FTIR spectroscopy at grazing incidence for surface chemical analysis

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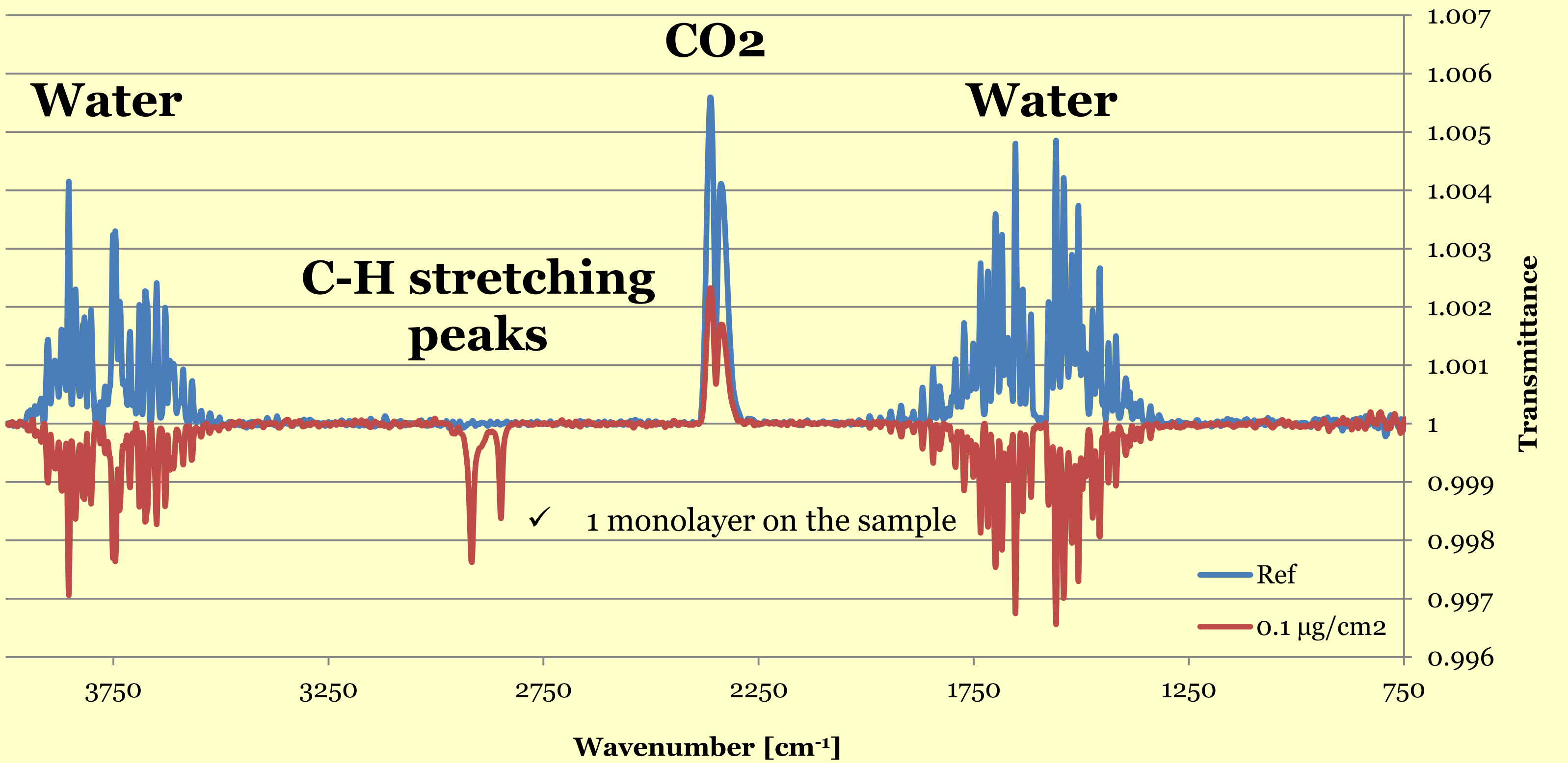
Introduction

- Current procedure for organic contamination:
  - Extraction with n-Hexane (304 ml/m^2)
  - Deposition of 2 drops of extraction solution on a ZnS cell
  - The n-Hexane evaporates from the cell
  - The organic contamination remains on the surface of the cell and is analysed with FTIR (in transmission)

Introduction

- Transmission spectrum for an organic contaminant



Introduction

- Disadvantages:
  - n-Hexane is toxic

  - The sample has to be dismounted and transported to the chemistry laboratory
  - Complex geometries can cause problems
  - Only the average surface contamination
  - Solubility in n-Hexane

Introduction

- The *portable* Agilent 4100 ExoScan FTIR

Diamond ATR

For the identification of polymers, powders

Diffuse Reflectance

For the measurement of rough surfaces

Grazing Angle 82°

For the measurement of thin films ($d < \lambda$)

Previous Study

- Detection of *Silicones* down to 0.1 µg/cm^2
  - Stainless Steel
  - Copper
  - Aluminum

V

0.1 µg/cm² = 1 monolayer

- Detection of *Hydrocarbons* down to 0.1 µg/cm^2
  - Copper
  - Aluminum

V

  - Stainless Steel → Problems

1 µg/cm² not visible!
= 10 monolayers

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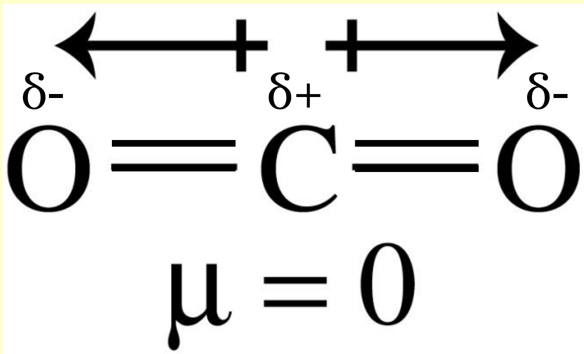
FTIR at grazing incidence

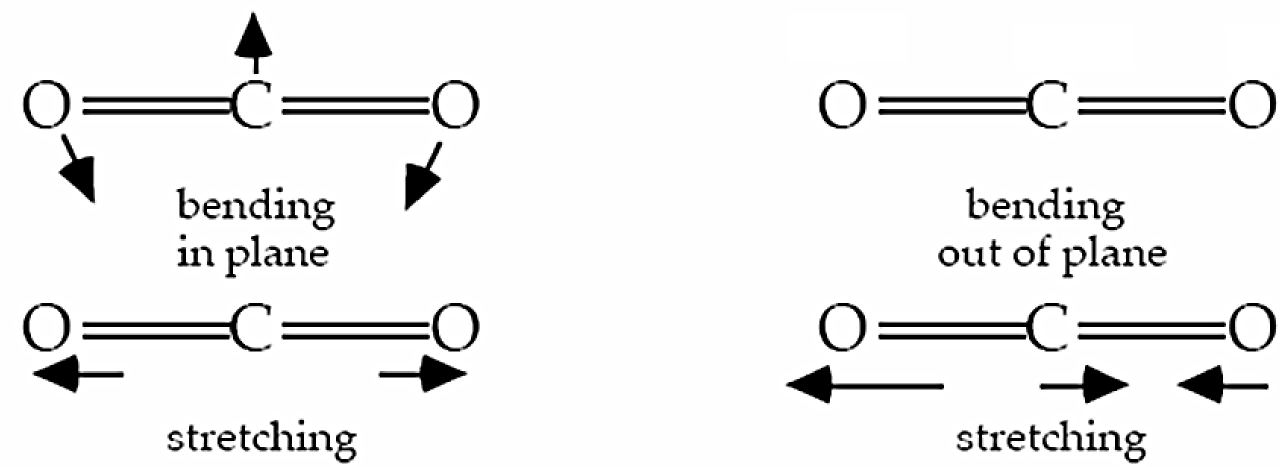
- **Vibrational Spectroscopy**



Requirements for excitation:

