Electron Energy Loss Spectroscopy –
A Versatile Tool for the (Atomic Level) Characterization of Chemical and Electronic Properties of Surfaces

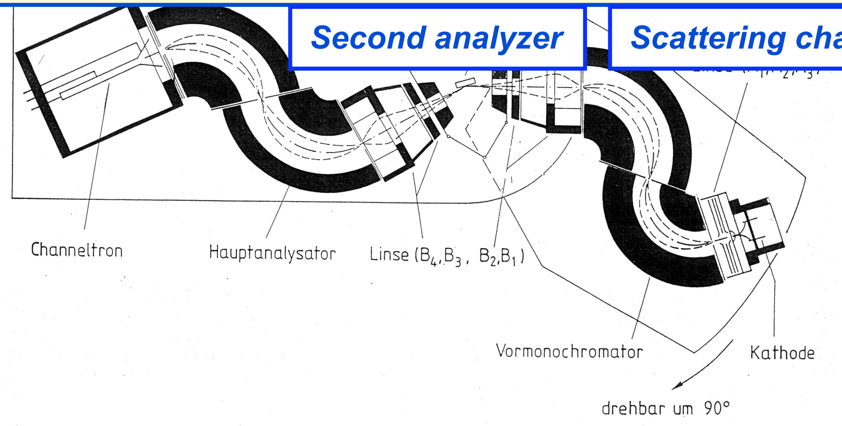
1. Electron spectrometers – principles and performance
3. Inelastic scattering of electrons – basic mechanisms
4. Resonance scattering: physisorbed molecules
4. Dipole scattering
    4.1 The dielectric halfspace: surface plasmons and FK-phonons
    4.2 Thin films: 2D plasmons, FK-phonons of oxide films
    4.3 Monolayers: surface chemistry
    - the most important application of EELS

Excursion to metal/electrolyte interface: water on stepped Au(11*n*) surfaces

5. Impact scattering: dispersion of surface phonons
6. Exchange scattering: spin-polarized EELS and surface magnons

Contributors and Collaborators in the field of EELS, the ultra-short-list:
experiment: Sieghart Lehwald *theory: Douglas L. Mills*
René Franchy *Jorge Müller*

1. Electron spectrometers – principles and performance



Second analyzer

Scattering chamber

Sample

Second monochromator

Cathode lenses

Channeltron

First Analyzer

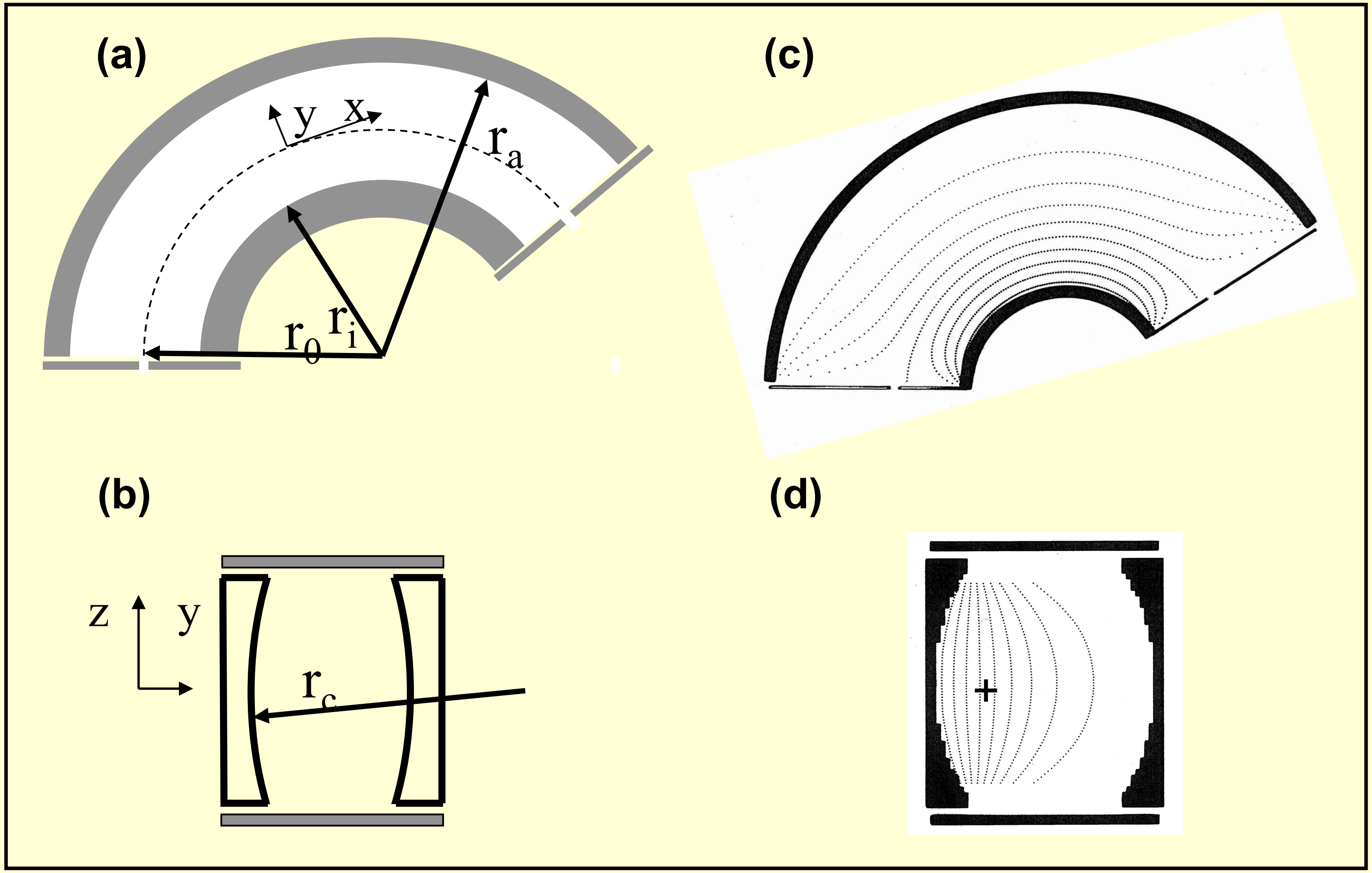
Lenses B_1 - B_4

First monochromator

Cathode

The art is in the details!

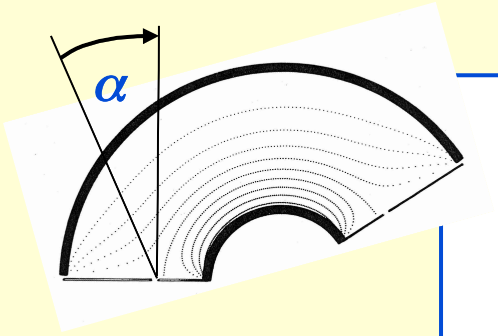
Example: the free-form electrostatic delectors



Features:

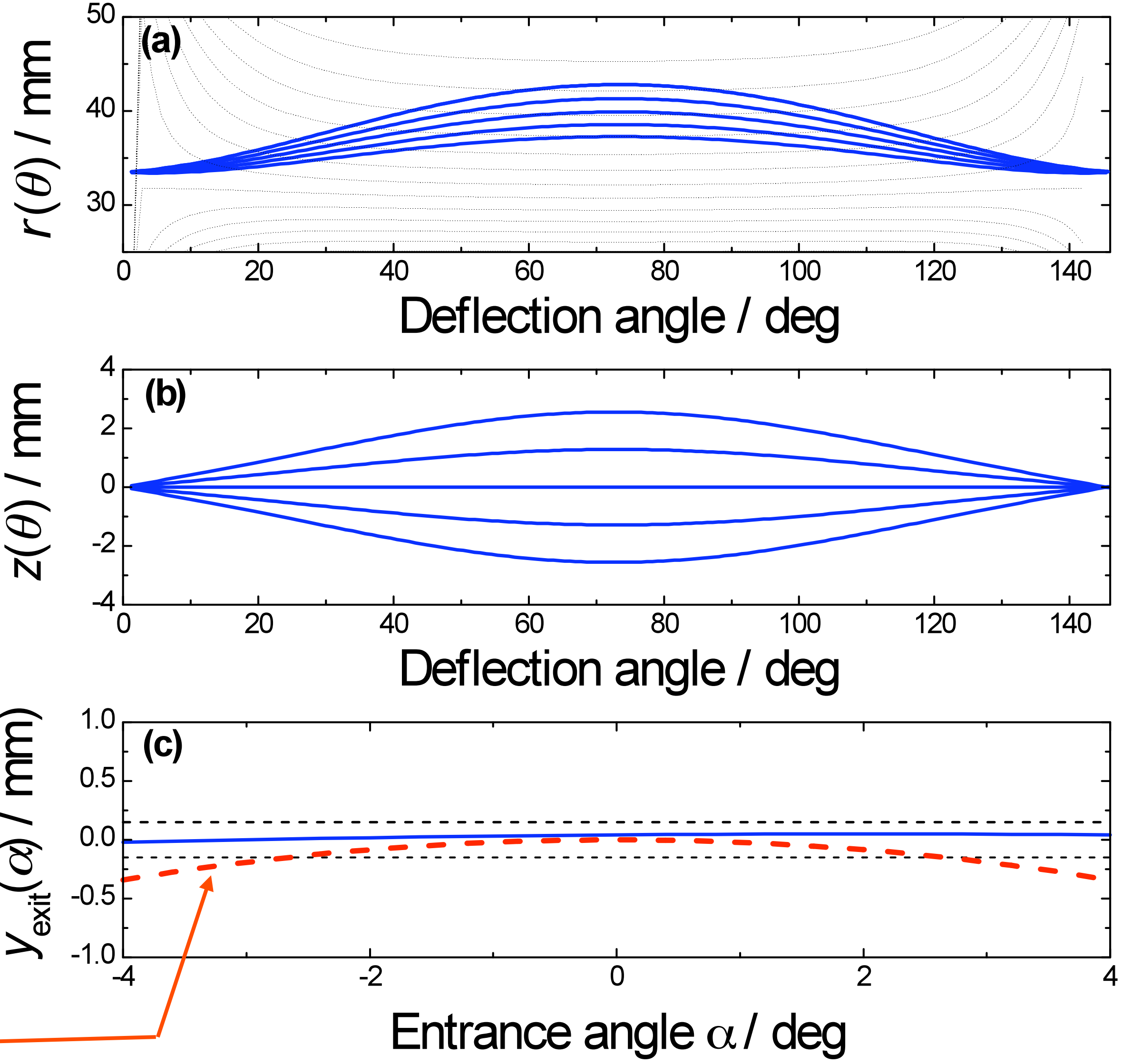
- metal apertures,
- stigmatic focussing even under higher current loads
- low angular aberration in dispersion plane

