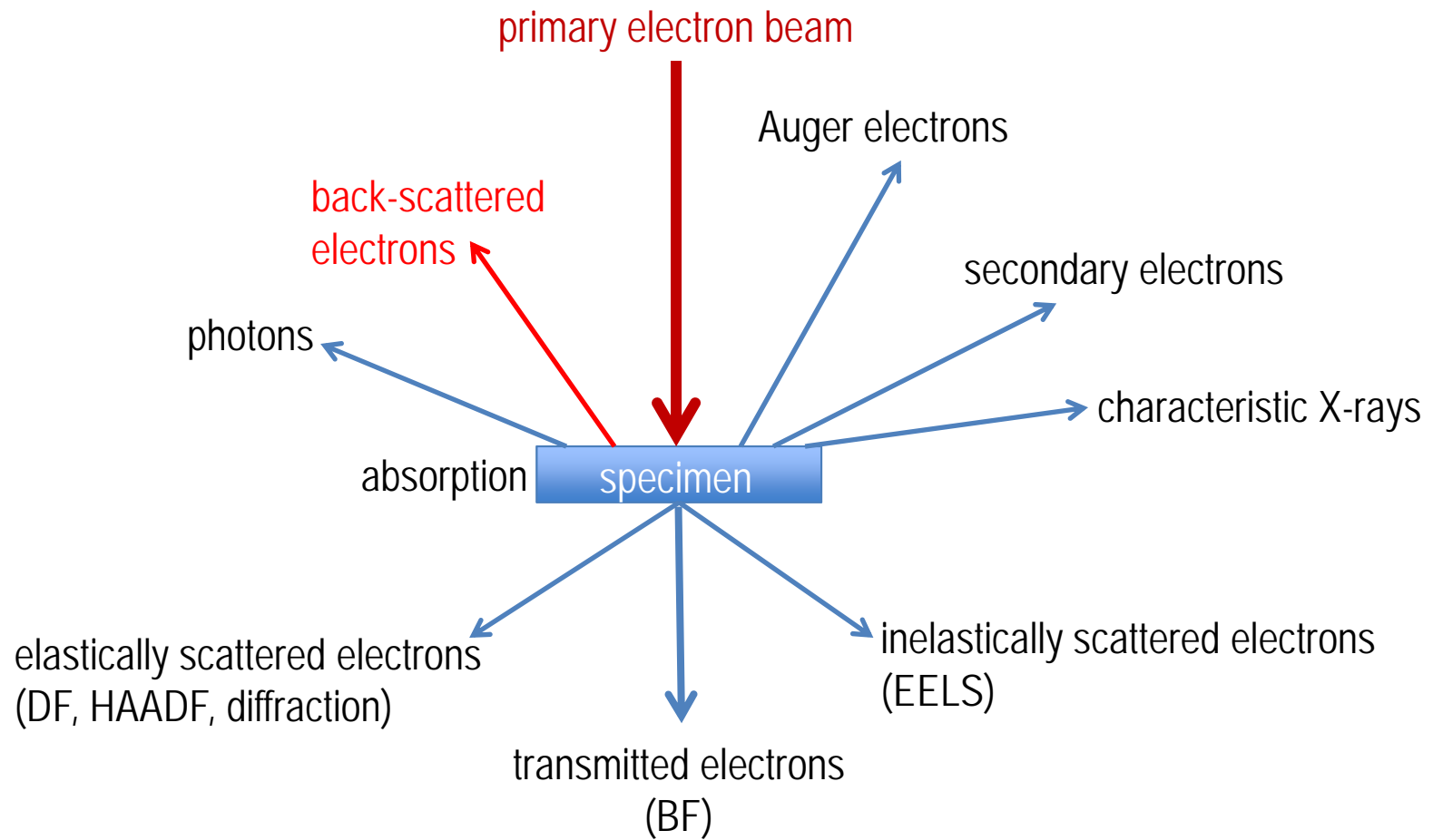


UHV Techniques

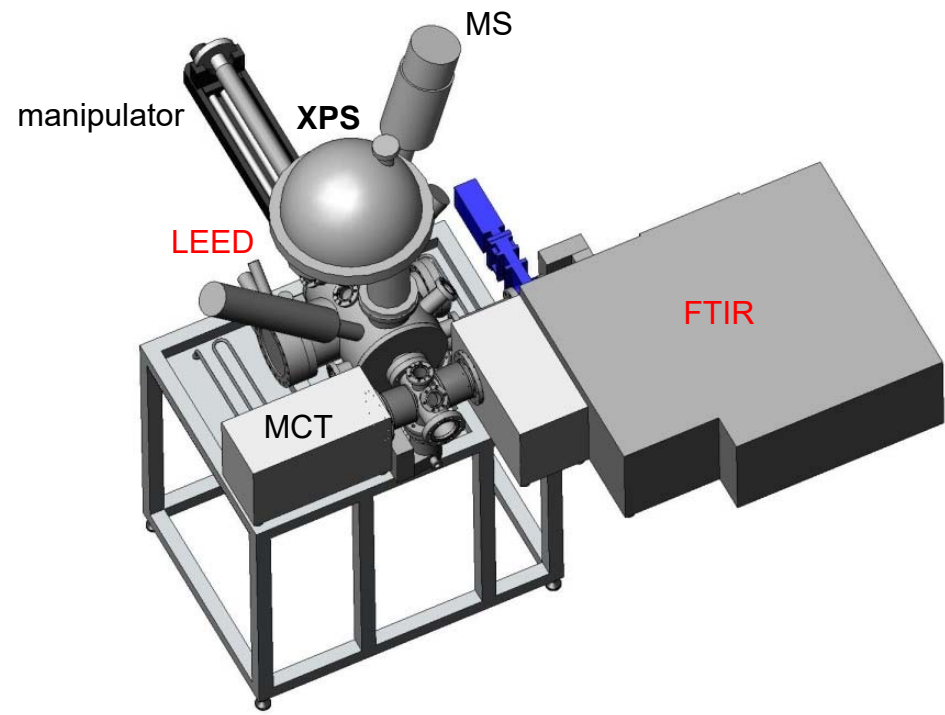
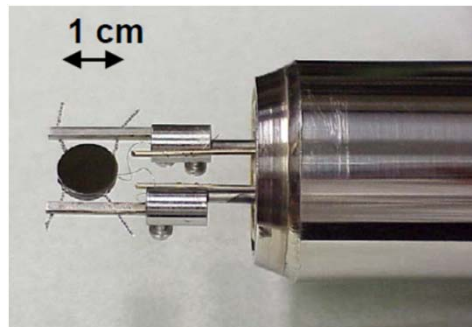
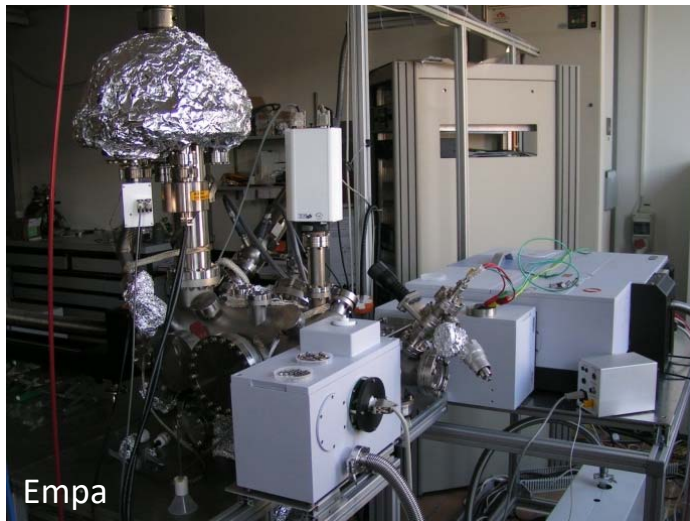
Dr. Davide Ferri
Paul Scherrer Institut
 056 310 27 81
 davide.ferri@psi.ch

Electrons-matter interaction



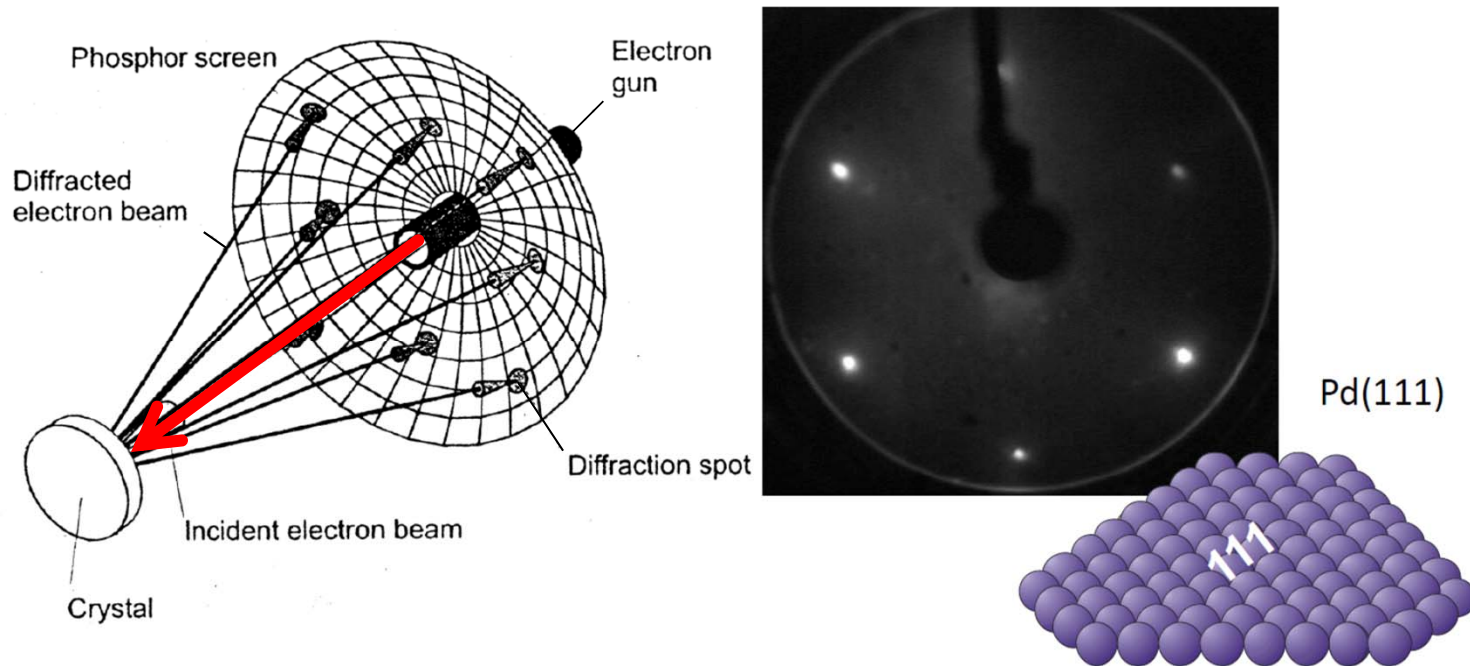
The UHV setup

- 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



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

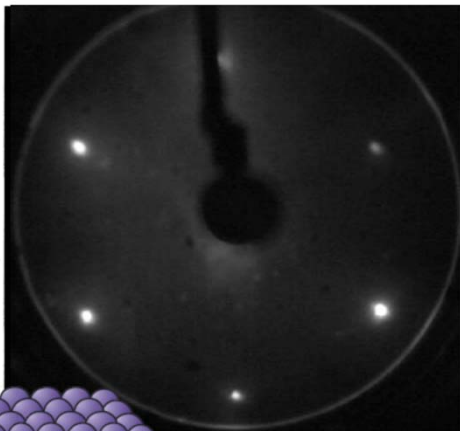
Collimated beam of low energy electrons (20-200 eV)

