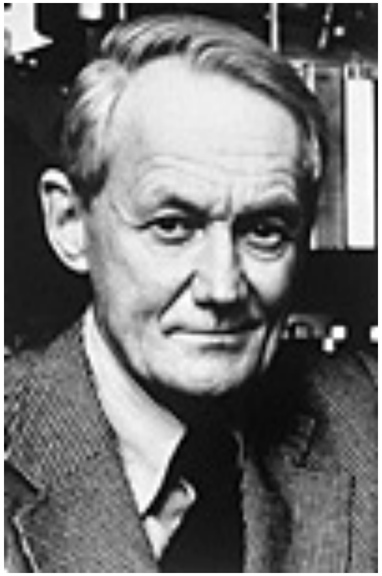
Lectures 12-13
Understanding surfaces



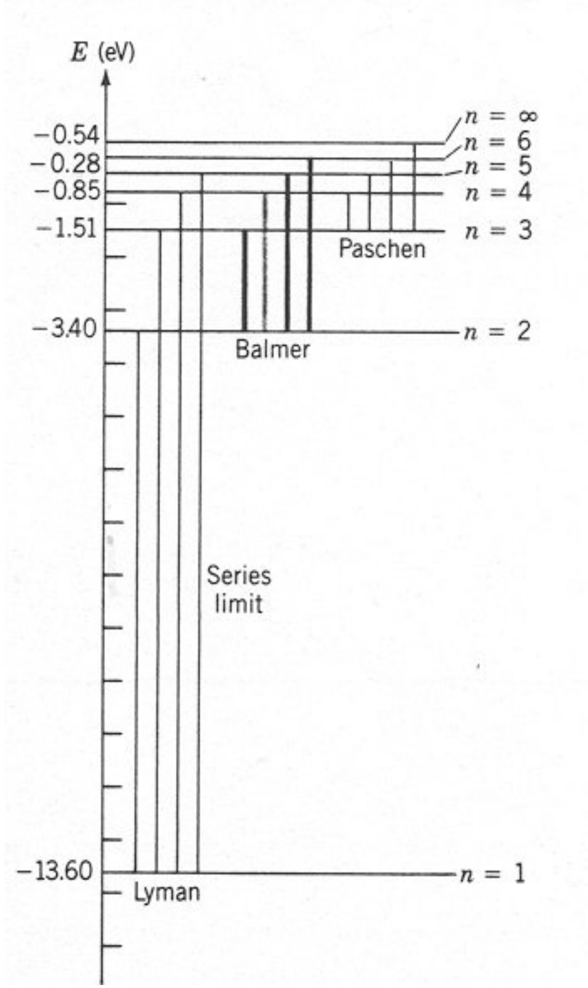
Kai M. Siegbahn (1918 - 2007)
Nobel Prize 1981 – High Resolution Electron Spectroscopy

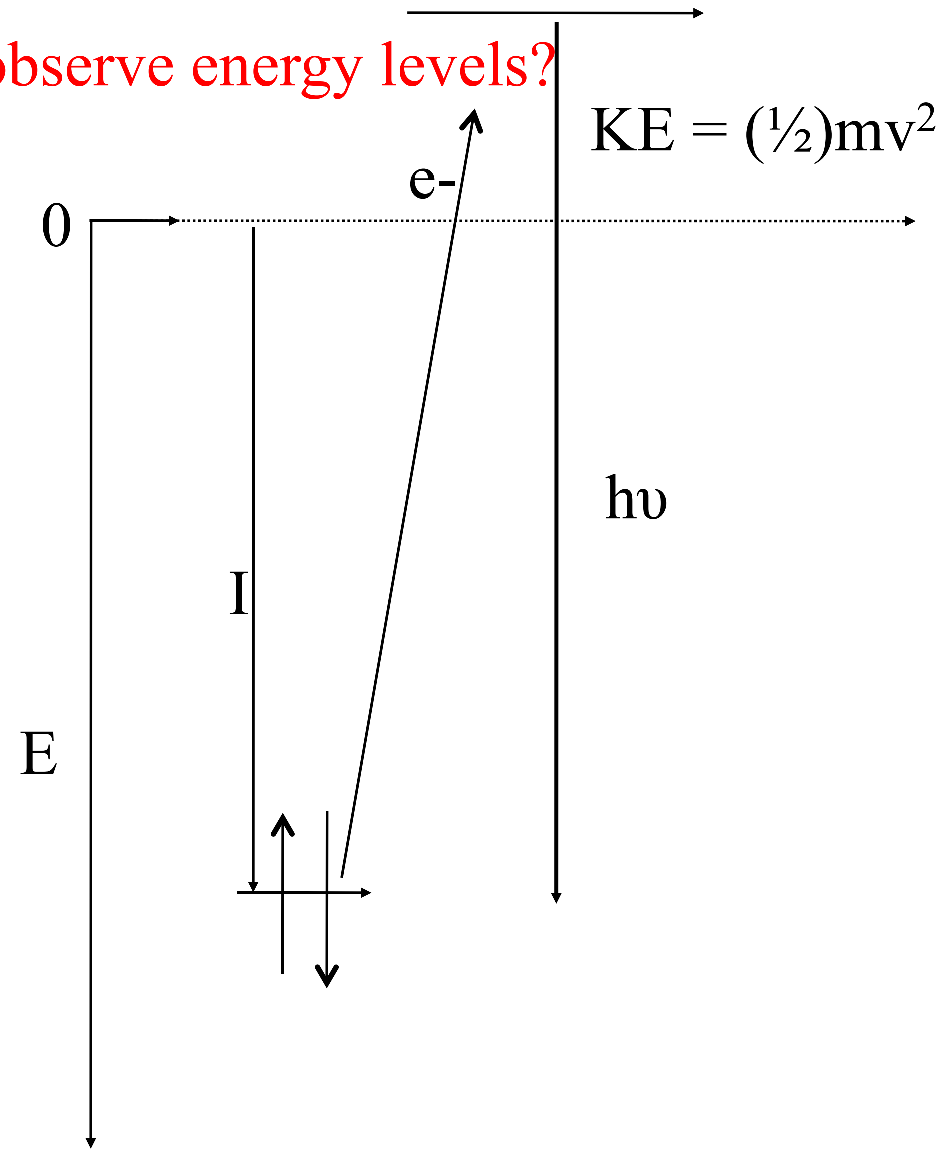
Surface science is an important component in physical sciences

