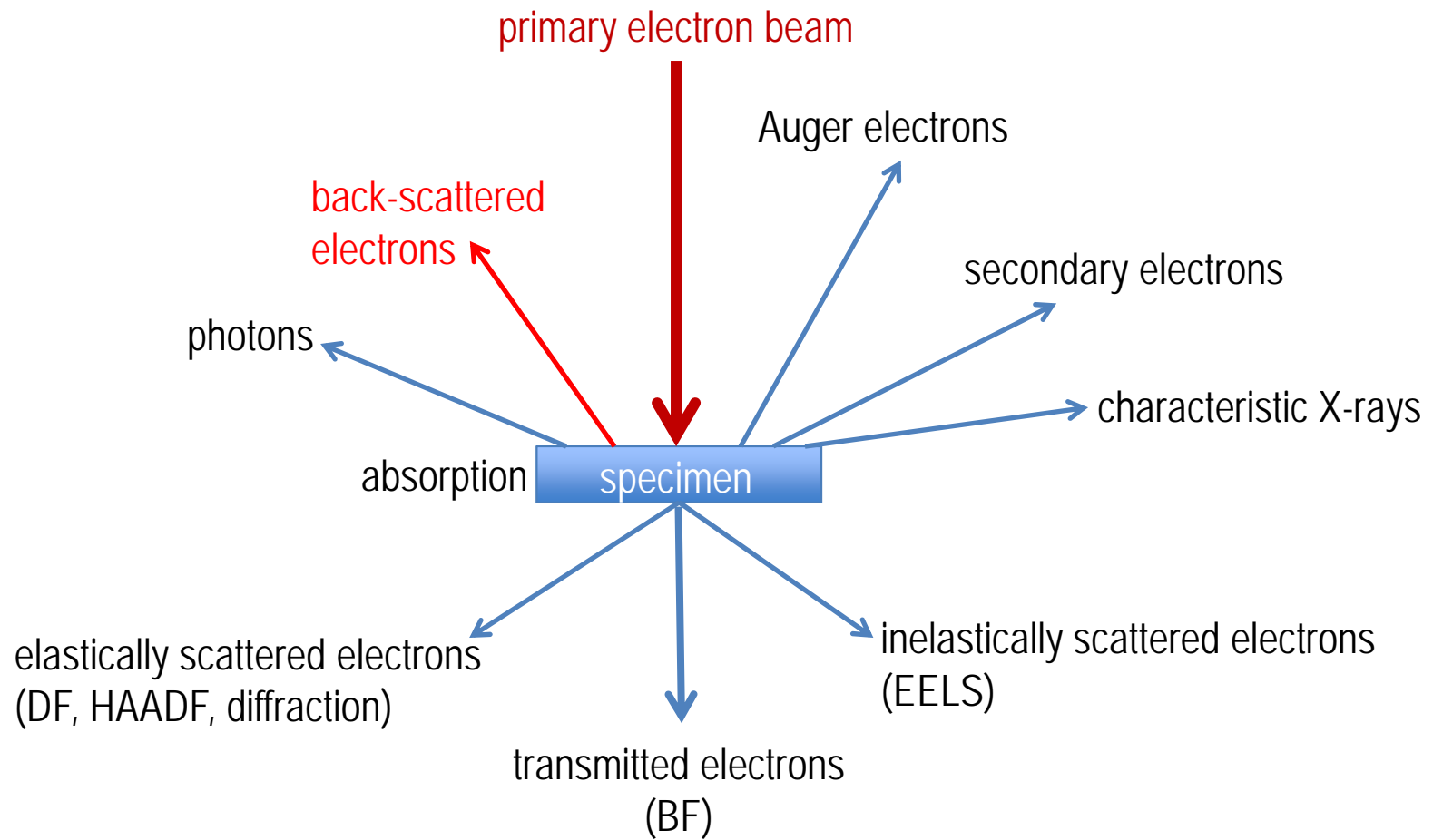


# UHV Techniques

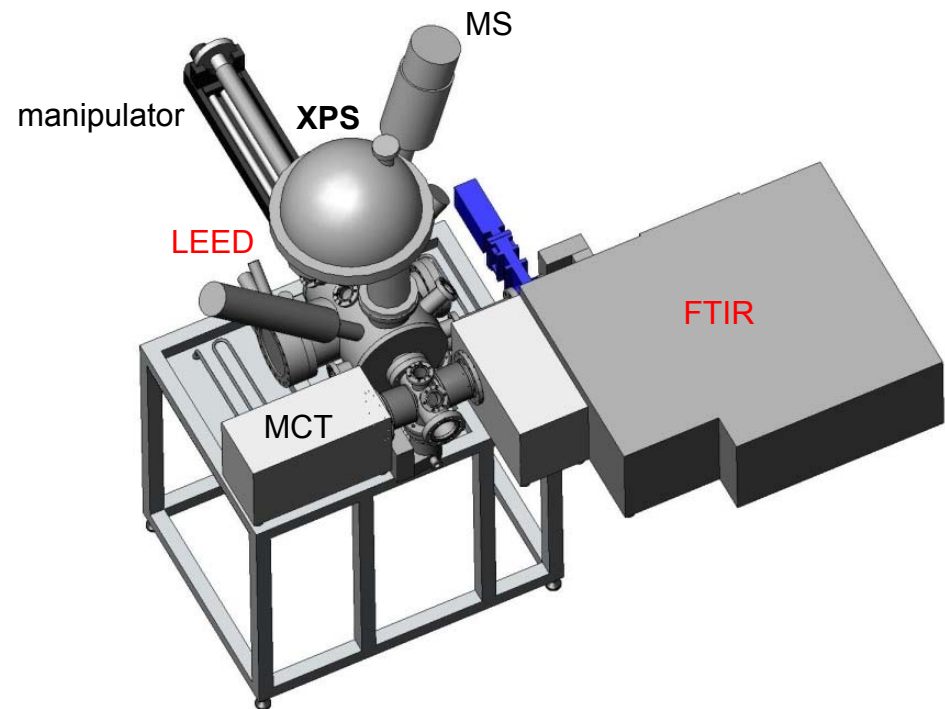
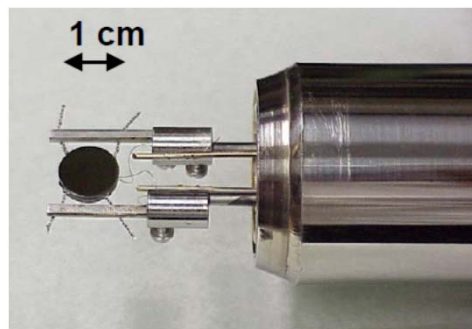
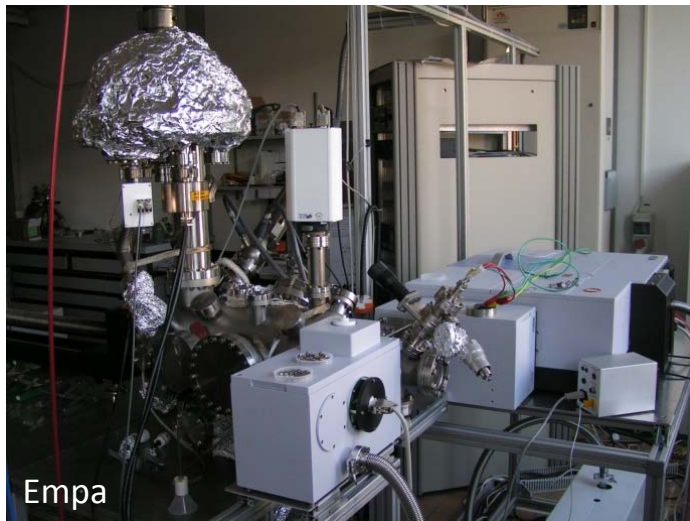
Dr. Davide Ferri  
Paul Scherrer Institut  
 056 310 27 81  
 [davide.ferri@psi.ch](mailto:davide.ferri@psi.ch)