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

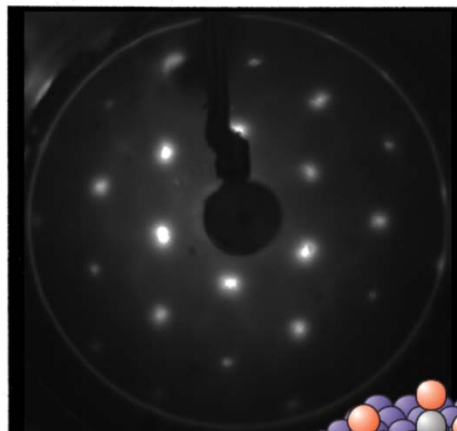
LEED

■ The structure of surfaces

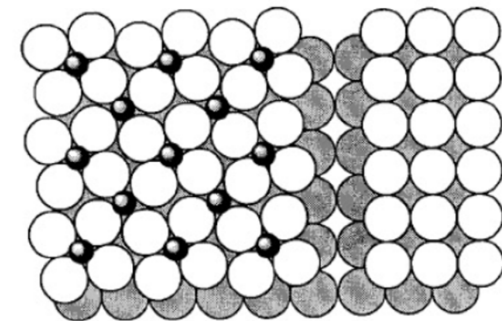
Pd(111) 1x1



(2x2) CO Pd(111)



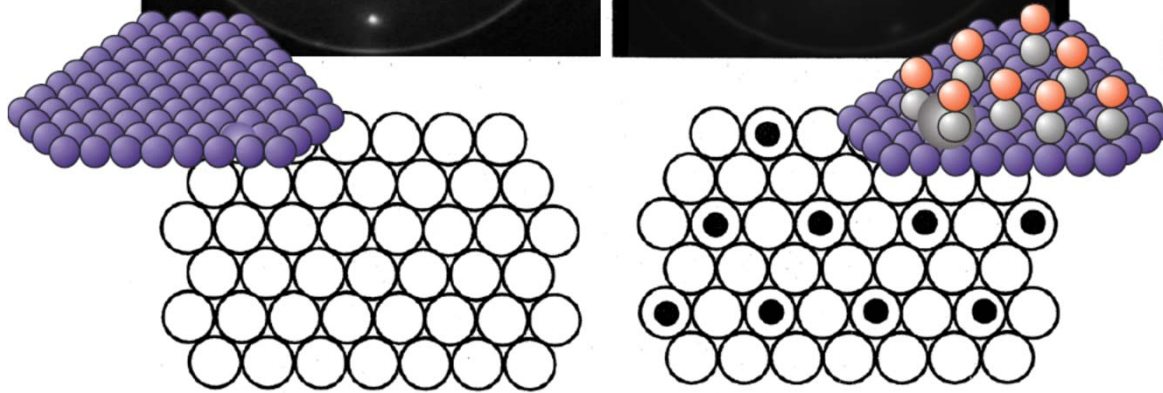
surface reconstruction



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

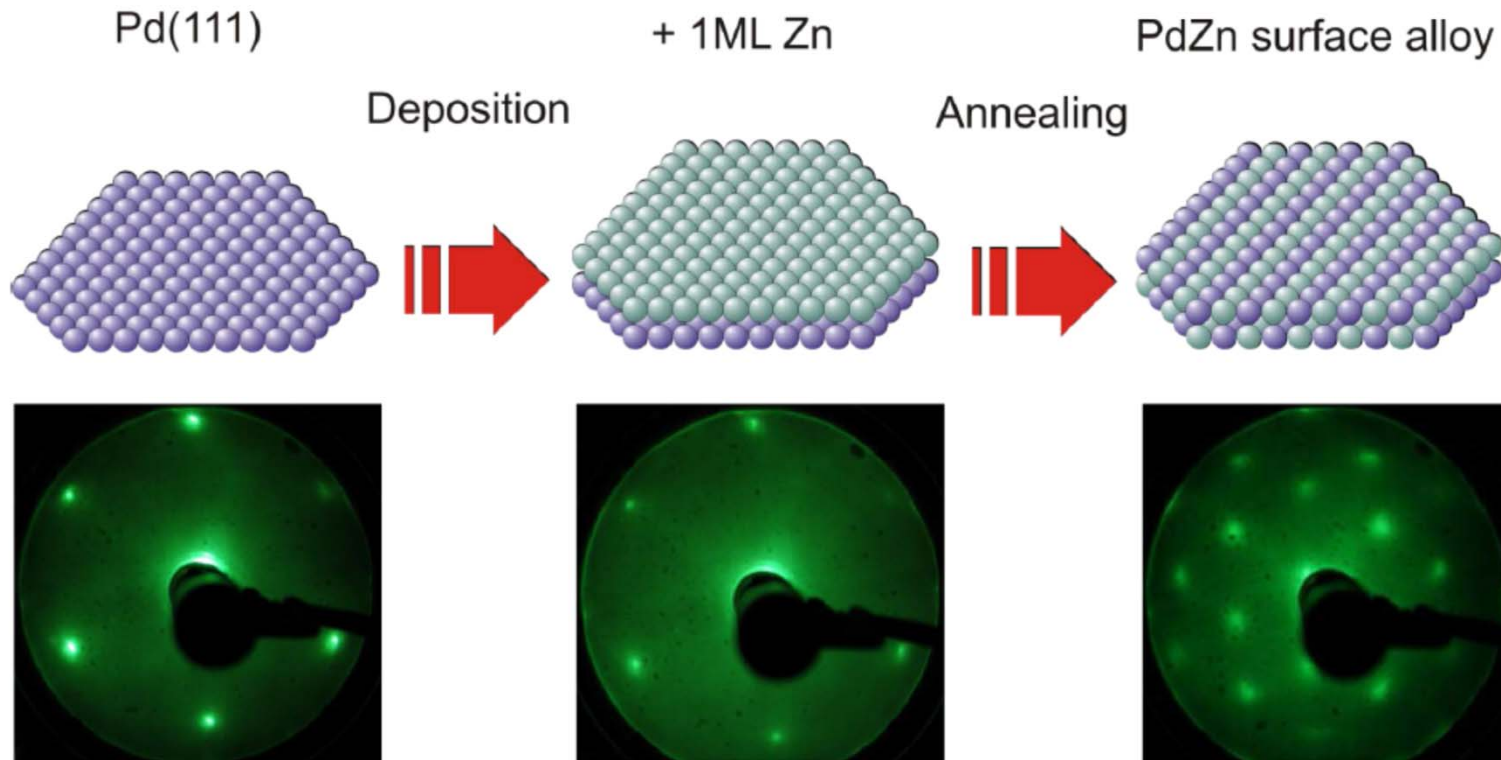
Ni(100)-(1x1)

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



LEED

■ Preparation of PdZn surface alloy for model studies

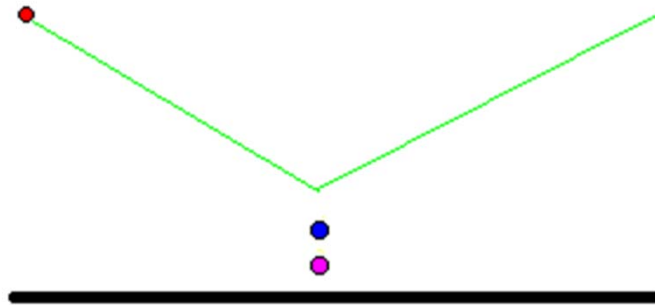


HREELS

- **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 energy is converted into vibrational motion of the adsorbed molecule
- The result is a characteristic loss peak in the HREEL spectrum

HREELS

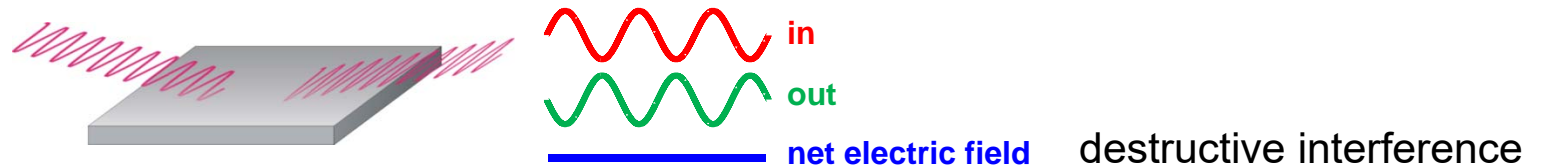
- **How it works – Interaction between electrons and molecules**
- Two scattering modes
- Dipole scattering
 - incident electron is like a electromagnetic wave interacting with oscillating dipoles (vibration of species at surface)
 - long-range effect mediated by the Coulomb field. The incoming electron 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



