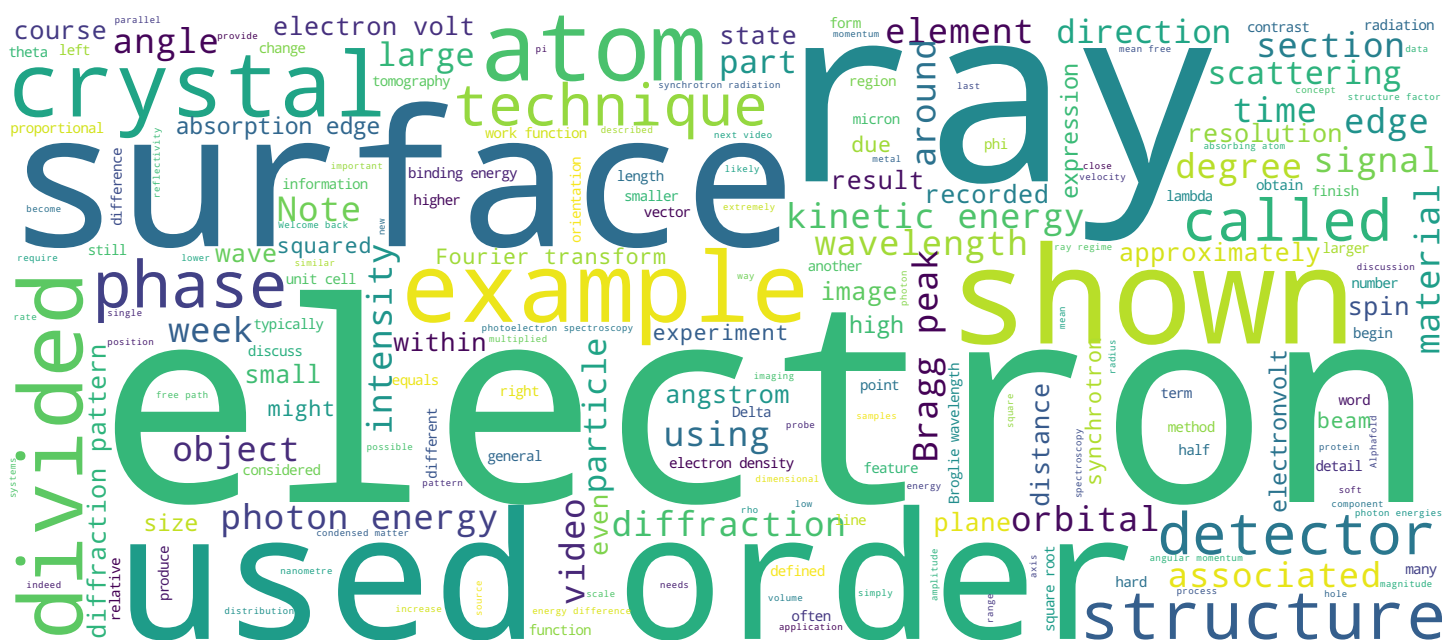


Prof. Philip Willmott



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Video



Contents and objectives of this video



- Energy balance in photoabsorption/emission
 - The work function
 - The photoelectric effect
- The de Broglie wavelength
 - Electrons as waves
- Absorption edges and synchrotron ranges
- Absorption edges and chemical states

Hi again. In this fourth video of section one of week three, we'll look at the photoelectric effect, the electron and other massive particles as against massless particles as waves, and recap absorption edges of the elements and information coded in these in identifying chemical states.

Notes

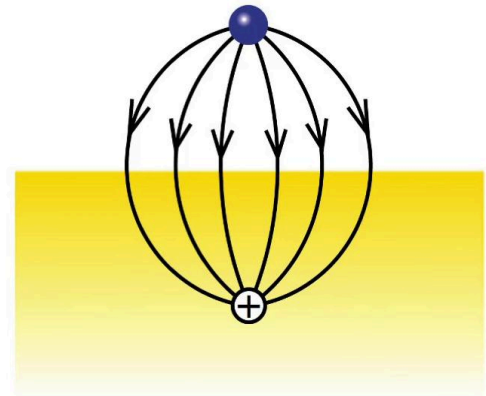
Summary



0m 05s

Photoemission

- Ejection of an electron out of the system due to photoabsorption of a photon with an energy larger than the binding energy
- In metals, the valence electrons are “free” (unbound)
 - The only phenomenon keeping them in the metal is the **work function**
 - Caused by the electron seeing a positively-charged mirror of itself as it tries to leave the surface due to a local rearrangement of the other electrons in the metal
 - Work function has values typically between $e\phi = 2 - 6$ eV for the metallic elements
 - $e\phi$ = minimum photon energy required by free electrons to induce the photoelectric effect



