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LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Studies of High Pressure CO Adsorption on Supported Pd Nanoparticles by Sum-Frequency Generation Spectroscopy

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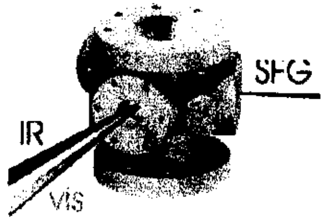
Outline:

1. Motivation
2. SFG vibrational spectroscopy
3. UHV grown Pd/Al_2O_3 model catalysts
4. SFG experiments: CO adsorption up to 200 mbar
5. Summary and conclusions

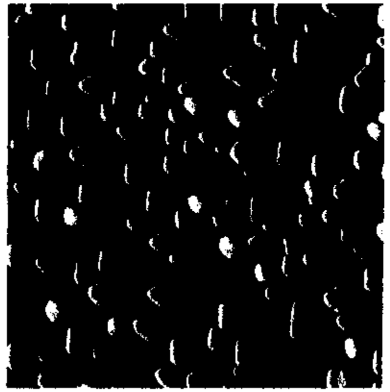


High pressure studies on model catalyst surfaces

Deposition of noble metal nanoparticles onto thin oxide films in UHV allows to prepare well-defined model catalysts

- well-defined structure and composition
- compatible to surface sensitive techniques (STM, LEED, AES, XPS, TDS, RAIRS, EELS, ...)
- including size, support and diffusion effects
- generally studied under UHV conditions (~ 10^{-6} mbar)

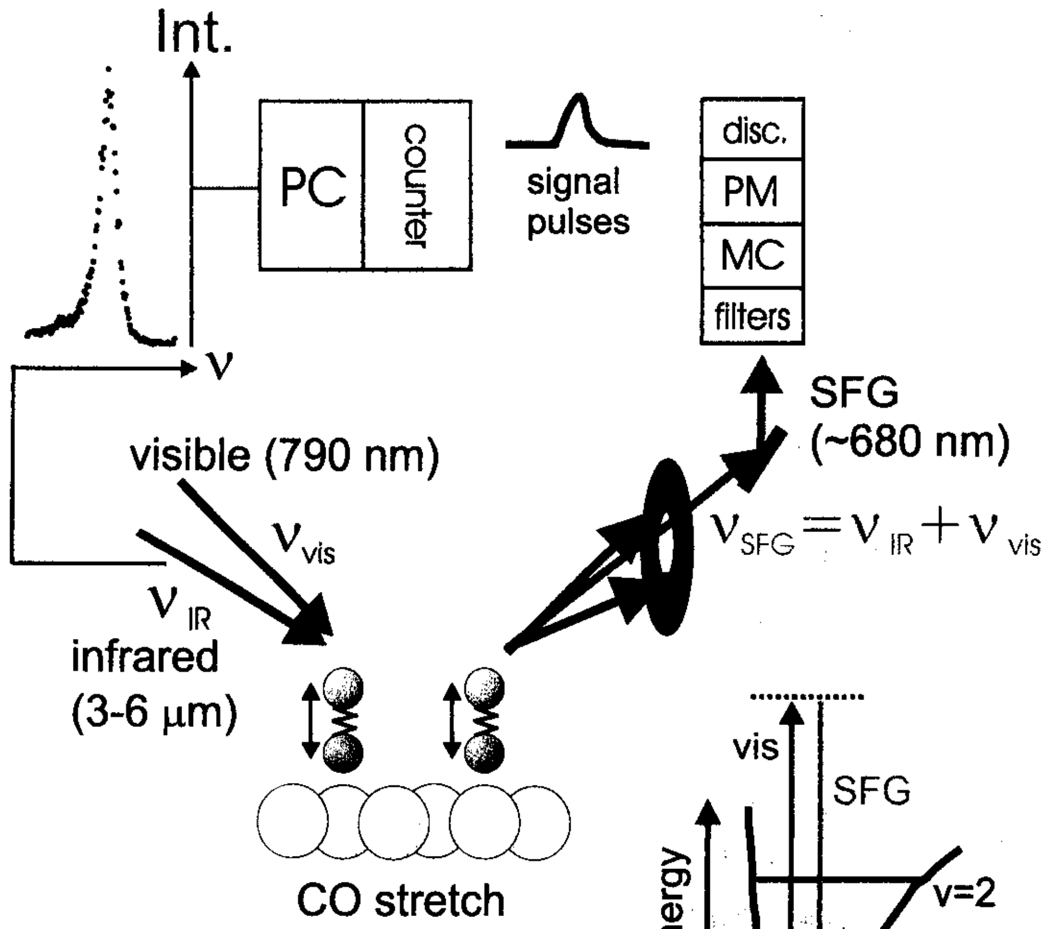
Freund, Bäumer, Kuhlenbeck, Adv. Catal. 45 (2000) 333

