SURFACE SCIENCE

"Adsorption on Surfaces"
Readings

1. Zangwill, Ch. 8 - Physisorption
   Ch. 9 - Chemisorption
   Ch. 14 - Kinetics and Dynamics

2. Attard and Barnes, pp. 1-17, 27-34, 71-75

3. G. A. Somorjai, "Introduction to Surface Chemistry and Catalysis", (Wiley 1994)

   Ch. 3.8, Thermodynamics of Monolayers
   Ch. 4, Dynamics at Surfaces
   4.3.4, ff: Surface Diffusion
   Ch. 6, The Surface Chemical Bond

4. R. I. Masel, "Principles of Adsorption and Reaction on Solid Surfaces", (Wiley, 1996)

   Ch. 3, Binding of Molecules to Surfaces
   Ch. 4, Adsorption Isotherms
   Ch. 5, Kinetics of Adsorption

5. B. Hammer and J. K. Norskov, "Theory of Adsorption and Surface Reactions", in R. M. Lambert and G. Pacchioni, eds., "Chemisorption and Reactivity on Supported Clusters and Thin Films", NATO ASI Series E: Applied Sciences Vol. 331 (Kluwer Academic Pub. Dordrecht 1997) p. 285-352.

6. Woodruff and Delchar, Ch. 5, p. 356 ff., Desorption Spectroscopies

7. M. R. Albert and J. T. Yates, Jr., "The Surface Scientist's Guide to Organometallic Chemistry" (American Chemical Society, Washington, DC, 1987).

Adsorption of Atoms and Molecules

Physisorption

Chemisorption

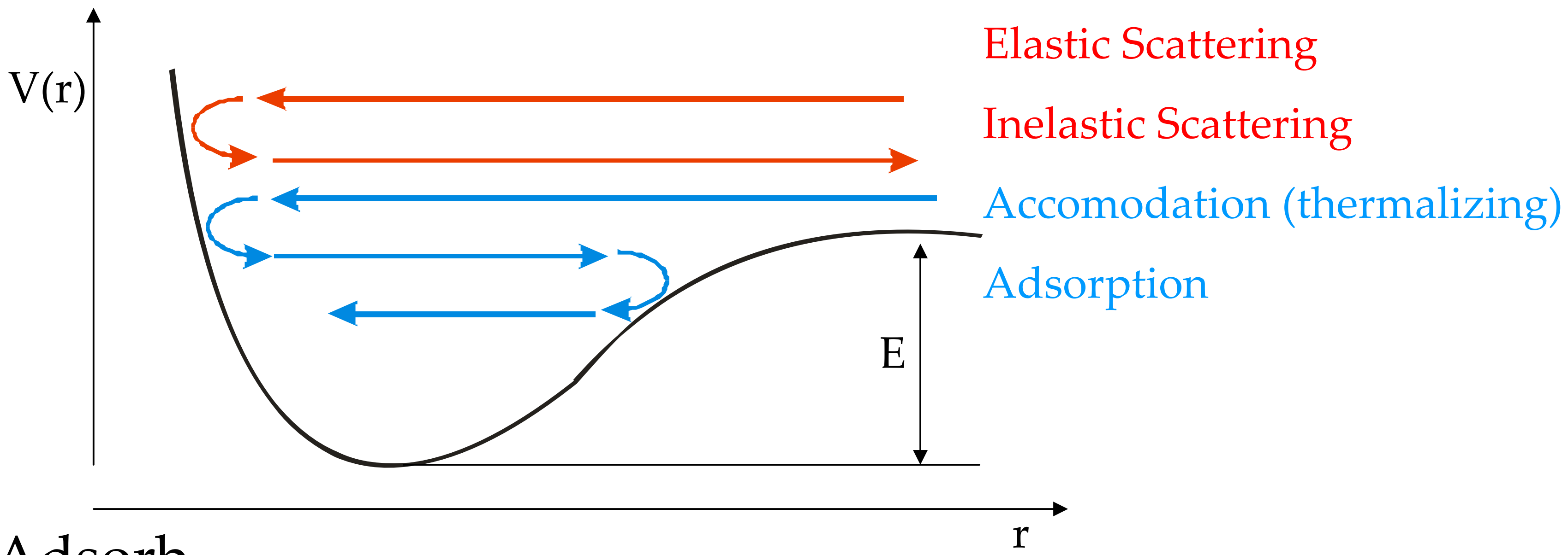
Surface Bonding

Kinetics of Adsorption/Diffusion/Desorption

(Scattering Dynamics)

Outcomes of Collision Process

Rebound (elastically or inelastically)



Adsorb

Physisorption

Chemisorption

Surface Reaction

Desorption

Physisorption of Atoms and Molecules

Weak bonding, Van der Waals Interaction

Binding Energy ~ Bulk (adsorbate) vaporization energy

Physisorption will occur for any gas-solid system for a suitable range of T, P.

Multilayers can form

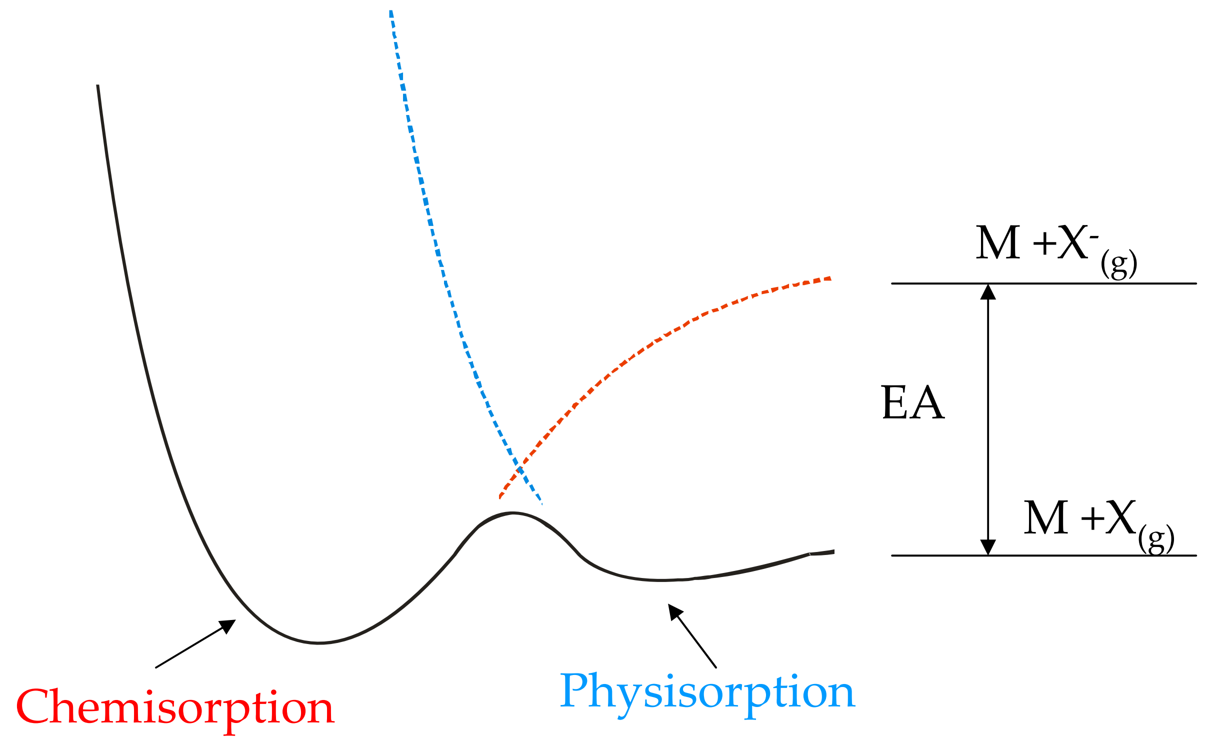
Typical E ~ 1 to 40 kJ mol^{-1}

Chemisorption of Atoms and Molecules

Chemisorption associated with charge transfer (see example below)

