UNIVERSITY OF ESWATINI

MAIN EXAMINATION 2018/2019

TITLE OF PAPER: THEORY OF SPECTROSCOPY

COURSE NUMBER: CHE342

TIME: THREE (3) HOURS

INSTRUCTIONS:

Answer all questions

NB: Each question should start on a new page.

A data sheet and a periodic table are attached

Non-programmable electronic calculator may be used

DO NOT OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1 [25Marks]

a) Briefly explain why the 2s and 2p subshells are degenerate in the H-atom but are not in an atom with two or more electrons [6]

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 Under what circumstances or conditions are L and S no longer valid as quantum numbers? State the reason for this [7]

c) The calcium atom has an excited state whose electron configuration is $[Ar]3d^1 4s^1$.

   i). Obtain the complete term symbol for this state and the ground state [6]

   ii). Discuss the possibility of spectroscopic transition from the excited state to the ground state. [2]

d) State whether the following transitions are allowed or forbidden. In each case, give a reason.

   i). $3d \rightarrow 2s$ and $3p \rightarrow 1s$ for the hydrogen atom [2]

   ii). $^1D \rightarrow {}^1S_0$ and $^3P_1 \rightarrow {}^3P_0$ for a carbon atom [2]

Question 2 [25 marks]

a) The spacing between two adjacent lines in the rotational spectrum of carbon monoxide is $1.15 \times 10^{11} s^{-1}$. Calculate

   i). The moment of inertia of the CO molecule

   ii). The internuclear distance [8]

   (The atomic masses for C and O are 12.000u and 15.9949u respectively)

b) The rotational constant for $H^{35}Cl$ is observed to be $10.5909 cm^{-1}$. What are the values of the rotational constant, B for $H^{37}Cl$ and for $^2D^{35}Cl$? The atomic masses are H=1.0078u, ^2D = 2.0140u, ^{35}Cl = 34.9688 and ^{37}Cl = 36.9651u [8]

c) The fundamental and first overtone of $^{14}N^{16}O$ are at 1876.06 cm^{-1} and 3724.20 cm^{-1}, respectively. Evaluate

   i). The equilibrium vibration frequency and the anhamornicity 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]

(the atomic masses of ^{14}N = 14.0031u and ^{16}O =15.9949u)

QUESTION 3 [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 [2]

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

c) Define the word laser. What is the main advantage of a four laser-level laser over a three-level laser? [5]

d) In the photoelectron spectrum of O_2, using 58.43nm light, electrons with kinetic energies 5.63 eV and 5.55 eV are observed. What are the ionization energies of these electrons (1eV = 1.602 x10^{-19}J) [5]

e) Suppose that the maximum molar absorption coefficient of a molecule containing a carbonyl group at a concentration of 1.00mol/L is 30Lmol^{-1}cm^{-1} near 280nm, calculate the thickness of the sample that will result in half the initial intensity.

[5]

Total Marks **/75/**

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}
		6.2364×10 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	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_o$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ 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	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^{\,2}$	$1.097\,37 \times 10^{7}$ 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

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											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								

TRANSITION ELEMENTS

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

*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.