Q.3/ The Frequency of absorption line in the rotational spectrum For the tran-sition $J=0 \longrightarrow J=1$ of $^{12}C^{16}O$ molecule is $(1.153 \times 10^{11} Hz)$ and the Frequency For the same transition in $^{X}C^{16}O$ is $(1.102 \times 10^{11} Hz)$. Find the mass of isotopic Carbon atom ^{X}C in $^{X}C O^{16}$ molecule (or Find the mass number of ^{X}C)

$\left(m_O = 16 \, gm/mole \right) \left(m_C \left(in \, ^{12}C^{16}O \right) = 12 \, gm/mole \right)$

$$\nu = 1.153 \times 10^{11} \text{ then } \tilde{\nu} = \frac{\nu}{c} = \frac{1.153 \times 10^{11}}{3 \times 10^{10}} = 3.84 \text{ cm}^{-1}$$

$$\tilde{\nu} = 1.102 \times 10^{11} \text{ Hence } \tilde{\nu}' = \frac{\nu'}{c} = \frac{1.102 \times 10^{11}}{3 \times 10^{10}} = 3.67 \text{ cm}^{-1}$$

$$3.84 = 2B(J+1) = 2B \quad \text{For } J=0$$

$$\text{and } 3.67 = 2\hat{B}(J+1) = 2\hat{B} \quad \text{Hence } B = \frac{3.84}{2} = 1.92 \text{ cm}^{-1}$$

$$\hat{B}' = \frac{3.67}{2} = 1.835 \text{ cm}^{-1}$$

$$\frac{B}{B'} = \frac{1.92}{1.835} = \frac{\mu'}{\mu} = 1.046$$

$$1.046 = \frac{(X)(16)}{(X+16)} \frac{1}{6.022 \times 10^{23}} \frac{(12+16)}{(12)(16)} \frac{6.022 \times 10^{23}}{1}$$

$$1.046 = 0.1458 \frac{(16)(X)}{(X+16)} \quad \text{and} \quad \frac{1.046}{(0.1458)} = \frac{(X)(16)}{(X+16)}$$

$$7.174 = \frac{X(16)}{X+16} \quad \text{then} \quad 7.174(X) + 7.174(16) = 16(X)$$

$$16(X) - 7.174(X) = 114.784$$

$$X(16 - 7.174) = 114.784$$

$$\text{then } X = \frac{114.784}{(16-7.174)} = \frac{114.784}{8.826} = 13.005$$

$$\boxed{X \simeq 13} \quad \text{or} \left(m_C^X = 13 \, gm/mole \right)$$

Q.4/ compute the wavelength For the First Four lines in rotational spectrum oF (NaCl) molecule, iF you know that the moment of inertia $(I = 12.9 \times 10^{-46} \, kg.m^2)$ and Find the bond length. atomic weight $(M_{Cl} = 35 \, , \, m_{Na} = 22)$

احسب الطول الموجي للخطوط الاربعة الاولى في طيف الدوران لجزيئة NaCl اذا كان عزم إنتعض الذاتي $(12.9 \times 10^{-46} \, kg.m^2)$ و أوجد طول الاصرة؟

$$B = \frac{h}{8\pi^2 I c} = \frac{6.63 \times 10^{-34}}{78.956 \times 12.9 \times 10^{-46} \times 3 \times 10^8} = 21.69 \, m^{-1}$$

$$\boxed{B = 21.7 \, m^{-1}}$$

thus $B = 0.217 \, cm^{-1}$, since $\tilde{v} = 2B(J+1)$ and $\lambda = \frac{1}{\tilde{v}}$

therefore line$_{(1)}$ $\tilde{v}_{J=0 \to 1} = 2B = 2(0.217) = 0.434 \, cm^{-1}$

$$\boxed{\lambda_{(1)} = \frac{1}{0.434} = 2.3 \, cm}$$

line$_{(2)}$ $\tilde{v}_{J=1 \to 2} = 2B(1+1) = 4B = 4(0.217) = 0.868 \, cm^{-1}$

$$\boxed{\lambda_{(2)} = \frac{1}{0.868} = 1.152 \, cm}$$

line$_{(3)}$ $\tilde{v}_{J=2 \to 3} = 2B(2+1) = 6B = 6(0.217) = 1.302 \, cm^{-1}$