Binding Energy E ~ 50 to 400 kJ mol^{-1}

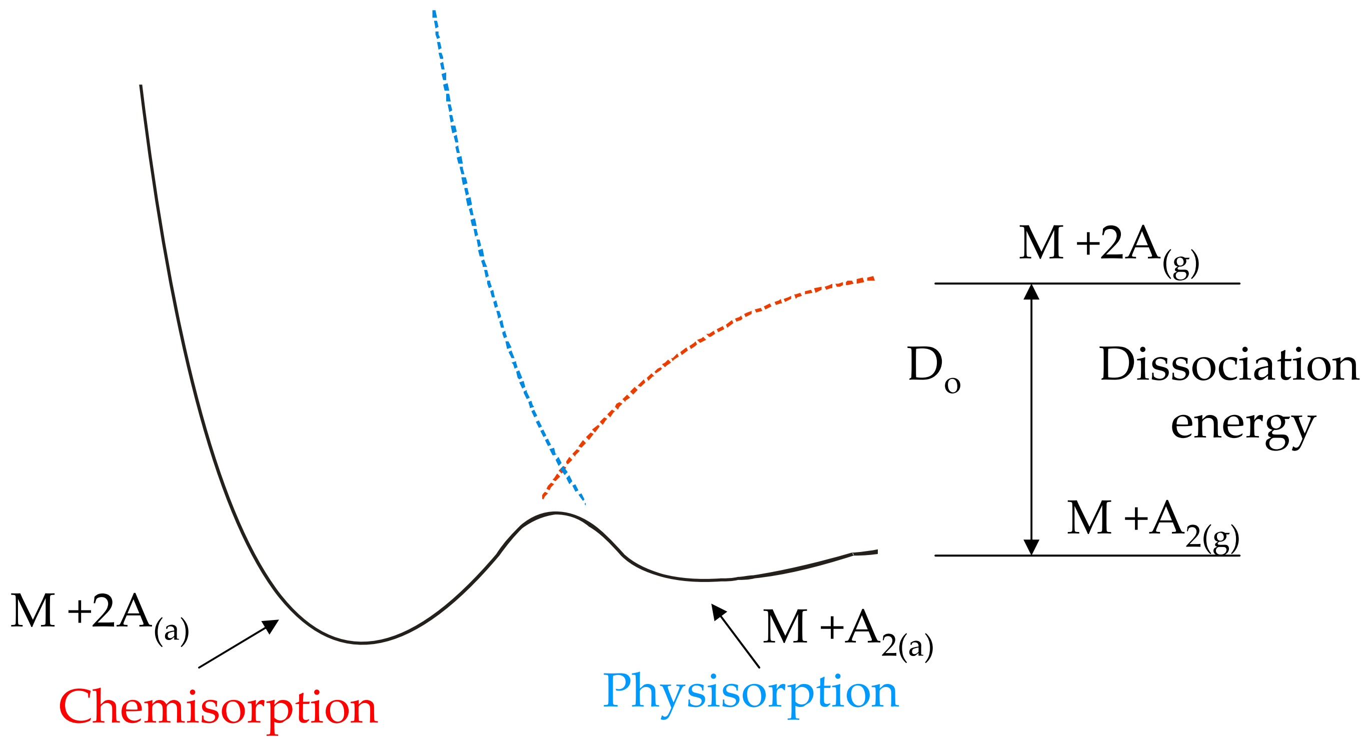
Chemisorbed layer ~ 1 atom (molecule) thick



Reactive Chemisorption of Molecules

Chemisorption possibly associated with molecular decomposition

E.g. Dissociative adsorption
(charge transfer will occur also!)



Other Reactive Processes

Catalysis ($A_2 + B_{2(ads)} \rightarrow 2AB$)

Substrate reaction (Oxidation etc)

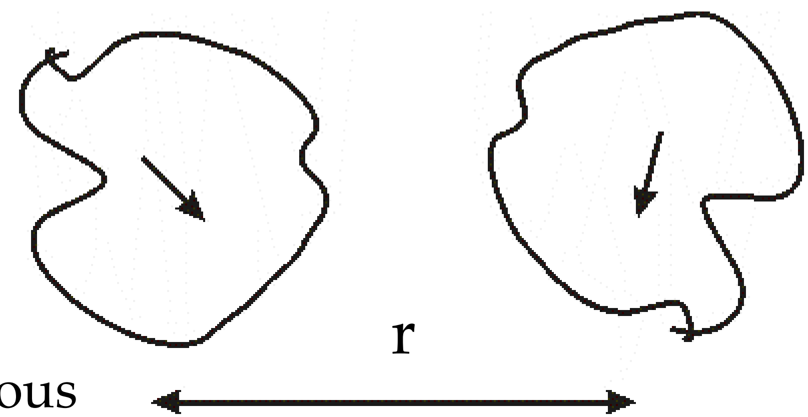
Desorption (+"Chemistry with a sledge hammer"!)

$$M + B_{2(a)} \xrightarrow{Xe} M + B_{2(g)}$$

$$M + B_{2(a)} \xrightarrow{Xe} M + 2B_{(a)}$$

Physisorption arises from dispersion forces

Consider non reacting species



Instantaneous fluctuations in charge distribution interact with instantaneous dipole moments (also multipole moments) in neighboring species.

Consequence: attractive interaction of the form

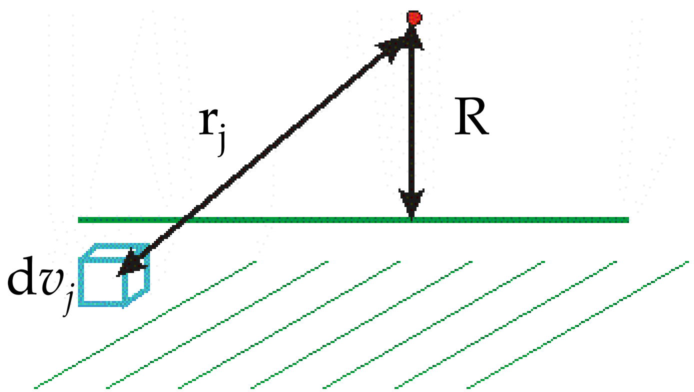
$$E = - C / r^6$$

where $C = f(I_i, \alpha_i, \mu_i)$ I = ionization potential,
α polarizability,
μ = dipole moment.

