Mahindra University Hyderabad

École Centrale School of Engineering
End-semester Regular Examination

Program: B. Tech. **Branch: All** **Year: I** **Semester: I**
Subject: Chemistry - I (CH-1101)

Date: 29/12/2022 **Start Time: 9:00 AM**
Time Duration: 3 Hours **Max. Marks: 100**

Instructions:

1) *No clarifications will be entertained during the examination.*
2) *If any information is missing make appropriate assumptions and proceed.*
3) *Some relevant physical constants and molecular spectroscopic data are given below.*

Fundamental constants:

Speed of light (c) = 2.997 x 10^{8} m s^{-1}
Mass of electron (m_e) = 9.109 x 10^{-31} kg
Plank's constant (h) = 6.626 x 10^{-34} J s
Rydberg Constant (R_H) = 109677 cm^{-1}
Avogadro's number (N_A) = 6.023 x 10^{23} mol^{-1}
Boltzmann constant (k_B) = 1.381 x 10^{-23} J K^{-1}

Typical functional group positions in IR spectra (cm^{-1}):
(s-strong; m-medium; w-weak in intensity)

3600–2500 (s)	–O–H stretch
3500–3330 (m)	–N–H stretch
3300–3200 (m)	≡C–H stretch (alkyne)
3100–3000 (w)	=C–H stretch (alkene)
3000–2850 (w)	–C–H stretch (alkane)
2250 – 2200 (s)	–C≡N stretch
2250–2100 (w)	–C≡C– stretch alkynes
1800–1600 (s)	–C=O stretch carbonyls
1700–1600 (w)	–C=C– stretch (alkenes)
1600–1400 (w)	–C=C– stretch (aromatic)
1300–1000 (s)	–C–O stretch

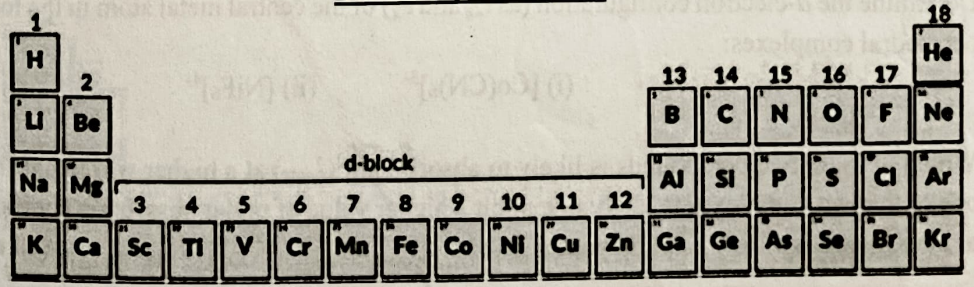
Some useful conversion factors:

1 eV = 1.602 x 10^{-19} J

^{1}H NMR chemical shift data (ppm):

C-H protons:	
Alkyl protons (–CH_3, –CH_2–, >CH–)	0.9 – 1.7
Alkyne protons (–C≡CH)	1.8 – 3.1
Alkyl attached to carbonyl (O=C–CH)	2.2 – 3.0
Alkyl attached to aromatic ring	2.3 – 3.0
Alkyl attached to electronegative atom	3.1 – 4.1
Alkene protons (C=CH)	4.6 – 5.9
Aromatic protons (Ph–H)	6.0 – 8.5
Aldehydic protons (R–CHO)	9.3 – 10.5
O-H protons:	
Alcohol (R–OH)	2.0 – 6.0
Phenol (Ar–OH)	4.0 – 12.0
Carboxylic acid (R–COOH)	10.0 – 13.2
N-H protons:	
Alkyl amine (R–NH_2)	1.0 – 5.0
Aryl amine (Ar–NH_2)	3.0 – 6.0
Amide (R–CO–NH_2)	5.0 – 12.0

***Truncated* periodic table**



Spectrochemical series (based on the strength of ligands):

(Weak ligand) $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^- < CO$ (Strong ligand)

1) Determine the energy changes, in cm^{-1}, of the lines of various series in the hydrogen atom spectrum for which n_2 values are given below: (a) Lyman, $n_2 = 5$; (b) Balmer, $n_2 = 8$; (c) Paschen, $n_2 = 4$; (d) Brackett, $n_2 = 8$; (e) Pfund, $n_2 = 6$. **(10 marks)**

2) Which of the following expressions are acceptable wavefunctions, and which are not? State why. **(10 marks)**

a. $\psi(x) = x^2 + 1$, where x can have any value

b. $\psi(x) = \pm\sqrt{x}$, where $x \geq 0$

c. $\psi(x) = \frac{1}{\sqrt{2}} sin\frac{x}{2}$, where $-\frac{\pi}{2} \leq x \leq \frac{\pi}{2}$

d. $\psi(x) = \frac{1}{4-x}$, where $0 \leq x \leq 10$

e. $\psi(x) = \frac{1}{4-x}$, where $0 \leq x \leq 3$

3) A particle is moving freely in a ring placed on a plane. Determine the normalization constant A for the wavefunction given below: **(10 marks)**

$$\psi(\phi) = Ae^{im_l\phi}$$

4) Vibrational ground state ($v = 0$) and first vibrational excited state ($v = 1$) in carbon monoxide are separated by an energy gap of about 2000 cm^{-1}. In a collection of carbon monoxide molecules, determine the temperature (in K) at which 5% of the molecules will be found in the $v = 1$ state. **(10 marks)**