$$\boxed{\lambda_{(3)} = \frac{1}{1.302} = 0.768 \, cm}$$

line$_{(4)}$ $\tilde{v}_{J=3 \to 4} = 2B(3+1) = 8B = 8(0.217) = 1.736 \, cm^{-1}$

$$\boxed{\lambda_{(4)} = \frac{1}{1.736} = 0.576 \, cm}$$

$\mu = \frac{(35)(22)}{(35+22)} \times 1.66 \times 10^{-27} = 2.242 \times 10^{-26} \, kg$ $\quad r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{12.9 \times 10^{-46}}{2.242 \times 10^{-26}}} = 2.39 \, \mathring{A}$

Molecule

Q.5/ compute the force constant For HCl^{35}, if you know that the vibrational Frequency is 8.667×10^{13} sec^{-1} and the reduced mass is 1.628×10^{-24} gm .

احسب ثابت القوة لجزيئة HCl^{35} اذا اعطيت ان لتردد الاهتزاز في هو $8.667 \times 10^{13} sec^{-1}$ و الكتلة المختزلة هي 1.628×10^{-24} gm .

Solution/

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

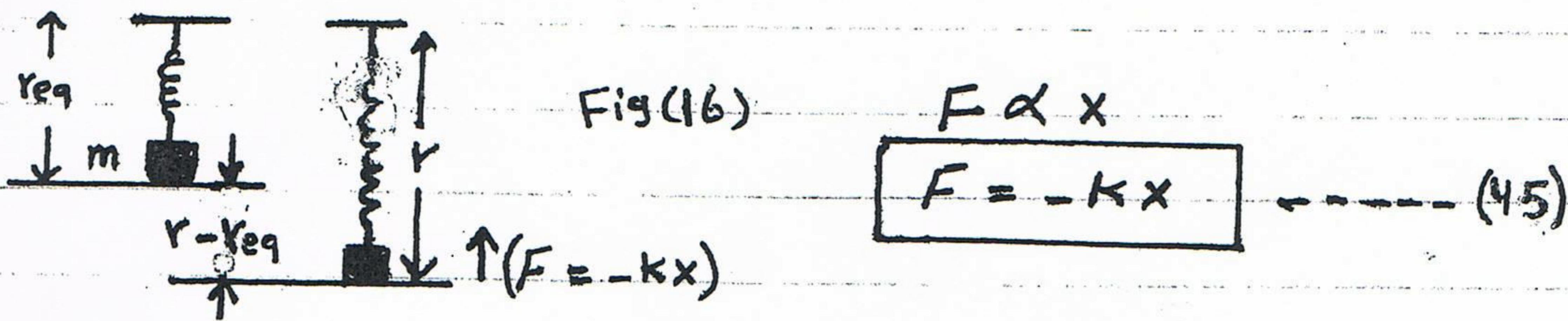$$K = (2\pi\nu)^2 \mu = (2 \times 3.14 \times 8.667 \times 10^{13})^2 \times 1.628 \times 10^{-24} \, gm$$

$$\boxed{k = 4.8229 \times 10^5 \, dyn/cm}$$

$$\text{or} \quad K = (2 \times 3.14 \times 8.667 \times 10^{13})^2 \times 1.628 \times 10^{-27} \, Kg$$

$$\boxed{K = 482.293 \, N/m}$$

Infra-red spectroscopy :-

Uibrational spectra :-

اذا ازیحت كتلة (m) معینة لجسم مربوط في سلك حلزوني اونابض . نشأ النابض سیعائي من قوة وذلك هـب ثانون هوك، تحاول ارجاع الجسم الى وضعه الطبیعي هیثأن

Fig (16)

$F \propto x$

$$F = -Kx \quad \text{----- (45)}$$

where F = applied Force For spring to mass , K = Force constant
X = displacement From the equilbrium position .
to determine the Force which required to restore the mass (m) to the equilbrium
position we must apply the second law of Newton's

$$F = ma = m\frac{dx^2}{dt^2} \quad \text{---- (48)}$$

but $F = -Kx$ there Fore $m\frac{dx^2}{dt^2} = -Kx$

Then $$M\frac{dx^2}{dt^2} + Kx = 0 \quad \text{------ (47)}$$

the equation (47) is differential equation, and we can consider one of the
solution of eq (47) as the following

$$X = A \sin 2\pi \nu t \quad \text{---- (48)}$$

or
$$X = A \sin \omega t \quad \text{----- (49)}$$

where $(w = 2\pi v)$ the angular frequency, and $v =$ linear vibrational frequency $A =$ maximum displacement (amplitude)

