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SMR. 628 - 16

Research Workshop in Condensed Matter, Atomic and Molecular Physics (22 June - 11 September 1992)

Working Party on: "Energy Transfer in Interactions with Surfaces and Adsorbates" (31 August - 11 September 1992)

"Inelastic Effects in the Electronic Spectra of Adsorbates" (Part I)

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INELASTIC EFFECTS in (1*(2)

1) the electronic spectra of adsorbates

2) electron and photon stimulated desorption from surfaces → (Dietrich)

Dietrich MENZEL

Inelastic effects ↔ transfer of energy and/or charge

i.e.: influences of
COUPLING
of a molecule to a substrate on

- excitation
- deexcitation] → 1)
- fragmentation → 2)

In time-dependent picture:
DYNAMIC EFFECTS

Study as function of coupling strength

Restrict to CORE excitations

CORE EXCITATION-INDUCED DYNAMICS IN SURFACE MOLECULES

DYNAMICS INDUCED IN MOLECULES BY ELECTRONIC EXCITATIONS:

- Electronic evolution
- Evolution of nuclear coordinates

Particularly interesting: comparable ≈

CORE-INDUCED DYNAMICS:

- Bound resonances vs. continuum exc.
- Decay spectra observable
- Coupling to vibration / dissociation (1)
- Decay times known: internal time mark

SURFACE MOLECULES:

Coupling to continuum causes:
shifts and broadening of levels
Energy and charge exchange

Time scales of these may again be comparable to internal time scales

Generally expected:

COUPLING

of discrete system with continuum

will lead to

SHIFTS and BROADENING

$\Delta + i\Gamma$

QUESTIONS:

What are the effects?

What are their mechanisms?

What physical picture implied?

Ingredients:

Polarization screening of charges

Charge transfer screening

Coupling to phonons and e-h exc. (w.a.)

Chemical interactions: in initial state
in final state

Variation of coupling strength

same surface, different (coad.) molecule:

CO vs. N_2 on TM

same molecule, different surfaces:

CO on Cu, Ru, Pt, Ni, Ni/O

same molecule, same surface, different state:

O_2 on Pt(111)

spacer layers: CO, N_2 on Xe (Ar) mono-l. or multil.

Varied hydrogen bonds: condensed H_2O, H_2S, NH_3, vs. CH_4, C_6H_6

Excitations:

Discrete (neutral(s))

Continuum (ionic f.s.)

Satellites

Deexcitations:

From discrete → 2 le, 1h (autoionization)

- cont. → 2h (Auger)

1. Excitations

Core excitations

no chemistry in initial state
well-defined decay processes (→ 2.)
internal time mark by core life time

Continuum excitations	Discrete excitations
Core ionization: XPS, SEXAFS, PED)	Neutral final state NEXAFS)

Valence excitations

chemical interaction in initial state possible: differential shifts
two-dim. overlap: 2D bands
(ARUPS)

Observations for (core) ionization: of adsorbates ("ionic" final states)

BE shifts

condensed multilayers: 1 - 1.5 eV
physisorbed monolayers/met: 1.5 - 2 eV
chemisorbed molec./metal: up to 8 eV(

difficulty: local potential

Broadening

loss of vibr. structure + few tenths eV

Explanations:

multilayer: polarization; phonon exc.
physis. monol.: image charge screening; phonon + eh exc.
chemisorbed: charge transfer screening; phonon + eh exc. (+ CI)
vibr. exc. of ad molecule

Consequence:

(dynamical counterpart of static scr.)

Additional satellite intensity
(for sudden excit.; sum rule)

image charge scr. → plasmon sat.
CT sat. → valence shake-up ("shake back")

"Grand satellites" (final state splitting) for intermediate coupling

こちらが転写面です。

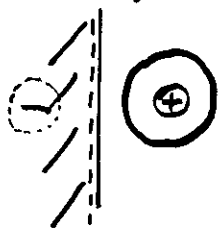
Change of E_B with adsorption:

$$\Delta E = \Delta E_i + \Delta E_f$$
$$= \Delta E_{ch} + \Delta E_p + \Delta E_f$$

ΔE_f : additional screening of core hole

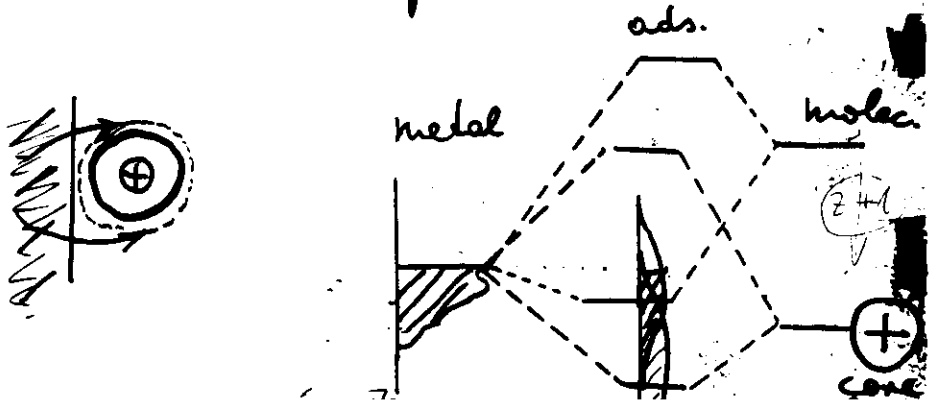
On metal surface:

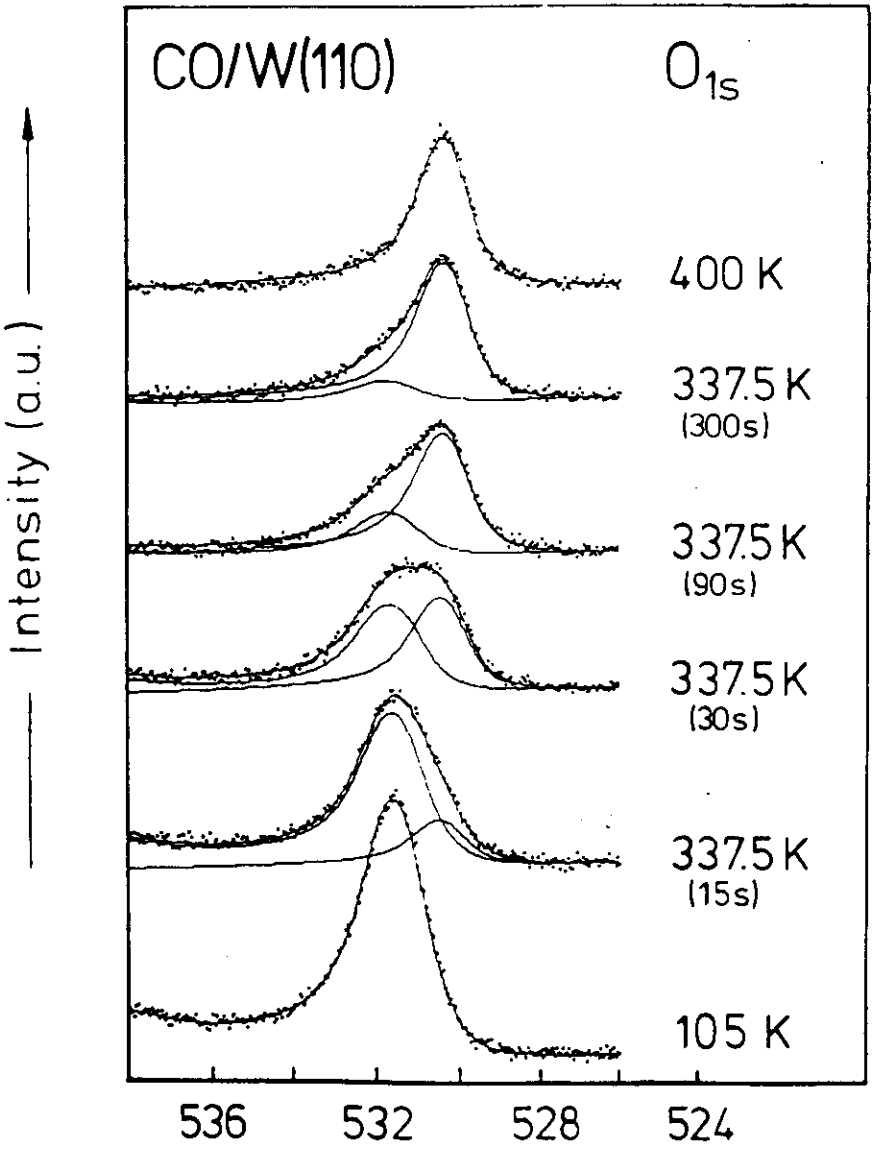
a) Image force (plasmons)



$$\Delta E = \frac{e^2}{4r} \approx 0{,}5\text{-}2\,eV$$

b) Charge transfer into unoccupied orbital on ads.





Adsorbate core level shifts:

ΔE_i (molecular vs. dissoc. CO)

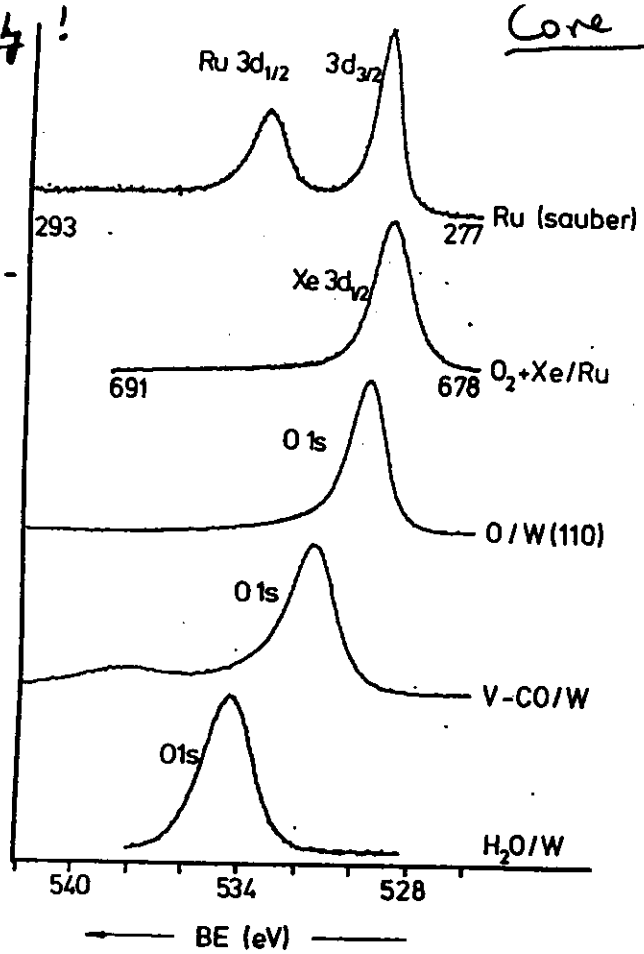


Abb.VI.4.1 Linienformanalyse an verschiedenen Substrat- und Adsorbatniveaus. Die Punkte entsprechen der Messung, die durchgezogenen Linien sind das Ergebnis der Fits. Die angegebenen Energiewerte beziehen sich auf die jeweiligen Anfangs- und Endpunkte der Kurven; für O_{1s} gilt die m-Skalierung

Core level line shapes : broadening
Asymmetry

Asymmetry $\propto$ polarizability

image charge screening (Gunnarsson - Newns) :

$$\alpha = \ln(1.6\, k_{TF} \cdot d)/8d^2k_{TF}^2$$

Expected ~ 0.03

Measured : Xe/Ru 0.05
Xe/O/Ru 0.04
N_2O/Ru 0.03

charge transfer screening (Schönhammer - Gunnarsson - Gunnarsson)

$$\alpha \sim |V_c \cdot g_{ns}(0)|^2$$

Expected : 0.1 - 0.3
Measured : 0.1 - 0.2

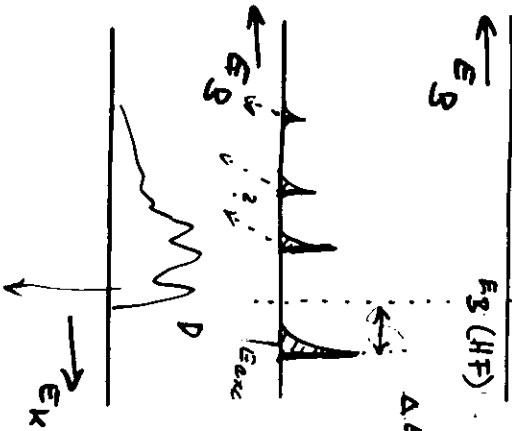
Umbach (1980)

