FT-IR Reflection Techniques

Vladimír Setnička

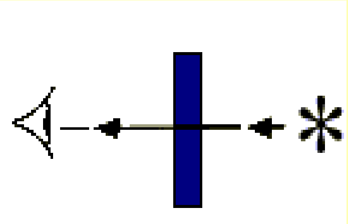
Overview – Main Principles of Reflection Techniques

Internal Reflection

External Reflection

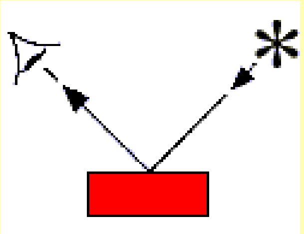
Summary

Differences Between Transmission and Reflection FT-IR Techniques



Transmission:
- Excellent for solids, liquids and gases
- The reference method for quantitative analysis
- Sample preparation can be difficult

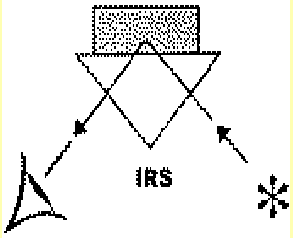
Reflection:
- Collect light reflected from an interface
  air/sample, solid/sample, liquid/sample
- Analyze liquids, solids, gels or coatings
- Minimal sample preparation
- Convenient for qualitative analysis, frequently used for quantitative analysis



FT-IR Reflection Techniques

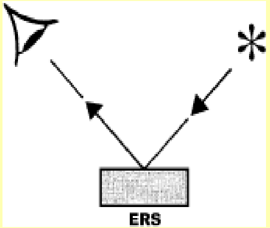
Internal Reflection Spectroscopy:

Attenuated Total Reflection (ATR)



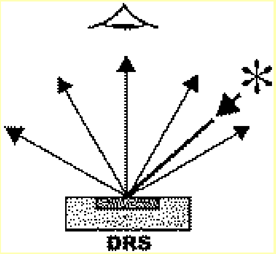
External Reflection Spectroscopy:

Specular Reflection (smooth surfaces)

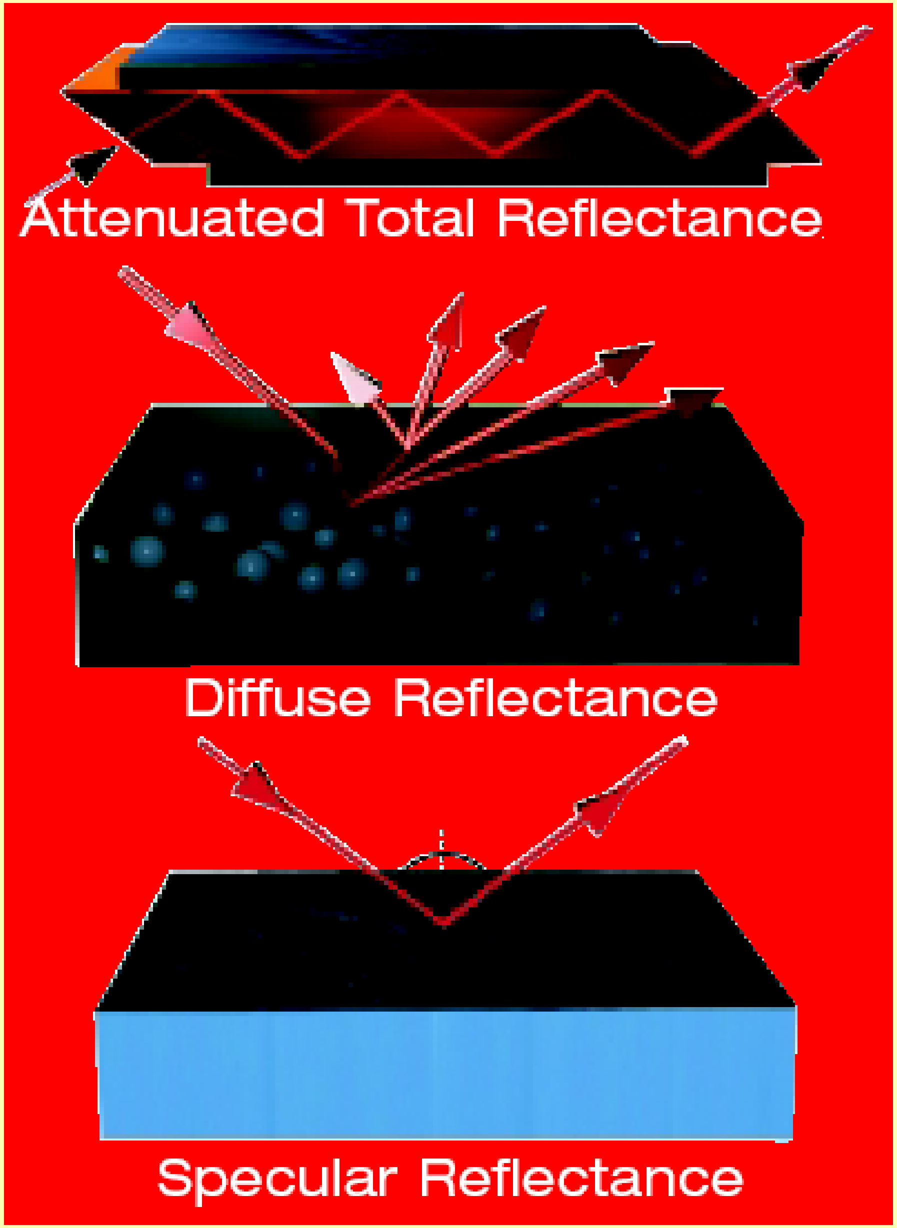


Combination of Internal and External Reflection:

Diffuse Reflection (DRIFTs) (rough surfaces)



FT-IR Reflection Techniques



- Infrared beam reflects from a interface via total internal reflectance
- Sample must be in optical contact with the crystal
- Collected information is from the **surface**

- Solids and powders, diluted in a IR transparent matrix if needed
- Information provided is from the **bulk matrix**

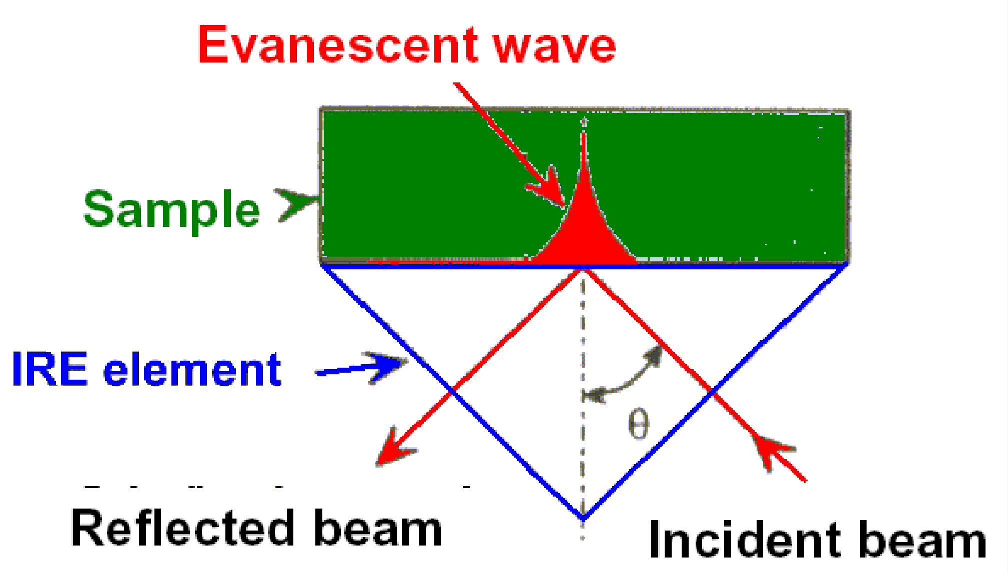
- Sample must be reflective or on a reflective surface
- Information provided is from the **thin layers**

Attenuated Total Reflection (ATR)

- introduced in the 1960s, now widely used
- light introduced into a suitable prism at an angle exceeding the **critical angle** for **internal reflection**

⇒ an **evanescent wave** at the reflecting surface

Single Bounce ATR

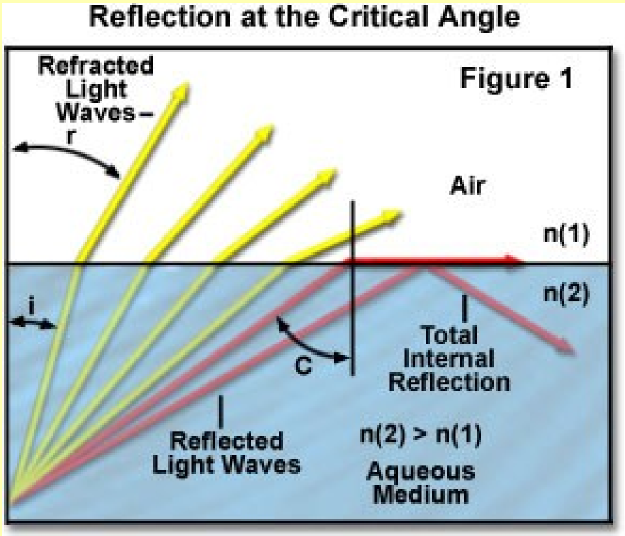


- sample in close contact with IRE
- from the interaction of the evanescent wave (exponential decay) with the sample, a spectrum can be recorded with little or no sample preparation

IRE – internal reflection element = ATR crystal

Attenuated Total Reflection (ATR)

Total internal reflection

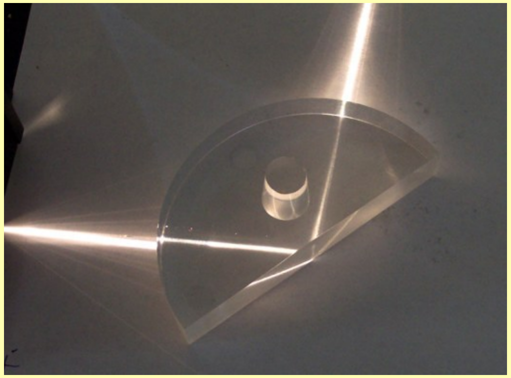


- **critical angle** - when the angle of refraction (**r**) becomes equal to 90 degrees and Snell's law reduces to:

sin(θ) = n(1)/n(2)   **n(1) ≠ n(2)**

where **(θ)** is termed the **critical angle c**

When the critical angle is exceeded for a particular light wave, it exhibits **total internal reflection** back into the medium.



The larger the angle to the normal, the smaller is the fraction of light transmitted, until the angle when **total internal reflection** occurs.

Attenuated Total Reflection (ATR)

Factors influencing ATR analysis

- **Wavelength** of IR radiation — λ
- **Refractive indexes** of sample and IRE — n_{smp}, n_{IRE}
- **Angle of incidence** of IR radiation — θ
- **Depth of penetration** (pathlength) — d_P
- **Sample and IRE contact efficiency**

When an incident ray is totally internally reflected at the interface between two materials of different refractive index, the intensity of the evanescent field extending into the medium of lower index decays exponentially with distance from the boundary:

$$I_{ev} = I_o \exp\left[-z/d_p\right]$$

– z is the distance normal to the optical interface,

– I_o is the intensity at $z = 0$,

– d_p is the penetration depth

Attenuated Total Reflection (ATR)

Depth of penetration (pathlength) of the infrared beam into the sample **depends on** λ, n_{smp}, n_{IRE}, θ

$$\boxed{dp = \frac{\lambda}{2\pi n_{IRE}\sqrt{\sin^2\theta - (n_{smp}/n_{IRE})^2}}}$$

d_P typically < 10 μm

The effective pathlength of the spectrum collected varies with the wavelength of the radiation:

- longer $\lambda \Rightarrow$ greater d_P: d_P lower at higher wavenumbers
  - ATR intensities decreased at higher wavenumbers if compared to transmission spectra

ATR correction accounts for this variation in effective pathlength by scaling the ATR spectrum accordingly. Most FTIR software packages incorporate an ATR correction algorithm.

Attenuated Total Reflection (ATR)

Critical Angle depends on n_{IRE} and n_{smp}

- increasing $n_{IRE} \Rightarrow$ decreasing θ and d_P

$$\boxed{\theta_c = \sin^{-1}\left(\frac{n_{smp}}{n_{IRE}}\right)}$$

$\Rightarrow$ high values of n_{IRE} needed

Materials of ATR crystals (IRE elements)

Table 1: MIRacle Crystal Plate Specifications

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

Attenuated Total Reflection (ATR)

Chart of Common Crystal Materials

Material	ATR Spectral Range (cm^{-1})	Refractive Index	Depth of Penetration (μ) (at 45° & 1000 cm^{-1})	Uses
Germanium	5,500 - 675	4	0.66	Good for most samples. Strong absorbing samples, such as dark polymers.
Silicon	8,900 - 1,500 & 360-120	3.4	0.85	Resistant to basic solutions.
AMTIR	11,000 - 725	2.5	1.77	Very resistant to acidic solutions.
ZnSe	15,000 - 650	2.4	2.01	General use.
Diamond	25,000 - 100	2.4	2.01	Good for most samples. Extremely caustic or hard samples.

Attenuated Total Reflection (ATR)

Materials of ATR crystals (IRE elements)

Zinc Selenide ZnSe

- preferred for all routine applications, limited use with strong acids and alkalies, surface etched during prolonged exposure to extremes of pH, complexing agents (ammonia and EDTA) will also erode its surface because of the formation of complexes with the zinc

AMTIR

- as a glass from selenium, germanium and arsenic, insolubility in water, similar refractive index to zinc selenide, can be used in measurements that involve strong acids

Attenuated Total Reflection (ATR)

Materials of ATR crystals (IRE elements)

Germanium Ge

- high refractive index, used when analyzing samples have a high refractive index

Silicon Si

- hard and brittle, chemically inert, affected only by strong oxidizers, well suited for applications requiring temperature changes as it withstands thermal shocks better then other ATR materials, hardest crystal material offered except for Diamond, which makes it well suited for abrasive samples that might otherwise scratch softer crystal materials, below 1500 cm^{-1} usefulness limited

Attenuated Total Reflection (ATR)

Materials of ATR crystals (IRE elements)

Diamond

- for analysis of a wide range of samples, including acids, bases, and oxidizing agents, scratch and abrasion resistant, expensive, intrinsic absorption from approximately 2300 to 1800 cm^{-1} limits its usefulness in this region (5% transmission)

Attenuated Total Reflection (ATR)

For thin films, the ATR spectra are the same as transmission spectra.

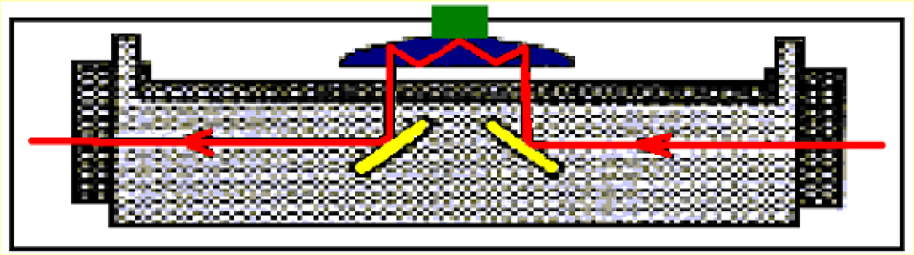
For thick films, the absorption bands are more intense at longer wavelengths.

