UHV Techniques

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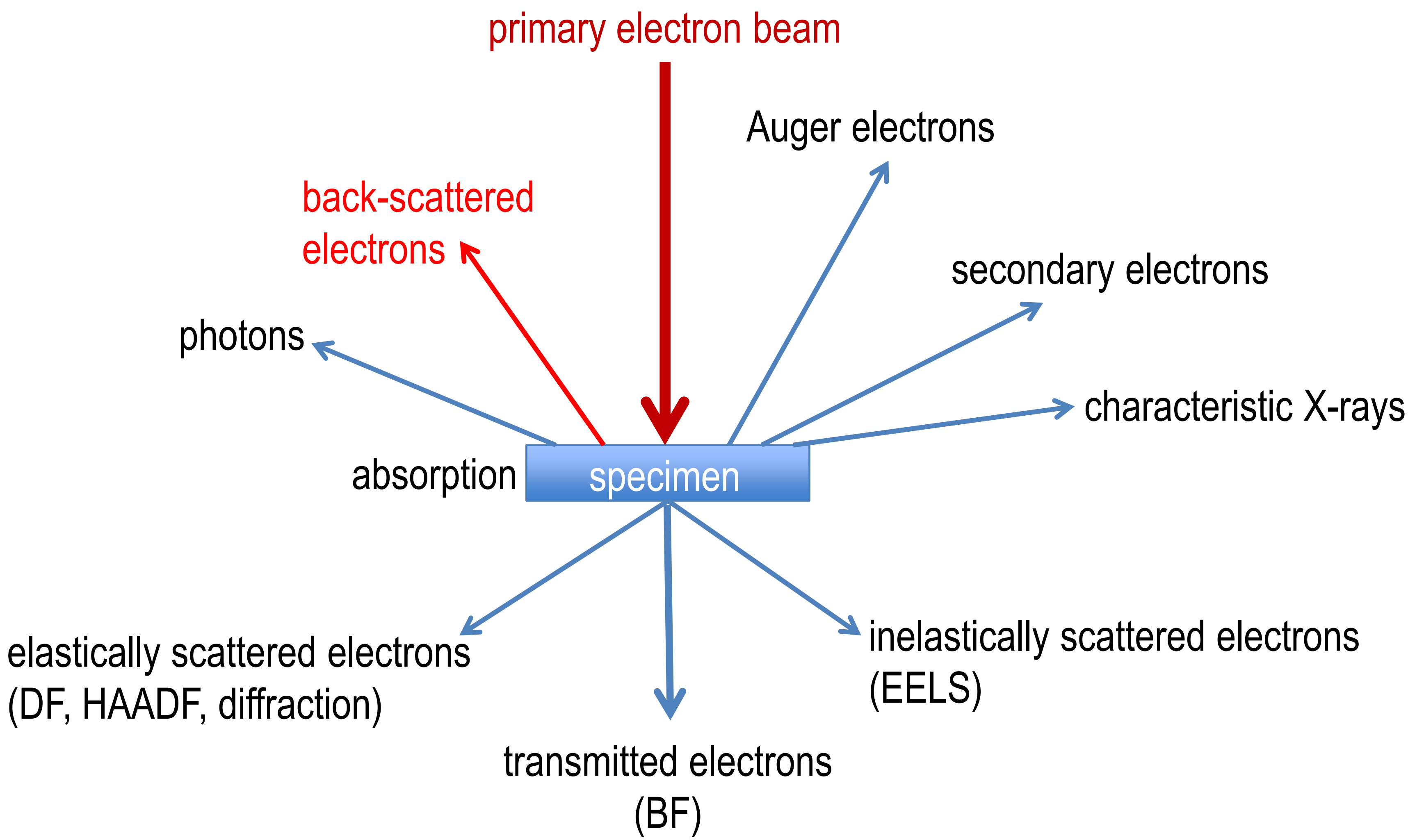
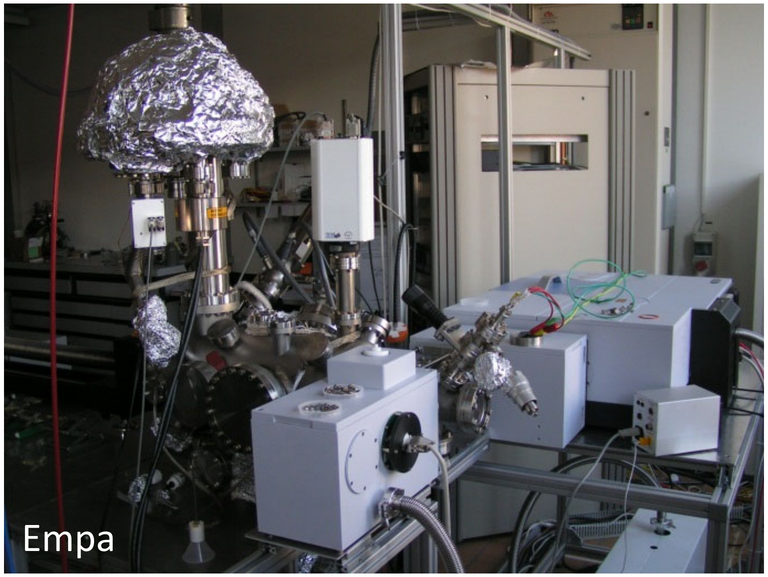
Electrons-matter interaction

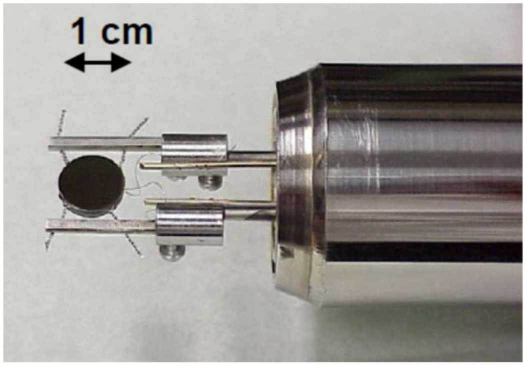


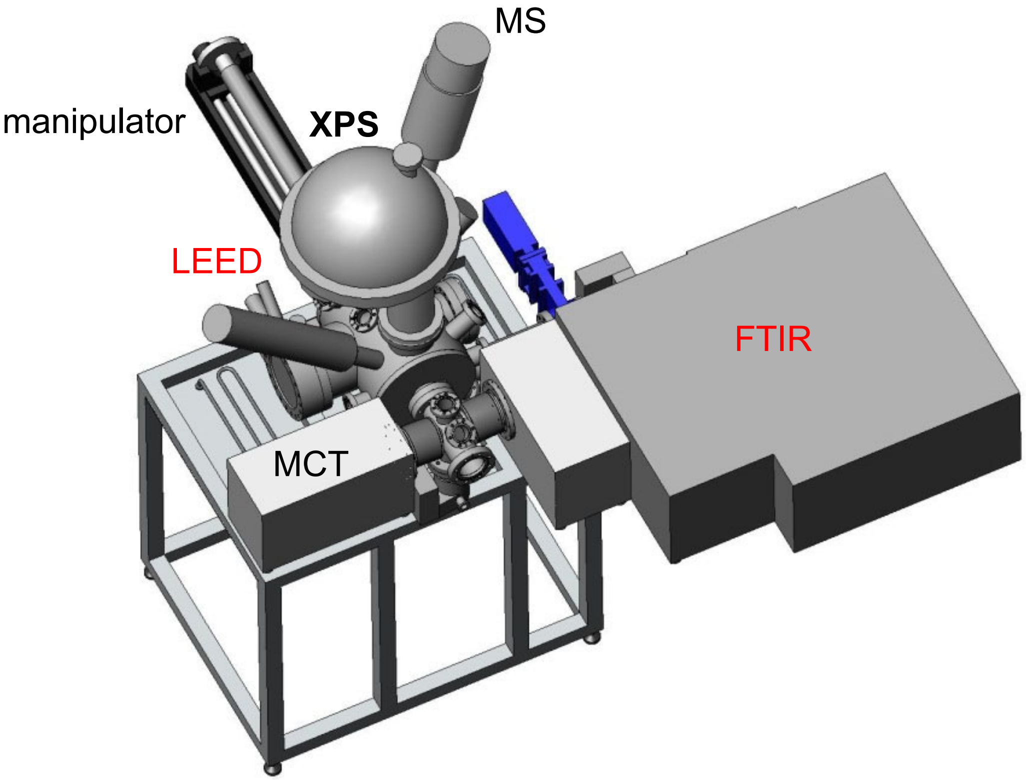
The UHV setup

- Stainless steel UHV setup with flanges, pumps, pressure gauges, …
- Typically, 10^{-10} to 10^{-11} mbar base pressure

- Tool and components:
  - preparation
  - characterization
  - sample manipulation
  - resistive heating

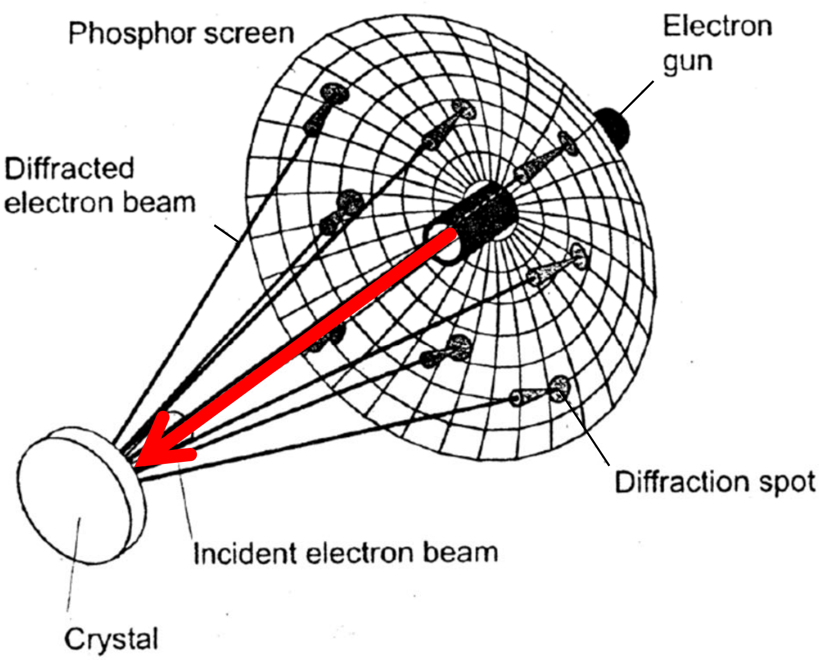


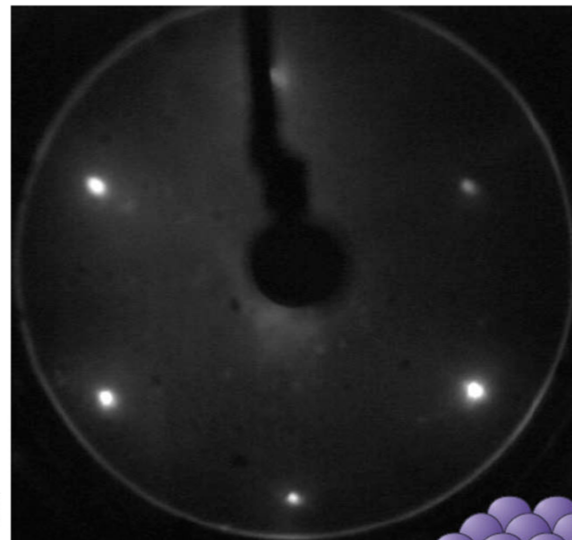




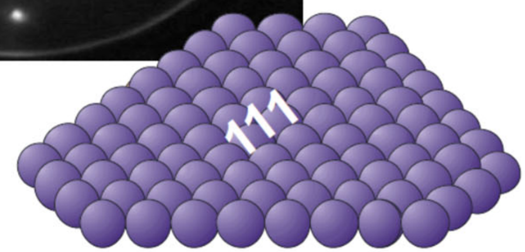
LEED

- **Low-energy electron diffraction**





Pd(111)



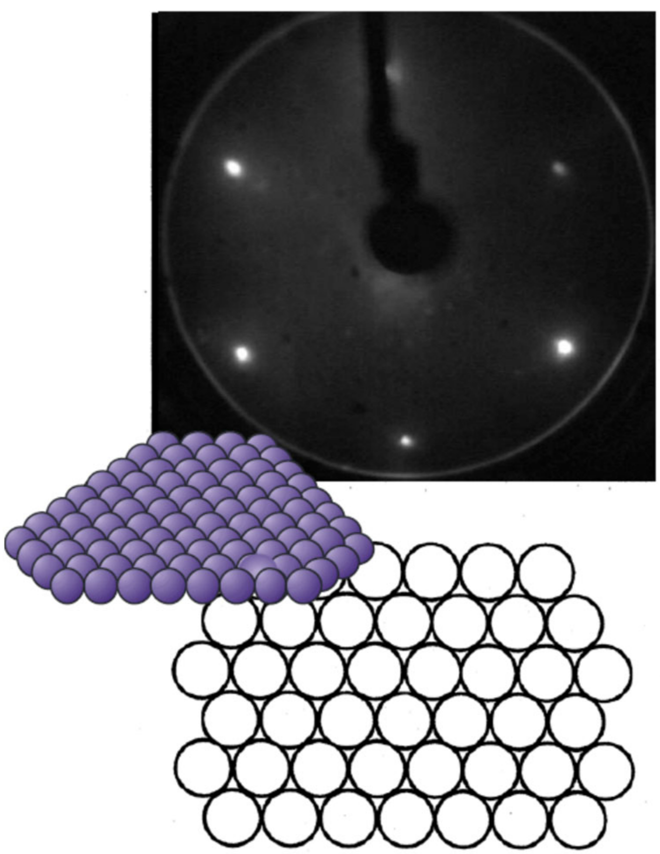
$$n\lambda = a \sin\alpha$$

Collimated beam of low energy electrons (20-200 eV)
Wavelength (λ) of 100 V electrons: ca. 1 Å, < interatomics distances

