x) = I_{\sigma_1}(\Delta x) + I_{\sigma_2}(\Delta x) = I_s(\sigma_1) + I_s(\sigma_2) + I_s(\sigma_1)\cos(2\pi\sigma_1\Delta x) + I_s(\sigma_2)\cos(2\pi\sigma_2\Delta x)$$

- For a multitude of frequencies: $I_d(\Delta x) = \sum_i I_s(\sigma_i) + \sum_i I_s(\sigma_i) \cos(2\pi\sigma_i\Delta x) = I_{s,total} + \mathcal{F}(I_s(\sigma))$ is the Fourier transform of the spectrum $I_s(\sigma)$.
- The **spectrum** is the *inverse Fourier transform* of the **interferogram** $I_d(\Delta x):I_s(\sigma)=\mathcal{F}^{-1}(I_d(\Delta x))$.

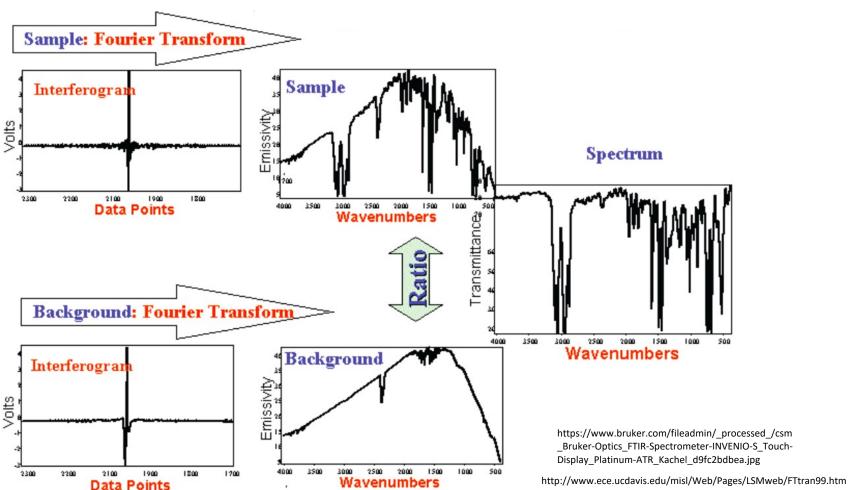




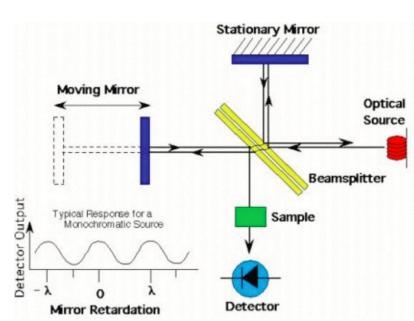


The FTIR spectrometer

The *FTIR spectrometer* is usually used to measure the absorption spectra of molecules. We measure the spectrum of a broadband (white) light source, then insert in the optical path the solution and measure again . The absorption spectrum is obtained as the ratio of the two spectra.







The FTIR spectrometer: performance

- The optical spectrum is calculated by a numerical Fourier transform (FFT) of the sampled interference pattern: $I_d(\Delta x) = \sum_i I_s(\sigma_i) + \sum_i I_s(\sigma_i) \cos(2\pi\sigma_i \Delta x) = I_{s,total} + \mathcal{F}(I_s(\sigma)).$
- For a broadband source, the detected signal has a maximum for Δx =0 (all wavelengths interfere positively).
- If δx is the sampling interval, the first data point after x=0 is at x= δx ; the corresponding frequency is: $\sigma_{max}\delta x = 1/2$, giving: $\sigma_{max} = \frac{1}{2\delta x}$, which is the highest detectable frequency. This results also from the Nyquist-Shannon sampling theorem.
- The ability to distinguish between two close frequencies is related to the maximal path $2\Delta x_{max}$: suppose that the frequencies σ_1 and σ_2 correspond to n and n+1 interference cycles: $\sigma_1 2\Delta x_{max} = n$ and $\sigma_2 2\Delta x_{max} = n+1$

. The difference is:
$$(\sigma_2 - \sigma_1)2\Delta x_{max} = 1$$
, or: $\Delta \sigma = \frac{1}{2\Delta x_{max}}$. The resolvance is then: $R = \frac{\lambda}{\Delta \lambda} = \frac{-\sigma}{\Delta \sigma} = \frac{2\Delta x_{max}}{\lambda}$,

