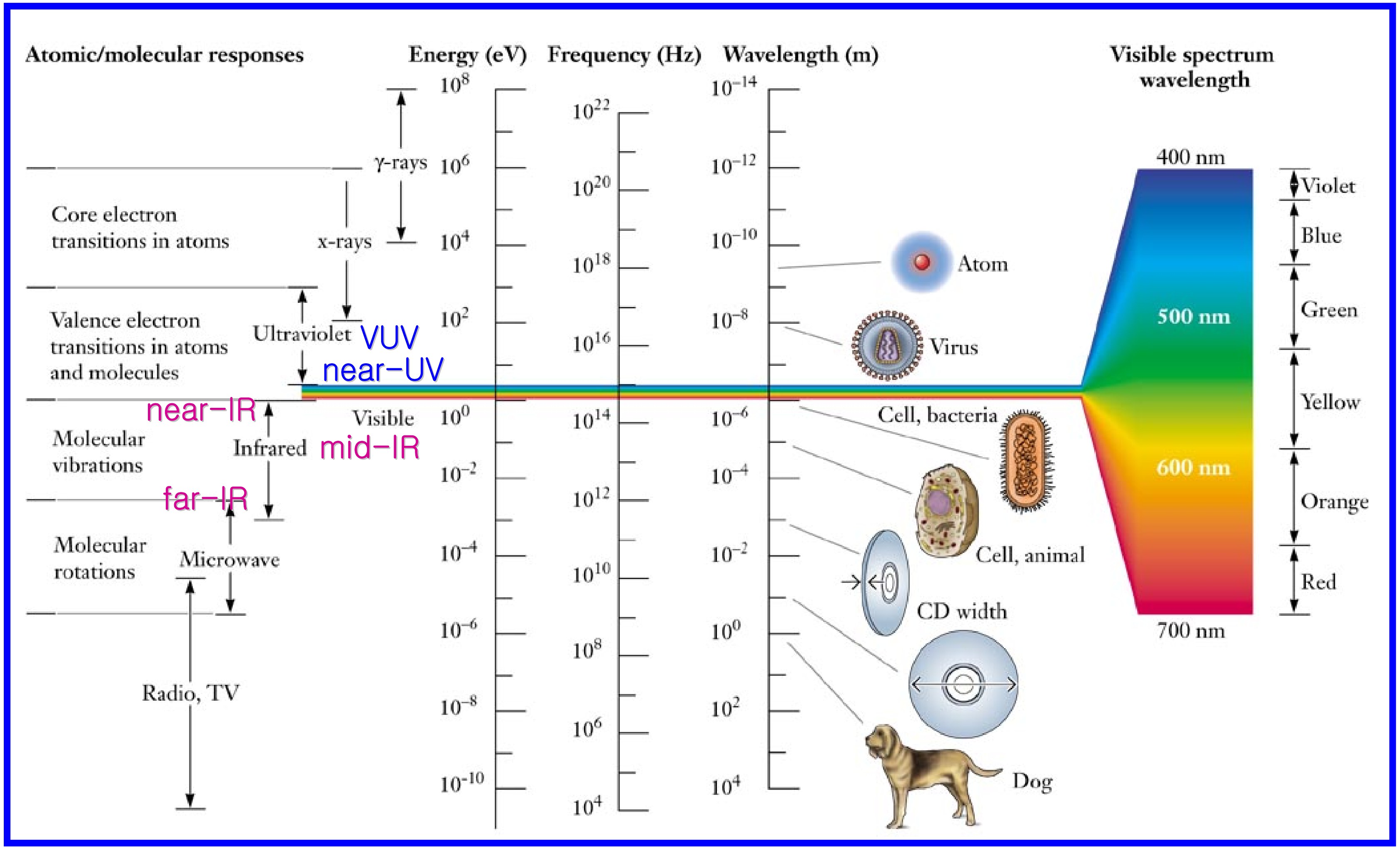
Basics-3

General Features of Experimental Methods

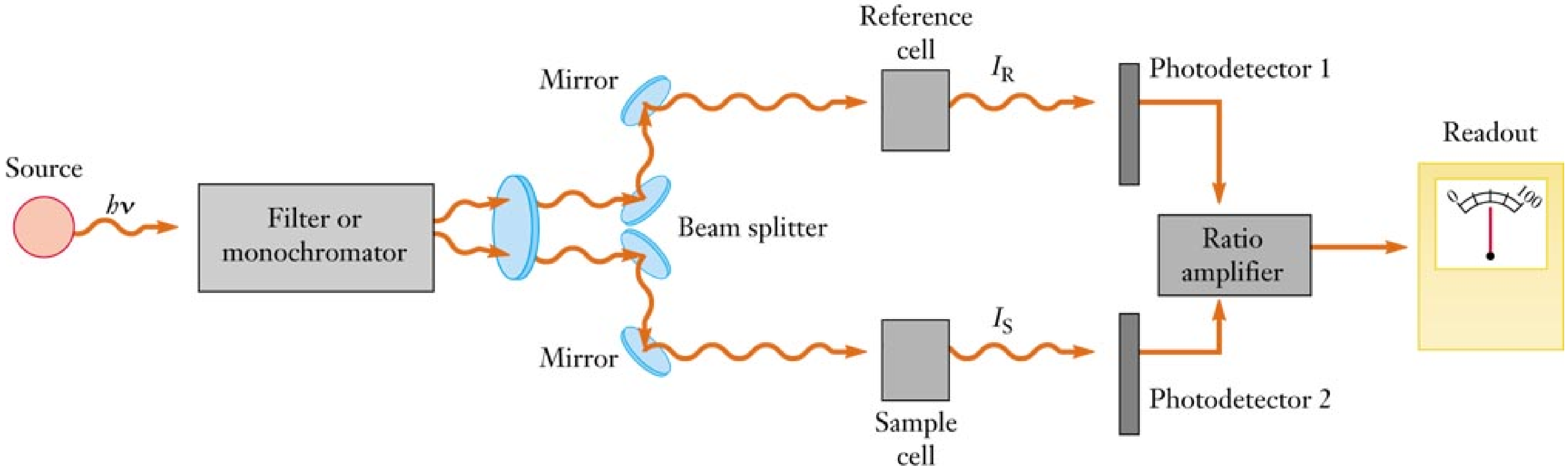
Reference: “Modern Spectroscopy” by Hollas, Chapter 3
“Principles of instrumental analysis” by Skoog
Chapter 7