As the angle of incidence approaches the critical angle, the bands tend to broaden on the long wavelength side and the minima are displaced to longer wavelengths (lower wavenumbers). Dispersion type spectra are observed very close to and below critical angle.

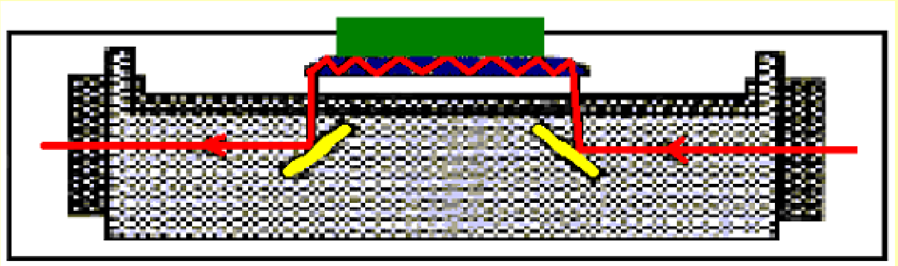
Attenuated Total Reflection (ATR)

Experimental Setup - horizontal arrangement (HATR)

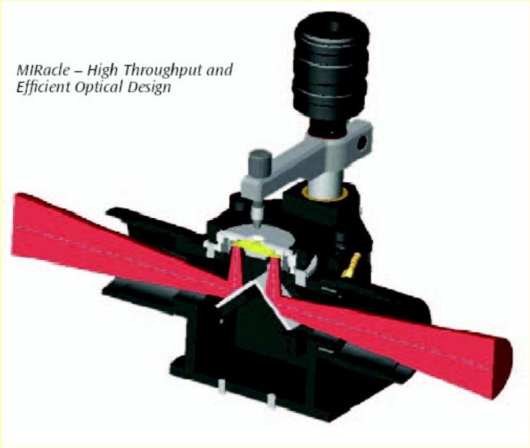
Single Bounce ATR



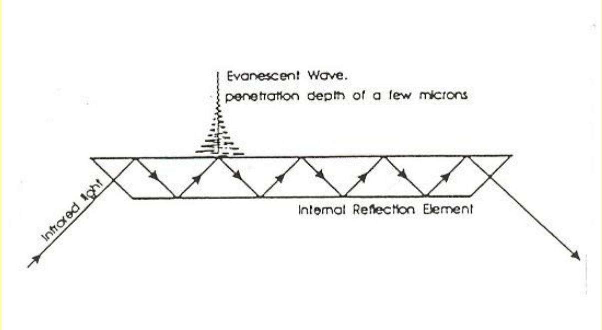
Multi-Bounce ATR



Small sampling area
- use for strong absorbers
- solid samples, liquids

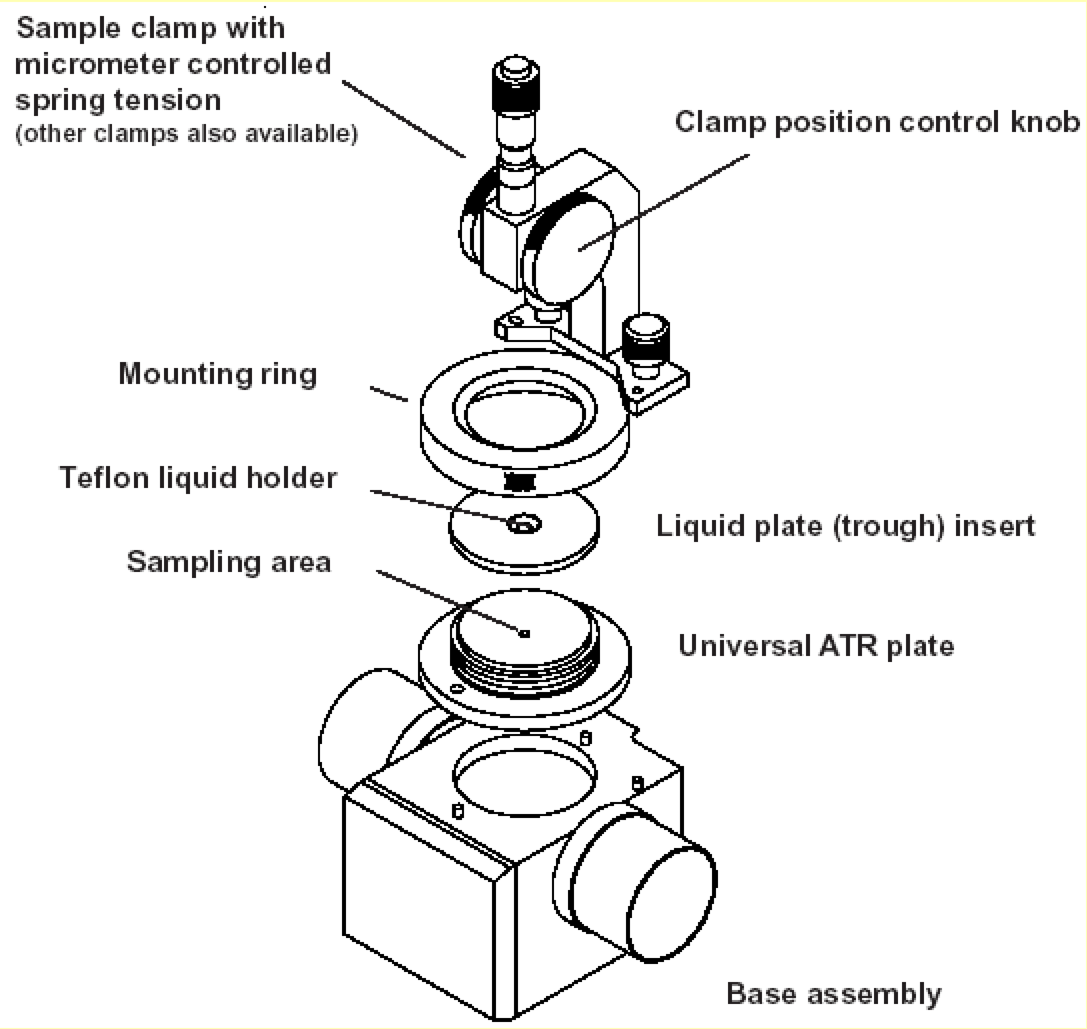


Broad sampling area provides
- greater contact with the sample
- use for weak absorbers or dilute solutions



Attenuated Total Reflection (ATR)

Experimental Setup



Single Reflection ATR Plate

3 Reflection ATR Plate
(includes 5mm swivel tip)

Attenuated Total Reflection (ATR)

MIRacle Pressure Clamps are Pinned-in-Place and Easily Upgraded

MIRacle Digital Clamp
Ideal for Controlled Pressure

MIRacle Rotating Clamp
Ideal for Cleaning Tip of Debris

MIRacle Viewing Clamp
Ideal for Placing Fibers or Crystals

MIRacle High-Pressure Clamp *– Ideal for Routine Sampling*

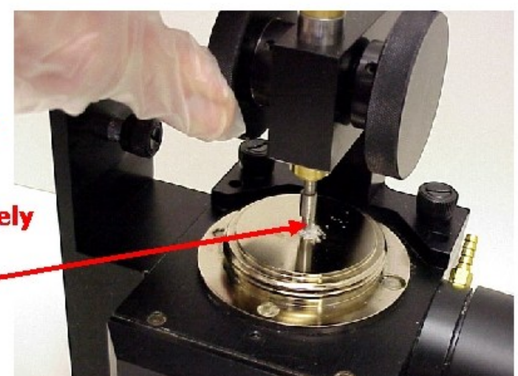
MIRacle Micrometer Clamp *– OK for Low Pressure Applications*

Slide 12

Sample should completely cover the ZnSe Crystal indicated with the arrow below.

Slide 13

Be sure that the press is rotated completely to the lowest level.

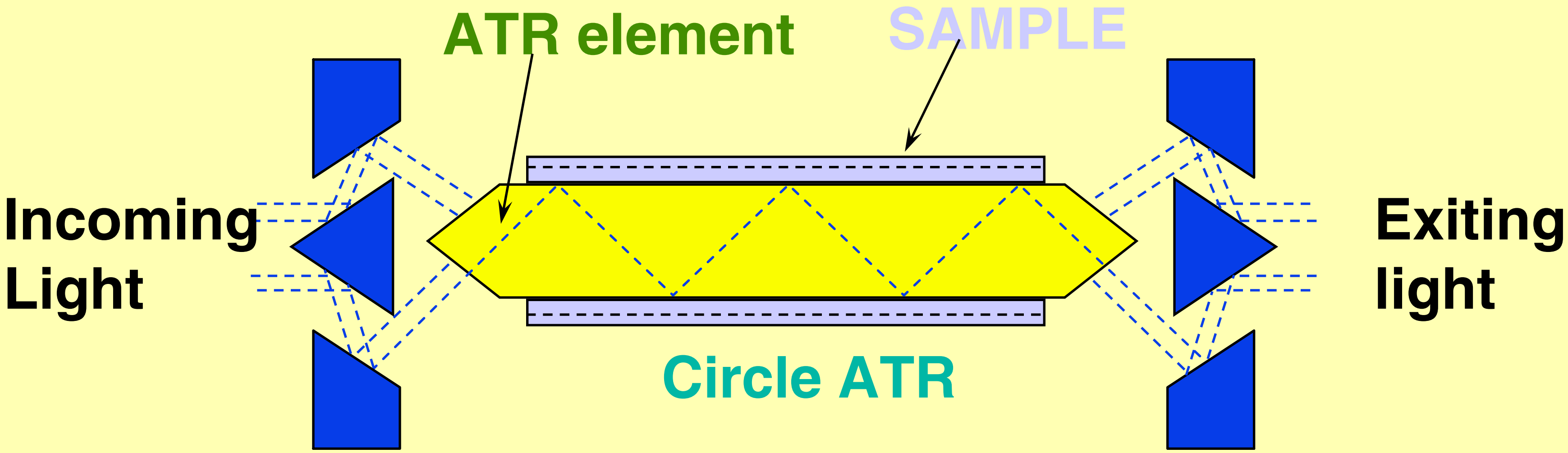


Attenuated Total Reflection (ATR)

Multi-Bounce ATR

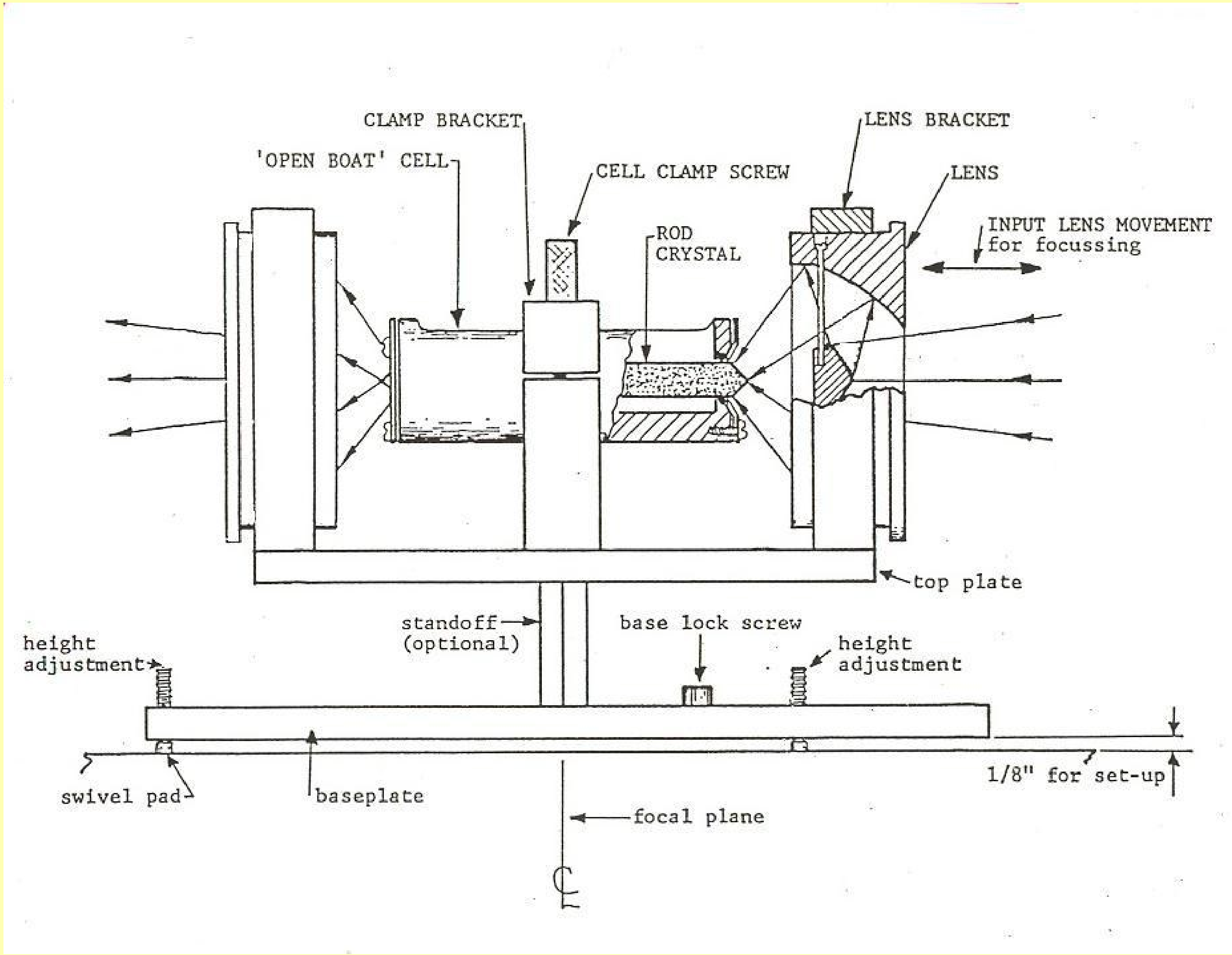
Attenuated Total Reflection (ATR)

