

# *Supplementary Course Topic 2:*

## Atomic Spectroscopy

- Identifying Atoms from their Spectra
- Atomic Absorption Spectroscopy.
- X-Ray Spectroscopy

# Spectroscopy and Electronic Transitions

We have already seen that the set of allowed energies corresponding to solutions of the wavefunction or electronic states for an atom are uniquely determined by its chemical character

- nuclear charge or atomic number
- electronic configuration

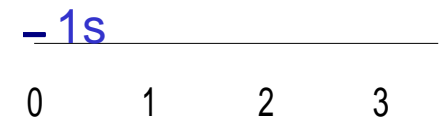
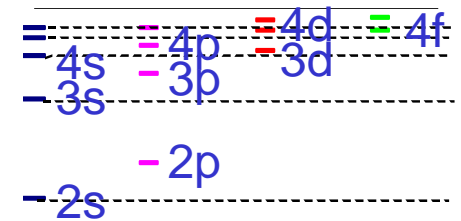
This also means that the set of allowed energy differences between states is unique to each element.

Spectroscopy probes the energy differences between allowed states, from which we can deduce the identity of the atom in two ways

- Precise  $\Delta E$  or wavelength measurements
- Measurements of multiple wavelengths

$$\Delta E = \frac{hc}{\lambda}$$

Energy (J)



# Absorption and Emission Measurements

Spectroscopic measurements can be divided into two broad classes.

An electronic transition occurs when an electron changes from one allowed state to another.

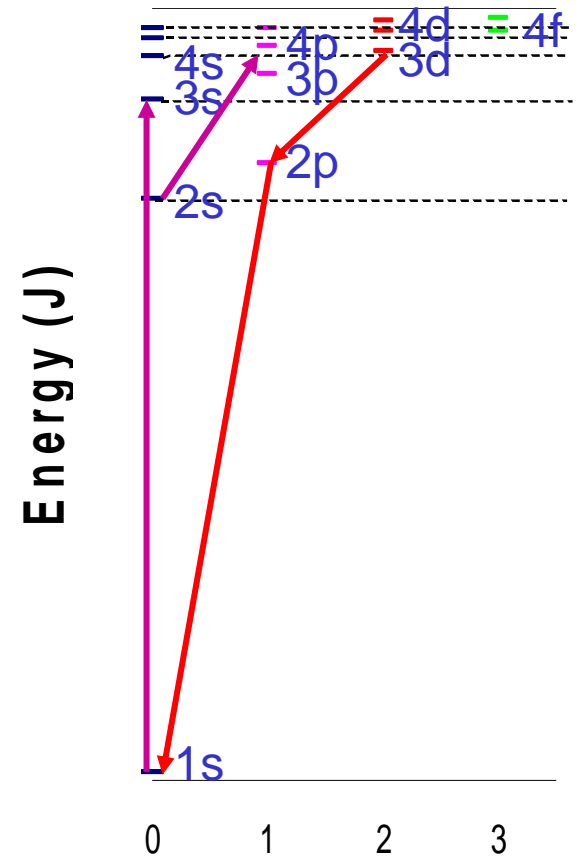
The orbital it is *leaving* must be partly filled (it contains at least one electron), and the orbital it is *entering* must be partly unfilled (it contains less than two electrons).

- Absorption or Absorbance

An electron absorbs the energy of a photon, and jumps from a lower into a higher energy orbital.

- Emission

An electron jumps from a higher into a lower orbital, and releases (emits) a photon of energy equal to the difference.



# Dispersion Spectrophotometry

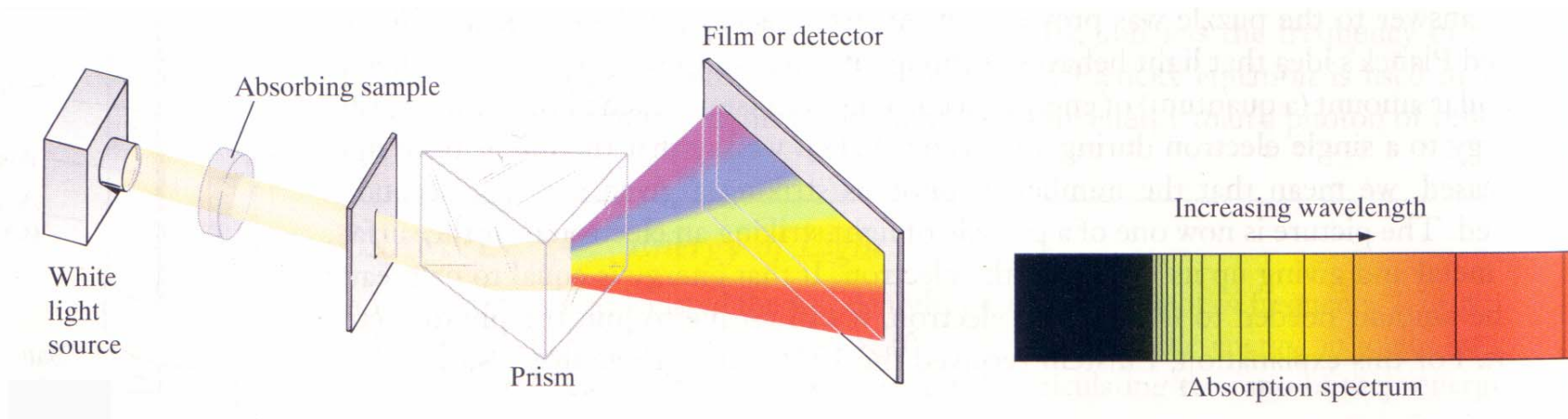
The principle of dispersion spectrophotometry is to take a light source that produces a broad, continuous spectrum (a “white source”), and then select and scan through the available range of wavelengths from the source.

