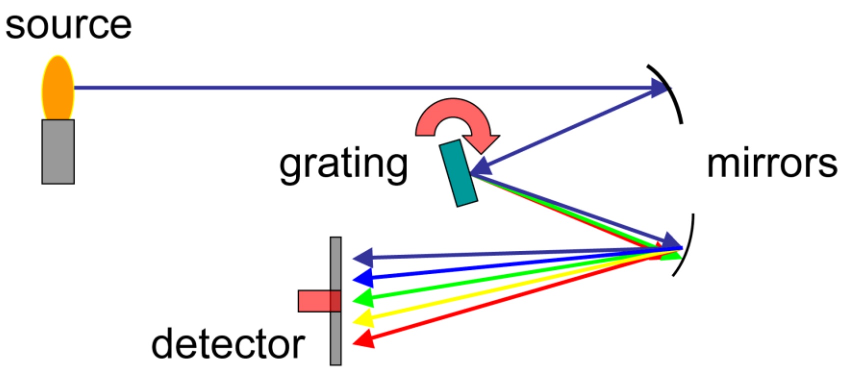
Ch3. General Features of Experimental Methods



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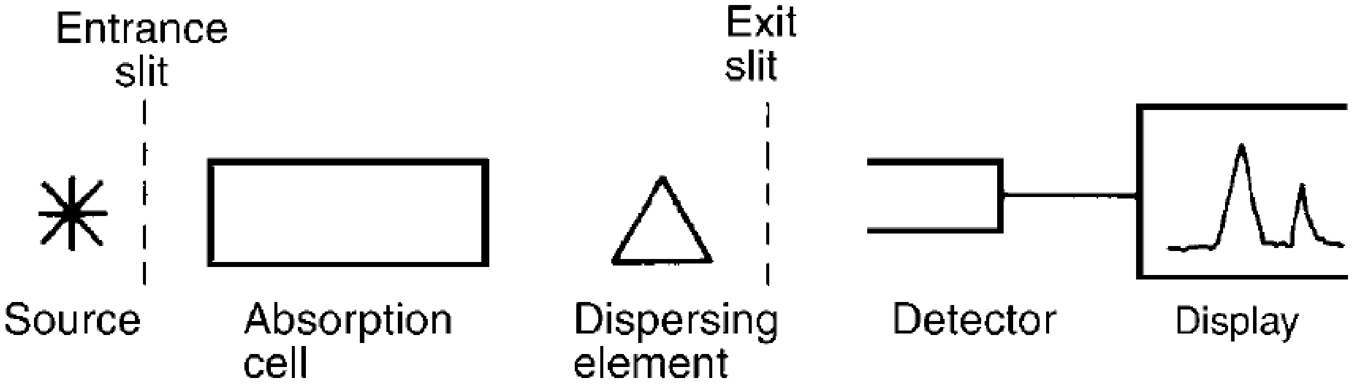
POSTECH

Components of absorption spectroscope

- Light source
- Absorption cell
- Dispersing element: prisms, grating, interferometer …
- Detector



Scheme of absorption spectrophotometer

Dispersing elements

When wavelengths λ and $\lambda + d\lambda$ are just observably separated, then the resolution is

- $\mathrm{d}\lambda$ (wavelength)
- $\mathrm{d}\nu$ (corresponding frequency interval)
- $\mathrm{d}\tilde{\nu}$ (corresponding wavenumber interval)

Resolving power (R)

$$R = \frac{\lambda}{\mathrm{d}\lambda} = \frac{\nu}{\mathrm{d}\nu} = \frac{\tilde{\nu}}{\mathrm{d}\tilde{\nu}}$$

