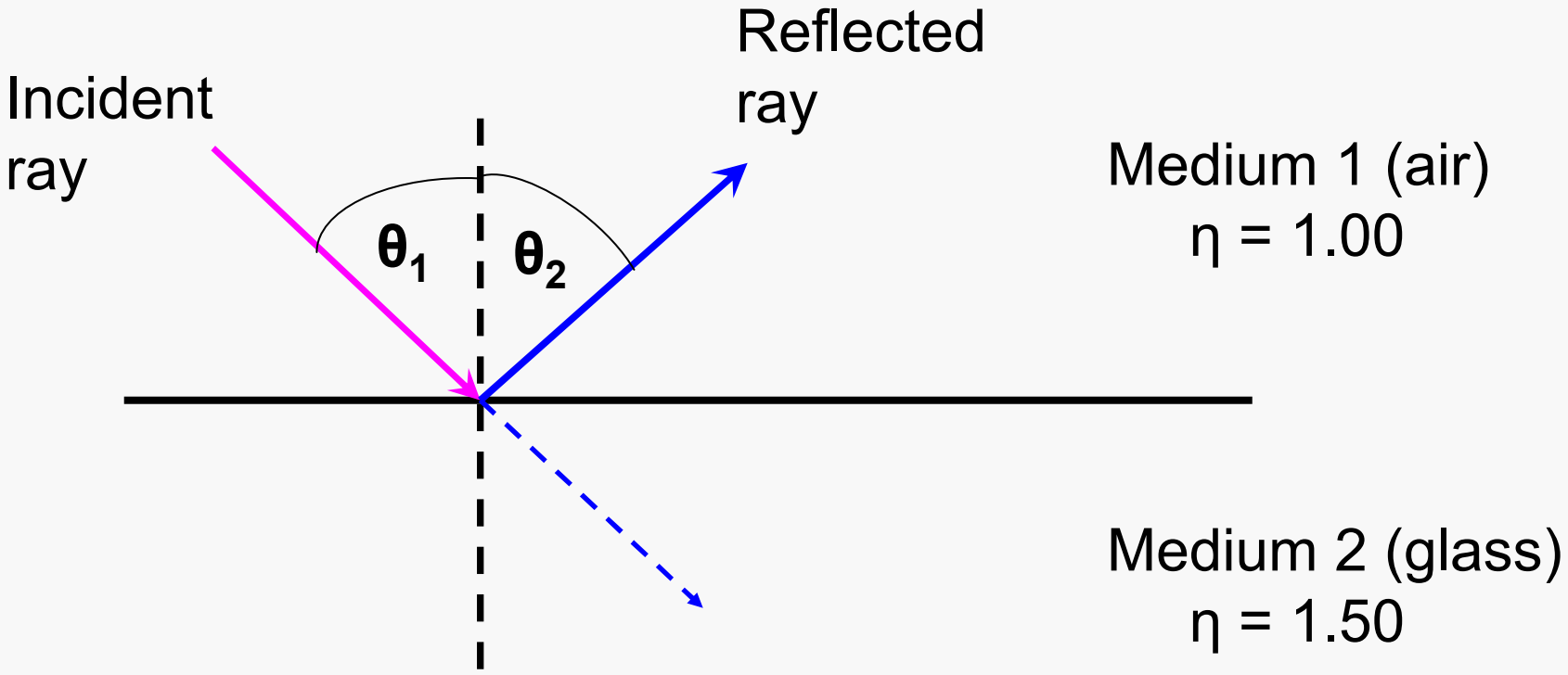
Reflection = EM strikes a boundary between two media differing in η and bounces back



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

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

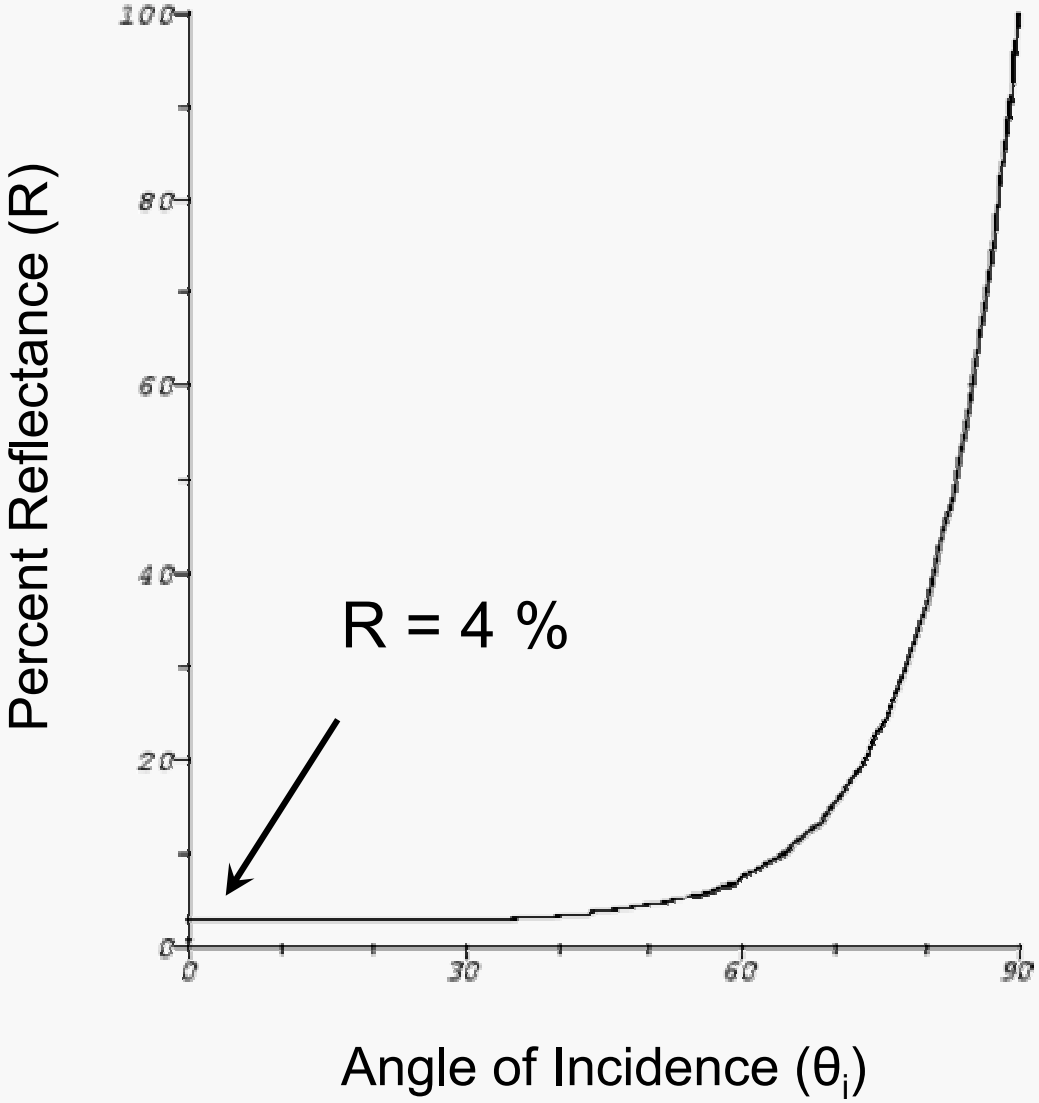
Where I_i and I_r = incident & reflected intensity

For radiation going from air ($\eta = 1.00$) to glass ($\eta = 1.50$) 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**.