# Electrons-matter interaction



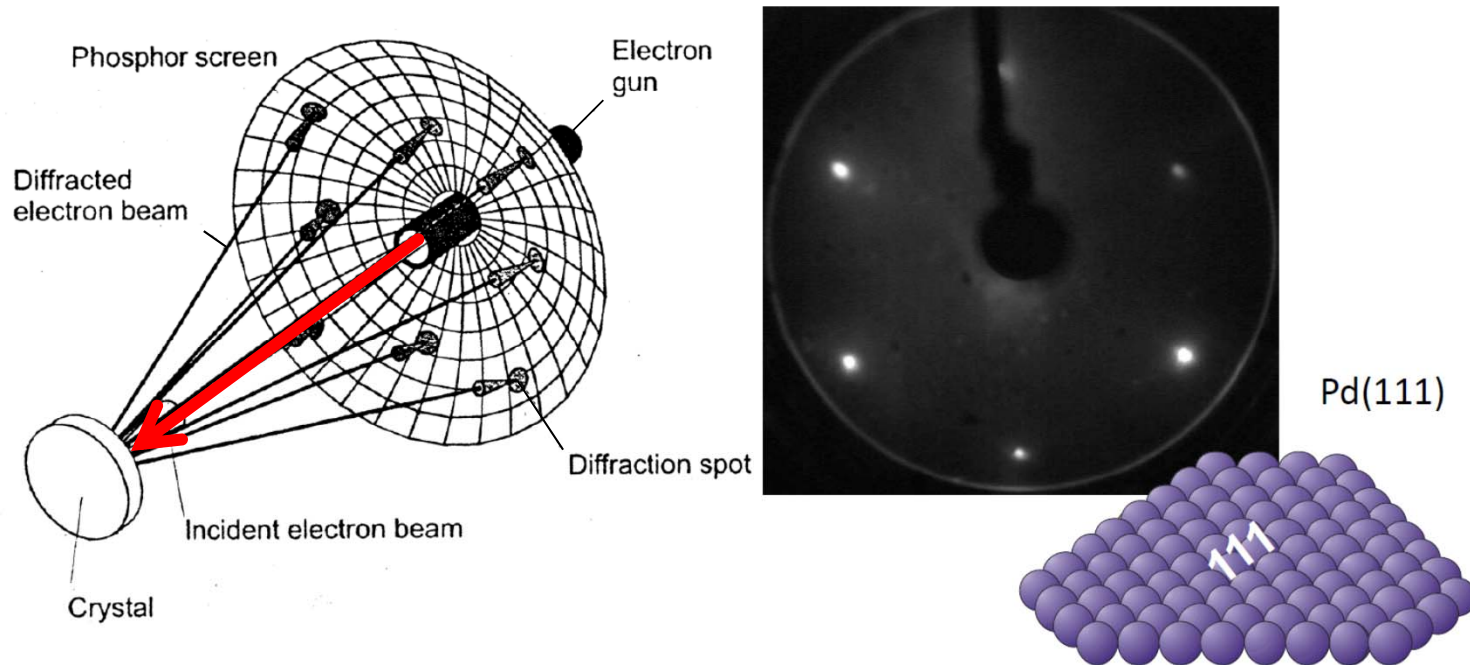
# The UHV setup

- 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



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

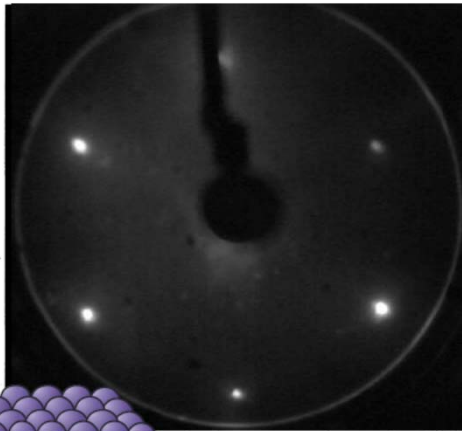
Collimated beam of low energy electrons (20-200 eV)

Wavelength ( $\lambda$ ) of 100 V electrons: ca. 1 Å, < interatomic distances

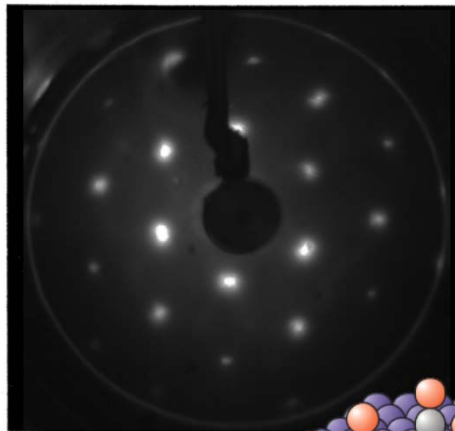
# LEED

## ■ The structure of surfaces

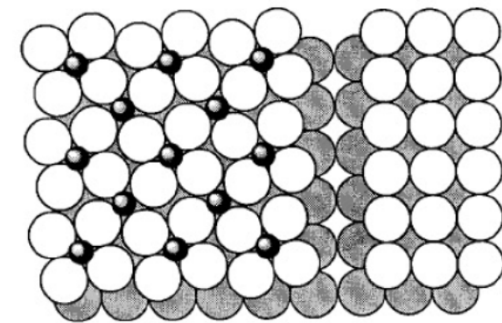
Pd(111) 1x1



(2x2) CO Pd(111)



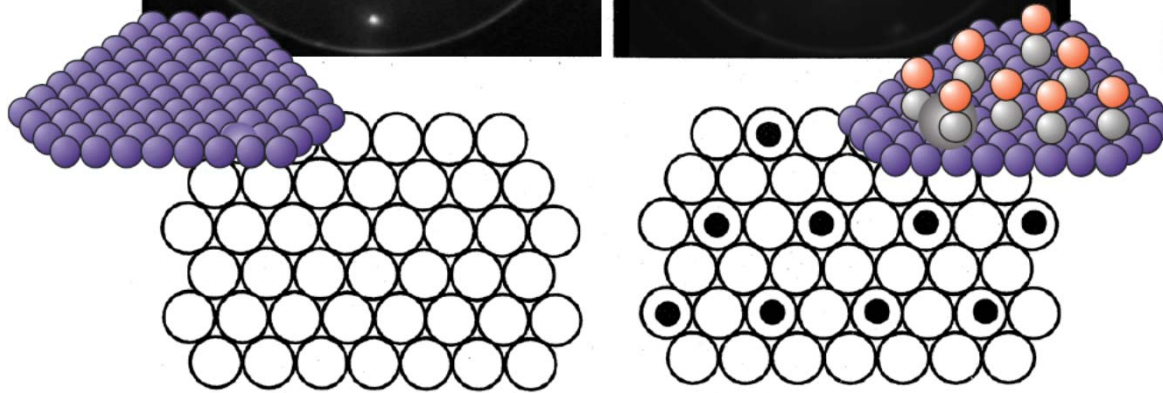
surface reconstruction



Ni(100)-p4g(2x2)-2C

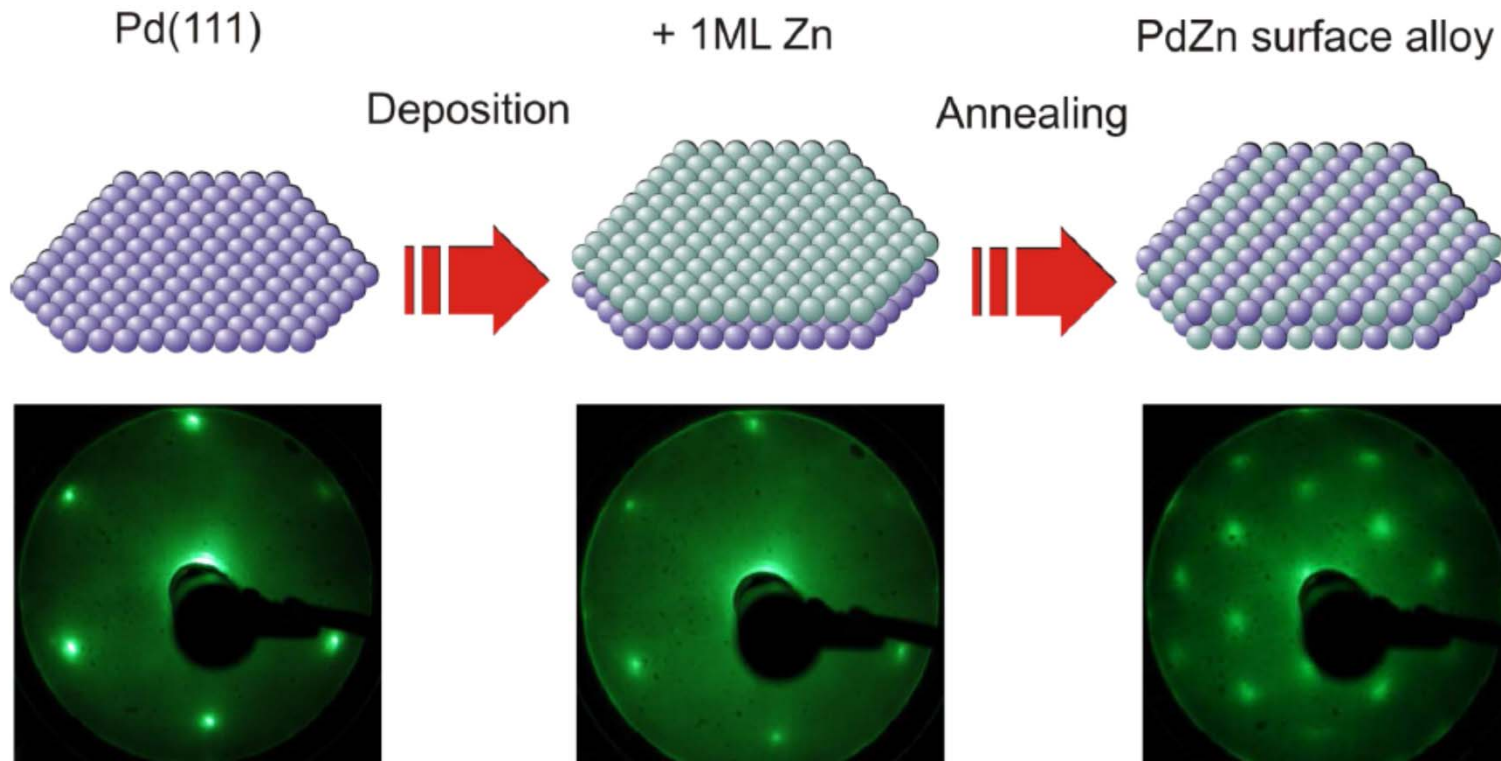
Ni(100)-(1x1)

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



# LEED

## ■ Preparation of PdZn surface alloy for model studies

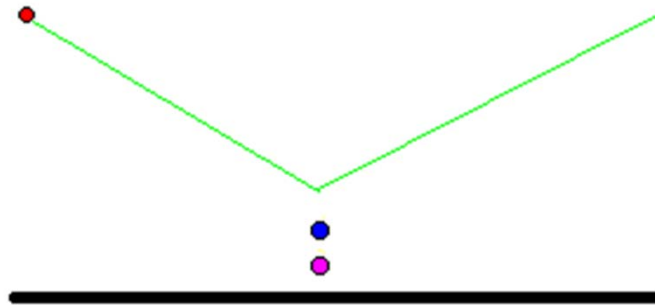


# HREELS

- **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

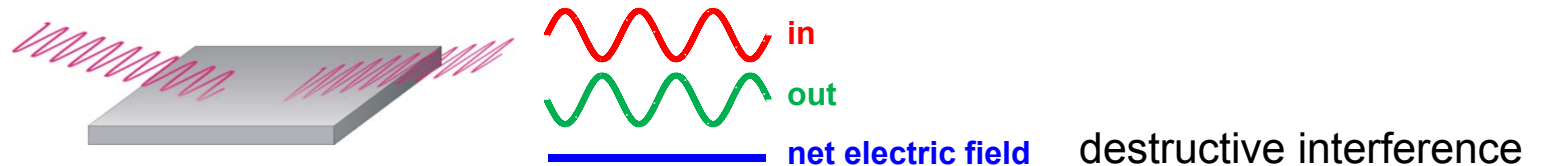


# HREELS

- **How it works – Interaction between electrons and molecule**
- 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 molecule**
- Two scattering modes
- Dipole scattering
  - identical information to a IR spectrum
  - same rules as IR spectroscopy
    - only fundamental transitions allowed
    - only vibrations accompanied by change in dipole moment allowed
    - s-polarized light undergoes  $180^\circ$  phase change upon reflection



