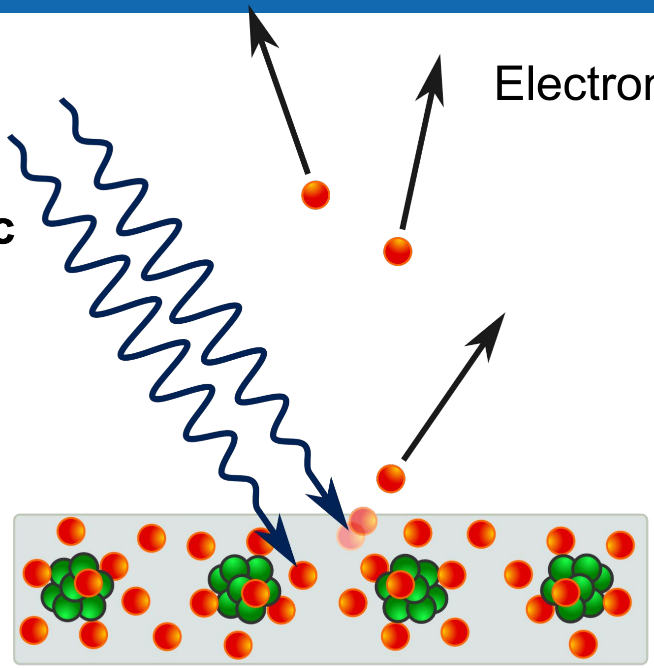


Electrons

Electromagnetic Radiation

Photoelectric Effect

Heinrich Hertz
First observed in 1887

Albert Einstein
Quantum explanation 1905

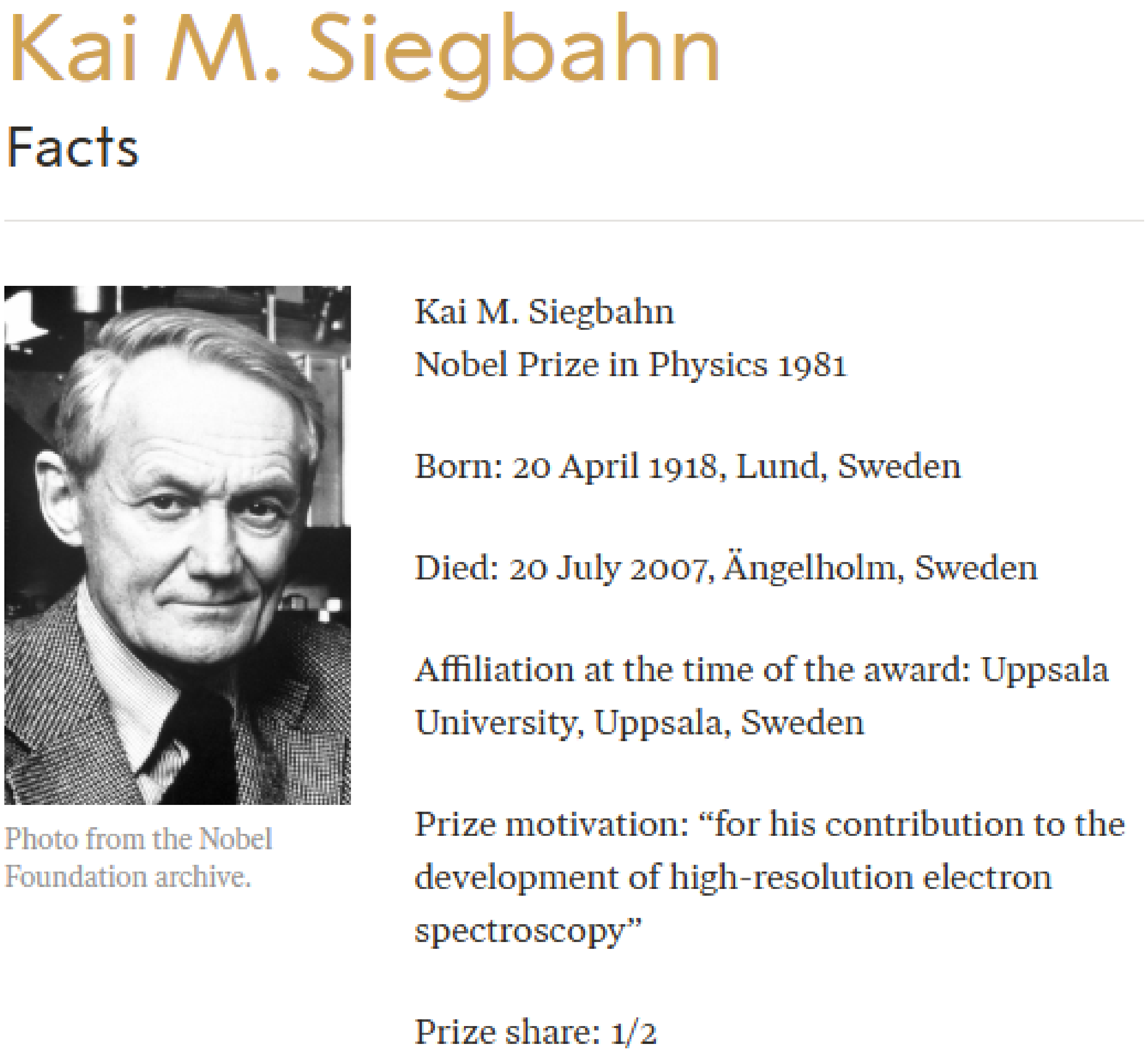
Karl Manne Georg Siegbahn

Nobel Prize in Physics 1924

Born: 3 December 1886, Örebro, Sweden
Died: 26 September 1978, Stockholm, Sweden
Affiliation at the time of the award: Uppsala University, Uppsala, Sweden

The Nobel Prize in Physics 1924 was awarded to Karl Manne Georg Siegbahn "for his discoveries and research in the field of X-ray spectroscopy"
Manne Siegbahn received his Nobel Prize one year later, in 1925. During the selection process in 1924, the Nobel Committee for Physics decided that none of the year's nominations met the criteria as outlined in the will of Alfred Nobel. According to the Nobel Foundation's statutes, the Nobel Prize can in such a case be reserved until the following year, and this statute was then applied. Manne Siegbahn therefore received his Nobel Prize for 1924 one year later, in 1925.

Source: nobelprize.org



Kai M. Siegbahn

Facts

Photo from the Nobel Foundation archive.

Kai M. Siegbahn
Nobel Prize in Physics 1981

Born: 20 April 1918, Lund, Sweden

Died: 20 July 2007, Ängelholm, Sweden

Affiliation at the time of the award: Uppsala University, Uppsala, Sweden

Prize motivation: “for his contribution to the development of high-resolution electron spectroscopy”

Prize share: 1/2

Source: nobelprize.org

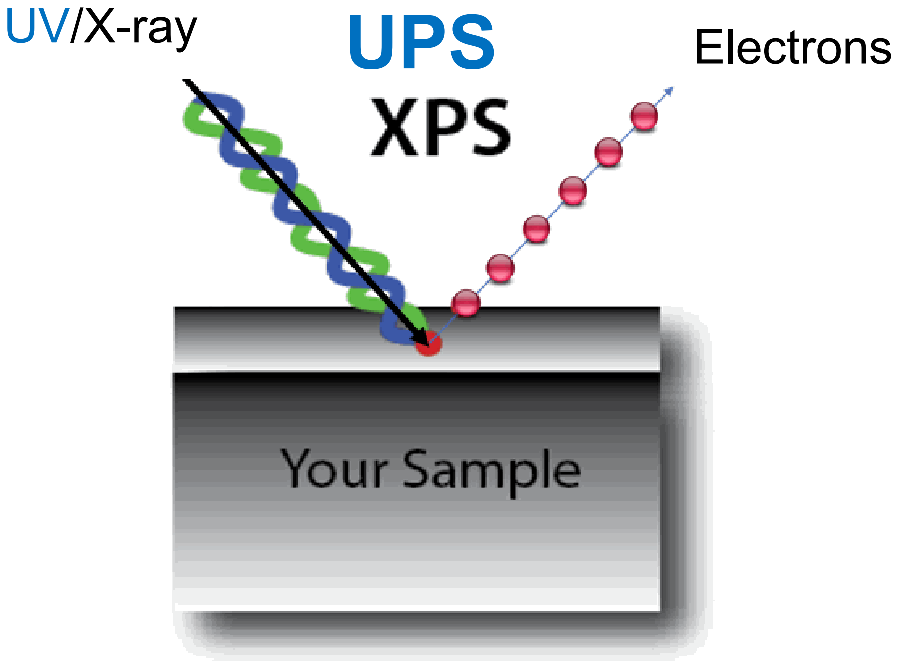
Photoelectron Spectroscopy

Principle

It is based on the photoelectric effect, i.e., emission of electron following excitation of electrons by photons