$$\text{K.E.} = h\nu - E_B - e\phi$$

Consider an electron that has been ejected from its parent atom as a result of photoabsorption of a photon with an energy equal to or greater than the electron's binding energy. Moreover, let the absorbing atom be a part of a condensed matter system, such as a nickel atom in a block of crystalline nickel. The electron's journey is not over yet, however. If an observer wants to detect this ejected electron, it also needs to escape the confines of the macroscopic object the atom finds itself in. Before we ask what this involves, let's think about electrons travelling through a copper wire in an electrical cable. Why, if one bends the wire at right angles, don't the electrons approaching this bend in the wire not simply continue in the same direction flow out of the corner? The reason is the so-called work function. This is, in principle, a matter of simple electrostatics. If an electron begins to pass through a surface, it will see a positively-charged mirror image of itself due to the other electrons in the neighbourhood rearranging themselves, which will pull it back in again. In general, an electron will need to expend another few electron volts in kinetic energy to overcome this electrostatic force trying to keep it within the body.

Notes

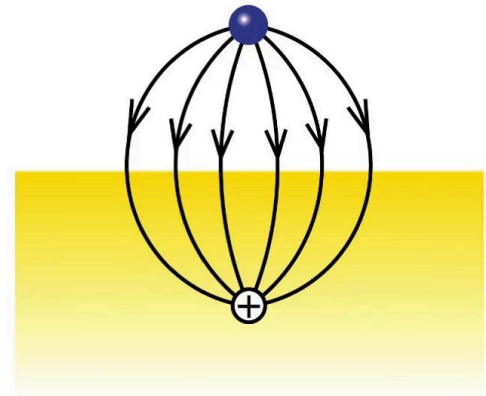
Summary



0m 24s

Photoemission

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This might not seem much, but when one realises that the electron needs to be approximately 100 angstroms removed from the surface before it can be considered to be free, one can immediately calculate that the electric field strength to pull electrons from a material needs to be of the order of five volts, say for the work function, divided by 100 angstroms, which is equal to 500,000,000 V/m. The kinetic energy of the electron, once it is fully ejected from the system, is therefore equal to the photon energy, minus the binding energy, minus the work function.

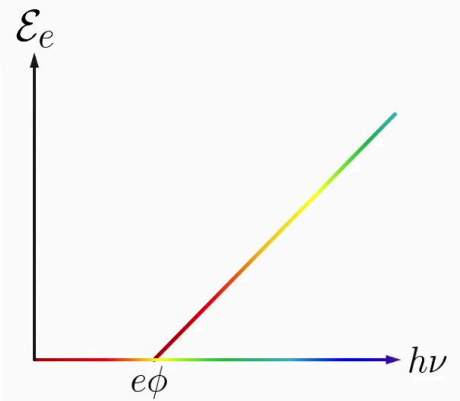
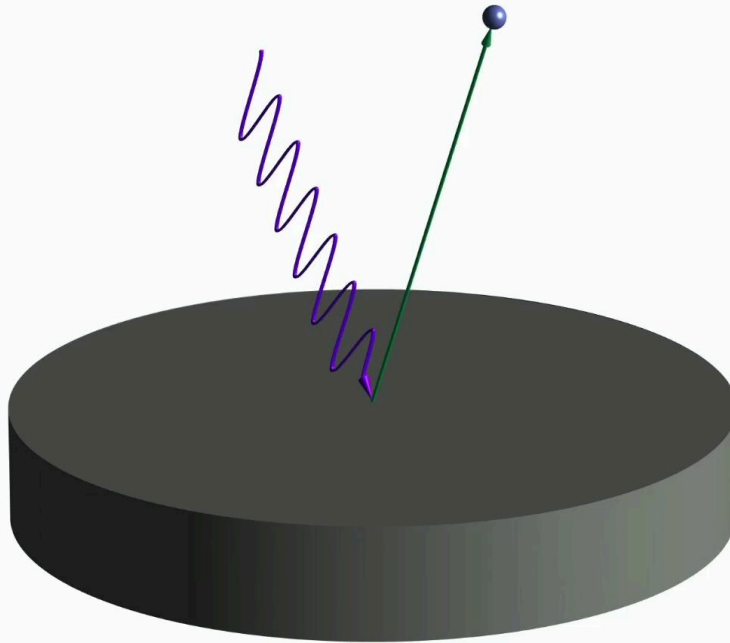
Notes