CORE IONISATION :

ADIABATIC EXCITATION

SUDDEN EXCITATION

DECAY



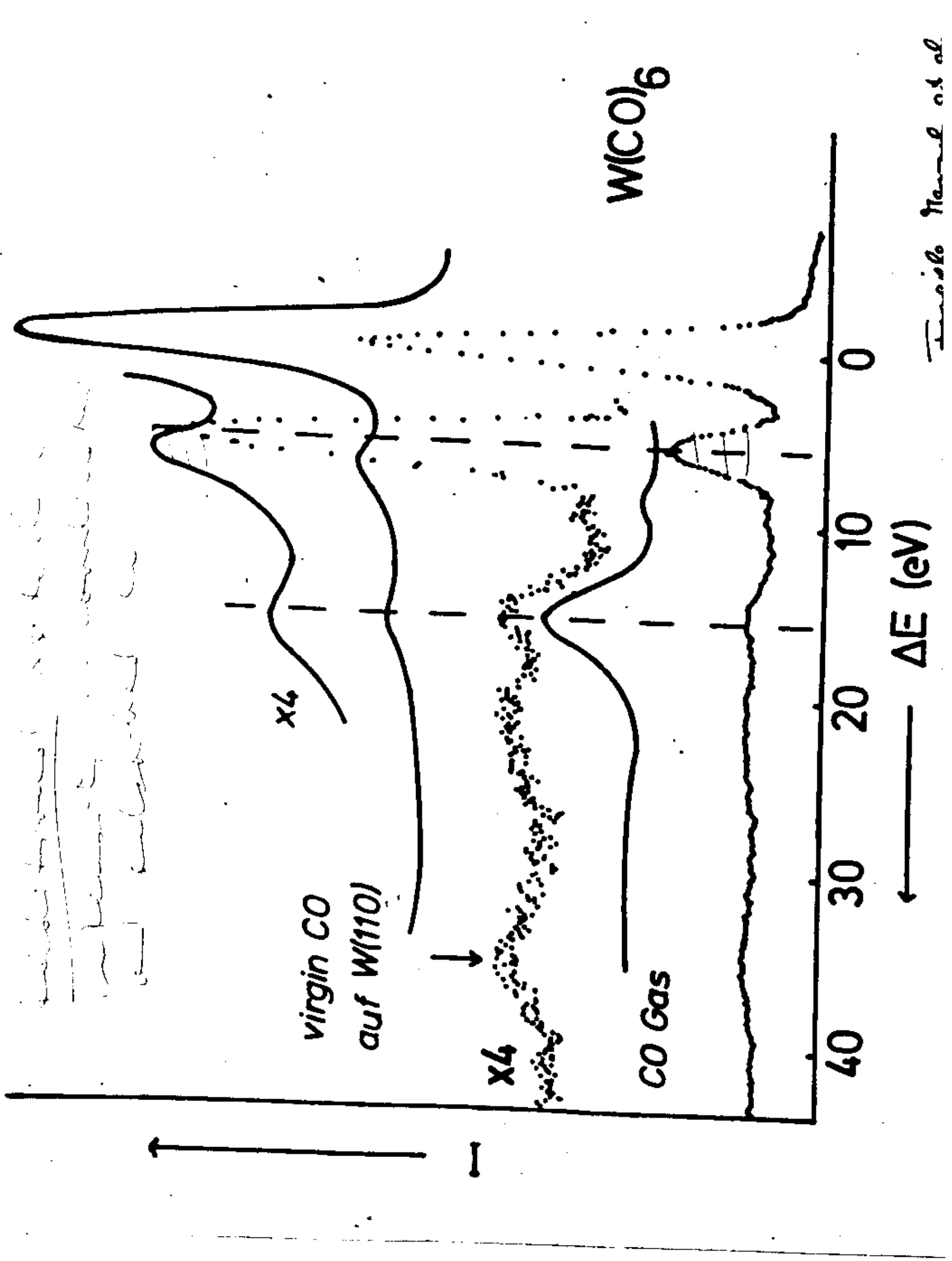
Highest energy line :
$E_K(max) = E_{exc} - 2E_V(min) - U_{eff}$