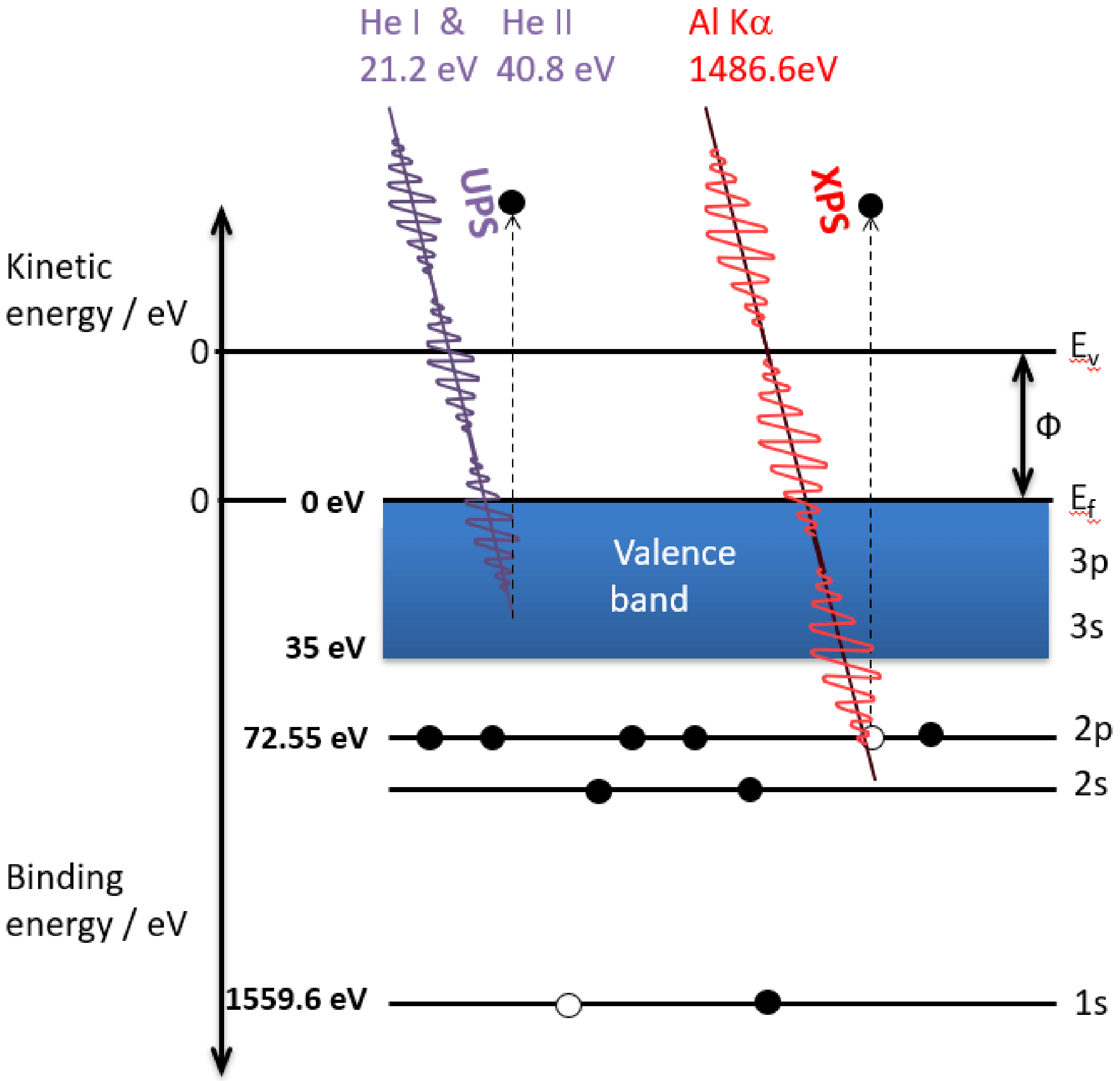
Surface sensitive

UHV



Photon IN
Electron OUT

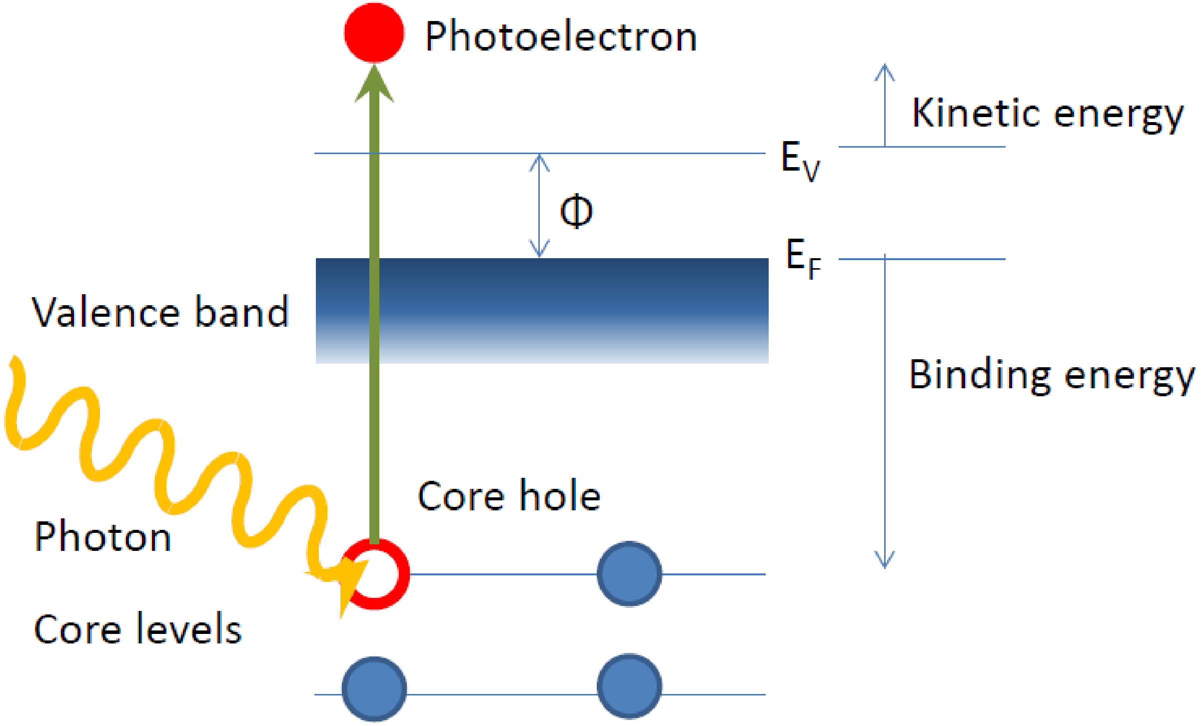
UPS = Ultra-violet photoelectron spectroscopy
XPS = X-ray photoelectron spectroscopy


He I & He II
21.2 eV 40.8 eV
Al Kα
1486.6eV
UPS
XPS
Kinetic energy / eV
0
0
0 eV
E_v
Φ
E_f
Valence band
3p
3s
35 eV
72.55 eV
2p
2s
Binding energy / eV
1559.6 eV
1s

Why do we need vacuum?

- Low pressure is required for operation of electron detectors
- Pressure must be low enough to allow mean-free-path of electrons through the analyzer i.e. to prevent attenuation of photoelectrons
- Ultra-high vacuum is required to lower surface contamination for condensed-phase spectroscopy

The Photoemission Process



KE = hν – BE – Φ for a solid

KE = hν – IP for a gas

Φ : photoelectric workfunction (4-6 eV)

Photoelectron Spectroscopy

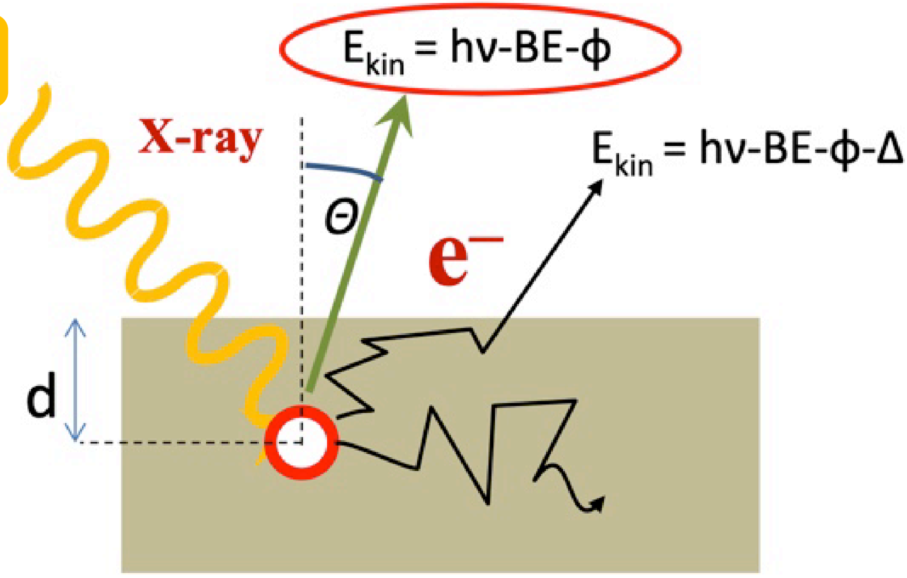
All these terms refer same

Probed depth

Sampling depth

Information depth

The depth from which 95% of all photoelectrons are scattered by the time before they reach the surface, which means that 95% of the photoelectrons come from the region above the information depth.



Effective attenuation length (EAL)
The average distance that an electron with a given energy travels between successive inelastic collisions.

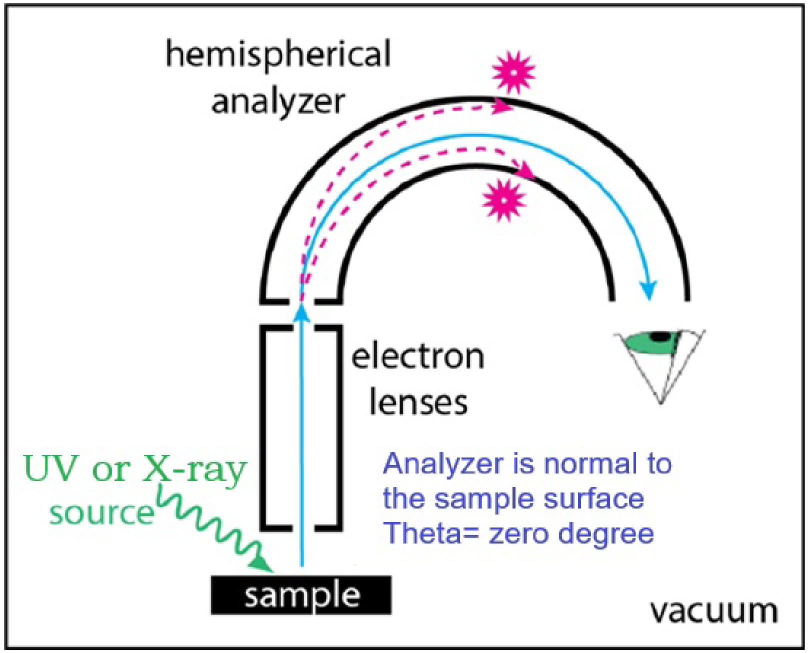
Contribution of atom in depth d to PE peak:

$$I = I_0 \exp\left(\frac{-d}{\lambda \cos\theta}\right)$$

The intensity (I) of photoelectrons emitted elastically from the substrate from depth *d* at angle *θ*, which is the angle between the sample normal and the perpendicular to the entrance of the energy analyzer, is given by the Beer-Lambert relationship:

$$I = I_0 e^{\frac{-d\cos\theta}{\lambda}}$$

where I_0 is photoelectron intensity that would occur from an infinitely thick, uniform substrate. As seen from equation, the contribution to the overall photoemission signal decreases exponentially as a function of depth. It may easily be shown that for photoelectrons detected normal to the surface (θ = 0), approximately 63, 86 and 95% of the signal arises from depths less than λ, 2λ and 3λ, respectively. The 3λ value is usually taken as the **"detection depth"** or **"sampling depth",** which for He I and He II UPS is in the range of 10–20 Å (1-2 nm).



