Skoog – Chapter 1 Introduction

- Basics of Instrumental Analysis
  - Properties Employed in Instrumental Methods
  - Numerical Criteria
  - Figures of Merit

Skip the following chapters

- Chapter 2 – Electrical Components and Circuits
- Chapter 3 – Operational Amplifiers in Chemical Instrumentation
- Chapter 4 – Digital Electronics and Microcomputers

Skoog – Chapter 5
Signals and Noise

- Signal to Noise Ratio

All instrumental measurements involve a signal

Unfortunately they always have noise present

Sometimes the noise is large

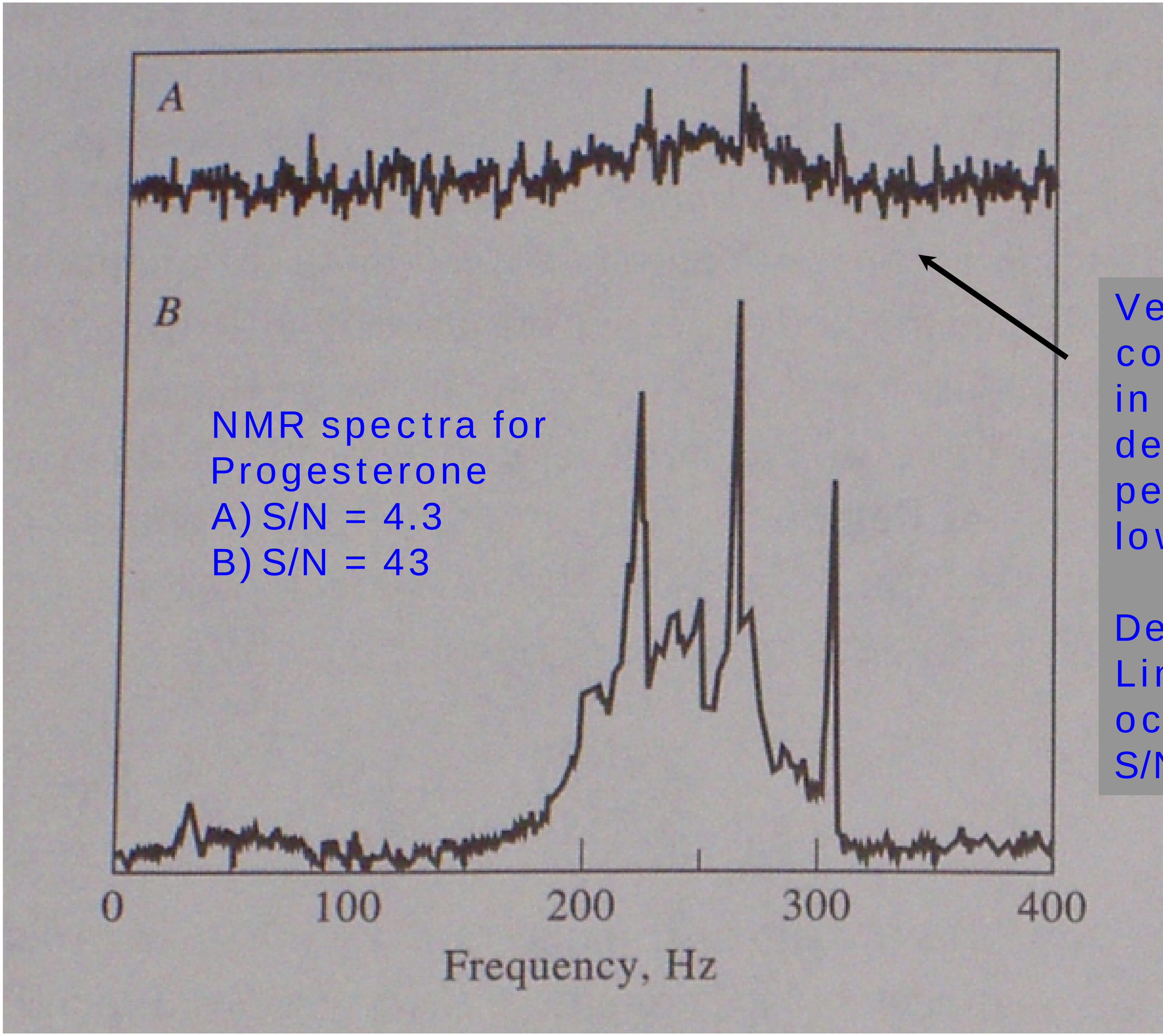
Sometimes it is so small you can't see it

Signal to Noise Ratio (S/N)

- Parameter describing quality of data
- Often referred to as “figure of merit”

$$\frac{S}{N} = \frac{\text{mean of signal}}{\text{standard deviation}} = \frac{\bar{x}}{s} = \frac{1}{RSD}$$