Electromagnetic Spectrum



$$\lambda = \frac{c}{\nu} = \frac{1}{\bar{\nu}} = \frac{\lambda_{vac}}{n} = \frac{c_{vac}}{n\nu}, \quad 1eV = 8065.54\ cm^{-1} = 2.4 \times 10^{14}\ Hz = 1240\ nm$$

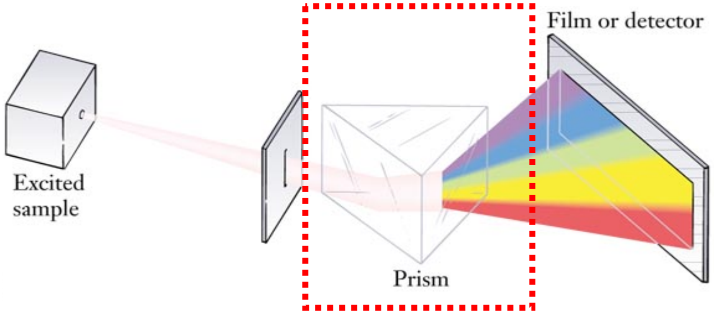
General Components of Absorption Experiment

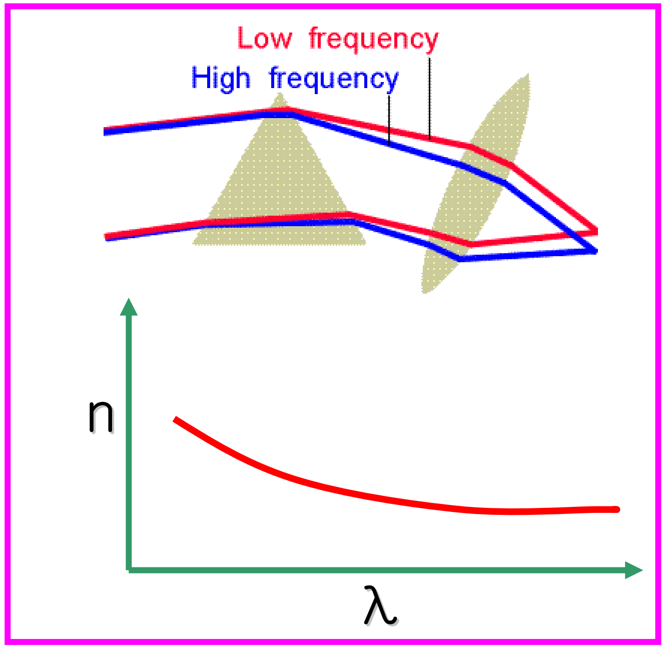


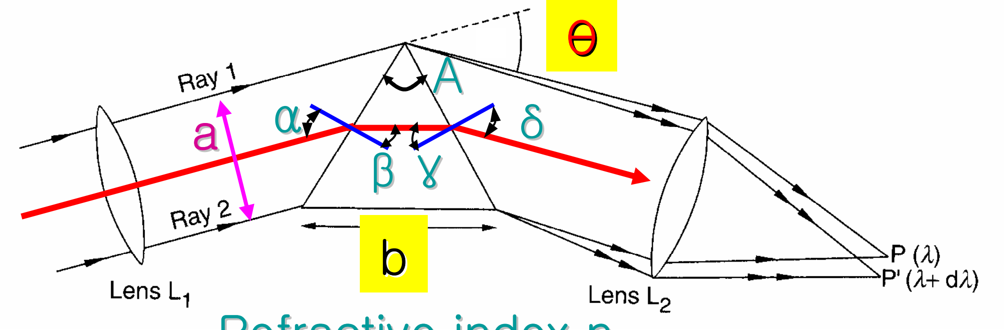
- Light Source (lamp, laser, etc)
- Sample Cell (gas cell, liquid cell, pellet, etc)
- Dispersing Element (prism, grating, interferometer, etc)
- Detector (photodiode, photomultiplier tube, CCD, etc)
- Display
- Optics (mirror, lens, filter, beam splitter, etc)

