Lecture Note #4 (Fall, 2022)

Chemisorption, Physisorption, & Dynamics

1. Type of interactions, binding sites, diffusion
2. Non-dissociative chemisorption
3. Dissociative chemisorption
4. Reactivity of metals
5. Atoms and molecules incident on a surface
6. Reaction mechanisms
7. Measurement of sticking coefficients

Reading: Kolasinski, ch.3

LN#1,2
Structure (ch.1)
Analysis (ch.2) LN#3

Chemical reaction mechanism (ch.3, ch.4) LN#4,5

Geometric structure → geometric effect
Electronic structure → electronic effect

Ensemble effect

Liquid & charged interface (ch.5) LN#6

Applications to catalysis, nano (ch.6-7) LN#7,8

Type of interactions

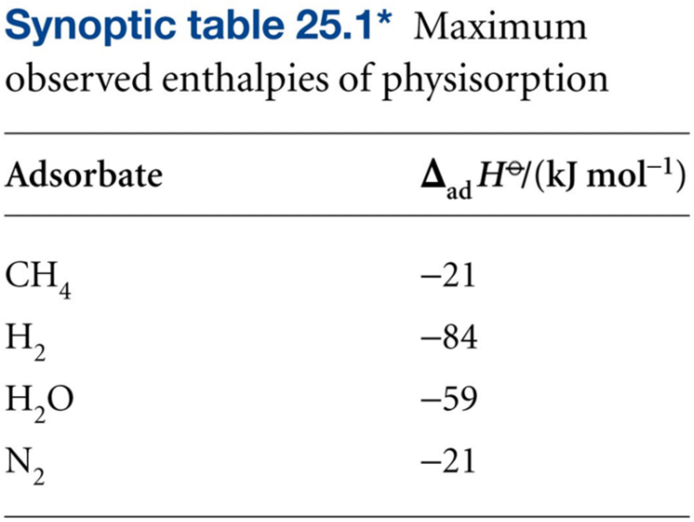
Physisorption vs. Chemisorption

Physisorption (physical adsorption)

- Van der Waals interaction (weak interaction)
- Small adsorption energy: ≤ 20 kJ/mole
- Similar to condensation
- Multilayer adsorption possible
- No charge transfer
- Substrate non-specific

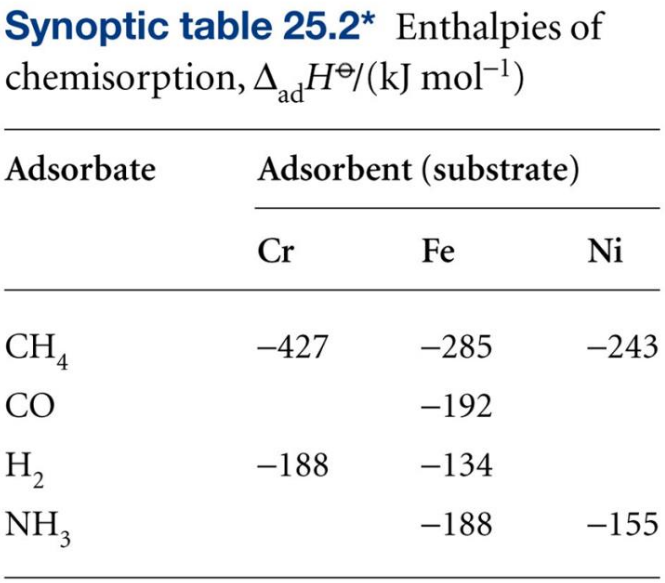
Chemisorption (chemical adsorption)

- Chemical bonding (covalent bonding)
- Large adsorption energy: ≥ 200 kJ/mole
- Charge transfer : work function change
- Limited to a monolayer
- Substrate specific
- Gas specific



Synoptic table 25.1* Maximum observed enthalpies of physisorption

Adsorbate	$\Delta_{ad}H^\ominus/(\mathrm{kJ\ mol^{-1}})$
CH_4	−21
H_2	−84
H_2O	−59
N_2	−21



Synoptic table 25.2* Enthalpies of chemisorption, $\Delta_{ad}H^\ominus/(\mathrm{kJ\ mol^{-1}})$

Adsorbate	Adsorbent (substrate)		
	Cr	Fe	Ni
CH_4	−427	−285	−243
CO		−192	
H_2	−188	−134	
NH_3		−188	−155

Atkins, Physical Chemistry

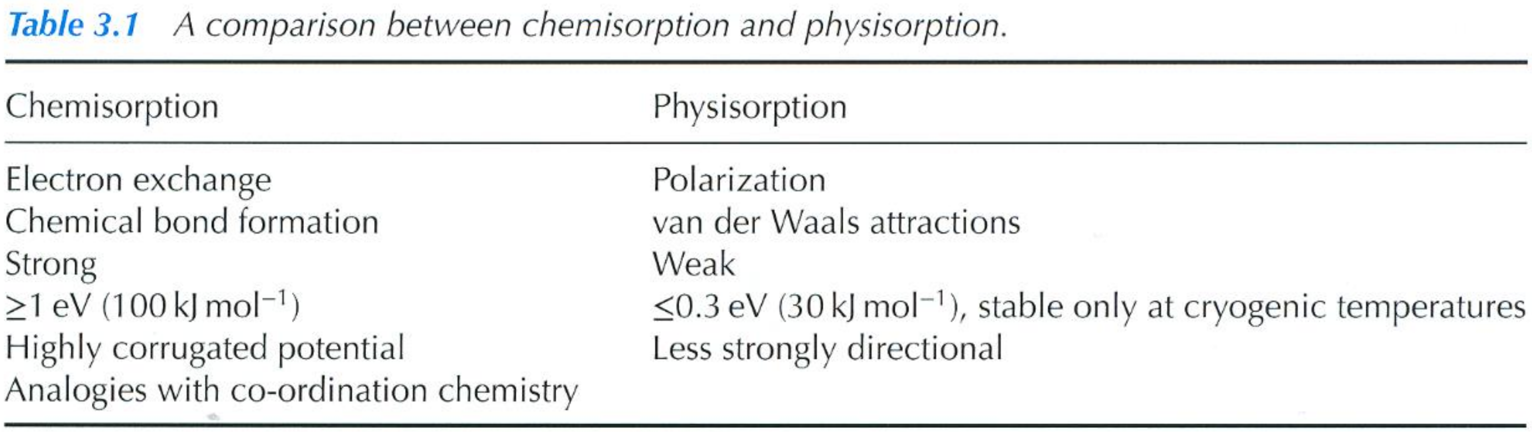


Table 3.1 *A comparison between chemisorption and physisorption.*

Chemisorption	Physisorption
Electron exchange	Polarization
Chemical bond formation	van der Waals attractions
Strong	Weak
≥1 eV (100 kJ mol^{-1})	≤0.3 eV (30 kJ mol^{-1}), stable only at cryogenic temperatures
Highly corrugated potential	Less strongly directional
Analogies with co-ordination chemistry	

1 eV = 1.6 x 10^{-19} J = 96.485 kJ/mol = 8065.5 cm^{-1}

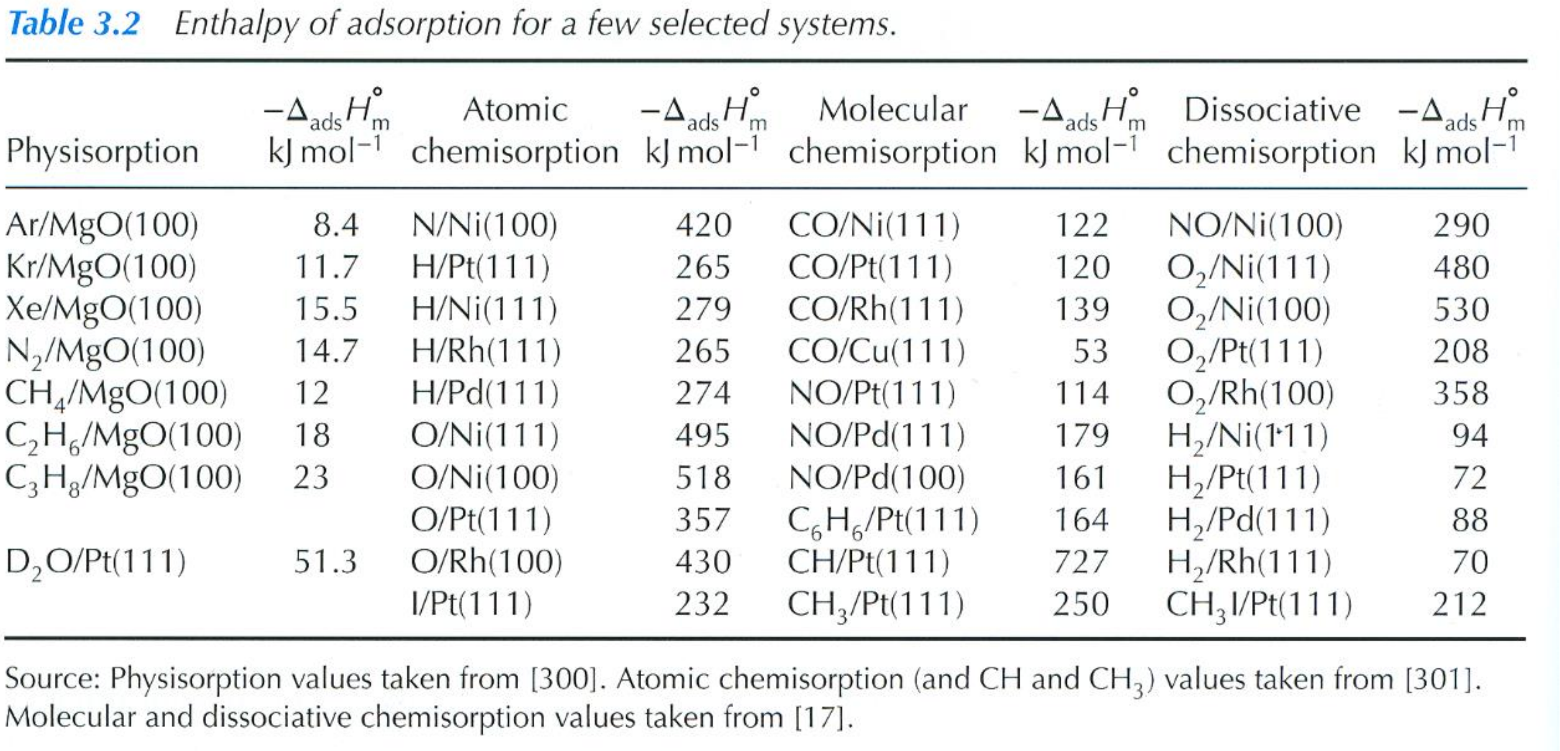


Table 3.2 *Enthalpy of adsorption for a few selected systems.*

Physisorption	$-\Delta_{ads}H^\circ_m$ kJ mol^{-1}	Atomic chemisorption	$-\Delta_{ads}H^\circ_m$ kJ mol^{-1}	Molecular chemisorption	$-\Delta_{ads}H^\circ_m$ kJ mol^{-1}	Dissociative chemisorption	$-\Delta_{ads}H^\circ_m$ kJ mol^{-1}
Ar/MgO(100)	8.4	N/Ni(100)	420	CO/Ni(111)	122	NO/Ni(100)	290
Kr/MgO(100)	11.7	H/Pt(111)	265	CO/Pt(111)	120	O_2/Ni(111)	480
Xe/MgO(100)	15.5	H/Ni(111)	279	CO/Rh(111)	139	O_2/Ni(100)	530
N_2/MgO(100)	14.7	H/Rh(111)	265	CO/Cu(111)	53	O_2/Pt(111)	208
CH_4/MgO(100)	12	H/Pd(111)	274	NO/Pt(111)	114	O_2/Rh(100)	358
C_2H_6/MgO(100)	18	O/Ni(111)	495	NO/Pd(111)	179	H_2/Ni(111)	94
C_3H_8/MgO(100)	23	O/Ni(100)	518	NO/Pd(100)	161	H_2/Pt(111)	72
		O/Pt(111)	357	C_6H_6/Pt(111)	164	H_2/Pd(111)	88
D_2O/Pt(111)	51.3	O/Rh(100)	430	CH/Pt(111)	727	H_2/Rh(111)	70
		I/Pt(111)	232	CH_3/Pt(111)	250	CH_3I/Pt(111)	212

Source: Physisorption values taken from [300]. Atomic chemisorption (and CH and CH_3) values taken from [301]. Molecular and dissociative chemisorption values taken from [17].

Cryogenic temperatures: liquid He (4K), liquid N_2 (77K)

- Adsorption, especially chemisorption → surface free energy↓→ surface tension, $\gamma\downarrow$

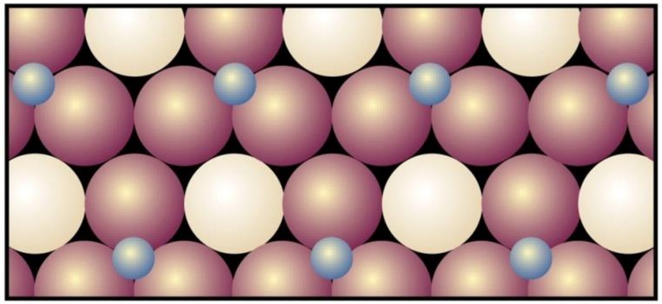
- Chemisorption → usually exothermic process → $\Delta S < 0$ (gas in 2D), $\Delta G < 0$ (constant T & P, free energy↓, spontaneous) → $\Delta G = \Delta H - T\Delta S$ → $\Delta H < 0$ (exothermic)

- Temperature↓ → Adsorption↑

- exception: dissociate adsorbates & high translational mobility on the surface ($\Delta S > 0$). Repulsion between adsorbates by coverage↑ → less exothermic

  e.g., H_2 on glass: endothermic, $H_2(g) \rightarrow 2H$ (glass), $\Delta S > 0 \rightarrow \Delta H > 0$

Terminology



- Adsorption site density

  N_s = # of sites /cm^2 ~ 10^{15} /cm^2

- Coverage

  fractional coverage $\theta = N_s / N$
  saturation coverage : $\theta_s = 1$

- Wall collision rate Z_w

  Z_w = # molecules striking a surface /$cm^2 \cdot s$
  $Z_w = P / (2\pi mkT)^{1/2}$ ~ 10^{15} molecules /$cm^2 \cdot s$
  @ 10^{-6} Torr and 298 K
  1 L (Langmuir) = 10^{-6} Torr·s of gas exposure (Lecture Note#1)

- Monolayer completion time ~ 1sec @ 10^{-6} Torr

  (1 atm = 1.013 x 10^5 Pa, 1 torr = 133.3 Pa)

Binding sites and diffusion

Surface sites are separated by energetic barriers → diffusion barrier

Potential energy surface (1-D and 2-D)

Diffusion

$$\boxed{D = D_0 \exp(-E_{diff}/RT)}$$

D: diffusion coefficient
D_0: diffusion pre-factor
E_{diff}: activation energy for diffusion

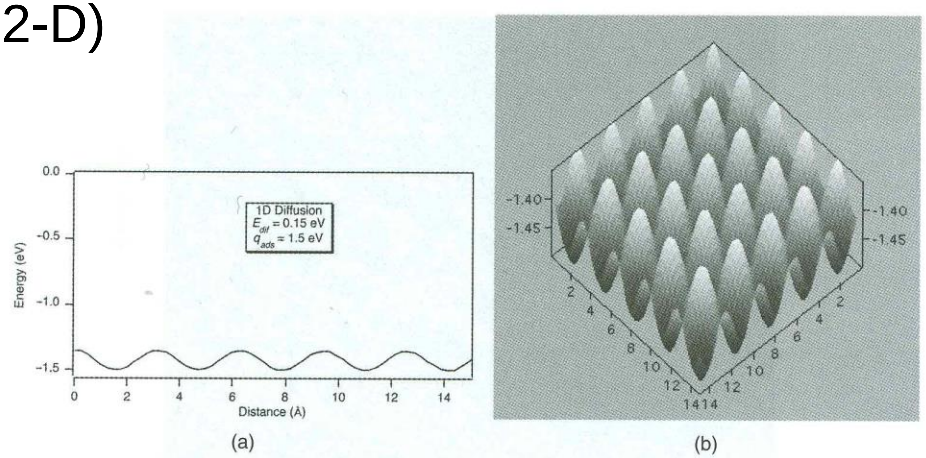


Figure 3.1 *The interaction potential of an adsorbate is corrugated as can be seen in these (a) 1D and (b) 2D representations of energy versus position on ideal defect-free surfaces.*

Generally, E_{diff} is small compared to E_{des} (desorption activation E)
If low temp limit, RT << E_{diff} → D ~ 0, adsorbate motion: vibrational only, localized to a binding site → adsorbate as a lattice gas
If very low temp for light adsorbates as H → quantum effects dominate → tunneling (diffusion is independent of temp)
As T↑, RT ~ E_{diff} → diffusional hoping between sites↑
If high temp (RT >> E_{diff}) → adsorbate translates freely across the surface (type of Brownian motion) → not bound in x & y directions (free 2D motion) → 2D gas

Chemisorbates experience greater diffusion barriers than physisorbates
Below the high-temp limit, D is related to the hoping frequency (v)

$$\boxed{D = vd^2 / 2b}$$

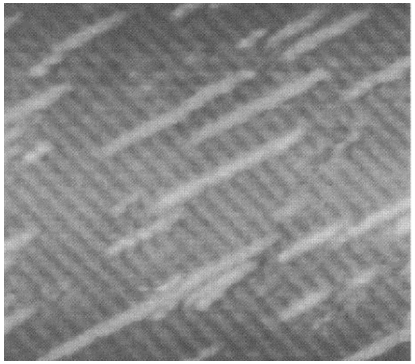
d: mean-square hoping length (related to the distance between sites)
b: dimensionality of diffusion (1D: b = 1, diffusion in a plane: b = 2)
The root mean square distance, $<x^2>^{1/2}$, in 1D in a time t

$$\boxed{<x^2>^{1/2} = \sqrt{(2Dt)}} \quad \text{(uniform 1D potential)}$$

For 2D potential energy surface(PES) (b = 2),

$$\boxed{<x^2>^{1/2} = \sqrt{(4Dt)}} \quad \text{(uniform 2D potential)}$$

Diffusion barrier is not always uniform across the surface
e.g. Si(100)(2 x 1):
easier diffusion along rows,
difficult across lows



Step-up diffusion (E_s)

