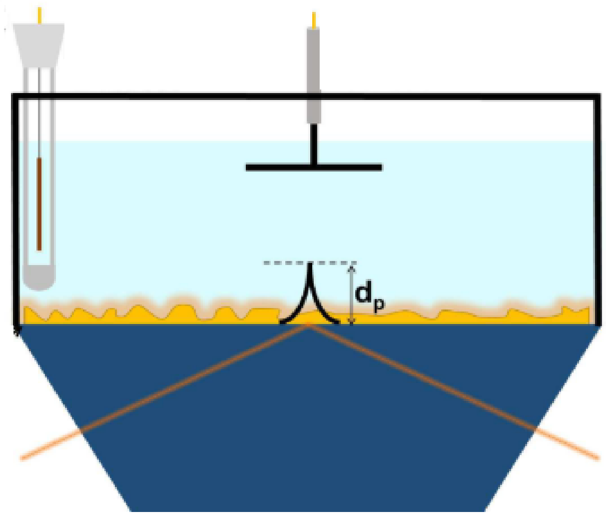
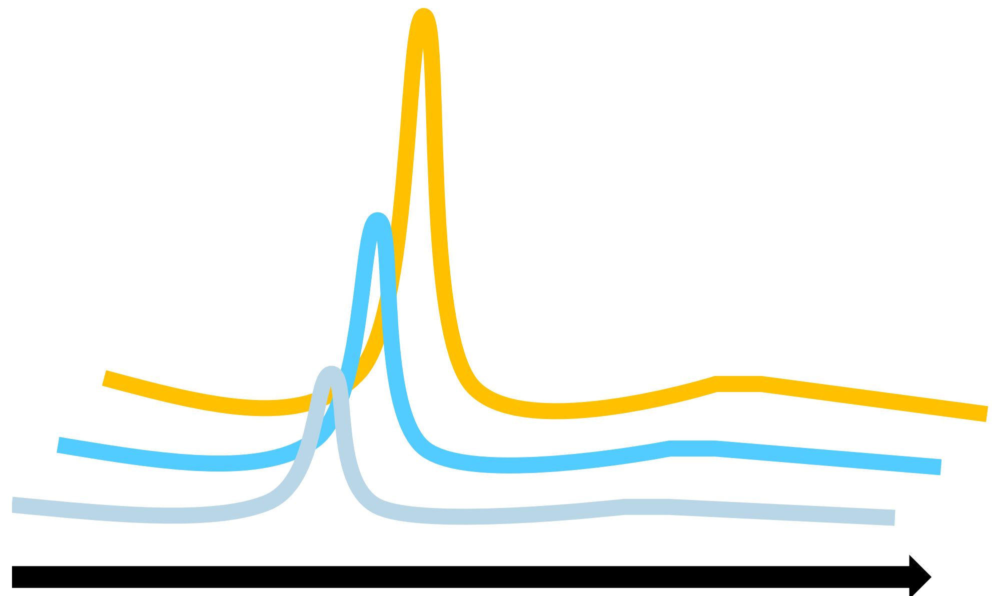
Where Electricity and Light Meet: The Power of Infrared Spectroelectrochemical Techniques in Observing Surface Chemistry





NACK webinar, April 21st
Asbury Group, Yujia Zhai (Jerry), 4th year graduate student

PennState

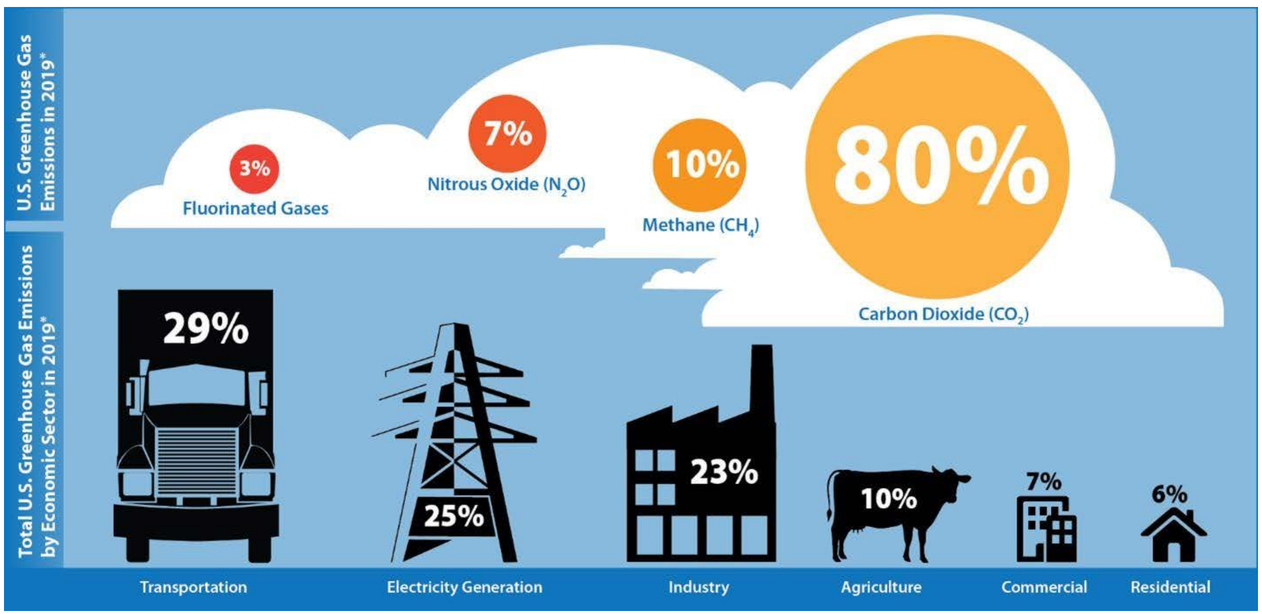
In 100 years, humans will have little reserves of fossil fu

Fossil Fuel Resources

Fossil Fuel	World Reserves	Annual World Consumption	Depletion Time
Coal	980 billion short tons	8.3 billion short tons	118 yrs
Nat. Gas	6700 trillion cubic feet	116 trillion cubic feet	58 yrs
Oil	1480 billion barrels	32 billion barrels	46 yrs

Fossil fuel data from 2011 US EIA wesbite (environmental information administration)

Greenhouse gas emissions cause global environmental issues.