Dispersing Elements

* Prisms (dispersion, right-angle, etc)







Refractive index n

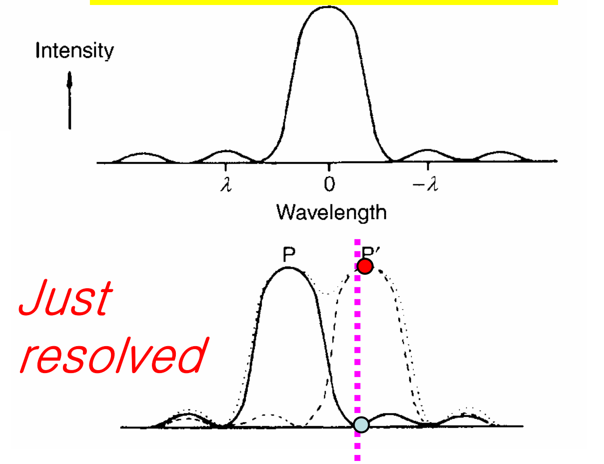
@ min deviation ($d\theta/d\alpha=0$): $\beta=\gamma=A/2$, $\alpha=\delta$, $\theta=2\alpha-A$

Resolving Power: ← *derived from Rayleigh criterion*

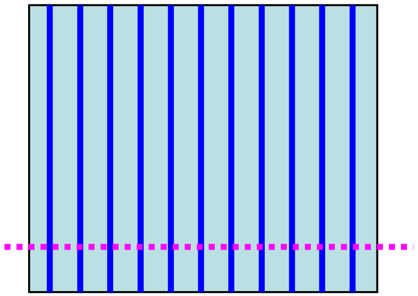
$$R \equiv \frac{\lambda}{\Delta\lambda} = a\frac{d\theta}{d\lambda} = a\frac{d\theta}{dn}\frac{dn}{d\lambda} \quad (a: aperture)$$

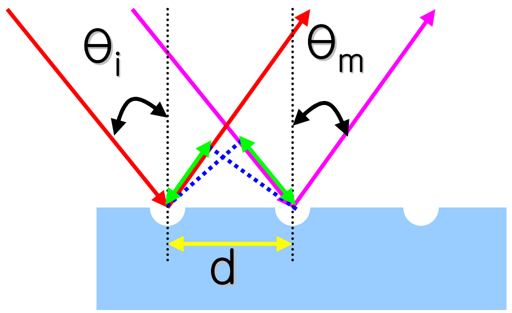
$$= b\frac{dn}{d\lambda} \quad (b: base\ length)$$

Rayleigh Criterion



* Diffraction Gratings





Constructive interference:

$$d(\sin\theta_m - \sin\theta_i) = m\lambda \quad (m = 0, 1, \ldots)$$

- Diffraction Order m

e.g. normal Incidence (θ_i=0)

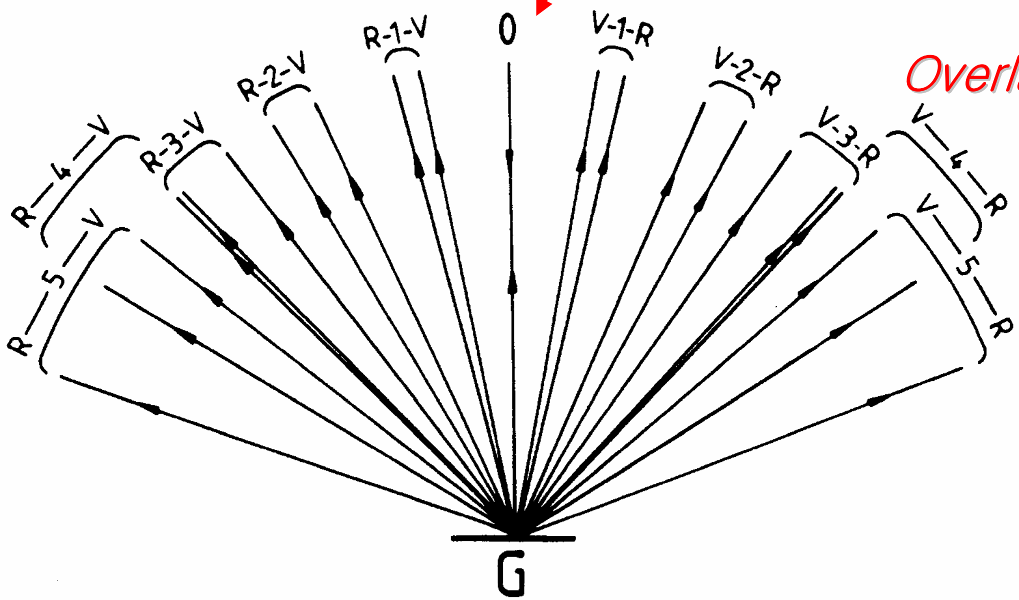
$$d\sin\theta_m = m\lambda$$

angular dispersion:

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

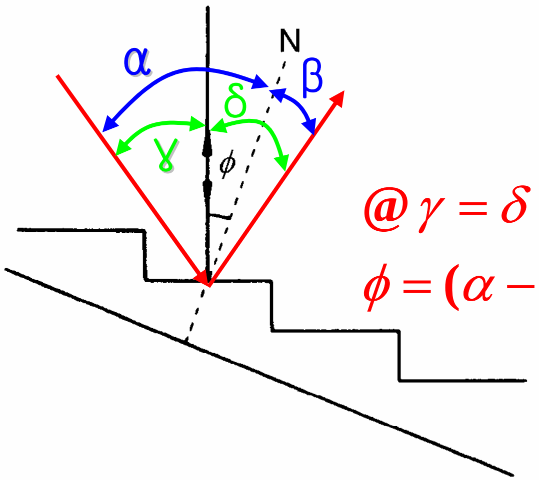
Specular reflection (no dispersion)

Overlap!