Steps, or defects: higher diffusion barriers

Lateral interactions of adsorbates:
Repulsive: D↑
Attractive: D↓

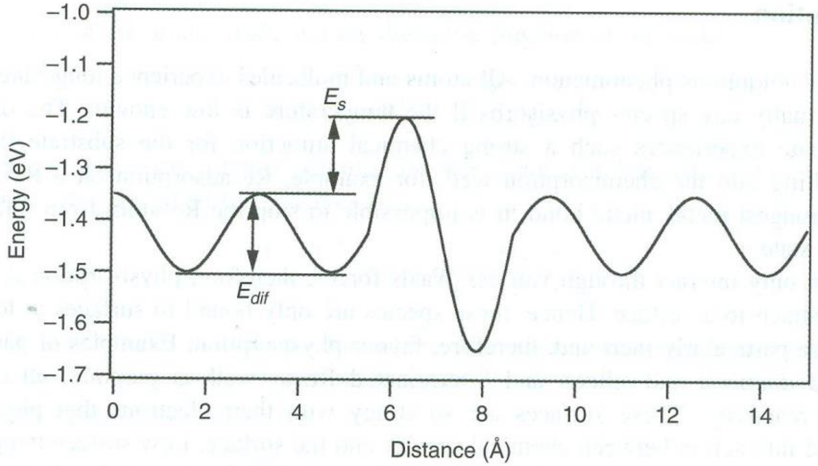


Figure 3.3 *A step changes the diffusion activation energy, E_{dif} [one-dimensional (1D) diffusion]. Step-up diffusion is often negligible because of the increased barrier; note also the increased binding strength at the bottom of the step – a feature that is often observed. E_s, Ehrlich-Schwoebel barrier.*

Diffusion for strongly interacting atoms (metal on metal)

→ exchange mechanism

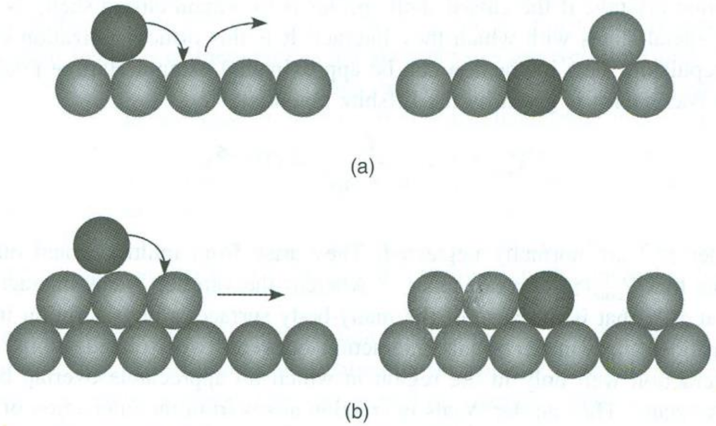
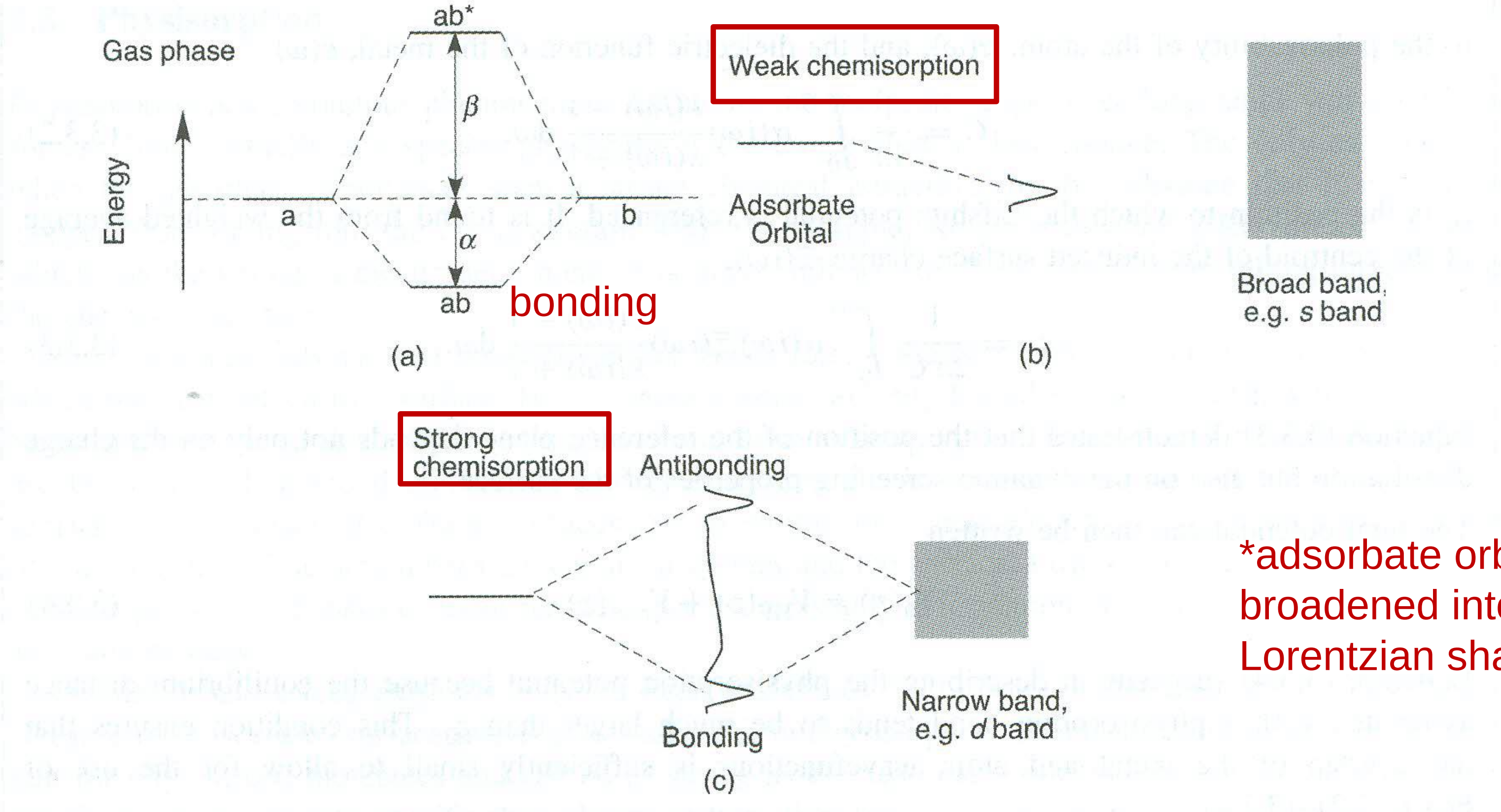


Figure 3.4 *The exchange mechanism of diffusion. Mass transport occurs via the replacement of one atom with another. This can happen either (a) on a terrace or (b) at a step*

Non-dissociative chemisorption

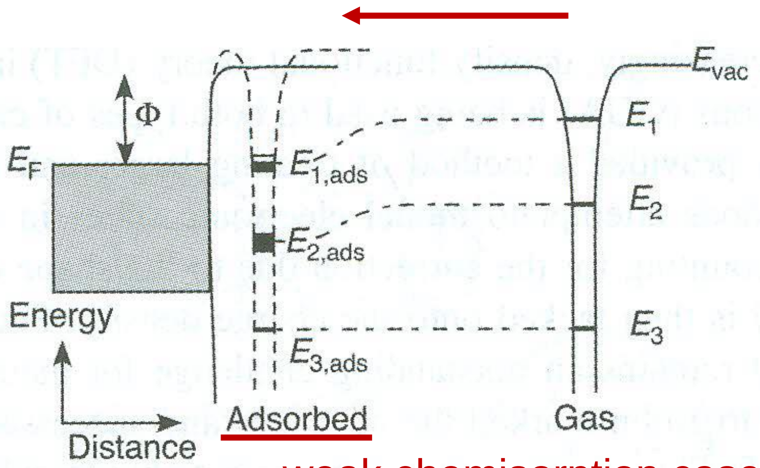
Theoretical treatment of chemisorption (Langmuir, Nobel Prize (1935))

Chemisorption → formation of a chemical bond between adsorbate & surface
→ molecular orbital formation



*adsorbate orbital is broadened into a Lorentzian shape

Figure 3.5 *Orbital interactions. (a) Gas phase. (b) Weak chemisorption. (c) Strong chemisorption. a, b, atomic orbitals; ab, ab*, bonding and antibonding molecular orbitals; α, β energy shifts of molecular orbitals with respect to the mean energy of a and b.*



weak chemisorption case

Figure 3.6 *Diagram of broadening and shifting of adsorbate levels as they approach a surface.* E_F*, Fermi energy;* E_{vac}*, vacuum energy;* Φ *work function of the surface material;* E_1, E_2, E_3*, energies of molecular orbitals 1, 2 and 3, respectively, of the molecule far from the surface;* $E_{1,ads}$, $E_{2,ads}$, $E_{3,ads}$ *energies of molecular orbitals 1, 2 and 3, respectively, of the adsorbed molecule; shaded area, occupied band (e.g. valence band).*

As a molecule approaches a surface, its electronic states interact with the electronic states of the metal
→ this broadens the MOs and it also lowers the energy of the MOs
→ the reason why MOs experience a shift and broadening is that they interact with the electron of the substrate

Core level → little interaction (e.g. E_3, core levels) → sharp MO

Blyholder model of CO chemisorption on a metal

CO: why non-dissociative molecular adsorption?

Electronic structure of gas-phase CO → modification of electronic structure on surface

HOMO(highest occupied MO): 5σ MO (non-bonding of C-O)

LUMO (lowest unoccupied MO): 2π* (antibonding of C-O)

Gas-phase CO

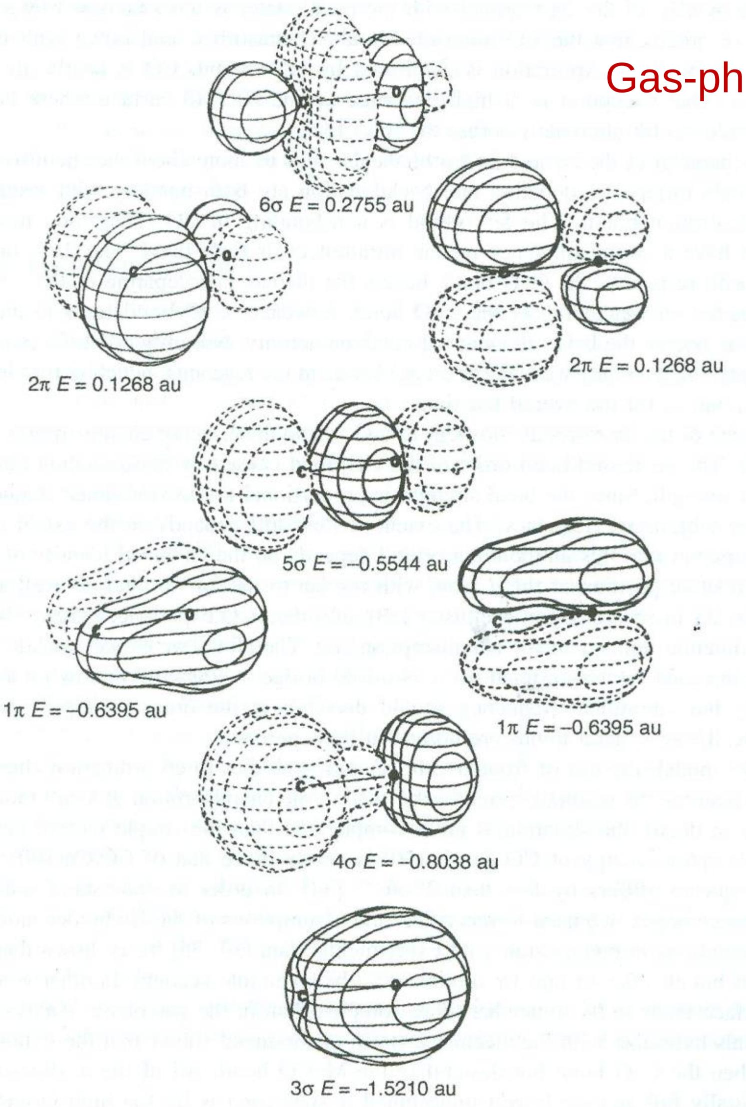
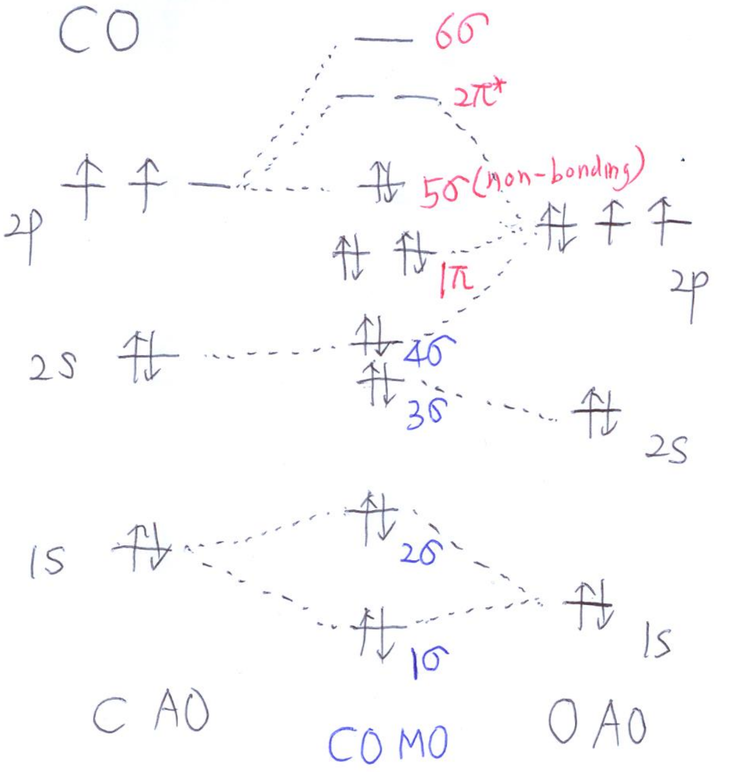


Figure 3.7 *The molecular orbitals of gas-phase CO. The wavefunction changes sign in going from the regions enclosed by solid lines to those enclosed by dashed lines. Energies, E, are given in atomic units (1 atomic unit = 27.21 eV). Orbitals with negative energies are occupied in the ground state of the neutral molecule. Reproduced from W. L. Jorgensen, L. Salem,* The Organic Chemist's Book of Orbitals, *Academic Press, New York. © (1973) with permission from Academic Press.*

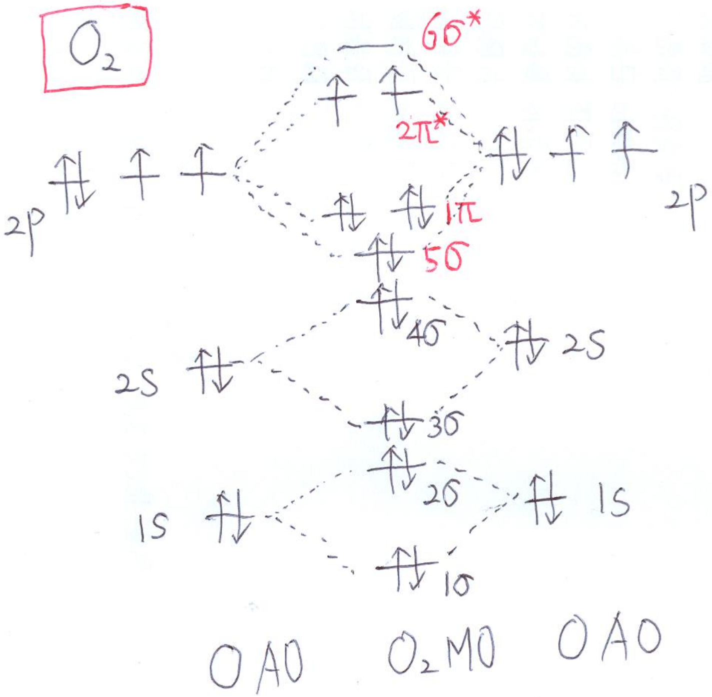
MO



CO: Stable MO → molecular adsorption

5σ↓ or 5σ e^- donation to metal

→ more stable



$2e^-$ in $2\pi^*$ antibonding MO

→ stable to donate $2\pi^*$ e^- $(2\pi^* e^- \uparrow)$

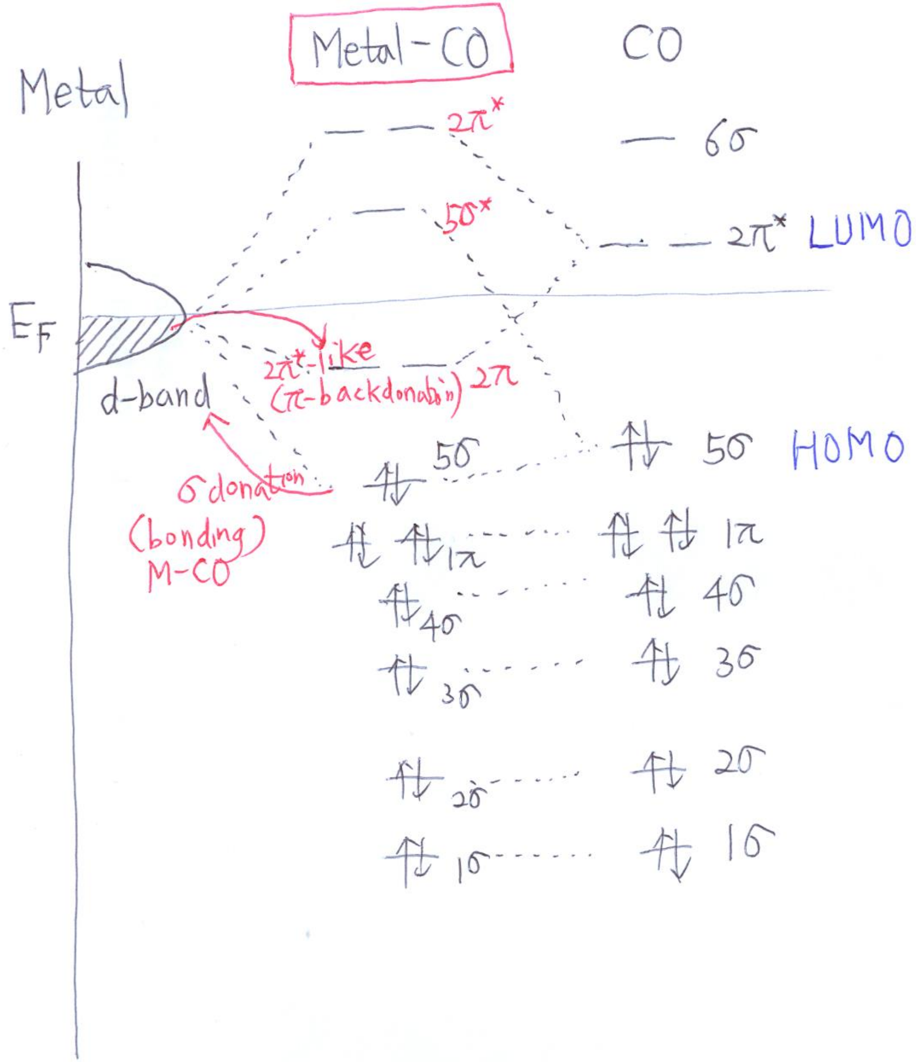
→ dissociative

HOMO & LUMO with respect to the surface

5σ orbital is localized on the C end of the molecule
2π* is symmetrically distributed along the molecular axis
→
5σ is completely occupied as it lies below E_F
2π* is partially occupied
→
(1) 5σ orbital interacts strongly with the metallic electronic states
5σ electron is donated to the metal and new hybrid electronic states are formed (donation)
→ localized C end of molecule
(2) 2π* orbital accept electron from the metal (backdonation)
→ new hybrid electronic states → localized about CO molecule

