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Indian Institute of Science Education and Research Mohali

CHM 201: Spectroscopy and other physical methods

END-SEM Examination, 7th DEC, 2021

Total marks: 50; Time: 9.00 AM – 11.00 AM

*(**Important note:** Please write your Name and Roll No. on the Q-paper; please return the Q-Paper along with the answer sheet.)*

PART A- Objective type (10 x 1 = 10 Marks):

1. The unit of molar extinction coefficient:
   a. cmM^{-1} b. $cm^{-1}M^{-1}$
   c. $cm^{-2}M^{-2}$ d. $cm^{-1}M$
2. The major *difference* of Echelle grating *over* Echellette grating:
   a. Reflection from the short axis of the grating normal.
   b. Transmission from the short axis of the grating normal.
   c. Reflection from the long axis of the grating normal.
   d. Transmission from the long axis of the grating normal.
3. The frequency range of a modulating signal from a Michelson interferometer with $V_m = 0.2$ *cm/s* and $\lambda = 16\ \mu m$.
   a. 2500 Hz b. 250 Hz
   c. 500 Hz d. 5000 Hz
4. CH_4 (methane) is a:
   a. Prolate symmetric top b. Asymmetric top
   c. Spherical top d. Oblate symmetric top
5. Which of the following statement is correct?
   a. H_2 molecule can show *microwave rotational* spectrum.
   b. H_2 molecule can show *infrared vibrational* spectrum.
   c. H_2 molecule can show *vibrational-Raman* spectrum.
   d. H_2 molecule can show *rotational-Raman* spectrum.
6. For *anharmonic oscillator model*, the *overtone energy* is expressed in cm^{-1} as:
   a. $\bar{\omega}_e(1-2x_e)$ b. $2\bar{\omega}_e(1-2x_e)$
   c. $2\bar{\omega}_e(1-3x_e)$ d. $\bar{\omega}_e(1-3x_e)$
7. The total No. of fundamental *vibrational bending modes* available for *a non-linear molecule*:
   a. 3N-5 b. 3N-6
   c. 2N-5 d. 2N-6
8. The line separation in a *rotational-Raman* fine structure for *a linear molecule* will be:
   a. B (5J+4) b. B (4J+6)
   c. B (4J+5) d. B (6J+4)
9. In a polarization experiment, N_2O molecule shows a very strong/polarized Raman band at 1285 cm^{-1}. The band will be a:
   a. Symmetric stretching mode. b. Asymmetric stretching mode.
   c. In-plane bending mode. d. Out of-plane bending mode.
10. For *a several electron molecular system*, the orbital angular momentum *(Λ)=1*; the spin angular momentum *(Σ)=1*. The corresponding term symbol will be:
    a. $^1\Sigma_0$ b. $^1\Pi_0$
    c. $^3\Pi_2$ d. $^3\Delta_0$

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PART B- Match the following (5 x 1 = 5 Marks):

11.

(a) Photon	(i) Simple harmonic
(b) H_2O	(ii) Anharmonic
(c) Overtone	(iii) R-branch
(d) ΔJ = +1	(iv) Rotational-Raman
(e) ΔJ = +2	(v) Transverse wave
	(vi) Longitudinal wave
	(vii) P-branch
	(viii) Symmetric top
	(ix) Vibrational-Raman
	(x) Asymmetric top

PART C- Subjective type (5 x 2 = 10 Marks):

Q.1 12. The transmittance of $KMnO_4$ at *540 nm* is *10 % (0.1)* for a 10^{-4} *molar* solution in a *1 cm* quartz cuvette.
(a) What is the absorbance?
(b) Calculate the molar extinction coefficient.

Q.2 13. Rotational-vibrational spectrum of CO (carbon monoxide) shows a separation ($\Delta\bar{\nu}$) of *55* cm^{-1} at *300 K*. Calculate the approximate rotational constant B.

14. For *linear polyatomic molecules*, ΔJ = 0 is allowed in the case of vibrational modes *perpendicular to the principal axis*. Why?

Q.3 15. How many fundamental vibrational modes are available to $CHCl_3$ (chloroform)? How many of them are Raman active?