RSD = relative standard deviation



NMR spectra for Progesterone
A) S/N = 4.3
B) S/N = 43

Very little confidence in ability to determine peaks at lower S/N

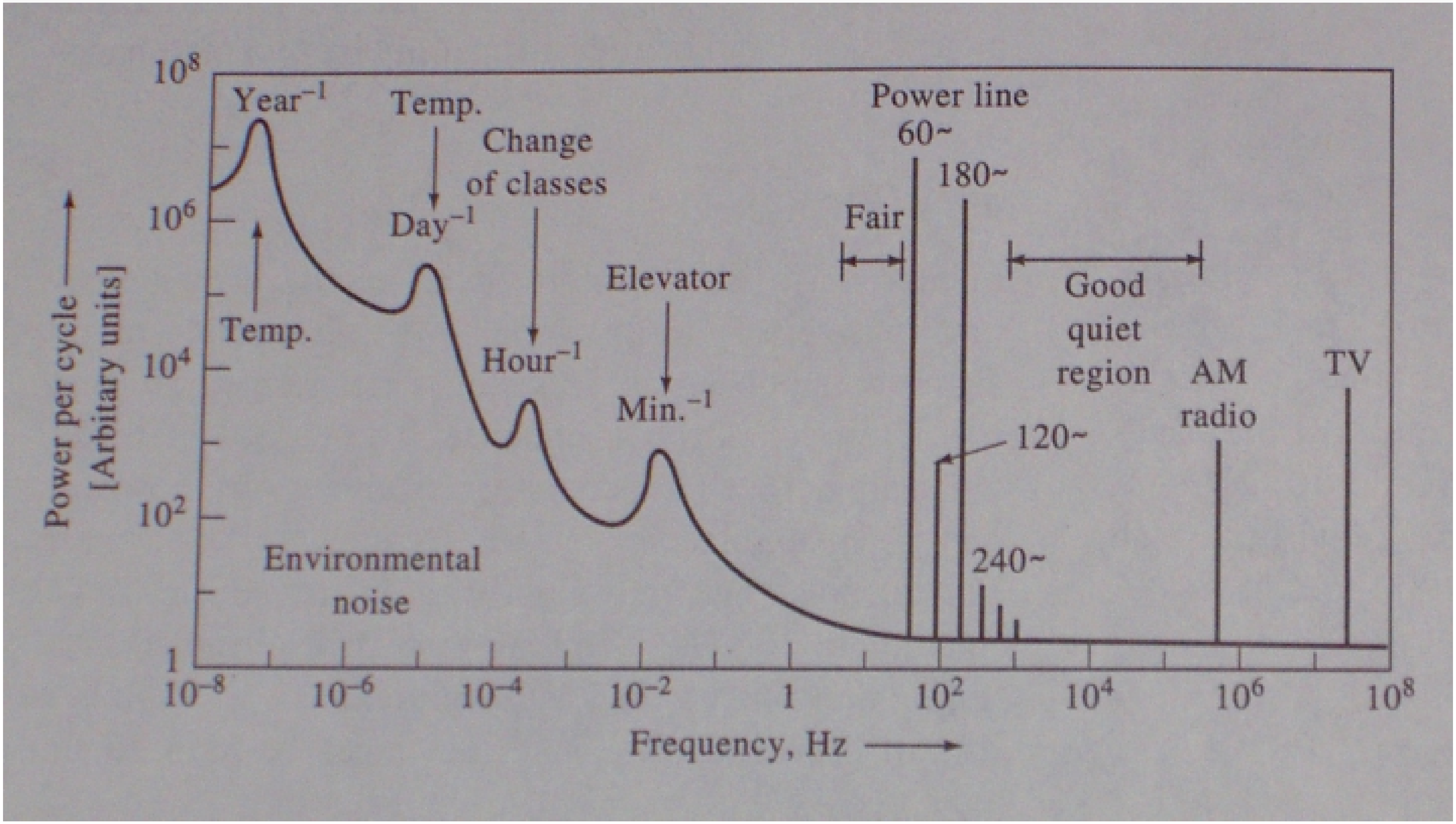
↓

Detection Limit occurs at S/N ~ 2 or 3

Sources of Noise

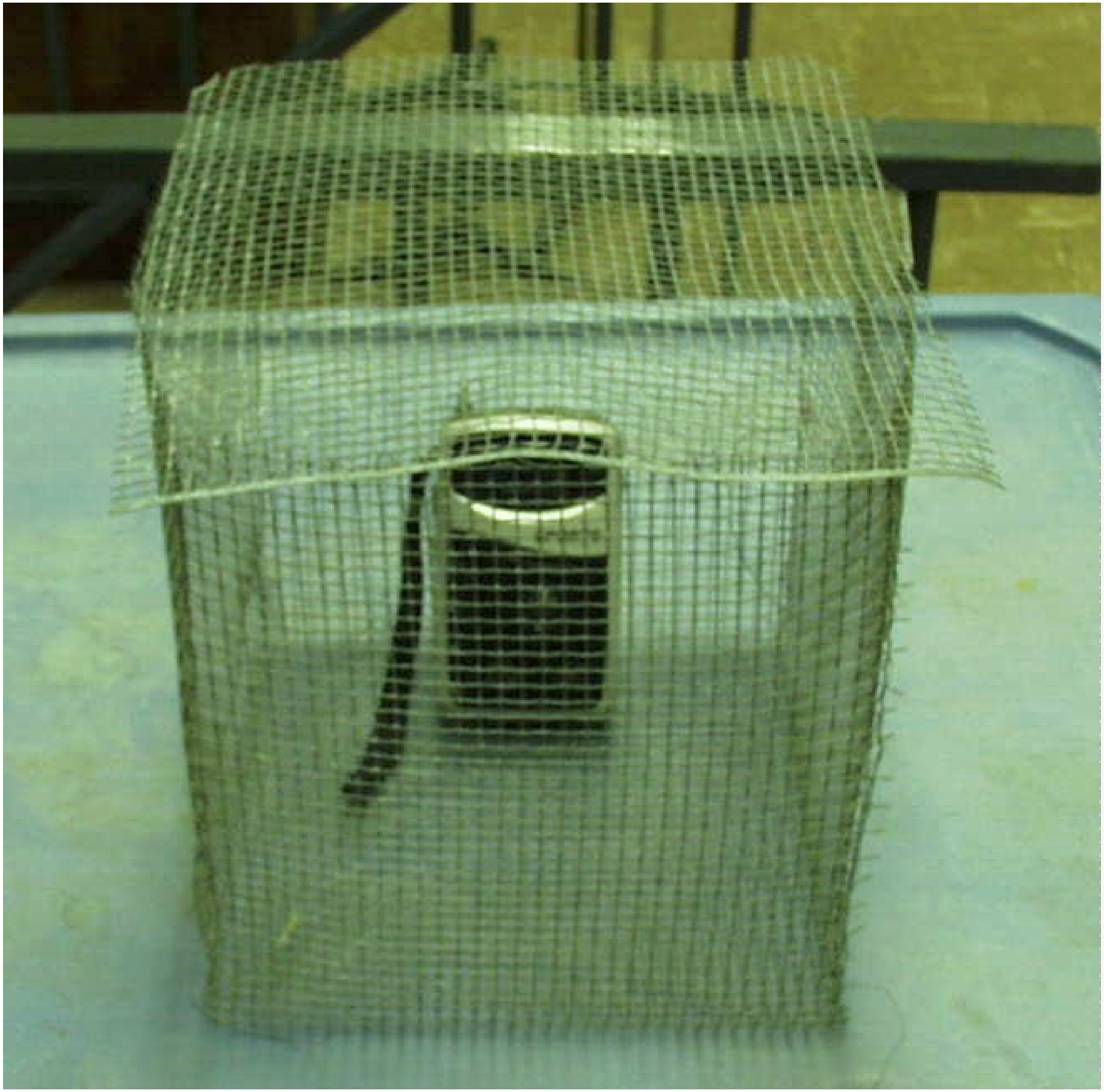
- Chemical noise – temp, pressure, humidity, etc. fluctuations = uncontrolled variables
- Instrumental noise – noise from instrumental components
  - Thermal noise (Johnson noise) – thermal motion of electrons in load resistor
  - Shot noise – movement of electrons across a junction
  - Flicker noise – any noise that is inversely proportional to signal 1/f
  - Environmental noise – many noise sources

Environmental noise sources (note frequency dependence)



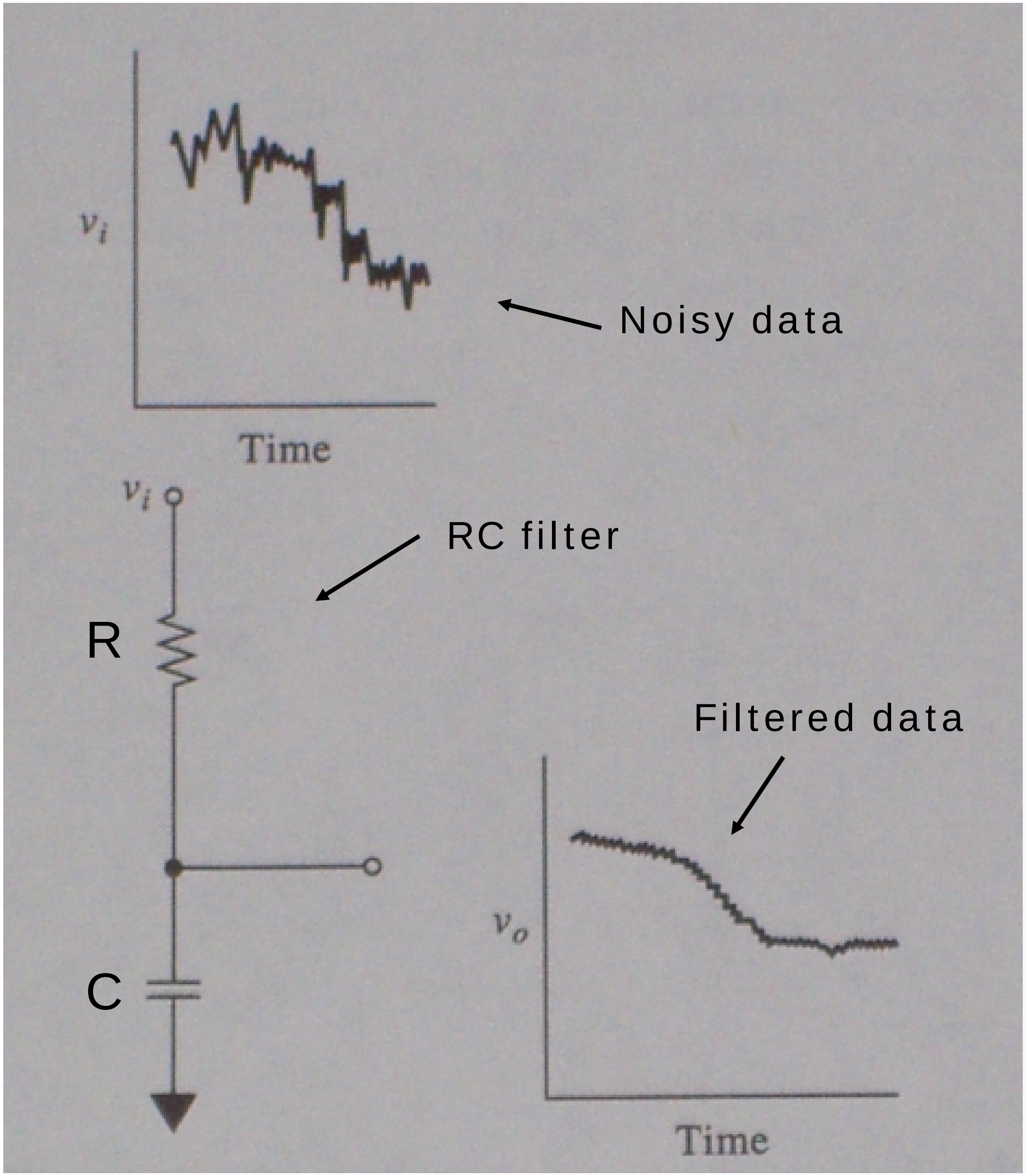
Improving S/N
hardware & software

- Hardware
  - Grounding & shielding – Faraday cage
  - Analog filtering – RC filtering
  - Modulation – convert DC signal to high frequency AC then demodulate
  - Signal chopping – rotating wheel to differentiate e.g. IR source from heat
  - Lock-in amplifiers

