84.514
Advanced Analytical Chemistry

Part II

Molecular Spectroscopy

Important Websites

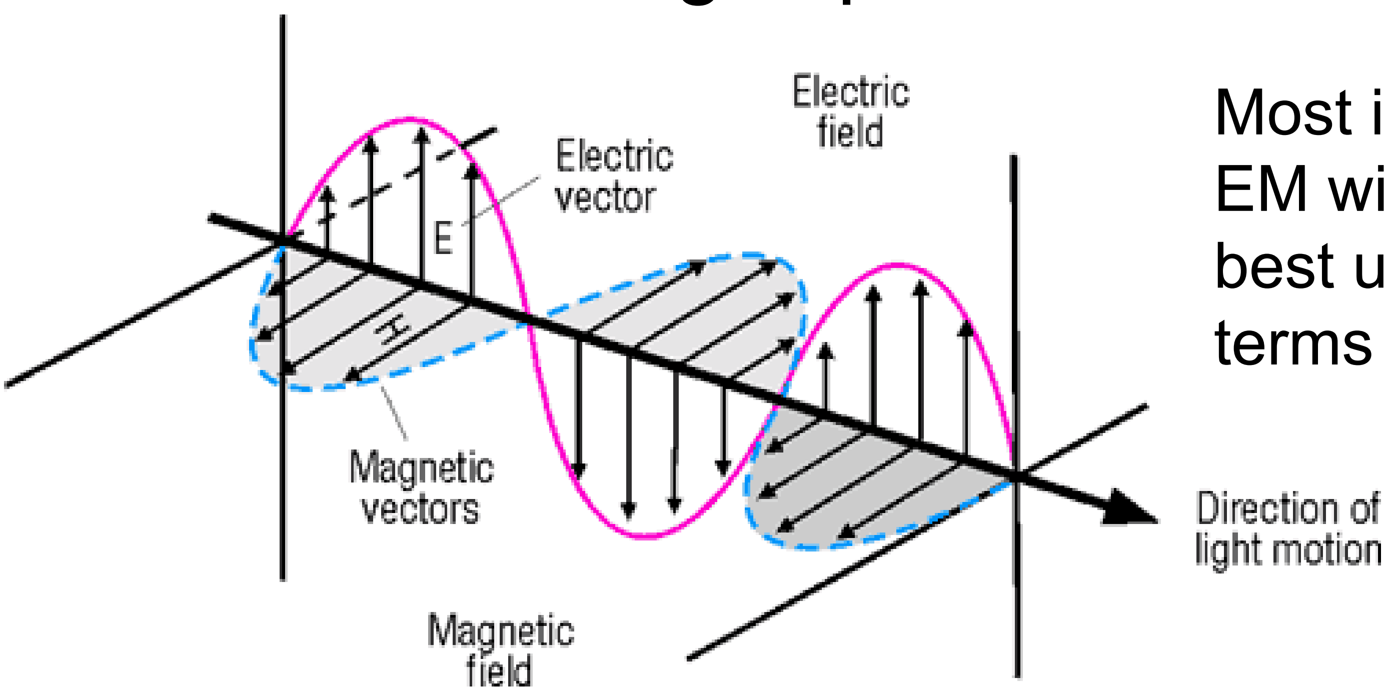
http://faculty.uml.edu/David_Ryan/84.514

http://cord.org/step_online/introduction/contents.htm

<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

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

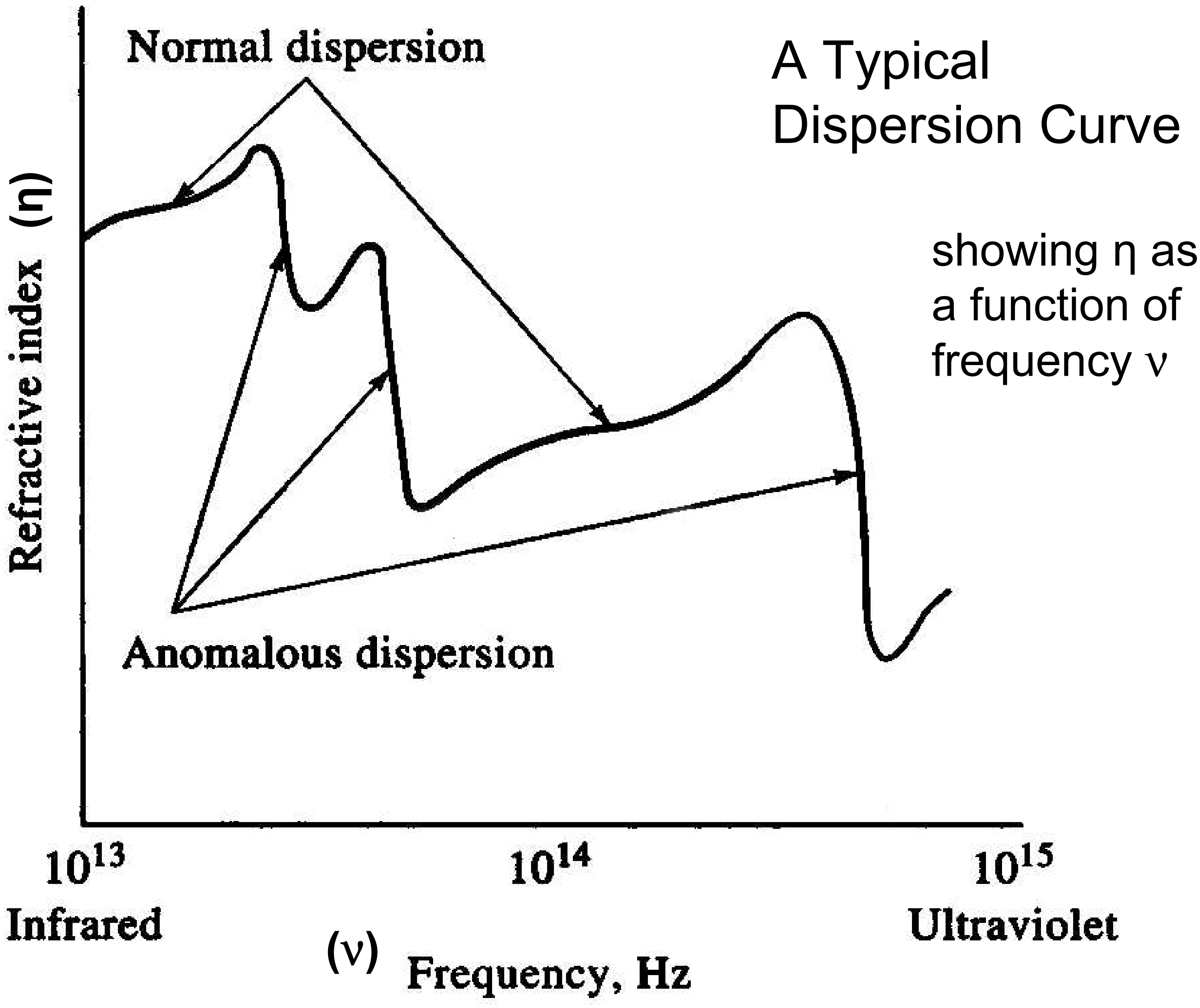
Where ν = frequency in cycles/s or Hz

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



A Typical
Dispersion Curve
showing η as
a function of
frequency ν
Normal dispersion
Anomalous dispersion
Refractive index (η)
10^13
10^14
10^15
Infrared
Ultraviolet
(ν)
Frequency, Hz