Summary



1m 53s

Photoelectric effect



The photoelectric effect therefore has a threshold photon energy which is equal to $e\phi$ for systems such as good metals, where the conduction electrons are essentially free within the metal. As the photon energy is tuned to higher energies above $e\phi$, the ejected electrons carry that excess energy away in the form of kinetic energy, \mathcal{E}_e , as indicated by the length and colour of the arrow in the cartoon on the left.

Notes

Summary



2m 30s

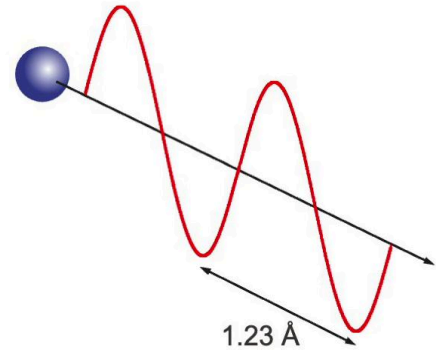
Particle-wave duality and the de-Broglie wavelength

- Any particle of mass m and velocity v has a “fuzziness” associated with a wavelength λ
- This wavelength is related to the particle’s momentum $p = mv$ by

$$p = mv = h/\lambda = \hbar k$$

Examples

- Electron with KE = 100 eV**
- Helium atom with velocity 5 km/s
- Smallest bacterium ($m = 10^{-15}$ kg) travelling at 0.05 mm/s
- Usain Bolt running at 40 m/s



e.g. EXAFS

This now brings us to the idea of an electron as being a wave in the concept of particle wave duality. Any particle of mass m not equal to zero and velocity v will have a fuzziness associated with it described by a wave function with a wavelength λ . The momentum of a particle is mv . That of a wave is h/λ , h being Planck's constant six times six, 6.63 times ten to the -34 joule-seconds. But λ is equal to two pi divided by k , where k is the wave vector. As an example, an electron with a kinetic energy of 100 electronvolts or 1.6 times ten to the -17 joules has a velocity of approximately 6,000 km per second. Now that's fast, but it's still only 2% of the speed of light. The associated wavelength is 1.23 angstroms. An electron with a kinetic energy of only one electron volt will have a wavelength of 12.3 angstroms, ten times larger. This wavelength is called the de-Broglie wavelength, after Louis de Broglie, the French physicist and aristocrat who made groundbreaking contributions to the quantum theory in the 1920s for which he would receive the Nobel Prize in physics in 1929. Note that the wavelike nature of electrons is exploited in many fields, including solid-state lasers and in this week's subject matter EXAFS and ARPES.

Notes

Summary



3m 02s

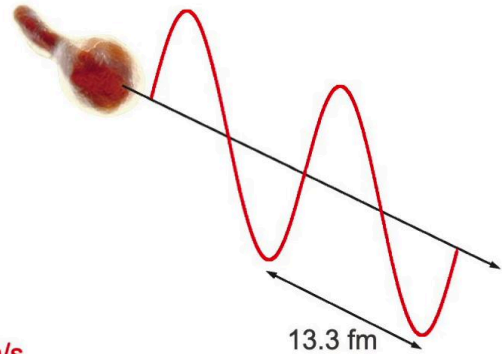
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Higher-mass particles such as helium atoms can be used in atomic-scattering experiments in which their velocity is filtered using a time of flight chopper system to very specific values. Helium interacts elastically with matter and their wavelike nature is such that at a speed of around a kilometre per second, they have a wavelength of around one angstrom, making them ideal for scattering experiments. Macroscopic objects, even ones as small as the tiniest bacteria with masses of the order of a picogram, travelling at a stately 50 microns per second still have extremely small de-Broglie wavelengths of the order of ten femtometres, some thousand to 2,000 times smaller than atomic radii.