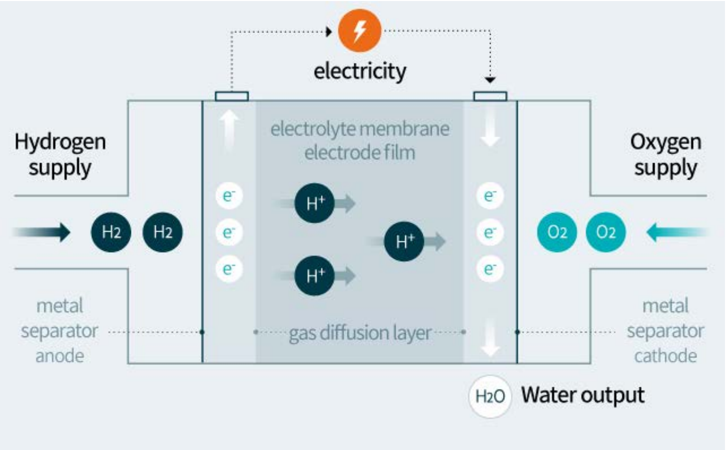
Renewable and clean energy will replace fossil fuels.

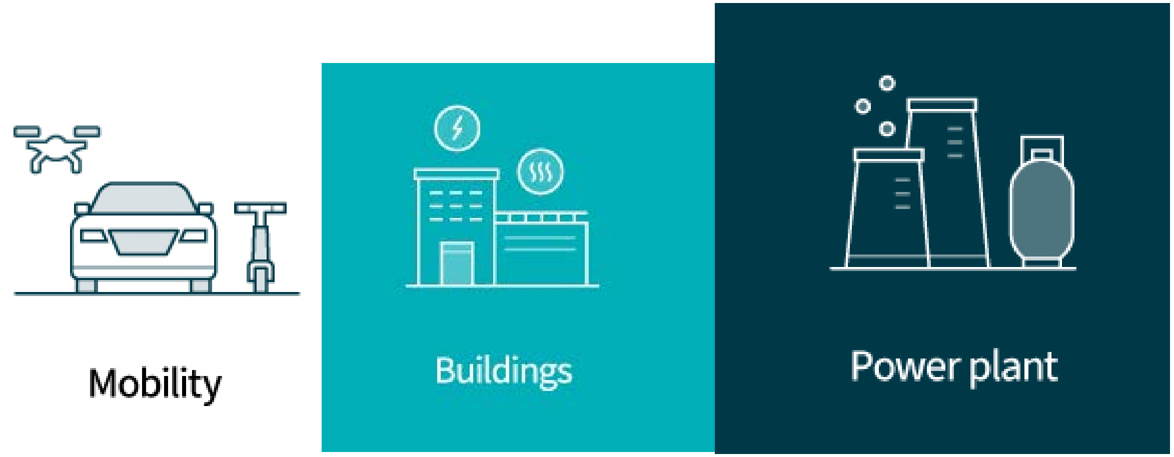
Wind energy

Solar energy

Hydropower energy

Electrocatalysis is promising for its low cost and wide range of usage.

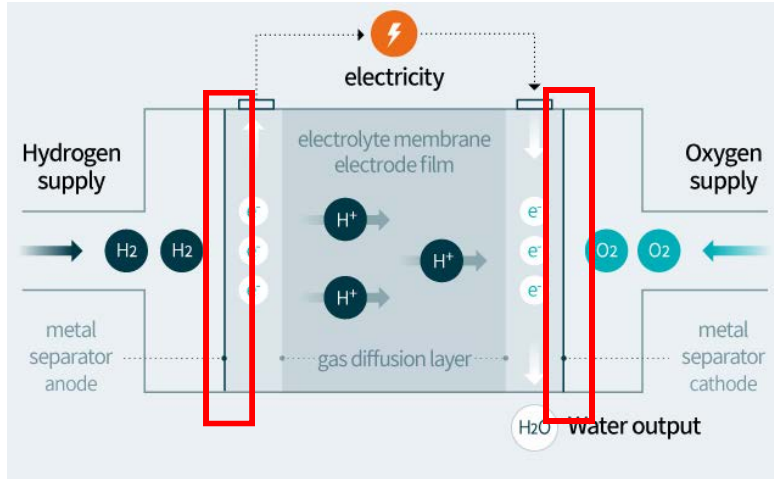




Electrochemistry is a branch of chemistry marked by the movement of electrons from one to other reactants.

