Observation of occupied covalent bonding states of CO molecule on Pt & Pt-Sn/Pt(111) surfaces

문 봉 진
Bongjin Simon Mun

Department of Physics and Photon Science
Center for Advanced X-ray Science

Gwangju Institute of Science and Technology
Gwangju, Korea

Collaboration

IBS CCES & Seoul National University, Korea

Changyoung Kim
Jongkeun Jeong
In Kyung Song
Won Shik Kyung
Soo Hyun Cho
Bum Seo Kim

Institut de Recherches sur la Catalyse et l'Environnement de Lyon

Francisco Jose Cadete Santos Aires
Eric Ehret

Univ. of West Bohemia, Czechoslovakia

Jan Minar
Laruent Nicolai

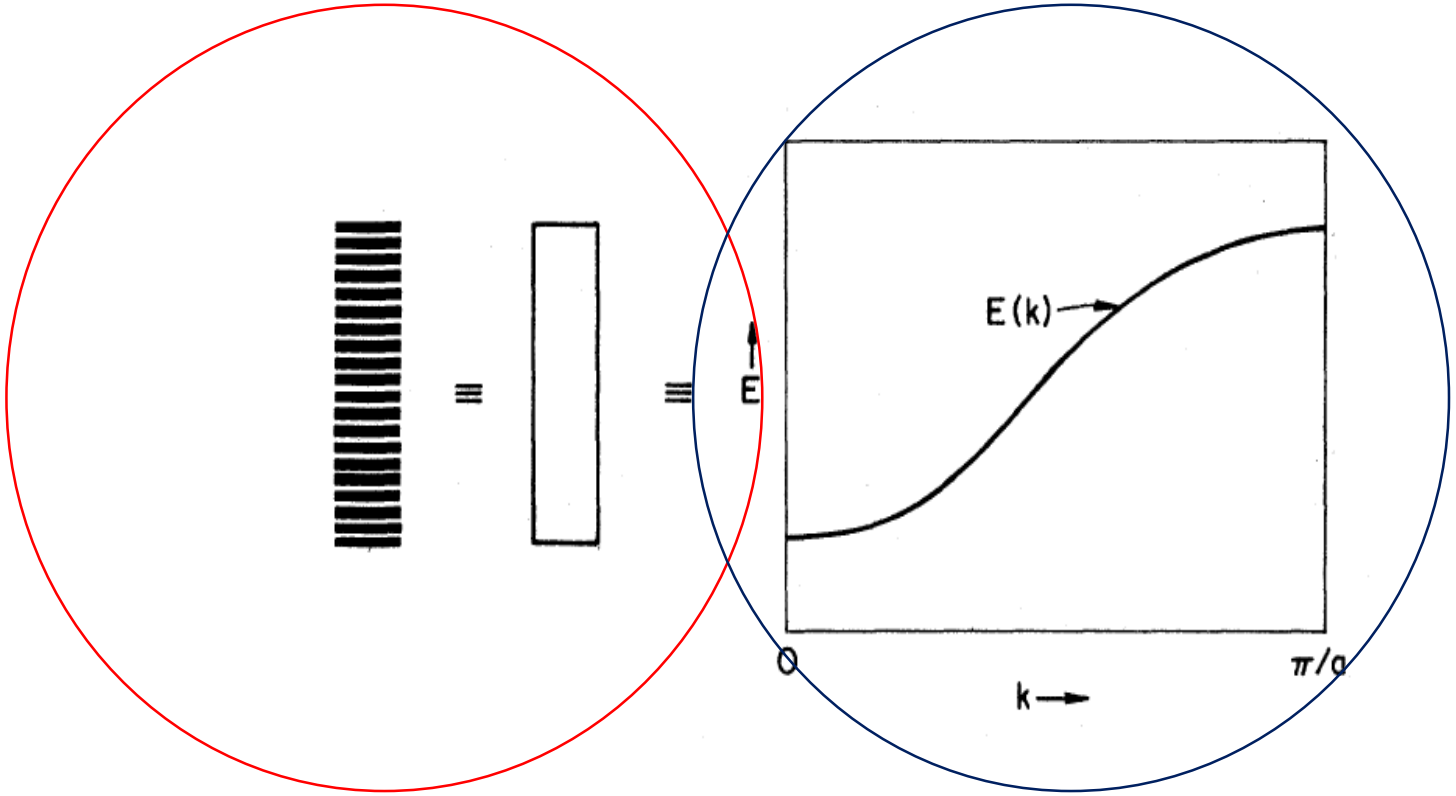
Advanced Light Source
Lawrence Berkeley National Laboratory

Jonathan Dellinger
Slavo Nemsak
Phil Ross Jr.

A chemical and theoretical way to look at bonding on surfaces

Roald Hoffmann

Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301



Chemist's point of view **Physicist's point of view**

Reviews of Modern Physics, Vol. 60, No. 3, July 1988

Heterogeneous Catalysis

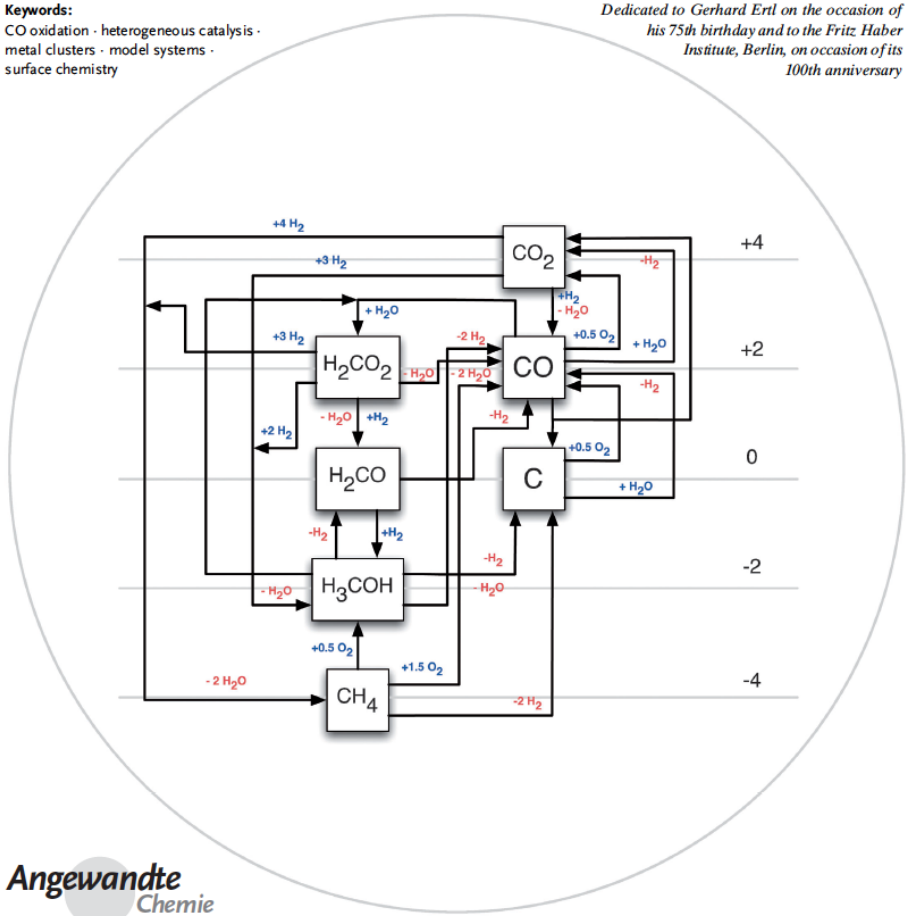
DOI: 10.1002/anie.201101378

CO Oxidation as a Prototypical Reaction for Heterogeneous Processes

Hans-Joachim Freund, Gerard Meijer,* Matthias Scheffler,* Robert Schlögl,* and Martin Wolf**

Keywords:
CO oxidation · heterogeneous catalysis · metal clusters · model systems · surface chemistry

Dedicated to Gerhard Ertl on the occasion of his 75th birthday and to the Fritz Haber Institute, Berlin, on occasion of its 100th anniversary



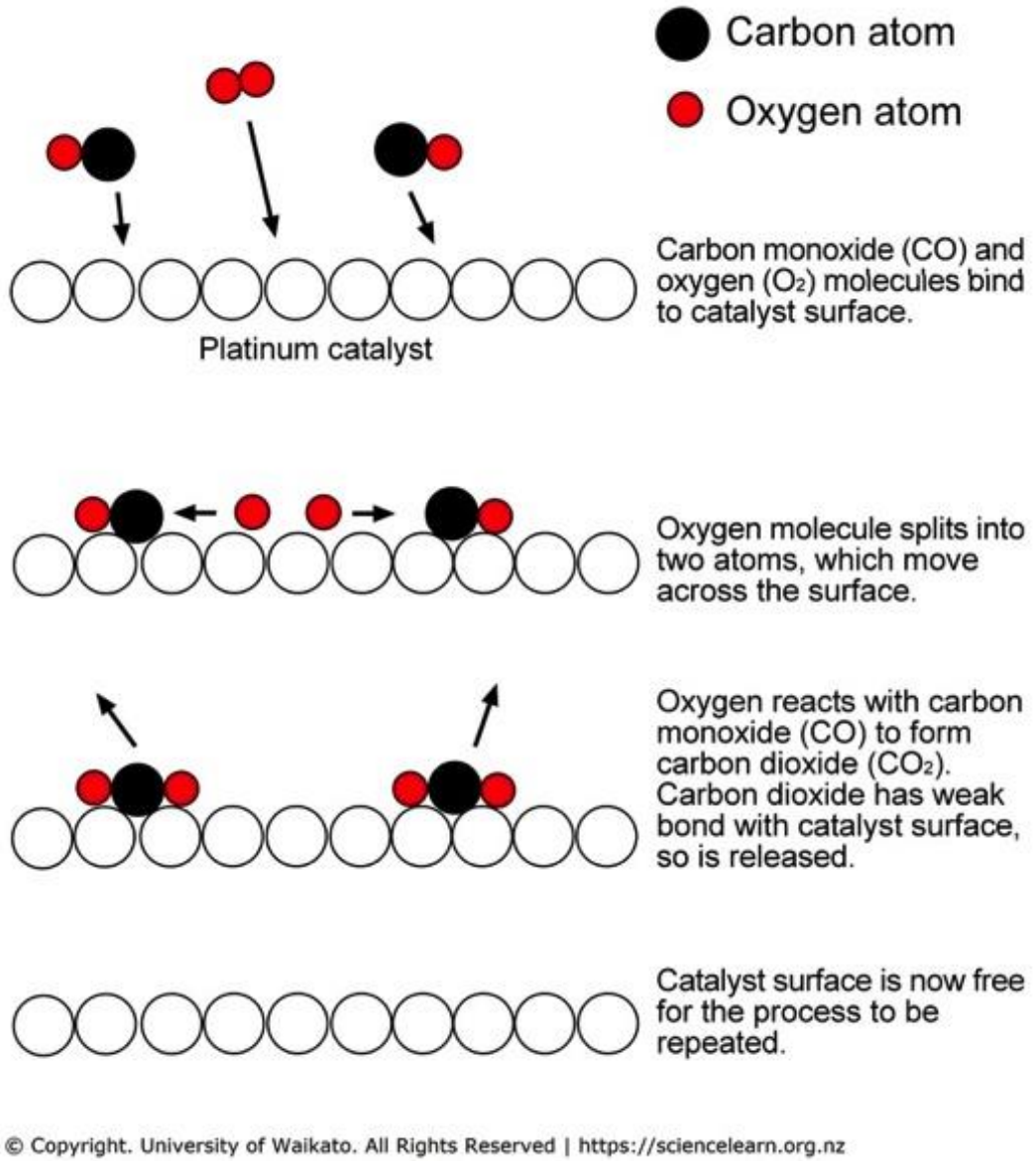
Why Pt is such a good catalyst ?

Model catalysis : CO oxidation

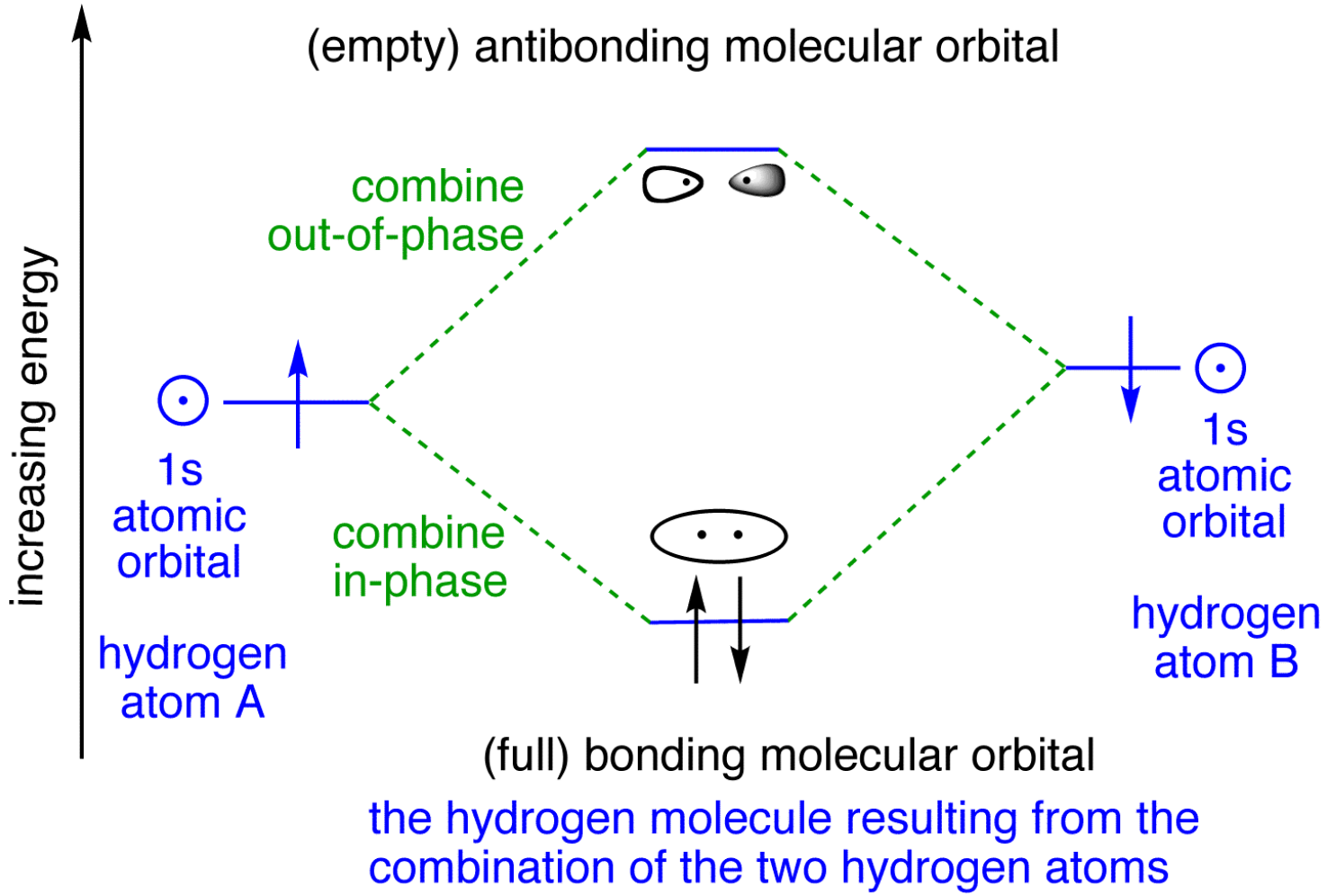
The roles of surface is critical.

Not too strong !
Not too weak !

