Electrochemical Energy Engineering, 2019

B

14. Spectroelectrochemistry (ch. 17B): *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

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

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 x 10^{-34} Js)
speed of light (c); 3 x 10^{8} m/s,
wavelength (λ); distance between the neighboring peaks of wave,

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

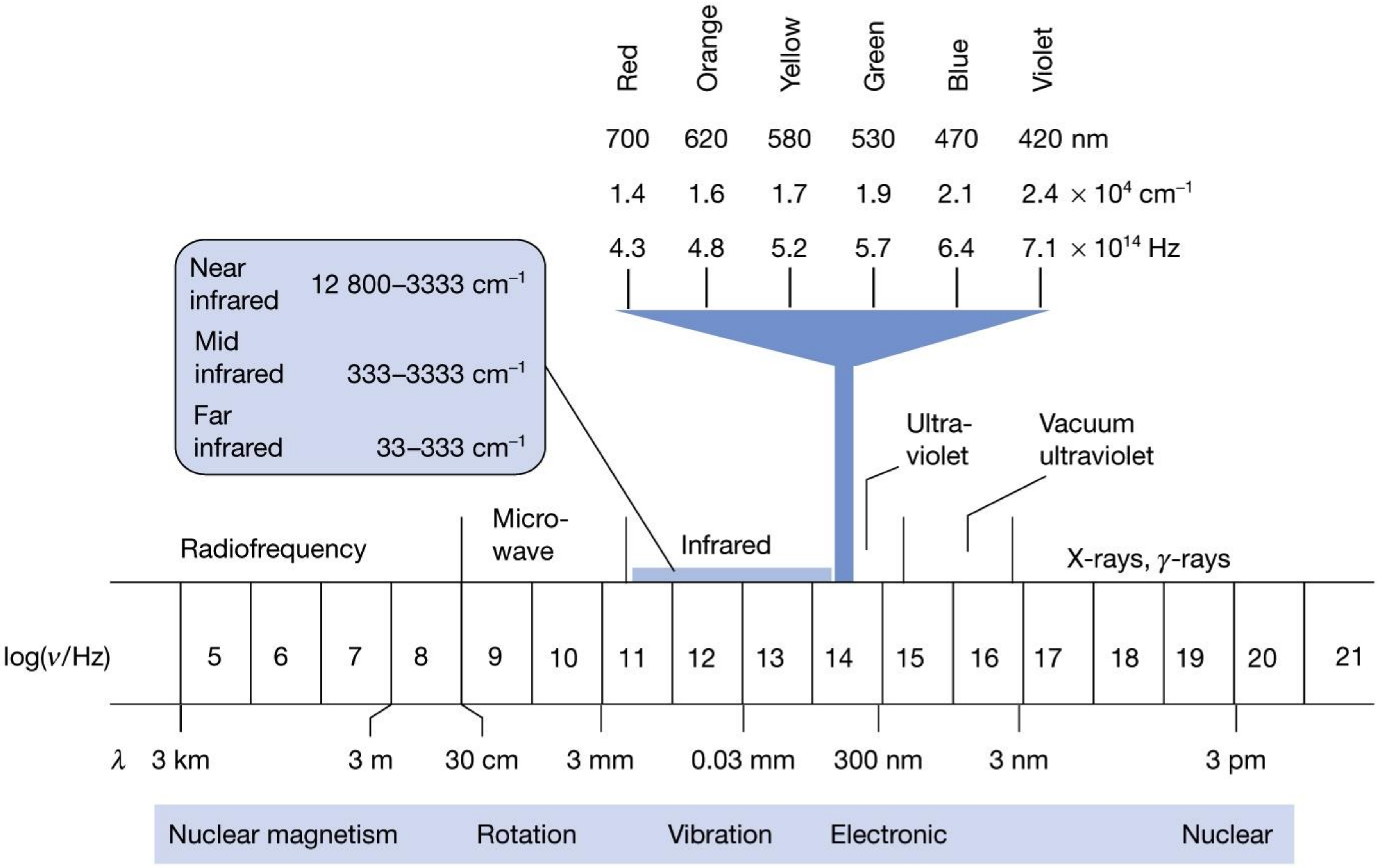
frequency (ν, Hz = 1 s^{-1}); number of times per second

$$\lambda\nu = c$$

wavenumber (cm^{-1}, reciprocal cm), $\nu\text{-bar} = \nu/c = 1/\lambda$
cf) 1 eV ~ 8066 cm^{-1}

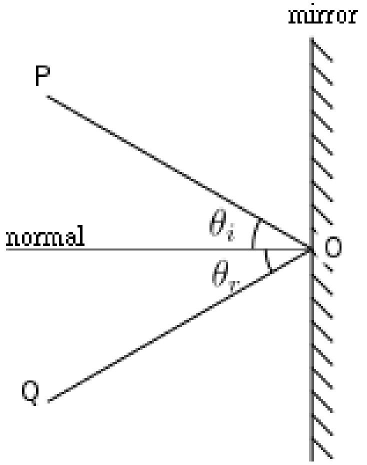
Wavelength (λ, nm) = 1240/band gap energy (eV)

Electromagnetic spectrum

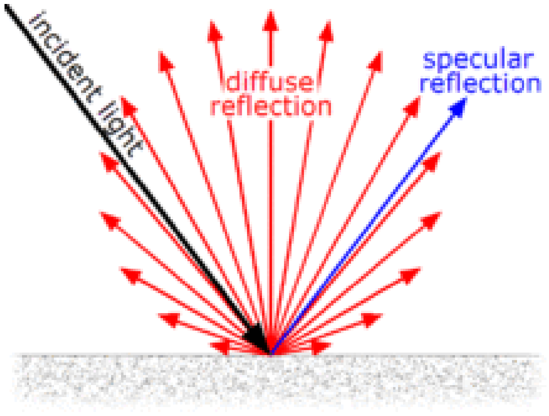


IR reflection spectrometry

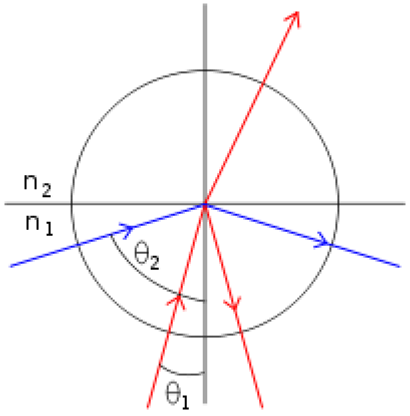
Four types:
Specular reflection: smooth surface
Diffuse reflection
Internal reflection
Attenuated total reflection (ATR)



Specular reflection



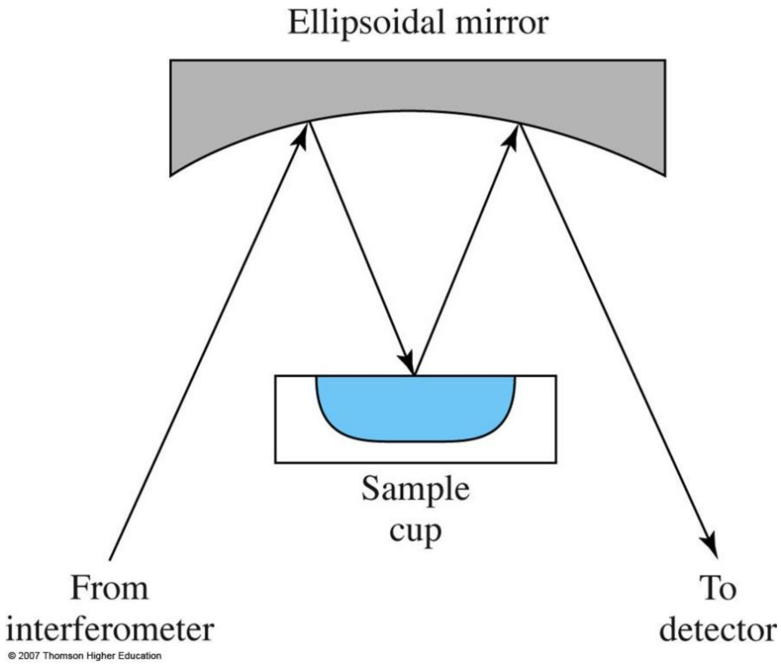
Diffuse reflection



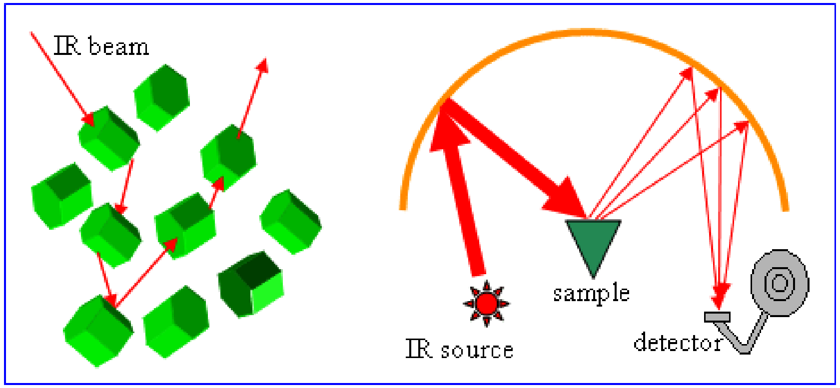
Internal reflection
(blue line)

Diffuse reflection

Diffuse-reflectance attachment



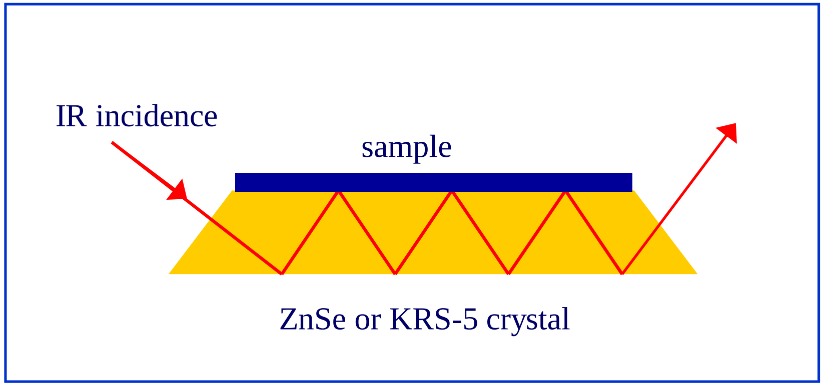
- Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT)



Powder sample

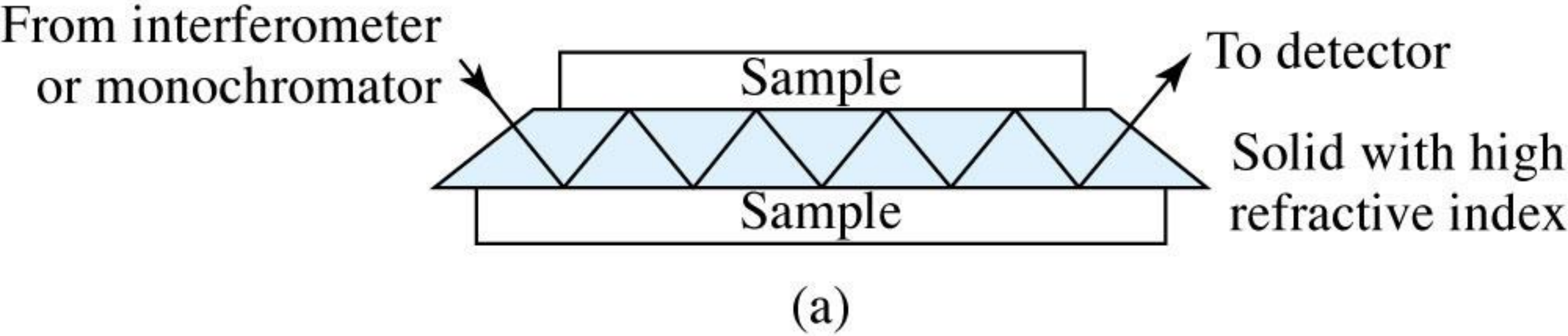
Attenuated total reflectance (ATR) is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid, liquid or gas state without further preparation

❖ Attenuated Total Reflectance Spectroscopy (ATR)

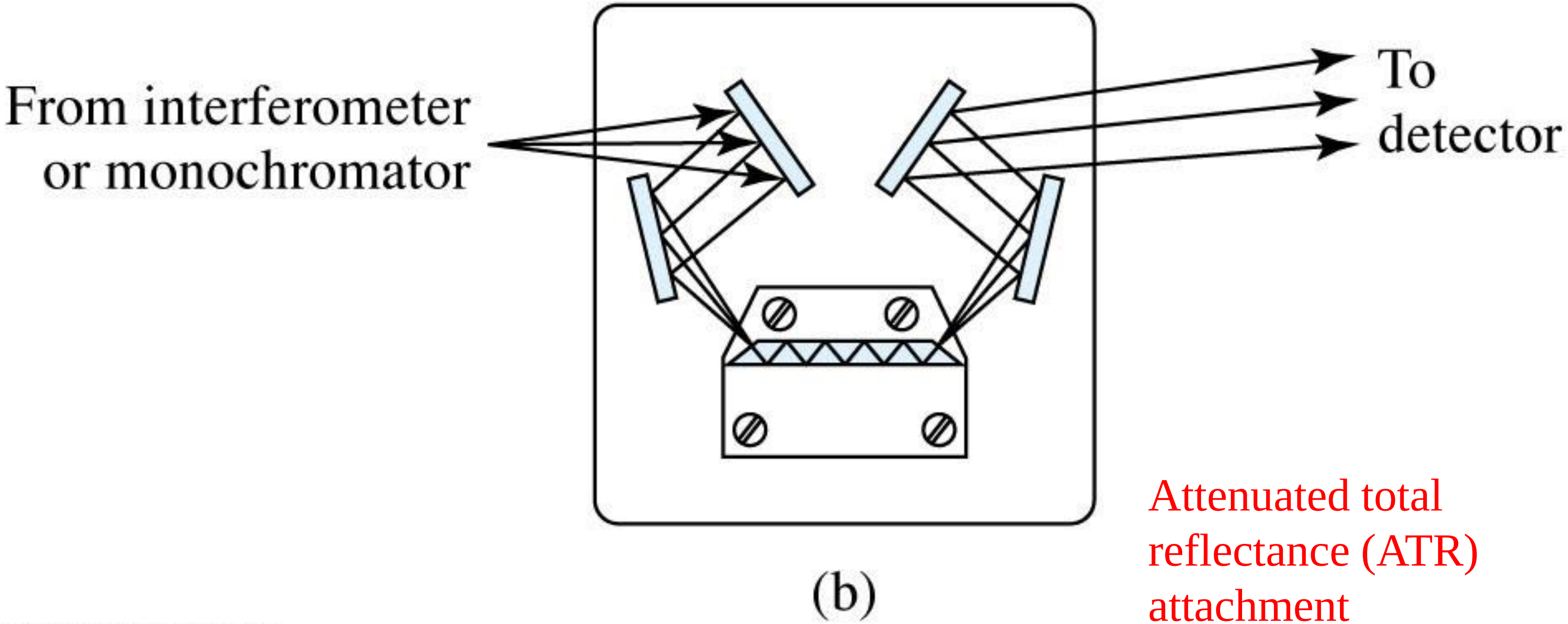


ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the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



(a)



(b)

Attenuated total reflectance (ATR) attachment

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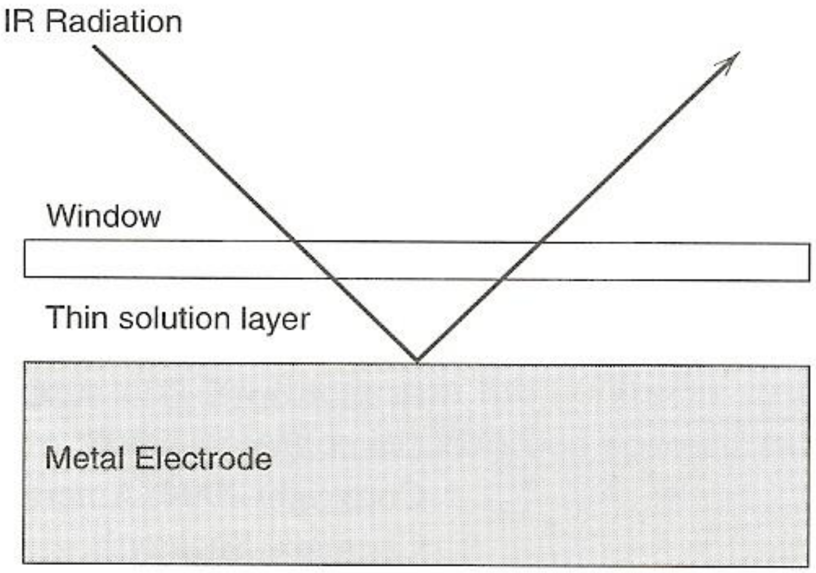
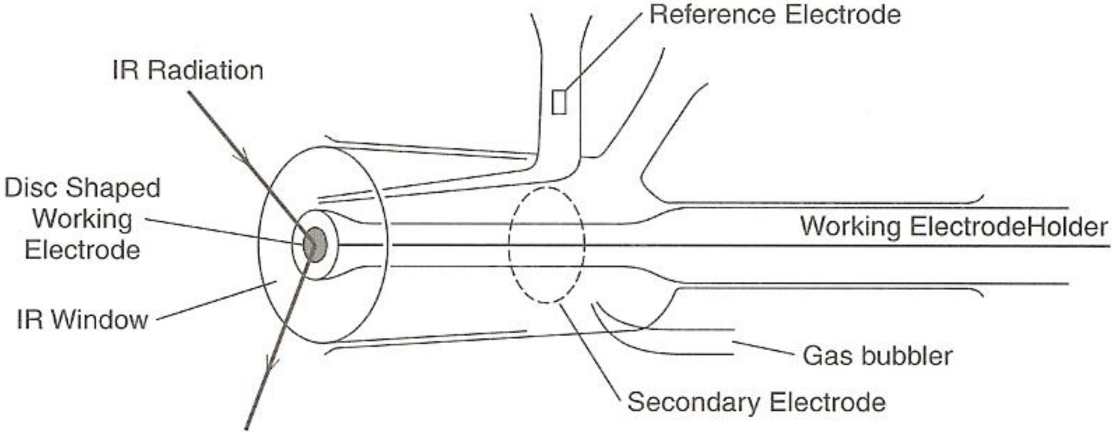
Infrared spectroelectrochemistry (IR-SEC)

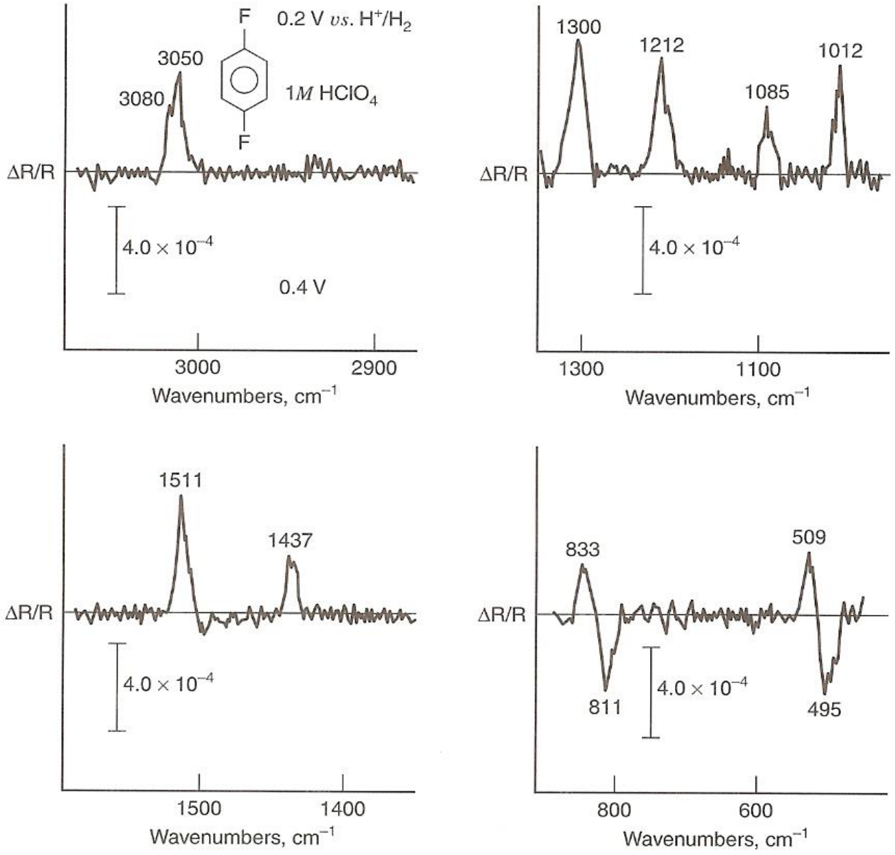


Cell for IR-SEC



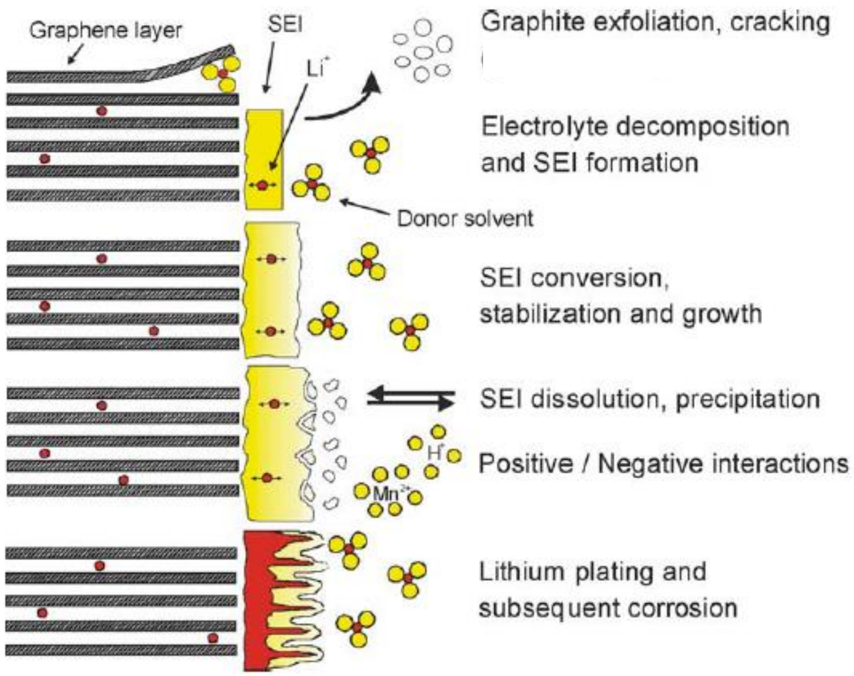
SEIRA (surface enhanced IR absorption)

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



P-difluorobenzene in 1 M $HClO_4$ at a Pt electrode

Why in-situ FT-IR spectroscopy ?



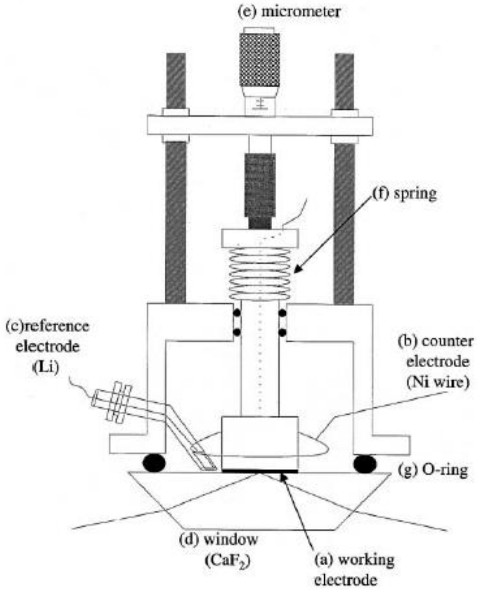
Changes at the anode/electrolyte interface

- *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 investigation*

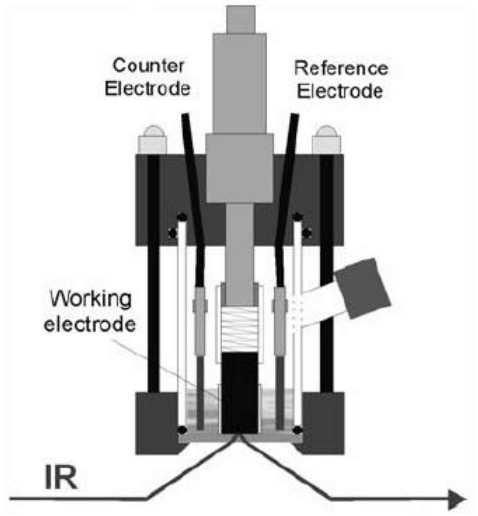
➢ *Necessity of In-situ FT- IR spectroscopy*

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

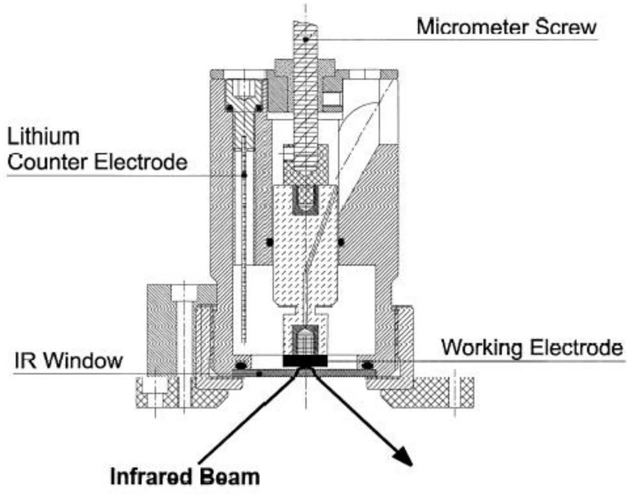
in-situ FT-IR Cell



Electrochim. Acta 47, 2001, 433
Kanamura group



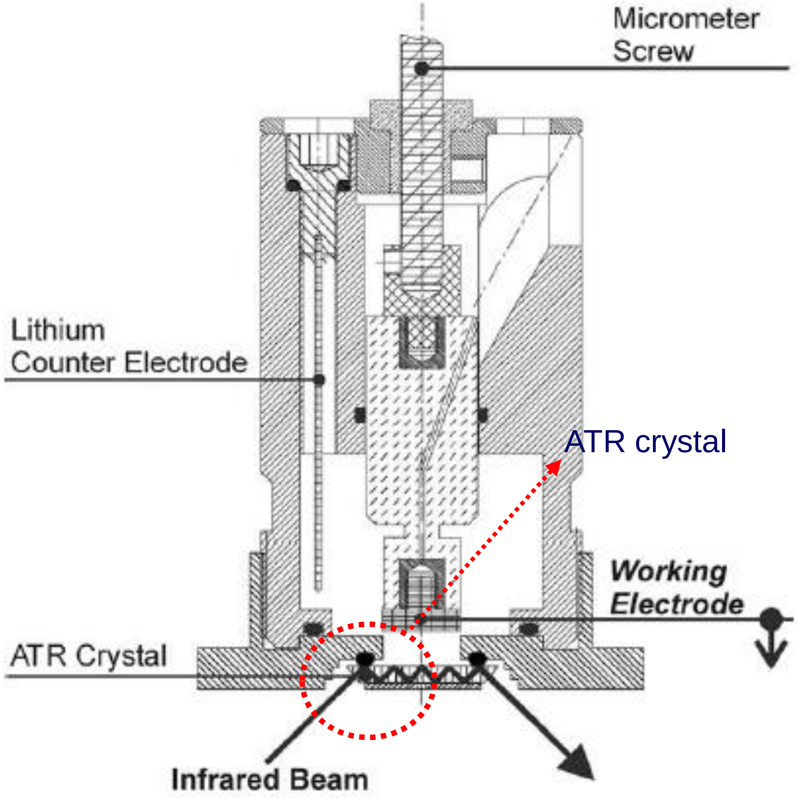
Anal. Bioanal. Chem. 379, 2004, 266
Moller group



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)