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

# The surface selection rule

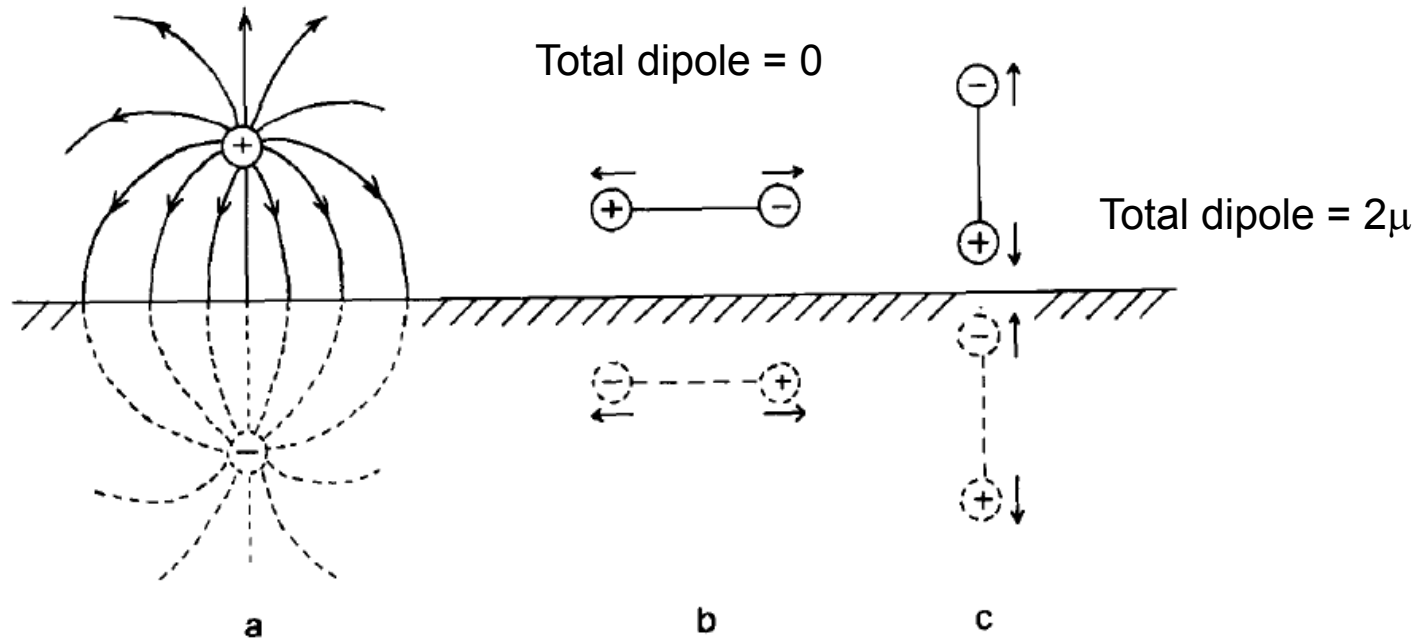


Fig. 1. (a) The lines of force and the electrical "image" resulting from a positive charge over the surface of a conductor (the metal surface is the upper line above the hatched area). (b) The changes during the vibration of a dipole parallel to the surface of the metal; the "image" dipole change is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

# HREELS

- **How it works – Interaction between electrons and molecule**

- 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

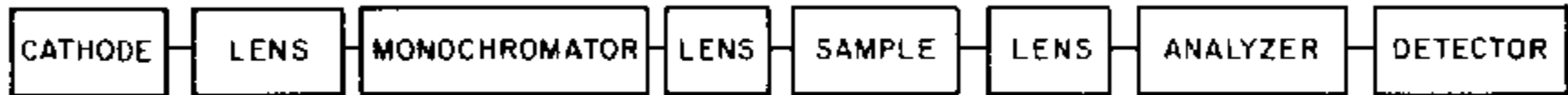
- isotropic (not in the specular direction, but everywhere) but the energy losses still reflect vibrational excitations in the adsorbate

- dominant at high vibrational energy

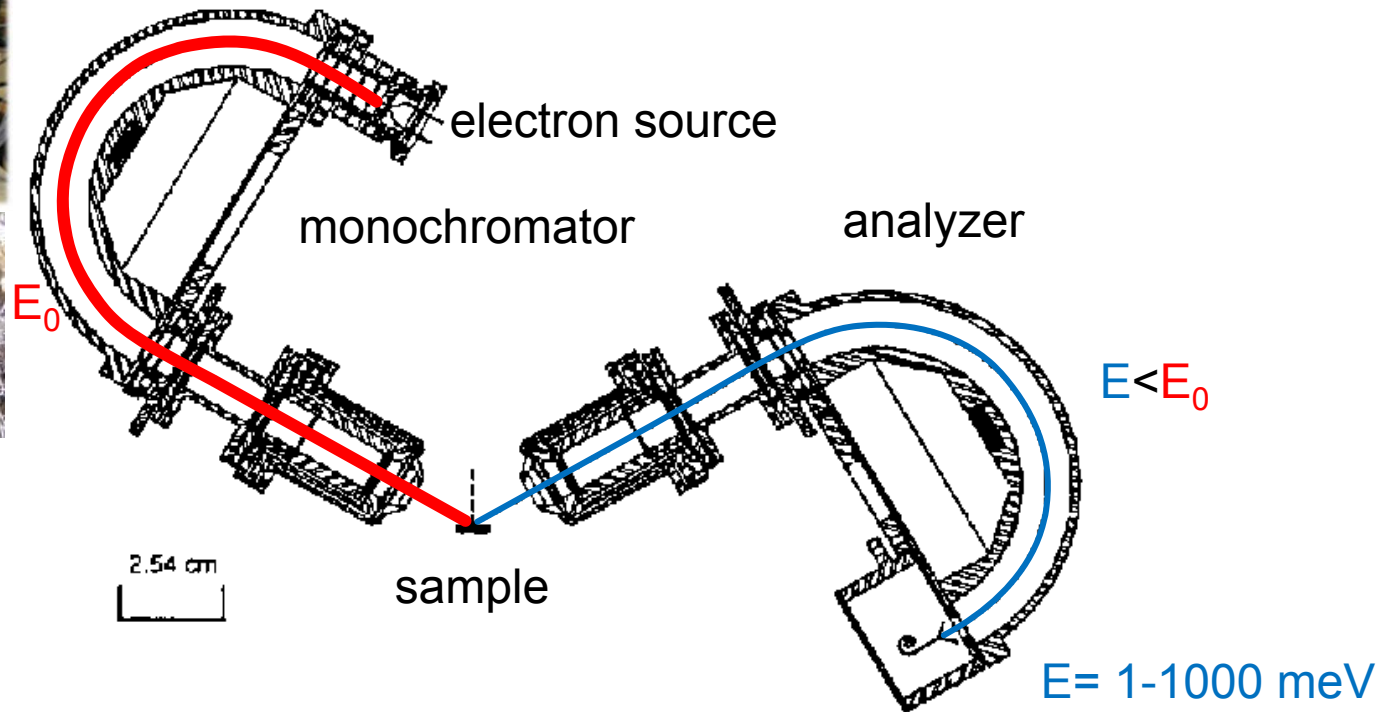
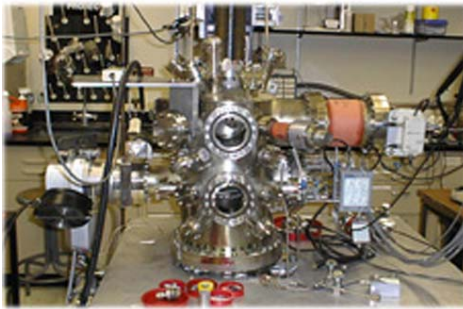
- strong dipole scatterers (CO) are weak impact scatterers

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

# Setup



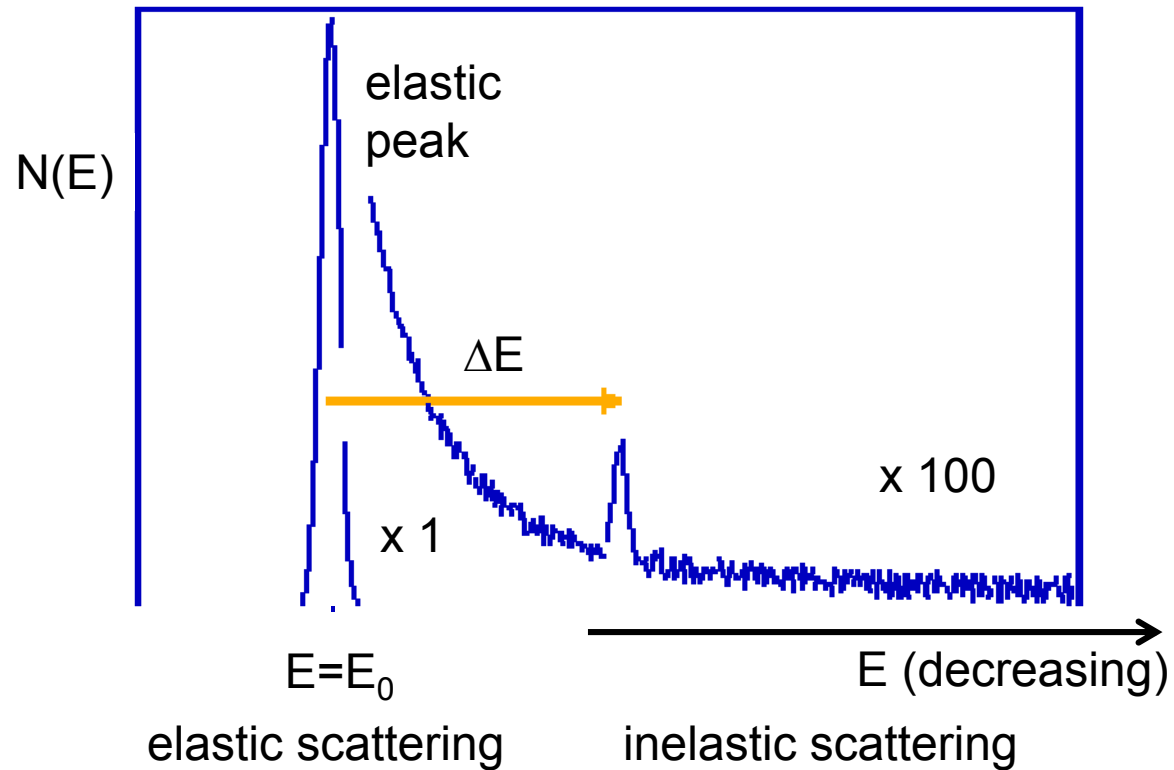
Block diagram of an electron energy loss spectrometer.