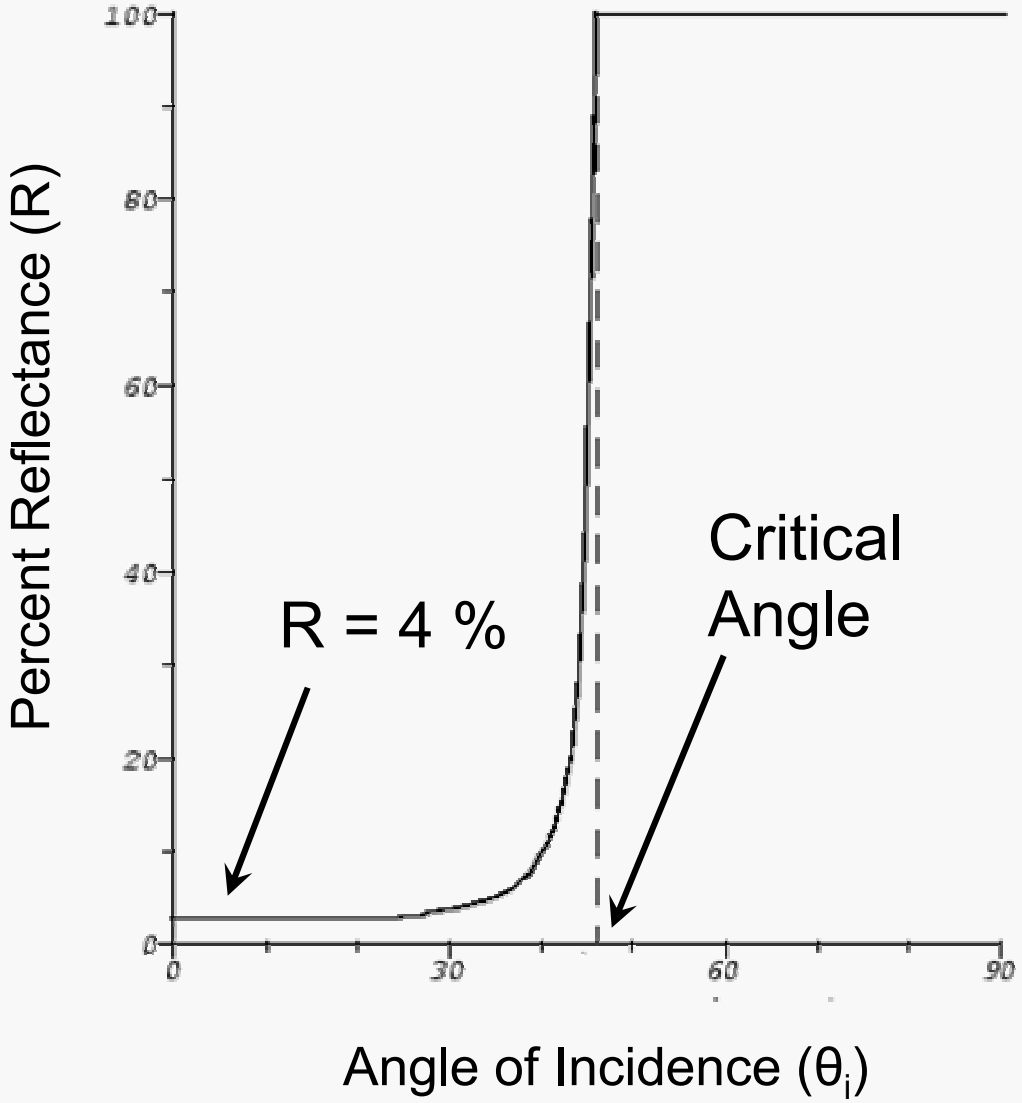
Reflectance varies with the angle of incidence



EM going from air ($\eta = 1.00$) to glass ($\eta = 1.50$)

For monochromatic radiation, as incident angle deviates from the normal, the R tends to increase

EM going from glass (η = 1.50) to air (η = 1.00)

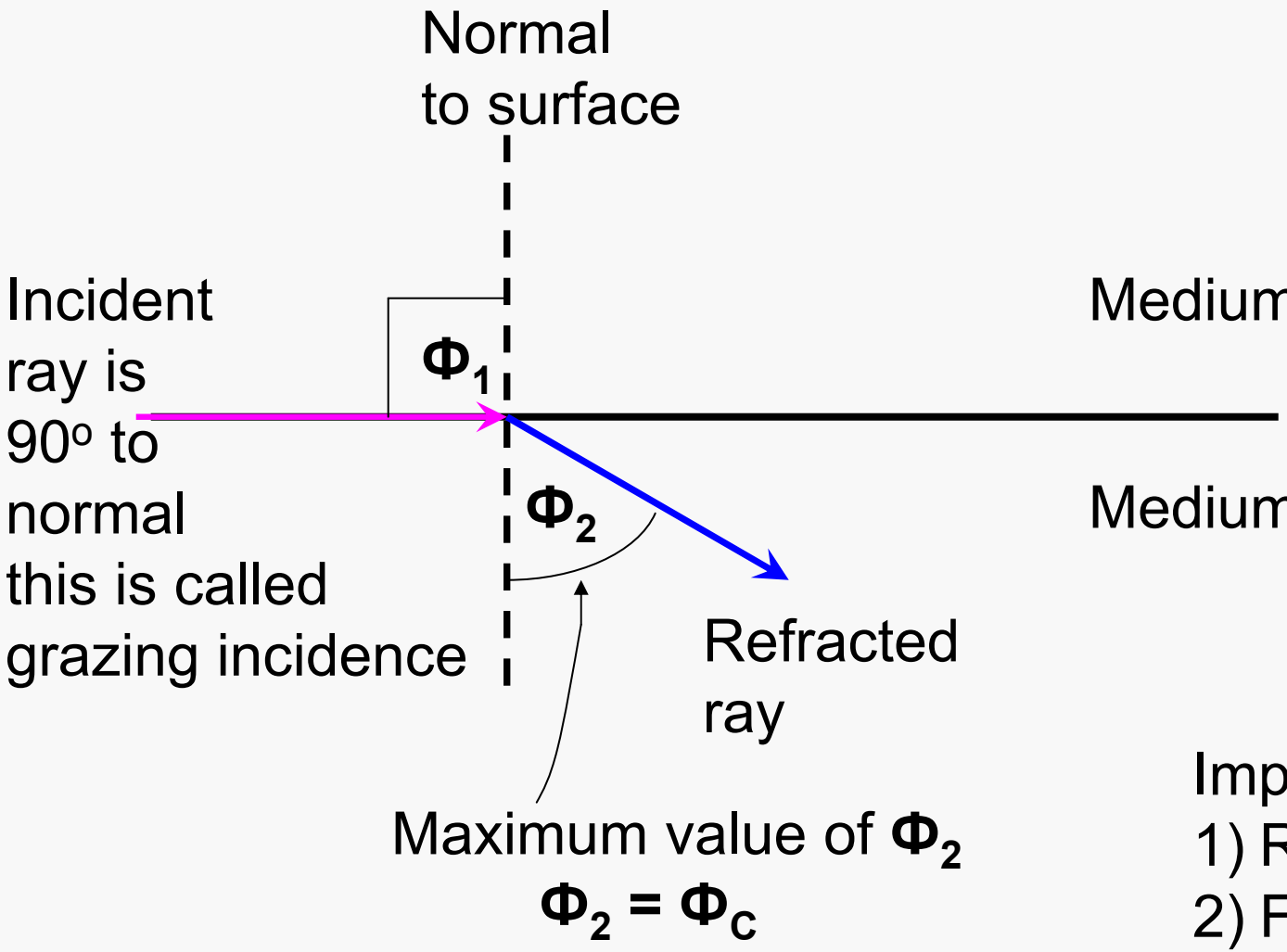


EM going from a medium of higher η to a medium of lower η, the angle of incidence can only increase to the critical angle before all of the light is completely reflected back

Critical Angle (Φ_C)