Normally η increases with ν and this is referred to as "Normal Dispersion"

When absorption occurs, the nature of the interaction changes

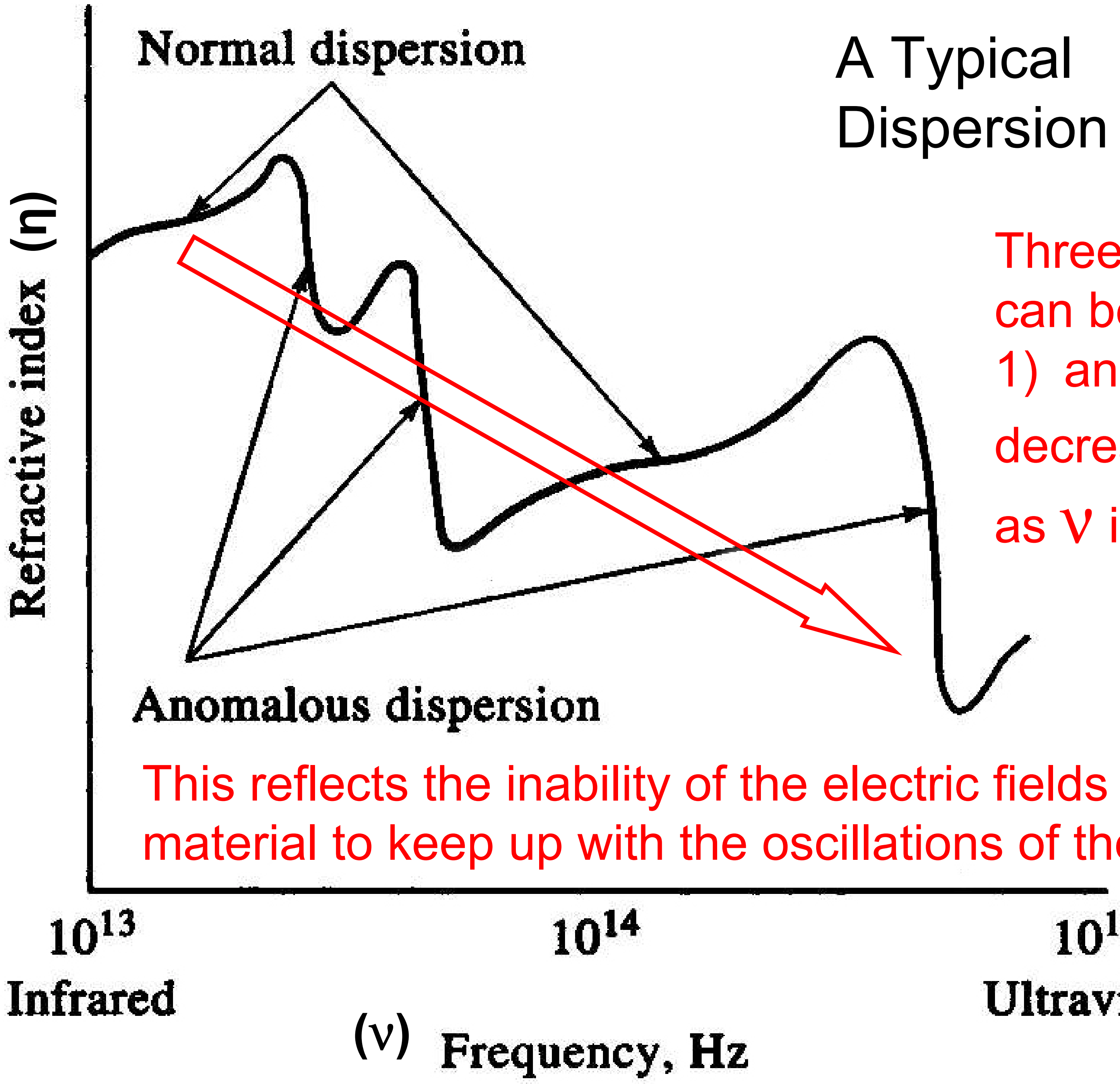
η is a measure of the extent to which the electric vector interacts with the medium & slows down

For a given frequency and medium, a larger η means more interaction with electric field & the medium is said to have greater **polarizability** i.e., is more able to follow the electric vector