Individual wavelengths (monochromatic light) are selected with a monochromator. A monochromator uses the interference of waves to select a very narrow band of wavelengths.

Conceptually, this is like dispersing white light through a prism, and then selecting a particular wavelength from its position in the resulting spectrum (rainbow).

# Absorbance Spectrometry

A sample is placed between a light source and a detector. If a particular wavelength of light promotes the electron into an excited state, then that wavelength is absorbed and does not appear (or appears at a reduced intensity) in the detected spectrum.



The attenuation of a beam by absorbance is typically represented in two ways.

- Fraction or Percent Transmission.
- Absorbance

# Transmission and Absorbance

**Transmission,  $T$** , is simply defined as the fraction of light that reaches a detector after passing through a sample

$$T = \frac{I}{I_0} \qquad \%T = 100 \frac{I}{I_0}$$

where  $I$  denotes intensity, and  $I_0$  is the intensity of a reference beam (no sample present).

**Absorbance,  $A$** , is a *logarithmic* scale that increases as the transmission decreases.

$$A = \log_{10} \left( \frac{I_0}{I} \right)$$

**Worked Example:** *What is the absorbance of a sample with a 1.0% transmission?*

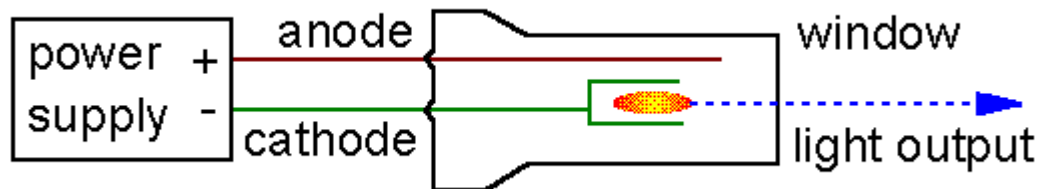
$$\%T = 1.0 \Rightarrow I/I_0 = 0.010 \text{ or } I_0/I = 100. \quad A = \log_{10}(100) = \underline{2.0}$$

# Atomic Absorbance Spectrophotometry (AAS)

AAS was developed in the 1950's by Dr. Alan Walsh of the CSIRO Division of Chemical Physics. It uses the narrow atomic absorbance lines to uniquely identify and measure the concentrations of atoms in a sample that may contain a complex mixture.

Each element is measured separately by a hollow cathode lamp that uses **the same element** to produce emission lines with its own unique wavelengths. In this way one element can be singled out of many.

The hollow cathode lamp works like a cathode ray tube. An electrical discharge is used to ionize gaseous atoms (+ve), which then impact onto a metal cathode (-ve). The metal is vaporised and electronically excited, and hence emits its characteristic wavelengths when it returns to its ground state.



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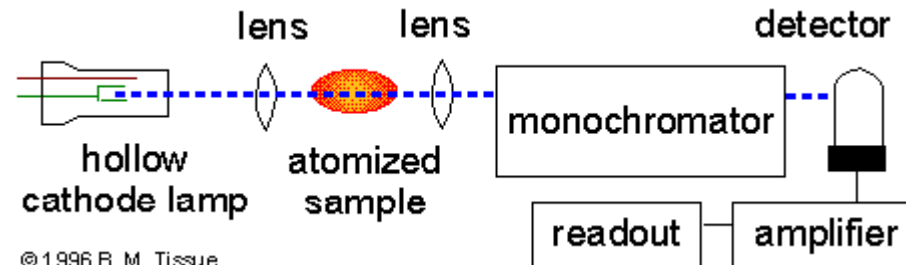
# Atomic Absorbance Spectrophotometry (AAS)

Samples for AAS analysis must be vapourised and atomised, so that they are not present as molecules or strongly interacting with other atoms or molecules, as these affect the electronic energy levels and hence the transition wavelengths. This is achieved in two ways.

**1. Flame.** Flame atomization heats the sample to  $\sim 1000^{\circ}\text{C}$ , which can vapourise solutions. Flame atomisers typically use a vacuum aspirator to suck solution with the element to be analysed into a slit flame ( $\sim 5\text{cm}$  long).

**2. Graphite Furnace.** A graphite furnace can work with solid or liquid samples, and smaller volumes than a flame. They also provide a better controlled environment. E.g. the furnace can be oxygen-free to prevent oxidation of the element of interest.

AAS is used *quantitatively*, to measure the concentration of one or more elements using the appropriate lamp.





# Trace Analysis of Elements by AAS

The concentration of an element in a sample can be determined from its absorbance by comparing with one or more standard solutions. This uses **Beer-Lambert Law**, that absorbance,  $A$ , is directly proportional to the optical path length,  $l$ , and concentration,  $c$ .

$$A = \epsilon cl$$

A slit flame is used to define and the optical path length.

The constant of proportionality is a property of the element being examined, and is called the **extinction coefficient**. In practice,  $\epsilon$  is determined by calibrating the instrument with one or more standard solutions.

# Applications of AAS

Flame AAS is routinely used to determine the concentrations of metals in particular in various water environments, and whether these exceed safe levels. E.g. The US Environmental Protection Agency limits lead in drinking water to a maximum of 15 parts per billion (ppb).

1 part per million (ppm) = 1 mg/kg

1 ppb = 1 mg/1000kg.

**Worked Example:** *Is the concentration of lead in a water sample with absorbance  $A = 0.0068$  within safe (US) limits? A reference 0.100 ppm standard solution has an absorbance of 0.165.*

We are not given the path length, so we treat the product  $\epsilon l$  as a constant.

Single-point calibration. For the standard:  $\epsilon l = A/c = 0.165/0.10\text{ppm} = 1.65\text{ppm}^{-1}$

For the unknown,  $c = A/\epsilon l = 0.0068/1.65 =$  0.0041ppm or 4.1 ppb.