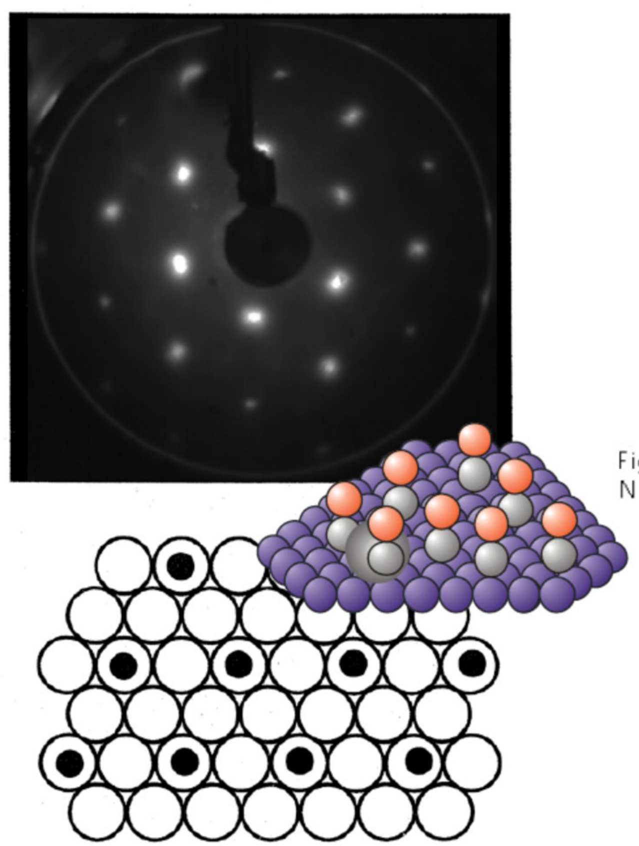
LEED

- **The structure of surfaces**

Pd(111) 1x1



(2x2) CO Pd(111)



surface reconstruction

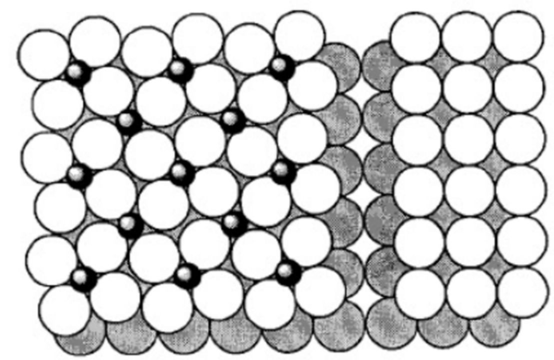
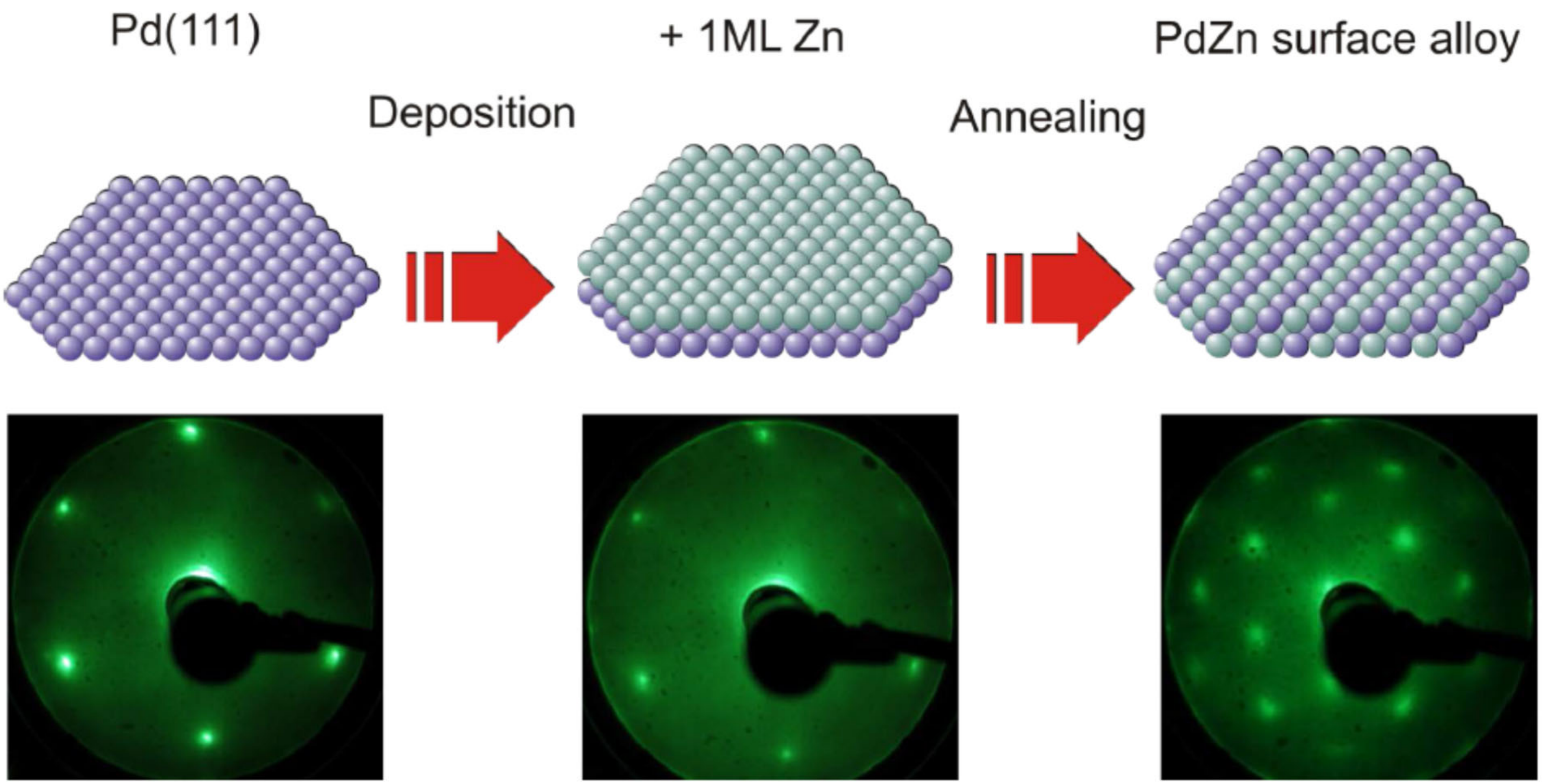


Figure 12. Carbon-chemisorption-induced restructuring of the Ni(100) surface.

LEED

- **Preparation of PdZn surface alloy for model studies**



Weilach et al., J. Phys. Chem. C 116 (2012) 18768

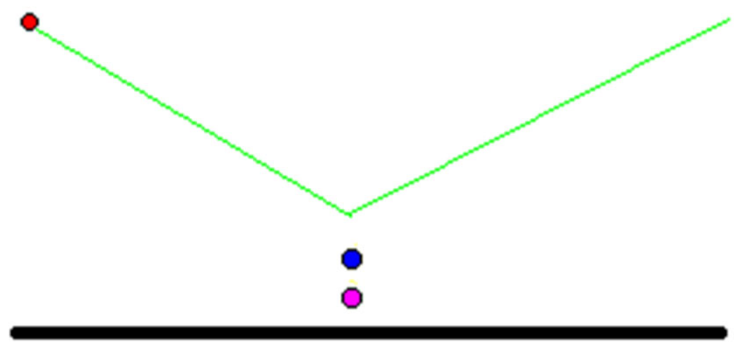
HREELS

- **High resolution electron energy loss spectroscopy**

- Interaction of low energy electrons with surfaces
- Backscattered electrons are detected
- Possible interactions are
  - the excitations of vibrations of adsorbed molecules
  - vibrations of the top layers of the substrate (surface phonons)
  - vibrations of the electrons in the substrate or in films or islands on the substrate surface (plasmons)
- UHV is required
- Surface sensitive technique
- Technique of choice to study adsorbates at single crystal surfaces

HREELS

- **How it works**



- Some of the electron beam's energy is converted into vibrational motion of the adsorbed molecule
- The result is a characteristic loss peak in the HREEL spectrum

University of Waterloo: http://www.chembio.uoguelph.ca/educmat/CHM729/eels/eels0.htm

HREELS

- **How it works – Interaction between electrons and molecules**
- Two scattering modes

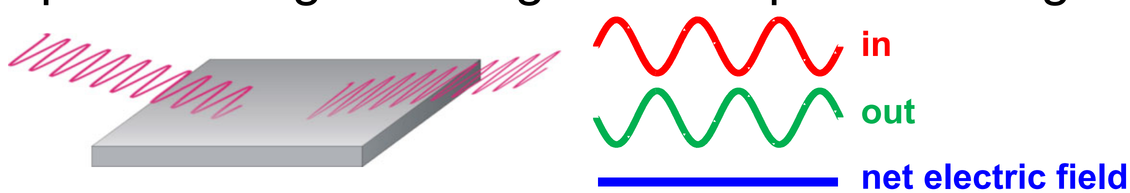
- Dipole scattering
  - incident electron is like a electromagnetic wave interacting with oscillating dipoles (vibration of species at surface)
  - long-range effect mediated by the Coulomb field. The incoming electron is influenced by a vibrating dipole at the surface.
  - electron is scattered specularly with an energy loss characteristic of the energy it delivered to the vibrational mode.

HREELS

- **How it works – Interaction between electrons and molecules**
- Two scattering modes

- Dipole scattering
  - identical information to IR spectrum

  - same rules as IR spectroscopy
    - only fundamental transitions allowed
    - only vibrations accompanied by change in dipole moment allowed
    - s-polarized light undergoes 180° phase change upon reflection



destructive interference

    - surface (normal) selection rule: only dipoles perpendicular (normal) to the surface are active
  - intensity is at maximum for specular reflection

The surface selection rule

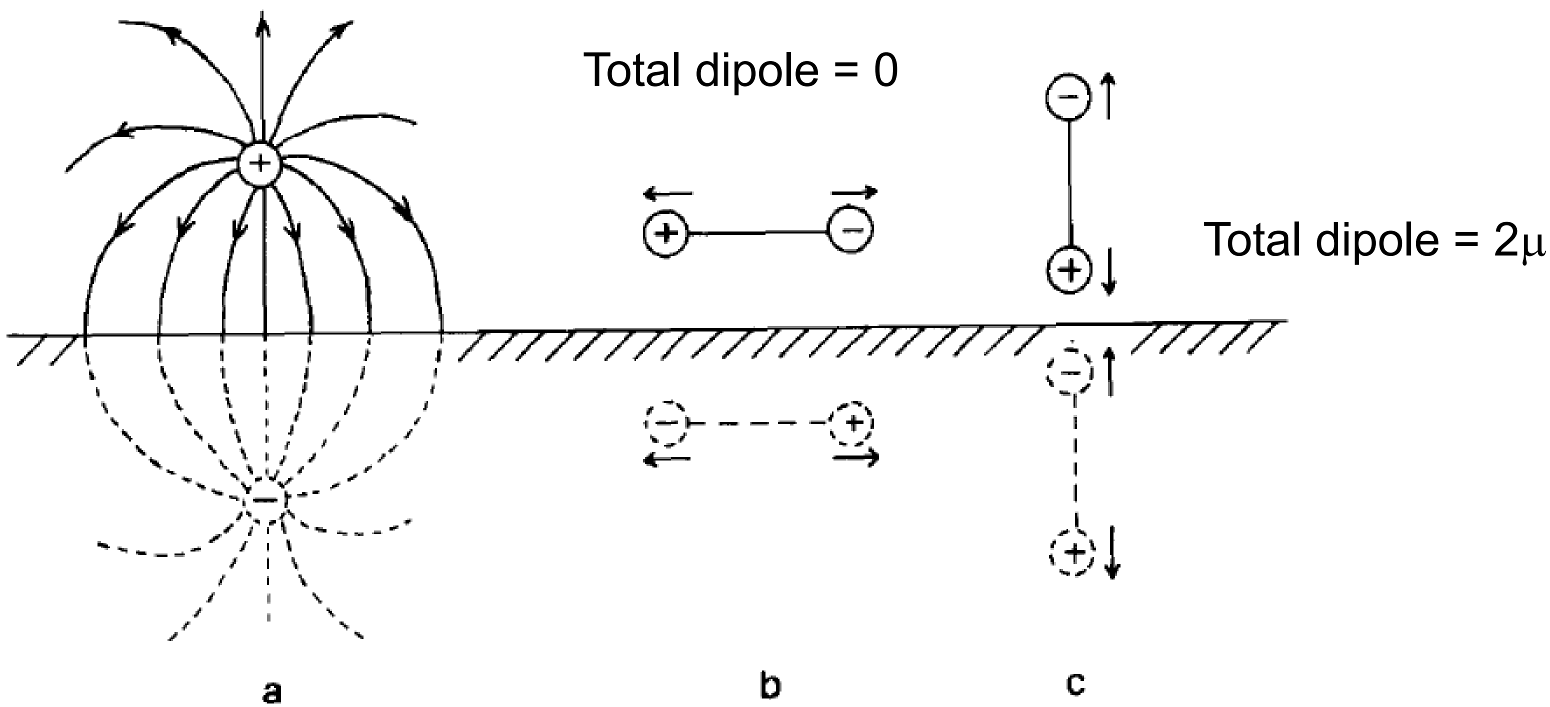


Fig. 1. (a) The lines of force and the electrical "image" resulting from a positive charge over the surface of a conductor (the metal surface is the upper line above the hatched area). (b) The changes during the vibration of a dipole parallel to the surface of the metal; the "image" dipole change is in the opposite direction to the original. (c) The changes during the vibration of a dipole perpendicular to the surface; the "image" dipole change is in the same direction as the original.