Notes

Summary



4m 38s

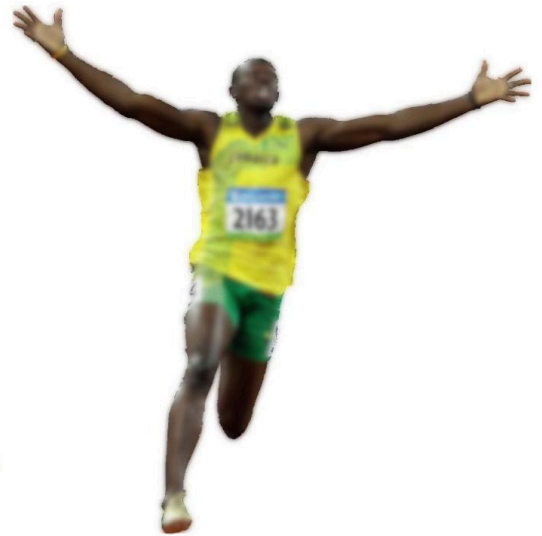
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- Examples

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$\lambda = 1.76 \times 10^{-37}$ m
100 x smaller than the Planck length
 10^{-22} x diameter of a proton

Now going still further, Usain Bolt at a hefty 90kg running at 40m/s, will fuzz out to an extent of around 2 times 10 to the -37 m. This is 100 times smaller than the Planck length, which is considered by many physicists to represent the fundamental granularity of space and below which lengths are actually meaningless.

Notes

Summary



5m 26s

Photoelectrons as waves

- Incident radiation $h\nu > E_B (+ e\phi)$
- Kinetic energy of a photoelectron

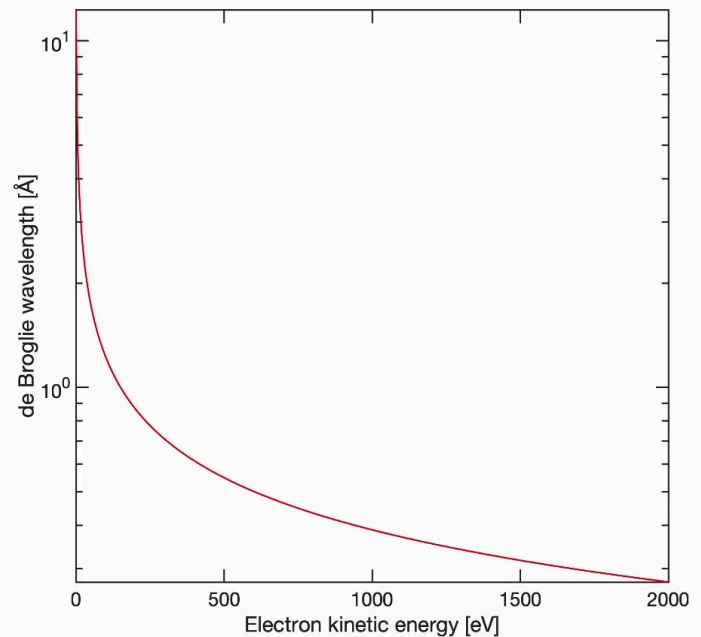
$$\mathcal{E}_e = h\nu - E_B (-e\phi)$$

- But

$$\mathcal{E}_e = \frac{m_e v^2}{2} = \frac{p^2}{2m_e} = \frac{\hbar^2 k_e^2}{2m_e}$$

$$\Rightarrow k_e = [2m_e(h\nu - E_B)]^{1/2} / \hbar$$

$$\Rightarrow \lambda_e = h [2m_e(h\nu - E_B)]^{-1/2}$$



But back to reality. The kinetic energy of a photoelectron is equal to the photon energy used to excite it, minus the binding energy and the additional small cost of the work function. Using simple Newtonian equations and adding a sprinkling of quantum mechanics in the form of P equals $\hbar k_e$, we quickly arrive at the expression for the de-Broglie wavelength of an electron being λ_e is equal to h divided by the square root of $2m_e$ times the electron kinetic energy which I have here, kept to the simpler $h\nu - E_B$. Ignoring the work function $e\phi$ for the moment. In practical units we see that the wavelength in angstroms is equal to 12.28 divided by the square root of the kinetic energy in electronvolts, or alternatively, the wavelength in reciprocal angstroms is equal to 0.512 times the square root of the kinetic energy in electronvolts.