- Blazed Grating (ϕ)

$$\theta_{reflection} = \theta_{diffraction}$$



$$@\,\gamma = \delta$$

$$\phi = (\alpha - \beta)/2$$

Specular reflection:
m≠0
"Intensity Increase"

Angular dispersion:

$$d\sin\beta - d\sin\alpha = m\lambda$$

$$\rightarrow \quad \frac{d\beta}{d\lambda} = \frac{m}{d\cos\beta}$$

Rayleigh criterion:

$$\Delta\beta = \frac{\lambda}{Nd\cos\beta}$$

$$\equiv \frac{d\beta}{d\lambda}\Delta\lambda$$

$$\therefore\; RP = \frac{\lambda}{\Delta\lambda} = mN$$

m: order of diffraction
N: # of grooves

Exercise

Suppose a grating w/ ruled area 10X10 cm^2 and 1000 grooves/mm runs in second order (m=2). What is theoretical spectral resolution and minimum spectral separation for λ=500 nm?

$$R = 2x10^5$$

$$\Delta\lambda = 500 \text{ nm} / 2x10^5 = 2.5x10^{-3} \text{ nm}$$

* Fourier Transformation and Interferometers

- Fourier Transform:

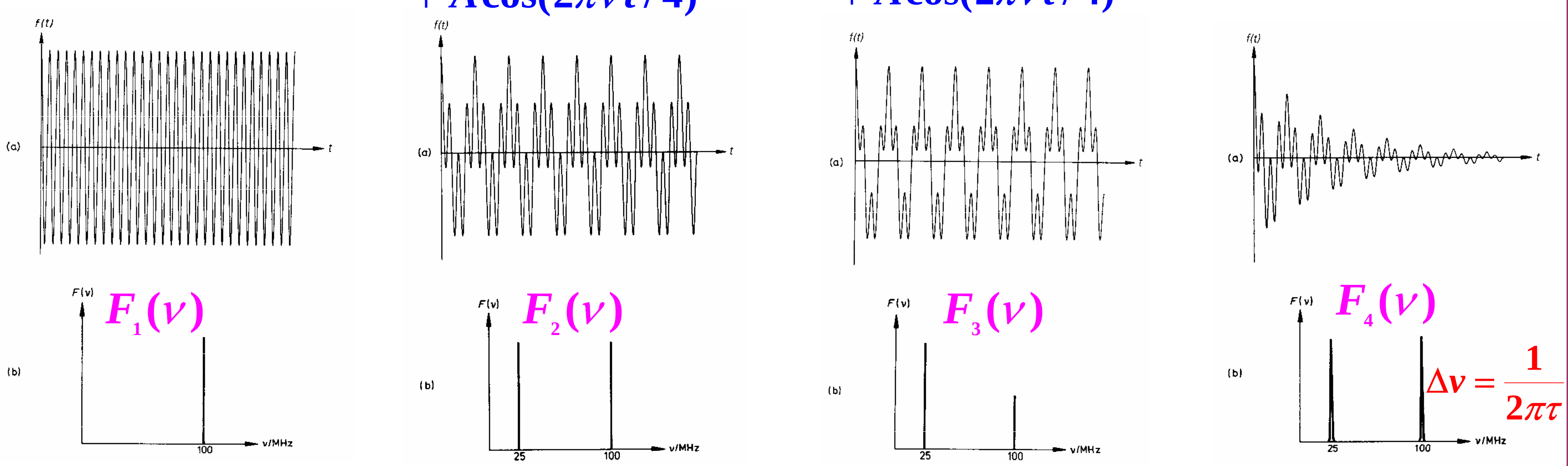
$$f(t) = \int_{-\infty}^{+\infty} F(\nu) e^{i2\pi\nu t} d\nu \leftrightarrow F(\nu) = \int_{-\infty}^{+\infty} f(t) e^{-i2\pi\nu t} dt$$