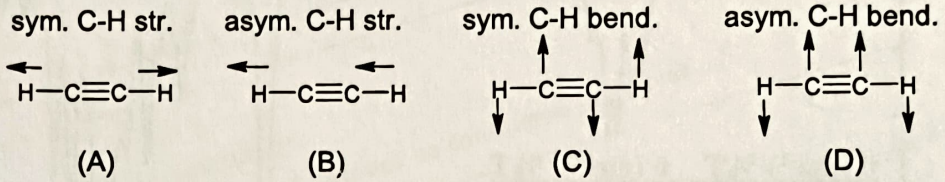
5) *1,3-Butadiene* (CH_2=CH–CH=CH_2) absorbs UV light at a wavelength (λ_{max}) of 217 nm. Assign this to an electronic transition. Qualitatively, where do you expect this transition to occur in *ethylene* (CH_2=CH_2) compared to *1,3-Butadiene* (CH_2=CH–CH=CH_2). UV-visible spectrum of a solution containing certain amount of *1,3-Butadiene* (measured using a sample cell of length 1.0 cm) shows an absorbance (A) of 1.05 at 217 nm. Determine the amount (in *milligrams*) of *1,3-Butadiene* present in 1.0 L of the solution, given that the molar absorption coefficient (ε) of *1,3-Butadiene* at 217 nm is 21,000 mol^{-1} L cm^{-1}. **(10 marks)**

6) Determine the *d*-electron configuration (as t_{2g} and e_g) of the central metal atom in the following octahedral complexes:

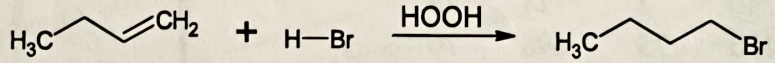
(i) $[Co(CN)_6]^{3-}$ (ii) $[NiF_6]^{4-}$

Which of these two compounds is likely to absorb light (λ_{max}) at a higher wavelength? Which one of the two complexes is likely to exhibit a higher value of molar absorption coefficient (ε) at their respective λ_{max}? Explain your answer. **(10 marks)**

7) How many normal modes of vibrations do you expect to see in acetylene (H–C≡C–H)? Four of the normal modes of acetylene are shown below (A) – (D). Determine whether each of them is IR active or IR inactive. Draw at least one other normal mode not listed below and specify its IR activity. If one of the hydrogens of acetylene is replaced by a fluorine (H–C≡C–F), determine the IR activity of the corresponding symmetric stretching mode (A). **(10 marks)**

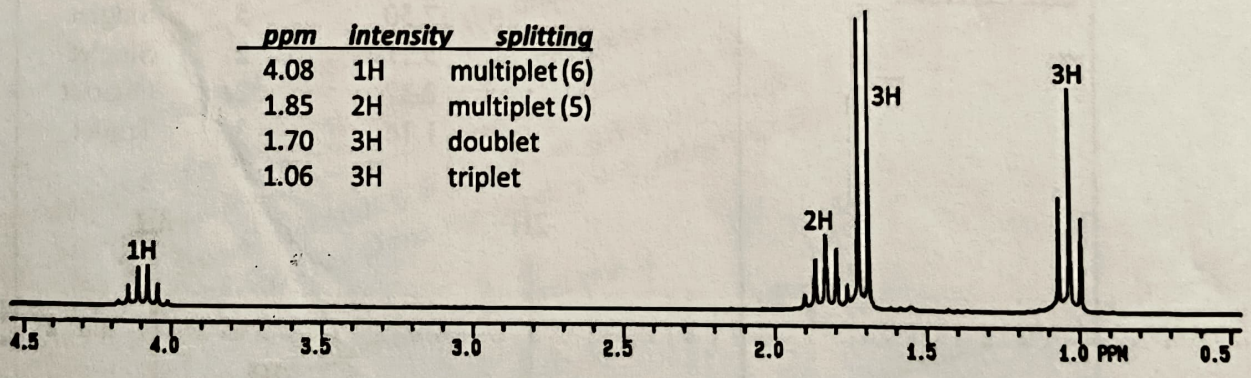


8) An organic chemist performs the following Anti-Markovnikov's addition reaction intending to obtain a product as per the below reaction.