Energy, chemicals, pharmaceuticals,….
Electron spectroscopy is the most important surfa
analysis tool

Ref. Atkins

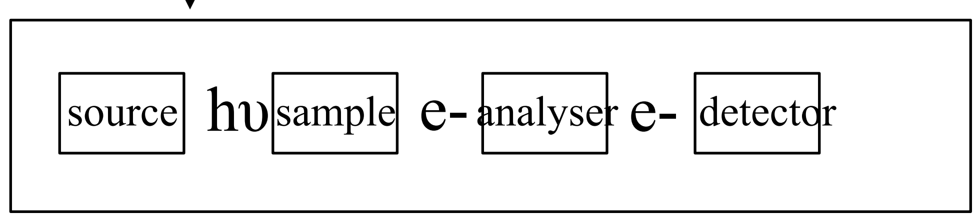
How to observe energy levels?





$$I = h\upsilon - (½)mv^2$$

Photoelectron equation
Koopmans' theorem



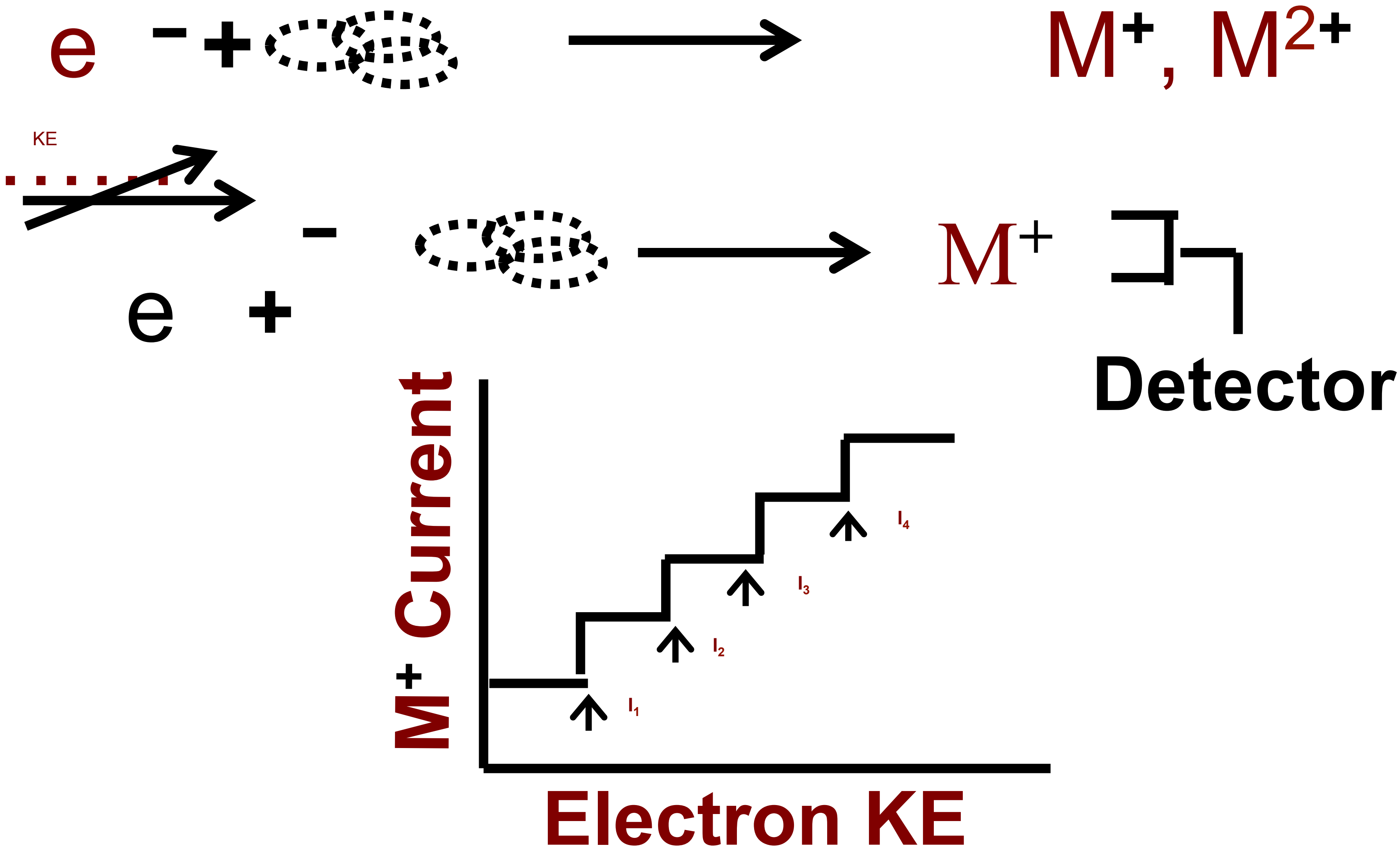
Structure and Properties of Matter

- *Spectroscopy*
- *Scattering*
