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# **Prof. Owoyomi's Part**



# Molecular Spectroscopy

## ~~Non magnetic Spectroscopy~~

- (1) Introduction
- (2) Rotational - Microwave Spectroscopy
- (3) Vibrational infrared Spectroscopy
- (4) Rotational Raman
- (5) Vibrational Raman
- (6) Electronic Spectroscopy

## Magnetic Spectroscopy

- (1) Nuclear
- (2) Electron Spin

prof. agunlusic

prof. Aoyami

Dr. Olusegun

## Texts

Fundamental of molecular spectroscopy by C.N. Banwell  
" " by Gordon Barrow  
" " P. W. Atkins

Spectroscopy is the study of interaction of electromagnetic radiation with matter.

One of the experimental probes for studying molecular structure.

\* It provides accurate information on the bond length and bond angles of small molecules

\* It provides information on

- The conformation such as <sup>planarity</sup> ~~primary~~ or non-planarity of large molecules
- Stability of cis and trans isomers

It is a very important tool for studying structures of molecules

### SCOPE

It is an experimental subject concerned with

- Absorption
  - Emission
  - Scattering
- of EMR.



## Assignment

Discuss extensively the electromagnetic spectrum.

$$E = h\nu = \frac{hc}{\lambda}$$

The UV region is that region of usually very low wavelength between 190, 240 ~~to~~ 325 nm

Visible region  $> 325 - 800$  nm

IR  $> 900 - 1100$  nm

Electromagnetic : Electric, Magnetic

An electron has an electric field and magnetic field, and they are perpendicular to one another

Electric component  $E_y = A \sin(2\pi\nu t - kx)$

Magnetic component  $H_z = A \sin(2\pi\nu t - kx)$

$$-E_y \perp H_z$$

When an electron is subjected to an external magnetic field, it has two orientations of magnetic

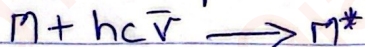
little

The transition of electron from lower energy level to higher energy level <sup>→ It becomes unstable</sup> is called Absorption (Absorption of radiation) which is due to interaction of electron with radiation. As it comes back to ground state, it emits radiation.

Induced by magnetic field

Three Important Processes Between Two Energy State

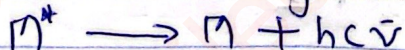
(1) Induced Absorption: No Natural Absorption



\* The blue colour of  $\text{CuSO}_4$  due to the absorption of the complementary colour, red.

$\text{CuSO}_4$  appears blue, cos it absorbs red

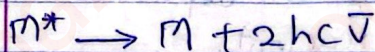
(2) Spontaneous Emission: It caused because the electron is not stable at the higher energy state



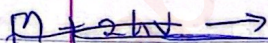
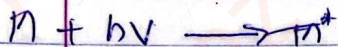
e.g Tungsten filament lamp etc



3) Induced emission



Seeding of cloud with AgI crystal to induce reaction



All these three process are going on simultaneously in any system

31/03/26



The rate of change of population of state  $n$  due to induced absorption is

$$\frac{dN_n}{dt} = N_m B_{mn} f(\bar{\nu})$$

The rate of formation of B depends on the concentration of the reactant



$$\text{rate} = k[A]$$

Therefore the rate of state  $n$  depends on the number of population of  $m$

$\rho(\nu)$  is the spectral density which is given according to Max Planck's equation as;

$$\rho(\nu) = \frac{8\pi h c \nu^3}{\exp\left(\frac{h c \nu}{k_B T}\right) - 1}$$

Similarly, for induced emission, rate is;

$$\frac{dN_n}{dt} = -N_n B_{nm} \rho(\nu)$$

The upper state population is being reduced as a result of emission, that the final population is less than the initial population. That is the reason for the minus sign in the rate of change of the population of upper state.



For spontaneous emission, the rate of change in the upper state is

$$\frac{dN_n}{dt} = -N_n A_{nm}$$

In the presence of radiation of wave number  $f(\nu)$ , all the three processes are going on at once. When the population have reached equilibrium values, the rate of change of population at the upper state is:

$$\frac{dN_n}{dt} = (N_m - N_n) B_{nm} f(\nu) - N_n A_{nm} = 0$$

The populations  $N_n$  and  $N_m$  are related through the Boltzmann's distribution law

$$\frac{N_n}{N_m} = \frac{g_n}{g_m} \exp\left(\frac{-\Delta E}{K_B T}\right)$$

Where  $g_n$  and  $g_m$  are the degeneracy of the upper and the lower energy state respectively

$K_B$  = Boltzmann's constant

For most simple systems,  $g_m = g_n = 1$ .

Consequently, the ratio of population of upper to lower state is given as

$$\frac{N_n}{N_m} = \exp\left(\frac{-\Delta E}{k_B T}\right)$$

The Einstein coefficient  $A_{nm}$  and  $B_{nm}$  can be obtained from all the various equations above as

$$A_{nm} = 8\pi h c \nu^3 B_{nm}$$

### Questions

- (1) The wavelength of the radiation absorbed during a particular spectroscopic transition is observed to be  $10 \text{ nm}$ . Express this in frequency and wave number, and calculate the energy change during the transition in  $\text{J molecule}^{-1}$  and  $\text{J mole}^{-1}$ .  
If the energy change were twice as large, what could be wavelength of the corresponding radiation.
- (2) A certain transition involves an energy change of  $4.005 \times 10^{-22} \text{ J/molecule}$ . If there are 1000 molecules in the groundstate. What is the approximate



equilibrium population of the excited state at temperatures

- (a) 29 K (b) 145 K (c) 290 K (d) 2900 K

Comment on your answers

- (3) As a function of frequency, the spectral radiation density is given as

$$\rho(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$

Calculate typical values of this spectral density in the microwave and near ultraviolet regions

$$\begin{aligned} \nu &= 50 \text{ GHz} \\ \nu &= 30000 \text{ cm}^{-1} \end{aligned} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{regions}$$

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The Einstein coefficients are related to the wavefunctions  $\psi_m$  and  $\psi_n$  of the combining states through the transition moment  $R^{nm}$ , a vector quantity by

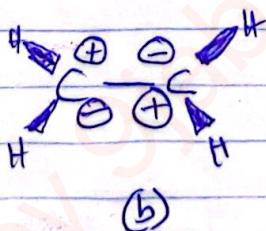
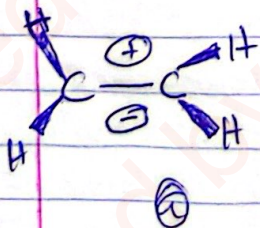
$$R^{nm} = \int \psi_n^* M \psi_m d\tau$$

for interaction with the electric component of the radiation

$$M = \sum q_i r_i \quad M = \text{dipole moment}$$

where  $q_i$  and  $r_i$  are the charge and position vector of the  $i$ th particle (electron or nucleus).

The transition moment can be thought of as the oscillating electric dipole moment due to the transition



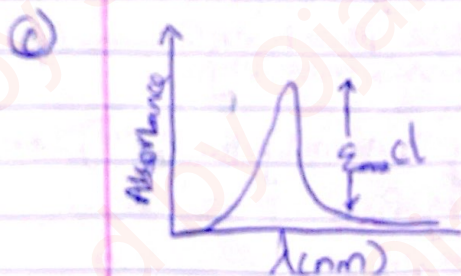
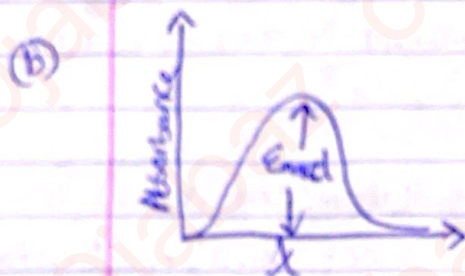
If a molecule is promoted from  $\pi \rightarrow \pi^*$  in an electronic transition, then we have corresponding dipole moment interaction







APP



(a) An absorption experiment (b) a broad (c) a narrow absorption band with the sum  $E_{max}$ ;  $c$  is the concentration of the absorbing material in the liquid state

$$\text{Absorbance (A)} = \log_{10} \left( \frac{I_0}{I} \right) = \epsilon l c \quad \left( \text{Beer-Lambert law} \right)$$

$$\log_{10} \left( \frac{I_0}{I} \right) \propto C$$

\* molecules are the ones that exhibit rotational motion

## MICROWAVE SPECTROSCOPY

It is also known as rotational spectroscopy

It arises from quantized rotation of molecules in 3D space

\* Atoms do not have rotational spectra (they do not undergo microwave spectroscopy, they only undergo translational motion)

\* Diatomic molecules have a simple rotational spectrum (rotation in only two dimensions)  $\rightarrow$  ( $\text{BF}_2, \text{BF}_3, \text{PF}_5$ )

\* For non-linear polyatomic molecules, they have one (highly symmetric) to three (for less symmetric species) different rotations in space

## Classification of Molecules for Rotation Spectra Study

Resolution of the rotation of a 3D body into rotational components along the 3 mutually perpendicular directions through the centre of gravity

This implies that a body has three principal moments



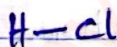
of inertia, one about each axis designated as  $I_A$ ,  $I_B$  and  $I_C$ .

Classification is then according to the relative values of the three principal moments of inertia.

This is equivalent to classifying them according to their shapes.

### Linear Molecules

Linear molecules: All atoms are arranged in a straight line such as HCl or OCS (Carbon oxysulphide)



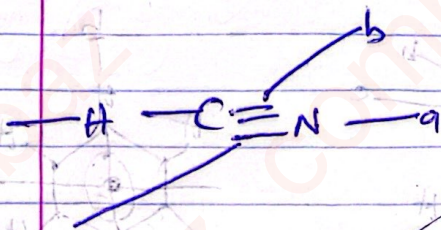
The 3 directions of rotation may be taken as

- About the bond axis ( $I_A$ )
- End over end in the plane ( $I_B$ )
- End over end rotation at right angles to the plane ( $I_C$ )

\* Evidently  $I_B = I_C$ , while  $I_A$  is very small and may be assumed (a very close approximation) to be equal to zero. Therefore, for linear molecules;

$$I_B = I_C; I_A = 0$$





$$I_c = I_b > I_a = 0$$

principal inertial axes of hydrogen cyanide - a linear molecule

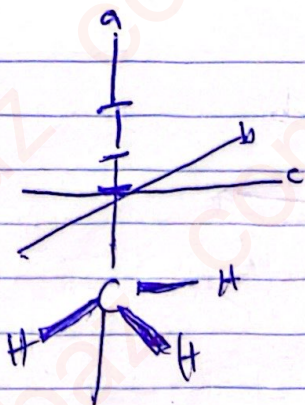
### Symmetric Tops

The end-over-end rotation in and out of the plane are identical

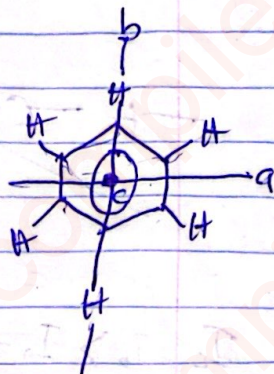
The moment of inertia about the principal axis of rotation is now not negligible. It's called a top because it's spinning about the principal axis of rotation. Therefore, for such molecules:

$$I_b = I_c \neq I_a \quad I_a \neq 0 \quad \dots (2)$$

- \* It is called a prolate <sup>symmetric top</sup> for  $I_b = I_c > I_a$  e.g. methyl fluoride
- \* An oblate for  $I_b = I_c < I_a$  e.g. boron trichloride, benzene



A prolate symmetric rotor



## Spherical Tops

\* All three moments of inertia are identical. A good example is methane — a tetrahedral molecule

$$I_a = I_b = I_c$$

\* No dipole moment due to their symmetry

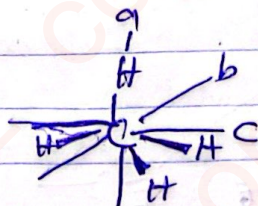
\* Rotation can produce no dipole change

\* No observable rotational spectrum

\* Therefore, they don't undergo microwave spectroscopy because they are highly symmetrical



Classification of molecules that undergo rotational spectroscopy

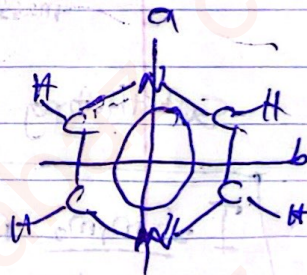
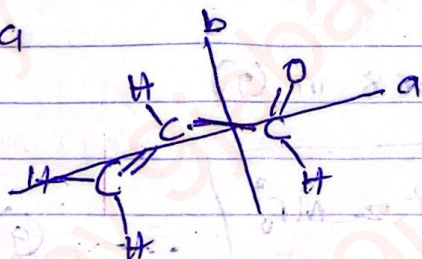
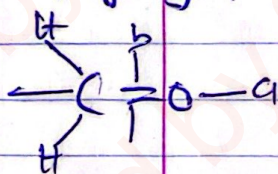


### Asymmetric Tops

All three moments of inertia are different

$$I_a \neq I_b \neq I_c \quad (*)$$

Therefore rotation will produce a net dipole moment & they will undergo MW spectroscopy  
Majority of substances are in this category.