Donation & backdonation → both bonding with respect to M-CO bond (chemisorption)
2π* backdonation weaken the C-O bond → weaker C-O bond leads to increased reactivity of the CO

2π* backdonation → C-O vibration frequency↓



Pt	$5d^9 6s^1$	empty d orbital
Au	$5d^{10} 6s^1$	
Pd	$4d^{10}$	
Ni	$3d^8 4s^2$	
Rh	$4d^8 5s^1$	

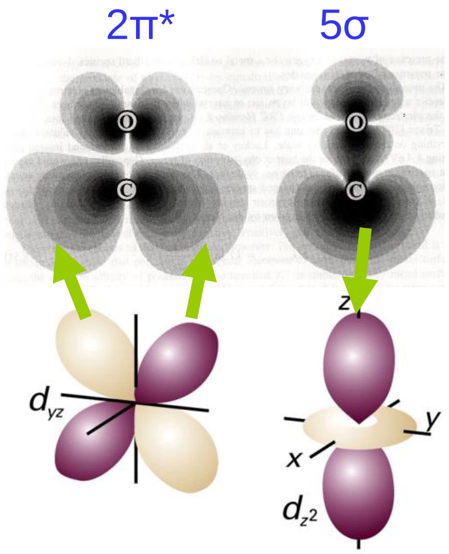
σ donation + π backdonation

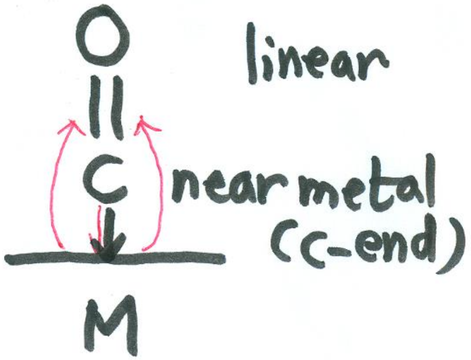
(1) To form strong chemical bond between metal surface and C of CO (M-CO)

(2) To weaken the C-O bond because of the charge depletion of the CO 5σ bonding orbital and charge increase CO 2π* antibonding orbital

- Charge transfer : work function change
- e^- donation + backdonation
- Orbital symmetry

- Transition & noble metal : d-band metal





Molecular oxygen chemisorption

- vibrational spectrum of O_2/Pd(111): O-O stretching peaks (Fig. 2.29)
- occupation of π*↑, M-O_2 bonding↑ → vibrational frequency↓
- O_2 dissociative at high temp (e.g. O_2/Pd dissociative > 180 K) → this related to the MO structure of O_2. two 2π* orbitals are half-filled and degenerate in the gas phase

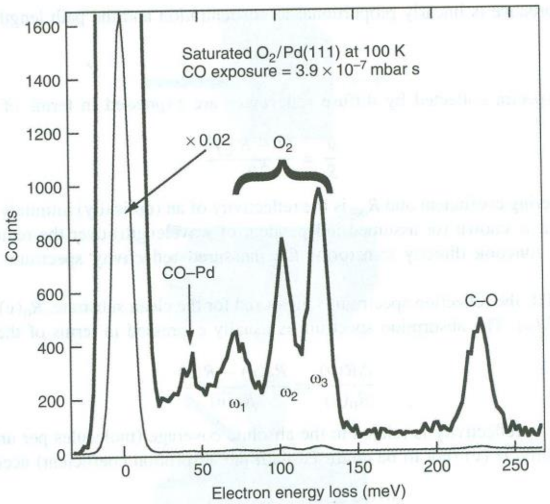


Figure 2.29 *The electron energy loss spectrum of co-adsorbed O_2 + CO on Pd(111). The species associated with ω_1, ω_2 and ω_3 are illustrated in Fig. 3.8. Adapted from K.W. Kolasinski, F. Cemič, A. de Meijere, E. Hasselbrink, Surf. Sci., 334, 19.* © *1995 with permission from Elsevier.*

ω_1 strongest M-O_2, weakest O-O

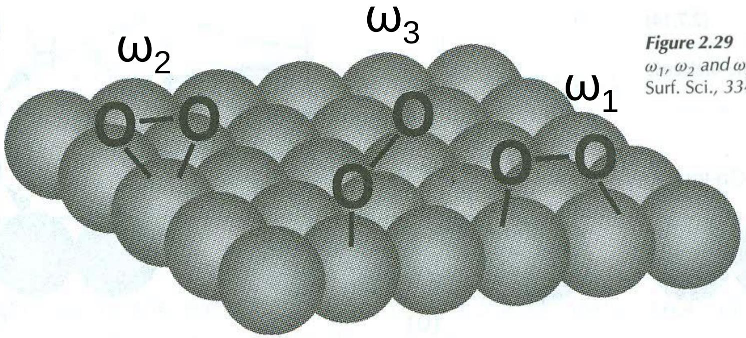


Figure 3.8 *O_2/Pd(111) adsorbate structure. The labelling of the three states (ω_1, ω_2 and ω_3) correlates with the loss peaks observed in the electron energy loss spectrum as shown in Fig. 2.30.*

The binding of ethene

- a model of the binding of polyatomic molecule to a surface

- Fig.3.9(a): -73 kJ/mol on Pt(111)
- Fig.3.9(b): π electron donated to the surface to form two σ bonds → structure of ethane (sp^3 hybridization), -117 kJ/mol on Pt(111) (~280 K)
- Fig.3.9(c): loss of H with T↑

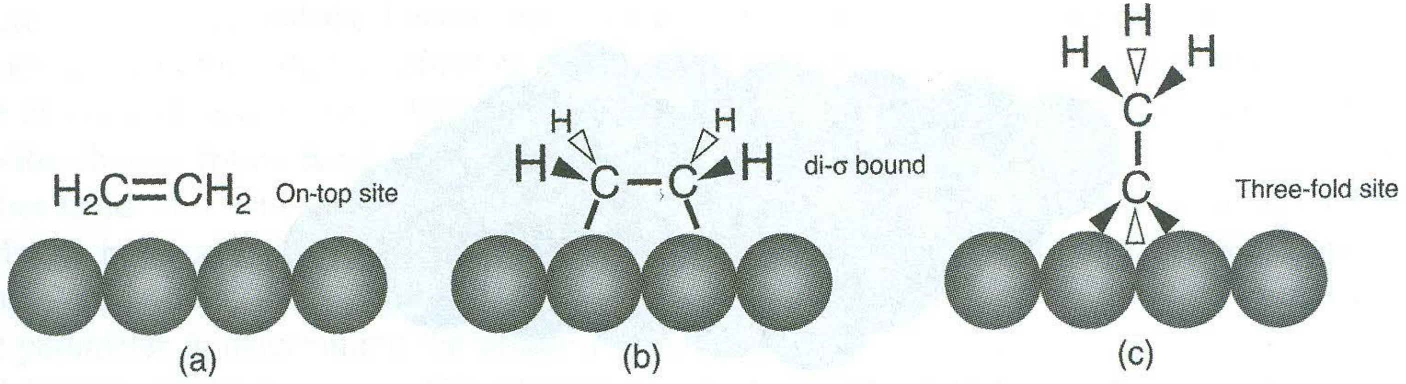


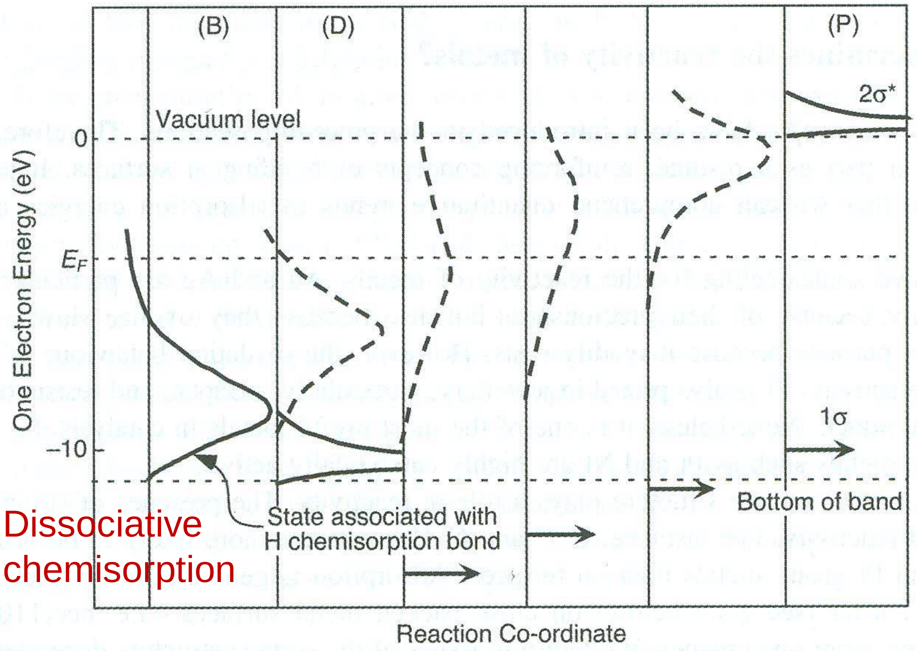
Figure 3.9 *The binding of ethene at a metal surface. (a) The weakly chemisorbed π-bonded C_2H_4. (b) The d*
σ-bonded chemisorbed state. (c) Ethylidyne.

Dissociative chemisorption: H_2 on a simple metal

- bonding + antibonding pair

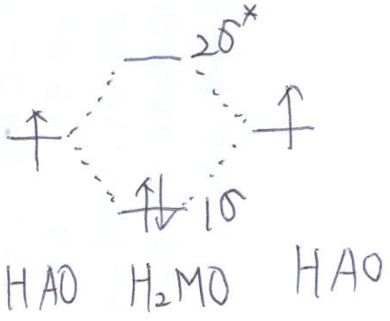
cf) CO: backdonation into π system is bonding with respect to the M-CO bond
but antibonding with respect to the C-O bond

- H_2: electron donation from the metal into the 2σ* antibonding orbital → weaken of H-H bond and strengthen the adsorbate/surface interaction → dissociation

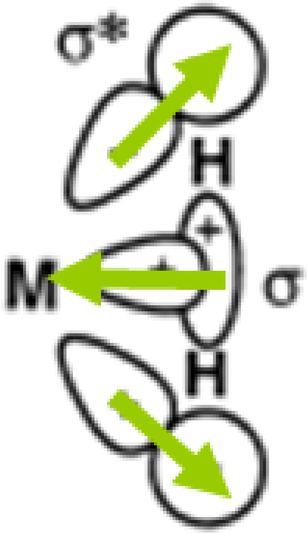


Dissociative chemisorption

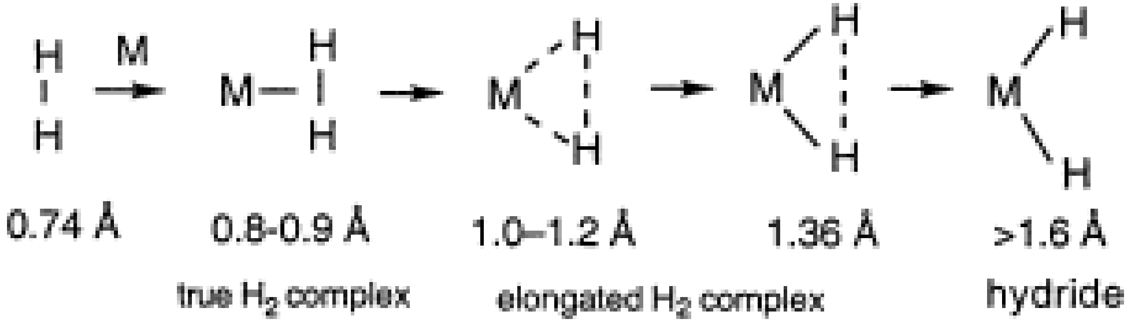
Figure 3.10 *Calculated changes in the electronic structure of the orbitals associated with H_2 as the molecule approaches a Mg surface. Moving to the left in the diagram represents motion toward the surface. Reproduced from J. K. Nørskov, A. Houmøller, P. K. Johansson, B. I. Lundqvist,* Phys. Rev. Lett., *46, 257. © 1981, with permission from the American Physical Society.*



- H_2 1σ and 2σ* orbitals shift and broaden as they approach the surface → electron transfer from the metal to the H_2 occurs because the 2σ* drops in energy and broadens as H_2 approaches the surface → As it drops below E_F, electrons begin to populate the orbital and H_2 bond grows progressively weaker while M-H bonds become progressively stronger



Kubas interaction



What determines the reactivity of metals?

- What makes Au so noble whereas Pt & Ni are highly catalytic active?

- Surface structure plays a role in reactivity: defects (steps, kinks) → enhance reactivity. Adsorption hindered on close packed (fcc(111), bcc(110), hcp(001))

Structural effect

- Also electronic structure plays a role in reactivity →
  e.g., Hammer & Nϕrskov → H, O adsorption on metal (s, d bands)

Electronic effect

H on metal: two step process

Step 1) H1s ↔ s band of the metal (s band in transition metals are very broad) → weak chemisorption

Step 2) H1s ↔ d band of the metal →

(a) Early transition metal: antibonding above E_F → antibonding: not-filled → chemisorption(bonding) attractive↑ → strong exothermic

(b) Coinage metal (Cu, Ag, Au…): antibonding below E_F
left to right in Periodic Table: filled electrons in antibonding↑ → chemisorption(bonding) repulsive↑(attractive↓) → weaken chemisorption

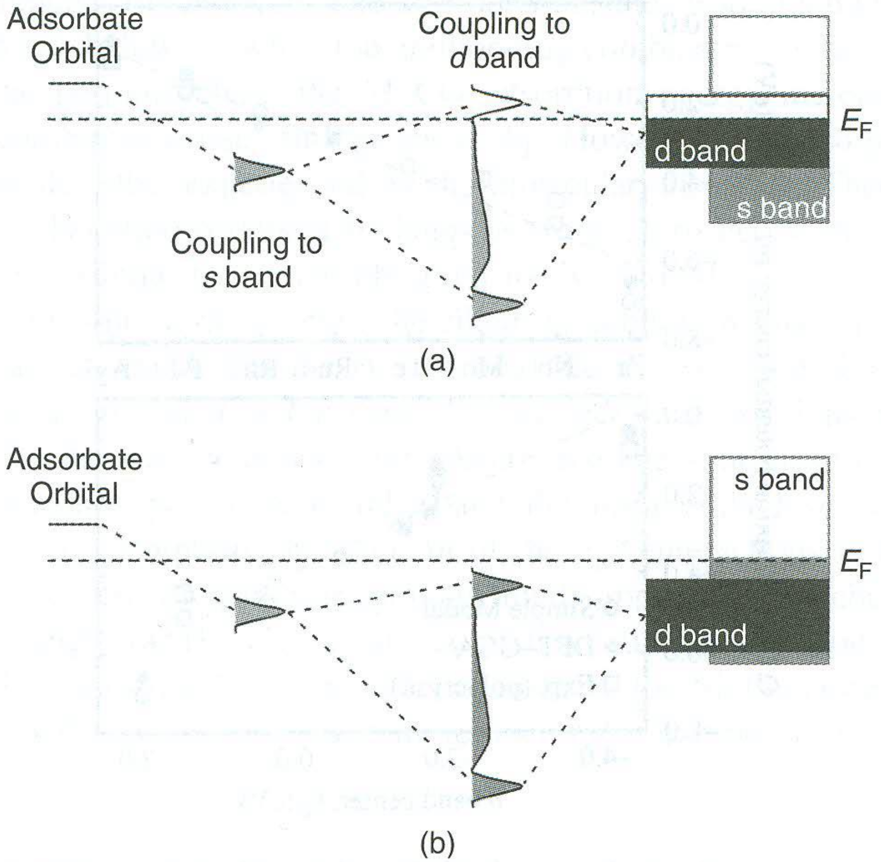


Figure 3.11 *The two-step conceptualization of chemisorption bond formation on transition metal surfaces. (a) Early transition metal. (b) Coinage metal.*

