

Lecture Note #11

B

Spectroelectrochemistry (ch. 17): *in situ & ex situ*

1. UV & visible spectroscopy

(1) Transmission experiments

(2) Ellipsometry

(3) Internal reflection spectroelectrochemistry: surface plasmon resonance

(4) Second harmonic spectroscopy

2. Vibrational spectroscopy:

(1) IR spectroscopy

(2) Raman spectroscopy

3. Electron & ion spectroscopy

XPS, AES, LEED, HREELS, mass spectroscopy

4. Magnetic resonance methods: ESR, NMR

5. Quartz crystal microbalance

6. X-ray methods: XAS, XRD

2. Vibration spectroscopy

(1) Infrared spectroscopy

Energy of electromagnetic field: oscillating electric & magnetic disturbance

$$E = h\nu = h c/\lambda$$

h ; Planck constant (6.6×10^{-34} Js)

speed of light (c); 3×10^8 m/s,

wavelength (λ); distance between the neighboring peaks of wave,

$$1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$$

frequency (ν , Hz = 1 s^{-1}); number of times per second

$$\lambda\nu = c$$

wavenumber (cm^{-1} , reciprocal cm), $\bar{\nu} = \nu/c = 1/\lambda$

cf) $1 \text{ eV} \sim 8066 \text{ cm}^{-1}$

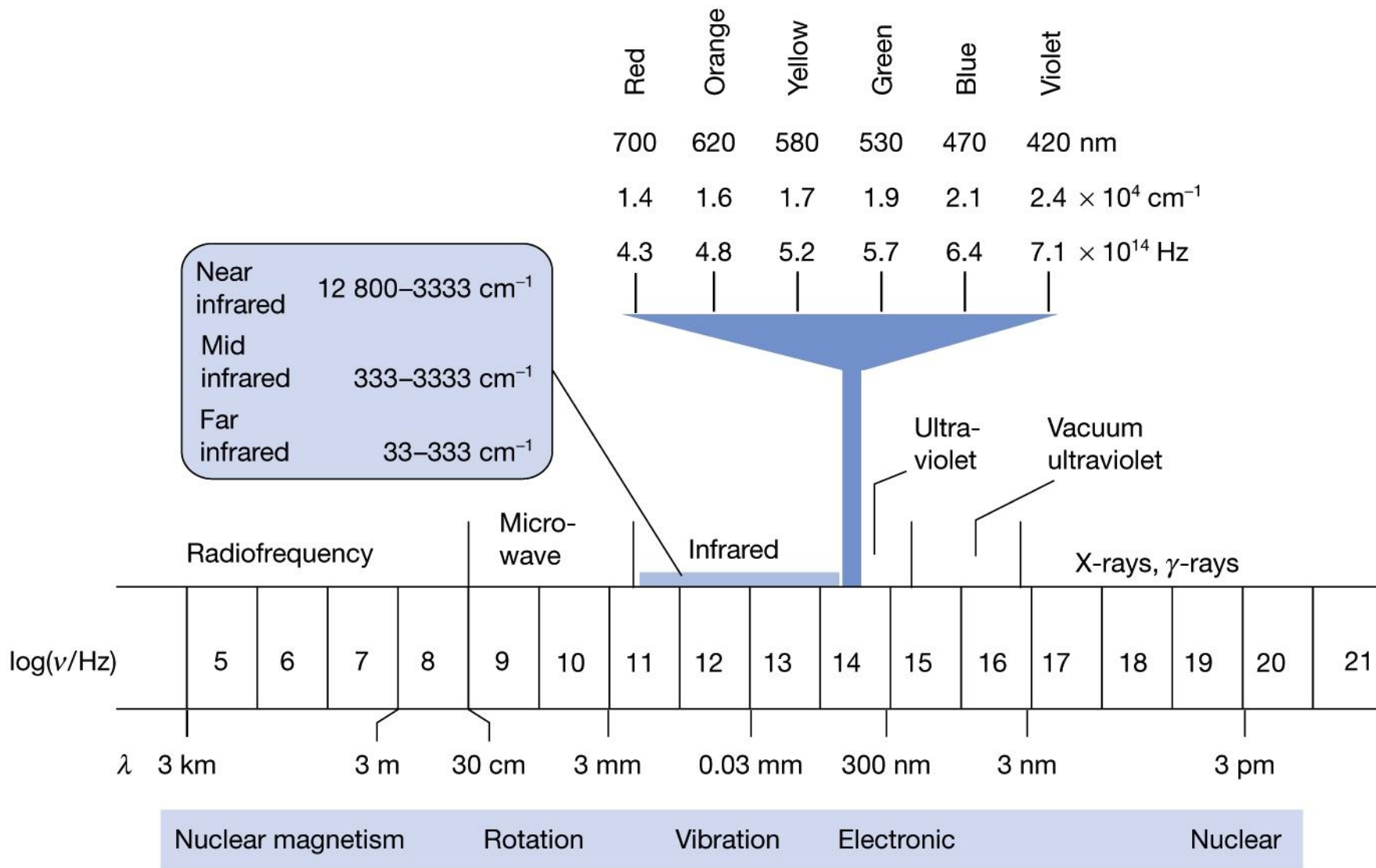
$$\text{Wavelength } (\lambda, \text{ nm}) = 1240/\text{band gap energy (eV)}$$

Widely used IR spectroscopy: mid-IR (670~4000 cm⁻¹(2.5 ~ 14.9 μm))

TABLE 17-1 Major Applications of IR Spectrometry

Spectral Regions	Measurement Type	Kind of Analysis	Applicable Samples
Near-IR	Diffuse reflectance	Quantitative	Solid or liquid commercial materials
	Absorption	Quantitative	Gaseous mixtures
Mid-IR	Absorption	Qualitative	Pure solid, liquid, or gases
		Quantitative	Complex liquid, solid, or gaseous mixtures
		Chromatographic	Complex liquid, solid, or gaseous mixtures
	Reflectance	Qualitative	Pure solids or liquids
Far-IR	Emission	Quantitative	Atmospheric samples
	Absorption	Qualitative	Pure inorganic or organometallic species

Electromagnetic spectrum



IR radiation ~ energy differences
for vibrational & rotational states

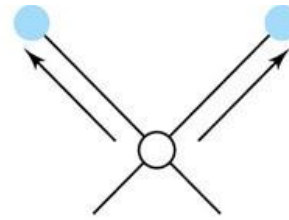
For absorption of IR radiation:
dipole moment change during
vibration

Dipole moment is determined by
the magnitude of the charge
difference and the distance
between two centers of charge

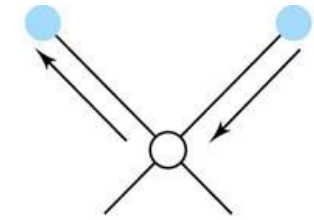
e.g) H-Cl (o)

O-O (x)

Types of vibration:
Stretching & bending

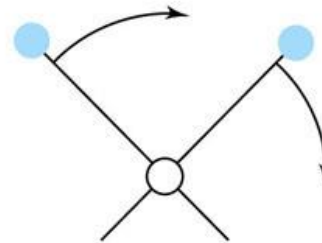


Symmetric

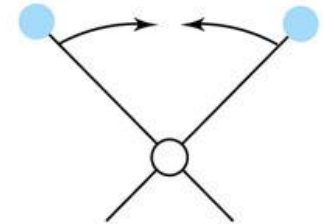


Asymmetric

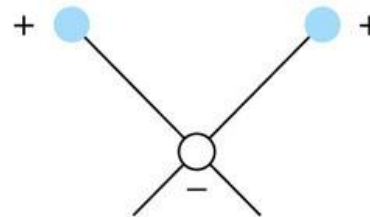
(a) Stretching vibrations



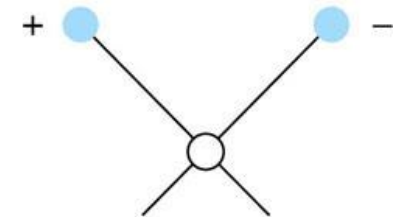
In-plane rocking



In-plane scissoring



Out-of-plane wagging



Out-of-plane twisting

(b) Bending vibrations

Harmonic oscillator

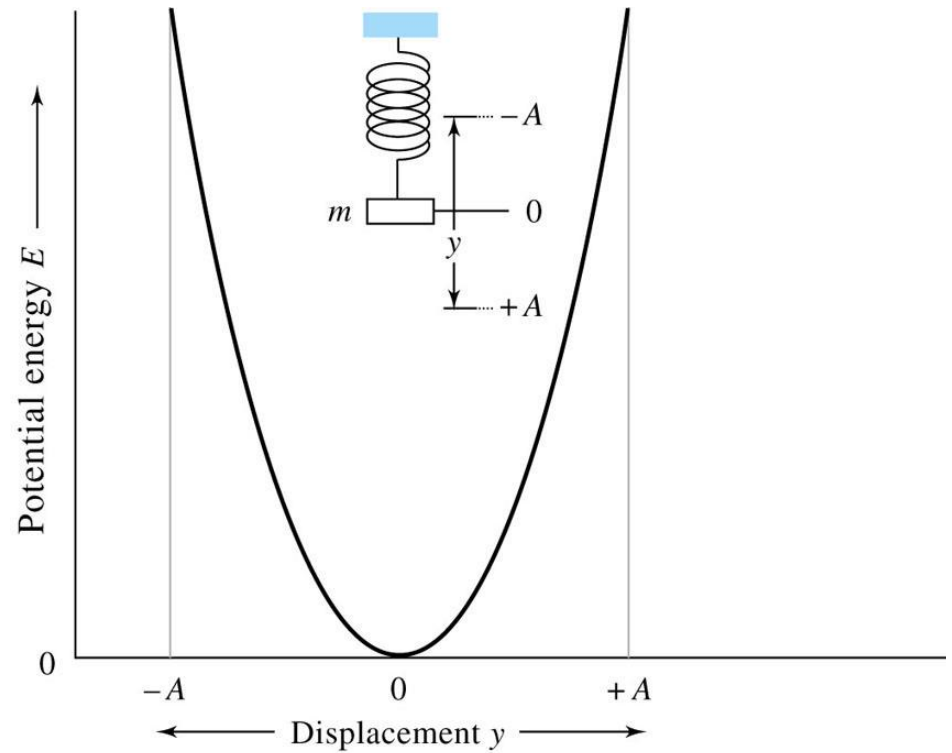
$$F = -ky \quad \text{Hooke's law}$$

k: force constant

-: opposite direction for the force

Potential energy:

$$E = \frac{1}{2} ky^2$$



(a)

Vibrational frequency

$$F = ma = m(d^2y/dt^2) = -ky$$

$$y = A\cos(2\pi vt)$$

Frequency of mechanical oscillator

$$v = (1/2\pi)\sqrt{(k/m)}$$

Reduced mass: $\mu = m_1m_2/(m_1 + m_2)$

$$v = (1/2\pi)\sqrt{(k/\mu)}$$

Quantum treatment of vibration:

$$E = (v + 1/2)(h/2\pi)\sqrt{(k/\mu)}$$

h : Planck's constant, v : vibrational quantum number

$$\Delta E = h\nu = (h/2\pi)\sqrt{(k/\mu)}$$

Ground state at $v = 0$:

$$E_0 = \frac{1}{2} h\nu$$

1st excited state ($v = 1$)

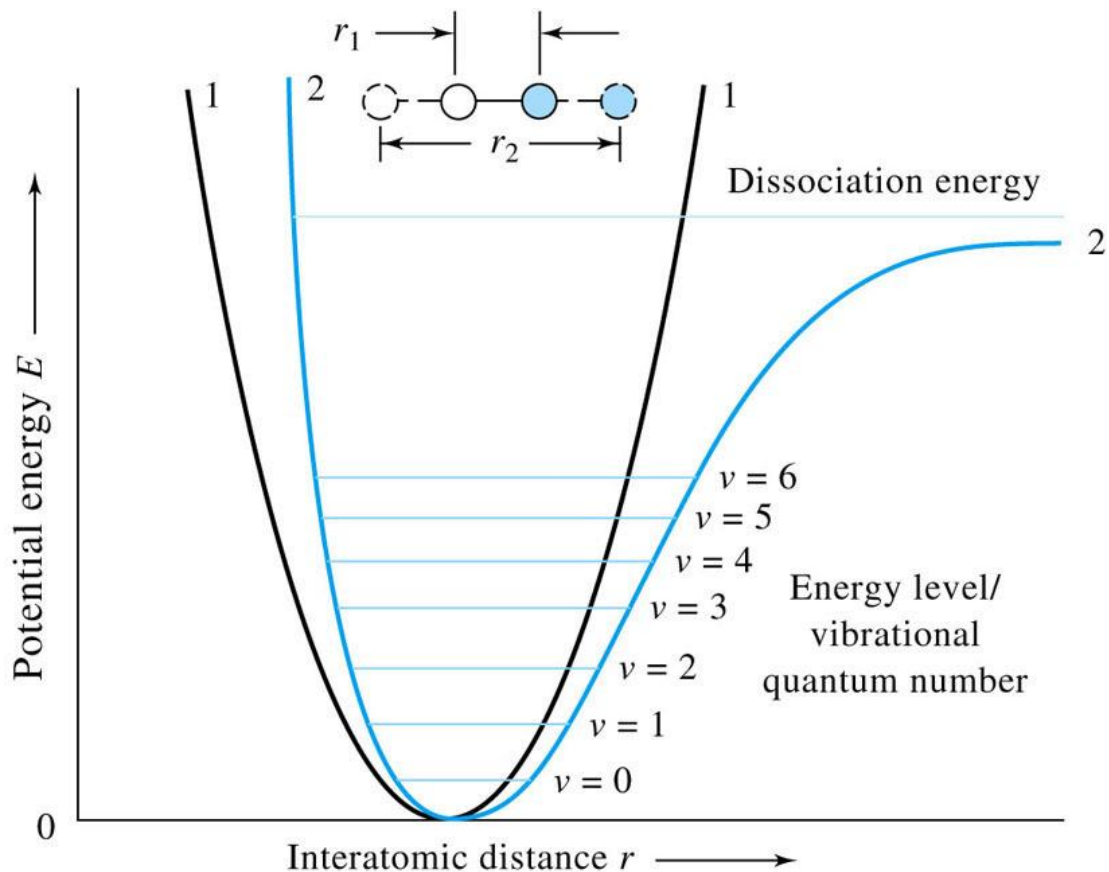
$$E_1 = \frac{3}{2} h\nu$$

Required radiation energy:

$$\begin{aligned} (3/2 - 1/2)h\nu &= h\nu \\ &= (h/2\pi)\sqrt{(k/\mu)} \end{aligned}$$

Wavenumber (cm^{-1}):

$$\begin{aligned} \bar{\nu} &= (1/2\pi c)\sqrt{(k/\mu)} \\ &= 5.3 \times 10^{-12}\sqrt{(k/\mu)} \end{aligned}$$



(b)

1. Harmonic oscillator
2. Anharmonic motion

Selection rules

Gross selection rule for IR: change of dipole moment

e.g., symmetric stretch of CO₂: no dipole moment change → IR inactive

antisymmetric stretch, bending modes → IR active

Specific selection rule $\Delta v_q = \pm 1$ in harmonic approximation

Molecules can be identified from characteristic frequencies and intensities

IR reflection spectrometry

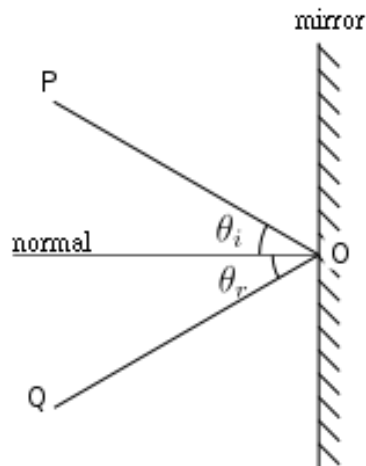
Four types:

Specular reflection: smooth surface

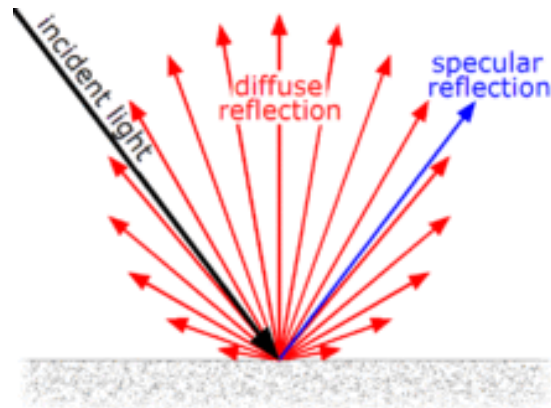
Diffuse reflection

Internal reflection

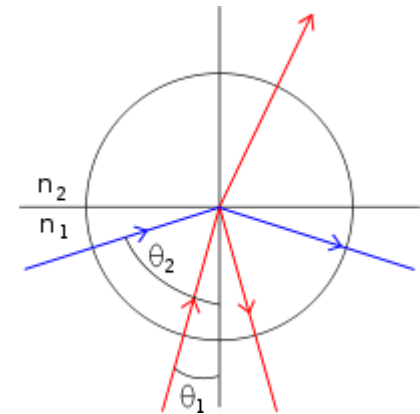
Attenuated total reflection (ATR)



Specular reflection



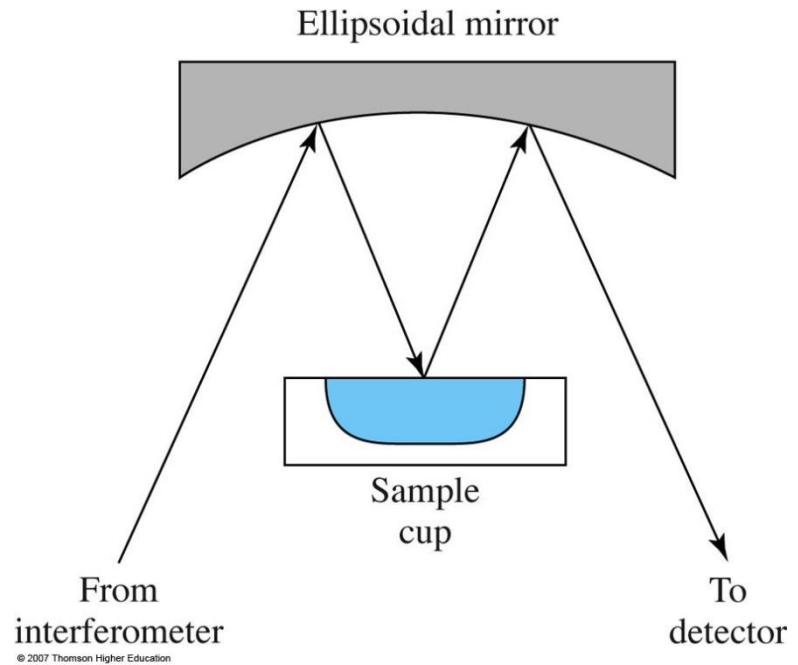
Diffuse reflection



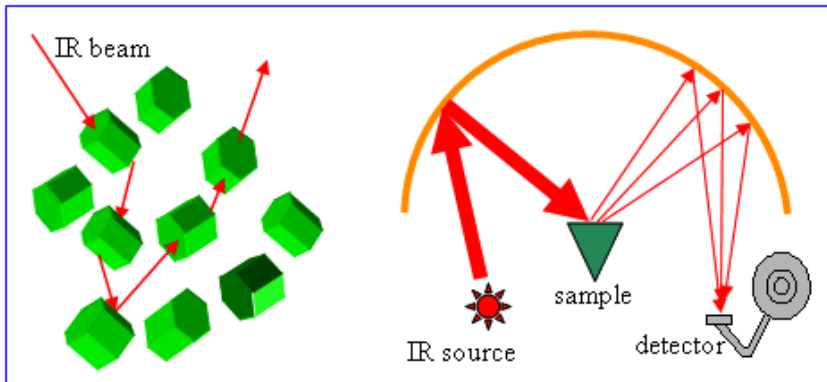
Internal reflection
(blue line)

Diffuse reflection

Diffuse-reflectance attachment



❖ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT)



Powder sample

Attenuated total reflectance (ATR) is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid, liquid or gas state without further preparation

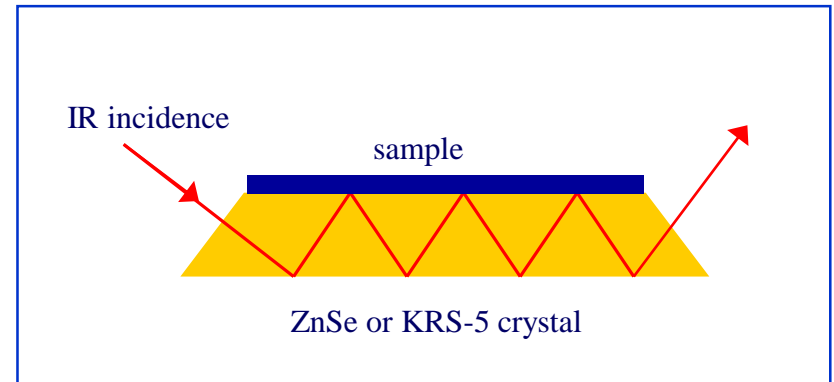
ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact

with the sample. This reflection forms the evanescent wave which extends into the sample. The penetration depth into the sample is typically between 0.5 and 2 micrometres, with the exact value being determined by the wavelength of light, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed. The number of reflections may be varied by varying the angle of incidence. The beam is then collected by a detector as it exits the crystal. Most modern infrared spectrometers can be converted to characterise samples via ATR by mounting the ATR accessory in the spectrometer's sample compartment. The accessibility of ATR-FTIR has led to substantial use by the scientific community.

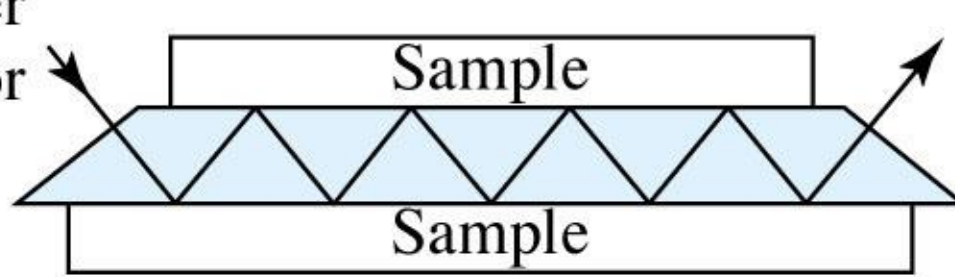
This evanescent effect only works if the crystal is made of an optical material with a higher refractive index than the sample being studied. Otherwise light is lost to the sample. In the case of a liquid sample, pouring a shallow amount over the surface of the crystal is sufficient. In the case of a solid sample, it is pressed into direct contact with the crystal. Because the evanescent wave into the solid sample is improved with a more intimate contact, solid samples are usually firmly clamped against the ATR crystal, so that trapped air is not the medium through which the evanescent wave travels, as that would distort the results.

Typical materials for ATR crystals include germanium, KRS-5 and zinc selenide, while silicon is ideal for use in the Far-IR region of the electromagnetic spectrum. The excellent mechanical properties of diamond make it an ideal material for ATR, particularly when studying very hard solids, but its much higher cost means it is less widely used. The shape of the crystal depends on the type of spectrometer and nature of the sample. With dispersive spectrometers, the crystal is a rectangular slab with chamfered edges, seen in cross-section in the illustrations. With FTIR cylindrical crystals are used with liquid samples. (출처: 위키백과)

❖ Attenuated Total Reflectance Spectroscopy (ATR)



From interferometer
or monochromator



To detector

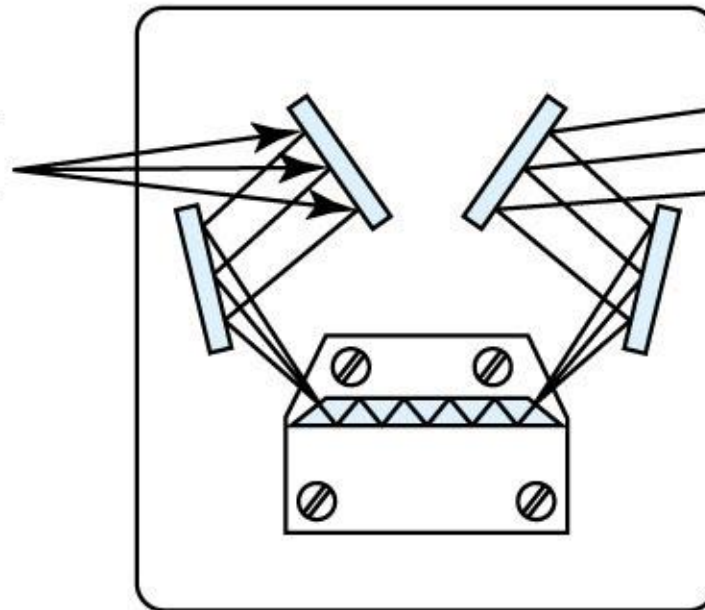
Solid with high
refractive index

Sample

Sample

(a)

From interferometer
or monochromator

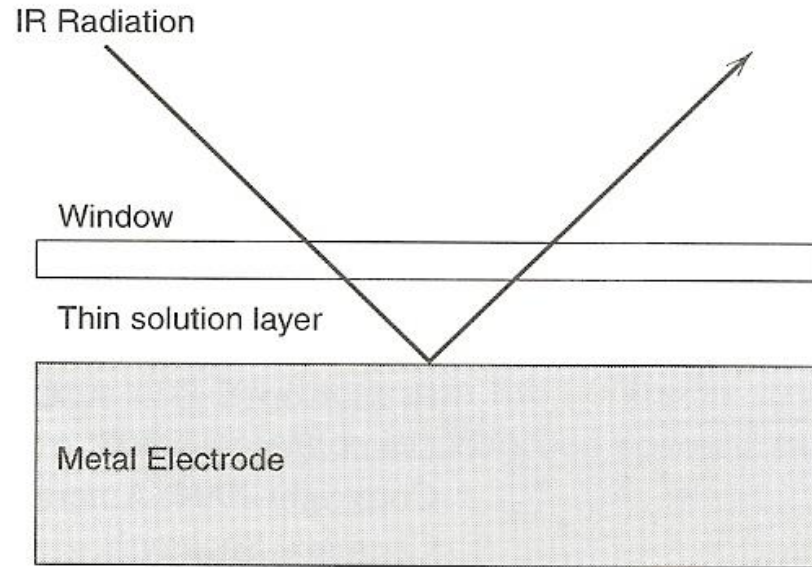


To
detector

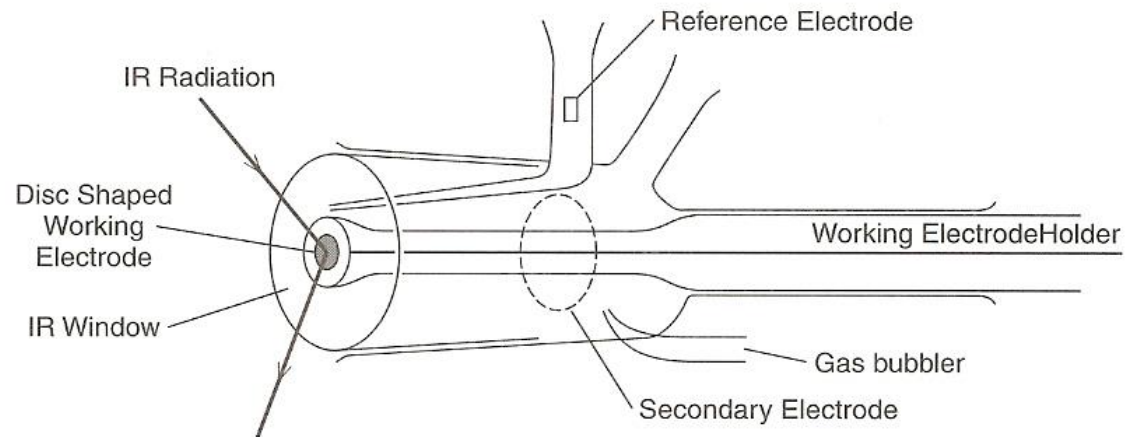
Attenuated total
reflectance (ATR)
attachment

(b)

Infrared spectroelectrochemistry (IR-SEC)

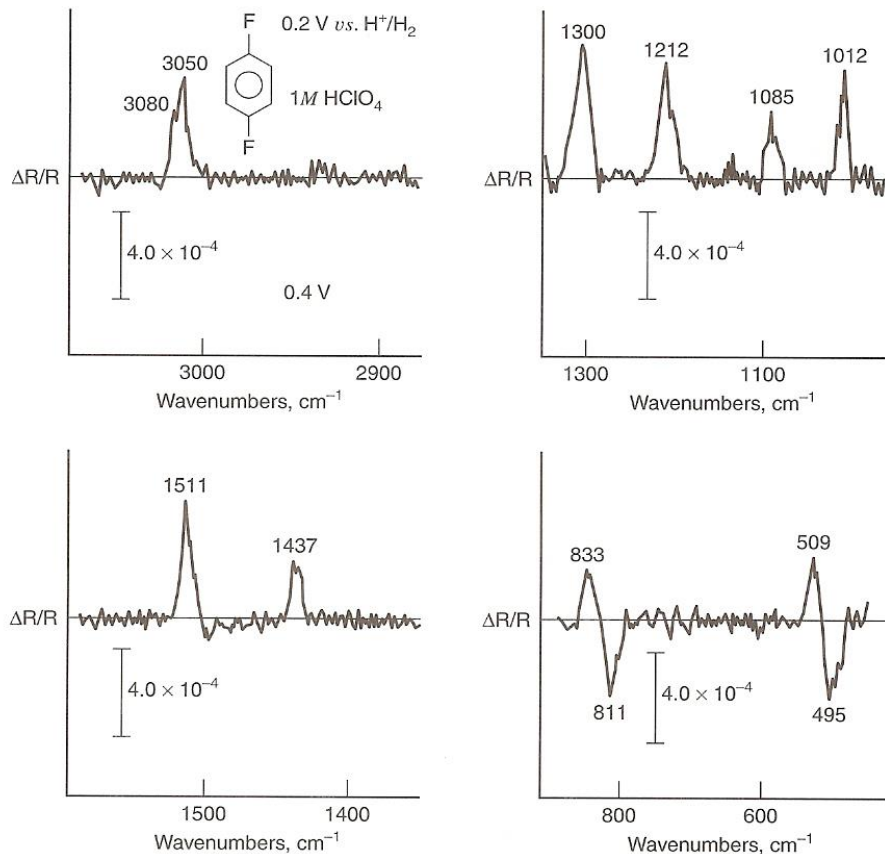


Cell for IR-SEC



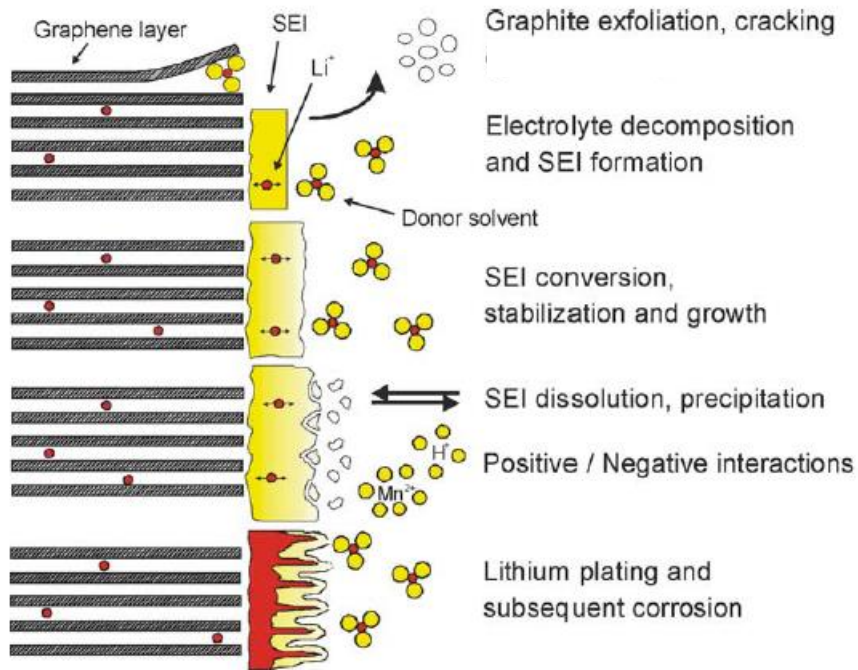
SEIRA (surface enhanced IR absorption)

IR to study adsorbed species (reactants, intermediates, products)
→ orientation & potential dependence of the adsorbed species



P-difluorobenzene in 1 M
HClO₄ at a Pt electrode

Why in-situ FT-IR spectroscopy ?



