Max-Planck-Gesellschaft

vibrational and rotational spectroscopy on surfaces

Thomas Risse

Fritz-Haber-Institut der Max-Planck Gesellschaft,
Abteilung Chemische Physik
Faradayweg 4-6
14195 Berlin

Outline

Max-Planck-Gesellschaft

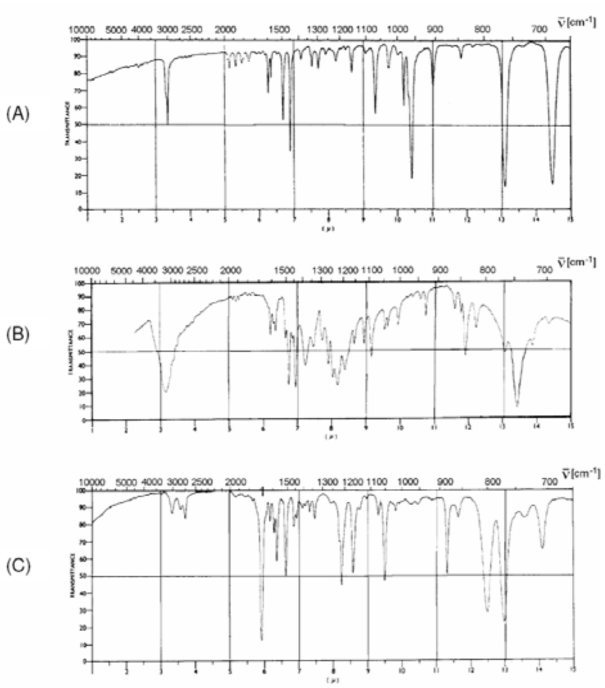
- Introduction
- electron energy loss spectroscopy (EELS)
- infrared spectroscopy
- helium atom scattering (HAS)
- tip enhanced Raman spectroscopy/SERS
- SFG (sum frequency generation)
- electron spin resonance

Introduction

Max-Planck-Gesellschaft

chemical perspective

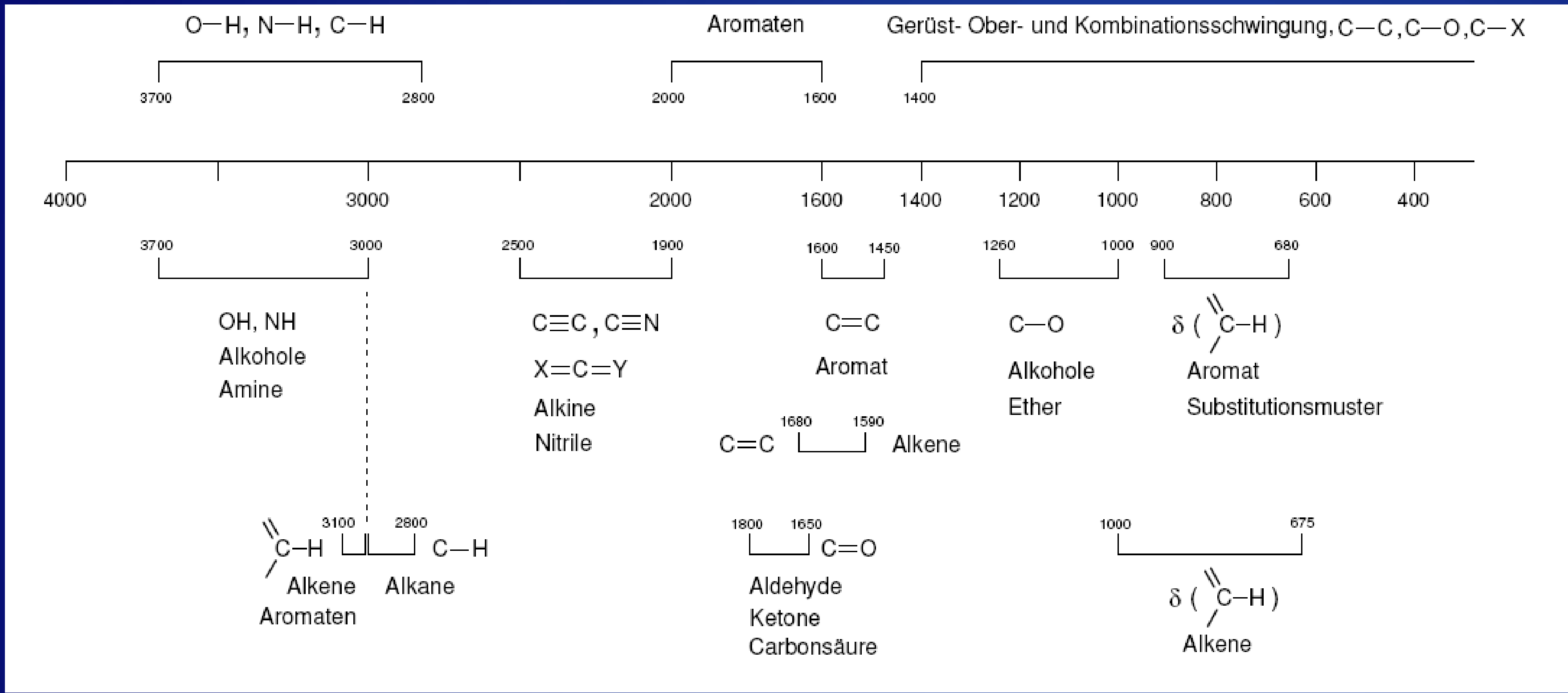
Aufgabe 2: Die dargestellten IR-Spektren können von 1-Naphthaldehyd, E-Zimtaldehyd, trans-Stilben, 2,4,6-Tri-t-butylphenol, 2,2´-Dihydroxybiphenyl und 4,4´-Dihydroxybiphenyl stammen. Welches Spektrum gehört zu welcher Substanz? Ordnen Sie die charakteristischen Banden zu.



Introduction

Max-Planck-Gesellschaft

chemical perspective

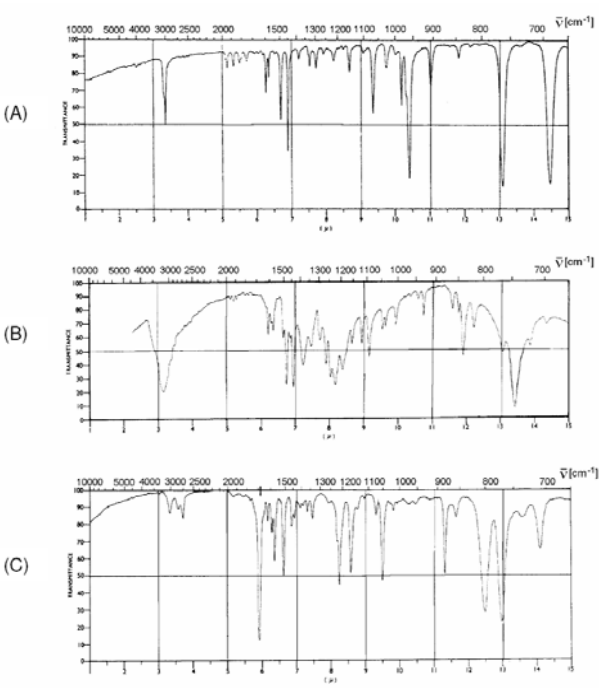


Introduction

Max-Planck-Gesellschaft

chemical perspective

Aufgabe 2: Die dargestellten IR-Spektren können von 1-Naphthaldehyd, E-Zimtaldehyd, trans-Stilben, 2,4,6-Tri-t-butylphenol, 2,2´-Dihydroxybiphenyl und 4,4´-Dihydroxybiphenyl stammen. Welches Spektrum gehört zu welcher Substanz? Ordnen Sie die charakteristischen Banden zu.



physical perspective

PHYSICAL REVIEW B **66**, 073414 (2002)

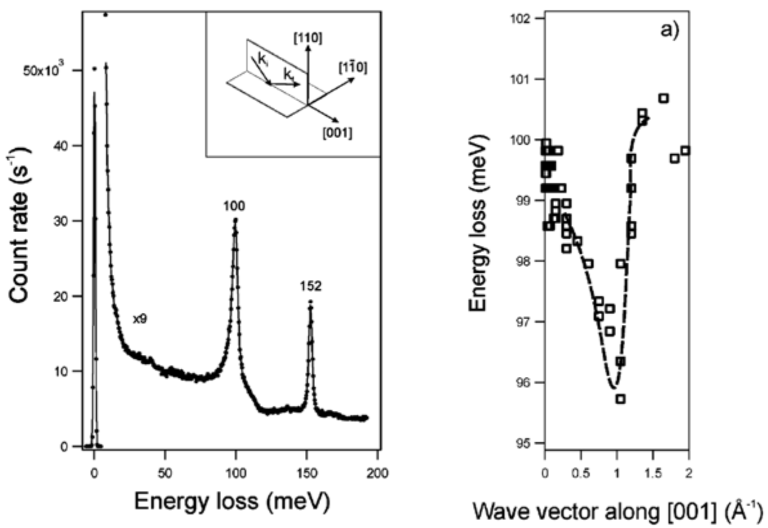
Anomalous dispersion of adsorbate phonons of Mo(110)-H

Jörg Kröger*
Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany

Sieghart Lehwald, Martin Balden, and Harald Ibach
Institut für Schichten und Grenzen, Forschungszentrum Jülich, D-52425 Jülich, Germany
(Received 8 November 2001; published 21 August 2002)

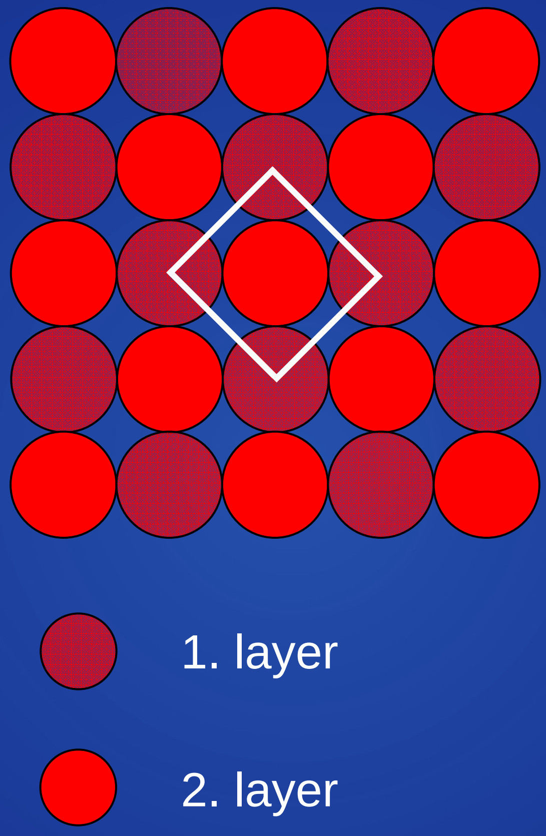
The dispersion curve of the longitudinal-optical adsorbate phonon on hydrogen-saturated Mo(110) along [001] is found to exhibit an anomalous indentation. The maximum indentation is observed at a wave vector, which coincides within the experimental angular resolution with the wave vector, at which the known giant Kohn anomaly for the transverse- and longitudinal-acoustic substrate surface phonons along [001] occurs.

DOI: 10.1103/PhysRevB.66.073414 PACS number(s): 68.35.Ja, 63.20.Kr, 68.43.Pq, 73.20.At



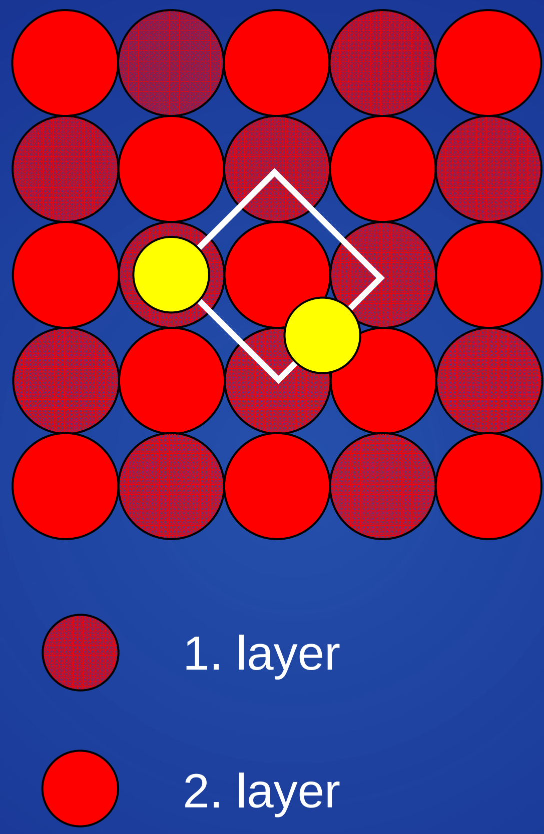
EELS

H on W(100)



EELS

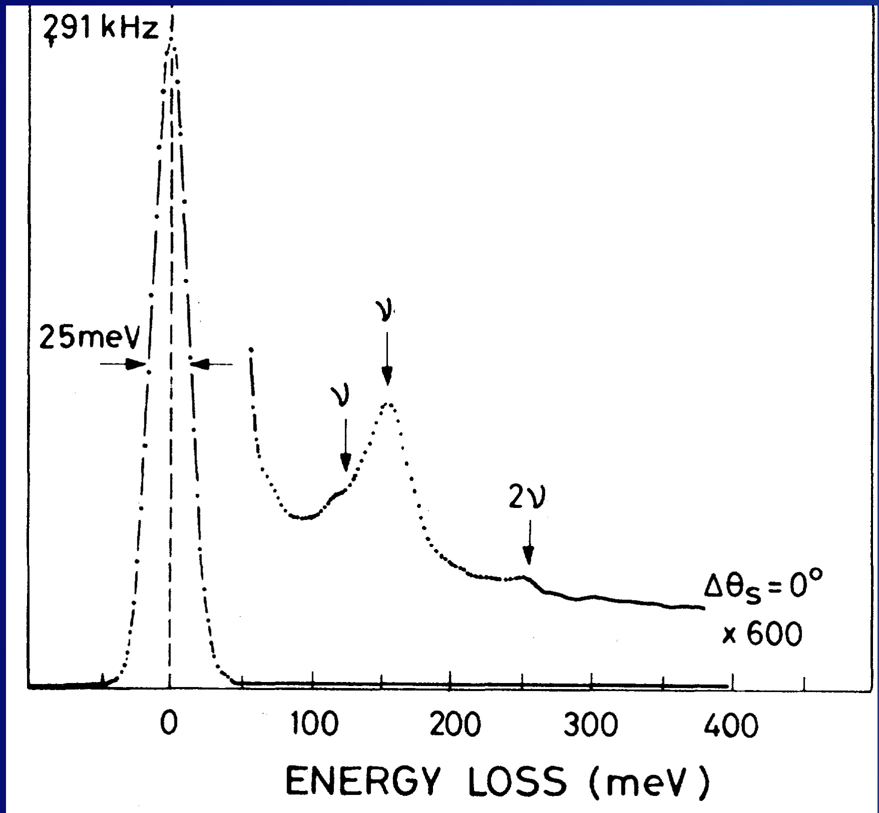
H on W(100)

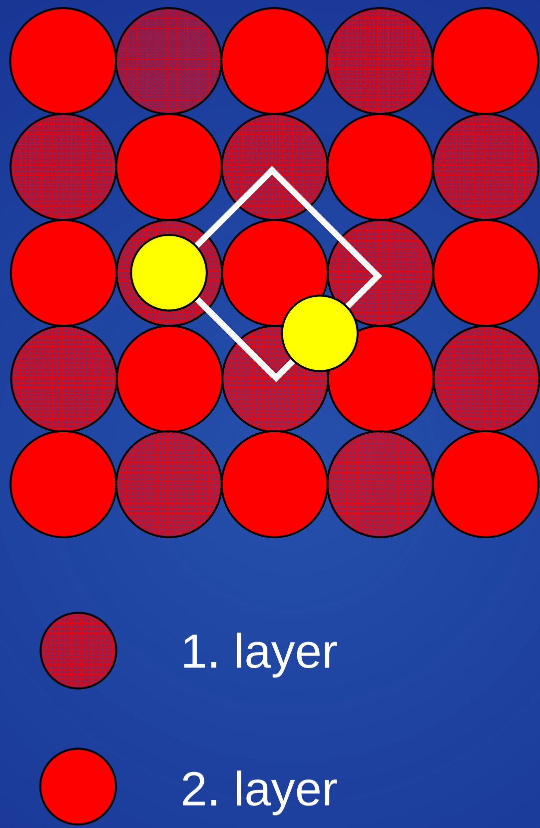


EELS

H on W(100)

Max-Planck-Gesellschaft

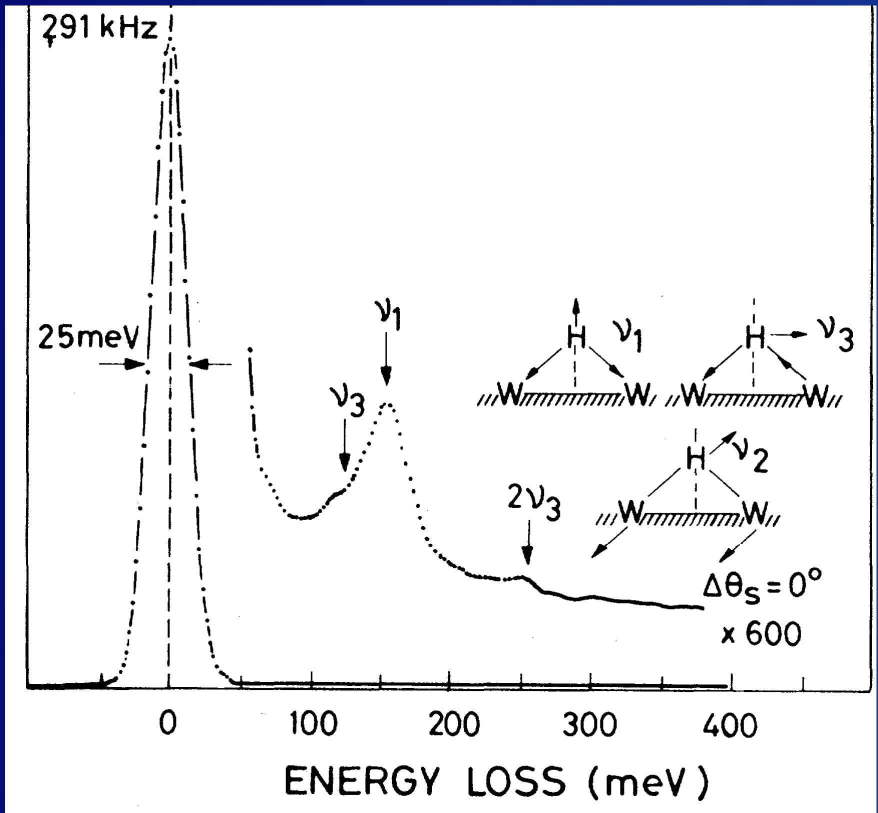


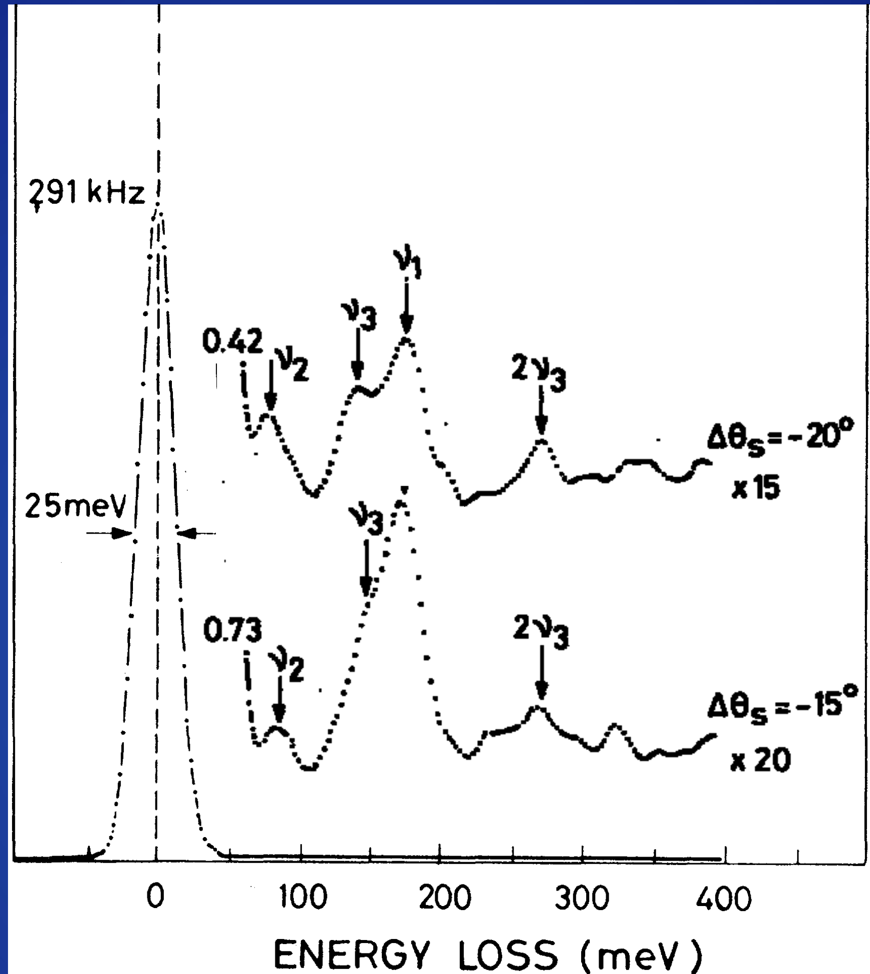


W. Ho, R. F. Willis, and E. W. Plummer, Phys. Rev. Lett. 40, 1463 (1978).

EELS

H on W(100)



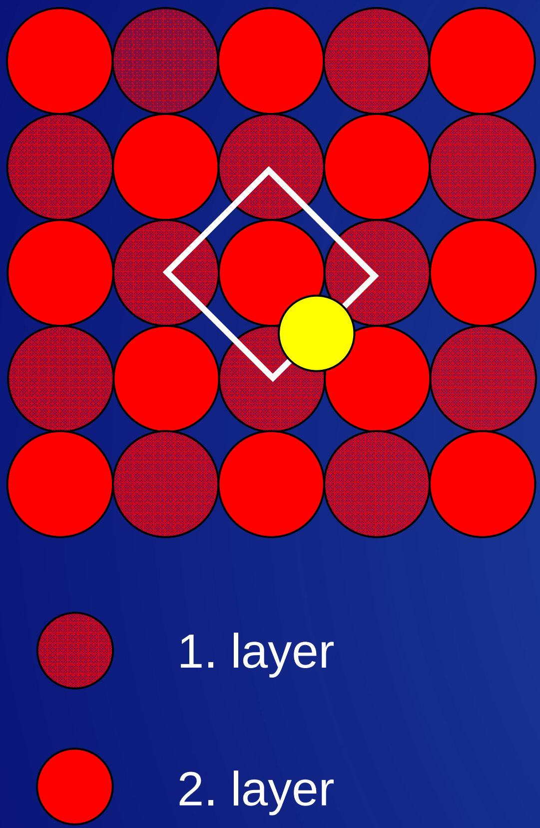


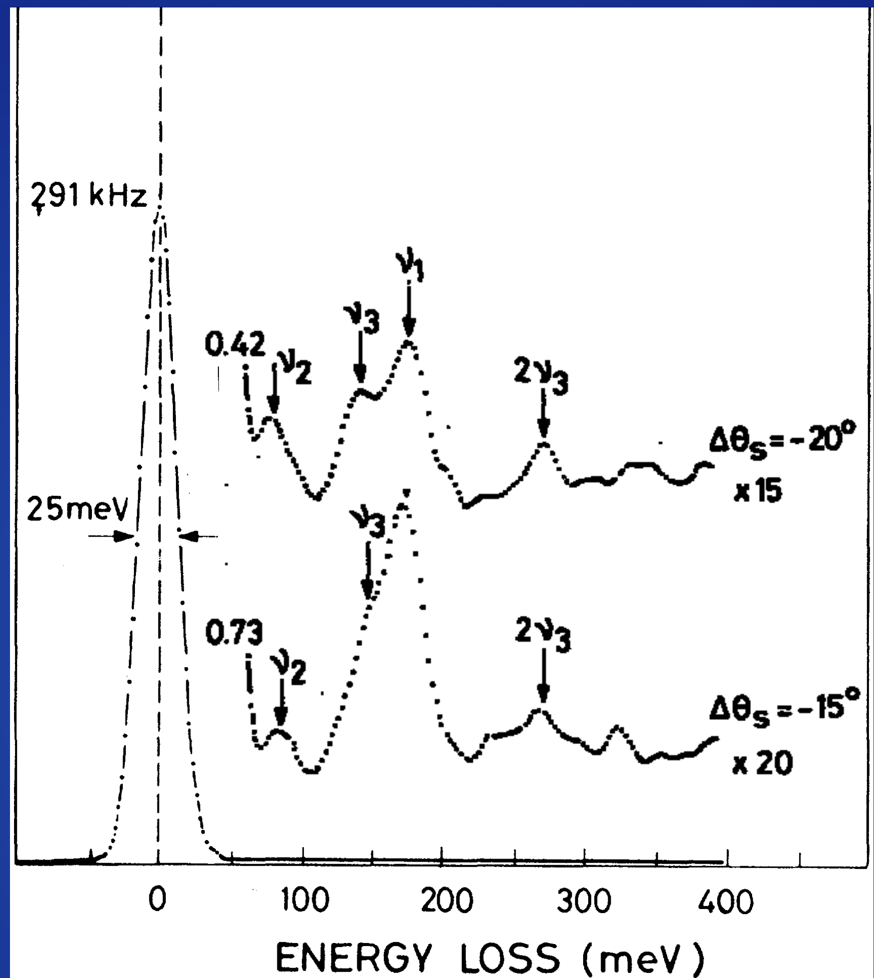
W. Ho, R. F. Willis, and E. W. Plummer, Phys. Rev. Lett. 40, 1463 (1978).

EELS

H on W(100)

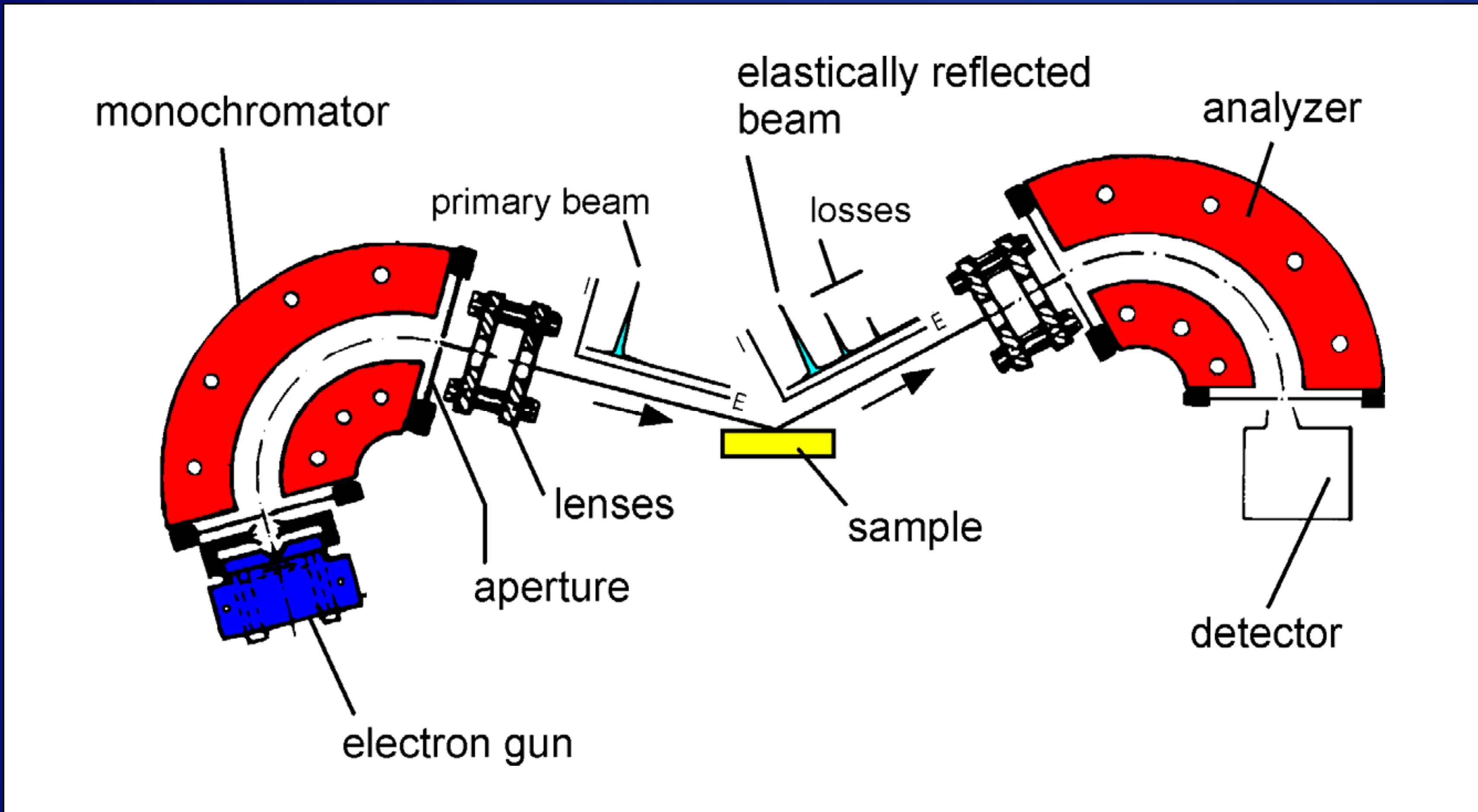
Max-Planck-Gesellschaft





EELS

principle setup



EELS

principles

Max-Planck-Gesellschaft

Why EELS? (pros and cons)

• lower energy vibrations detectable (down to appox. 100 cm^{-1})

• dipole selection rule applies only in specular geometry

• off specular geometry allows detection of non IR active modes

• energy resolution to the best 4 cm^{-1} (0.5 meV)

• electron current on the sample decreases with resolution in a power law behavior :
$(I \propto (\Delta E - \Delta E_{min})^{5/2}$

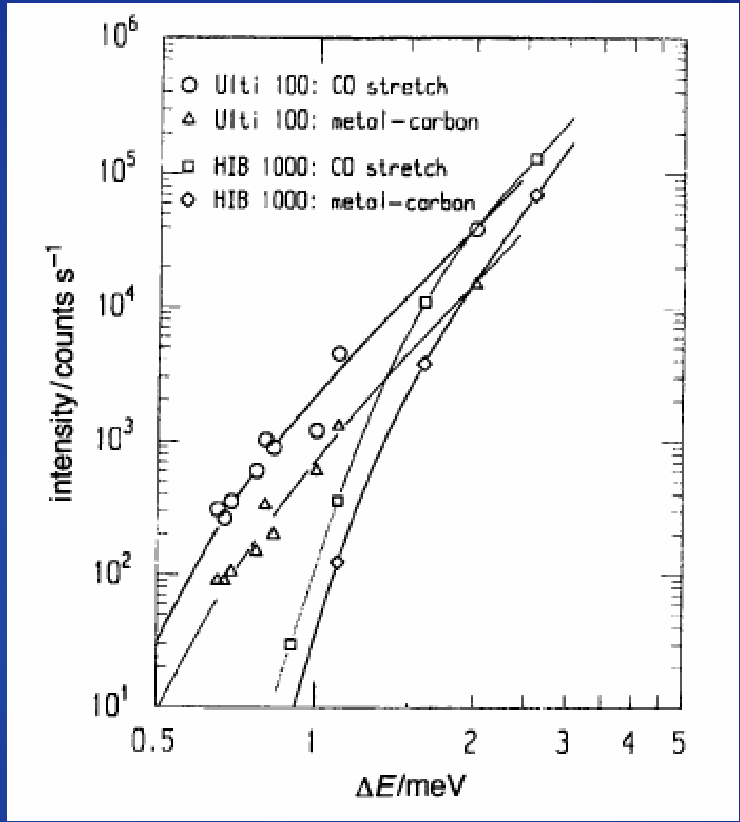
EELS

principles

Max-Planck-Gesellschaft

Why EELS? (pros and cons)

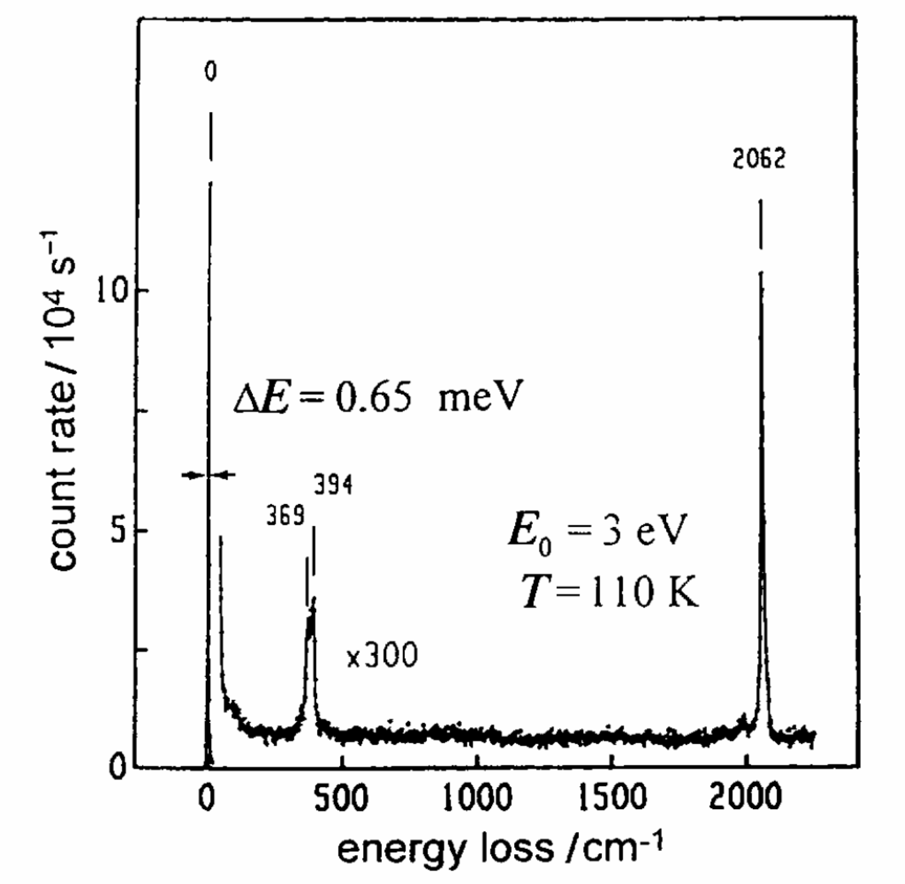
- lower energy vibrations detectable (down to appox. 100 cm^{-1})
- dipole selection rule applies only in specular geometry
- off specular geometry allows detection of non IR active modes
- energy resolution to the best 4 cm^{-1} (0.5 meV)
- electron current on the sample decreases with resolution in a power law behavior : ($I \propto (\Delta E - \Delta E_{min})^{5/2}$

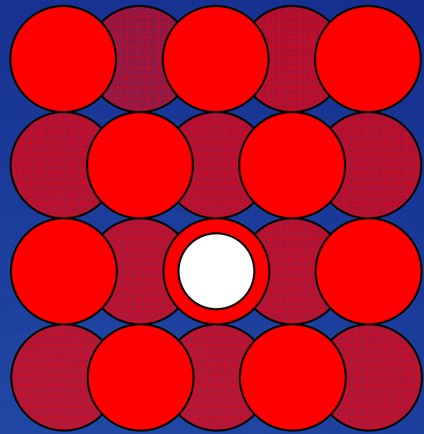


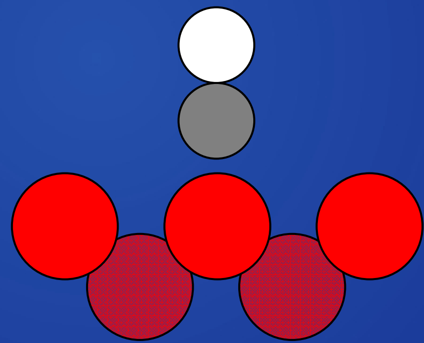
H. Ibach, M. Balden, S. Lehwald, J. Chem. Soc.-Faraday Trans. **92,** 4771 (1996).

