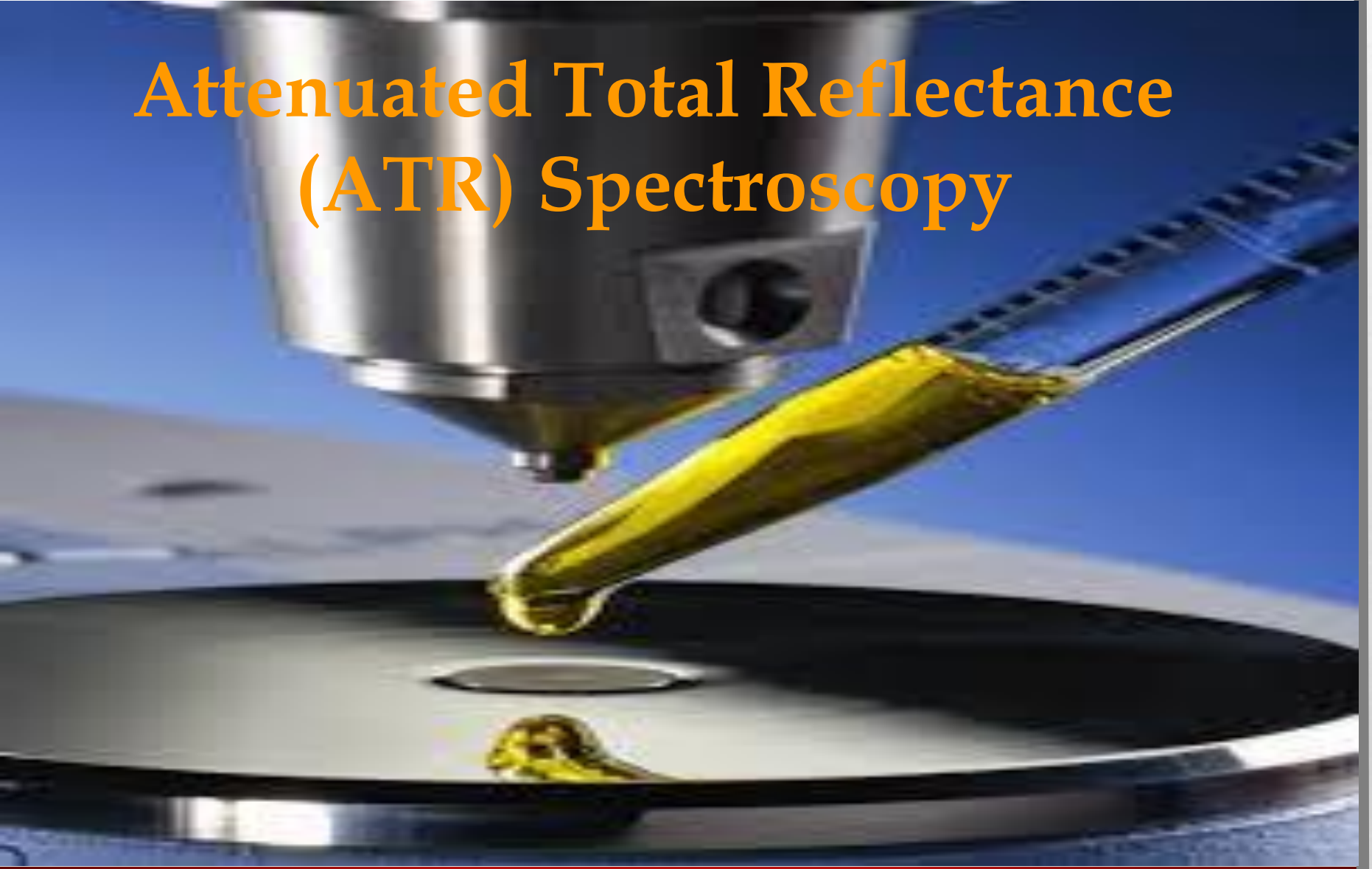
Attenuated Total Reflectance (ATR) Spectroscopy