Changes at the anode/electrolyte interface

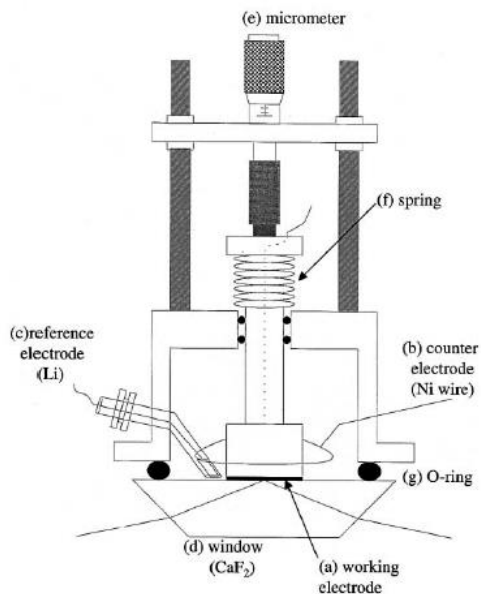
- ◆ *Electrolyte decomposition occurs at the electrode/electrolyte interfaces*
- ◆ *Formation of SEI (solid electrolyte interface)*
- ◆ *Mechanisms of the electrolyte decomposition process have been the subject of many investigations*



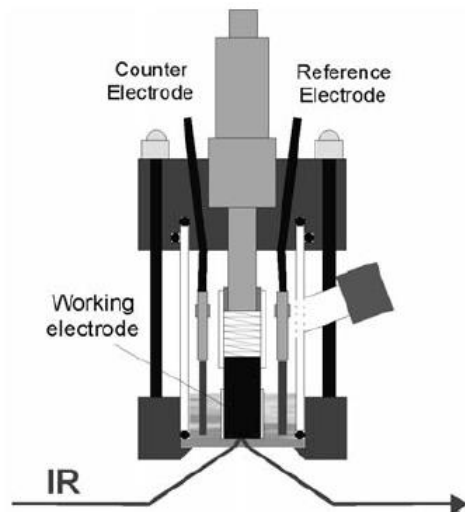
➤ *Necessity of In-situ FT-IR spectroscopy*

- 1. Investigation of electrolyte at the electrode surface without contamination*
- 2. information about electrolyte decomposition*
- 3. formation of SEI*

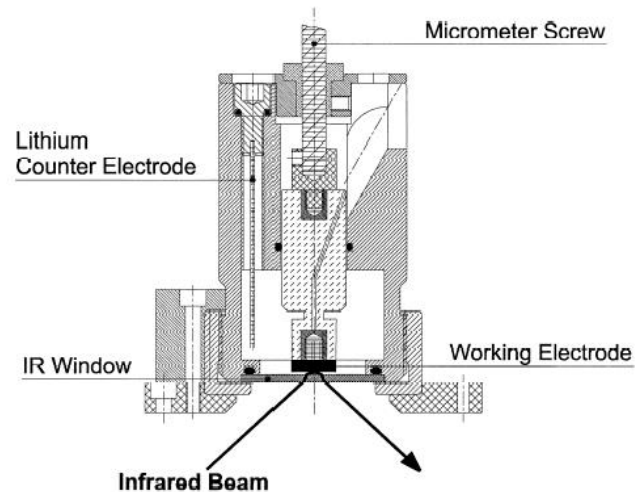
in-situ FT-IR Cell



Electrochim. Acta 47, 2001, 433
Kanamura group



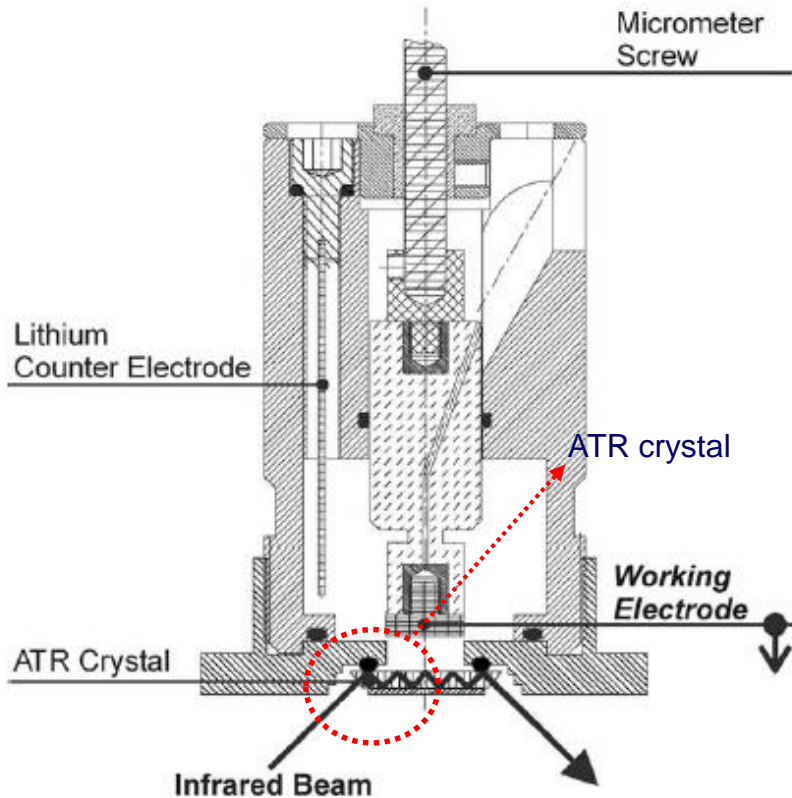
Anal. Bioanal. Chem. 379, 2004, 266
Moller group



J. Power sources 90, 2002, 52
P. Novak group (PSI)

➤ Disadvantage: weak sensitivity (single beam)

Cell model of In-situ FT-IR



J. Power sources , ASAP
P. Novak group (PSI)

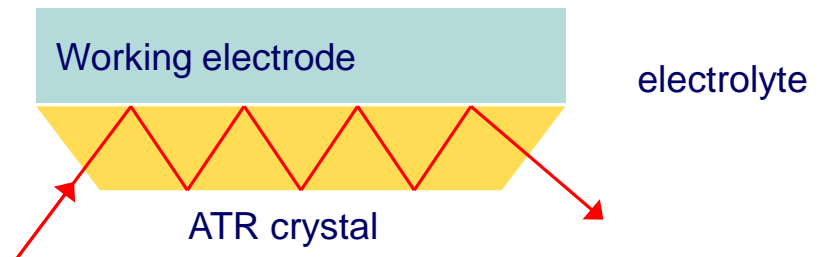
The decisive innovation is the use of an ATR crystal as the optical window. Five reflections can be increasing, thus, the sensitivity significantly. (P.Novak group)

❖ Selection of ATR crystal

Materials	Frequency Range(cm^{-1})	Index of Refraction	Characteristics
KRS-5	16,500-250	2.4	wide frequency Range
ZnSe	20,000-650	2.4	water insoluble

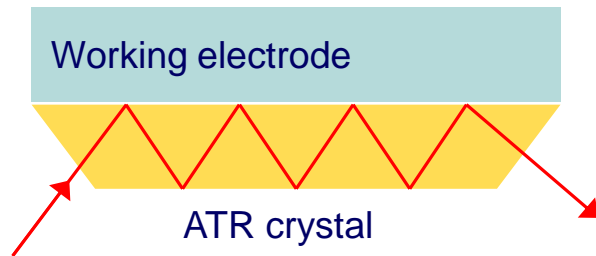
❖ Sealing problem

❖ Diffusion problem

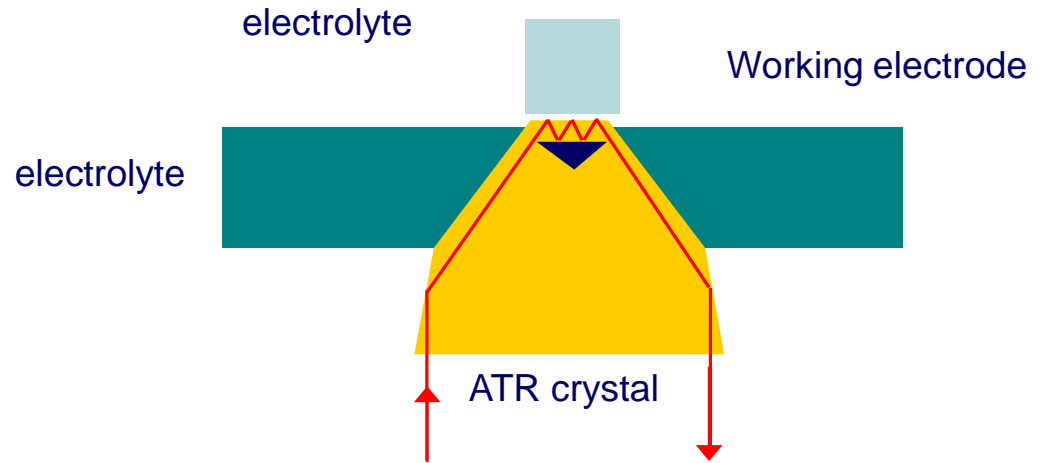


Cell model of In-situ FT-IR

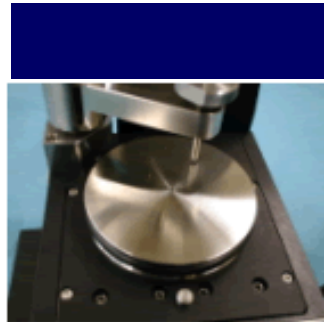
❖ Diffusion problem



- Small size working electrode
- Three –reflection hexagon ATR crystal



❖ Beam alignment



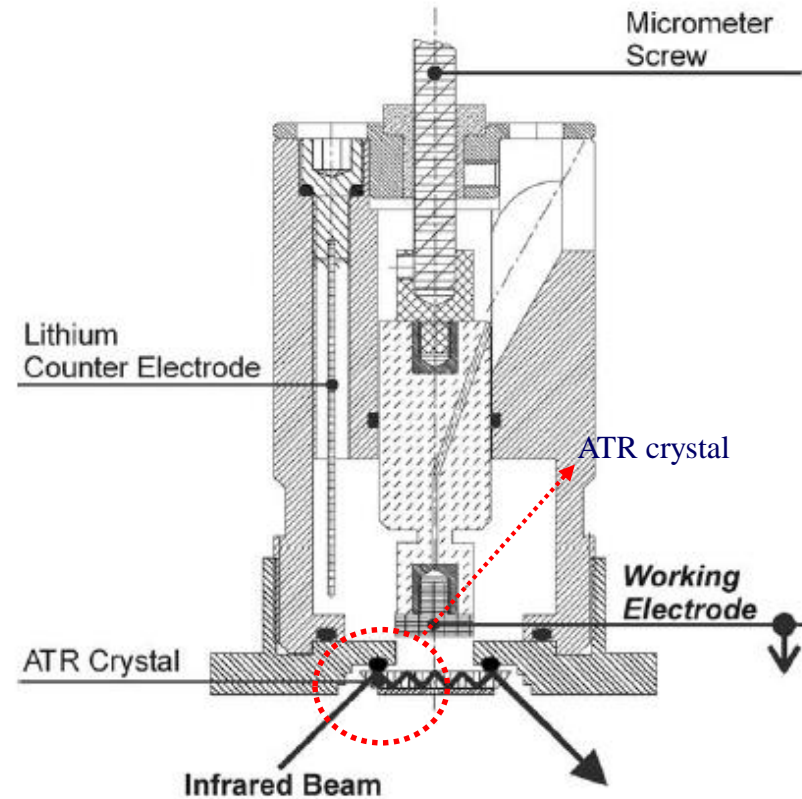
MIRacle™ ATR
PIKE technologies /USA

In situ FT-IR (SNU)

- Nicolet 5700 (thermo electron co.)
- ATR,DRIFT, in situ analysis
- 7,800~350cm⁻¹ (DLaTGS w/KBr Detector)

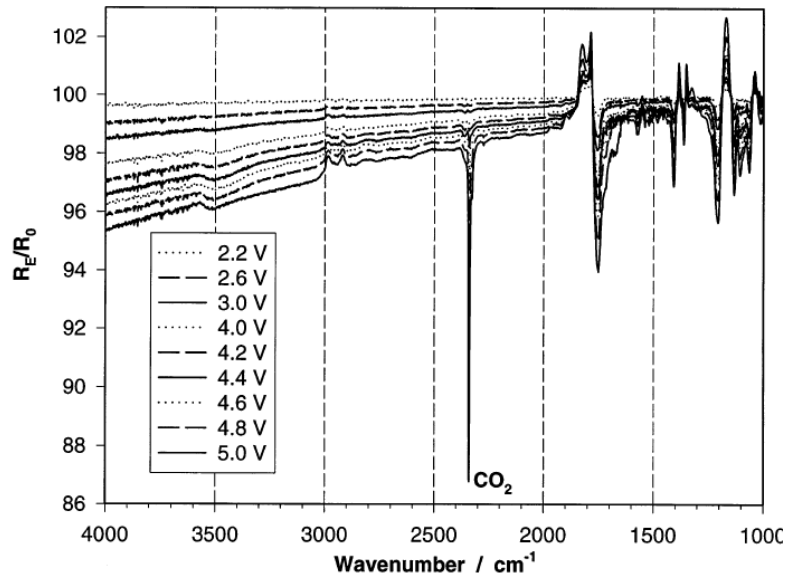


In situ FT IR cell

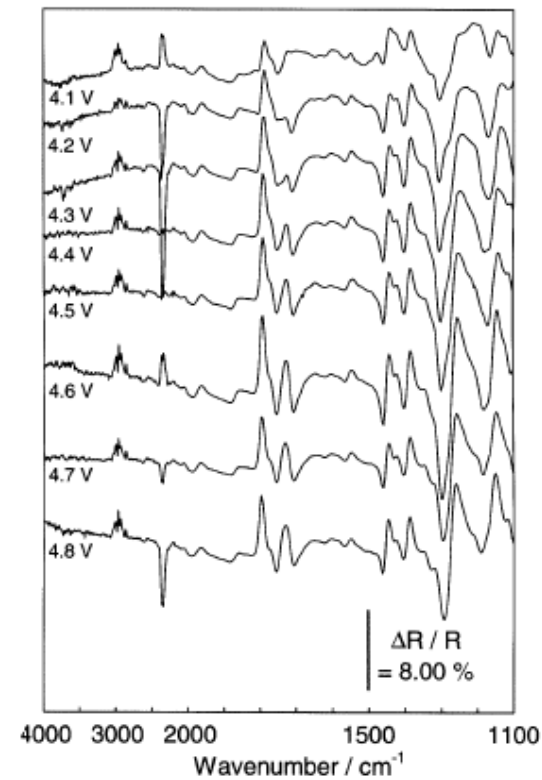


in-situ FT-IR spectroscopy

■ 활용의 예

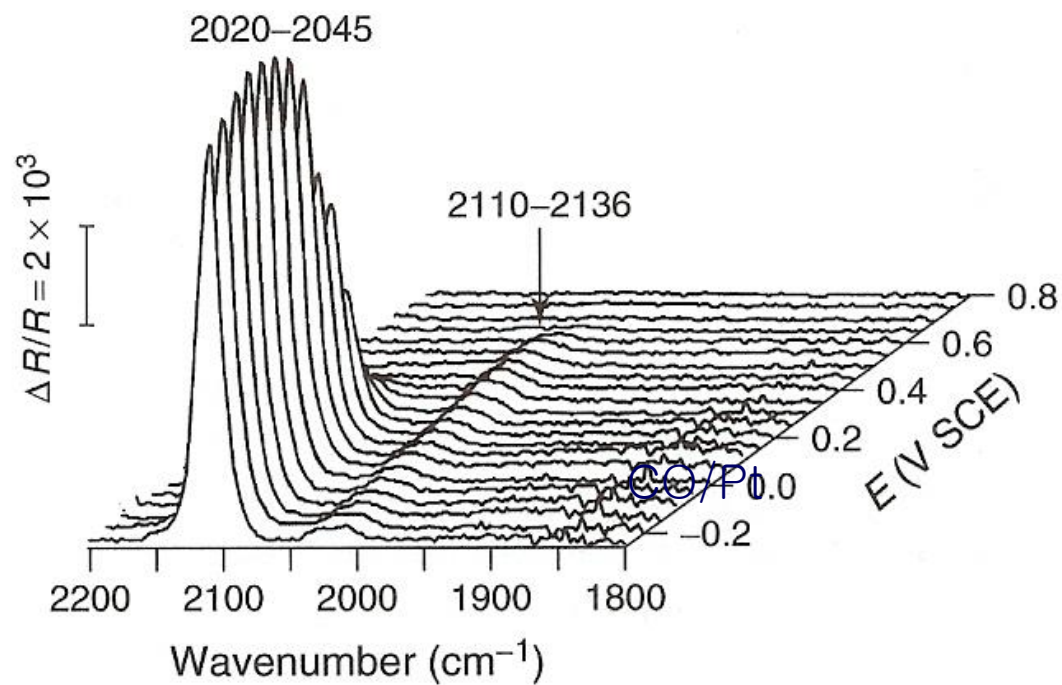


In situ FTIR spectra on a polished nickel electrode
Electrolyte solution, 1 M LiClO_4 in PC (Electrochim. acta
45, 2000, 3589), Novak group



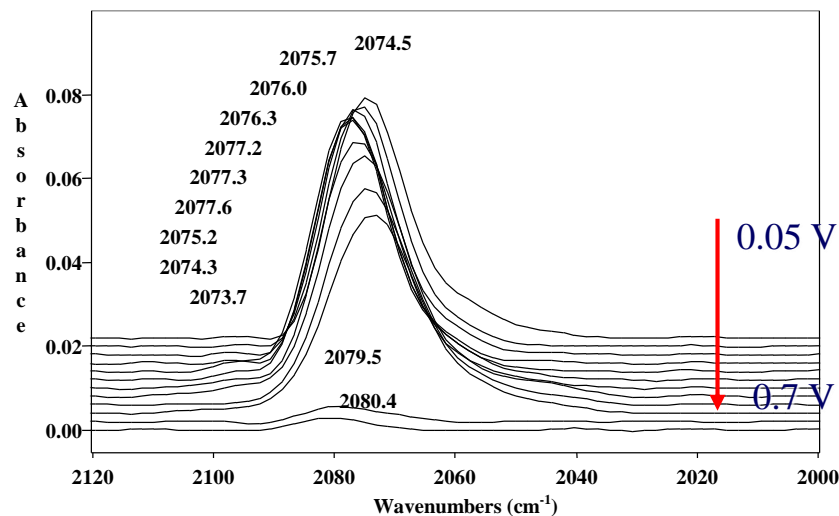
FTIR spectra for the electrochemical oxidation
of 1.0 mol dm^{-3} LiPF_6 /propylene carbonate on the
 LiCoO_2 film electrode

➤ In situ FT-IR

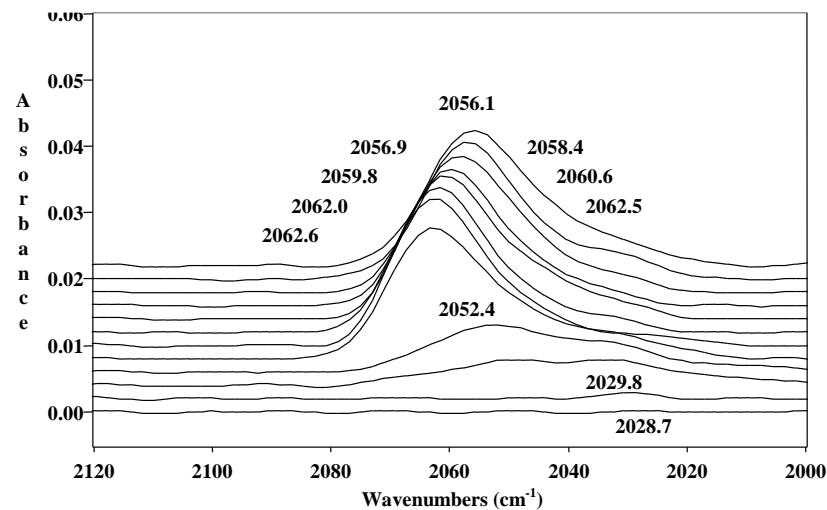


➤ In situ FT-IR

CO/Pt



Pure Pt, 50 % CO

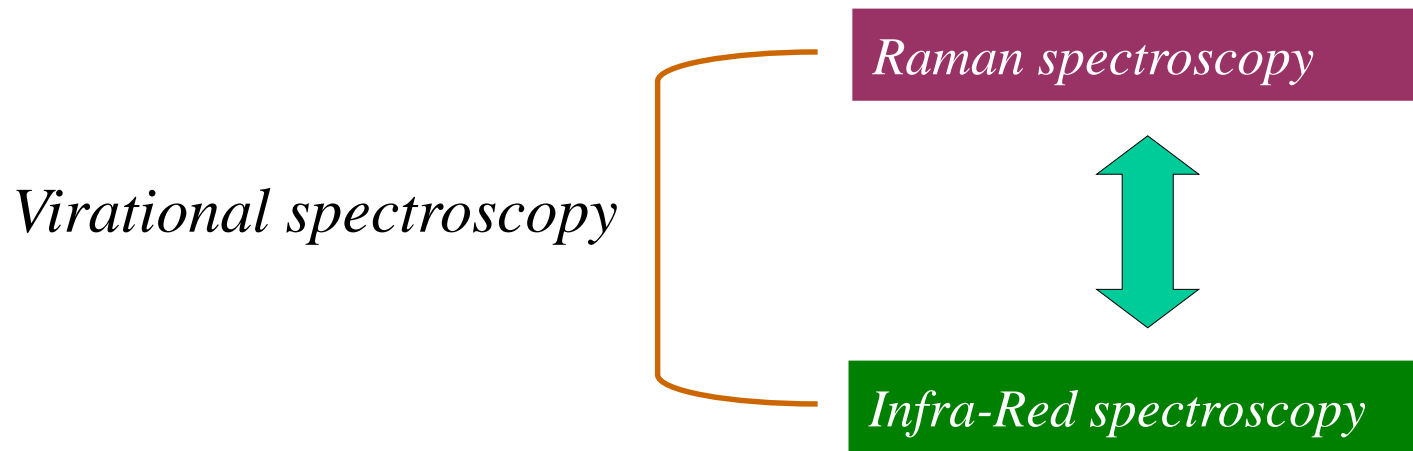


PtRu(1:1), 50 % CO

Change of bonding energy of CO-Pt

2. Vibration spectroscopy

(2) Raman spectroscopy



Comparison: IR vs. Raman

Infra-Red spectroscopy

- Absorption
- IR source
- Change of dipole moment, charge distribution



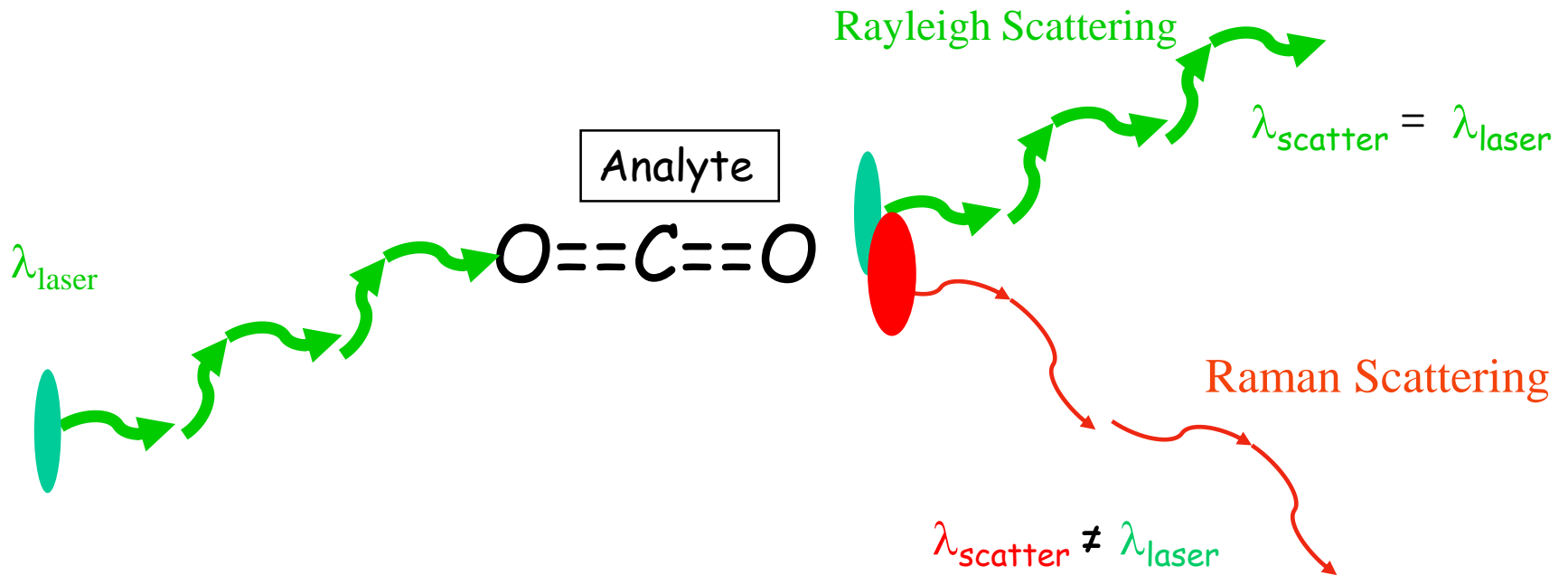
Raman spectroscopy

- Scattering
- Visible or NIR source.
- Change of polarizability



In case of homonuclear molecule, IR inactive, Raman active

What is Raman effect ?



A Light Scattering Process: A photon (Laser source at only one wavelength) bounces off a molecule and loses a small amount of energy equal to the vibrational energy of the molecule.

