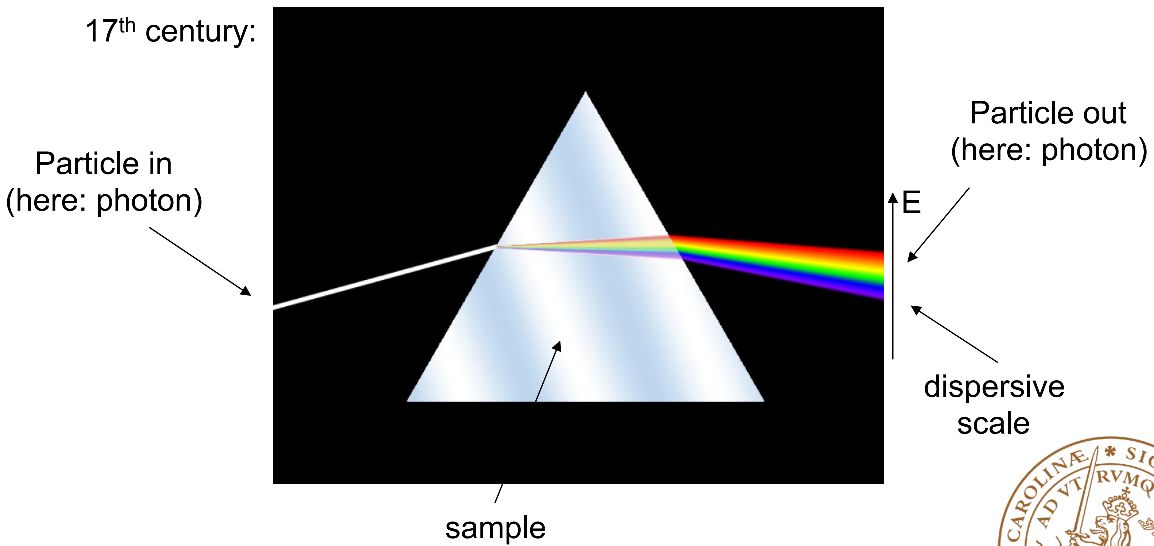
Spectroscopy
Photoelectron spectroscopy
X-ray absorption spectroscopy

What is spectroscopy?

”Spectrum” is Latin and means ”appearance”, ”apparition”

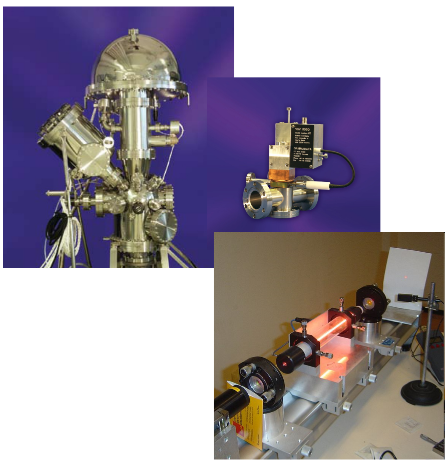
17th century:



Spectroscopy ”methods” that you have mentioned

Photoelectron spectroscopy
Mass spectroscopy
Absorption spectroscopy
X-ray diffraction XRD
X-ray spectroscopy
Neutron spectroscopy
Absorption spectroscopy
Emission spectroscopy
Alpha, Beta, Gamma spectroscopy
IR spectroscopy
NMR spectroscopy

Photon sources



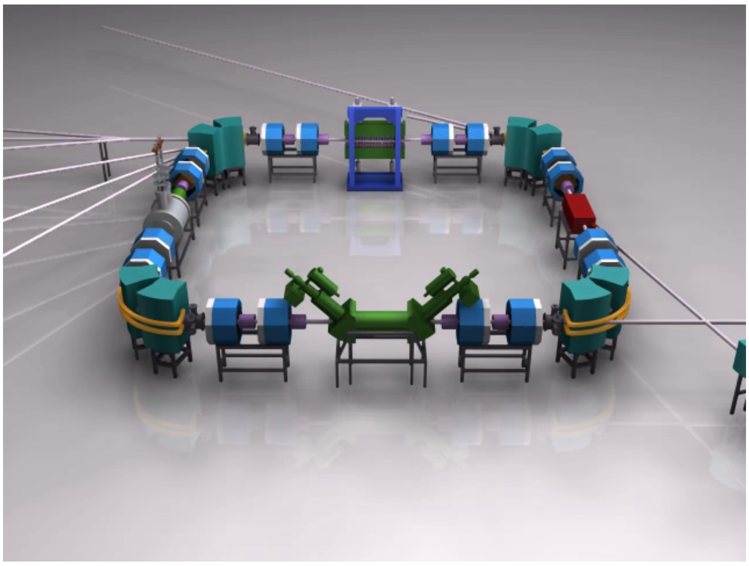
Lab sources:

photons emitted from an electronically excited material (lasers, x-ray anodes, helium lamps)

Advantage: cheap, can be used in home Lab, easy to use

Disadvantage: only certain energies are available, the intensities and energy resolution of x-ray tubes are limited

Photon sources



Synchrotron light sources:

Advantages: wide range of energies, high intensity, high resolution
Disadvantages: expensive, not readily available