Scheme of the Circle ATR Cell



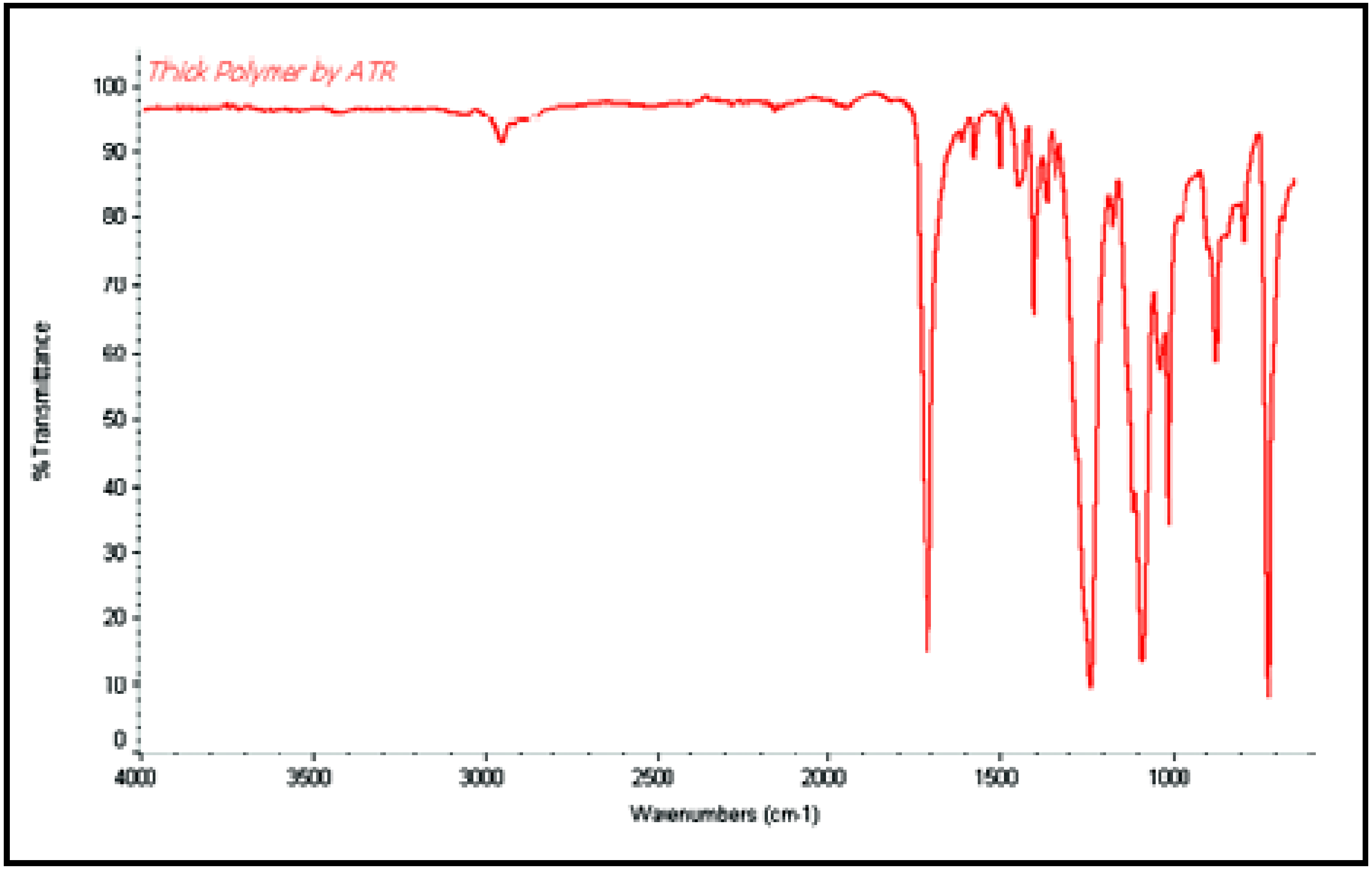
Attenuated Total Reflection (ATR)

Scheme of the Circle ATR Cell



Attenuated Total Reflection (ATR)

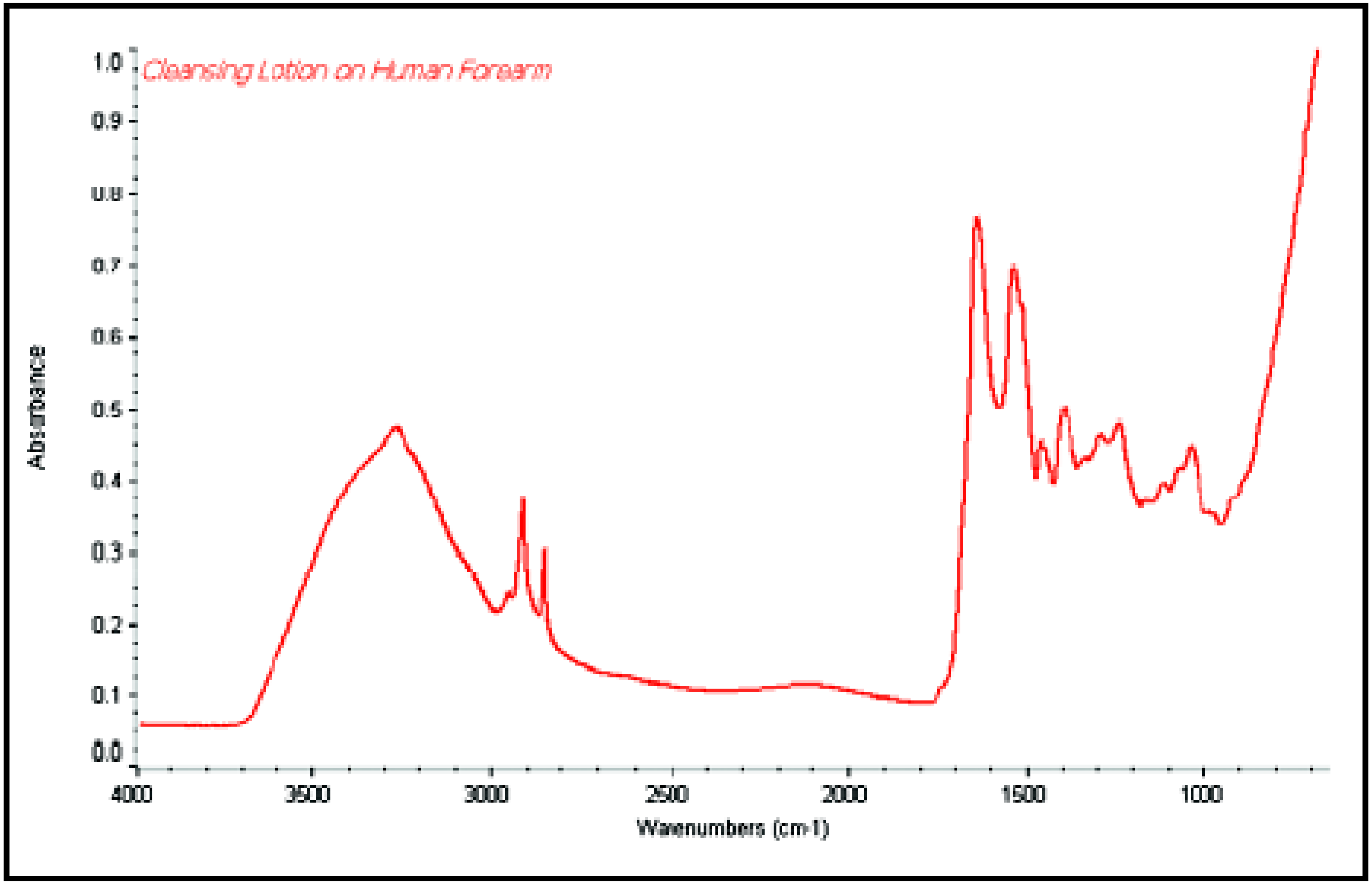
ATR Spectra



Thick Polymer Sample, using MIRacle with AMTIR Crystal and High-Pressure Clamp – No Sample Preparation.

Attenuated Total Reflection (ATR)

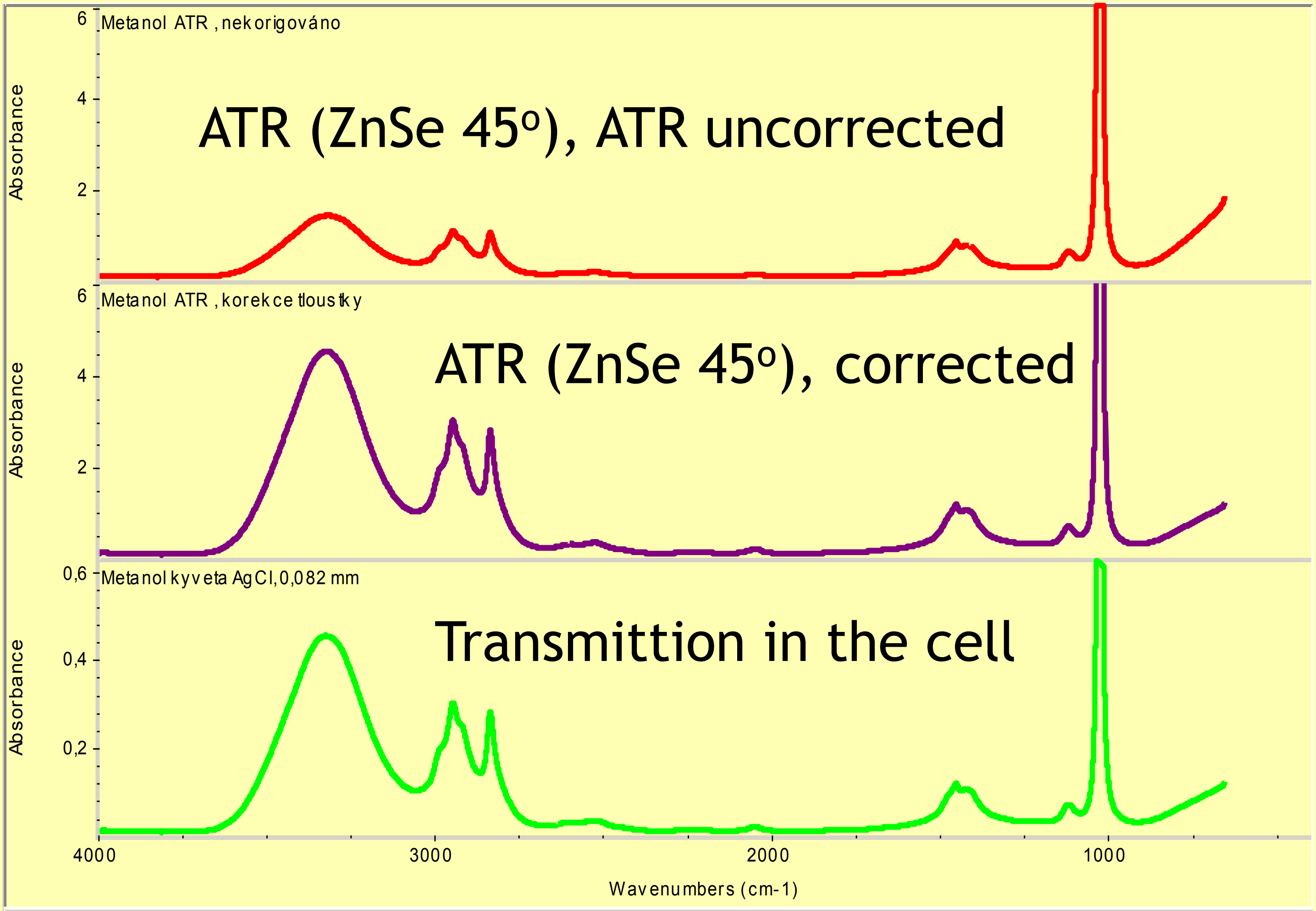
ATR Spectra



FTIR spectrum of cleansing lotion on human forearm – using the HATRPlus with flat plate Ge crystal.

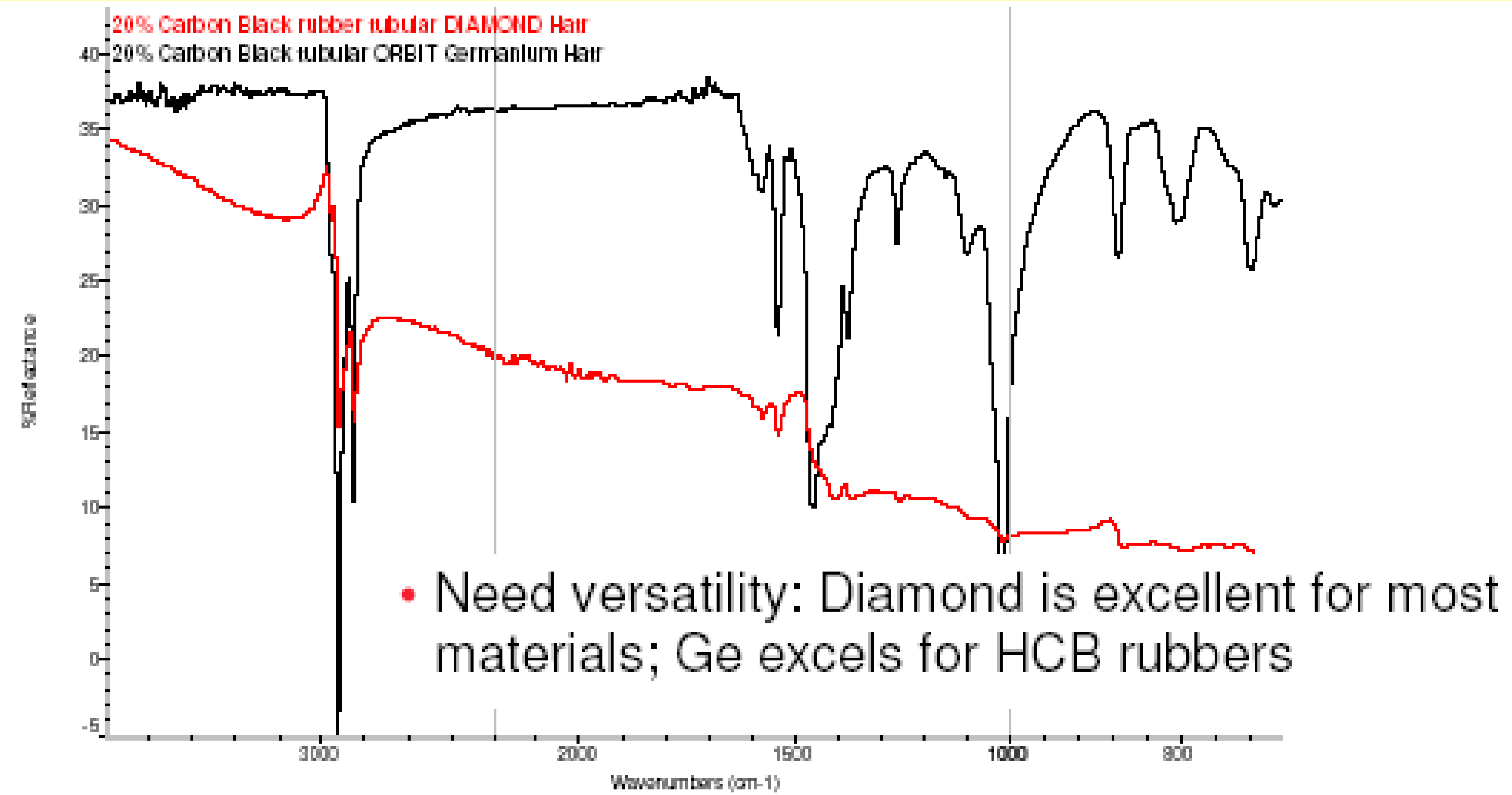
Attenuated Total Reflection (ATR)

IR Spectra of Methanol



Attenuated Total Reflection (ATR)

ATR Spectra of Rubber - Diamond vs Germanium IRE



- Need versatility: Diamond is excellent for most materials; Ge excels for HCB rubbers

Refractive indexes: Ge=4

Diamond=2.4

Attenuated Total Reflection (ATR)

Summary:

- Versatile and ***non-destructive*** technique for variety of materials – soft solid materials, liquids, powders, gels, pastes, surface layers, polymer films, samples after evaporation of a solvent …..

