NACK CENTER
Building College-University Partnerships for Nanotechnology Workforce Development

Wave-Based Characterization

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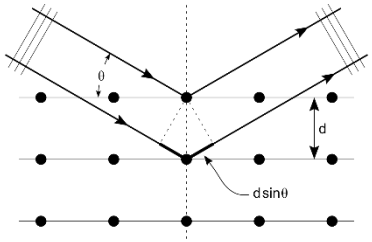
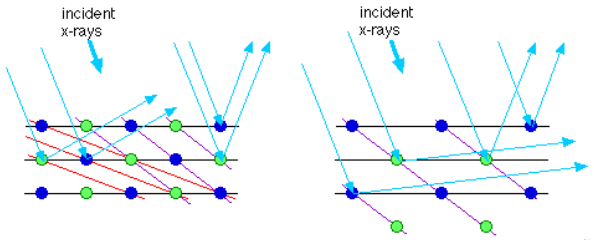
Classroom Resources

X-Ray Diffraction

- What is it and Why is it important?
  - A very frequently used tool in order to determine
    - Crystal structure
    - Crystal size
    - Internal stress
    - Composition
  - Elastic scattering (Bragg diffraction) of the X-rays from the examined materials are collected. Reflected X-rays will interfere and possess information about the crystallography.





X-Ray Diffraction

- Examining Interference from two sources separated by a distance
  - Phet University of Colorado Boulder offers excellent illustrative tools to explain how the local positioning of the light sources can have an effect on the collected far-field diffraction patterns on a screen. This example can be linked to the reflection from the periodic atomic configurations: crystals. Wave Interference (colorado.edu)

PhET INTERACTIVE SIMULATIONS

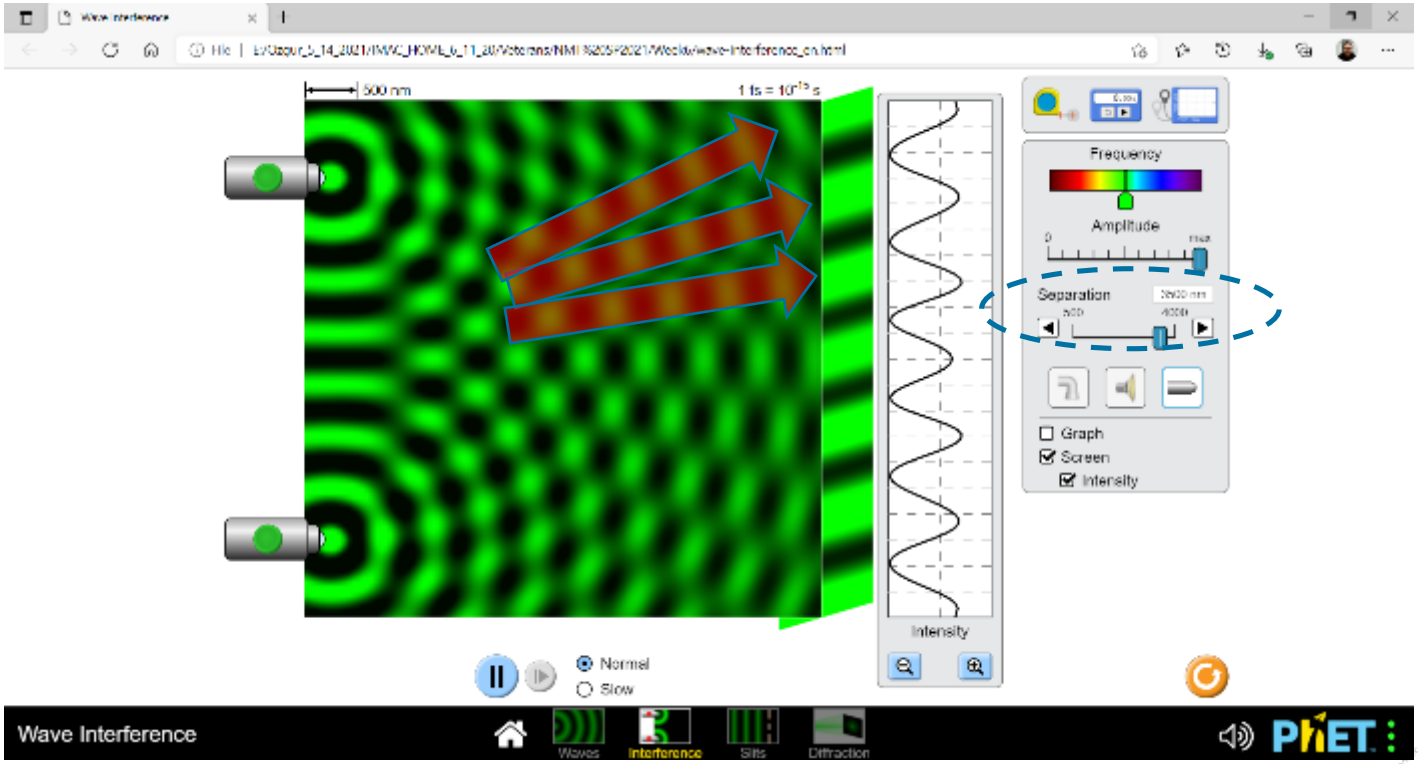
University of Colorado Boulder

Grand Valley State University
Seymour and Esther Padnos College of Engineering and Computing

PennState

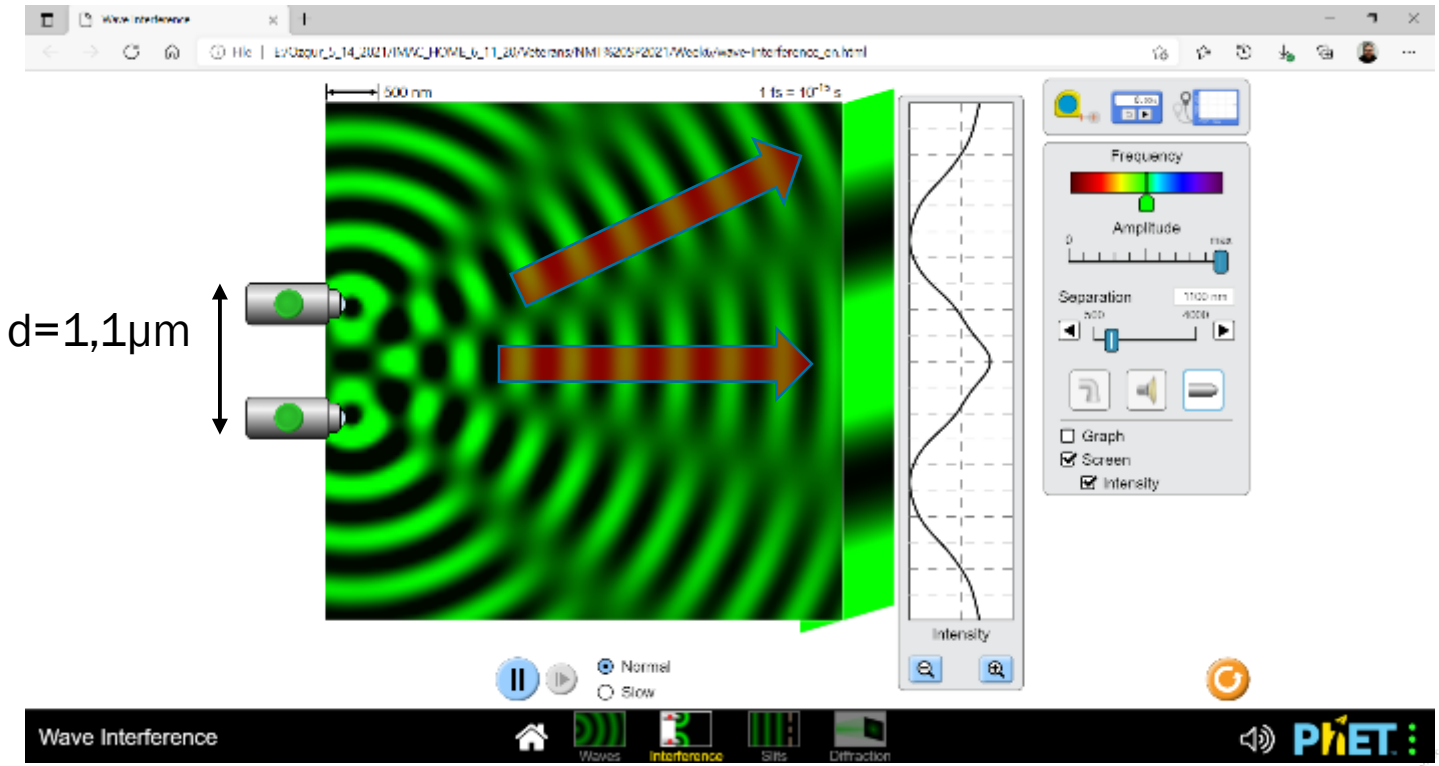
X-Ray Diffraction

- Examining Interference from two sources separated by a distance
  - Two sources separated by 3,5μm yields interference patterns that survive waves in the shown propagation directions (arrows).



X-Ray Diffraction

- Examining Interference from two sources separated by a distance
  - Two sources separated by 1,1 μm yields the given intensity profile on the screen.



X-Ray Diffraction

- Examining Interference from two sources separated by a distance
  - Students can deduce that d and arrow directions, which constitute the diffraction pattern are related to each other. As d increases, the arrows make a larger angle (θ) wrt the horizontal axis. Accordingly:

$$d \propto \theta^{-1}$$ **(inversely proportional to each other)**

  - Similarly, the reflections from planes of arranged atoms scattering rays 1-3 in the figure below can also be thought of the same form. The collection angle (θ) is related to the separation between these planes.

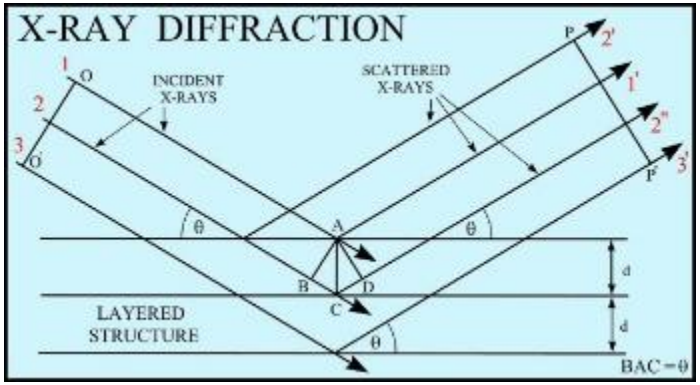


Image taken from Bragg Diffraction | PhysicsOpenLab

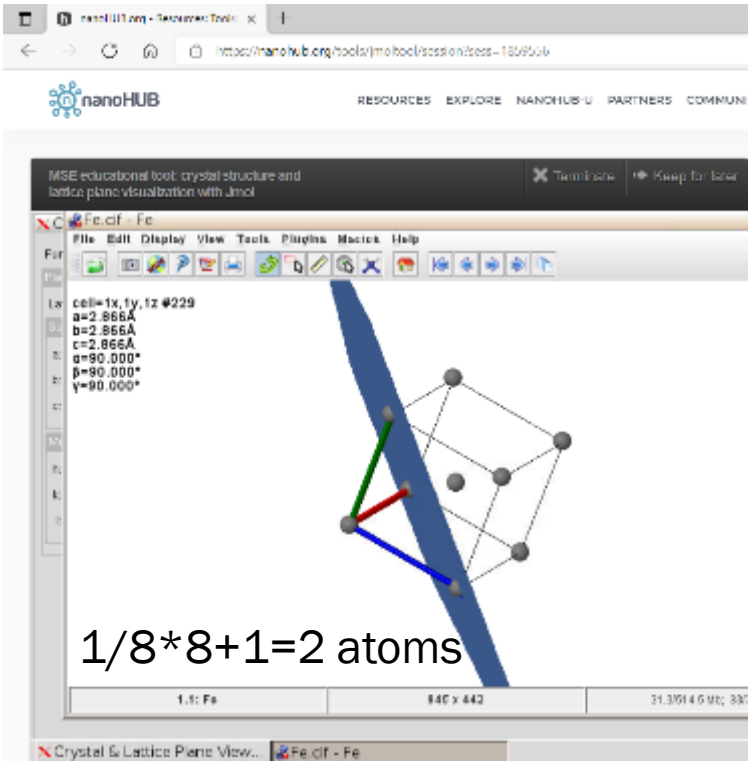
X-Ray Diffraction

- Examining Interference from two sources separated by a distance
  - Nanohub offers nanoHUB.org - Resources: MSE educational tool: crystal structure and lattice plane visualization with Jmol that helps easy visualization of the crystal planes and Bravais lattices.

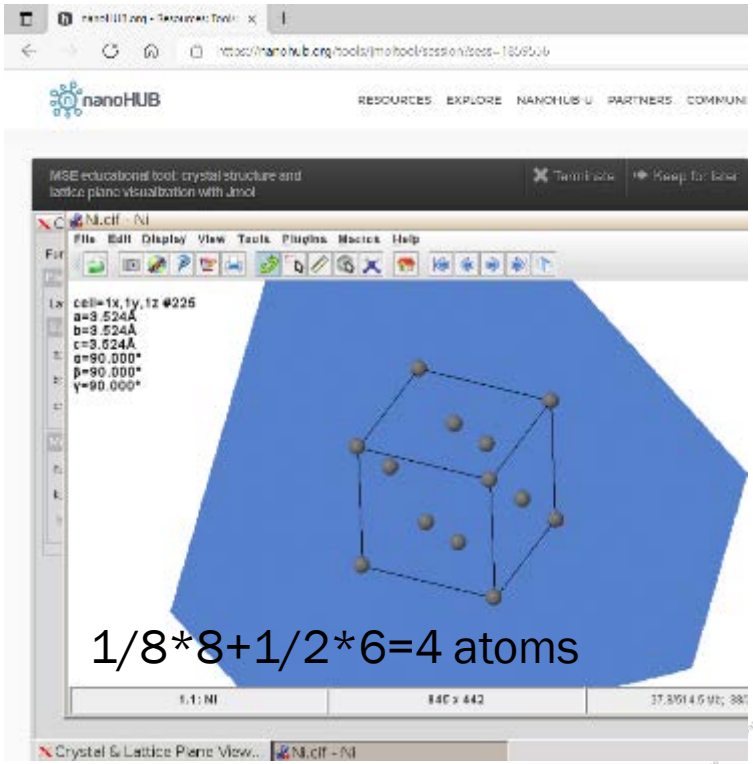
X-Ray Diffraction

- **JMOL Exercise1:** Counting number of atoms in BCC and FCC unit lattices.

BCC



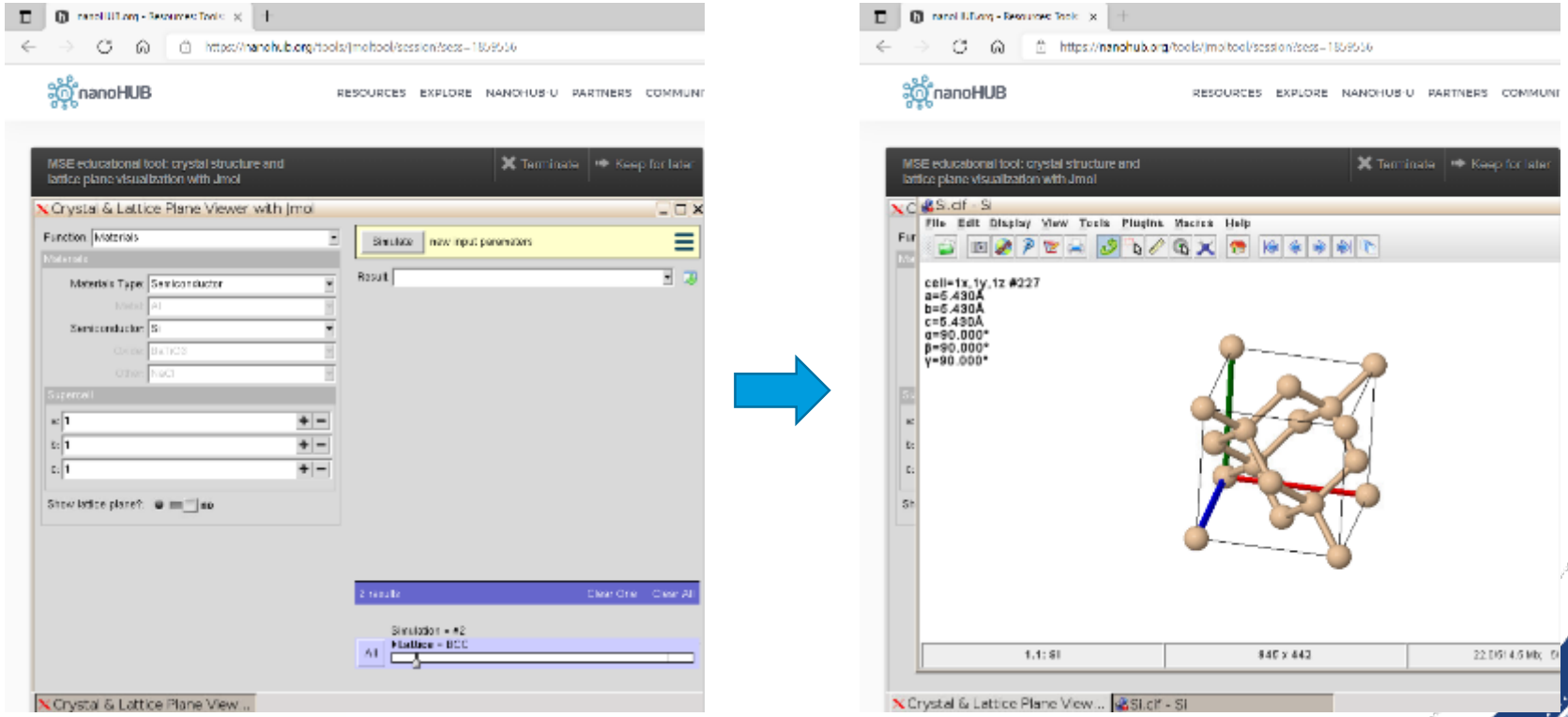
FCC



X-Ray Diffraction

- **JMOL Exercise2:** Si crystal structure and shortest distance between atoms.

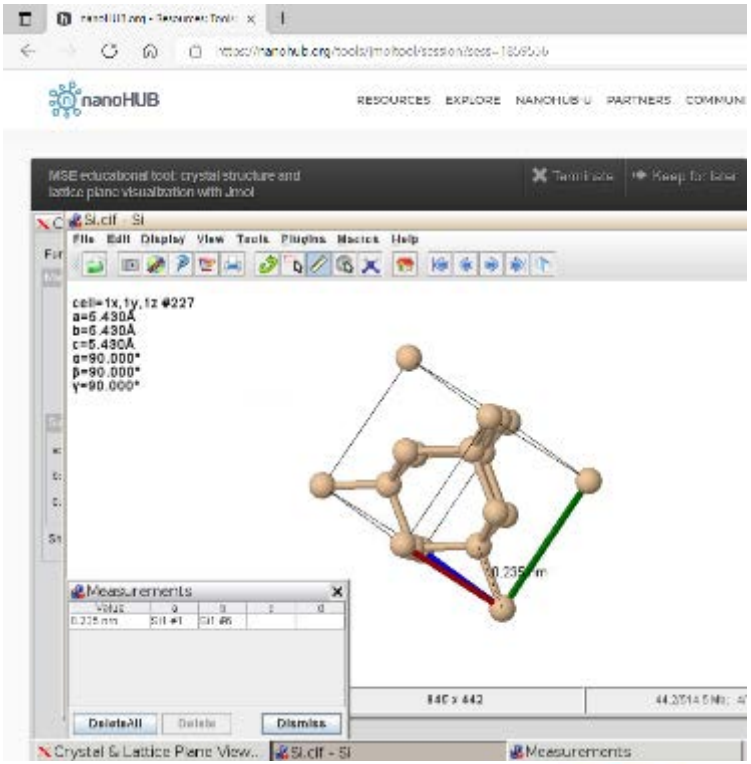
Diamond lattice



X-Ray Diffraction

- **JMOL Exercise3:** Si crystal structure and shortest distance between atoms.

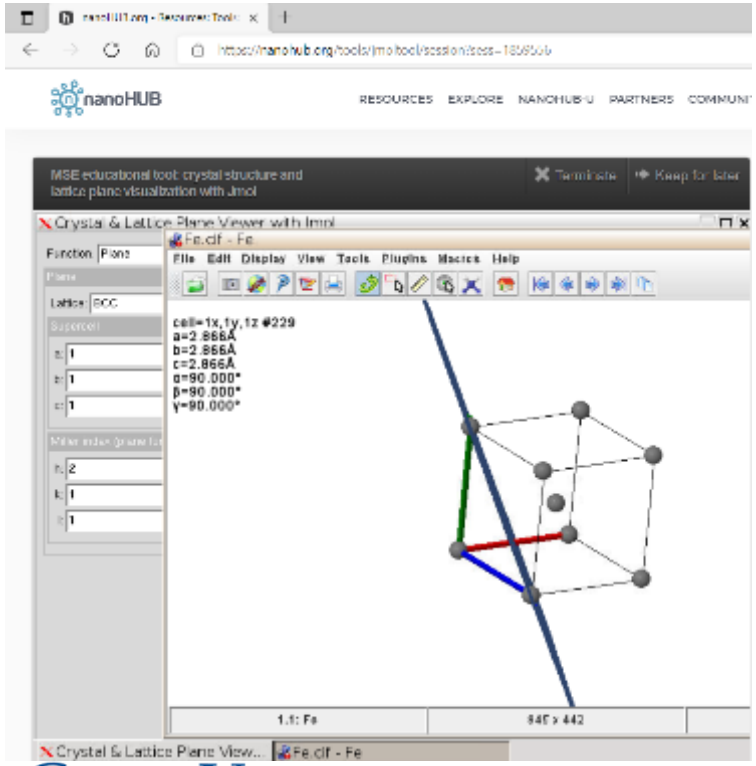
Shortest Distance: 0.235nm



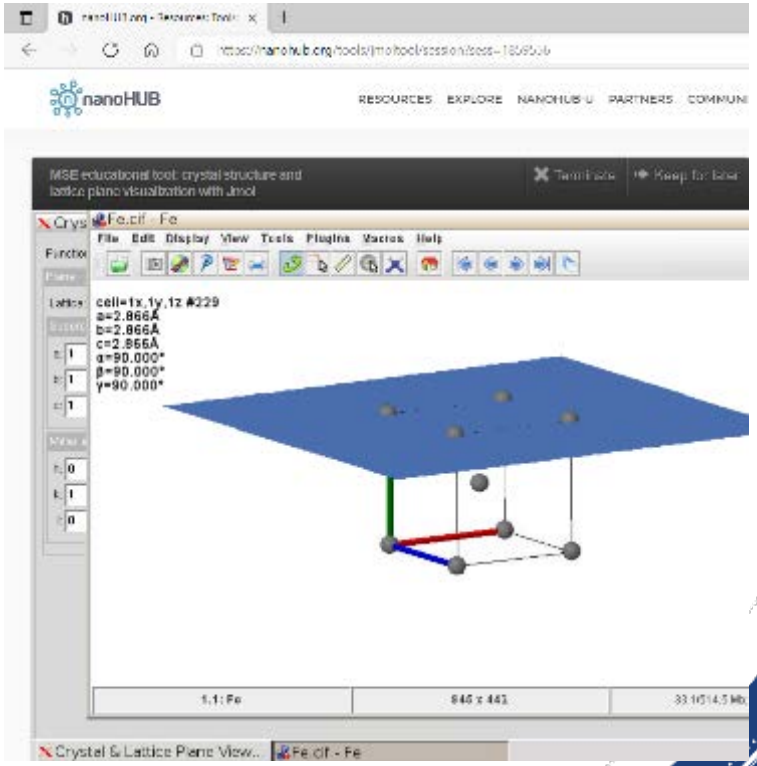
X-Ray Diffraction

- **JMOL Exercise4:** Draw Miller planes for
  - (211) and (010) planes on BCC lattice.

