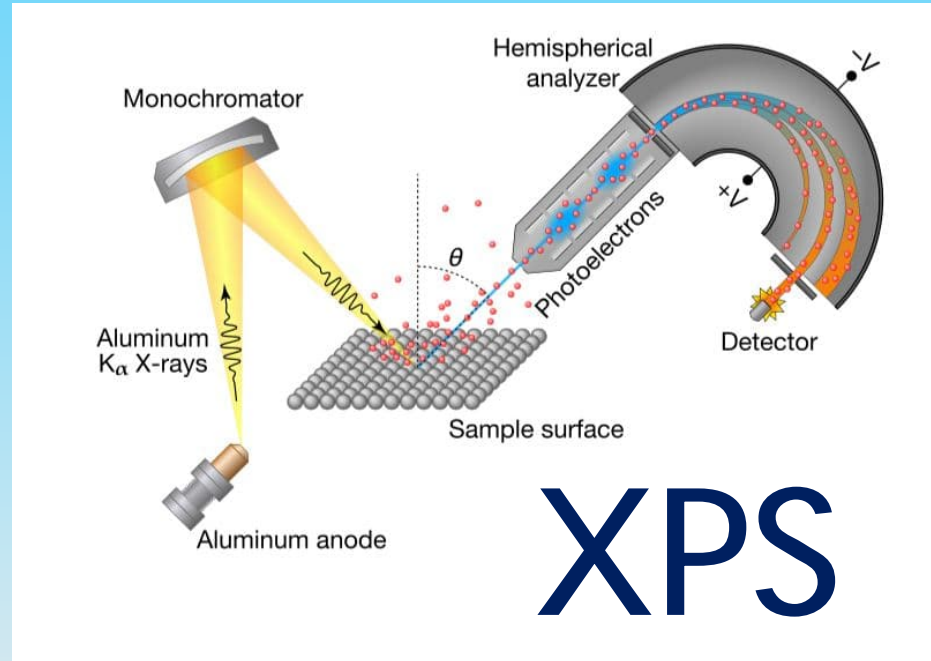


CHEM-E4205 Crystallography Basics and Structural Characterization



Outline

- ❖ *Principle of the technique*
- ❖ *Type of information gained*
- ❖ *Interpretation of data*
- ❖ *Strengths and limitations*