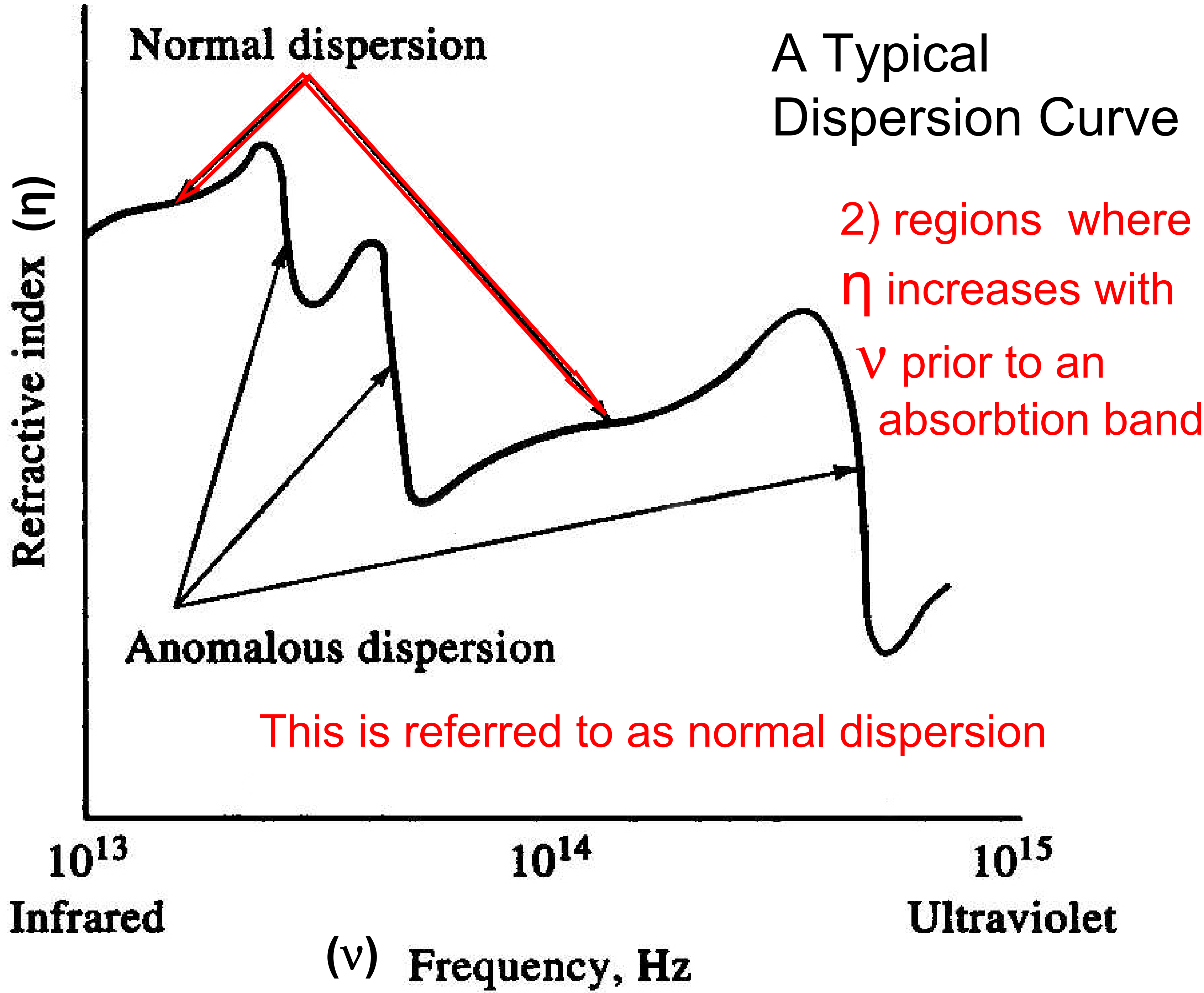
A Typical Dispersion Curve

Three trends can be seen

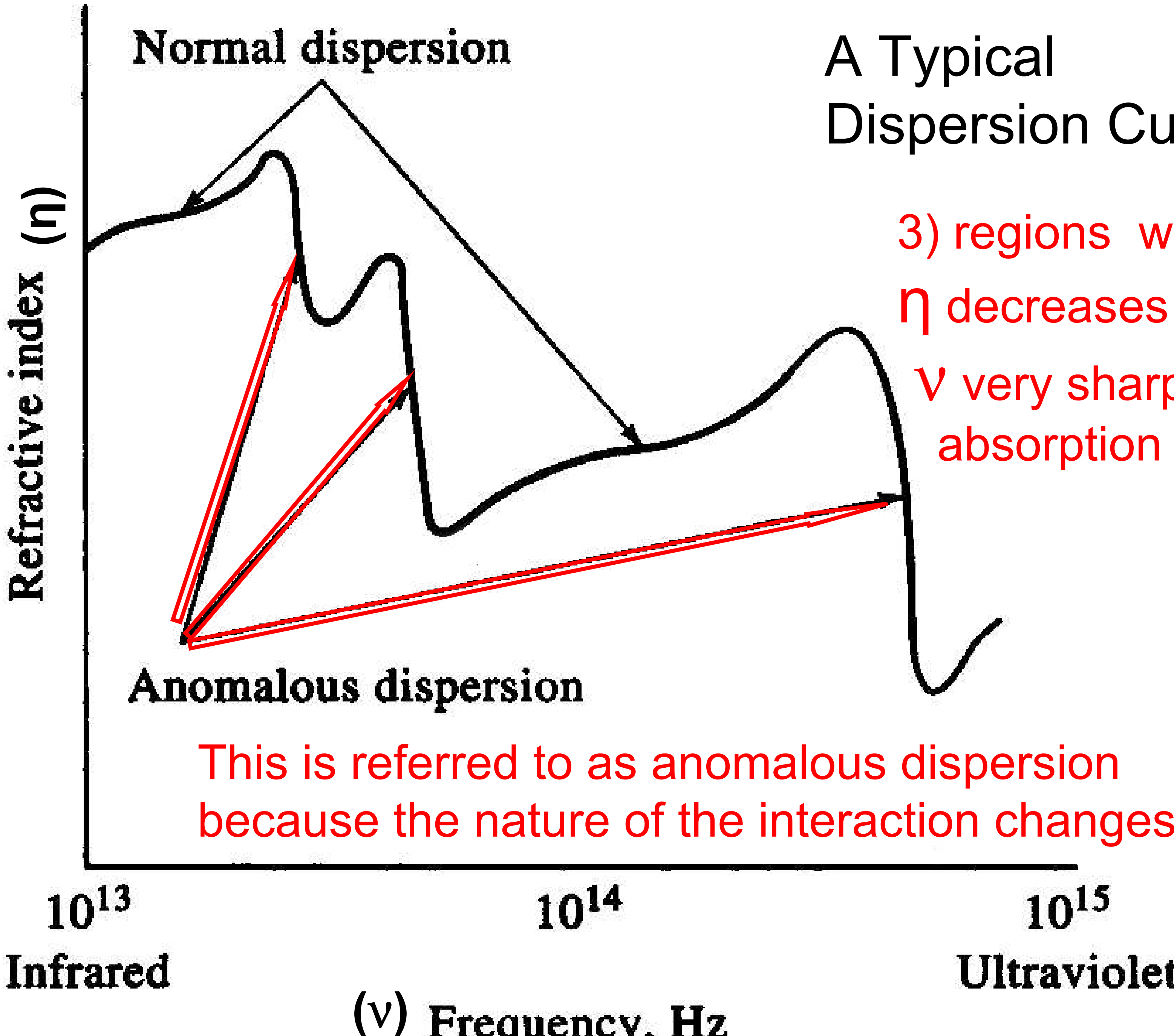
1) an overall decrease in η as ν increases



This reflects the inability of the electric fields in the material to keep up with the oscillations of the EM


Normal dispersion
A Typical
Dispersion Curve
2) regions where
η increases with
ν prior to an
absorbtion band
Refractive index (η)
Anomalous dispersion
This is referred to as normal dispersion
10^{13}
10^{14}
10^{15}
Infrared
Ultraviolet
(ν) Frequency, Hz

