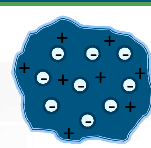
bl26

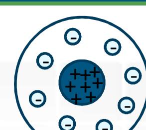
Introduction to Photoelectron Spectroscopy (PES)

Various Models of the Atom

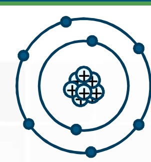
Dalton



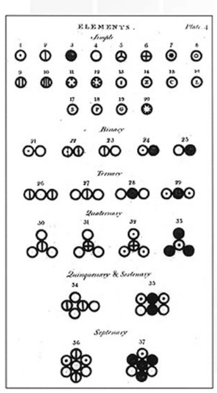
Thomson

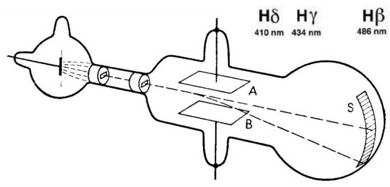


Rutherford



Bohr





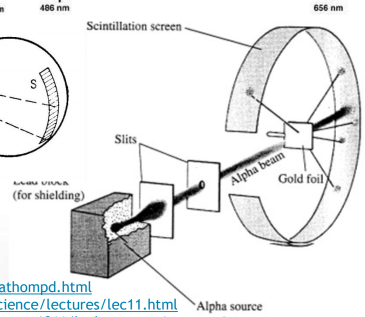


Image sources:
http://library.thinkquest.org/13394/angielsk/athompd.html
http://abyss.uoregon.edu/~js/21st_century_science/lectures/lec11.html
http://mail.colonial.net/~hkaiter/astronomyimages1011/hydrogen_emis_spect.jpg
http://upload.wikimedia.org/wikipedia/commons/9/97/A_New_System_of_Chemical_Philosophy_fp.jpg

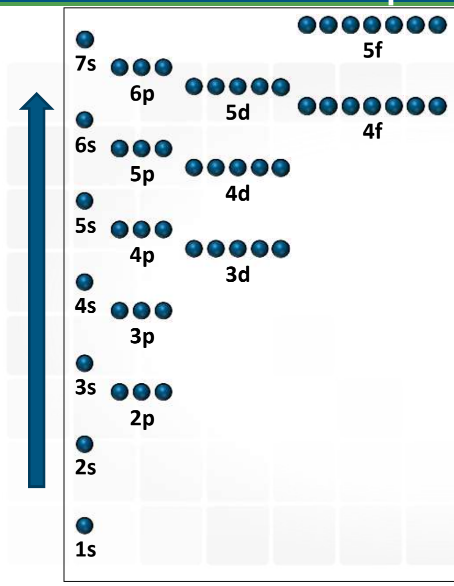
Slide 1

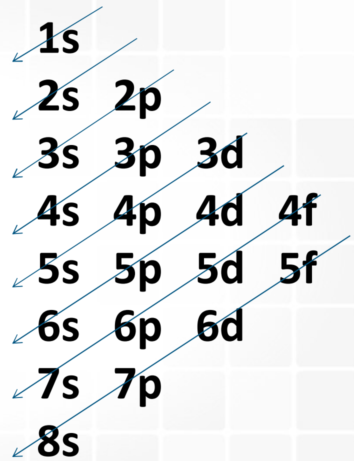
---

bl26 Jamie - in the next section, I took the text from the detailed outline and put it with the corresponding slide. This could be the text you use when you narrate the slides.
blankenau, 10/21/2013

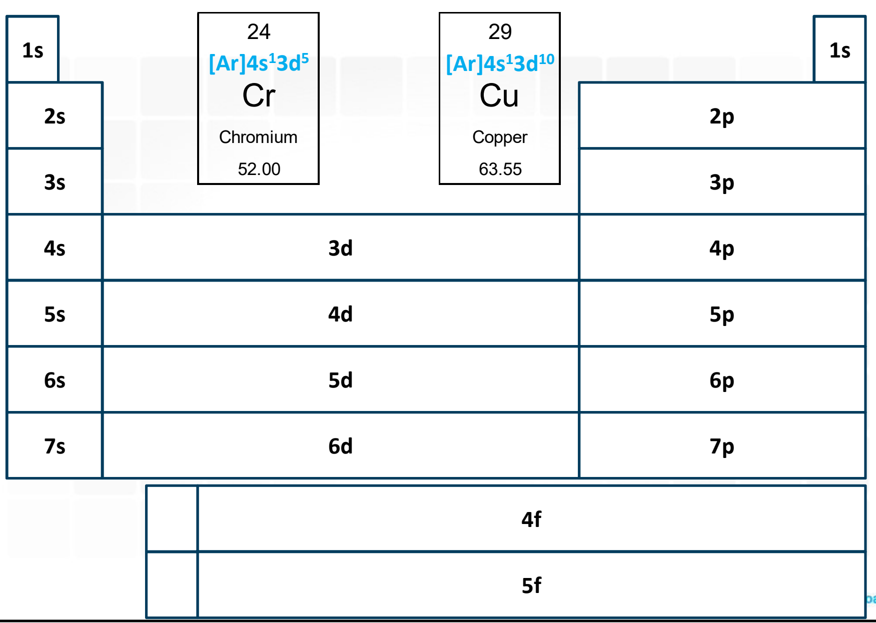
Further refinements to these models have occurred with new experimental results

bl19





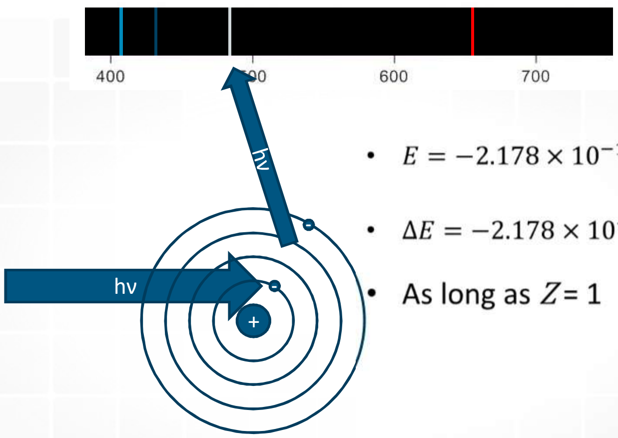
But not all elements 'follow the rules'



Slide 3

bl19 Jamie - not sure how you want to use this slide
blankenau, 10/16/2013

How do we know?



