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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O. B. 589 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2940-1
CABLE: CENTRATOM - TELEX 400692 - I

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WORKSHOP ON
"SURFACE SCIENCE AND CATALYSIS"
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24* RESONANCE FEATURES IN THE
ELECTRONIC SPECTRA OF CHEMISORBED CO

B. GURHALTER
Institute of Physics
University of Zagreb
Bijenicka 46
P.O. Box 304
41001 Zagreb
Yugoslavia

These are preliminary lecture notes, intended only for distribution to participants.

2nd* resonance features in the electronic spectra of chemisorbed CO

(A Surface Science Study of)
CO chemisorption metals

B. Gumhalter

Institute of Physics of the University, Zagreb, YU

K. Wandelt

Fritz-Haber-Institut der MPG, D-1000 Berlin 33

Ph. Avouris

IBM Research Center, Yorktown Heights, N.Y.

Motivation

As in any other science, the attempts in surface science to study some typical, model systems the understanding of which may serve as a prerequisite for a description of more complicated and technologically relevant systems.

Such a typical adsorption system frequently encountered in surface science is

CO/metals.

In connection with such a system one wants to understand: e.g.:

- adsorption/desorption (kinetics)
- adsorbate electronic structure
- effect of the adsorbate on the substrate and vice-versa, on the coadsorbates and neighbouring gas phase atoms, etc.

Investigation of adsorption systems and their properties by means of surface sensitive analytical methods.

Development of theoretical models and

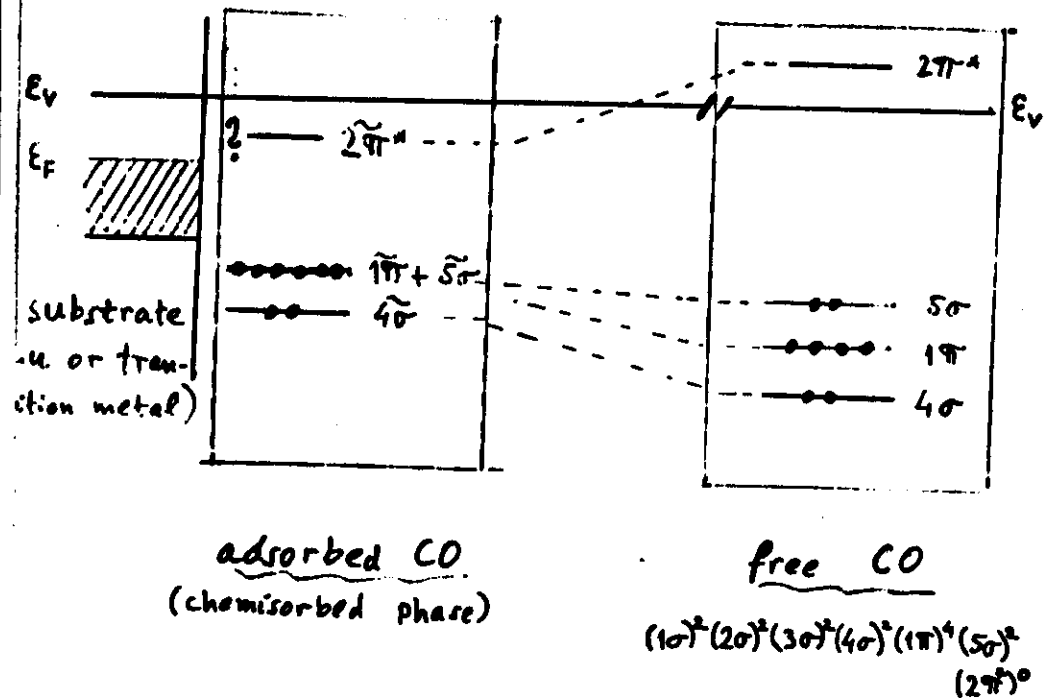
Why studies of CO adsorption on metals?

- i) CO adsorption on noble and some transition metals is a typical example of nondissociative molecular adsorption.
- ii) CO adsorption (in particular chemisorption) on metals and alloys is encountered in many processes of great practical and technological importance as e.g. corrosion, heterogeneous catalysis, etc.
- iii) Adsorbed CO is often used as a model system for testing our understanding of the processes of chemisorption and desorption, dissociation, reaction kinetics, etc. Due to its relatively simple structure this system can easily be studied by modern experimental analytical techniques and also quantified theoretically.
- iv) etc.

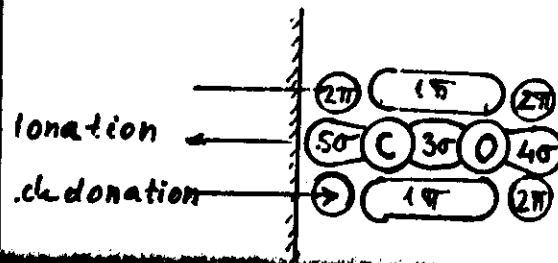
Primary goal of this studies:

Give a description and develop the understanding of the CO-metal bonding mechanism and the electronic structure of the adsorption complex.

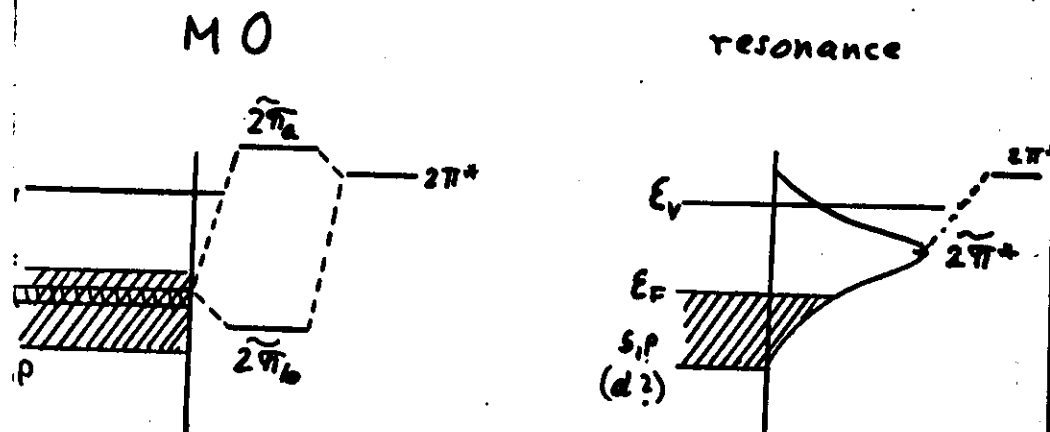
Valence levels of free and chemisorbed CO



Current models of CO chemisorption on Cu and transition metals are based on indication and evidence (exp. & theor.) that the chemisorptive bonding is primarily due to charge "backdonation" into the $2\pi^*$ derived levels of adsorbed CO.