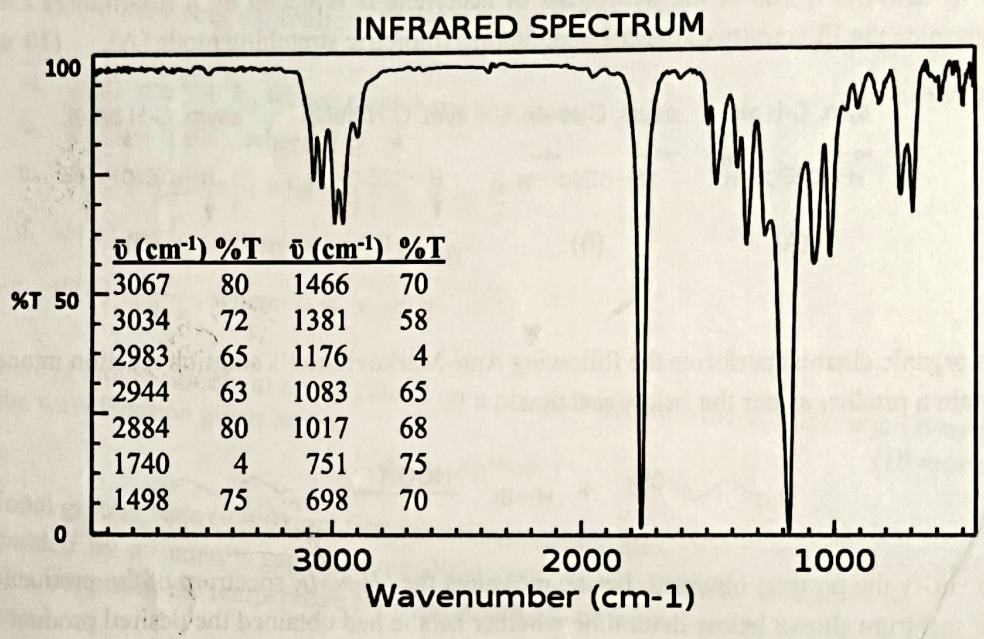


To verify the product obtained, he/she measures the *^{1}H-NMR* spectrum of the product. Using the spectrum shown below determine whether he/she had obtained the desired product or not. Explain your answer in detail by interpreting all the peaks in the spectrum. **(10 marks)**

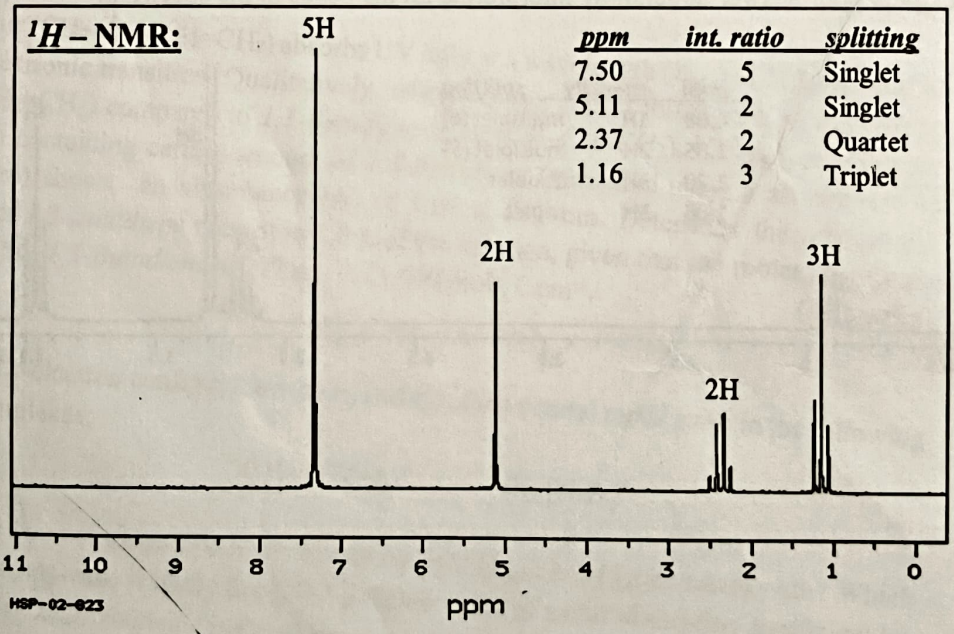
ppm	intensity	splitting
4.08	1H	multiplet (6)
1.85	2H	multiplet (5)
1.70	3H	doublet
1.06	3H	triplet



2) Determine the exact chemical structure of the organic compound of molecular formula $C_{10}H_{12}O_2$ from the IR and ^1H-NMR spectrum given below. Explain your answer in detail. Important spectroscopic peaks are listed along with the spectra for clarity. **(20 marks)**



$\bar{\upsilon}$ (cm^{-1})	%T	$\bar{\upsilon}$ (cm^{-1})	%T
3067	80	1466	70
3034	72	1381	58
2983	65	1176	4
2944	63	1083	65
2884	80	1017	68
1740	4	751	75
1498	75	698	70



ppm	*int. ratio*	*splitting*
7.50	5	Singlet
5.11	2	Singlet
2.37	2	Quartet
1.16	3	Triplet