Pearce and Sheppard, Surf. Sci. 59 (1976) 205

HREELS

- **How it works – Interaction between electrons and molecules**
- Two scattering modes

- Impact Scattering
  - transfer of energy between electron and molecule while the electron is in the molecule
  - short range scattering process from the ion core
  - quantum mechanical formalism required for the theory

  - vanishes in specular direction
  - isotropic (not in the specular direction, but everywhere) but the energy losses still reflect vibrational excitations in the adsorbate
  - dominant at high vibrational energy
  - strong dipole scatterers (CO) are weak impact scatterers

  The angular distribution of peaks around the specular direction can distinguish between peaks which result from different scattering modes

Setup

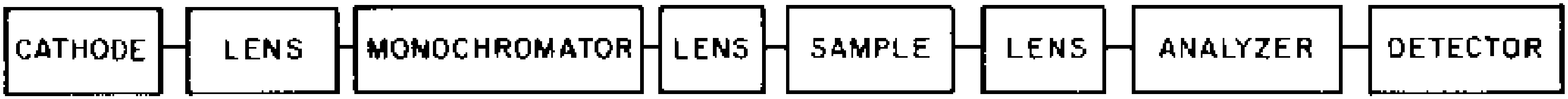
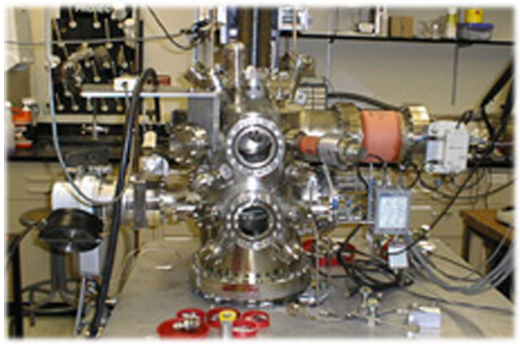
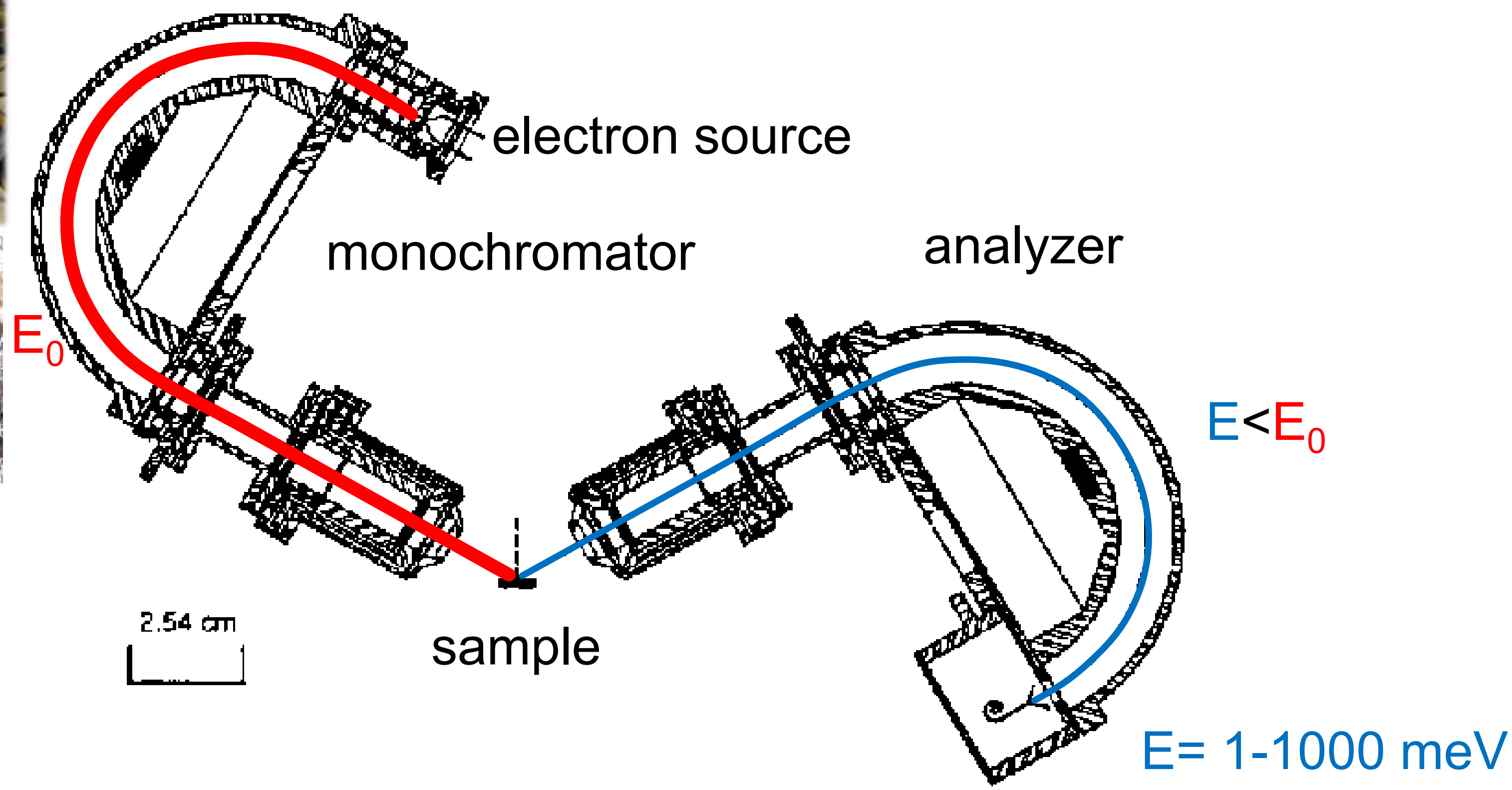


Diagram of an electron energy loss spectrometer

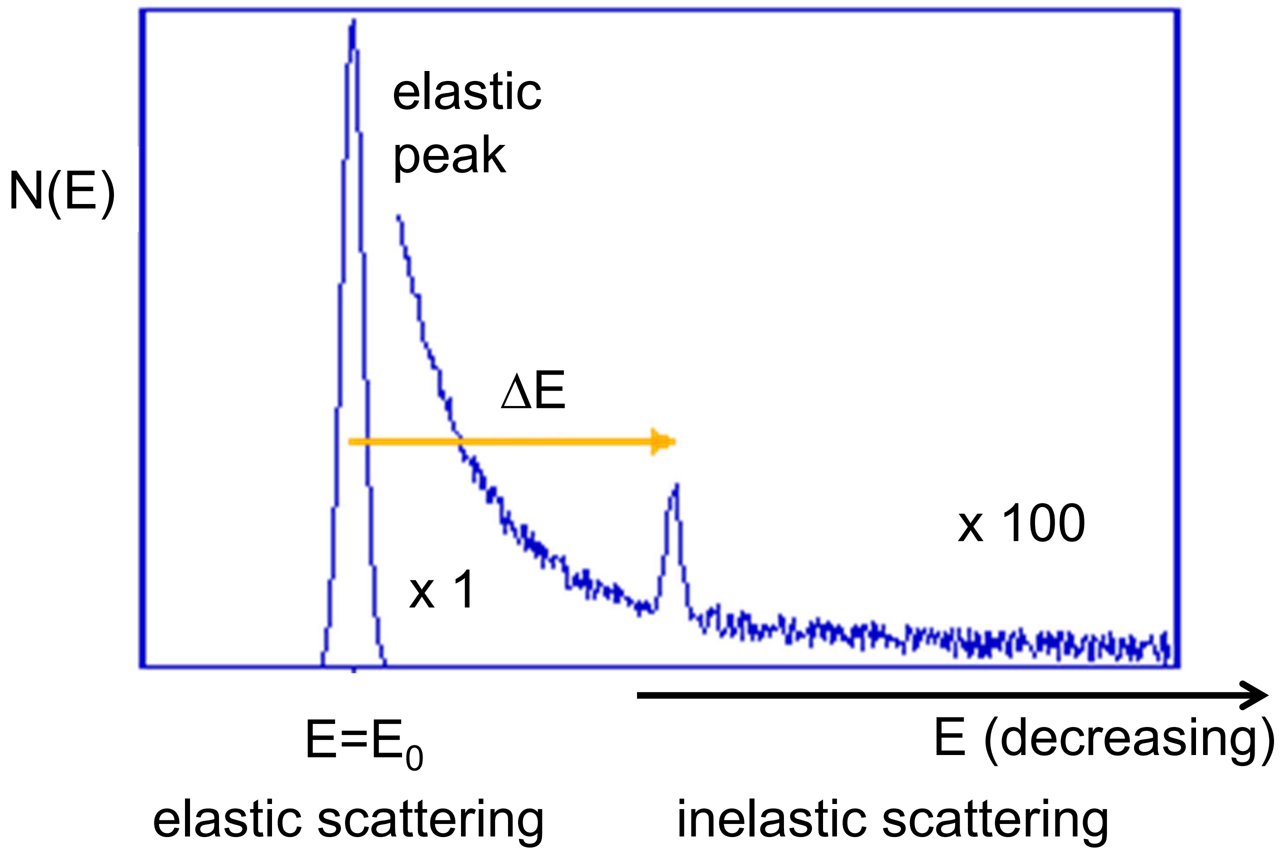




E_0= 5-10 eV

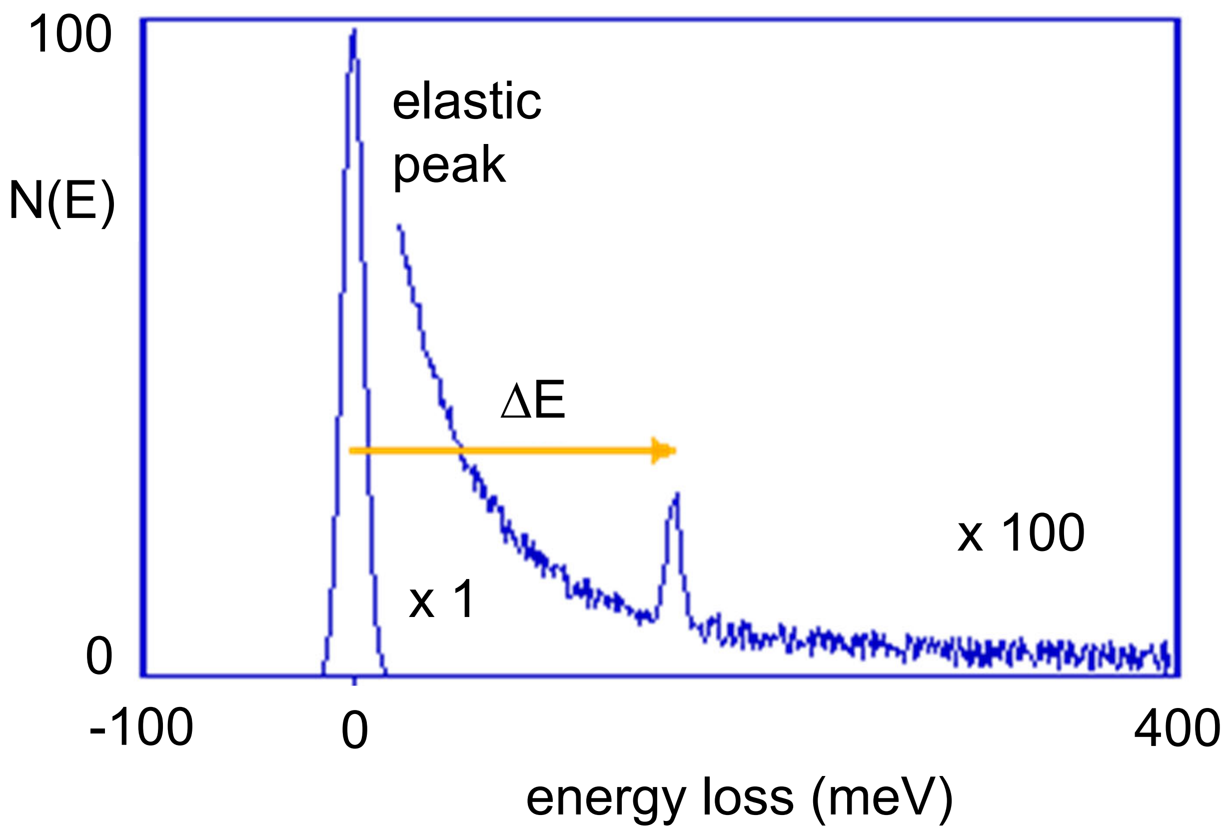
Electrons from a cathode pass through a monochromator, strike the sample, and the energy spectrum of the scattered electrons is probed by a second monochromator.