### Rotational Spectra of Diatomic Molecules

$$r_1 + r_2 = r_0 \quad \text{..... (5)}$$

$$m_1 r_1 = m_2 r_2 \quad \text{..... (6)}$$

The moment of inertia about the center of gravity

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{..... (7)}$$

$$= m_1 r_1 r_0 + m_2 r_2 r_0 \quad \text{..... (7)}$$



$$A \xrightarrow{r_A} | \xrightarrow{r_B} B$$

$$r_0 = r_A + r_B$$

5

From equations 5 and 6

$$\text{The } m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

$$\therefore r_1 = \frac{m_2 r_0}{m_1 + m_2}, \quad r_2 = \frac{m_1 r_0}{m_1 + m_2} \quad \dots (8)$$

$$I = M r_0^2$$

↓  
reduced  
mass

$$N = \frac{m_1 m_2}{m_1 + m_2}$$

Substituting for 8 in (7)

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = N r_0^2 \quad \dots (9)$$

## Energy of Rotation

The solution to the Schrodinger equation for the rigid rotor is given as

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joules}, \quad J = 0, 1, 2, \dots \quad (10)$$

In the rotational region spectra, the allowed energies are usually discussed in terms of wave number. Therefore equation (10) is expressed as:

$$E_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1}, \quad J = 0, 1, 2, 3, \dots \quad (11)$$

$$\left[ \bar{\nu} = \frac{1}{\lambda} \Rightarrow \bar{\nu} = \frac{E}{hc} \right]$$

Equation (11) is usually abbreviated to

$$E_J = B J(J+1) \text{ cm}^{-1} \dots \dots (12)$$

where  $B = \frac{h}{8\pi^2 I_B c} \text{ cm}^{-1}$

(B is only constant for a particular molecule - ...  
I varies and B is a function of I)

The quantity B is known as the rotational constant. Its determination by spectroscopic means results in determination



of inter-nuclear distances and represents a very powerful structural technique

### Illustration

Calculate the rotational energy levels, in joules for  $J=0, 1$  and  $2$  for  $^{12}\text{C}, ^{16}\text{O}$ . Convert these to units of  $\text{cm}^{-1}$ . If the bond length is  $1.1283 \text{ \AA}$  (Relative atomic mass:  $\text{C} = 12; \text{O} = 15.999$ )

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$I = Mr_0^2 \Rightarrow \frac{m_1 m_2}{m_1 + m_2} r_0^2 \quad (r_0 = \text{bond length})$$

$$I = \frac{m_{\text{C}} m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} \times (1.1283 \times 10^{-10} \text{ m})^2$$

Since we are looking for a single molecule, not  $^n$  mols of the atom

$$m_{\text{C}} = \frac{12.01 \times 10^{-3} \text{ kg}}{6.02 \times 10^{23}}; \quad m_{\text{O}} = \frac{15.999 \times 10^{-3} \text{ kg}}{6.02 \times 10^{23}}$$

$$\frac{m_e m_0}{N_A} = (m_e + m_0)$$

$$I = \left( \frac{m_e m_0}{m_e + m_0} \right) \frac{1}{N_A} \times r_0^2 \quad (\text{Note that } m \text{ is in kg})$$

$$I = \left( \frac{12.0 \times 10^{-3} \times 16 \times 10^{-3}}{12.0 \times 10^{-3} + 16 \times 10^{-3}} \right) \frac{1}{6.03 \times 10^{23}} \times (1.283 \times 10^{-10})^2$$

$$I = 1.4501 \times 10^{-46}$$

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1); \quad \text{when } J=0, E=0$$

$$\text{when } J=1$$

$$E_J = \frac{(6.626 \times 10^{-34})^2}{8\pi^2 \times 1.4501 \times 10^{-46}} \times 1(1+1)$$

$$E_J = 7.67 \times 10^{-3} \text{ J}$$

$$\text{when } J=2$$

$$E_J = \frac{(6.626 \times 10^{-34})^2}{8\pi^2 \times 1.4501 \times 10^{-46}} \times 2(2+1)$$

$$E_J = 2.301 \times 10^{-22} \text{ J}$$



~~The differ~~

The energy in a rotational transition is the difference in energy of two adjacent state, for a diatomic or linear molecule

For absorption, the transition can be labeled as  $E(J) \rightarrow E(J+1)$ , and the difference in energy is given by the difference between final and initial states, such that

$$\Delta E = E_{J+1} - E_J$$

$$= \frac{h^2}{8\pi^2 I} \{ (J+1)(J+1+1) - J(J+1) \}$$

$$= \frac{h^2}{8\pi^2 I} \{ (J+1)(J+2) - J(J+1) \}$$

$$= \frac{h^2}{8\pi^2 I} \{ J^2 + 3J + 2 - J^2 - J \}$$

$$\Delta E = \frac{h^2}{8\pi^2 I} (2J+2)$$

$$\Delta E_z = \frac{h^2}{8\pi^2 I} (2)(J+1)$$

$$\Delta E_z = \left( \frac{h^2}{8\pi^2 I_c} \right) (J+1)$$

$$\therefore \Delta E = 2B(2)(J+1) \\ = 2B(J+1) \text{ cm}^{-1}$$

For absorption spectroscopy, the minimum  $J$  value is  $J \geq 0$

$$E_c \geq 2B(J+1) \quad (\text{where } J \text{ is the lower energy state})$$

$$\text{from } J = 0 \rightarrow J = 1$$

$$\Delta E_J = 2B[(1+1) - (0+1)] \\ = 2B(2-1) \\ = 2B$$

$$E = 2B(0+1)$$

$$E = 2B$$

$$\Delta E_{J=1 \rightarrow J'=2} = 2B(2+1) \quad ; \quad J=1 \rightarrow J'=2$$

$$E = 2B(1+1)$$

$$E = 4B$$

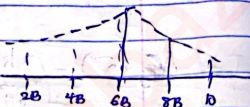


$$J=2 \rightarrow J'=(J+1)$$

$$\Delta E = 2B(2+1) \\ = 6B$$

$$J=3 \rightarrow J'=(J+1)$$

$$\Delta E = 2B(3+1) \\ = 8B$$



### Illustration

Some of the lines in the rotational spectrum of HCl appear at  $83.03$ ,  $104.1$ ,  $124.3$ ,  $145.0$  and  $165.5 \text{ cm}^{-1}$

The first line is the  $J=3 \rightarrow J=4$  transition, so it equals  $8B$ . Determine the average value of  $B$  from this data and calculate the length of the HCl bond (which gives a good idea of the size of the molecule).

Assume that these data are for  $^1\text{H}$  and  $^{35}\text{Cl}$

$$E_J (\text{cm}^{-1}) = 2B(J+1)$$

$$= 8B = 83.03 \text{ cm}^{-1} \Rightarrow B_1 = 10.37875$$

$$4 \rightarrow 5 = 10B = 104.1 \text{ cm}^{-1}$$

$$5 \rightarrow 6 = 12B = 124.3 \text{ cm}^{-1}$$

$$6 \rightarrow 7 = 14B = 145.0 \text{ cm}^{-1}$$

$$7 \rightarrow 8 = 16B = 165.5 \text{ cm}^{-1}$$

$$B = \frac{B_1 + B_2 + B_3 + B_4}{5}$$

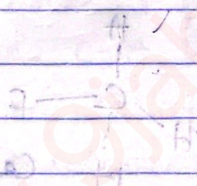
$$\gamma \rightarrow 8 \approx 16B \approx 165.5 \text{ cm}^{-1}$$

of similar frequency. A 12.1% of signal band is seen on

$$\hat{B}_2 = \underline{B_1 + B_2 + B_3 + B_4 + B_5}$$

5 - 11.7 for the same frequency

At 12.1% of signal

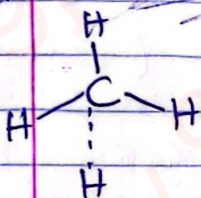




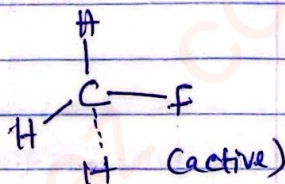
NO has a bond length of  $1.157 \text{ \AA}$ . Predict where the first four lines of the pure rotational spectrum of NO will appear, in units of  $\text{GHz}$ .

13th April, 2026

$C=2.5$   
 $H=2.1$



and



one of these will be spectroscopically active, why?  
Before a compound can be spectroscopically active it has to have a net dipole moment: the transition state of molecules is not zero

Selection Rule: It is related to any transition probability

when  $|R^{nm}|^2 = 0$  ----- forbidden

when  $|R^{nm}|^2 \neq 0$  ----- allowed

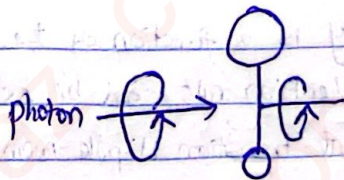
The transition probability is a function of the electric dipole moment ( $M$ ). The selection rule can be established by considering the relevant transition dipole moment. The gross selection rule, for the observation of a pure rotational transition is that a molecule must have a permanent dipole moment.

For C-H bond, there is a form of polarity because of the difference in electronegativity. <sup>it cancels each other, zero dipole moment</sup> Because we have four C-H bonds, there is no net ~~the~~ dipole moment, therefore it can never exhibit pure rotational spectroscopy.

For the second compound, which have C-F have a large difference in the electronegativity values ( $F=4.0, C=2.5$ ), it has strong polarity, therefore there is a permanent dipole moment, and the  $CF_3F$  can ~~be~~ examined using rotational spectroscopy.

The classical basis of this rule, is that a polar molecule appears to possess a fluctuating dipole when rotating but a non polar molecule does not.





The photon is absorbed by a molecule and the angular momentum of the combined system is conserved.

If the molecule is rotating in the same sense as the spin of the incoming photon, then the rotational quantum number  $J$  increases by 1.

$$i.e. J \rightarrow J+1$$

The transition  $\Delta J = (J' - J) = +1$  corresponds to absorption ~~and~~ and the transition;

$$\Delta J = -1 \text{ corresponds to emission}$$

Therefore the allowed transition is equal to  $+1$  or  $-1$ . When the transition moment is evaluated for all possible relative orientations of the molecule to the line of flight of the photon, <sup>like</sup> on the image above, it is found that the total  $(J+1) \leftrightarrow J$  transition intensity is proportional to

$$|M_{J+1 \leftrightarrow J}|^2 = \left( \frac{J+1}{2J+1} \right) M_0^2$$

Intensity is dependent on  $M_0$  (dipole moment)

where  $M_0$  is the permanent electric dipole <sup>moment</sup> of the molecule

What is the implication of this statement?

The greater the dipole moment/polarity, the more intense the signal associated molecule will be in the microwave spectroscopy. Since polarity is determined by the number of dipole moment (intensity is proportional to the square of dipole moment)

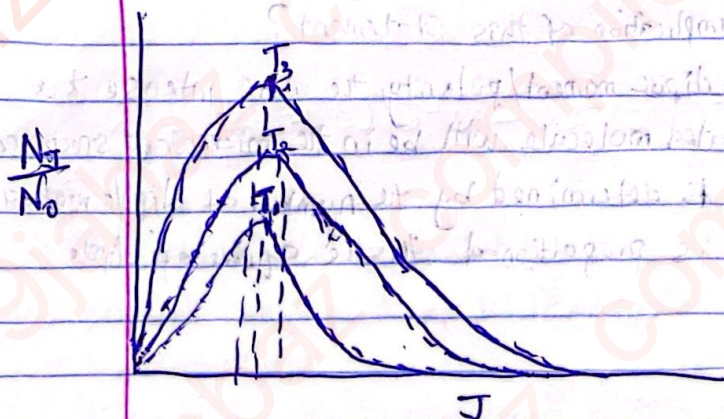
\* molecule is

The intensity pattern of a rotational spectral is due to the number of molecules having a certain rotational state, this is called population of the state, and because the population of each rotational state is different, the number of molecules absorbing radiation and becoming excited to the next state is different.