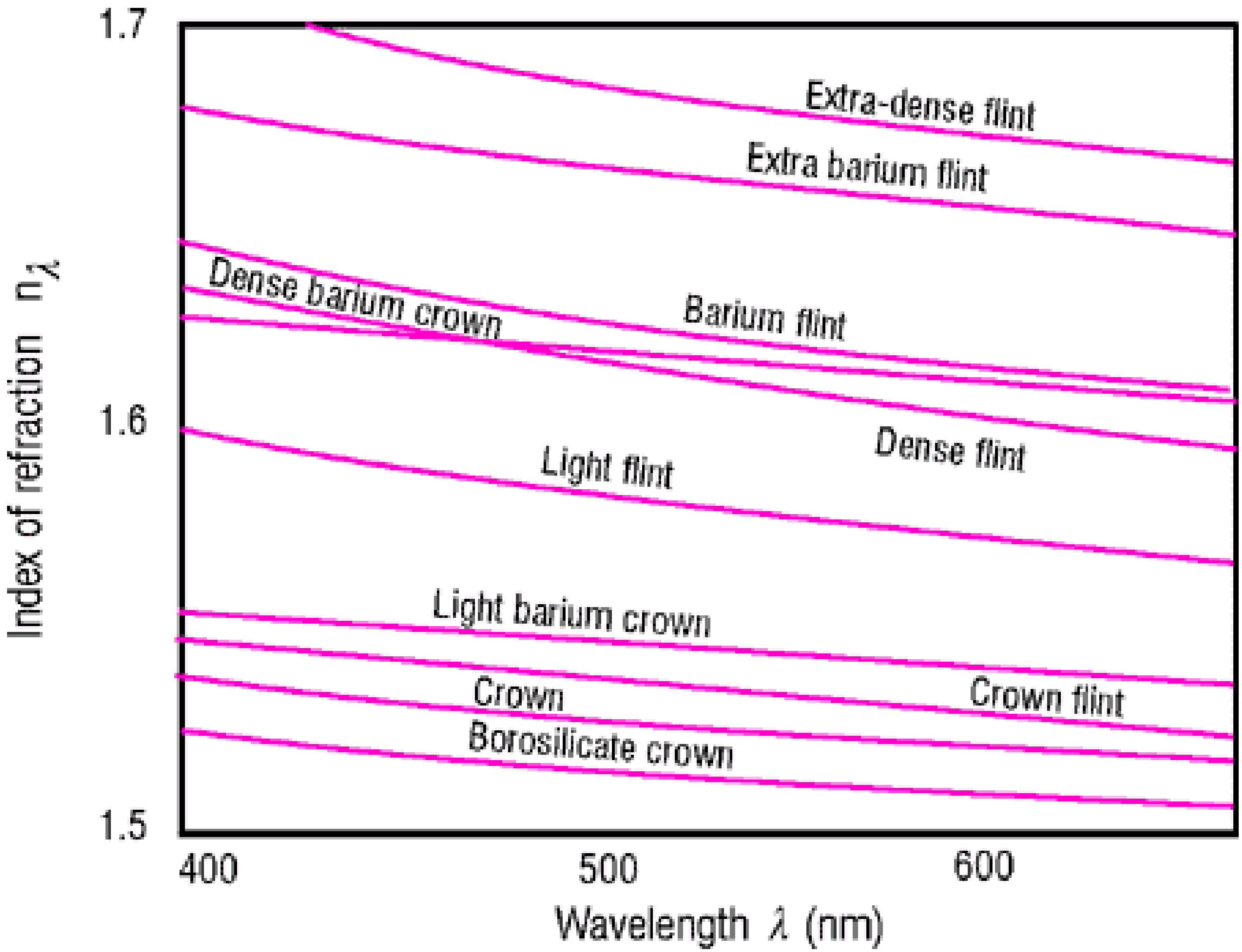
A Typical Dispersion Curve



3) regions where η decreases with ν very sharply at absorption bands

This is referred to as anomalous dispersion because the nature of the interaction changes

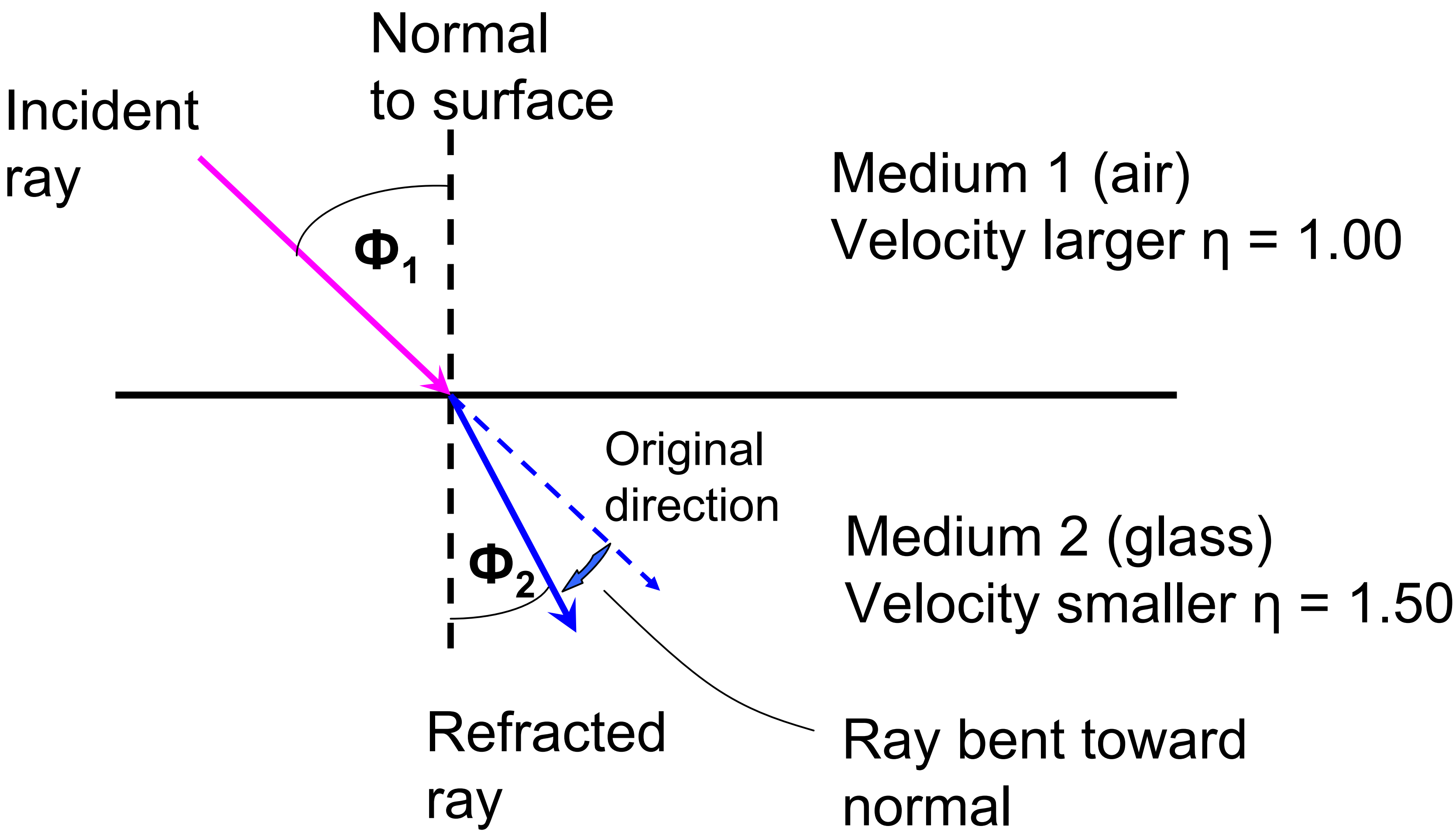
Variation in the Refractive index (η) with wavelength (λ) for several types of glass



Refractive indices (η) for various substances at 589 nm (the sodium D line)

Substance	η
air	1.00027
water, 20 ^{o}C	1.33336
NaCl crystal	1.544
benzene	1.501
quartz (fused)	1.46
glass (crown)	1.52
ethyl alcohol	1.36
carbon disulfide	1.63