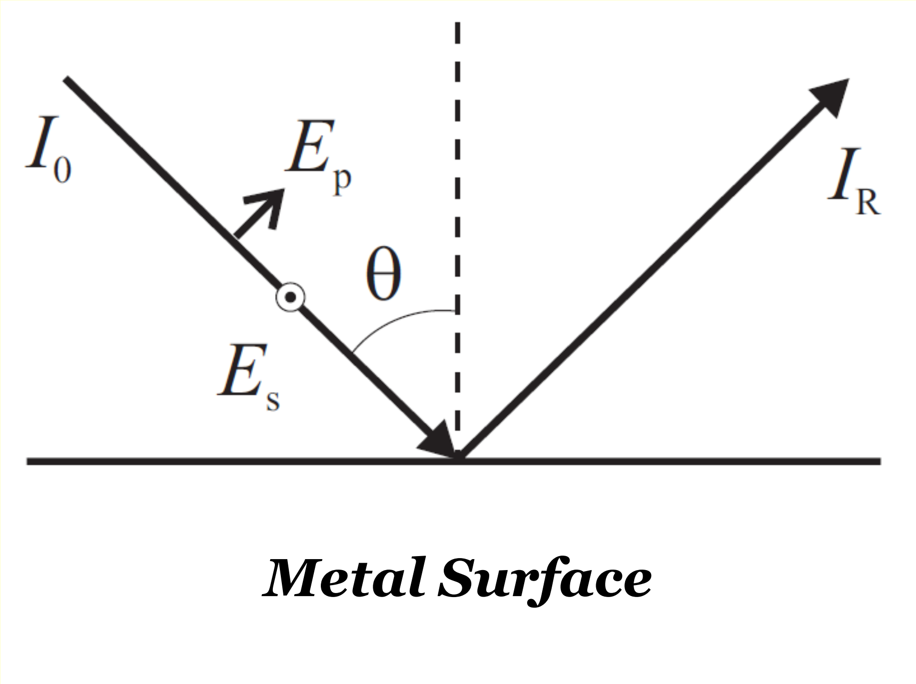
- Oscillating dipole moment μ
- Alignment of the electric field vector of the radiation with the oscillating dipole

For CO_2, which is a linear molecule, there are 3(3) – 5 = 4 fundamental vibrations:



FTIR at grazing incidence

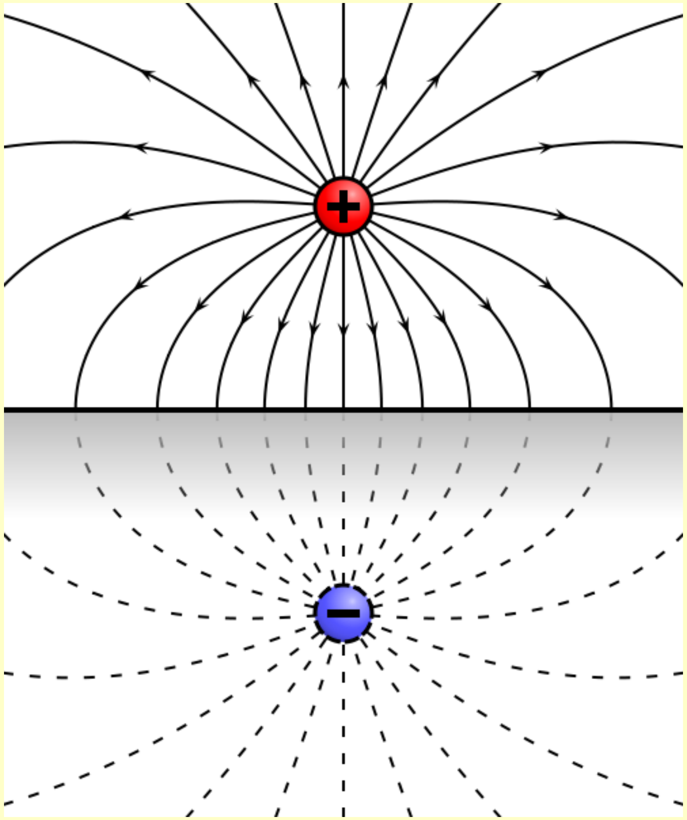
- Polarization of light



- P-polarized light → *parallel* to the plane of incidence
- S-polarized light → *perpendicular* to the plane of incidence