Scattering of radiation (산란)

The transmission of radiation in matter → momentary retention of the radiation energy by atoms, ions, and molecules → reemission of the radiation in all directions as the particles return to their original state: scattering

Rayleigh scattering: scattering smaller than the wavelength of the radiation . 파장에 비하여 작은 미립자에 의한 현상으로 산광의 세기가 파장의 4제곱에 반비례, 단파장의 빛일수록 강하게 산란.

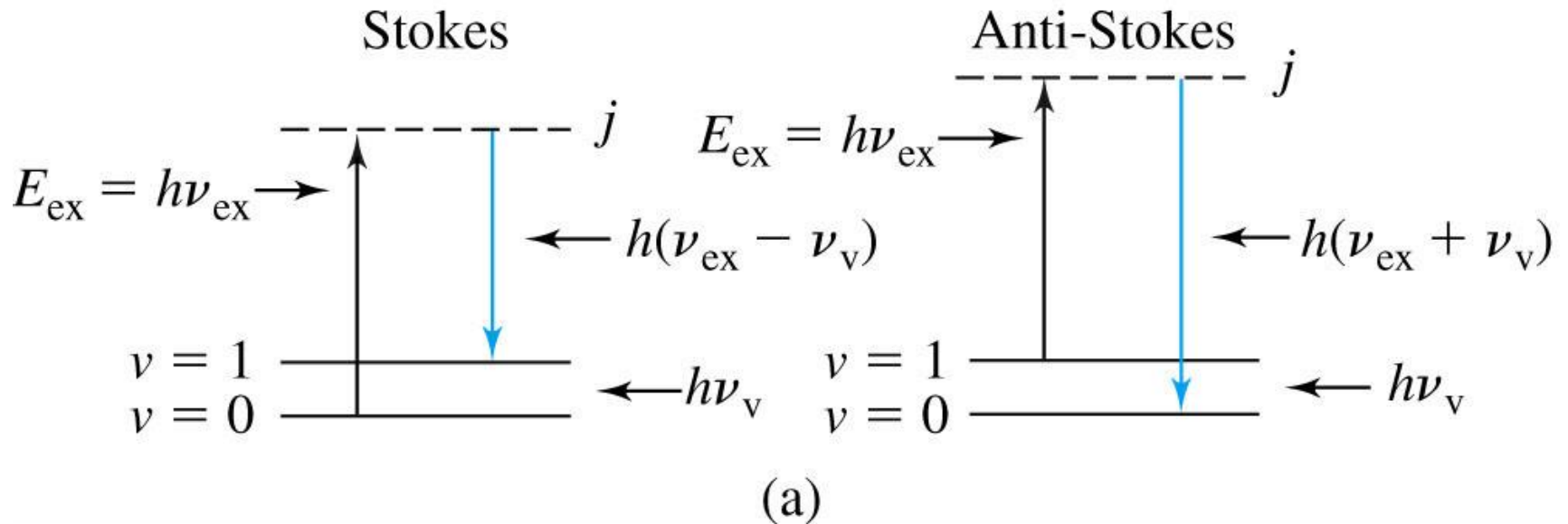
e.g., blue color of the sky: greater scattering of the shorter wavelength of visible spectrum
아침/저녁놀: 단파장 산란, 장파장 투과하기 때문에 붉게 보임

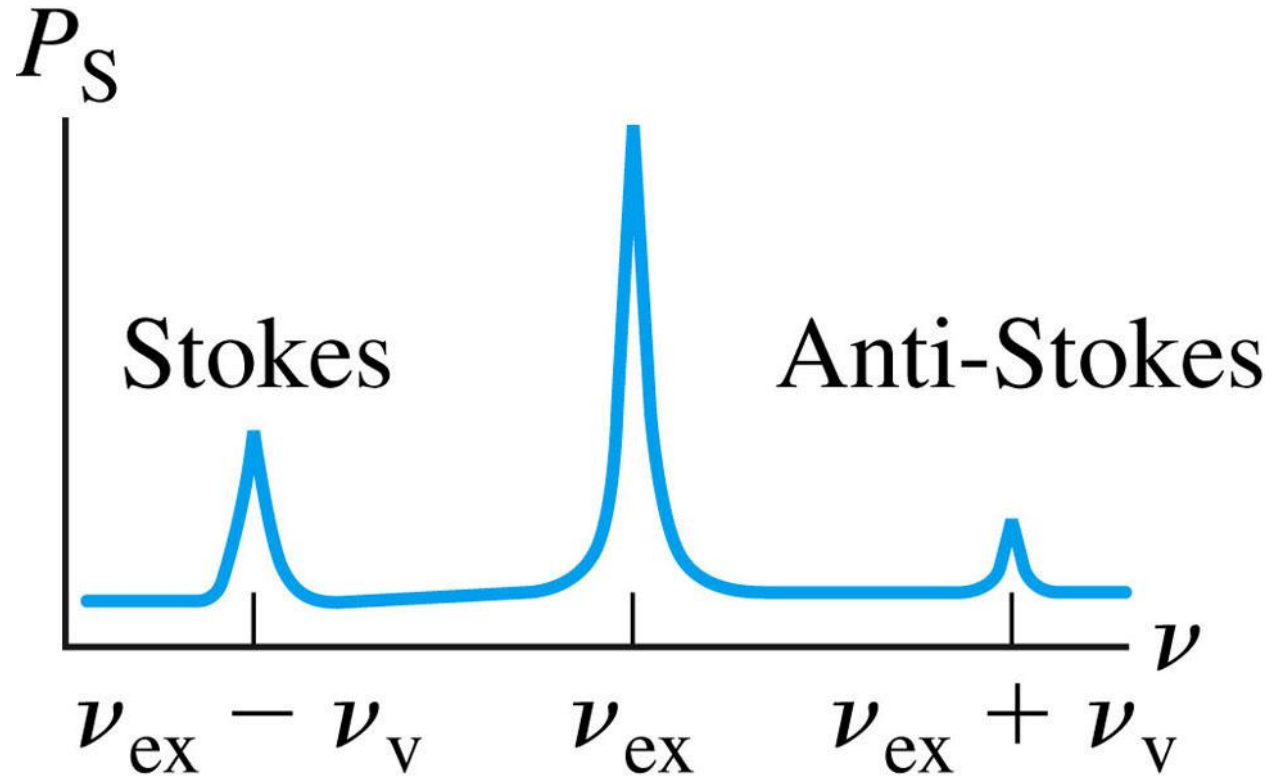
Scattering by large molecules: With large particle, scattering can be different in different directions (Mie scattering, 빛의 파장과 거의 같은 크기의 입자들에 의해 일어나는 산란 현상. 대기오염 물질이 많을 때 대기가 회색을 띠는 예) → used to determine the size and shape of large molecules and colloidal particles

Raman scattering: from vibrational energy level transitions that occur in the molecules as a consequence of the polarization process. Raman spectroscopy에 이용. (대부분 산란은 입사광선의 파장과 같지만 라만효과는 입사광선과 파장이 다름

Monochromatic beam of energy $h\nu_{\text{ex}}$ \rightarrow excitation to a virtual state j \rightarrow scattering

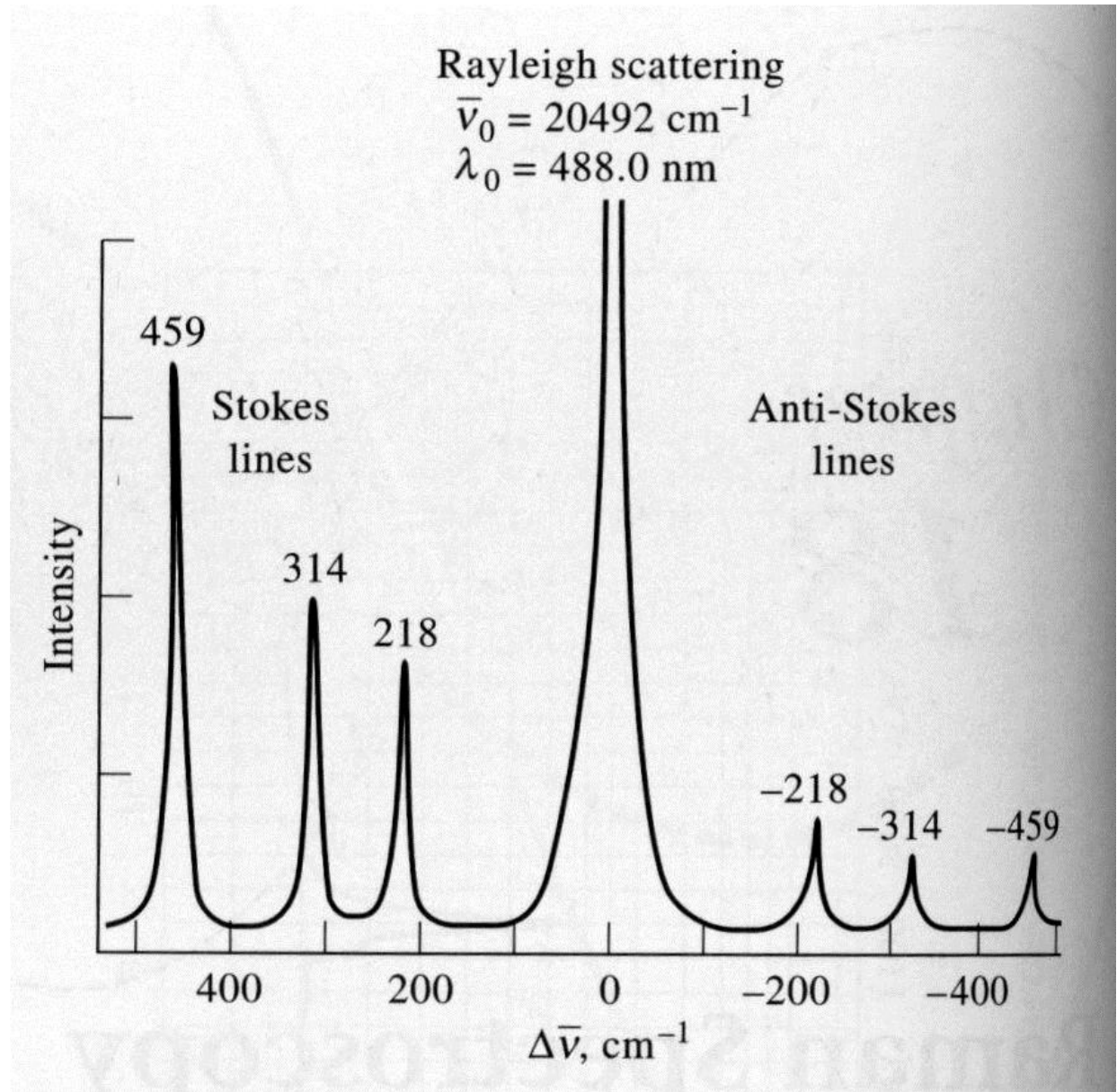
Frequency shift of inelastic scattering = vibrational frequency



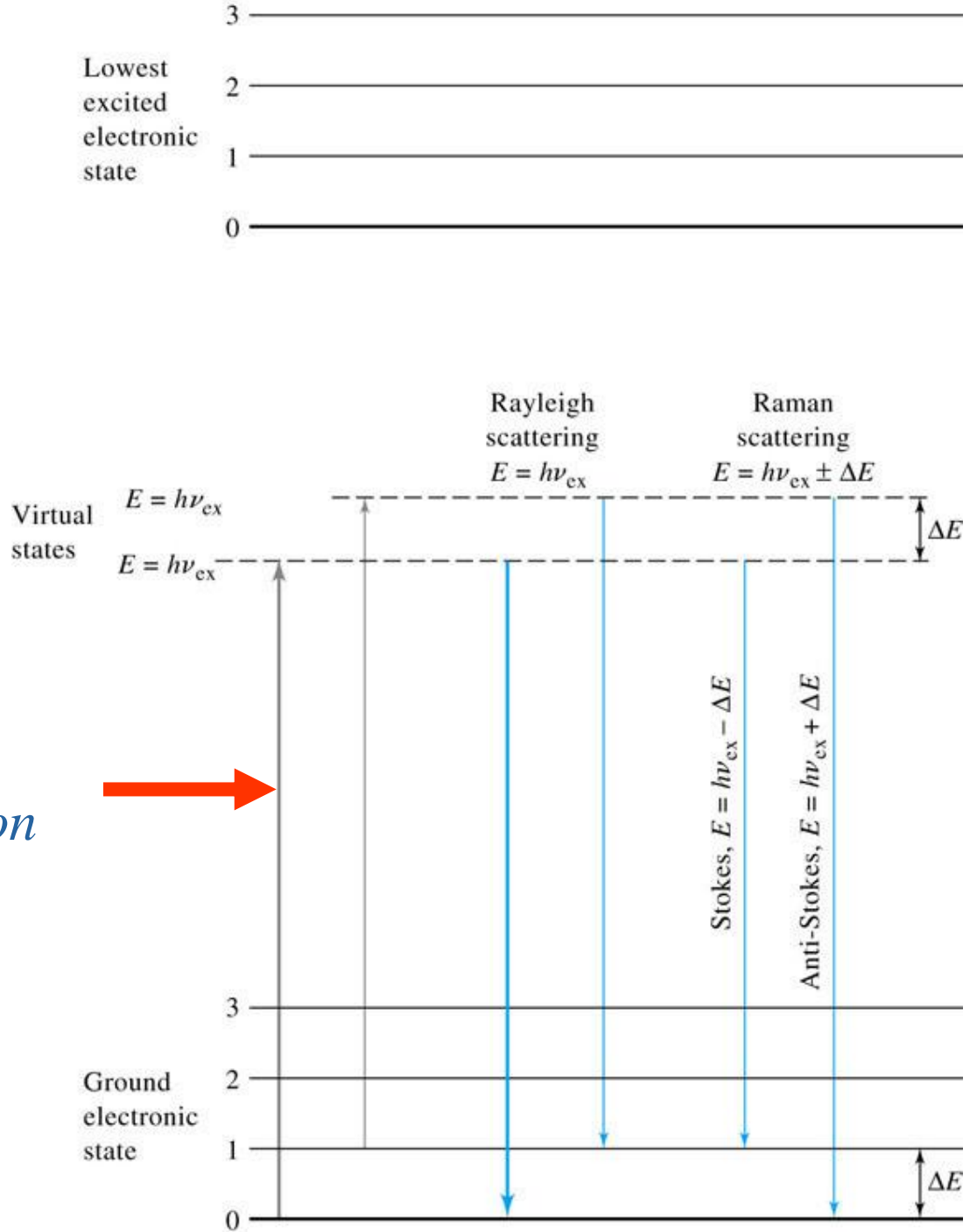


(b)

CCl_4
Excited by laser
(488 nm (= 20492
 cm^{-1}))



Temporal polarization

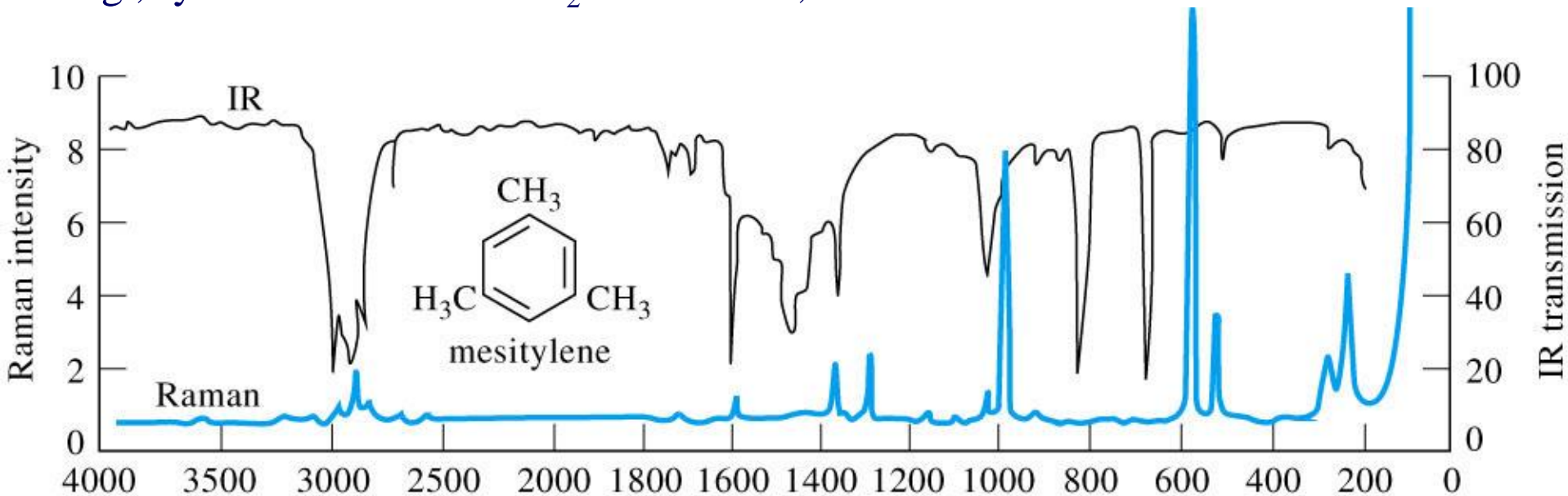


IR vs. Raman

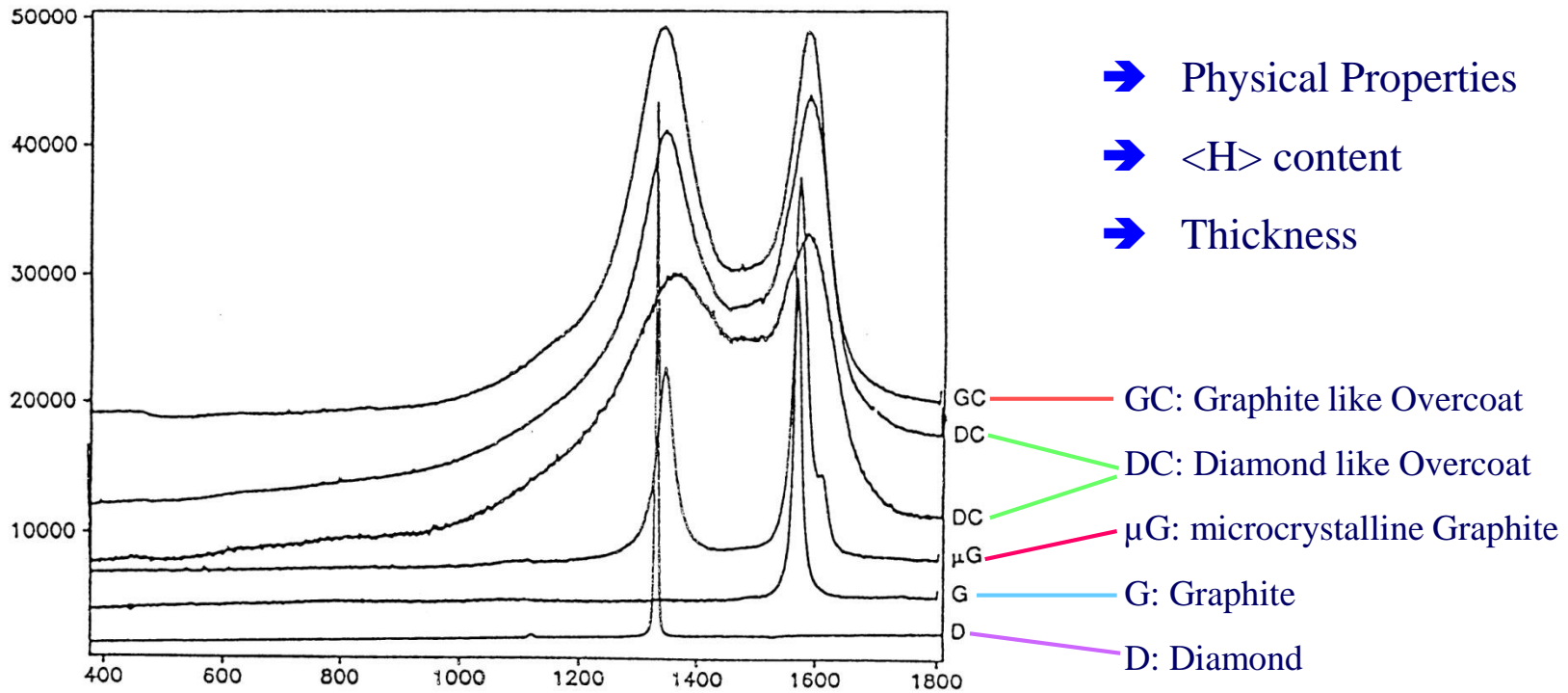
Similar, different intensities

Different in some peaks: IR active or inactive, Raman active or inactive

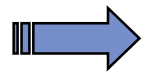
e.g., symmetric mode of CO₂: IR inactive, Raman active



Raman Spectra of different modifications of carbon

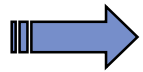


What is Raman Spectroscopy offering?



Qualitative results

- ✓ Identification
- ✓ Nature of functional groups
- ✓ Structure: crystalline or amorphous phases
- ✓ Specific physical properties



Quantitative results (calibration is necessary)

Benefits of Raman Spectroscopy

No need for sample preparation.

- Water inactive.

Non-destructive, non-invasive technique.

- Laser energy is low so the sample remains intact.

What can Raman Spectra tell us ?

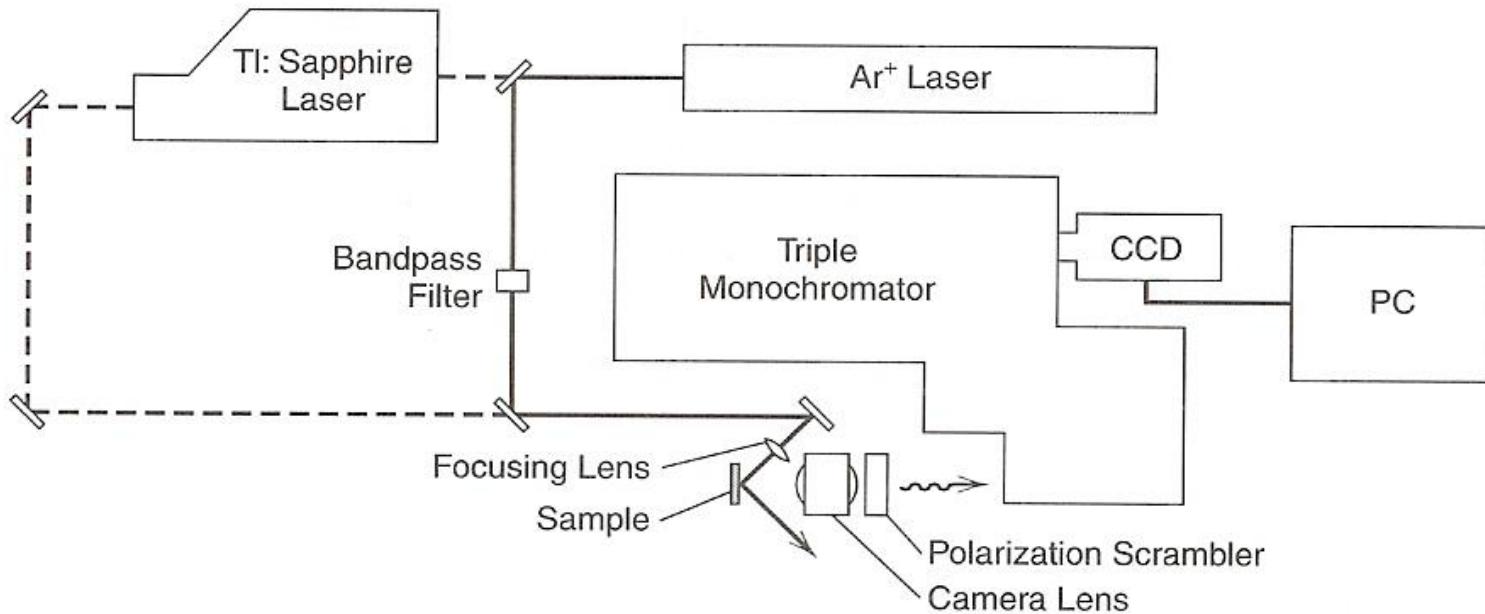
- Vibrational frequencies are characteristic of chemical bonds or groups of bonds in a specific molecule: normal modes
- A Raman spectrum provides a fingerprint of the set of bonds present in the material
- Vibrational frequencies are sensitive to details of the local environment of a molecule, such as crystal phase, local strain, and degree of crystallinity.
- Relative intensities within a spectrum can quantify the orientation of the bond w.r.t. the incoming laser polarization
- Raman spectroscopy can be complementary to IR

Raman spectroscopy: molecular vibrational information complementing IR spec.

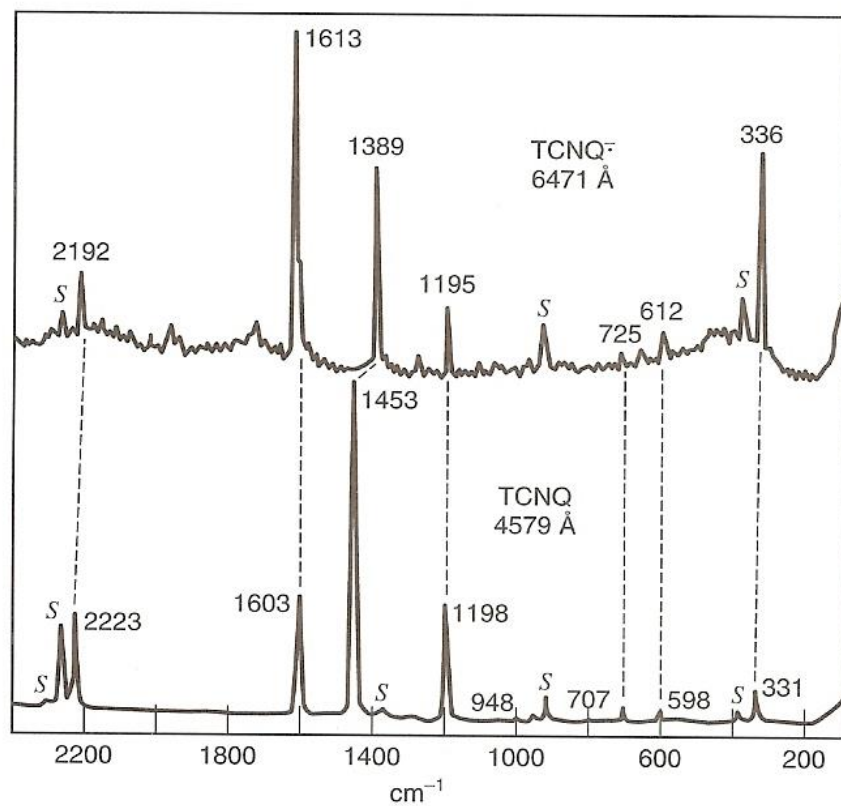
Raman in electrochemical system: signal enhancement

- Resonance Raman spectroscopy (RRS)

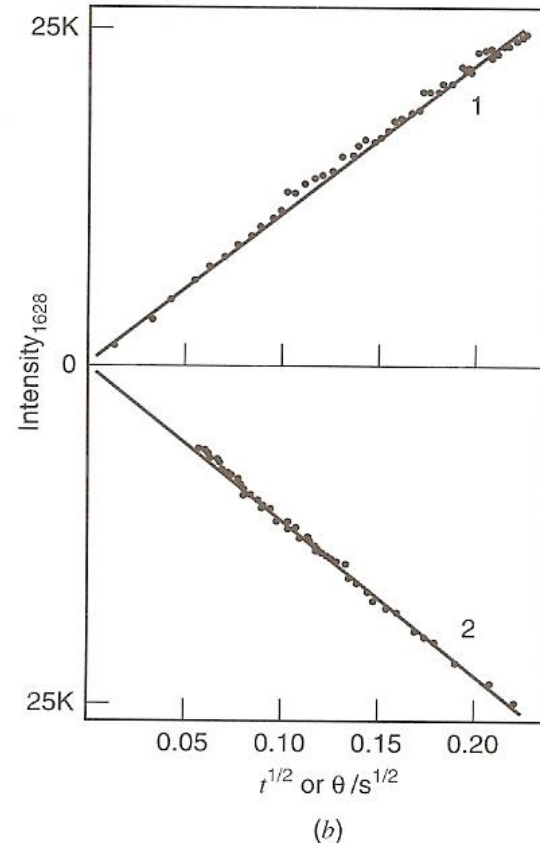
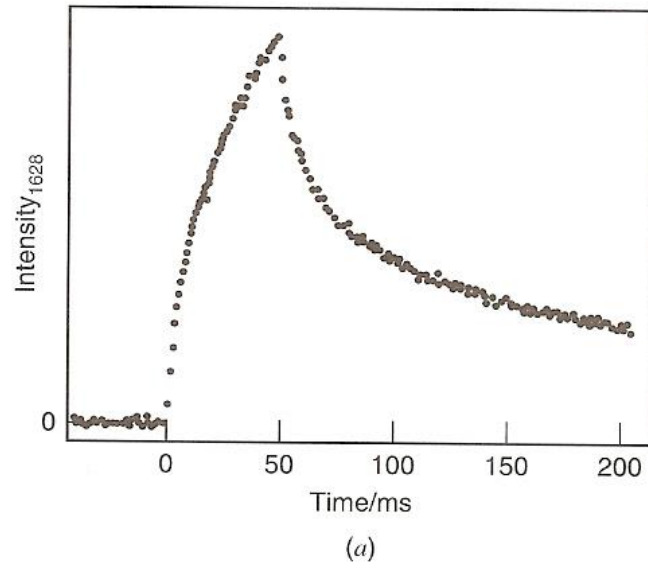
- Surface enhanced Raman spec. (SERS): molecules adsorbed on certain surfaces
(Ag or Au)