This population difference is responsible for the varying intensities of each rotational spectra line. The population  $N_J$  of the  $J^{\text{th}}$  level relative to  $N_0$  (population at the ground state) is determined by the Boltzmann distribution law

$$\frac{N_J}{N_0} = (2J+1) \exp\left(-\frac{\Delta E_J}{K_B T}\right) \quad \text{where } K_B \text{ is Boltzmann Constant}$$





The relative population increases as temperature increases.

The relative population does not increase linearly with  $J$ . For every population, there is a particular  $J$  value where you have maximum population.

$$\frac{d \frac{N_J}{N_0}}{dJ} = 0$$

$$\frac{N_J}{N_0} = (2J+1) \exp \left( -\frac{AE}{k_B T} \right)$$

Show that;

$$J_{\max} = \left( \frac{k_B T}{2hcB} \right)^{1/2} - \frac{1}{2}$$

\* J value must be a whole number, it is quantized

$$J = 22.4 \times \quad J = 22 \checkmark$$

Assumption: The bond in a molecule is rigid (like a rigid rotor) - this is idealized

In real sense, there is a force that tends to pull these molecules from their rotational path. This force is

called Centrifugal distortion.

14th April, 2026

The rigid rotor model is an idealized one suggesting that the rotational spectra are very simple. Complications however arise when dealing with real systems, as molecules have larger and larger rotational quantum numbers ( $J$ ) corresponding to higher energies, the molecules distort slightly but not enough to change the energy levels noticeably. This effect is called Centrifugal distortion.

The Schrödinger wave equation shows that the rotational energy levels for a non-rigid molecule are

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2$$



OR (in terms of wave number);

$$E_J = \frac{E}{hc} = BJ(J+1) - DJ^2(J+1)^2$$

where  $D = \frac{h^3}{32\pi^4 I^2 r^2 K}$  cm<sup>-1</sup>

Centrifugal distortion  
constant

K = force constant  
(from Hooke's law).

\* A bond is rather considered as a vibrating spring, not a rigid rotor. The frequency of vibration can then be calculated using the force constant K.

For an elastic bond, the molecule may have vibrational energy, i.e. a periodical stretching and compression with a certain fundamental frequency in which the force constant K for the vibration if harmonic is given as

$$K = 4\pi^2 \bar{\omega}^2 \epsilon^2 M$$



16th April, 2026

$$D = \frac{4B^3}{W^2}$$

The positions of the rotational spectral lines are then given as

$$E_J = BJ(J+1) - DJ^2(J+1)^2$$

$$E_{J+1} - E_J$$



(1) The silver hydride diatomic molecule,  $^{197}\text{Ag}^1\text{H}$ , has an internuclear bond distance of  $1.617 \text{ \AA}$ . Predict the energies, in joules, of its first four rotational levels

(2) Diatomic Sulphur,  $\text{S}_2$  was detected in the tail of Halley's comet when it last approached Earth in 1985-86. It has a bond length of  $1.880 \times 10^{-10} \text{ m}$ . Calculate the value of  $B$ , in units of  $\text{cm}^{-1}$  and  $\text{J}$ , for  $\text{S}_2$ .

(3) Three consecutive lines in the rotational spectrum of  $^1\text{H}$   $^{79}\text{Br}$  are observed at  $84.544$ ,  $101.35$  and  $118.112 \text{ cm}^{-1}$ . Assign the lines to their approximate  $J''$  to  $J'$  transitions, then deduce values for  $B$  and  $D$ , and hence evaluate the bond length and approximate vibrational frequency of the molecule.

(4)  $\text{LiH}$  in the gas phase has a pure rotational spectrum consisting of lines spaced by  $15.26 \text{ cm}^{-1}$

(a) Calculate the bond distance of  $\text{LiH}$

(b) Determine the first four absorptions in the pure rotational spectrum of  $\text{LiH}$

(c) Determine the most populated rotational level,  $J_{\text{max}}$  for a sample of  $\text{LiH}$  at (i)  $298 \text{ K}$  (ii)  $1036 \text{ K}$  (iii)  $5000 \text{ K}$

## (Infrared)

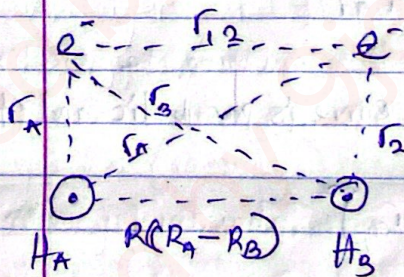
Vibrational Spectroscopy - The average spectroscopic technique in the IR region

Formation of stable covalent bond between atoms in a diatomic molecule involve some internal electronic rearrangement

The stability of the bond is due to the phenomenon of balance of forces which include

- nuclei-nuclei interaction
- Electron-electron interaction
- Nuclei-electron interaction

The two atoms settle at a mean internuclear distance such that these forces are just balanced and the energy of the system is at a minimum



(The forces balance each other, that the energy of the system is at equilibrium)

### Interactions in a single bond

The movement of the nuclei is negligibly small compared to the movement of electrons



At the minimum the inter-nuclear distance is referred to as the equilibrium distance  $r_{eq}$ , or simply as the bond length.

The vibrations (compression and expansion) of diatomic molecules can be treated as harmonic, Hooke's law-type oscillators.

That is,

- The molecules are moving back and forth about their center of mass
- The force opposing the motion is proportional to the distance away from ~~some~~ minimum energy, equilibrium distance

$$f = -k(r - r_{eq})$$

⊗

$$V = - \int f \cdot r \, dr$$

Therefore, the energy curve is parabolic and of the form

$$E = \frac{1}{2} k(r - r_{eq})^2$$

In simple harmonic approximation, an elastic bond, like a spring has a certain vibration frequency given classically as

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{M}} \text{ Hz}$$

To convert the frequency to wavenumber, the unit most frequently used in vibrational spectroscopy

$$\bar{\omega}_{\text{osc}} = \frac{1}{2\pi c} \sqrt{\frac{k}{M}} \text{ cm}^{-1} \quad \left( \begin{array}{l} \gamma = \frac{c}{\lambda} \\ \Rightarrow \frac{\gamma}{c} = \frac{1}{\lambda} \text{ cm}^{-1} \end{array} \right)$$

Vibrational energy, like any molecular energy is quantized and the allowed vibrational energy may be calculated from the Schrodinger's equation's

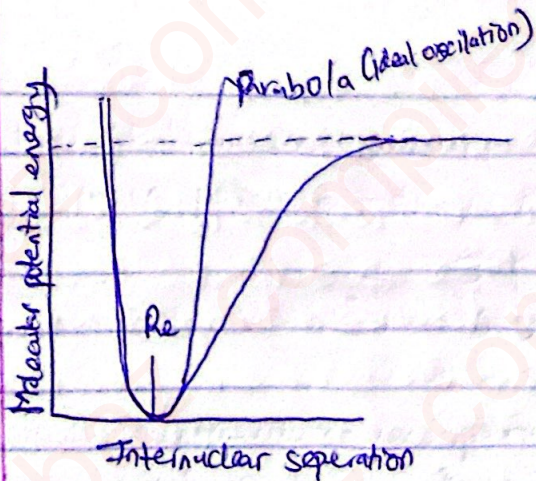
$$E_v = \left(n + \frac{1}{2}\right) h \omega_{\text{osc}} \text{ joules } (n = 0, 1, 2, \dots)$$

$n$  = vibrational quantum number

Converting to spectroscopic units,  $\text{cm}^{-1}$  to have;

$$E_v = \frac{E_v}{hc} = \left(n + \frac{1}{2}\right) \bar{\omega}_{\text{osc}} \text{ cm}^{-1}$$





### Selection Rule 1

From the Schrodinger's equation

Change in the vibration quantum number must be equal to  $\pm 1$  ~ Selection rule

From the Schrodinger's equation, the selection rule for a simple harmonic oscillator is given as

$$\Delta v = \pm 1$$

Applying the selection rule to have (for emission)

$$E_{v+1} \rightarrow v = \left( v+1 + \frac{1}{2} \right) \bar{h} \omega_{osc} - \left( v + \frac{1}{2} \right) \bar{h} \omega_{osc}$$



$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega_{osc}$$

$$E_{n+1} = \left(n + 1 + \frac{1}{2}\right) \hbar \omega_{osc}$$

$$= \left(n + \frac{3}{2}\right) \hbar \omega_{osc}$$

$$\Delta E = E_{n+1} - E_n$$

$$= \left(n + \frac{1}{2}\right) \hbar \omega_{osc} - \left(n + \frac{3}{2}\right) \hbar \omega_{osc}$$

$$= \hbar \omega_{osc} \left\{ n + \frac{1}{2} - n - \frac{3}{2} \right\}$$

$$= \hbar \omega_{osc} (-1) = -\hbar \omega_{osc}$$

$$= -\hbar \omega_{osc}$$

$$\frac{2}{1/04/26} = \dots$$

In the actual sense, the negative is just to show or account for the loss of energy,  $\hbar \omega_{osc}$  is never negative

It is a negative value, but it is not a negative value.

It is a negative value, but it is not a negative value.

It is a negative value, but it is not a negative value.

$$(1) \dots \dots \dots \left(n + \frac{1}{2}\right) \hbar \omega_{osc} - \left(n + \frac{3}{2}\right) \hbar \omega_{osc} = -\hbar \omega_{osc}$$

$$\hbar \omega_{osc} = \dots \dots \dots$$

$$\hbar \omega_{osc} = \dots \dots \dots$$



## The Anharmonic Oscillator

Real molecules do not obey exact law of SHM, why?  
Because bonds can be broken (pull apart).

Then bond dissociation  $E$  can be determined by breaking the bond. As a bond is stretched it becomes weaker and the restoring force is reduced, this is called ANHARMONICITY

A purely empirical expression that accounts for this anharmonicity is known as a Morse function

The morse function is of the form;

$$V(R) = D_e \left\{ 1 - \exp(-\beta(R - R_e)) \right\}^2$$

\* you don't  
need the derivation  
cos it is advised

$$V(R) = D_e \left\{ 1 - \exp(-\beta(R - R_e)) \right\}^2$$

$$H\psi = E\psi$$

$E$  = eigenvalue

where  $D_e$  = dissociation energy

$\beta$  = Anharmonicity constant

Measure of deviation of a ~~atom~~ true bond from an idealical bond is known as anharmonicity constant, i.e.  $\chi_e$

The specific value for this function is

$$G = \left( v + \frac{1}{2} \right) \bar{\omega}_e - \left( v + \frac{1}{2} \right)^2 \bar{\omega}_e \chi_e \dots (x)$$

$$v = 0, 1, 2 \dots v_{\max}$$

$v$  = vibrational quantum number

$\chi_e \propto \beta \equiv$  anharmonicity constant

$$\chi_e = \frac{\bar{\omega}_e}{4D_e}$$

$\bar{\omega}$  = equilibrium vibrational frequency in  $\text{cm}^{-1}$   
 $D_e$  = dissociation

Comparing the equation of an harmonic oscillator (6) to this equation (xx)

$$E = \left(v + \frac{1}{2}\right) \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \chi_e$$

$$= \left(v + \frac{1}{2}\right) \bar{\omega}_e \left[1 - \left(v + \frac{1}{2}\right) \chi_e\right]$$

compared with

$$E_v = \left(v + \frac{1}{2}\right) \bar{\omega}_{\text{osc}} \text{ cm}^{-1}$$

$$\bar{\omega}_{\text{osc}} = \bar{\omega}_e \left[1 - \left(v + \frac{1}{2}\right) \chi_e\right] \text{ This shows the deviation from an ideal band}$$

$\bar{\omega}_e$  is the frequency if the bond were to behave like an anharmonic oscillator

From the last equation, it can be seen that an anharmonic oscillator behaves like the harmonic oscillator, but with an oscillator frequency which decreases steadily with increasing vibrational quantum number



What is the selection rule for anharmonic oscillator?