$E_0 = 5-10 \text{ eV}$

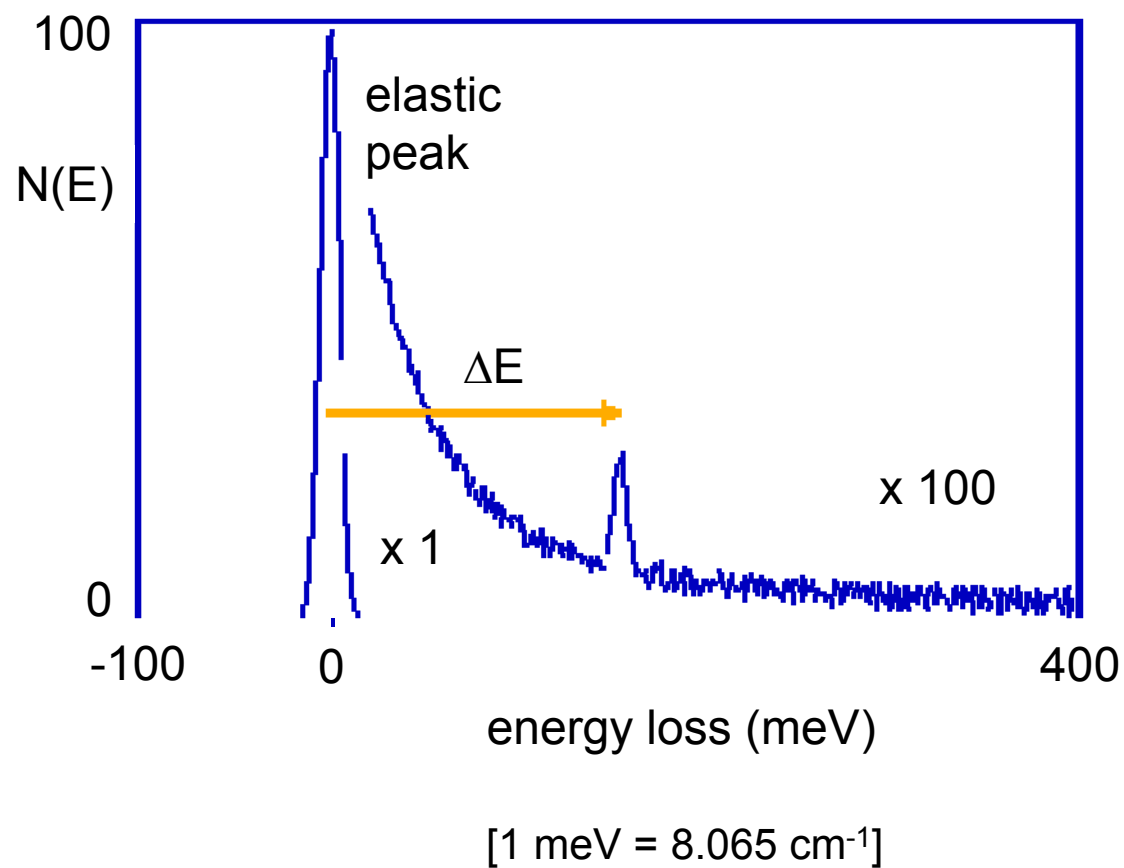
Electrons from a cathode pass through a monochromator, strike the sample, and the energy spectrum of the scattered electrons is probed by a second monochromator.

# The HREELS spectrum



# The HREELS spectrum

$\Delta E$  = energy of vibrational mode of excited adsorbate upon inelastic scattering



# HREELS vs. RAIRS

## ▪ HREELS

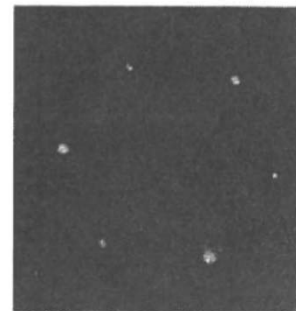
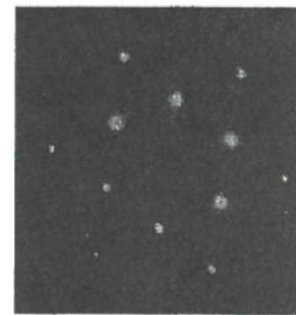
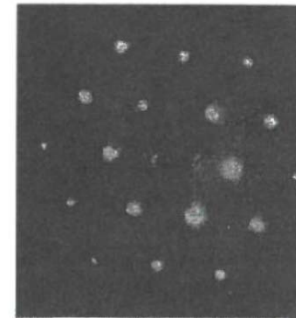
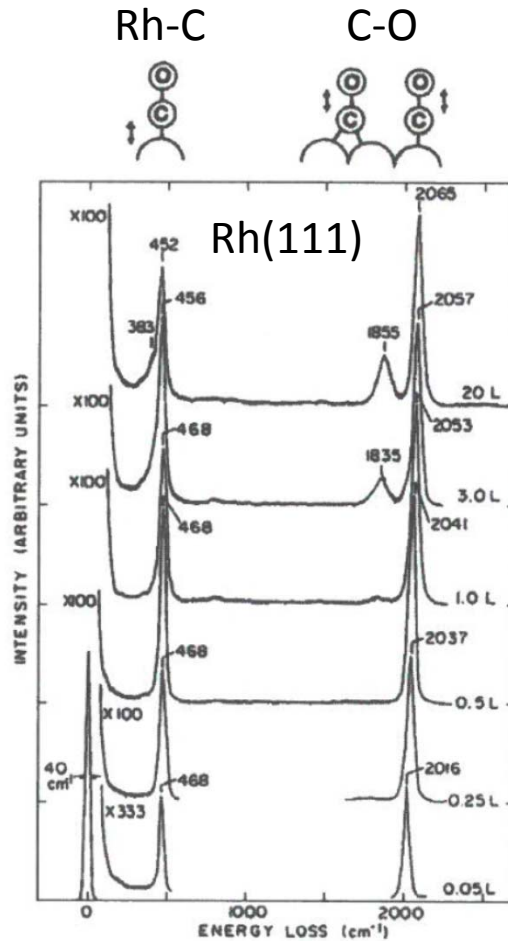
- access to low vibrational energy, e.g. of O (few meV)
- low energy resolution ( $\approx 4$  meV;  $<30$   $\text{cm}^{-1}$ )
- 0.0001 monolayer of CO
- specialised setup (UHV)

## ▪ RAIRS

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



# Examples

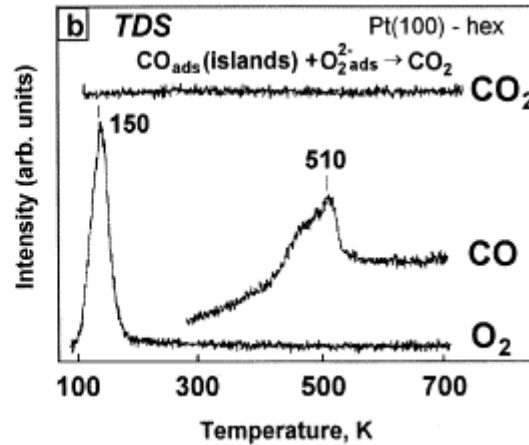
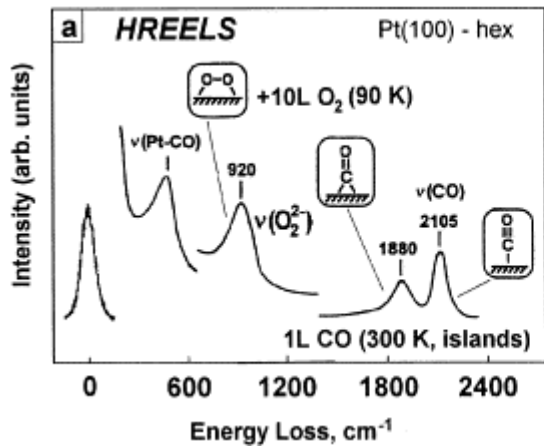


surface structure is known at all points of the experiment (LEED)