I - X-ray photoelectron spectroscopy

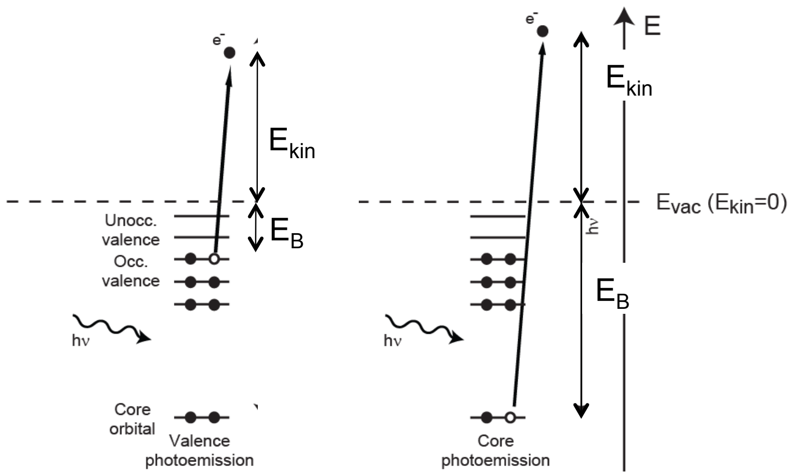
Photoelectron spectroscopy = Photoemission spectroscopy

Hard x-ray:
approx. 1200 – 250,000 eV

Soft x-rays:
approx. 20 – 1200 eV

Vacuum ultraviolet:
approx. 6 – 20 eV

Ultraviolet:
approx. 3 – 6 eV



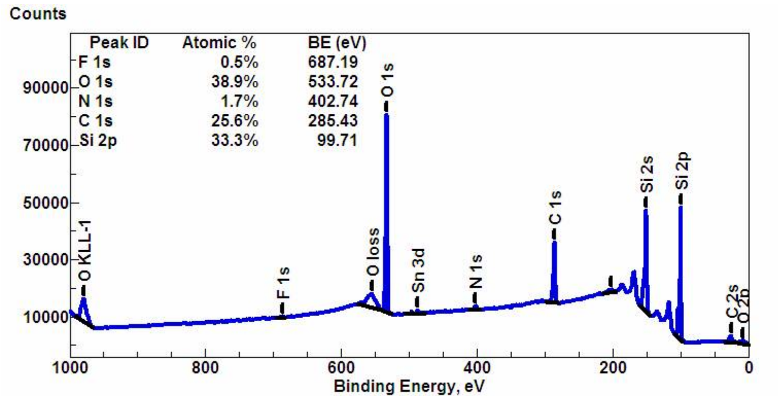
UPS = Ultraviolet photoelectron spectroscopy

XPS = X-ray photoelectron spectroscopy

Overview

Extension of the photoelectric effect

$$|E_B| = h\nu - E_{kin} = \text{ Ionization Potential}$$



Al $K\alpha$ radiation $h\nu \approx 1486$ eV

Core level binding energies:

characteristic for the elements

Binding energies																					
		1s	2s	2p1	2p3	3s	3p1	3p3	3d3	3d5	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3	
1	H	14																			H
2	He	25																			He
3	Li	55																			Li
4	Be	112																			Be
5	B	188																			B
6	C	284																			C
7	N	410	2s	2p1	2p3	3s	3p1	3p3	3d3	3d5	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3	N
8	O	543	23																		O
9	F	686	30																		F
10	Ne	863	41	14	14																Ne
11	Na	1072	64	31	31																Na
12	Mg		90	51	51																Mg
13	Al		119	74	74																Al
14	Si		153	103	102																Si
15	P		191	134	133	14															P
16	S		229	166	165	17															S
17	Cl		270	201	199	17															Cl
18	Ar		319	243	241	22	3p1	3p3	3d3	3d5	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3	Ar
19	K		378	296	293	33	17	17													K
20	Ca		439	350	347	44	25	25													Ca
21	Sc		501	407	402	53	31	31													Sc
22	Ti		565	464	458	62	37	37													Ti
23	V		630	523	515	69	40	40													V
24	Cr		698	586	577	77	46	45													Cr
25	Mn		770	652	641	83	49	48													Mn
26	Fe		847	723	710	93	56	55													Fe
27	Co		927	796	781	103	63	61													Co
28	Ni		1009	873	855	112	69	67													Ni
29	Cu		1098	954	934	124	79	77													Cu
30	Zn		1196	1045	1022	140	92	89	10	10											Zn
31	Ga			1144	1117	160	108	105	20	20											Ga
32	Ge					184	128	124	32	31											Ge
33	As					207	148	143	45	44											As
34	Se					232	169	163	58	57											Se
35	Br					256	189	182	70	69	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3	Br
36	Kr					287	216	208	89	88	22										Kr
37	Rb					322	247	238	111	110	29	14	14								Rb
38	Sf					358	280	269	135	133	37	20	20								Sf
39	Y					395	313	301	160	158	45	25	25								Y
40	Zr					431	345	331	183	181	51	29	29								Zr
41	Nb					470	379	364	209	206	59	35	35								Nb
42	Mo					508	413	396	233	230	65	38	38								Mo
43	Tc					544	445	425	257	253	68	39	39								Tc
44	Ru					587	485	463	286	282	77	45	45								Ru
45	Rh					629	522	498	314	309	83	49	49								Rh
46	Pd					673	561	534	342	337	88	54	54								Pd
47	Ag					718	604	573	374	368	97	58	58	4d3	4d5	4f5	4f7	5s	5p1	5p3	Ag
48	Cd					772	652	618	412	405	109	68	68	11	11						Cd
49	In					828	704	666	453	445	123	79	79	19	19						In
50	Sn					884	757	715	494	486	137	91	91	26	25						Sn
51	Sb					946	814	768	539	530	155	105	105	35	34						Sb
52	Te					1009	873	822	585	575	171	114	114	44	43			14			Te
53	I					1071	930	874	630	619	186	123	123	52	50			16			I
54	Xe					1144	997	936	685	672	209	141	141	65	63			19			Xe

