**Question 15**          **14 marks**
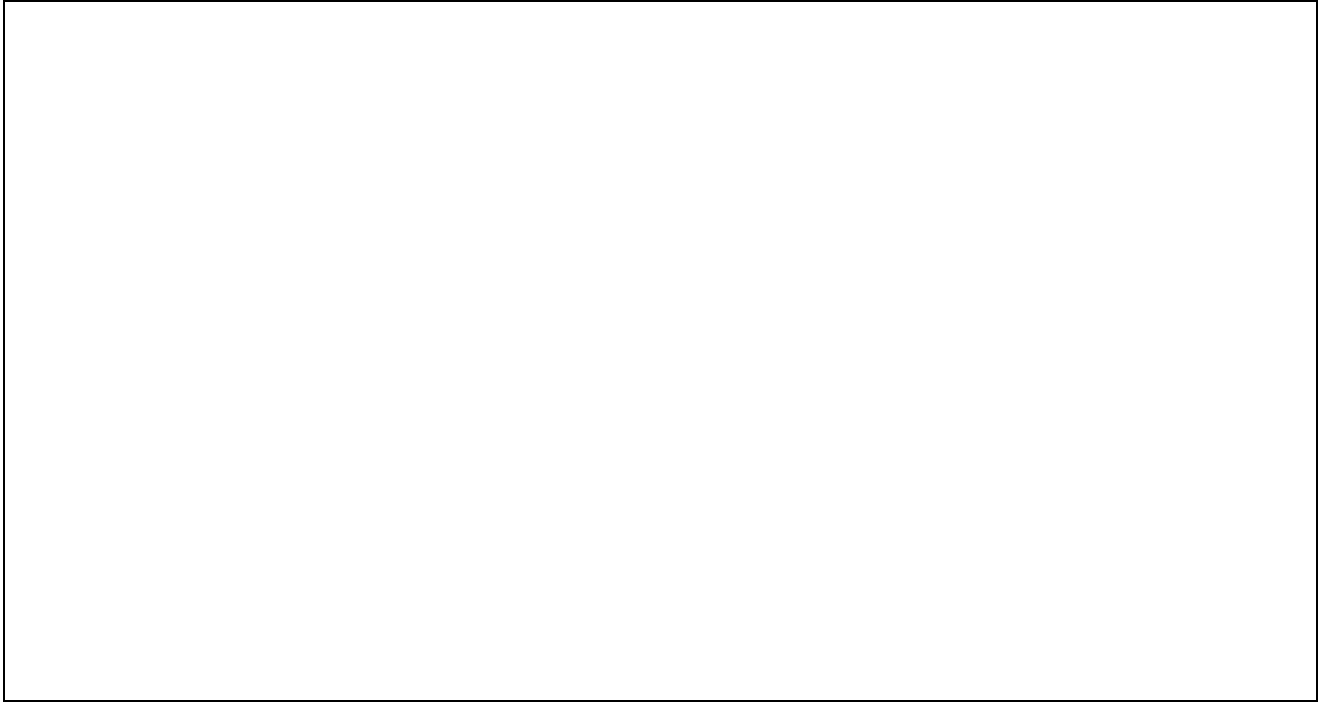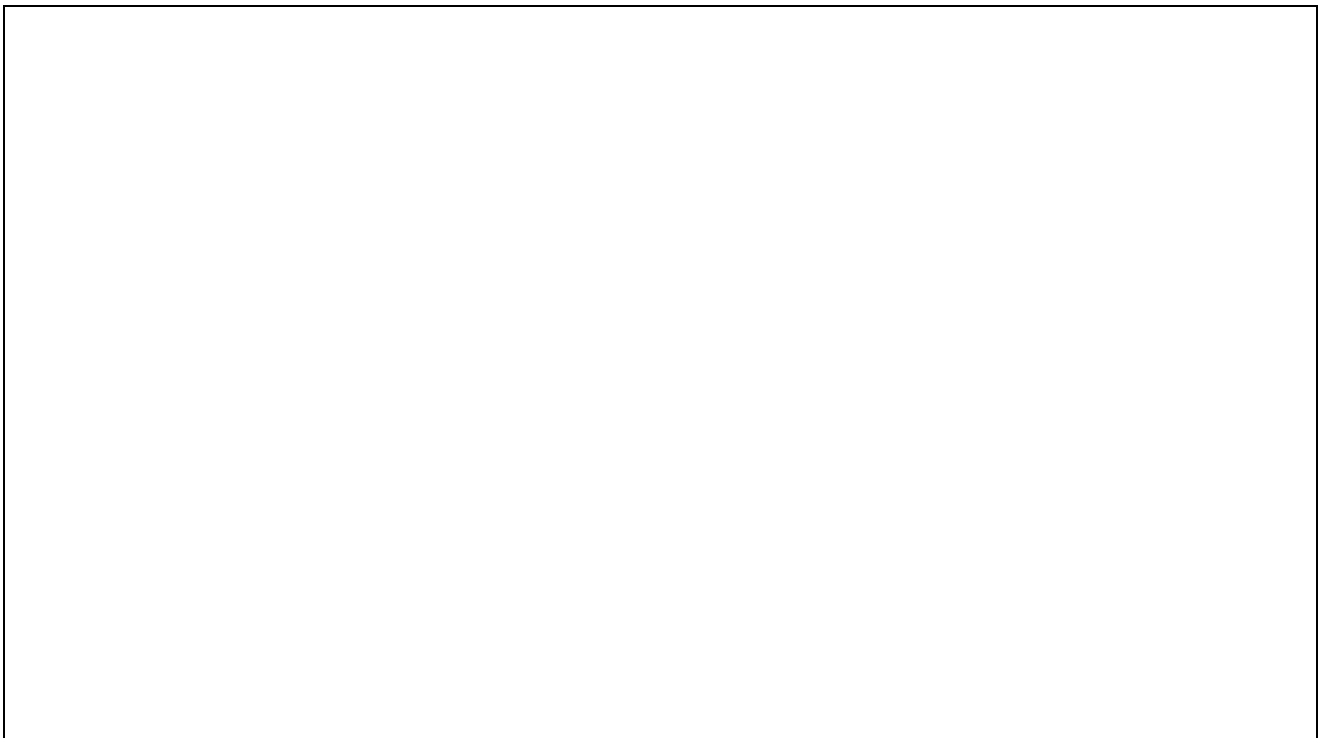
(a)      Use de Broglie's equation, $p = mv = h/\lambda$, to show that