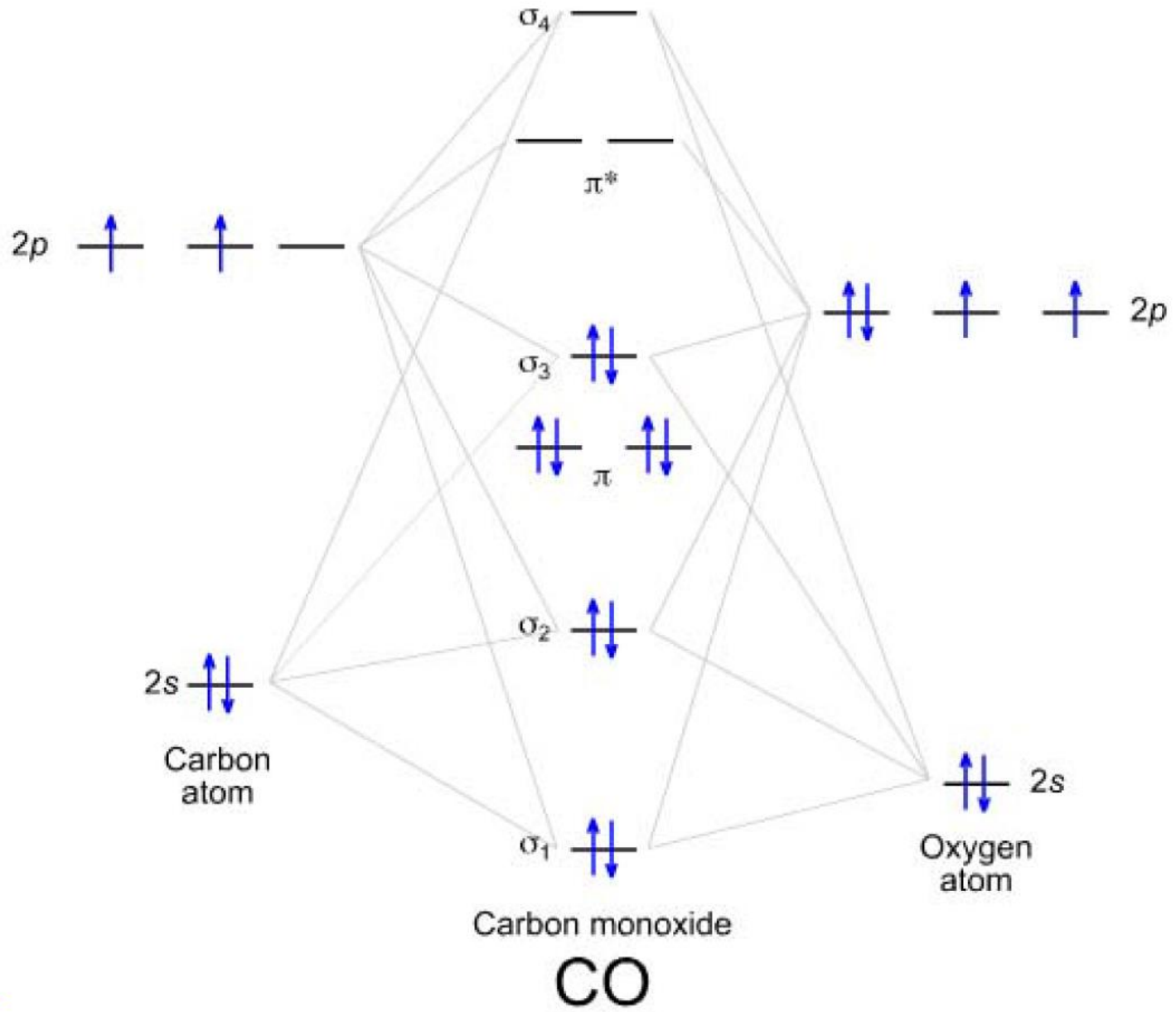
Correlation between
surface chemical properties
and
surface electronic structure

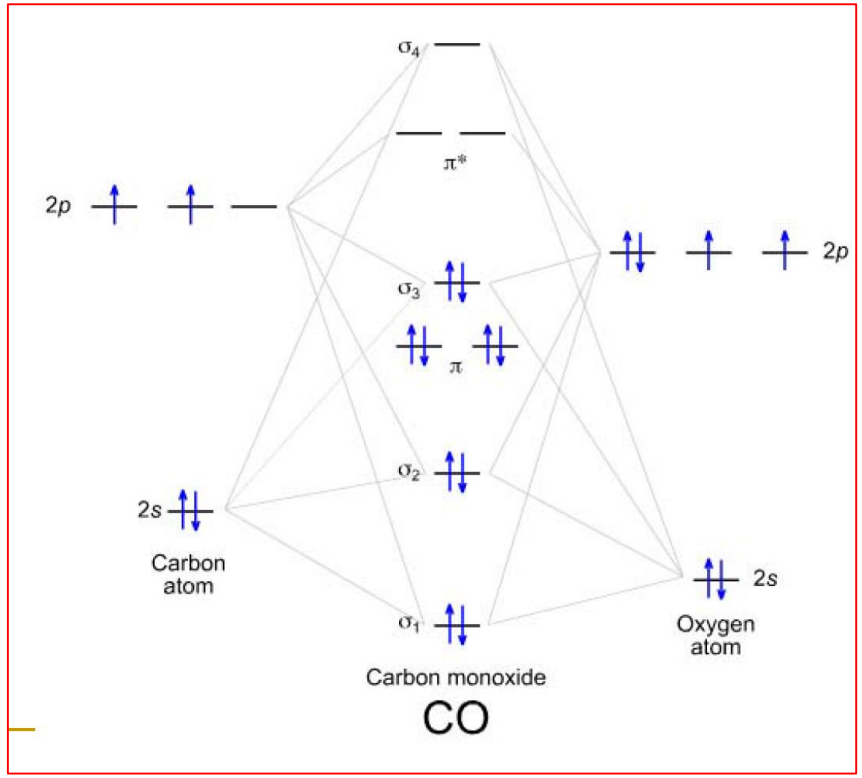


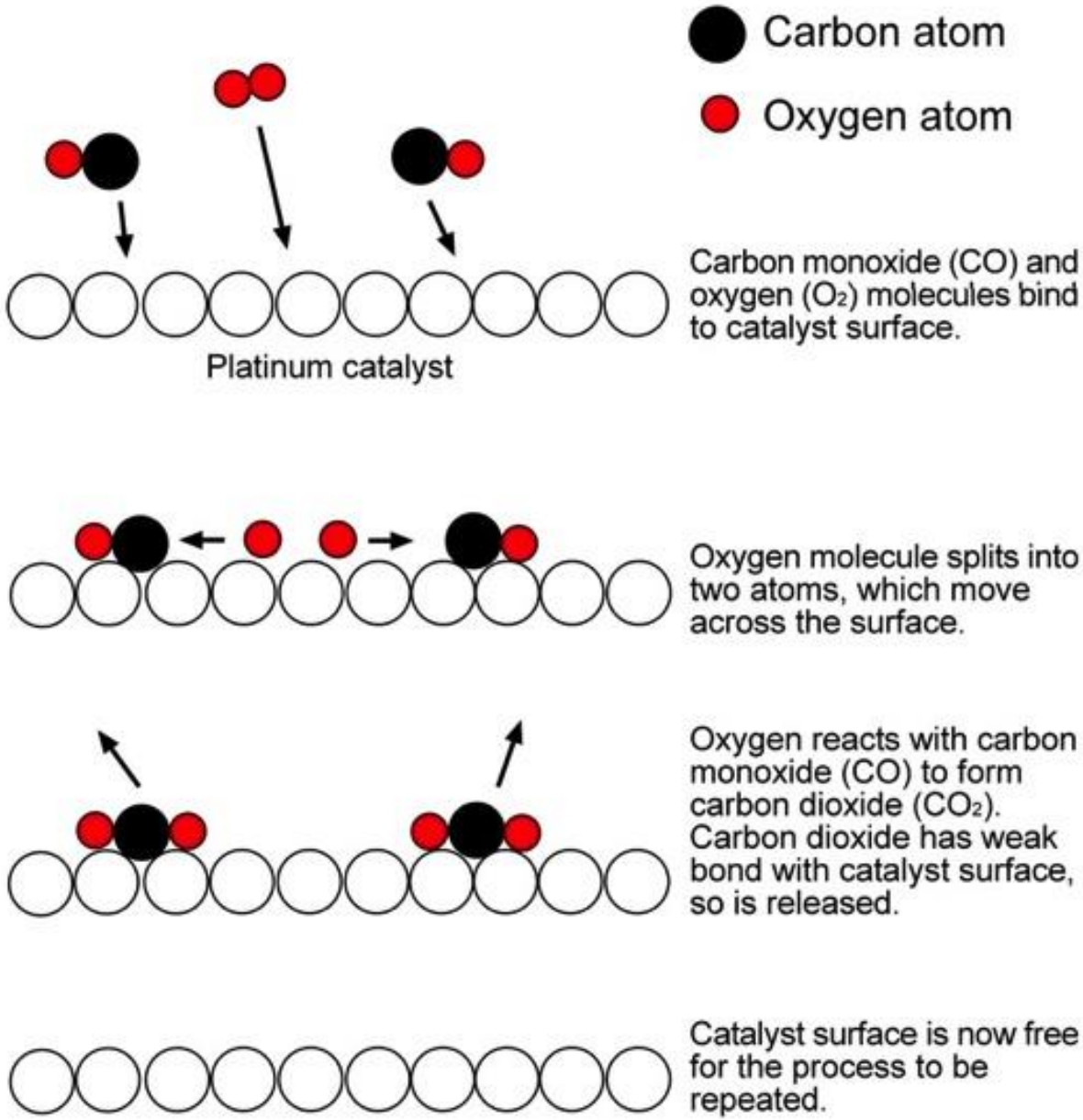
Molecular Orbital Theory



the hydrogen molecule resulting from the combination of the two hydrogen atoms


σ4
π*
2p
2p
σ3
π
σ2
2s
2s
Carbon
atom
Oxygen
atom
σ1
Carbon monoxide
CO

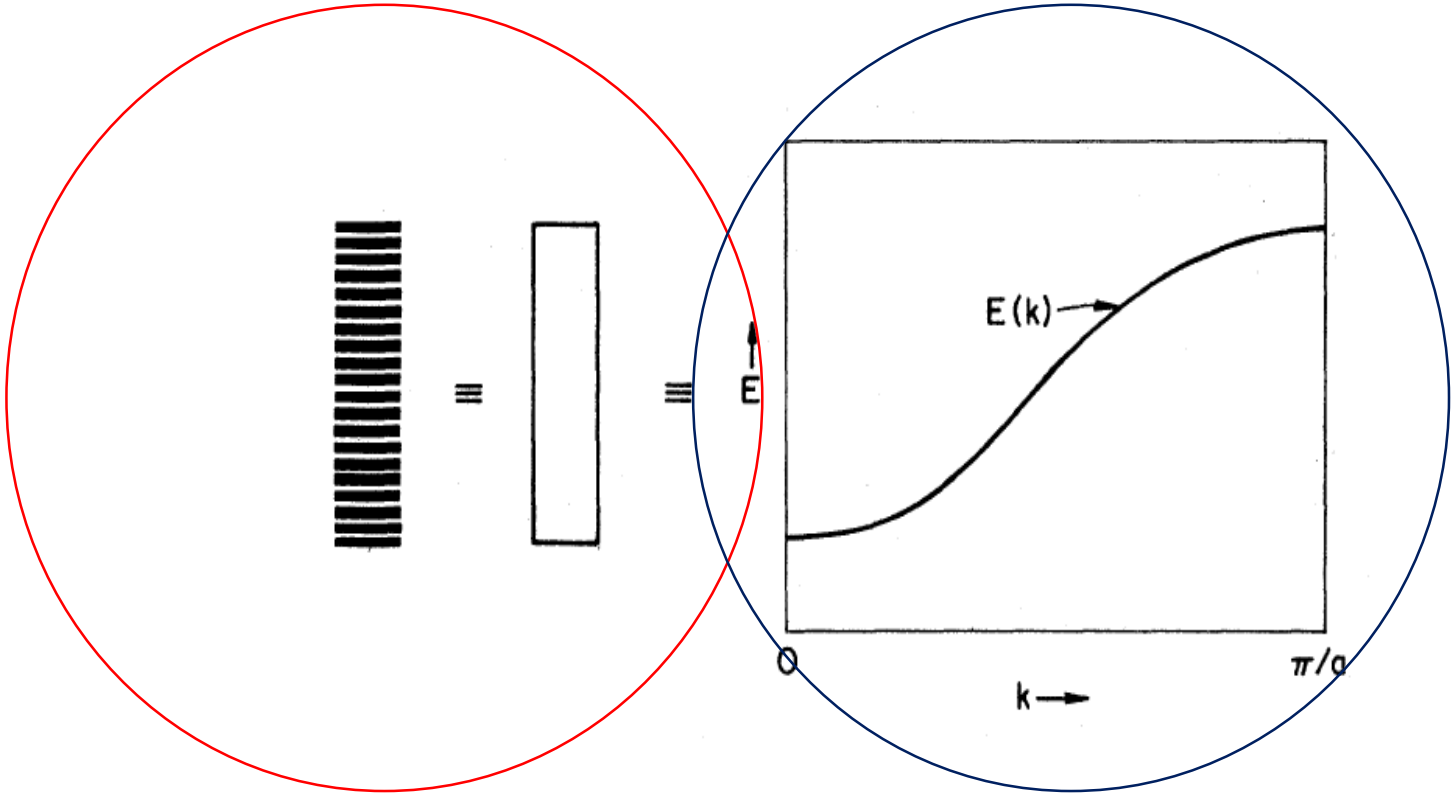




A chemical and theoretical way to look at bonding on surfaces

Roald Hoffmann

Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301



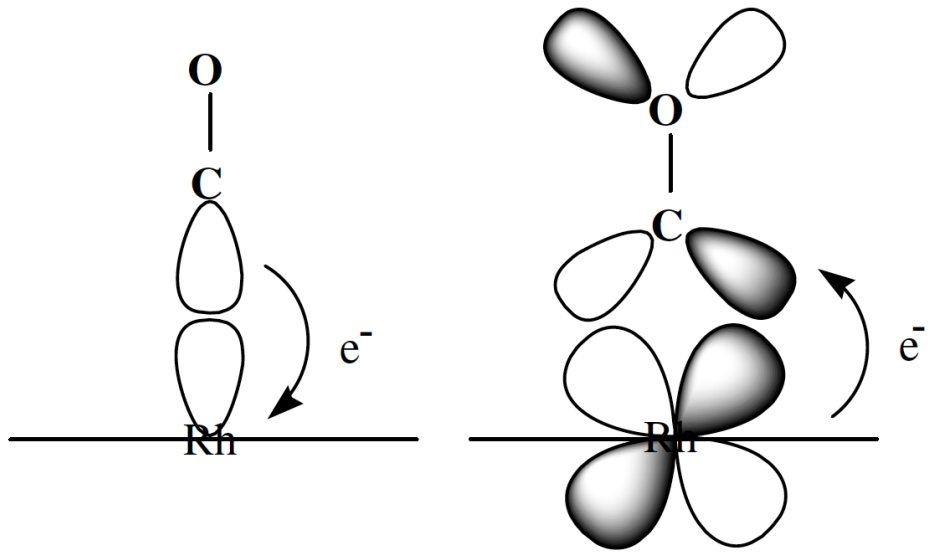
Chemist's point of view **Physicist's point of view**

Reviews of Modern Physics, Vol. 60, No. 3, July 1988

Molecular Orbital View of Chemisorbed Carbon Monoxide

by George Blyholder

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas *(Received February 26, 1964)*



Scheme 1. The resembled Blyholder model of CO molecule adsorbed on the 4Rh/CeO_2(Rh-cluster) surface.

Chemical Physics 348 (2008) 161–168

Frontier Molecular Orbitals

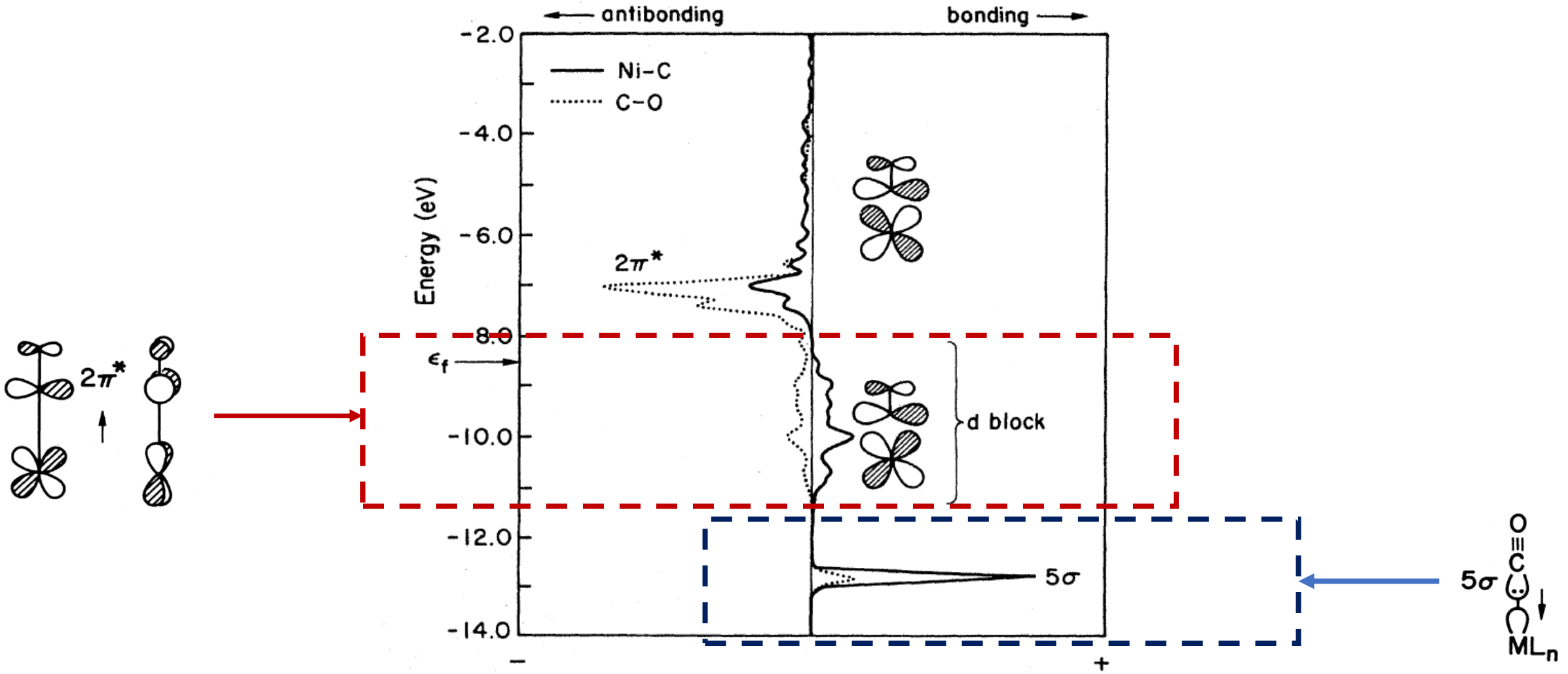


FIG. 10. Crystal orbital overlap population for CO, on top, in a $c(2\times2)$CO-Ni(100) model. Representative orbital combinations are drawn.