Molecular Orbital (Blyholder) versus $2\pi^*$ resonance picture of CO chemisorption



Simple MO picture refuted by several groups of authors as inadequate (c.f. Ishi et al. Surf. Sci. 161 (1985) 349)!

Question:

Can the $2\pi^*$ resonance model be verified and tested by observing characteristic $2\pi^*$ resonance features in various electronic spectra of chemisorbed CO?

Answer:

Resonance model can be tested by analysing and discussing the CO/metal electronic spectra recorded by various spectroscopic techniques for typical CO adsorption systems, e.g.

weak chemisorption

CO/Cu

strong chemisorption

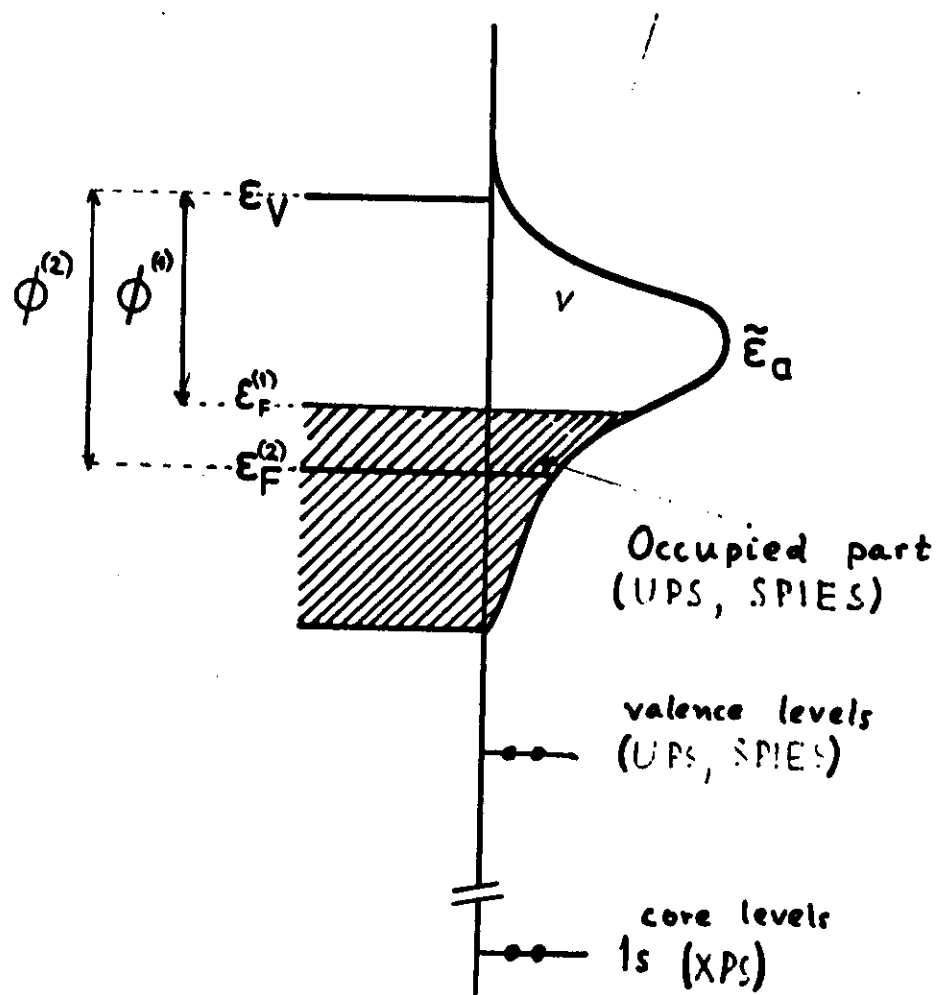
CO/Ni
Pd

Experimental techniques & methods:

- UV photoemission (UPS*)
- Penning ionization spectroscopy (SPIES)
- XPS* or ESCA*
- Inverse photoemission (BIS or IPES)
- core-to-valence excitation spectroscopy (NEXAFS* or XANES*)

* often carried out with synchrotron radiation

Unoccupied part
(EEL, NEXAFS)

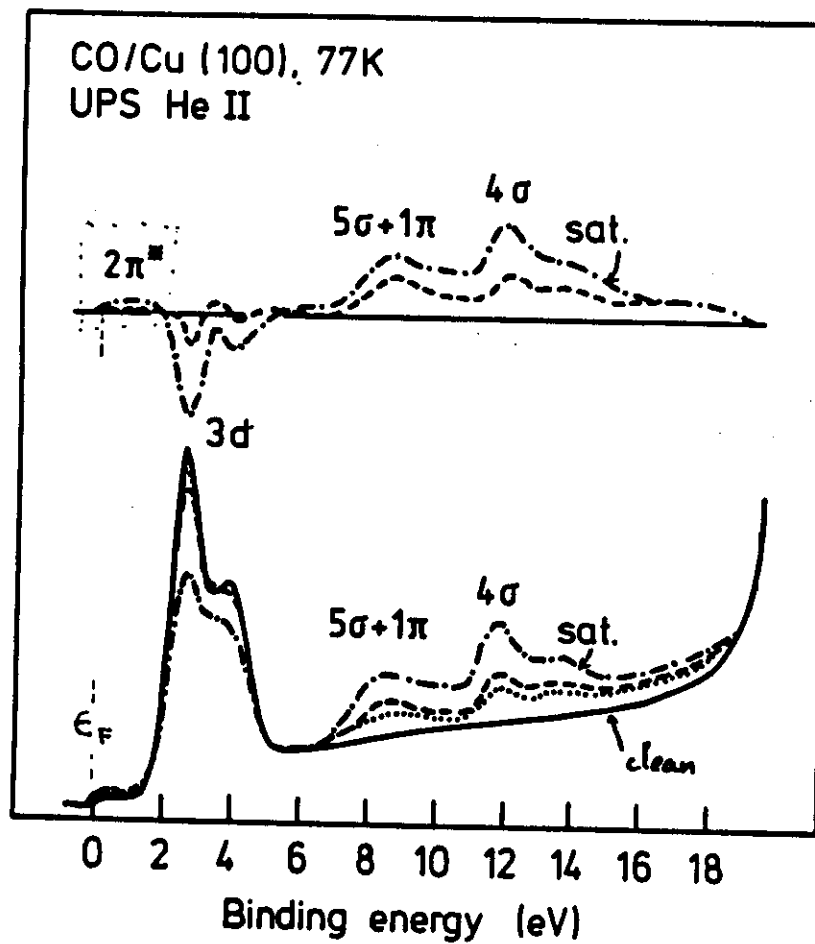


Density of states of occupied
adsorbate levels

Occupation of the resonance may vary
due to different position of the resonance
maximum relative to E_F of various substrates
(c.f. Gumhalter & Wandelt, PRL 57, 2318 (1986))