16. At higher vibrational quantum number 'v', the quantum and classical picture merge for a molecular system. Justify this statement and show it pictorially.

PART D- Descriptive type (2 x 5 = 10 Marks):

Q.4 17. (a) What are Stokes and Anti-Stokes lines in Raman spectroscopy?
(b) Show that: $\nu_{spec} = \nu_{ex} \pm \nu_{vib}$ (if $E = E_0 sin 2\pi\nu_{ex} t$) and define the Stokes and Anti-Stokes.
(c) What are the fundamental Raman and infrared active bands for CO_2 and H_2O molecules?

18. (a) What is Franck-Condon principle?
(b) What are the FOUR possible situations to get a vibrational progression due to Franck-Condon principle? Represent it pictorially.
(c) Is (0,0) transition is possible in a molecular electronic excitation? Why?
(d) What are the TWO major factors controlling the intensity of an electron transition other than Franck-Condon principle?

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PART E- Numerical problems (3 x 5 = 15 Marks):

Q.5

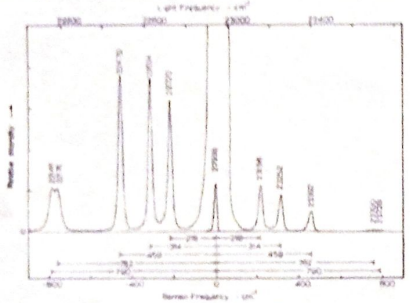
19. The vibrational wavenumbers of the following molecules in their $v = 0$ states are: HCl: 2885 cm^{-1}; DCl: 1990 cm^{-1}; D_2: 2990 cm^{-1} and HD: 3627 cm^{-1}. Calculate the energy change in *kJ/mol.*, of the reaction,

$$HCl + D_2 \longrightarrow DCl + HD$$

and determine whether energy is liberated or absorbed in this isotope exchange reaction.

Q.6

20. Vibrational-Raman bands of CCl_4 (carbon tetrachloride) is given below. Stokes and anti-Stokes lines are represented -δ and +δ, respectively.



(a) How many fundamental vibrational modes are available for CCl_4. Represent them in the form of a table given below:

Mode	Frequency (cm^{-1})	Degeneracy	Description	IR active	Raman active

(b) For temperature 20℃ and 40℃, calculate the ratio of intensity of Stokes and anti-Stokes lines for CCl_4 at (i) 218 cm^{-1} and (ii) 459 cm^{-1}. (*Hint: use Maxwell-Boltzmann distribution law*)

(c) Raman band at 790 cm^{-1} is not a fundamental mode. Guess what it would be?

Q.7

21. The value of $\overline{\omega_e}$ and x_e in the ground state ($^3\Pi_u$) and a particular excited state ($^3\Pi_g$) of C_2 are:

	$\overline{\omega_e}$	x_e
Ground state	1641·4 cm^{-1}	$7{\cdot}11 \times 10^{-3}$
Excited state	1788·2 cm^{-1}	$9{\cdot}19 \times 10^{-3}$

Use the equation, $v_{max} = \frac{1}{2x_e} - 1$, to find the number of vibrational energy levels below the dissociation limit and hence the ground state dissociation energy (D_0'') of C_2 extracted from both ground state and exited state.

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Important Formulae and universal constants:

1. $\varepsilon_J = BJ(J+1)$; $B = \frac{h}{8\pi^2 Ic}$
2. SHO, $\overline{\omega_{obs}} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$
3. Anharmonic; $\varepsilon_v = \left(v + \frac{1}{2}\right)\omega_e - x_e\left(v + \frac{1}{2}\right)^2 \omega_e$
4. Maxwell-Boltzmann distribution;

Rotational: $J_{max} = \sqrt{\frac{k_B T}{2hcB}} - \frac{1}{2}$

Rotational-vibrational: $v_{max} = \omega_0 \pm 2B\sqrt{\frac{k_B T}{2hcB}} + \frac{1}{2}$

5. $h = 6.626 * 10^{-34} Js$
6. $k_B = 1.38 * 10^{-23} J/K$
7. $c = 2.998 * 10^8 m/s$