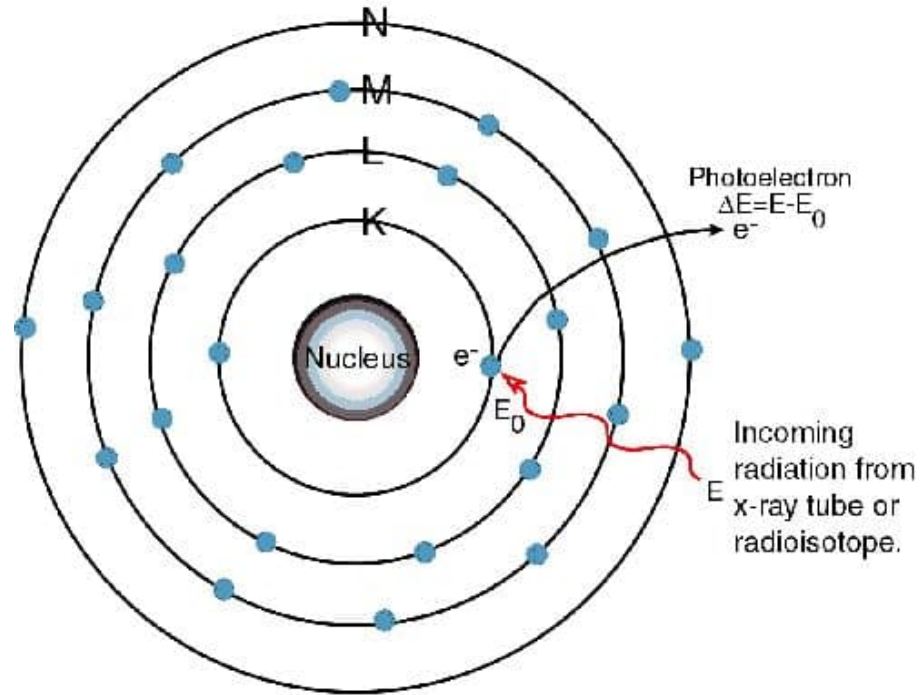
Introduction to the concept

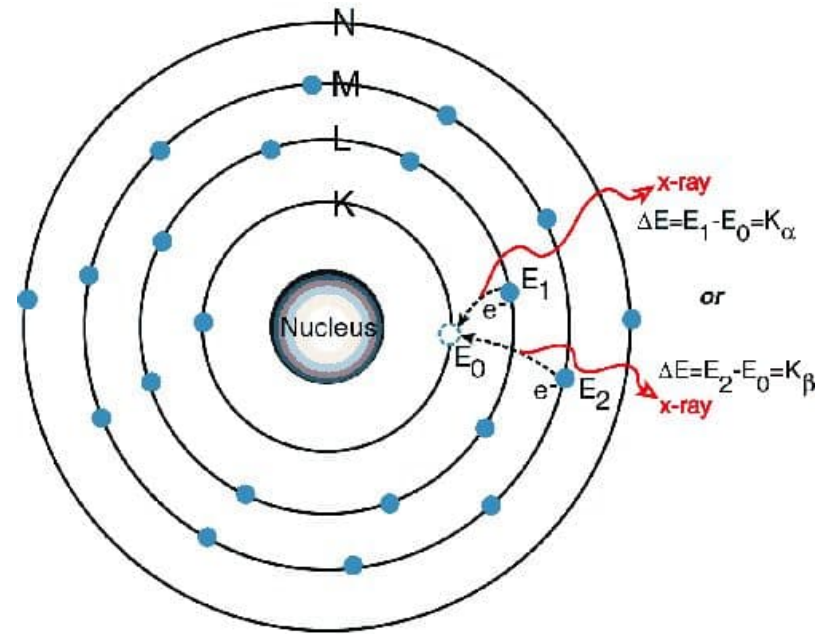
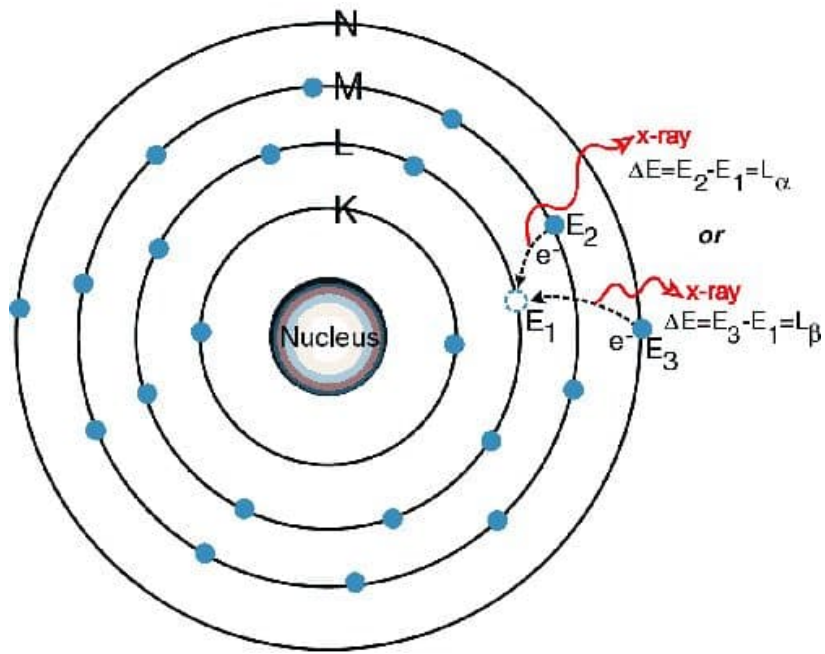
- XPS - X ray Photoelectron Spectroscopy.
- One of the major chemical characterization techniques of surfaces and thin films.
- Provide information of chemical bonding and valence state.
- Known as ESCA-(**Electron Spectroscopy for Chemical Analysis**).

| XPS | |
|------------------------------|-------------------------------------|
| Elemental sensitivity | Li-U |
| Detection limit | 0.1-1 atom % |
| Lateral resolution | 100 μm |
| Effective probe depth | <10nm |

Theory of XPS

- Based on atomic core-electron spectroscopy.





- Consider about the electron transition by emitting X-rays.
 - K_α X-rays, $L \longrightarrow K$
 - K_β X-rays, $M \longrightarrow K$
 - L_α X-rays, $M \longrightarrow L$

Facts:

1. The energy difference between the levels involved in the electron transition determines the energy of the emitted X-ray.
2. The emitted X-rays are characteristic of the particular atom undergoing emission.

- Characteristic X rays known as fluorescent X rays when excited by incident photons.
- X rays have relatively low energy.

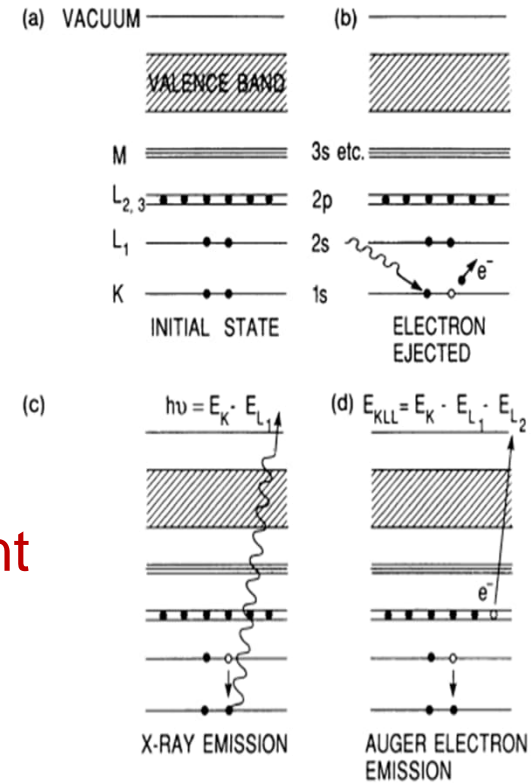
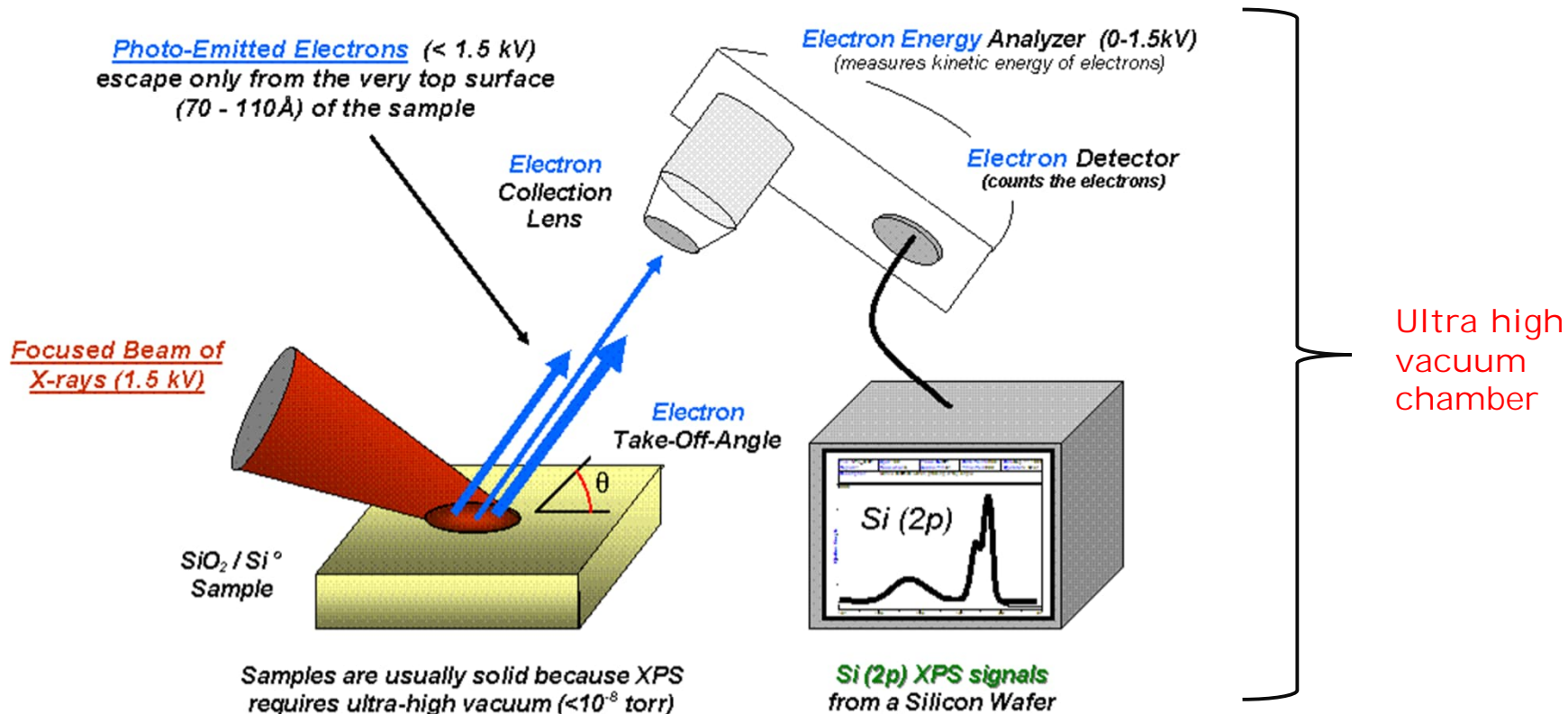


