Polarization Modulation Infrared Reflectance Absorption Spectroscopy(PMIRRAS)

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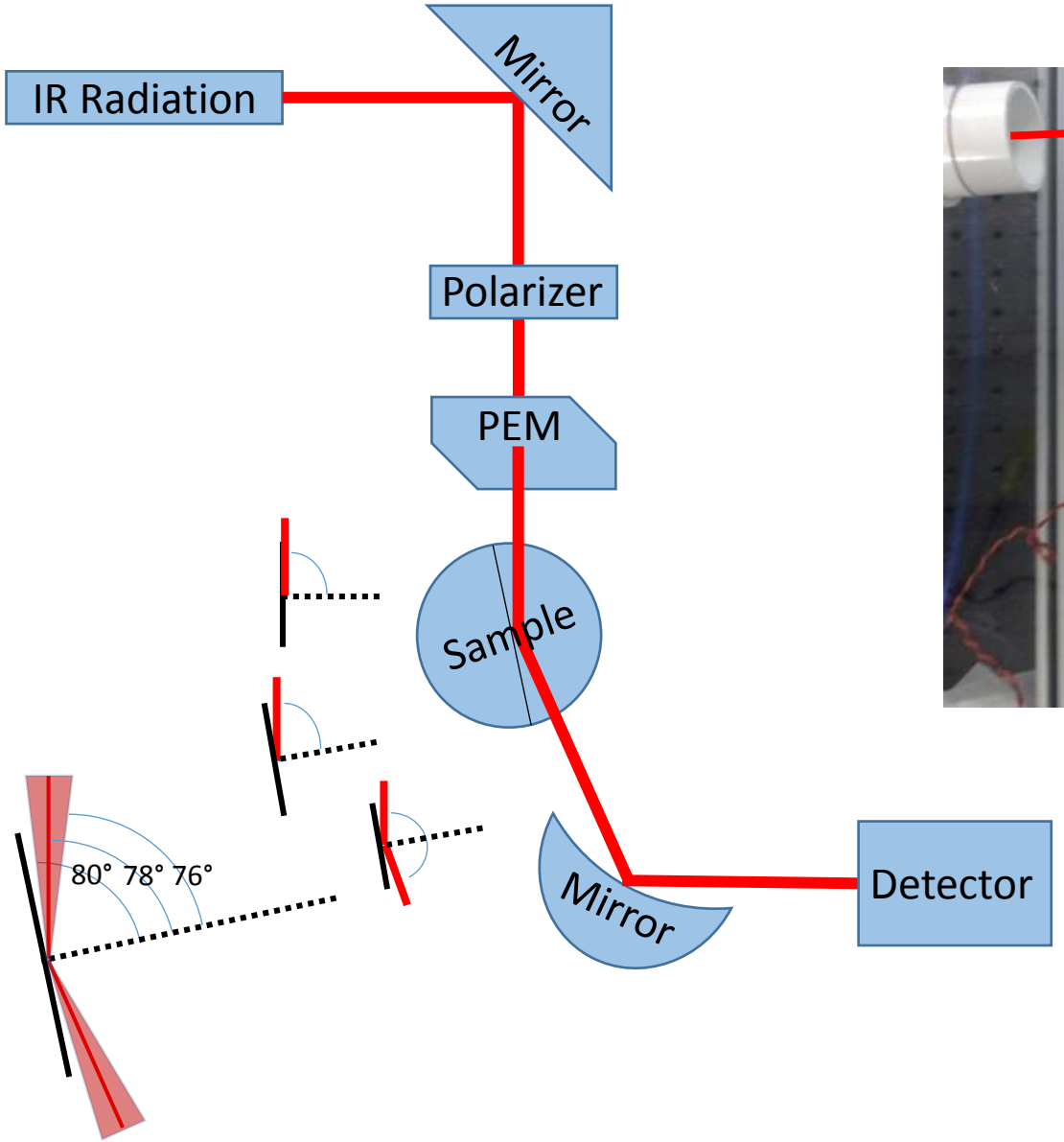
Shaw Group Meeting

