X-ray photoelectron spectroscopy for elemental analysis
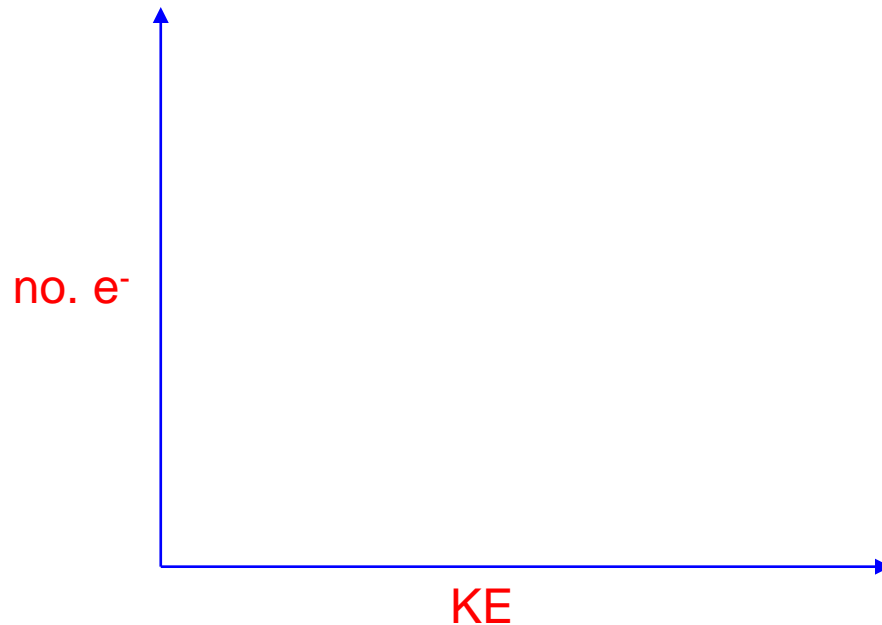
Textbook 6th ed Chapter 21 (Section 21C-1)
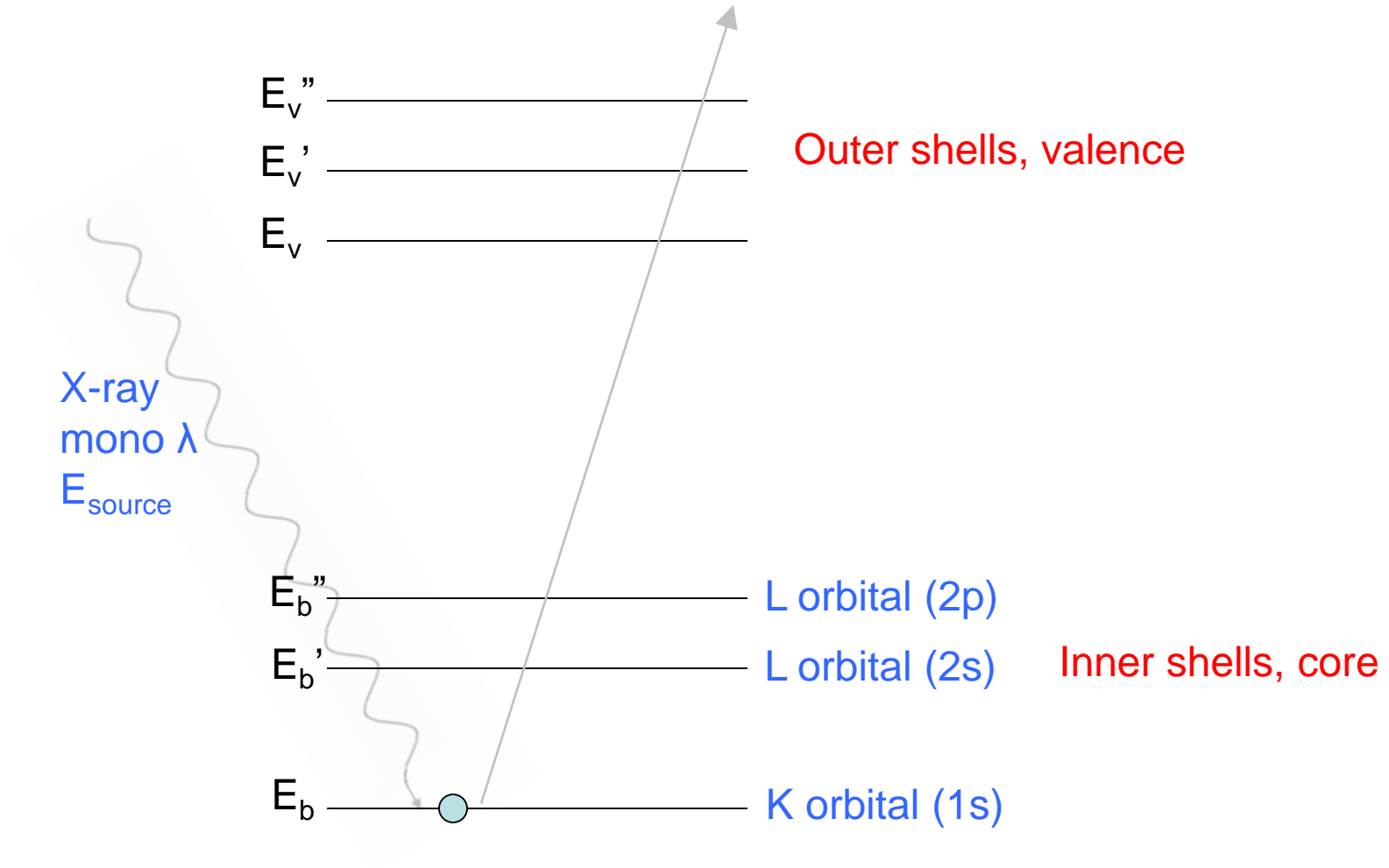
X-ray photoelectron spectroscopy

- Photo-ionization of solid sample by X-rays
- Uses soft X-rays (200-2000 eV) to examine core levels
- Emission of photoelectrons from sample's atomic cores
- Energy-dispersive analysis of photoelectrons
- Info of composition and electronic state of sample surface.

In XPS the photon is absorbed by an atom in a molecular or mineral solid, leading to ionization and the emission of a core (inner shell) electron = photoelectron.

The KE distribution of photoelectrons can be measured using an appropriate electron energy analyzer. A photoelectron spectrum is recorded.

no. e⁻

KE

Re: Fig. 21.3

E_v'' ——————————

E_v' ——————————   Outer shells, valence

E_v ——————————

X-ray
mono λ
E_{source}

E_b'' —————————— L orbital (2p)

E_b' —————————— L orbital (2s)   Inner shells, core

E_b —————————— K orbital (1s)

XPS uses monochromatic sources of X-ray radiation*:

Mg K_α radiation : E = 1253.6 eV

or

Al K_α radiation : E = 1486.6 eV

The emitted photoelectrons will then have KE in the range of 0 - 1253 eV or 0 - 1486 eV.

*In XPS instruments, X-rays are generated by bombarding a metallic anode with high-energy electrons. The energy of the emitted X-rays depends on the anode material and beam intensity depends on the electron current striking the anode and its energy. (https://xpssimplified.com/xray_generation.php)

One way is to look at photoionization is as follows:

$$A + \text{X-ray} \rightarrow A^+ + e^-$$

Conservation of energy:

$$E(A) + E_{source} = E(A^+) + E(e^-)$$

The photoelectron's energy is solely kinetic energy (KE):

$$E(A) + E_{source} = E(A^+) + KE$$

$$KE = E_{source} + E(A) - E(A^+)$$

$$KE = E_{source} - (E(A^+) - E(A))$$

The term in parentheses is the difference in energy between the ionized and neutral atoms. It is generally called the *binding energy* (BE) of the electron.