- $E = -2.178 \times 10^{-18}\text{J}\left(\frac{Z}{n}\right)^2$
- $\Delta E = -2.178 \times 10^{-18}\text{J}\left(\frac{Z^2}{n_f^{\ 2}} - \frac{Z^2}{n_i^{\ 2}}\right)$
- As long as $Z = 1$

Ionization Energy

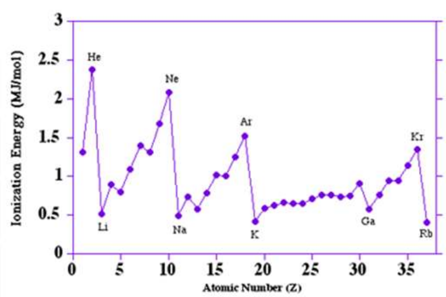


Image source:
http://chemistry.beloit.edu/stars/images/IEexpand.gif

Image source: Dayah, Michael. “Dynamic Periodic Table.” Accessed Sept. 5, 2013. http://ptable.com/#Property/Ionization

Ionization Energy

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
Na	495	4,560					
Mg	735	1,445	7,730				
Al	580	1,815	2,740	11,600			
Si	780	1,575	3,220	4,350	16,100		
P	1,060	1,890	2,905	4,950	6,270	21,200	
S	1,005	2,260	3,375	4,565	6,950	8,490	27,000
Cl	1,255	2,295	3,850	5,160	6,560	9,360	11,000
Ar	1,527	2,665	3,945	5,770	7,230	8,780	12,000

LO 1.5 - The student is able to explain the distribution of electrons in an atom or ion based upon data.

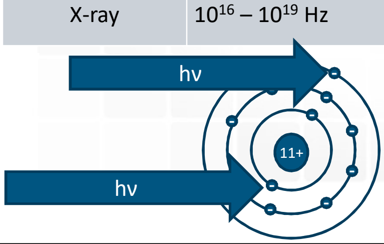
LO 1.6 - The student is able to analyze data relating to electron energies for patterns or relationships.

bl20

How do we probe further into the atom?

$$E = h\nu$$

Radiation Type	ν	E	Aspects Probed
Microwaves	$10^9 – 10^{11}$ Hz	$10^{-7} – 10^{-4}$ MJ/mol	Molecular rotations
Infrared (IR)	$10^{11} – 10^{14}$ Hz	$10^{-4} – 10^{-1}$ MJ/mol	Molecular vibrations
Visible (ROYGBV)	$4 \times 10^{14} – 7.5 \times 10^{14}$ Hz	0.2 - 0.3 MJ/mol	Valence electron transitions in atoms and molecules
Ultraviolet (UV)	$10^{14} – 10^{16}$ Hz	0.3 – 100 MJ/mol	Valence electron transitions in atoms and molecules
X-ray	$10^{16} – 10^{19}$ Hz	$10^2 – 10^5$ MJ/mol	Core electron transitions in atoms



$$E = h\nu$$

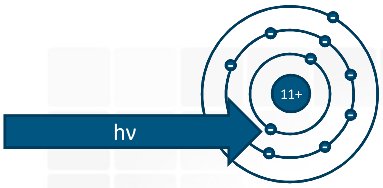
IE_1 = 495 kJ/mol

IE_1 = 0.495 MJ/mol

Slide 8

bl20 Jamie - not sure this build is correct
blankenau, 10/16/2013

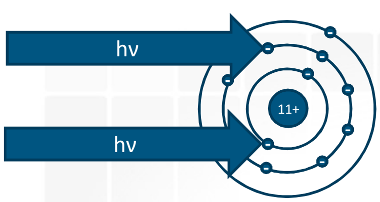
Removing Core Electrons



$$E = 103.3\ MJ/mol$$
$$E = 1.033 \cdot 10^{8}\ J/mol$$
$$\nu = \frac{E}{h} = \frac{1.033 \cdot 10^{8} J/mol}{6.626 \cdot 10^{-34} J \cdot s}$$
$$\nu = 1.559 \cdot 10^{41} mol^{-1} \cdot s^{-1}$$
$$\nu = 1.559 \cdot 10^{41} mol^{-1} \cdot s^{-1} \times \frac{1\ mol}{6.022 \cdot 10^{23} e^{-}}$$
$$\nu_{min} = 2.59 \cdot 10^{17} Hz$$

Radiation Type	ν	E	Aspects Probed
X-ray	$10^{16} – 10^{19}$ Hz	$10^{2} – 10^{5}$ MJ/mol	Core electron transitions in atoms

Removing Core Electrons



$$E_{1st} = 103.3\ MJ/mol$$
$$E_{2nd} = 3 - 6\ MJ/mol$$

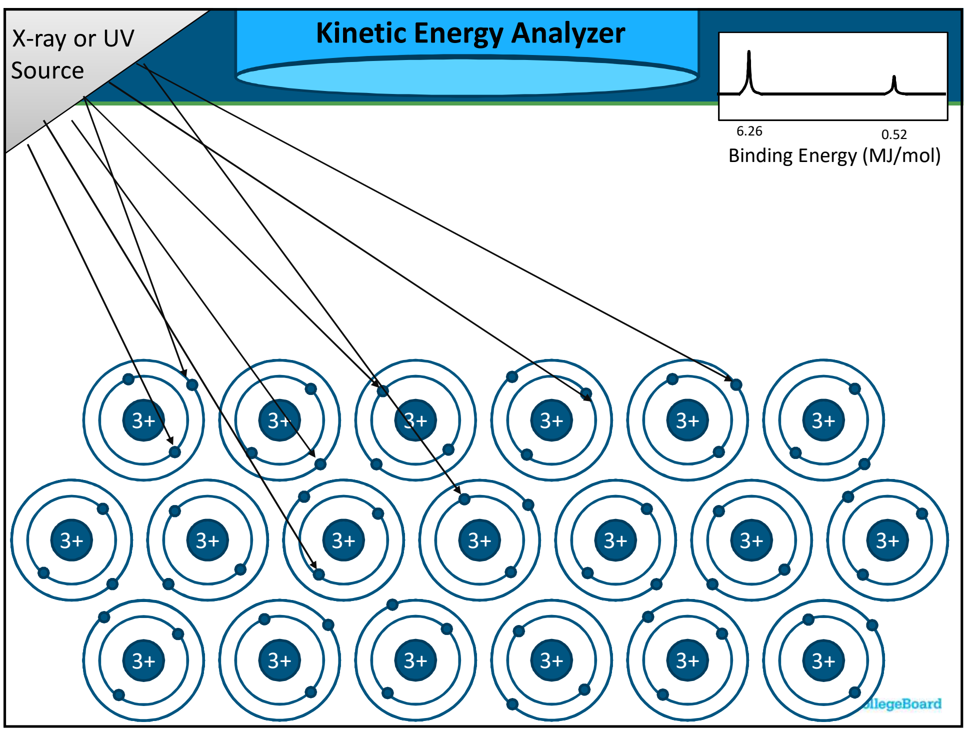
Any frequency of light that is sufficient to remove electrons from the 1^{st} shell can remove electrons from any of the other shells.