(211)



(010)



X-Ray Diffraction

- XRD simulations:
  - A typical configuration is shown below with the x-ray source on the left hand side and the detector on the right hand side. Optical elements are used to control the beam divergence.

Image taken from Wikipedia

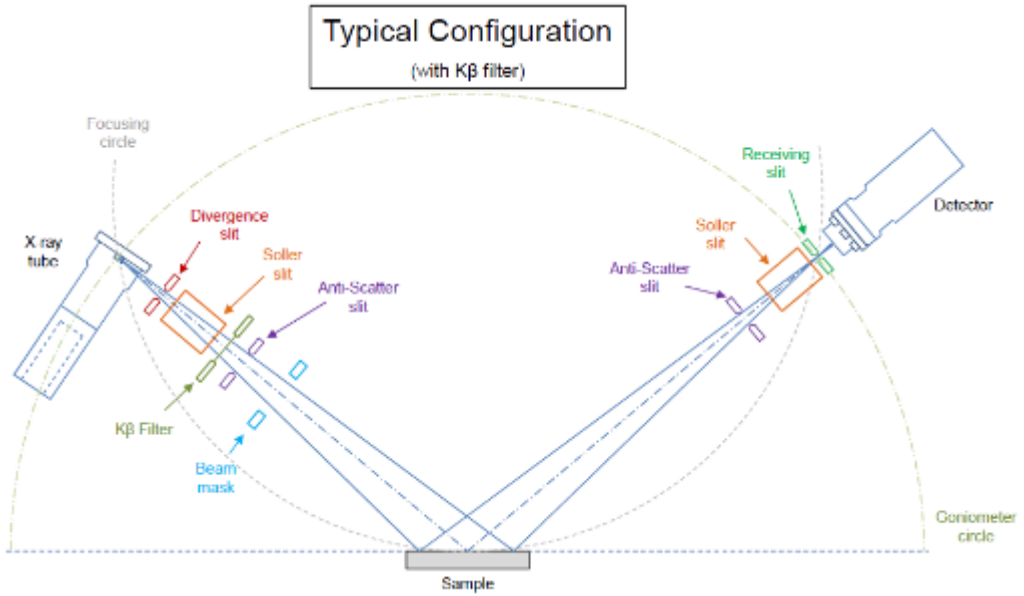
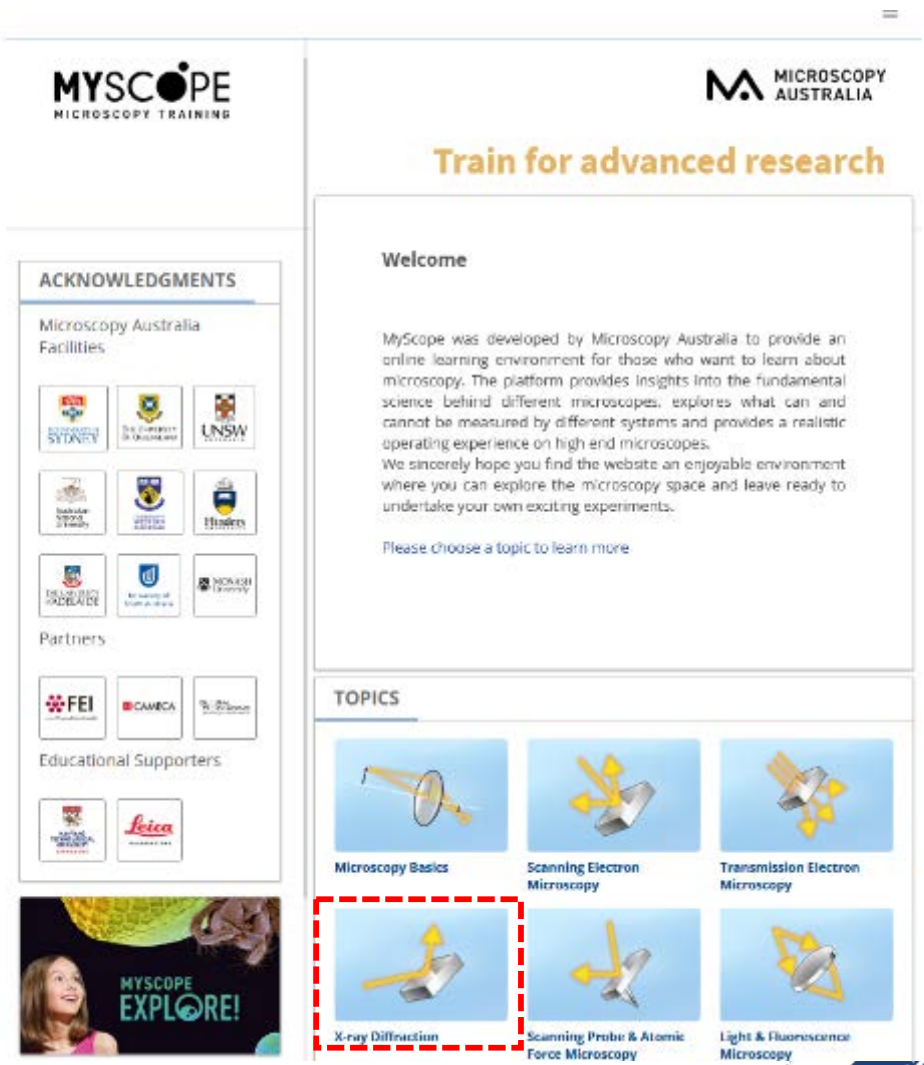


Image taken from RMS Foundation XRD Lecture Notes

X-Ray Diffraction

MYSCOPE
MICROSCOPY TRAINING

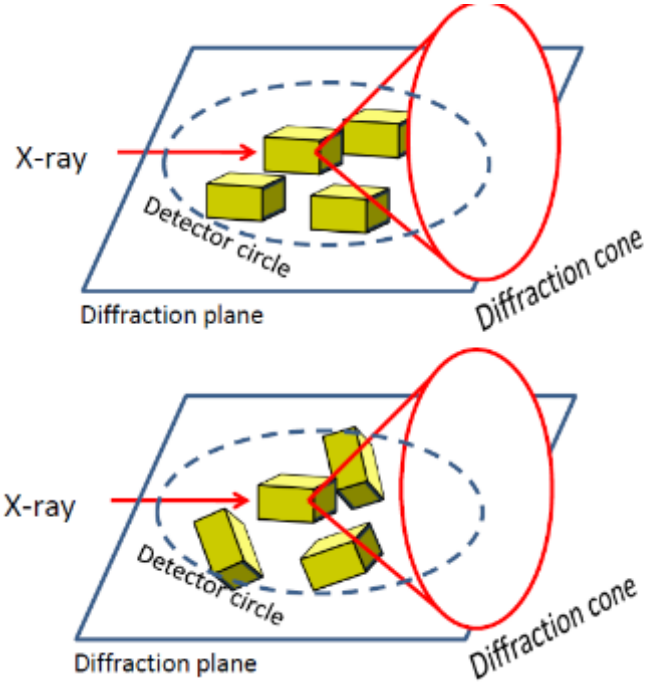


GRAND VALLEY STATE UNIVERSITY
SEYMOUR AND ESTHER PADNOS COLLEGE OF ENGINEERING AND COMPUTING

PennState

X-Ray Diffraction

- XRD simulations:
  - Students get convinced that the planes of reflections will create different diffraction cones at the exit side. Crystalline structures will generate point inside the diffraction cone. [nanoHUB.org - Resources: MSE educational tool: X-ray diffraction (XRD) pattern]



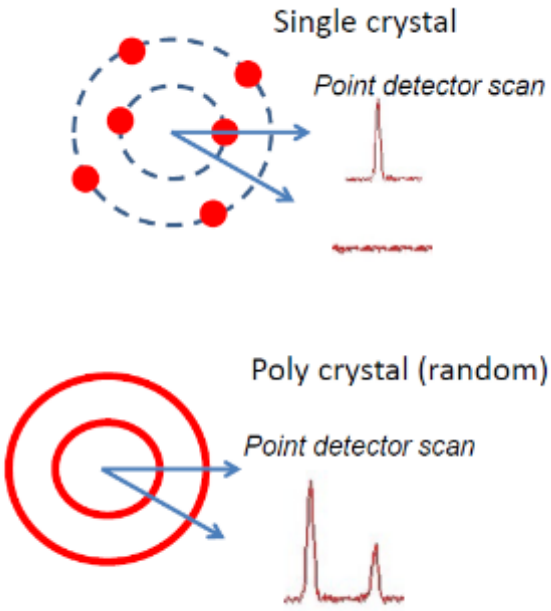
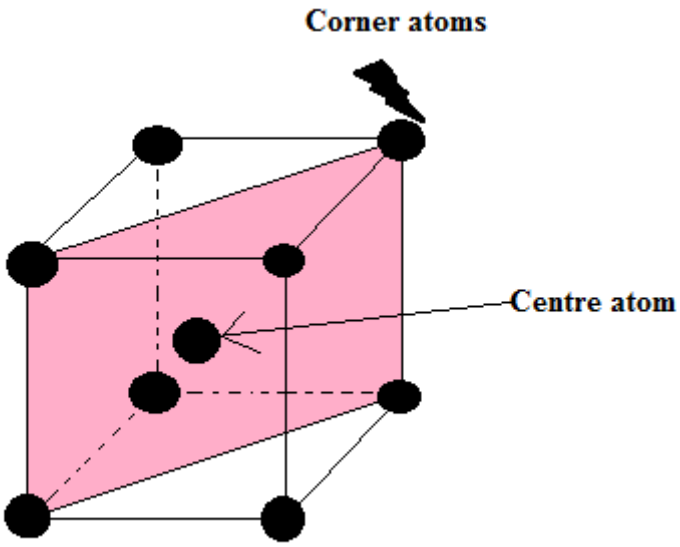


Image taken from Mauro Serdala's XRD lecture notes

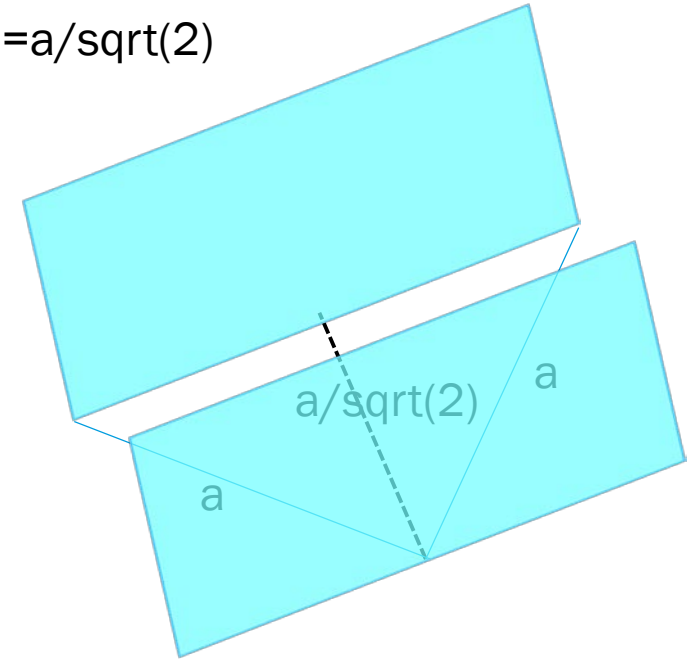
X-Ray Diffraction

- **XRD Exercise1:** Collect peak locations for BCC and verify for (110) plane.



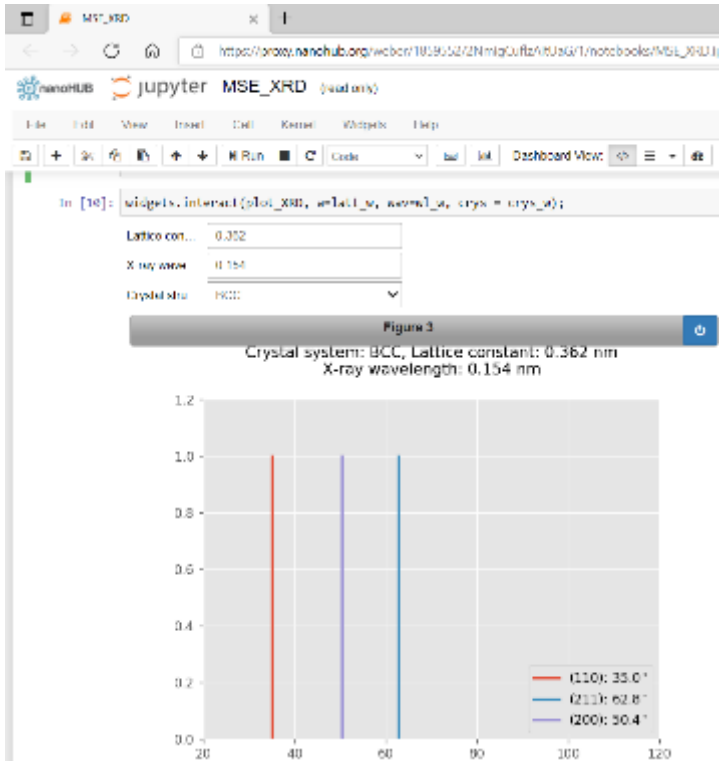
(100) plane

These reflection planes are separated by a distance d of:
d=a/sqrt(2)



X-Ray Diffraction

- **XRD Exercise1:** Collect peak locations for BCC and verify for (110) plane.



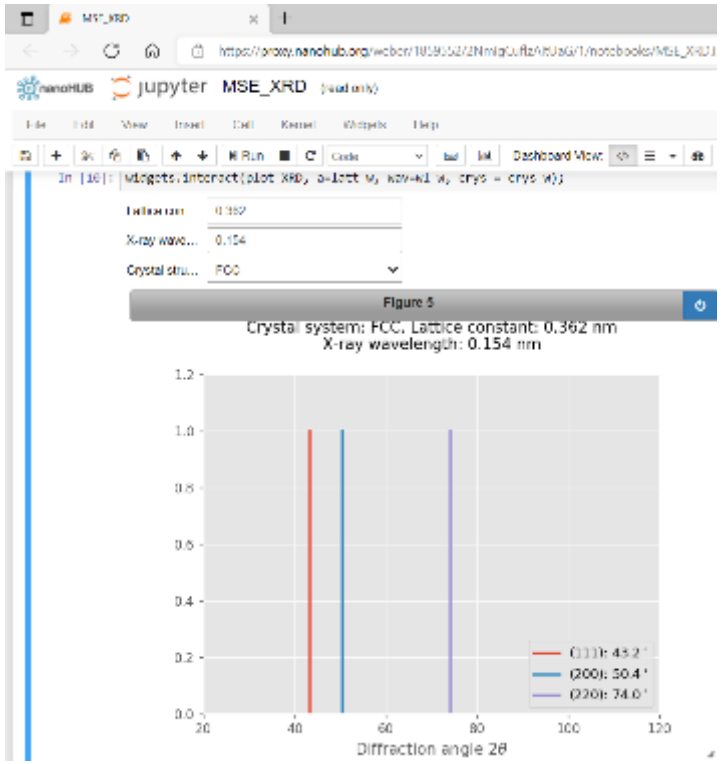
$$2d\sin\theta = n\lambda$$

According to Bragg formula:
n=1, λ=0.154nm (CuKα), d=a/sqrt(2), a=0.362nm

$\theta=\sin^{-1}(0.154/(2*0.362/\sqrt{2}))=17.5$ degrees

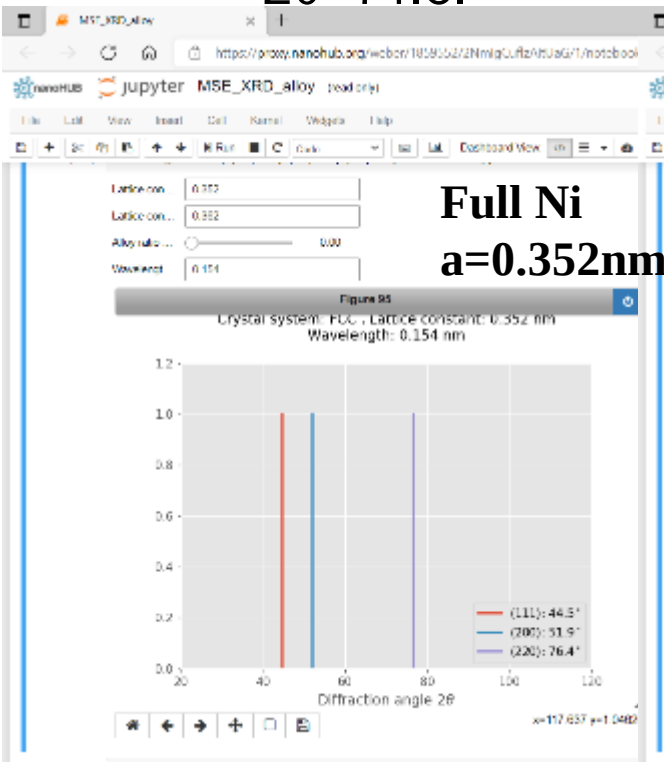
X-Ray Diffraction

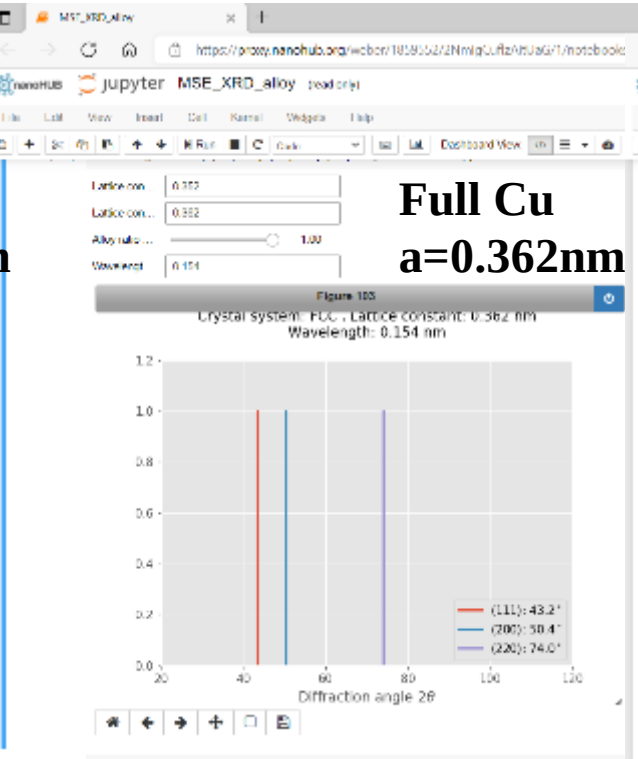
- **XRD Exercise2:** Collect peak locations for FCC

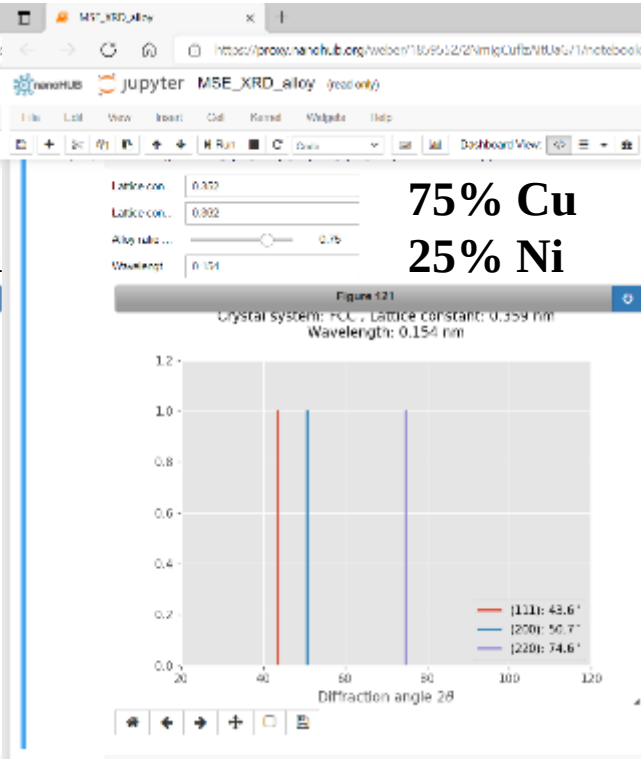


X-Ray Diffraction

- **XRD Exercise3:** Finding alloy ratio of Ni-Cu alloy
  - Instructor comes up with a hidden alloy ratio and asks students to figure it out by intelligent trials remembering that d and θ are inversely proportional to each other. Let us say (220) plane 2θ=74.6.

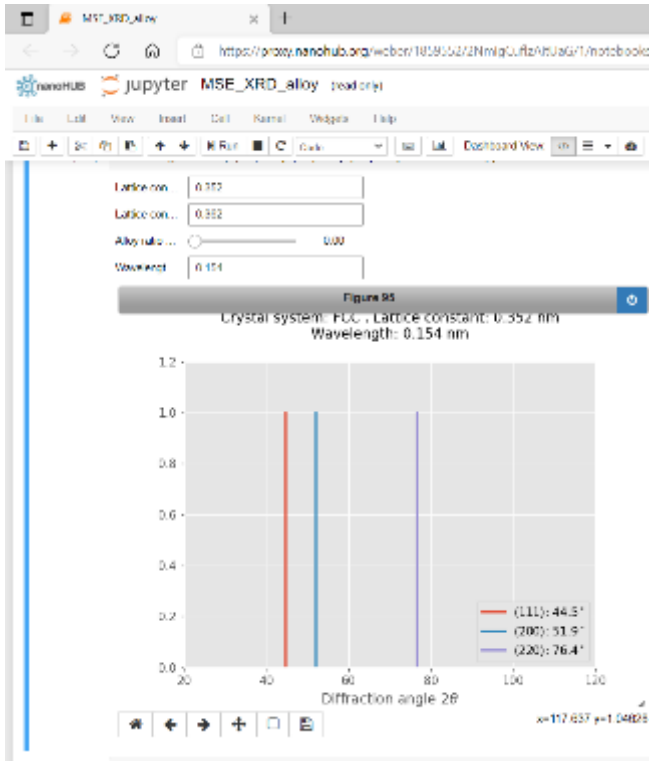


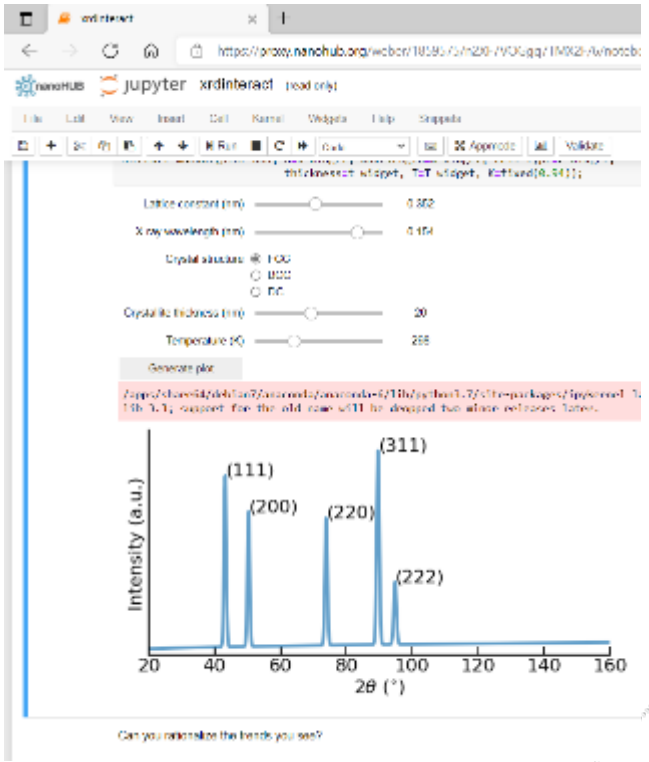




X-Ray Diffraction

- nanoHUB.org - Resources: XRD interactive trends plot
  - XRD interactive trends enables a simple calculation of the more realistic peaks with valid amplitudes.