### Selection Rule

$$\Delta v = \boxed{\pm 1}, \boxed{\pm 2, \pm 3}$$

These are intense  
and it is called  
fundamental

These are weaker  
and they are called  
overtone

The overtones though predicted by theory are observed to be of rapidly diminishing probability. The spacing between vibrational levels is of the order of  $10^3 \text{ cm}^{-1}$ . At room temperature, the ratio of the population between levels is given by the Boltzmann distribution equation;

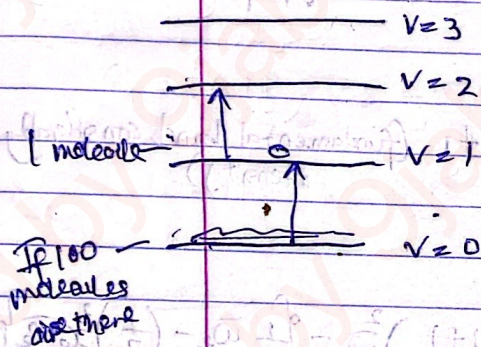
$$\frac{N_{v=1}}{N_{v=0}} = \exp \left\{ \frac{-\Delta E_v}{k_B T} \right\}$$

$$\frac{N_{v=1}}{N_{v=0}} = \exp \left\{ \frac{-6.626 \times 10^{-34} \times 2.998 \times 10^{10} \times 10^3}{1.38 \times 10^{-23} \times 300} \right\}$$
$$\approx 0.008$$

The meaning of this is that the upper state is barely populated as a result of vibration i.e. even as a result

of vibration, the bulk of the population remain at the lower energy state

This implies that the population of the  $v=1$  is nearly 1% of the ground state population



As a result of vibrational transition, only one out of 100 molecules will undergo transition, so if the transition from  $v=1$  to 2 is impossible and if it happens it is known as ~~hot~~ band

This shows that all transitions originating from  $v < 1$  or more are negligible and are called ~~hot~~ bands

23rd April, 2026

The allowed transition that occurs between the ground vibrational state ( $v=0$ ) and the first excited vibrational state ( $v=1$ ) of a diatomic molecule, the resulting set of spectral lines is called the fundamental band

The spectral band corresponding to  $\Delta v = \pm 2$  is called



a first overtone, one corresponding to  $\Delta v = \pm 3$  is called a second overtone and so on.

Bands for which the lower value of  $v$  is larger than zero are called hot bands.

Hot bands are generally not seen in absorption spectra near room temperature because of the small population of vibrational states.

$v=0 \rightarrow v=1$ ,  $\Delta v = \pm 1$  (fundamental band, considerably intensity)

$$\Delta E = E_{v=1} - E_{v=0}$$

$$= \left(1 + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(1 + \frac{1}{2}\right)^2 \bar{\omega}_e - \left[\frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e\right]$$

$$G_{v=1} = \bar{\omega}_e \left[1 - x_e \left(v + \frac{1}{2}\right)\right] \left[v + \frac{1}{2}\right]$$

$$G_{v=1} = \bar{\omega}_e \left[1 - x_e \left(\frac{3}{2}\right)\right] \left[\frac{3}{2}\right]$$

$$\cancel{E = \frac{3}{2} \bar{\omega}_e} \Rightarrow E = \bar{\omega}_e \left(\frac{3}{2} - \frac{9}{4} x_e\right)$$

When  $v=0$

$$E = \bar{\omega}_e \left[ 1 - x_e \left( \frac{1}{2} \right) \right] \left[ \frac{1}{2} \right] \quad -\frac{9}{4} + \frac{1}{4}$$

$$E = \bar{\omega}_e \left[ \frac{1}{2} - \frac{1}{4} x_e \right]$$

$$\Delta E_{v=1-v=0} = \bar{\omega}_e \left( \frac{3}{2} - \frac{9}{4} x_e \right) - \bar{\omega}_e \left( \frac{1}{2} - \frac{1}{4} x_e \right)$$

$$= \frac{3}{2} \bar{\omega}_e - \frac{9}{4} \bar{\omega}_e x_e - \frac{1}{2} \bar{\omega}_e + \frac{1}{4} \bar{\omega}_e x_e$$

$$\Delta E_v = \frac{2}{2} \bar{\omega}_e - \frac{8}{4} \bar{\omega}_e x_e$$

$$\Delta E_v = \bar{\omega}_e - 2 \bar{\omega}_e x_e$$

$$\Delta E_v = \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

$v=0 \rightarrow v=2$   $\Delta v = \pm 2$  (first overtone with)

$$E = \bar{\omega}_e \left[ 1 - x_e \left( v + \frac{1}{2} \right) \right] \left[ v + \frac{1}{2} \right]$$

$$E = \bar{\omega}_e \left[ 1 - x_e \left( 2 + \frac{1}{2} \right) \right] \left( 2 + \frac{1}{2} \right)$$

$$E = \bar{\omega}_e \left[ 1 - \frac{5}{2} x_e \right] \left[ \frac{5}{2} \right]$$

~~3/2~~



$$E \frac{5\bar{\omega}_e}{2} - \frac{25}{4} \omega_e x_e$$

$$\Delta E_{v=2 \rightarrow v=0} = \frac{5\bar{\omega}_e}{2} - \frac{25}{4} \omega_e x_e - \frac{1}{2} \bar{\omega}_e + \frac{1}{4} \bar{\omega}_e x_e$$

$$= \frac{4}{2} \bar{\omega}_e - \frac{24}{4} \omega_e x_e$$

$$\Delta E_{v=2 \rightarrow v=0} = 2\bar{\omega}_e - 6\omega_e x_e$$

$$= 2\bar{\omega}_e (1 - 3x_e)$$

$$= 2\bar{\omega}_e (1 - 3x_e) \text{ cm}^{-1}$$

$v=0 \rightarrow v=3$ ;  $\Delta v = +3$  (second overtone)

$$\Delta E = \left(3 + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(3 + \frac{1}{2}\right)^2 - \frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e$$

$$\Delta E = 3\bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1}$$

For  $^{16}\text{O}_2$ ,  $\Delta E_v$  for  $v=1 \leftarrow 0$   $1556.22 \text{ cm}^{-1}$

$v=2 \leftarrow 0$   $3088.28 \text{ cm}^{-1}$

$v=3 \leftarrow 0$   $4596.21 \text{ cm}^{-1}$

Calculate  $\bar{\omega}_e$  and  $x_e$

$$\Delta E_{v(1 \leftarrow 0)} = \bar{\omega}_e (1 - 2x_e) = 1556.22 \text{ cm}^{-1} \quad (1)$$

$$\Delta E_{v(2 \leftarrow 0)} = 2\bar{\omega}_e (1 - 3x_e) = 3088.28 \text{ cm}^{-1} \quad (2)$$

$$\Delta E_{v(3 \leftarrow 0)} = 3\bar{\omega}_e (1 - 4x_e) = 4596.21 \text{ cm}^{-1} \quad (3)$$

Dividing eqn (2) by eqn (1)

$$\frac{2\bar{\omega}_e (1 - 3x_e)}{\bar{\omega}_e (1 - 2x_e)} = \frac{3088.28}{1556.22}$$

$$\frac{2(1 - 3x_e)}{1 - 2x_e} = \frac{3088.28}{1556.22}$$

$$3088.28(1 - 2x_e) = 1556.22 \times 2(1 - 3x_e)$$

$$0.99224(1 - 2x_e) = 1 - 3x_e$$

$$0.99224 - 1.98448x_e = 1 - 3x_e$$

$$3x_e - 1.98448x_e = 1 - 0.99224$$

$$1.01552x_e = 7.76 \times 10^{-3}$$

$$x_e = 7.64 \times 10^{-3}$$



- (i) The fundamental and first overtone transitions of  $^{14}\text{N}^{16}\text{O}$  are centered at  $1876.06\text{cm}^{-1}$  and  $3724.20\text{cm}^{-1}$  respectively. Evaluate the equilibrium vibration frequency, the anharmonicity, the exact zero point energy, and the force constant of the molecule

- (ii) The vibrational wavenumbers of the following molecules in their  $v=0$  states are;  $\text{HCl}$  ( $2885\text{cm}^{-1}$ ),  $\text{DCl}$  ( $1990\text{cm}^{-1}$ ),  $\text{D}_2$  ( $2990\text{cm}^{-1}$ ) and  $\text{HD}$  ( $3627\text{cm}^{-1}$ ). Calculate the energy change in  $\text{kJ mol}^{-1}$  of the reaction



Determine whether energy is liberated or absorbed

Q

## The Diatomic Vibrating Rotator

For a normal rotational energy separation transition is in the order of  $1-10\text{cm}^{-1}$ , However if the molecule is vibrating the energy of rotation is in the order of  $10^3\text{cm}^{-1}$

Therefore during vibration, many rotation would have taken place.

As a first approximation, a diatomic molecule may execute rotations and vibrations quite independently due to the wide difference in the energies of the two motions. This is called Born-Oppenheimer approximation (including electronic energies)

The above is equivalent to assuming that the combined rotational vibrational energy is the sum of the separate energies

$$E_{\text{total}} \approx E_{\text{rot}} + E_{\text{vib}}$$

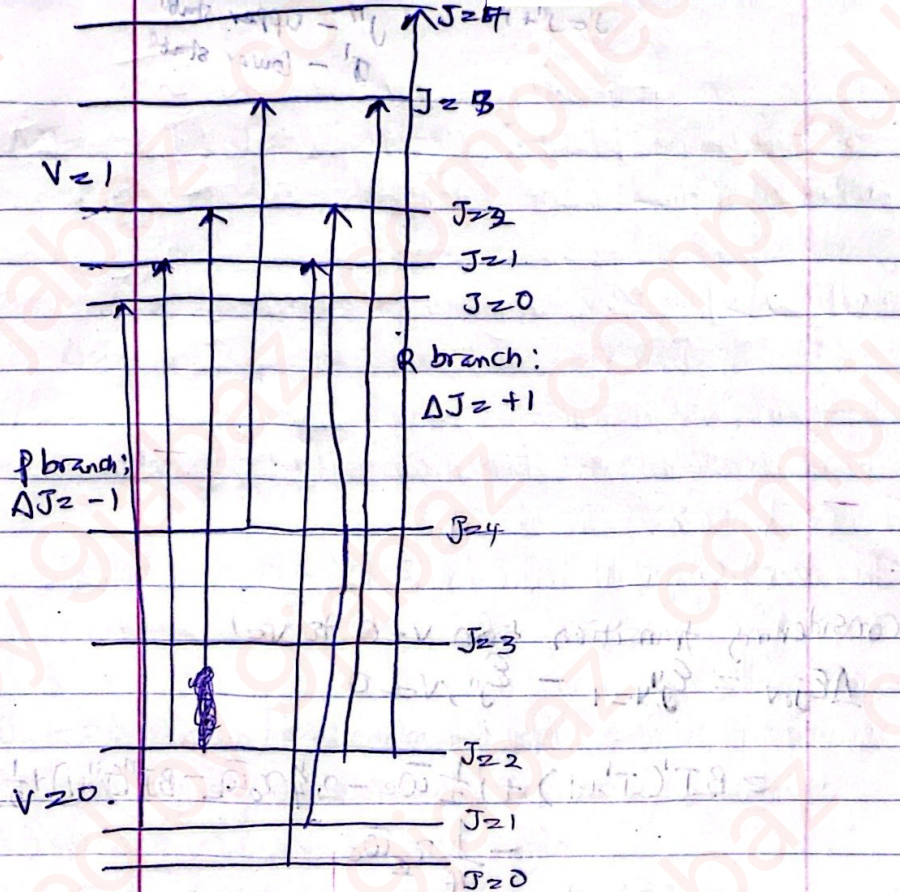
$$E_{\text{total}} \approx E_{\text{rot}} + E_{\text{vib}}$$

Taking the separate expressions for the energies of rotations and vibrations

$$E_{J,v} \approx E_J + E_v$$

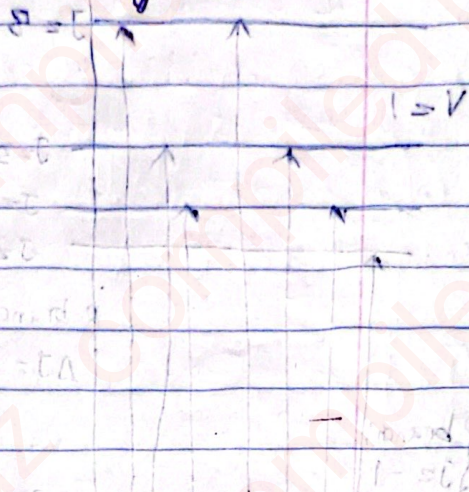
$$\approx \boxed{BJ(J+1)} + \boxed{v + \frac{1}{2} \bar{\omega}_e - x_e \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e}$$





If the spacing between the P transition is too big and the spacing between the R transition is too big. The middle of the transition spacing is  $4B$ .

