Molecular spectroscopy

~~Non magnetic spectroscopy~~

1. Introduction
2. Rotational - Microware spectroscopy
3. Vibrational infrared spectroscopy

} prof. Aooyemi

4. Rotational Raman
5. Vibrational Raman
6. Electronic Spectrosopy

} Dr. Olusegun

Magnetic spectroscopy

1. Nuclear
2. Electron Spin

} prof. ogunlusi

Textbo

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 ~~planarity~~ planarity or non-planarity of large molecules
- Stability of cis and trans isomers

It is a very important tools 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 ~~t~~ 325nm

Visible region > 325 - 800nm

IR : 900 - 1100nm

Electromagnetic : Electronic, 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 orientation of magnetic

~~lthe~~

The transition of electron from lower energy level to higher energy level is called Absorption (Absorption of radiation) which is due to interaction of electromag radiation.

→ It becomes unstable

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

$$M + hc\bar{\nu} \longrightarrow M^*$$

* The blue colour of $CuSO_4$ due to the absorption of the complementary colour, red.

$CuSO_4$ appears blue, cos it absorbs red

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

$$M^* \longrightarrow M + hc\bar{\nu}$$

e.g Tungsten filament lamp etc

3) Induced emission

$$M^* \longrightarrow M + 2hc\bar{\nu}$$

Seeding of Cloud with AgI cryscstal to induce reaction

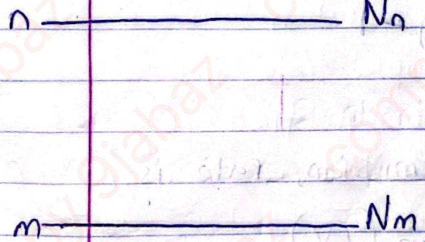
$$M + h\nu \longrightarrow M^*$$

$$M^* + h\nu \longrightarrow M + 2h\nu$$

~~$M + 2h\nu$~~ $\longrightarrow$

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

$$\frac{dN_n}{dt} = N_m B_{nm} \rho(\bar{\nu})$$

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

$$A \longrightarrow B$$

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

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

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

$$\rho(\bar{\nu}) = \frac{8\pi hc\bar{\nu}^3}{\exp\left(\frac{hc\bar{\nu}}{K_BT}\right)-1}$$

Similarly, for induced emission, rate is;

$$\frac{dN_n}{dt} = -N_nB_{nm}\rho(\bar{\nu})$$

The upper state populalation 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

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

In the presence of radiation of wave number $\rho(\bar{\nu})$, 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:

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

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

$$A_{nm} = 8\pi hc\bar{\nu}^3 B_{nm}$$

Questions

(1) The wavelength of the radiation absorbed during a particular spectroscopic transition is observed to be 10 Nm. Express this in frequency and wave number, and calculate the energy change during the transition in $J\,molecule^{-1}$ and $J\,mole^{-1}$. 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 4.005×10^{-22} J/molecule. If there are 1000 molecules in the groundstate. What is the approximate equilibrium population of the excited state at temperatures

ⓐ 29 K ⓑ 145 K ⓒ 290 K ⓓ 2900 K

Comment on your answers

③ As a function of frequency, the spectral radiation
[illegible] density is given as

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

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

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

02/04/26

The Eistein coefficients are related to the wavefunctions ψ_m and ψ_n of the combining states through the transition moment R^{nm}, a vector quantity by

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

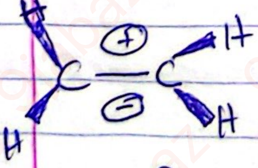
for interaction with the electric component of the radiation

$$M = \sum_i q_i r_i$$

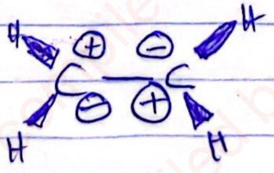
M = dipole moment

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

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



(a)



(b)

It ~~an~~ molecule ~~electron~~ is promoted from π → π* in an electronic transition, the we have corresponding dipole momen ~~t~~ interaction

$\left(\begin{array}{c}\text{no dipole moment} \\ \text{molecule}\end{array}\right) \longrightarrow$

A transition moment may be non-zero, even though the permanent ~~electric~~ dipole moment is zero in both the m an n state

$\overset{\delta^-}{O}\overset{\leftarrow}{\equiv}C=\overset{\delta^-}{O}$ (net dipole moment is zero)

even though $M = 0$, its R^{nm} is not zero, and therefore can be peaked spectroscopically