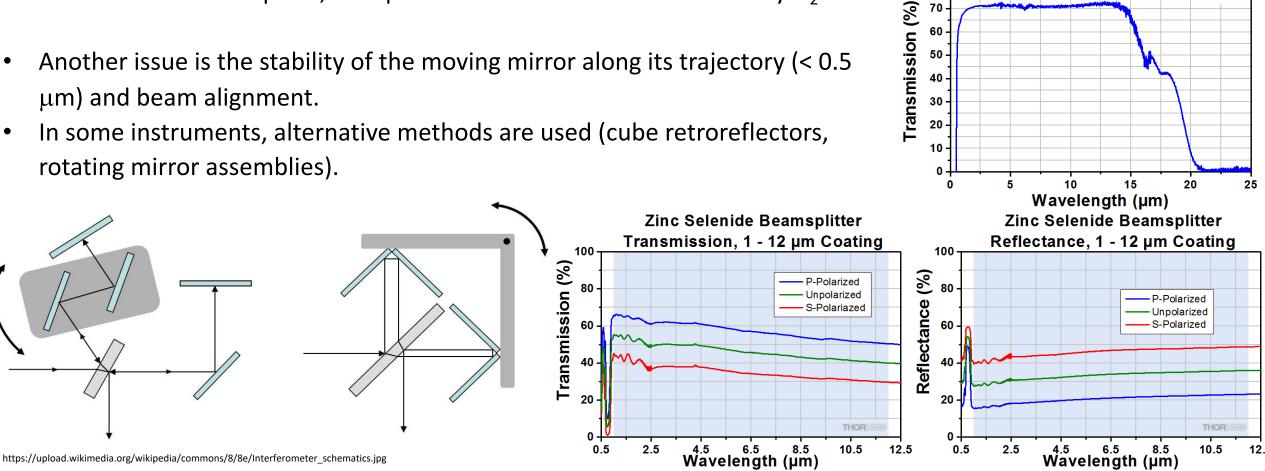
$$R_{max} = \frac{\Delta x_{max}}{\delta x}$$
.

Typical values for FTIR spectrometers:

δ x (μm)	ΔX_{max} (cm)	$\sigma_{min}\!\!=\!\!\Delta\sigma$	(cm ⁻¹)	σ _{max} (cm ⁻¹)	λ _{min} (μm)	R
0.633	0.3	1.7		$7.9 \cdot 10^3$	1.27	4.7·10 ³
0.633	3	0.17		7.9·10 ³	1.27	4.7·10 ⁴
0.633	30	0.017		$7.9 \cdot 10^3$	1.27	4.7·10 ⁵

Material and structure issues

- The performance of the FTIR cspectrometer depends on the beam splitter
- To work at long IR wavelengths, special materials are needed: ZnSe (to 20 μm), KBr (to 25 μ m), CsI (to 50 μ m).
- The detector should also be broadband (vis to FIR), usually a bolometer.
- To avoid water absorption, the spectrometer volume is filled with dry N_2 .
- Another issue is the stability of the moving mirror along its trajectory (< 0.5) μm) and beam alignment.



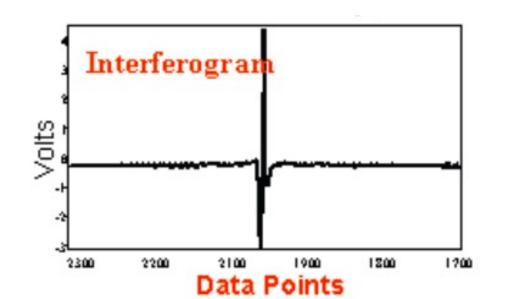
https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=4805

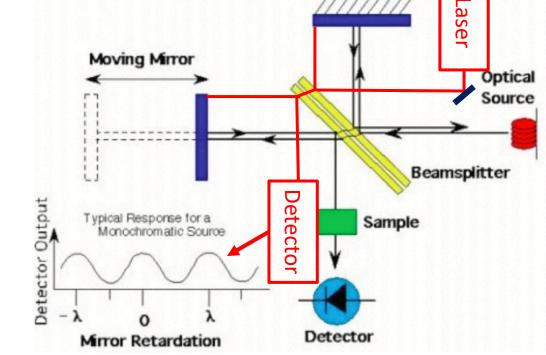
ZnSe Transmission (10 mm Thick Sample)

How to increase resolution

- To obtain high resolution at long wavelength, we need a long mirror trajectory with high-resolution, stable linear movement. This is not easy to achieve!
- A simple method to overcome the mechanical deficiencies is to add an internal standard. Usually it's a HeNe laser, emitting at 632.816 nm. It passes through the interferometer in parallel to the source beam, and into a separate detector, which provides a reference sinusoidal voltage corresponding to the spatial frequency of λ =0.633 μ m, which gives the precise position of the mirror independent of the mechanics.
- The zero point of the mirror path $\Delta x=0$ is also detected as the strong maximum of the interferogram at that point, which also coincides with a maximum of the reference

signal.