- Requires minimal or ***no sample preparation***

- Useful for ***surface*** characterization, opaque samples

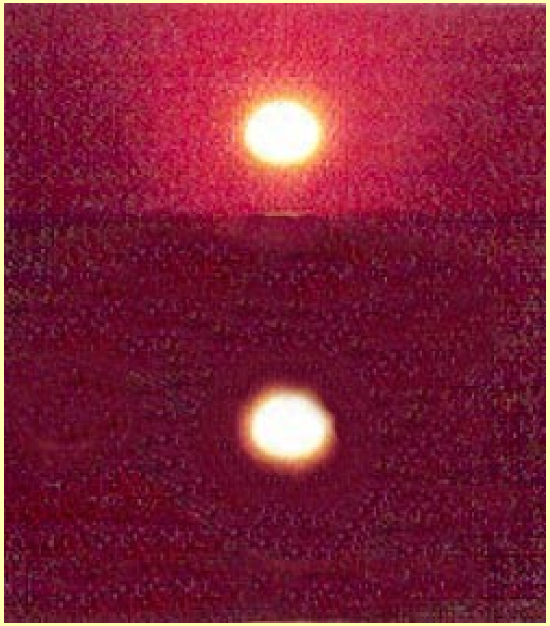
Limitation: sensitivity is typically 3-4 orders of magnitude less than transmission

Specular vs Diffuse Reflection

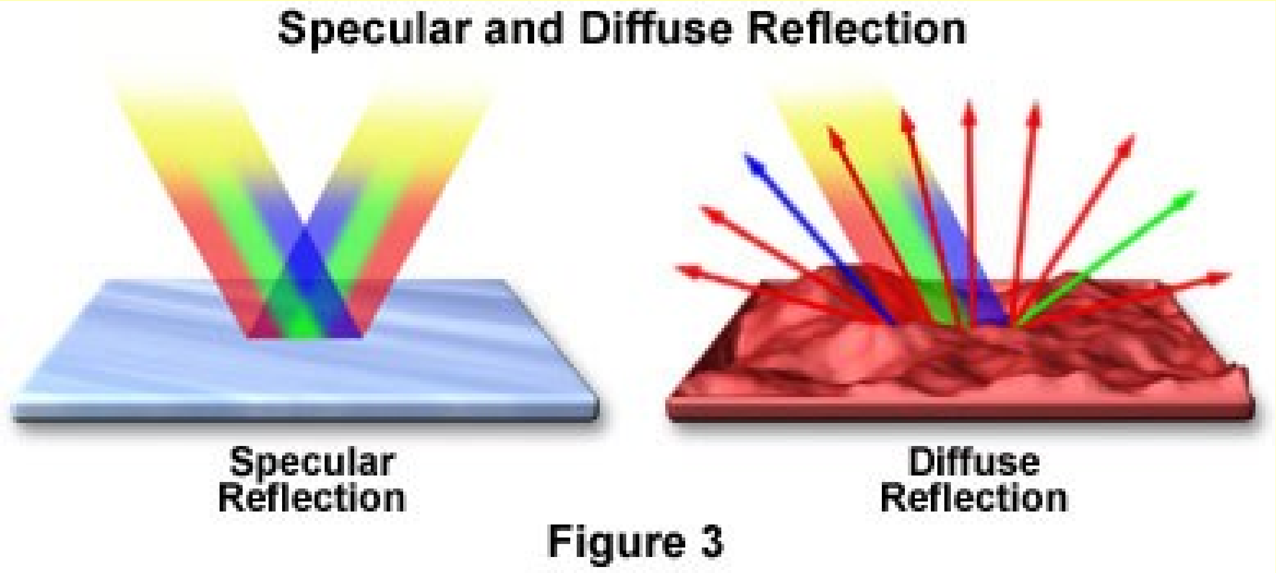
Specular reflection is defined as light reflected from a smooth surface (such as a mirror, any irregularities in the surface are small compared to λ) at a definite angle, whereas **diffuse reflection** is produced by rough surfaces that tend to reflect light in all directions. There are far more occurrences of diffuse reflection than specular reflection in our everyday environment.

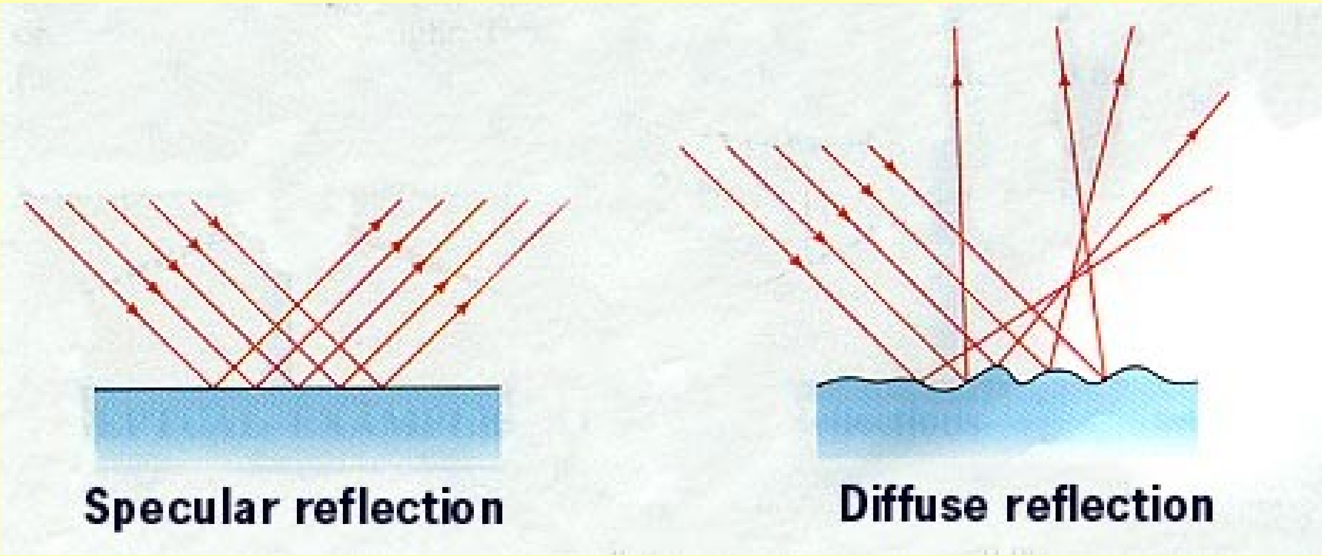
What kind of reflections account for the column of light reflected off the water?

What would we see on the water if it were perfectly flat, unmoving?



Specular vs Diffuse Reflection

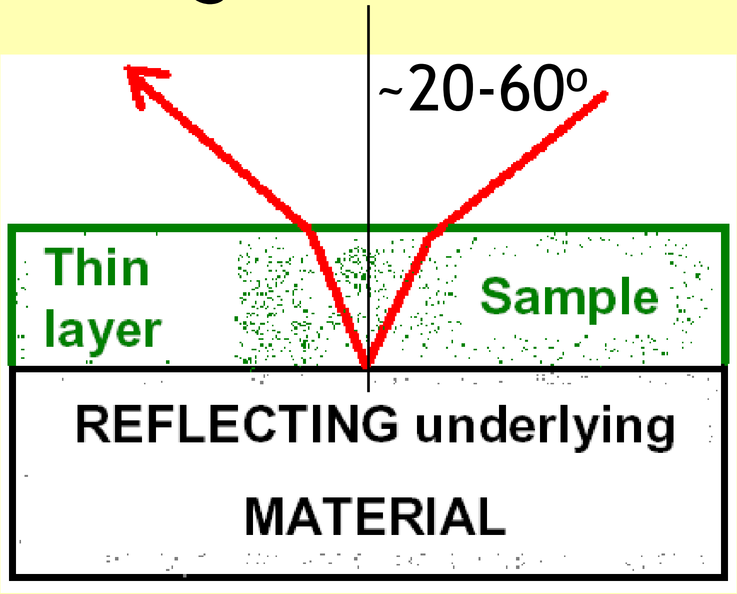




Specular Reflection

= External Reflection Spectroscopy

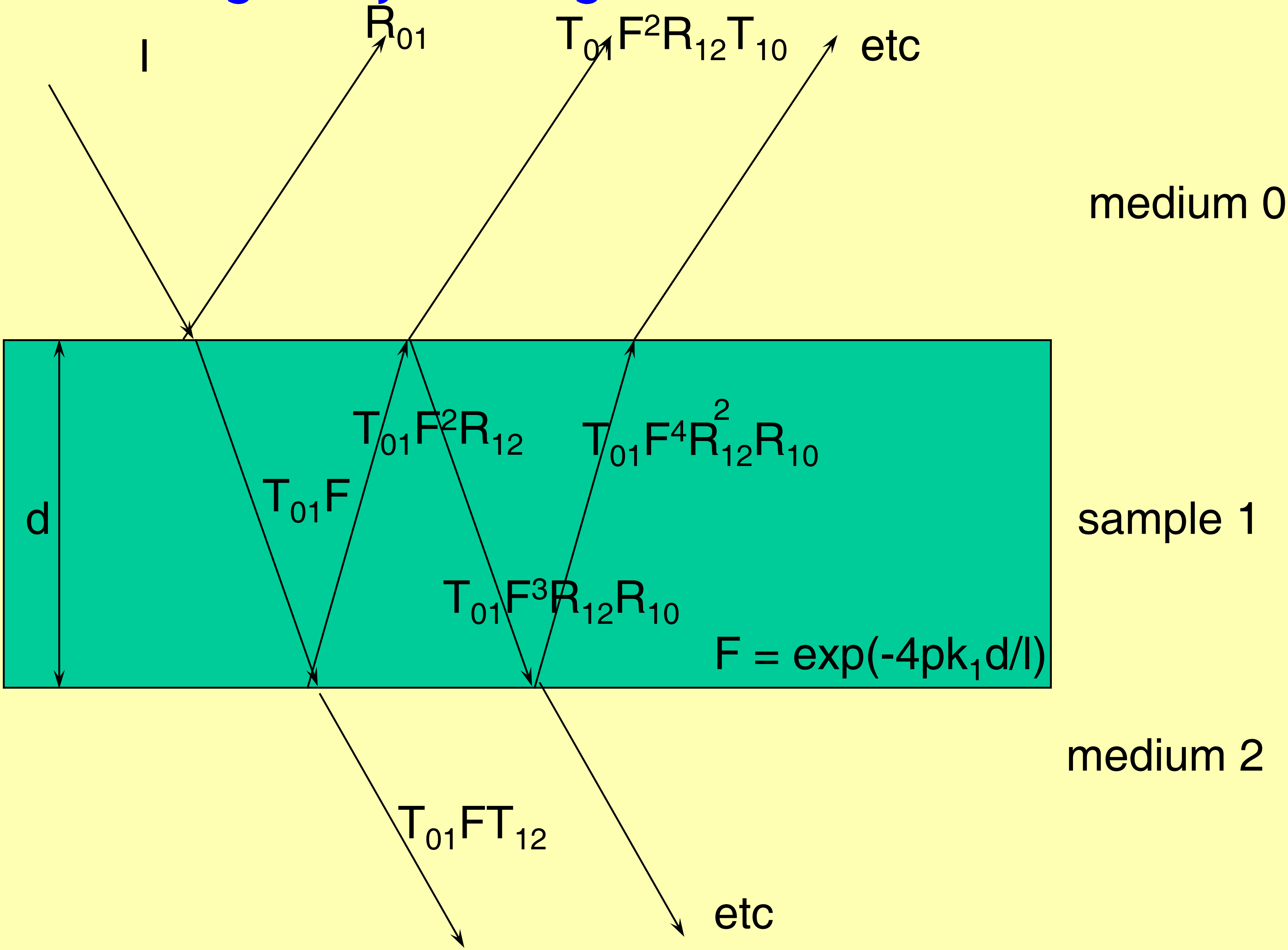
- introduced in the 1960s, much wider use in the 1970s
- light is **reflected from a smooth** (mirror-like) sample at a definite angle to record its spectrum
- spectroscopic technique for **films** deposited on, or pressed against reflective surfaces



- if surface absorbs a wavelength of light ⇒ its relative intensity is decreased

Angle of incidence = Angle of reflection

Light Rays Through Thin Films



Specular Reflection

If the surface is smooth like a mirror:

– reflection and the incidence angles are equal

– reflected beam retains the polarization characteristics of the incidence beam

Thin layers: 0.5-20 μm ⇒ angle ~20-60° ⇒ spectra similar to transmission ones

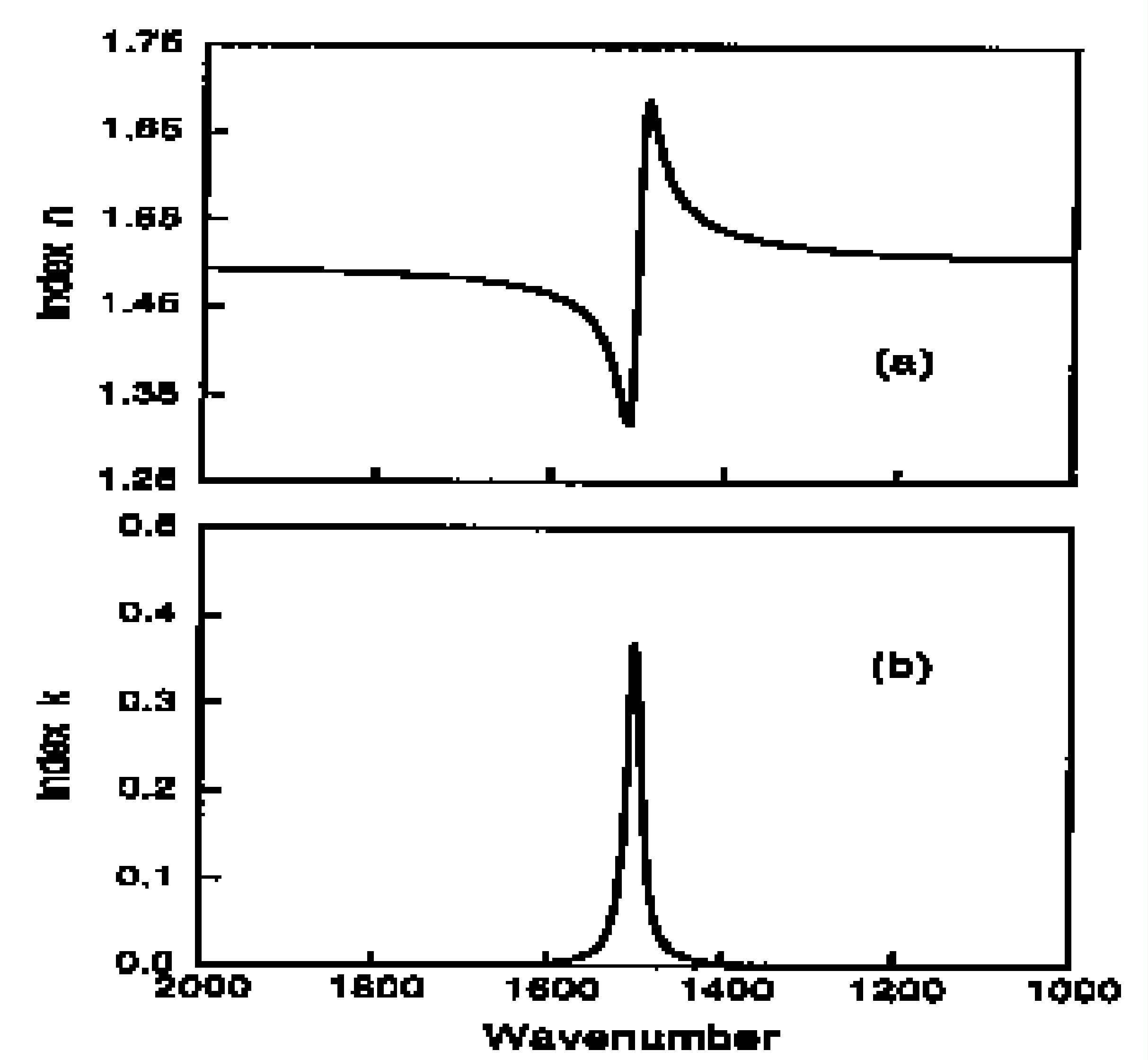
Monomolecular layers: angle ~60-85° ⇒ spectra predominatly a function of the **refractive index**