$M \neq 0, \; R^{nm} = 0$ can't be peaked spectroscopicaly
{transition probability}

The transition probability is given by the $(R^{nm})^2$ and is related to Eistein coefficient ~~probability~~ Bnm

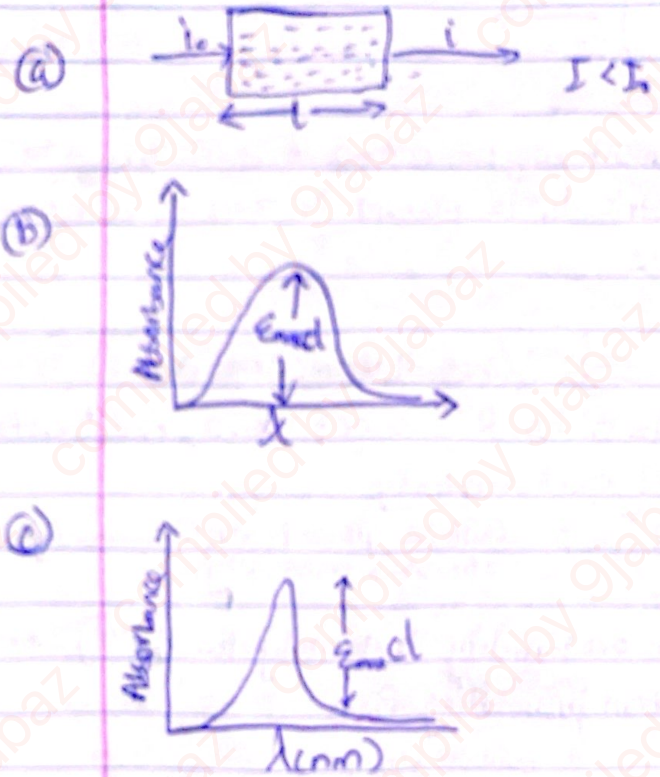
Recall,

$B_{nm} = B_{mn}$ } induced absorption / induced emission

$A_{nm} \Rightarrow$ Spontaneous emission

$$B_{nm} = \frac{8\pi^3}{(4\pi\varepsilon_0)^3 h^2} \left| R^{nm} \right|^2$$

AP



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

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

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

* 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 molecule have a simple rotational spectrum (rotation in only two dimensions) → (BF_2, BF_3, PF_5)

* For non-linear polyatomic molecules, they have one (highly symmetric) to three (for less symmetric species) diffrent 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 striaght line such as HCl or OCS (carbon oxysulphide)

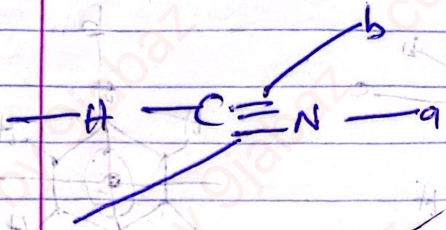
H—Cl   O—C—S

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 (to a very close approxiamation) to be equal to zero. Therefore, for linear molecules;

$$I_B = I_C ; I_A = 0$$



$I_c = I_b > I_a = 0$

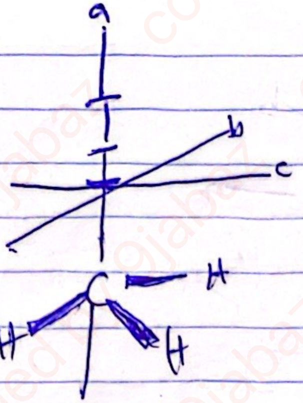
principal inertial axes of hydrogen cyanide - a linear molecule

Symmetric Tops

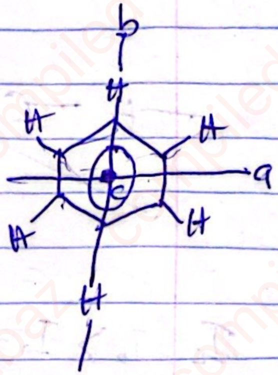
- The end-over-end rotation in and out of the plane are identical
- The moment of inertia about the principal axis of rotation is now not negligible. It's called a top because it's spinning about the principal axis of rotation. Therefore, for such molecules:

$$I_B = I_C \neq I_A \quad I_A \neq 0 \quad \ldots (2)$$

* It is called a prolate symmetric tops 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