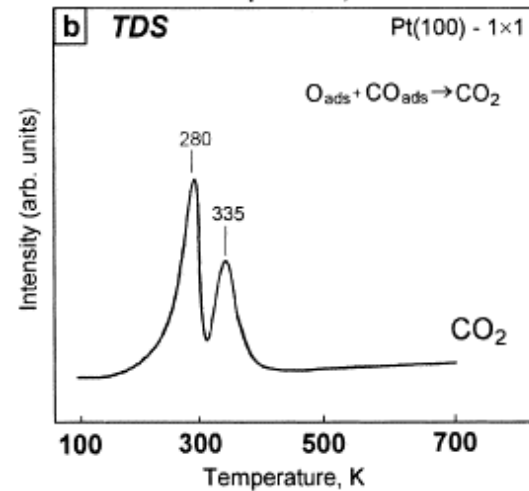
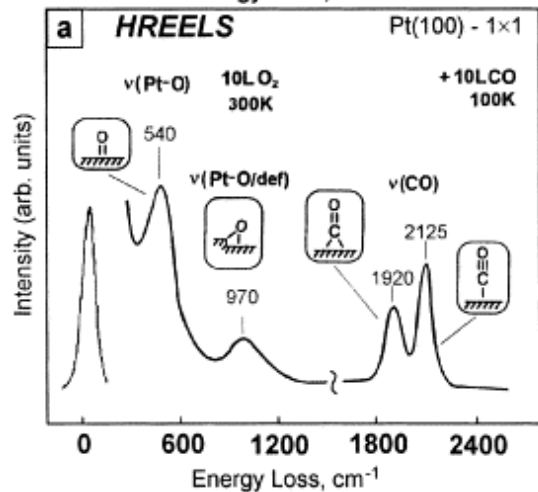
enhanced frequency range compared to FTIR

# Examples

## ■ Access to low vibrational energy

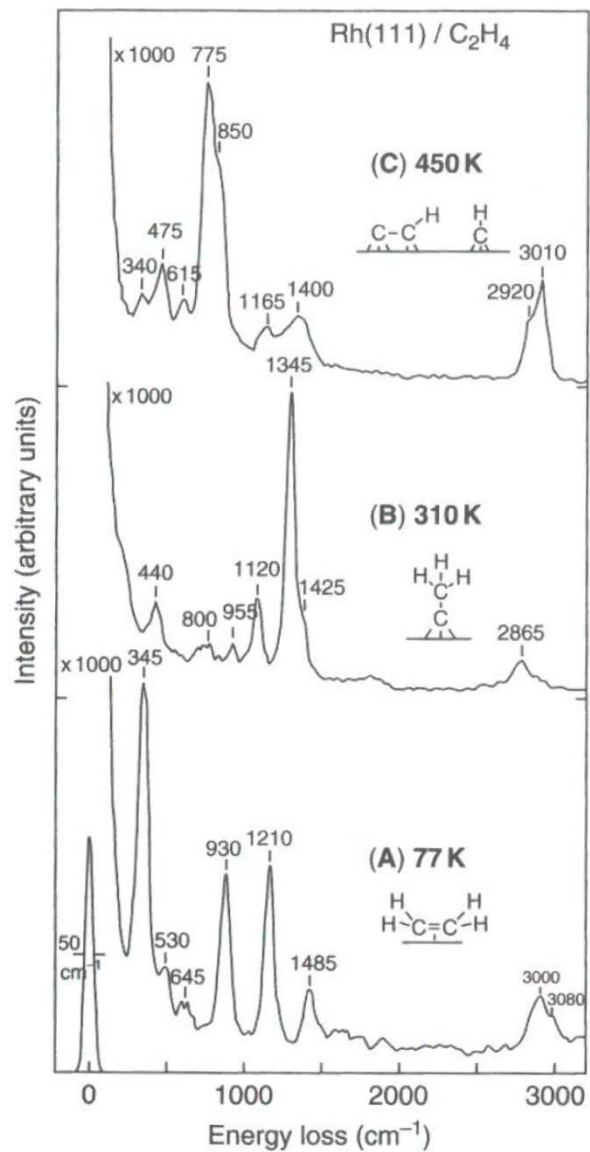


1. CO adsorption at 300 K
2. Pt(100)-(hex) surface covered by CO/(1x1) islands
3. O<sub>2</sub> adsorption at 90 K



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

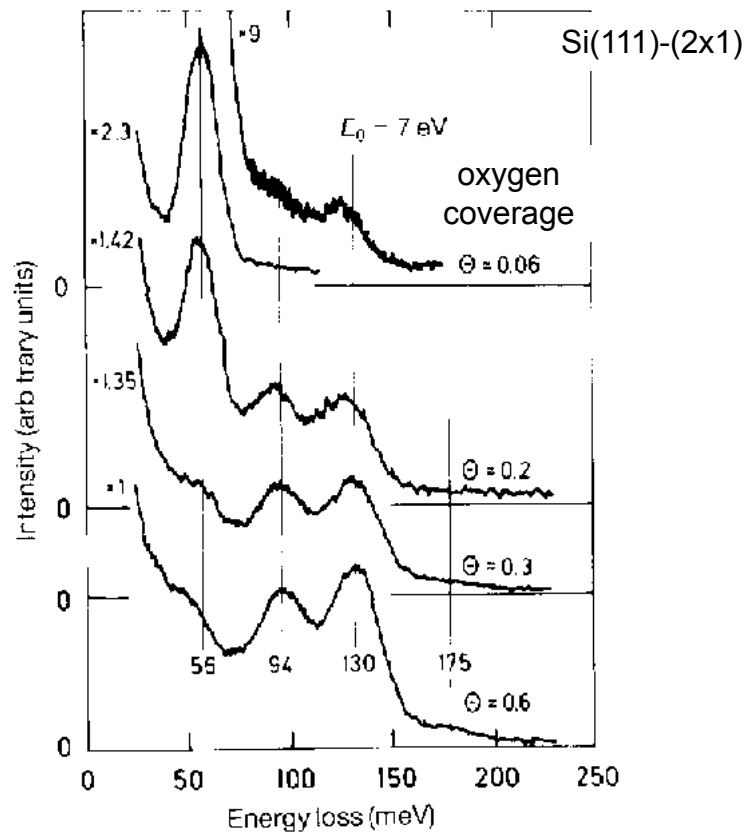
# HREELS | Examples



# Examples

## ■ HREELS of surfaces

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



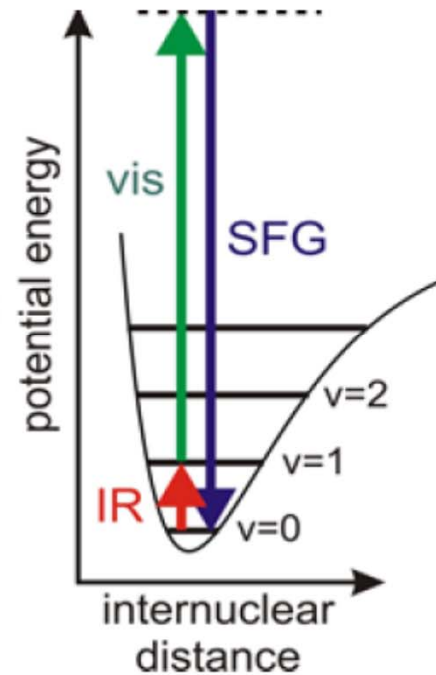
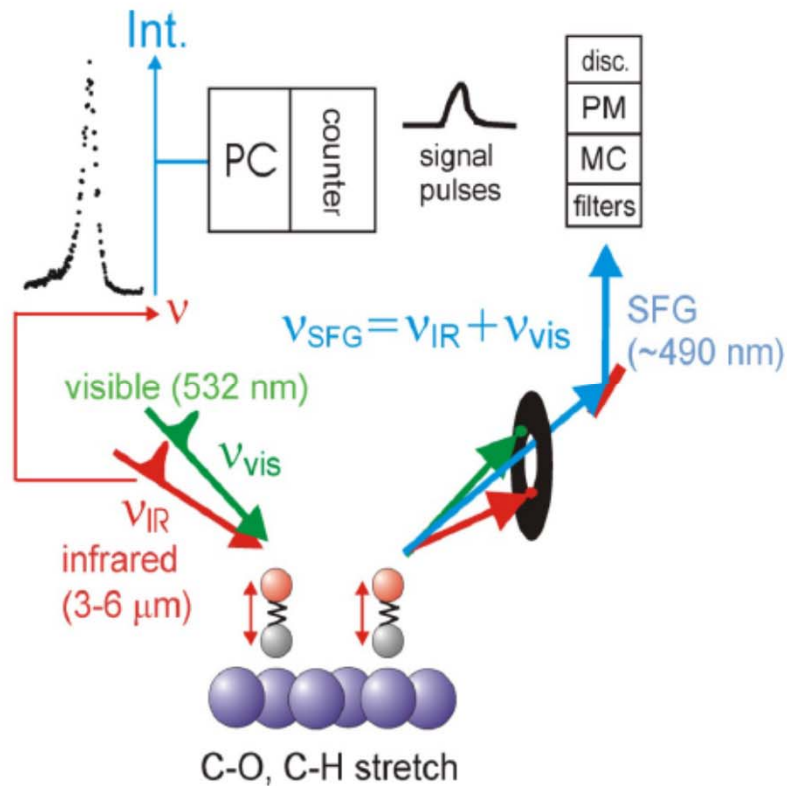
# SFG