At 90° incidence sin $\Phi_1 = 1.0$

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

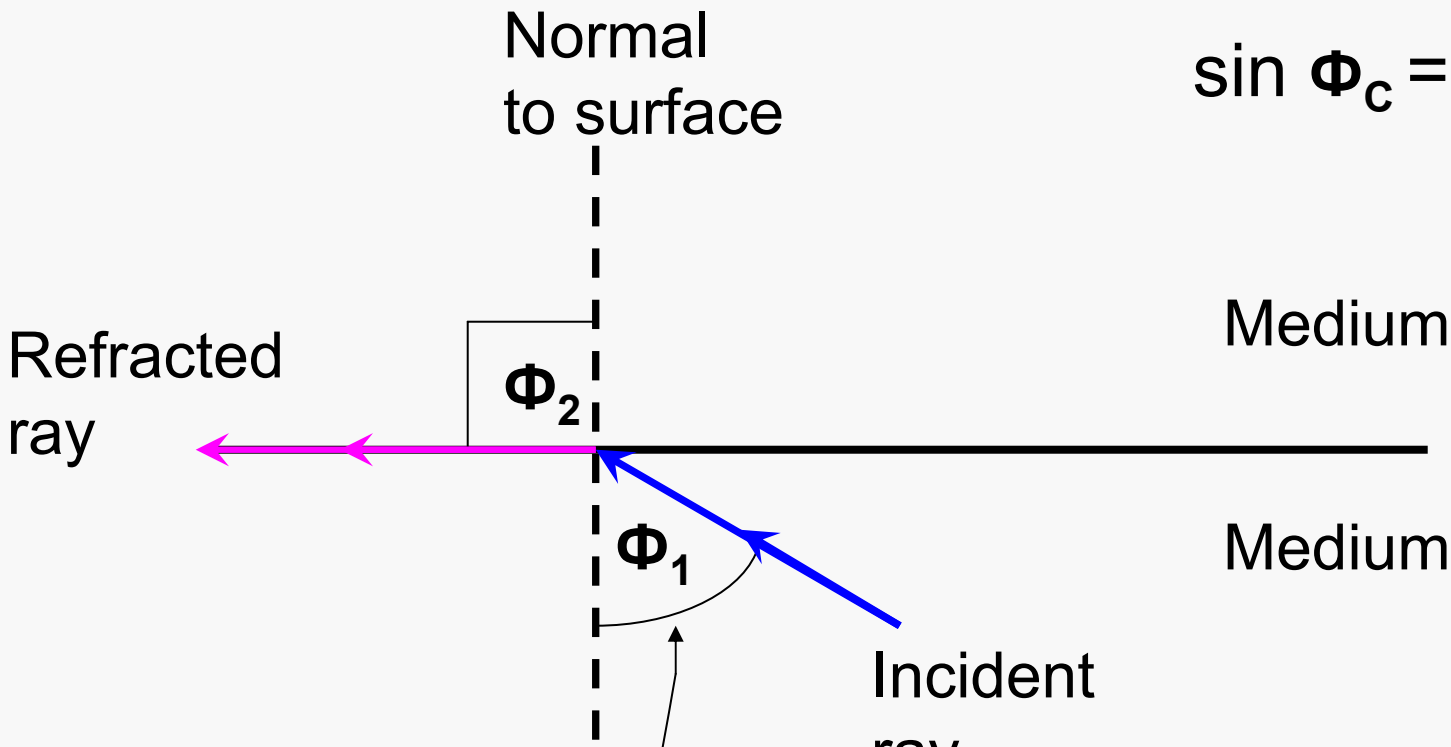


Important for:
1) Refractometers
2) Fiber Optics

Critical Angle (Φ_c)

When incidence is at the Critical angle, refraction is at 90°

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

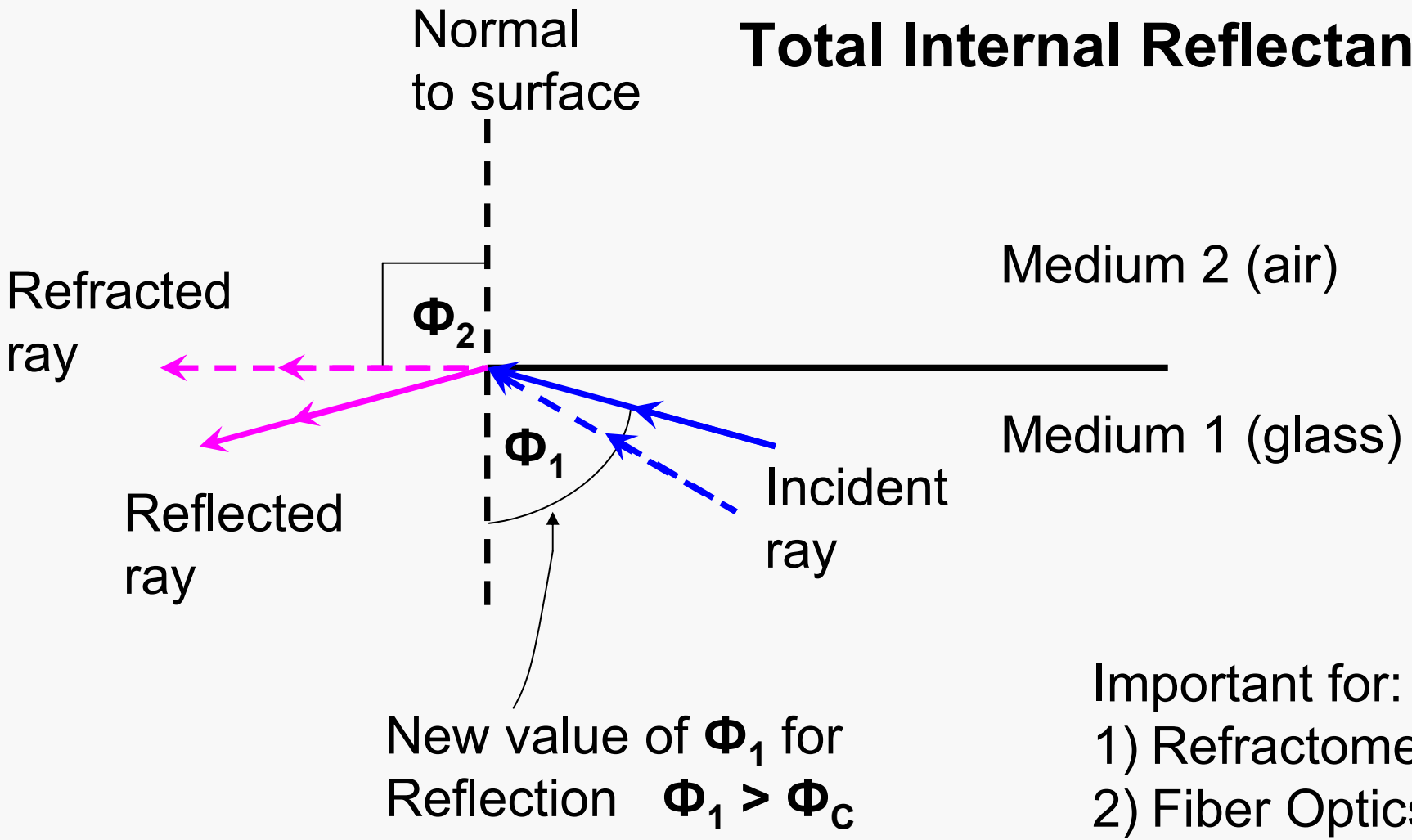


Maximum value of Φ_1 for Refraction $\Phi_1 = \Phi_c$

Important for:
1) Refractometers
2) Fiber Optics

Critical Angle (Φ_C)

