

## CEM 924 (Spring 2001) - Problem Set #3 (KEY)

- (1) (a) (5 points) XPS is usually performed using soft x-ray radiation from either a Mg or Al anode. What are the characteristic photon energies of the K<sub>1,2</sub> lines from these materials?

$$\text{Mg K}_{1,2} = 1253.6 \text{ eV}, \text{ Al K}_{1,2} = 1486.6 \text{ eV}$$

- (b) (5 points) The Mg K<sub>1,2</sub> line is really an unresolved doublet in which the K<sub>1</sub> line is more intense than the K<sub>2</sub> line. Which atomic transition is associated with each of these lines? From what you know about spin-orbit splitting, will the K<sub>1</sub> or K<sub>2</sub> line have the highest photon energy?

The transitions responsible for the K<sub>1</sub> peak is a Mg 2p<sub>3/2</sub> → 1s transition of highest photon energy. The transition responsible for the K<sub>2</sub> peak is a Mg 2p<sub>1/2</sub> → 1s transition of lower photon energy.

- (c) (10 points) Write down the atomic and x-ray notation for the expected spin-orbit split levels corresponding to a subshell with quantum numbers  $n = 4$ , and  $l = 3$ .

There are two levels given by  $n l_j$  where  $j = |l \pm s|$ . 4f<sub>7/2</sub> and 4f<sub>5/2</sub>. The x-ray notation for these levels are N<sub>7</sub> and N<sub>6</sub>, respectively.

- (d) (10 points) Using Mg K<sub>1,2</sub> radiation, photoelectrons with kinetic energies of 1165.5 eV and 1161.9 eV are observed from a pure metal. Assuming the workfunction of this metal is 4.3 eV, what are the binding energies of these peaks? What kinetic and binding energies would be measured using Al K<sub>1,2</sub> radiation?

$$\begin{aligned} \text{KE} &= h\nu - \text{BE} - \phi \\ \text{BE} &= h\nu - \phi - \text{KE} \\ &= 1253.6 - 4.3 - 1165.5 \\ &= 83.8 \text{ eV} \\ &= 1253.6 - 4.3 - 1161.9 \\ &= 87.4 \text{ eV} \end{aligned}$$

Using Al radiation, the measured BE's would be the same (since they are unique to each element) but the KE's would be

$$\begin{aligned} \text{KE} &= h\nu - \text{BE} - \phi \\ &= 1486.6 - 83.8 - 4.3 \\ &= 1398.5 \text{ eV} \\ &= 1486.6 - 87.5 - 4.3 \\ &= 1394.8 \text{ eV} \end{aligned}$$

- (e) (5 points) The two peaks in part (d) above form a doublet and have experimentally measured peak areas of 1023 and 766 counts·s<sup>-1</sup>·eV. From what subshell (1s, 2s, 2p etc.) do these peaks originate?

Spin-orbit coupling splits the p, d, f... subshells into a doublet and the intensities observed in each corresponds to the degeneracy of each subshell,  $2j+1$ . In this case, the ratio of the areas is  $766/1023=0.748$  or very close to  $3/4$ . This is the ratio expected for the spin-orbit split f electrons since  $j = |l \pm s| = 7/2$  or  $5/2$  for f electrons so  $2j+1 = 6$  or  $8$  (check: there are 14 f electrons). You cannot determine  $n$  so we don't know if these are 4f, 5f, 6f... electrons.

(f) (5 points) Would you expect the binding energy of the doublet in part (e) to be higher or lower in an element with higher atomic number  $Z$ ? Explain. Would you expect the spin-orbit splitting (the separation between the doublet peaks) to be larger or smaller in an element with higher  $Z$ ? Explain.

The binding energies of the doublet would be higher - a higher  $Z$  implies increased nuclear charge which attracts all electrons more strongly. Similarly, since spin-orbit coupling depends on nuclear charge, the magnitude of the coupling increases with binding energy - the spin-orbit splitting will be larger for the higher  $Z$  element.

- (2) (a) (10 points) A thin film of Ag was deposited onto a clean Pt surface in a layer-by-layer fashion and the surface investigated by Al  $K_{1,2}$  excited XPS. The intensity of the original Pt  $4p_{1/2}$  (BE = 610 eV) peak was still observed but with only 25 % of the intensity of the original uncoated surface. If the electron energy analyzer was set to collect photoelectrons emitted at  $30^\circ$  from the surface normal, what was the thickness of the film? (You will have to estimate an inelastic mean free path,  $\lambda$ , for the photoelectrons)

$$I = I_0 \exp \frac{-d}{\lambda \sin \theta}$$

$$\ln \frac{I}{I_0} = \frac{-d}{\lambda \sin \theta}$$

$$\ln 0.25 = \frac{-d}{\lambda \sin 60}$$

Examination of the "universal curve" for electrons of about 875 eV KE (1486 - 610 eV) gives an estimate for  $\lambda$  of about  $15 \text{ \AA}$ . Therefore

$$\ln 0.25 \sin 60 = \frac{-d}{\lambda}$$

$$\frac{d}{\lambda} = 1.2$$

$$d = 18 \text{ \AA}$$

- (3) Briefly define (two or three sentences) the following terms:

(a) (2 points) X-ray satellite

"Ghost peaks" (weak features) created in the XPS spectrum (low BE side) due to the presence of various emission lines in a non-monochromatic x-ray source

(b) (2 points) Shake-up satellite

Satellite feature that appears at higher BE than main line and associated with electronic excitation during the photoemission process

(c) (2 points) Electron energy analyzer pass energy

The energy that all electrons are decelerated to before entering a hemispherical analyzer. Electrons with the pass energy travel the central path between the hemispheres.

(d) (2 points) Sampling depth

The depth from which approximately 95 % of all the photoelectrons of energy KE originated. Equivalent to  $3\lambda$  since  $-\ln(0.05) = 3$ .

(e) (2 points) Core level chemical shift

Perturbation of the BE's of all core levels due to modulation of the net charge on the atom by chemical environment (number and nature of substituents/neighbors)

- (4) (10 points) Using XPS analysis, I obtained the following 1s binding energies and component peak areas for an organic sample. No other peaks were observed. Using the abbreviated table of binding energies for organic samples given in the lecture notes (page 9.17), and the table of atomic sensitivity factors (page 9.35), suggest a reasonable structure for the material based on a calculated stoichiometry.

Peak Binding Energy (eV)	Area (counts·s <sup>-1</sup> ·eV)
285.0 (C-H)	102,945
289.0 (O-C=O)	24,998
293.5 (CF <sub>3</sub> )	25,770
532.2 (C=O)	79,195
532.8 (C-OH)	80,044
690.0 (F)	366,330

You do not need the identity of the 690.0 eV peak but can you suggest an identity?

Stoichiometry obtained after dividing each Area by the ASF value for that core level - 4 aliphatic C, 1 acid C, 1 fluorinated C, 1 carbonyl O, 1 alcohol O, 3 F. A possible structure might be CF<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>H. The missing peak at 690 eV must be F (not H).

Total 70 points