Linear dispersion: $\frac{dl}{\mathrm{d}\lambda}$

Angular dispersion: $\frac{d\theta}{\mathrm{d}\lambda}$

For a prism,

$$R = b\frac{\mathrm{d}n}{\mathrm{d}\lambda}$$

b: length of base

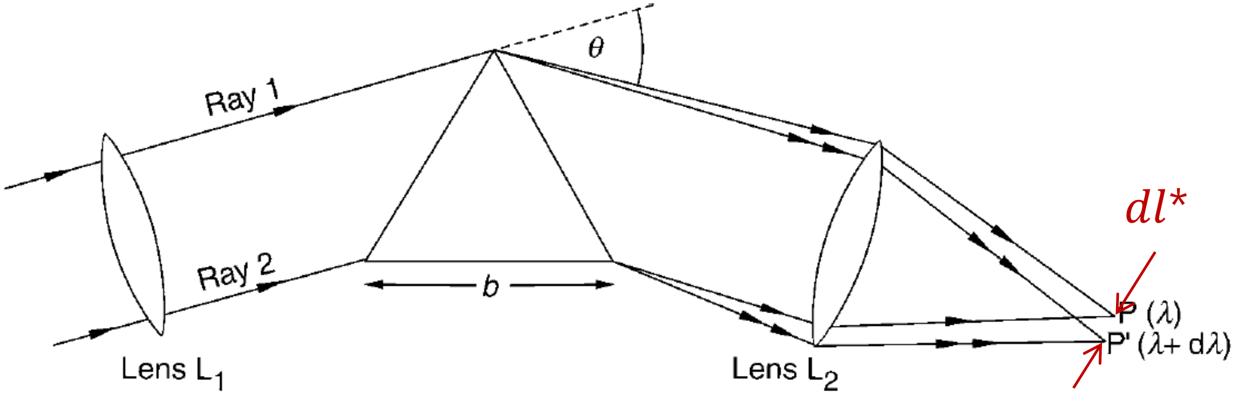
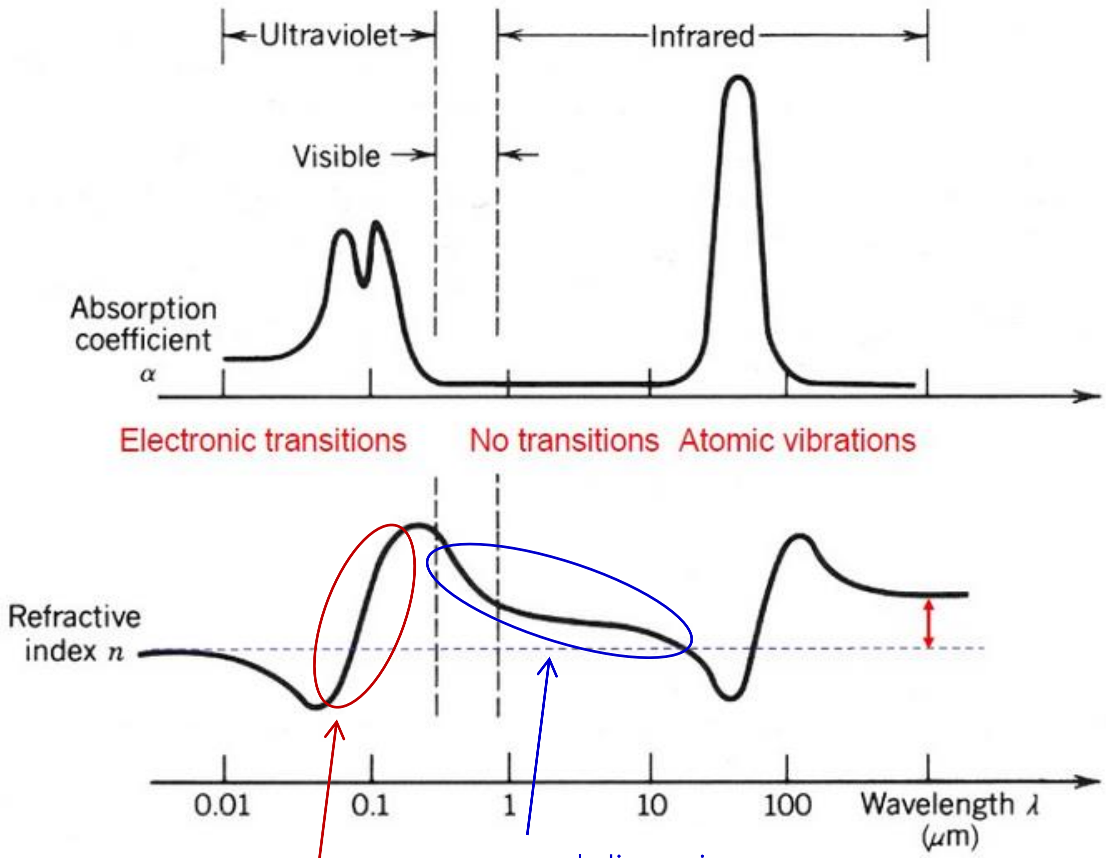