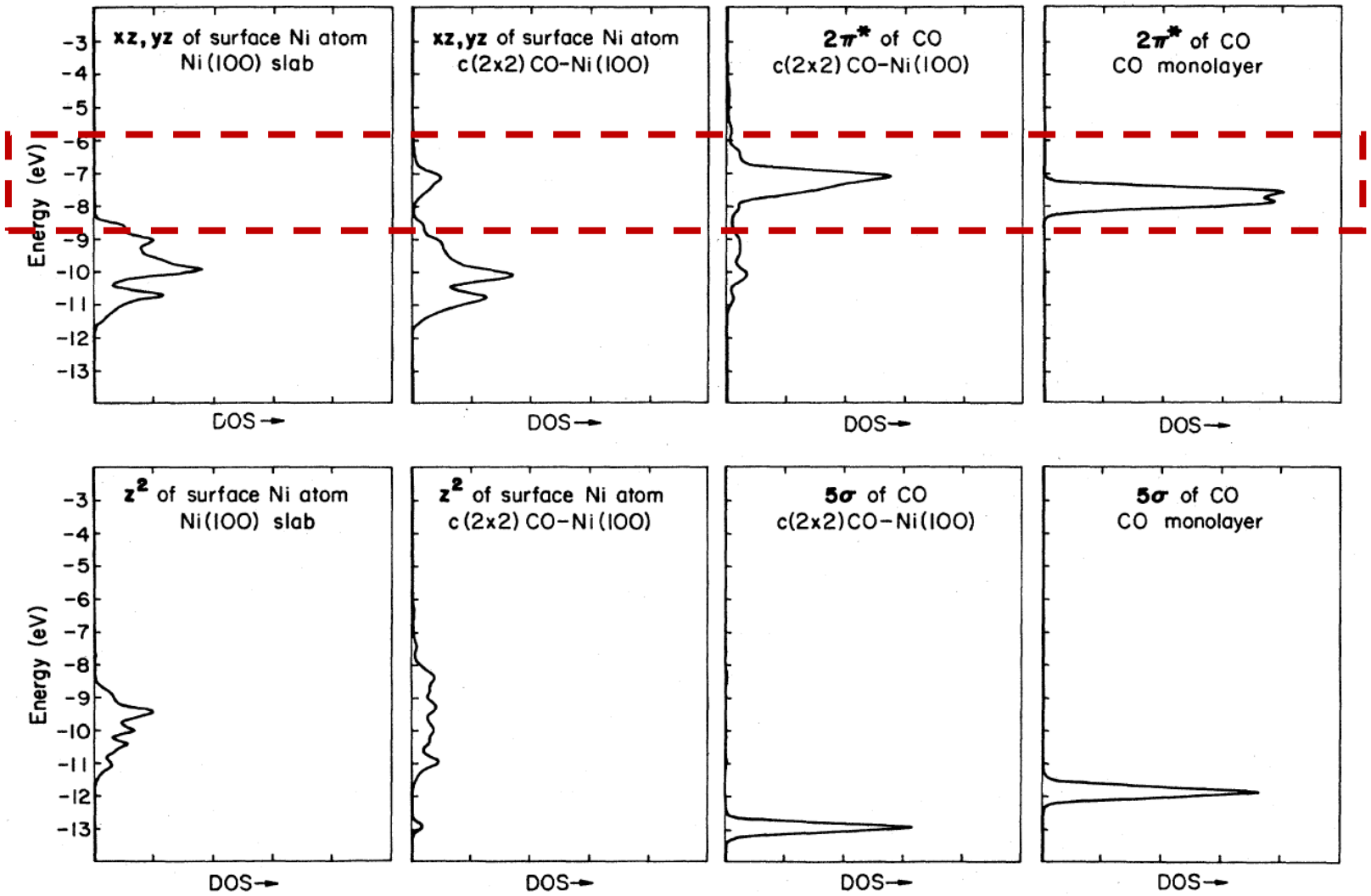
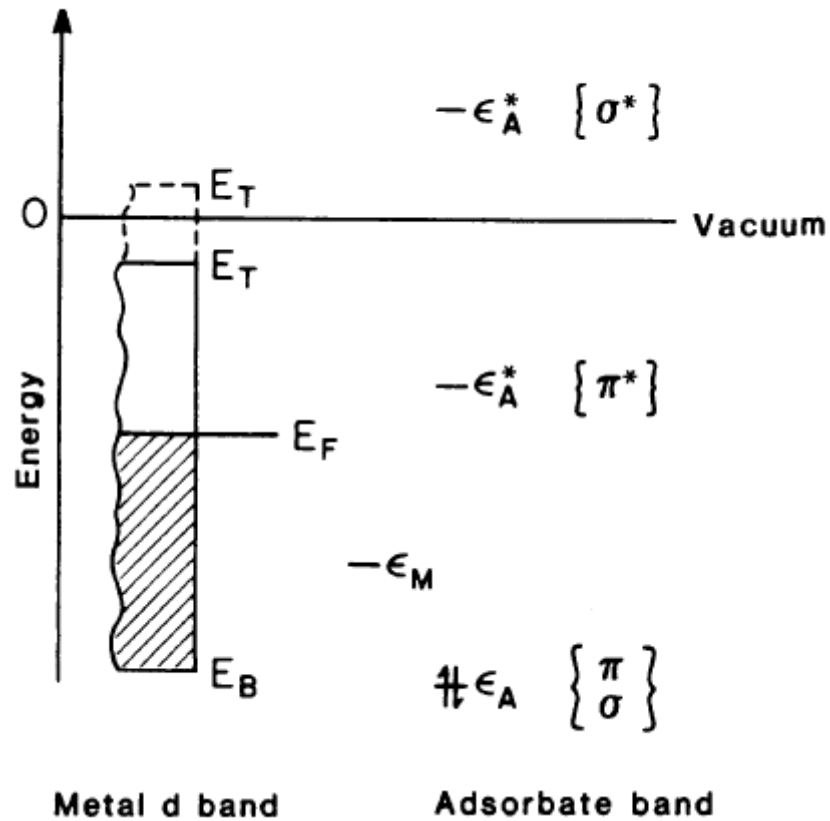


FIG. 6. "Interaction diagrams" for 5σ and $2\pi^*$ of $c(2\times2)$CO-Ni(100). The extreme left and right panels in each case show the contributions of the appropriate orbitals (z^2 for 5σ, xz,yz for $2\pi^*$) of a surface metal atom (left), and of the corresponding isolated CO monolayer MO. The middle two panels then show the contributions of the same fragment MO's to the DOS of the composite chemisorption system.

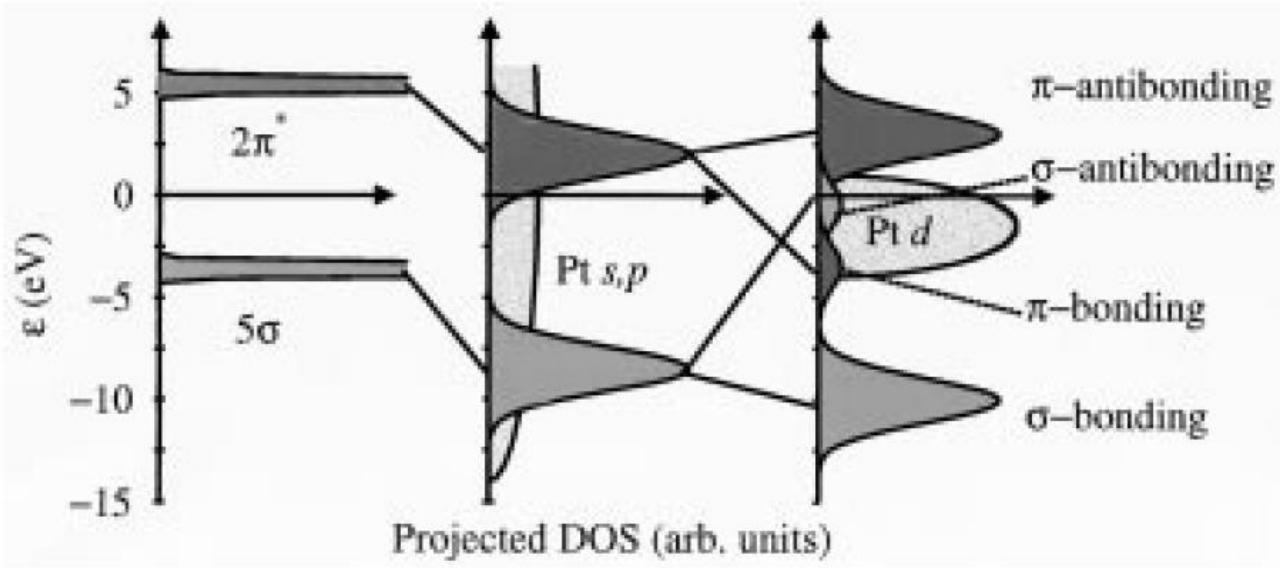
Toward A Coherent Theory of Chemisorption

Evgeny Shustorovich and Roger C. Baetzold

SCIENCE, VOL. 227 878



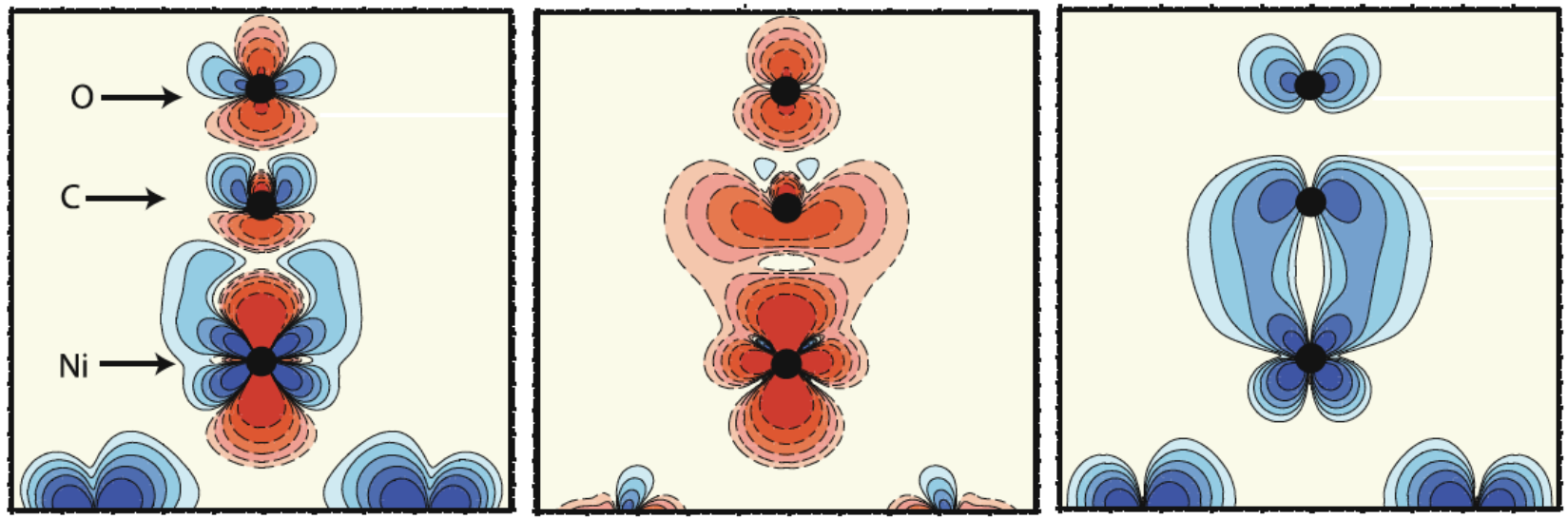
d-Band Model : Explaining the trend of surface reactivity



J. K. Norskov et al. Catalysis Letters **46** (1997) 31-35

A Molecular Perspective on the *d*-Band Model: Synergy Between Experiment and Theory

Lars Gunnar Moody Pettersson · Anders Nilsson

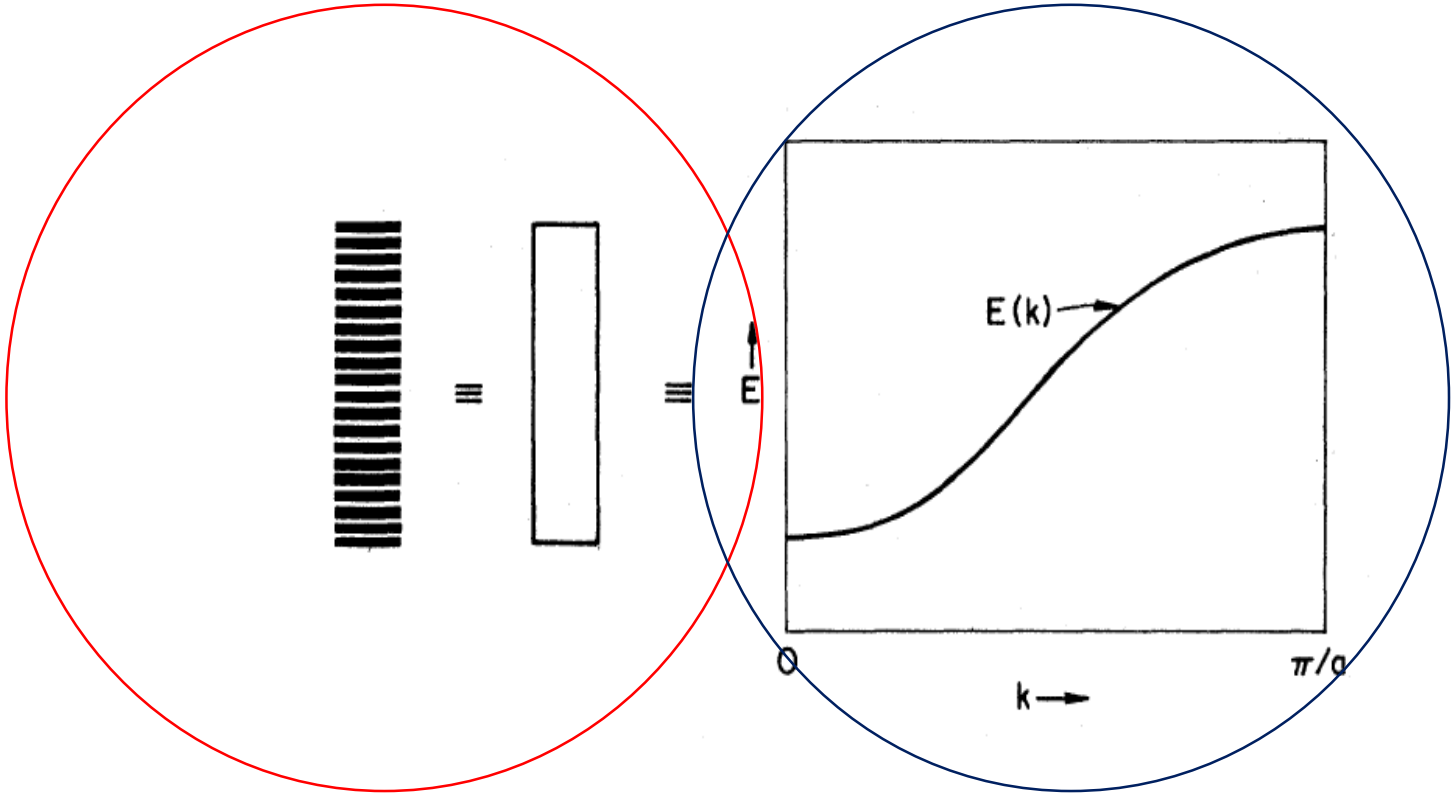


Top Catal (2014) 57:2–13
DOI 10.1007/s11244-013-0157-4

A chemical and theoretical way to look at bonding on surfaces

Roald Hoffmann

Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301



Chemist's point of view **Physicist's point of view**

Reviews of Modern Physics, Vol. 60, No. 3, July 1988

much to tell them about bonding in the solid state. I would disagree. Chemists have built up a great deal of under-

spaced polymer, then s
ity, called a Peierls di

as there are microscopic unit cells in the macroscopic crystal. So let us say Avogadro's number (N_A), give or take a few. There is an energy level for each value of k (actually a degenerate pair of levels for each pair of positive and negative k values). There is an easily proved theorem that

ate symmetry-adapted linear combinations ψ (remem- translation is just as good a symmetry operation as any ier one we know) are given in **6**. Here a is the lattice icing (the unit cell being in one dimension) and k is an lex which labels which irreducible representation of the nslation group ψ transforms as. We will see in a mo-

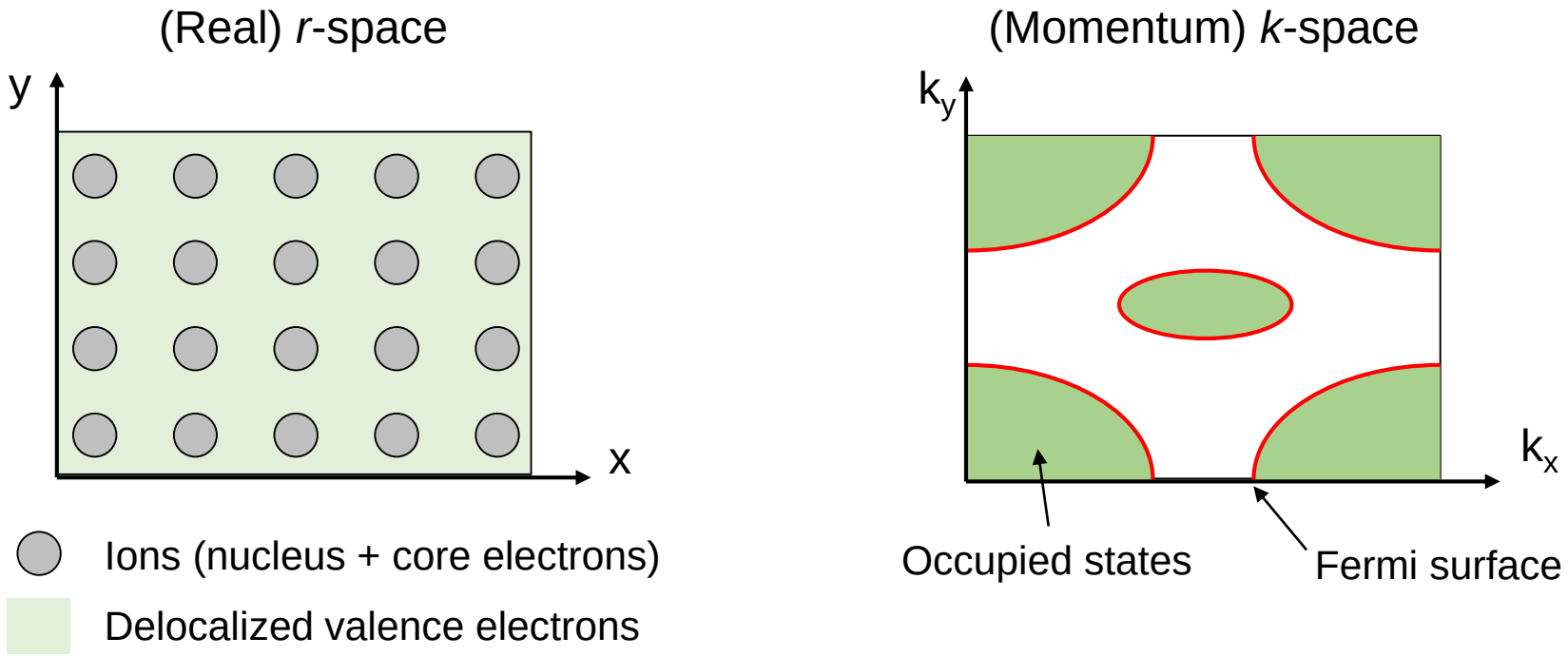
block instead of N_A lines), the physicist will alternatively draw as an E(k) vs. k diagram at right in **8**. Recall that k is quantized, and there is a finite but large number of levels in the diagram at right. The reason it looks continuous is that this is a fine "dot matrix" printer—there are N_A points jammed in there, and so it's no wonder we see a line.

