Introduction to Soft X-ray Techniques (G. Held)

Exercises

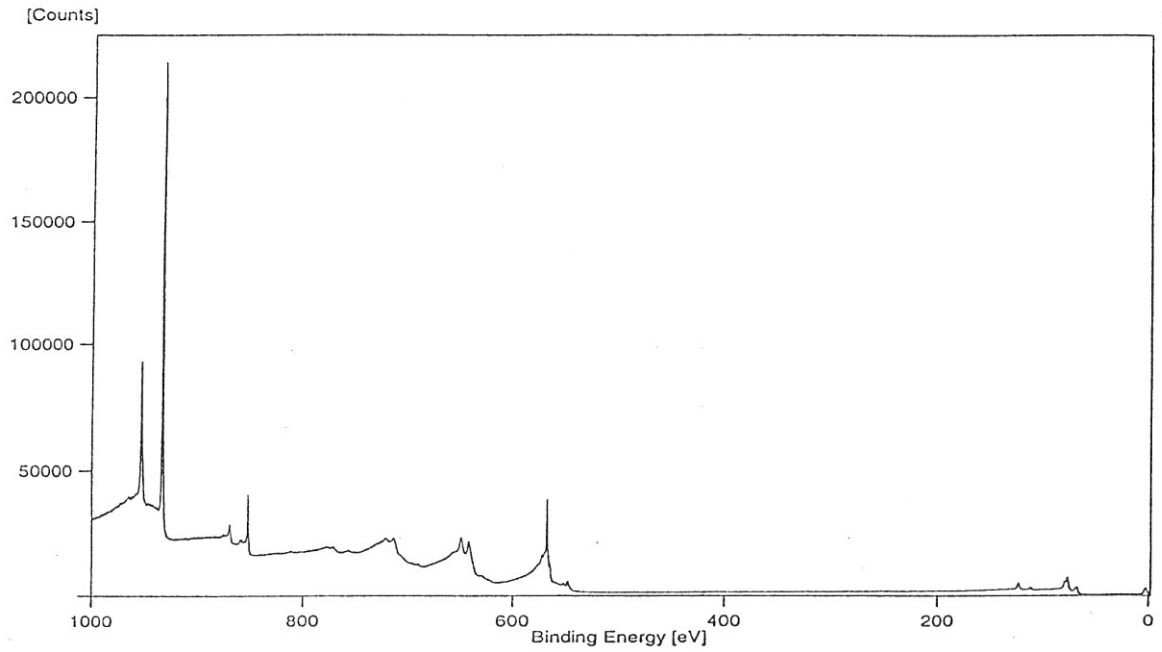
Question 1 (XPS)

Use a suitable labelled energy diagram to explain the energy transfer in the photoelectric effect and, from this derive an equation linking the kinetic energy of the emitted electron with the photon energy and the binding energy of the electron prior to excitation.

The Figure below shows a XP spectrum recorded using Al Kα X-ray radiation (1486.6 eV).

(a) Assign the main peaks above 800 eV and below 200 eV using the table of binding energies below and determine which 2 elements are present at the surface.