$$h\nu = IE + KE$$

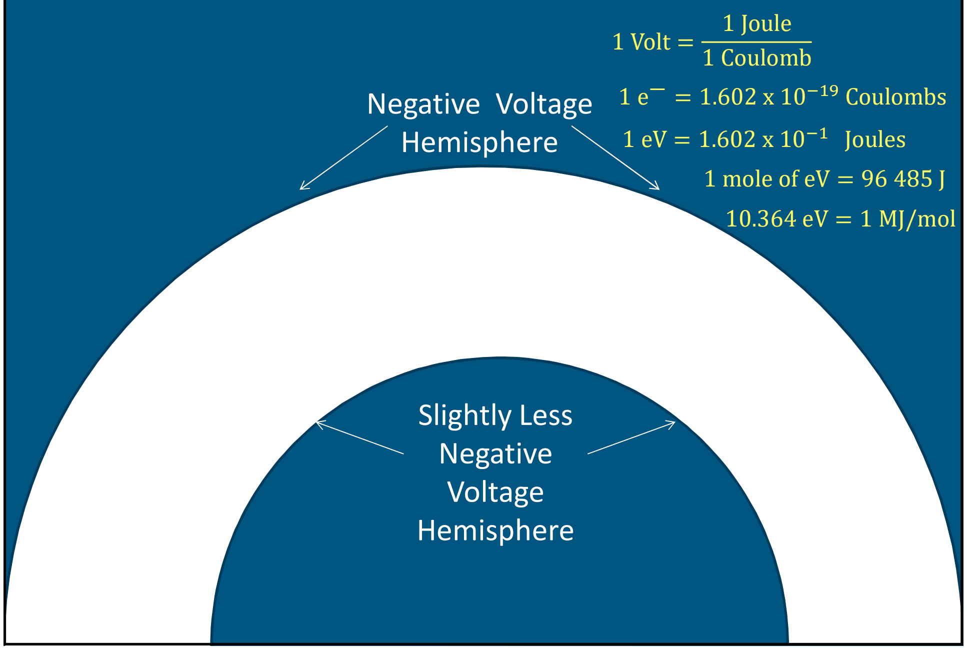
PES Instrument

Image Source: SPECS GmbH, http://www.specs.de/cms/front_content.php?idart=267

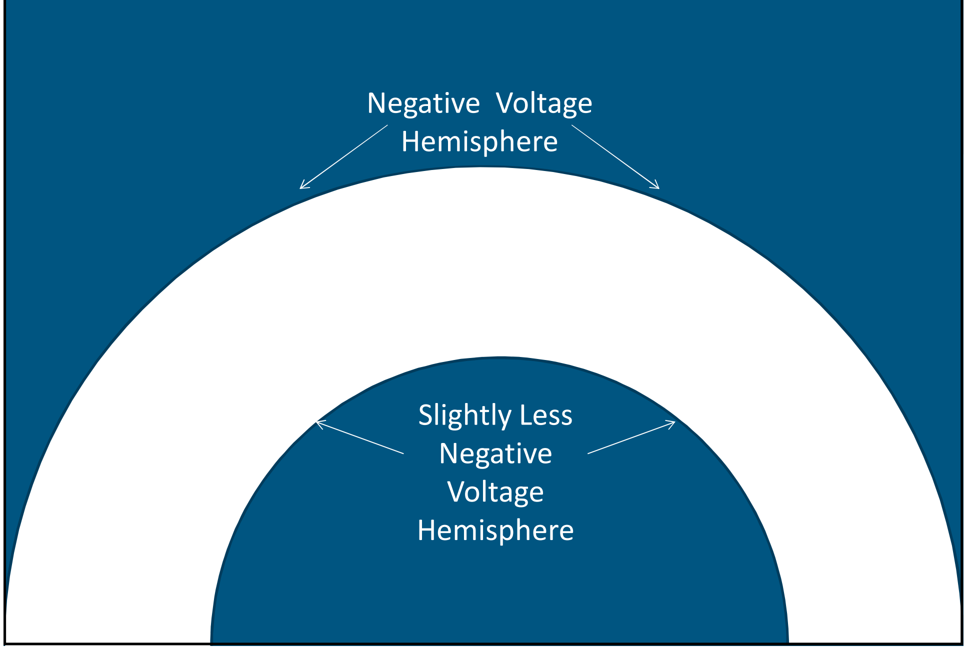
CollegeBoard

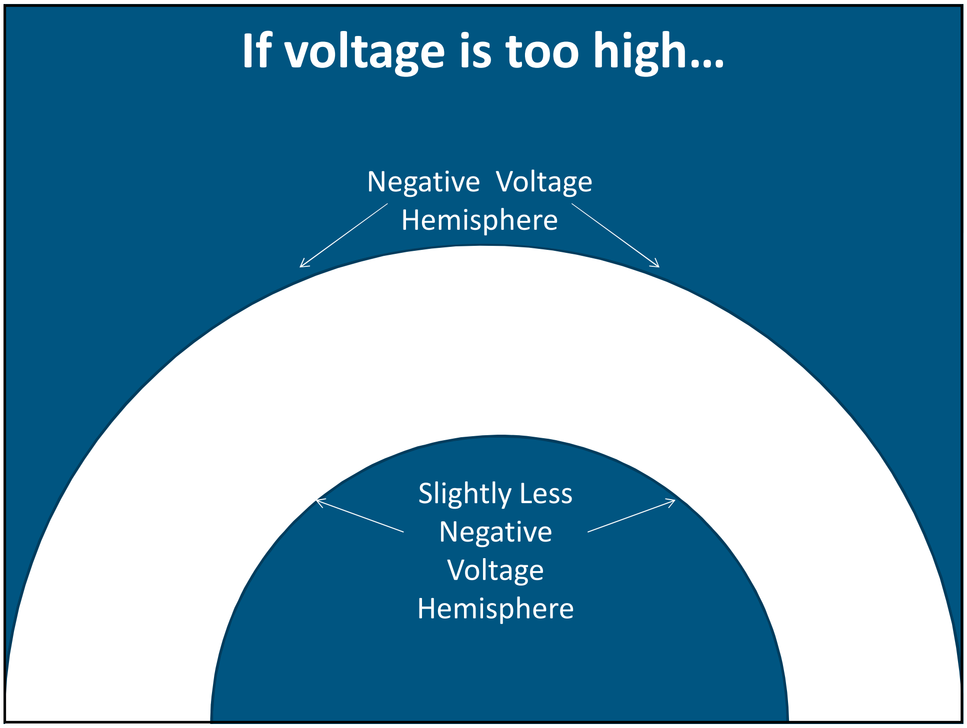


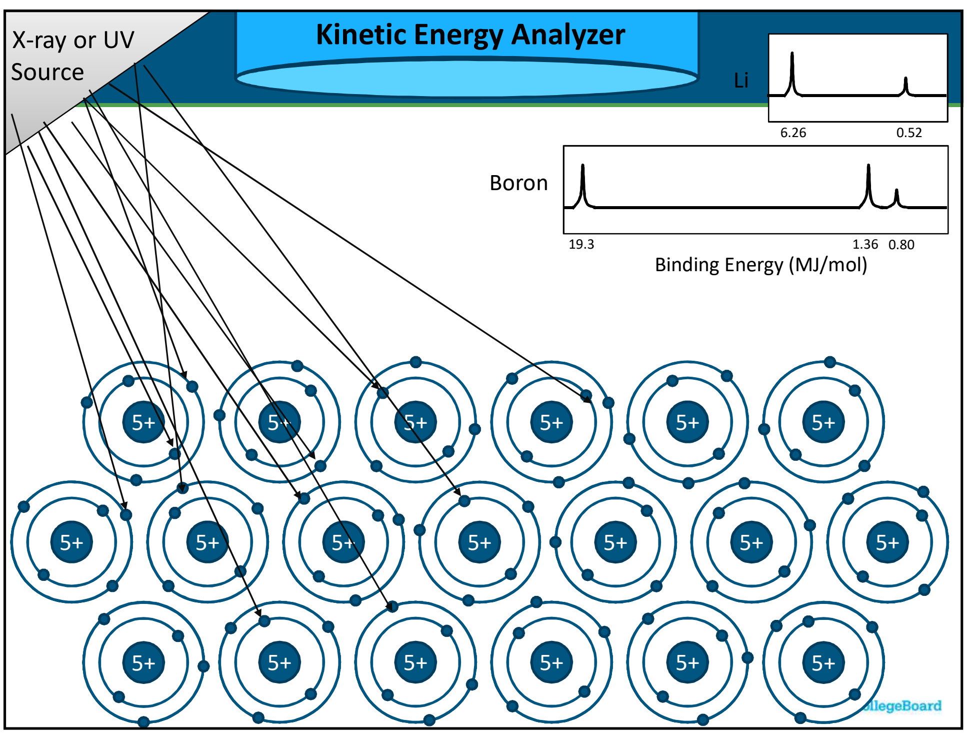
Kinetic Energy Analyzer



If Kinetic energy is too high…

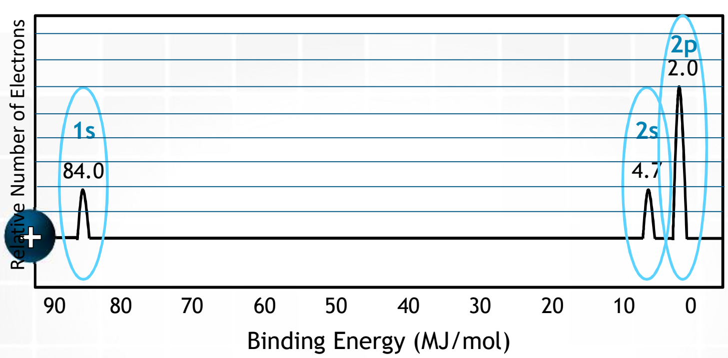