EELS

CO/W(110)





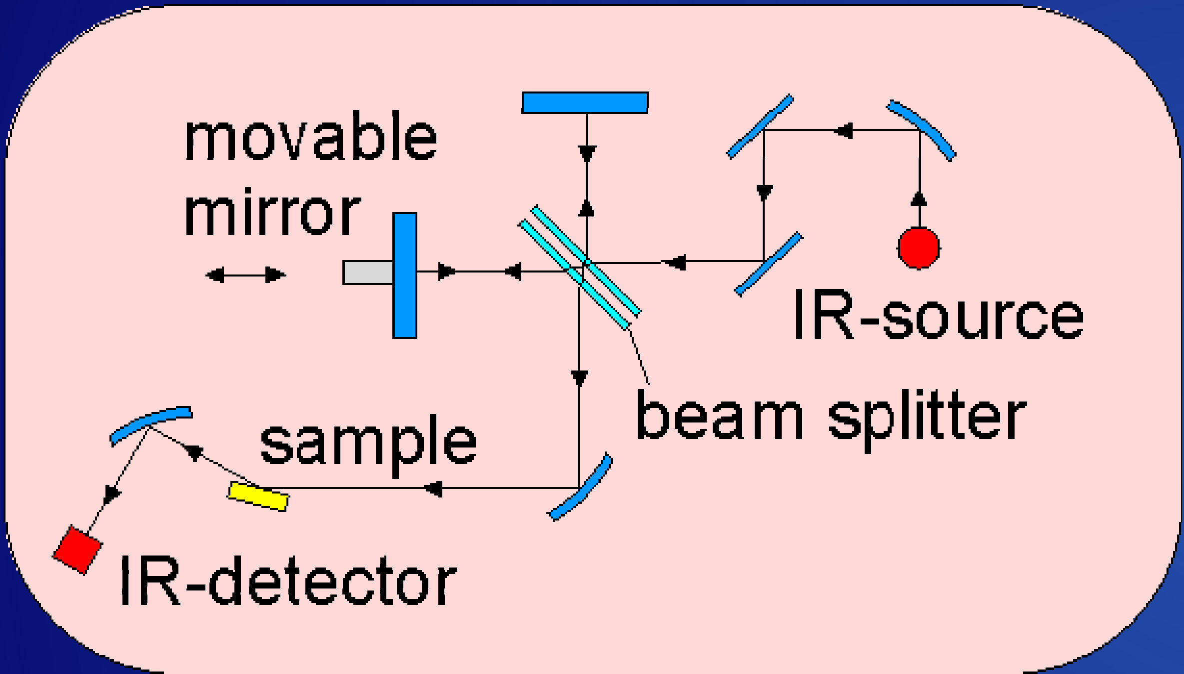


H. Ibach, M. Balden, S. Lehwald, J. Chem. Soc.-Faraday Trans. **92,** 4771 (1996).

surface vibrations

IRAS

principle experimental setup



source (white source)

- globar
- Nernst rod

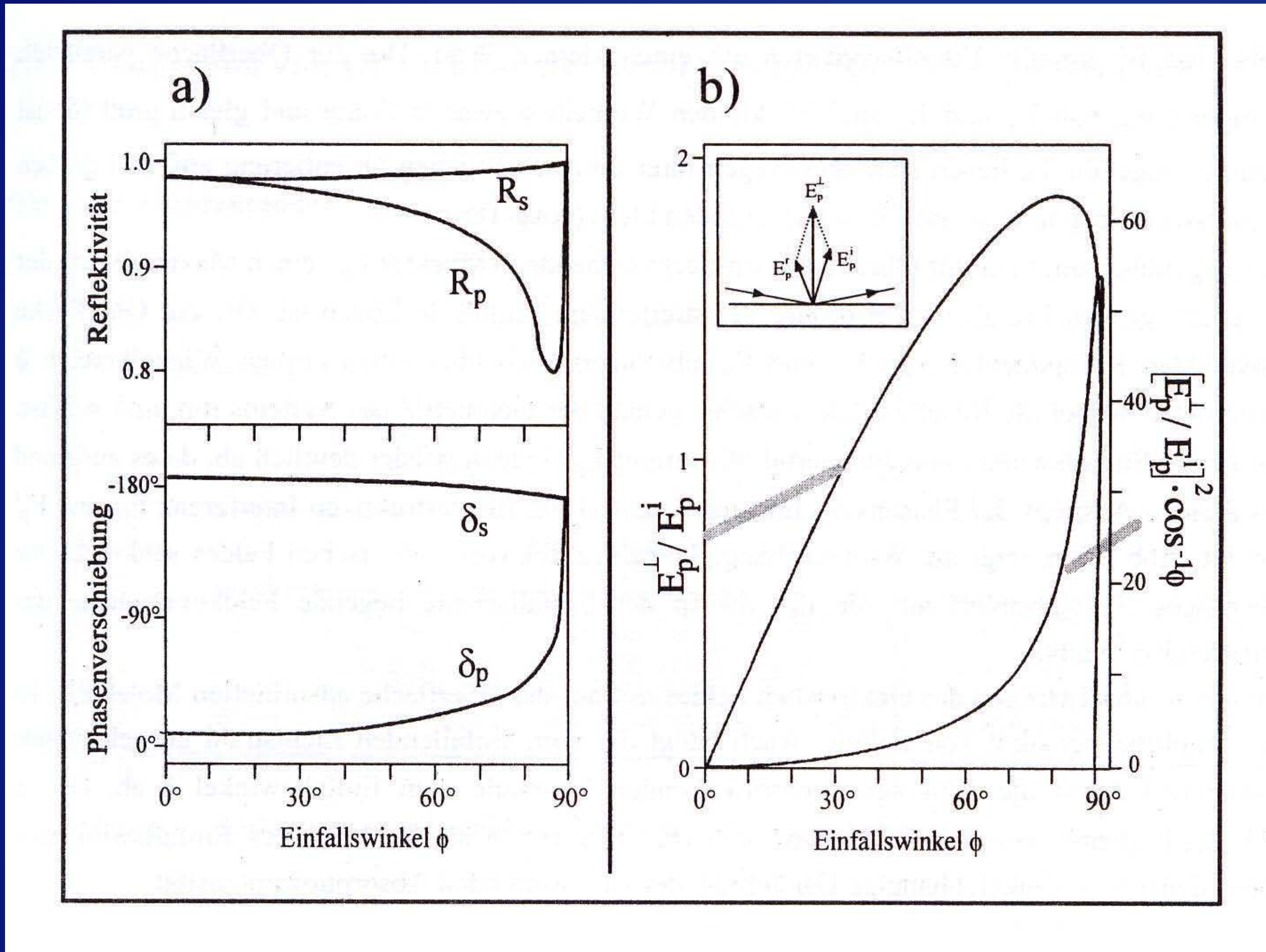
detector

- semiconductor, broad band e.g. MCT, InSb, GeCu
- bolometer (higher sensitivity especially for low frequencies; narrow band)

surface vibrations

IRAS

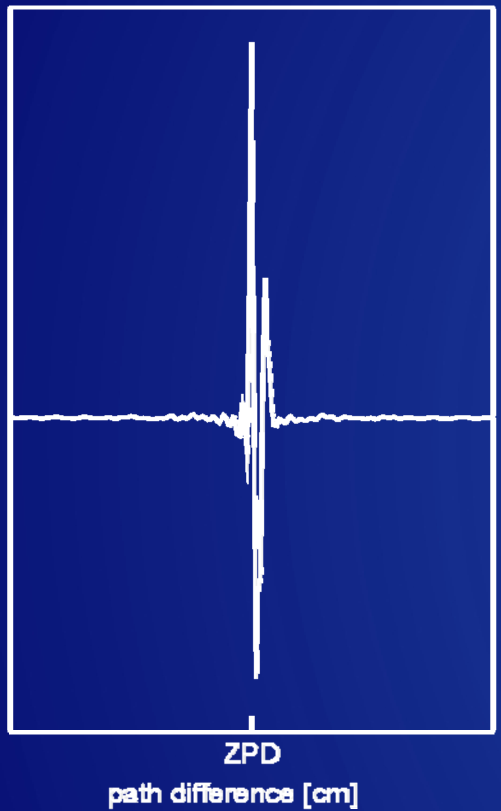
Max-Planck-Gesellschaft



surface vibrations

IRAS

interferogram



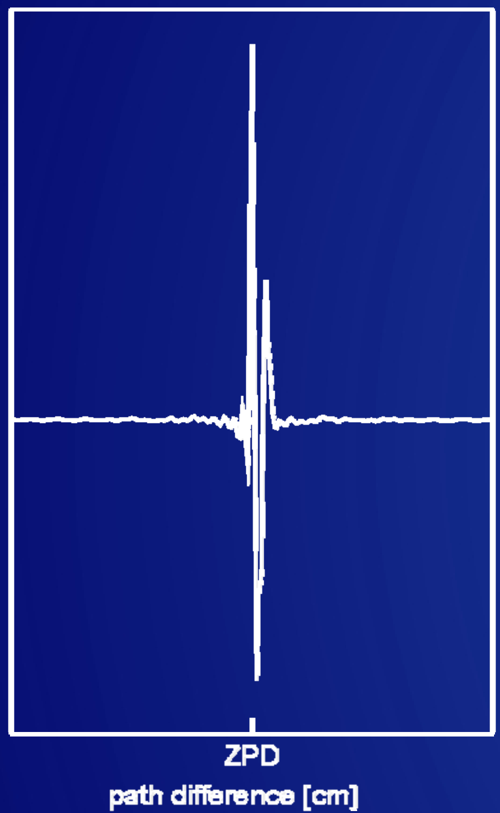
Max-Planck-Gesellschaft

surface vibrations

IRAS

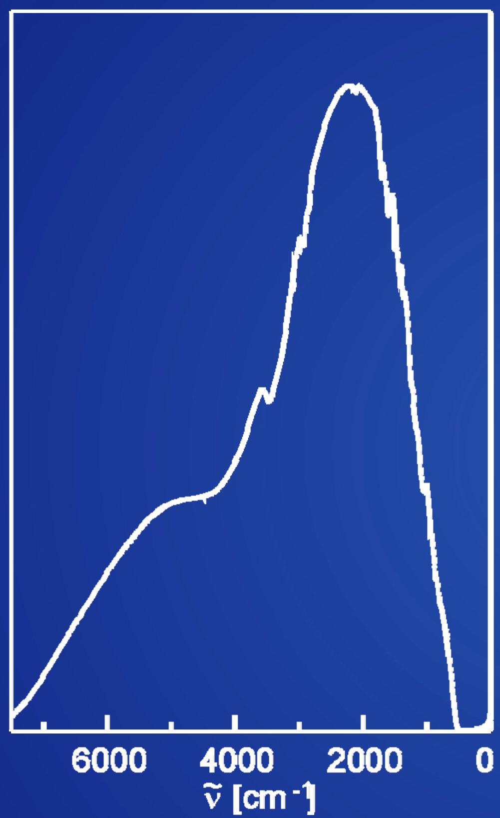
Max-Planck-Gesellschaft

interferogram



FFT

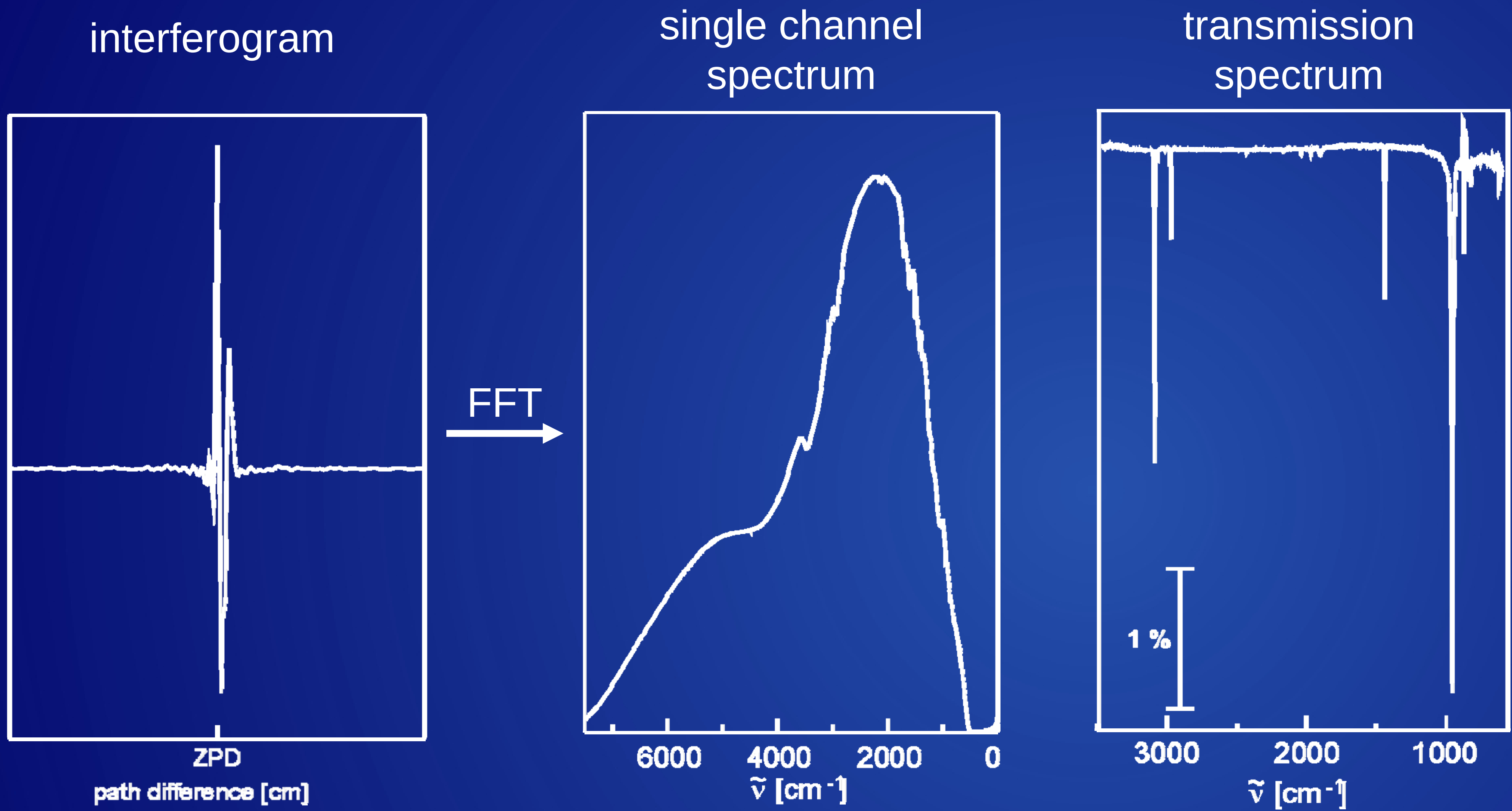
single channel spectrum



surface vibrations

IRAS

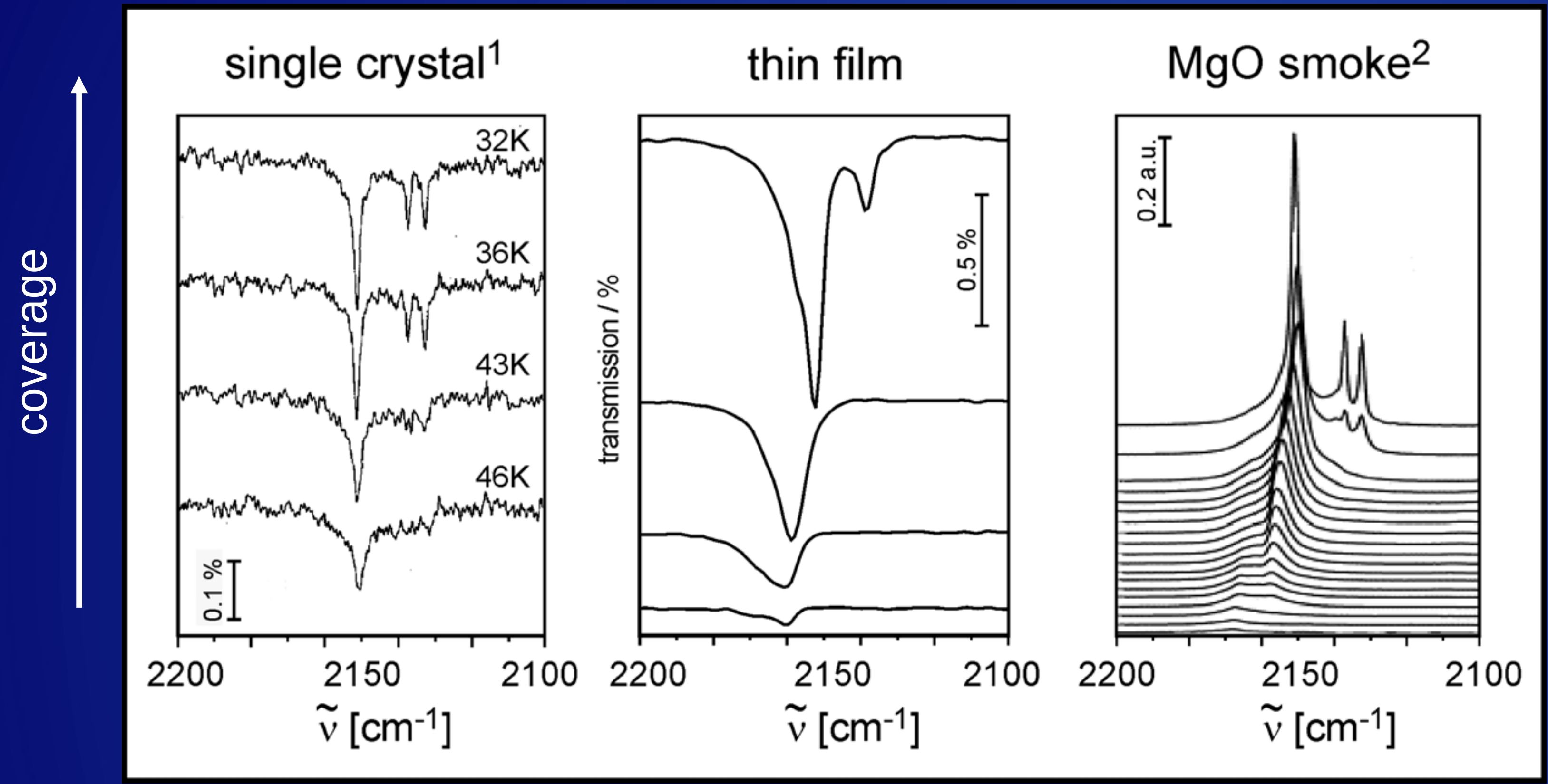
Max-Planck-Gesellschaft



IRAS

CO on MgO(001)

Max-Planck-Gesellschaft

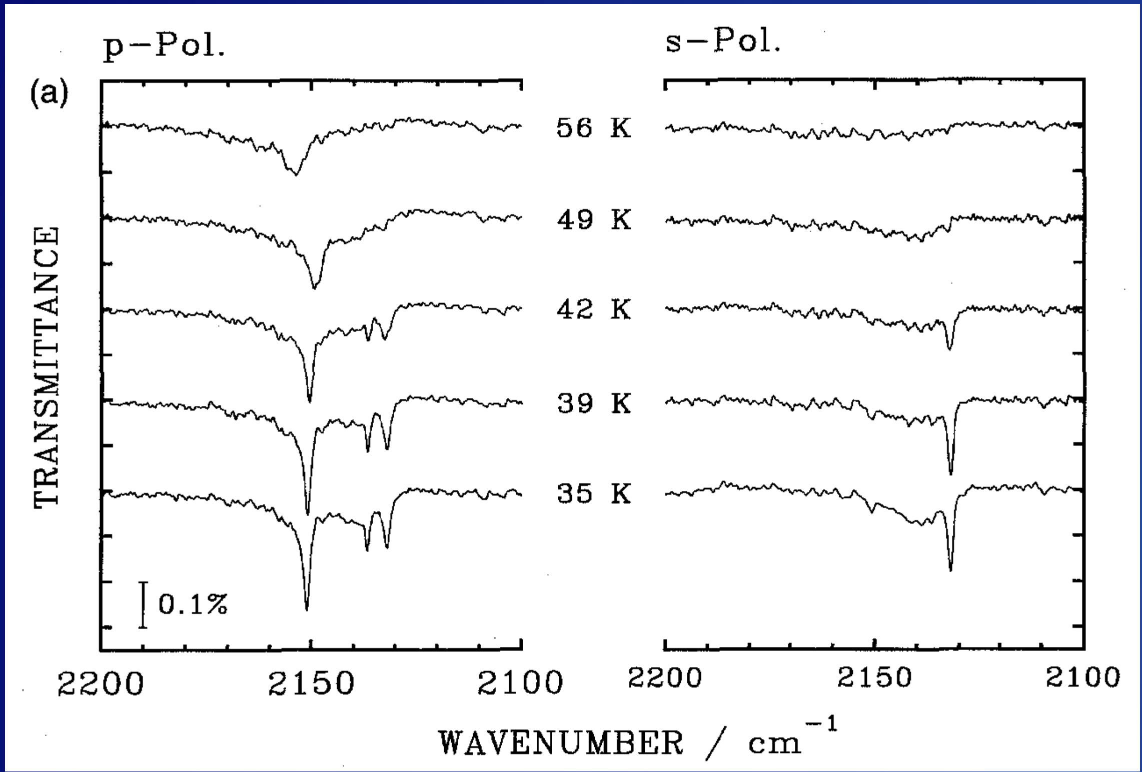


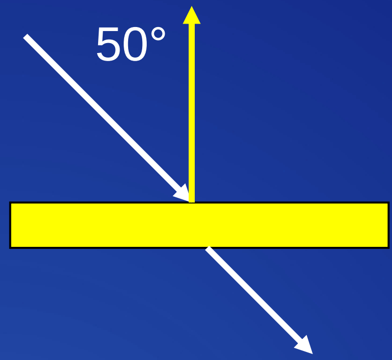
[1] J. Heidberg et al. *Surf. Sci.* **331-333**, 1467 (1995).
[2] G. Spoto et al. *Prog. Surf. Sci*. **76**, 71, (2004).
M. Sterrer et al. Surf. Sci. **596**, 222 (2005).

IRAS

CO on MgO(001)

transmission experiment





- c(4x2) superstructure (LEED)
- 3 molecules in the unit cell (LEED, HAS)
- 1 molecule perpendicular
- 2 molecules tilted

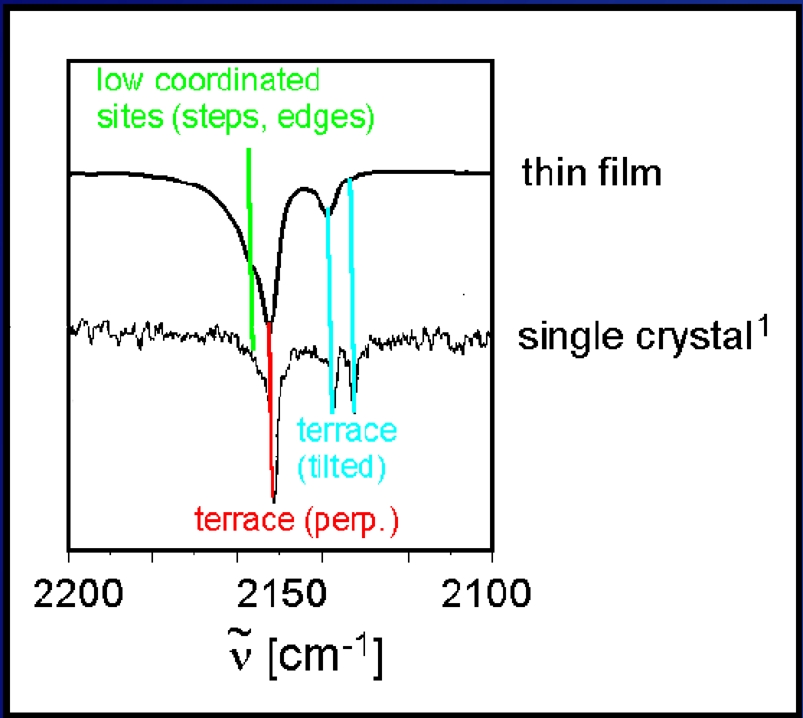
[1] J. Heidberg et al. *Surf. Sci.* **331-333**, 1467 (1995).

IRAS

CO on MgO(100)

Max-Planck-Gesellschaft

IR

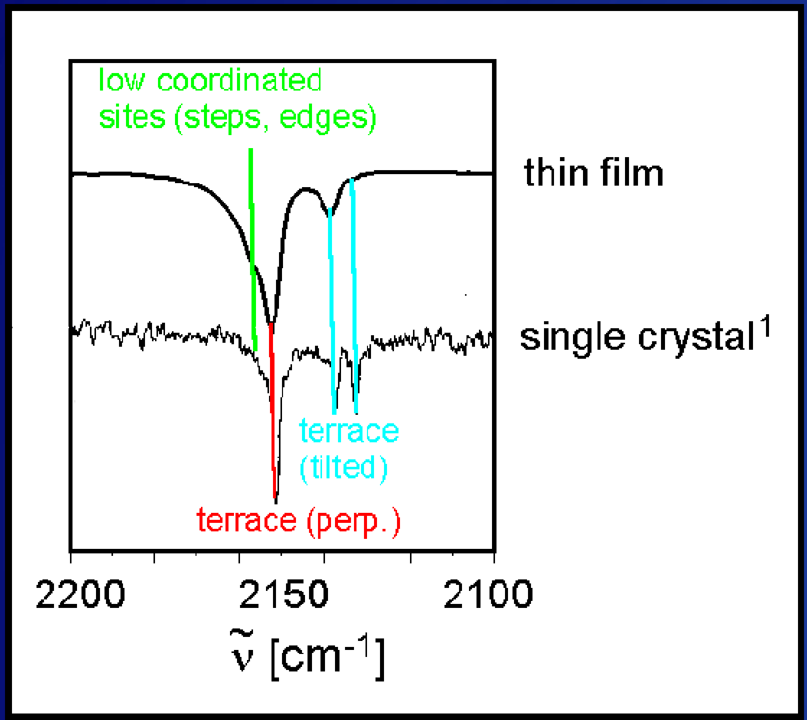


[1] J. Heidberg et al. *Surf. Sci.* **331-333**, 1467 (1995).
M. Sterrer et al. Surf. Sci. **596**, 222 (2005).

IRAS

CO on MgO(100)

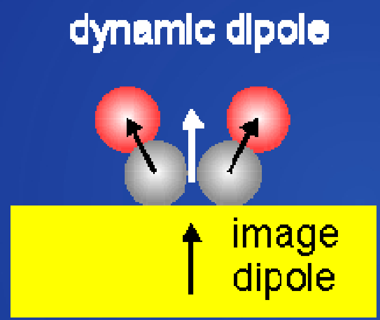
IR



2 tilted molecules

symmetric stretch

high frequency



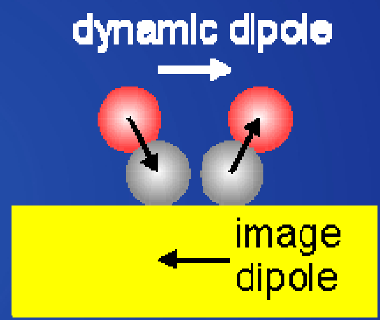
metal

$\mu_{dyndip} > 0$

IR active

asymmetric stretch

low frequency



metal

$\mu_{dyndip} = 0$

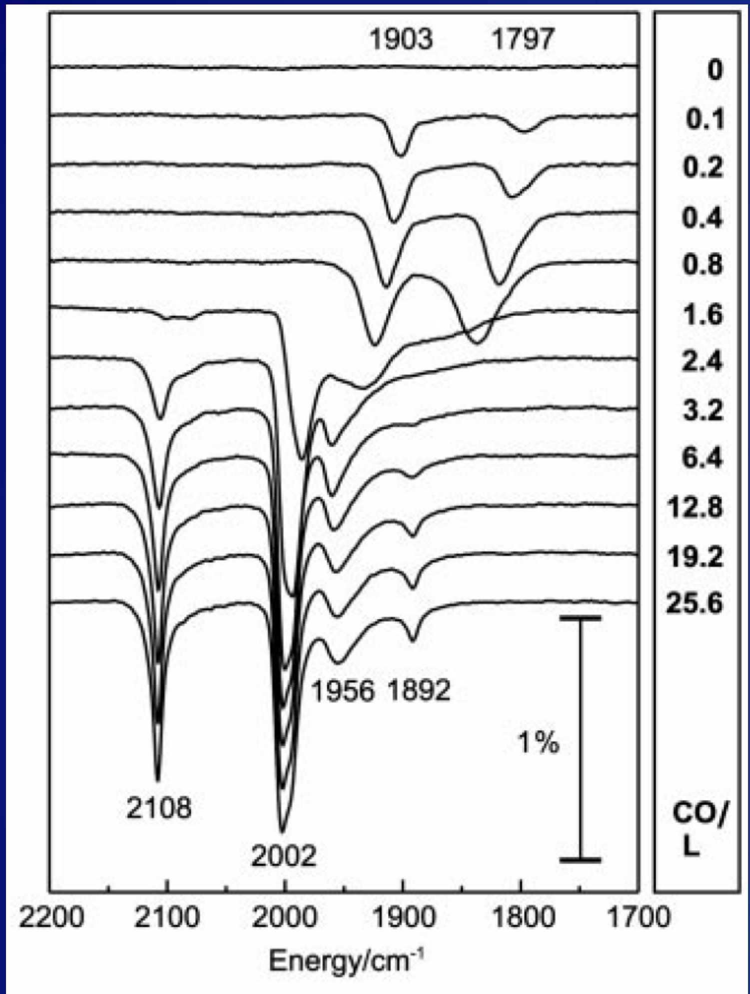
IR inactive

[1] J. Heidberg et al. *Surf. Sci.* **331-333**, 1467 (1995).
M. Sterrer et al. Surf. Sci. **596**, 222 (2005).

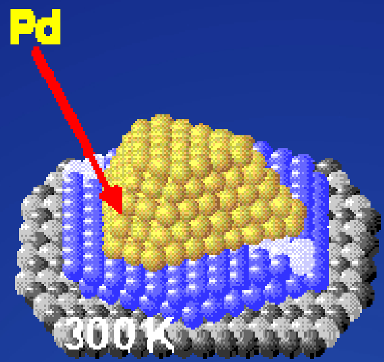
Pd particles on thin alumina

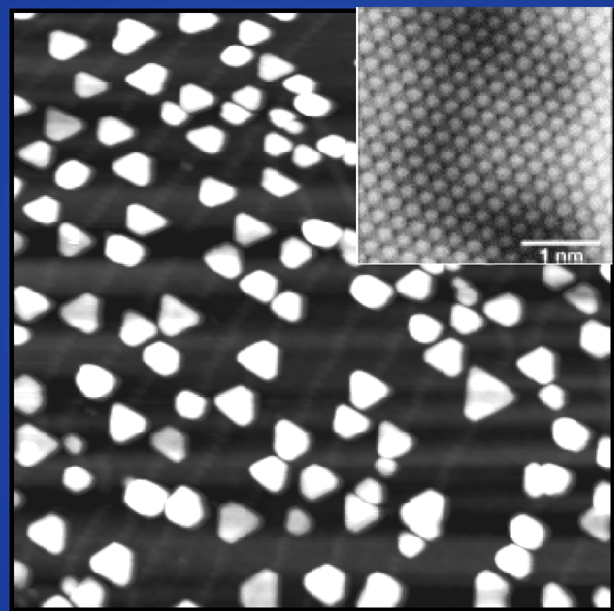
CO IRAS

Max-Planck-Gesellschaft



M. Frank and M. Bäumer, PCCP **2**, 3723 (2000).



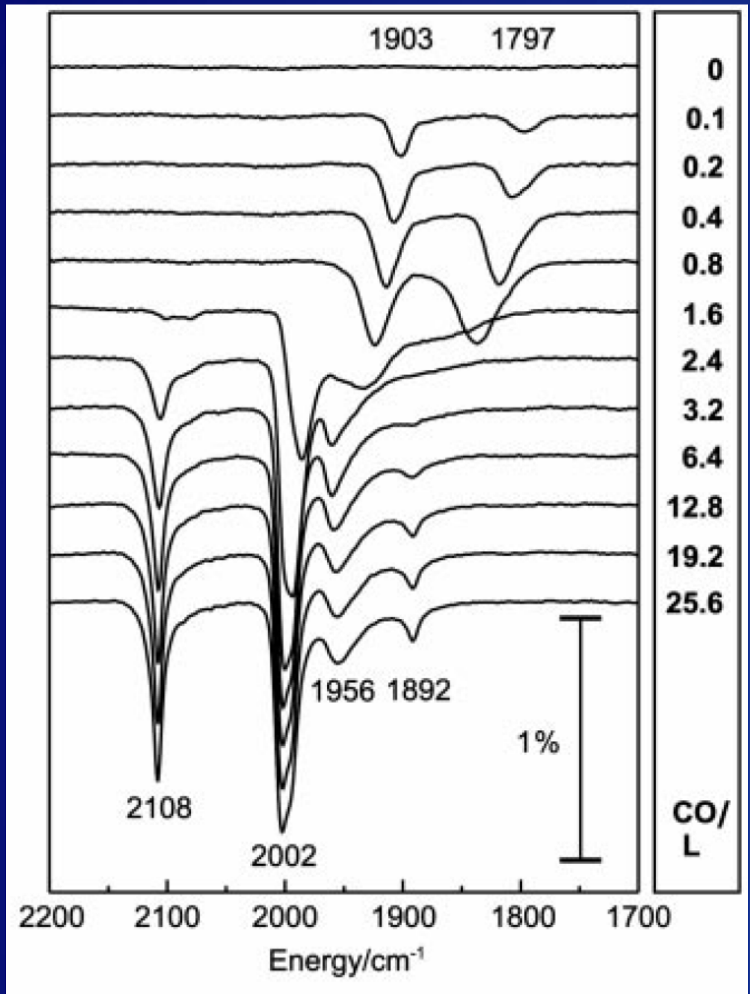


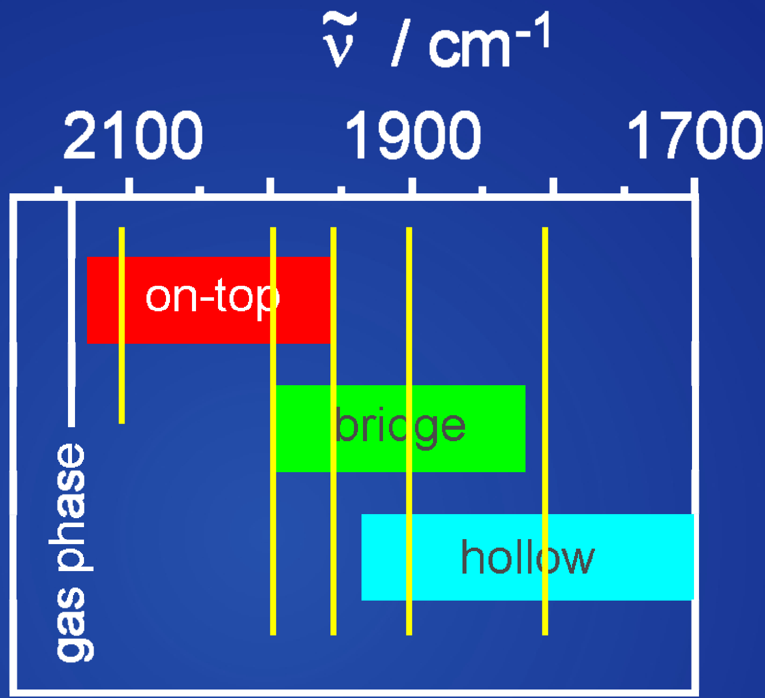
K. H. Hansen *et al.* Phys. Rev. Lett. **83**, 4120 (1999).