- *Physical Properties*

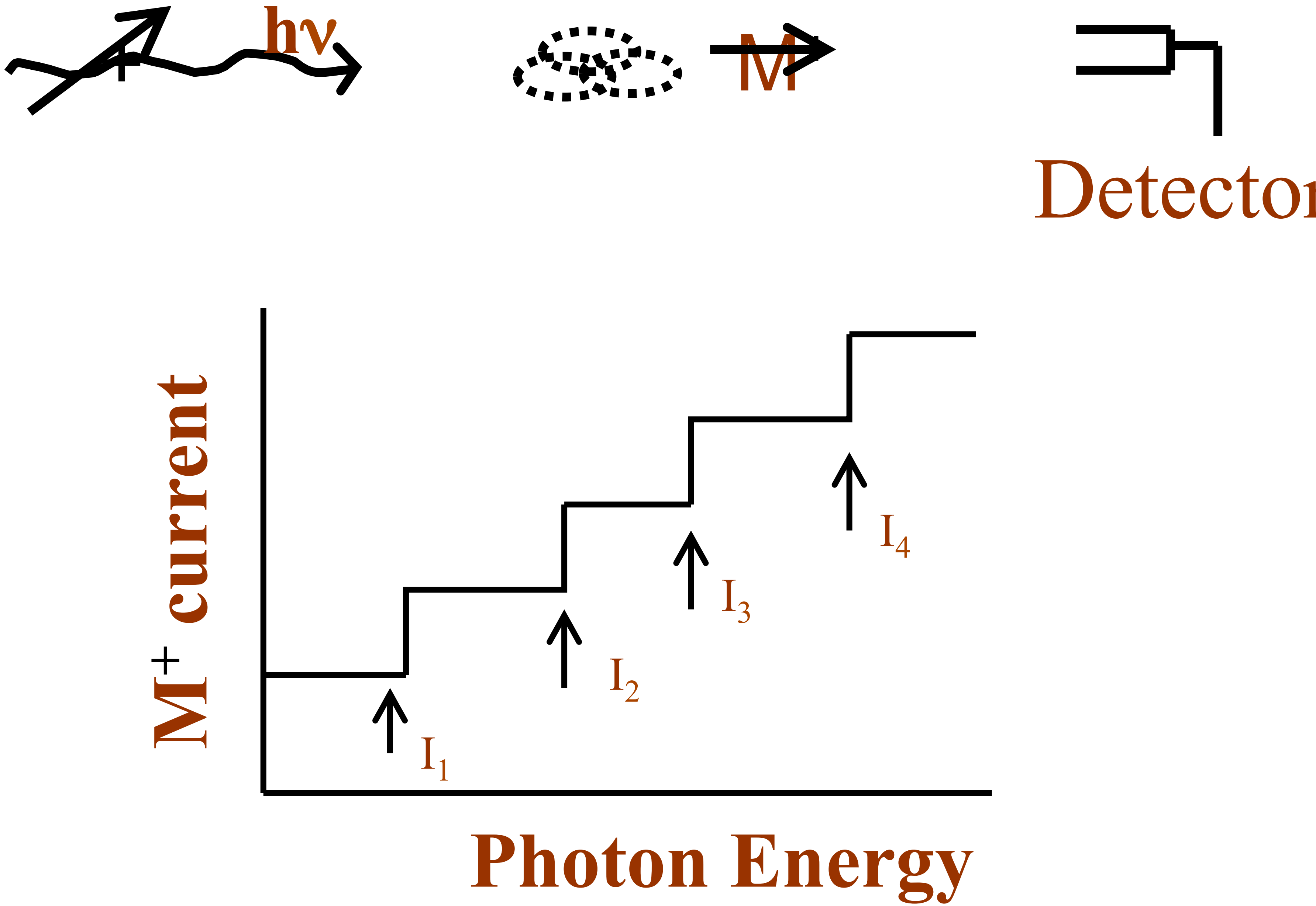
Spectroscopy (pre-1965)

- *Absorption*
- *Magnetic*
- *Mass*

Spectroscopy using electrons

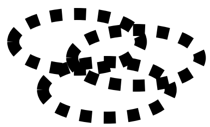


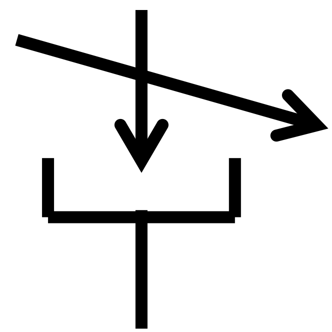
Ionization efficiency curves


hν
M
Detecto
M+ current
I1
I2
I3
I4
Photon Energy

$$h\nu + M \longrightarrow M^{+} + e^{-}$$

(No M^{2+}, generally)