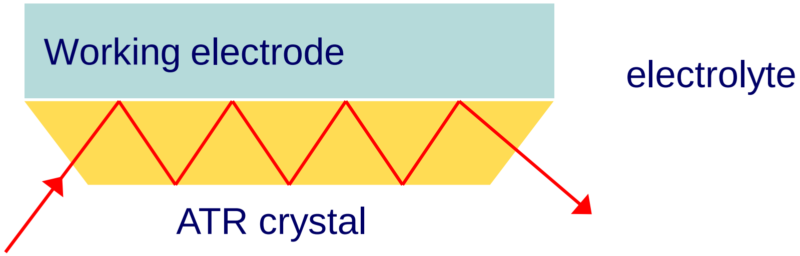
The decisive innovation is the use of an ATR crystal as the optical window. Five reflections can he increasing, thus, the sensitivity significantly. (P.Novak group)

❖ Selection of ATR crystal

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

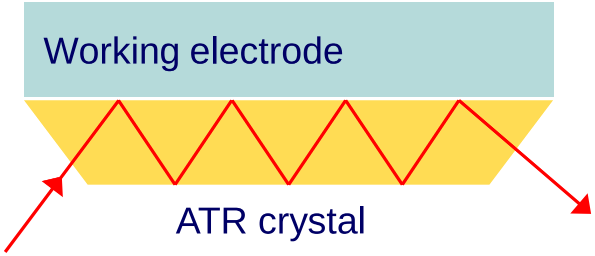
❖ Sealing problem

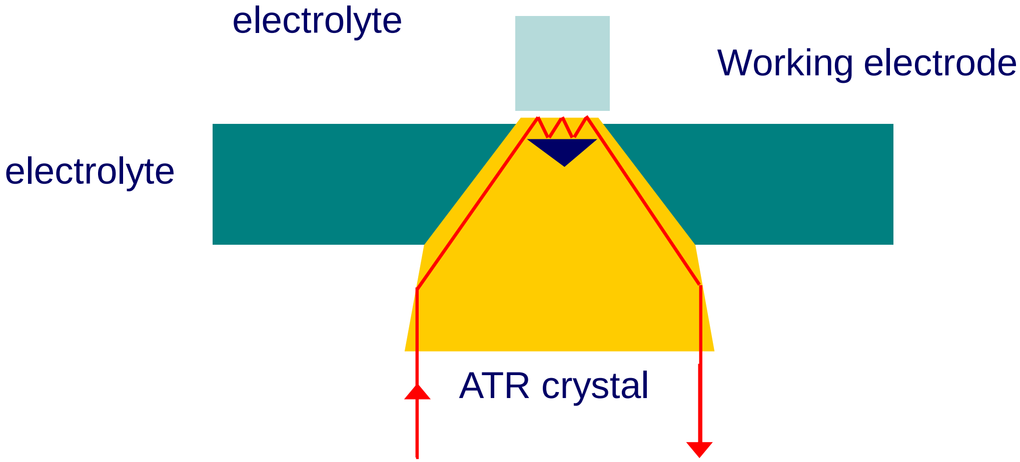
❖ Diffusion problem



Cell model of In-situ FT-IR

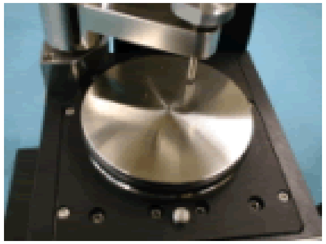
- Diffusion problem





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

- Beam alignment

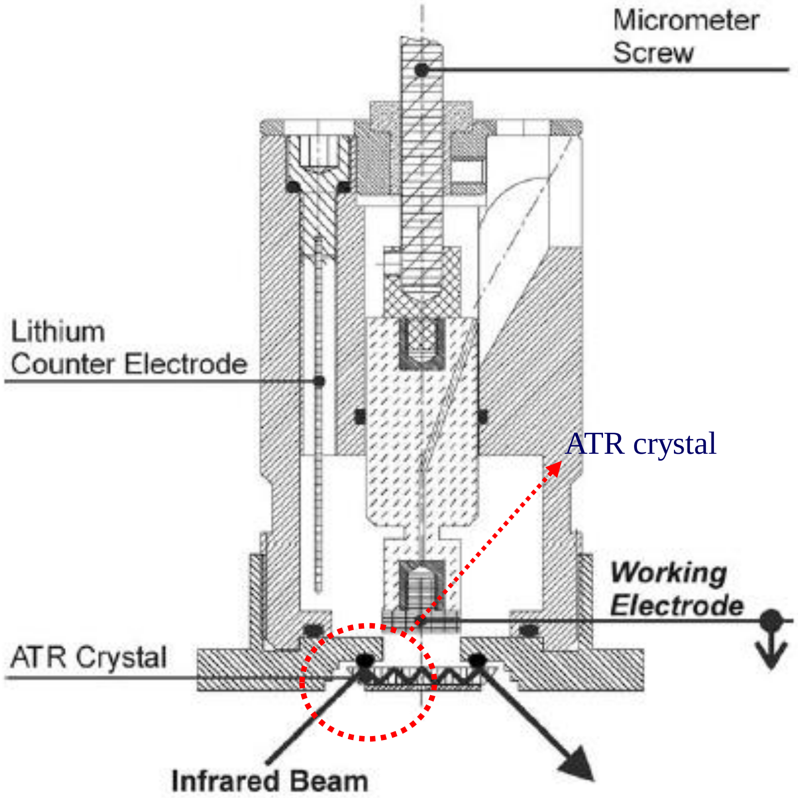


MIRacle^{TM} ATR
PIKE technologies /USA

In situ FT-IR (SNU)

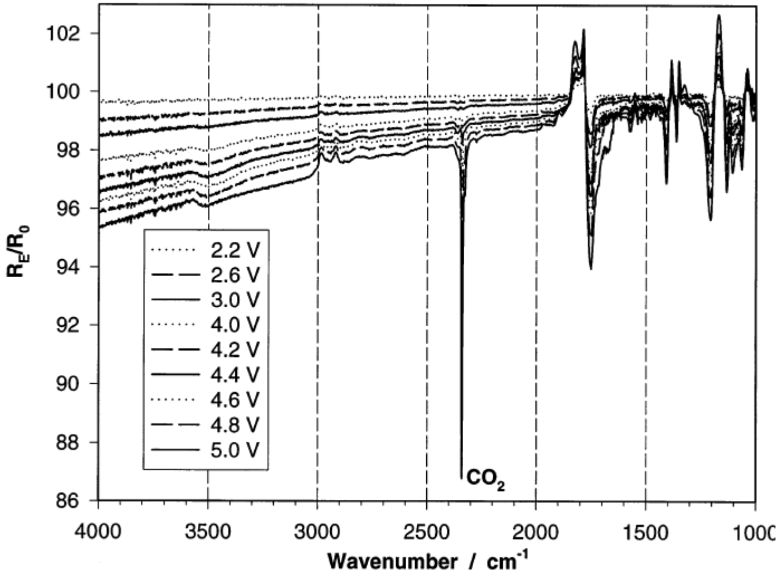
- Nicolet 5700 (thermo electron co.)
- ATR,DRIFT, in situ analysis
- 7,800~350cm-1 (DLaTGS w/KBr Detector)

In situ FT IR cell

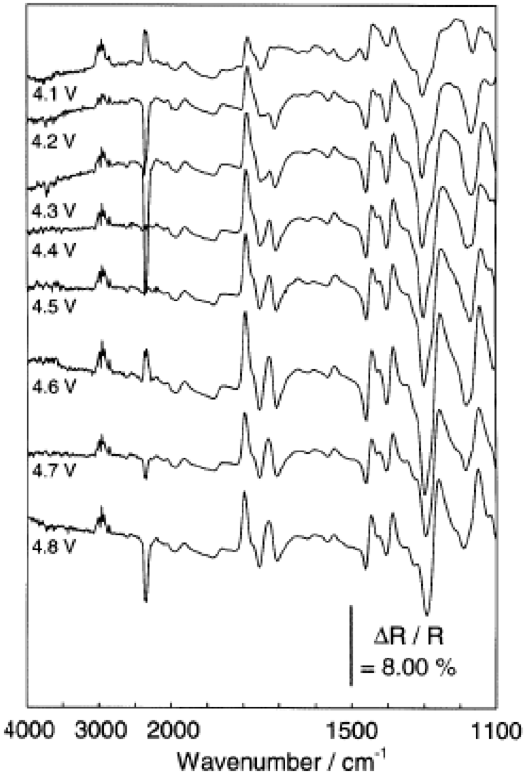


in-situ FT-IR spectroscopy

- 활용의 예

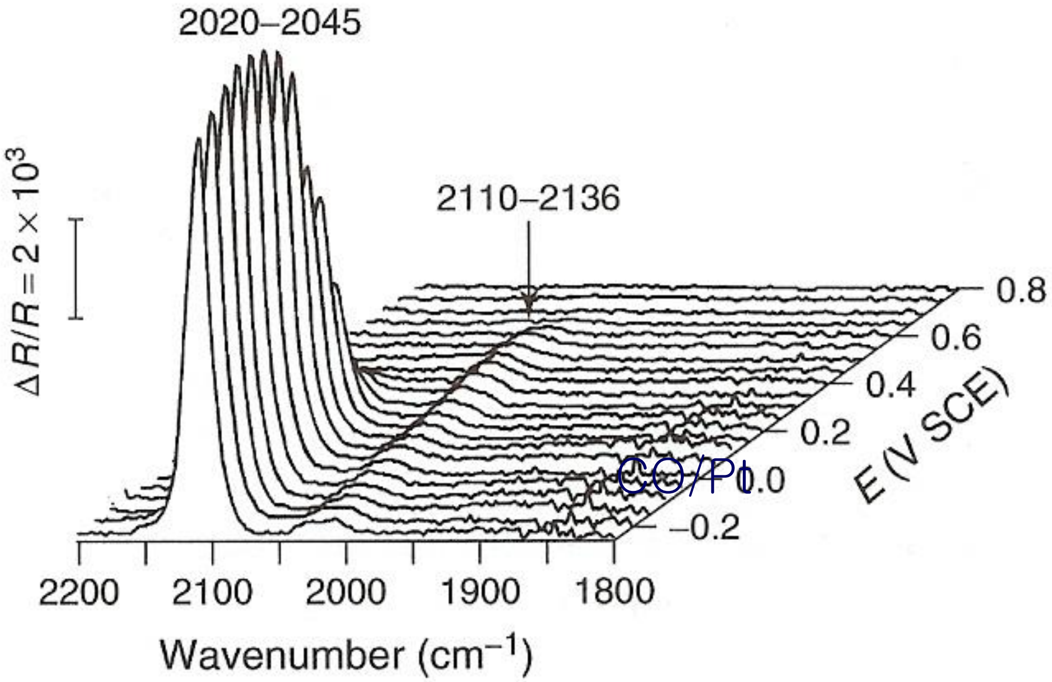


In situ FTIR spectra on a polished nickel electrode Electrolyte solution, 1 M $LiClO_4$ in PC (Electrochim. acta 45, 2000, 3589), Novak group



FTIR spectra for the electrochemical oxidation of 1.0 mol dm^{-3} LiPF6/propylene carbonate on the $LiCoO_2$ film electrode

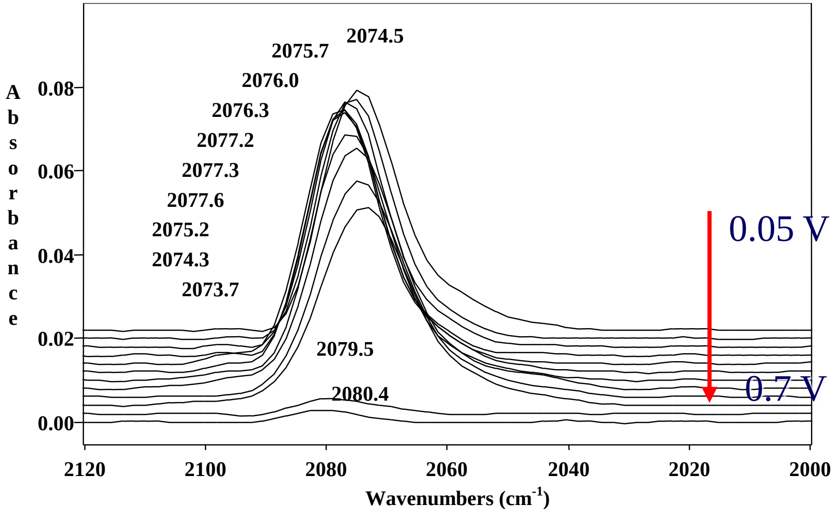
In situ FT-IR



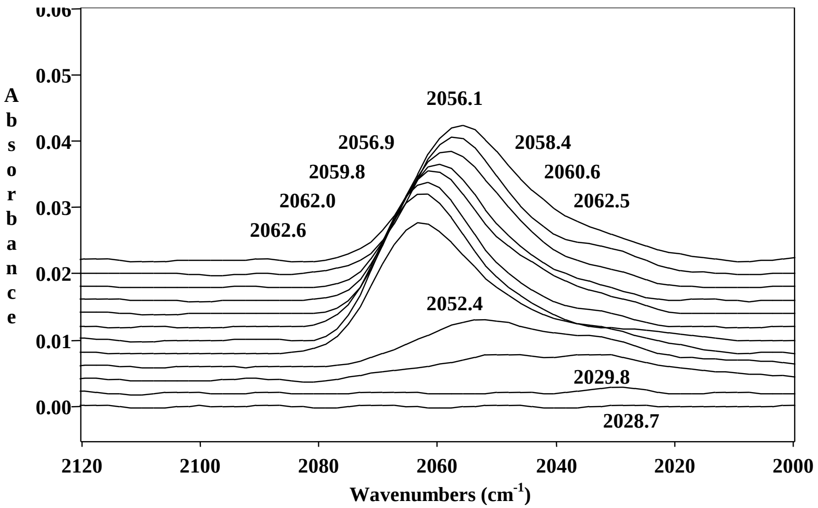
CO/Pt

In situ FT-IR

CO/Pt



Pure Pt, 50 % CO

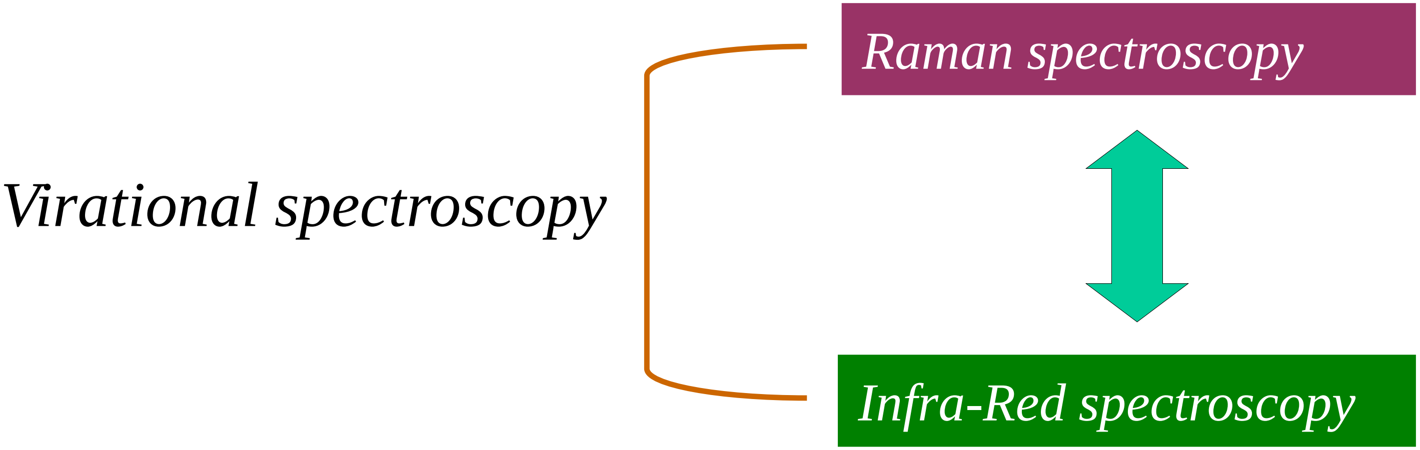


PtRu(1:1), 50 % CO

Change of bonding energy of CO-Pt

2. Vibration spectroscopy

(2) Raman spectroscopy



Virational spectroscopy

Raman spectroscopy

Infra-Red spectroscopy

Comparison: IR vs. Raman

Infra-Red spectroscopy

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

O C O

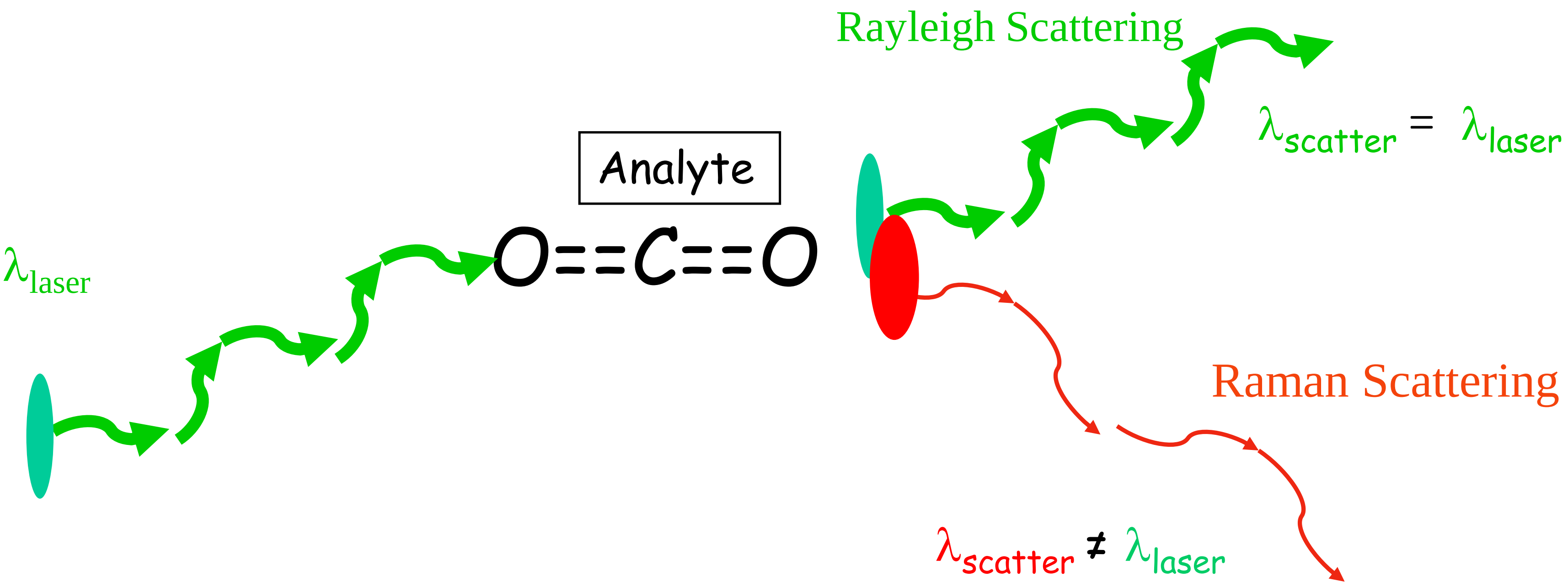
Raman spectroscopy

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

O C O

In case of homonuclear molecule, IR inactive, Raman active

What is Raman effect ?



λ_{laser}

Analyte

O==C==O

Rayleigh Scattering

$\lambda_{scatter} = \lambda_{laser}$

Raman Scattering

$\lambda_{scatter} \neq \lambda_{laser}$

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

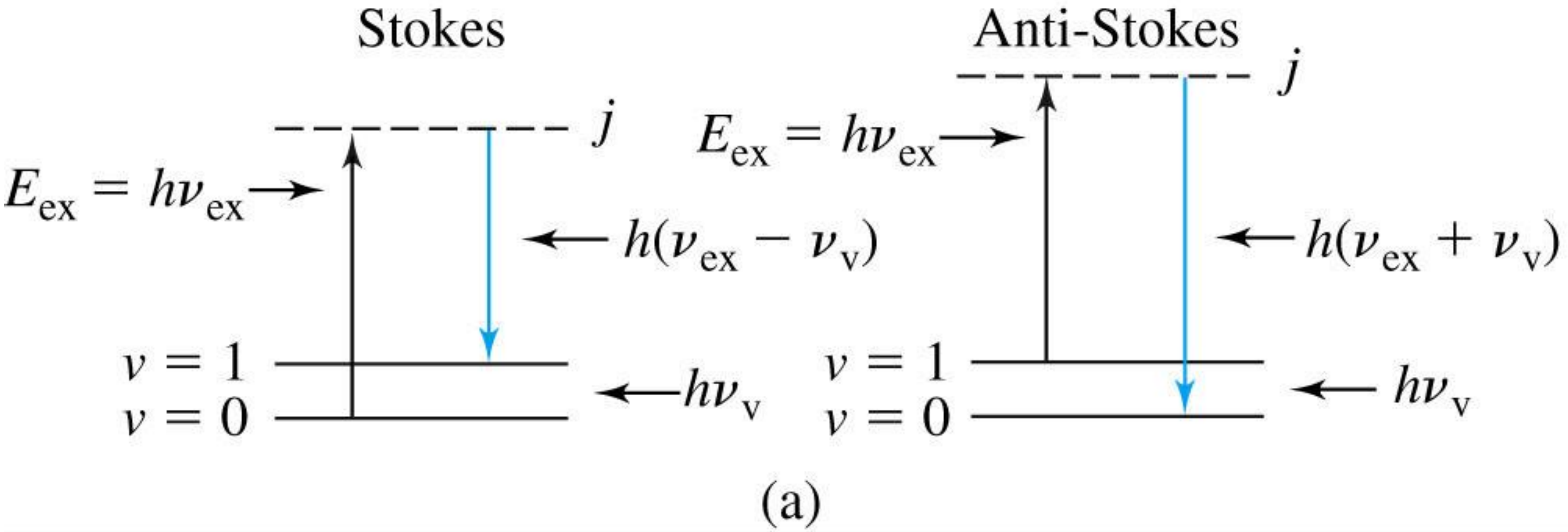
아침/저녁놀: 단파장 산란, 장파장 투과하기 때문에 붉게 보임

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 띄는 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 $h\nu_{ex}$ → excitation to a virtual state j → scattering

Frequency shift of inelastic scattering = vibrational frequency



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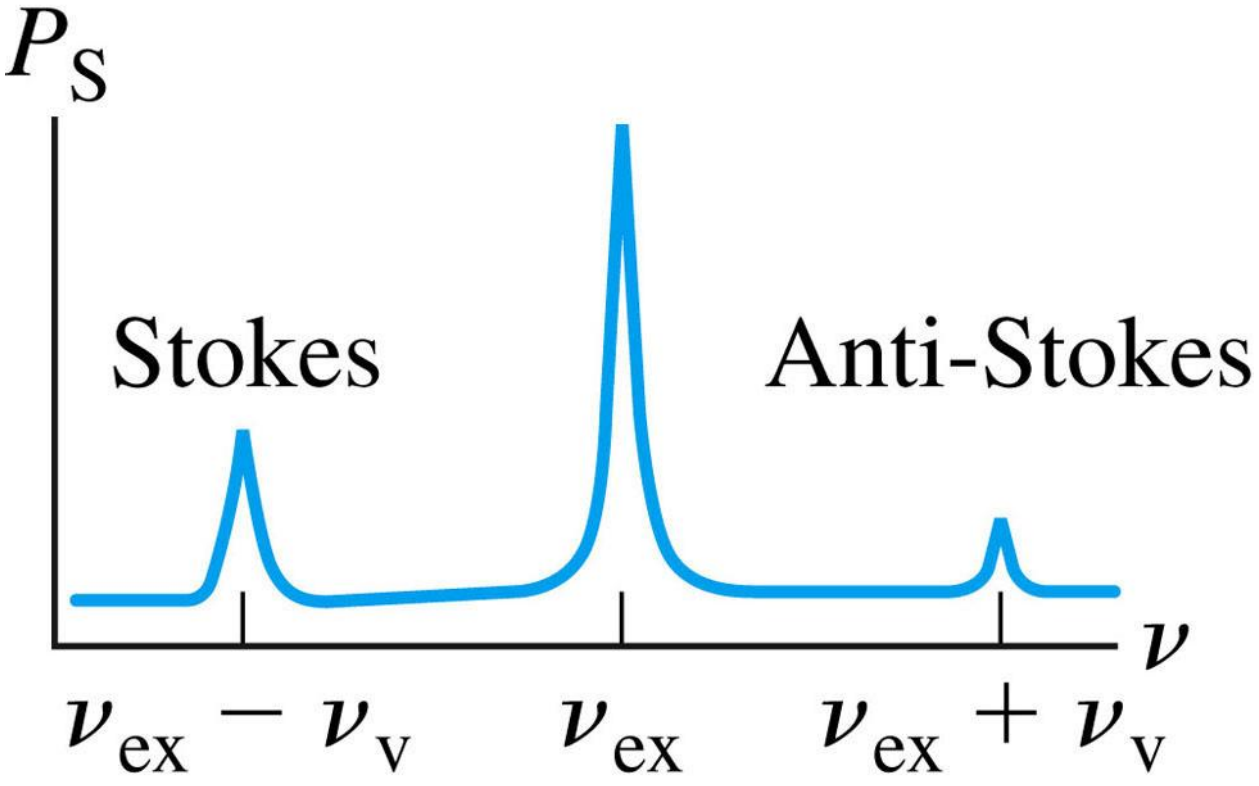

(b)

