

UNIVERSITY COLLEGE LONDON

EXAMINATION FOR INTERNAL STUDENTS

MODULE CODE : PHAS4431

MODULE NAME : Molecular Physics

DATE : 17-May-07

TIME : 10:00

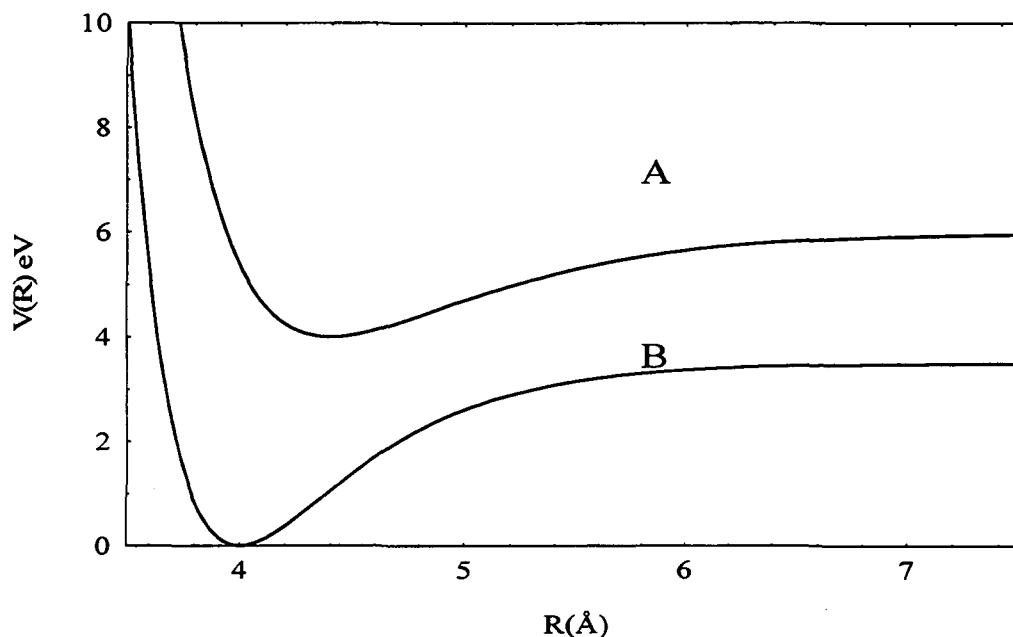
TIME ALLOWED : 2 Hours 30 Minutes

Answer any THREE questions

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

1 State the **Born Oppenheimer Approximation** as applied to the wavefunctions and energies of molecules and explain how it gives rise to the concept of a molecular potential energy surface.

[4]



The diagram above shows potential energy curves for two diatomic molecules A and B which both have the same reduced mass μ , indicate explaining your reasons which molecule has;

- (a) The shorter equilibrium bond length R_e
- (b) The larger zero point energy
- (c) The lower dissociation energy D_e
- (d) The larger rotational constant.

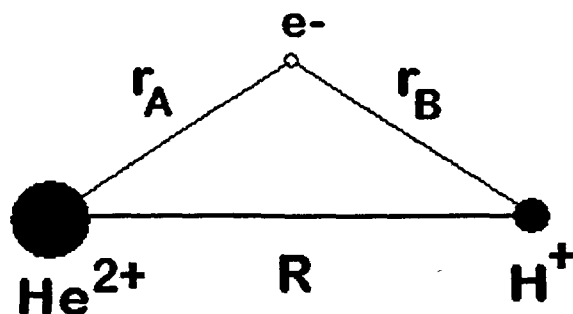
[8]

Give an expression for the rotational energy of a diatomic molecule in terms of μ , R_e and the rotational angular momentum quantum number J . In its lowest energy state H^{35}Cl strongly absorbs radiation at 10.483 cm^{-1} . At what frequency would you expect the corresponding transition in H^{37}Cl to occur? Be careful to state any assumptions that you have made.

[8]

2. Explain what is understood by the Linear Combination of Atomic Orbitals (LCAO) approach to constructing molecular electronic wavefunctions. What does such an approximation imply physically about the electronic interactions in multi-electron molecules? Briefly explain how the trial wavefunctions may be refined to yield accurate results [5]

The helium hydride molecular ion HeH^{2+} consists of an alpha particle, a proton and an electron as depicted below



With reference to this diagram, write down the electronic Hamiltonian for the system and identify the physical origin of the terms. [4]

At large internuclear separations the two lowest electronic states of HeH^{2+} correlate with what dissociation products? State, giving your reasons, which of these is the lower in energy, and give the asymptotic form of the electronic wavefunction in both instances. At close internuclear separations what are the limiting forms of the wavefunctions? [8]

Only one of these states gives rise to a stable molecular ion. By considering the differences in the interactions between the dissociated particles in each case, identify the bonding solution. [3]

You may wish to make use of the following information:

The dipole polarisability α of a hydrogen-like atom of atomic number Z is given by $\alpha = \frac{A}{Z^4}$ where A is a constant of proportionality.

3 Explain briefly what is understood by the **electric dipole approximation** as applied to the interaction of electromagnetic radiation with molecules. [3]

From Fermi's Golden Rule, the transition rate between two molecular eigenstates i and f induced by a radiation field of angular frequency ω , wavevector \vec{k} , propagation direction \vec{r} and polarisation vector \vec{e} is given by

$$R_{if} = \frac{\pi}{\epsilon_0 \hbar^2} |\langle f | \vec{\mu} \cdot \vec{e} \times \exp(i\vec{k} \cdot \vec{r}) | i \rangle|^2 \rho(\omega_{fi})$$

where $\rho(\omega_{fi})$ is the average energy density per unit angular frequency in the region of $\omega = (E_f - E_i)/\hbar$ and $\vec{\mu}$ is the dipole moment operator.