Dispersion forces above a surface

The 6-12 Lennard-Jones potential is commonly used to describe both Van der Waals and overlap repulsive interaction potentials

$$E = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



For pairwise interactions

with all surface species:

$$E = \sum_j E_j \qquad E = \int_{V_{substrate}} \left(Dr^{-12} - Cr^{-6}\right) N dv$$

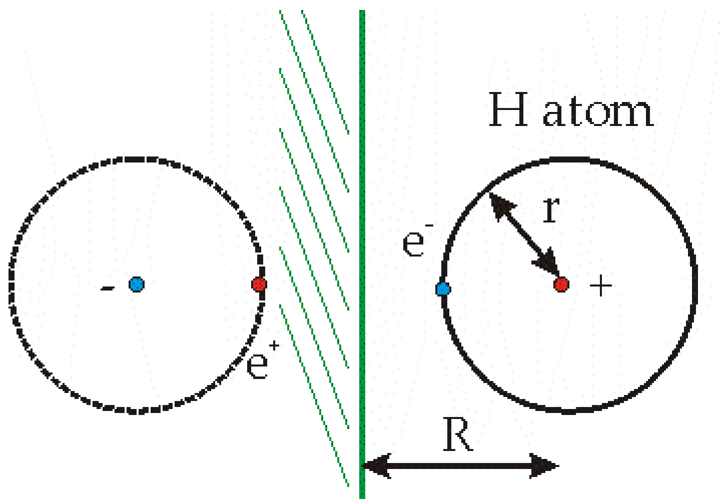
Substrate atoms/unit volume

$$\Rightarrow \quad E \simeq \left[\frac{C_1}{R^9} - \frac{C_2}{R^3}\right]$$

Works best for insulating substrates

Electrostatic interaction(s) give rise to attractive forces above metallic faces also

E.g. H above a perfect conductor substrate a



$$V(R) = -\frac{1}{8}\frac{e^2 r^2}{R^3}$$

Compare E_{LJ} α $1/R^3$

Physisorption energy (of Xe) on a metal face

1eV/atom(molecule)

= 23.05 kcal/mol

= 96.47 kJ/mol.

Factors affecting binding energy

Roughness

Local adsorbate density

Proximity of substrate

Bulk vaporization energy

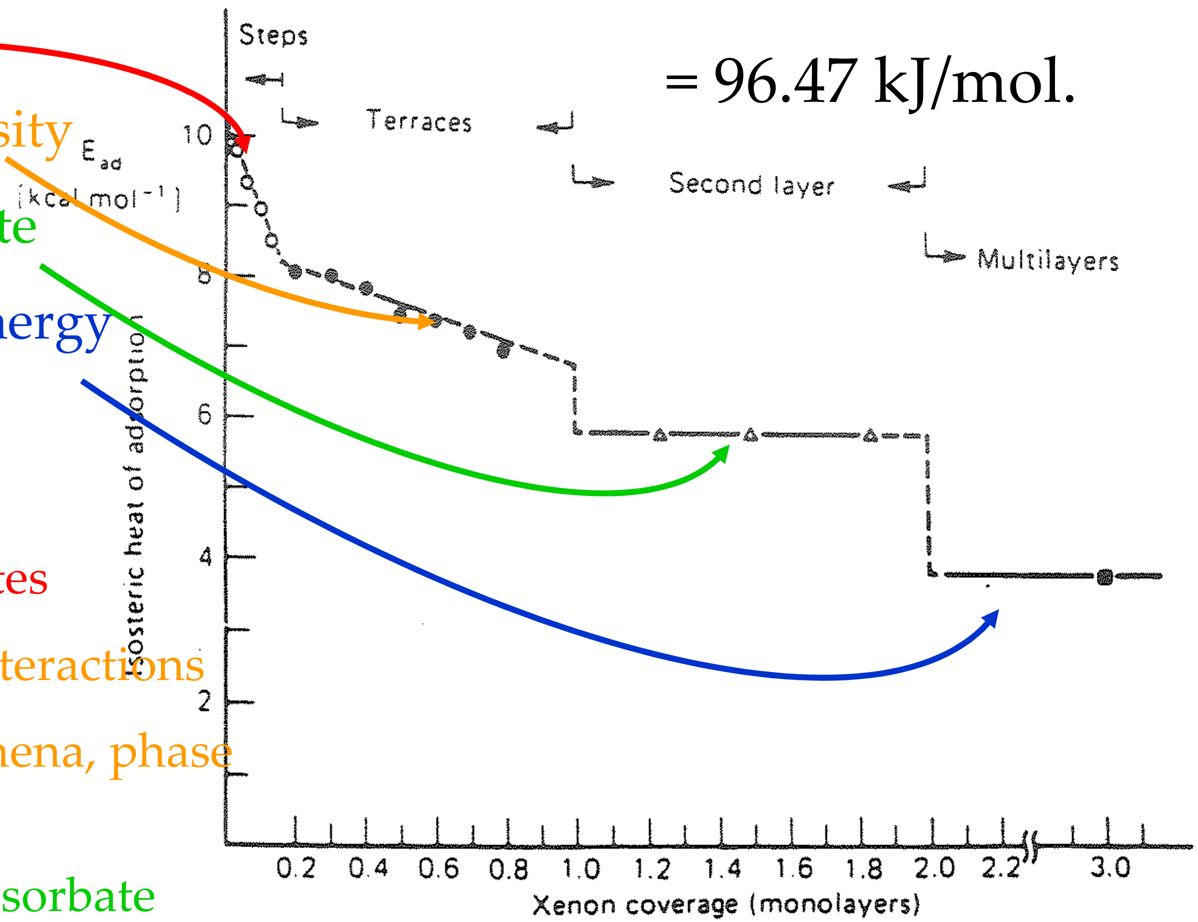


Figure 6.29. Heat of xenon adsorption on the stepped palladium 8(100) × (110) surface as a function of coverage [45].