If voltage is too high…
Negative Voltage Hemisphere
Slightly Less Negative Voltage Hemisphere


X-ray or UV Source
Kinetic Energy Analyzer
Li
6.26
0.52
Boron
19.3
1.36
0.80
Binding Energy (MJ/mol)
5+

Analyzing Data from PES Experiments

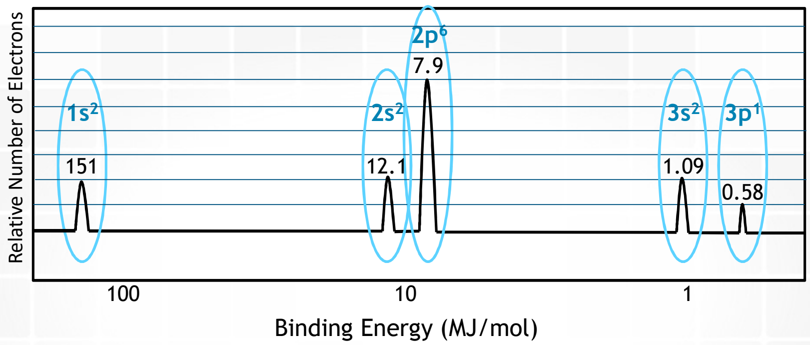
Analyzing data from PES



Which of the following elements might this spectrum represent?

