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14 (CHM-1) 105

2021
(Held in 2022)

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 eight*** of the following questions : 5×8=40

(a) What are the units of Einstein co-efficient A and B ? Can a three-level system lead to population inversion at equilibrium?

Contd.

- (b) The spectral line shape is never perfectly Gaussian or Lorentzian but is a convolution of Gaussian and Lorentzian line shape function. Briefly explain this statement. Calculate the full width at half maximum of the following homogeneous line function.

$$f(\nu - \nu_0) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(\nu - \nu_0)^2 / (2\sigma^2)}$$

- (c) Write the rate expression for an absorption process that relates rate of transition per unit time with transition moment integral in two-level system. Briefly explain its significance. Use this expression further to show that Einstein co-efficient for absorption and stimulated emission processes are identical.

- (d) State Raman Effect. How is the quantum mechanical construct "virtual state" different from "a stationary state"? Sketch suitable energy level diagram to depict the origin of Stokes and anti-Stokes lines.

- (e) Using the C_{2v} character table of the H_2O molecule, deduce the expression for the irreducible representation of vibrational modes. Indicate the IR activity of these vibrational modes.

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

- (f) Why is it difficult to observe the anti-Stokes lines in vibrational Raman spectroscopy? Which type of vibrational spectroscopy (IR or Raman) would one use to measure the vibrational frequency of the following bonds?

The stretching frequency of $^{14}N-^{15}N$

The $C=O$ stretch in acetone, CH_3COCH_3

The $C\equiv C$ stretch in ethyne, C_2H_2

- (g) Describe very briefly, two different sample preparation methods for IR measurement.

(h) Why is it difficult to measure time domain spectrum directly with infrared radiations? How do you solve this problem to measure signal in Fourier transform IR measurement? Sketch the Fourier transformation of a cosine wave.

(i) Pick the microwave active molecules of the following molecules and classify them on the basis of moment of inertia. H_2 , HCl , CH_4 , CH_3Cl , $CH_2=CHCl$, H_2O and BCl_3 .

(j) Using the following total energy eigenfunctions for the three-dimensional rigid rotor, show that $J=0 \rightarrow J=1$ transition is allowed, and that $J=0 \rightarrow J=2$ transition is forbidden. For calculating transition moment integral, assume that electromagnetic field lies along z-axis.

$$Y_0^0(\theta, \varphi) = \frac{1}{(4\pi)^{1/2}}$$

$$Y_1^0(\theta, \varphi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos(\theta)$$

$$Y_2^0(\theta, \varphi) = \left(\frac{5}{16\pi}\right)^{1/2} [3\cos^2(\theta) - 1]$$

(k) The microwave spectrum of the carbon oxysulphide (OCS) is shown in the following data table.

$J \rightarrow J+1$	$\bar{\nu}_{obs.} (cm^{-1})$	$\Delta\bar{\nu}$	$B (cm^{-1})$
$0 \rightarrow 1$		2×0.4055	0.2027
$1 \rightarrow 2$	0.8109	0.4054	0.2027
$2 \rightarrow 3$	1.2163	0.4054	0.2027
$3 \rightarrow 4$	1.6217	0.4054	0.2027
$4 \rightarrow 5$	0.0271		

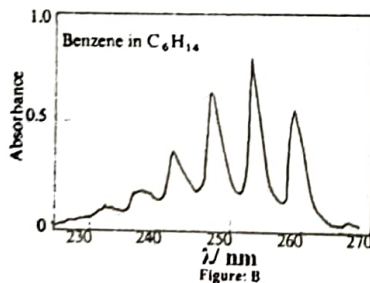
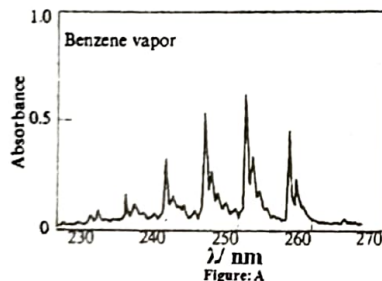
From this data, can you comment about the impact of centrifugal distortion on B values? Calculate the moment of inertia from the B value. How can you calculate the individual CO and CS bond distances for OCS?

(l) How do you distinguish a hydrogen-bonded OH group from a free OH group in an IR spectrum? Explain why the C=O stretching vibration of an aldehyde gives rise to very strong absorption in the infra-red, yet the absorption due to C=C vibration in an alkene is normally very weak.

(m) Can one measure rotational spectrum of a molecule in a liquid or solid phase? Sketch the rotational spectrum of (i) natural abundant CO and (ii) 50% C labeled CO.

2. Explain **any four** of the following questions :
5×4=20

(a) State Franck-Condon principle. Benzene vapour (Figure A) and benzene in n-hexane (Figure B) display electronic absorption spectra as given below. Justify the vibrational signatures observed in the electronic spectra. 1+4=5



(b) Show how increase in conjugation results in red shift of the $\pi-\pi^*$ transition in a molecule with the help of suitable examples. Draw a representative electronic absorption spectrum of lycopene and comment on the observed wavelength of maximum absorption (λ_{max}). 3+2=5

(c) Illustrate with the help of suitable examples how change in pH and polarity of solvent can lead to significant changes in the electronic absorption spectra of chromophores. 2.5×2=5

(d) Draw a Perrin-Jablonski diagram showing various photophysical processes. Comment on the time-scale and lifetime of various processes. 2+3=5

(e) What is Stokes shift? Discuss how extend of π -electron system and presence of heavy atoms as substituents on aromatic hydrocarbons affect their fluorescence emission. 1+4=5

(f) What are static and dynamic quenching of fluorescence? How can you differentiate between them by measurement of fluorescence lifetime of a fluorophore in presence of a quencher?
2+3=5

(g) How is CD different from ORD? Draw the CD and ORD curves for a pair of enantiomers. Write the minimum amount of samples required for each technique.
2+2+1=5