Pd particles on thin alumina

CO IRAS

Max-Planck-Gesellschaft



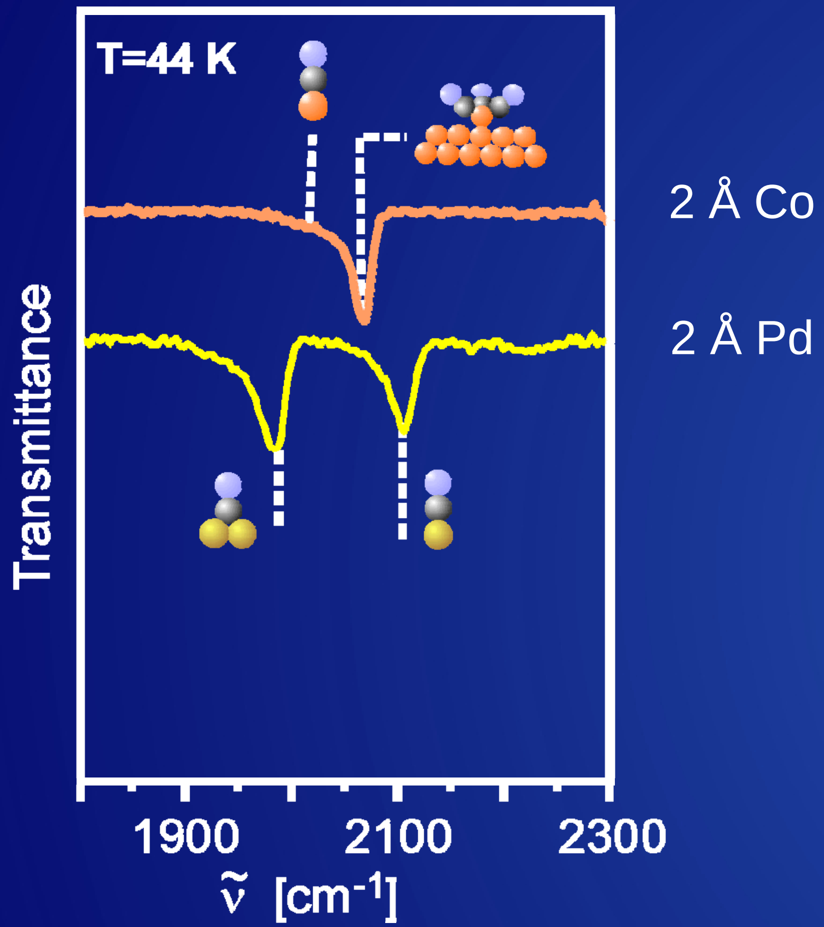


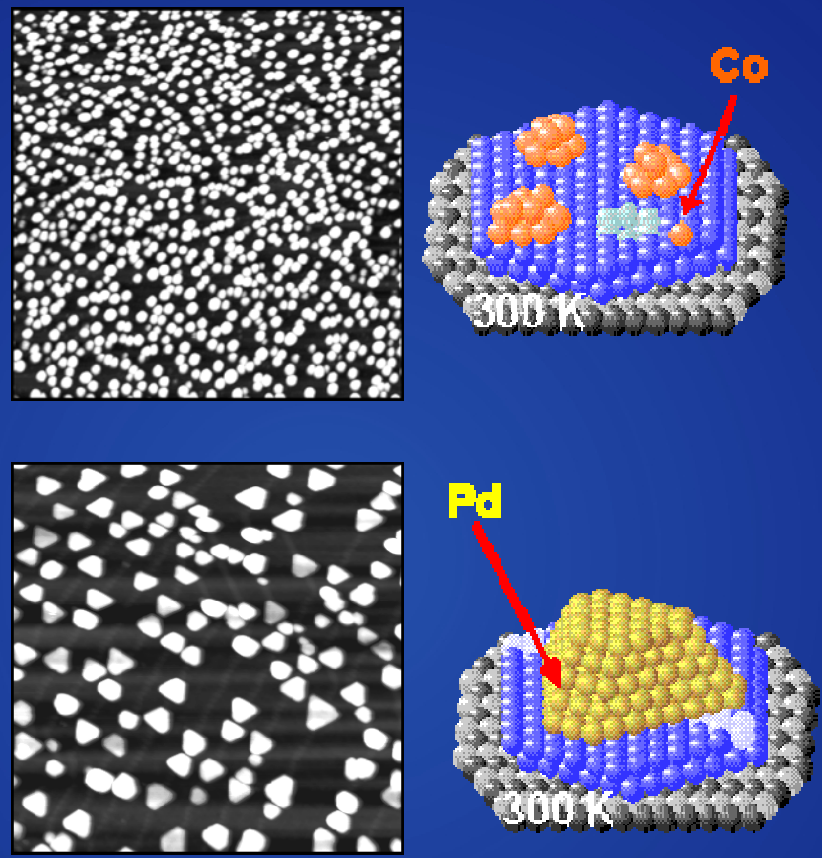
M. Frank and M. Bäumer, PCCP **2**, 3723 (2000).

Metal particles

CO IRAS

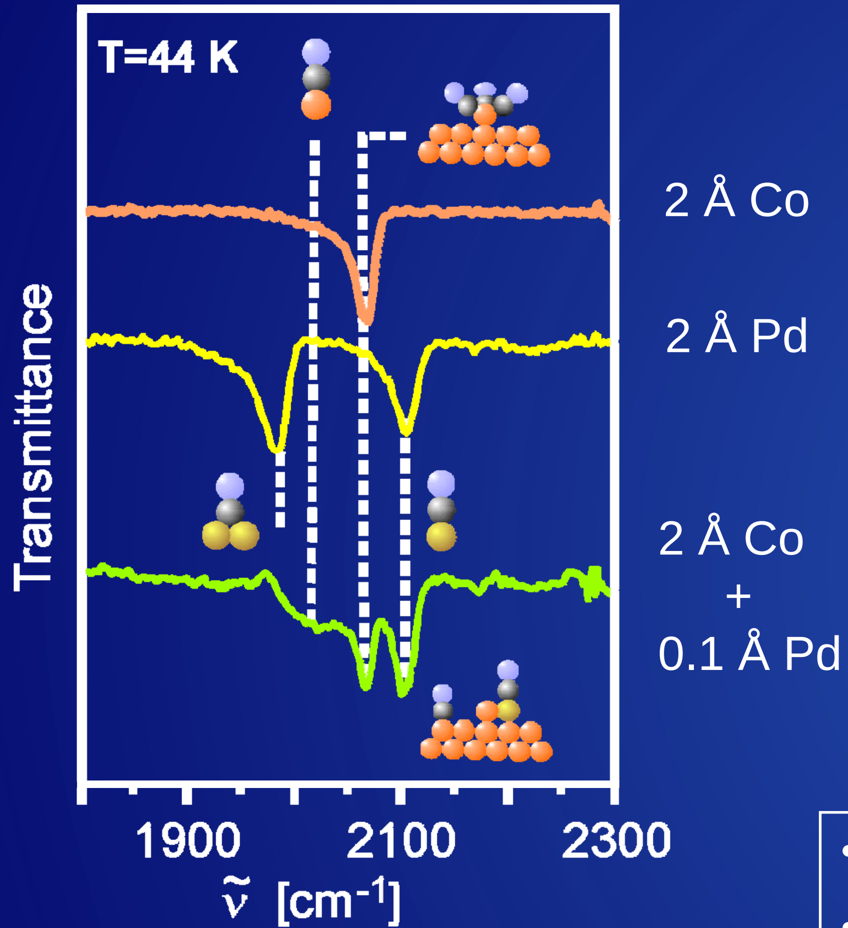
Max-Planck-Gesellschaft





Metal particles

CO IRAS

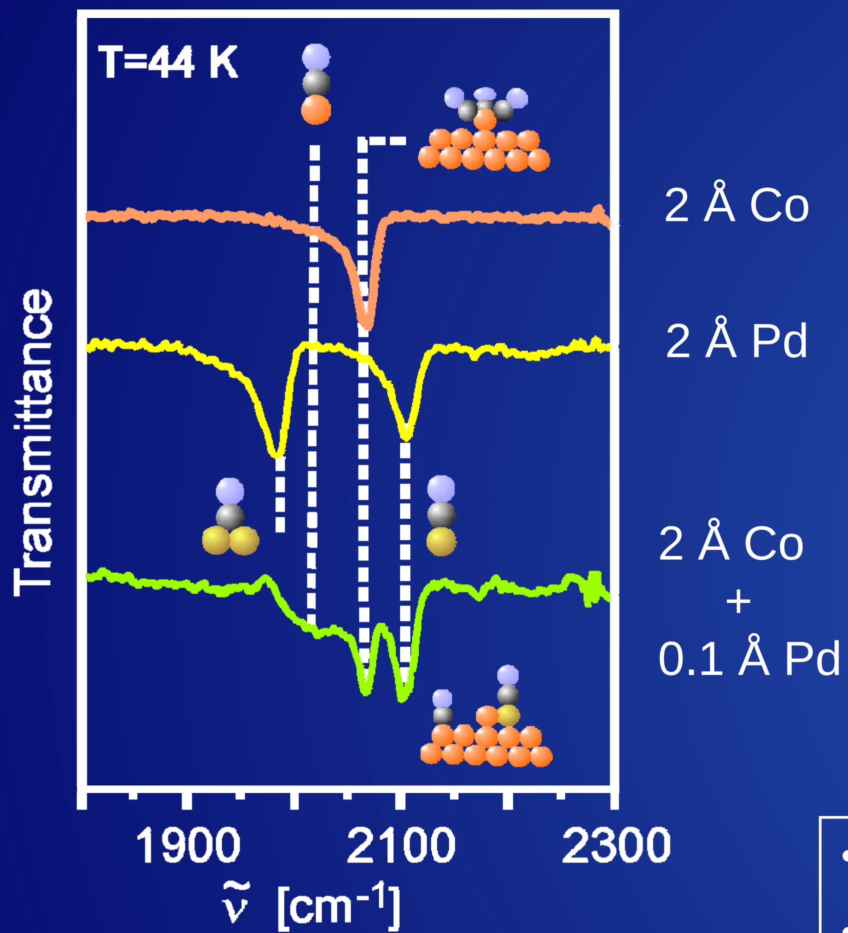


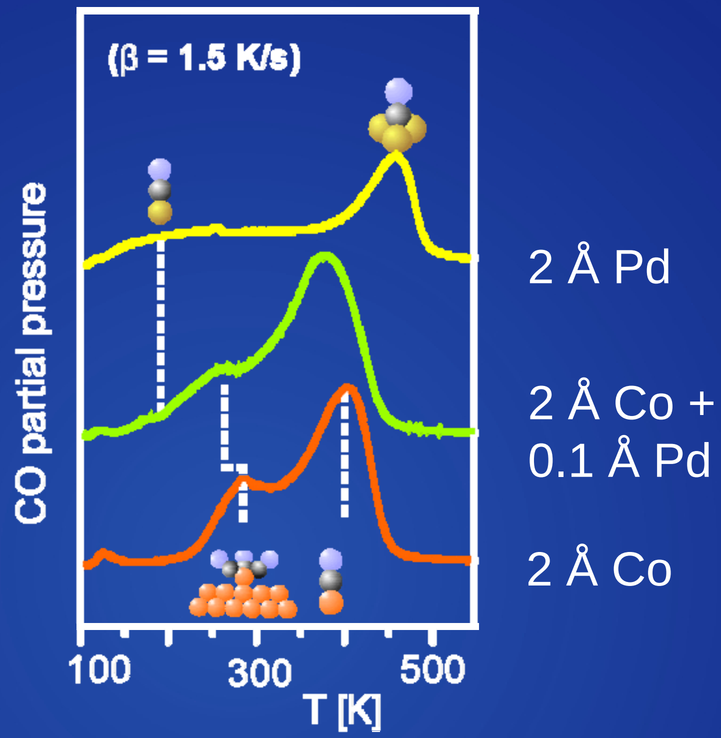
- Pd nucleates at low coordinated Co sites
- virtually no chemical contrast!

Metal particles

CO IRAS

Max-Planck-Gesellschaft



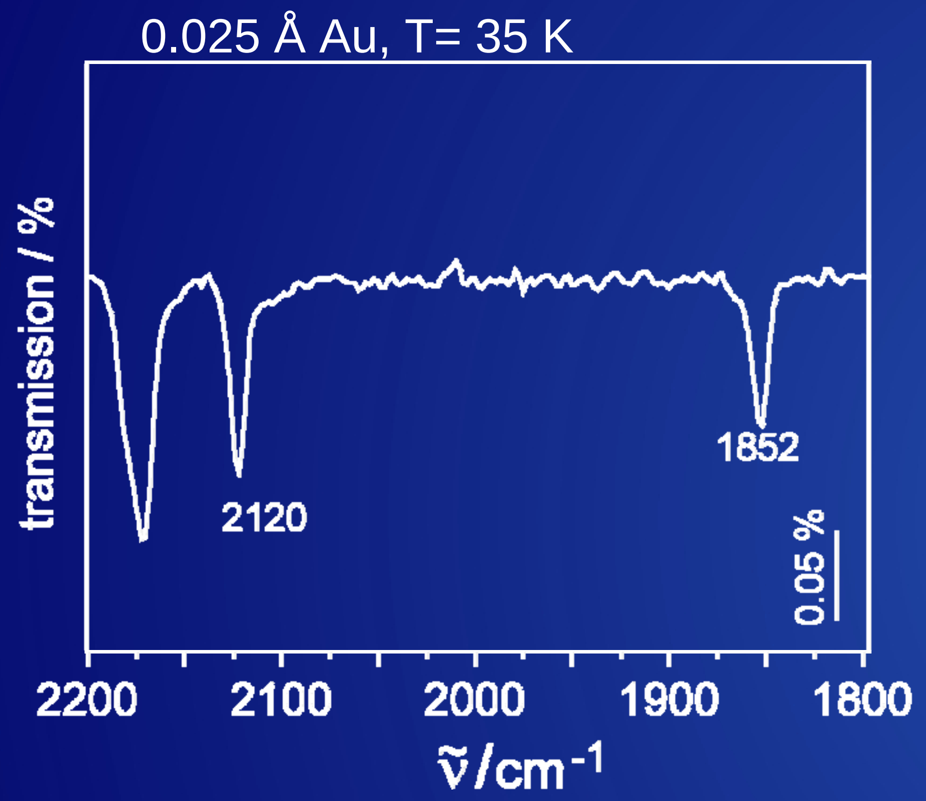


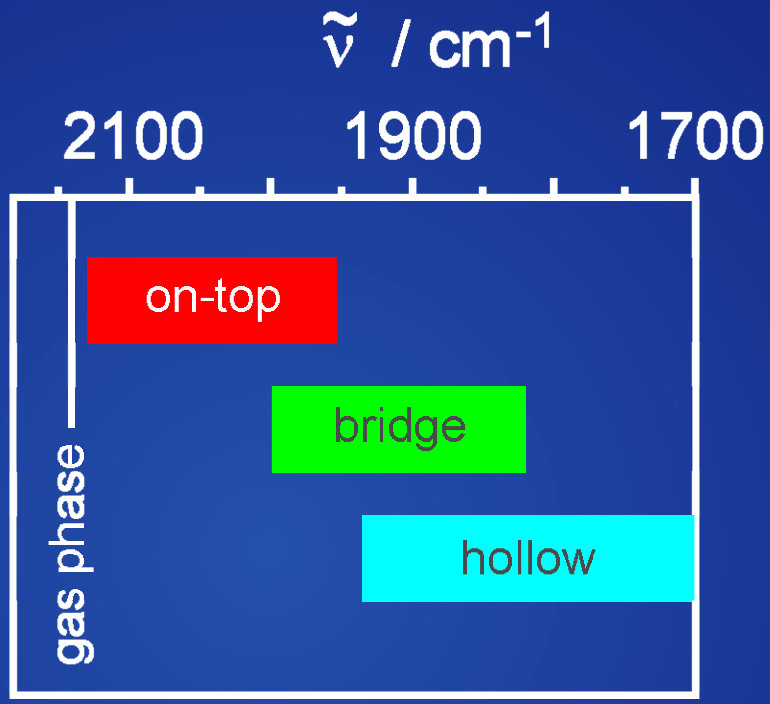
- Pd nucleates at low coordinated Co sites
- virtually no chemical contrast!

Au/MgO(001)/Mo(001)

CO IRAS

Max-Planck-Gesellschaft

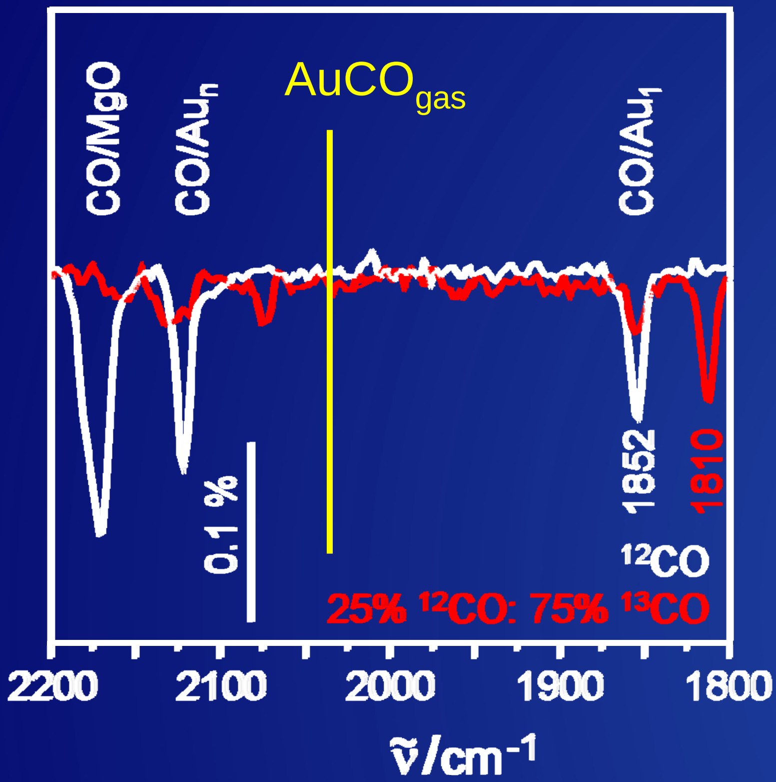




M. Sterrer et al. Angew. Chem. Int. Ed. **45**, 2633 (2006)

Au/MgO(001)/Mo(001)

CO IRAS

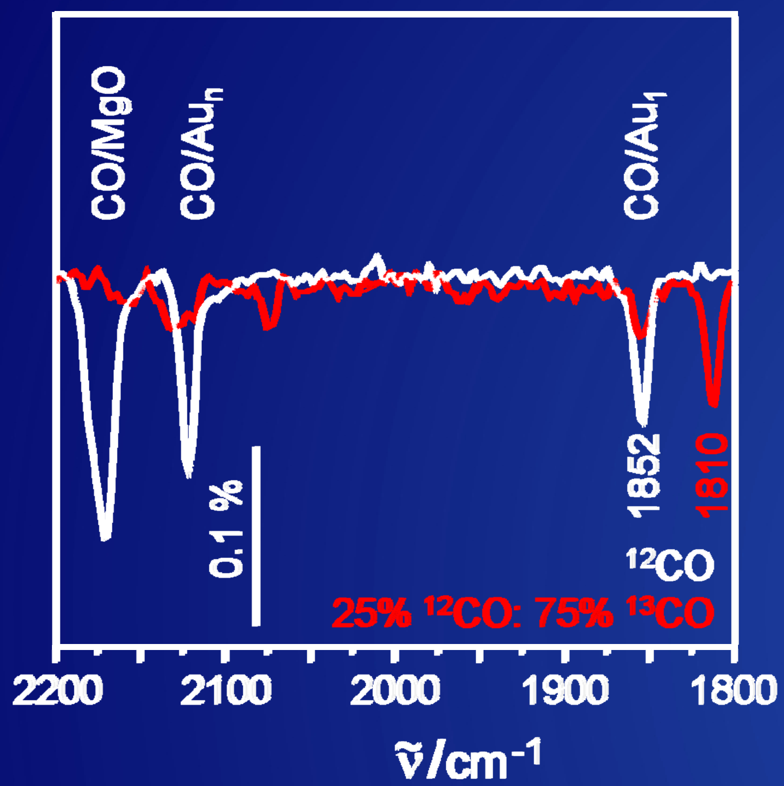


red-shift of CO streching frequency by 187 cm^{-1}
with respect to gas phase AuCO carbonyl

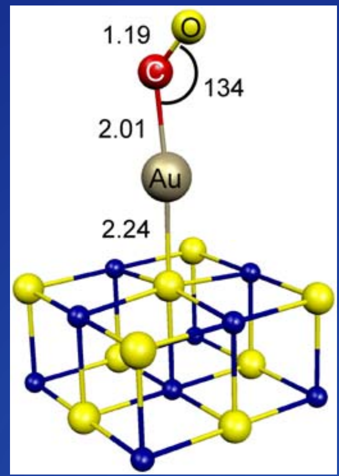
M. Sterrer et al. Angew. Chem. Int. Ed. **45**, 2633 (2006)

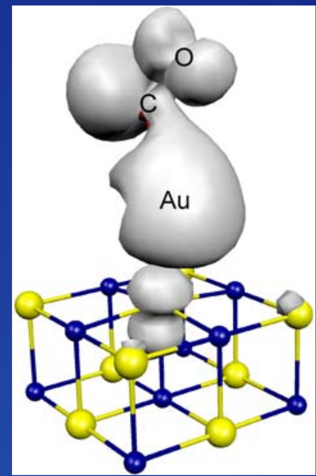
MgO(001)/Mo(001)

IR of Au atoms



red-shift of CO streching frequency by 291 cm^{-1} with respect to gas phase





Theory prediction:

- red-shift of 286 cm^{-1} to gas phase
- large electron transfer to Au/CO complex

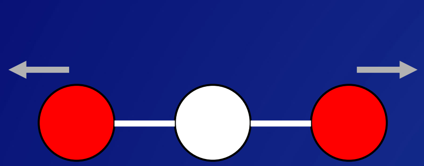
=> CO induces the charge transfer

M. Sterrer et al. Angew. Chem. Int. Ed. **45**, 2633 (2006)

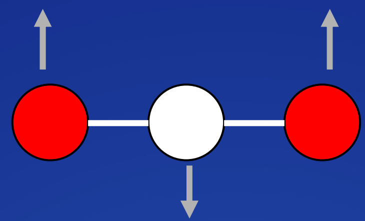
IRAS

CO_2 on NaCl(001)

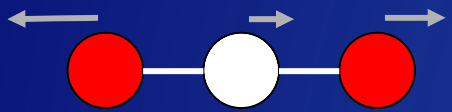
Max-Planck-Gesellschaft



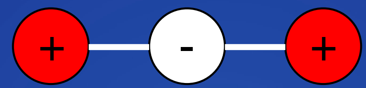
1288 cm^{-1}



667 cm^{-1}



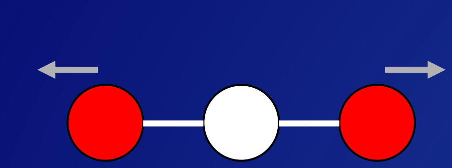
2349 cm^{-1}



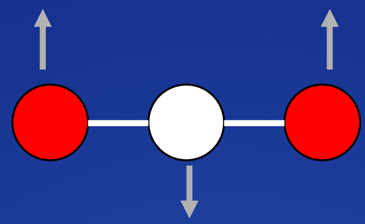
667 cm^{-1}

IRAS

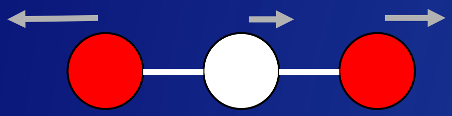
CO_2 on NaCl(001)



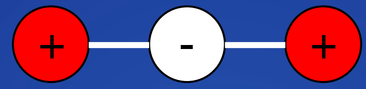
1288 cm^{-1}



667 cm^{-1}



2349 cm^{-1}



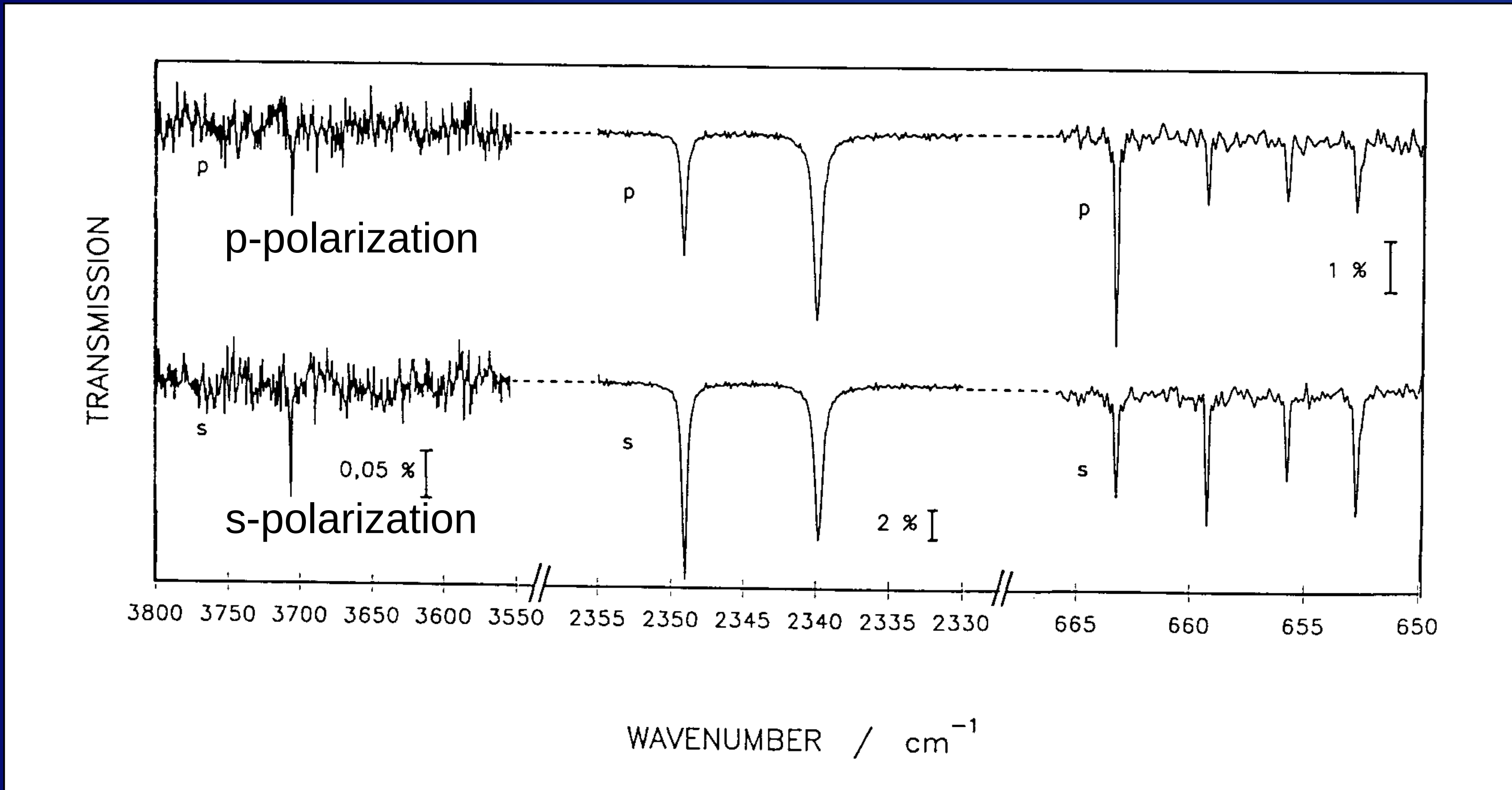
667 cm^{-1}

What is expected?

IRAS

CO_2 on NaCl(001)

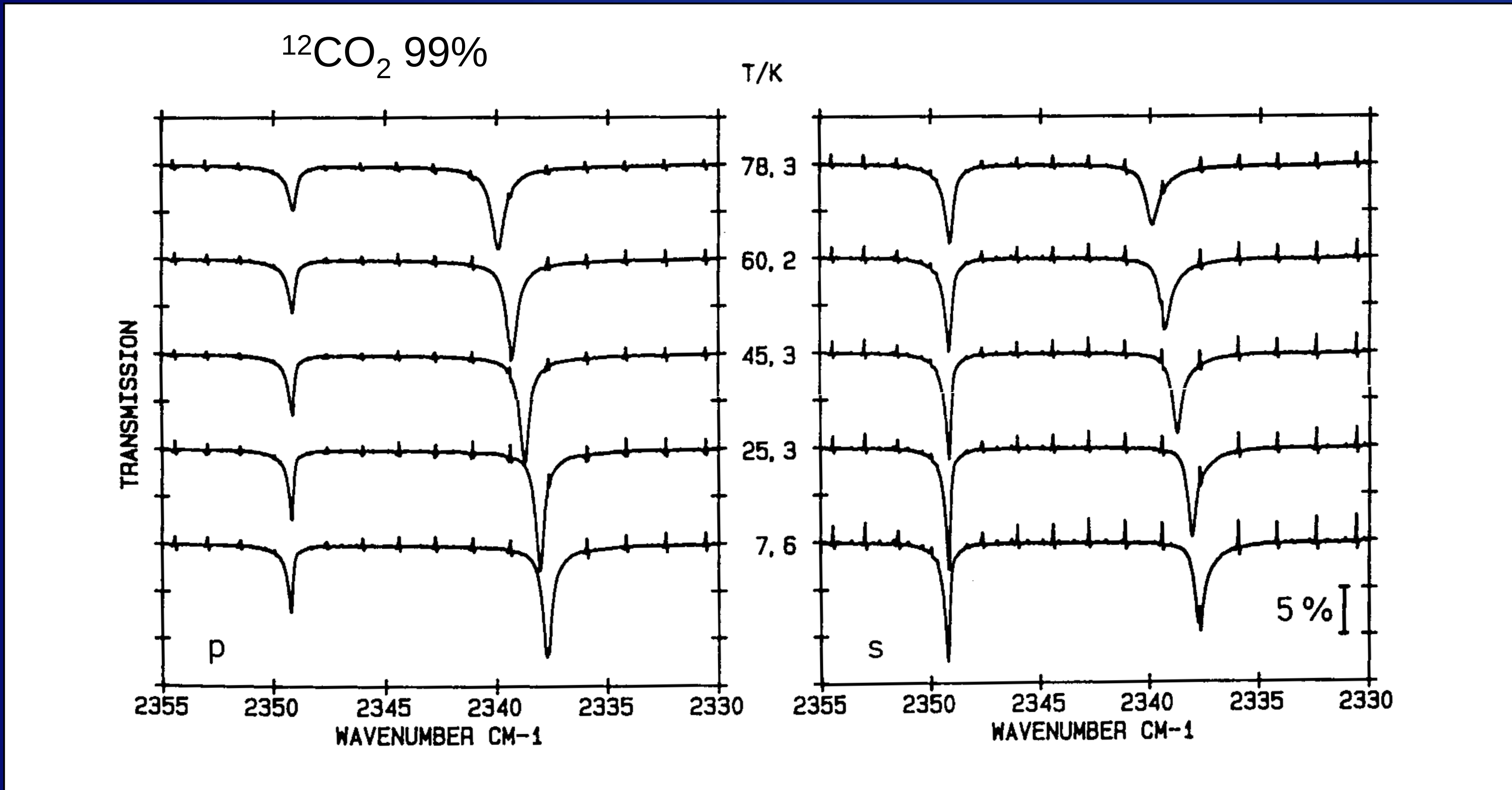
Max-Planck-Gesellschaft



J. Heidberg et al. *J. Electr. Spec. Rel. Phenom.* 64/65, 341 (1993).

IRAS

CO_2 on NaCl(001)

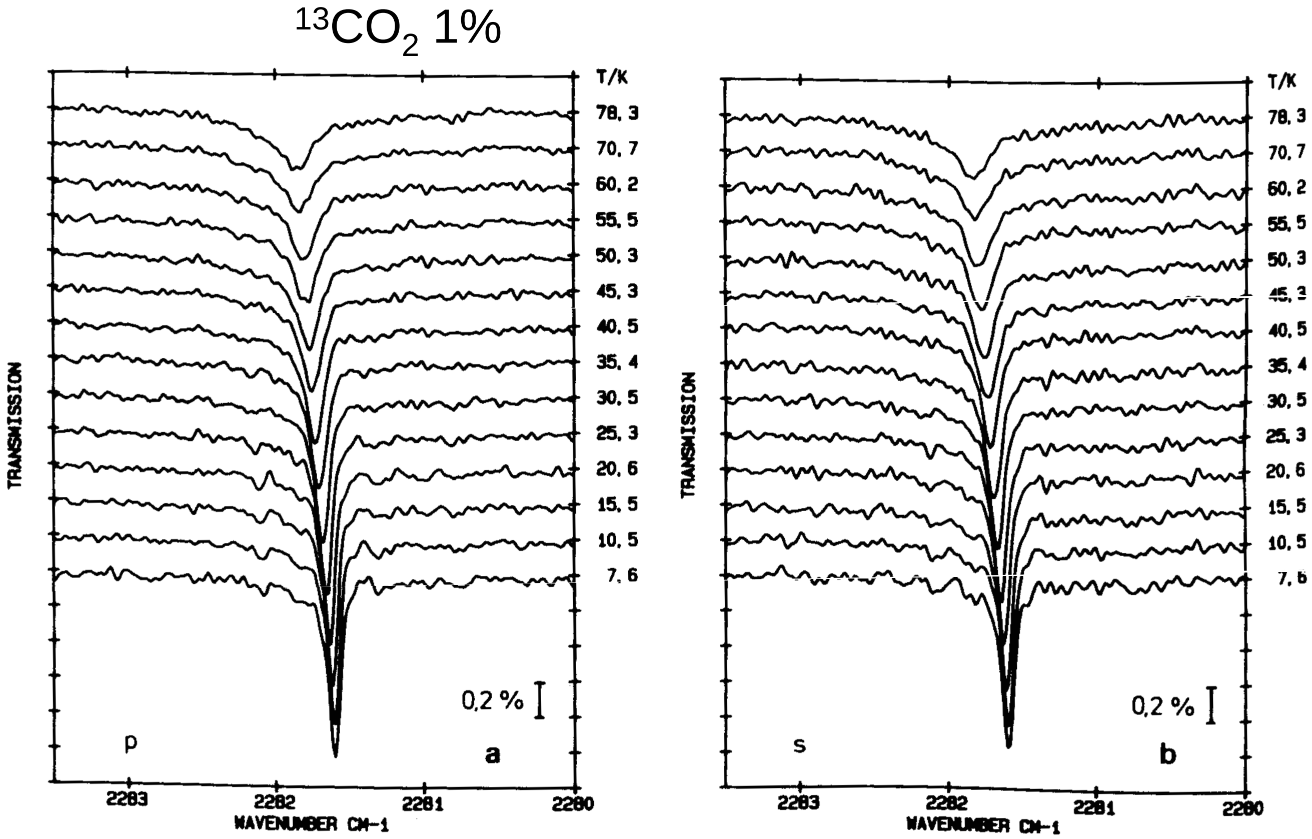


J. Heidberg et al. *J. Electr. Spec. Rel. Phenom.* 64/65, 341 (1993).

IRAS

CO_2 on NaCl(001)

