Atomic and Molecular Physics
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Lecture - 51
Electronic spectra of a molecule

Today, we learn about the Electronic Spectroscopy of a molecule.

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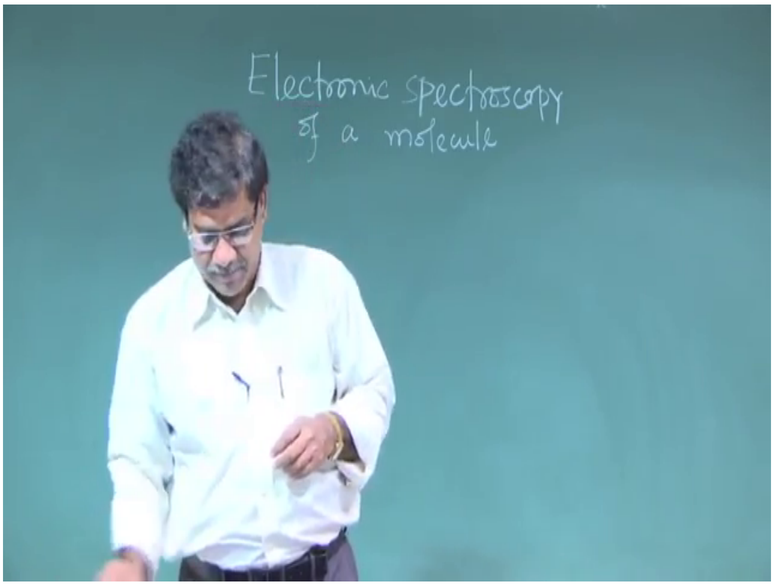

So, before starting this electronic spectroscopy of a molecule, let us summarize the vibrational and rotational spectra of a diatomic molecules whatever we have learned so far.

So, basically in case of rotation we have considered a two models a rigid rotator and non rigid rotator. So, in case of rigid rotor so diatomic molecule mass m 1 m 2 and this bond length is r 0.

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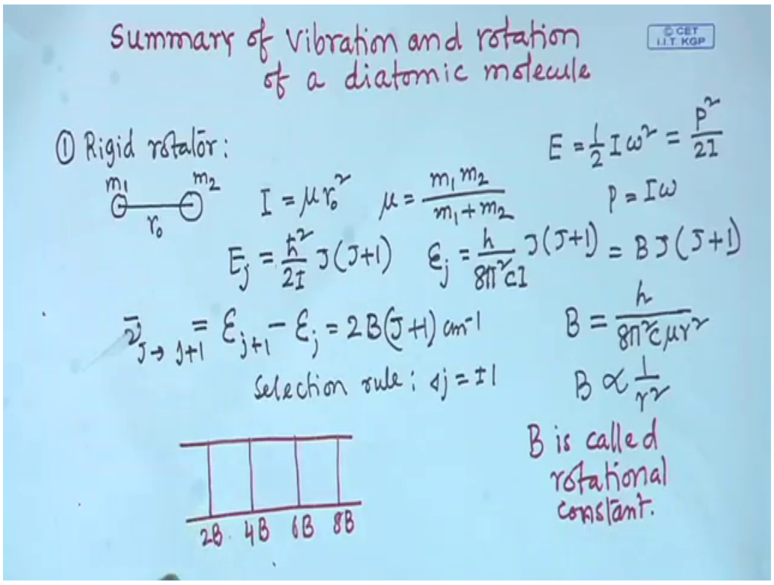

Summary of Vibration and rotation of a diatomic molecule

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① Rigid rotator:

m_1 m_2 r_0

$$E = \frac{1}{2} I \omega^2 = \frac{p^2}{2I}$$

$$I = \mu r_0^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad p = I\omega$$

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad \varepsilon_J = \frac{h}{8\pi^2 c I} J(J+1) = BJ(J+1)$$

$$\bar{\nu}_{J \to J+1} = \varepsilon_{J+1} - \varepsilon_J = 2B(J+1)\ \text{cm}^{-1} \quad B = \frac{h}{8\pi^2 c \mu r^2}$$

Selection rule: $\Delta j = \pm 1$

$$B \propto \frac{1}{r^2}$$

B is called rotational constant.

So, this it is reduced to 1 mass problem 1 body problem and this reduced mass is mu mu equal to m 1 m 2 by m 1 plus m 2 and moment of inertia I equal to mu r 0 square and energy of course, this like this translational motion whatever energy is half mv square. So, m is replaced by I moment of inertia and E is replaced by omega angular velocity. So, energy is half I omega square is basically p square by 2 I p is not linear momentum is angular momentum.

So, p equal to whatever m v, so m is replaced by I E is replaced by omega so p equal to I v ok. So, using quantum mechanics one can find out the quantized energy of the rotator. So this Ej, Ej that we have seen this equal to a cross square by 2 I it just like a square by 2 m in case of linear motion, in case of angular motion angular k. So, is a cross square same is replaced by I, so 2 I J plus 1 that is in energy if we express in joule.

So, this is the expression now we are interested to express this energy in terms of centimetre inverse means in terms of wave number. So, that is Ej. So, this different notation for E is used, so Ej equal to h by eight pi square cI J J plus 1. So, this we have written as a constant B. So, BJ J plus 1 whereas, b is this so here we have put I equal to mu r square. So, here basically we are seeing this b is this is proportional to 1 by r square this means if r is higher. So, this b will be smaller so b is called the rotational constant ok.

So, rotational constant is very sensitive to the distance between the 2 atom, it is exchanges is varies with square of the distance r square and that we have seen this what will be the spectral lines what will be the energy or wave number of the spectral lines. So, just transition from J 2 J plus 1 states. So, this will be 2BJ plus one. So, following the selection rule del J equal to plus minus 1. So, one can get this spectral lines rotational spectral lines and their separation are constant that is to B ok.