the energy levels of a particle inside a one-dimensional box of length $L$ and infinitely high sides are given by:
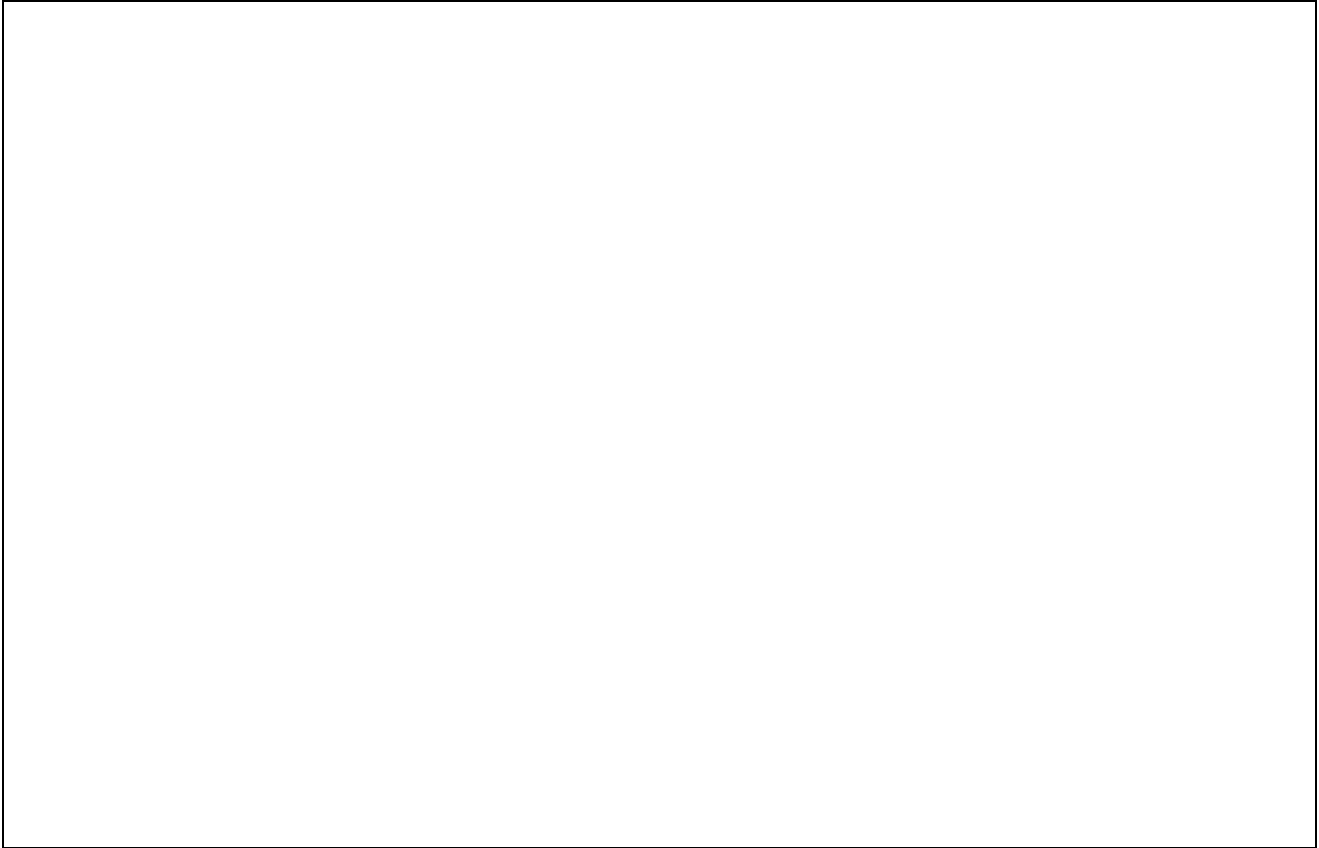
$$E_n = \frac{h^2 n^2}{8mL^2}$$