Anode reaction:

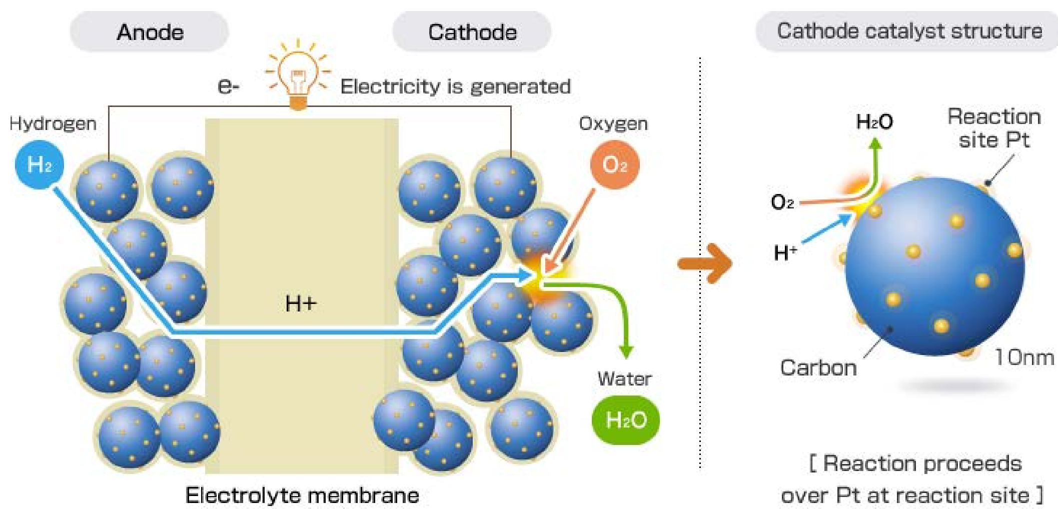
$$H_2 \rightarrow 2H^+ + 2e^-$$



Cathode reaction:

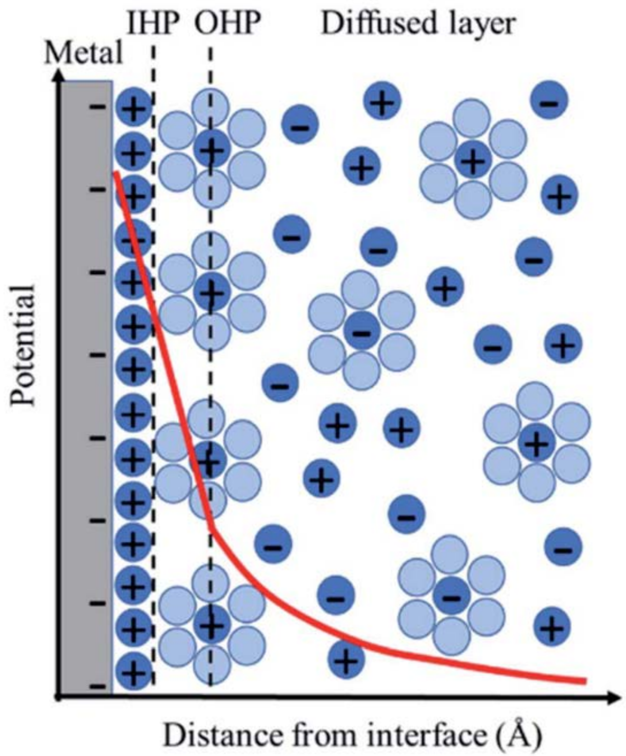
$$1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Electrocatalysis improves both reaction rate and selectivity.

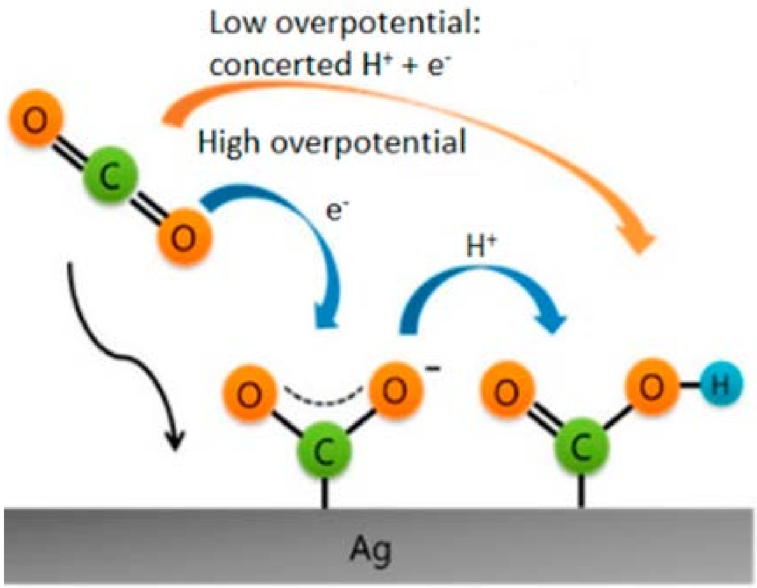


Electrocatalysis/electrochemistry is a complex surface chemistry problem.

Electrical Double layer



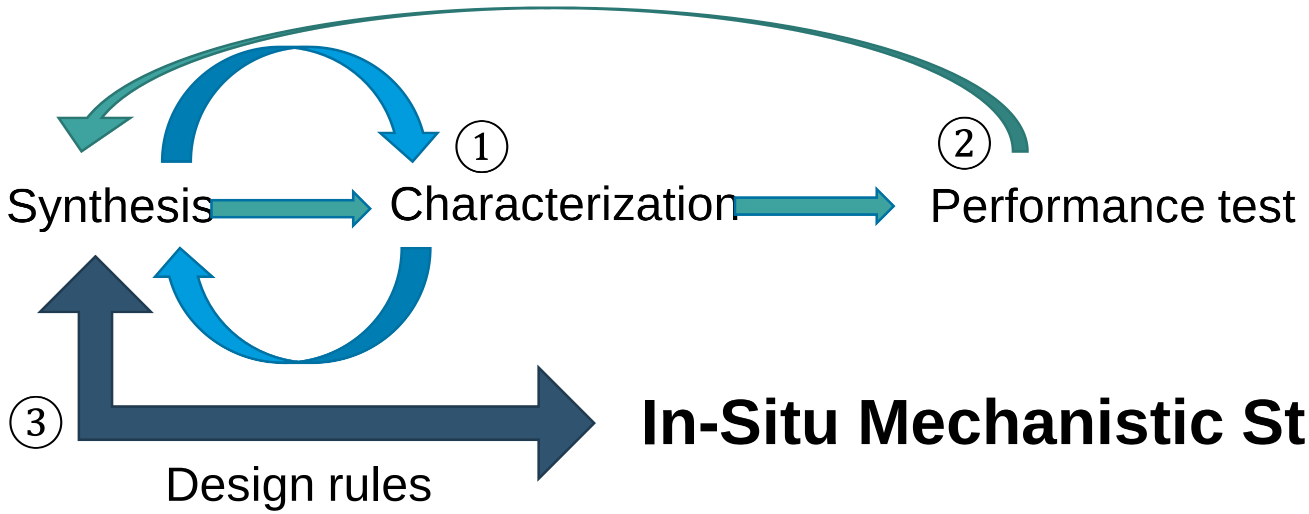
Adsorption of reactive species and intermediate