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

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

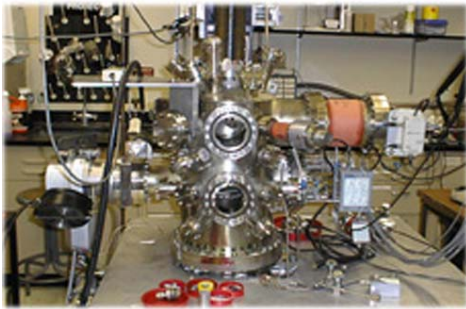
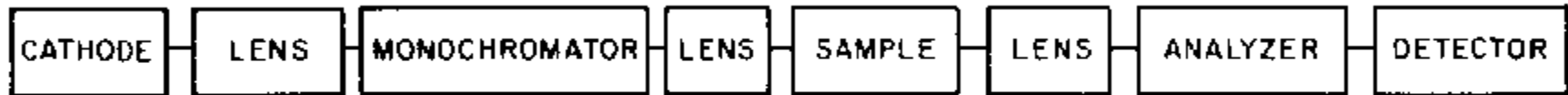
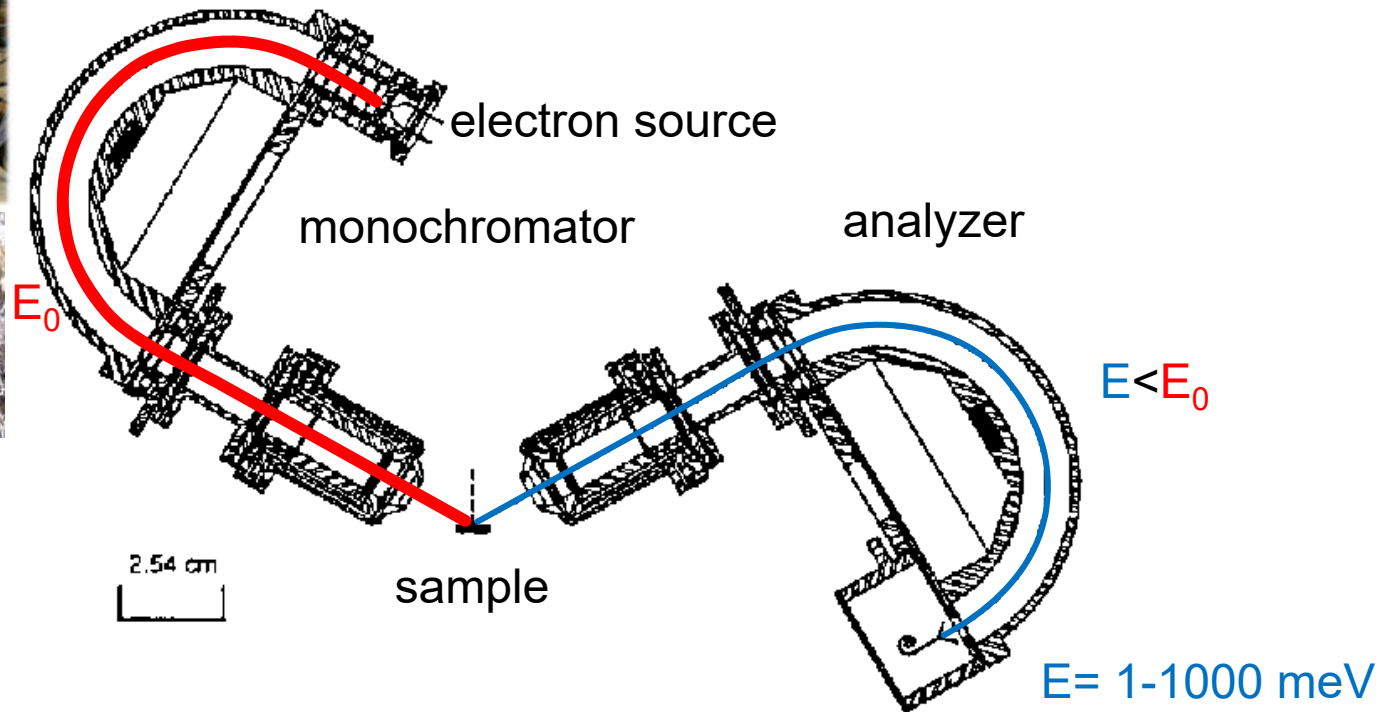


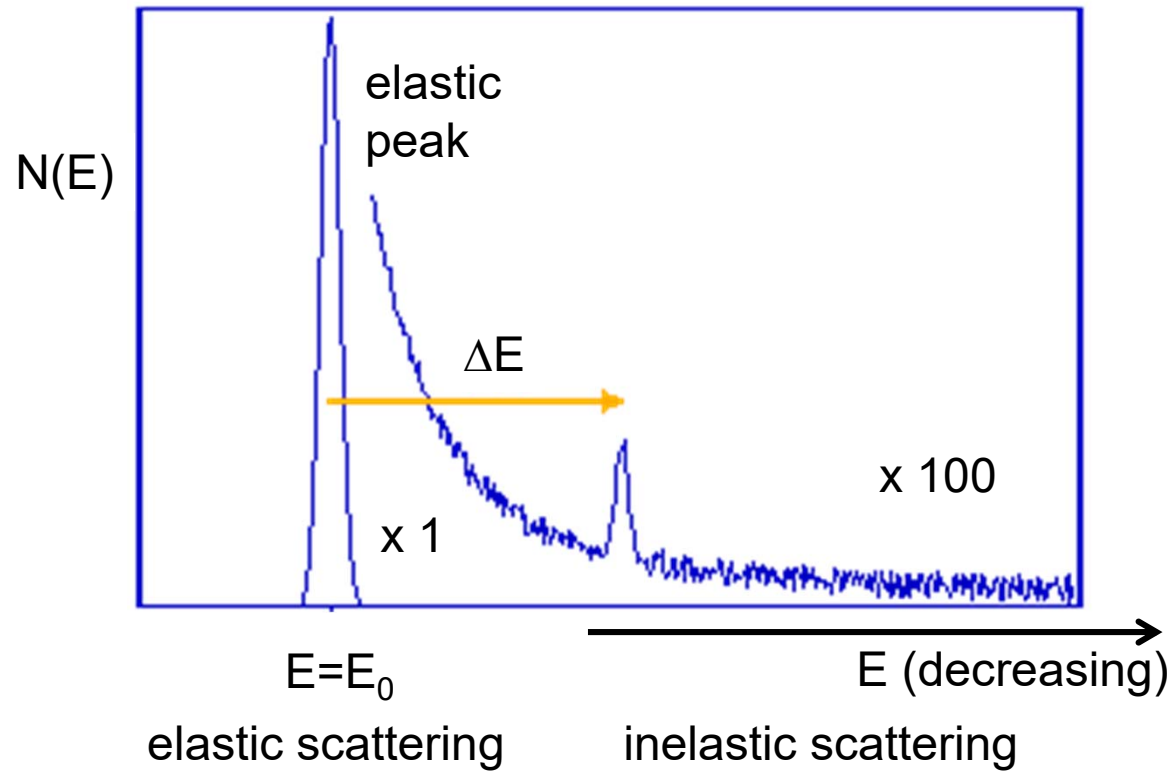
Diagram of an electron energy loss spectrometer



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

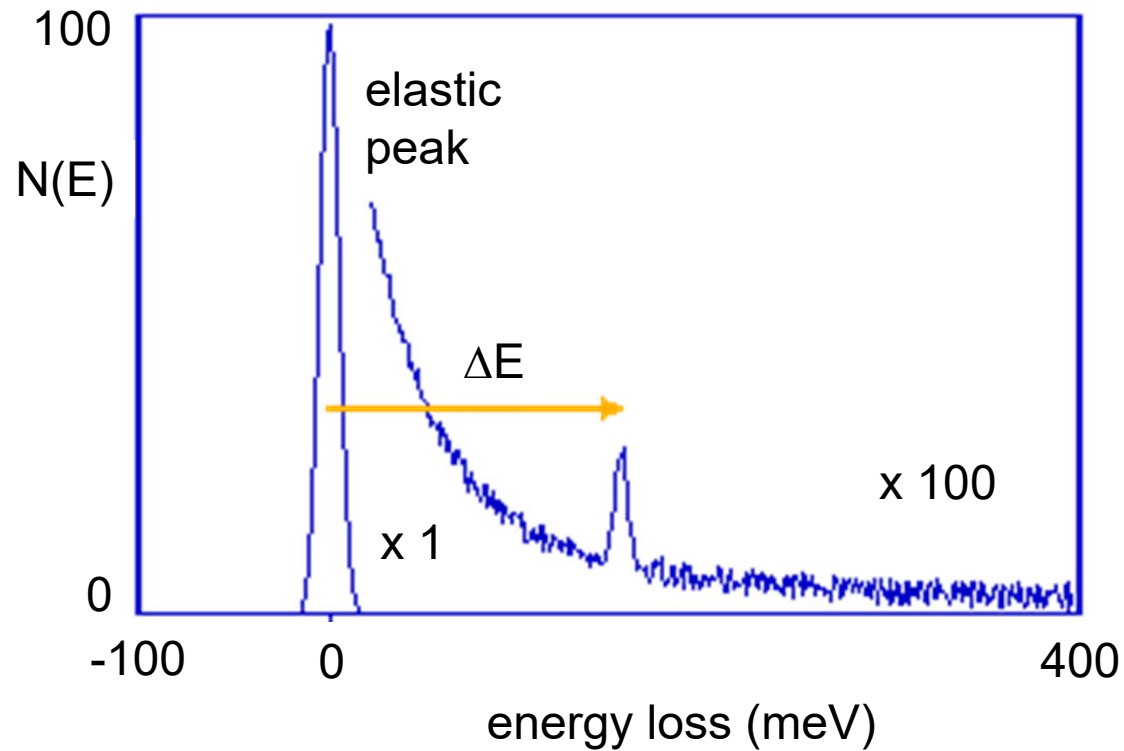
Electrons from a cathode pass through a monochromator, strike the sample, and the energy spectrum of the scattered electrons is probed by a second monochromator.

The HREELS spectrum



The HREELS spectrum

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



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

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)