Max-Planck-Gesellschaft

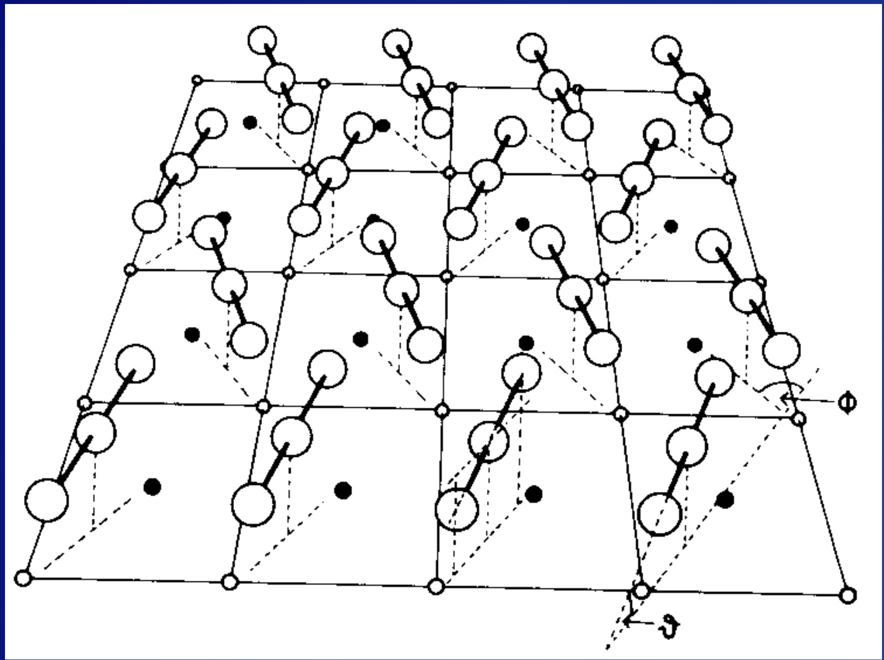


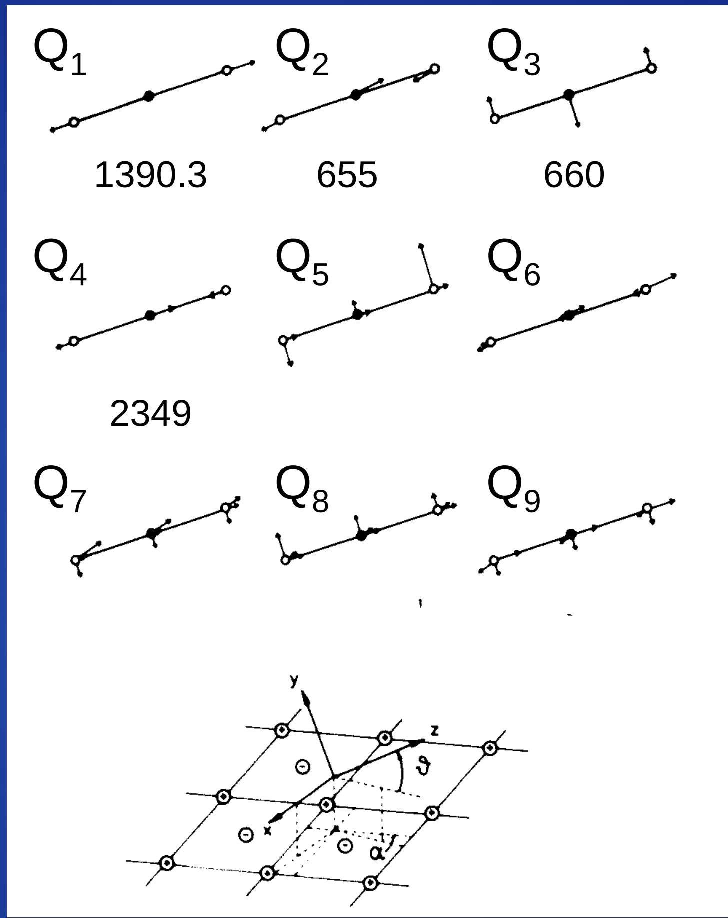
- two lines for $^{12}CO_2$; one line for highly diluted $^{13}CO_2$
- Peak area constant with T
- same shift for s and p polarization

J. Heidberg et al. *J. Electr. Spec. Rel. Phenom.* 64/65, 341 (1993).

IRAS

CO_2 on NaCl(001)





from structural analysis (LEED):

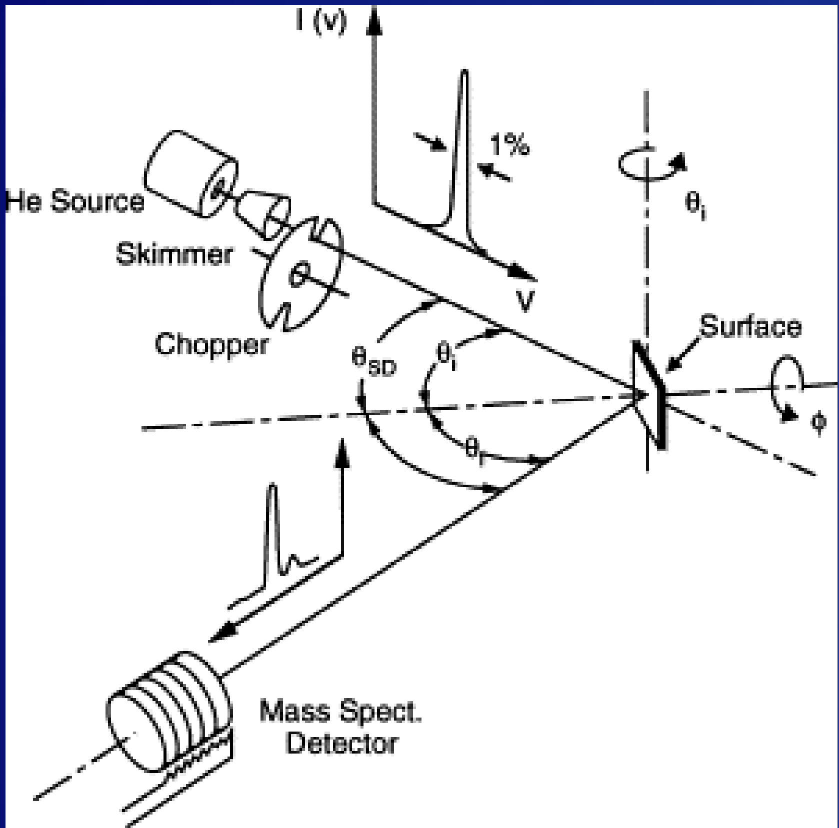
• glide mirror plane (pg symmetry)

J. Heidberg et al. *Surf. Sci.* 269/270, 120 (1992).

Helium atom scattering (HAS)

experimental setup

Max-Planck-Gesellschaft



- energy of the primary beam is ca. 10-40 meV
- inelastic losses by means of a TOF analysis
- Energy resolution: approx 100 μeV
- There is also momentum transfer

For fixed scattering angle of 90°:

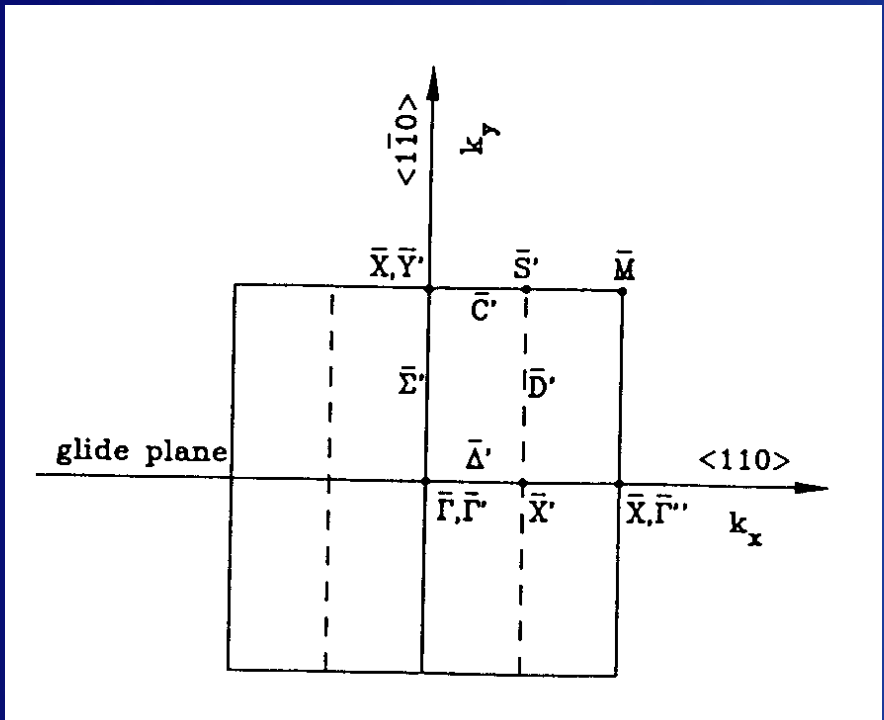
$$\Delta E/E_i = \frac{(\sin(\theta_i)+\Delta k/k_i)^2}{\cos^2(\theta_i)} - 1$$

A. Graham *Surf. Sci. Rep.* 49, 115 (2003).

HAS

CO_2 on NaCl(001)

Max-Planck-Gesellschaft



How many “external” modes to expect?

• two molecules in the unit cell, each five external modes

$\Rightarrow$ 10 modes

additionally: symmetry equivalent islands (along Δ’ and Σ’)

along Δ’ (glide plane) symmetry applies: only five modes

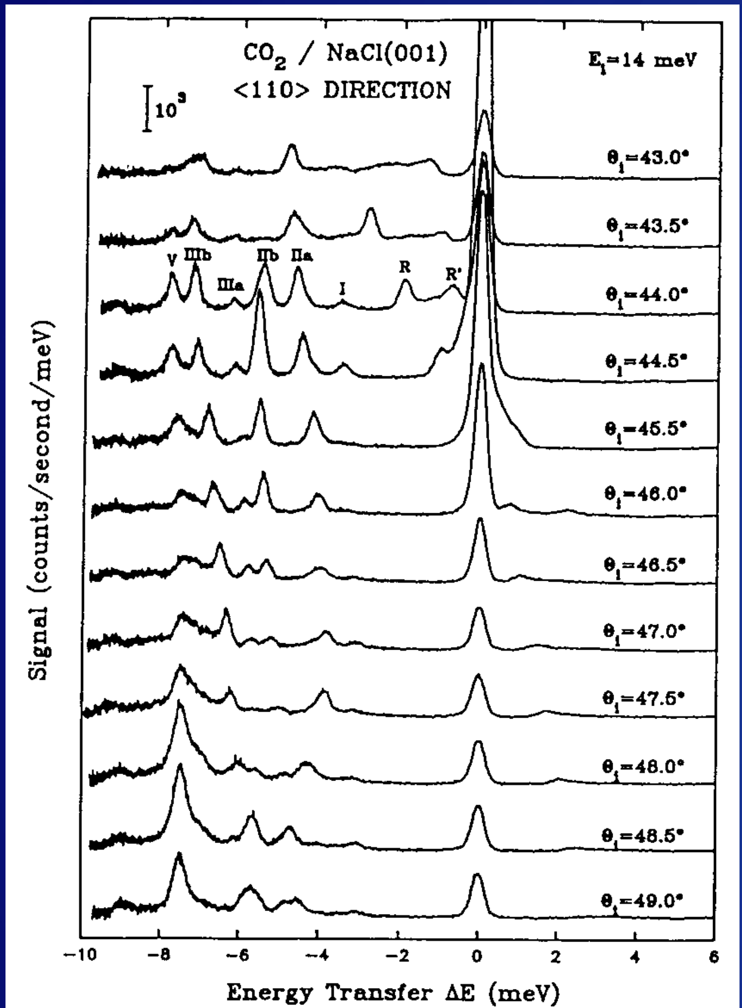
=> 15 modes in total

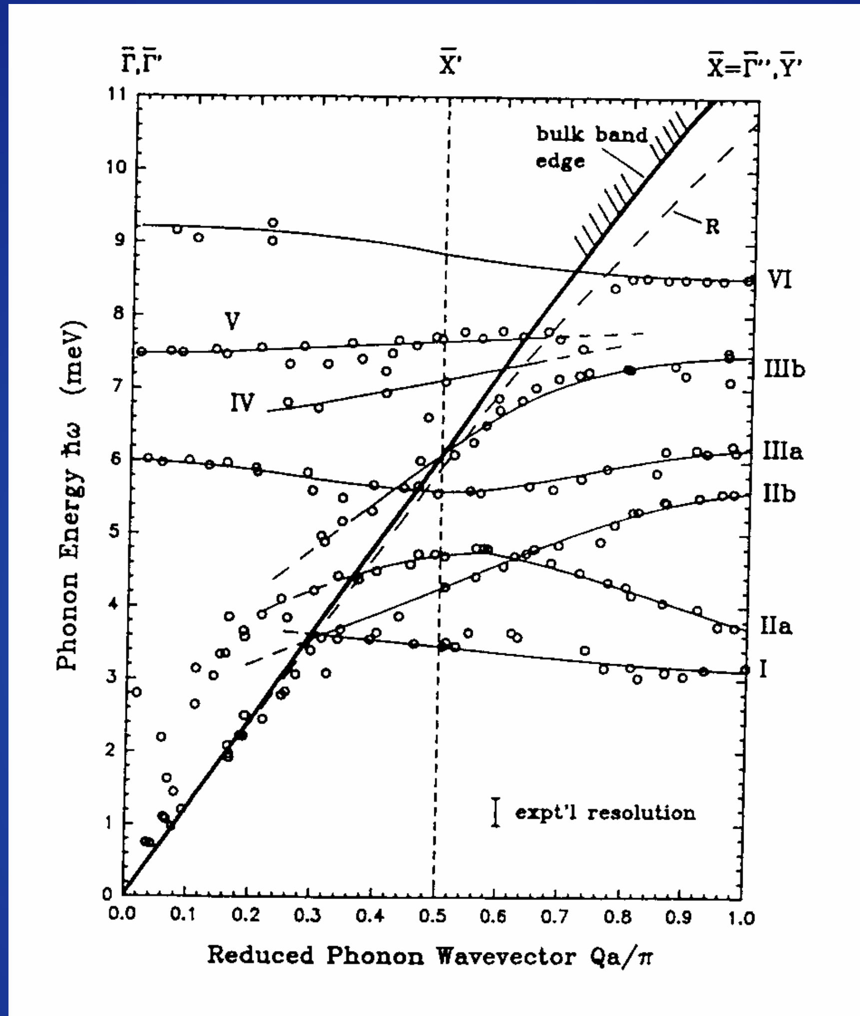
J. Heidberg et al. *J. Electr. Spec. Rel. Phenom.* 64/65, 341 (1993).

HAS

CO_2 on NaCl(001)

Max-Planck-Gesellschaft



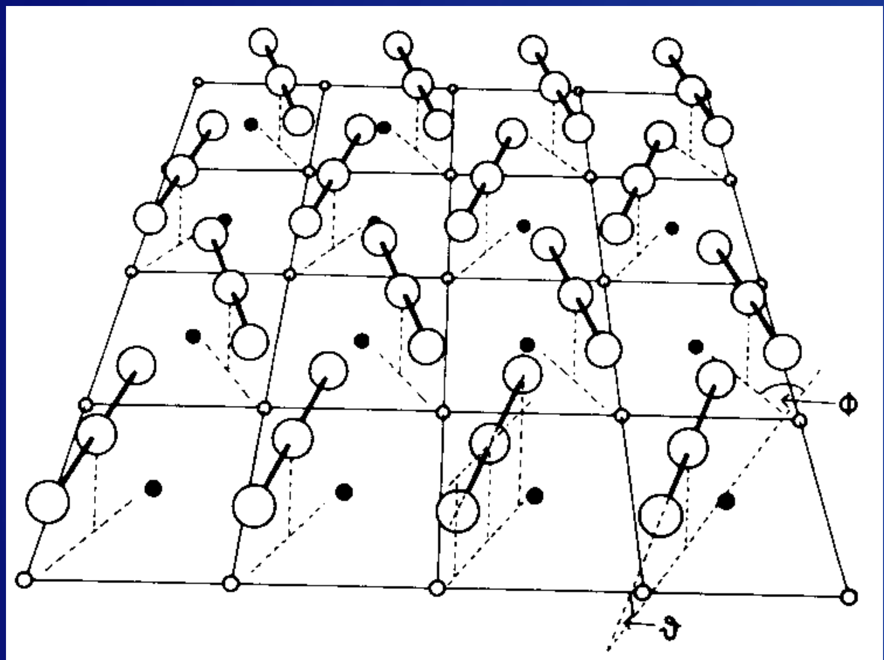


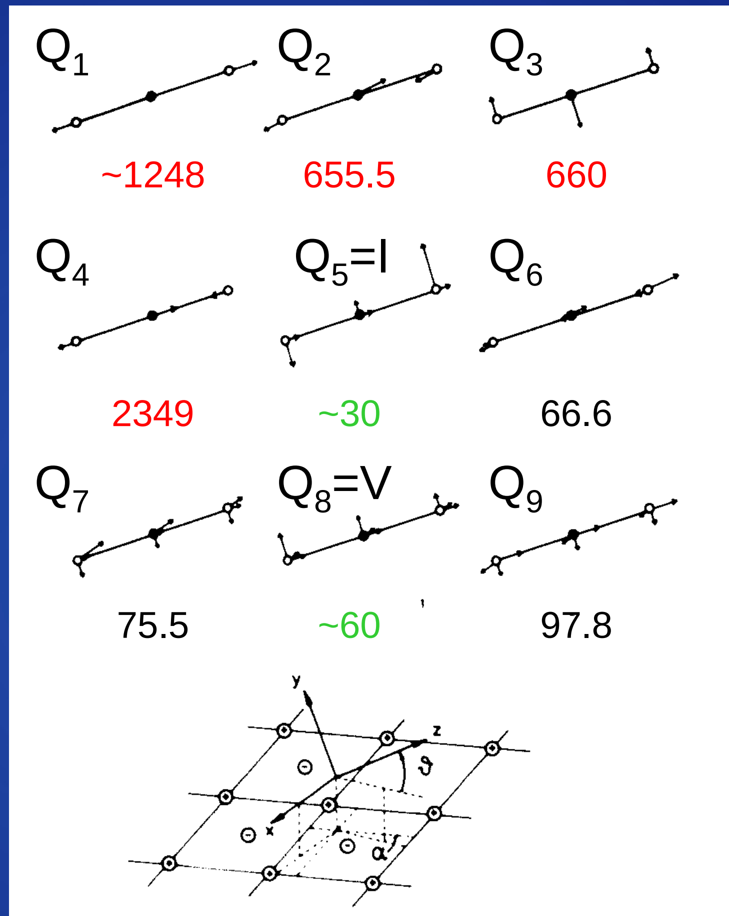
J. Heidberg et al. *J. Electr. Spec. Rel. Phenom.* 64/65, 341 (1993).

IRAS

CO_2 on NaCl(001)

Max-Planck-Gesellschaft





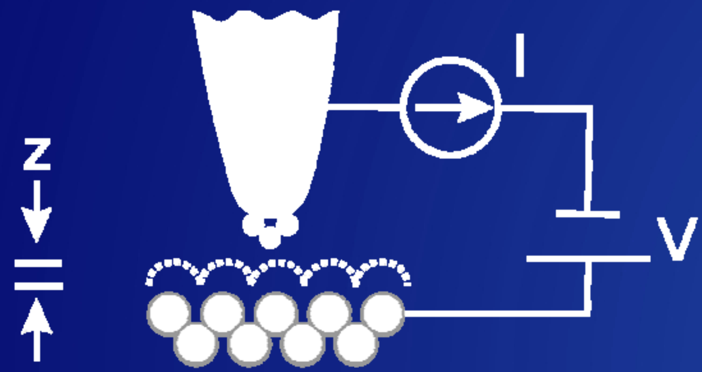
J. Heidberg et al. *Surf. Sci.* 269/270, 120 (1992).

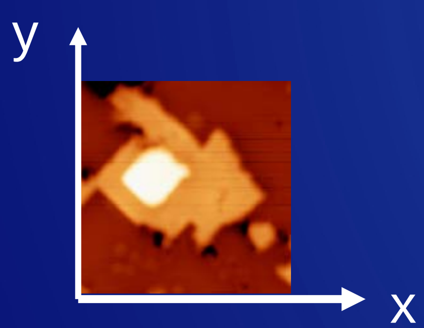
Single molecule vibrations

STM/STS

STM

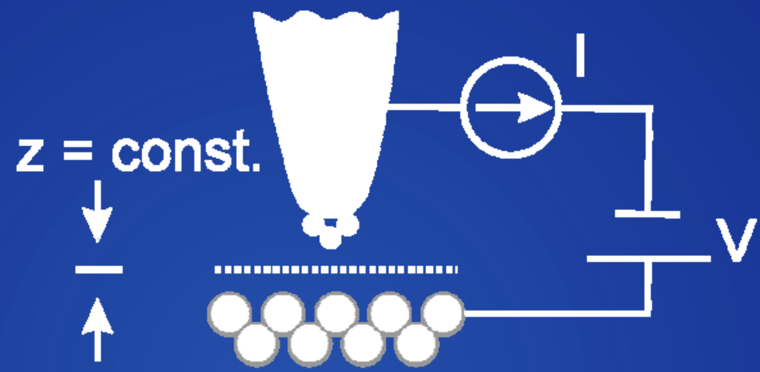
constant current mode



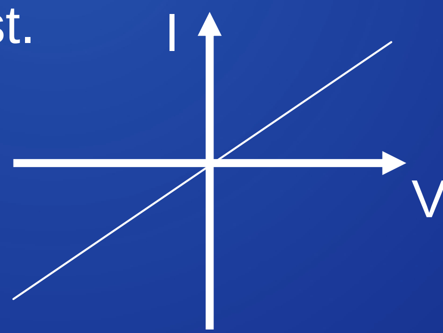


STS

constant height mode



x, y = const.

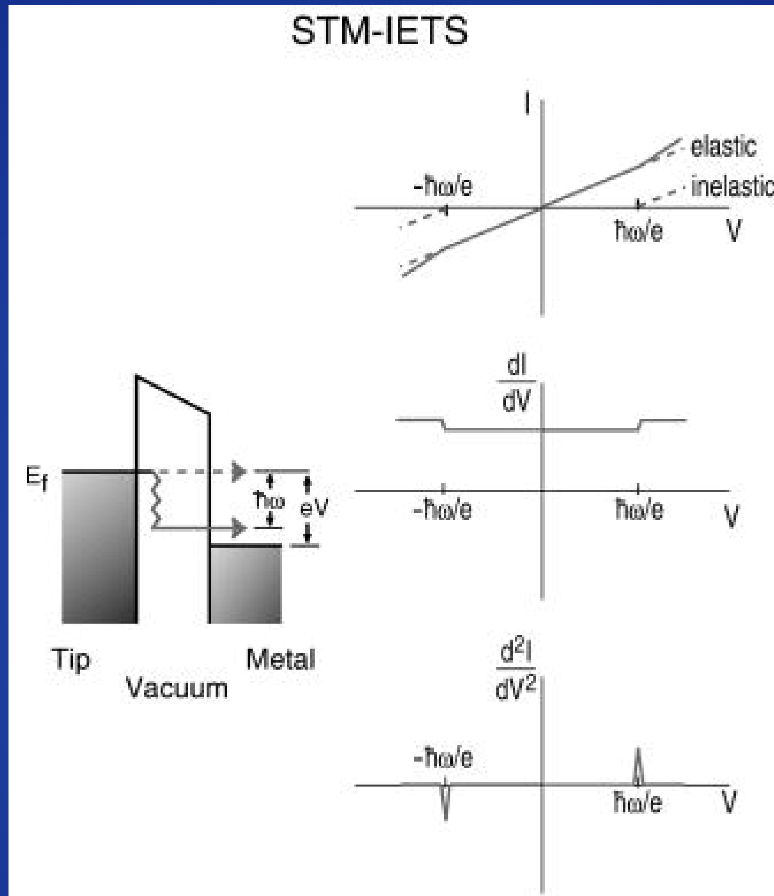


Single molecule vibrations

STM-IETS

Max-Planck-Gesellschaft

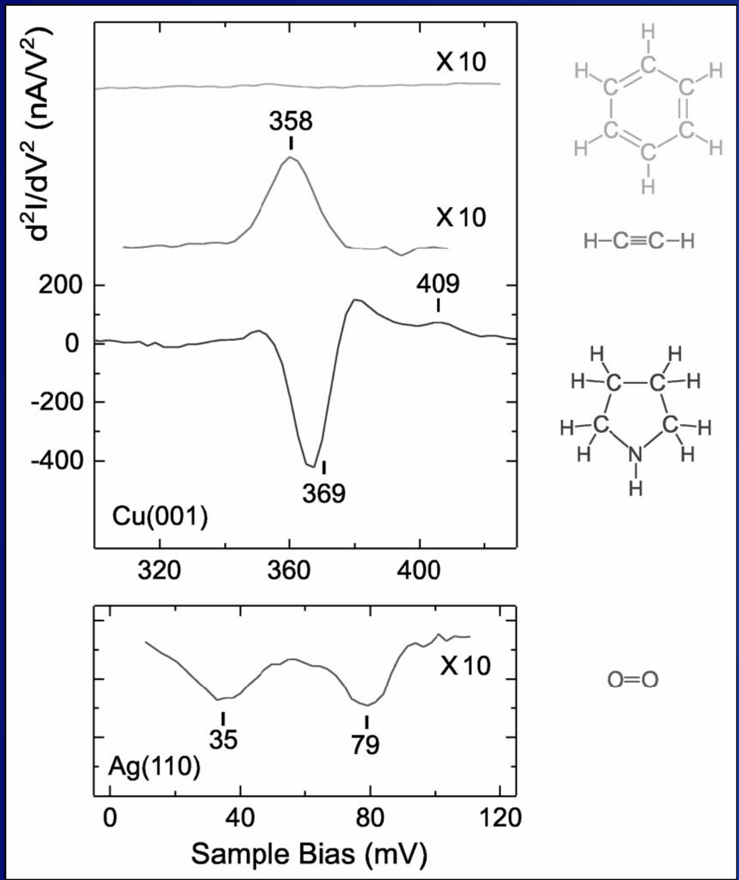
threshold spectroscopy

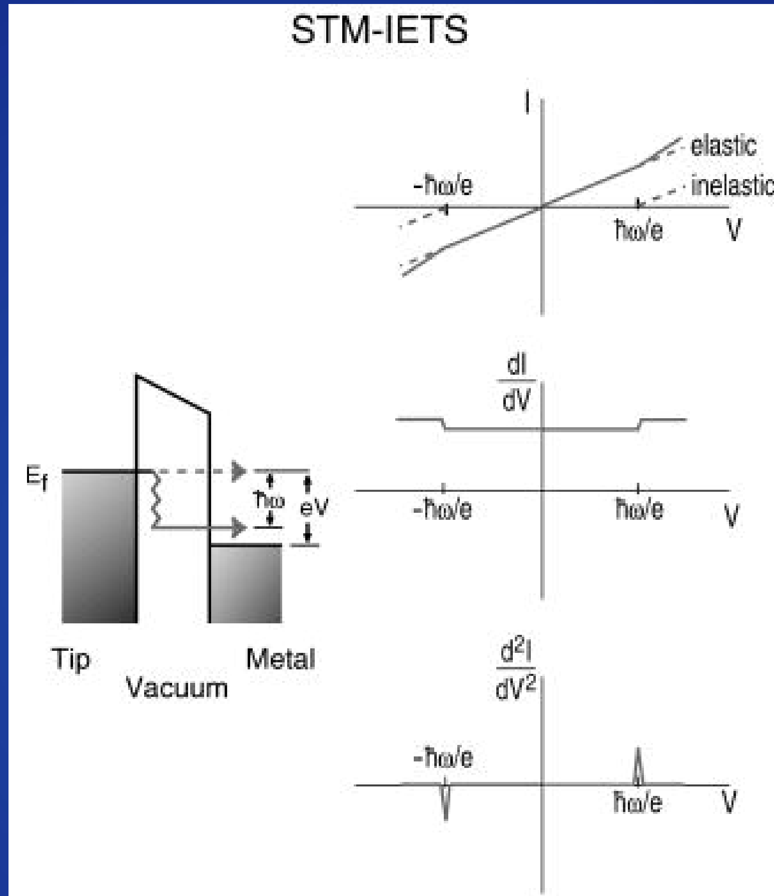


W. Ho J. Chem. Phys. 117, 11033 (2003).

Single molecule vibrations

STM-IETS

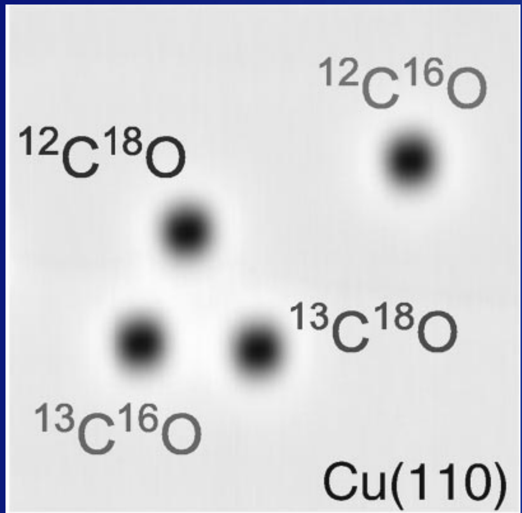


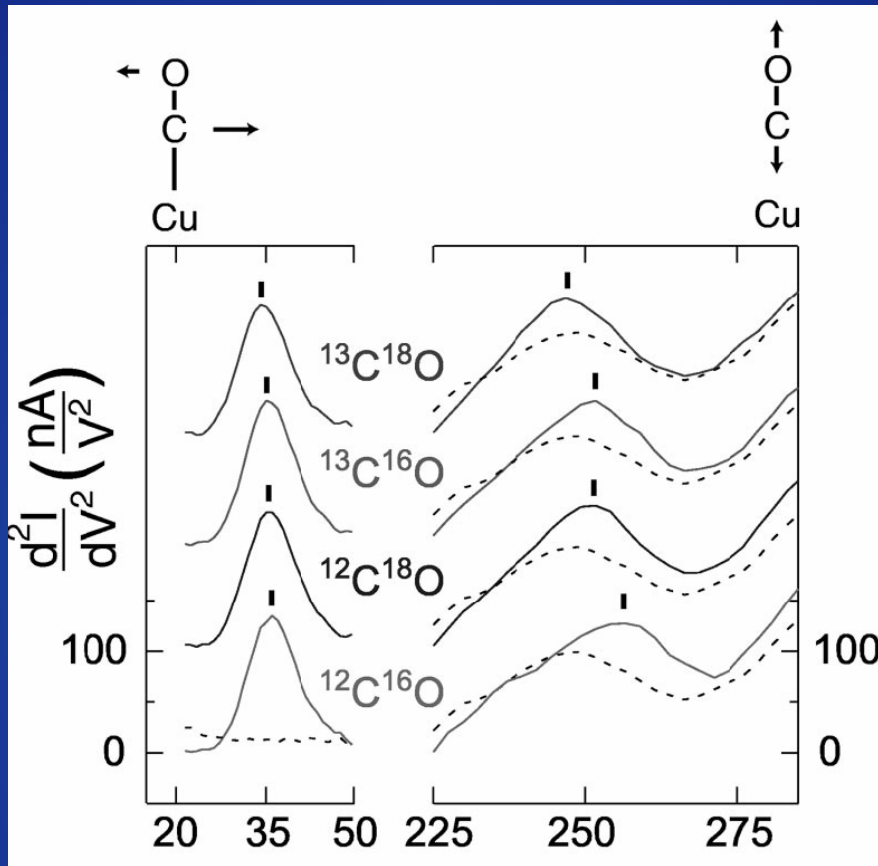


W. Ho J. Chem. Phys. 117, 11033 (2003).

Single molecule vibrations

STM-IETS





W. Ho J. Chem. Phys. 117, 11033 (2003).

Max-Planck-Gesellschaft

vibrational and rotational dynamics of adsorbates on surfaces

Part II

Thomas Risse

Fritz-Haber-Institut der Max-Planck Gesellschaft,
Abteilung Chemische Physik
Faradayweg 4-6
14195 Berlin

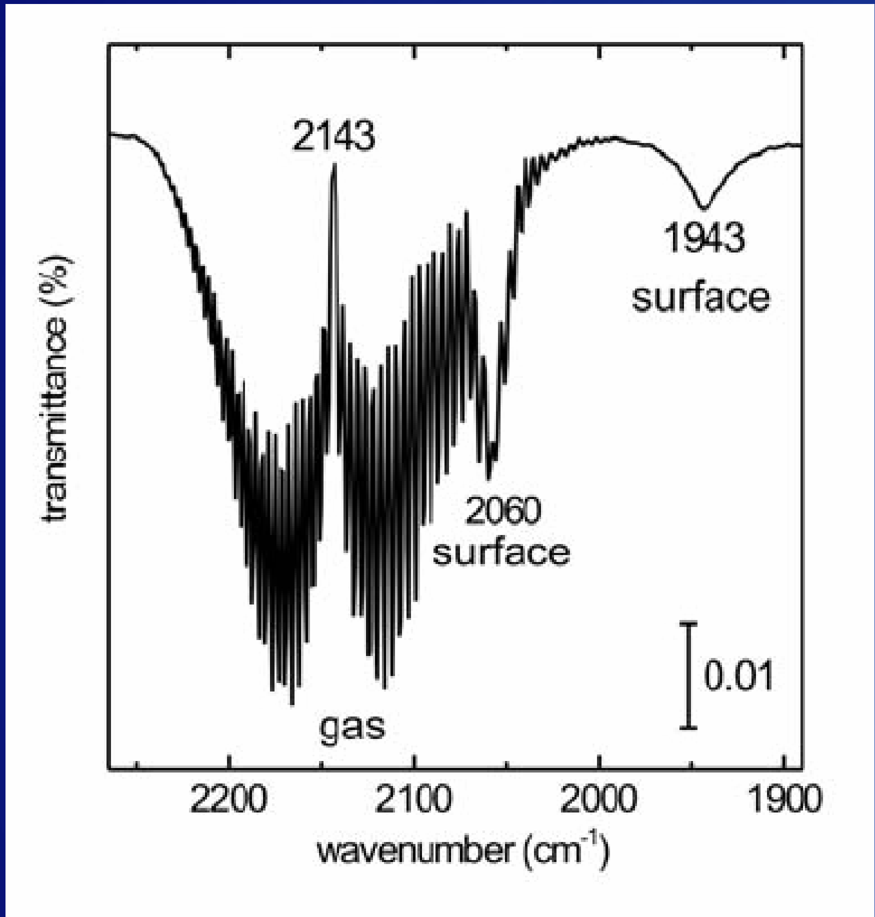
Outline

Max-Planck-Gesellschaft

- Introduction
- electron energy loss spectroscopy (EELS)
- infrared spectroscopy
- helium atom scattering (HAS)
- PMIRAS
- SFG
- Raman
- scanning tunneling spectroscopy
- electron spin resonance