$J' = J'' + 1$  or  $J' = J''$   
 $J''$  - upper state  
 $J'$  - lower state



Considering transition from  $v=0$  to  $v=1$

$$\Delta E_{J',v} = E_{J',v=1} - E_{J'',v=0}$$

$$= BJ'(J'+1) + \frac{1}{2}\bar{\omega}_e - 2\frac{1}{4}\bar{\omega}_e - BJ''(J''+1) + \frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e$$

$$= \bar{\omega}_0 + B(J' - J'')(J' + J'' + 1) \text{ cm}^{-1}$$

where  $\bar{\omega}_0 = \bar{\omega}_e(1 - 2x_e)$

(1)  $\Delta J = +1$ , i.e.  $J' = J'' + 1$  or  $J' - J'' = +1$  hence

$$\Delta E_{J',v} = \bar{\omega}_0 + 2B(J'' + 1) \text{ cm}^{-1}, J'' = 0, 1, 2, \dots, 20$$

Given that;  $J' = J'' + 1$

$$\Rightarrow \Delta E = \bar{\omega}_0 + [B(1)(2J'' + 3)] = \bar{\omega}_0 + 2B(J'' + 1) \text{ cm}^{-1}$$



(ii)  $\Delta J = -1$ , i.e.  $J'' = J' + 1$  or  $J' - J'' = -1$  and  
 $\Delta E_{J,v} = \bar{\omega}_0 - 2B(J' + 1) \text{ cm}^{-1}$ ,  $J' = 0, 1, 2, \dots, 20b$

These two expressions can be combined into

$$\Delta E_{J,v} = \bar{\nu}_{\text{spec}} = \bar{\omega}_0 + 2B_m \text{ cm}^{-1}, \quad m = \pm 1, \pm 2, \dots,$$

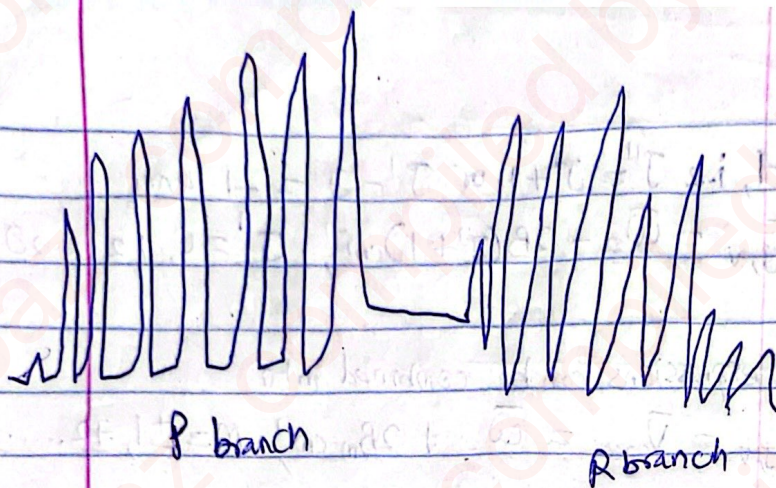
where  $m$ , replacing  $J'' + 1$  in 20a and  $J' + 1$  in 20b

$\bar{\omega}_0 \rightarrow$  band origin / band centre and implies that the spectrum consists of equally spaced lines and the spacing equals to  $2B$  on each side of the band origin.

Lines to the ~~known~~ frequency of the band origin.

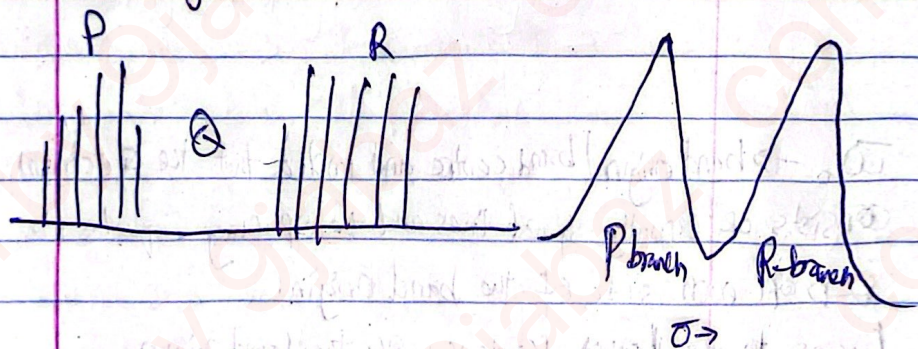
$m = -ve$  and  $\Delta J = -1$  are referred to as the P-branch

Lines to the high frequency side of the band origin with  $m = +ve$  and  $\Delta J = +1$  are referred to as the R-branch.



~~The Q branch is the band origin~~

The band origin is called the Q branch



In eqn 20a & 20b above it has been assumed that the rotational constant  $B$  at the ground and excited vibrational levels are the same. Similarly the Centrifugal distortion constant has been assumed negligible





The bond length of  $^{12}\text{C}^{14}\text{N}$  is  $117\text{pm}$  and its force constant is  $1630\text{N m}^{-1}$ . Predict the vibrational-rotational spectrum of the molecule.

22/05/26

### Vibrational Spectroscopy of Polyatomic Molecules

For a molecule that has  $n$  atoms, it is important to take note of the coordinate of the motion of the molecules.

We need the coordinates to describe the motion of vibration.

Every molecule has  $3N$  degrees of freedom.

For any change in position, the number of necessary changes in coordinate is the same.

For a molecule having  $n$  atoms, each atom's change in position can be broken down into changes ~~in~~  $\Delta x$ ,  $\Delta y$ , and  $\Delta z$  in coordinate. Although, these changes in coordinate may have different values and an  $n$ -atom molecule needs a total of  $3N$  changes in coordinates to describe its ~~coordi~~ motion, because the atoms are free to move in  $3N$  different independent directions, the molecule is said to have  $3N$  degrees of freedom.

The combined motion of all atoms for three of the  $3N$  ways

corresponds to all of the atoms moving in either the x, y or z direction. This three out of the  $3N$  ways accounts for the translational motion of the molecule as a whole

$3 \equiv$  translational motion of the molecule -  
which remains  $3N - 3$

For rotational motion, if the molecule is a linear molecule, they are two possible ways of rotation for a linear molecule while there are three rotational degree of freedom for non-linear molecule and that implies that accounting for translational and rotational, there remains  $3N - 5$  degree of freedom for a linear molecule and  $3N - 6$  degree of freedom for a non-linear molecule

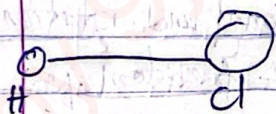
The above leaves either  $3N - 5$  for linear molecules or  $3N - 6$  for non-linear molecules. This remaining degree of freedom accounts for the normal mode of vibrational degrees for freedom.

For translational and rotation, the atoms in the molecule does not move independently for



However, for vibrational motion, each atoms can move independently for one another.

That is, the vibration of all molecules can be described as independent motion, such that for each motion, the frequency of vibration for all atoms is the same. To a very good approximation, the frequencies of light that are absorbed due to vibrational motion of atom in molecules are those that have the same frequency as the normal mode of vibration.



Because of the electronegativity differences of these two atoms, they are vibrating. If the bond is vibrating at a certain frequency, it can only absorb light of the same energy.

Two molecules cannot absorb the same energy, therefore no two bonds can vibrate at the same frequency.

How many vibrational mode will there be in HCl

# is linear;  $3N - 5$  ( $N \geq 2$ )

$$= 3 \times 2 - 5$$

$$= 1 \quad 58$$

group

$$\frac{c}{\lambda}$$

$$f = \frac{c}{\lambda}$$

If has only one vibrational mode, it is called stretching vibration mode.

\* If the frequency of vibration in the HCl molecule is equals  $8.65 \times 10^{13}$  Hz. Calculate the wave number of the radiation that can absorbed by this molecule.

The wave number of the absorbed radiation =

¶

Possible Vibrations of Three Atoms in Water molecule.

How many distinct frequency of absorption is present in water molecule?

Non linear,  $3N - 6$

$$3 \times 3 - 6 = 9 - 6 = 3$$

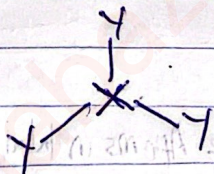
Three distinct absorption frequency which occurs at 3756, 3657 and 1595  $\text{cm}^{-1}$ . These three modes of vibration are generally referred to as asymmetric <sup>higher energy</sup> stretching mode, symmetric <sup>stretching</sup> stretching mode, and bending mode.



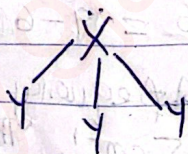
Suggest a structure for  $XY_3$  molecule so that:

- (i) It gives a rotational spectrum
- (ii) Does not give a rotational spectrum

(i) When  $XY_3$  is trigonal planar, it will not give rotational spectrum because it will have no dipole moment. It has a net dipole moment of zero.



(ii) When  $XY_3$  is trigonal pyramidal, it has a net dipole moment, therefore it will give a rotational spectrum.



# **Dr. Olusegun's Part**



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# Raman Spectroscopy

Raman deals with both vibrational and rotational motion. We want to determine the motion of the molecule can we understand the theoretical principle of Raman.

## Introduction

The light source in Raman is laser.

In all spectroscopic method, there's always a light source which interacts with the molecules leading to three possibilities

(i) Absorption (ii) Transmission (iii) Scattering - Raman deals with this.

$\nu$  will have same as the light source (Rayleigh)

Light source has the  $\nu$  below the frequency of the scattered

~~that~~

The three basis

- (i) frequency of scattering = frequency of light source
- (ii) frequency of light source > frequency of scattered light
- (iii) frequency of scattered light > frequency of light source

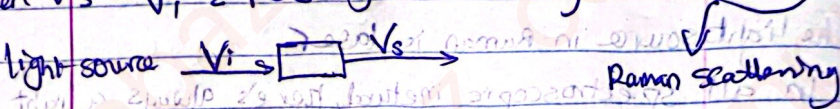


When the frequency of the scattered light is  $<$  than frequency of the incident light is called Stokes scattering

$\nu_s < \nu_i$  = Raman scattering (Stokes scattering)

when  $\nu_s > \nu_i$  = anti-Stokes scattering

when  $\nu_s = \nu_i$  = Rayleigh scattering



The combination of the three is called Raman spectroscopy

There are two ways in which Raman scattering effect can be explained

(i) Classical theory

(ii) Quantum theory

## Classical Theory

For a molecule to be Raman active, it must not have a permanent dipole moment, but rather an induced dipole moment.

Eg polar molecules like  $\text{O}-\text{H}$  will not show positive Raman

But molecules like  $\text{H}-\text{H}$  will undergo polarization and thereby will have an induced (temporary) dipole.

This can be caused using light source to induce dipole into the molecule.

polarization will cause electron cloud to shift to one side, causing each atom to have temporary positive and negative charge.

In other words, for the molecule to be Raman active, it must be non-polar and must be easily polarized in order to induce dipole moment.

Normally, solids and liquids usually have strong Raman line, gases usually have weak Raman line.

IR and Raman are usually opposite, some molecules active to IR will not be active to Raman.