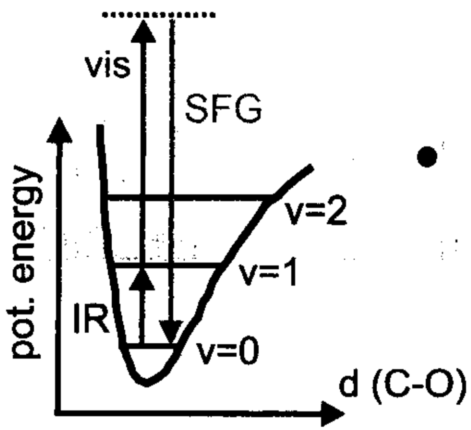


STM: Pd on Al_2O_3

Studies at "high pressure" (~ 1 bar) are needed to reveal the characteristics of model catalysts under reaction conditions

- structure: high pressure STM *(single crystals: Somorjai, Besenbacher)*
- vibrational spectroscopy of adsorbates:
  Reflection Absorption InfraRed Spectroscopy (PM-mode)
  Sum-Frequency Generation





Ti:Sa: 790 nm, 200 μJ, 2ps, 500 Hz
OPG/OPA: 3-6 μm, 15 μJ @ 5 μm

- allows to acquire vibrational spectra of adsorbates from UHV to high pressure
- inherently surface sensitive due to 2nd order optical nonlinearity (SFG not allowed in media with inversion symmetry)

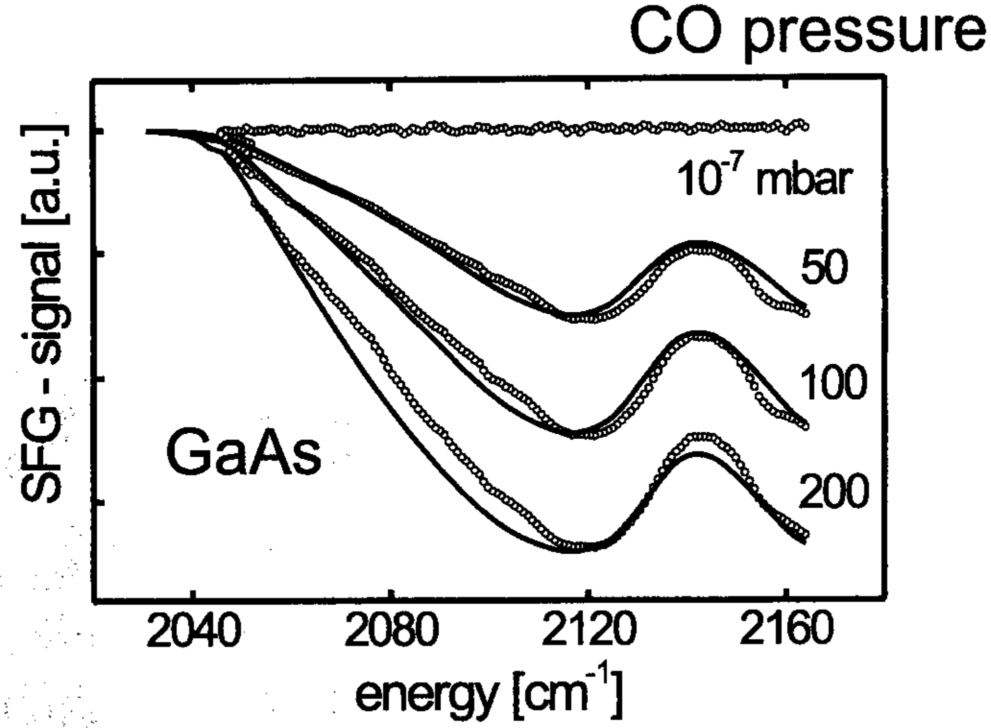
$$I(SFG) \sim \left|\chi_s^{(2)}\right|^2 \sim \frac{\partial \mu_n}{\partial q} \frac{\partial \alpha_{lm}^{(1)}}{\partial q}$$