$f_1(t) = A\cos 2\pi\nu t$

$f_2(t) = A\cos 2\pi\nu t + A\cos(2\pi\nu t/4)$

$f_3(t) = (A/2)\cos 2\pi\nu t + A\cos(2\pi\nu t/4)$

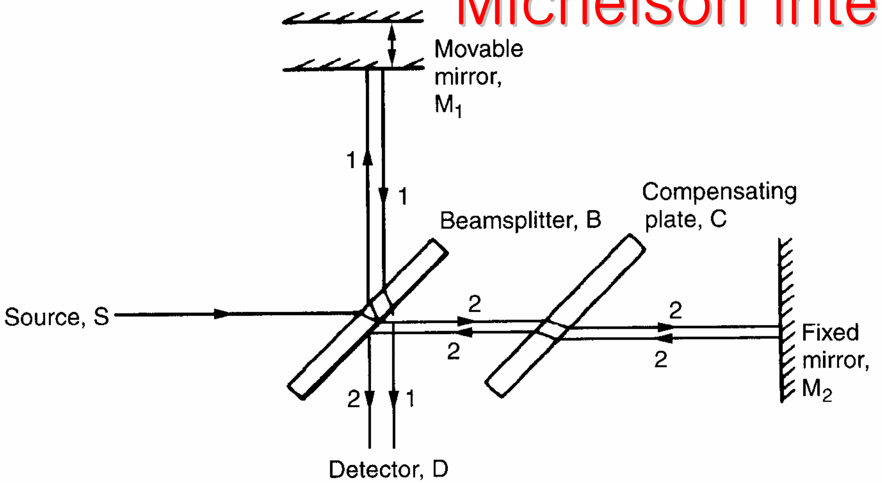
$f_4(t) = f_2(t) e^{-t/\tau}$



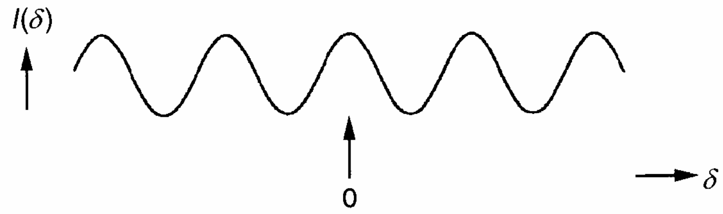
" … By FT, any complex spectra (containing many resonant frequencies and time-decay features) are easily convertible between time and frequency domains…"

– Interferometers:

Michelson Interferometer



Interferogram: $I(\delta)$ vs δ

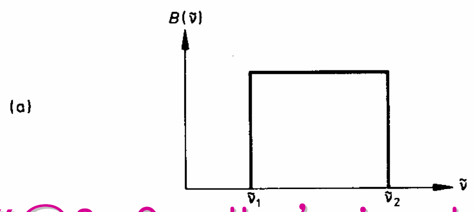


$$I(\delta) = \int_0^\infty B(\bar{\nu}) \cos 2\pi\bar{\nu}\delta \, d\bar{\nu}$$

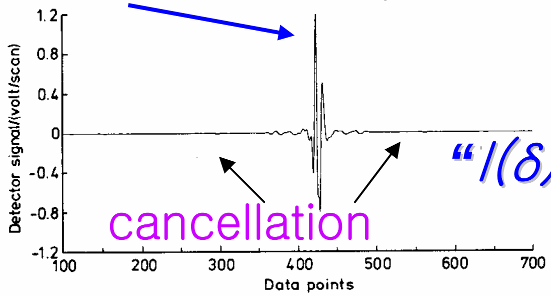
$$B(\bar{\nu}) = 2\int_0^\infty I(\delta) \cos 2\pi\bar{\nu}\delta \, d\delta$$

Application: FT-IR

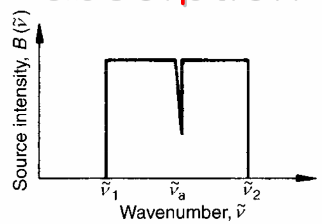
Broad band source



"@δ=0, all ν's in phase"

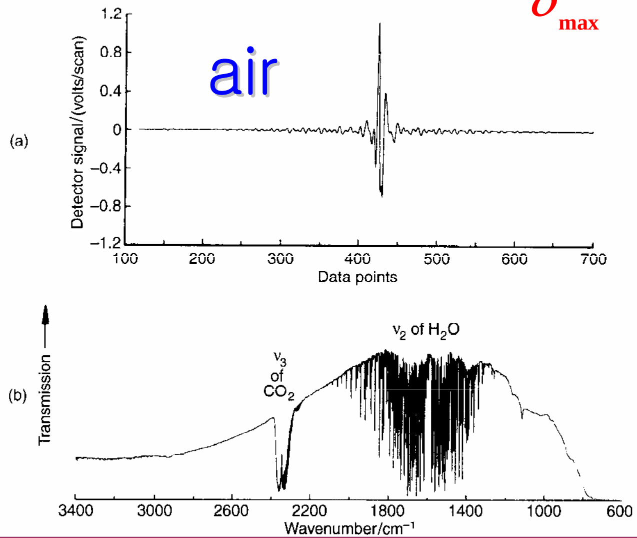


"absorption"



"$I(\delta)$ pattern change"

Resolution: $\Delta\bar{\nu} = \dfrac{1}{\delta_{max}}$



Components of Absorption Experiments

Region	Source	Absorption cell window	Dispersing element	Detector
Microwave	Klystron; backward wave oscillator	Mica	None	Crystal diode
Millimetre wave	Klyston (frequency multiplied); backward wave oscillator	Mica; polymer	None	Crystal diode; Golay cell; thermocouple; bolometer; pyroelectric
Far-infrared	Mercury arc	Polymer	Grating; interferometer	Golay cell; thermocouple bolometer; pyroelectric
Mid- and near-infrared	Nernst filament; globar	NaCl or KBr	Grating; interferometer	Golay cell; thermocouple; bolometer; pyroelectric; photoconductive semiconductor
Visible	Tungsten filament; xenon arc	Glass	Prism; grating; interferometer	Photomultiplier; photodiode; photographic plate
Near-ultraviolet	Deuterium discharge; xenon arc	Quartz	Prism; grating; interferometer	Photomultiplier; photodiode; photographic plate
Far-ultraviolet	Microwave discharge in noble gases; Lyman discharge	LiF (or no windows)	Grating	Photomultiplier; photodiode; photographic plate