(A) He
(B) N
(C) Ne
(D) Ar

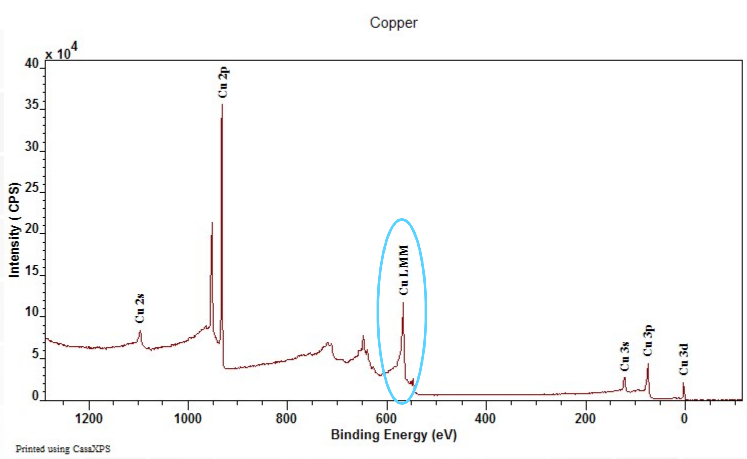
Analyzing data from PES



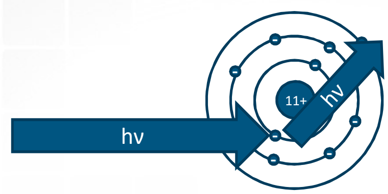
Given the spectrum above, identify the element and its electron configuration:

(A) B
(B) Al
(C) Si
(D) Na

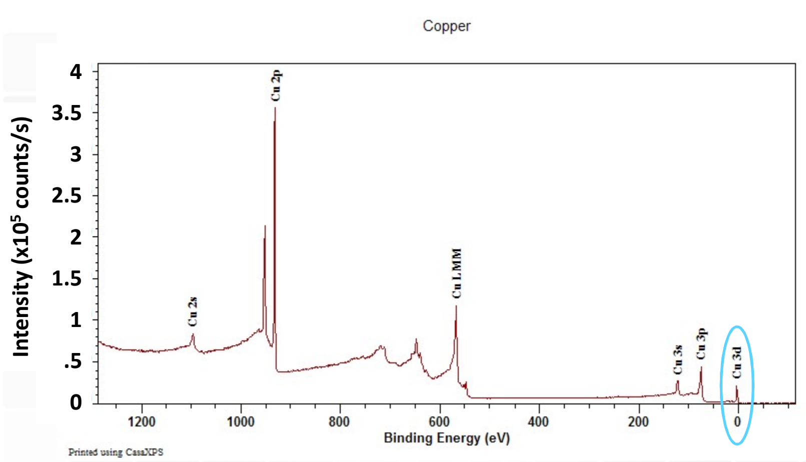
Real Spectrum



Auger Transitions

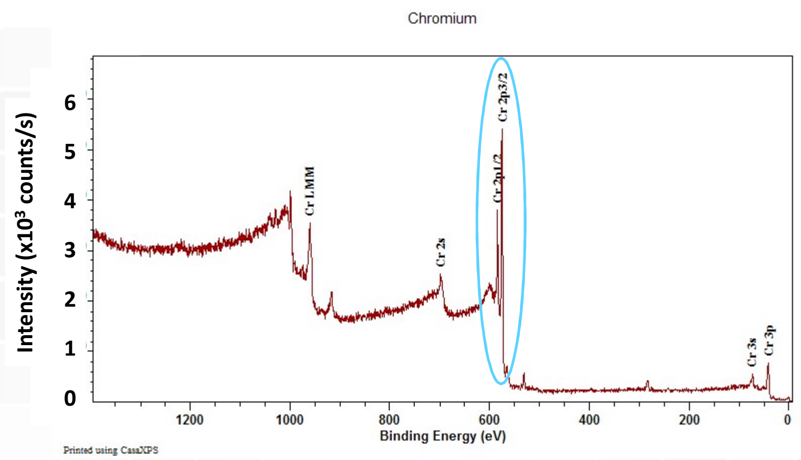


Real Spectrum

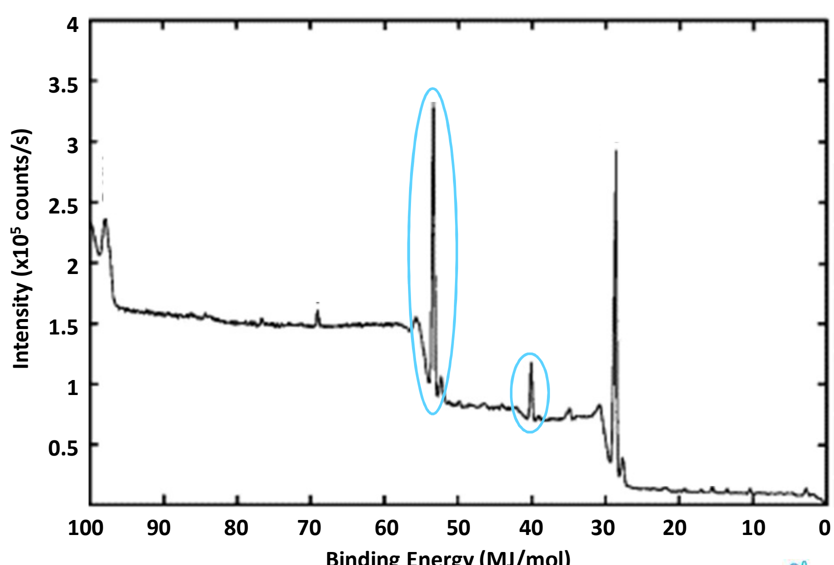


JB1

Copper vs. Chromium



Mixtures of Elements



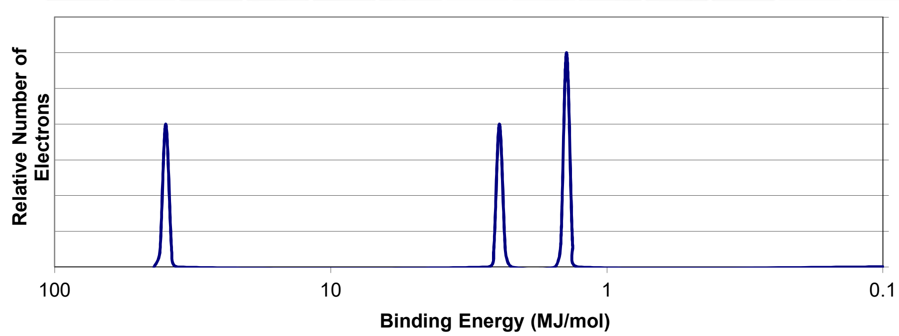
Slide 23

JB1 You never get entirely pure samples. This Chromium has some carbon in it, so the C KLL and C 1s peaks appear. I blanked them out with a rectangle to minimize confusion.
Jamie Benigna, 9/25/2013

PES Sample Questions

Sample Question #1

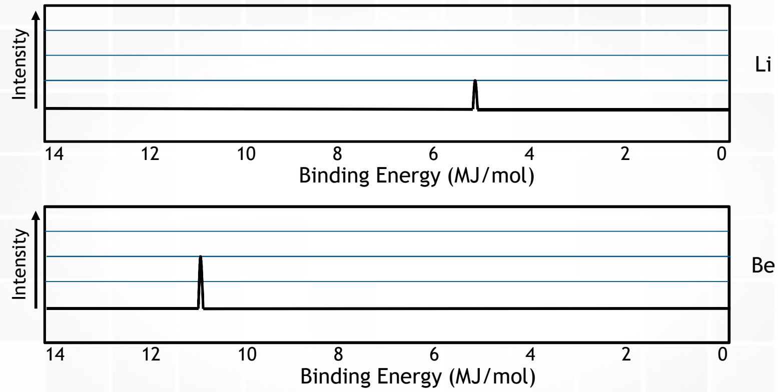
Which element could be represented by the complete PES spectrum below?



