Polarization Modulation Infrared Reflectance Absorption Spectroscopy (PMIRRAS)

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140908 How it Works
What is PMIRRAS and why do we use it?

• A surface sensitive spectroscopy technique
  • Less than 1 µm from surface
  • Estimated from $\frac{1}{4}$ or $\frac{1}{2}$ of the wavelength of the incident radiation

• Modulation of the source gives both S- and P-polarized light

• Only molecular vibrations with some fraction of a dipole moment perpendicular to the surface are active
  • molecular orientation

• Insensitive to atmospheric H$_2$O and CO$_2$ in the vapor phase
Instrument set up

IR Radiation → Mirror

Mirror → Polarizer

Polarizer → PEM

PEM → Sample

Sample → Mirror

Mirror → Detector
Polarizer and PEM

• Made of piezoelectric transducer which is glue to ZnSe crystal
• Piezo element converts periodic voltage to a periodic mechanical wave
  • Compresses or expands crystal
• Operates at 50 kHz resonant frequency
• Half-retardation occurs at
  • Compressed crystal (angle +45°)
  • Expanded crystal (angle -45°)

\[ I_D(\varphi) = \frac{I_S + I_P}{2} + \frac{I_P - I_S}{2} \cos \varphi \]

Instrument set up

- IR Radiation
- Polarizer
- PEM
- Sample
- Mirror
- Detector

Angles:
- 80°, 78°, 76°
Surface Selection Rules

• Electric Field
  • $E_p$: parallel to surface normal
    • Enhanced
  • $E_s$: perpendicular to surface normal
    • Cancelled

• Only occurs on metals
• Allows for orientational studies

Instrument set up

IR Radiation → Mirror → Polarizer → PEM → Sample → Mirror → Detector
Mean Squared Electric Field Strength (MSEFS)

- MSEFS for the $E_p$ is maximized around $80^\circ$ but drops off drastically from there
- MSEFS for $E_s$ is negligible at this angle.

Relevant Equations

• Law of reflection: $\theta_1^i = \theta_1^r$

• Snell’s Law of refraction: $n_2 \sin \theta_2^t = n_1 \sin \theta_1^i$

• Fresnel Equations for reflection ($r$) and transmission ($t$)

\[
\begin{align*}
    r_s &= \frac{E_{s1}^r}{E_{s1}^i} = \frac{\xi_1 - \xi_2}{\xi_1 + \xi_2} &
    r_p &= \frac{E_{p1}^r}{E_{p1}^i} = \frac{\hat{n}_2^2 \xi_1 - \hat{n}_1^2 \xi_2}{\hat{n}_2^2 \xi_1 + \hat{n}_1^2 \xi_2} \\
    t_s &= \frac{E_{s1}^t}{E_{s1}^i} = \frac{2 \xi_1}{\xi_1 + \xi_2} &
    t_p &= \frac{E_{p1}^t}{E_{p1}^i} = \frac{2 \hat{n}_2^2 \xi_1}{\hat{n}_2^2 \xi_1 + \hat{n}_1^2 \xi_2} \left(\frac{\hat{n}_1}{\hat{n}_2}\right)
\end{align*}
\]

where $\xi_j = \hat{n}_j \cos \theta_j^t = \sqrt{\hat{n}_j^2 - \hat{n}_1^2 \sin^2 \theta_1^t}$

Sample Preparation and Pre-Data collection

- Dry surface with nitrogen and place in cell with dry capillary
- Pick wavelength on PEM controller that will allow your peaks to be near the max of the Bessel function but still in the linear portion for easy base lining
- Alignment
  - Want to optimize to get the focal point on the surface
- Check Peak to Peak (between 2-10)
  - Under Experimental Setup- Bench
Sample Preparation and Pre-Data collection

• Check Phase
  • Plug in Phase cords from oscilloscope
  • Adjust using knob on top left of SSD box
    • Tip: Found best when the phase looks like that in the top image and the phase is at 5-510

• Check Bessel Function
  • Move Switch from local and Sum to Ext and Diff
  • Check “External A” in SST menu
  • Experimental Setup- Bench- Single Beam

• Before you start collecting, Check Dual Channel
  • Want A channel to be larger than B by adjusting gain knobs on SSD box
Wetting

• Take PMIRRAS and IRRAS of bare silver sample with nitrogen purge
  • IRRAS will stand for a background for when doing saturation
• Saturate cell
  • Turn off nitrogen
  • Allowing drops to be dispensed from capillary to bottom of the cell
    • Try not to squirt onto the sample for condensation layer studies
  • Take IRRAS spectra since vapor phase is the crucial state
  • Take PMIRRAS before wetting to analyze for condensation layer
• Start wetting
Ratio A and B channel to get spectra

- Once scan has finished, you need to ratio the spectra (SST menu)

\[
\frac{B}{A} = \frac{\Delta R}{< R >} = \frac{|R_p - R_s|}{(R_s + R_p)} \frac{1}{2}
\]

Base lining

• To get rid of the Bessel function
  • Process- Baseline Correct
  • Put points along Bessel- BE CAREFUL around peaks