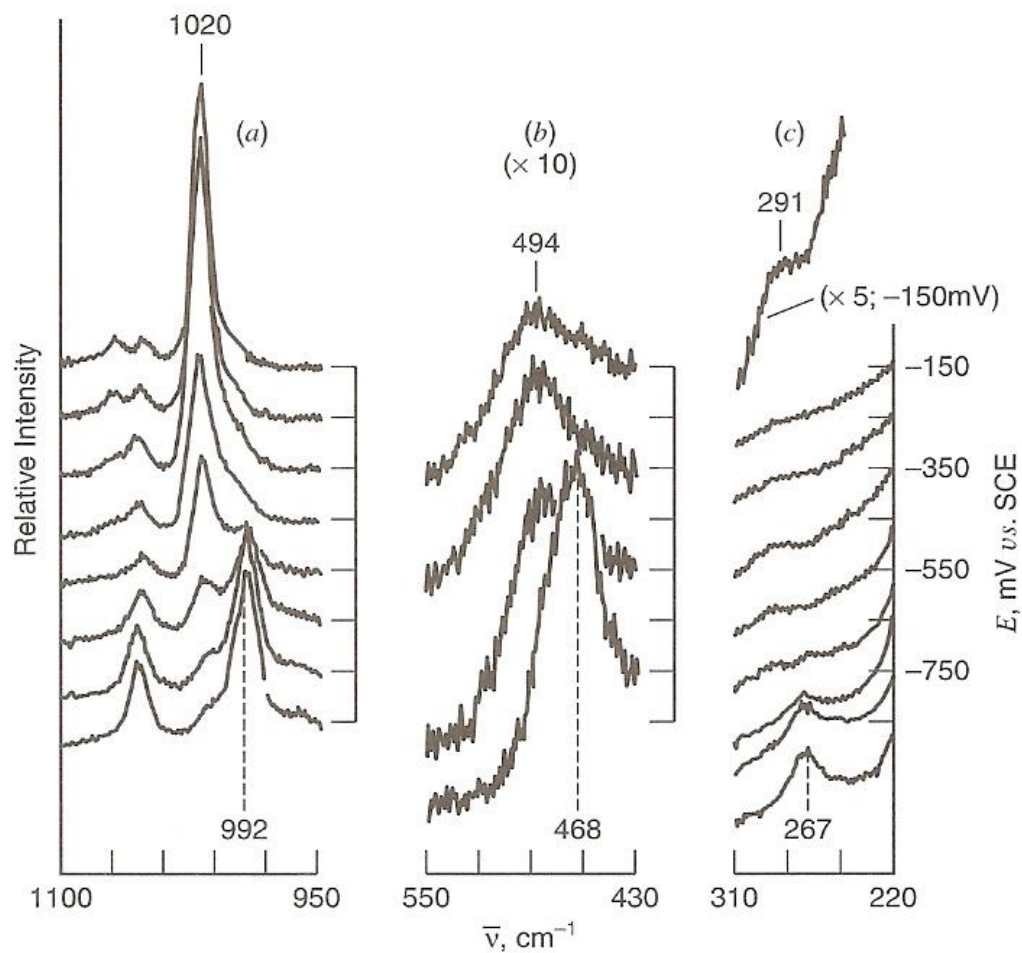
RRS of TCNQ & electrochemically generated TCNQ⁻



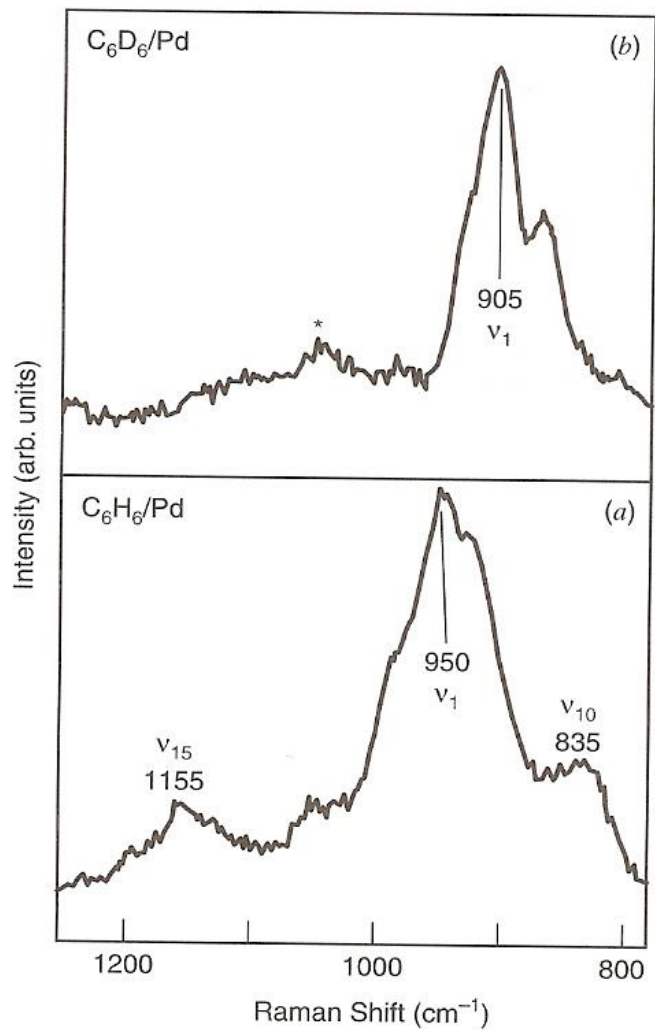
Transients in Raman intensity



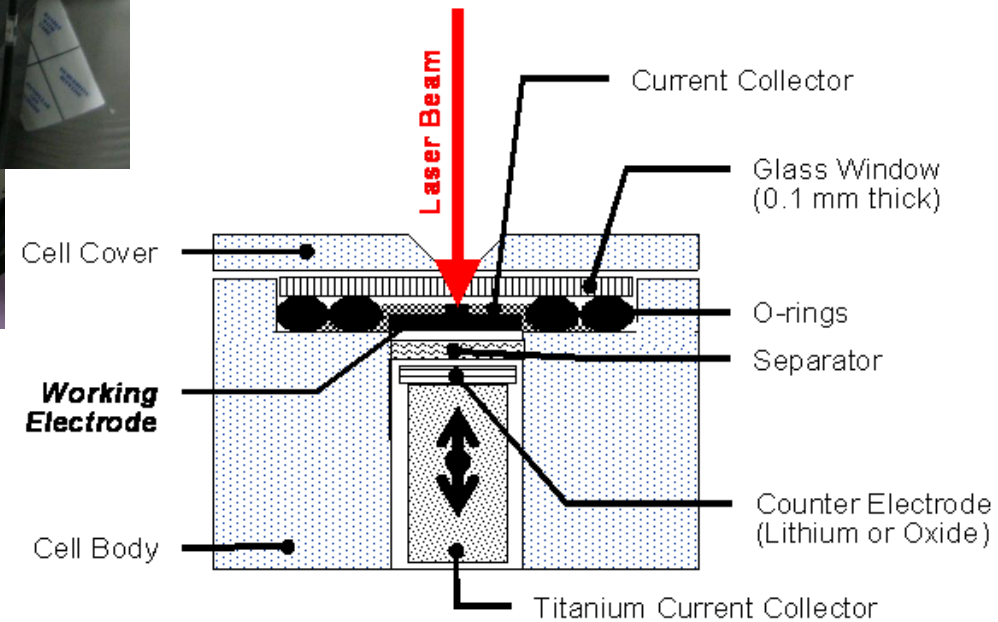
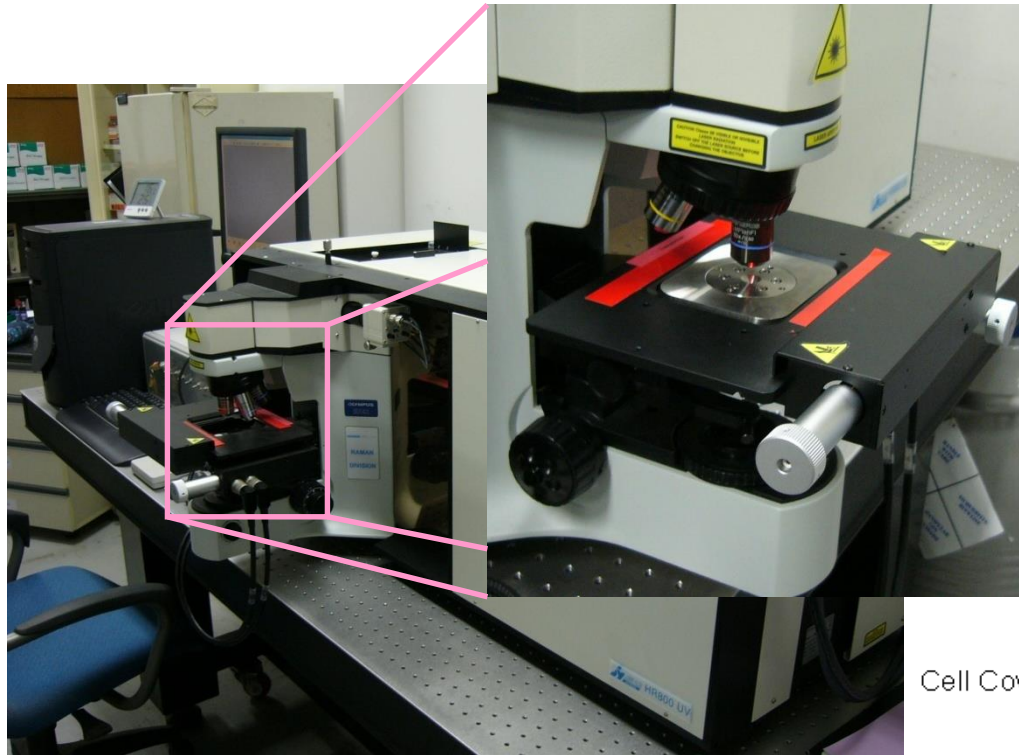
SERS for Os compound on Ag electrode as ftn of potential



SER spectra for benzene on Pd



In-situ Raman Spectroscopy (SNU)

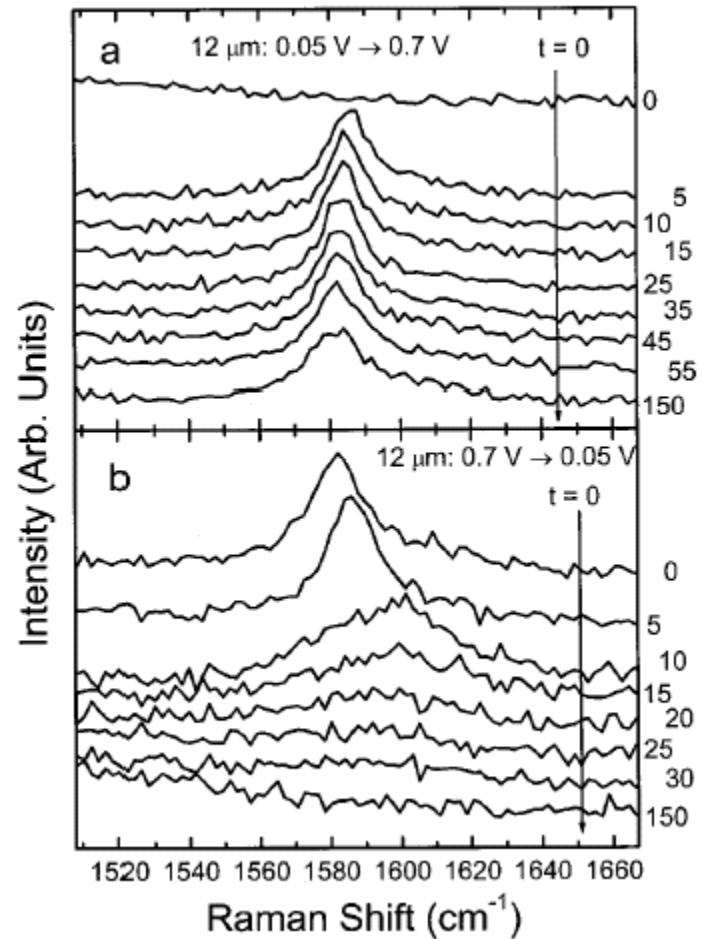
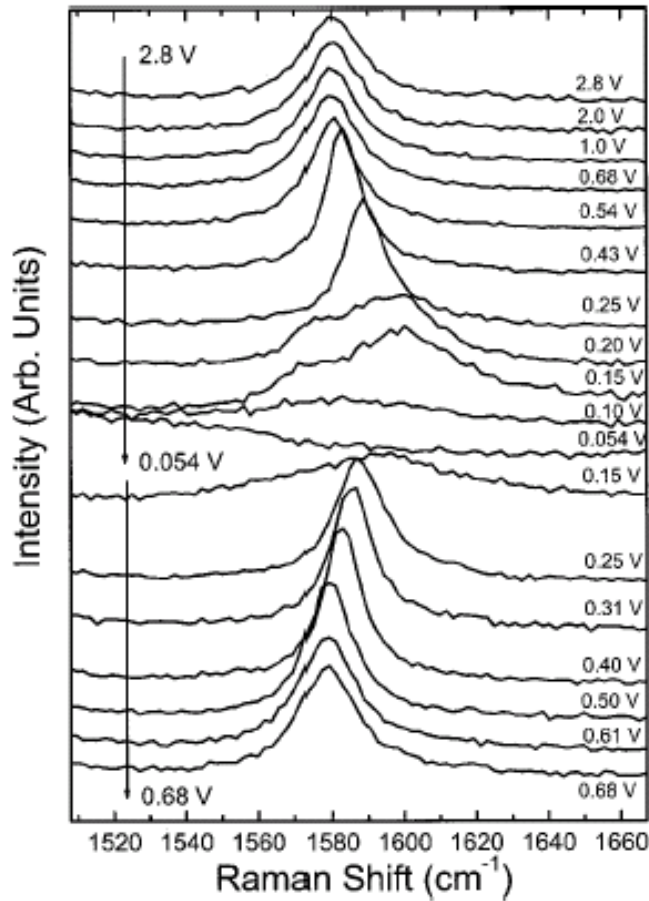


Specifications of HR LabRam

- ➡ Covering spectral range from 200-1600 nm
- ➡ Laser : Ar ion laser : 514.5 nm (green), 50 mW.
He/Ne laser : 632.8 nm (red), 17 mW.
- ➡ Grating : 1800 gr/mm, 600 gr/mm
- ➡ Visible objective : 10X, 50X, 100X, 50X LWD
- ➡ CCD detector : a multichannel LN₂ cooled (-133 °C)
1024 × 256 pixels

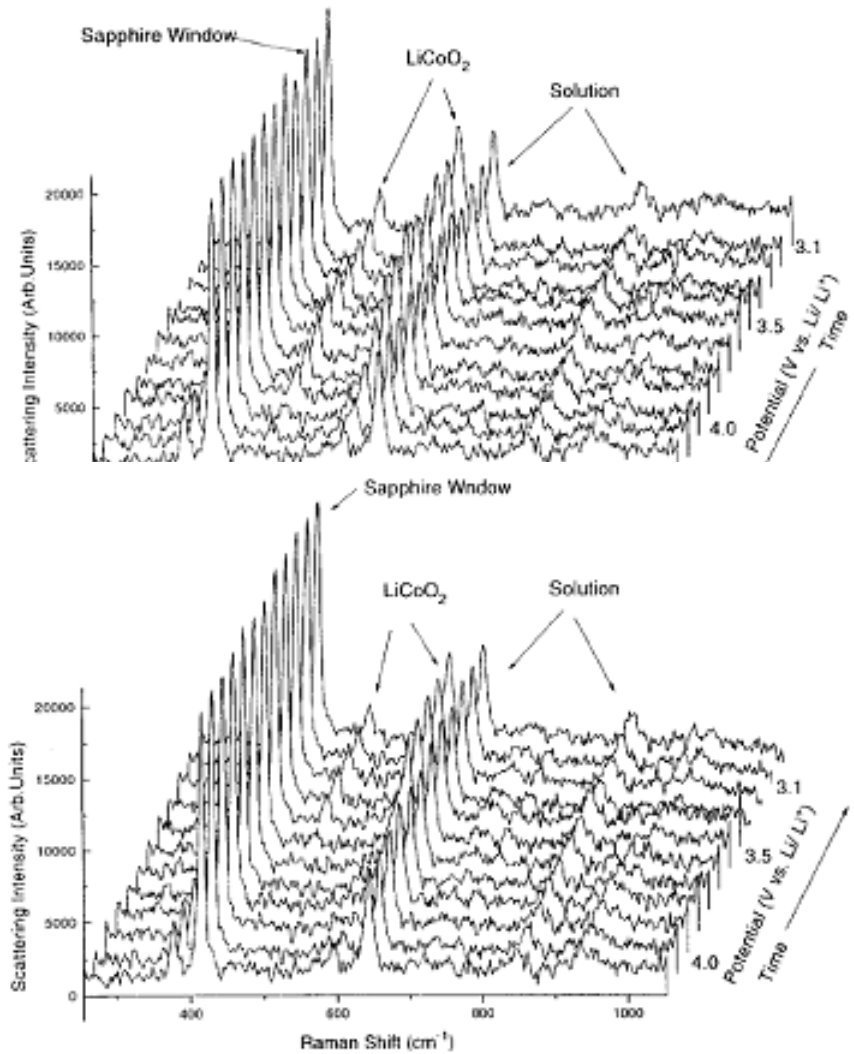
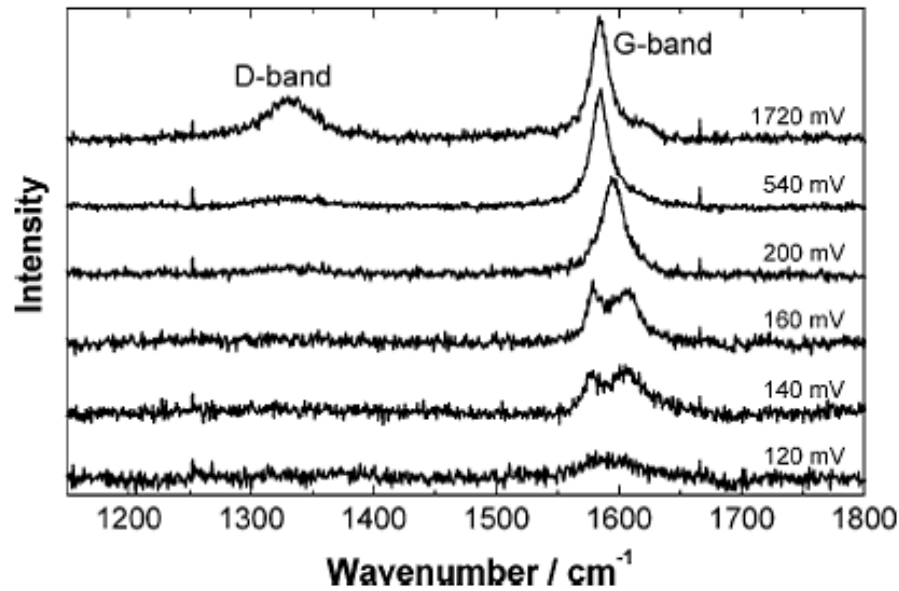
Structural Changes according to Li⁺ intercalation

➤ Li⁺ intercalation

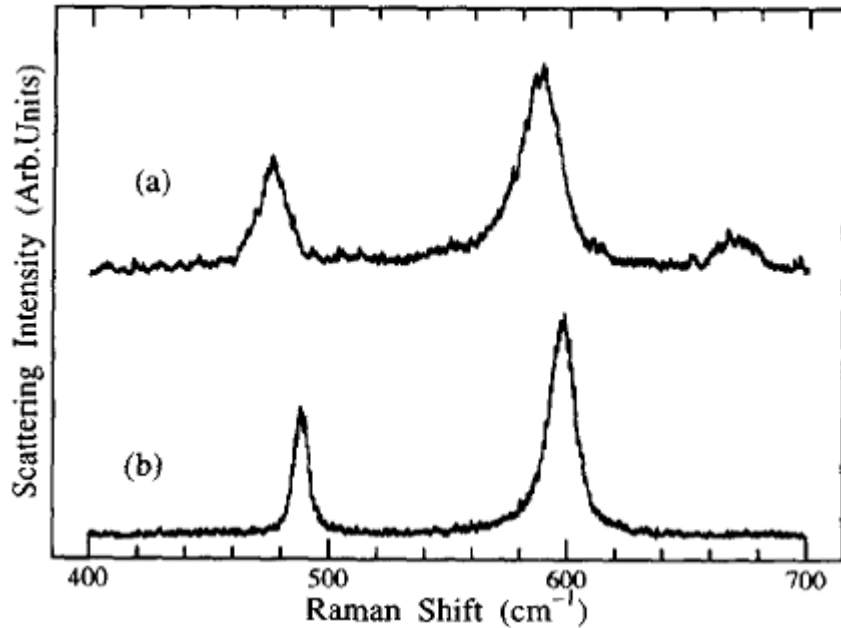


Scherson (2002)

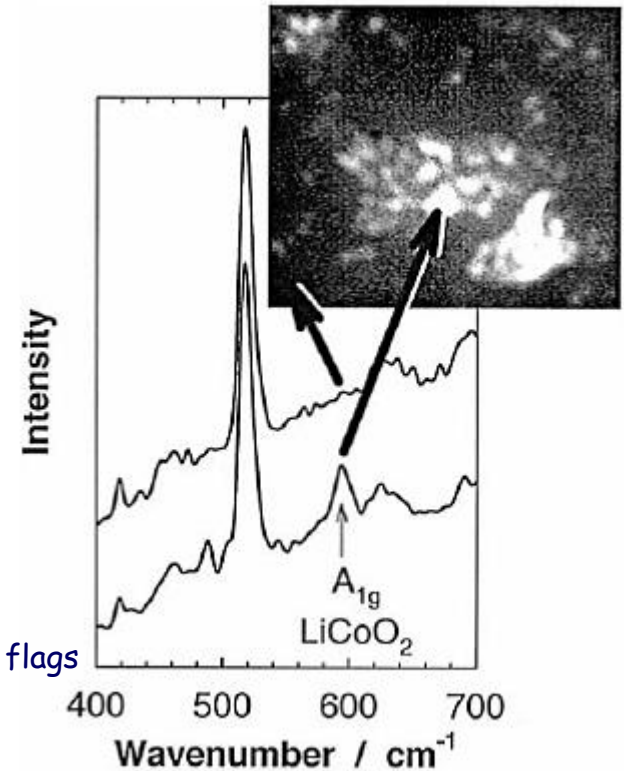
Structural Changes according to Li⁺ intercalation



LiCoO₂



Variation of Raman spectra of (a) powder and (b) thin film of LiCoO₂ on gold flags



LiCoO₂ unit cell의 전체 진동 모드 : $A_{1g} + E_g + 2A_{2u} + 2E_u$

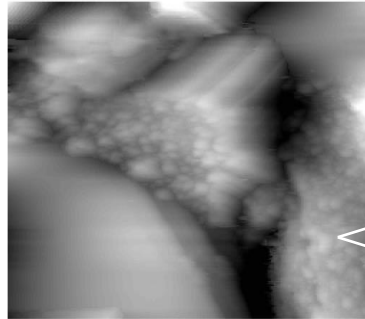
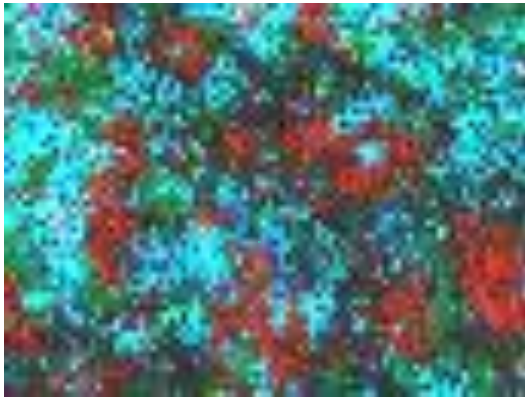
A_{1g}, E_g 모드는 Raman active, $2A_{2u}, 2E_u$ 모드는 IR active.

485cm⁻¹ 와 597 cm⁻¹ 에서의 라만 라인은 각각 A_{1g}, E_g 모드에 해당.

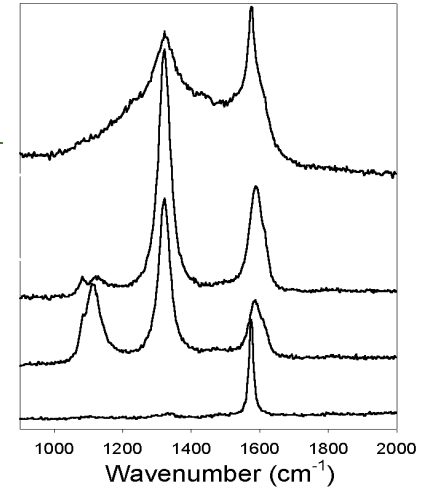
Peak의 shift와 width 차이 -> Film의 결정성이 뛰어나기 때문에

➤ In situ Raman microscopy

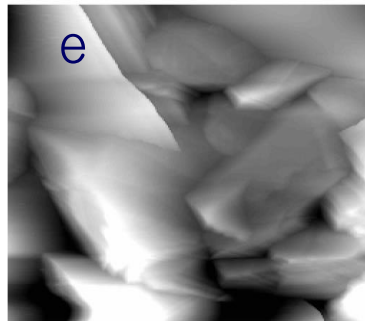
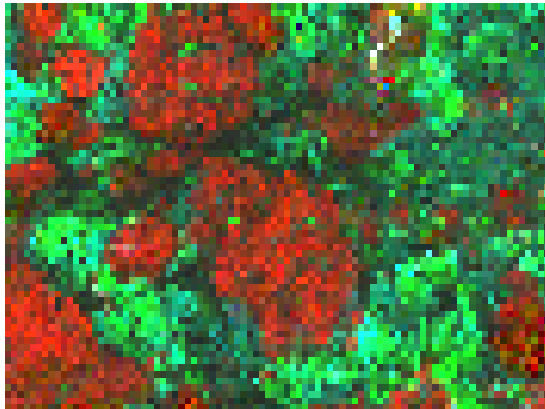
25°C



μm
0.8
0.4
0.0



60°C



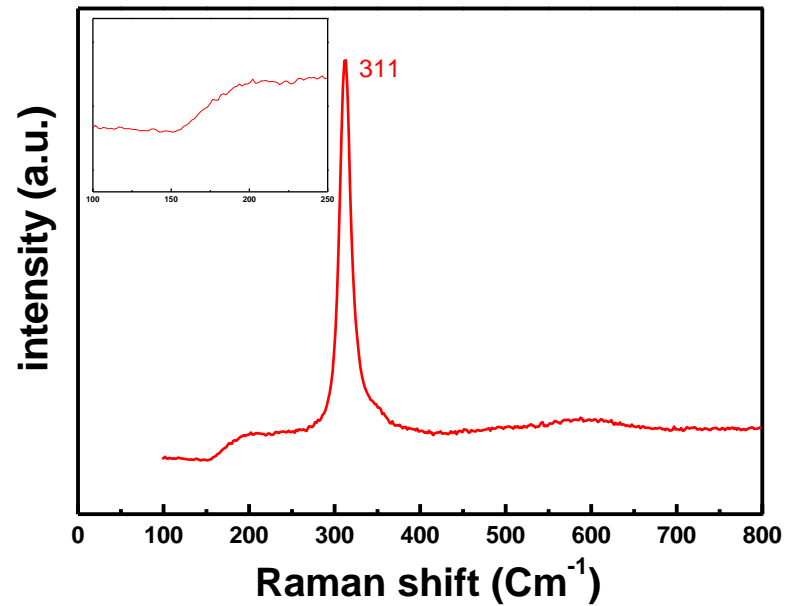
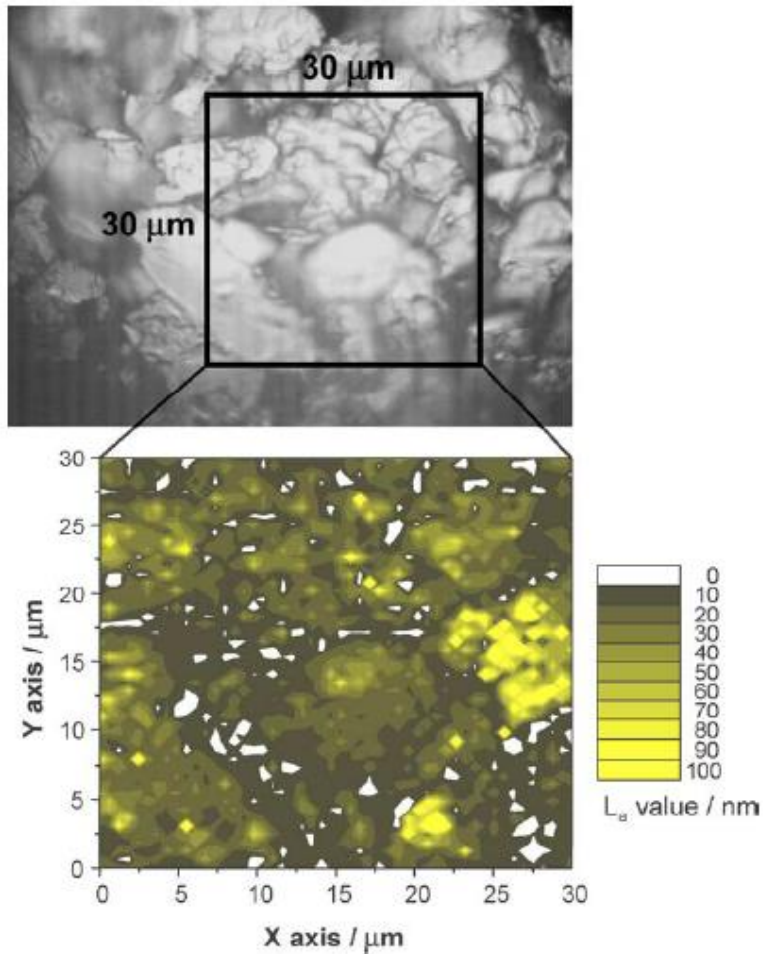
Fresh anode