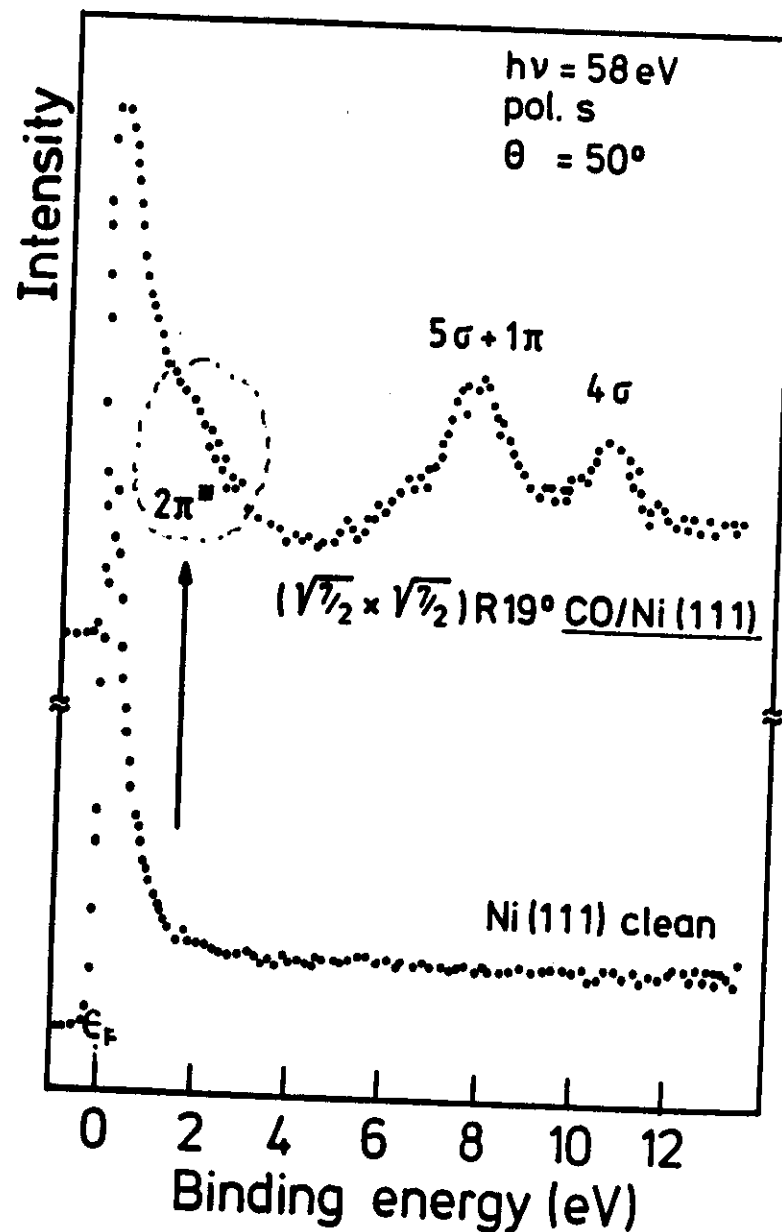
Valence levels

UPS

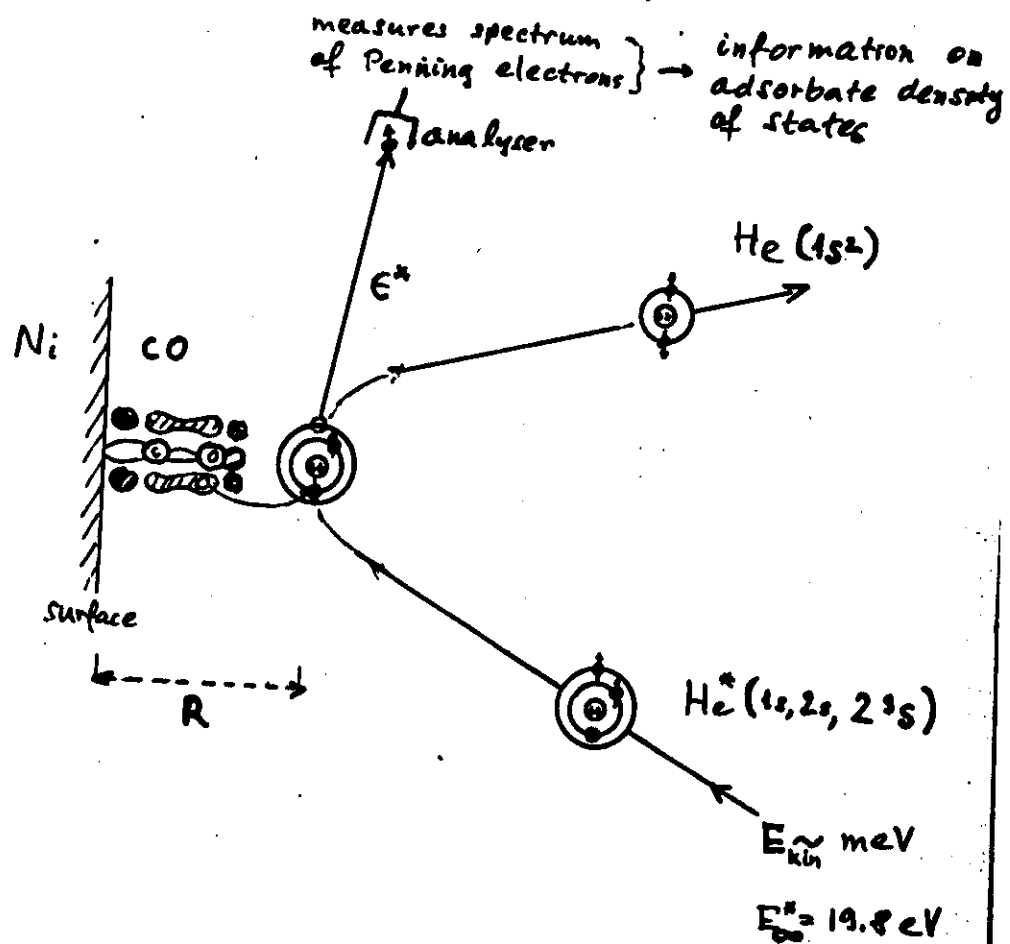


difference spectra

2 π^* feature above the Cu d-band

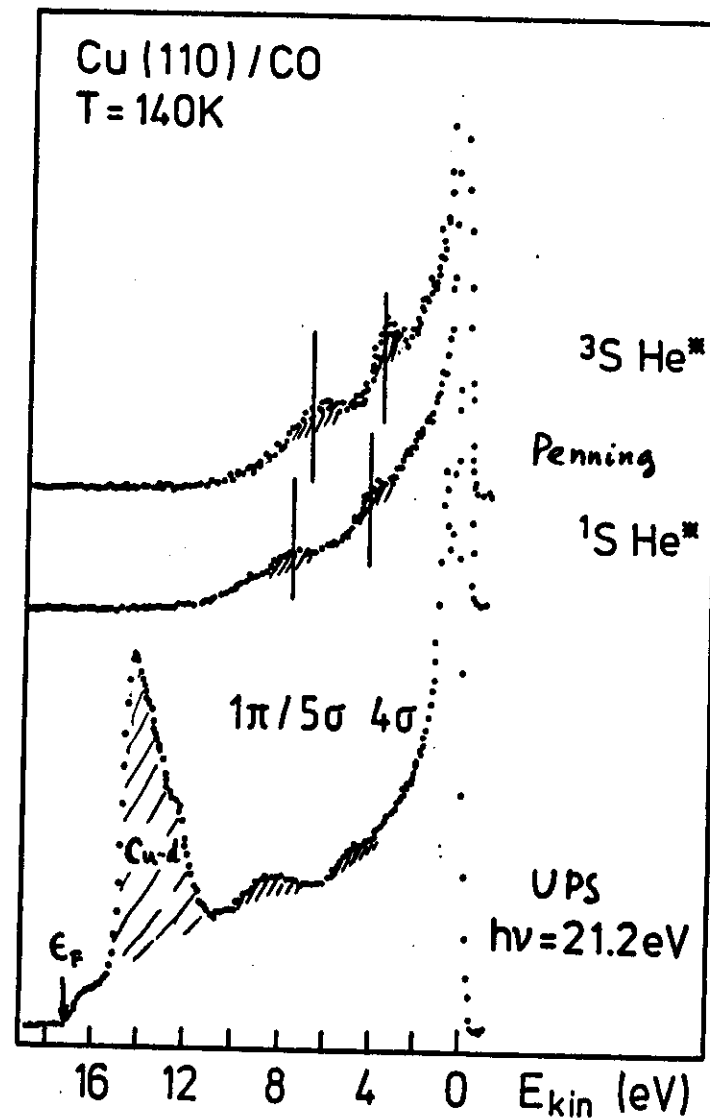


Penning (SPIES)

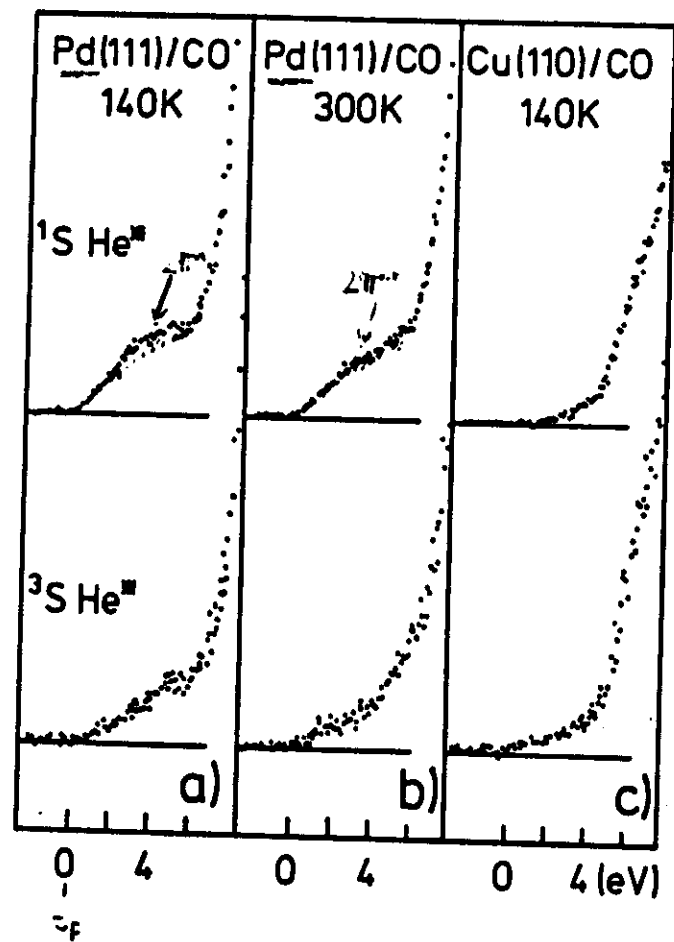


Penning spectroscopy of adsorbates:

- Adsorbate final state the same as in UPS (one hole in valence states)
- Extremely surface sensitive