HeNe

Stationary Mirror

The use of the FTIR spectrometer

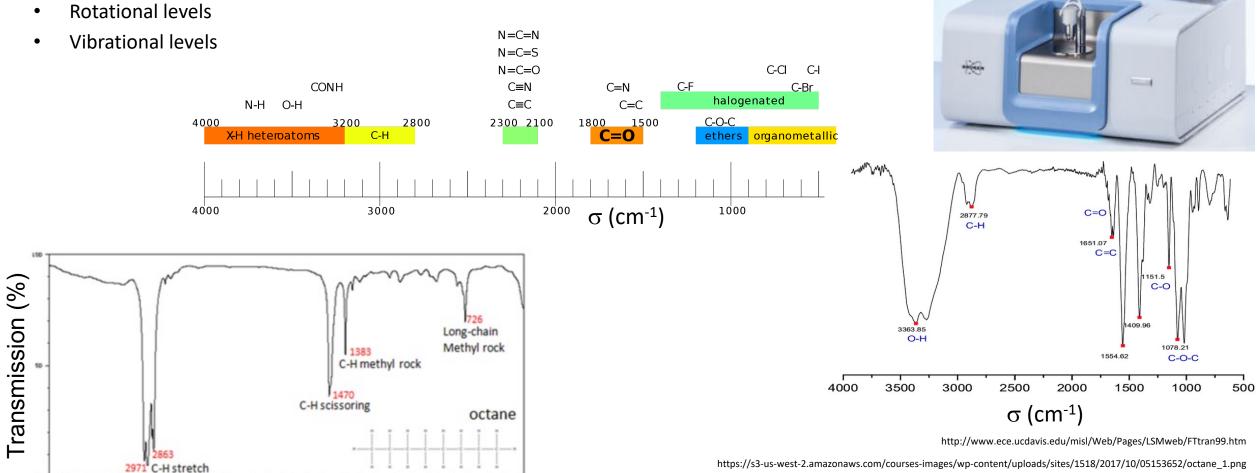
• The FTIR spectrometer is usually used to measure the absorption spectra of molecules

as the ratio of the light passing through the molecules and the source's light.

• Typical absorption peaks are related to molecular properties:

 σ (cm⁻¹)

ypical absorption peaks are related to inforecular properties



https://www.bruker.com/fileadmin/ processed /csm Bruker-Optics FTIR-Spectrometer-INVENIO-S Touch-Display Platinum-ATR Kachel d9fc2bdbea.jpg

https://upload.wikimedia.org/wikipedia/commons/thumb/d/d9/IR-spectroscopy-sample.svg/2880px-IR-spectroscopy-sample.svg.png

Summary of FTIR properties

Advantages:

- High transmittance (full beam size is used, no slits)
- Hi speed (full spectrum taken in one fast sweep), averaging can be used to reduce noise.
- Wide wavelength range (1 \rightarrow >10 μ m)
- No strange resonances

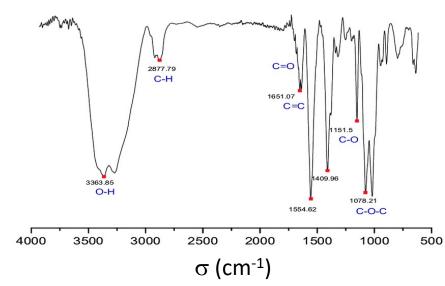
Disadvantages:

- Low resolvance, unless long trajectory
- Needs good alignment and stability of moving mirror path

Main applications:

- Organic chemistry and bio-chemistry laboratories
- Forensic laboratories





The prism spectrometer

- The oldest (Newton 1670) and simplest spectrometer is the prism spectrometer.
- It uses the dispersion of light by a glass prism.



The refractive prism - physics(1)

70

60-

50

37,18

30

40

 $i_1 = 48,59$

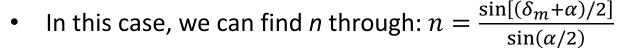
32

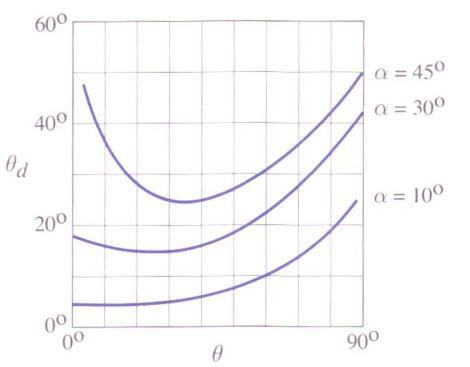
 $i_1 = 27,92$

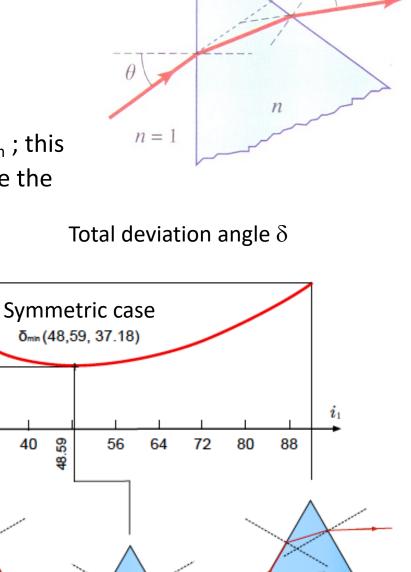
- The simple glass prism can be used as a dispersive element.
- The deviation angle de of light passing through a prism is:

$$\delta \equiv \theta_d = \theta - \alpha + \sin^{-1} \left[\sqrt{n^2 - \sin^2 \theta} \sin \alpha - \sin \theta \cos \alpha \right]$$

 δ depends on θ , α and n. The dependence of δ on θ has a minimum at $\delta = \delta_m$; this angle corresponds to the symmetrical situation when the beam travels inside the prism parallel to its base.