55	Cs	1064	997	738	724	230	170	158	77	75			24			Cs
56	Ba	1137	1062	795	780	254	192	179	92	90			23			Ba
57	La		1126	851	834	274	210	195	104	101			34	17	17	La
58	Ce		1184	900	882	290	222	207	112	108			37	18	18	Ce
59	Pr			950	930	305	237	218	114	114			38	20	20	Pr
60	Nd			1001	980	318	248	227	120	120			38	23	23	Nd
61	Pm			1060	1034	337	264	242	129	129			38	22	22	Pm
62	Sm			1110	1083	349	283	250	132	132			41	20	20	Sm
63	Eu			1166	1136	366	289	261	136	136			34	24	24	Eu
64	Gd				1186	380	301	270	141	141			36	21	21	Gd
65	Tb					398	317	284	150	150			42	28	28	Tb
66	Dy					412	329	293	154	154			63	26	26	Dy
67	Ho					431	345	306	161	161			51	20	20	Ho
68	Er					451	362	320	169	169			61	25	25	Er
69	Tm					470	378	333	180	180			54	32	26	Tm
70	Yb					483	392	342	194	185			55	33	26	Yb
71	Lu					507	412	359	207	197			58	34	27	Lu
72	Hf					537	437	382	224	213	19	17	64	37	30	Hf
73	Ta					566	464	403	241	229	27	25	71	45	37	Ta
74	W					594	491	425	257	245	36	34	77	47	37	W
75	Re					628	521	449	277	263	45	43	81	44	33	Re
76	Os					657	549	475	294	279	55	52	86	60	48	Os
77	Ir					692	579	497	313	297	65	62	98	65	53	Ir
78	Pt					726	610	521	333	316	76	73	105	69	54	Pt
79	Au					763	643	547	354	336	89	85	110	75	57	Au
80	Hg					803	681	577	379	359	104	100	127	84	65	Hg
81	Tl					845	721	608	406	385	122	118	137	100	76	Tl
82	Pb					893	762	645	435	413	143	138	148	107	84	Pb
83	Bi					942	807	681	467	443	164	159	161	120	94	Bi
84	Po											184				Po
85	At											210				At
86	Rn											238				Rn
87	Fr											268				Fr
88	Ra											299				Ra
89	Ac											319				Ac
90	Th											333				Th
91	Pa						1168	968	714	677	344	335	290	226	179	Pa
92	U							1046	781	739	391	380	325	262	197	U
93	Np							1086	816	771	414	402			206	Np
94	Pu							1121	850	802	439	427			216	Pu
95	Am								883	832	463	449			216	Am
96	Cm								919	865	487	473			232	Cm

Do we actually measure the orbital energy ?

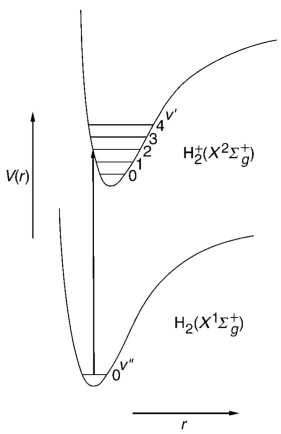
- **Koopmans theorem**

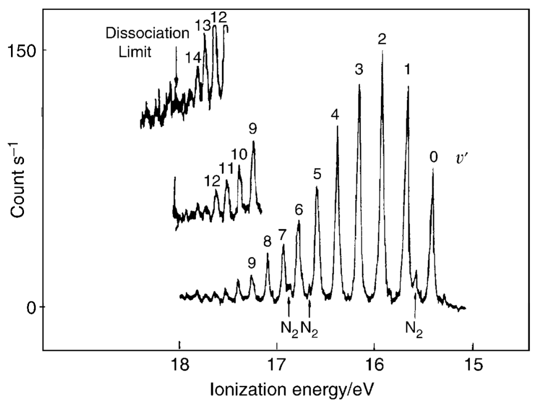
" For a closed-shell molecule the ionization energy of an electron in a particle orbital is approximately equal to the negative of the orbital energy calculated by a self-consistent field method, or for orbital i, $I_i \approx -\varepsilon_i^{SCF}$ "

- **Approximations:**
  - Electron reorganization: I_i measure the difference in energy between M and M^+ but the M^+ orbital are not quite the same as the M orbital
  - Electron correlations: Electrons in an atom or a molecule do not move entirely independently
  - Relativistic effect : particularly important for core orbital

UPS in molecules

H_2 - $(1\sigma_g)^2$



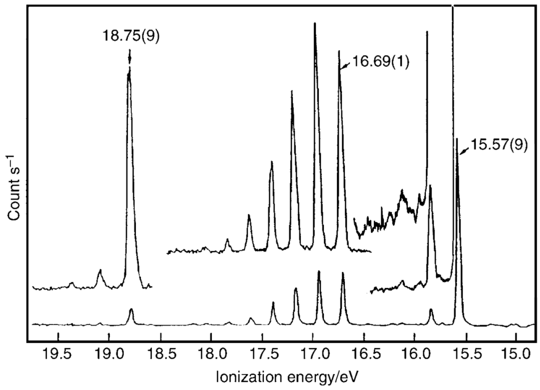


The He I ultraviolet photoelectron spectrum of H_2. (Reproduced from Turner, D. W., Baker, C., Baker, A. D. and Brundle, C. R., *Molecular Photoelectron Spectroscopy*, p. 44, John Wiley, London, 1970)

The vertical ionization energy, to which Koopman's theorem refers, corresponds to the transition at the centre of gravity of the band system.