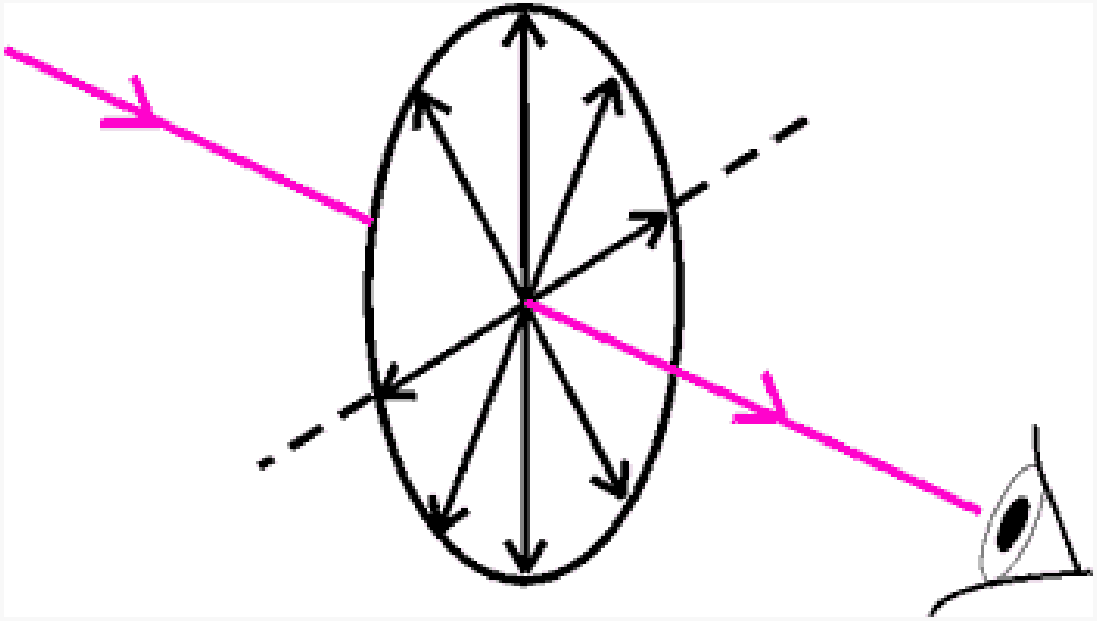
At angles greater than the Critical angle, 100 % reflection occurs or **Total Internal Reflectance**



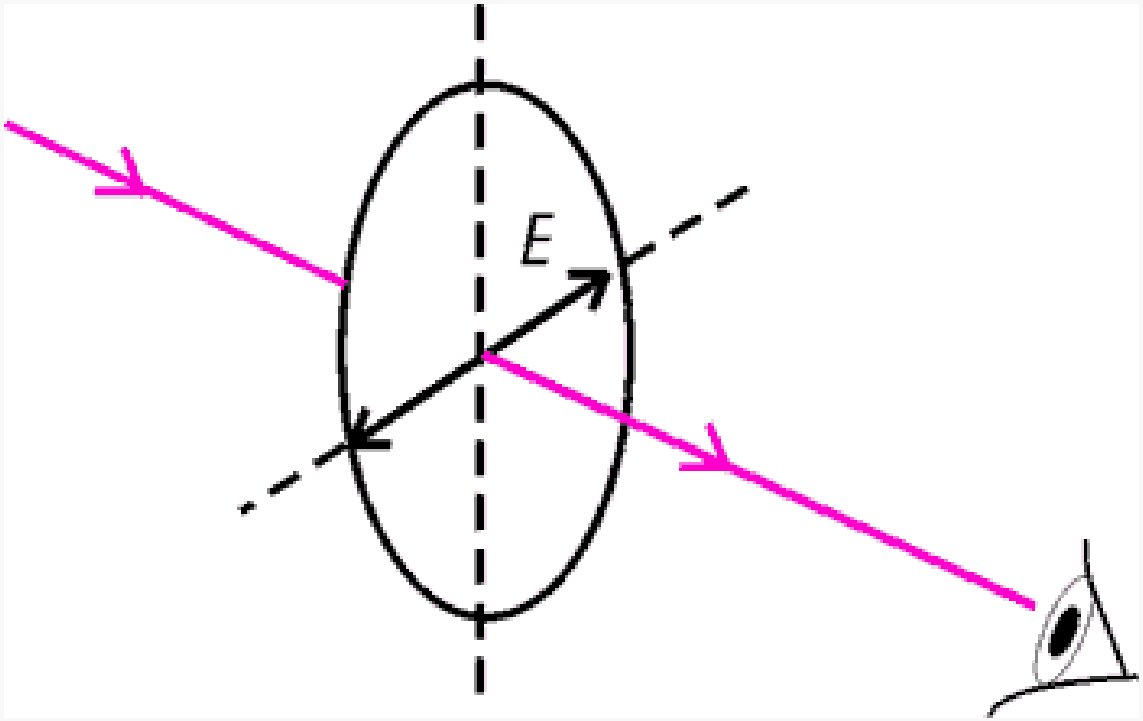
Important for:
1) Refractometers
2) Fiber Optics

Polarization

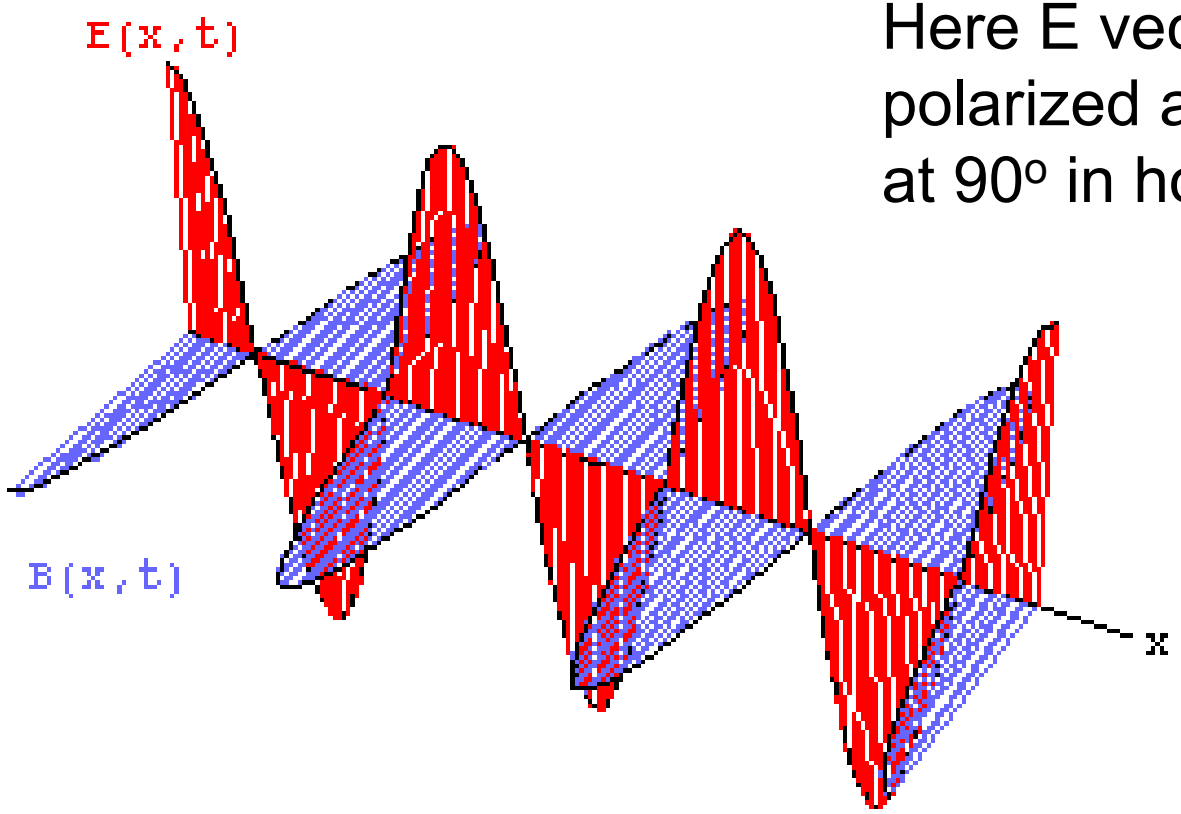
EM is said to be unpolarized if its electric vectors and magnetic vectors occur with equal amplitude in all direction