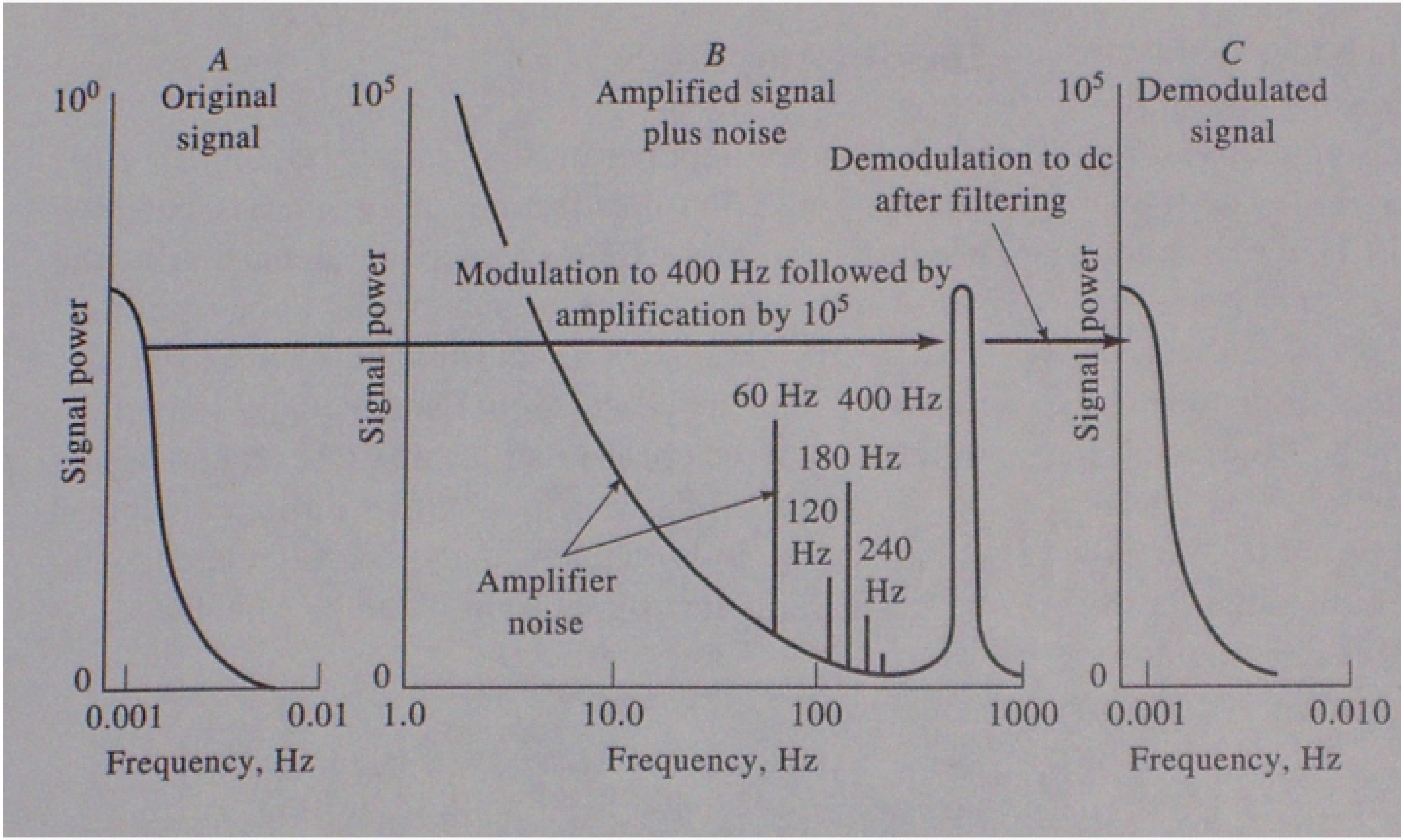


Primitive Faraday Cage

Analog Filtering or RC Filtering

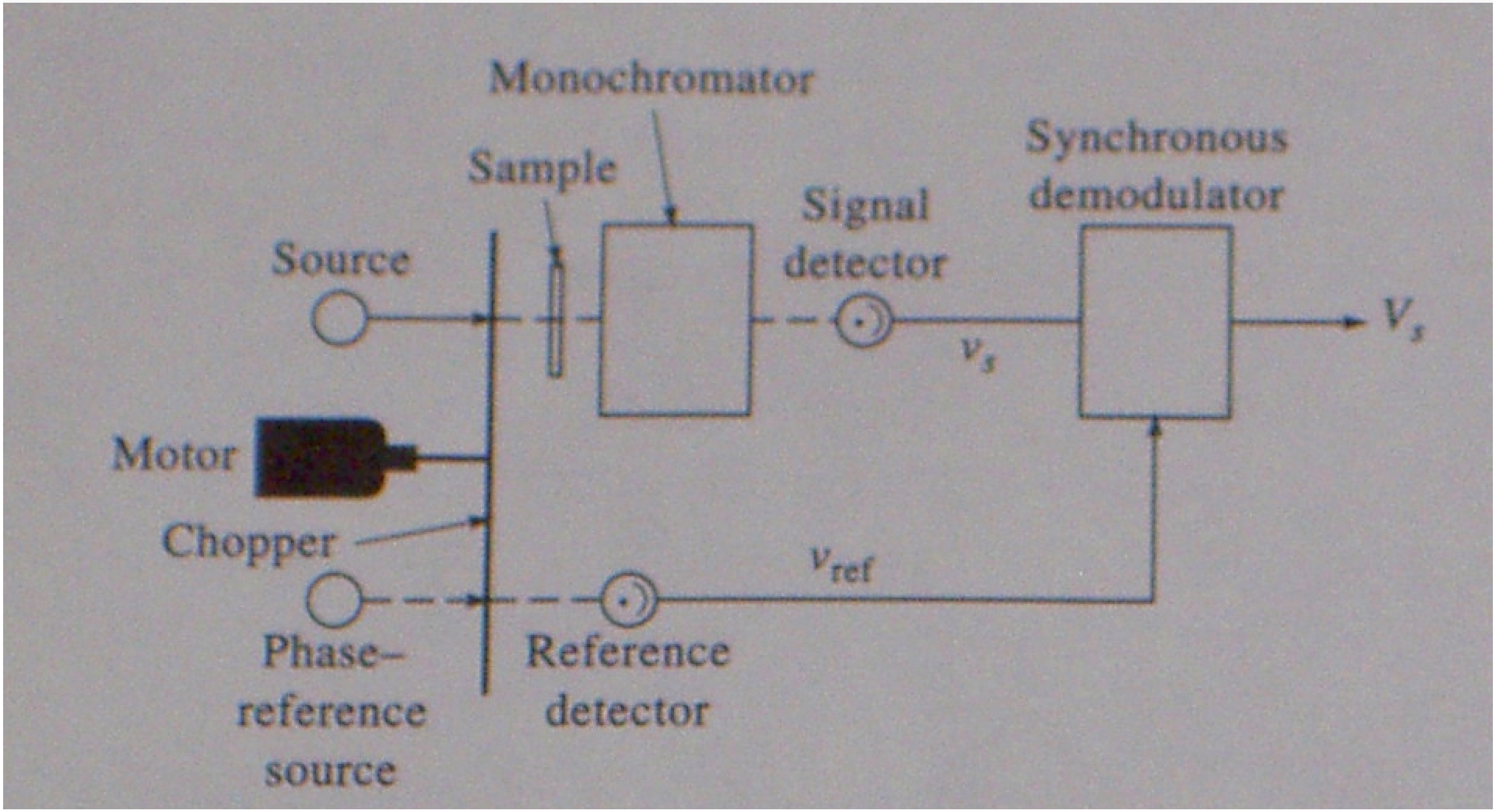


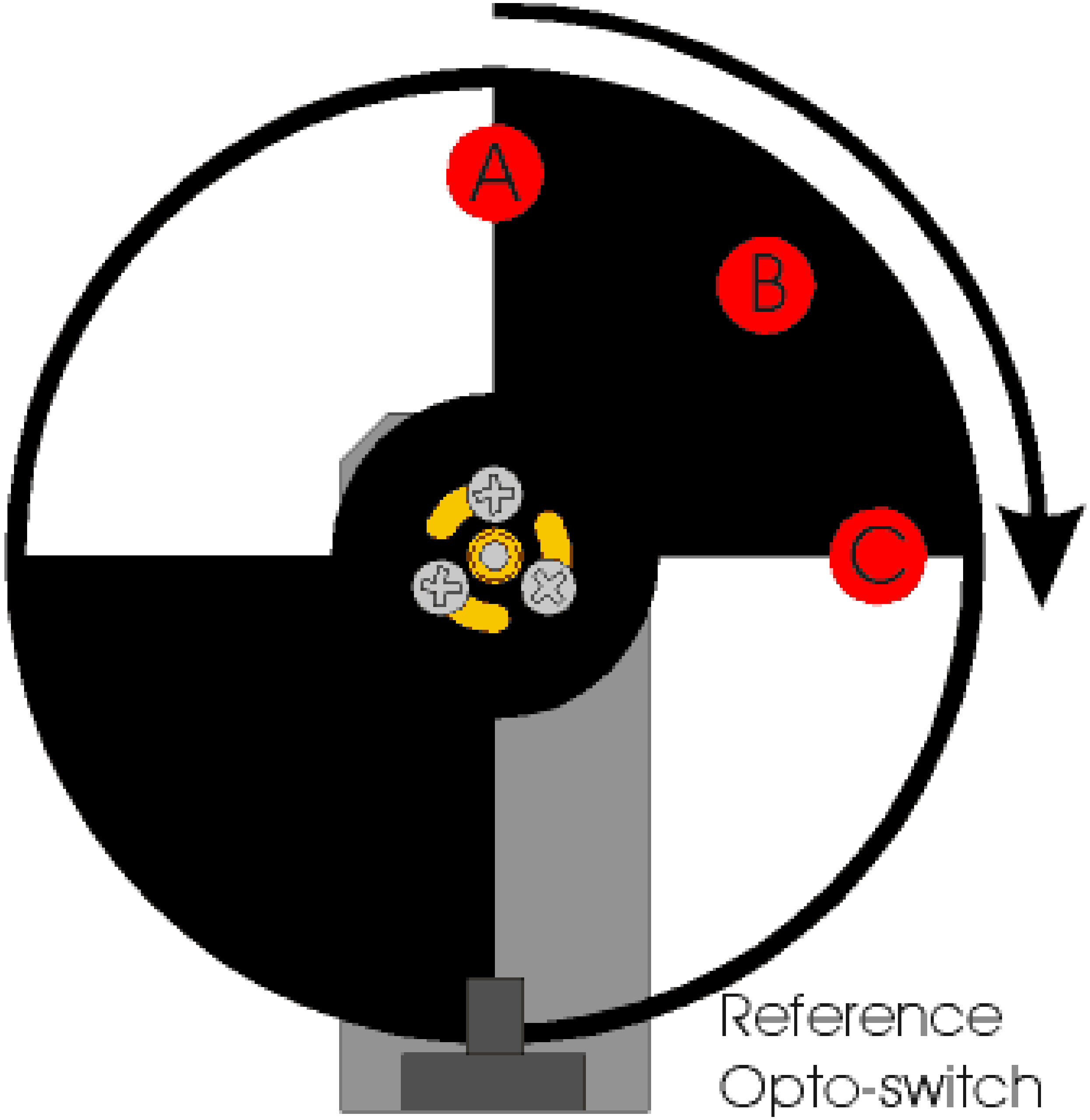
Modulation



A
Original signal
10^0
Signal power
0
0.001
0.01
Frequency, Hz
B
Amplified signal plus noise
10^5
Signal power
Modulation to 400 Hz followed by amplification by 10^5
60 Hz
400 Hz
180 Hz
120 Hz
240 Hz
Amplifier noise
0
1.0
10.0
100
1000
Frequency, Hz
Demodulation to dc after filtering
C
Demodulated signal
10^5
Signal power
0
0.001
0.010
Frequency, Hz