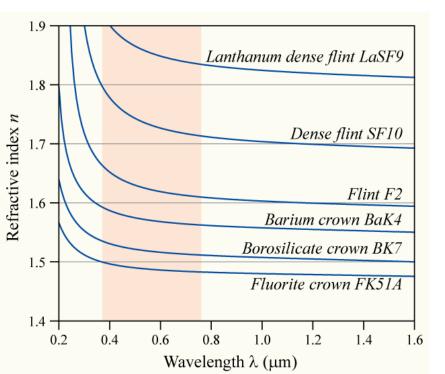
 $i_1 = 90$

The refractive prism – physics(2)

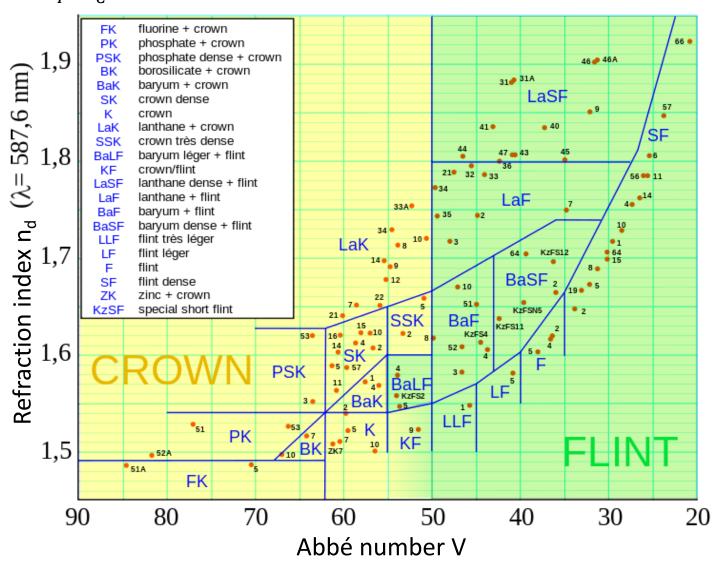
- The usefullness of the prism in spectroscopy is beacause n depends on wavelength: $n=n(\lambda)$
- The relation between $\delta_{\rm m}$ and n produces:

$$\sin[(\delta_m + \alpha)/2] = \frac{n(\lambda)}{\sin(\alpha/2)}$$

- Choice of the prism material allows to get the wanted change in $n(\lambda)$.
- Dense glasses (La-doped) are best



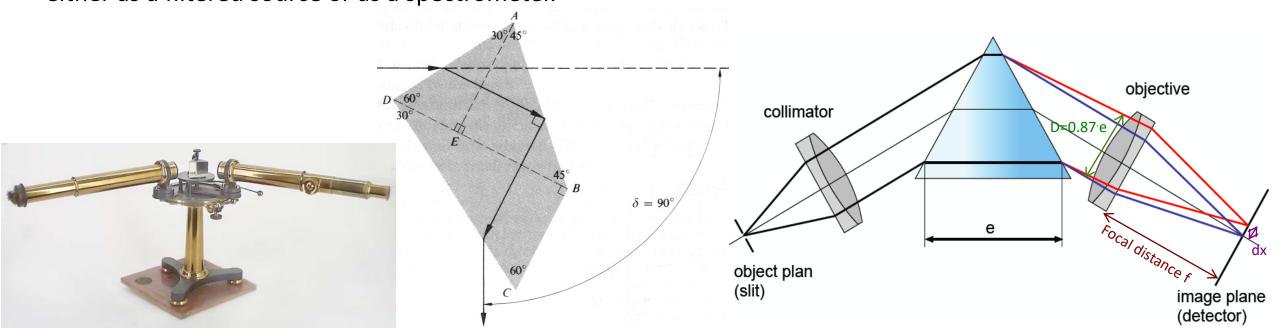
A way to characterize glasses is by the Abbé number: $V_d = \frac{n_d-1}{n_F-n_C}$; d, F, C = atomic spectral lines (587.6, 486.1, 656.3 nm)



Using the prism spectrometer

- A lens is used to transform light coming from an entrance slit to a parallel beam entering the prism. A similar lens focuses the parallel beam coming from the prism onto an exit slit.
- To maintain the condition of minimum deviation, both entrance and exit angles should change simultaneously.

 This is not very convenient!
- A solution of this problem is the Pellin-Broca prism, which is a double 30° top prism plus internal reflection at 90°. In this prism, the beam deviation is always $\delta_m = 90^\circ$ if: $\sin(\theta_i) = n/2$.
- In this configuration, we keep entrance and exit optics at 90° to each other, and turn the prism to satisfy the refraction condition $\sin(\theta_i) = n(\lambda)/2$. This allows to filter a single wavelength(according to the slit width), either as a filtered source or as a spectrometer.