Linearly polarized light oscillates in one plane only as it moves through space

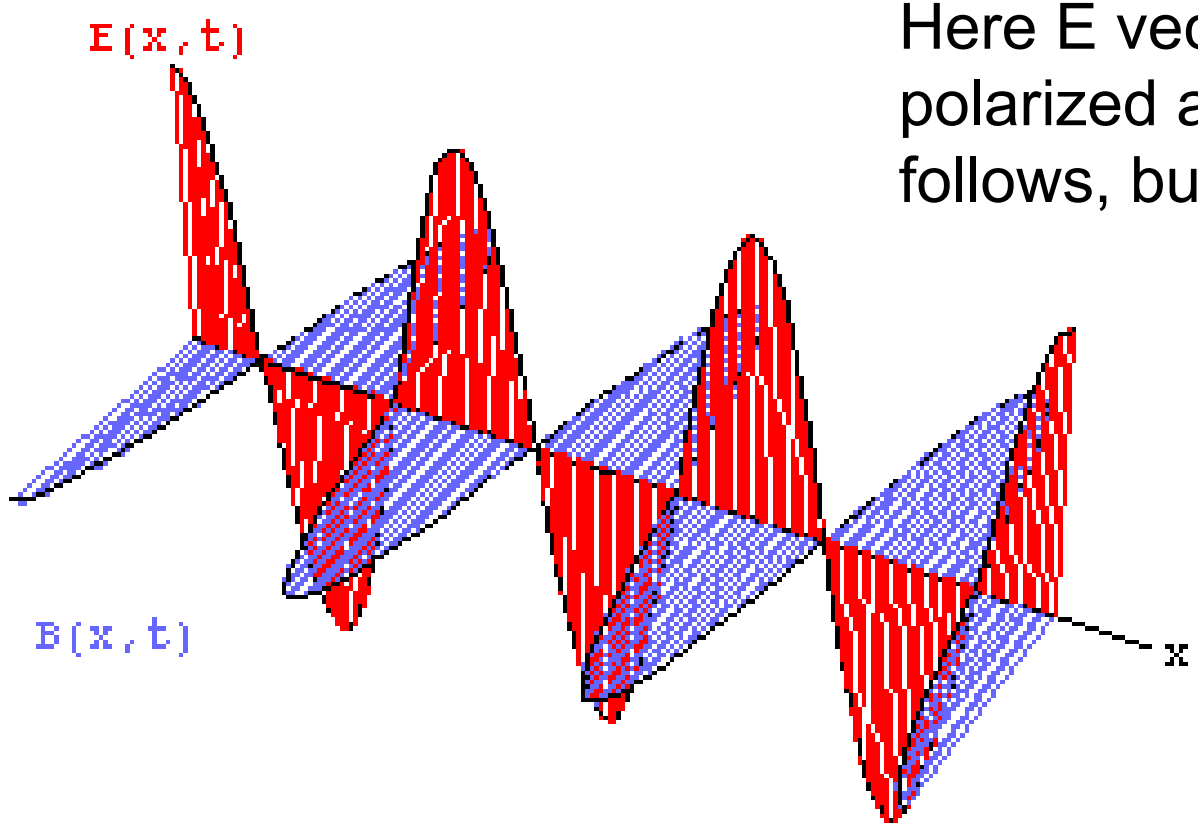


Linearly polarized light oscillates in one plane only as it moves through space



Here E vector is vertically polarized and H vector is at 90^{o} in horizontal plane

Circularly polarized light rotates in either a left handed or right handed spiral as it moves through space



Here E vector is circularly polarized and H vector follows, but is offset by 90^{o}

Combining equal beams where one is right circularly polarized and the other left, results in linearly polarized radiation

Polarization is particularly important for studying optically active materials using

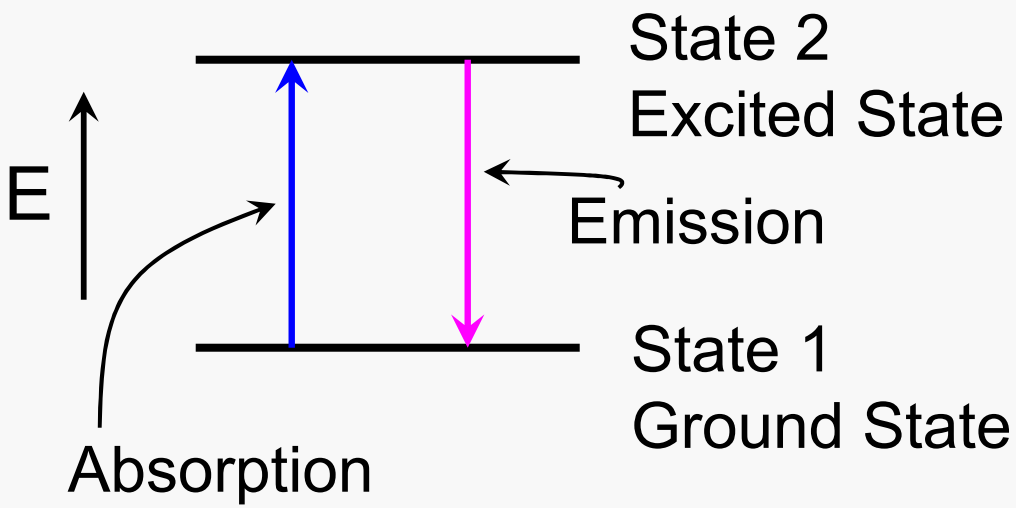
- Optical Rotatory Dispersion (ORD)
- Circular Dichroism (CD)
- Fluorescence Polarization