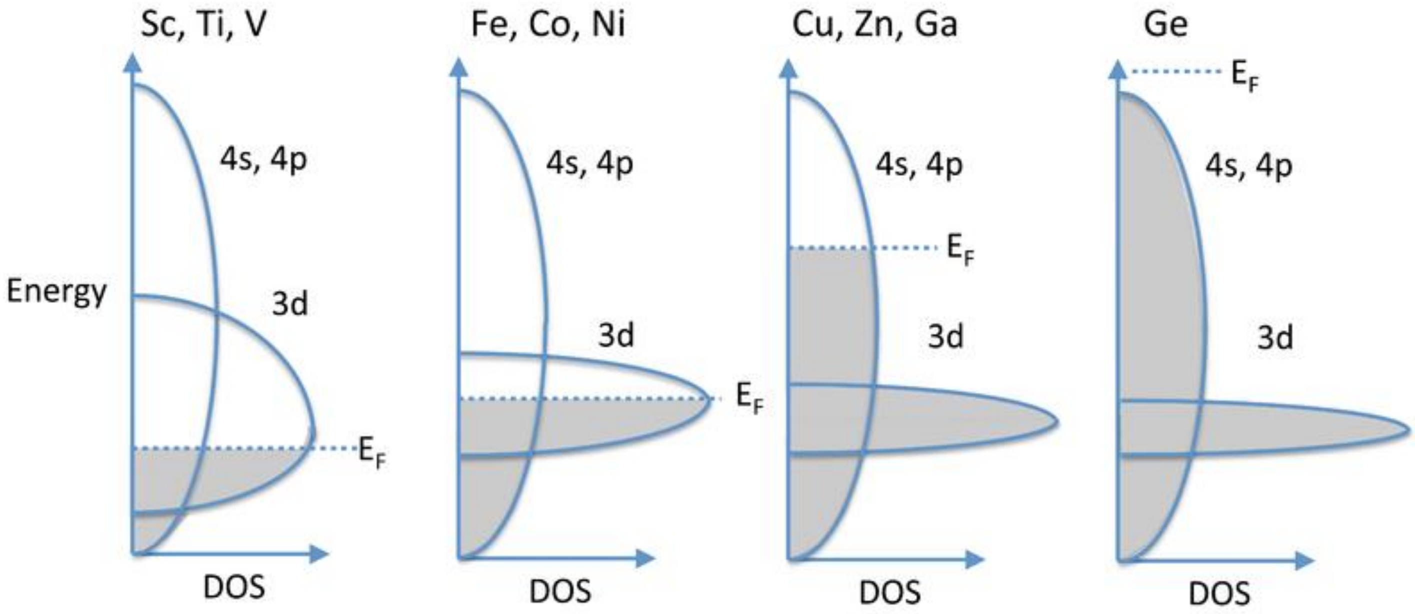
Adsorption energy, $\Delta E = \Delta E_{sp} + \Delta E_d$

ΔE_{sp}, ΔE_d : coupling to the sp states & d states

Coupling to the d band, $\Delta E_d = \Delta E_d^{hyb} + \Delta E_d^{orth}$

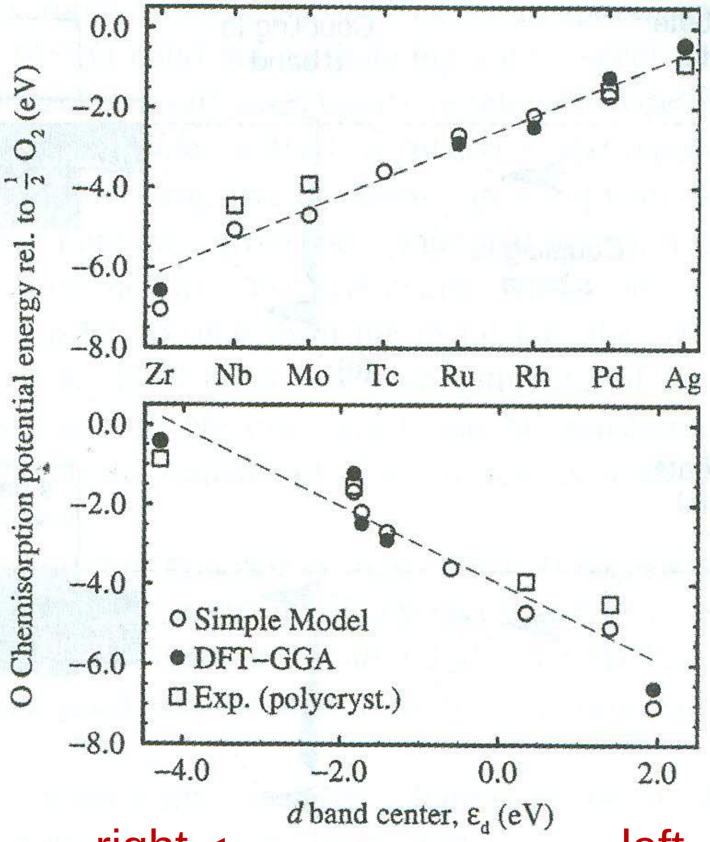
ΔE_d^{hyb}, ΔE_d^{orth} : attractive hybridization term & repulsive orthogonalization term

Shift of d band center



Source: Wikimedia Commons

left → right



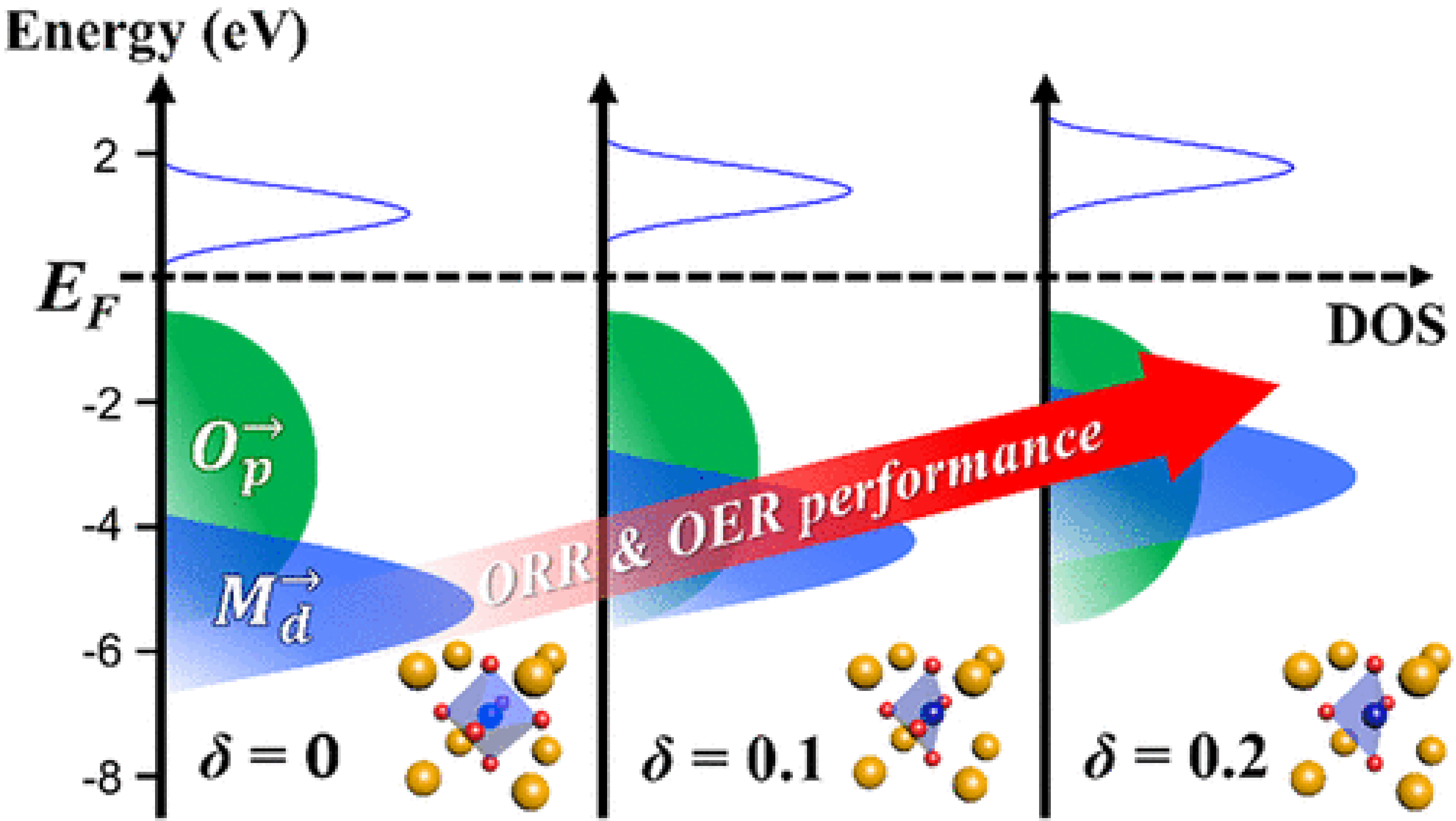
weaker adsorption ↑

(-): d band center↓

right ← left

Figure 3.12 *The interaction strength of chemisorbed O and how it varies across a row of transition metals. In the upper panel, the good agreement between experimental and theoretical results is shown. In the lower panel, the linear relationship between interaction strength and the d band centre is demonstrated. Source of data for experimental results: I. Toyoshima, G. A. Somorjai,* Catal. Rev – Sci. Eng., *19 (1979) 105. Reprinted from B. Hammer and J. K. Nørskov, Theoretical surface science and catalysis – Calculations and concepts,* Adv. Catal., *Vol. 45 (Eds B. C. Gates, H. Knözinger), Academic Press, Boston, p. 71. © 2000 with permission from Academic Press.*

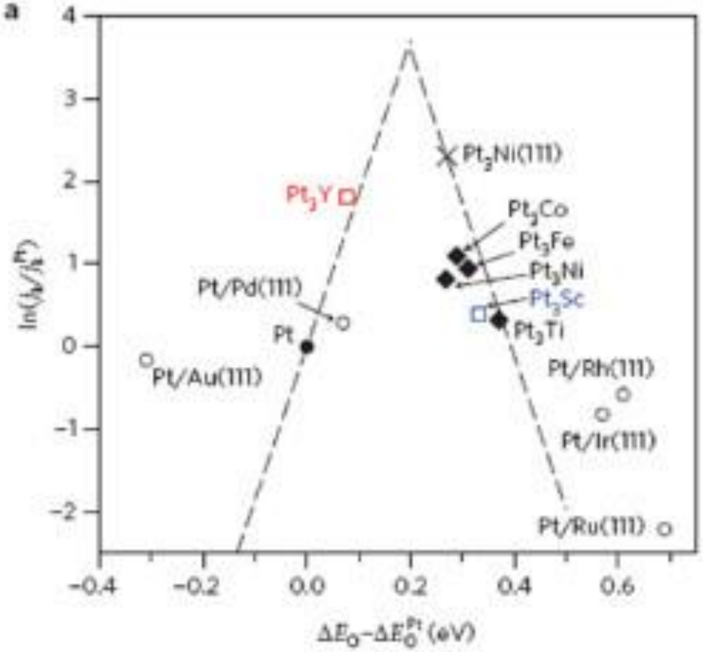
d band center vs. catalytic activity

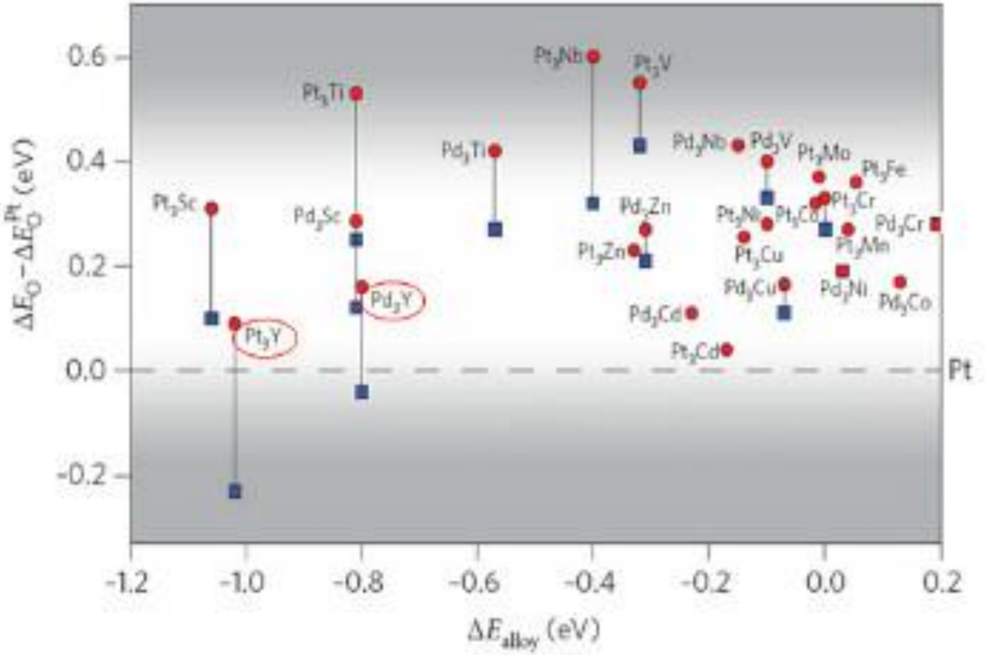


Enhancing Bifunctional Electrocatalytic Activities via Metal d-Band Center Lift Induced by Oxygen Vacancy on the Subsurface of Perovskites

Hansol Lee *et al*, *ACS Catal.* 2020, 10, 8, 4664–4670.

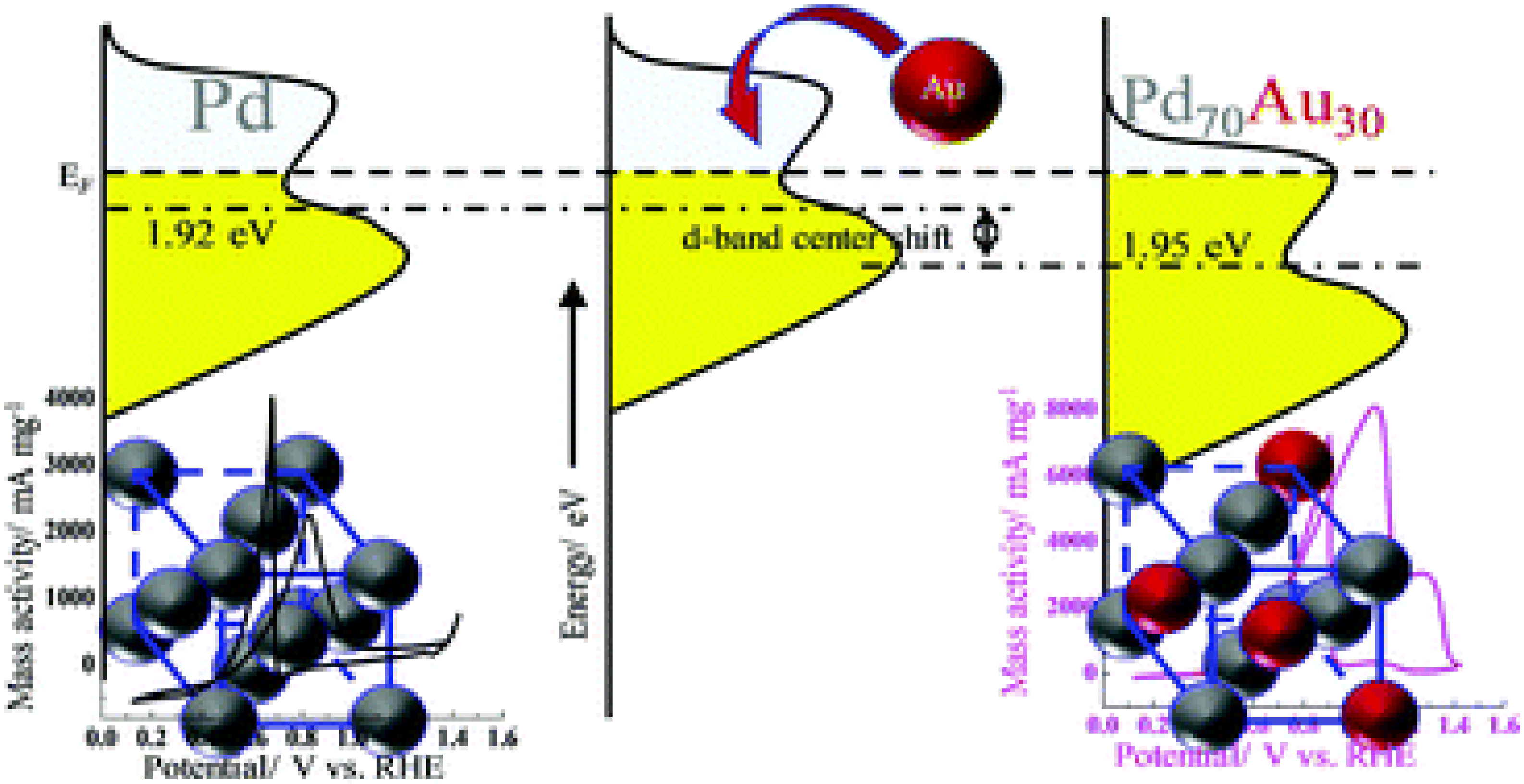
d band center vs. catalytic activity





Source: 신소재경제(2018.4.5)

d band center vs. catalytic activity



Electrochemical tuning of Pd$_{100-x}$Au$_x$ bimetallics towards ethanol oxidation: effect of an induced d-band center shift and oxophilicity

Sreejith P. Babu *et al*, *PCCP.* 2019, 16

- In Cu(3d), Ag(4d), Au(5d), why Au is more noble than Cu?
- 3d→5d, core→valence, wider band in valence
- orthogonalization energy between adsorbate & metal d orbitals, which is repulsive, increases with increasing coupling strength → this energy increases as the d orbitals become more extended → 5d orbitals of Au are more extended than the 3d orbitals of Cu, which renders Au less reactive than Cu because of the higher energy cost of orthogonalization between the H1s & Au 5d orbitals

- Two criteria influencing the strength of the chemisorption interaction

(i) The degree of filling of the antibonding adsorbate-metal d states
(ii) The strength of the coupling