- Effective deexcitation energy ϵ^* system specific (in contrast to UPS)



Sesselmann et al. Surf. Sci. 146 (1994) 17



Sesselman et al. *Surf. Sci.* 146(1984) 17

Core levels

Screening of the core hole in XPS by valence electron density

Temporal components of relaxation

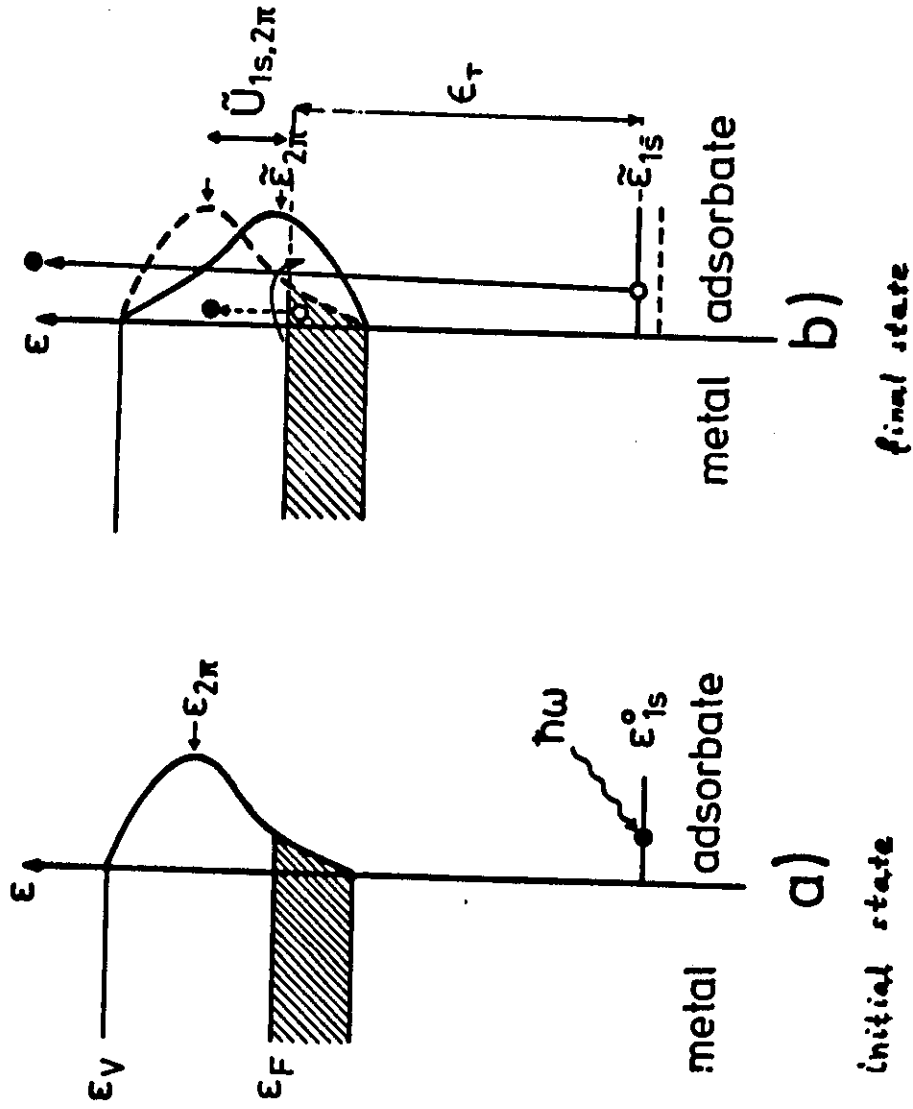
adiabatic
(long time response) transient
(short time response)