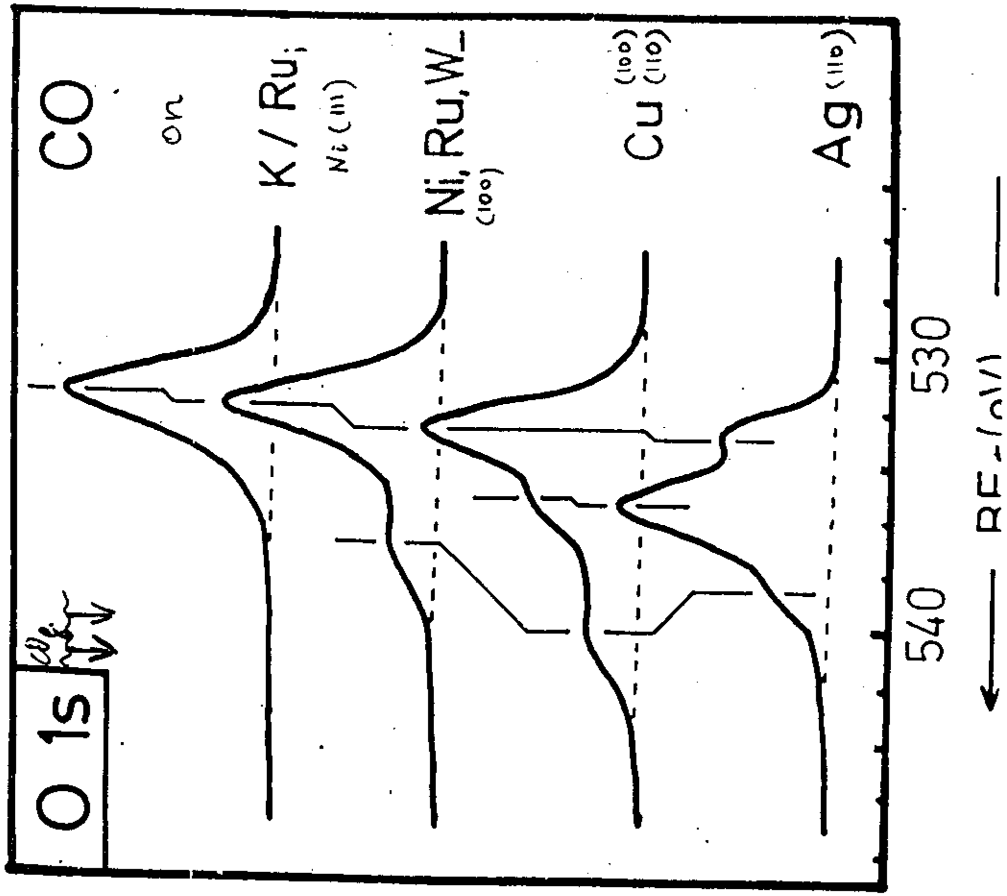
Adsorbates :

Additional relaxation
- image charge screening
- inhomogen screening
- charge transfer screening

Additional shake-up

2. Influence on decay spectra ?





Final state splitting
(screened – "unscreened")
for strong – intermediate – weak
coupling

SURFACE EFFECTS in DISCRETE CORE EXCITATION:

("NEXAFS" (orientation); neutral final states)

Shifts: small to negligible (nature of exc. state) surface vs. bulk

Broadening: Loss of vibr. structure (phonon, e-h coupling
- sharpness of Rydberg (↑) life time!

→ transfer of exc. en.?

Examples: Ar (ΔE, surface vs. bulk; inner and outer continua 2p bands)

N_2 (vibr. structure; Rydberg)

CO (loss of - + broadening)

(NH_3, H_2O, C_6H_6); O_2/Pt

⇒ Broadening

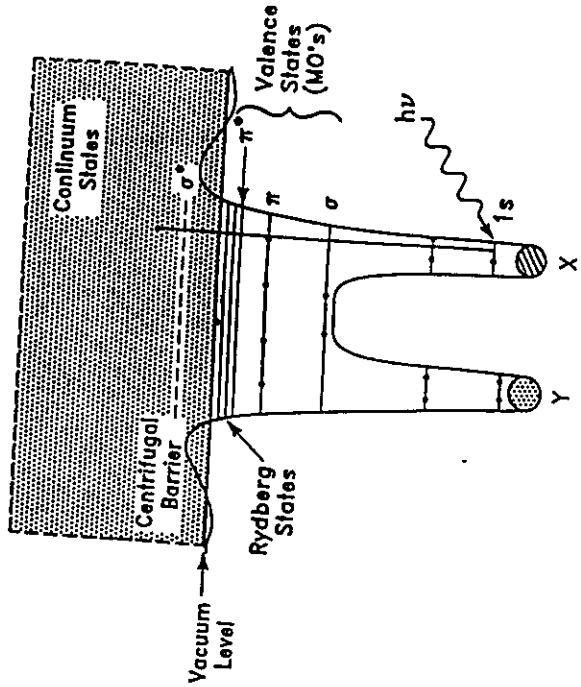
Small for multilayer and physis. ML or ads. on RG ML (vibr. structure preserved)
⇒ $\tau_e > \tau_c$

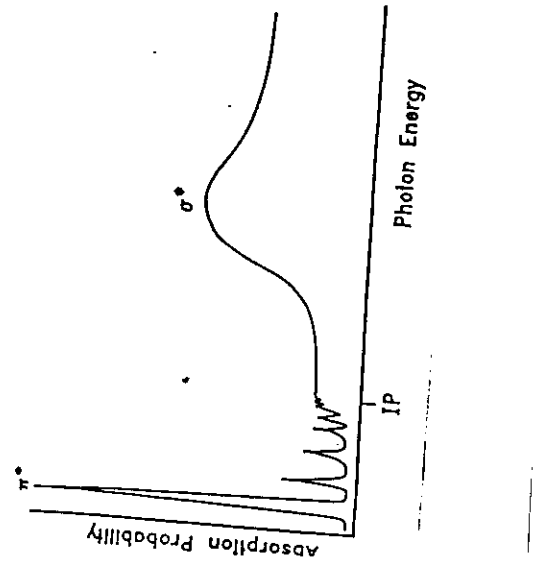
Large for chemisorbed ML ⇒ consequences for decay sp.
⇒ $\tau_e < \tau_c$

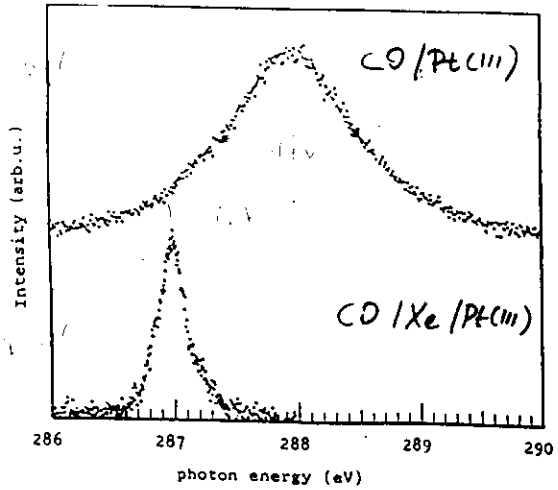
But: for chemis. ML observed:
$\Delta E_{direct} > \Delta E_{coul}$
(=)

Consequence: two ionization thresholds!