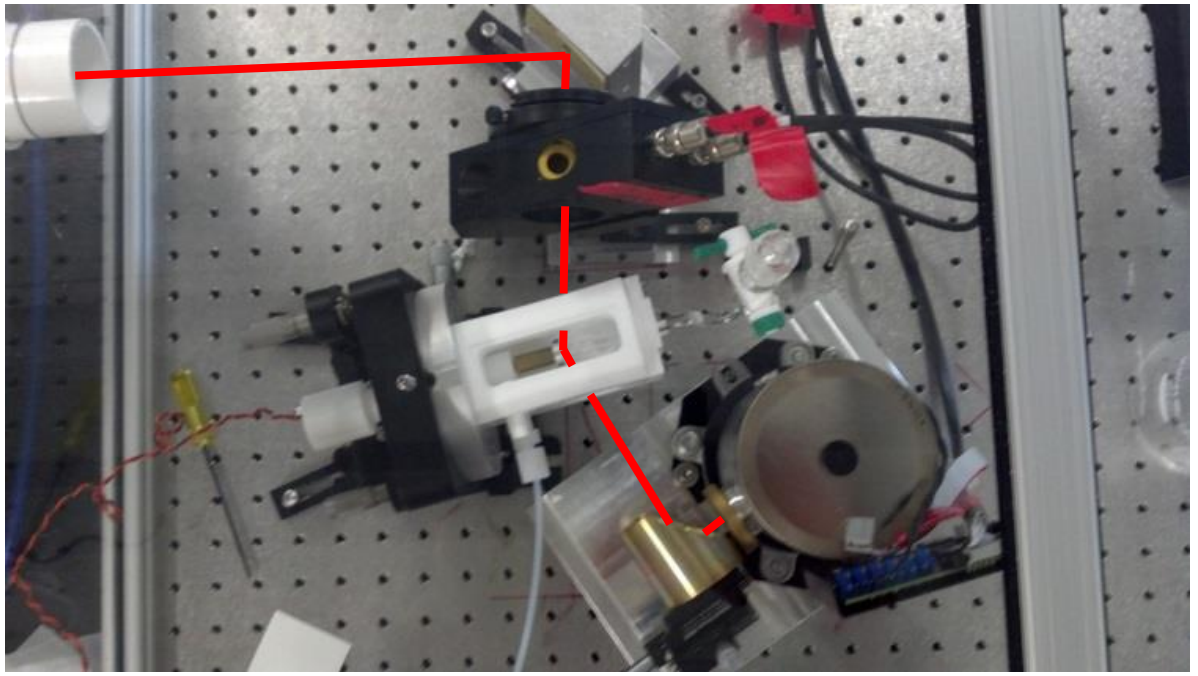
140908 How it Works

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_2O and CO_2 in the vapor phase

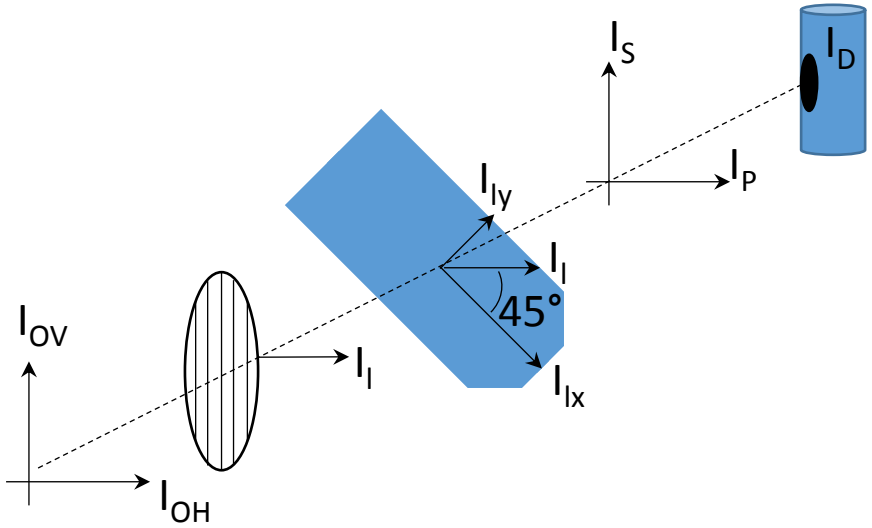
Instrument set up





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°)



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

Zamlynny, V.; Lipkowski, J., In *Advances in Electrochemical Science and Engineering*, WILEY-VCH: Weinheim, 2006.