Trajectories in the free-form deflector



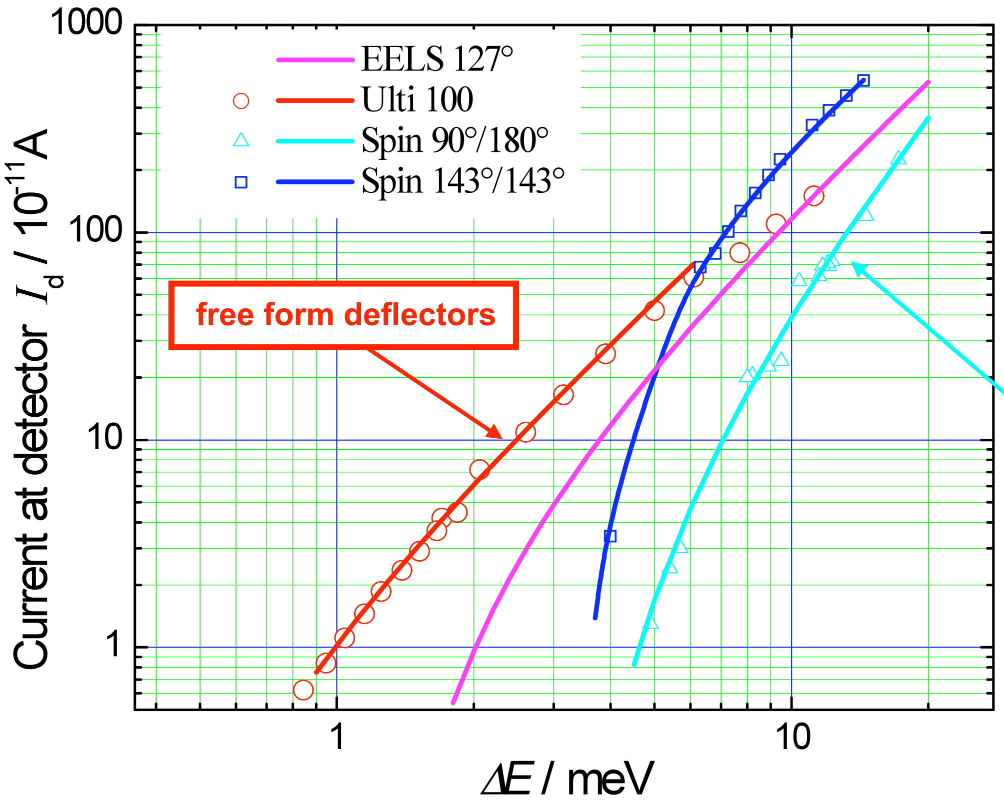
α= -4°,-2°,0°,+2°,+4°

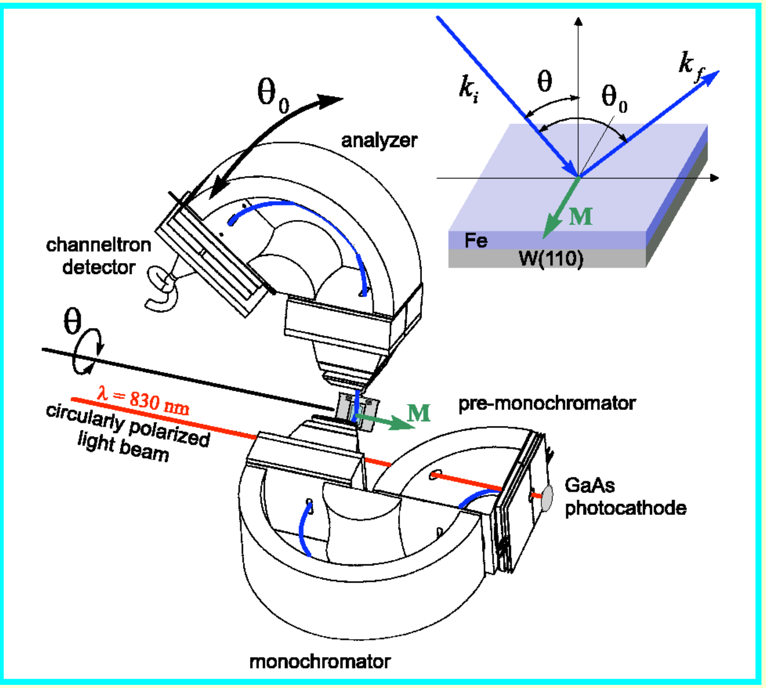
β=-4°,-2°,0°,+2°,+4°



spherical deflector

Performance of various spectrometer types

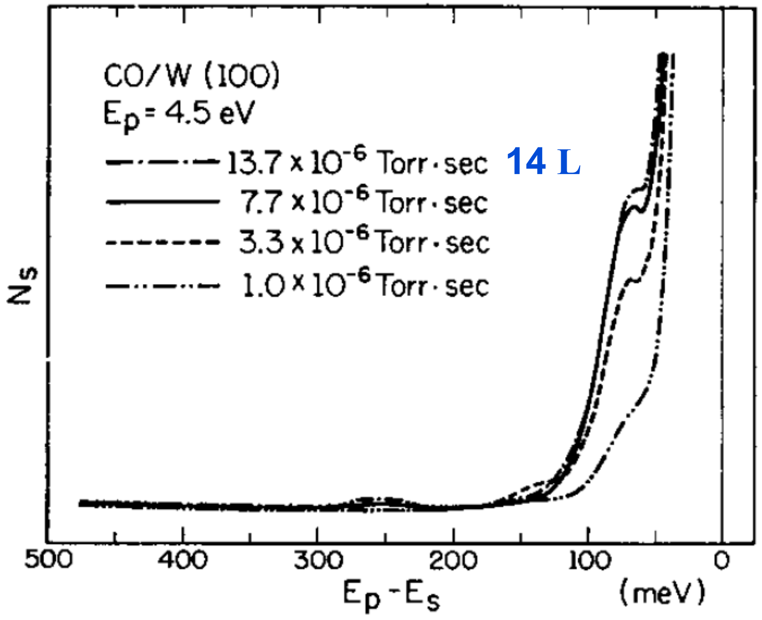


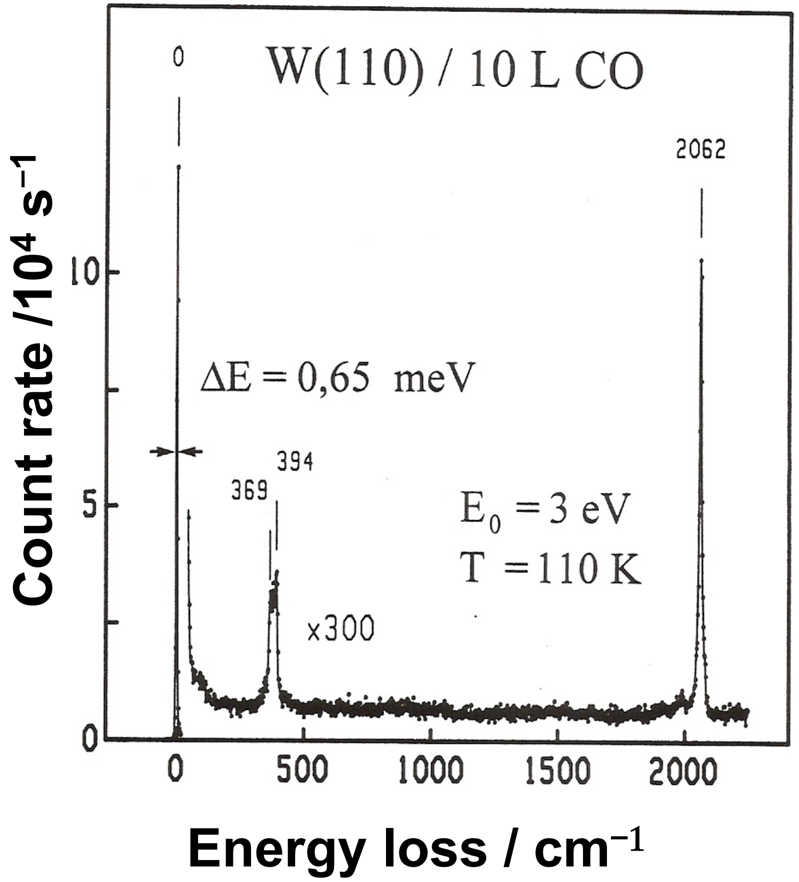


Demonstration of performance with physisorbed CO on W

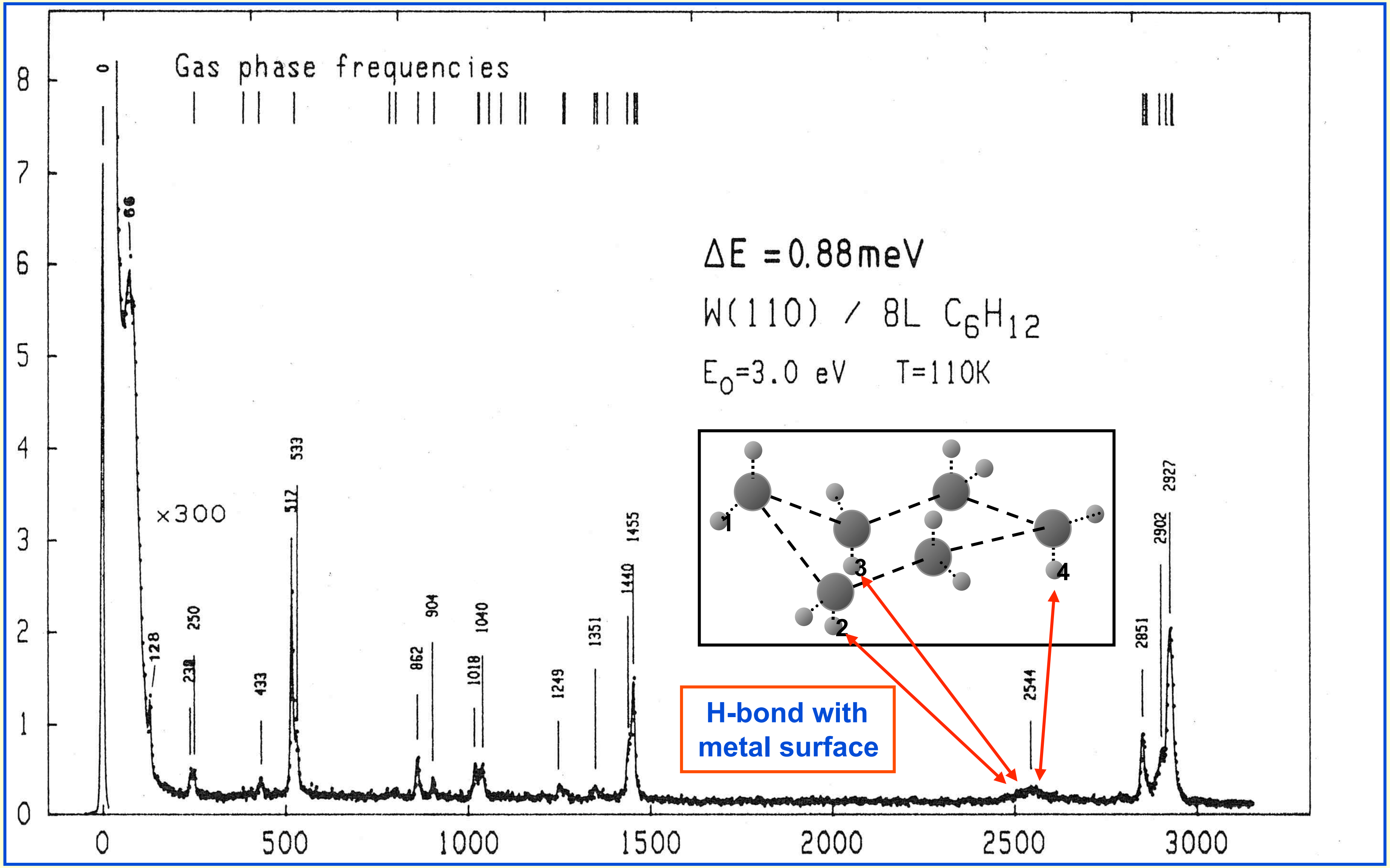
F. M. Propst, T. C. Piper,
J. Vac. Sci. Technol. 4 (1967) 53

H. Ibach, M. Balden, S. Lehwald,
J. Chem. Soc., Faraday Trans. 92 (1996) 4771





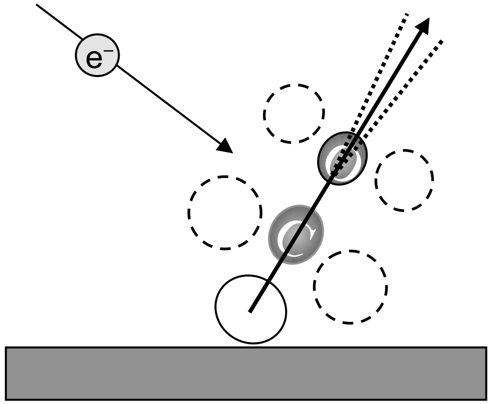
High performance spectra, here: cyclohexane on W(110)



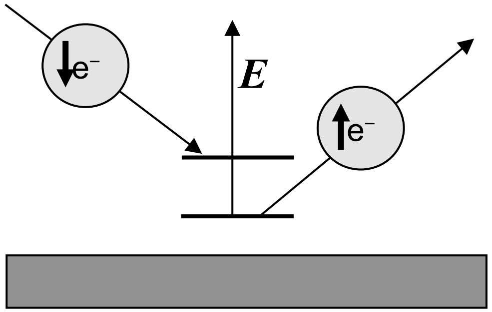
H-bond with metal surface

see also: J. E. Demuth, H. Ibach, S. Lehwald, Phys. Rev. Lett. 40 (1978) 1044

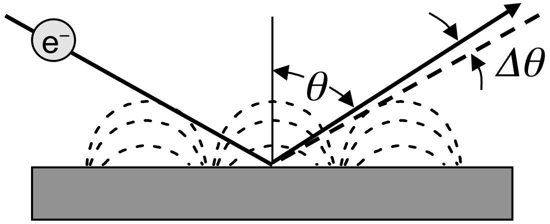
2. Inelastic scattering of electrons – basic mechanisms



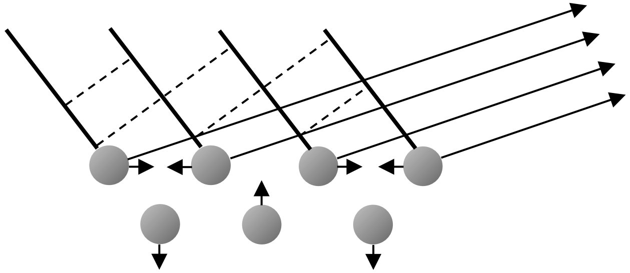
Resonance scattering



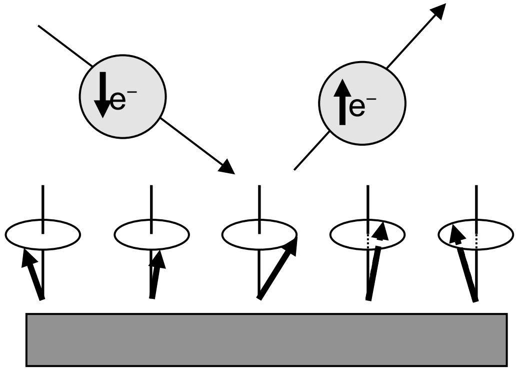
Exchange scattering Stoner-excitations



Dipole scattering

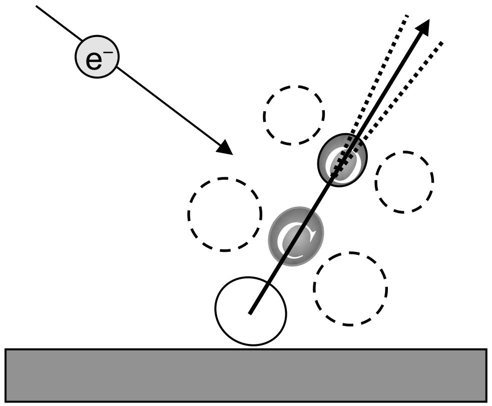


Impact scattering



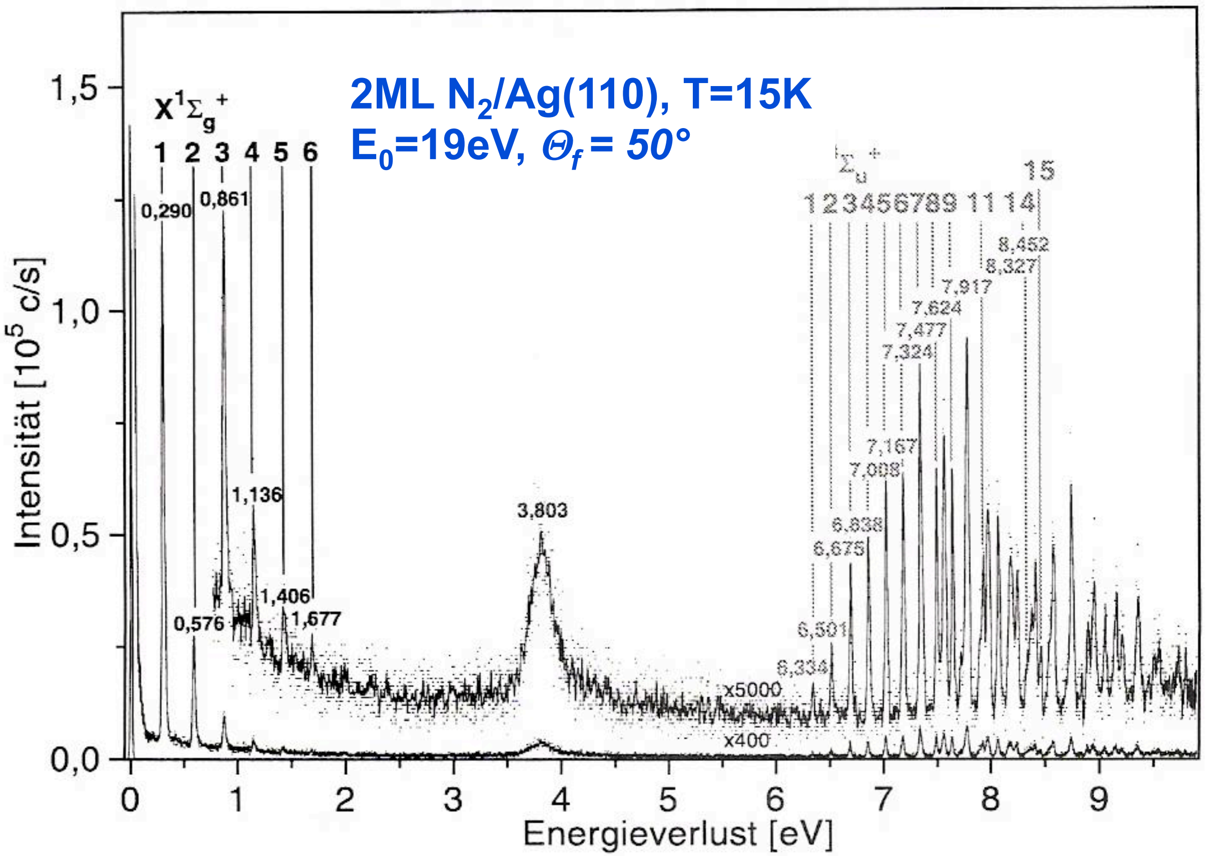
Exchange scattering spin-waves

Resonance scattering

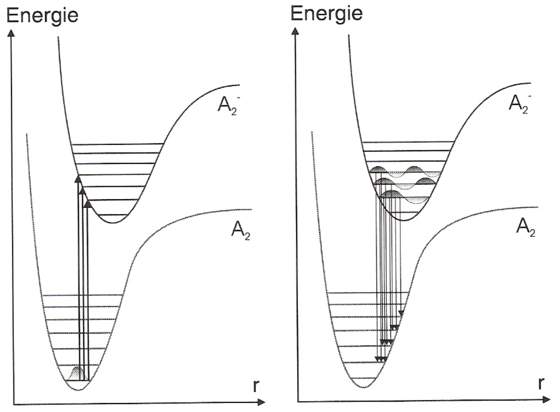


Electron and molecule form a short-living negative ion compound, the re-emitted electron has lost memory of its incident state, yet carries information about excited states of molecule

$$\tau\,(A_2^-) \cong 10^{-15}\text{-}10^{-14}\ \mathrm{s}$$

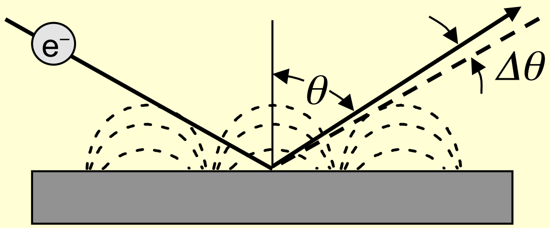


2ML N_2/Ag(110), T=15K
E_0=19eV, Θ_f = 50°



F. Bartolucci, R. Franchy, et al., J. Chem. Phys. 108 (1998) 2251

Dipole scattering



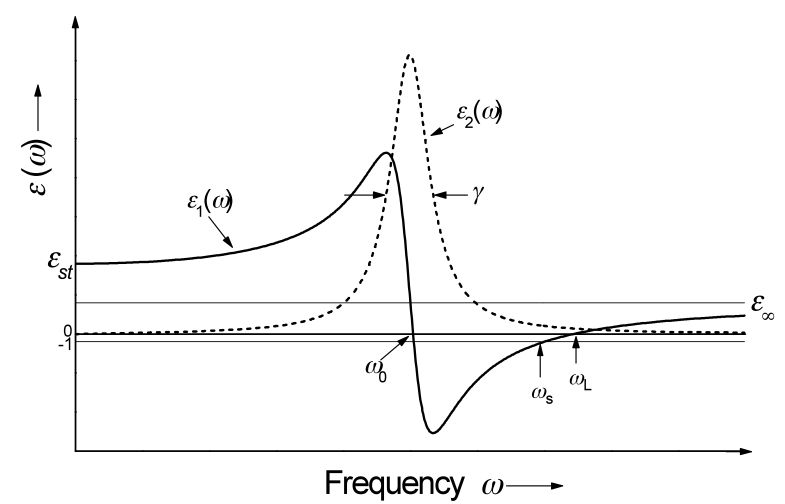
4.1 The dielectric halfspace: surface plasmons and Fuchs Kliewer- phonons