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 $\eta_1 = 1.0$

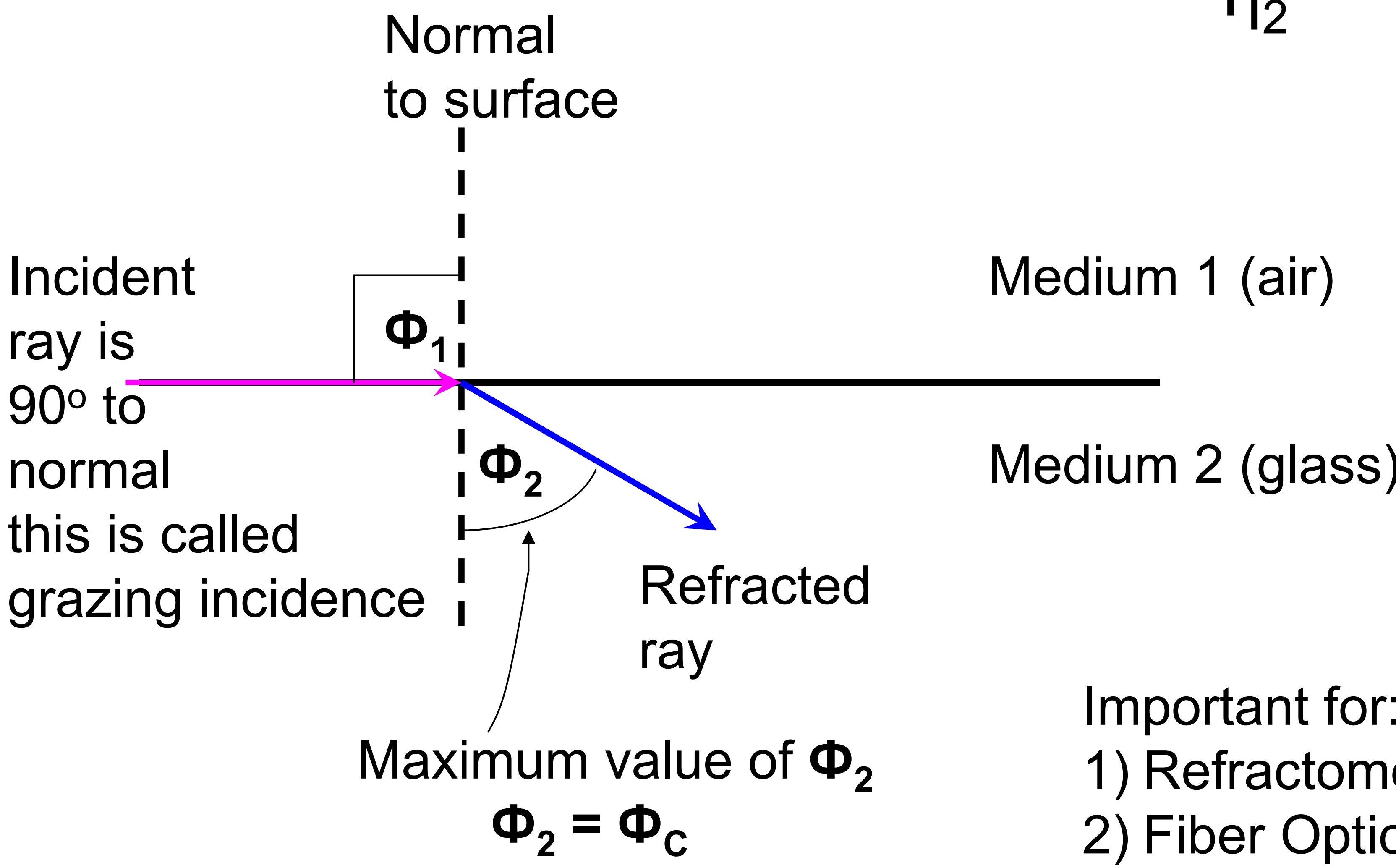
Magnitude of the direction change (i.e., size of the angle depends on wavelength (shown in equation as ν) this is how a prism works

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.

Critical Angle (Φ_C)

At 90^o incidence $\sin \Phi_1 = 1.0$

$$\sin \Phi_C = \frac{\eta_1}{\eta_2}$$



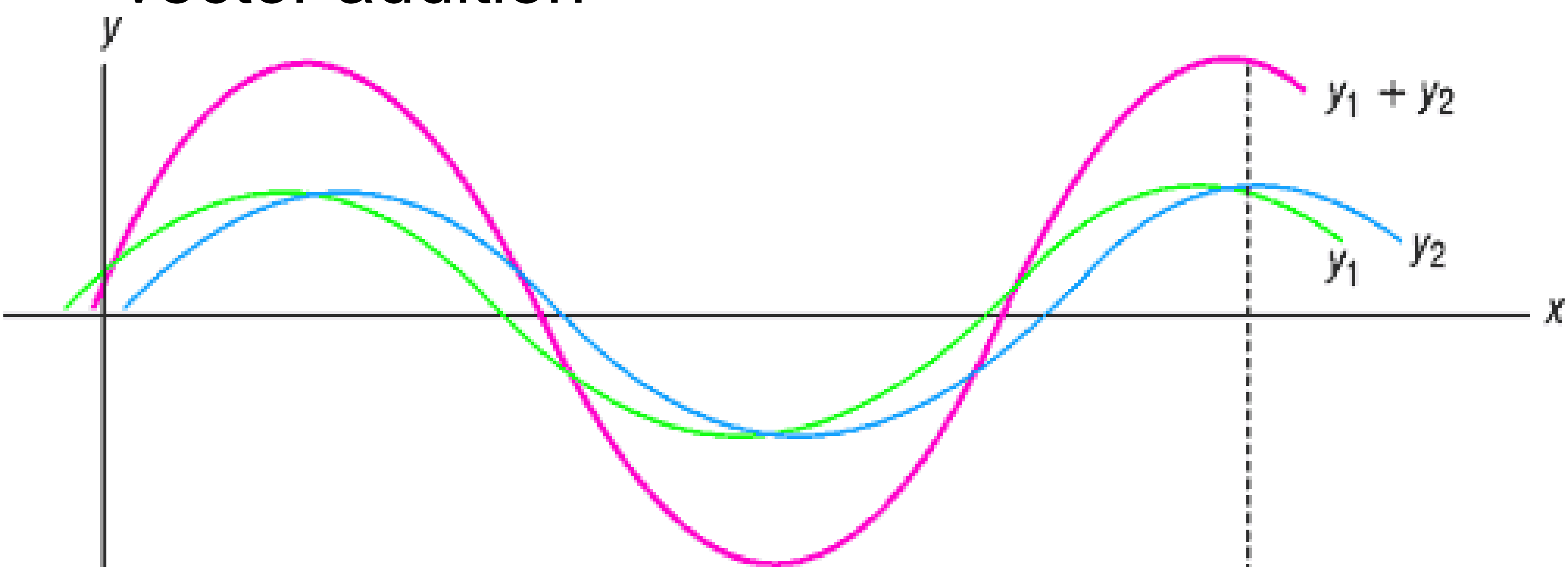
Important for:
1) Refractometers
2) Fiber Optics