Geometry in binding sites

Adsorbate-adsorbate interactions

Order/disorder phenomena, phase transitions

Distinction between adsorbate and substrate

Long + short range interactions

Chemisorption: the chemical bond

Chemisorption is system specific

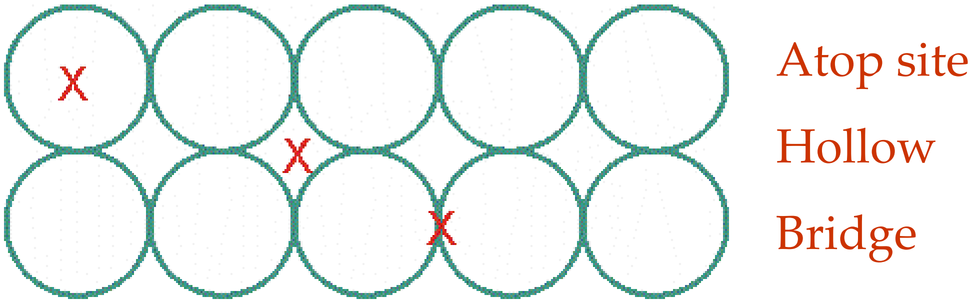
The Activities of Metal Films in Chemisorption*

Metals	Gases					
	N_2	H_2	CO	C_2H_4	C_2H_2	O_2
W, Ta, Mo, Ti, Zr, Fe, Ca, Ba	+	+	+	+	+	+
Ni, Pt, Rh, Pd	−	+	+	+	+	+
Cu, Al	−	−	+	+	+	+
K	−	−	−	−	+	+
Zn, Cd, In, Sn, Pb, Ag	−	−	−	−	−	+
Au	−	−	+	+	+	−

* Table taken from Ref. 194, p. 231; data based on adsorption studies on metal films. (+) Gas chemisorbed. Chemisorption takes place over a large part of the surface with great rapidity. (−) Gas not chemisorbed. Little or no adsorption observed between 0°C and temperatures at which physical adsorption occurs.

Chemisorption: the chemical bond

Chemisorption is site specific



Sequential filling of binding sites

Binding energies depend on crystal face

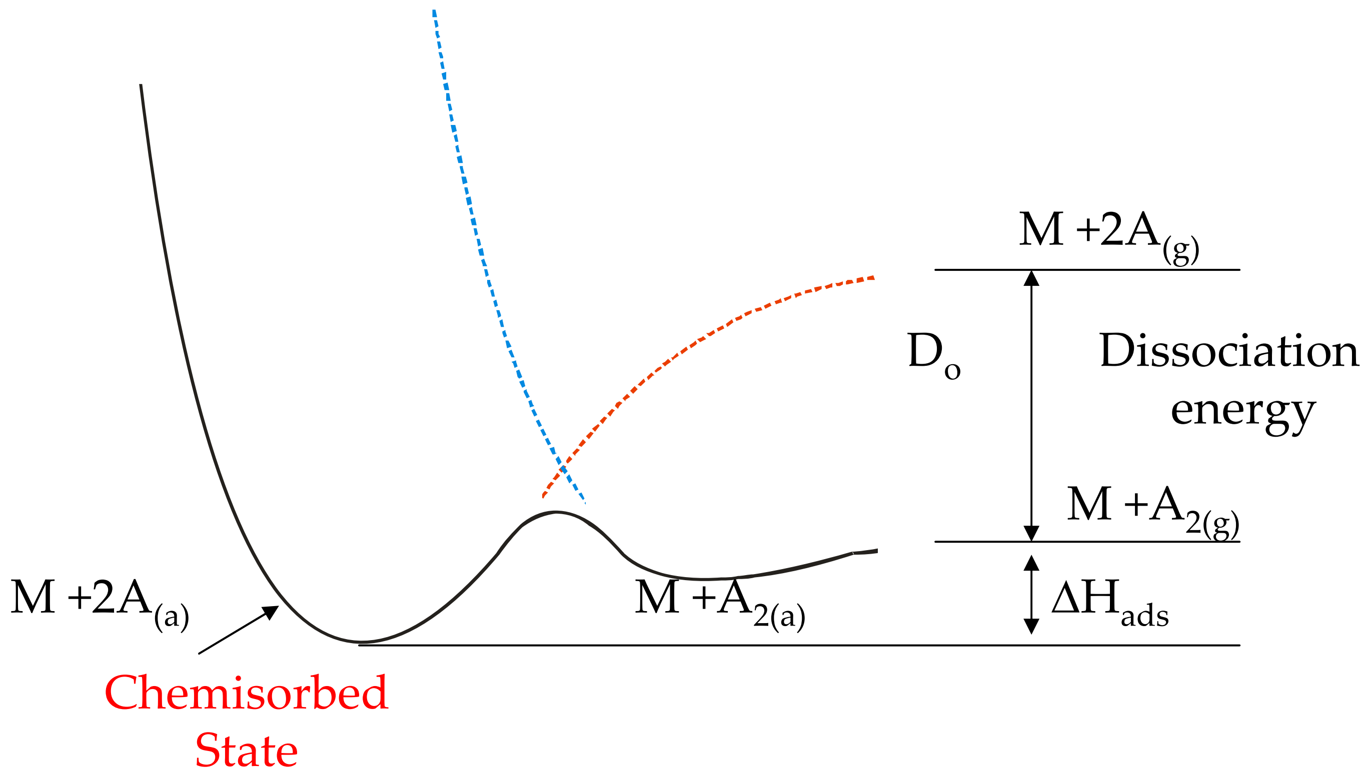
Steps, defects affect adsorption energies

2-D alloyed layers, compound layers can exist when no such bulk phase is known

Adsorption chemistry on extended surface is often very analogous to inorganic/cluster chemistry

Heats of Chemisorption

E.g. again dissociative adsorption



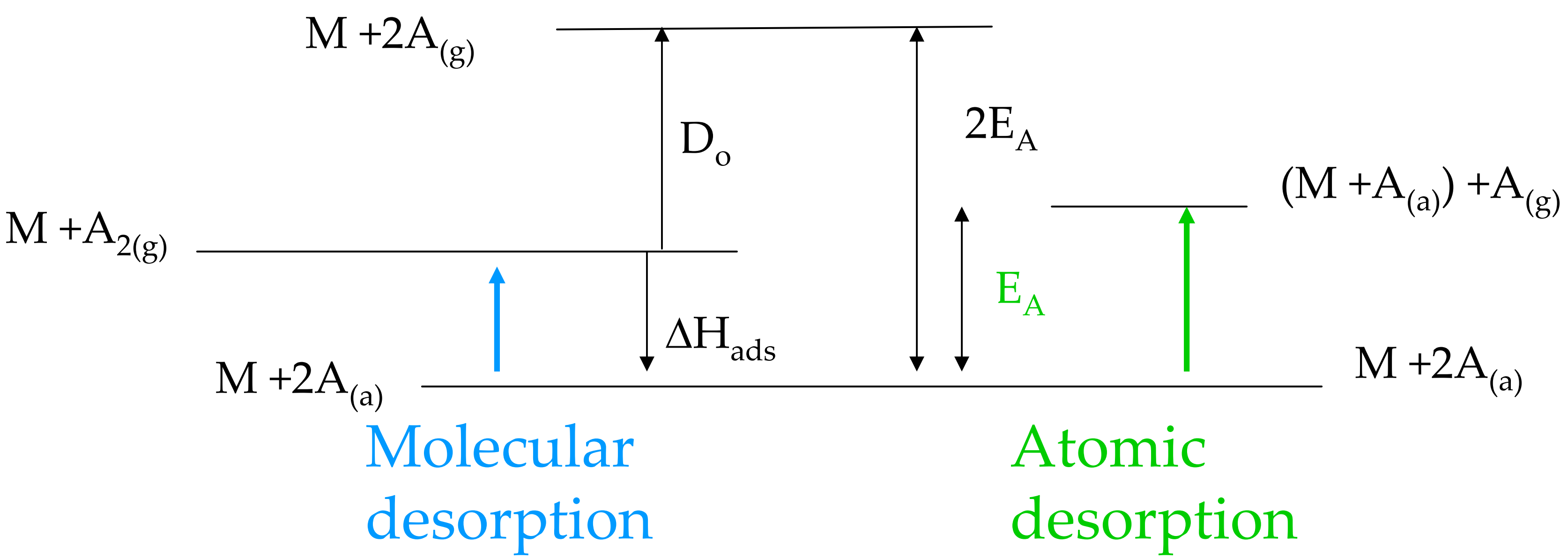
Predictions from Heats of Adsorption

Given dissociative adsorption,

is molecular or atomic desorption preferred?

