Adsorption

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Program

- **Thermodynamics**
- **Dynamics**
- **Electronic Structure**

Adsorption

Ideal Gas Theory

number of molecules colliding with a unit surface area:

$$F_i'' = \frac{P_i}{\sqrt{2\pi m_A k_B T}}$$

P_i: pressure of species:

$$r_A = F_i'' \sigma$$

σ: sticking coefficient

molecules per unit surface and per unit time

$$r_A = F_i'' \sigma^0(T) f(\theta) = \frac{P_i \sigma^0(T) f(\theta)}{\sqrt{2\pi m_A k_B T}}$$

rate constant:

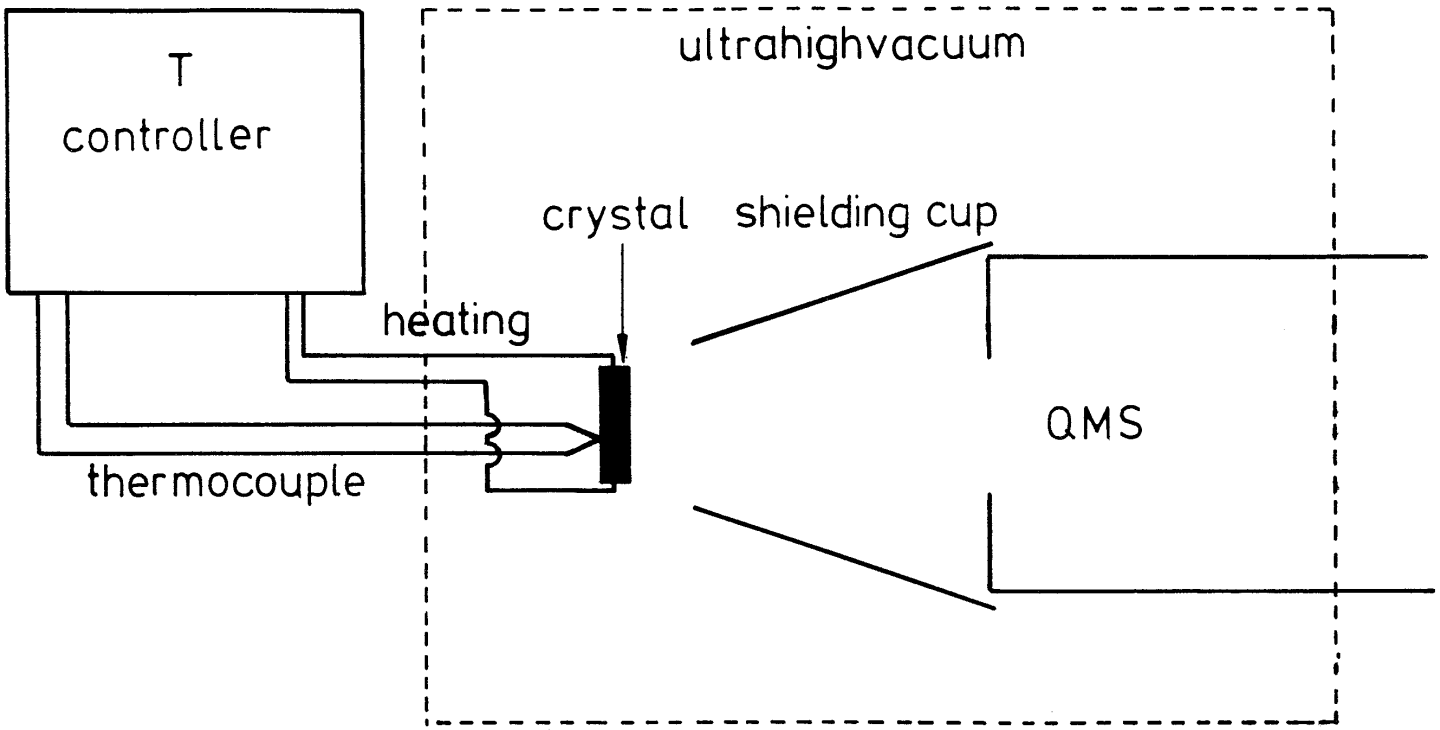
$$k_A = \frac{\sigma^0(T)}{\sqrt{2\pi m_A k_B T}}$$

$0 \le \sigma^0(T) \le 1$

unit: per pascal per cm^2 per second

Surface Coverage

Experimental Setup



Adsorption Isotherm

Clausius-Clapeyron

Assumption: adsorbate phase in equilibrium with the gas-phase and switching to partial molecular quantities

$$\left(\frac{\partial 1nP}{\partial T}\right) = \frac{\left(S_g - S_s\right)}{RT} = \frac{\left(h_g - h_s\right)}{RT^2} = -\frac{\Delta h_{ads}}{RT^2}$$

$$\Theta = \frac{n_s}{n_a}$$

$$\tilde{v}_s = \left(\frac{\partial v}{\partial n_s}\right)_{T,P,n_a}$$

leads to:

$$\left(\frac{\partial 1nP}{\partial T}\right)_{\Theta} = \frac{\left(S_g - \tilde{S}_s\right)}{RT} = \frac{\left(h_g - \tilde{h}_s\right)}{RT^2} = \frac{-q_{st}}{RT^2}$$

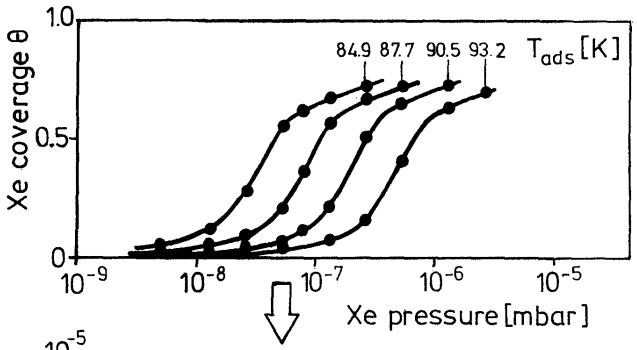
$$\frac{dP}{P} = \left(\frac{-q_{st}}{RT^2}\right)dT$$

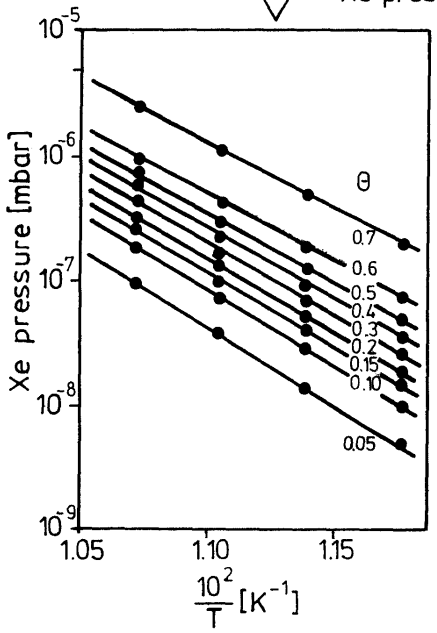
Integration leads to:

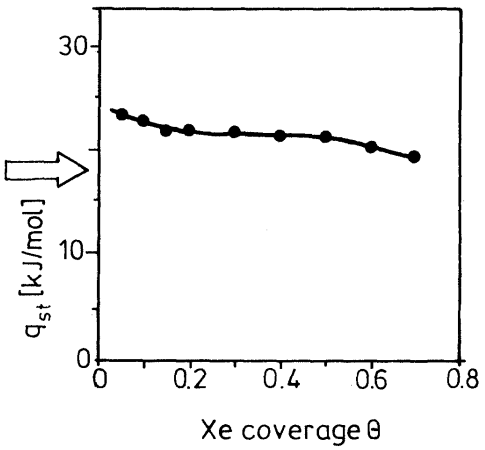
$$1n\left(\frac{P_1}{P_2}\right) = \frac{q_{st}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Isosteric Heat of Adsorption

Xe/Ni(100)







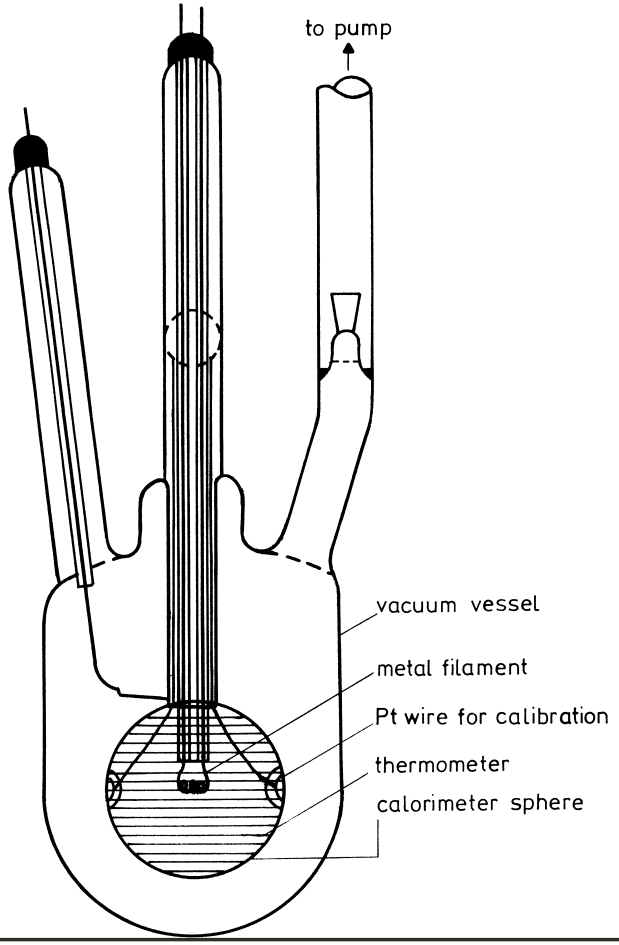
Clausius-Clapeyron

$$ln\left(\frac{P_1}{P_2}\right) = \frac{q_{st}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

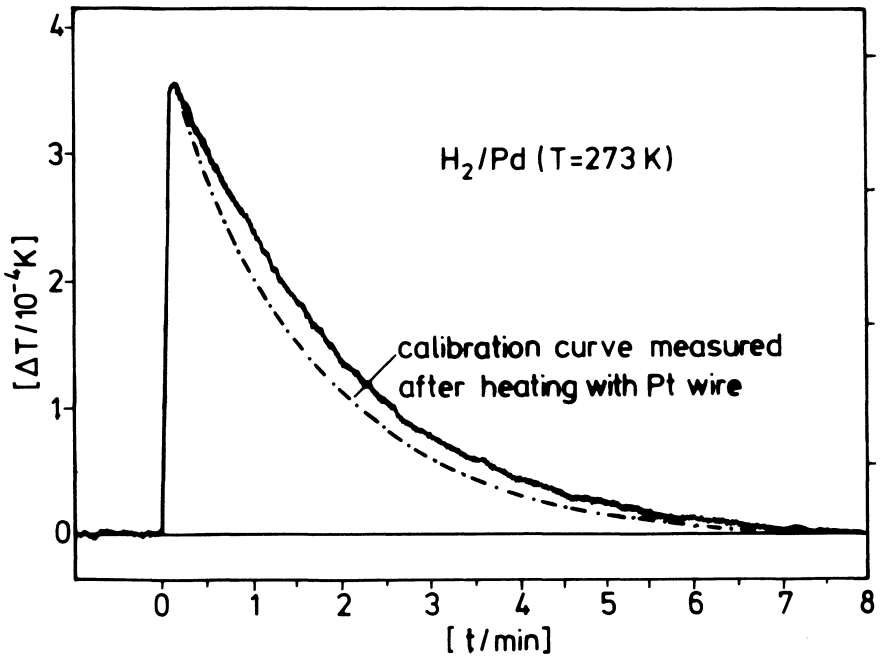
K. Christmann, J.E. Demuth, *Surf. Sci.* **1982,** *120*, 291

Heats of Adsorption (Evaporated Films)

Calorimeter (after Wedler)



$$Q_{integr} = \int_{o}^{ns} q_{st}\, dn_s$$



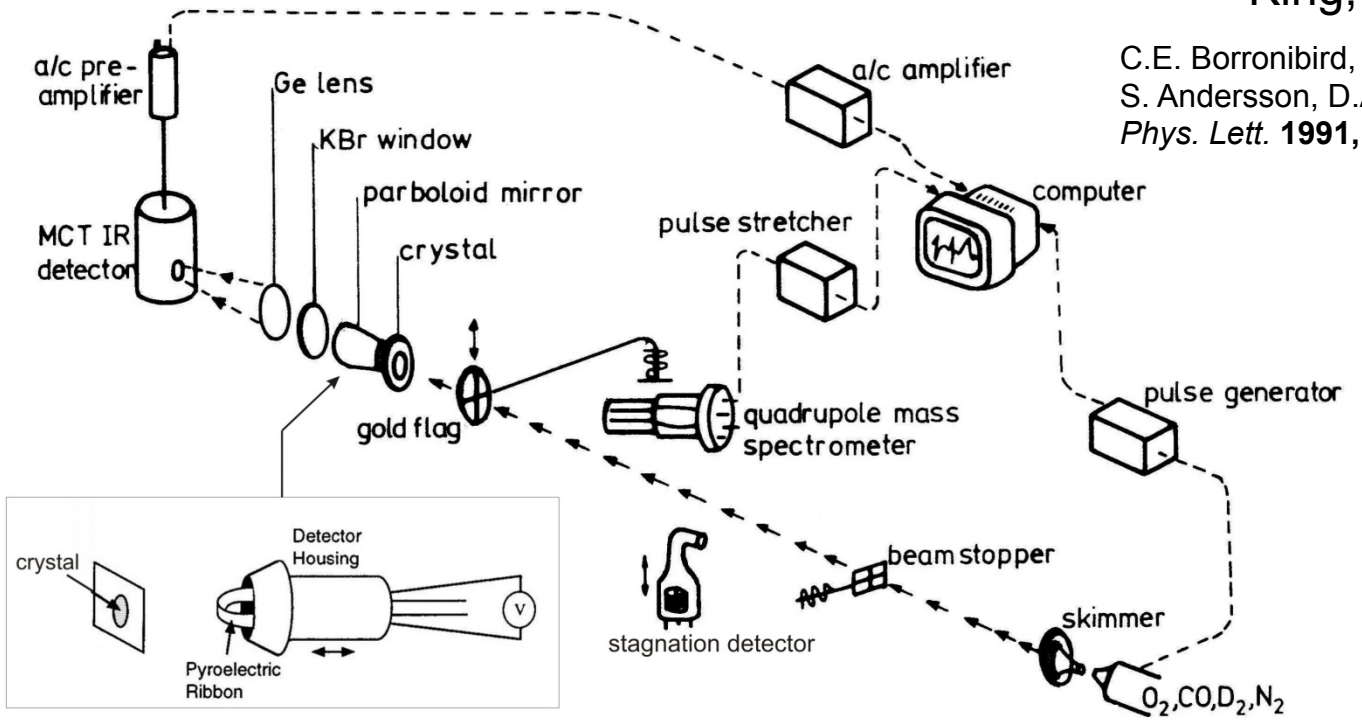
G. Wedler, H. Strothenk, *Ber. Bunsenges. Phys. Chem.* **1966,** *70*, 214; C. Pluntke, G. Wedler, G. Rau, *Surf. Sci.* **1983**, *134*, 145

Heat of Adsorption (Single Crystal)

Microcalorimetry

King, 1991

C.E. Borronibird, N. Alsarraf, S. Andersson, D.A. King, *Chem. Phys. Lett.* **1991,** *183*, 516

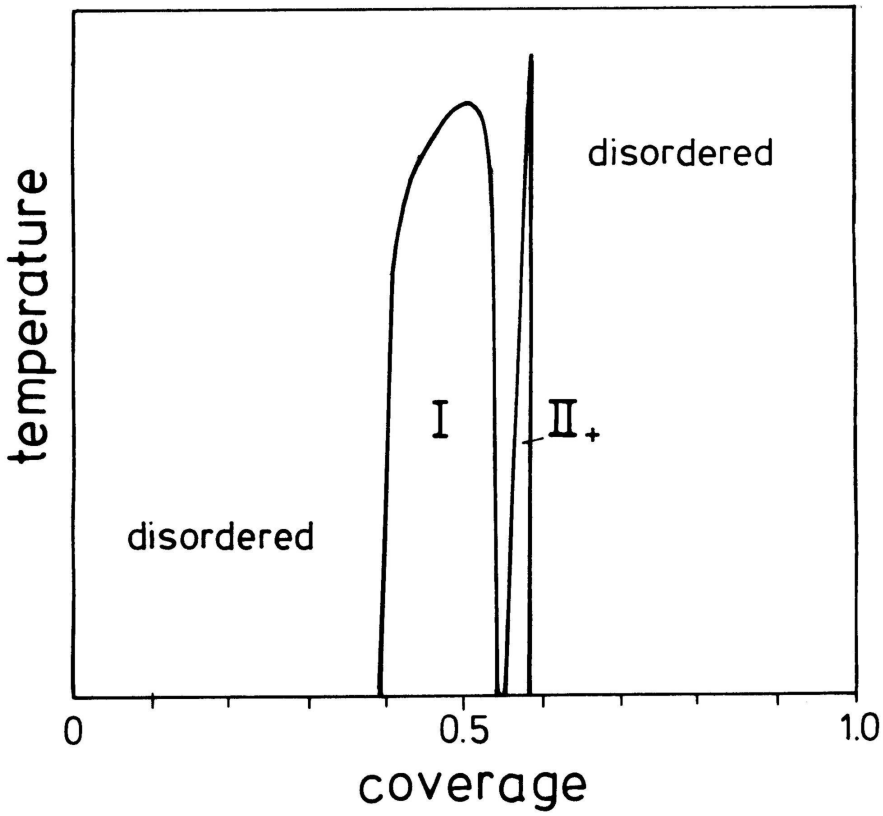


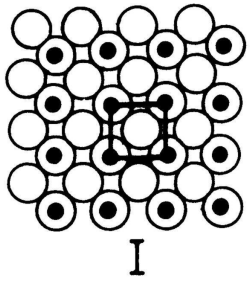
Campbell, 1998

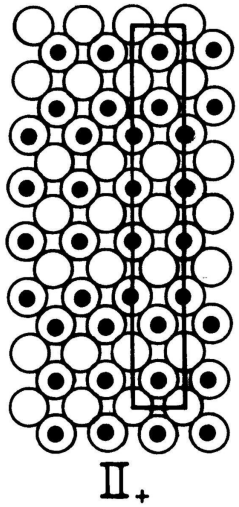
J.T. Stuckless, N.A. Frei, C.T. Campbell, *Rev. Sci. Inst.* **1998,** *69*, 2427

Surface Phase Diagram

CO/Cu(100)







B.N.J. Persson, *Surf. Sci.* **1991,** *258*, 451

Adsorption Isotherm

after Langmuir

Adsorption rate: $$r_{ad} = \frac{d\sigma_s}{dt} = \frac{P}{\sqrt{2\pi mkT}} s_o f(\sigma_s)$$