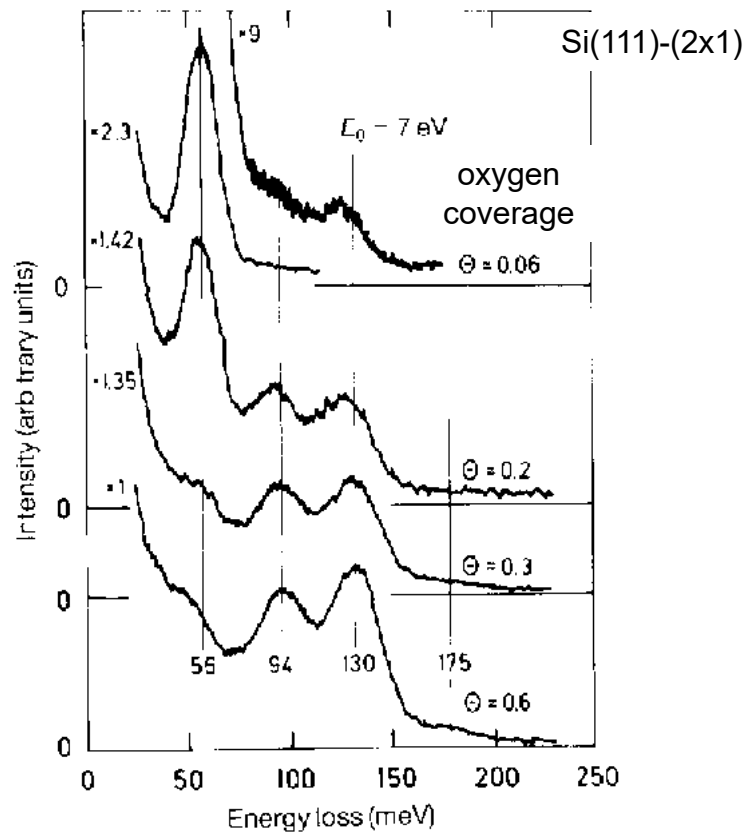
▪ RAIRS

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

Examples

■ HREELS of surfaces

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



SFG

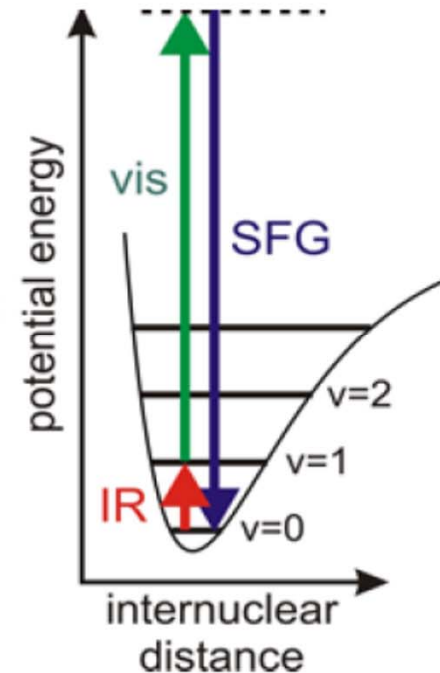
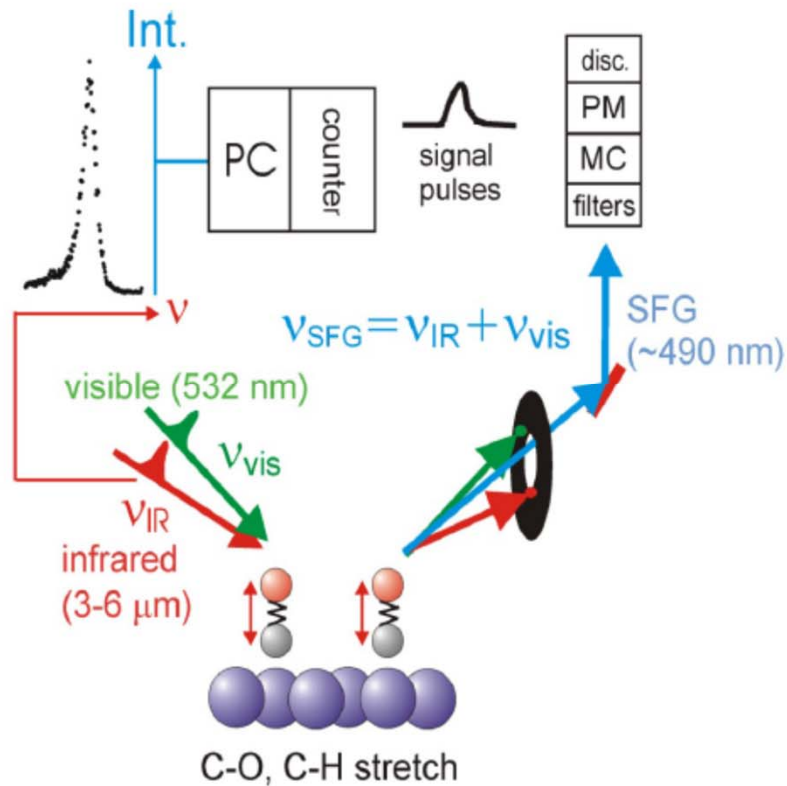
- **Sum frequency generation**