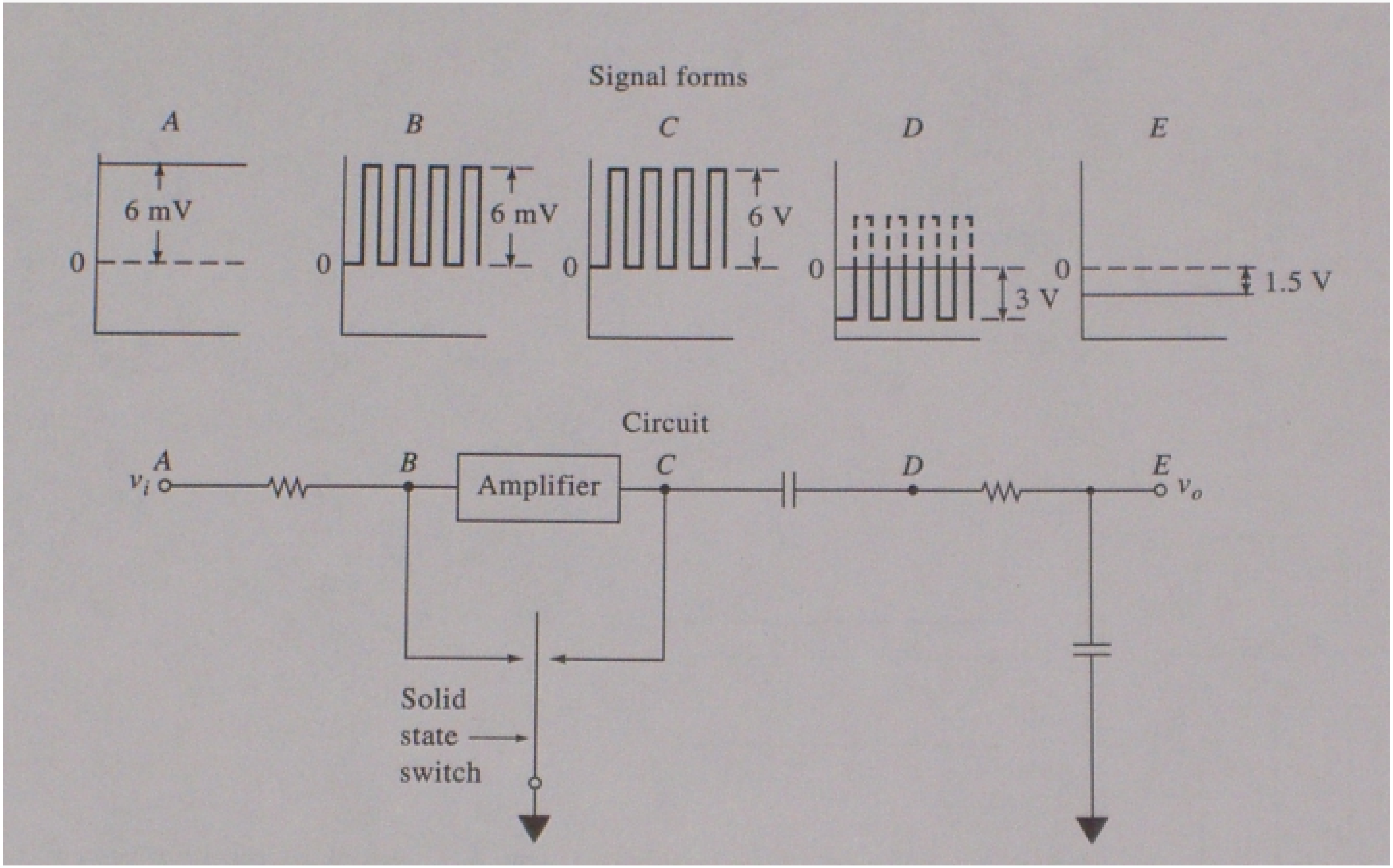
Signal chopping in an IR spectrophotometer





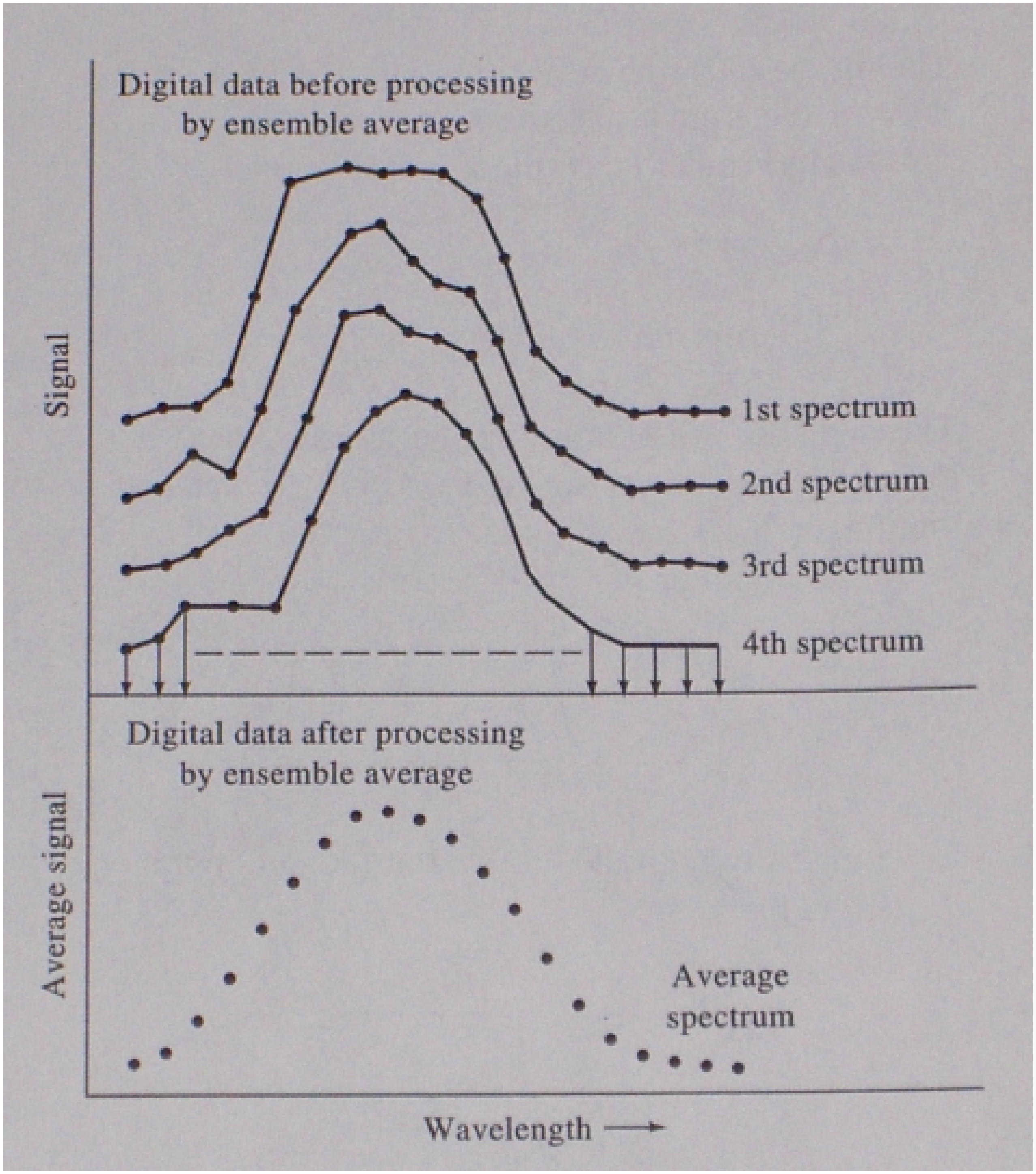
Rotating Chopper

Chopper amplifier

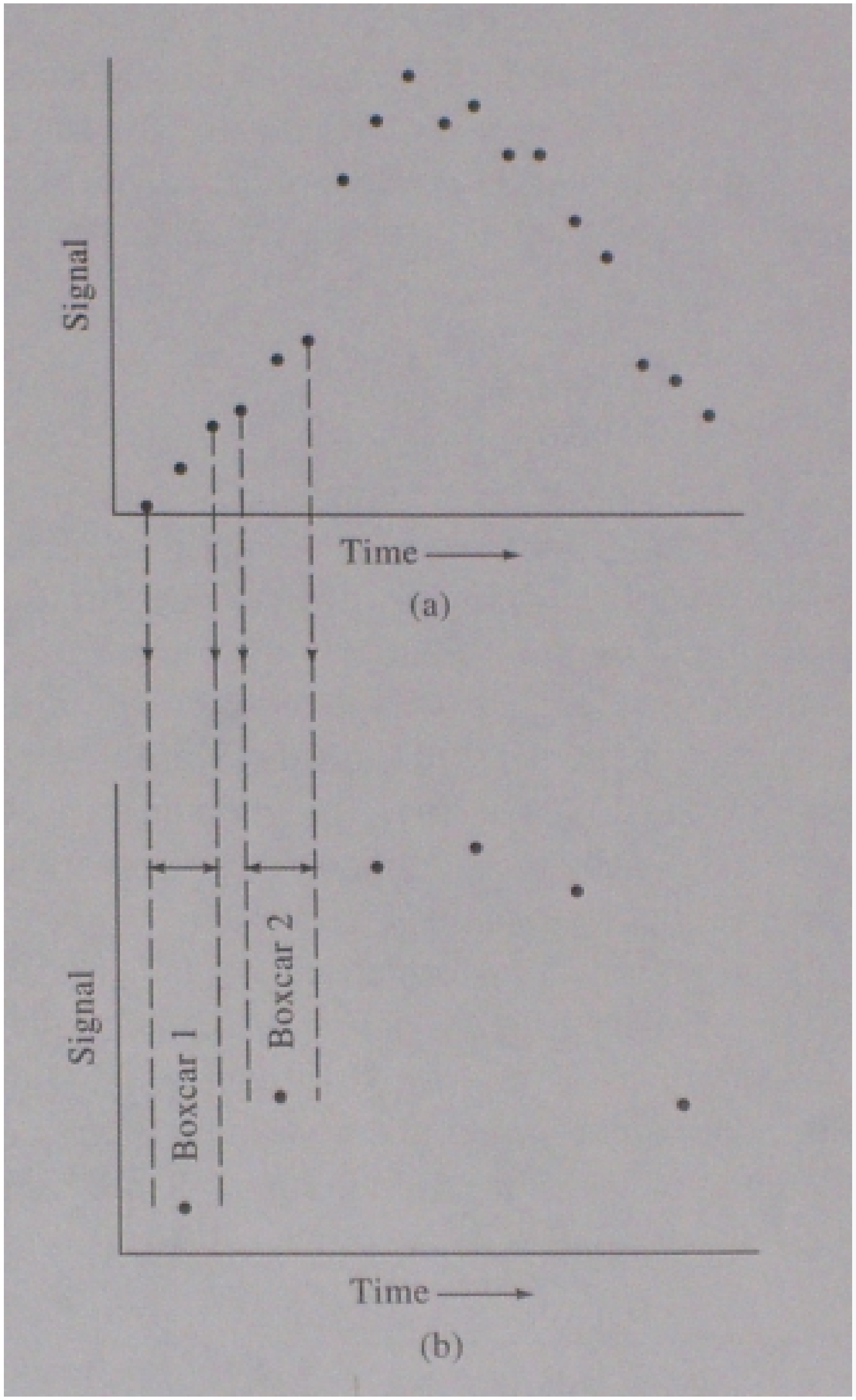


Improving S/N
hardware & software

- Software
  - Ensemble averaging – adding spectra
  - Boxcar averaging –
  - Digital filtering – moving window, sliding average
  - Correlation methods



