CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 345: MOLECULAR SPECTROSCOPY

STREAMS: BSC. CHEM **TIME: 2 HOURS**

DAY/DATE: WEDNESDAY 16/04/2025 **8.30 A.M. – 10.30 A.M.**

INSTRUCTIONS

- Answer question **ONE** and any other **TWO** questions
- Useful data

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^{8}	$m\ s^{-1}$
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^{4}	$C\ mol^{-1}$
Boltzmann's constant	k	1.380 65	10^{-23}	$J\ K^{-1}$
Gas constant	$R = N_A k$	8.314 47		$J\ K^{-1}\ mol^{-1}$
		8.314 47	10^{-2}	$dm^3\ bar\ K^{-1}\ mol^{-1}$
		8.205 74	10^{-2}	$dm^3\ atm\ K^{-1}\ mol^{-1}$
		6.236 37	10	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	8.854 19	10^{-12}	$J^{-1}\ C^2\ m^{-1}$
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	$J^{-1}\ C^2\ m^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$J\ s^2\ C^{-2}\ m^{-1}\ (= T^2\ J^{-1}\ m^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	$J\ T^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	$J\ T^{-1}$
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^{2}	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3c^2$	5.670 51	10^{-8}	$W\ m^{-2}\ K^{-4}$
Rydberg constant	$R = m_e e^4/8h^3c\varepsilon_0^2$	1.097 37	10^{5}	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		$m\ s^{-2}$
Gravitational constant	G	6.673	10^{-11}	$N\ m^2\ kg^{-2}$

Exact value

QUESTION ONE (30 MARKS)

(a) i) Write notes on fundamental vibration of nonlinear molecule using suitable examples. (3 marks)

ii) Explain why aniline absorbs at 280 nm (εmax 8600), however in acidic solution, the main absorption band is seen at 203 nm. (2 marks)

iii) The position of absorption of acetone shift in different solvent 279 nm (hexane), 272 nm (ethanol), and 264.5 nm (water). Explain. (3 marks)

(b) i) The carbonyl stretching vibration of trans-2-hexenal appears at 1669 cm^{-1} (5.99 μm). Determine the force constant of the C=O bond. ($1\frac{1}{2}$marks)

ii) Explain why the carbonyl stretching frequency is always strong. (3 marks)

c) i) Identify and explain three important criteria for selecting suitable ATR crystals. ($1\frac{1}{2}$marks)

ii) Summarize the advantages and disadvantages to KBr disc and Nujol mull sample preparations. (4 marks)

iii) Determine the normal modes of vibration of the following molecules; ($1\frac{1}{2}$marks)

I. prop-2-ynenitrile

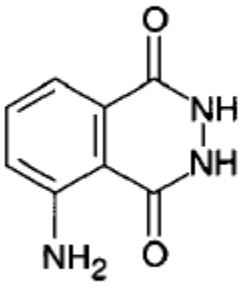
II. Propanone

III. Methylbenzene

iv) For $^{1}H^{35}Cl$, the rotational constant B_0=10.44 cm^{-1} and B_1=10.13 cm^{-1} for the v = 0 and 1 vibrational levels, respectively, and the separation of these vibrational levels, ω0, is 2886.04 cm^{-1}. Calculate the wavenumbers of the first two members of each of the O and S branches in the Raman vibration–rotation spectrum. (3 marks)

d) i) The first line in rotational spectrum of carbon monoxide has a frequency of 3.8424 cm^{-1} Calculate the rotational constant and hence the C-O band length in carbon monoxide. Avogadro number is 6.022x 10^{23} mole. (2 marks)

ii) Ferrous iron catalyses the oxidation of luminol (see below) by hydrogen peroxide. The intensity of the chemiluminescence which follows increases linearly with the concentration of Fe (II) as it rises from 10^{-10}M to 10^{-8} M. To measure a solution of unknown content in Fe (II), 2 mL of the solution was extracted and then introduced to 1 mL of water, followed by the addition of 2 mL of hydrogen peroxide and finally 1 mL of an alkali solution of luminol. The luminescence signal is emitted and integrated over a period of 10 seconds giving a value of 16.1 (arbitrary units). In a second attempt, 2 mL of the unknown Fe (II) solution is again extracted and on this occasion it was added to 1 mL of a solution 515×10^{-5}M in Fe (II) and the same quantities of hydrogen peroxide and luminol were introduced as before. The signal, integrated over 10 seconds, was measured as 29.6.Calculate the molar concentration of Fe (II) in the original solution. (2 marks)



luminol

iii) At a wavelength number of 33400cm^{-1} a sample, contained in a cell 6.45× 10^{-3}m long, absorbs 76.4% of the incident radiation. The sample is in the liquid phase in solution with a concentration of 1.76× 10^{-4} mol dm^{-3}. Determine the value of the molar absorption coefficient with units of mol^{-1} dm^{3} cm^{-1}. (2 marks)

iv) Explain why homonuclear diatomic molecules are IR-inactive and Raman active. (1$\frac{1}{2}$marks)