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\omega_0^2(\varepsilon_{\mathrm{st}} - \varepsilon_\infty)}{\omega_0^2 - \omega^2 - \mathrm{i}\gamma\omega}$$

$\operatorname{div} \boldsymbol{P} \neq 0, \ \operatorname{curl} \boldsymbol{P} = 0$ $\varepsilon(\omega) = 0$ **: longitudinal modes**

$\operatorname{div} \boldsymbol{P} = 0, \ \operatorname{curl} \boldsymbol{P} \neq 0$ $\varepsilon(\omega) = \infty$ **: transverse modes**

$\operatorname{div} \mathrm{E} = 0, \ \operatorname{curl} \mathrm{E} = 0$ $\varepsilon(\omega) = -1$ **: surface modes**



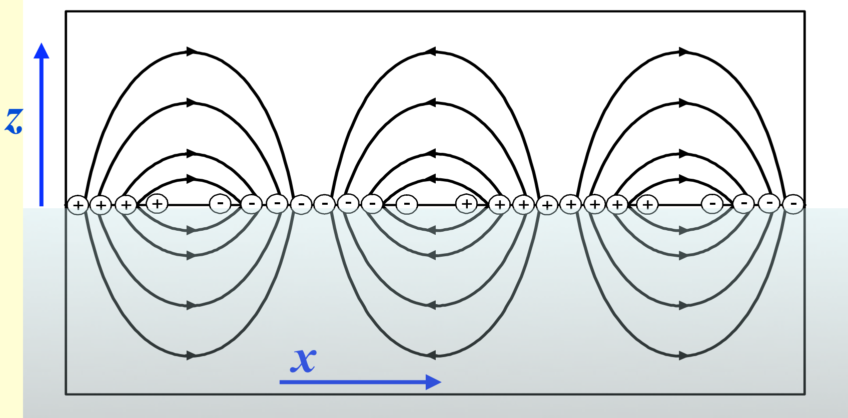
$$\boxed{\Delta\varphi = 0}$$

$$\boxed{\varphi(x,z,t) = \varphi_0 \mathrm{e}^{-q|z|} \mathrm{e}^{\mathrm{i}(qx - \omega t)}}$$

Surface plasmons
Fuchs-Kliewer phonons of ionic materials

Maximum interaction: $v_{||}^{(el)} = \omega / q$
q is small, small angle scattering, inelastic events are found near specular reflection!

field lines of a surface modes on a dielectric halfspace



Two classic experiments on a dielectric halfspace

Plasmon excitations after reflection from aluminum

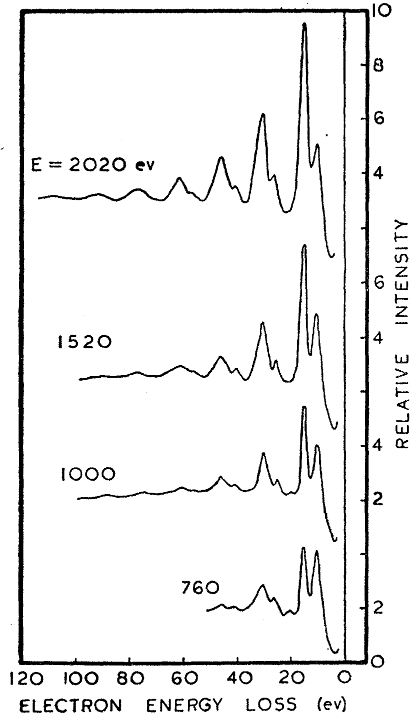
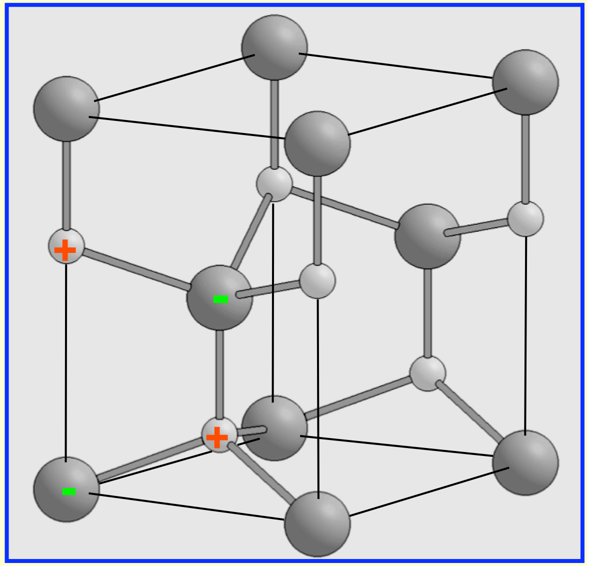


FIG. 1. Characteristic electron energy loss spectra for primary electron energies of 760, 1000, 1520, and 2020 ev. The peak of elastically scattered electrons (not shown) has been adjusted to an intensity of 25 units in each case.

C. J. Powell, J. B. Swan, Phys. Rev. 115 (1959) 869

Surface phonons of ZnO



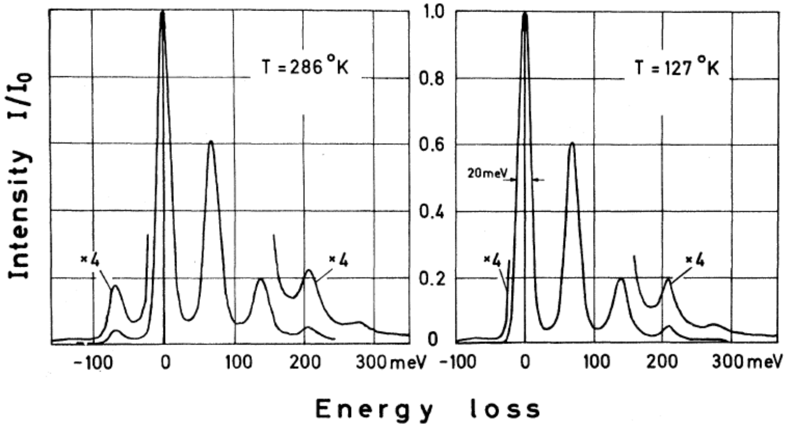
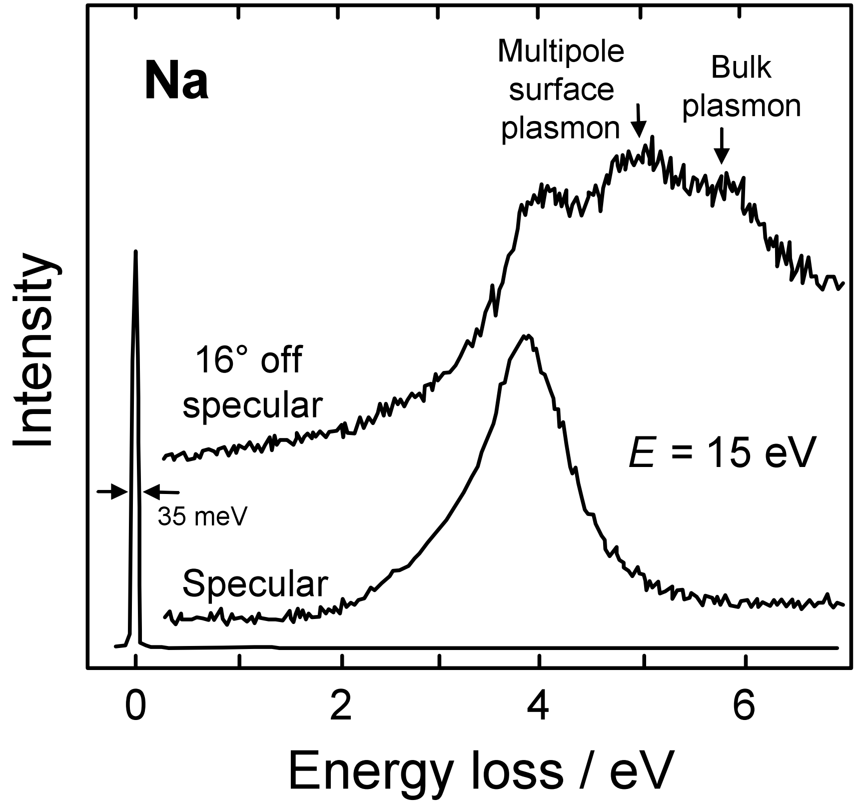


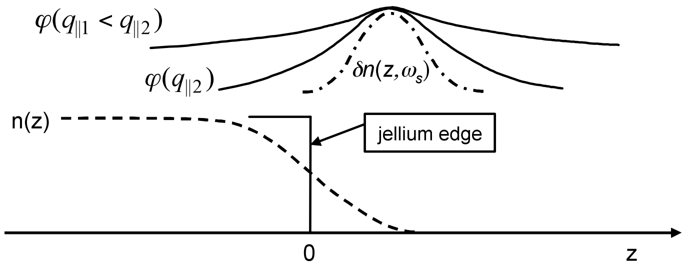
FIG. 1. Energy-loss spectrum of 7.5-eV electrons after specular reflection from the $(1\bar{1}00)$ surface of a ZnO crystal (recorder trace). The angle of incidence is approximately 45°.

H. Ibach, Phys. Rev. Lett. 27 (1971) 253

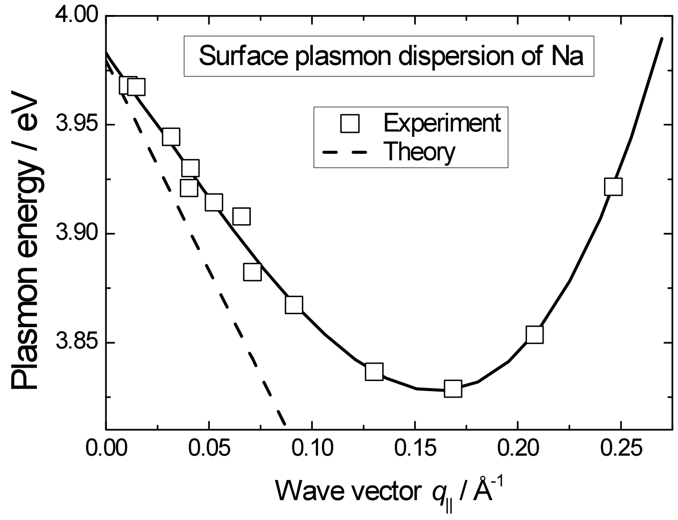
Dispersion of plasmons on free-electron metals

$$\omega_s(q_{\|}) = \omega_s(0)(1 - q_{\|} d(\omega_s)/2\ldots)$$





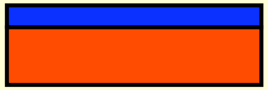
K. D. Tsuei, E. W. Plummer, P. J. Feibelman, Phys. Rev. Lett. 63 (1989) 2256
K.-D. Tsuei, et al., Surf. Sci. 247 (1991) 302



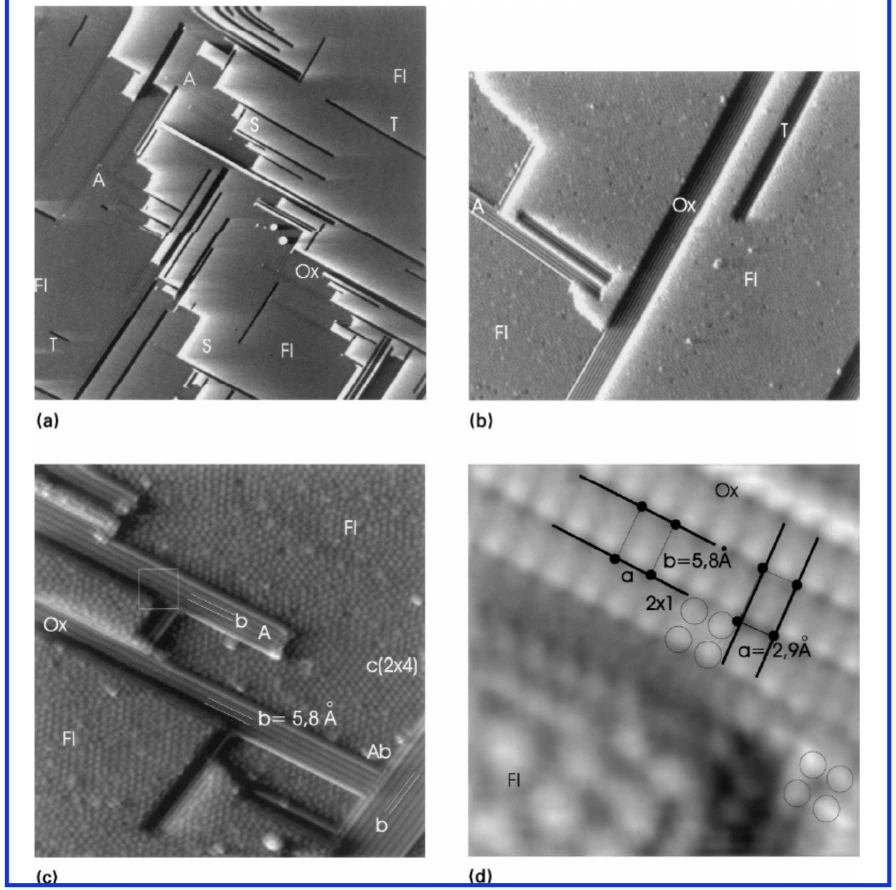
4.2 Dielectric losses of thin films

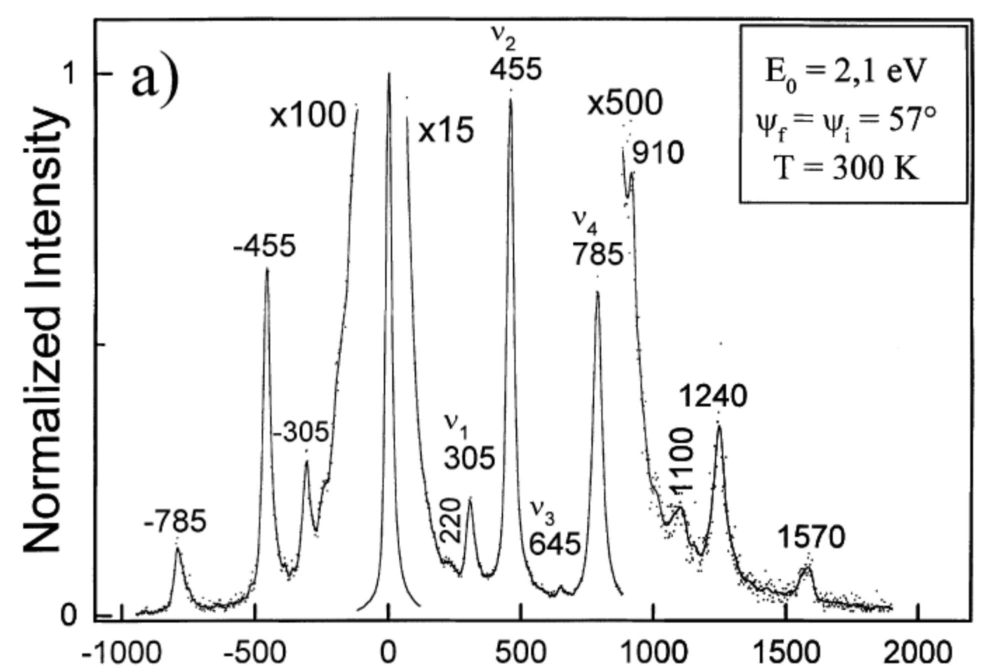
a.) Vibration spectra of oxide films

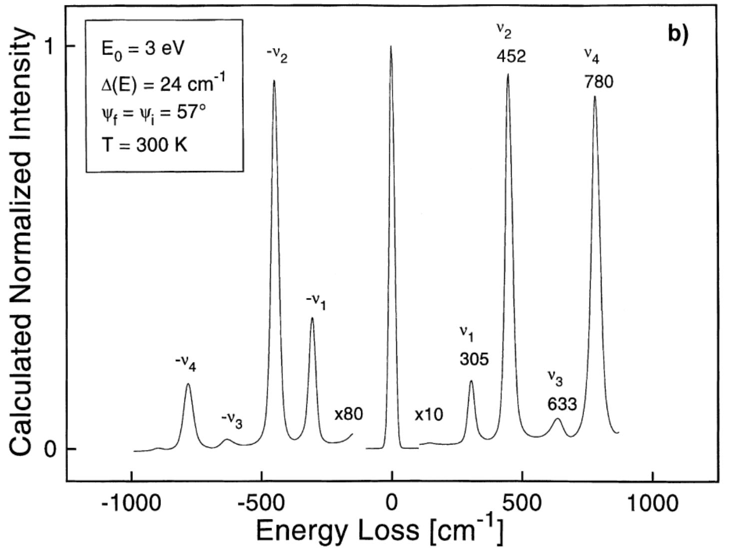
β-Ga_2O_3 on CoGa (1 0 0)