Performance of the prism spectrometer

- The prism equation: $\sin[(\delta_m + \alpha)/2] = n \sin(\alpha/2)$ allows us to calculate the prism **dispersion** (difference in angle for a given wavelength change) is: $\frac{d\delta_m}{d\lambda} = 2(1/\sin^2(\alpha/2) n^2)^{-1/2} \frac{dn}{d\lambda} = K \frac{dn}{d\lambda}$. Typical values for α =60°, n=1.5: K = 0.756. If the focal length of the focusing lens is f, the linear dispersion is: $\frac{dx}{d\lambda} = Kf \frac{dn}{d\lambda}$.
- The **resolution** is given by the size of the diffraction-limited focused spot: $dx_{min} = 1.2 \frac{\lambda}{NA} = 1.2 \frac{\lambda}{D/2f}$. Using the equation above, we get the **resolution**: $\Delta \lambda = \frac{2.4\lambda}{KD\frac{dn}{d\lambda}}$, and the **resolvance**: $R \equiv \frac{\lambda}{\Delta \lambda} = \frac{KD}{2.4} \frac{dn}{d\lambda}$. Typical values at

 λ =500nm: K=0.756, D=76mm, $\frac{dn}{d\lambda} = 5.6 \cdot 10^{-2} \, \mu \text{m}^{-1}$; $\Delta\lambda$ =0.37 nm , R=1340 .

collimator

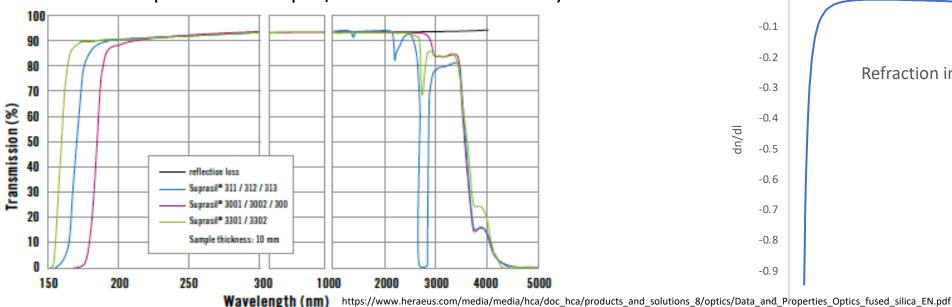
objective

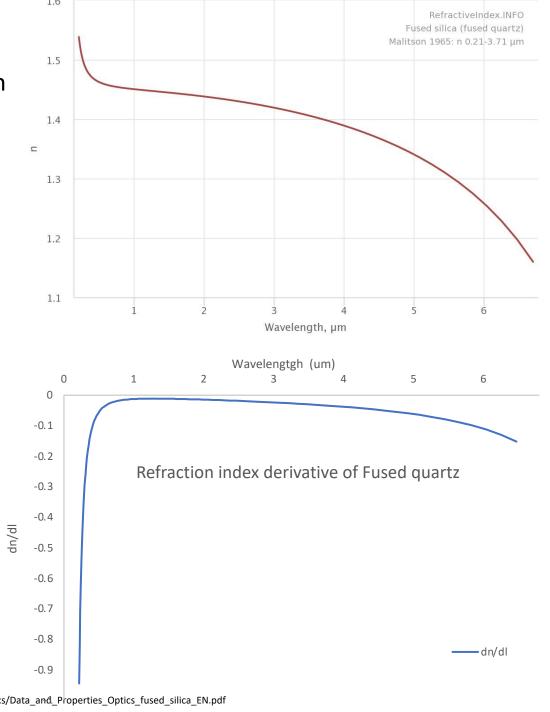
object plan (slit)

image plane (detector)

Material issues

- The performance of a prism cspectrometer depends directly on the material properties:
 - The resolvance is proportional to: $\frac{dn}{d\lambda}$ (in most materials it's non-linear, changing strongly with wavelength).
 - The material should be transparent at the required wavelength (limited wavelength range).
 - Typical example: Fused quartz
 - Can be used from UV (200 nm) to IR (3.5μm).
 - Refraction index varies a lot (from 0.95 μ m⁻¹ at λ = 220 nm to 0.011 μ m⁻¹ at λ =1.3 μ m) and in a non-linear way.





Summary of prism spectrometer properties

Advantages:

- High transmission efficiency (close to 100%)
- Large spectral range
- Cheap

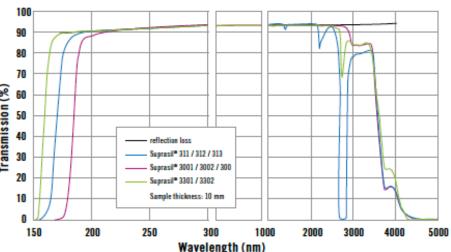
• Disadvantages:

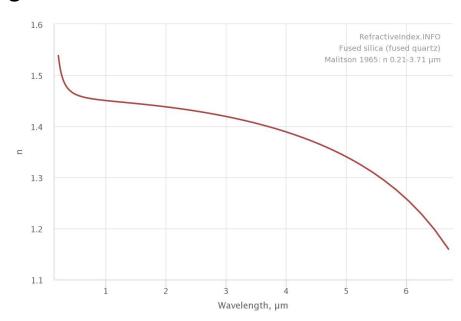
- Transmission wavelength range depends on prism material
- Non-linear dispersion, depends on $n(\lambda)$ curve.
- Medium resolvance
- Resolvance depends on material, can vary a lot for different wavelengths