Commonly quoted equation : $KE = E_{source} - BE$

Experimental Details

The basic requirements for a photoemission experiment (XPS or UPS) are:

1. a source of fixed-energy X-ray radiation

2. an e^- energy analyzer (which can disperse the emitted electrons according to their kinetic energy and measure the flux of emitted electrons of each particular energy)

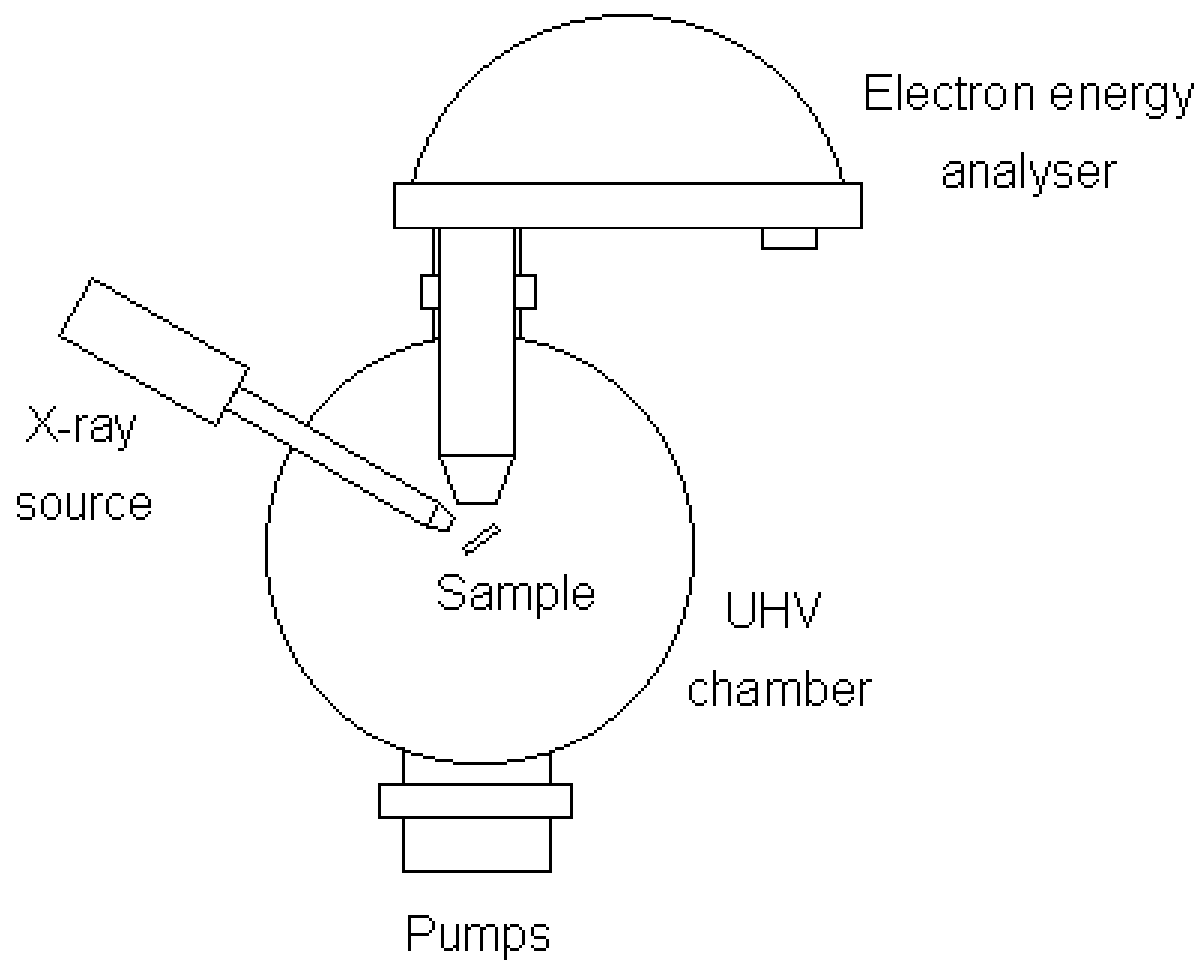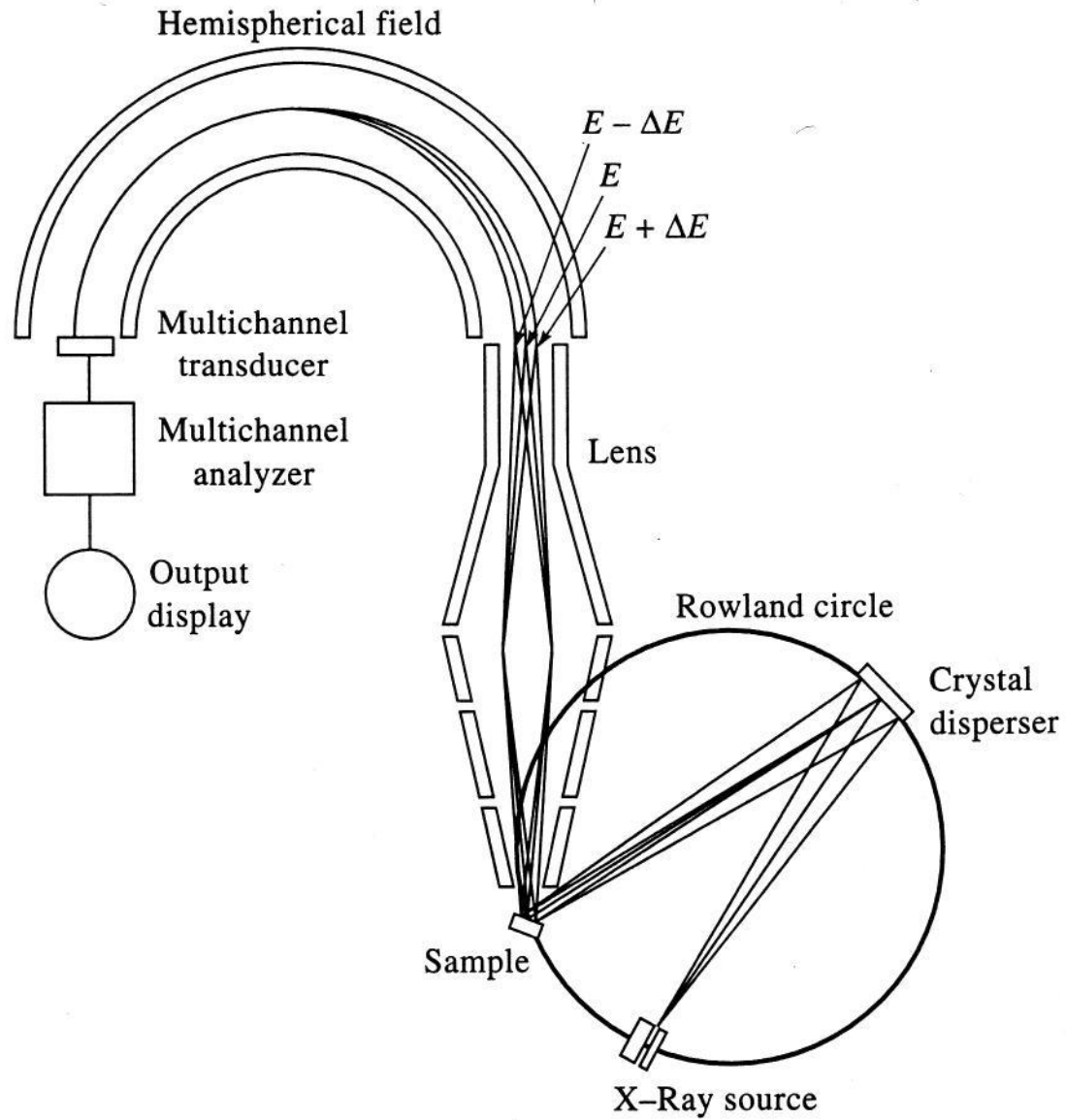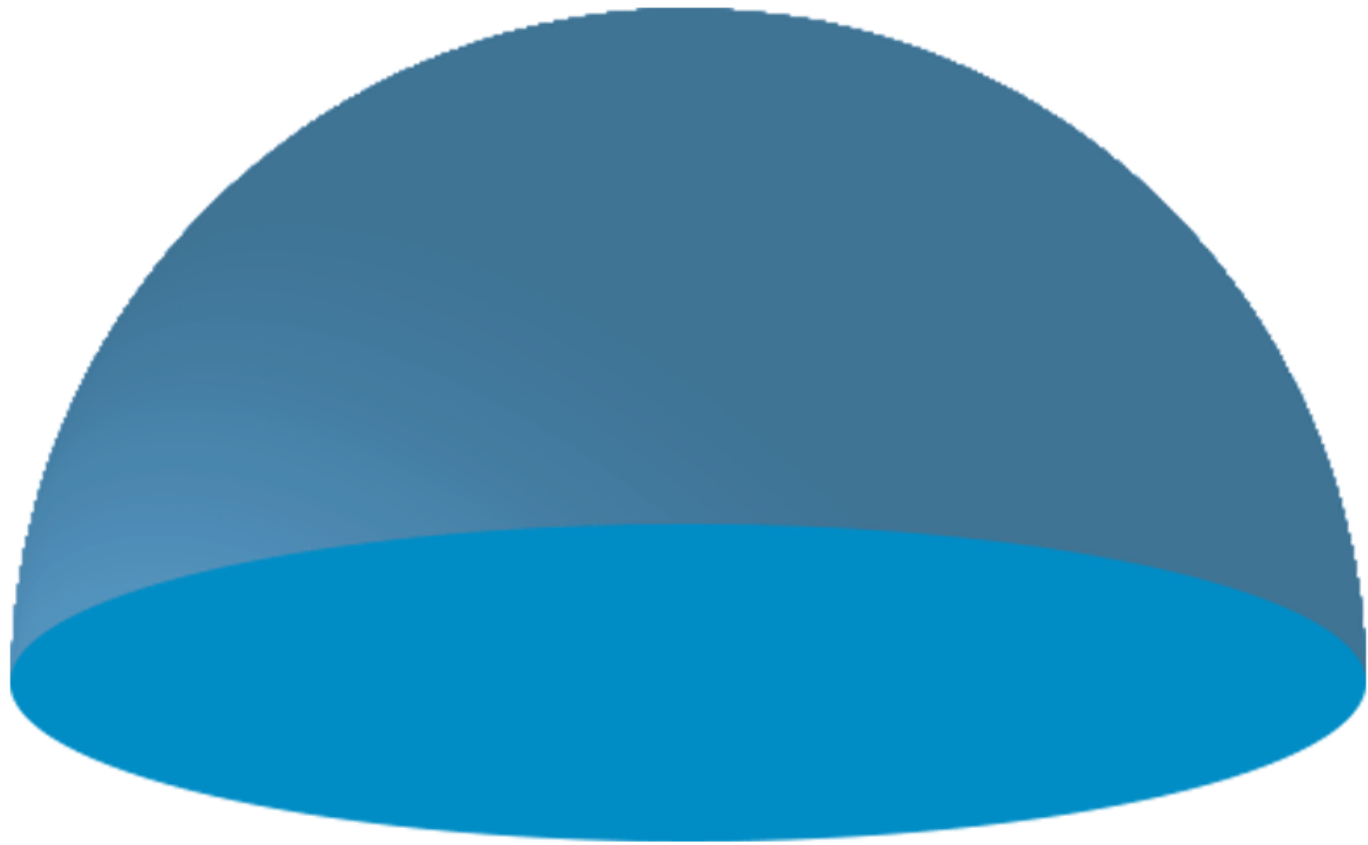3. a high vacuum environment (no gas phase collisions)