Notes

Summary

5m 52s



Photoelectrons as waves

- Incident radiation $h\nu > E_B (+ e\phi)$
- Kinetic energy of a photoelectron

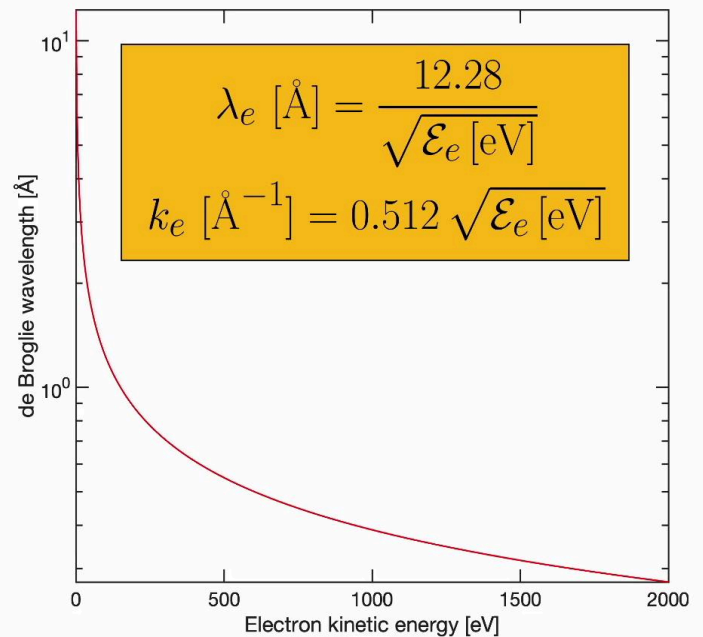
$$\mathcal{E}_e = h\nu - E_B (-e\phi)$$

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$$\Rightarrow k_e = [2m_e(h\nu - E_B)]^{1/2} / \hbar$$

$$\Rightarrow \lambda_e = h [2m_e(h\nu - E_B)]^{-1/2}$$



Note that a 151 electronvolt electron has a de-Broglie wavelength of one angstrom. Keep this in mind. Keep this number in mind when we discuss XFELs in section two of this week's videos.

Notes

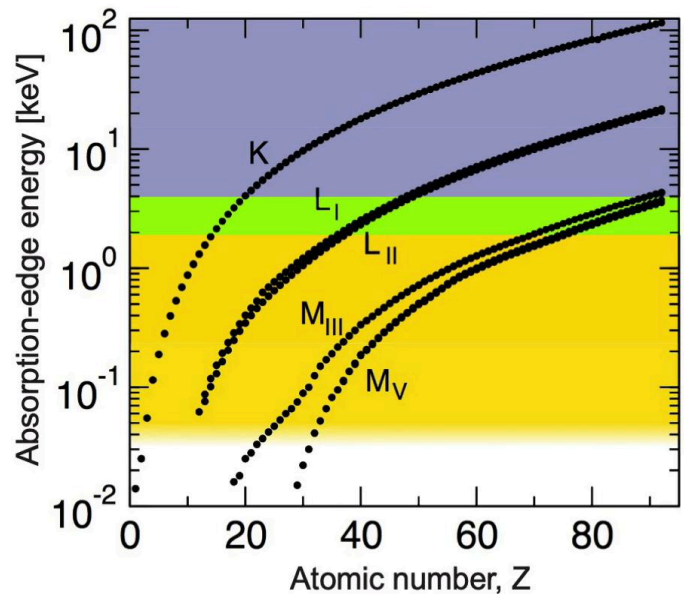
Summary



6m 59s

Absorption edges and synchrotron ranges

- Soft x-rays (+ VUV)
 - 10 – 2000 eV
 - C, N, O K-edges, up to Si/P
 - L-edges $Z = 22 - 30$, important 1st-row transition metals
- Tender x-rays
 - 2000 – 4000 eV
 - S, Cl, Ca K-edges (biology)
 - L-edges 2nd-row transition metals
- Hard x-rays
 - 4 keV – 500 keV
 - K-edges above $Z = 20$ (Ca)
 - L-edges above $Z = 48$ (Cd)