- **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

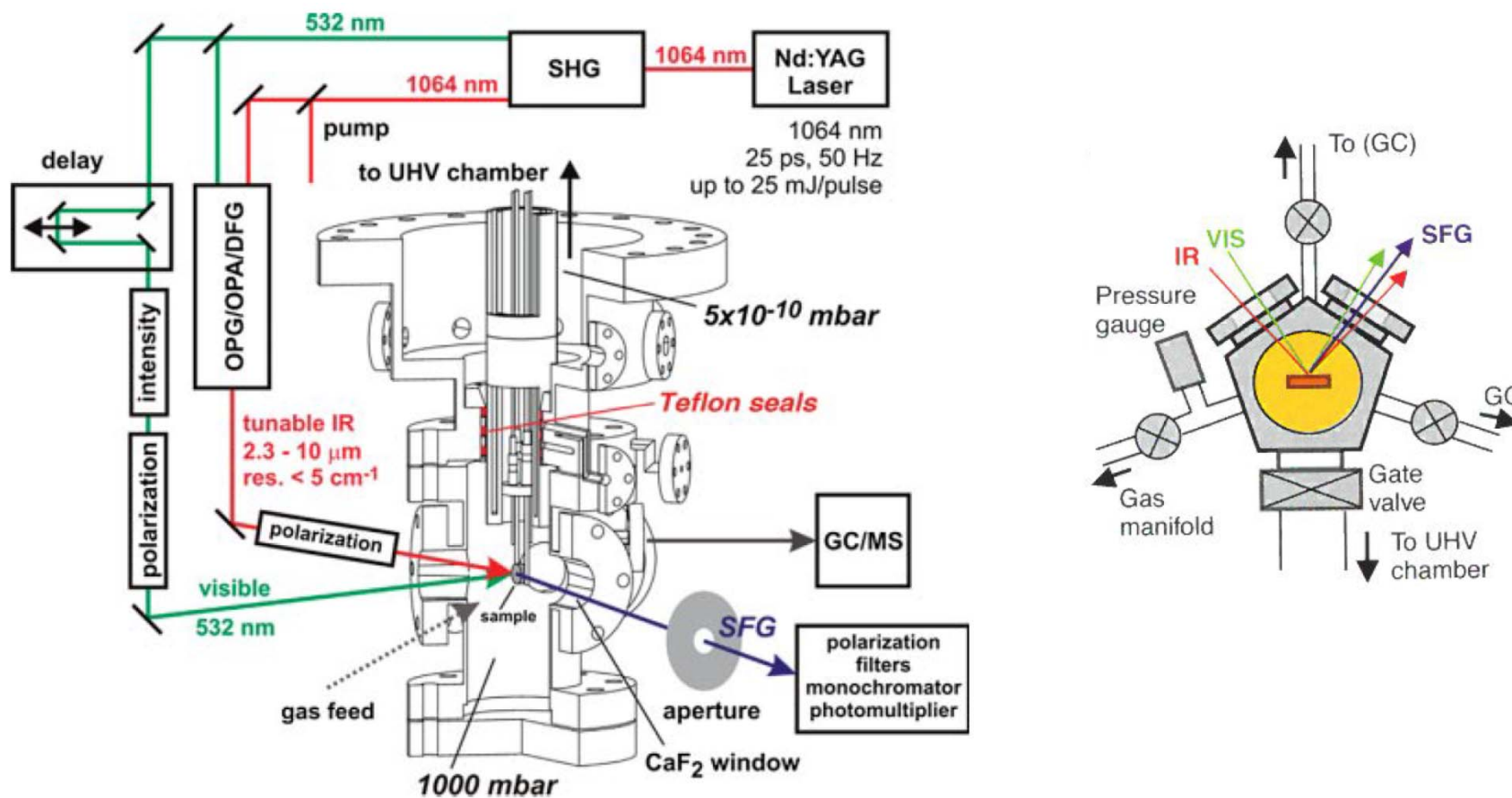
# SFG

## ■ 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

# SFG

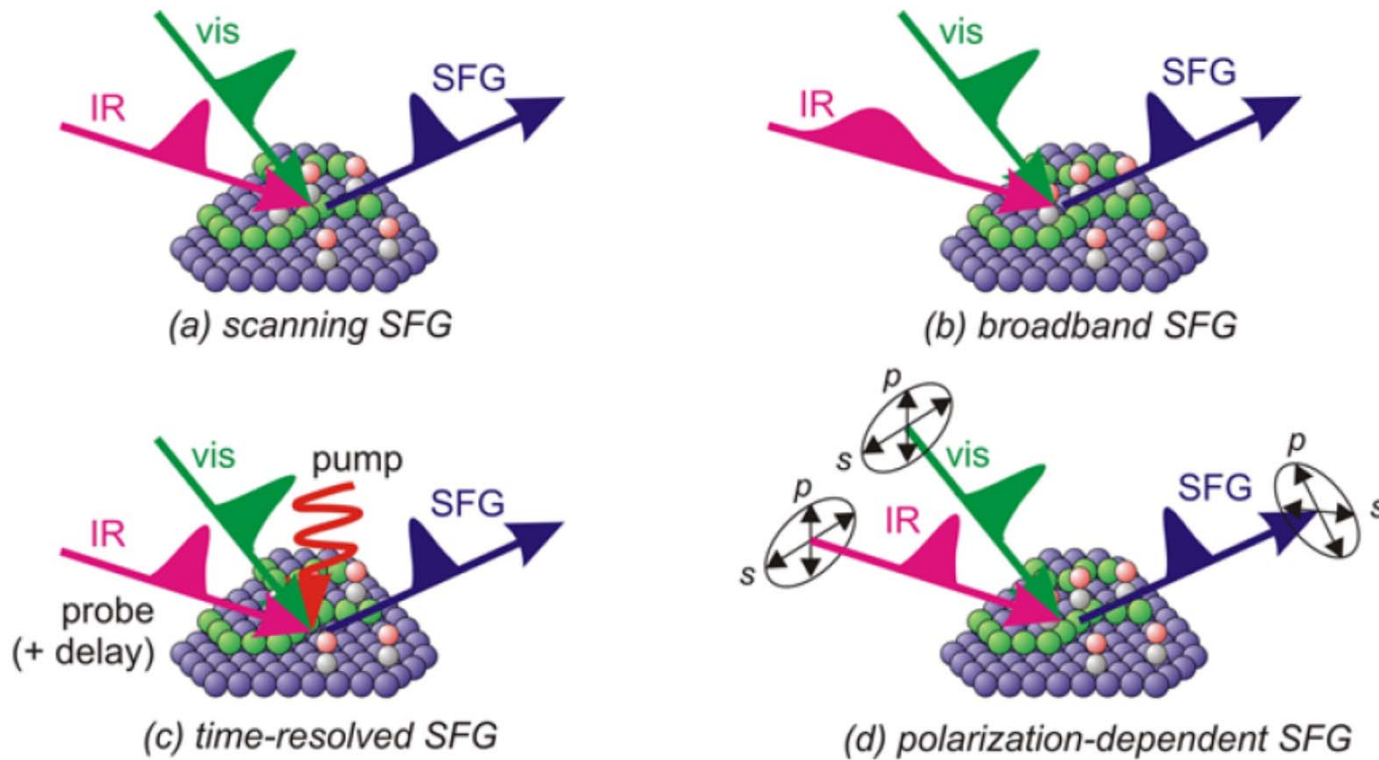
## ■ Setup





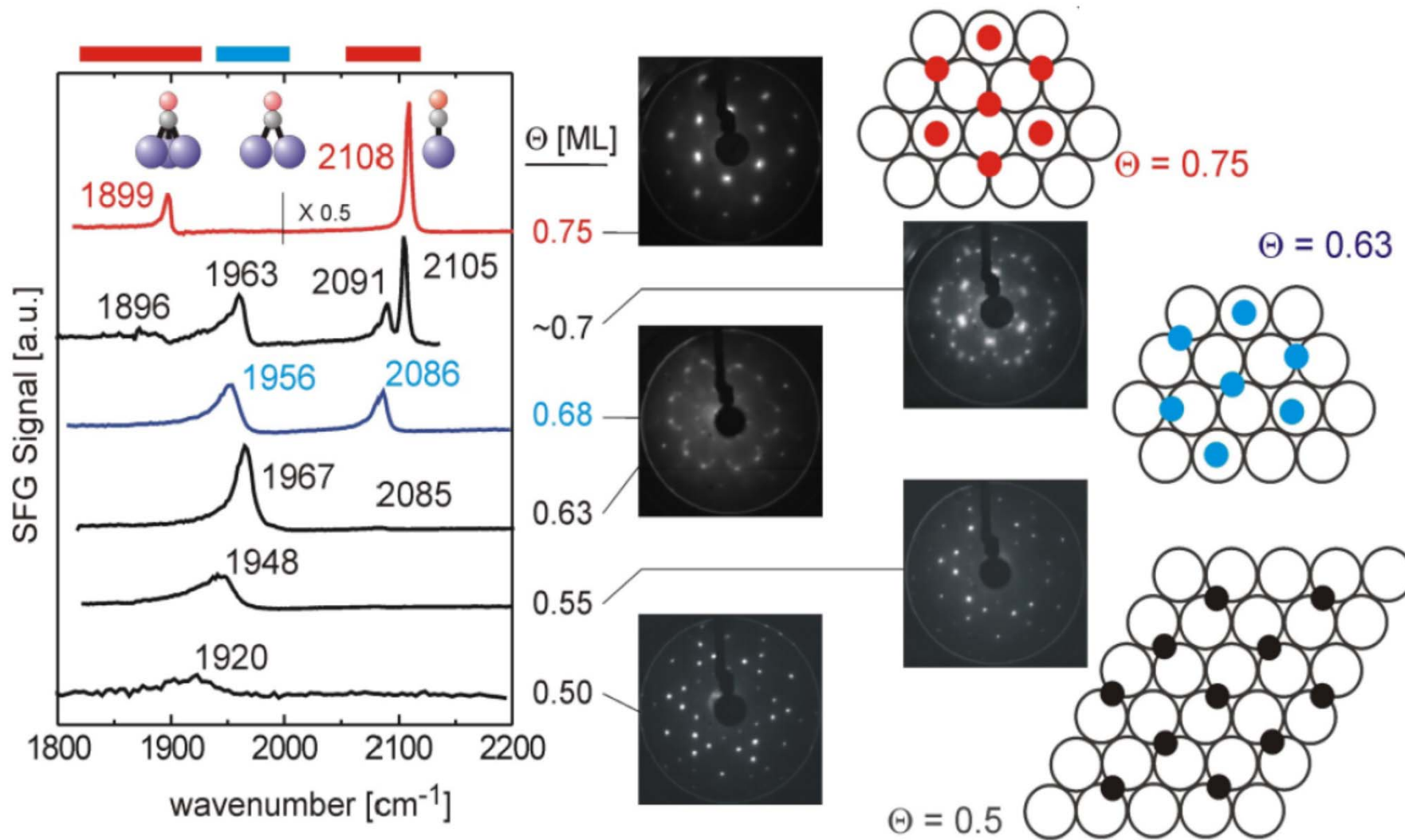
# SFG

## ■ Modes of operation



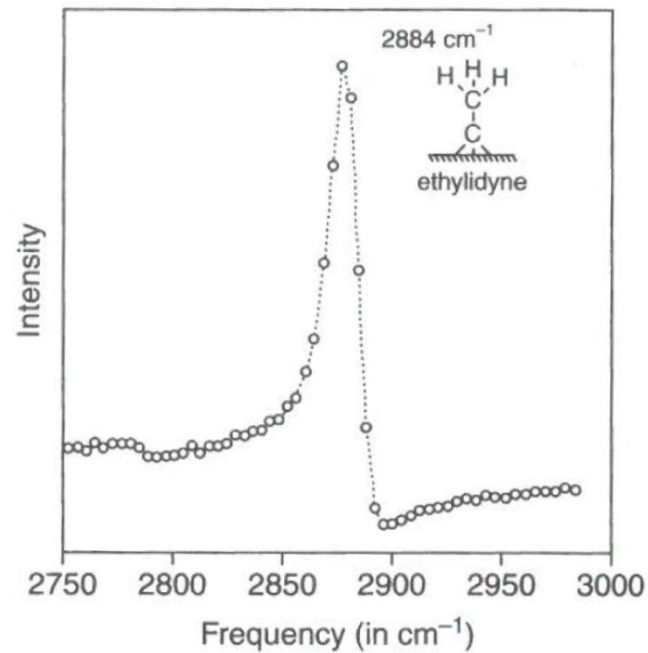
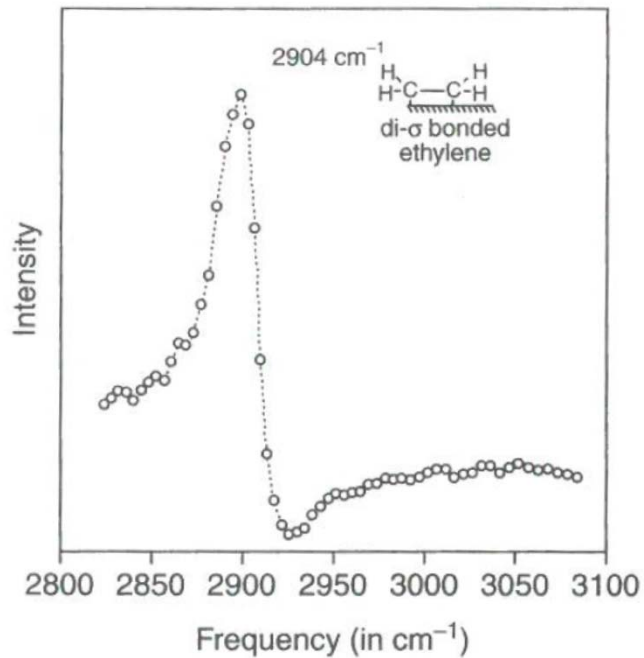
# SFG

## ■ Structure assignment in combination with LEED



# SFG

## ■ Hydrocarbon fragments on Pt(111)



# RAIRS

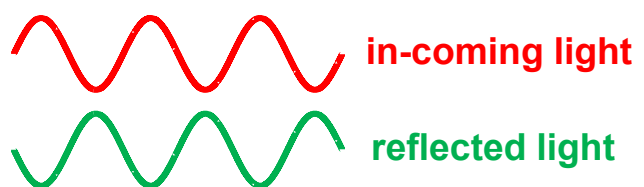
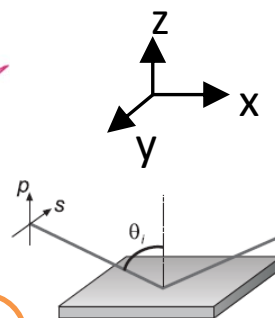
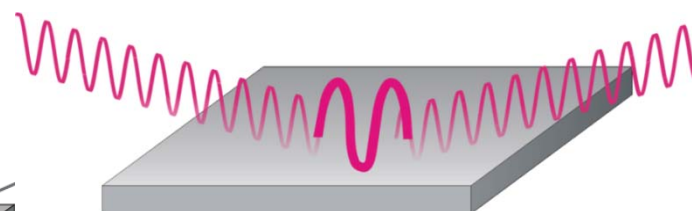