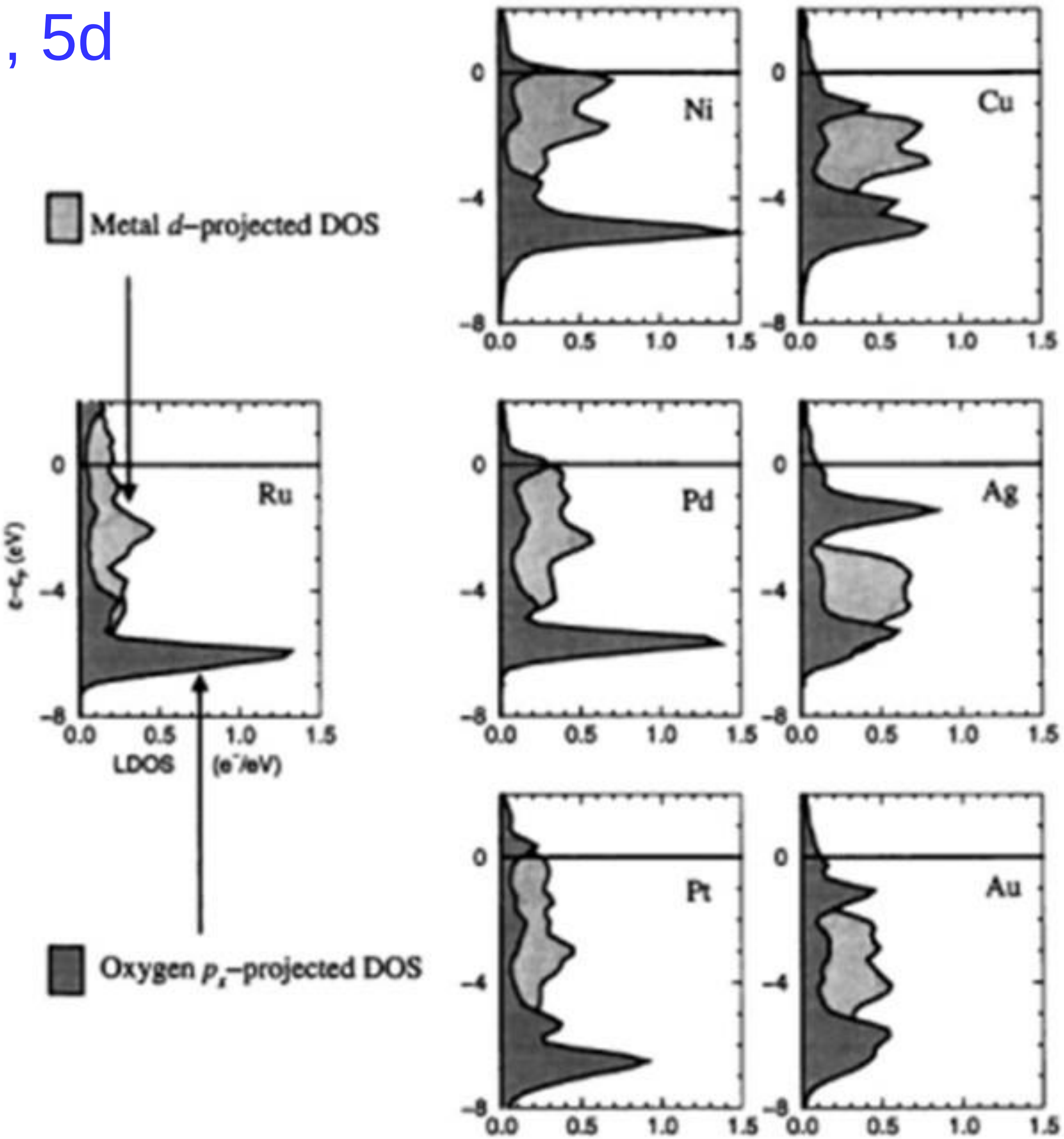
→ the filling increases in going from left to right across a row of transition metals in the periodic table and is complete for the coinage metals (Cu, Ag, Au). The coupling increases in going down a column in the periodic table. It also increases in going to the right across a period

Same principle can be extended to molecular adsorption
e.g. CO, Blyholder model (next page) →

d band: 3d, 4d, 5d

Ni $3d^8 4s^2$
Pd $4d^{10} 4s^0$
Pt $5d^9 6s^1$

Cu $3d^{10} 4s^1$
Ag $4d^{10} 5s^1$
Au $5d^{10} 6s^1$



Source: 신소재경제(2018.4.5)

- 5σ derived states (bonding & antibonding combinations) are predominantly below E_F, and, therefore, lead to a repulsive interaction
- 2π* derived states lead to attractive interaction because the bonding combination lies below E_F while the antibonding combination is (at least partially) above E_F

→ Moving to the left in the periodic table, the M-CO adsorption energy increases as the filling of the 2π*-metal antibonding combination rises further above E_F. However, the adsorption energy of C and O increases at a greater rate than that experienced by the molecular adsorbate

→ therefore, a crossover from molecular to dissociative adsorption occurs

→ this happens from Co to Fe for the 3d transition, Ru to Mo for 4d and Re to W for 5d

→ similar trends are observed for N_2 and NO

- In dissociative chemisorption of H_2 both the filled σ_g orbital and the unfilled σ_u* MO must be considered

→ σ_g orbital acts like H1s orbital
  σ_u* orbital undergoes similar hybridization

→ the strength of the σ_u* interactions is the dominant factor that determines the height of the activation barrier

Atoms and molecules incident on a surface

- Atoms & molecules incident on a surface → adsorption & desorption

Scattering channels

- Elastic scattering: no energy is exchanged → equal angle (incident & reflection) → specular scattering → return to the gas phase (no adsorption) (special case of elastic scattering: diffraction for light particles)
- Inelastic scattering: energy is exchanged

(i) Direct inelastic scattering: particle either gains or loses energy and returned to the gas phase. e.g. He atoms scattering to investigate surface phonons

(ii) Trapping or sticking: particle loses enough energy to be trapped in the adsorption well at the surface

- Sticking probability or initial sticking coefficient

$$\boxed{s_0 = \lim_{\theta\to 0}\frac{N_{\text{stick}}}{N_{\text{inc}}} = \lim_{\theta\to 0}\frac{N_{\text{stick}}}{N_{\text{el}}+N_{\text{in}}+N_{\text{stick}}}} \qquad (3.7.$$

where N_{stick} is the number of particles that stick to the surface, N_{inc} is the total number incident c the surface, N_{el} is the number scattered elastically, and N_{in} is the number scattered inelastically bu which do not stick. Values of s_0, even for simple molecules such as H_2 and O_2, can vary between 1 ar $<10^{-10}$. This extreme range of sticking probabilities indicates that sticking is extremely sensitive to tl

$1 \sim 10^{-10}$ for H_2, O_2

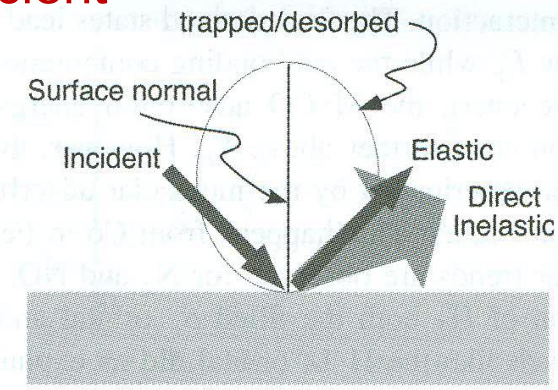
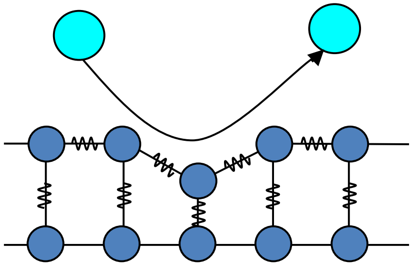
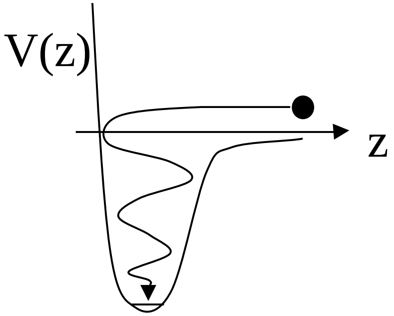


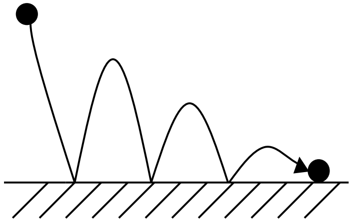
Figure 3.13 *Scattering channels for a molecule incident upon a surface.*

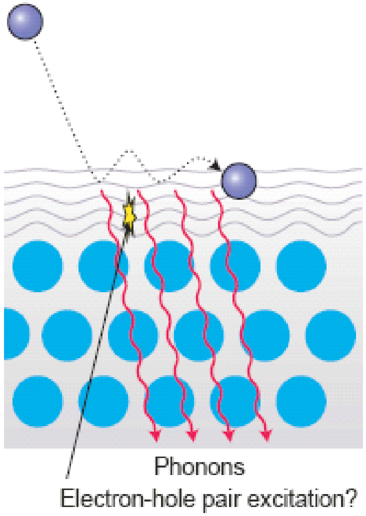
Adsorption dynamics

- The outcome of the gas-surface collisions;
  1) Trapping: becoming a bound state after the 1st collision
  2) Direct reflection to the gas phase
- The trapping probability is determined by the amount of the energy transfer to the surface
- Energy transfer occurs via multiphonon excitations









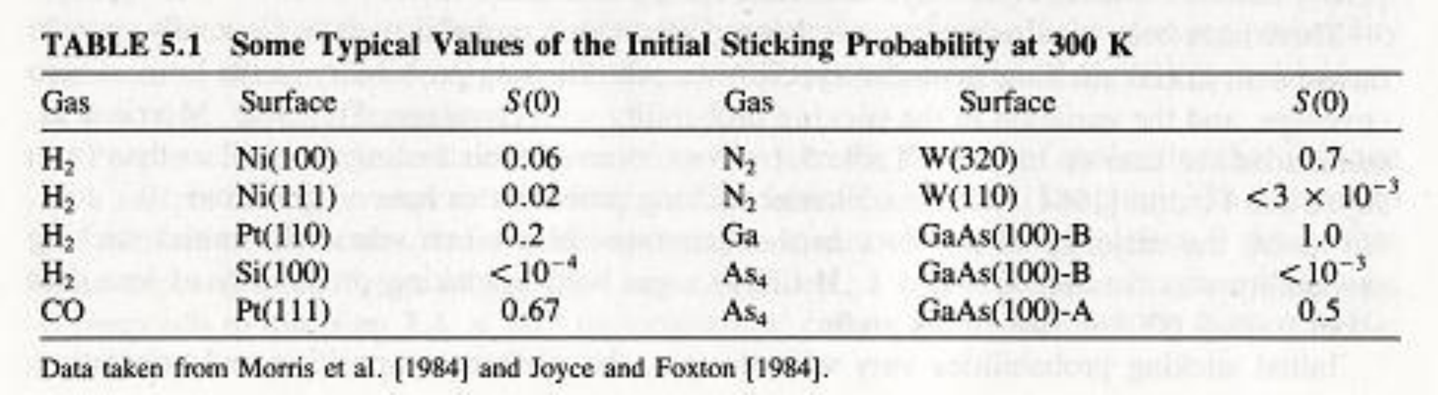


TABLE 5.1 Some Typical Values of the Initial Sticking Probability at 300 K

Gas	Surface	$S(0)$	Gas	Surface	$S(0)$
H_2	Ni(100)	0.06	N_2	W(320)	0.7
H_2	Ni(111)	0.02	N_2	W(110)	$<3 \times 10^{-3}$
H_2	Pt(110)	0.2	Ga	GaAs(100)-B	1.0
H_2	Si(100)	$<10^{-4}$	As_4	GaAs(100)-B	$<10^{-3}$
CO	Pt(111)	0.67	As_4	GaAs(100)-A	0.5

Data taken from Morris et al. [1984] and Joyce and Foxton [1984].

Non-activated adsorption

No energetic barrier

1D potential
(Lennard-Jones diagram)

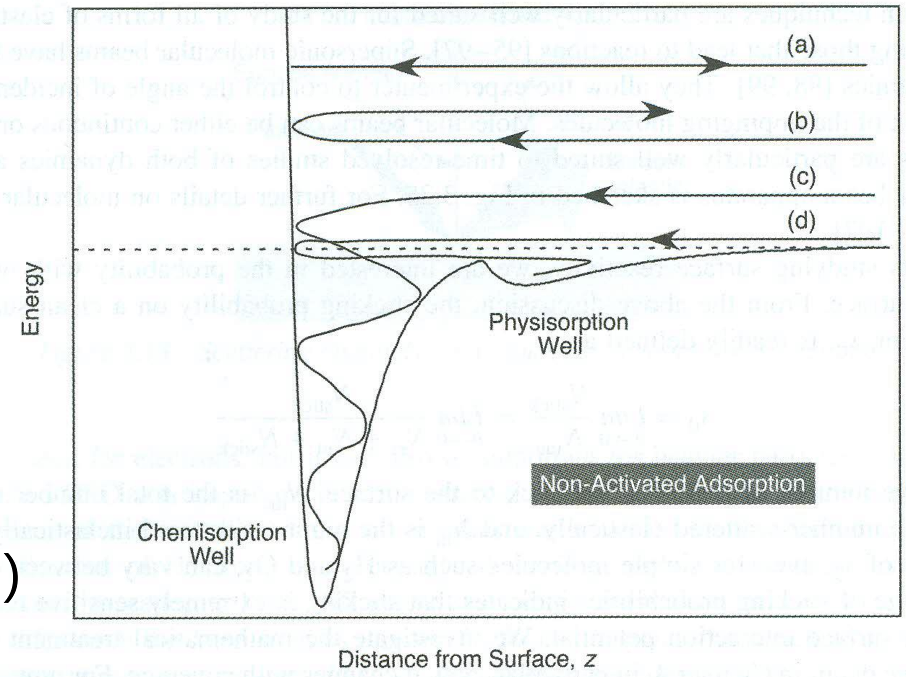
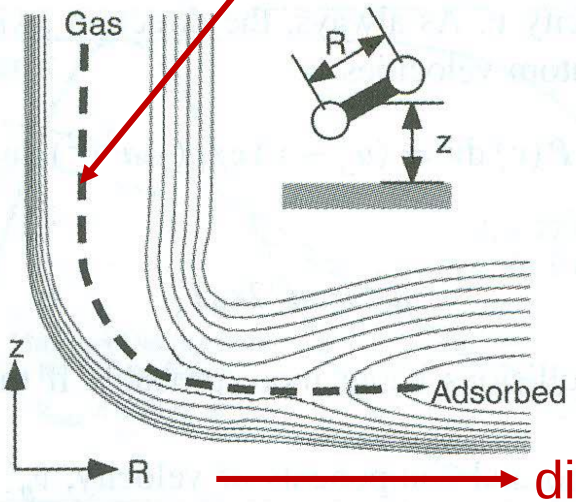


Figure 3.14 *A one-dimensional representation of non-activated adsorption: (a) elastic scattering trajectory; (b) direct inelastic scattering trajectory; (c) sticking event (chemisorption); (d) sticking event (physisorption).*

2D potential energy hyperstructure (PES) → to describe dissociative adsorption



path of minimum energy that connect the gas-phase molecules to the adsorbed phase

far from the surface

dissociation

Figure 3.15 *2D PES for non-activated dissociative adsorption. z is the distance from the molecular centre of mass to the surface. R is the internuclear distance between the atoms of the molecule.*

Hard cube model for non-activated adsorption: surface is modeled by a cube of mass m

Activated adsorption

Low sticking coefficient

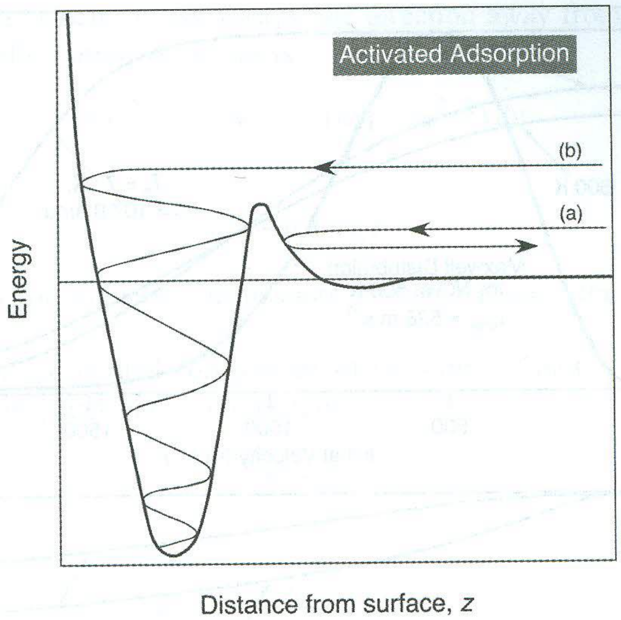


Figure 3.17 *A Lennard-Jones diagram is a one-dimensional representation of the potential energy. In the case shown here, the one dimension is taken as the distance above the surface. A barrier separating the chemisorption well from the gas phase distinguishes activated adsorption. Also shown in the diagram are the energies of two hypothetical trajectories at (a) low and (b) high kinetic energy. Classically, only high energy trajectories can overcome the adsorption barrier.*

Activated adsorption

$X_2\ (g) \rightarrow 2\ X_{ad}$

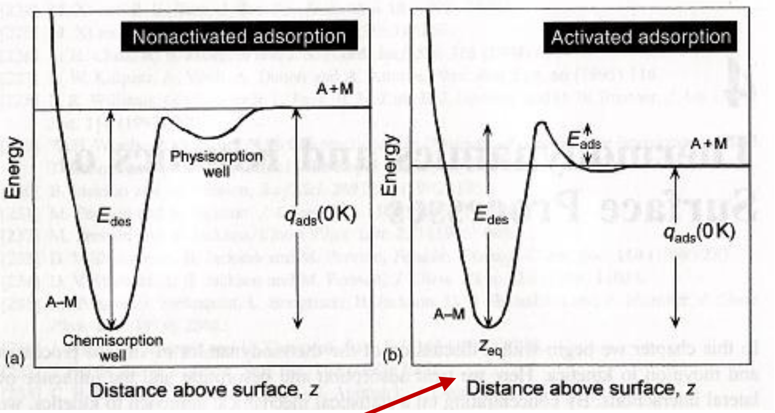
- Important process in heterogeneous catalysis
- Very small s_0 due to the presence of an adsorption barrier

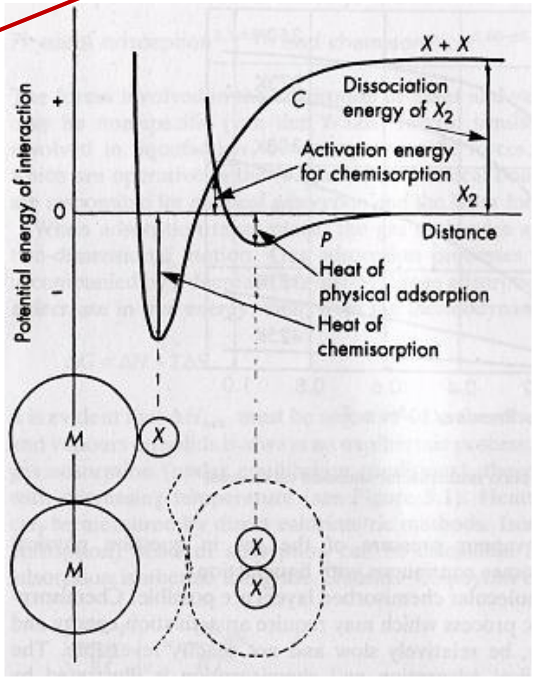
- A fast N_2 can overcome the barrier to directly populate the atomic state