$f(\sigma_s)$ **accounts for the loss of empty sites**

$$s_o = {}^{o}s \exp\left(-\frac{{}^{ads}E_{act}}{kT}\right)$$

Sticking depents on many factors:

$$s(v, E_e, T) = \sum_v F_B(v, T) s_a(v, E_e)$$

E_e is the effective translation energy.

$$E_e = E_i \cos^n(\vartheta_i)$$

Assumptions: **each particle one site**
no interaction

$$r_{ad}(\Theta) = \frac{d\Theta}{dt} = \frac{P}{\sqrt{2\pi mkT}} s_o f(\Theta)$$

$f(\Theta)$ **: associate adsorption:** $(1-\Theta)$

: dissociate adsorption: $(1-\Theta)^2$

$$r_{ad} = r_{des}$$

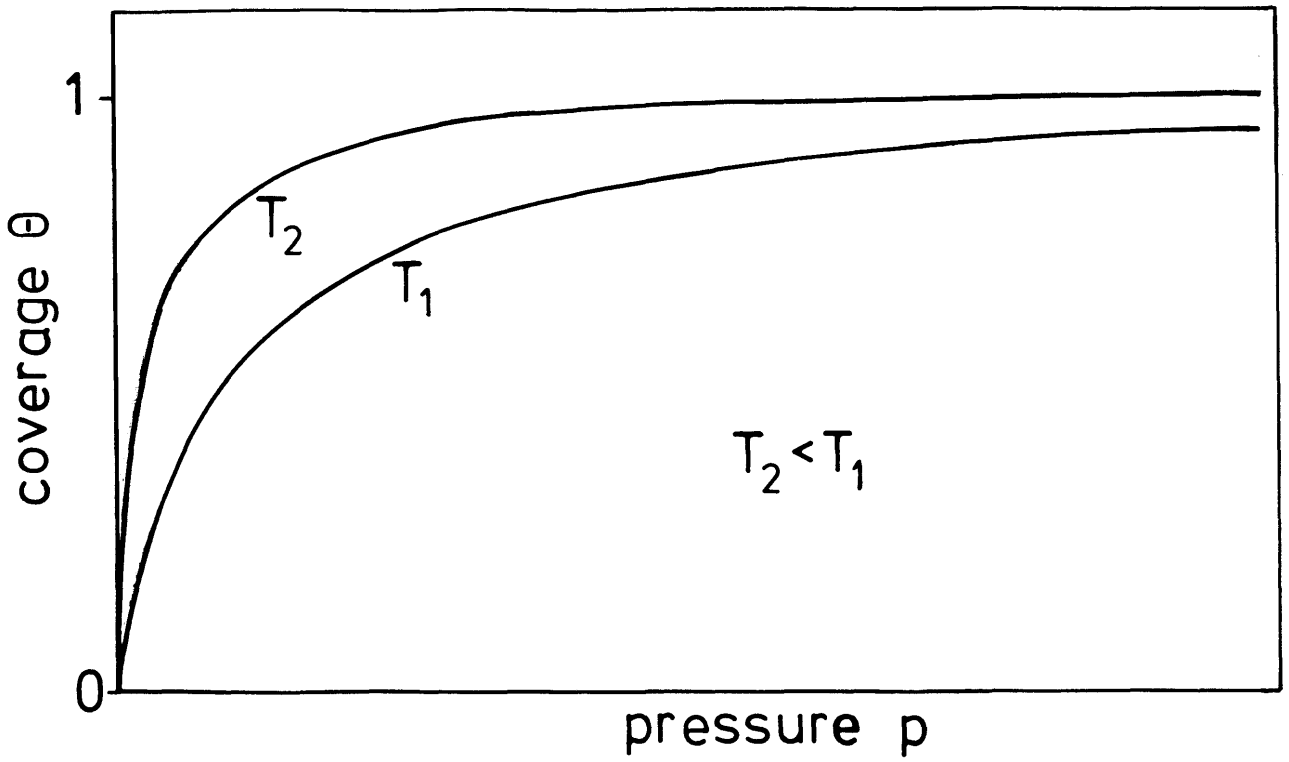
$$(\Theta) = \frac{b(T)P}{1 + b(T)P}$$

with

$$b(T) = \frac{{}^{o}s}{\upsilon\sqrt{2\pi mkT}} \exp\left(-\frac{{}^{ads}E_{act} - {}^{des}E_{act}}{kT}\right)$$

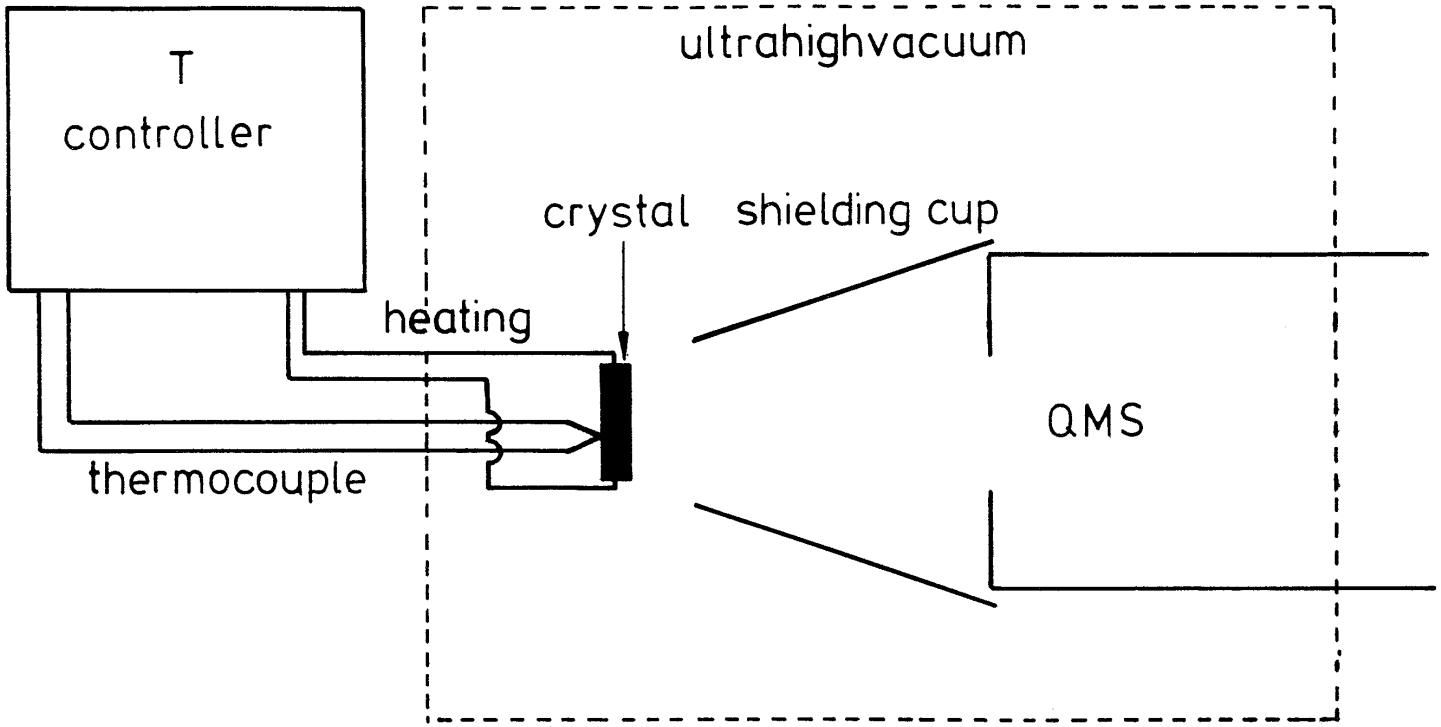
Adsorption Isotherms

after Langmuir



Thermal Desorption Spectrocopy

Experimental Setups



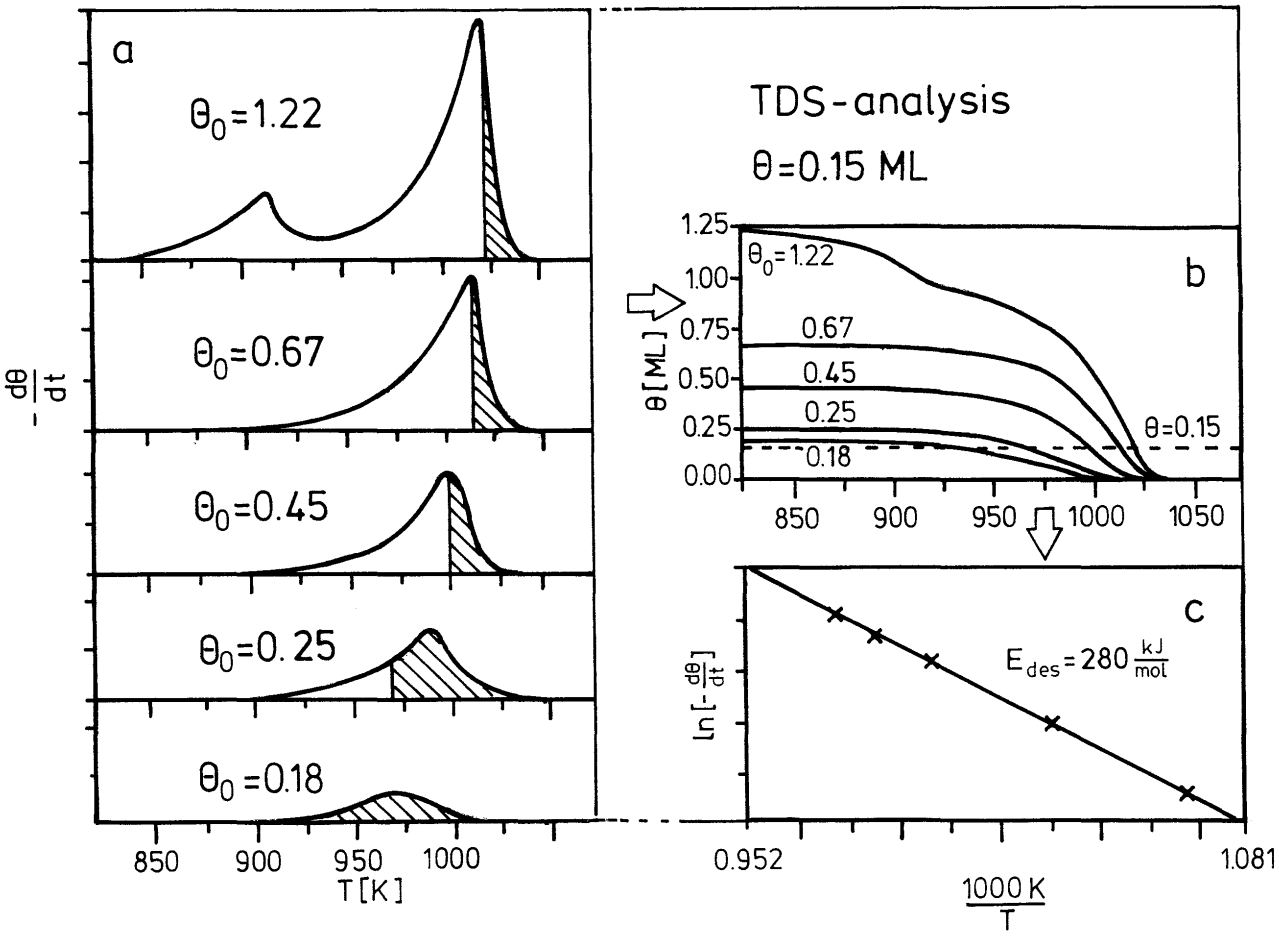
$$r_{des} = -\frac{d\Theta}{dt} = k_{des}\Theta^{n} = \nu(\Theta)\Theta^{n}\exp\left\{-\frac{E_{des}(\Theta)}{RT}\right\}$$

$$E_{des} = RT_{\max}\left[1n\left(\nu T_{\max}/\beta\right) - 3.46\right]$$

$$T = T_o + \beta t$$

Thermal Desorption Spectrocopy

Data Evaluation



D.A. King, *Surf. Sci.* **1975**, *47*, 384

Enthalpies of Adsorption

Adsorbate	Substrate	q(kJmo1^{-})		Remarks
CO	Ni(111)	111	(±5)	WF[1]
		130		Microcalorimetry
	Ni(100)	125	(0±5)	WF
		115		TDS[2]
		119		TDS
		138		TDS
		109		isosteric E_{ad}
		123		isosteric E_{ad}
		130		isosteric E_{ad}
		134		isosteric E_{ad}
		123		Microcalorimetry
	Ni(110)	133		Microcalorimetry
	Pd(100)	150	(±5)	WF
		161	(±8)	WF, TDS, LEED
	Pd(111)	142	(±3)	WF
	Ru(0001)	160	(±10)	WF
	Ru(10$\underline{1}$0)	157	(±10)	Contact-pot., TDS
	Cu(106)	58	(±10)	WF
	Fe(111)	325		273 K (dissociative)
	Fe(111)	200		195 K (partially diss.)

Adsorbate	Substrate	q(kJmo1^{-})		Remarks
	Fe(111)	100		(not dissociative)
CO/K	Ni(100)	190		Microcalorimetry
CO_2	Fe	300		195 K (dissociative)
H_2	Ni(100)	96.3	(±5)	WF
	Ni(110)	90.0	(±5)	WF
	Ni(111)	96.3	(±5)	WF
		85	(±5)	
	Ni	75...176		
	Pd(111)	88	(±5)	WF
	Pd(110)	103	(±5)	WF
	Pd(100)	102	(±5)	WF
	Rh(110)	92	(±5)	WF, TDS
	Ru(10$\underline{1}$0)	80	(±5)	
	Co(10$\underline{1}$0)	80	(±5)	
	Ta	188.1		
	W	188.1		
	Cr	188.1		
	Fe	133.8		
	Fe	100		dissociative (273 K)
	Fe	97	(±3)	

[1] WF, work function; [2] TDS, thermal desorption spectroscopy

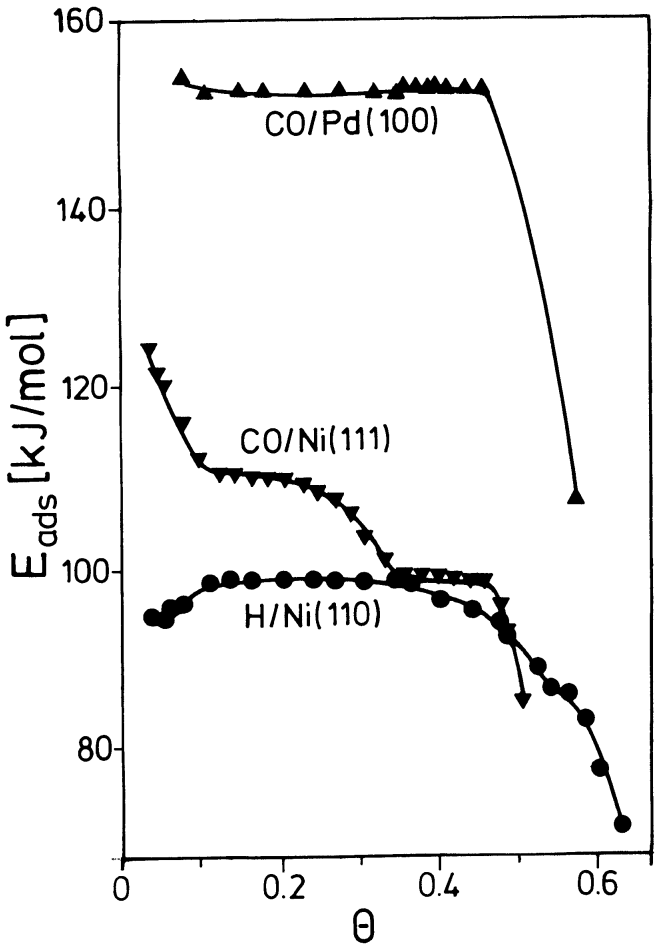
Enthalpies of Adsorption

Adsorbate	Substrate	q(kJmo1^{-})		Remarks
	Pd	80/96		
Na	W	133.8		
Cs		267.5		
O	Ni(100)	532	(±5)	IR (300K)
	Pd	80/96		
		≈ 432		IR (100 K)
		532	(±5)	
	Ni(l11)	470	(±15)	
	Ni(110)	498	(±5)	
O_2/CO	Fe(111)	490		273 K

[1] WF, work function; [2] TDS, thermal desorption spectroscopy

Heats of Adsorption

CO on Transition Metal Surfaces



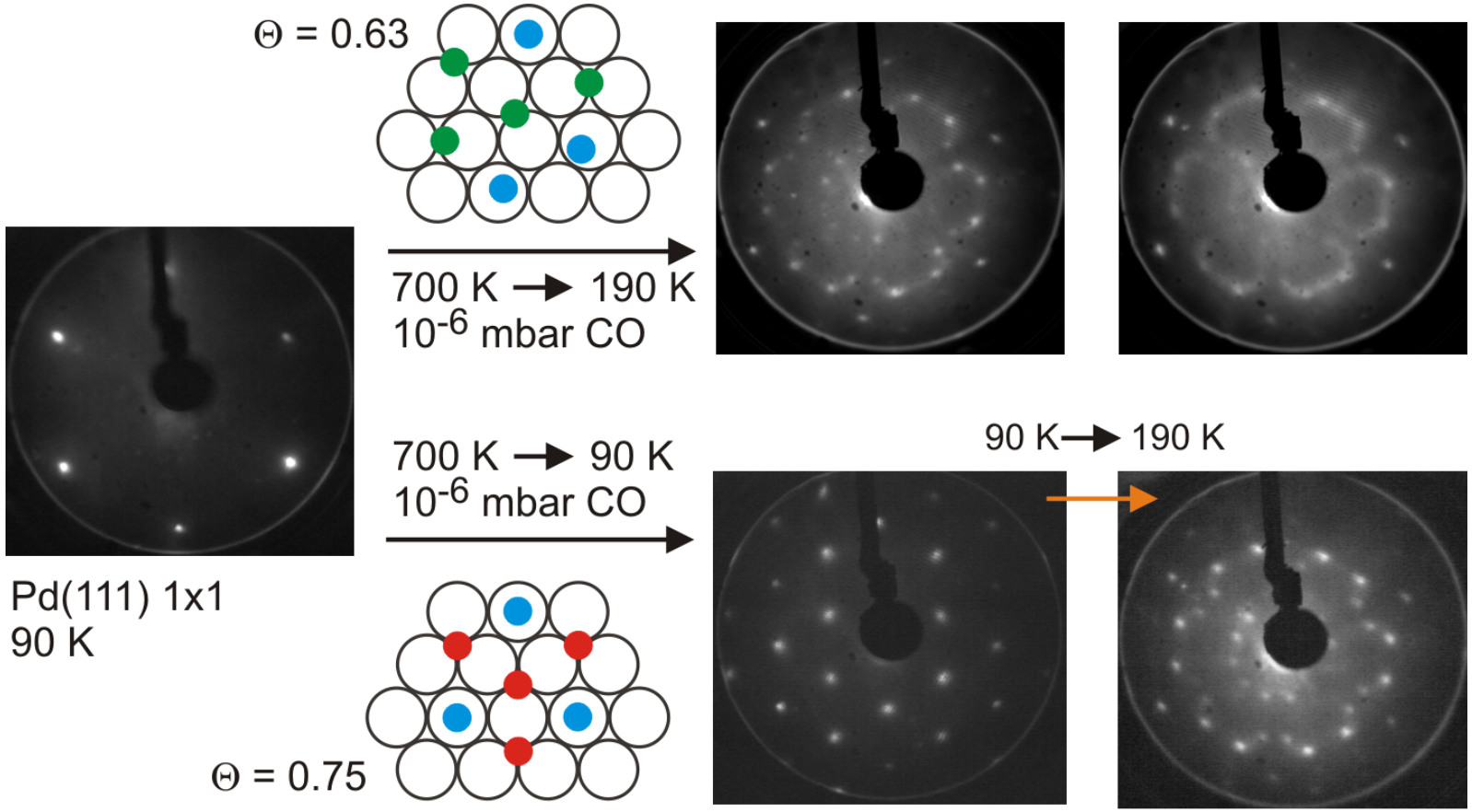
K. Christmann, *Introduction to Surface Physical Chemistry*, Topics in Physical Chemistry, Vol. 1, Steinkopff Verlag, Darmstadt, **1991**;