X-Ray Diffraction

- nanoHUB.org - Resources: XRD interactive trends plot
  - XRD interactive trends enables a simple calculation of the more realistic peaks with valid amplitudes. Sherrer's equation is also integrated to take into account the grain sizes (thickness parameter)

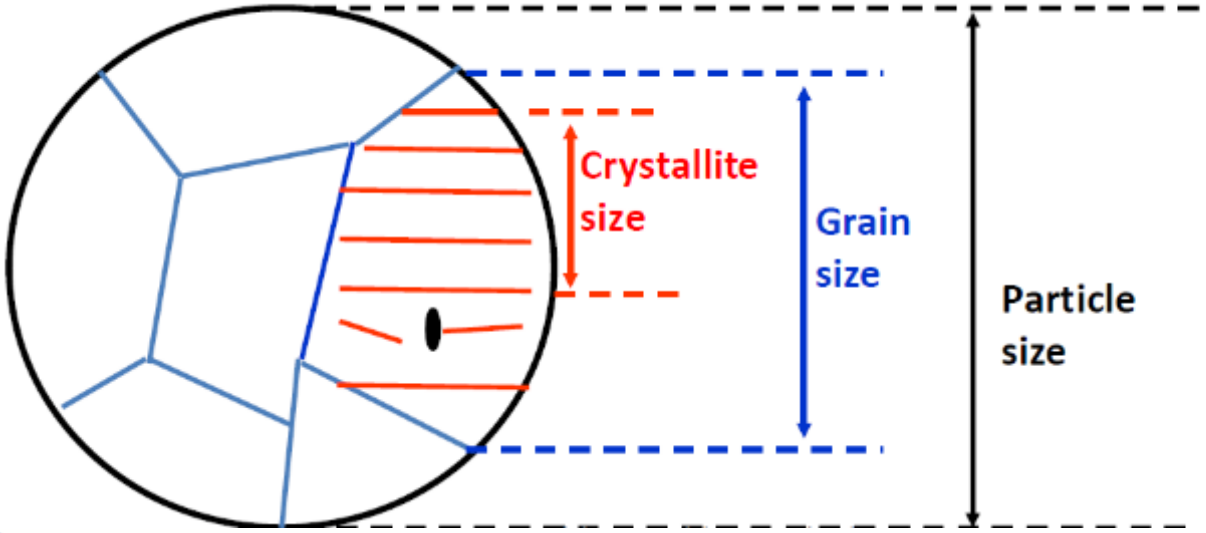


Image taken from Mauro Serdala's XRD lecture notes

X-Ray Diffraction

- **XRD Exercise4:** Comparing the grain size effects on FWHM
  - Grain size determines the peak broadening

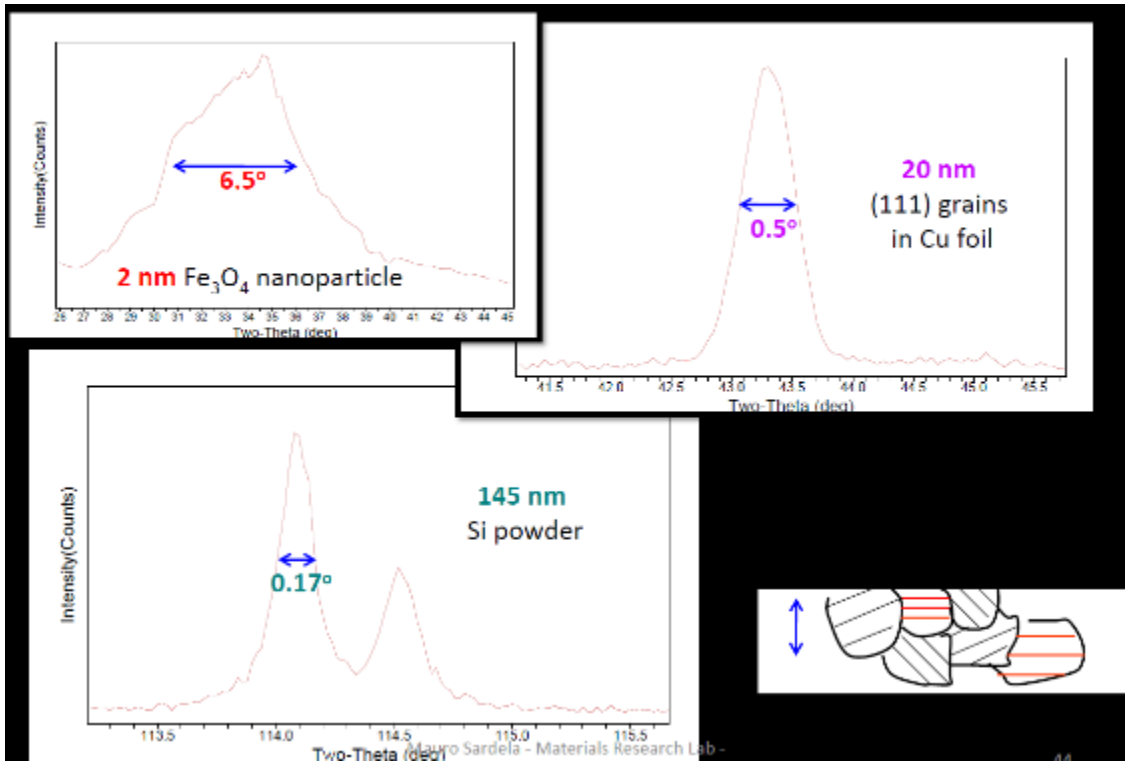
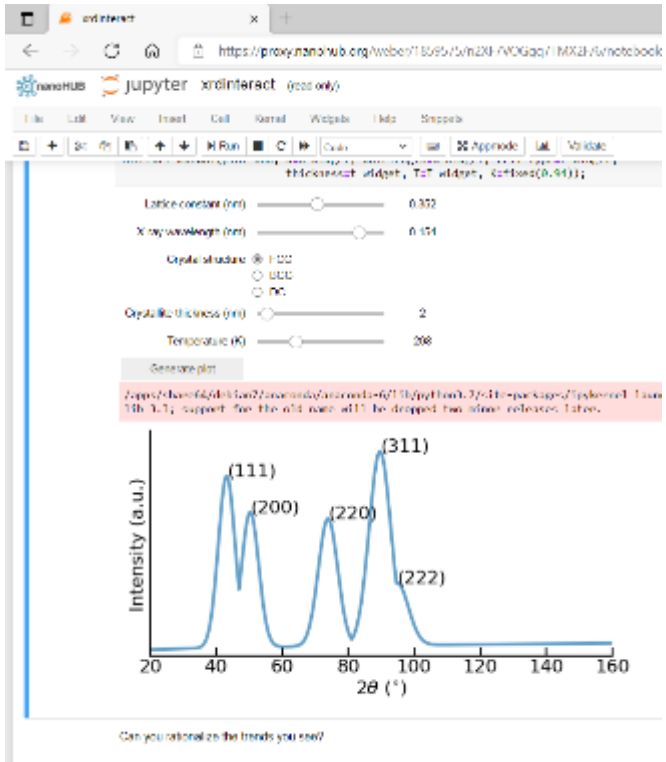
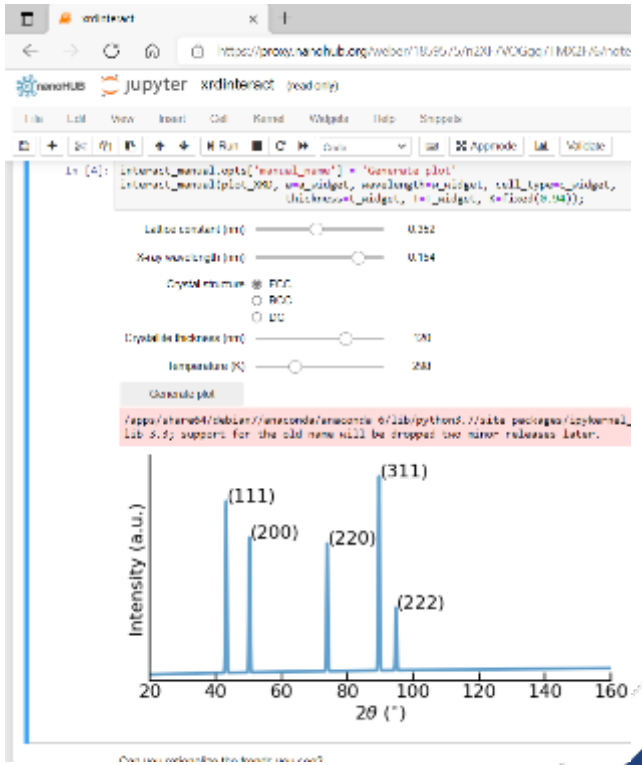


Image taken from Mauro Serdala's XRD lecture notes

X-Ray Diffraction

- **XRD Exercise4:** Comparing the grain size effects on FWHM
  - Students observe the changes when grain size is entered as 2nm and 120nm



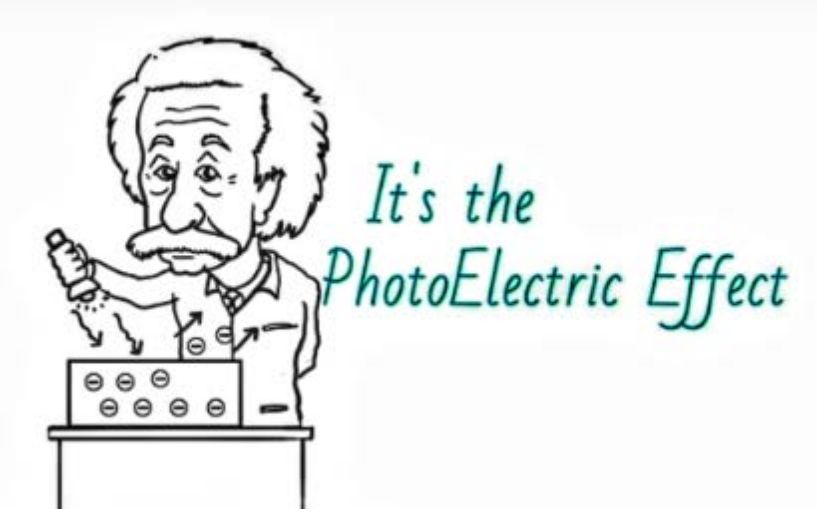


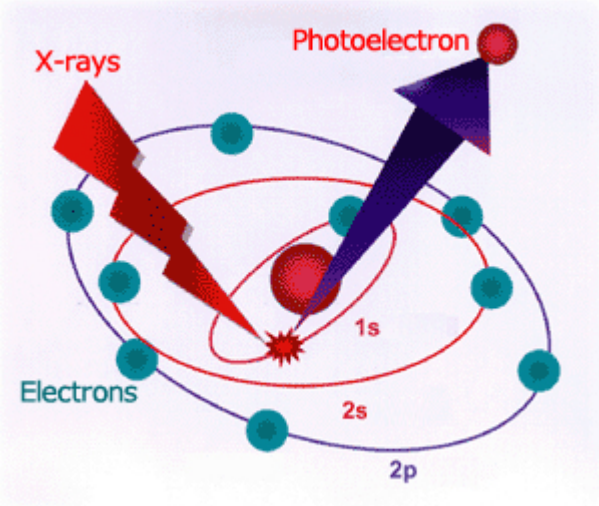
X-Ray Photoelectron Spectroscopy

- What is it and why is it important?
  - Developed in 1960s as a surface analysis technique.
  - Also known as Electron Spectroscopy for chemical analysis (ESCA).
  - One of the most frequently used chemical analysis tool in order to determine
    - Elemental composition
    - Stoichiometry
    - Chemical state (e.g. oxidation state)
    - Electronic state of the elements

X-Ray Photoelectron Spectroscopy

- What is it and why is it important?
  - Relies on the Photoelectric Effect: Shining a torchlight on any surface splashes away some surface electrons due to the acquired energy from the incident light.





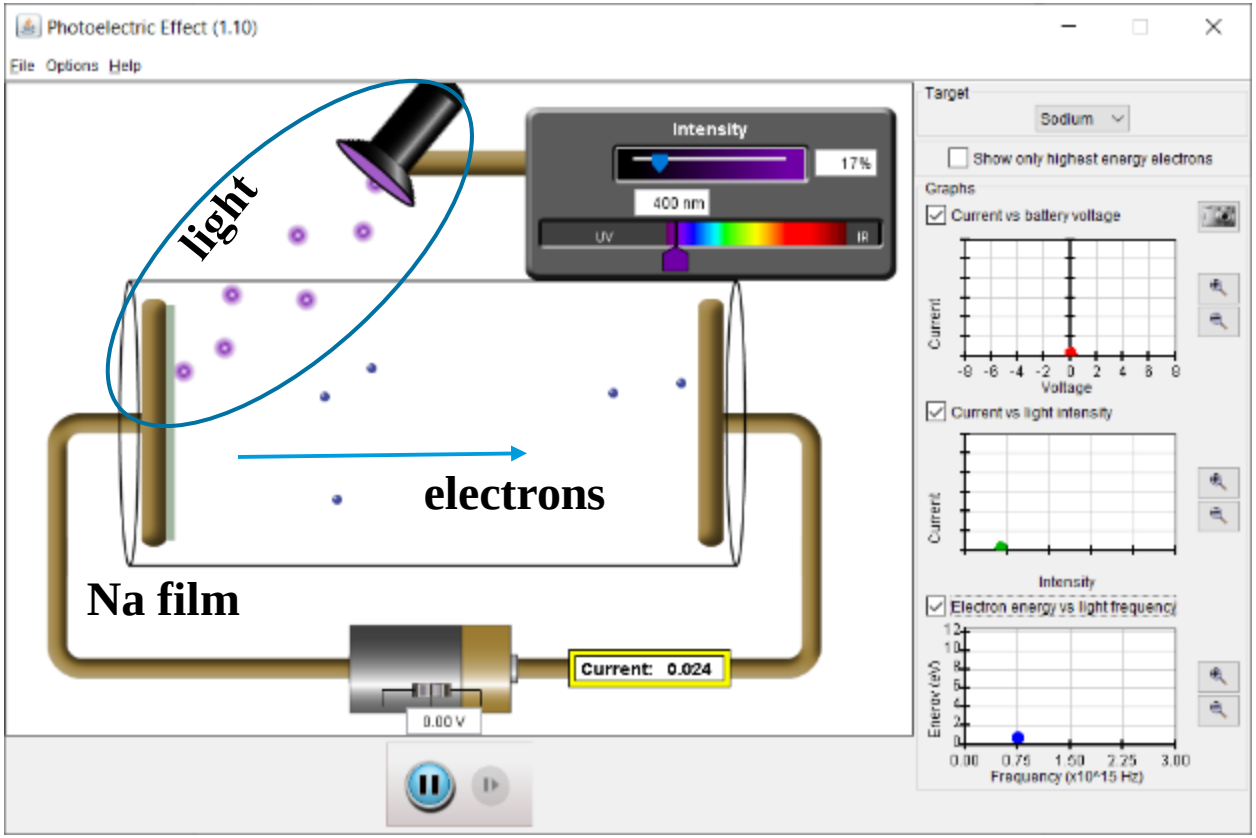
Photoelectron Spectrometer (ESCA) | Introduction to JEOL Products | JEOL Ltd.

X-Ray Photoelectron Spectroscopy

- Examining the Photoelectric Effect
  - Phet University of Colorado Boulder offers excellent simulations on Photoelectric Effect - Light | Quantum Mechanics | Photons - PhET Interactive Simulations (colorado.edu)
  - Explore the rest of the simulation APPs here: Browse - PhET Interactive Simulations (colorado.edu)

X-Ray Photoelectron Spectroscopy

- Examining the Photoelectric Effect



Case1: Illuminating Na (Sodium)

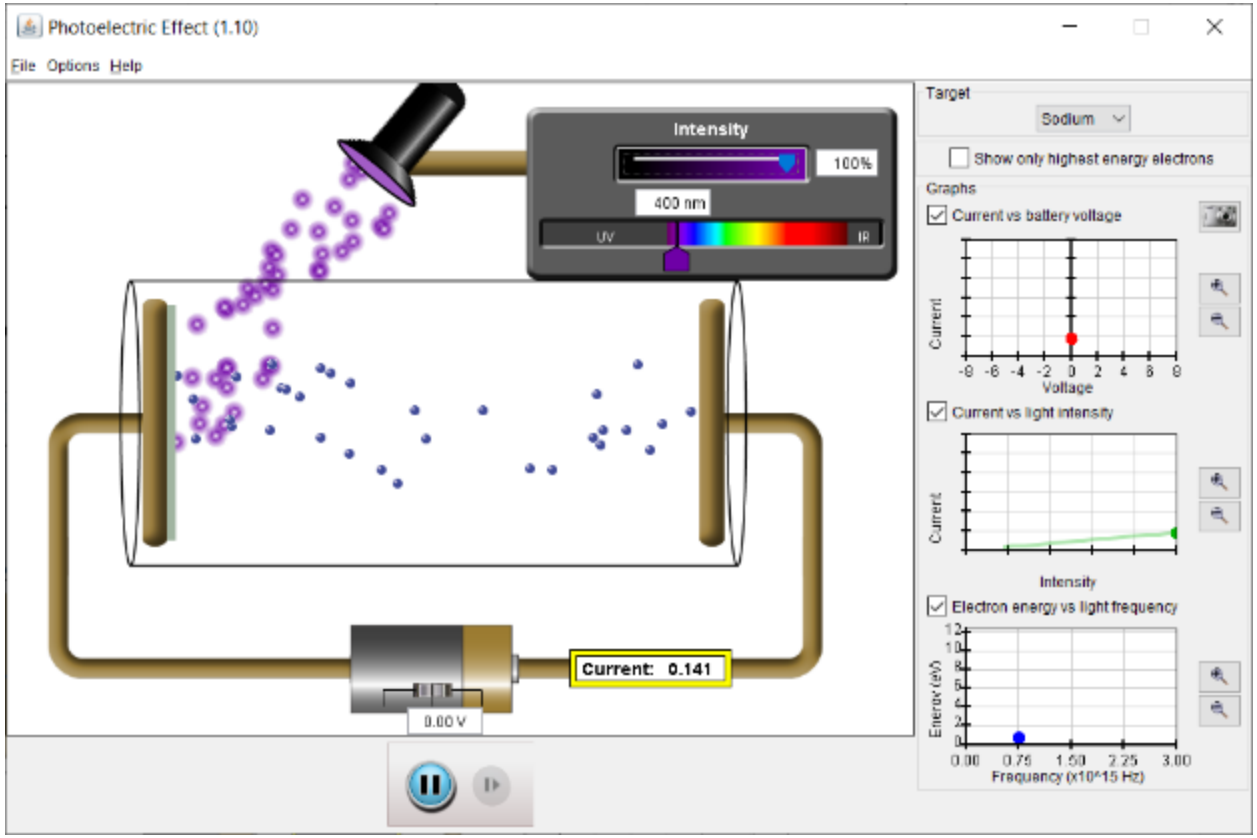
Light impinges on a thin Na film.

Electrons are extracted thanks to the illumination at 400nm wavelength with 17% intensity.

Displaced electrons go to the other electrode and yield current conduction of 0.024 Amperes.

X-Ray Photoelectron Spectroscopy

- Examining the Photoelectric Effect

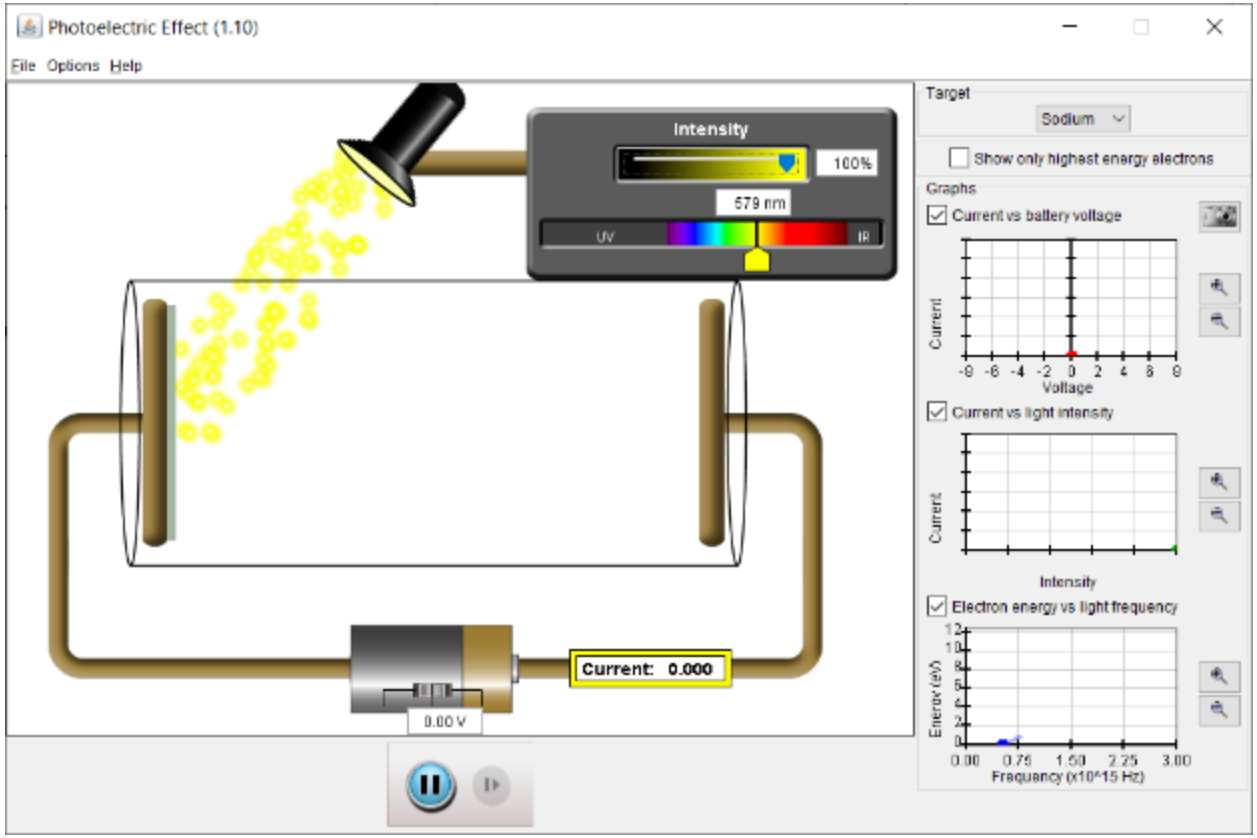


Case1: Illuminating Na (Sodium)

Increased intensity to 100% yields more electrons to be extracted. Thereby more current reading by the students. More photons impinging on the Na film extracts more electrons.
More Intensity => More Light => More Electrons Extracted => More Current

