THE UNIVERSITY OF IOWA

How to do IRRAS & PMIRRAS for in-situ Spectro-electrochemical studies

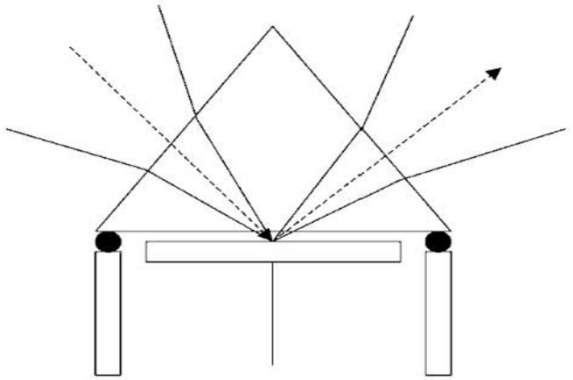
Ramin O. Seyedlar
Shaw Group

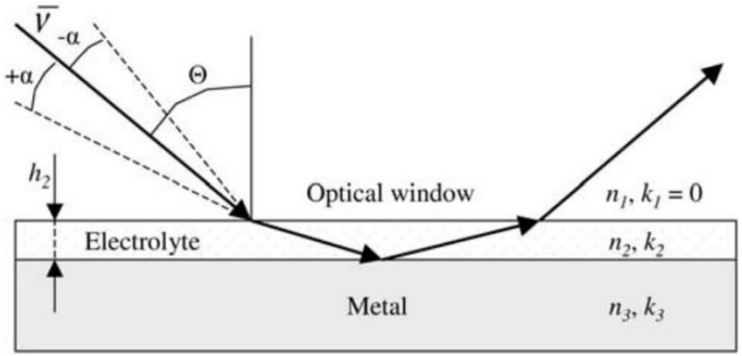
How it works

10.27.2020

What is Infrared Reflectance Absorption Spectroscopy (IRRAS)?

- An optical technique used to study thin films (often submonolayer) adsorbed on the reflective substrates (metals)
- Measuring the change in the reflectance spectrum of the substrate that accompanies adsorption (We need a Background spectrum)
- Only those vibrational modes that have a component of their dipole change prependicular to the surface can be detected
- Various acronyms IRAS,IRRAS, RAIRS
- Inadequate for studies less than 600 cm^{-1} (because of the light source)