Scaling up electrocatalytic processes for industrial processes and electricity generation is still challenging.

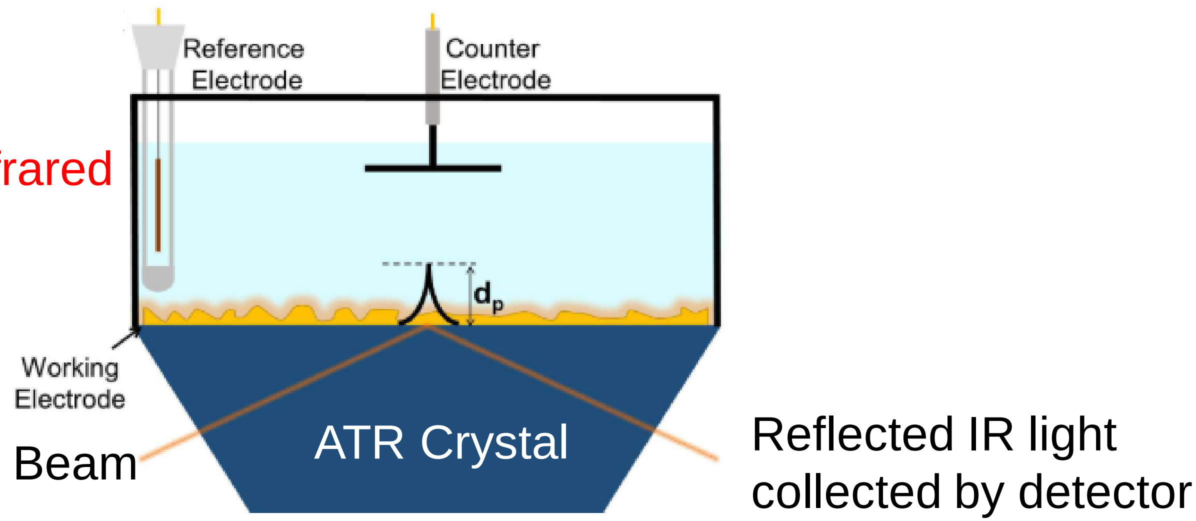
Chem. Sci., 2021,**12**, 10131-10149
ACS Catal. 2017, 7, 606−612

Challenges to improve selectivity and activity of electrocatalyst remain in the field.



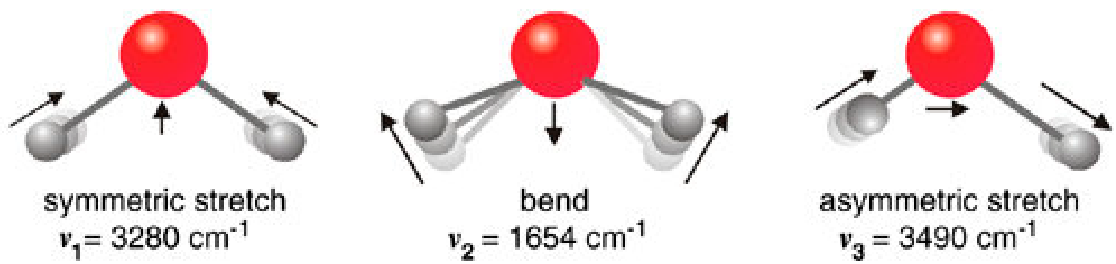
In-Situ Mechanistic Studies

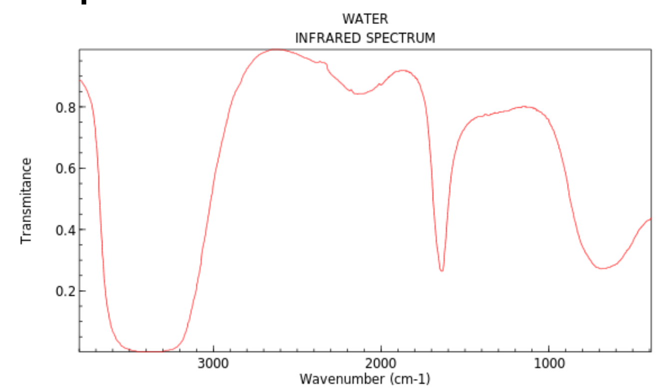
Attenuated Total Reflectance Infrared Spectroscopy (ATR-SEIRAS)



Why do we use Infrared Spectroscopy?

Molecular vibrations at certain frequencies happen upon interaction with infrared light.