Figure 3.3 Dispersion by a prism

*separation in detector plane

Dispersion & absorption in dielectrics



normal dispersion

$$\frac{dn}{d\lambda} < 0$$

anomalous dispersion

$$\frac{dn}{d\lambda} > 0$$

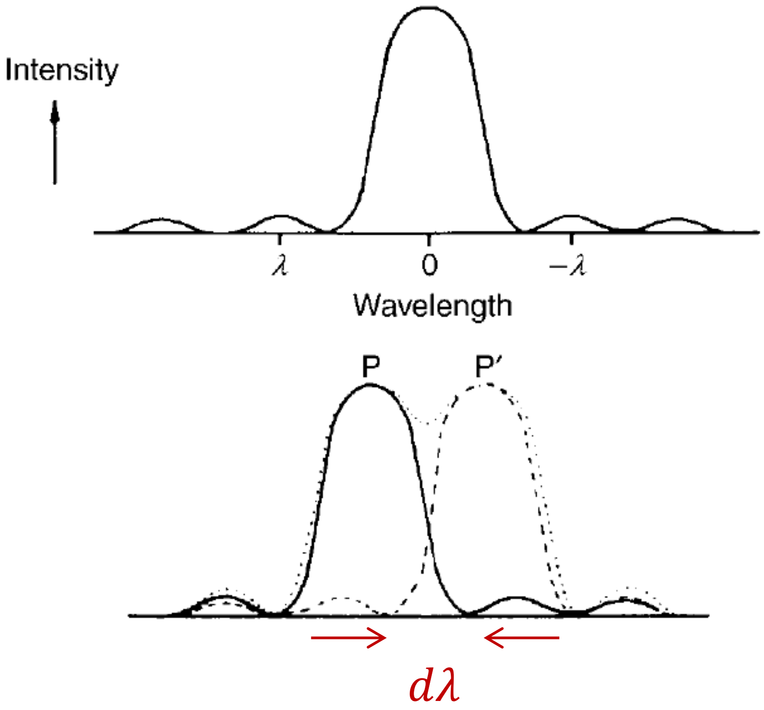
*insulators vs dielectrics

(Vladimir M. Shalaev @ Purdue Univ.)

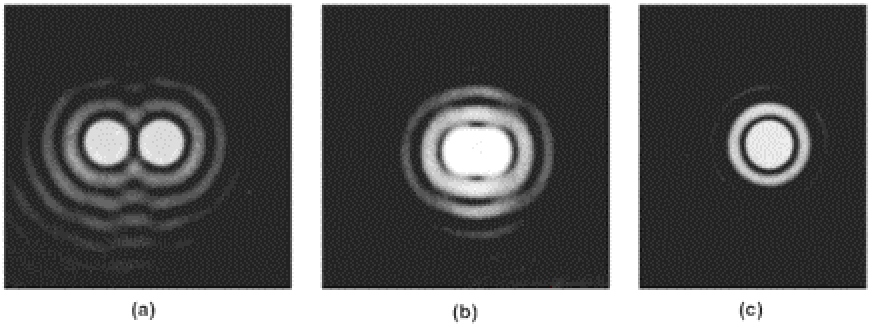
Rayleigh criterion of resolution

- Two point sources are regarded as just resolved when the principal diffraction maximum of one image coincides with the first minimum of the other

Diffraction through a slit



Diffraction through a circular hole (Airy patterns)


well resolved
just resolved
unresolved

Diffraction gratings

- consist of a series of parallel grooves ruled on a hard glassy or metallic material
- 100 ~ 2000 grooves/mm (spacing: 0.5 ~10 μm)

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

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

$$R = m \cdot n \cdot w_G = m \cdot N$$

m: order of diffraction
d: groove spacing
i: incidence angle
θ: diffraction angle
n: groove density
w_G: width of illuminated area
N: total number of grooves illuminated

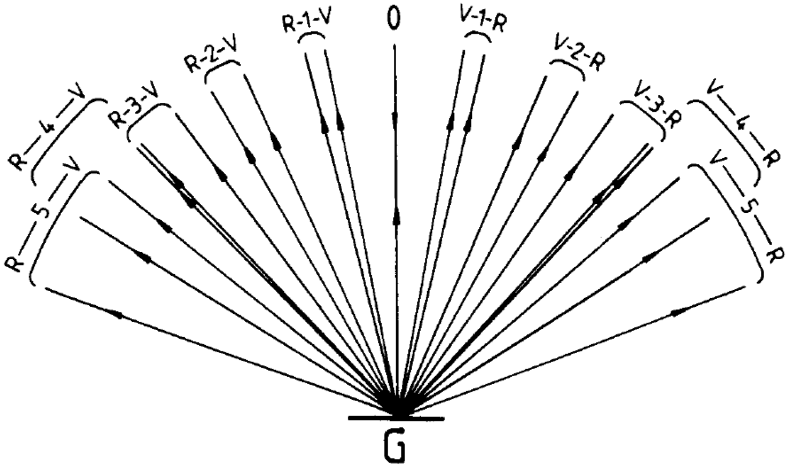
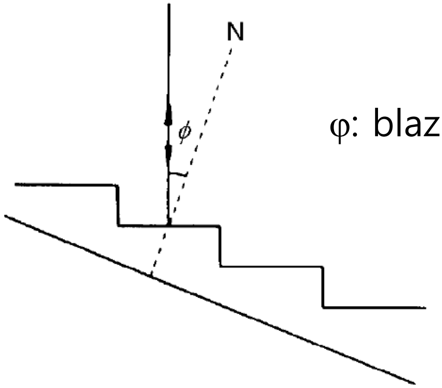


Figure 3.5 Various orders of diffraction from a plane reflection grating G; R indicates the red end of the spectrum; V indicates the violet end of the spectrum; the central number is the order of diffraction

Blazed gratings:

- allow preferential diffraction at a designed angle



φ: blaze angle

Worked example 3.1

Question. A diffraction grating has a ruled area that is 10.40 cm wide, has 600.0 grooves per millimetre and is blazed at an angle of 45.00°.

(a) What is the wavelength of radiation diffracted at the blaze angle in the first, fourth and ninth orders?

(b) What is the resolving power in these orders?