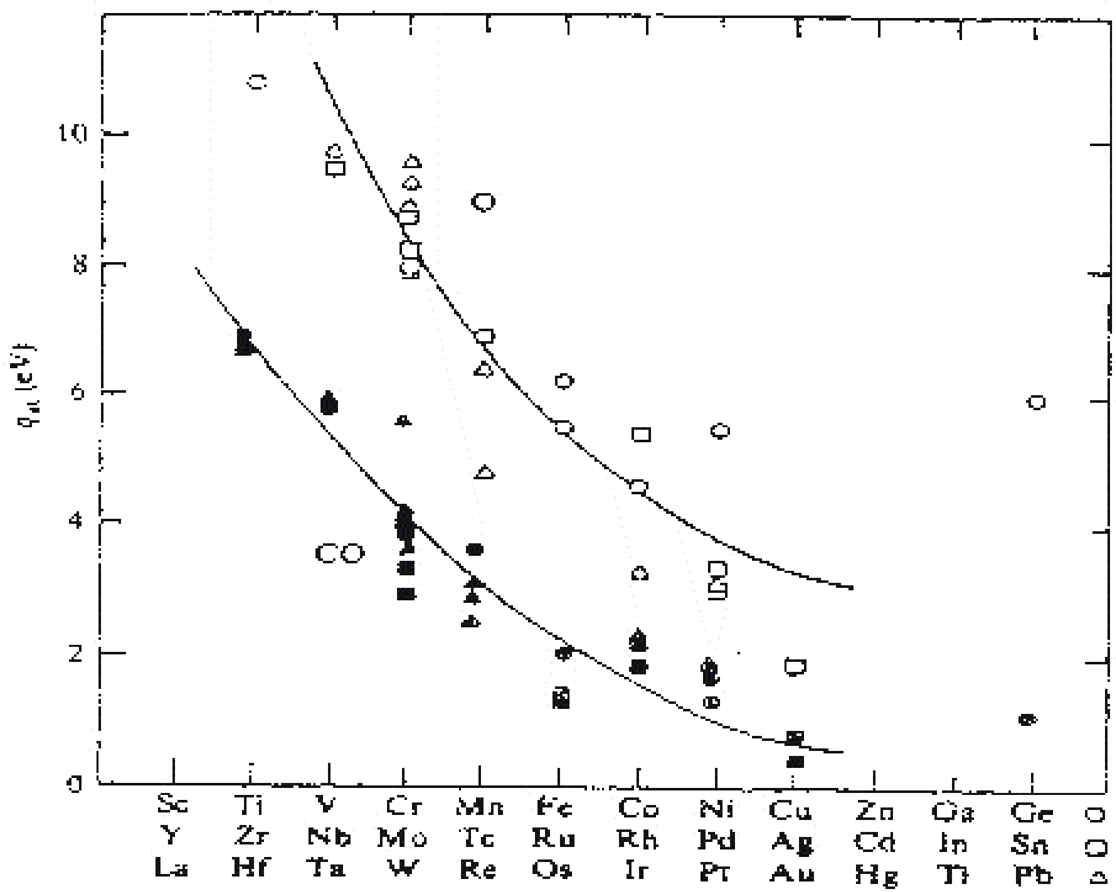
Is $|\Delta H_{ads}| < E_A$ or $|\Delta H_{ads}| > E_A$?