Although we discussed photo absorption in the first part of this course, it bears repetition here. Synchrotron radiation can be divided into three broad energy regions. The lowest energy range covers the vacuum ultraviolet and soft x rays between about 10 and 2,000 electron volts. This regime, in terms of spectroscopy, is used to probe valence electrons, particularly in angular resolved photoelectron spectroscopy. The carbon, nitrogen, oxygen edges, notably in scanning transmission, X-ray microscopy and the L-edges of some of the most important first-row transition metals. The tender X-ray regime covers the transition to hard X-rays. Its bounds differ according to which scientist you speak to, but normally cover about approximately two to four kiloelectronvolts. This range is particularly important for the sulphur, chlorine and calcium K-edges in biological studies and the L-edges of the second-row transition metals. The hard X-ray regime covers all photon energies above about four kilo electron volts and can probe the K-edges of calcium and heavier elements and the L-edges from elements above cadmium.

Notes

Summary



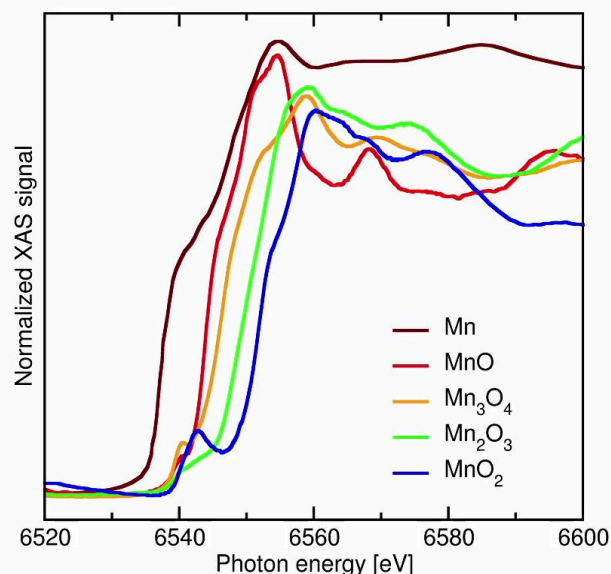
Absorption edges and chemistry

■ Oxidation state

- High? Lower electron density around absorbing atom
 - Less repelled by electron cloud
- Low? Higher electron density around absorbing atom
 - More repelled by electron cloud



Oxidation Is Loss
Reduction Is Gain



The precise position of an absorption edge is influenced by the local electron density around the absorbing atom. This can shift the edge by up to 10 or 20 electronvolts, depending on the system. On the right is shown different oxidation states of manganese. One sees that the higher the oxidation state, the higher is the absorption energy. Oxidation is associated with the oxidised atom being an electron donor to the electron acceptor of oxygen. This means that the electron density around the absorbing atom is lower and hence the emitted photoelectron sees less electrons to repel it and send it on its way from the atom. It is therefore more strongly bound to the atom, and has a higher absorption energy as we see in this graph here.