FTIR at grazing incidence

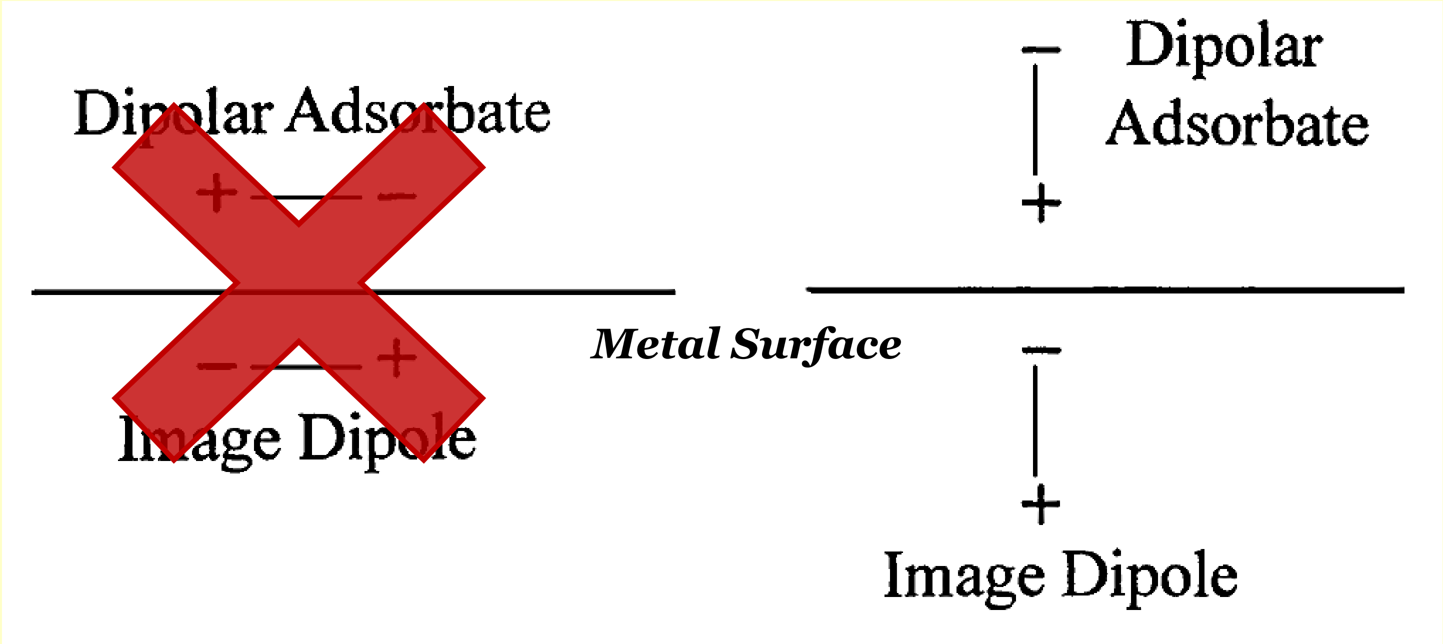
- **Image charge**



A conducting surface

FTIR at grazing incidence

- The effect of the image charge

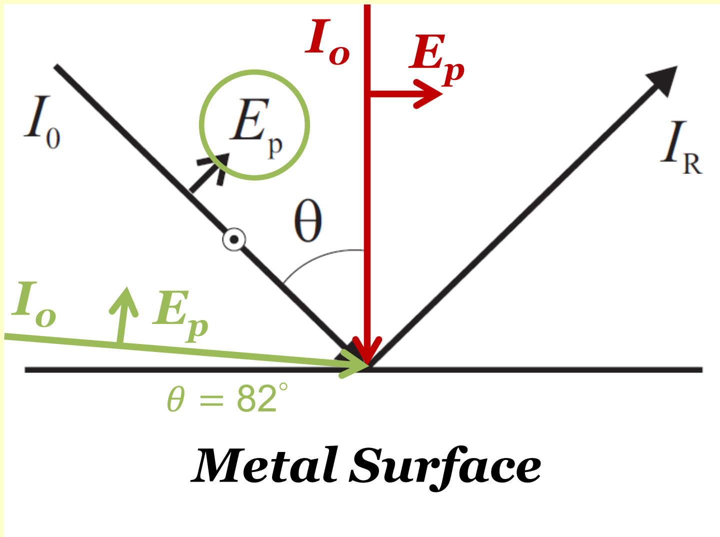


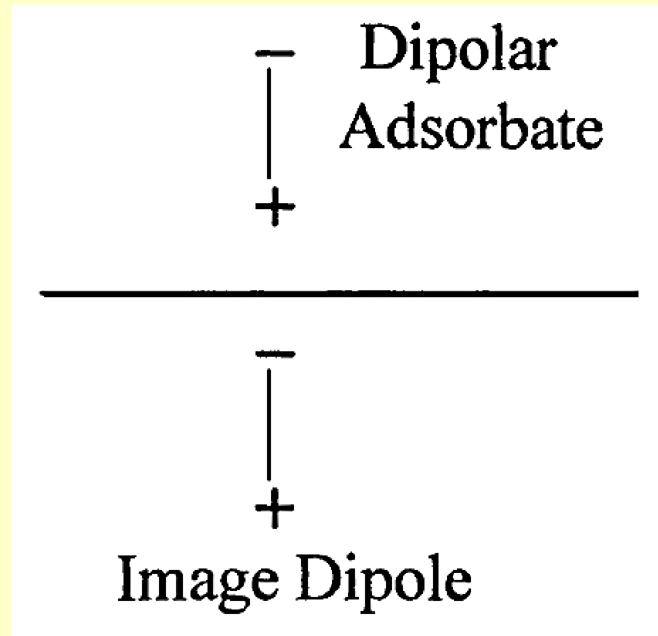
No net dipole oscillation
No absorption

The dipole oscillation
is amplified

FTIR at grazing incidence

- **How to excite this vibration?**





But… You need an angle θ > 0

In conclusion:
Good absorbance only for a large angle of incidence θ

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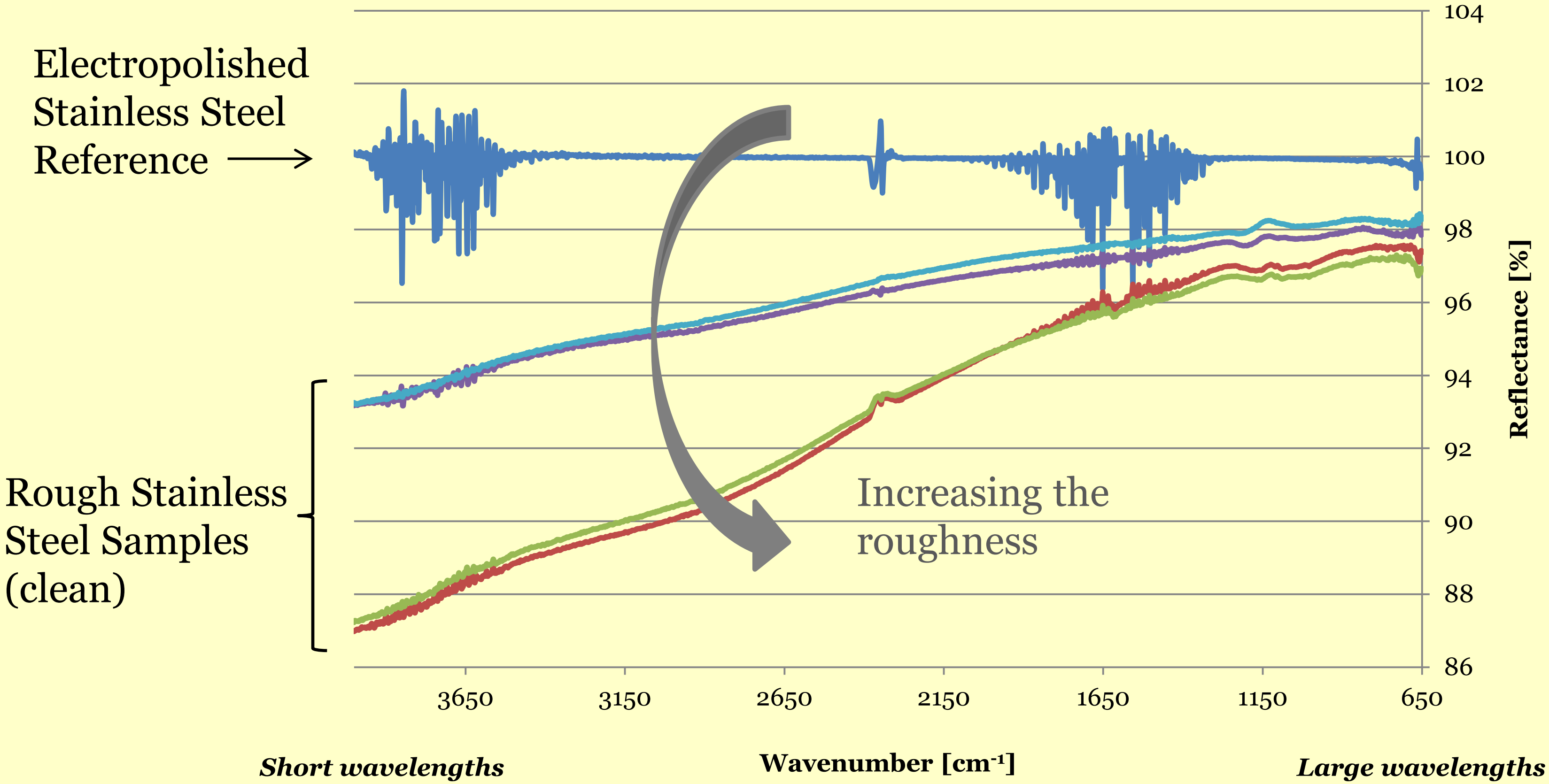
Baseline Distortions