Ni-H_2 or W-O_2

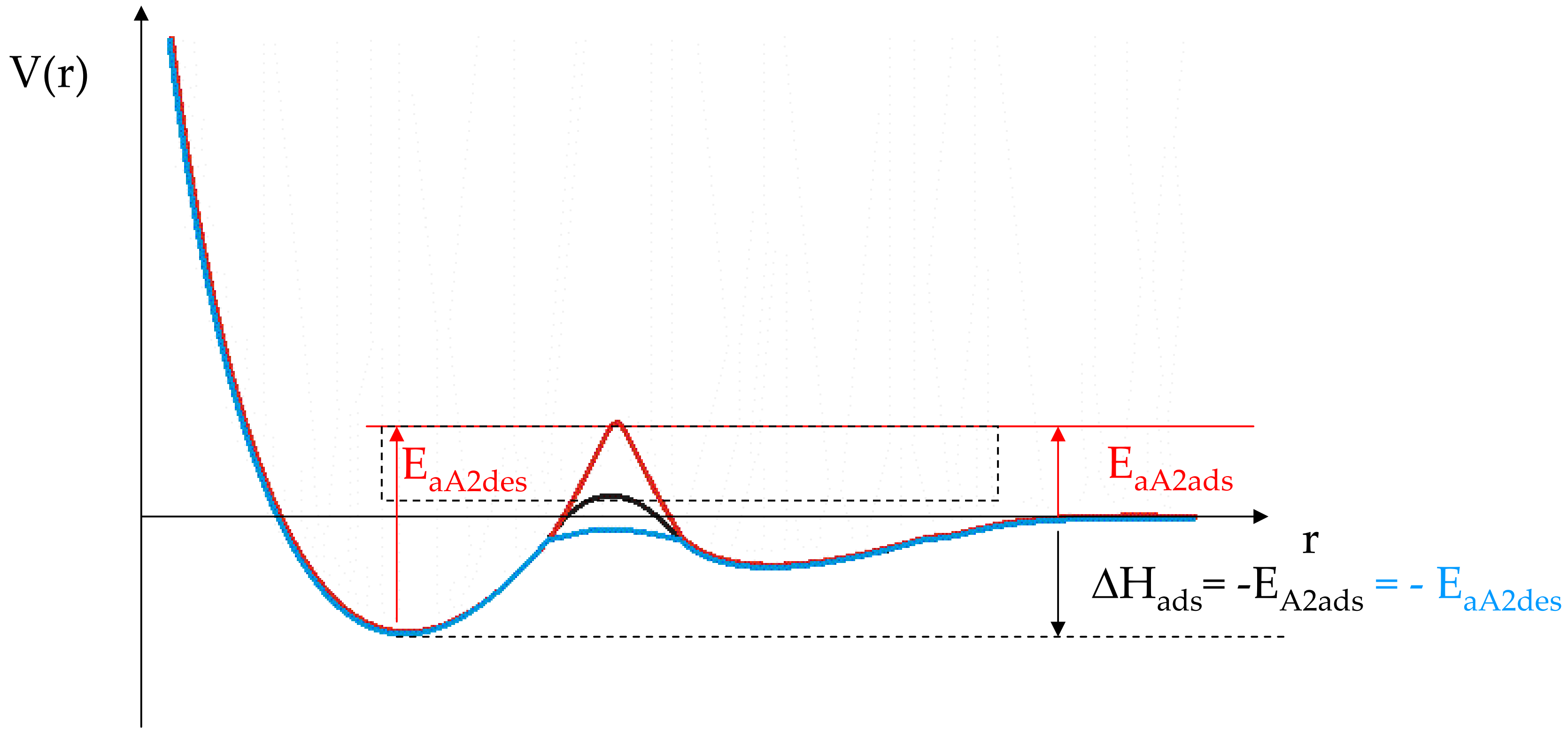


Trends in Heats of Adsorption

Fig. 9.4. Heat of adsorption of CO and O on polycrystalline metal surfaces (Toyoshima & Somorjai, 1979).

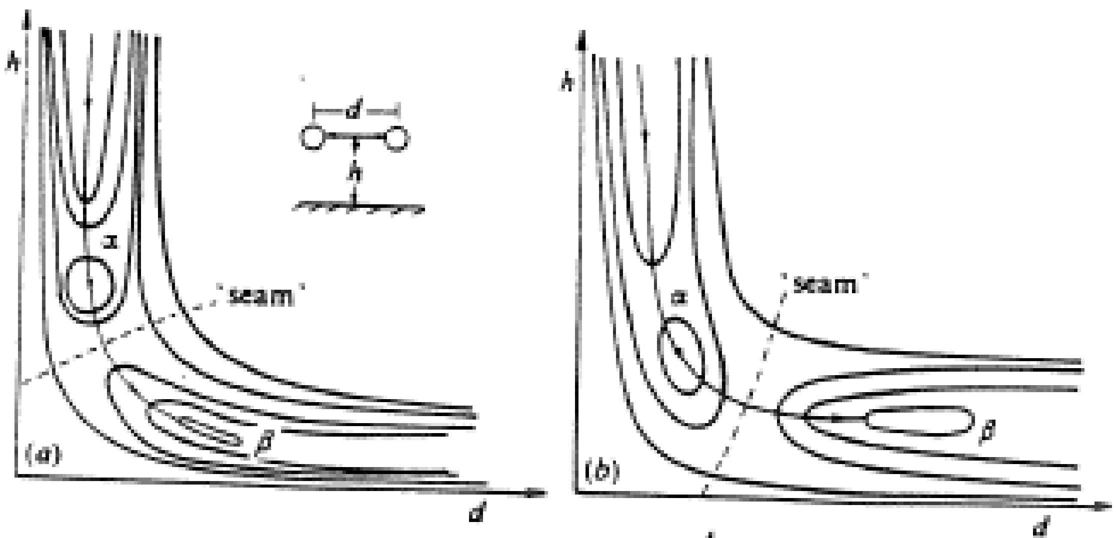


Activated dissociative adsorption



Routes for Activated dissociative adsorption

Fig. 14.12. Schematic two-dimensional potential energy diagrams for dissociative chemisorption. Both situations exhibit a physisorbed state (α) and a chemisorbed state (β). The barrier to adsorption can occur in the (*a*) entrance channel or the (*b*) exit channel (Ertl, 1982).



cf. Zangwill, p. 374

increased translational energy promotes dissociation
H_2/Cu (100)

?

increased vibrational energy promotes dissociation
CH_4/Pt (111)

Charge transfer on adsorption:

Electropositive adsorbate

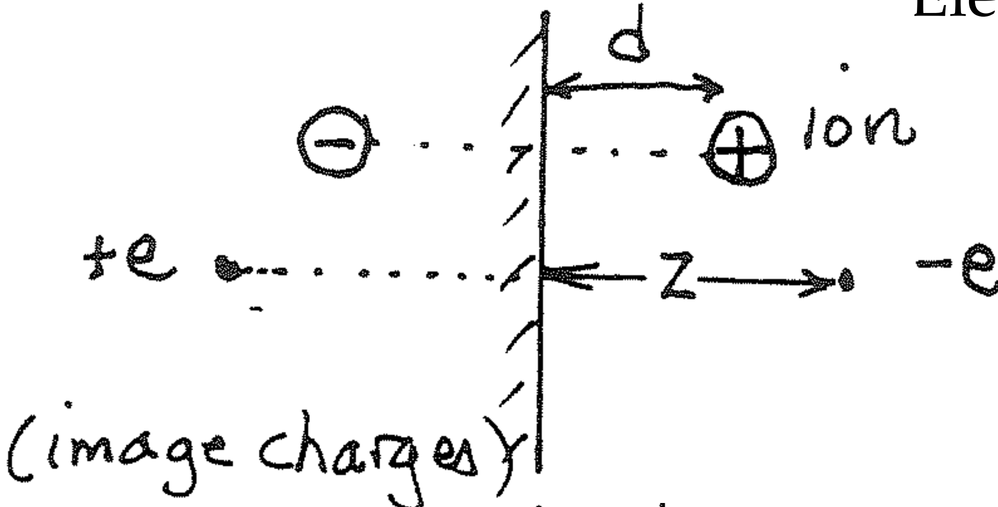
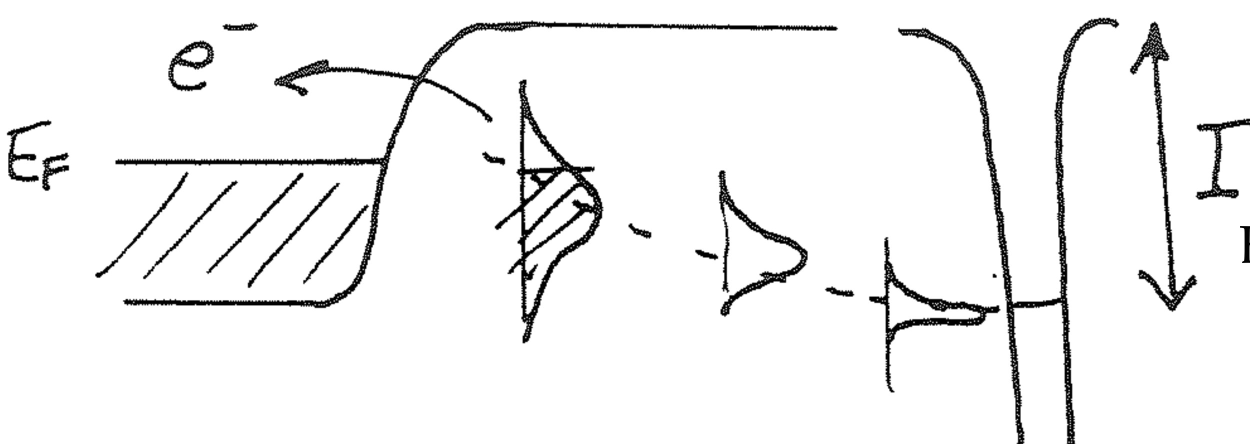


