Answer TWO questions.

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

Constants:

Boltzmann constant	k	$= 1.38 \times 10^{-23}$ J K^{-1}
Planck constant	h	$= 6.6 \times 10^{-34}$ Js
Speed of light in vacuum	c	$= 3.0 \times 10^{8}$ m s^{-1}

[Part marks]

1. In the Separated Atom approximation two different atoms, A and B, can be brought together adiabatically to form a molecule AB. If A is in a D state and B is in a P state determine the molecular levels produced. Explain carefully the role of parity in the classification of any Σ states. [5]

   Describe the main features of the potential V(r) existing in a typical molecule AB. [3]

   Expand V(r) using Taylor's series and obtain an expression for the force constant k for small vibrations about the equilibrium position r_e. [3]

   Given the empirical Morse potential function

   $$V(r) = D_e\left[1 - e^{-a(r-r_e)}\right]^2$$

   (i) Show that it describes the main features of a typical molecular potential,

   (ii) Determine k in terms of the dissociation energies, D_e, and the variable constant a,

   (iii) Assuming the formulae

   $$\omega_e x_e = \frac{1}{24}\left\{5\left(\frac{V'''}{V''}\right)^2 - 3\left(\frac{V''''}{V''}\right)\right\}\frac{h}{8\pi^2 c\mu}$$ [9]

   derive an expression for the vibrational levels of the anharmonic oscillator.

2. Write down the Hamiltonian for the H_2^+ molecular ion. [2]

   Use the Heitler-London method of molecular bonding to determine the [8]

bonding and anti-bonding orbitals of the ground state of H_2^+ in terms of the atomic orbital

$$\phi = \frac{1}{\sqrt{\pi}} e^{-r}.$$

Derive the Virial Theorem.

[8]

Hence, or otherwise, show that in the case of a single particle in a Coulomb potential, *V*, that [2]

$$< T > = 0.5 <V>$$

You may assume Euler's Theorem.

3. Explain what is meant by an Eximer molecular state and the roles of the Ionic and Metastable channels in the formation of eximer molecules. [6]

Describe the operation of the Krypton Fluoride laser. [6]

Explain and distinguish between the Symmetric, Asymmetric and Bending modes in the CO_2 molecule. Which modes in CO_2 are Raman Active and Infrared Active? Justify your answer. [3]

Describe the molecular processes by which a population inversion is produced in the Carbon Dioxide laser. [5]