Ensemble averaging i.e. adding or averaging signal

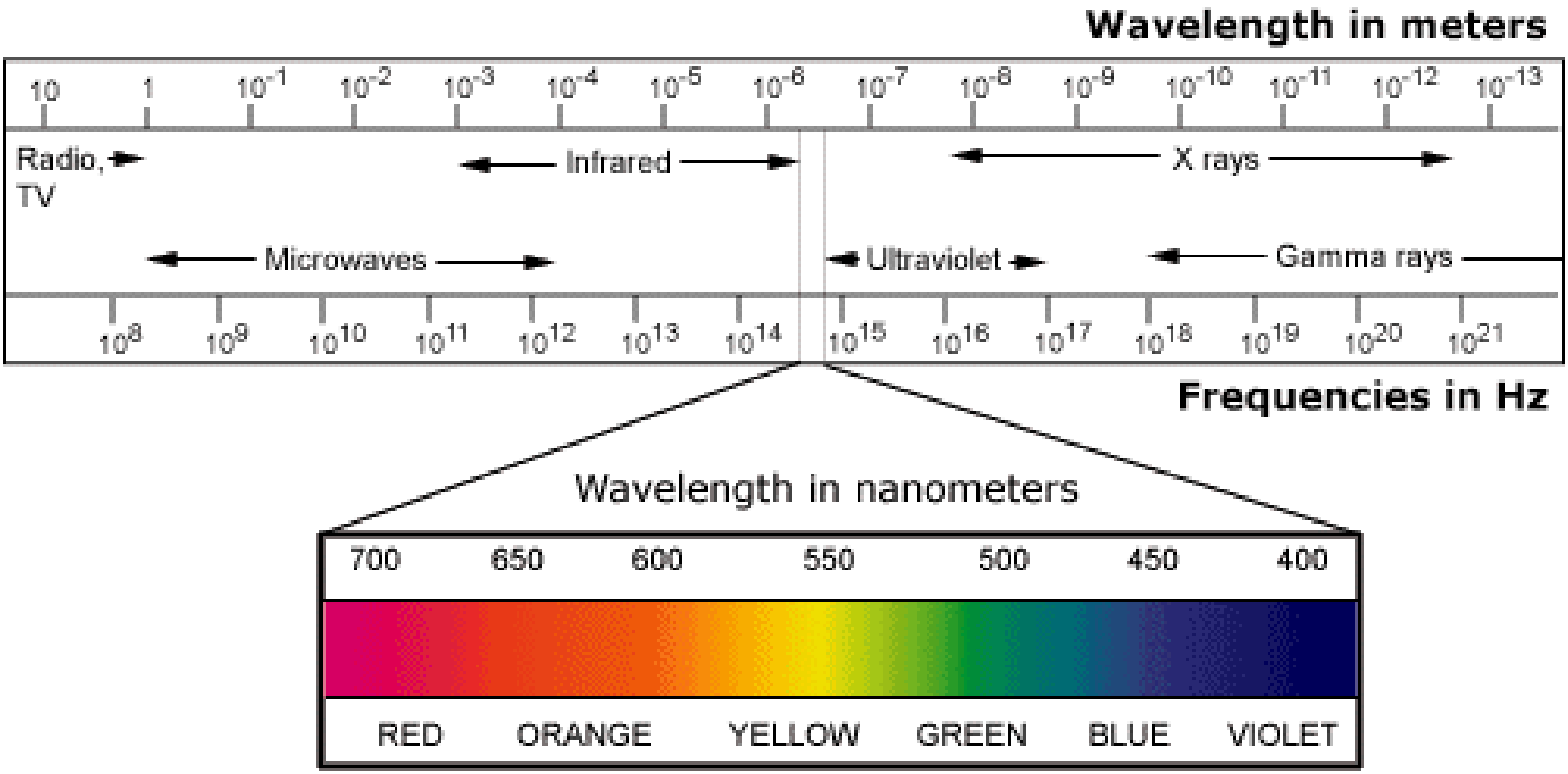


Boxcar averaging

Skoog – Chapter 6
Intro to Spectrometric Methods

- General Properties of Electromagnetic Radiation (EM)
- Wave Properties of EM
- Quantum-Mechanical Properties of EM
- Quantitative Aspects of Spectrochemical Measurements

Spin States	Molecular Rotations	Molecular Vibrations	Outer Shell Electrons	Inner Shell Electrons	Nuclear Transitions
NMR EPR	Microwave Absorption Spectroscopy	Infrared Absorption Spectroscopy	UV-vis Absorption, Fluorescence	X-Ray Absorption, Fluorescence	Gamma Ray Spectroscopy

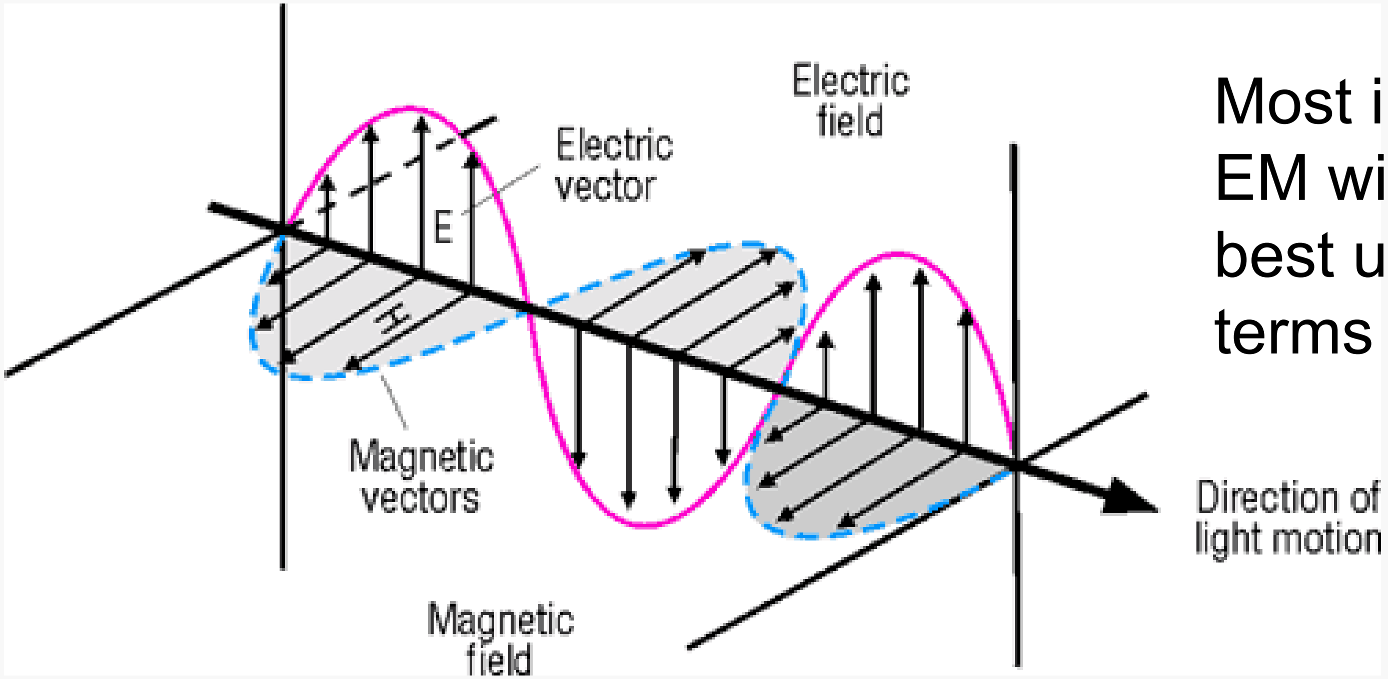


R O Y G B V

<u>Spectroscopy</u> = methods based on the interaction of electromagnetic radiation (EM) and matter

<u>Electromagnetic Radiation</u> = form of energy with both wave and particle properties

EM moves through space as a wave



Most interactions of EM with matter are best understood in terms of electric vector

Relationship between various wave properties

$$\nu \lambda_i = \frac{C}{\eta_i}$$

Where ν = frequency in cycles/s or Hz

λ_i = wavelength in medium i

η_i = refractive index of medium i

C = speed of light in vacuum (2.99×10^{10} cm/s)