R. Franchy, Surf. Sci. Rep. 38 (2000) 195



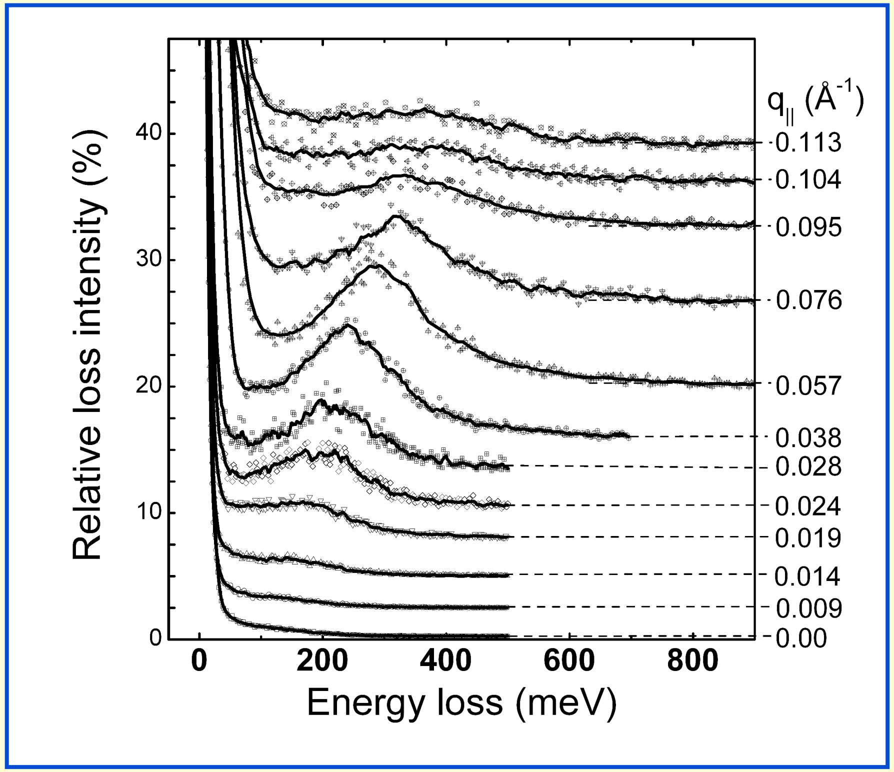


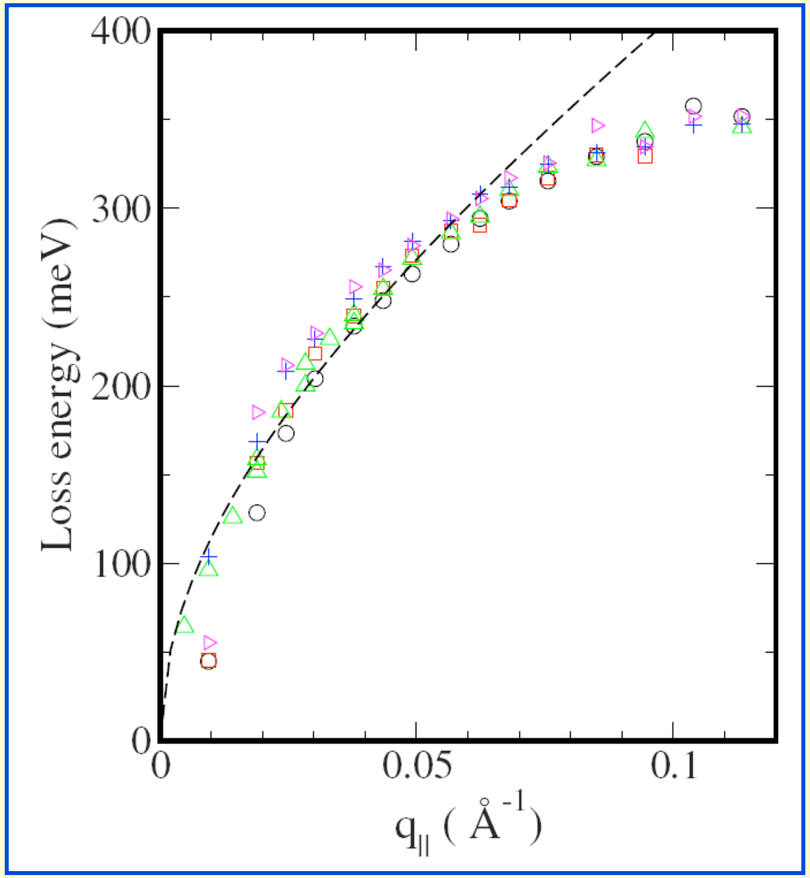


$$P(\boldsymbol{q}_{\|},\omega) = \frac{4e^2}{\hbar^2\pi^2}\frac{q_{\|}^2 v_{\perp}^2}{((\omega - \boldsymbol{q}_{\|}\cdot\boldsymbol{v}_{\|})^2 + q_{\|}^2 v_{\perp}^2)^2}\, d\,\mathrm{Im}(\varepsilon_{s\perp}(\omega))^{-1}$$

b.) 2D-plasmons in thin metallic films on insulators, here $DySi_2$ on Si(111)

E. P. Rugeramigabo, T. Nagao, H. Pfnür, Phys. Rev. B 78 (2008) 155402

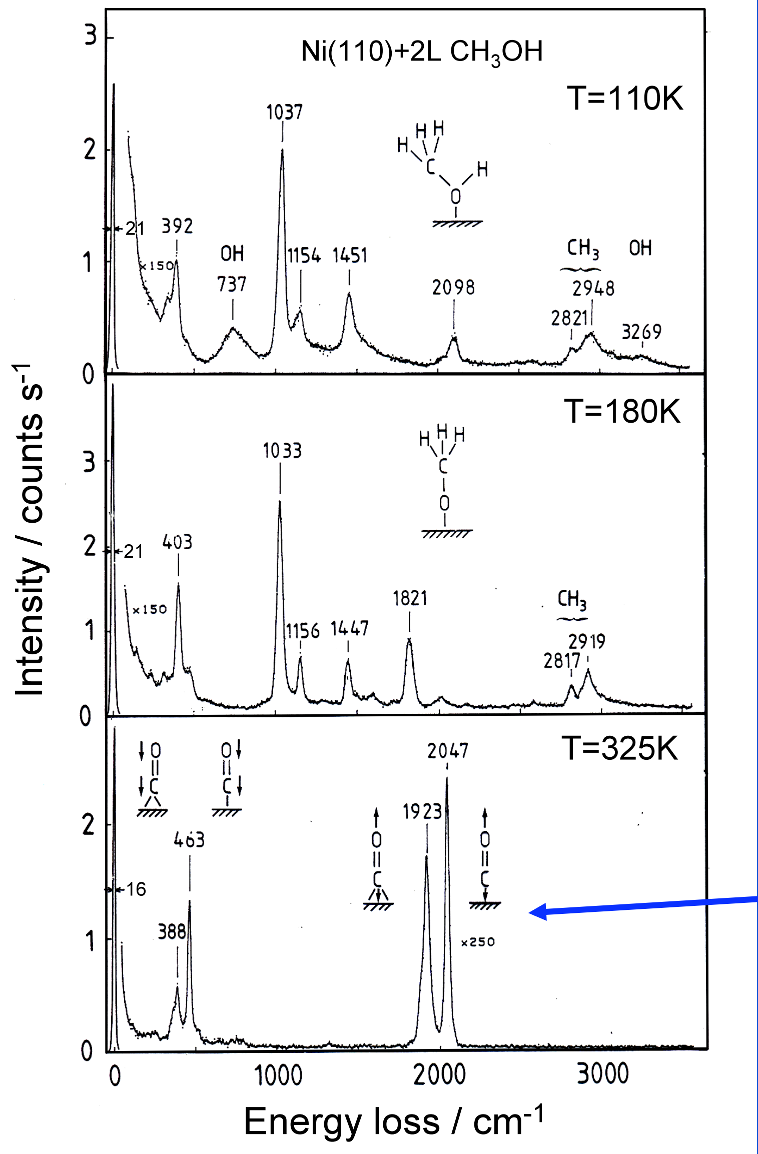




$$\omega^2(q_{\|}) = \frac{e^2}{\varepsilon_0(1+\varepsilon_{Si})}\frac{n_{2D}}{m^*}\left|q_{\|}\right| + 6\hbar^2\pi\frac{n_{2D}}{(2m^*)^2}q_{\|}^2$$

no restoring force on electron for $q_{\|}$ = 0!

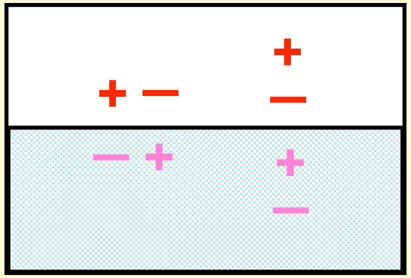
4.3 Dipole scattering from monolayers: Surface chemistry - the most important application of EELS



Example: gradual decomposition of methanol on Ni

Selection rule for dipole scattering on metal surfaces: dipole moment of the mode must be perpendicular to surface!
In the language of group theory these are the modes that belong to the totally symmetric representation of the surface point group of the species !

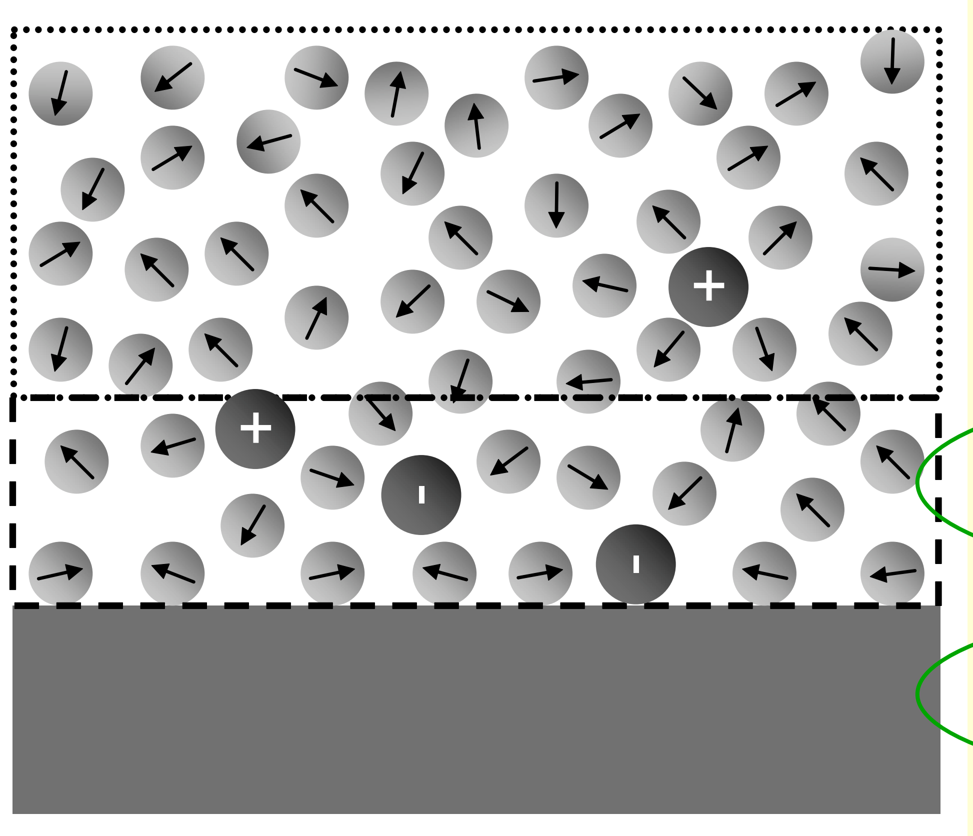
Note:
the surface selection rule is not the same as for molecules in vacuum!!



Utilizing the selection rule:
CO stands upright on surface in head-on and bridging position

Excursion to the metal/electrolyte interface

What are the issues ?



Outline of the problems
(aqueous electrolytes):

Liquid water ✓
solvated ions ✓

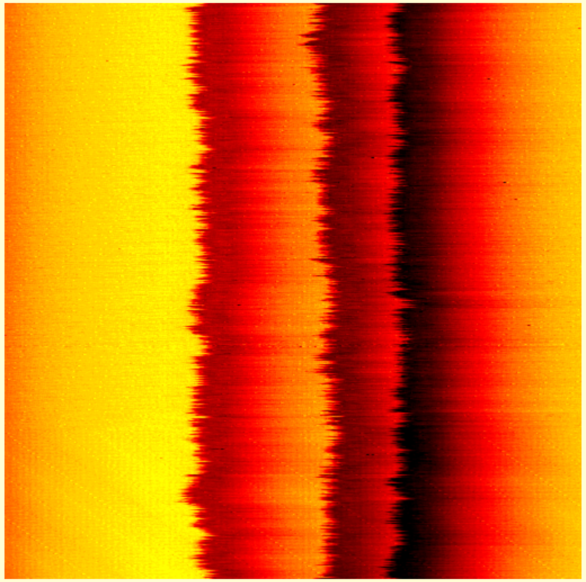
Structure and electric properties of water near surface ???

