

End-Sem-2021 - ANSWER KEY -

CHM-201 - Spectroscopy & other Physical Methods

Part A.

1. (b)  $\text{cm}^{-1} \text{m}^{-1}$
2. (a) Reflection from the short axis of the going normal.
3. (b)  $250 \text{ Hz}$  [ Hint:  $\frac{2\sqrt{m}}{\pi \cdot e} = f \Rightarrow \frac{2 \times 0.2 (\text{cm/s})}{16(\mu\text{m}) \times 10^{-8} (\text{cm}/\mu\text{m})} = 250 \text{ Hz}$  ]
4. (c) Spherical top
5. (d)  $\text{H}_2$ -molecules show rotational-Raman spectrum.
6. (c)  $2\bar{\omega}_e (1 - 3\chi_e)$
7. (c)  $2N - 5$
8. (b)  $B(4S + 6)$
9. (a) Sym. stretching mode.
10. (c)  ${}^3\pi_2$ .

Part B

11. (a) Photon ————— (ii) Transverse
- (b)  $\text{H}_2\text{O}$  ————— (x) Asymmetric top
- (c) overtones ————— (ii') Anharmonic
- (d)  $\Delta J = +1$  ————— (ii') R-branch
- (e)  $\Delta J = +2$  ————— (iv) Rotational-Raman.

### Part C

12.  $\text{KMnO}_4$  at 540 nm.

$$(a) \text{ Transmittance} = \frac{I}{I_0} = 0.1$$

$$\therefore \text{Absorbance} = \log_{10} \left( \frac{1}{T} \right) = \log_{10} \left( \frac{1}{0.1} \right) = \underline{\underline{1.0D}}$$

(b) Here  $A = \underline{\underline{1.0D}}$ .

$A = \text{E. e. l.}$

$$\text{So, } E = \frac{A}{c \cdot l} = \frac{1}{10^{-4} \text{ molar} \text{ cm}} = \underline{\underline{10,000 \text{ cm}^{-1} \text{ M}^{-1}}}$$

13. For Rotational - Vibrational spectrum.

Maxwell-Boltzmann distribution is :

$$v_{max} = \omega_0 \pm 2B \sqrt{\frac{k_B T}{2\pi c B}} + \nu_2$$

The separation b/w two maxima,

(Already given in the last session)

$$\Delta\nu = 4B \left( \sqrt{\frac{k_B T}{2Bhc}} + \nu_2 \right)$$

$$= \sqrt{\frac{8Bk_B T}{hc}} + 2B$$

if  $B$  is small,

$$\Delta\nu \approx \sqrt{8Bk_B T/hc}$$

$$\text{u, } B = \frac{h\nu_c (\Delta\nu)^2}{8k_B T} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{10} \text{ cm/s} \times (55 \text{ cm})^2}{8 \times 1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K}}$$

$$= \underline{\underline{1.8155 \text{ cm}^{-1}}}$$

14. In the case of vibration along the principal axis principle bond axis, there is an effective change in the vibrational dipole with no simultaneous rotational transition. i.e.,  $\Delta J = 0$ .

This result in a Q-branch with no fine-rotational lines.

$$\text{Here, } \Delta E = E_{J, 2J+1} - E_{J, J}.$$

$$= \left\{ 1/2 \bar{\omega}_e - 2 \frac{1}{4} x_e \bar{\omega}_e + BJ(J+1) \right\} -$$

$$\left\{ \frac{1}{2} \bar{\omega}_e - \frac{1}{4} x_e \bar{\omega}_e + BJ(J+1) \right\}$$

$$\bar{\nu}_Q = \bar{\omega}_e \text{ cm}^{-1} \text{ for all } J \text{ (for linear molecule)} \\ \text{in SHO model.}$$