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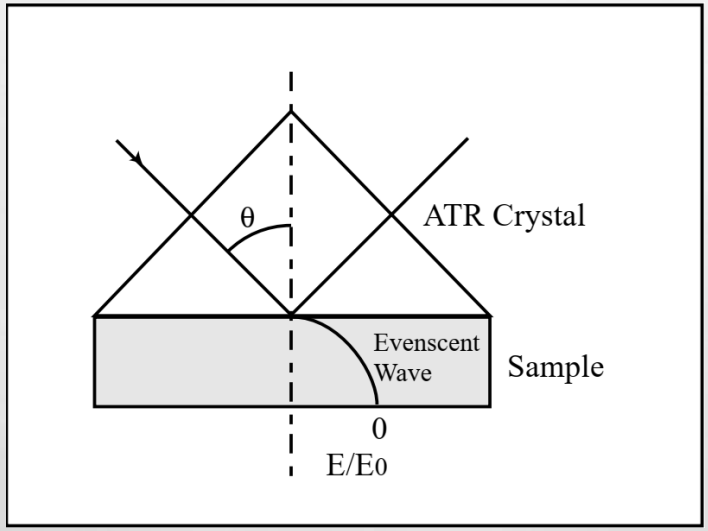
What is ATR spectroscopy ?

- ATR spectroscopy uses the phenomenon of **total internal reflection**.
- It is a versatile and powerful technique for infrared spectroscopy which enables sample to be examined directly in the solid or liquid state with minimal or no sample preparation.
- It measures the change that occurs in a totally internally reflected infrared beam when the beam comes in contact with the sample.

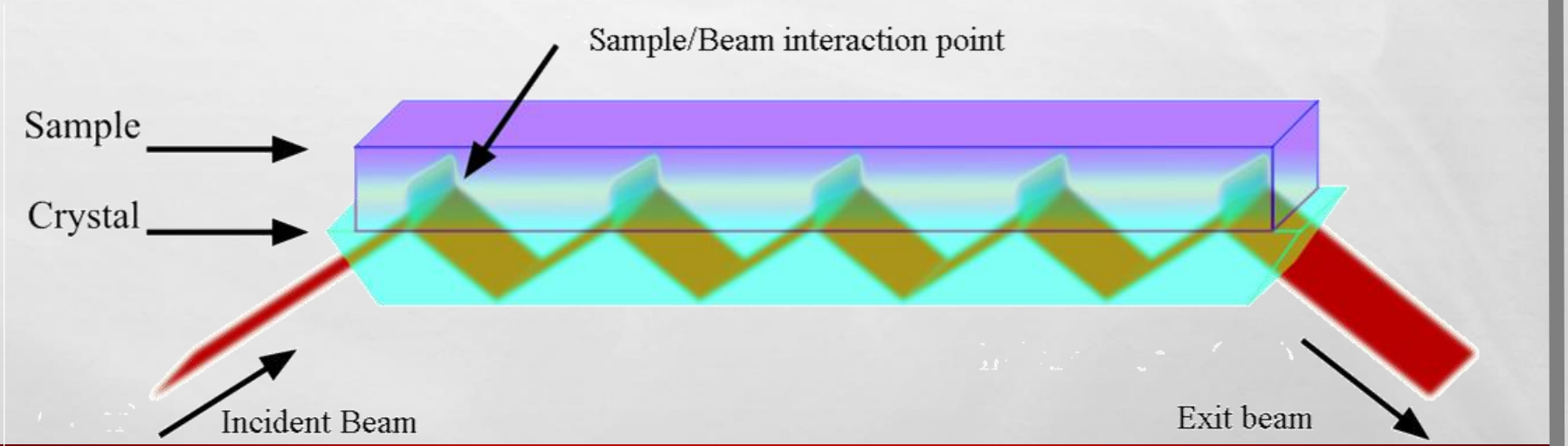
Total Internal Reflection and Evanescent waves



- When angle of incidence (θ) is greater than critical angle (θ_c) results into total internal reflection.
- An oscillating electric or magnetic field that does not propagate as an electromagnetic wave but whose energy is spatially concentrated in the vicinity of the source (here ATR crystal).

