IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2010, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

ADVANCED CHEMISTRY THEORY IIA

Inorganic Chemistry

Wednesday 13th January 2010, 14:00-15:30

Answer ONE question from each attended course

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

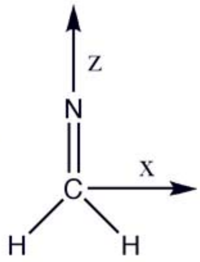
Year 2/0110 **Turn Over**

2.I1 – Molecular Orbitals in Inorganic Chemistry

Answer part a) and **EITHER** part b) **OR** part c)

a) Construct and **annotate** a valence MO diagram for H_2CN^-. Use it to explain why the neutral radical $H_2CN\bullet$ is more stable than the anion. Use the axial system defined in **A**, H_2C and N molecular fragments and assume the MOs of H_2CN^- do not undergo mixing.

A

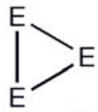


y-axis coming out of the page

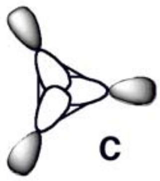
(13 marks)

b) Answer **ALL** parts of this question.

A fragment E_3 belongs to the D_{3h} point group and consists of three atoms (E) arranged in an equilateral triangle as shown in **B**.



B



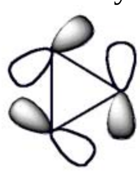
C

i) Determine the reducible representation ($\Gamma_{\mathbf{C}}$) for the basis set **C** consisting of three p AOs.

(1 mark)

ii) The reducible representation ($\Gamma_{\mathbf{D}}$) for the basis set **D** consisting of three p AOs is given below. Determine the contributing irreducible representations. Use the reduction formula at least once, where appropriate use "short-cuts" and show your working.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\mathbf{D}}$	3	0	-1	3	0	-1



D

(4 marks)

iii) Use the projection formula to determine ONE wavefunction for the degenerate irreducible representation. Show your working. The wavefunction does not need to be normalised. Draw the molecular orbital.

(7 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts of this question.

i) The octahedral point group has $8C_3$ operations. Illustrate **ONE** of the C_3 axes on a diagram and clearly **describe** how all 8 C_3 operations can be identified.

(4 marks)

ii) For an octahedral transition metal (M) complex with six sigma-bonding ligands (L): ML_6, draw the antibonding e_g MOs, annotate **ONE** of your diagrams describing the bonding and antibonding character of the MO.

(4 marks)

iii) For the octahedral complex ML_6 with **six sigma-bonding** ligands, define the octahedral splitting parameter and discuss (using MO theory) how the size of Δ_{oct} can be affected.

(4 marks)

2.IS1 – NMR and EPR Spectroscopy

Answer part a) **AND** b), and **EITHER** part c) **OR** part d)

a) Answer **ALL** parts of this question.

Describe and sketch the following:

i) the ^{1}H NMR spectrum of AlH_4^- (4 marks)
ii) the ^{1}H NMR spectrum of GaH_4^- (8 marks)
iii) the ^{27}Al NMR spectrum of AlH_4^- (2 marks)

On each spectrum indicate the position of the chemical shift, label the couplings using the $^{n}J_{X\text{-}Y}$ notation and give the relative intensities of signals. If more than one coupling is present in a spectrum give their relative magnitudes.

(Assume that ^{1}H is 100% abundant, I = ½; ^{27}Al is 100% I = 5/2; ^{69}Ga is 60% abundant I = 3/2, γ = 6.0 ^{71}Ga is 40% abundant I = 3/2, γ = 8.0; units for γ are 10^{7} rad T^{-1} s^{-1}.)

b) Describe and sketch the **hydride** region of the ^{1}H NMR spectrum of the square planar cation $[PtH(PMe_3)_3]^+$. Label the couplings using the $^{n}J_{X\text{-}Y}$ notation, give the relative intensities of signals and the relative magnitudes of any couplings present. Assume that no coupling greater than ^{2}J is observed.

(Assume that ^{1}H and ^{31}P are both 100% abundant, I = ½; ^{195}Pt is 33% abundant I = ½, and that all other nuclei present are I = 0.)

(6 marks)

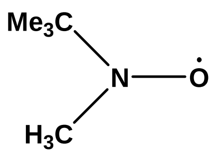
c) Describe and sketch the ^{1}H and the ^{2}D NMR spectra for a dilute solution of water (99% deuterated) in an inert solvent. Indicate on each sketch chemical shift positions and any coupling using the $^{n}J_{X\text{-}Y}$ notation.

(Assume that that ^{1}H has I = ½ and ^{2}D has I = 1.)

(5 marks)

d) Describe and sketch the EPR spectrum of the free radical, **1**, shown below. Indicate any couplings and the relative intensities of signals on the sketch. Assume that no coupling beyond three bonds is observed.

(Assume that ^{1}H is 100% abundant, I = ½; ^{14}N is 100% abundant, I = 1; and that all other nuclei present are I = 0.)



1

(5 marks)