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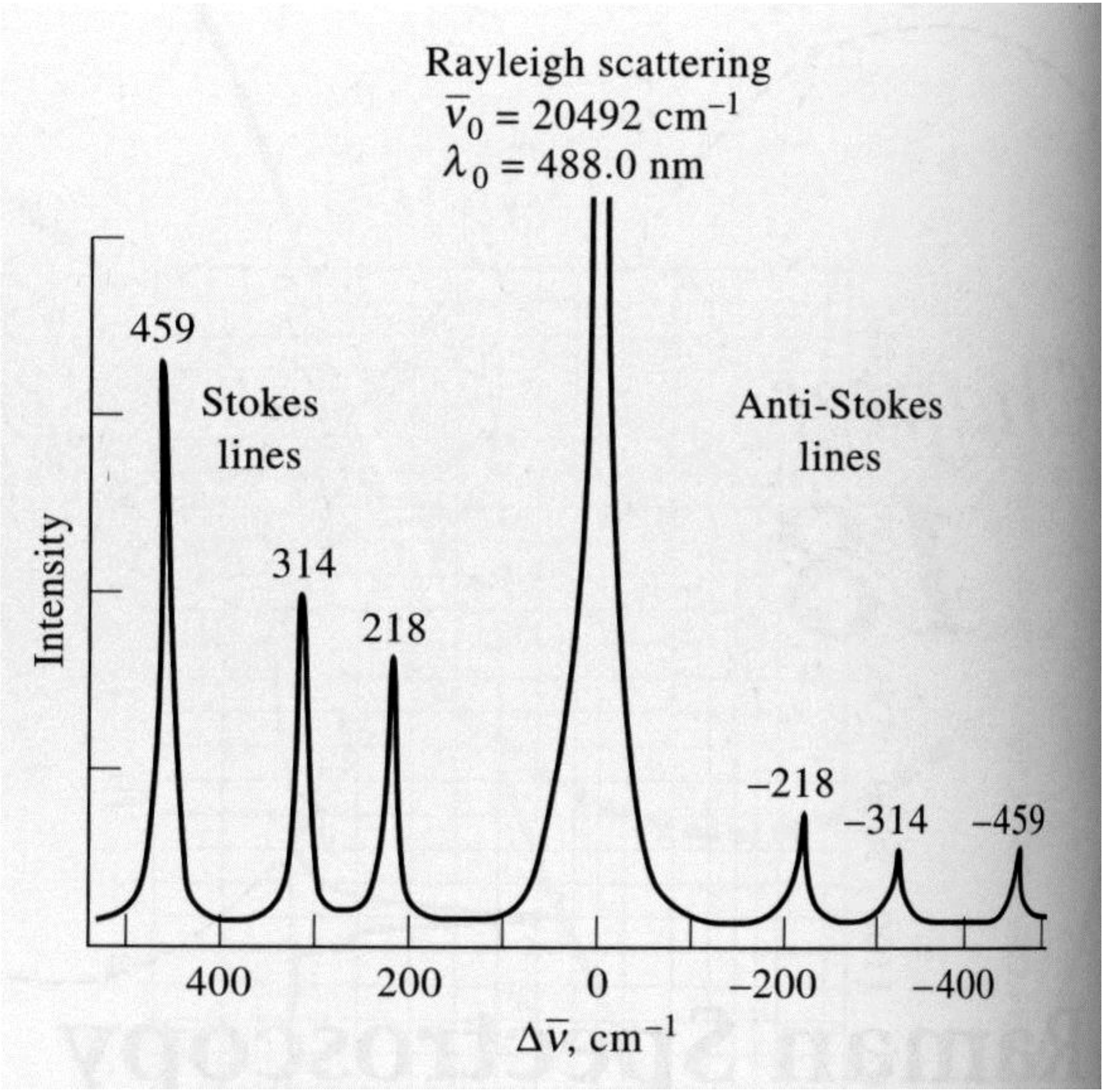
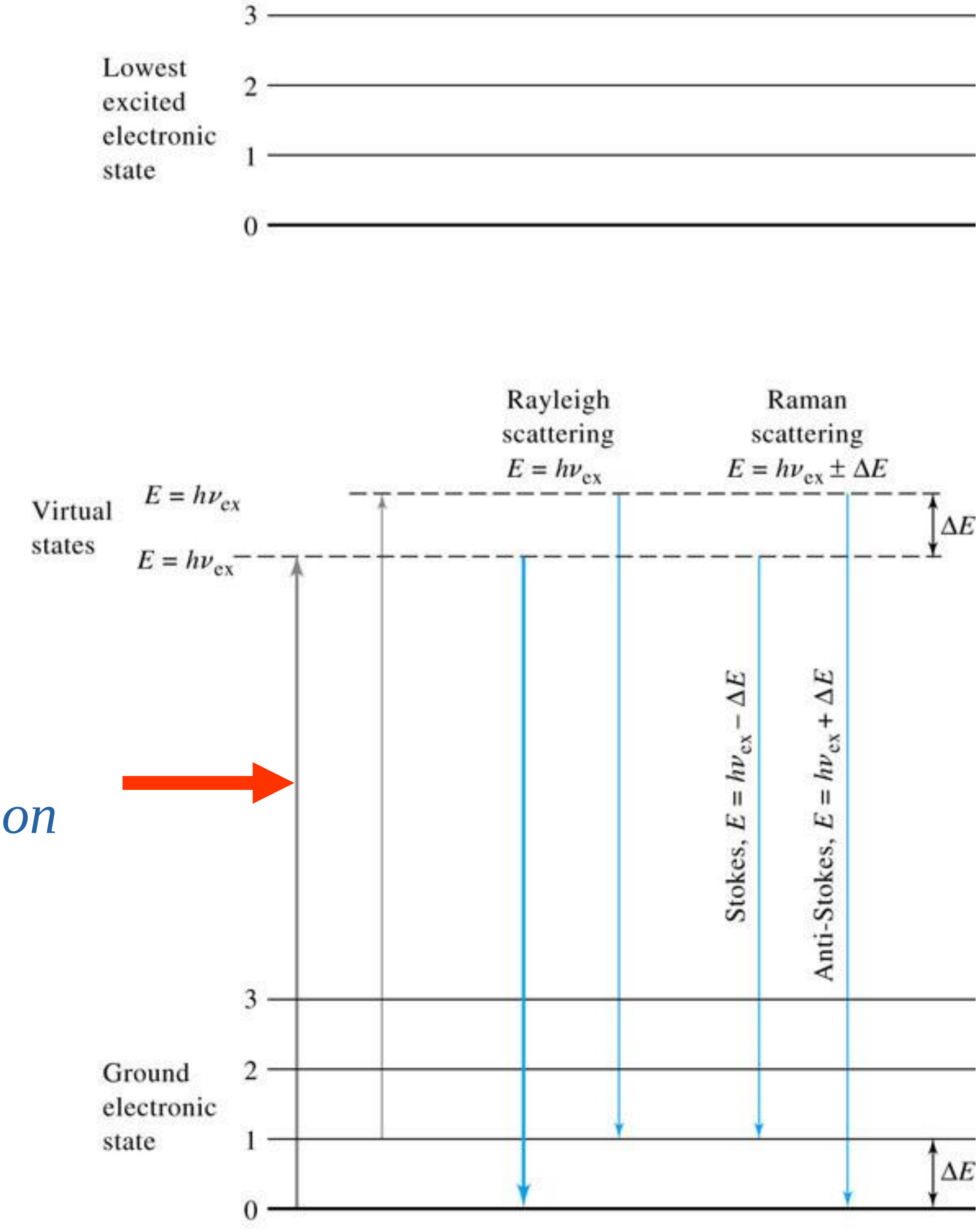


CCl_4
Excited by laser
(488 nm (= 20492
cm^{-1})

Temporal polarization



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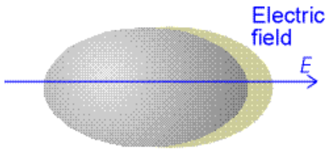
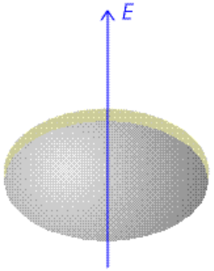
Scattering Model



(a)



(b)

Induced dipole moment (m)

$$E = E_0 \cos(2\pi\nu_{ex} t)$$

E : Laser electric field

$$m = \alpha E = \alpha E_0 \cos(2\pi\nu_{ex} t)$$

m : Dipole moment

α : Polarizability

$$\alpha = \alpha_0 + (r - r_{eq})\left(\frac{\partial \alpha}{\partial r}\right) \qquad r - r_{eq} = r_m \cos(2\pi\nu_v t)$$

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial r}\right) r_m \cos(2\pi\nu_v t)$$

$$m = \alpha_0 E_0 \cos(2\pi\nu_{ex} t) + E_0 r_m \left(\frac{\partial \alpha}{\partial r}\right) \cos(2\pi\nu_v t)\cos(2\pi\nu_{ex} t)$$

$$m = \underset{\textit{Rayleigh line}}{\alpha_0 E_0 \cos(2\pi\nu_{ex} t)} + \frac{E_0}{2} r_m \left(\frac{\partial \alpha}{\partial r}\right) \cos[2\pi \underset{\textit{Stokes line}}{\underline{(\nu_{ex} - \nu_v)t}}] + \frac{E_0}{2} r_m \left(\frac{\partial \alpha}{\partial r}\right) \cos[2\pi \underset{\textit{Anti-stokes line}}{\underline{(\nu_{ex} + \nu_v)t}}]$$

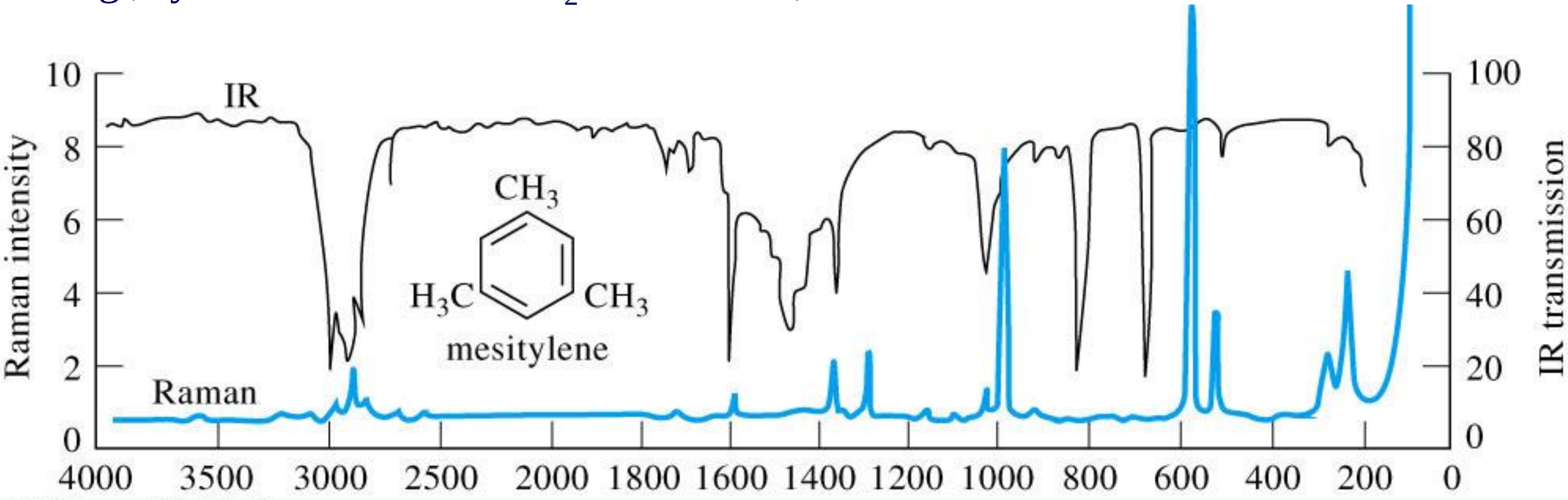
$$\boxed{\frac{\partial \alpha}{\partial r} \neq 0 \quad \text{: Raman에 active하기 위한 조건}}$$

IR vs. Raman

Similar, different intensities

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

e.g., symmetric mode of CO_2: IR inactive, Raman active



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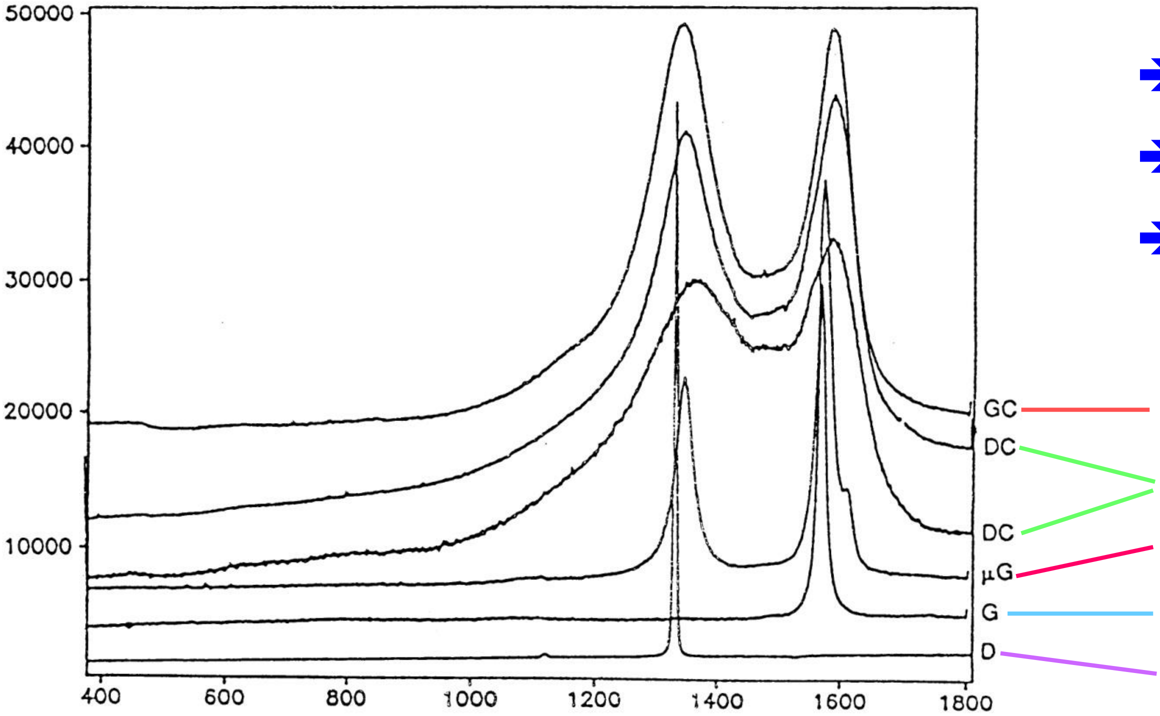
Raman Spectra of different modifications of carbon



- Physical Properties
- <H> content
- Thickness

GC: Graphite like Overcoat

DC: Diamond like Overcoat

μG: microcrystalline Graphite

G: Graphite

D: Diamond

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.

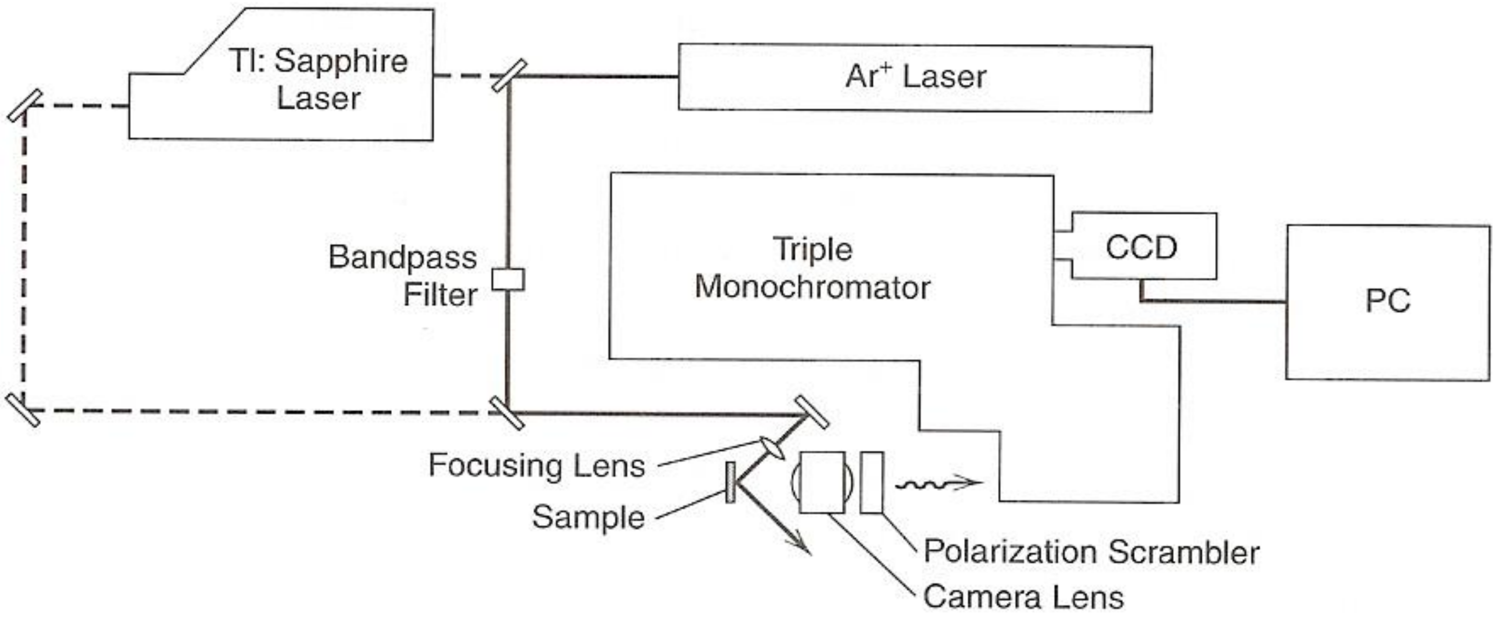
- Laser energy is low so the sample remains intact.

What can Raman Spectra tell us ?

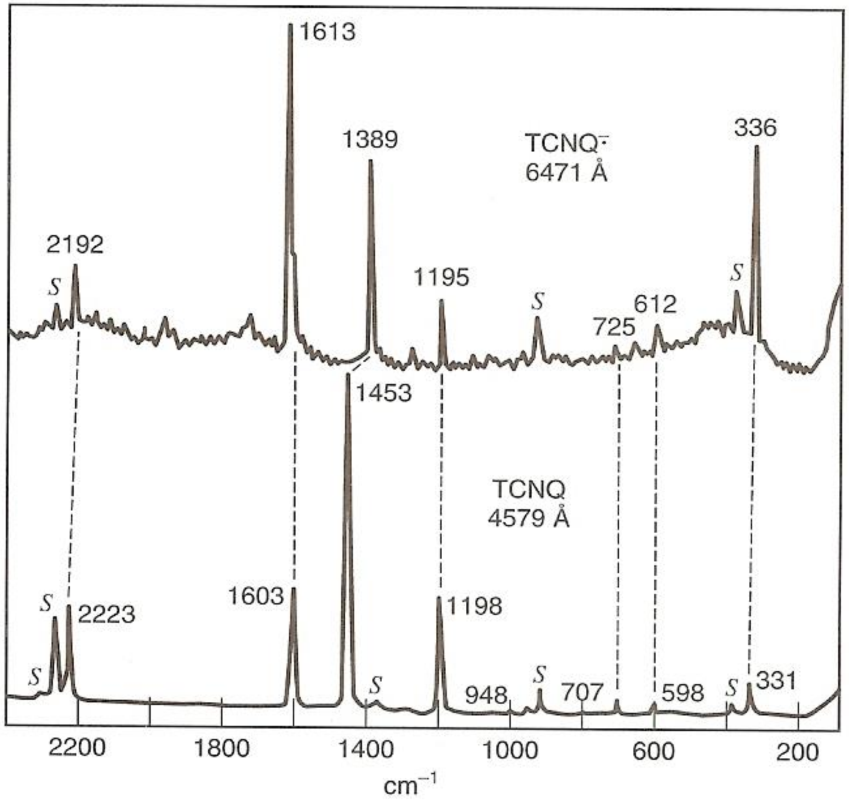
- Vibrational frequencies are characteristic of chemical bonds or groups of bonds in a specific molecule: normal modes
- A Raman spectrum provides a fingerprint of the set of bonds present in the material
- Vibrational frequencies are sensitive to details of the local environment of a molecule, such 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

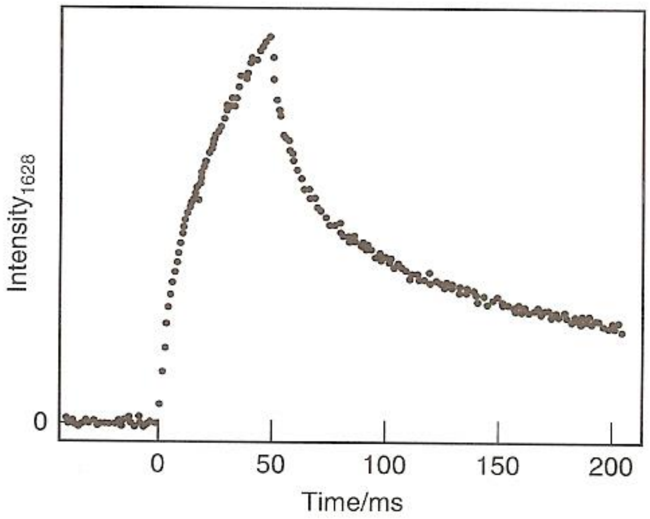
- Resonance Raman spectroscopy (RRS)
- Surface enhanced Raman spec. (SERS): molecules adsorbed on certain surfaces (Ag or Au)



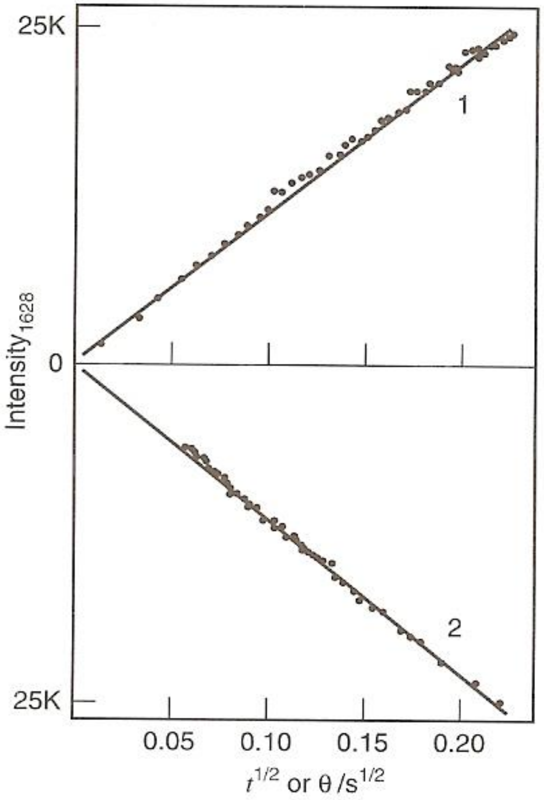
RRS of TCNQ & electrochemically generated TCNQ$^-$



Transients in Raman intensity

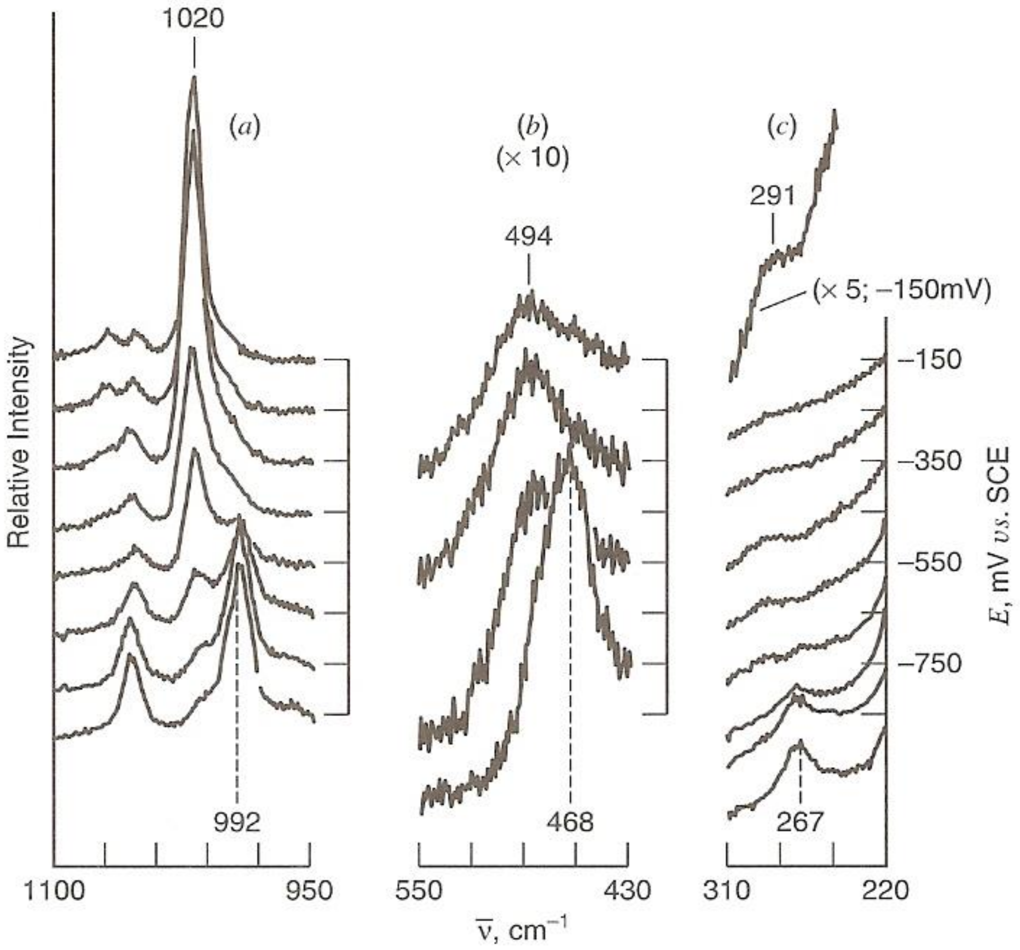


(a)

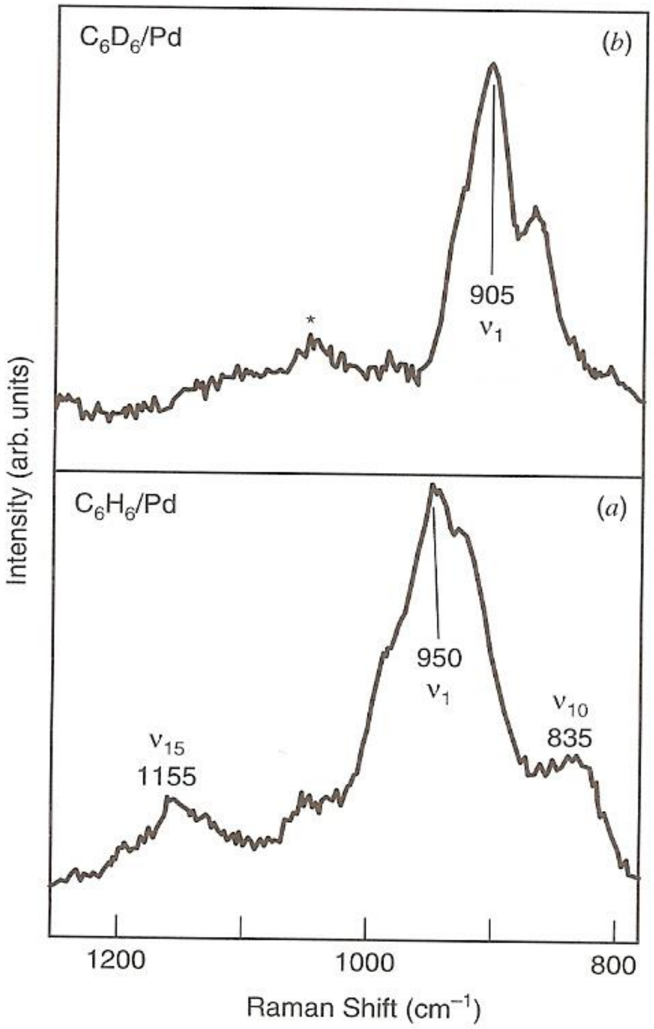


(b)

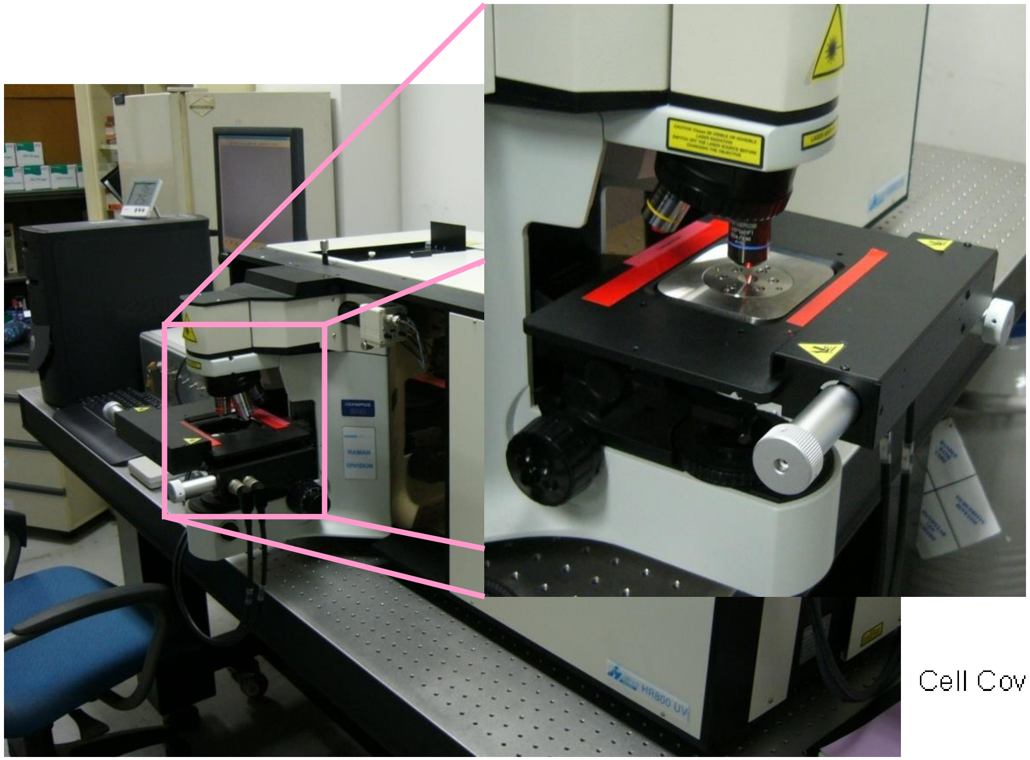
SERS for Os compound on Ag electrode as ftn of potential