μm
0.8
0.4
0.0

- LiCoO₂
- graphite
- acetylene black

Brodd (2003)

in-situ Raman

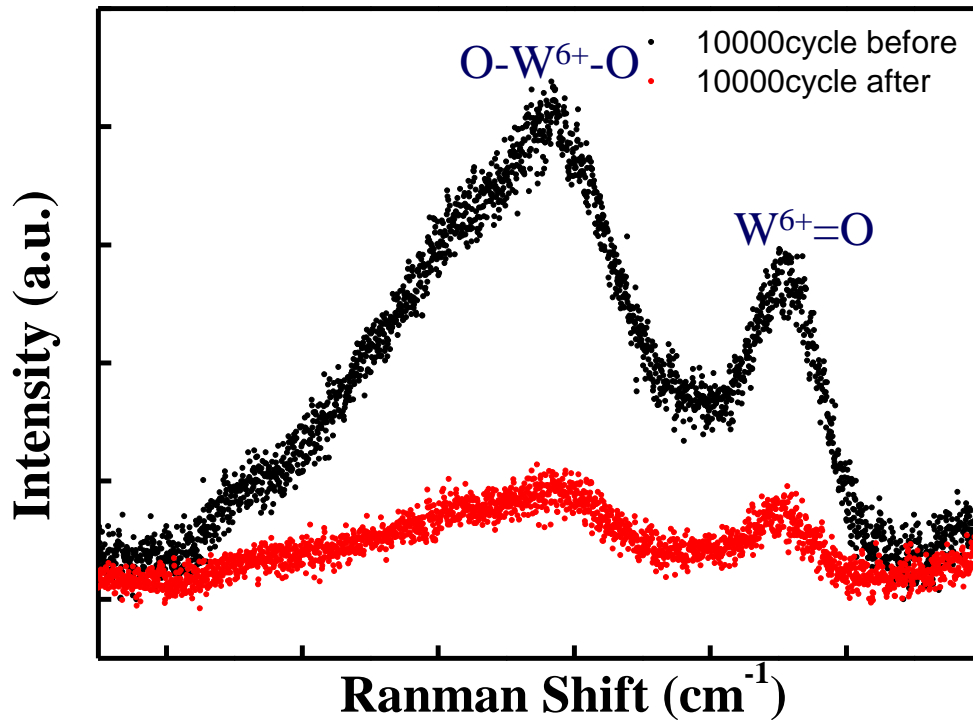


Raman spectra of SnS₂ nanopowder by solvothermal synthesis

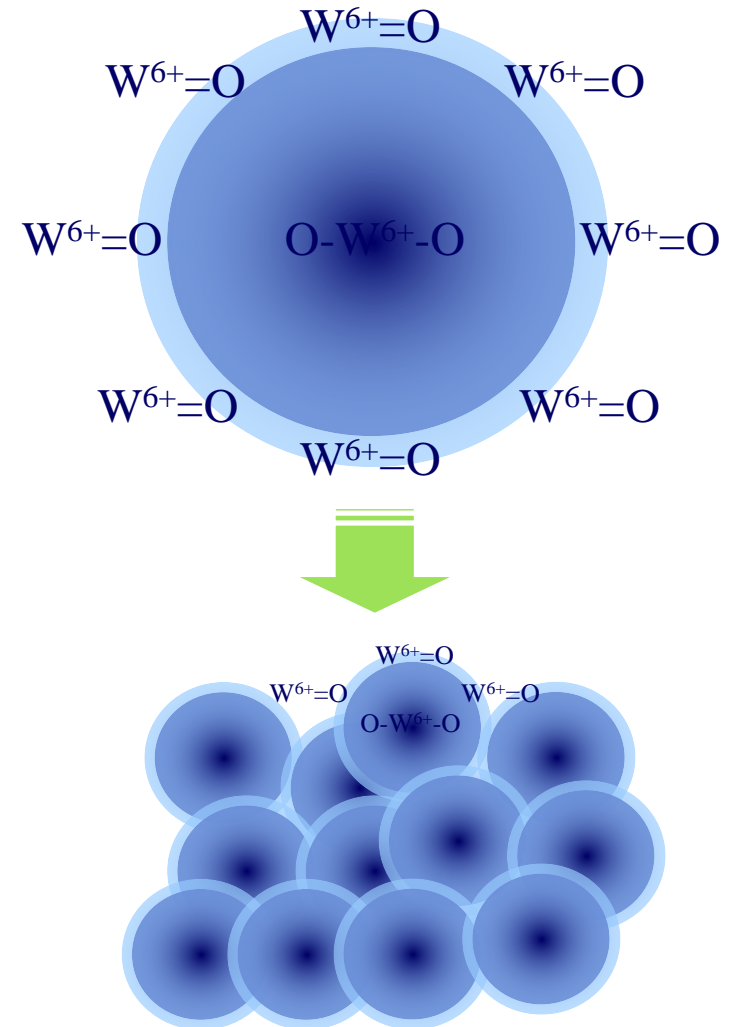
2005 CMAB

Raman mapping of graphite surface: a graphite sample (top) and spatial distribution plot of the L_a values

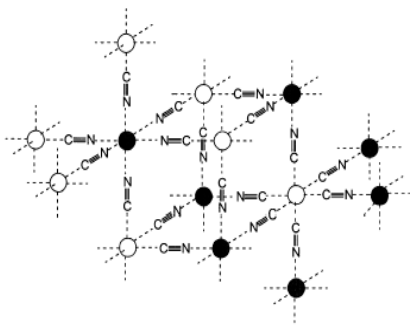
In situ Raman - WO_3



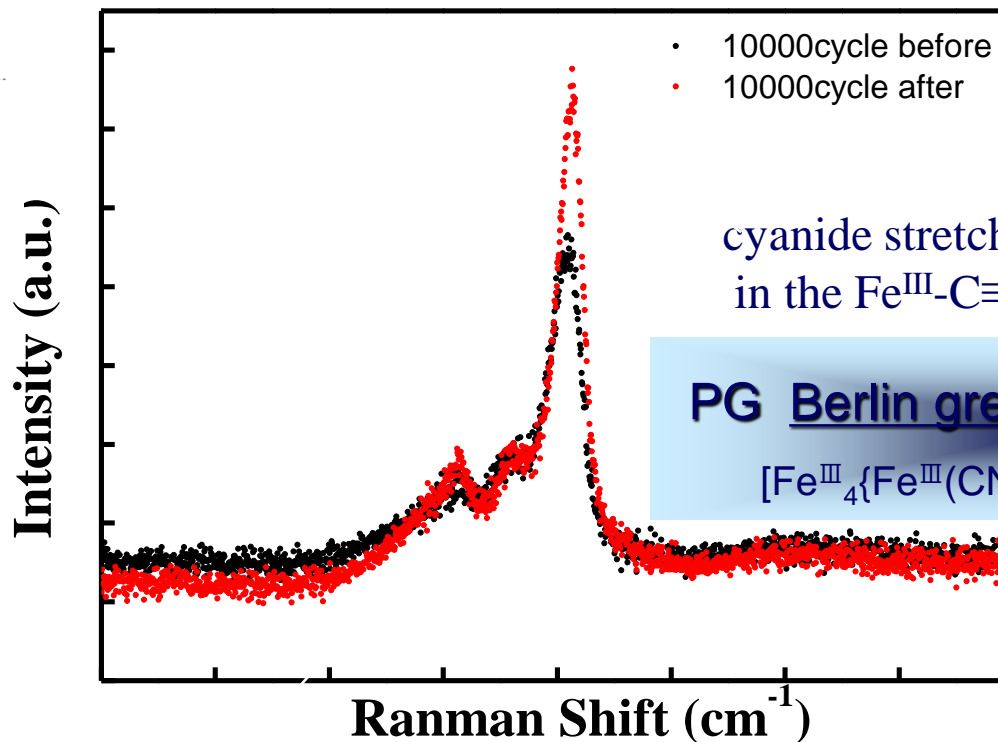
- The $\text{W}^{6+}=\text{O}/\text{O}-\text{W}^{6+}-\text{O}$ ratio \rightarrow increase
- The grain size \rightarrow decrease



Raman data - PB



- **PB** Prussian blue
[Fe^{III}Fe^{II}(CN)₆]⁻
- **PW** Prussian white
[Fe^{II}Fe^{II}(CN)₆]²⁻



cyanide stretching vibration
in the Fe^{III}-C≡N-Fe^{II}

PG Berlin green



cyanide stretching vibration
in the Fe^{III}-N≡C-Fe^{II}

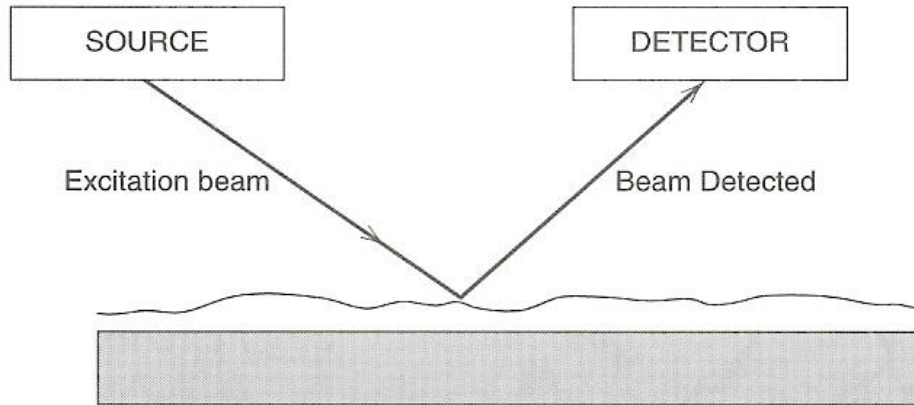
PB Prussian blue



Structure unstable

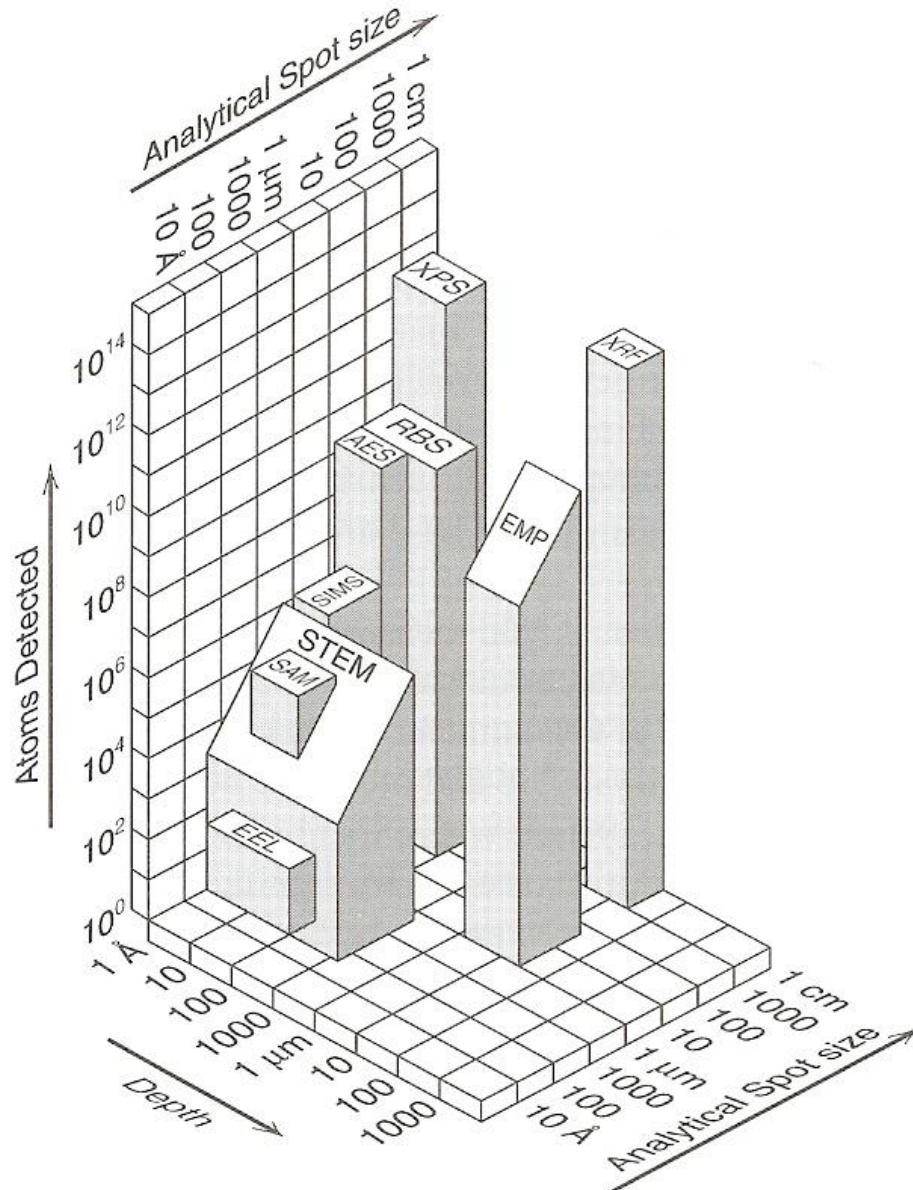
Electron and ion spectrometry

Ultra high vacuum (UHV)

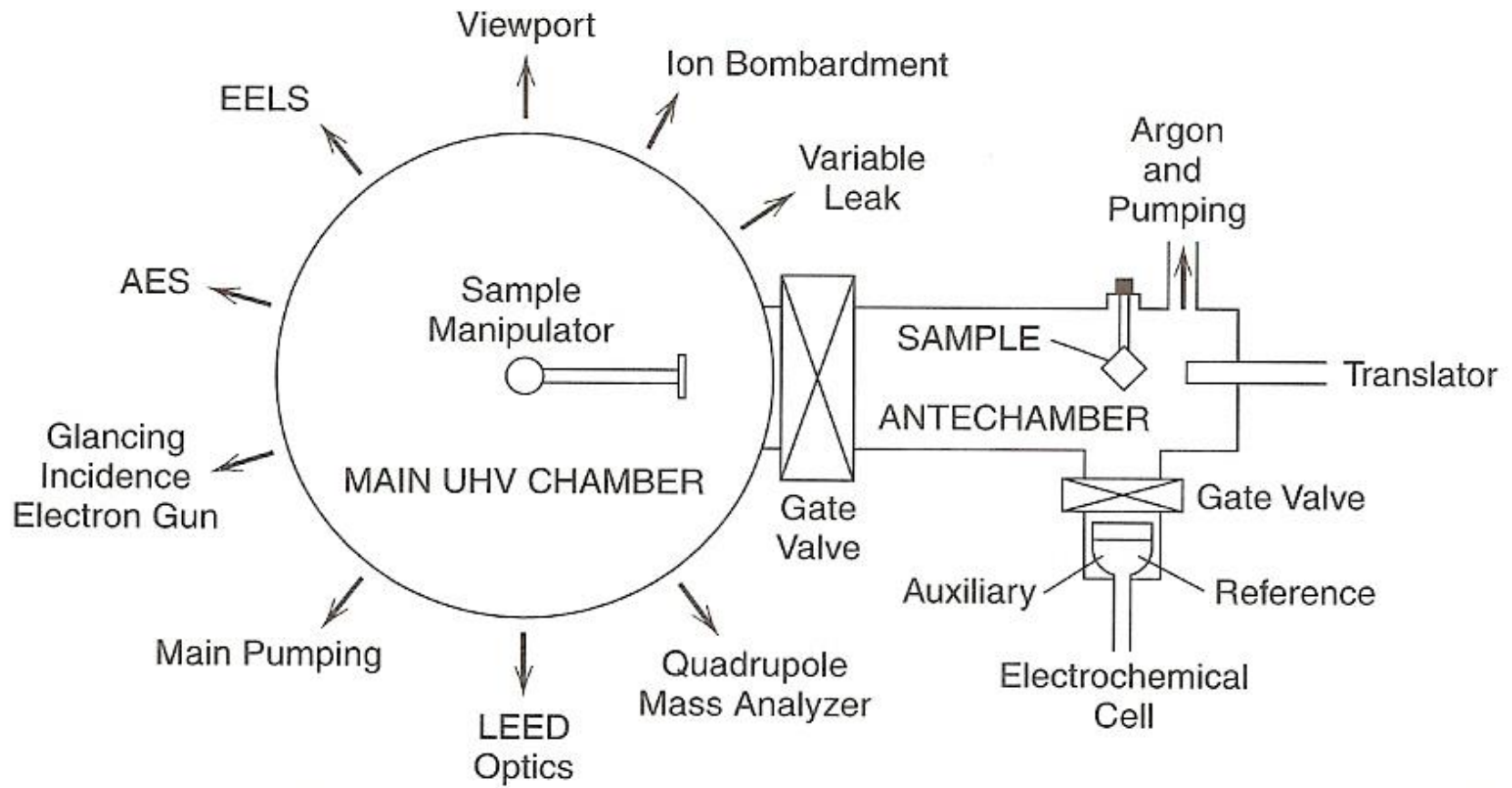


	Excitation	Detection
X-ray photoelectron spectroscopy (XPS)	Photons(X-ray)	Electrons
UV photoelectron spectroscopy (UPS)	Photons (UV)	Electrons
Auger electron spectroscopy (AES)	Electrons	Electrons
Low-energy electron diffraction (LEED)	Electrons	Electrons
High resolution e ⁻ E loss spec. (HREELS)	Electrons	Electrons
Rutherford backscattering (RBS)	H ⁺ or He ⁺	H ⁺ or He ⁺
Secondary ion mass spec. (SIMS)	Ions	Ions
Laser desorption mass spec. (LDMS)	Photons	Ions

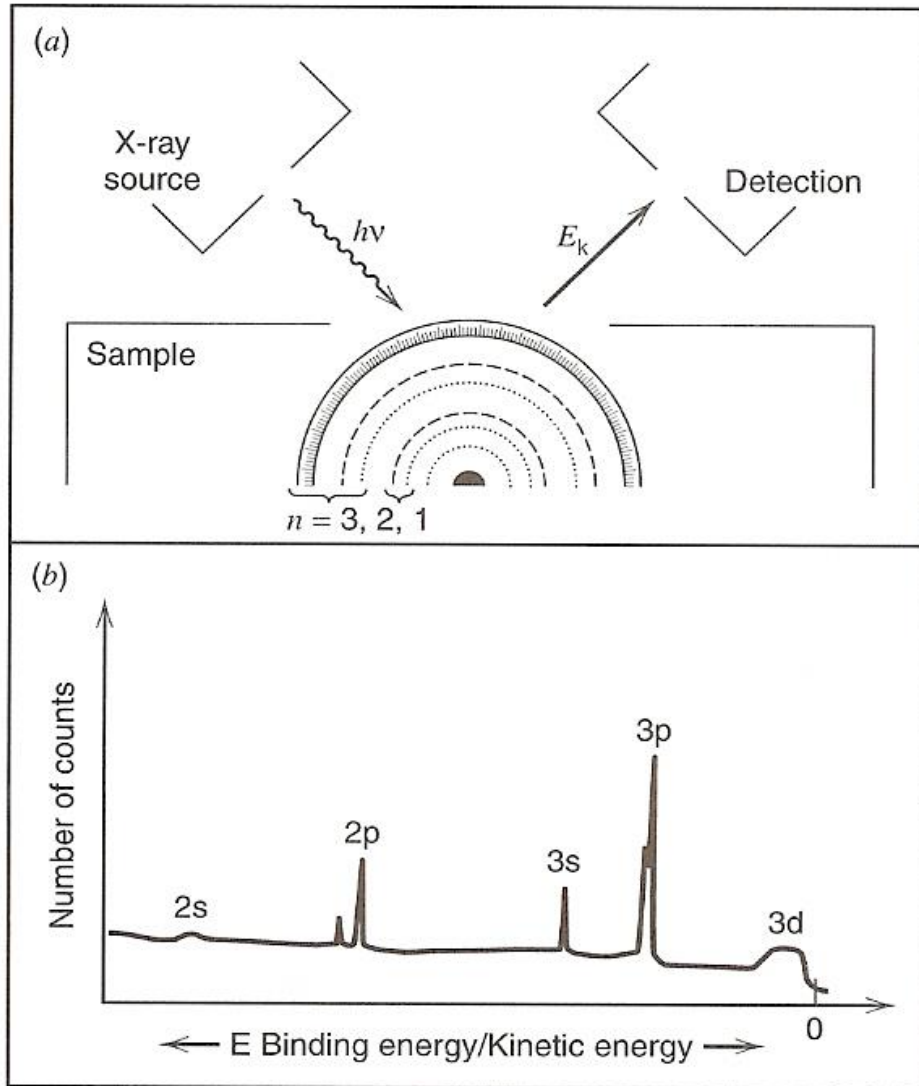
Detection limits, sampling depth, spot size (spatial resolution)



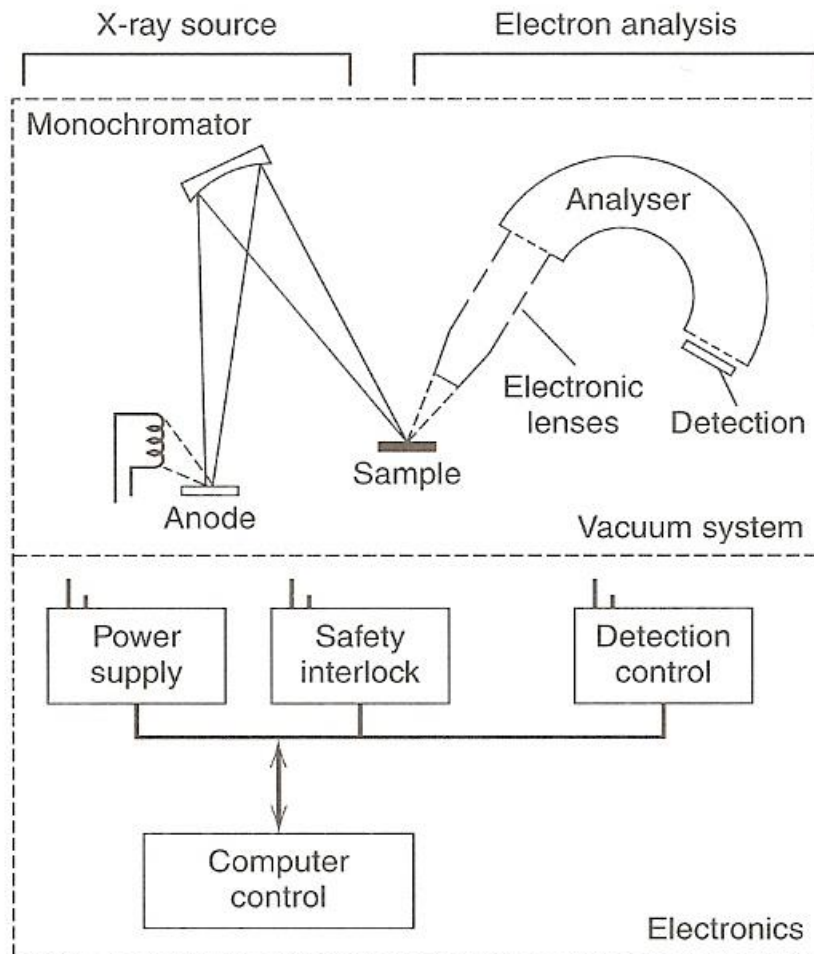
UHV-electrochemistry



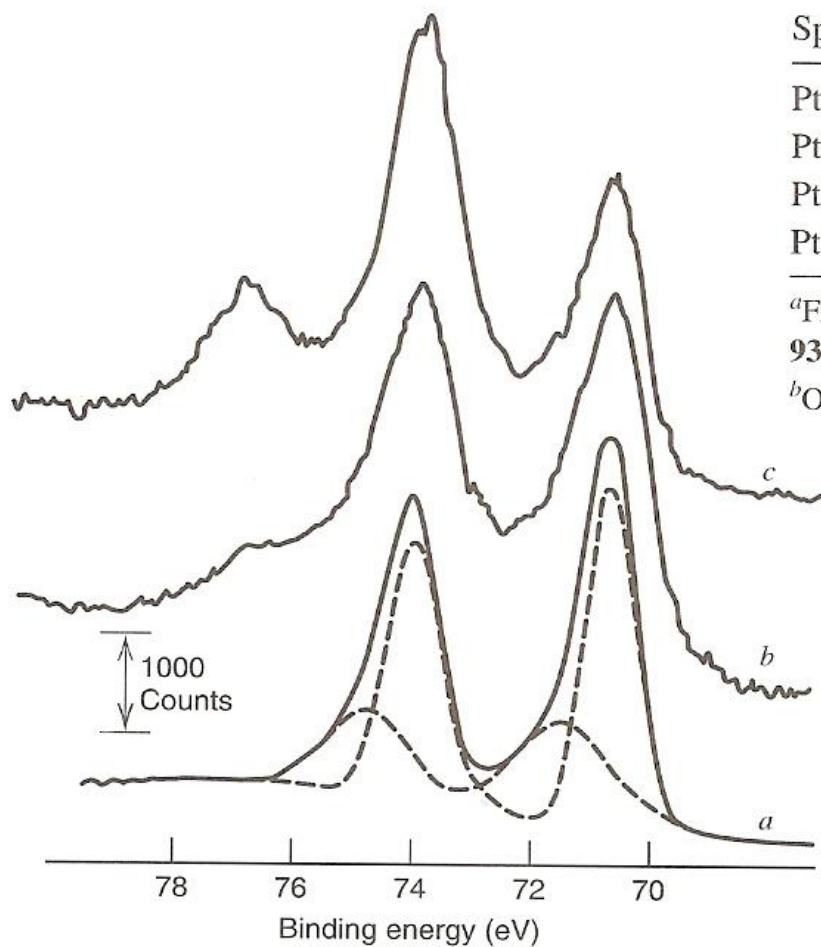
X-ray photoelectron spectroscopy (XPS, or ESCA)



Schematic diagram of XPS



XPS for Pt 4f levels:

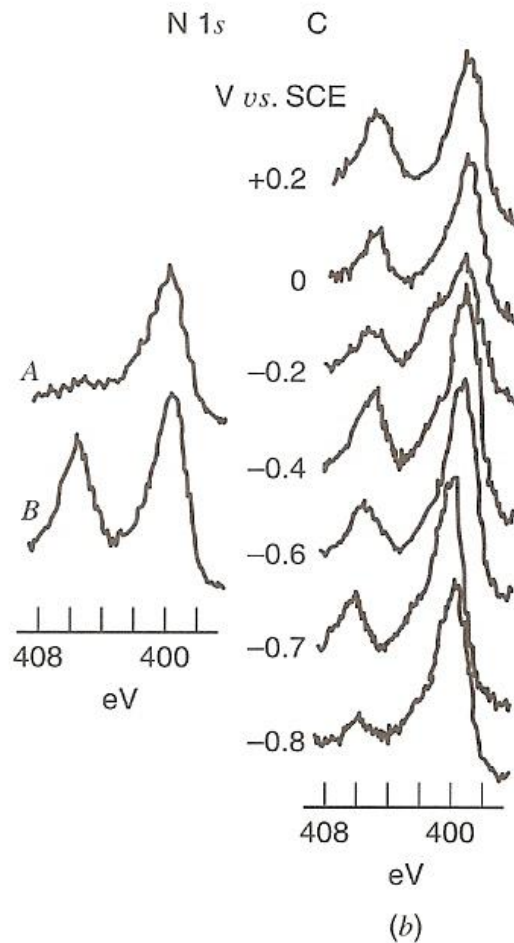
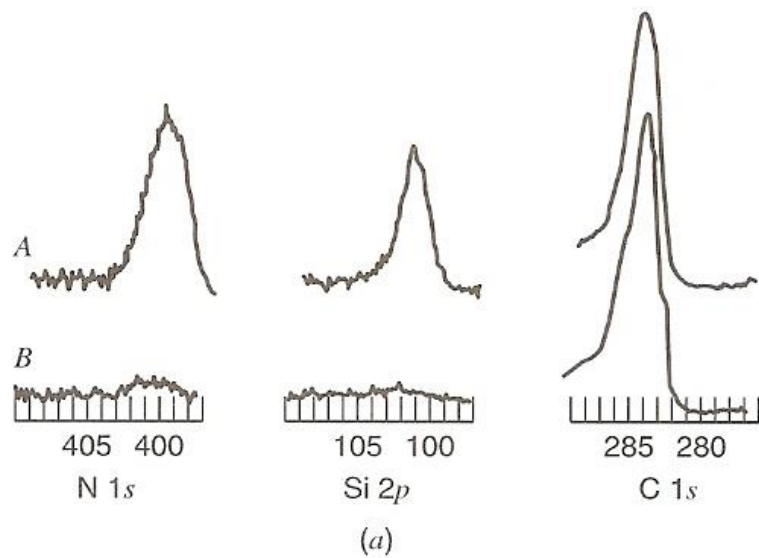


Species	Binding Energy, eV		Relative Peak Areas ^b		
	4f (7/2)	4f (5/2)	+0.7 V	+1.2 V	+2.2 V
Pt	70.7	74.0	56	39	34
PtO _{ads}	71.6	74.9	39	37	24
PtO	73.3	76.6	<5	24	22
PtO ₂	74.1	77.4	0	0	20

^aFrom K. S. Kim, N. Winograd, and R. E. Davis, *J. Am. Chem. Soc.*, **93**, 6296 (1971).