# Applications of AAS

AAS can be used to in studies of toxicity, again particularly for heavy metals. Heavy metals like mercury, arsenic, lead, and chromium are not easily stored within the body, so they accumulate in the hair and fingernails. These can be prepared for flame AAS analysis by digestion in concentrated acid, or combusted in an oven.

Samples of the hair and fingernails were taken from the body of the arctic explorer Charles Hall, who died under mysterious circumstances on an expedition in 1871.

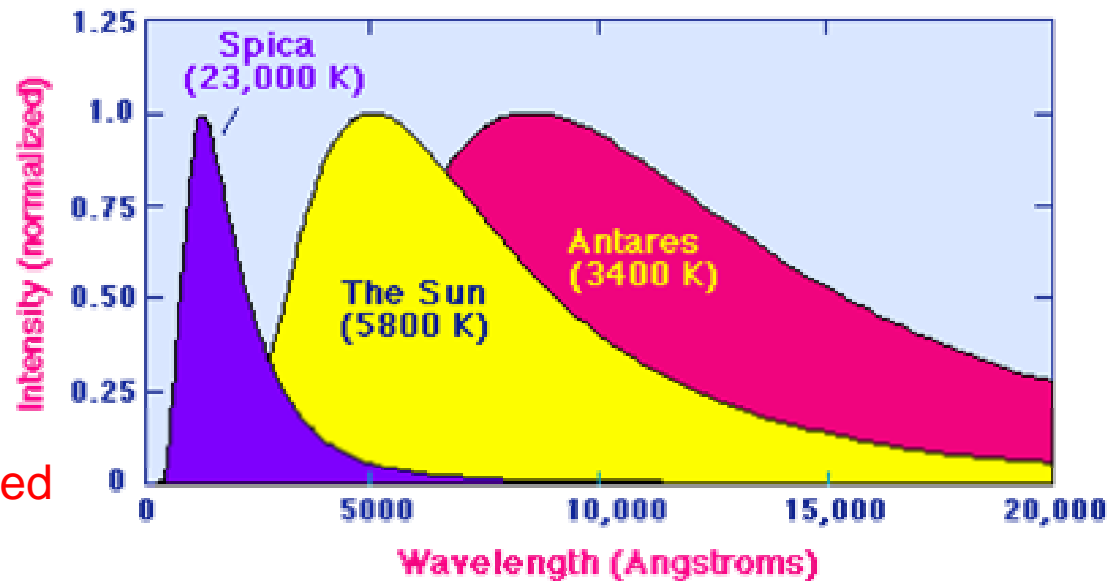
The fingernail was found to have 24.6 ppm As at its tip, but 76.7 ppm As at its base. Similar results were found for the hair, suggesting that he had been given a massive dose of the poison in the last two weeks of his life.

# Spectra of Stars

Stars **emit** a broad (so-called “black-body) spectrum of radiation that depends on their temperature. Higher temperatures shift this emission spectrum towards shorter wavelengths.

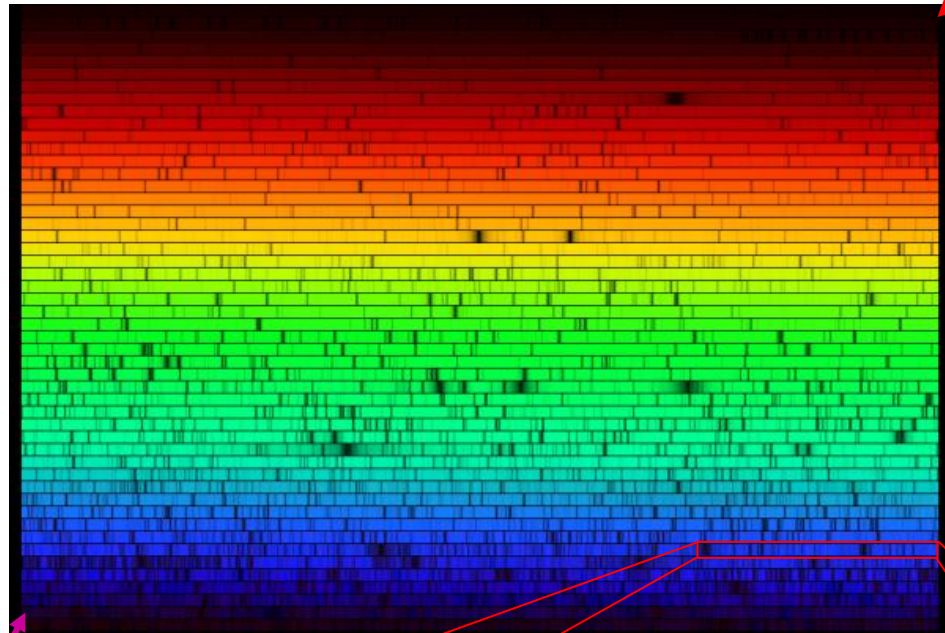
Elements (atoms and ions) in the star **absorb** certain wavelengths, leading to a pattern of dark lines in the continuous spectrum.

These *Fraunhofer Lines* can be used to deduce both the identity and relative concentration of the various elements present.



# Composition of the Sun

The expanded solar spectrum shown below includes series of absorbance lines from many elements.



700 nm

400 nm

Balmer H-gamma

$n=3 \rightarrow n=2$

Solar Elemental Abundances

Element	Number %	Mass %
Hydrogen	92.0	73.4
Helium	7.8	25.0
Carbon	0.02	0.20
Nitrogen	0.008	0.09
Oxygen	0.06	0.8
Neon	0.01	0.16
Magnesium	0.003	0.06
Silicon	0.004	0.09
Sulfur	0.002	0.05
Iron	0.003	0.14

# Emission Spectra and Flame Tests

Emission can only occur when electrons have been excited from their ground electronic configuration into higher energy levels. When these electrons return to a lower state, they emit photons of the same wavelength as those absorbed. (It's the same energy difference, and the same effect as used to make AAS hollow cathode lamps.)