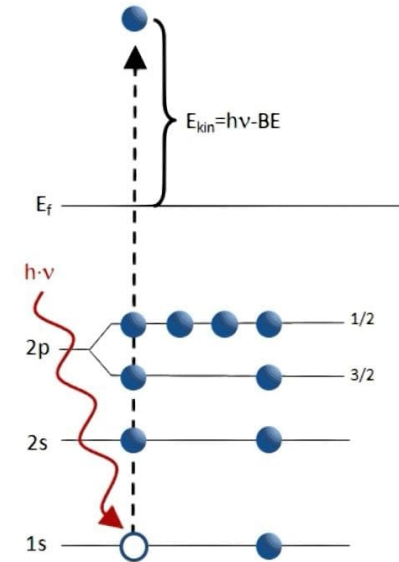
Figure 10-24 Schematic of electron energy transitions: (a) initial state; (b) incident photon (or electron) ejects K shell electron; (c) X-ray emission when 2s electron fills vacancy; (d) Auger electron emission. KLL transition shown.



Excitation source : beam of Mg or Al K α X-rays
 Eject photoelectrons from the outermost atomic orbitals of the atoms in the sample - **photoelectric effect.**

- ❖ Detect the number of emitted photoelectrons and kinetic energy of them. **Quantitative and Qualitative detection**
- ❖ The x rays have sufficient energy ($h\nu$) to ionize core electrons(BE) and kinetic energy of ejected electrons (KE)

$$BE = h\nu - KE$$



- ❖ Identification of elements possible as binding energies of the core electrons are unique for every element.

XPS Spectra

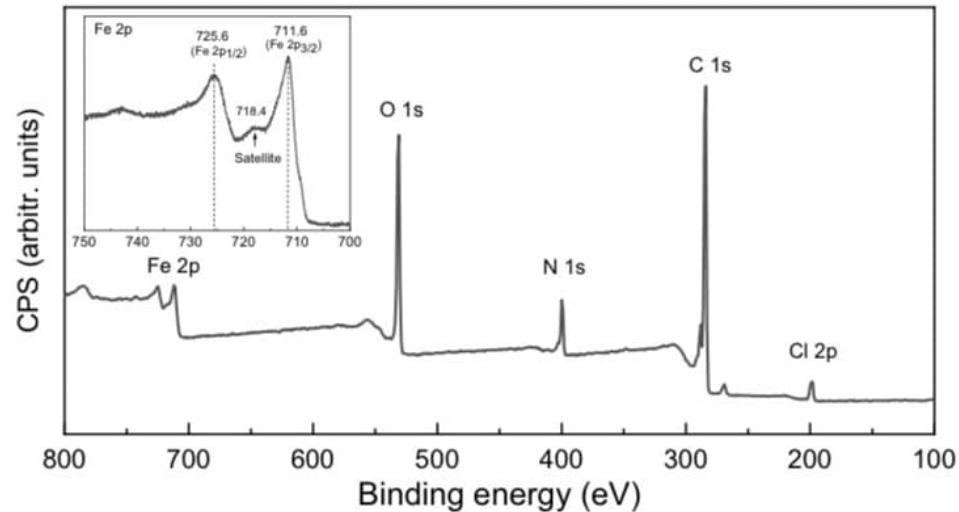
Only detect electrons that escape from the sample.

Elemental signals from the surface are stronger than deeper in the sample.

The X axis (**Peak position**) : Binding energy (eV) – **plot from the highest to the lowest.**

The Y axis (**Peak intensity**) : total number of photoelectron counts per second.