Hence

$$\frac{dX}{dt} = Aw\cos wt \quad , \text{and} \quad \frac{d^2X}{dt^2} = -Aw^2\sin wt$$ —— (50)

After substitue the eq (50) in the equation of energy for vibrational motion which is

$$E = \frac{1}{2}mv^2 + \frac{1}{2}Kx^2$$ ——(51)

we get $E = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 + \frac{1}{2}Kx^2$

$$E = \frac{1}{2}mA^2w^2\cos^2 wt + \frac{1}{2}KA^2\sin^2 wt$$

since $w = \sqrt{\frac{K}{m}}$, and $K = mw^2$

then $E = \frac{1}{2}mA^2w^2\cos^2 wt + \frac{1}{2}mw^2A^2\sin^2 wt$

$$E = \frac{1}{2}A^2mw^2(\underbrace{\cos^2 wt + \sin^2 wt}_{=1})$$

$$E = \frac{1}{2}KA^2$$ ——— (52)

to prove that $w = \sqrt{\frac{K}{m}}$, we substituting the value X of equation (48) in the Newton's second law of the force, as the following

$$m\frac{d^2X}{dt^2} + Kx = 0$$

$$m\frac{d^2}{dt^2}(A\sin 2\pi vt) + KA\sin 2\pi vt = 0$$

$$-mA(2\pi\nu)^2 \sin 2\pi\nu t + KA \sin 2\pi\nu t = 0$$

$$-mA\, 4\pi^2\nu^2 \sin 2\pi\nu t = -KA \sin 2\pi\nu t$$

$$m\,4\pi^2\nu^2 = K \quad \text{and} \quad \left(4\pi^2\nu^2 = \frac{K}{m}\right) \quad \text{also} \quad \left(2\pi\nu = \sqrt{\frac{K}{m}}\,\right)$$

thus $\boxed{\omega = \sqrt{\frac{K}{m}}}$ or $\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{K}{m}}}$

ν : is the linear Frequency or (Vibrational Frequency)

since $\nu = \dfrac{c}{\lambda}$ hence $\dfrac{1}{\lambda} = \dfrac{1}{2\pi c}\sqrt{\dfrac{K}{m}} \quad cm^{-1}$

or $\boxed{\bar{\omega} = \dfrac{1}{2\pi c}\sqrt{\dfrac{K}{m}}}$ --------(53)

$\bar{\omega}_e$ is the vibrational Frequency in cm^{-1} unit thus

$$\boxed{\begin{array}{l} c\,\bar{\omega} = \nu \\ 2\pi c\,\bar{\omega} = \omega \end{array}} \quad ------(54)$$

Vibration oF Diatomic molecule :

When two atoms combine to Form a stable covalent molecule (e.g., HCl gas), we may simply look on the phenomenon as a balancing oF Forces Repulsion and Attraction, repulsive between the positively charged nuclei oF both atoms, and between the negative electron clouds, attractive is between the nucleus oF one atom and the electrons of the other. iF attempt to squeeze the atoms more closely together, the repulsive Force rises rapidly or pull the Further apart, the attractive Force will rises. in either case an attempt to distort the bond requires an input oF energy. the compression and extension oF bond may be likened to the behaviour oF spring by assuming that the bond, like