(4 marks)

(b)      Draw the corresponding wavefunctions and probability densities for $n = 1 - 3$. Mark the positions of the nodes for each function. (3 marks)

(c)    Explain why (i) the energy levels of a particle in a box are quantized but the energy levels of a free particle are not and (ii) the lowest possible energy for a particle in a box is not zero. (4 marks)
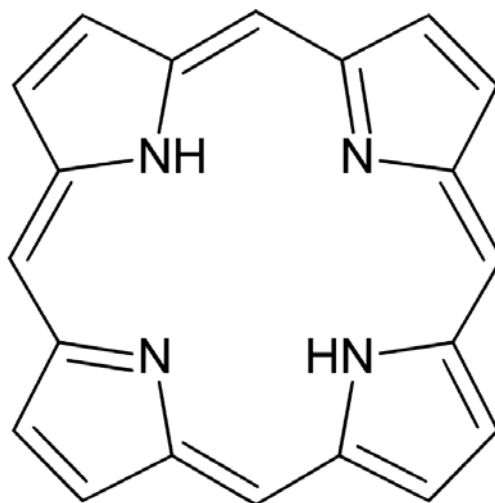
**Question 15 (continued)**

(d)    By considering the effect of large *n* and *L* for a particle in a box, discuss how the classical and quantum mechanical pictures can be reconciled. (3 marks)

**Question 16**            **27 marks**

Porphyrins are naturally occurring chromophores featuring a highly conjugated $\pi$-system. The simplest porphyrin structure is porphin (pictured).