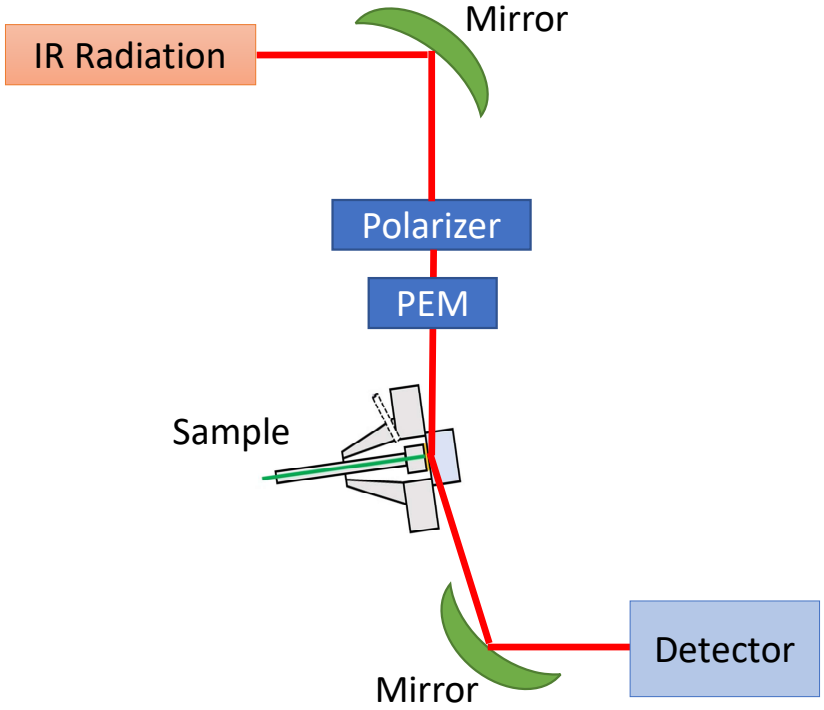


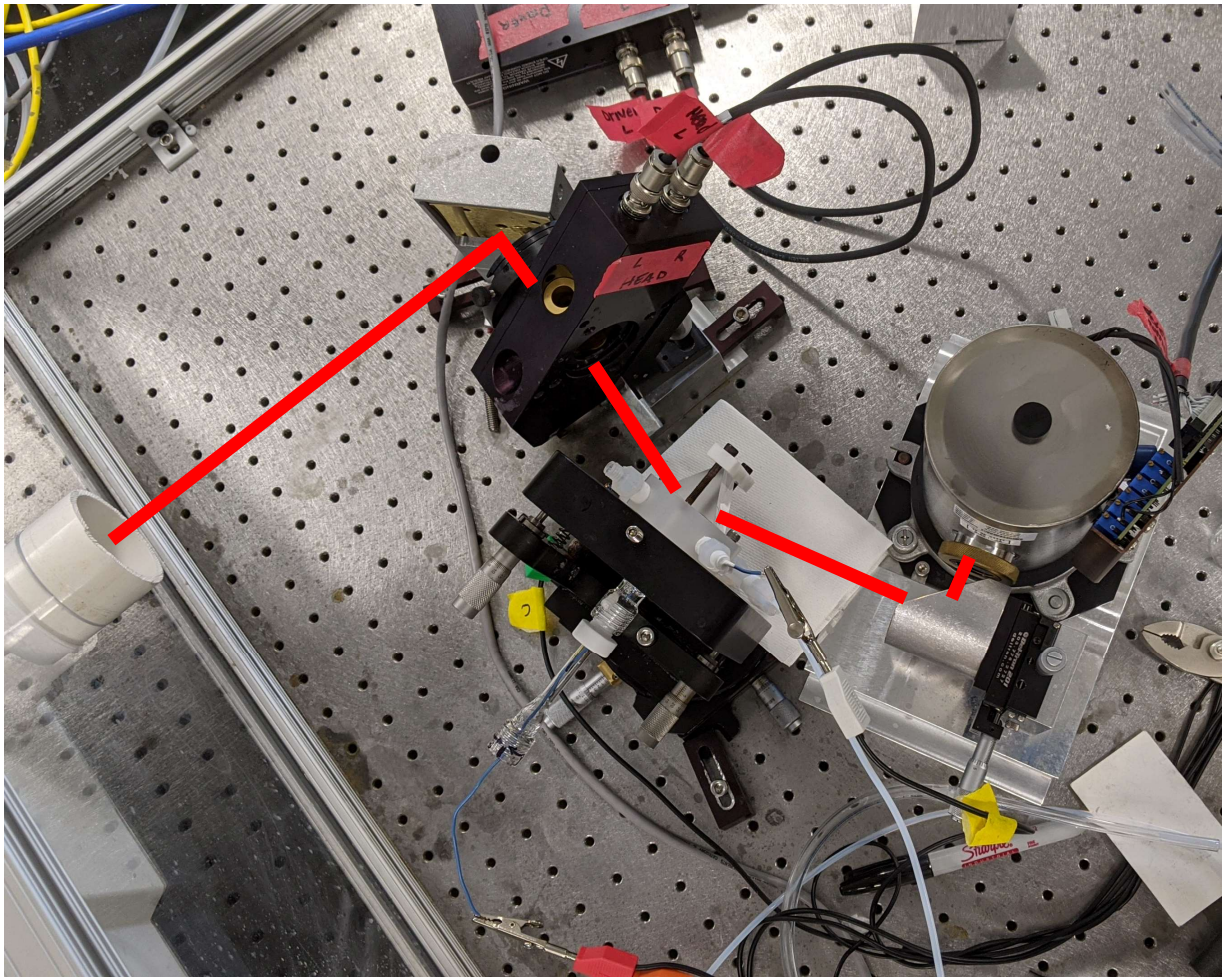


γ the wavenumber, α convergence, θ angle of incidence, n refractive index, k attenuation coefficient, h thickness

Hollins, Peter. "Infrared reflection–absorption spectroscopy." *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation* (2006).
Zamlynny, V.; Lipkowski, J., In *Advances in Electrochemical Science and Engineering*, WILEY-VCH: Weinheim, 2006.

Instrument set up





What happens on the surface?

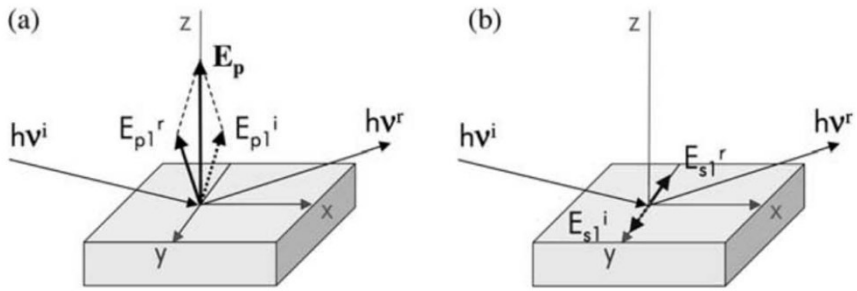
- Electric Field

  E_p : parallel to plan of incidence
  Enhanced

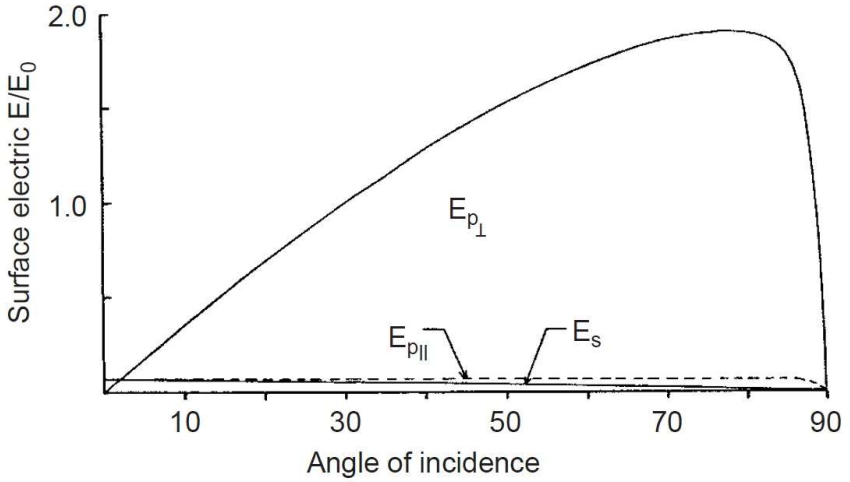
  E_s : perpendicular to plan of incidence
  Cancelled

- To maximize sensetivity, the reflection is

usually performed at grazing incidence angle (~78- 80°)



IR beams at the air/gold interface for a) p-polarized light and b)s-polarized light



Electric fields relative to the incident field E_0 for infrared radiation incident on a metal with optical constants appropriate to copper at 2000 cm^{-1} (n=3; k=30)

Ep_{II} and Ep_1 are the components parallel and perpendicular to the surface from p-polarized radiation

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

Relevant Equations

Generic equation for measuring intensity for an absorption band in IRRAS

$$A = \int_{\tilde{\nu}} \ln\left(\frac{R_1}{R_2}\right) d\tilde{\nu}$$

R_1 and R_2 are respectively the surface reflectivities in the absence and presence of the adsorbate, and γ represents wavenumber

For a submonolayer film with the dipoles oriented perpendicular to the surface

$$A = \frac{1}{4\pi\varepsilon_0} \frac{4\pi^2 n_s \tilde{\nu}_p \mu^2 \sin\theta \tan\theta}{c\hbar}$$

n_s is the adlayer density (molecules per unit area), γ_p the wavenumber of the peak absorbance and μ the dynamic dipole