⇒ derivative shape of the bands arising from superposition of extinction coefficient and dispersion of refractive index

Specular Reflection

Refractive index

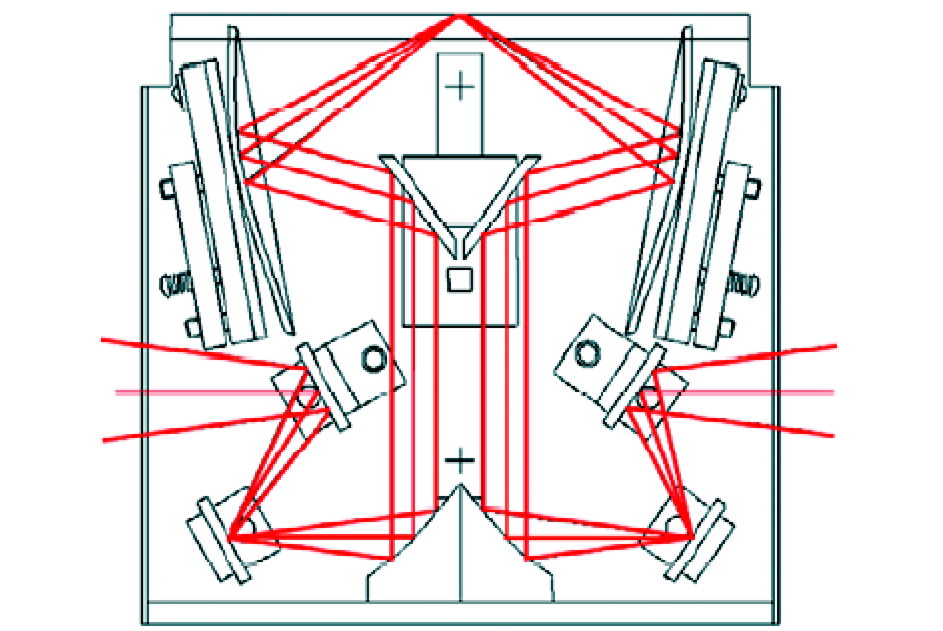
Absorbance index



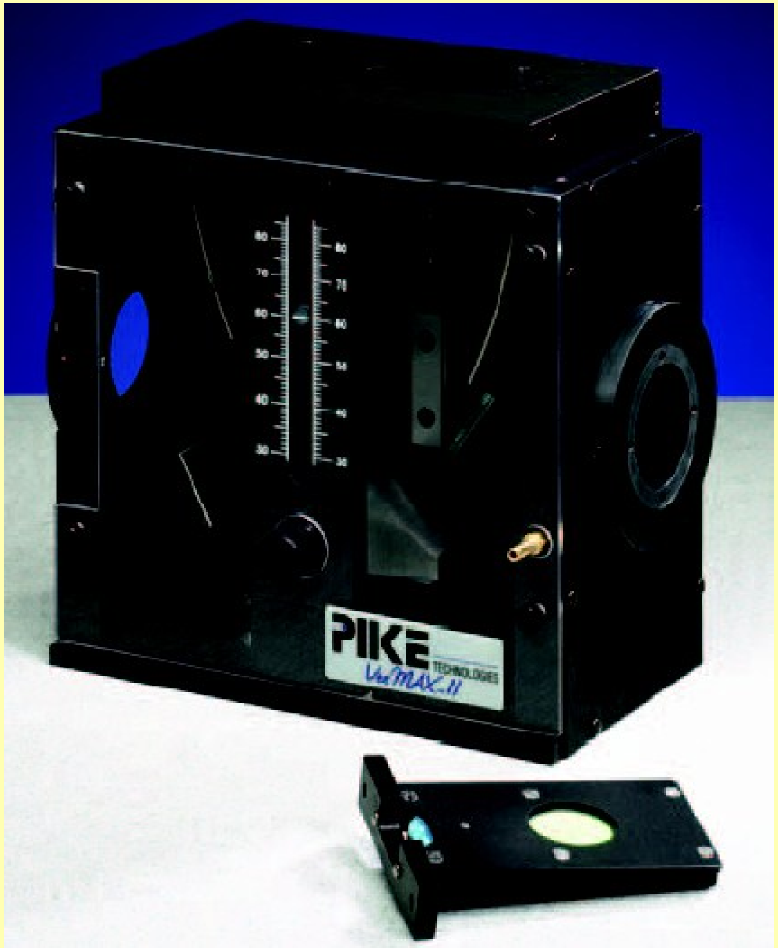
K. Yamamoto and H. Ishida, Vibrational Spectrosc., 8, 1 (1994)

Specular Reflection

Experimental Setup



Proprietary beam path within the VeeMax II Specular Reflectance accessory



- selection of incident angle

Incident angle influences
- effective pathlength
- polarized IR response

Specular Reflection

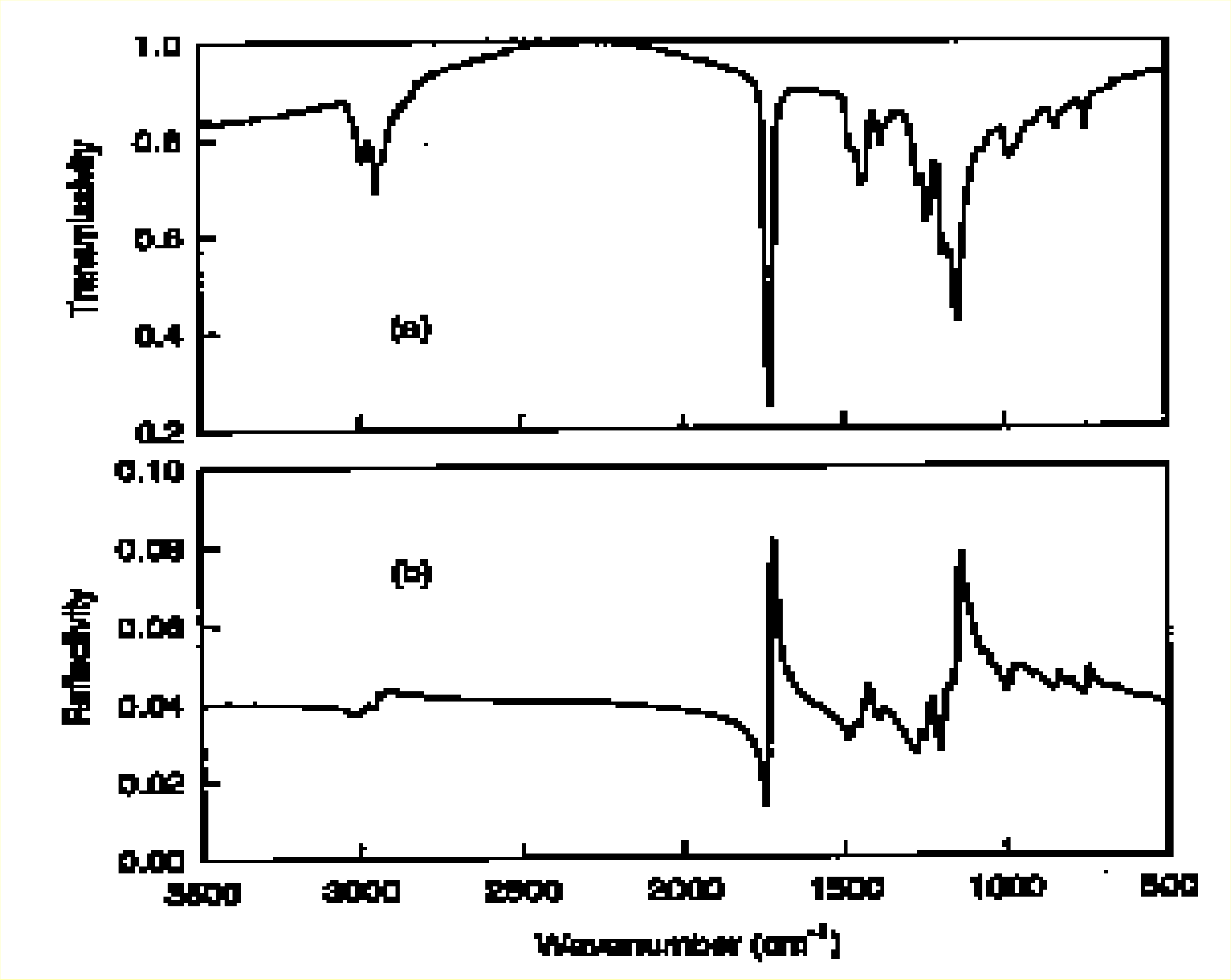
Experimental Setup

Specular Reflection

Specular Reflection Spectra

Absorbance index

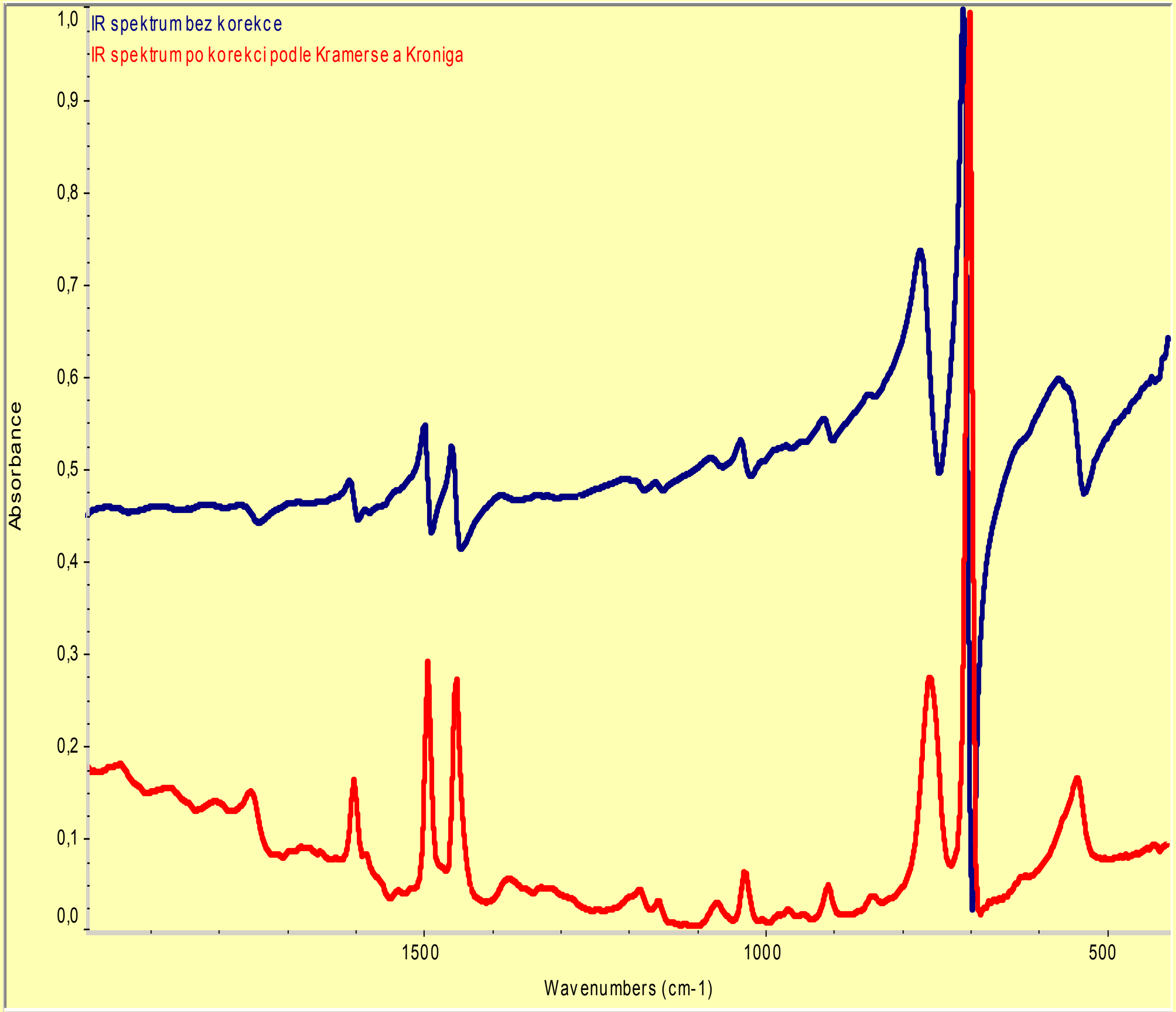
Refractive index



K. Yamamoto and H. Ishida, Vibrational Spectrosc., 8, 1 (1994)

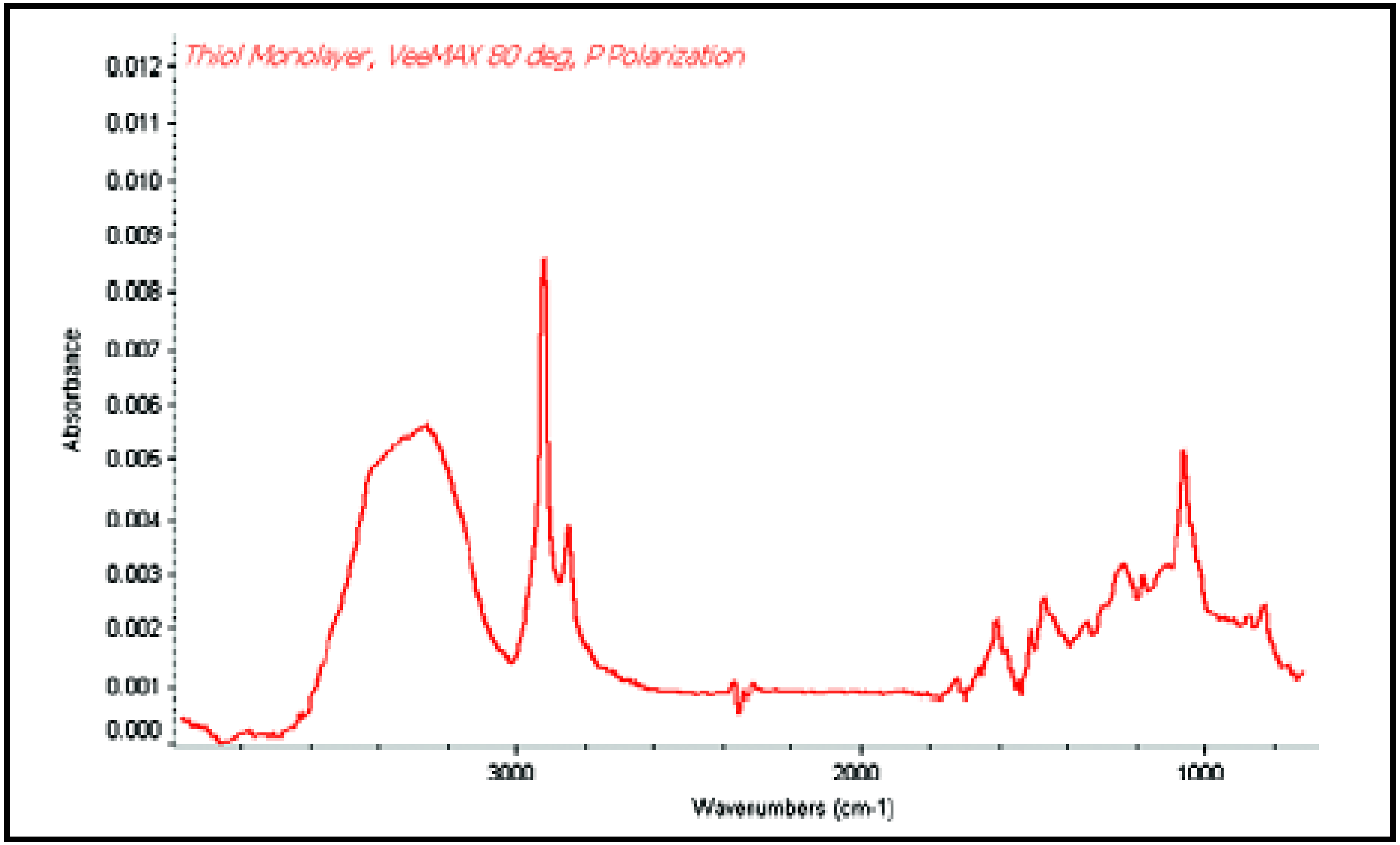
Specular Reflection

Correction of „Restrahlen „ bands



Specular Reflection

Specular Reflection Spectra



FTIR spectrum of thiol monolayer measured using the VeeMAX II specular reflectance accessory set at 80 degrees angle of incidence, ZnSe polarizer and MCT detector.