Analyzer is normal to the sample surface Theta= zero degree

Fundamental Equations

Gas

$E_{photon} = h\nu = I + KE$

E_{photon} = energy of incident radiation

h = Planck's constant

ν = frequency of incident radiation

I = ionization energy

KE = kinetic energy of ejected electron

Solid

$E_{photon} = h\nu = BE + KE + \Phi$

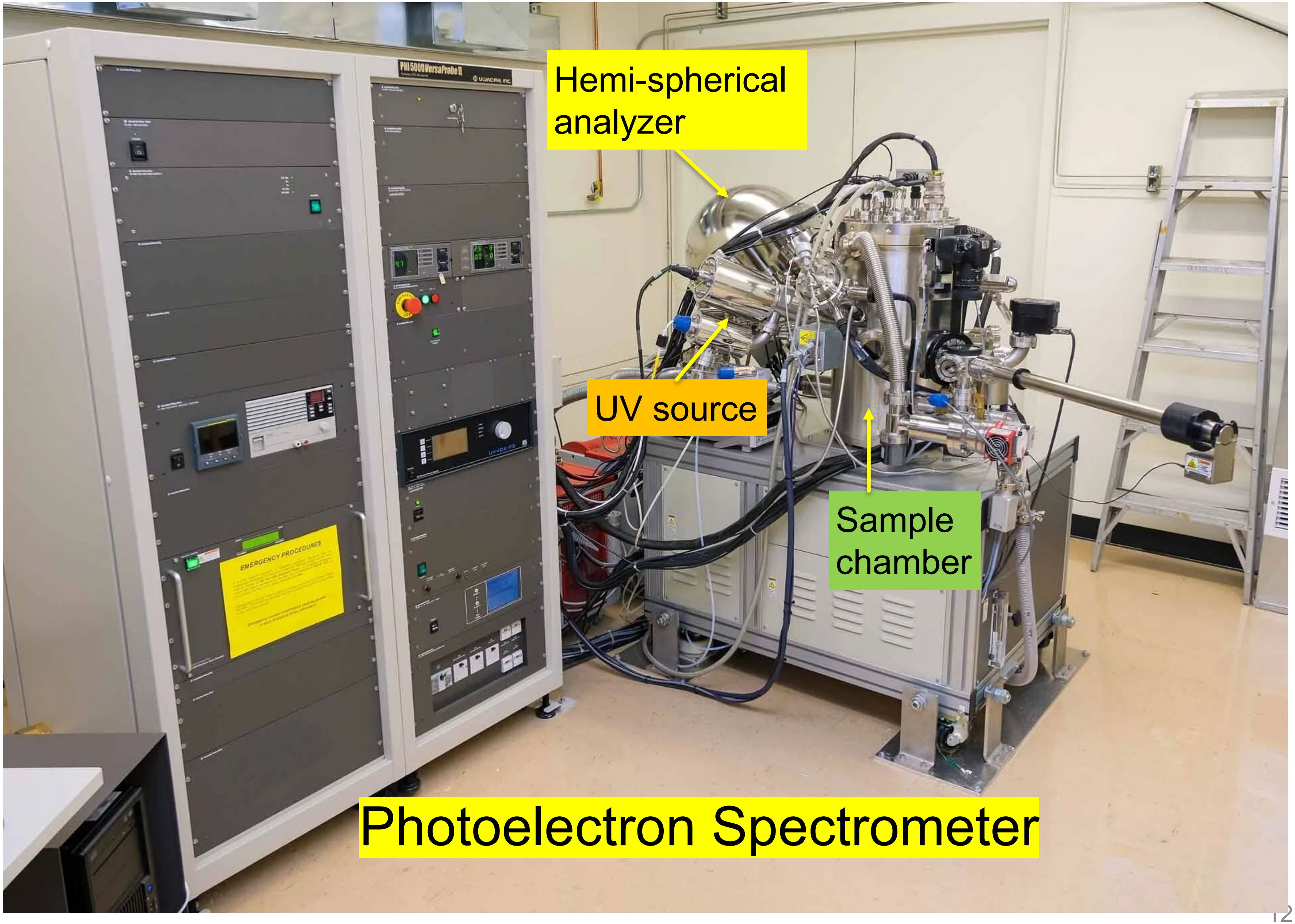
KE = kinetic energy of ejected electron

BE= Binding energy

Φ= *work function*

Ultra-violet photoelectron spectroscopy (UPS or UVPES)

- Low incident photon energy
- Low K.E. of photoelectrons, smaller probed depth than XPS
- Access mostly valence level



Hemi-spherical analyzer

UV source

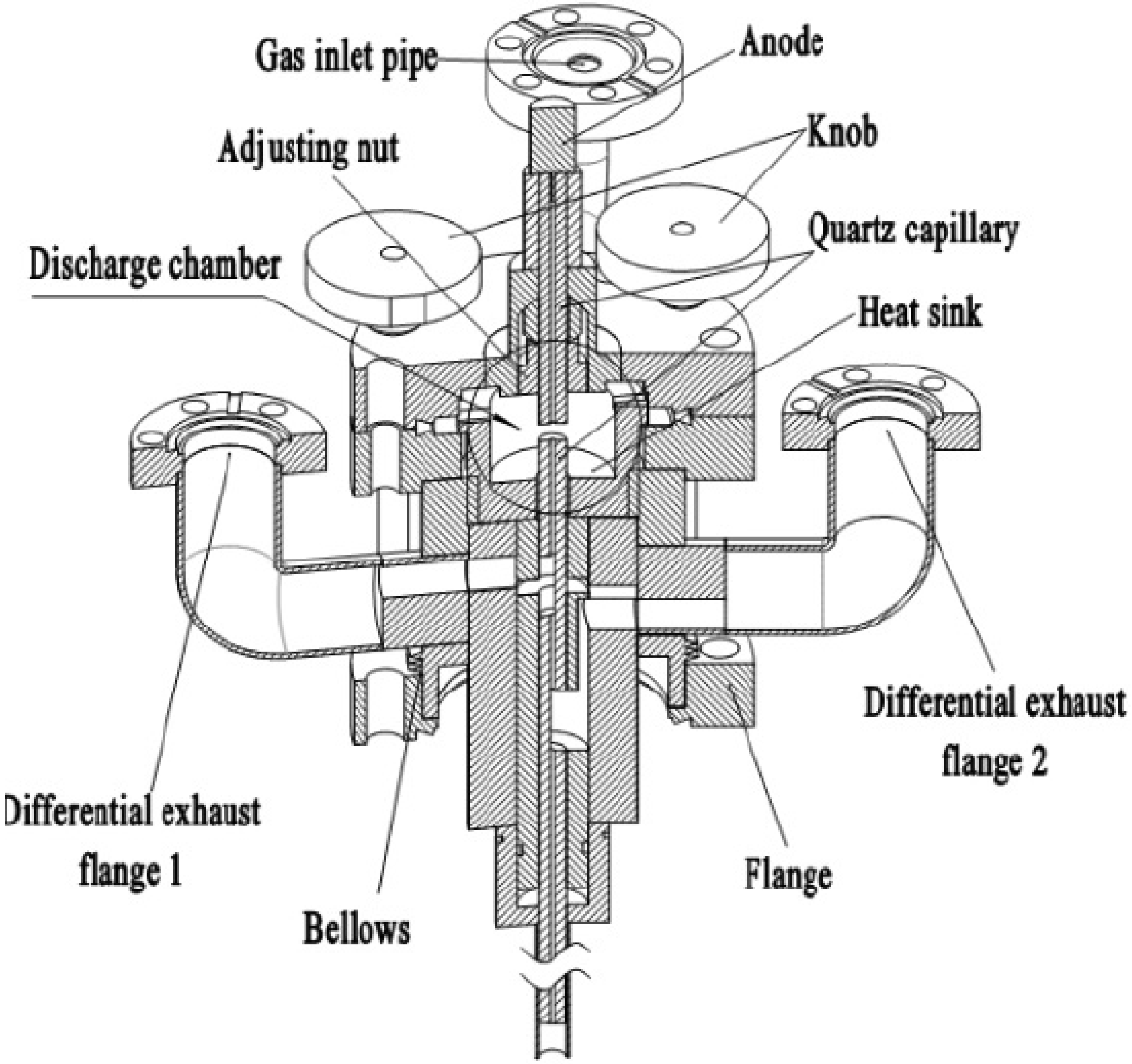
Sample chamber

Photoelectron Spectrometer

Helium gas discharge lamp

UV source for UPS

(Inside) capillary


Gas inlet pipe
Anode
Knob
Adjusting nut
Quartz capillary
Discharge chamber
Heat sink
Differential exhaust flange 2
Differential exhaust flange 1
Flange
Bellows

Ultra-violet Sources

Some conversion factors to remember

$$1\ eV \equiv 96.584\ kJmol^{-1} \equiv 8065.54\ cm^{-1}$$

$$cm^{-1} = \frac{10^7}{nm} \qquad eV = \frac{1240}{nm}$$

Gas discharge sources: ~ 0.005 eV resolution (40 cm^{-1})

He I: 21.2 eV (energy) or 58.43 nm (Wavelength)(most common for UPS)

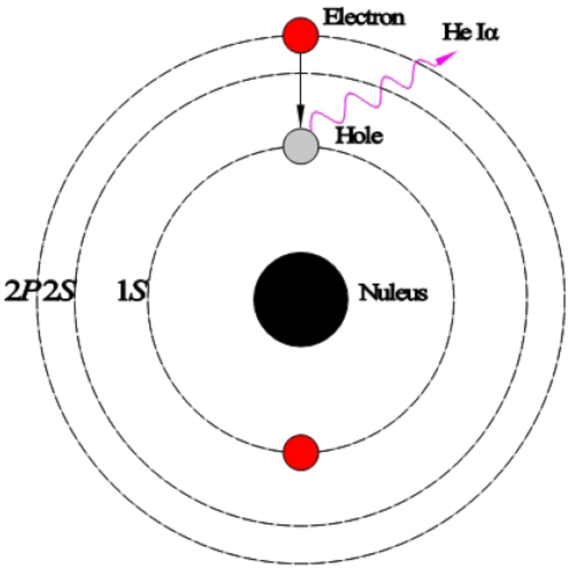
(light emitted from the neutral atoms)

He II: 40.8 eV or 30.38 nm

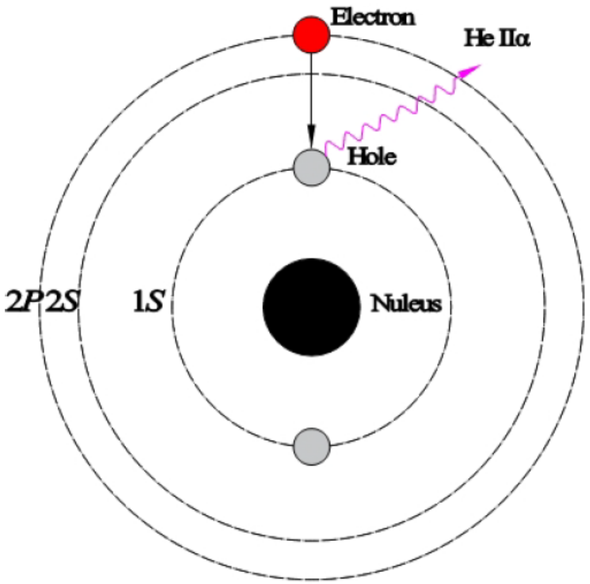
(light emitted from the singly ionized atoms)

Ne I: 16.7 eV

He I and He II



Neutral Helium



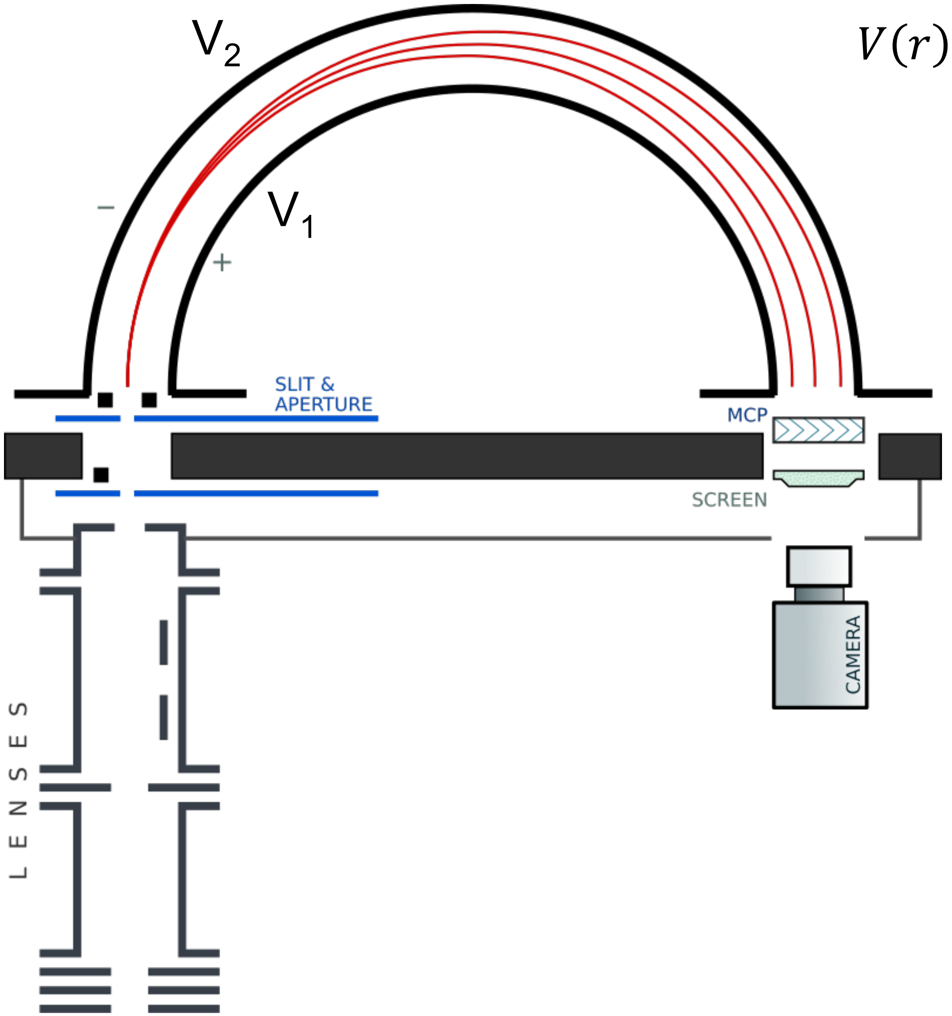
Singly ionized helium

	Energy [eV]	Satellite shift [eV]	Relative Intensity [%]
He I α	21.22	0	100
He I β	23.09	1.87	1.5
He I γ	23.74	2.52	0.5
He II α	40.81	0	100
He II β	48.37	7.56	<10
He II γ	51.02	10.2	<1

He I (21.2 eV) and He II (40.8 eV) lines can be produced by cold cathode capillary discharge lamps. The resonance fluorescence occurs when the gas is excited in the discharge and then decays back to its ground state.