Beer-Lambert's law tell us information about concentration of samp

$$A = \varepsilon c l$$

A	Absorbance	
ε	Molar absorption coefficient	M^{-1}cm^{-1}
c	Molar concentration	M
l	optical path length	cm

Wavenumber/frequency of molecular vibration is related to the mass and spring constant of cher

Hooke's Law

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}}$$

ν = frequency
c = speed of light
f = force constant (bond strength)
μ = reduced mass = $\frac{m_1 m_2}{m_1 + m_2}$

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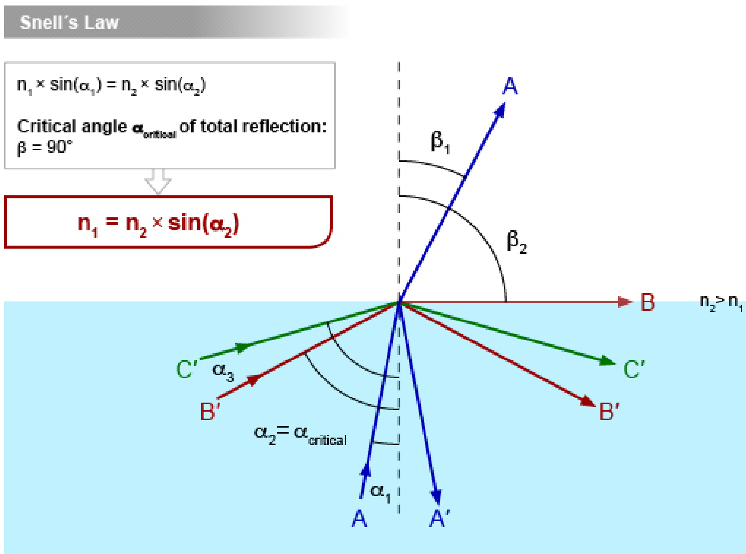
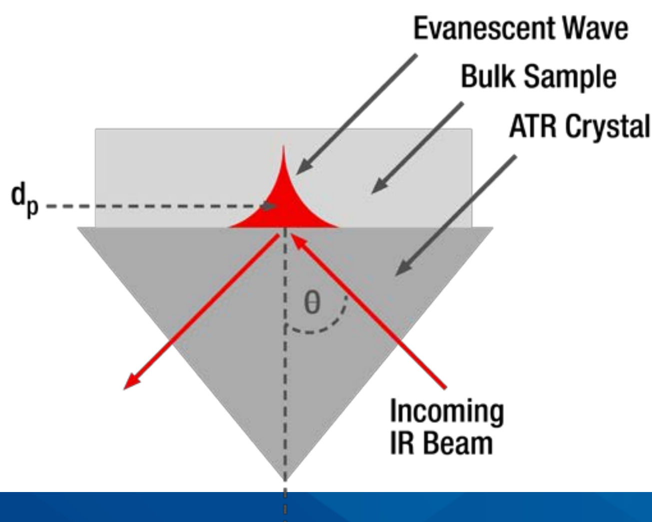
https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Type=IR-SPEC&Index=1

ATR geometry of IR measurements

Total internal reflection and Evanescent Waves



ATR crystals	Refractive Index	α $_{critical}$ when n_1=1.5
Zinc selenide (ZnSe)	2.40	40°
Germanium (Ge)	4.00	22°
Silicon (Si)	3.41	26°
Diamond	2.41	40°

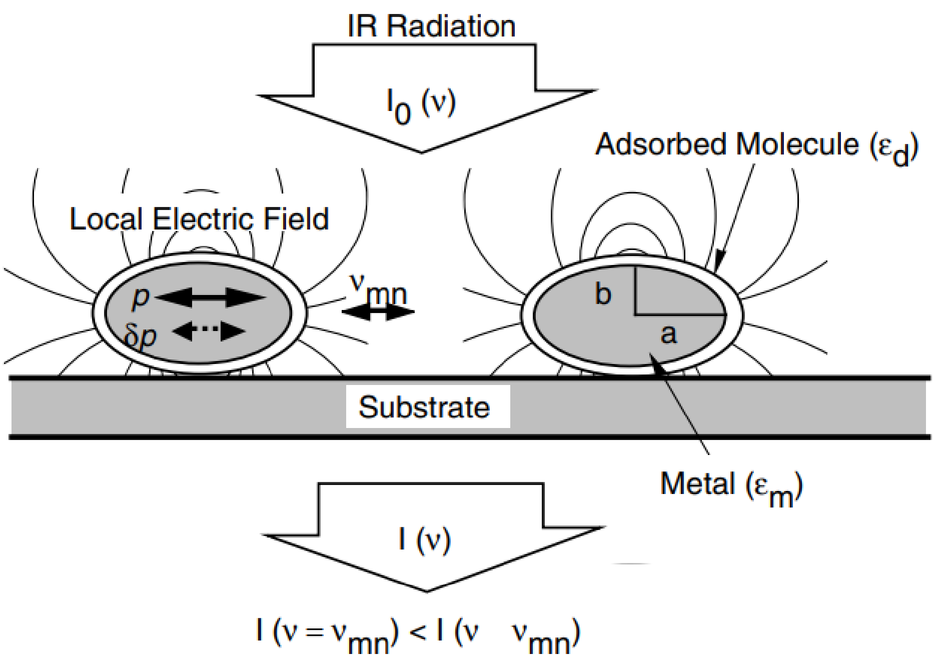


$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{sin^2\theta - (\frac{n_1}{n_2})^2}}$$