QUESTION TWO (20 MARKS)

a) i) Discuss the various types of electronic transitions and explain the effect of the polarity of the solvent on the each type of transition. (6 marks)

ii) Using the given data, calculate the v=0, 1, and 2 vibrational term values and compare the v=1-0 and 2-1 separations for each molecule.

I. 1_{H_2} for which ωe=4401.2 cm^{-1}, χe=121.3cm^{-1}, ye=0.8 cm^{-1} (2$\frac{1}{2}$marks)

II. 79_{Br_2} For which ωe=325.32 cm^{-1}, χe=1.08cm^{-1}, ye=-0.002 cm^{-1} (2$\frac{1}{2}$marks)

iii) Two adjacent lines in the rotational absorption spectrum of $^{14}N^{1}H$ are at 98.036 and 130.714 Cm^{-1}. Calculate the equilibrium bond length of HF, Ro, and the rotational quantum numbers of the lower states of the two transitions. (4 marks)

b) i) Deduce all the types of electron transitions which are allowed for which the lower state is 3_{Δ_u} in H_2 and I_2. (2 marks)

ii) Explain how you can account for the fact that the two sets of high-resolution NMR triplets of SF4 merge into one peak upon heating. (3 marks)

QUESTION THREE (20 MARKS)

a) i) Describe general regions of the fundamental vibrational spectrum with some characteristic group frequencies. (5 marks)

ii) I. From the value for B_0 of 1.923 604$\pm$0.000 027 cm^{-1}, obtained from the rotational Raman spectrum of $^{14}N^{15}N$, calculate the bond length r_0. (2 marks)

II. Explain why it differs from r_0 for $14N_2$. ($\frac{1}{2}$ Mark)

III. Explain if there will be an intensity alternation in the spectrum of $^{14}N^{15}N$. ($\frac{1}{2}$ Mark)

IV. Explain whether $^{14}N^{15}N$ will show a rotational infrared spectrum. ($\frac{1}{2}$ Mark)

iii) I. The first rotational line of $^{12}C\ ^{16}O$ is observed at 3.84235$cm^{-1}$and that of $^{13}C\ ^{16}O$ at 3.67337cm^{-1}. Calculate the atomic weight of $^{13}C\ ^{16}O$, assuming the mass of ^{16}O to be 15.9949. (2 marks)

II. Treating each molecule as a rigid rotor, calculate the frequency of the 1-0, 3-2 and 5-4 rotational transitions of $^{12}C^{16}O$ (B=57.64GHz), $^{1}H^{35}Cl$ (B=313.0GHz) and $^{27}Al^{19}F$ (B=16.56GHz) and indicate the region of the spectrum in which they appear. (3 marks)

b) i) Use the separation of the R(2) and P(3) lines of $^{1}H^{35}Cl$ figure 10.2 to obtain an estimate of the bond length. Given that m (^{1}H) =1.01u and m (^{35}Cl) =34.97u. Explain why it would not be beneficial to use the separation of lines with larger J-values. ($3\frac{1}{2}$ marks)