(A) Li (B) B (C) N (D) Ne

Sample Question #2

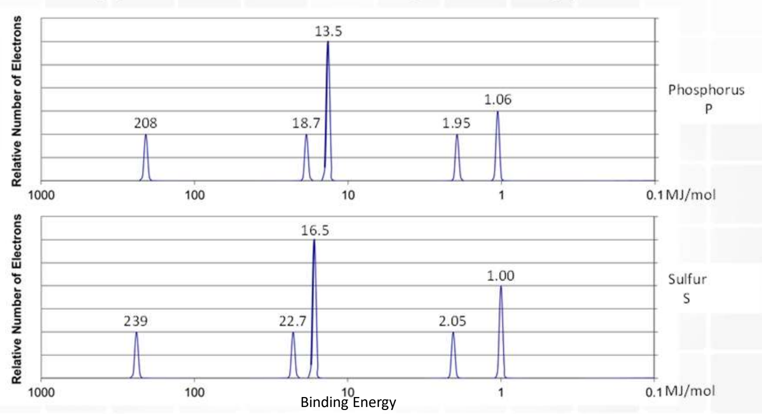
Which of the following best explains the relative positioning and intensity of the 2s peaks in the following spectra?



(A) Be has a greater nuclear charge than Li and more electrons in the 2s orbital
(B) Be electrons experience greater electron-electron repulsions than Li electrons
(C) Li has a greater pull from the nucleus on the 2s electrons, so they are harder to remove
(D) Li has greater electron shielding by the 1s orbital, so the 2s electrons are easier to remove

Sample Question #3

Given the photoelectron spectra above for phosphorus, P, and sulfur, S, which of the following best explains why the 2p peak for S is further to the left than the 2p peak for P, *but the 3p peak for S is further to the right than the 3p peak for P?*



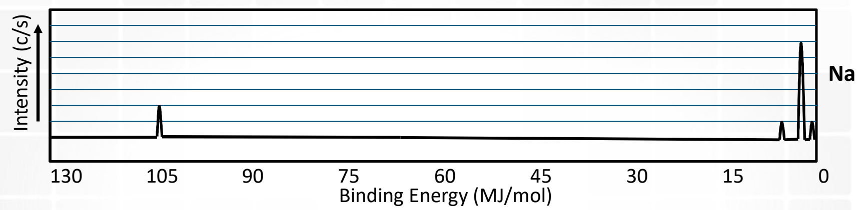
(A) S has a greater effective nuclear charge than P, and the 3p sublevel in S has greater electron repulsions than in P.
(B) S has a greater effective nuclear charge than P, and the 3p sublevel is more heavily shielded in S than in P.
(C) S has a greater number of electrons than P, so the third energy level is further from the nucleus in S than in P.
(D) S has a greater number of electrons than P, so the Coulombic attraction between the electron cloud and the nucleus is greater in S than in P.

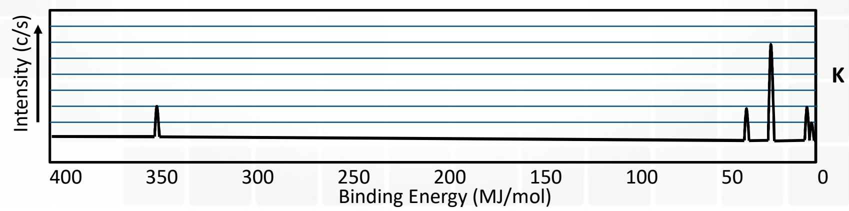
JB2

bl21

Sample Question #4

Looking at the complete spectra for Na and K below, which of the following would best explain the relative positioning of the 3s electrons?



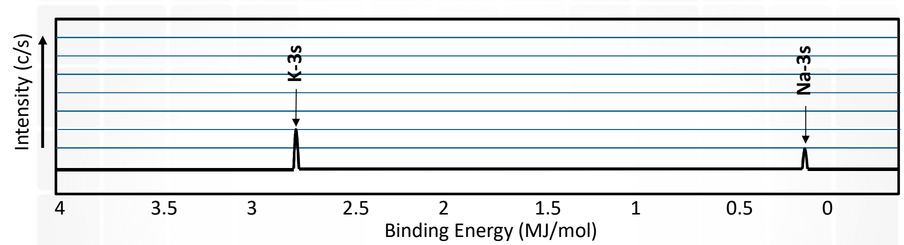


CollegeBoard

JB3

Sample Question #4a

Looking at the spectra for Na and K below, which of the following would best explain the difference in binding energy for the 3s electrons?



(A) K has a greater nuclear charge than Na
(B) K has more electron-electron repulsions than Na
(C) Na has one valence electron in the 3s sublevel
(D) Na has less electron shielding than K

CollegeBoard

Slide 29

JB2 I at first want teachers to consider the question without choices. In the script, I indicate that at the scale, it is very difficult to determine what is happening since so many peaks overlap at the righthand side. The next slide zooms in and compares the 3s sublevel for Na and K directly.
Jamie Benigna, 9/25/2013

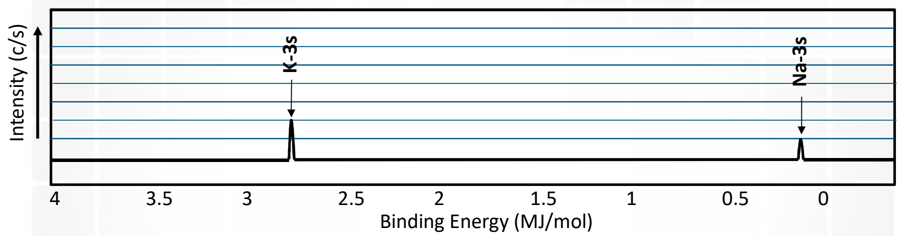
bl21 Jamie - not sure if I have set this up properly
blankenau, 10/17/2013

Slide 30

JB3 Updated the references in the outline. Note that with the addition of the title slide and biographical info, all slides have been bumped back by 2 from what is written in the outline.
Jamie Benigna, 9/25/2013

Sample Question #4b

Looking at the spectra for Na and K below, which of the following would best explain the difference in ***signal intensity*** for the 3s electrons?