<u>Wave Interaction</u> - 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

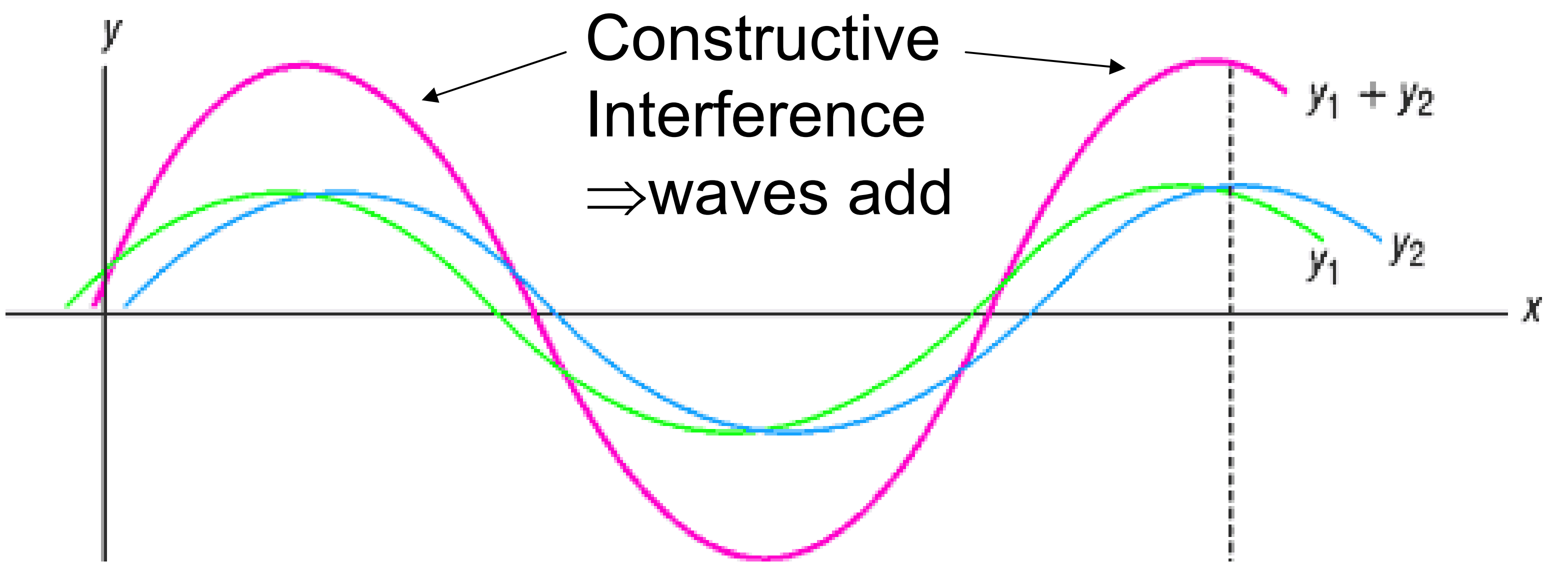
α = phase angle

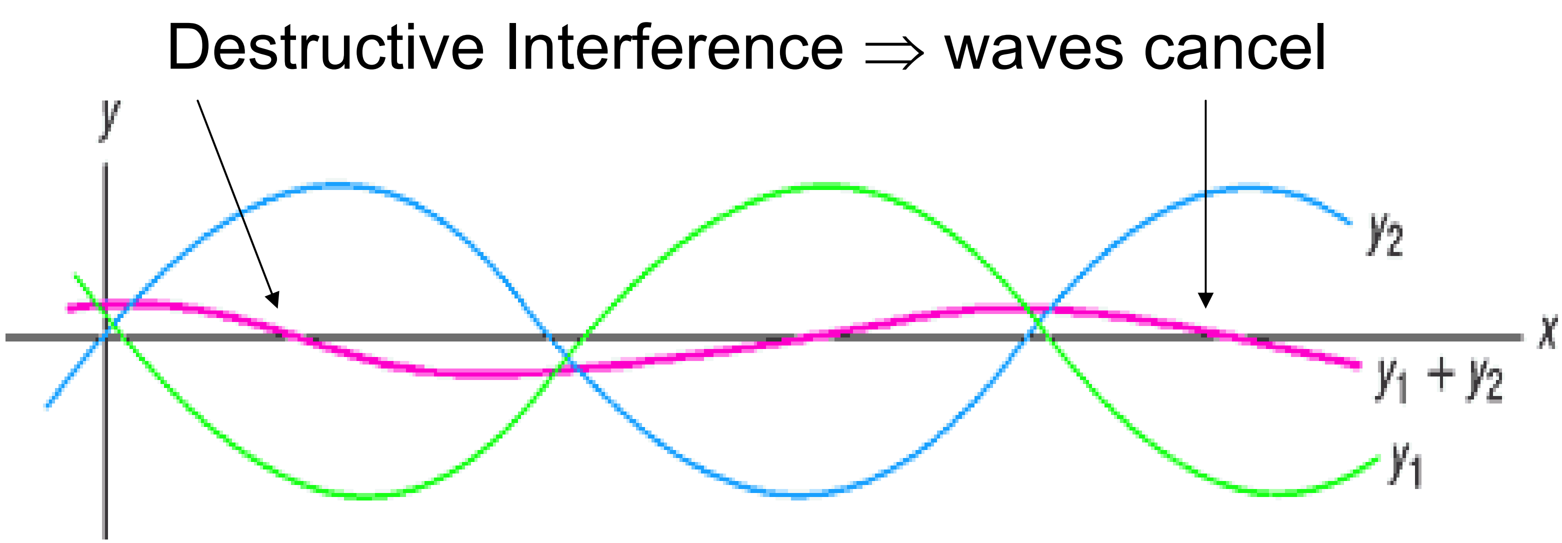
t = time

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

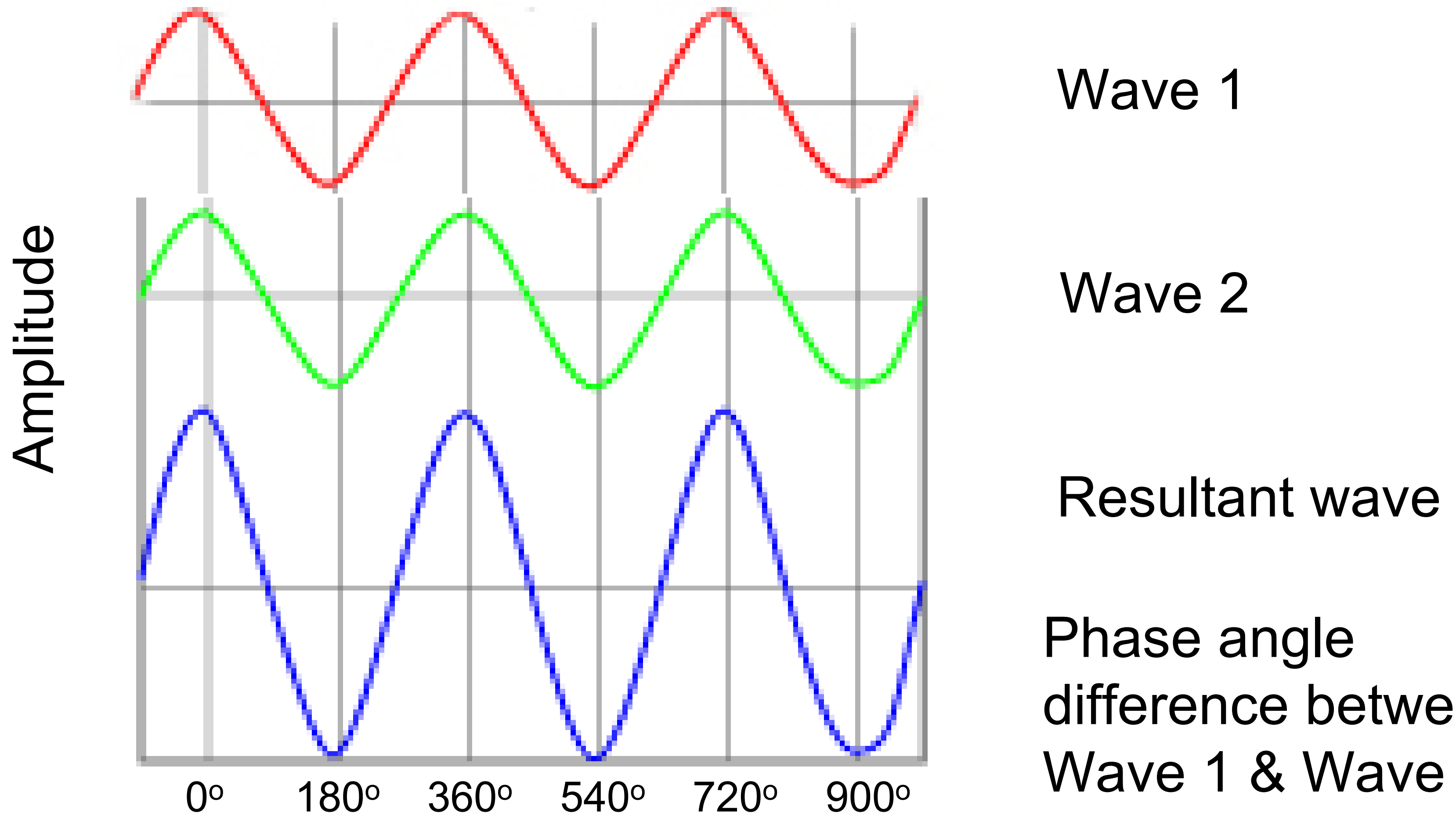
$$y = A_1 \sin(\omega_1 t + \alpha_1) + A_2 \sin(\omega_2 t + \alpha_2) + \ldots$$