Peaks have discrete well defined energies



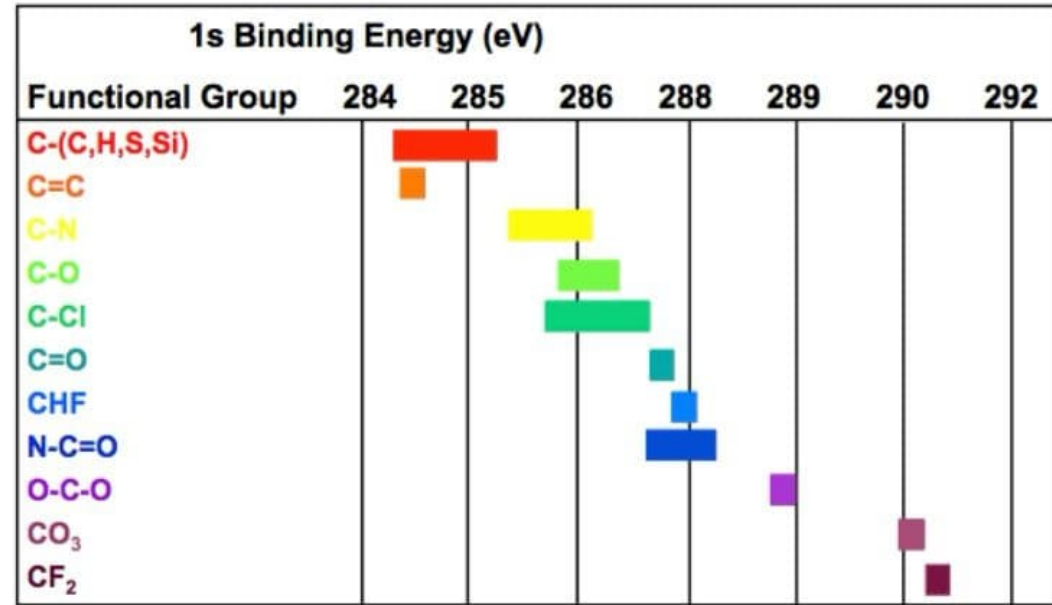
XPS Analysis

- ❖ Peaks indicate the presence of a specific element on the sample.
- ❖ Intensity of peaks is directly related to the concentration of the element within the sampled region.
- ❖ **Line widths are considerably narrow – high resolution analysis.**
- ❖ The shape of each peak and the binding energy can be slightly altered by the chemical bonding with neighboring atoms and the valence of these atoms – **chemical shift**.

Chemical shift

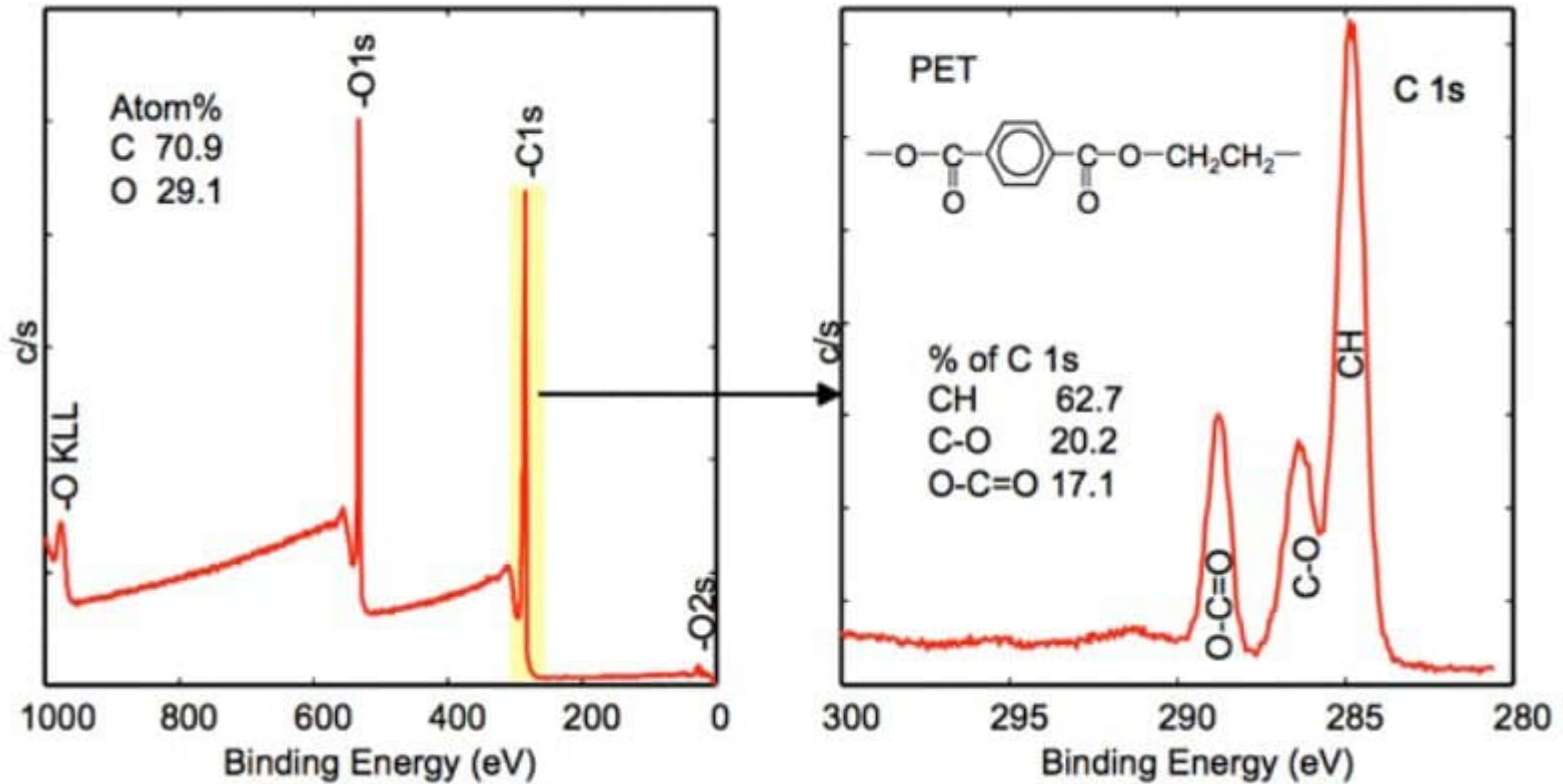
Change of binding energy of core electron due to the change of chemical environment.