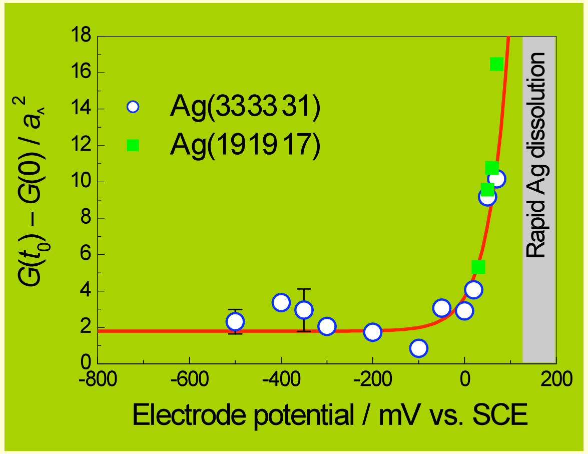
Structure and dynamics of metals in contact with an electrolyte: ✓

For metals in contact with an electrolyte,
a new parameter appears: the electrode potential ϕ

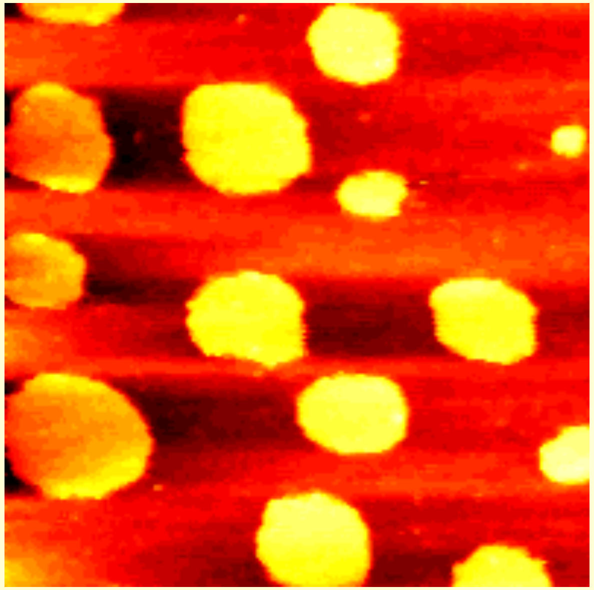
Atom transport dynamics on electrodes

Step equilibrium fluctuations





Coalescense



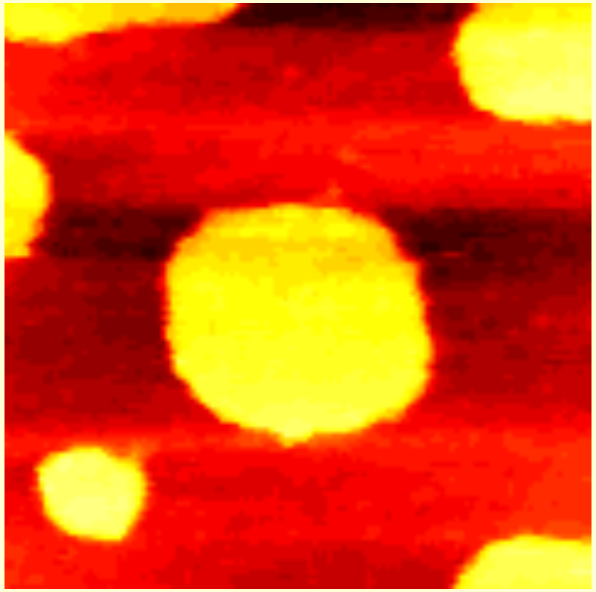
Reason for the potential dependence:

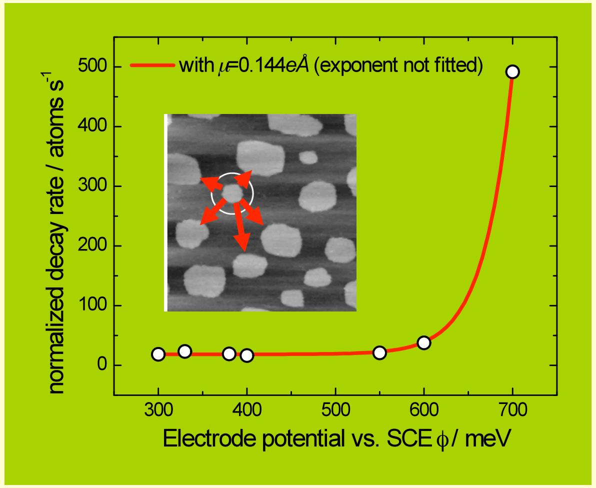
$$E_{act} = E_{act}^{(0)} - p_z \underbrace{\sigma(\phi)}_{\propto\phi} / \varepsilon_0$$

J. E. Müller, H. Ibach, Phys. Rev. B 74 (2006) 085408

M. Giesen et al., Surf. Sci. 595 (2005) 127

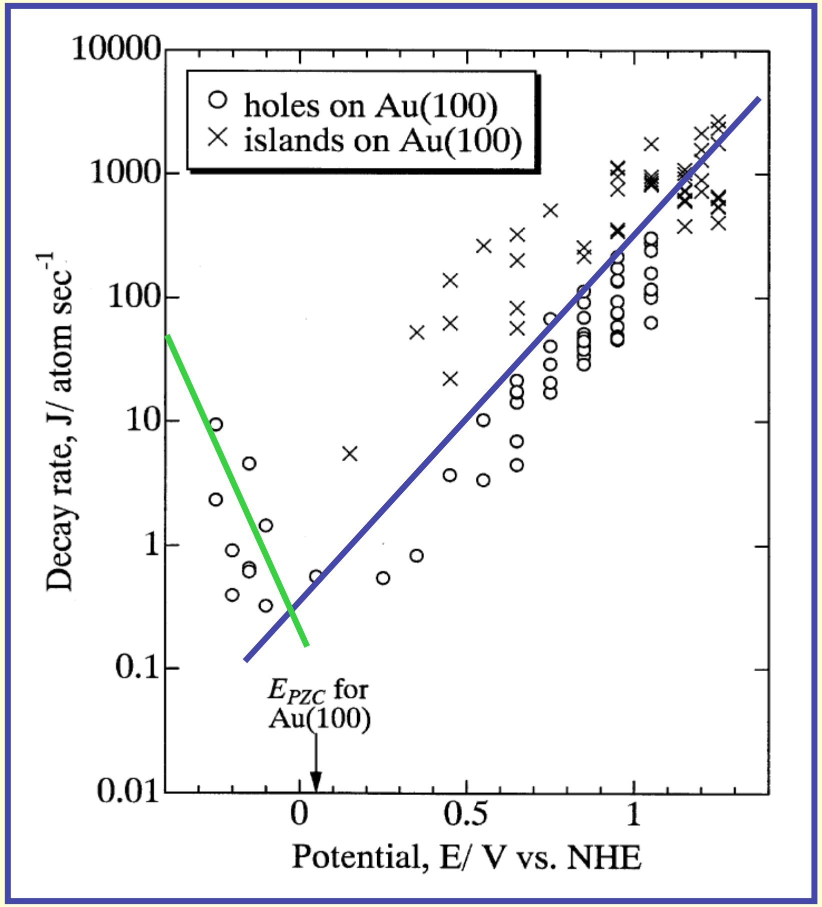
Ostwald ripening





Electrochemical annealing processes

N. Hirai, K.-I. Watanabe, S. Hara,
Surf. Sci. 493 (2001) 568

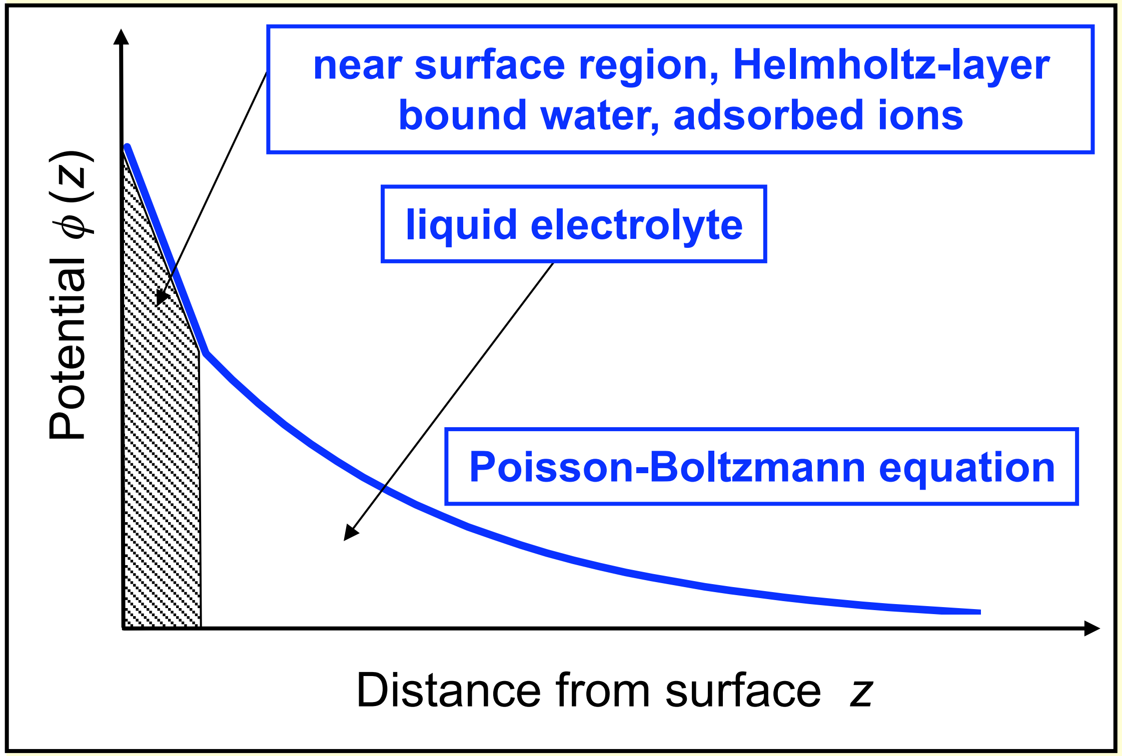


$$E_{act} = E_{act}^{(0)} - p_z \underbrace{\sigma(\phi)}_{\propto\phi} / \varepsilon_0$$

$$\sigma(\phi) = \int_{\phi_{pzc}}^{\phi} C(\tilde{\phi}) \mathrm{d}\tilde{\phi}$$

It is important to understand the capacitance of the metal/electrolyte interface!
Easy to measure, but hard on theory!

Classical (incorrect) picture of solid-electrolyte interface



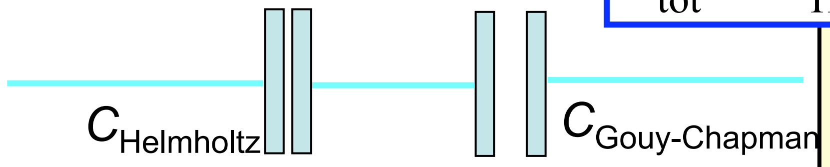
near surface region, Helmholtz-layer bound water, adsorbed ions

liquid electrolyte

Poisson-Boltzmann equation

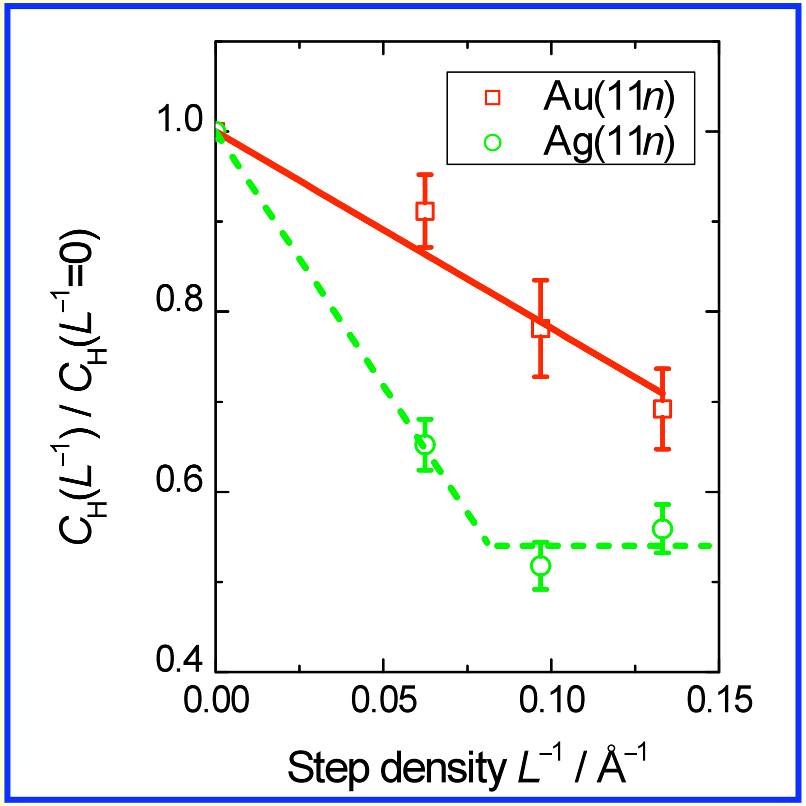
Equivalent circuit

$$\frac{1}{C_{\mathrm{tot}}} = \frac{1}{C_{\mathrm{H}}} + \frac{1}{C_{\mathrm{GCh}}}$$



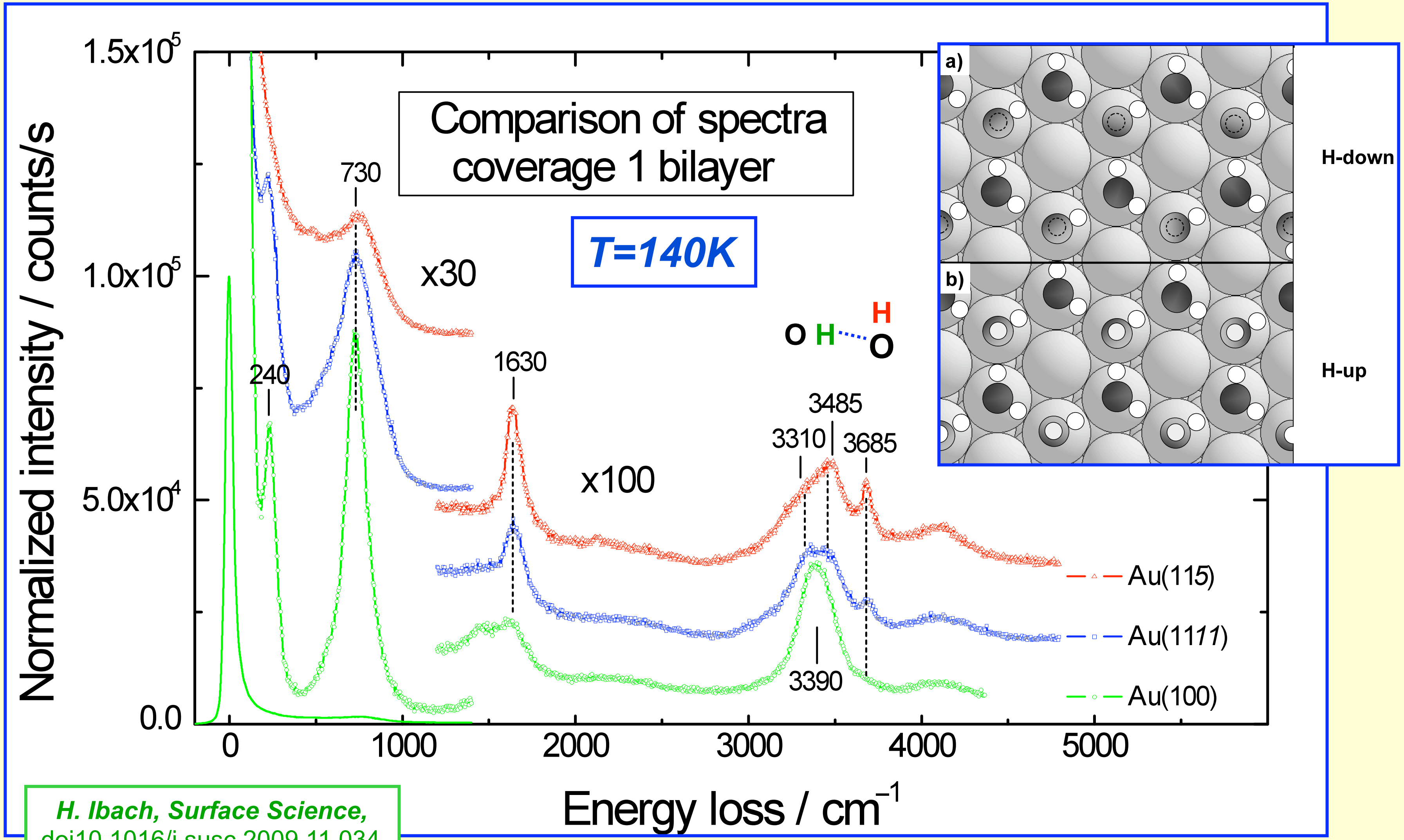
Experiment on stepped surfaces

G. Beltramo, M. Giesen, H. Ibach
Electrochim. Acta 54 (2009) 4305



Why ???

EELS spectra of of adsorbed H_2O on Au(100), Au(11 11) and Au(115)



H. Ibach, Surface Science,
doi10.1016/j.susc.2009.11.034

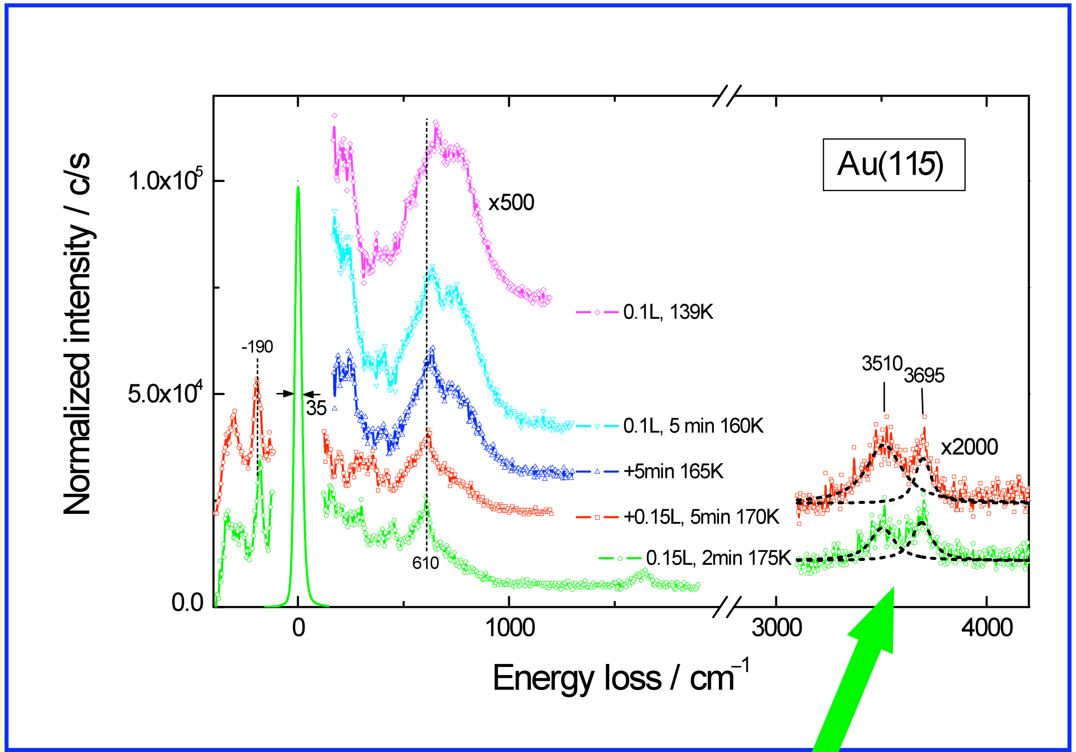
Au(100) realizes the H-down bilayer!