The HREELS spectrum



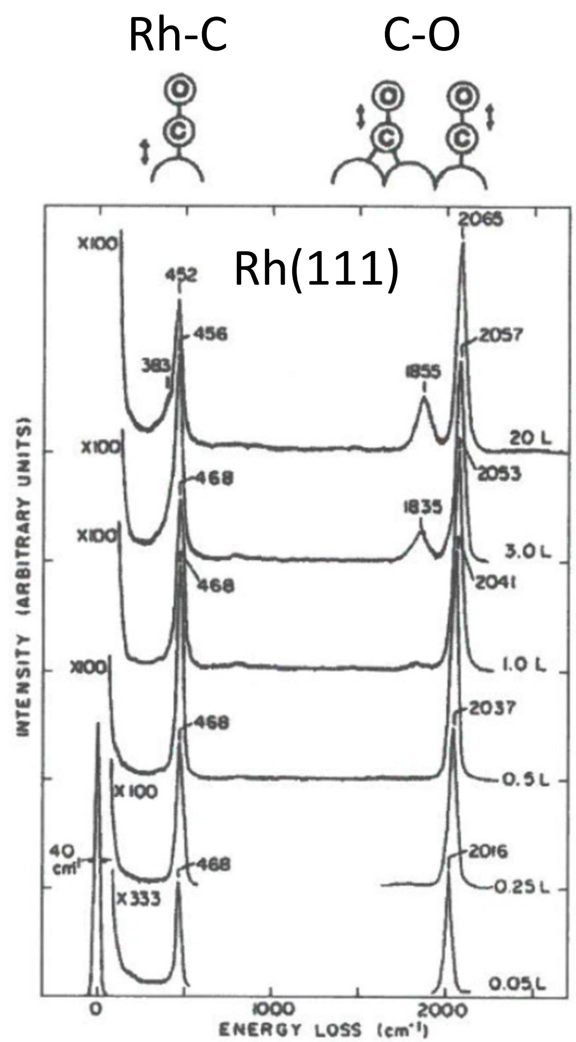
The HREELS spectrum

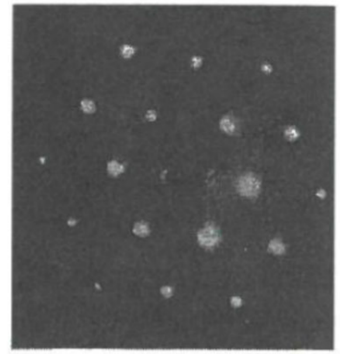
ΔE= energy of vibrational mode of excited adsorbate upon inelastic scattering



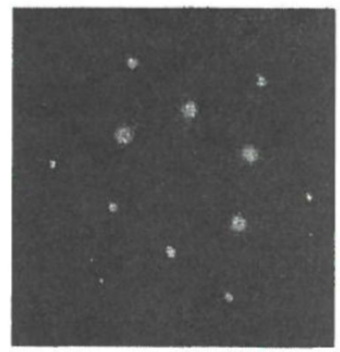
[1 meV = 8.065 cm^{-1}]

Examples

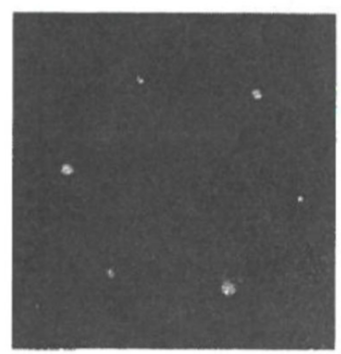




(2x2)



(√3x√3)R30°



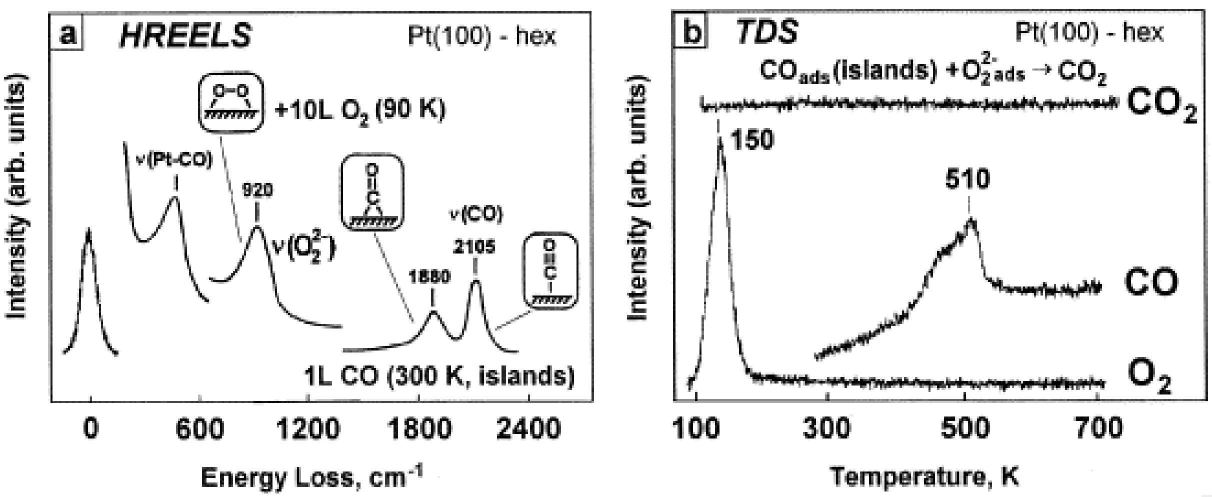
Clean Rh(111)

surface structure is known
at all points of the experiment (LEED)

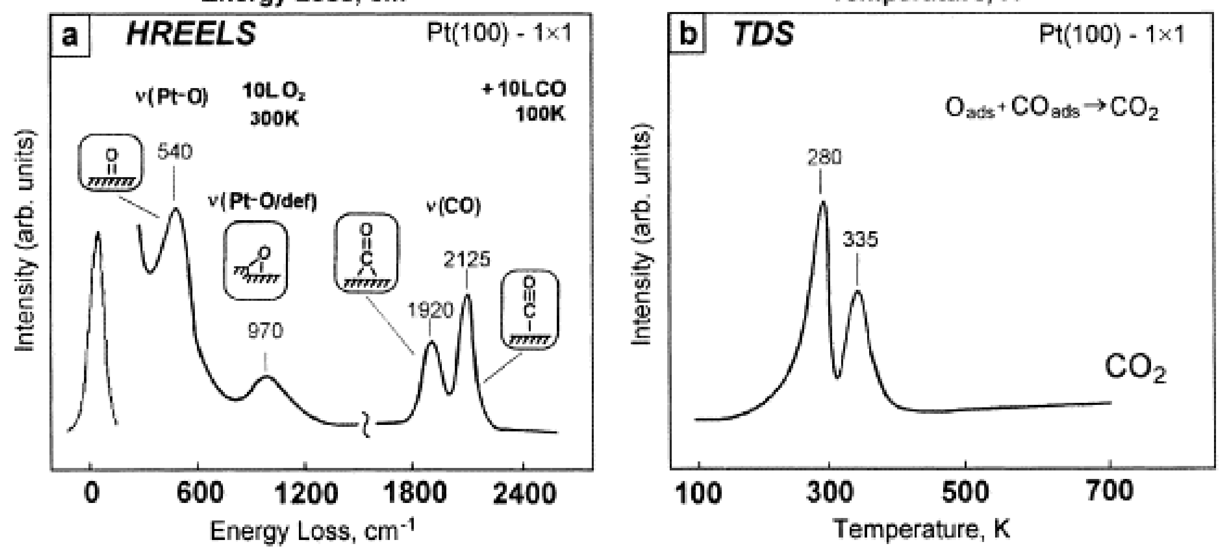
enhanced frequency range compared to FTIR

Examples

- **Access to low vibrational energy**



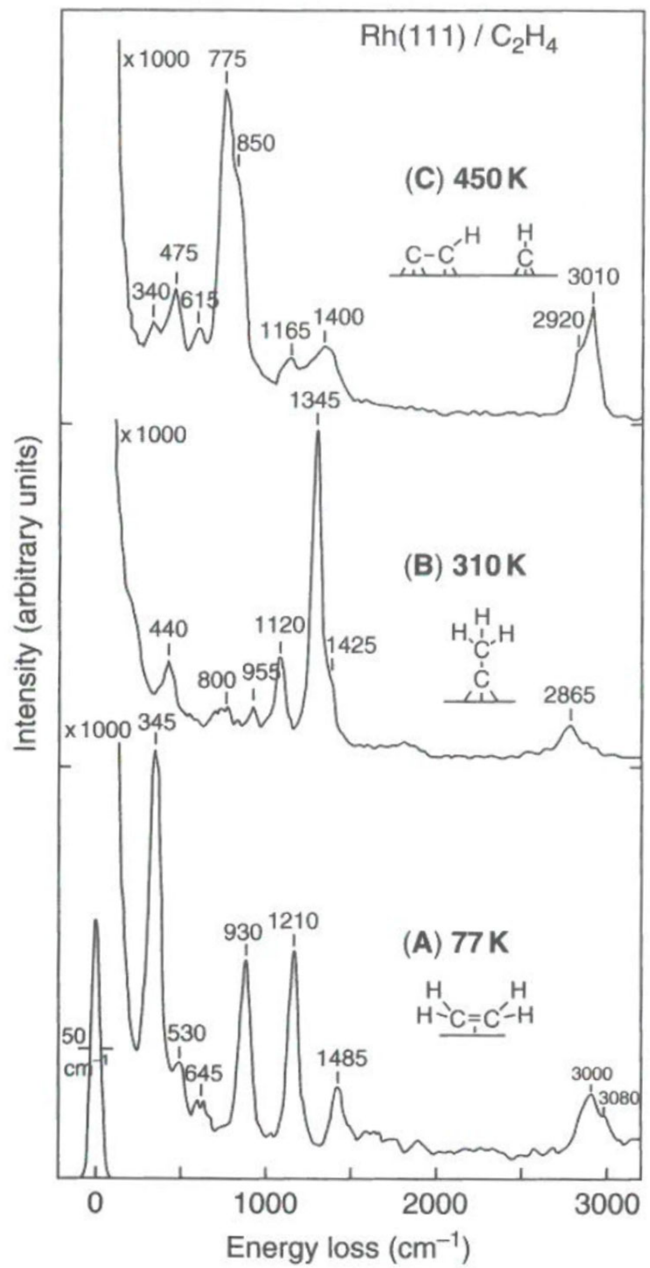
1. CO adsorption at 300 K
2. Pt(100)-(hex) surface covered by CO/(1x1) islands
3. O_2 adsorption at 90 K