Interference - amplitude of the resulting wave depends on phase difference α_1 - α_2





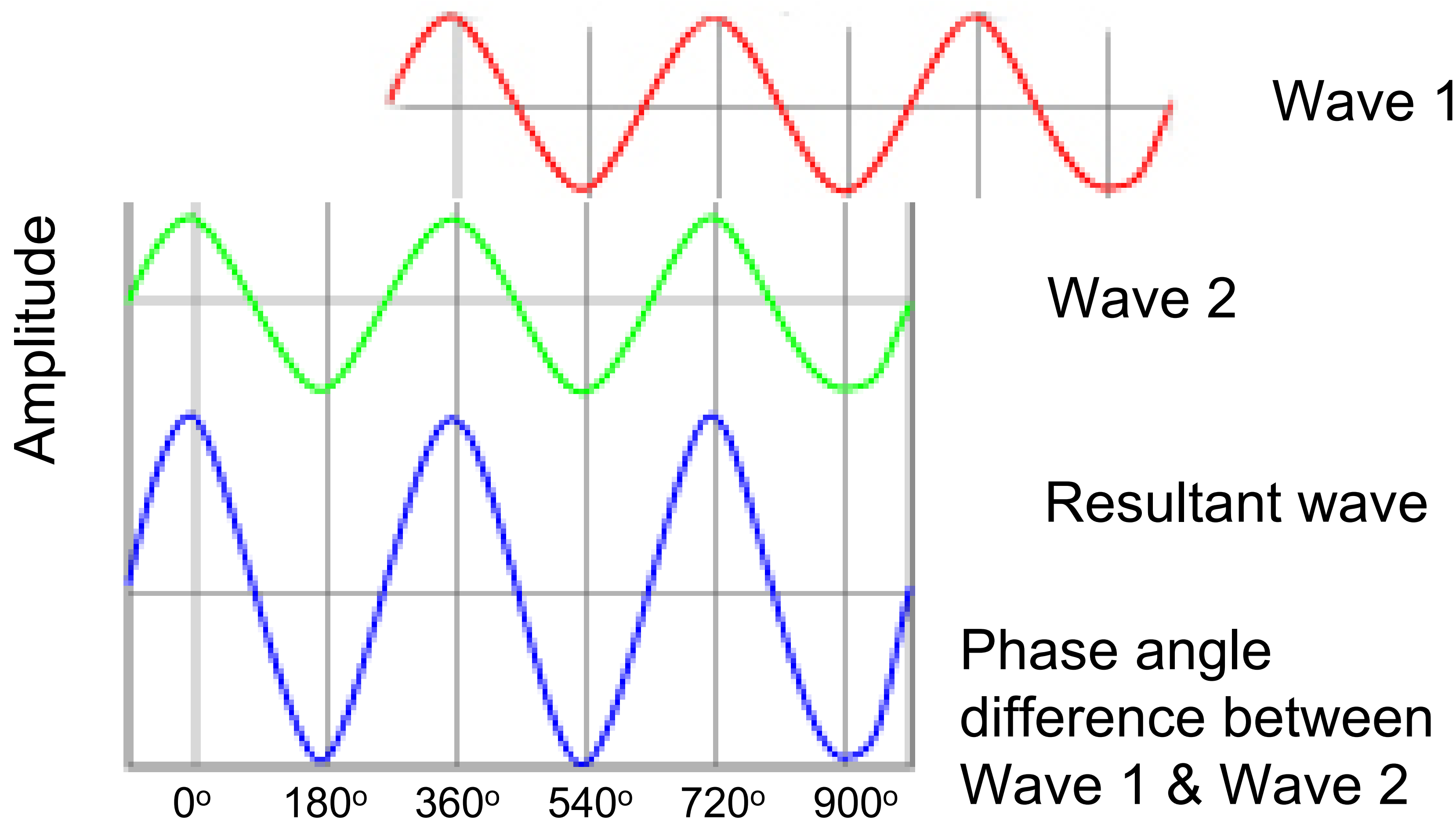
At $\alpha_1 - \alpha_2 = 0^o$ adding of waves gives <u>Maximum Constructive Interference</u>



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

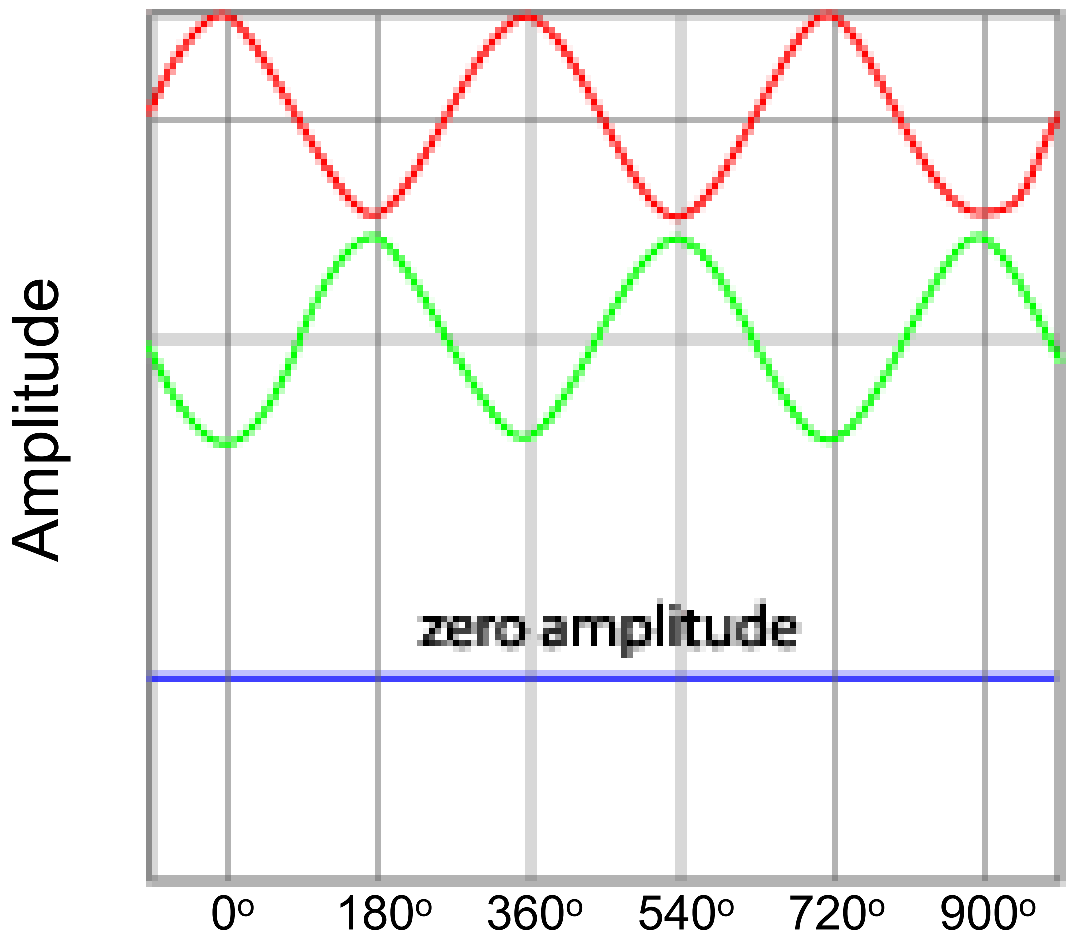
Also at α_1 - α_2 = 360° adding of waves gives