Atomic emission spectra are most commonly used as qualitative visual tests for the presence of an element in a sample, but they can be used quantitatively.

**Flame Tests.** An small sample is introduced into a flame. This excites a small fraction of electrons out of their ground state. Emissions in the visible range of wavelengths give the flame a characteristic colour. These wavelengths can be quantified by dispersion onto a detector.

The fraction of atoms excited in the flame is constant, and depends only on flame temperature. Hence the intensity of the emission is directly proportional to the number of atoms in the flame, and so can also be used to measure concentration in the aspirated sample.

# Visible versus X-ray Spectrometry

Other atomic electron energy levels can be used to identify atoms:

Atomic spectrophotometry for identifying and measuring concentrations of elements suffers under some important practical constraints.

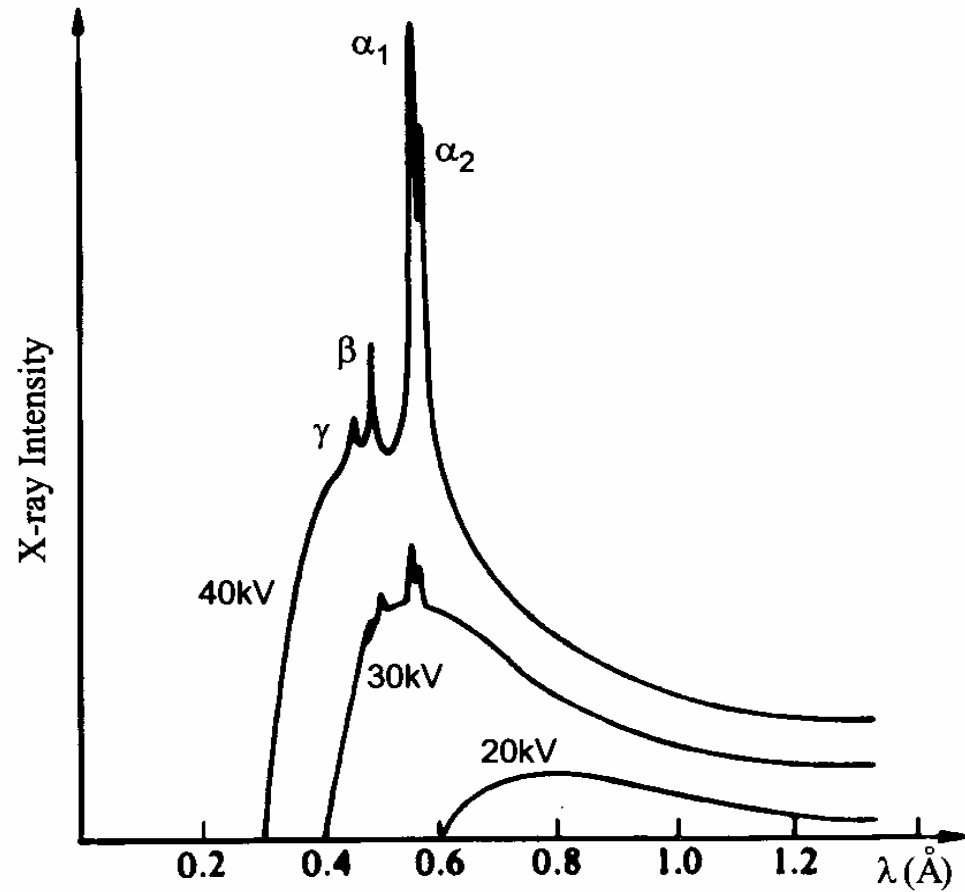
The visible and UV wavelength range corresponds to changes in *outer* electron configurations for most atoms. The energies involved are similar to or less than the ionization energy of the element. The samples to be analysed must therefore be decomposed into their constituent atoms. Sample preparation for AAS relies on breaking chemical bonds so that the electronic configurations are of atoms and not molecules.

X-rays probe much higher energy changes in core electron configurations. These are insensitive to bonding (which mainly effects outer shell electrons), so elaborate preparations are not required. Other restrictions arise when working with x-ray and higher energies.

# Generation of X-rays

## *Electron Bombardment*

X-rays are generated in a “cathode ray tube” by accelerating electrons from a cathode into a metal target anode. When the electrons strike the anode they collide and emit *Bremsstrahlung* or “braking” radiation in the x-ray wavelength range.



Braking may occur by one or more collisions, leading to a broad spectrum of emitted x-rays which have a well defined maximum energy (or minimum wavelength) corresponding to stopping by one collision.

$$E_{\max} = \frac{hc}{\lambda_{\min}}$$



## Worked Example: Bremsstrahlung Wavelengths

*What is the minimum x-ray wavelength obtained when 30keV electrons impact on a Cu target?*

The material used for the target is irrelevant to the bremsstrahlung minimum wavelength.

30keV electrons have been accelerated by a 30,000V potential difference

$$E = 30,000 \text{ eV} \times 1.609 \times 10^{-19} \text{ J/eV} = 4.83 \times 10^{-15} \text{ J}$$

The maximum x-ray energy or minimum wavelength correspond to complete stopping in one collision, i.e.