- ❖ Binding energy increases with electronegativity of neighboring atoms.
- ❖ Higher valence oxidation state species has high binding energy compared with more reduced state



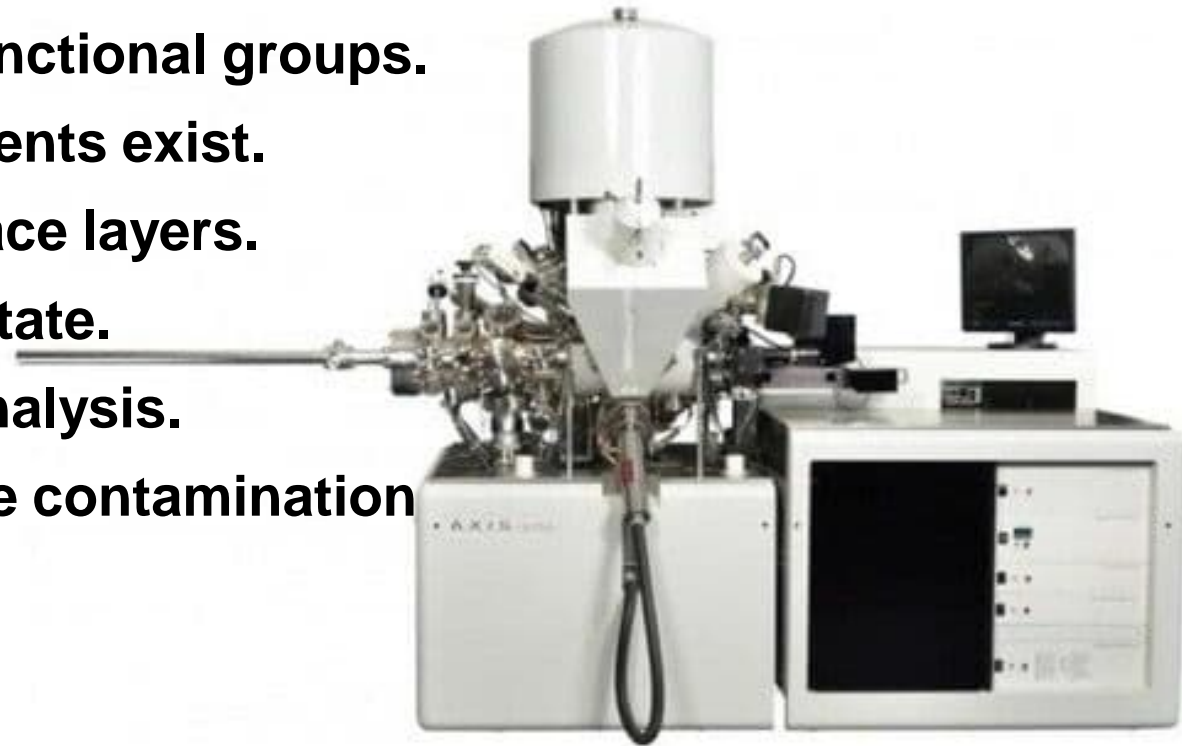
Carbon chemical state (C1s binding energy shift (chemical shift))

Chemical bonding information can be determined from the chemical shift.- ESCA



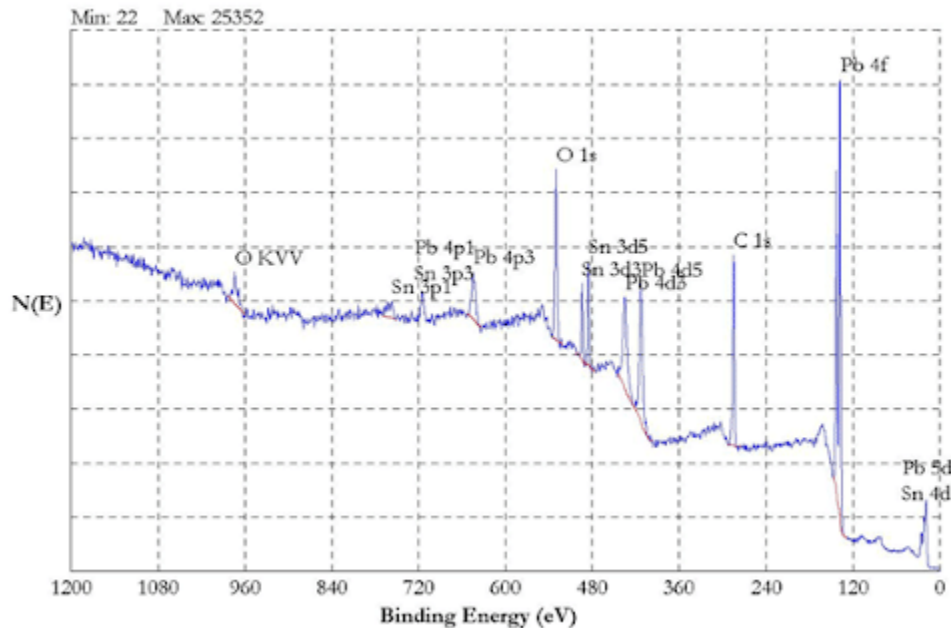
Information from XPS

- ✓ Elemental composition.
- ✓ Chemical bonding information.
- ✓ Detection of surface functional groups.
- ✓ Chemical state of elements exist.
- ✓ Depth profiling of surface layers.
- ✓ Analysis of oxidation state.
- ✓ Surface morphology analysis.
- ✓ Identification of surface contamination