$h\nu$ (Constant) +  $\longrightarrow M^{+} + e^{-}$



Photoelectron Spectroscopy

Photoelectric effect

Early experiments in 1887

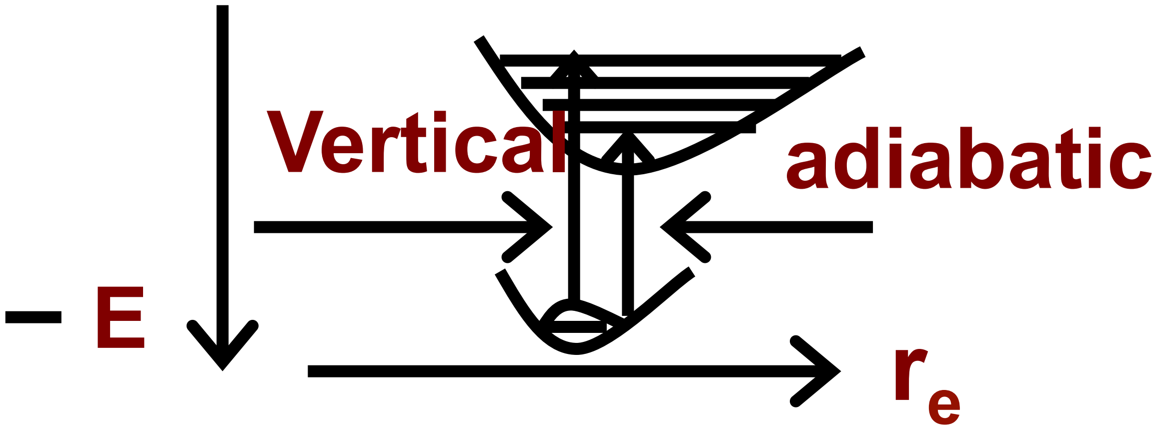
$h\nu = KE + \phi$ 1905

Photoion can be excited

$$M + h\nu \longrightarrow M^{+}(E_{int}) + e$$

elec vib rot

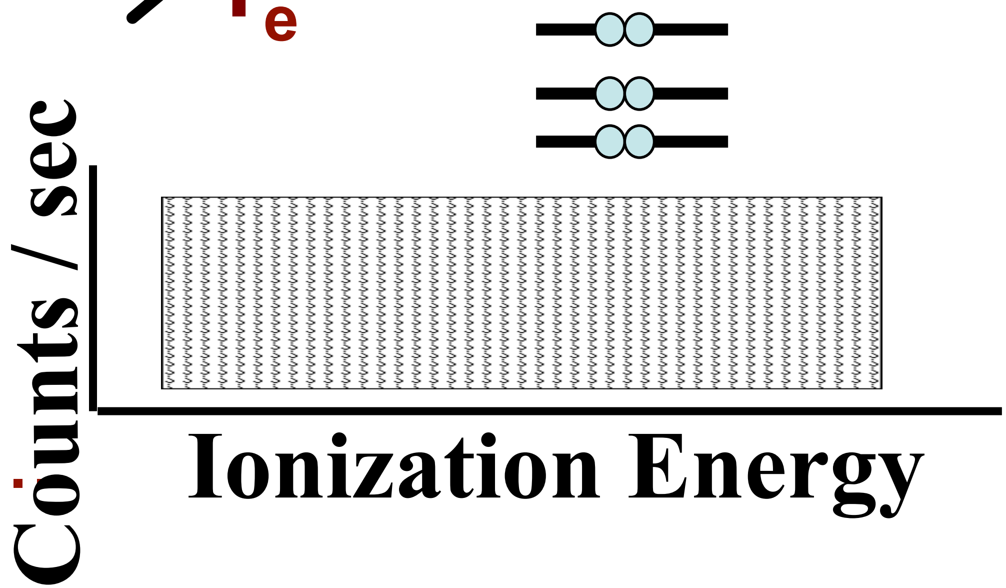
$$h\nu - I - E_{int} = \text{KE of the electron}$$



$h\nu$ - KE_1 IP_1

$h\nu$ - KE_2 IP_2

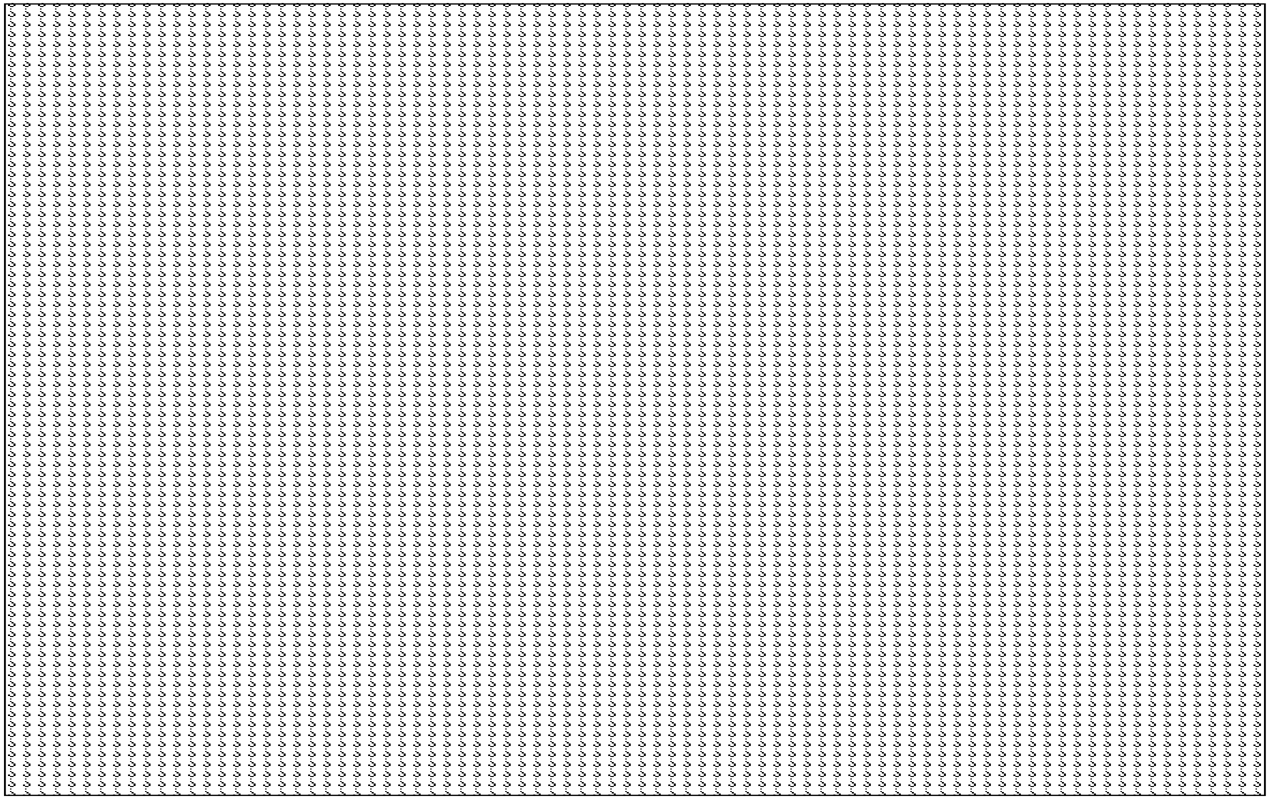
$h\nu$ - KE_3 IP_3 .....