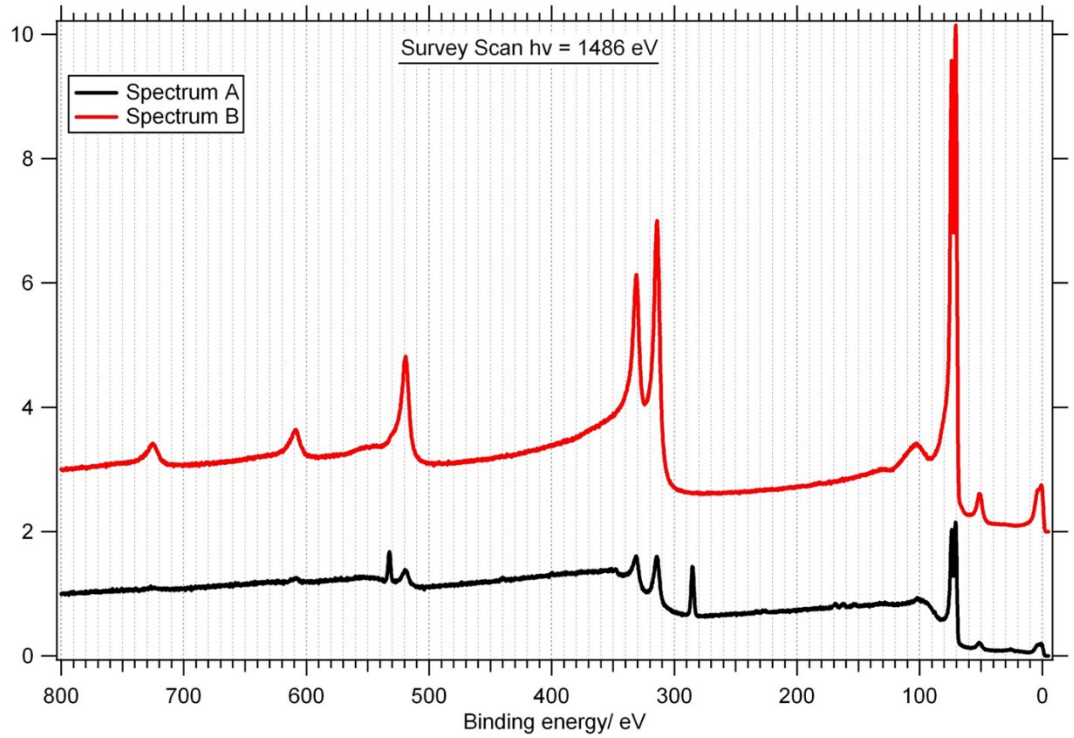
(b) Explain the peaks between 500 and 800 eV and assign them.



(c) How could one determine whether one atomic species is covering the other (layered structure) or both are present in the surface layer?

Question 2 (XPS)

Assign all the XPS peaks in the spectra below.
Why are there no Auger peaks in the spectra?



Question 3 (XPS)

(a) A thin film of PdO is grown on Pd foil when it is heated in a low pressure oxygen atmosphere. When foil is exposed to Mg Kα X-rays of hν = 1253.6 eV the photoelectron spectrum shows peaks at binding energies 335.2 eV, 336.5 eV, 340.5 eV, and 341.8 eV, which are assigned to Pd 3d lines (Pd $3d_{3/2}$ and Pd $3d_{5/2}$) of metallic Pd and PdO. The workfunction was measured to be 5 eV.

(i) Assign the binding energies to Pd and PdO, respectively, and justify your assignment.
(ii) Explain the reason for the splitting of the Pd 3d signal. What intensity ratio is expected between the Pd $3d_{3/2}$ and the Pd $3d_{5/2}$ signals?
(iii) Calculate the range of kinetic energies for the Pd 3d photoelectrons.

(b) When the foil is annealed in vacuum the sample is fully reduced and the Pd 3d photoelectron signal of metallic Pd increases by a factor of 7 with respect to the oxidised sample. Given that the inelastic mean free path of the photoelectrons through PdO is 1.7 nm, calculate the thickness of the PdO film on the oxidised sample.

Question 4 (NEXAFS)

CO has a strong NEXAFS resonance at 288 eV which is due to the excitation C 1s → 2π* (LUMO). When CO is adsorbed on a flat Ni single crystal surface at low temperatures this resonance is only observed if the polarisation vector of the X-ray beam has a component parallel to the surface. The resonance grows in intensity when the parallel component increases. For Ni powders exposed to CO the same resonance is observed for all orientations of the polarisation vector. Explain this behaviour using a diagram and discuss what conclusions can be drawn about the orientation of the molecules.

Question 5 (NEXAFS)

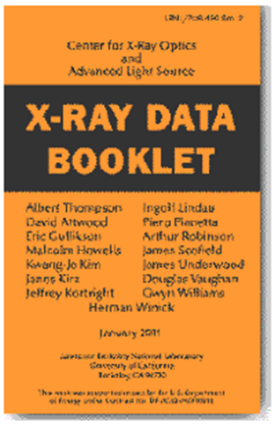
Chemisorbed layers of (aromatic) benzene molecules (C_6H_6) are adsorbed upright on iridium single crystal surfaces, whereby two of the 6 carbon atoms have lost their H atoms and form bonds with two nearest neighbour Ir atoms in the surface layer.
Draw the possible orientations of such benzene molecules on Ir{111}, Ir{100} and Ir{110} surfaces.

The NEXAFS signal of benzene has a strong resonance associated with the π electrons at 284 eV. The resonance is strongest when the polarization vector of the exciting X-ray beam is perpendicular to the molecular plane and changes proportional to $(\sin \gamma)^2$, where γ is the angle between the polarization vector and the molecular plane.