Absorption and Emission

Two most interesting and most useful processes when EM interacts with matter

Atoms and molecules can exist in many possible energy states

Consider two states



For absorption of EM

$$\Delta E = E_2 - E_1 = h\nu$$

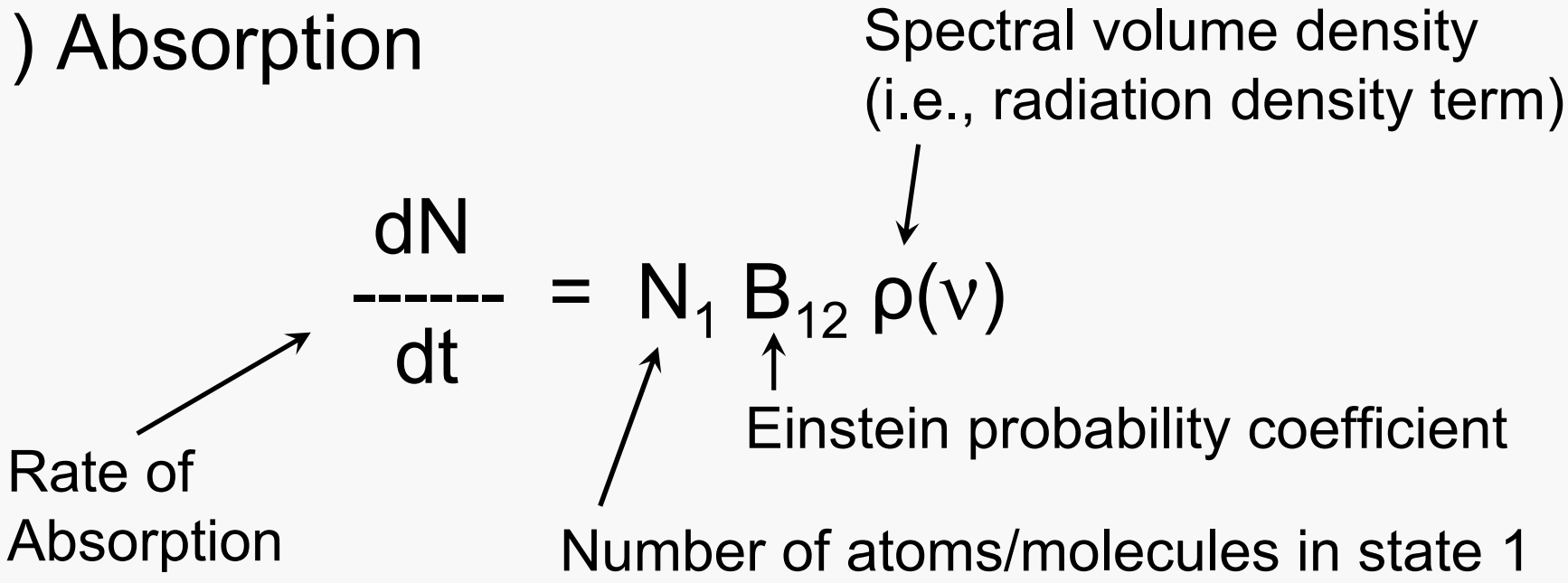
Where E_1 & E_2 are energies of states & h is Planck's constant ν is the frequency

Have to consider particle nature of EM for absorption – consider EM to be a bundle of photons with energy $h\nu$

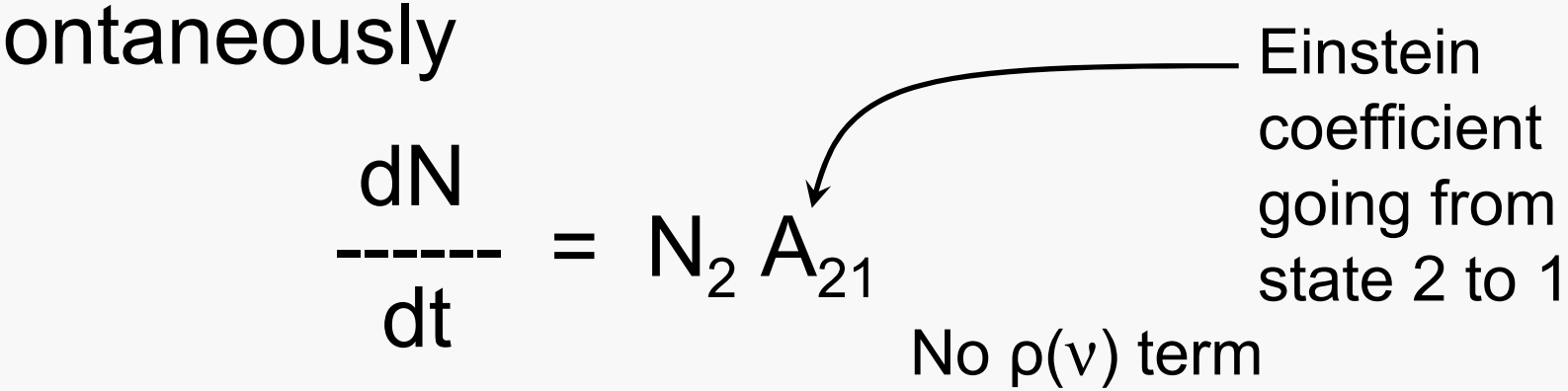
The rate of absorption or emission depends on:

1) Number of atoms/molecules in initial state
2) Probability that is characteristic of the particular transition
3) Radiation density

1) Absorption



2) Spontaneous Emission – goes back down spontaneously



3) Stimulated Emission - photon strikes state 2 causing it to emit

$$\frac{dN}{dt} = N_2 B_{21} \rho(\nu)$$

Relationship between probability coefficients

$$B_{12} = B_{21}$$

Absorption → B_{12} = B_{21} ← Stimulated Emission

$$A_{21} = 8 \pi h \sigma^3 B_{12}$$

Boltzmann Distribution – relative population of states 1 & 2 is dependent on energy difference and temperature at equilibrium

$$\frac{N_1}{N_2} = \frac{e^{-E_1/kT}}{e^{-E_2/kT}}$$

K = Boltzmann's constant (8.62×10^{-5} eV/^{o}K)

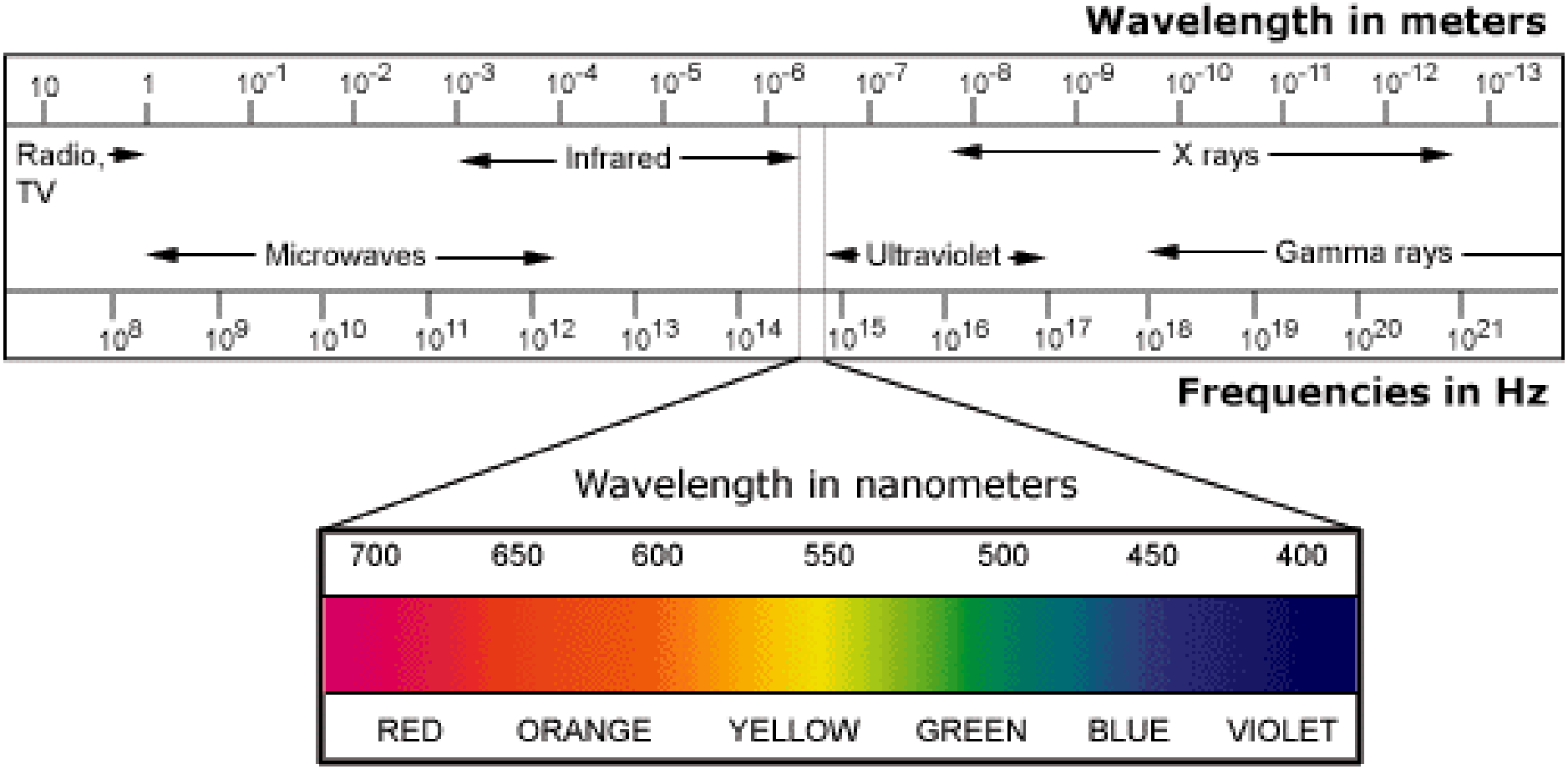
T = absolute temperature (298 ^{o}K = 25 ^{o}C)

