

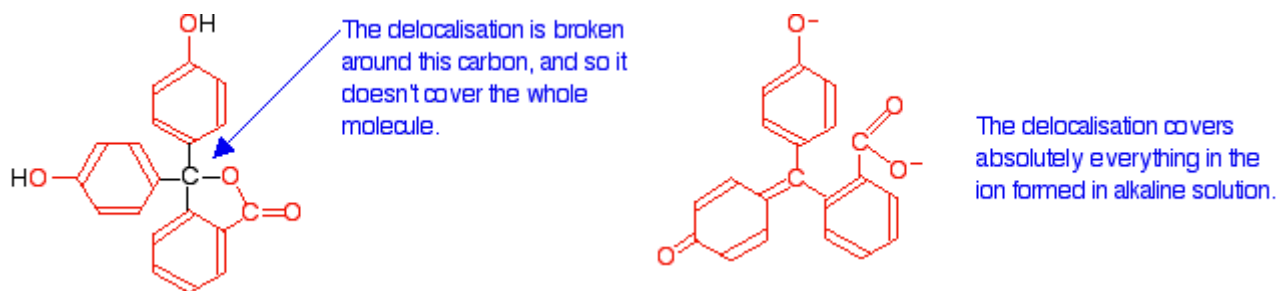
## Chemguide – answers

### UV-VISIBLE SPECTROSCOPY – SPECTRA

- From sigma bonding to sigma anti-bonding.
  - From sigma bonding to sigma anti-bonding. Energy is related to frequency by the equation  $E=h\nu$  and so the greater the energy jump, the higher the frequency.
  - This will be the smallest jump – from a non-bonding orbital to a pi anti-bonding orbital. The relationship between the wavelength and the frequency is  $\lambda=c/\nu$ . The smallest jump will be due to absorbing light of the smallest frequency, which corresponds to the highest wavelength.
  - These would be the result of absorbing the shortest wavelengths, and these lie in the UV outside the range normally measured by a UV/visible spectrometer.
  - This would be a jump from a pi bonding orbital into a pi non-bonding orbital. This is the shortest jump possible given the structure of the molecule, and therefore produces absorption at the greatest wavelength. Any other jumps would be caused by UV absorption out of the range of the spectrometer at less than 200 nm.
  - These are obviously the jumps producing absorption at the highest possible wavelengths, and therefore having the lowest possible energies. In this case, the lowest energy jump is from a non-bonding orbital (an oxygen lone pair) to a pi anti-bonding orbital and so that will produce the peak at 290 nm. The other peak at 180 nm will therefore be the one from the pi bonding orbital to the pi anti-bonding orbital.
- This is simply because the number of pi electrons increases from ethene to hexa-1,3,5-triene. In ethene you are creating a pi bond from two atomic orbitals, and must therefore produce two molecular orbitals – a pi bonding orbital, and a pi anti-bonding orbital. Both of the electrons will normally be in the bonding orbital. By the time you get to hexa-1,3,5-triene, six atomic orbitals are involved in creating the pi bonds, and therefore there have to be six molecular pi orbitals – three bonding and three anti-bonding. Again the electrons will normally all be found in the three bonding orbitals.
  - The energy diagram shows that as you go from ethene to hexa-1,3,5-triene, the gap between the highest occupied molecular orbital and the lowest unoccupied one is getting less. This is an effect of increasing delocalisation. The result is that the energy needed to promote an electron gets less, and so the wavelength absorbed gets longer.
- Beta-carotene is absorbing light mainly in the top end of the blue region, getting towards the cyan region. What you see can often be worked out using complementary colours. The complementary colour to blue is yellow, and the complementary colour of cyan is red. It would therefore seem reasonable that the complementary colour of those being absorbed might be seen as orange.

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4. a) Taking the corresponding diagrams from the Chemguide page:



b) More delocalisation shifts the absorption from a lower to a higher wavelength. The colourless form of the phenolphthalein doesn't absorb in the visible region because the delocalisation is broken up into smaller bits. The magenta form is absorbing in the visible region because the delocalisation covers the whole structure. Magenta is the complementary colour of cyan, and so this form must be absorbing in the cyan region of the spectrum from 500 – 520 nm (from the table in an earlier question).

c) (i) The absorption peak at 440 nm is in the blue region of the spectrum, and so the observed appearance will be the complementary colour to blue - which is yellow. The absorption peak at 520 nm is in the cyan region of the spectrum, and its complementary colour is red.

(ii) The one with the higher absorption wavelength has the greater amount of delocalisation – in this case, the red form.