- Roughness Induced Baseline Distortions
- Film Induced Baseline Distortions

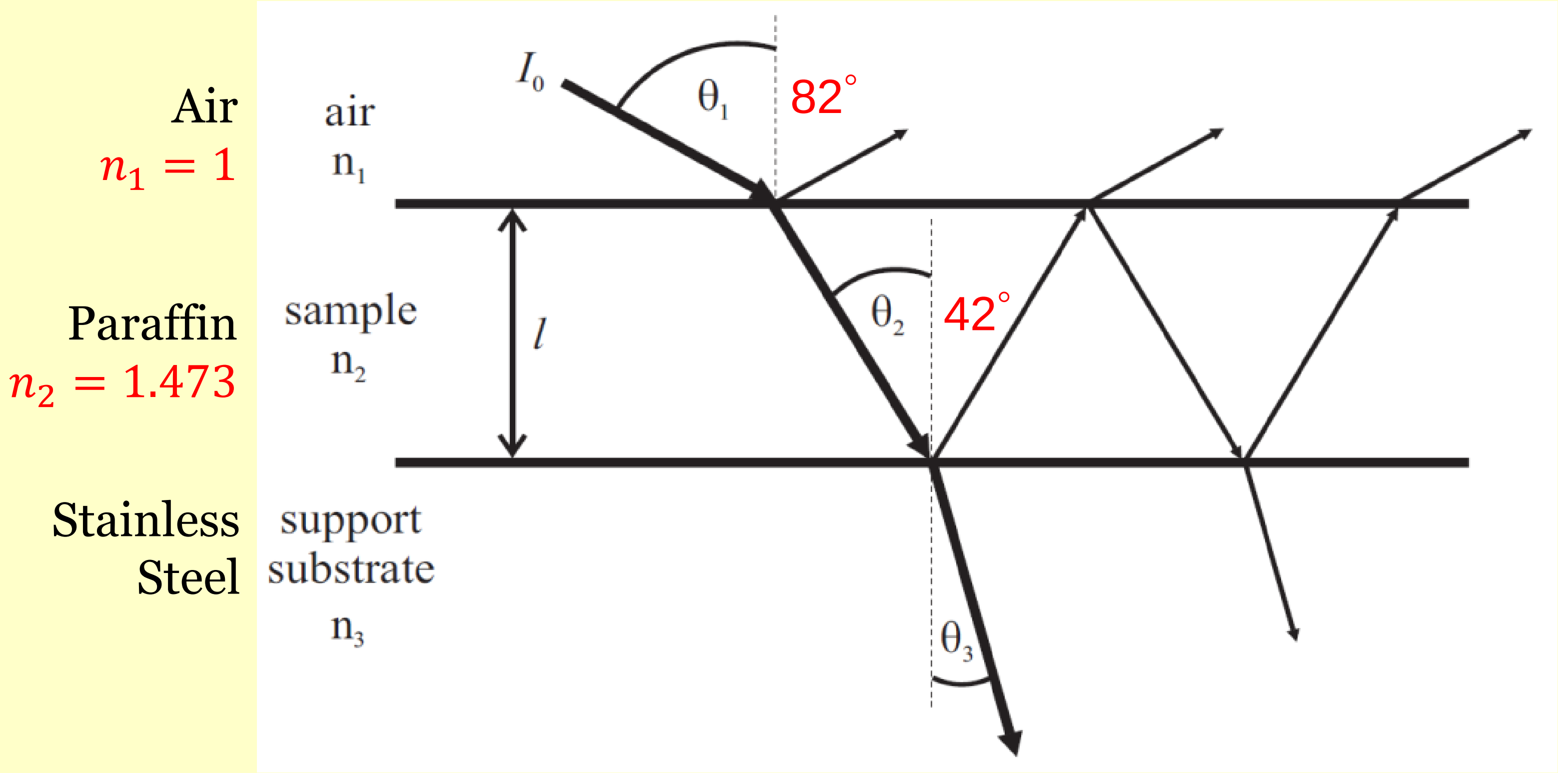
Baseline Distortions

- Roughness Induced Baseline Distortions



Light only 'sees' objects larger or approximately equal to its wavelength

- Film Induced Baseline Distortions



- The angle of incidence for the metal surface changes
- Higher refractive index

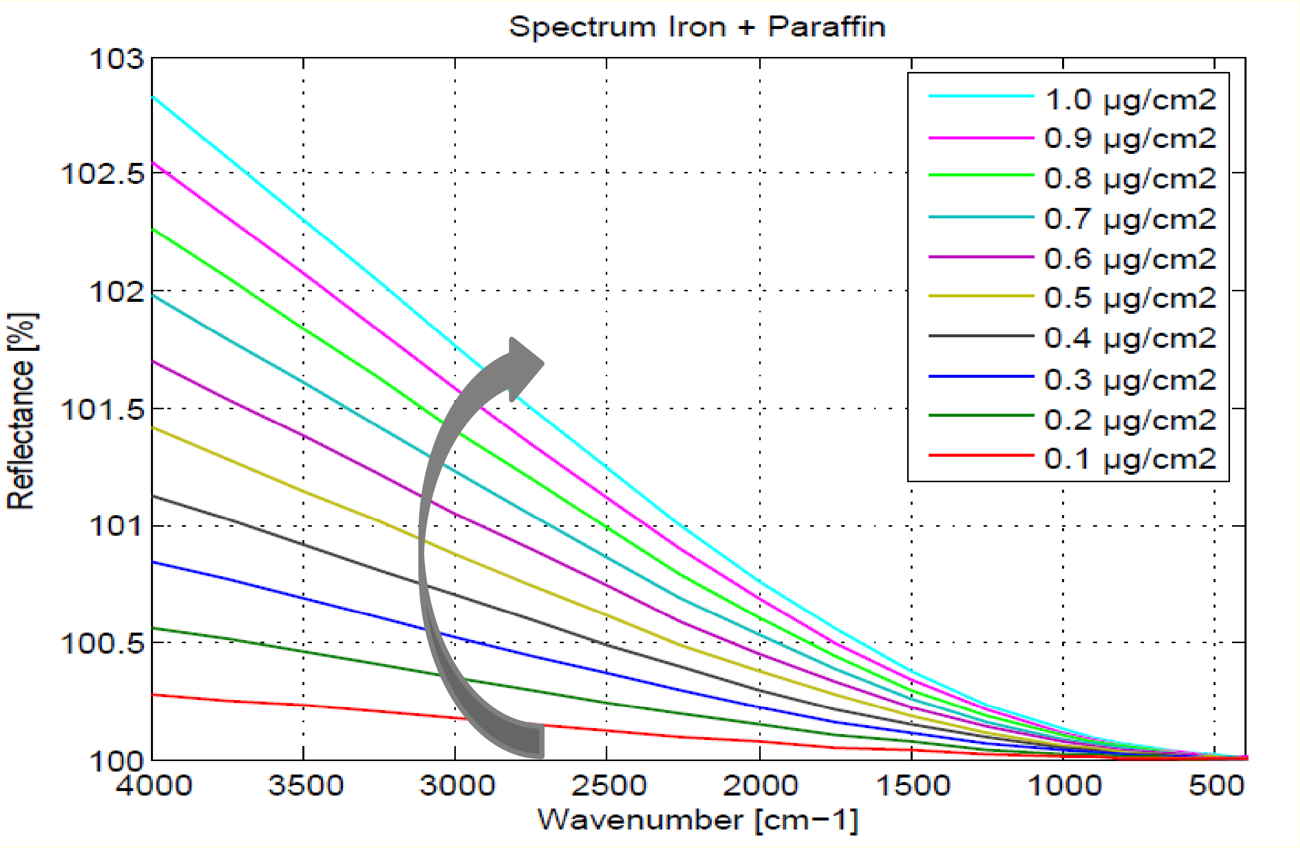
Baseline Distortions

- Calculation of the baseline (MATLAB)
  - Approximations:
    - The complex refractive index of ***iron*** as a function of wavenumber
    - The refractive index of Paraffin: $n_2 = 1.473$ (n20/D)

The calculation will yield:
Only the baseline, not the carbon-hydrogen stretching peaks

Baseline Distortions

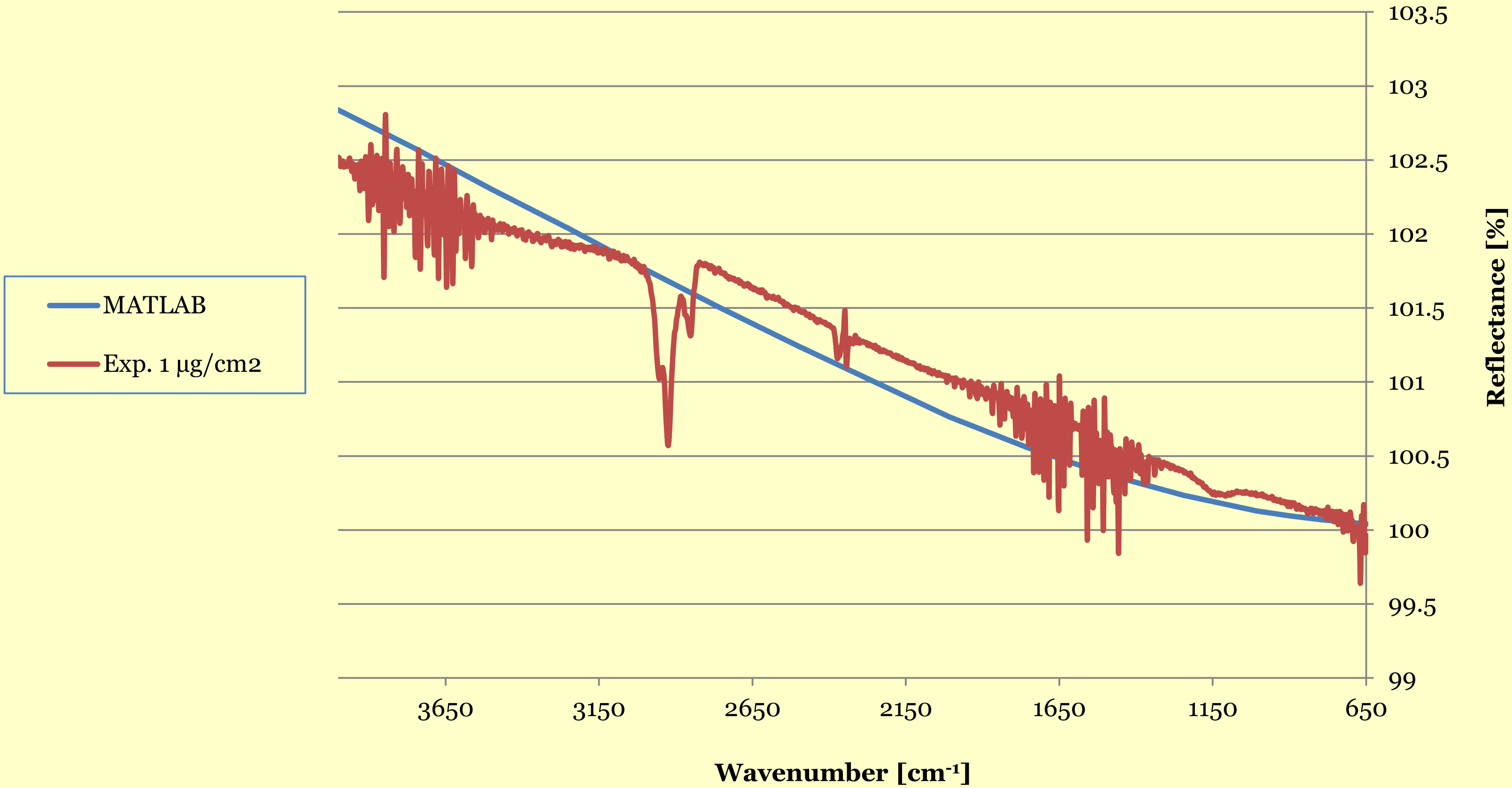
- Calculation of the baseline (MATLAB)



The higher the concentration, the bigger the baseline distortion
But negligible compared to the effect of the roughness

Baseline Distortions

- Calculation of the baseline (MATLAB)