(a)    *Shade* the pathway of unhybridized p-orbitals in porphin (all nitrogens are $sp^2$). (2 marks)

(b)    How many $\pi$ electrons are there in porphin? (2 marks)

(c)    Despite the Hückel $4n+2$ rule strictly applying to monocyclic systems, in each resonance form there is a path around the molecule which follows alternating single and double bonds. How many bonds comprise this path and how many $\pi$ electrons are *along this path*? Does this path obey the Hückel rule? (4 marks)

**Question 16 (continued)**

(d)    Approximating porphin as the cyclic system from (c), the allowed energy levels form
        degenerate pairs. Fill the following electronic energy diagram with $\pi$ electrons. (2 marks)

$$\underline{\qquad} \quad \underline{\qquad} \quad j = 7$$

$$\underline{\qquad} \quad \underline{\qquad} \quad j = 6$$

$$\underline{\qquad} \quad \underline{\qquad} \quad j = 5$$

$$\underline{\qquad} \quad \underline{\qquad} \quad j = 4$$

$$\underline{\qquad} \quad \underline{\qquad} \quad j = 3$$

$$\underline{\qquad} \quad \underline{\qquad} \quad j = 2$$

$$\underline{\qquad} \quad \underline{\qquad} \quad j = 1$$

$$\underline{\qquad} \quad j = 0$$
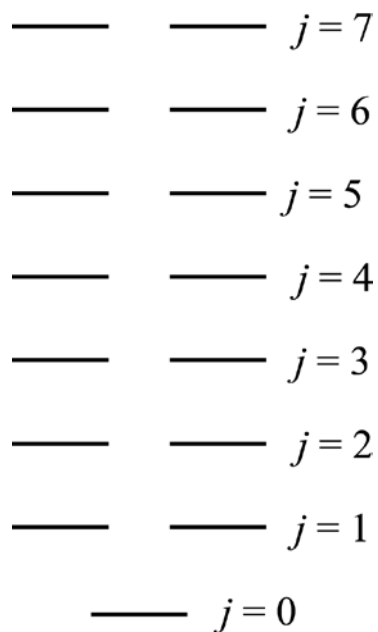
(e)    What are the $j$ quantum numbers for the HOMO and LUMO? (2 marks)

**Question 16 (continued)**

(f)     From molecular orbital theory, the energy levels are given by:

$$\varepsilon_j = \alpha + 2\beta \cos\left(\frac{2\pi j}{N}\right).$$

If benzene absorbs at 260 nm, with a transition of $-2\beta$ magnitude, calculate where porphin is expected to absorb given the above approximations. (4 marks)
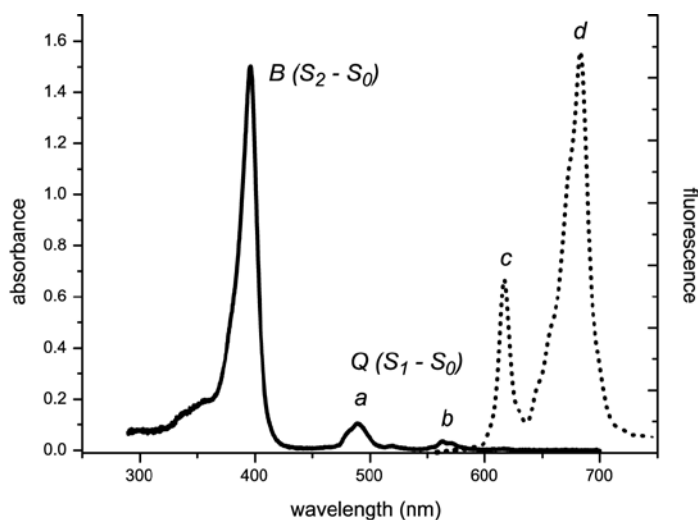


**Fig.** The absorption spectrum of porphin (solid line), and the fluorescence spectrum obtained by 396nm excitation (dashed line). Both peaks *a* and *b* belong to the Q band ($S_1$-$S_0$).