a spring . obeys Hooke's law , we may then write

$$F = -K (r - r_{eq})$$

F: — is the restoring Force ,(r):- the internuclear distance ,(r_eq):- equilbrium distance (bond length)
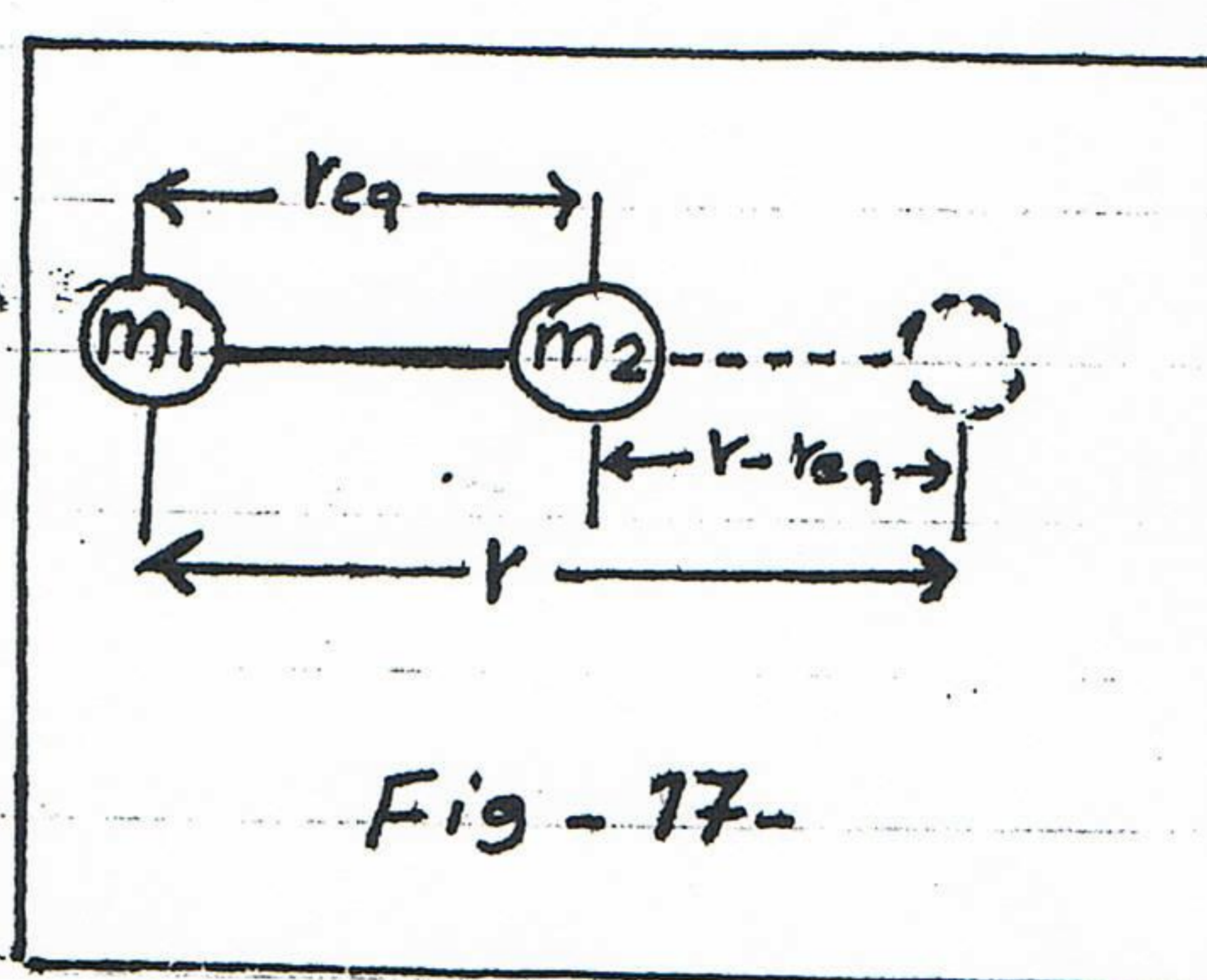