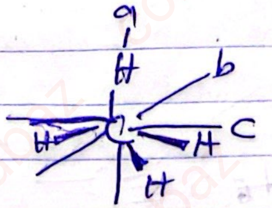
Spherical Tops

* 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~~ of molecules that undergo rotational Spectroscopy



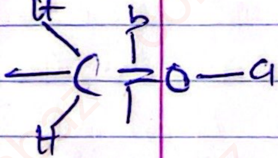
Assymetric Tops

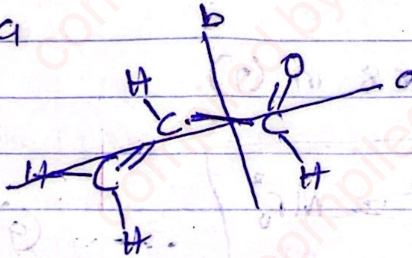
All three moment of inertial are different

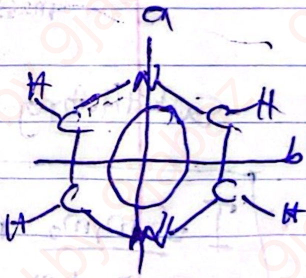
$$I_A \neq I_B \neq I_C \quad (4)$$

Therefore rotation will produce a net dipole moment so they will undergo MW spectroscopy

Majority of substances are in this category.







~~Re~~

Rotational Spectra of Diatomic Molecules

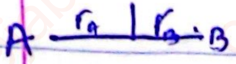
$r_1 + r_2 = r_0$ .... (5)

$m_1 r_1 = m_2 r_2$ .... (6)

The moment of inertia about the center of gravity

$I = m_1 r_1^2 + m_2 r_2^2$ ....~~(7)~~

$= m_2 r_2 r_1 + m_1 r_1 r_2$ .... (7)



$r_0 = r_A + r_B$

From equations 5 and 6

~~The~~ $m_1 r_1 = m_2 r_2 = m_2(r_0 - r_1)$

$\therefore r_1 = \frac{m_2 r_0}{m_1 + m_2}$; $r_2 = \frac{m_1 r_0}{m_1 + m_2}$ ...... (8)

$I = \underset{\substack{\downarrow \\ \text{reduced} \\ \text{mass}}}{\mu} r_0^2$ $\qquad N = \frac{m_1 m_2}{m_1 + m_2}$

Substituting for 8 in (7)

$$\boxed{I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = M r_0^2} \quad \text{......} \ (9)$$

07/04/26

Energy of Rotation

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

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

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

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1}, \quad J = 0, 1, 2, 3 \ldots (1$$

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

Equation (11) is usually abbreviated to

$$\varepsilon_J = BJ(J+1) \text{ cm}^{-1} \ldots\ldots (12)$$

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}C, ^{16}O. Convert these to units of cm^{-1} If the bond length is 1.1283 Å (Relative atomic mass: C = 12; O = 15.999)

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

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

$$I = \frac{m_C m_O}{m_C + m_O} \times (1.1283 \times 10^{-10} m)^2$$

Since we are looking for a single molecule, not in a mole of the atom

$m_C = \frac{12.01 \times 10^{-3} kg}{6.02 \times 10^{23}}$, ~~$m_O = 15.999$~~ $m_O = \frac{16 \times 10^{-3}}{6.02 \times 10^{23}} kg$

$$\frac{m_c m_o}{N_{a}^2} \div (m_c + m_o)$$

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

$$I = \left(\frac{12.01\times10^{-3} \times 16\times10^{-3}}{12.01\times10^{-3} + 16\times10^{-3}}\right) \frac{1}{6.03\times10^{23}} \times \left(1.1283\times10^{-10}\right)^2$$

$$I = 1.4501\times10^{-46}$$

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

when $J = 1$

$$E_J = \frac{(6.626\times10^{-34})^2}{8\pi^2 \times 1.4501\times10^{-46}} \times 1(1+1)$$

$$E_J = 7.67\times10^{-3}\,J$$

when $J = 2$

$$E_J = \frac{(6.626\times10^{-34})^2}{8\pi^2 \times 1.4501\times10^{-4}} \times 2(2+1)$$

$$E_J = 2.301\times10^{-22}\,J$$

~~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

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

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

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

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

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

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

$$\Delta \varepsilon_J(\bar{\nu}) = \underbrace{\left(\frac{h}{8\pi^2 I_c}\right)}_{B}(2)(J+1)$$