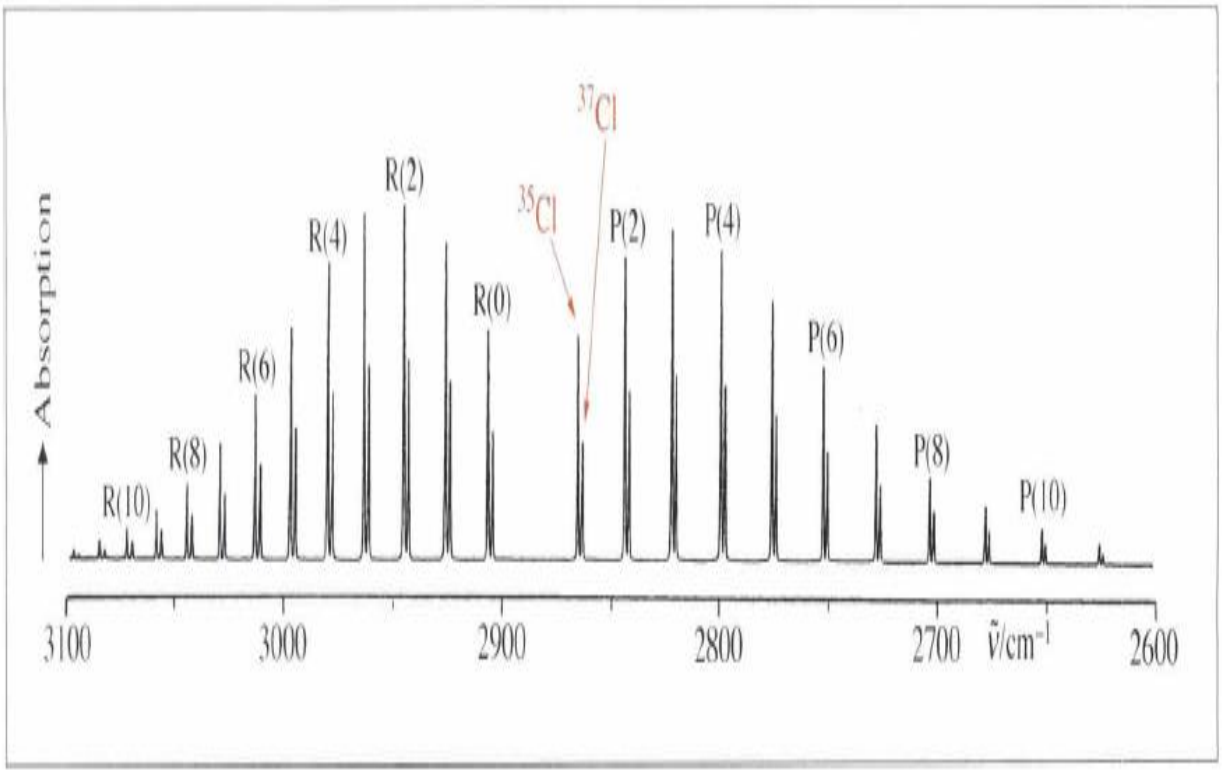


Figure 10.2: Rotational fine structure of the v=1-0 infrared spectrum of HCl

ii) Explain how nuclear quadrupole can be used for studying the nature of chemical bond.

(3 marks)

QUESTION FOUR (20 MARKS)

(a) i) Discuss the theory of microwave spectroscopy. (3 marks)

ii) Describe the common instrumentation features amongst near infrared, the fundamental infrared and far infrared and state their differences. (4 marks)

iii) Explain why in Raman spectra the stoke's lines are far more intense than the antistoke's lines which are sometimes too weak to be observed. (2 marks

iv) I. Explain why spectra of solutions in the ultraviolet and visible regions tend to consist of a few broad peaks whereas the same solutions measured using infrared show many sharp peaks.

(2 marks)

II. Explain why the ultraviolet spectrum of benzene vapour contains many sharp bands whereas the same spectrum of benzene solution in alcohol lacks fine detail and consists only of broad peaks.

(2 marks)

(b) i) Explain the mechanism of hyperfine interaction in the ESR spectra of organic radicals. (3 marks)

ii) Explain why nuclei such as ^{12}C, ^{16}O which do not possess nuclear spin do not show NMR spectra. (1 mark)

iii) Consider the following reaction;

$N_2F_4 \rightleftharpoons 2NF_2$. Suggest an ESR experiment to obtain the various thermodynamic quantities. (3 marks)

Table F.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	1 kg m^{-1} s^{-2} 1 N m^{-2}	pascal, Pa
Energy	1 kg m^2 s^{-2} 1 N m 1 Pa m^3	joule, J
Power	1 kg m^2 s^{-3} 1 J s^{-1}	watt, W

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

Table F.3 Common SI prefixes

Prefix	y	z	a	f	p	n	μ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}
Prefix	**da**	**h**	**k**	**M**	**G**	**T**	**P**	**E**	**Z**	**Y**
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10^2	10^3	10^6	10^9	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