Image force acting on outgoing electron at distance z is

$$F = \underbrace{-\frac{e^2}{4z^2}}_{\text{attractive}} + \underbrace{\frac{e^2}{(d+z)^2}}_{\text{repulsive}}$$

ionization energy is decreased by

$$W = \int_d^\infty F\,dz = e^2/4d = -V_{im}$$



Electron transfer to surface

e.g. alkali metals

Charge transfer on adsorption:

Electro<u>negative</u> adsorbate

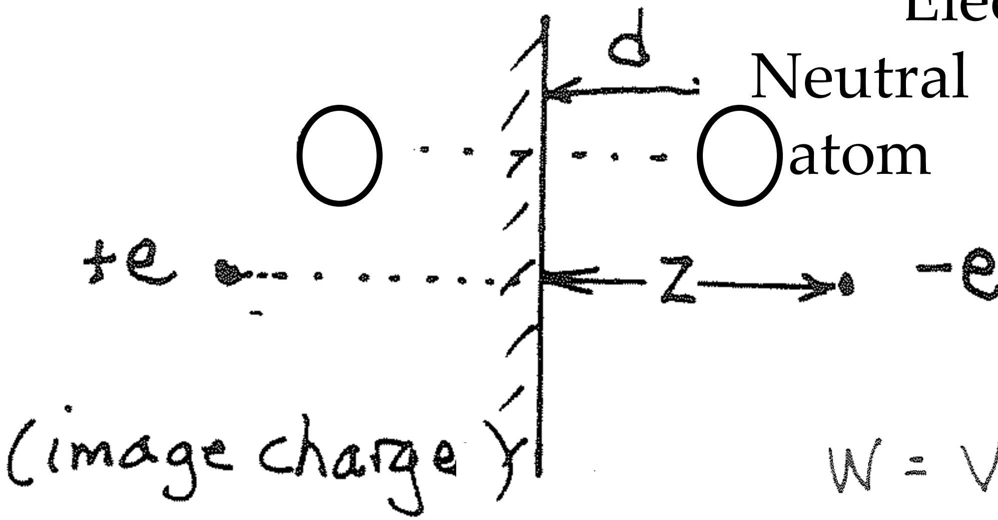


Image force acting on outgoing electron at distance z is

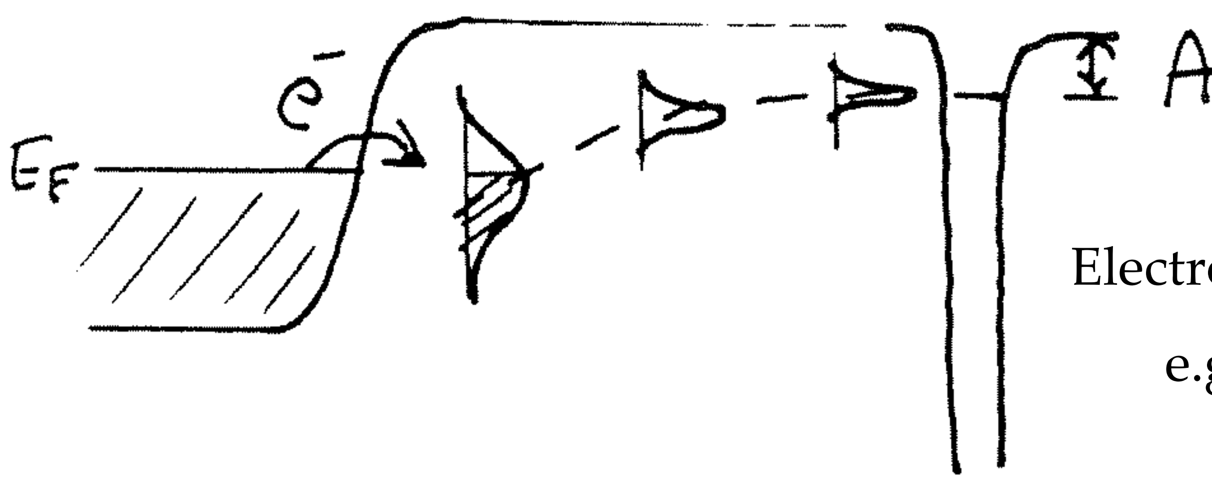
$$F = -\frac{e^2}{4z^2}$$

attractive

$W = V_{im}$

effective affinity level $A_{eff} = A + V_{im}$

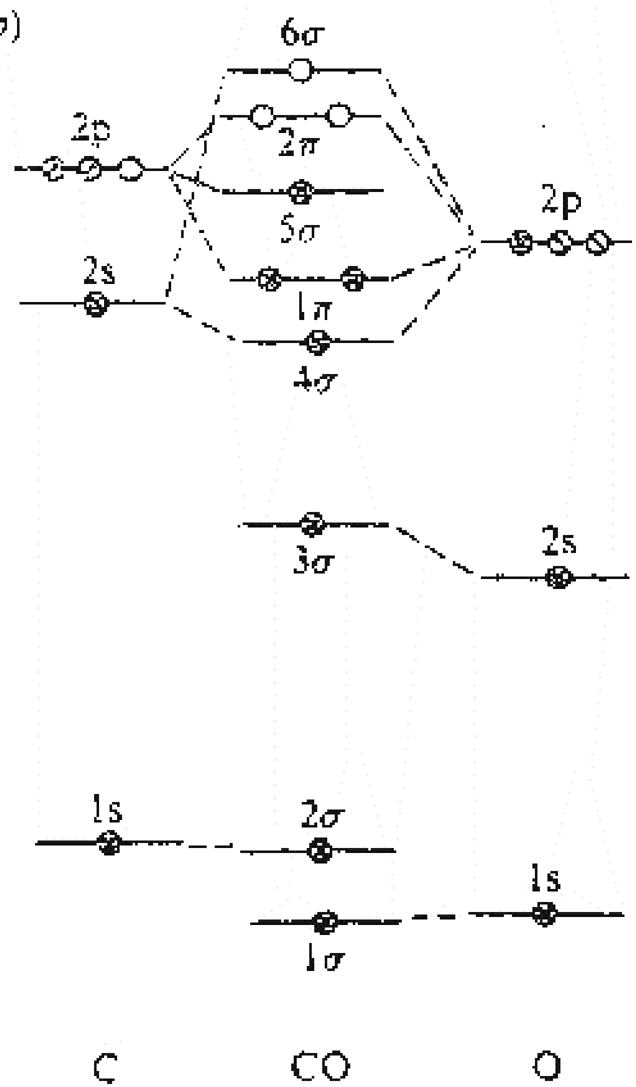
$\Rightarrow$ A level shifts <u>down</u>