↓
Determines the relaxation
shift of the level

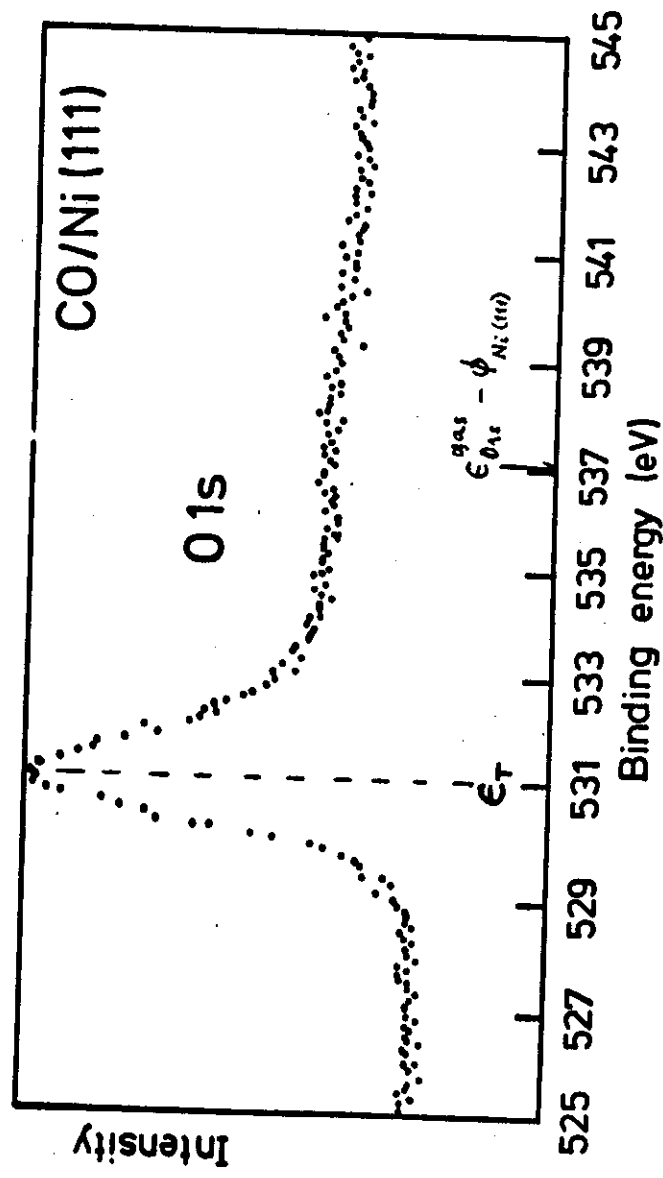
↓
Determines spectral
shape at threshold

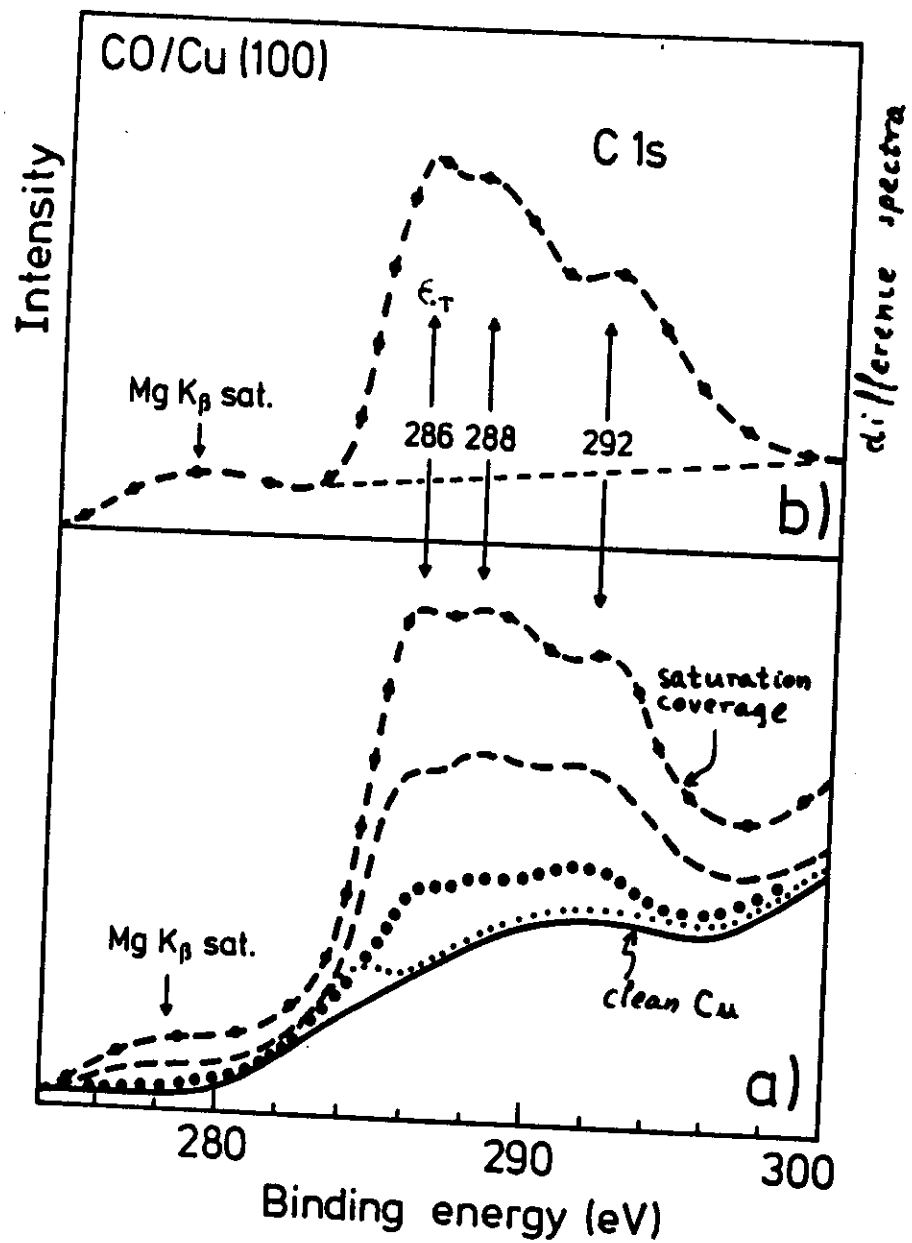
Both components show up in the
measured spectra