(g)     Experimental porphin spectra are shown above. Comment on how your prediction compares to the lowest absorptions of porphin? (2 marks)

**Question 16 (continued)**

(h)     Experimentally, the HOMO-LUMO transitions give rise to two distinct band systems. The higher energy one is known as the Soret, or *B* band, and the lower energy one is known as the *Q* band. These are evident in the absorption spectrum. With the aid of a Jablonski diagram, explain how absorption in the *B* band yields fluorescence consistent with population with the upper state of the *Q* band system. Name all processes involved. (4 marks)

(i)     The fluorescence yield of porphin is only 0.043. Explain possible processes which may explain non-unity fluorescence yield. (2 marks)

**Question 16 (continued)**

(j)     Peaks *b* and *c*, as indicated, correspond to transitions between the ground vibrational levels in $S_1$ and $S_0$, with the small Stokes shift being due to solvent reorganization. With the aid of diagrams, and invoking the Franck-Condon principle, explain why bands *a* and *d* appear more intense than *b* and *c*. (3 marks)
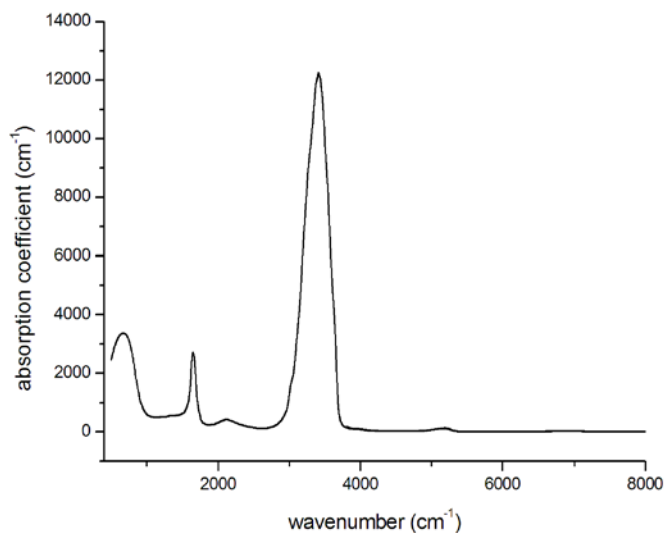
**Question 17                15 marks**

The vibrational absorption spectrum of liquid water extends from the infrared into the visible region. The spectrum of the liquid is largely explained by that of the water monomer, albeit in a hydrogen-bonded environment. The water molecule (in water) has three vibrational modes:

| mode | frequency | description |
|------|-----------|-------------|
| $v_1$ | 3277 | symmetric stretch |
| $v_2$ | 1645 | bend |
| $v_3$ | 3490 | asymmetric stretch |

Additionally, there are *librations* – vibrations of the entire framework of $H_2O$ about its equilibrium position in the liquid environment. Important librations occur at 396 cm$^{-1}$ and 686 cm$^{-1}$.

(a)     The highly heterogeneous environment causes the symmetric and antisymmetric O-H stretches to blend into one feature, while the bend remains distinct. Indicate these features as $v_1/v_3$ and $v_2$ on the following spectrum. (2 marks)