15.  $\text{CHCl}_3$  - (Non-linear) - Symmetric top

$$3N-6 = 3 \times 5 - 6 = 9 \text{ Modes.}$$

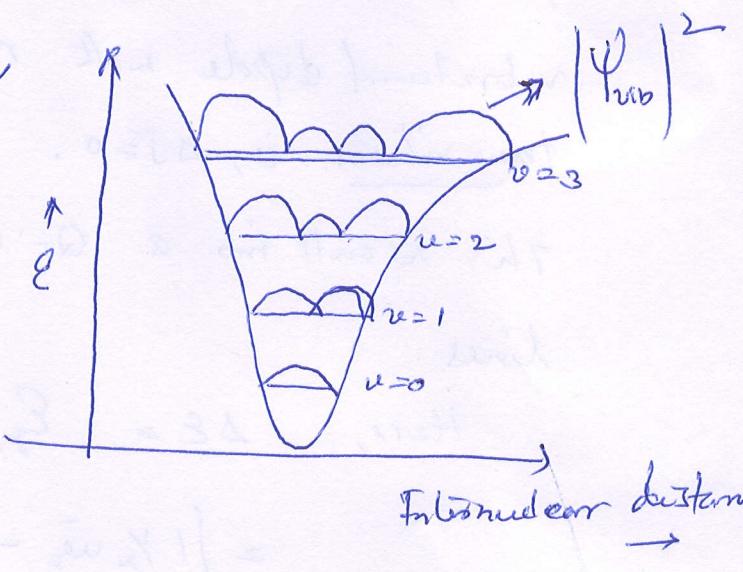
Here, 3- if the vibrations are doubly-degenerate -

Plane - total 6-modes - } All are Raman active  
 $(3+3)$  visible }

16. This happens due to elastic Nature of chemical bond - Another saying, the anharmonicity in the bond make the system classically behave at high ' $v$ '.

In a classical oscillator the atom spend more time at the turning point of the motion. (more slower at this point)

This can be represented as,



### Part B

17. (a) Stokes - Energy lost due to vib/rotation of the molecule in a Raman expt.

(Mark) Anti-Stokes - Energy gained due to "

- (b) The electric field of an incident beam

$$E = E_0 \sin 2\pi v t.$$

(2 Marks) Induced dipole moment  $\mu = \alpha \cdot E$ .

$$\Rightarrow \alpha \cdot E_0 \sin 2\pi v t.$$

Suppose a molecule has vibrations & hence,

$$\omega = \omega_0 + \beta \sin 2\pi(v_{\text{vib}})t \quad [\text{Then, } \beta = \frac{d\omega}{dQ_K}]$$

$\alpha_0 \rightarrow$  is the spm. polarizability.

$$\text{Now, } \mu = \alpha \cdot E = (\omega_0 + \beta \sin 2\pi(v_{\text{vib}})t) \cdot E_0 \sin 2\pi v t$$

$$\text{Now, } \sin A \sin B = \frac{1}{2} \left\{ \cos(A-B) - \cos(A+B) \right\}$$

$$\therefore \mu_2 \propto E_0 \sin 2\pi vt + \frac{1}{2} \beta E_0 \left\{ \cos 2\pi(v-v_{wb})t - \cos 2\pi(v+v_{wb})t \right\}$$

$$0, \mu_2 \propto E_0 \sin 2\pi vt + \frac{1}{2} \beta E_0 \left\{ \cos 2\pi(v-v_{wb})t - \cos 2\pi(v+v_{wb})t \right\}$$

Rayleigh                    Stokes                    Anti-Stokes

(c)  $\text{CO}_2$  - (linear triatomic)

$$3N-5 \text{ modes} = 3 \times 3 - 5 = 4 \text{ modes.}$$

The modes are:

(2 Modes)	Sy. str.	1 mode	- Raman active
	Asy. str.	1 mode	- IR active
	Bending	$\frac{2 \text{ modes (degenerate)}}{4 \text{ modes}}$	- Both Raman & IR active

$\text{H}_2\text{O}$  - bond (non-linear)

$$3N-6 \text{ modes} = 3 \times 3 - 6 = 3 \text{ modes.}$$

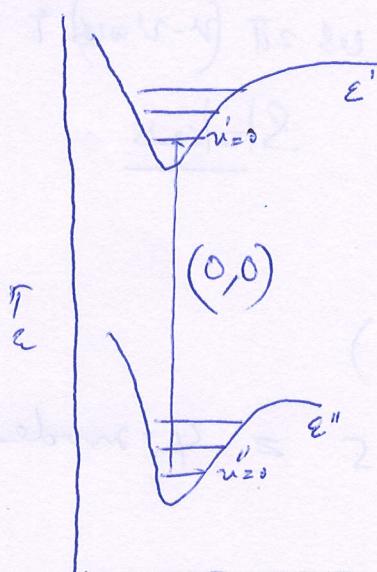
Modes are:

Sy. str.	2 modes	- Raman & IR active
Asy. str.	1 mode	"
Bending.	$\frac{1 \text{ mode}}{3 \text{ Modes.}}$	"