• Main applications:

- Simple spectrometer in demonstration laboratories
- As a filter to choose the diffraction order of a grating
- Filtered light sources







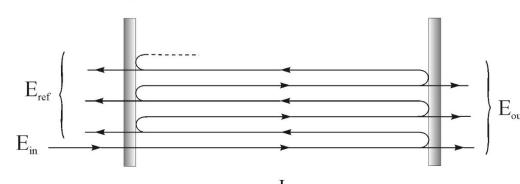
The Fabri-Pérot cavity spectrometer: principles (1)

- The Fabry-Pérot cavity is made of two high-reflectivity mirrors, each with transmission t and reflection r, separated by a distance L. The light beam enters the cavity from the left, and gets partially reflected and partially transmitted at each passage, exiting at the right.
- Each passage (back and forth) in the cavity contributes a component: $E_{out_j} = E_{out_{j-1}} r^2 e^{i2kL}$. The total output field is: $E_{out} = E_0 t^2 e^{ikL} \sum_{j=0}^{\infty} (r^2 e^{i2kL})^j = E_0 t^2 e^{i\Delta\varphi/2} \sum_{j=0}^{\infty} r^{2j} e^{i\Delta\varphi j} = E_0 t^2 e^{i\Delta\varphi/2} \frac{1}{1-r^2 e^{i\Delta\varphi}}$, with $\Delta\varphi = 2kL$.
- $\text{ The output intensity is: } I_{out} = I_0 t^4 \left| \frac{1}{1-r^2 e^{i\Delta \varphi}} \right|^2 = \frac{I_0 t^4}{(1-r^2 e^{i\Delta \varphi})(1-r^2 e^{-i\Delta \varphi})} = \frac{I_0 t^4}{1+r^4-r^2 (e^{i\Delta \varphi}+e^{-i\Delta \varphi})} = \frac{I_0 t^4}{1+r^4-2r^2 (e^{i\Delta \varphi}$

and $\mathcal{F} \equiv \frac{\pi r}{1-r^2} = \frac{\pi \cdot \sqrt{R}}{1-\sqrt{R}}$, where R=r² is the mirror reflectivity.

- To increase \mathcal{F} , R should be close to 1:
- To reach such high R, dielectric mirrors are needed.

R	${\mathcal F}$	
0.73134	10	
0.9690737	100	
0.99686334	1000	
0.99000334	1000	



reflectance

reflectance r_2

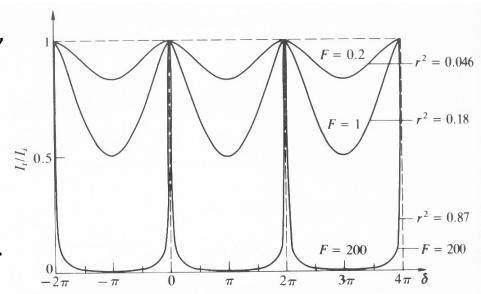
The Fabri-Pérot cavity spectrometer: principles (2)

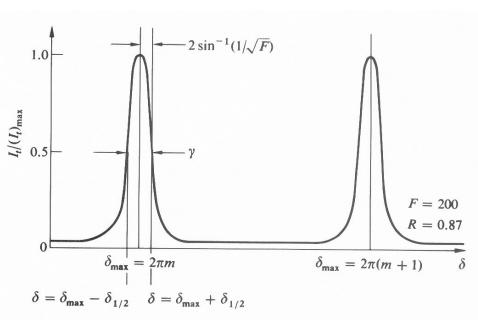
• The output intensity: $I_{out} = \frac{I_{max}}{1 + \left(\frac{2\mathcal{F}}{\pi}\right)^2 \sin^2 \Delta \varphi / 2}$, with: $\Delta \varphi = 2kL = \frac{4\pi L}{\lambda}$,

$$\mathcal{F} \equiv \frac{\pi r}{1 - r^2} = \frac{\pi \cdot \sqrt{R}}{1 - \sqrt{R}} .$$

- We have maximal intensity $I_{out}=I_{max}$ when: $\sin^2\Delta\varphi/2=0$, or: $\Delta\phi_{\text{max}}=2\pi m$ (m=1,2,3,...) . This corresponds to: L= $\lambda m/2$. The phase difference between peaks is thus: $\Delta\phi_{\text{p-p}}=2\pi$, corresponding to $\Delta L=\lambda$.
- The width at half-maximum is obtained when: $\left(\frac{2\mathcal{F}}{\pi}\right)^2\sin^2\Delta\phi_{1/2}/2=1$. For $\mathcal{F}>4$ we can use the linear approximation of the sinus, giving: $\Delta\phi_{1/2}=\pi/\mathcal{F}$. The ratio of p-p distance and full width at half-maximum (FWHM) $\delta\phi=2\Delta\phi_{1/2}$ is: $R=\Delta\phi_{\text{p-p}}/\delta\phi=\mathcal{F}$.
- As the width at half-maximum is small, most of the phase values lead to low intensity, with the minimal intensity occurring when:

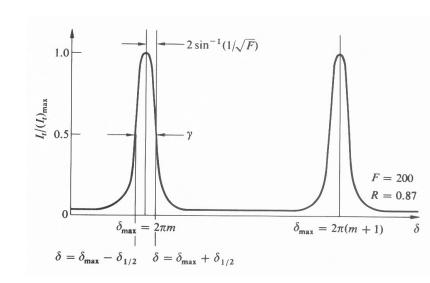
 $\sin^2 \Delta \varphi / 2 = 1$, or: $\Delta \varphi_{\min} = \pi (2m+1)$ (m=1,2,3,...) , or: $L=\lambda (2m+1)/4$.

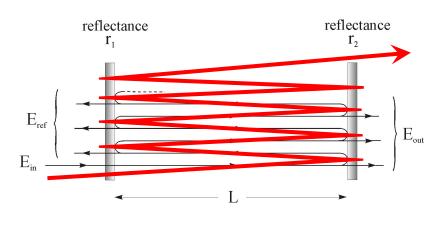




The Fabri-Pérot cavity spectrometer: principles (3)

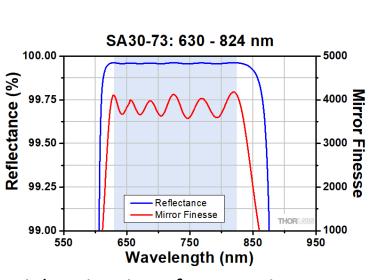
- We saw that the maxima correspond to: $L=\lambda m/2$. Typically, L=10mm, so: $m=2L/\lambda=2\cdot10^4$.
- To pass from one maximum to the next, we need to change L by $\lambda/2$, or change the wavelength by: $\Delta\lambda = \lambda^2/2L$. We call $\Delta\lambda$ the **free spectral range** (FSR). In our example, L=10mm, $\lambda=1$ μ m, so $\Delta\lambda=50$ pm!
- The wavelength **resolution** is the FWHM: $\delta\lambda = \Delta\lambda/\mathcal{F}$. In our example, and with \mathcal{F} =1000, $\delta\lambda$ =50fm! The **resolvance** is $R = \mathcal{F}$.
- Due to the small values of $\Delta\lambda$ and $\delta\lambda$, we often state them in MHz/GHz $(f=c/\lambda)$: $\Delta f=c\Delta\lambda/\lambda^2=3.10^{20}\Delta\lambda$. In our example: $\Delta f=15$ GHz, $\delta f=15$ MHz.
- In a plane mirrors cavity, if the angle between the beam and the mirror is not precisely 90°, the beam will go out of the cavity after several reflections, which will reduce \mathcal{F} to a much smaller value.
- To maintain a finesse \mathcal{F} , the maximal angle error is : $\alpha_{\text{max}} = \text{tg}^{-1}(H/2FL)$, where H is the mirror radius. In our example, for H= c cm, \mathcal{F} =1000, we get: $\alpha_{\text{max}} = 0.06^{\circ}$!

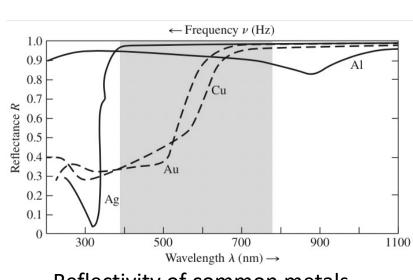


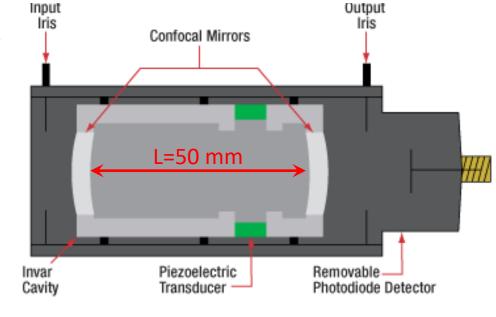


The Fabri-Pérot cavity spectrometer: instrument

- We saw that the maxima correspond to: $L=\lambda m/2$. Typically, L=10mm, so: $m=2L/\lambda=2\cdot10^4$.
- The Fabri-Pérot spectrometer is usually constructed with spherical mirrors, to avoid the sensitivity to beam misalignment. This design often doubles the optical path, giving the condition for maxima: $L=\lambda m/4$.
- To obtain precise cavity tuning, a piezoelectric actuator is used to displace the mirrors. Typical movement range is of a few μ m, with a resolution of a few nm.
- Only dielectric mirrors have sufficient reflectivity needed for a high finesse value.