INTERNATIONAL ATOMIC MASSES*

Name	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	[227]
Aluminium	Al	13	26.9815385(7)
Americium	Am	95	[243]
Antimony	Sb	51	121.760(1)
Argon	Ar	18	39.948(1)
Arsenic	As	33	74.921595(6)
Astatine	At	85	[210]
Barium	Ba	56	137.327(7)
Berkelium	Bk	97	[247]
Beryllium	Be	4	9.0121831(5)
Bismuth	Bi	83	208.98040(1)
Bohrium	Bh	107	[270]
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.414(4)
Calcium	Ca	20	40.078(4)
Californium	Cf	98	[251]
Carbon	C	6	12.011
Cerium	Ce	58	140.116(1)
Cesium	Cs	55	132.90545196(6)
Chlorine	Cl	17	35.45
Chromium	Cr	24	51.9961(6)
Cobalt	Co	27	58.933194(4)
Copernicum	Cn	112	[285]
Copper	Cu	29	63.546(3)
Curium	Cm	96	[247]
Darmstadtium	Ds	110	[281]
Dubnium	Db	105	[270]
Dysprosium	Dy	66	162.500(1)
Einsteinium	Es	99	[252]
Erbium	Er	68	167.259(3)
Europium	Eu	63	151.964(1)
Fermium	Fm	100	[257]
Flerovium	Fl	114	[289]
Fluorine	F	9	18.998403163(6)
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.25(3)
Gallium	Ga	31	69.723(1)
Germanium	Ge	32	72.630(8)
Gold	Au	79	196.966569(5)
Hafnium	Hf	72	178.49(2)
Hassium	Hs	108	[270]
Helium	He	2	4.002602(2)
Holmium	Ho	67	164.93033(2)
Hydrogen	H	1	1.008
Indium	In	49	114.818(1)
Iodine	I	53	126.90447(3)
Iridium	Ir	77	192.217(3)
Iron	Fe	26	55.845(2)
Krypton	Kr	36	83.798(2)
Lanthanum	La	57	138.90547(7)
Lawrencium	Lr	103	[262]
Lead	Pb	82	207.2(1)
Lithium	Li	3	6.94
Livermorium	Lv	116	[293]
Lutetium	Lu	71	174.9668(1)
Magnesium	Mg	12	24.305
Manganese	Mn	25	54.938044(3)
Meitnerium	Mt	109	[278]
Mendelevium	Md	101	[258]
Mercury	Hg	80	200.592(3)
Molybdenum	Mo	42	95.95(1)
Neodymium	Nd	60	144.242(3)
Neon	Ne	10	20.1797(6)
Neptunium	Np	93	[237]
Nickel	Ni	28	58.6934(4)
Niobium	Nb	41	92.90637(2)
Nitrogen	N	7	14.007
Nobelium	No	102	[259]
Osmium	Os	76	190.23(3)
Oxygen	O	8	15.999
Palladium	Pd	46	106.42(1)
Phosphorus	P	15	30.973761998(5)
Platinum	Pt	78	195.084(9)
Plutonium	Pu	94	[244]
Polonium	Po	84	[209]
Potassium	K	19	39.0983(1)
Praseodymium	Pr	59	140.90766(2)
Promethium	Pm	61	[145]
Protactinium	Pa	91	231.03588(2)
Radium	Ra	88	[226]
Radon	Rn	86	[222]
Rhenium	Re	75	186.207(1)
Rhodium	Rh	45	102.90550(2)
Roentgenium	Rg	111	[281]
Rubidium	Rb	37	85.4678(3)
Ruthenium	Ru	44	101.07(2)
Rutherfordium	Rf	104	[267]
Samarium	Sm	62	150.36(2)
Scandium	Sc	21	44.955908(5)
Seaborgium	Sg	106	[269]
Selenium	Se	34	78.971(8)
Silicon	Si	14	28.085
Silver	Ag	47	107.8682(2)
Sodium	Na	11	22.98976928(2)
Strontium	Sr	38	87.62(1)
Sulfur	S	16	32.06
Tantalum	Ta	73	180.94788(2)
Technetium	Tc	43	[97]
Tellurium	Te	52	127.60(3)
Terbium	Tb	65	158.92535(2)
Thallium	Tl	81	204.38
Thorium	Th	90	232.0377(4)
Thulium	Tm	69	168.93422(2)
Tin	Sn	50	118.710(7)
Titanium	Ti	22	47.867(1)
Tungsten	W	74	183.84(1)
Ununoctium	Uuo	118	[294]
Ununpentium	Uup	115	[289]
Ununtrium	Uut	113	[285]
Uranium	U	92	238.02891(3)
Vanadium	V	23	50.9415(1)
Xenon	Xe	54	131.293(6)
Ytterbium	Yb	70	173.045(10)
Yttrium	Y	39	88.90584(2)
Zinc	Zn	30	65.38(2)
Zirconium	Zr	40	91.224(2)