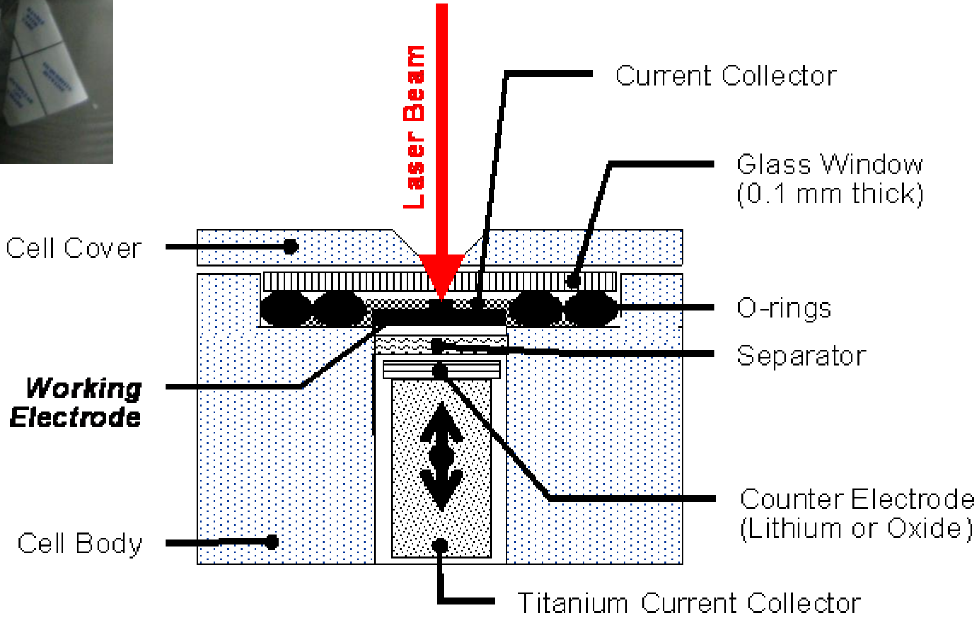


SER spectra for benzene on Pd



In-situ Raman Spectroscopy (SNU)



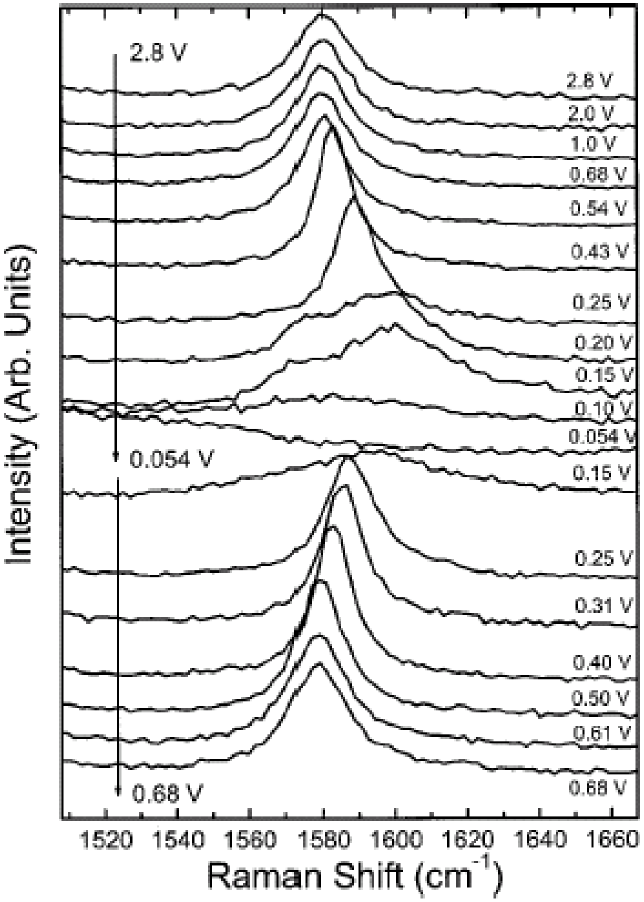


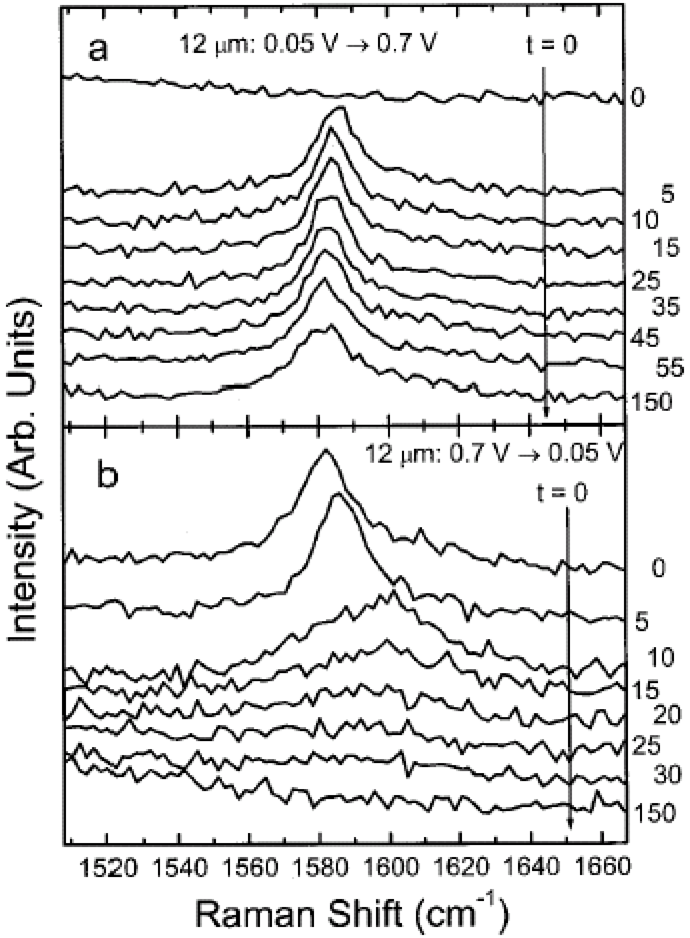
Specifications of HR LabRam

- 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 objetive : 10X, 50X, 100X, 50X LWD
- CCD detector : a multichannel LN_2 cooled (-133 ^{o}C)
  1024 × 256 pixels

Structural Changes according to Li+ intercalation

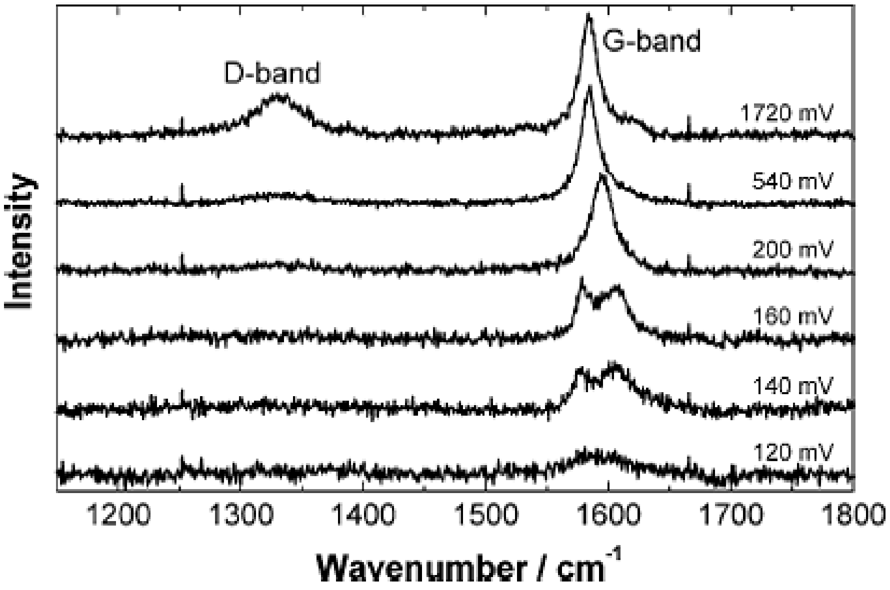
- Li^+ intercalation

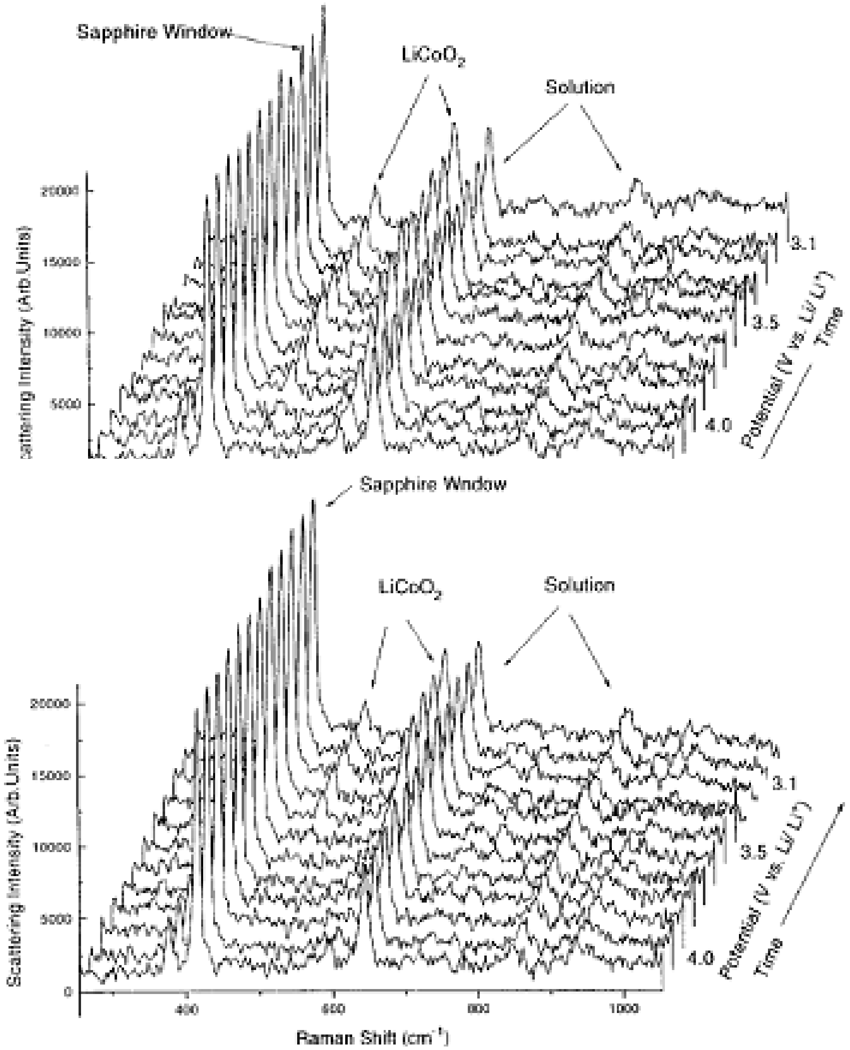




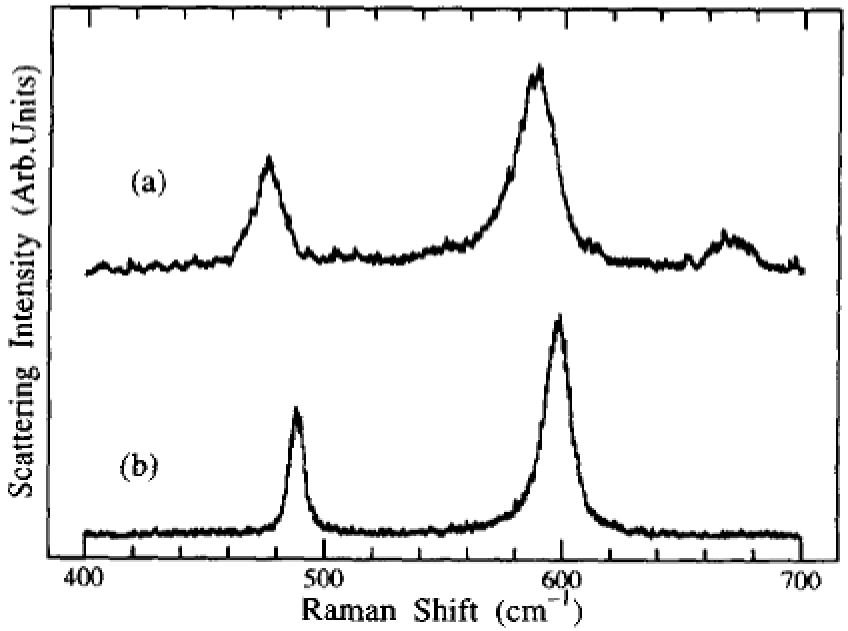
Scherson (2002)

Structural Changes according to Li+ intercalation

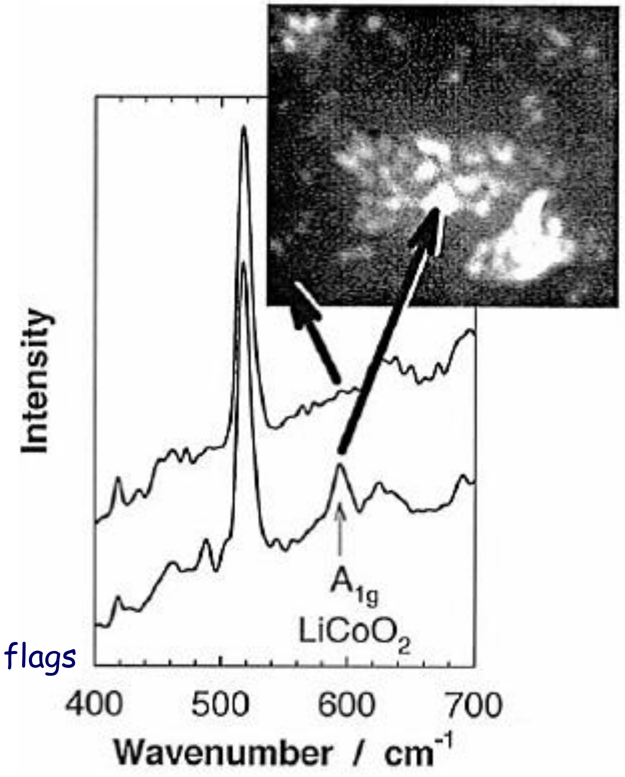




LiCoO$_2$



Variation of Raman spectra of (a) powder and (b) thin film of LiCoO$_2$ on gold flags



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

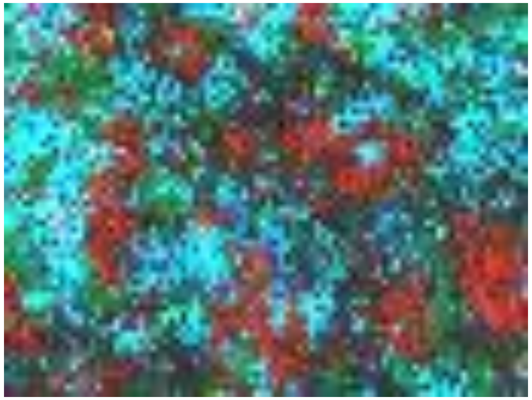
A_{1g}, E_g 모드는 Raman active, $2A_{2u}$, $2E_u$ 모드는 IR active.

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

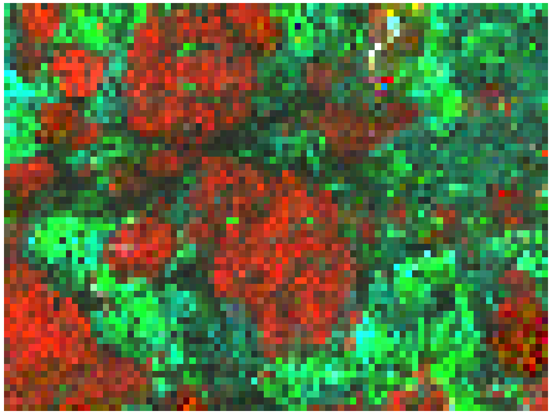
Peak의 shift와 width 차이 -> Film의 결정성이 뛰어나기 때문에

- In situ Raman microscopy

25°C

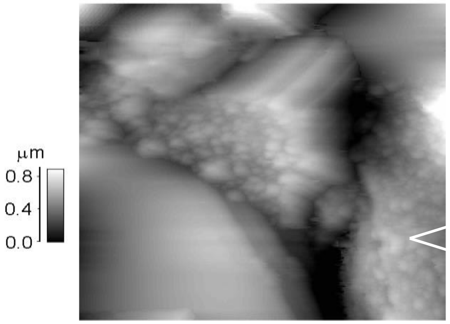


60°C

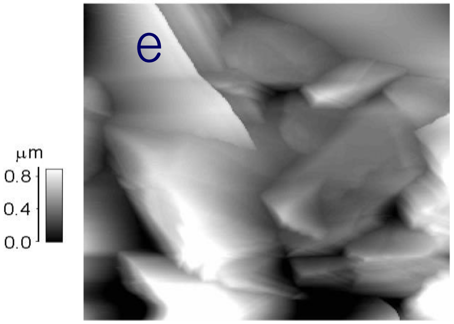


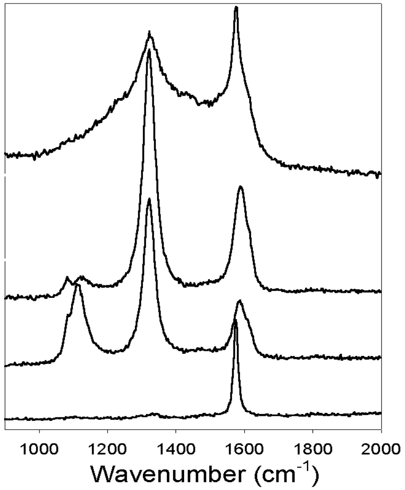
- $LiCoO_2$
- graphite
- acetylene black

Brodd (2003)

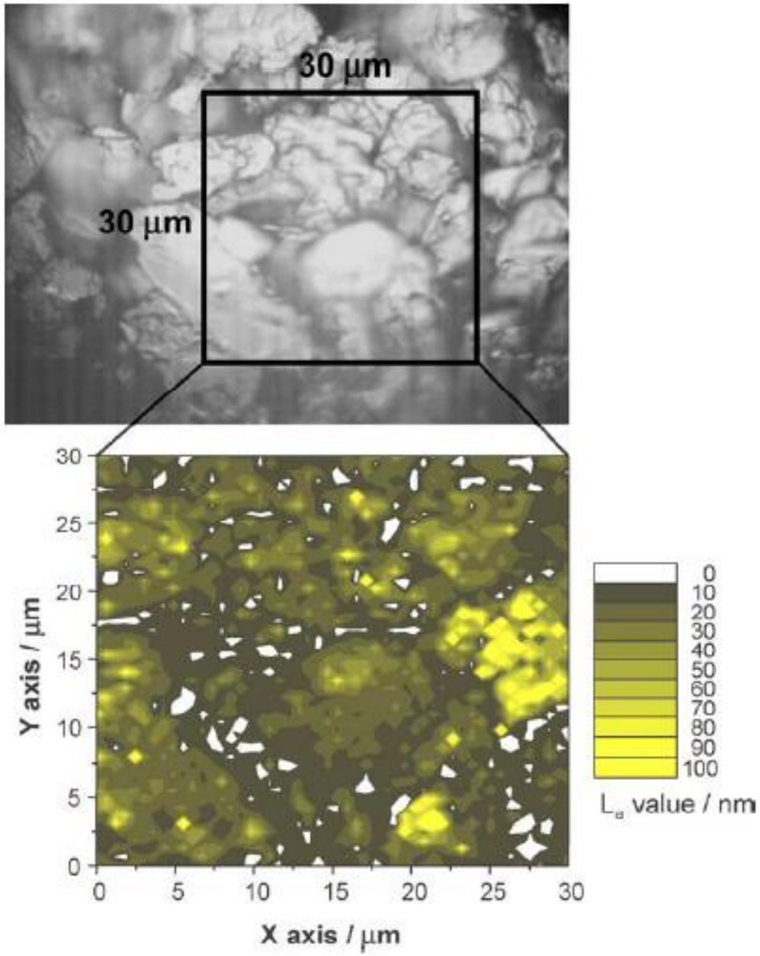


Fresh anode

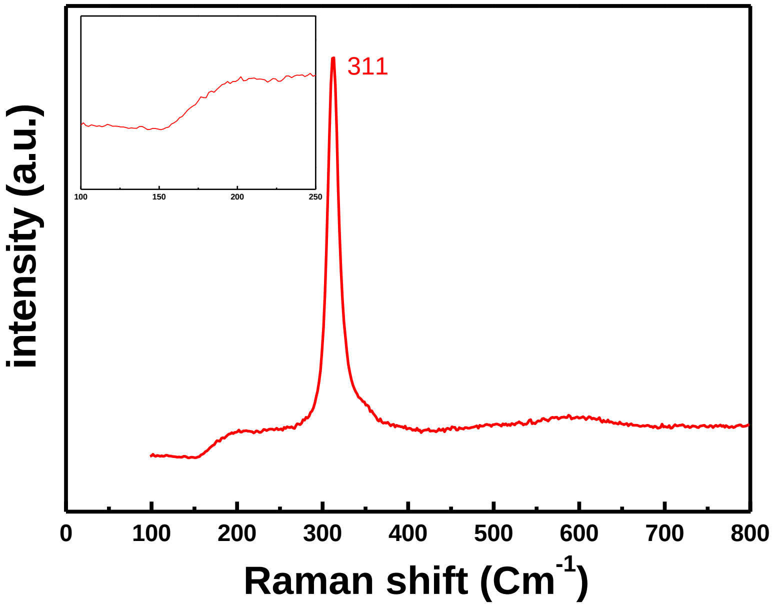




in-situ Raman

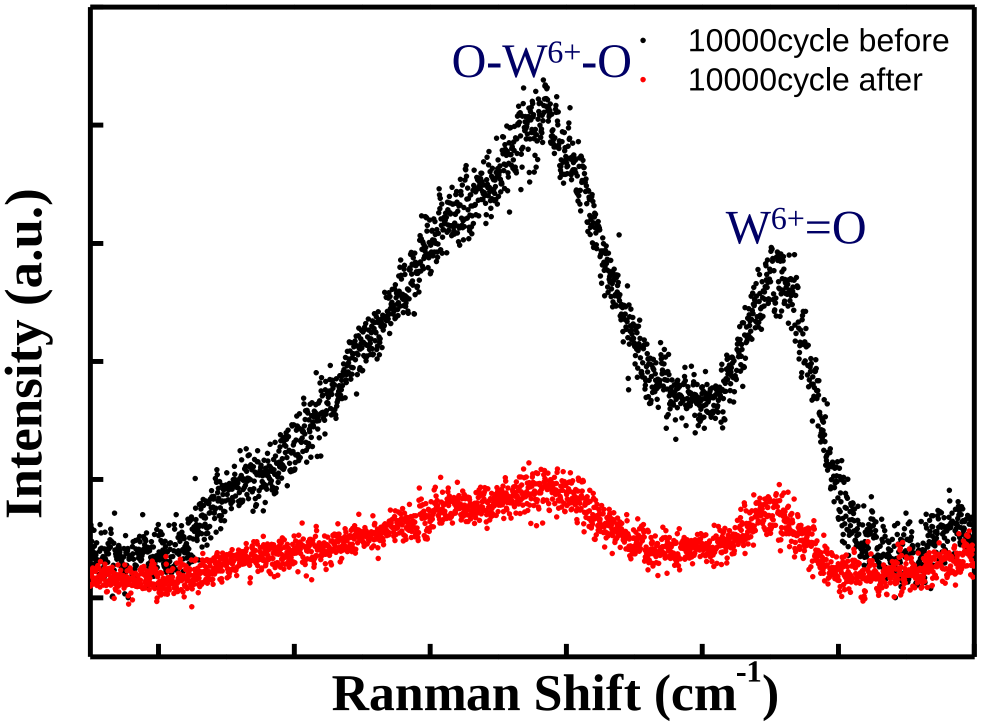


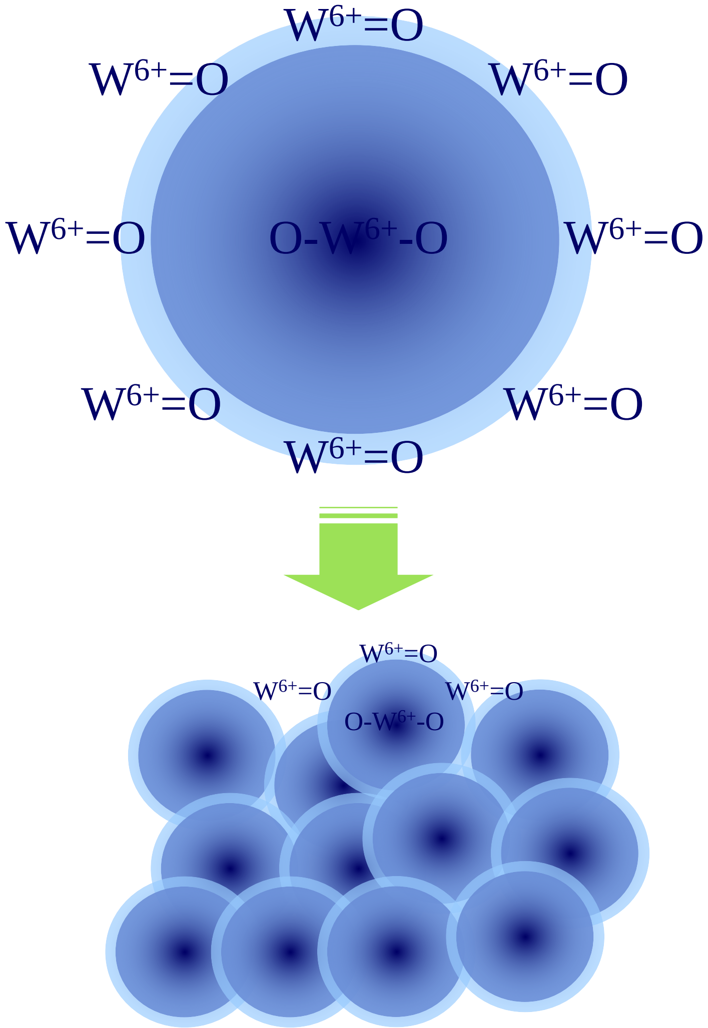
Raman mapping of graphite surface: a graphite sample (top) and spatial distribution plot of the L_a values