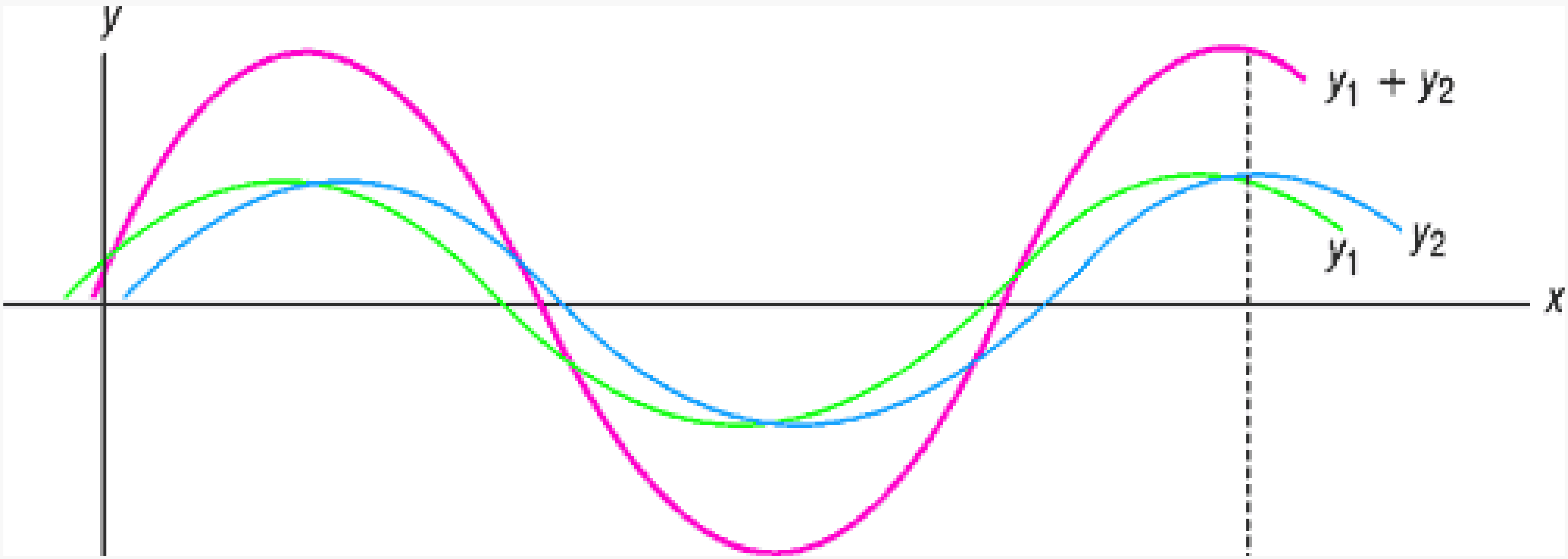
EM slows down in media other than vacuum because electric vector interacts with electric fields in the medium (matter) → this effect is greatest in solids & liquids, in gases (air) velocity similar to vacuum

Wave Interaction - interaction between waves

- waves must have similar ν but can be out of phase (i.e., they start in different places)

Principle of superposition = vectors add

- wave y_1+y_2 formed by adding y_1 & y_2 by vector addition



Wave Equation

$$y = A \sin(\omega t + \alpha)$$

Where A = amplitude

ω = angular frequency

α = phase angle

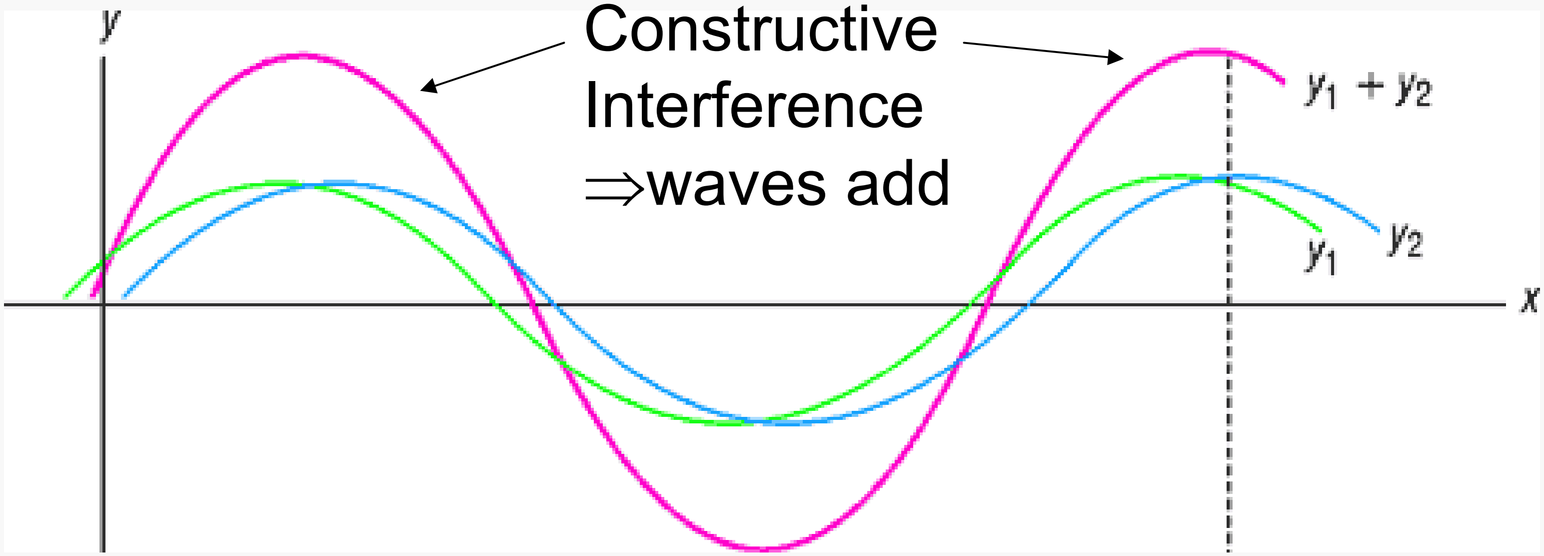
t = time

For a collection of waves the resulting position y at a given t can be calculated by

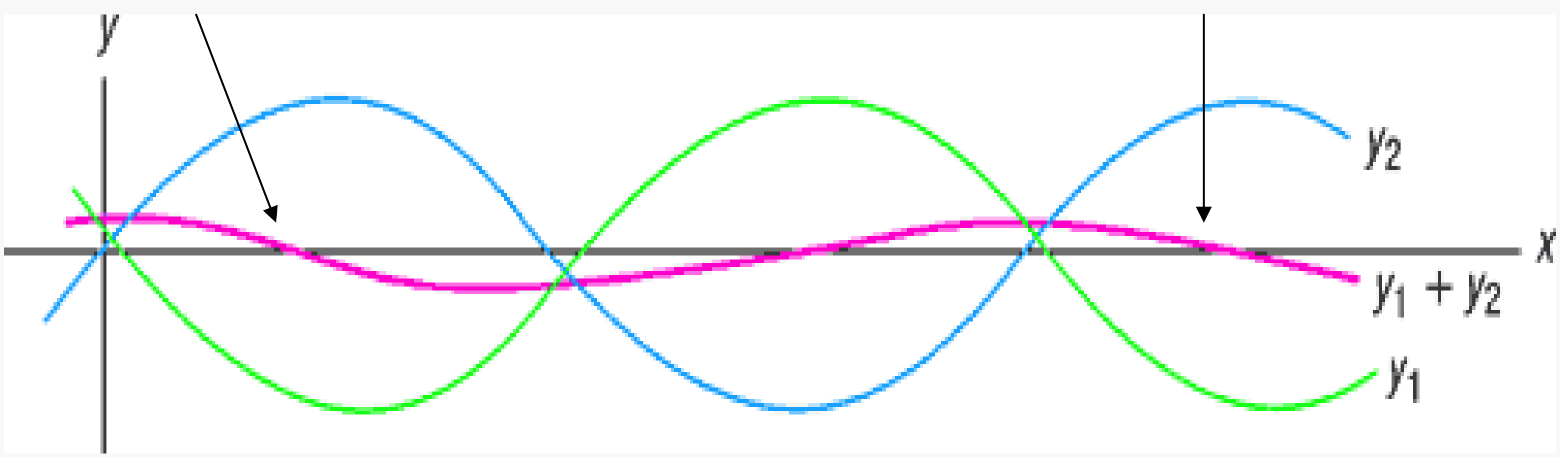
$$y = A_1 \sin(\omega_1 t + \alpha_1) + A_2 \sin(\omega_2 t + \alpha_2) + \dots$$

Interference - amplitude of the resulting wave depends on phase difference $\alpha_1 - \alpha_2$

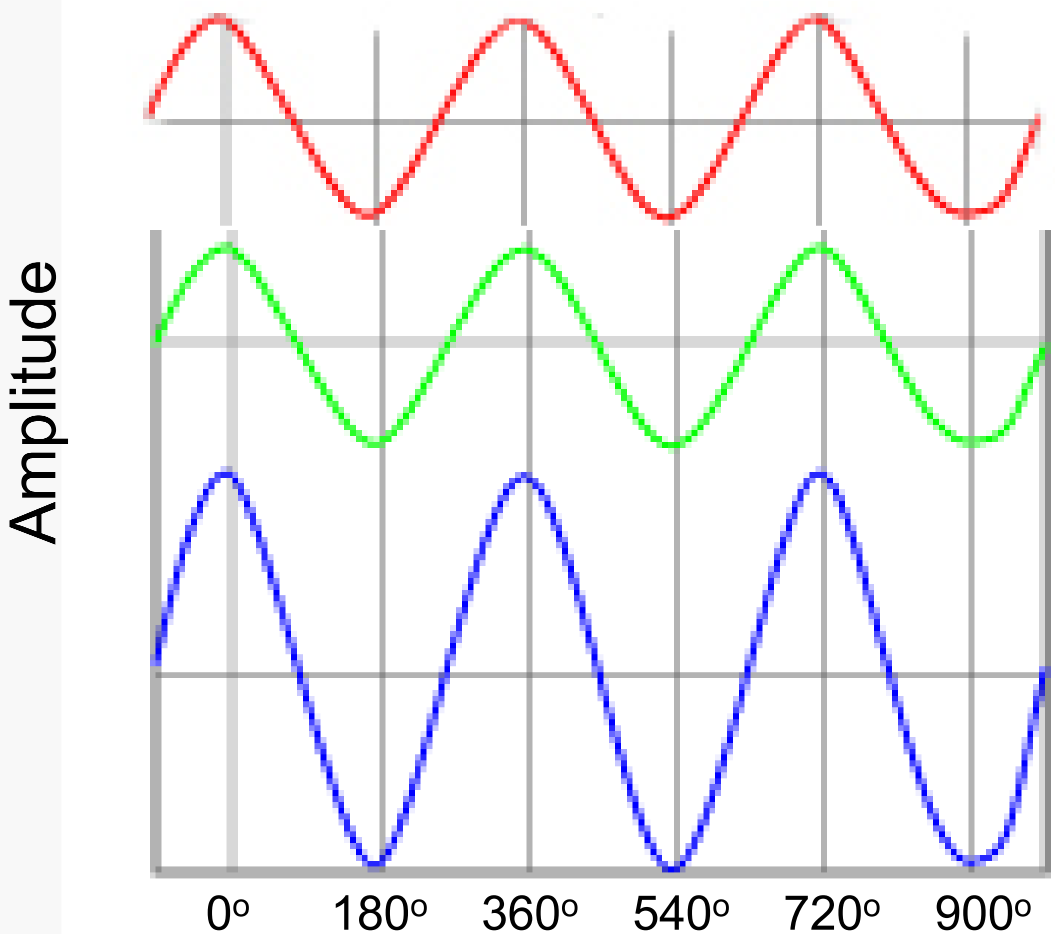
Constructive Interference
$\Rightarrow$waves add