Which angular dependence of the resonance would one expect if the polarization vector is rotated within the surface plane:

(a) for a single molecule
(b) for equal numbers of molecules in all possible orientations on Ir{111}, {100} and {110}?

Binding Energies in eV



(on blackboard)

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$
1 H	13.6											
2 He	24.6*											
3 Li	54.7*											
4 Be	111.5*											
5 B	188*											
6 C	284.2*											
7 N	409.9*	37.3*										
8 O	543.1*	41.6*										
9 F	696.7*											
10 Ne	870.2*	48.5*	21.7*	21.6*								
11 Na	1070.8†	63.5†	30.65	30.81								
12 Mg	1303.0†	88.7	49.78	49.50								
13 Al	1559.6	117.8	72.95	72.55								
14 Si	1839	149.7*b	99.82	99.42								
15 P	2145.5	189*	136*	135*								
16 S	2472	230.9	163.6*	162.5*								
17 Cl	2822.4	270*	202*	200*								
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*		15.9*		15.7*			
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*		18.3*		18.3*			
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †		25.4†		25.4†			
21 Sc	4492	498.0*	403.6*	398.7*	51.1*		28.3*		28.3*			
22 Ti	4966	560.9†	460.2†	453.8†	58.7†		32.6†		32.6†			
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†					
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†					
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†					
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†					
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†					
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†	68.0†	66.2†					
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†					
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*			
31 Ga	10367	1299.0*b	1143.2†	1116.4†	159.5†	103.5†	100.0†	18.7†	18.7†			
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8	29.2			
33 As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*			
34 Se	12658	1652.0*b	1474.3*b	1433.9*b	229.6*	166.5*	160.7*	55.5*	54.6*			
35 Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*			
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*	27.5*	14.1*	14.1*
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*	30.5*	16.3*	15.3 *
38 Sr	16105	2216	2007	1940	358.7†	280.3†	270.0†	136.0†	134.2†	38.9†	21.3	20.1†
39 Y	17038	2373	2156	2080	392.0*b	310.6*	298.8*	157.7†	155.8†	43.8*	24.4*	23.1*
40 Zr	17998	2532	2307	2223	430.3†	343.5†	329.8†	181.1†	178.8†	50.6†	28.5†	27.1†
41 Nb	18986	2698	2465	2371	466.6†	376.1†	360.6†	205.0†	202.3†	56.4†	32.6†	30.8†
42 Mo	20000	2866	2625	2520	506.3†	411.6†	394.0†	231.1†	227.9†	63.2†	37.6†	35.5†
43 Tc	21044	3043	2793	2677	544*	447.6	417.7	257.6	253.9*	69.5*	42.3*	39.9*
44 Ru	22117	3224	2967	2838	586.1*	483.5†	461.4†	284.2†	280.0†	75.0†	46.3†	43.2†
45 Rh	23220	3412	3146	3004	628.1†	521.3†	496.5†	311.9†	307.2†	81.4*b	50.5†	47.3†
46 Pd	24350	3604	3330	3173	671.6†	559.9†	532.3†	340.5†	335.2†	87.1*b	55.7†a	50.9†
47 Ag	25514	3806	3524	3351	719.0†	603.8†	573.0†	374.0†	368.3	97.0†	63.7†	58.3†