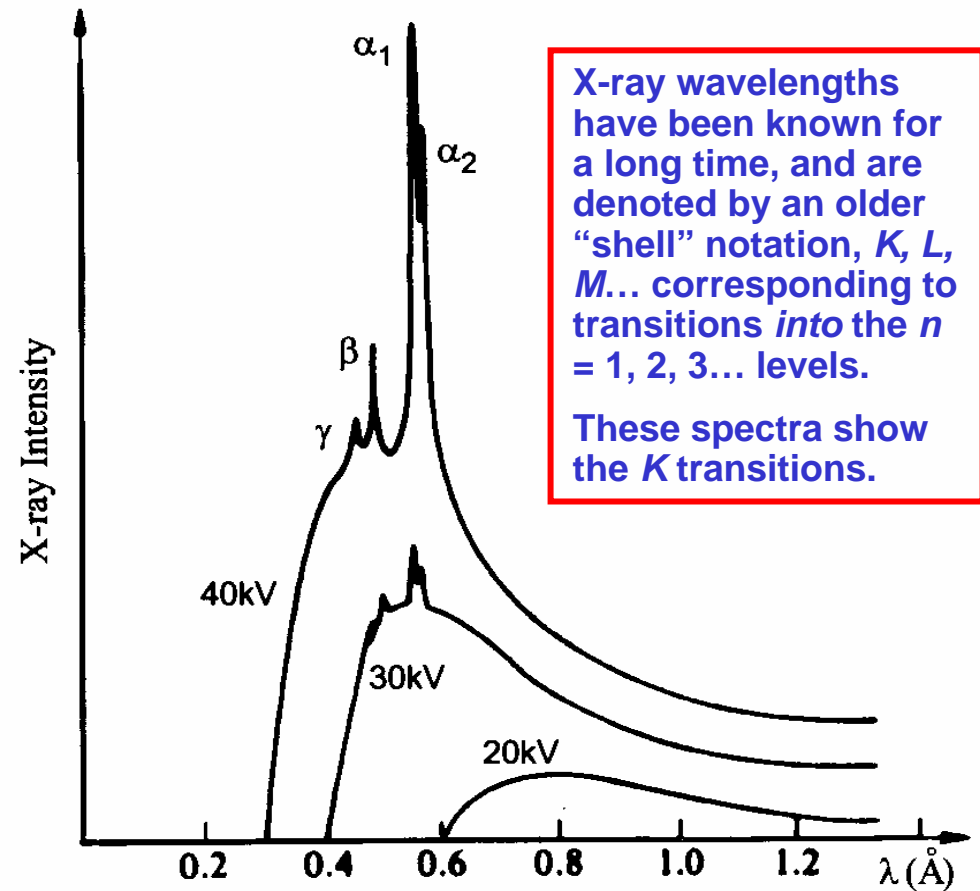
$$\lambda_{\min} = \frac{hc}{E_{\max}} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{4.83 \times 10^{-15}} = 4.11 \times 10^{-11} \text{ m}$$

or 0.411 Å or 0.0411 nm.

# X-Ray Fluorescence

In addition to the broad spectrum Bremsstrahlung, target anodes may exhibit sharp lines characteristic of the atom(s) in the anode.

These arise when incident electrons have enough energy to ionise the atom by *ejecting an electron from a core (e.g. 1s) atomic orbital*.



X-ray wavelengths have been known for a long time, and are denoted by an older “shell” notation, *K*, *L*, *M*... corresponding to transitions *into* the  $n = 1, 2, 3 \dots$  levels.

These spectra show the *K* transitions.

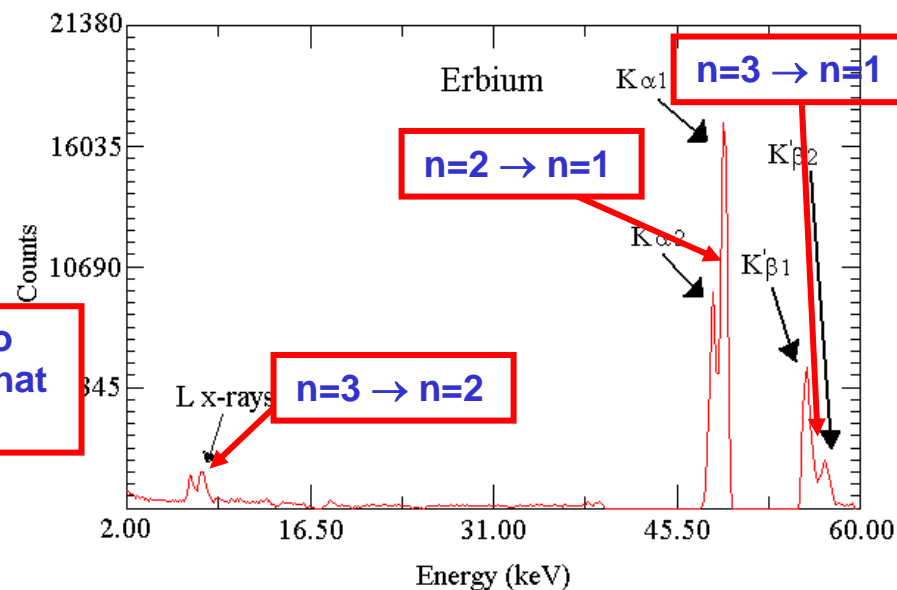
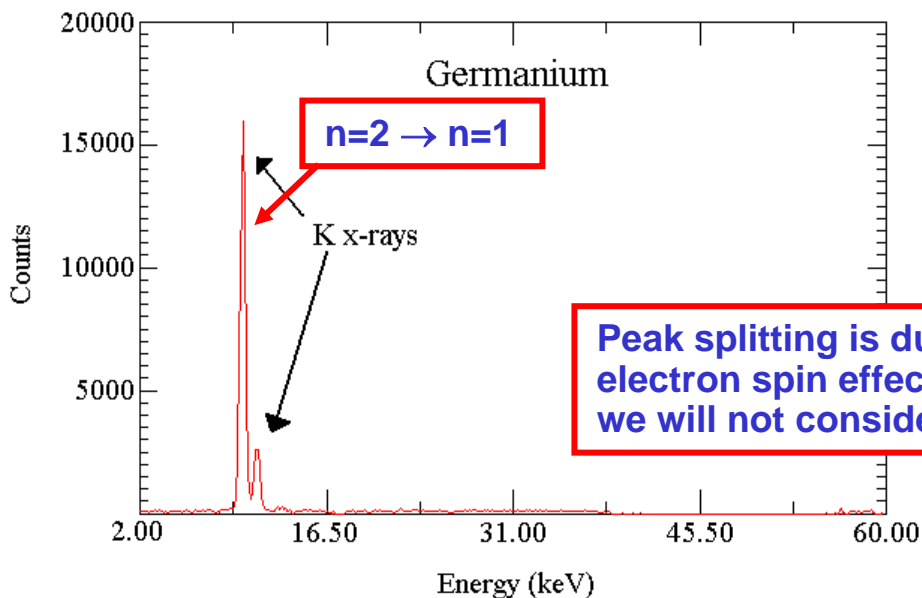
X-ray photons are emitted when electrons drop from higher energy orbitals to fill the vacancy. Because these wavelengths are characteristic of core orbital energies, they are relatively unaffected by any changes in outer (valence) electron energies associated with bonding.