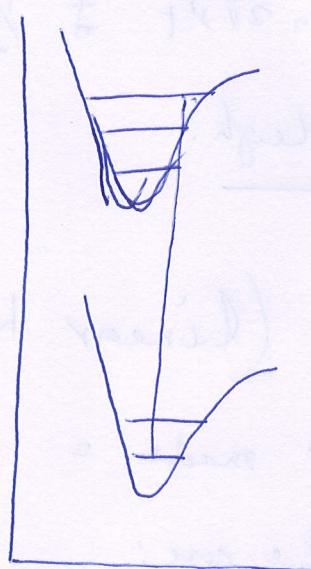
18. (a). Electronic transitions take place so rapidly that a vibrating molecule doesn't change its internuclear distance - is called Franck-Cordon principle.

This result in vertical excitation. ~~in mole~~

(b)



(2 marks)

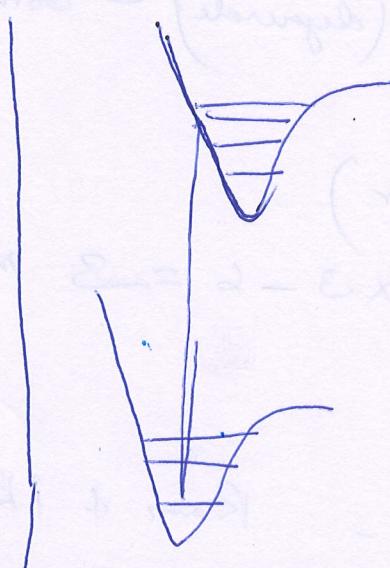


i) Internuclear  
distance is the same.

- result in  $(0,0)$  transition.

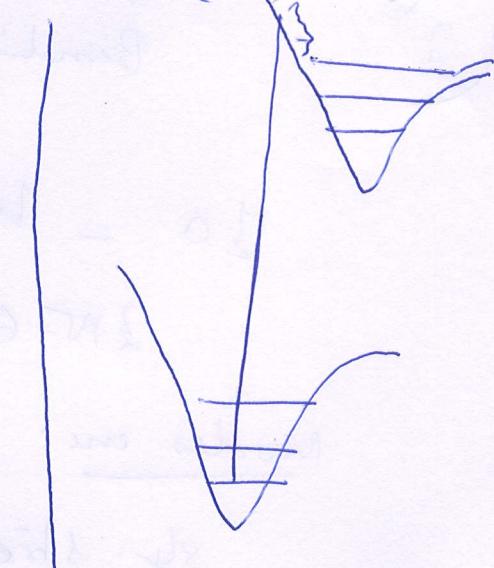
ii) upper state is

a little less than the  
g.s. - result in higher order  
transition,  $(0,2)$



(iii) upper state is a little  
greater than the lower  
state -

Result in higher order  
transition like  $(0,2)$



iv) upper state is far up  
from the lower state -

result in continuum.

$$\text{Now, } \sin A \sin B = \frac{1}{2} \left\{ \cos(A-B) - \cos(A+B) \right\}$$

$$\therefore \mu_2 \propto E_0 \sin 2\pi vt + \frac{1}{2} \beta E_0 \left\{ \cos 2\pi(v-v_{wb})t - \cos 2\pi(v+v_{wb})t \right\}$$

$$0, \mu_2 \propto E_0 \sin 2\pi vt + \frac{1}{2} \beta E_0 \left\{ \cos 2\pi(v-v_{wb})t - \cos 2\pi(v+v_{wb})t \right\}$$

Rayleigh.                   Stokes                   Anti-Stokes

(e)  $\text{CO}_2$  - (linear triatomic)

$$3N-5 \text{ modes} = 3 \times 3 - 5 = 4 \text{ modes.}$$

The modes are:

(2 Modes)	Sy. str.	1 mode	- Raman active
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	Bending	2 modes (degenerate) 4 modes	- Both Raman & IR active

$\text{H}_2\text{O}$  - bond (non-linear)

$$3N-6 \text{ modes} = 3 \times 3 - 6 = 3 \text{ modes.}$$

Modes are:

Sy. str.	2 modes	- Raman & IR active
Asy. str.	1 mode	
Bending.	1 mode 3 Modes.	4

18. contd. (c)  $(0,0)$  transitions is possible.

(1 mark)  $\Delta v = 0, \pm 1, \pm 2, \text{ etc.}$  is allowed in electronic transitions

- (d) i) Orbital angular momentum selection rule.  
 (1 mark) ii) Spin angular momentum selection rule.