1. O_2 adsorption at 300 K
2. Pt(100)-(1x1) surface covered by atomic O layer
3. CO adsorption at 100 K

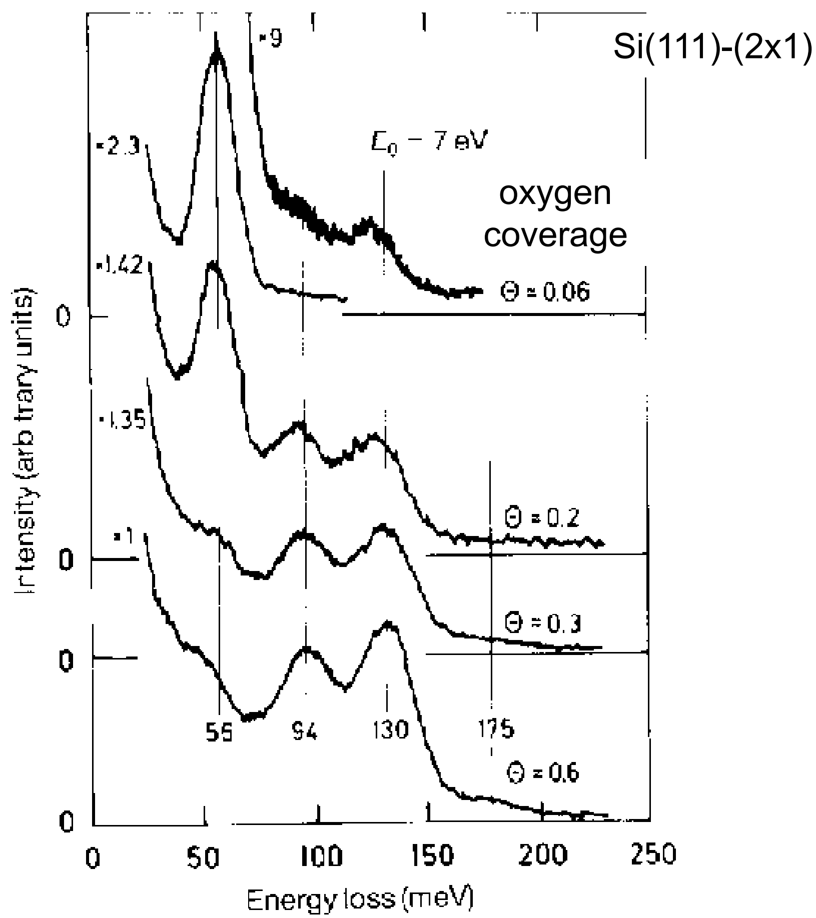
Gorodetski et al., Appl. Catal. A 188 (1999) 267

HREELS | Examples



Examples

- **HREELS of surfaces**
  - Phonons: elementary vibrational motion in which a lattice of atoms or molecules uniformly oscillates at a single frequency

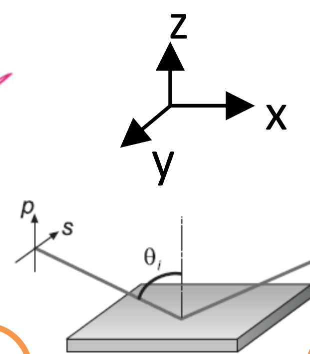


Ibach et al., Electron Energy Loss Spectroscopy and Surface Vibrations, Academic Press, New York, 1982

RAIRS

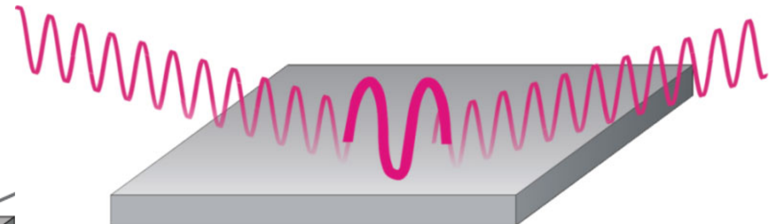
- **Reflection absorption IR spectroscopy**
  - Specular/external reflection method

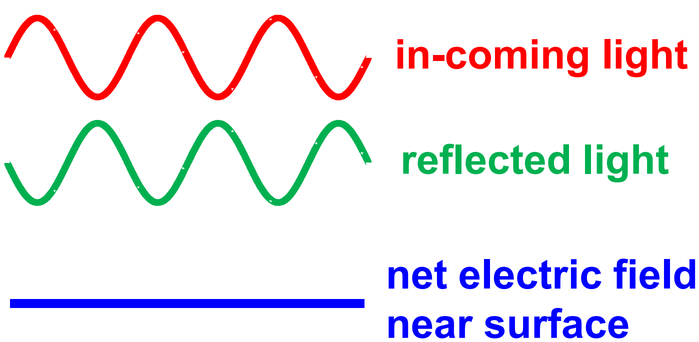
Perpendicular (s-) polarization (y-axis)



Parallel (*p*-) polarization (x, z-axis)

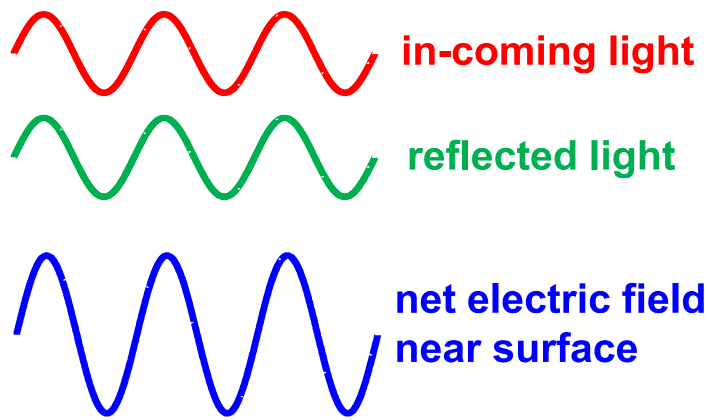
Parallel: parallel to the plane of incident light





destructive interference

This *s*-polarization does not contain information about surface species (180° phase change)



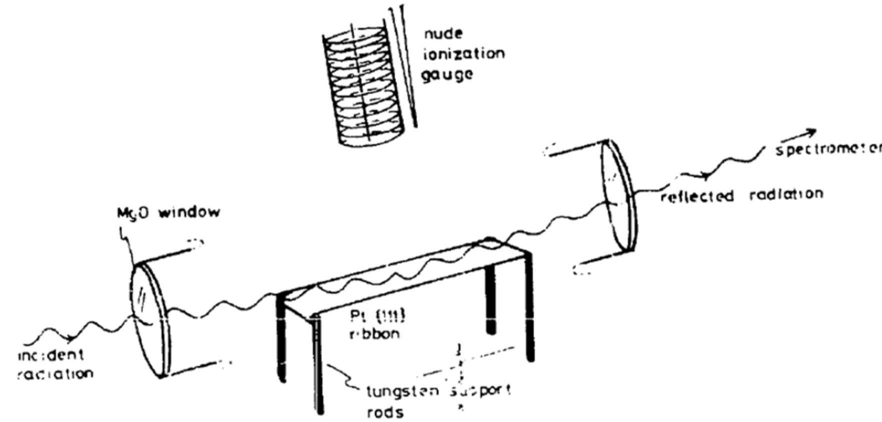
constructive interference

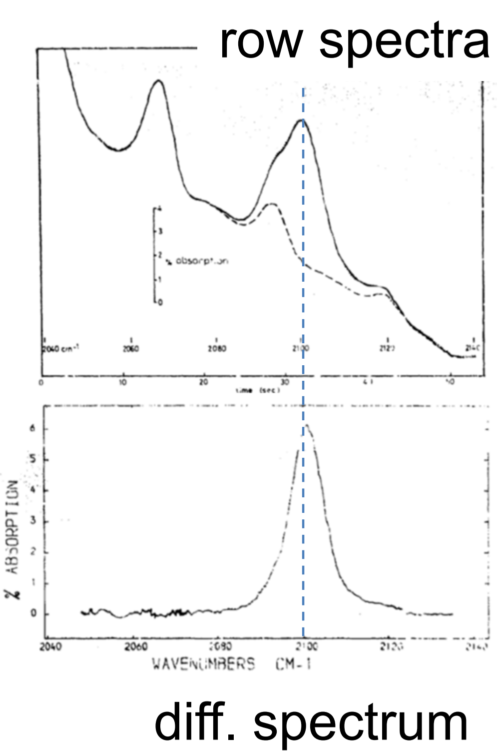
p-polarization is exploited

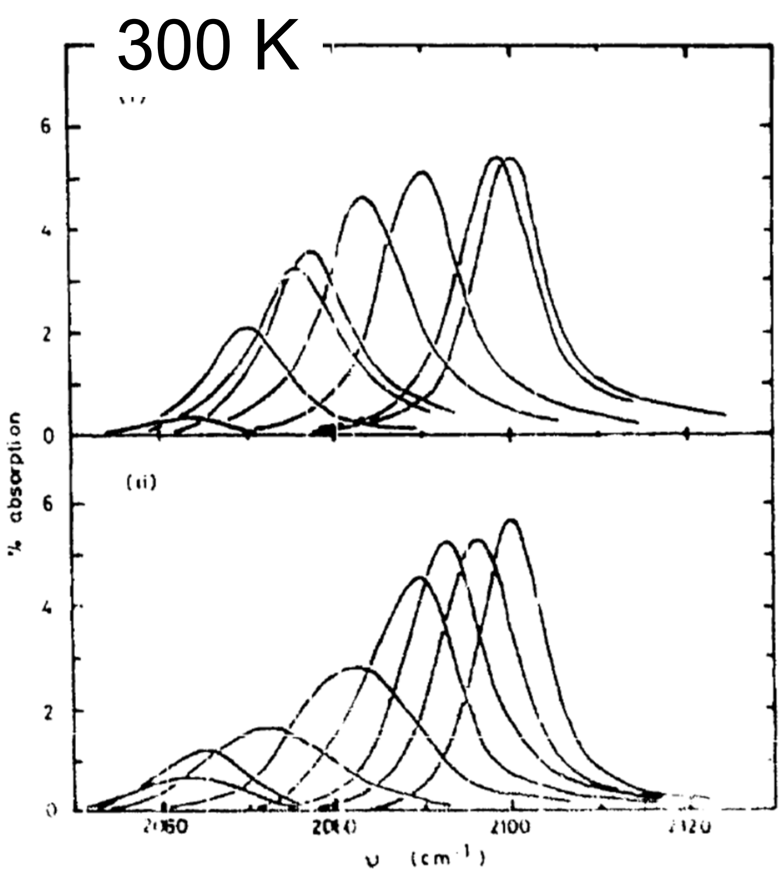
Greenler, *J. Chem. Phys.* 44 (1966) 310

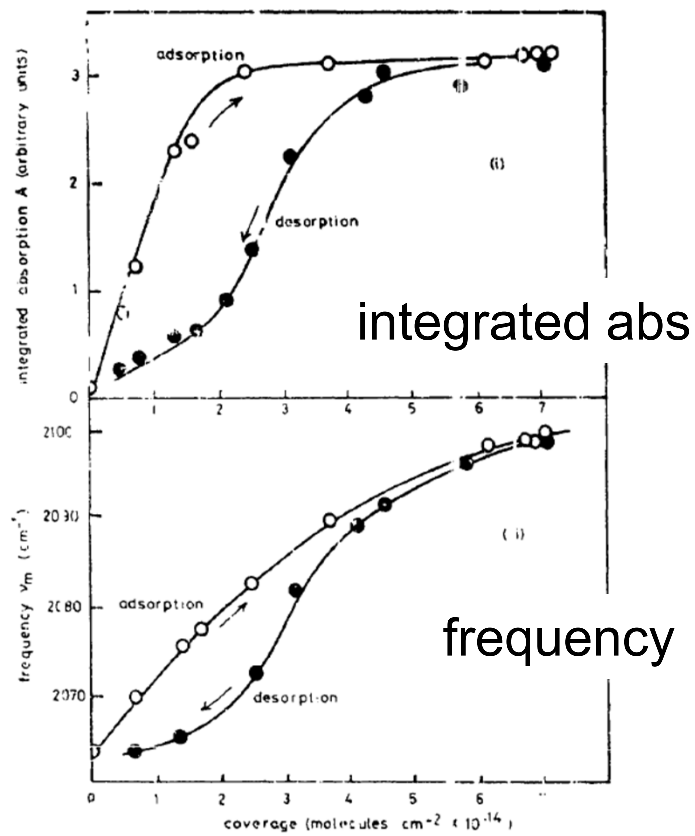
CO adsorption on Pt(111)

- ν(CO) blue-shifts with increasing coverage
  - dipole-dipole interactions
- linear increase of intensity up to 1/3 of full surface coverage, then only shift
- ads/des hysteresis