X-ray wavelengths are characteristic of the element being bombarded, and an x-ray fluorescence spectrum can be used to identify elements in a sample.

# X-Ray Fluorescence - Minerals and Materials

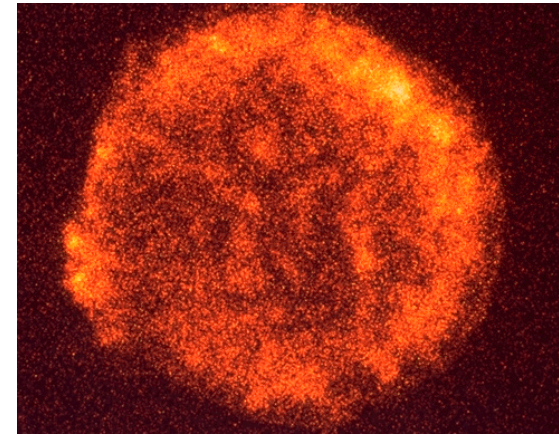
The x-ray  $K$  emissions arise from  $2p \rightarrow 1s$  transitions, and these are enough to identify elements in minerals that cannot be vapourised. The energy of these transitions increases with  $Z^2$  (as demonstrated by Moseley). For H this series is in the UV, and for heavier elements it moves into the x-ray range.

Core (1s) ionization that leads to x-ray fluorescence can be generated by UV excitation at low  $Z$ , electron or x-ray bombardment for intermediate  $Z$ , and  $\gamma$ -radiation for heavier elements.

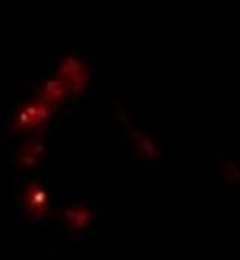


# Astrochemistry - X-ray spectroscopy of the Universe

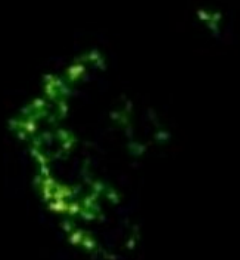
X-ray fluorescence is used to identify elements in stars, galaxies, and other features by their characteristic wavelengths. The supernova Tycho, observed in 1572, exhibits a broad x-ray spectrum as shown at right.



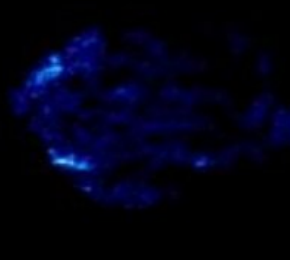
Resolving the x-ray spectrum into its characteristic wavelengths, it is possible to map the distribution of various elements around the supernova remnant. Some representative elements identified in this way are shown below.



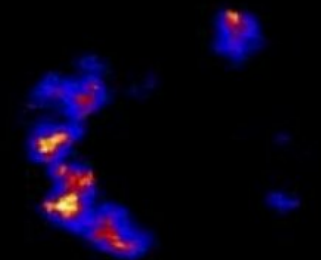
Calcium



Sulphur



Silicon



Iron

# “White” Light Sources

White, incandescent, or broad-spectrum sources seem to emit a continuum of wavelengths quite unlike the discrete lines seen in atomic spectra. (In fact these are due to different kinds of quantum states that we will encounter later, and that are so closely spaced that the spectrum seems continuous.)

These emissions are known as thermal radiation; we are familiar with this idea from terms like “red hot” and “white hot.”

Thermal energy is characterised by the temperature in absolute units (Kelvin or K), multiplied by the Boltzmann constant,  $k_B$ . The maximum intensity in a thermal spectrum is *approximately* at a transition energy  $\Delta E = 4.5k_B T$ , or

$$4.5k_B T \approx \frac{hc}{\lambda}$$

$$T \text{ (K)} = T \text{ (}^\circ\text{C)} + 273.15$$

$$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

## Worked Example: What is the energy range corresponding to visible light (in J and eV)?

To emit a photon in the visible range of wavelengths, a source must have **two states whose energies are separated by** at least

$$\begin{aligned}\Delta E &= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{750 \times 10^{-9}} = 2.65 \times 10^{-19} \text{ J} \\ &= \frac{2.65 \times 10^{-19}}{1.602 \times 10^{-19}} = 1.65 \text{ eV}\end{aligned}$$

...and not separated by more than

$$\begin{aligned}\Delta E &= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{400 \times 10^{-9}} = 4.97 \times 10^{-19} \text{ J} \\ &= \frac{4.97 \times 10^{-19}}{1.602 \times 10^{-19}} = 3.10 \text{ eV}\end{aligned}$$

**This range of energies is typical of the quantum states of bound electrons, and particularly of outer shell and valence electrons involved in bonding.**

# Absorbance, Colour and Transparency of Materials

**Transparent materials** absorb no light in the visible wavelength range, and hence have no energy states separated by between 1.65 and 3.10eV.