We do not use aqueous solution due to interference, it can be used with IR. That makes Raman very important



## Principles Behind Raman Spectroscopy

Lord Rayleigh discovered Rayleigh Scattering, he discovered that when light interacts with substance scatters

Smickel (Schae) → not only that light scatter, some of the frequency of light source are not always equal to incident light

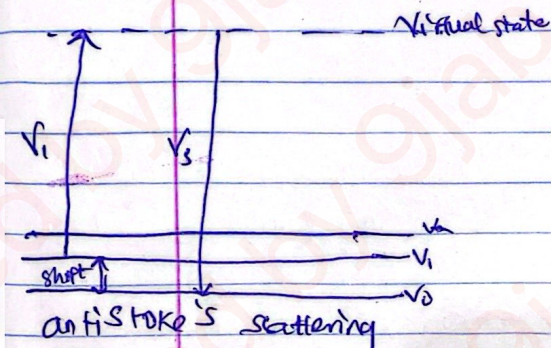
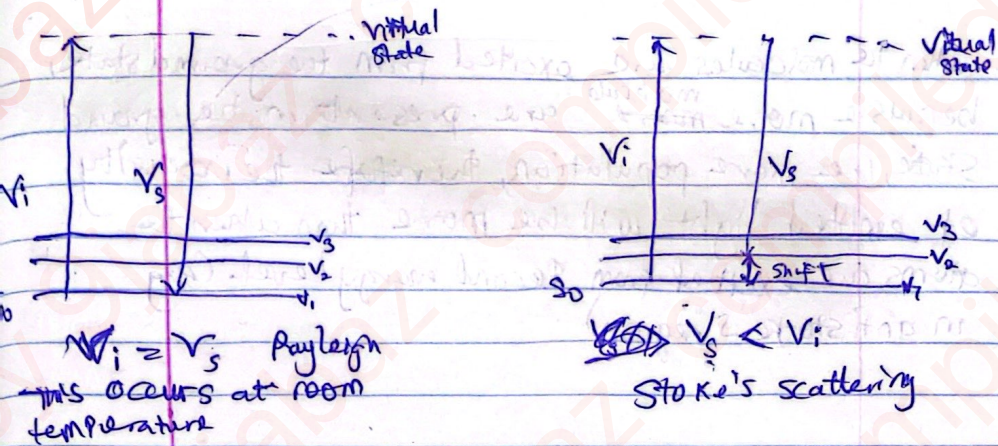
Smickel (1923)  
When light interacts, some of it will have frequency as frequency of incident light & some will have lower frequency of it and some higher than incident light

C. V Raman

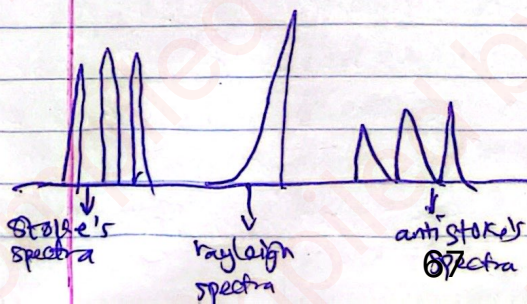
He puts a theoretical basis to both Smickel and Rayleigh theory. His source of experiment was sun, a polychromatic light. In 1930, C. V. Raman was awarded Nobel prize in physics.

Laser used in Raman is polychromator but monochromator is used to allow light of single wavelength to interact

Scattering below and above the incident light is called (Raman scattering) effect



When the temperature is high, we have more molecule in the anti-stoke's than the stoke's region.



The spectra lines depends on the intensity of the light admitted.



when the molecules are excited from the ground state, because a more ~~more~~ <sup>molecule</sup> are present in the ground state, i.e. more population, therefore the intensity of emitted light will be more than when the atoms are excited from second energy level. (Carg in anti-Stokes region).

3/06/26

Raman spectroscopy does not destroy the material

The natural phenomenon that portrays Rayleigh is the blue sky. The sun is a polychromator. When we see a blue sky, it is because blue is the most scattered

\* Based on your understanding of Raman spectroscopy, explain the concept of a blue sky

Why is it Rayleigh? It is because the frequency of the light coming from the sun is equal to the frequency of the scattered blue light seen.

In Stokes's scattering the molecule has absorbed some of the incident light, so it does not return back to the ~~any~~ ground state.

### Characteristics of Raman Light

- Intensity of Stokes > that of anti-Stokes (because majority of the population are in the ground state in Stokes)

\* Every Raman shift is specific for different molecules

\* IR and Raman are usually in the same energy space and they are complementary to each other

- ~~The~~ Stokes's occurs at a lower energy (ground state)



compared to anti-stokes (which is already excited).  
Therefore Stokes occurs at longer wavelength, and anti-stokes at shorter wavelength.

— for a molecule to be Raman active, it must be easily polarized, <sup>dipole induced,</sup> ~~then the molecules~~ then the molecules can be scattered.

How do we relate the induced dipole to the energy that is supplied to the molecule?

The induced dipole ( $\mu$ )  $\propto E$  (Energy of the scattered light)  
 $\Rightarrow \mu = \alpha E$   $\alpha$  = polarization constant or molecular polarization

$\mu$  or  $M$  is a vector quantity, it has magnitude and direction, it is this magnitude and direction that determines the polarization.

Anisotropy  $\Rightarrow$  occurs when the physical and chemical properties ~~is determined by~~ the changes with the direction of measurement. The direction of measurement determines the properties of the molecule. Anisotropy molecule will cause induced dipole, easily polarized.

For a molecule to show positive Raman, it must be anisotropic in nature

~~For an~~

Isotropy: The properties of the molecules remain the same regardless of the direction of measurement. They are usually spherical; the molecule will not be easily polarized

$$P(t) \propto E(t)$$

and  $E_2(t) = E_0 \cos \omega t$

$$P(t) \propto E_0 \cos \omega t$$

(This is the induced dipole for Rayleigh scattering)  
Only useful for elastic scattering

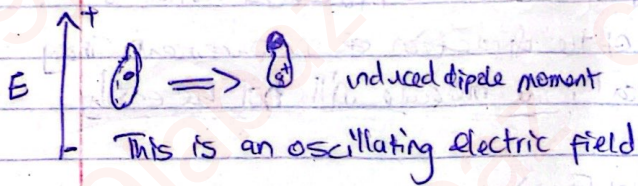
Elastic Scattering: This occurs with Rayleigh, when  $v$  of incident =  $v$  of scattered

Inelastic Scattering: It occurs with Stokes and anti-Stokes



05/06/26

Polarization is separation of charge, electrons migrate towards the positive pole leaving behind the positive charge in the negative pole



When an electric field is applied to a molecule, it causes distortion. Therefore, we can say the molecule has undergone polarization, causing it to have an induced dipole moment.

$$p(t) = \alpha E$$

$$E = E_0 \cos \omega t \quad \omega = \text{angular frequency, } \omega = 2\pi \nu_0$$

$$p = \alpha E_0 \cos 2\pi \nu_0 t \quad (\text{This is the induced dipole moment caused by Rayleigh scattering})$$

when  $\nu_0 = \nu_s$

Effect of Vibration As a Result of Electric Field

$$p = \alpha E_0 \cos 2\pi \nu_0 t$$

$$\alpha = \alpha_0 \cdot \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q + \dots \quad \text{using Taylor's series}$$

Substituting this, we have

$$\alpha = \left( \alpha_0 + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 \cos 2\pi \gamma_m t + \dots \right)$$

$$P = \left( \alpha_0 + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 \cos(2\pi \gamma_m t) \right) E_0 \cos(2\pi \gamma_0 t)$$

$$P = \alpha_0 E_0 \cos 2\pi \gamma_0 t + \left( \frac{\partial \alpha}{\partial Q} \right)_0 E_0 Q_0 (\cos 2\pi \gamma_m t) (\cos 2\pi \gamma_0 t)$$

$$\begin{aligned} \sin A \sin B &= \frac{1}{2} (\cos(A-B) - \cos(A+B)) \\ \cos A \cos B &= \frac{1}{2} (\cos(A-B) + \cos(A+B)) \end{aligned}$$

$$P = \alpha_0 E_0 \cos(2\pi \gamma_0 t) + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 E_0 \frac{1}{2} [\cos 2\pi (\gamma_0 - \gamma_m) t + \cos 2\pi (\gamma_0 + \gamma_m) t]$$



$$\cos(0.6/2c)$$

$$P = \left[ \alpha_0 + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 \cos(2\pi \nu_m t) \right] E_0 \cos(2\pi \nu_0 t)$$

$$P = \alpha_0 E_0 \cos(2\pi \nu_0 t) + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 E_0 \cos(2\pi \nu_m t) \cos(2\pi \nu_0 t)$$

$$P = \alpha_0 E$$

Polarization has 3 frequency components

- $\nu = \nu_0$  Rayleigh line
- $\nu = \nu_0 - \nu_m$  Raman Stokes lines
- $\nu = \nu_0 + \nu_m$  Raman anti-Stokes lines

If  $\left( \frac{\partial \alpha}{\partial Q} \right)$  is zero, no Raman lines will be observed

For a molecule to be Raman active, it must cause a change in a component of the polarizability (either magnitude or direction)

8/08/26

~~the~~ The polarization varies with the angle of rotation.  
The frequency of rotation is usually twice that of vibration.

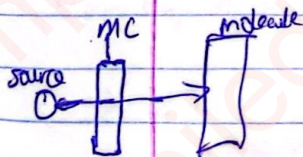
Raman shift will be equal to twice the frequency of rotation.

$$P \propto \alpha_0 E_0 \cos(2\pi \nu_0 t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 E_0 \cos 2\pi$$

~~The essence~~

Because the classical theory does not account for the intensities of the various lights, which is the essence of the quantum theory.

## Quantum Theory of Raman Effect



The molecule itself has its own energy before also the light. As soon as the photon hits the molecule, if the photon loses its photon to the molecule. The energy of



22/20/8

The scattered light is lesser than the incident light, which is a Stokes' scattering. But if the photon interacts with the molecule and the molecule adds its own energy with that of the photon, the energy of the scattered light is greater which is anti-Stokes scattering.

Difference between quantum and classical

Light source is now looked at as photon, which is both a matter and energy. Therefore, it both interacts with the molecule.

$$E_p + \frac{1}{2}mv^2 + h\nu = E_q + \frac{1}{2}mv'^2 + h\nu'$$

If the  $\Delta v$  is negligible

$$\Rightarrow E_p + h\nu = E_q + h\nu' \quad \therefore \nu = \nu'$$

$$E_p - E_q = h(\nu' - \nu)$$

$$(\nu' - \nu) = \frac{E_p - E_q}{h}$$

$$\nu' = \nu + \frac{E_p - E_q}{h}$$

$$\left( \frac{E_p - E_q}{h} \right) \neq \Delta \left( \frac{E_p - E_q}{h} \right) \approx \frac{\Delta E}{h} \approx \Delta \nu$$

$$\Rightarrow \nu' = \nu \pm \Delta \nu$$

$$\Rightarrow \nu' = \nu \pm \Delta \nu$$

(i)  $E_p = E_q$ , Rayleigh (molecule deflects the photon; no exchange of energy - Elastic collision)  
 $\nu' = \nu$

(ii)  $E_p > E_q$  anti-stokes (molecule was previously excited)  
 $\nu' = \nu + \Delta \nu$

(iii)  $E_p < E_q$  Stokes  
 $\nu' = \nu - \Delta \nu$

$$E_p - E_q = \pm h \nu_c$$

$\nu_c \approx$  Char frequency of molecule  
 $n \approx 1$

Incident freq  $\approx$  Scattered frequency  $\approx$  characteristic frequency of molecule.



\* Raman lines are equidistant from parent line and other side at distances equal to characteristic frequency of molecule equals

IR absorption line of scatter

$$\nu_A \pm \nu = \nu' < \nu$$

\* If Virtual state = real state of the system  $\therefore$  Resonance Raman effect

\* Annihilation of incident photon and creation of scattered photon is simultaneous

\* Intensity of spectral = Initial population of the state from which transition

state (i)  $E_i < E_f$  (i)

$$\nu_A + \nu = \nu'$$

state (ii)  $E_i > E_f$  (ii)

$$\nu_A - \nu = \nu'$$

$$\nu' = \nu \pm \nu_A$$

characteristic frequency of molecule  $\nu_A$

$$\nu' = \nu$$

frequency of scattered photon = characteristic frequency of molecule

Vibration made of:  $\text{CO}_2$  molecules

①.

Symmetric Stretching  $\text{CO}_2$  is Raman active, but IR inactive

Asymmetric " of  $\text{CO}_2$  is IR active but Raman inactive

Bending mode is both IR and Raman active

Mutual exclusion principle states that if a molecule has a center of symmetry, then Raman active vibrations are IR inactive and vice versa. If there is no center of symmetry then some vibrations may be

[Question]

① Predict the form of the rotational Raman spectrum of  $^{35}\text{Cl}_2$  for which  $B = 0.975 \text{ cm}^{-1}$  when it is exposed to  $336.732 \text{ nm}$  laser radiation

② The first three Stokes lines in the rotational Raman spectrum of  ~~$\text{H}_2\text{O}$~~   $^{16}\text{O}_2$  are separated by  $14.4 \text{ cm}^{-1}$ ,  $25.8 \text{ cm}^{-1}$  and  $31.4 \text{ cm}^{-1}$  from the exciting radiation. Using the rigid rotor approximation obtain a value for  $I_0$



9/06/26

## Raman Spectroscopy

### Pure Rotational / Raman Spectra

Gross selection rule: The molecule must be anisotropically polarizable eg  $N_2$ ,  $H_2$ ,  $O_2$  etc. If the molecule is isotropically polarized it will not show any rotational Raman Spectroscopy.