R.J. Behm, K. Christmann, G. Ertl, M.A. van Hove, *J. Chem. Phys.* **1980**, *73*, 2984;

K. Christmann, O. Schober, G. Ertl, M. Neumann, *J. Chem. Phys.* **1974**, *60*, 4528

Adsorption under UHV Conditions

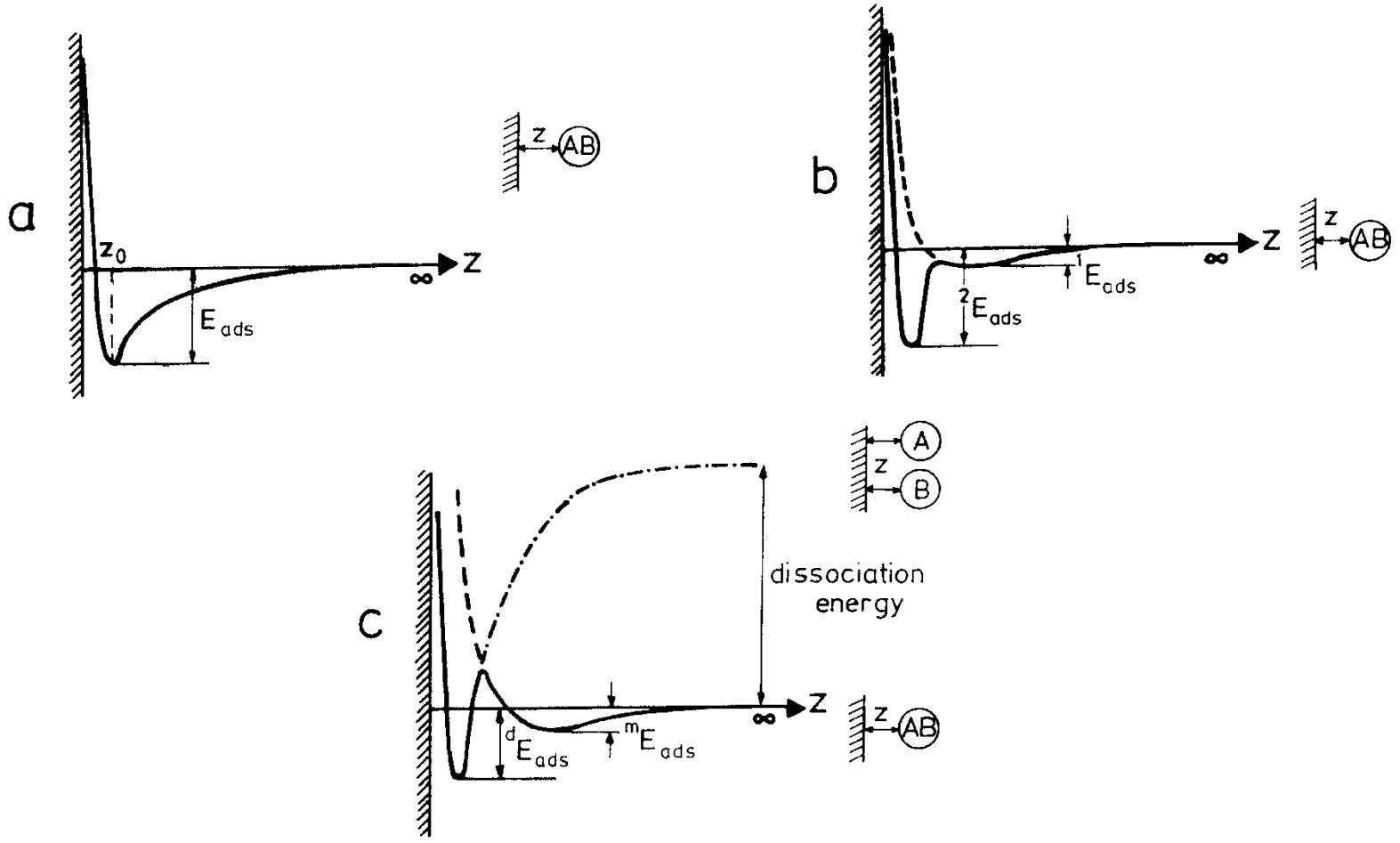
LEED Studies



T. Tüshaus, W. Berndt, H. Conrad, A.M. Bradshaw, B. Persson, *Appl. Phys. A* **1990,** *51*, 91

Model Potentials

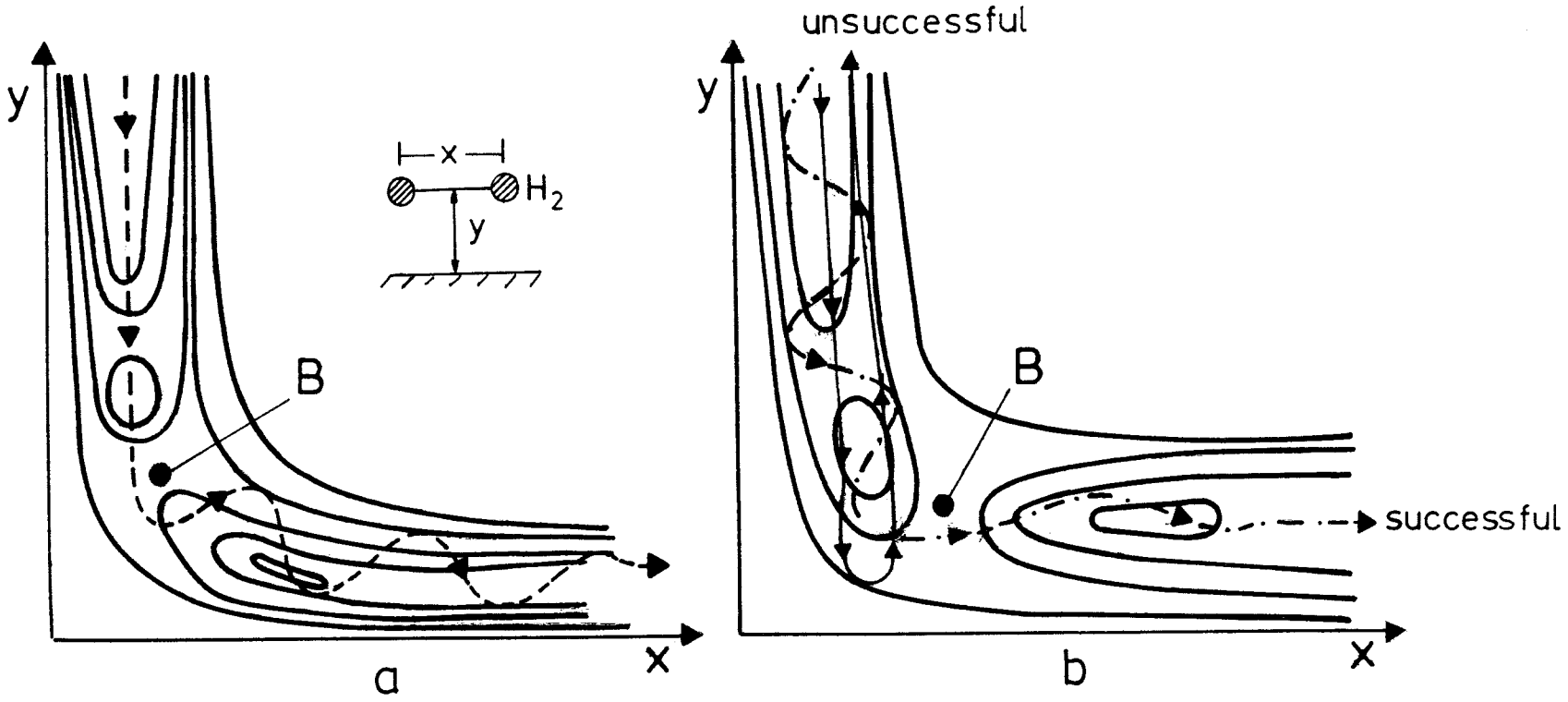
One Dimensional



J.E. Lennard-Jones, *Trans. Faraday Soc.* **1932,** *28*, 333

Model Potentials

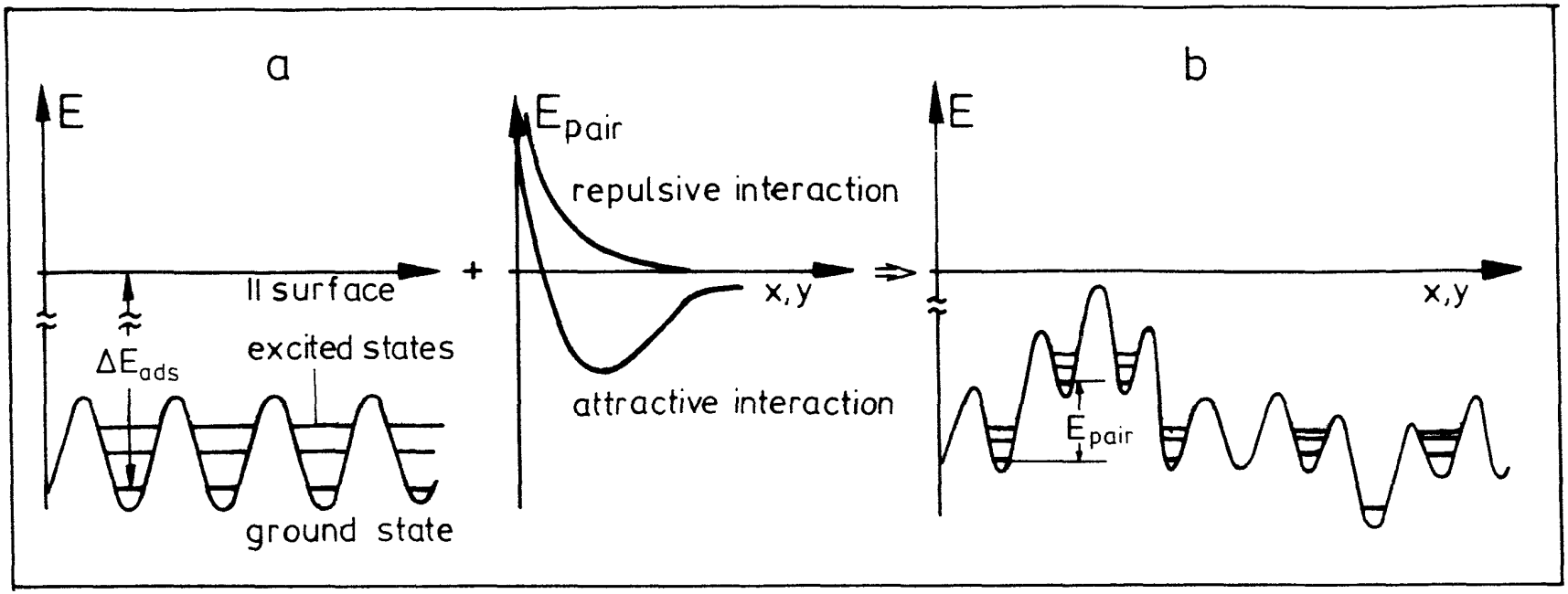
Two Dimensional



J.C. Polanyi, *Science* **1987,** *236*, 680

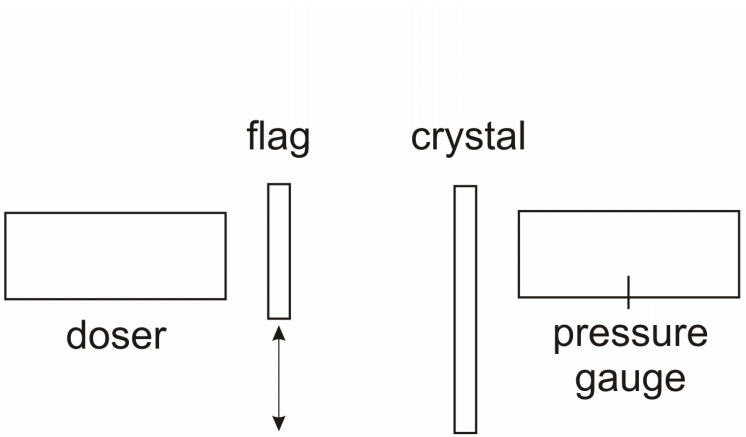
Model Potentials

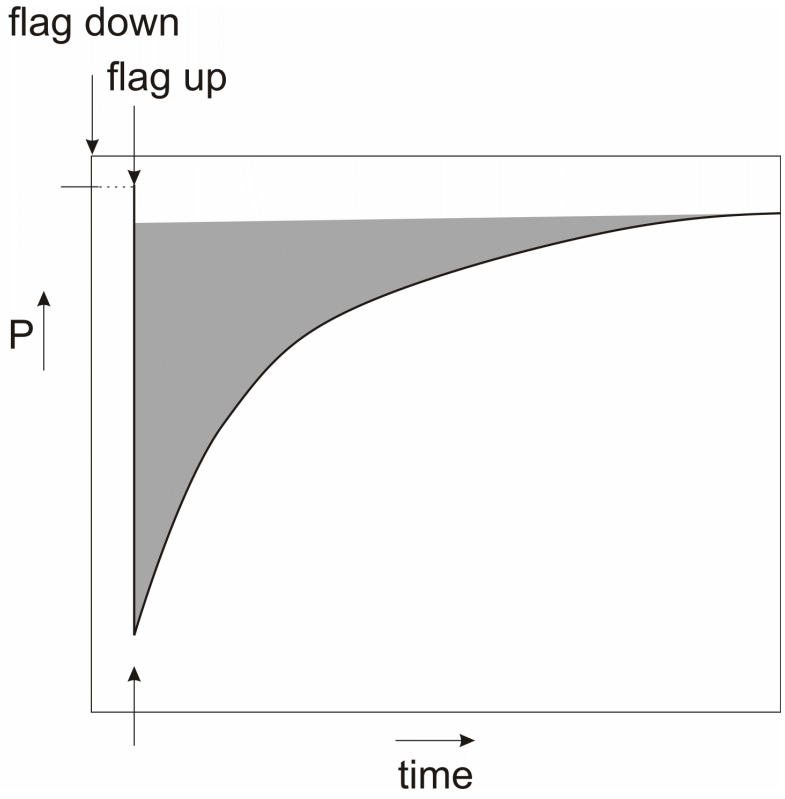
Diffusion



Sticking Coefficient

after King & Wells





D.A. King, M.G. Wells, *Surf. Sci.* **1972,** *29*, 454

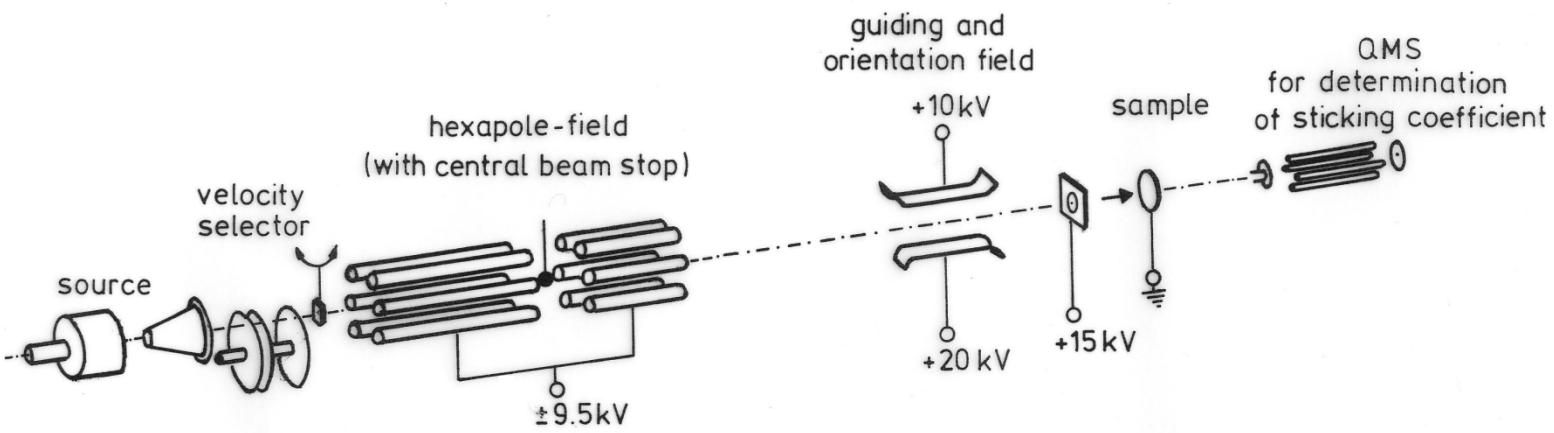
Initial Sticking Coefficients

Adsorbate	Substrate	Sticking coefficient	Remarks
H	Ni(100)	0.06	
	Ni(1 11)	≥ 0.01	
	Ni(110)	≈ 1	
		0.96	
	Pt(111)	0.1	
		≤ 0.0001	
	Rh(1 10)	≈ 1	
	Ru(10_1 0)	≈ 1	
	Co(10_1 0)	0.75 (±20%)	
	W(100)	1	
O	Cu(100)	0.03	300 K
	Ni(100)	1	
	Pt(111)	0.2	
CO	Ni(111)	1	
	Ni(110)	0.89	

Adsorbate	Substrate	Sticking coefficient	Remarks
	Pd(100)	0.6	
	Pd(111)	0.96	
	Ru(10$\underline{1}$0)	1	
	Pt(111)	1	
N	W(100)	0.2-0.6	
	W(110)	$1\text{-}5\times10^{-3}$	β-N_2
		0.22	γ-N_z
	W(111)	0.08	
N_2	Fe(100)	10^{-6}-10^{-7}	
	Fe(111)	10^{-6}-10^{-7}	
	Fe(1 11) > (100) > (110)	10^{-6}-10^{-8}	

