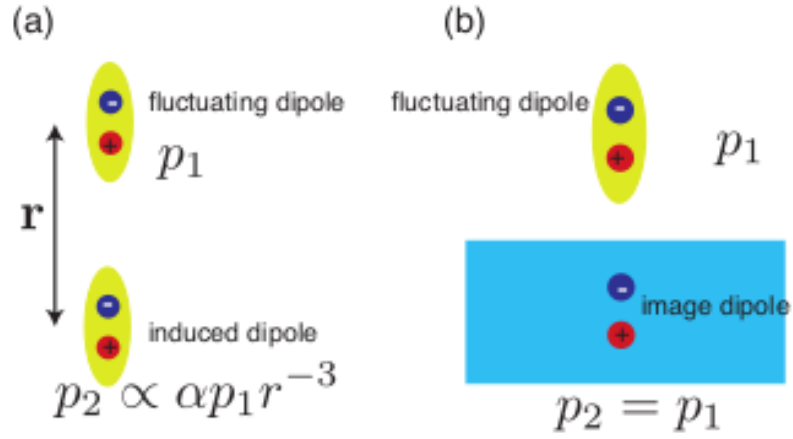


1 Physisorbtion

This is simmlar to van der Walls bonding, in normal vdW a molecule form a dipole p_1 , with $E_1 \propto r^{-3}$, and then induces a dipole in the other molecule $p_2 \propto \alpha p_1 r^{-3}$ so $U \propto p_2 E_1 \propto r^{-6}$. In physisorption however, the second dipole is not induced, but an image dipole, so $p_2 = p_1$ thus $U \propto p_2 E_1 \propto r^{-3}$ and it becomes a stronger and longer ranged (several Å force than the normal vdW.

It has the order of 10 meV–100 meV, and as the room temperature energy $k_b T = 25$ meV the temperature must be low for it to have an effect.



2 Chemisorption

2.1 Newns Anderson model

chemisorption is akin to the chemical bond formed between two molecules, where the surface can be viewed as a single large molecule.

$$\psi = c_m \psi_m + c_a \psi_a$$

where m is the metal and a is the adsorbate. The system then has the energies:

$$\begin{aligned} E_m &= \int \psi_m^* H \psi_m d\mathbf{r} \\ E_a &= \int \psi_a^* H \psi_a d\mathbf{r} \\ -V &= \int \psi_a^* H \psi_m d\mathbf{r} = \int \psi_m^* H \psi_a d\mathbf{r} \end{aligned}$$

And the overlap

$$S = \int \psi_m^* \psi_a d\mathbf{r}$$

$$H\psi = E\psi$$

$$\int \psi_a^* H\psi = -c_m V + c_a E_a = E_a (S c_m + c_a)$$

$$\int \psi_m^* H\psi = -c_a V + c_m E_m = E_m (S c_a + c_m)$$

Or in matrix form:

$$\begin{bmatrix} E - E_a & V - ES \\ V - SE & E - E_m \end{bmatrix} = 0$$

For simplicity $S = 0$ can be assumed

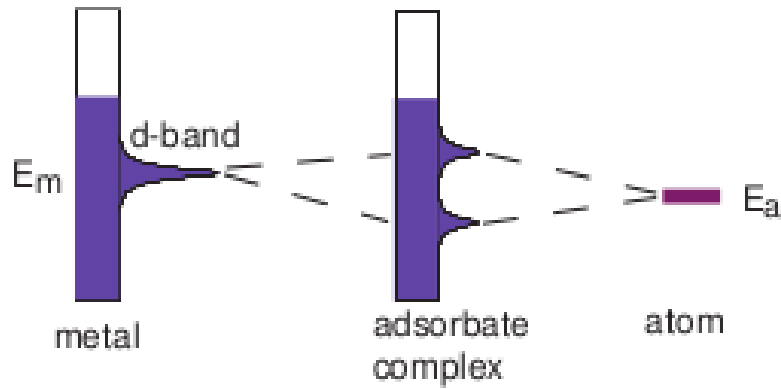
$$E_{1,2} = \frac{E_a + E_m}{2} \pm \sqrt{\left(\frac{E_a - E_m}{2}\right)^2 + V^2}$$