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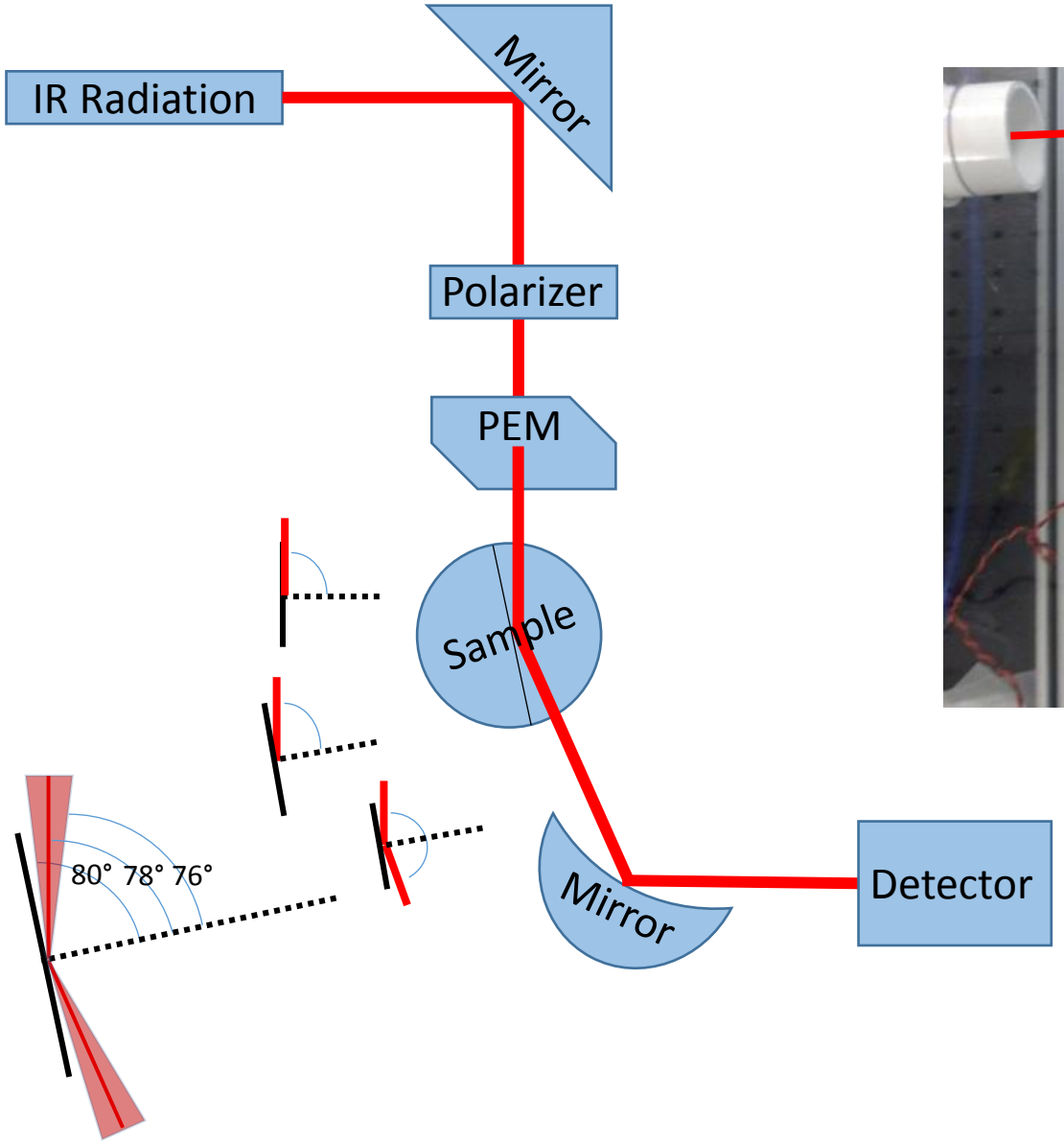
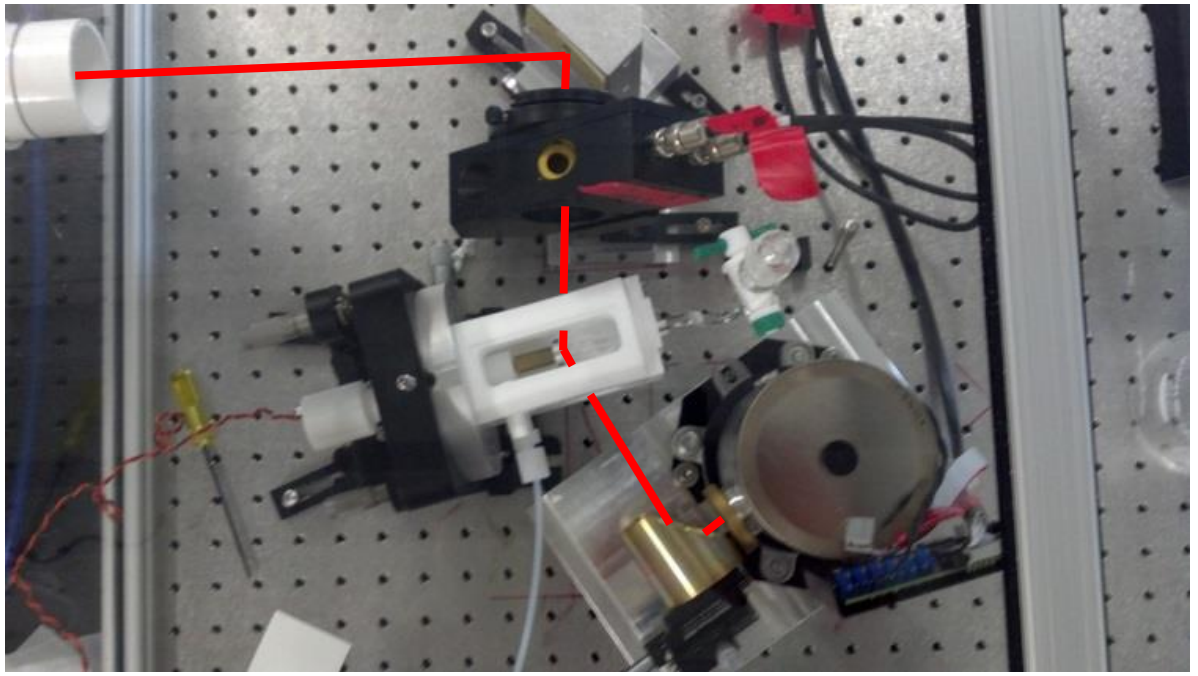
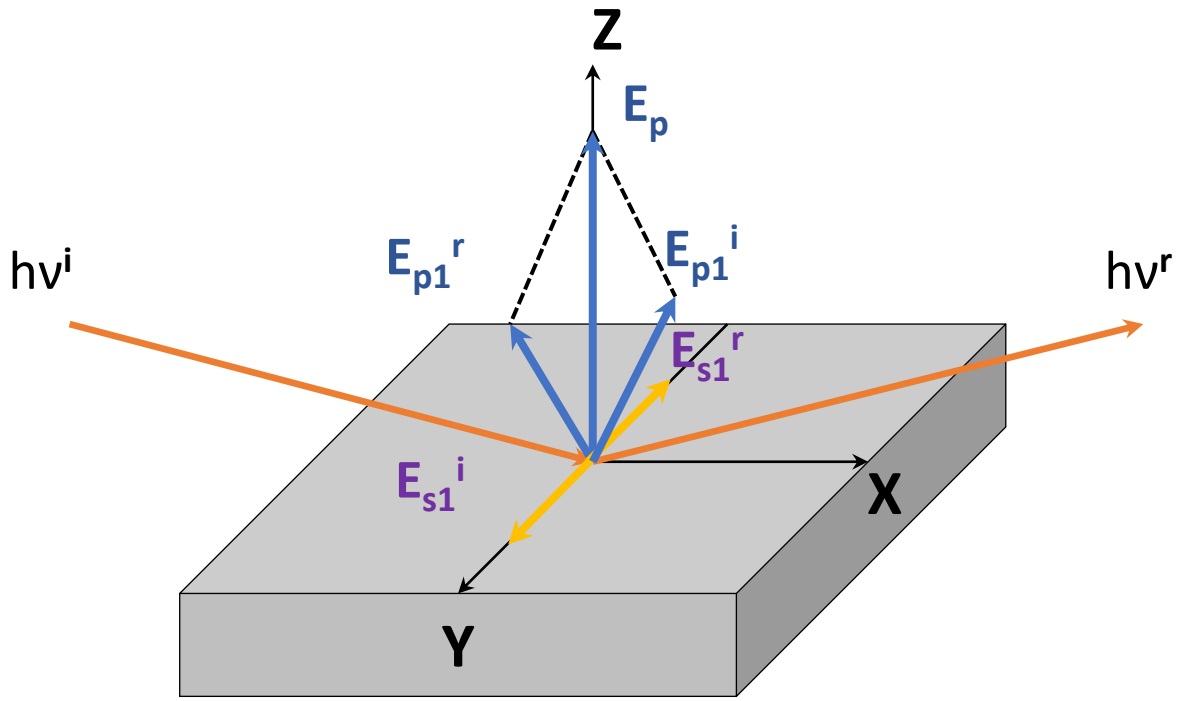