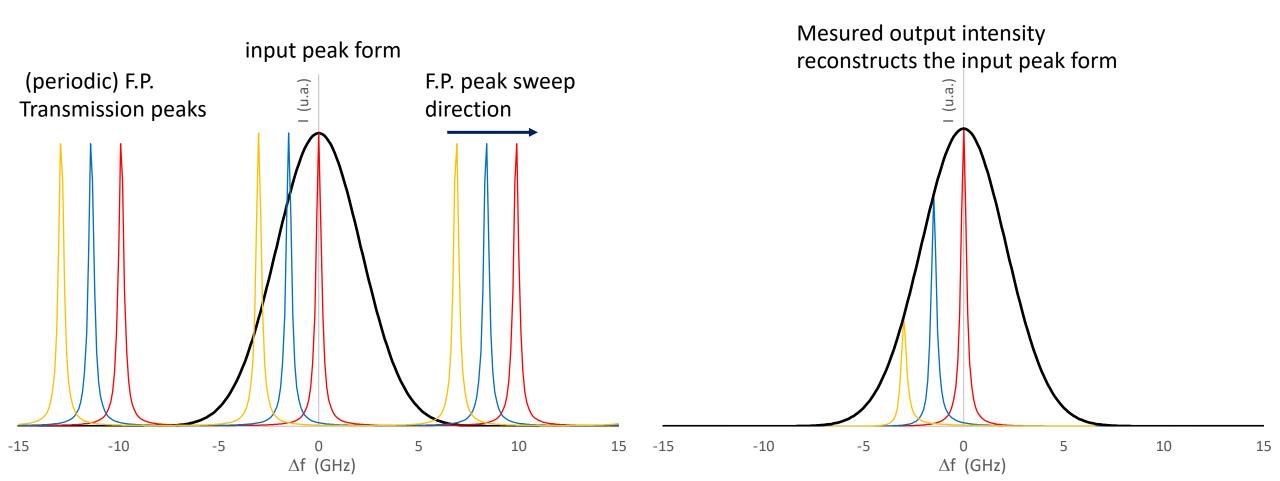


Dielectric mirror for FP cavity

Reflectivity of common metals

The Fabri-Pérot cavity spectrometer: use

- The special property of the Fabry-Pérot spectrometer: periodic series of very narrow transmission peaks.
- The main use: linewidth analysis of light sources (e.g. lasers, quantum dots). The cavity is a very narrow filter, and we sweep the transmission peak through a small wavelength range to trace the form of the measured spectrum. The FWHM (resolution) of the transmission peak must be much smaller than the measured linewidth.



Summary of Fabri-Pérot cavity spectrometer properties

Advantages:

- High transmission efficiency (close to 100%)
- Extremely high resolution better than other spectrometers.

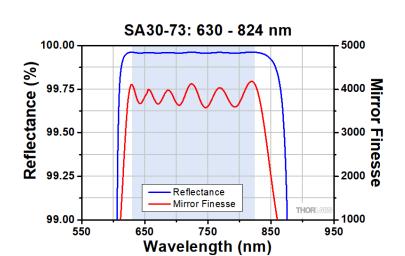
• Disadvantages:

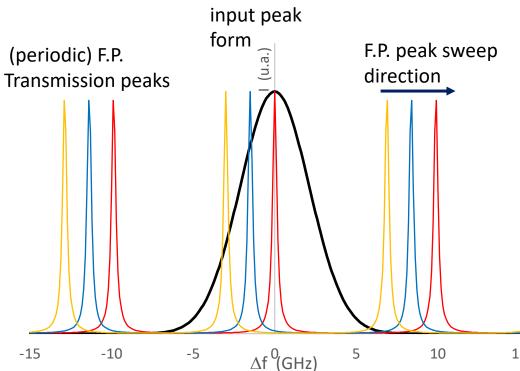
- Periodic transmission peaks no absolute wavelength measurement.
- The high-reflectivity mirrors can work over a limited wavelength range (about 20% of the center wavelength).

Invar Piezoelectric Removable Photodiode Detector

Main applications:

Linewidth measurement of narrow emission lines.





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Comparison of spectrometer types

		Prism spectrometer Pellin-Broca	Grating spectrometer iHR 320 (Horiba-Jobin-Yvon)	Interferential Spectrometer PF -Thorlabs SA210-3B	FTIR IRTracer-100 [Shimadzu]
	Price	low	medium	medium / high	medium / high
	absorption mode	yes	yes	yes	yes
r	emission mode	yes	yes	yes	no
	simplicity	simple	intermediate	sophisticated	sophisticated
	stability (mechanical)	low	intermediate	high	high
	stability (thermal)	low	intermediate	high	high
	spectral domain	0.19 μm - 2.5 μm (max 5 μm)	0.15 μm - 1.5 μm (max 40 μm)	0.3 μm - 2.5 μm	0.8 μm - 25 μm
	detector	PM - CCD/CMOS - bolometer	PM - CCD/CMOS - bolometer	PM, Avalanche diode	InGaAs, bolometer, Golay
	resolvance	2135 [0.06 nm at 435 nm]	7250 [0.06 nm at 435 nm]	10* [60 MHz at 6x10	3200 (0.25 cm-1 at nm at 800 cm-1)
	dispersive element size	25 mm (F2 glass)	68mm x 68 mm (1200g/mm)	1 mm beam Ø	1mm beam Ø
			(HR 320	SA.300	
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