- no signal from isotropic gas phase and centrosymmetric substrate

Y.R. Shen
Surf. Sci. 299/300 (1994) 551

GaAs reference spectra

$$I(SFG) \sim \left|\chi_s^{(2)}\right|^2 I_{IR}\, I_{vis}$$



SFG process is insensitive to the gas phase but CO gas phase absorption lowers IR intensity on the surface

Pd - Al_2O_3 - NiAl(110)

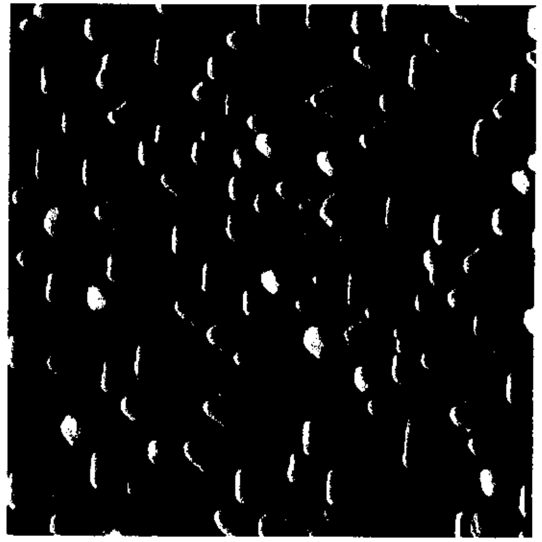
Three steps:

1. Conducting Substrate: NiAl(110) single crystal

2. Support: Thin, well-ordered Al_2O_3 film
Oxidation of NiAl(110)

3. Particle growth: Pd deposition at 90 K or 300 K

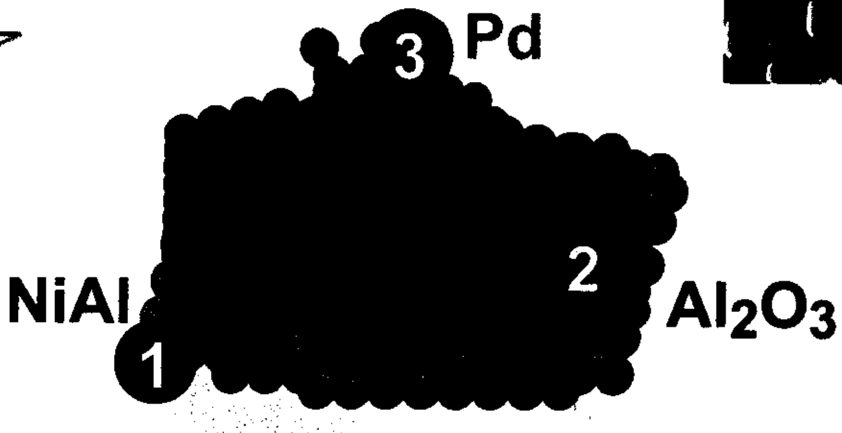
STM



100 x 100 nm
M. Heemeier, FHI

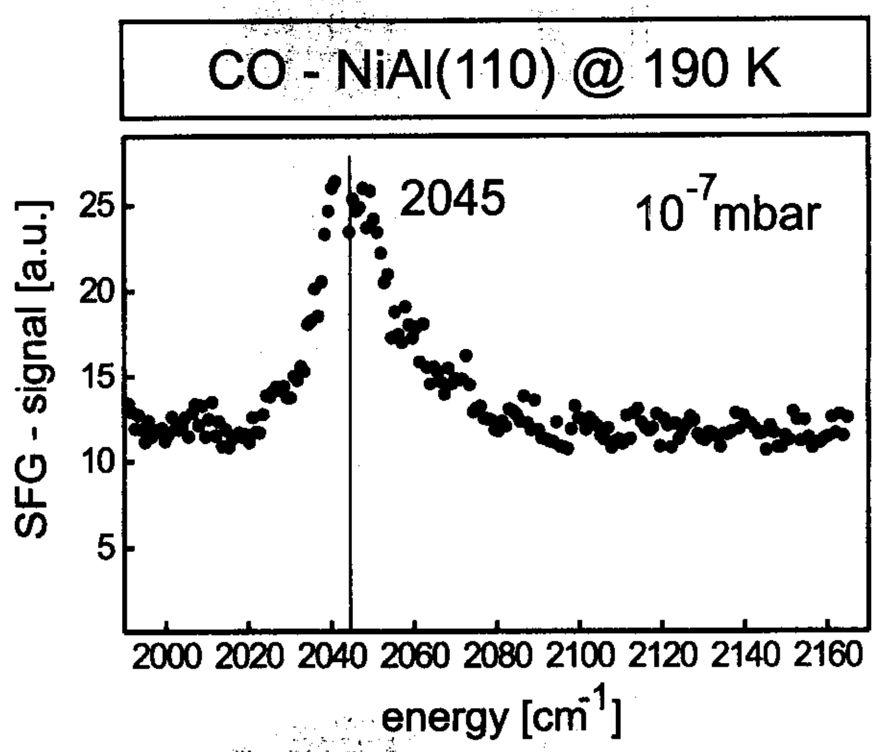
growth temperature →
island density
morphology / structure