(c.f. B. Gumhalter, *Progress in Surf.
Sci.* 15(1984) 1)



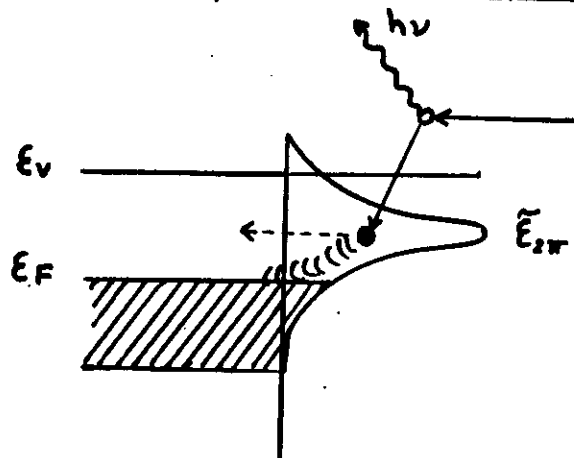
XPS





*Density of states of un-occupied
adsorbate levels*

Inverse photoemission from CO $2\pi^*$ resonance



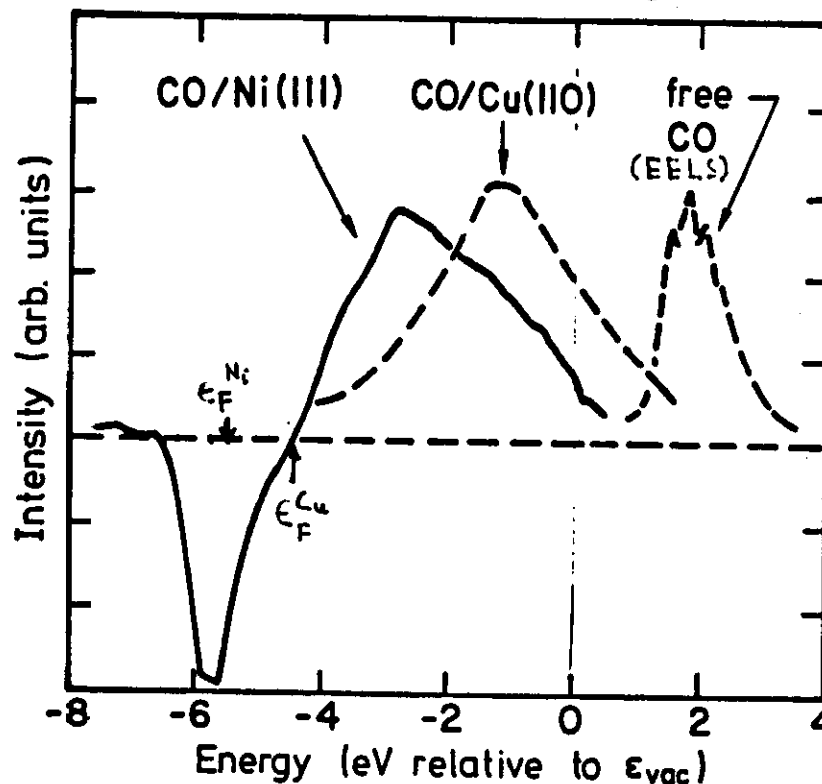
BIS spectra affected by:

- (i) Initial state (chemical) effects
(shift and resonance-and line-width)
- (ii) Final state (relaxation) effects
(relaxation shift and line shapes)

(c.f. B. Gumhalter, *Surf. Sci.* 157 (1985) 2355)