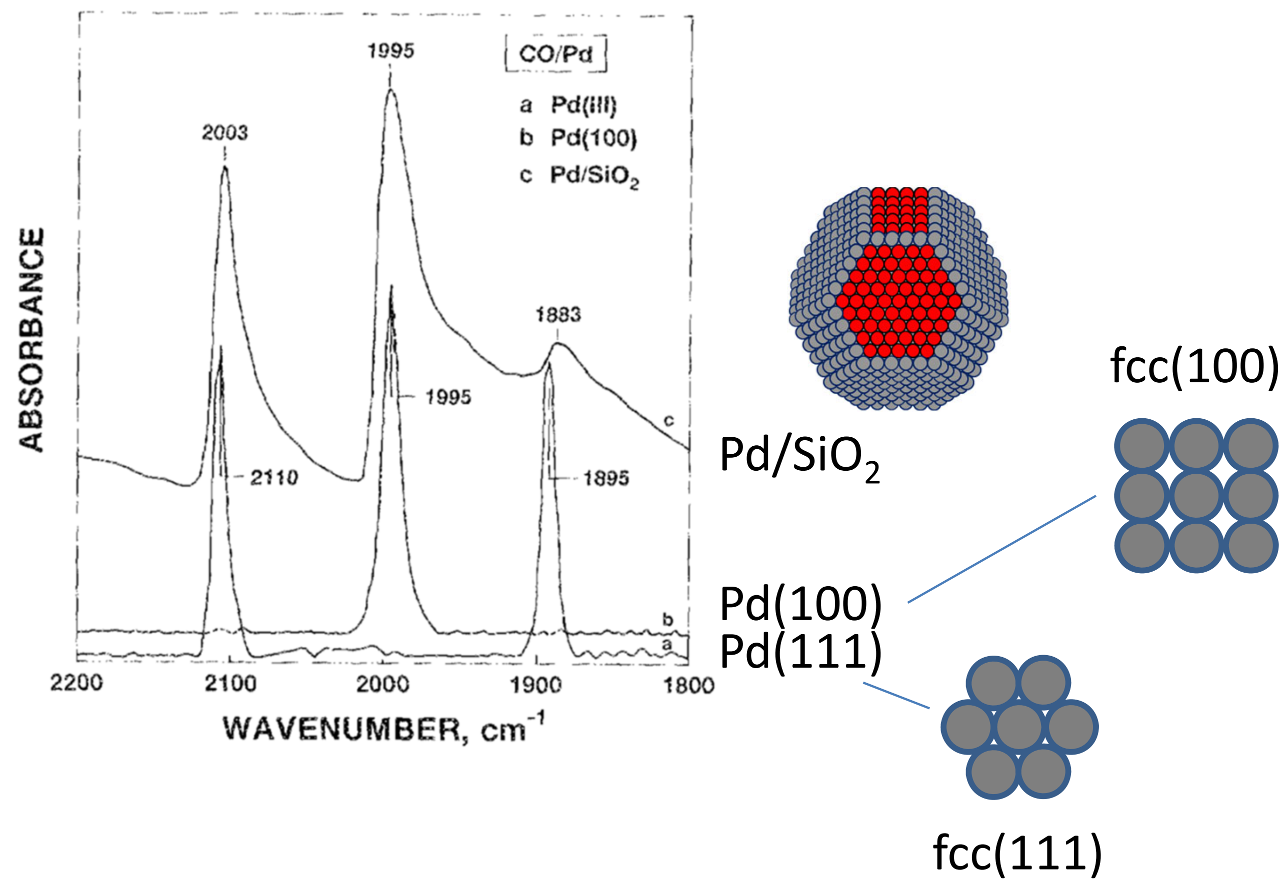




Shigeishi et al., Surf. Sci. 58 (1976) 379

RAIRS

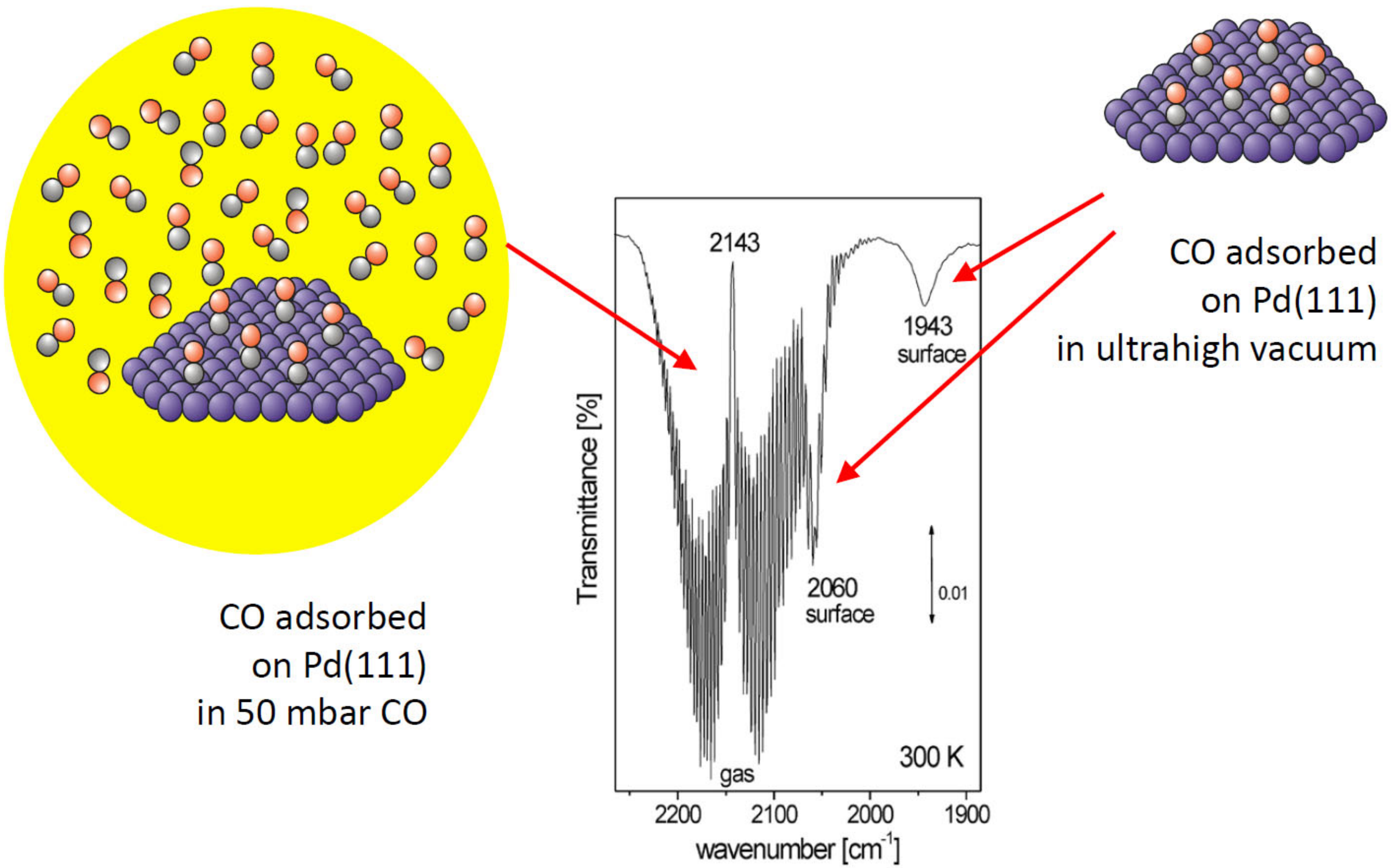
- **Single crystal vs. Powder**
  - reference for assignment of signals on technical catalysts!



Szanyi et al., J. Vac. Sci. Technol. A 11 (1993) 1969

RAIRS

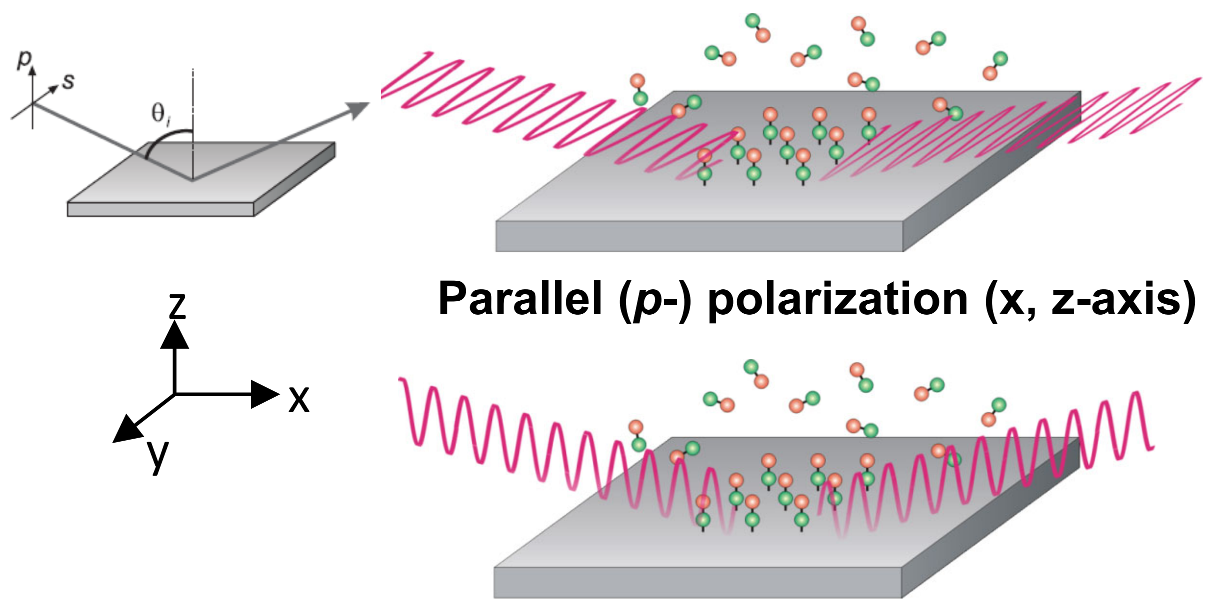
- **Non-UHV conditions**
  - Superposition of contributions from surface and gas phase



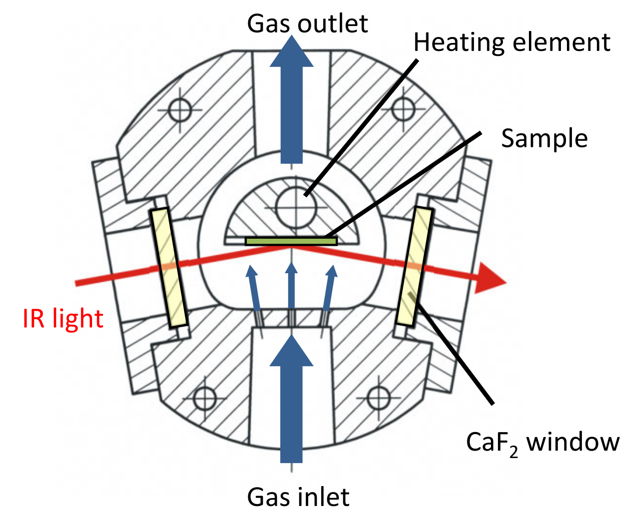
Polarization-modulation IRRAS (PM-IRRAS)

- **Non-UHV experiments**
  - continuous generation of 2 polarizations (photoelastic modulator)
  - excellent gas-phase compensation
  - highly sensitive, time-resolved

Perpendicular (*s*-) polarization (y-axis)



Parallel (*p*-) polarization (x, z-axis)



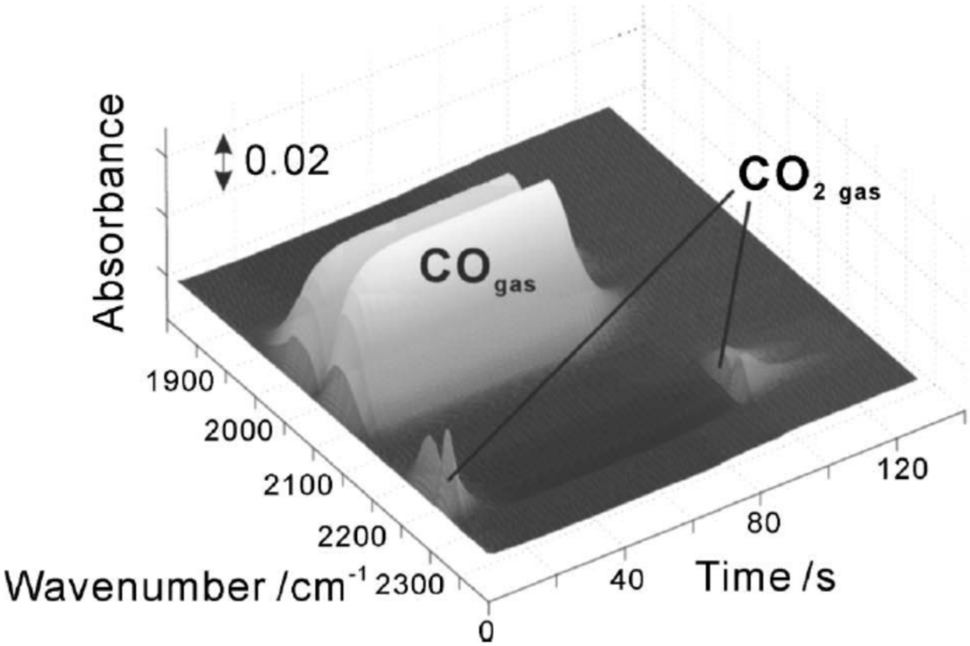
Urakawa et al., J. Chem. Phys. 124 (2006) 054717

