UNIVERSITY OF SWAZILAND

MAIN 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 3 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

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

QUESTION 1 [25 MARKS]

a) Calculate the frequency in wavenumbers of the line in the spectrum of a Li^{2+} ion that is emitted when the ion makes a transition from the stationary state n=2 to the ground state [4]

b) State whether the following transitions are allowed or forbidden. Give reasons for your answers.

i. $3d \leftarrow 2s$ and $3p \leftarrow 1s$ [3]

ii. $^1D \leftarrow {}^1S$ and $^3P_1 \leftarrow {}^3P_0$ [3]

c) the term symbol for particular states of different atoms are quoted as follows:

i. $^4S_1$

ii. $^2D_{7/2}$

iii. $^0P_1$

Explain why these are wrong [9]

d) Give term symbols for the following

i. The lithium in its first excited state:$1s^2 2p^1$ [3]

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

QUESTION 2 [25MARKS]

a) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centered at 1876.06 and 3724.20 /cm, respectively. The atomic masses for ^{14}N and ^{16}O are 14.0031 u and 15.9949 u, respectively. Calculate

i. The equilibrium vibrational frequency [3]

ii. The anhamornicity constant [3]

iii. The exact zero point energy in kJ/mol [3]

iv. The force constant of the molecule [3]

b) Compare the species O_2^+, O_2 and O_2^{2-} in terms of the ground state configuration, bond order, stability, bond length and magnetic properties [13]

QUESTION 3 [25MARKS]

a) Give the gross and specific selection rules for pure rotational spectroscopy[4]

b) Which of the following molecules show pure rotational spectra? Explain your choices

i. H_2, HCl, CH_3Cl, CH_2Cl_2, H_2O, NH_3 [6]

c) The average spacing between adjacent lines in the rotational spectra of $^1H^{19}F$ is 41.912 /cm. Calculate the bond length of the HF molecule. [given that the atomic masses are ^1H =1.0078 u and ^{19}F = 18.9984 u] [8]

d) Assuming the bond length is independent of isotopic substitution; calculate the spacing between adjacent lines in the rotational spectra of $^{2}H^{19}F$. Atomic mass ^{2}H = 2.0140 u [7]

QUESTION 4 [25MARKS]

a) Write down the rotational energy levels of a diatomic molecule assumed to be rigid [3]

b) What is degeneracy? What is the physical interpretation of this degeneracy [3]

c) Obtain a general expression for the change in energy of the R-branch in HCl in the lowest vibrational state [4]

d) The highest temperature microwave spectrum of $^{39}K^{35}Cl$ vapor shows an absorption at 7687.94 MHz that can be identified with the J=0 to J=1 transition. Calculate the moment of inertia and the bond length of KCl. [Atomic masses are ^{39}K =38.9637 u and ^{35}Cl =3409688 u] [15]

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	$F = N_A e$	$9.6485 \times 10^{4}\ C\ mol^{-1}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23}\ J\ K^{-1}$
Gas constant	$R = N_A k$	$8.314\,51\ J\ K^{-1}\ mol^{-1}$
		$8.205\,78 \times 10^{-2}\ dm^{3}\ atm\ K^{-1}\ mol^{-1}$
		$6.2364 \times 10\ L\ Torr\ K^{-1}\ mol^{-1}$
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	=	$1 \times 10^{-7}\ J$
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.