IRAS

Ambient pressures

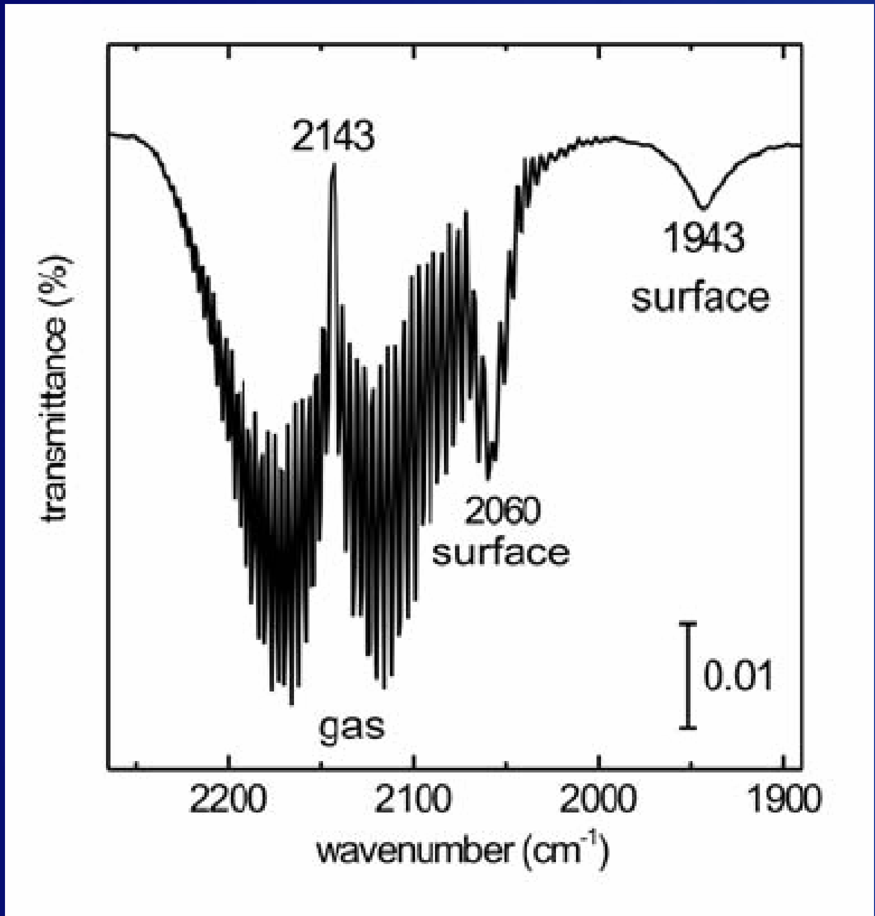


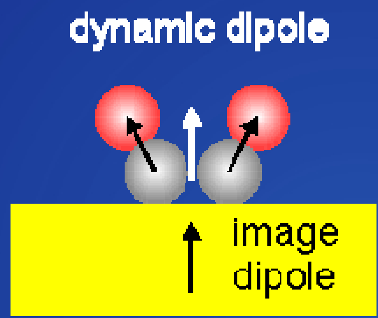
50 mbar CO on Pd(111) at 300 K

M. Borasio, PhD-thesis, FU-Berlin (2006)

IRAS

Ambient pressures

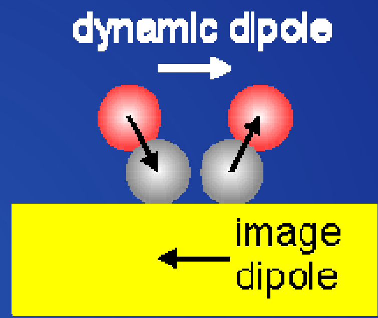




metal

$\mu_{dyndip} > 0$

IR active



metal

$\mu_{dyndip} = 0$

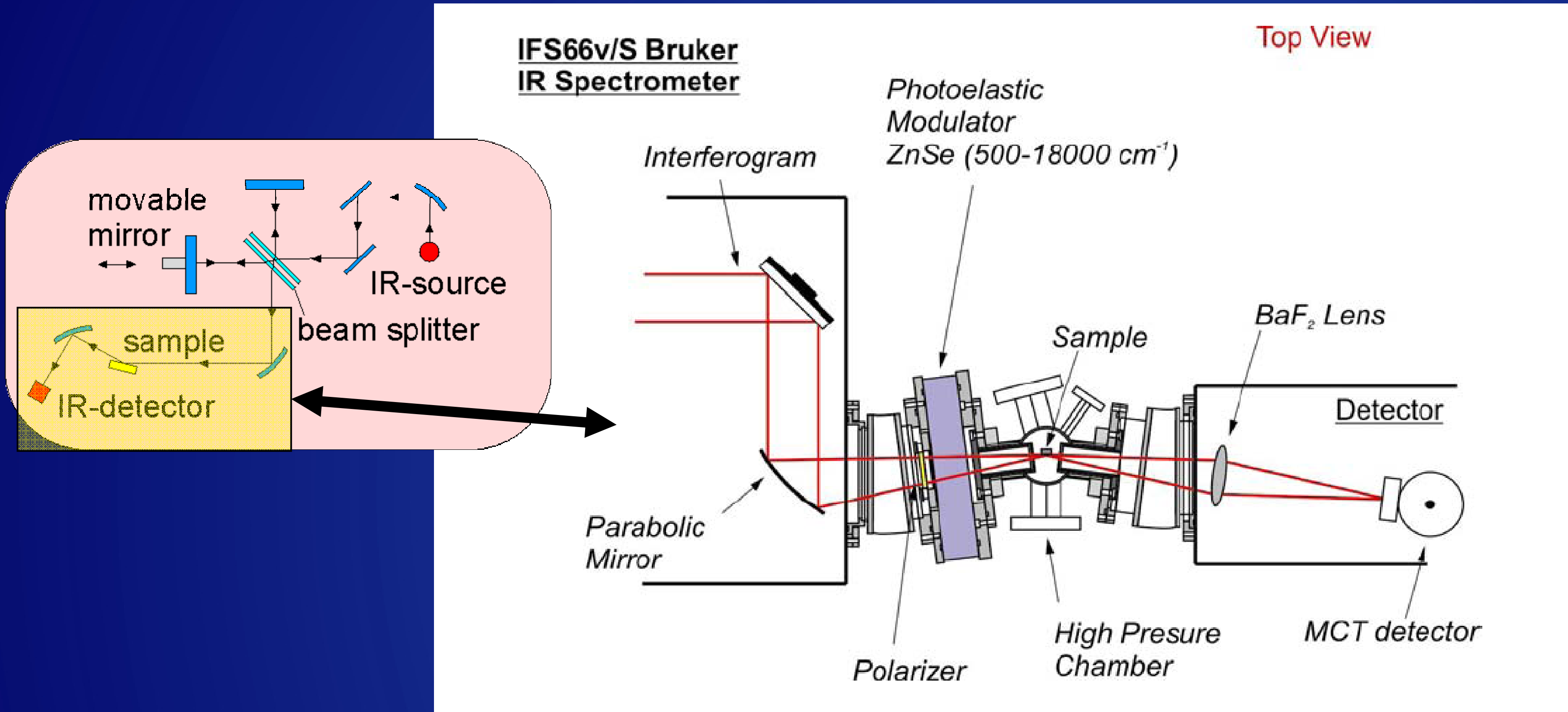
IR inactive

M. Borasio, PhD-thesis, FU-Berlin (2006)

IRAS

PMIRAS

Max-Planck-Gesellschaft

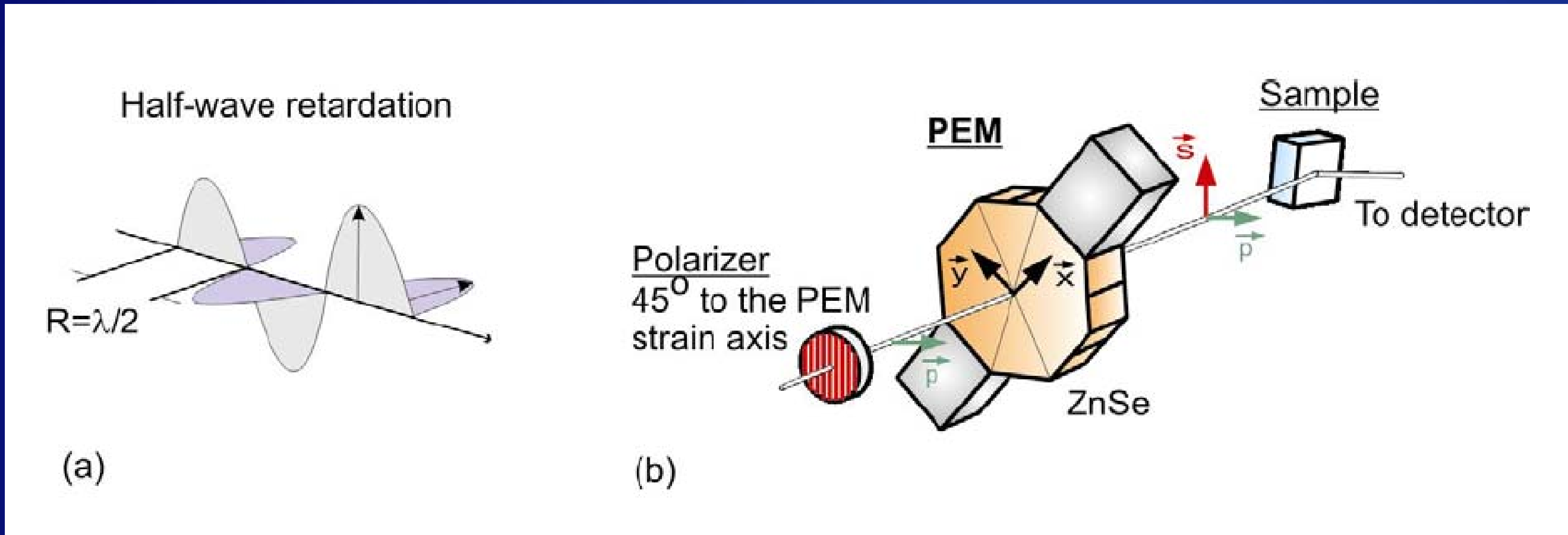


M. Borasio, PhD-thesis, FU-Berlin (2006)

IRAS

PMIRAS

central part: photoacustic modulator

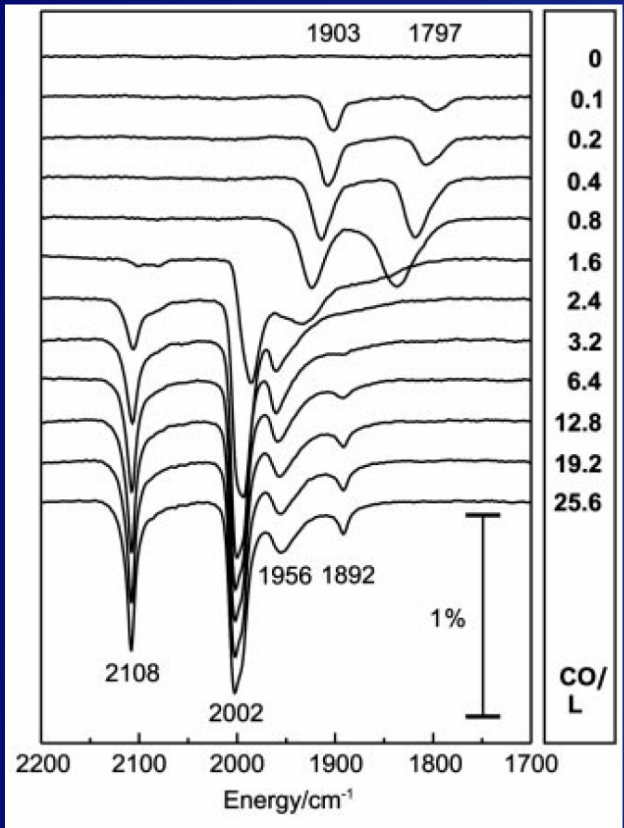


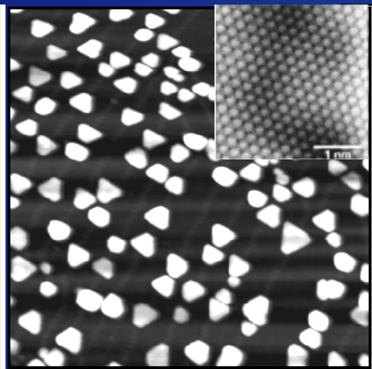
M. Borasio, PhD-thesis, FU-Berlin (2006)

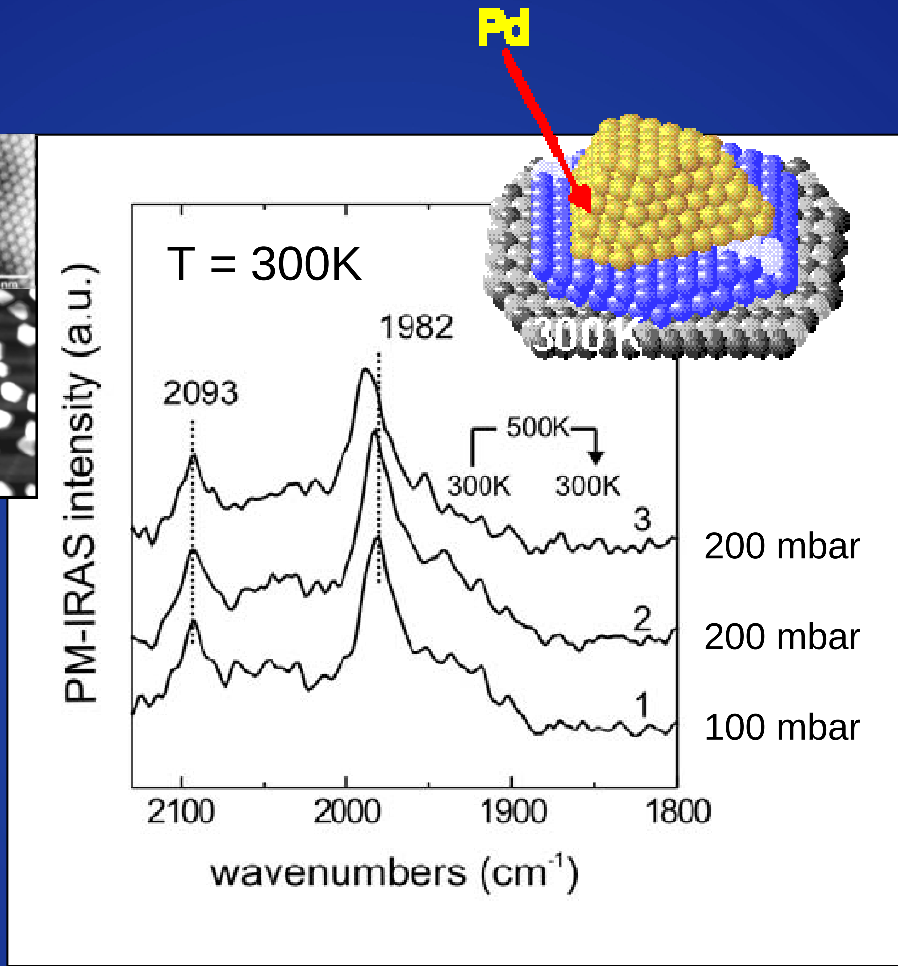
PMIRAS

$CO/Pd/Al_2O_3/NiAl(110)$

Max-Planck-Gesellschaft







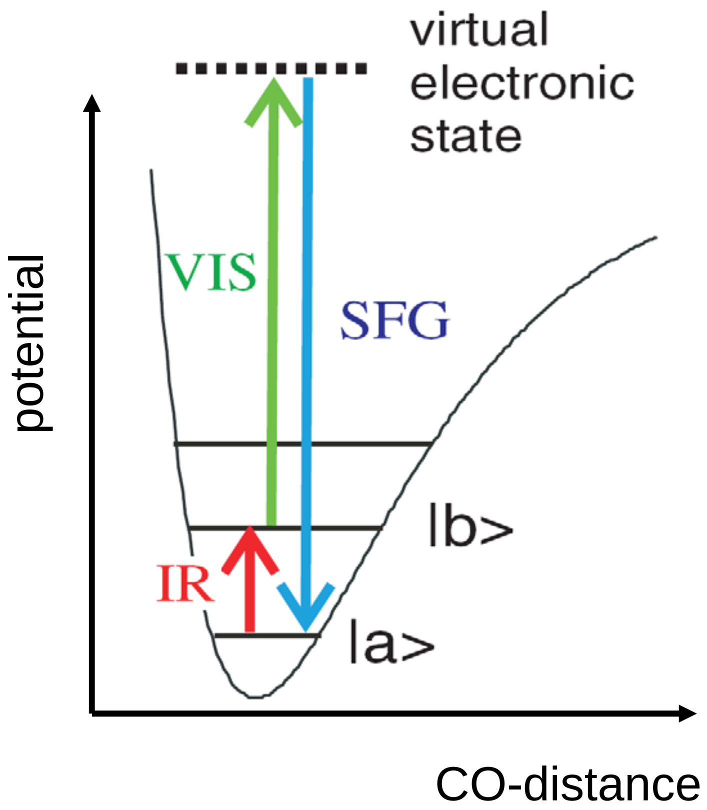
M. Frank and M. Bäumer, PCCP **2**, 3723 (2000).

M. Borasio, PhD-thesis, FU-Berlin (2006)

Vibrational spectroscopy

Sum frequency generation

Max-Planck-Gesellschaft



Second order non optical linear process

$$P^{(2)}_{\omega_{SFG}} = \chi^{(2)}_{\omega_{SFG}} E_{\omega_{IR}} E_{\omega_{VIS}}$$

Surface sensitive method

SFG is symmetry forbidden in isotropic (bulk) media (dipole approximation)

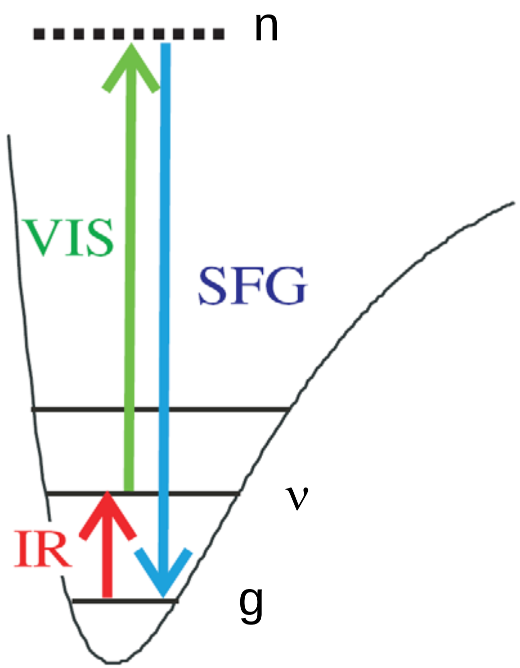
Vibrational spectroscopy

Sum frequency generation

Max-Planck-Gesellschaft

$$\mathbf{P}^{(2)}_{\omega_{SFG}} = \chi^{(2)}_{\omega_{SFG}} \mathbf{E}_{\omega_{IR}} \mathbf{E}_{\omega_{VIS}}$$

$$\chi^{(2)}_{ijk}(-\omega_{SF};\omega_{vis},\omega_{IR}) = \frac{N}{2\varepsilon_0\hbar^2}\sum_n \rho^0_{gg} \times \left\{ \frac{\mu^i_{gn}\mu^j_{n\nu}\mu^k_{\nu g}}{[(\omega_{ng}-\omega_{SF})-i\gamma_{ng}][(\omega_{\nu g}-\omega_{IR})-i\gamma_{\nu g}]} + \frac{\mu^j_{gn}\mu^i_{n\nu}\mu^k_{\nu g}}{[(\omega_{n\nu}+\omega_{SF})+i\gamma_{n\nu}][(\omega_{\nu g}-\omega_{IR})-i\gamma_{\nu g}]} \right\}$$



- molecules in the vibronic ground state g
- IR light in resonance with a vibration

R.W. Boyd *Nonlinear Optics*, Academic Press, New York, 1992.

Vibrational spectroscopy

Sum frequency generation

Max-Planck-Gesellschaft

$$\mathbf{P}^{(2)}_{\omega_{SFG}} = \chi^{(2)}_{\omega_{SFG}} \mathbf{E}_{\omega_{IR}} \mathbf{E}_{\omega_{VIS}}$$

$$\chi^{(2)}_{ijk}(-\omega_{SF};\omega_{vis},\omega_{IR}) = \frac{N\rho^0_{gg}}{2\varepsilon_0\hbar^2} \frac{\mu^k_{\nu g}}{[(\omega_{\nu g}-\omega_{IR})-i\gamma_{\nu g}]} \times \sum_n \left\{ \frac{\mu^i_{gn}\mu^j_{n\nu}}{[(\omega_{ng}-\omega_{SF})-i\gamma_{ng}]} + \frac{\mu^j_{gn}\mu^i_{n\nu}}{[(\omega_{n\nu}+\omega_{SF})+i\gamma_{n\nu}]} \right\}.$$

$$\chi^{(2)}_{ijk}(-\omega_{SF};\omega_{vis},\omega_{IR}) = \frac{N\rho^0_{gg}}{2\varepsilon_0\hbar} \frac{\mu^k_{\nu g}}{[(\omega_{\nu g}-\omega_{IR})-i\gamma_{\nu g}]} \alpha^{ij}_{g\nu}(-\omega_{SF};\omega_{vis})$$

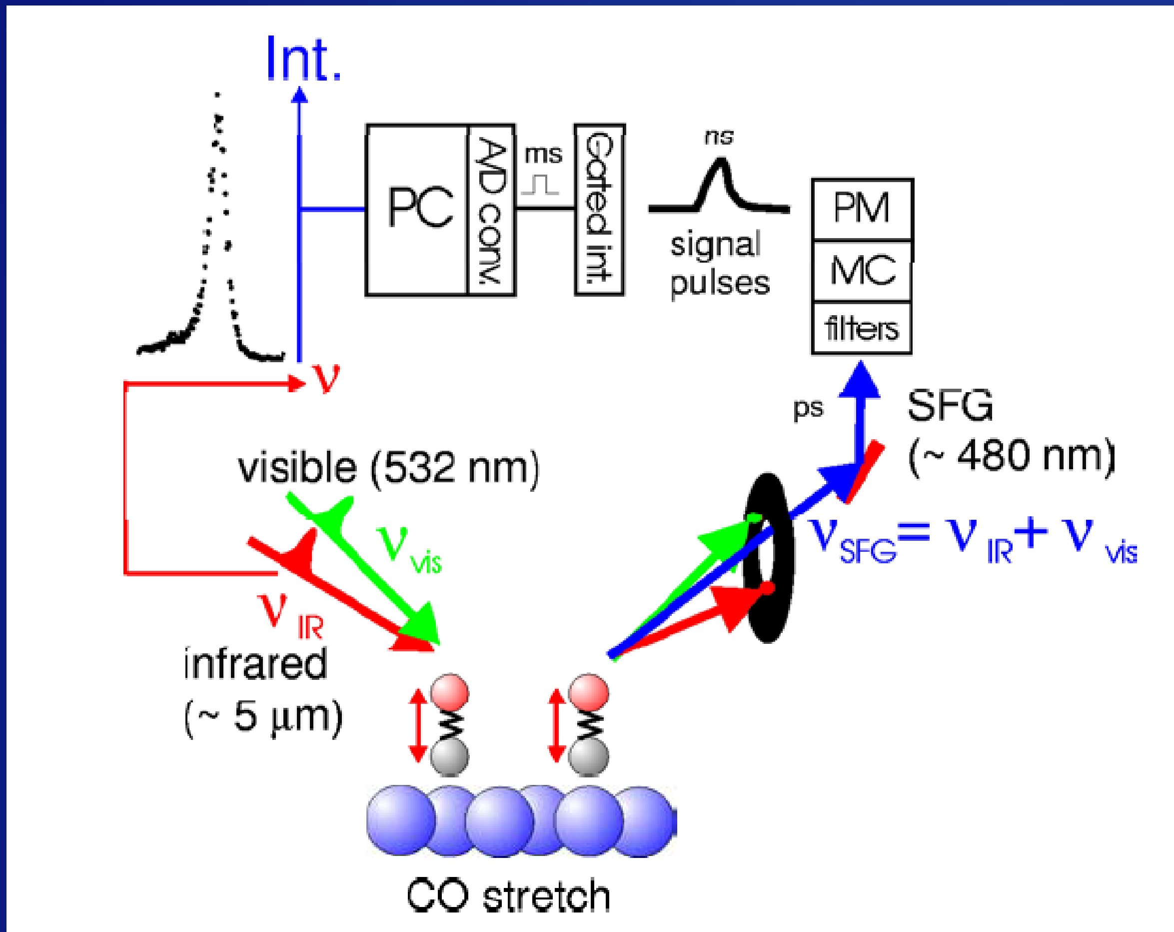
$$\alpha^{ij}_{g\nu}(-\omega_{SF};\omega_{vis}) = \frac{1}{\hbar} \sum_n \left\{ \frac{\mu^i_{gn}\mu^j_{n\nu}}{(\omega_{ng}-\omega_{SF})} + \frac{\mu^j_{gn}\mu^i_{n\nu}}{(\omega_{ng}+\omega_{vis})} \right\}.$$

a_{gv}: 1. order hyperpolarizability (anti Stokes Raman intensity)

R.W. Boyd *Nonlinear Optics*, Academic Press, New York, 1992.

Vibrational spectroscopy

Sum frequency generation

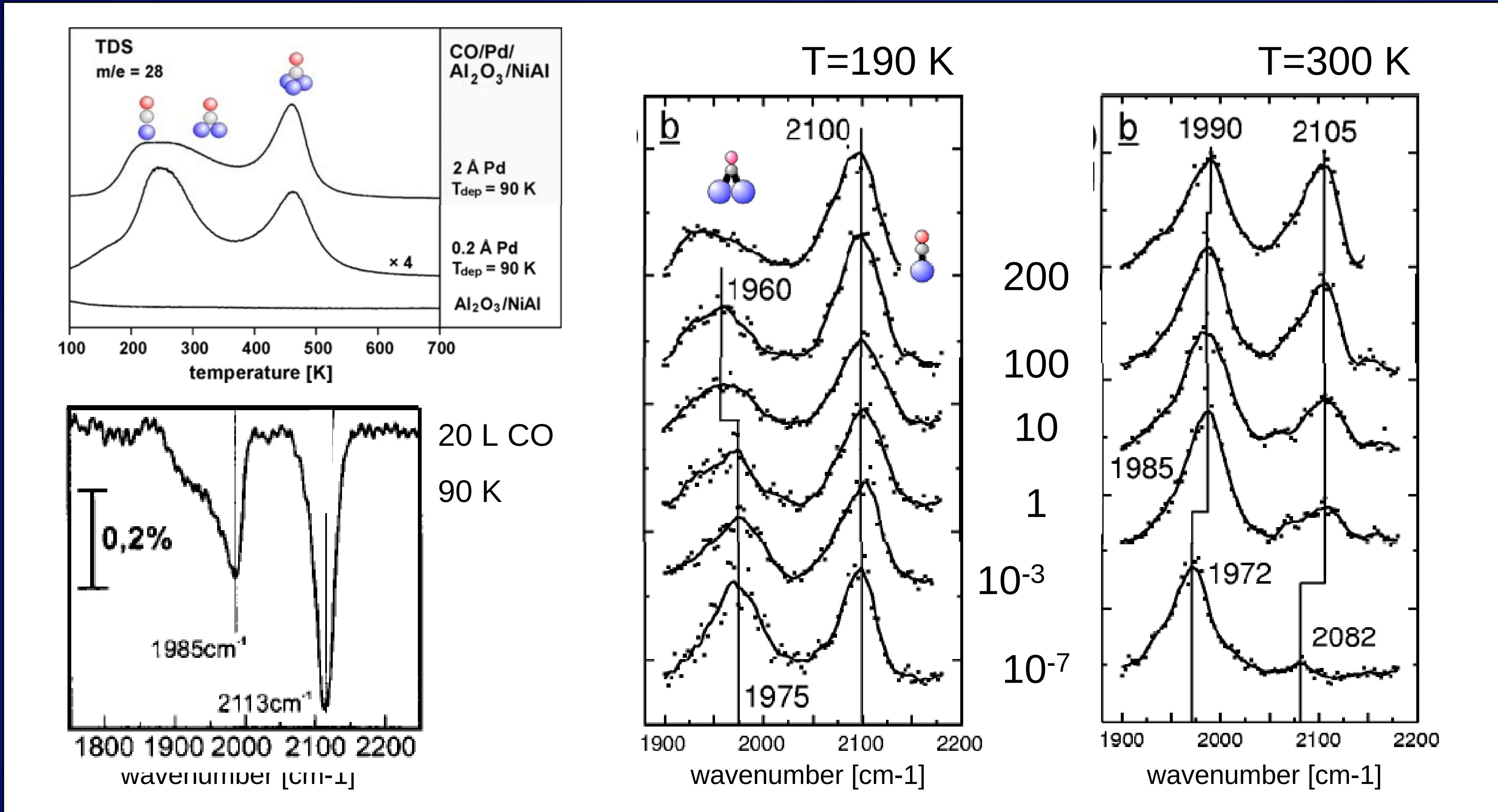


H. Unterhalt, PhD-thesis, FU-Berlin (2002)

SFG

$CO/Pd/Al_2O_3/NiAl(110)$

Max-Planck-Gesellschaft



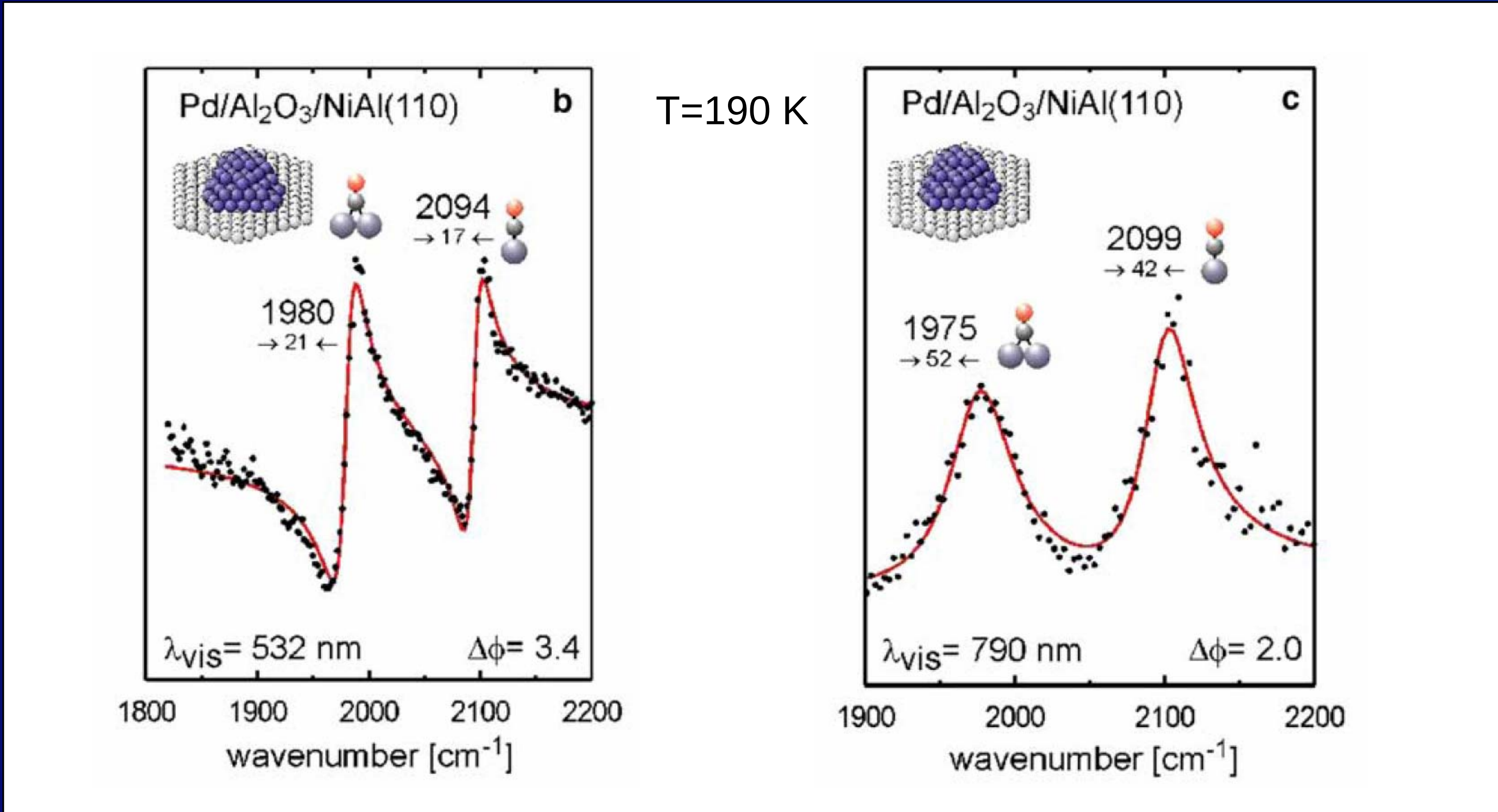
K. Wolter et al. Surf. Sci. **399**, 190 (1998).