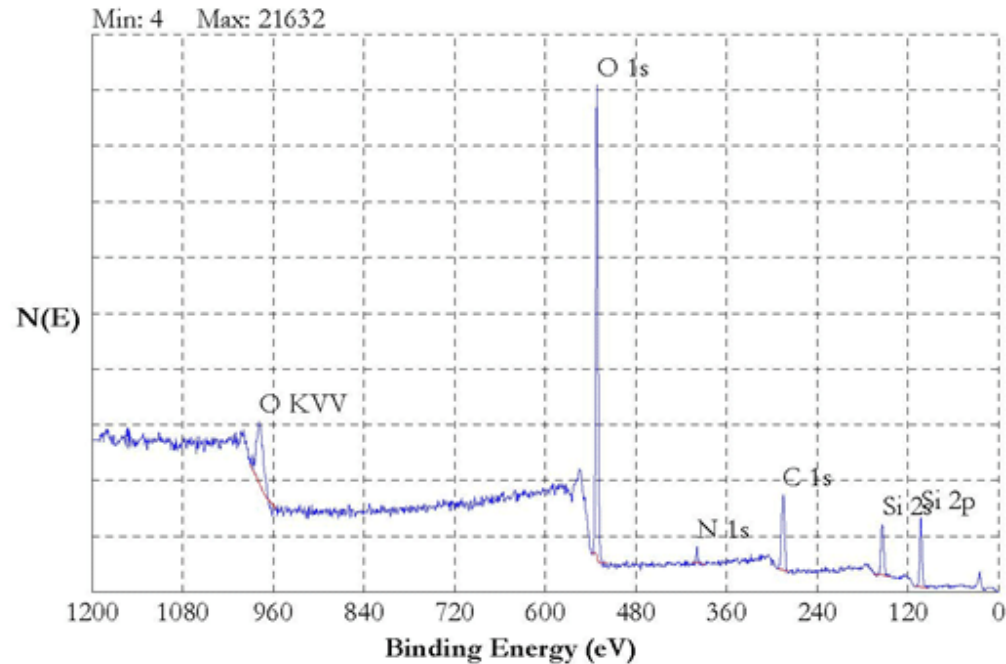
Interpretation of Data

- Peak position → elemental composition
- Peak Area → concentration/proportion of element
- Overlapping peaks → use peak models



Interpretation of Data

- More than one elemental peak → select transition with largest peak



- Some instrumentation have peak identification feature. Otherwise standards of different material required.

Interpretation of Data

➤ **Satellite peak**

- provide information about electronic structure and chemical bonding

➤ **Auger lines**

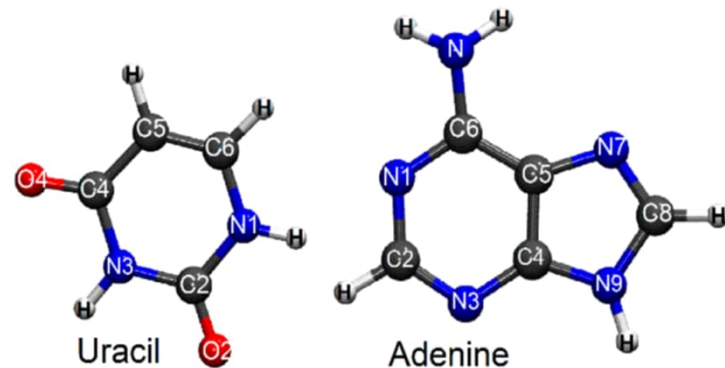
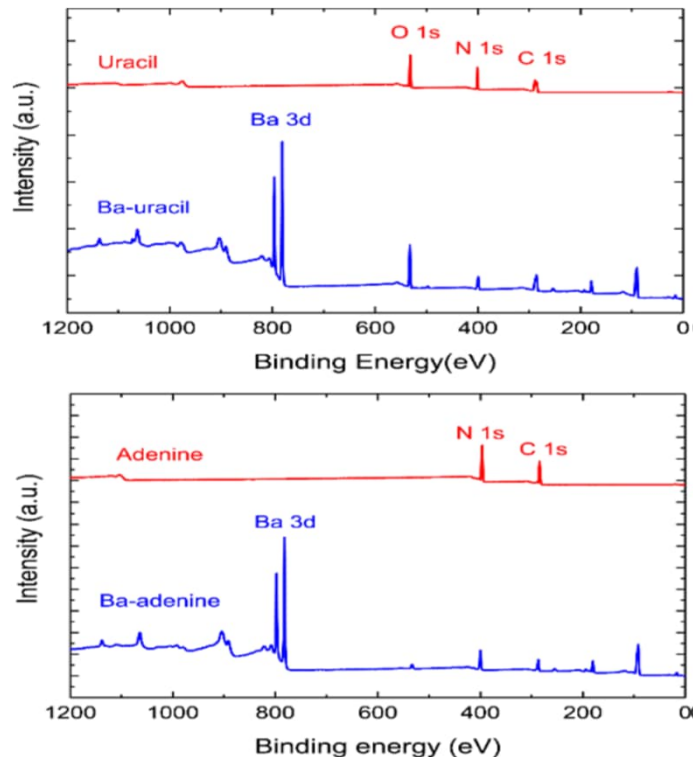
- Arise due to intra atom transitions
- 2 different x-ray sources needs to distinguish auger peaks from photoelectron peaks

➤ **Energy loss lines**

- Arise due to inelastic scattering process
- Provide information on electronic structure