An additional term is add to the right side of the equation if there is more than one state with the same energy = degeneracy

Energy Separation and Relative Population of States

Type of Transition	Energy of Transition			Population Ratio N_2/N_1
	cm^{-1}	eV	kJ/mol	at 25 ^oC
Electronic	20,000	2.6	240	10^{-41}
Vibrational	1,000	0.12	12	10^{-2}
Rotational	10	1.2×10^{-3}	0.12	0.95
Electron Spin	0.1	1.2×10^{-5}	1.2×10^{-3}	0.9995
Nuclear Spin	1×10^{-3}	1.2×10^{-7}	1.2×10^{-5}	0.999995

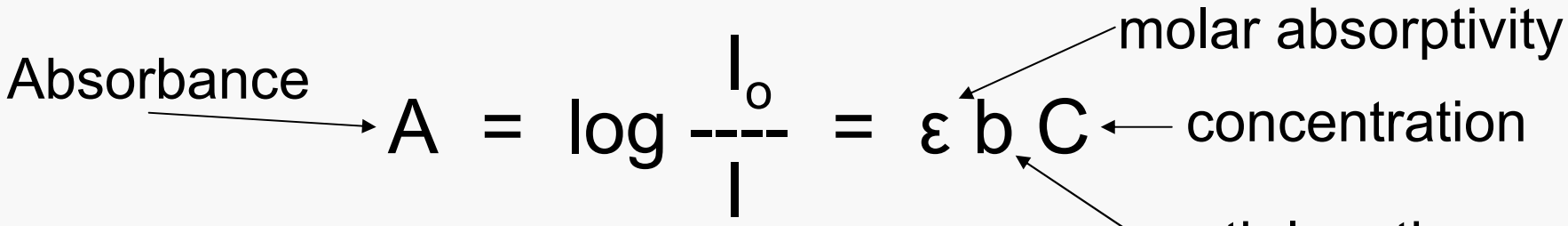
Spin States	Molecular Rotations	Molecular Vibrations	Outer Shell Electrons	Inner Shell Electrons	Nuclear Transitions
NMR EPR	Microwave Absorption Spectroscopy	Infrared Absorption Spectroscopy	UV-vis Absorption, Fluorescence	X-Ray Absorption, Fluorescence	Gamma Ray Spectroscopy



R O Y G B V

Quantitative Aspects of Absoption

Beer-Lambert Law (or Beer's Law)



Transmittance

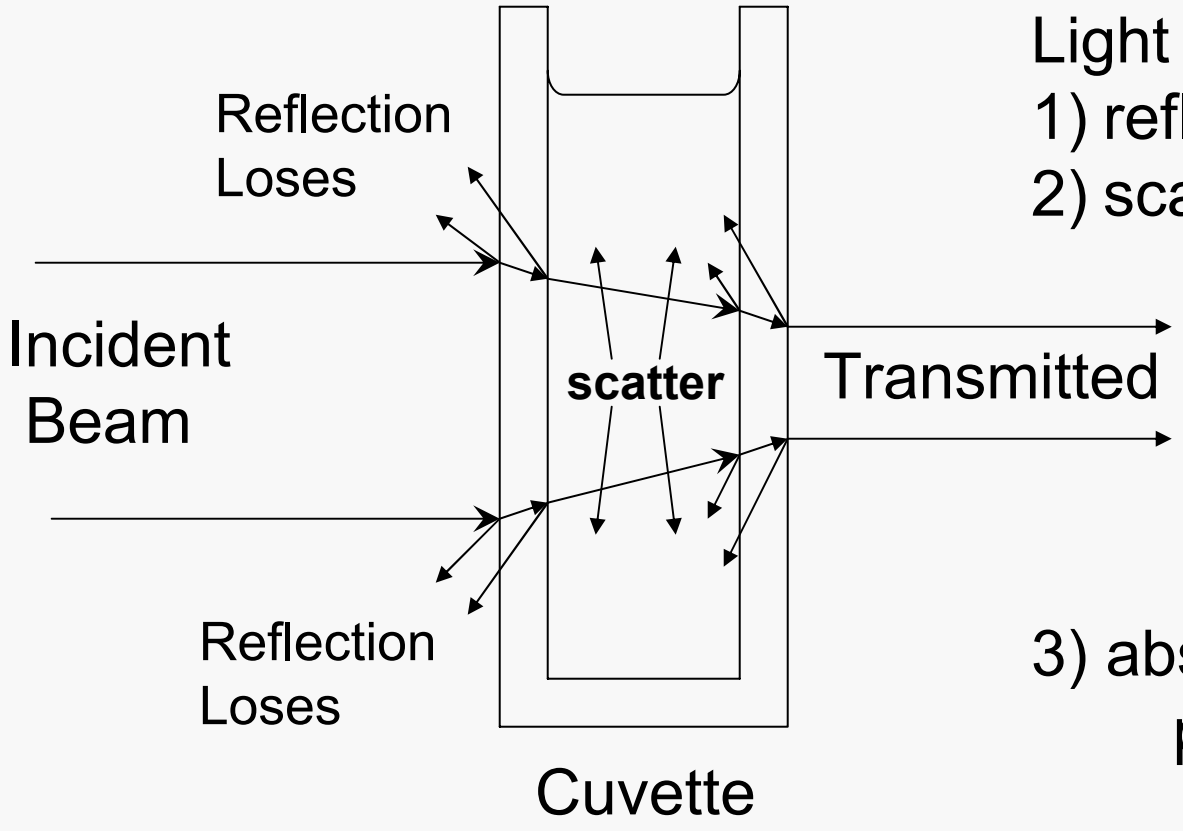
$$T = \frac{I}{I_o} \qquad \%T = T \times 100$$

I_o = measured source intensity

I = measured intensity after absorption

Intensity change does not change absorbance

Effects other than absorption that reduce source intensity (i.e., scattering, reflection) may also be measured as absorbance and must be accounted for when measuring I & I_o



Light loses occur due to:
1) reflection at boundaries
2) scattering by molecules or particles
3) absorption which is process of interest

- Absorbance & Transmittance are unitless
- If C is mol/L & b is in cm then ε is L/mol-cm
- To minimize the effect of light loses from reflection the procedure followed in UV-vis spectrophotometry is to measure I_o with a reference blank of pure solvent in the light path & then measure I under the same conditions – cuvettes should be optically matched if using 2 & clean, free of scratches, lint, fingerprints, etc.