Stepped surfaces feature non-H-bonded hydrogen!

Low coverage, modest annealing:

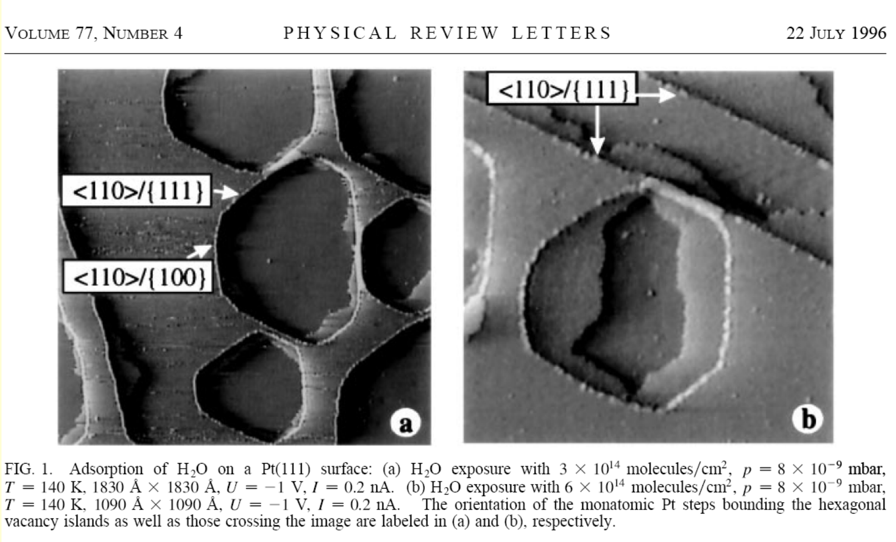
water chains at steps

Spectrum matches proposal from DFT



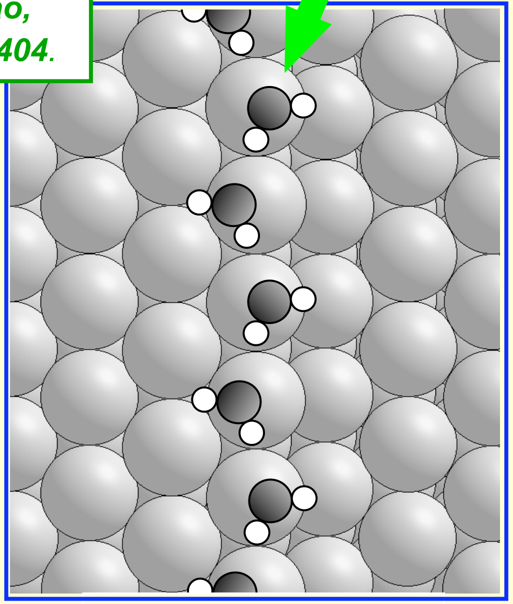
M. Morgenstern, T. Michely, G. Comsa, Phys. Rev. Lett. 77 (1996) 703

S. Meng, E. G. Wang, S. Gao, Phys. Rev. B 69 (2004) 195404.

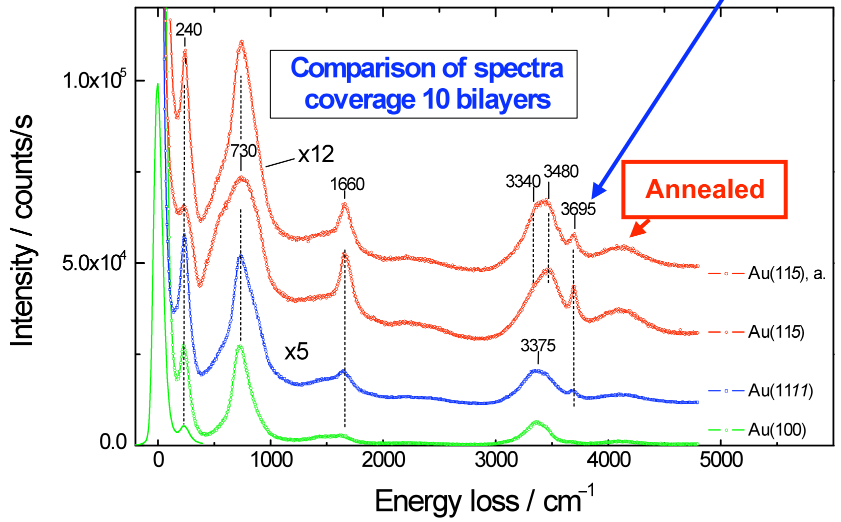


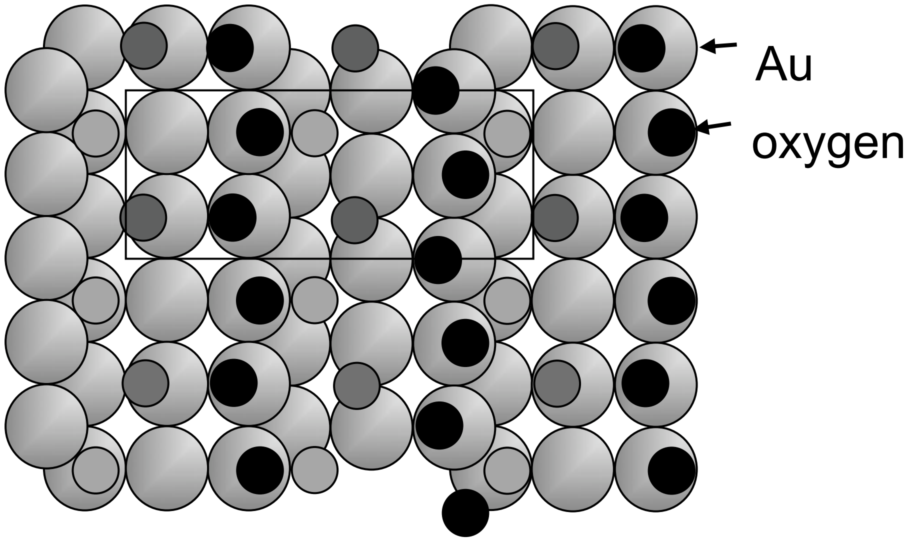
VOLUME 77, NUMBER 4 PHYSICAL REVIEW LETTERS 22 JULY 1996

FIG. 1. Adsorption of H_2O on a Pt(111) surface: (a) H_2O exposure with 3×10^{14} molecules/cm^2, $p = 8 \times 10^{-9}$ mbar, $T = 140$ K, 1830 Å × 1830 Å, $U = -1$ V, $I = 0.2$ nA. (b) H_2O exposure with 6×10^{14} molecules/cm^2, $p = 8 \times 10^{-9}$ mbar, $T = 140$ K, 1090 Å × 1090 Å, $U = -1$ V, $I = 0.2$ nA. The orientation of the monatomic Pt steps bounding the hexagonal vacancy islands as well as those crossing the image are labeled in (a) and (b), respectively.



Non-H-bonded hydrogen atoms at any coverage!





The safe conclusion:

there is a crucial difference between water at stepped and flat surfaces!

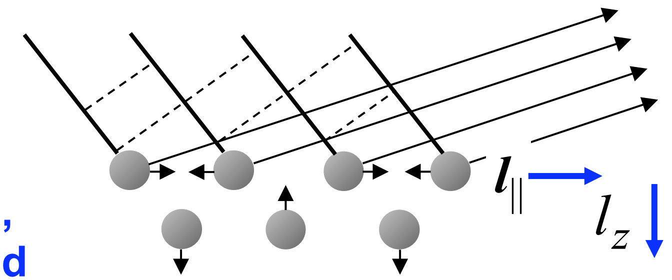
Speculation:

Lower polarizability of water due to non-H-bonded hydrogen atoms??

Therefore lower Helmholtz-capacitance??

Current collaboration with Sebastien Filhol
Axel Gross
Wolfgang Schmickler
on this and related issues

5. Impact scattering, the method to study the dispersion of surface phonons



Similar to inelastic neutron scattering, however complicated by multiple elastic scattering

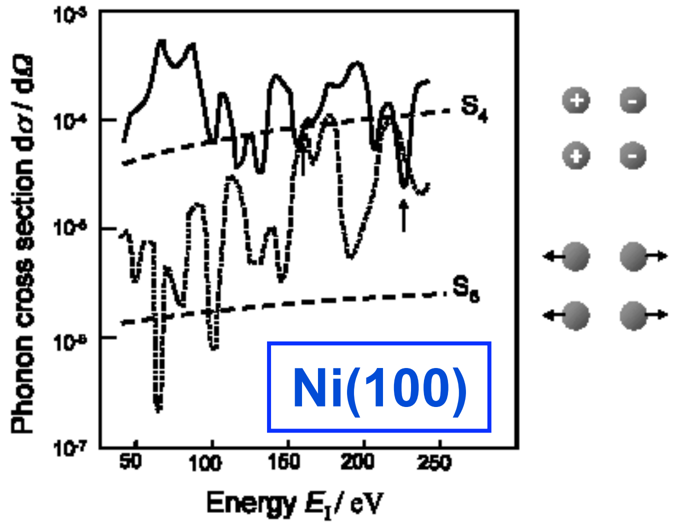
$$f = f_0 e^{-i\omega_0 t} \sum_{\boldsymbol{l}_{\|}, l_z, \kappa} e^{-i\boldsymbol{K}\cdot\boldsymbol{r}(\boldsymbol{l}_{\|} l_z \kappa, t)}$$

$$\boldsymbol{r}(\boldsymbol{l}_{\|} l_z \kappa, t) = \boldsymbol{r}_0(\boldsymbol{l}_{\|} l_z \kappa) + \boldsymbol{u}_0(\boldsymbol{q}_{\|} l_z \kappa) e^{\pm i(\boldsymbol{q}_{\|}\cdot \boldsymbol{r}_0(\boldsymbol{l}_{\|} l_z \kappa) - \omega(\boldsymbol{q}_{\|}) t)}$$

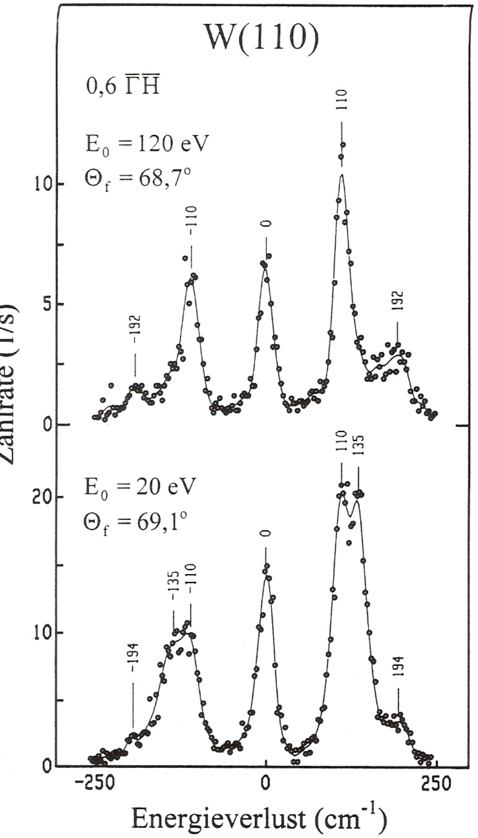
$$f = f_0 e^{-i\omega_0 t} \delta(\boldsymbol{K}_{\|}) \sum_{l_z, \kappa} e^{-i\boldsymbol{K}\cdot\boldsymbol{r}(0 l_z \kappa)} + f_0 e^{-i(\omega_0 \pm \omega(\boldsymbol{q}_{\|}))t} \delta(\boldsymbol{K}_{\|} \mp \boldsymbol{q}_{\|}) \sum_{l_z, \kappa} \boldsymbol{K}\cdot\boldsymbol{u}_0(\boldsymbol{q}_{\|} l_z \kappa) e^{-i\boldsymbol{K}\cdot\boldsymbol{r}(0 l_z \kappa)}$$

Multiple elastic scattering causes strong oscillations in intensity!
here: theory confirmed by experiment

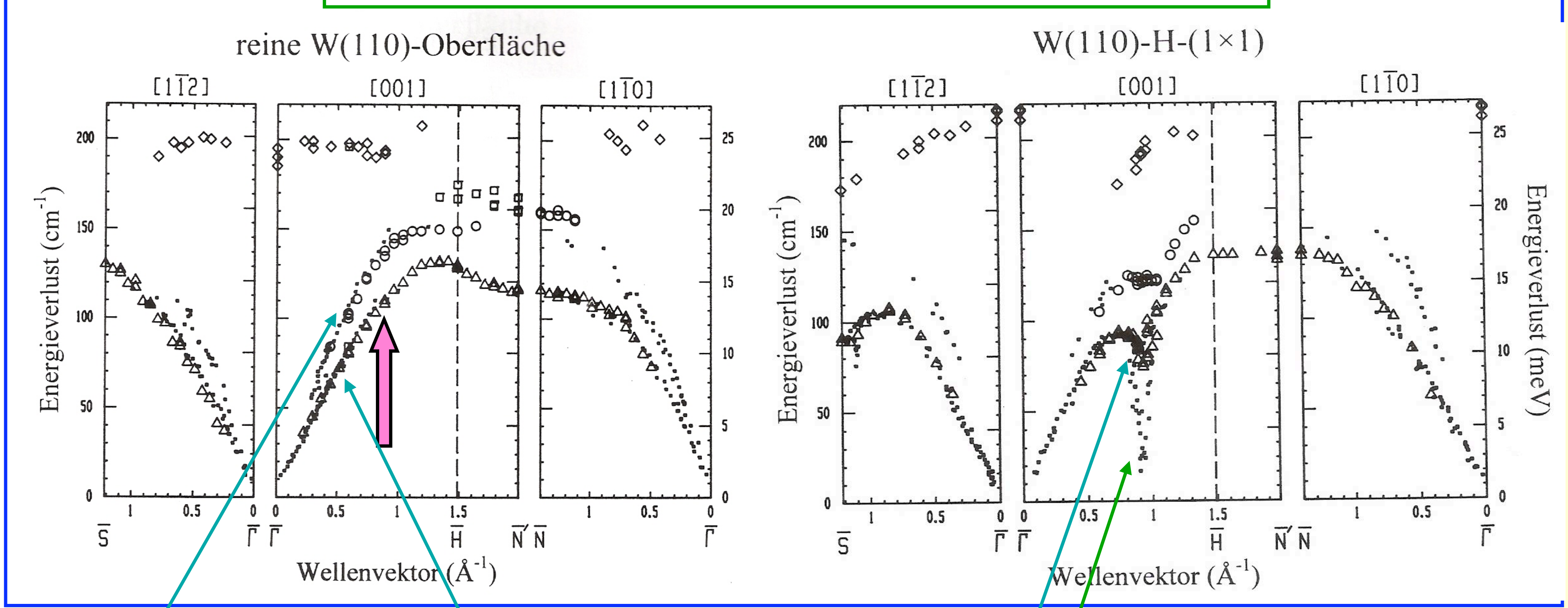
M.L.Xu et al., Phys. Rev. Lett. 54 (1985) 1171



Experimental example: W(110) at $q_{\|} = 0.9$Å^{-1}, two different electron energies



M. Balden, S. Lehwald, E. Preuss, H. Ibach, Surf. Sci. 307-309 (1994) 1141
M. Balden, S. Lehwald, H. Ibach, Phys. Rev. B 53 (1996) 7479