Fig - 17 -

this model of a vibrating diatomic molecule so - called (simple harmonic oscillator model). the distance of bond From the equilbrium location is :-
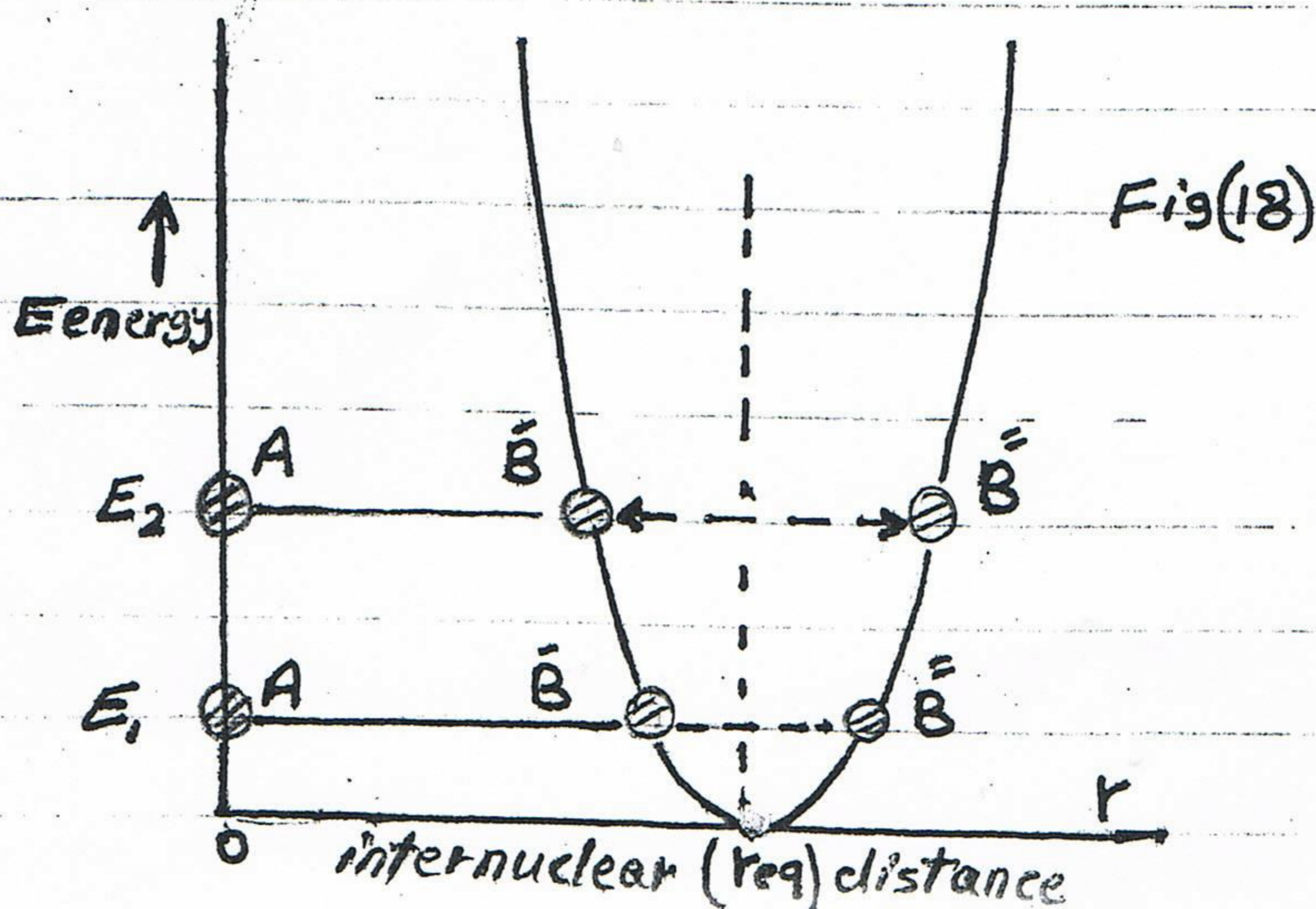
$$r - r_{eq} = A \sin 2\pi v t \qquad \text{------- (55)}$$

and the Frequency of the vibrational system (diatomic molecule) will be given by the Formula

$$v = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \qquad \text{------(56)}$$

this equation analogue to the equation of vibrating of single mass except here the reduce mass (μ) inplace of (m) . and in this case the energy curve is parabolic Fig (18) , and has the Form

$$E = \frac{1}{2} K (r - r_{eq})^2 \qquad (57)$$

Fig(18)

internuclear (r_eq) distance

its clear from the Fig(18) the zero of curve and equation is found at$(r = req)$ and any energy in excess of this, such as E_1, arises because of extension or compression of the bond, Furthermore the Fig(18) shows that if one atom (A) is considered to be stationary on the $r=0$ axis, the other will oscillate between $\acute{B}$ and $\ddot{B}$. and if the energy is increased to E_2, its mean the oscillation degree of compression and extension will be greater, but the vibrational frequency will not change $\left\{ \nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \right\}$, because its dependent on the mass of the system and the force constant.