UPS in molecules

N_2 - $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$



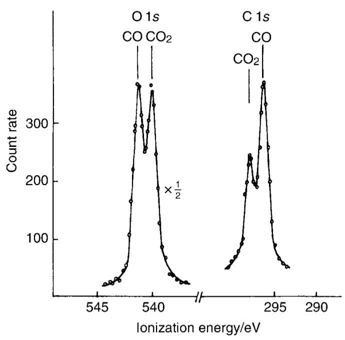
The He I ultraviolet photoelectron spectrum of N_2. (Reproduced from Turner, D. W., Baker, C., Baker, A. D. and Brundle, C. R., *Molecular Photoelectron Spectroscopy*, p. 46, John Wiley, London, 1970)

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

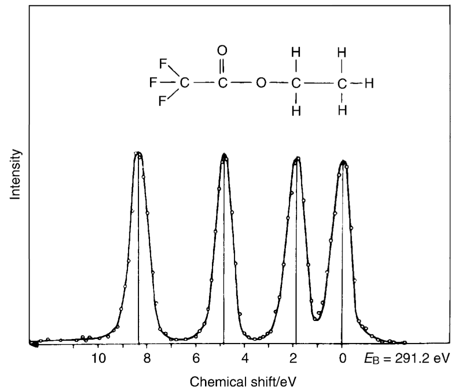
Note: MO, molecular orbital.

MO calculation of the SCF type for N_2^+ place the $A^2\Pi_u$ stale below the $X^2\Sigma_g^+$ state – breakdown of the Koopman's theorem

XPS in molecule – chemical shift



The MgKα oxygen 1s and carbon 1s X-ray photoelectron spectra of a 2 : 1 mixture of CO and CO_2 gases. (Reproduced, with permission, from Allan, C. J. and Siegbahn, K. (November 1971), *Publication No. UUIP–754*, p. 48, Uppsala University Institute of Physics)

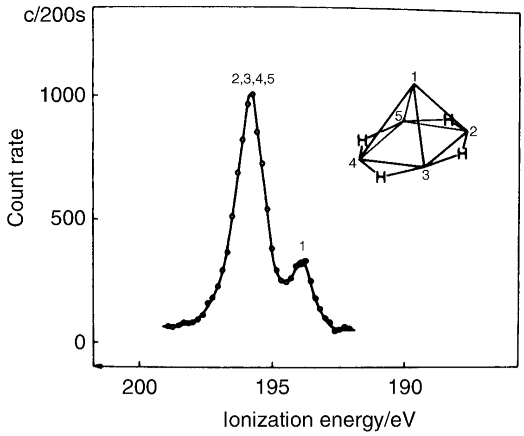


The monochromatized AlKα carbon 1s X-ray photoelectron spectrum of ethyltrifluoroacetate showing the chemical shifts relative to an ionization energy of 291.2 eV. (Reproduced, with permission, from Gelius, U., Basilier, E., Svensson, S., Bergmark, T. and Siegbahn, K., *J. Electron Spectrosc.*, **2**, 405, 1974)

The chemical shift (ΔE_{nl}) is measured relative to the ionization energy of the corresponding orbital of the free atom A

$$\Delta E_{nl} = \left[E_{nl}(M^+) - E_{nl}(M)\right] - \left[E_{nl}(A^+) - E_{nl}(A)\right]$$
$$\approx -\varepsilon_{nl}(M) + \varepsilon_{nl}(A)$$

XPS in molecule – structure determination



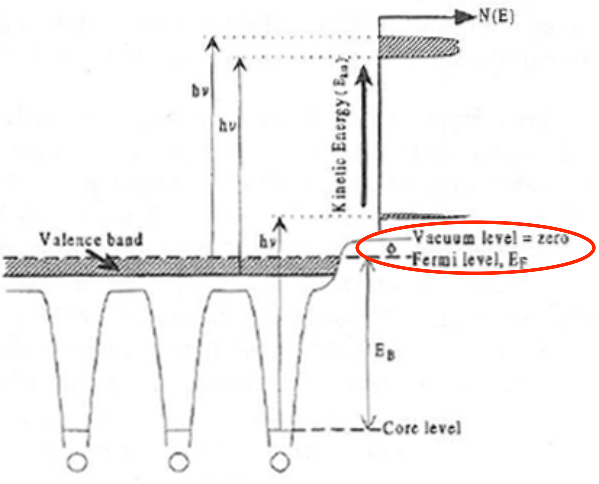
The Mg$K\alpha$ boron 1s X-ray photoelectron spectrum of B_5H_9. (Reproduced, with permission, from Allison, D. A., Johansson, G., Allan, C. J., Gelius, U., Siegbahn, H., Allison, J. and Siegbahn, K., *J. Electron Spectrosc.*, **1**, 269, 1972–73)