metal amount →
particle size



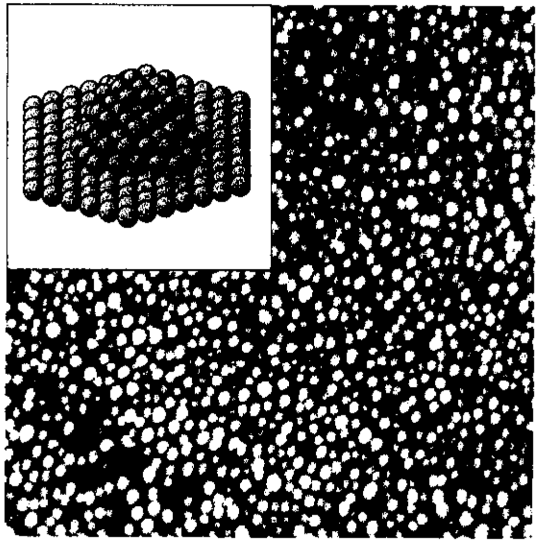
Bäumer/Freund
Progr. Surf. Sci.
61 (1999) 127

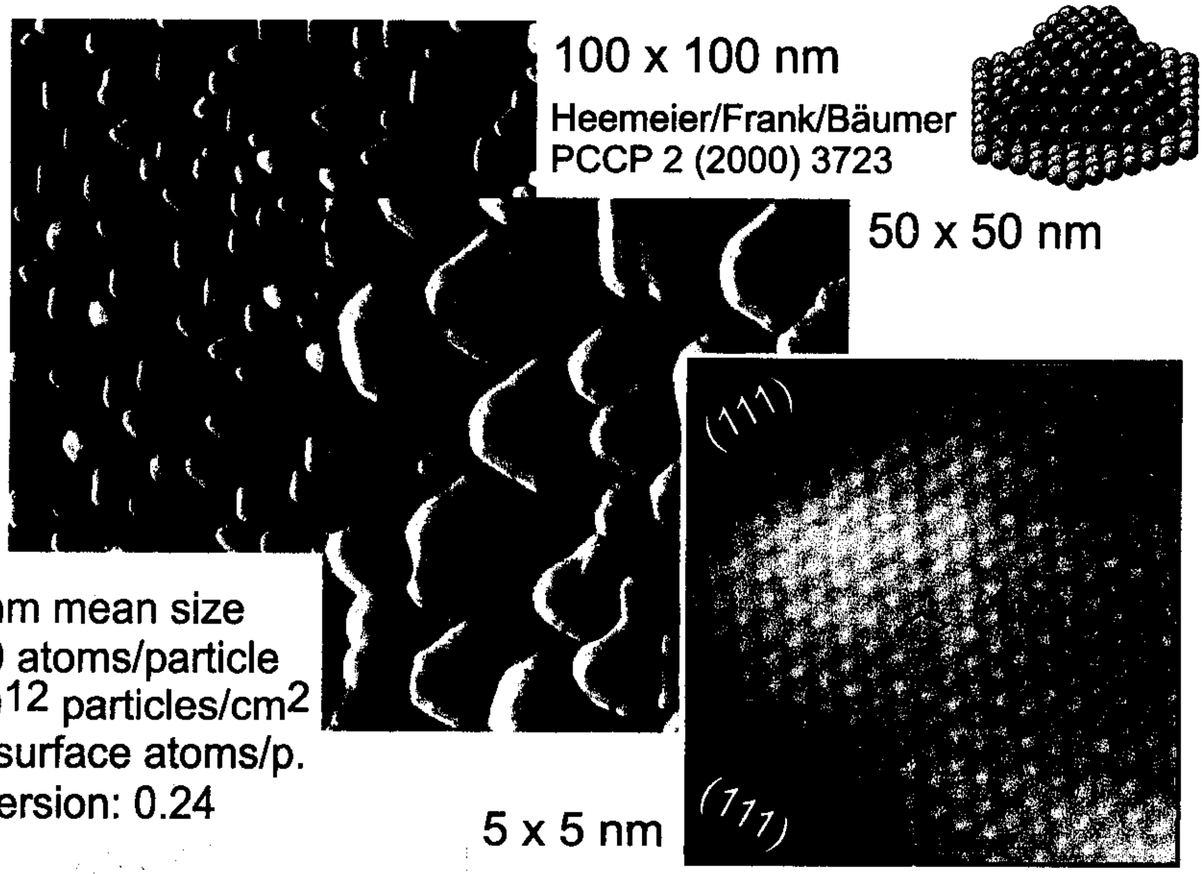
SFG spectroscopy



The absence of the 2045 cm^{-1} peak after oxidation proves that the aluminum oxide film is complete.

grown at 90 K grown at 300 K





100 x 100 nm

Heemeier/Frank/Bäumer
PCCP 2 (2000) 3723

50 x 50 nm

