

Total number of printed pages-15

14 (CHM-1) 105

2018

CHEMISTRY

Paper : CH 105

(Spectroscopy-I)

Full Marks : 60

Time : 2½ hours

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

1. Answer **any two** questions : 2×3=6

- (a) What is the difference between spontaneous and stimulated emissions? Give examples.
- (b) Explain how the Doppler effect causes line broadening.
- (c) Why is the frequency spread for an excited electronic state is much larger than that of an excited rotational state? Explain using appropriate mathematical expression.

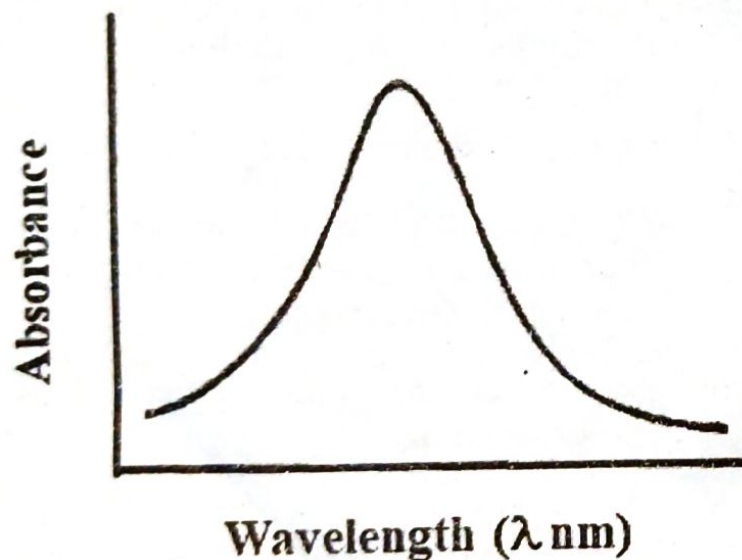
Contd.

2. Answer **any one** question :

2

(a) For Fourier transformation, the signal is recorded in the length domain instead of a time domain in IR spectroscopy. Explain briefly why.

(b) Sketch the first order and second order derivative spectrum of the following absorption spectrum. Write one advantage of a such spectrum representation.



(c) How does the oscillator strength provide information in UV-visible spectroscopy? Explain briefly.

3. Benzene. C_6H_6 belongs to the D_{6h} group. The character table for this point group is shown below. The reducible representation for the vibration modes is

4

$$\Gamma_{\text{reducible}} = 2A_{1g} + A_{2g} + A_{2u} + 2B_{1u} + 2B_{2g} + 2B_{2u} + E_{1g} + 3E_{1u} + 4E_{2g} + 2E_{2u}$$

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	σ_h	$2S_6$	$2S_6^5$	σ_v	$3\sigma_v$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1		
B_{1g}	1	-1	1	1	-1	-1	1	-1	1	1	-1	-1		
B_{2g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
E_{1g}	2	1	-1	2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1		
B_{2u}	1	-1	1	-1	1	-1	-1	-1	1	-1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
E_{2u}	2	-1	-1	-2	0	0	-2	1	-1	-2	0	0		

Answer the following questions with very brief explanations :

- How many of these modes are infrared active and to which representation do they belong?
- Which of the infrared active modes are degenerated in energy and what is the degeneracy for each?
- How many of these modes are Raman active and to which representation do they belong?
- Which of the infrared modes are also Raman active?

Or

NH_3 belongs to the C_{3v} group for which the character table is shown below. Show that reducible representation for vibrational modes is $\Gamma_{\text{reducible}} = 2A_1 + 2E$

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2-y^2, xy), (xz, yz)$

4. For the following questions, find the correct answer and provide justification for your answer : (Answer **any four** questions)

$$4 \times 5 = 20$$

- (a) The transition moment integral for a rotational transition between $J=1; M_j=0$ and $J=2; M_j=0$ states for a diatomic molecule along the z -axis is proportional to

A) $\int_0^\pi \cos^2 \theta (3\cos^2 \theta - 1) d\theta$
B) $\int_0^\pi \cos^2 \theta (3\cos^2 \theta - 1) \sin \theta d\theta$
C) $\int_0^\pi \cos \theta (3\cos^2 \theta - 1) \sin \theta d\theta$
D) $\int_0^\pi \cos \theta (3\cos^2 \theta - 1) \sin^2 \theta d\theta$