Adsorption of oriented Molecules

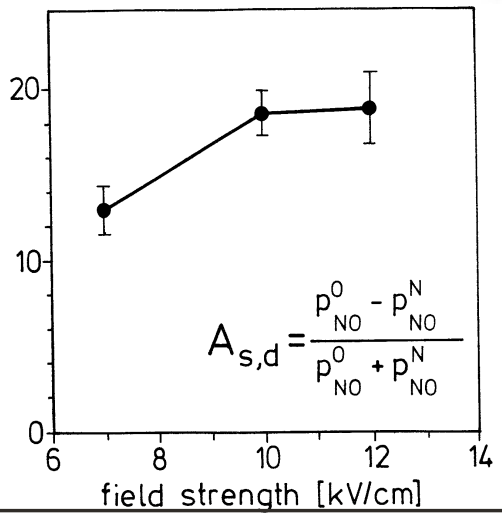
Experimental Setup

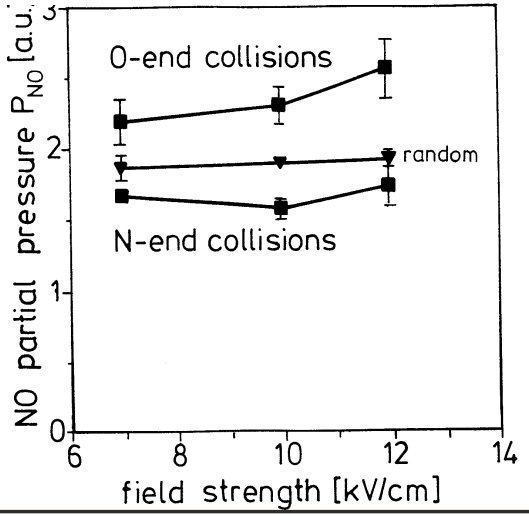


G.H. Fecher, N. Bowering, M. Volkmer, B. Pawlitzky, U. Heinzmann, *Surf. Sci.* **1990**, *230*, L169

H. Muller, B. Dierks, F. Hamza, G. Zagatta, G.H. Fecher, N. Bowering, U. Heinzmann, *Surf. Sci.* **1992,** *270*, 207;

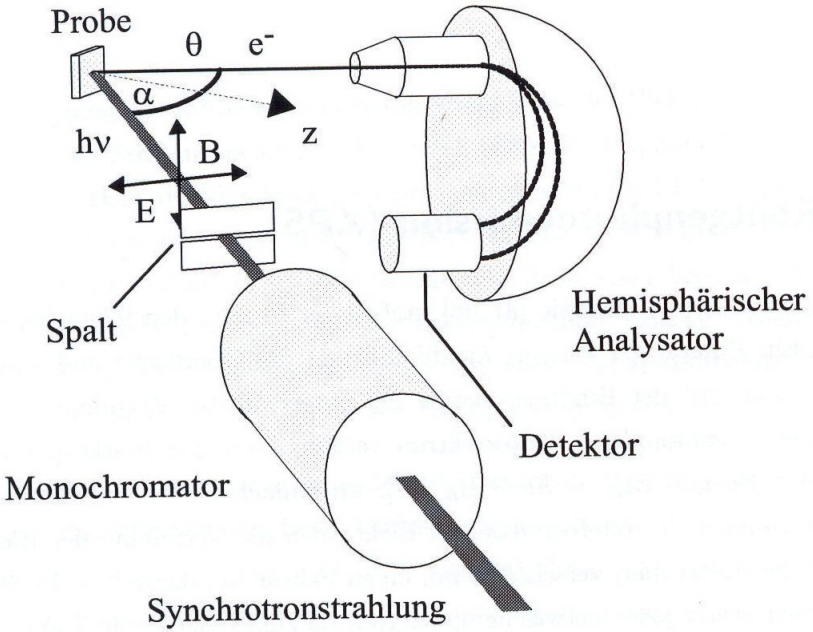
H. Muller, G. Zagatta, N. Bowering, U. Heinzmann, *Chem. Phys. Lett.* **1994**, *223*, 197

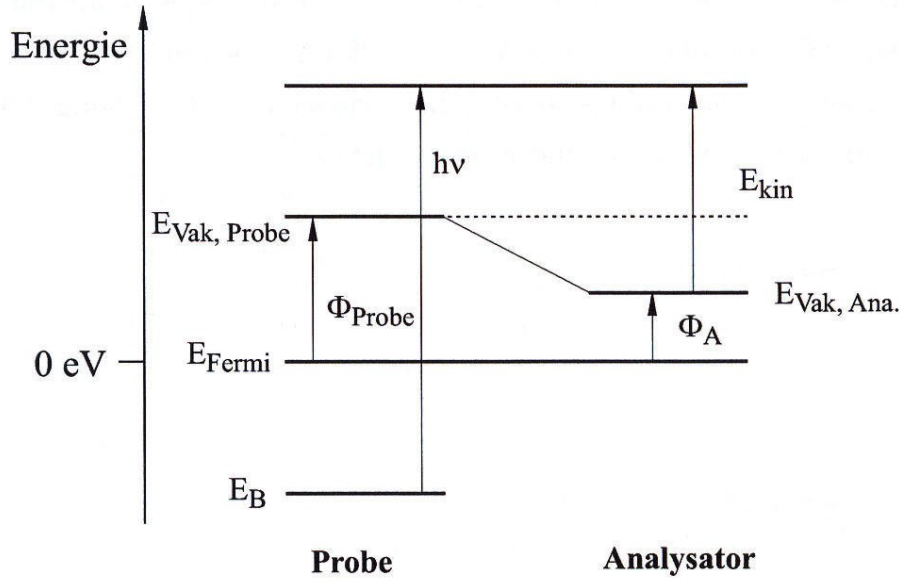




Photoemission

Principles

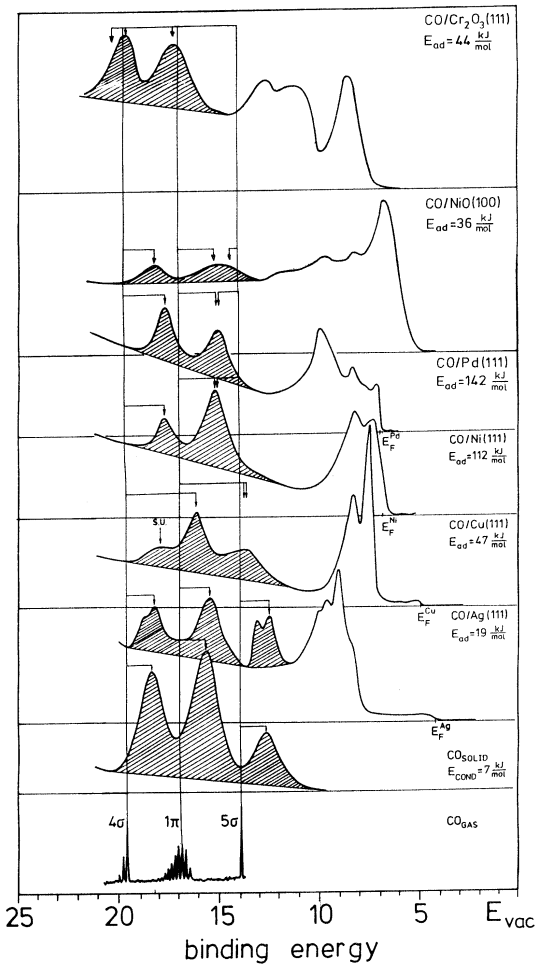


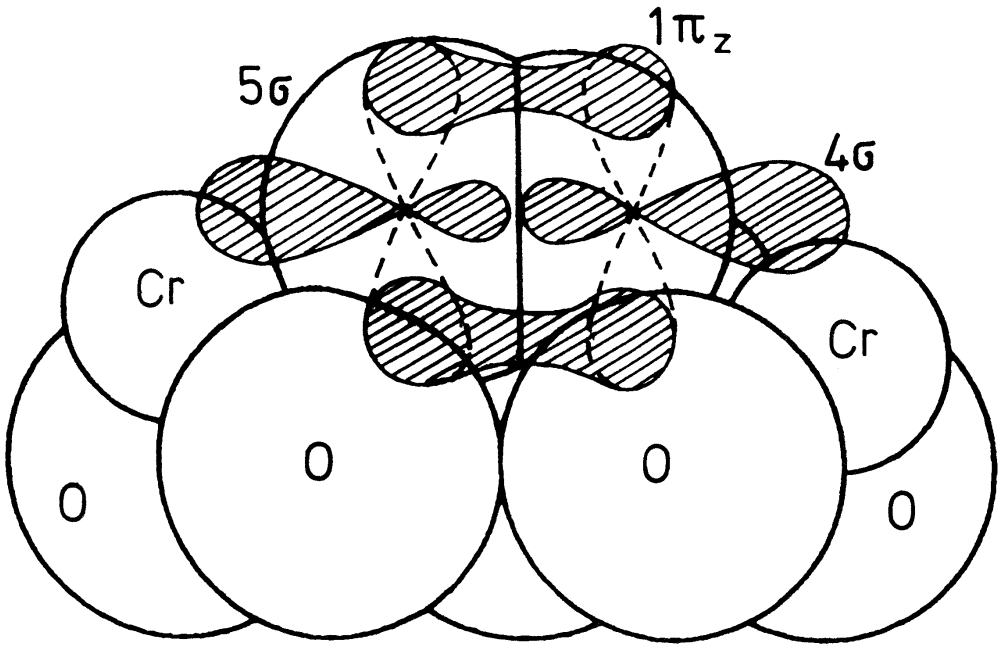


$$\hbar\omega = E_{kin} - E_B$$

Electronic Structure

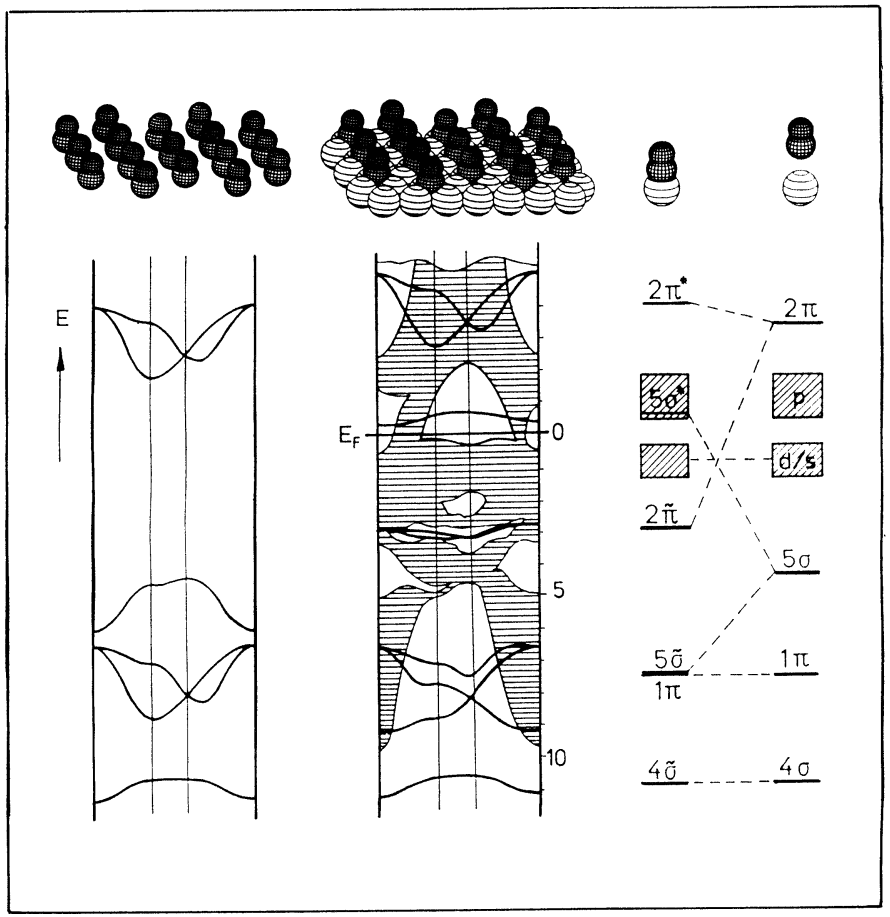
Photoelectron Spectroscopy





Ordered Adsorbate Layers

Formation of Two-dimensional Band-structures

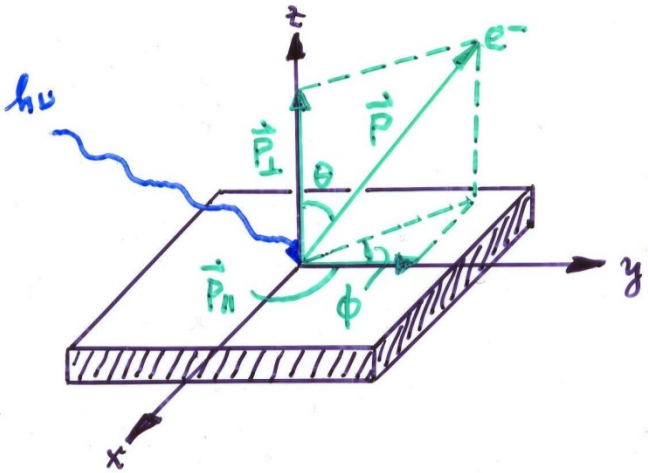


H.J. Freund, M. Neumann, *Appl. Phys. A* **1988,** *47*, 3

Photoemission

Principle of Bandstructure Measurement

Angle resolved photoemission



$$\vec{p} = \vec{p}_{\parallel} + \vec{p}_{\perp} \; ; \quad \vec{p}_{\parallel} = |\vec{p}| \cdot \sin\theta$$

$$E_{kin} = \frac{p^2}{2m}$$

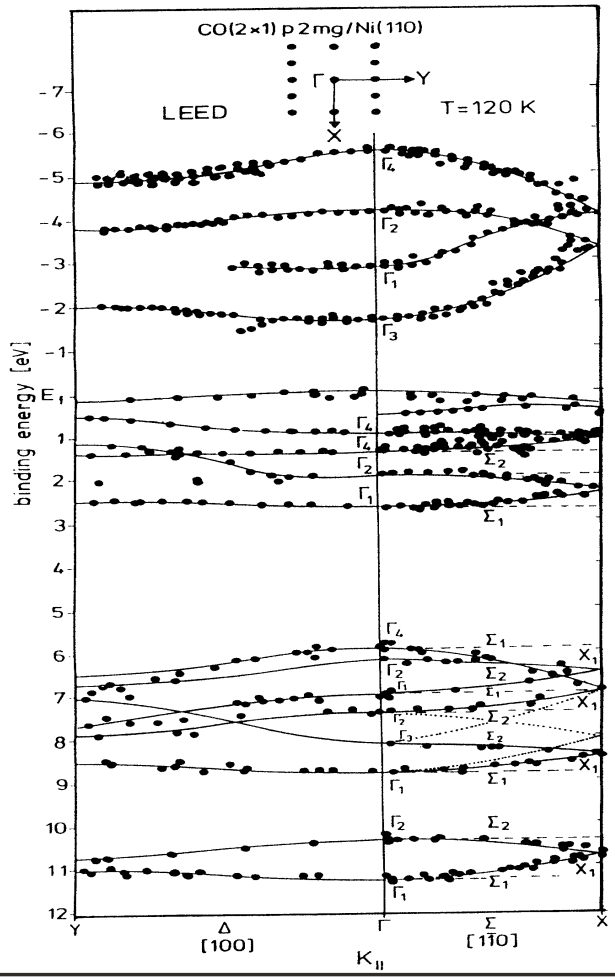
$$\vec{p} = \hbar\vec{k}$$

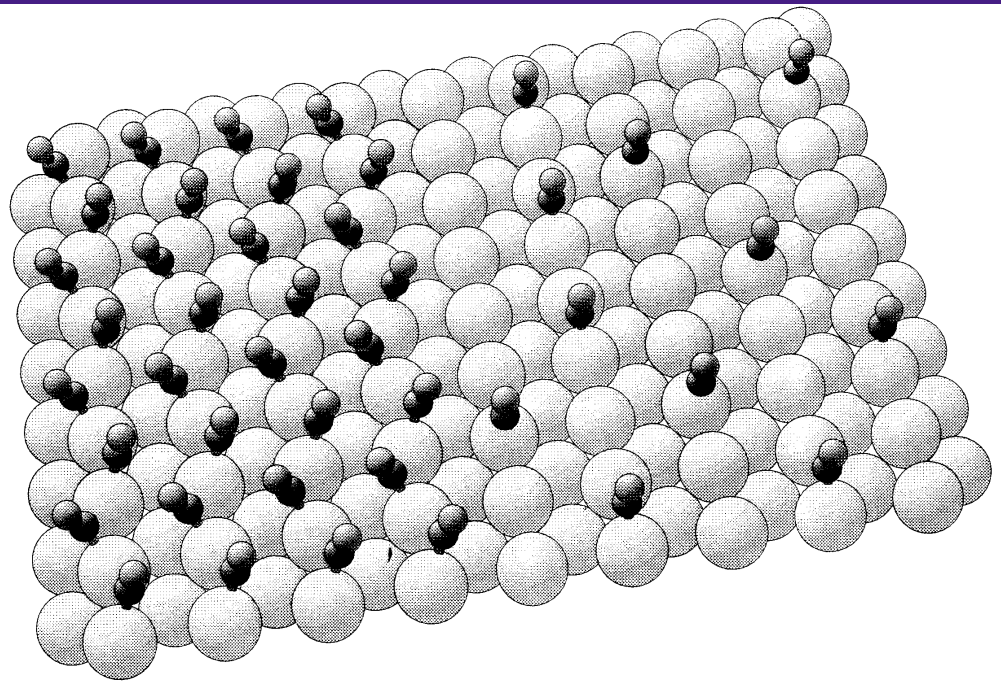
$$k_{\parallel} = \left(\frac{2m}{\hbar^2} E_{kin}\right)^{1/2} \sin\theta$$

$k_{\parallel}$ is conserved

Intermolecular Interaction at Surfaces

Two-dimensional band structure COp_{2mg}/Ni(110)