Electron energy analyser

X-ray source

Sample

UHV chamber

Pumps

Figure 21-4

Hemispherical field

$E - \Delta E$

E

$E + \Delta E$

Multichannel transducer

Multichannel analyzer

Lens

Output display

Rowland circle

Crystal disperser

Sample

X–Ray source

https://minalab.fbk.eu/x-ray-photoelectron-spectroscopy-xps

$$KE = \frac{1}{2}mv^2$$

$$\frac{mv^2}{r} = eE$$

$$2KE = reE$$

$$KE = \frac{reE}{2} = Const* E$$

X-ray Photoelectron Spectroscopy (XPS)

- For each element, there is a characteristic BE associated with each core atomic orbital

- Each element will produce a characteristic set of peaks KE values determined by E_{source} and BE values.

- Peaks at particular energies indicate the presence of a specific element in the sample under study

- The intensity of peaks is related to the concentration of the elements within the sampled region

- This technique provides *quantitative analysis of the surface composition.*

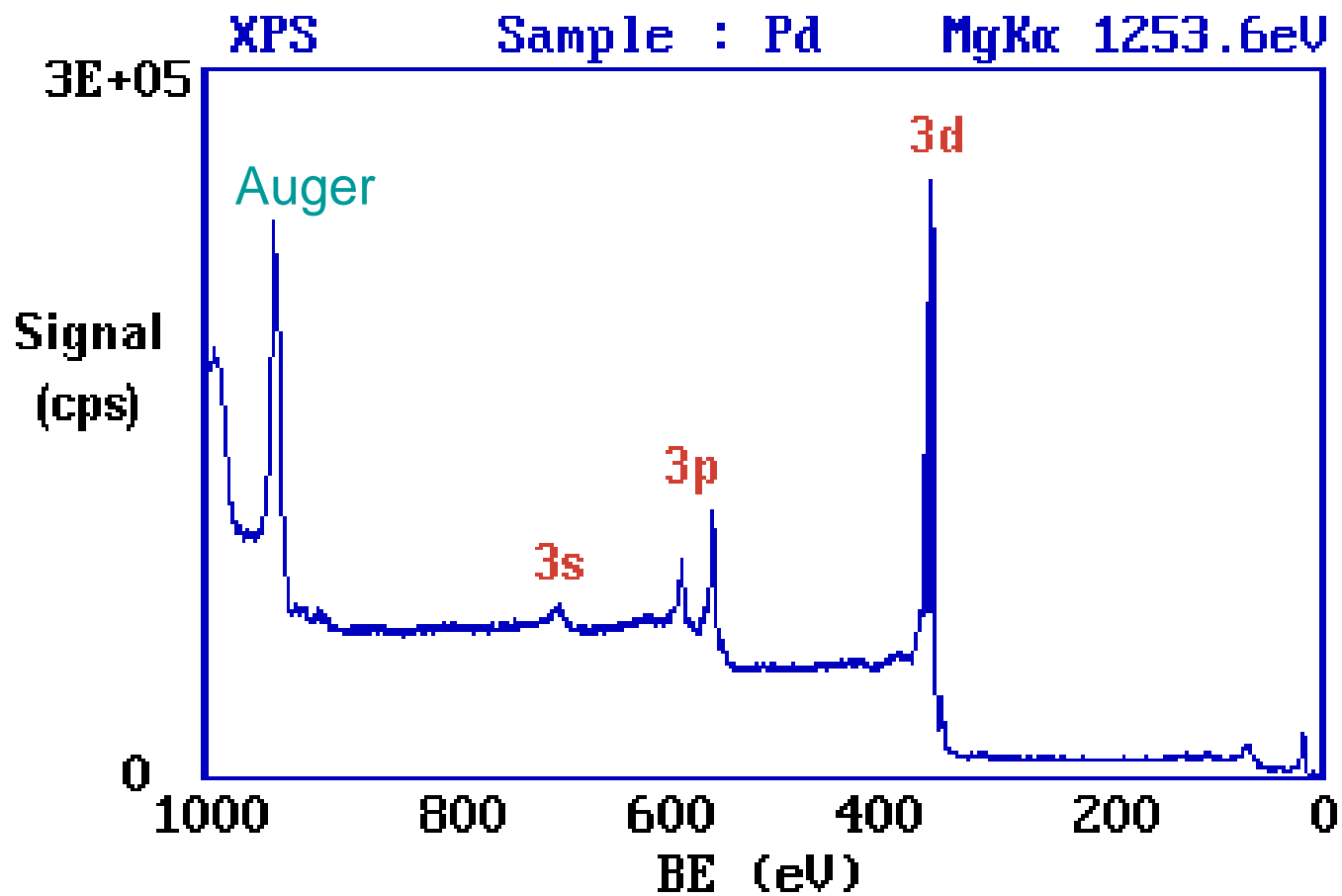- *Alternative acronym: ESCA (Electron Spectroscopy for Chemical Analysis).*

XPS spectrum obtained from a Pd metal sample using Mg Kα radiation

XPS   Sample : Pd   MgKα 1253.6eV

3E+05

Signal
(cps)

