Lecture 10: Atomic Spectroscopy with visible and x-ray light

Lecture 11: Electronic Structure and Properties of Compounds
  • Colour
  • Conductivity
  • Magnetic Character

Lecture 12: Quantum Theory of Bonding
  • Bonding in $\text{H}_2$
Where Does Colour Come From?

Colour is a subjective description of light in the visible wavelength range, 400-750nm.

We identify pure colours according to their place in that wavelength range, but our brains register and interpret colour in two ways.

1. As a direct or pure colour, which arises when a single wavelength or narrow band of wavelengths is detected.

2. As a complementary colour. When a single colour is missing from white light, then our brain interprets the rest as its complementary colour. This is the colour opposite the missing one on the colour wheel (shown above). E.g. If blue is missing from a white light source, then our brain perceives orange.
Absorption and Emission

A material may be coloured because it emits light of a particular wavelength or range of wavelengths. To emit, the material must jump from a higher (excited) to a lower energy state, so it must have been excited by an external energy source in the first place.

Excitation can have a number of causes, e.g.

- **Heat**
  - An incandescent light bulb (3000 K)
  - A flame (1000 K)
  - A star (sun, 6000 K)

- **Electrical Discharge**
  - An x-ray (Bremsstrahlung) generator
  - A neon sign.

- **Light**
  - A laser.
  - A fluorescent dye.
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

$$\Delta E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{750 \times 10^{-9}} = 2.65 \times 10^{-19} \text{ J}$$

$$= \frac{2.65 \times 10^{-19}}{1.602 \times 10^{-19}} = 1.65 \text{ eV}$$

...and not separated by more than

$$\Delta E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{400 \times 10^{-9}} = 4.97 \times 10^{-19} \text{ J}$$

$$= \frac{4.97 \times 10^{-19}}{1.602 \times 10^{-19}} = 3.10 \text{ eV}$$

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

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

$$T \,(K) = T(°C) + 273.15$$

$$k_B = 1.381 \times 10^{-23} \, J \, K^{-1}$$
“White” Light Sources: Worked Examples

1. Estimate the most intense wavelength emitted by the continuous spectrum of the sun \((T=6000K)\)

\[
\lambda \, \Delta \, \frac{hc}{4.5k_B T} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{4.5 \times 1.381 \times 10^{-23} \times 6000}
\]

\[
= 530 \times 10^{-9} \, m = 530 \, nm = 5300 \, \AA
\]

2. Estimate the most intense wavelength emitted by an electric light bulb \((T=3000K)\)

\[
\lambda \, \Delta \, \frac{hc}{4.5k_B T} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{4.5 \times 1.381 \times 10^{-23} \times 3000}
\]

\[
= 1100 \times 10^{-9} \, m = 1100 \, nm = 11000 \, \AA
\]
Atomic Absorption and Emission Spectra

In atomic systems we recognise flame colours because they are pure emissions of a discrete wavelength (colour), *even though only very few atoms emit.*

However we do not *see* colour due to atomic absorbance because only very few discrete wavelengths are *missing* from the white spectrum.

Even stars look white to us, although they also have many wavelengths missing due to atomic absorption lines. (e.g. Arcturus A or the sun [Lecture 9])
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. SiO₂ (glass, quartz); C (diamond); H₂O; 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.

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

See Lecture 13
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.
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.
Absorbance of SiO$_2$

Glass absorbs in the UV below about 350 nm, as shown in the *transmission* experiment below. Perspex plastic begins absorbing at slightly higher wavelengths, but both are transparent across the visible range.

Quartz is transparent to UV light down to around 200nm.
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.
Electrical Conductivity of Materials

Electrical conductivity is sensitive to the mobility of charge when a sample is placed in an electric circuit. It is related to current, \( I \), and voltage, \( V \), in a circuit through Ohm’s Law

\[ V = IR \]

where \( R \) is the resistance in the circuit. Conductivity, \( \kappa = k/R \), where \( k \) is cell constant describing the shape of the resistor. Where resistance depends on the shape of a material, conductivity can be used to compare materials with each other directly.

1. Ionic Conductivity. This is important in ionic solutions and molten electrolytes. Mobile ions act as charge carriers between electrodes. In solids the ions are fixed in place, so ionic solids are non-conducting.

2. Electron Conductivity. This is important in metals and semiconductors, including conducting polymers, and novel “molecular wires.” In such materials electrons may not be bound to individual nuclei, and can act as charge carriers in both the solid and liquid states.

See Lecture 13
Conductors and Insulators

Conductivities can vary by a huge amount between materials. The Table below gives an indication of the range of conductivities for materials at 20°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (ohm(^{-1}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (metal)</td>
<td>5.9 x 10(^5)</td>
</tr>
<tr>
<td>Ag (metal)</td>
<td>6.3 x 10(^5)</td>
</tr>
<tr>
<td>Pb (metal)</td>
<td>4.6 x 10(^4)</td>
</tr>
<tr>
<td>Ge (semiconductor)</td>
<td>1</td>
</tr>
<tr>
<td>SiO(_2) (insulator)</td>
<td>10(^{-12})</td>
</tr>
</tbody>
</table>

Very sensitive to impurities.
Graphite and Diamond

Graphite and Diamond are *allotropes* of carbon. That is, two different crystalline or molecular forms of the same substance.

Graphite and diamond differ in the nature of their bonding (electronic structure), which significantly affects many of their properties.

<table>
<thead>
<tr>
<th></th>
<th>Graphite</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>black &amp; opaque</td>
<td>transparent and clear</td>
</tr>
<tr>
<td>Conductivity</td>
<td>highly conducting (along two directions)</td>
<td>insulator</td>
</tr>
<tr>
<td>Density</td>
<td>low density (2.27 g cm(^{-3}))</td>
<td>high density (3.51 g cm(^{-3}))</td>
</tr>
<tr>
<td>Melting point</td>
<td>melts at 4100K</td>
<td>melts at 4100K</td>
</tr>
<tr>
<td>Hardness</td>
<td>soft solid</td>
<td>hardest solid</td>
</tr>
</tbody>
</table>

The connection between strength or hardness and bonding includes many factors. We will examine these later after the models for bonding are finished.
Magnetism

Hund’s Rule for electrons in atoms tells us to maximise the number of parallel spins in degenerate orbitals of an atom. Why is this important?

Electron spin conveys magnetic character to a chemical species.

Atoms or compounds with unpaired spins are *paramagnetic*. They are attracted into a magnetic field.

Chemical species with paired spins are *diamagnetic*. They are unaffected or weakly repelled by a magnetic field.

These characteristics do not include a permanent magnetic moment, but only the response to an external magnetic field. [*Ferromagnetism* or the formation of permanent magnets is a property of concentrated systems and not individual atoms or molecules.]
Summary

You should now be able to

• Explain complementary colours
• Explain the origins of discrete and continuous spectra
• Relate wavelength of a photon to energy difference (again, or still).
• Describe the qualitative differences between atomic and molecular electronic spectra
• Define conductivity, paramagnetism and diamagnetism
• Recognise conductors and insulators by their conductivity.
• Define an allotrope.
• Know the difference between UV-A, -B, and -C radiation.

Next

We will build up a picture of bonding and molecular properties, beginning with the simplest molecule, H$_2$. 