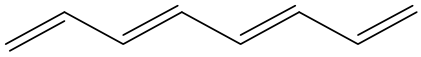
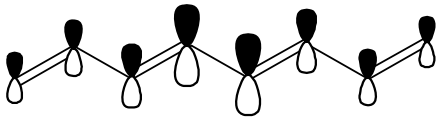
Question 16 20 marks

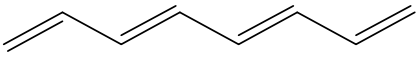
The energy levels of the π orbitals of a polyene such as octatetraene, pictured below, can be approximated to those of a particle in a one-dimensional box whose length is equal to the sum of the bonds in the conjugated system.



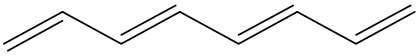
a) Draw the second and third lowest-energy wavefunctions for octatetraene, showing the position of any nodes relative to the position of the carbon atoms in the molecule. The lowest energy wavefunction is drawn for you. (3 marks)



$n = 1$



$n = 2$



$n = 3$

b) What is the wavelength for $n = 2$ electrons, if the π-electrons are modelled as a particle inside a one-dimensional box of length L? (1 mark)

c) What is the wavelength for $n = 3$ electrons, if the π-electrons are modelled as a particle inside a one-dimensional box of length L? (1 mark)

d) What is the general formula for the wavelength of the electrons with quantum number n, if the π-electrons are modelled as a particle inside a one-dimensional box of length L. (1 mark)

Question continues on next page.

e) How many π-electrons are there in octatetraene, and therefore, what is the quantum number, n_{HOMO}, of the highest occupied molecular orbital, if the π-electrons are modelled as a particle inside a one-dimensional box? (2 marks)

f) If each C-C bond is 0.139 nm in length, what is the length of the box for octatetraene? (2 marks)

g) Noting that $E = p^2/2m$, for a particle with no potential energy, use de Broglie's equation, $p = mv = h/\lambda$, to show that the separation between adjacent energy levels (n, n+1) for a particle inside a one-dimensional box of length L and infinitely high sides is given by:

$$\Delta E = \frac{h^2(2n+1)}{8mL^2}$$

(3 marks)

h) To what does the m in the above equation refer? What is its value in kg? (1 mark)

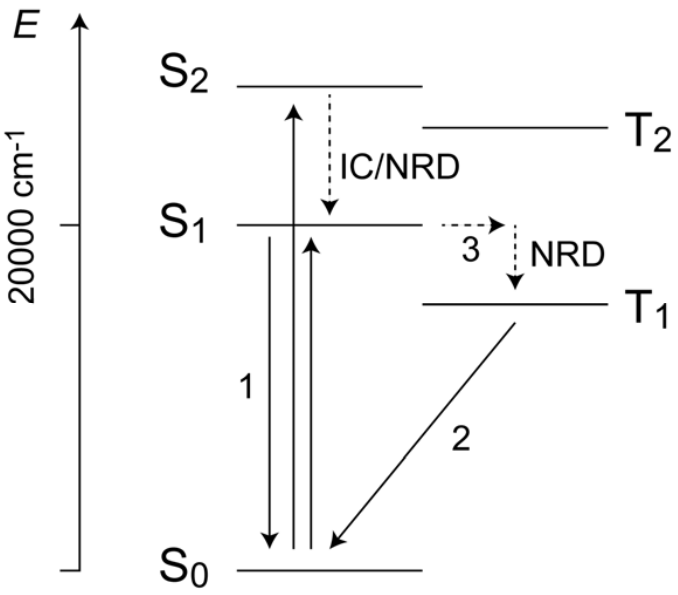
i) Calculate the energy of a photon emitted when an electron relaxes from the n_{HOMO}+1 level to the n_{HOMO} level in octatetraene. (2 marks)

Question continues on next page.

j) Predict what will happen to the energy of the equivalent transition as the length of the polyene increases. Explain your answer. (2 marks)

k) Taking the limit of infinite (~N_A carbons) chain length, within the particle-in-a-box model, do you expect the resulting material to be a conductor, insulator, or semiconductor? Explain your answer with reference to terminology used for the electronic structure of network solids such as silicon. (3 marks)