$\leftarrow$  (this much is enough for 1 mark)  
 full work 2

$$|N_{g.s.e.s}|^2 = \left[ \int \psi_{\text{orb}}^* \psi_{\text{orb}} d\tau_e \int \psi_{\text{el}}^* \psi_{\text{el}} d\tau_e \right] \psi_{\text{ls}}^* \psi_{\text{ls}} d\tau_s$$

f.c. factor      orbital      spin-

### Part E

19.  $HCl = 2885 \text{ cm}^{-1}$

$$\text{Z.P.E} = \frac{2885}{2} = 1442.5 \text{ cm}^{-1}$$

$$D_2 = 2990$$

$$\text{ZPE} = \cancel{995}$$

$$(HCl + D_2) \text{ ZPE} = \cancel{2437.5} \text{ cm}^{-1} \quad \underline{\underline{2937.5 \text{ cm}^{-1}}} \quad (1)$$

(3 marks)  $DCl = 1990 \text{ cm}^{-1}$

$$\text{ZPE} = 995 \text{ cm}^{-1}$$

$$\begin{cases} HD = 3627 \text{ cm}^{-1} \\ \text{ZPE} = 1813.5 \end{cases}$$

$$DCl + HD = \underline{\underline{2808.5 \text{ cm}^{-1}}} \quad (2)$$

$$(1) - (2) \rightarrow \pm 129 \text{ cm}^{-1}$$

(2 marks)  $\rightarrow \frac{h.c.}{\text{NA}} \times 129 \text{ cm}^{-1} \times \cancel{10} =$

$$6.626 \times 10^{-34} \text{ J} \times \frac{1}{3} \times 10^{10} \text{ cm}^{-1}$$

$$\times \cancel{129 \text{ cm}^{-1}} \times 6.023 \times 10^{23} / \text{mol}$$

$$= \underline{\underline{1.544 \text{ kJ/mol}}}$$

(2 marks)

-8-

		freqency ( $\text{cm}^{-1}$ )	Degeneracy	Des.	IR active	Raman active
20. (a) mode						
1.		218 $\text{cm}^{-1}$	2	lissoring	N	Y
2.		314 $\text{cm}^{-1}$	3	Rock/umbrella	Y	Y
3.		459 $\text{cm}^{-1}$	1	Sym. Str.	N	Y
4.		762 $\text{cm}^{-1}$	3	Anti-Sym. Str.	Y	Y
				Total = 9 modes.		

(b) (2 marks)

$$\frac{N_{\text{Anti-stokes}}}{N_{\text{Stokes}}} = \exp \left\{ - \frac{\Delta E}{k_B T} \right\} = \exp \left\{ - \frac{h.c. \nu (\text{cm}^{-1})}{k_B T} \right\}$$

$$\text{At } 20^\circ\text{C} = 293 \text{ K}$$

$$\text{Intensity ratio} = \exp \left\{ \frac{-6.626 \times 10^{-34} \times 3 \times 10^{10} \times 218}{1.38 \times 10^{-23} \times 293 \text{ K}} \right\} \\ = \exp \{-1.072\} = \underline{\underline{0.342 \text{ at } 20^\circ\text{C}}}$$

$$\text{At } 40^\circ\text{C} = 313 \text{ K} \Rightarrow 0.367$$

(c) (1 mark) It is a combination band.  $(459 + 314)$

(Sym. Str. + Rocking modes)

$$21. \text{ for g.s. } \bar{\omega}_e = 1641.4 \text{ cm}^{-1}$$

$$\chi_e = 7.11 \times 10^{-3}$$

$$\nu_{\text{max}} = \frac{1}{2\chi_e} - 1 = \frac{1}{2(7.11 \times 10^{-3})} - 1 = 70 - 1 = 69$$

$$\text{We know, } \epsilon_v = (v + 1/2) \bar{\omega}_e - \chi_e (v + 1/2)^2 \bar{\omega}_e \text{ cm}^{-1}$$

$$\text{for } v = 69 \Rightarrow \epsilon_{69} = (69 + 1/2) 1641.4 - 7.11 \times 10^{-3} (69 + 1/2)^2 1641.4$$

$$\epsilon_{69} = 57,707 \text{ cm}^{-1} = (\text{h.c. } N_A) \times 57,707 \text{ KJ/mol}$$

$$\therefore D'' = \underline{\underline{690.32 \text{ KJ/mol}}}$$