X-Ray Photoelectron Spectroscopy

- Examining the Photoelectric Effect

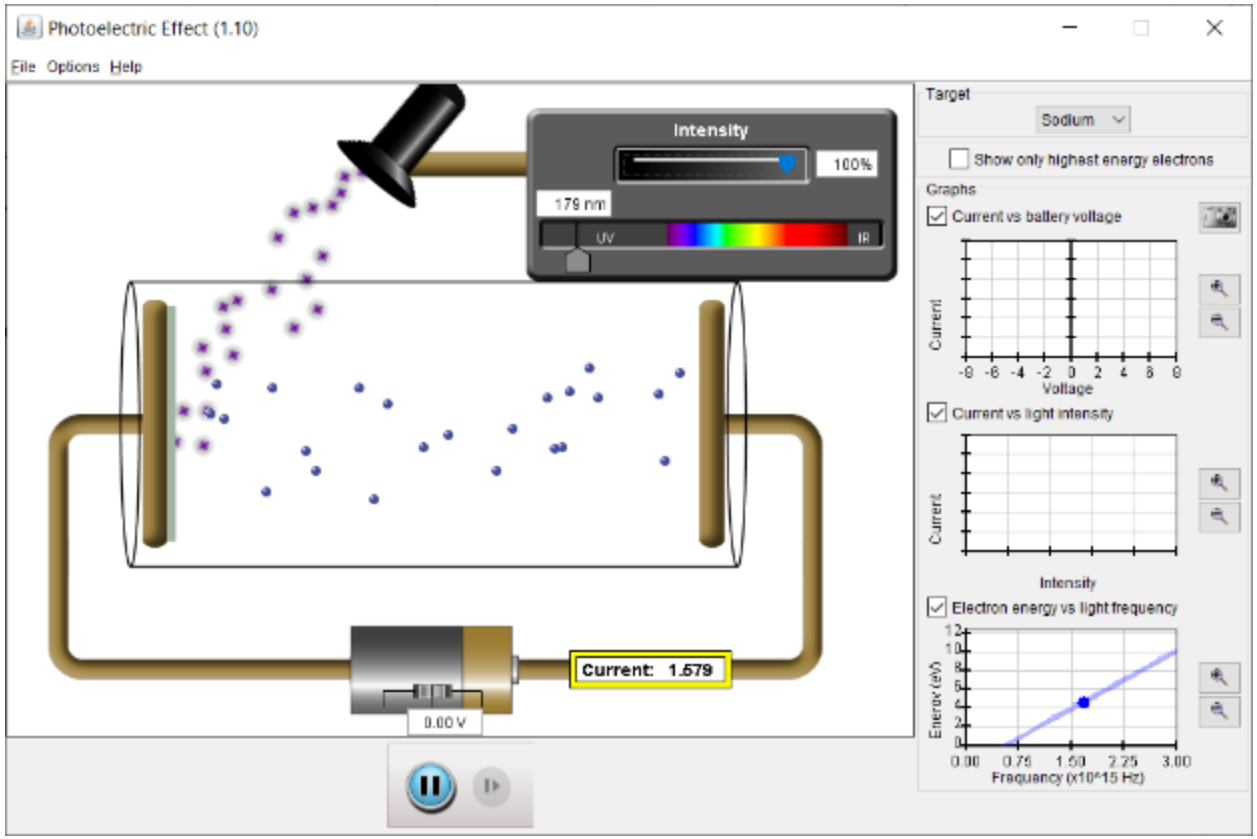


Case1: Illuminating Na (Sodium)

Increasing the wavelength of impinging light to 579nm. There is no electron extraction! Higher wavelength of light possesses lower energy, hence less or no electrons are extracted. Higher Wavelength => Less Energy of Light => Less or No Electrons Extracted => Less or No Current

X-Ray Photoelectron Spectroscopy

- Examining the Photoelectric Effect

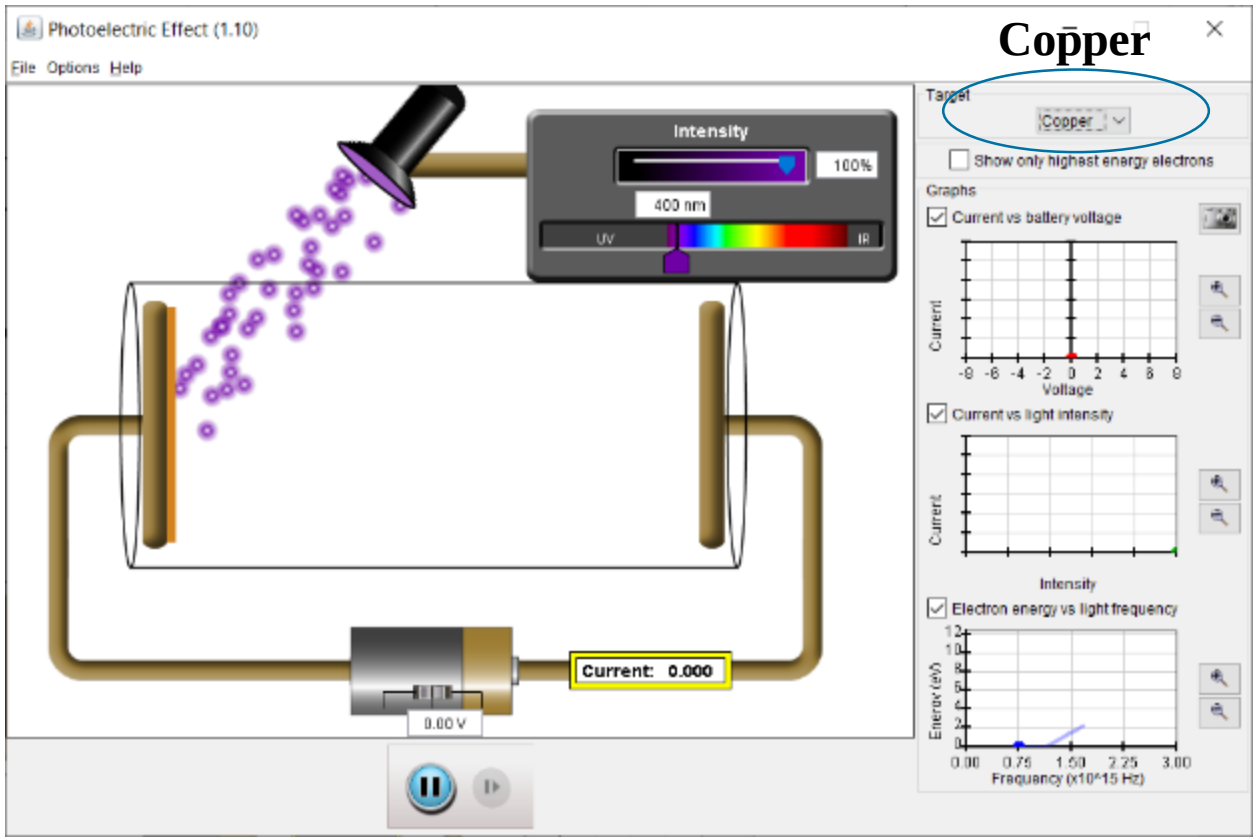


Case1: Illuminating Na (Sodium)

Opposite is also *generally* true (there are secondary effects outside of the scope). Lower wavelength => Higher Energy of Light => More Electrons Extracted => More Current

X-Ray Photoelectron Spectroscopy

- Examining the Photoelectric Effect



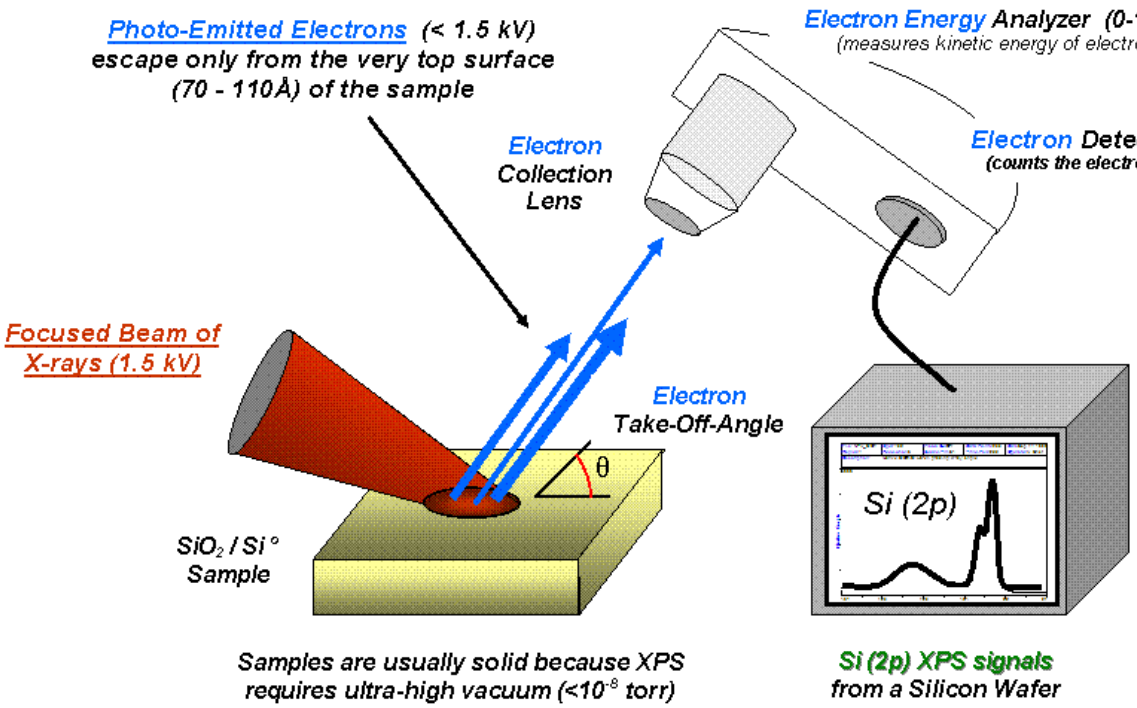
Case2: Illuminating Cu (Copper)

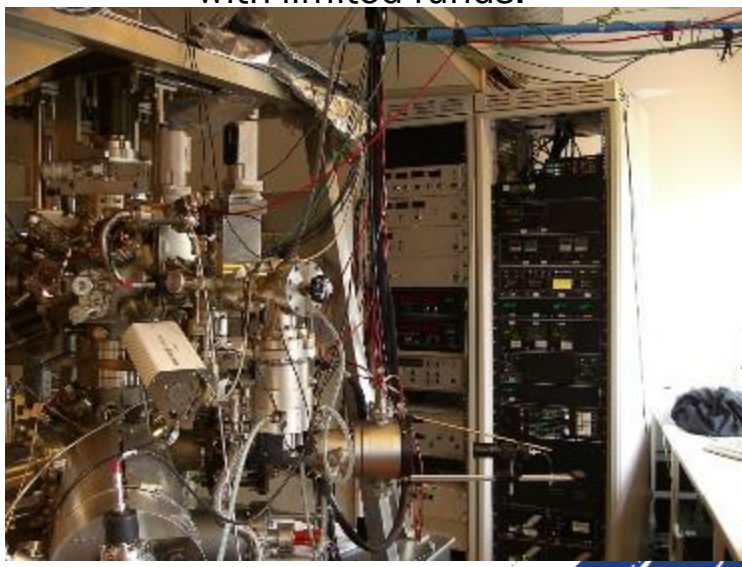
At wavelength of 400nm, Cu does not yield any current. No electrons extracted. Cu has higher atomic number (Z) and requires higher energy to extract the electrons. In other words, Cu has higher **binding energy** (E_B)!

X-Ray Photoelectron Spectroscopy

- XPS tool and exposure for the students

Illuminating the surface with x-rays to extract core electrons to fulfill an elemental analysis. Might be challenging to give the exposure to the students with limited funds.





Images taken from Wikipedia

X-Ray Photoelectron Spectroscopy

- XPS tool and exposure for the students

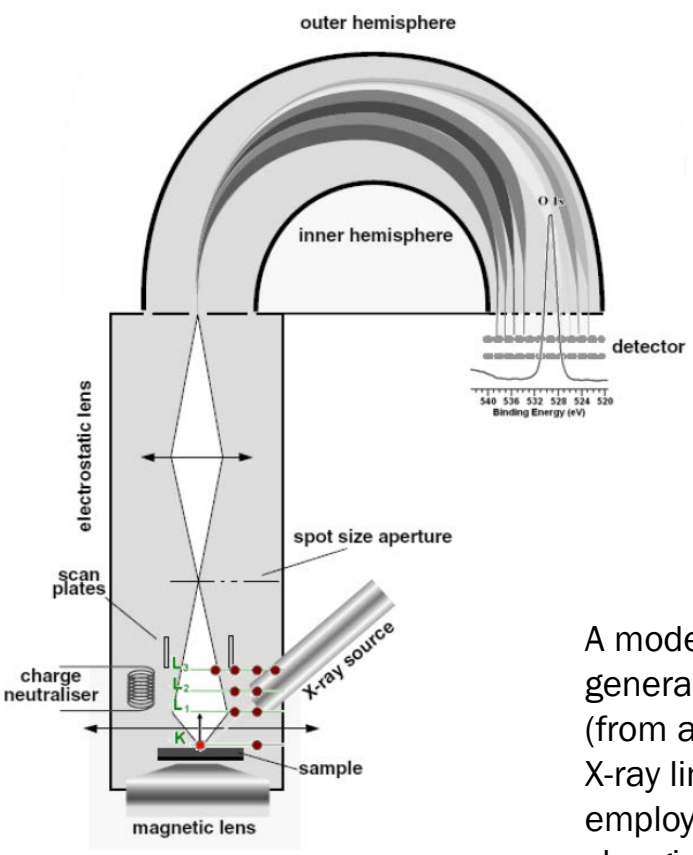


Image taken from Teignmouth Science and Technology Center

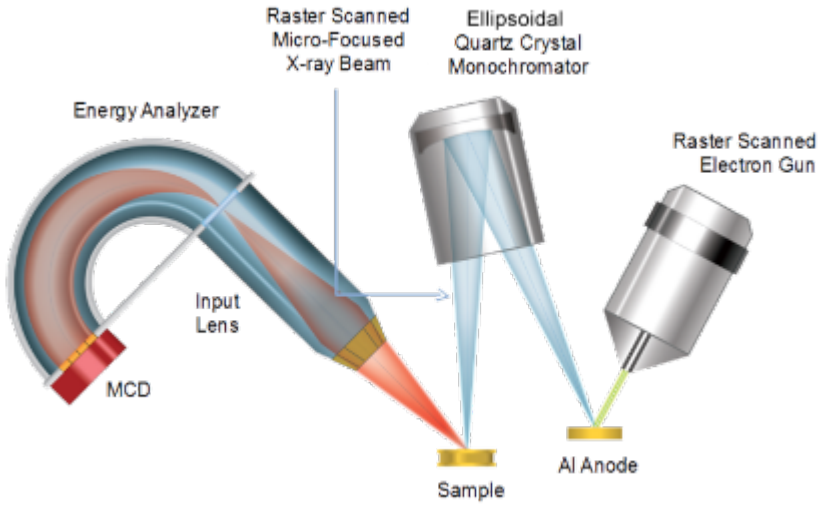


Image taken from X-Ray Photoelectron Spectroscopy (XPS) Surface Analysis Technique (phi.com)

A modern XPS operating under Ultra High Vacuum with an X-ray source generally emitted from Al or Mg anodes after receiving e-beam emission (from a Tungsten or LaB_6) filament. Quartz Monochromator produces a thin X-ray line width. Hemispherical sector analyzer with an electron lens are employed on the receiver side. Charge neutralizer might be needed for charging problems.

X-Ray Photoelectron Spectroscopy

- SESSA: Simulation of the Electron Spectra for Surface Analysis
  - Go to NIST Standard Reference Database 100 | NIST to download the proper version to your computer.

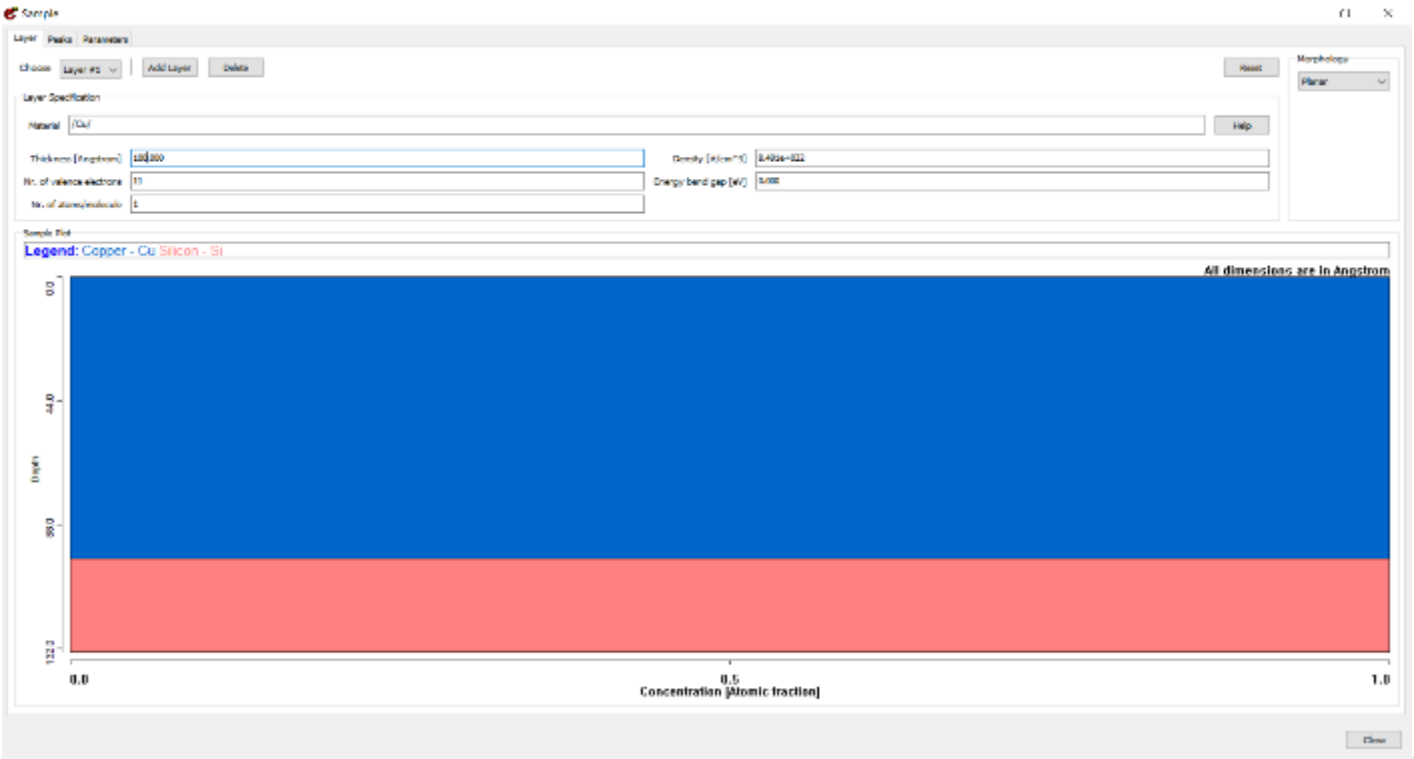
NIST National Institute of Standards and Technology U.S. Department of Commerce

Grand Valley State University
Seymour and Esther Padnos College of Engineering and Computing

PennState

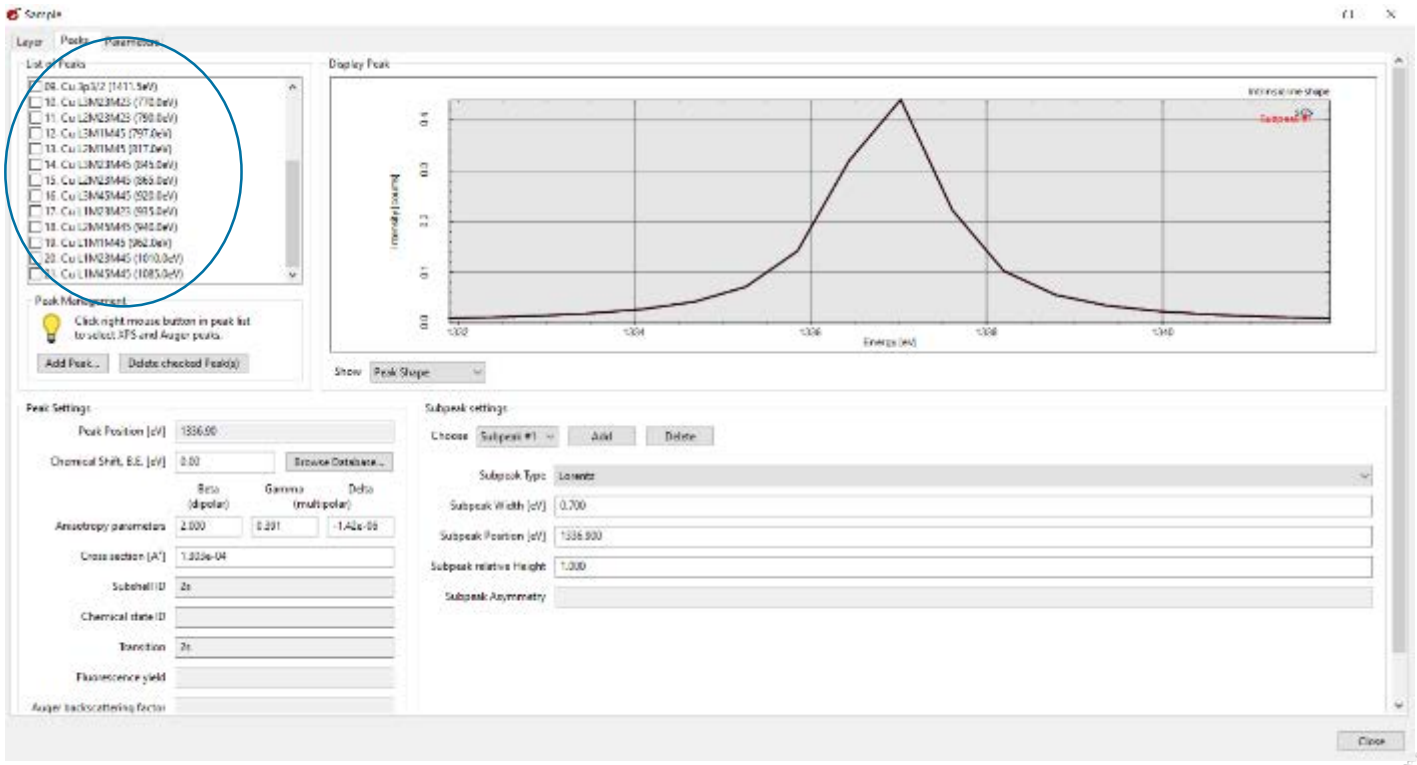
X-Ray Photoelectron Spectroscopy

- **SESSA Exercise1:** Cu survey result
  - Set up a 10nm (thick) Cu layer on Si substrate from Sample tab.



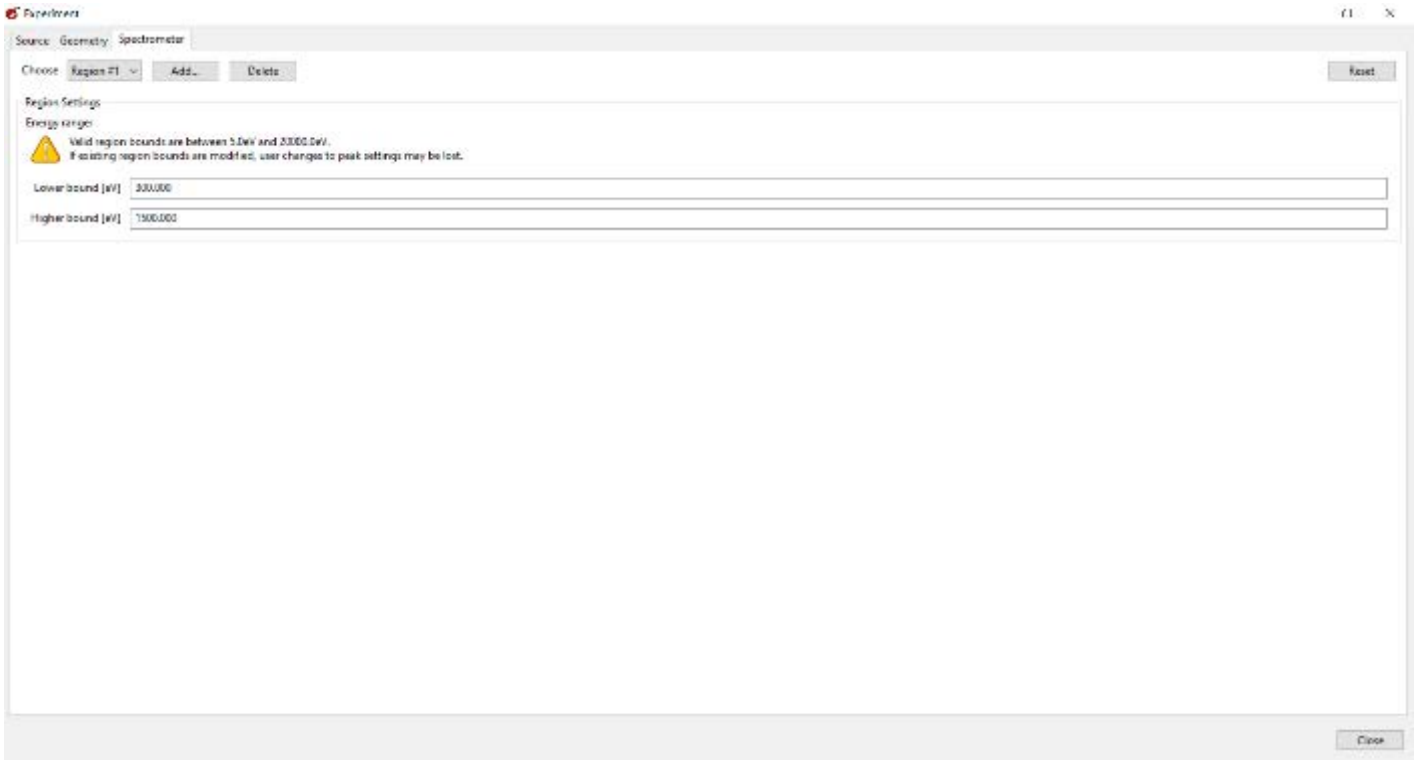
X-Ray Photoelectron Spectroscopy

- **SESSA Exercise1:** Cu survey result
  - Go to Peaks tab, you will see that there are various Auger peaks, aside from the XPS peaks.