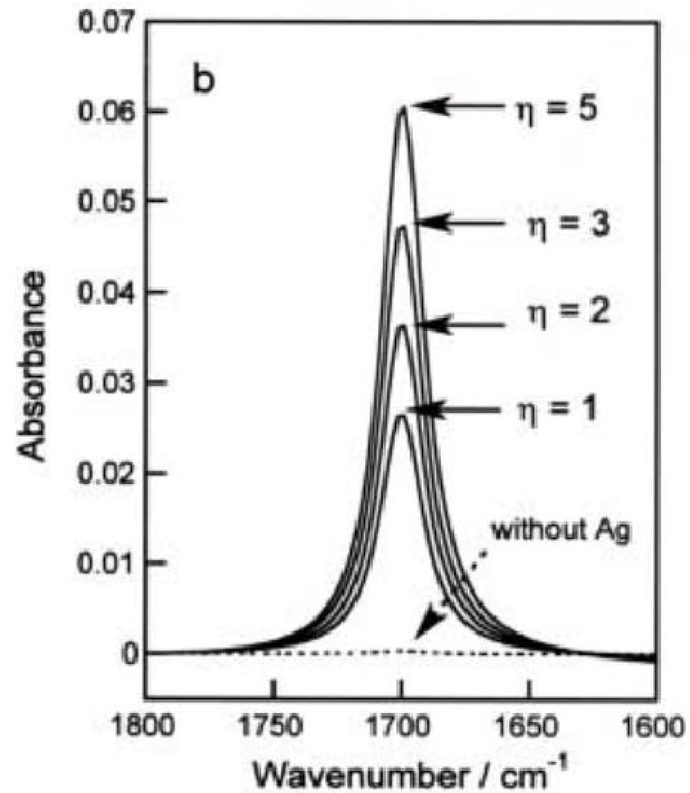
λ … wavelength of incident light in vacuum
n_1 … refractive index of ATR crystal (dense medium)
n_2 … refractive index of sample (rare medium)
ϴ … angle of incidence

Surface enhancement principles

Localized Surface Plasmon Resonance (Au, Ag, Cu, etc…)



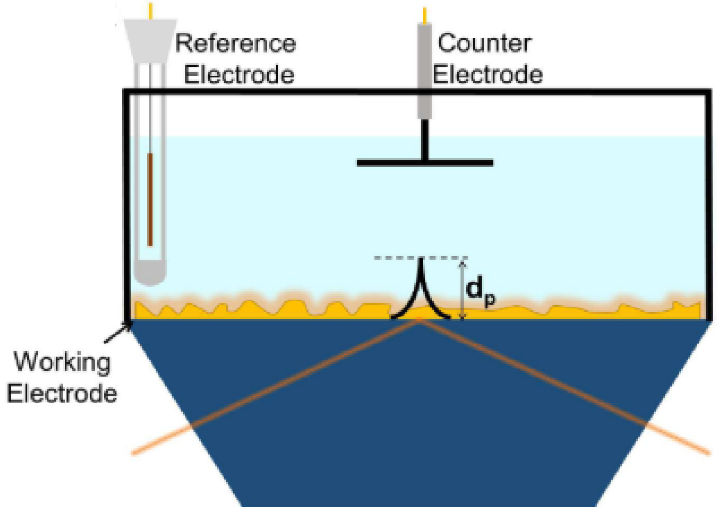
SEIRAS achieves 10–100 × enhancement of vibrational bands.

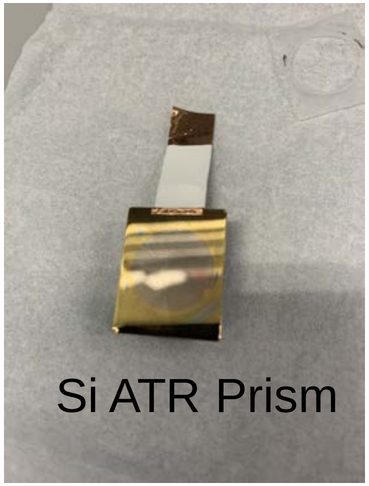


η represents the aspect ratio of the metal ellipsoid (lightning rod effect)