Graphs of E(k) vs. k are called band structures. You can be sure that they can be much more complicated than this simple one, but no matter how complicated, they can be understood.

Band Width

One very important feature of a band is its *dispersion*, or *band width*, the difference in energy between the highest and lowest levels in the band. What determines the width of bands? The same thing that determines the splitting of levels in a "dimer," ethylene or H_2, namely, the overlap

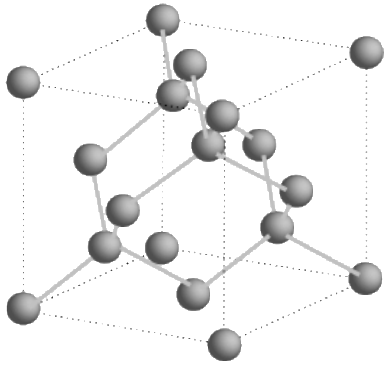
Physicist's point of view on matter



- Periodic arrays of atoms ➔ Periodic potential
- Electrons (waves) in a periodic potential
- (Periodic) electronic band structure formed
- Many physical properties determined by the electronic structure

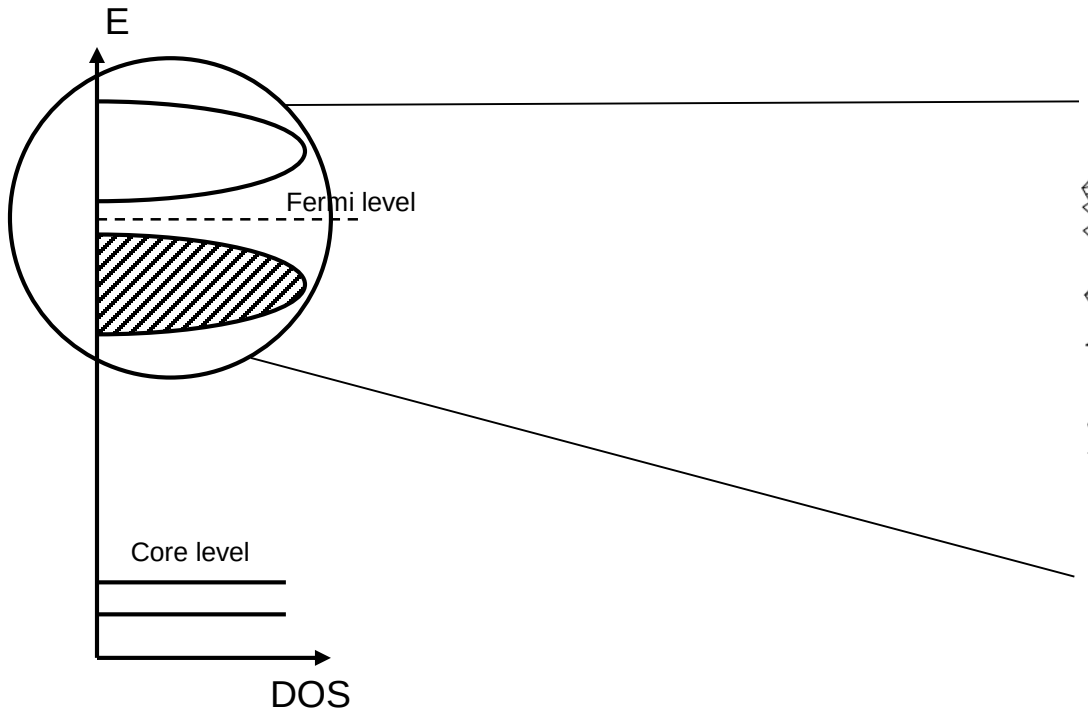
We want to know this

Electronic structure



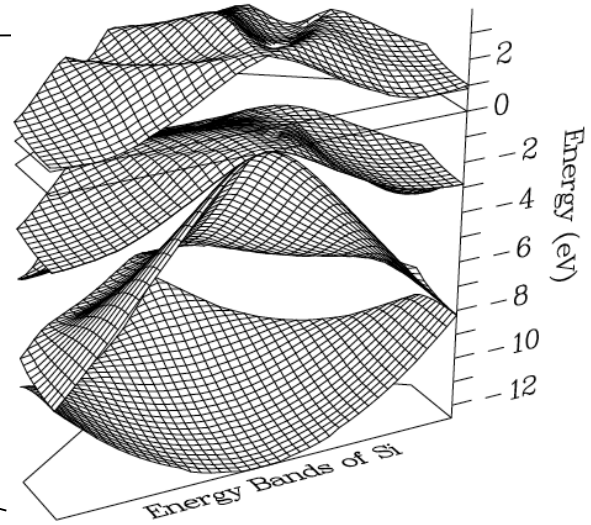
Silicon

Density of States (DOS)



Electronic structure

Band structure



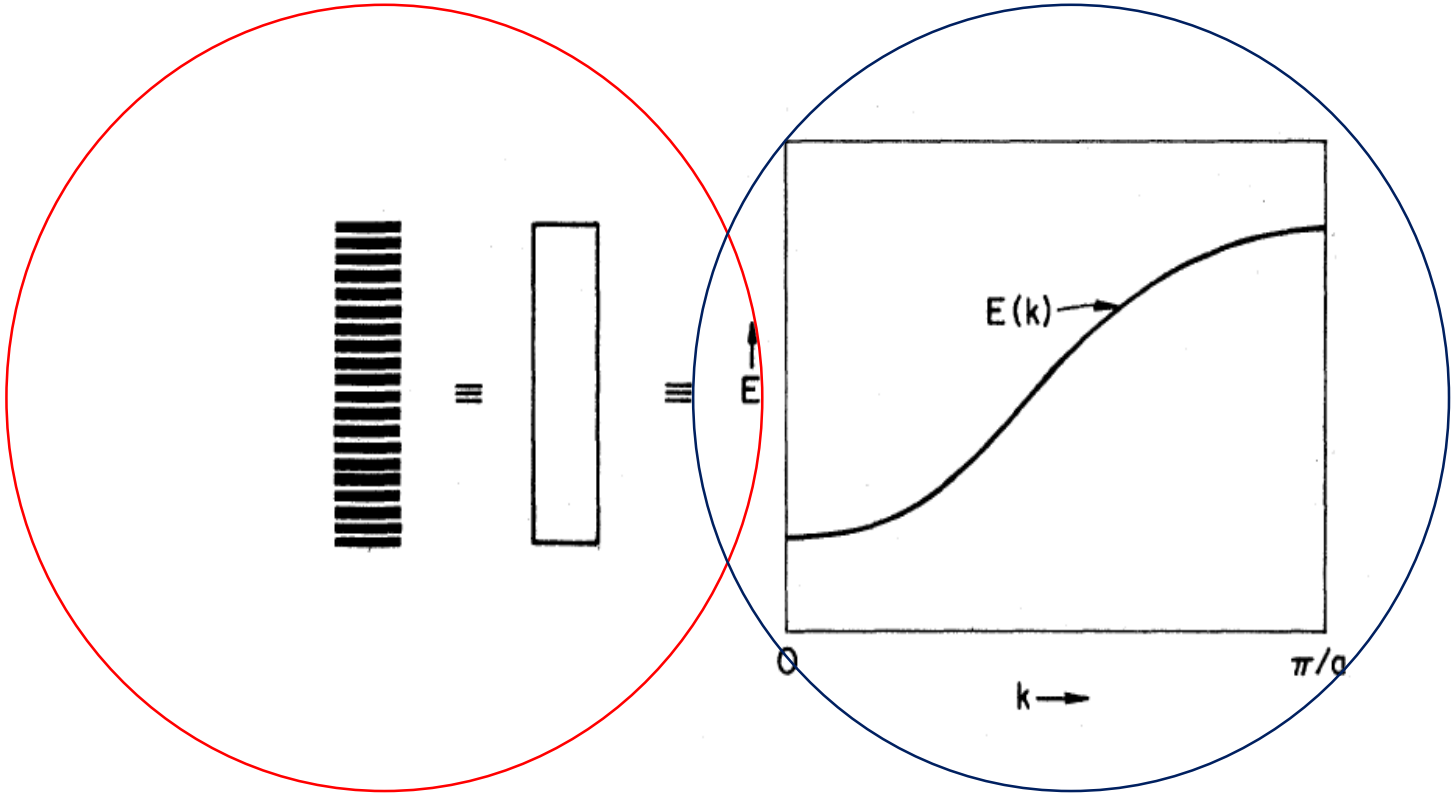
Electronic structure

C. Y. Kim (IBS, SNU)

A chemical and theoretical way to look at bonding on surfaces

Roald Hoffmann

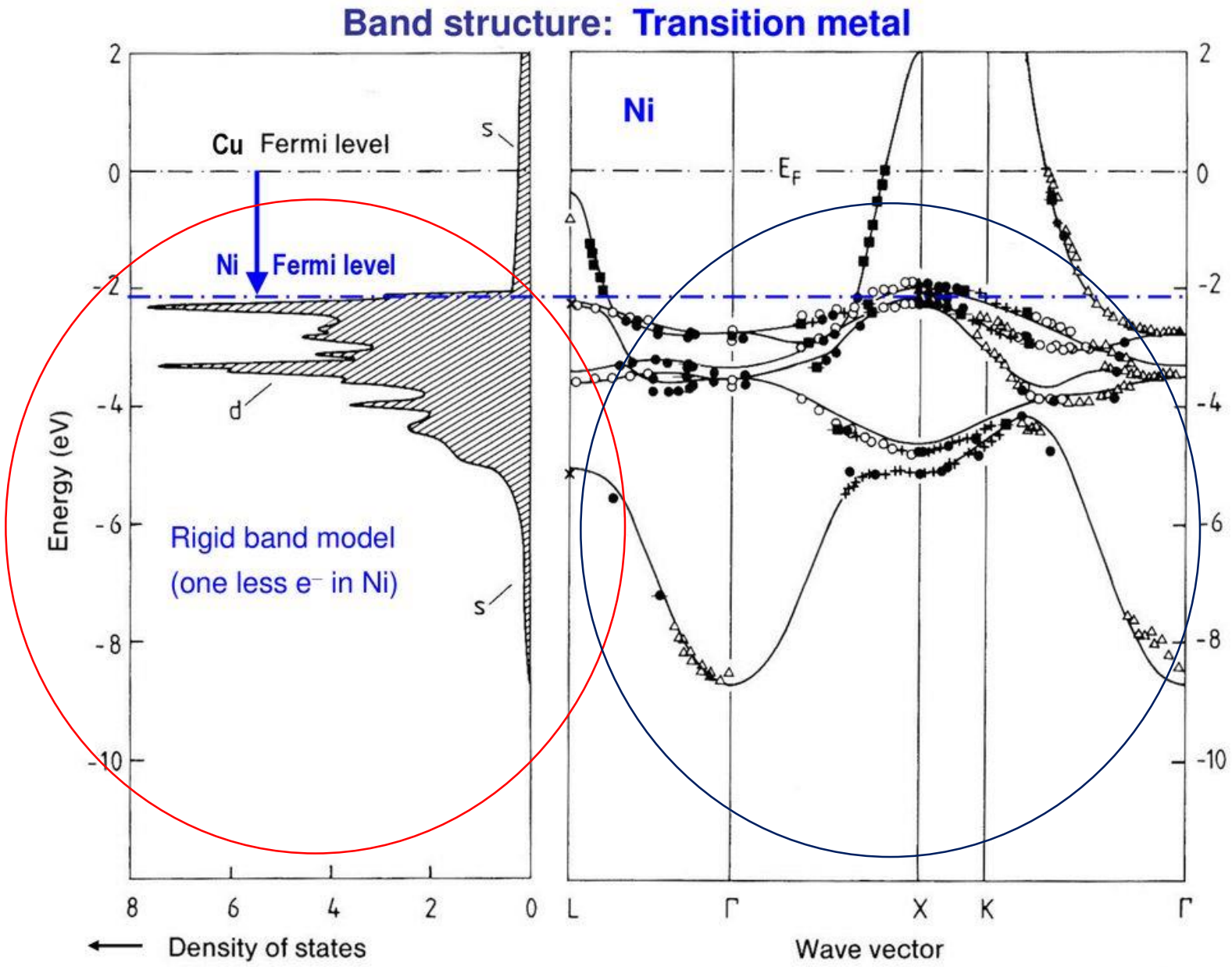
Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301



Chemist's point of view **Physicist's point of view**

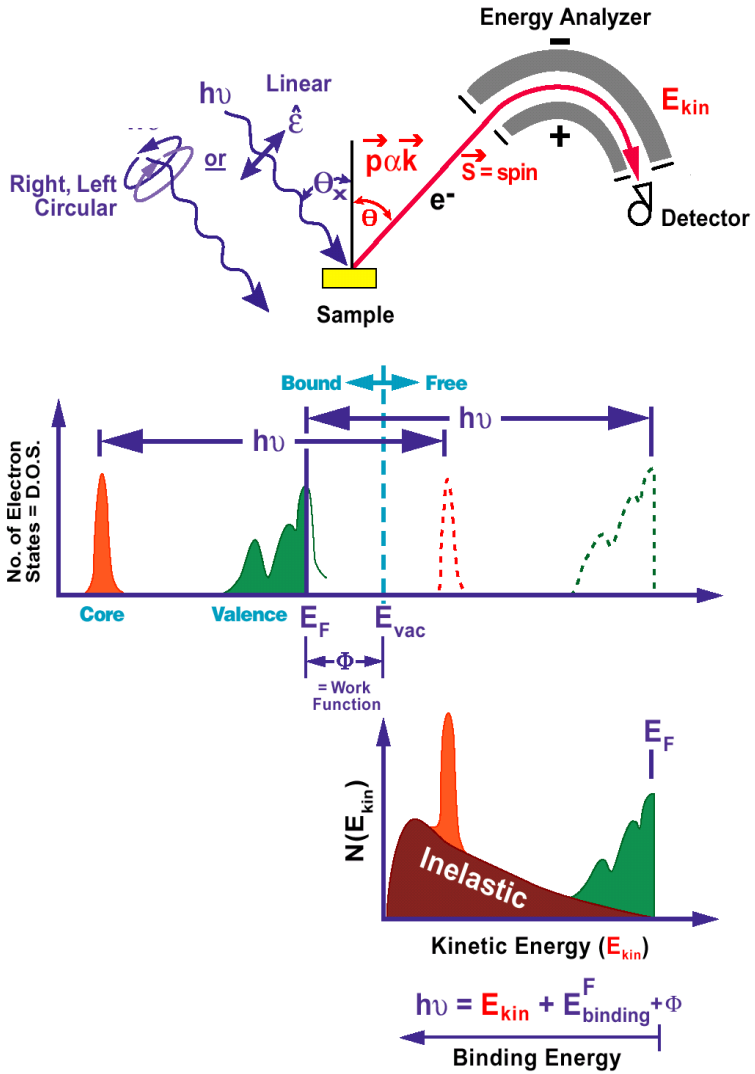
Reviews of Modern Physics, Vol. 60, No. 3, July 1988

Real Life



Chemist's point of view **Physicist's point of view**

X-ray Photoelectron Spectroscopy (XPS)