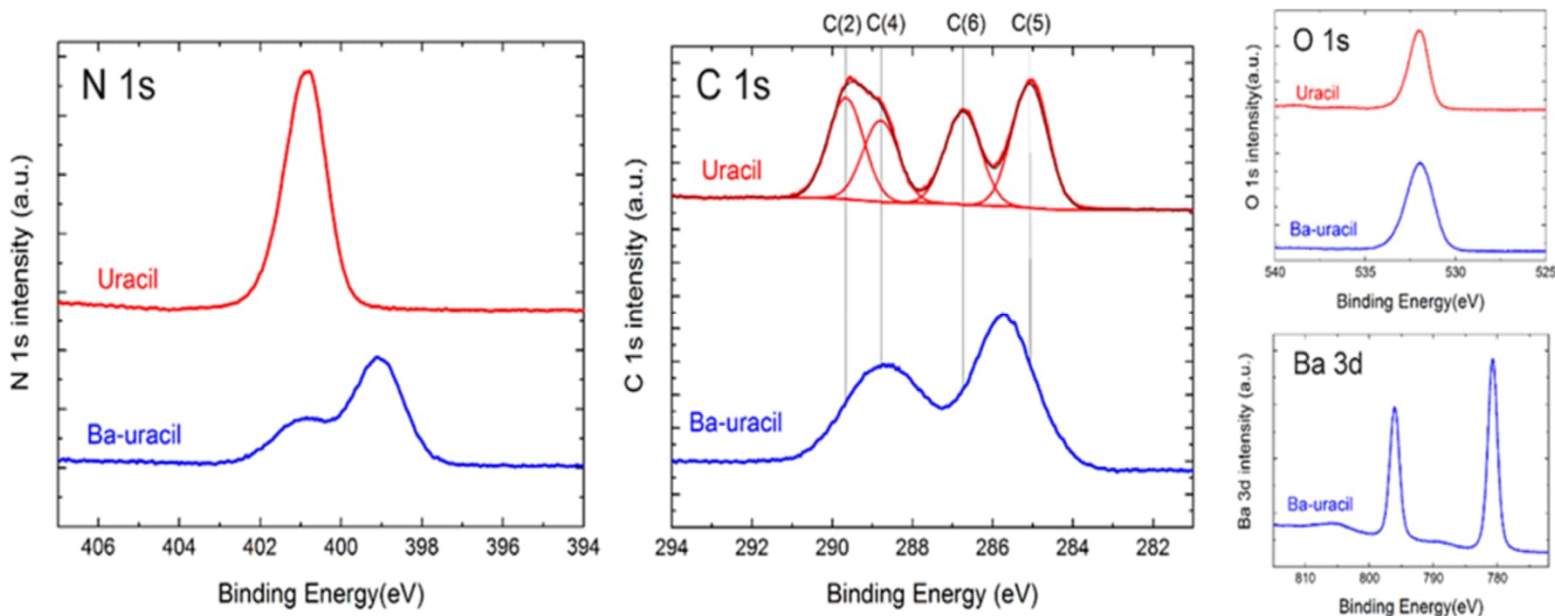
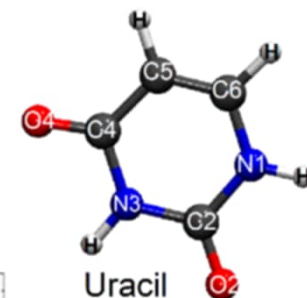
Interpretation of Data

1. Luminescent Metal-nucleobase network thin films by Atomic/molecular layer deposition



XPS survey spectra for the Ba-uracil and Ba-adenine thin films as well as for the uracil and adenine precursors for comparison.

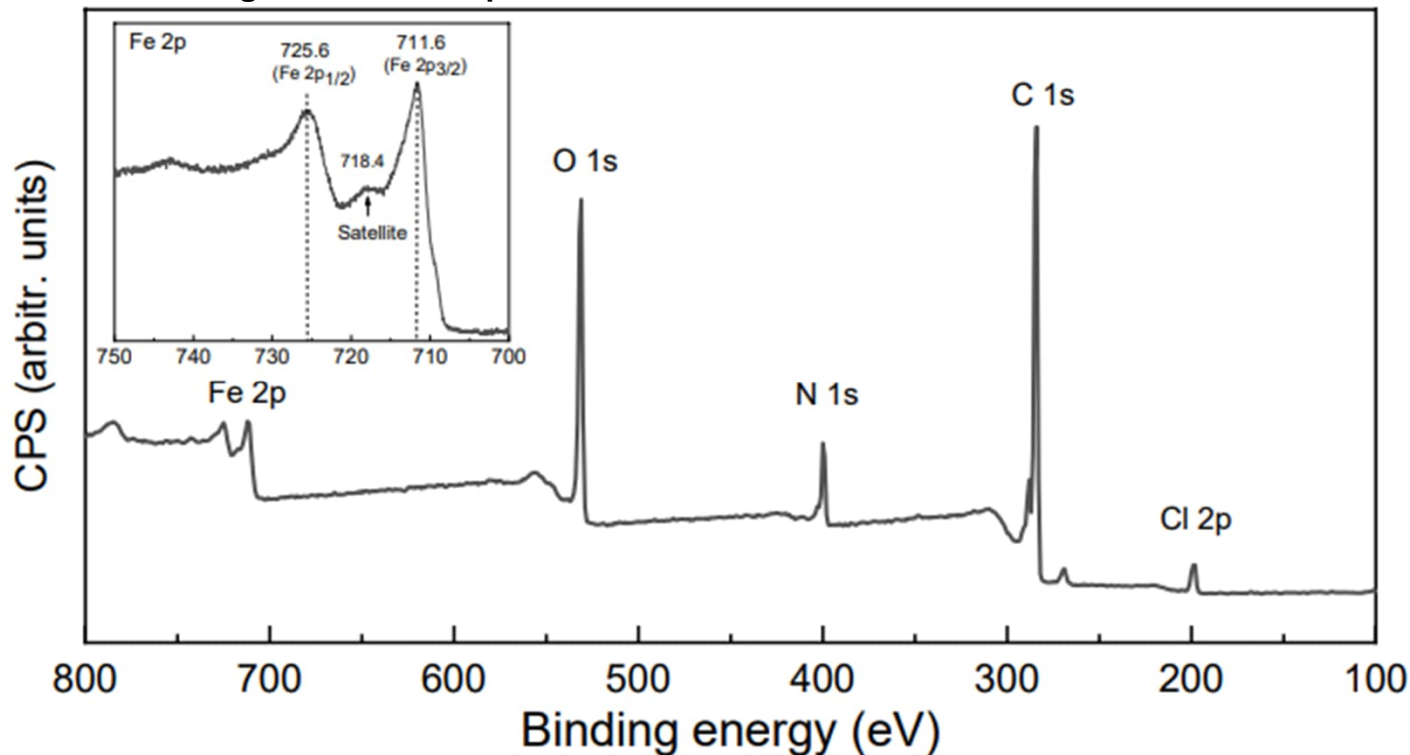
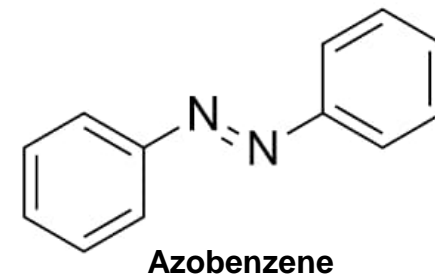
Interpretation of Data



spectra of the N 1s, C 1s, O 1s, and Ba 3d regions for uracil (top, red) and of Ba-uracil film (bottom, blue)

