FT-IR SAMPLING TECHNIQUES

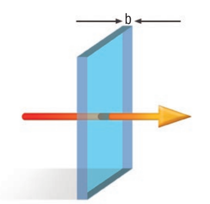
Shorter Wavelengths | **Near-IR** | **Mid-IR** | **Far-IR** | Longer Wavelengths

UV-Vis | **X-H Overtones and Combination Bands** | **Fundamental Vibrations, Overtone and Combination Bands** | **Fundamental and Heavy Atom Vibration Bands** | Microwave

Wavelength	0.7 µm	2.5 µm	25 µm	1000 µm
Wavenumber	14000 cm^{-1}	4000 cm^{-1}	400 cm^{-1}	10 cm^{-1}
Frequency	10^{9} MHz	10^{8} MHz	10^{7} MHz	10^{6} MHz
Energy	1.771 eV	0.496 eV	0.050 eV	0.001 eV

Transmission/Absorption

Sample is positioned directly in the beam of the FT-IR spectrometer



Beer-Lambert Law

$A = a \times b \times c$

A - Absorbance
a - absorptivity
b - pathlength
c - concentration

Absorbance is linearly proportional to sample concentration and pathlength.

Attributes

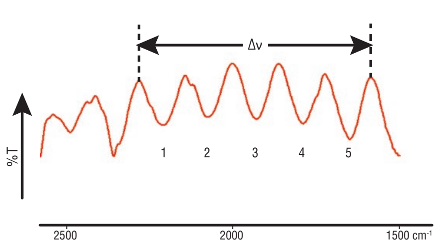
- High quality, representative spectral data, compatible with many digital libraries
- Spectra represent bulk sample composition
- Ability to control sample thickness – intensity of spectral features/sensitivity

Special Considerations

- Thick samples may absorb totally and need to be thinned-out or diluted
- Original material may be destroyed in sample preparation process
- Pellet making and other sample preparation methods require skill and time
- Beer's law is limited to simple, linearly absorbing samples

Applications

- Solids, gels, pastes, liquids and gases
- Film thickness and liquid cell pathlength
- Qualitative and quantitative



Transmission Ranges of Popular IR Windows

NaCl	52600-455 cm^{-1}
KBr	48000-345 cm^{-1}
CaF_2	79500-895 cm^{-1}
BaF_2	66600-690 cm^{-1}
ZnSe	15000-460 cm^{-1}

Free Standing Film Thickness (µ)

$T = (N \times 10{,}000)/(2n \times \Delta v)$

T - thickness of polymer film (µ)
Δv - wavenumber range of fringes count (cm^{-1})
N - number of fringes within Δv
n - refractive index of polymer

Cell Pathlength (mm)

$P = (N \times 10)/(2 \times \Delta v)$

P - cell pathlength (mm)
Δv - wavenumber range of fringes count (cm^{-1})
N - number of fringes within Δv

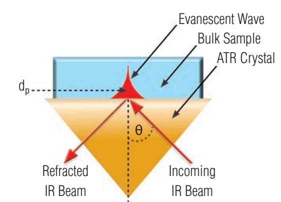
Sample Handling

- Films, thin materials – direct placement in the transmission sample holders
- Powder and solid samples: KBr pellets, (solid samples require processing), mulls
- Gels/pastes: smears on IR transparent windows
- Liquids: liquid cells
- Gases: short- and long-path gas cells

Attenuated Total Reflection (ATR)

(internal reflection)

Sample is placed in intimate contact with the internal reflection element (IRE)



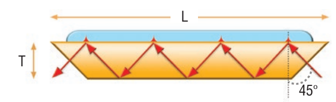
Depth of Penetration

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

d_p - depth of penetration
λ - wavelength of light
θ - angle of incidence
n_1 - refractive index of crystal
n_2 - refractive index of sample

Depth of penetration can be controlled by changing angle of incidence beam and/or use of crystals with different refractive indices.

Number of Reflections



$r_n = L/(2T \tan\theta)$

r_n - number of reflections
L - crystal length
T - crystal thickness
θ - angle of incidence

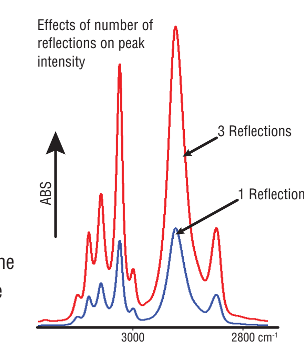
Refractive Index and Critical Angle

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

θ_c - critical angle
n_1 - refractive index of crystal
n_2 - refractive index of sample

Attributes

- Minimal sample preparation
- Short sampling time and easy cleaning
- High versatility, non destructive sampling



Special Considerations

- The angle of incidence must exceed the critical angle to produce good quality spectra
- ATR is not a bulk technique; it measures only the surface of a potentially inhomogeneous sample
- Correction needs to be applied to spectra for direct comparison with transmission data
- ATR crystals must be cleaned between samples to avoid contamination and carry-over
- Spectral ranges and properties of ATR crystals vary and need to be considered when working with specific samples

Applications

- Solids, gels, pastes and liquids
- Qualitative and quantitative

Transmission Ranges of Popular ATR Crystals

ZnSe	52600-650 cm^{-1}
Ge	5500-780 cm^{-1}
Diamond	30000-50 cm^{-1}
Si	8900-1460 cm^{-1}