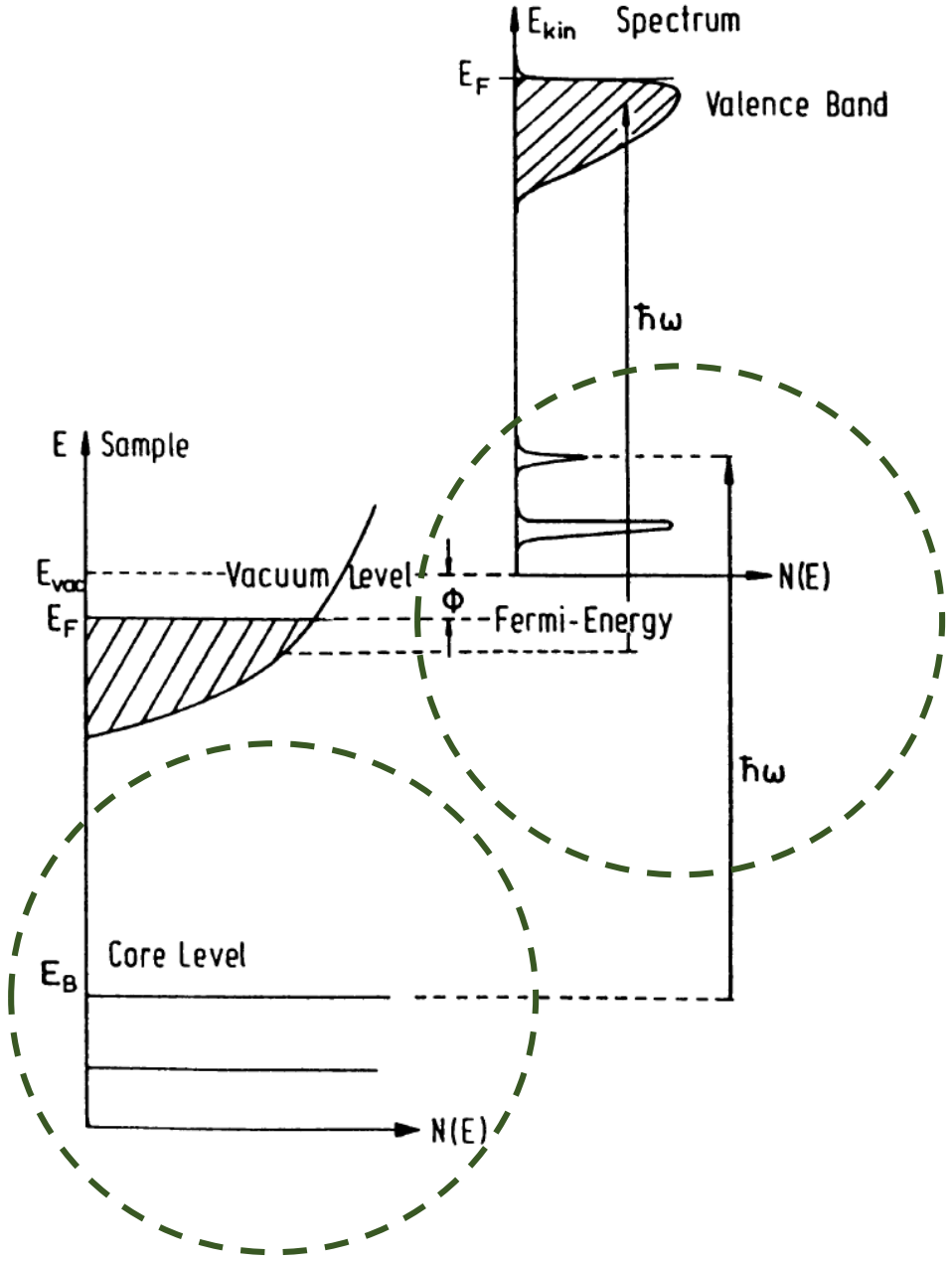
Photoelectric Effect : Einstein (1905)

E(K.E.) = E(hv) – E(B.E.) – Work function

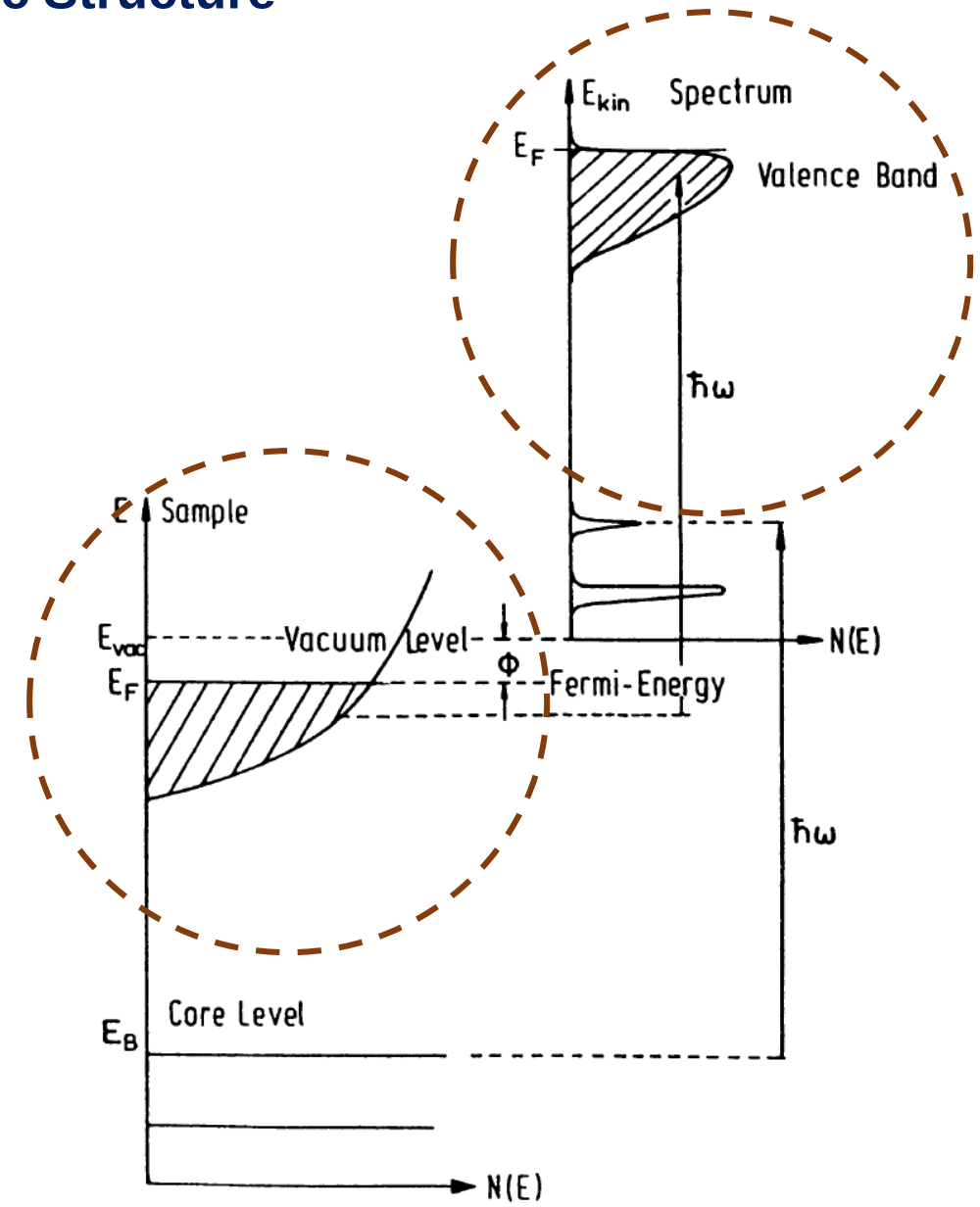
$$I \propto \sum_{f,i} |< f \mid p \cdot A \mid i >|^2 \, \delta(E_k^0 - E_m^0 - \mathrm{h}\omega)$$

***f* = final states**
***i* = initial states**
***p* = momentum of photoelectron**
***A* = vector potential of photon**
(Electric fields)

XPS Core-Level : Element Specific Chemical Information

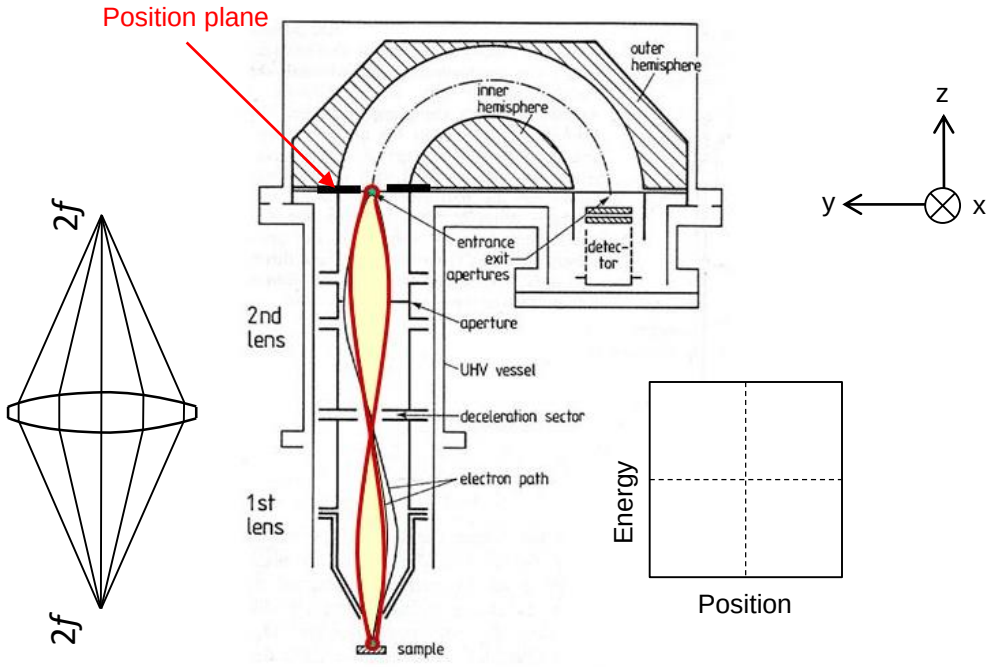


XPS Valence Band : Electronic Structure



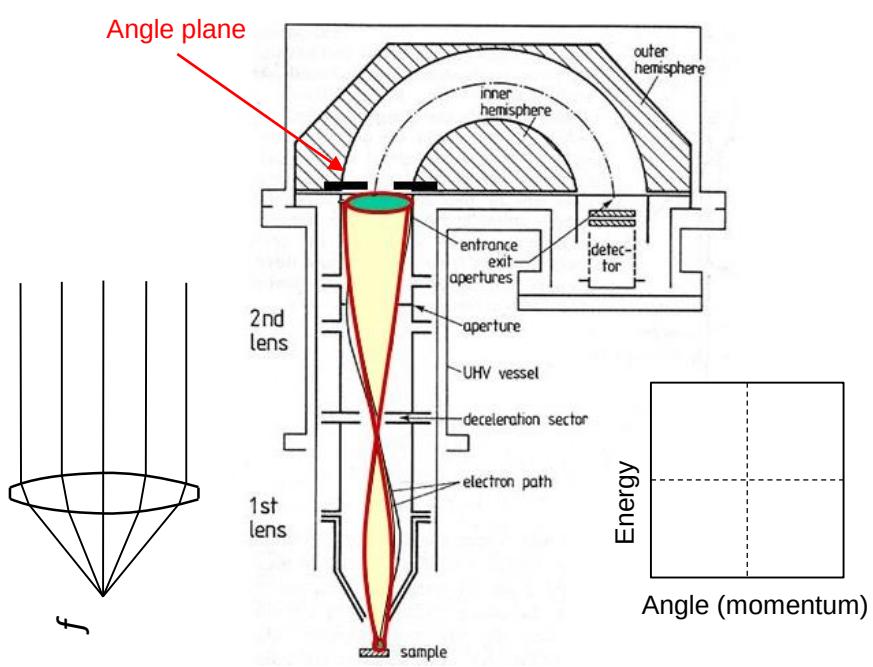
Transmission vs angle modes

Transmission mode



- x-position @ sample → x-position @slit → x-position @ detector

Angle mode

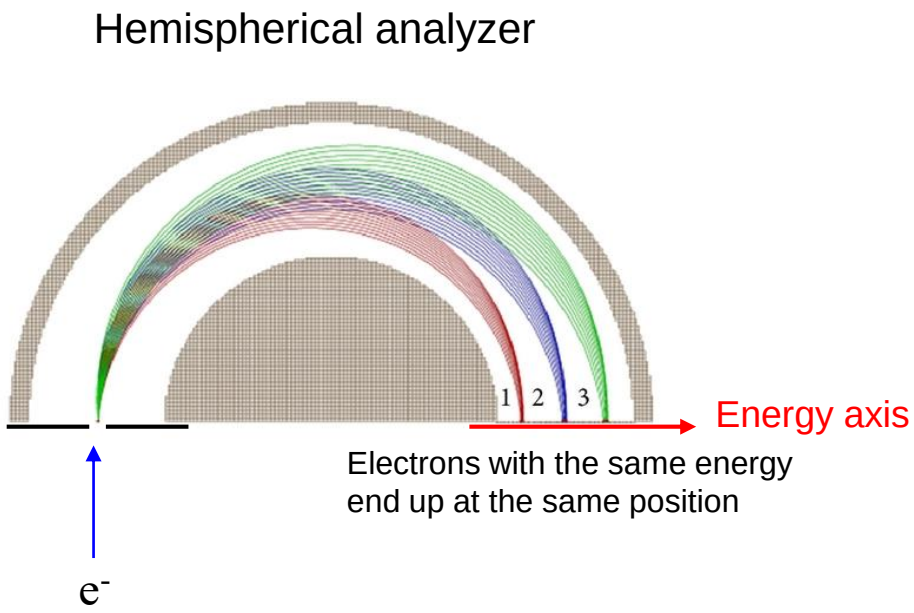


- Angle @ sample → position @ slit → position @ detector

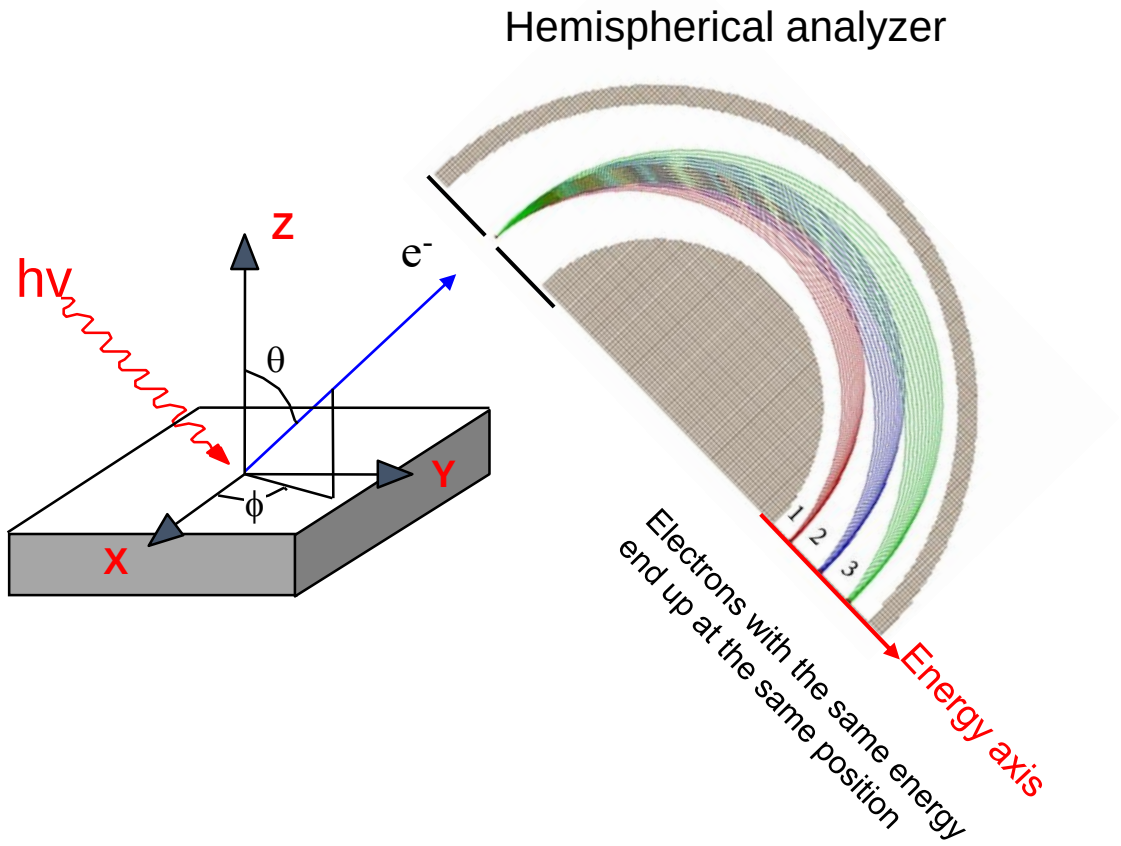
Google images

C. Y. Kim (IBS, SNU)

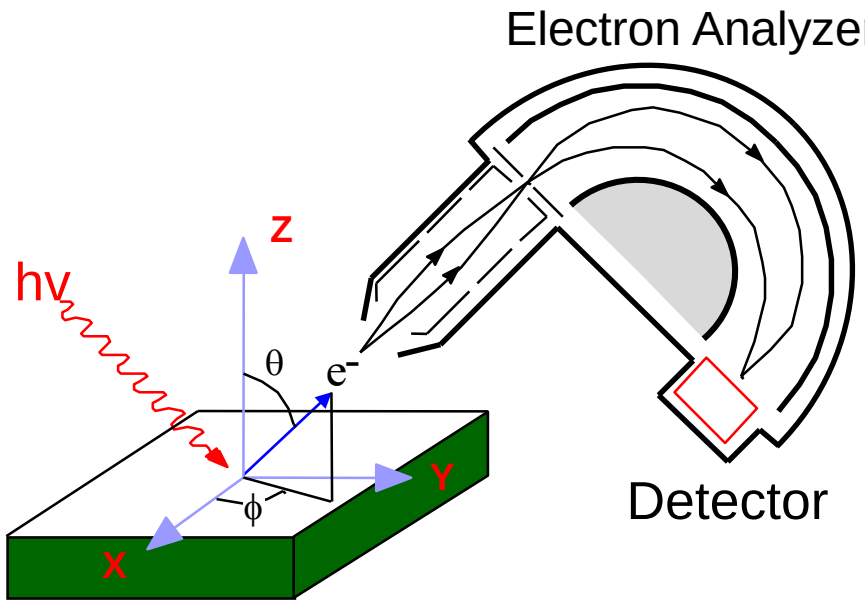
Measuring electron (kinetic) energy

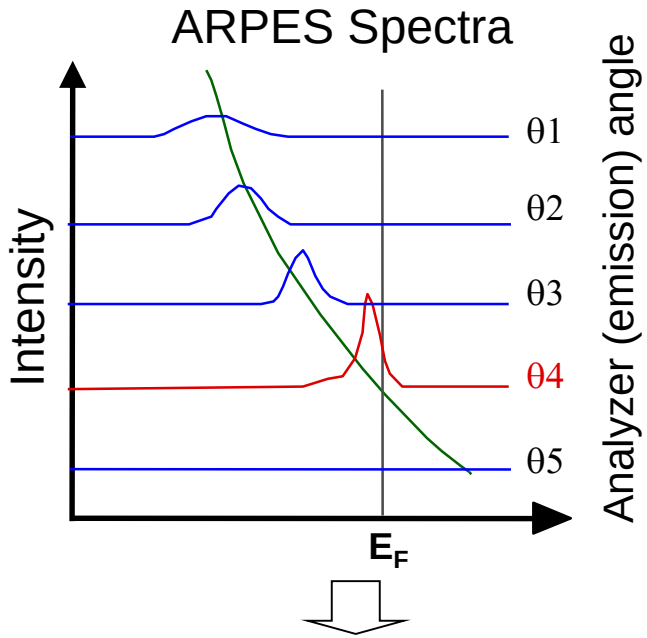


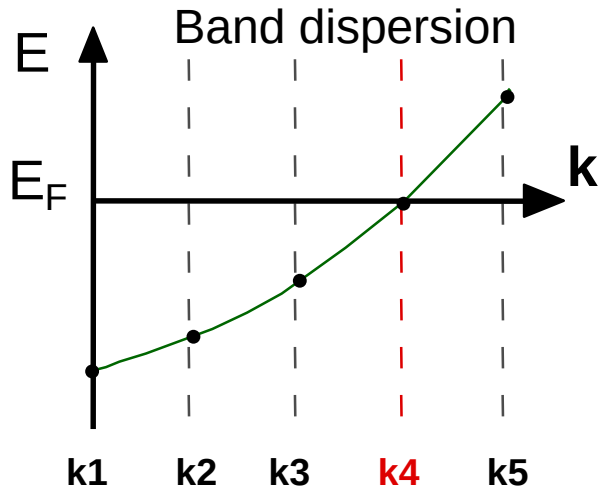
Measuring electron (kinetic) energy



Angle (momentum) resolved PES







- Photoelectron kinetic energy is measured
- Emission angle of photo electron is measured
- Momentum is obtained from energy and emission angle