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$	N_4 $4d_{3/2}$	N_5 $4d_{5/2}$	N_6 $4f_{5/2}$	N_7 $4f_{7/2}$	O_1 5s	O_2 $5p_{1/2}$	O_3 $5p_{3/2}$
48 Cd	26711	4018	3727	3538	772.0†	652.6†	618.4†	411.9†	405.2†	109.8†	63.9†a	63.9†a	11.7†	10.7†					
49 In	27940	4238	3938	3730	827.2†	703.2†	665.3†	451.4†	443.9†	122.9†	73.5†a	73.5†a	17.7†	16.9†					
50 Sn	29200	4465	4156	3929	884.7†	756.5†	714.6†	493.2†	484.9†	137.1†	83.6†a	83.6†a	24.9†	23.9†					
51 Sb	30491	4698	4380	4132	946†	812.7†	766.4†	537.5†	528.2†	153.2†	95.6†a	95.6†a	33.3†	32.1†					
52 Te	31814	4939	4612	4341	1006†	870.8†	820.0†	583.4†	573.0†	169.4†	103.3†a	103.3†a	41.9†	40.4†					
53 I	33169	5188	4852	4557	1072*	931*	875*	630.8	619.3	186*	123*	123*	50.6	48.9					
54 Xe	34561	5453	5107	4786	1148.7*	1002.1*	940.6*	689.0*	676.4*	213.2*	146.7	145.5*	69.5*	67.5*	—	—	23.3*	13.4*	12.1*
55 Cs	35985	5714	5359	5012	1211*b	1071*	1003*	740.5*	726.6*	232.3*	172.4*	161.3*	79.8*	77.5*	—	—	22.7	14.2*	12.1*
56 Ba	37441	5989	5624	5247	1293*b	1137*b	1063*b	795.7†	780.5*	253.5†	192	178.6†	92.6†	89.9†	—	—	30.3†	17.0†	14.8†
57 La	38925	6266	5891	5483	1362*b	1209*b	1128*b	853*	836*	274.7*	205.8	196.0*	105.3*	102.5*	—	—	34.3*	19.3*	16.8*
58 Ce	40443	6549	6164	5723	1436*b	1274*b	1187*b	902.4*	883.8*	291.0*	223.2	206.5*	109*	—	0.1	0.1	37.8	19.8*	17.0*
59 Pr	41991	6835	6440	5964	1511	1337	1242	948.3*	928.8*	304.5	236.3	217.6	115.1*	115.1*	2.0	2.0	37.4	22.3	22.3
60 Nd	43569	7126	6722	6208	1575	1403	1297	1003.3*	980.4*	319.2*	243.3	224.6	120.5*	120.5*	1.5	1.5	37.5	21.1	21.1
61 Pm	45184	7428	7013	6459	—	1471	1357	1052	1027	—	242	242	120	120	—	—	—	—	—
62 Sm	46834	7737	7312	6716	1723	1541	1420	1110.9*	1083.4*	347.2*	265.6	247.4	129	129	5.2	5.2	37.4	21.3	21.3
63 Eu	48519	8052	7617	6977	1800	1614	1481	1158.6*	1127.5*	360	284	257	133	127.7*	0	0	32	22	22
64 Gd	50239	8376	7930	7243	1881	1688	1544	1221.9*	1189.6*	378.6*	286	271	—	142.6*	8.6*	8.6*	36	28	21
65 Tb	51996	8708	8252	7514	1968	1768	1611	1276.9*	1241.1*	396.0*	322.4*	284.1*	150.5*	150.5*	7.7*	2.4*	45.6*	28.7*	22.6*
66 Dy	53789	9046	8581	7790	2047	1842	1676	1333	1292.6*	414.2*	333.5*	293.2*	153.6*	153.6*	8.0*	4.3*	49.9*	26.3	26.3
67 Ho	55618	9394	8918	8071	2128	1923	1741	1392	1351	432.4*	343.5	308.2*	160*	160*	8.6*	5.2*	49.3*	30.8*	24.1*
68 Er	57486	9751	9264	8358	2207	2006	1812	1453	1409	449.8*	366.2	320.2*	167.6*	167.6*	—	4.7*	50.6*	31.4*	24.7*
69 Tm	59390	10116	9617	8648	2307	2090	1885	1515	1468	470.9*	385.9*	332.6*	175.5*	175.5*	—	4.6	54.7*	31.8*	25.0*
70 Yb	61332	10486	9978	8944	2398	2173	1950	1576	1528	480.5*	388.7*	339.7*	191.2*	182.4*	2.5*	1.3*	52.0*	30.3*	24.1*