Depth of analysis depends on photon energy

He I	21.2 eV	$2^1P \rightarrow 1\,^1S$
He II	40.8 eV	$2\,P \rightarrow 1\,S$ of He^+
Al $K_{\alpha 1,2}$	1486.6 eV	$^3/_2\,2\,^1/_2\,P \rightarrow 1\,S$
Mg $K_{\alpha 1,2}$	1253.6 eV	”
Na $K_{\alpha 1,2}$	1041.0 eV	”
Si $K_{\alpha 1,2}$	1739.5 eV	”

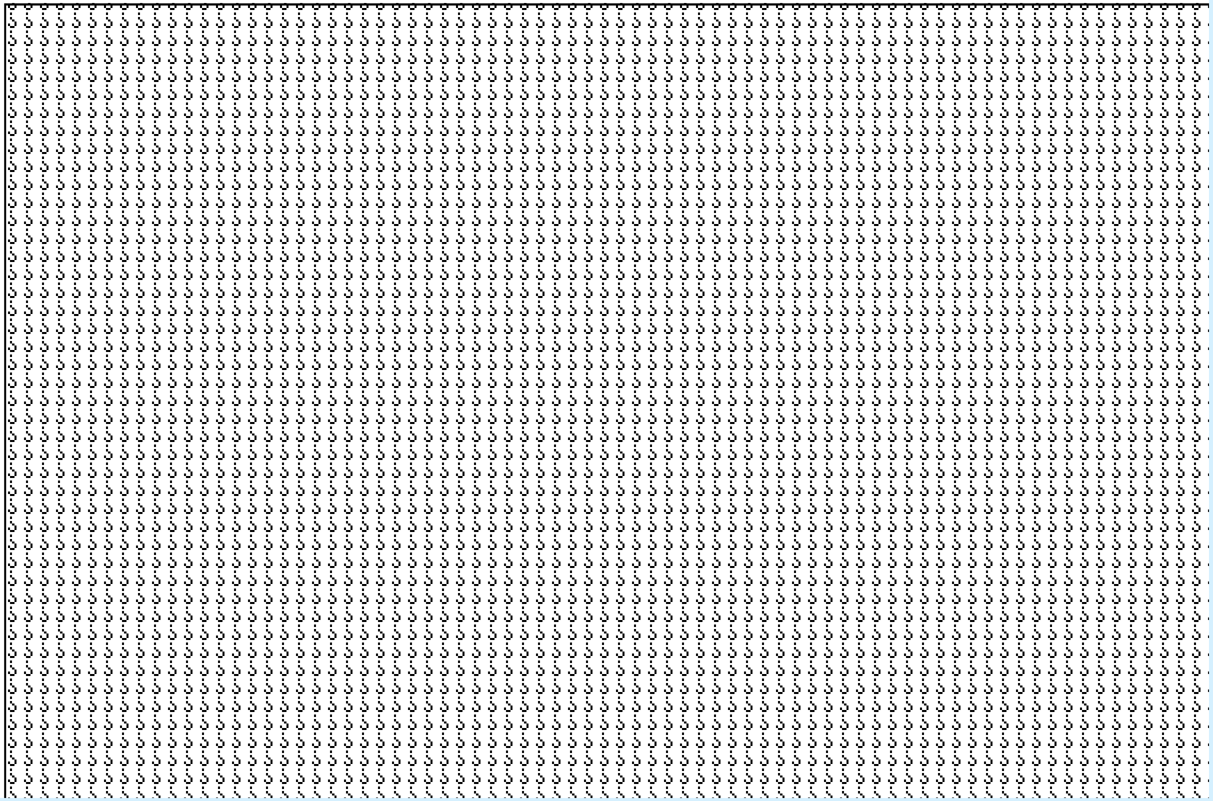
Photoelectron spectrum is a reflection of the potential energy surfaces