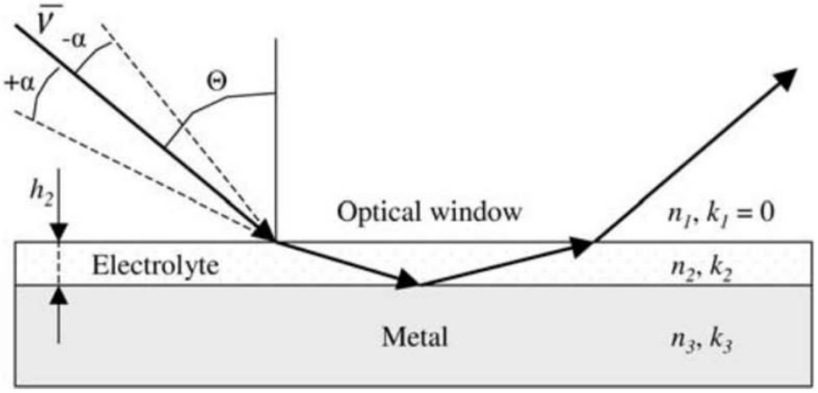
Zamlynny, V.; Lipkowski, J., In *Advances in Electrochemical Science and Engineering*, WILEY-VCH: Weinheim, 2006.

What is Polarization Modulation Infrared Reflectance Absorption Spectroscopy(PMIRRAS)?

- Less than 1 μm from surface
- 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

Advantages compared to IRRAS:

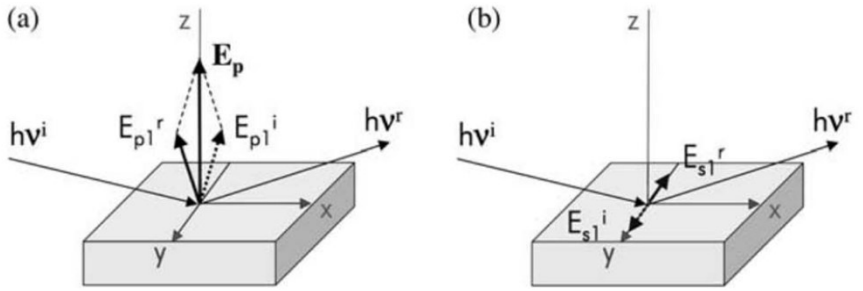
- Insensitive to atmospheric H_2O and CO_2 in the vapor phase



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

Surface Selection Rules

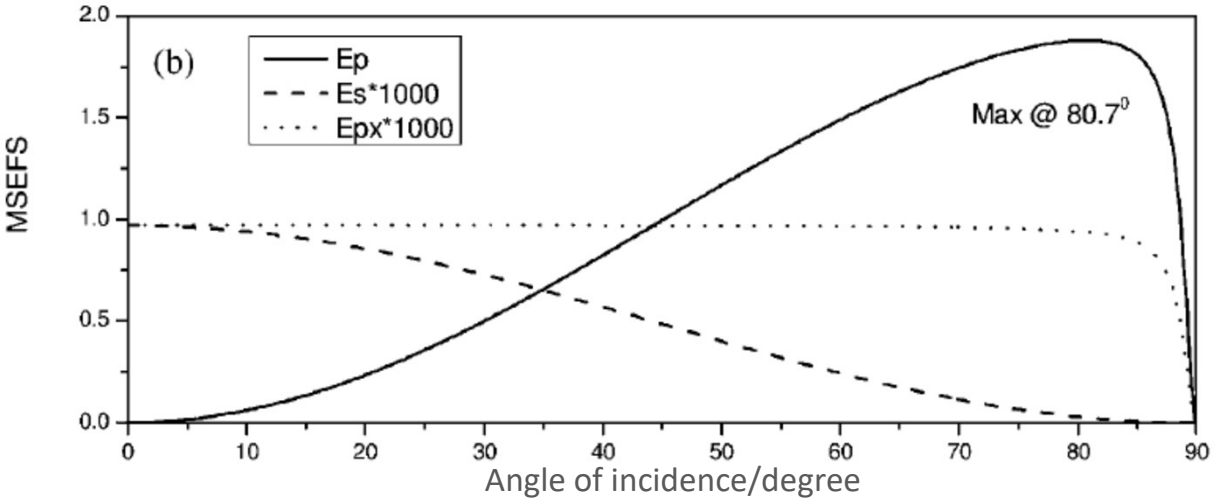
- S-polarized IR beam vanishes while the p-pol beam is enhanced
- First component of the modulated signal is insensitive to the film (being used as a background)
- The other component can be used to obtain the spectrum of the film



IR beams at the air/gold interface for a) p-polarized light and b)s-polarized light

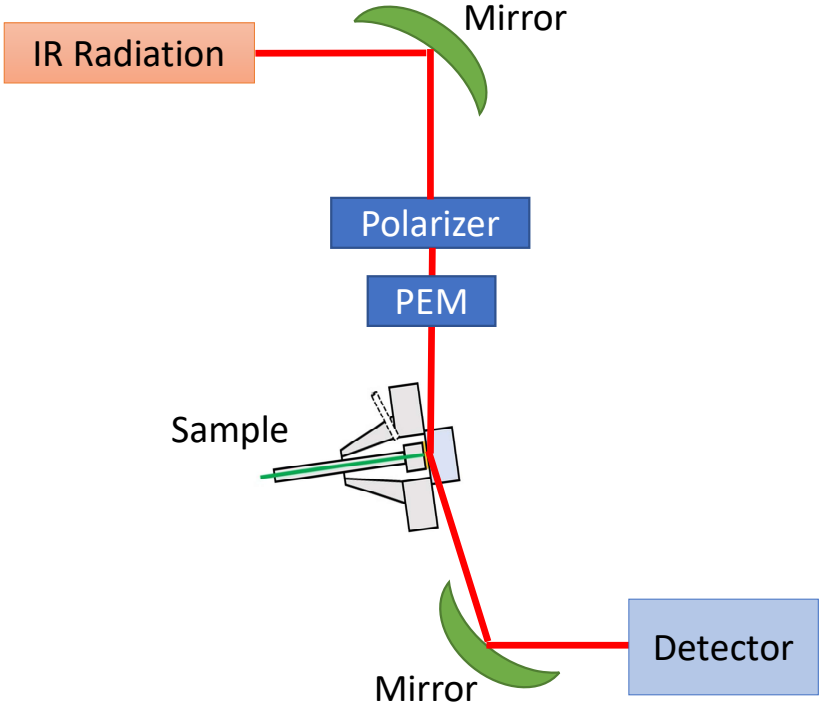
$$\frac{\Delta R}{\langle R \rangle} = \frac{|R_s - R_p|}{(R_s + R_p)/2}$$