Instrumentation of ATR

- ✓ A beam passes through the crystal and undergoes total internal reflection through the crystal.
- ✓ An evanescent wave is created which protrudes only a few microns beyond the crystal surface.
- ✓ The radiation that penetrates a fraction of a wavelength beyond the surface of the crystal enters the sample that is placed on its surface.
- ✓ Part of the radiation will be absorbed by the sample and it produced absorption spectrum.
- ✓ Modified infrared reflected light will be detected by sensor.



Common equations and terms used in ATR spectroscopy

1) **Critical angle –** A function of refractive indices of the sample and ATR crystal.

$$\theta_c = \sin^{-1} \frac{n2}{n1}$$

where, n1 and n2 are refractive indices of ATR crystal and sample, respectively

2) **Depth of penetration –** The depth which the evanescent waves extend into the sample. It is also defined as the distance from the crystal-sample interface where the intensity of the evanescent waves decays to 1/e of its original value.

$$d_p = \frac{\lambda}{2\pi(n_1^2 \sin^2\theta - n_2^2)^{1/2}}$$

where λ is the wavelength of infrared radiation and θ is the angle of incidence

3) **Effective pathlength –** It is used as an approximate comparison between the expected absorbance intensity of an ATR spectrum and a transmission spectrum. It is directly related to intensity of spectrum.

EPL = penetration depth x number of reflections

Factors affecting the ATR spectrum

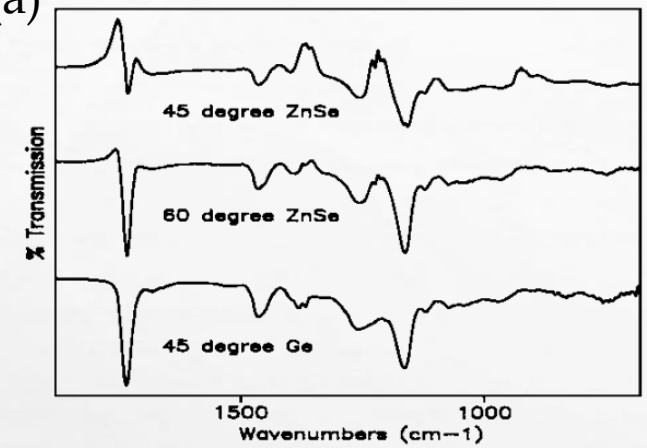
The factors which effect the results obtained in an ATR experiment are the:

- o Wavelength of Infrared Radiation
- o Refractive Index of the ATR crystal
- o Angle of Incidence
- o Efficiency of Sample Contact
- o Area of Sample Contact
- o ATR Crystal Material

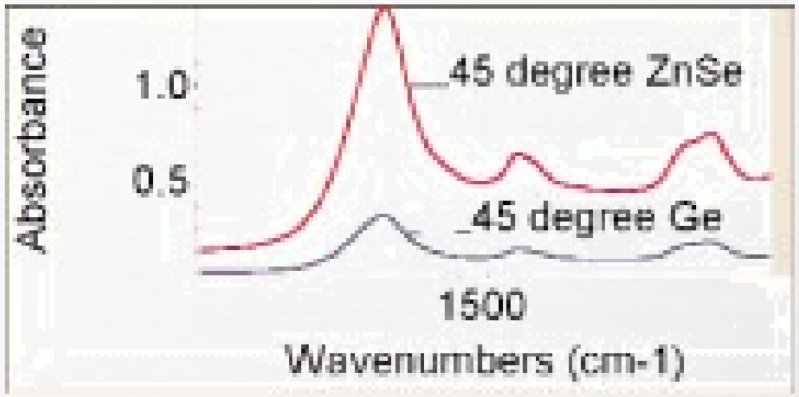
1. Wavelength of IR – (a) Penetration depth (d_p) of IR energy onto sample is wavelength-dependent.
(b) With increase in wavelength of IR, d_p also increases hence relative intensities of band increases.