0

270   1270

KE (eV)
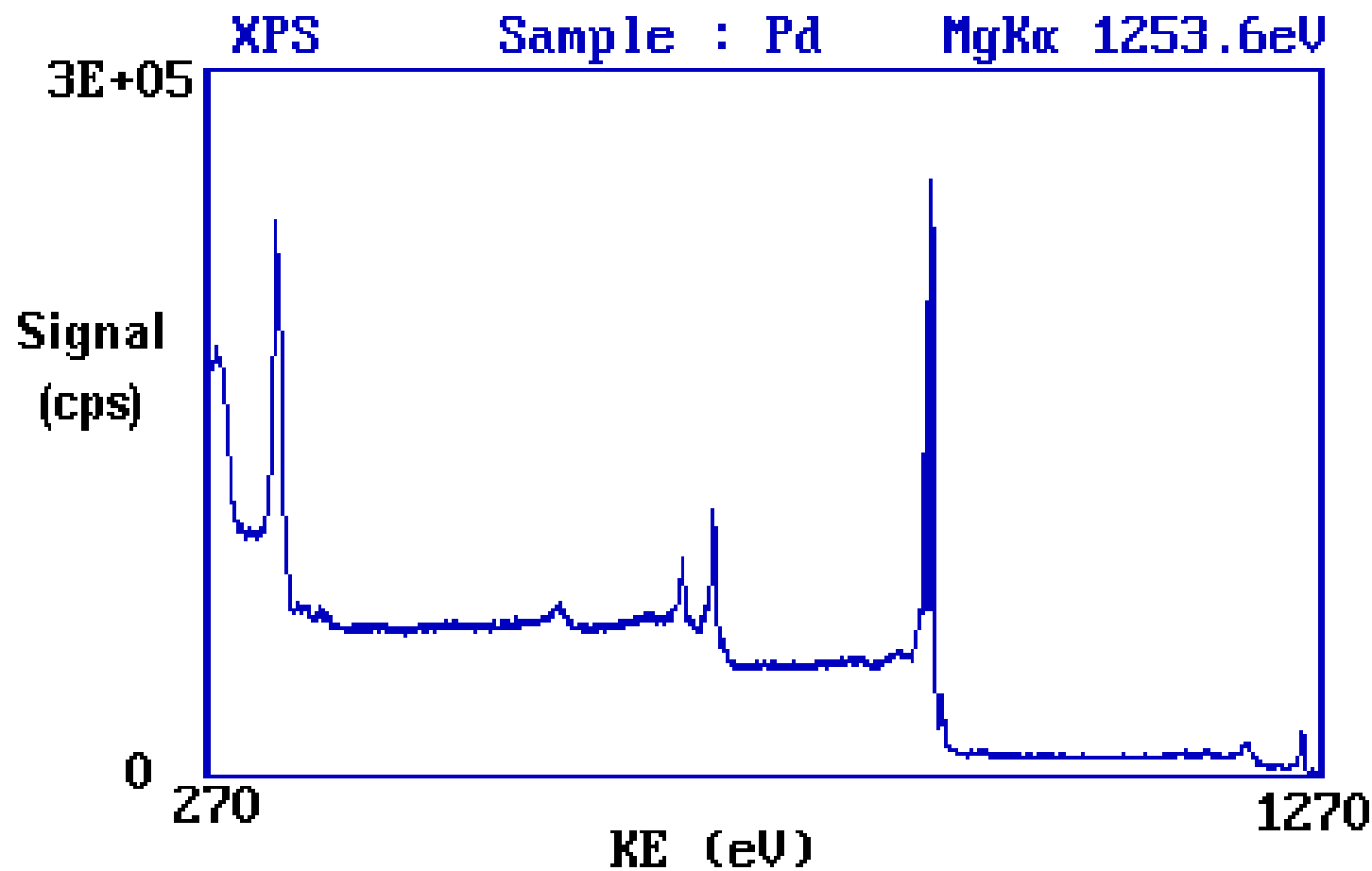
XPS spectrum obtained from a Pd metal sample using Mg Kα radiation
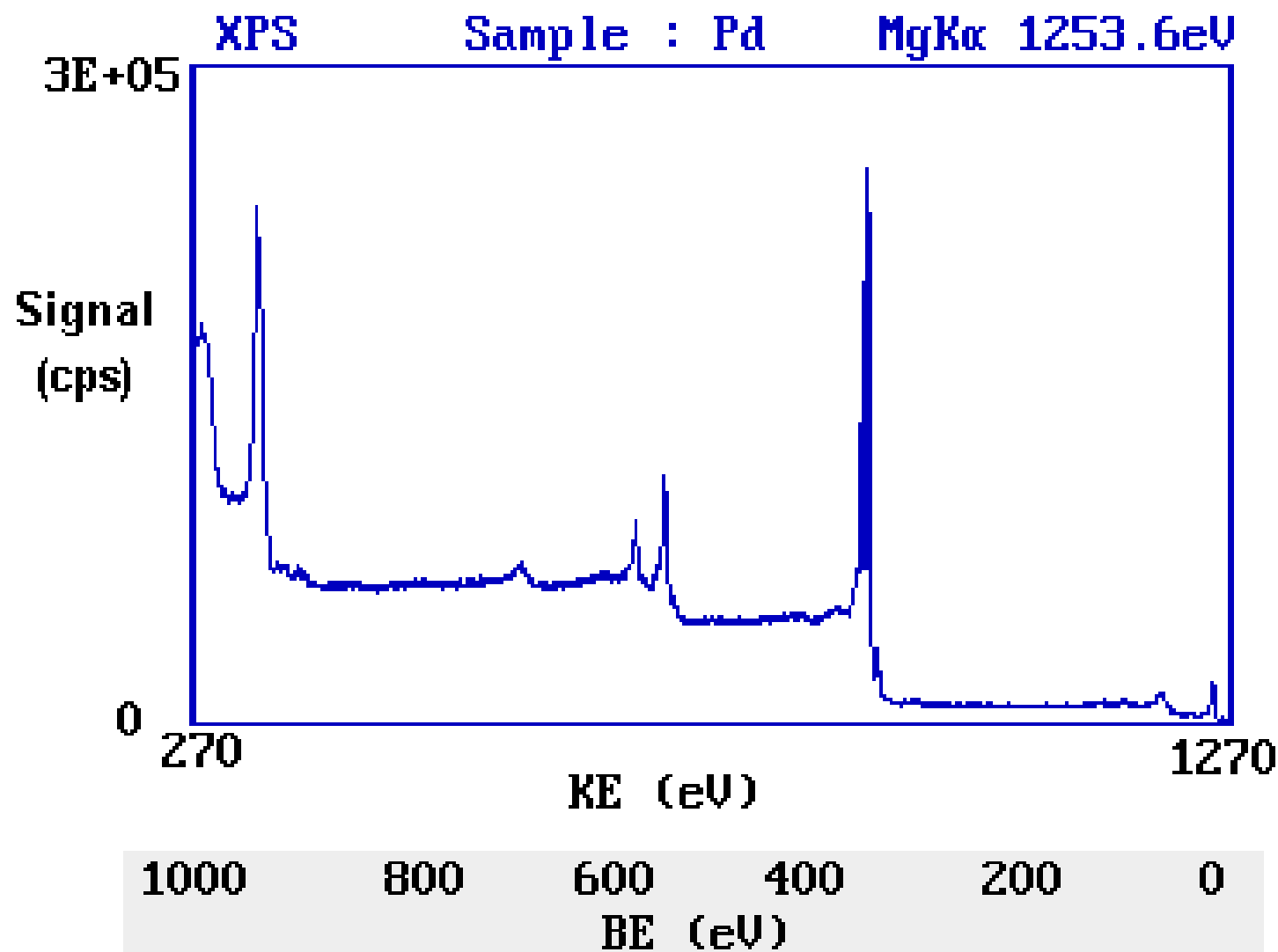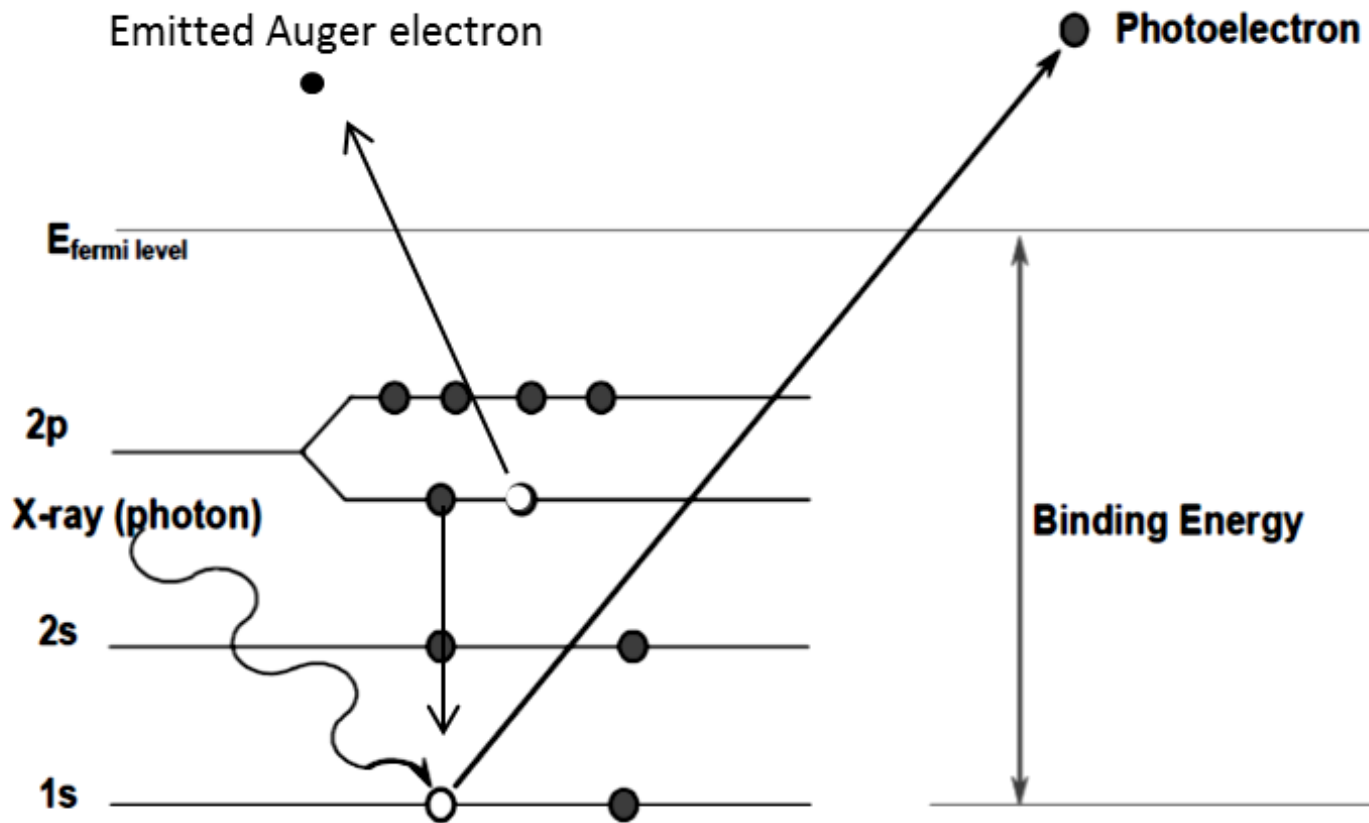
Peak assignments:

The highest peak at ca. 335 eV is due to emission from the 3d levels of the Pd atoms.
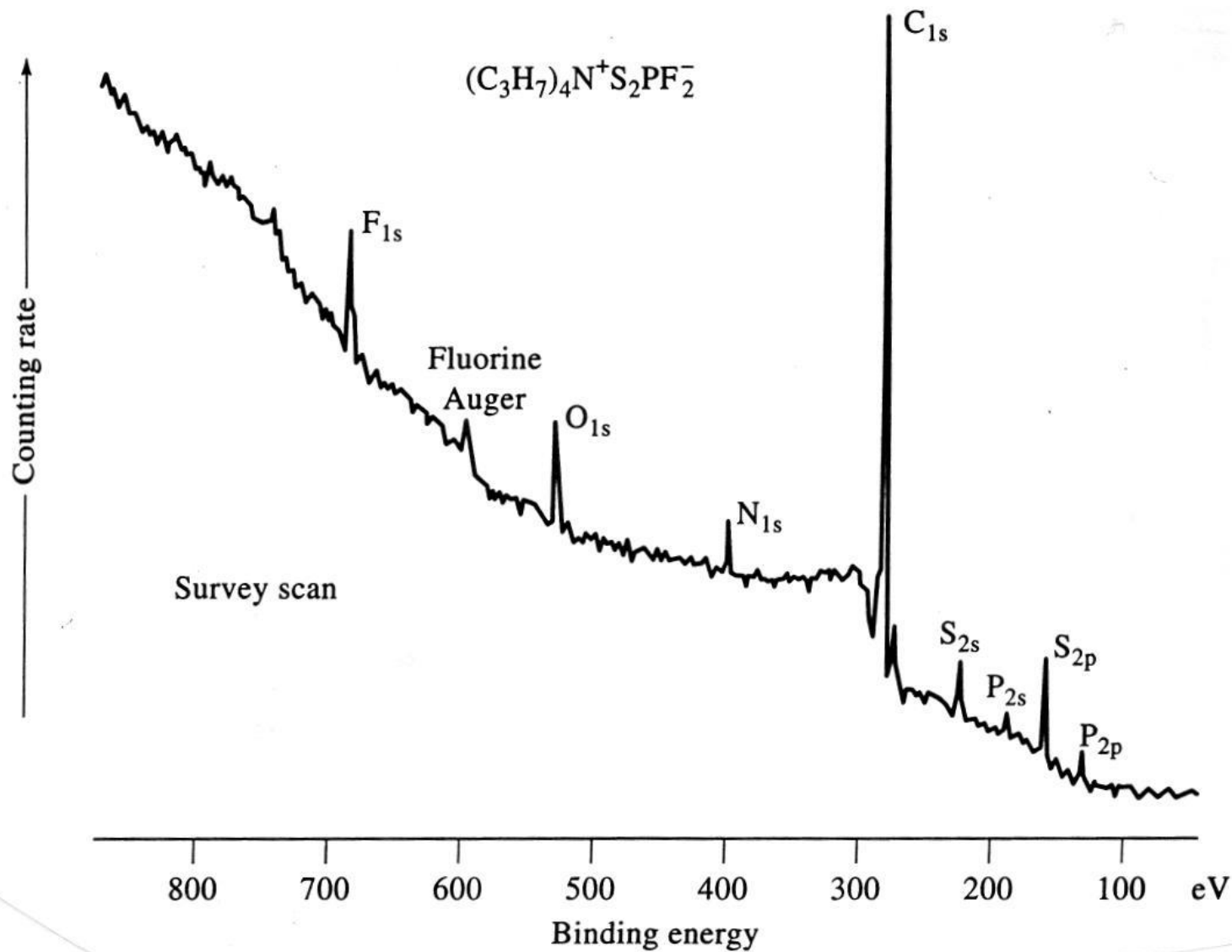
The 3p and 3s levels give rise to the peaks at ca. 534/561 eV and 673 eV.

The remaining peak arises from X-ray induced Auger emission. It occurs at a kinetic energy of ca. 330 eV and does not relate to binding energies.

Figure 21-2

$(C_3H_7)_4N^+S_2PF_2^-$

C_1s

F_1s

Fluorine Auger

O_1s

N_1s

Survey scan

S_2s

P_2s

S_2p

P_2p

800   700   600   500   400   300   200   100   eV

Binding energy

In general, BE for one type of orbital (e.g. 1s) increases with nuclear size.

The spectrum shows 6 elements.

Presence of O: oxidation must have occurred

BE values for 1s electrons increase with the atomic no. because of the larger positive charge in the nucleus.

Chemical Shifts

The binding energy of an electron depends upon the photoemission orbital level, but also upon :

1. oxidation state of the atom
2. local chemical and physical environment

Changes in either (1) or (2) produce small shifts in peak positions - so-called *chemical shifts.*

Atoms of higher positive oxidation have higher binding energies due to the extra coulombic interaction between the photoelectron and the ion core.

This ability to discriminate between different oxidation states and chemical environments is one of the major strengths of XPS.

Ti 2p XP Spectra

Mg Kα

Ti metal

TiO$_2$

Binding Energy / eV
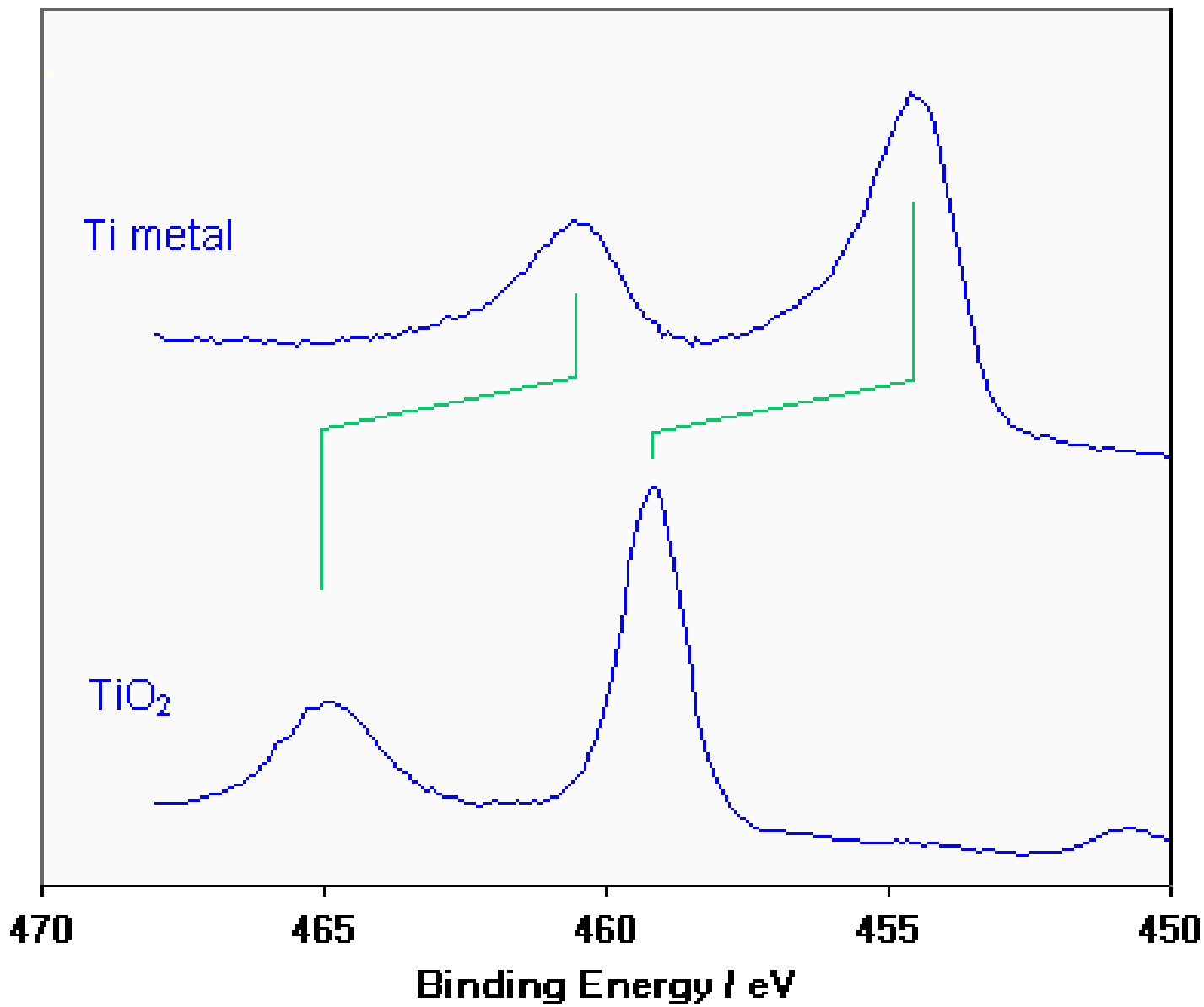
TABLE 21-2 Chemical Shifts as a Function of Oxidation State[a]

| Element[b]	Oxidation State									
	−2	−1	0	+1	+2	+3	+4	+5	+6	+7
Nitrogen (1s)	—	*0[c]	—	+4.5[d]	—	+5.1	—	+8.0	—	—
Sulfur (1s)	−2.0	—	*0	—	—	—	+4.5	—	+5.8	—
Chlorine (2p)	—	*0	—	—	—	+3.8	—	+7.1	—	+9.5
Copper (1s)	—	—	*0	+0.7	+4.4	—	—	—	—	—
Iodine (4s)	—	*0	—	—	—	—	—	+5.3	—	+6.5
Europium (3d)	—	—	—	—	*0	+9.6	—	—	—	—