XPS on surfaces

The photoelectric effect
(Einstein, 1905)

$$h\nu = E_B + E_{kin} + \phi$$

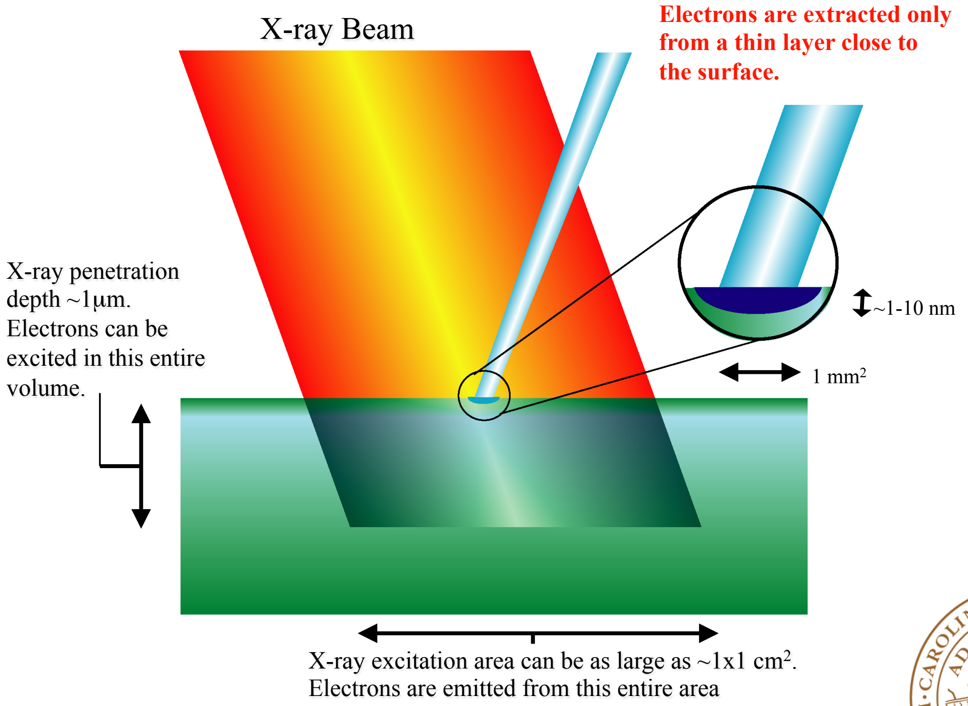
Work function



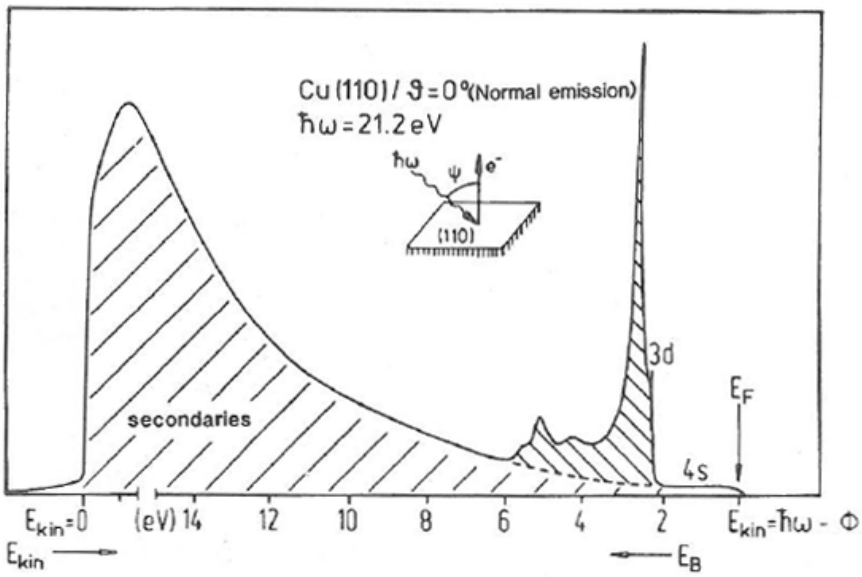
ϕ = work function
$N(E)$ = number of electrons with a particular kinetic energy
E_B = binding energy

The energetics of an X-ray photoemission experiment.