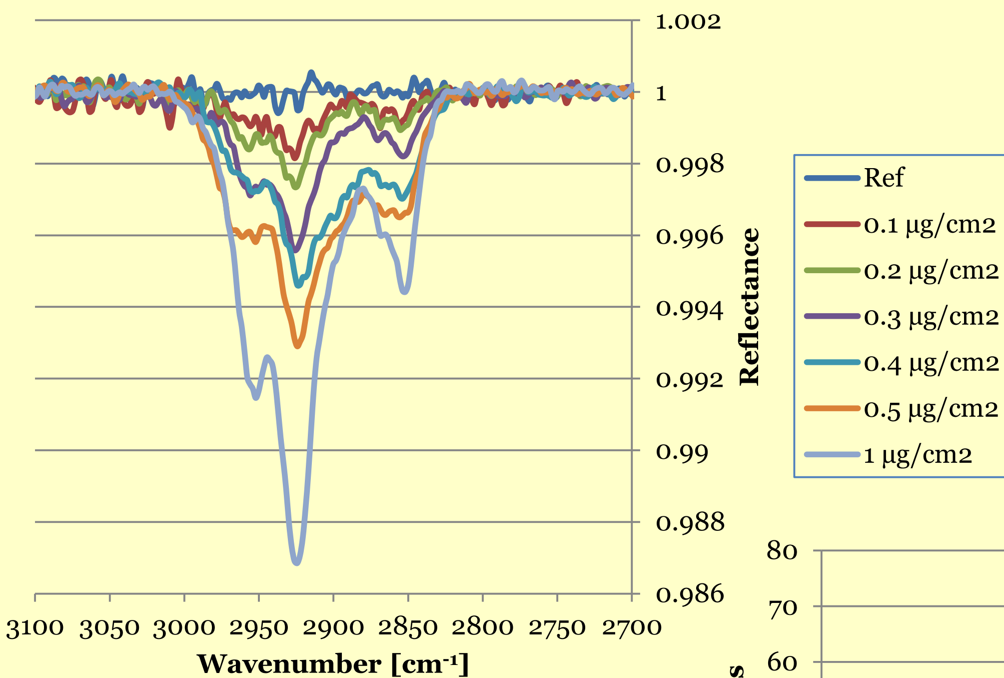
Comparison with a Paraffin film on a *electropolished* Stainless Steel surface (experiment)

The Contamination

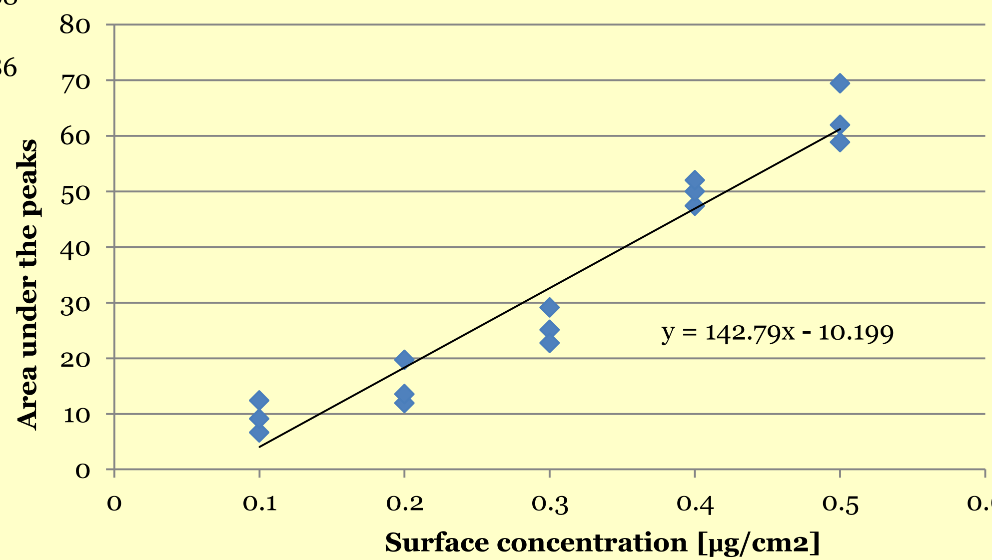
- The contamination standard for hydrocarbons:
  - Cutting oil: *Blasocut BC 35 LF SW* (33 vol%)
  - Machine oil: *Shell Vitrea 150* (33 vol%)
  - Bearing grease: *Kluber Isoflex NBU 15* (33 vol%)
- Dissolve in n-Hexane (for spectroscopy)
- Switch to Paraffin (for spectroscopy)

Detection Limit

- Electropolished Stainless Steel Surface



Stainless Steel is *not* the cause of the problems!