Core-to-valence excitation of free molecule

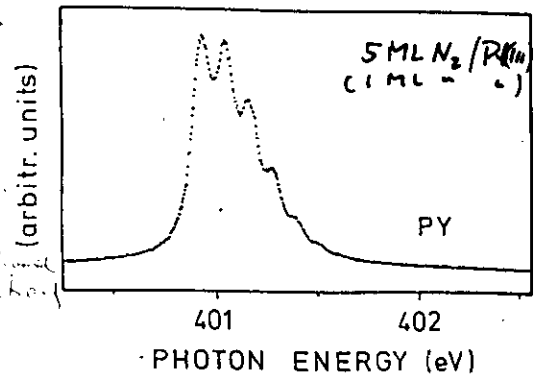




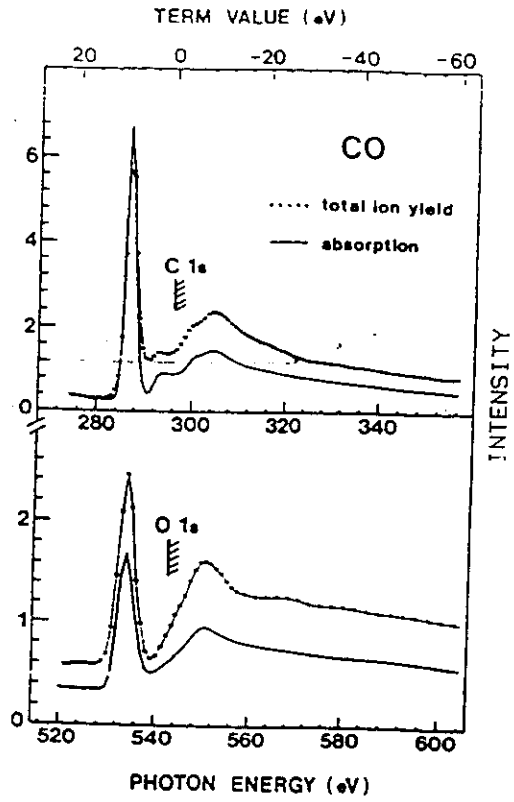


Wurth, Feulner, DH, IWASES91

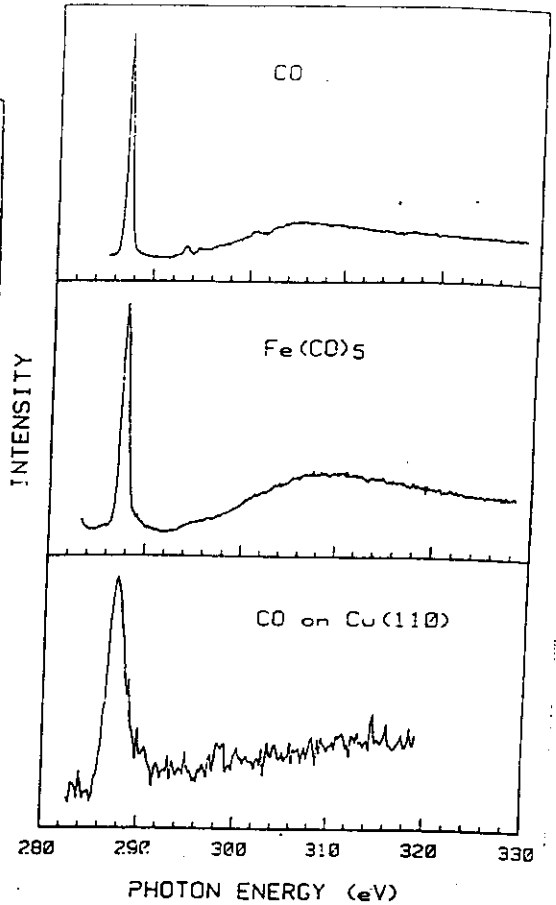
(Phys. Scr. 92) T41 (92) 213



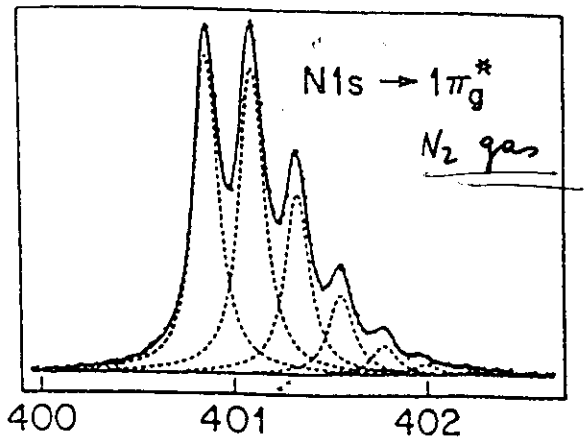
Schoenerer et al. 1992



Hitchcock et al.



Eberhardt et al.



Chen et al. PRA(1989)

	CO_{gas}	CO/Cu(100)	CO/Ru(001)	CO/Ni(111)	CO+K/Ni(111)
C 1s	296.2 [a]	286.3	285.7	285.5	285.2
C1s→2π	287.3 [b]	286.4	286.5	287.0	286.7
O1s	541.6 [a]	533.3	532.0	531.1	531.0
O1s→2π	534.1 [b]	532.9	532.6	532.6	532.2

a) From ref.6; referred to the Vacuum level.
b) From ref.7.

Wurth et al.