- 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

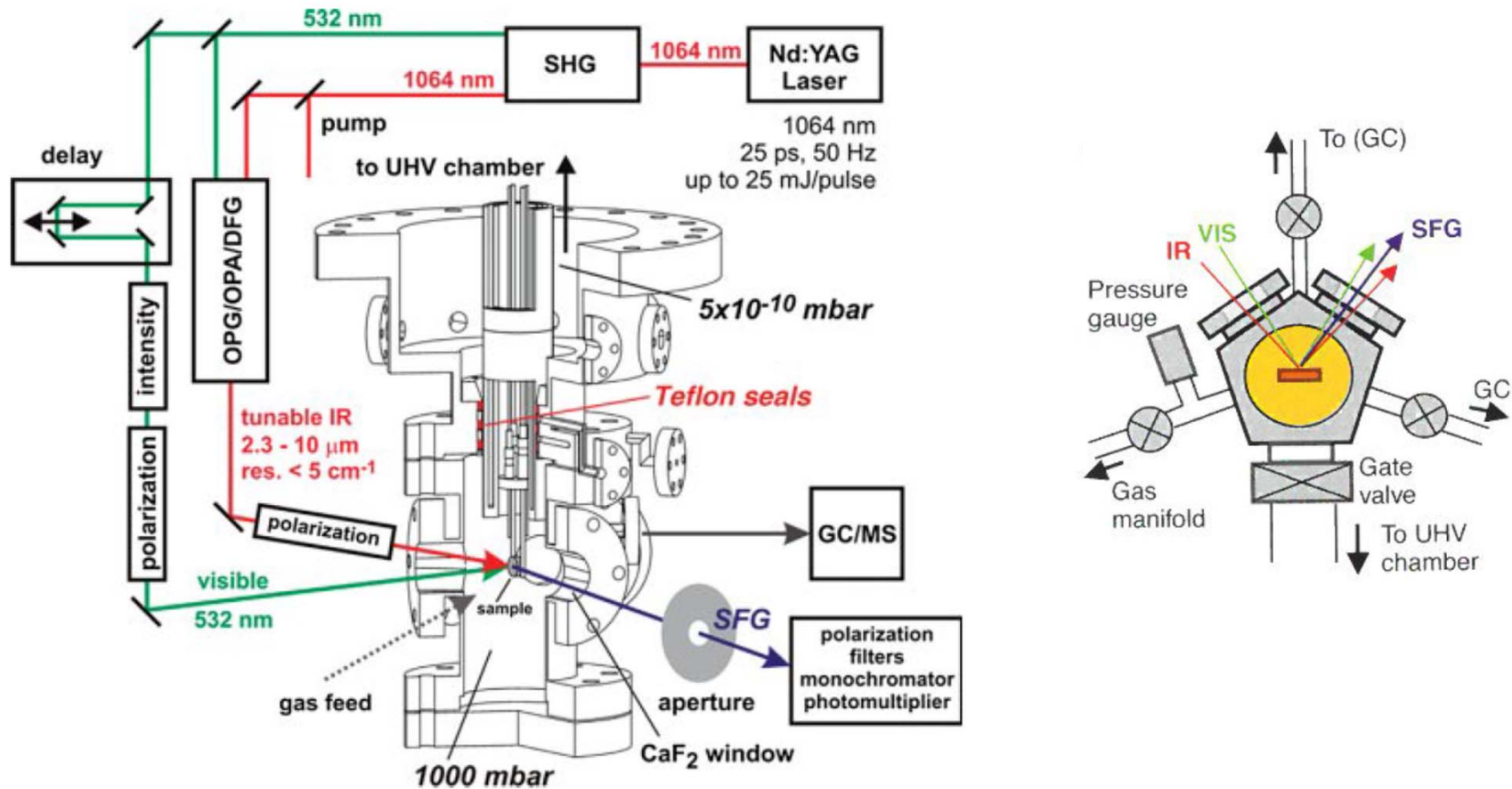
SFG

■ 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

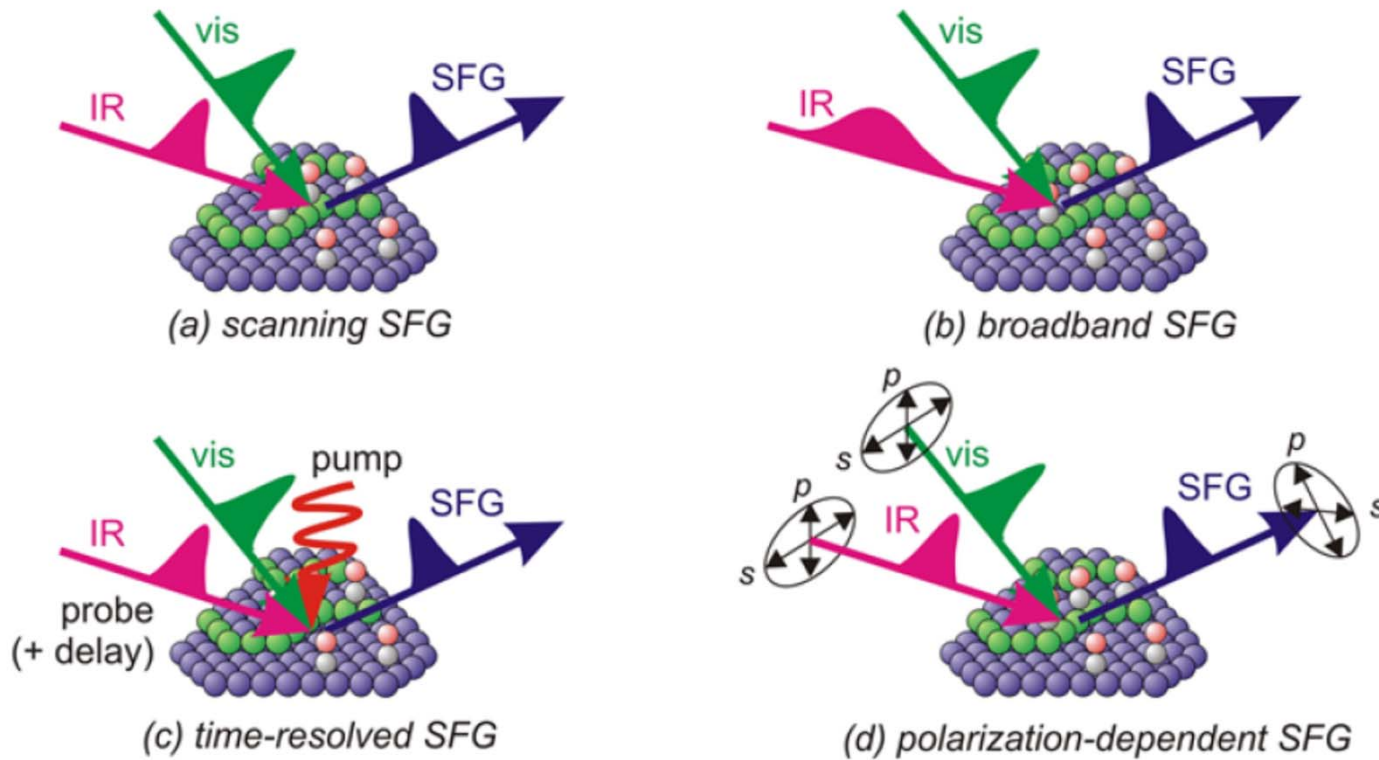
SFG

■ Setup



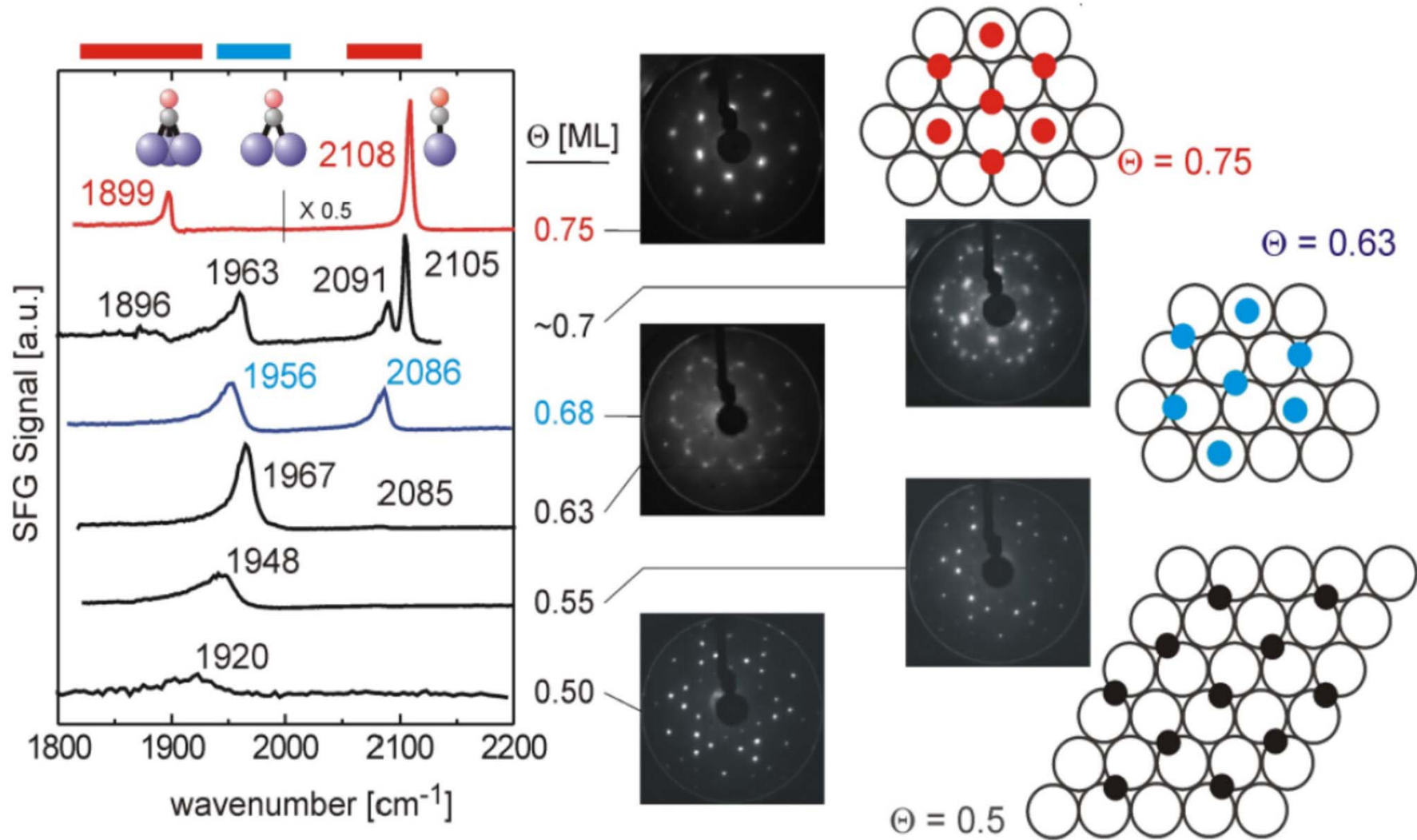
SFG

■ Modes of operation



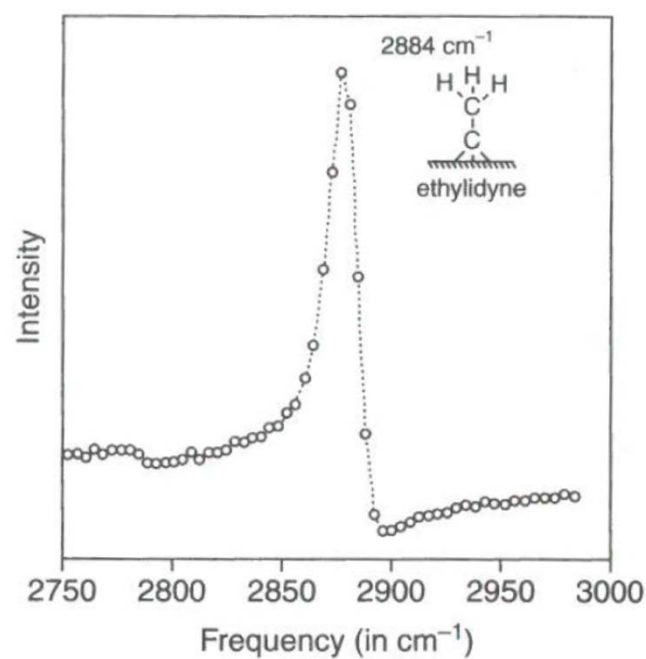
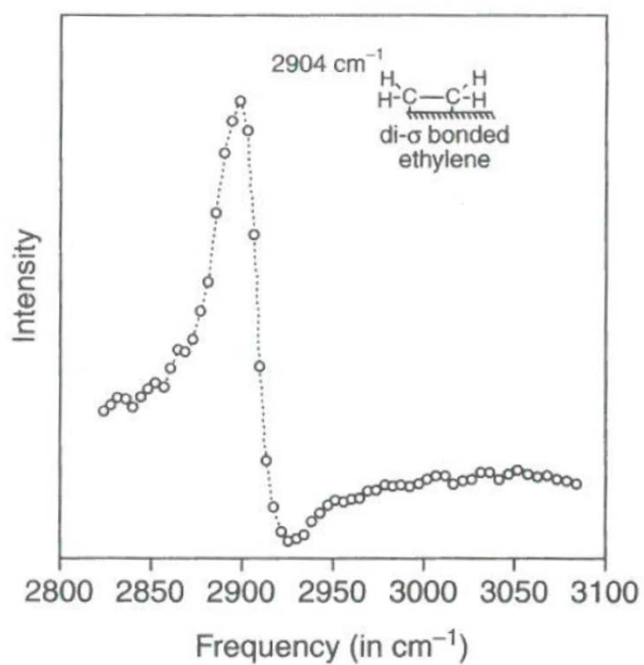
SFG

■ Structure assignment in combination with LEED



SFG

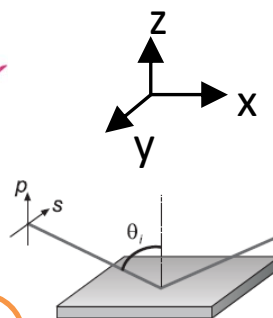
■ Hydrocarbon fragments on Pt(111)



RAIRS

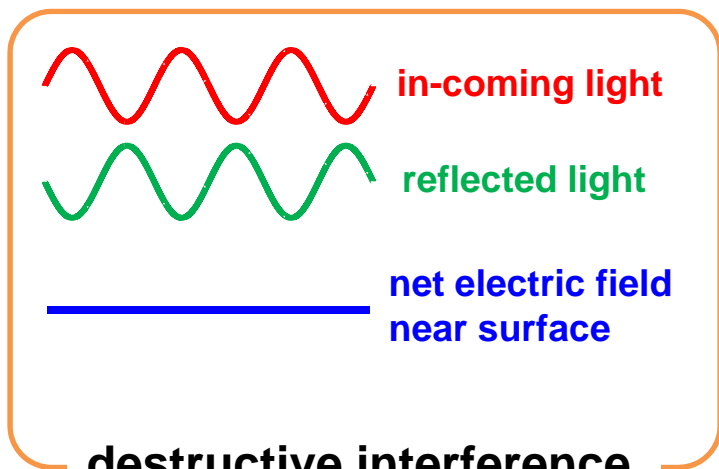
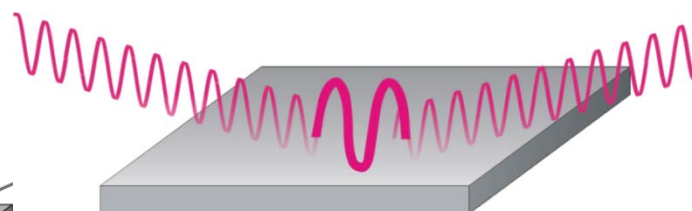
- Reflection absorption IR spectroscopy
 - Specular/external reflection method

Perpendicular (s-) polarization (y-axis)

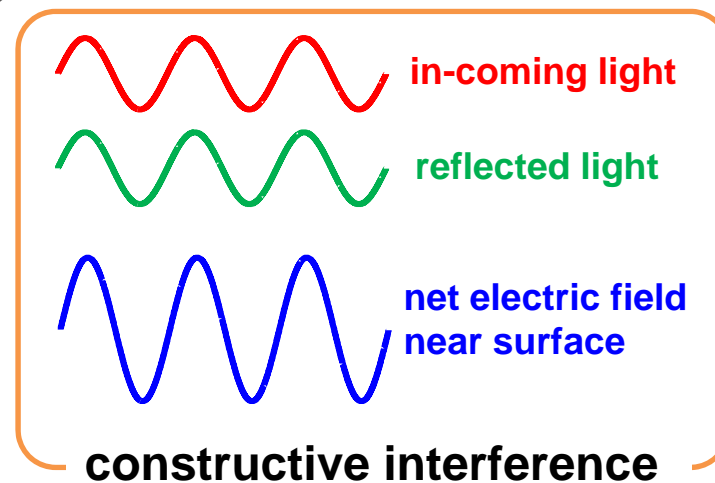


Parallel (p -) polarization (x, z-axis)