Photoemission spectroscopy is surface sensitive

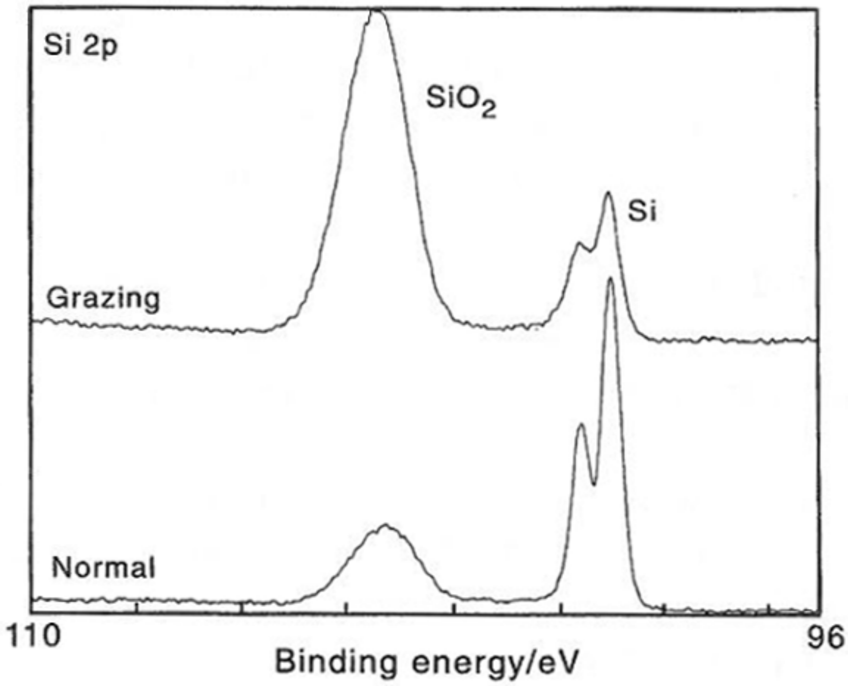


A photoelectron spectrum over the entire available energy range

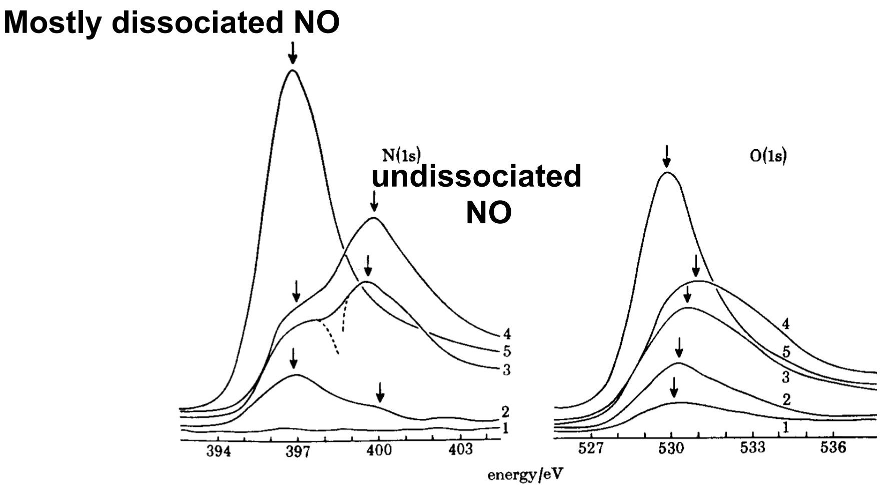


Secondary electrons: electrons which have lost energy due to scattering on their way out of the solid into the vacuum

XPS - Chemical shifts



XPS - Chemical shifts and temperature



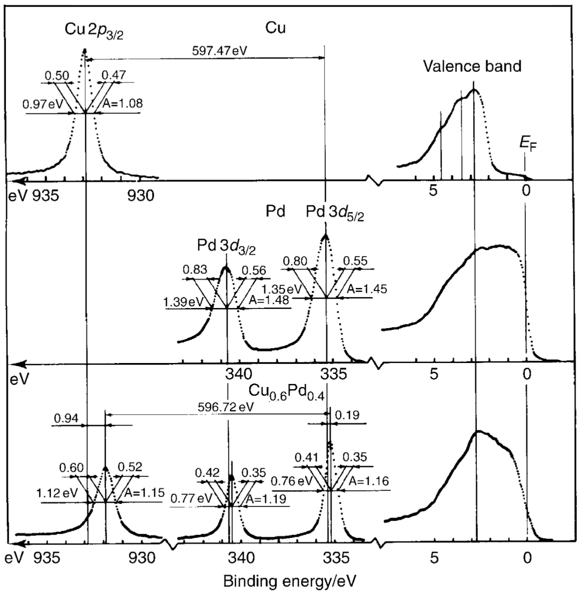
Nitrogen 1*s* and oxygen 1*s* X-ray photoelectron spectra of nitric oxide (NO) adsorbed on an iron surface. 1, Fe surface at 85 K; 2, exposed at 85 K to NO at 2.65 × 10^{-5} Pa for 80 s; 3, as for 2 but exposed for 200 s; 4, as for 2 but exposed for 480 s; 5, after warming to 280 K. (Reproduced, with permission, from Kishi, K. and Roberts, M. W., *Proc. R. Soc. Lond.*, **A352**, 289, 1976)

XPS - (Sub) Femtosecond dynamics

Copper surface

Palladium surface

Copper-Palladium alloy

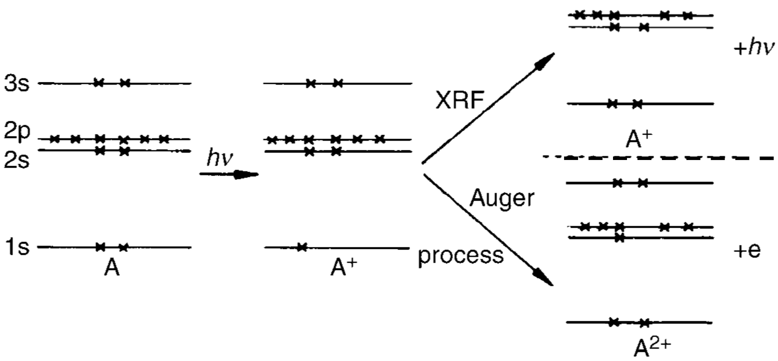


X-ray photoelectron spectrum, showing core and valence electron ionization energies, of Cu, Pd, and a 60% Cu and 40% Pd alloy (face-centred cubic lattice). The 'binding energy' is the ionization energy relative to the Fermi energy, E_F, of Cu. (Reproduced, with permission, from Siegbahn, K., *J. Electron Spectrosc.*, **5**, 3, 1974)