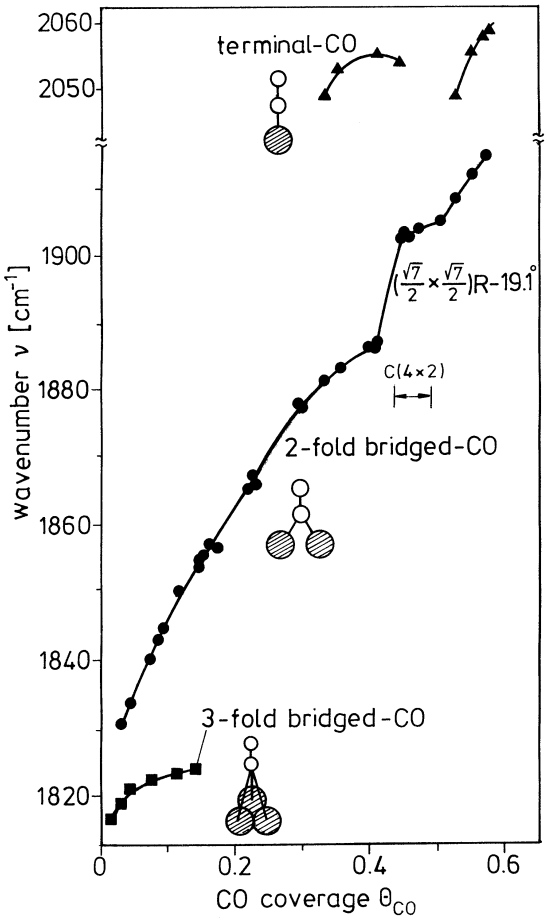


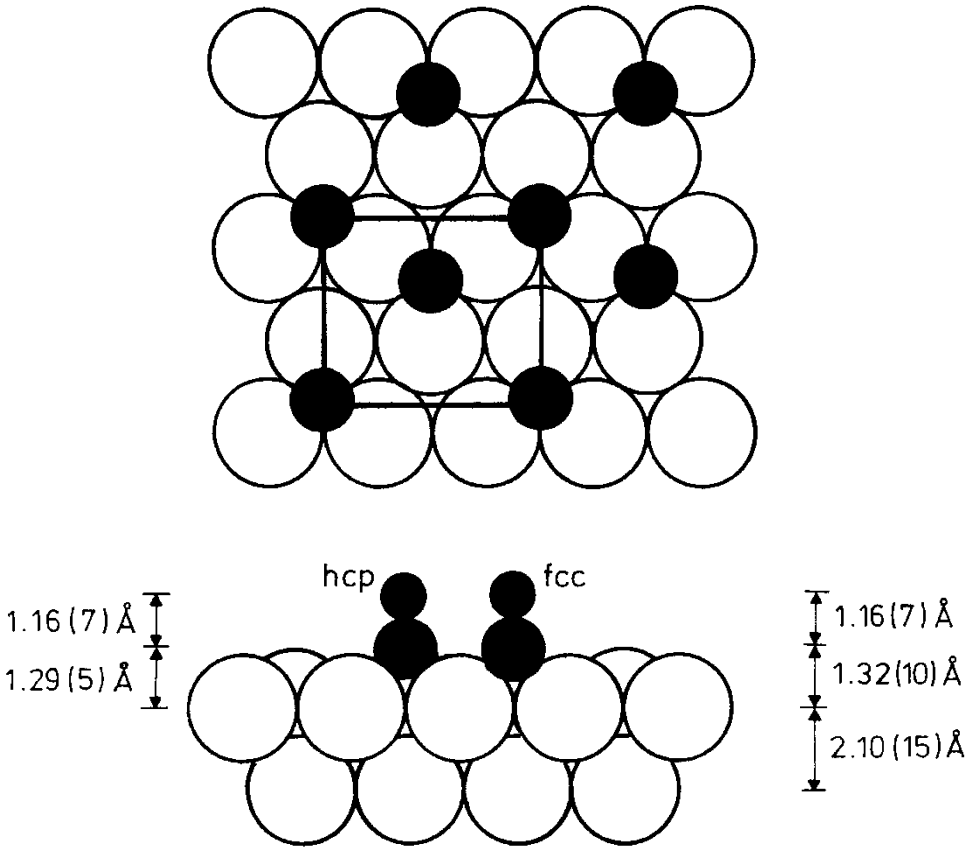
H. Kuhlenbeck, H.B. Saalfeld, U. Buskotte, M. Neumann, H.J. Freund, E.W. Plummer, *Phys. Rev. B* **1989,** *39*, 3475;

N. Memmel, G. Rangelov, E. Bertel, V. Dose, K. Kometer, N. Roesch, *Phys. Rev. Lett.* **1989,** *63*, 1884

Determination of Adsorption Size

Vibrational Spectroscopy CO/Ni(111)



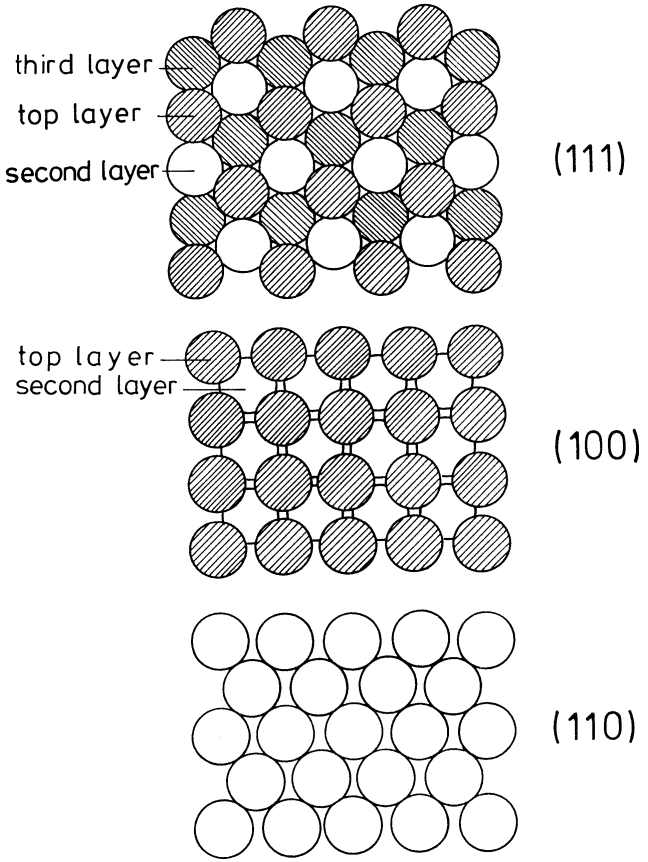


K.M. Schindler, P. Hofmann, V. Fritzsche, S. Bao, S. Kulkarni, A.M. Bradshaw, D.P. Woodruff, *Phys. Rev. Lett.* **1993,** *71*, 205

L. Surnev, Z. Xu, J.T. Yates, *Surf. Sci.* **1988,** *201*, 1

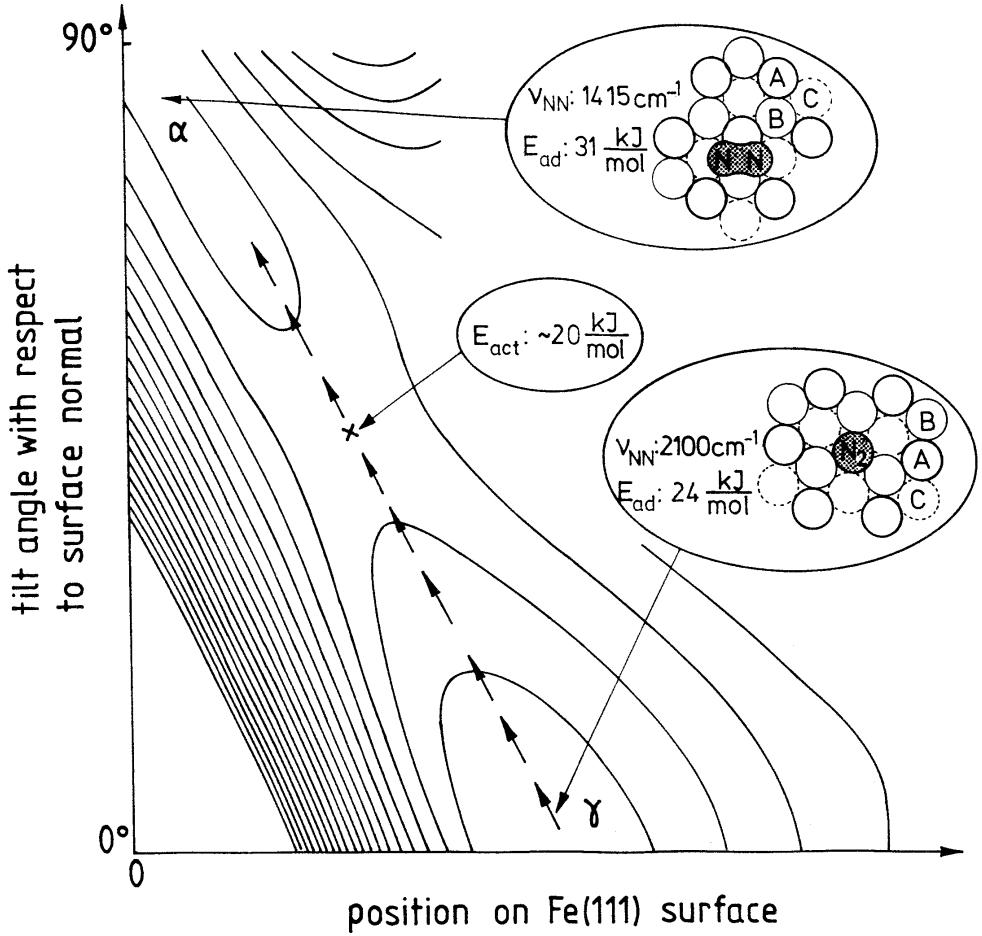
Surface Structure

bcc(hkl)



Model Potential

N_2/Fe(111)



M. Grunze, M. Golze, W. Hirschwald, H.J. Freund, H. Pulm, U. Seip, M.C. Tsai, G. Ertl, J. Kuppers, *Phys. Rev. Lett.* **1984,** *53*, 85;

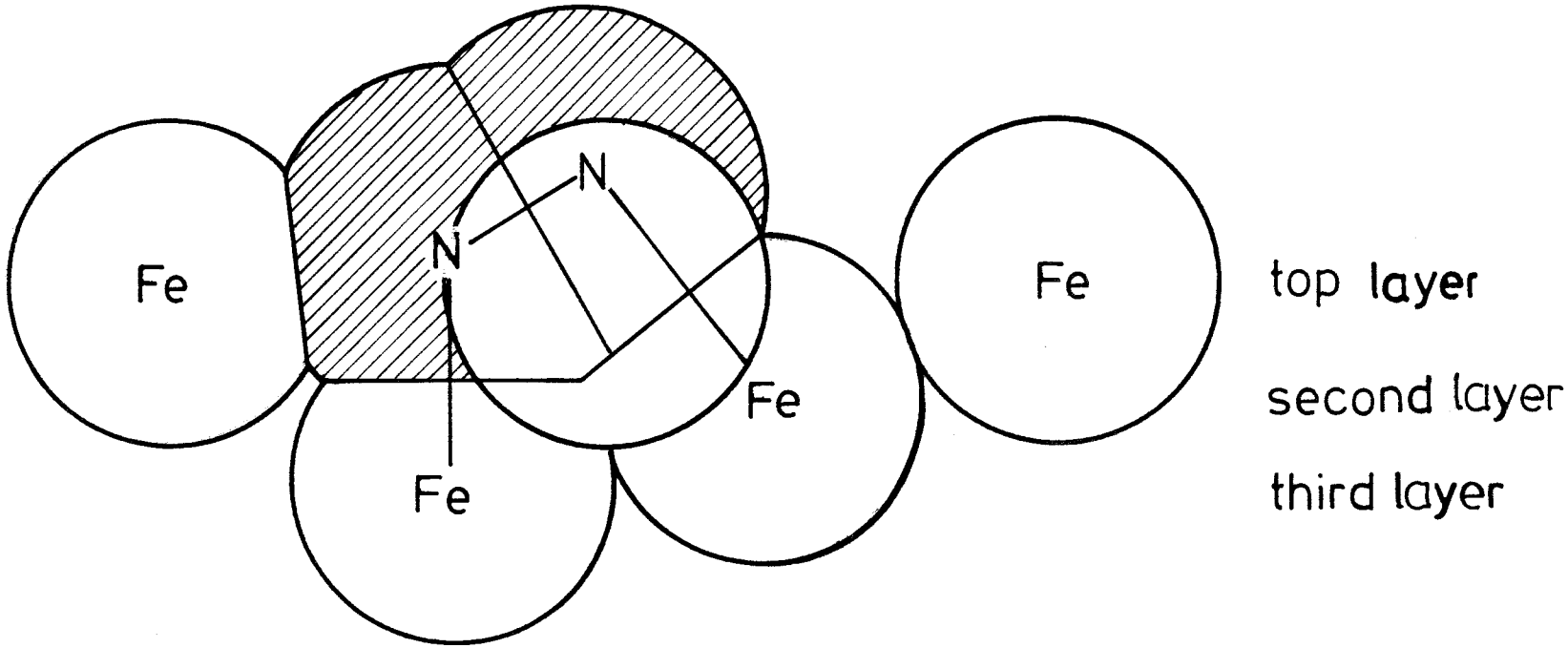
M.C. Tsai, U. Seip, I.C. Bassignana, J. Kuppers, G. Ertl, *Surf. Sci.* **1985**, *155*, 387.

L.J. Whitman, C.E. Bartosch, W. Ho, G. Strasser, M. Grunze, *Phys. Rev. Lett.* **1986**, *56*, 1984.

D. Tomanek, K.H. Bennemann, *Phys. Rev. B* **1985**, *31*, 2488

Adsorbate Structure

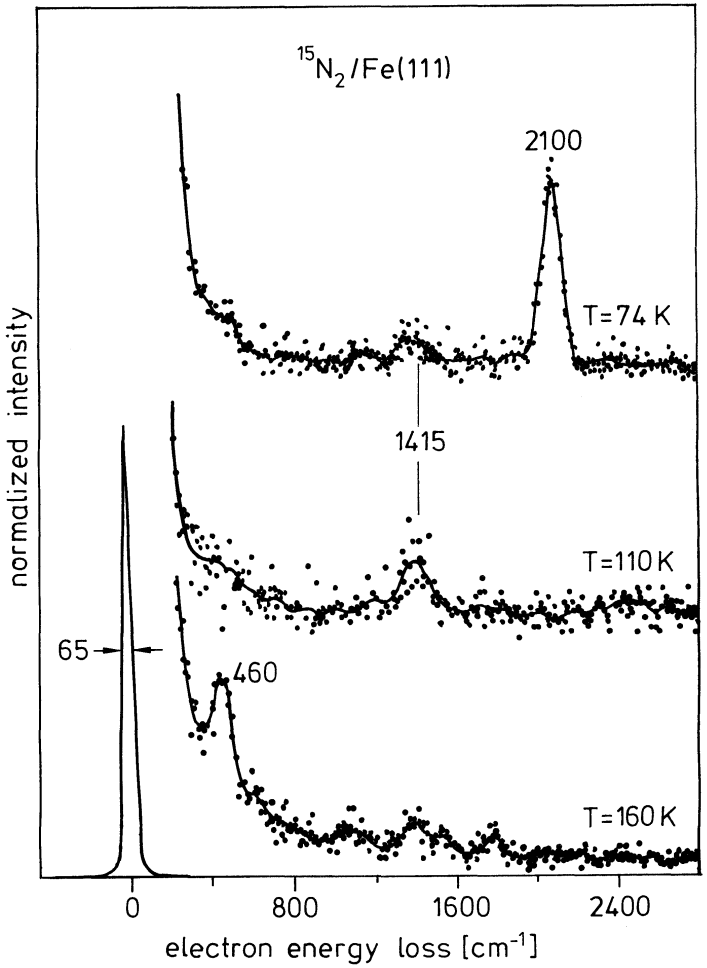
N_2/Fe(111)



H.J. Freund, B. Bartos, R.P. Messmer, M. Grunze, H. Kuhlenbeck, M. Neumann, *Surf. Sci.* **1987,** *185*, 187

Vibrational Spectroscopy (EELS)

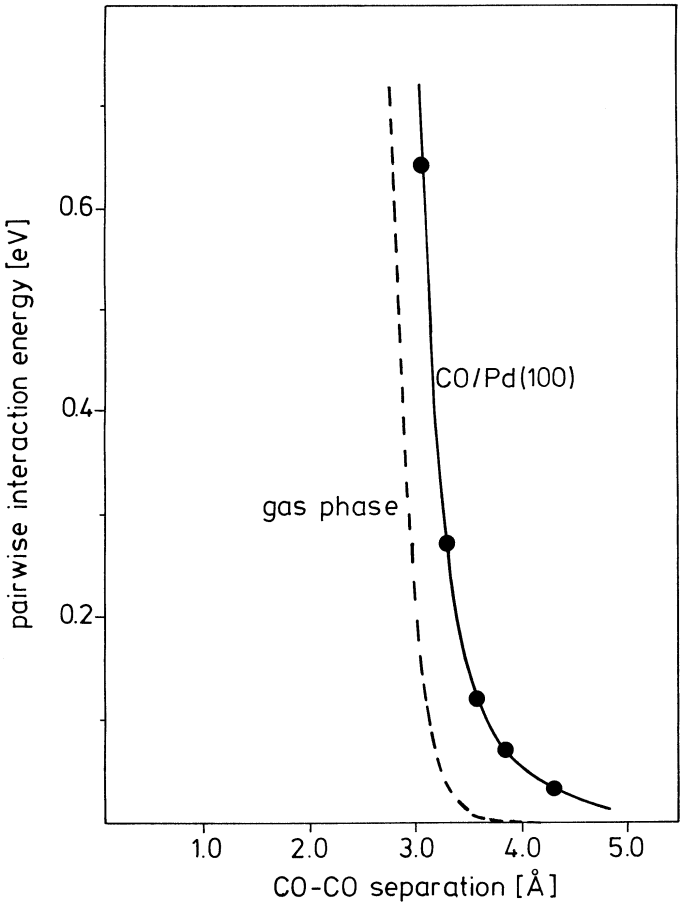
N_2/Fe(111)



L.J. Whitman, C.E. Bartosch, W. Ho, G. Strasser, M. Grunze, *Phys. Rev. Lett.* **1986,** *56*, 1984