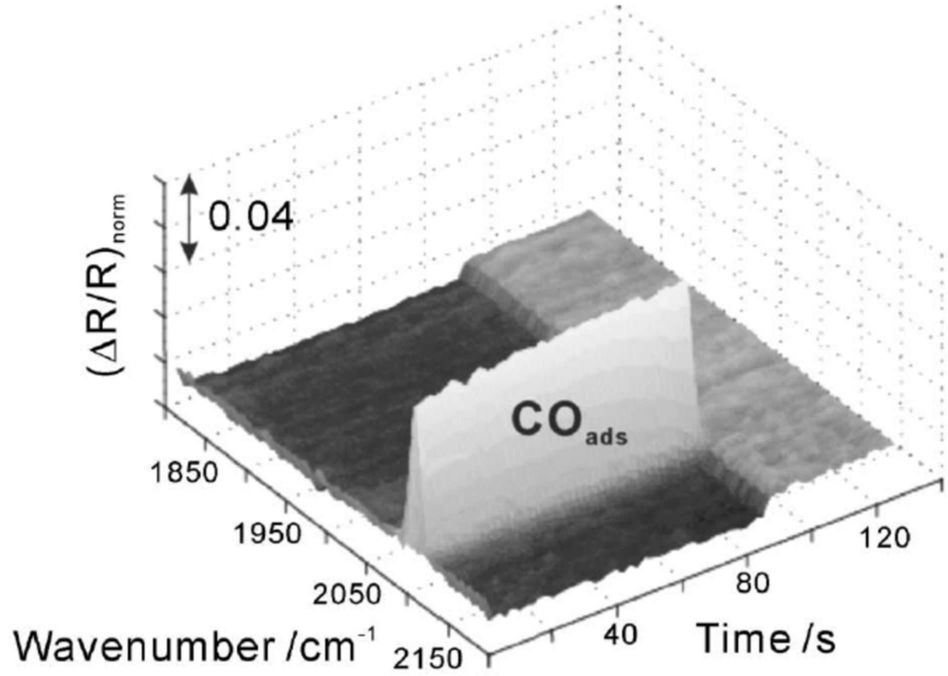
R_p	-	R_s	=	ΔR
Parallel polarization		**Perpendicular polarization**		**Difference**
surface + gas		gas		surface

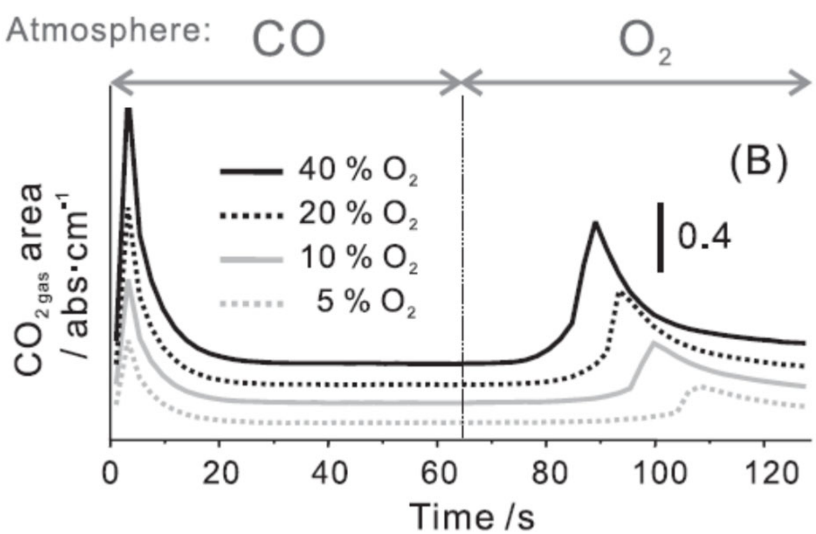
The surface spectra are often shown in $\Delta R/R$ ($R=R_s+R_p$)

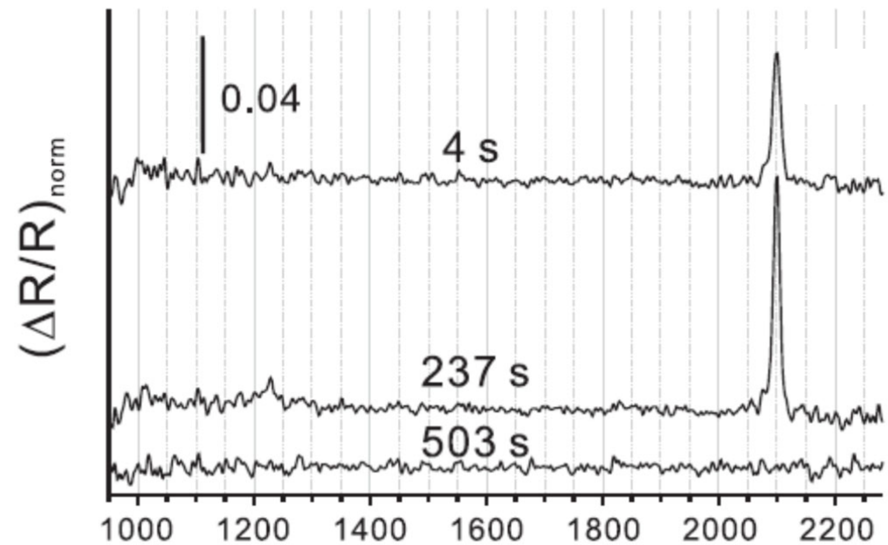
RAIRS

- **Isolation of surface contribution**









Urakawa et al., J. Chem. Phys. 124 (2006) 054717

HREELS vs. RAIRS

- HREELS
  - access to low vibrational energy, e.g. of O (few meV)
  - low energy resolution (≈ 4 meV; <30 cm^{-1})
  - 0.0001 monolayer of CO
  - specialised setup (UHV)

- RAIRS
  - detectors limited to 400 cm^{-1}
  - high energy resolution (4 cm^{-1})
  - 0.01 monolayer of CO
  - also ambient pressure

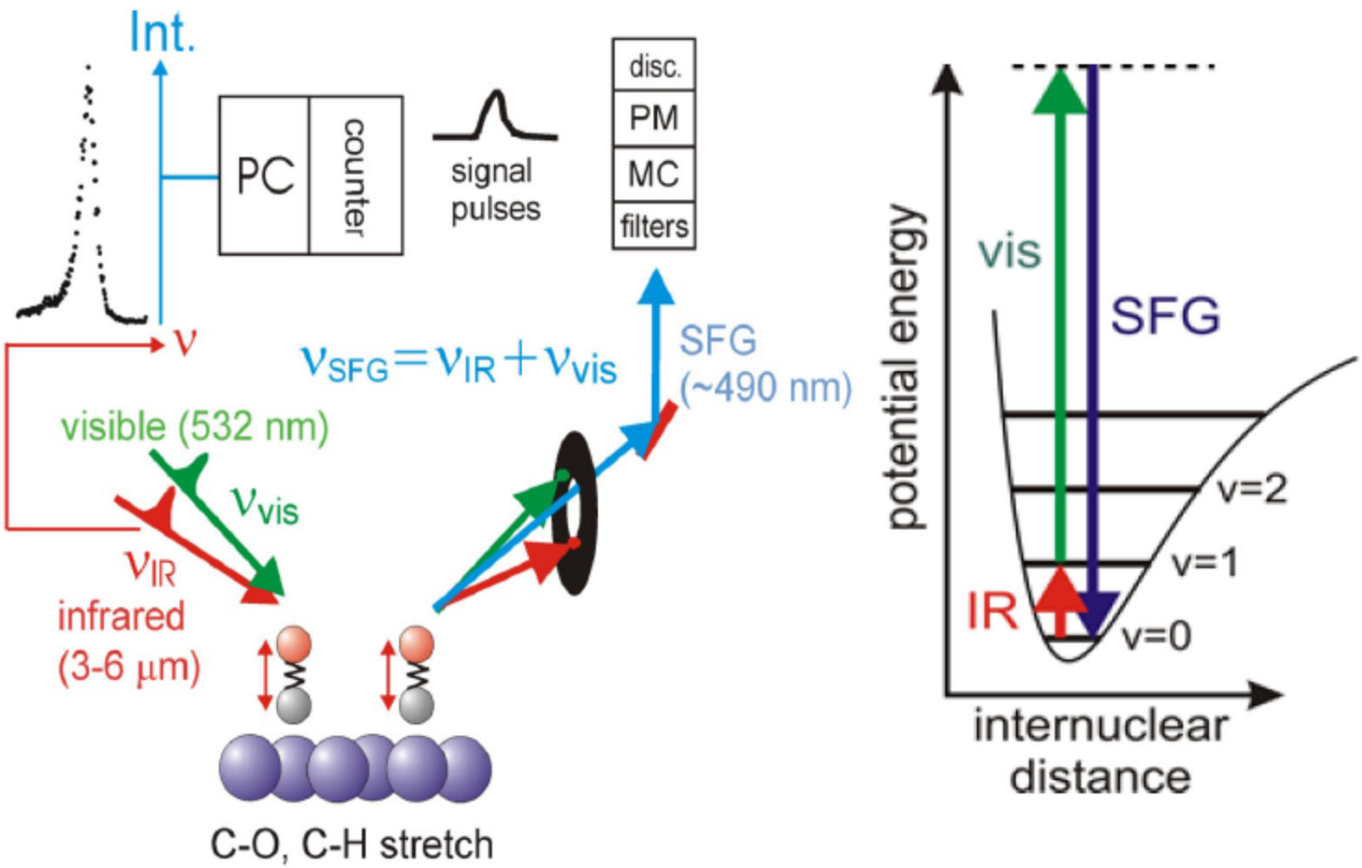
SFG

- **Sum frequency generation**

- Two laser beams mix at a surface and generate an output beam with a frequency equal to the sum of the two input frequencies
- Advantages
  - ability to be monolayer surface sensitive
  - ability to be performed in situ (for example aqueous surfaces and in gases)
  - does not cause much sample damage
- SFG gives complementary information to FTIR and Raman spectroscopy

SFG

- **IR-vis SFG laser spectroscopy**
  - no signal from isotropic gas phase
  - no signal from centrosymmetric solid
  - only adsorbates! (UHV to 1 bar)



- laser required: non-linear process is weak

courtesy: K. Föttinger (TUVienna)

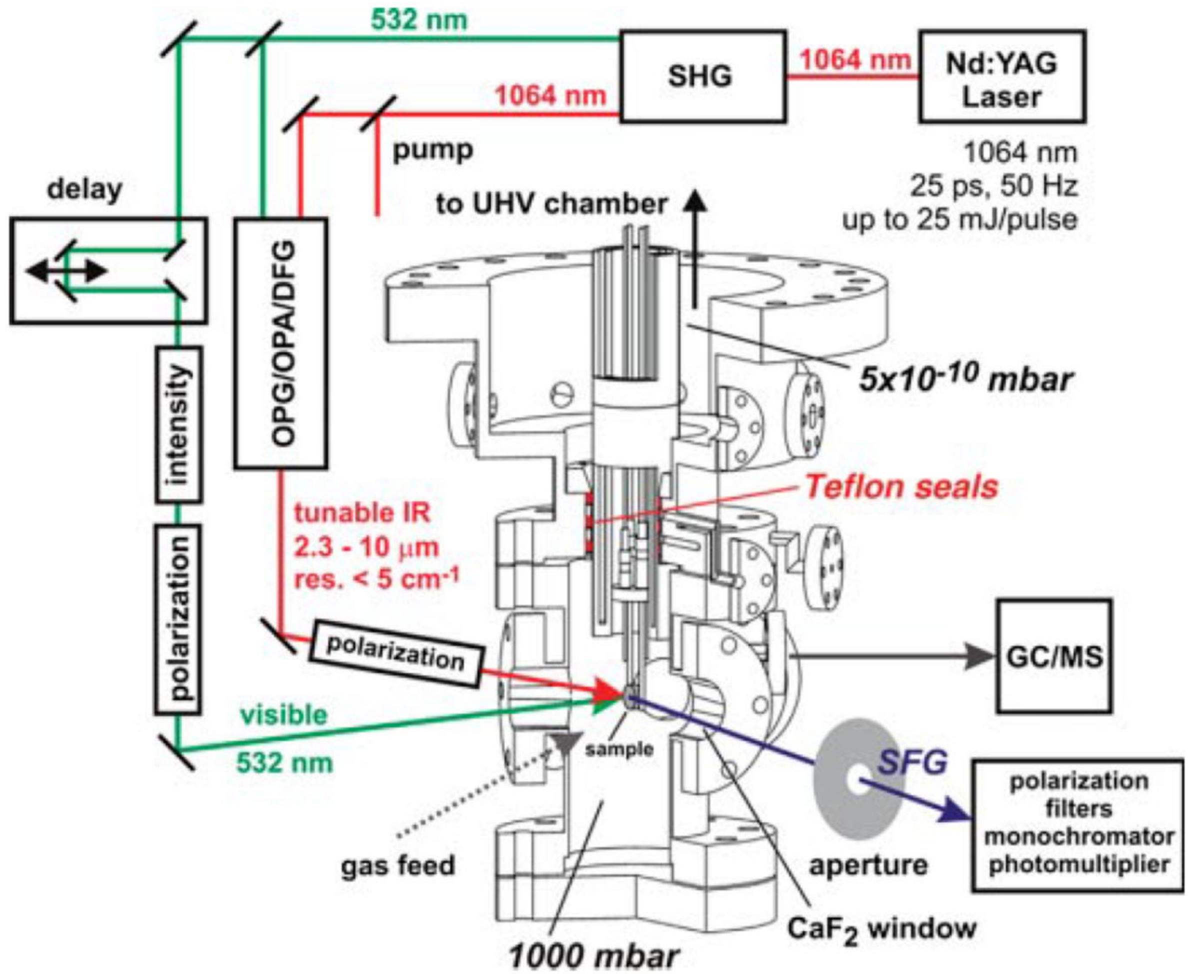
SFG

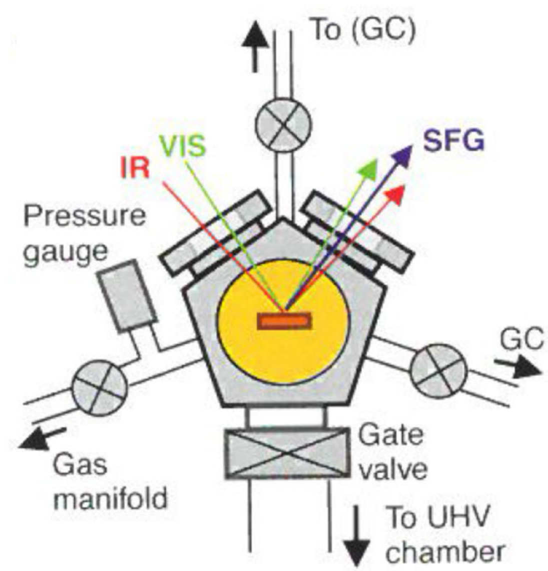
- **Information**
  - composition
  - orientation distributions
  - structural information of molecules (vibrational spectroscopy)
  - gas-solid, gas-liquid, liquid-solid
  - selection rule: in order to generate a sum frequency emission, the excited vibrational mode must be both IR and Raman active