Rough Surfaces

Electropolished

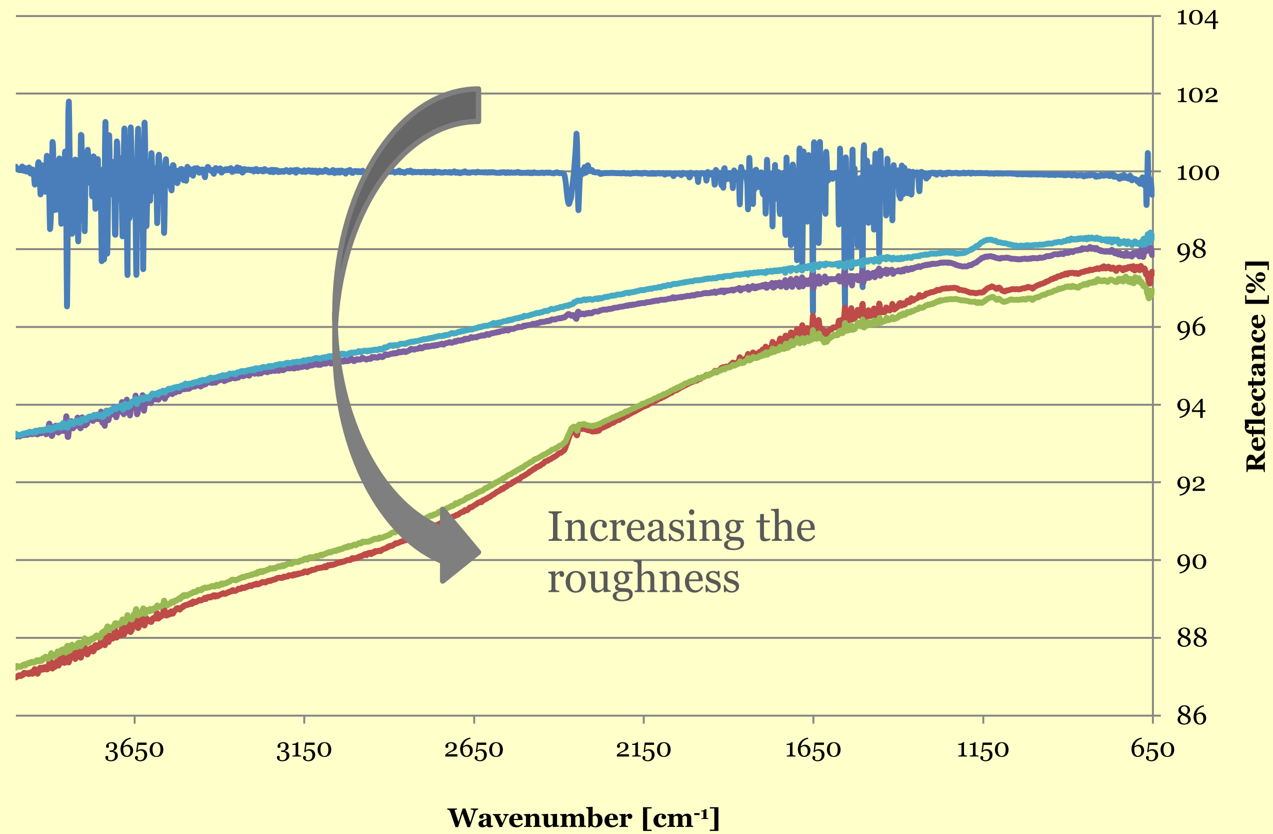
Rough Surface

Sandblasted

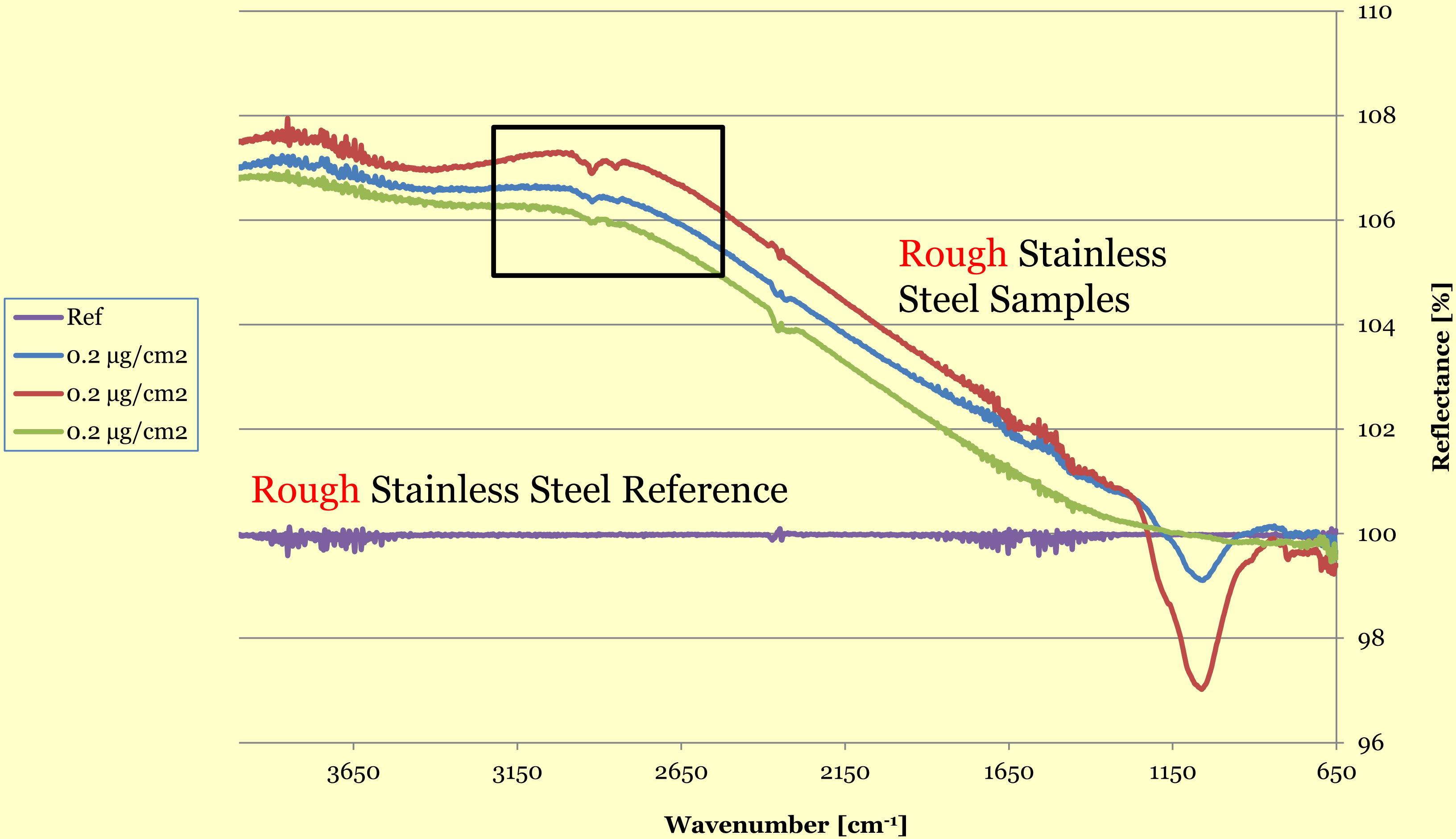
Rough Surfaces

Electropolished Stainless Steel Reference

Rough Stainless Steel Samples (clean)



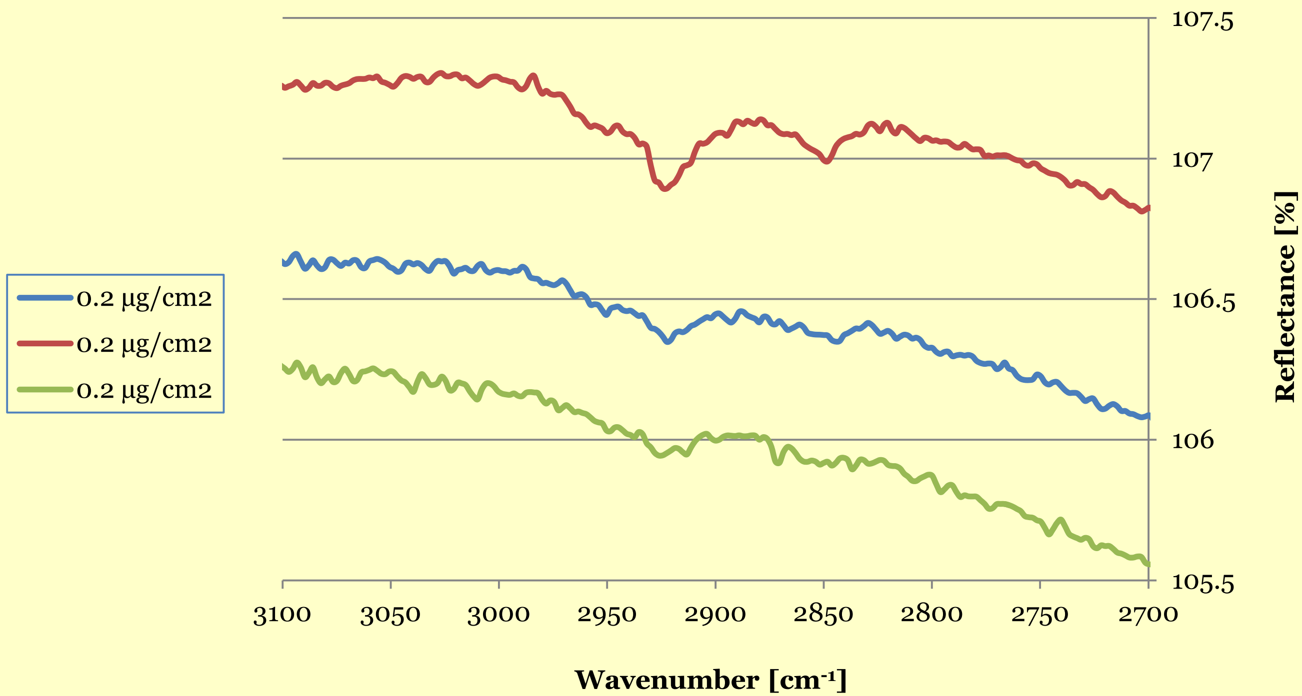
Rough Surfaces



The samples are rougher than the reference

Rough Surfaces

- Rough Stainless Steel Sample & Rough Stainless Steel Reference



The more signal is lost, the smaller the peaks become.

Conclusion

- Detection of *Hydrocarbons* on *smooth Stainless Steel* surfaces is possible down to 0.1 µg/cm^2 (= 1 monolayer)

- Detection on rough surfaces is an issue for
  - Stainless Steel

  But possibly also for
  - Copper
  - Aluminum

Questions ?

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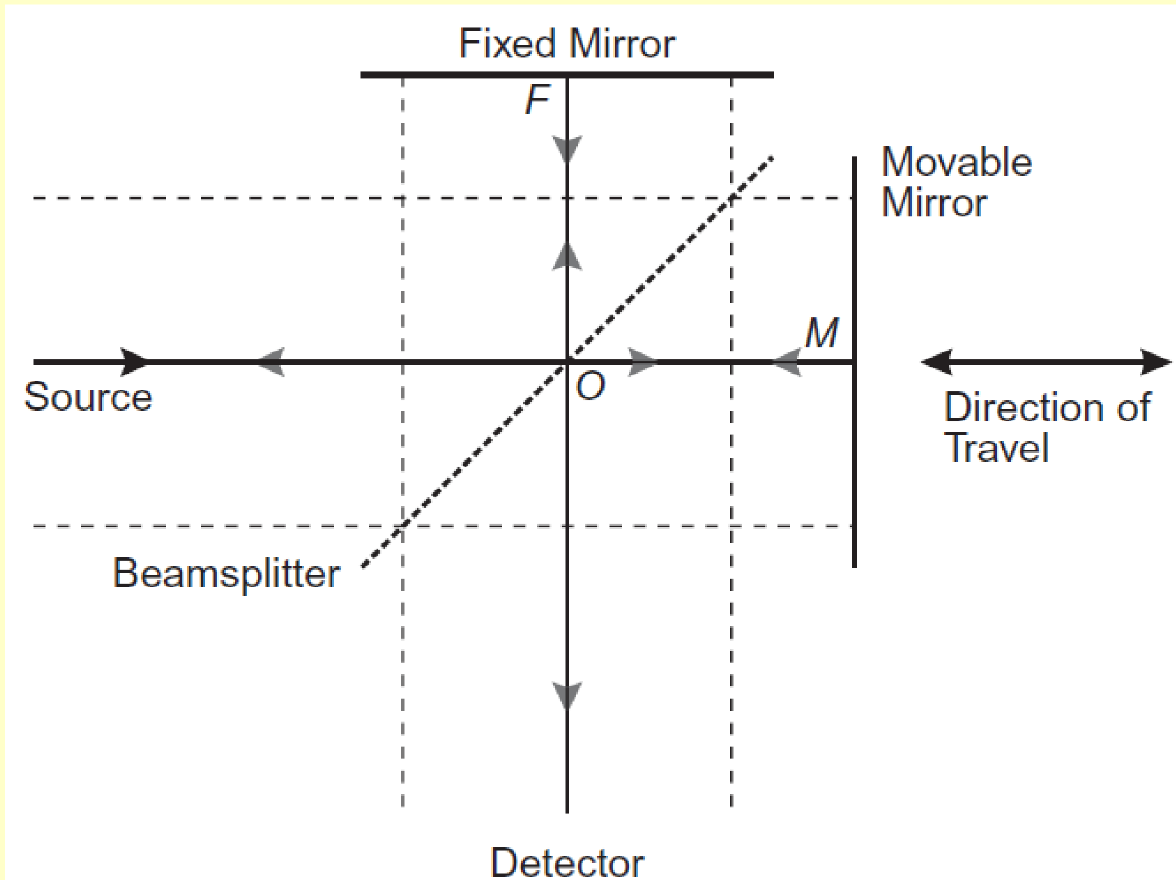
The Surface Treatment Workshop:

Florent Fesquet, Pierre Maurin & Jacky Carosone

The Polymer Laboratory

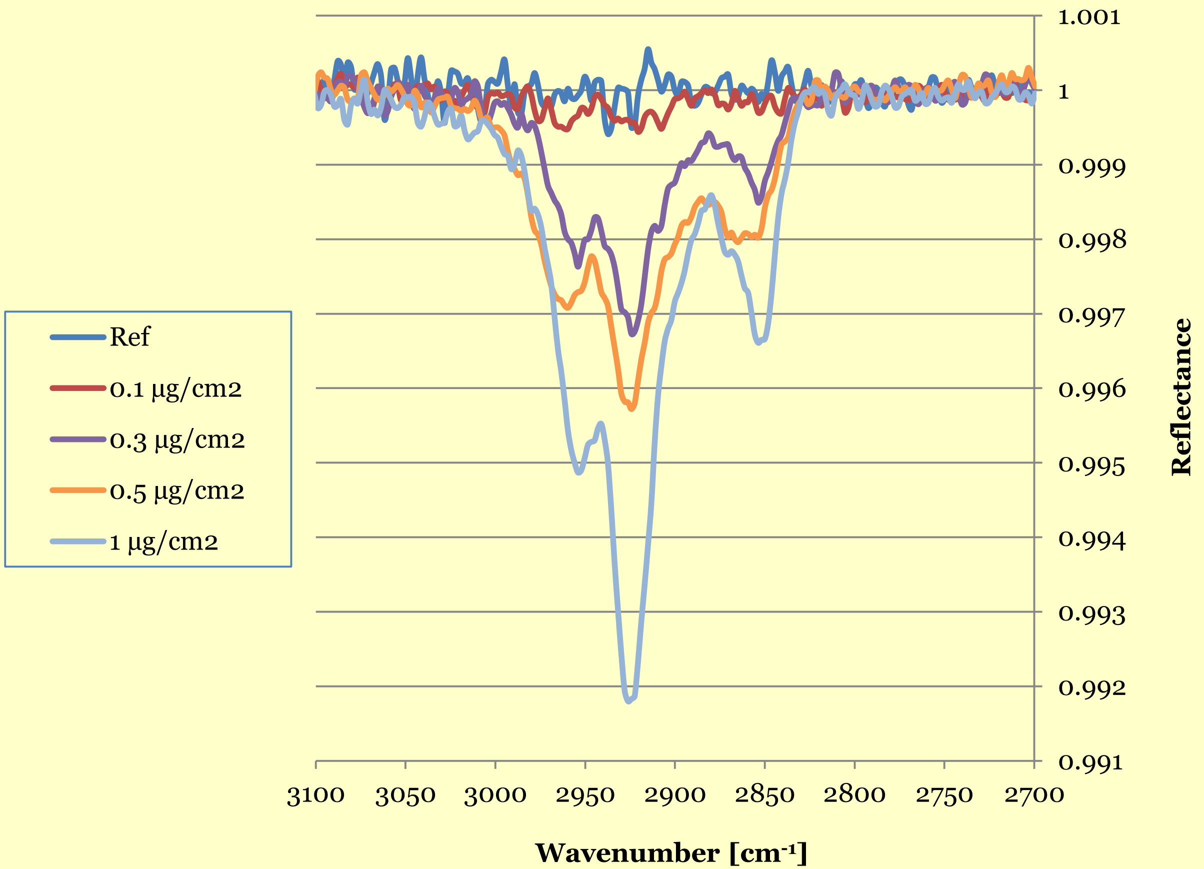
FTIR Spectroscopy

- Why *Fourier Transform?*



Oxidized Stainless Steel

- Electropolished stainless steel plates
- 300°C for 2.5 days



The Calculation

- The Fresnel equations

$$r_p = \frac{(n_2 \cdot cos(\theta_1) - n_1 \cdot cos(\theta_2))}{(n_2 \cdot cos(\theta_1) + n_1 \cdot cos(\theta_2))}$$

$$r_s = \frac{(n_1 \cdot cos(\theta_1) - n_2 \cdot cos(\theta_2))}{(n_1 \cdot cos(\theta_1) + n_2 \cdot cos(\theta_2))}$$

- Snell's law

$$n_1 \cdot sin(\theta_1) = n_2 \cdot sin(\theta_2)$$

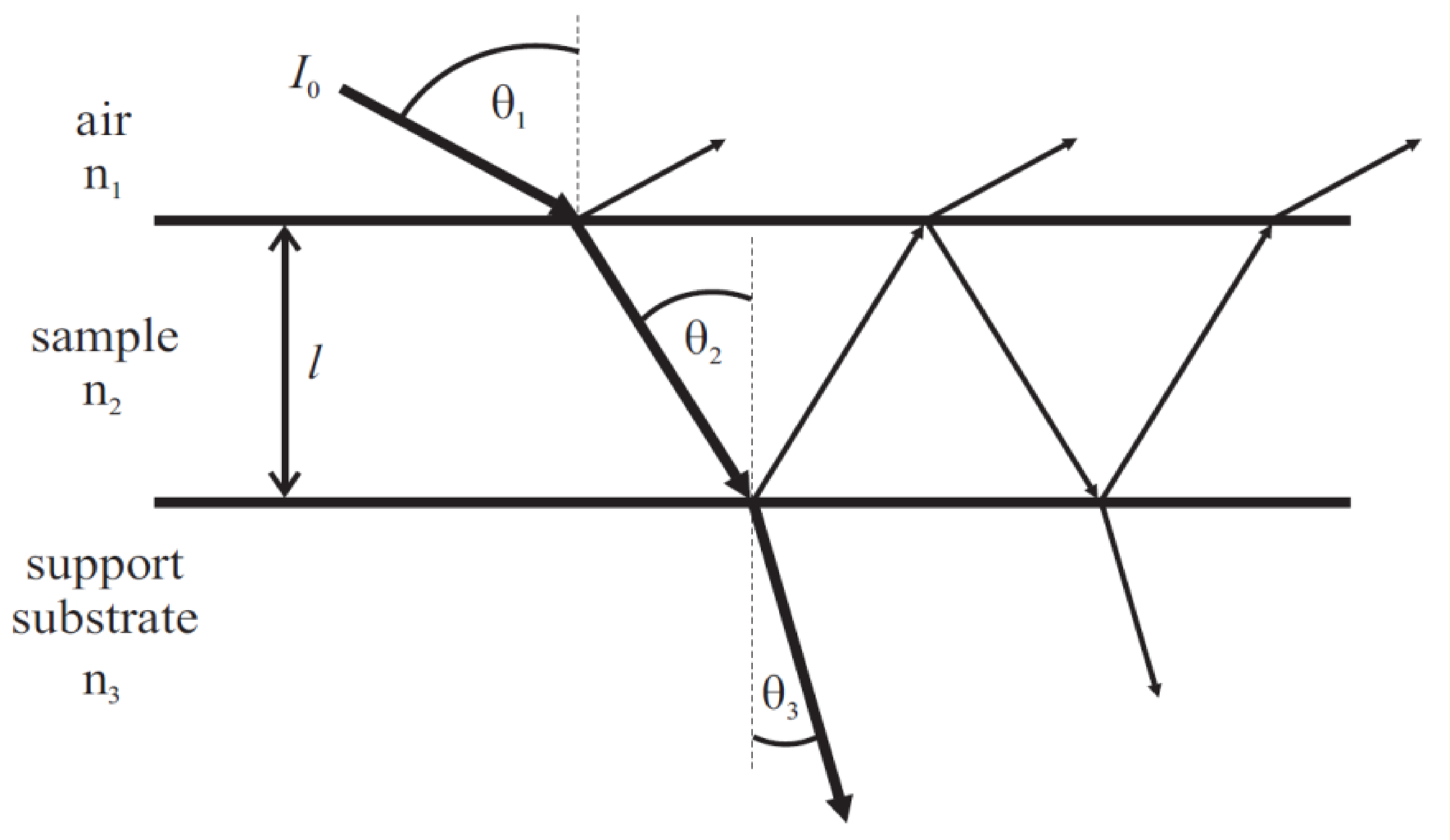
The Calculation

- The reflectance of a thin film on a metal surface (= stratified medium)