Parallel: parallel to the plane of incident light



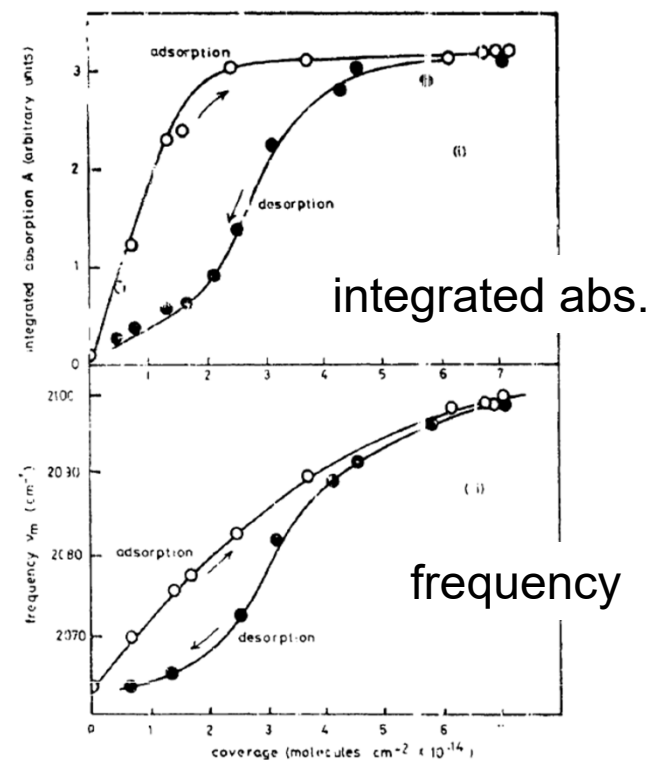
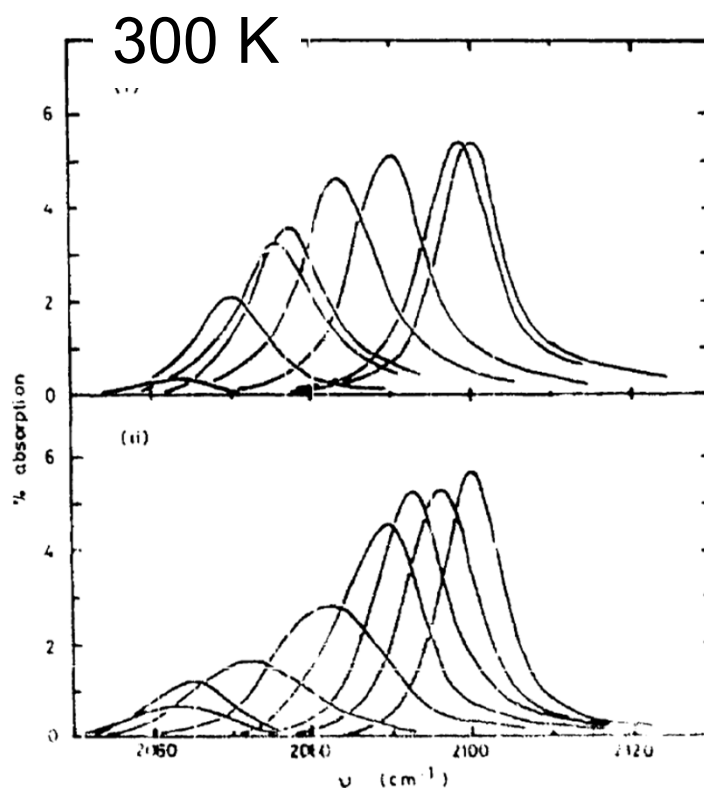
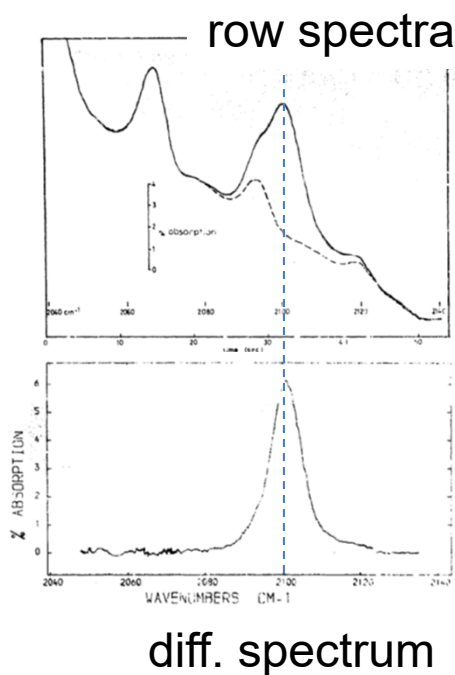
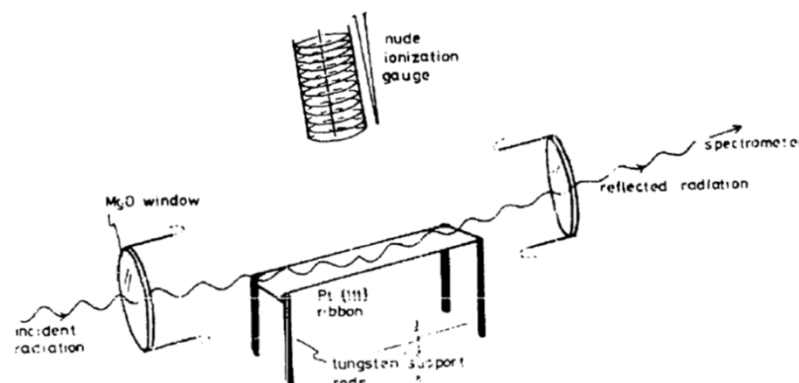
destructive interference
This s-polarization does not contain information about surface species
(180° phase change)



constructive interference
 p -polarization is exploited
Ideally no gas phase present (UHV)

CO adsorption on Pt(111)

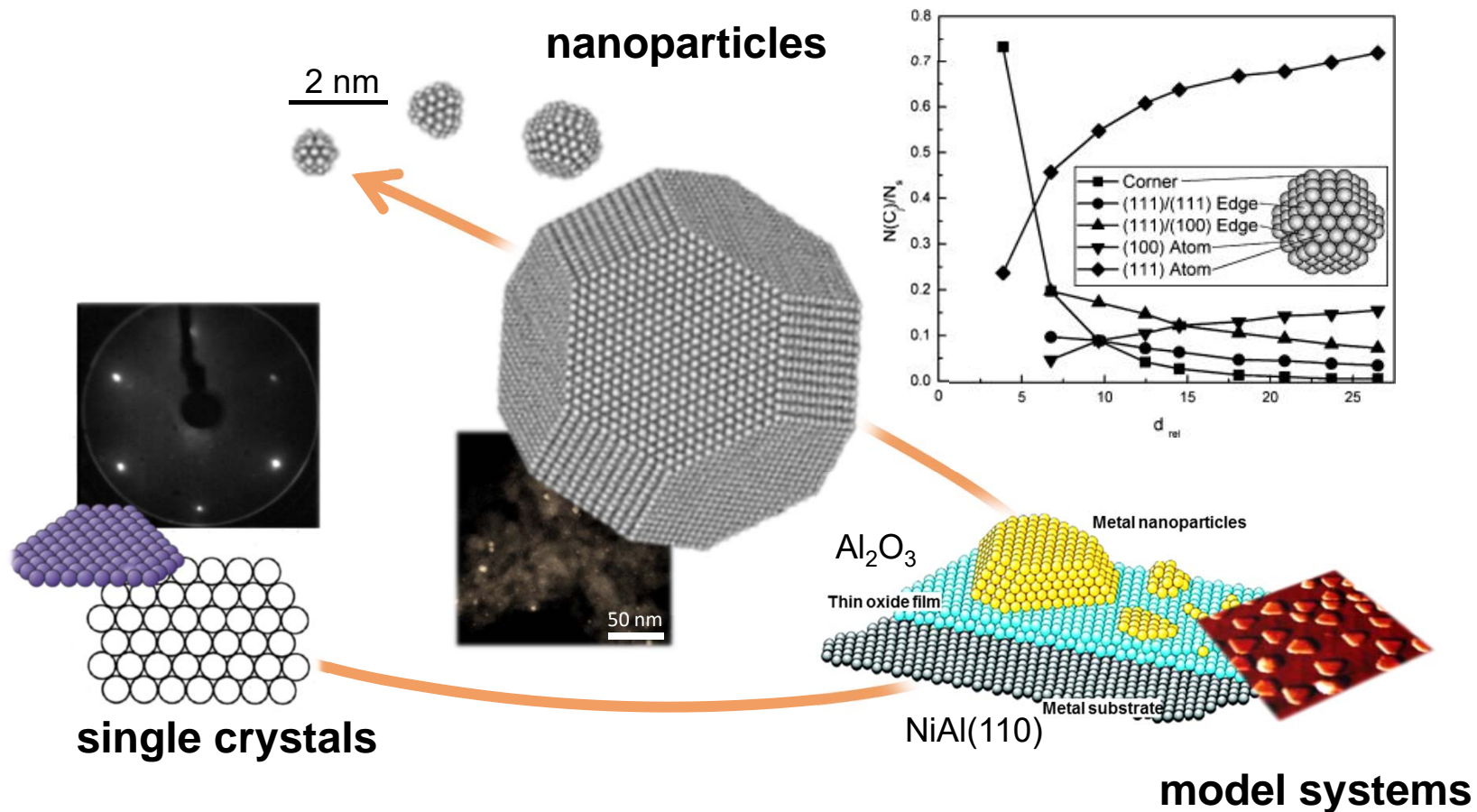
- $\nu(\text{CO})$ blue-shifts with increasing coverage - dipole-dipole interactions
- linear increase of intensity up to 1/3 of full surface coverage, then only shift
- ads/des hysteresis



CO adsorption

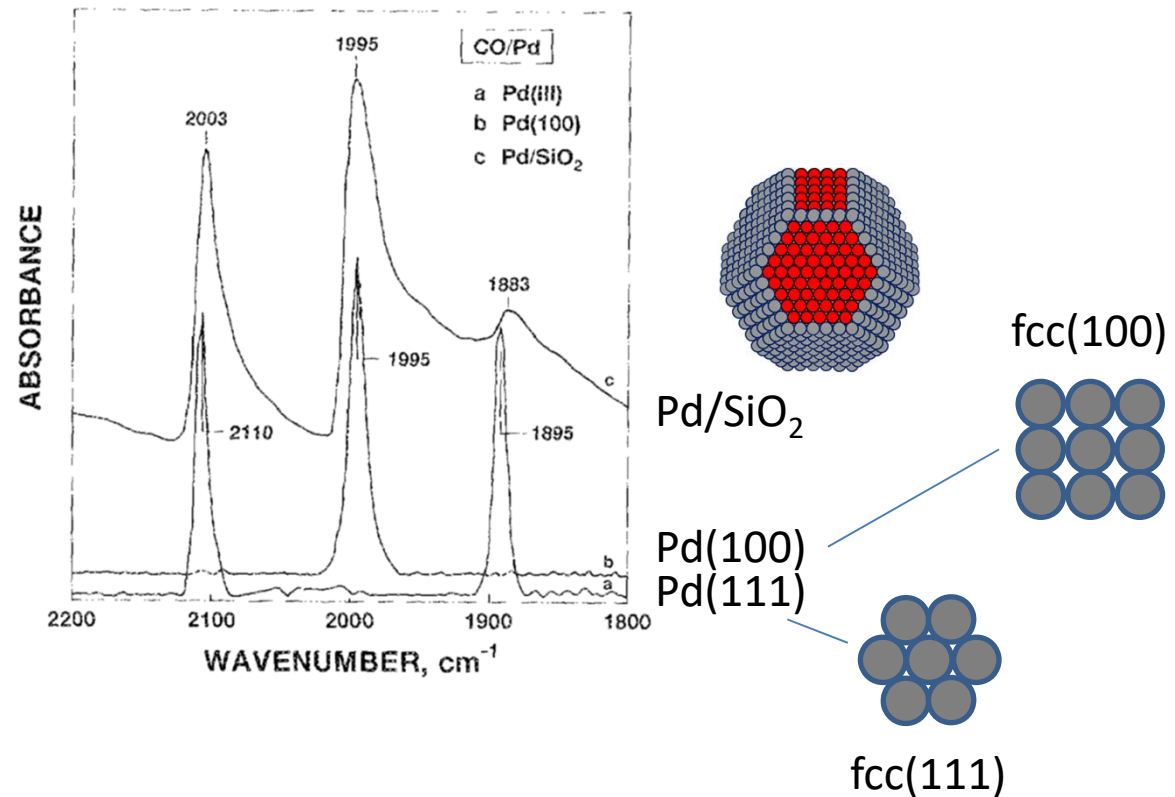
■ Single crystal vs Powder

- reference for assignment of signals on technical catalysts!