Thermonuclear Interaction

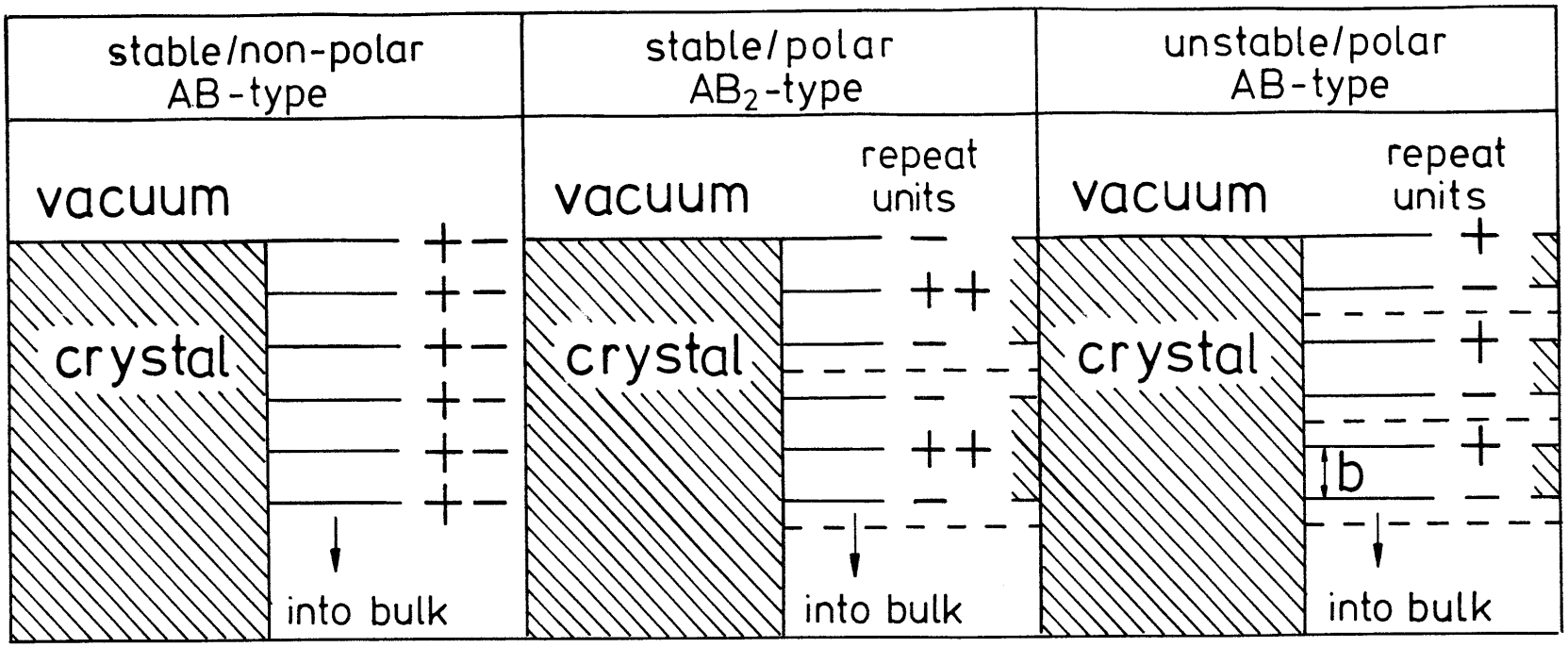
CO in Gas-phase and on Surface



J.C. Tracy, P.W. Palmberg, *J. Chem. Phys.* **1969,** *51*, 4852

Stability of Oxide Surfaces

Electrostatic Considerations

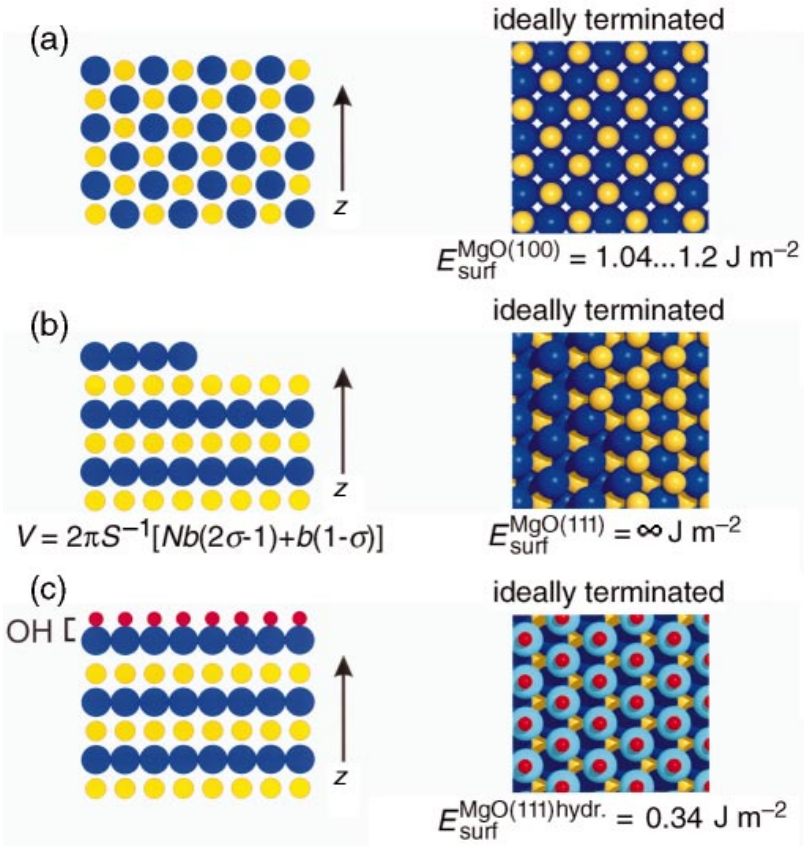


$$V = \frac{2\pi}{S}\left[Nb\left(2\sigma - 1\right) + \left(1 - \sigma\right)b\right]$$

P.W. Tasker, *Philos. Mag. A* **1979,** *39*, 119; P.W. Tasker, *J. Phys. C: Solid State Phys.* **1978,** *12*, 4977

Oxide Surface Structure

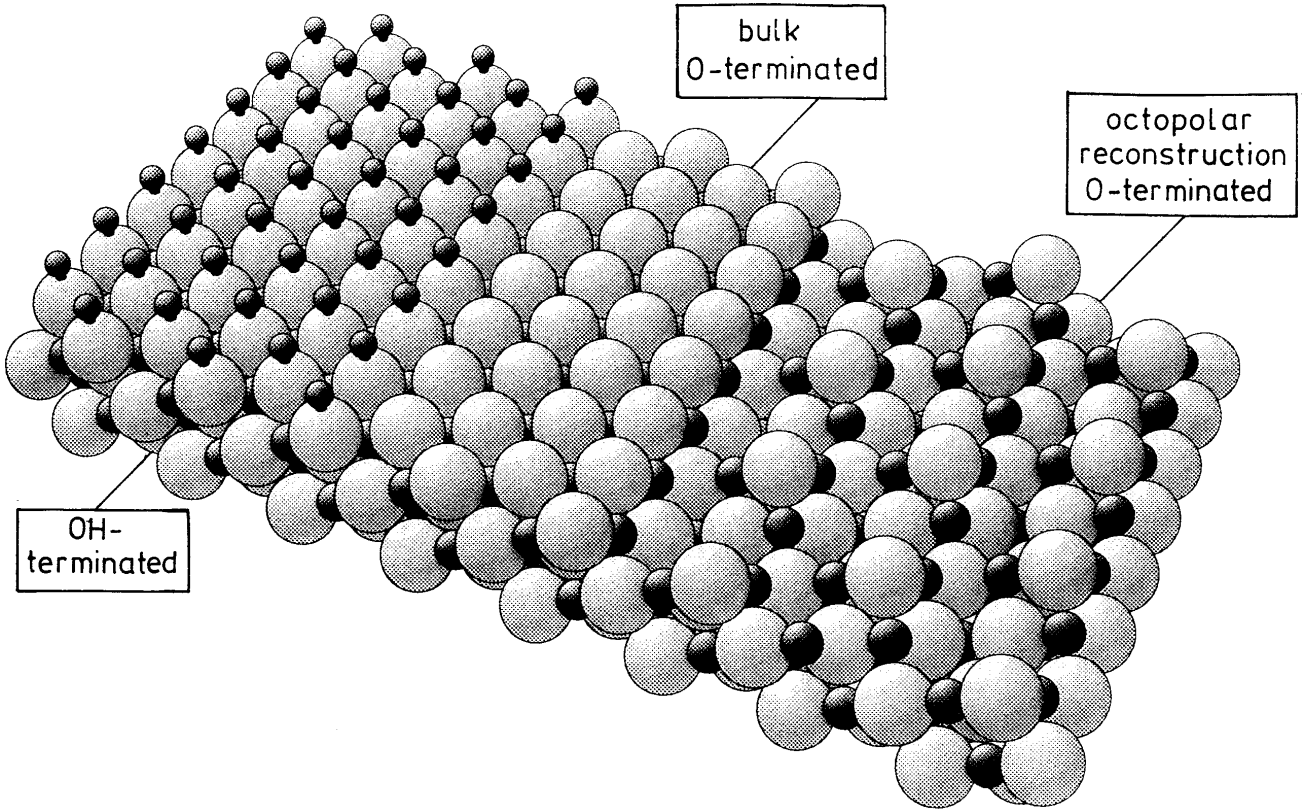
Energy in AO(nkl) surfaces



H.-J. Freund, Faraday Discuss. **114** (1999)

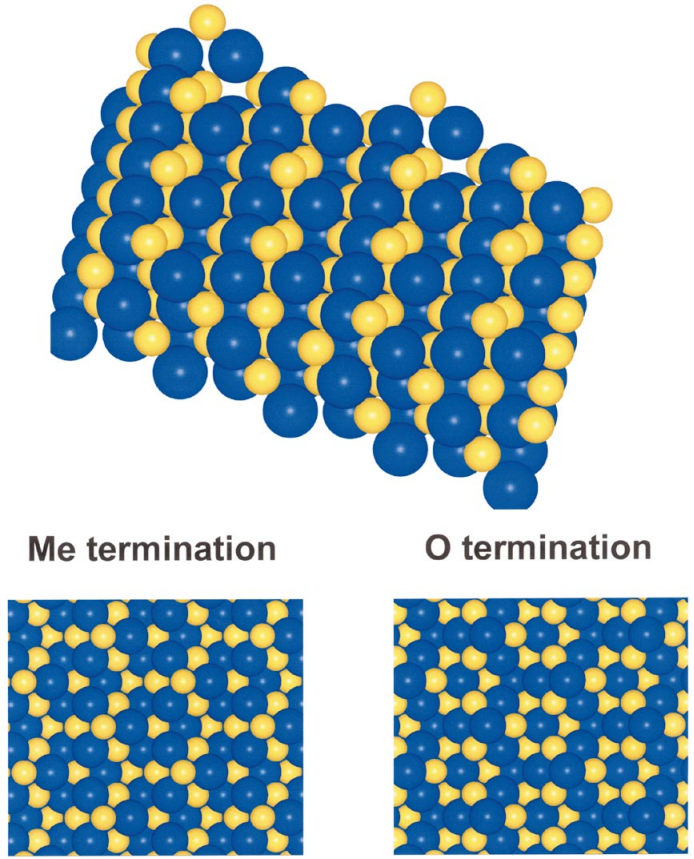
Stability of Oxide Surfaces

Corundum Type Surfaces



Oxide Surface Structure

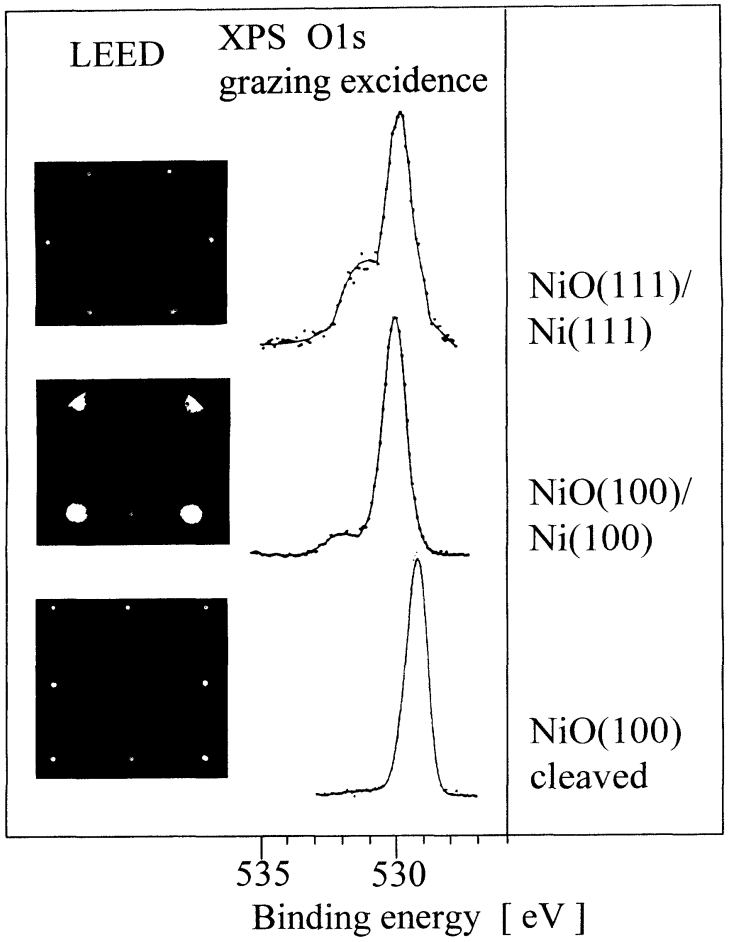
Reconstruction of AO(111)



H.-J. Freund, Faraday Discuss. **114** (1999)

Oxide Surface Preparation

Single Crystal vs. Thin Films

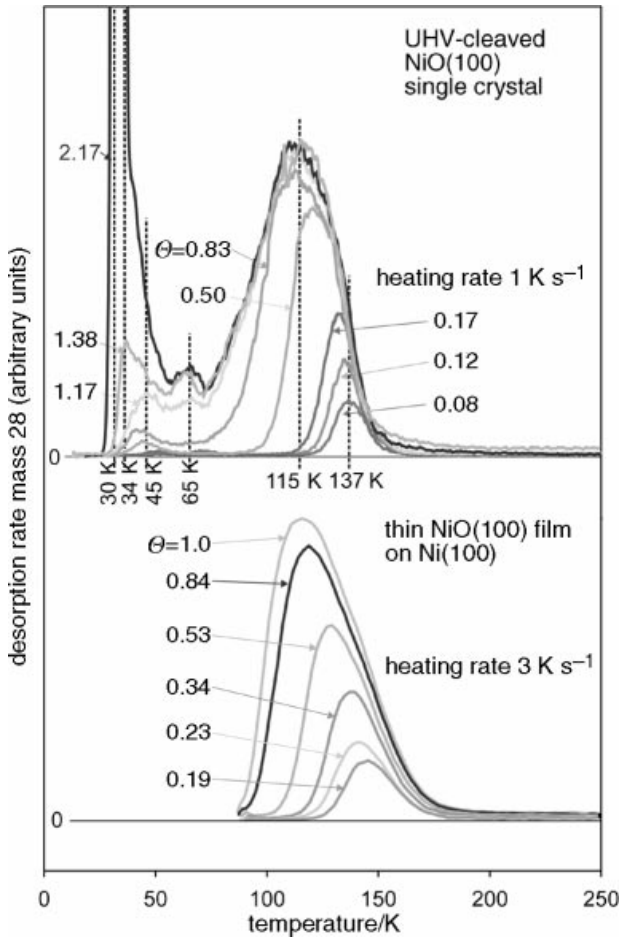


F. Rohr, K. Wirth, J. Libuda, D. Cappus, M. Bäumer, H.-J. Freund, *Surf. Sci.* **1994,** *315*, L977;

D. Cappus, M. Haßel, E. Neuhaus, M. Heber, F. Rohr, H.-J. Freund, *Surf. Sci.* **1995**, *337*, 268

CO/NiO(100)

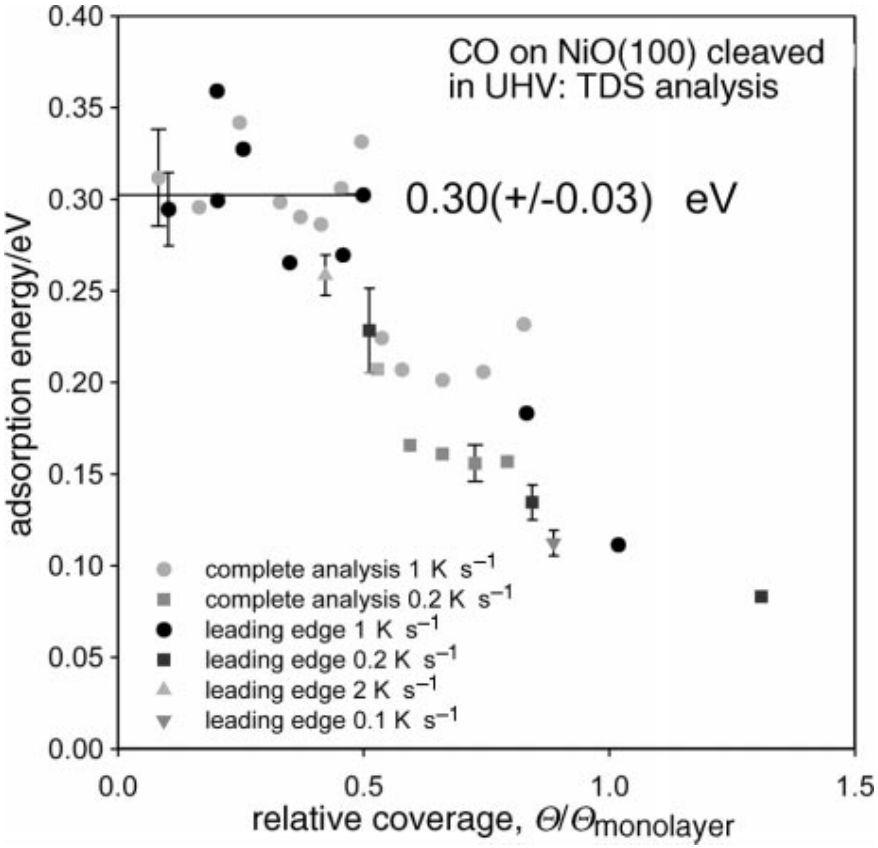
TDS comparison between bulk single crystals and thin films



H.-J. Freund, Faraday Discuss. **114** (1999)

CO/NiO(100)

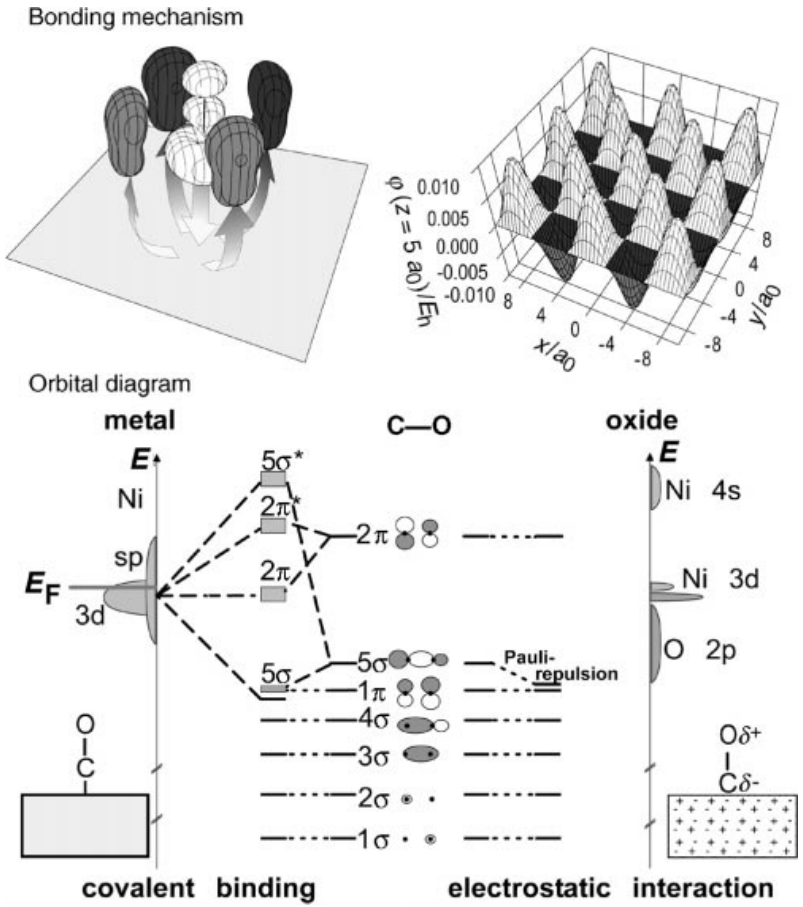
TDS coverage dependence



H.-J. Freund, Faraday Discuss. **114** (1999)