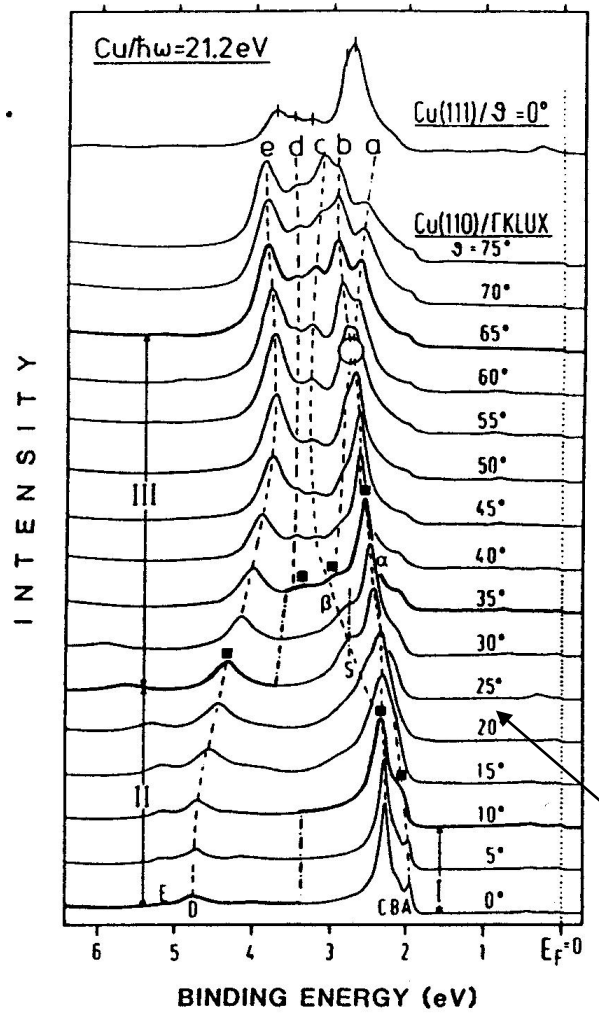
Quick overview

C. Y. Kim (IBS, SNU)

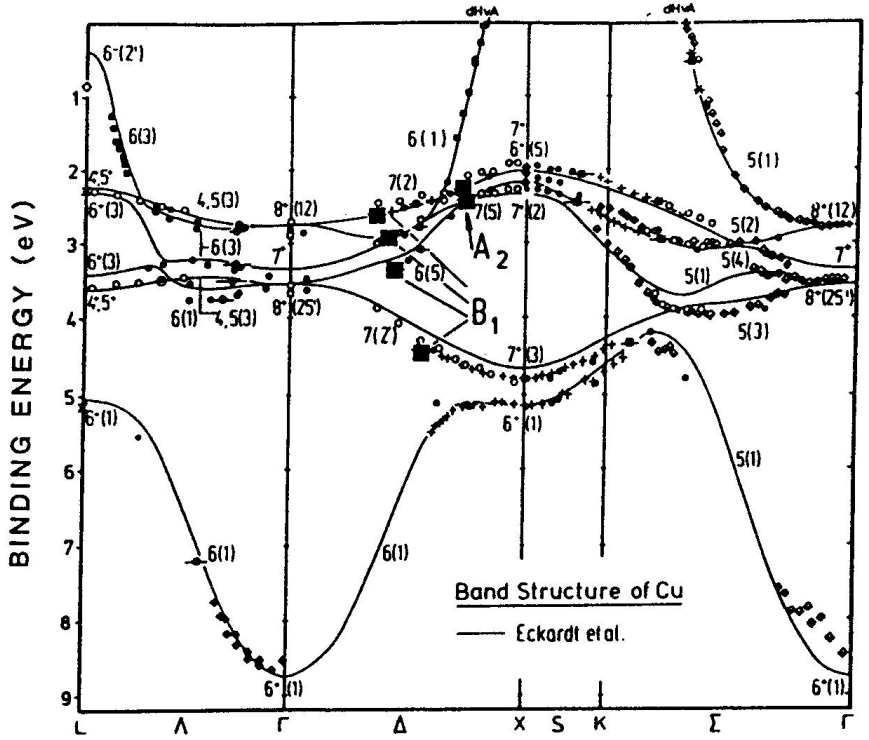
When all are considered…

EDCs at different angles

* Peak positions give the bands



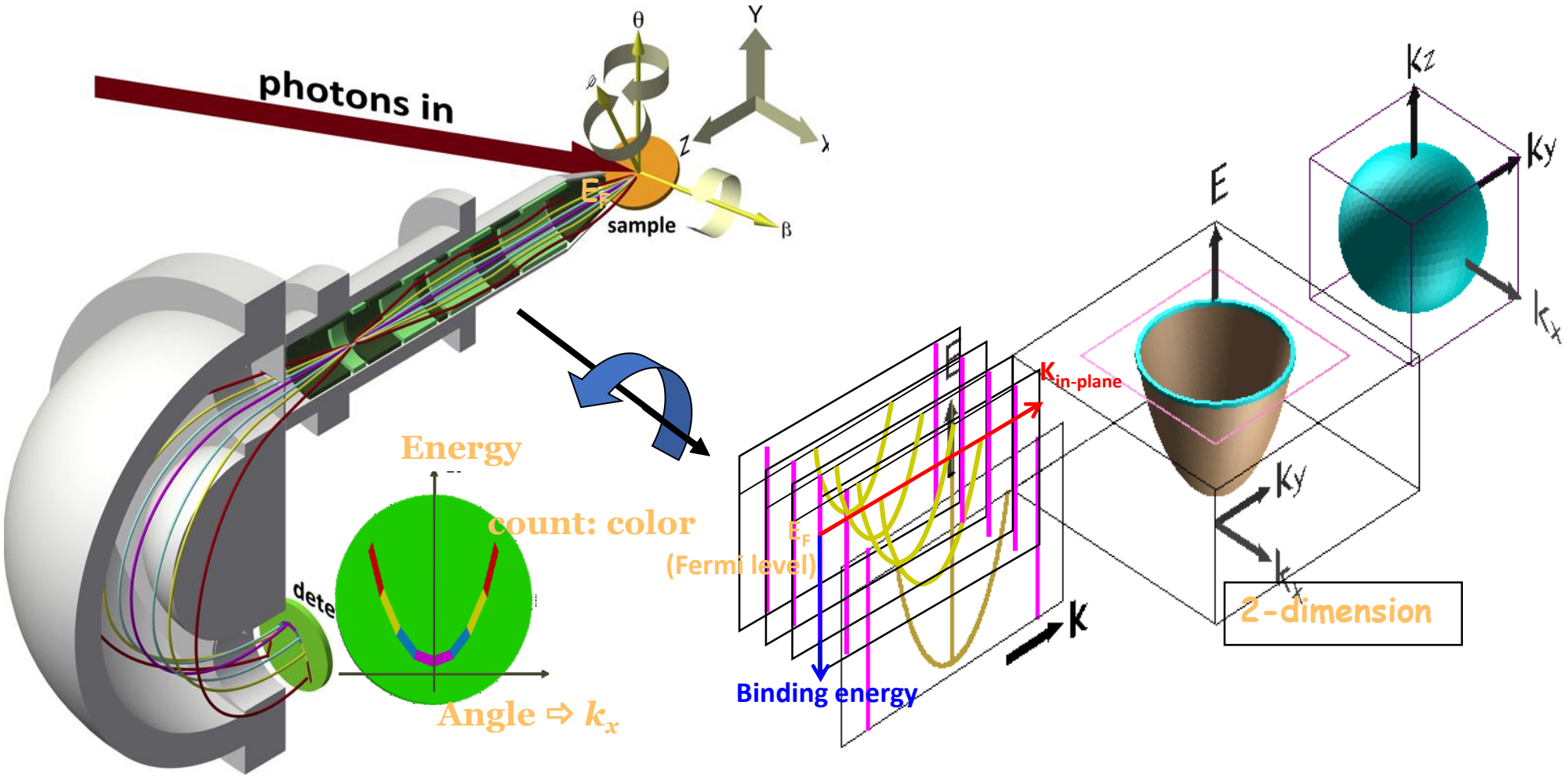
Measured bands



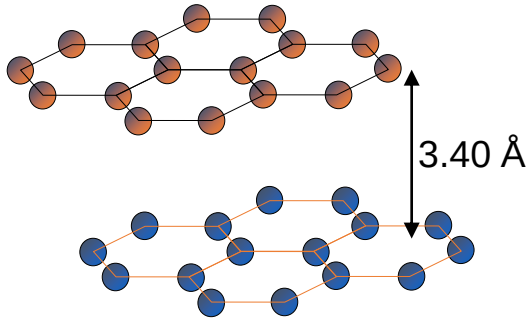
Electron emission angles

From Hufner's book

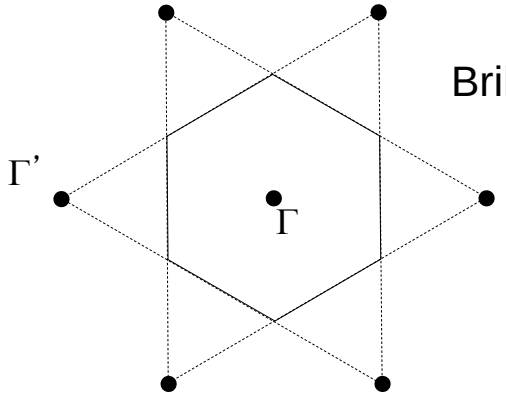
Angle Resolved Photoemission Spectroscopy (ARPES)