RAIRS

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



The surface selection rule

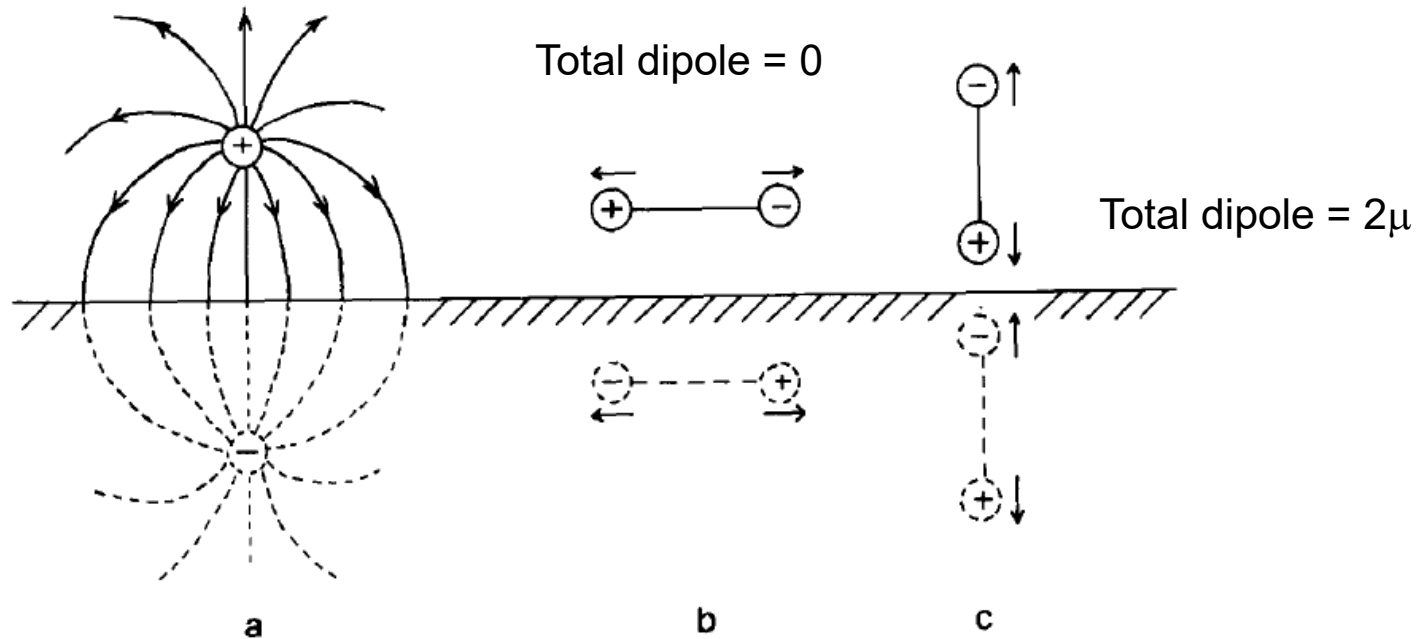
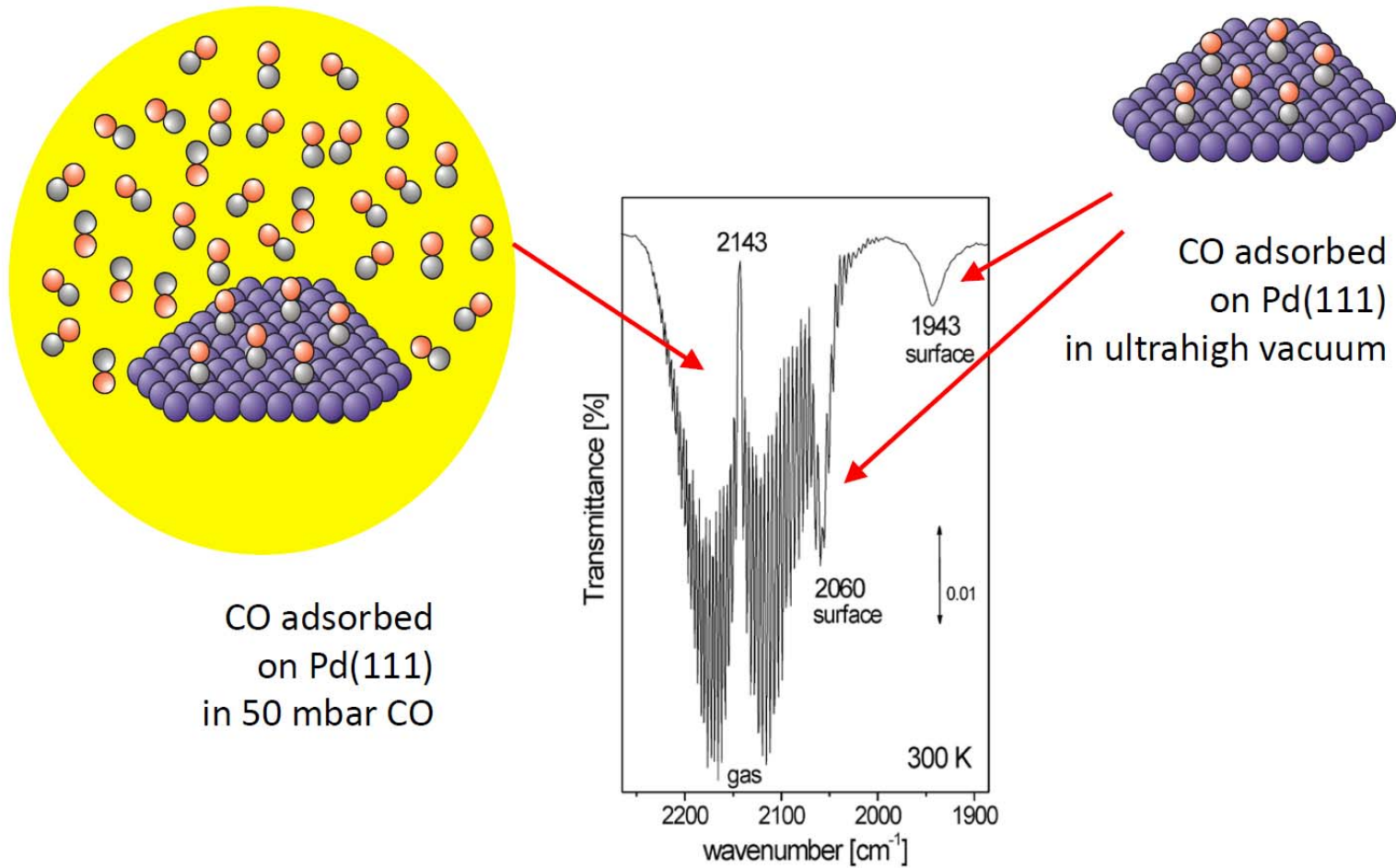


Fig. 1. (a) The lines of force and the electrical "image" resulting from a positive charge over the surface of a conductor (the metal surface is the upper line above the hatched area). (b) The changes during the vibration of a dipole parallel to the surface of the metal; the "image" dipole change is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

RAIRS

- **Non-UHV conditions**

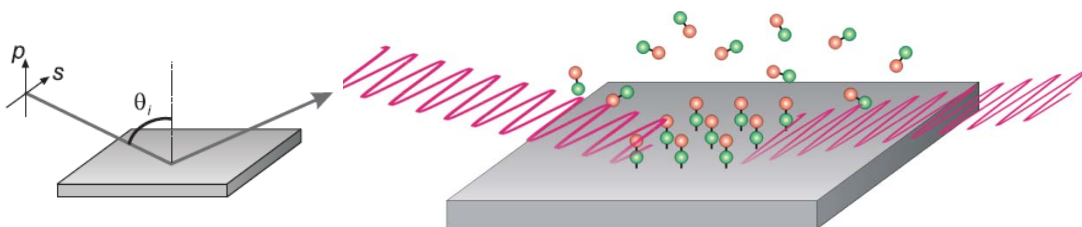
- Superposition of contributions from surface and gas phase



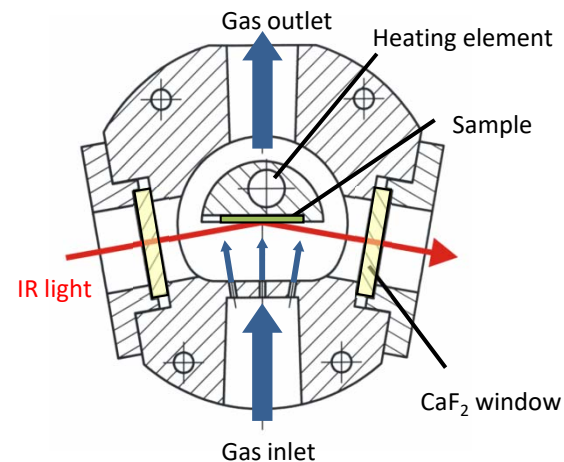
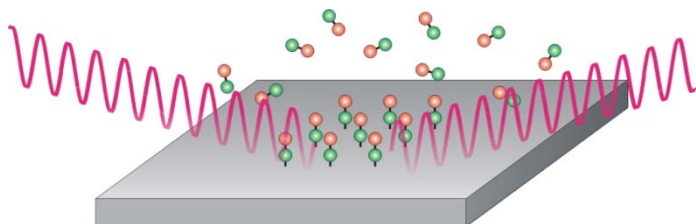
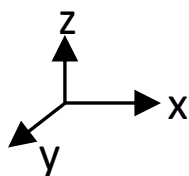
Polarization-modulation IRRAS (PM-IRRAS)