CO/Ni(100) vs. CO/NiO(100)

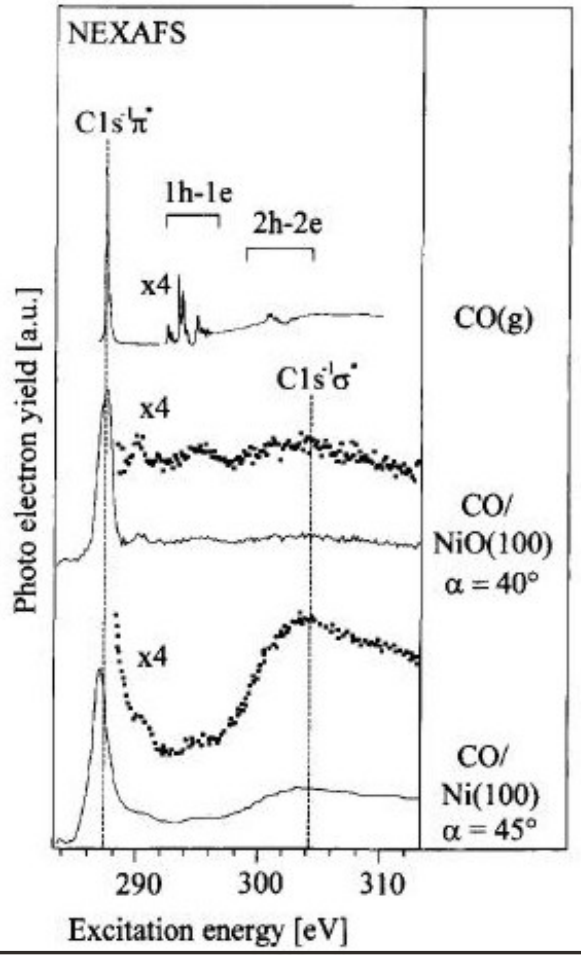
Bonding characteristics



H.-J. Freund, Faraday Discuss. **114** (1999)

CO/NiO(100)

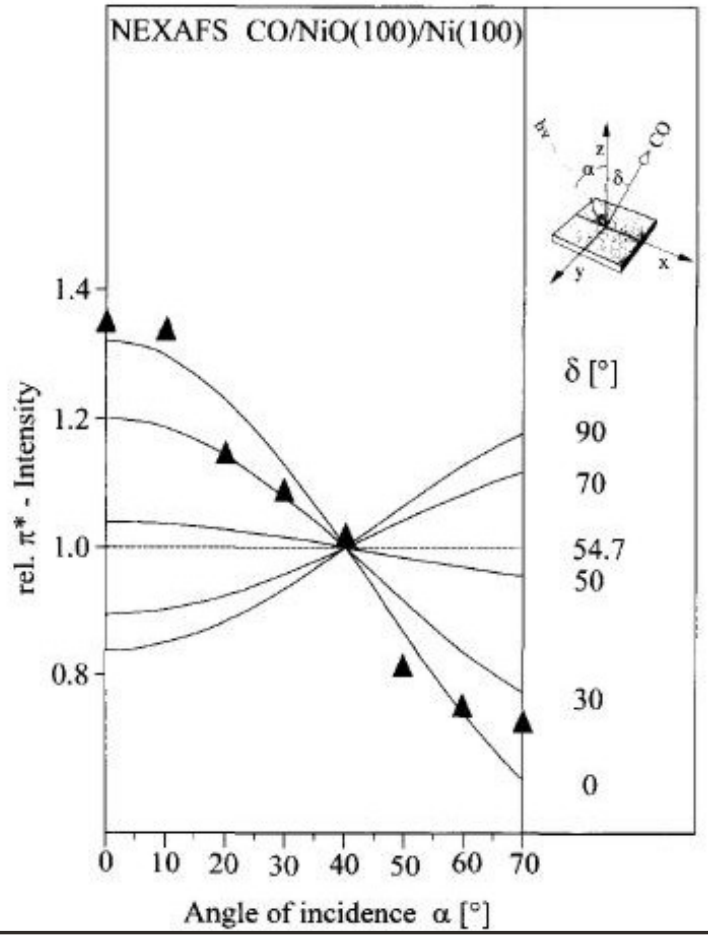
Comparison with CO/Ni(100) and free CO



D. Cappus et al, Surf. Sci. **325** (1995)

CO/NiO(100)

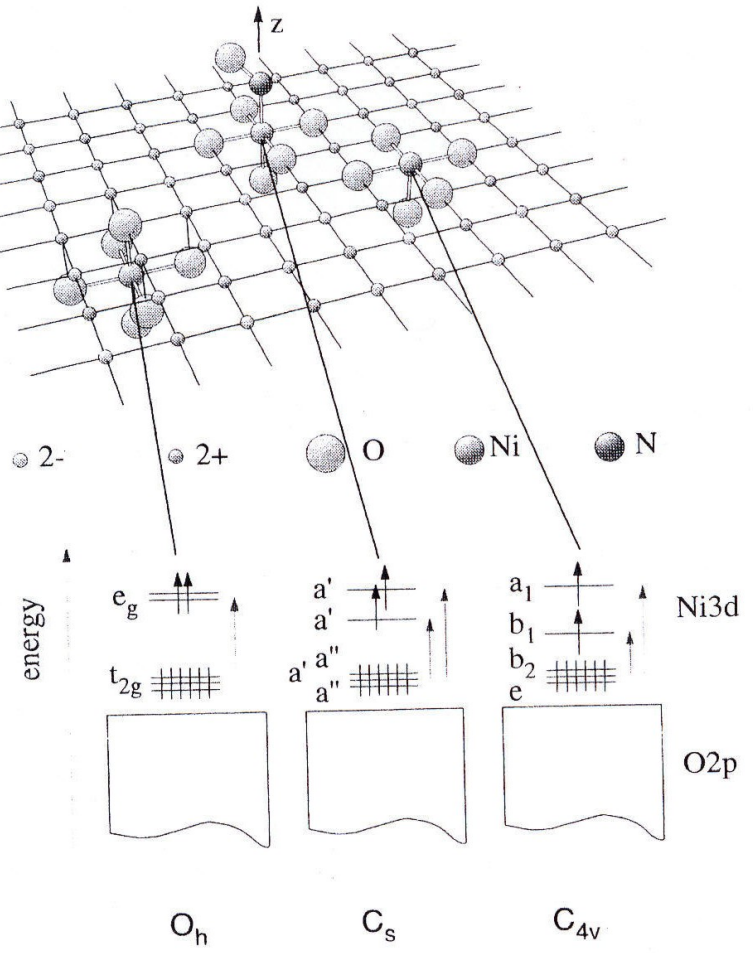
Angular dependent NEXAFS



D. Cappus et al, Surf. Sci. **325** (1995)

NiO(100)

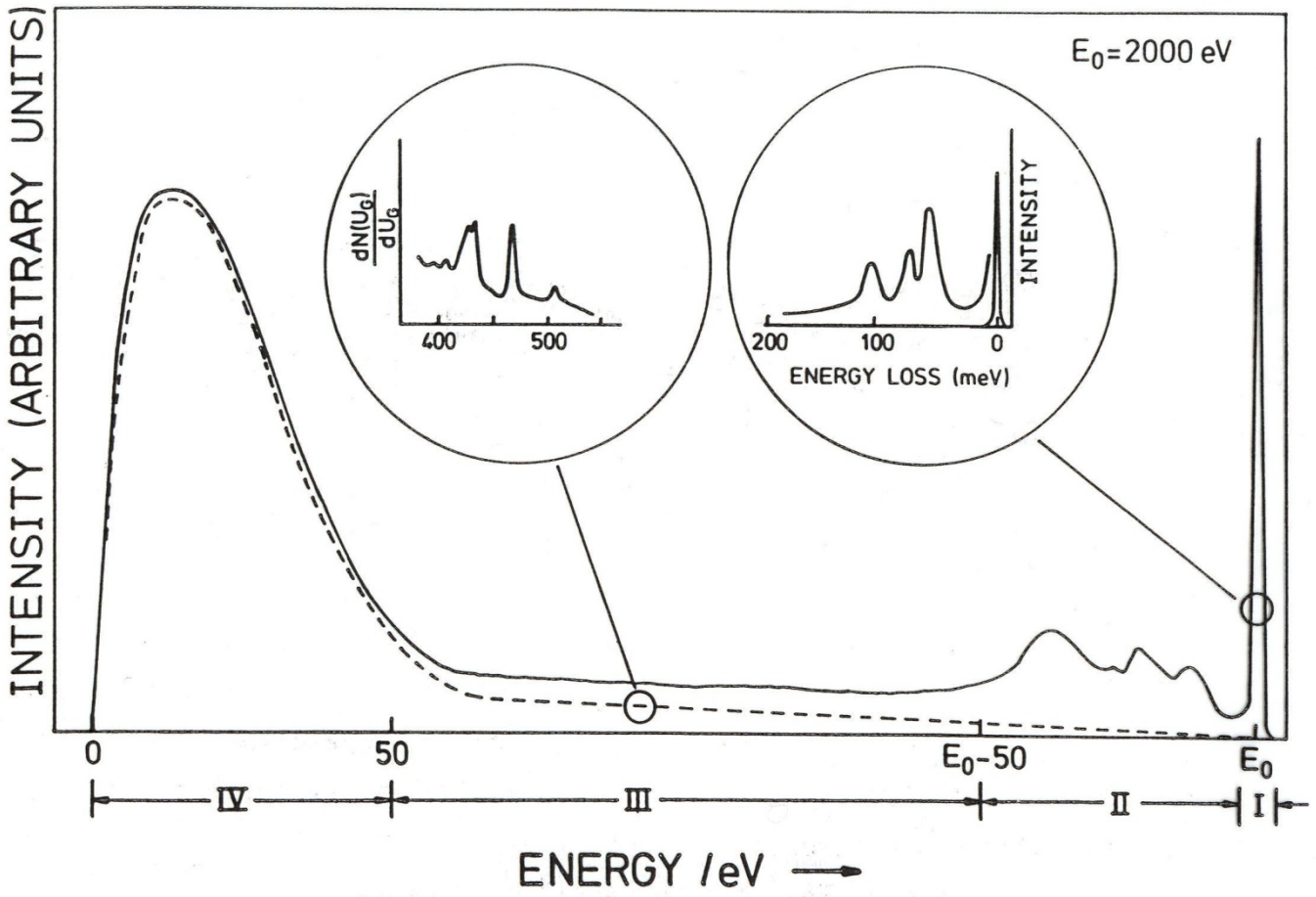
d-derived surfaces states



H.-J. Freund et al., Reports on Progress in Physics, **59** (1996)

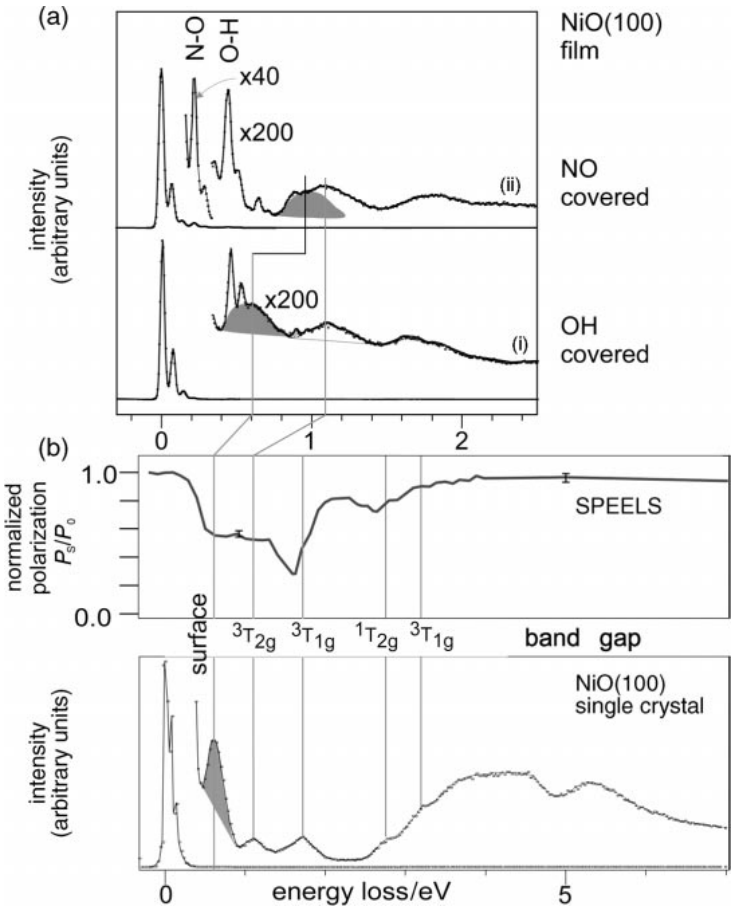
Electron Scattering

Loss Mechanisms



CO/NiO(100)

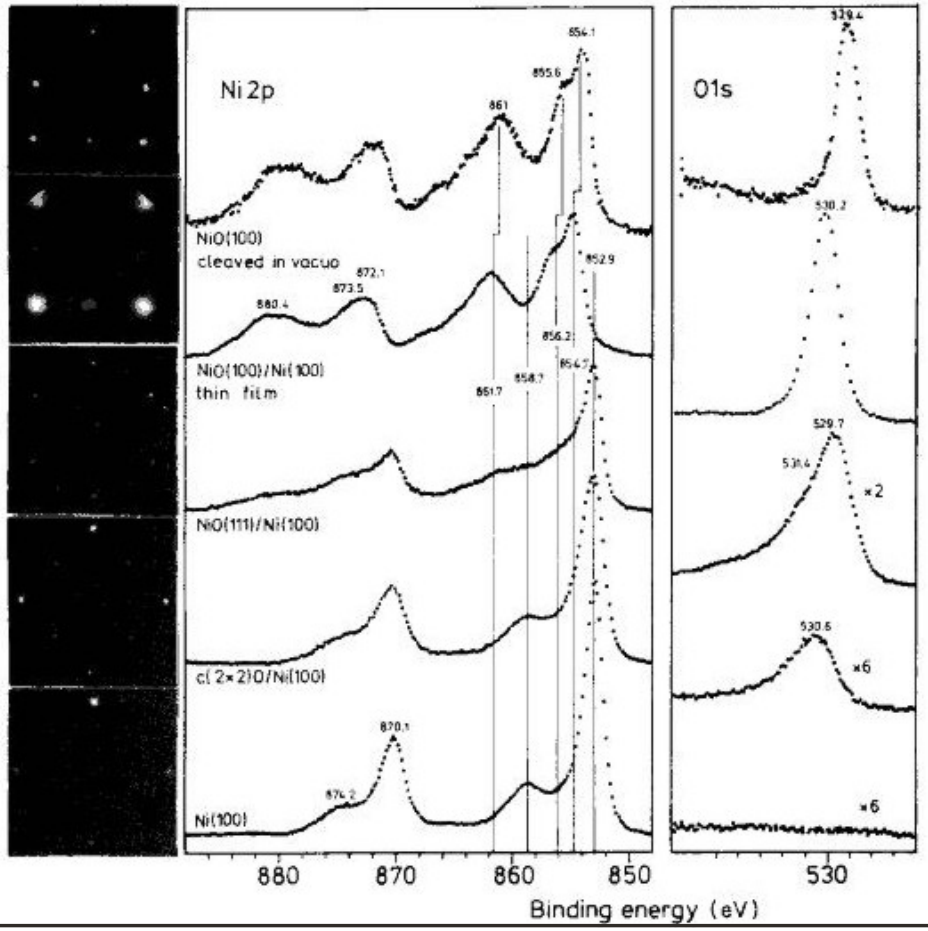
EELS/SPEELS

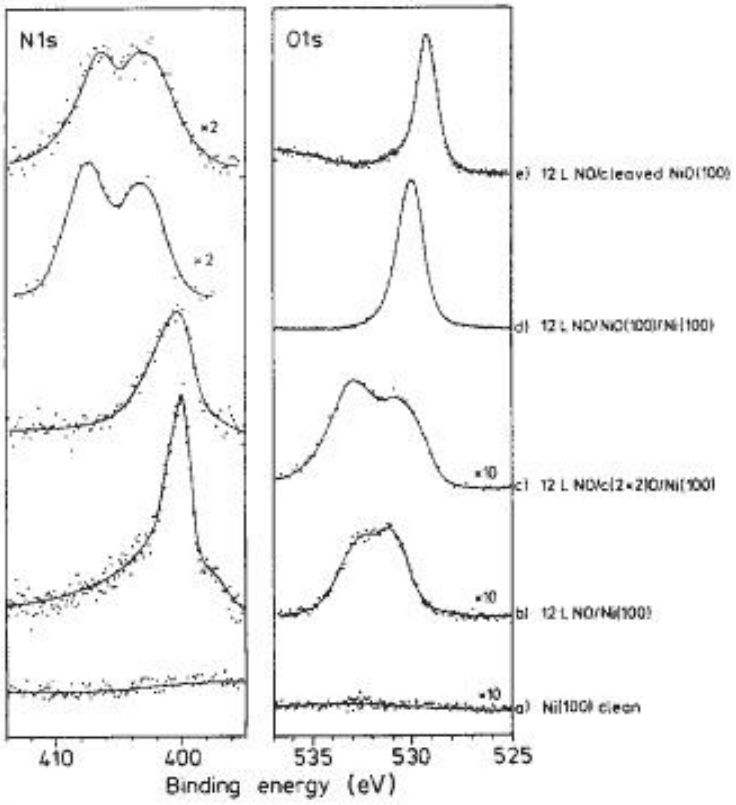


H.-J. Freund, Faraday Discuss. **114** (1999)

Photoemission

NiO(100) and NO/NIO(100)