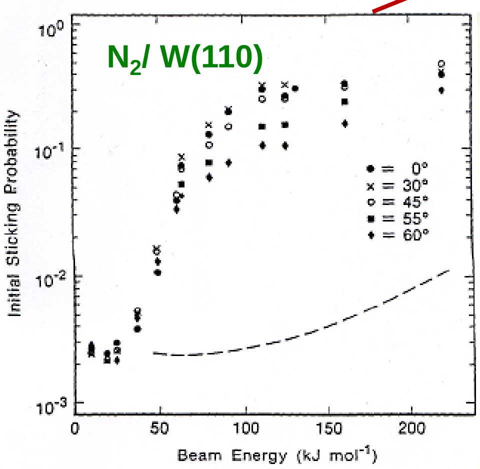
- A large kinetic energy dependence of s_0

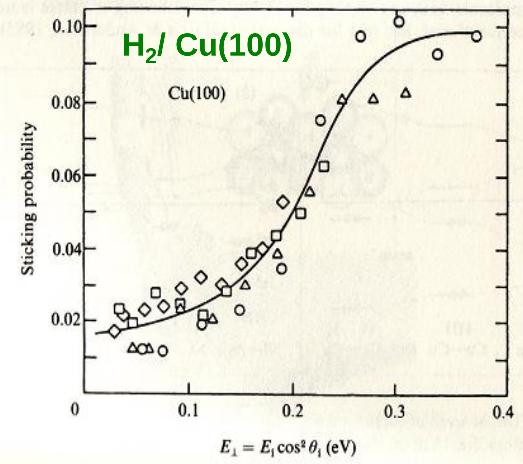
fast chemisorption
gas on clean metal

slow chemisorption
H_2 on Cu
20~40 kJ/mol E_a









2D PES of activated dissociative adsorption: different position of the barrier

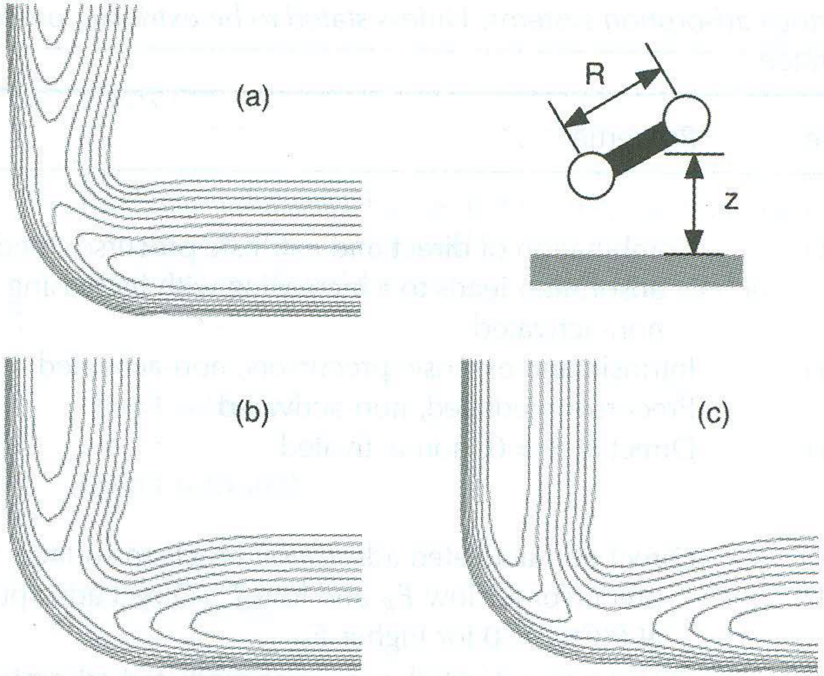


Figure 3.18 *Potential energy surfaces (PESs) for activated dissociative adsorption with (a) early, (b) middle and (c) late barriers. z, the distance from the molecular centre of mass to the surface (vertical axis); R, internuclear distance between the atoms of the (diatomic) molecule (horizontal axis). George Darling is thanked for providing these very fine model PESs.*

Direct vs. precursor mediated adsorption (Table 3.3)

- Direct adsorption corresponds to the case in which a molecule makes the decision to stick or scatter upon its first encounter with the surface
→ a molecule hit the surface, loses energy, and adsorbs at the site where it lands or hop sites away from the point of impact

- Precursor mediated adsorption: a molecule loses sufficient energy → trapped into a mobile precursor state → hop or migrate

Table 3.3 *A survey of various adsorption systems. Unless stated to be extrinsic, precursor refers to the sticking behaviour on the clean surface.*

Species	Surface	Properties	Reference
Atomic			
Xe	Pt(111)	Combination of direct and extrinsic precursor mediated adsorption leads to *s* increasing with increasing coverage, non-activated	[125]
Kr	Pt(111)	Intrinsic and extrinsic precursors, non-activated	[126]
Cs	W	Precursor mediated, non-activated	[127]
Ir, Re, W, Pd	Ir(111)	Direct at $\theta = 0$, non-activated	[128]
Molecular			
CO	Ni(100) Pt(111)	Direct non-activated adsorption on clean surface. Extrinsic precursor for low E_K and low T_s. Direct adsorption possible at $\theta(\mathrm{CO}) > 0$ for higher E_K	[125][129, 130]
CO_2	Cu(110)	Direct non-activated, precursor mediated adsorption. Below 91 K *s* increases with increasing coverage.	[131]
	Ni(111)	Precursor mediated, non-activated	[132]
N_2	Fe(111)	Direct into first molecular state, activated transfer into second molecular state, K co-adsorption lowers barrier to transfer	[133, 134]

NO	Pt(111)	Direct non-activated	[135]
	Pt(110)	Precursor mediated, $s_0 = 0.87$	[136]
	Pt(100)-(1 × 1)	Direct non-activated, $s_0 = 0.68$	[136]
	Pt(100)-hex	Precursor mediated, $s_0 = 0.86$	[136]
	Pd(100)	Direct non-activated, $s_0 = 0.85$	[136]
	Ni(100)	Dissociative at 300 K up to $\theta = 0.16$ ML, molecular above 0.16 ML	[136]
O_2	Ag(111)	Activation barrier between physisorbed and chemisorbed molecular states	[137]
	Pt(111)	Precursor mediated switching to direct for high E_K	[138]
	Pt(100)	s_0 two orders of magnitude lower on HEX-R0.7° reconstruction compared to (1 × 1), precursor switches to direct for high E_K	[139]
n-alkanes	Pt(111)	Precursor mediated, non-activated, s increases with coverage for C_2H_6 and C_3H_8	[125]
Si_2H_6	Si(111(–(7 × 7)	Precursor mediated, non-activated	[140]
Dissociative			
H_2	Si(111(–(7 × 7) Si(100)-(2 × 1)	Direct activated, large barrier on clean terraces, lower barrier at steps, lower barrier in neighbourhood of adsorbed H	[141–144]
	Ni(997)	Precursor mediated	[125]
	Cu(100) Cu(111)	Direct activated, $E_{ads} = 0.74$ eV (100), 0.63 eV (111)	[48, 145]
	Ge(100)-(2 × 1)	Direct activated, large barrier	[146]

Competitive adsorption & collision induced processes

- e.g. O_2 + CO on Pd(111)

  O_2 on Pd(111) at 100 K → 3 states $\xrightarrow{CO\uparrow}$ CO can displace O_2 from the surface

→ remain ω_3 (most able to compete with CO for adsorption sites)

→ CO and O_2 compete for sites on Pd surface

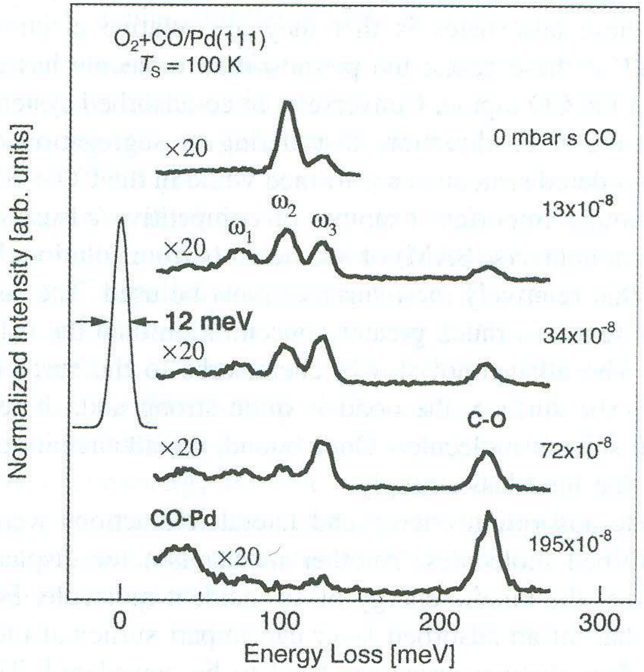


Figure 3.23 *Competitive adsorption in the CO + O_2/Pd(111) system is investigated by electron energy loss spectroscopy (EELS). The species associated with species ω_1, ω_2 and ω_3 are illustrated in Fig. 3.8. arb units, arbitrary units; T_s, surface temperature. Reproduced from K. W. Kolasinski, F. Cemič, A. de Meijere, E. Hasselbrink, Surf. Sci., 334, 19. © 1995, with permission from Elsevier.*

Classification of reaction mechanism

Langmuir-Hinshelwood mechanism (LH mechanism)

- Most common surface reaction mechanism → both reactants are adsorbed on the surface where they collide and form products → adsorption, desorption and surface diffusion play essential roles in the LH mechanism

$$\boxed{A(a) + B(a) \rightarrow AB(a)}$$

- Reaction rate should depend on the surface coverage of both species

$$\boxed{R = k\theta_A\theta_B}$$

- RDS (rate determining step): adsorption or adsorbate decomposition or diffusion of an adsorbate to a reactive site or desorption of a product

e.g. NH_3 synthesis: N_2 adsorption(RDS)

O_2 + CO to form CO_2 on Pt group

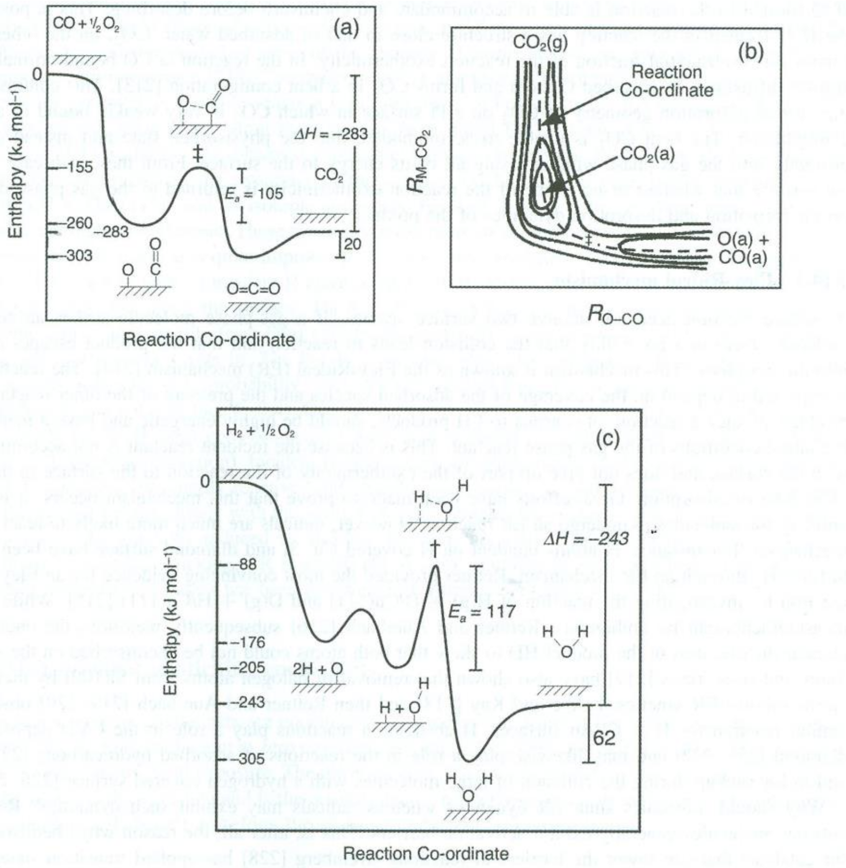


Figure 3.24 *The oxidation of CO to form CO_2 and H_2 to form H_2O on Pt(111) follow Langmuir-Hinshelwood mechanisms. The changes in energy along the reaction pathway are as follows. (a) Enthalpy changes associated with CO + O_2 reaction. The transition state ‡ is a stretched and bent CO_2 entity. (b) A two-dimensional potential energy surface of the CO + O_2 reaction, portraying the energetic changes as a function of the CO_2–surface distance [r(M–CO_2)] and the forming OC bond length [r(O–CO)]. (c) Enthalpy changes associated with the H_2 + O_2 reaction. Two intermediates (2H + O, and H + OH) are formed during the reaction. The transition state † reached prior to the formation of H_2O(a) is also bent and stretched; however † resembles H_2O(a) more closely than ‡ resembles CO_2(a). Parts (a) and (b) Reproduced with permission from G. Ertl, Ber. Bunsenges. Phys. Chem. 86 (1982) 425. © 1982 Wiley VCH. Values for (c) taken from M. P. D'Evelyn and R. J. Madix, Surf. Sci. Rep. 3 (1983) 413.*

Eley-Rideal mechanism

- A surface reaction need not involve two surface species→ if a gas-phase molecule sticks an adsorbed molecule, the collision leads to reaction and that the product escapes directly into the gas phase

$$\boxed{A(a) + B(g) \rightarrow AB(g)}$$

→ reaction rate is expected to depend on the coverage of the adsorbed species and the pressure of the other reactant

$$\boxed{R = k\theta_A P_B}$$

Hot atom mechanism

- Mechanism between LH and ER → one of the reactants were adsorbed while the other was not yet fully accommodated to the surface → hot precursor or hot atom mechanism

$$\boxed{A(a) + B(hot) \rightarrow AB(g)}$$

e.g. O atoms incident on CO/Pt(111)

Measurement of sticking coefficients

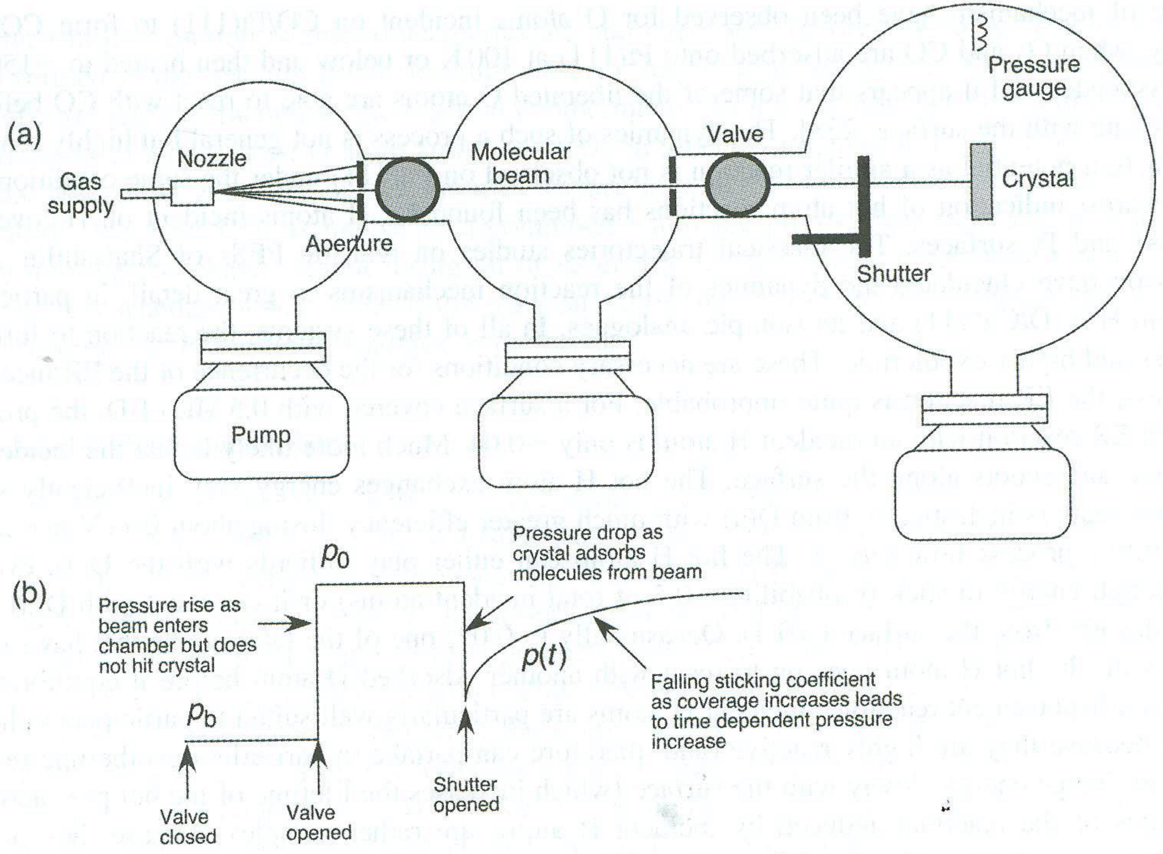


Figure 3.25 *The King and Wells method of sticking coefficient determination: (a) apparatus, (b) pressure curve.*

$$s(t) = \frac{p_0 - p(t)}{p_0 - p_b}$$

- Sticking probability

  s = # molecules adsorbed / # molecules impinging on a surface
- Molecular beam method, in which the partial pressure change is monitored with a QMS (quadrupole mass spectroscopy)