The resonance line He I produced by transition from the first excited state to the ground state is usually the most intense. Additional lines (satellites) are always produced in the gas discharge but these are of relatively low intensity. By reducing the gas pressure the relative proportion of singly ionized atoms in the discharge chamber can be significantly increased to generate usable photon yields of He II.

Concentric Hemispherical Analyzer



$$V(r) = -\left[\frac{V_2 - V_1}{R_2 - R_1}\right] \cdot \frac{R_1 R_2}{r} + const.$$

$$|\mathbf{E}(r)| = -\left[\frac{V_2 - V_1}{R_2 - R_1}\right] \cdot \frac{R_1 R_2}{r^2}$$

The voltages are set in such a way that the electrons with kinetic energy E_k equal to the so-called *pass energy* E_P follow a circular trajectory of radius

$$R_P = \frac{1}{2}(R_1 + R_2)$$

The centripetal force along the path is imposed by the electric field $-e\mathbf{E}(r)$. With this in mind

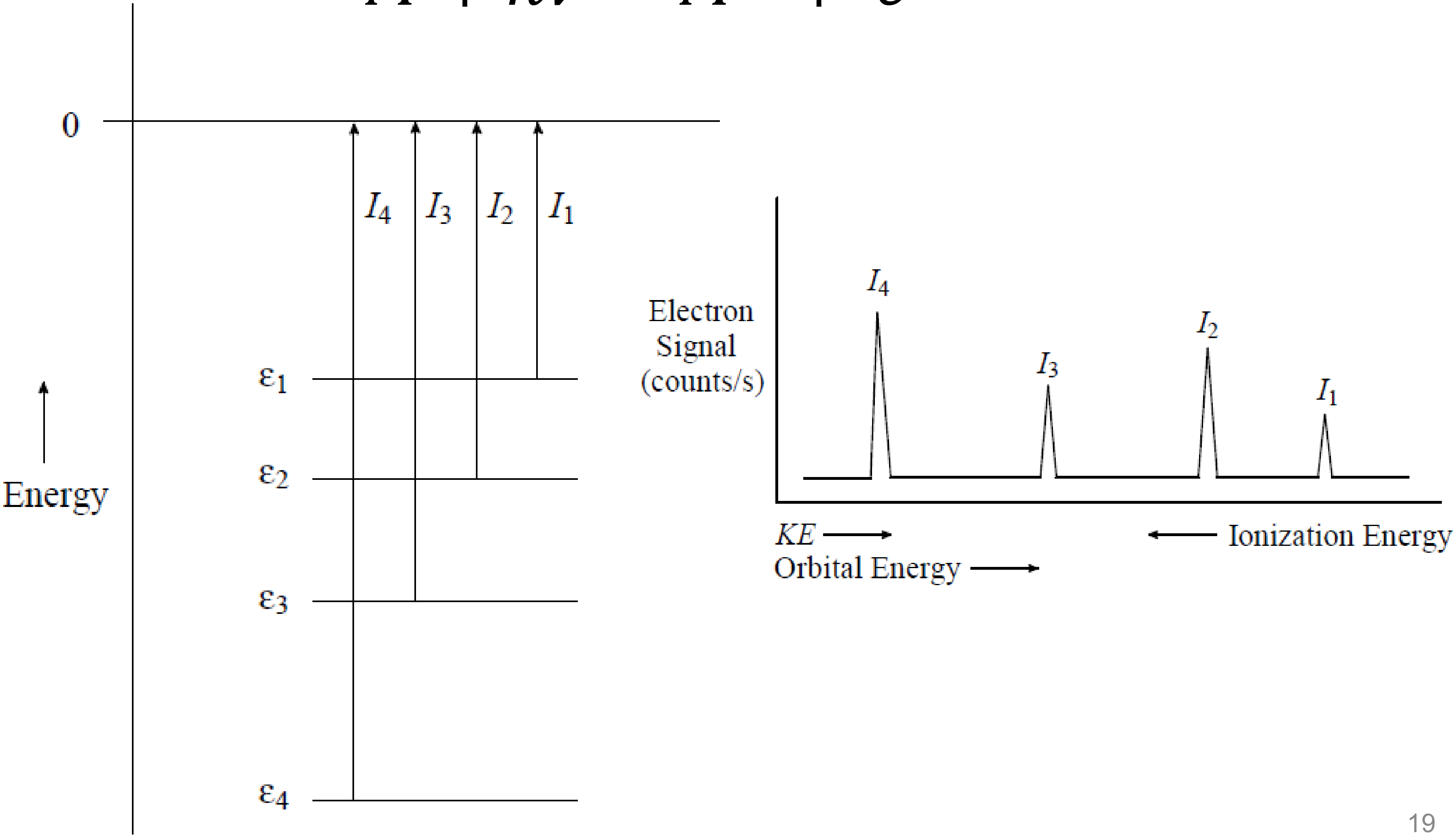
$$V(r) = \frac{E_P}{e}\frac{R_P}{r} + const.$$

The potential difference between the two hemispheres needs to be

$$V_1 - V_2 = \frac{1}{e}\left(\frac{R_2}{R_1} - \frac{R_1}{R_2}\right) E_P$$

Ionizations from a set of orbitals

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



Koopmans' Theorem

The binding energy of an electron in state *i* is equal to the negative of the orbital energy of the *ith* state.

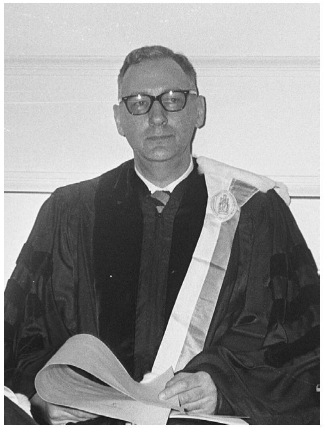
$I_i = -\varepsilon_i$

(the ion is represented by (N-1) frozen orbitals)

Koopmans' theorem makes possible the identification of calculated orbital energies with ionization potentials.

But it does not allow for electronic relaxation.

The ionization energy for the removal of electrons from different orbitals in a molecule is given by the energy difference between the initial state of the neutral molecule (in the ground state) and the final state that is the state of the ionized molecule.



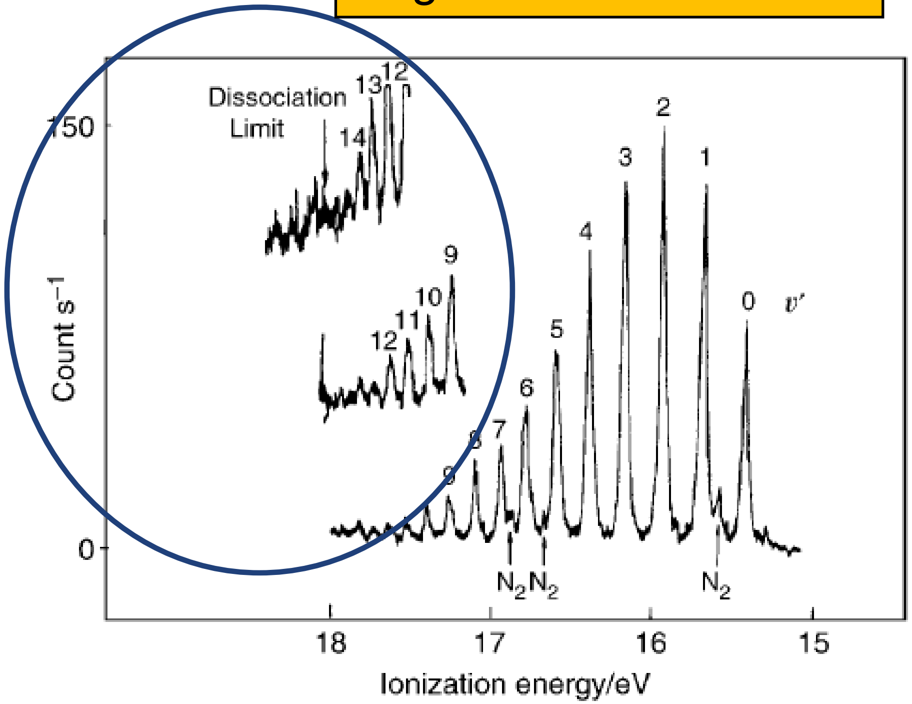
Tjalling Koopmans

Dutch American
Mathematician and
Economist

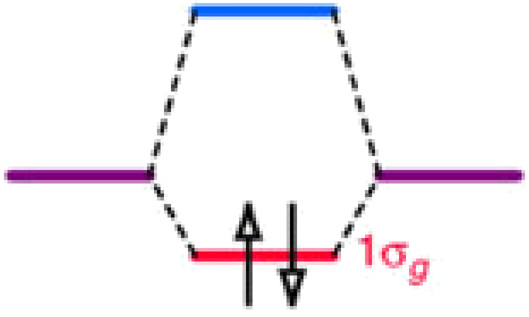
Ultraviolet photoelectron spectra of molecules in **gas phase**

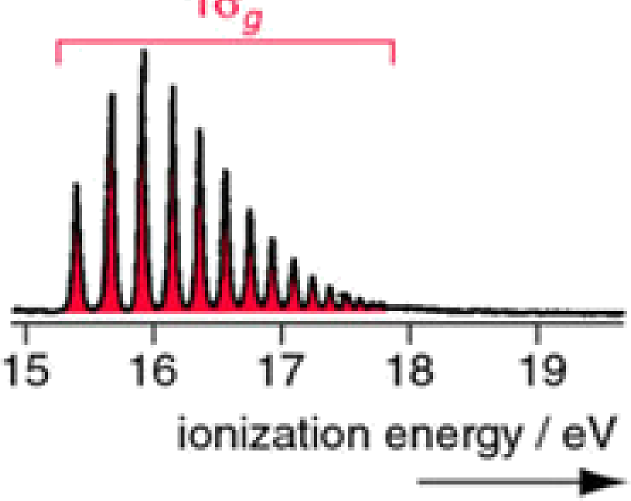
H_2

Some peaks are magnified for better view



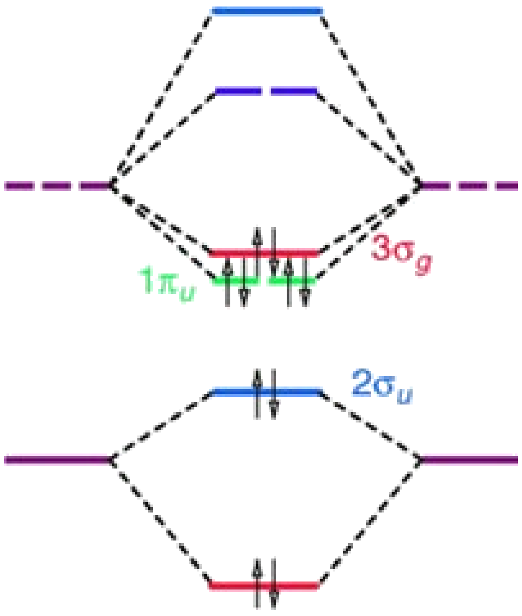
He I ultraviolet photoelectron spectrum of H_2
Refer to book by Hollas Chapter 8