- (b) The microwave spectrum of a molecule gives three rotational constants. The molecule is,

A) Prolate symmetric top
B) Oblate symmetric top
C) Spherical top
D) Asymmetric top

- (c) For a diatomic molecule HBr , the energy for the rotational transition from $J=0$ to $J=1$ state is 10 cm^{-1} . The energy for the rotational transition from $J=3$ to $J=4$ state would be,

A) 10 cm^{-1}
B) 20 cm^{-1}
C) 30 cm^{-1}
D) 40 cm^{-1}

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D) 40 cm^{-1}

(d) For which of the following molecule, the conjugation effect increases the CO stretching frequency in IR spectrum,

A)	
B)	
C)	
D)	

(e) Which of the following pair of molecules provide highest and lowest CO stretching frequencies in IR spectra, respectively,

A)	
B)	
C)	
D)	

(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, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Vibrational transition from the ground state of A_1 symmetry to excited state of B_2 symmetry is possible only if

A) Allowed with x polarization
B) Allowed with y polarization
C) Allowed with z polarization
D) None of the above

5. Answer **any two** of the following questions :

3×2=6

- How do you distinguish between *cis*- and *trans*-dichloroethene using microwave and IR spectroscopy?
- Which vibrational spectroscopic method would be most appropriate in order to study the following systems? Explain why.

K_2PdBr_4 , O_2 and Very dilute samples

c) The Raman spectra of C_6D_6 absorbed on the Ag surface gives two bands? Write the approximate frequencies and intensities of these bands? What are different types of vibrations for which these bands were observed?

d) Raman spectrum of $[Co(NH_3)_5O_2]^{5+}$ shows a strong band at 1122 cm^{-1} , but this band is absent in IR spectrum. Mention the nature of dioxygen present and the structure of the compound.

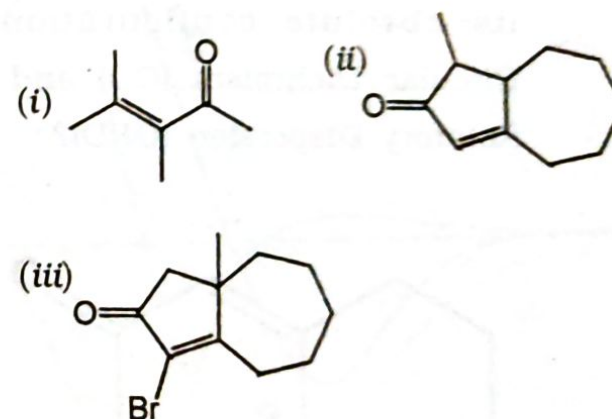
6. Explain **very briefly any five** of the following observations : 2×5=10

- The λ_{max} of Biphenyl is at 252 nm with an ϵ_{max} of 19,000 whereas λ_{max} of 2,2'-Dimethylbiphenyl is at 270 nm with an ϵ_{max} of 800.
- The $\pi \rightarrow \pi^*$ transition for anthracene shows bathochromic shift when the solvent is changed from hexane to methanol.

- c) Tetracyanoethylene is colorless by itself but it gives a blue colored solution in aniline.
- d) Phosphorescence quantum yield of molecules increase greatly in frozen solvents.
- e) Fluorescence quantum yield of naphthalene is 0.55 whereas that of 1-Bromonaphthalene is 0.0016.
- f) The λ_{max} of 4-Nitroaniline is red-shifted compared to that of 2-Nitroaniline.
- g) The fine structures of Benzene in its liquid form are blurred out whereas the structures are well resolved in vapor phase.
- h) 1, 3-dialkyl substitution of butadiene is accompanied with bathochromic shift and hypochromic effect.

7. Answer **any two** the following questions :
3×2=6

- a) With the help of a neat diagram explain why BeH_2 in its ground state or BeH_2^+ are linear but BeH_2 in its excited state is bent.
- b) Calculate the λ_{max} values for the following. Use the table provided in the appendix.