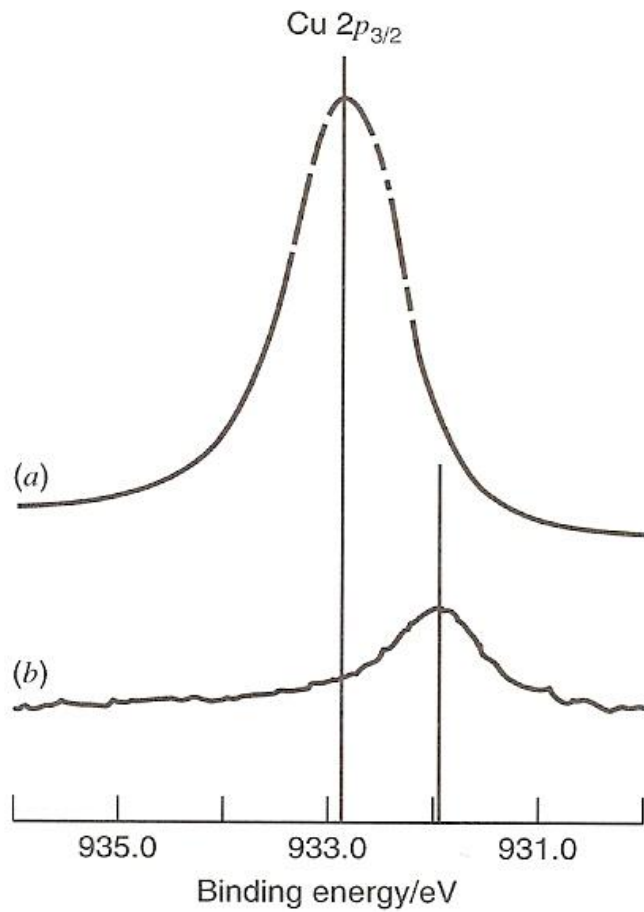
^bOxidation carried out at indicated potential (vs. SCE) for 3 min.

XPS for gassy carbon electrodes

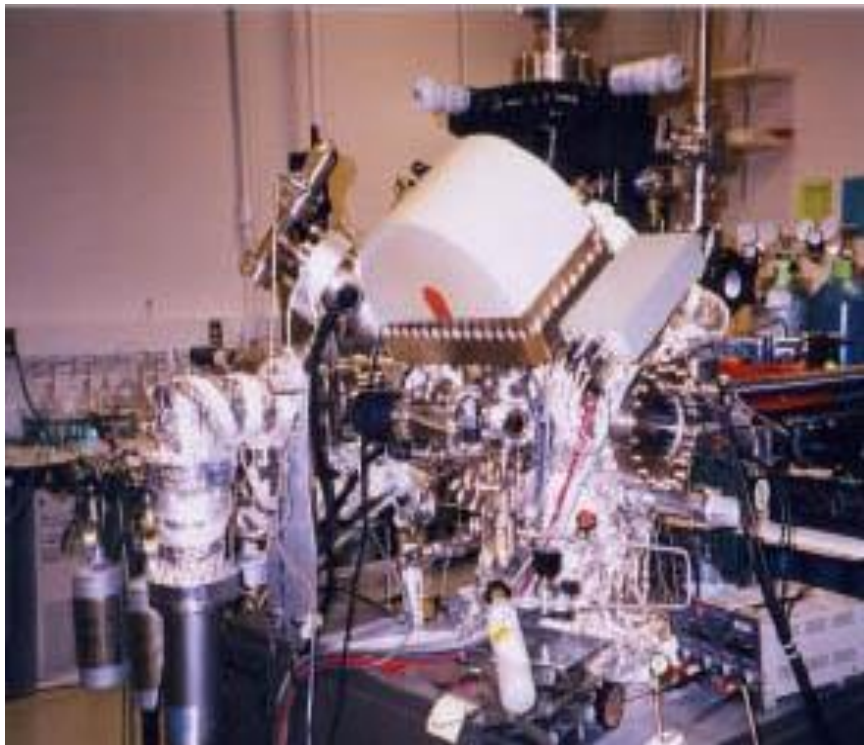


XPS for copper electrodeposition

(a) Bulk Cu (b) Cu UPD



Electrochemical X-ray Photoelectron Spectroscopy



Univ. of Illinois

Electrochemical XPS (SNU)



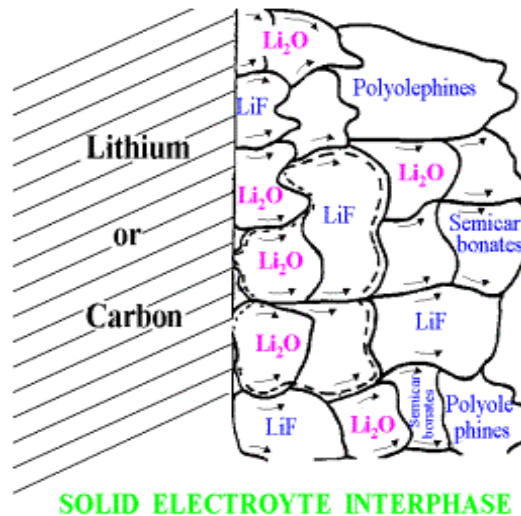
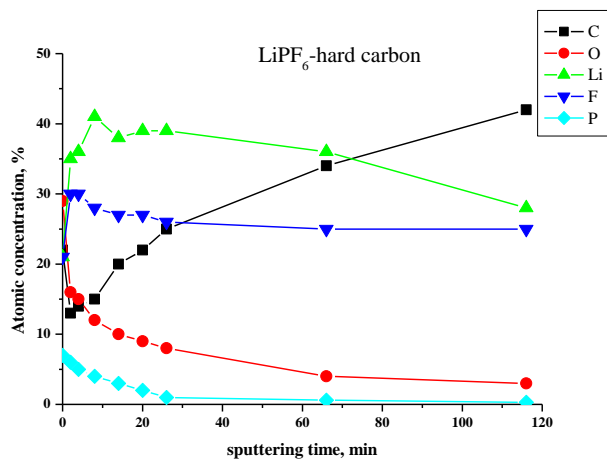
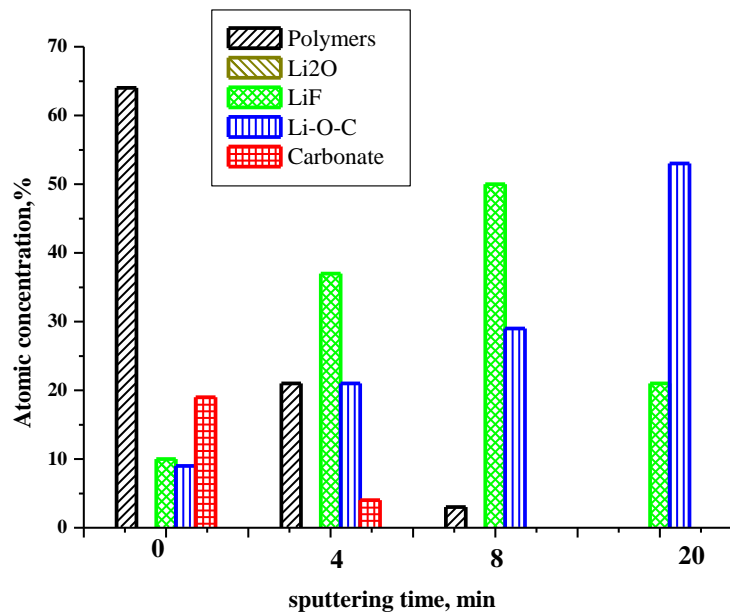
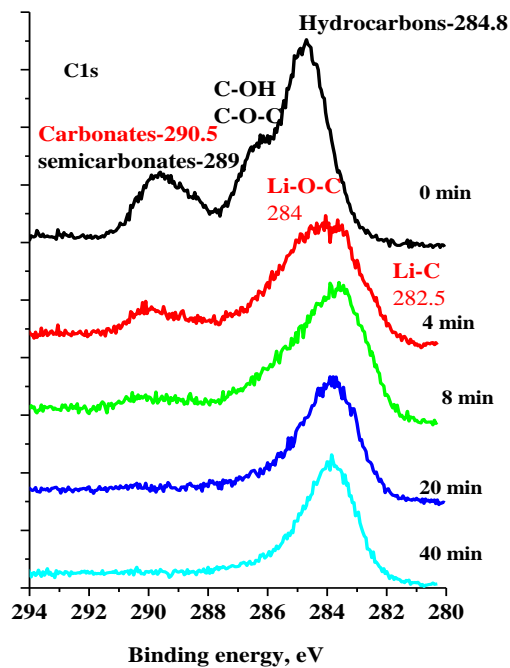
UHV-XPS

Glove Box



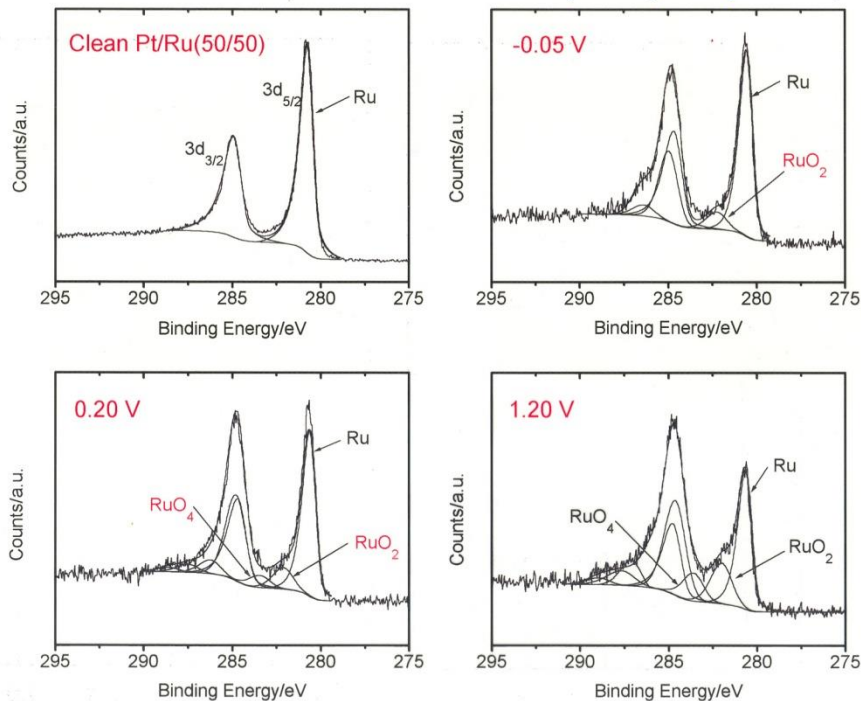
***Ex-situ* Analysis without Contamination**

Electrochemical XPS

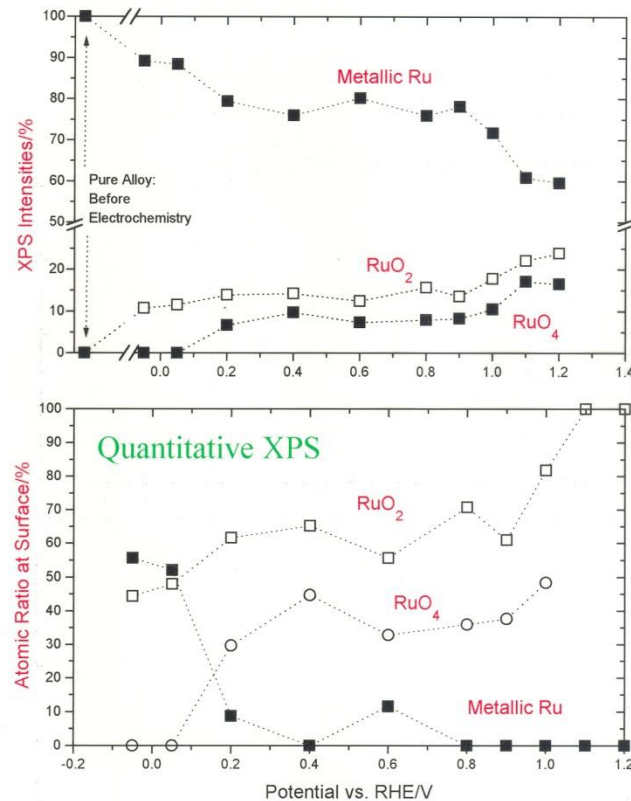


Peled (2003)

XPS of Ru3d Levels for Pt/Ru(50/50) Alloy : Ru

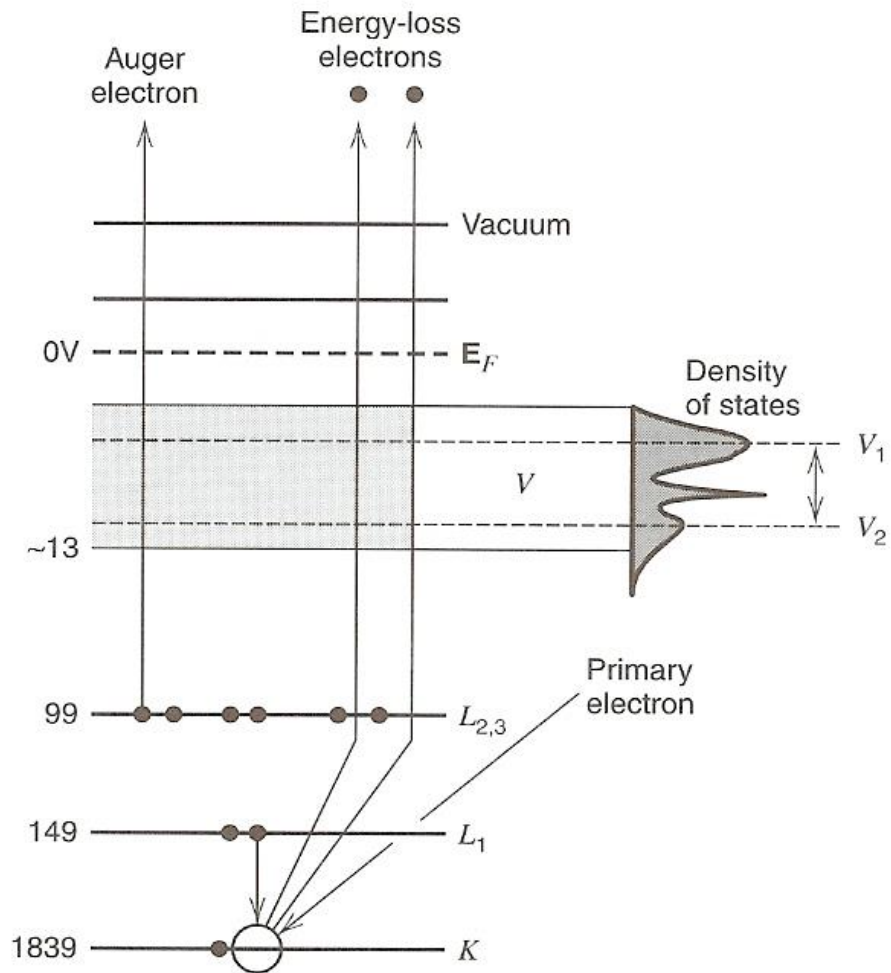


Relative Amount of Ru Species

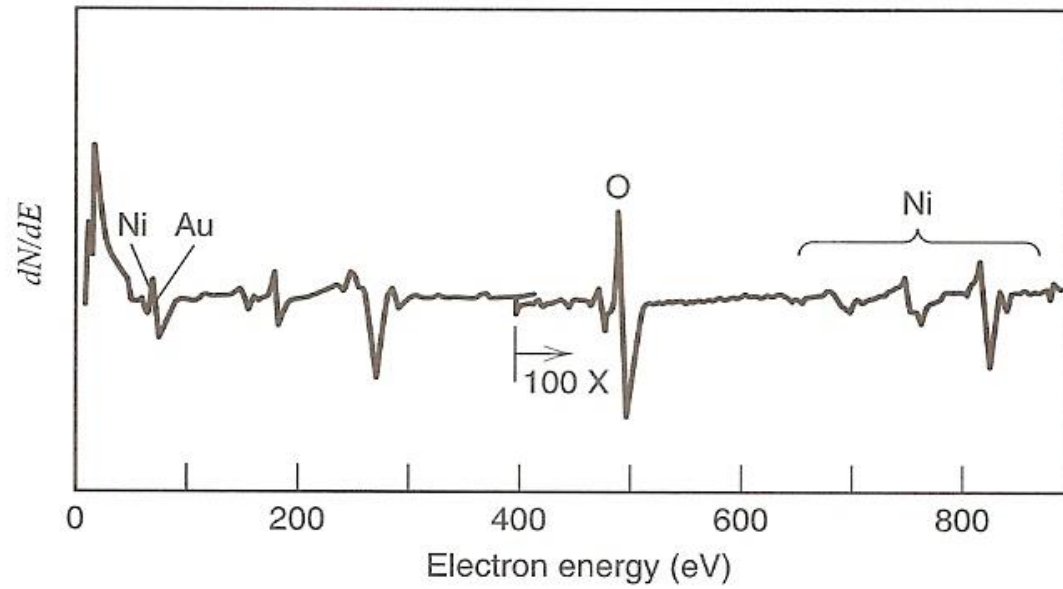


PtRu during Electrochemistry

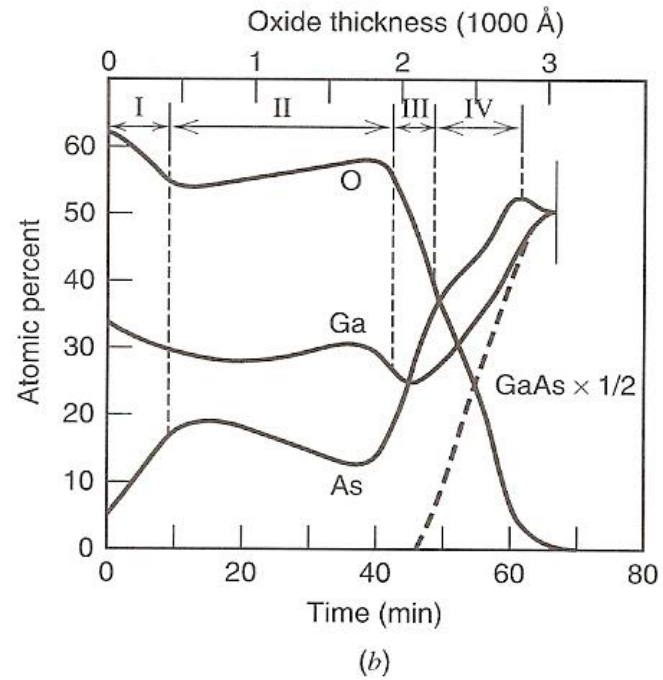
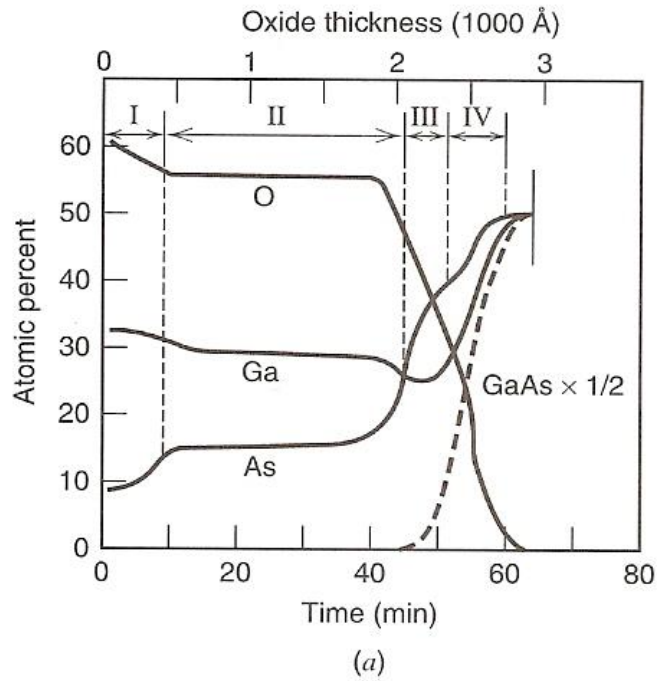
Auger electron spectroscopy



