Lecture 14
Some typical XPS studies
Photoelectron spectroscopy is surface sensitive, to the extent that it can distinguish monolayers. It is also possible to distinguish one layer from the next layer, etc.
Surface sensitivity enhancement is possible by tilting the sample.

Fig. 2.32. Surface sensitivity of XPS, demonstrated by changing the electron detection angle relative to the surface for a slightly oxidized surface of Al. At 7.5°, the Al 2s signals from Al metal and oxidized Al have the same magnitude, while at 51.5° the oxide signal is hardly visible [2.74].
We can study evolution of surface species. This helps us to understand the origin of reactivity.

Fig. 2.33. Oxidation of a (111) surface of Al monitored via the Al 2p level with $h\omega = 130$ eV synchrotron radiation [2.75]. The development of a chemisorbed state and subsequent oxide formation can be observed.
The difference between the main line and the satellite is the same for several core holes indicating that the configurations are the same.

Fig. 3.13. XPS spectra of the 3d, 3p, 3s, 2p\textsubscript{3/2} and 2p\textsubscript{1/2} levels of Ni metal [3.10]. The main lines have been lined up to demonstrate the constant distance of the satellite position (even for the 3d valence band)
This is explained schematically here.

Fig. 3.14. Schematic density of states of Ni, indicating the origin of the main line and the satellite for core ionization (c⁻¹); for valence band ionization see also Fig. 3.19. The initial state is c3d⁹4s and the two final states are c⁻¹3d⁹4s² (satellite) and c⁻¹3d¹⁰4s (main line); c denotes a core level, c⁻¹ a core hole.
Satellite can be used to distinguish oxidation state.

Fig. 3.2. XPS spectrum of the Cu 2p<sub>1/2</sub>–2p<sub>3/2</sub> core levels in Cu<sub>2</sub>O (bottom) with a d<sup>10</sup> configuration and CuO (top) with a d<sup>9</sup> configuration [3.32]. The CuO spectrum shows strong satellites.
Multiplet slitting can be complex, but comparison with the elements can help.
Multiplet can arise in the XPS valence band of simple solids.
Evolution of band structure

CH$_4$ $(1s\ a_1)^2\ (2s\ a_1)^2\ (2p\ t_2)^6$
C$_2$H$_6$ $(1a_2n)^2\ (1a_1g)^2\ (2a_1g)^2\ (2a_2n)^2$
$(1e_n)^4\ (3a_1g)^2\ (1e_g)^4/2p$

Fig.5.20. (a) EDCs of a number of linear polymers [5.30]: CH$_4$, C$_2$H$_6$, C$_3$H$_8$ and C$_4$H$_{10}$; (b) comparison with the ab initio calculation of their valence bands. The C 2s orbital nicely shows the splitting expected into 1, 2, 3 and 4 levels. (c) For higher members of this family the single orbitals originating from the C 2s level can no longer be resolved and lead to a structure seen e.g. in the gas phase spectrum of C$_{13}$H$_{28}$. This spectrum is very similar to the one observed in solid samples such as C$_{38}$H$_7$. 
You can see the orbitals clearly in UPS

Fig. 5.21. UPS (21.2eV) spectrum of \( \text{C}_2\text{H}_6 \) to study the structure in the 2p-derived orbitals [5.1]. The three expected orbitals can barely be discerned.