- Reflection absorption IR spectroscopy
  - Specular/external reflection method

Perpendicular (s-) polarization (y-axis)



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

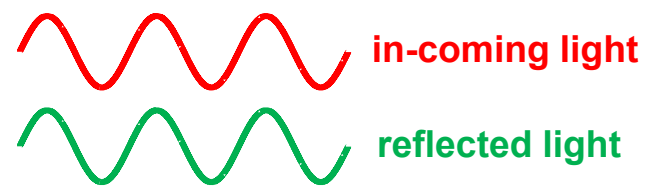
Parallel: parallel to the plane of incident light



net electric field  
near surface

**destructive interference**

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



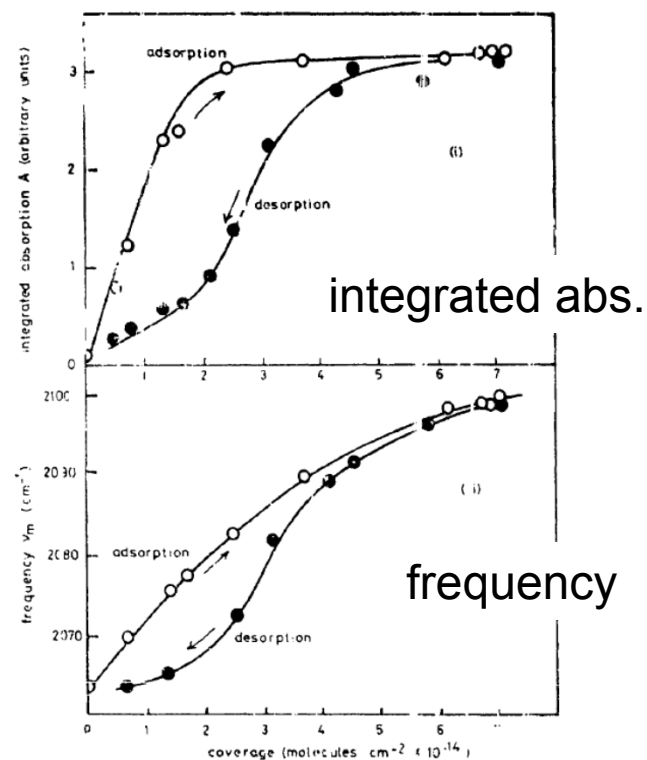
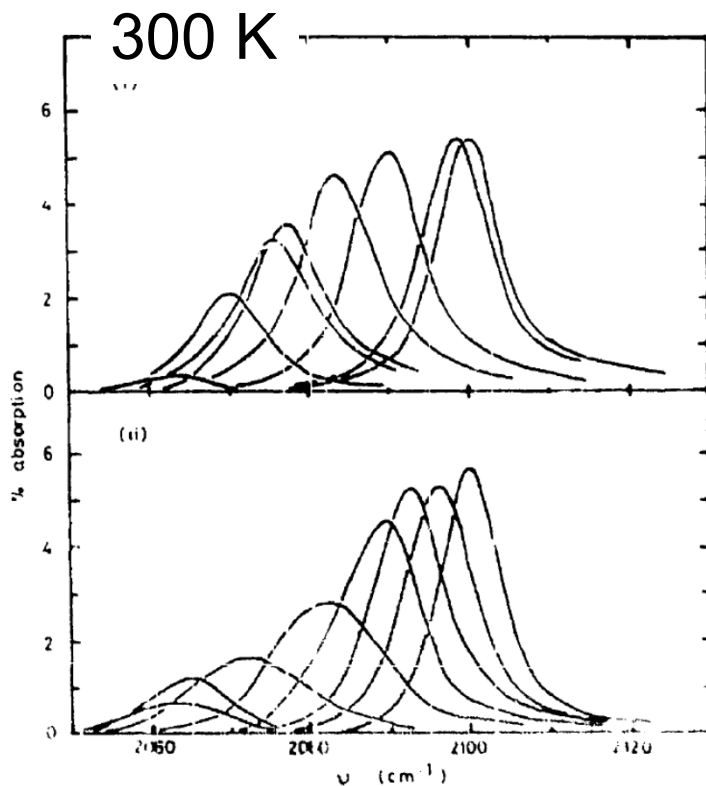
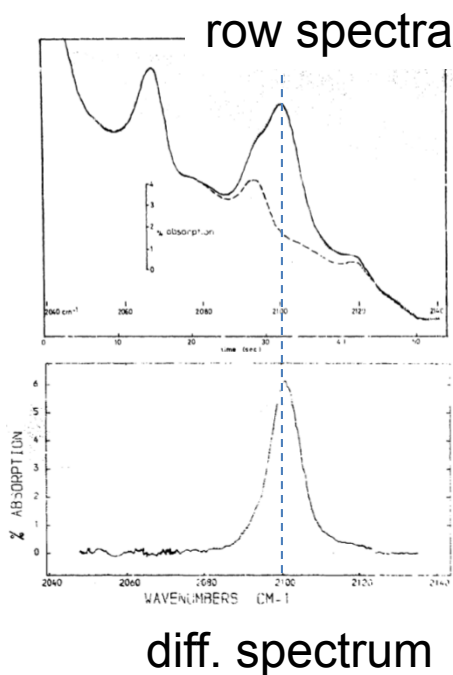
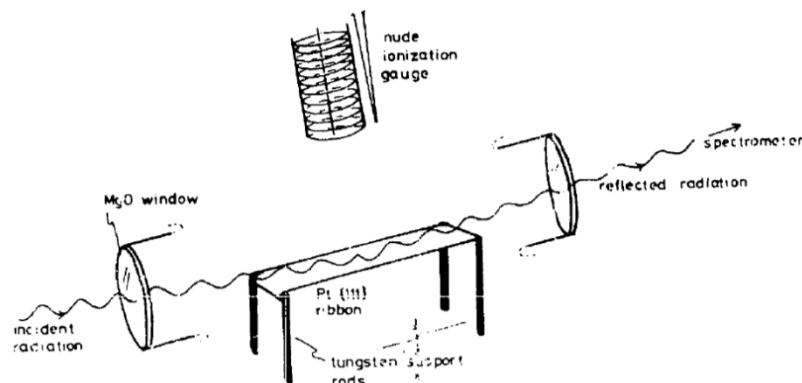
net electric field  
near surface