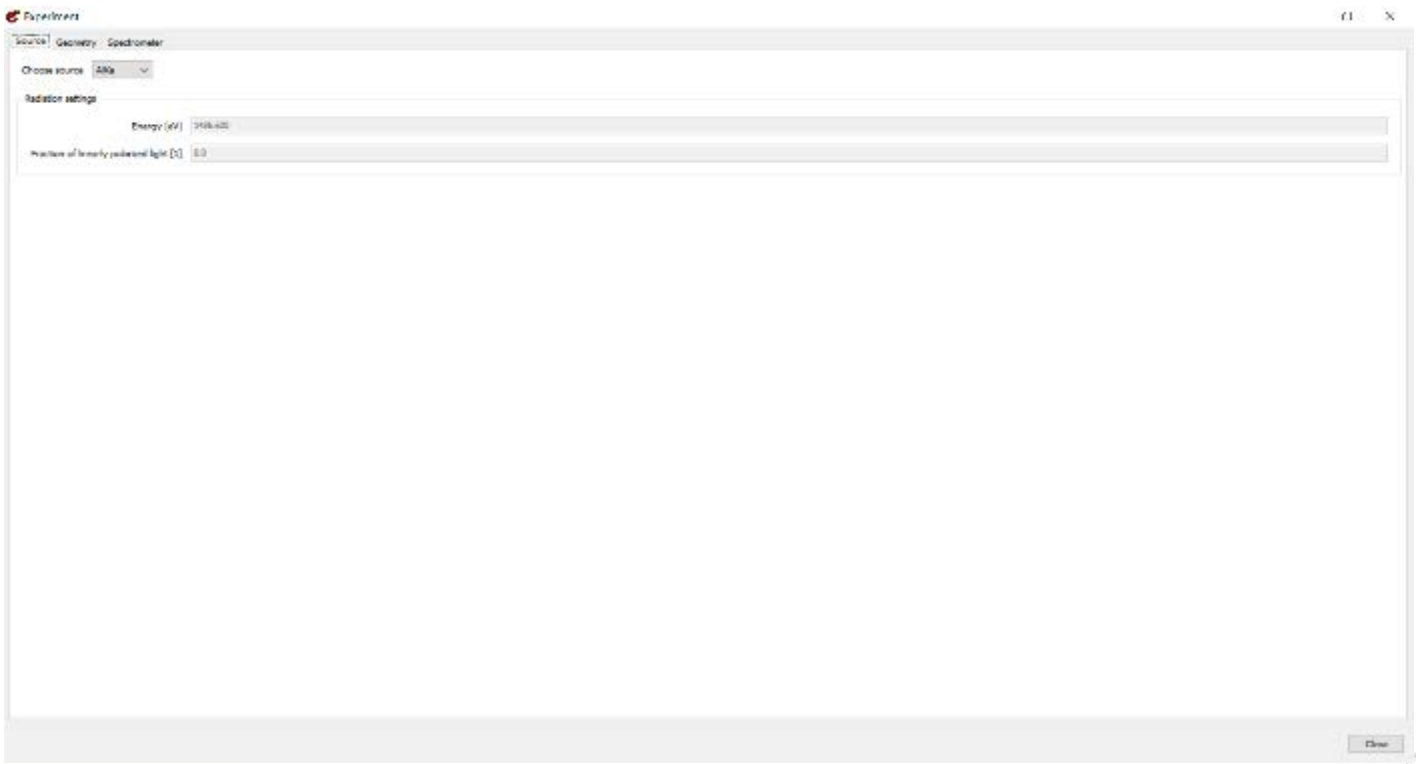
X-Ray Photoelectron Spectroscopy

- **SESSA Exercise1:** Cu survey result
  - Go to Spectrometer and set the lower and upper boundaries as 300eV and 1.2keV, respectively.



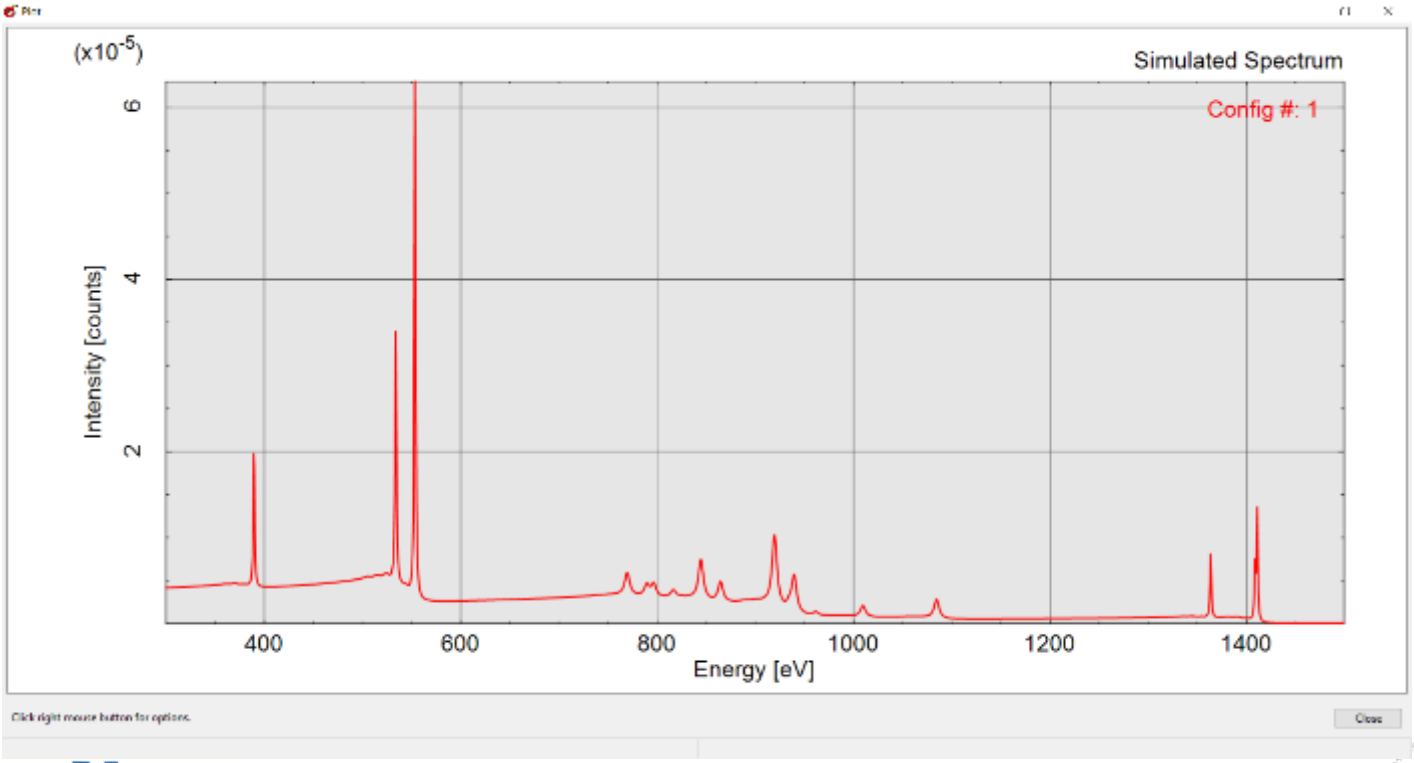
X-Ray Photoelectron Spectroscopy

- **SESSA Exercise1:** Cu survey result
  - Go to Source and observe the incident X-ray source, which is an AlKα source with an incident energy (E_i) of 1486eV.



X-Ray Photoelectron Spectroscopy

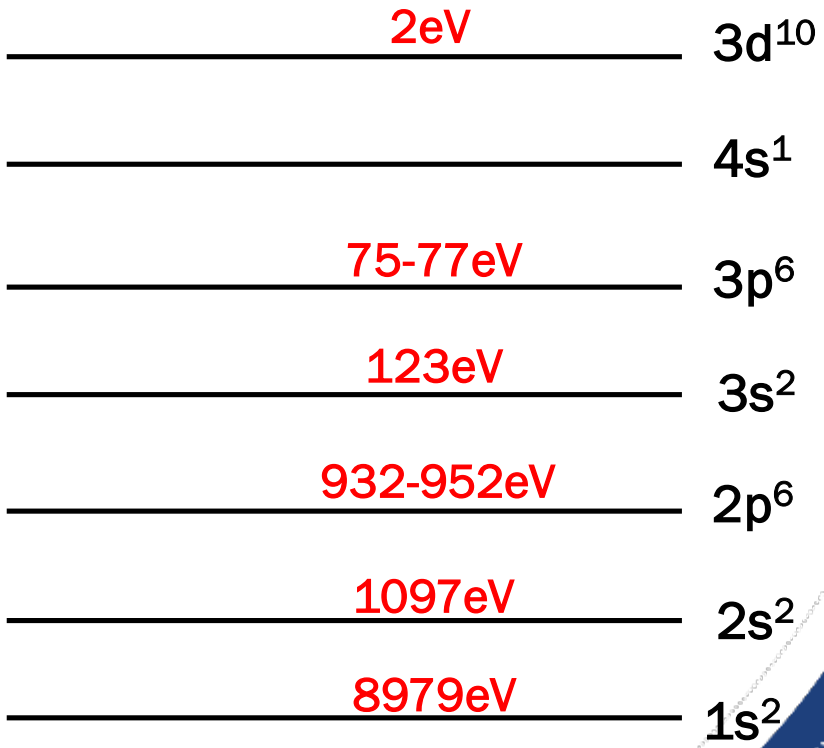
- **SESSA Exercise1:** Cu survey result
  - Go to Simulation tab and hit Start Simulation, you should obtain the following plot. Students can extract the peak values and corresponding energy values with the help of the mouse.



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise1:** Cu survey result
  - Referring back to the Periodic Table, Cu can be arranged as:
    $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

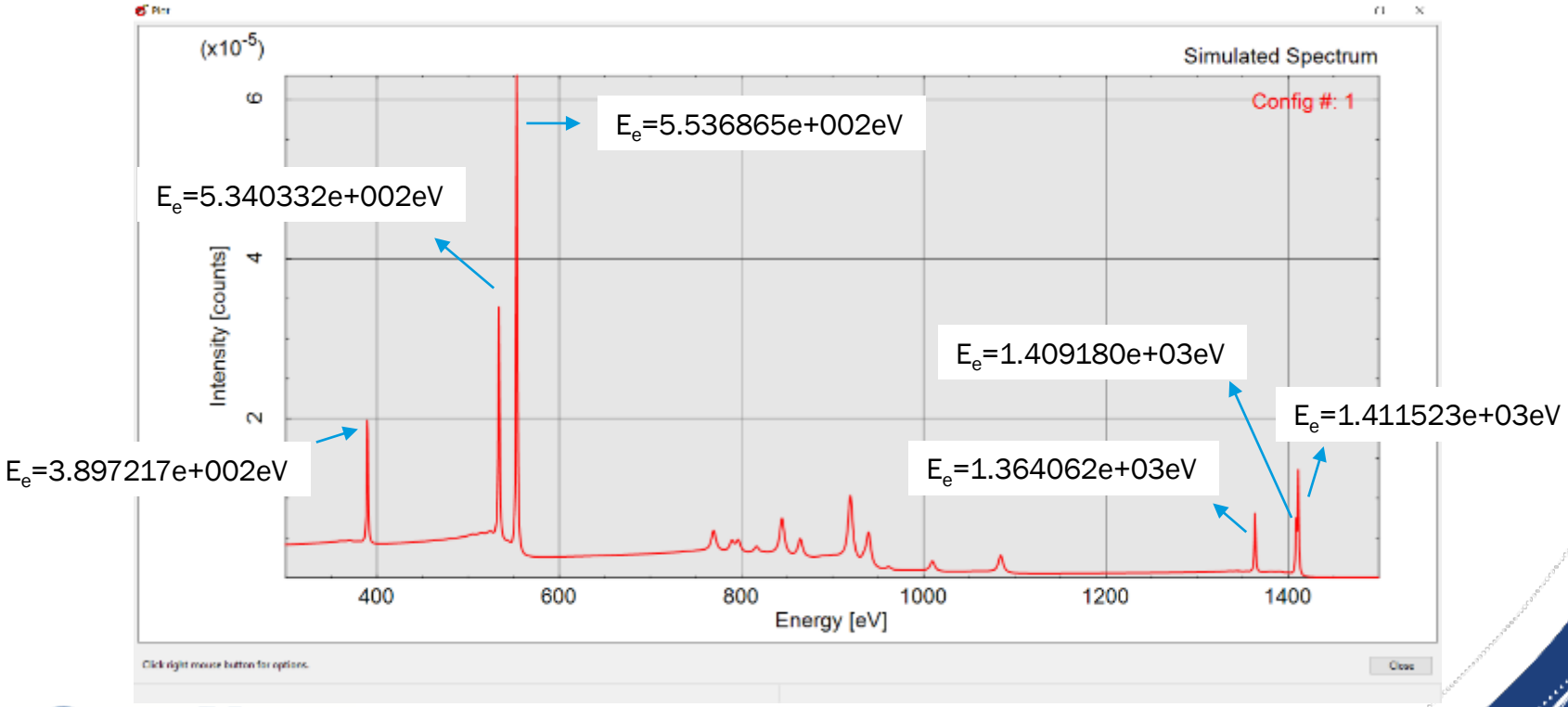
Image taken from Copper – The Element We can Count on : Chemical Industry Digest (chemindigest.com)



Red labeled energy values are the binding E_B values of the electrons.

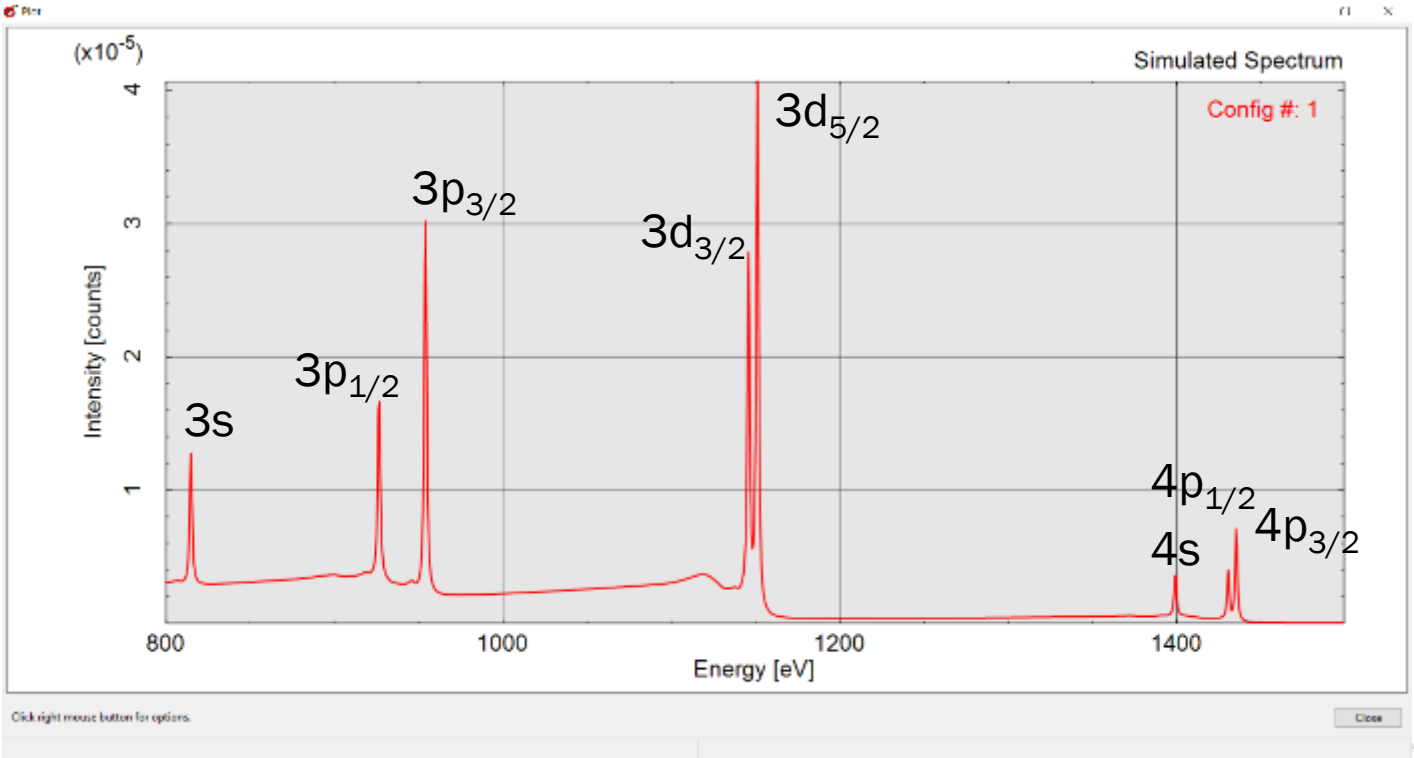
X-Ray Photoelectron Spectroscopy

- **SESSA Exercise1:** Cu survey result
  - Retrieved peaks (photoelectron Energy values) E_e and E_b values from the previous slide match? Energy should be conserved.
    - 1st peak => $E_e=E_i- E_b$ => 1486eV-1097eV=389eV => This is 2s photoelectron!
    - Other shown peaks can be checked and found that they are 2p, 3s and 3p photoelectrons!



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise2:** Pd survey result and spin-orbit splitting
  - Follow similar steps for 10nm Pd instead of Cu and collect the results. Should collect 8 peaks. The peaks are associated with orbits.



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise2:** Pd survey result and spin-orbit splitting
  - Pd is a heavy atom with the dominant effect observed as L-S Coupling. More detailed reading can be found here: Angular Momentum Coupling (gsu.edu)

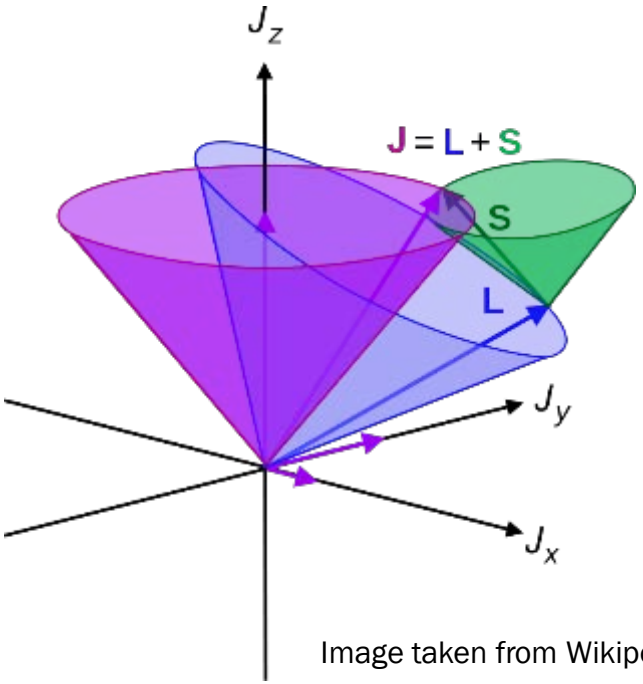


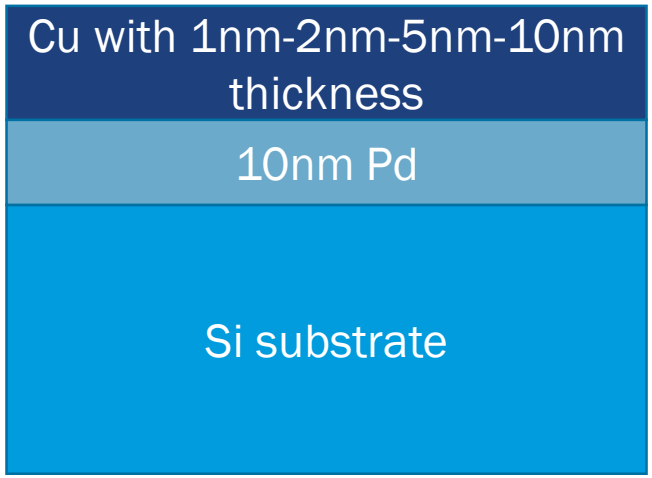
Image taken from Wikipedia

Inner core electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$... will remove an electron from 3d

Total Angular Momentum:
d orbit => L=2
S (spin)=1/2
|L-S| and |L+S| splitting will occur => $3d_{5/2}$ and $3d_{3/2}$
p orbit => L=1
S=1/2
|L-S| and |L+S| splitting will occur => $3p_{1/2}$ and $3p_{3/2}$

X-Ray Photoelectron Spectroscopy

- **SESSA Exercise3:** Escape length, mean free path and surface sensing.
  - This exercise shows the surface sensing capability of XPS.
  - On top of the Pd layer stack a Cu layer with changing thicknesses from 1nm, 2nm, 5nm to 10nm. We will quickly lose the peaks from Pd layer as the top Cu layer is getting thicker. The photoelectrons will not be able to escape the surface.