INTERNUCLEAR DISTANCE

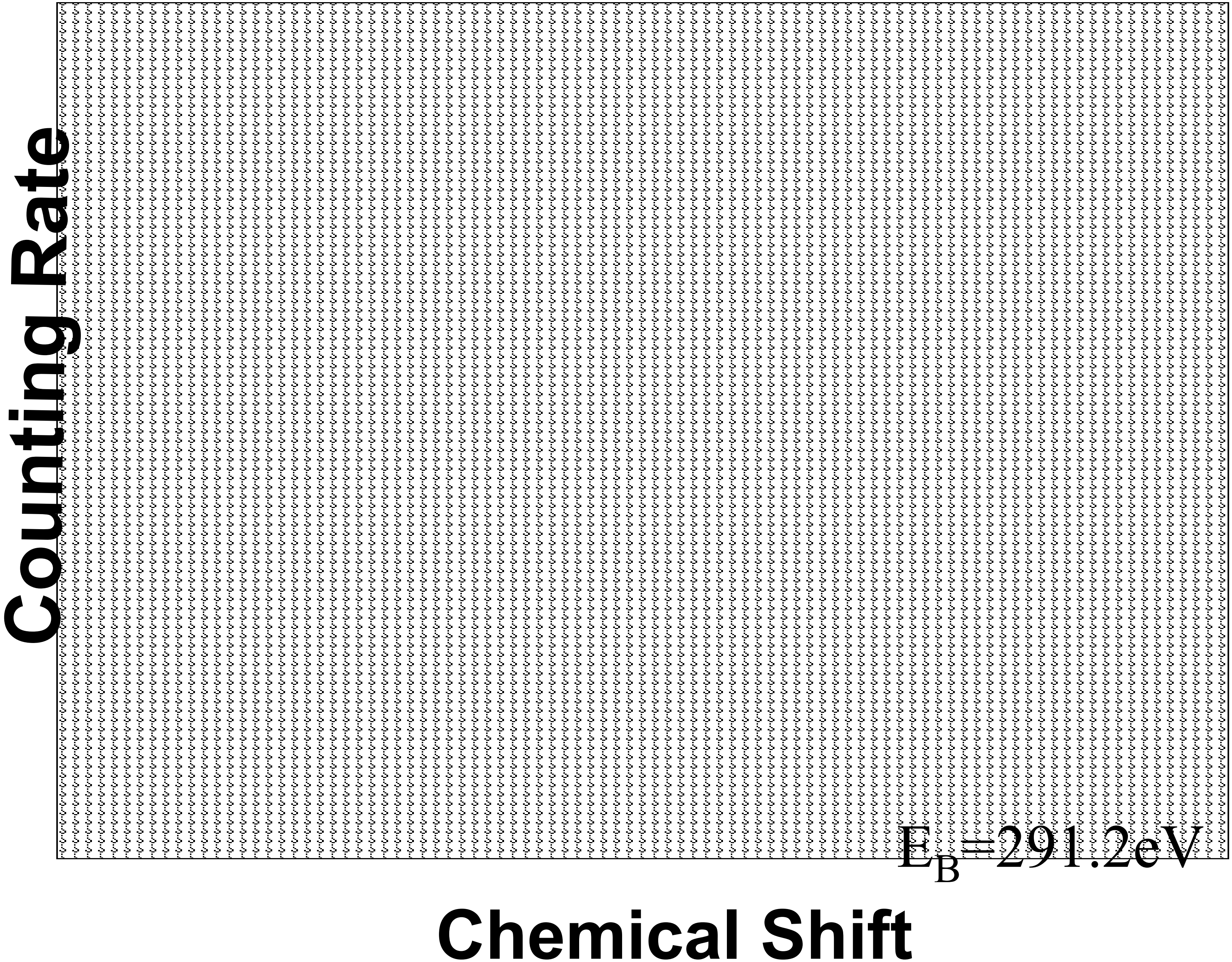
UPS

XPS



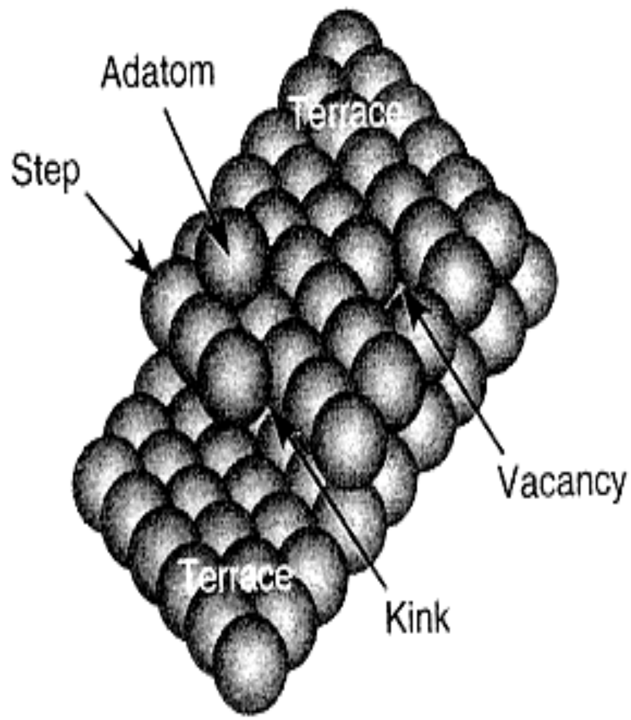
XPS-spectra of the 1s core levels of Li, Be, B, C, N, O, F.

Chemical analysis – ESCA (qualitative, quantitative)


Counting Rate
E_B=291.2eV
Chemical Shift

Surface sensitivity
Inelastic mean free path

Steps, kinks and defects

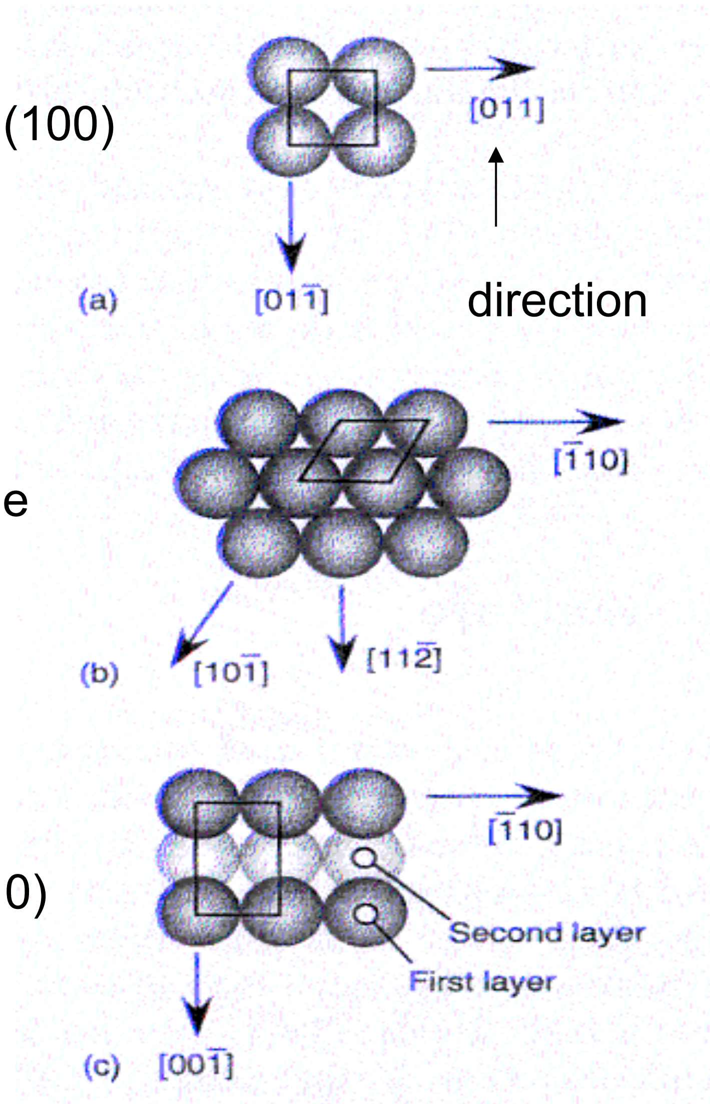


fcc unit cell

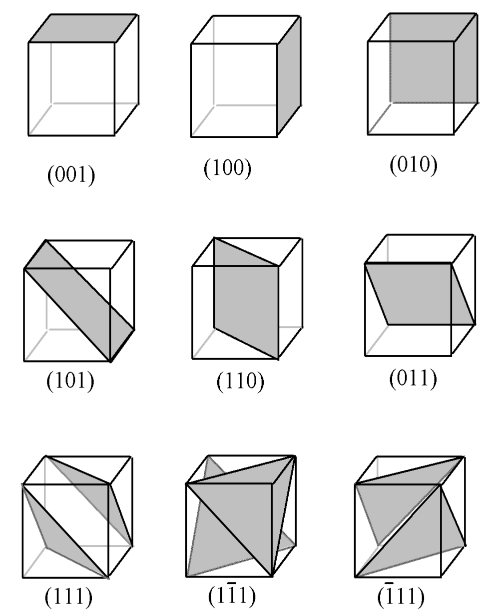
plane → (100)