S. Kawata (Ed.): Near-Field Optics and Surface Plasmon Polaritons, Topics Appl. Phys. 81, 163–187 (2001)

To achieve surface enhancement, electrode underlayer need to be prepare

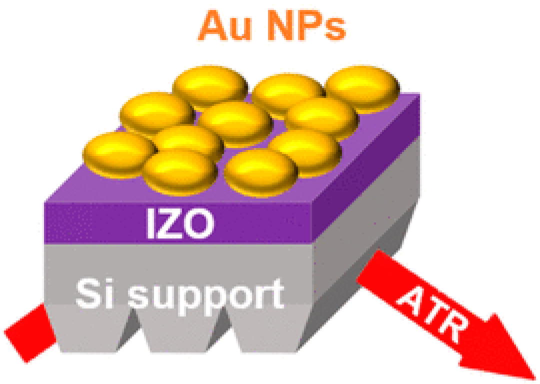




Magnetron Sputtering

Electroless plating

Electrodeposition

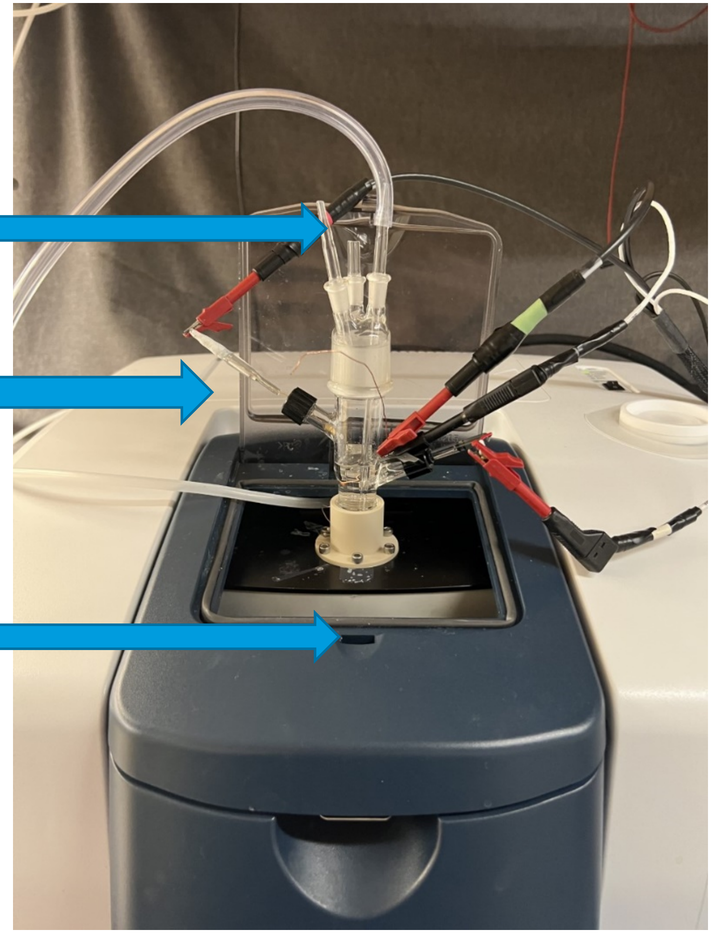


The setup of ATR-SEIRAS = ATR geometry + conductive metal film + **reaction cell**

①Gas Inlet and Outlet

②Reaction Cell
(PEEK+ Glass parts)

③ Veemax ATR Accessory



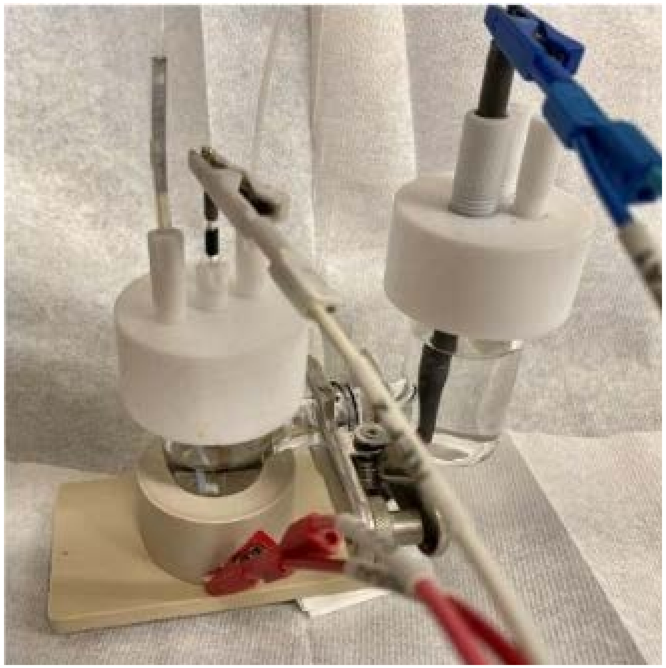
④ Counter electrode

⑤ Reference
Electrode

⑥Working Electrode

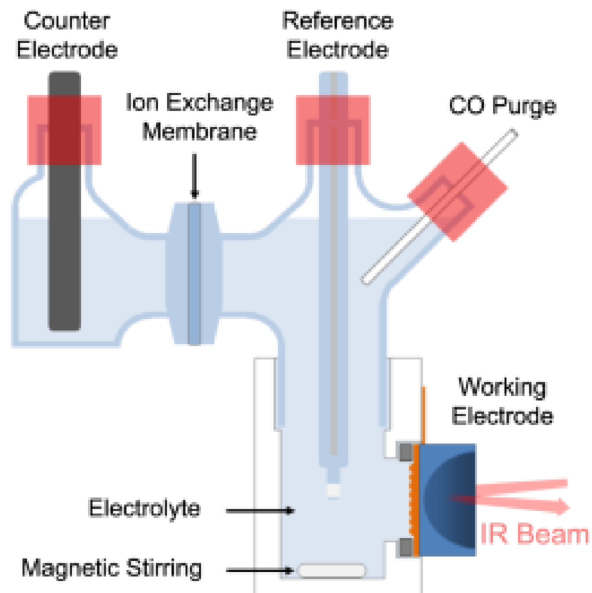
Reaction cell design can be customized for different purposes.

H-cell design Cell: Prevent Cross Contamination



J. Am. Chem. Soc. 2022, 144, 8641−8648

Stirring Cell: Improve Mass Transport



Nature Communications volume 13, Article number: 2656 (2022)

Procedures for a typical ATR-SEIRAS measurement:

Sample Preparation

Assembly of the ATR crystal in a cell

Addition of electrolyte and purging gas

Operation of potentiostat and FTIR

After a series of experiment, we will gather data like below:

Collecting background spectrum

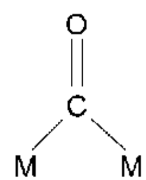
Background spectrum taken at 0.9 V vs RHE