**constructive interference**

p-polarization is exploited

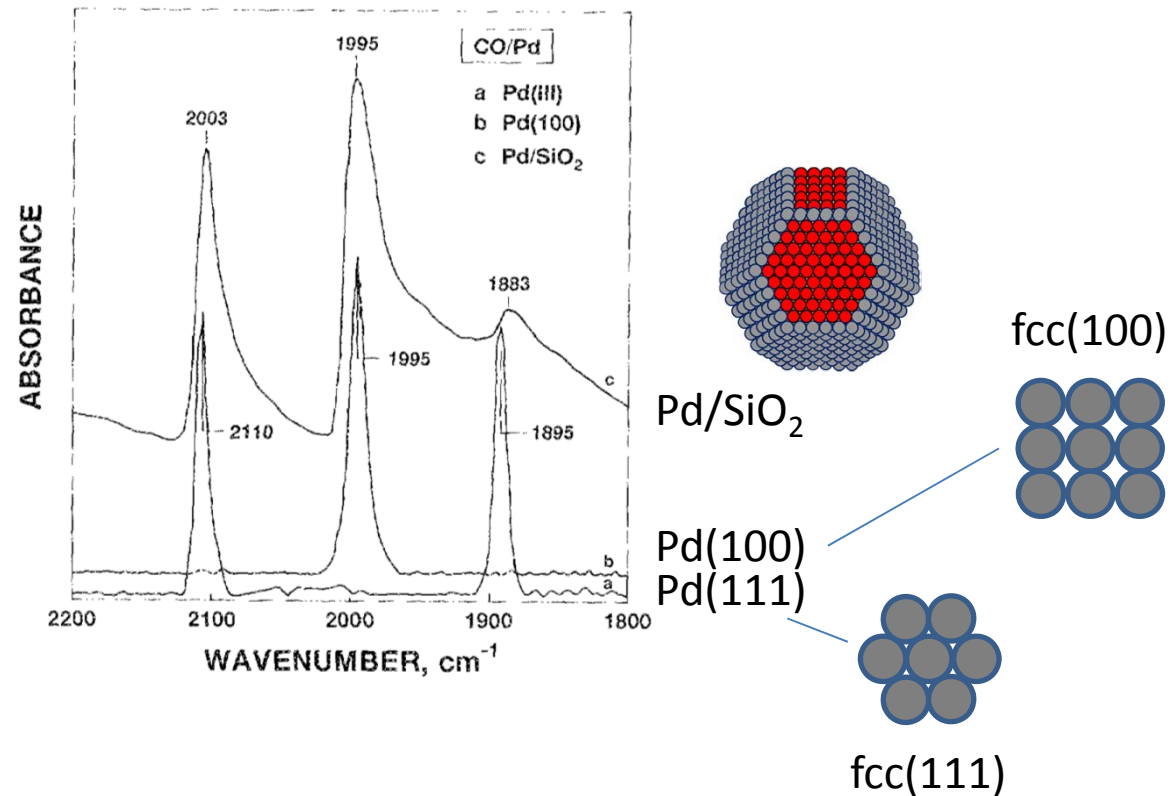
# CO adsorption on Pt(111)

- $\nu(\text{CO})$  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



# RAIRS

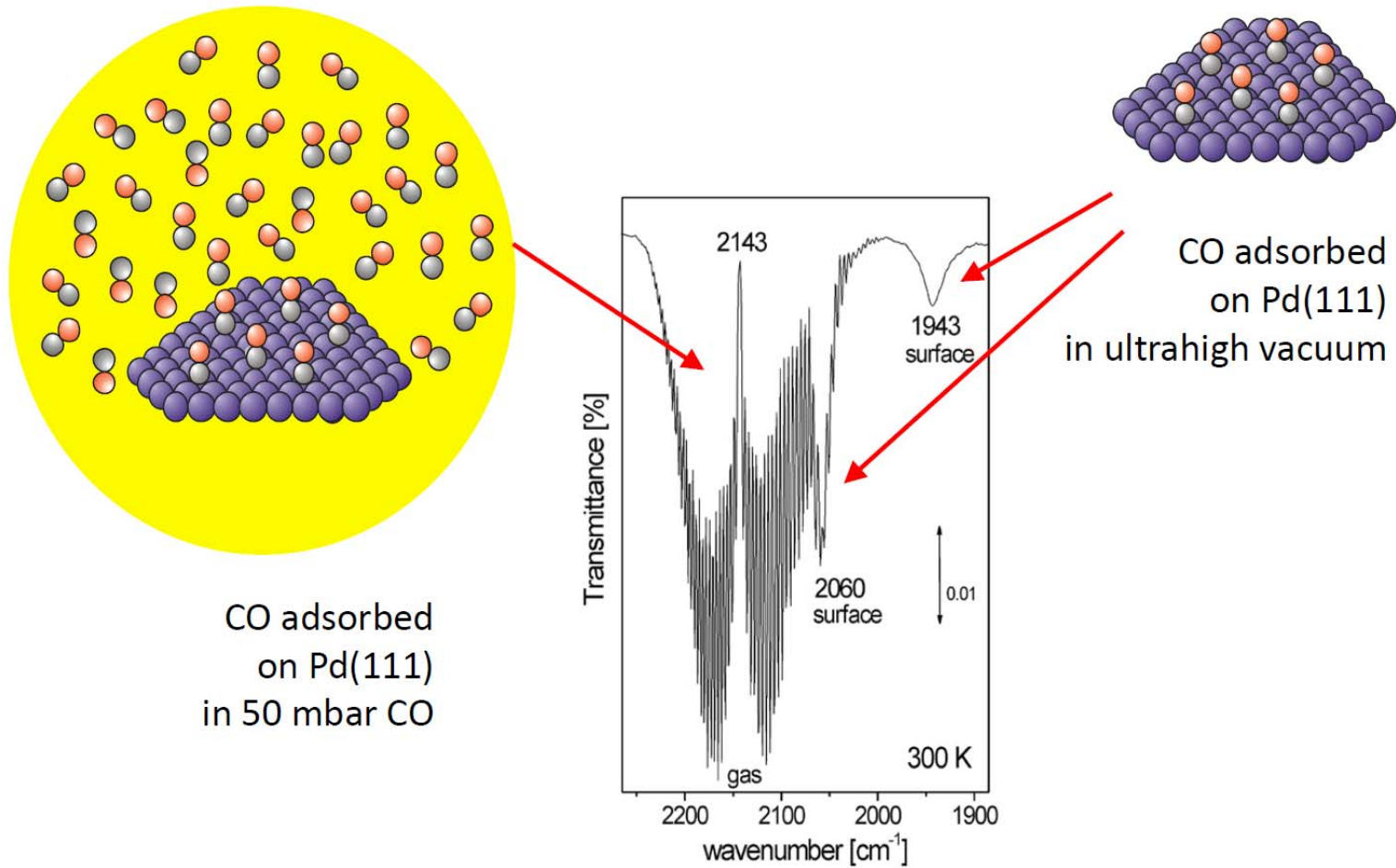
- **Single crystal vs. Powder**
  - reference for assignment of signals on technical catalysts!



# RAIRS

- **Non-UHV conditions**

- Superposition of contributions from surface and gas phase



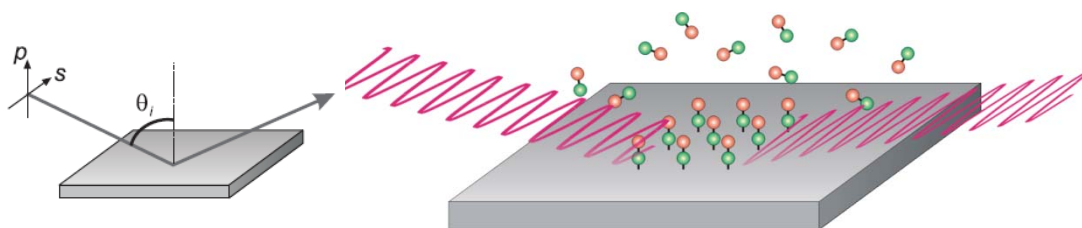


# Phase-modulation IRRAS (PM-IRRAS)

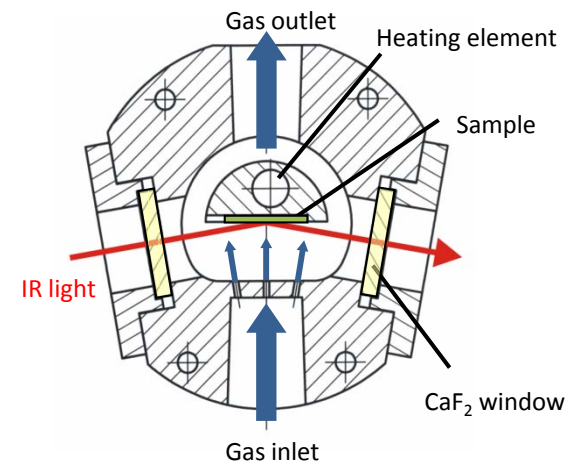
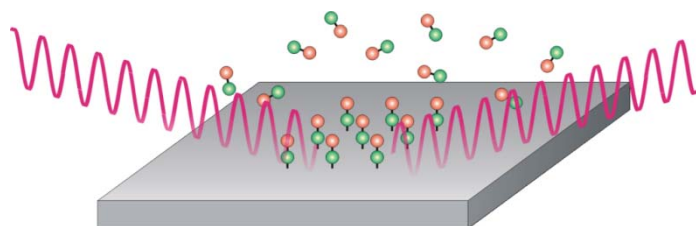
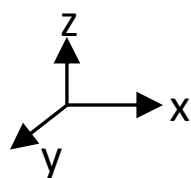
## ■ Non-UHV experiments

- 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

$$R_p - R_s = \Delta R$$

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