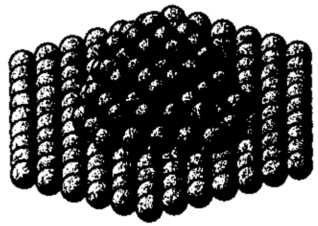
5 x 5 nm

90 K	300 K
3.3 nm mean size	5.6 nm mean size
650 atoms/particle	2700 atoms/particle
$4x10^{12}$ particles/cm^2	$1x10^{12}$ particles/cm^2
250 surface atoms/p.	640 surface atoms/p.
Dispersion: 0.37	Dispersion: 0.24

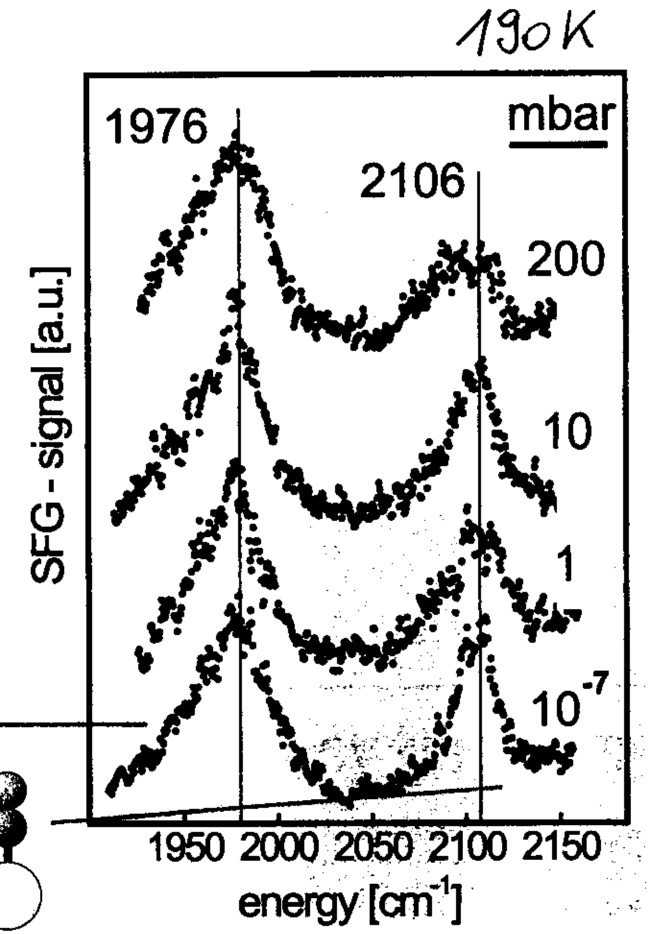
surface area of half spherical particles:
$1x10^{15}$ $6x10^{14}$ surface Pd atoms/cm^2