E.g. SiO<sub>2</sub> (glass, quartz); C (diamond); H<sub>2</sub>O; poly(methyl methacrylate) (perspex); poly(ethylene terephthalate) (PET)

**Metals are opaque.** They absorb light in all the visible wavelength range, and hence have many energy states separated by between 1.65 and 3.10eV.

- C(graphite) also absorbs light at all wavelengths, but is black and not reflective like a metal.
- Some metals (Cu, Au...) are coloured as well as reflective.

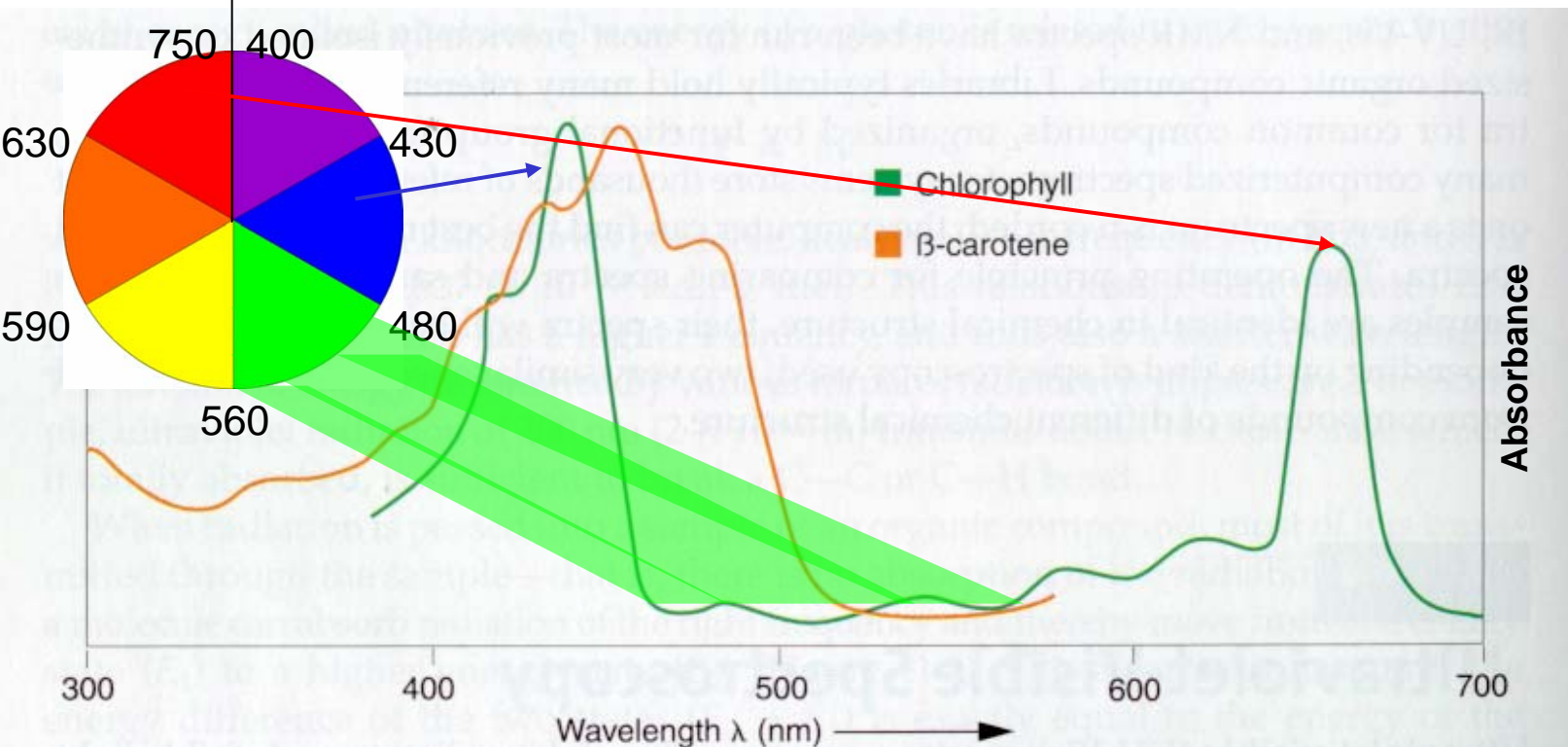
See Lecture 13

**Dyes, ceramics, pigments, gems (ruby, emerald)** and many other materials may be coloured because they absorb some of the wavelengths in the visible range.

# Absorbance by Molecules: Chlorophyll A

Chlorophyll A is the molecule responsible for the colour green in leaves.

It absorbs light in the blue (400-430 nm) and red (650-680 nm) ranges. A solution of chlorophyll A is transparent, and **transmits green**. Leaves, crystals or other solid material containing chlorophyll A **reflect** the unabsorbed green light.