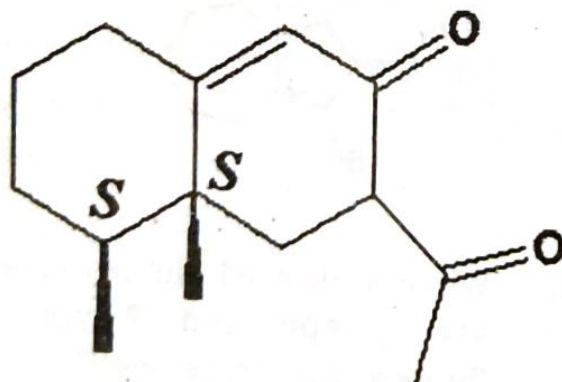


- c) What is delayed fluorescence? What are E-type and P-type delayed fluorescence processes?

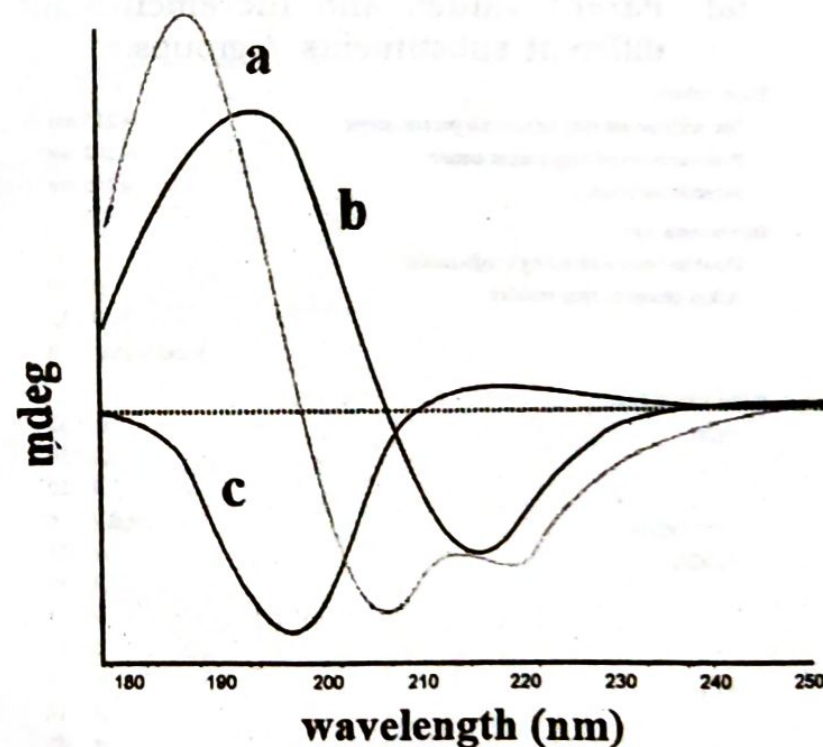
- d) What is static fluorescence quenching?
How is it different from dynamic quenching?

8. Answer **any two** of the following questions :
3×2=6

- a) Two stereogenic centers of following molecule have a relative configuration of SS (or RR)? How do you ascertain its absolute configuration using Circular Dichroism (CD) and Optical Rotatory Dispersion (ORD)?



- b) The CD curve of a protein is shown below. Assign the curves for α -helix, β -sheet and random coil structure? Mention about the type of electronic transitions for these CD curve.



- c) Define briefly CD. What is the necessary condition for a molecule, which is not pre-requisite in the case of ORD, to show CD effect? Mention about the sensitivity of a CD measurement in comparison with an ORD measurement.

Appendix :

- (a) Parent values and increments for different substituents / groups.

Base values:

Six-membered ring or acyclic parent enone	= 215 nm
Five-membered ring parent enone	= 202 nm
Acyclic dienone	= 245 nm

Increments for:

Double-bond-extending conjugation	30
Alkyl group or ring residue	α 10
	β 12
	γ and higher 18

Polar groupings:

-OH	α 35
	β 30
	δ 50
-OCOCH ₃	α, β, δ 6
-OCH ₃	α 35
	β 30
	γ 17
	δ 31
-Cl	α 15
	β 12
-Br	α 25
	β 30
-NR ₂	β 95
Exocyclic double bond	5
Homocyclic diene component	39

- b) Spherical harmonics

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

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