$$E_{1,2} = \bar{E} \pm \Delta$$

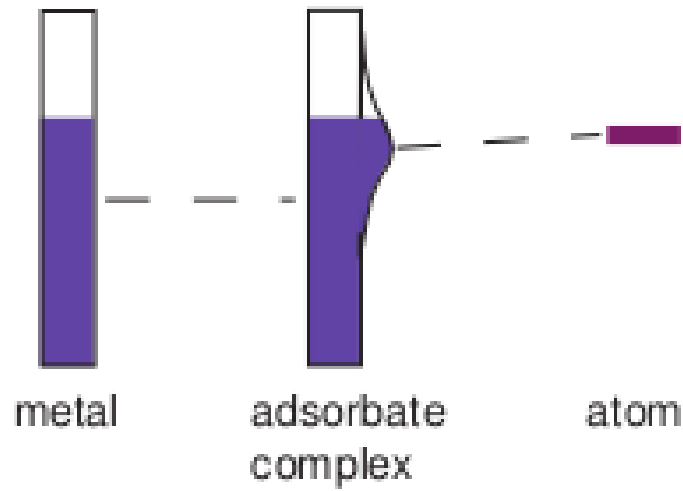
$$c_a = c_m \frac{E_1 - E_m}{V} \quad \text{For the lower state}$$

$$c_a = c_m \frac{E_2 - E_m}{V} \quad \text{For the upper state}$$

The above is the Newns-Anderson model for metals with d-electrons. Here one will see a split, and a broadening+shift due to the sp orbitals:



If there is no d-electrons, only a broadening+shift will be seen:



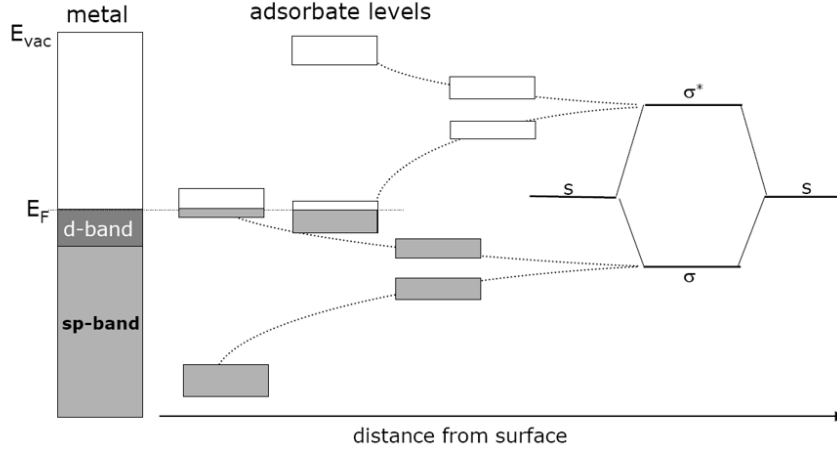
2.2 d-band model

In the d-band model $\Delta E = \Delta E_{sp} + \Delta E_{d-h}$. First the molecule couples to the s orbital (giving shift and broadening) then to the d orbital (giving a splitting into binding and antibonding orbitals) it can then be projected onto the metal DOS.

2.3 dissociative adsorption

When the antibonding orbitals in the molecules are filled enough to break the molecule on the surface.

Dissociative Adsorption



3 Kinetics: Langmuir model

3.1 absorption

The coverage Θ changes over time:

$$\frac{d\Theta}{dt} = S \frac{dN}{dt} = S \frac{P}{\sqrt{2\pi M k_b T}}$$

where, N is the number of sites (N_0 would be the number of sites on a clean surface), S is the sticking coefficient:

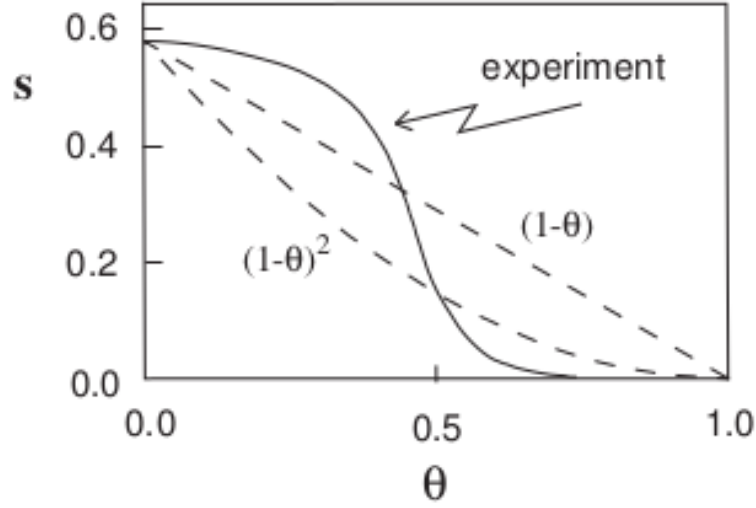
$$S = c(1 - \Theta)^n e^{\frac{E_a}{k_b T}} = S_0(1 - \Theta)^n$$

S_0 is the sticking coefficient on a clean surface. c is the fraction of incoming molecules adsorbed on a clean surface. $(1 - \Theta)^n$ takes care of the fact that the adsorption probability changes with coverage. The n describes the order; at zeroth order new adsorbants can sit on top of old adsorbants, at first order the adsorption is associative, at second order the adsorption is dissociative. The last factor is the energy requirement for the process, in total this gives:

$$\frac{d\Theta}{dt} = \frac{P}{\sqrt{2\pi M k_b T}} c(1 - \Theta)^n e^{\frac{E_a}{k_b T}}$$

c , E_a and n are unknown.

This model is often too simple, as it doesn't mind physisorption. Physisorption can act as a precursor to chemisorption and thus making binding more likely at lower coverages and less likely at higher coverages.



3.2 desorption

$$-\frac{d\Theta}{dt} = \nu\Theta^n e^{-\frac{E_d}{k_b T}}$$

maximum at:

$$\begin{aligned} \frac{d^2\Theta}{dt^2} &= 0 \\ \Downarrow \quad n &= 1 \\ E_d &= kT_m \ln \left(\frac{kT_m^2 \nu}{E_d \beta} \right) \end{aligned}$$

ν is the attempt rate, Θ the coverage, E_d the dissociation barrier. To study the dissociation one uses

Thermal desorption spectroscopy/ Temperature programmed desorption

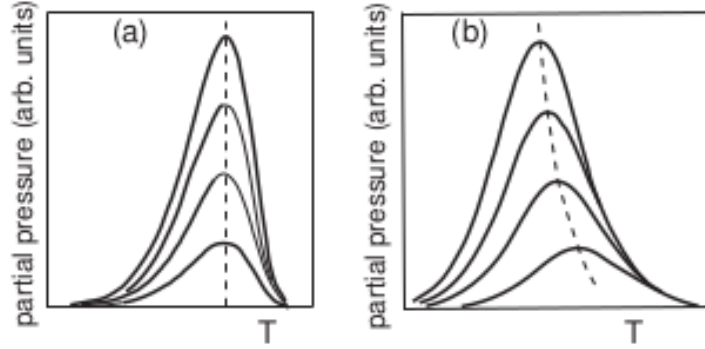
here the temperature is linearly changed:

$$T = T_0 + \beta t$$

If the UHV pump is very fast, then:

$$-\frac{d\Theta}{dt} \propto P_{\text{partial}}$$

this leads to the following:



Where the left picture is $n = 1$ and the right is $n = 2$. The difference is due to the two atoms needing to meet on the right picture.

Each peak is an adsorption state, and there can be many more, each complicating the situation.

3.3 Desorption Adsorption equilibrium

At equilibrium:

$$\nu \Theta^n e^{-\frac{E_d}{k_b T}} = \frac{P}{\sqrt{2\pi M k_b T}} c (1 - \Theta)^n e^{\frac{E_a}{k_b T}}$$

Or:

$$P = \frac{\sqrt{2\pi M k_b T}}{c} \nu_n \left(\frac{\Theta}{1 - \Theta} \right)^n e^{-\frac{E_d - E_a}{k_b T}}$$

$$E_d - E_a = -k \left(\frac{\partial \ln(P)}{\partial \frac{1}{T}} \right) \Big|_{\Theta}$$

the above is the Clausius-Claperyon formulæ