

Total number of printed pages-9

14 (CHM-1) CH 105

2019

CHEMISTRY

Paper : CH-105

(Spectroscopy-I)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

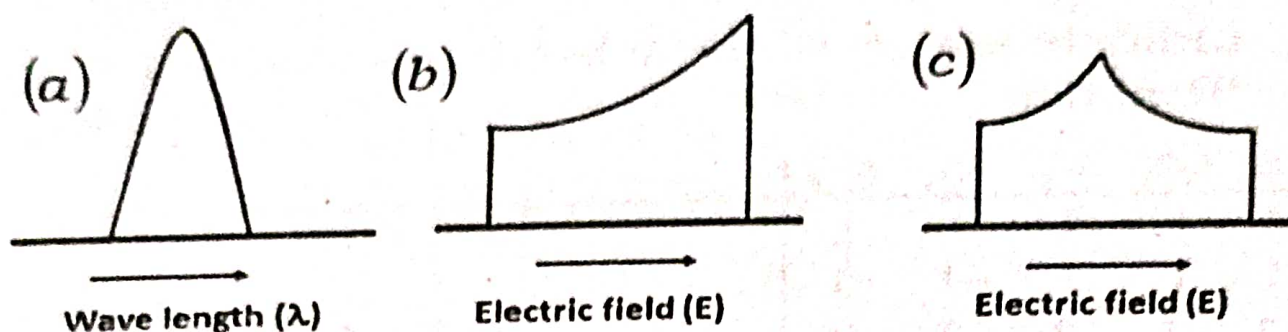
1. Answer **any five** questions : $3 \times 5 = 15$

- (a) How is stimulated emission different from induced emission? Give one example for each of these emissions.

Contd.

- (b) Using an appropriate mathematical expression, explain how the natural line broadening of spectral line depends on frequency. Write the typical values for the frequency spread for excited electronic and rotational states.
- (c) In IR spectroscopy, the signal is recorded as a function of length domain instead of a time domain. Explain why. Sketch the curve you would expect from the Fourier transformation of a sine wave.
- (d) Explain why the $C=O$ stretching vibration of an aldehyde gives rise to very strong absorption in the infra-red, but the absorption due to $C=C$ vibration in an alkene is normally very weak.
- (e) Describe very briefly one method for the preparation of a solid sample for IR measurement. Write one disadvantage of the Nujol mull method.
- (f) How does the stretching frequency of dioxygen change upon its binding with hemoglobin and hemerythrin in Raman spectrum ?

(g) Sketch the first order derivative of the following absorption spectra :



2. Which type of vibrational spectroscopy (IR or Raman) would one use to measure the vibrational frequency of the following bonds ?

3

- (i) The stretching frequency of $^{14}\text{N}-^{15}\text{N}$
- (ii) The $\text{C}=\text{O}$ stretch in acetone, CH_3COCH_3
- (iii) The $\text{C}\equiv\text{C}$ stretch in ethyne, C_2H_2

OR

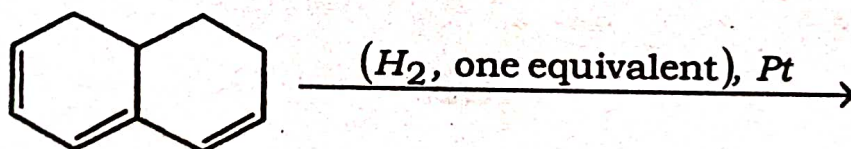
A space probe equipped with a microwave spectrometer was designed to seek the atmospheric CO in Saturn. Find the wavenumbers for first three rotational lines which will confirm its presence. What resolution would be required to determine the isotopic ratio of ^{13}C to ^{12}C in Saturn by measuring the first three rotational lines ? (Bond length of CO is 112.8 pm.)

3. CH_4 belongs to the T_d group. Using the character table for this point group, obtain the representation for the vibration modes. Indicate which of the vibrational modes are IR active. 4

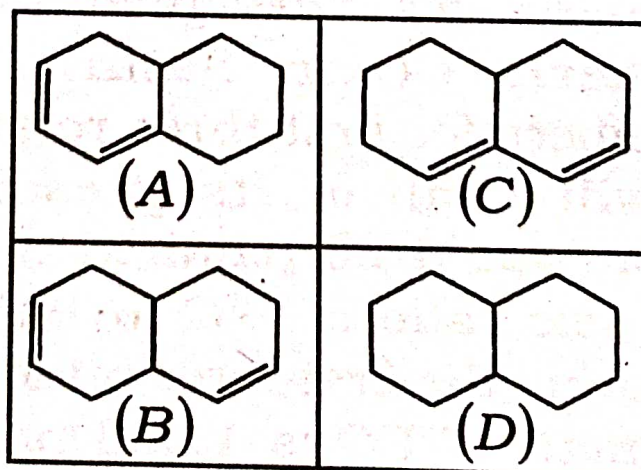
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xz, yz, xy)

4. For the following questions, find the correct answer and provide short justification for your answer. (Answer **any five** questions) $4 \times 5 = 20$

- (a) The λ_{max} of the product of the following hydrogenation reaction is 234 nm.



The correct reaction product is



- (b) Which of the following pairs of molecules provide two and three rotational constants in the microwave spectra, respectively ?