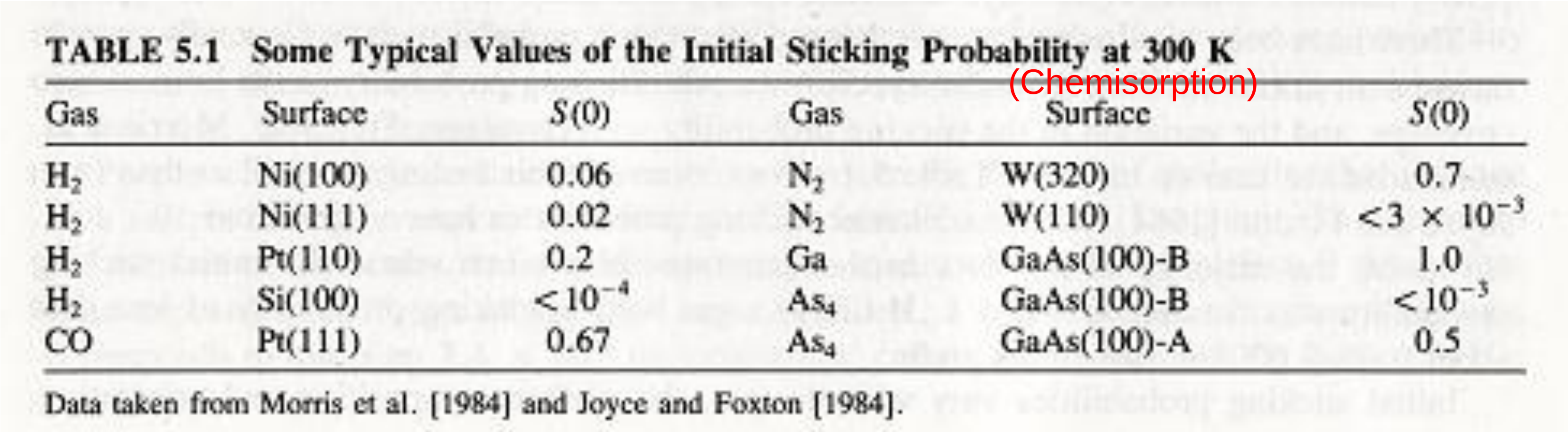


TABLE 5.1 Some Typical Values of the Initial Sticking Probability at 300 K

(Chemisorption)

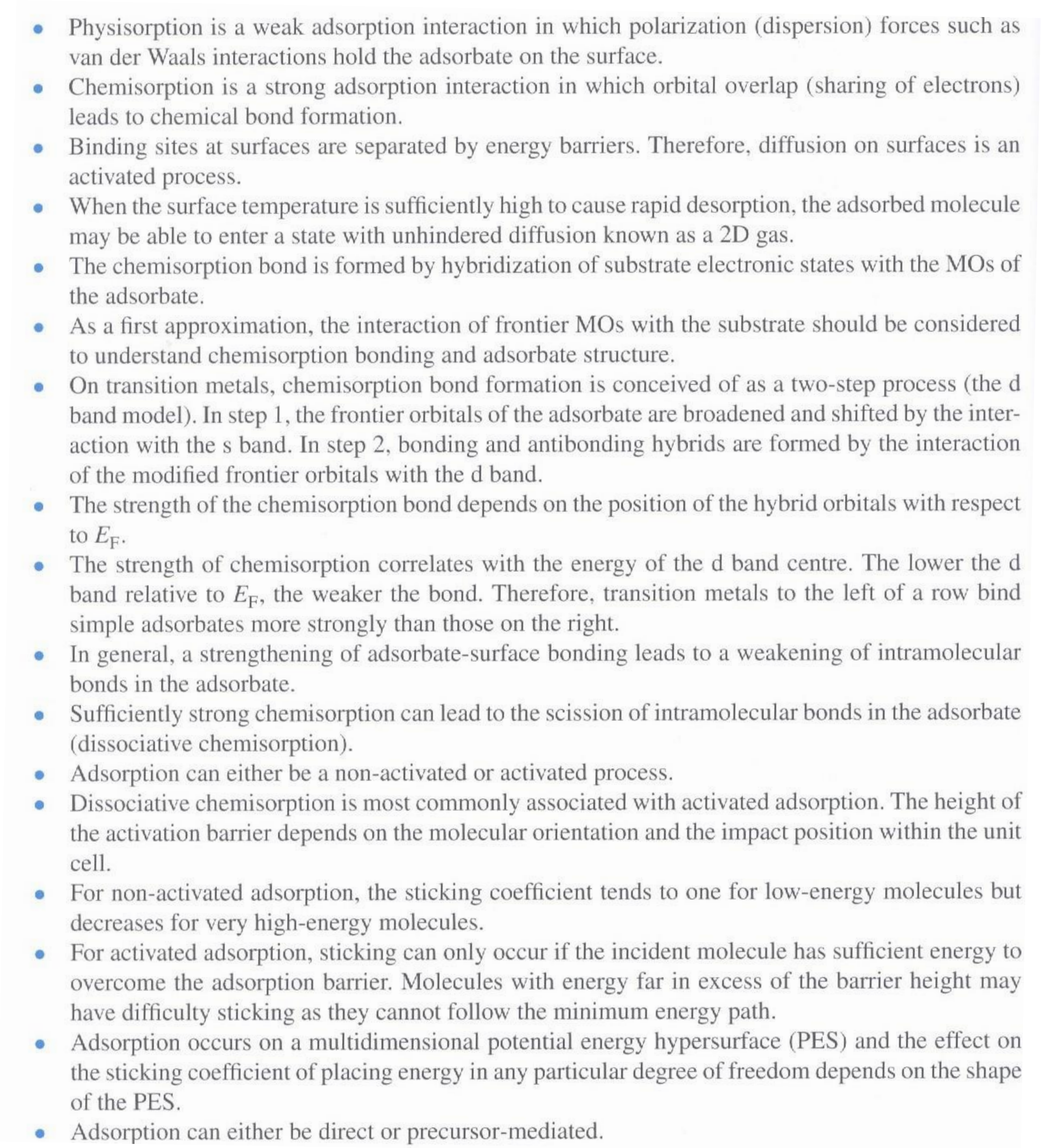
Gas	Surface	$S(0)$	Gas	Surface	$S(0)$
H_2	Ni(100)	0.06	N_2	W(320)	0.7
H_2	Ni(111)	0.02	N_2	W(110)	$<3 \times 10^{-3}$
H_2	Pt(110)	0.2	Ga	GaAs(100)-B	1.0
H_2	Si(100)	$<10^{-4}$	As_4	GaAs(100)-B	$<10^{-3}$
CO	Pt(111)	0.67	As_4	GaAs(100)-A	0.5

Data taken from Morris et al. [1984] and Joyce and Foxton [1984].

Factors influencing s_0 in chemisorption

- Gas- surface combination
- Efficiency of energy transfer in gas-surface collisions
- Surface orientation of the surface for a given single crystal material
- Presence of an energy barrier for dissociative adsorption: activated adsorption

Summary

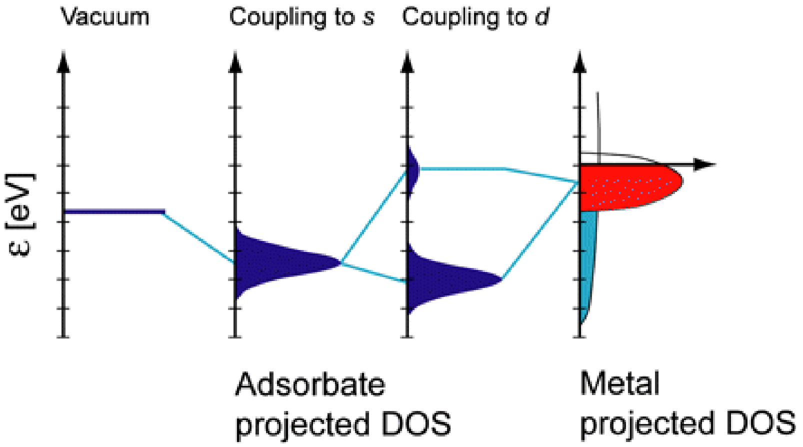


- Physisorption is a weak adsorption interaction in which polarization (dispersion) forces such as van der Waals interactions hold the adsorbate on the surface.
- Chemisorption is a strong adsorption interaction in which orbital overlap (sharing of electrons) leads to chemical bond formation.
- Binding sites at surfaces are separated by energy barriers. Therefore, diffusion on surfaces is an activated process.
- When the surface temperature is sufficiently high to cause rapid desorption, the adsorbed molecule may be able to enter a state with unhindered diffusion known as a 2D gas.
- The chemisorption bond is formed by hybridization of substrate electronic states with the MOs of the adsorbate.
- As a first approximation, the interaction of frontier MOs with the substrate should be considered to understand chemisorption bonding and adsorbate structure.
- On transition metals, chemisorption bond formation is conceived of as a two-step process (the d band model). In step 1, the frontier orbitals of the adsorbate are broadened and shifted by the interaction with the s band. In step 2, bonding and antibonding hybrids are formed by the interaction of the modified frontier orbitals with the d band.
- The strength of the chemisorption bond depends on the position of the hybrid orbitals with respect to E_F.
- The strength of chemisorption correlates with the energy of the d band centre. The lower the d band relative to E_F, the weaker the bond. Therefore, transition metals to the left of a row bind simple adsorbates more strongly than those on the right.
- In general, a strengthening of adsorbate-surface bonding leads to a weakening of intramolecular bonds in the adsorbate.
- Sufficiently strong chemisorption can lead to the scission of intramolecular bonds in the adsorbate (dissociative chemisorption).
- Adsorption can either be a non-activated or activated process.
- Dissociative chemisorption is most commonly associated with activated adsorption. The height of the activation barrier depends on the molecular orientation and the impact position within the unit cell.
- For non-activated adsorption, the sticking coefficient tends to one for low-energy molecules but decreases for very high-energy molecules.
- For activated adsorption, sticking can only occur if the incident molecule has sufficient energy to overcome the adsorption barrier. Molecules with energy far in excess of the barrier height may have difficulty sticking as they cannot follow the minimum energy path.
- Adsorption occurs on a multidimensional potential energy hypersurface (PES) and the effect on the sticking coefficient of placing energy in any particular degree of freedom depends on the shape of the PES.
- Adsorption can either be direct or precursor-mediated.

- Adsorption and desorption are connected by microscopic reversibility.
- In any system for which the sticking coefficient is a function of energy, the desorbed molecules do not have an energy distribution corresponding to an equilibrium distribution at the surface temperature.
- Corrugation is the variation of barrier heights across the surface.
- Whereas initial sticking coefficient values for activated adsorption may exhibit Arrhenius behaviour over some range of temperature, a more general expectation is that they follow the sigmoidal form of Eq. (3.15.3).

Additional Note

Norskov, PNAS January 18, 2011, 108 (3) 937-943



Bond formation at a transition-metal surface. Schematic illustration of the formation of a chemical bond between an adsorbate valence level and the *s* and *d* states of a transition-metal surface. The bond is characterized by the degree to which the antibonding state between the adsorbate state and the metal *d* states is occupied. The higher the *d* states are in energy relative to the Fermi level, the more empty the antibonding states and the stronger the adsorption bond. DOS, density of states.

It can be described by two terms: covalent attraction due to the orbital hybridization and repulsion due to the energy cost associated with the orbital orthogonalization (this term is sometimes referred to as Pauli repulsion).

weaker

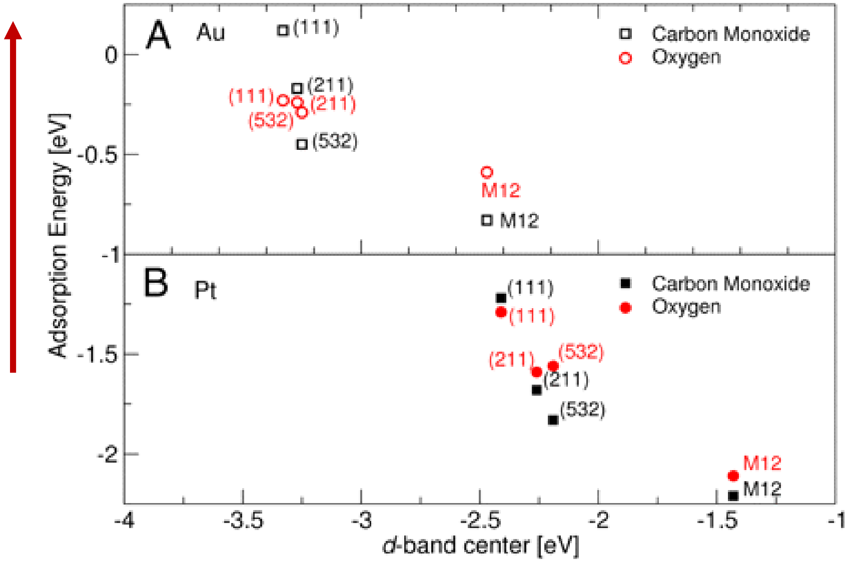


Illustration of the extent of the *d*-band model. Calculated CO and O adsorption energies for a range of different Au (*A*) and Pt (*B*) surfaces including 12 atom clusters are seen to correlate with the calculated *d*-band center (ε_d).

- In Cu(3d), Ag(4d), Au(5d), why Au is more noble than Cu?
- 3d→5d, core → valence, wider band in valence
- orthogonalization energy between adsorbate & metal d orbitals, which is repulsive, increases with increasing coupling strength → this energy increases as the d orbitals become more extended → 5d orbitals of Au are more extended than the 3d orbitals of Cu, which renders Au less reactive than Cu because of the higher energy cost of orthogonalization between the H1s & Au 5d orbitals

- Two criteria influencing the strength of the chemisorption interaction

(i) The degree of filling of the antibonding adsorbate-metal d states
(ii) The strength of the coupling

→ the filling increases in going from left to right across a row of transition metals in the periodic table and is complete for the coinage metals (Cu, Ag, Au). The coupling increases in going down a column in the periodic table. It also increases in going to the right across a period

Same principle can be extended to molecular adsorption
e.g. CO, Blyholder model (next page) →

Why gold is the noblest of all the metals

- B. Hammer & J. K. Norskov

Nature **volume 376**, pages238–240(1995)

…nobleness is related to two factors: the degree of filling of the antibonding states on adsorption, and the degree of orbital overlap with the adsorbate. These two factors, which determine both the strength of the adsorbate-metal interaction and the energy barrier for dissociation, operate together to the maxima detriment of adsorbate binding and subsequent reactivity on gold.

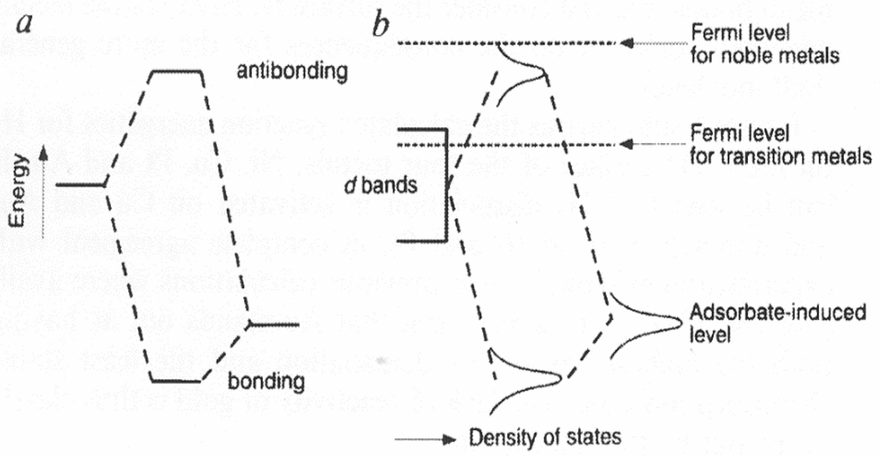


FIG. 2 Schematic illustration of the interaction between two electronic states. The down-shift of the bonding state is smaller than the up-shift of the antibonding state because the overlap of the initial states gives rise to an energy cost related to the orthogonalization of the two states. Both the energy associated with the orthogonalization, and the hybridization energy associated with the formation of bonding and antibonding states, scale with the square of the coupling matrix element. *a*, The simple case of two sharp atomic or molecular states. *b*, The interaction between a state of an adsorbate outside a metal surface, which has been broadened out to a resonance owing to the interaction with the metal *s* band, and the metal *d* bands.

FIG. 3 The density of one-electron states (DOS) (solid lines) for H atomically chemisorbed on the (111) surface of Ni, Cu, Pt and Au. The DOS is projected onto the atomic H 1*s* state. The surface *d* bands DOS (dashed lines) of the four clean metal surfaces are shown for comparison. The dominant features are the H 1*s*–metal *d* bonding resonances at energies, ε, between −5 and −10 eV. Also prominent are the H 1*s*-metal *d* antibonding DOS peaks (indicated by arrows) directly above the metal *d* bands. These antibonding states cause repulsion on Cu and Au, where they are filled. As indicated by the grey-shading, only states below the Fermi energy (which is the energy zero in all cases) are filled.

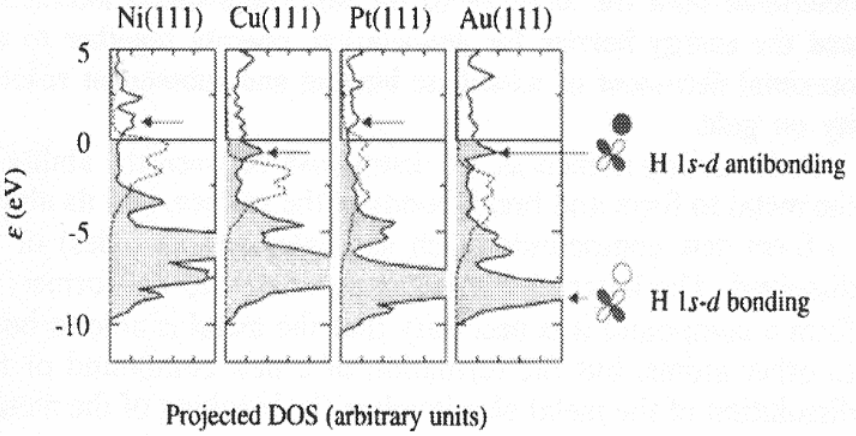
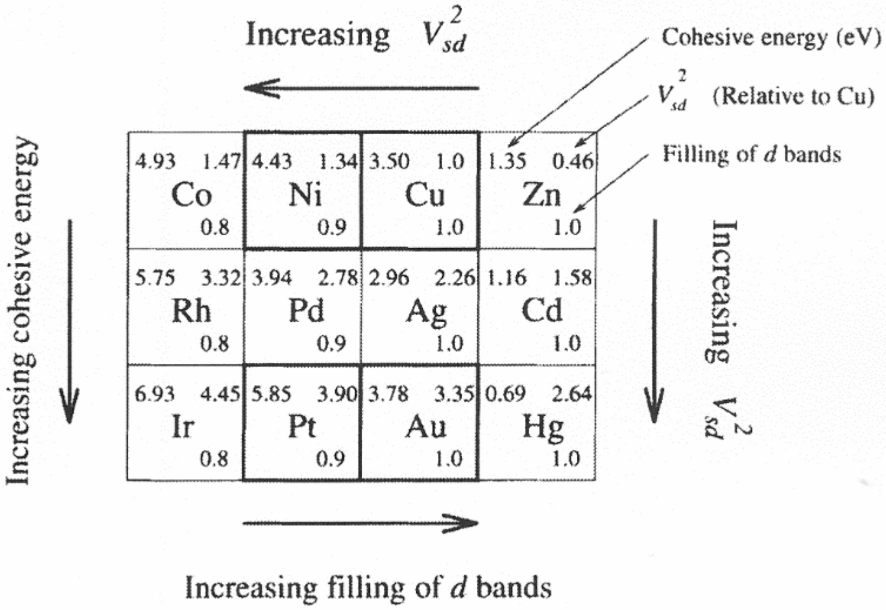


FIG. 4 The *s*–*d* coupling matrix element (V_{sd}^2; refs 17, 18), the filling of the metal *d* bands and the cohesive energy[22] for metals in the vicinity of gold in the periodic table. The filling of the metal *d* bands is taken as a measure of the filling of the adsorbate–metal *d* antibonding state. The largest adsorbate–metal *d* repulsion, and hence the largest nobleness in terms of the surface reactivity, is obtained by maximizing V_{sd}^2 and having an antibonding state filling of one. This is obtained for gold. The nobleness in terms of ability to resist corrosion and dissolution further involves the cohesive energy of the metals. This energy is largest for the 5*d* metals like Ir and Pt and adds particularly to the nobleness of these metals.