Question 17 24 marks



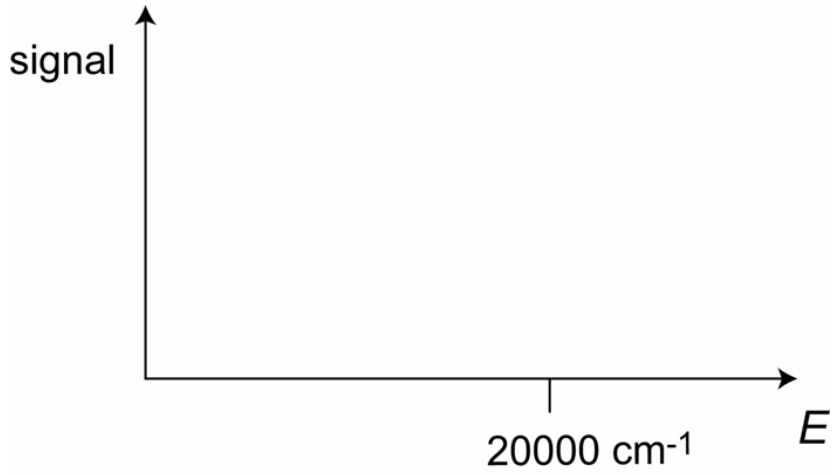
a) A generic Jablonski diagram is shown above for an organic dye molecule. If the process labelled as **1** is fluorescence, name processes **2** and **3**. (2 marks)

b) What do the abbreviations IC and NRD stand for? (2 marks)

c) What is the essential difference between processes marked with solid lines and dashed lines in the above diagram? (1 mark)

Question continues on next page.

d) On the diagram below, draw an absorption spectrum for the molecule, given that the $S_0 \rightarrow S_2$ transition occurs with twice the intensity as $S_0 \rightarrow S_1$. Both bands possess some vibrational structure. (4 marks)



e) Draw and clearly label the fluorescence spectrum on the same diagram. (2 marks)

f) Process **3** competes with process **1** to depopulate the S_1 state. If both rates are the same, and process **2** is 100% efficient, draw the spectrum of emitted light due to process **2** on the same diagram. Clearly label the spectrum either with a '**2**' or with its name. (3 marks)

g) What wavelength corresponds to 20000 cm^{-1}? (1 mark)

h) The S_1 state may be described principally as the result of the excitation of an electron from the HOMO to the LUMO. What do HOMO and LUMO stand for? (2 marks)

i) In the T_1 state, are the HOMO and LUMO electrons of the same or different spin? (Let $S_z = \pm 1$) (1 mark)

Question continues on next page.

j) What colour is this substance in transmitted light? (1 mark)

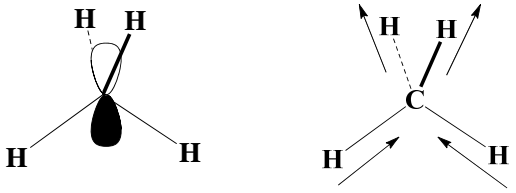
k) An experiment is performed which shows that blue light is emitted for about 500 femtoseconds following excitation of the molecule with 300 nm light. Explain this phenomenon. (2 marks)

l) Subsequently, green light is emitted with a 20 nanosecond lifetime, followed by dull red luminescence with a 10 microsecond lifetime. Explain these phenomena. (3 marks)

Question 18 22 marks

The infrared spectrum of $CH_4(g)$ contains a single strong band in the C-H stretching region, at 3020 cm^{-1}. The Raman spectrum shows a band at 2914 cm^{-1}.

The form of the vibrational modes can be obtained using their relationship to the atomic orbitals on the central atom. The example below illustrates this relationship using one of the stretching modes and one of the carbon *p*-orbitals.



a) Sketch the form of the remaining stretching modes for methane. (3 marks)

b) Three of the stretching modes have the same vibrational frequency. Clearly identify these vibrations above and briefly explain why this occurs. (2 marks)

Question continues on next page.

c) Identify which of the vibrational mode(s) corresponds to the infrared band at 3020 cm^{-1} and which mode(s) correspond to the Raman band at 2914 cm^{-1}. Briefly explain your assignment. (3 marks)

d) Briefly explain why there is only one band in the C-H region of the infrared spectrum, even though there are four C-H bonds in methane. (2 marks)

e) For a harmonic oscillator, the wavenumber, $\bar{\nu}$, is given by the equation below.

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Does the band in the Raman spectrum of deuterated methane, CD_4 occur at higher or lower wavenumber than that in the spectrum of CH_4? Briefly explain your answer. (2 marks)

Question continues on next page.

f) Use this equation to predict the wavenumber for the band in the Raman spectrum of CD_4. (3 marks)

g) The first and second overtones of the infrared active mode occur at 6006 and 9047 cm^{-1}. Using a suitable energy level diagram, explain the origin of these transitions and qualitatively account for their energies. (4 marks)

Question continues on next page.

h) The main constituents of the atmosphere of the gas planet Uranus are methane, hydrogen and helium. The blue colour of this planet is thought to be due to methane. Explain how this colour arises and why the other atmospheric gases are not thought to contribute. (4 marks)