Raman spectra of SnS_2 nanopowder by solvothermal synthesis

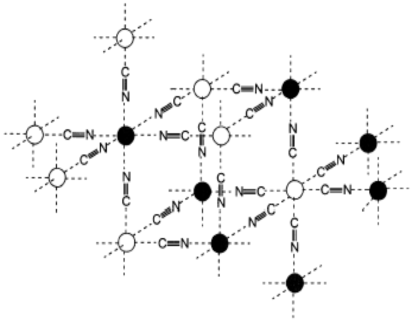
In situ Raman - WO_3



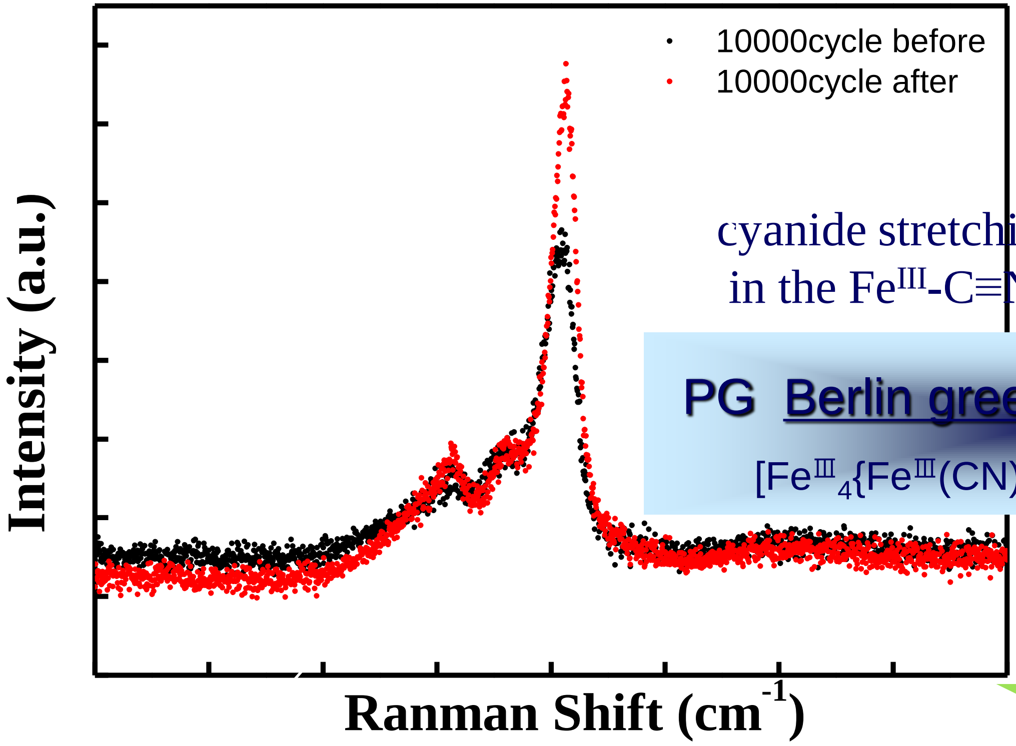


- The $W^{6+}=O/O–W^{6+}–O$ ratio ➔ increase
- The grain size ➔ decrease

Raman data - PB



- **PB** Prussian blue
  [FeⅢFeⅡ(CN)6]-
- PW Prussian white
  [FeⅡFeⅡ(CN)6]2-



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

PG Berlin green

$[Fe^{III}_4\{Fe^{III}(CN)_6\}_2\{Fe^{II}(CN)_6\}]^-$

Structure unstable

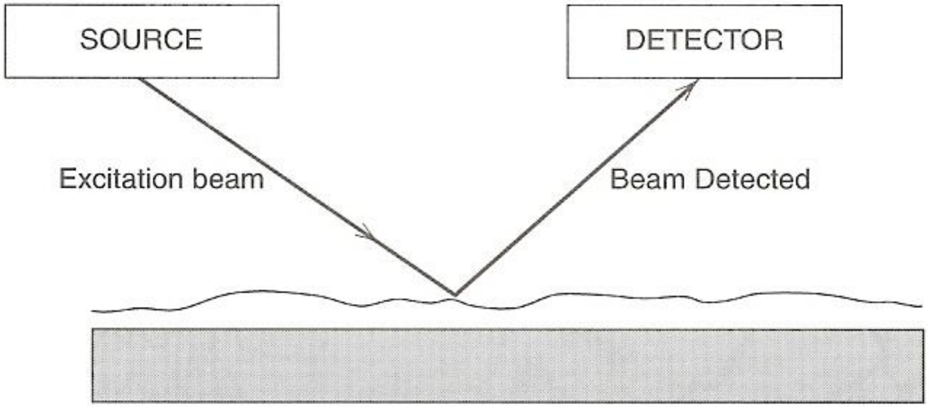
cyanide stretching vibration
in the Fe^{III}-N≡C-Fe^{II}

PB Prussian blue

$[Fe^{III}Fe^{II}(CN)_6]^-$

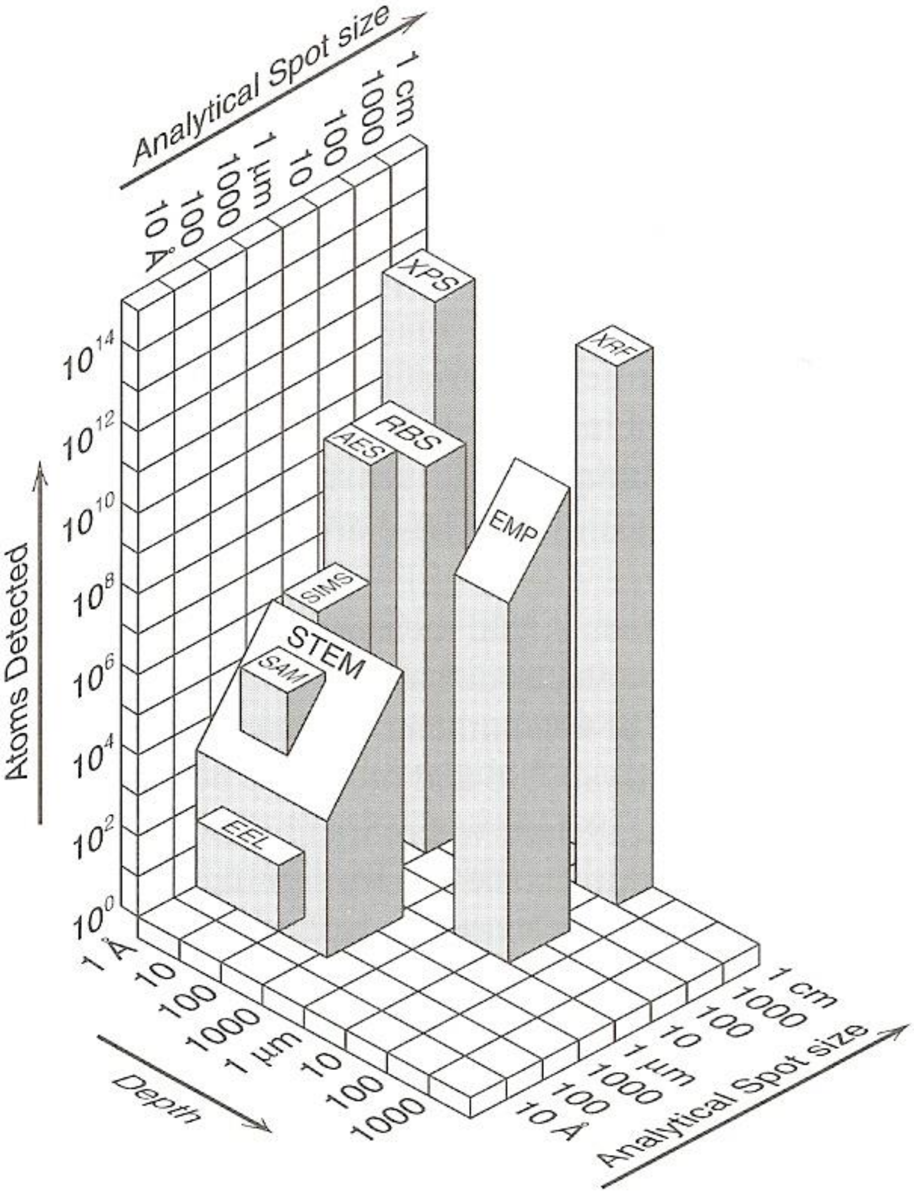
Electron and ion spectrometry

Ultra high vacuum (UHV)

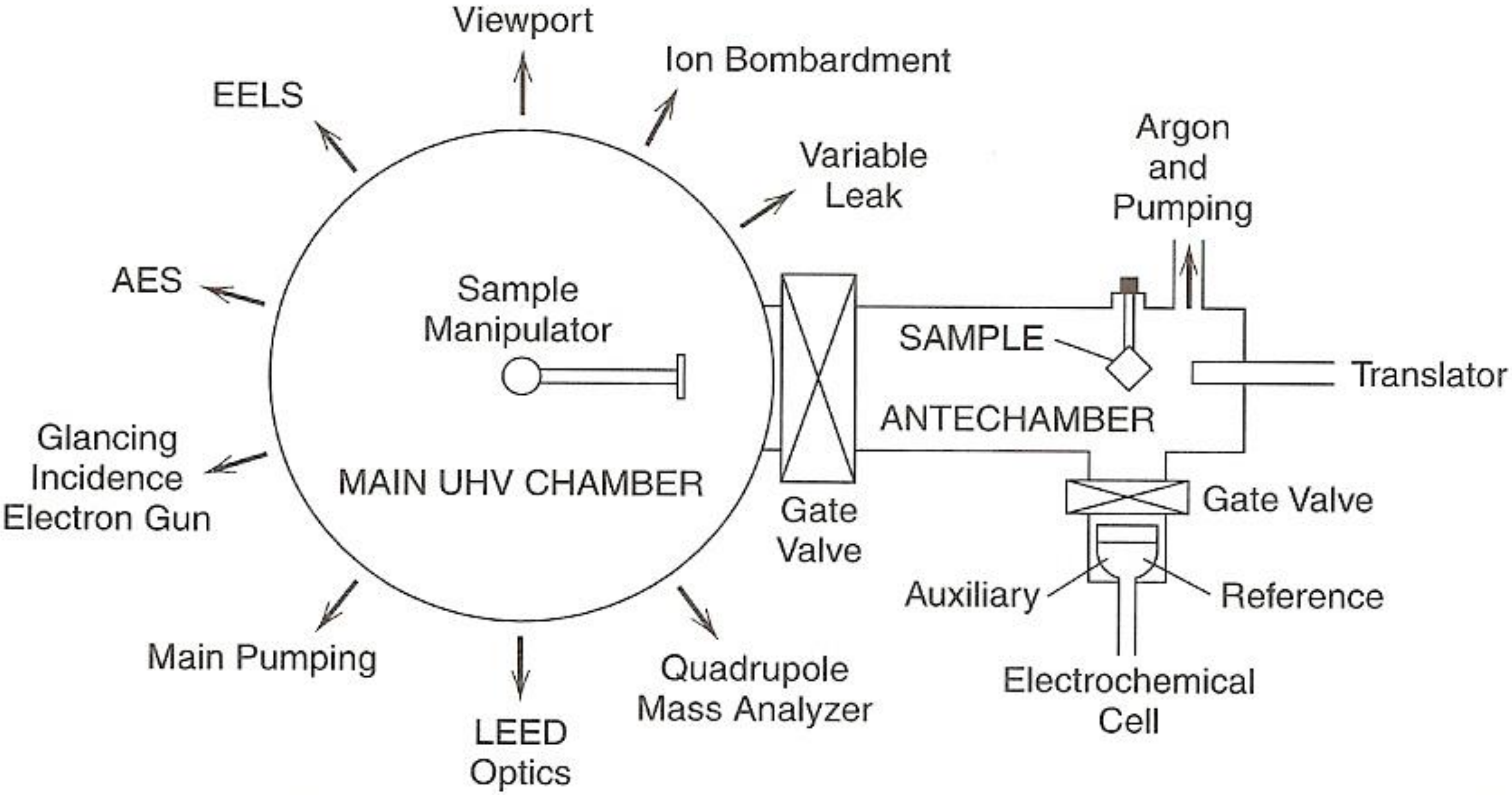


	Excitation	Detection
X-ray photoelectron spectroscopy (XPS)	Photons(X-ray)	Electrons
UV photoelectron spectroscopy (UPS)	Photons (UV)	Electrons
Auger electron spectroscopy (AES)	Electrons	Electrons
Low-energy electron diffraction (LEED)	Electrons	Electrons
High resolution e^- E loss spec. (HREELS)	Electrons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

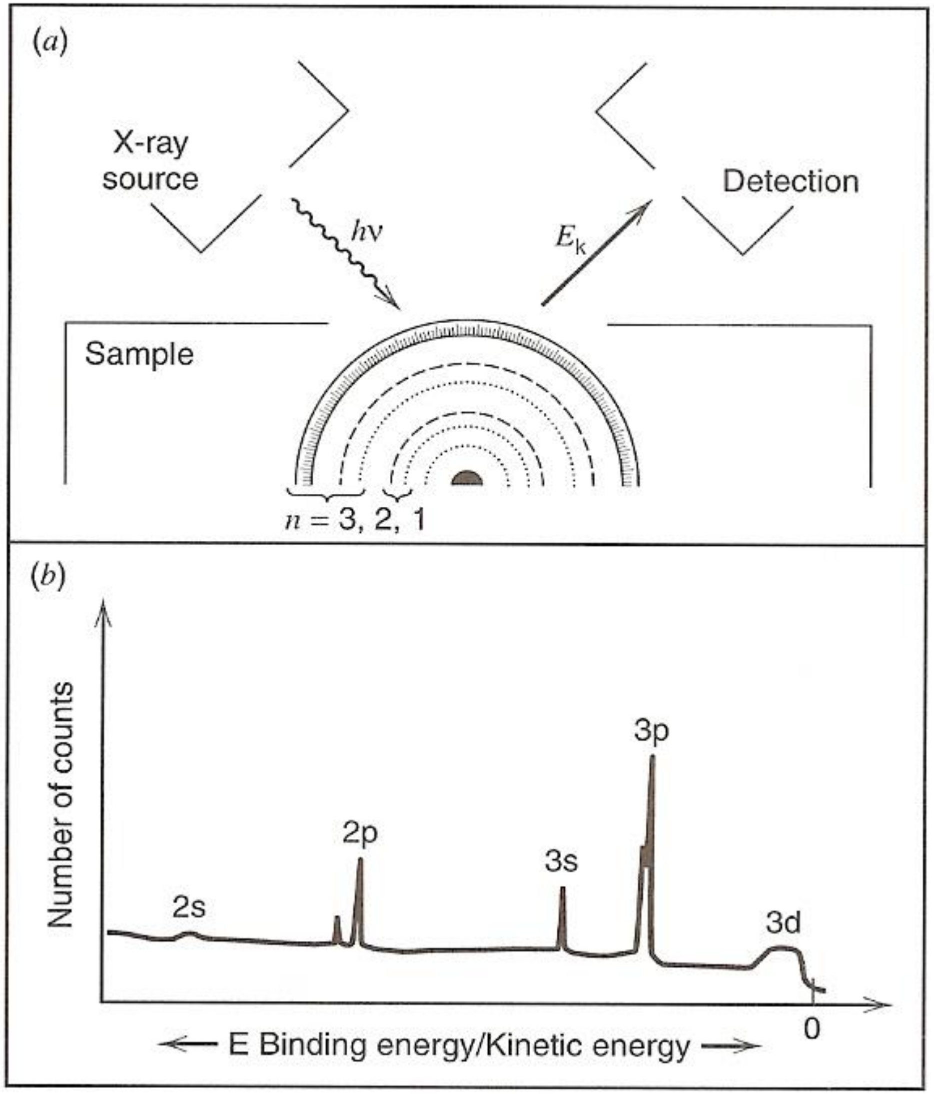
Detection limits, sampling depth, spot size (spatial resolution)



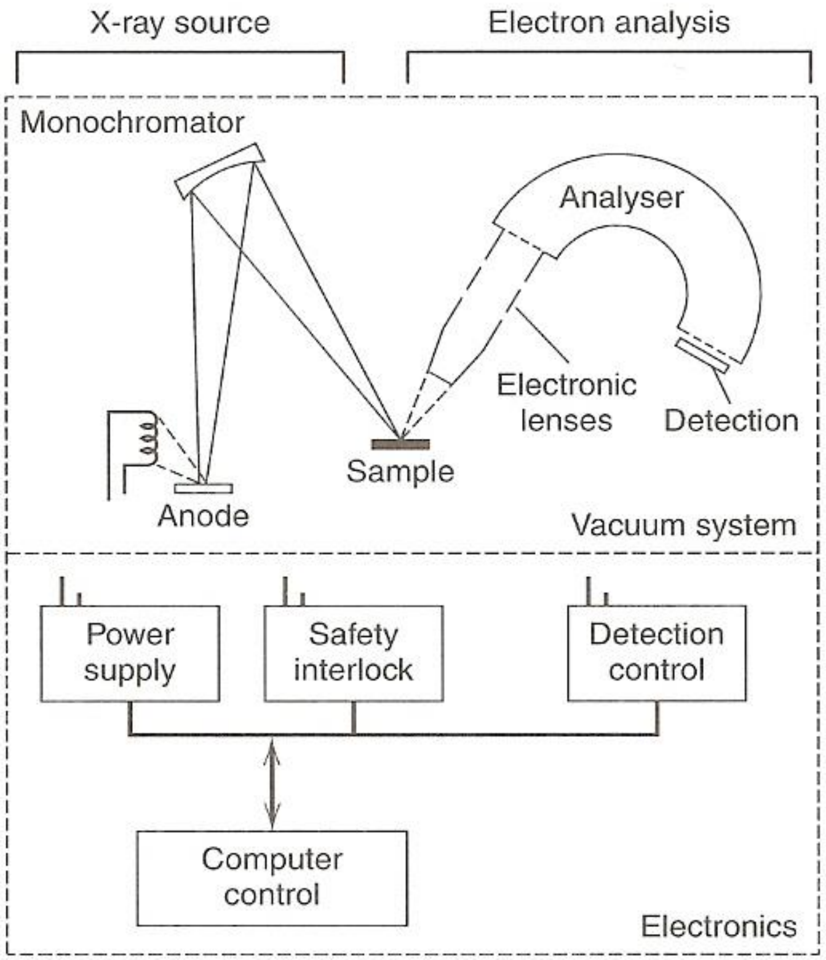
UHV-electrochemistry



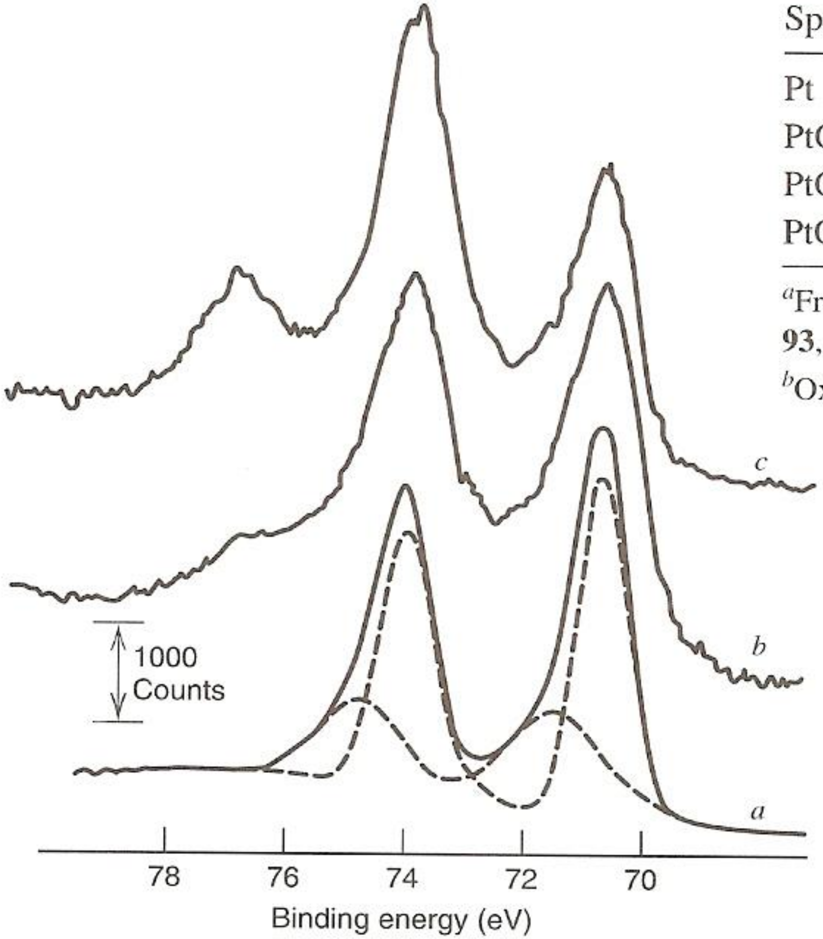
X-ray photoelectron spectroscopy (XPS, or ESCA)

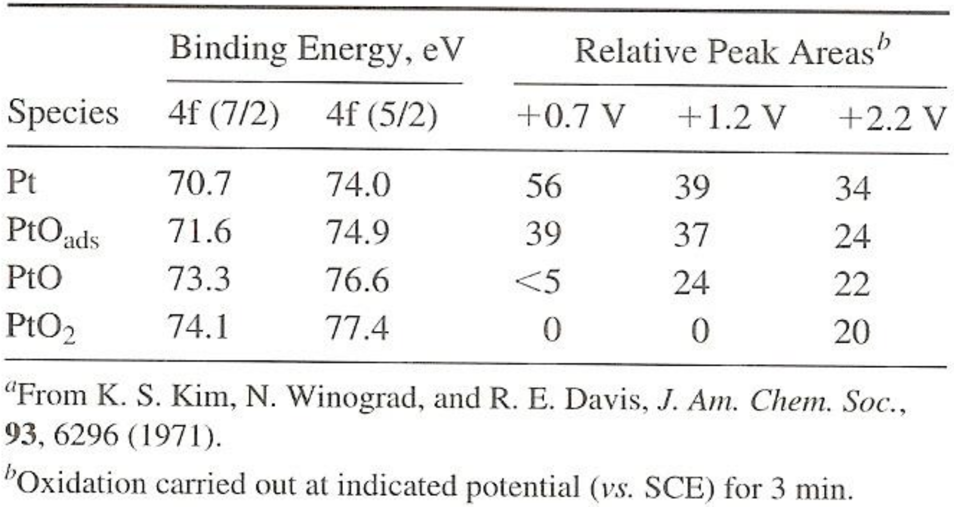


Schematic diagram of XPS



XPS for Pt 4f levels:



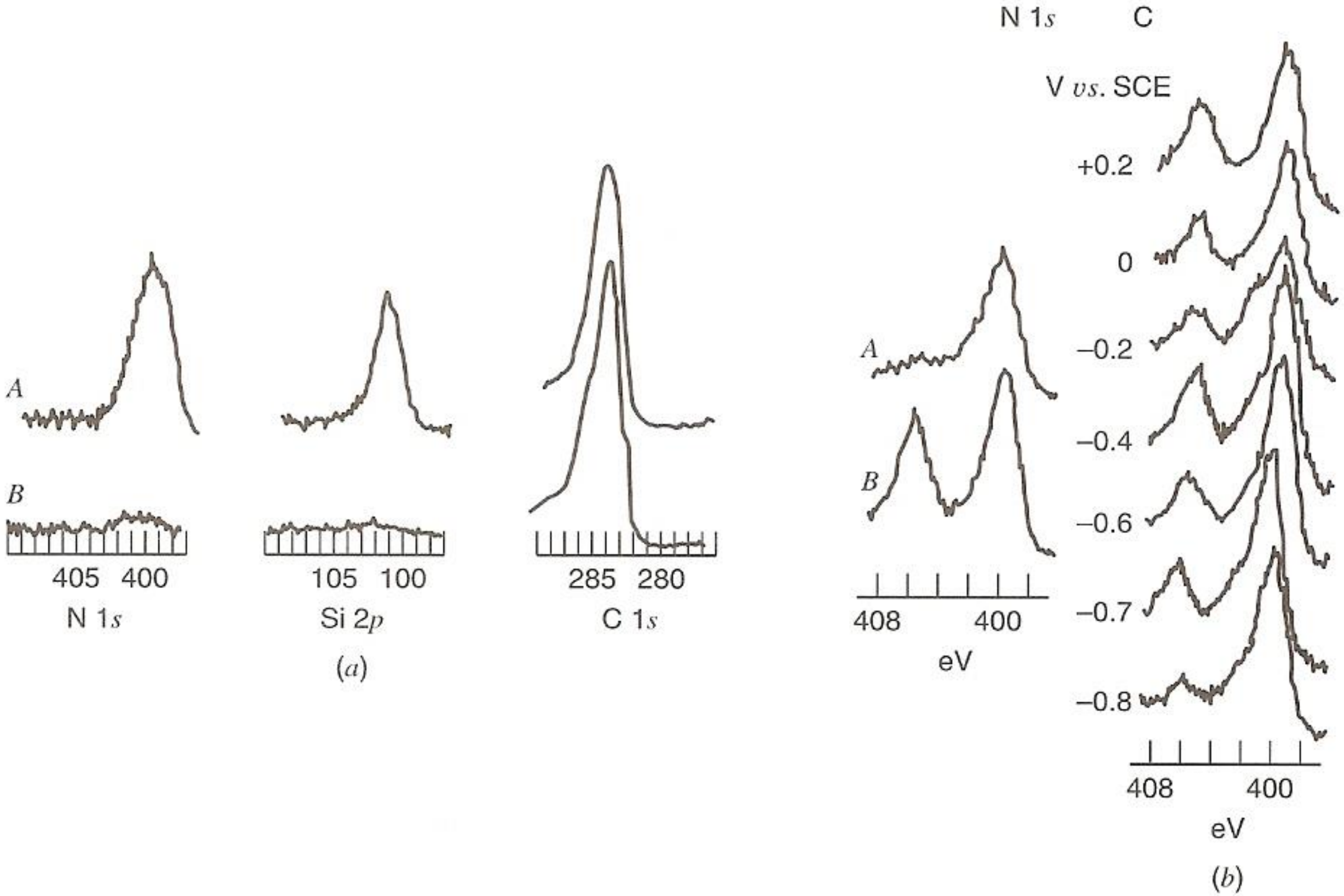


Species	Binding Energy, eV		Relative Peak Areas[b]		
	4f (7/2)	4f (5/2)	+0.7 V	+1.2 V	+2.2 V
Pt	70.7	74.0	56	39	34
PtO_{ads}	71.6	74.9	39	37	24
PtO	73.3	76.6	<5	24	22
PtO_2	74.1	77.4	0	0	20

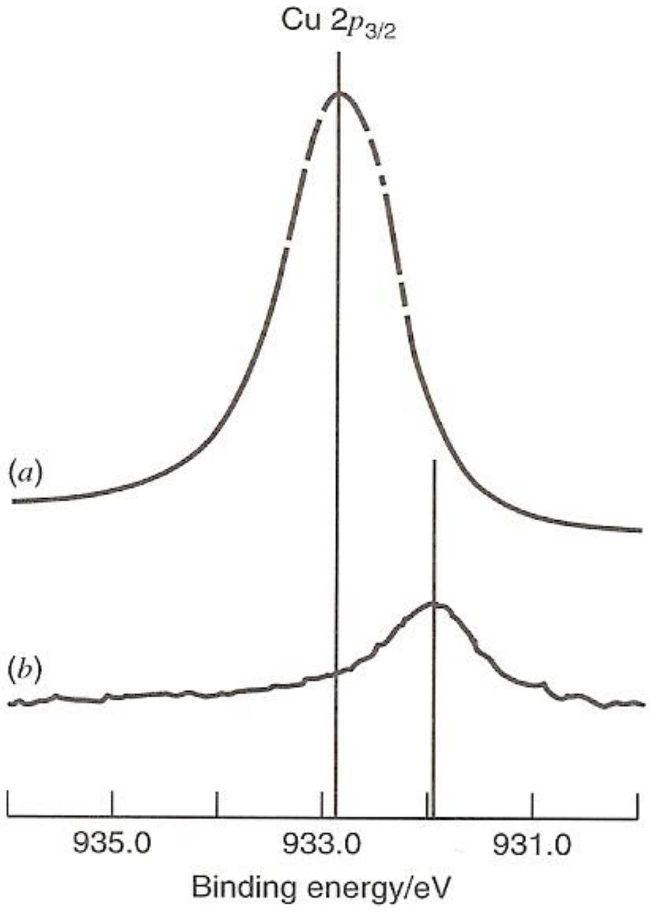
[a] From K. S. Kim, N. Winograd, and R. E. Davis, *J. Am. Chem. Soc.*, **93**, 6296 (1971).

[b] Oxidation carried out at indicated potential (*vs.* SCE) for 3 min.