(A) K has a greater nuclear charge than Na
(B) K has more electron-electron repulsions than Na
(C) Na has one valence electron in the 3s sublevel
(D) Na has less electron shielding than K

Sample Question #5

Given the photoelectron spectrum below, which of the following best explains the relative positioning of the peaks on the horizontal axis?

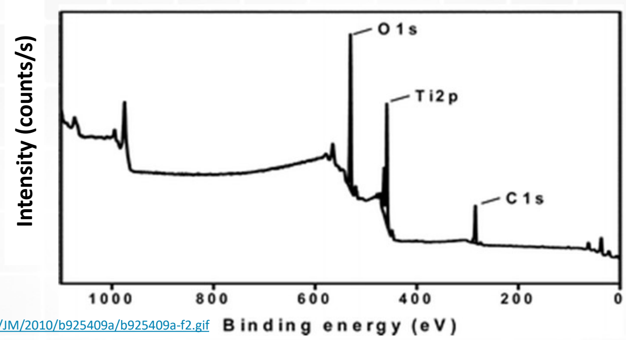


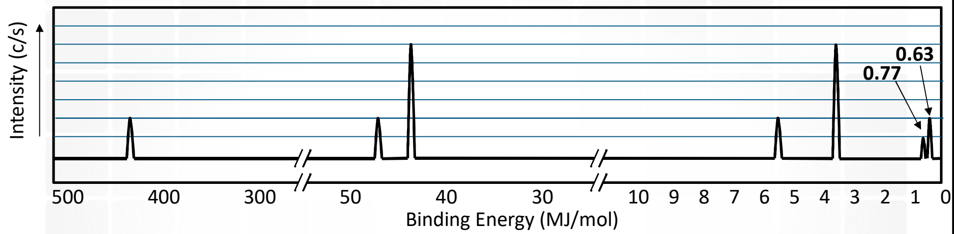
Image source: http://www.rsc.org/ej/JM/2010/b925409a/b925409a-f2.gif

(A) O has more valence electrons than Ti or C, so more energy is required to remove them
(B) O has more electron-electron repulsions in the 2p sublevel than Ti and C
(C) Ti atoms are present in a greater quantity than O can C in the mixture.
(D) Ti has a greater nuclear charge, but the 2p sublevel experiences greater shielding than the 1s sublevel.

JB9

Sample Question #6

Given the photoelectron spectrum of scandium below, which of the following best explains why Scandium commonly makes a 3+ ion as opposed to a 2+ ion?



(A) Removing 3 electrons releases more energy than removing 2 electrons.

(B) Scandium is in Group 3, and atoms only lose the number of electrons that will result in a noble gas electron configuration

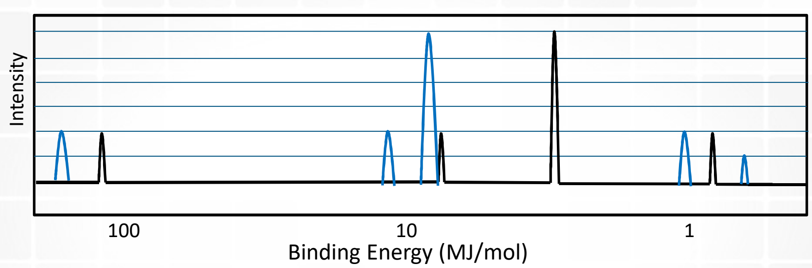
(C) The amount of energy required to remove an electron from the 3d sublevel is close to that for the 4s sublevel, but significantly more energy is needed to remove electrons from the 3p sublevel.

(D) Removing 2 electrons alleviates the spin-pairing repulsions in the 4s sublevel, so it is not as energetically favorable as emptying the 4s sublevel completely.

CollegeBoard

Example Formative Assessment

On the photoelectron spectrum of magnesium below, draw the spectrum for aluminum



Hint: for additional formative assessments, use spectra from previous multiple choice questions

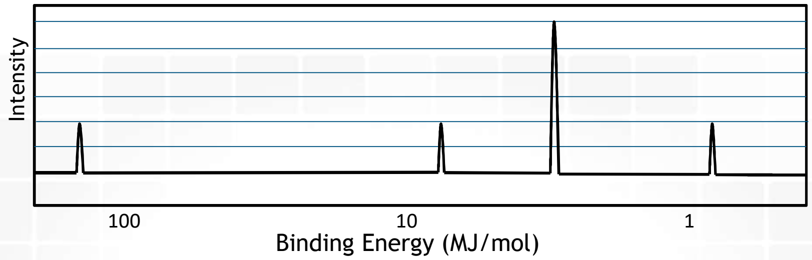
CollegeBoard

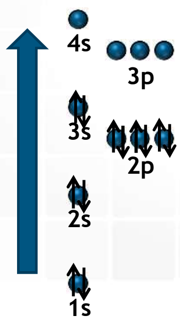
Slide 33

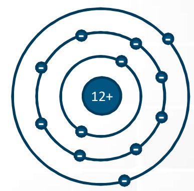
JB9 I changed the language of choice C significantly on this slide. Not sure if this has to be updated elsewhere.

Jamie Benigna, 11/3/2013

Quick Check - Can You Now Translate Between These Representations of Mg?