## The Simple Harmonic Oscillator :

the vibrational energies, like all other molecular energies, are quantized, and the allowed vibrational energies for any particular system are calculated from the schrödinger equation. For the simple harmonic oscillator these turn out to be :

$$E_U = \left(U + \frac{1}{2}\right) h\nu \quad \text{joules} \quad \nu = 0, 1, 2, 3, \ldots \quad \text{------(58)}$$

where (U) is called the vibrational quantum number. converting to the spectroscopic units, cm^{-1}, we have

$$G(\nu) = \frac{E_\nu}{hc} = \left(U + \frac{1}{2}\right) \bar{\omega} \quad cm^{-1} \quad \text{------(59)}$$

the energies allowed to a simple harmonic vibrator, are shown in Fig (19)

Fig (19)
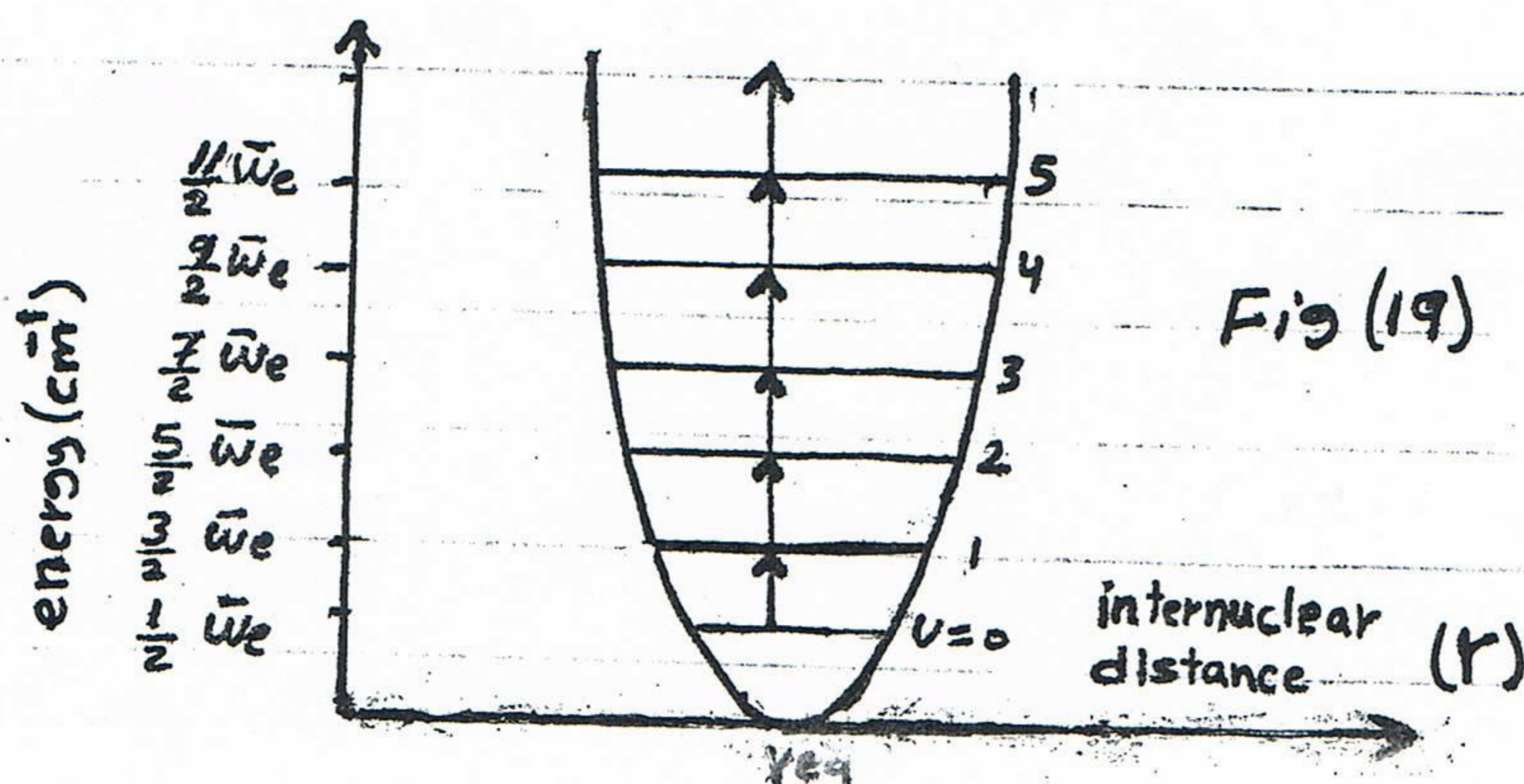
its should be notice, that the lowest vibrational energy, which obtained by putting $v = 0$ in Eq (58) or (59) is.