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$	N_4 $4d_{3/2}$	N_5 $4d_{5/2}$	N_6 $4f_{5/2}$	N_7 $4f_{7/2}$	O_1 5s	O_2 $5p_{1/2}$	O_3 $5p_{3/2}$	O_4 $5d_{3/2}$	O_5 $5d_{5/2}$	P_1 6s	P_2 $6p_{1/2}$	P_3 $6p_{3/2}$
71 Lu	63314	10870	10349	9244	2491	2264	2024	1639	1589	506.8*	412.4*	359.2*	206.1*	196.3*	8.9*	7.5*	57.3*	33.6*	26.7*					
72 Hf	65351	11271	10739	9561	2601	2365	2108	1716	1662	538*	438.2†	380.7†	220.0†	211.5†	15.9†	14.2†	64.2†	38*	29.9†					
73 Ta	67416	11682	11136	9881	2708	2469	2194	1793	1735	563.4†	463.4†	400.9†	237.9†	226.4†	23.5†	21.6†	69.7†	42.2*	32.7†					
74 W	69525	12100	11544	10207	2820	2575	2281	1872	1809	594.1†	490.4†	423.6†	255.9†	243.5†	33.6*	31.4†	75.6†	45.3*b	36.8†					
75 Re	71676	12527	11959	10535	2932	2682	2367	1949	1883	625.4†	518.7†	446.8†	273.9†	260.5†	42.9*	40.5*	83†	45.6*	34.6*b					
76 Os	73871	12968	12385	10871	3049	2792	2457	2031	1960	658.2†	549.1†	470.7†	293.1†	278.5†	53.4†	50.7†	84*	58*	44.5†					
77 Ir	76111	13419	12824	11215	3174	2909	2551	2116	2040	691.1†	577.8†	495.8†	311.9†	296.3†	63.8†	60.8†	95.2*b	63.0*b	48.0†					
78 Pt	78395	13880	13273	11564	3296	3027	2645	2202	2122	725.4†	609.1†	519.4†	331.6†	314.6†	74.5†	71.2†	101.7*b	65.3*b	51.7†					
79 Au	80725	14353	13734	11919	3425	3148	2743	2291	2206	762.1†	642.7†	546.3†	353.2†	335.1†	87.6†	84.0	107.2*b	74.2†	57.2†					
80 Hg	83102	14839	14209	12284	3562	3279	2847	2385	2295	802.2†	680.2†	576.6†	378.2†	358.8†	104.0†	99.9†	127†	83.1†	64.5†	9.6†	7.8†			
81 Tl	85530	15347	14698	12658	3704	3416	2957	2485	2389	846.2†	720.5†	609.5†	405.7†	385.0†	122.2†	117.8†	136.0*b	94.6†	73.5†	14.7†	12.5†			
82 Pb	88005	15861	15200	13035	3851	3554	3066	2586	2484	891.8†	761.9†	643.5†	434.3†	412.2†	141.7†	136.9†	147*b	106.4†	83.3†	20.7†	18.1†			
83 Bi	90524	16388	15711	13419	3999	3696	3177	2688	2580	939†	805.2†	678.8†	464.0†	440.1†	162.3†	157.0†	159.3*b	119.0†	92.6†	26.9†	23.8†			
84 Po	93105	16939	16244	13814	4149	3854	3302	2798	2683	995*	851*	705*	500*	473*	184*	184*	177*	132*	104*	31*	31*			
85 At	95730	17493	16785	14214	4317	4008	3426	2909	2787	1042*	886*	740*	533*	507	210*	210*	195*	148*	115*	40*	40*			
86 Rn	98404	18049	17337	14619	4482	4159	3538	3022	2892	1097*	929*	768*	567*	541*	238*	238*	214*	164*	127*	48*	48*	26		
87 Fr	101137	18639	17907	15031	4652	4327	3663	3136	3000	1153*	980*	810*	603*	577*	268*	268*	234*	182*	140*	58*	58*	34	15	15
88 Ra	103922	19237	18484	15444	4822	4490	3792	3248	3105	1208*	1058	879*	636*	603*	299*	299*	254*	200*	153*	68*	68*	44	19	19
89 Ac	106755	19840	19083	15871	5002	4656	3909	3370	3219	1269*	1080*	890*	675*	639*	319*	319*	272*	215*	167*	80*	80*	—	—	—
90 Th	109651	20472	19693	16300	5182	4830	4046	3491	3332	1330*	1168*	966.4†	712.1†	675.2†	342.4†	333.1†	290*a	229*a	182*a	92.5†	85.4†	41.4†	24.5†	16.6†
91 Pa	112601	21105	20314	16733	5367	5001	4174	3611	3442	1387*	1224*	1007*	743*	708*	371*	360*	310*	232*	232*	94*	94*	—	—	—
92 U	115606	21757	20948	17166	5548	5182	4303	3728	3552	1439*b	1271*b	1043†	778.3†	736.2†	388.2*	377.4†	321*ab	257*ab	192*ab	102.8†	94.2†	43.9†	26.8†	16.8†