Destructive Interference $\Rightarrow$ waves cancel



At $\alpha_1 - \alpha_2 = 0^o$ adding of waves gives Maximum Constructive Interference



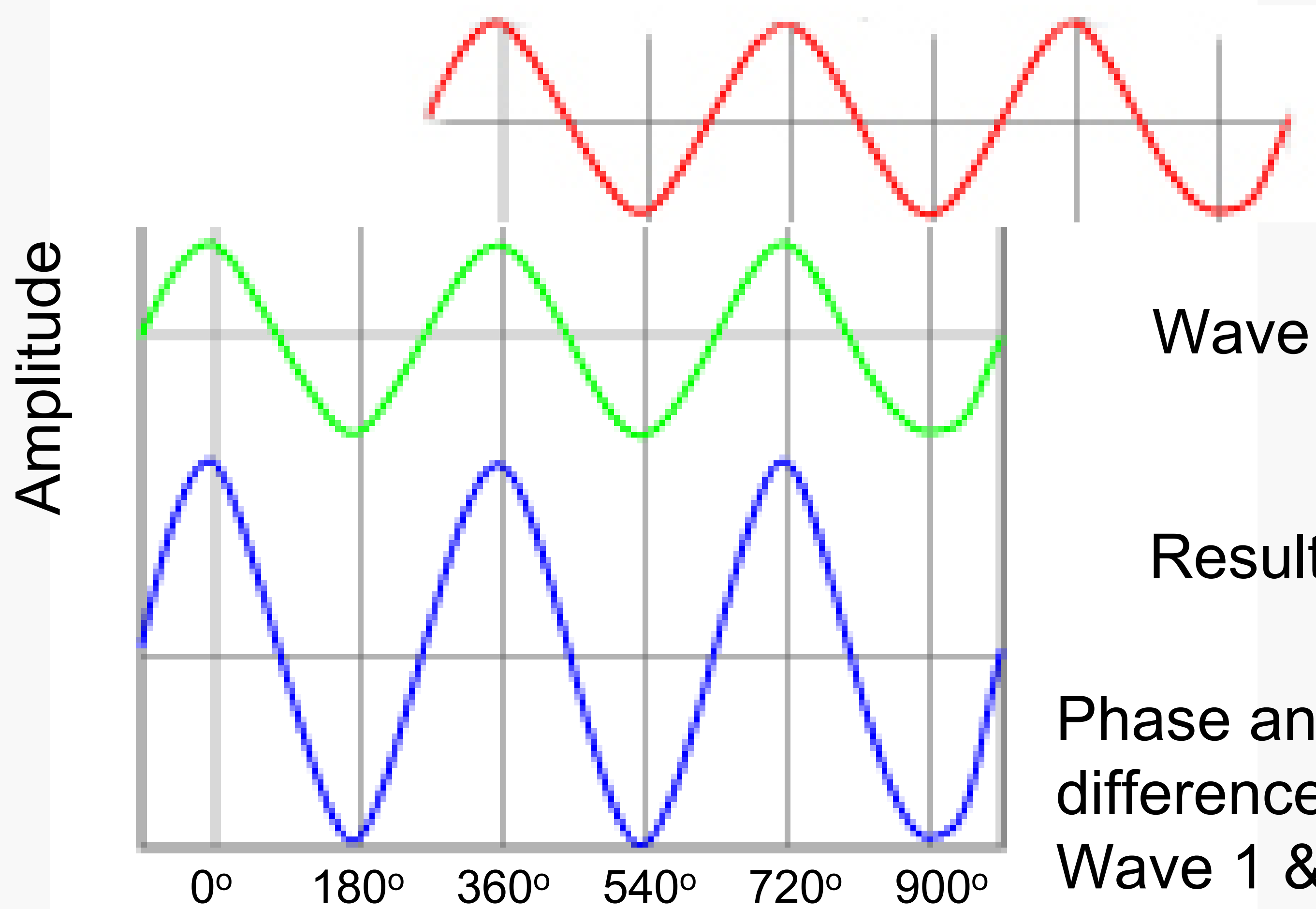
Wave 1

Wave 2

Resultant wave

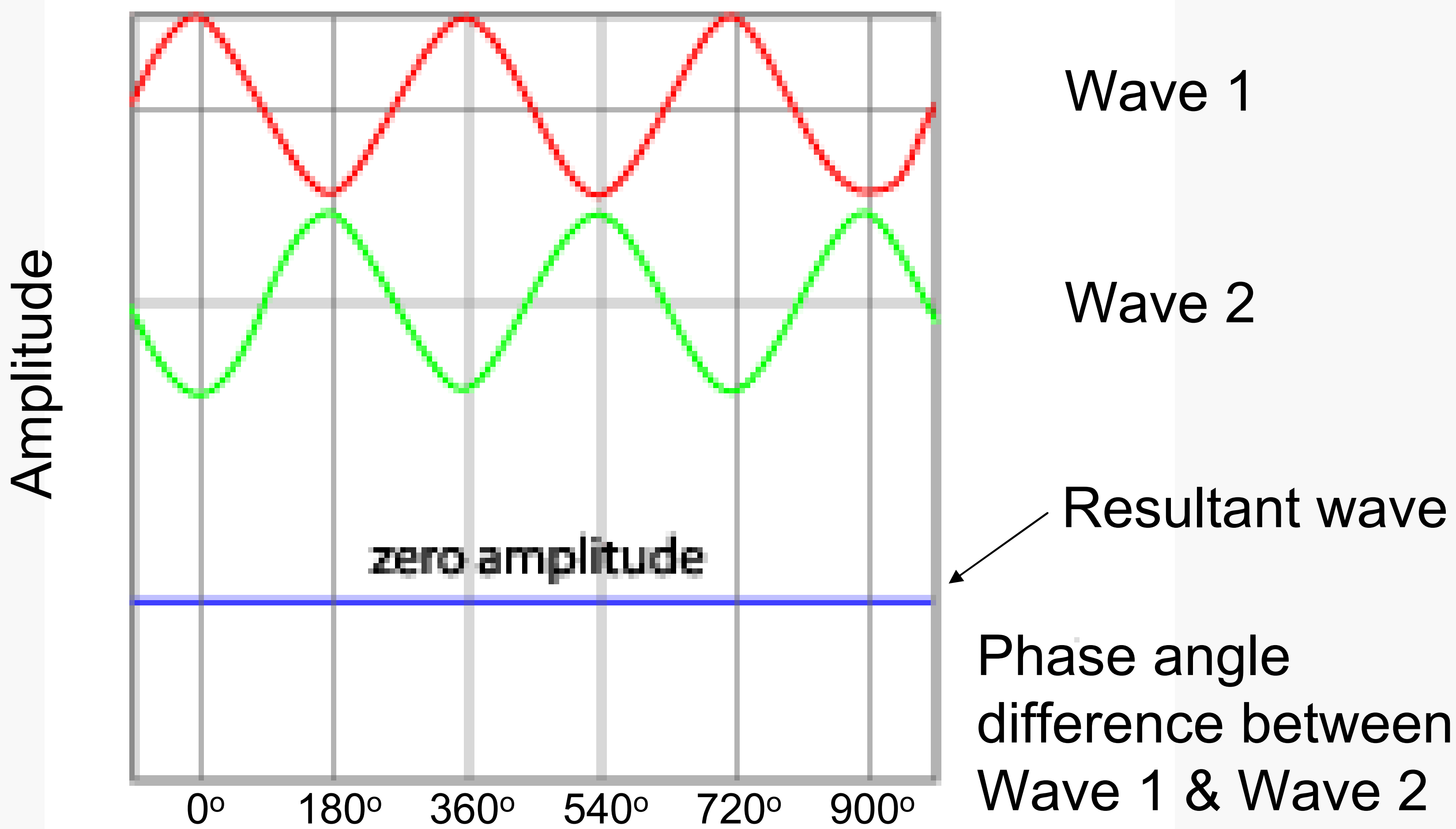
Phase angle difference between Wave 1 & Wave 2 is zero $\alpha_1 - \alpha_2 = 0^o$

Also at $\alpha_1 - \alpha_2 = 360^o$ adding of waves gives **Maximum Constructive Interference**