Remember: Our discussion is only limited to gas-phase UPS of simple molecules

N_2



Some peaks are magnified for better view

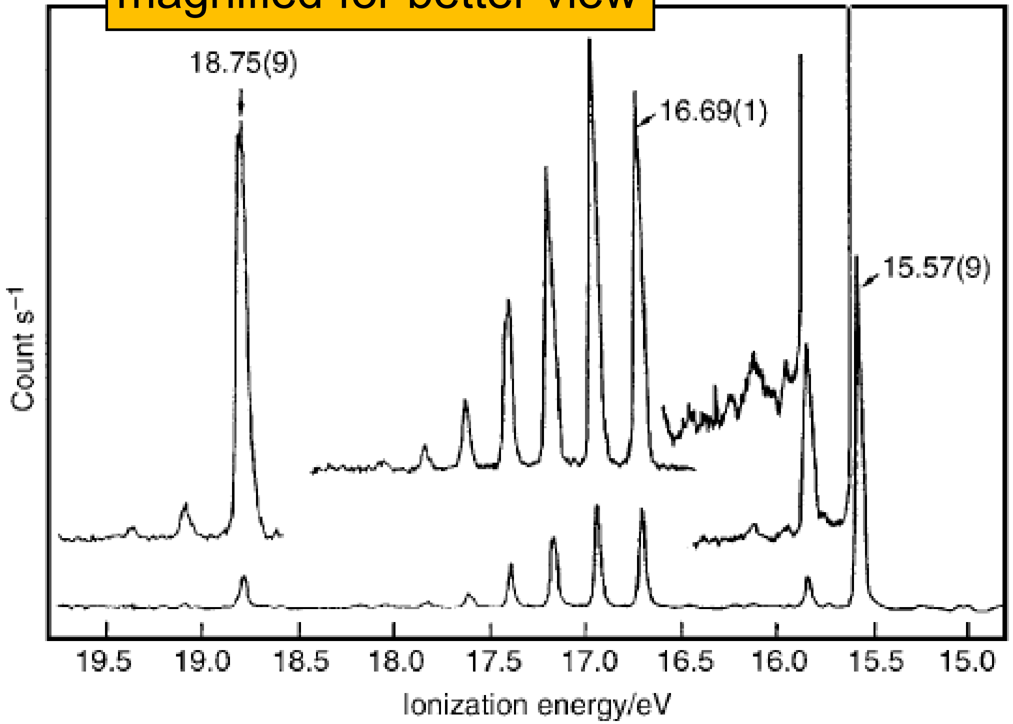
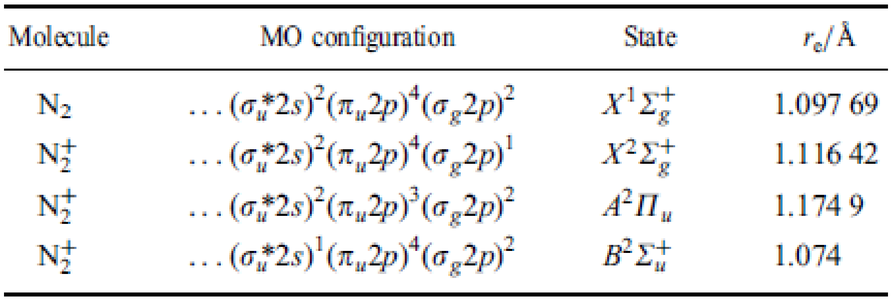


Table 8.2 Bond lengths, r_e, of N_2^+ and N_2 in various electronic states



Molecule	MO configuration	State	r_e/Å
N_2	$\ldots(\sigma_u^*2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$	$X^1\Sigma_g^+$	1.097 69
N_2^+	$\ldots(\sigma_u^*2s)^2(\pi_u 2p)^4(\sigma_g 2p)^1$	$X^2\Sigma_g^+$	1.116 42
N_2^+	$\ldots(\sigma_u^*2s)^2(\pi_u 2p)^3(\sigma_g 2p)^2$	$A^2\Pi_u$	1.174 9
N_2^+	$\ldots(\sigma_u^*2s)^1(\pi_u 2p)^4(\sigma_g 2p)^2$	$B^2\Sigma_u^+$	1.074

Note: MO, molecular orbital.

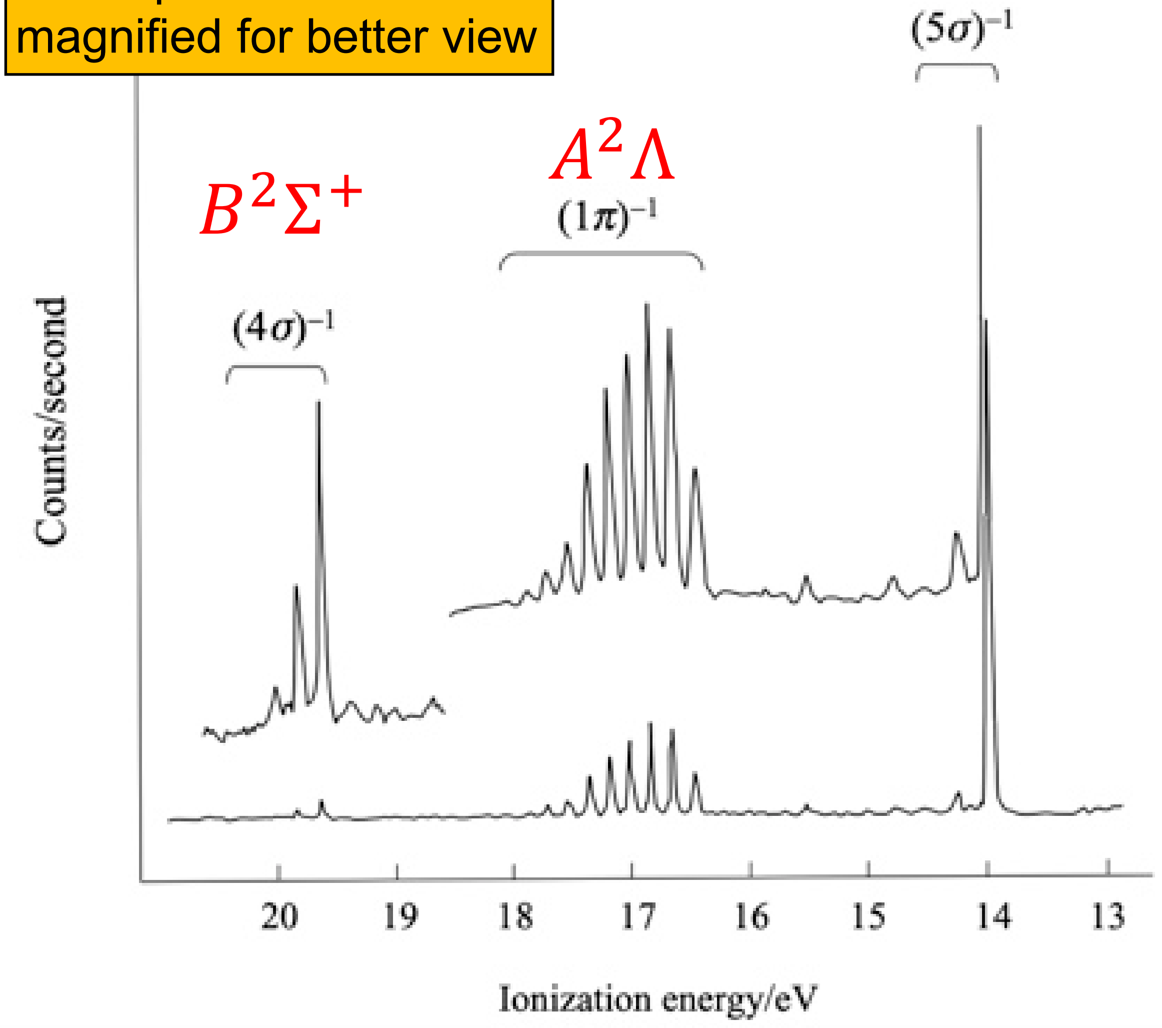
UPS of CO gas

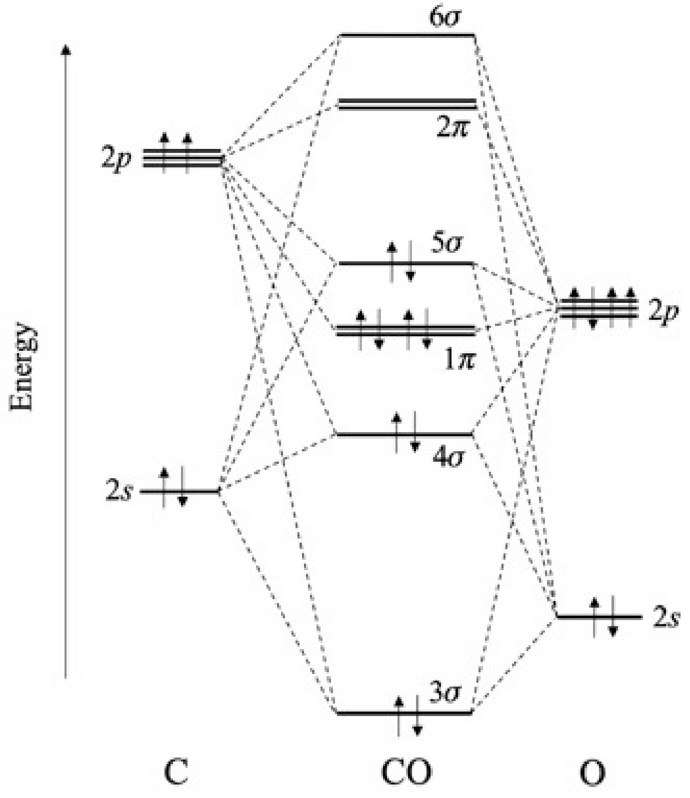
Some peaks are magnified for better view