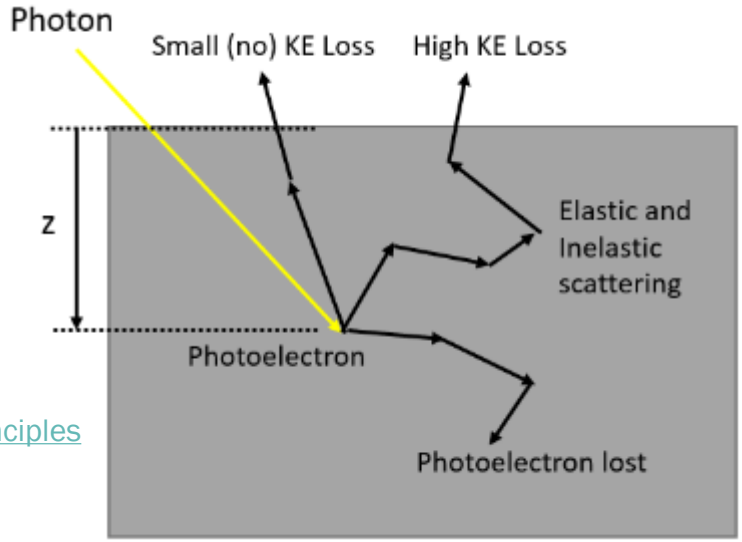
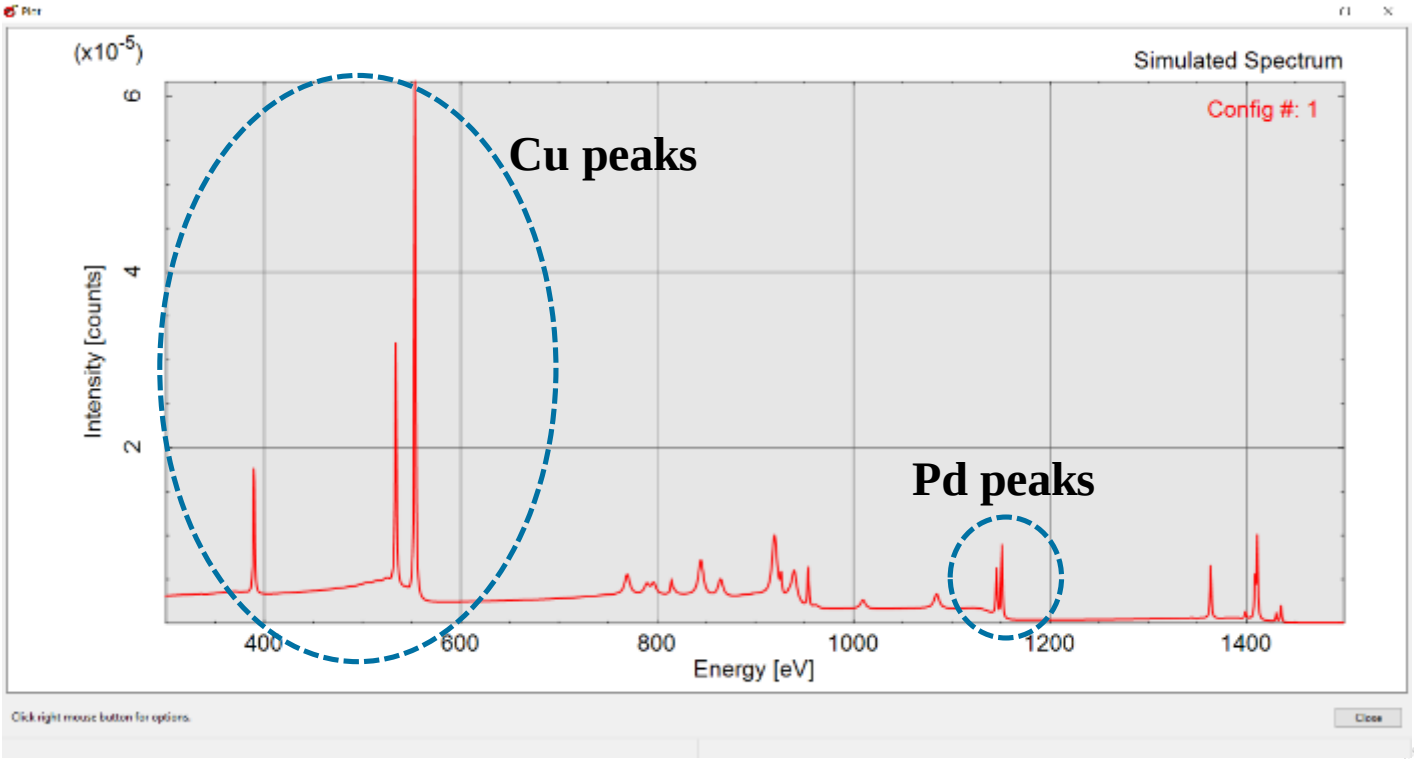


Image taken from Principles of XPS: Effective Attenuation Length

X-Ray Photoelectron Spectroscopy

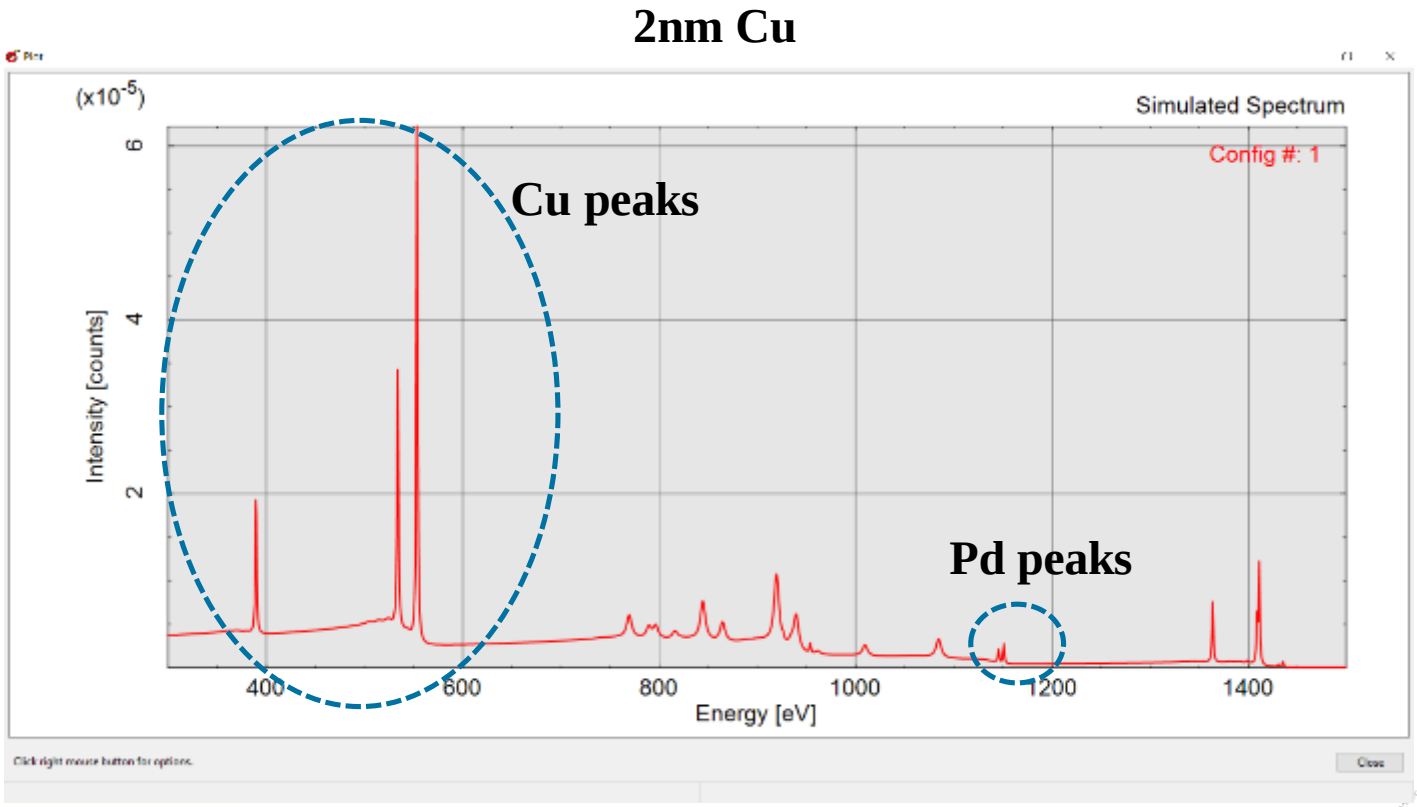
- **SESSA Exercise3:** Escape length, mean free path and surface sensing.

1nm Cu



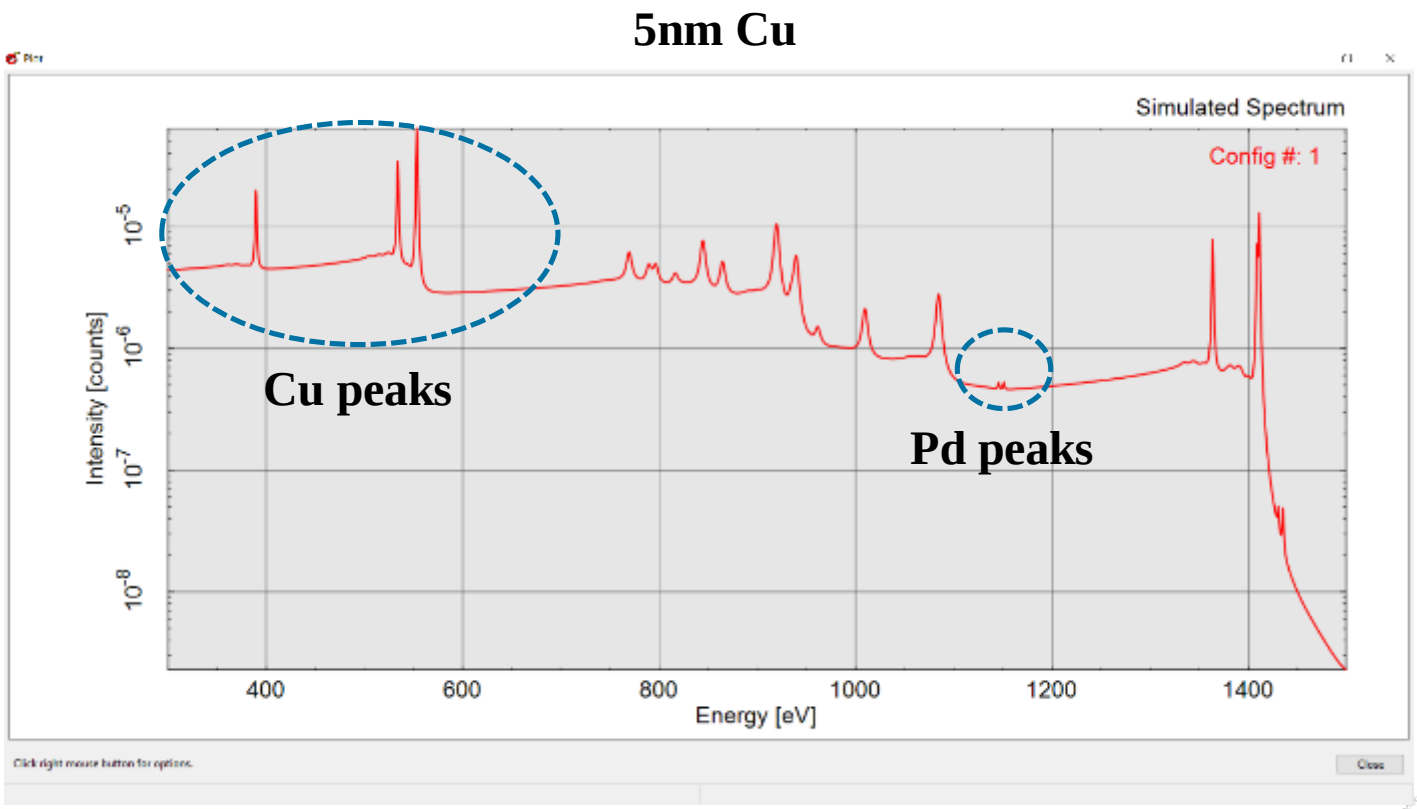
X-Ray Photoelectron Spectroscopy

- **SESSA Exercise3:** Escape length, mean free path and surface sensing.



X-Ray Photoelectron Spectroscopy

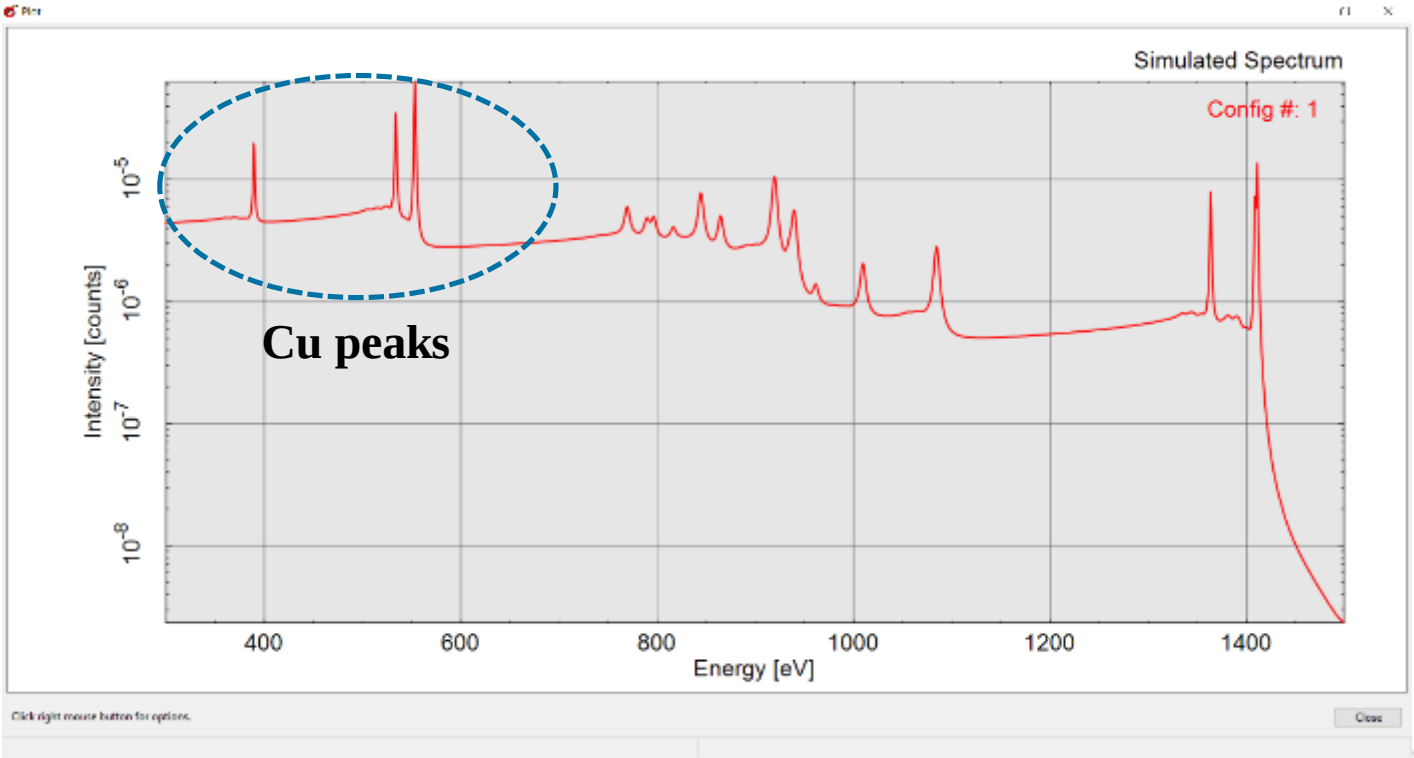
- **SESSA Exercise3:** Escape length, mean free path and surface sensing.



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise3:** Escape length, mean free path and surface sensing.

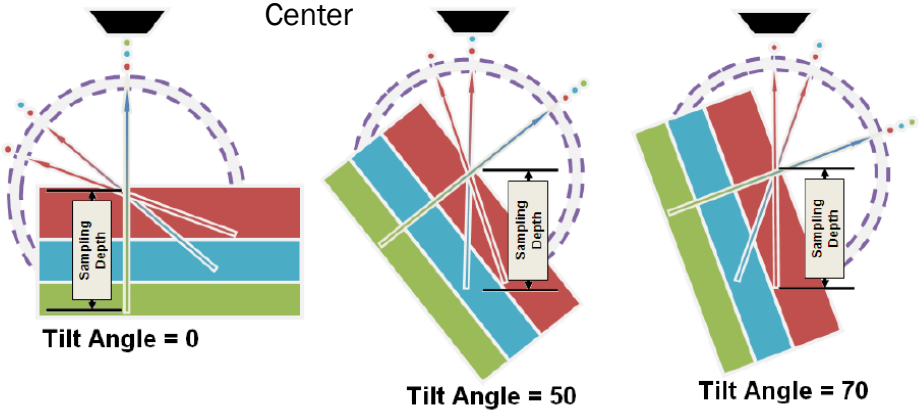
10nm Cu

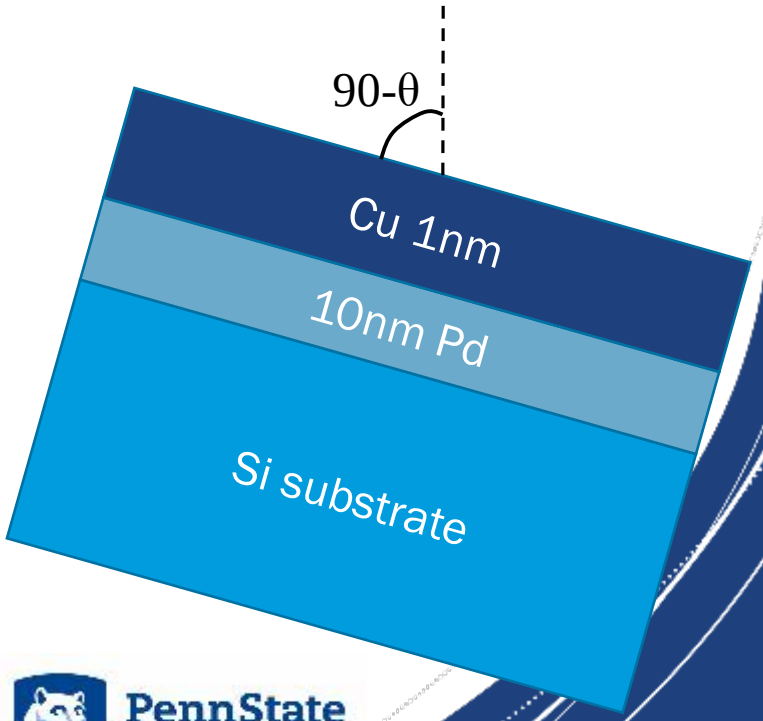


X-Ray Photoelectron Spectroscopy

- **SESSA Exercise4:** Depth Profiling
  - Students can observe the sampling depth changes with the modifications done to the angle resolved XPS. The escape depth shrinks down with the tilted sample as schematically shown below.
  - Change the tilt angle (Theta) from 0 to 30 to 60 degrees from Configurations tab.

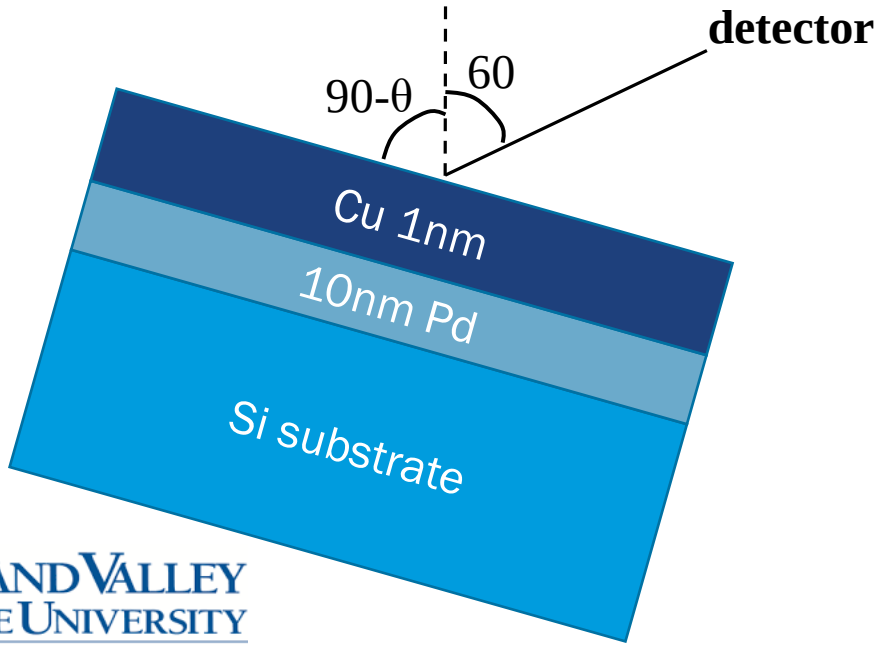
Image taken from Teignmouth Science and Technology Center





X-Ray Photoelectron Spectroscopy

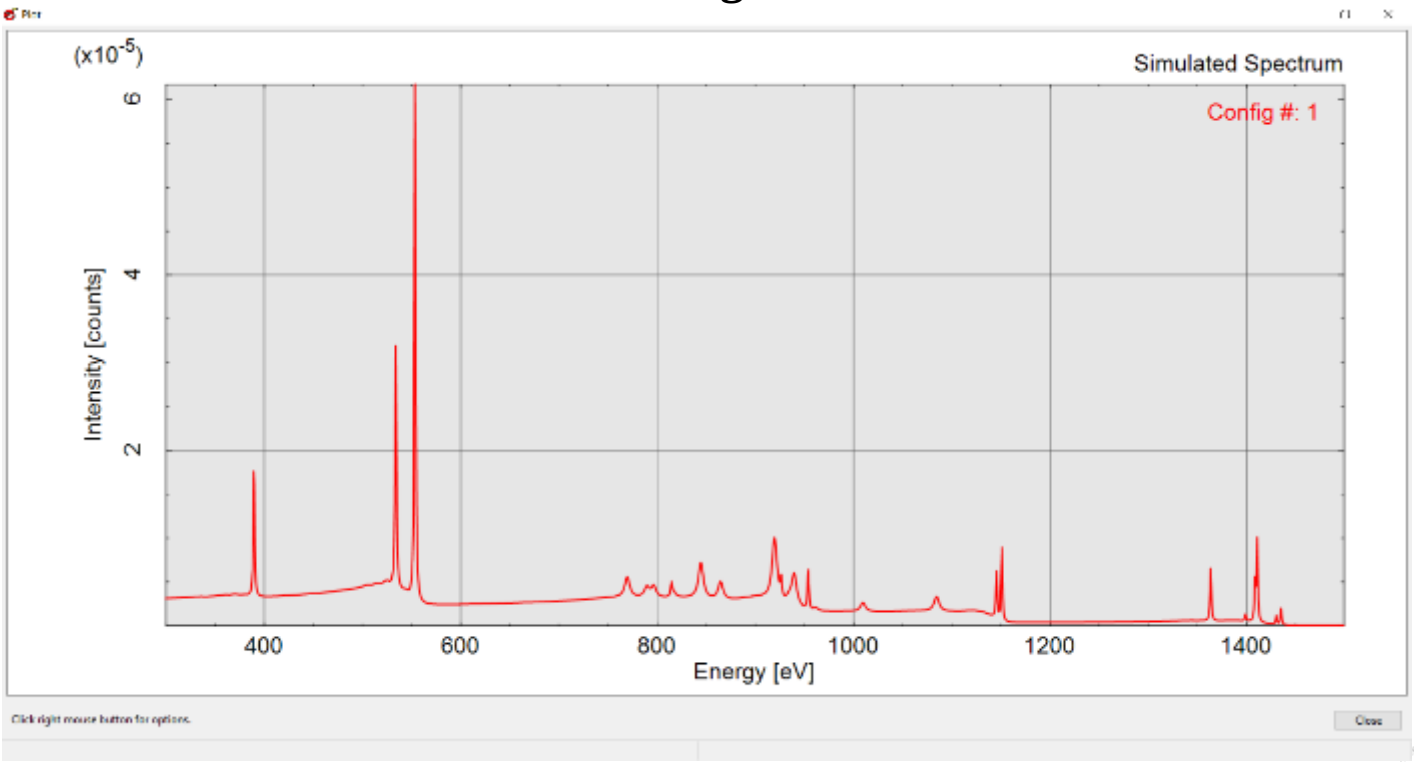
- **SESSA Exercise4:** Depth Profiling
  - Change the tilt angle (Theta) from 0 to 30 to 60 degrees from Configurations tab. Observe the changes in the signal intensity.
  - Since the detector is already at a position with θ=60 degrees, the highest signal intensity will be collected from the underlying Pd layer when the sample is also tilted the same amount.