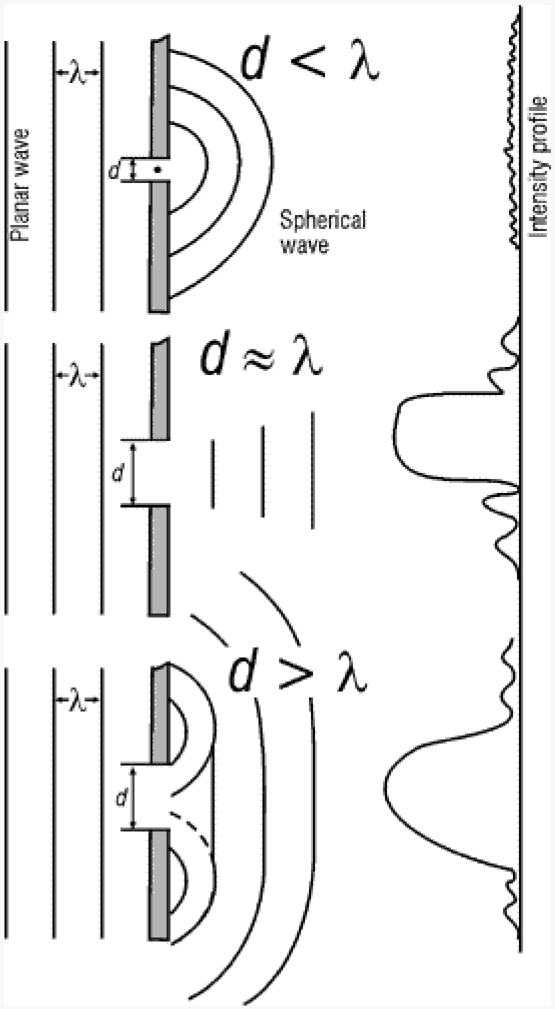
Phase angle difference between Wave 1 & Wave 2 is 360^o ($\alpha_1 - \alpha_2 = 360^o$)

When $\alpha_1 - \alpha_2 = 180^o$ or 540^o adding of waves gives <u>Maximum Destructive Interference</u>



Phase angle difference between Wave 1 & Wave 2 is 180^o ($\alpha_1 - \alpha_2 = 180^o$)

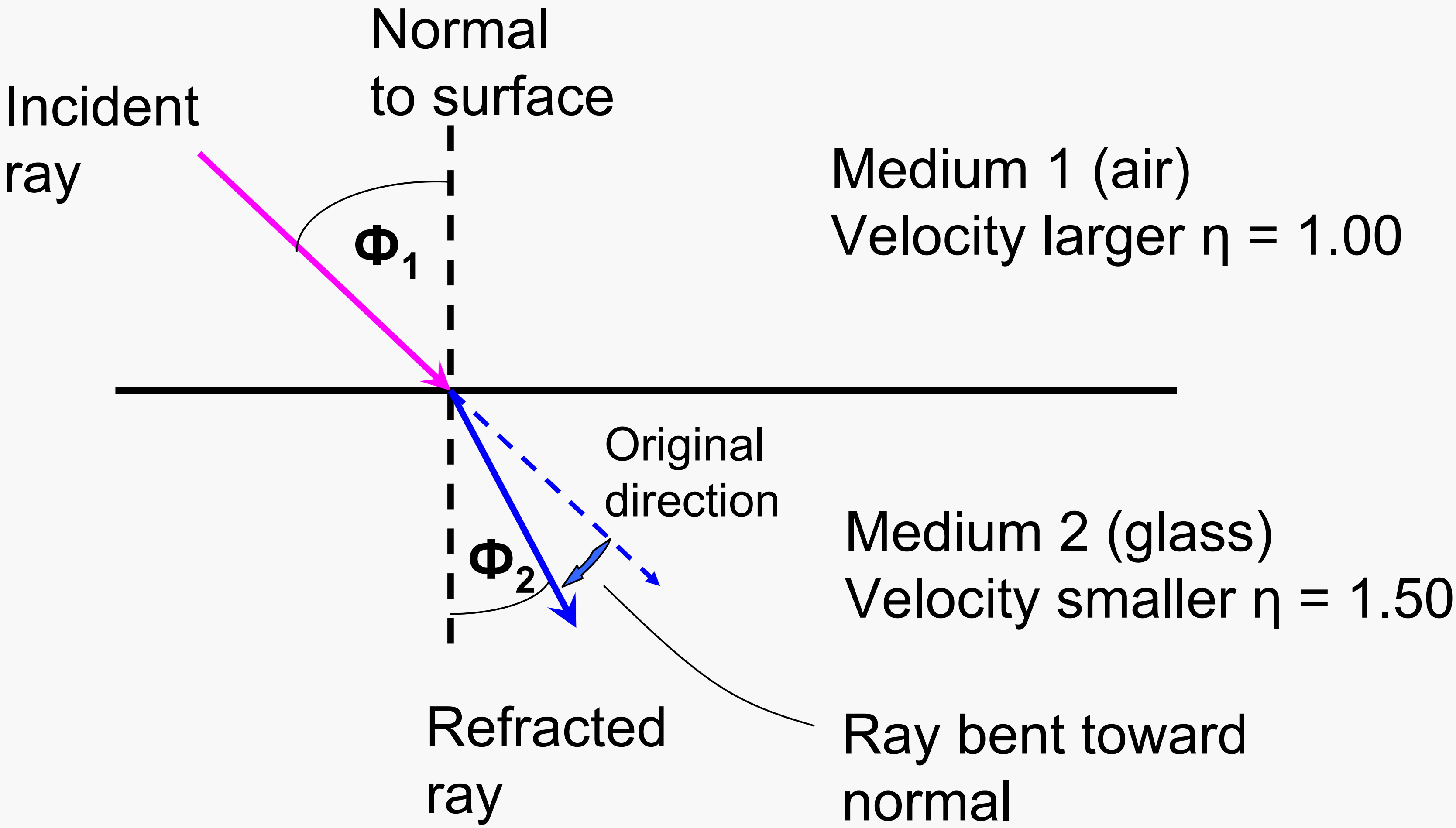
Diffraction = EM going past an edge or through a slit (2 edges) tends to spread



The combination of diffraction effects & interference effects are important in spectroscopy for

1) diffraction gratings
2) slit width considerations

Refraction = change in velocity of EM as it goes from one medium to another



Equation for Refraction

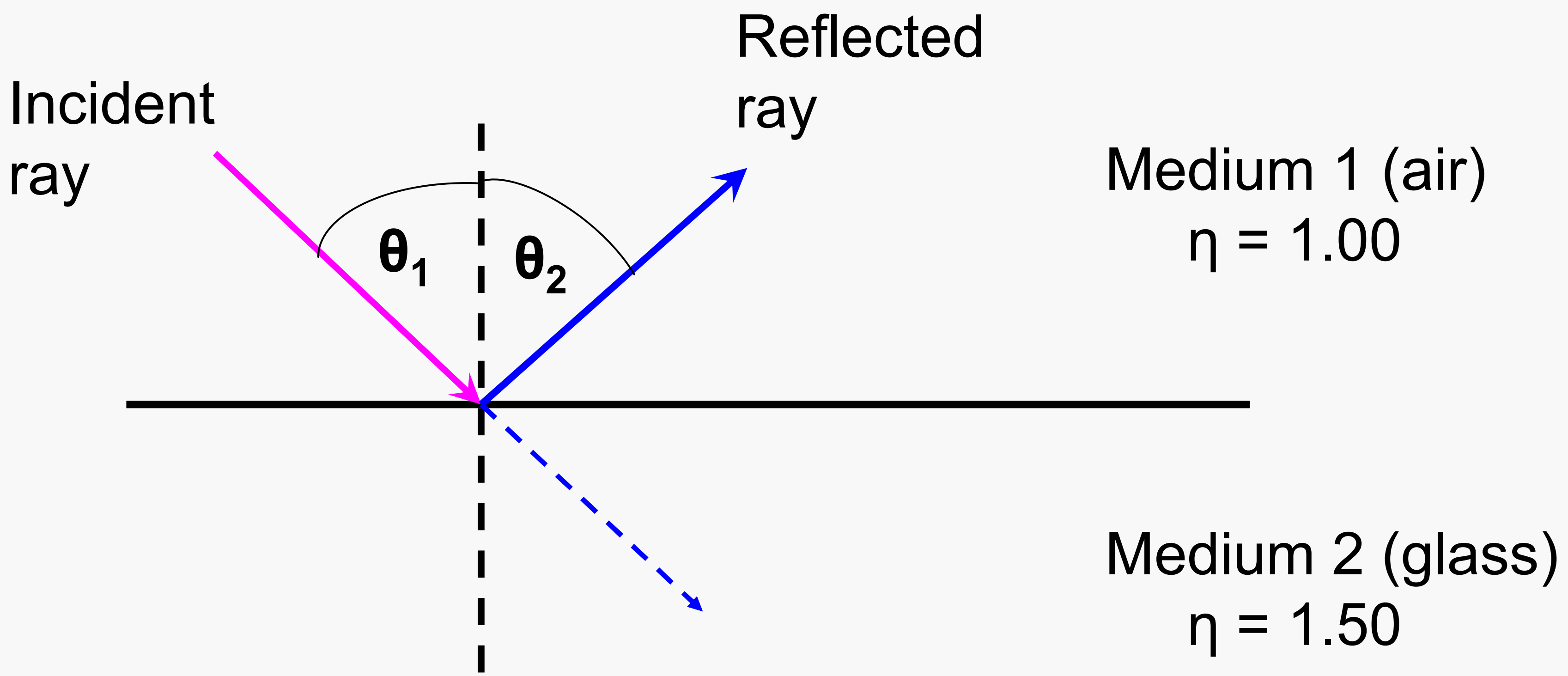
$$\frac{\sin \Phi_1}{\sin \Phi_2} = \frac{\nu_1}{\nu_2} = \frac{\eta_2}{\eta_1} = \eta_2$$

if medium 1 is air $\eta_1 = 1.0$

Magnitude of the direction change (i.e., size of the angle depends on wavelength (shown in equation as ν) this is how a prism works

Direction of bending depends on relative values of η for each medium. Going from low η to higher, the ray bends toward the normal. Going from higher η to lower the ray bends away from the normal.

Reflection = EM strikes a boundary between two media differing in η and bounces back



Specular reflection = situation where angle of incidence (θ_i) equals angle of reflection (θ_r)

$$\text{Reflectance} = R = \frac{I_r}{I_i} = \frac{(\eta_2 - \eta_1)^2}{(\eta_2 + \eta_1)^2}$$

Where I_i and I_r = incident & reflected intensity

For radiation going from air (η = 1.00) to glass (η = 1.50) as shown in previous slide

$$R = 0.04 = 4\ \%$$

Many surfaces at 4 % each (i.e., many lenses) can cause serious light losses in a spectrometer. This generates **stray radiation** or **stray light**.