- Generation of 2 polarizations (photoelastic modulator)
 - excellent gas-phase compensation
 - non-UHV experiments possible
 - highly sensitive, time-resolved

Perpendicular (s-) polarization (y-axis)



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



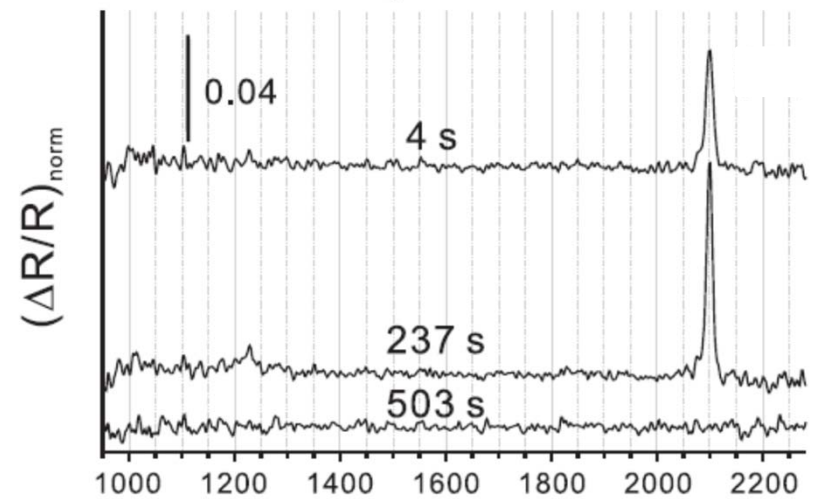
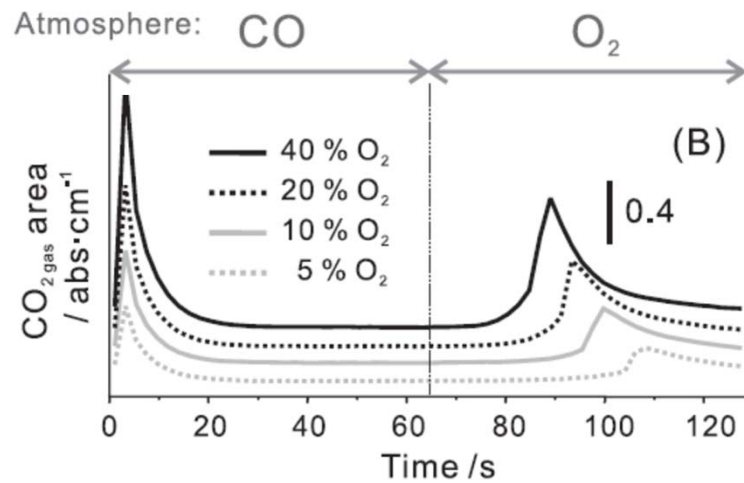
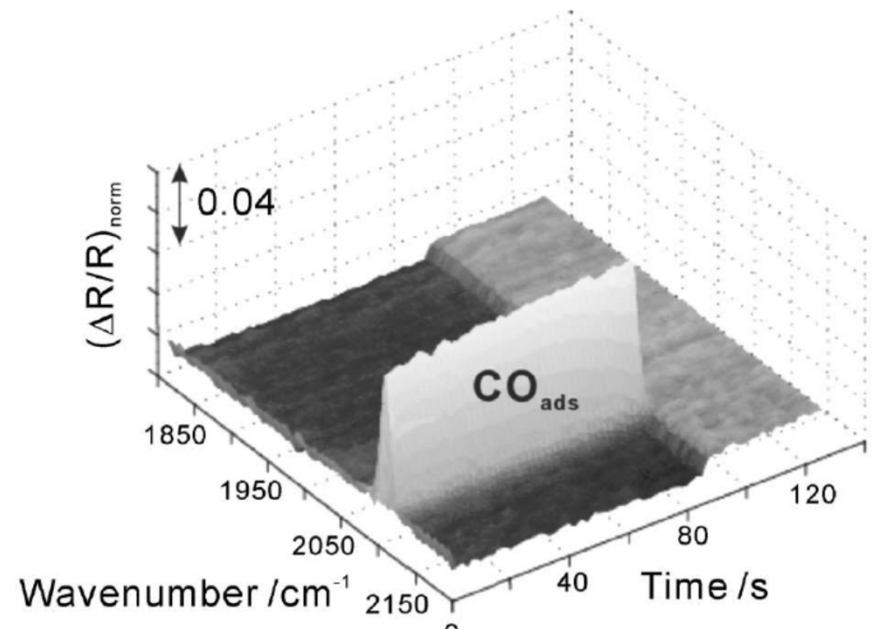
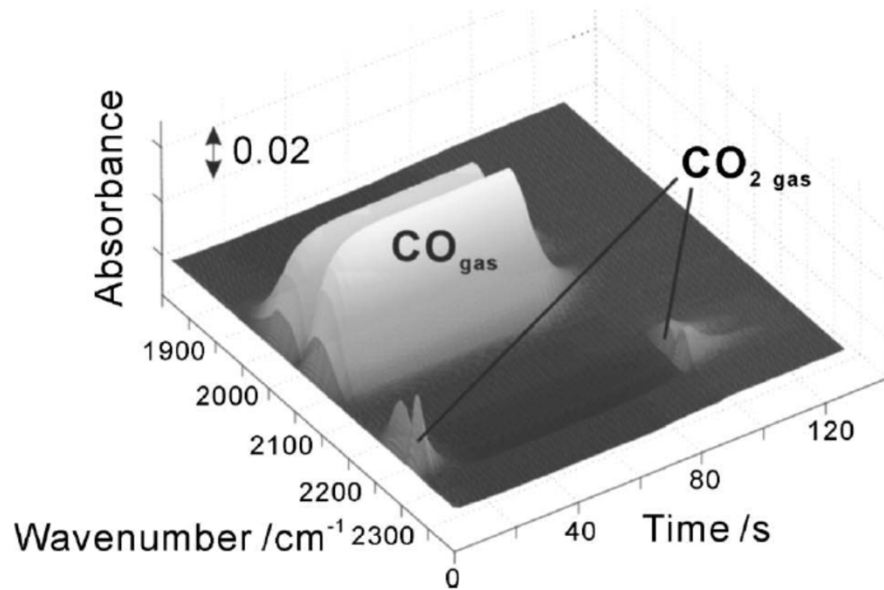
Urakawa et al., J. Chem. Phys. 124 (2006) 054717

$$\begin{array}{ccccc} R_p & - & R_s & = & \Delta R \\ \text{Parallel polarization} & & \text{Perpendicular polarization} & & \text{Difference} \\ \text{surface + gas} & & \text{gas} & & \text{surface} \end{array}$$

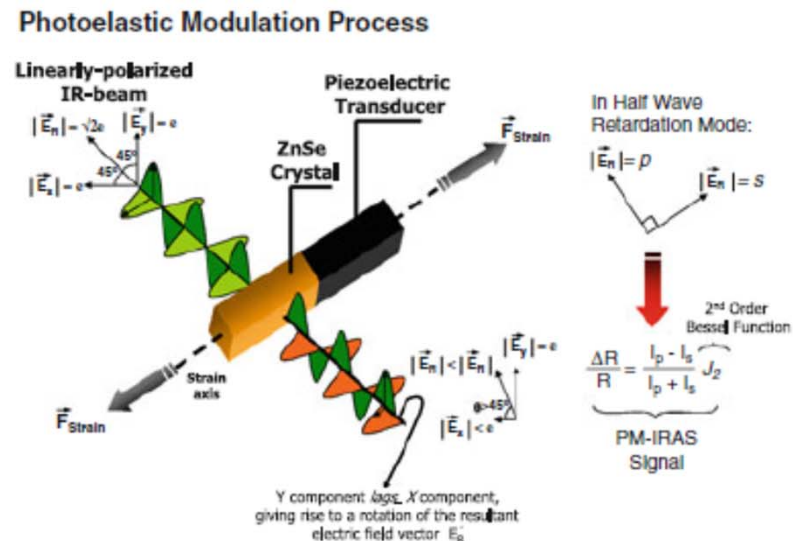
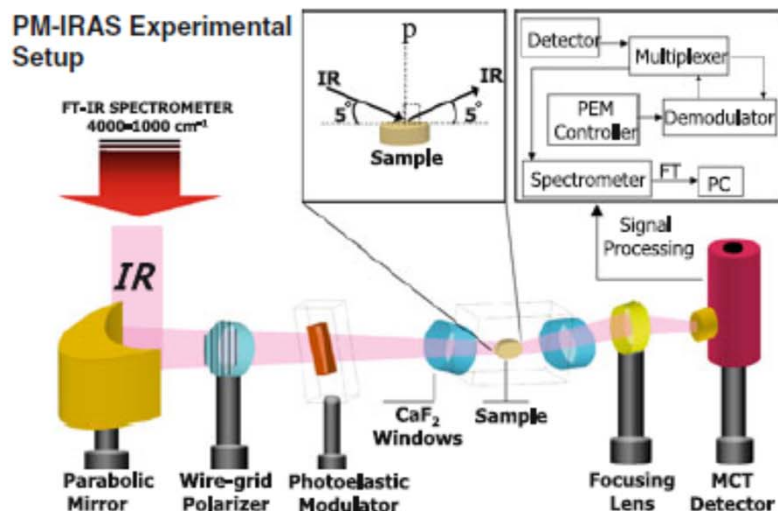
The surface spectra are often shown in $\Delta R/R$ ($R=R_s+R_p$)

RAIRS

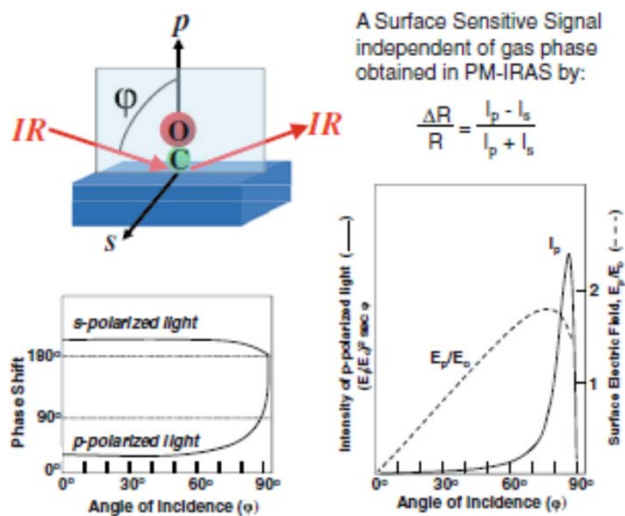
■ Isolation of surface contribution



Polarization-modulation IRRAS (PM-IRRAS)



Origin of Surface Sensitivity of PM-IRRAS and Surface Selection Rules



PM-IRRAS Data Acquisition