(c) What is the resolution in terms of wavelength (nm), wavenumber (cm^{-1}) and frequency (GHz) in the ninth order at 300 nm?

(a) The grating is 104.0 mm wide. Thus the total number of grooves is given by

$$N = 104.0\ \mathrm{mm} \times 600.0\ \mathrm{mm}^{-1} = 62\,400$$

and the spacing between grooves by

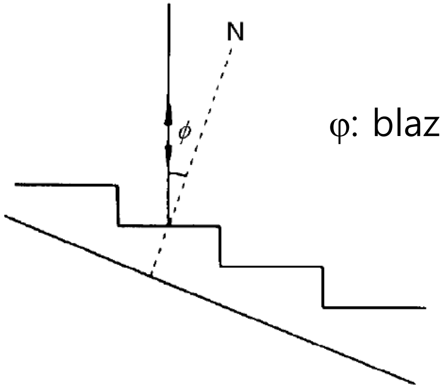
$$\begin{aligned} d &= \frac{0.1040\ \mathrm{m}}{62\,400} \\ &= 1.6667 \times 10^{-6}\ \mathrm{m} \\ &= 1666.7\ \mathrm{nm} \end{aligned}$$

The Bragg equation for diffraction is given by Equation (3.9):

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

$$\begin{aligned} m\lambda &= 2d\sin\theta \\ &= 2 \times 1666.7\,\text{nm} \times 0.70711 \\ &= 2357.1\ \text{nm} \end{aligned}$$

$$\therefore \quad \lambda = \begin{cases} 2357\,\text{nm} & \text{for } m = 1 \\ 589.3\,\text{nm} & \text{for } m = 4 \\ 261.9\,\text{nm} & \text{for } m = 9 \end{cases}$$



φ: blaze angle

(b) The resolving power R of the grating is given by Equation (3.8) as

$$\begin{aligned} R &= mN \\ &= 62\,400m \end{aligned}$$

$$\therefore \quad R = \begin{cases} 62\,400 & \text{for } m = 1 \\ 249\,600 & \text{for } m = 4 \\ 561\,600 & \text{for } m = 9 \end{cases}$$

(c) The resolution $\mathrm{d}\lambda$, $\mathrm{d}\tilde{\nu}$ or $\mathrm{d}\nu$ is obtained from the resolving power by using Equation (3.3)

$$R = \frac{\lambda}{\mathrm{d}\lambda} = \frac{\tilde{\nu}}{\mathrm{d}\tilde{\nu}} = \frac{\nu}{\mathrm{d}\nu}$$

$$\therefore \quad \mathrm{d}\lambda = \frac{\lambda}{R} = \frac{300.0 \text{ nm}}{561\,600}$$

$$= 5.342 \times 10^{-4} \text{ nm}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{300.0 \text{ nm}} = \frac{1}{300.0 \times 10^{-7} \text{ cm}} = 33\,333 \text{ cm}^{-1}$$

$$\therefore \quad \mathrm{d}\tilde{\nu} = \frac{\tilde{\nu}}{R} = \frac{33\,333 \text{ cm}^{-1}}{561\,600}$$

$$= 0.05935 \text{ cm}^{-1}$$

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10} \text{ cm s}^{-1}}{300.0 \times 10^{-7} \text{ cm}} = 9.9933 \times 10^{14} \text{ s}^{-1}$$

$$= 9.9933 \times 10^{5} \text{ GHz}$$

$$\therefore \quad \mathrm{d}\nu = \frac{\nu}{R} = \frac{9.9933 \times 10^{5} \text{ GHz}}{561\,600}$$

$$= 1.779 \text{ GHz}$$

Czerny–Turner spectrometer

- Using planar gratings
- Scanning wavelength by rotating the grating
- Most popular in compact spectrometers