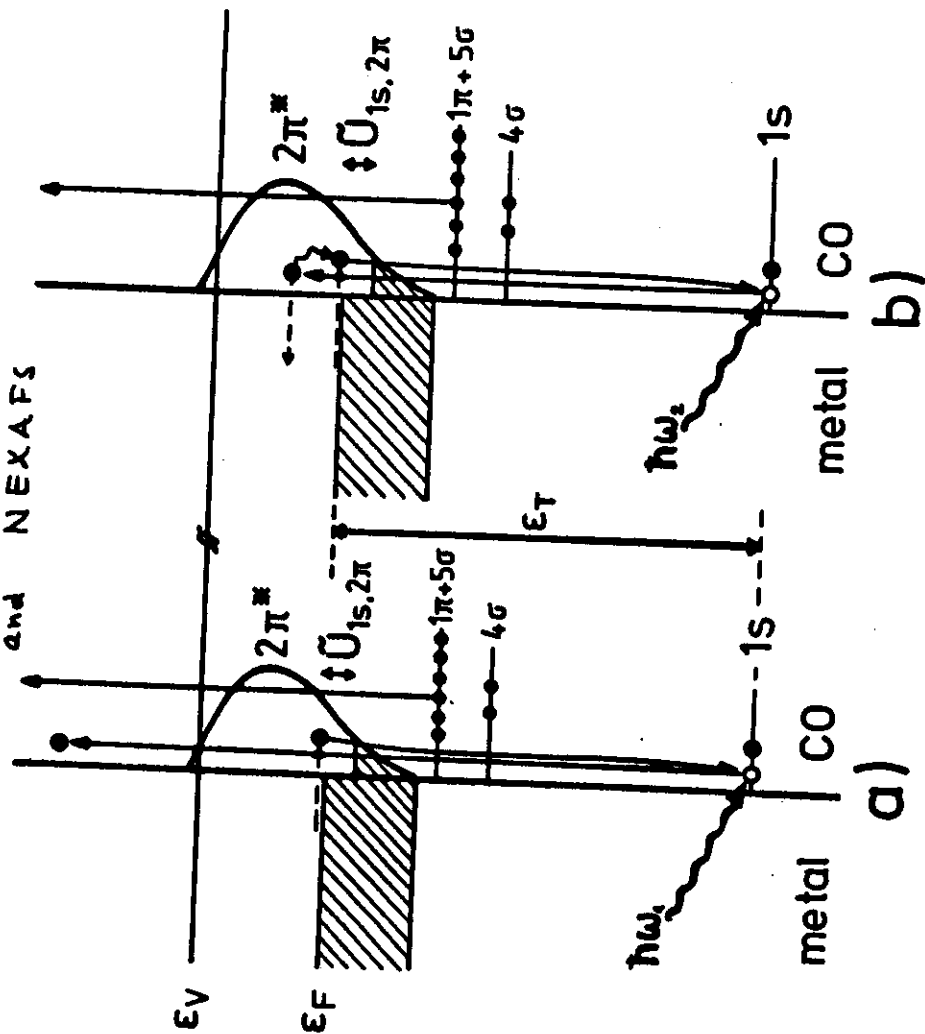
2.3.1.1

Energy of the $2\pi^*$ orbital
of free and bound CO



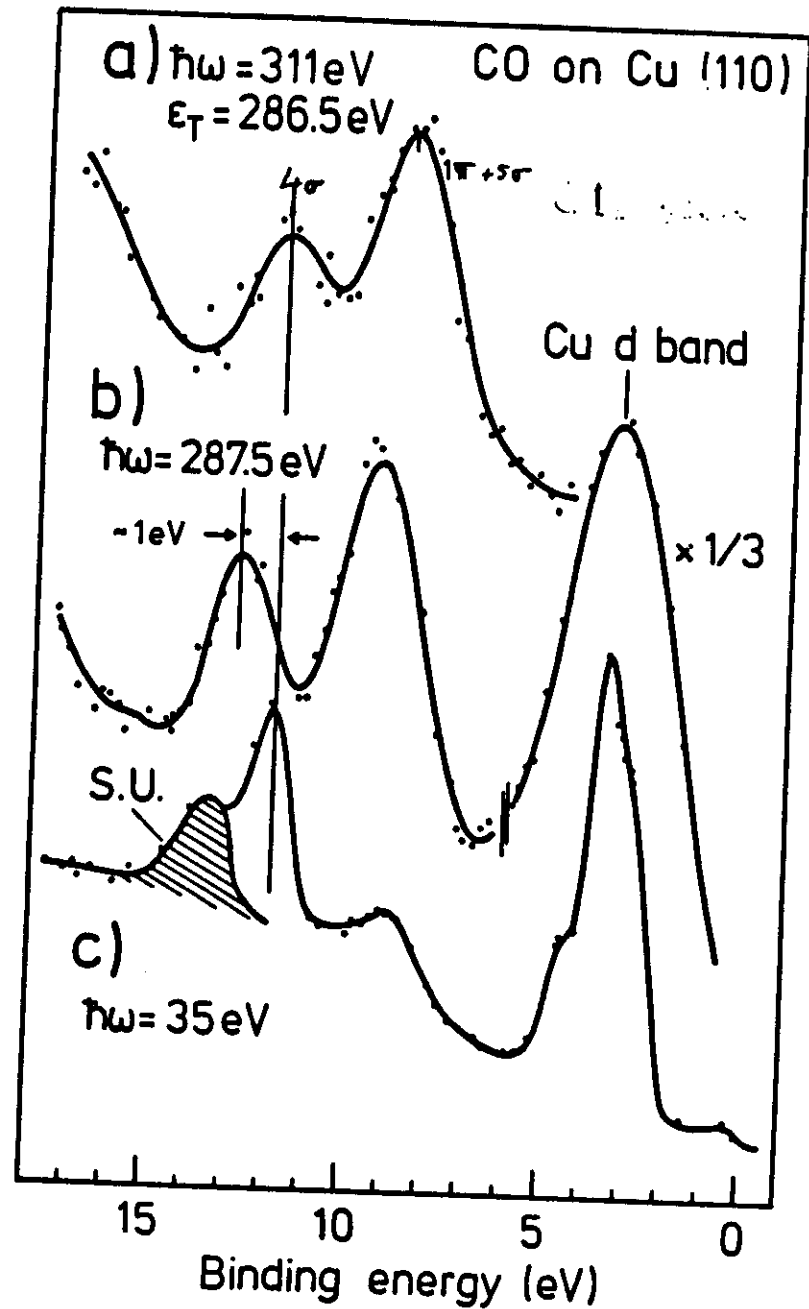
Resonance widths cannot be explained by
final state relaxation effects only!

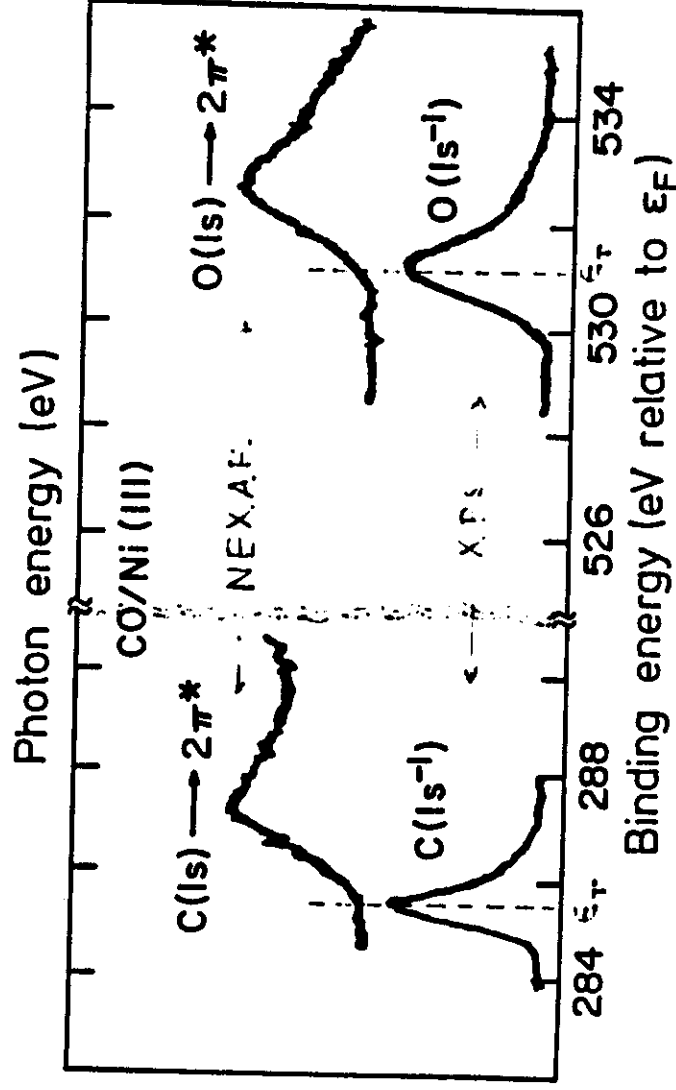
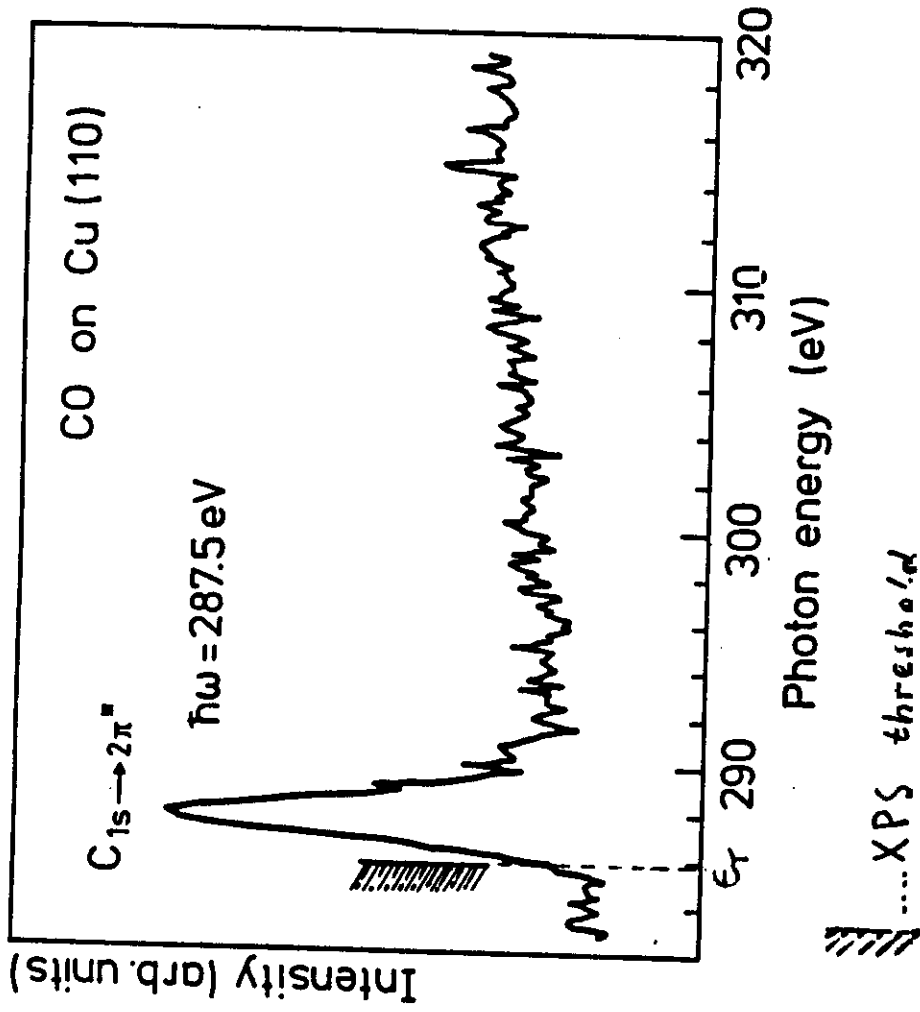
⇒ Initial state resonance broadening present!
i.e. evidence for $2\pi^*$ resonance