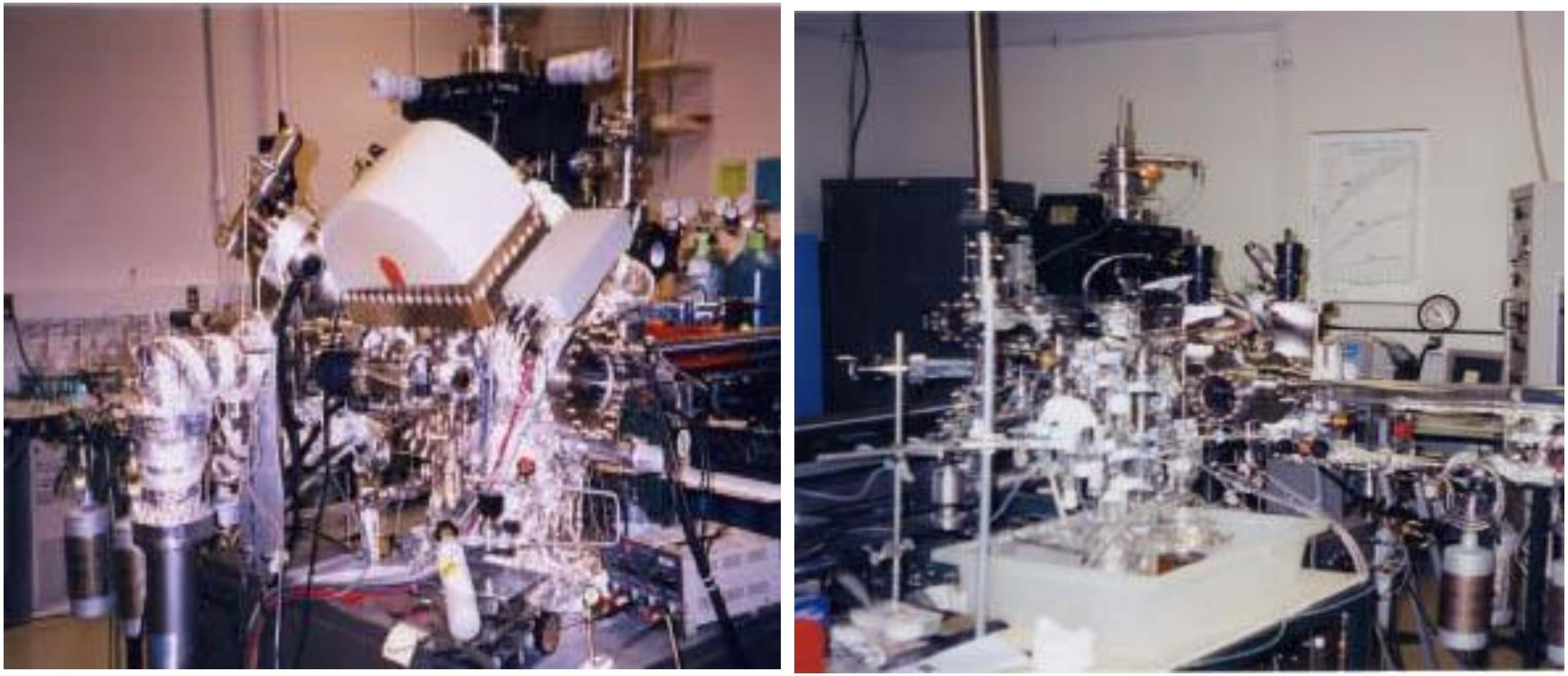
XPS for gassy carbon electrodes



XPS for copper electrodeposition
(a) Bulk Cu (b) Cu UPD



Electrochemical X-ray Photoelectron Spectroscopy



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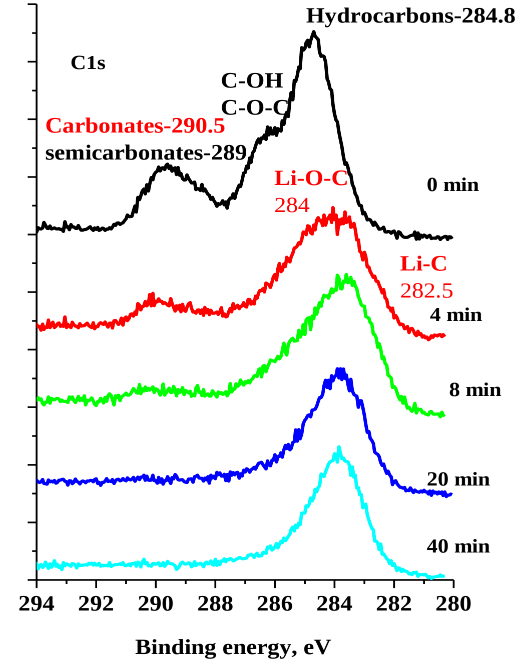
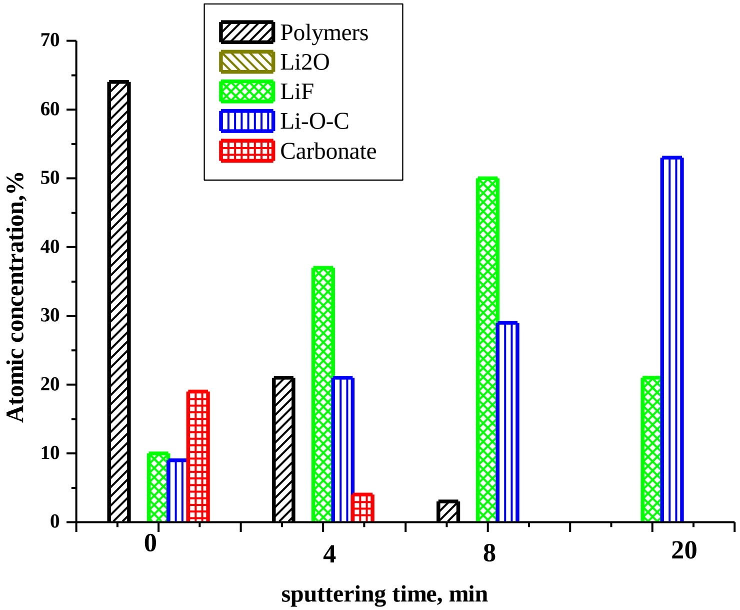
Electrochemical XPS (SNU)

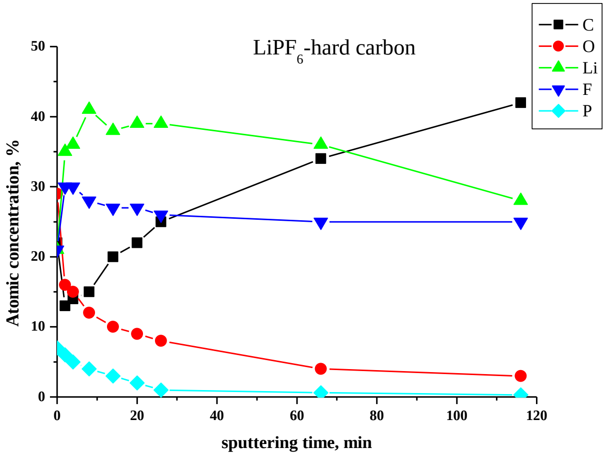
UHV-XPS **Glove Box**

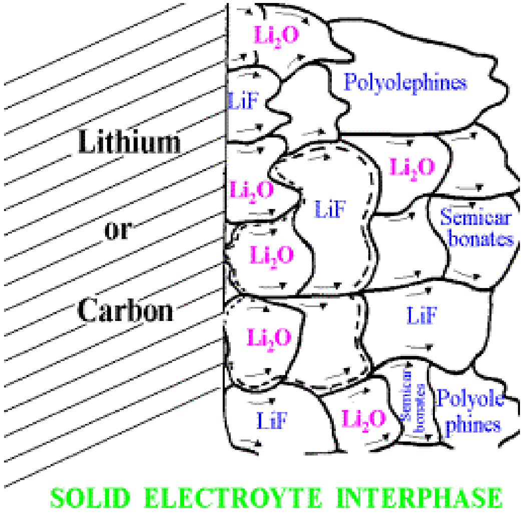
Ex-situ **Analysis without Contamination**

Electrochemical XPS



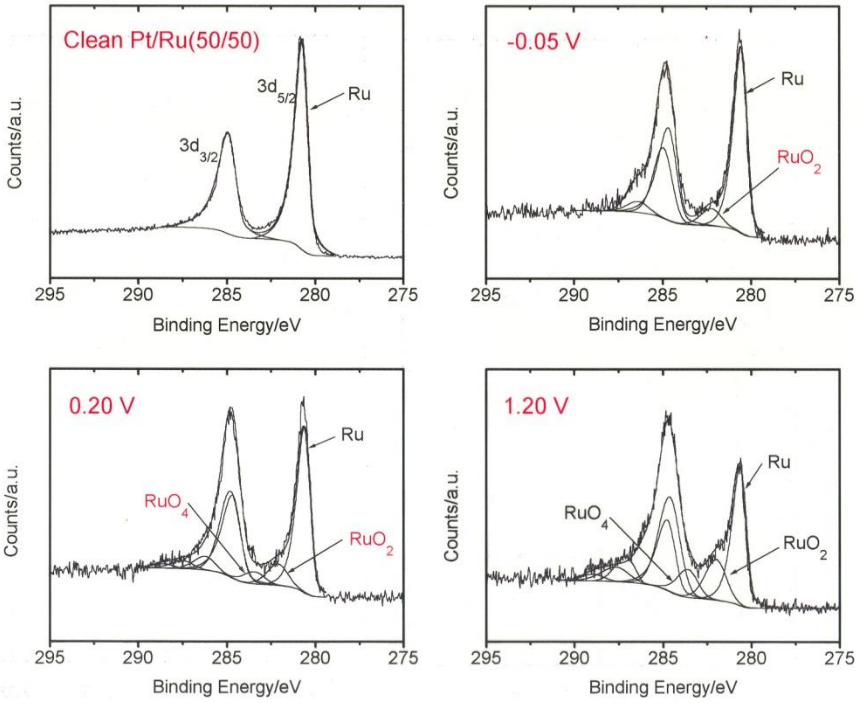




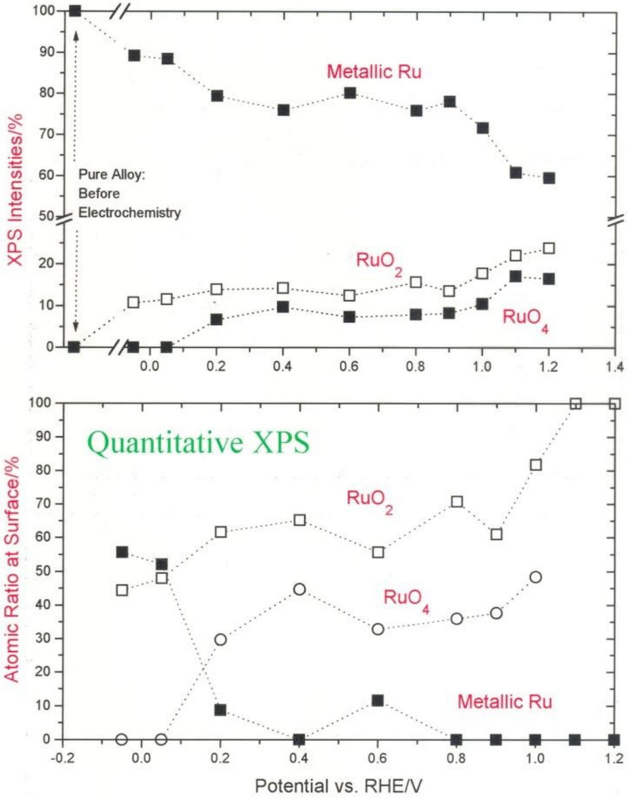


Peled (2003)

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

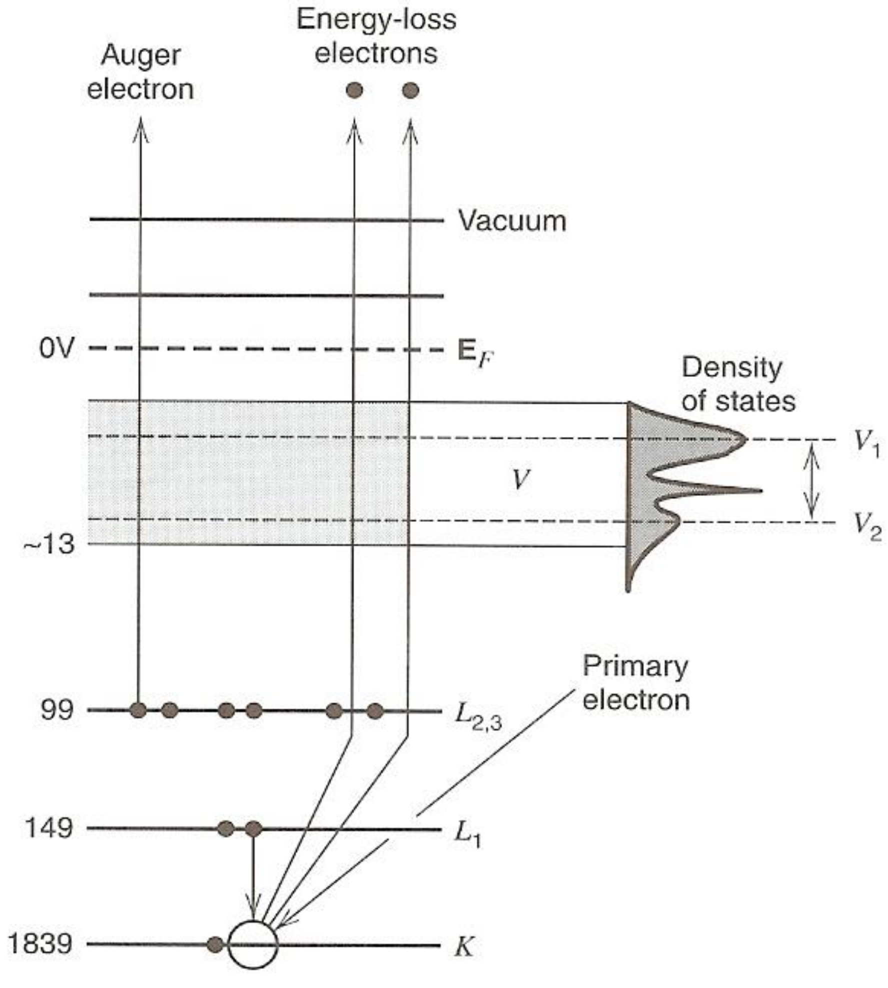


Relative Amount of Ru Species

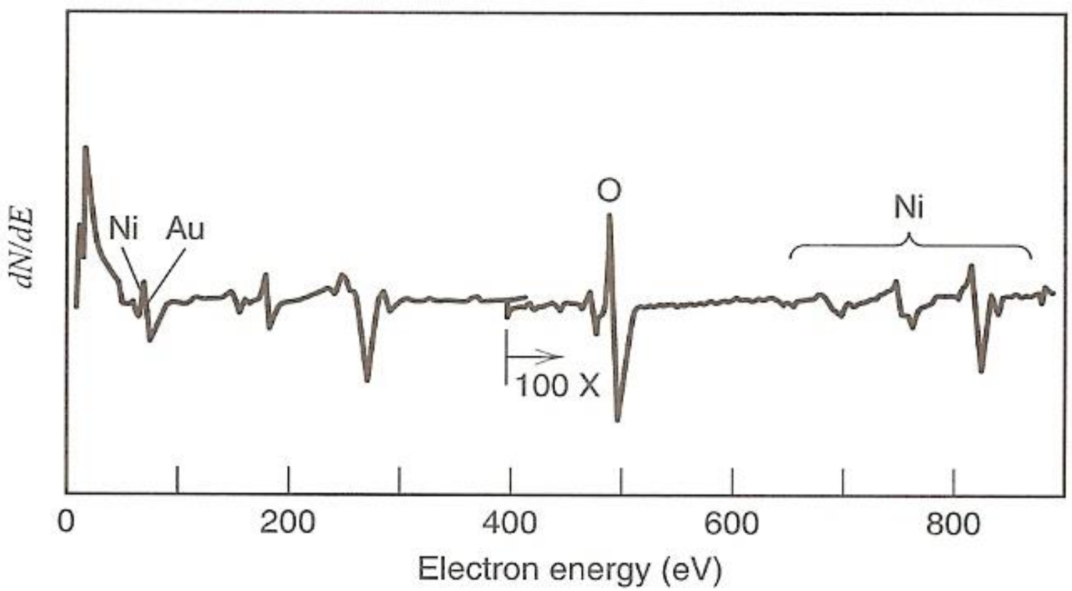


PtRu during Electrochemistry

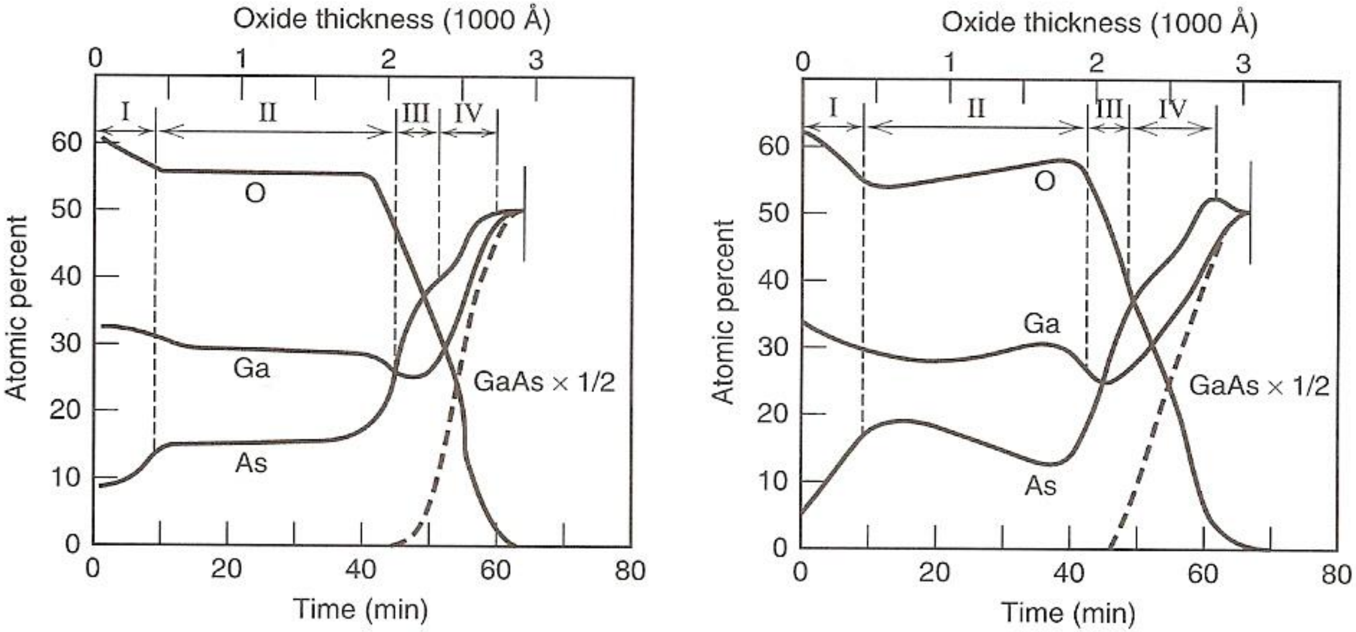
Auger electron spectroscopy



Ni oxide on Au

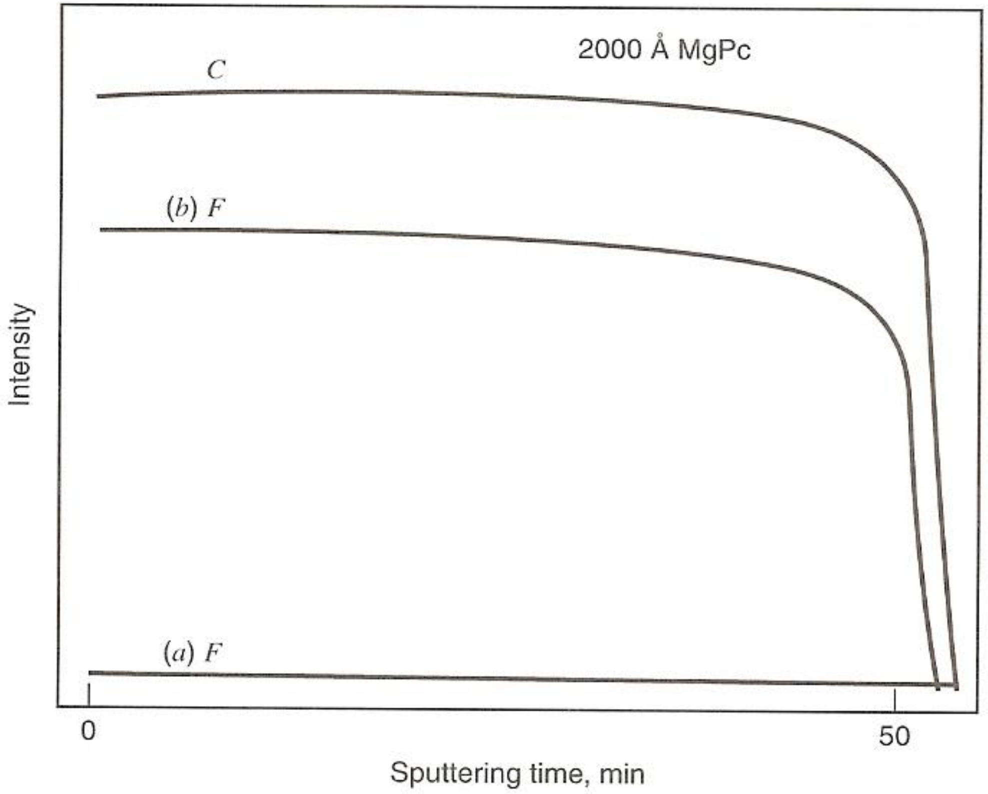


AES Depth profiles for GaAs

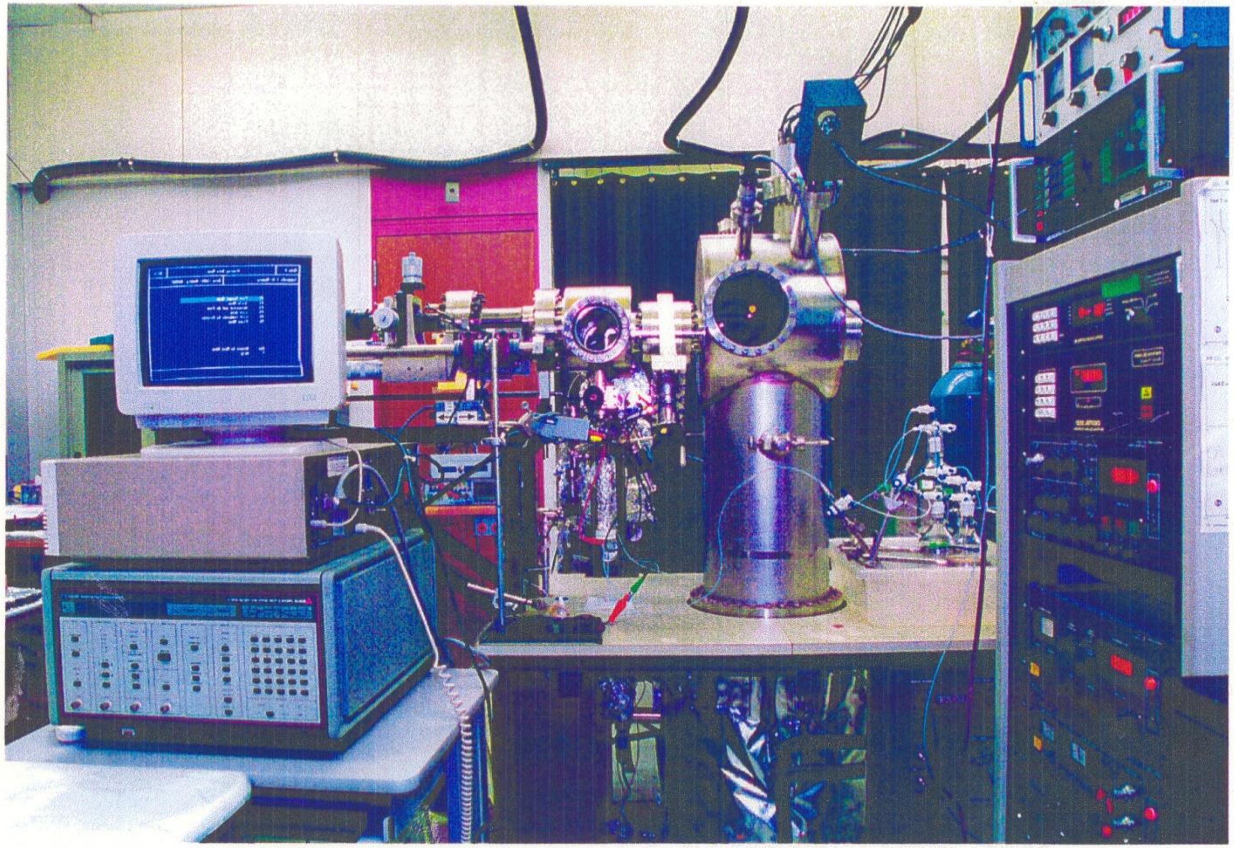


(a) (b)

AES depth profiles for MgPc



Electrochemical Auger Electron Spectroscopy



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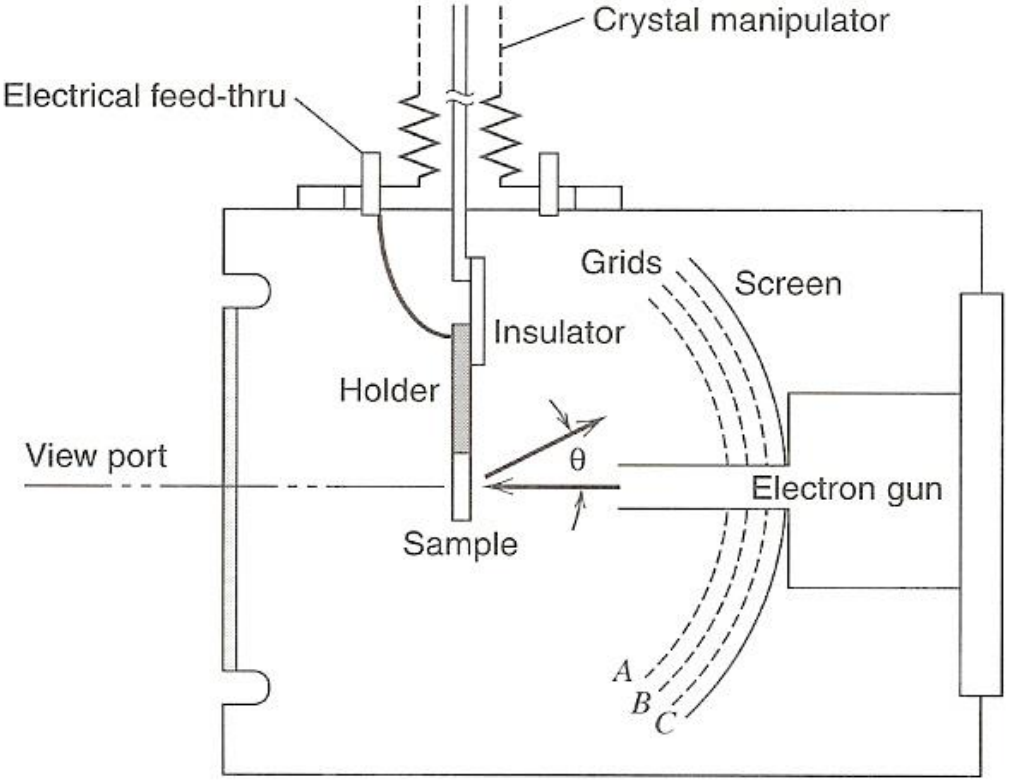
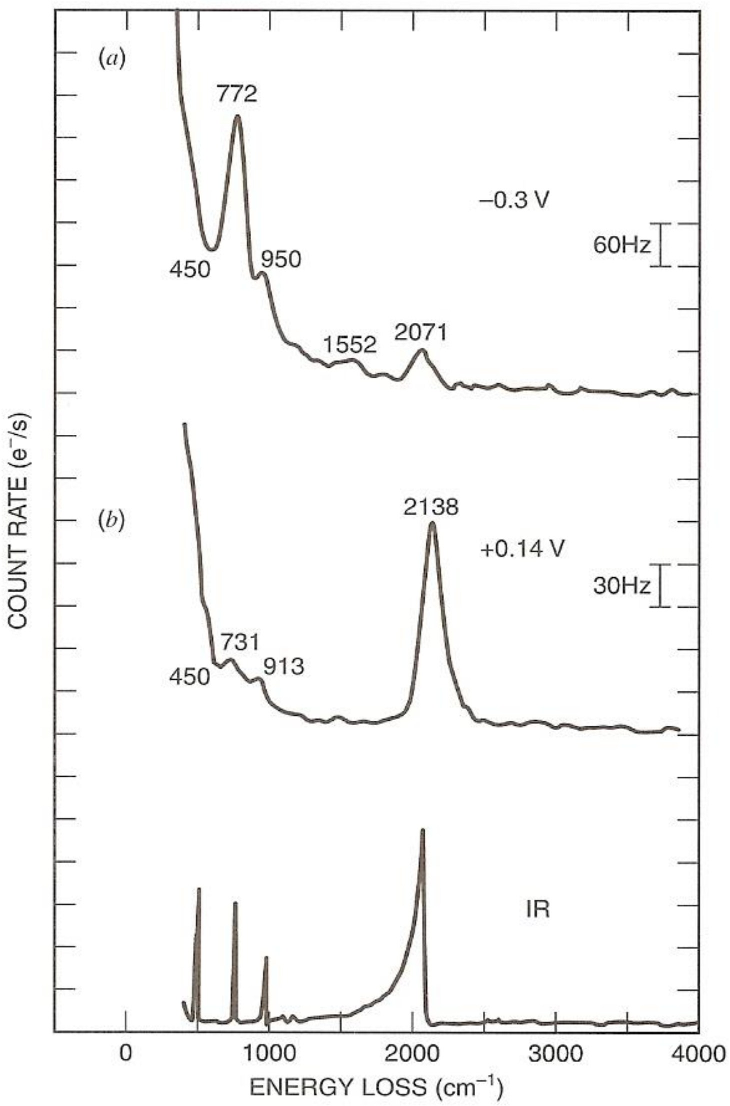
Low-energy electron diffraction