Energie of neutral vs ionic core excitation of CO (free and adsorbed)

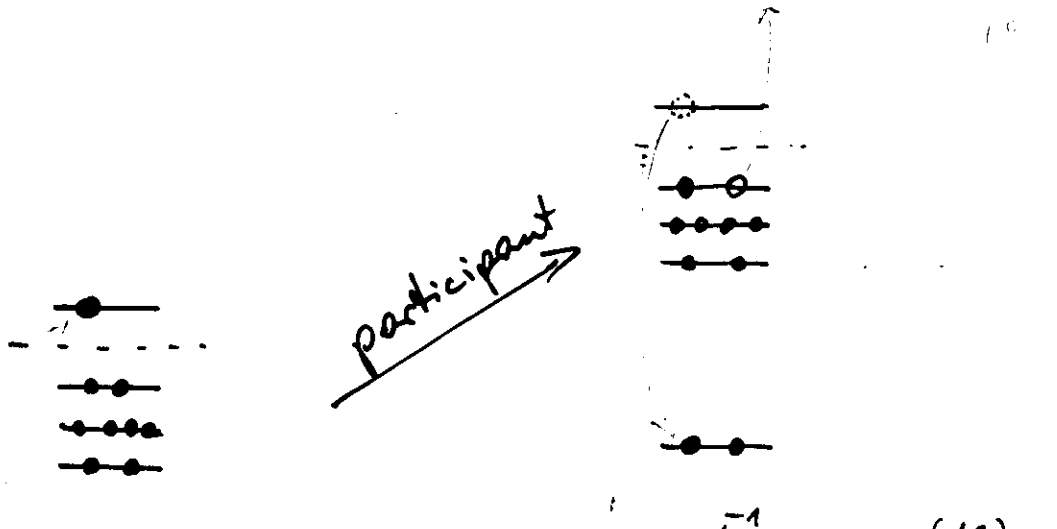
2. Electronic evolution: deexcitation of core holes

Remember:
Isolated atom / molecules

Decay of core ion: Auger 2h states

Decay of core-to-bound: Autoionization, neutral
- Participant → 1h
- Spectator → 2h 1e

Competing satellites, cascades)



Observations on surface:

Chemisorbate on metal:

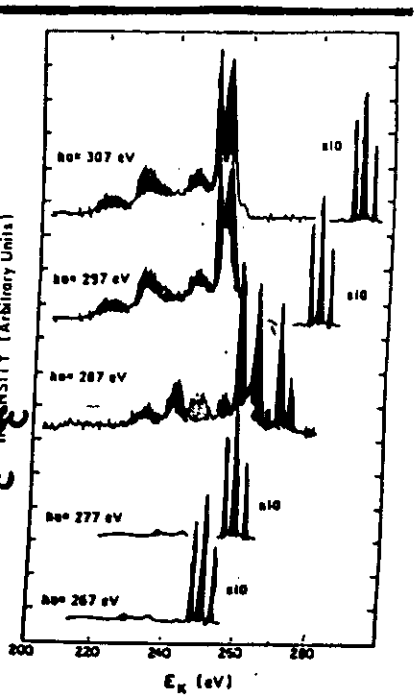
Normal and resonant Auger are IDENTICAL !
both for strong and intermediate coupling (satellites have decayed !)
Even for rare gas monolayers !
but not for molecular physisorbates (N_2) and decoupled molecules