Surface Selection Rules

- Electric Field
  - E_p : parallel to surface normal
    - Enhanced
  - E_s : perpendicular to surface normal
    - Cancelled
- Only occurs on metals
- Allows for orientational studies



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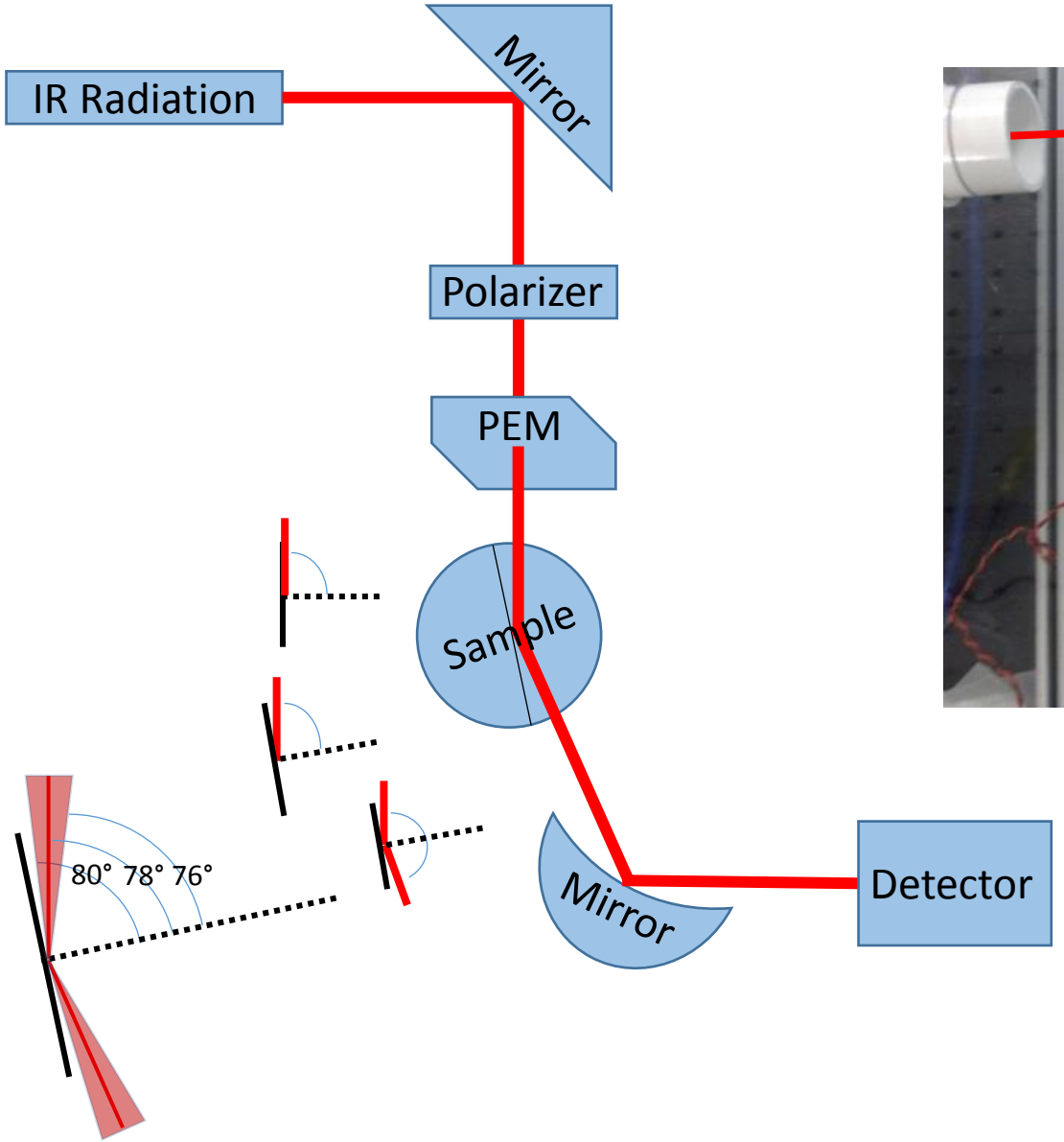
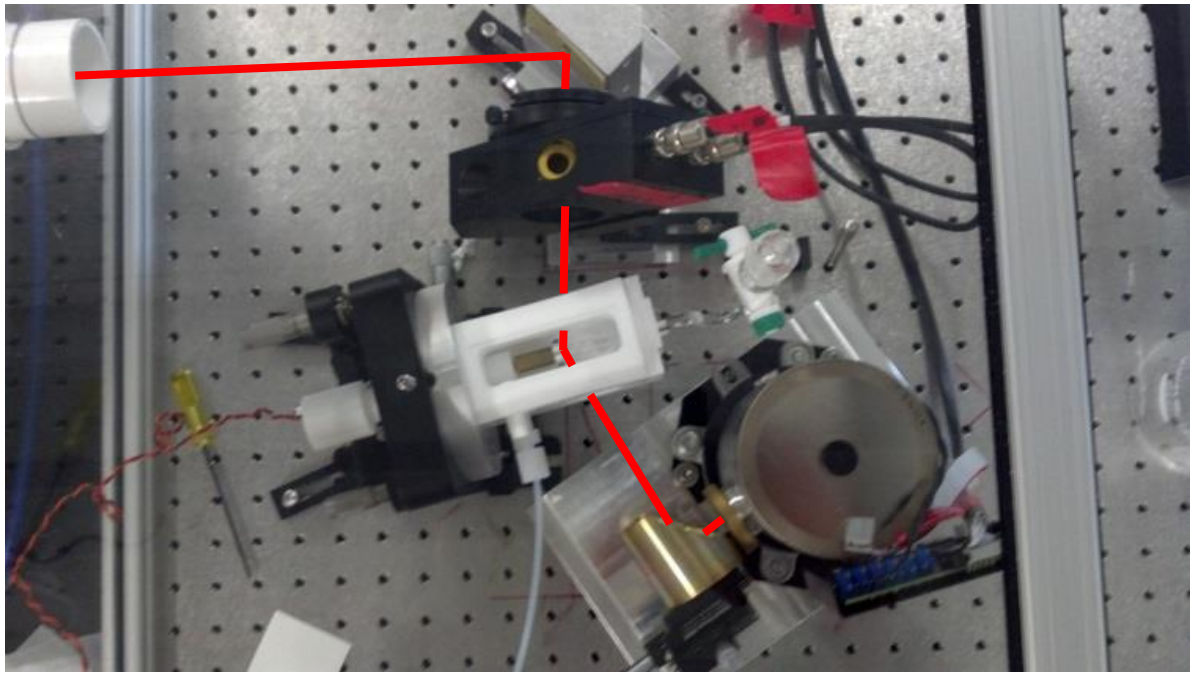
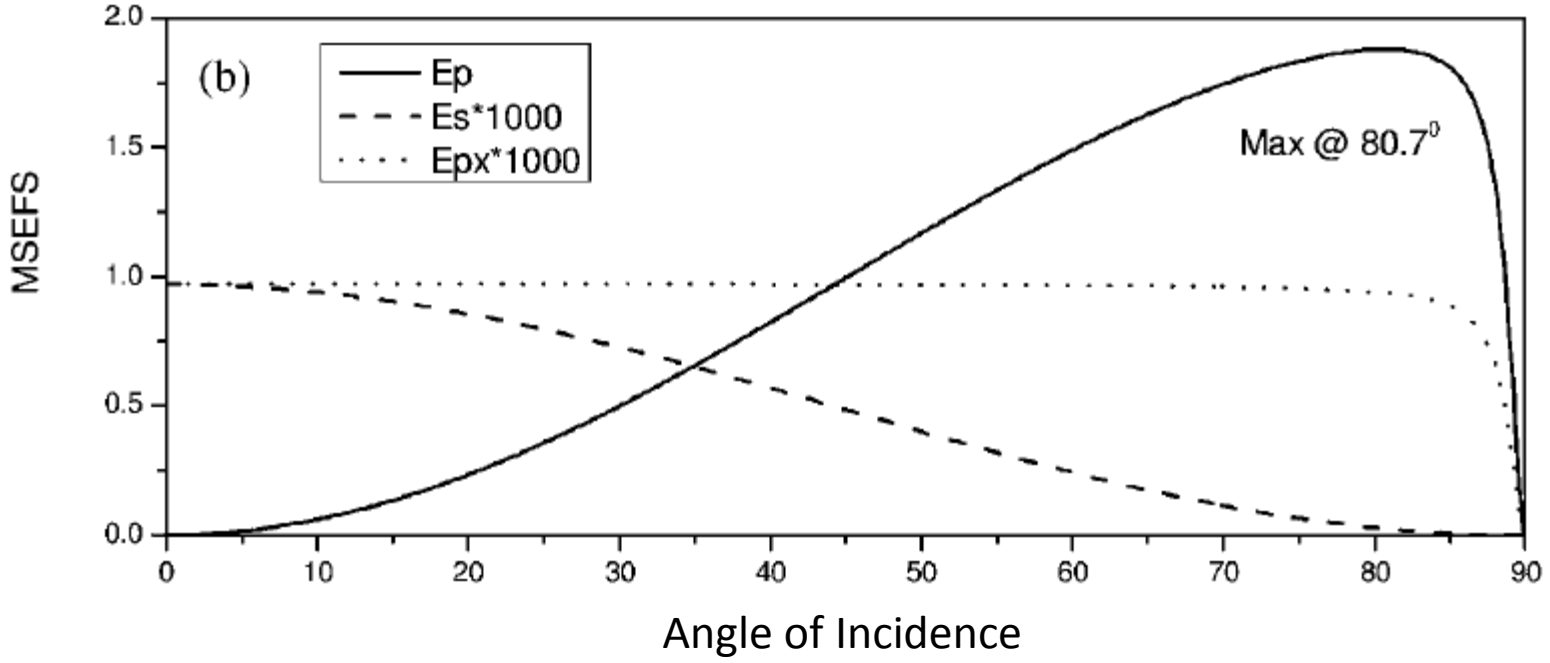
Instrument set up