Specular Reflection

Summary:

- **non-destructive** measurement of thin layers or monolayers
    - coatings on polished metals $\Rightarrow$ *e.g.*varnishes
    - surface characterization

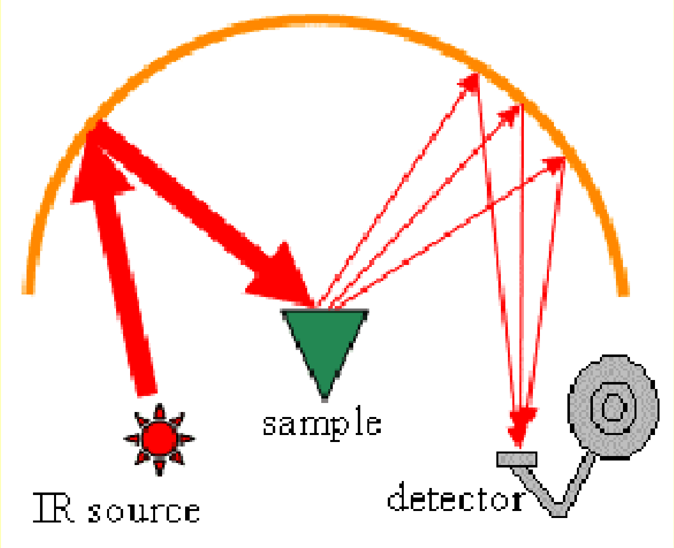
Limitation: Spectra depend on **refractive index**

- used for testing of lubricated surfaces of hard disks, to degradation studies of a protective coating on the surface; analysis of polymers on the surface of food containers and many others

Diffuse Reflection

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTs)

Spectra of **powders** and rough surfaces can be recorded by illuminating these surfaces and **collecting sufficient scattered** radiation with ellipsoids and paraboloids.



- fast measurement of powdered samples
- low repeatability of spectral data
- complicated physical description of the effect

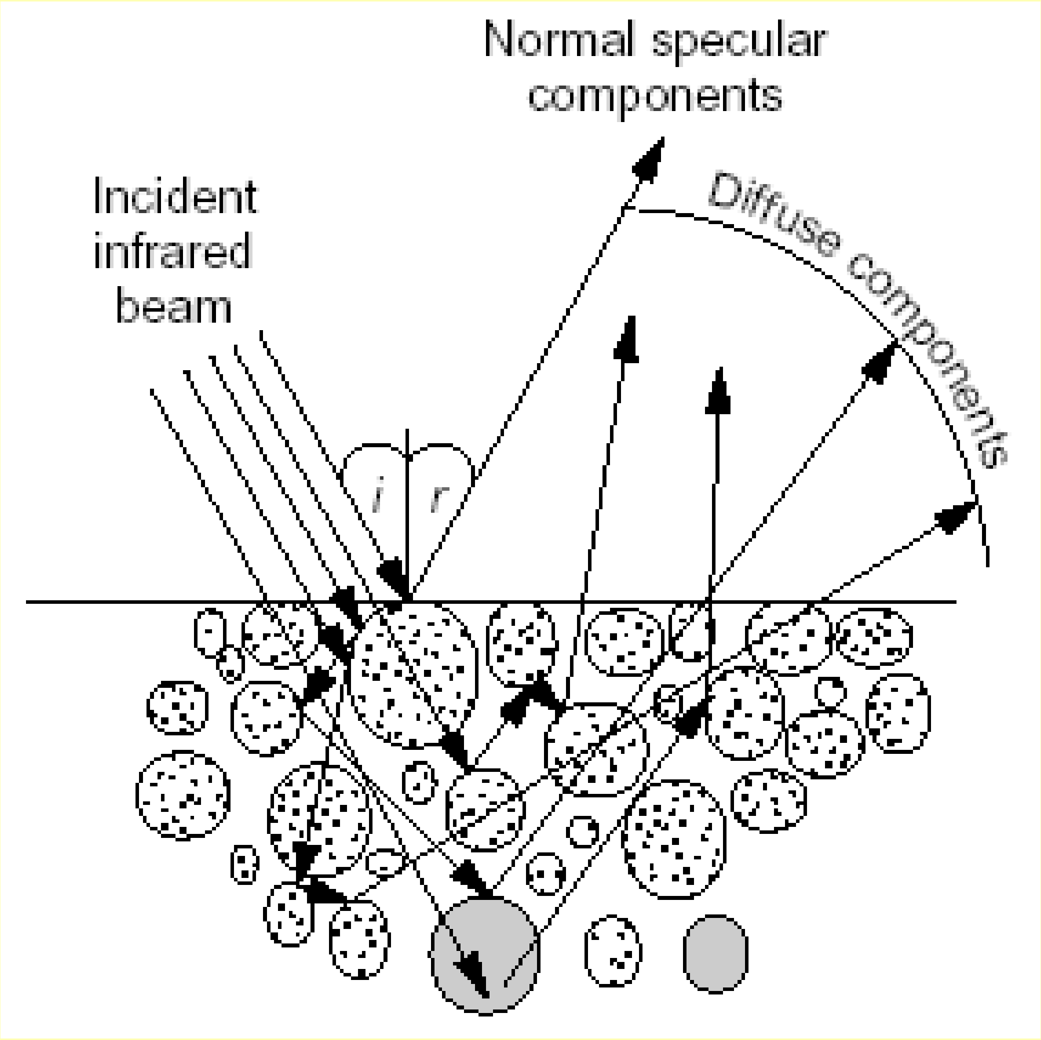
shape of particles, compactness of samples

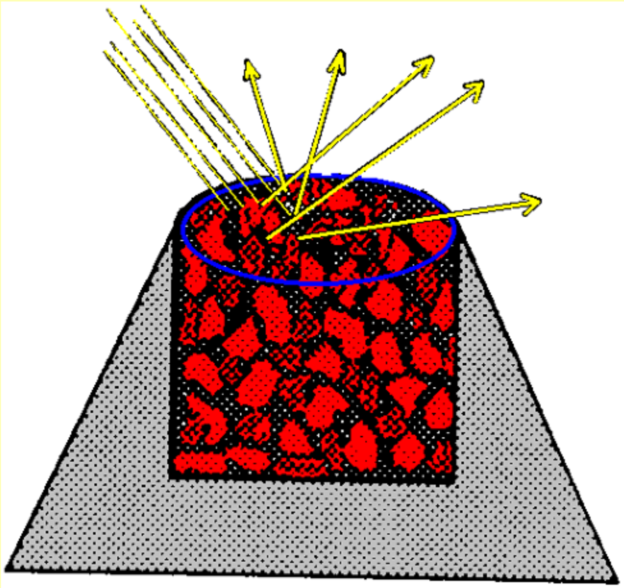
refractive index of particles

reflectivity and absorption characteristics of particles

Diffuse Reflection

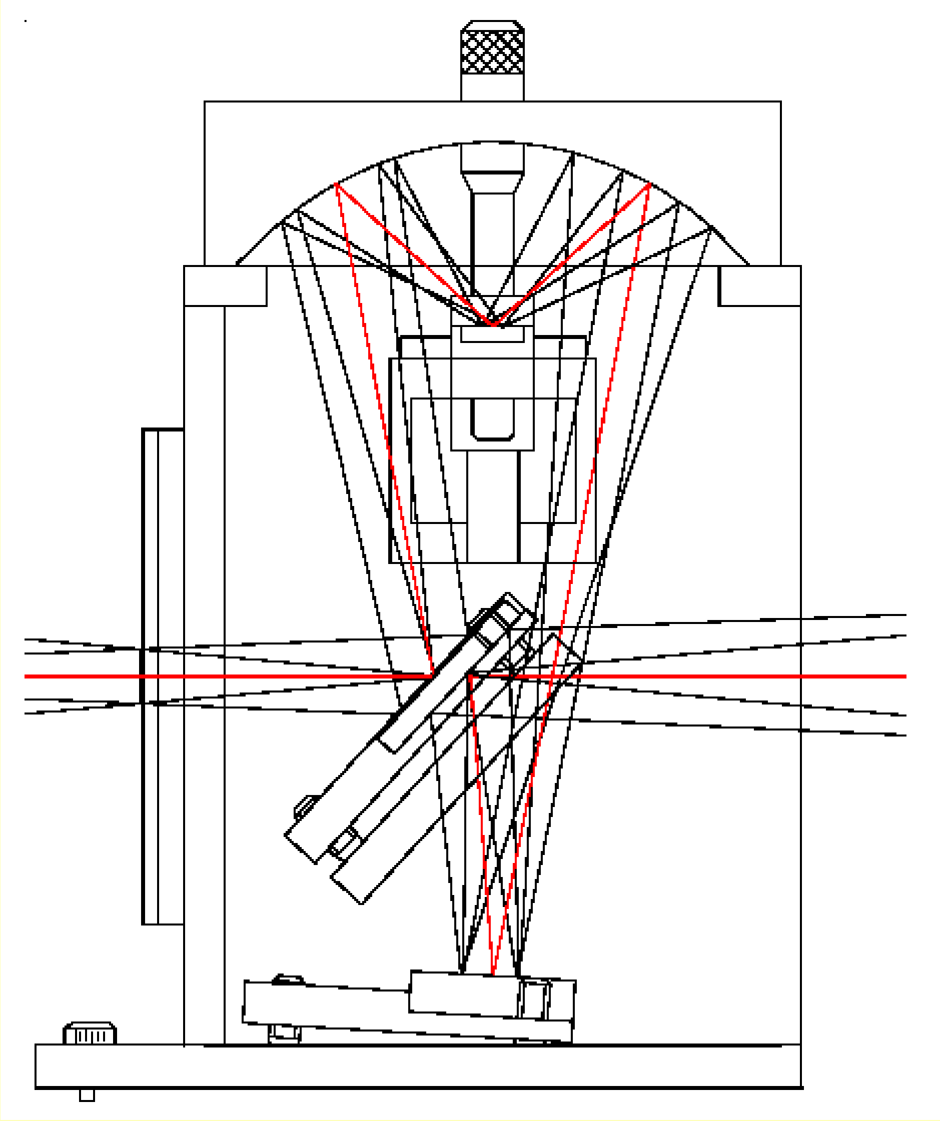
Mechanisms generating infrared spectrum of a powder

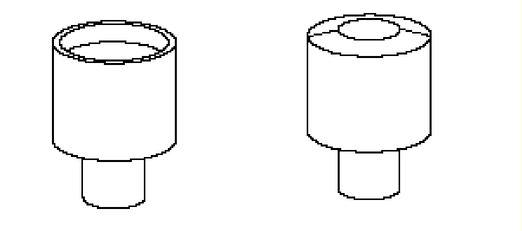




Diffuse Reflection

Experimental Setup

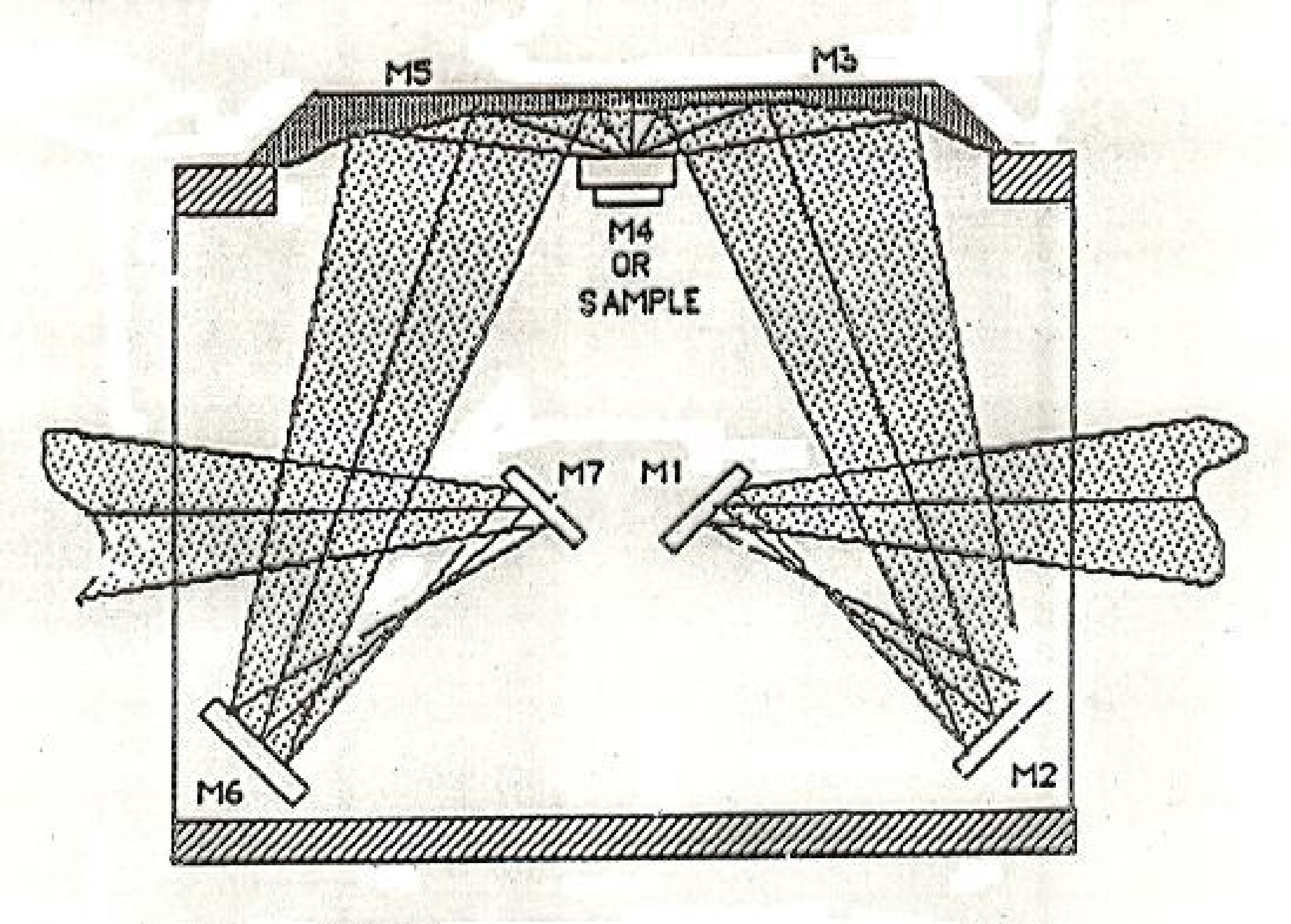




Large and Small Sample Cups

Diffuse Reflection

Experimental Setup – Different Geometry



Diffuse Reflection

DRIFTs Sample Preparation

- powder **simply placed** into the sample cup and analyzed (no sample preparation)
- if the sample is too absorbent, it must be diluted in a nonabsorbent matrix (KBr, KCl,...)
  - no pellet pressing required