$X^2\Sigma^+$

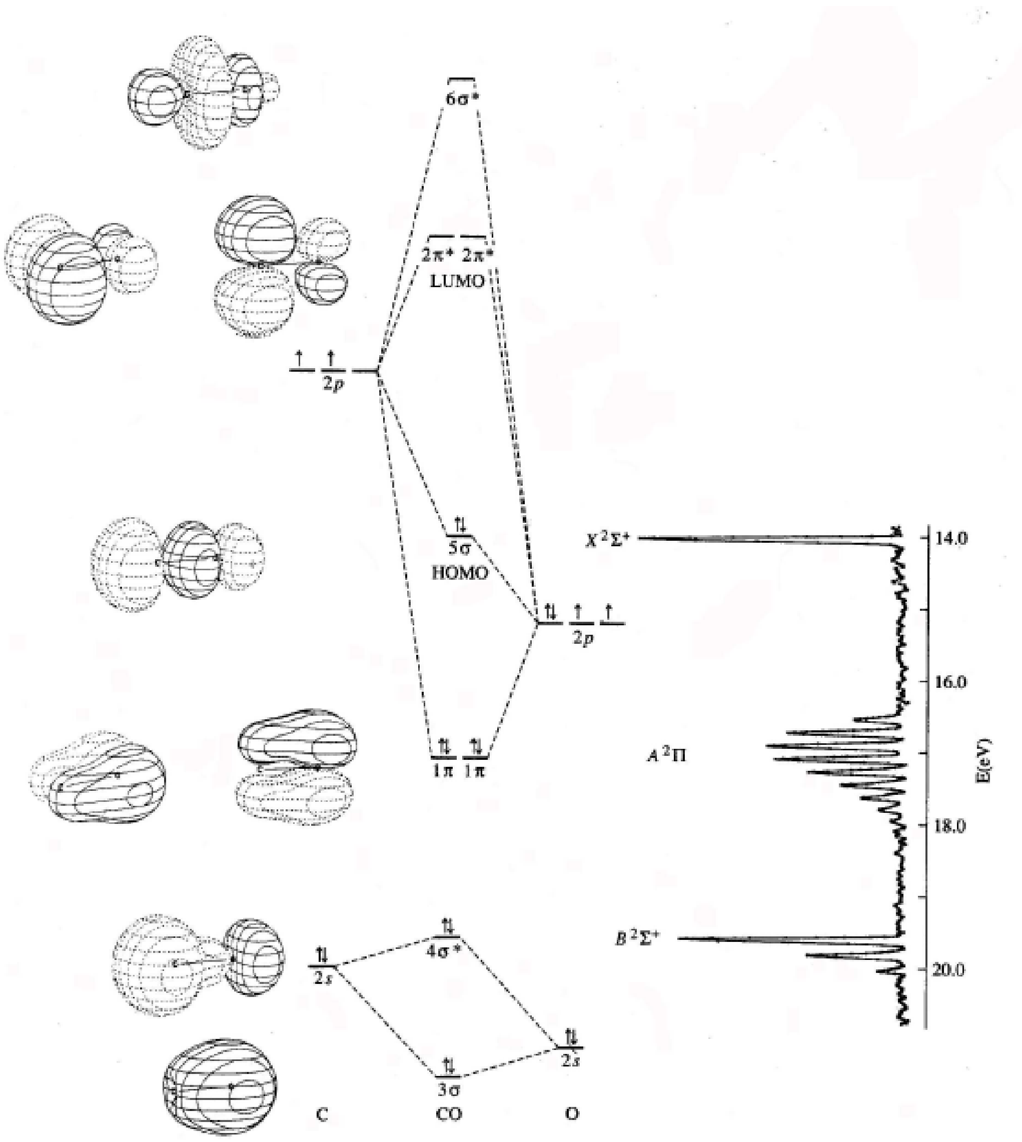
$A^2\Lambda$

$B^2\Sigma^+$

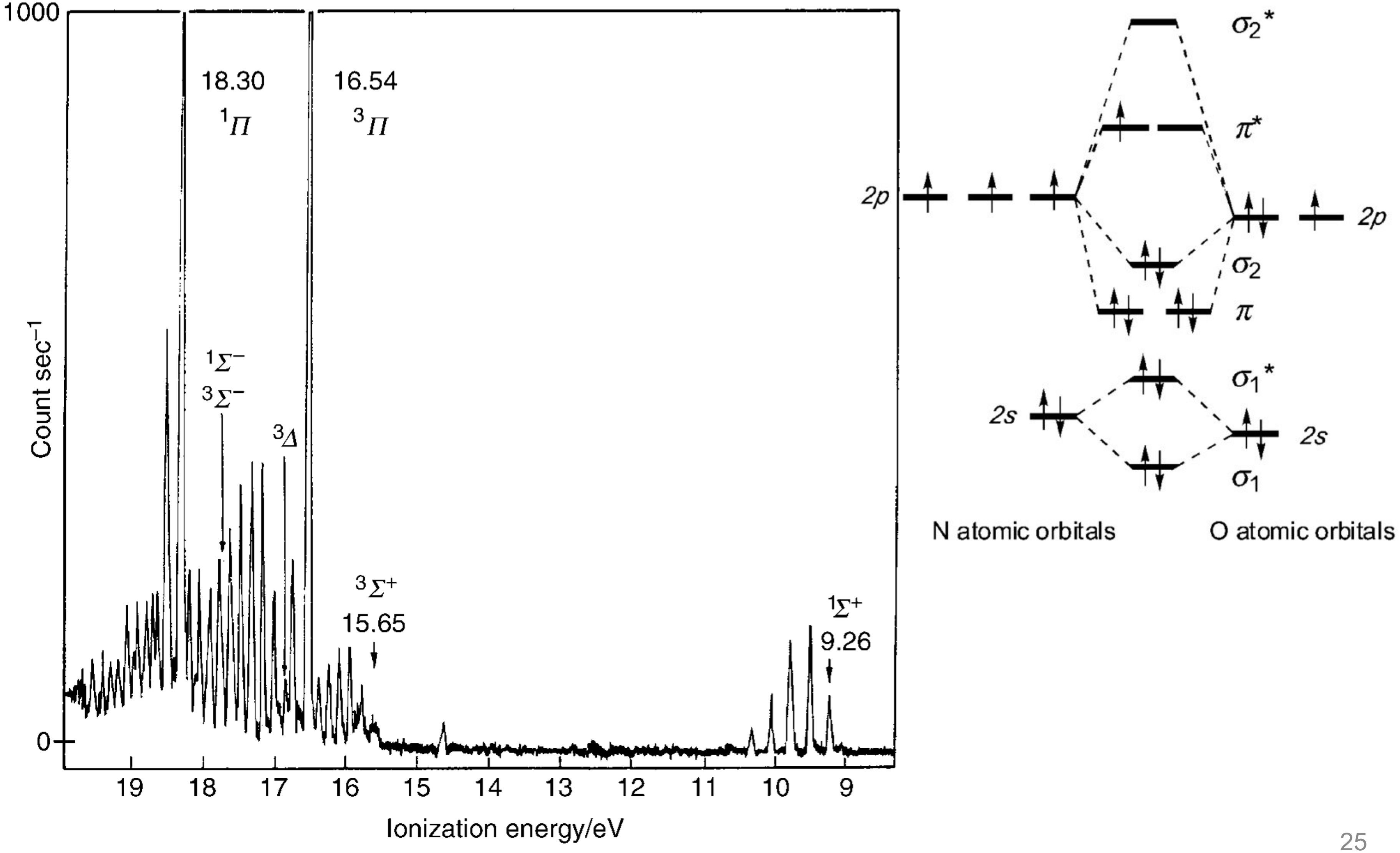




PES of CO


6σ*
2π* 2π*
LUMO
2p
5σ
HOMO
2p
1π 1π
2s
4σ*
3σ
2s
C
CO
O
X ²Σ⁺
A ²Π
B ²Σ⁺
14.0
16.0
18.0
20.0
E(eV)

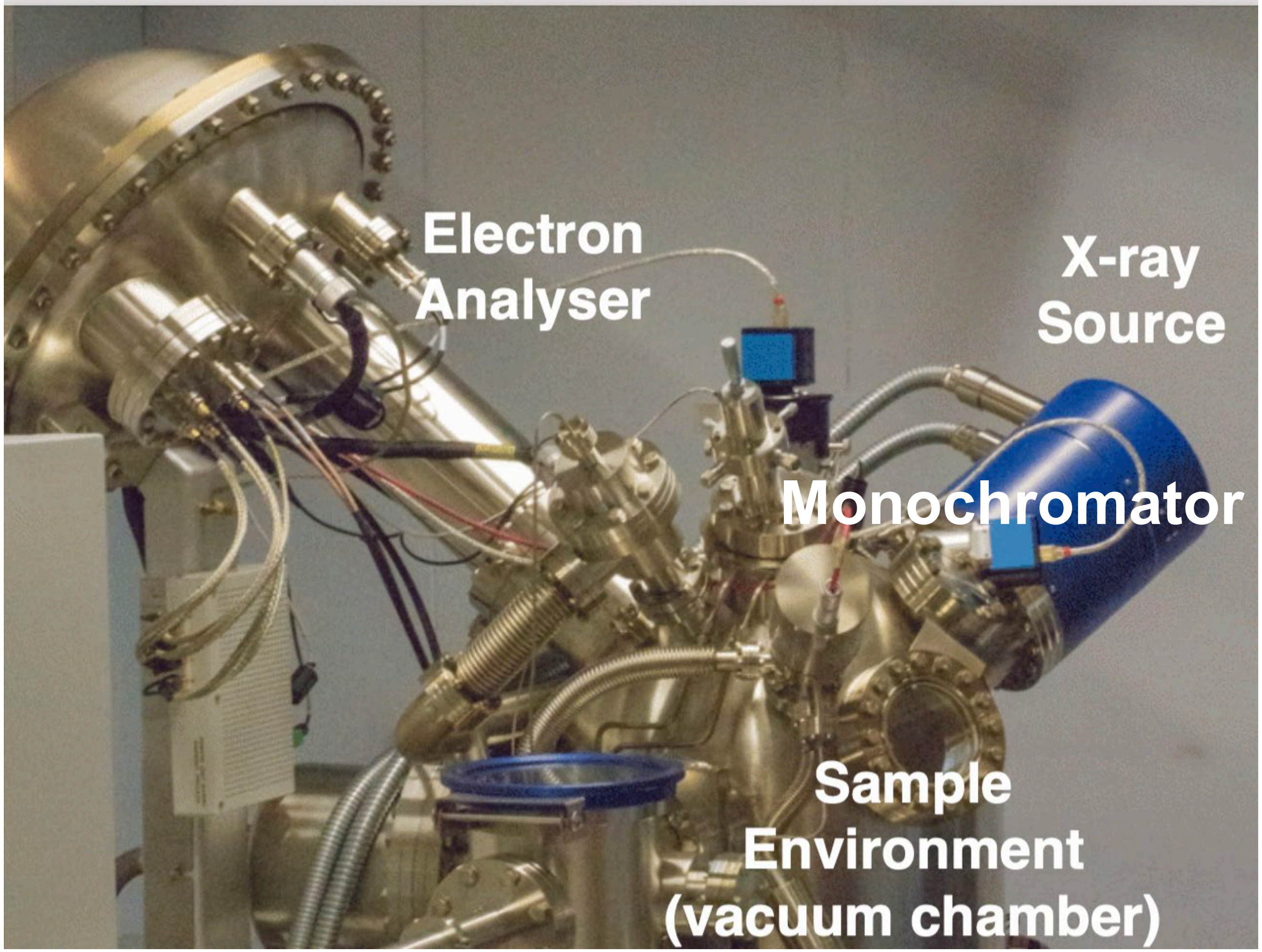
NO


1000
0
Count sec^{-1}
18.30
$^1\Pi$
16.54
$^3\Pi$
$^1\Sigma^-$
$^3\Sigma^-$
$^3\Delta$
$^3\Sigma^+$
15.65
$^1\Sigma^+$
9.26
19
18
17
16
15
14
13
12
11
10
9
Ionization energy/eV
σ_2^*
π^*
2p
2p
σ_2
π
σ_1^*
2s
2s
σ_1
N atomic orbitals
O atomic orbitals

X-ray Photoelectron Spectroscopy (XPS)

- Incident photon energy is higher compared to UPS
- The probed depth is higher compared to UPS.
- Used for investigation of core levels.