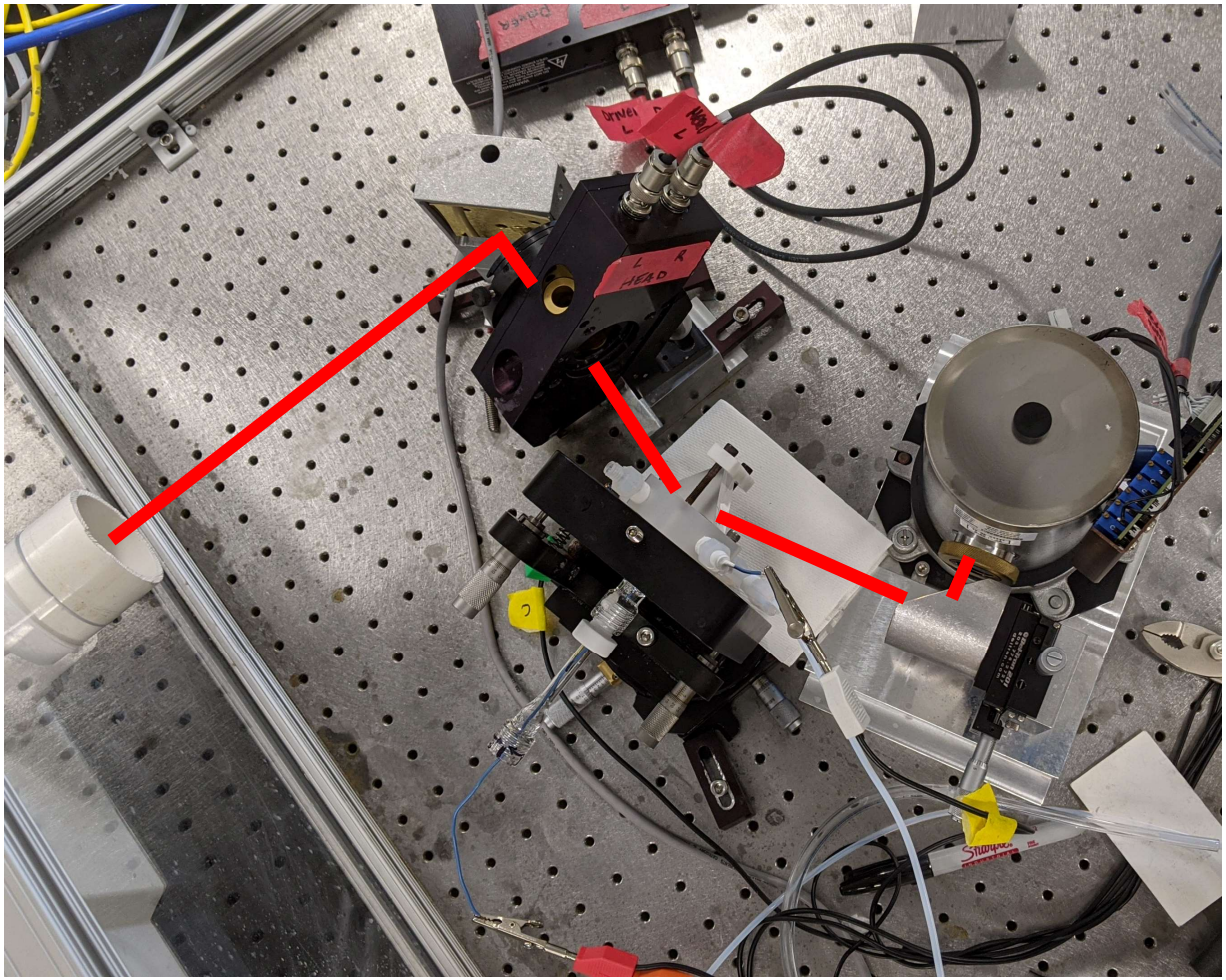
R_s and R_p: Reflectivities of the s- and p- components of the modulated infrared beam



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

Instrument set up



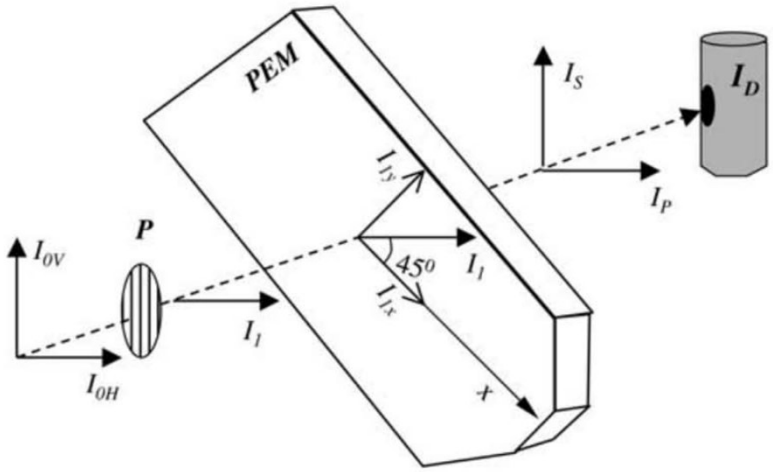


Polarizer and Photoelastic Modulator (PEM)

- Made of piezoelectric transducer which is glued 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.