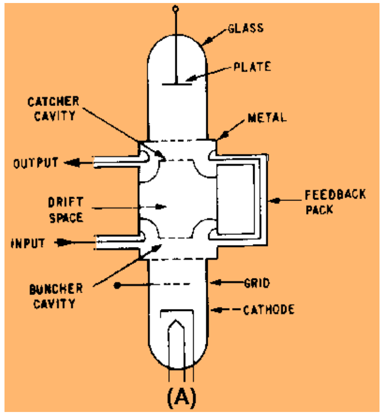
Lasers

CCD

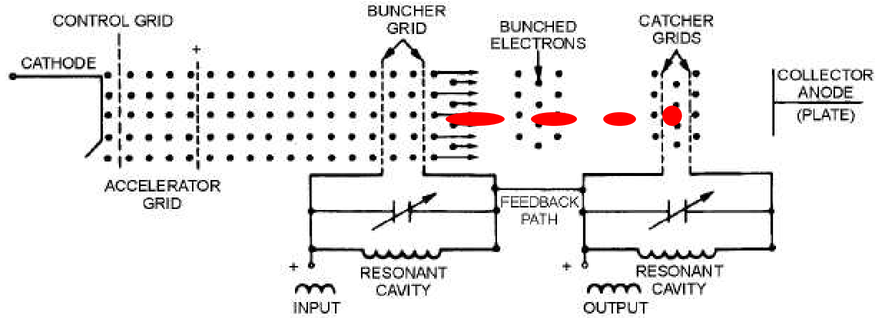
* Microwave region (molecular rotation, electron spin)

$$\nu = 10 - 100\,GHz,\ \bar{\nu} = 0.1 - 1\ cm^{-1}$$

-Source: Klystron



"Use of velocity-modulated electron beam"



-Detector (electronic circuit): crystal diode rectifier

-Optics: window – mica / rectangular waveguide

waveguide

crystal diode

* Far-infrared (hindered rotations; vdW vibrations)

$$\bar{\nu} = 10 - 100\ cm^{-1},\ \nu = 1 - 10THz$$

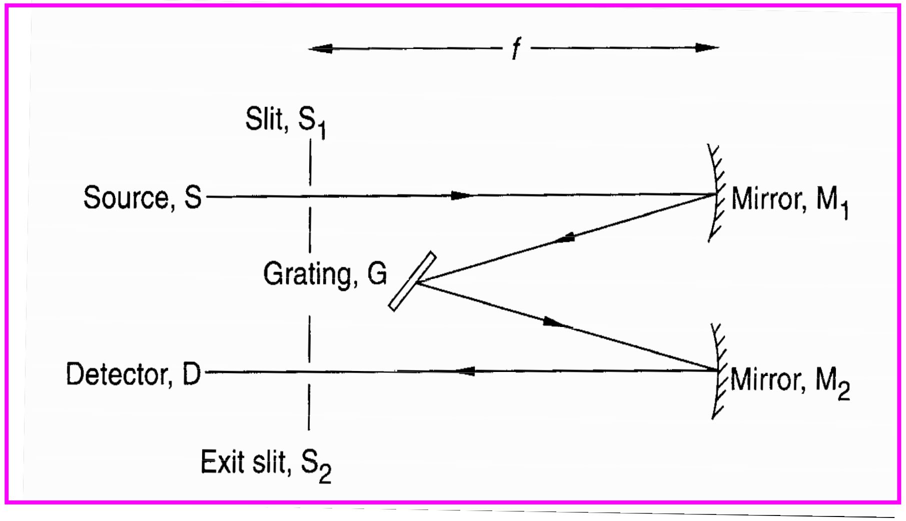
-Source: Mercury arc discharge, Laser

-Detector (heat sensor): Golay cell, bolometer, thermocouple,

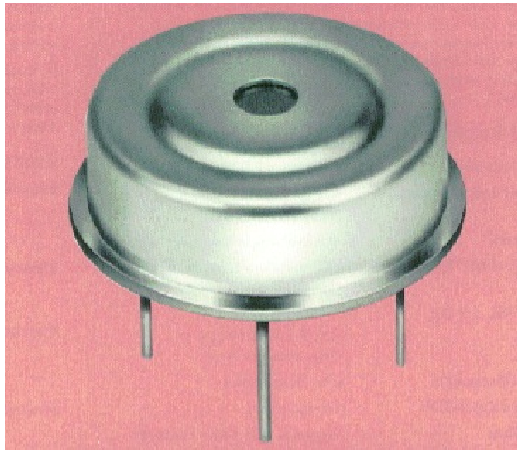
-Optics: window – polyethylene, Terylene, polystyrene
mirror – coated metal, etc

-Dispersion: Michelson-type interferometer

Czerny-Turner System



FIR thermistor



* Infrared region (vibrations)