[a]All shifts are in electron volts measured relative to the oxidation states indicated by (*). (Reprinted with permission from D. M. Hercules, *Anal. Chem.*, **1970**, *42*, 28A. Copyright 1970 American Chemical Society.)
[b]Type of electrons given in parentheses.
[c]Arbitrary zero for measurement, end nitrogen in NaN_3.
[d]*Middle nitrogen in NaN_3.*

Figure 21-5
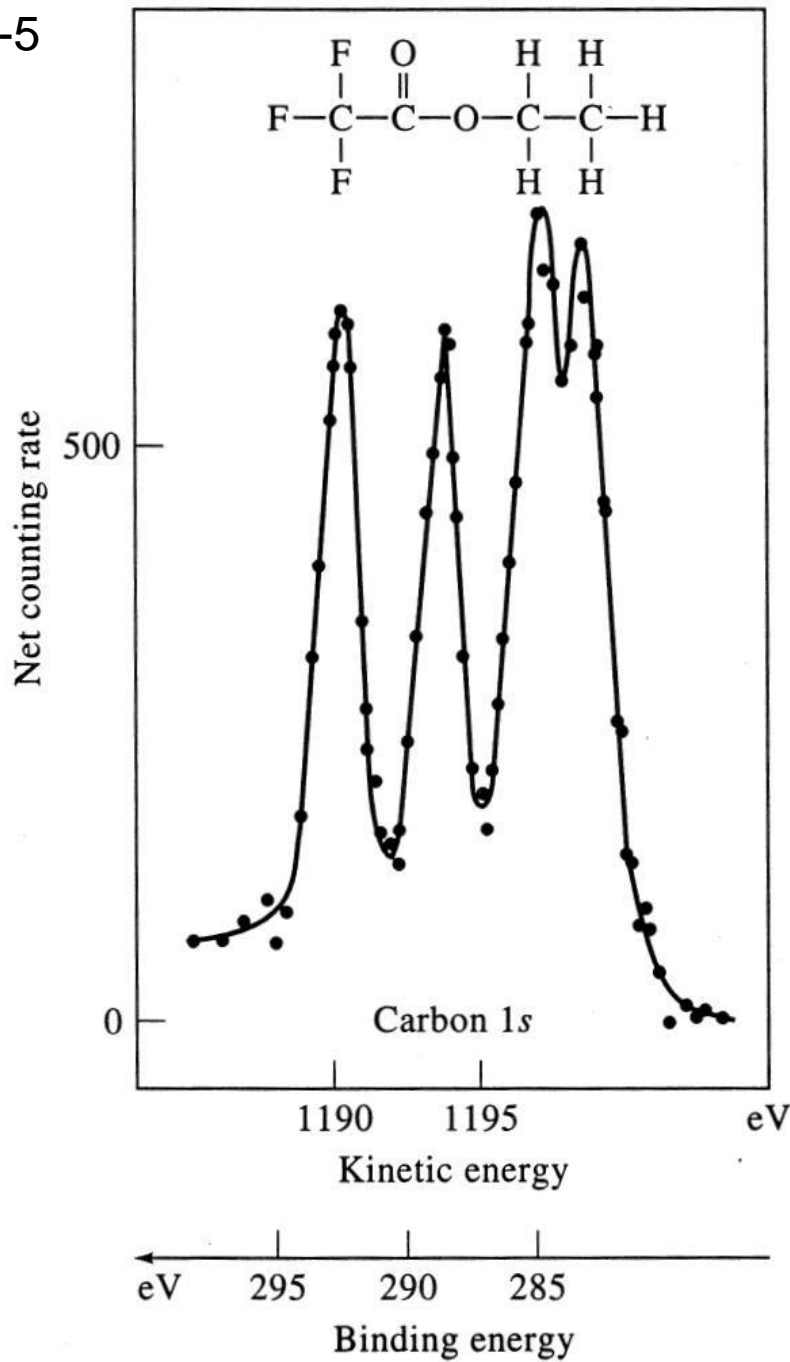
F withdraws the most electron density from C, making the effective nuclear attraction on the 1s electron greater.

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http://www.kratos.com/Axis/AXISUltra.html   http://umanitoba.ca/interdisciplinary/research/mim/infrastructure/axisultra.html

Research Article

Differentiating calcium carbonate polymorphs by surface analysis techniques – an XPS and TOF-SIMS study

Ming Ni[a] and Buddy D. Ratner[a,b]*

Calcium carbonate has evoked interest owing to its use as a biomaterial, and for its potential in biomineralization. Three polymorphs of calcium carbonate, i.e. calcite, aragonite, and vaterite were synthesized. Three conventional bulk analysis techniques, Fourier transform infrared (FTIR), X-ray diffraction (XRD), and SEM, were used to confirm the crystal phase of each polymorphic calcium carbonate. Two surface analysis techniques, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS), were used to differentiate the surfaces of these three polymorphs of calcium carbonate. XPS results clearly demonstrate that the surfaces of these three polymorphs are different as seen in the Ca(2p) and O(1s) core-level spectra. The different atomic arrangement in the crystal lattice, which provides for a different chemical environment, can explain this surface difference. Principal component analysis (PCA) was used to analyze the TOF-SIMS data. Three polymorphs of calcium carbonate cluster into three different groups by PCA scores. This suggests that surface analysis techniques are as powerful as conventional bulk analysis to discriminate calcium carbonate polymorphs. Copyright © 2008 John Wiley & Sons, Ltd.

XPS

Al Kα X-rays were used as the source (E_{source} = 1486.6 eV).

All binding energies (BEs) for the samples were referenced by setting the adventitious carbon C(1s) peak to 285 eV.

The Bes were measured with a precision of±0.2 eV.

The XPS data were acquired at a take off angle of 55°.