Sample Preparation

- Mechanically polish working electrode to a mirror finish using 9.5, 3.0, 1.0, and 0.3 µm alumina powder slurry.
- Chemically polish the W.E.
  - Au & Pt by Piranha solution (H_2SO_4: H_2O_2 = 3:1)
  - Ag with following process:

    1- 5 min in H_2SO_4 then rinse

    2- 15 sec in $HClO_4$

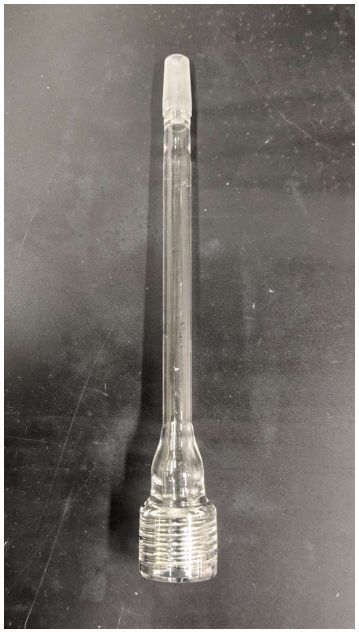
    3- 1 min in Chromic/HCl + Jig then rinse and sonicate

    4- 5 min in NH_4OH then rinse

    5- 5 min in H_2SO_4 then rinse

Parts of the Spec-e-chem cell

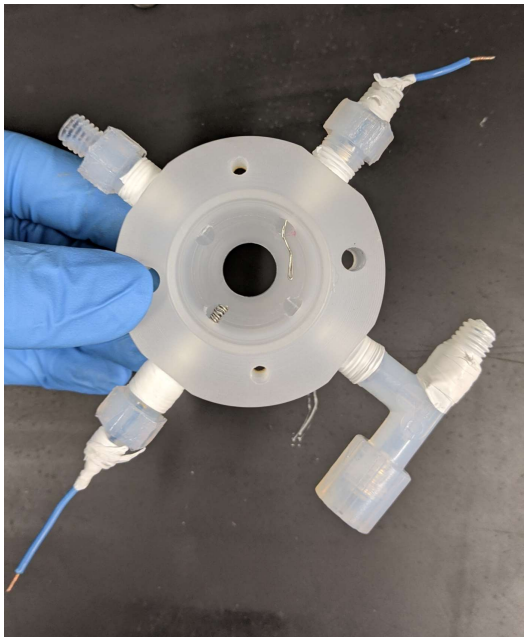
Kel-F bottom piece



Plunger

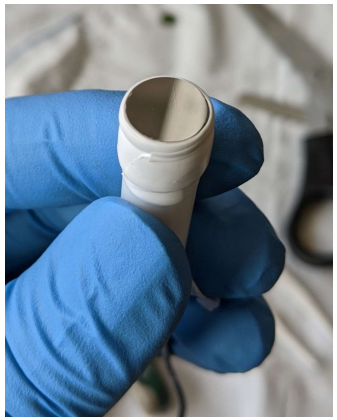
Glass cell

Threaded Kel-F vacuum adapter

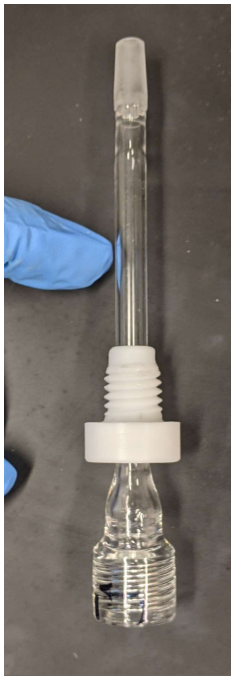


Kel-F base & the fittings

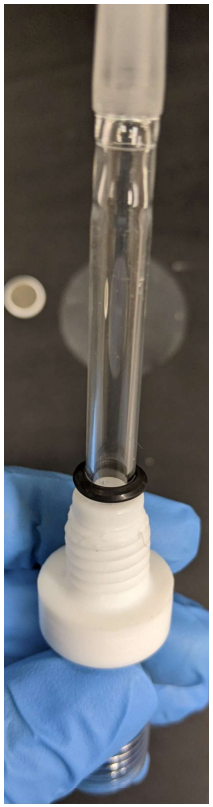
Assembling spec-e-chem cell



1. Wrap the W.E. to Kel-F bottom piece with Teflon tape

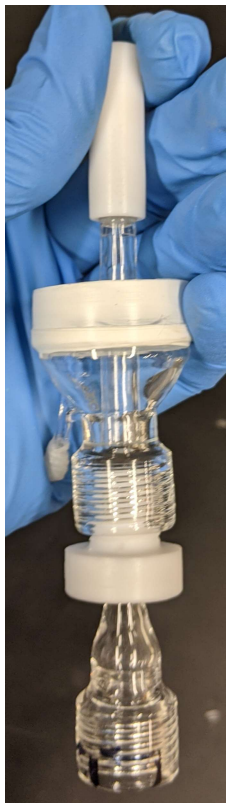


2. Attach threaded Kel-F vacuum adapter to the plunger



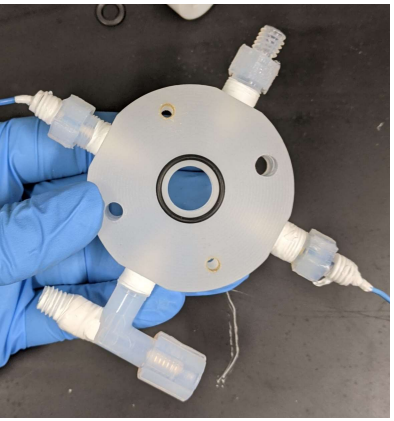
3. Put the rubber piece

4. Attach the glass cell & tighten it to the threaded Kel-F vacuum adapter with the rubber piece in between to seal it

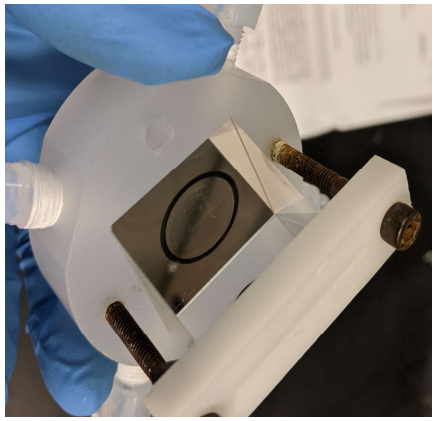


5. Attach the Kel-F piece to the end of the plunger

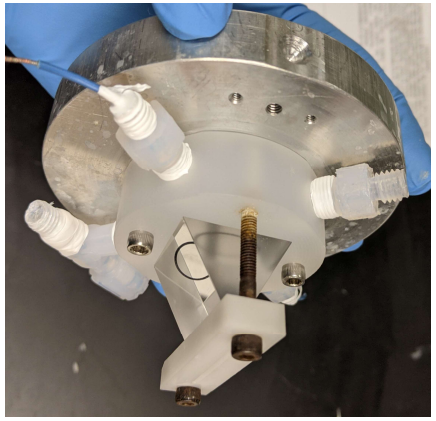