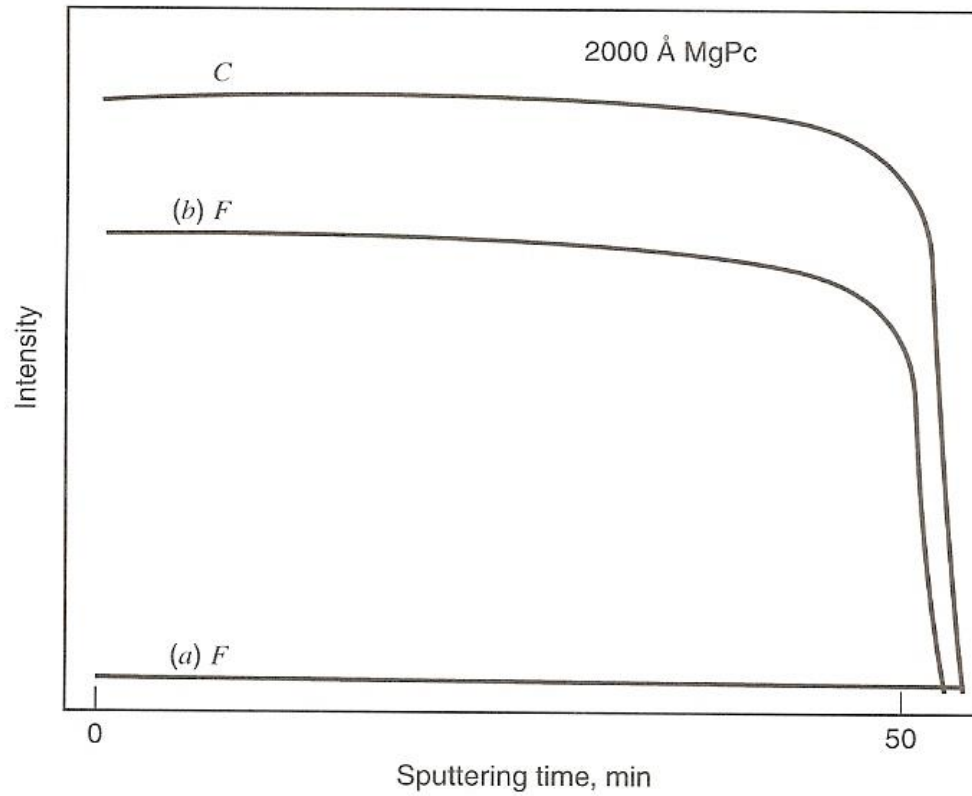
Ni oxide on Au



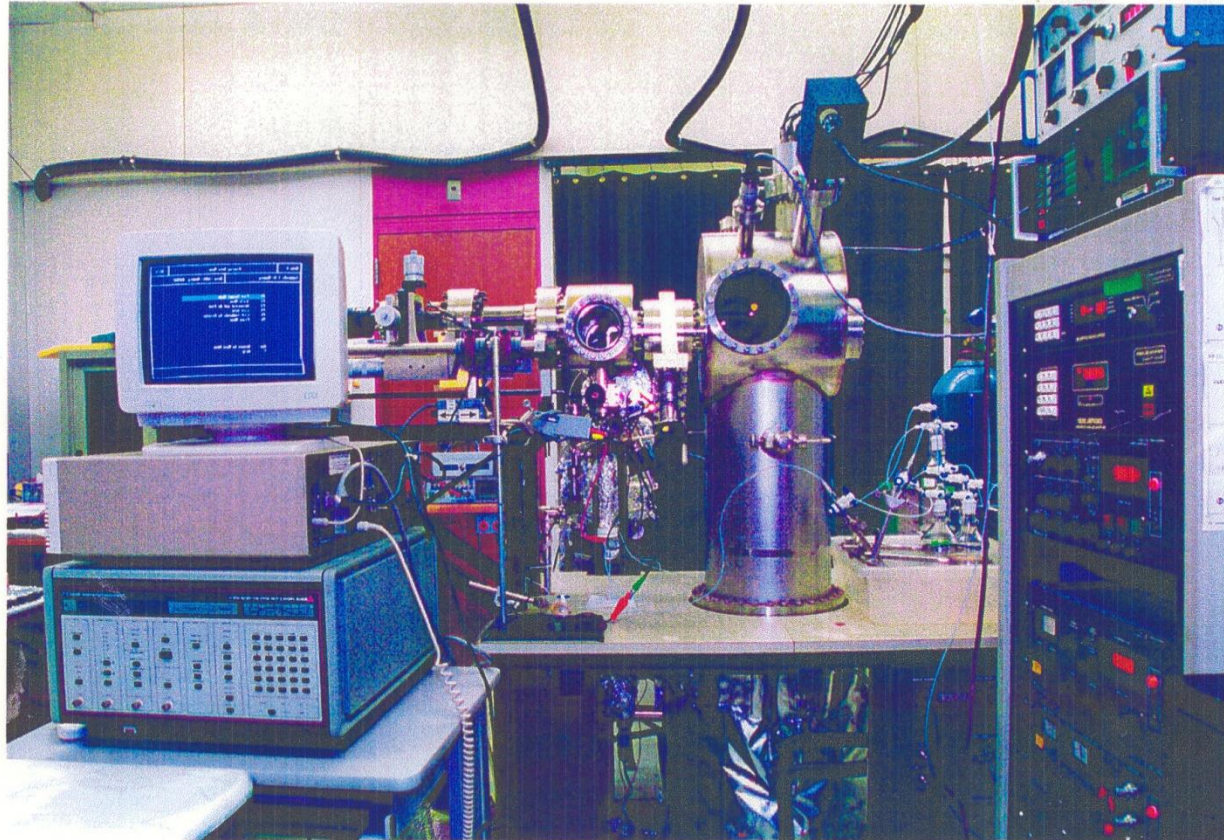
AES Depth profiles for GaAs



AES depth profiles for MgPc

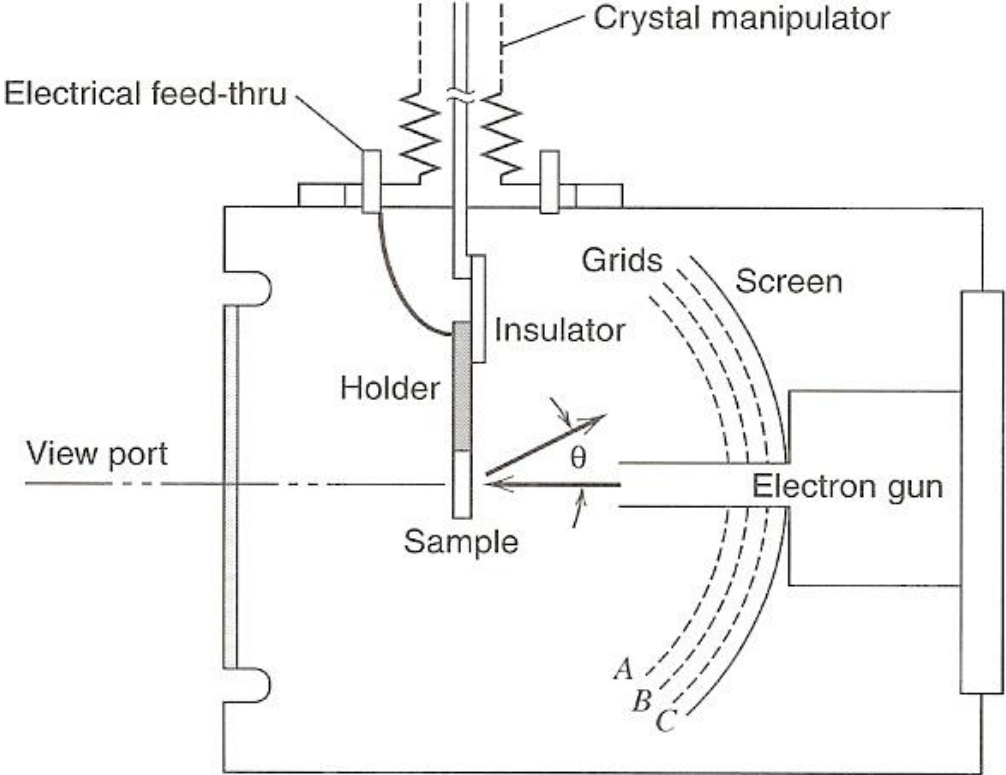


Electrochemical Auger Electron Spectroscopy

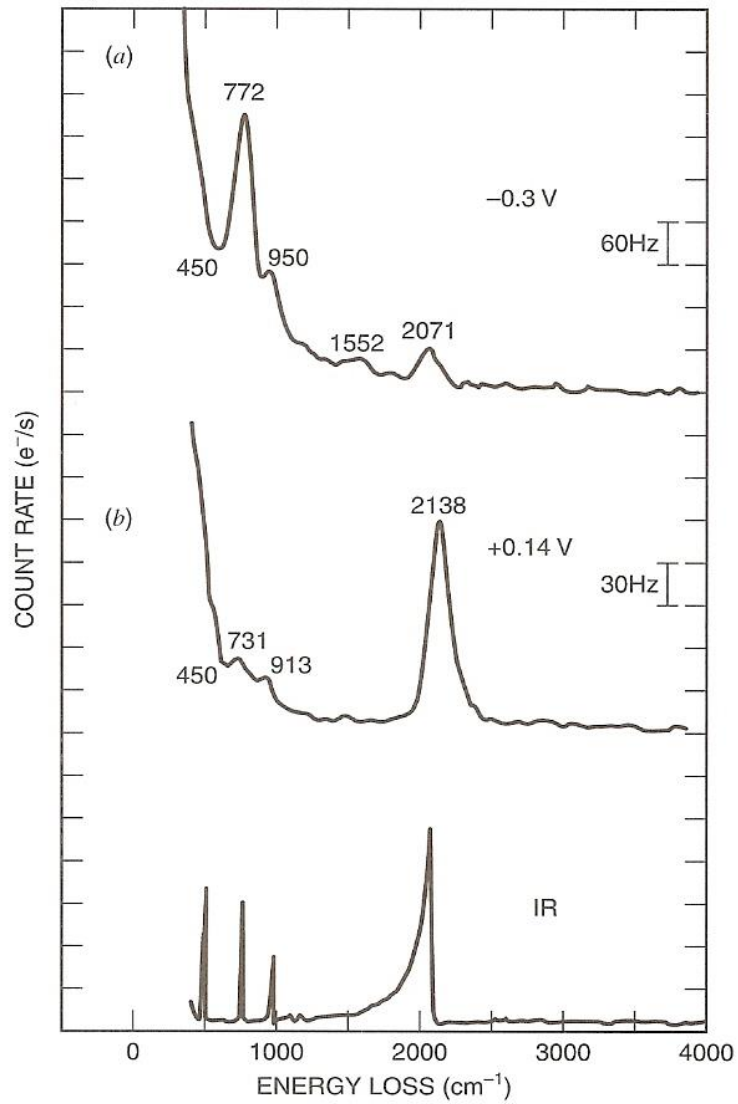


Univ. of Illinois

Low-energy electron diffraction



High resolution electron energy loss spectroscopy



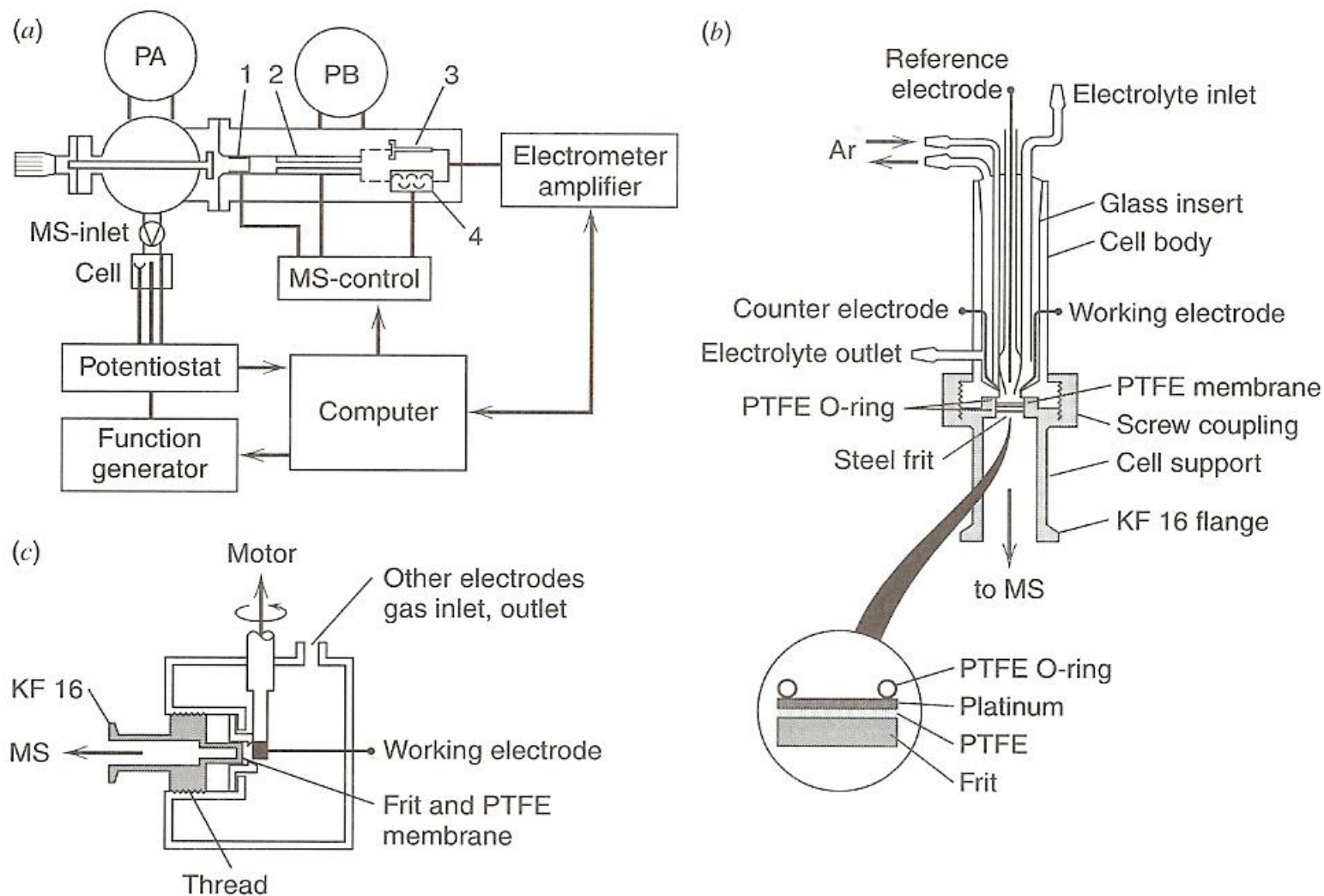
SCN⁻ on Ag(111)

(a) -0.3 V

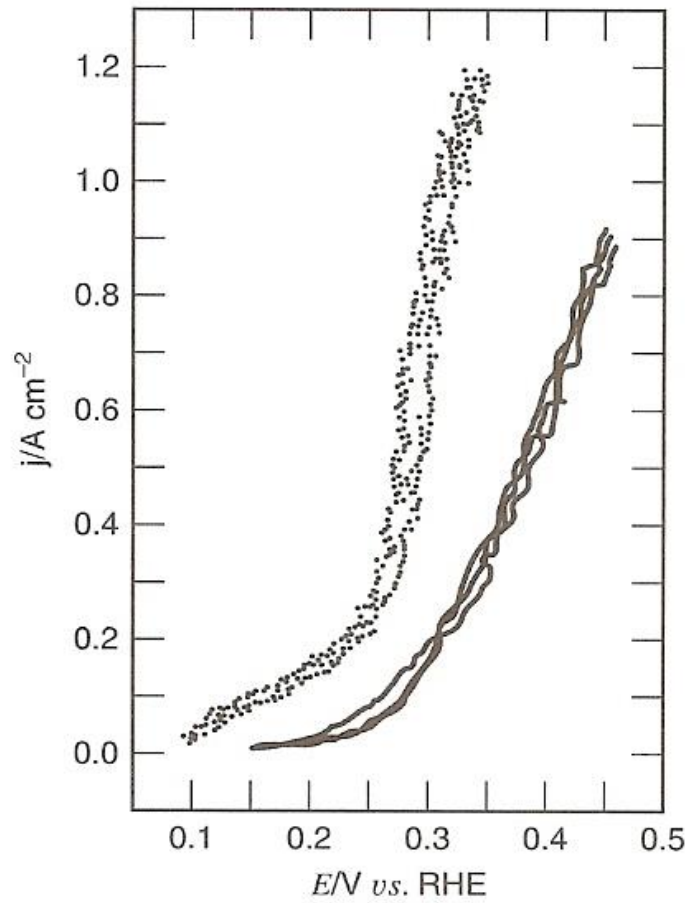
(b) +0.14 V

Mass spectrometry

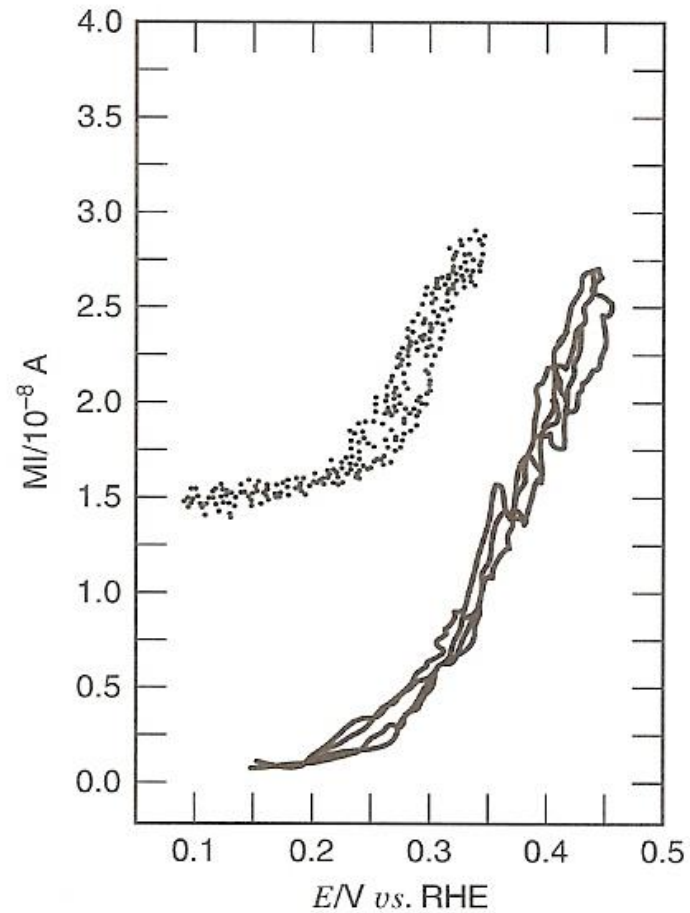
Differential electrochemical mass spectrometry (DEMS)



DEMS: fuel cell catalysts for methanol(solid) & formic acid(dotted) oxidation

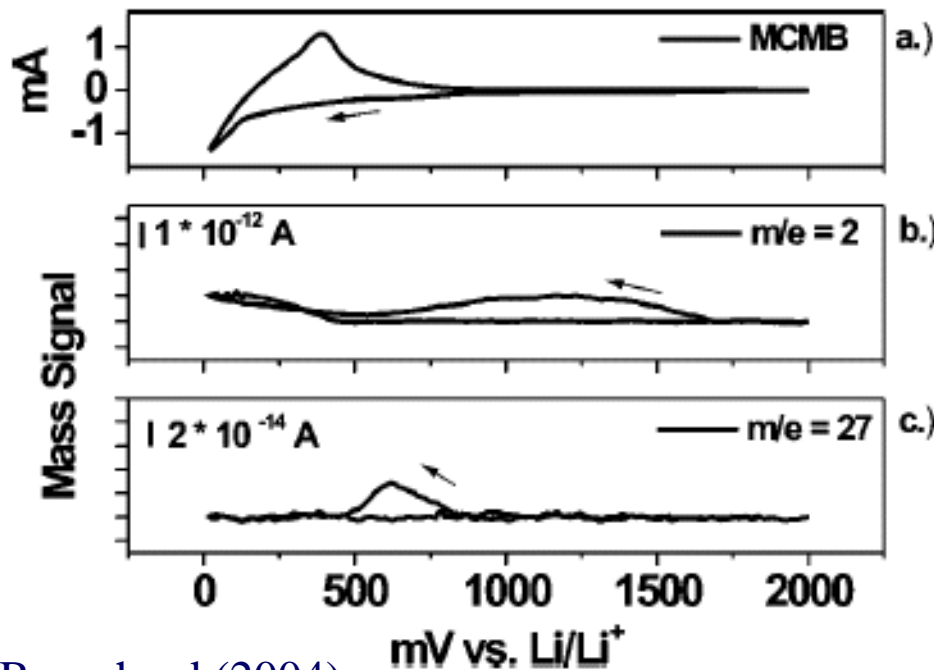


(a) Current density

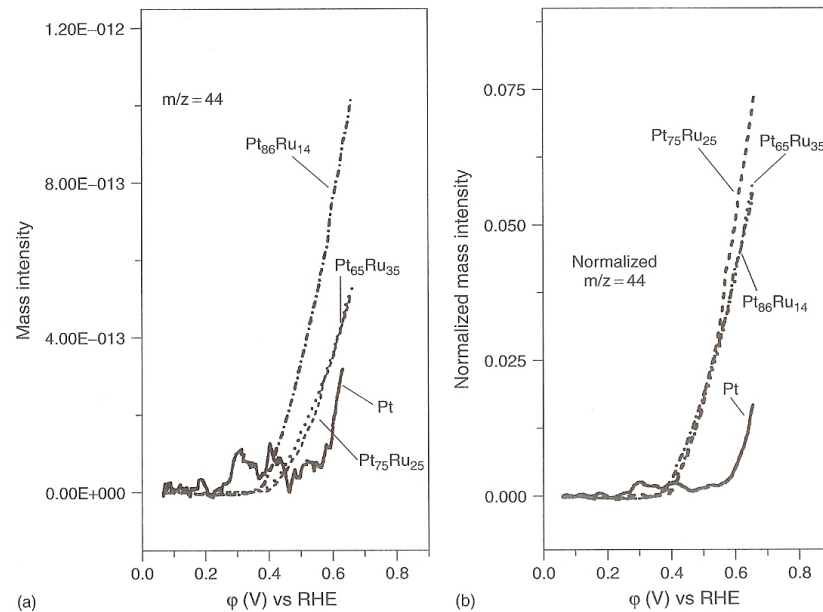


(b) $m/e = 44$; CO_2

➤ In situ DEMS (differential electrochemical mass spectrometry)

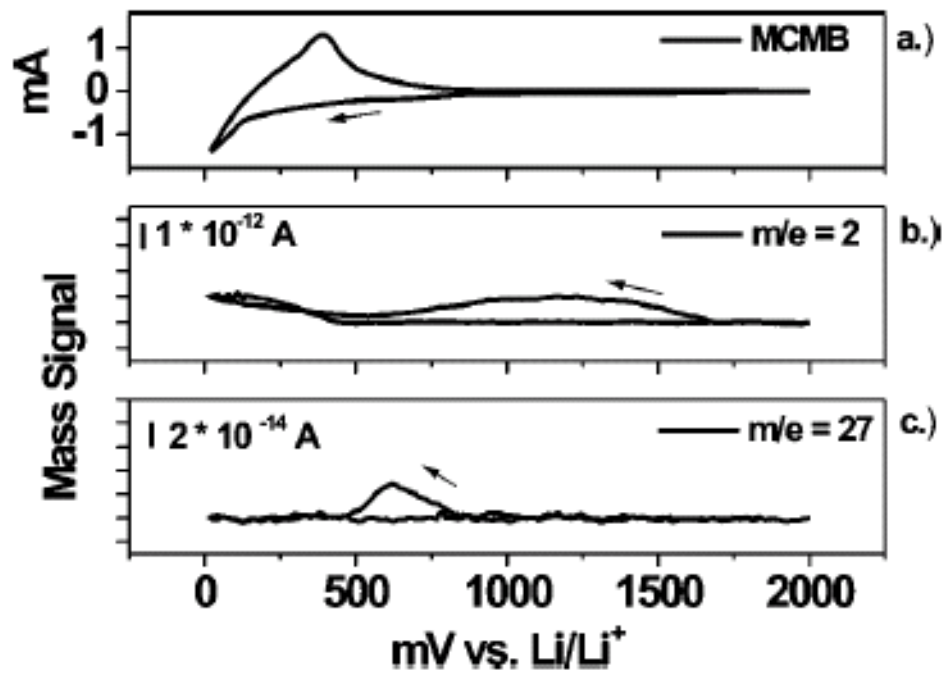
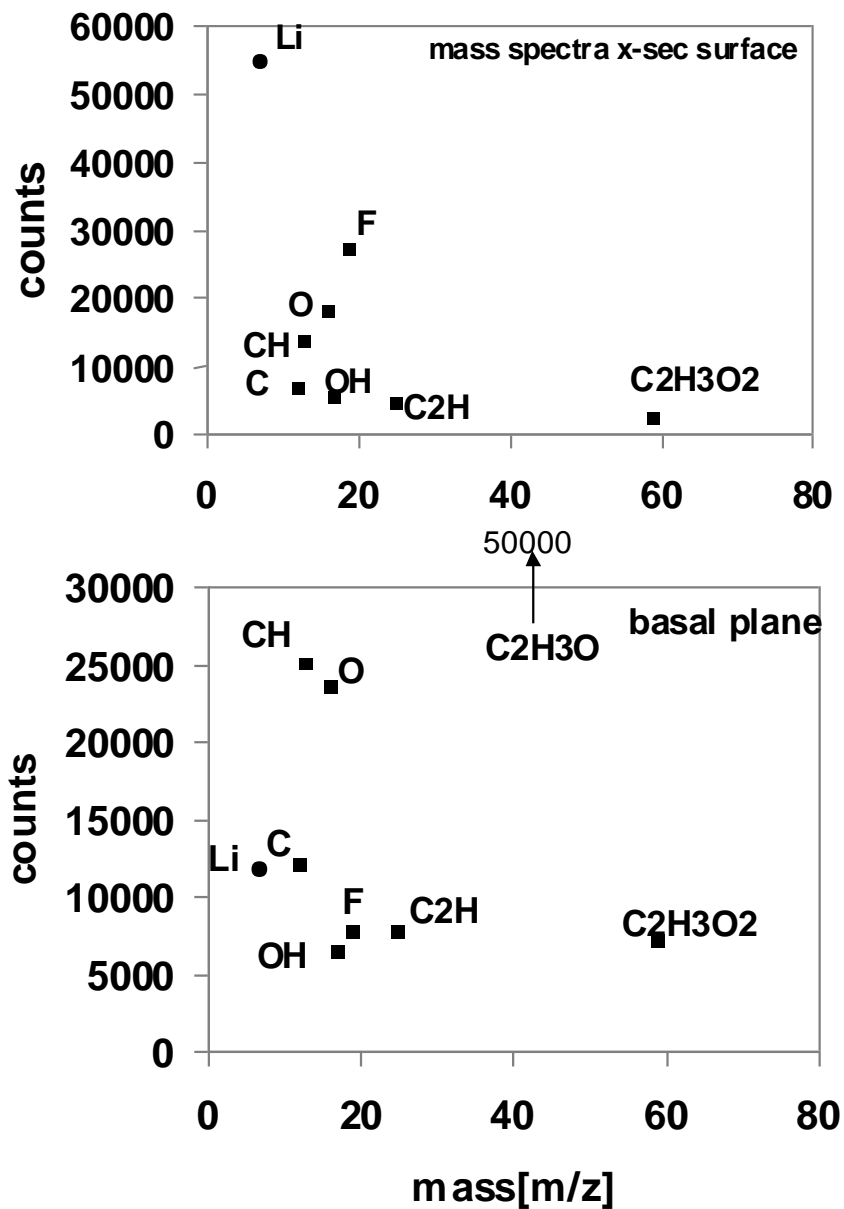


Besenhard (2004)



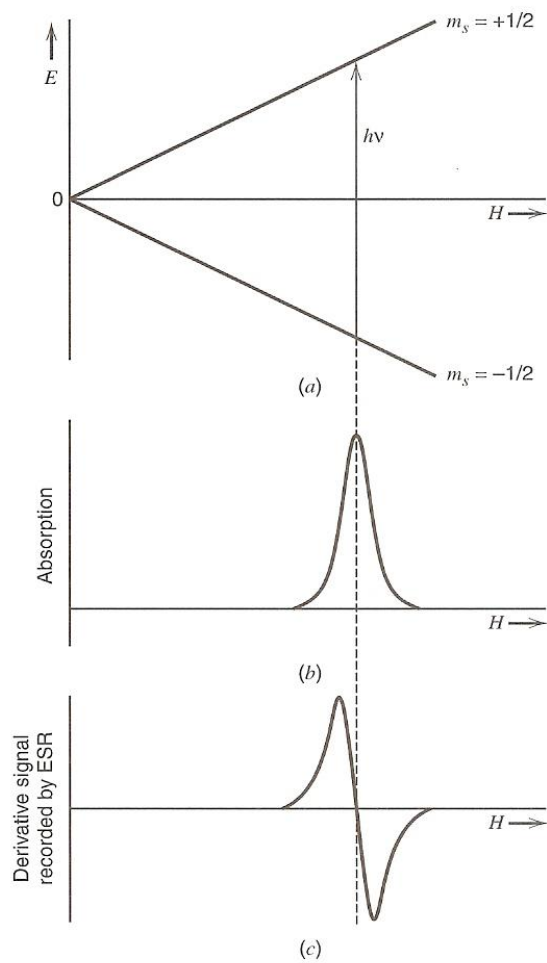
MeOH oxidation

➤ in-situ DEMS (differential electrochemical mass spectroscopy)

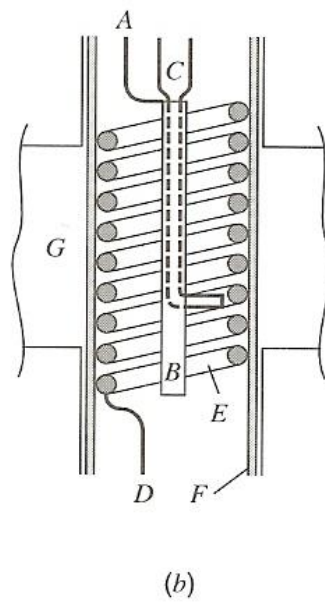
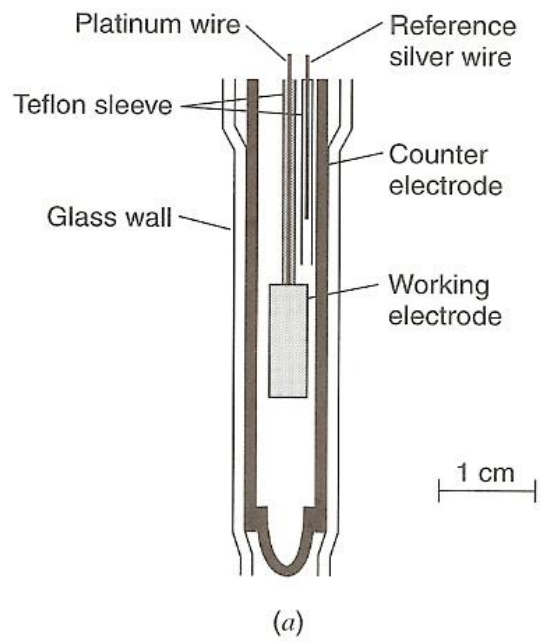


Magnetic resonance methods

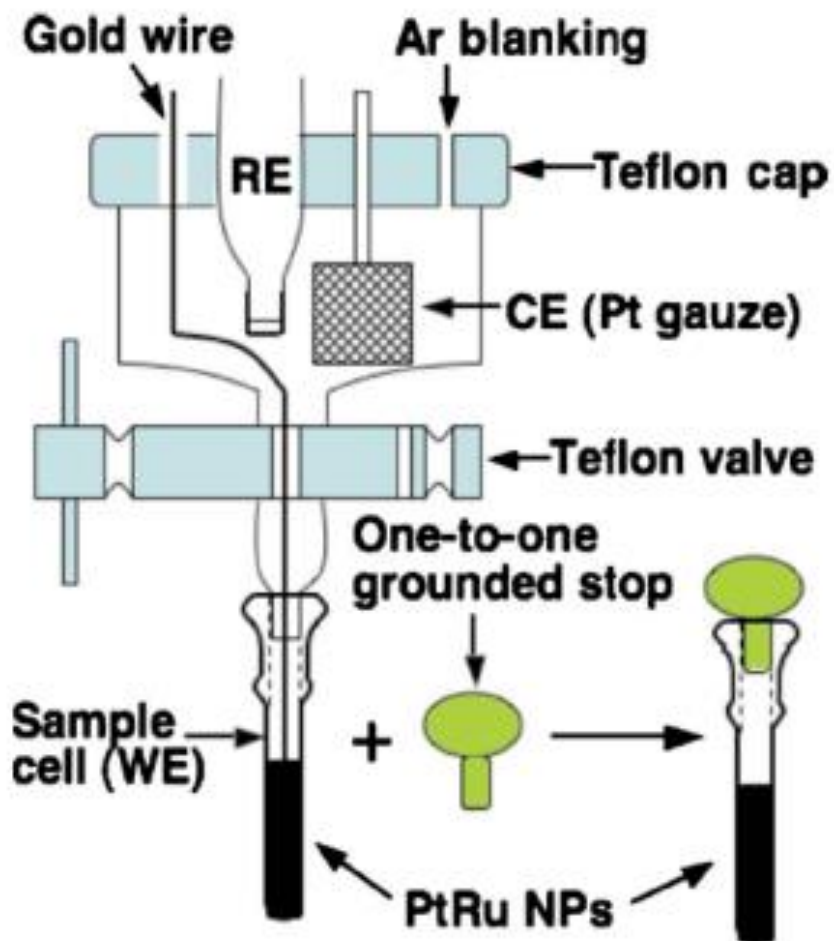
Electron spin resonance & NMR



Electrochemical ESR

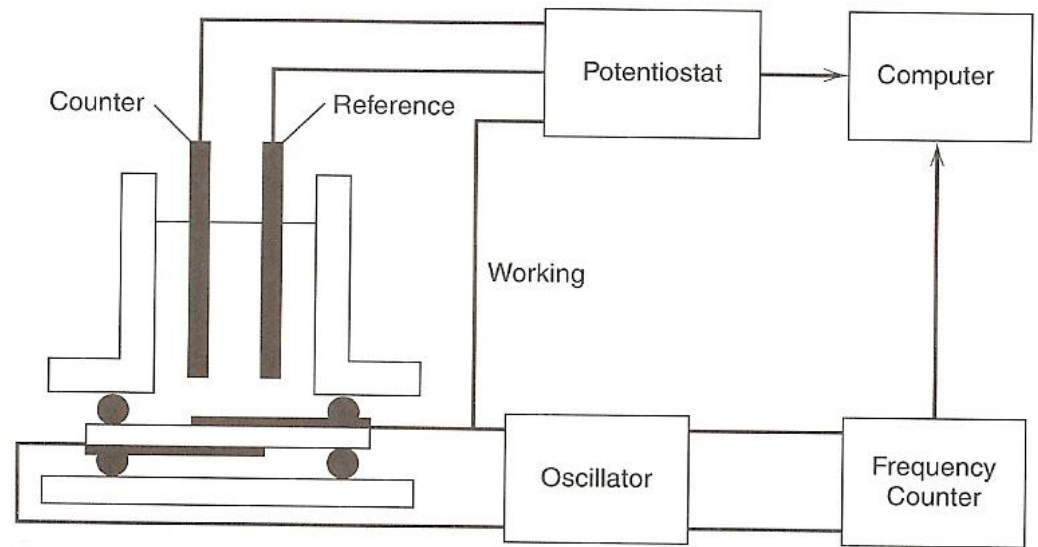
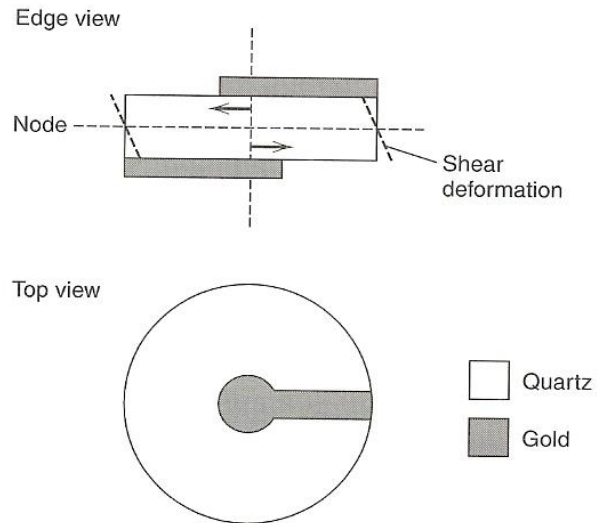


in-situ NMR

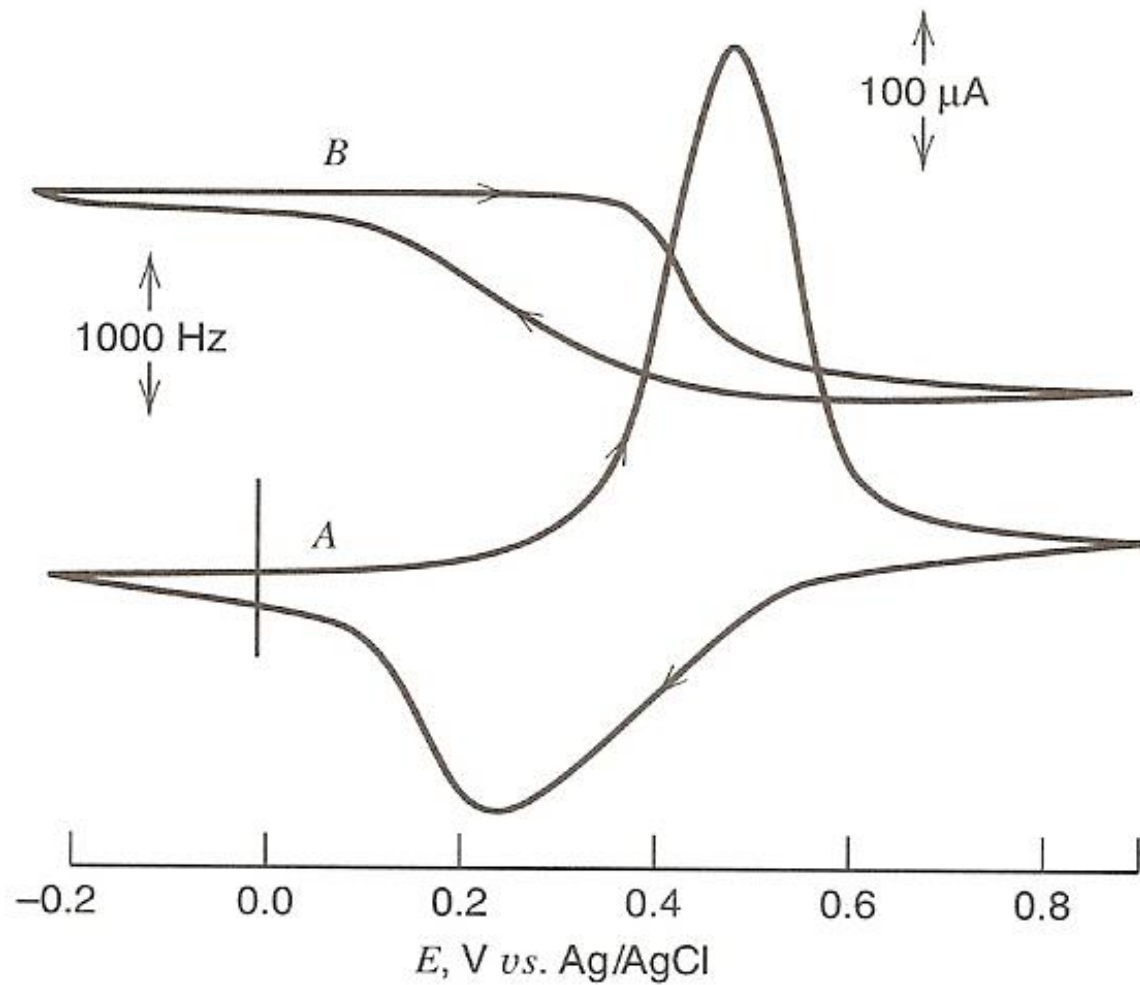


(with Prof. YuYe Tong (Georgetown University))