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise4:** Depth Profiling
  - Focusing on the Pd peaks only

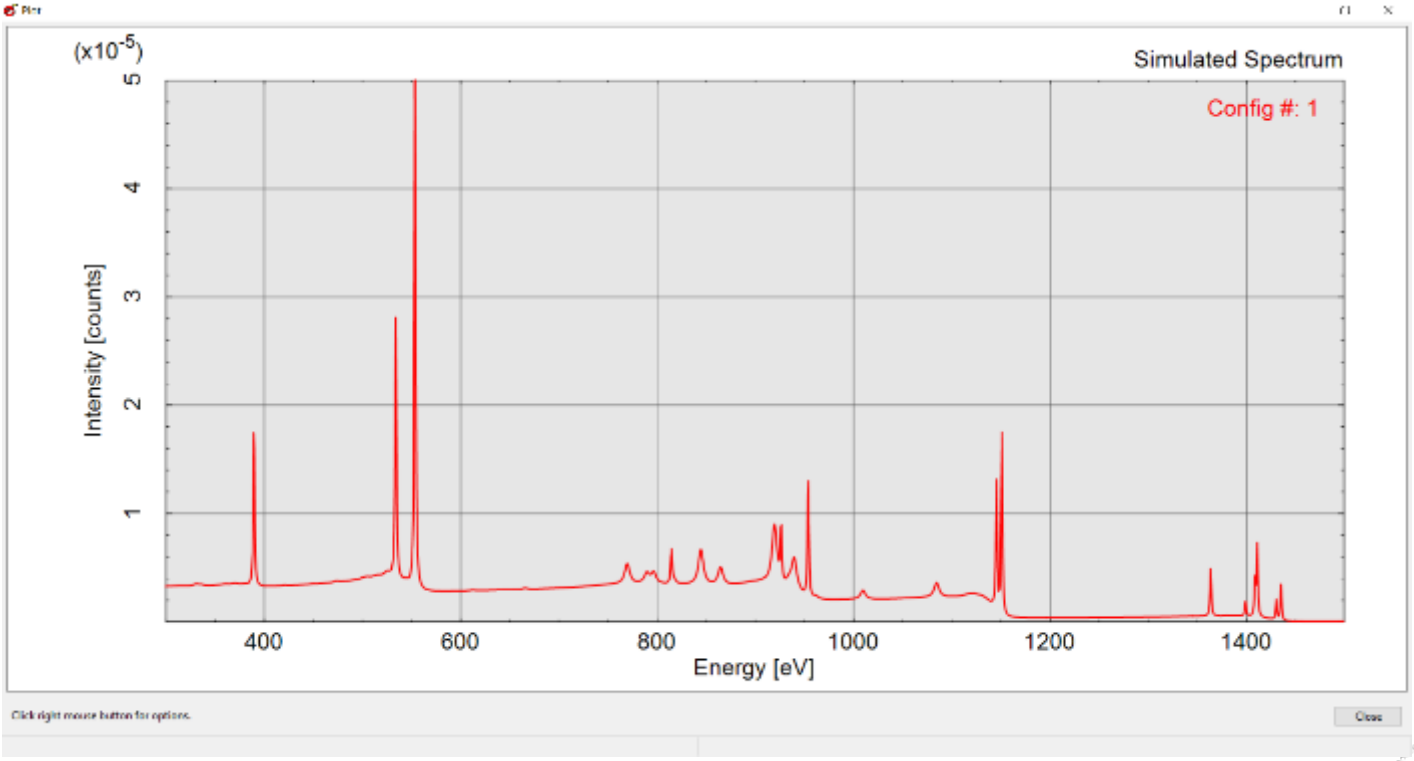
θ=0 degrees



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise4:** Depth Profiling
  - Focusing on the Pd peaks only

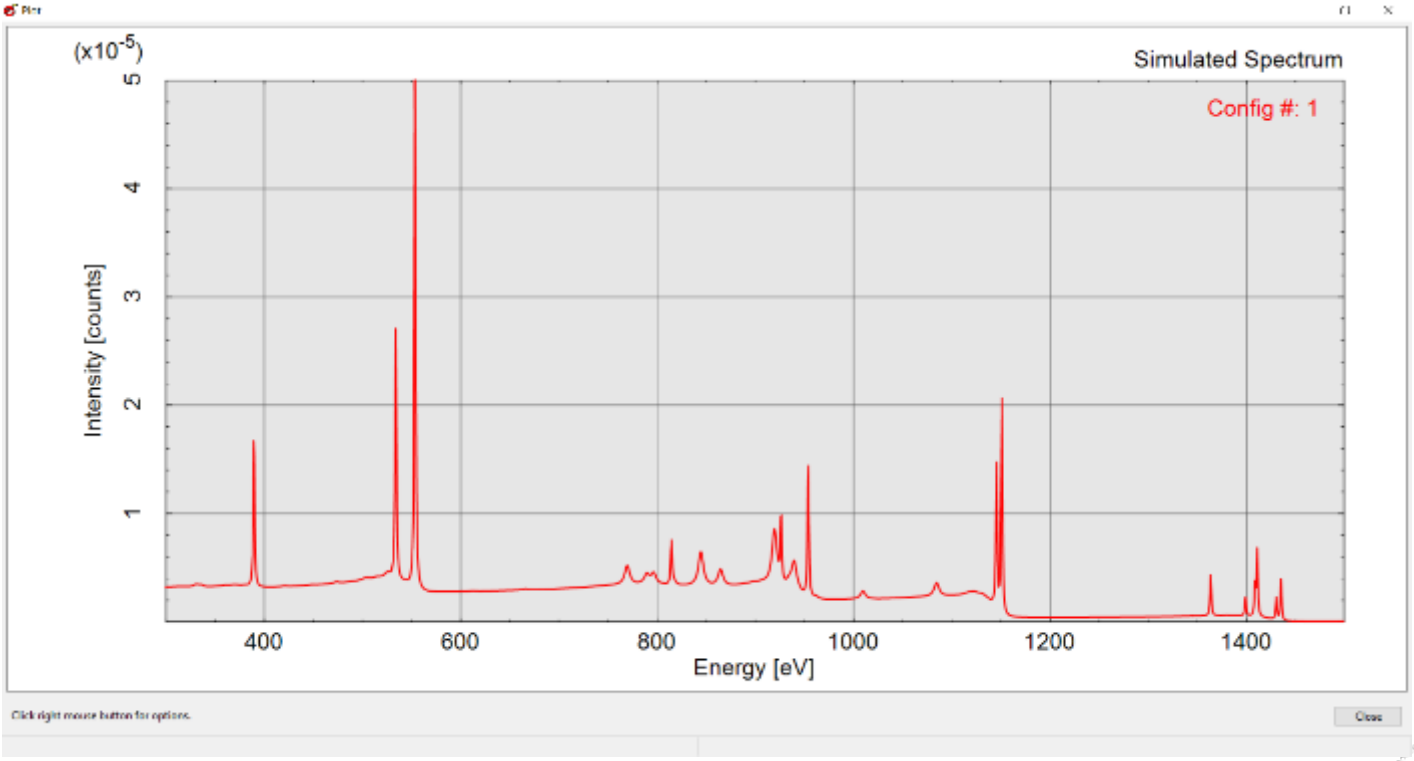
θ=30 degrees



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise4:** Depth Profiling
  - Focusing on the Pd peaks only

θ=60 degrees



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise5:** Chemical Shift
  - Students can observe the effect of the electronegativity on the binding energy as shown below for the same C atom binding to F as the most electronegative partner with the highest binding energy.

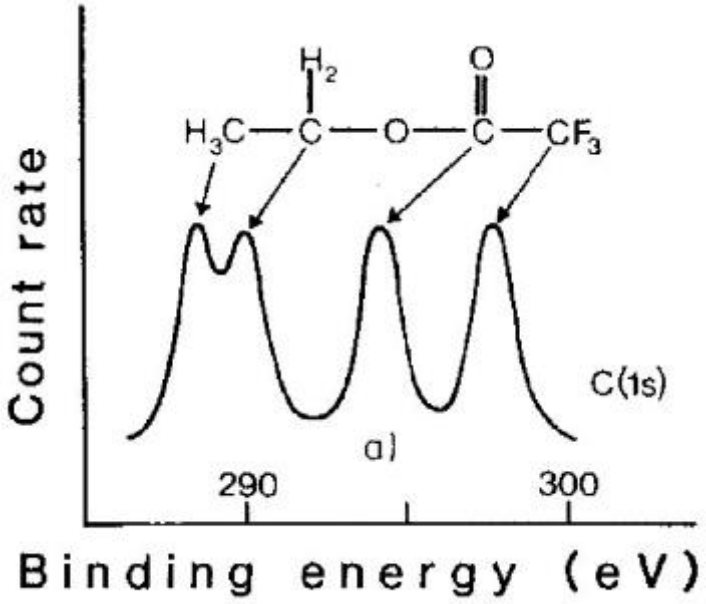


Image taken from Alessandro Kovtun's PhD thesis: 2D Graphene-based Materials. Interplay between Composition and Electrical Properties

- Go to Sources tab and change the X-ray source to MgKα which is at E_i=1253.6eV
- We will observe the chemical shift as Si is oxidized.
- Go to Sample tab and change the material (single layer) to /Si[oxide]/O2/ for oxide

Si substrate	SiO_2 oxidized state

X-Ray Photoelectron Spectroscopy

- **SESSA Exercise5:** Chemical Shift
  - Go to the Peaks tab and under Si 2p peaks click on the Chemical Shift and choose a Good estimation peak for the O bonded Si.

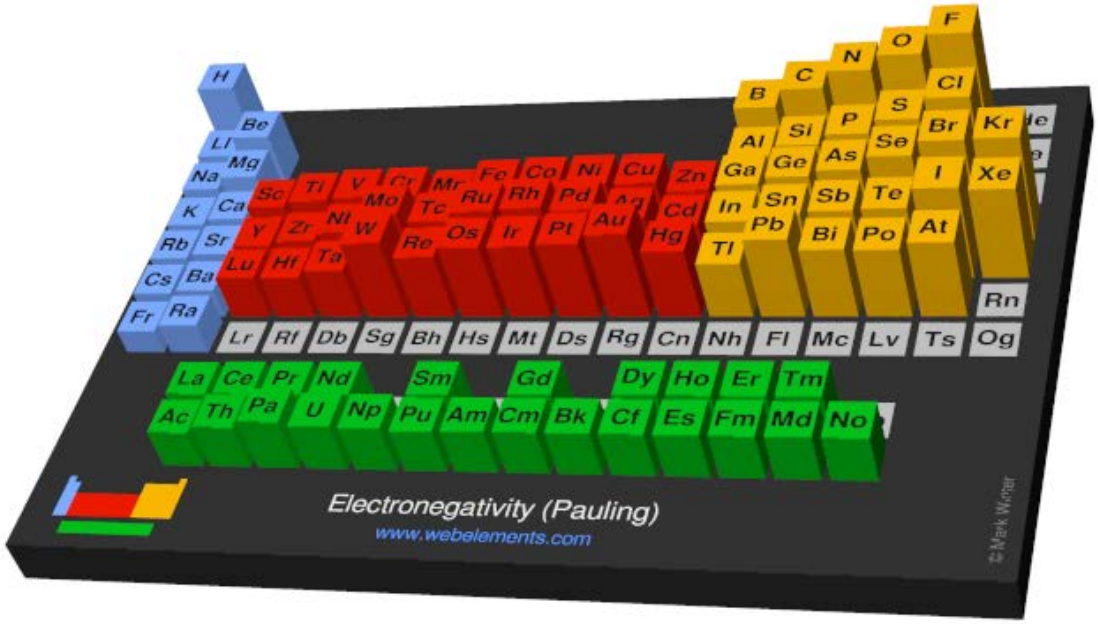
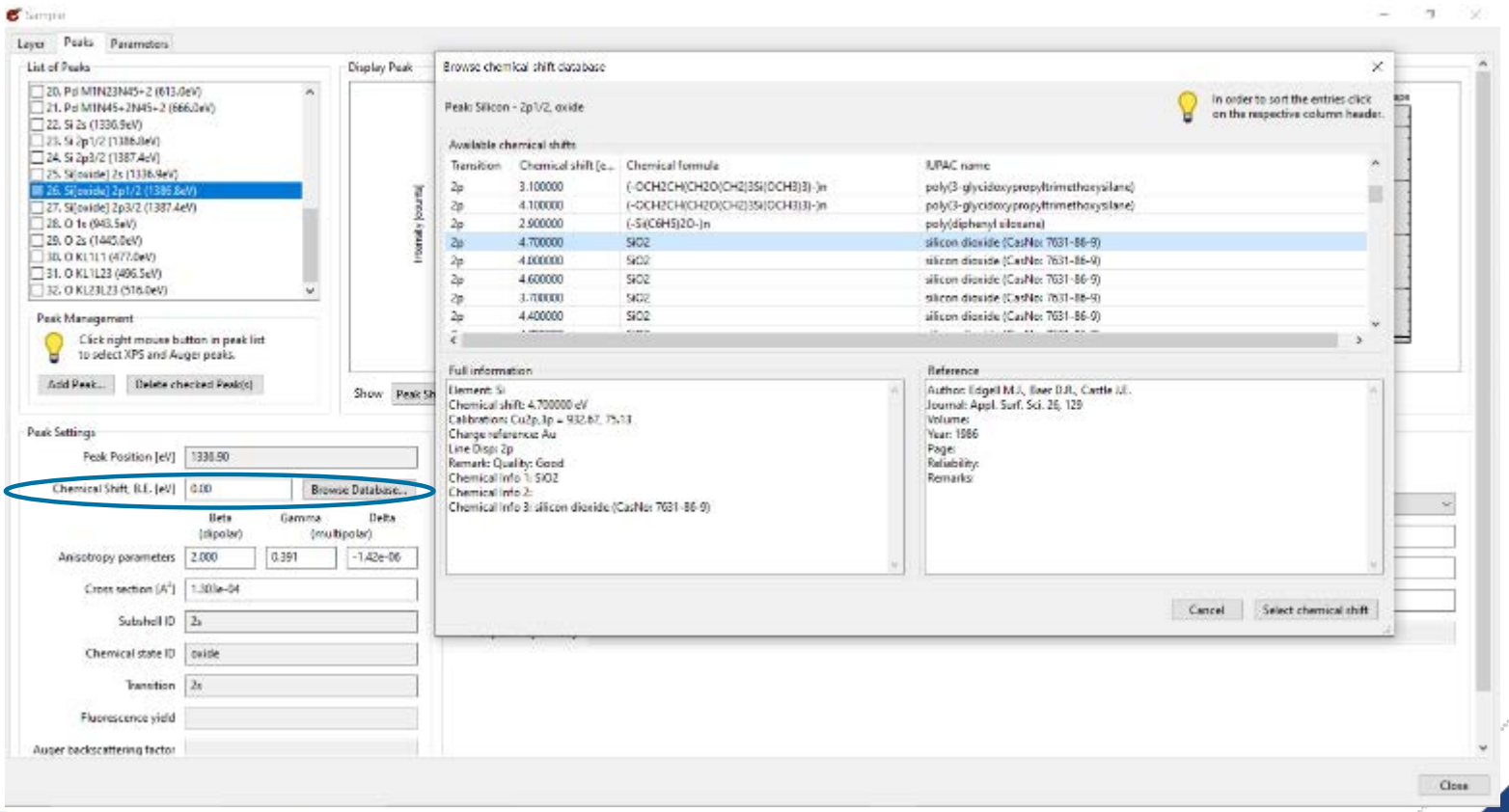


Image taken from WebElements Periodic Table » Periodicity » Electronegativity (Pauling) » Periodic table gallery

X-Ray Photoelectron Spectroscopy

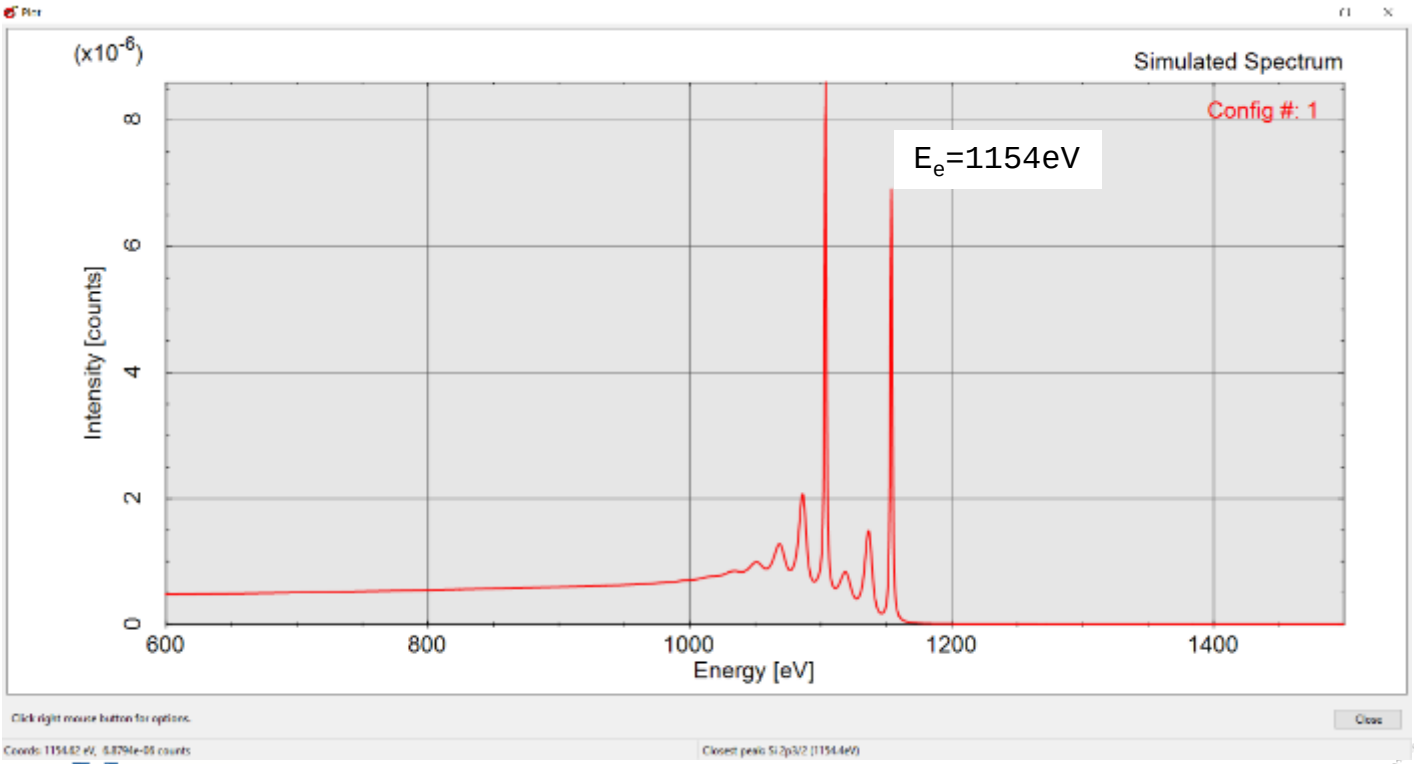
- **SESSA Exercise5:** Chemical Shift
  - Go to the Peaks tab and under Si 2p peaks click on the Chemical Shift and choose a Good estimation peak for the O bonded Si.



X-Ray Photoelectron Spectroscopy

- **SESSA Exercise5:** Chemical Shift
  - Notice that 2p states are very close to each other for Si and yield a seemingly single peak.

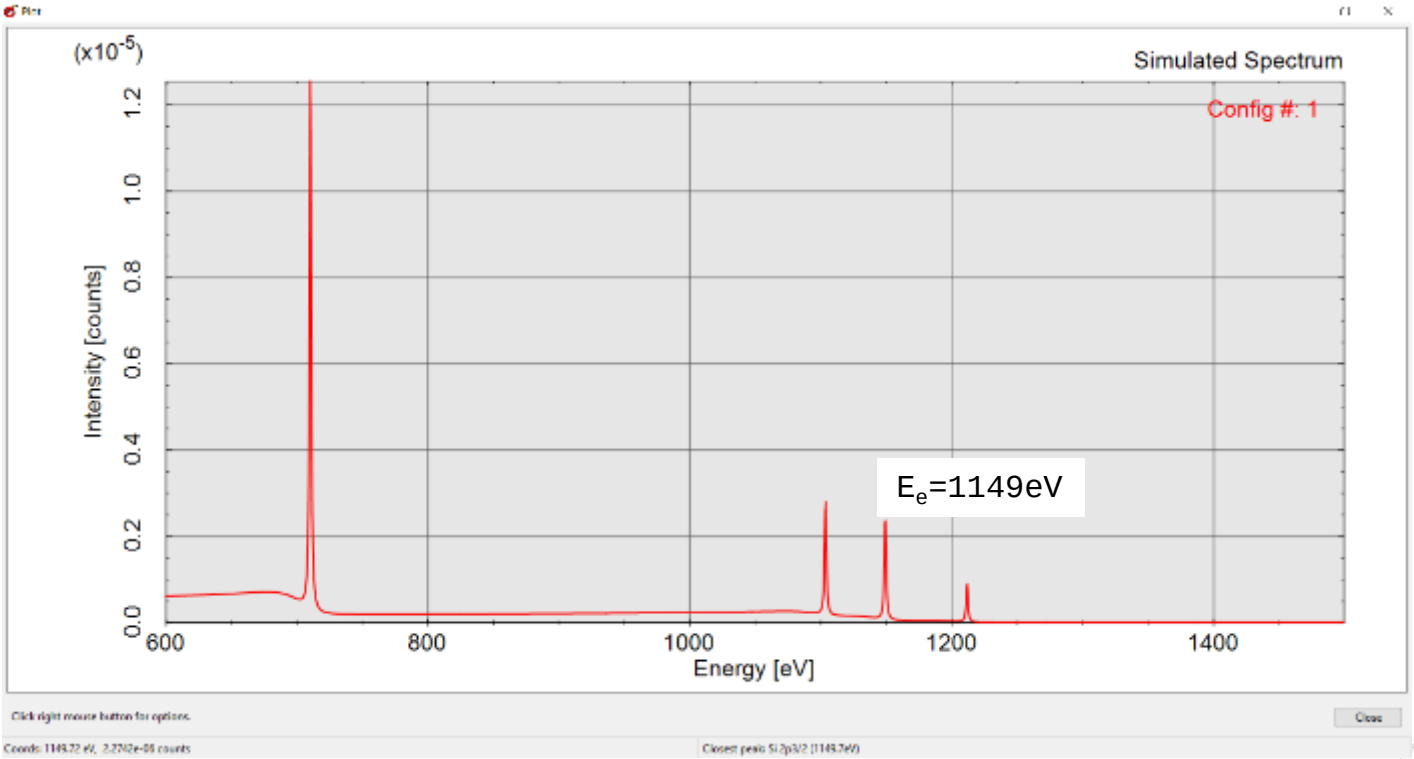
Bare Si



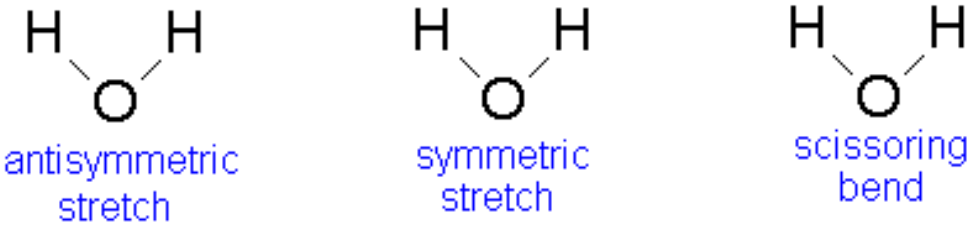
X-Ray Photoelectron Spectroscopy

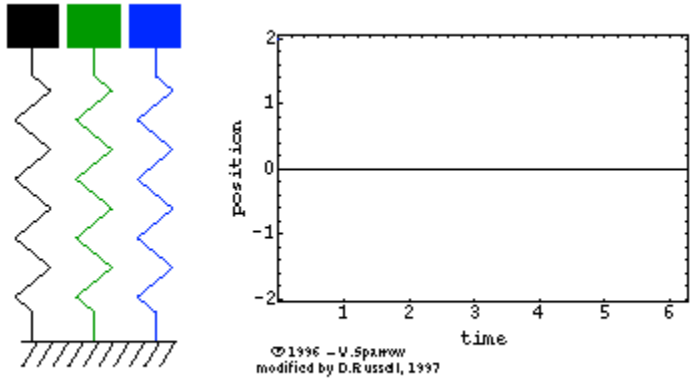
- **SESSA Exercise5:** Chemical Shift
  - Notice that 2p states are shifted by around 5eV to lower values, meaning that E_B is increased as a result of the O bond to the Si.