H. Unterhalt *et al.* J. Phys. Chem. B **106**, 356 (2002).

M. Bäumer *et al.* Ber. Bunsenges. Phys. Chem. **99**, 1381 (1995).

SFG

CO/Pd/Al_2O_3/NiAl(110)

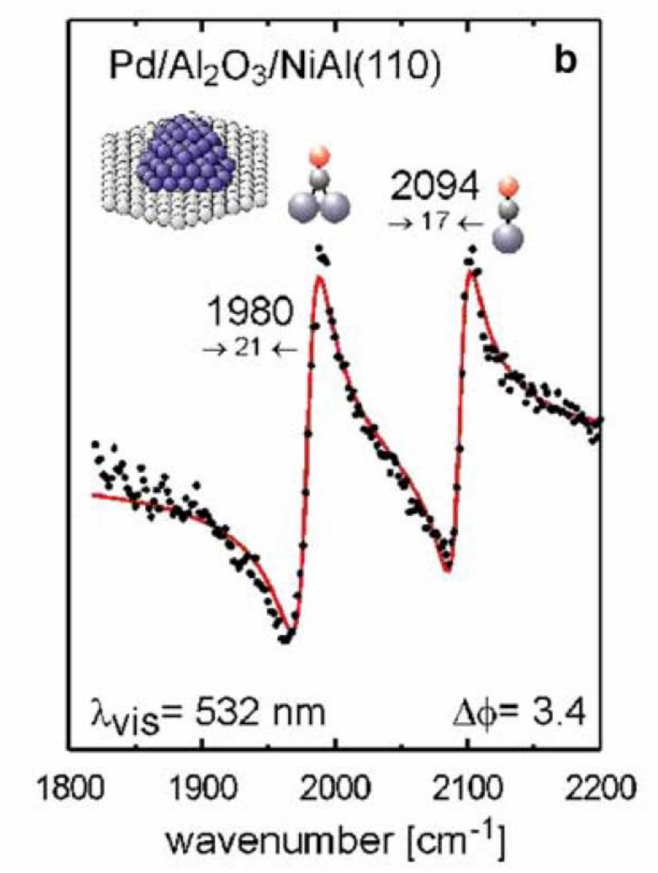


M. Morkel et al. Surf. Sci. **586**, 146 (2005).

SFG

$CO/Pd/Al_2O_3/NiAl(110)$

Max-Planck-Gesellschaft



$$\chi_s^{(2)} = \chi_{NR}^{(2)} + \chi_R^{(2)} = A_{NR} \cdot e^{i\phi_0} + \sum_q \frac{A_q \cdot e^{i\phi_q}}{(\omega_q - \omega_{IR}) - i\Gamma_q}$$

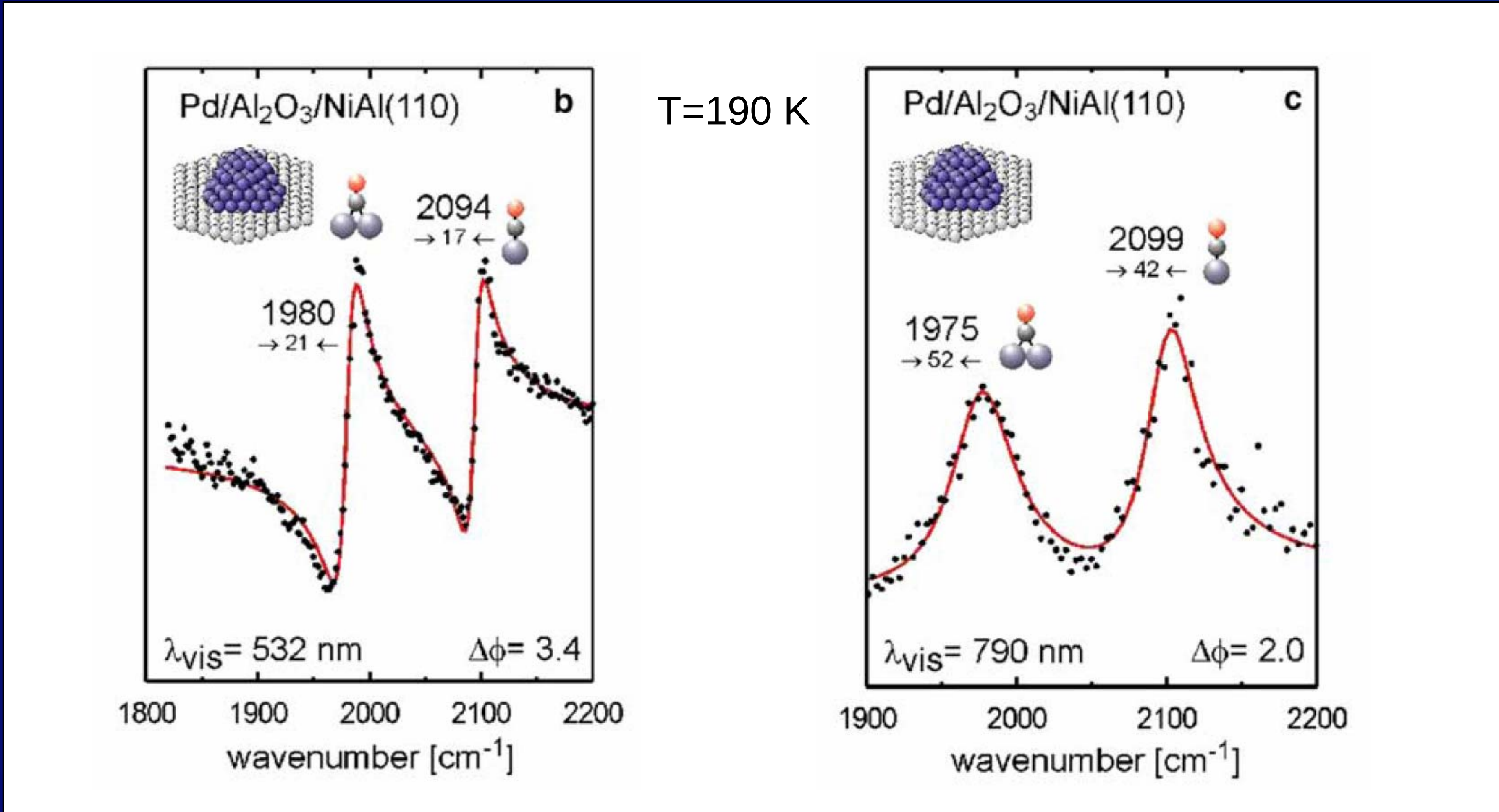
In case the phase of the non resonant background is constant I_{SFG} does only depent on the phase difference $\Delta\phi_{0q}$:

$$I_{SFG} \propto \left| A_{NR} + \sum_q \frac{A_q \cdot e^{i\Delta\phi_{0q}}}{(\omega_q - \omega_{IR}) - i\Gamma_q} \right|^2 \cdot I_{vis} \cdot I_{IR}$$

M. Morkel et al. Surf. Sci. **586**, 146 (2005).

SFG

$CO/Pd/Al_2O_3/NiAl(110)$

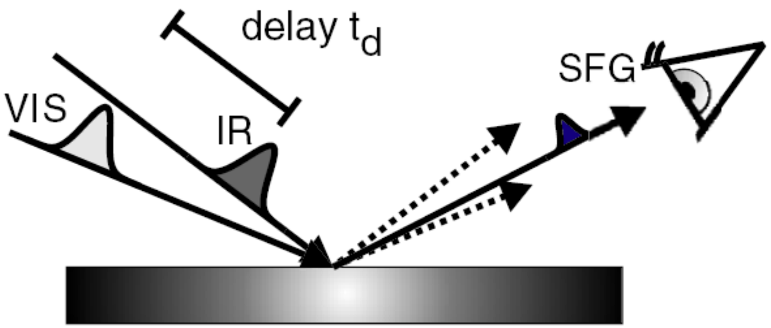


M. Morkel et al. Surf. Sci. **586**, 146 (2005).

SFG

Time resolved measurements

Max-Planck-Gesellschaft



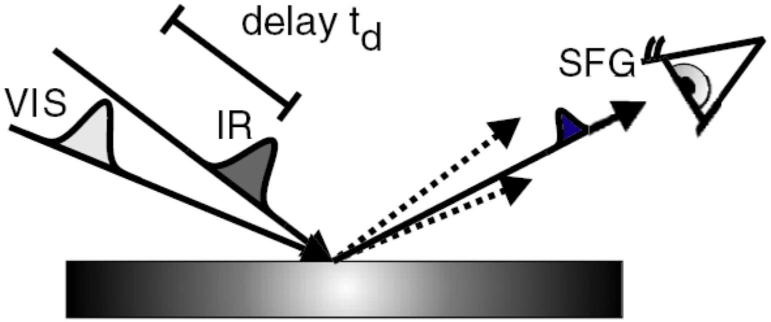
What happens if both pulses are fs in duration?

M. Bonn *et al.* J. Phys.: Condens. Mat. **17**, S201 (2005).

SFG

Time resolved measurements

Max-Planck-Gesellschaft

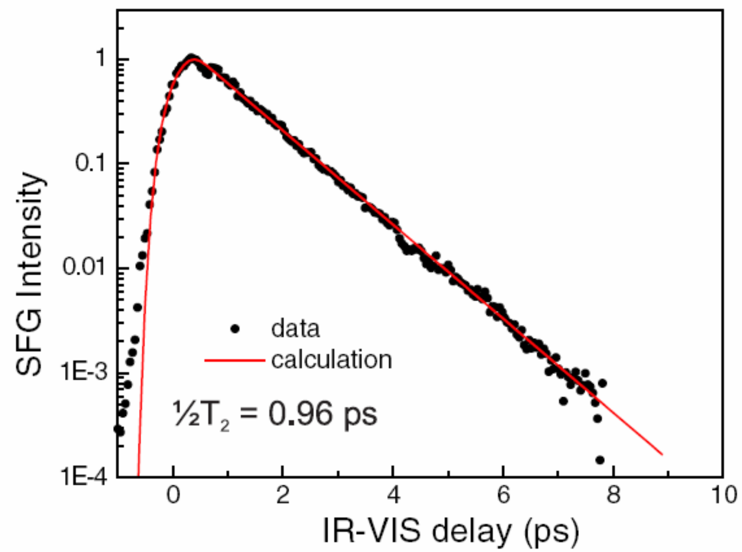


What happens if both pulses are fs in duration?

⇒ Loss of spectral resolution!

For 200 fs spectral width: 165 cm^{-1}

CO/Ru(0001)



M. Bonn *et al.* J. Phys.: Condens. Mat. **17**, S201 (2005).

SFG

Time resolved measurements

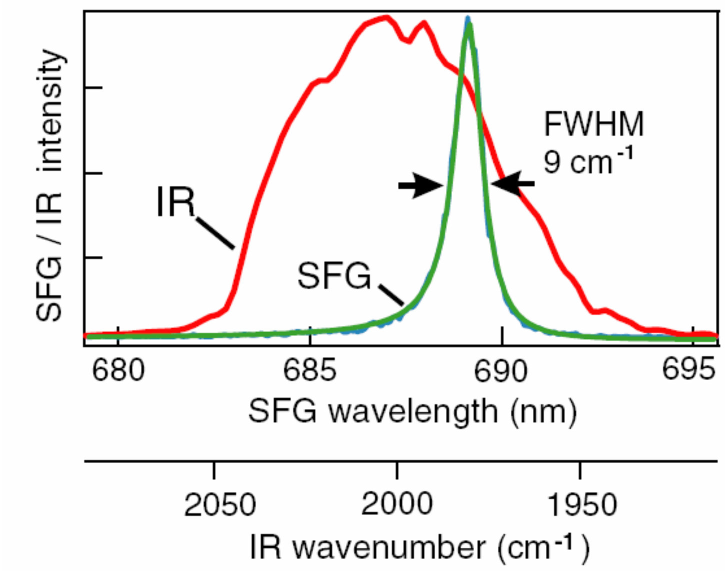
Max-Planck-Gesellschaft

How to measure a frequency domain spectrum?

fs IR pulse: broad spectral width

long VIS pulse (ps; pulse shaper)
(narrow spectral width appox. 7 cm^{-1})

CO/Ru(0001)



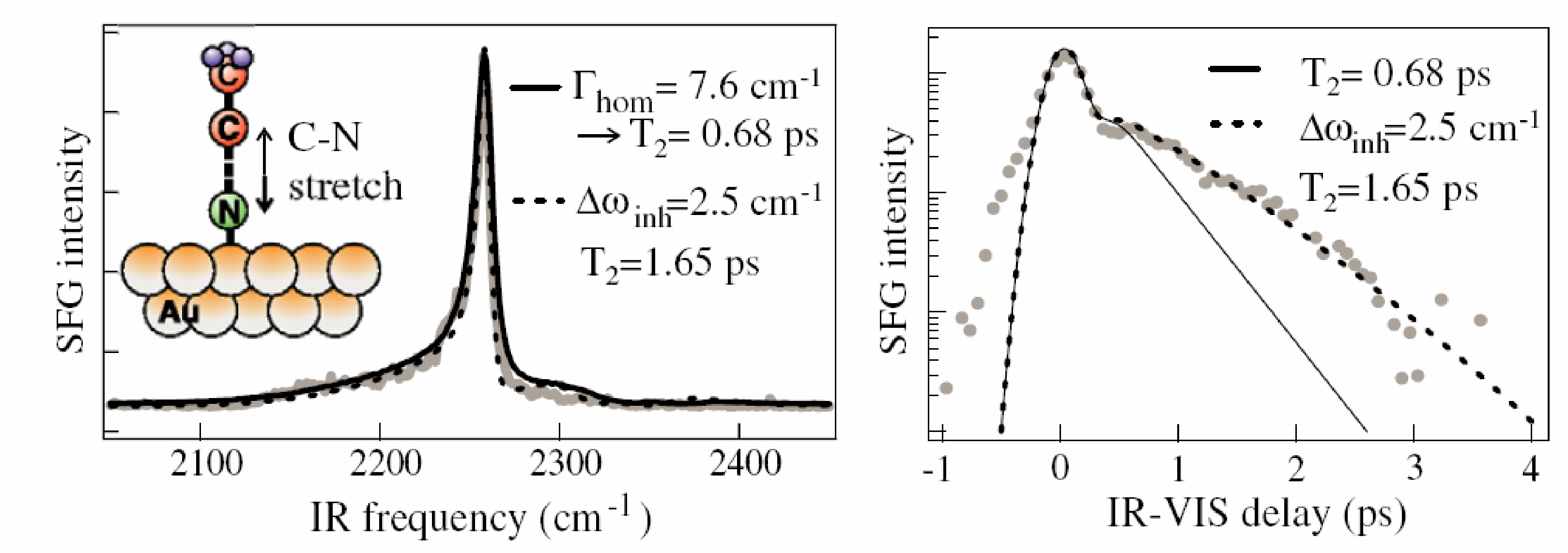
M. Bonn *et al.* J. Phys.: Condens. Mat. **17**, S201 (2005).

SFG

Time resolved measurements

Max-Planck-Gesellschaft

What method is better suited?

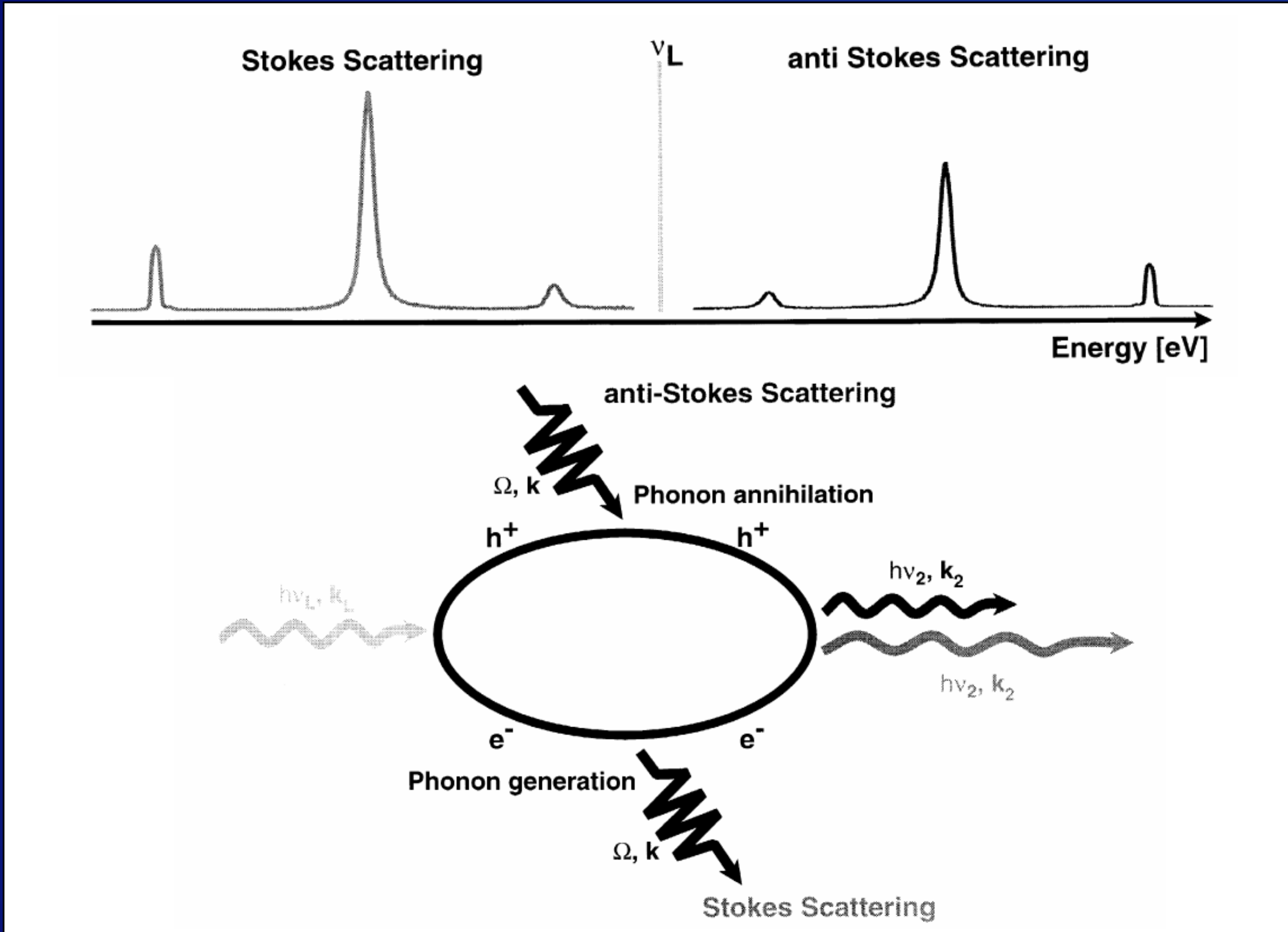


M. Bonn *et al.* J. Phys.: Condens. Mat. **17**, S201 (2005).

Raman spectroscopy

Basic aspects

Max-Planck-Gesellschaft



Raman spectroscopy

Basic aspects

Max-Planck-Gesellschaft

Pro

- wide spectral range 50 – 5000 cm^{-1}
- negligile gas phase scattering
- quartz is a very weak Raman scatterer; cells/windows can be made out of quartz
- can be done also at high temperatures (e.g. 1000 °C) because of detection in the optical regime; no perturbation by blackbody radiation
- catalysis: typical oxide supports (silca, alumina) are weak scatteres

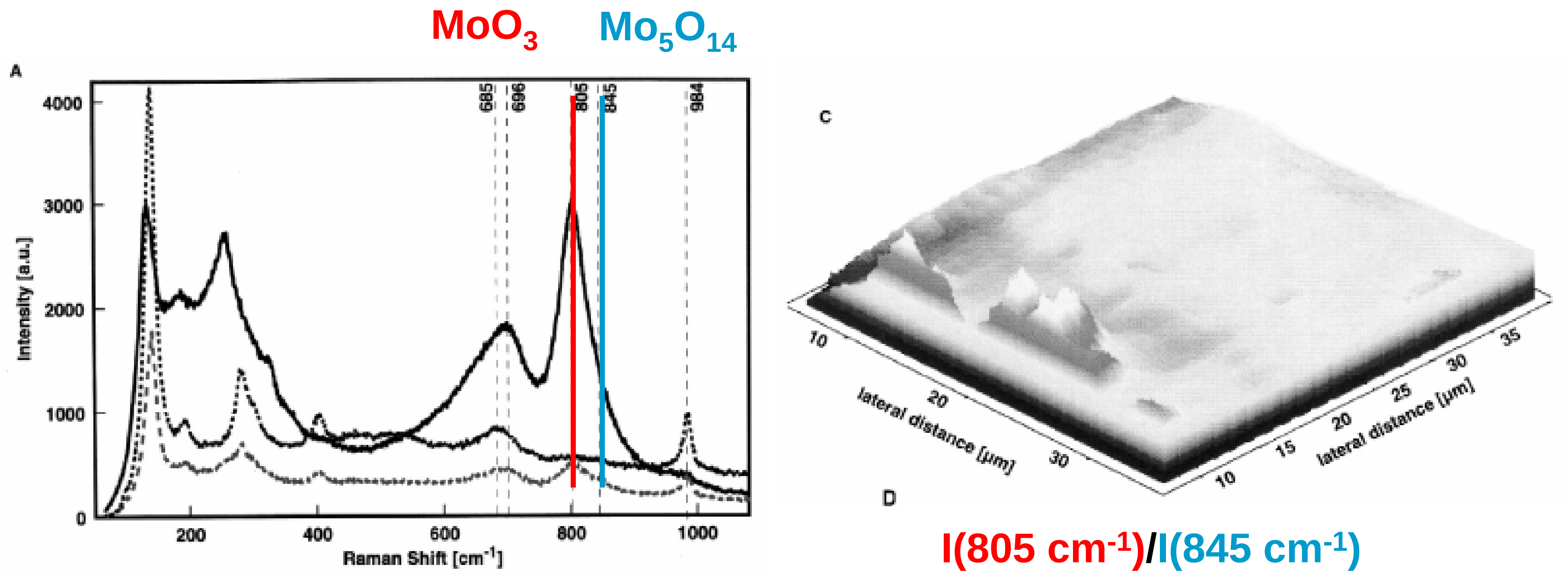
Con

- low intrinsic cross section
- $(d\sigma/d\Omega)_{NRS} \approx 10^{-28}$ cm^2 sr^{-1} ($I \propto \nu^4$)
- susceptible to fluorescence (can be up to 10^6 higher; especially coke has a high fluorescence yield)
- heating due to intense lasers
- quantification of Raman intensities is very diffcult (even with reference samples, because of possible electronic effects of the substrate)

Raman spectroscopy

Material characterization

Max-Planck-Gesellschaft

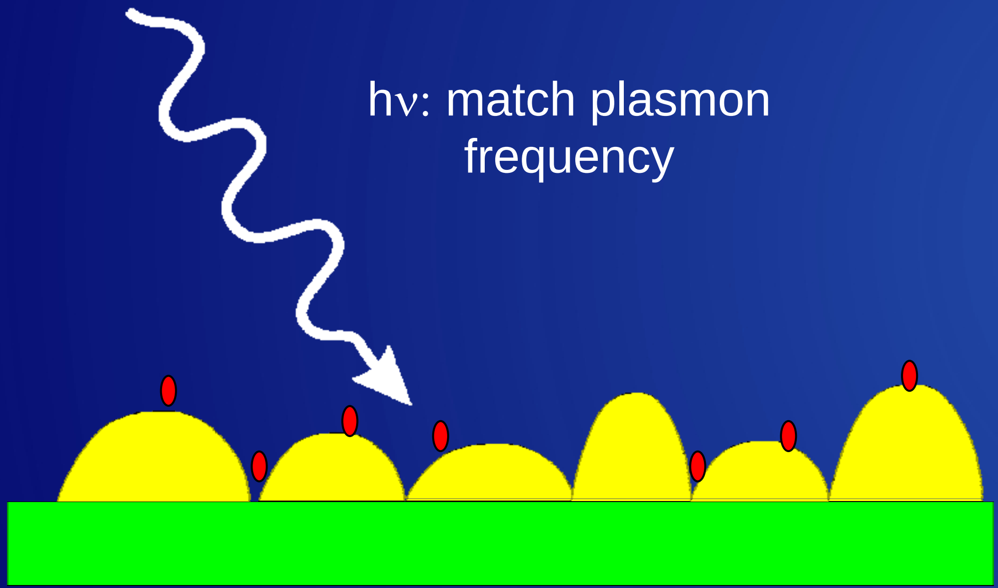


G. Mestl, J. Mol. Catal. A 158, 45 (2000).

Raman spectroscopy

Surface enhancement, SERS

Max-Planck-Gesellschaft



Works for rough surfaces of coinage metals (Cu, Ag, Au)

Idea: excitation of local surface plasmons

Field enhancement by plasmons in particular in between particles (gap states)

Enhancement: average effect approx 10^7 (gap mode may influence only a small number of molecules => local effects even much higher)

Raman spectroscopy

Surface enhancement, TERS

Max-Planck-Gesellschaft

Idea: using the enhancement due to gap modes and combine an STM with a Raman spectrometer

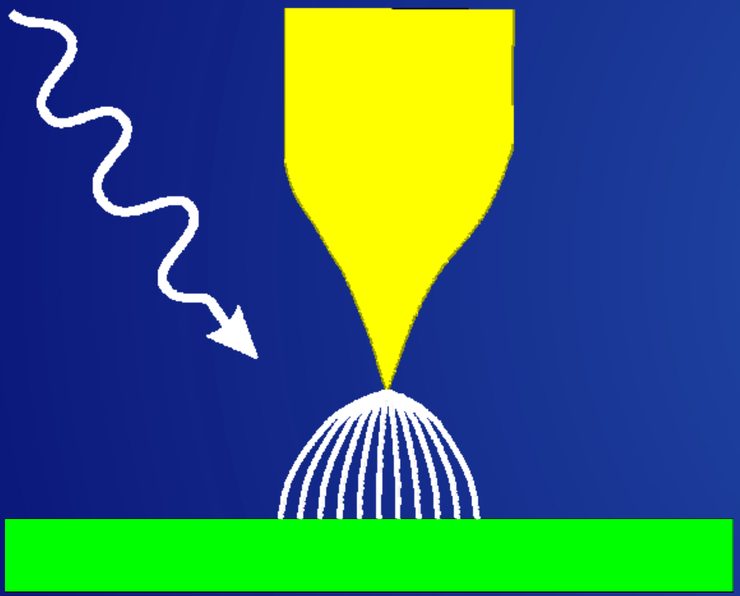
(Tip Enhanced Raman Spectroscopy)

Raman spectroscopy
Surface enhancement, TERS

Max-Planck-Gesellschaft

Idea: using the enhancement due to gap modes and combine an STM with a Raman spectrometer

(Tip Enhanced Raman Spectroscopy)



B. Pettinger et al.: Single Molec. **3**, 285 (2002).

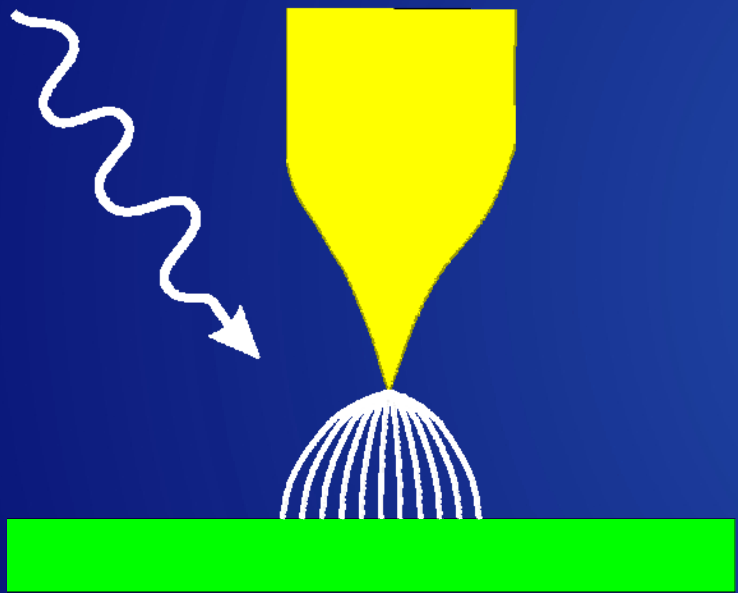
Raman spectroscopy

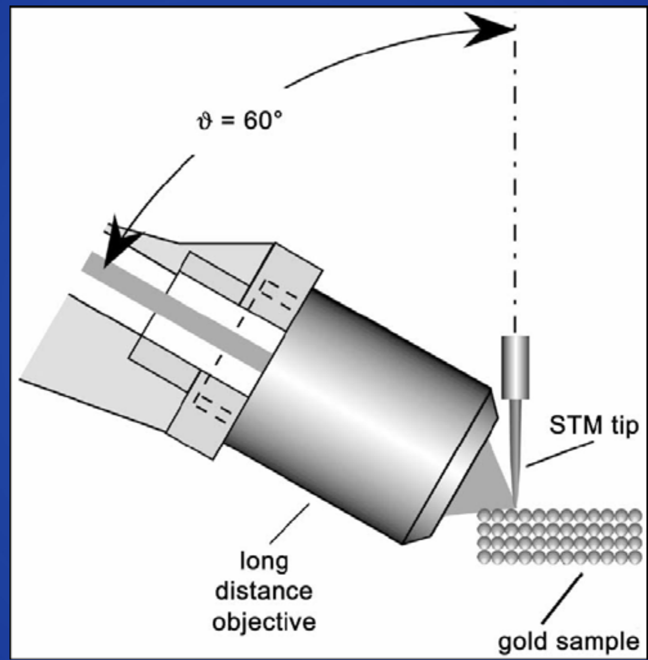
Surface enhancement, TERS

Max-Planck-Gesellschaft

Idea: using the enhancement due to gap modes and combine an STM with a Raman spectrometer

(Tip Enhanced Raman Spectroscopy)





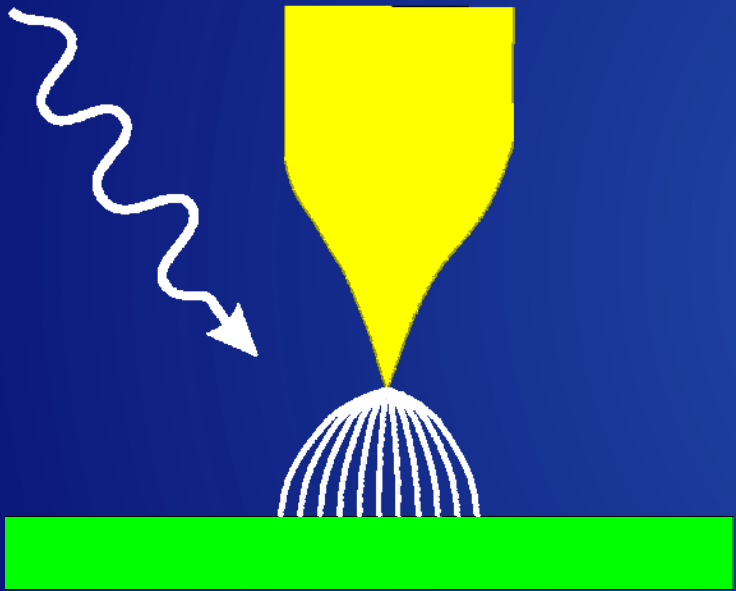
B. Pettinger et al. Phys. Rev. Lett. **92**, 096101 (2004).

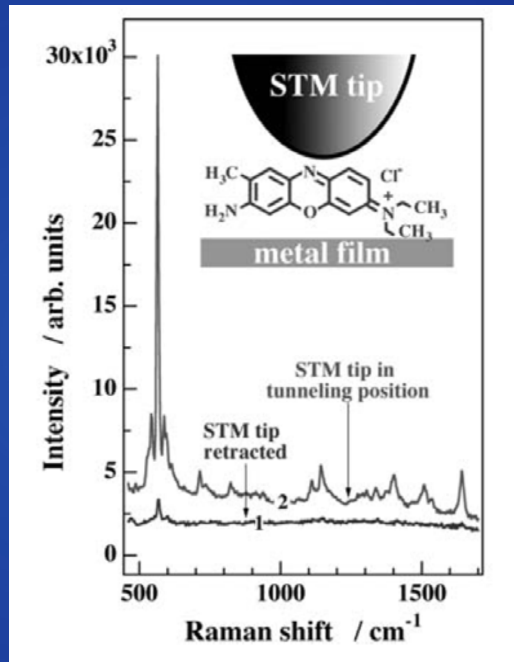
Raman spectroscopy

Surface enhancement, TERS

Idea: using the enhancement due to gap modes and combine an STM with a Raman spectrometer

(Tip Enhanced Raman Spectroscopy)



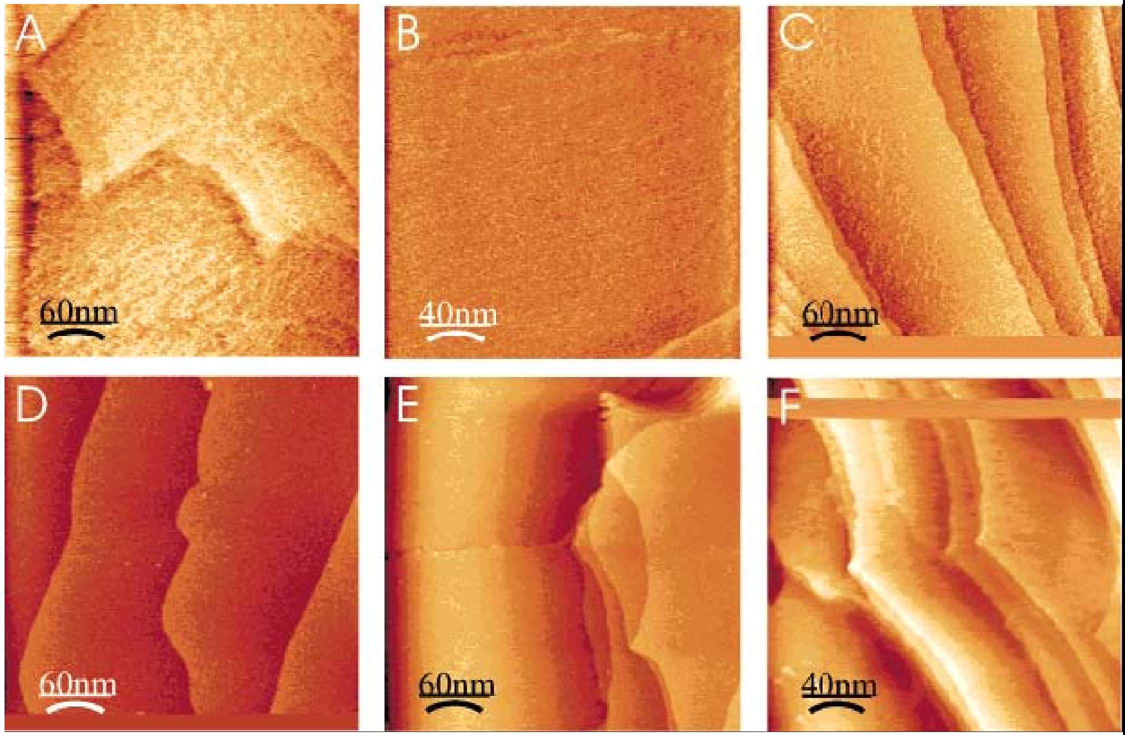


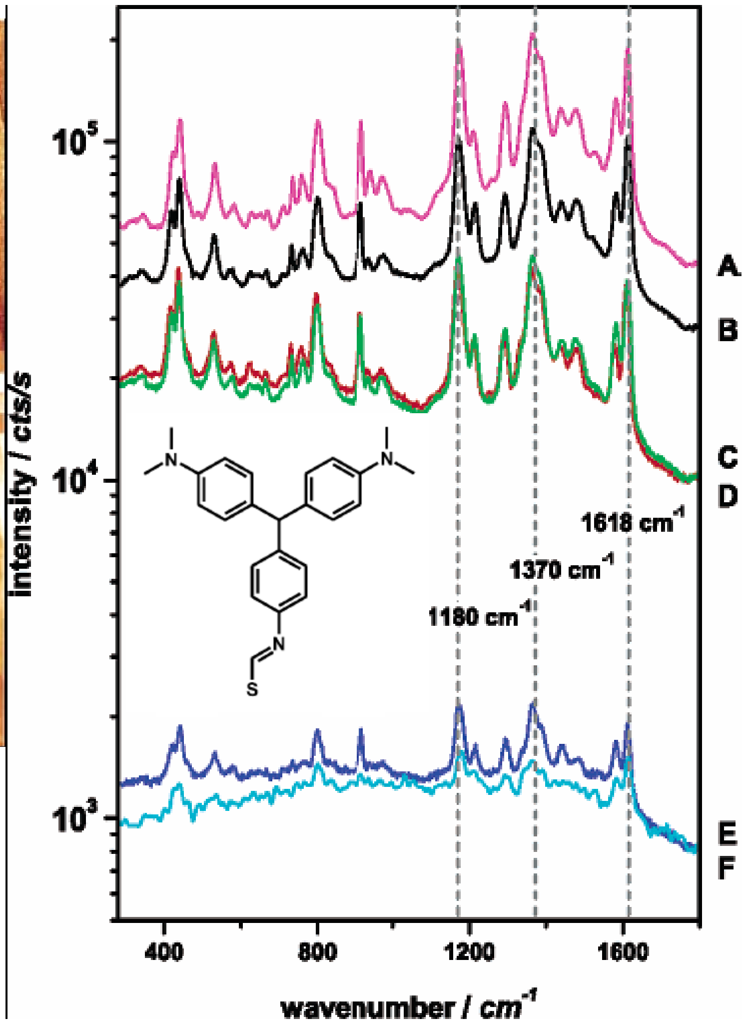
B. Pettinger et al.: Single Molec. **3**, 285 (2002).