$1s^2\ 2s^2\ 2p^6\ 3s^2$

Using Data to Makes Conclusions About Atomic Structure

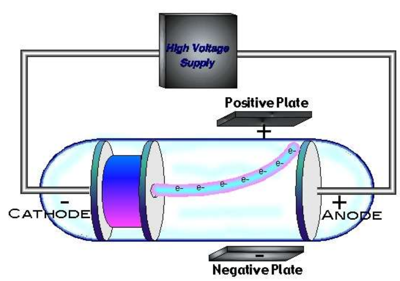
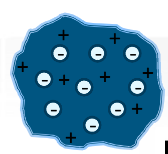
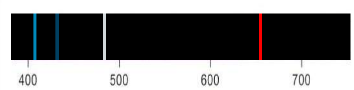
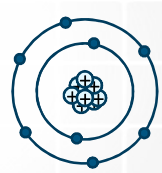


image source: http://ericsaltchemistry.blogspot.com/2010/10/jj-thomsons-experiments-with-cathode.html

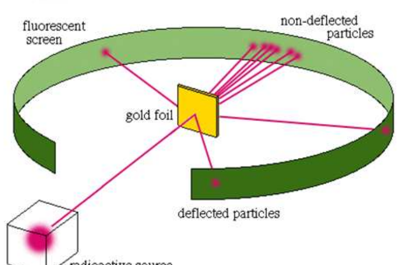


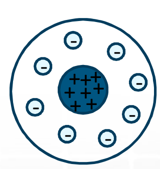
Thomson





Bohr

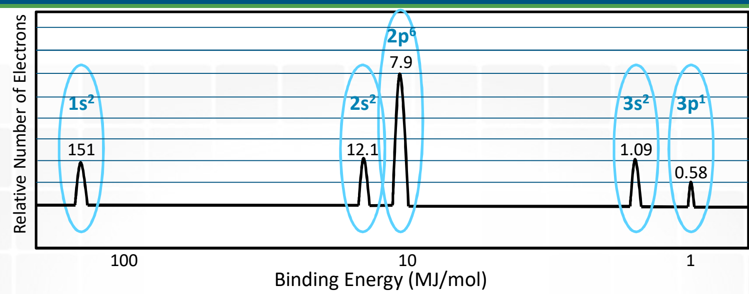




Rutherford

http://84d1f3.medialib.glogster.com/media/f9/f9a5f2402eb205269b648b14072d9fb3a2f556367849d7feb5cfa4a8e2b3fd29/yooouu.gif

PES - Data that Shells are Divided into Subshells



Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
Na	495	4560					
Mg	735	1445	7730				
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

Applicable Science Practices

From the AP Chemistry Curriculum Framework:

- SP 3.2
  - The student can refine scientific questions
- SP 3.3
  - The student can evaluate scientific questions
- SP 6.3
  - The student can articulate the reasons that scientific explanations are refined or replaced.

Wrap up and Take Aways

AP

CollegeBoard

Applicable Learning Objectives

AP

From the AP Chemistry Curriculum Framework:

- 1.5 – The student is able to explain the distribution of electrons in an atom or ion based upon data.
- 1.6 – The student is able to analyze data relating to electron energies for patterns and relationships.
- 1.7 – The student is able to describe the electronic structure of the atom, using PES data, ionization energy data, and/or Coulomb's law to construct explanations of how the energies of electrons within shells in atoms vary.
- 1.8 – The student is able to explain the distribution of electrons using Coulomb's law to analyze measured energies.
- 1.12 – The student is able to explain why a given set of data suggests, or does not suggest, the need to refine the atomic model from a classical shell model with the quantum mechanical model.
- 1.13 – Given information about a particular model of the atom, the student is able to determine if the model is consistent with specified evidence.
- 1.14 – The student can justify the selection of a particular type of spectroscopy to measure properties associated with vibrational or electronic motions of molecules.

CollegeBoard

Supporting Resources

Download and use the webcast handouts

- Classroom activities
  - Shells Class Activity
  - From Shells to Subshells Class Activity
- Teacher resources
  - Spectrum generator spreadsheet
  - Peaks compiled (80 elements)
  - Frequently asked questions
- Testing items
  - Sample items referenced in this webcast (for classroom use, formative, or summative assessments)

CollegeBoard

Supporting Resources (cont.)

- Arizona simulated photoelectron spectra
  http://www.chem.arizona.edu/chemt/Flash/photoelectron.html
- Guided inquiry activities on PES
  - John Gelder (Oklahoma State University)
  - Moog and Farrell, *Chemistry: A Guided Inquiry*
  - POGIL
- Books on PES technical specs
  - Van der Heide, Paul. *X-Ray Photoelectron Spectroscopy: An Introduction to Principles and Practices*. New Jersey: John Wiley & Sons, Inc, 2012.
  - Ellis, Andrew M., Miklos Feher, and Timothy Wright. *Electronic and Photoelectron Spectroscopy: Fundamentals and Case Studies*. New York: Cambridge University Press, 2005.

CollegeBoard

Supporting Resources (cont.)

AP

- AP Chemistry Teacher Community (resources section)
  https://apcommunity.collegeboard.org/web/apchem
- Spectra search strings
  - XPS
  - X-ray photoelectron spectroscopy
  - UVPS
  - ESCA spectroscopy
  - ESCA spectra
  - Photoelectron spectrum
  - Photoelectron spectroscopy

CollegeBoard

Supporting Resources (cont.)

AP

bl29

JB10

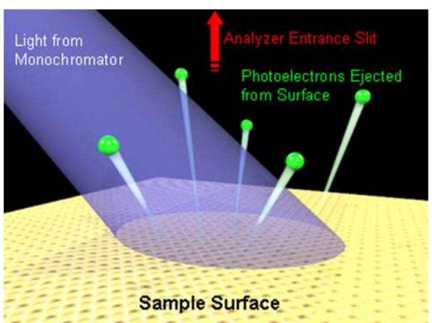


Image Source: Shen Laboratory, Stanford University and SLAC National Accelerator Laboratory http://arpes.stanford.edu/facilities_ssrl.html

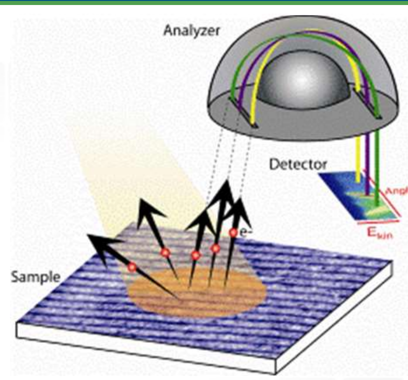


Image source: Inna M Vishik
http://www.stanford.edu/~ivishik/inna_vishik_files/Page452.htm

CollegeBoard

Slide 44

---

bl29 Jamie - not sure how you wanted to use these images
blankenau, 10/21/2013

JB10 I will use this as a lead-in to the next slide
Jamie Benigna, 11/3/2013

Take Away

You should now feel confident

- Explaining how data informs our understanding of the atom
- Using PES and experimental evidence to build mental models of atomic structure
- Explaining how a PES instrument collects data and how to analyze spectra