Oxidized Si



FTIR



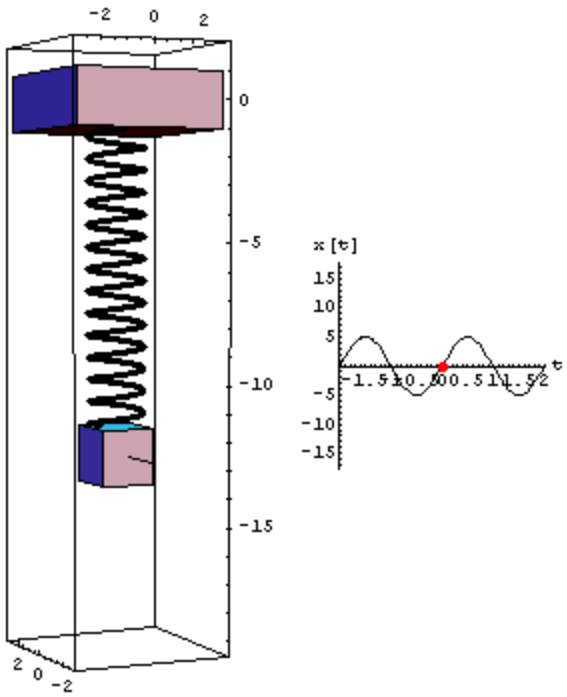


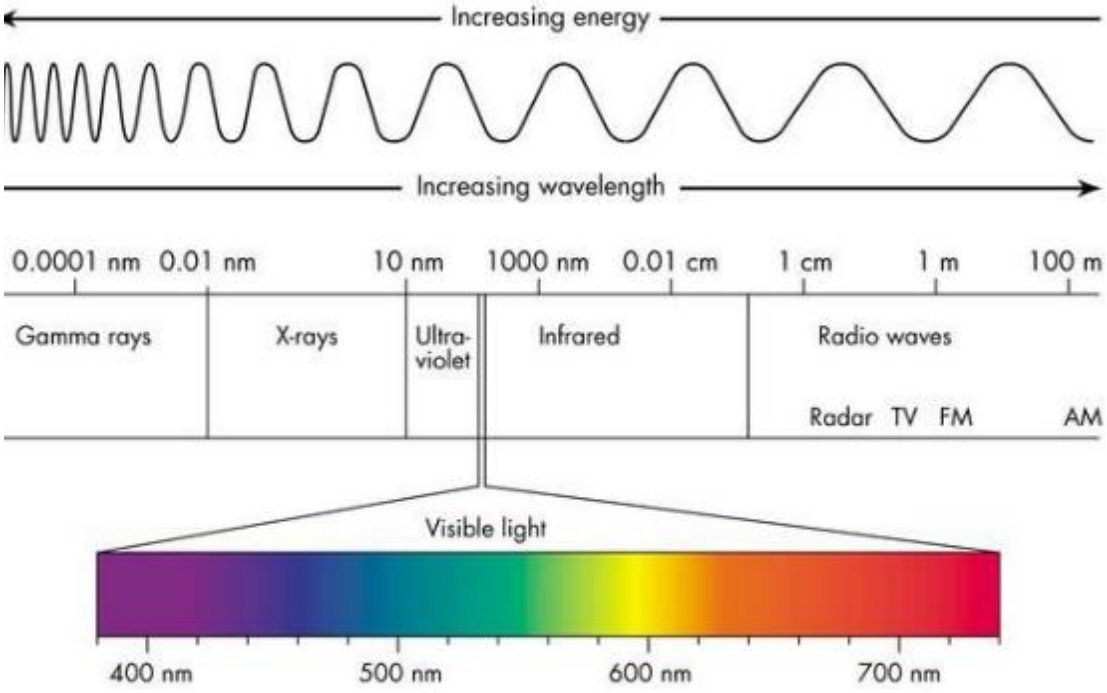
$$\omega = \sqrt{\frac{k}{m}}$$

The stronger the spring the faster the vibration and the higher the frequency

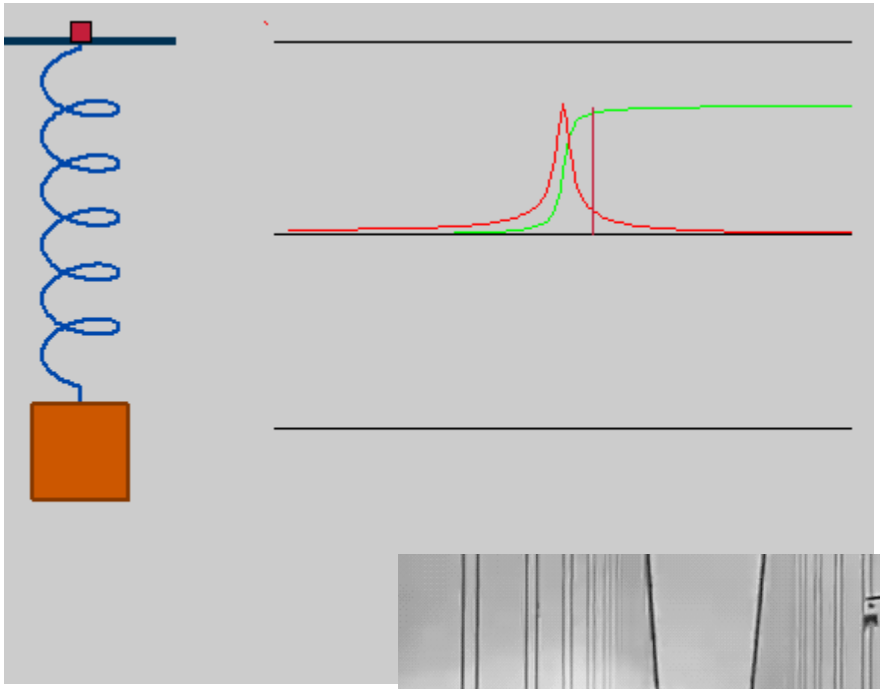
Masses and springs

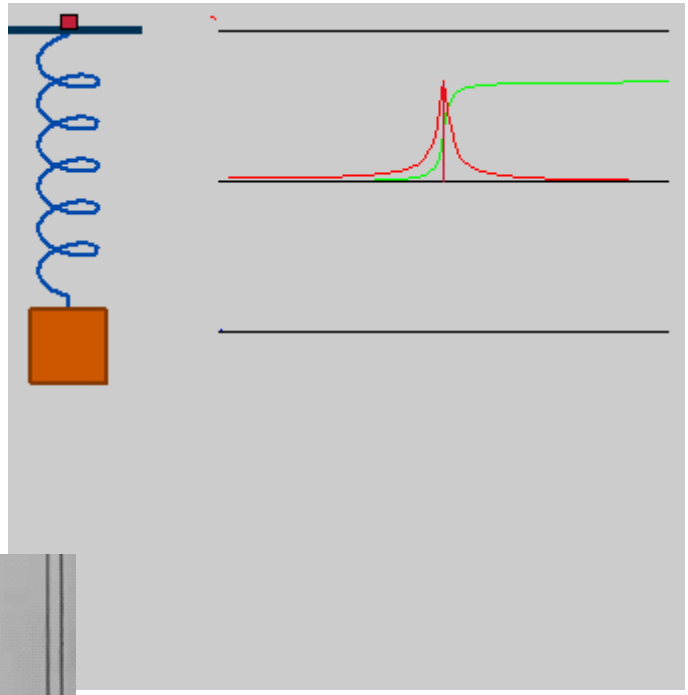
FTIR


-2 0 2
0
-5
-10
-15
2 0 -2
x [t]
15
10
5
-5
-10
-15
-1.5 -1 -0.5 0 0.5 1 1.5 2
t


Increasing energy
Increasing wavelength
0.0001 nm
0.01 nm
10 nm
1000 nm
0.01 cm
1 cm
1 m
100 m
Gamma rays
X-rays
Ultra-violet
Infrared
Radio waves
Radar
TV
FM
AM
Visible light
400 nm
500 nm
600 nm
700 nm

FTIR



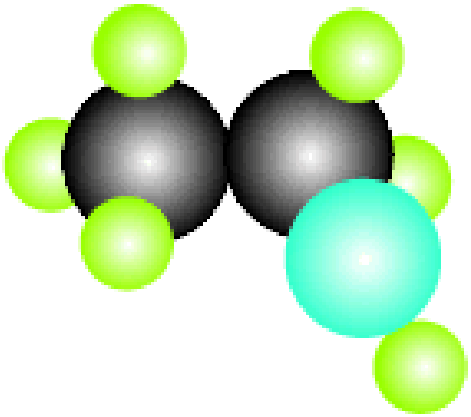


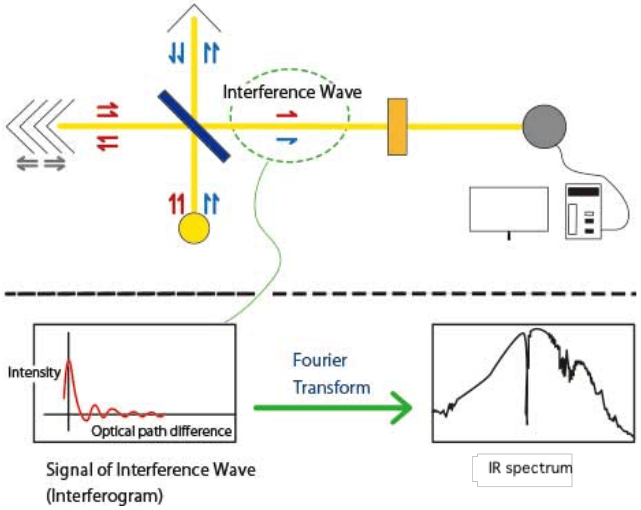
Molecules and light

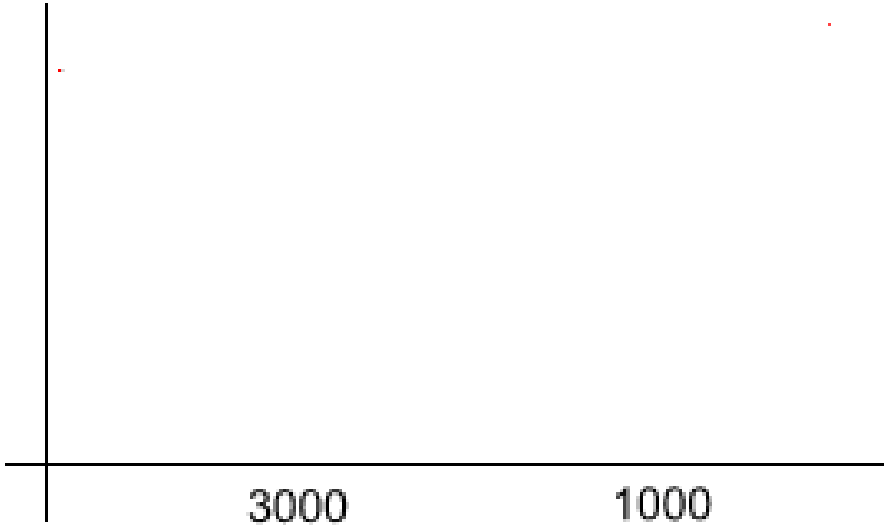
FTIR

JOSEPH FOURIER(1768-1830)

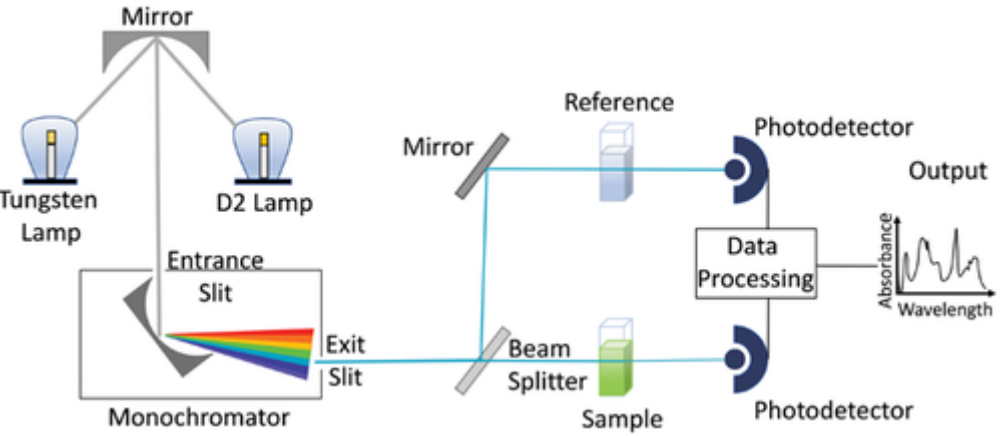
IR Spectra
FFT example

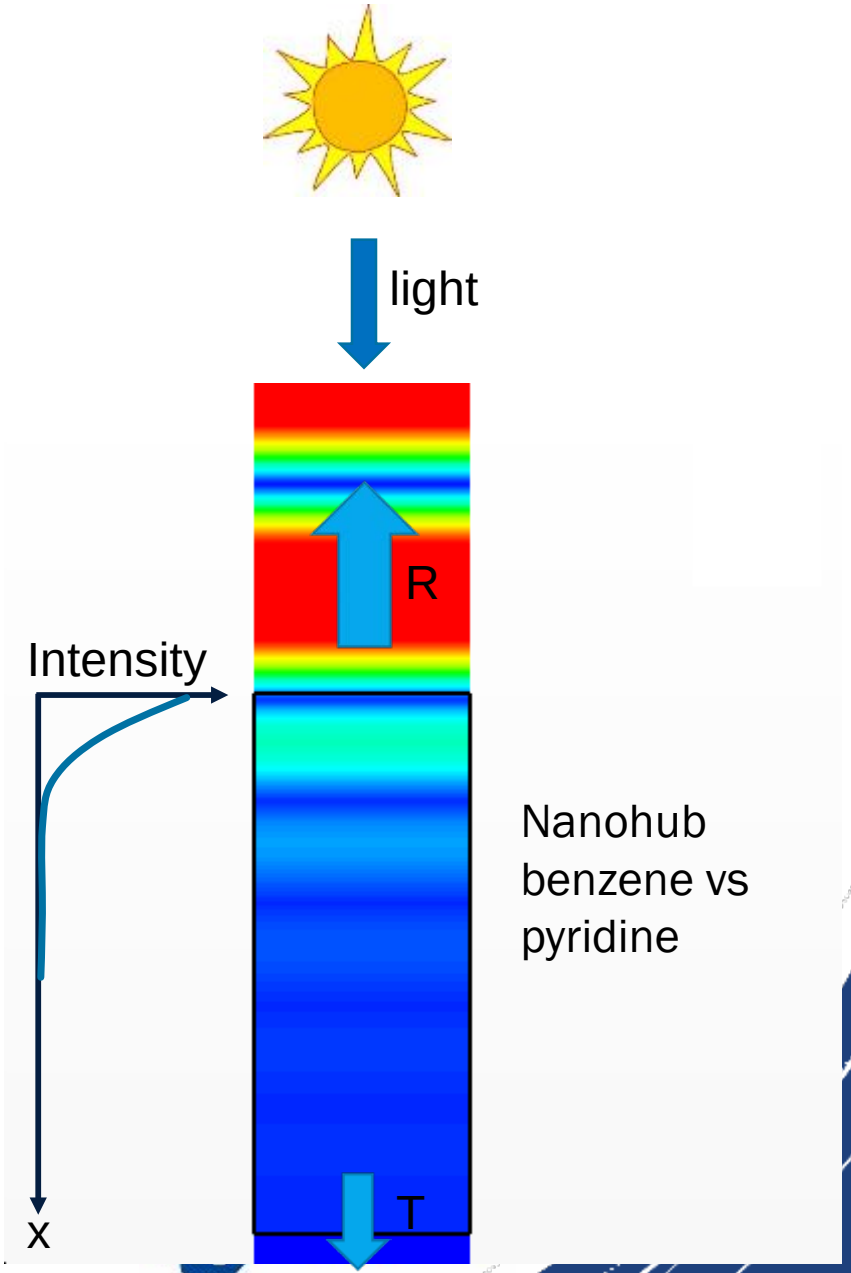






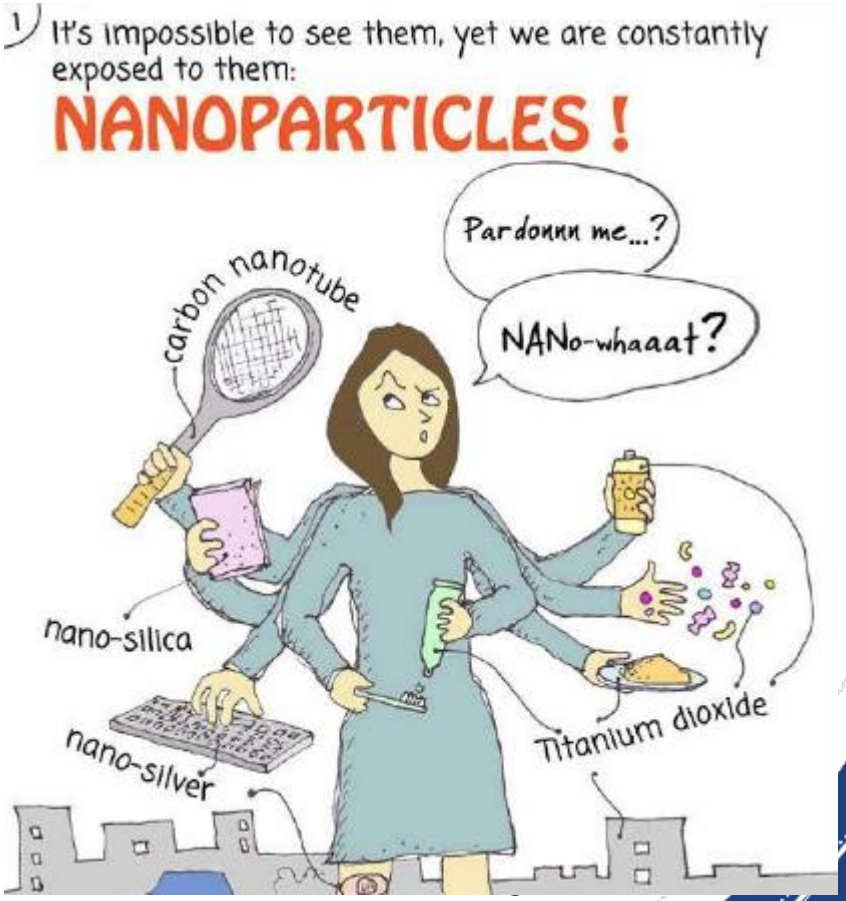
Uvvis



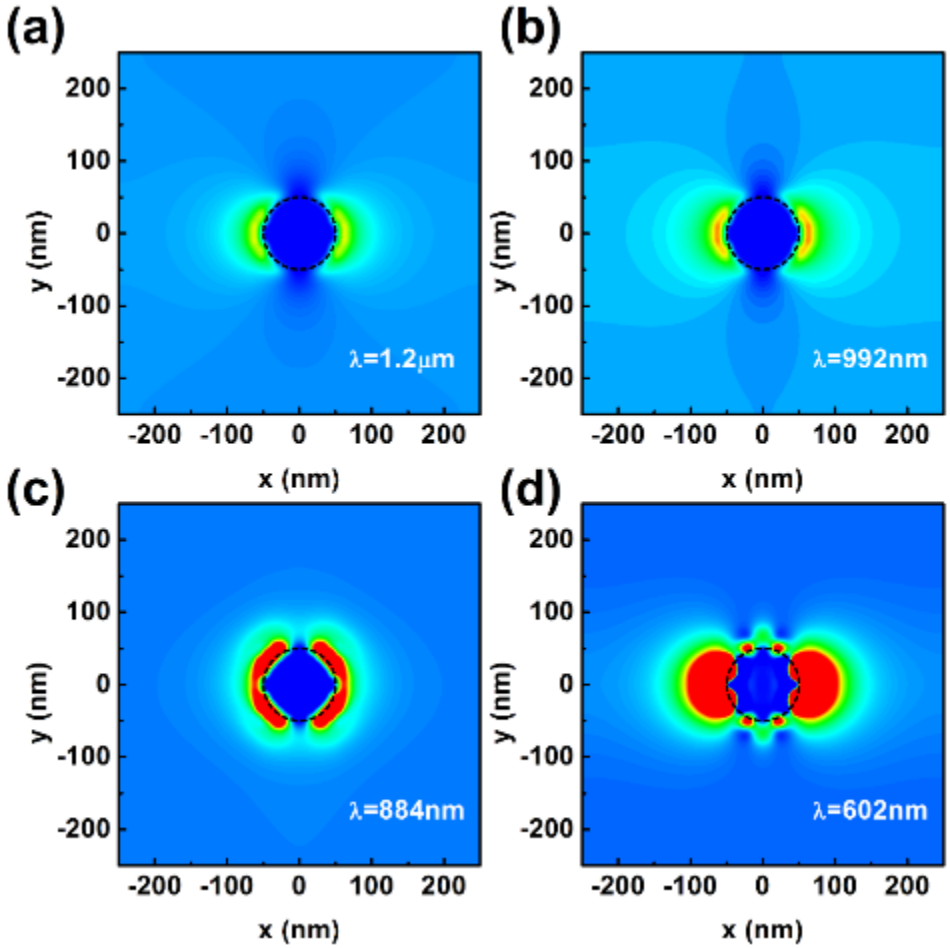


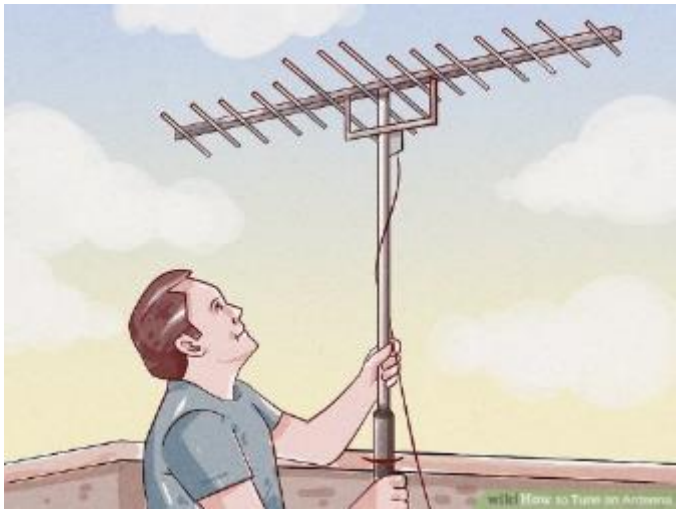
Nanohub benzene vs pyridine

Uvvis


It's impossible to see them, yet we are constantly exposed to them:
NANOPARTICLES !
Pardonnn me...?
NANo-whaaat?
carbon nanotube
nano-silica
nano-silver
Titanium dioxide

Uvvis





Nanoantennas! => [Nanohub Nanosphere Lab]

Summary

- XRD => Send X-ray and look at the diffraction patterns
  - Crystal structure
  - Crystal size
  - Internal stress
  - Composition
- XPS => Send X-ray and look at the extracted electrons (photoelectrons)
  - Elemental composition
  - Stoichiometry
  - Chemical state (e.g. oxidation state)
  - Electronic state of the elements
- FTIR => Send IR light and vibrate the chem. bonds and inspect the absorption (loss) of light. Uses Fourier Transform on Interference Patterns.
  - Identify bonds
  - Identify compounds, organics and polymers
  - Identify contamination, oxidation
- UV vis => Send UV and visible spectrum light, look at transmission and absorption. Identify how much a substance absorbs light.

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GRAND VALLEY STATE UNIVERSITY
SEYMOUR AND ESTHER PADNOS COLLEGE OF ENGINEERING AND COMPUTING

PennState