For linear and diatomic molecules

$$E_J = hc B J(J+1) \text{ Joules}$$

$$J = 0, 1, 2, 3, \dots$$

$$B = \frac{h}{8\pi^2 I c}, \quad I = Mr_o^2$$

$$M = \frac{m_1 \times m_2}{m_1 + m_2}$$

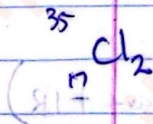
$$S. R = [\Delta J = 0, \pm 2]$$

Stokes = +ve (+2)  $J = 0, 1, 2, 3, \dots$   
 anti-Stokes = -ve (-2)  $J = 2, 4, 6, \dots$

Nuclear spin



The atomic mass and atomic number is even, atom's like that have nuclear spin <sup>of</sup> zero (Bosons)



odd atomic mass and atomic number (fermions)  
Nuclear spin is  $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$



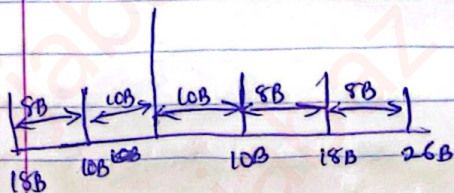
11/06/26

When  $I=0$ , the even lines will be empty

$$\bar{\nu} = \bar{\nu} + B(4J+6) \text{ cm}^{-1}$$

$J=0, 2, 4, 6 \dots$  even empty

$J=1, 3, 5, 7 \dots$



when  $I$  is non zero, both the odd and even lines are occupied but the odd is weak

~~even~~

neutron & proton number is even,  $I=0$

neutron and proton number is odd  $I=1$

neutron is odd and proton is even or vice versa,  $I=1/2$

### Vibrational Raman spectra

Raman is rotational + vibration, (i.e. microwave + IR)

Energy for vibrational is higher than that of rotational.

For a linear and diatomic

$\Delta V = \pm 1, \pm 2, \pm 3, \dots$  Selection rule  $\rightarrow$  overtones / hot bands

We must consider when  $\Delta V = \pm 1$

when  $\Delta V = 0$ , it is Rayleigh

$-ve = \text{Stokes}$   
 $+ve = \text{anti-Stokes}$

$$\nu_{\text{fundamental}} = \nu_{\text{existing}} + \Delta E_{\text{fundamental}}$$

### Summary

Vibrational Raman involves transition where  $\Delta V = \pm$  (fundamental)  
with possible accompanying rotational changes

A vibration that is Raman active is the one that is symmetrical  
but any other asymmetric motion is IR active but Raman  
inactive

Vibration that shows Raman active will be IR inactive

Stokes line  $\rightarrow$  O-branch

anti-Stokes line  $\rightarrow$  S-branch

Rayleigh line  $\rightarrow$  O-branch

Difference Betw.



## Difference Between Raman and IR Spectra

### Raman

- ① Due to scattering by vibrating molecules
- ② Caused by induced dipole (Change in polarizability)
- ③ Water can be used as solvent
- ④ Vibrational frequencies of large molecules are measured
- ⑤ Very accurate but not very sensitive
- ⑥ Raman lines are weak; concentrated solutions needed to increase the intensity of Raman lines
- ⑦ Optical systems are made of glass or quartz

### IR

- ① Due to absorption by vibrating molecules
- ② Change in intrinsic dipole moment
- ③ Water cannot be used as solvent
- ④ Vibrational frequencies of large molecules cannot be measured
- ⑤ Very accurate and sensitive
- ⑥ Dilute solutions are preferred

It has a great  
grating which  
helps disperse light

Differentiate between dispersive Raman and near IR

15/06/26

Electronic spectroscopy studies transition between different electronic states of molecules induced by absorption or emission of UV or

visible light

\* transition occurs within wavelength of  $100 - 800 \text{ nm}$

\* Transition goes from bonding/non-bonding to free antibonding orbital.

\* Spectra often show broad bands

very insignificant

rotational < vibrational < electronic

energy increases

Usefulness of ESR

- (i) determining electronic structure
- (ii) identifying chromophores
- (iii) quantitative analysis



According to Born-Oppenheimer approximation

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

Electronic energies:  $\sim 10^1 - 10^5$  (UV-Visible region)

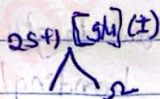
Vibrational energies:  $10^3 \text{ cm}^{-1}$  (IR region)

Rotational energies:  $1 - 10 \text{ cm}^{-1}$  (microwave region)

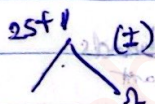
### Term Symbol

For diatomic molecules

The general form



(homonuclear diatomic molecules with center of inversion)



(heteronuclear diatomic molecules with no center of inversion)

where

$S$  = Total spin angular momentum (sum of all electron spins)

$2S+1$  = Spin multiplicity (singlet, doublet, triplet etc)

$\Lambda$  = orbital angular momentum projection along molecular axis

$\Omega$  = total angular momentum projection ( $\Omega = \Lambda + \Sigma$ )

$g/u$  = Symmetry under inversion (gerade/ungerade)

$+$  = Symmetry under reflection (for  $\Sigma$  states only)

A molecule with point of inversion also has point of reflection

$$2$$

$$-2, -1, 0$$

$\Lambda$ : projection of orbital angular momentum along the internuclear axis.  $\Lambda = (\sum l_i)$  is the projection for each electron ( $\sigma$ :  $l=0$ ,  $\pi$ :  $l=\pm 1$ ,  $\delta$ :  $l=\pm 2$ , etc.).

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$

for  $H_2$ :

Ground state:  $1\sigma_g$

$$\sigma_{1s}^2, \sigma_{1s}^{*0}$$

$$S=0, 2S+1=1$$

Since they are occupying bonding, it will be g  
for molecules; occupying the  $\sigma$  state, reflection +

Therefore,  $\sum g$

for excited state of  $O_2$

$$^3 \sum_g$$

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s} \sigma_{2p_z}^2$$



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25-11

Homonuclear diatomic molecules

the symmetry under inversion

$\Sigma, \pi, \Delta, \phi$

(i) Heteronuclear diatomic molecule without center of inversion

For  $\leq 14 \text{ e}^-$

$\sigma_g$  is  $\sigma_u^*$  is  $\sigma_g$   $\sigma_u^*$   $(\pi_u 2p_z = \pi_u 2p_y)$   $\sigma_g 2p_z$   $(\pi_g 2p_z = \pi_g 2p_y)$   $\sigma_u^*$

For  $> 14 \text{ e}^-$

$\sigma_g$  is  $\sigma_u^*$  is  $\sigma_g$   $\sigma_u^*$   $\sigma_g 2p_z$   $\pi_u 2p_z = \pi_u 2p_y$   $\pi_g^* 2p_z = \pi_g^* 2p_y$   $\sigma_u^* 4p_z$

Rules

- (1) If the symbol is  $\Sigma$ , then only  $+$  or  $-$  superscript will be used
- (2) g and u is referred to the orbital of the least electron filled
- (3) You only have - superscript only when the last electron is occupying a  $\pi$ -orbital
- (4) If two unpaired electrons lie in different orbital, then the rule applies that.

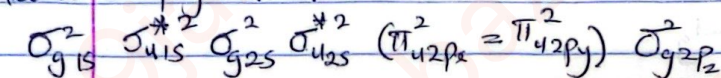
$g \times g = g, g \times u = u, u \times u = g$   
(most when dealing with excited molecules)

$$\Lambda_z / \sum |l_i|$$

\* For diatomic molecule that has completely filled orbitals e.g.  $H_2$ ,  $CO$ ,  $N_2$ , has the same term symbol

For  $N_2$  (G.S.)

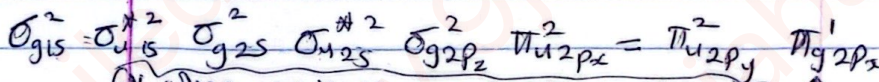
molecular configuration:



$1 \Sigma_g^+$  — Same as  $H_2$  term symbol

Which of the following have the same term symbol?

For NO  $7+8=15$



\* when you have less than half electrons in an orbital  $\Omega = 1/2$

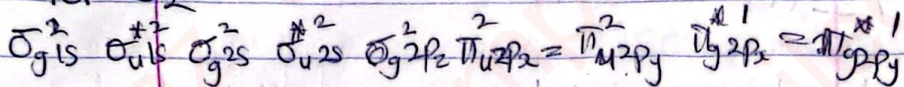
\* when you have more than half electrons in the orbital  $\Omega = 3/2$

For  $O_2$





For  $O_2$



$$\Lambda_z / \Sigma \text{ Li}^+$$

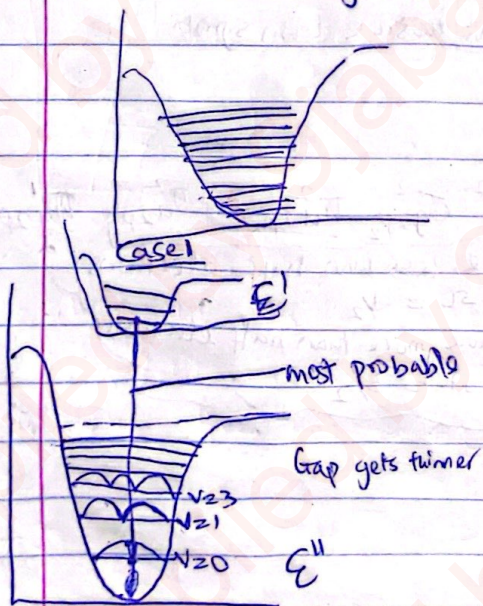
$$\Lambda_z (+1 + -1) = 0$$

$$\Lambda_z S = \sum 2S + 1 \quad \cancel{2(1) + 1 = 3}$$

$$\Rightarrow 2(1) + 1 = 3$$

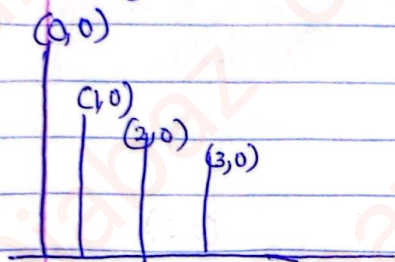
$$3 \sum_g$$

\* Electronic motion is faster than nuclear mo  
 \* transition occurs vertically on a Morse curve



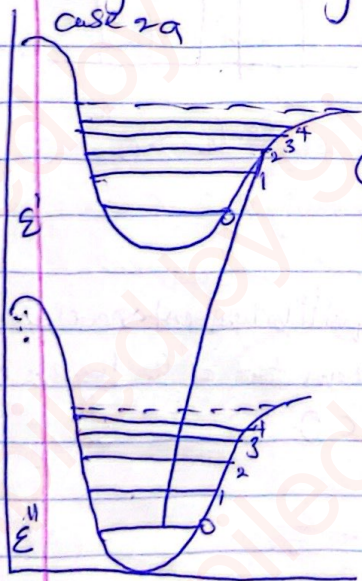
internuclear distance

In case 1, the upper electronic state have the same equilibrium internuclear distance as the lower state. This transition is the most probable and it will have the highest frequency.



$$r_e' = r_e'' \quad (r = \text{internuclear distance})$$

normally exhibited by  $O_2$  molecule  
case 2a



$$(v', v'')$$

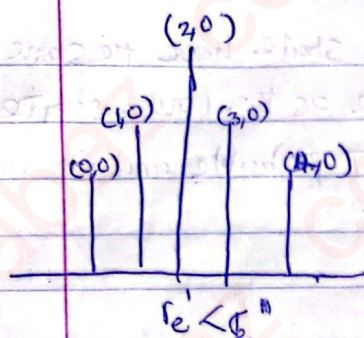
$$(2, 0)$$

$$r_e' \neq r_e''$$

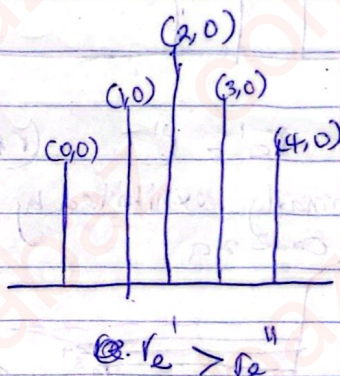
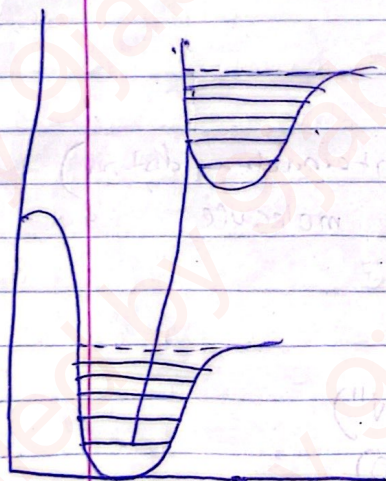
The lower equilibrium internuclear distance of the upper electronic state is a little greater than the lower one.