Assembling the Spec-e-chem cell



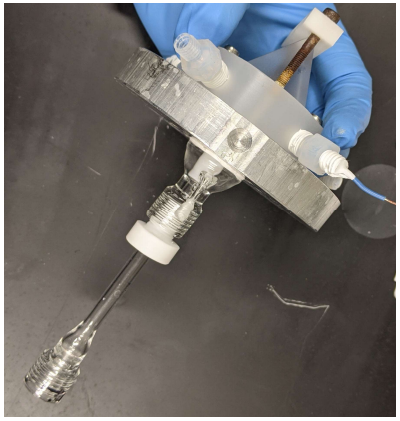
6. Attach R.E., C.E. and the fittings to the Kel-F base



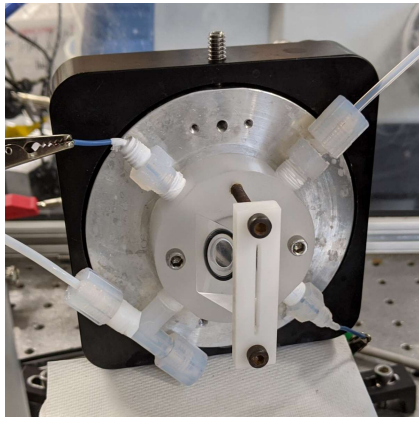
7. Screw in the prism with a rubber piece to the main Kel-F piece (make sure to use the appropriate rubber piece in between the prism). **CaF_2** Prism (transmission range 76900-1100 cm^{-1})



8. Screw the Kel-F base to the metal base



9. Attach the glass cell and everything on it to the Kel-F base (make sure to use Teflon tape to seal it)



10. Attach the spec-e-chem cell to the base in the IR box (attach in and out gas line)

How to do IRRAS?

1- Pour in the detector with liquid N2 before starting the experiment (half an hour or an hour prior to the experiment)

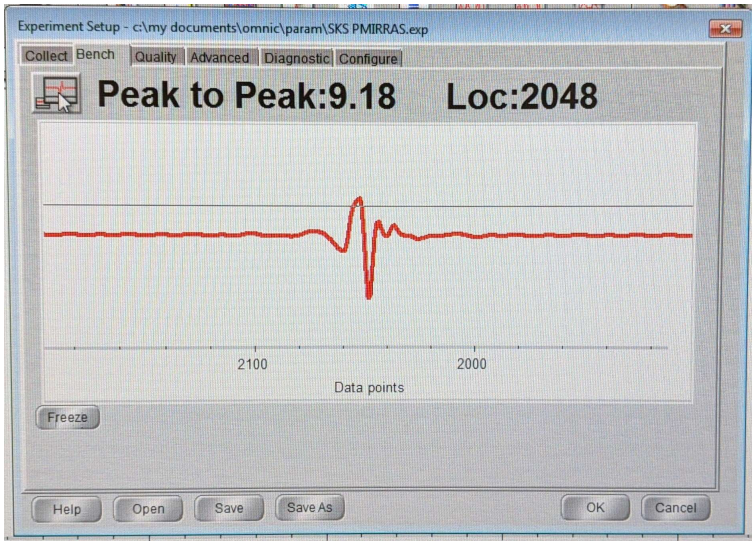
2- Alignment:

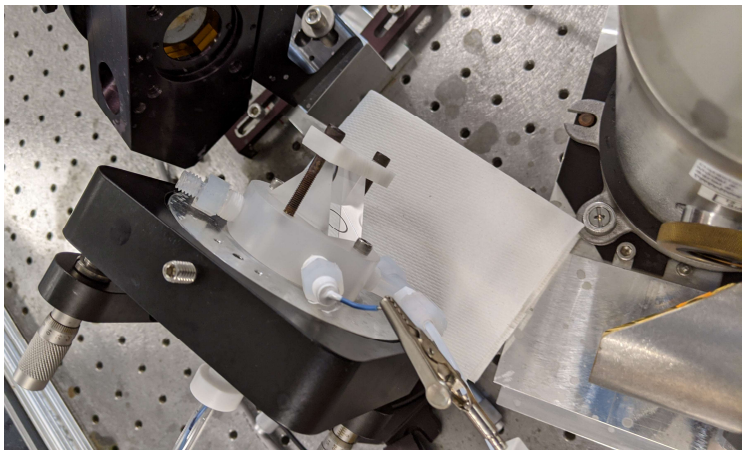
- Make sure to push the W.E. all the way until it touches the prism

- Get the focal point on the surface

- Get a Peak to Peak between 2-10 (Go to OMNIC/Experiment/SKS IRRAS/Expt Set/Bench/Peak to Peak

3- Collect a background of the dry cell (Click on Col Bkg)





How to do IRRAS?

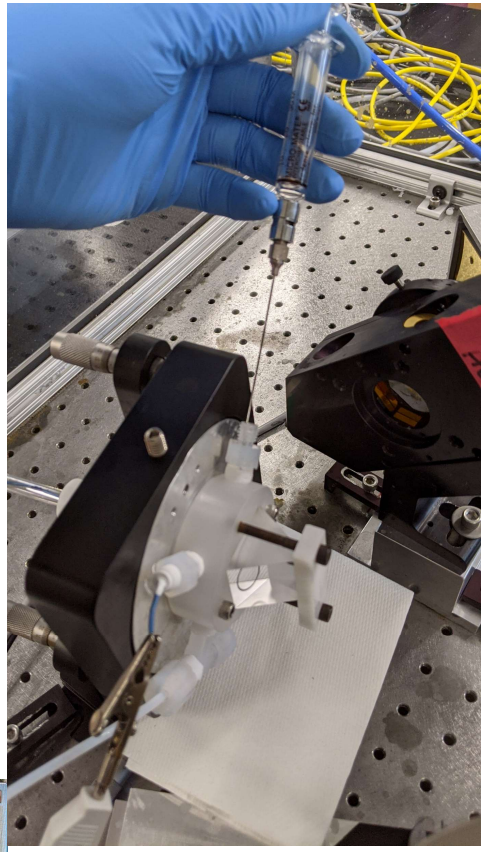
4- Inject the solution to the Spec-e-chem cell (make sure there are no bubbles forming on the surface of the W.E.)

