UNIVERSITY OF SWAZILAND

Re-Sit EXAMINATION 2017/2018

TITLE OF PAPER: THEORY OF SPECTROSCOPY

COURSE NUMBER: CHE342

TIME: THREE (3) HOURS

INSTRUCTIONS:

This paper consists of five (5) questions in 4 pages. **Answer any four (4) questions**

NB: Each question should start on a new page.

A data sheet and a periodic table are attached

A non-programmable electronic calculator may be used

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QUESTION 1 [25 MARKS]

a) The technique of photoelectron spectroscopy may be used to estimate the orbital energies of molecules. Explain how this may be achieved. [4]

b) Consider the following molecules: B_2, OF and CN.

i. Give the electron configuration and bond order of each molecule [6]

ii. State whether the molecule is paramagnetic or diamagnetic and give the number of unpaired electrons [3]

iii. Which of these molecules would you expect to become more stable if an electron is added? If an electron is removed? In each case give a reason [6]

c) the term symbol for particular state of an atom is quoted as follows:

i. $^{0}P_{1}$

Explain why this is incorrect [3]

d) Give term symbols for the following

i. Ground state scandium:[Ar]$3d^{1}4s^{2}$ [3]

QUESTION 2 [25 MARKS]

a) Briefly explain why the 2s and 2p subshells are degenerate in the H-atom but are not in an atom of two or more electrons [7]

b) Define the quantum numbers L and S as applied to atoms, indicating the kind of values they may have. State their physical meaning in quantitative terms. Under what conditions are the L and S no longer valid as quantum numbers? State this in a sentence or two. [7]

c) The Calcium atom has an excited state whose electron configuration is [Ar]$3d^{1}$4s1

i. Obtain the complete term symbols for this state and the ground state [5]

ii. Discuss the possibility of a spectroscopic transition from the excited state to the ground state [4]

d) State whether the following transition is allowed or forbidden. Provide an explanation for your answer

i. 3d→2s and 3p→1s for a hydrogen atom. [2]

QUESTION 3 [25 MARKS]

a) The spacing between two adjacent lines in the rotational spectrum of CO is 1.15 x 10^{11} Hz. The atomic masses of C and O are 12.0000u and 15.9949 u respectively. Calculate

i. The moment of inertia of the CO molecule [3]
ii. The internuclear distance [5]

b) The rotational constant for $H^{35}Cl$ is observed to be 10.5909 /cm. What are the values of the rotational constant, B, for the $H^{37}Cl$ and $^{2}D^{35}Cl$? The atomic masses are H=1.0078 u, ^{2}D =2.0140 u ^{35}Cl = 34.9688 u and ^{37}Cl = 36.9651 [8]

c) The fundamental and first overtone of $^{14}N^{16}O$ are centered at 1876.06 /cm and 3724.20 /cm, respectively. Evaluate

i. The equilibrium vibration frequency and the anharmonicity constant [3]
ii. The exact zero point energy [2]
iii. The force constant of the molecule [2]
iv. The approximate bond dissociation energy of the molecule [2]

QUESTION 4 [25 MARKS]

a) Consider the molecule B_2 (Z=5) in its ground state and determine

i. The molecular orbital electron configuration [2]
ii. The bond order [2]
iii. The term symbol [3]

b) Use the electron configuration of NO and N_2 to predict which is likely to have a shorter bond length (Atomic number Z for N=7 and O =8) [4]

c) Define the word laser. What is the main advantage of a four laser over a three laser? [4]

d) In the photoelectron spectrum of O_2 using the 58.43 nm light, electrons with kinetic energies 5.63 eV and 5.55 eV are observed. What are the ionization energies of these electrons? [5]

e) Suppose that the maximum molar absorption coefficient of a molecule containing a carbonyl group at a concentration of 1.00mol/Lcm near 280 nm, calculate the thickness of a sample that will result in half the intensity. [5]

QUESTION 5 [25 MARKS]

a) Give the number of vibrational modes of the following

i. SO_2
ii. C_2F_2
iii. CCl_4 [3]

b) Sketch and name the vibrational modes of SO_2. Indicate which are IR and which are Raman active [6]

c) Explain how you can use infrared and Raman spectroscopy to determine the structure of a triatomic AB_2 molecule [6]

d) State the selection rules for rotational Raman spectroscopy [2]

e) The pure rotational Raman spectrum of $^{14}N_2$ shows a spacing 7.99 /cm between adjacent rotational lines.

i. Find the value of the rotational constant B [2]

ii. What is the spacing between the unshifted line v_{ex} and pure rotational lines closest to v_{ex} [2]

iii. If 540.8 nm radiation from an Argon laser is used as the exciting radiation, find the wavelengths of the two pure rotational Raman lines nearest the unshifted lines. [4]

Total Marks **/100/**

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_A k$	8.314 51 J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
		6.2364 X 10 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ Kg
Mass		
electron	m_e	$9.109\,39 \times 10^{-31}$ Kg
proton	m_p	$1.672\,62 \times 10^{-27}$ Kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Vacuum permeability	μ_0	$4\pi \times 10^{-7}$ J s^2 C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^2 J^{-1} m^3
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
g value	g_e	2.002 32
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\,37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	9.806 65 m s^{-2}
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^2 Kg^{-2}

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\,2 \times 10^{-19}$ J	1 eV/molecule	=	96 485 kJ mol^{-1}

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12	TRANSITION ELEMENTS										26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.