Changing applied potential and take a new spectrum

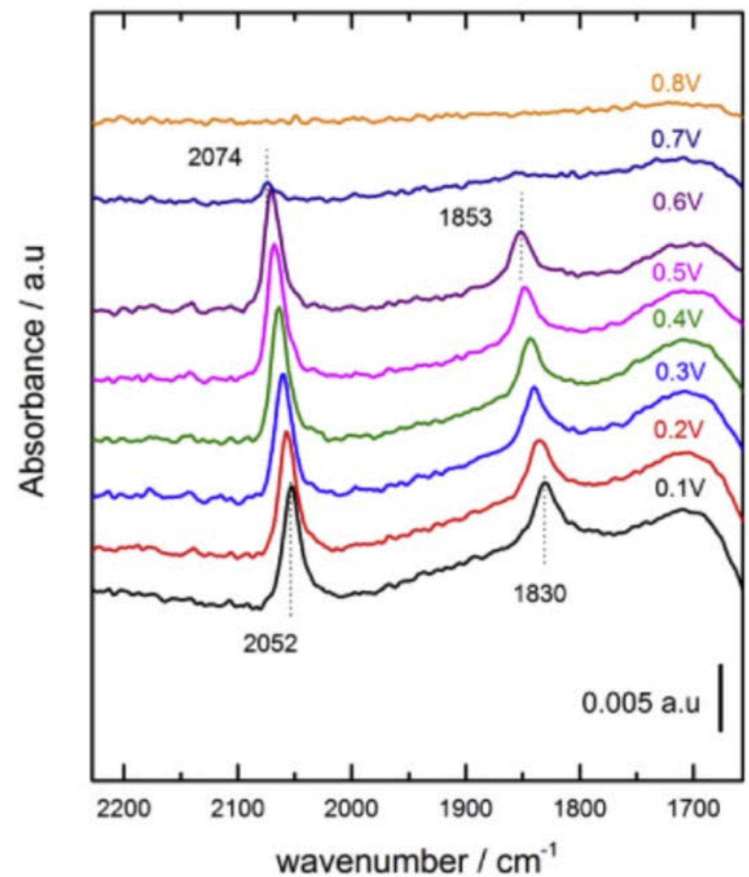
CO adsorption on Pt at different potentials

Subtracting the old spectrum from the new spectrum

Linear-bonded

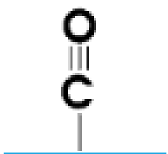


Bridge-bonded

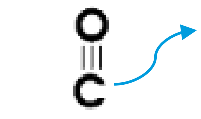


Electrochim. Acta **2018**, *281*, 127– 132,

On different metals, different mechanisms were observed for the same reaction conditions.


Au

CO desorption due to weak interaction between Au and CO

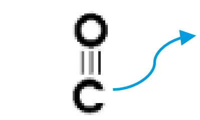

CO Gas

Au

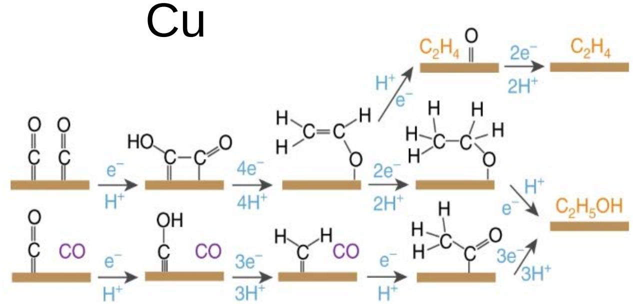
Linear-bonded CO stretch observed near 2100 cm^{-1}, no other peaks observed in the literature


Cu

Optimal CO binding on Cu surfaces


CO Gas

Cu

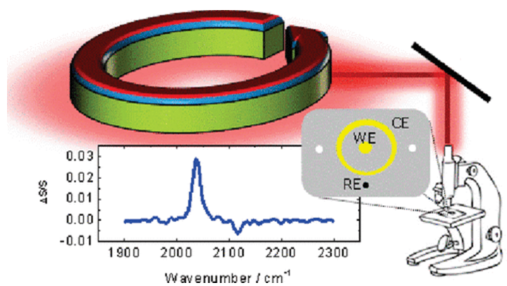


Linear-bonded CO stretch observed 2070-2040 cm^{-1} Multicarbon product intermediate peak reported using ATR-SEIRAS and Gas Chromatography

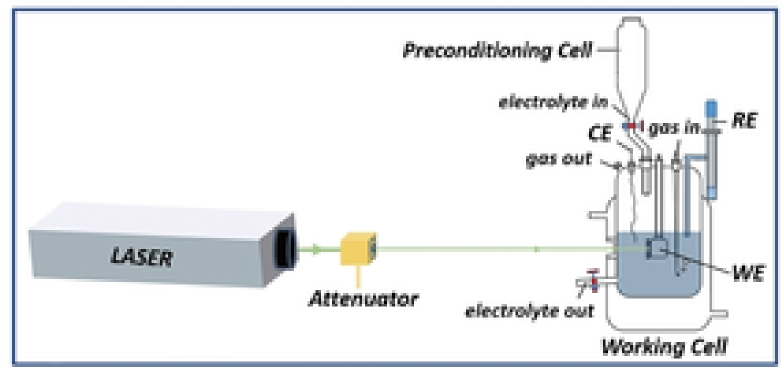
ATR-SEIRAS is powerful, but still limited to ensemble studies for long timescales.

Higher

ATR-IRSEC microscope



Anal. Chem. 2011, 83, 10, 3632–3639



Laser-induced potential jump

ChemElectroChem **2022**, *9*, e202101175.

Spatial Resolution

ATR-SEIRAS

Lower

Slower

Time Resolution

Faster

Tips for starting ATR-SEIRAS:

1. Know the system and theories
2. Build/Machine the cell and test its performance using samples
3. Prepare samples and prove its integrity throughout the experiment
4. Collect data under controlled reaction conditions
5. Pair With Gas Chromatography and Mass Spectrometry to detect volatile and dilute products
6. Be patient

Questions?

Join us for the next webinar!

Recent Advances in Surface Emitting Lasers

When: May 19, 2023 at 1 pm ET

Speaker: Amirhossein Ghods, staff research scientist
R&D division of ams-OSRAM

For more information, visit:
www.cneu.psu.edu/webinars

Upcoming Professional Development Opportunities

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- NACK Hands-on-Site Workshops, Aug 7-9, register at www.cneu.psu.edu/workshops

- HI-TEC 2023, July 24-27 in Atlanta, GA. www.highimpact-tec.org/. To apply for a registration discount code, visit: https://forms.gle/fhELvXcCsEDYi73k9

- MNT-EC Journal Writing Workshop, Sept 12-14, 10am-noon PST, online. To register, visit https://micronanoeducation.org/calendar