Valence: Electronic Spectroscopy and Hückel Theory

Section A

Work through the notes on the variation principle and Huckel molecular orbital theory. It is important that you understand this material since it forms the basis for almost all current theories of chemical bonding.

Section B

Q1. a) Sketch the molecular orbital diagrams of the hydrogen and oxygen molecules, H_2 and O_2. Give the term symbols of the ground states of each molecule, explaining the meaning of each label you use.

b) O_2 possesses two low-lying excited electronic states, at 7900 cm^{-1} and 13200 cm^{-1} above the ground state. Give the term symbols for the two excited electronic states, and rationalise the energy ordering of the ground state and the two excited states. Why are the two low-lying excited electronic states of O_2 expected to have long radiative lifetimes?

c) The highest electron kinetic energy features in the photoelectron spectra of H_2 and O_2, associated with the transitions to the lowest electronic states of the ions, both display progressions of bands. For H_2 many bands are observed, and the lower bands in the progression are separated by 2300 cm^{-1}. For O_2 only a small number of bands are observed, and the bands are separated by 1900 cm^{-1}. At higher resolution each of the bands in O_2 is found to be doubled. The vibrational wavenumbers for H_2 and O_2 in their ground electronic states are 4400 cm^{-1} and 1600 cm^{-1}, respectively.

For each spectrum give the term symbol(s) for the state(s) of the ion involved. Rationalise the spectral features (both the number of bands and band separations) observed.

Q2. a) The lowest three electronic states of the N_2^+ ion have the symmetries $^2\Sigma_g^+$, $^2\Pi_u$, and $^2\Sigma_u^+$, and each can be accessed by removal of one electron from the ground electron configuration of N_2. Identify the electronic configurations giving rise to each, and discuss the meaning of the term symbols employed.

b) The vibrational wavenumbers and rotational constants for these states are listed below.

State	ω_e / cm^{-1}	B_e / cm^{-1}
$^2\Sigma_g^+$	2207.0	1.9317
$^2\Pi_u$	1903.7	1.7444
$^2\Sigma_u^+$	2419.8	2.0746

For the ground state of N_2, ω_e = 2358.6 cm^{-1} and B_e = 1.998 cm^{-1}. Discuss these values in terms of the molecular orbital diagram for N_2 and N_2^+.

c) The electronic emission spectrum of N_2^+ involving the states listed above shows one band with an origin at 9015.5 cm^{-1} with a band head in the R branch, while another band occurs at 25 556 cm^{-1} with a band head in the P branch. Identify the electronic states involved, giving reasons for your assignment.

[Note that the wavenumbers of transitions in the R branch are given by

$$\bar{\nu}_J = \bar{\nu}_0 + (B' + B'')(J+1) + (B' - B'')(J+1)^2$$

where B' and B'' are the rotational constants for the upper and lower states and $\bar{\nu}_0$ is the band origin.]

Q3. a) The Ar^{2+} ion in the gas phase has the configuration $1s^2 2s^2 2p^6 3s^2 3p^4$ in its ground state. Predict the following, explaining your reasoning.

i) The *terms* arising from that configuration and their energy ordering

ii) The J quantum number for the lowest energy level.

b) The lowest energy *fully-allowed* electric-dipole transition in the *absorption* spectrum of Ar^{2+} is of the type $3s^1 3p^5 \leftarrow 3s^2 3p^4$ and occurs at a wavenumber of approximately 115 000 cm⁻¹. Deduce the term symbols for the two states involved in this transition and draw a diagram showing the allowed transitions between all the levels of the two terms.

c) A series of transitions are observed in the emission spectrum of Ar^{2+} of the type $3s^2 3p^3 nf[^3F_4] \rightarrow 3s^2 3p^3 3d^1[^3D_3]$.

n	$\bar{\nu}$ /cm^{-1}
4	111 290
5	133 527
6	145 605
7	152 887

The quantum defect for the upper $^3F_4$ levels may be assumed to be zero and the ionization energy of Ar^{2+} is 329 966 cm⁻¹. Use a graphical procedure with the data given above to determine the energy required to ionize the Ar^{2+} ion from the $3s^2 3p^3 3d^1[^3D_3]$ level, and hence determine the excitation energy from the ground state to this level.

Q4. a) For a trial wavefunction of the form $\psi = c_A\phi_A + c_B\phi_B$, where ϕ_A and ϕ_B are normalised atomic orbitals on different atoms, and c_A and c_B are coefficients, derive the secular equations.

b) Show that the roots of these equations when the orbitals ϕ_A and ϕ_B are orthogonal (S_{AB}=0) are given by

$$E_\pm = \frac{H_{AA}+H_{BB}}{2} \pm \frac{1}{2}[\,(H_{AA} - H_{BB})^2 + 4H_{AB}^2\,]^{1/2}$$

c) Find the coefficients c_A and c_B for the molecular orbitals associated with E_+ and E_- for the special cases

i) $H_{AA} = H_{BB}$ (homonuclear diatomics)

ii) $H_{AA} = 2H_{BB} = \alpha$, $H_{AB} = \alpha/4$.

For i) above, describe and explain the variations in the relative magnitudes of c_A and c_B as the electronegativity of atom A increases relative to atom B.

Q5. a) The *k*th molecular orbital for a linear chain of *N* carbon atoms has the form

$$\psi_k \propto \sum_{m=1}^{N} \phi_m \sin\left(\frac{mk\pi}{N+1}\right)$$

where ϕ_m is a p_z orbital on atom m. Find its energy within Hückel theory by substitution into the secular equations.

b) Sketch the lowest three orbitals for a six-membered chain. By considering the relative phases of each molecular orbital on the first and last atoms, show that orbitals with odd values of *k* are stabilized and those with even values of *k* are destabilized if the chain is converted to a ring.