Interpretation of Data

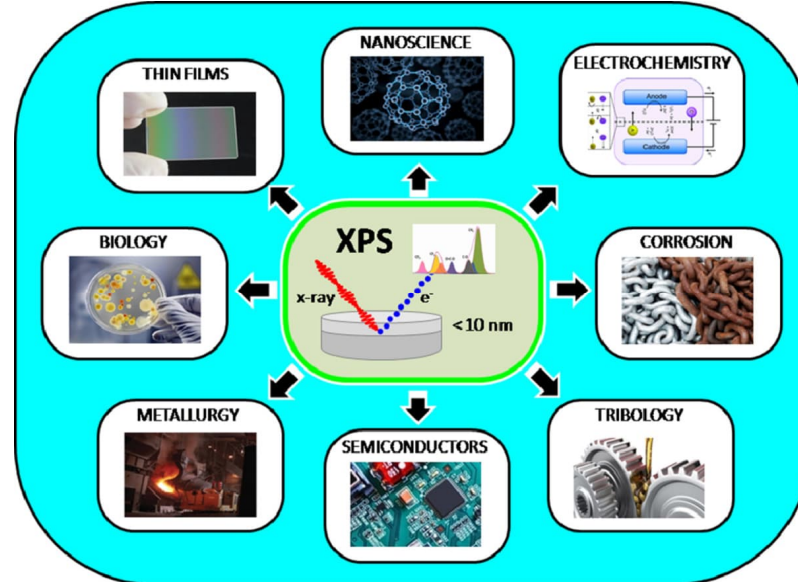
2. Atomic/molecular layer deposited iron–azobenzene framework thin films for stimuli-induced gas molecule capture/release.



Strengths of XPS

1. Wide range of applications

- Analyzing surfaces, thin films and coatings, depth profiling
- Studying corrosion
- Identifying contaminants
- Materials: Inorganic compounds, metal alloys, semiconductors, Polymers



Strengths of XPS

2. Elemental range – Li-U
3. Surface sensitivity (10-100 Å)
4. Relatively non destructive technique
5. Qualitative and quantitative measurements can be obtained
6. Little/ no sample preparation is required

Limitations of XPS

1. Samples must be compatible with Ultra High Vacuum(UHV environment)

- UHV is used for prevention contamination and maximize the mean free path of photoelectrons
- **Volatile samples** cannot be analyzed

2. H and He cannot be detected

- Lower energy of photoelectrons

3. Expensive technique

Limitations of XPS

4. Larger analysis area is required

5. Charge effects

- leads distortion/ broadening of peaks

6. High processing time

- Specially for depth profiling and analyzing complex samples

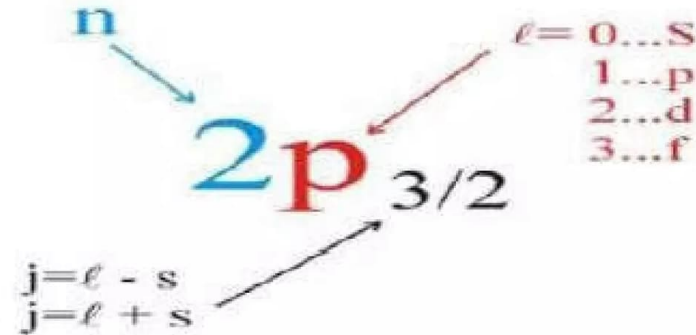
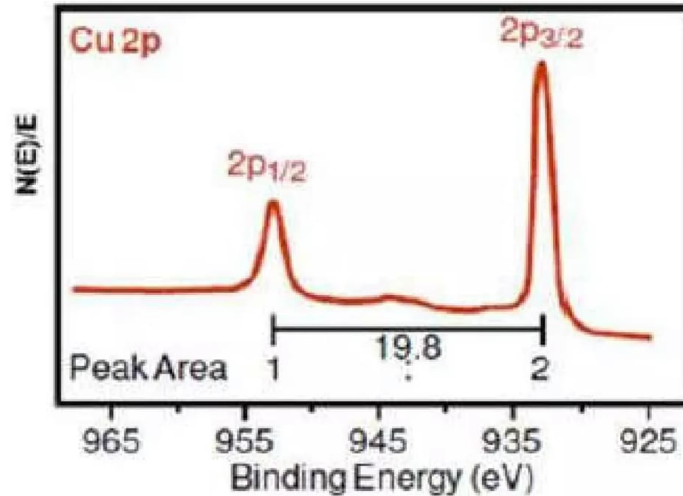
References

- [1] M. Ohring, *The materials science of thin films*. San Diego, Calif. ; London: Academic, 2002. ISBN: 9780125249751
- [2] J. F. Watts, J. Wolstenholme, and J. Wiley, *An introduction to surface analysis by XPS and AES*. Hoboken ; Chichester: Wiley, 2020. ISBN: 9781119417583
- [3] Giedraityte, Z., Sainio, J., Hagen, D., & Karppinen, M. (2017). Luminescent Metal-nucleobase network thin films by Atomic/molecular layer deposition. *The Journal of Physical Chemistry C*, 121(32), 17538–17545. <https://doi.org/10.1021/acs.jpcc.7b06129>
- [4] Khayyami, A., Philip, A., & Karppinen, M. (2019). Atomic/molecular layer deposited iron–azobenzene framework thin films for stimuli-induced gas molecule capture/release. *Angewandte Chemie*, 131(38), 13534–13538. <https://doi.org/10.1002/ange.201908164>
- [5] Krishna, D. N., & Philip, J. (2022). Review on surface-characterization applications of X-ray photoelectron spectroscopy (XPS): Recent developments and challenges. *Applied Surface Science Advances*, 12, 100332. <https://doi.org/10.1016/j.apsadv.2022.100332>
- [6] Seah, M. P. (1980). The quantitative analysis of surfaces by XPS: A Review. *Surface and Interface Analysis*, 2(6), 222–239. <https://doi.org/10.1002/sia.740020607>

Thank you

Extra slides.

Spin-orbit coupling – In XPS, spin of core level electrons interacts with orbit motion, resulting splitting of energy levels into multiple sub levels.



Total angular momentum = J

Orbital angular momentum = L

Spin angular momentum = S