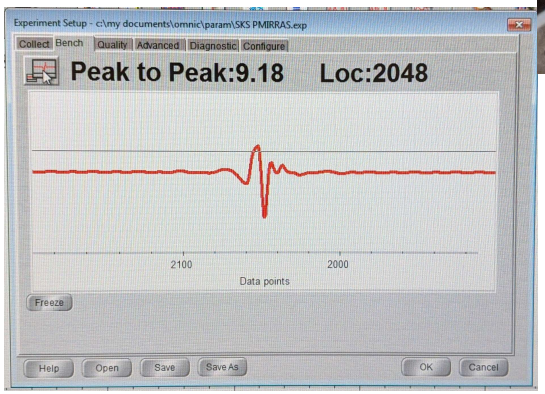
5- Check Peak to Peak again & align it if necessary

6- Check the connection for W.E., R.E., and C.E. (Ohmmeter) and connect them to the potentiostat

7- Collect sample (Go to Exp Set/Collect/Choose your Background data/OK/Col Smp)

8- Save (Click Save on the main page)





How to do PMIRRAS?

1- Cool down the detector

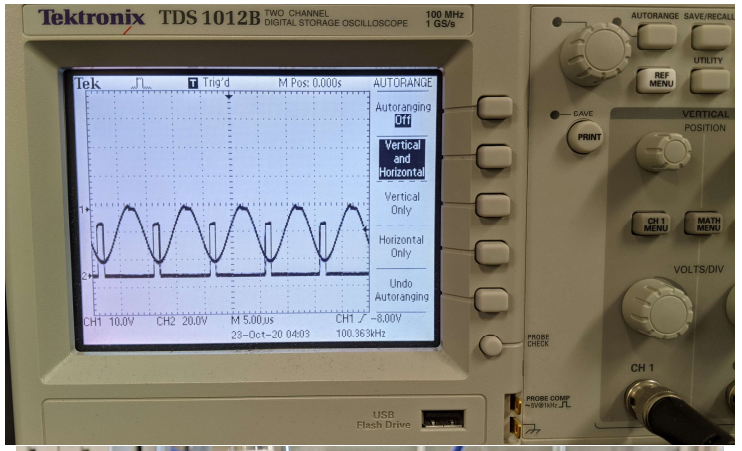
2- Alignment:

- Get the focal point on the surface
- Get a Peak to Peak between 2-10 (Go to OMNIC/Experiment/SKS PMIRRAS/Expt Set/Bench/Peak to Peak)

3- Check Phase (make sure PEM-100 Controller and SSD box are both turned on)

4- Plug in Phase cords from oscilloscope

5- Adjust using knob on top left of SSD box (Phase ADJ)



How to do PMIRRAS?

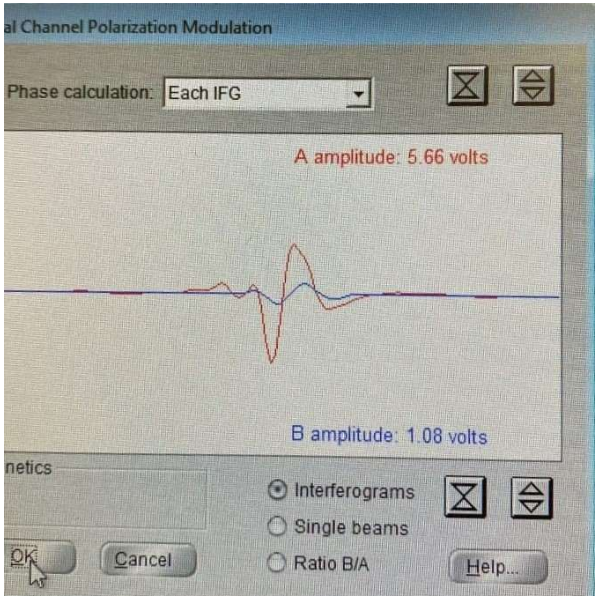
6- Check Dual Channel (Go to SST/Dual Channel Polarization Modulation)

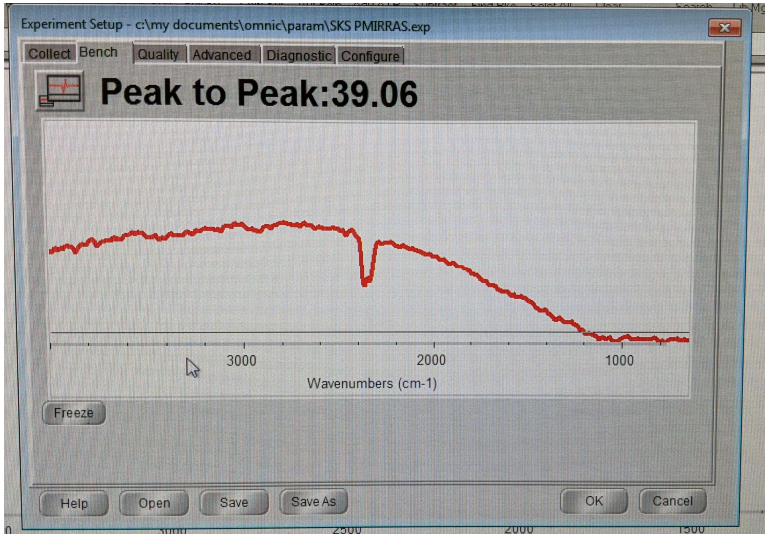
- Want A channel to be larger than B by adjusting (input &output) gain knobs on SSD box (B should be 50-70% of A)

7- Check Bessel Function

- Move Switch from local and Sum to Ext and Diff on the SSD box
- Check “External A” in SST menu
- Experimental Setup- Bench- Single Beam
- Pick a 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

8- Collect a sample of the dry cell (Click SSD/ /Dual Channel Polarization Modulation/Collect sample)





How to do PMIRRAS?