Beer's Law applies to all absorption processes

Assumptions made in deriving Beer's Law:

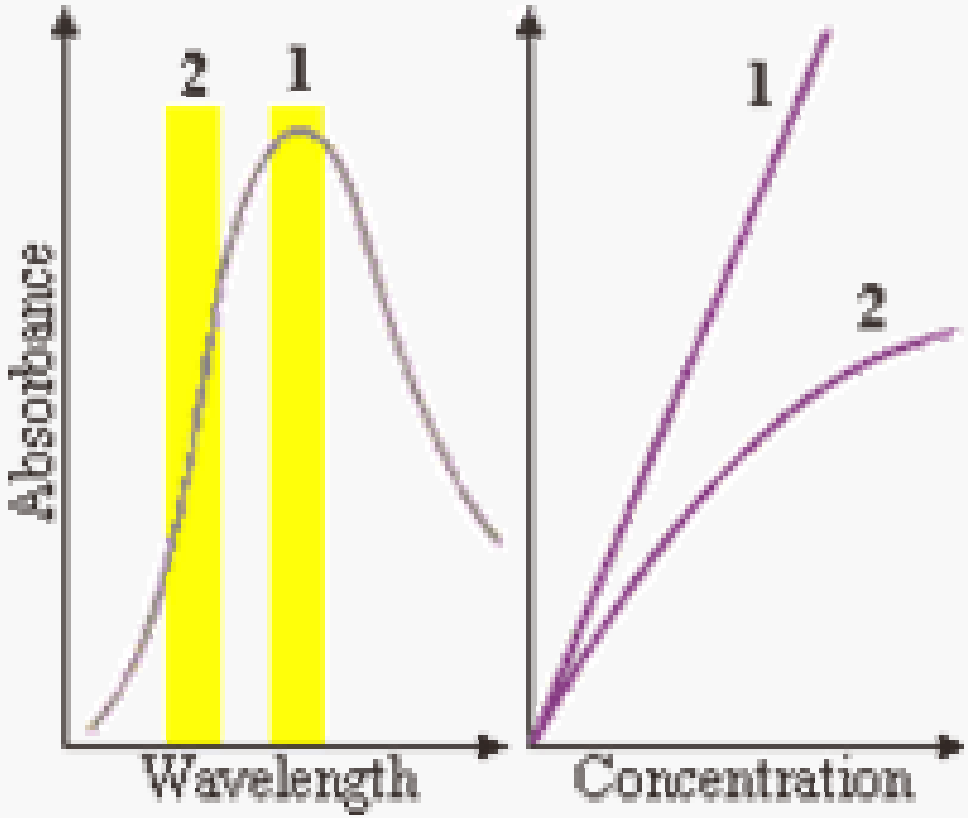
1) Only interaction between radiation (light) and the absorber (sample) is absorption. This breaks down if reflection and scattering are not compensated for. Also breaks down if the absorbed radiation is reemitted as fluorescence (not normally a problem) or if stray light in the instrument reaches detector

Assumptions made in deriving Beer's Law:

2) Monochromatic radiation – in reality this condition is only approximated, instrument measures a narrow band of radiation

ε varies with λ so the best place to measure A is at 1 where A is nearly constant with λ

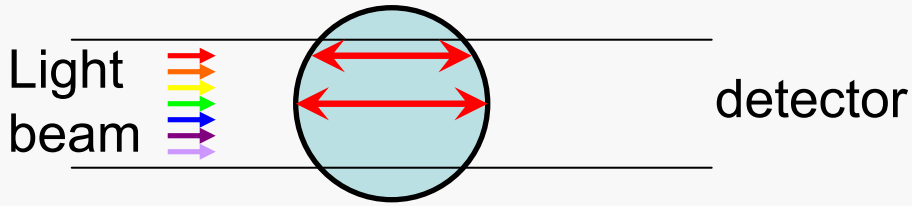
Measurements at 2 suffer from the variation in ε over the bandwidth



Assumptions made in deriving Beer's Law:

3) Pathlength is the same over the volume being measured – this becomes a problem with round cells

λ varies across the bandwidth so some wavelengths pass through more solution than others (b varies)

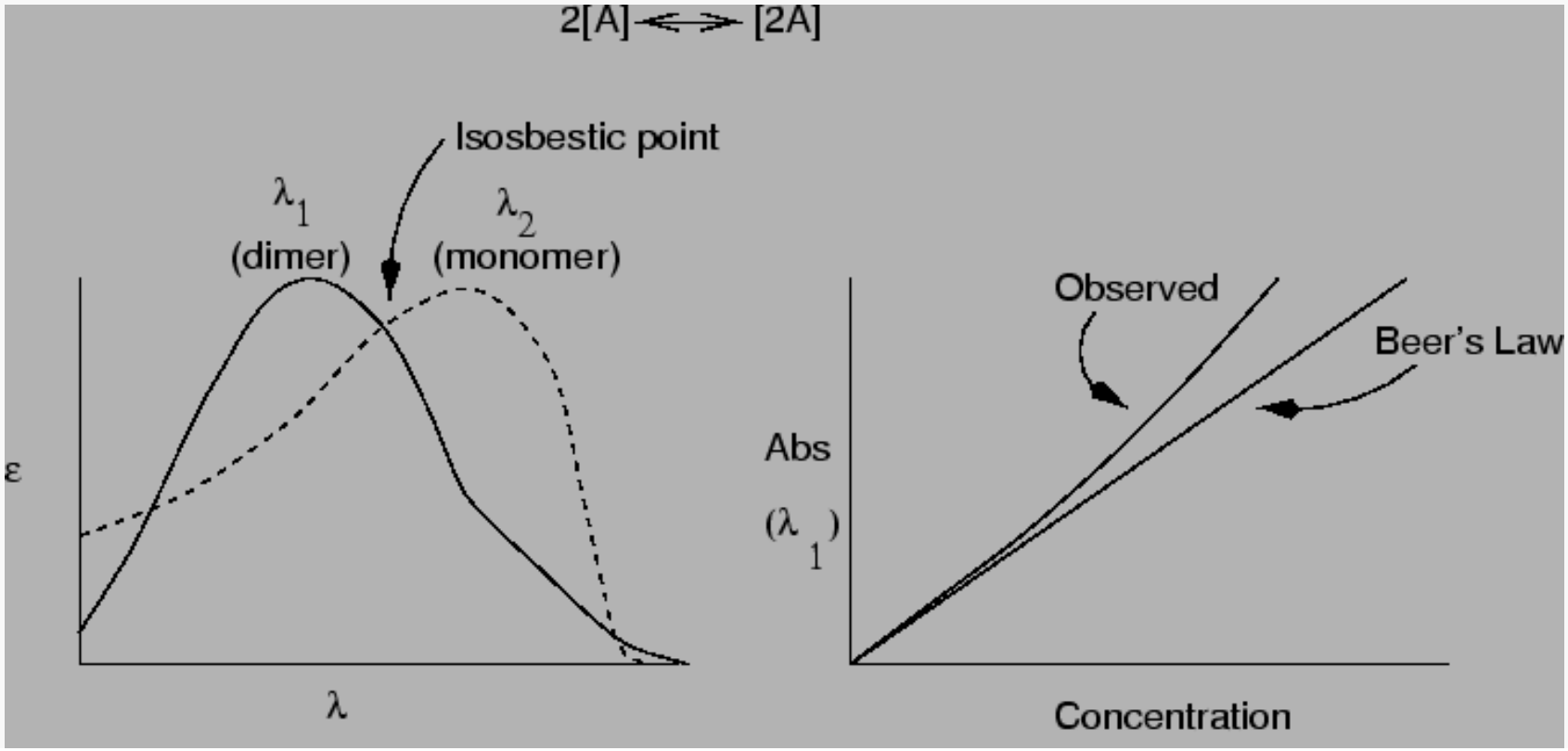


Round cell

The consequence is the same as for polychromatic radiation = curved response

Different components of the incident beam are absorbent with different efficiencies

4) The nature of the absorber does not change with concentration – a variety of effects can cause this assumption to break down, e.g. dimerization, acid-base or complexation equilibria



All of the above mentioned deviations from Beer's Law (or instrumental deviations) are really only deviations in the sense that the experimental conditions deviate from the conditions that have been assumed in deriving Beer's Law

Beer's Law always holds