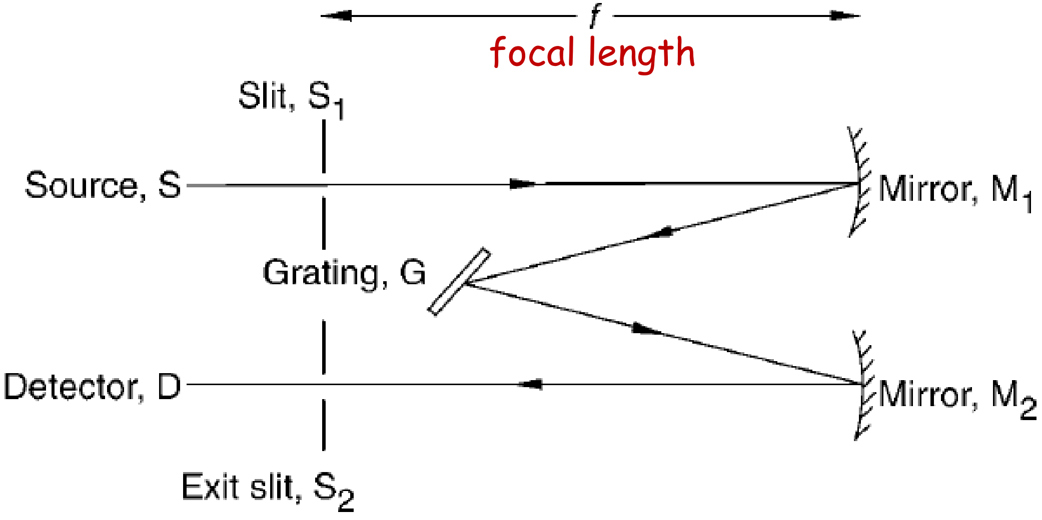


Figure 3.17 The Czerny–Turner grating mounting

Detectors for UV or Vis

- Photomultipliers: photoelectrons from metals with low work function are multiplied several times
  (high gain → high sensitivity)
- CCD (charge coupled device): silicon photosensors
  2-dim arrays → multiplex advantage

*multiplex advantage:

- an improvement in signal to noise ratio that is gained when taking multiplexed measurements rather than direct measurements using scanning monochromator

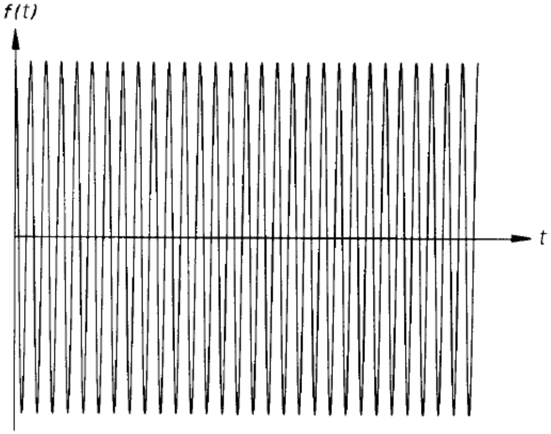
Fourier transformation

$$f(t) = A\cos 2\pi\nu t \qquad\qquad f(t) = A[\cos 2\pi\nu t + \cos 2\pi(\tfrac{1}{4}\nu)t]$$

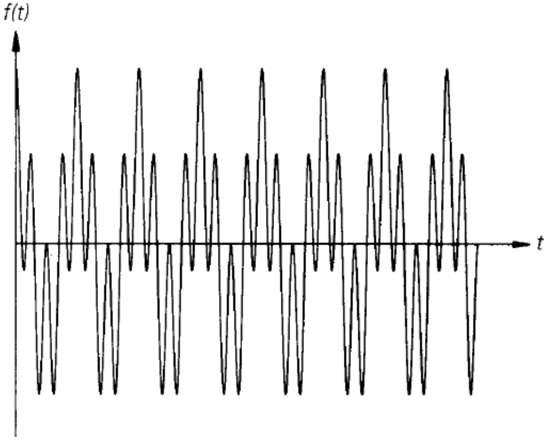
Time-domain spectrum:

$$f(t) = \int_{-\infty}^{+\infty} F(\nu)\exp(\mathrm{i}2\pi\nu t)\mathrm{d}\nu$$

(a)



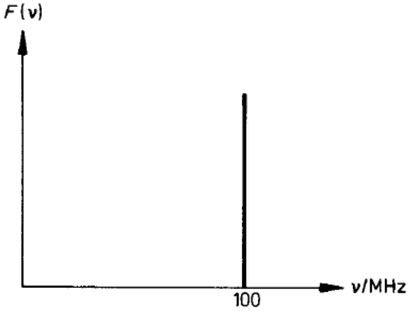
(a)



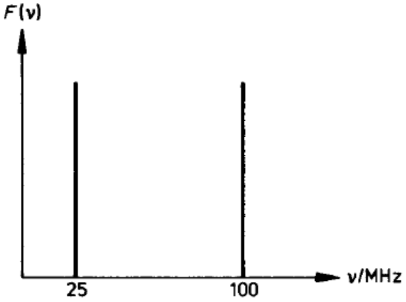
Frequency-domain spectrum:

$$F(\nu) = \int_{-\infty}^{+\infty} f(t)\exp(-\mathrm{i}2\pi\nu t)\mathrm{d}t$$

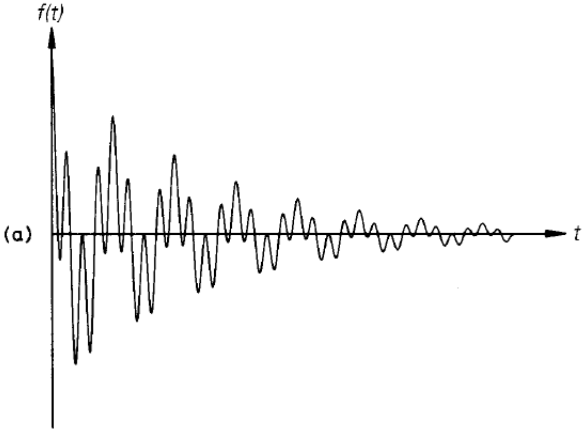
(b)