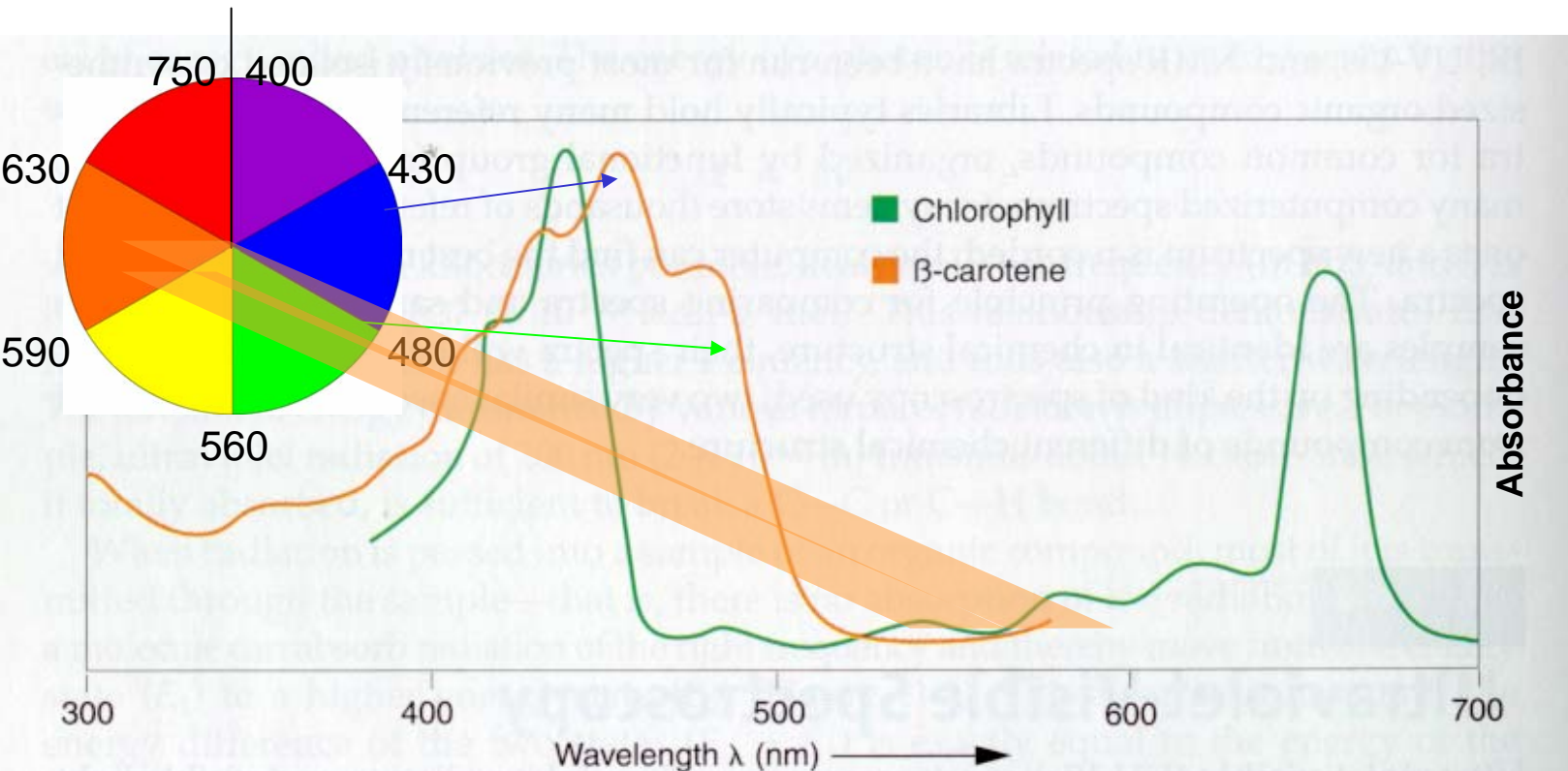




# Absorbance by Molecules: Carotene

Carotene is the molecule responsible for the colour orange in carrots.

It absorbs light in the blue (400-430 nm) and green (430-500 nm) ranges. Carotene transmits or reflects longer wavelengths, and appears orange.



# UV Absorbance - Sunscreens

While not important for colour, absorbance in the ultraviolet range has other significance. UV is higher energy light, and UV absorbance can lead to *photochemical reactions* and the formation of highly reactive free radicals. As with ionizing radiation these can lead to cell damage and (skin) cancer.

Sunscreens contain a mixture of compounds that absorb UV light from the solar spectrum.

UV-A (320-400 nm) and UV-B (280-320 nm), UV-C (<280 nm).

Longest wavelength range abutting the visible (violet) end of the spectrum.

Sunscreens seek to block this region of the spectrum.  
UV-B levels are sensitive to ozone concentrations in the upper atmosphere.

Most energetic photons. Little solar UV-C reaches the surface of the Earth as it is absorbed in the atmosphere.

# Electronic Absorbance Spectra.

Absorption spectra in the visible, UV and x-ray wavelengths are used to gain information about the *electronic quantum states* of materials.

It is only recently that extensive quantum calculations have become readily available on desktop computers. Many aspects are still being developed, so that theory and experiment are used in tandem.

**Theoretical modeling.** We can use quantum theory to predict the allowed energy states and energy differences, and then use this to *design materials* with particular optical characteristics: transparency and colour.

**Measurement of electronic properties.** Using quantum theory we can take measurements of absorbance wavelengths (i.e.  $\Delta E$ ), and use these to determine the electronic structure and the bonding in stable molecules and ions, or in transient (short-lived) reactive species.

# Summary

You should now be able to

- Explain the difference between core and valence electrons.
- Distinguish between absorbance and emission spectra.
- Explain how AAS works
- Convert experimental data between transmission, absorbance, and concentration if given appropriate information.
- Calculate the minimum wavelength of bremsstrahlung radiation.
- Explain how the elements in stars and other celestial objects can be identified and their abundances measured from visible and x-ray spectrometry.
- Relate wavelength of a photon to energy difference.
- Describe the qualitative differences between atomic and molecular electronic spectra