- particle size smaller than 10 μm (i.e. not exceeding the wavelength of the incident radiation) preferred

- or **paper disc** coated on a surface by SiC as an abrasive material ⇒ grinding of sample

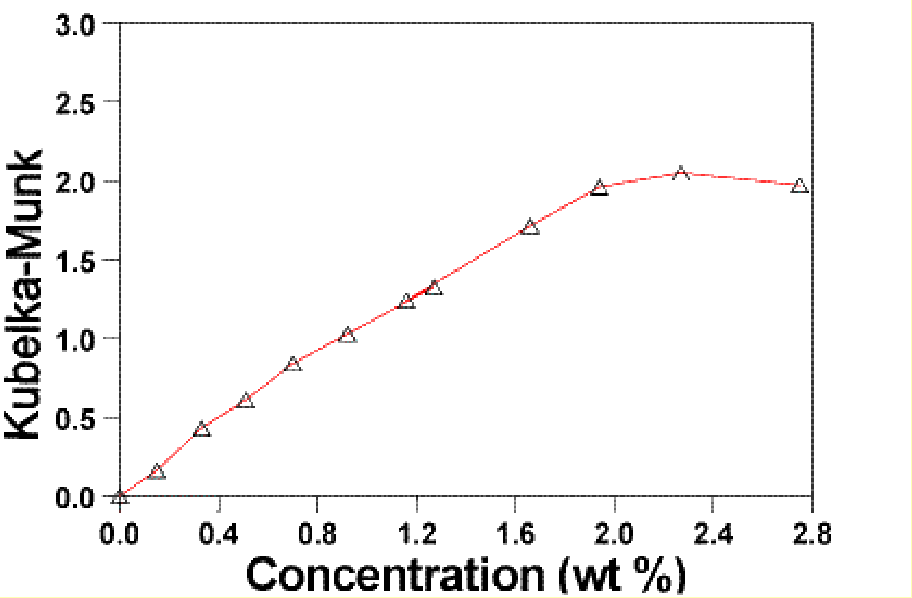
- ideal for pharmaceutical and forensic applications

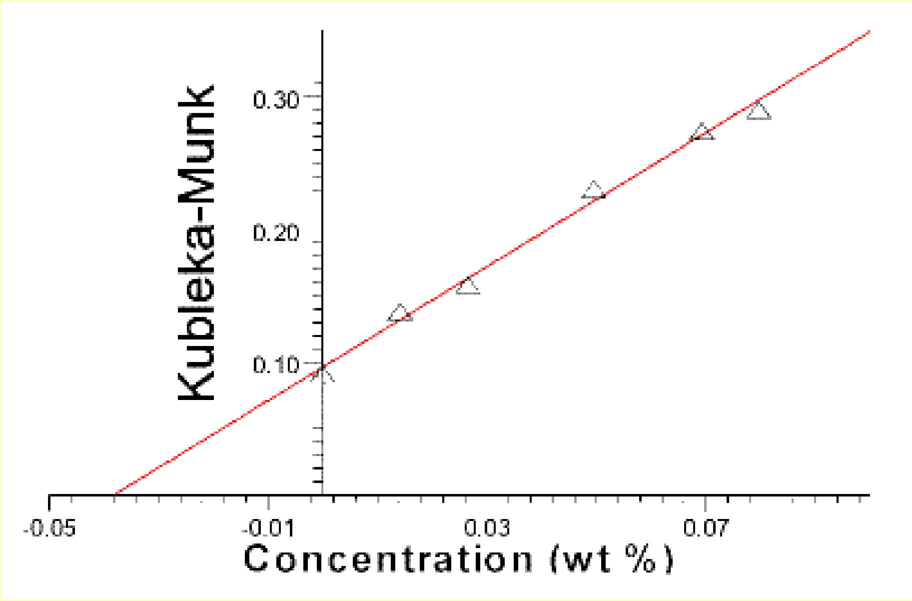
Diffuse Reflection

DRIFTs Spectra - y axe units

From the theoretical standpoint, there is no linear relation between band intensity and concentration (as valid in transmission), and quantitative analyses by the DRIFTS method are therefore rather complicated.

- expressed in linear units **Kubelka-Munk** (roughly correspond to absorbance in transmission KBr pellet technique)





Diffuse Reflection

DRIFTs Spectra - y axe units

- DRIFTs bands stronger than expected absorption from weak IR bands $\Rightarrow$ compensation by **Kubelka-Munk** conversion

$$f(R) = \frac{(1 - R_\infty)^2}{2R_\infty} = 2.303\,a\,.\frac{c}{s} = \frac{k}{s}$$

$$k = 2.303\ a\ c$$

$$f(R) = 2.303\ a\ c/s$$

- $f(R)$ is called **Kubelka-Munk** function

R_∞ … **absolute reflectance** of the sampled layer

k … **molar absorption coefficient** a … **absorptivity**

- proportional to the fraction of transmitted light

s … **diffusion** (scattering) **coefficient**

- proportional to the fraction of diffused light

$\Rightarrow$ creates a **linear relationship** for spectral intensity relative to sample concentration $s \sim const. \Rightarrow \boldsymbol{f(R) = 2.303\ a\ c}$

Diffuse Reflection

DRIFTs Spectra - y axe units

linear relationship assumed when:

- infinite sample dilution in a non-absorbing matrix, *i.e*. KCl, KBr, … (such that k = 0 and R = 1)
- a constant scattering coefficient
- "infinitely thick" sample layer

These conditions achieved for:

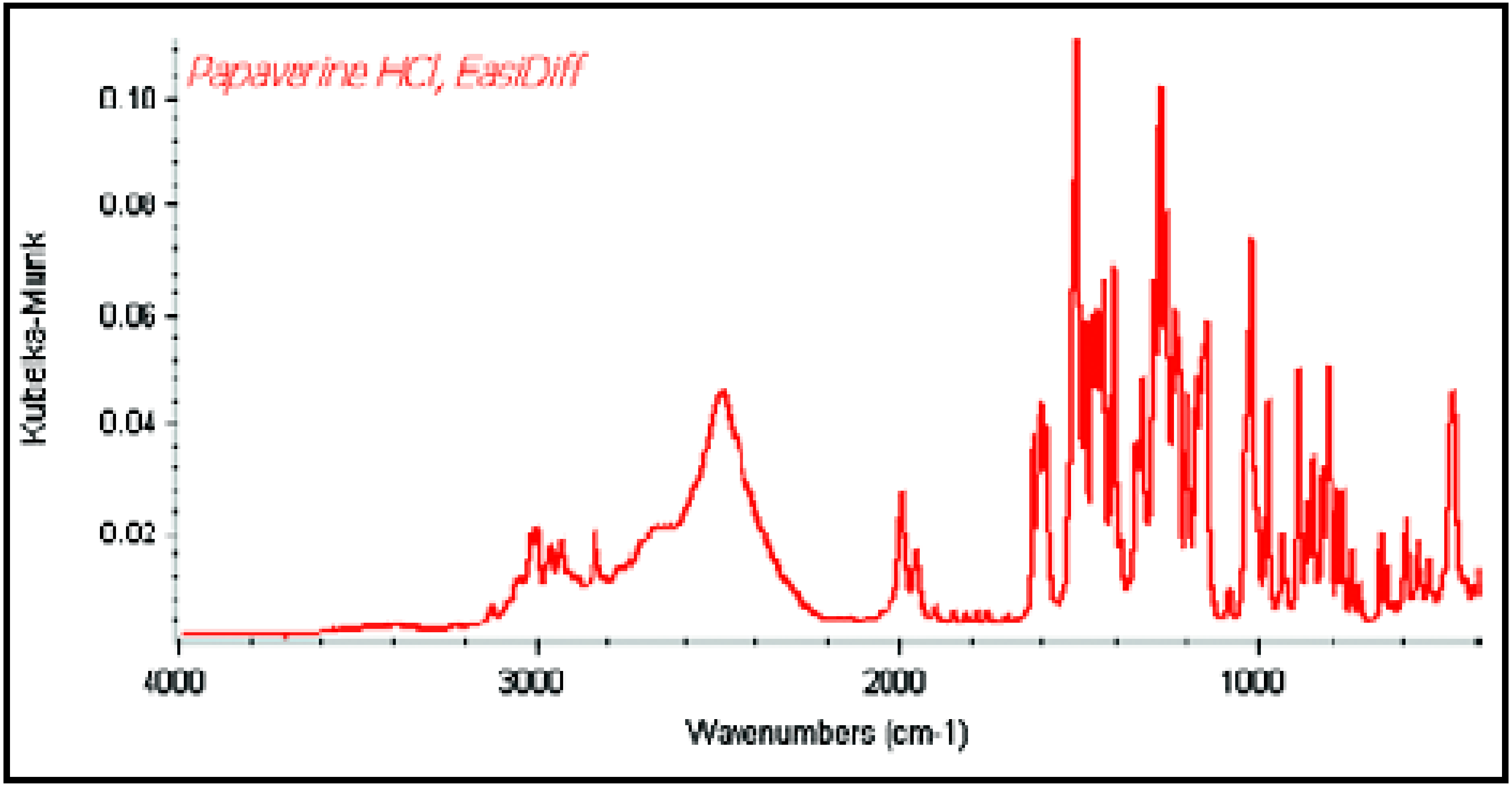
- highly diluted samples
- small particle samples (the scattering coefficient is a function of sample size and packing)
- sample layer of at least 1.5 mm

With proper sample preparation DRIFTs can provide ppm sensitivity and high quality results.

T Armaroli et al. Oil & Gas Science and Technology – Rev. IFP, 59 (2004), 215.

Diffuse Reflection

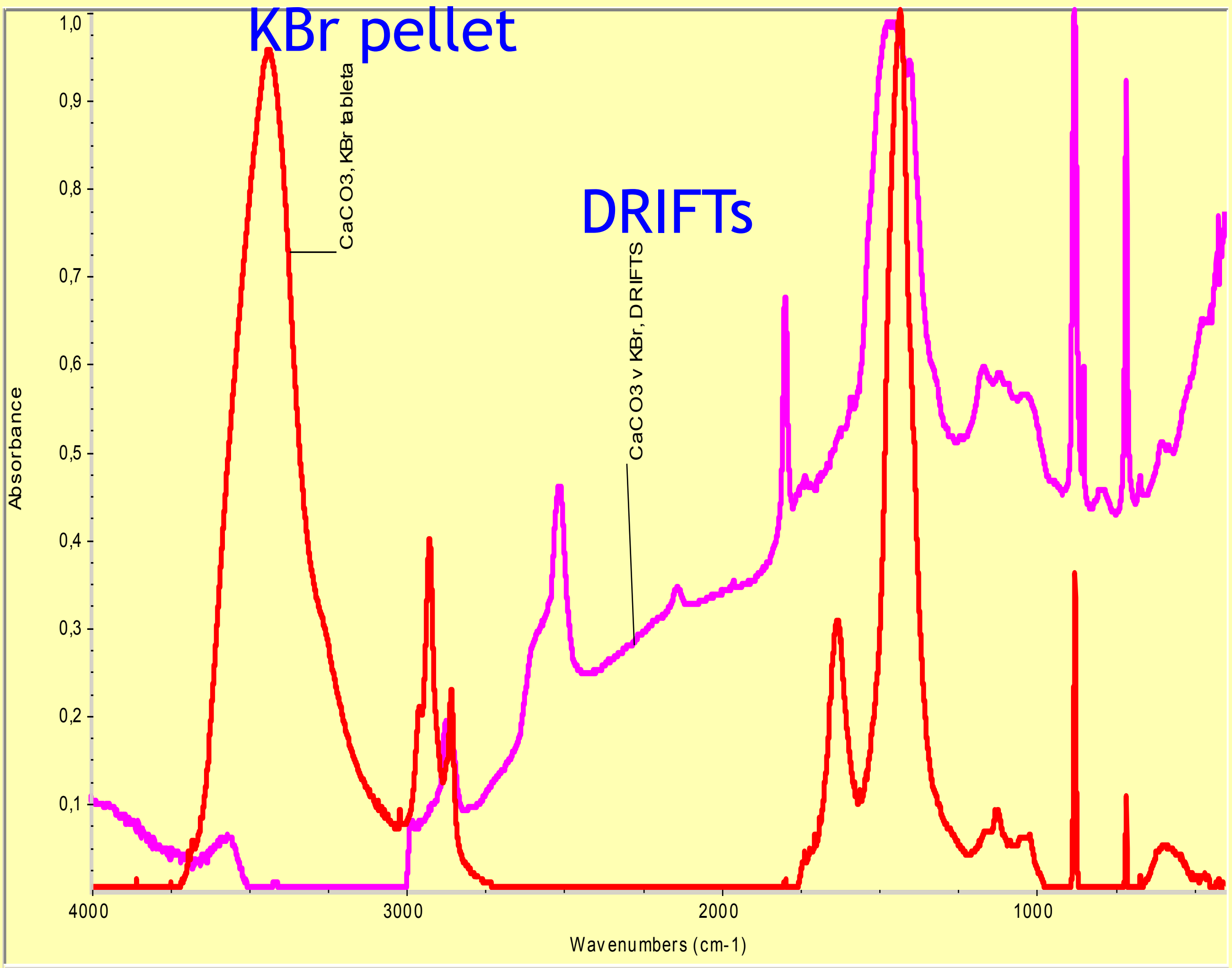
DRIFTs Spectra



A special version of the EasiDiff for NIR measurements (gold coated optics) is also available