**Question 17 (continued)**

The smaller features are much more easily shown using a logarithmic absorption axis. The following spectrum extends into the visible region.
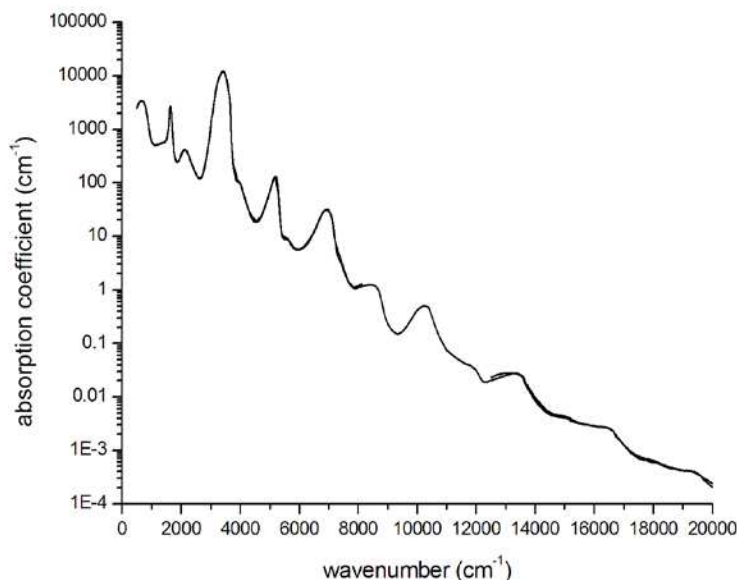
(b)      Indicate on this spectrum the onset of visible light (700 nm). (2 marks)

(c)      The following table assigns the observed vibrational absorption features of liquid water, noting that multiple quanta of $v_1$ and $v_3$ are not resolved, and simply denoted $v_S$. There are five features left unassigned. Write assignments for these features in the table, using the assigned features as a guide. (5 marks)

| Assignment of the IR vibrational absorption spectrum of liquid water | | | | | |
|---|---|---|---|---|---|
| **Wavelength** | **cm$^{-1}$** | **Assignment** | **Wavelength** | **cm$^{-1}$** | **Assignment** |
| 0.2 mm | 50 | intermolecular bend | 1470 nm | 6800 | $2v_S$ |
| 55 μm | 183.4 | intermolecular stretch | 1200 nm | 8330 | $2v_S + v_2$ |
| 25 μm | 395.5 | $L_1$, librations | 970 nm | 10310 |  |
| 15 μm | 686.3 | $L_2$, librations | 836 nm | 11960 |  |
| 6.08 μm | 1645 | $v_2$, bend | 739 nm | 13530 |  |
| 4.65 μm | 2150 | $v_2 + L_2$ | 660 nm | 15150 |  |
| 3.05 μm | 3277 | $v_1$, symmetric stretch | 606 nm | 16500 |  |
| 2.87 μm | 3490 | $v_3$, asymmetric stretch | 514 nm | 19460 | $6v_S$ |
| 1900 nm | 5260 | $v_S + v_2$ | | | |

**Question 17 (continued)**

(d)    It turns out that, if one looks at white light through a long pathlength of pure water, one perceives a blue coloration. What is responsible for this blue colour? (2 marks)

(e)    Using that data in the above table, calculate effective spectroscopic constants, $\omega_e$ and $\omega_e x_e$, for the OH stretching motion for water (in water). Use the average of the symmetric and antisymmetric stretches, (3277+3490)/2, as the fundamental anharmonic frequency. (4 marks)

**Question 18**          **12 marks**

The vibrational spectrum of a triatomic molecule $XY_2$ contains three strong bands. Two bands, at 667.3 and 2349.3 cm$^{-1}$, are only observed in its IR spectrum. The third band, at 1340 cm$^{-1}$, is only observed in its Raman spectrum.

(a)     Is $XY_2$ a linear or bent molecule? Briefly explain your answer including an explanation for the observation of *only* three bands. (2 marks)

(b)     Assign, with explanation, the observed bands to the symmetric and antisymmetric stretches and the bending vibration of the molecule. (2 marks)

(c)     For each of these vibrations, explain why they are IR or Raman active or inactive. (4 marks)

**Question 18 (continued)**

(d)     The molecule $N_2O$ is linear with the form NNO. Predict the number of bands in its IR and Raman spectrum. Briefly explain your answer. (4 marks)