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

For absorption spectroscopy, the minimum J value is J = 0

$\Delta \varepsilon = 2B(J+1)$ (where J is the lower energy state)

from $J = 0 \rightarrow J = 1$

~~$\Delta \varepsilon_J = 2B\{(1+1)-(0+1)\}$~~

~~$= 2B(2-1)$~~

~~$= 2B$~~

$$\varepsilon = 2B(0+1)$$
$$\varepsilon = 2B$$

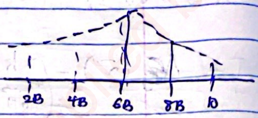
$\Delta \varepsilon_{J=1 \rightarrow J'=(J+1)}$; $J = 1 \rightarrow J' = (1+1)$

$$\varepsilon = 2B(1+1)$$
$$\varepsilon = 4B$$

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

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

$= 6B$



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

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

$= 8B$

Illustration

Some of the lines in the rotational spectrum of HCl appear at 83.03, 104.1, 124.3, 145.0 and 165.5 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}H and ^{35}Cl

for $3 \rightarrow 4$

$E_J (cm^{-1}) = 2B(3+1)$

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

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

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

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

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

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

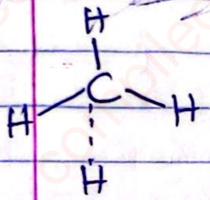
$7 \to 8 = 16B = 165.5\,cm^{-1}$

$$\hat{B} = \frac{B_1 + B_2 + B_3 + B_4 + B_5}{5}$$

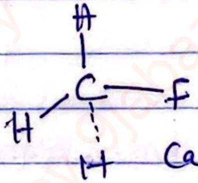
NO has a bond length of 1.151 Å. predict where the first four lines of the pure rotational spectrum of NO will appear, in units of GHz

13th April, 2026

C = 2.5
H = 2.1



and



(active)

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

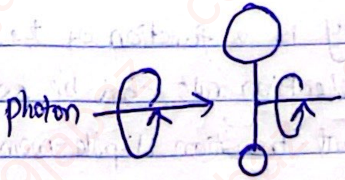
when $|R^{nm}|^2 = 0$ ------ forbidden

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. Because we have four C-H bond, it cancels each other, there is no net ~~the~~ zero dipole moment dipole moment, therefore it can never exihibit 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 CH_3F can be examined using rotational spectroscopy
The classical basics of this rule, is that a polar molecule appears to possess a flunctuating 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 $J \longrightarrow J+1$

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

$\Delta J = -1$ 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 like 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 moment 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 propoltional to the square of dipole moment)

~~* Molecule~~ ω

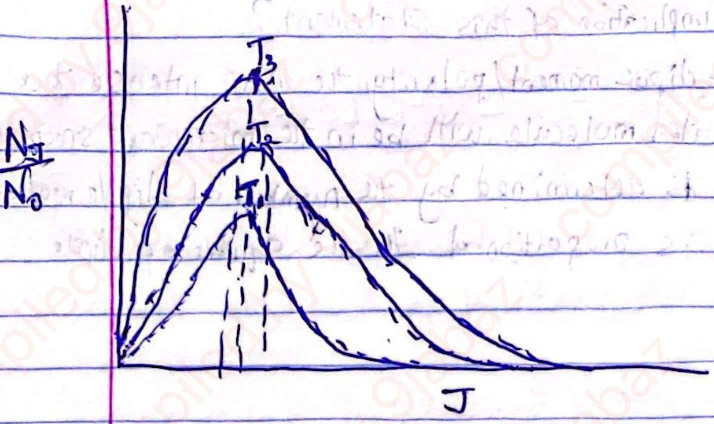
The intensity pattern of a rotational spectral is due to the number of molecules having a certain rotational state, this is called population of the state, and because the population of each rotational state is different, the number of molecules absorbing radiation and becoming excited to the next state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

This population difference is responsible for the varying intensities of each rotational spectra line

The population N_J of the ~~Jth~~ J level relative to N_0 (population at the ground state) is ~~to~~ determined by the Boltzmann distribution law

$$\frac{N_J}{N_0} = (2J+1)\exp\left(-\frac{\Delta E_r}{K_B T}\right)$$

where K_B 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

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

$$\frac{N_J}{N_0} = (2J+1)\exp -\left(\frac{\Delta E}{K_BT}\right)$$

Show that;

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

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

$J = 22.4$ ✗ $J = 22$ ✓

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 this molecules from their rotational path. This force is Called Centrifugal distortion.