The XPS peaks with multiple components were resolved by a peak-fitting program assuming 100% Gaussian peak shape.
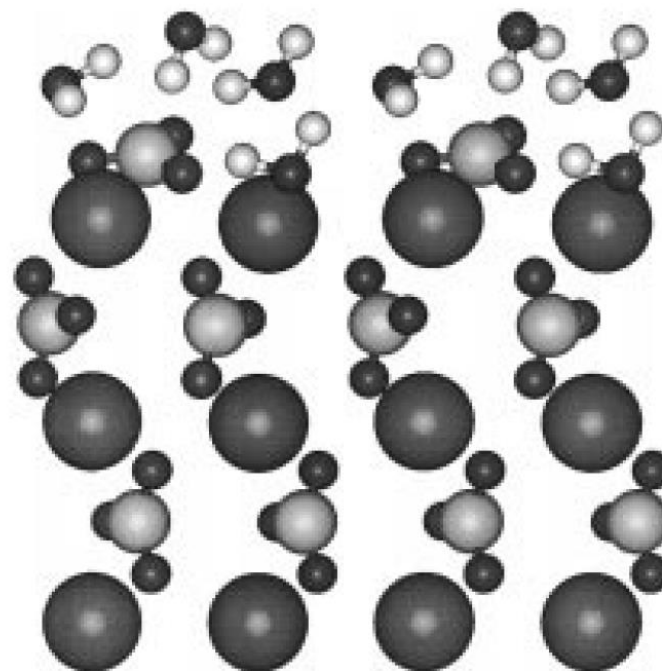
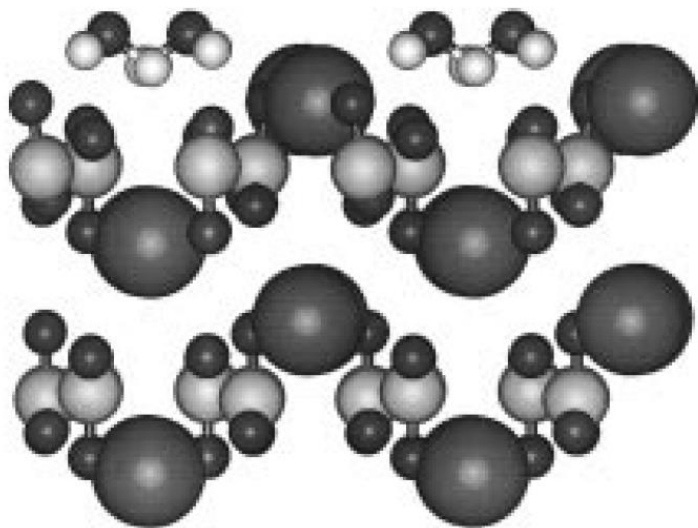Three identical experiments were performed for each type of calcium carbonate.
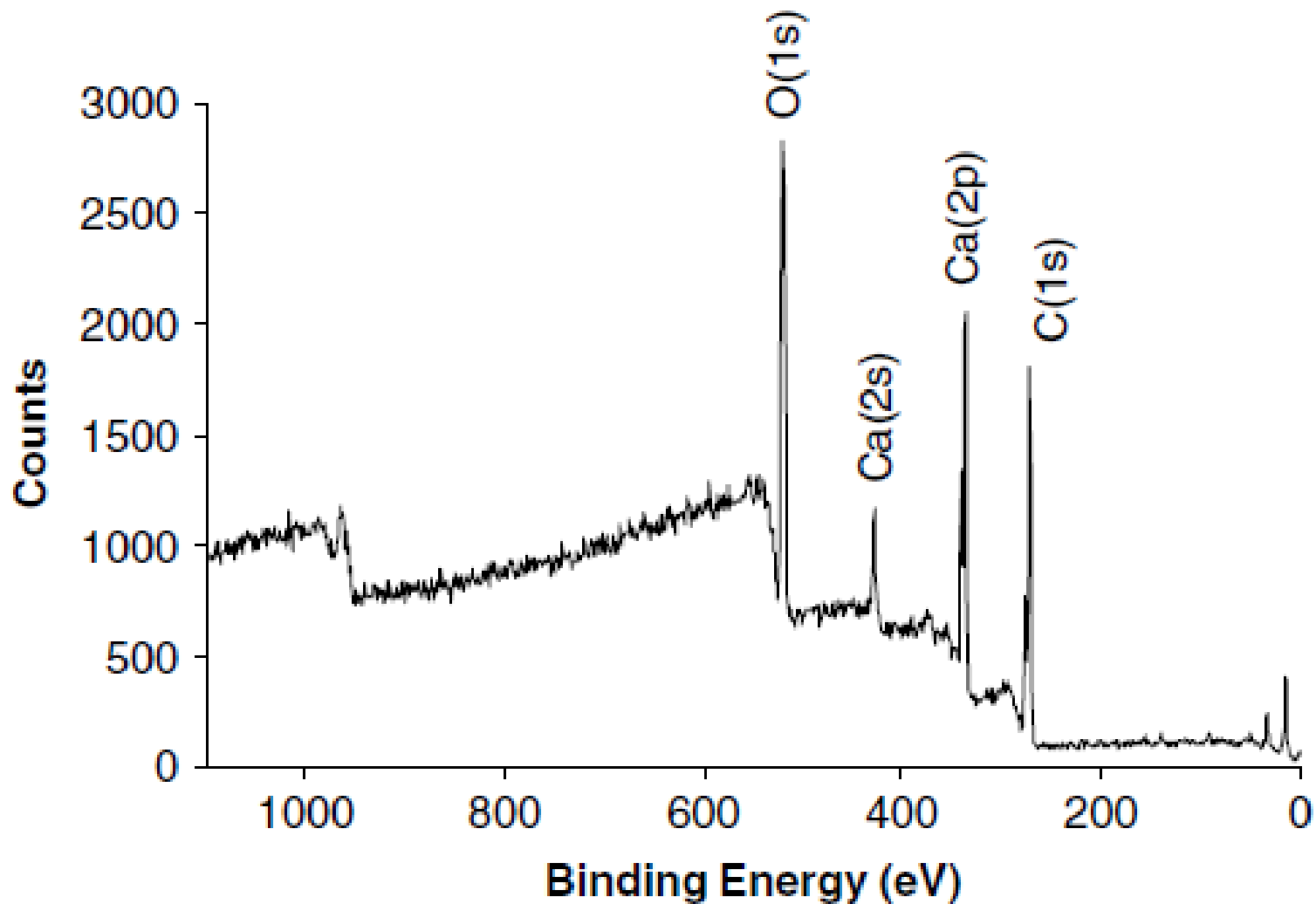
Figure 4. XPS wide scan of calcite showing that Ca, C, and O, the three compositional elements of calcium carbonate, are present.
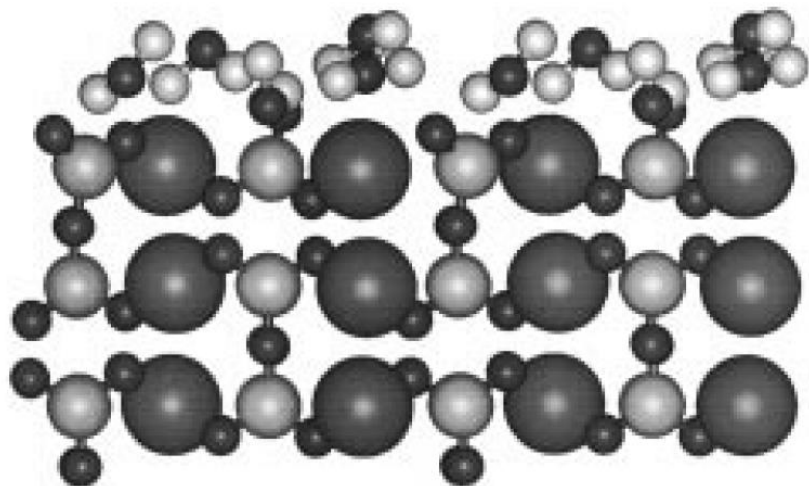
Figure 3. Hydrated calcite {11$\bar{2}$0} surface showing bulk termination of the surface and different adsorption modes of the water molecules (Ca = large medium gray, C = medium sized pale gray, O = small dark gray, H = small white).


Figure 4. Hydrated calcium terminated aragonite {110} surface, showing bridgelike adsorption of the water molecules (Ca = large medium gray, C = medium sized pale gray, O = small dark gray, H = small white).