2. Refractive index of crystal (Eg. ZnSe, Ge, Si diamond etc.) – It affects in two ways -
(a) Increasing the n, the θ_c decreases. And distortions in spectra appear if θ does not exceed the θ_c
(b) By increase in n, penetration depth decreases hence relative absorbance intensity decreases.

(a)



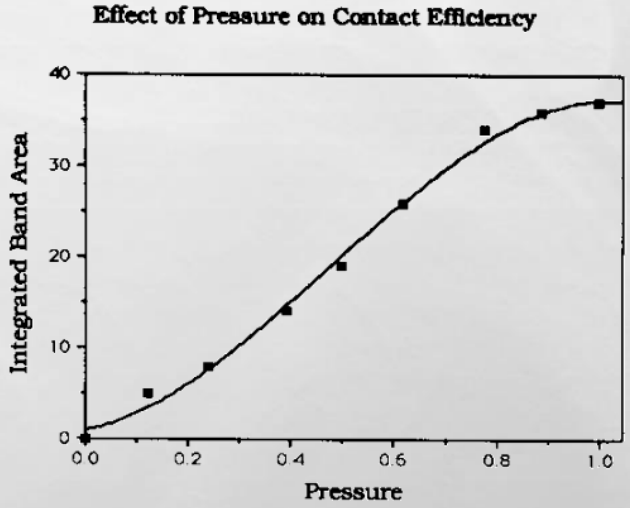
(b)



n of ZnSe – 2.4
n of Ge – 4
For n of sample – 1.5, θ_c = 38.7 (ZnSe), 22.0 (Ge)

3. Efficiency of sample contact – Since evanescent waves decays with distance from crystal surface, hence it is important to have intimate contact of sample with crystal.

(a) This is easily achieved with most liquids since they wet the surface of the ATR crystal.
(b) For solids, it is important to use a pressure device which presses the sample against the crystal to enhance contact efficiency.



4. **Area of contact**– It directly affects the intensity of the absorbance spectrum. For reproducibility of data, entire crystal surface should be covered with sample.

5. **ATR crystal material**– The material from which the ATR crystal is made from will affect the refractive index, the infrared transmission range, as well as the chemical properties of the crystal. A crystal material must have a high index of refraction to allow internal reflectance. Materials with a refractive index greater than 2.2 are normally chosen as ATR crystals.

MIRacle Crystal Plate	Application	Hardness kg/mm²	Cutoff cm⁻¹, Spectral Range	Refractive Index @ 1000 cm⁻¹	Depth of Penetration @ 45°,μ	pH Range of Sample
AMTIR	Harder than ZnSe, ok with acid samples	170	630	2.5	1.70	1 – 9
Diamond/KRS-5	When you need full mid-IR spectral range	5700	250	2.4	2.00	1 – 14
Diamond/ZnSe	Ideal for hard samples, acids or alkaline	5700	525	2.4	2.00	1 – 14
Ge	General purpose and carbon filled or rubber	550	575	4.0	0.66	1 – 14
Si/ZnSe	General purpose – only below diamond for hardness	1150	550	3.4	0.85	1 – 12
Si	Excellent for far-IR spectral measurement	1150	8900-1500, 475-40	3.4	0.85	1 – 12
ZnSe	General purpose ATR crystal	120	520	2.4	2.00	5 – 9

Application of ATR spectroscopy- Used in FT IR techniques.

Thank you