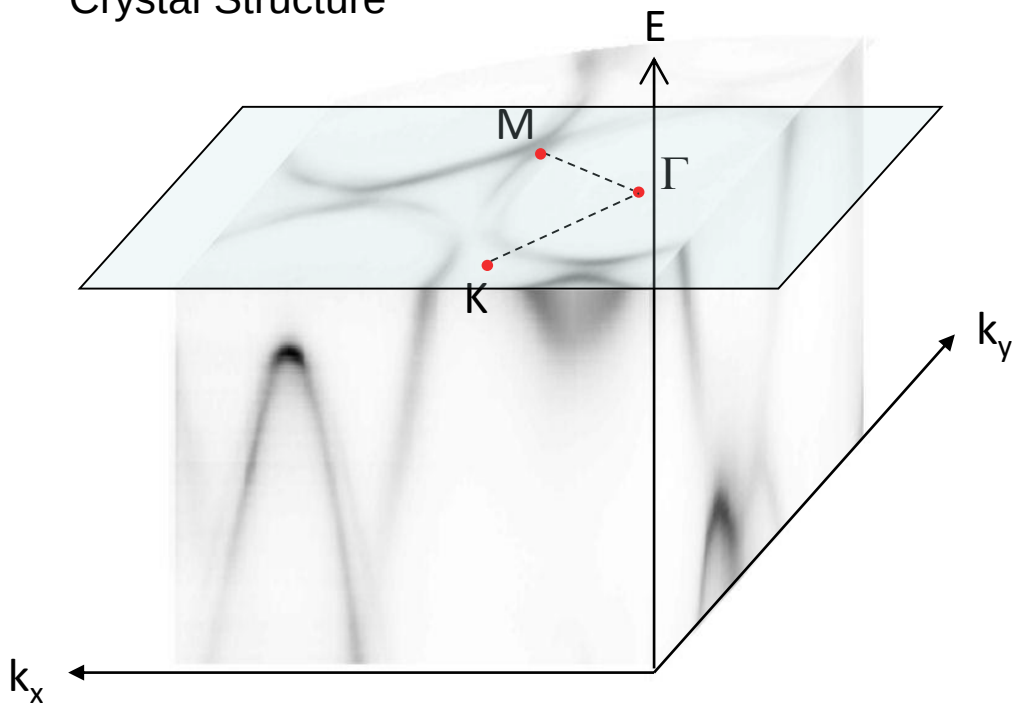
Graphite

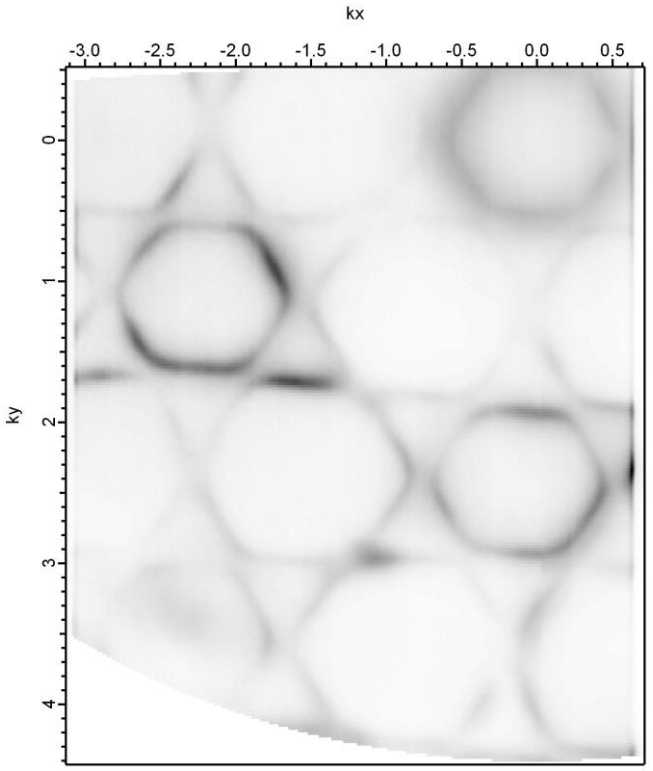


Crystal Structure



Brillouin zone

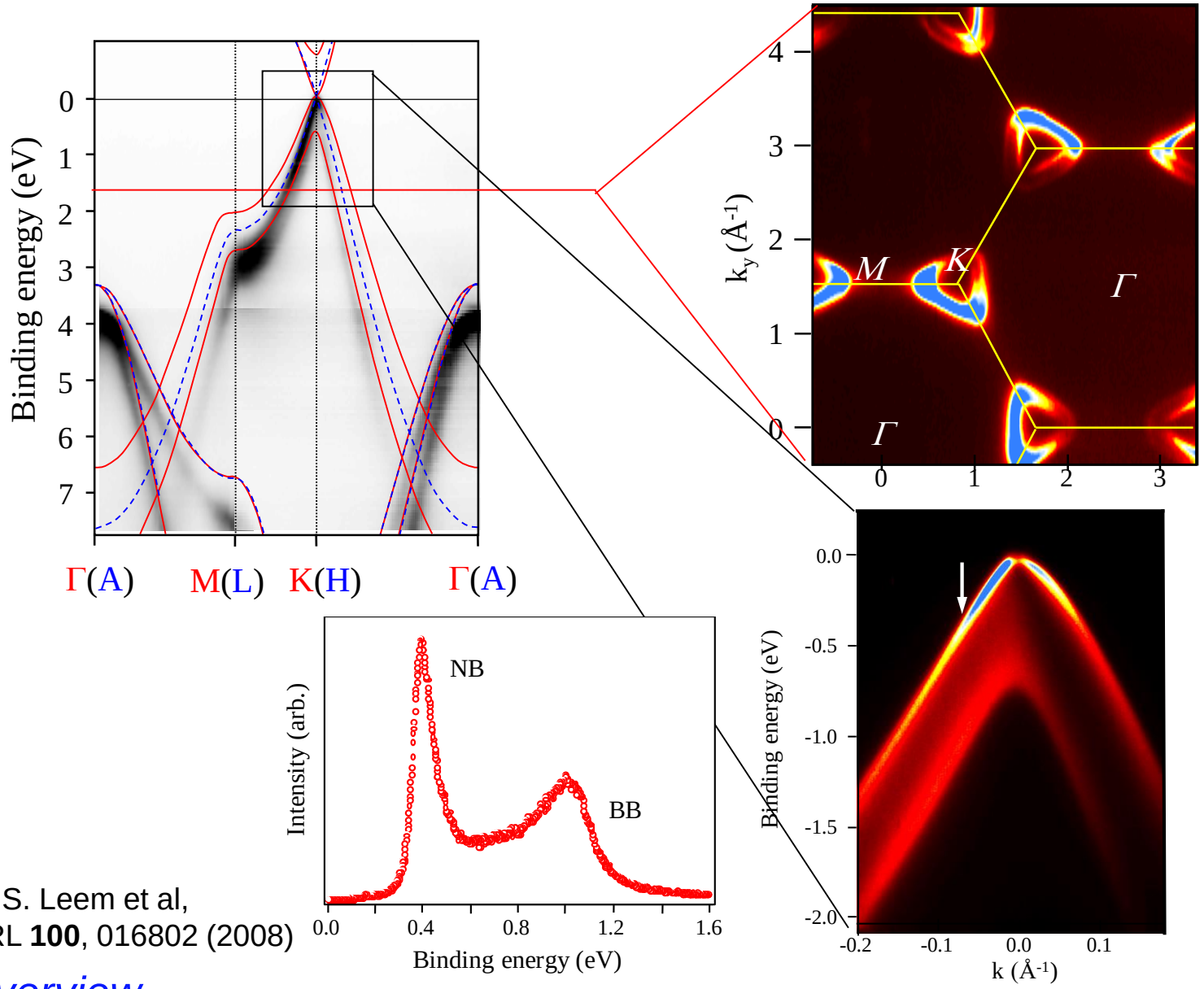




Quick overview

C. Y. Kim (IBS, SNU)

Graphite band structure

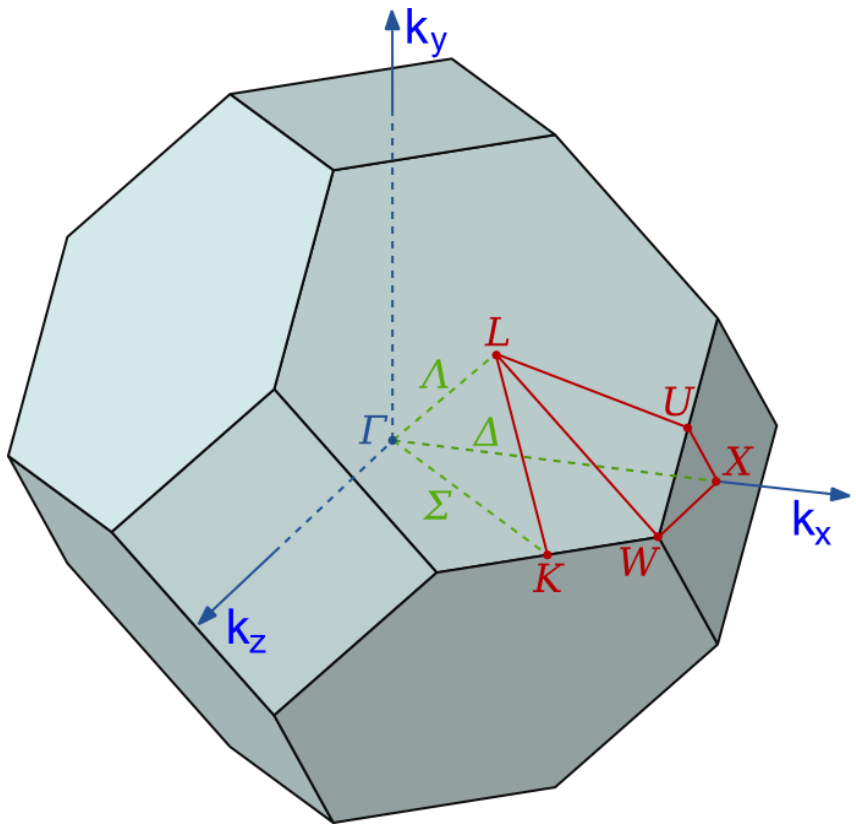


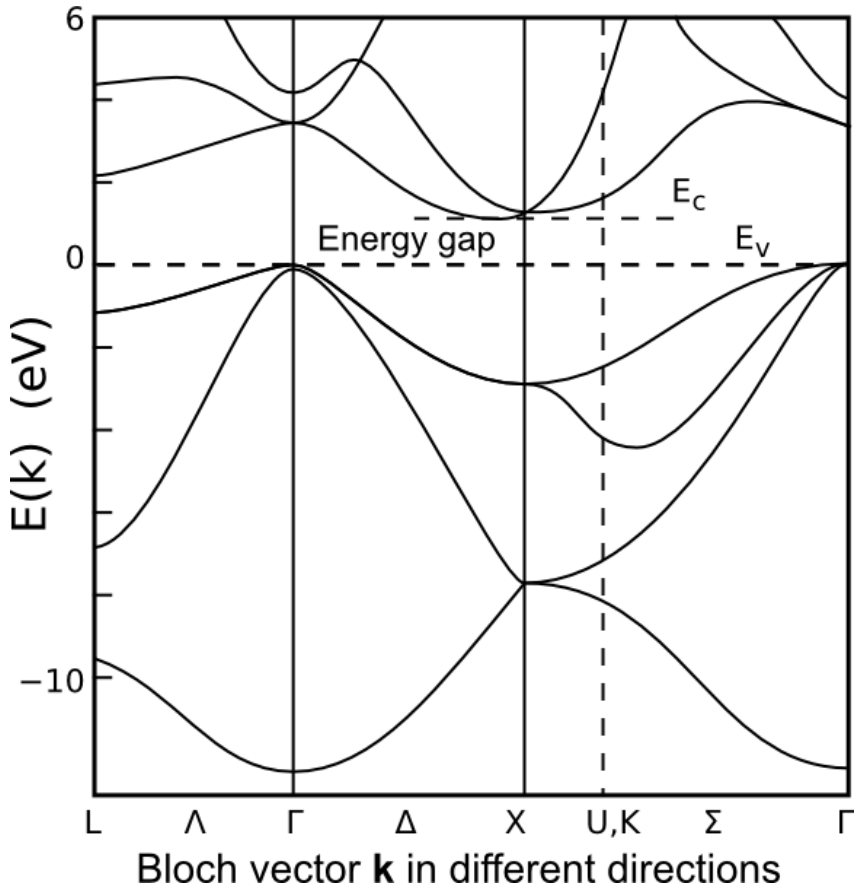
C. S. Leem et al,
PRL **100**, 016802 (2008)

Quick overview

C. Y. Kim (IBS, SNU)

Notations of Symmetry



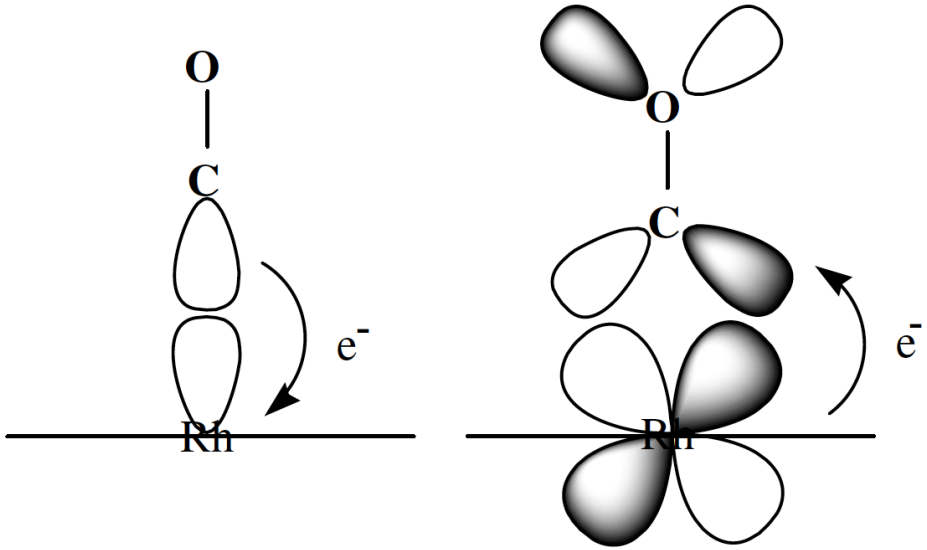


Silicon

Molecular Orbital View of Chemisorbed Carbon Monoxide

by George Blyholder

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas *(Received February 26, 1964)*



Scheme 1. The resembled Blyholder model of CO molecule adsorbed on the 4Rh/CeO_2(Rh-cluster) surface.

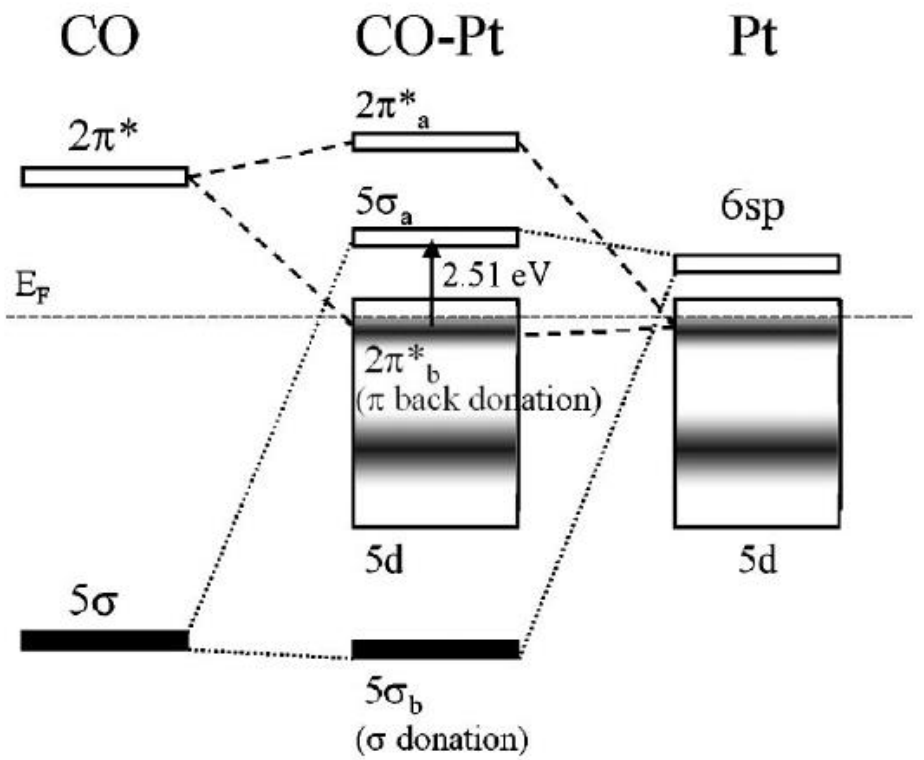
Chemical Physics 348 (2008) 161–168

Frontier Molecular Orbitals

Can we see these orbitals ?

Probing the charge-transfer state of CO on Pt(111) by two-dimensional infrared-visible sum frequency generation spectroscopy

K. C. Chou,[1,3,*] S. Westerberg,[1,3] Y. R. Shen,[2,3] P. N. Ross,[3] and G. A. Somorjai[1,3,†]



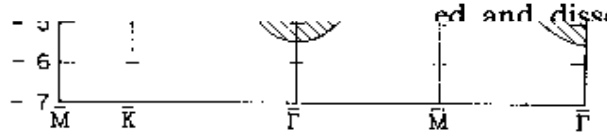
PHYSICAL REVIEW B **69**, 153413 (2004)

Previous Reports

I. INTRODUCTION

on of H with the bulk of Pd has been in-
oughly due to the high solubility of H in
re of the adsorbed H and the relationship
ed and dissolved H is not as well under-

Pd(111).[3] The atomic adsorption energy
Pd(111) has been measured by Conrad *et*
at low coverages, while the heat of solu
($\Delta\overline{H}$) is 0.20 eV.[1] The chemisorbed H
more tightly than the dissolved H, but t
surface well will depend upon the H con
surface. Engel and Kuipers showed that
their molecular-beam data predicted a va



(b) H_2 ADSORPTION

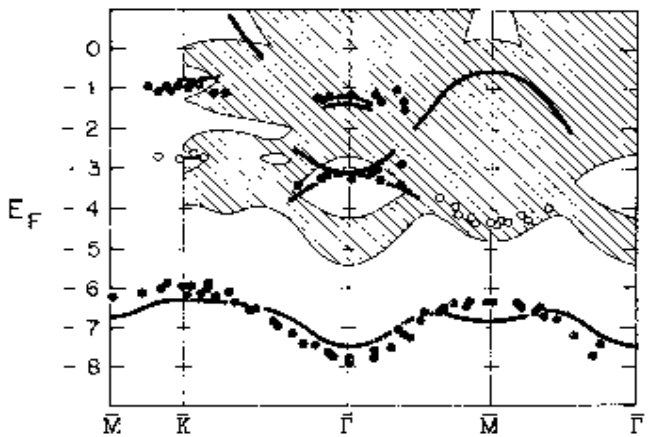
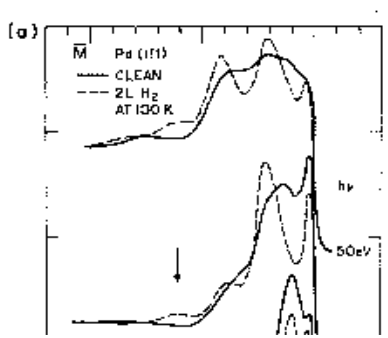


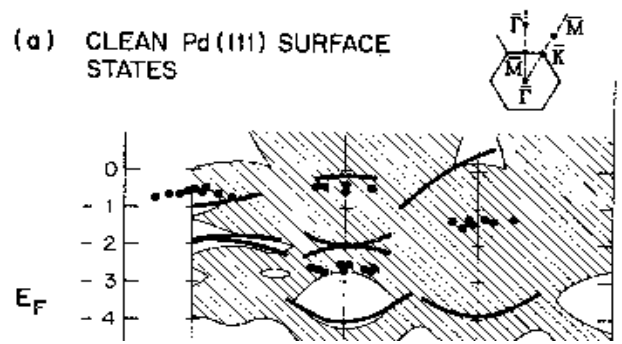
FIG. 5. Calculated and measured surface states fo
(111) and (b) H(1×1) Pd(111) (Ref. 13). The shaded re
e the calculated projection of the bulk bands onto the
rface. The solid lines are calculated surface states or
nces, the solid circles are data. The open circles ind
aks with some uncertainty.

e intensity of the H 1*s* split-off state, which is very v
$\hbar\omega = 30$ eV. The peak in the clean $\hbar\omega = 30$ eV spect

INTERACTION OF HYDROGEN WITH A Pd(111) SURFACE



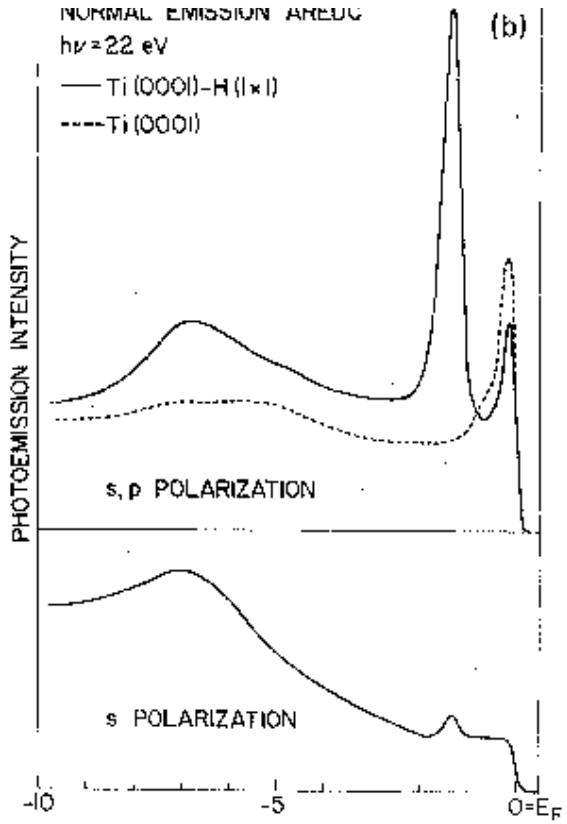
(a) CLEAN Pd(111) SURFACE STATES

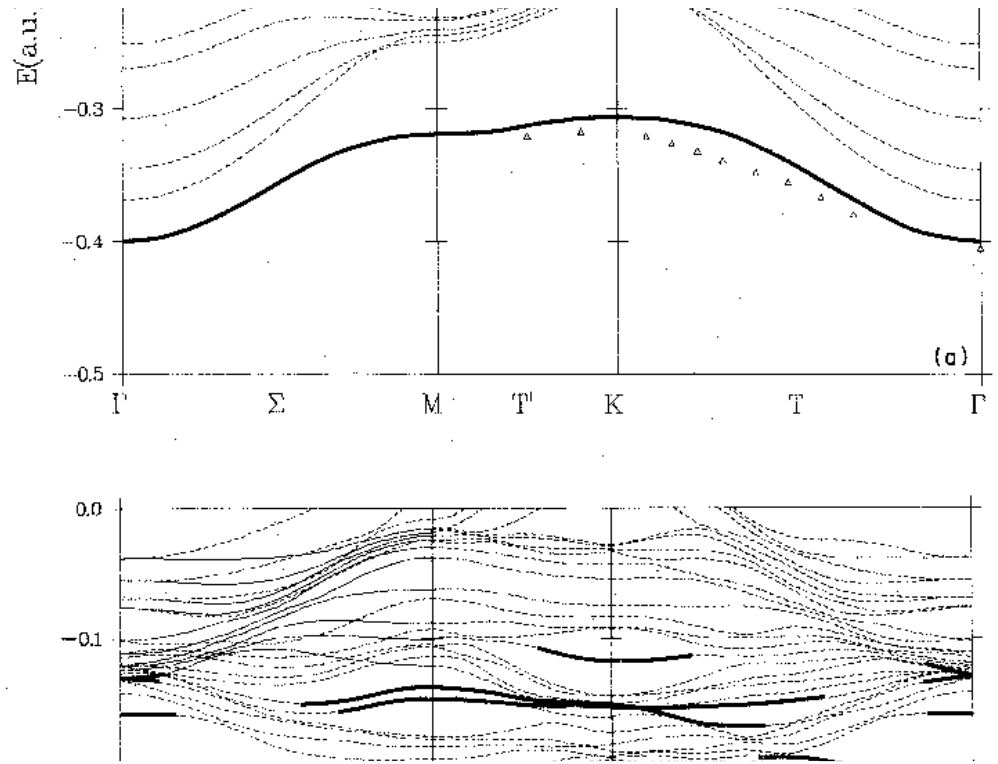


photoemission-spectroscopy (PARUPS) data provide a great deal more information (level symmetries, orderings, and dispersions) than is available in ordinary angle-integrated ultraviolet-photoemission spectroscopy (UPS). A complete set of PARUPS measurements thus presents a much more stringent test of a hypothetical geometry and corresponding electronic-structure analysis.