Mid-IR $\lambda \approx 3 - 30\,\mu m, \bar{\nu} = 300 - 4000\,cm^{-1}$

Near-IR $\lambda \approx 0.8 - 3\,\mu m, \bar{\nu} = 4000 - 12000\,cm^{-1}$

-Source: Nernst filament, Globar, Laser, etc

-Detector (heat): thermocouple, bolometer, Golay cell, etc

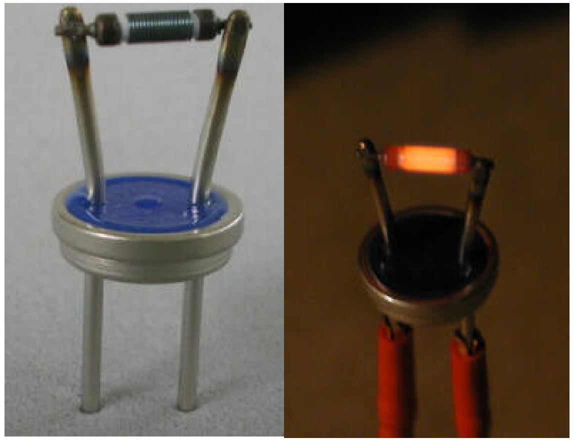
(heat-electrical): pyroelectric detector,

(electrical): photoconductive semiconductor, etc.