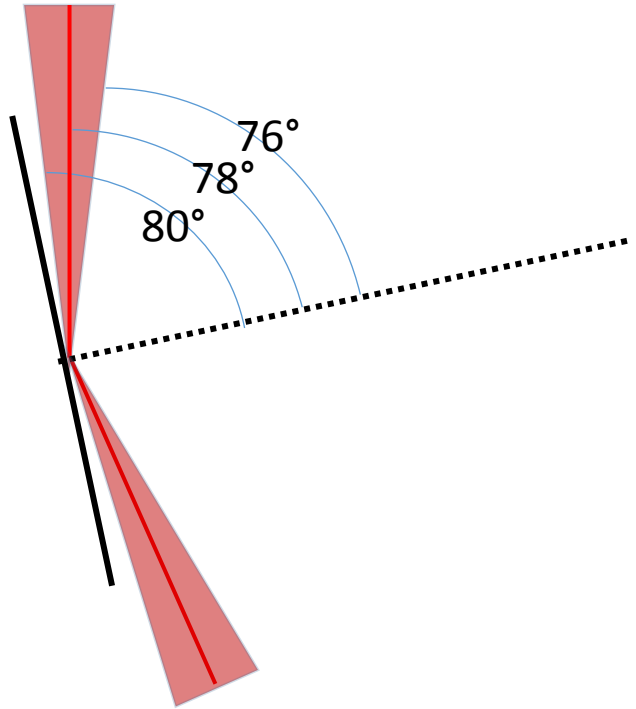




Mean Squared Electric Field Strength (MSEFS)

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





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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)

$$r_s = \frac{E_{s1}^r}{E_{s1}^i} = \frac{\xi_1 - \xi_2}{\xi_1 + \xi_2} \qquad r_p = \frac{E_{p1}^r}{E_{p1}^i} = \frac{\hat{n}_2^2\xi_1 - \hat{n}_1^2\xi_2}{\hat{n}_2^2\xi_1 + \hat{n}_1^2\xi_2}$$