Figure 6. Hydrated carbonate terminated vaterite {001} surface, showing rotated surface carbonate groups and water molecules adsorbing in surface vacancies (Ca = large medium gray, C = medium sized pale gray, O = small dark gray, H = small white).
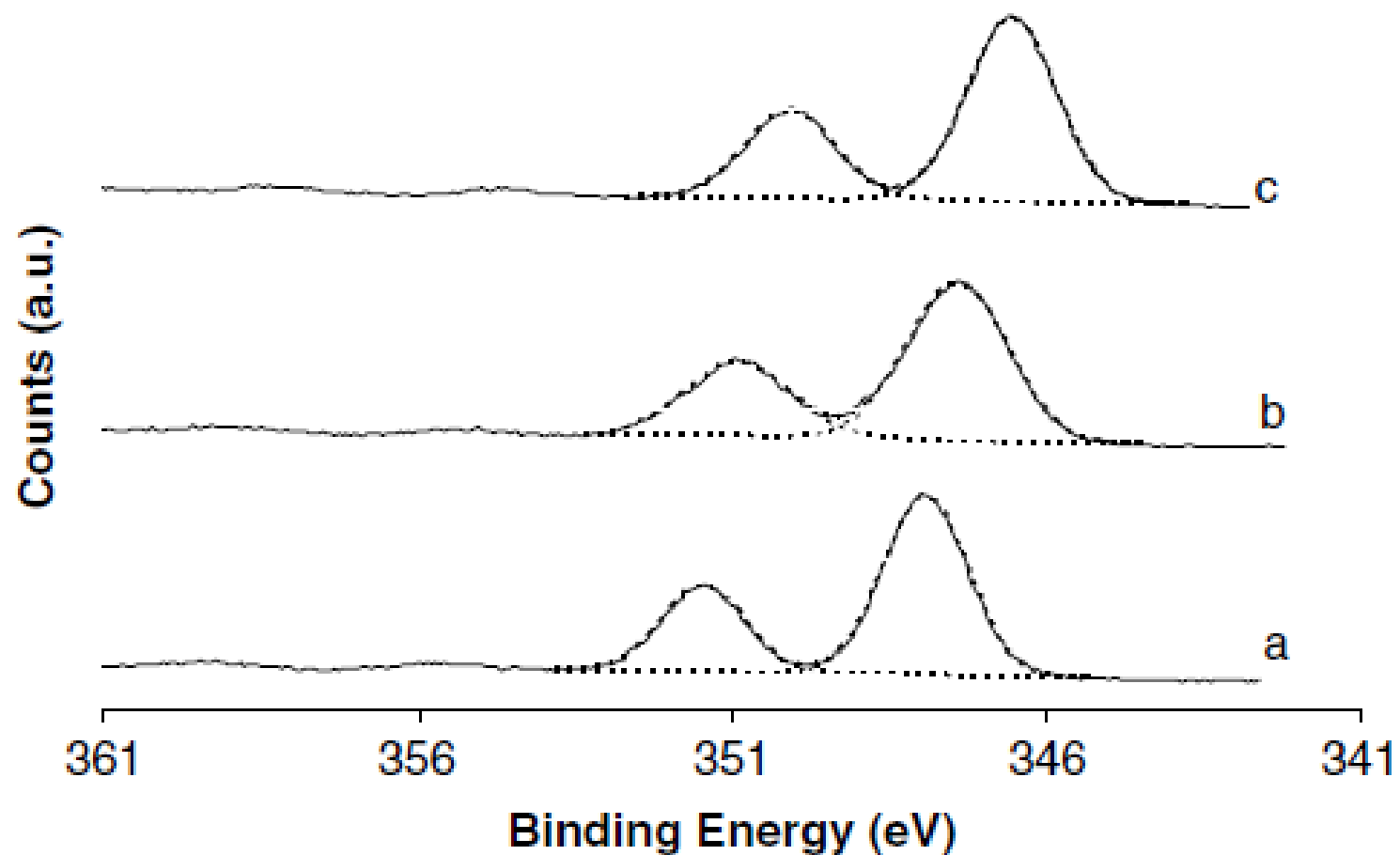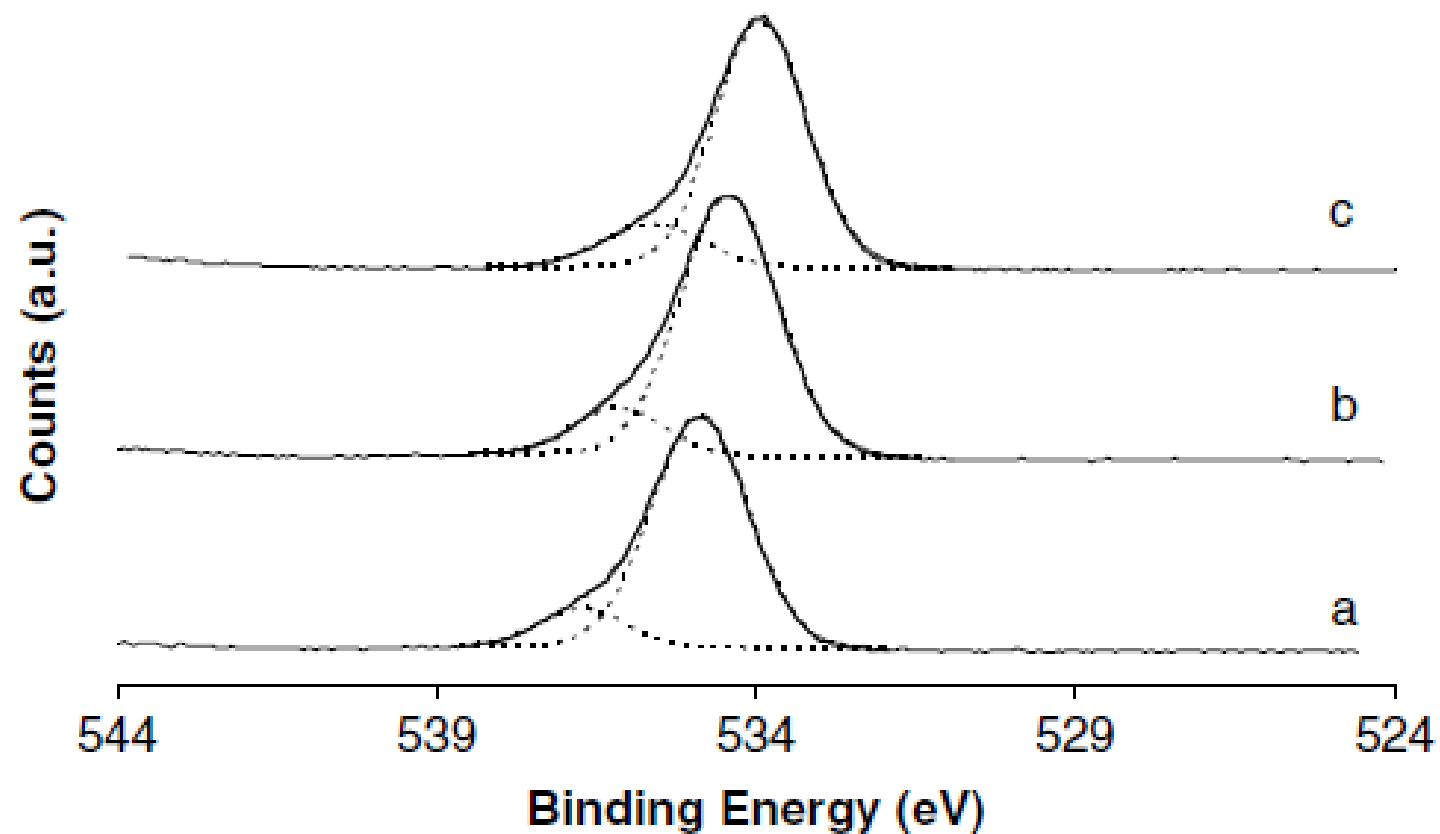
Figure 5. XPS Ca2p core-level spectra of (a) aragonite (b) vaterite, and (c) calcite. Dashed lines show the fitting results.
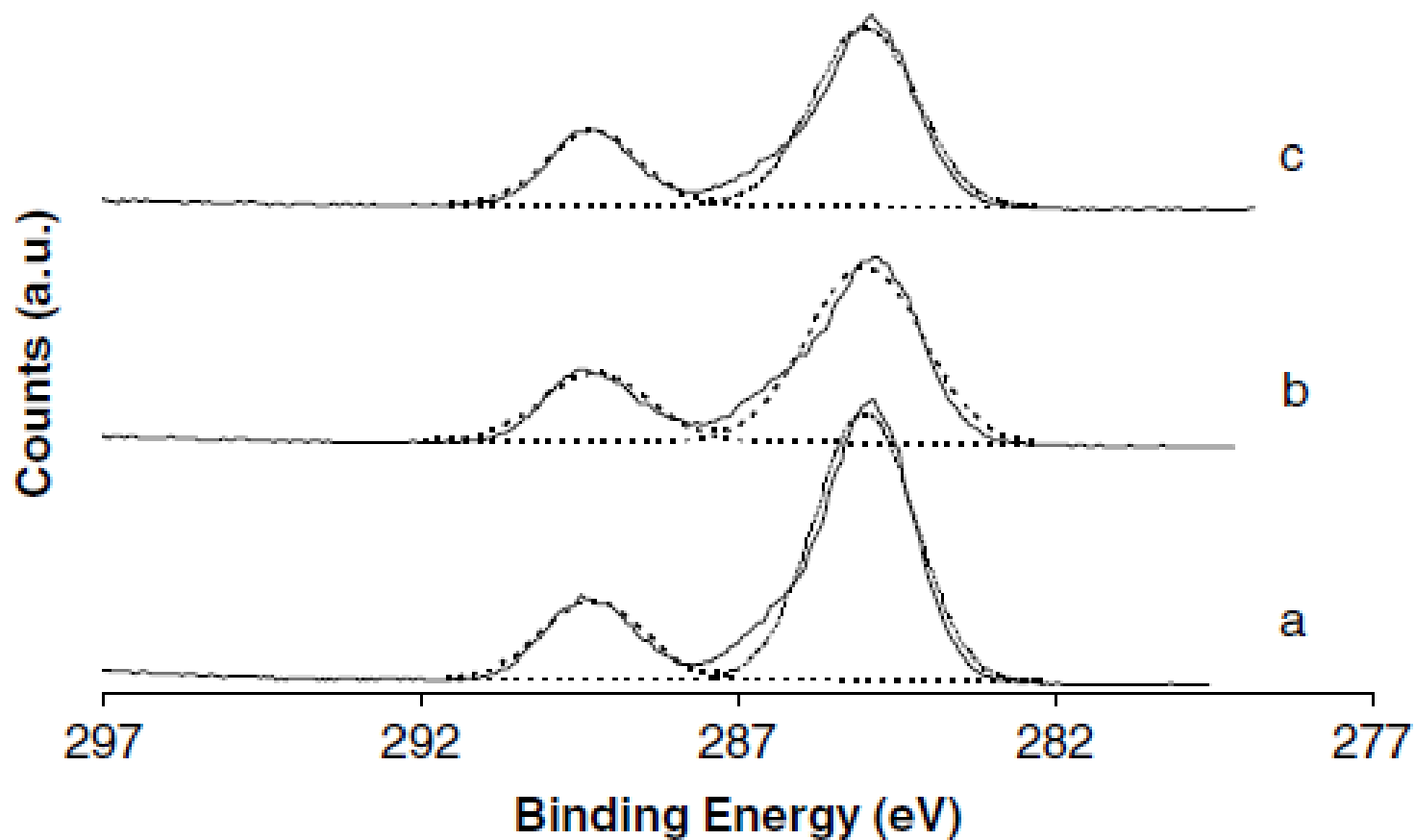
Figure 6. XPS C1s core-level spectra of (a) aragonite, (b) vaterite, and (c) calcite.

Figure 7. XPS O1s core-level spectra of (a) aragonite, (b) vaterite, and (c) calcite.

In summary, the surfaces of the three calcium carbonate polymorphs can be differentiated with XPS.

The Ca 2p XP spectra can be used for CaCO3 polymorph identification. The O1s spectra can also be used.

To sum up on XPS:

- Applicable to solid samples for elemental analysis
- Analysis possible with attached microscope
- Quantitative/qualitative analysis of elements
- Quantitative analysis of oxidation states
- Calibration curves necessary for each element

- High cost and high-maintenance
- Occupies significant space

Questions

1. For the following molecule, give the order of increasing binding energies for carbon 1s photoelectrons.

$$F_3C\text{---}\overset{H_2}{C}\text{---}CCl_3$$
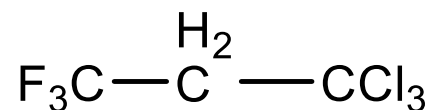
2. Calculate the kinetic energy of photoelectrons showing a binding energy of 650 eV, if the X-Ray source used is at 1253.6 eV and the work function of the instrument is 18 eV.