$$E_0 = \frac{1}{2} h\nu \quad \text{joules} \quad (\nu \text{ in Hertz})$$

$$G_0 = \frac{1}{2} \bar{\omega} \quad cm^{-1} \quad (\bar{\omega} \text{ in } cm^{-1})$$

$$\text{----} \quad (60)$$

its mean that the diatomic molecule can never have zero vibrational energy , and the atoms can never be completely at rest relative to each other. the quantity $\left(\frac{1}{2} h\nu\right)$ or $\left(\frac{1}{2}\bar{\omega}\right)$ is called or known as the (zero-point energy), and it depends only on the classical vibration frequency and hence on the force constant (strength of the chemical bond) and the atomic masses.

Further use of the schrodinger equation leads to the simple selection rule for the harmonic oscillator undergoing vibrational changes ,

$$\Delta v = \mp 1 \qquad \text{----} \quad (61)$$

applying the selection rule we have immediately

$$G_{v+1 \to v} = \left(v + 1 + \frac{1}{2}\right)\bar{\omega} - \left(v + \frac{1}{2}\right)\bar{\omega}$$
$$= \bar{\omega} \quad cm^{-1}$$

$$\text{----} \quad (62)$$

For emission and

$$G_{v \to v+1} = \bar{\omega} \quad cm^{-1} \qquad \text{----} \quad (63)$$

For absorption, whatever the initial value of (v). this simple result is obvious in Fig (19), since the vibrational levels are equally spaced, the transitions between any two neighbouring states will give the same energy change

which is $\bar{\omega}$ cm^{1} Further this difference gives directly the wavenumber of the spectral line absorbed or emitted.

$$\boxed{\bar{\nu} = \Delta G = \bar{\omega} \; \text{cm}^{1}}$$ ————— (64)

Finally the result in the spectrum shows one line which represent the (Fundamental vibrational Frequency).

أن أطياف الاهتزاز تنتج من التغيرات في مستويات الطاقة الاهتزازية ومع ذلك فأنه يمكن الحصول على أطياف الامتصاص والانبعاث فقط للجزيئات ذات الذرتين التي يصاحب مركبها الاهتزازية تغيراً في عزم ثنائي القطبين. اذ أن عزم ثنائي القطبين المتذبذب يعطي ميكانيكية للاتحاد بين الجزيئات والاشعاع الكهرومغناطيسي. لذلك فأن الجزيئات ذات الذرتين المتماثلتين في مكوناتهما مثل H_2، O_2، N_2 والتي لها عزم ثنائي القطبين مساوياً للصفر لأي طول من الطوال الاهزة لايمكنها أن تتحد مع الشعاع الكهرومغناطيسي. ايضنا من ناحية اخرى فأن الجزيئات ذات الذرتين المجيينتين (heteronuclear) التي تتملك عزما ثنائي القطب متذبذباً يعقد على الماعنة البينية يمكن أن تنتج طيفاً اهتزازياً، وبصورة عامة يمكن وضع قاعدة لامتصاص وأنبعاث الاشعاع بواسطة الجزيئة كنتيجة للتغير في حالتها الاهتزازية بالشكل التالي [أن الاشعاع الكهرومغناطيسي يمكن أن يُمتص او أن ينبعث فيما لو كان هنالك تغيراً في حالة الاهتزاز مصحوباً بتغير في عزم ثنائي القطبين للجزيئة].