High resolution electron energy loss spectroscopy

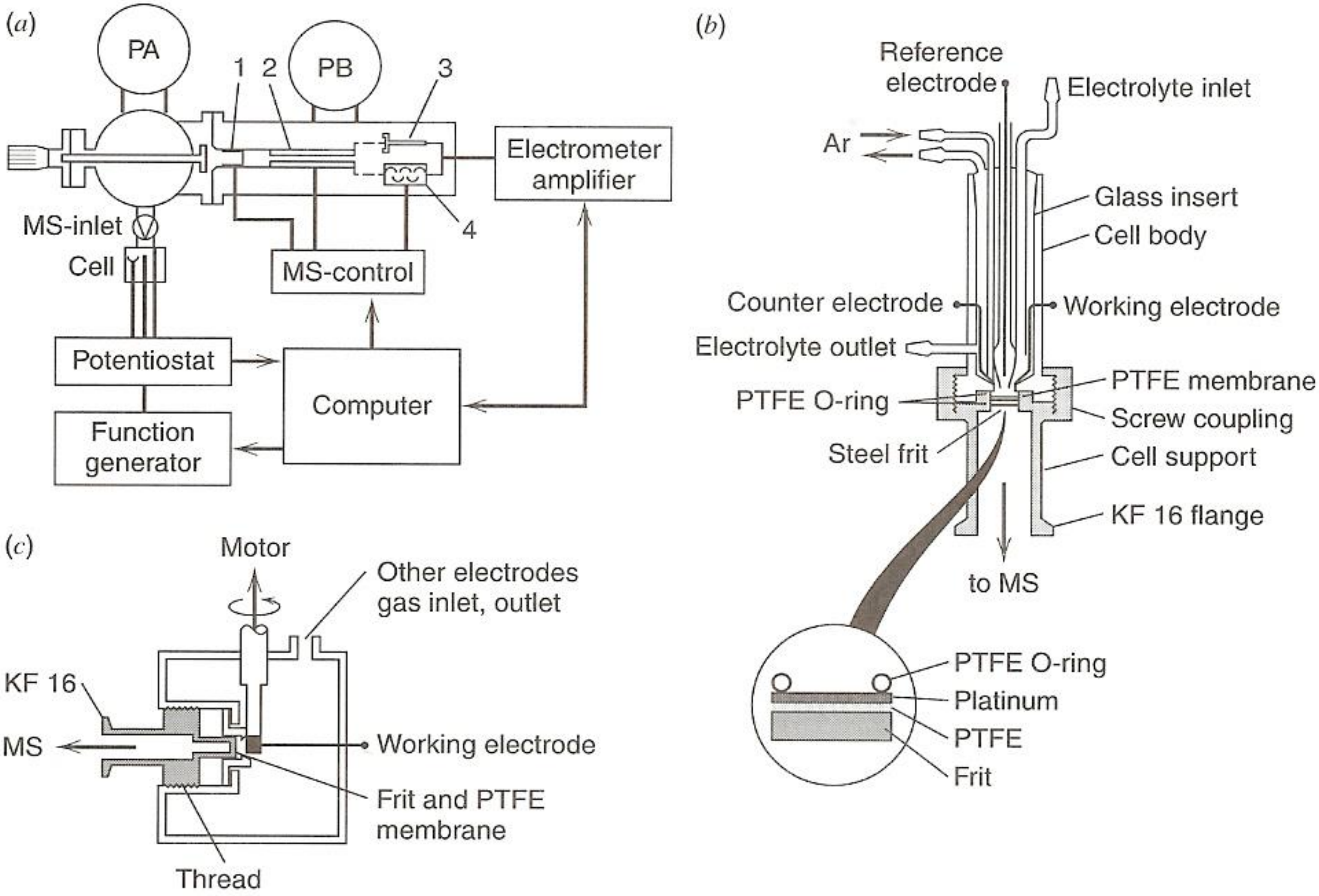


SCN$^-$ on Ag(111)

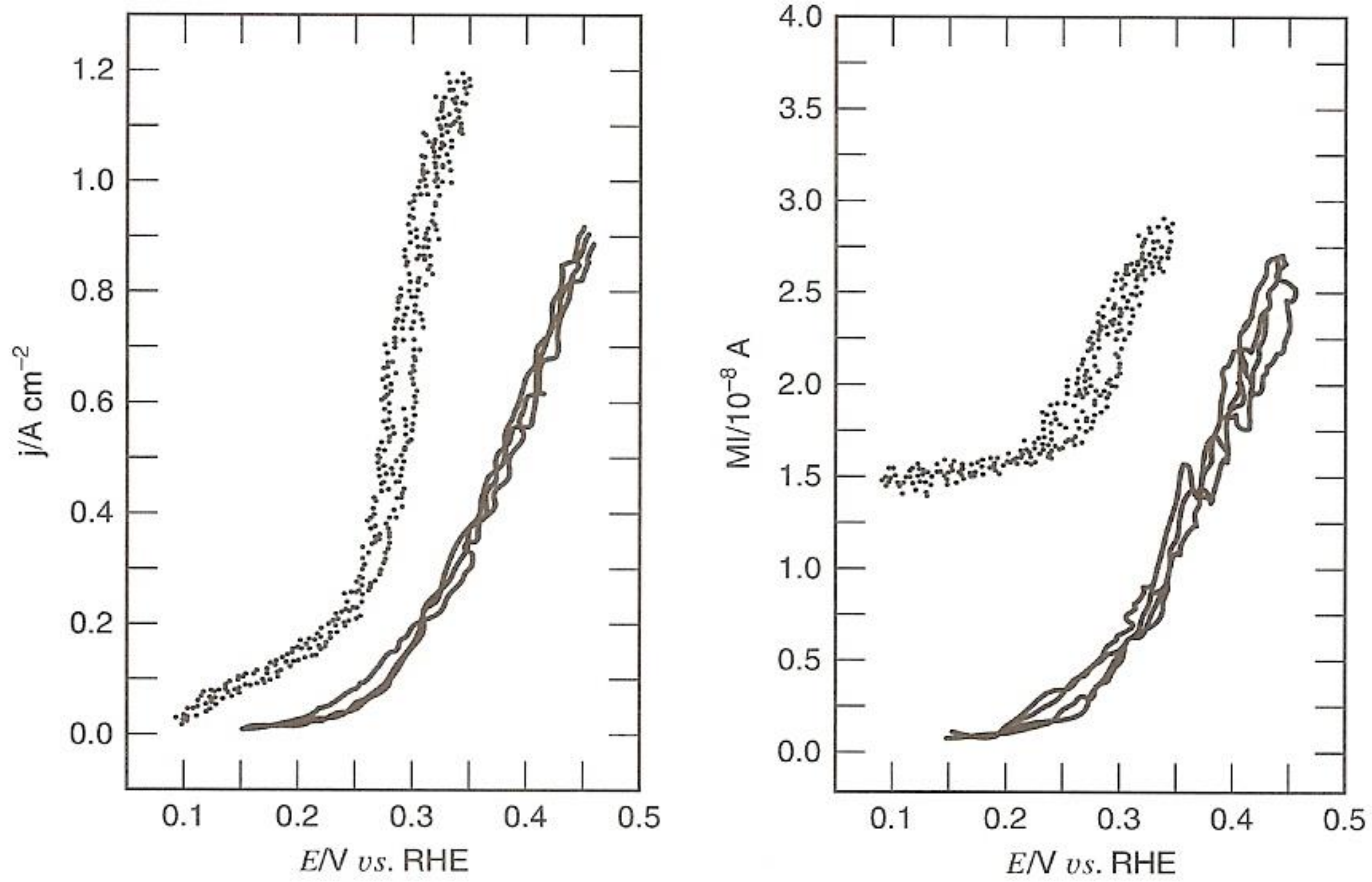
(a) -0.3 V
(b) +0.14 V

Mass spectrometry

Differential electrochemical mass spectrometry (DEMS)



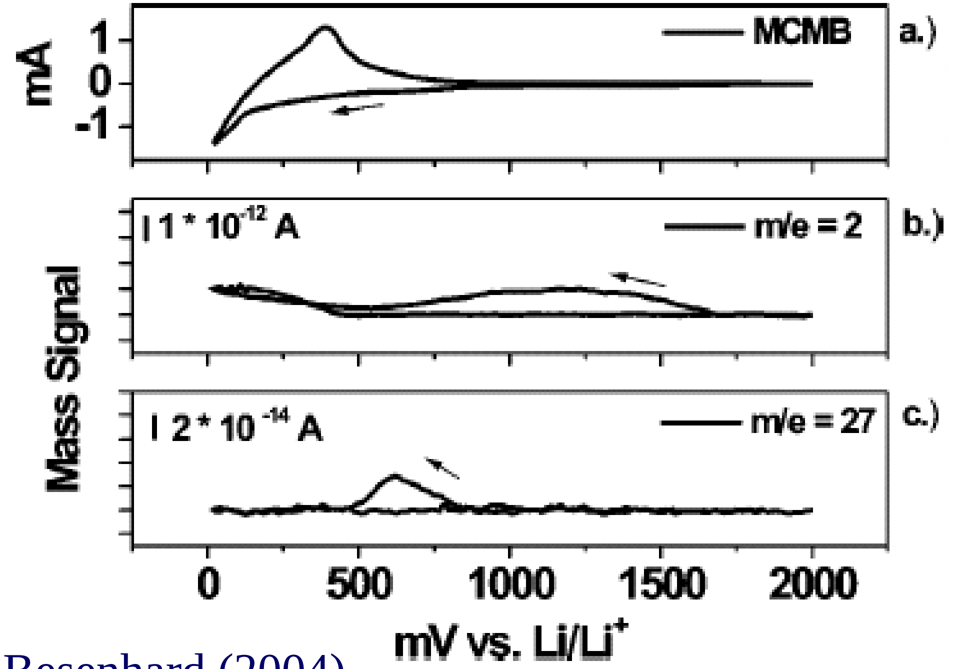
DEMS: fuel cell catalysts for methanol(solid) & formic acid(dotted) oxidation



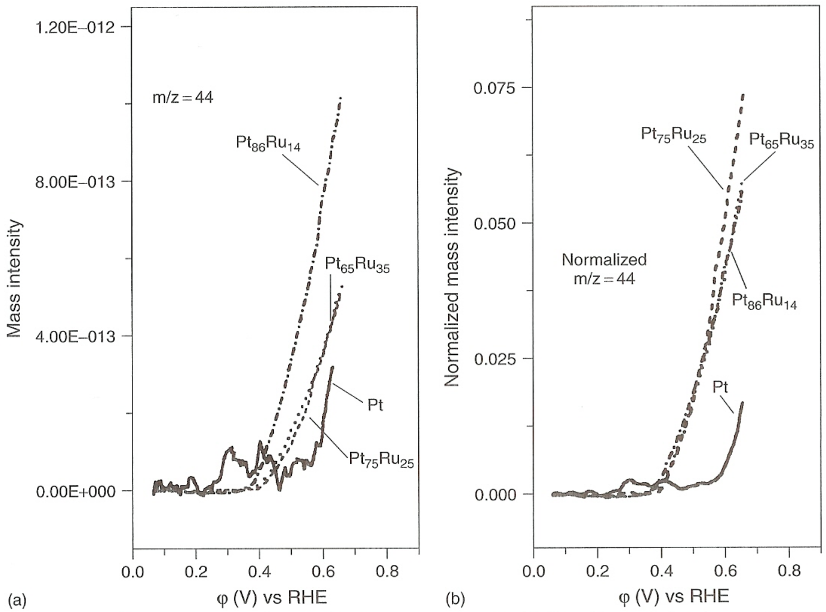
(*a*) Current density

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

- In situ DEMS (differential electrochemical mass spectroscopy)

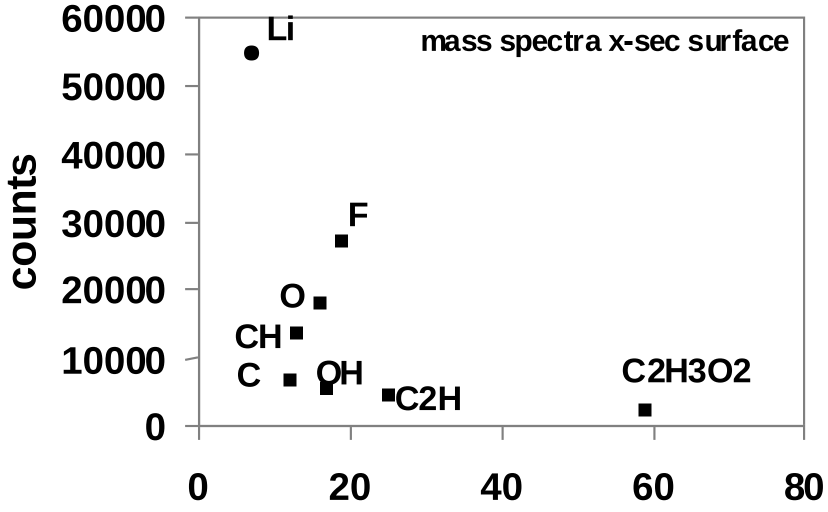


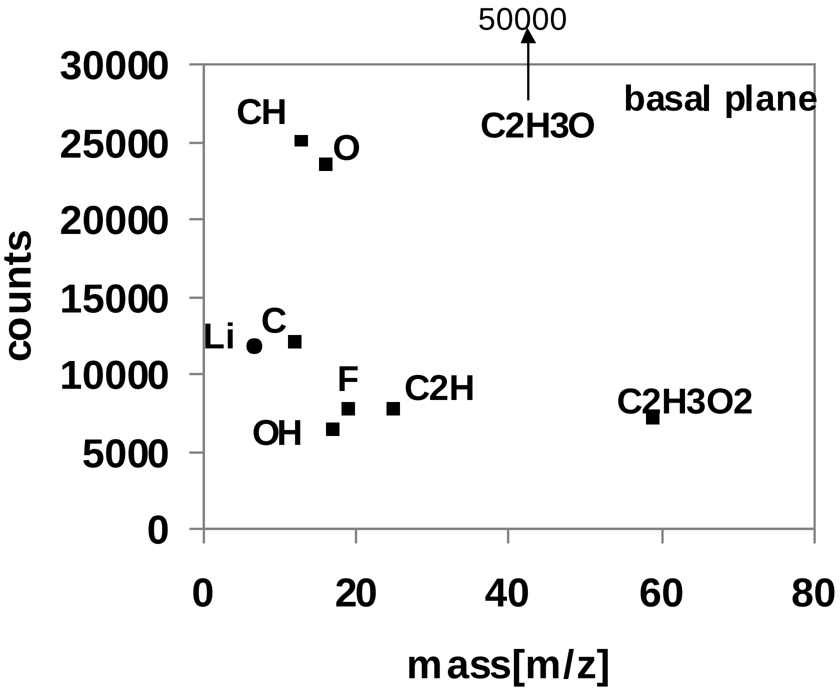
Besenhard (2004)

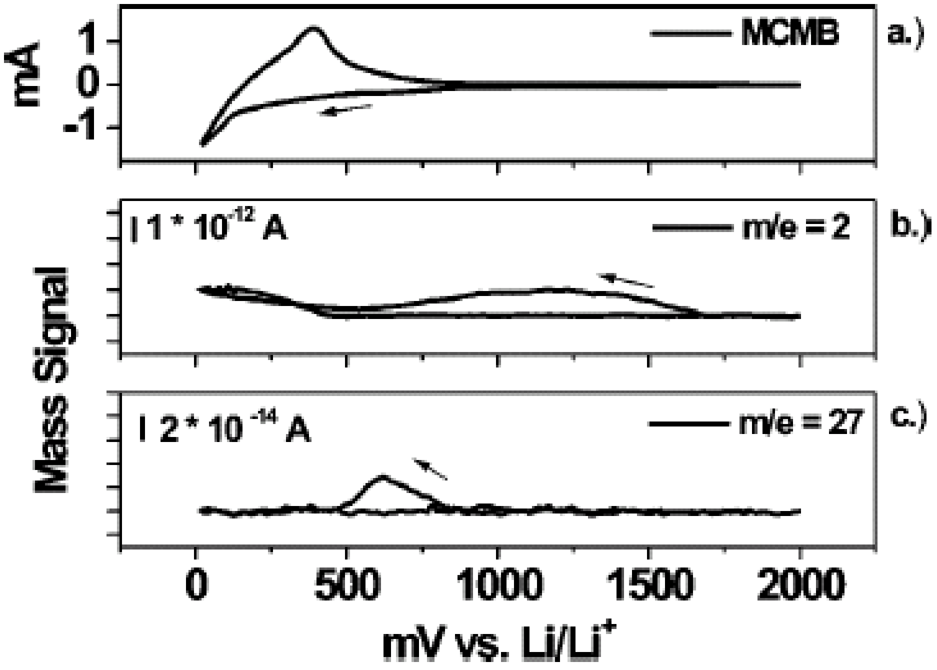


MeOH oxidation

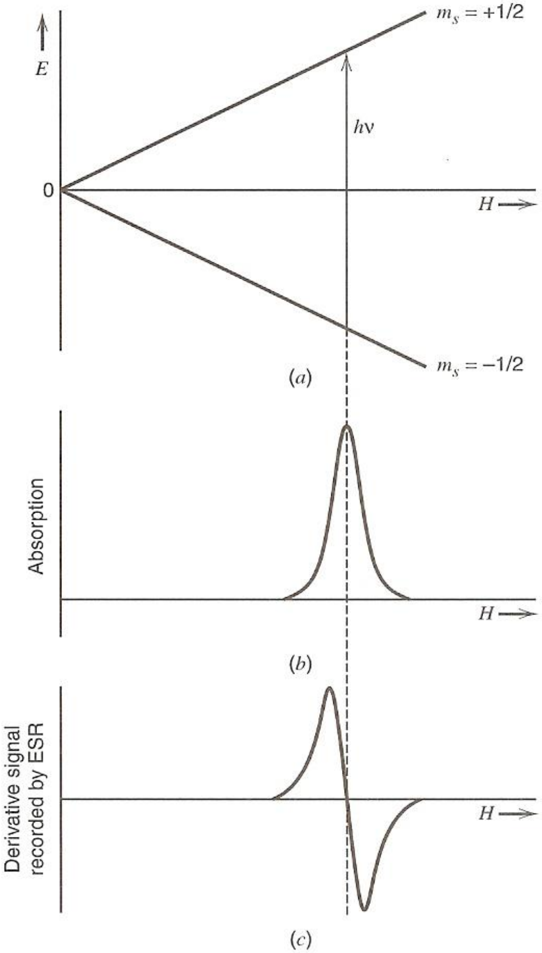
in-situ DEMS (differential electrochemical mass spectroscopy)







Magnetic resonance methods
Electron spin resonance & NMR



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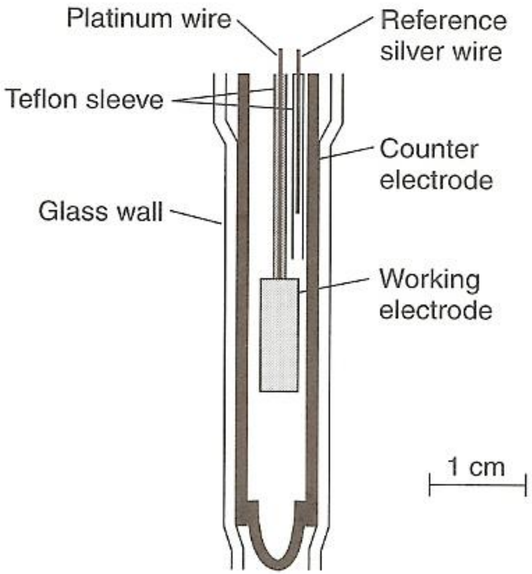
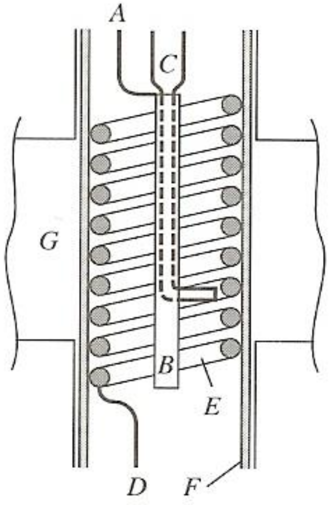
[4] First edition, pp. 615–621.

Electrochemical ESR

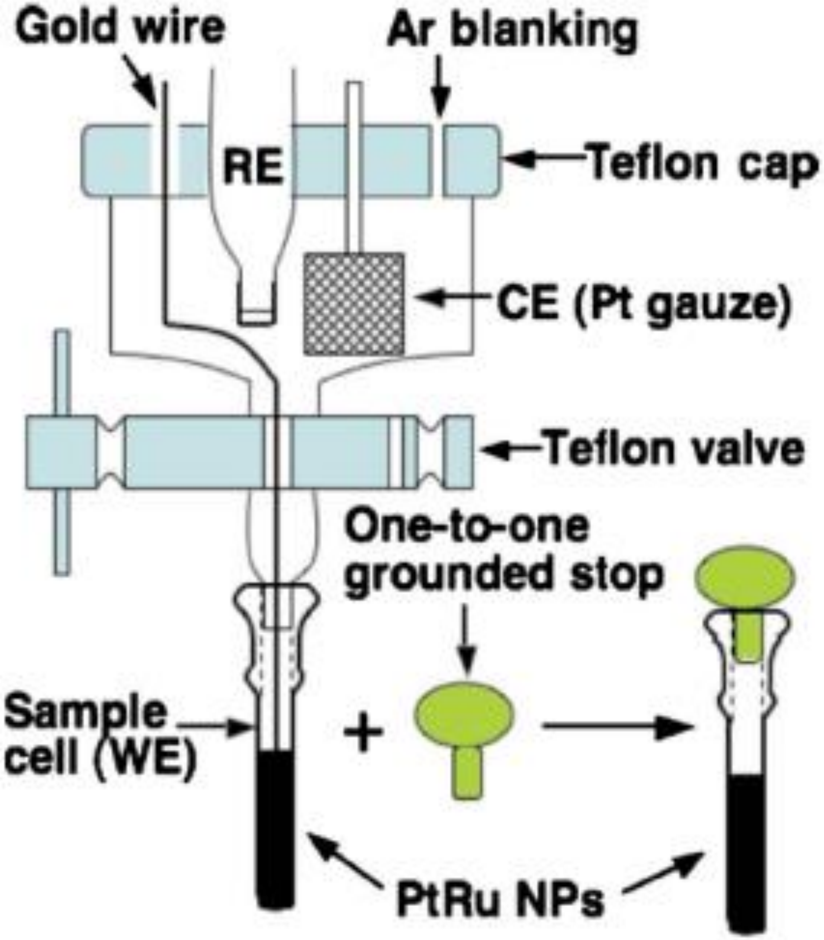


(*a*)



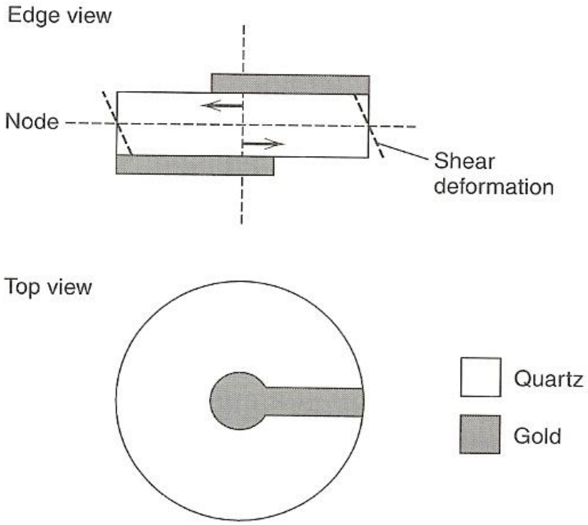
(*b*)