Föttinger et al., Introduction to surface chemistry and catalysis, Wiley, Hoboken, New Jersey, 2010

SFG

- **Setup**

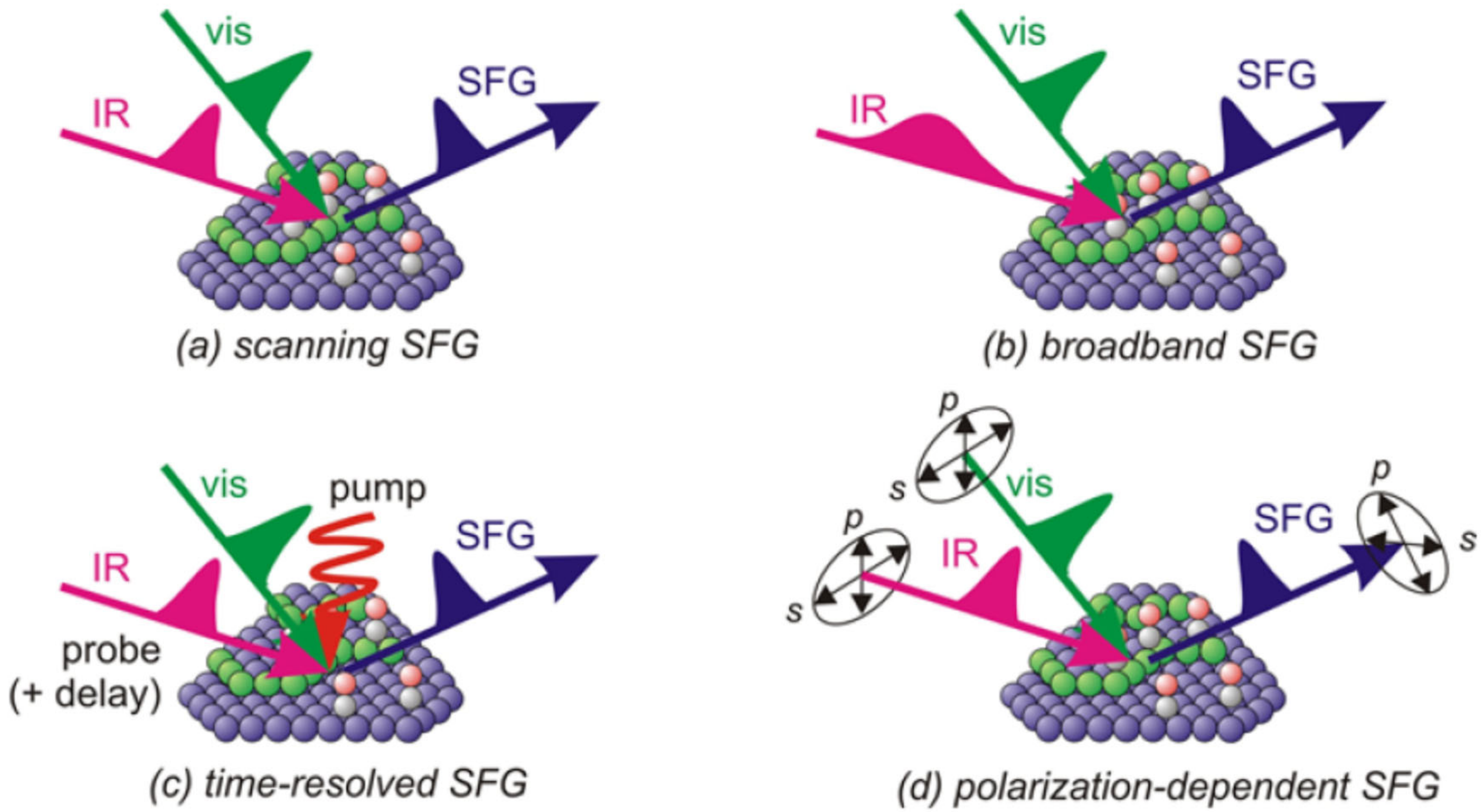




Föttinger et al., Characterization of Solid Materials and Heterogeneous Catalysts, 2012, Wiley-VCH Verlag

SFG

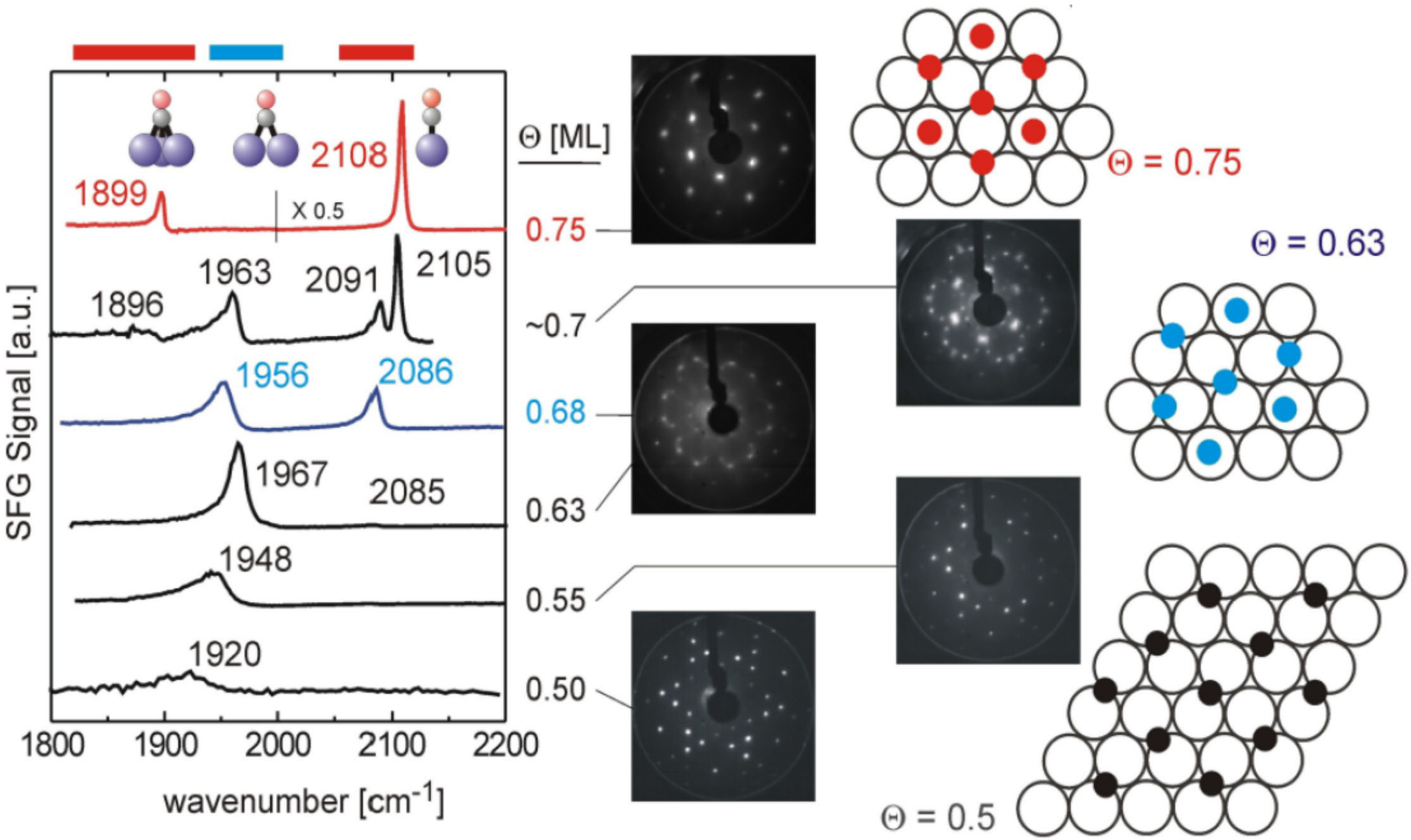
- **Modes of operation**



Föttinger et al., Characterization of Solid Materials and Heterogeneous Catalysts, 2012, Wiley-VCH Verlag

SFG

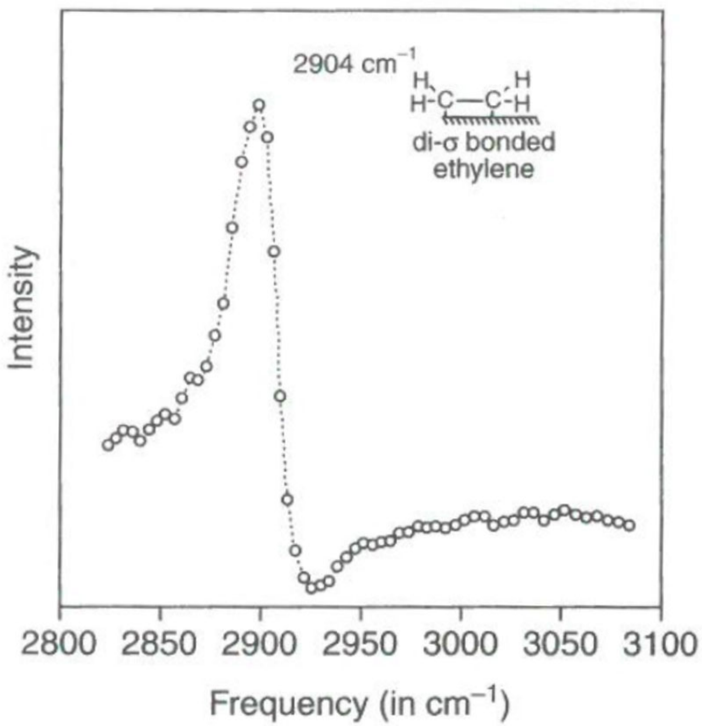
- **Structure assignment in combination with LEED**

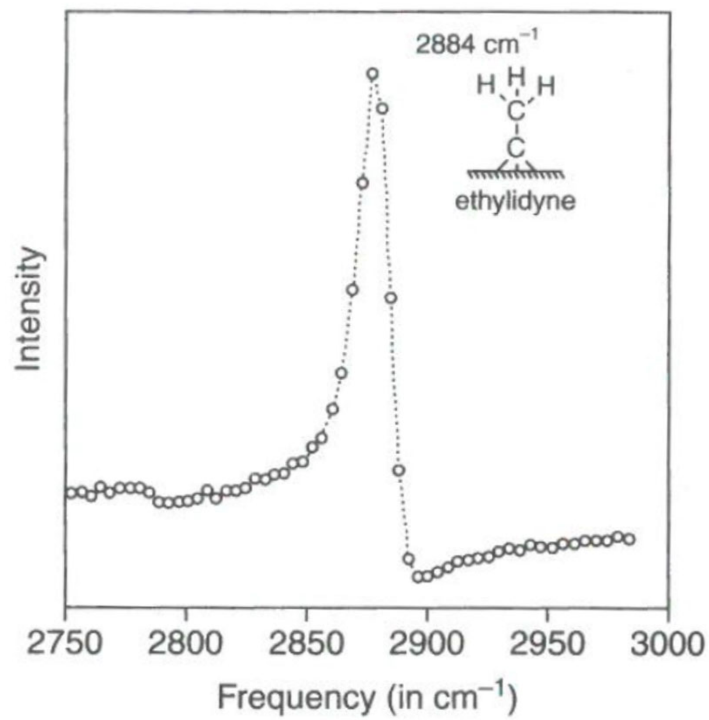


Rupprechter, *PCCP* 3 (2001) 4621; Unterhalt et al., J. Phys. Chem. B 106 (2002) 356

SFG

- Hydrocarbon fragments on Pt(111)





Somorjai et al., Introduction to surface chemistry and catalysis, Wiley, Hoboken, New Jersey, 2010