14th April, 2026

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

The Scrodinger 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);

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

where $D = \dfrac{h^3}{32\pi^4 I^2 r^2 K c}$ cm^{-1}

$\downarrow$

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:

$$K = 4\pi^2 \bar{w}^2 c^2 M$$

16th April, 2026

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

The positions of the rotational spectral lines are then given as

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

$\varepsilon_{J+1} - \varepsilon_J$

① The silver hydride diatomic molecule, $^{197}Ag^{1}H$, has an inter nuclear bond distance of 1.617Å. predict the energies, in joules, of its first four rotational levels

②. Diatomic Sulphur, 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 1.880×10^{-10} m. Calculate the value of B, in units of cm^{-1} and J, for S_2.

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

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

ⓐ calculate the bond distance of LiH

ⓑ Determine the first four absorptions in the pure rotational spectrum of LiH

ⓒ Determine the most populated rotational level, J_{max} for a sample of LiH @ (i) 298K (ii) 10[illegible] K (iii) 5000K

(Infrared)

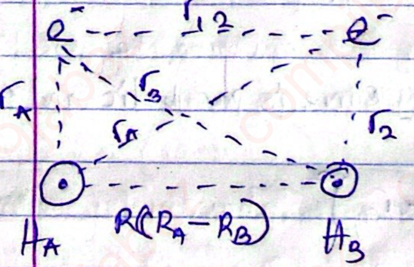
Vibrational Spectroscopy – The average spectroscopic technique in the IR region

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 interaction
- Electron – electron interaction
- Nuclei – electron interaction

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



(The forces balances 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 eletrons

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

The vibrations (compression and expansion) of diatomic molecules can be treated as hamonic, Hook'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

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

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

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

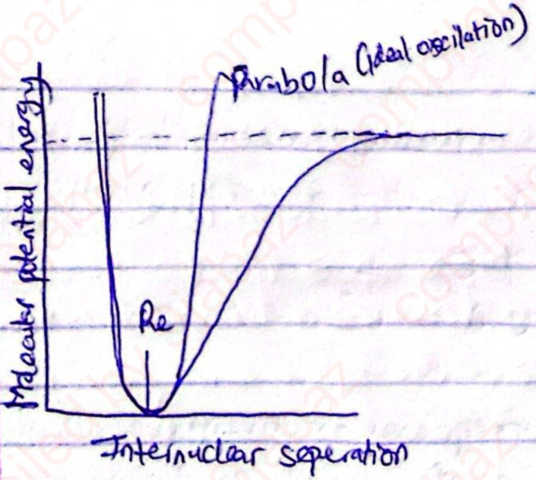
Vibrational energy, like any molecular energy is quantized and the allowed vibrational energy may be calculated from the Schroedinger's equation is

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

n = Vibrational quantum number

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

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



Selection Rule 1

~~From the Schroendinger's equation~~

Change in the Vibration quantum number must be equal to ± 1 ~ Selection rule

From the Schroendinger'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)

$$\varepsilon_{v+1 \to v} = \left(\cancel{v}+1+\frac{1}{2}\right)\bar{\omega}_{osc} - \left(\cancel{v}+\frac{1}{2}\right)\bar{\omega}_{osc}$$

$$\varepsilon_v = \left(v+\frac{1}{2}\right)\bar{\omega}_{osc}$$

$$\varepsilon_{v+1} = \left(v+1+\frac{1}{2}\right)\bar{\omega}_{osc}$$

$$= \left(v+\frac{3}{2}\right)\bar{\omega}_{osc}$$

$$\Delta\varepsilon_v = \varepsilon_v + \varepsilon_{v+1}$$

$$= \left(v+\frac{1}{2}\right)\bar{\omega}_{osc} - \left(v+3/2\right)\bar{\omega}_{osc}$$

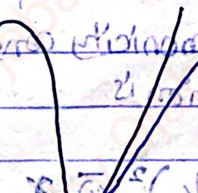
$$= \bar{\omega}_{osc}\left\{n+\frac{1}{2}-n-3/2\right\}$$

$$= \bar{\omega}_{osc}(1)$$

$$= \bar{\omega}_{osc}$$

21/04/26

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



morse function

The Anhamonic 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 rotating force is reduced, this is called ANHAMONICITY