Show that in the electric dipole approximation the Einstein coefficient for the induced transition probability is given by

$$B_{if} = \frac{\pi}{\epsilon_0 \hbar^2} |\langle f | \vec{\mu} \cdot \vec{e} | i \rangle|^2 \quad [2]$$

With reference to this result give an explanation for the following observations:

In diatomic molecules such as HCl the absorption of linearly polarised microwave radiation at moderate temperatures predominantly involves the excitation of $M_J = 0$ rotational states

[5]

In heteronuclear diatomic molecules the probability for the absorption of infra-red vibrational transition in the transition $\nu \rightarrow \nu + 1$ rises with increasing ν .

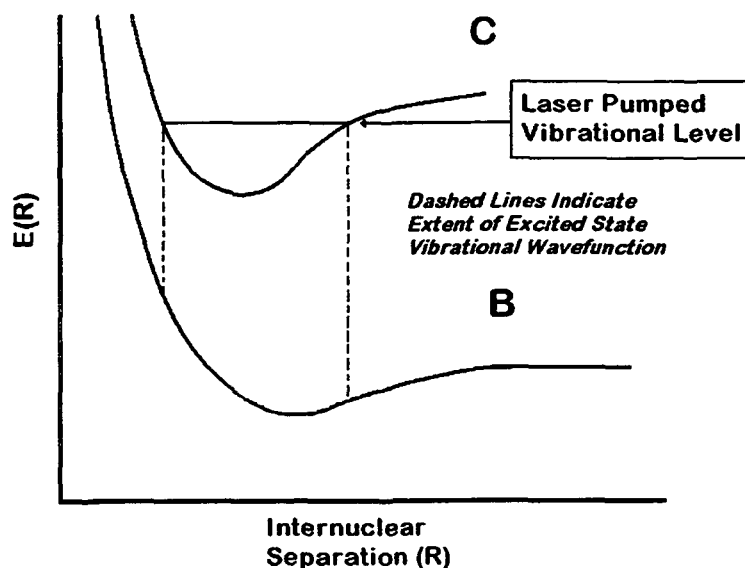
[5]

Oxygen molecules do not absorb microwave or infrared radiation, but show a complex absorption spectrum in the ultraviolet.

[5]

4. Explain the **Franck-Condon Principle** as applied to the prediction of the intensity of vibrational transitions between the electronic states of a molecule. [3]

The diagram below shows the potential energy curves of two excited electronic states of a diatomic molecule, a high-lying vibrational level in the upper C state is populated by laser excitation from another state and subsequently relaxes to the B state by spontaneous emission.



- Sketch the form of the **C**→**B** emission spectrum [3]

Molecular electronic absorption spectra often display a band head. Explain how this may arise. [3]

Nitrogen molecules undergo an electronic transition from their $X^1\Sigma_g^+$ electronic ground state to the $b^1\Sigma_u^+$ excited state; there is no Q branch for the transition. The potential energy minima for these states are separated by 103678.9 cm^{-1} . The energy levels of the excited state are characterised by $h\nu = 2359.6\text{ cm}^{-1}$ and $B = 2.010\text{ cm}^{-1}$; the corresponding parameters for the excited state are given by $h\nu = 751.7\text{ cm}^{-1}$ and $B = 1.145\text{ cm}^{-1}$. You may assume that both states behave as harmonic oscillators and rigid rotors.

A spectrum is recorded using cold N_2 such that only levels up to $J'' = 2$ are occupied in the ground state. Calculate the wavenumbers of the spectral lines you would expect to observe in the transition to the $v' = 0$ level of the excited state. [8]

The absorption spectrum of N_2 , even at warm temperatures, does not show a band head. Why is this? [3]

5. Briefly explain the physical principles by which the fluorescence arising from the absorption of short (picosecond) linearly polarised laser pulses by an initially isotropic distribution of molecules is polarised. [3]

For single photon absorption the initial distribution of excited molecular orientations in the laboratory frame axis system is given by

$$P(\theta, \phi, T = 0) = \frac{3}{4\pi} \cos^2 \theta,$$

where θ denotes the angle between the polarisation vector of the light and the absorption transition dipole moment direction in the molecular frame. The fluorescence anisotropy R for a population of molecular probes at time T after excitation is given by

$$R(T) = \frac{1}{2} [3 \langle \cos^2 \theta \rangle_T - 1]$$

where $\langle \rangle$ denotes the ensemble average value of $\cos^2 \theta$ at time T given by

$$\int_0^{2\pi} d\phi \int_0^\pi P(\theta, \phi, T) \cos^2 \theta \sin \theta d\theta = \langle \cos^2 \theta \rangle_T$$

Show that the initial fluorescence anisotropy is 2/5. [3]

What differences and similarities are there in the time resolved fluorescence polarisation signals observed from fluorescent molecules in the gas phase and in solution and what is their origin? [6]

Sketch the time resolved fluorescence anisotropy signal you would expect to observe from

(a) a fluorescent probe embedded in the nematic phase of a liquid crystal

(b) a fluorescent molecule constrained within a protein in solution

(c) a fluorescent probe in isotropic solution where the absorption and emission transition dipole moments in the molecular frame are orthogonal.

(d) emission from a yellow fluorescent protein molecule excited by **intra-molecular** resonance energy transfer from a green fluorescent protein molecule; both chromophores are attached to a large protein and the angle between their respective absorption transition dipole moments is 35°.

[8]

END OF PAPER