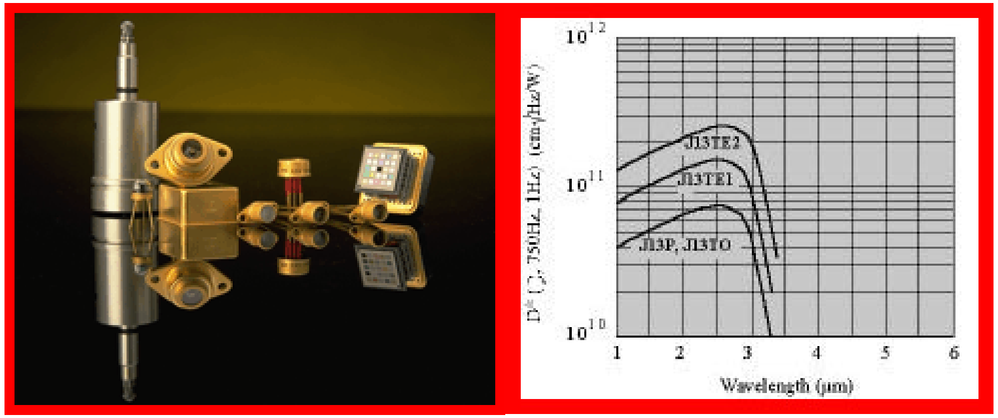
-Optics: mirror – Au, Ag, ZnSe, etc

window, lens – NaCl, KBr, etc

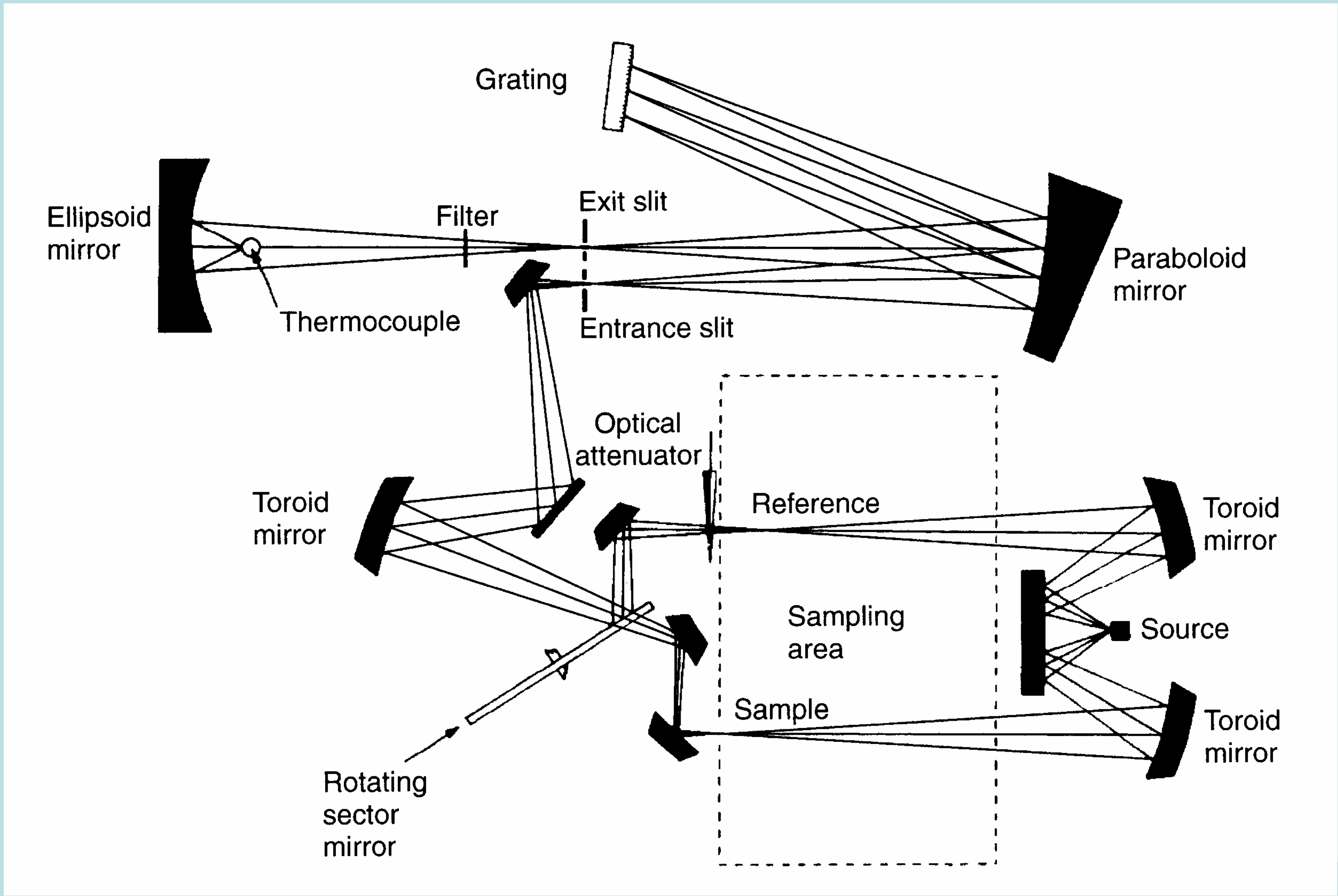
Heating filament



PbS photoconductor



Double Beam IR Spectrophotometer



* Visible and near-ultraviolet (valence electron)

Visible $\lambda \approx 400 - 700\ nm$

Near-UV $\lambda \approx 200 - 400\ nm$

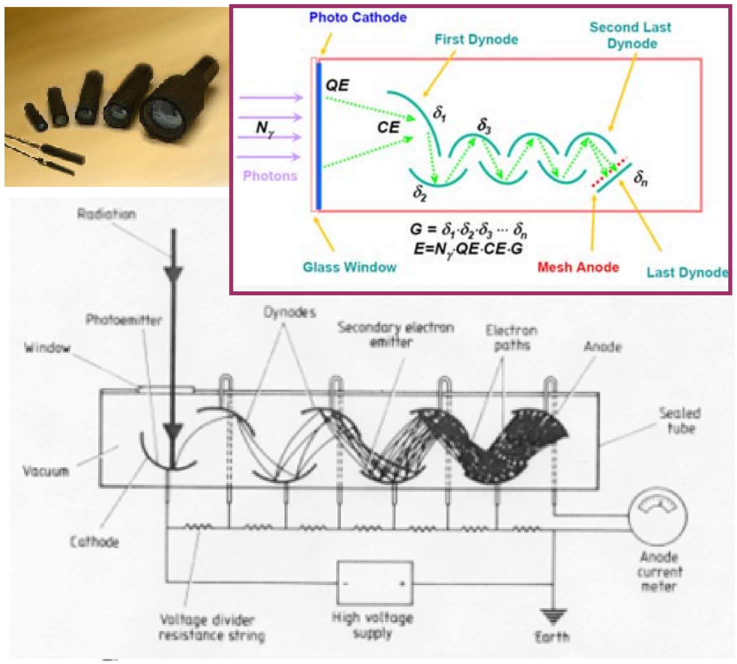
-Source: Lamp (W, W-I_2 filament, D_2-discharge), Laser, etc

-Detector (optoelectric): PMT, CCD, photodiode, etc

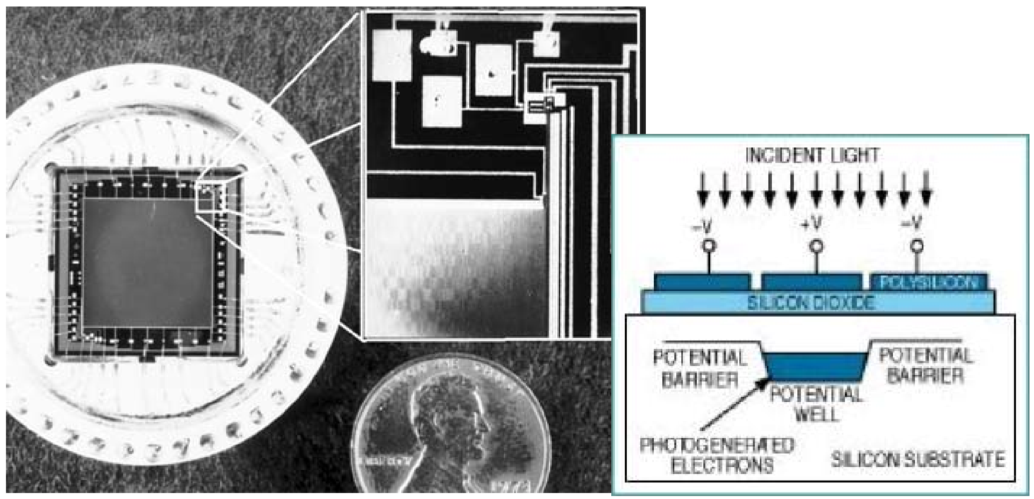
-Optics: mirror – Al, Au, Ag, etc

window, lens – glass, quartz etc

PMT



CCD



Double Beam UV-VIS Spectrophotometer