Direction and plane

(110)



(111)



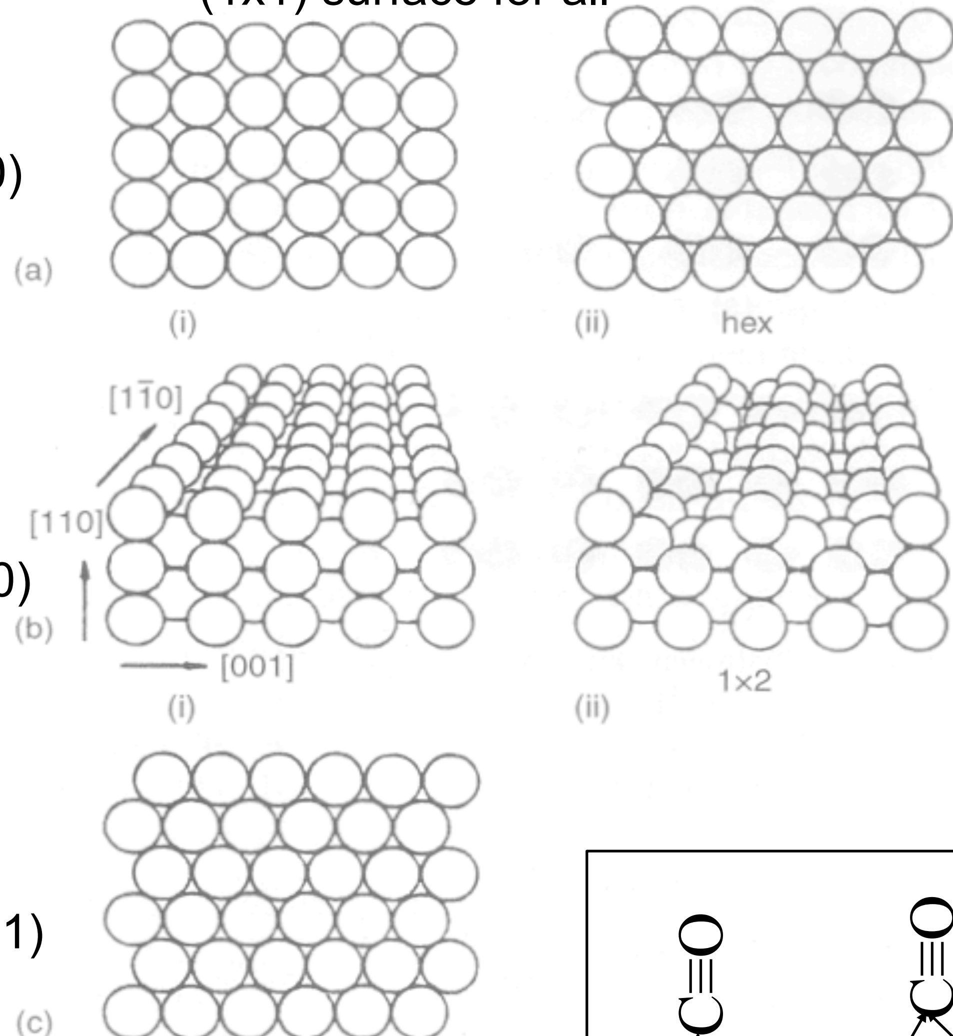
(1x1) surface for all

Reconstruction

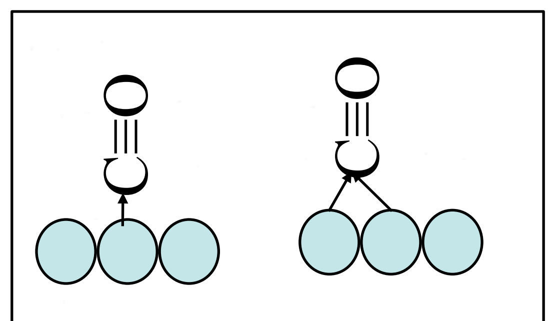
(100)

(110)

(111)



planes



Adsorbate structure

Determination of surface structure

- AES
- IR (RAIRS)
- LEED
- EELS and surface vibrations
- SPM (STM, AFM)
- SEXAFS

Surface Dynamics

Irving Langmuir 1881–1957

Nobel Prize in Chemistry 1932 "for his discoveries and investigations in surface chemistry".

Concepts of adsorption, desorption, various kinds of adsorption, energetics of adsorption, adsorption isotherms

$$A + S = AS \qquad \Delta_{ads} H < 0$$

Adsorption isotherms

Concept of theta, Θ surface coverage

Langmuir adsorption isotherm

Assumptions

1. Adsorption does not occur beyond monolayer
2. Sites are equivalent and surface is uniform
3. Adsorption at one site is independent of occupancy at another site