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

The morse function is of the form;

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

* you don't need the derivation cos it is advanced

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

$$H\psi = E\psi$$

E = eigen valu

where D_e = dissociation energy

β = Anharmonicity constant

Measure of deviation of a ~~atom~~ true bond from an identical → bond is known as anharmonicity constant, i.e χ_e

The specific value for this function is

$$\varepsilon = (v+\tfrac{1}{2})\bar{\omega}_e - (v+\tfrac{1}{2})^2\bar{\omega}\chi_e \quad ---(**)$$

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

v = vibrational quantum number

$\chi_e \alpha \beta$ = anharmonicity constant

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

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

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

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

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

compared with

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

$$\bar{\omega}_{osc} = \bar{\omega}_e\left\{1-\left(v+\tfrac{1}{2}\right)\chi_e\right\}$$ This shows the deviation from an idea bond

$\bar{\omega}_e$ 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

$$\Delta V = \underbrace{\boxed{\pm 1}}_{\text{these are intense and it is called fundamental}}, \underbrace{\boxed{\pm 2, +3}}_{\text{these are weaker and they are called overtone}}$$

The overtones though predicted by theory are observed to be of rapidly diminishing probability. The spacing between vibrational levels is of the order of $10^3 cm^{-1}$

At room temperature, the ratio of the population between levels is given by the Boltzman distribution equation;

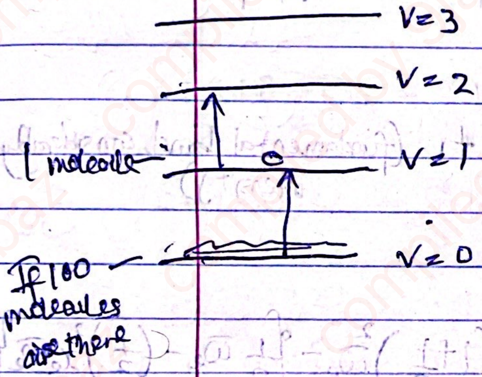
$$\frac{N_{v=1}}{N_{v=0}} = \exp\left\{\frac{-\Delta E_v}{K_B T}\right\}$$

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

$$\simeq 0.008$$

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 ~~to~~ transit from $v=1$ to 2 is impossible and if it happen it is known as cold 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 occur 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 band are generally not seen in absorption spectra near room temperature because of the small population of vibrational states.

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

$$\Delta \mathcal{E} = \mathcal{E}_{v=1} - \mathcal{E}_{v=0}$$

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

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

$v = 1$

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

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

when v = 0

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

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

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

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

$$\Delta\mathcal{E}_v = \frac{2}{2}\bar{\omega}_e - \frac{8}{4}\omega_e x_e$$

$$\Delta\mathcal{E}_v = \omega_e - 2\omega_e x_e$$

$$\Delta\mathcal{E}_v = \omega_e(1 - 2x_e)\ \text{cm}^{-1}$$

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

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

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

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

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

$\Delta\mathcal{E}_{v=2 \to v=0} = \frac{5}{2}\bar{\omega}_e - \frac{25}{4}\omega_e x_e - \frac{1}{2}\omega_e + \frac{1}{4}\bar{\omega}_e x_e$

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

$\Delta\mathcal{E}_{v=2 \to v=0} = 2\bar{\omega}_e - 6\omega_e x_e$

~~$= 2\bar{\omega}_e(\omega_e - 3$~~

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

$v = 0 \to v = 3$; $\Delta v = +3$ (second overtone,

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

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

For $^{16}O_2$, $\Delta\varepsilon_v$ for $v = 1 \leftarrow 0$ $1556.22\ cm^{-1}$

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

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

Calculate $\bar{\omega}_{osc}$ and x_e

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

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

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

Dividing eqn (2) by eqn (1)