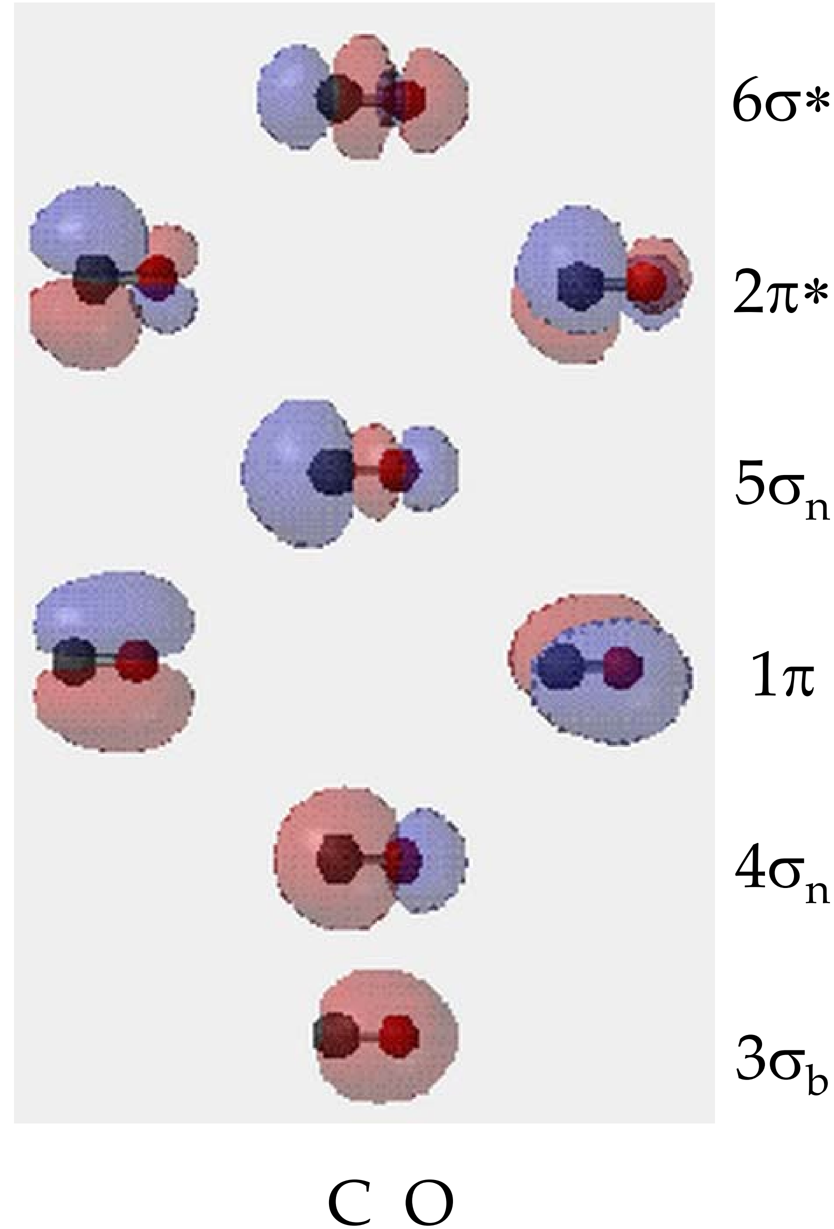


Electron transfer to adsorbate

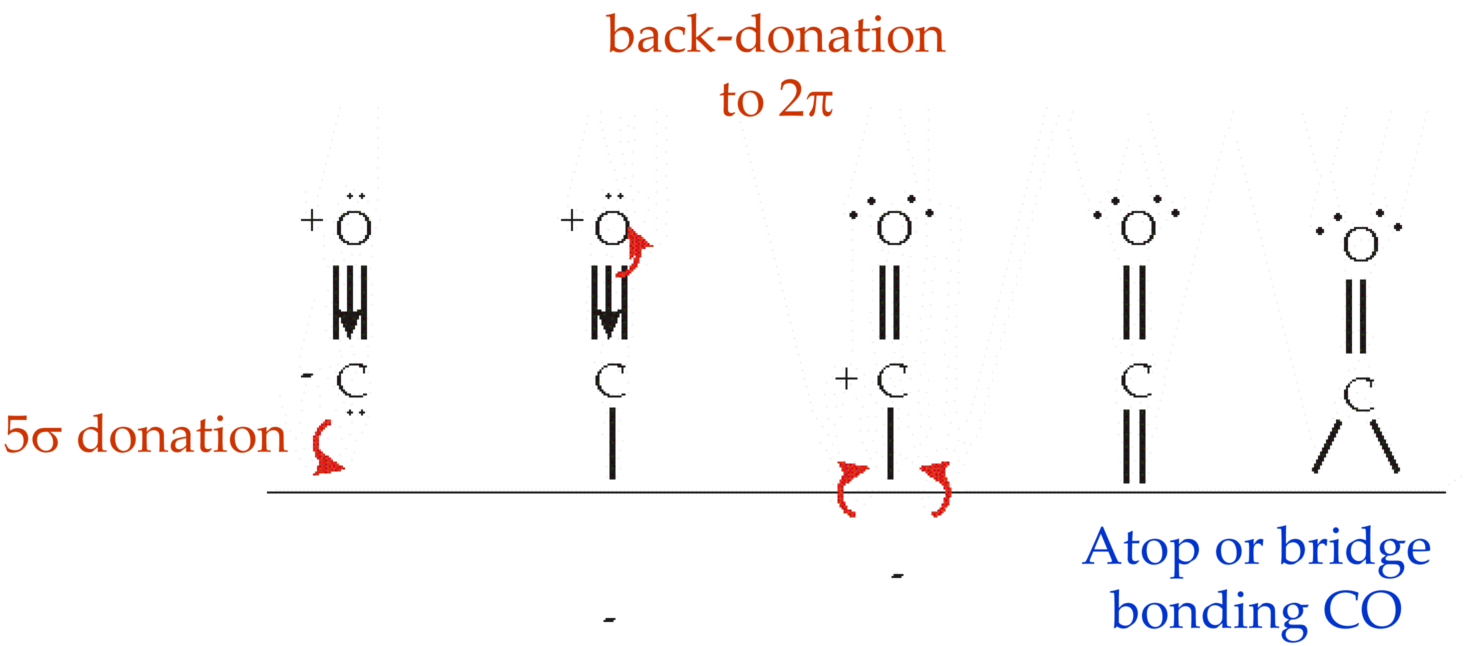
e.g. adsorbed O, Cl, F

Isolated CO


6σ
2p
2π
5σ
2p
2s
1π
4σ
3σ
2s
1s
2σ
1s
1σ
C
CO
O


$6\sigma*$
$2\pi*$
$5\sigma_n$
1π
$4\sigma_n$
$3\sigma_b$
C O

CO-Surface bonding



Blyholder model