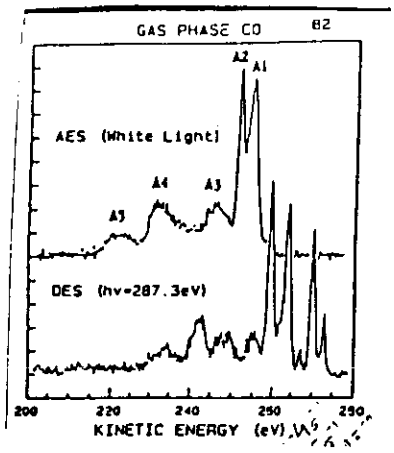
⟹ Evolution during τ_c

Decay of core resonance

Normal Auger
Valence PE

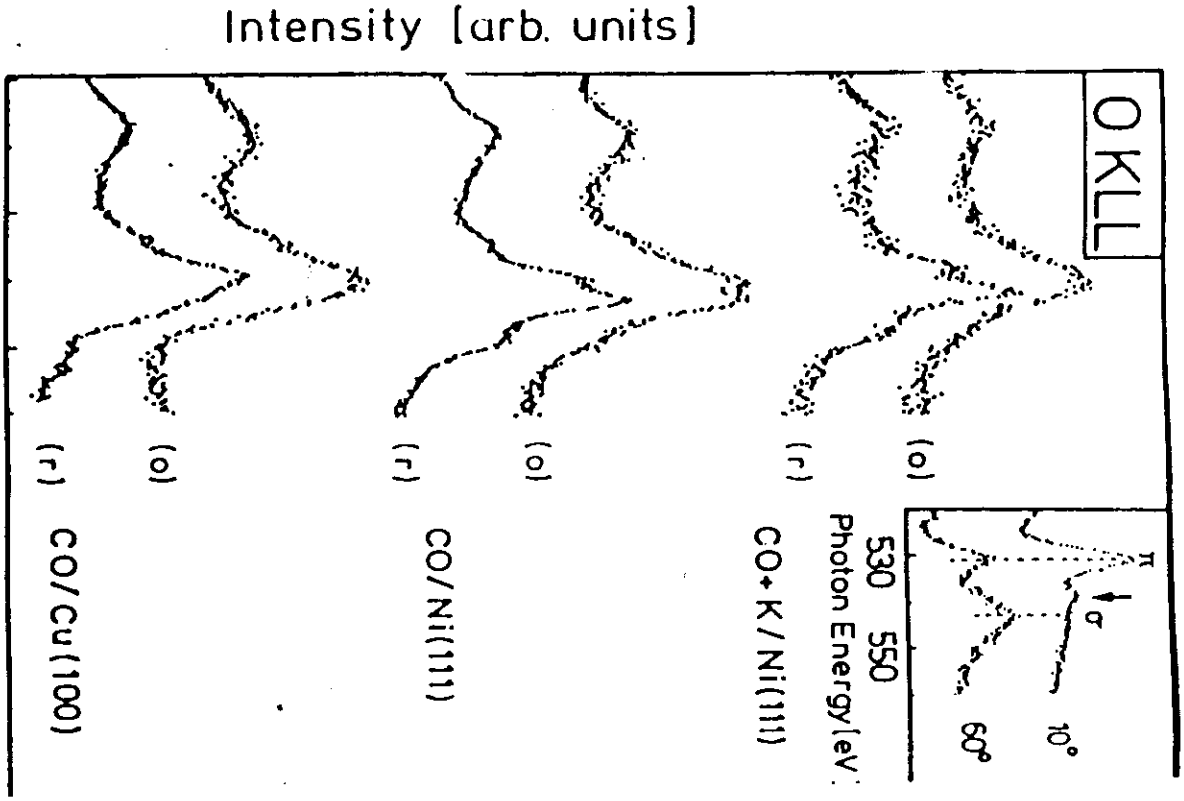
participant Auger
spectator Auger





Gas phase CO, autoionization vs. Auger

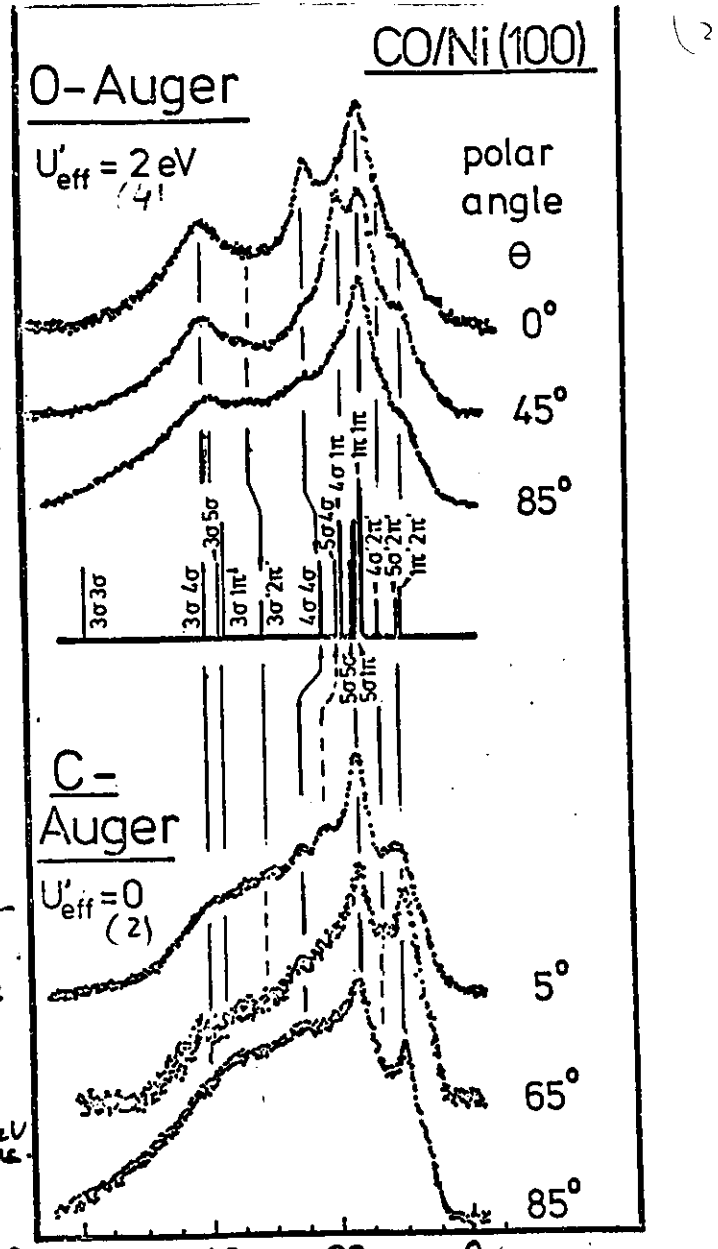
Eberhardt et al.



adsorbed CO
no difference
between gas
phase core-to-bound
and continuum

CVV

ASSIGNMENT OF THE CVV AUGER FINAL STATES FROM ANGULAR DISTRIBUTIONS



$W_{fi} = |\langle V_1 V_2 | \frac{e^2}{r} | c\,\beta \rangle|^2$

Monopde selection rules

Screening energy ≈ 12eV → 3 × E_{1s}

$U'_{eff} = E_B^{(2)} - \sum E_B^{(1)}$

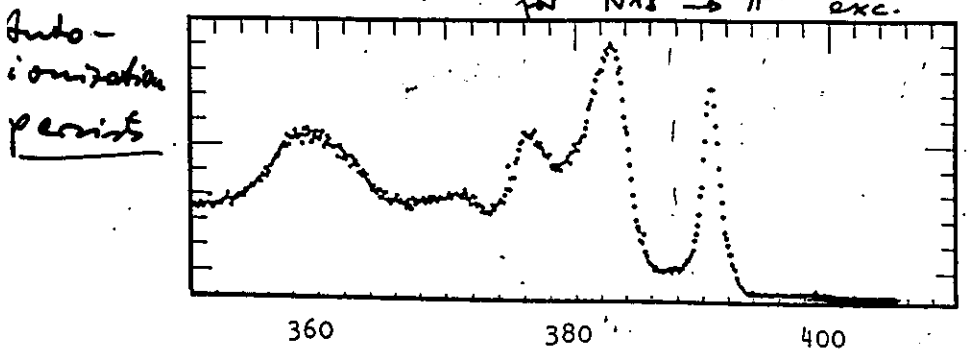
Relax: ~18eV → 2-4eV charge-

Lines derived from screening orbital!

generally: high energy shoulders

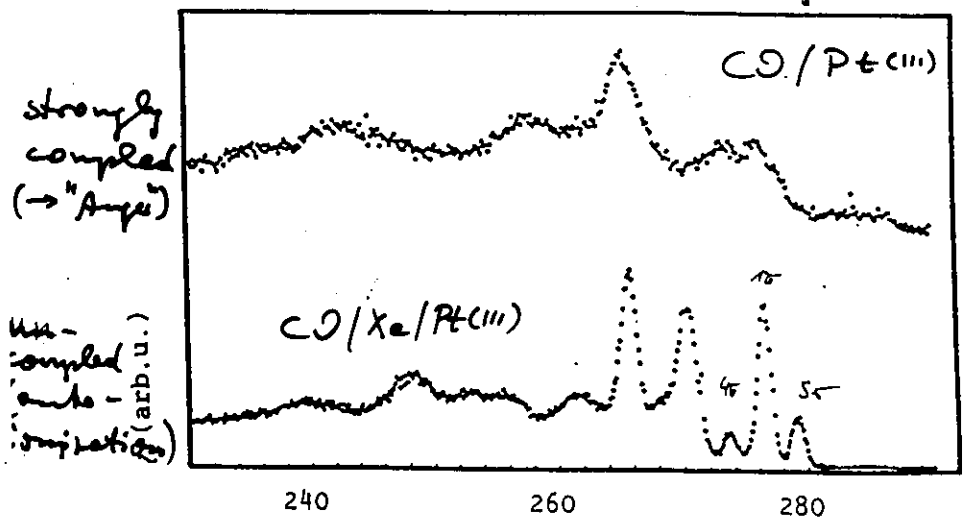
Kumbach u. Hussein (1984)
PRL 52 (1984) 457

