IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2010, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

ADVANCED CHEMISTRY THEORY IIIA

Physical Chemistry

Monday 11th January 2010, 09:00-12:00

Answer ONE question from each attended course

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

3.P1 – Modern Analytical Techniques

Answer any **TWO** of the three parts a), b) and c)

a) Answer **ALL** parts of this question.

   i)   Derive an equation for FRET efficiency (E) only in terms of the fluorescence lifetime of the donor (τ_d) and fluorescent lifetime of the donor in the presence of the acceptor (τ_{da}).

(5 marks)

ii)   A single strand of DNA has been internally modified to contain both a donor and acceptor. The free donor dye has a lifetime of 4 ns and the lifetime of the donor in the presence of acceptor is 2 ns. If the Forster radius for this dye combination is 5 nm, what is the distance between the donor and the acceptor?

(3.5 marks)

iii)   In point form, describe what makes a good FRET pair. Use a diagram if necessary.

(4 marks)

b) Answer **ALL** parts of this question.

i)   What is a virtual state in Raman spectroscopy?

(2 marks)

ii)   Use an energy level diagram to illustrate the virtual state and how Stokes and anti-Stokes lines are generated.

(3.5 marks)

iii)   If a laser of 647 nm is used as the excitation source, and ΔE of the vibrational energy level is 421 cm^{-1}, calculate the Rayleigh and Raman lines in both wavelength and wavenumbers. Assume there is only one vibrational state above the ground state.

(4 marks)

iv)   The same sample as in iii) is excited with a 488 nm laser instead of a 647 nm laser. Which excitation source will result in a larger wavelength shift of the 421 cm^{-1} energy level?

(3 marks)

c) Answer **ALL** parts of this question.

i)   Draw a generalized block diagram of a mass spectrometer, and indicate which components should be contained in a vacuum. Briefly explain the function of each component.

(5 marks)

ii)   In a magnetic sector mass analyzer, the kinetic energy, KE, is given by: $KE = zeV = 0.5mv^2$. The magnetic force, F_m and the balancing centripetal force, F_c, are given by $F_m = Bzev$ and $F_c = mv^2/r$ respectively. What parameters can be changed to allow different ions to go through the magnetic sector analyzer? Briefly explain.

(4.5 marks)

iii)   Name two other different types of mass analyzer and name at least one advantage and disadvantage for each.

(3 marks)

3.P2 – Quantum Chemistry Part 2

UNLESS OTHERWISE STATED YOU MAY OMIT NORMALISATION CONSTANTS IN YOUR ANSWER TO THIS QUESTION.

Answer part a) and **EITHER** b) **OR** c)

a)   Answer **ALL** parts of this question.

   i)   Explain briefly what is meant by the pi electron approximation for conjugated systems.

   (4 marks)

   ii)   State the Hückel approximations, defining clearly in your answer the symbols α and β.

   (4 marks)

   iii)   Write down the secular determinant for butadiene in the Hückel approximation in terms of α and β, and hence obtain the orbital energies. You may wish to use the result:

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} \cong (x - 0.618)(x + 0.618)(x - 1.618)(x + 1.618)$$

   (4 marks)

   iv)   Calculate the stabilisation energy per electron for butadiene and hence comment whether you would expect it to be more or less reactive than ethene.

   (3 marks)

QUESTION CONTINUED OVERLEAF

b)   Answer **ALL** parts of this question.

      i)   Using a minimal basis set, write down an approximate expression for the $1\sigma_g$ ground state molecular orbital of H_2^+.

                                                      (1 mark)

      ii)   Using the independent electron model, write down the ground-state wave function of H_2 in terms of the $1\sigma_g$ molecular orbital of H_2^+ and the spin wave functions α and β. Comment on the symmetry of the spin and space terms and the overall symmetry of the wavefunction.

                                                        (3 marks)

      iii)   Using your expression for $1\sigma_g$ from b i), show that the space part of the H_2 ground-state wavefunction may be written as a linear combination of ionic and covalent terms. Comment upon whether this molecular orbital wavefunction is a good description of a real H_2 molecule.

                                                        (4 marks)

      iv)   List two ways in which you could modify the LCAO expression to obtain a better approximation to the true molecular orbital for ground-state hydrogen.

                                                        (2 marks)

c) Answer **ALL** parts of this question.

      i)   Sketch the energy level diagram for O_2 and hence explain why molecular oxygen is paramagnetic. Label each energy level fully.

                                                          (5 marks)

      ii)   Why is the $3\sigma_g - 3\sigma_u$ splitting larger than the $1\pi_g - 1\pi_u$ splitting?

                                                           (2 marks)

      iii)   Why is the ordering of the orbital energies different for diatomic molecules formed from smaller atoms? What important implication does this have for B_2?

                                                          (3 marks)

3.P9 – Photochemistry

Answer part (a) **AND EITHER** part (b) **OR** part (c)

a) Answer **ALL** parts of this question.

i) The observed fluorescence lifetime for a given chromophore is 500 picoseconds. The fluorescence quantum yield is 0.4. Determine the natural radiative lifetime of the chromophore.

(2 marks)

ii) How many photons are there in a light pulse of energy 5 mJ at a wavelength of 600 nm?

(2 marks)

iii) With the aid of a suitable diagram define the terms singlet and triplet states, internal conversion, intersystem crossing, fluorescence and phosphorescence.

(6 marks)

iv) Explain why emission spectra from molecules in solution are red shifted relative to their corresponding absorption spectra.

(3 marks)

b) Answer the following question

i) With reference to suitable diagrams and equations, describe the Förster energy transfer mechanism.

(6 marks)

ii) The following data was obtained for a family of compounds with the general composition A-(bridge)-B in which the distance R between A and B was varied by increasing the length of the bridge. E_T refers to the efficiency of energy transfer.

R / nm	1	1.5	2	2.5	3	3.5	4	4.5
E_T	0.99	0.96	0.92	0.87	0.74	0.55	0.3	0.18

Show that these data are consistent with Forster theory and determine R_o for the A-B pair.

(3 marks)

iii) With the aid of a suitable diagram and equation explain how the rate of electron transfer depends on the spatial separation between an electron donor / acceptor pair.

(3 marks)

c) Answer **ALL** parts of this question

i) Explain why bimolecular photochemistry normally originates from triplet states rather than singlet states.

(3 marks)

ii) Give the equation for Fermi's Golden Rule, defining all terms used.

(3 marks)

iii) The rate of electron transfer is given by the following equation:

$$k_{elec} \propto e^{(-\beta r)} \times e^{\left(\frac{-(\Delta G^{\circ} + \lambda)^2}{4\lambda k_b T}\right)}$$

With the aid of a suitable diagram explain the physical meaning of the terms ΔG and λ in the above equation.

(6 marks)