Notes

Summary



8m 31s

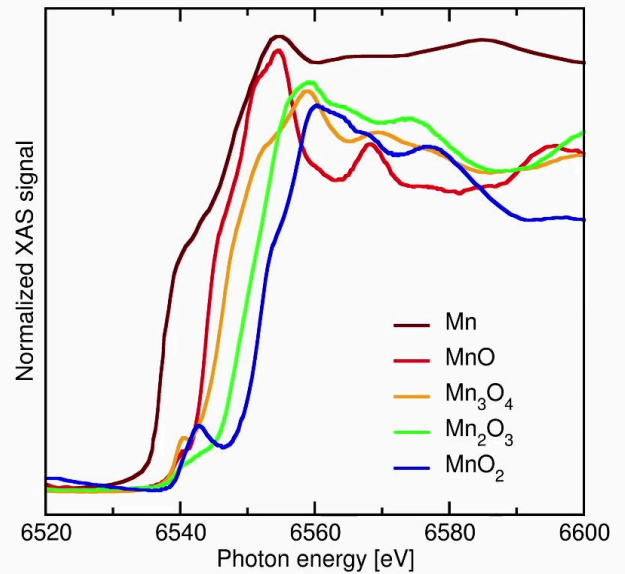
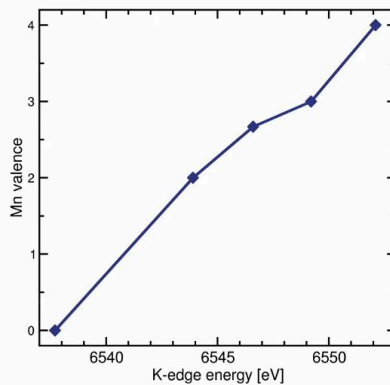
Absorption edges and chemistry

■ Oxidation state

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Oxidation Is Loss
Reduction Is Gain



Conversely, low valence states are associated with weaker binding energies. Hence, detailed absorption spectroscopies can provide important chemical information.

Notes

Summary



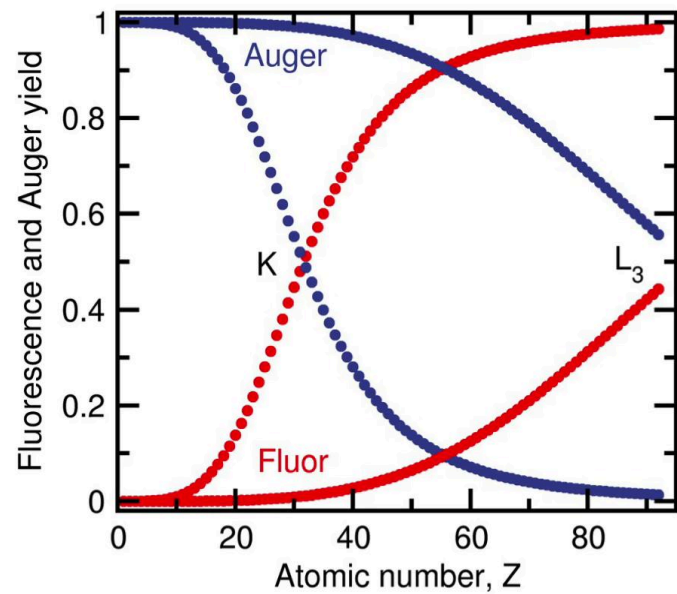
9m 24s

What happens next?

- Excited state, photoelectron ejected
- Then?
 - Fluorescence, or...
 - Auger emission
- Fluorescence
 - Spontaneous process, determined by "Einstein A-coefficient" A_{21}
 - $A_{21} \propto h\nu^3$
 - Dominates for relaxation to empty K-states in high-Z elements

$$Y_{K,L_3} = \frac{Z^4}{A_{K,L_3} + Z^4}$$

$A_K \approx 10^6$ $A_{L_3} \approx 9 \times 10^7$



Now what happens after the ejection of a photoelectron? The hole which is left behind by the electron can be filled by another electron falling into it from a higher orbital. The energy released in this process can be in the form of the emission of another photon in fluorescence, or it can cause yet another electron from a higher orbital to be ejected in an Auger emission process. Which process is more likely to happen depends on the energy difference between the hole and the higher energy level from which the electron decays, and on the atomic number. Fluorescence dominates for high energy differences as its rate is proportional to the Einstein A coefficient, A_{21} which is proportional to the cube of the energy difference. Hence, fluorescence dominates for electrons falling into empty K-edge holes and for high-Z elements, while Auger electron emission is more likely for the decay into L-holes and for low-Z elements.

Notes

Summary



9m 40s

In the next video...



In the following video, the last of this section, we revisit the inelastic mean free path for electrons moving through condensed matter. We look also at the electron angular momentum, both orbital and spin and how these, couple to one another, and finish with a brief summary of s and p polarisations of electromagnetic radiation.

Notes

Summary



10m 43s