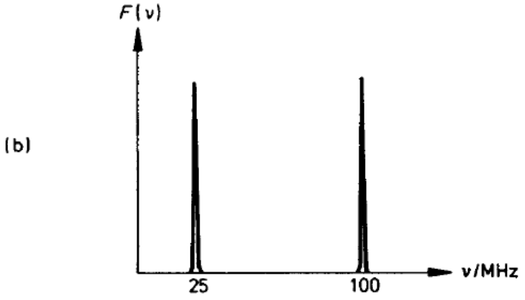


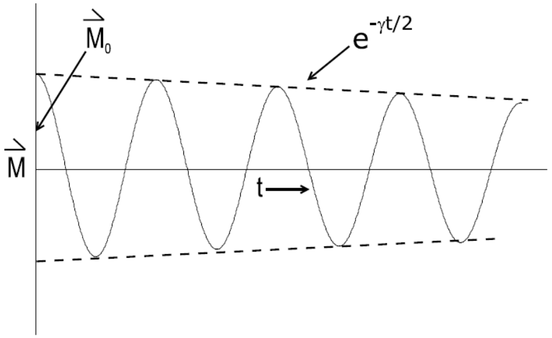
(b)



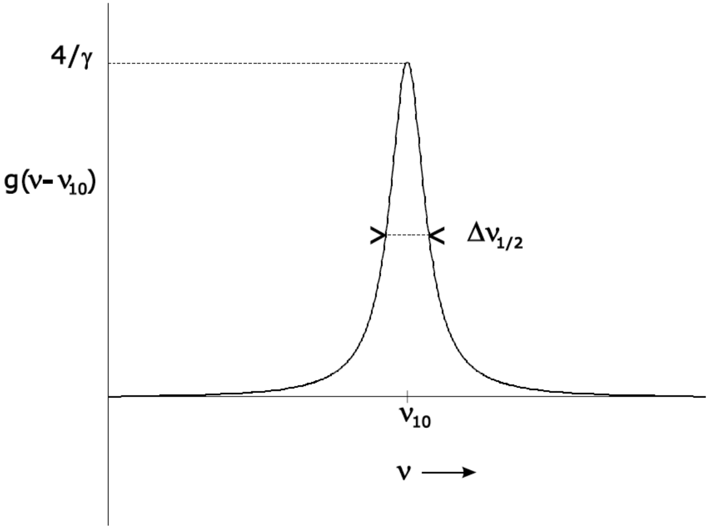
FT of exponentially decaying signals*







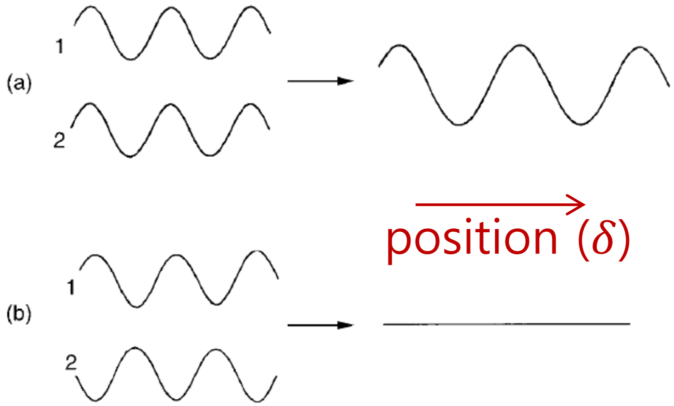
Slowly damped oscillating dipole moment



$$g(\nu - \nu_0) = \frac{\Delta\nu_{1/2}/(2\pi)}{(\Delta\nu_{1/2}/2)^2 + (\nu - \nu_0)^2}$$

* Light emission or free induction decay (FID) in pulsed NMR spectroscopy

Interferometer-based FT spectrometer



$\xrightarrow{\hspace{2cm}}$
position (δ)

time vs frequency

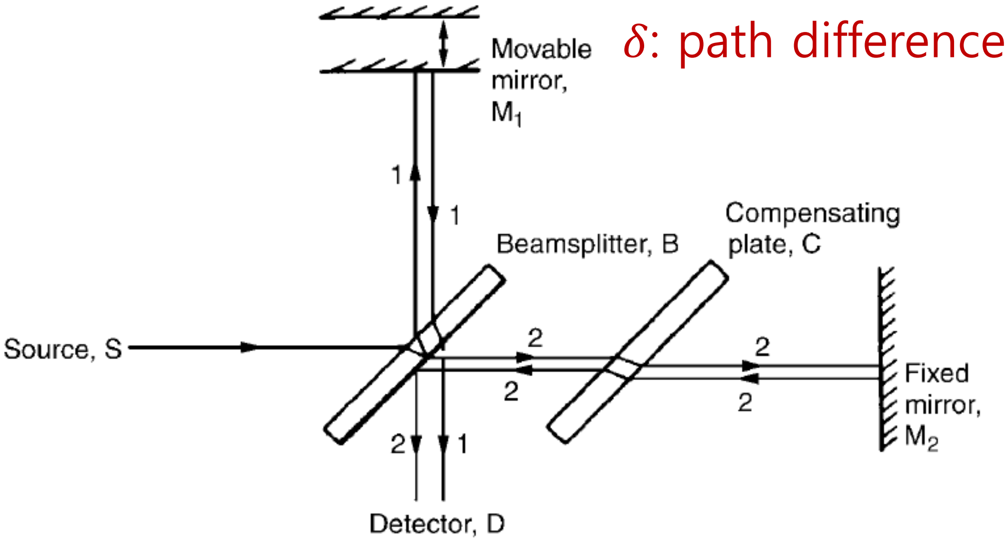
$$f(t) = \int_{-\infty}^{+\infty} F(\nu)\exp(\mathrm{i}2\pi\nu t)\mathrm{d}\nu$$