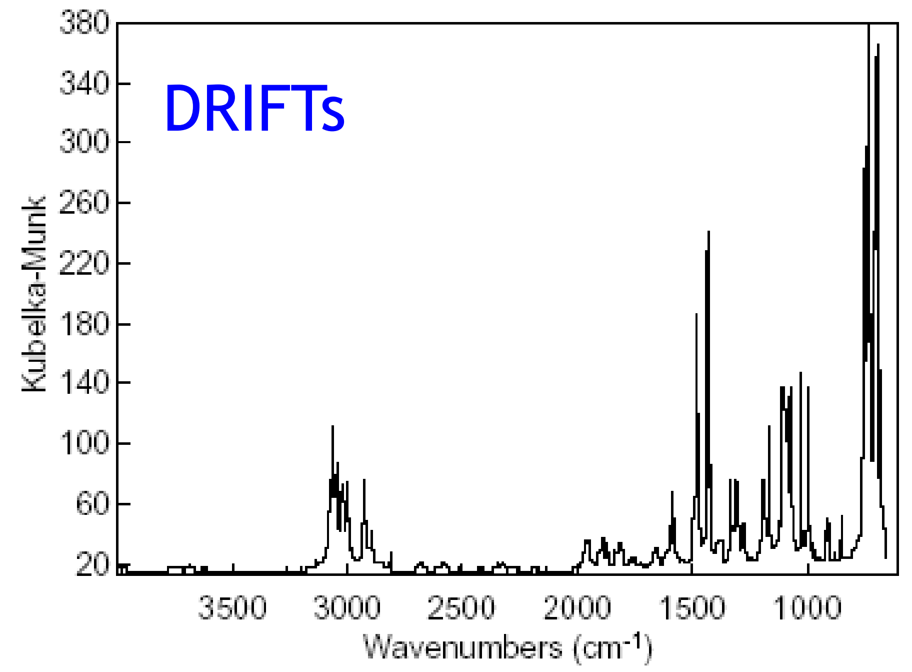
Diffuse Reflection

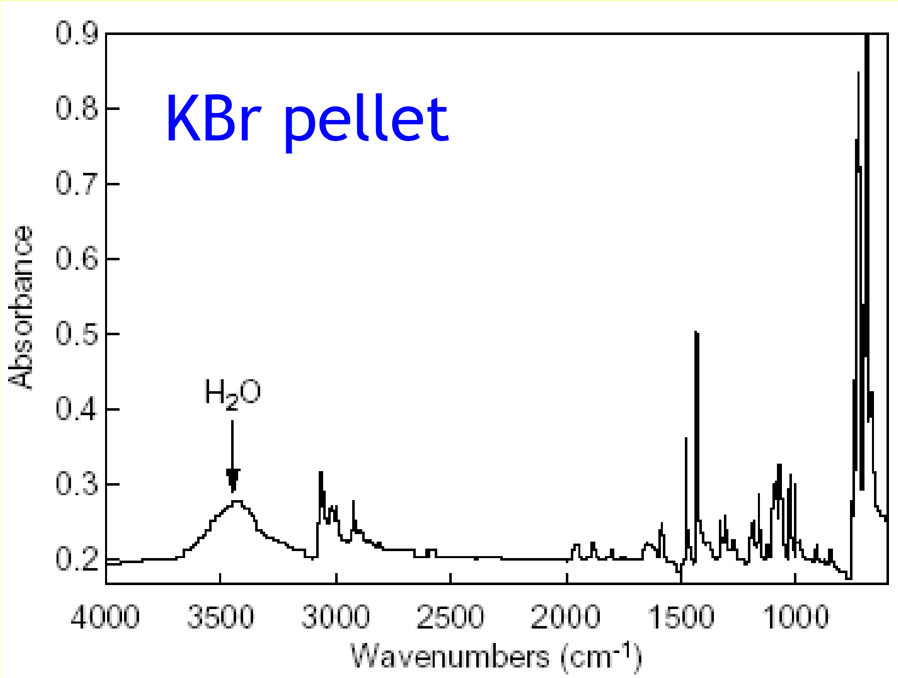
IR Spectra of $CaCO_3$



Diffuse Reflection

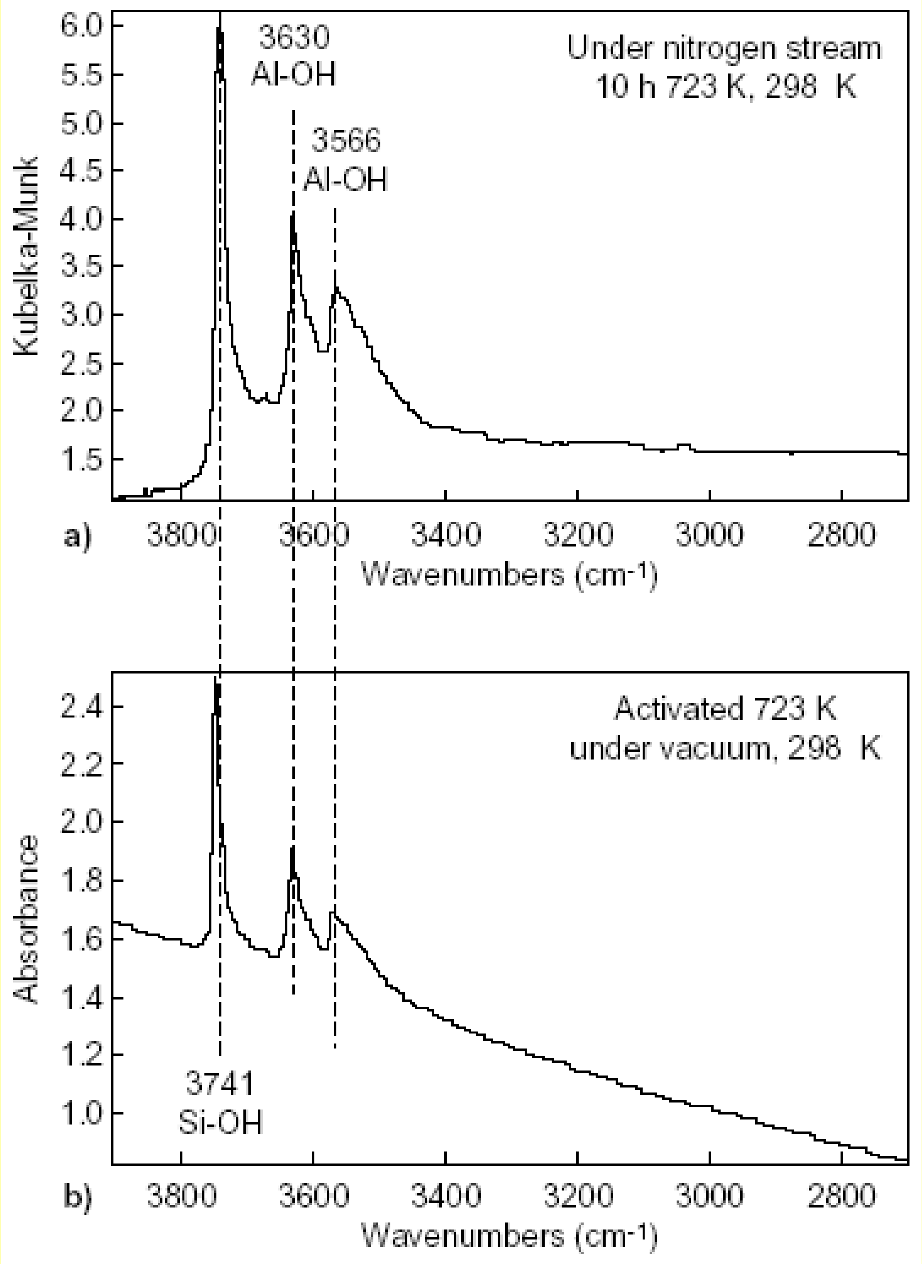
IR Spectra of 1,2-Bis(diphenyl phosphino)ethane





T Armaroli et al. Oil & Gas Science and Technology – Rev. IFP, 59 (2004), 215.

Diffuse Reflection vs Transmission



Zeolite Y14 (Si/Al of 13.6)

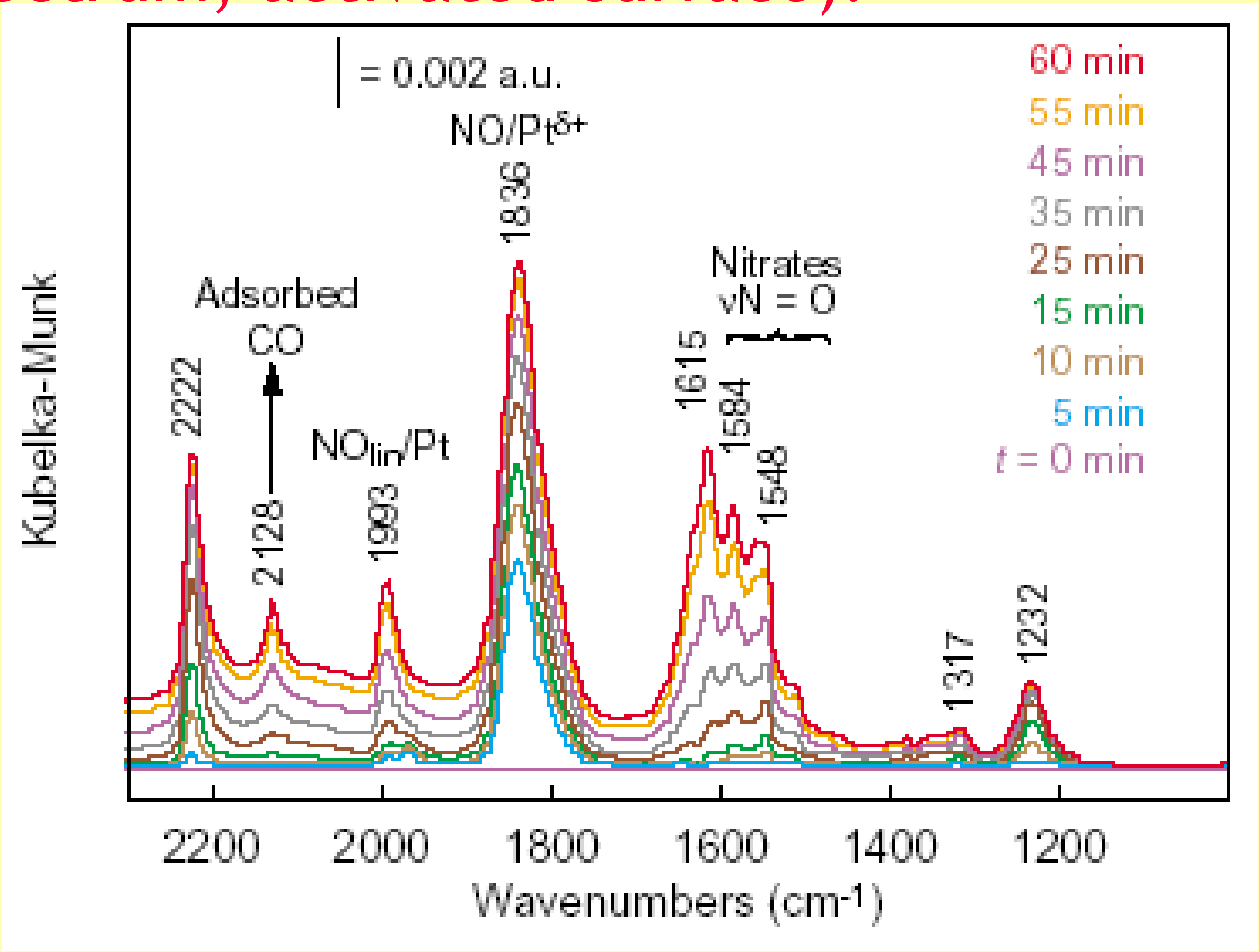
a) transmission spectrum, selfsupported pure powder pellet, after overnight activation at 723 K under vacuum

b) diffuse reflection spectrum after 10 h activation under nitrogen.

spectra recorded at 298 K

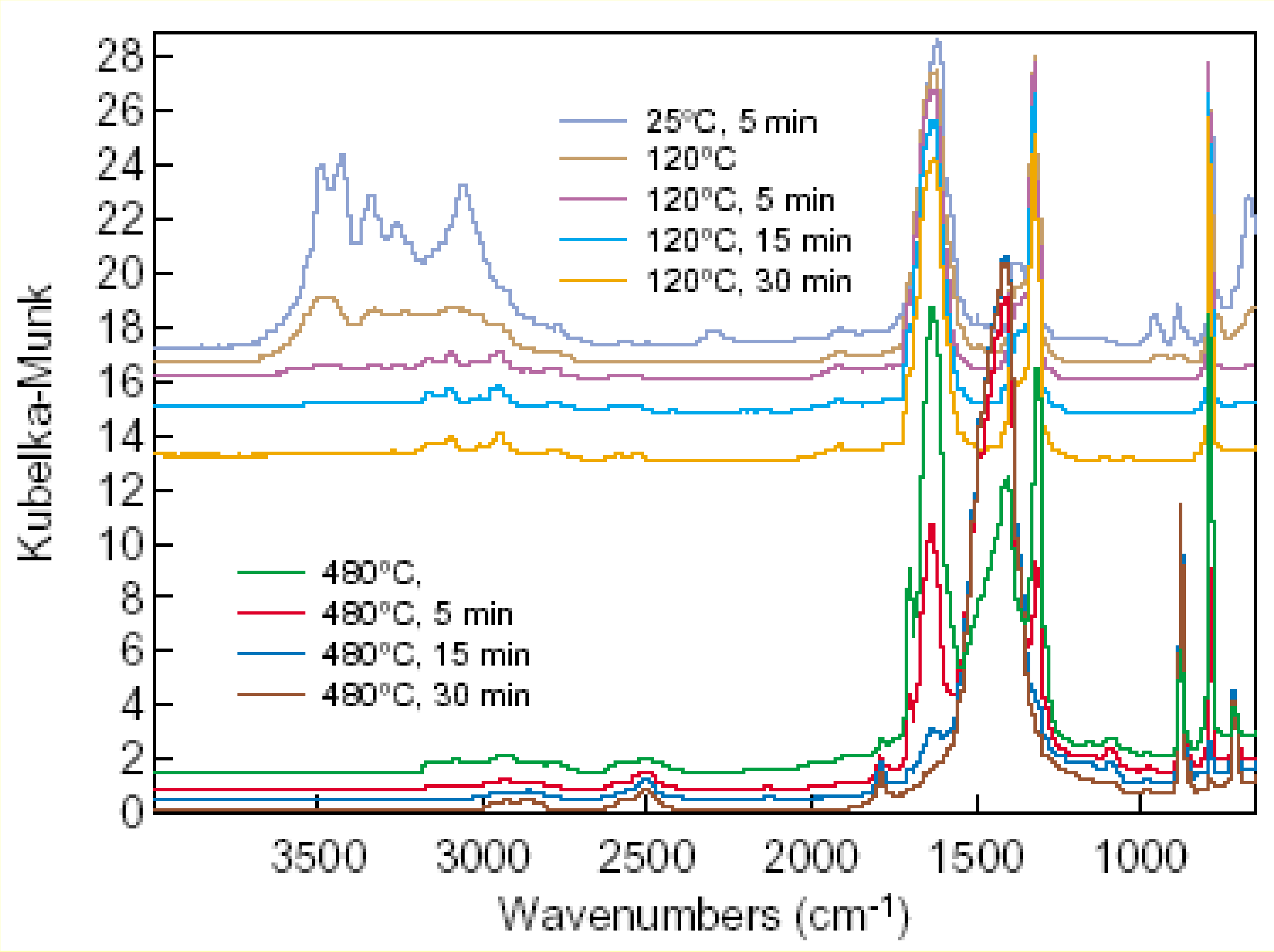
Diffuse Reflection

Pt/Al_2O_3 DRIFTs spectra, variation in species at the surface during 1 h of nitration at 423 K (background first spectrum, activated surface).



Diffuse Reflection

DRIFTs spectra of Ca oxalate + KBr (5/95 w/w)



FT-IR Reflection Techniques

Summary:

Attenuated Total Reflection (ATR)

- structural information from the **surface - thick layers**

Specular Reflection (smooth surfaces)

- measurement of **thin layers or monolayers** (coatings on metals, surface characterization)

Diffuse Reflection (DRIFTs) (rough surfaces)

- structural information is from the **bulk matrix**