ΔE>2 eV

Δt<1fs

II – Electronic relaxation – *"in short"*



High Z

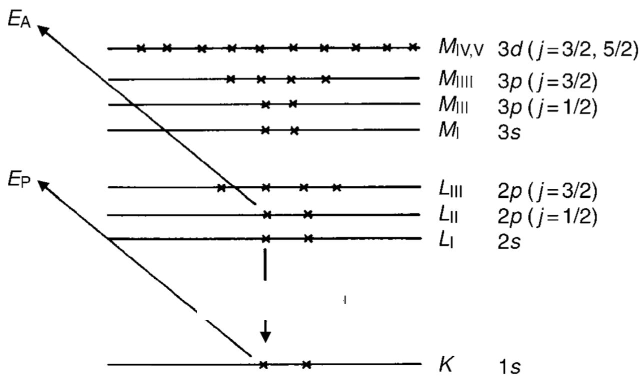
Bulk & Liquid

Low Z

Surface

Normal Auger

(Pierre Auger, 1925)



The auger electron kinetic energy E_A is given by

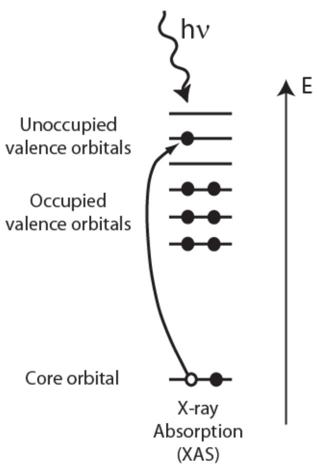
$$E_K - E_{L_I} = E^{+}_{L_{II}} + E_A$$

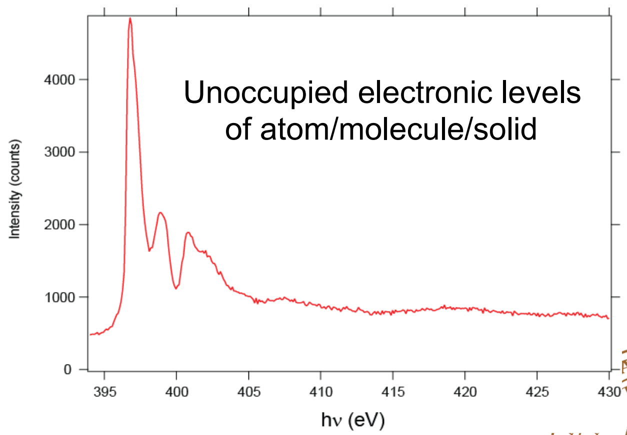
No photon energy dependence ←

→ **Chemical shift effect**

III- X-ray absorption spectroscopy

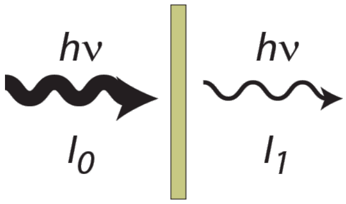
XANES = X-ray Absorption Near Edge Structure
NEXAFS = Near Edge X-ray Absorption Fine Structure
XAS = X-ray Absorption Spectroscopy





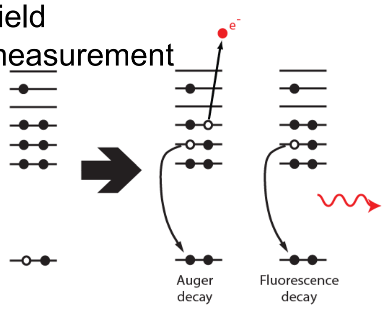
How to measure x-ray absorption spectra

(a) True absorption measurement

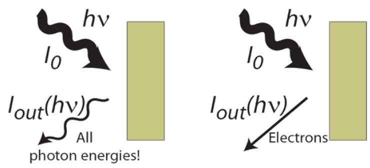


Measure $I_1(h\nu)$-$I_0(h\nu)$.

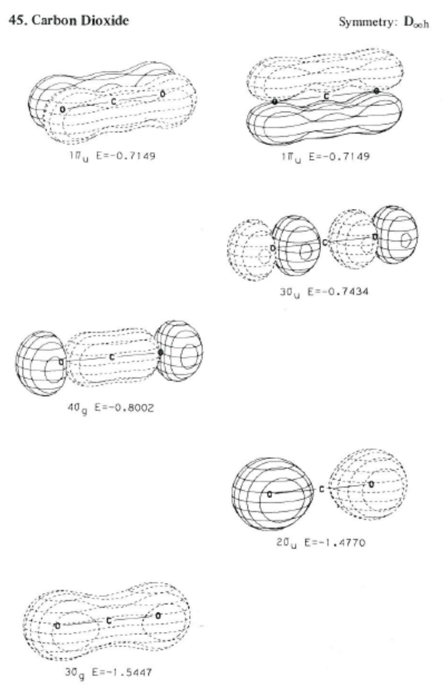
(b) Electron yield or fluorescence yield measurement