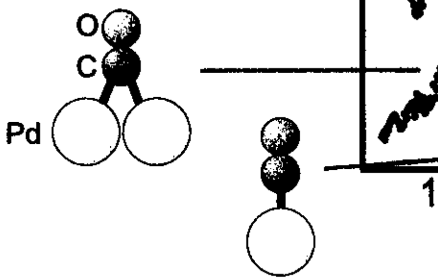
Højrup Hansen/Freund/Besenbacher
et al. PRL 83 (1999) 4120

vibrational spectra of CO on Pd-Al_2O_3-NiAl(110) @

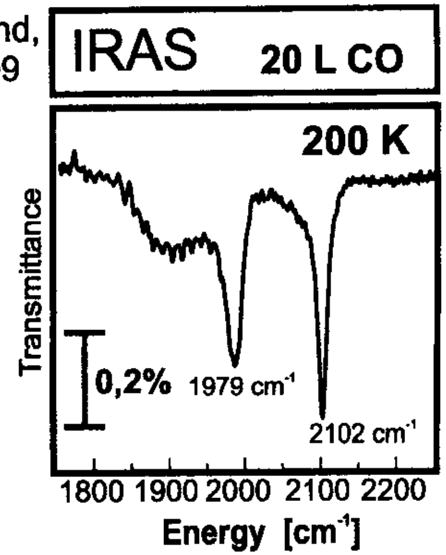


3 nm Pd particles grown at 90 K: ***defective***





Wolter/Freund, Surf. Sci. 399 (1998) 190)



difference to CO on Pd single crystals:
(Tüshaus/Bradshaw, Appl. Phys. A. 51 (1990) 91; Goodman et al. Surf. Sci. Lett. 274 (1992) L611; J. Vac. Sci. Technol. A 14 (1996) 1184; etc.)

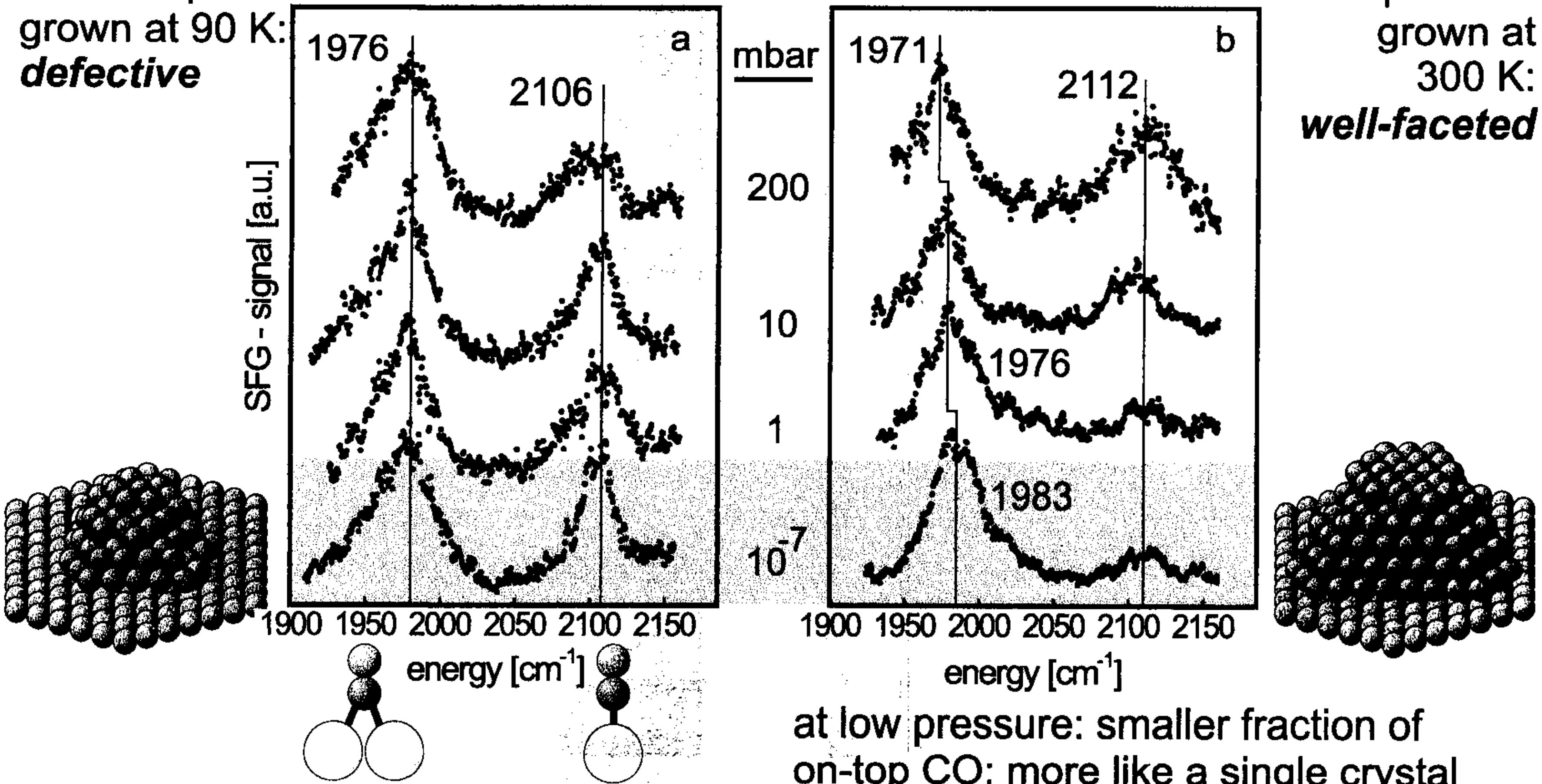
coexistence of bridge bonded and on-top CO attributed to the particle structure (defects) or a reduced lateral CO interaction on nanoparticles