$$F(\nu) = \int_{-\infty}^{+\infty} f(t)\exp(-\mathrm{i}2\pi\nu t)\mathrm{d}t$$

position vs wave number

$$I(\delta) = \int_{0}^{\infty} B(\tilde{\nu})\cos 2\pi\tilde{\nu}\delta\ \mathrm{d}\tilde{\nu}$$

$$B(\tilde{\nu}) = 2\int_{0}^{\infty} I(\delta)\cos 2\pi\tilde{\nu}\delta\ \mathrm{d}\delta$$

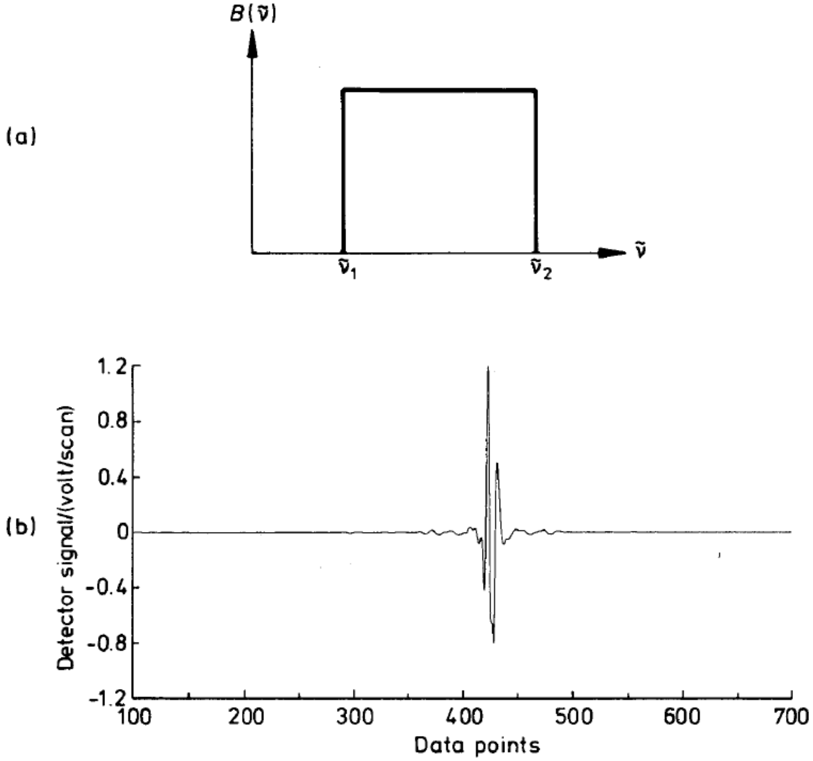


δ: path difference

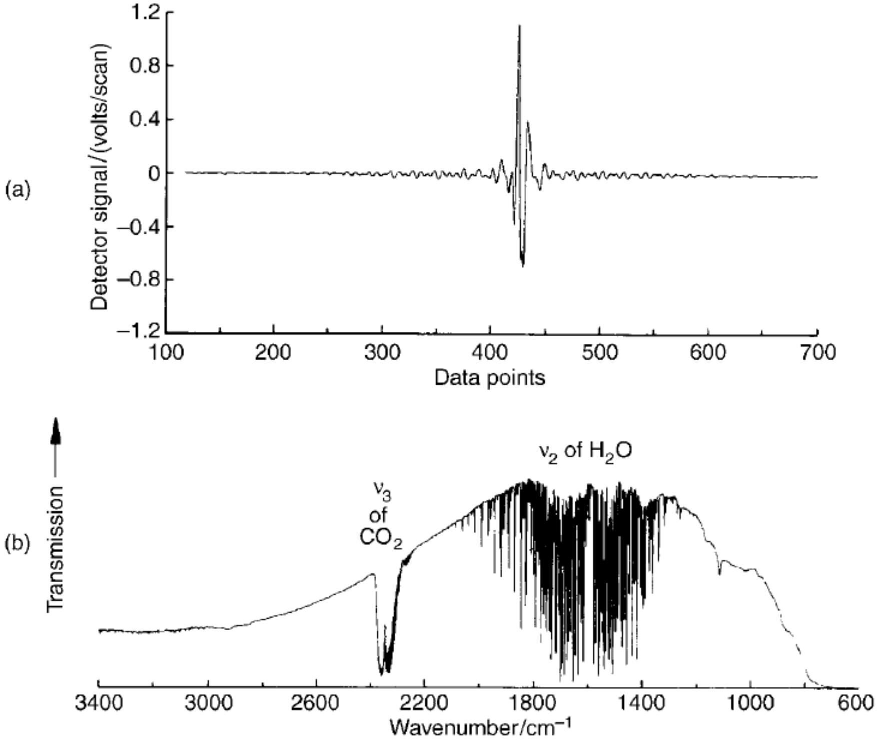
Figure 3.11 Michelson interferometer