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

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

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

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

$$0.99224 - 1.9845x_e = 1 - 3x_e$$

$$3x_e - 1.9845x_e = 1 - 0.99224$$

$$1.0155x_e = 7.76\times10^{-3}$$

$$x_e = 7.641\times10^{-3}$$

(i) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centered at 1876.06 cm^{-1} and 3724.20 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; HCl (2885 cm^{-1}), DCl (1990 cm^{-1}), D_2 (2990 cm^{-1}) and ~~HA~~ HD (3627 cm^{-1}). Calculate the energy change in ~~k~~ kJ mol^{-1} of the reaction

$$HCl + D_2 \rightarrow DCl + HD$$

Determine whether energy is liberated or absorbed

The Diatomic Vibrating Rotator

For a normal rotational energy seperation transition is in the order of 1-10cm^{-1}, However if the molecule is vibrating the energy of rotation is in the order of 10^3cm^{-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 is assuming that the combined rotational vibrational energy is the sum of the seperate energies

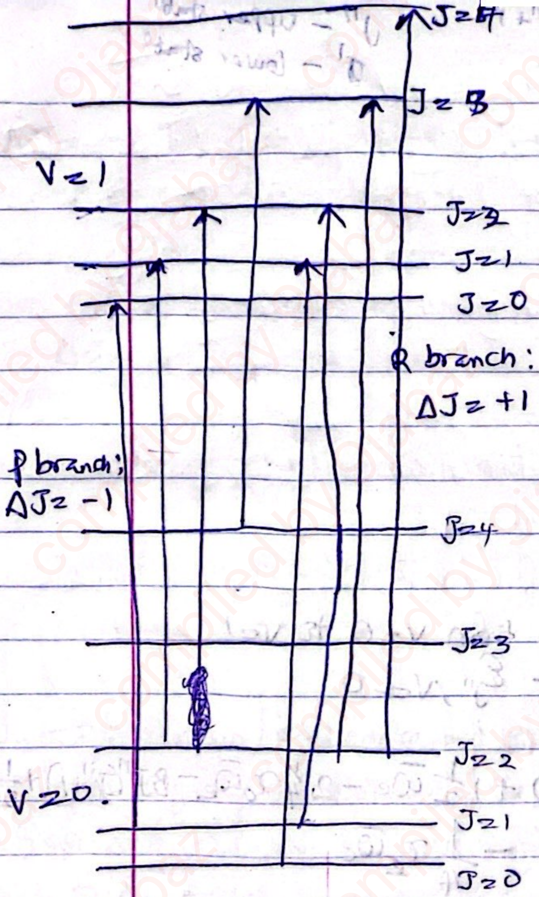
$$E_{total} = E_{rot} + E_{vib}$$

$$\varepsilon_{total} = \varepsilon_{rot} + \varepsilon_{vib}$$

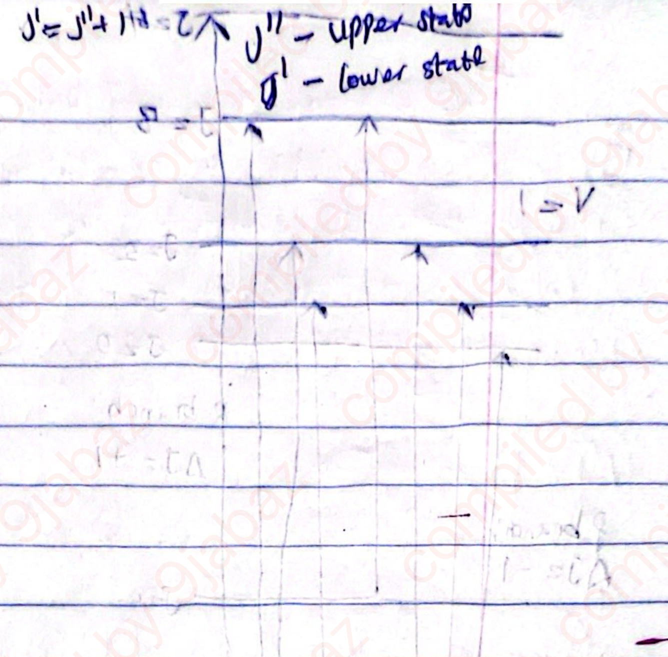
Taking the seperate expressions for the energies of rotations and vibrations

$$\varepsilon_{J,v} = \varepsilon_J + \varepsilon_v$$

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



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



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

$$\Delta\mathcal{E}_{J,V} = \mathcal{E}_{J',V=1} - \mathcal{E}_{J'',V=0}$$

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

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

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

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

$$\Delta\mathcal{E}_{J,V} = \bar{\omega}_0 + 2B(J''+1)\text{cm}^{-1},\ J'' = 0, 1, 2 \ldots 20\ \text{a}$$