XPS Instrumentation

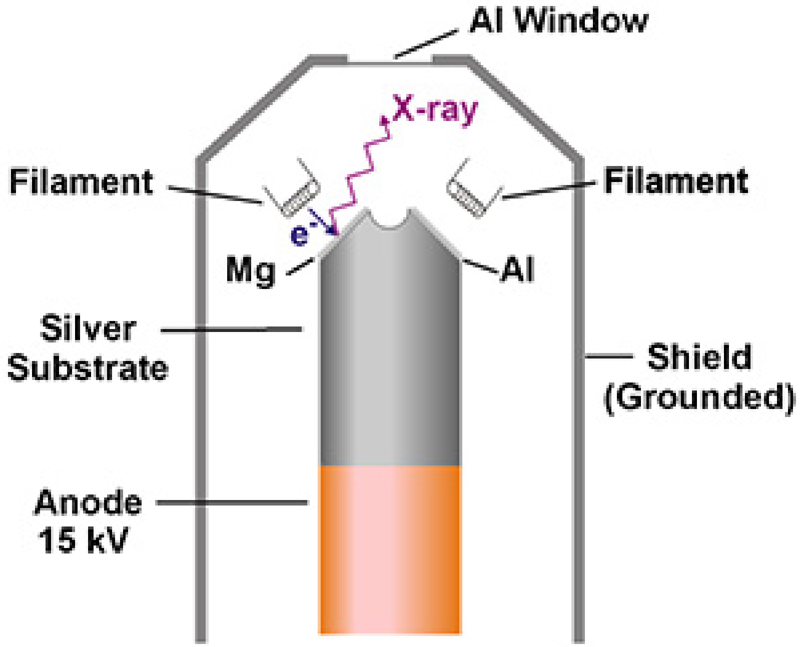


Laboratory Sources (Non-monochromatic)

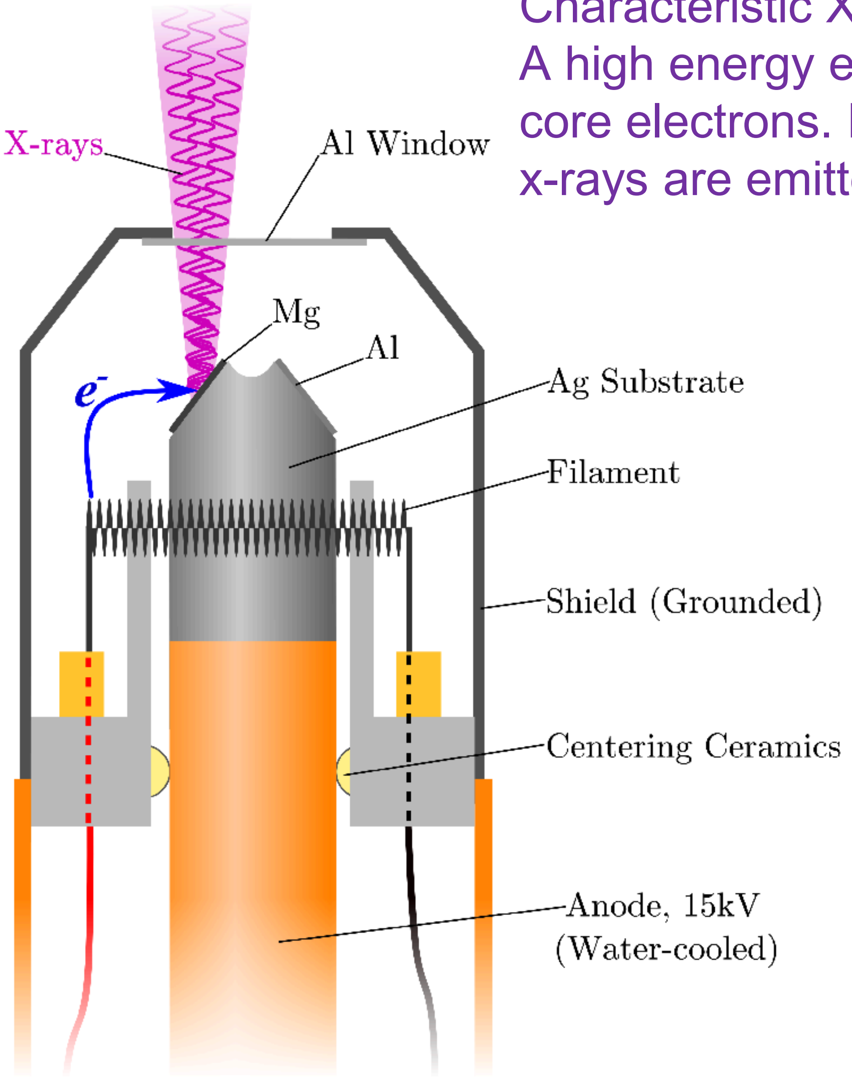
X-ray guns, Twin anode Non-monochromatic

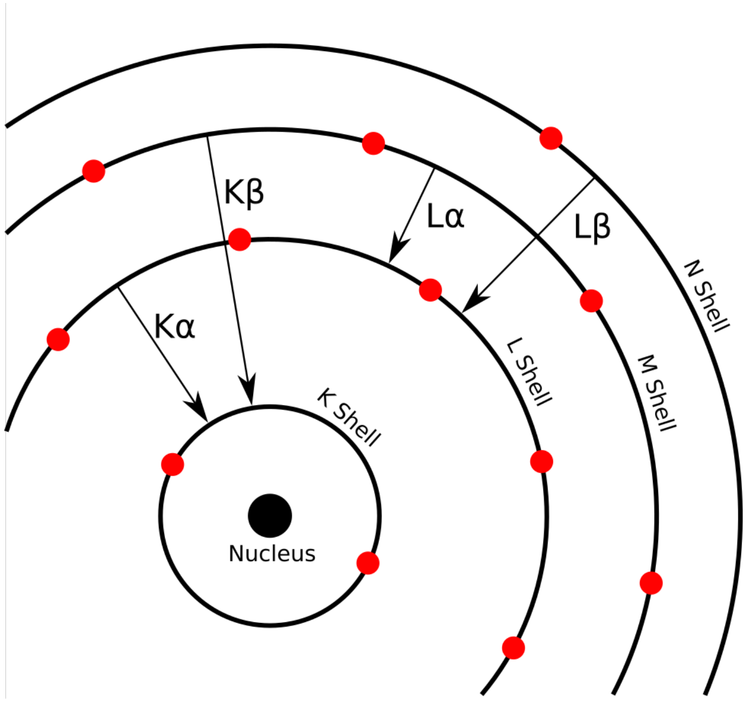
Most used are: Mg Kα (1253.7 eV); Al Kα (1486.6 eV)

The twin anodes commonly have Mg (Magnesium) and Al (Aluminium) anodes. And at a time, one anode is operated.

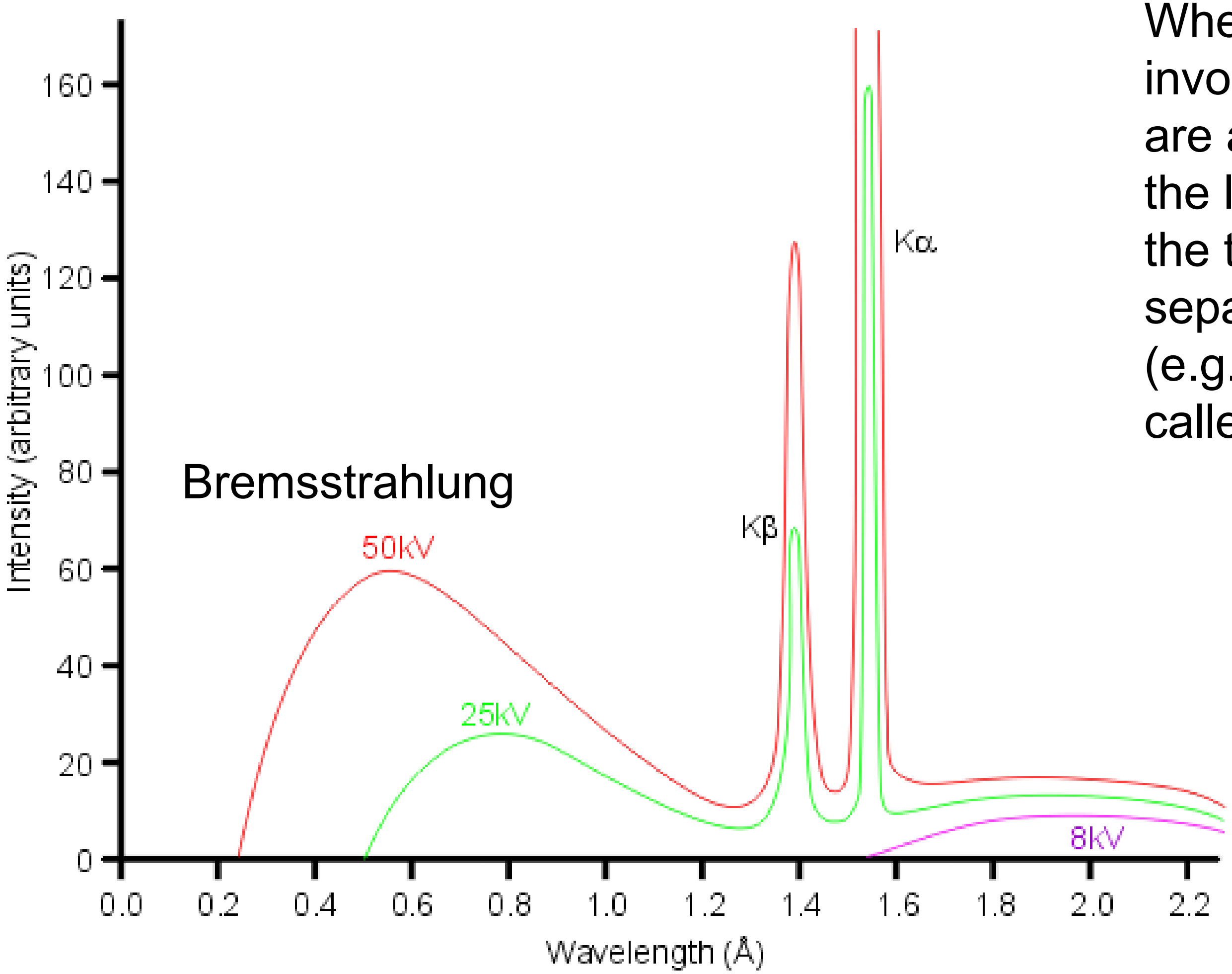


Characteristic X-rays are generated from a target anode, A high energy electron flow hits the anode and excites its core electrons. During relaxation of the excited electron, x-rays are emitted.





Characteristic X-ray



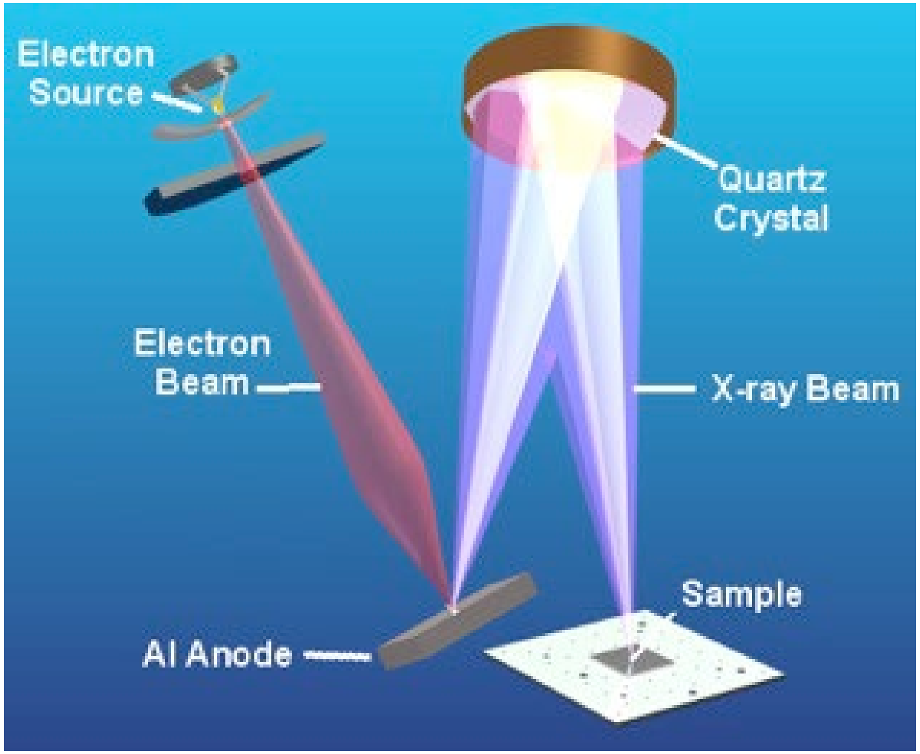
When the two orbitals involved in the transition are adjacent (e.g. 2 → 1), the line is called α. When the two orbitals are separated by another shell (e.g. 3 → 1), the line is called β.