(A) H_2O and CH_4
(B) CH_3I and C_6H_6
(C) HCl and $HCHO$
(D) C_6H_6 and H_2O

- (c) A molecule A_2B_2 has infra-red absorptions and Raman spectral lines as given in the following table :

cm^{-1}	Infra-red	Raman
3374	—	Strong
3287	Very strong, <i>PR</i> contour	—
1973	—	Very strong
729	Very strong, <i>PQR</i> contour	—
612	—	Weak

The structure of A_2B_2 corresponds to

(A) $CH \equiv CH$
(B) $CH \equiv CCl$
(C) $ClC \equiv CCl$
(D) $(CN)_2$

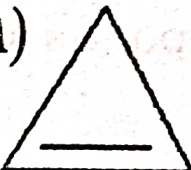
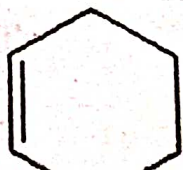
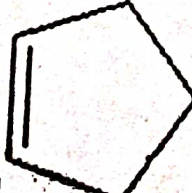
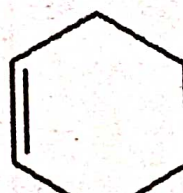
(d) HCHO belongs to the C_{2v} group, for which the character table is shown below :

C_{3v}	E	C_2	$\sigma_v(x, z)$	$\sigma'_v(y, z)$		
A_1	1	1	1	1	z	xx, yy, zz
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The labelling of the transition which results from $n \rightarrow \pi^*$ electronic transition is

(A) $A_2 \leftarrow A_1$
(B) $A_1 \leftarrow A_2$
(C) $A_2 \leftarrow B_1$
(D) $B_2 \leftarrow B_1$

(e) Which of the following pairs of molecules provide highest and lowest internal double bond absorption frequencies in IR spectra, respectively ?

(A)  and 	(C)  and 
(B)  and 	(D)  and 

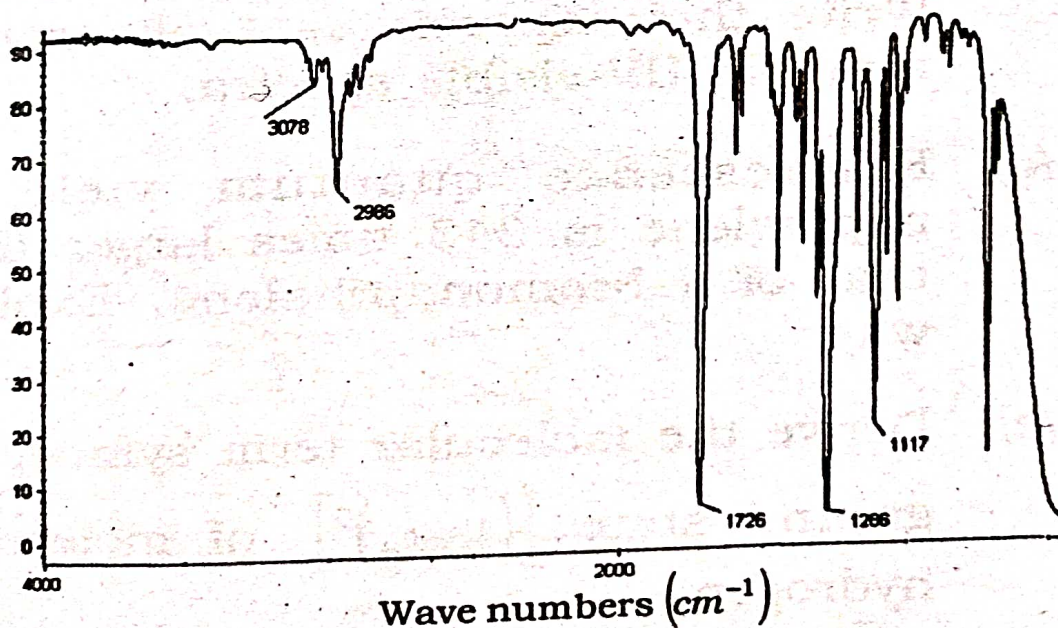
- (f) H_2O belongs to the C_{2v} group, for which the character table is shown below :

C_{3v}	E	C_2	$\sigma_v(x, z)$	$\sigma'_v(y, z)$		
A_1	1	1	1	1	z	xx, yy, zz
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, Ry	xz
B_2	1	-1	-1	1	y, R_x	yz

The Mulliken symbol for the asymmetric stretching vibration is

- | |
|-----------|
| (A) A_1 |
| (B) A_2 |
| (C) B_1 |
| (D) B_2 |

- (g) In the following IR spectrum of ethyl benzoate, peaks at 2986, 1726 and 1117 cm^{-1} correspond to



(A) CH stretch (alkyl), C = O stretch and C-O stretch
(B) CH stretch (aromatic), C = O stretch and C-O stretch
(C) CH stretch (aromatic), C = O stretch and CH ₂ bending
(D) CH stretch (alkyl), C = O stretch and CH ₂ stretch

5. Answer **any six** questions :

3×6=18

- (a) Using a suitable energy scheme, explain why longer the conjugated system greater is the wavelength of absorption maxima.
- (b) What are two light sources used in fluorescence spectroscopy? Why is the fluorescence measured at 90° to the incident beam?
- (c) Write *two* different classes of chromophores present in proteins. Write their approximate absorption range in UV-visible spectra.
- (d) Fluorescence quantum yield of naphthalene is 343 times larger than that of 1-bromonaphthalene. Explain why.
- (e) Derive the molecular term symbol for ground state $\left[(1s\sigma_g)^2\right]$ of molecular hydrogen.

(f) Chloromethane has an absorption maximum at 172 nm, bromomethane shows an absorption at 204 nm, and iodomethane shows a band at 258 nm. What type of transition is responsible for each band? How can the trend of absorption be explained?

(g) What is static fluorescence quenching? How is it different from dynamic quenching?

(h) Draw the CD and ORD curves for a pair of enantiomers.

(i) How is CD different from ORD? Write the minimum amount of samples required for each technique.

(j) Using octant rule, determine the sign of the Cotton effect of