Adsorption,

$d\Theta/dt = k_a PN(1- \Theta)$

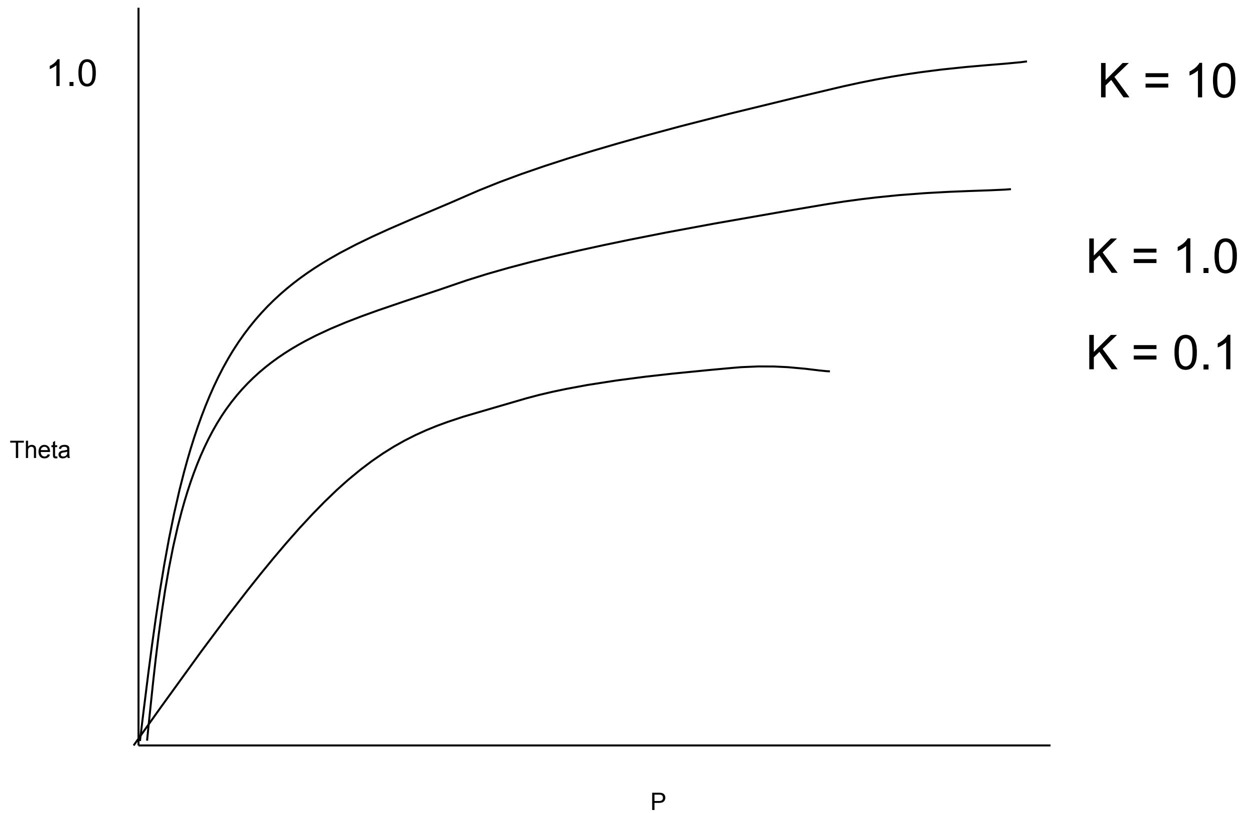
Desorption,

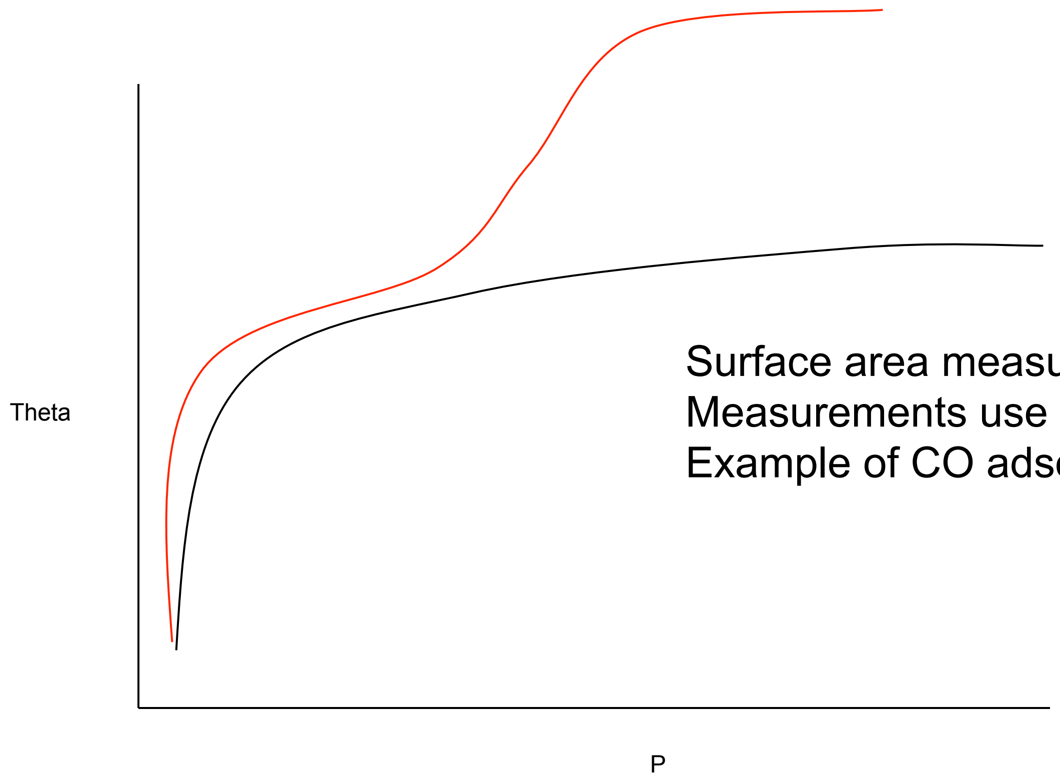
$d\Theta/dt = -k_d N\Theta$

$K = k_a/k_d$

$$P = \frac{\Theta}{K(1-\Theta)} \quad or \quad \Theta = \frac{KP}{1+KP}$$

It is possible to deduce this equation from first principles.


1.0
K = 10
K = 1.0
K = 0.1
Theta
P



Surface area measurements
Measurements use often pressure of the gas.
Example of CO adsorption on charcoal.

Methods to measure adsorption
Flash desorption
Gravimetry – quartz crystal microbalance

Dissociative Adsorption

$$kd\Theta^2 = ka(1-\Theta)^2 P$$

$$\frac{\Theta}{1-\Theta} = \frac{ka^{1/2} P^{1/2}}{kd^{1/2}}$$

$$\Theta = \frac{(KP)^{1/2}}{1+(KP)^{1/2}}$$

$K = (k_a/k_d)^{1/2}$

Adsorption and reaction