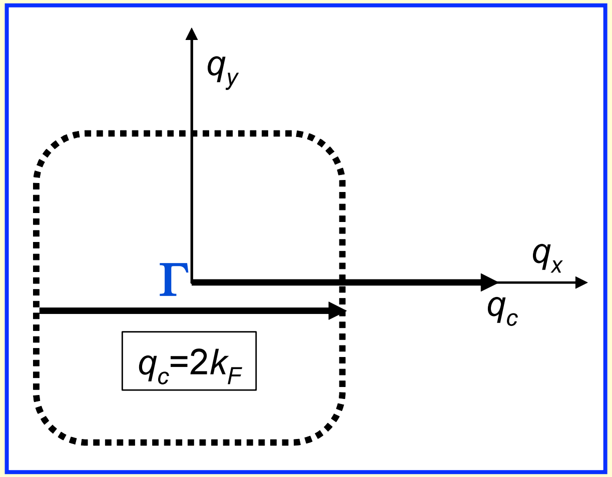
longitudinal surface phonon

Rayleigh mode

Kohn anomaly

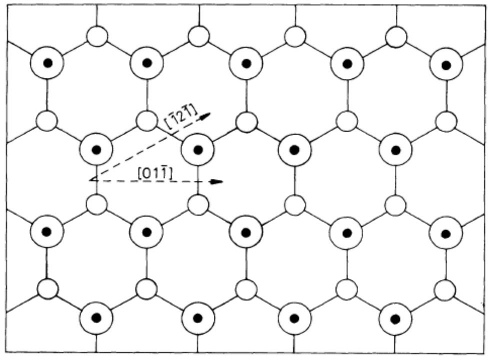
E. Hulpke, J. Lüdecke, Phys. Rev. Lett. 68 (1992) 2846

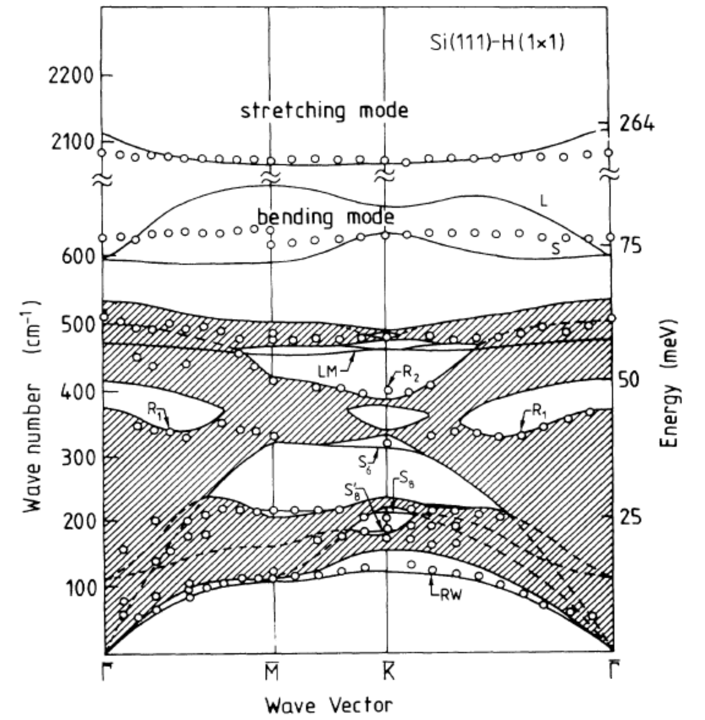
$q_{||}$ -vector of e-h excitation matches $q_{||}$ of surface phonon. Depending electron- phonon coupling and the dimensionality, one has a dip in the the dispersion.



Two more examples

The H-terminated Si(111) surface



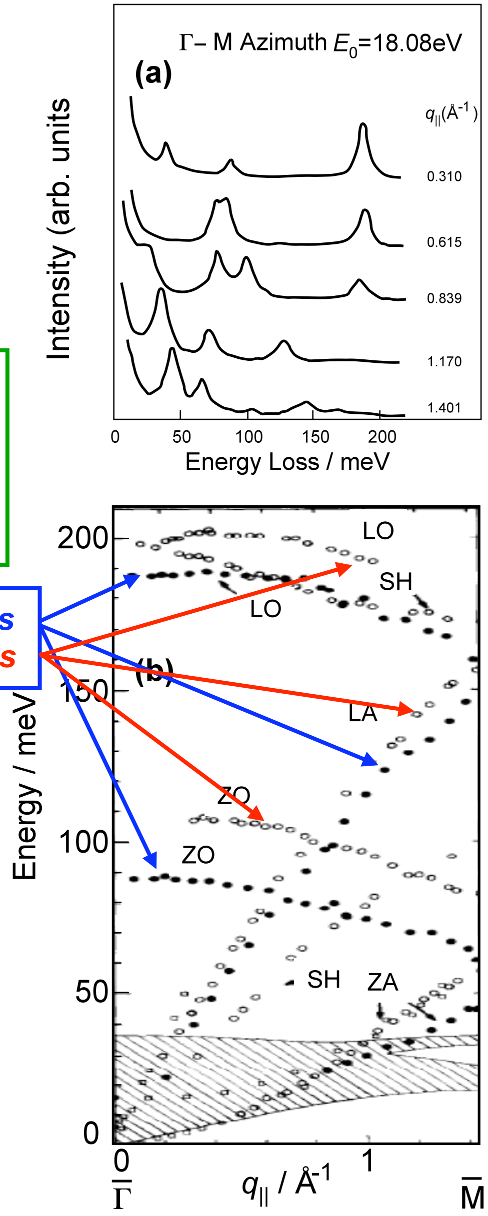


C. Stuhlmann, et al., Phys. Rev. B 45 (1992) 6786.

Monolayer of graphite on Ni(111): "Graphene"

T. Aizawa et al.,
H. Hirano et al.,
Ch. Oshima
Surface Science 237
(1990) 194

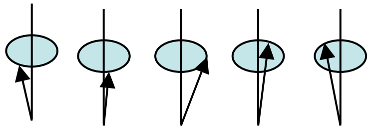
Graphene: solid symbols
Graphite: open sysmbols

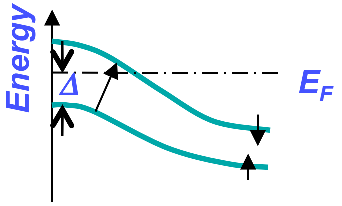


6. Spin-polarized EELS and surface magnons

Spin-polarized EELS explores a hitherto inaccessible region in the $E(q_{||})$ space at surfaces!

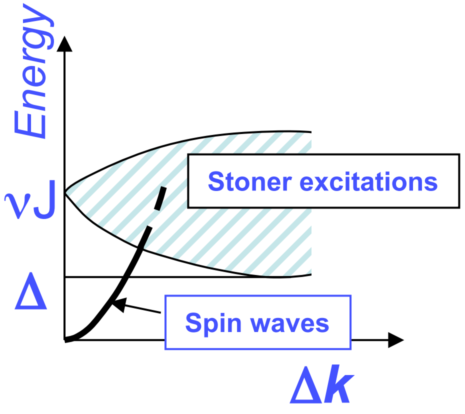
Spin-waves and Stoner excitations

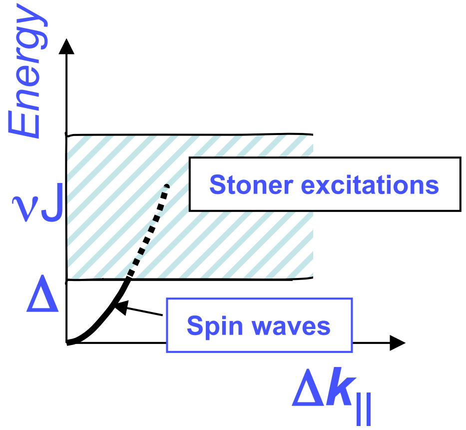


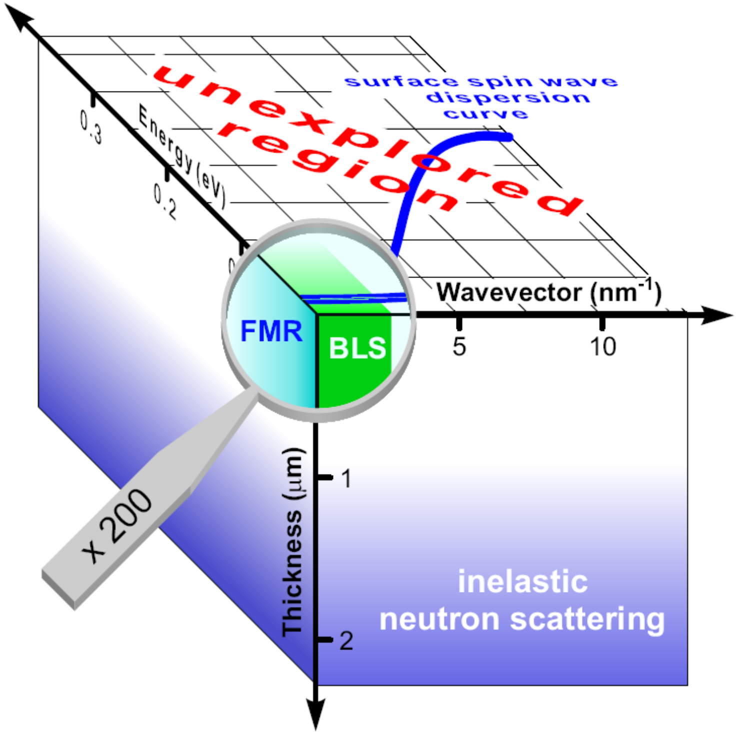


Bulk: Full *k*-conservation

Surface, thin films: only $k_{||}$ is conserved

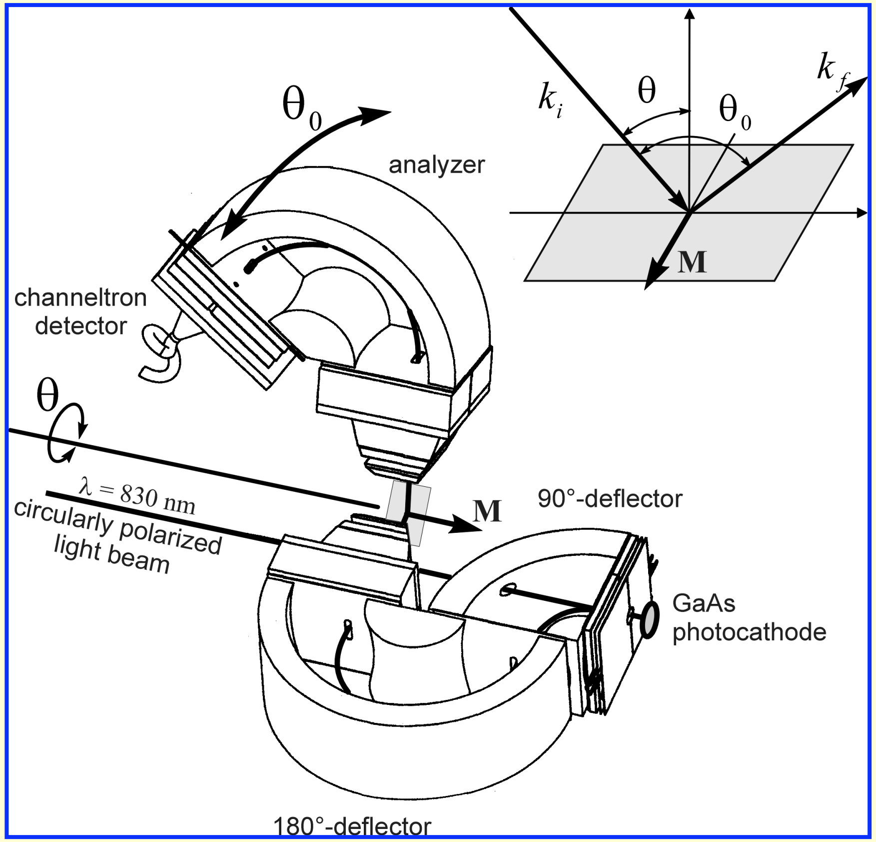






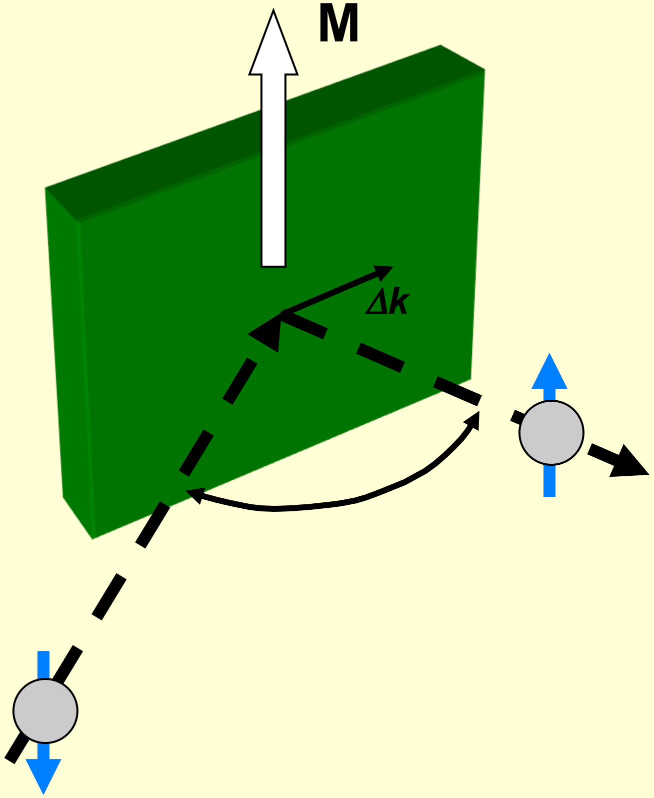
Courtesy of Rüdiger Vollmer (†)

The first spin-polarized EEL Spectrometer



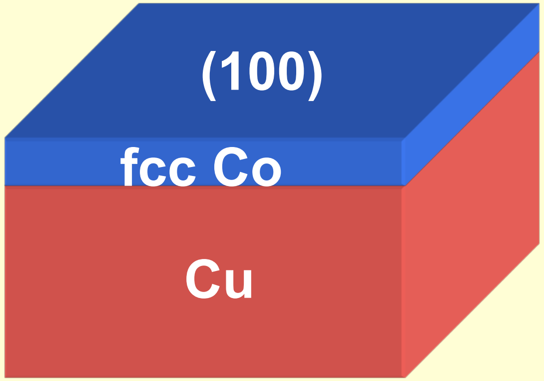
H. Ibach et al., Rev. Sci. Instrum. 74 (2003) 4089