9- Inject the solution to the Spec-e-chem cell

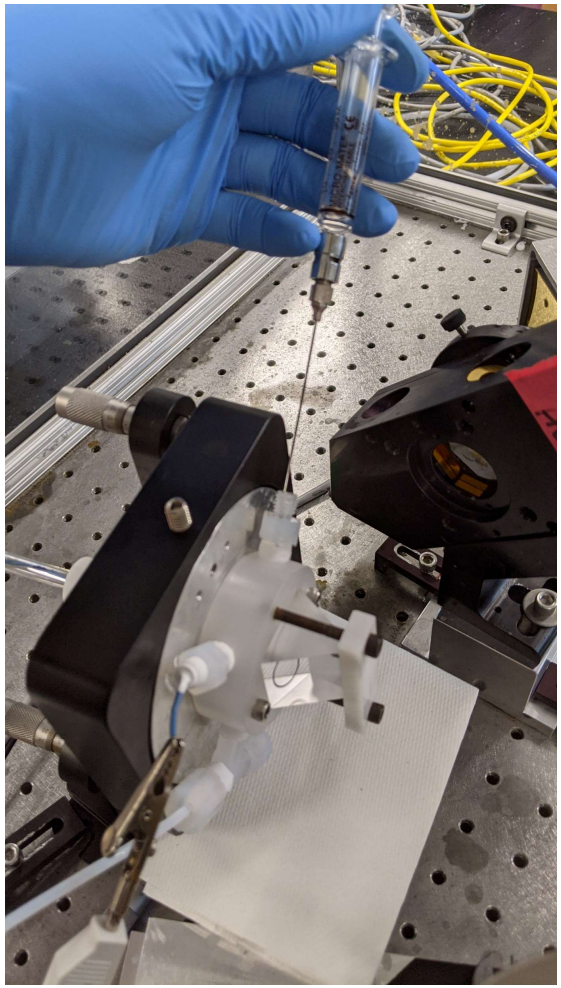
- make sure there are no bubbles forming on the surface of the W.E.

10- Check the connection for W.E., R.E., and C.E. and connect them to the potentiostat

11- Check Peak to Peak again & align it if necessary

12- Repeat steps 3 to 7

13- Collect sample



Ratio A and B channel to get spectra & Save

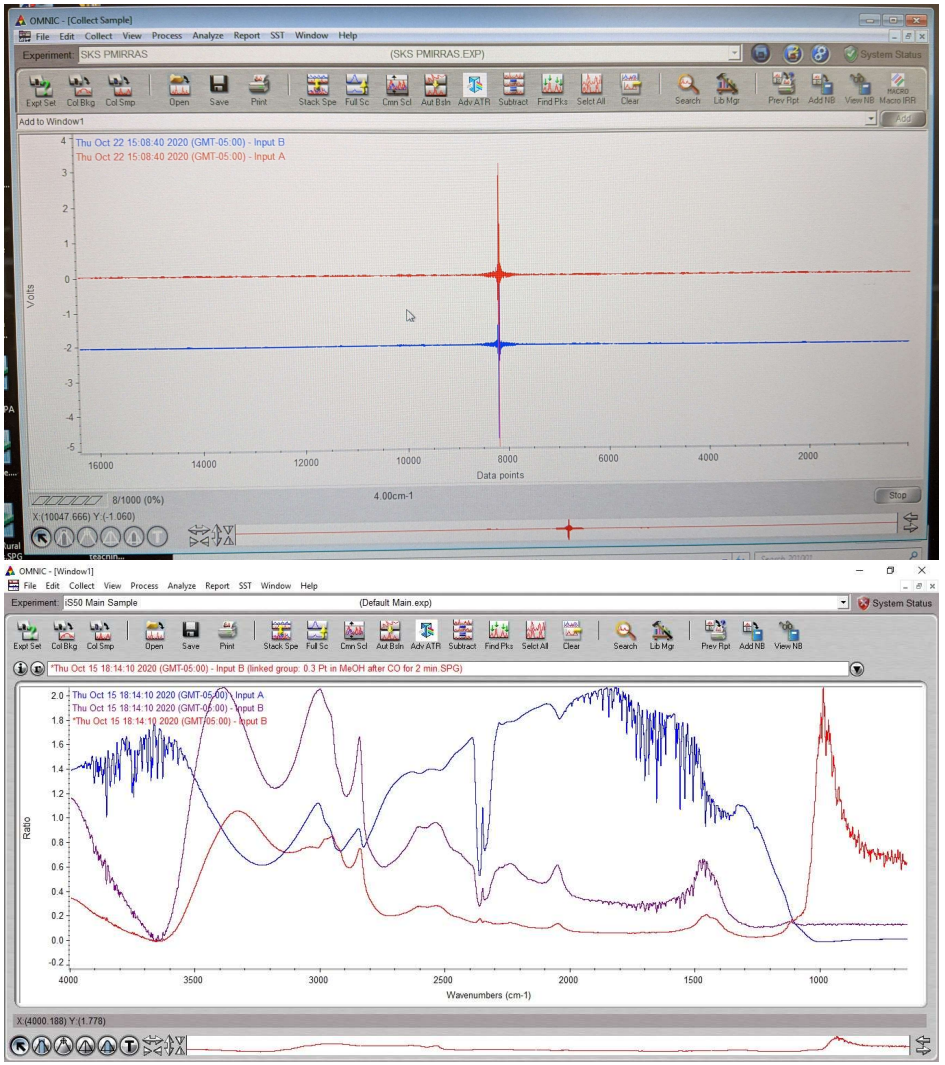
14- Once done click Yes to add a window

15- Check Ratio Spectra & make sure B is over A, then click Yes.

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

16- Save (File/Save as/Browse/Save)

17- Group save (Select all/File/Save Group/Browse/Save)



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

Base lining

To cancel the Bessel function(Go to Process/Baseline Correct)

- Put points along Bessel
- Be careful around peaks (do not go into peaks, just the very first point where peak starts and the end point of the week)