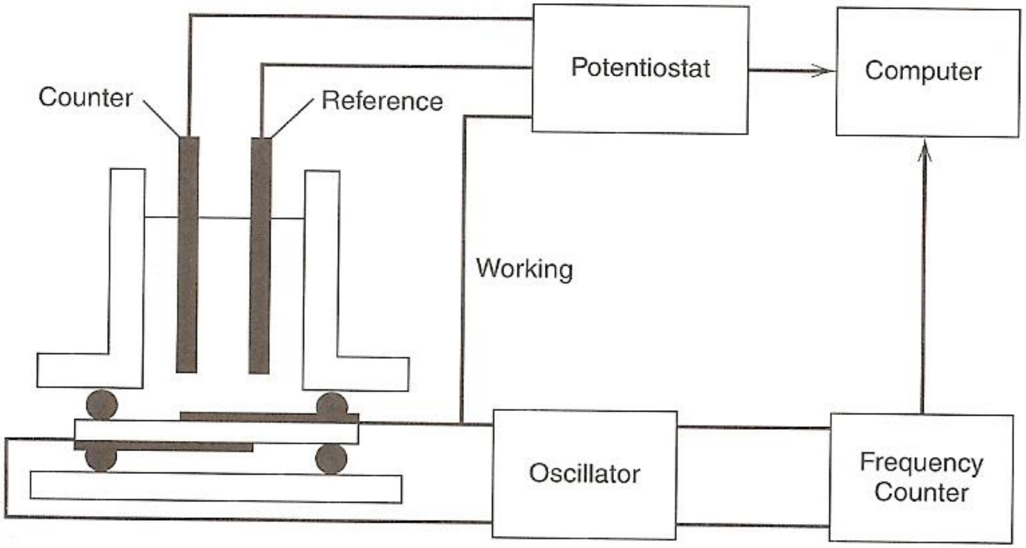
in-situ NMR



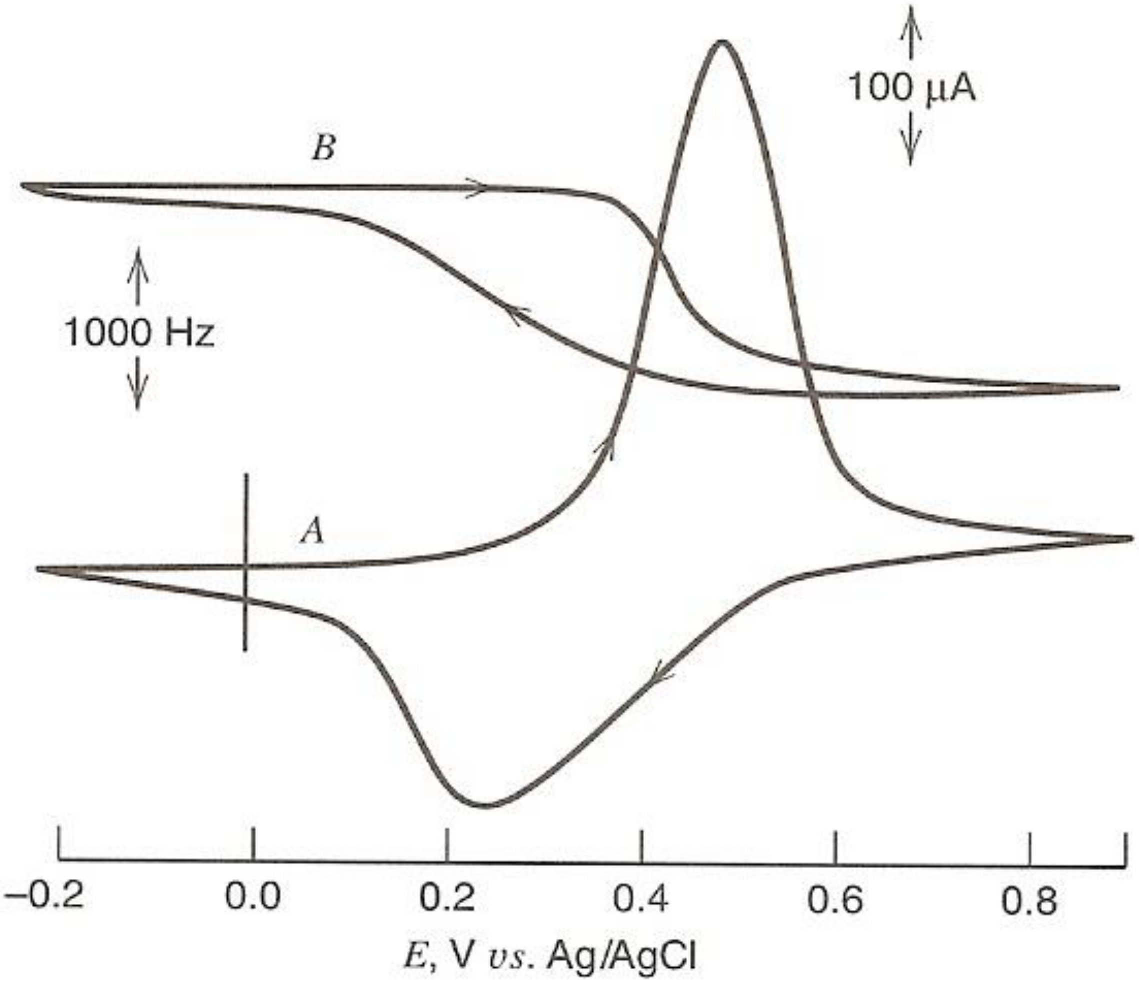
(with Prof. YuYe Tong (Georgetown University))

Quartz crystal microbalance





QCM: PVF on Au



X-ray methods

Synchrotron

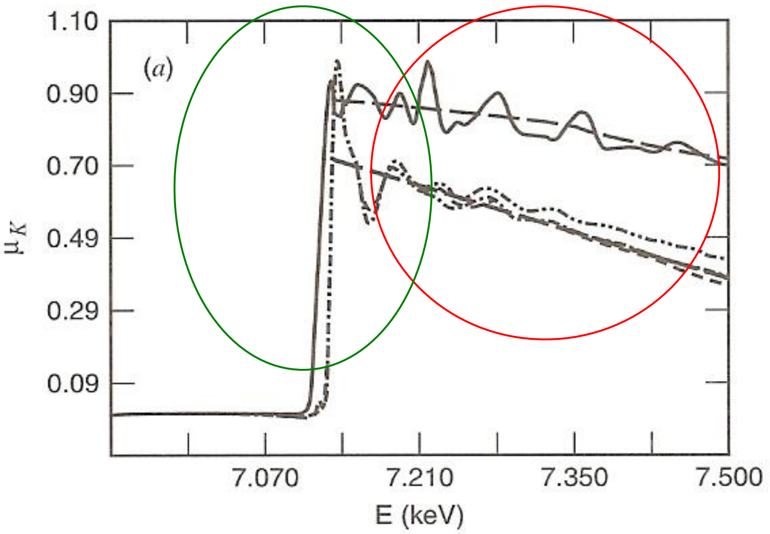
X-ray absorption spectroscopy

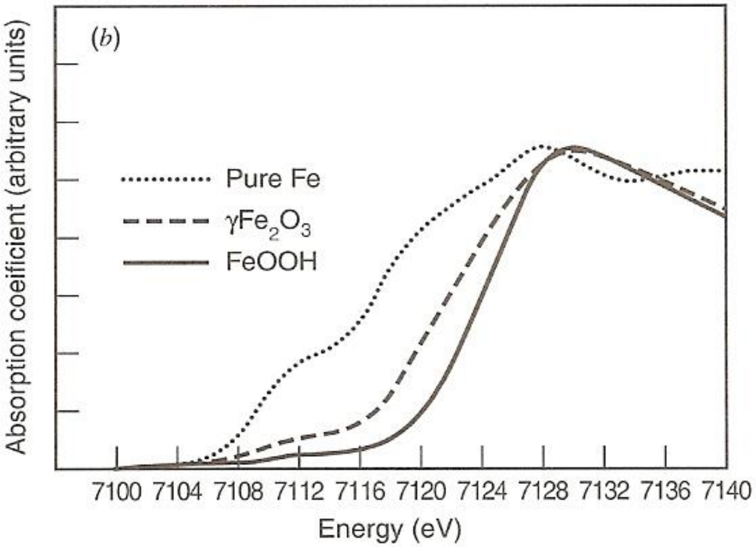
Absorption edge (energy that is just needed to eject a particular core electron, e.g., 1s e^- (K edge), $2p_{3/2}$ e^- (L_3 edge)

Fe & Fe oxides
K-edge: 7.112 keV

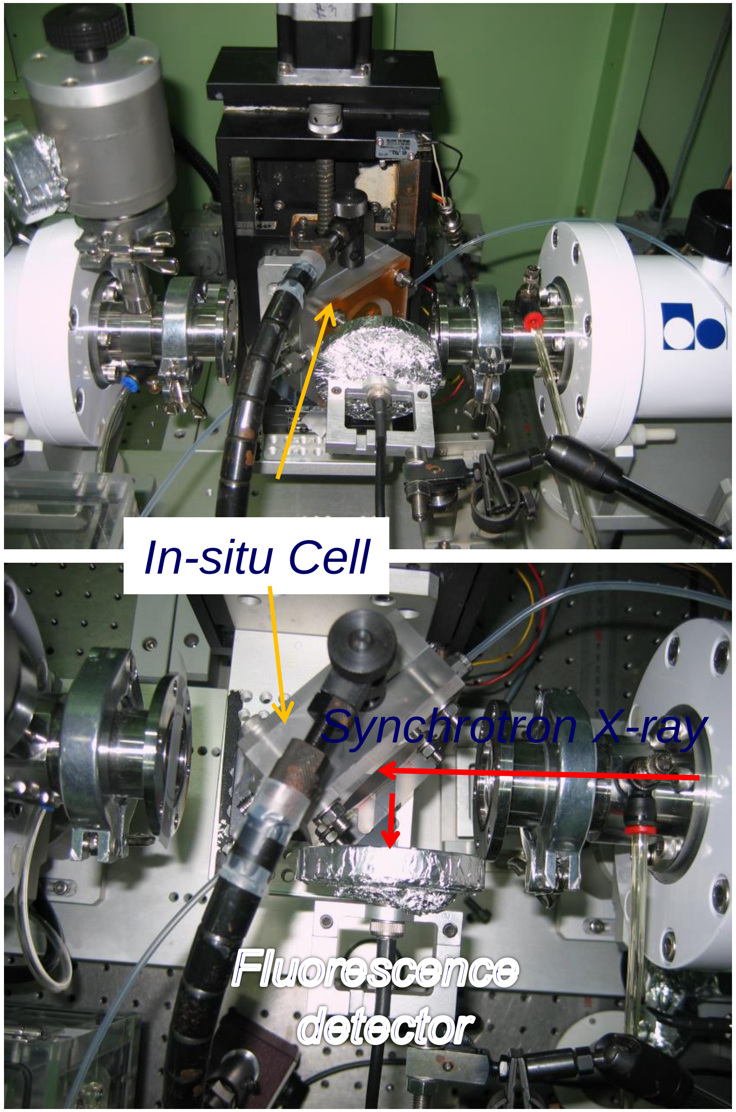
Within 10-40 eV: X-ray absorption near-edge structure (**XANES**) (or near-edge absorption fine structure (**NEXAFS**))
→ oxidation state & ligand envirionment

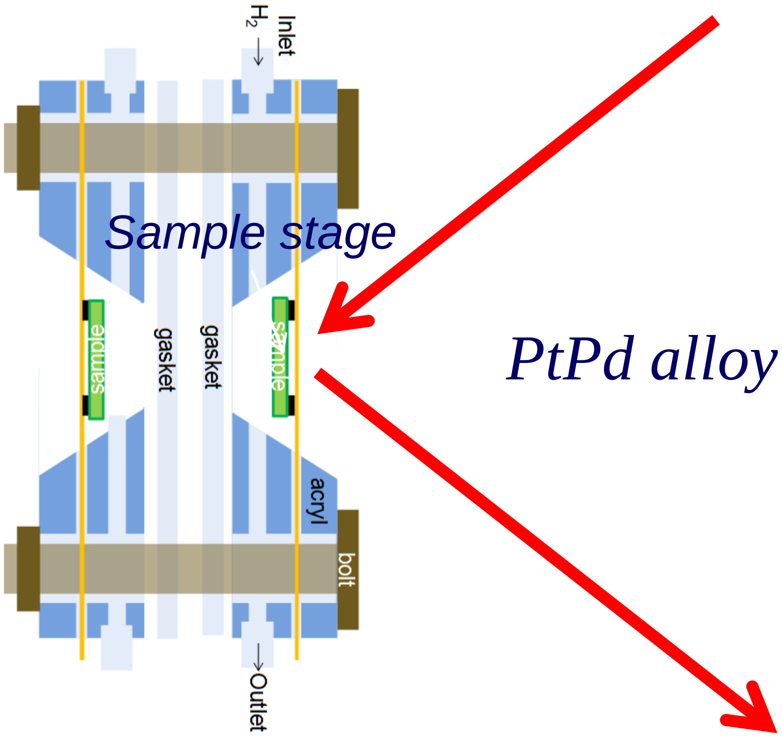
About 50 keV: extended X-ray absorption Fine structure (**EXAFS**)
→ distance & arrangement of atoms





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



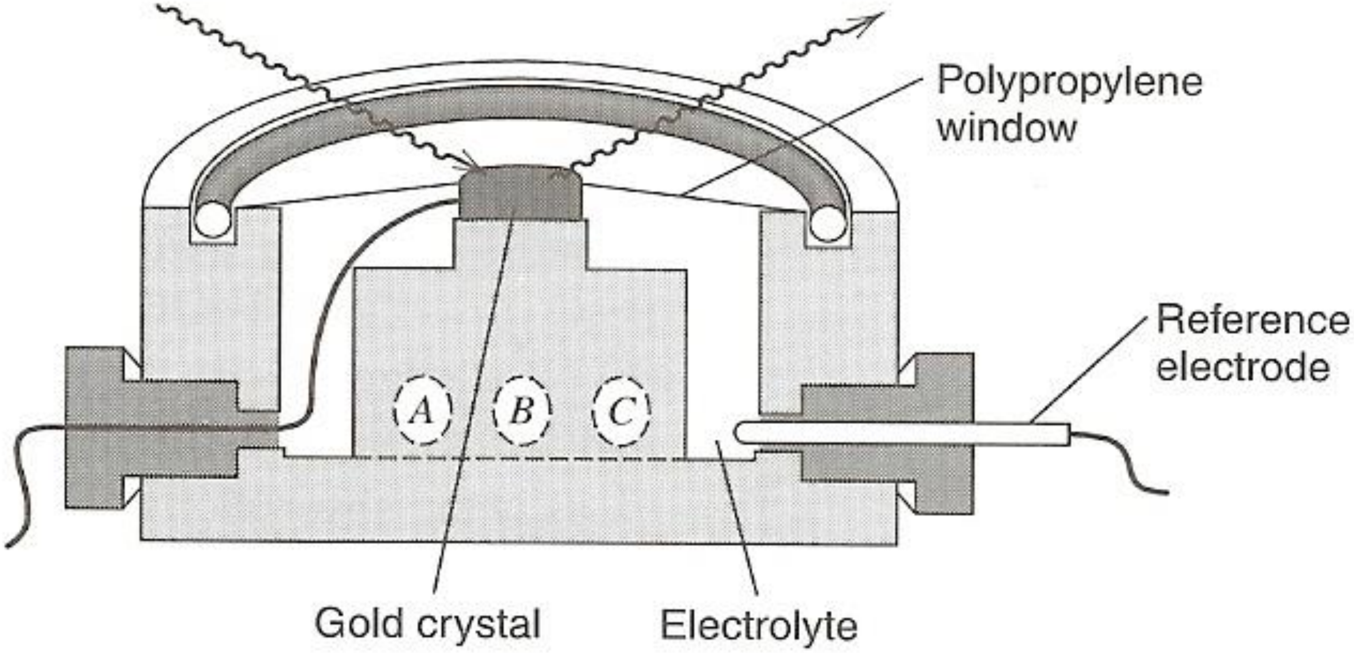


Synchrotron X-ray

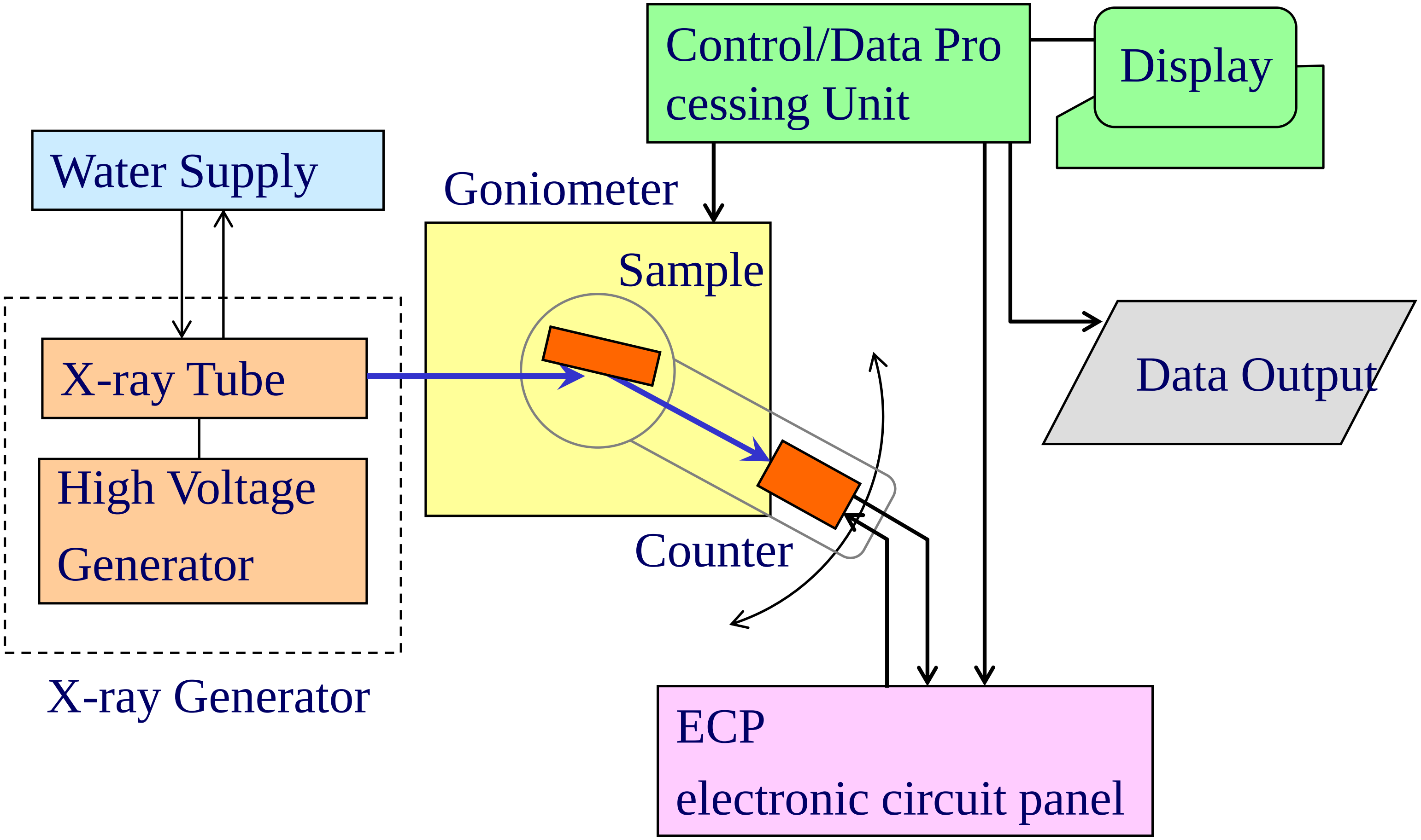
PtPd alloy

Fluorescence detector

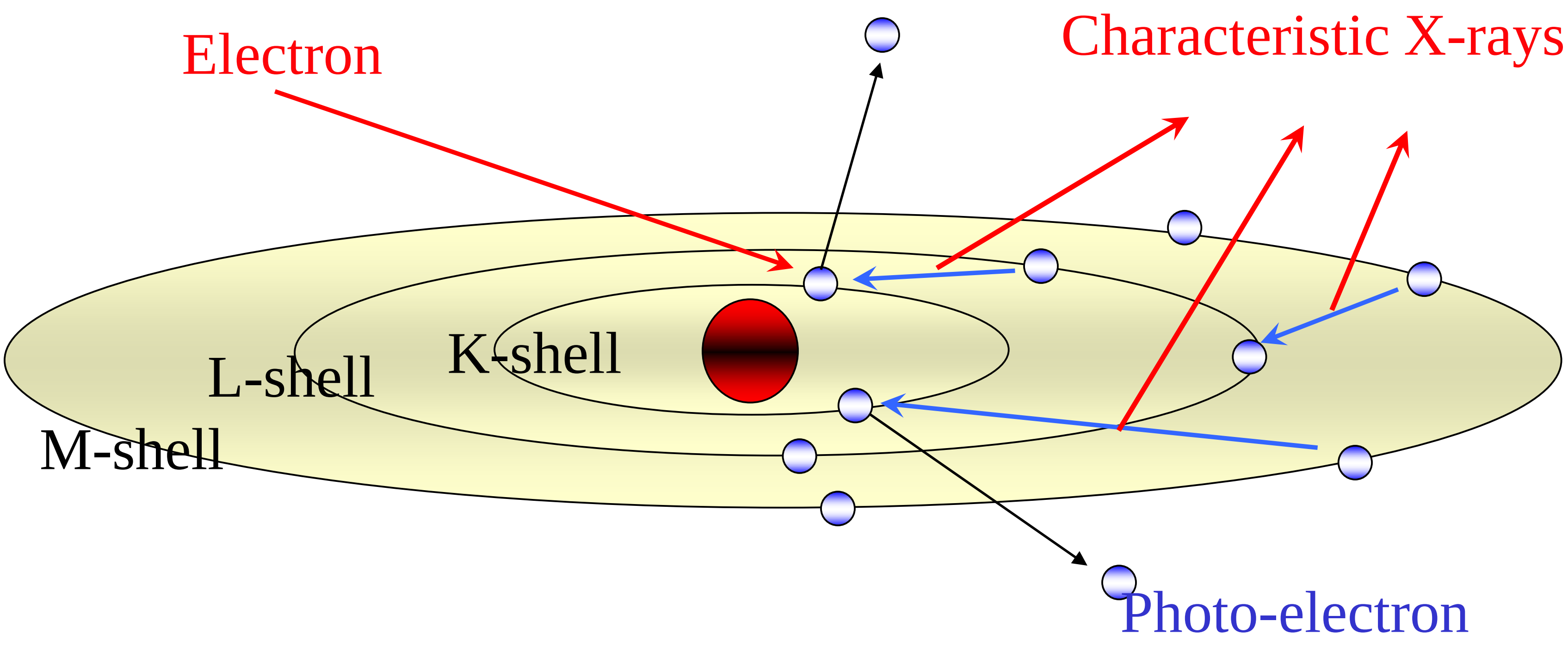
X-ray diffraction techniques



X-Ray Diffractometer



Characteristic X-ray



X-ray diffraction (Bragg's Law)

λ(wavelength)

Known

θ(diffration angle)

measured

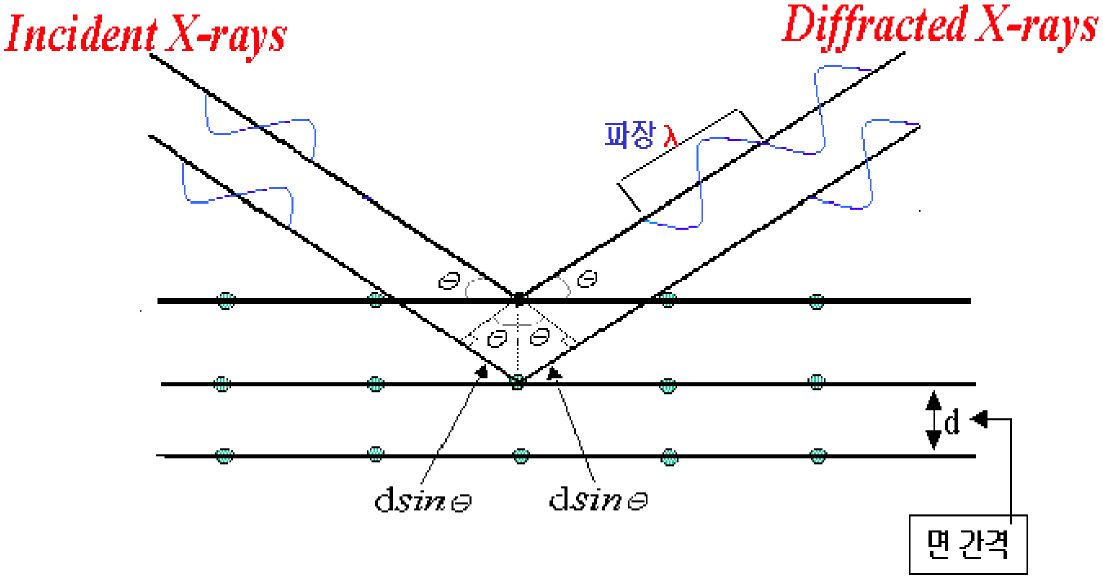
Diffraction condition

(Bragg's Law)

2dsinθ = n λ (n:1,2,3….)

d(→ lattice constant)

calculated



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

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

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

$$ACB' = n\lambda$$ Amplification

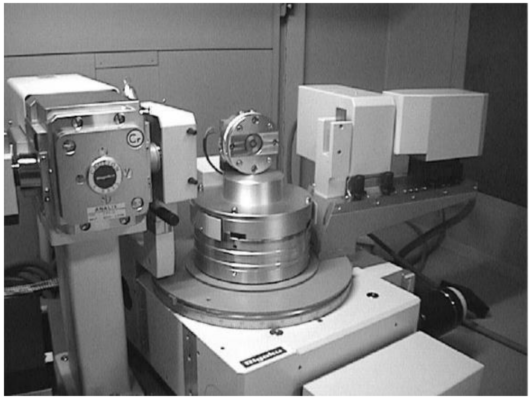
Rigaku - D/MAX 2500/PC (SNU)

Large enclosure type – Two goniometer

- 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

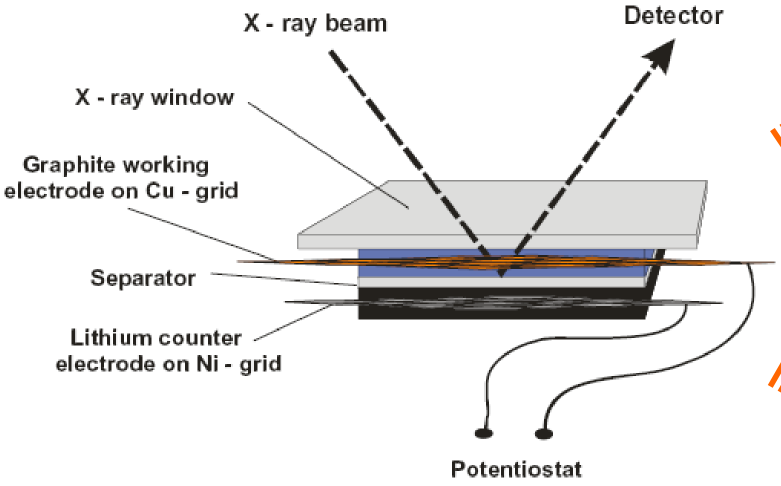
in situ XRD (SNU)

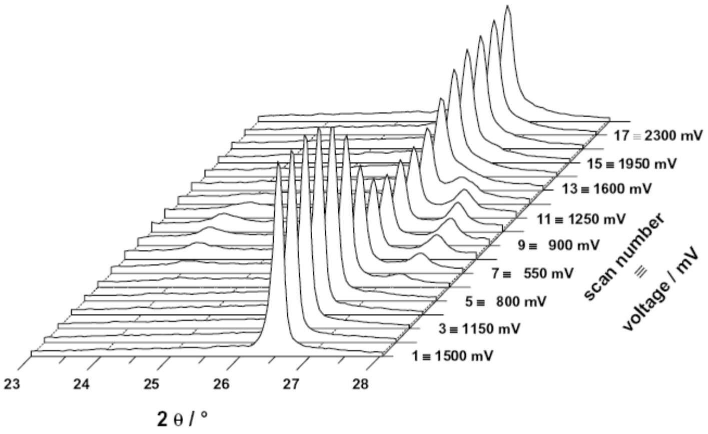
- powder X-Ray Diffractometer, D/MAX 2500/PC
- powder, thin film, in situ analysis



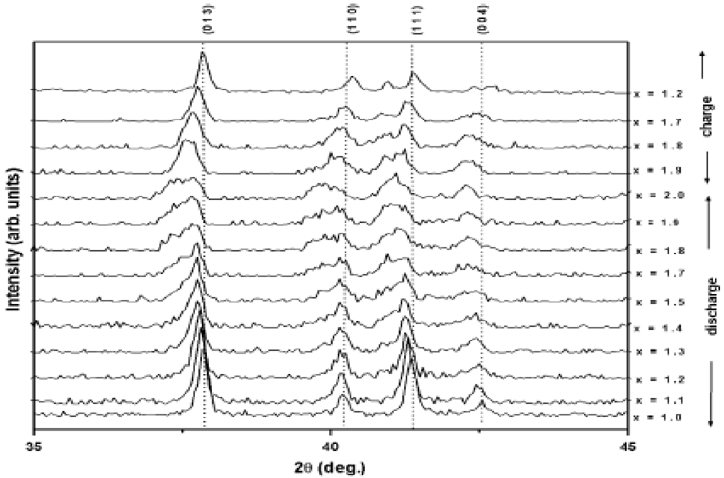
In situ cell

❑ Schematic of in situ XRD cell





Cascade of in situ XRD data vs. the scan number



In-situ XRD patterns of Li_xFeSnO_4 during initial lithium intercalation and deintercalation.