vibrational spectra of CO on Pd-Al_2O_3-NiAl(110) @

190 K

3 nm Pd particles grown at 90 K: ***defective***

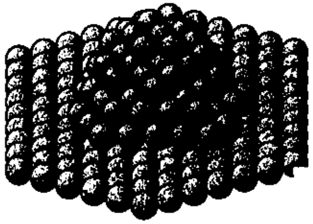
6 nm Pd particles grown at 300 K: ***well-faceted***

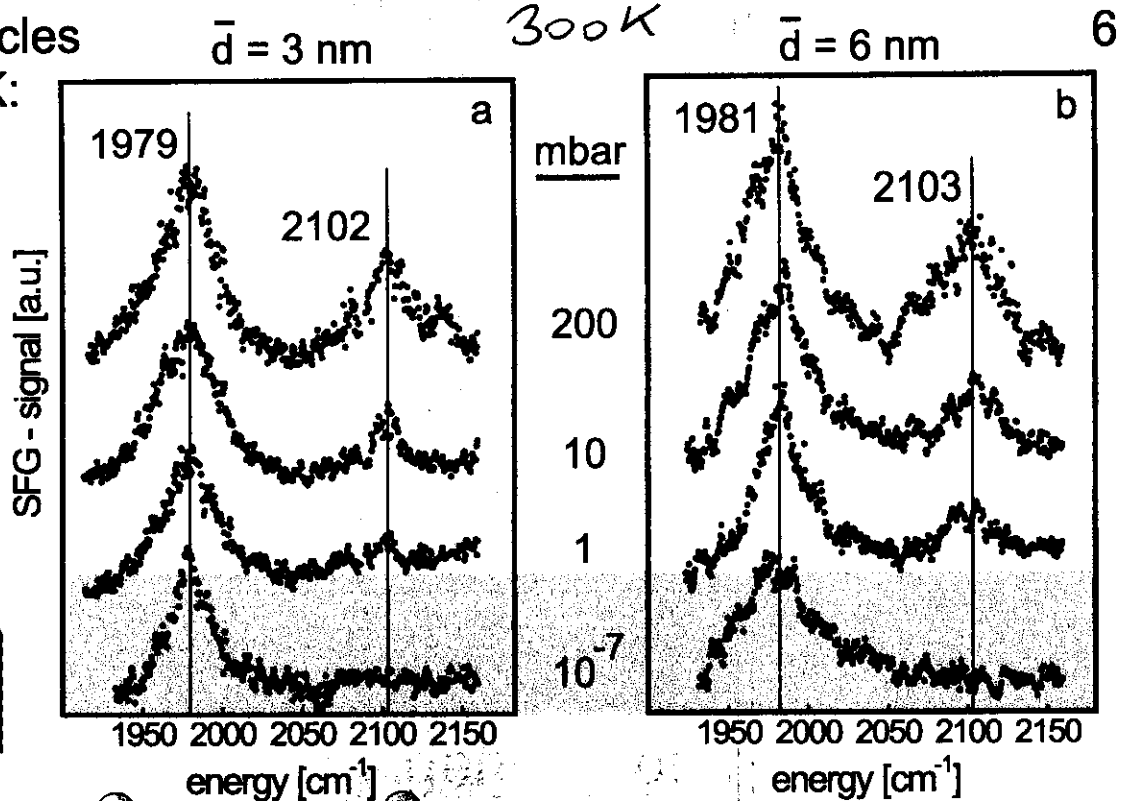


at low pressure: smaller fraction of on-top CO; more like a single crystal

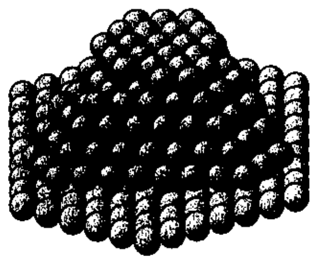
vibrational spectra of CO on Pd-Al_2O_3-NiAl(110) @ 300K

3 nm Pd particles grown at 90 K: ***defective***



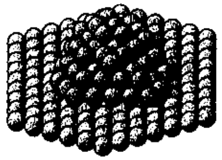


6 nm Pd particles grown at 300 K: ***well-faceted***

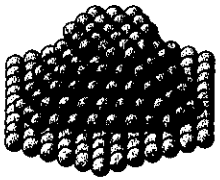


at low pressure: only bridged CO;
on-top CO repopulated ≥ 1 mbar

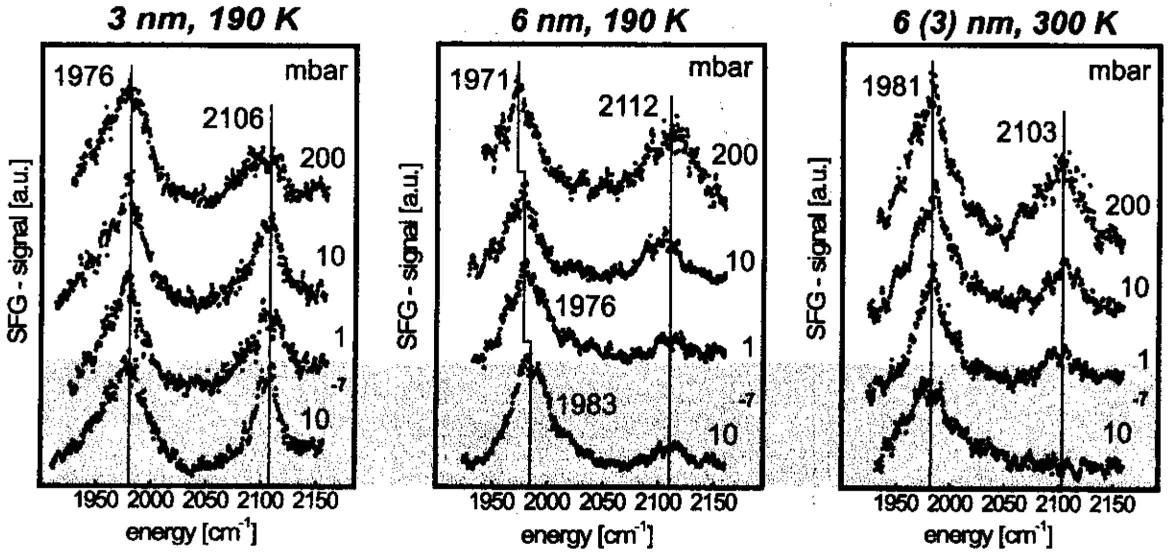
5. Summary and Conclusions



3 nm



6 nm



Dellwig, Rupprechter, Unterhalt, Freund
PRL *85 (2000) 776*

- 10^{-7} mbar: adsorption site distribution depends strongly on particle size, structure and temperature; more on-top adsorption on small, defective Pd aggregates
- above ~250 K, on-top sites are vacant under UHV conditions but are re-populated $\geq$ 1 mbar
- 200 mbar: adsorption site occupancy nearly independent of the structural properties and the temperature of the Pd particles
- high gas pressures may lead to surface coverages that exceed the "saturation coverage" of UHV studies; adsorbate geometries may form that can not be detected under UHV
- a simple extrapolation of UHV results to reaction conditions is not correct

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Michael Heemeier
Martin Frank

Hajo Freund

Max Planck Society
German Science Foundation