Raman spectroscopy

Surface enhancement, TERS

Max-Planck-Gesellschaft



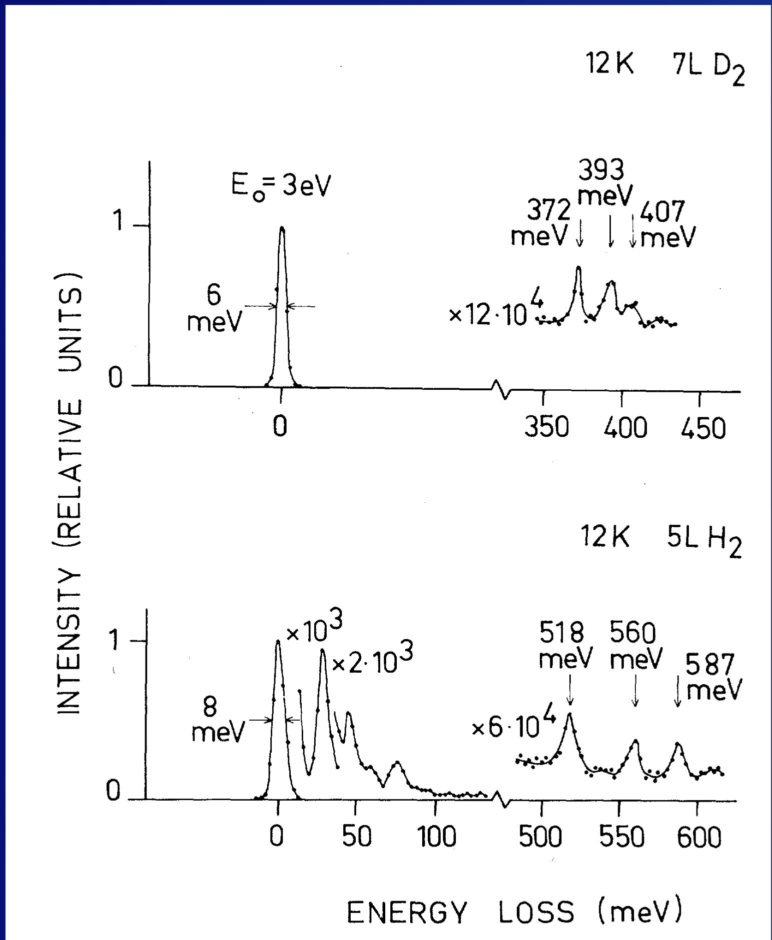


K. F. Domke et al. J. Am. Chem. Soc. **128**, 14721 (2006).

EELS

H_2 on Cu(100)

Max-Planck-Gesellschaft



- D_2-strech at 372 meV
- 21-23 meV is close to gas phase rotation form J(0->2)

- H_2-strech at 518 meV
- 42 meV is close to gas phase rotation form J(0->2)
- 69 meV is close to gas phase rotation form J(1->3)

S. Andersson, J. Harris, Phys. Rev. Lett. 48, 545 (1982).

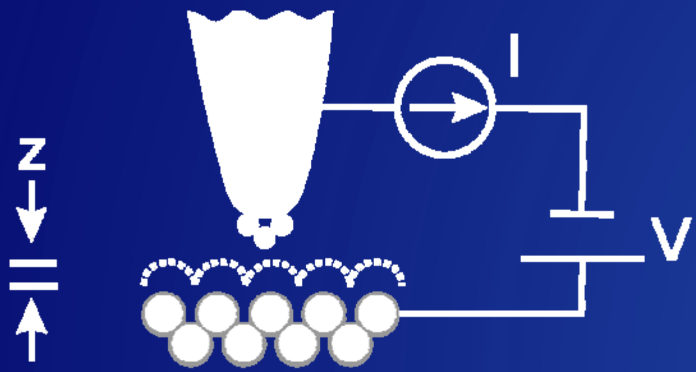
STM/STS

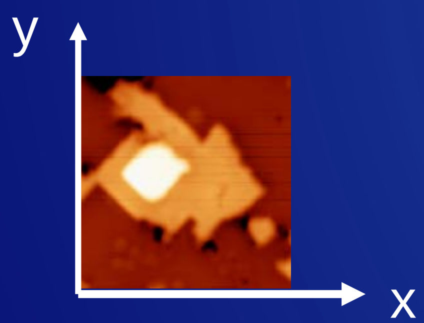
modes of operation

Max-Planck-Gesellschaft

STM

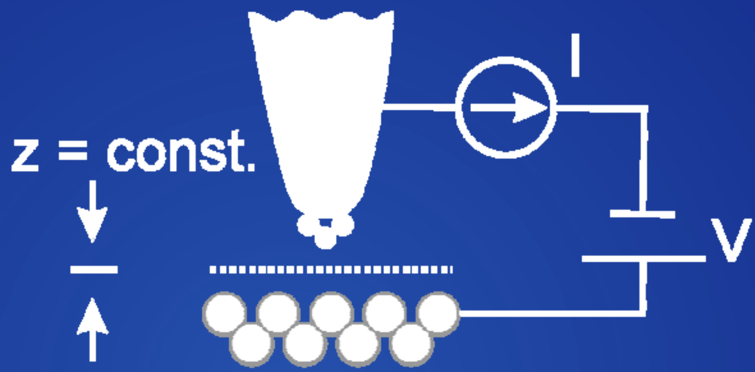
constant current mode



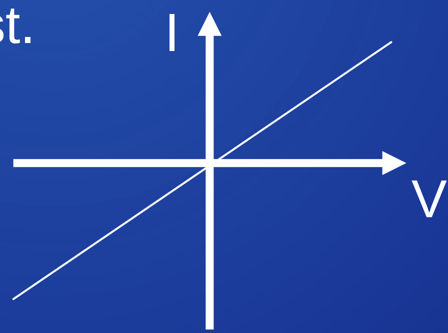


STS

constant height mode



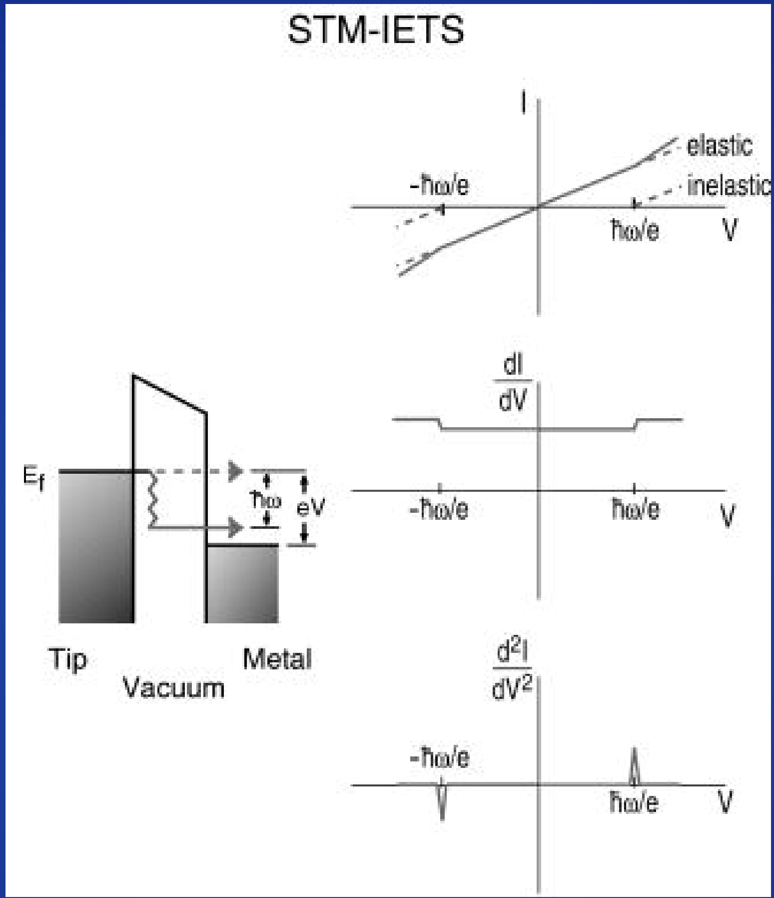
x, y = const.



STS

inelastic tunneling processes

threshold spectroscopy

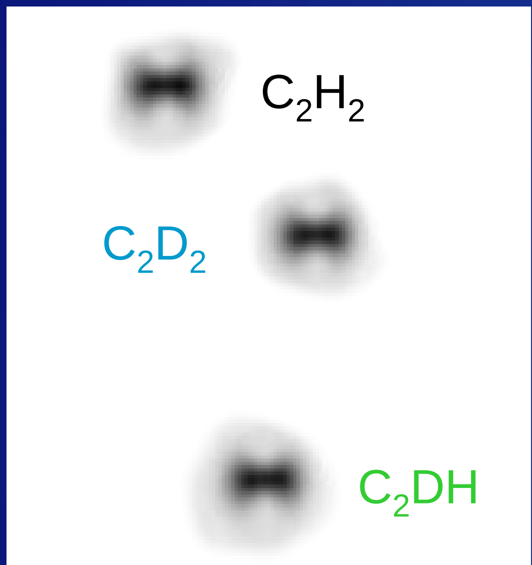


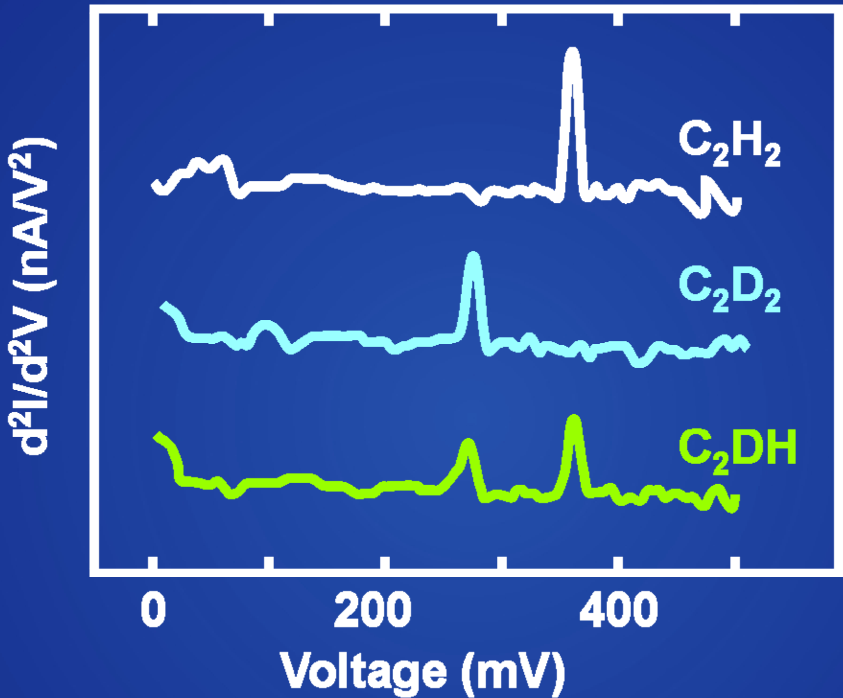
W. Ho J. Chem. Phys. 117, 11033 (2003).

STS

acetylene/Cu(001)

Max-Planck-Gesellschaft



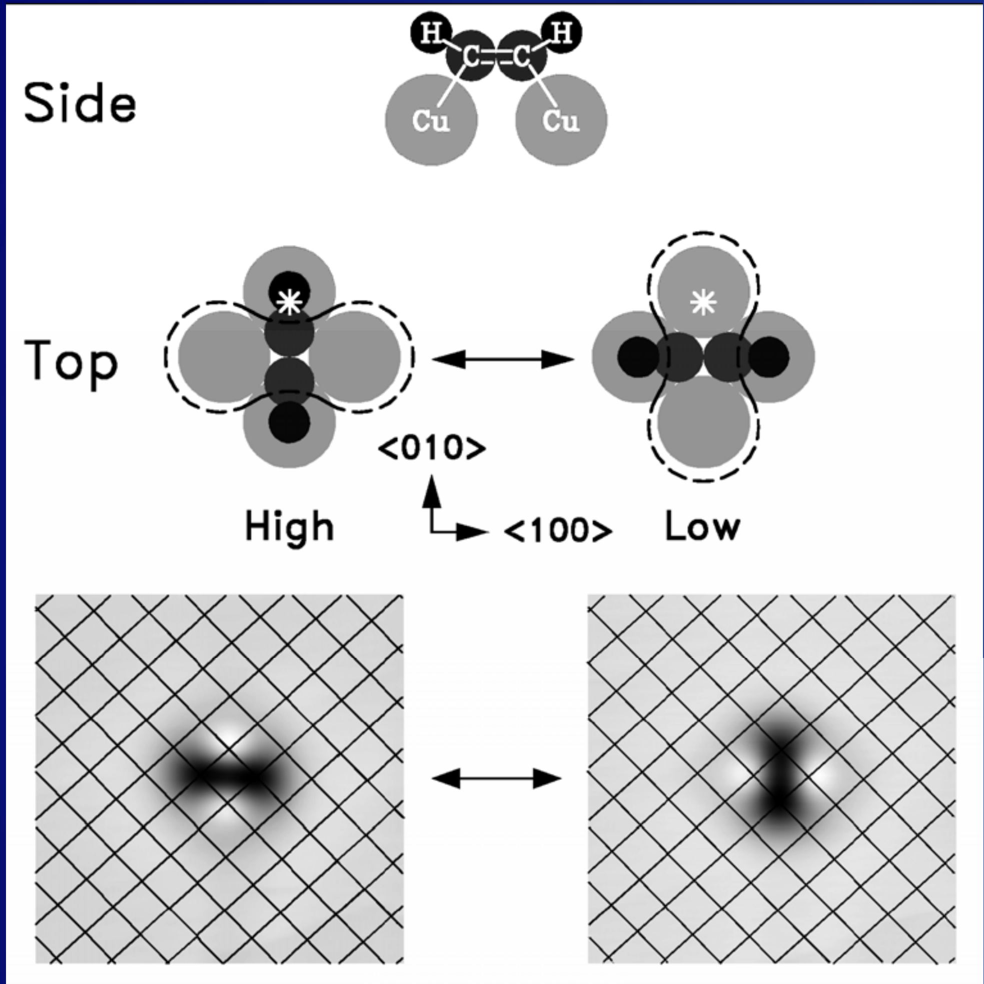


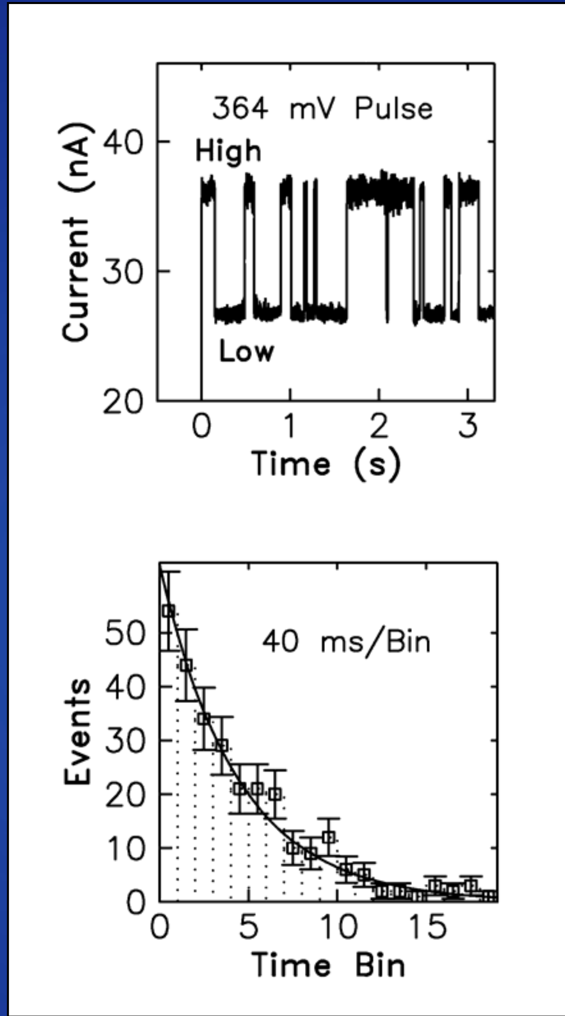
W. Ho J. Chem. Phys. 117, 11033 (2003).

STS

acetylene/Cu(001)

Max-Planck-Gesellschaft

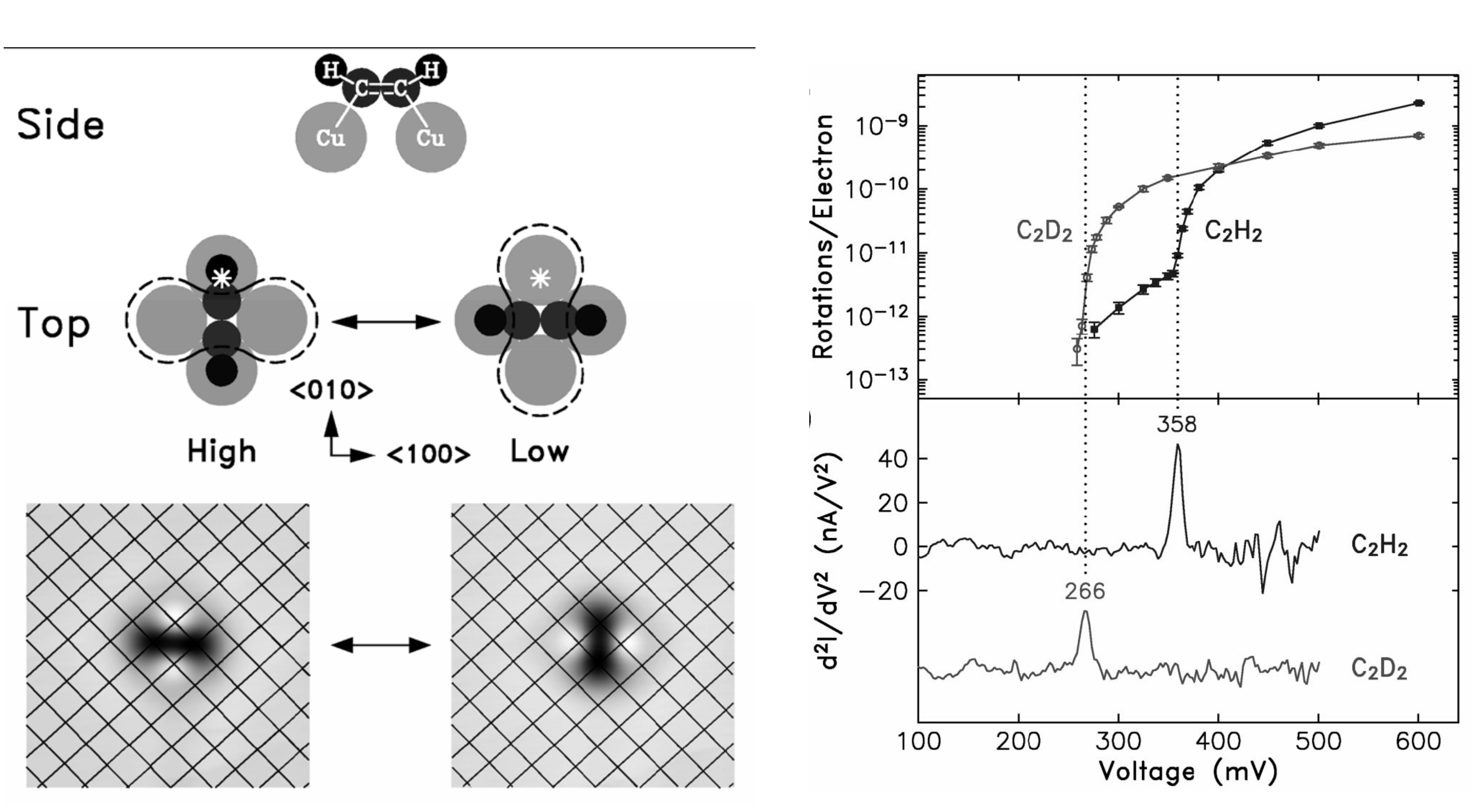




B.C. Stipe et al., Phys. Rev. Lett. 81, 1263 (1998)

STS

acetylene/Cu(001)

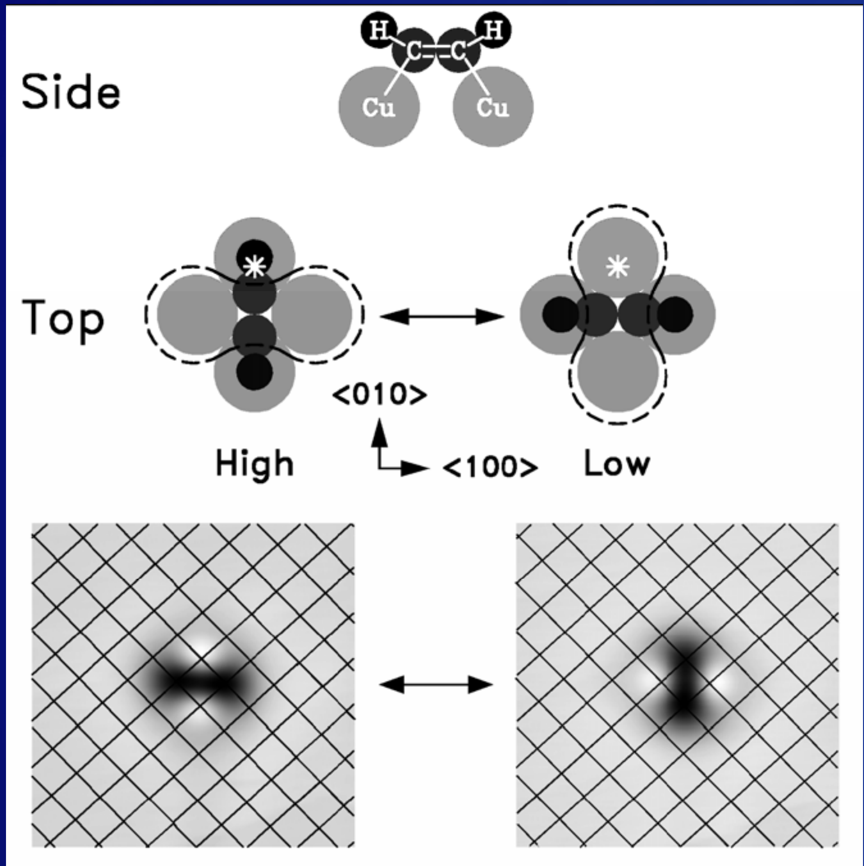


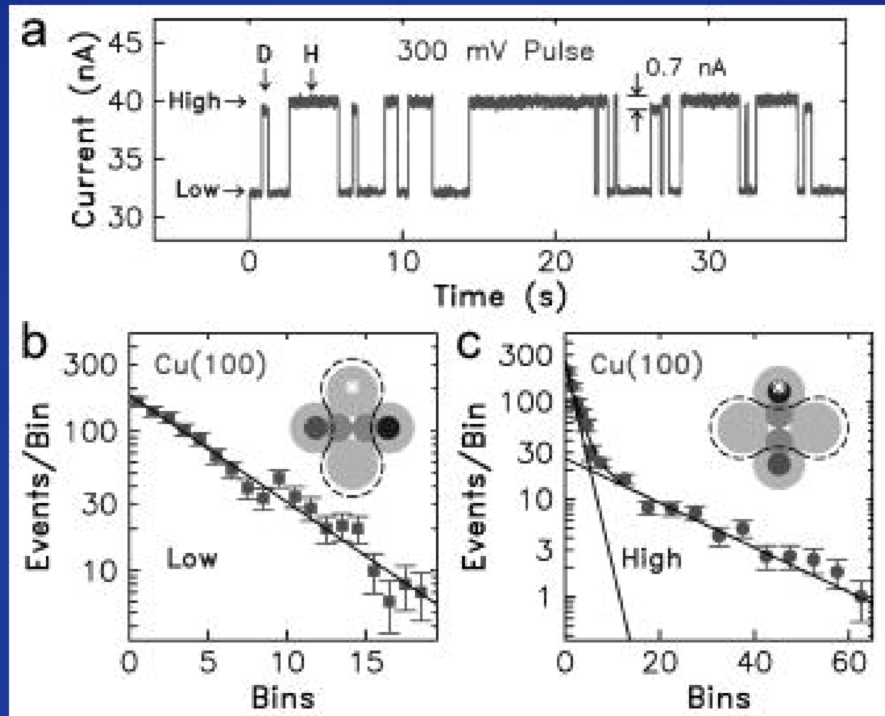
B.C. Stipe et al., Phys. Rev. Lett. 81, 1263 (1998)

STS

acetylene/Cu(001)

Max-Planck-Gesellschaft



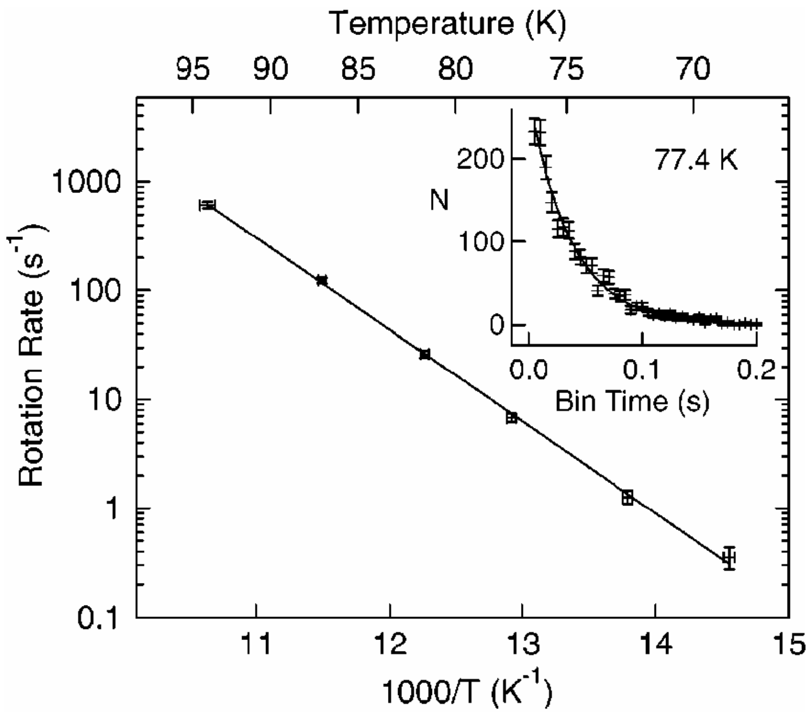


B.C. Stipe et al., Phys. Rev. Lett. 81, 1263 (1998)

STS

acetylene/Cu(001)

temperature induced rotation



E_a = 169 meV; $\nu = 10^{11.8}\ s^{-1}$

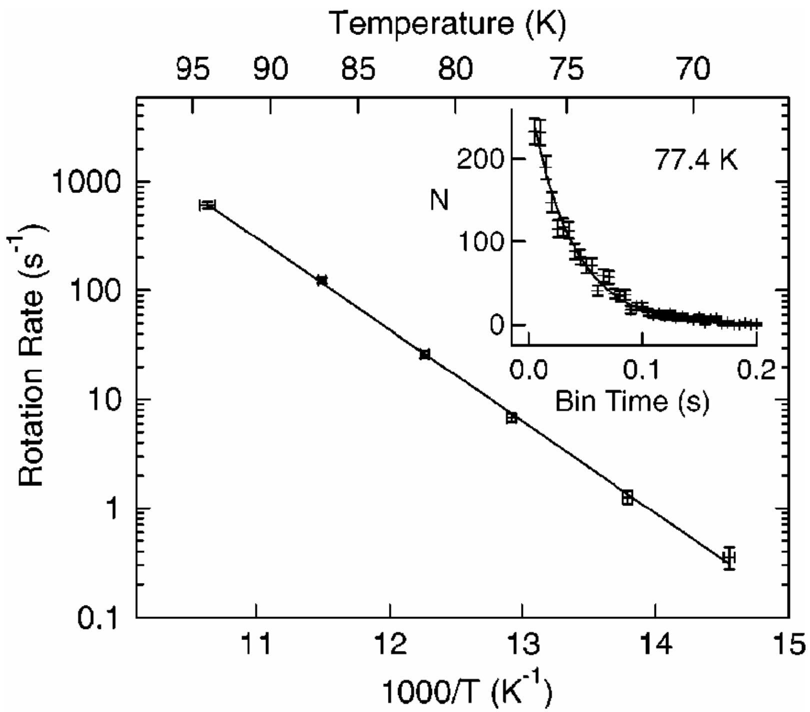
L. J. Lauhon and W. Ho, J. Chem. Phys. 111, 5633 (1999)

STS

acetylene/Cu(001)

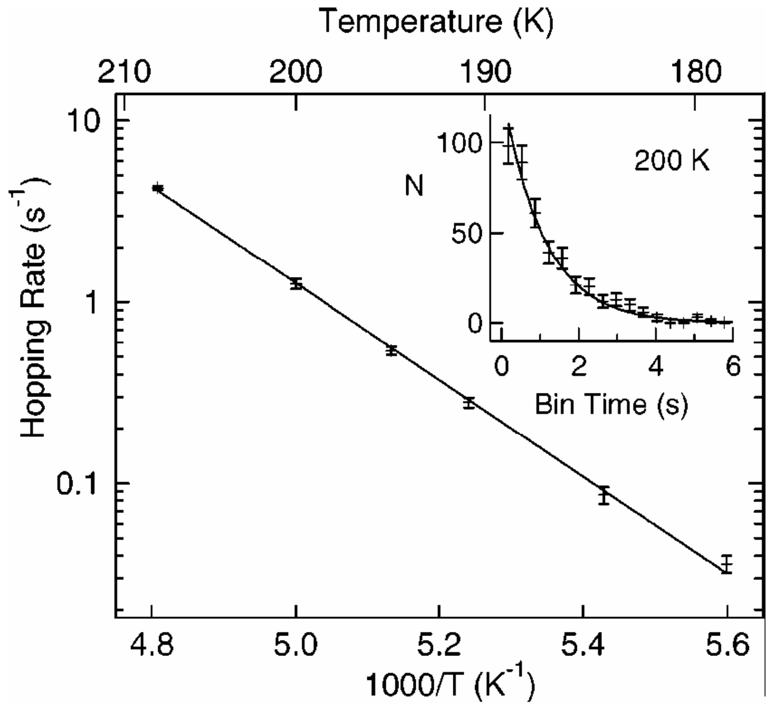
Max-Planck-Gesellschaft

temperature induced rotation



E_a = 169 meV; $\nu = 10^{11.8}$ s^{-1}

temperature induced translation



E_a = 560 meV; $\nu = 10^{13.6}$ s^{-1}

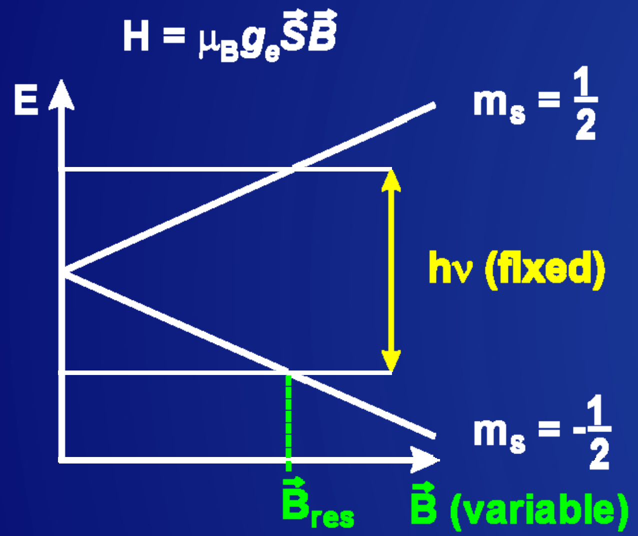
L. J. Lauhon and W. Ho, J. Chem. Phys. 111, 5633 (1999)