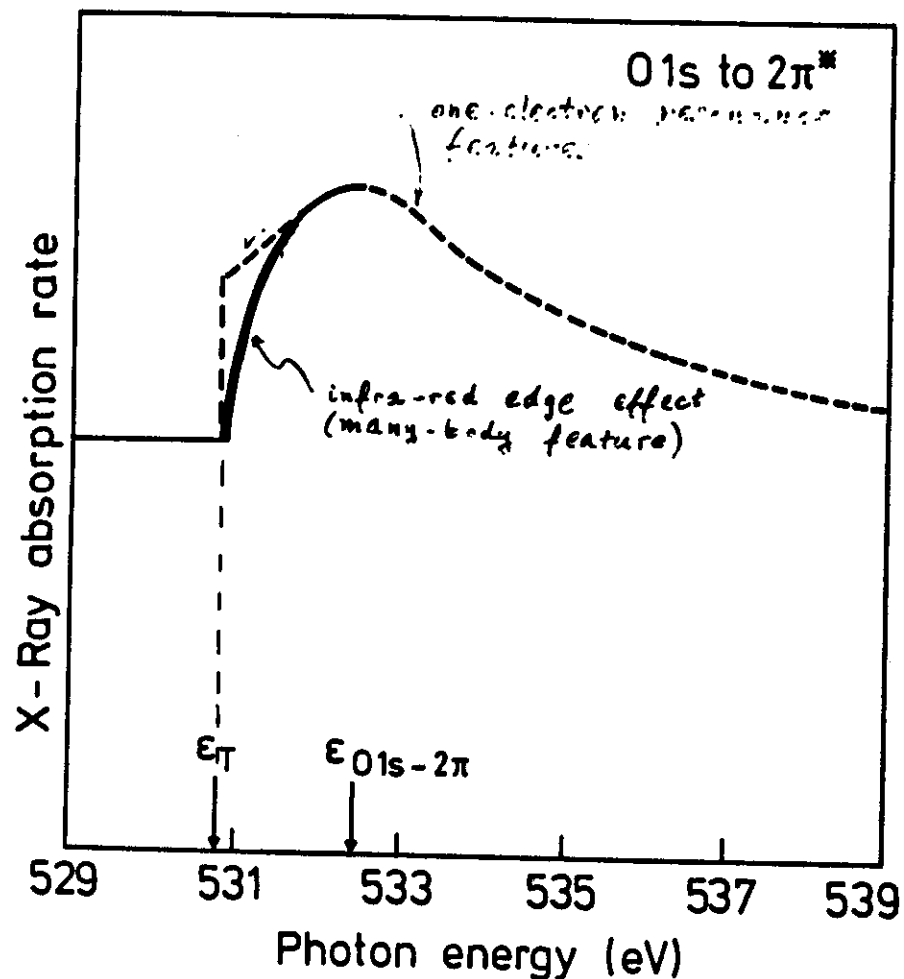


XPS

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/... resonance quenching at E_T :
 manifestation of infra-red singularity
 or Anderson orthogonality block
 25

Energetics of CO adsorption in
 physisorbed and chemisorbed (Ni) phase
 (energies relative to the vacuum level)

	CO chemisorbed on Ni(111)		CO physisorbed on noble metals		CO free molecule	
	E(eV)	Γ (eV)	E(eV)	Γ (eV)	E(eV)	Γ (eV)
$O 1s \rightarrow 2\pi^*$	532.4	3.5	534.1	1.15 (j)	534.1 (o) 534.1 (a) 534.0 (d)	1.15 (j) 1.3 (a,j)
$O 1s$	-536.7 (e) -536.8 (f)	<2.1 (h)	-538.3 (i)	1.5 (l)	-542.6 (b) -542.1 (g)	
$Cl 1s \rightarrow 2\pi^*$	287.0	2.2	287.3	<0.18	287.3 (a) 287.4 (c) 287.3 (d)	0.095 (a) 0.10 (c)
$Cl 1s$	-291.2 (e) -291.2 (f)	<1.85 (h)	-292.1 (i)	1.5 (l)	-296.2 (b) -295.9 (g)	
$2\pi^*$	-2.8 (l)	3.1 (l)	+1.3 (m)	0.6 (m)	+1.9 (n)	1.1 (n,j)

(c.f. B. Gumhalter, PRB 33(1986) 5245)