Since characteristic x-ray is polychromatic, sometimes they produce ghost peaks in XPS and show low resolution. Monochromatic x-ray is therefore preferred.

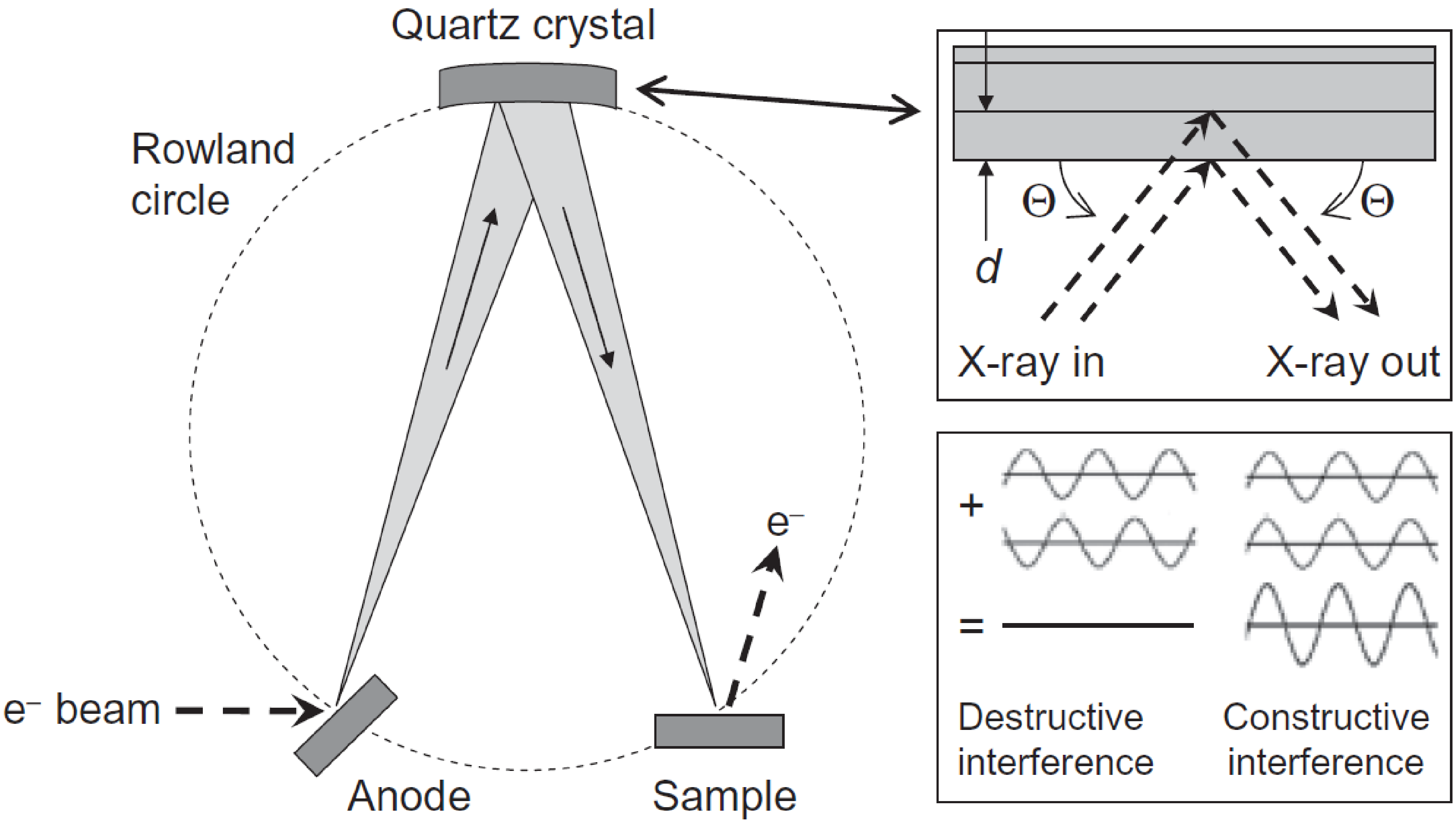
Laboratory Sources (Monochromatic)

Monochromatic X-ray

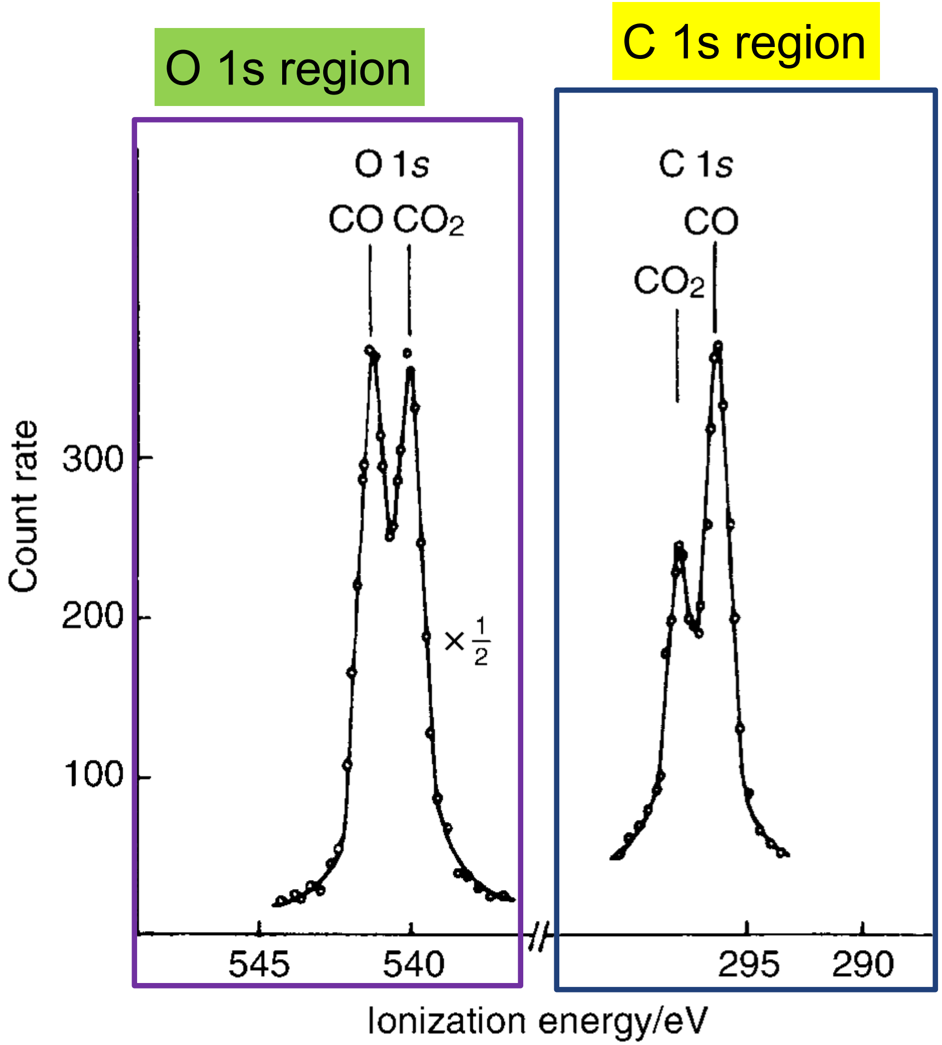
Most used is: Al Kα (1486.6 eV)



Monochromator Geometry



XPS Spectra of Gases

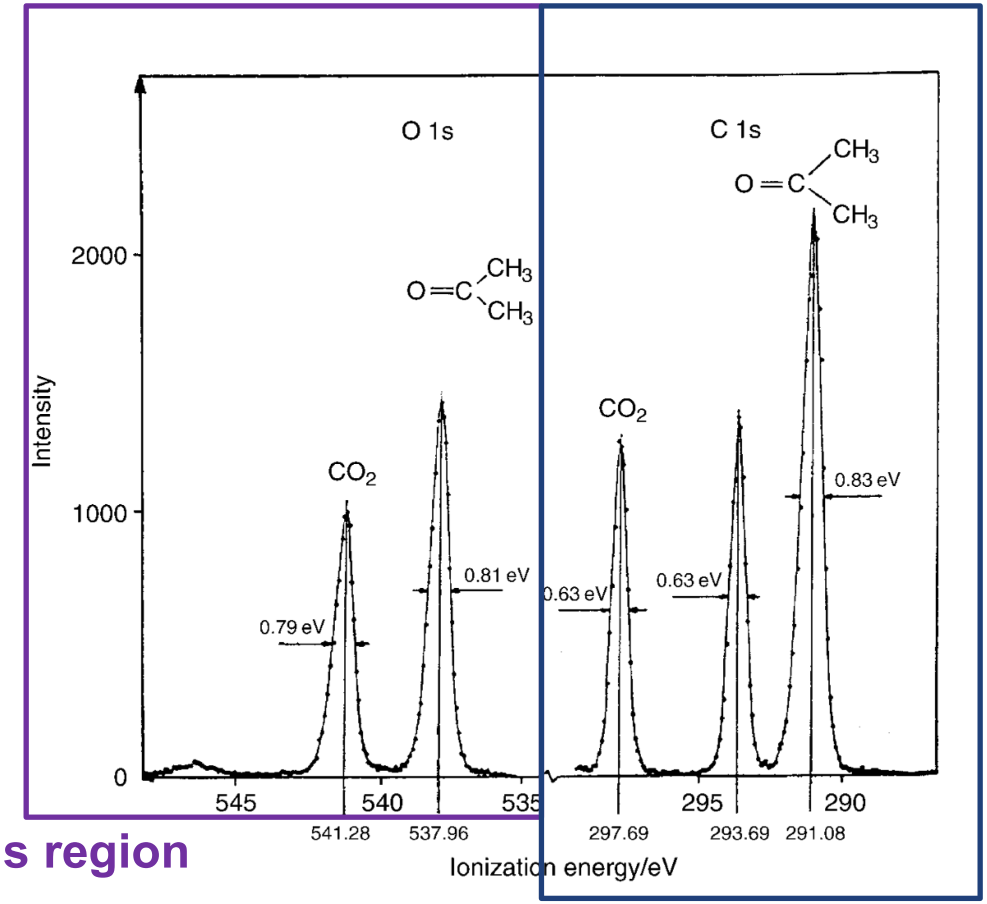


C 1s region =275 -310 eV
O 1s region= 525-545 eV

X-ray photoelectron spectrum of a 2 : 1 mixture of CO and CO_2 gases obtained with Mg Kα (1253.7 eV) source radiation. The ionization energy for removal of an electron from the 1s orbital on a carbon atom, referred to as the C 1s ionization energy, is 295.8 eV in CO and 297.8 eV in CO_2, these being quite comfortably resolved. The O 1s ionization energy is 541.1 eV in CO and 539.8 eV in CO_2, which are also resolved.

In this figure O 1s and C 1s regions are shown together. You can also plot separately in two different figures.

XPS Spectra of Gases



O 1s region

C 1s region

X-ray photoelectron spectra of a mixture of acetone and carbon dioxide gases, explain what you would expect to observe regarding the relative ionization energies (binding energies) and intensities in the C 1s and O 1s spectra.

In this figure O 1s and C 1s regions are shown together. You can also plot separately in two different figures.