

Answer any THREE questions.

The numbers in square brackets in the right-hand margin indicate the provisional allocation of maximum marks per sub-section of a question.

1. Describe the **Franck-Condon Principle** as it applies to the intensity of transitions within the electronic spectrum of a diatomic molecule. Suggest one other process for which Franck-Condon factors may be important. [5]

The ground electronic state of the astronomically important CH molecule is X $^2\Pi$ and has an equilibrium bondlength $R_e(X)$. Absorptions by cold CH molecules are observed from the ground electronic state to the following excited electronic states:

- (a) The a $^4\Sigma^-$ state which has an equilibrium bondlength very close to $R_e(X)$;
- (b) The E $^2\Pi$ state which has an equilibrium bondlength significantly larger than $R_e(X)$;
- (c) The G $^2\Sigma$ state which is purely dissociative.

Explain what vibrational structure you would expect to observe in each case. One set of transitions are found to be much weaker than the others, explain which you expect this to be. [7]

The X $^2\Pi$ to E $^2\Pi$ band is observed at high resolution. There is no Q branch for this band. The potential energy minima of these two electronic states are separated by $T_e = 65945.0 \text{ cm}^{-1}$. The energy levels of the X $^2\Pi$ ground state can be characterised by the constants $\hbar\omega'' = 2858.6 \text{ cm}^{-1}$ and $B'' = 14.5 \text{ cm}^{-1}$; the corresponding levels for the E $^2\Pi$ excited state are $\hbar\omega' = 1794.8 \text{ cm}^{-1}$ and $B' = 12.6 \text{ cm}^{-1}$. You may assume that both states behave as rigid rotors and harmonic oscillators. An absorption spectrum is recorded for cold CH, for which only the $J'' = 0$ and $J'' = 1$ rotational levels are occupied. Estimate the wavenumbers of the transitions to the $v' = 0$ and 1 vibrational levels of the excited electronic state. [8]

2. Define what is meant by the **reduced mass** of a system containing two particles of masses M_A and M_B . [2]

Within the rigid rotor approximation, all molecules can be classified as belonging to one of four classes of rotor according to their moments of inertia. Explain what these four classes are and, for each class, state a molecule belonging to it. [6]

The $J = 1 - 0$ transition of the molecule ${}^7\text{Li}{}^{19}\text{F}$ is observed at 2.690 cm^{-1} . Estimate the wavenumber of (a) the $J = 2 - 1$ transition of ${}^7\text{Li}{}^{19}\text{F}$, (b) the $J = 1 - 0$ transition of ${}^6\text{Li}{}^{19}\text{F}$. Be careful to state any assumptions you make. [7]

How can observation of these transitions be helpful for establishing an accurate value for the equilibrium bondlength of LiF? What other information could be obtained by observing several rotational transitions of LiF? [5]

3. At an internuclear separation of R , a diatomic molecule has two electronic states with wavefunctions $\Psi_1(R)$ and $\Psi_2(R)$. Without proof, explain why in general the potential energy curves associated with $\Psi_1(R)$ and $\Psi_2(R)$ do not cross. Give a sketch of potential energy curves in the vicinity of an avoided crossing and explain how the nature of the wavefunction changes in this region. Under what circumstances can curves cross? [7]

The wavefunctions of two excited singlet states of H_2 can be represented as:

$$\begin{aligned}\Psi_1 &= \phi_a(1)\phi_a(2)\chi^S \\ \Psi_2 &= N (\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)) \chi^S\end{aligned}$$

where N is a normalisation constant. Explain the meaning of the other terms used in these expressions. Obtain an expression for N in terms of the integral

$$S(R) = \langle \phi_a(1) | \phi_b(1) \rangle .$$

[6]

The wavefunctions $\Psi_1(R)$ and $\Psi_2(R)$ interact via a one-electron spatial operator \hat{o} . Obtain an expression for the matrix element

$$H_{12}(R) = \langle \Psi_1 | \hat{o} | \Psi_2 \rangle$$

using the following integrals:

$$\begin{aligned}I_{aa}(R) &= \langle \phi_a | \hat{o} | \phi_a \rangle \\ I_{ab}(R) &= \langle \phi_a | \hat{o} | \phi_b \rangle\end{aligned}$$

[7]

4. State the **Pauli Principle** as it applies to the wavefunction of a many-electron system and show how it leads to the exclusion principle. [4]
Explain what is meant by the phrase **linear combination of atomic orbitals** (LCAO) when representing the electronic structure of a molecule. [2]

The ground state of Li_2 is designated $X^1\Sigma_g^+$ in spectroscopic notation. Explain carefully what each of these symbols represent. The bonding in Li_2 comes from the doubly occupied $2\sigma_g$ orbital. Suggest a form for this orbital in terms of the $2s$ orbitals of the lithium atoms. The first excited state of Li_2 involves promoting one electron from the $2\sigma_g$ orbital to the $2\sigma_u$ orbital. Give a possible designation for this electronic state, explaining your reasons for choosing it. [7]

Atomic nitrogen has two isotopes: ^{14}N with nuclear spin 1 and ^{15}N with nuclear spin $\frac{1}{2}$. Given that the ground electronic state of the N_2 molecule is $X^1\Sigma_g^+$, how would you expect the distribution of rotational states to differ between the molecules $^{14}\text{N}_2$, $^{15}\text{N}_2$ and $^{15}\text{N}^{14}\text{N}$? [7]

5. Define the terms **total cross section**, **differential cross section** and **elastic cross section** when applied to the scattering of an electron from a molecule. For electron impacts below the ionisation threshold of the molecule, explain which processes contribute to the total cross section but not the elastic cross section. [6]

Describe an experimental method for measuring the total cross section to high accuracy. [4]

Low-energy electrons collide with the following molecular targets: (a) H_2^+ , (b) H_2 , (c) HF . For each target give the form of the dominant long-range interaction. How would you expect this to change for a positron rather than an electron collision?

What are the dominant interactions that need to be considered when the electron is close to the molecular target? How do these differ for positron scattering? [7]

A differential cross section for electron collisions with a molecule at 5 eV is measured as $(1 + \cos\theta) \times 1.2 \times 10^{-18} \text{ m}^2\text{sr}^{-1}$, where θ is the angle between the incoming and outgoing electrons. What is the total cross section for this process? [3]