$$E' < E''$$





Case 2b

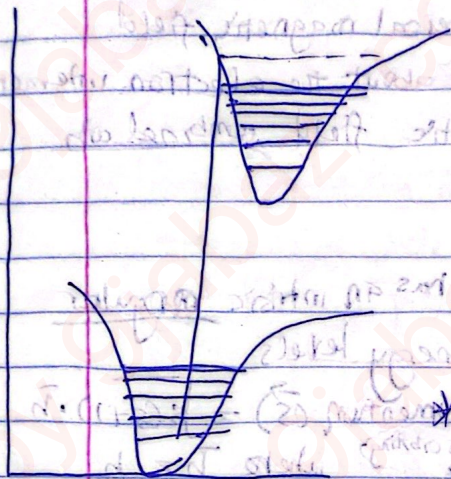


In case 2b, the upper state equilibrium internuclear distance is a little greater than that of the lower state molecules like that is CO

Case

The  $r_1' \gg r_2''$

case 3



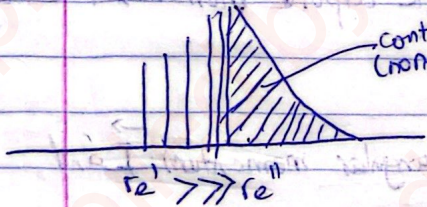
\* In this case, the excited molecule has energy in excess of its own dissociation energy

\* The molecule will dissociate without vibrating

\* The transition in this case, are not quantized, since the atoms which are formed may take up any value of kinetic energy.

$r_1' \gg r_2''$

The atoms that are formed in that state are stable but the energy is not quantized



continuum (non-quantizable)

This mostly occurs with  $I_2$

The Franck-Condon principle is important in calculating the energies and intensities of the electronic spectra



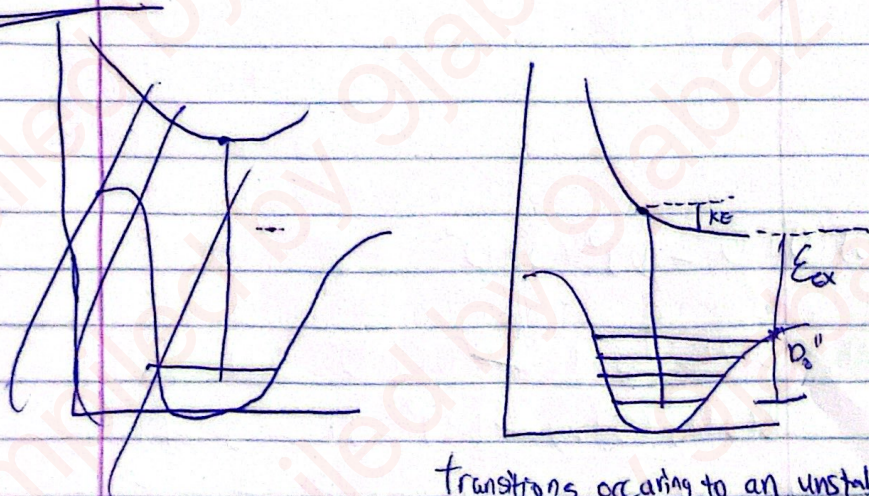
Dissociation energy is the energy required to separate a stable diatomic molecule  $AB$  in the  $v''=0$  vibrational state into two unexcited atoms  $A$  and  $B$ . The energy is represented as  $G(v'')$  and  $G(v')$

The total energy of the dissociated product from the upper state is greater by an amount  $E_x$  than that in the lower state. The lower wave number represents the continuum

The dissociation product separates with zero kinetic energy.

$$V_{\text{continuum limit}} = D_0'' + E_x \text{ (cm}^{-1}\text{)}$$

Case 4



Transitions occurring to an unstable upper electronic state.

When a molecule is raised to this state by excitation, it dissociates into product with total excitation energy  $E_x$ . The dissociation products fly apart with kinetic energy ( $E_{KE}$ ) which represents the excess energy in the final state above that needed just to dissociate the ~~product~~ molecule.

The  $E_{KE}$  is not quantized so, the whole spectrum will exhibit a continuum.



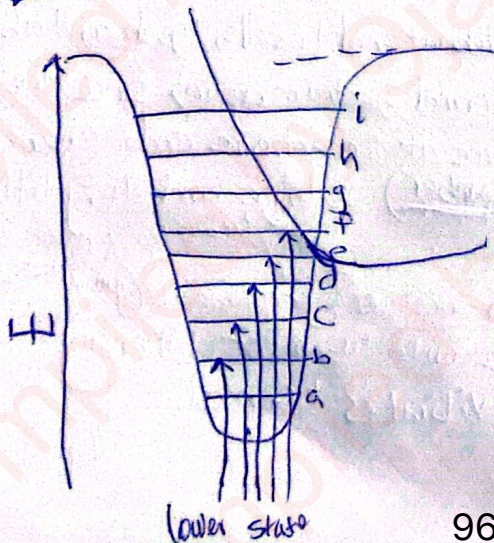
Electronic Spectroscopy\* Discuss predissociation  
part the drawingPredissociation (PD)

predissociation takes place with absorption/emission photo

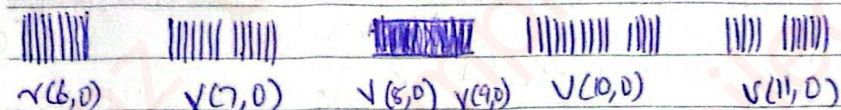
Predissociation is when molecules dissociates spontaneous with absorption.

A continuum <sup>or direct</sup> at high wave number would correspond to ordinary dissociation but the central continuum occurring at energies well below the true dissociation limit is referred to as predissociation.

Predissociation can arise when the Morse curve of a particular molecule in two different excited state intercept. One of the excited state is stable since it has a minimum in the curve and the other is continuous.







If a transition takes place into the levels a, b, or c a normal vibrational electronic spectrum occurs with rotational fine structure.

If the transition is to levels d, e, or f, the molecule may "cross over" onto the continuum curve and thus dissociates. This transition from one curve to another curve is a radiationless transfer, i.e., no energy is absorbed or emitted during the transfer.

Predissociation will occur before the molecule rotates. All ~~the~~ rotational fine structure will be destroyed in the spectrum.

Transition into ~~high~~ vibrational levels, g, h and above will give rise to a normal spectrum again, since the molecule spends most time at the extreme ends where  $v(\text{vibrational quantum number})$  is large and very little time in between.   
 details in the note.

\* Absorption Spectroscopy approach (grand selection)  
 $v_{\text{max}}$  is the vibrational line with the most intensity, where the molecule vibrates the most

≡≡≡



\* At dissociation limit, the vibration occurs so vigorously that it pulls apart

\* ~~Emission Spectroscopy Approach~~  
(excited  $\rightarrow$  ground state)

### \* Birge-Sponer Extrapolation

Vibrational level spacing decreases as  $v$  increases

\* Birge-Sponer overestimated the dissociation energy by 20%. The corrected value is gotten by multiplying their answer by 0.8

\* Convert the unit of dissociation to KJ/mole

$$0.01996$$

#### Problem 1

$$\omega_e = 2990 \text{ cm}^{-1}$$

$$\omega_e x_e = 52 \text{ cm}^{-1}$$

calculate  $D_e$  using Birge-Sponer method

$$D_e = \frac{\omega_e}{4x_e} = \frac{\omega_e^2}{4\omega_e x_e}$$

$$D_e = \frac{(2990)^2}{4 \times 52} \times 0.8 \times 0.01996$$

$\uparrow$  to correct value       $\uparrow$  to convert to KJ/mol

At some point the difference won't be constant, that is where extrapolation takes place

Date / /

Problem 2

$$\Delta G(0) = G(1) - G(0) \\ = 15,420 - 14,970 = 450$$

$$\Delta G(1) = G(2) - G(1) \\ = 15,860 - 15,420 = 440$$

$$\Delta G(2) = G(3) - G(2) \\ = 16,290 - 15,860 = 430$$

$$\Delta G(3) = G(4) - G(3) \\ = 16,710 - 16,290 = 420$$

$y = \text{intercept} + \text{slope}$

$$\Delta G(V') = 450 - 10V'$$

↓
↓  
 intercept      slope



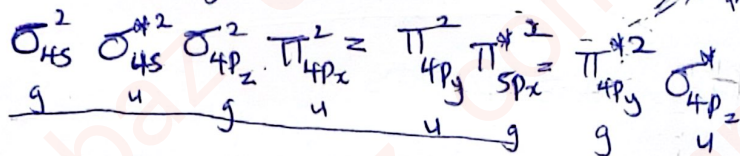
\* Term symbols (rules, allowed, forbidden).

\* Determine the term symbol for  $\text{Br}_2$

$_{35}\text{Br}$   $\text{Br} = 7$  Valence electrons;

$\text{Br}_2 = 14$  Valence electrons.

Molecular configuration



$$\Lambda = +1 - 1 + 1 - 1 = 0$$

\* For  $\Lambda = 0$ , we have term  $\Rightarrow \Sigma$

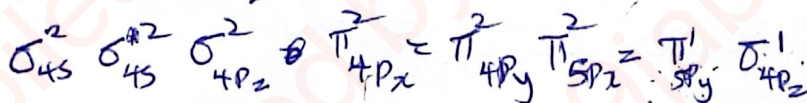
$$\begin{aligned} \text{multiplicity} &= 2S + 1 \quad (S = 0) \\ &= 2 \times 0 + 1 = 1 \Rightarrow \Sigma \end{aligned}$$

$$* g \otimes g = g$$

\* Because the last electron is on  $\pi$ , we have

$$a \Rightarrow \sum_g^+$$

Determine the term symbol of the first excited state of  $\text{Br}_2$ .



$$\Lambda = +1 + 0 = 1$$

For  $\Lambda = 1$ , we have term  $\Rightarrow \Pi$

$$\begin{aligned} \text{multiplicity} &= 2S + 1 \quad (S = 1) \\ &= 2 \times 1 + 1 = 3 \end{aligned}$$

$$\begin{aligned} p_x &= -1 \\ p_y &= +1 \\ p_z &= 0 \end{aligned}$$

7/6

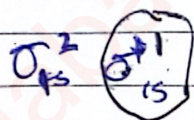
For 14 or greater than 14

$$* g \times u = u$$

\* If does not have purity



For  $\text{He}_2^+$  = 3 electrons



\* Last electron is on  $\sigma$ , Term =  $\Sigma$

\* Multiplicity =  $2S+1$  ( $S = 1/2$ )

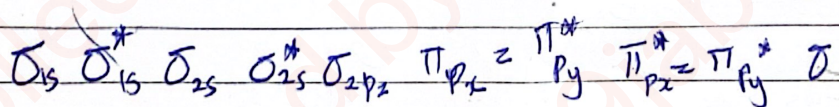
$$2(1/2) + 1 = 2$$

\* u

\* Last electron on  $\sigma = +$

Term symbol  ${}^2\Sigma_u^+$

For  $\text{O}_2^{\bullet}$  (first excited state)





\* Draw Morse curve when the equilibrium distance btw excited state and lower state is equal,  
Give example

\* Predissociation

\* Diffraction gratings, interferometer diffraction

\* Calculate  $\lambda_{max}$  of a molecule, for,



benzene is 255nm

With Cl  $\Rightarrow 255\text{nm} + 10 = 265\text{nm}$

\* Types electronic transition in polycyclic molecule, why they show broader bands.

\* Beer Lambert equation

$$A = \epsilon c l = \log \frac{I_0}{I}$$

$\nearrow$  incident intensity  
 $\searrow$  transmitted intensity

\* Substituent effect, chromophore and auxochrome  
know it offhand

For test

\* ~~Raman~~

\* Electronic spectroscopy

\* Transition

# **Check slides for Prof. Ogunlusi's Part**