EPR spectroscopy

basic aspects

Max-Planck-Gesellschaft

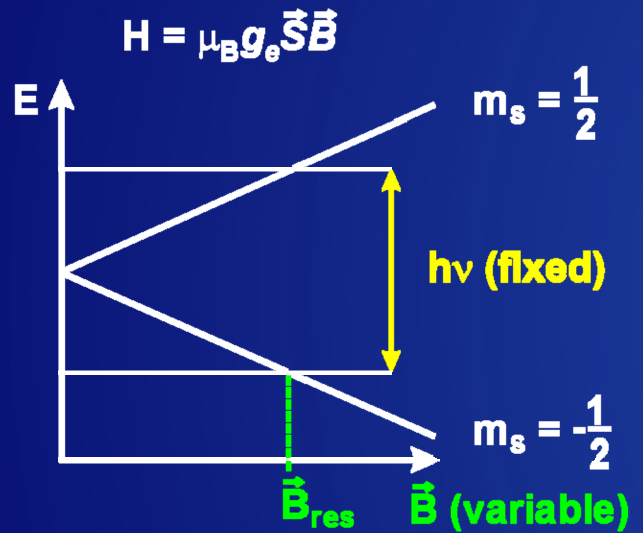
free electron



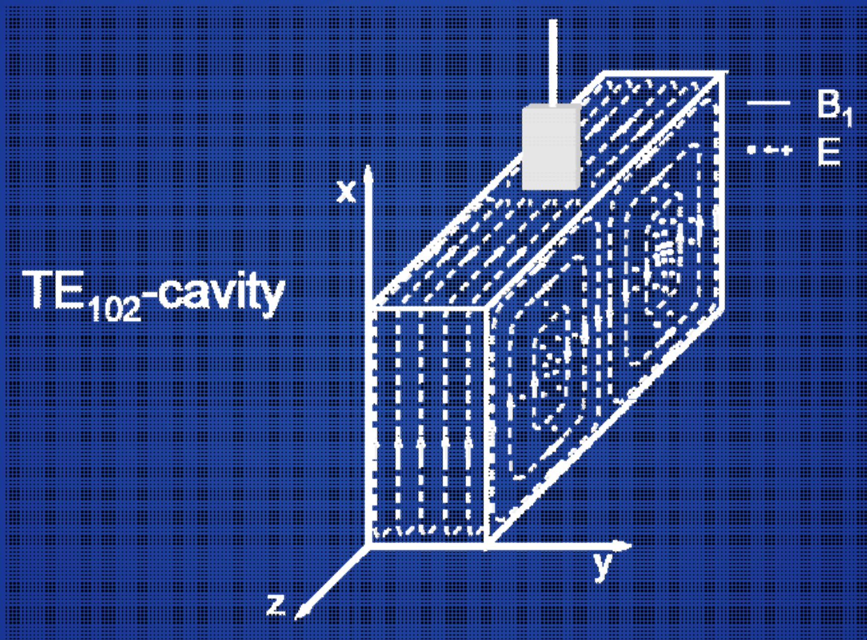
EPR spectroscopy

basic aspects

free electron



field distribution in a microwave resonator

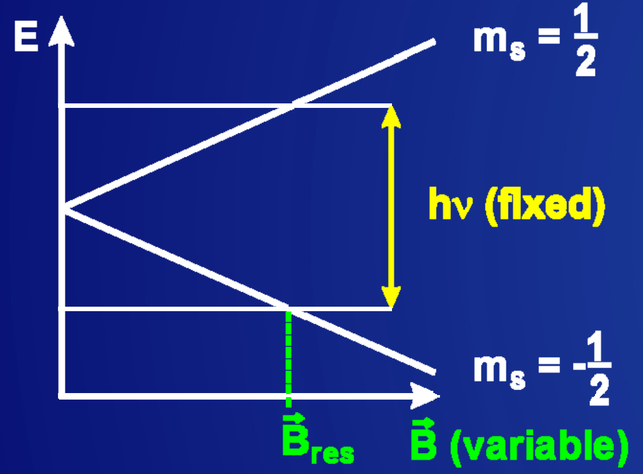


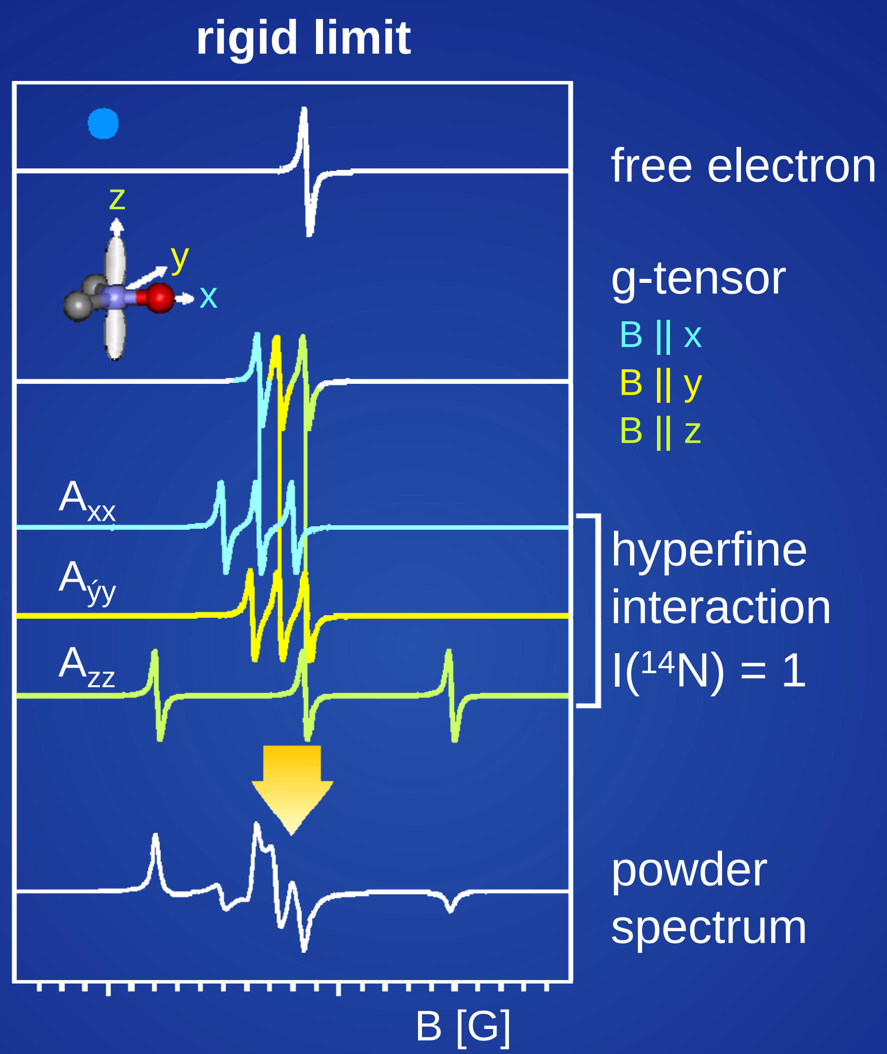
EPR spectroscopy

basic aspects

free electron

$$H = \mu_B g_e \vec{S}\vec{B}$$





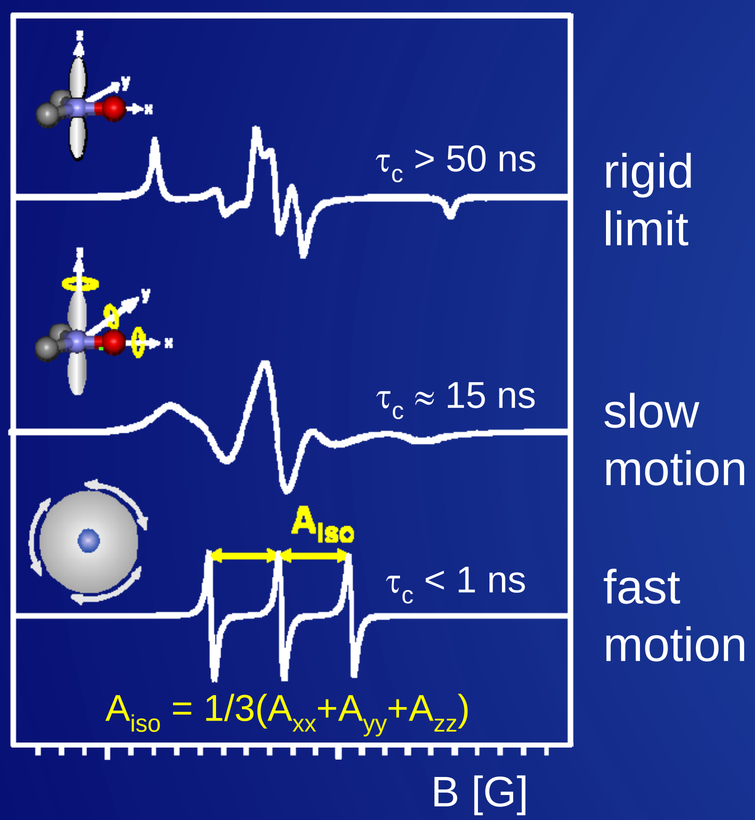
EPR spectroscopy

effect of rotational motion

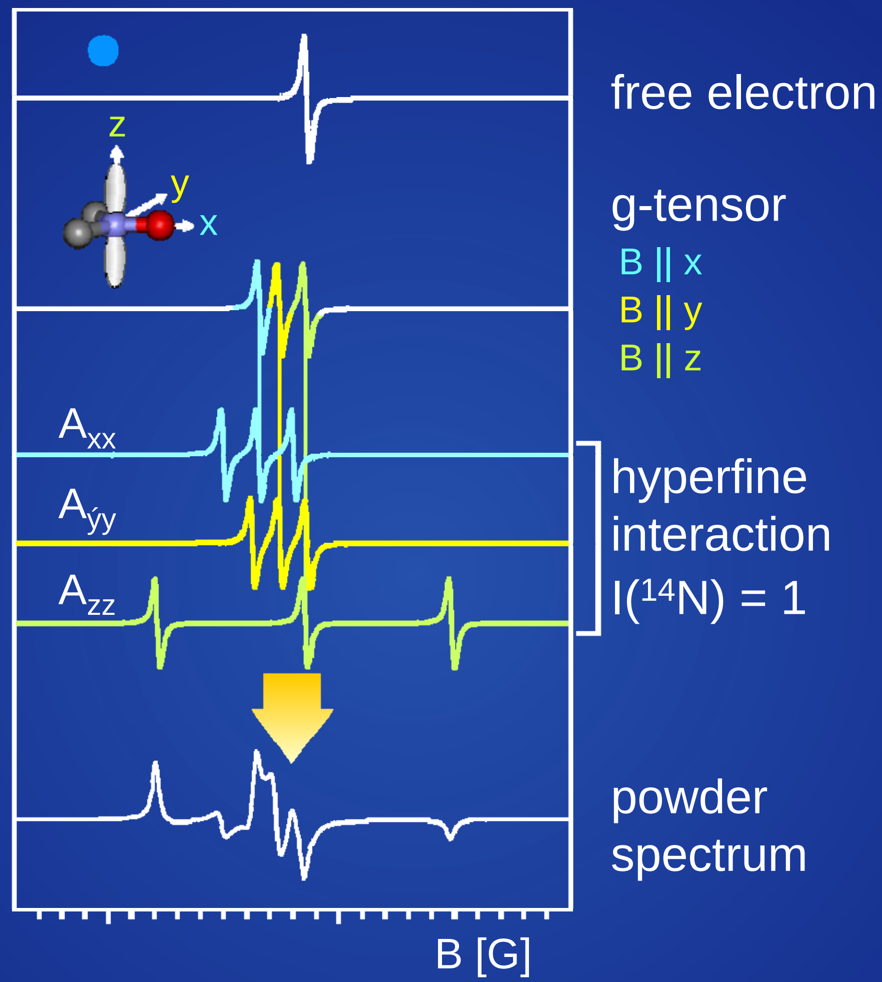
Max-Planck-Gesellschaft

rotational motion

isotropic rotation



rigid limit

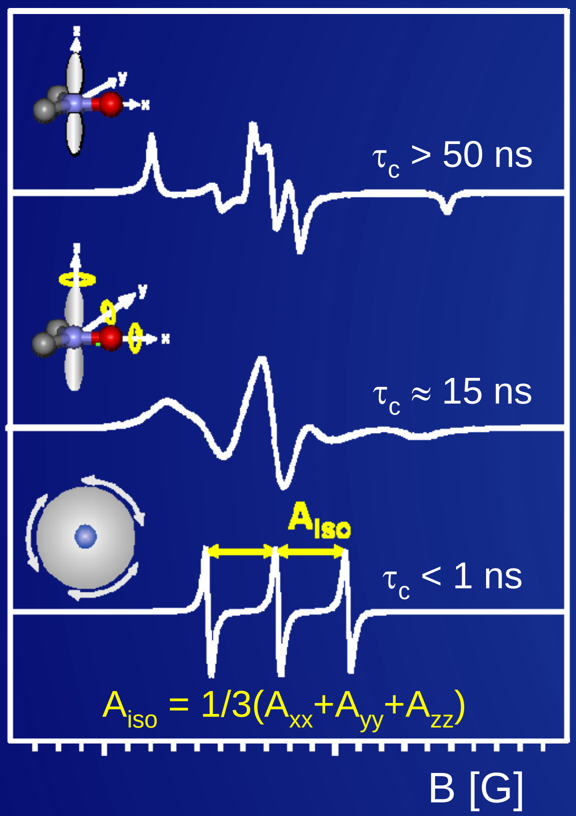


EPR spectroscopy

effects of rotational motion

Max-Planck-Gesellschaft

isotropic rotation

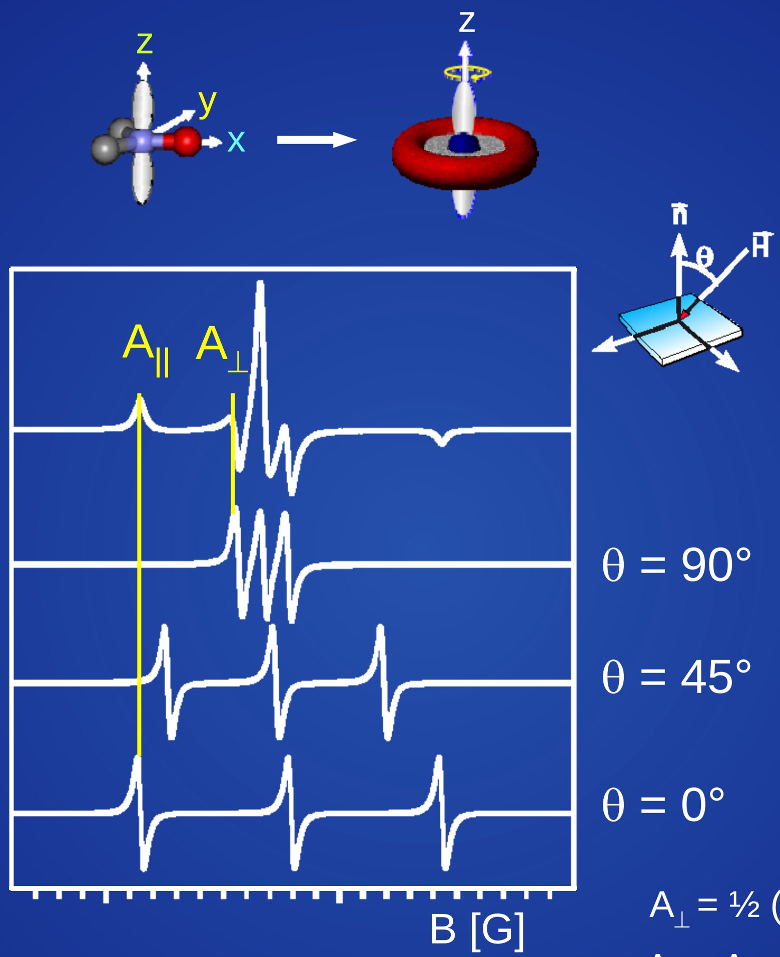


rigid limit

slow motion

fast motion

fast motion around z-axis



$\theta = 90°$

$\theta = 45°$

$\theta = 0°$

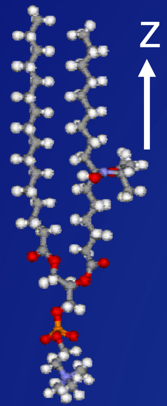
$A_{\perp} = ½ (A_{xx} + A_{yy})$

$A_{||} = A_{zz}$

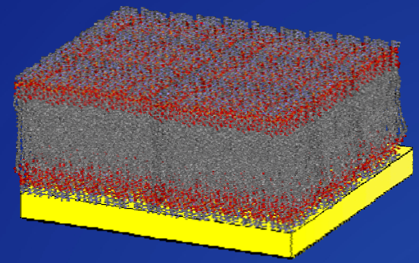
Introduction

Why ESR spectroscopy?

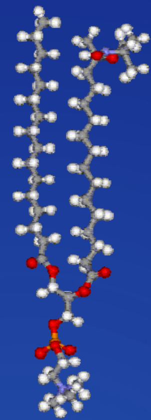
(7-doxyl-PSPC)
spin labeled lipid



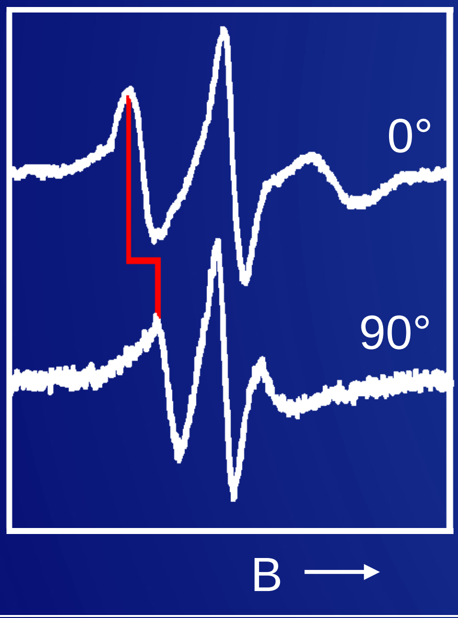
fluid lipid bilayer

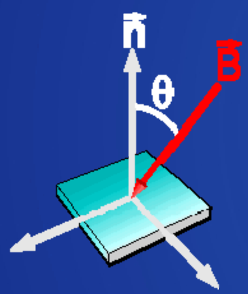


quartz surface

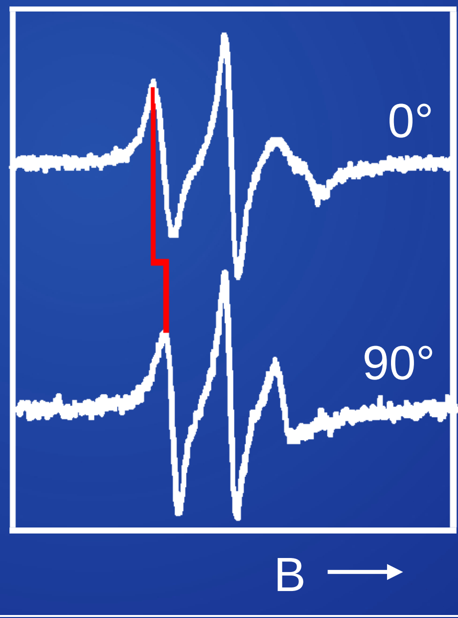


(14-doxyl-PSPC)
spin labeled lipid





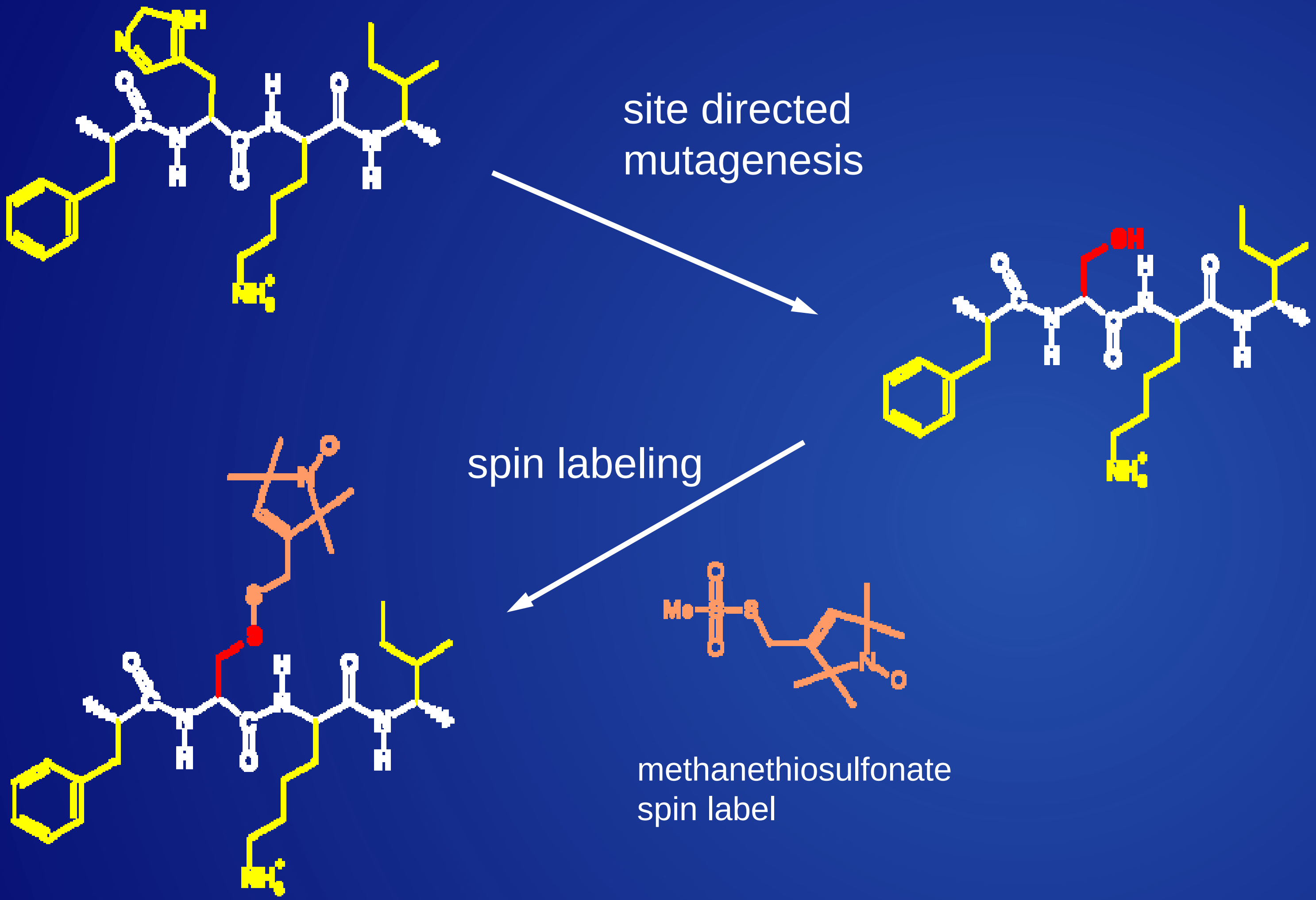
Increase of the rotational dynamics along the alkyl chain



Site Directed Spin Labeling (SDSL)

strategy

Max-Planck-Gesellschaft

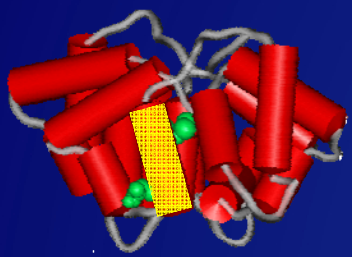


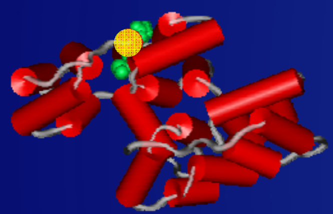
EPR Annexin 12

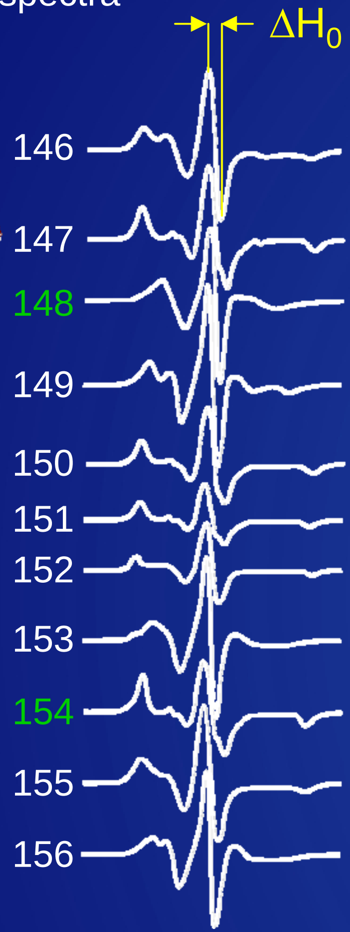
secondary structure from line shape analysis

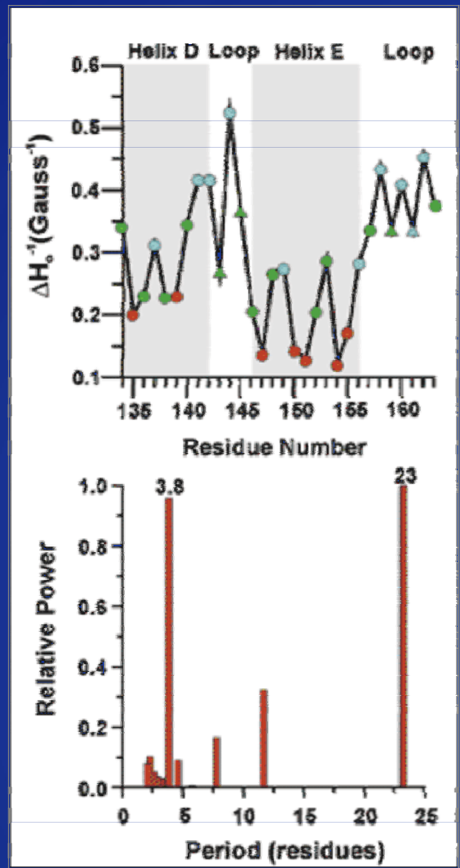
Max-Planck-Gesellschaft

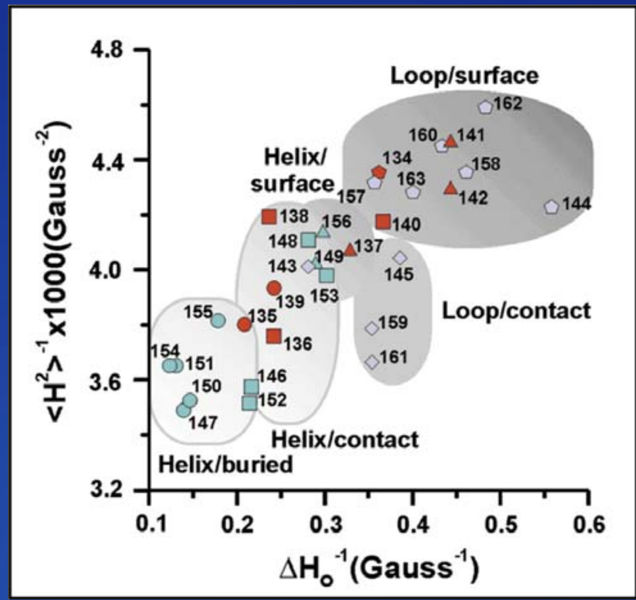
Solution spectra
helix E











EPR data: Isas, J. M et al. Biochemistry **41**, 1464 (2002).

EPR T4 Lysozyme on Surface

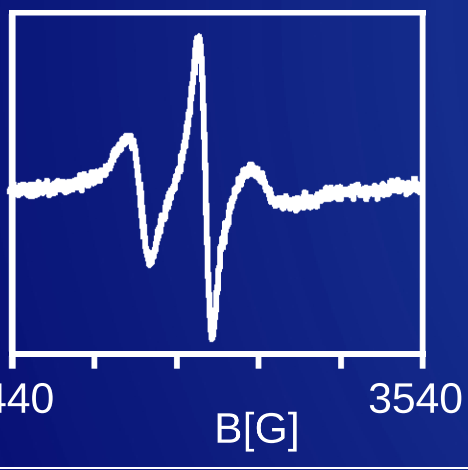
Angular Dependence

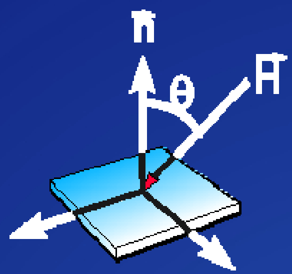
Max-Planck-Gesellschaft

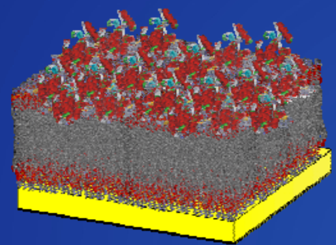
76 Cys

MTSSL

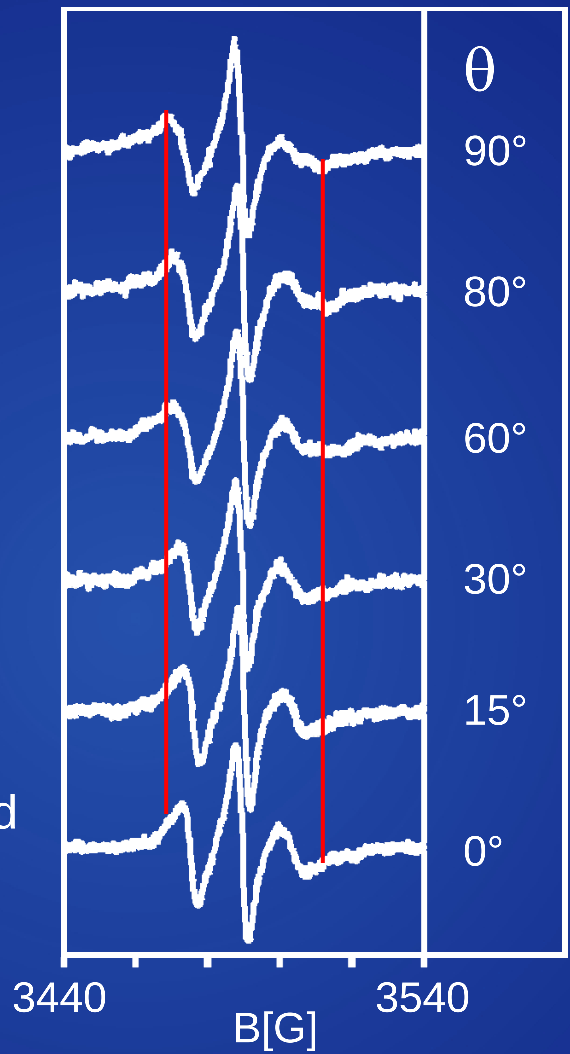
solution







- Angular dependent EPR spectra
- Intensity correspond to 80% of a dense protein layer

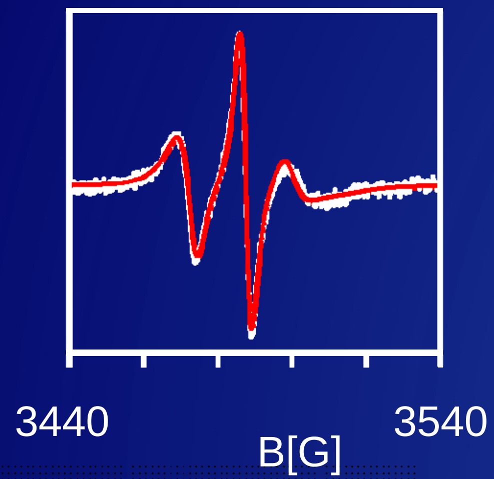


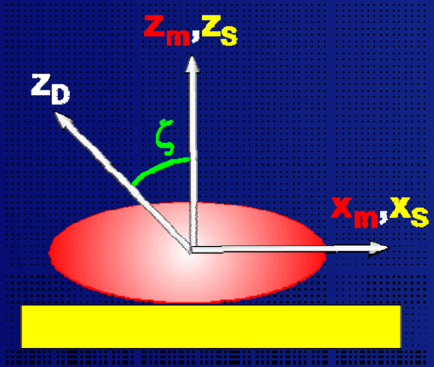
Simulations

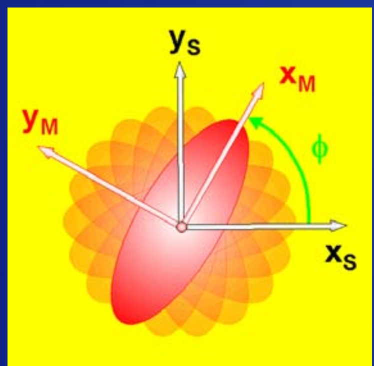
Surface – Results: 76 Cys

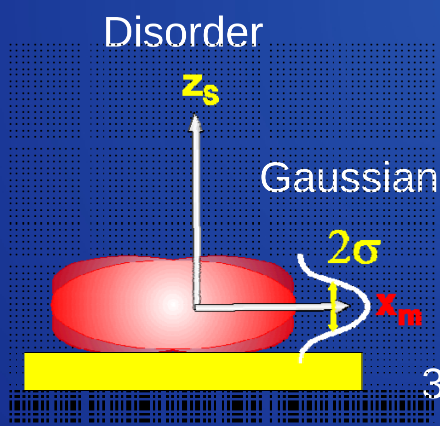
Max-Planck-Gesellschaft

Dynamic model parameters from solution







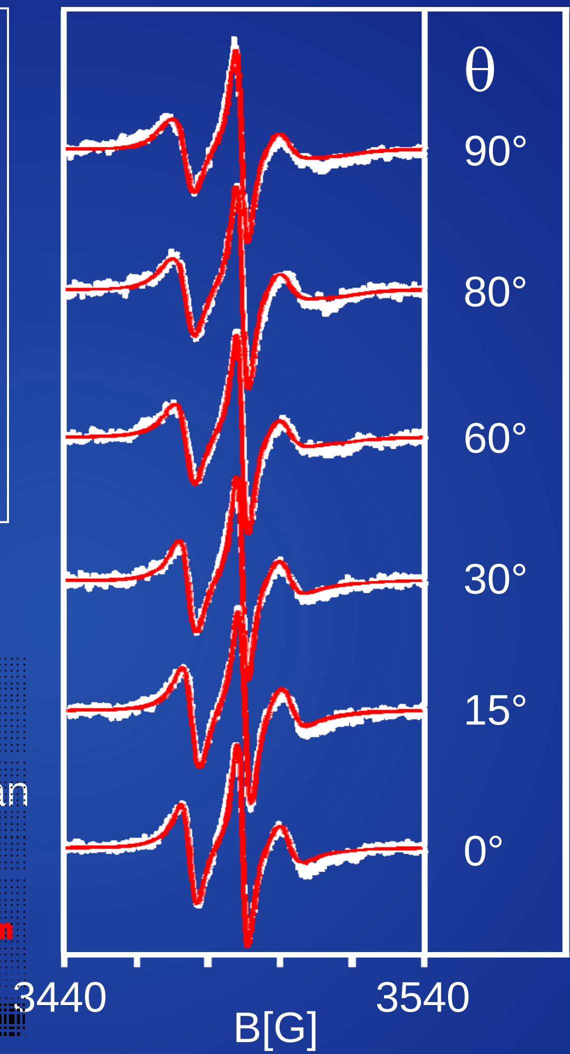


Surface model

- tilt angle of director (ζ)
- azimuthal average (ϕ)
- Gaussian disorder profile (σ)

Result of global fit T4L 76:

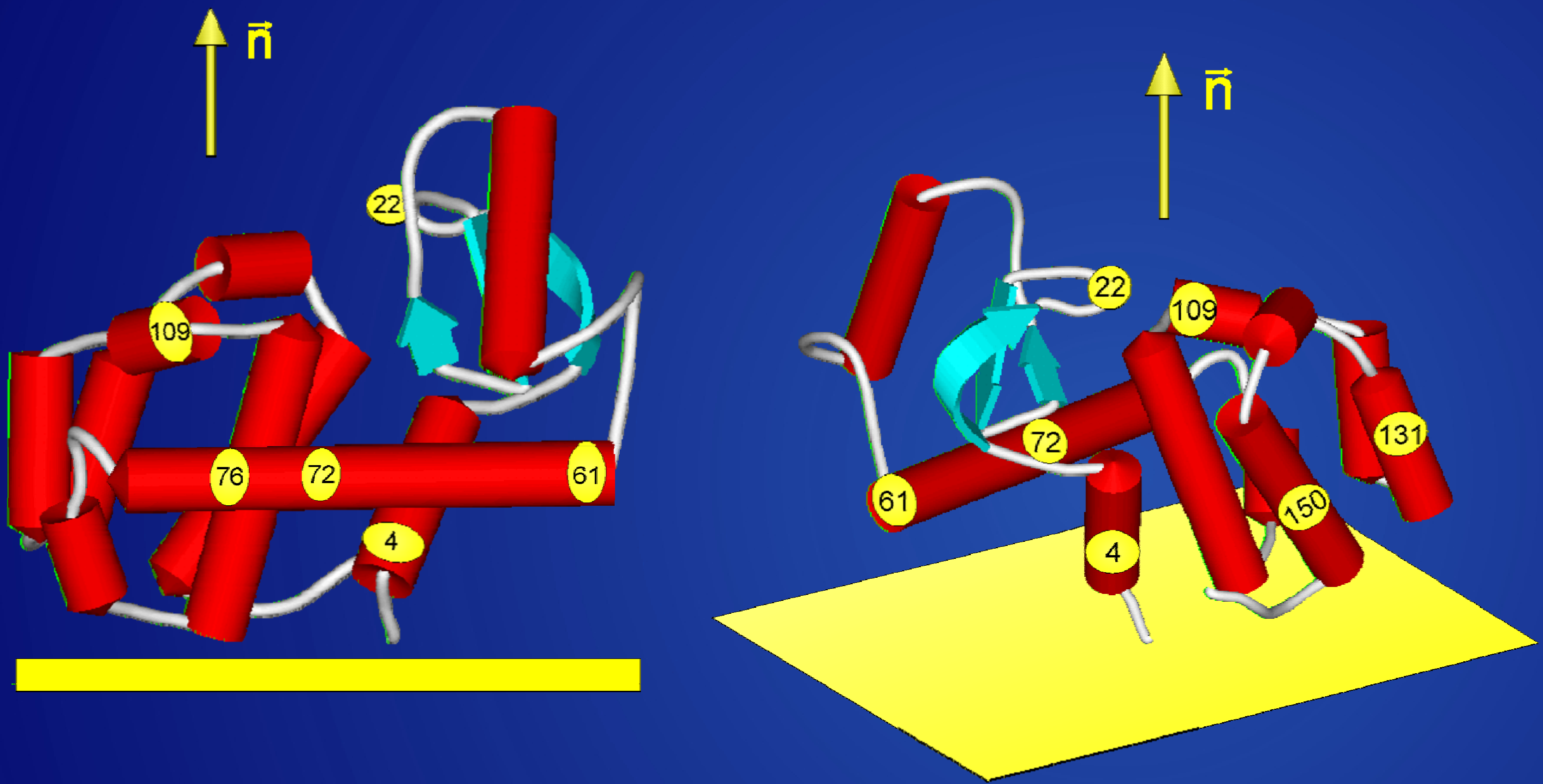
- $\zeta = 90°$, $\sigma = 15°$



T4Lysozyme on Model Surface

orientation of the molecule on the surface

Max-Planck-Gesellschaft



Conclusions

Max-Planck-Gesellschaft

Vibrations

- IRAS

  optimal range from 700 – 3500 cm^{-1}; restricted to dipole allowed excitations (metal surface selection rule)

- HAS

  powerful for low energy vibration such as frustrated translations or rotations energy resolution approx. 0.1 - 0.5 cm^{-1}

- EELS

  complementary to IR; lower frequencies; non dipole transitions possible.

- Raman

  comparatively low sensitivity; wide spectral range (50 – 5000 cm^{-1}); enhanced surface sensitivity by plasmon excitation (combination with STM allows resolution down to a few nm)

- SFG

  intrinsic surface sensitive; background free detection; suitable for time resolution down to the fs-regime.

Conclusions

Max-Planck-Gesellschaft

Rotations:

• EELS

does only work for very light molecules with large rotational quanta (H_2, D_2)

• STM,STS

single molecule resolution; rotation (coupling to vibrations. Becomes complex for more complicated molecules.

• EPR

can provide information on the rotational dynamics in the ns-regime; can be used e.g. to characterize large molecules.