$$r_j = \frac{r_{12,j} + r_{23,j} \cdot e^{2 \cdot i \cdot \beta}}{1 + r_{12,j} \cdot r_{23,j} \cdot e^{2 \cdot i \cdot \beta}} \quad with \quad (j = p \; or \; s)$$

$$\beta = \frac{2\pi}{\lambda_0} \cdot n_2 \cdot l \cdot cos(\theta_2)$$

The Calculation



The Calculation

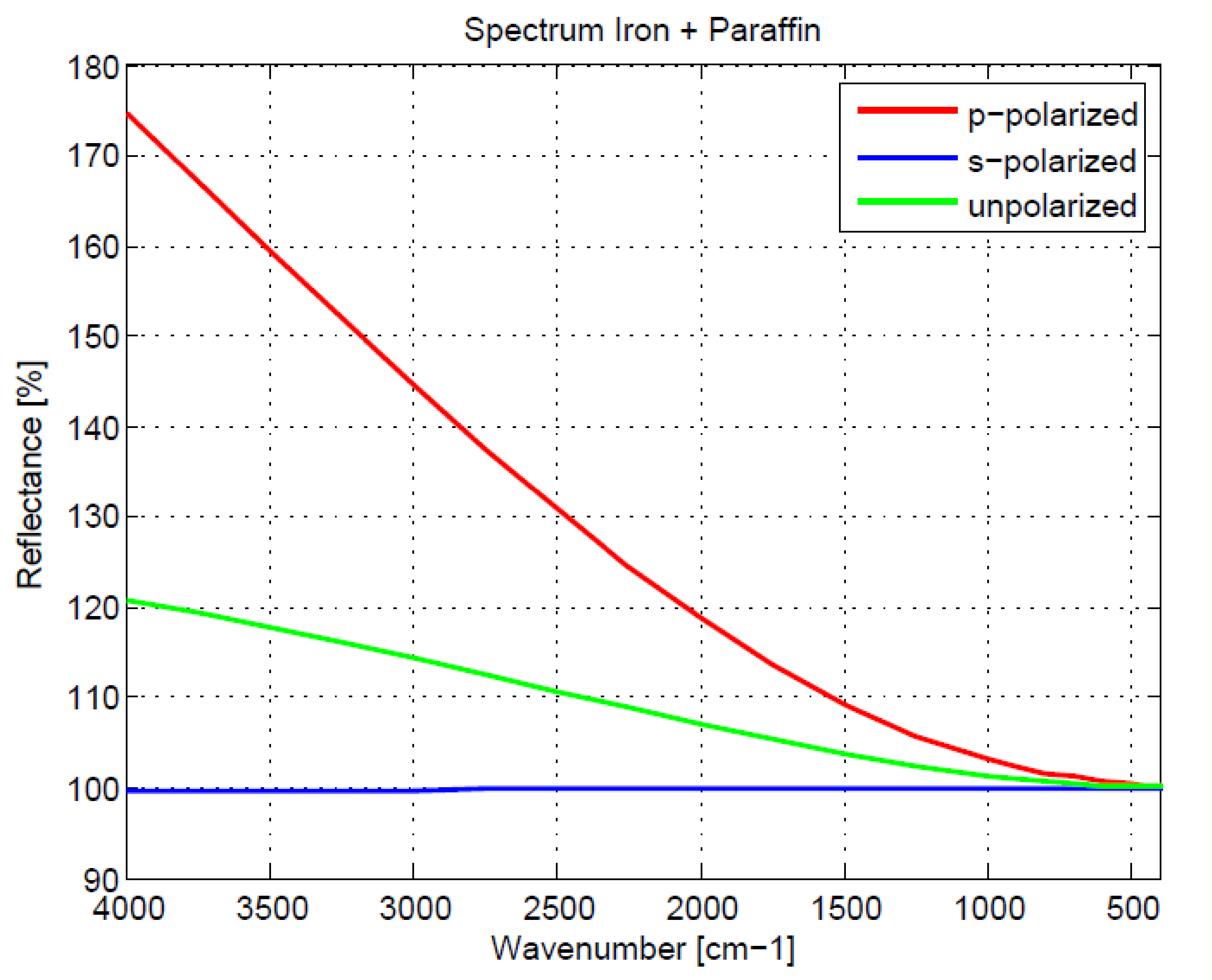
- The reflectance

$$R_j = |r_j|^2$$

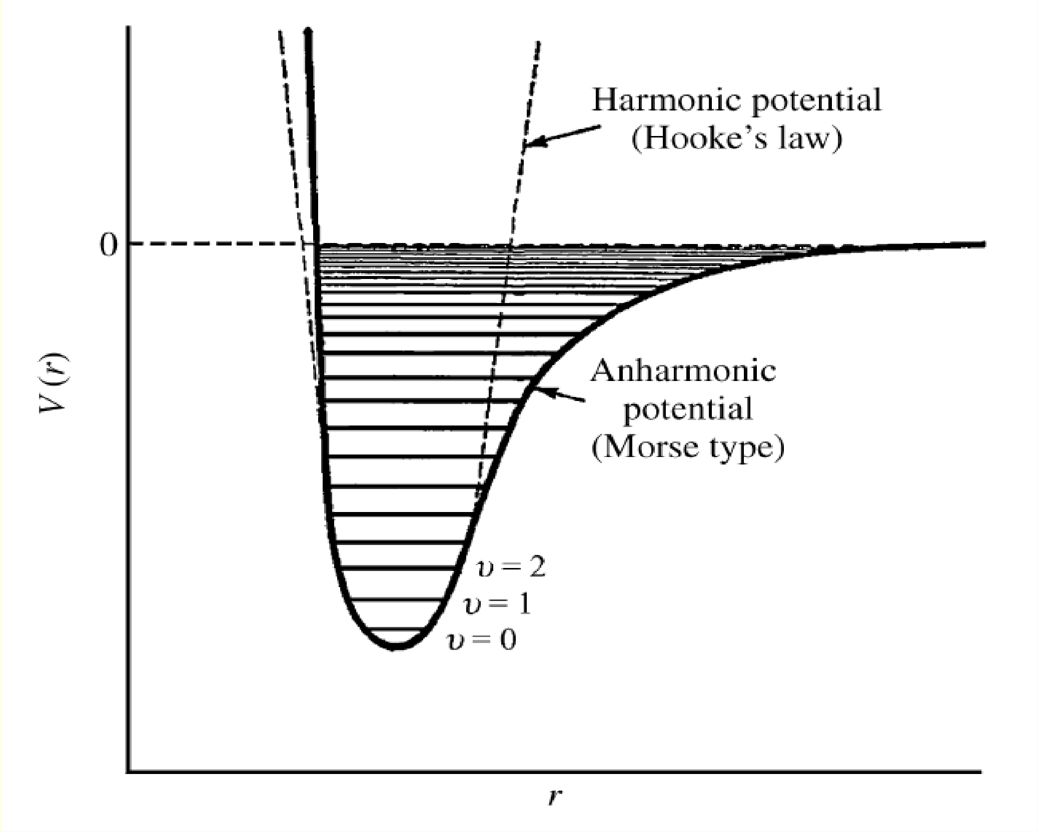
$$R_u = \frac{R_p + R_s}{2}$$

$$Spectrum = \frac{R_{p,film} + R_{s,film}}{R_{p,no\ film} + R_{s,no\ film}}$$

The Calculation



Vibrational Spectroscopy



$$V_{iv} = h\nu_i\left(v_i + \frac{1}{2}\right) + h\nu_i x_i\left(v_i + \frac{1}{2}\right)^2$$

Raw Spectra

- Bruker Vertex 70