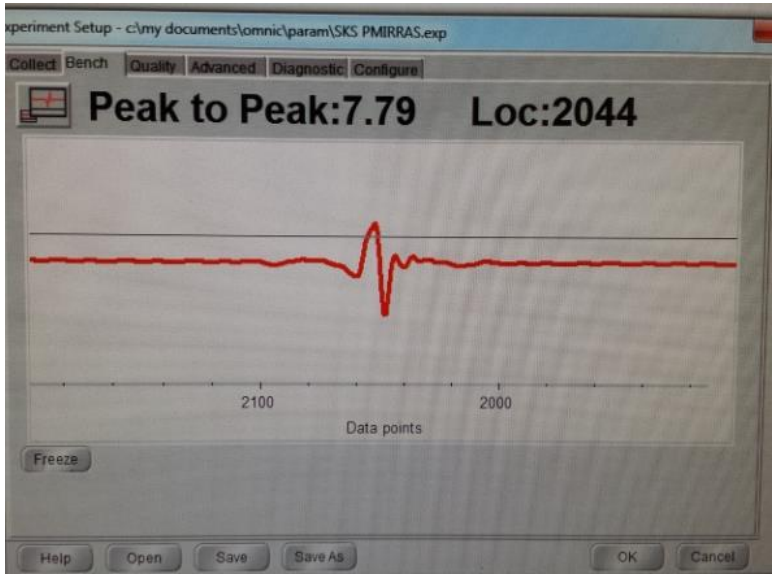
$$t_s = \frac{E_{s1}^t}{E_{s1}^i} = \frac{2\xi_1}{\xi_1 + \xi_2} \qquad t_p = \frac{E_{p1}^t}{E_{p1}^i} = \frac{2\hat{n}_2^2\xi_1}{\hat{n}_2^2\xi_1 + \hat{n}_1^2\xi_2}\left(\frac{\hat{n}_1}{\hat{n}_2}\right)$$

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

Zamlynny, V.; Lipkowski, J., In *Advances in Electrochemical Science and Engineering*, WILEY-VCH: Weinheim, 2006.

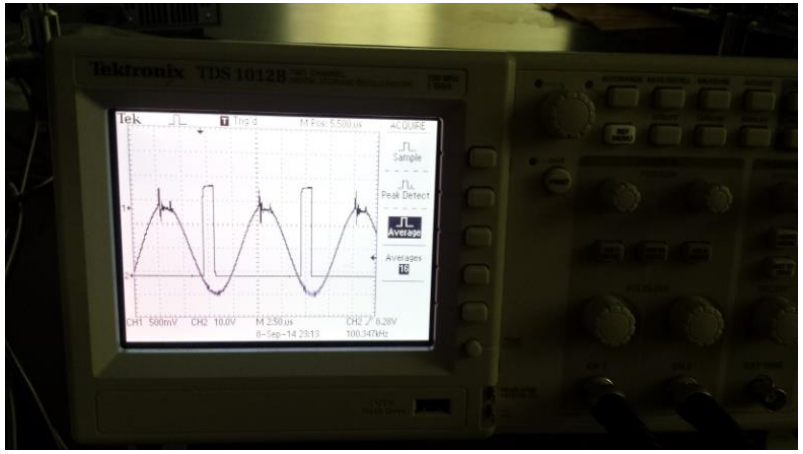
Sample Preparation and Pre-Data collection

- 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



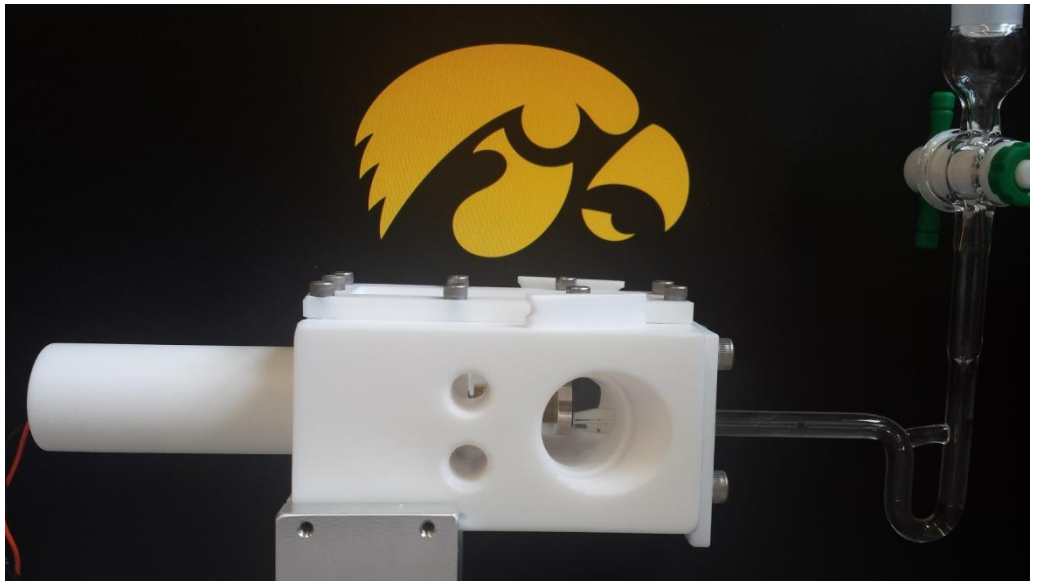
Sample Preparation and Pre-Data collection