Interferogram: I(δ)- δ plot

Emission spectrum of flat broad band source



Absorption spectrum of air



- Resolution limit:

$$\Delta\tilde{\nu} = \frac{1}{\delta_{\max}}$$

δ_{max}: maximum displacement (δ) of the mirror M_1

UV/Vis spectrophotometer (double-beam type)

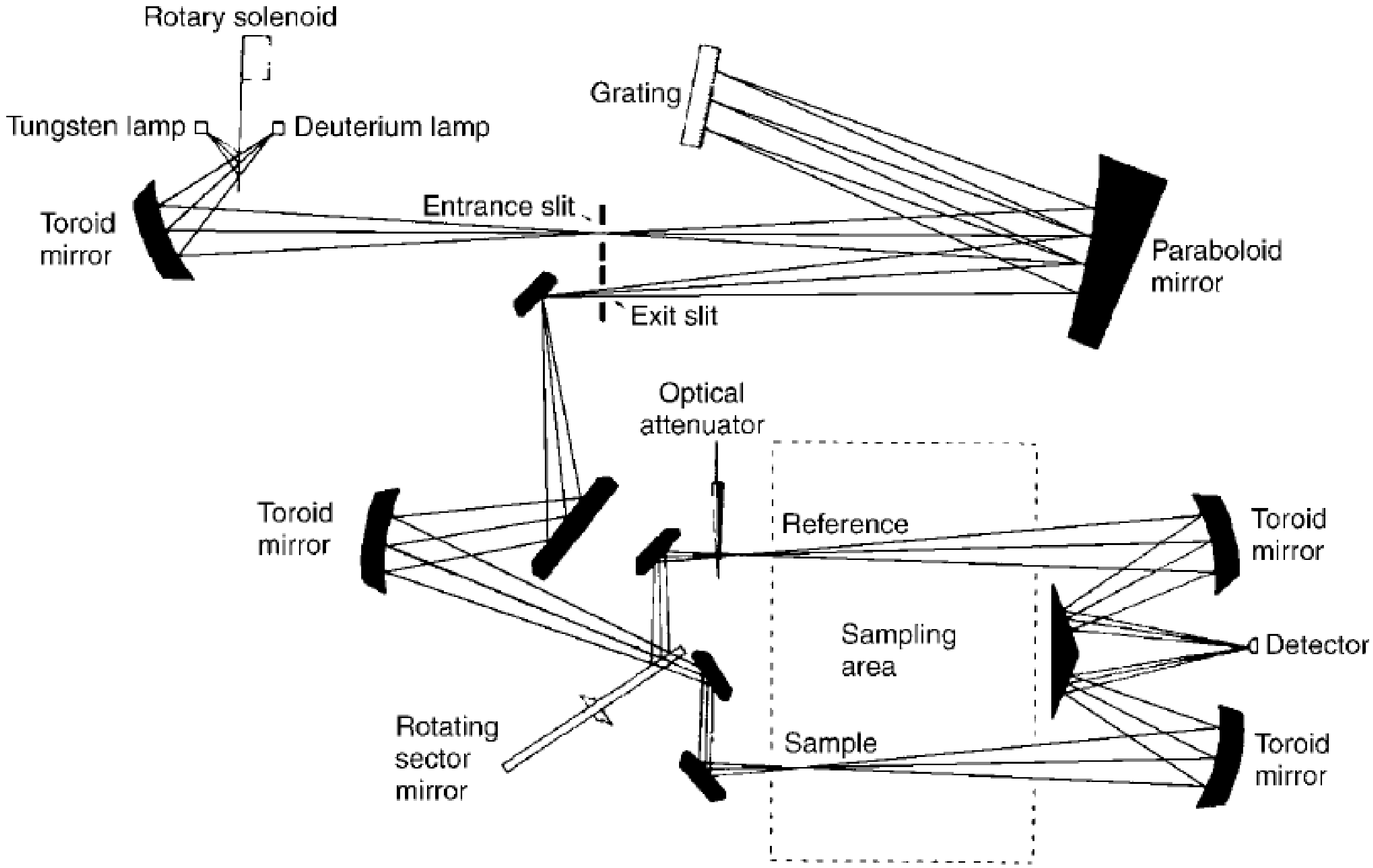


Figure 3.24 A typical double-beam recording visible and near-ultraviolet spectrophotometer