Nevertheless in the present work, for H on single crystal Ti (0001), we find that even an extensive set of PARUPS results is not enough to determine the bonding geometry unambiguously. Comparison of spectroscopic predictions to PARUPS surface-band positions and dispersions of the bonding-antibonding pair increases, ultimately driving the antibonding state out of a large bulk band gap up into a bulk band wherein it disappears as an observable surface feature. The sensitivity of these spectral features to bonding geometry makes it easy to tell in advance which geometries will yield reasonable spectroscopic predictions and several do. Satisfyingly, the minimum total-energy configuration is one of those which is spectroscopically acceptable.

Our calculations predict the observed work function difference of about 0.2 eV between the clean and H-covered Ti (0001) films, although the cal-





Previous Reports

A Direct Observation of the Two-Dimensional $\pi - d$ Bands for Adsorbed CO

H. Kuhlenbeck, H. B. Saalfeld, and M. Neumann

Fachbereich Physik, Universität, Barbarastrasse 7, D-4500 Osnabrück, Fed. Rep. Germany

H.-J. Freund and E. W. Plummer

Institut für Physikalische und Theoretische Chemie, Universität, Egerlandstrasse 3, D-8520 Erlangen, Fed. Rep. Germany

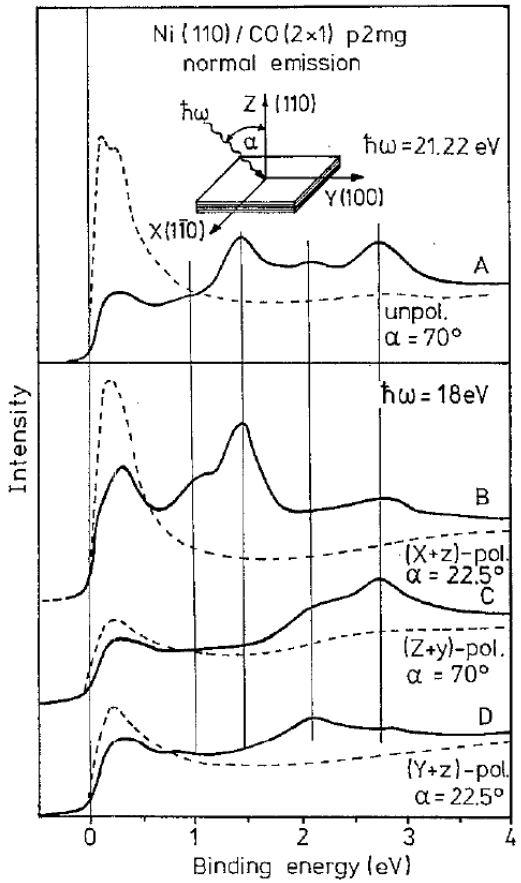


Fig. 1. Photoemission spectra of the valence band region of Ni for clean *(dashed)* and CO covered *(solid)* Ni(110) in normal emission. Curves *B*, *C*, and *D* are spectra taken with various polarizations of the incident light [9]. The notation *Y+z* means

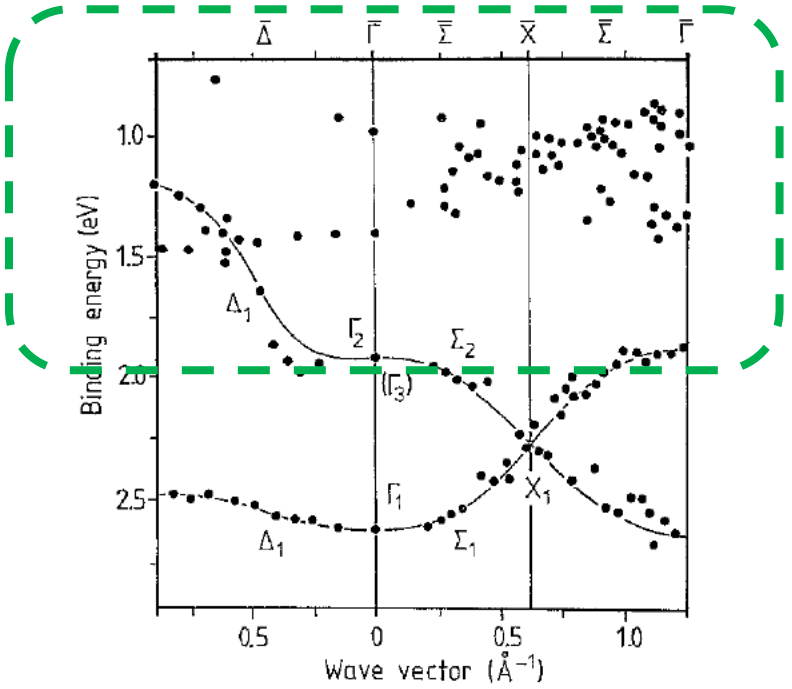


Fig. 2. Dispersion of the *d*-band features along the two high symmetry directions in the SBZ. Labelling is in accordance with [8] (Litvin's convention)

Table 1. Possible linear combinations of unoccupied CO states and Nickel *d*-band levels for bridge bonded CO at $\bar{\Gamma}$, $\bar{X}$ and along $\bar{\Sigma}$ and $\bar{\Delta}$, and the dipole selection rules. The notations of the *d* states are in accordance with those given by Salem and Leforestier [12] for the [110] direction of fcc crystals

Symmetry	Unoccupied CO state	Nickel *d*-states	Orientation of the electric field vector
Γ_1	$2\pi_y^-$	$d_{z^2}^+, d_{xy}^-, d_{x^2-y^2}^+$	$E \parallel z$
Γ_2	$2\pi_y^+$	d_{xz}^-, d_{yz}^+	$E \parallel y$
Γ_3	$2\pi_x^-$	$d_{z^2}^-, d_{xy}^+, d_{x^2-y^2}^-$	Forbidden
Γ_4	$2\pi_x^+$	d_{xz}^+, d_{yz}^-	$E \parallel x$
Σ_1	$2\pi_y^-, 2\pi_x^+$	$d_{z^2}^+, d_{xy}^-, d_{x^2-y^2}^+, d_{xz}^+, d_{yz}^-$	$E \parallel z$, or x
Σ_2	$2\pi_y^+, 2\pi_x^-$	$d_{z^2}^-, d_{xy}^+, d_{x^2-y^2}^-, d_{xz}^-, d_{yz}^+$	$E \parallel y$
X_1	All of Σ_1 and Σ_2		$E \parallel y, z$ or x
Δ_1	$2\pi_y^-, 2\pi_y^+$	$d_{z^2}^+, d_{xy}^-, d_{x^2-y^2}^+, d_{xz}^-, d_{yz}^+$	$E \parallel y$ or z
Δ_2	$2\pi_x^-, 2\pi_x^+$	$d_{z^2}^-, d_{xy}^+, d_{x^2-y^2}^-, d_{xz}^+, d_{yz}^-$	$E \parallel x$

Surface Science Letters

Probing the modifier precursor state: adsorption of CO on Sn/Pt(111) surface alloys

Chen Xu, Bruce E. Koel *

Surface Science Letters 304 (1994) L505–L511

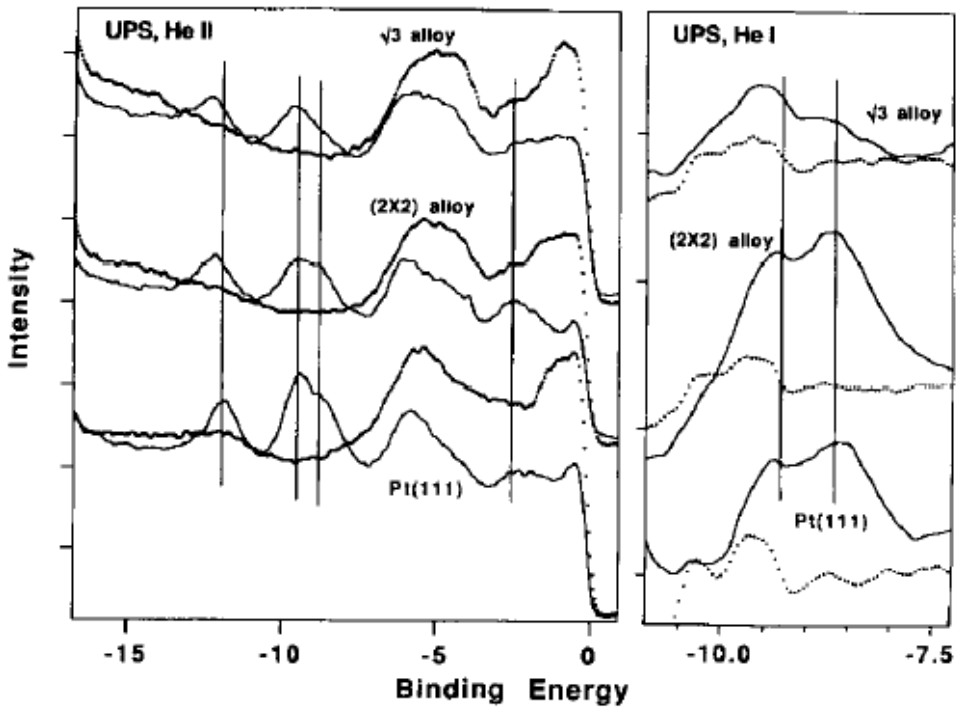
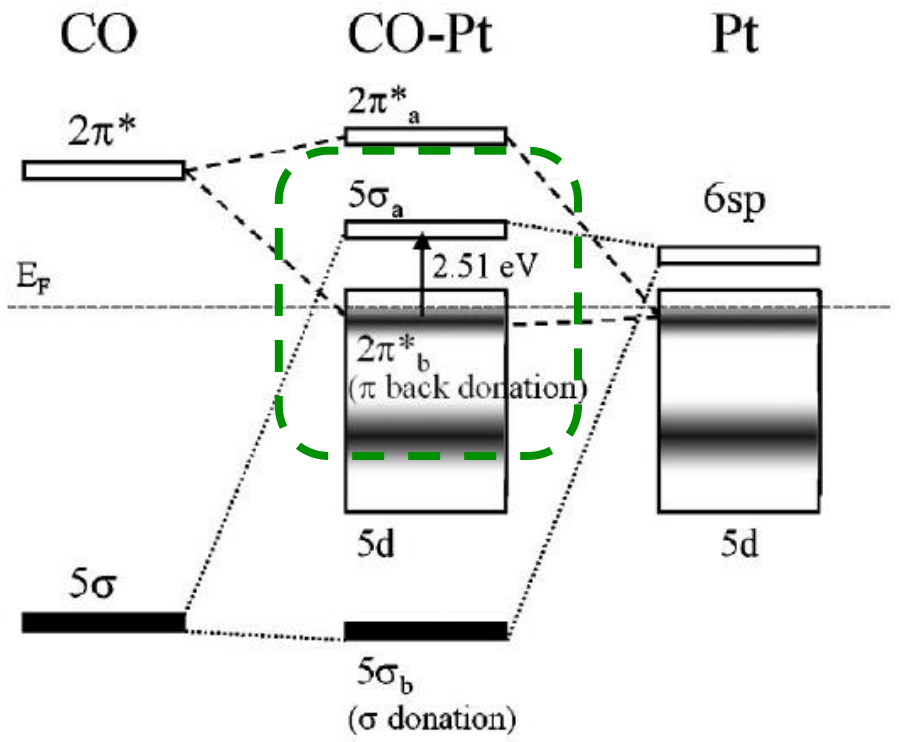


Fig. 2. He I and He II UPS spectra of CO saturation coverages on the Pt(111) surface and the (2×2) and $\sqrt{3}$ surface alloys.

on CO/Pd(111) to a shifted Pd surface state. A recent careful investigation of such a state on CO/Ni(110) by Kuhlenbeck et al. [24] using ARUPS and synchrotron light has identified this state unambiguously to be the $2\tilde{\pi}^*$–d surface band. Accordingly, we tentatively assign the peak at 2 eV in Fig. 2 to the $2\tilde{\pi}^*$ state. A definitive assignment would require careful ARUPS measurements. In any case, this CO-induced peak at 2 eV does not change significantly from Pt(111) to the Sn/Pt(111) surface alloys.

Probing the charge-transfer state of CO on Pt(111) by two-dimensional infrared-visible sum frequency generation spectroscopy

K. C. Chou,[1,3,*] S. Westerberg,[1,3] Y. R. Shen,[2,3] P. N. Ross,[3] and G. A. Somorjai[1,3,†]



PHYSICAL REVIEW B **69**, 153413 (2004)

Theoretical study on the photostimulated desorption of CO from a Pt surface

H. Nakatsuji
Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan and Institute for Fundamental Chemistry, 34-4, Tankano-Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan

H. Morita and H. Nakai
Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Y. Murata and K. Fukutani
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

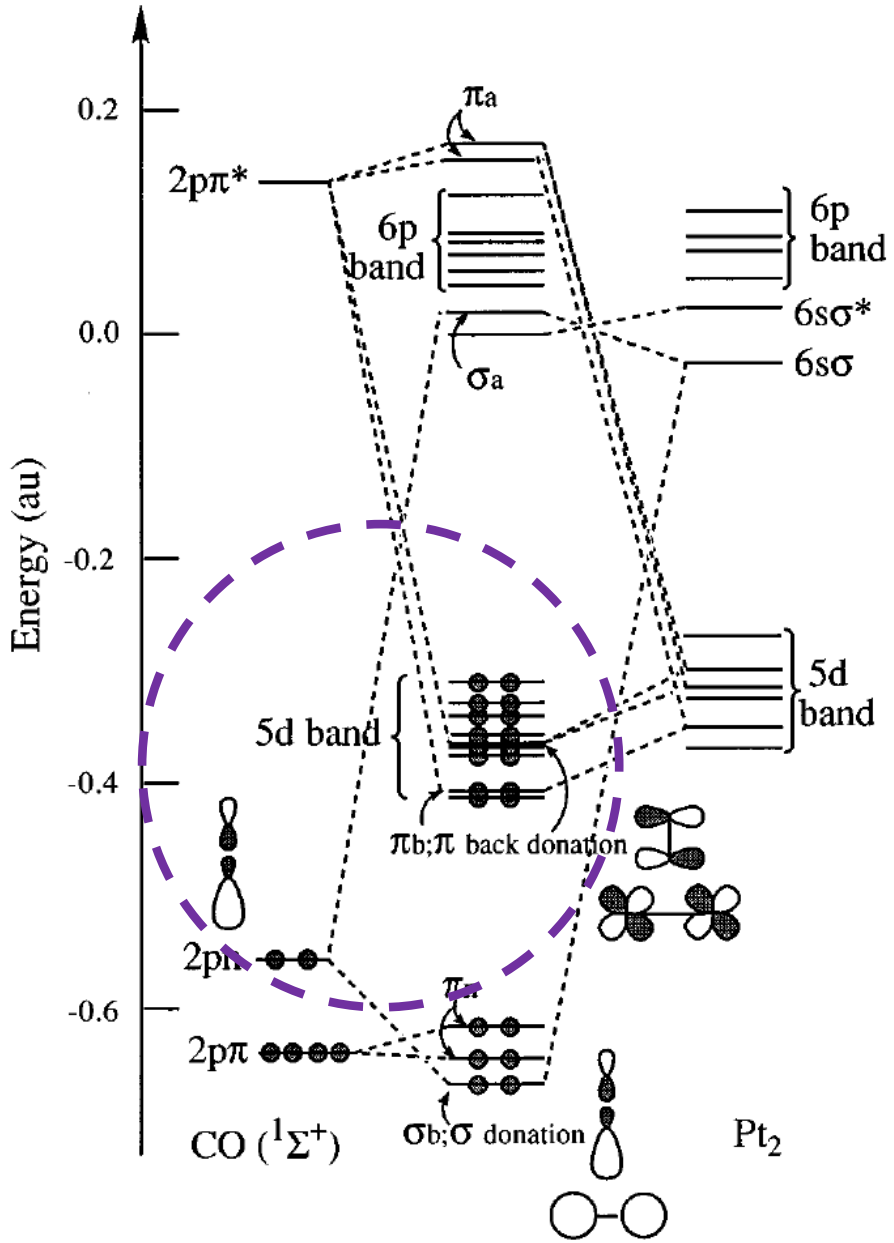


FIG. 2. A schematic orbital correlation diagram for the interaction between CO and Pt_2 in the bridge-site adsorption.

Summary

1. Electronic structure of CO on Pt(111) and PtSn surface alloys are measured.
2. Bonding state of back-donation is observed as CO adsorption increase.
3. The energy level of observed bonding state shows agreement with previous calculation results
4. DFT calculation (KKR method) shows good agreement on clean surface.
5. Supercell calculation of CO/Pt, PtSn will refine our interpretation.