- 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

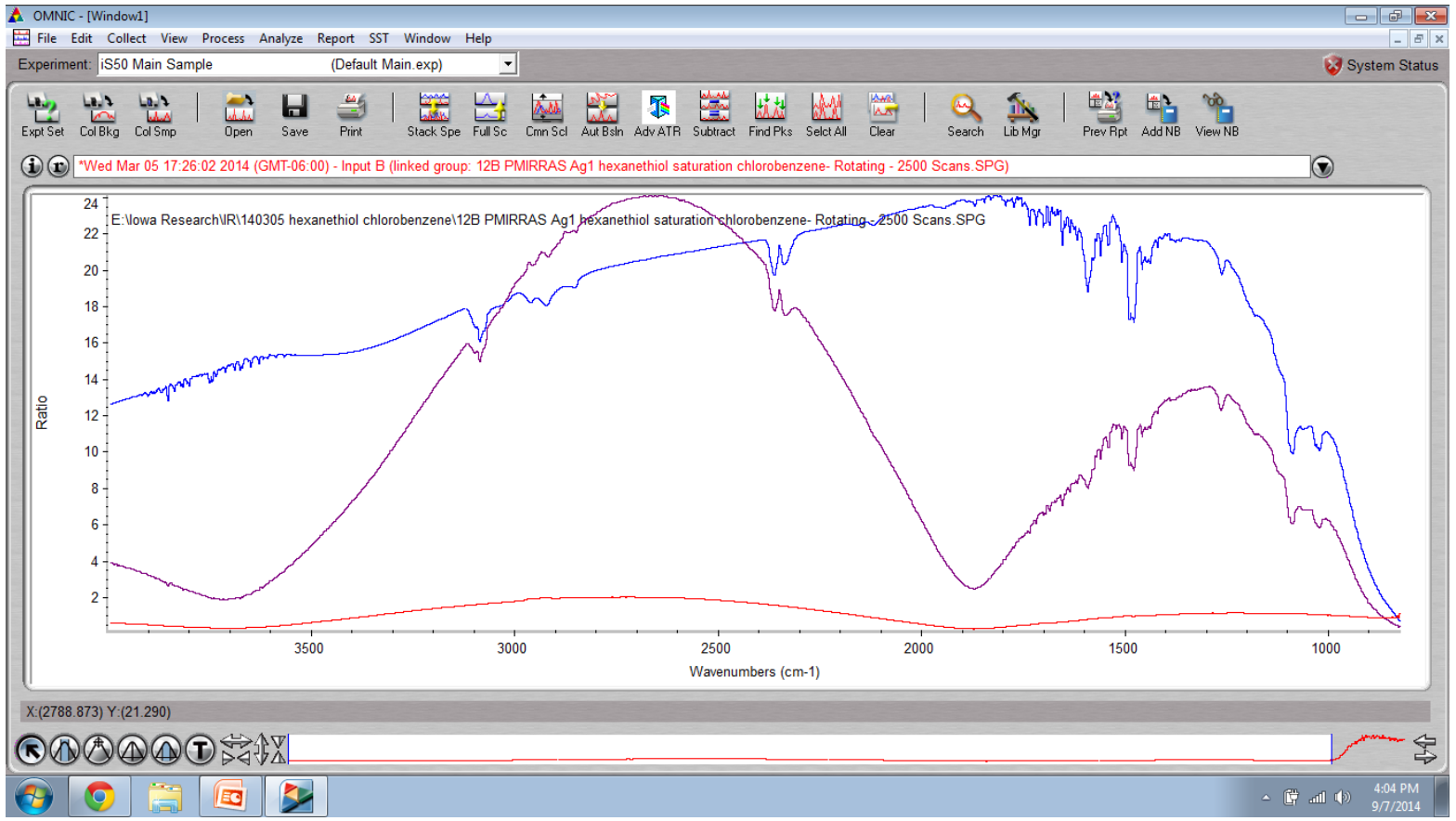
- Take PMIRRAS and IRRAS of bare silver sample with nitrogen purge
  - IRRAS will stand for a background for when doing saturation
- Saturate cell
  - Turn off nitrogen
  - Allowing drops to be dispensed from capillary to bottom of the cell
    - Try not to squirt onto the sample for condensation layer 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)

$$\frac{B}{A} = \frac{\Delta R}{< R >} = \frac{\left| R_p - R_s \right|}{(R_s + R_p)/2}$$



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Base lining

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