<u>Maximum Constructive Interference</u>



Phase angle difference between Wave 1 & Wave 2 is 360° (α_1 - α_2 = 360°)

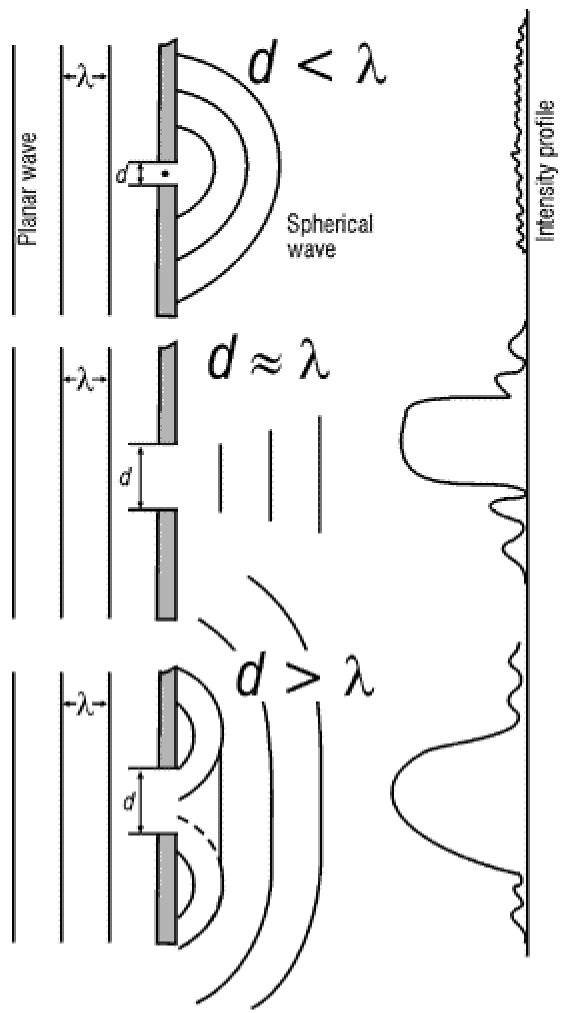
When α_1 - α_2 = 180^o or 540^o adding of waves gives Maximum Destructive Interference



Phase angle difference between Wave 1 & Wave 2 is 180^o (α_1 - α_2 = 180^o)

Fourier Analysis – mathematical process of resolving a combination of waves of various frequencies into their individual frequencies. This requires a Fourier integral and is important in all Fourier Transform (FT) methods like FTIR and FT NMR. Requires complex mathematics and a computer to figure out amplitudes of various component frequencies.

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

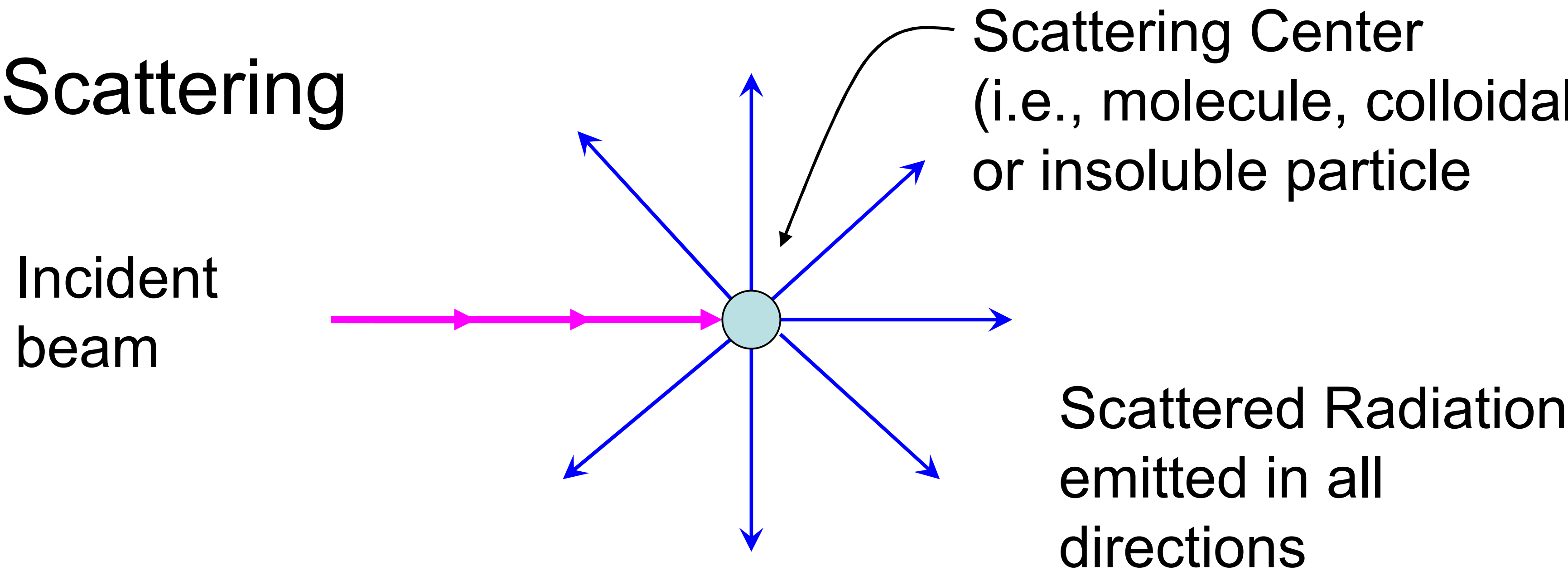
Scattering = EM interacts with matter and changes direction, usually without changing energy

This can be described using both the wave or particle nature of light:

1) Wave – EM induces oscillations in electrical charge of matter ⇒ resulting in oscillating dipoles which in turn radiate secondary waves in all directions = scattered radiation
2) Particle (or Quantum) – EM interacts with matter to form a virtual state (lifetime 10^{-14} s) which reemits in all directions.

Raman effect = when some molecules return to a different state ⇒ change in frequency

Scattering



Many types of scattering exist depending on several parameters characterizing the system, we will be concerned with:
Rayleigh Scattering and Large Particle Scattering

Rayleigh Scattering – scattering by particles whose longest dimension is < 5 % to 10 % of λ with no change in observed frequency

$$I_s = \frac{8 \pi^4 \alpha^2}{\lambda^4 r^2} (1 + \cos^2 \theta) I_o$$

- scattering intensity → I_s
- polarizability → α
- angle between incident beam & scattered beam → θ
- wavelength → λ
- distance from scattering center to detector → r
- incident beam intensity → I_o

Notice the fourth power dependence on wavelength meaning short wavelengths are scattered more efficiently ⇒ sky is blue

Polarizability (α) is measure of how well a given frequency induces a dipole in a substance

α Tends to be large for large molecules (e.g., proteins)

Large Particle Scattering – particle dimensions < 10 % λ to 1.5 λ

Applies in techniques like turbidimetry and nephelometry

Large particles do not act as a point source & give rise to various interference phenomena

Forward scatter becomes greater than back scatter