4.93 1.47 Co 0.8	4.43 1.34 Ni 0.9	3.50 1.0 Cu 1.0	1.35 0.46 Zn 1.0
5.75 3.32 Rh 0.8	3.94 2.78 Pd 0.9	2.96 2.26 Ag 1.0	1.16 1.58 Cd 1.0
6.93 4.45 Ir 0.8	5.85 3.90 Pt 0.9	3.78 3.35 Au 1.0	0.69 2.64 Hg 1.0

Coupling to the d band, $\Delta E_d = \Delta E_d^{hyb} + \Delta E_d^{orth}$

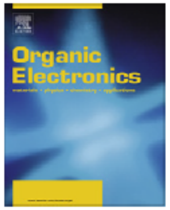
ΔE_d^{hyb}, ΔE_d^{orth} : attractive hybridization term & repulsive orthogonalization term

Organic Electronics 9 (2008) 783–789

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



A role of metal d-band in the interfacial electronic structure at organic/metal interface: PTCDA on Au, Ag and Cu

Eiji Kawabe [a,*], Hiroyuki Yamane [a,1], Ryohei Sumii [b,2], Kenji Koizumi [a], Yukio Ouchi [a], Kazuhiko Seki [a], Kaname Kanai [b]

[a] *Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*
[b] *Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*

ABSTRACT

We analyzed the vacuum level shift (Δ) induced by the dipole layer at the interfaces between perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and noble metals (Au, Ag and Cu). The variation of Δ observed by ultraviolet photoelectron spectroscopy does not show a simple dependence on the metal work function, which contradicts the prediction by the induced density of interface states (IDIS) model proposed by Vázquez et al. [H. Vázquez, F. Flores, R. Oszwaldowski, J. Ortega, R. Pérez and A. Kahn, Appl. Surf. Sci 234 (2004) 107]. We found that two factors, (1) the energy separation between the lowest unoccupied molecular orbital (LUMO) of PTCDA and the metal d-band states, which results in the attractive effect due to the orbital hybridization, and (2) the coupling matrix element between the adsorbate states and the metal d-band states, which result in the repulsive effect due to the orbital orthogonalization between the adsorbate states and the metal d-band states, have a clear correlation with the Δ formation. Our results indicate that the interactions between the molecular orbitals of PTCDA and the metal d-band states play an important role in determining the interfacial electronic structure, which has not been taken into account within the framework of the IDIS model.

As an example for such interaction with the metal d-band, we consider the H_2 adsorption on noble and transition metals [8–10]. The hydrogen 1s-state is broadened into resonances and shifted down in energy by the interaction with the broad continuum of metal sp-bands, and the broadened adsorbate state interacts with the metal d-band states resulting in the formation of the bonding and anti-bonding states. For these systems, it is well known that three parameters, (i) the centroid of the metal d-band states (ε_d), (ii) the filling of the metal d-band (f_d) and (iii) the coupling matrix element (V_{ad}) between the adsorbate states and the metal d-band states, govern the interaction energy between the adsorbate state with the filling f_a at the energy ε_a and the metal d-band state with the filling f_d at the energy ε_d as

$$E_{\text{d-hyb}} = -C(f_a, f_d)\frac{V_{ad}^2}{|\varepsilon_a - \varepsilon_d|} + \alpha V_{ad}^2, \tag{3}$$

where $C(f_a,f_d)$ only depends on the number of electrons in the adsorbate state and the metal d-band state. The first term gives the hybridization energy leading to the attraction if the anti-bonding state is not completely filled, while the second term gives the repulsion due to the orthogonalization between the adsorbate states and the metal d-band states. We can see that ε_d is a key parameter to investigate such interaction with the metal d-band. For a given adsorbate f_a is fixed, and for noble metals f_d is also fixed; the interaction energy $E_{\text{d-hyb}}$ between the adsorbate states and the metal d-band states is governed by the delicate balance of $|\varepsilon_a - \varepsilon_d|$ and V_{ad}^2.

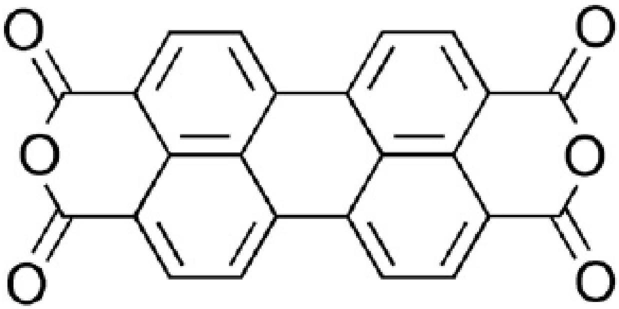


Fig. 1. Molecular structure of PTCDA.

face is not yet well understood. Narioka et al. found the vacuum level (VL) shift at the O/M interface due to the

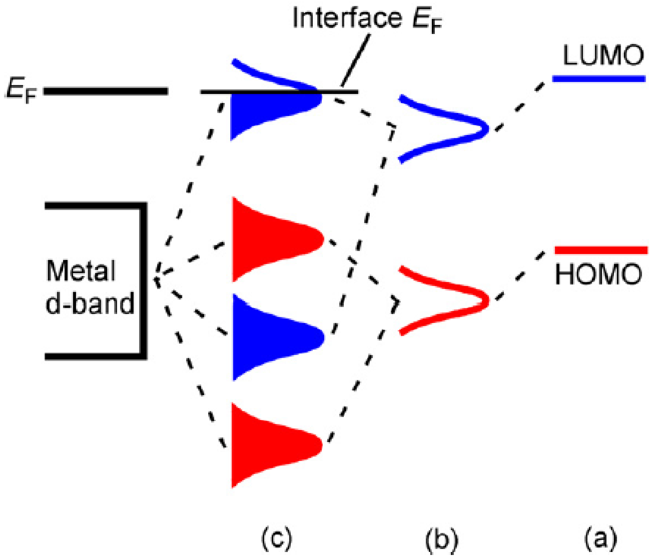


Fig. 2. Schematic illustrations of the interactions between the metal d-band and the HOMO and LUMO of the organic molecule: (a) original molecular states; (b) formation of the broadened molecular states by the interaction with the broad continuum of the metal sp-bands; (c) formation of the bonding and anti-bonding states by the interaction with the metal d-band states. The interface E_F position depends on the system. The interfacial interaction is governed by the occupation of the anti-bonding state originated from the hybridization between the LUMO and the metal d-band states.

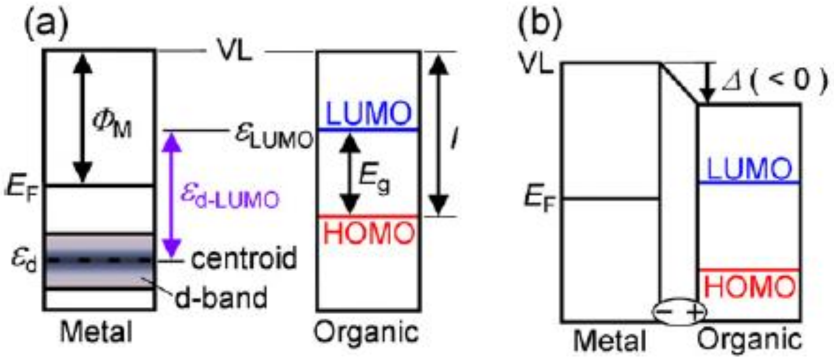


Table 1
Experimentally obtained and estimated energy parameters

	Φ_M	Δ	ε_d	$\varepsilon_{d\text{-LUMO}}$
Au	5.31	−0.52	3.56	4.98
Ag	4.24	0.27	4.30	4.58
Cu	4.58	0.29	2.67	3.40

Φ_M and Δ are the observed values of the metal work function and the vacuum level shift; ε_d is the reported value of the centroid energy of the metal d-band with respect to the Fermi level [10] and $\varepsilon_{d\text{-LUMO}}$ is the estimated energy separation between the LUMO of PTCDA and the ε_d. All values are written in eV.

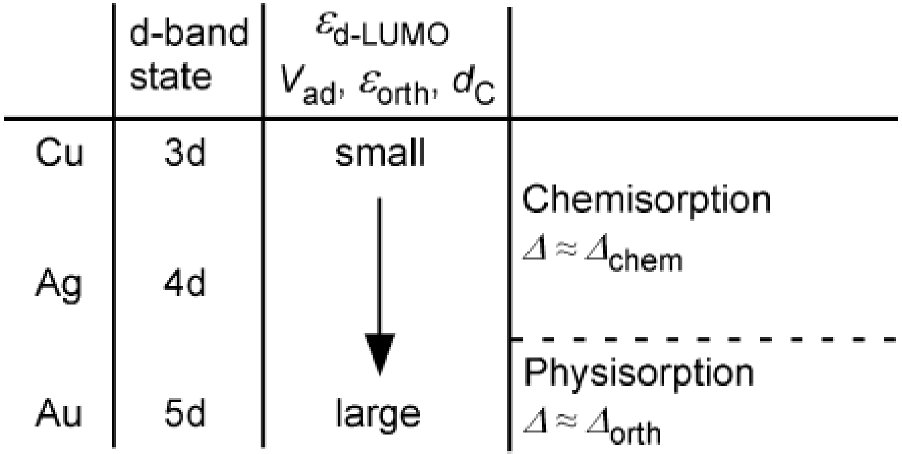
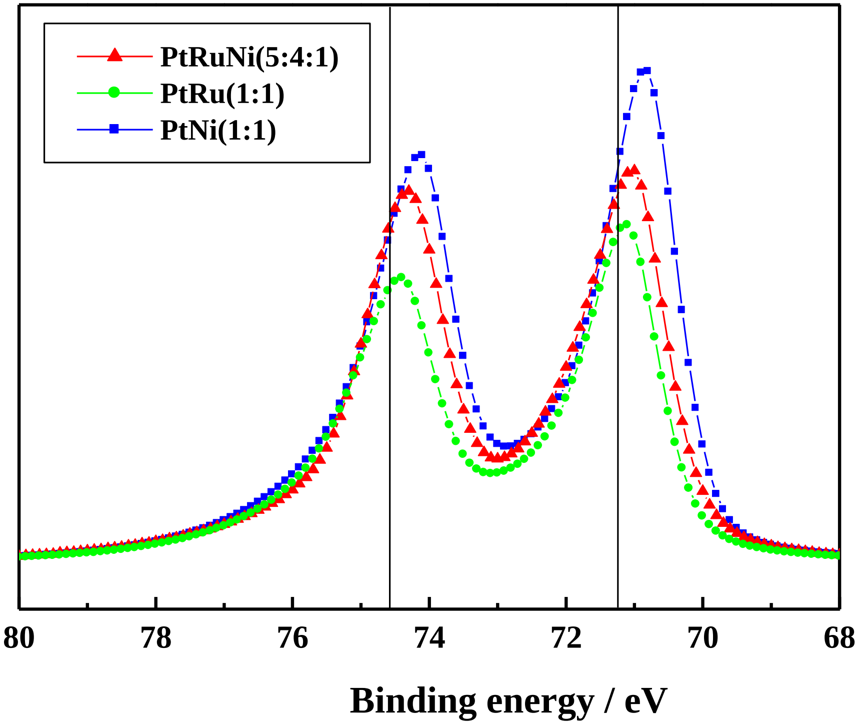


Fig. 7. Schematic view of the correlation among $\varepsilon_{d\text{-LUMO}}$, V_{ad}, d_C and ε_{orth}. These parameters increase with n. The dominant origins of Δ are determined by the delicate valence of these factors.

PtNi nanoparticles

using UHV Electrochemistry (XPS + EC chamber)



▶**Pt 4f peak shift to lower BE**

PtNi ~ 0.4 eV

PtRuNi ~ 0.2 eV

PtRu ~ 0.09 eV

*Electronegativity

Ni(1.92) < Ru(2.2) < Pt(2.28)

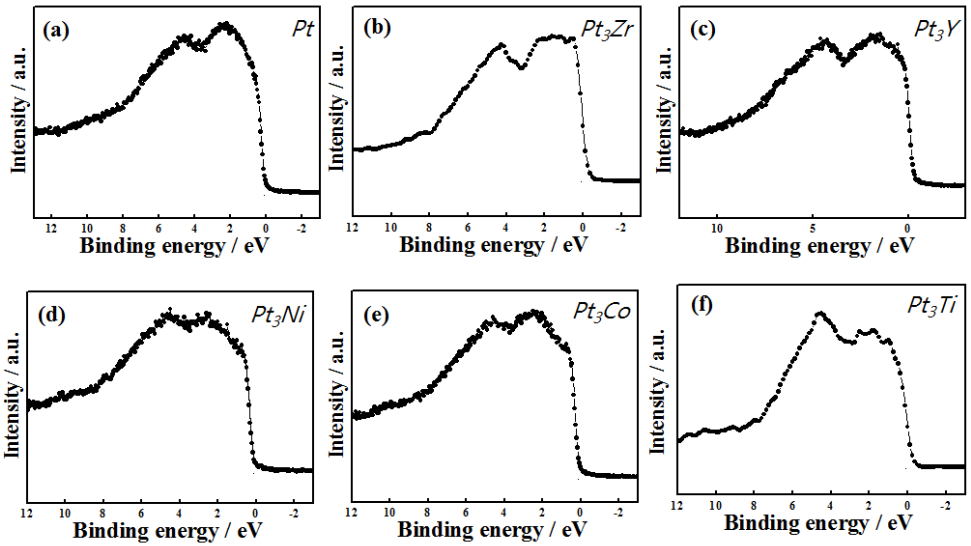
- **Modified Pt : *Au-like?***
- **CO binding energy**

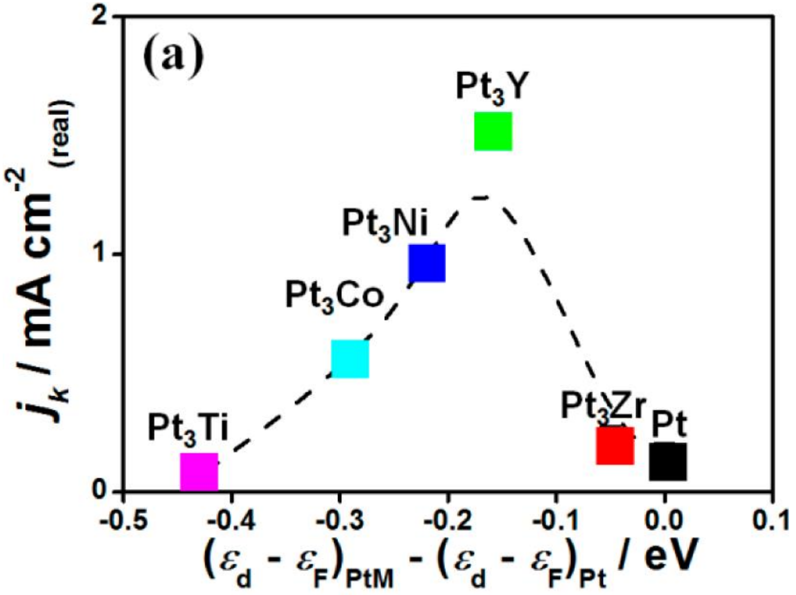
Ir	>	Pt	>	Au
2.22		**1.76**		**0.37 eV**

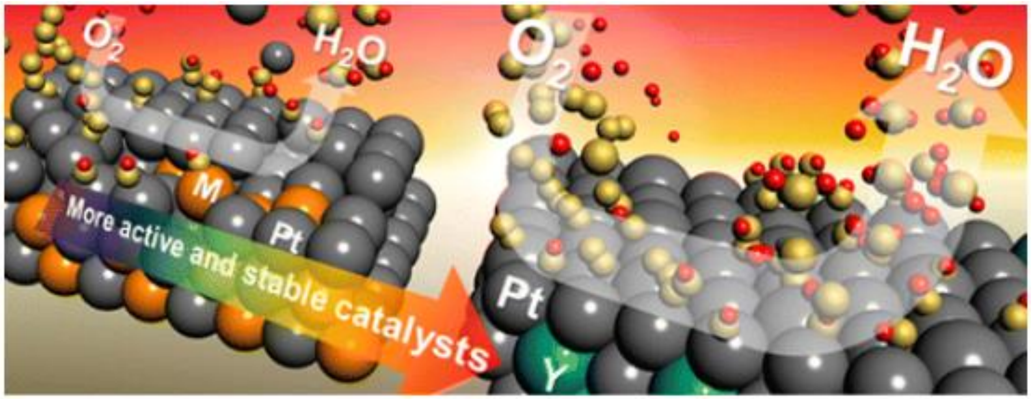
J. Phys. Chem. B, **2002**, *106*, 1869.

cited ~949

Pt-Based Alloy Nanocatalysts for Oxygen Reduction







Pt_3M alloy d-band characterization by synchrotron-based XPS directly correlates the catalytic ORR activity variations with variations in Pt_3M alloys.

J. Am. Chem. Soc., **2012**, *134*, 19508.