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

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

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

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

These two expressions can be combined into

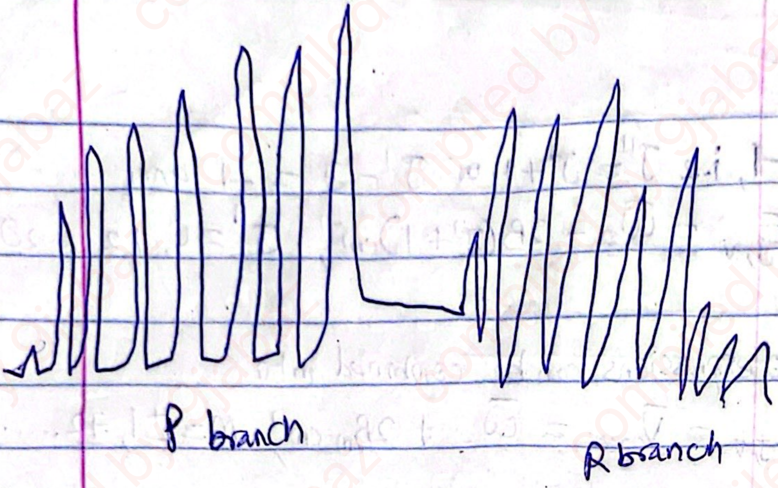
$$\Delta \varepsilon_{J,v} = \bar{\nu}_{spec} = \bar{\omega}_0 + 2Bm\,cm^{-1}, \quad m = \pm 1, \pm 2 \ldots,$$

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

$\bar{\omega}_0$ → 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.

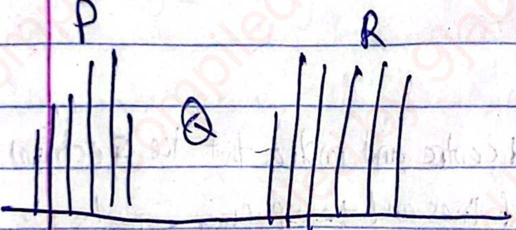
Lines to the lower frequency of the band origin. m = -ve and $\Delta J = -1$ are referred to as the p-branch

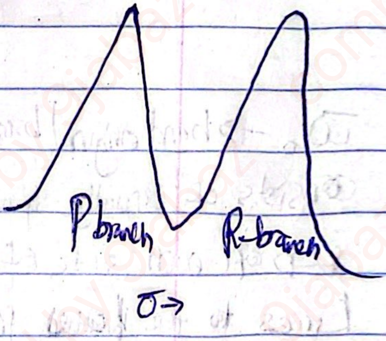
Lines to the high frequency side of the band origin with m = +ve and $\Delta J = +1$ are referred to as the R-branch.



~~The Q branch is the band or~~

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 distortional constant has been assumed negligible

$C \equiv N$

The bondlength of $^{12}C^{14}N$ is 117pm and it's force constant is $1630 Nm^{-1}$. 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 have 3N degree of freedom

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

For a molecule having n atoms, each atoms change in position can be broken down into ~~change in Δx~~ Δx, Δy, and Δz in coordinate. Although, this changes in coordinate may have different values and 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 ≡ 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

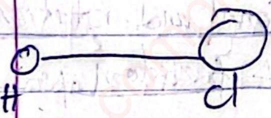
and 3N − 6 degree of freedom for a non-linear molecule

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 ~~[illegible]~~ molecule does not move independently fo

However, for Vibrational motion, each atoms can move independe
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 fequencies of light that are absorbed due to vibrational motion of atom in molecules are those that have the same frequency at the normal mode of vibration



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

It is linear; $3N - 5$ $(N = 2)$

$= 3 \times 2 - 5$

$= 1$

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

It has only one vibrational mode, it is called stretching vibration mod

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

The wavenumber of the absorbed radiation =

Q

Possible Vibrations of Three Atoms in Water molecule.

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

non linear ; $3N - 6$

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

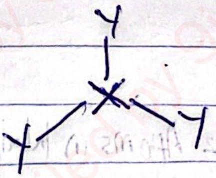
Three distinct absorption frequency which occurs at 3756, 3657 and 1595 cm^{-1}. This three modes of vibration are generally referred to as → higher energy assymetric stretching mode, symmetric stretching, and bending mode.

Suggest a structure for ~~XY~~ 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 ~~tra~~ 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