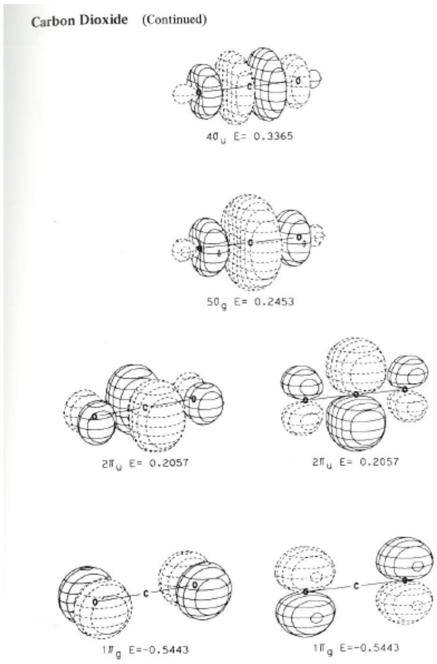


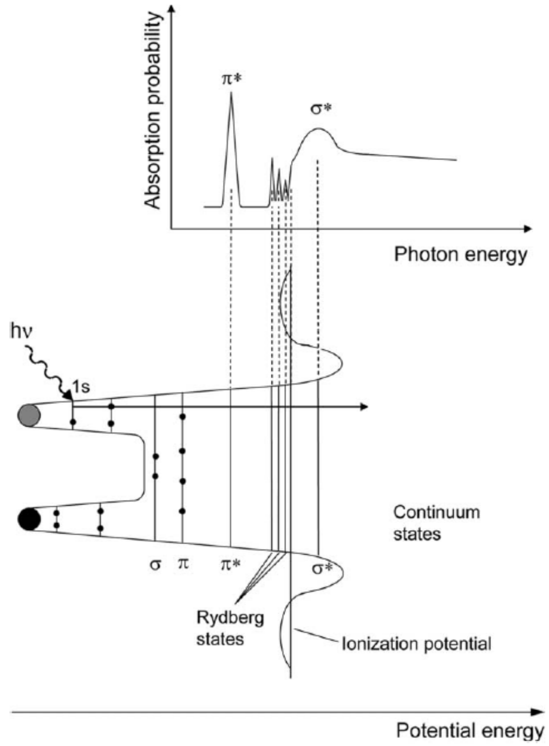
The number of decays (as a function of photon energy) is (exactly) proportional to the number of excitations (as a function of photon energy)!

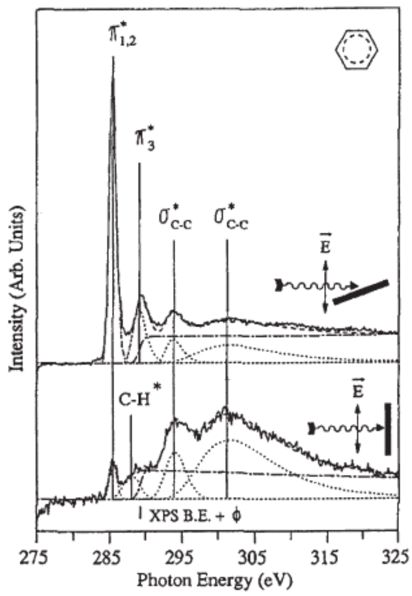


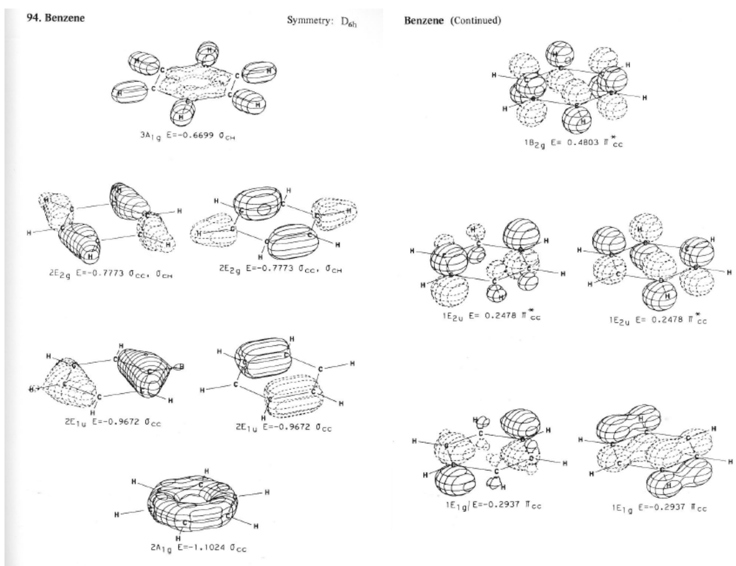
σ* and π* orbitals






Absorption probability
π*
σ*
Photon energy
hν
1s
Continuum
states
σ
π
π*
σ*
Rydberg
states
Ionization potential
Potential energy


$\pi^*_{1,2}$
π^*_3
σ^*_{C-C}
σ^*_{C-C}
E
C-H*
E
XPS B.E. + ϕ
Intensity (Arb. Units)
275
285
295
305
315
325
Photon Energy (eV)


94. Benzene
Symmetry: D_{6h}
Benzene (Continued)