Quartz crystal microbalance



QCM: PVF on Au



X-ray methods

Synchrotron

X-ray absorption spectroscopy

Absorption edge (energy that is just needed to eject a particular core electron, e.g., $1s$ e⁻ (K edge), $2p_{3/2}$ e⁻ (L_3 edge))

Fe & Fe oxides

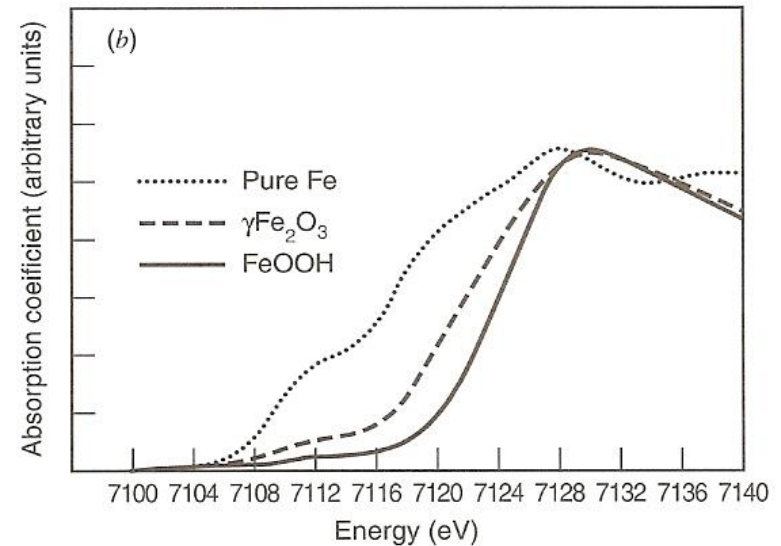
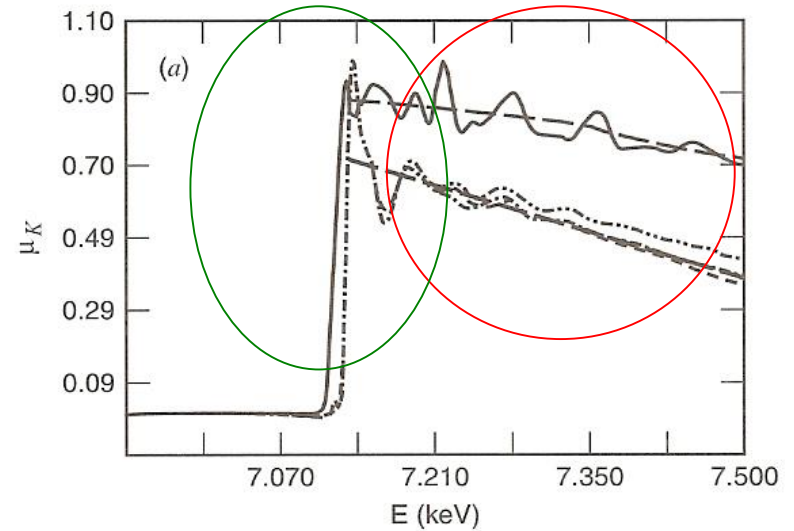
K-edge: 7.112 keV

Within 10-40 eV: X-ray absorption near-edge structure (**XANES**) (or near-edge absorption fine structure (**NEXAFS**))

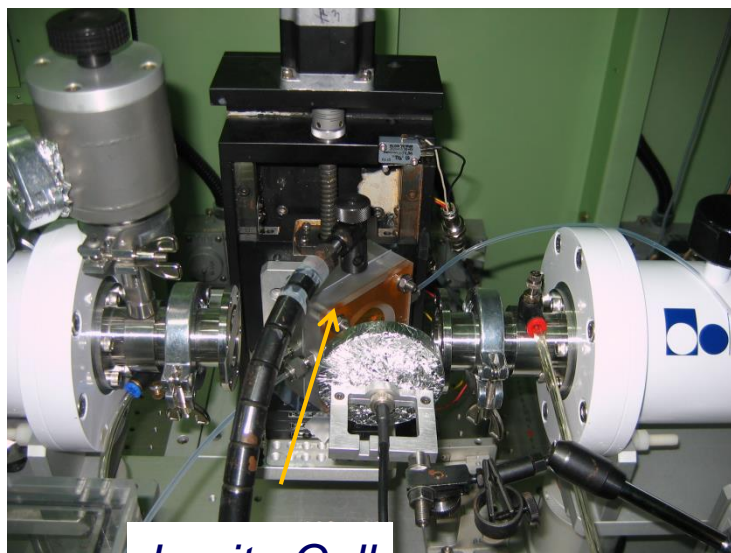
→ oxidation state & ligand environment

About 50 keV: extended X-ray absorption fine structure (**EXAFS**)

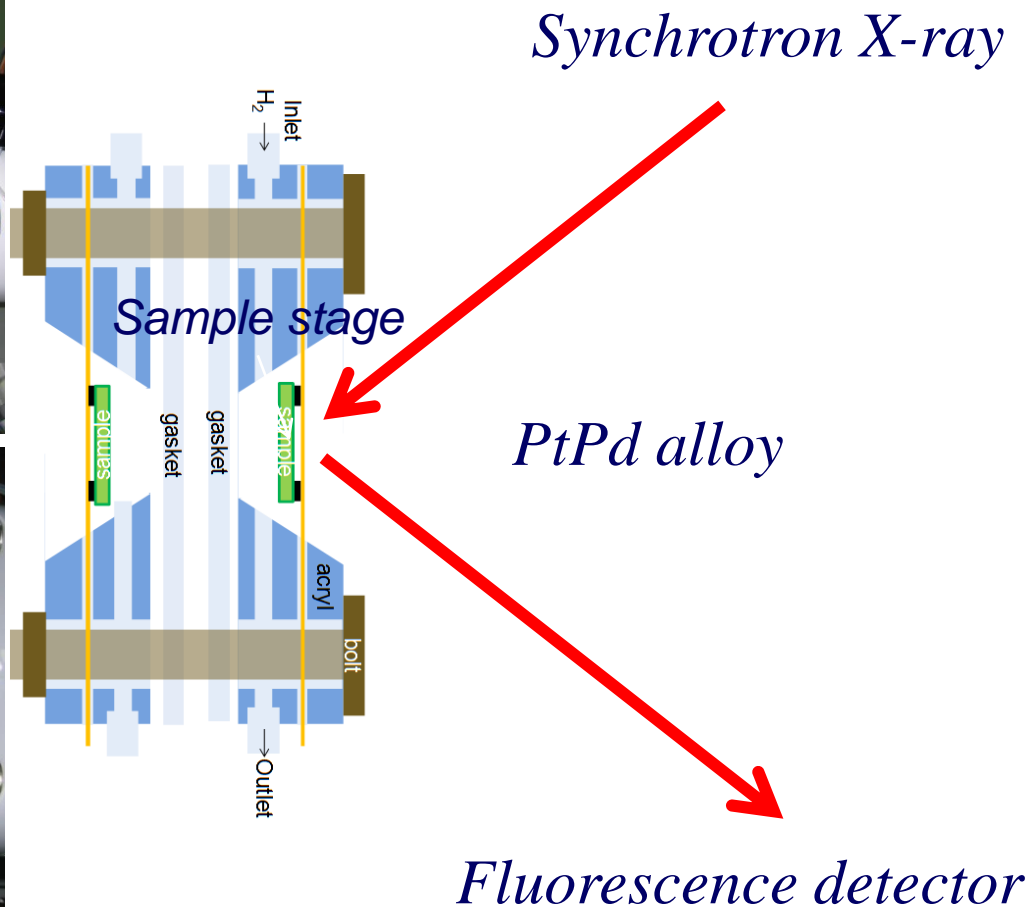
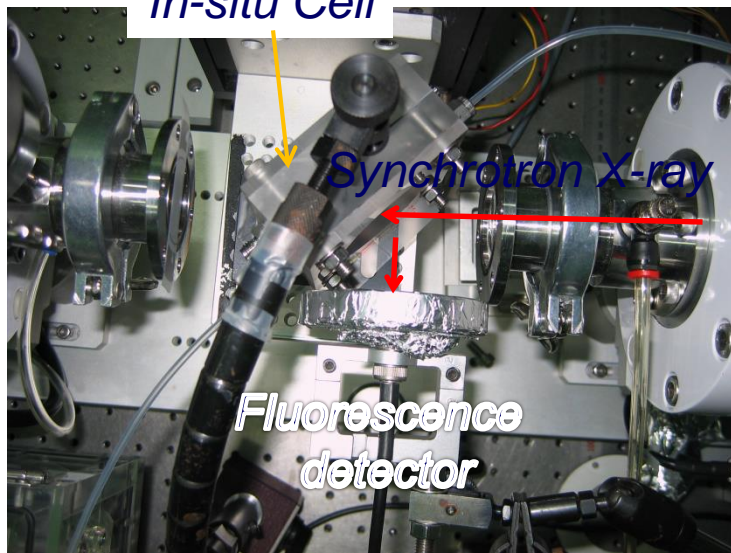
→ distance & arrangement of atoms



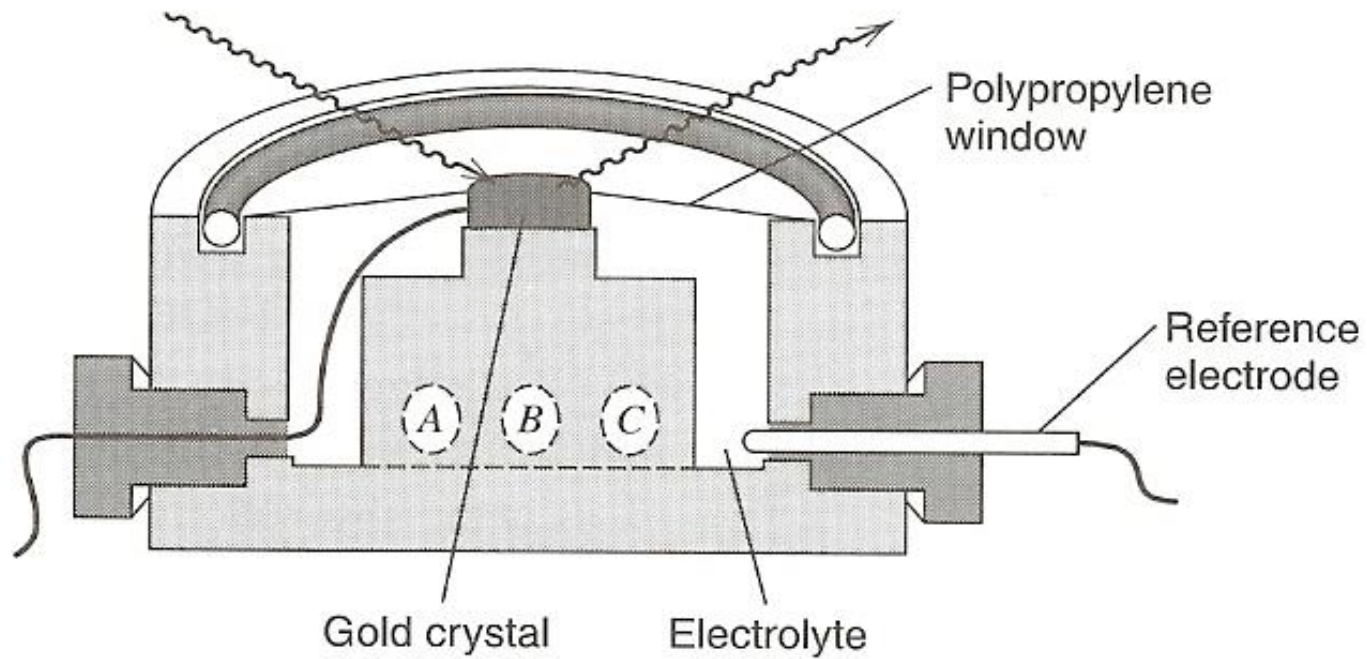
In-situ XANES (X-ray Absorption Near-Edge Structure)



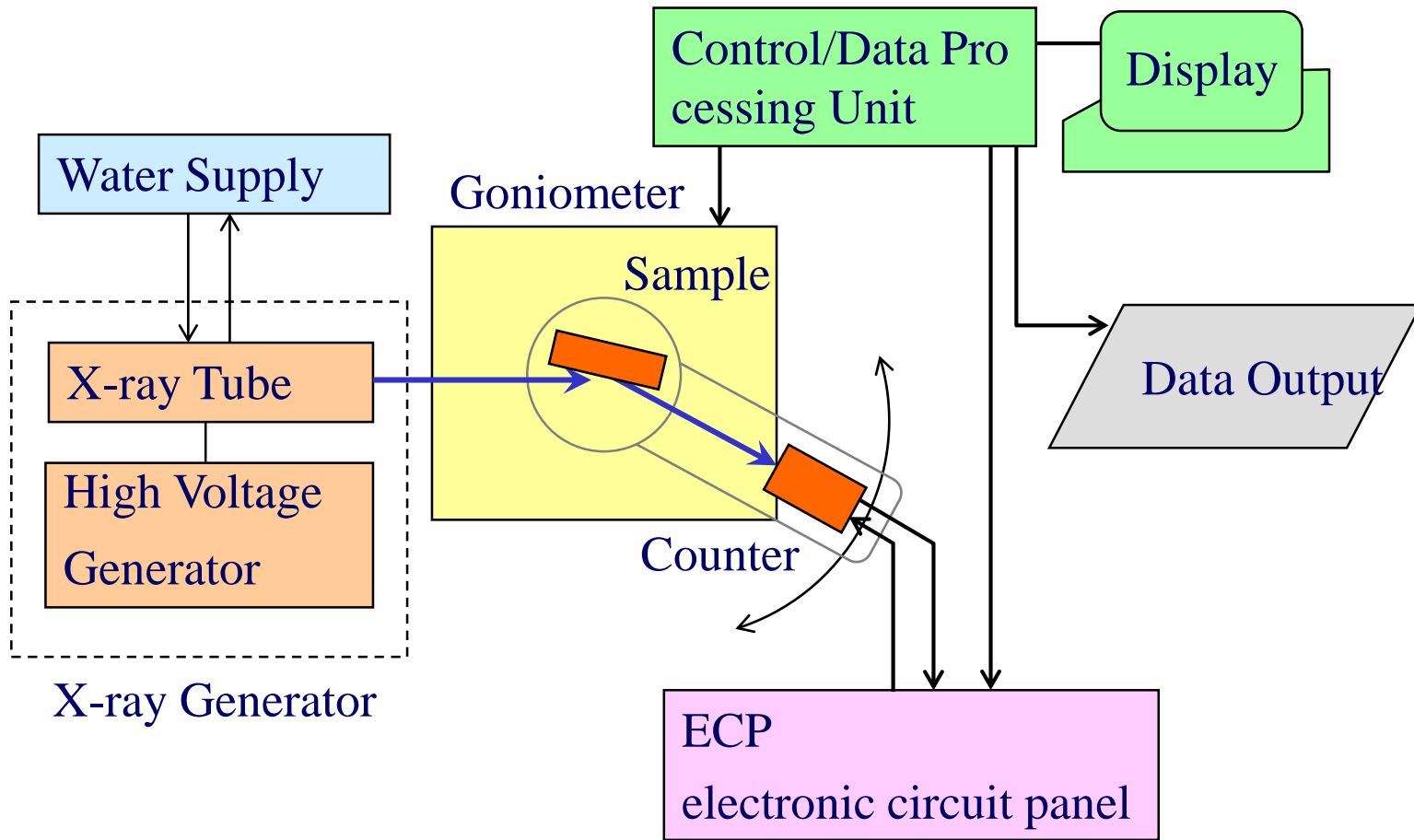
In-situ Cell



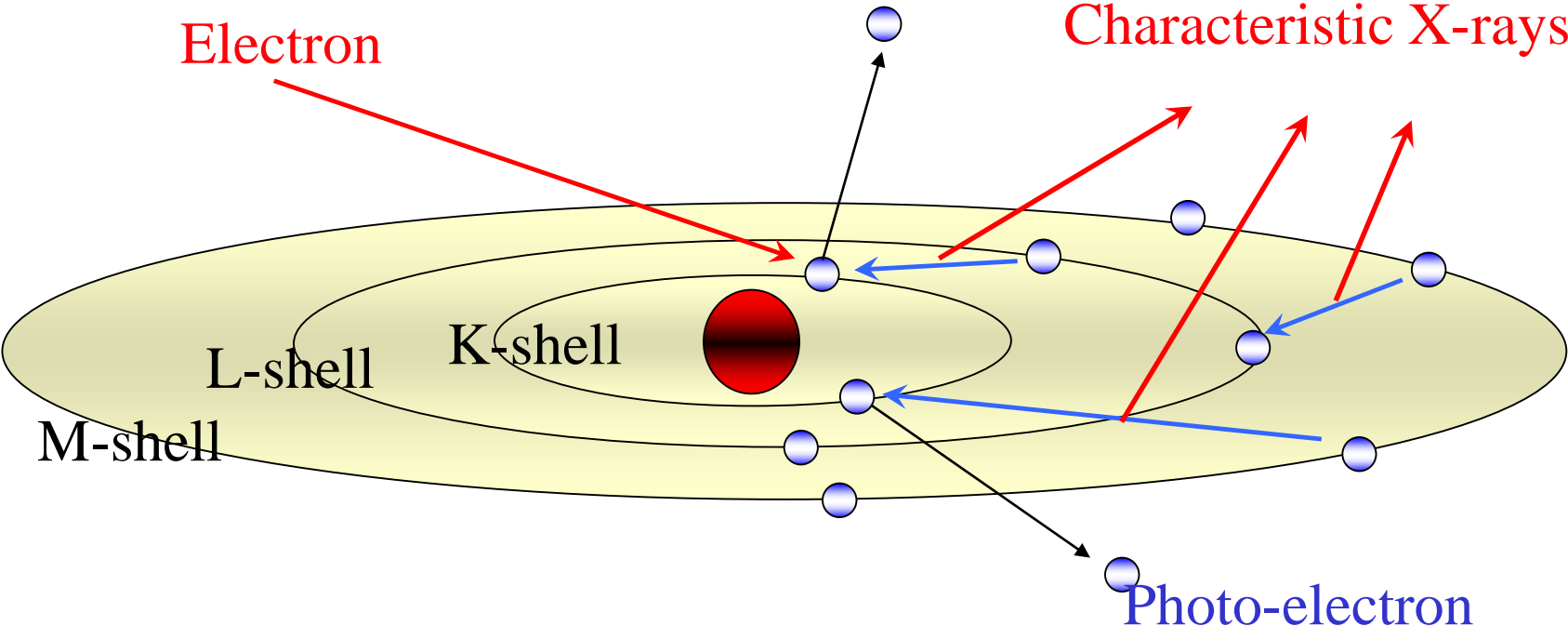
X-ray diffraction techniques



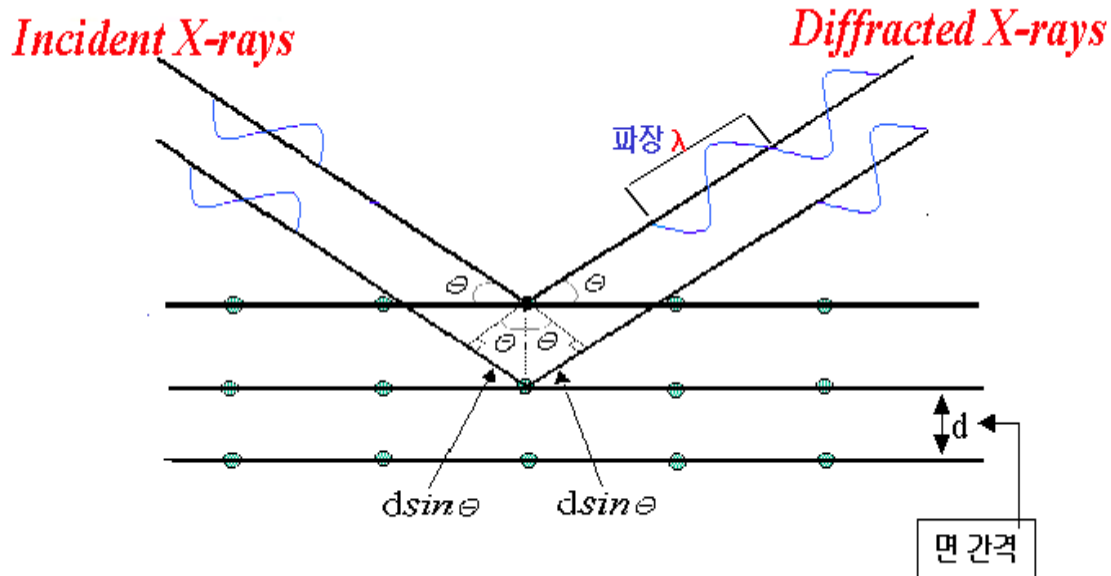
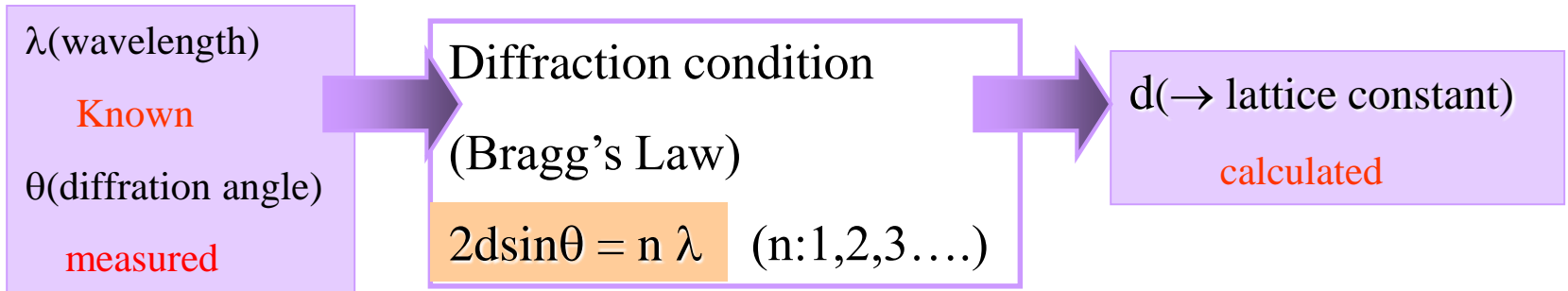
X-Ray Diffractometer



Characteristic X-ray



X-ray diffraction (Bragg's Law)



$$\frac{AC'}{d} = \sin \Theta$$

$$AC' = d \sin \Theta$$

$$ACB' = 2d \sin \Theta$$

$$ACB' = n\lambda \quad \text{Amplification}$$

Rigaku - D/MAX 2500/PC (SNU)



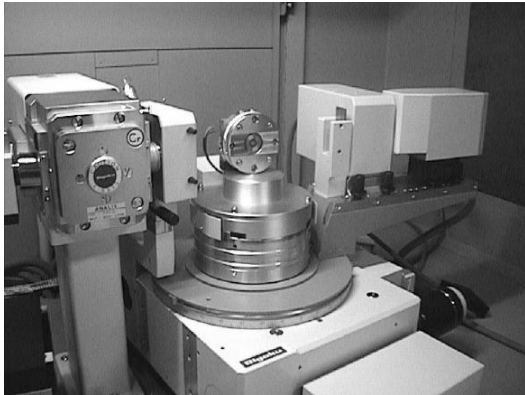
- 18kW X-ray generator
 - high frequency type
 - rotating anode(Cu etc.)
- High power generator
 - rapid, highly accurate
 - enhance S/N ratio
 - trace analysis
 - analysis of weakly diffracting material
- Goniometer
 - vertical type

Large enclosure type – Two goniometer

in situ XRD (SNU)

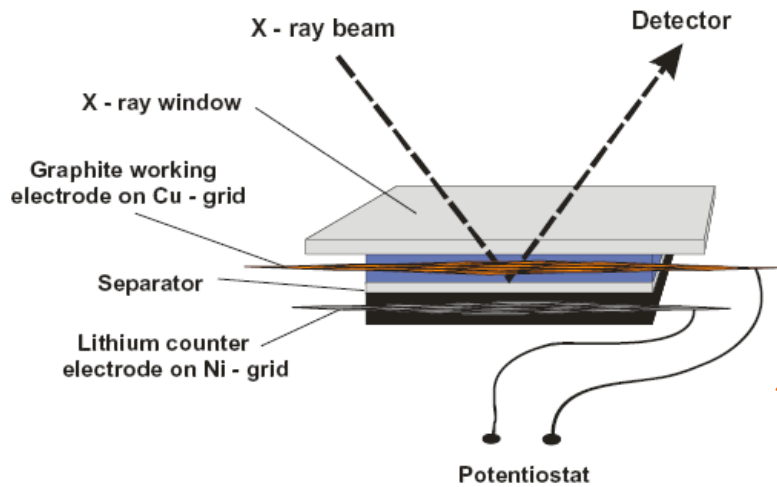


- powder X-Ray Diffractometer, D/MAX 2500/PC
- powder, thin film, in situ analysis

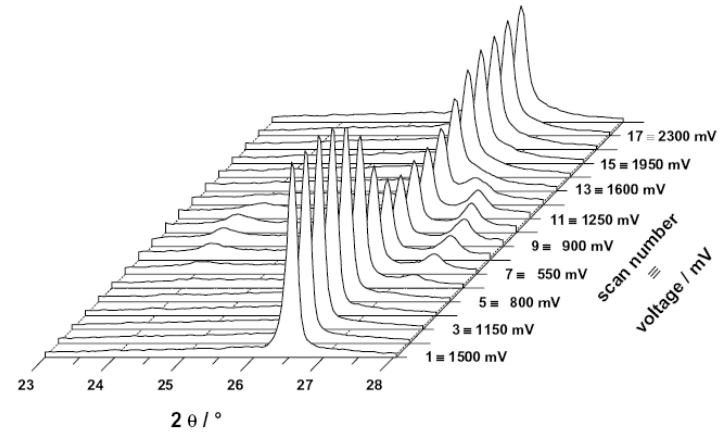


In situ cell

□ Schematic of in situ XRD cell



In-situ XRD patterns of $\text{Li}_x\text{FeSnO}_4$ during initial lithium intercalation and deintercalation.



Cascade of in situ XRD data vs. the scan number