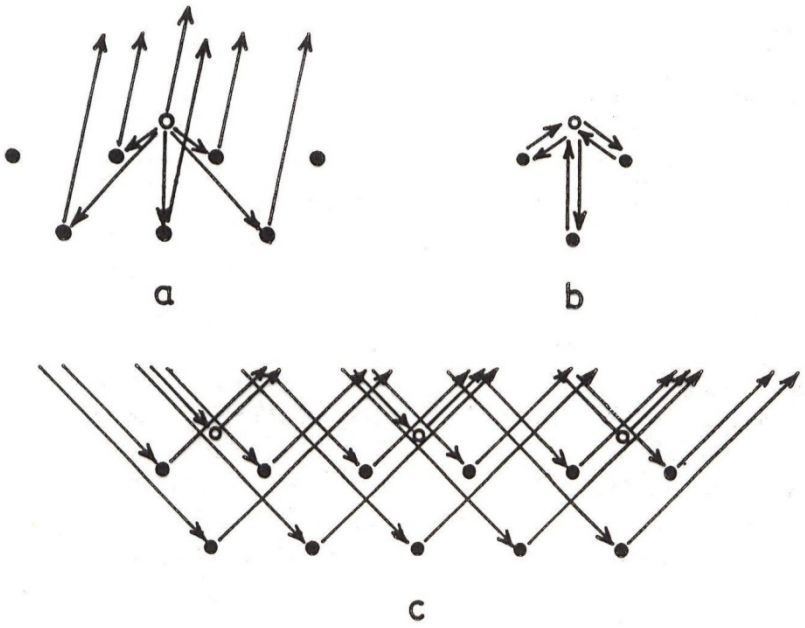


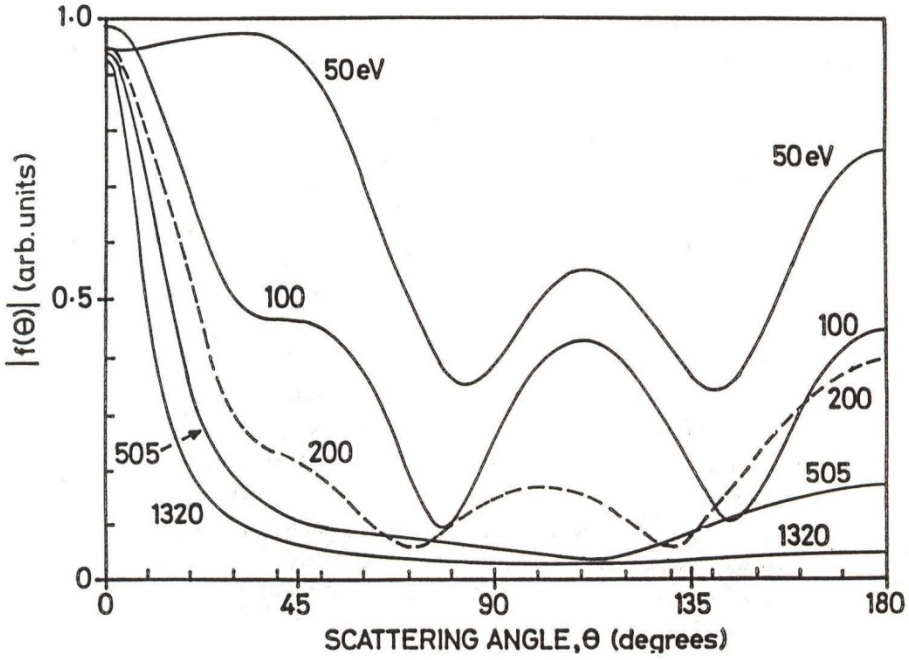


H. Kuhlenbeck et al., Phys. Rev. B **43** (1991), 1969

Photoelectron Diffraction

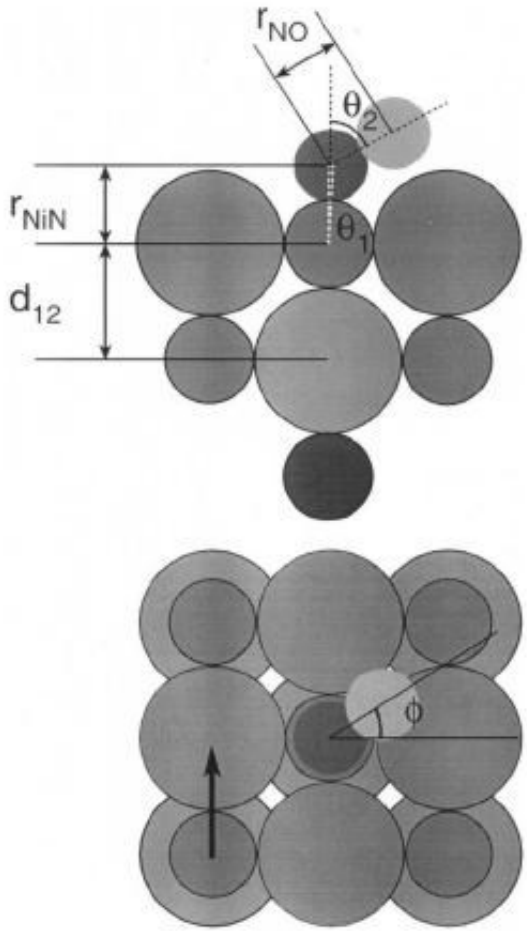
Schematic and Scattering factors

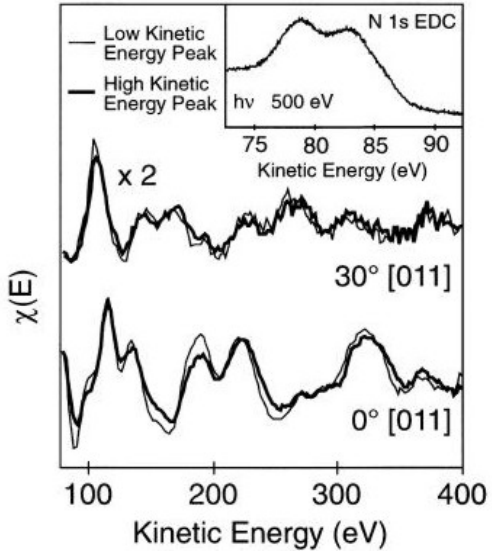




Photoelectron Diffraction

NO/NiO(100)



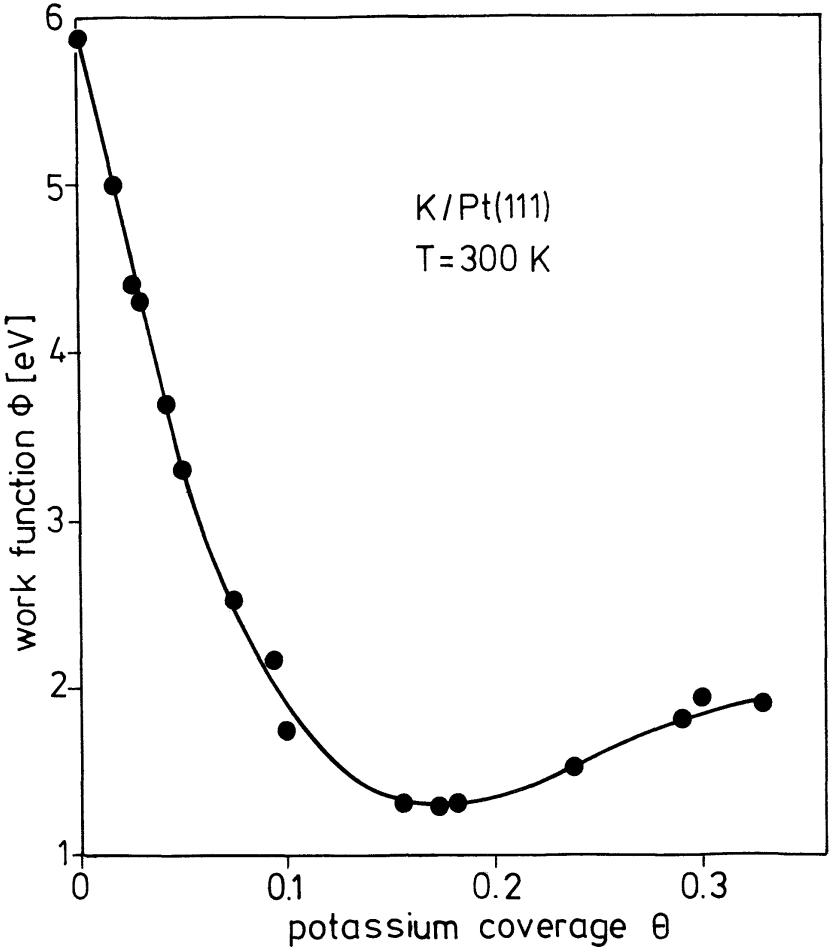


Parameter	Value
r_{NiN} (Å)	1.88 ± 0.02
Θ_1(°)	+3 / -8
r_{NO}(Å)	1.12+*/-0.15
Θ_2(°)	59 + 31/-17**
D_{12} (Å)	2.07 ± 0.04
	(1.8 + 4.2/-1.8) x 10^{-2}
	(3.8 ± 1.9) x 10^{-3}

R. Lindsay et al., Surf. Sci. **425** (1999), L401

Work Function Changes

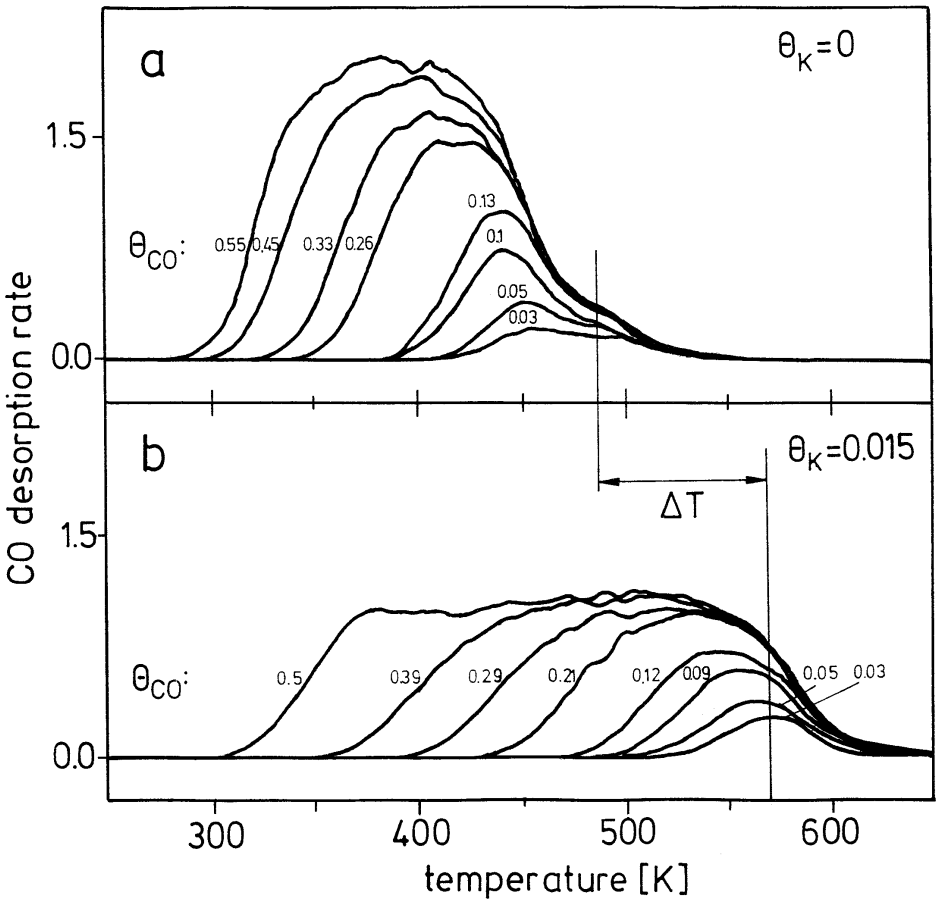
Alkali Adsorption



M. Kiskinova, G. Pirug, H.P. Bonzel, *Surf. Sci.* **1983,** *133*, 321

Thermal Adsorption Spectra

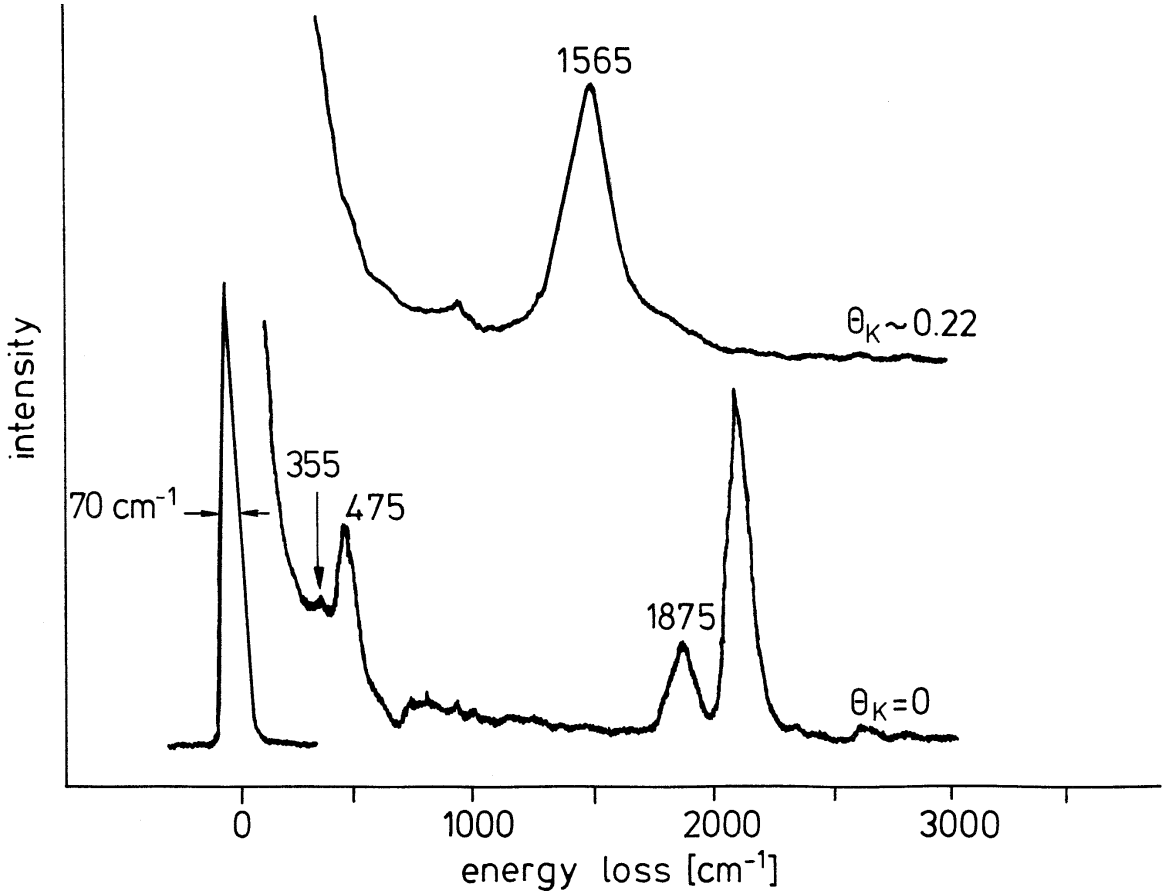
K/Pt(111) as a Function of K Coverage



L.J. Whitman, W. Ho, *J. Chem. Phys.* **1989,** *90*, 6018

Alkali-molecule Interactions at Surfaces

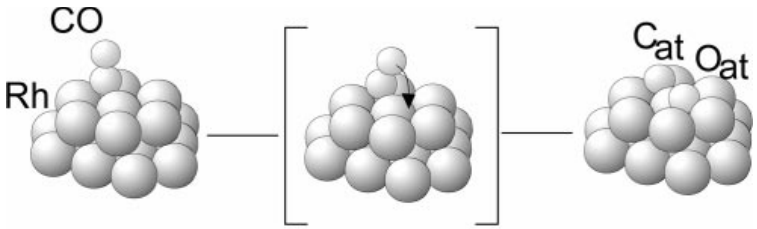
CO/K/Pt(111) EELS

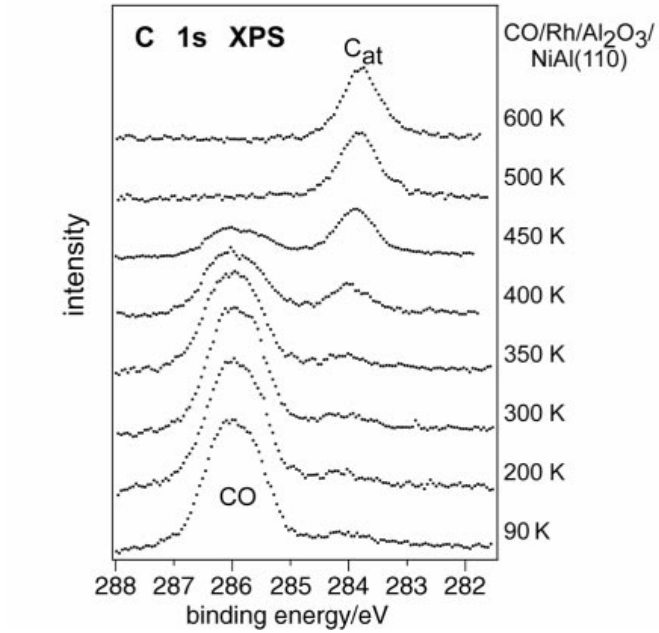


J.E. Crowell, E.L. Garfunkel, G.A. Somorjai, *Surf. Sci.* **1982,** *121*, 303

Photoemission

CO/Rh/ alumina Temperature Dependence

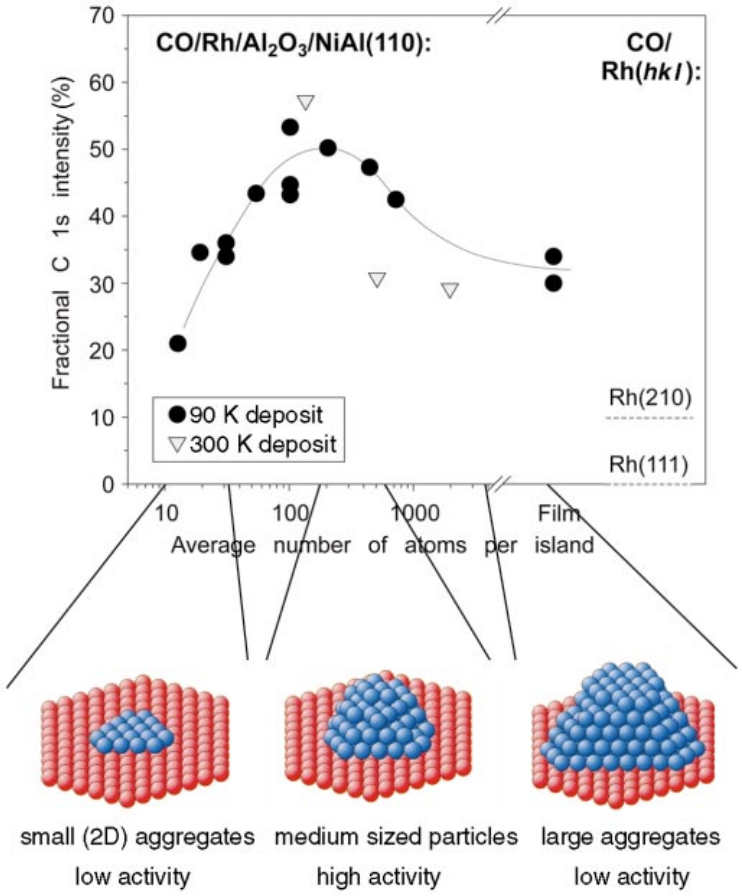




H.-J. Freund, Faraday Discuss. **114** (1999)

Photoemission

CO/Rh/ alumina Size Dependence



H.-J. Freund, Faraday Discuss. **114** (1999)

Microcalorimetry

CO/Pd/ ironoxide Size Dependence