tranverse polarization of beam

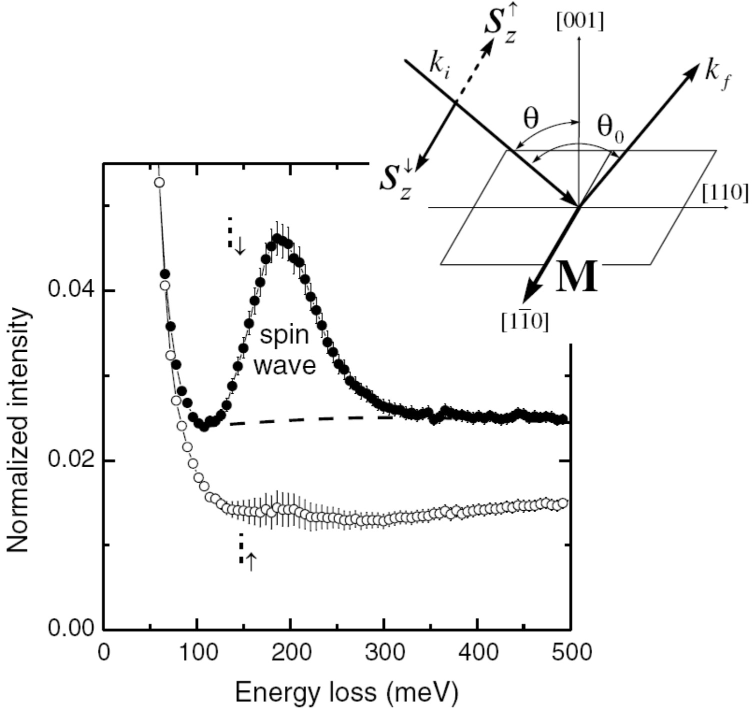


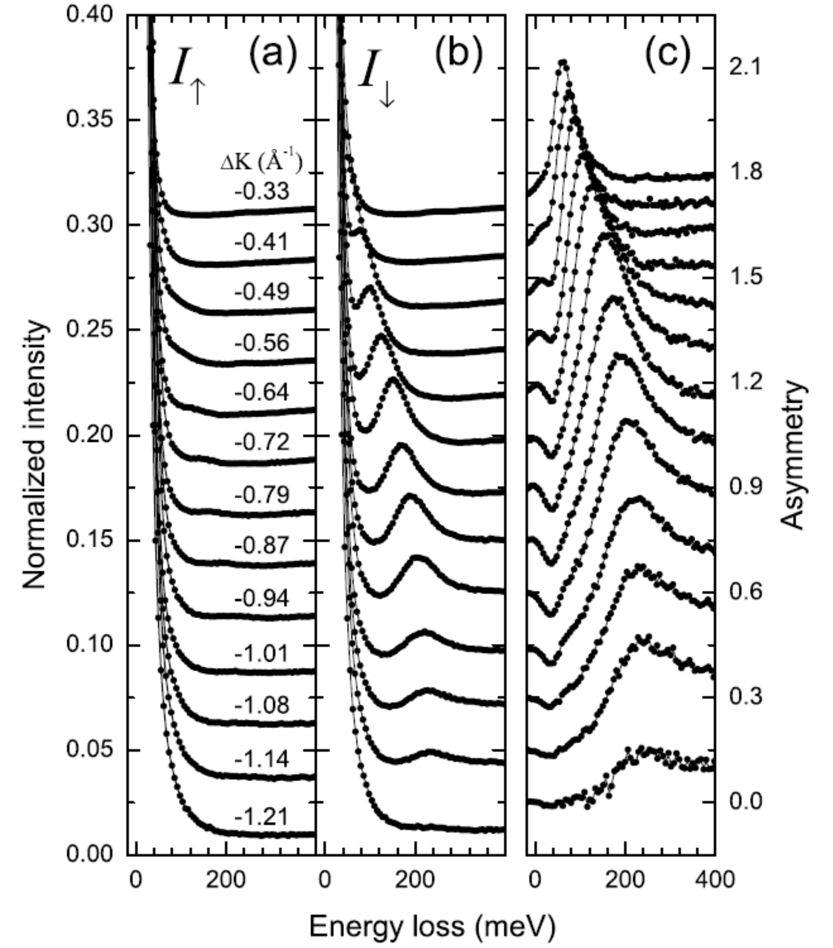
Transverse polarization and spin perpendicular to the scattering plane has the advantage that $\vec{P} \cdot \vec{M}$ stays constant in $q_{||}$ -scan

Spin waves on 8 ML fcc Co on Cu(100)



Deposited at 300 K, annealed to 450 K for 5 min

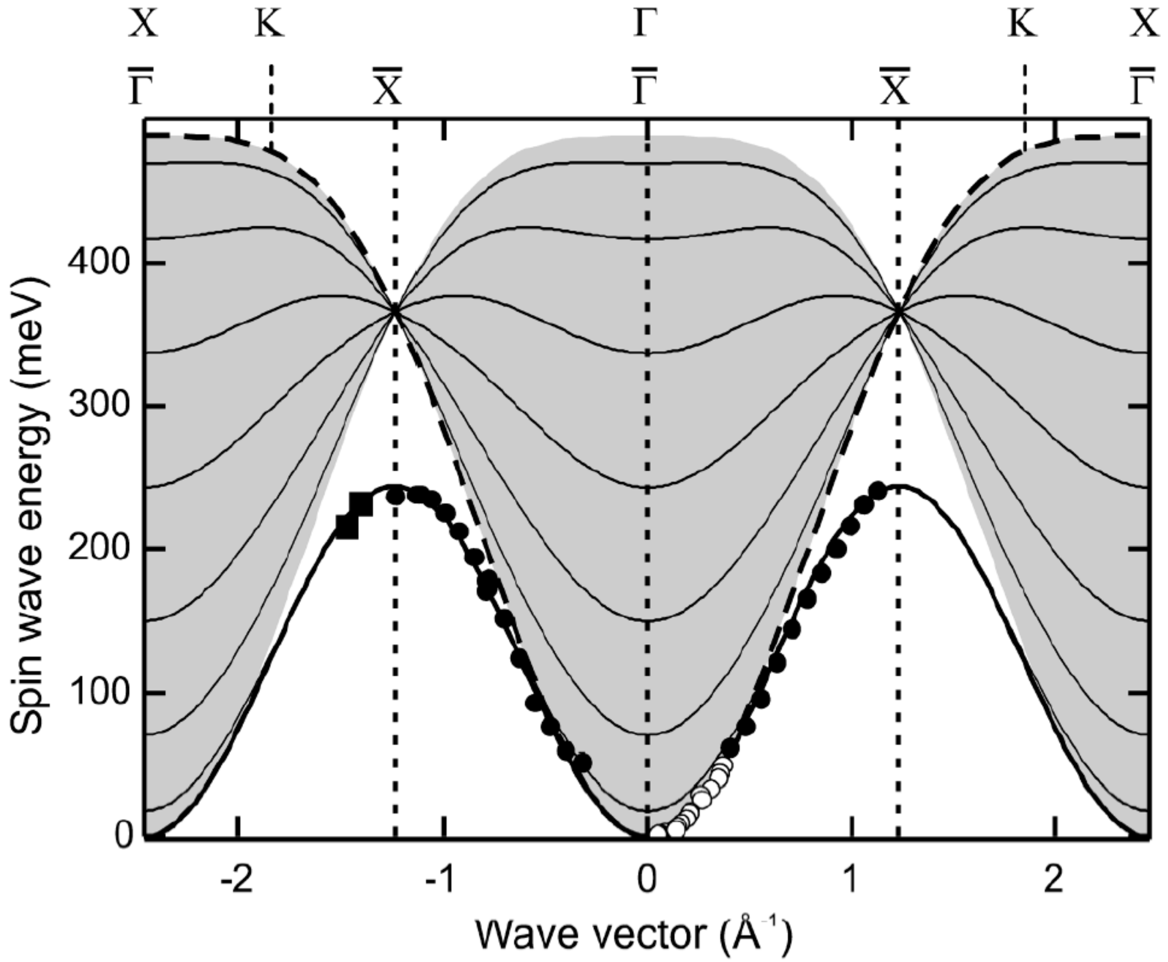




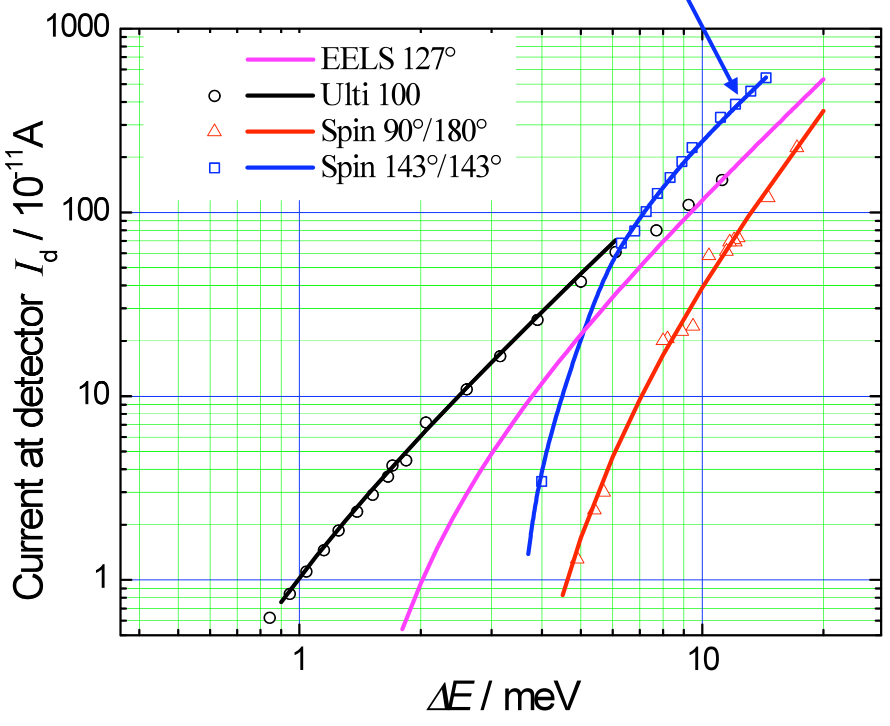
$$I_{\uparrow(\downarrow)} = \left[I'_{\uparrow(\downarrow)}(P+1) + I'_{\downarrow(\uparrow)}(P-1)\right]/2P$$

R. Vollmer et al., PRL 91 (2003) 147201

The observed spin wave branch is a surface mode of the film!

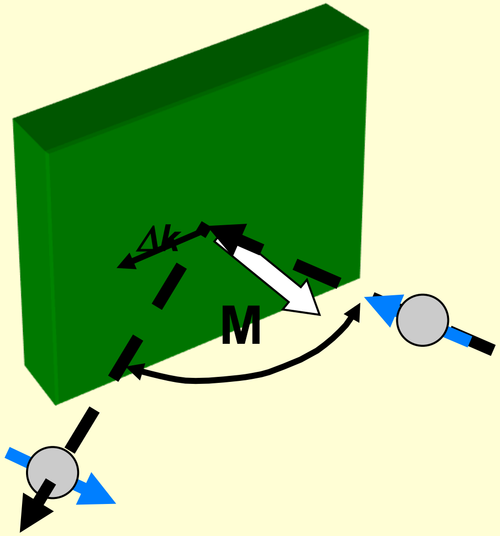


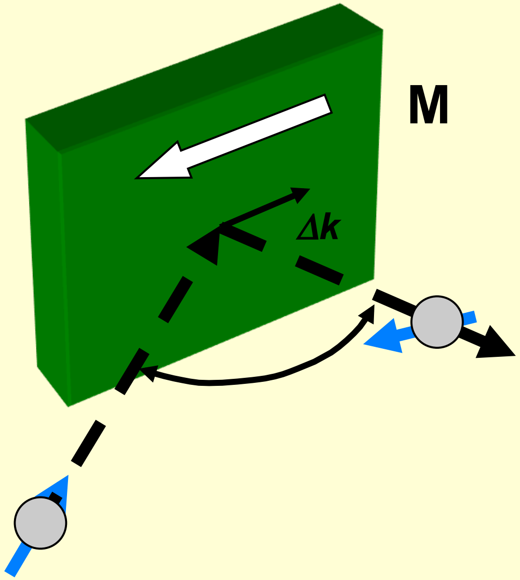
New high current spectrometer in conventional design



In conventional spectrometers
spin is longitudinal to the beam!

Disadvantage: ***P·M*** **not at maximum**
Advantages: much higher currents!
perpendicular polarized films can be studied!

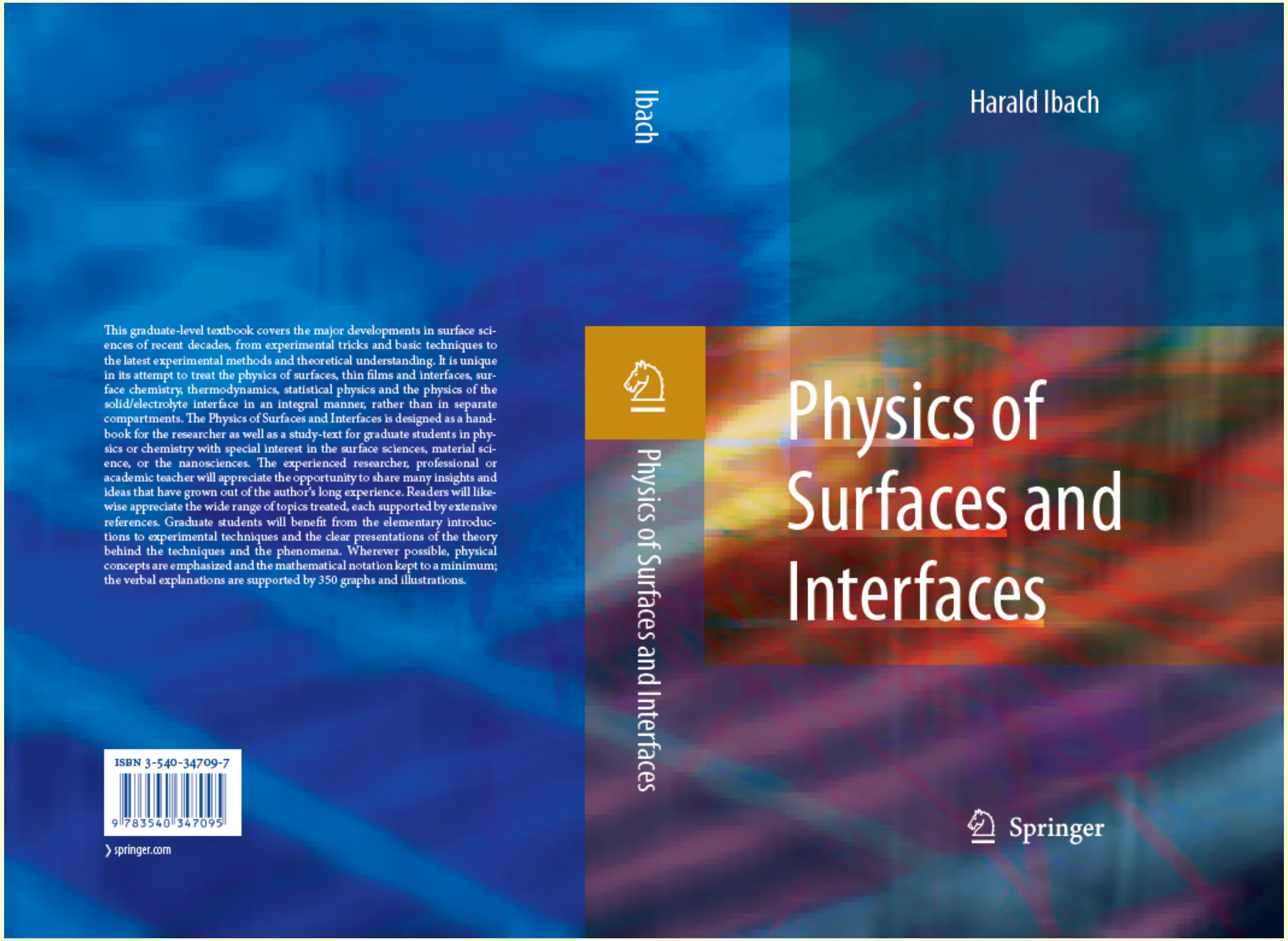




Summary

- Electron energy loss spectroscopy is a mature technique for the *Atomic Level Characterization of Surfaces*
- Capable of resolution down to 1 meV
- Rather versatile tool as different scattering mechanism may be employed
- Most important application is vibration spectroscopy of surfaces and adsorbed species
  sensitivity ranges down to less than 1/100 of a monolayer
- EELS has played (and still does) a crucial role in surface chemistry
- The full dispersion of surface phonons on ordered surfaces explored
- Surface plasmons at surfaces, in thin films and even 1D wires, interesting future ahead concerning nano-systems!
- For the first time: Full dispersion of surface magnetic excitations, spin waves in ultrathin films, molecular magnet systems

For more on EELS and Interface Science in general including solid electrolyte interface see: Springer 2006, 650 pages, ~75$



This graduate-level textbook covers the major developments in surface sciences of recent decades, from experimental tricks and basic techniques to the latest experimental methods and theoretical understanding. It is unique in its attempt to treat the physics of surfaces, thin films and interfaces, surface chemistry, thermodynamics, statistical physics and the physics of the solid/electrolyte interface in an integral manner, rather than in separate compartments. The Physics of Surfaces and Interfaces is designed as a handbook for the researcher as well as a study-text for graduate students in physics or chemistry with special interest in the surface sciences, material science, or the nanosciences. The experienced researcher, professional or academic teacher will appreciate the opportunity to share many insights and ideas that have grown out of the author's long experience. Readers will likewise appreciate the wide range of topics treated, each supported by extensive references. Graduate students will benefit from the elementary introductions to experimental techniques and the clear presentations of the theory behind the techniques and the phenomena. Wherever possible, physical concepts are emphasized and the mathematical notation kept to a minimum; the verbal explanations are supported by 350 graphs and illustrations.

ISBN 3-540-34709-7

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