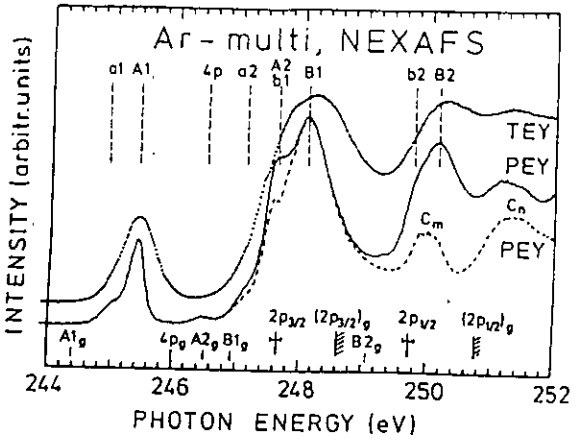
Decay spectrum of 1 ML N_2 / Pt(111) for $N_{1s} \rightarrow \pi^*$ exc.

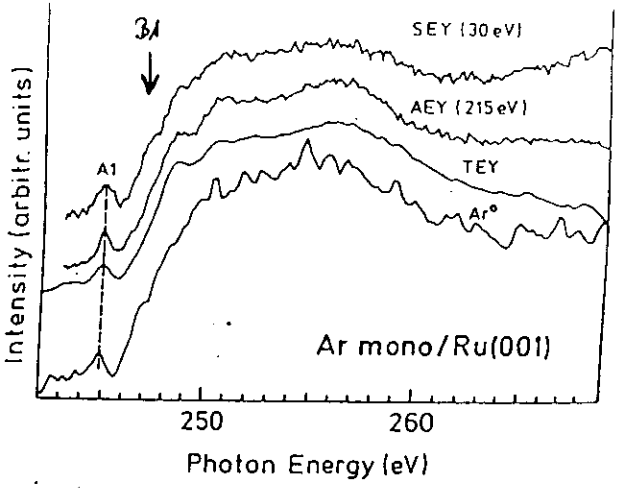


Unwin et al.
Phys. Script. T41 (92) 21.

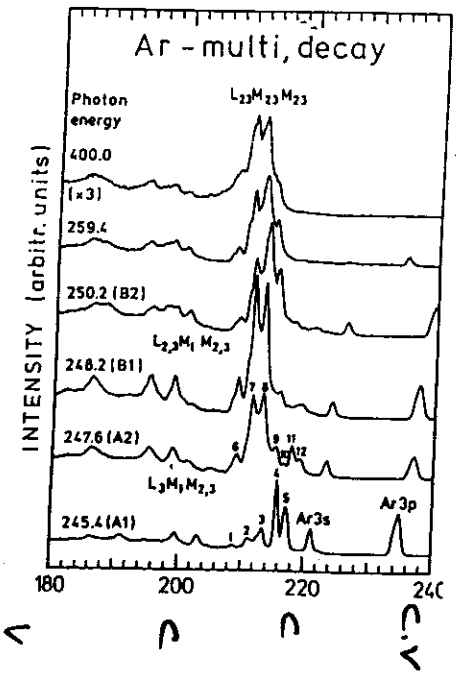
Decay spectra after C1s → π* exc for

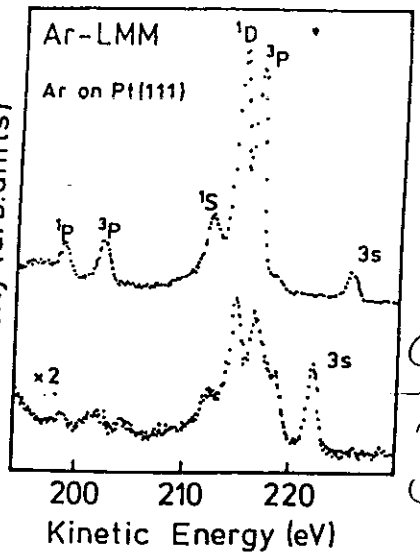






Roche et al. 1990





Wurth et al. 1992

Res. B1 ($2p_{3/2} \rightarrow 3d_{3/2}$)

Res. A1 ($2p_{3/2} \rightarrow 4s$)

SUMMARY

Coupling of atom and molecules at surfaces to molecular substrate leads to change in excitation and deexcitation behaviour, which depend on type of substrate (energie el. densities of states) and on coupling strength.

Excitation
Ionic states
Broadening of final state by coupling to phonons and e-h pairs
Screening of f.s. by polarization/image charge or by charge transfer
New satellite states as dynamic correlate to screening
Giant satellites (final state explicitly) for intermediate coupling of molecules to metal surface
Chemical interactions for valence states: "Vertical" interaction → chemical bond (differential shifts)
Lateral interaction → 2D band formation

Excitation, neutral states

Broadening dependent on coupling strength (vibr. resol.) and overlap

Shifts of E_{ex} through influences on final state ($\pm$); E_{ex} usually not identical to E_B even for CT screening

But resonances persist in all cases

Deexcitation

Difference between decay spectra of resonant and nonresonant (nominally neutral and nominally ionic) state disappears in many cases

The same is the case for different states of same system (main line, and satellites)

$\Rightarrow$ differences must decay during core life time
("bail-down" for ads/metal;
CT for condensate $\rightarrow$ ionic.)

$\Rightarrow$ TIME SCALES FOR REARRANGEMENTS IN COUPLED SYSTEM COMPARABLE TO CORE LIFE TIMES (1-10 fs)

So important as basis of discussion of effects on dissociation