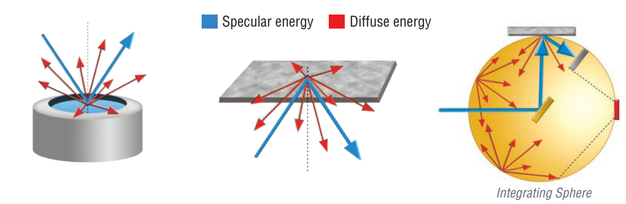
Sample Handling

- Intimate contact between the sample and the ATR crystal is required

Diffuse Reflection

(scattered reflection)

Sample is diluted with KBr (or similar) and placed in a cup for analysis
Large surface areas can be analyzed directly



Attributes

- Simplified sample preparation
- Direct measurement of large samples
- Representative sample spectra (not a surface measurement)
- Sensitivity and versatility

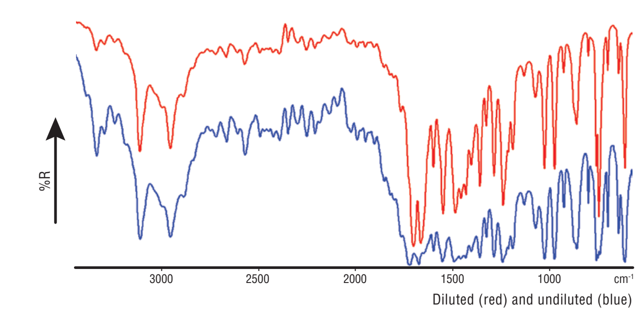
Kubelka-Munk Equation

$$f(R) = \frac{(1-R)^2}{2R} = \frac{k}{s}$$

R - absolute reflectance of the layer
k - molar absorption coeffecient
s - scattering coefficient

Special Considerations

- Diffuse reflection spectra will appear different to their transmission equivalents
- Kubelka-Munk conversion brings spectra to transmission-like format
- If not eliminated, specular reflection component may distort spectra
- Spectra of samples with high refractive indices require higher dilution to reduce distortion



Diluted (red) and undiluted (blue) spectra of caffeine

Applications

- Measurements of powdered samples
- Selected liquids/liquid residues
- Rough surface solids/coated surfaces
- Abrasion measurements
- Temperature and catalytic studies

Sample Handling

- Powders – 1% to 3% dilution in KBr, KCl or similar matrix
- Small particle size (50 µ or less) and homogeneous mixture
- Maintain more than 2 mm sample depth, even and loose packing in the cup
- Liquids – dispense small amount on top of KBr powder located in the sampling cup
- Large samples placed directly on top of upward looking diffuse reflection accessory or integrating sphere

Specular Reflection

(mirror-like reflection)

Sample is placed on top of the specular reflection accessory

Reflection

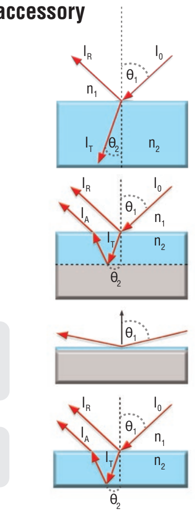
- Incident beam angle = reflected beam angle
- Angle of incident beam transmitted into a sample is reflected by Snell's Law

Reflection-Absorption at Near-Normal and Grazing Angle (< 65°)

- Beam enters and exits sample deposited on reflective substrate
- Equivalent to double-pass transmission measurement

Reflection in Free Standing Films

- Beam enters sample and reflects from top and bottom surfaces of the film
- Constructive and destructive interference generate fringe pattern



I_0 - Incident beam
I_T - Transmitted beam
I_R - Reflected beam (1)
I_A - Reflected beam (2)
θ_1 - angle of incidence
θ_2 - angle of trans. light
n_1 - refr. index of air
n_2 - refr. index of sample

Snell's law indicates that the angle of the incident beam into the sample is equal to the angle of reflection: $n_1 \sin\theta_1 = n_2 \sin\theta_2$

Attributes

- No or limited sample preparation
- Measurement simplicity/versatility
- Sensitivity/ability to look at very thin samples
- Non-destructive sampling

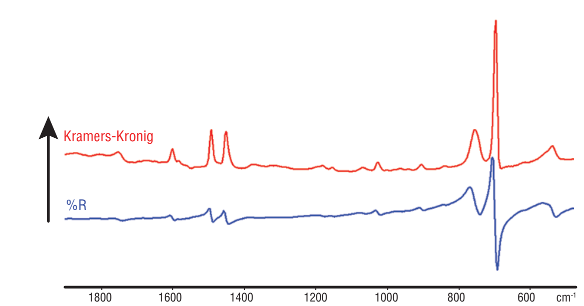
Film Thickness (µm)

$$T = \frac{10{,}000 \times N}{(2 \times \Delta v)(n^2 - \sin^2\theta)^{1/2}}$$

T - thickness of film (µm)
Δv - wavenumber range of fringes count (cm^{-1})
N - number of fringes within Δv
n - refractive index of polymer

Special Considerations

- Specular reflection spectra of thick reflecting samples may be distorted due to anomalous dispersion. Kramers-Kronig transform brings spectra to absorption-like format.



Applications

- Measurements of thin and thick film composition and thin film thickness
- Analysis of monolayers on reflective substrates
- Reflectance measurements – coatings, optical components/glass, EPI, lubricants on hard drives

Sample Handling

- Polarized light is recommended for grazing angle measurements

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