So, equi spaced spectral lines will see if it is rigid rotator , but in reality really we found very very small number of molecules which are which behave like rigid rotator, but most of them behave like non rigid rotator means during rotation due to centrifugal force. So, this bond length is changed, so if we consider that 1.

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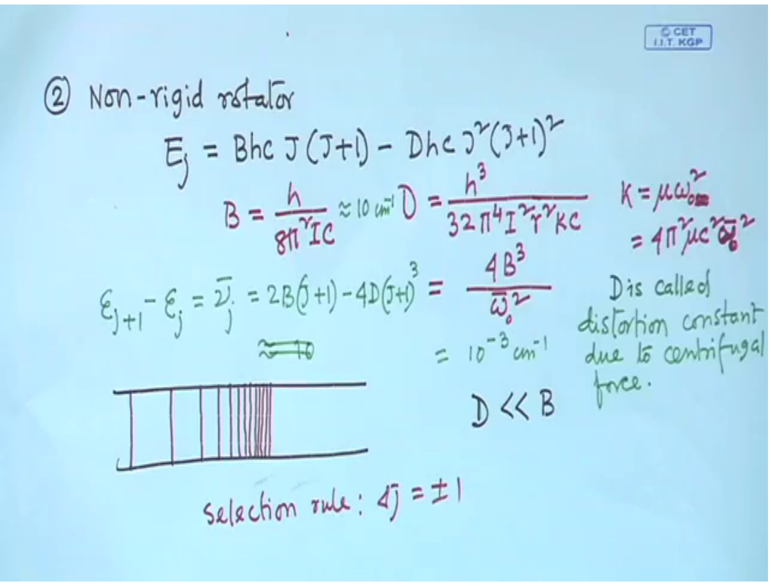

② Non-rigid rotator

$$E_J = BhcJ(J+1) - DhcJ^2(J+1)^2$$

$$B = \frac{h}{8\pi^2 Ic} \approx 10\ \text{cm}^{-1} \quad D = \frac{h^3}{32\pi^4 I^2 r^2 kc}$$

$$k = \mu\omega_0^2$$
$$= 4\pi^2\mu c^2\bar{\omega}_0^2$$

$$\epsilon_{J+1} - \epsilon_J = \bar{\nu}_J = 2B(J+1) - 4D(J+1)^3 = \frac{4B^3}{\bar{\omega}_0^2}$$
$$\cancel{\approx 10}$$
$$= 10^{-3}\ \text{cm}^{-1}$$

$$D \ll B$$

D is called distortion constant due to centrifugal force.

Selection rule: $\Delta J = \pm 1$

So, that is that will be basically non rigid rotator and in case of non rigid rotator. So, this energy will be corrected by these factors ok. So, that is minus Dhc J square J plus 1 whole square ok. So, in this case D is called distortion constant due to centrifugal force and here k we have written. So, it is as if we consider the spring mass system it is the stretching due to rotation. So, this spring constant that is basically is k k is omega mu omega 0 square, so mu 0 is natural frequency.

So, that you know this mu 0 equal to square root of k by mu, so this you will get in terms of wave number. So, this mu 0 bar we have written so this will be the k value and one can show that using b and omega 0 bar value. So, this D is basically depends on b as well as this omega 0 square this is this is the relation and in case of this energy of the spectral lines will be this, so 2BJ plus 1 2BJ plus 1 minus 2dJ plus 1 cube. So, for lower value of J this rotational quantum number so you will get basically you will not get much deviation of spectral line from the from the spectral line of rigid rotator, but for higher value of J you see this value this value 2 D J plus 1 cube, so this will increase for higher value of J.

So, this total value will; this energy of the spectral lines in centimetre inverse so that will decrease ok. So, whatever the whatever the spectral lines we have seen for rigid rotator. So, they are equi spaced now here they are there they will not be equi spaced.

So, their separation will decrease with higher J value ok. So, that is the difference one can see and seeing the spectral seeing the spectra in spectrometer, one can say one can say that whether the molecules behaving like rigid rotator or non rigid rotator ok. So, next we have we have seen for vibrational spectra of a molecule.

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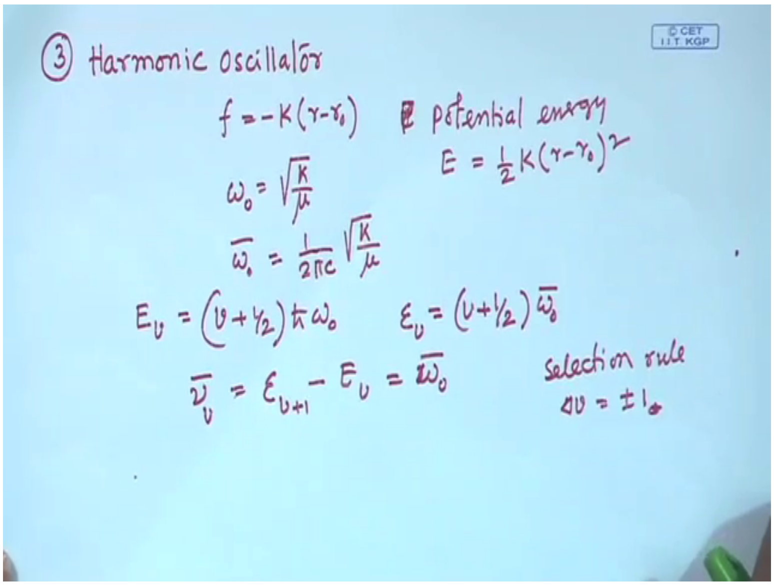

③ Harmonic oscillator

$f = -K(r - r_0)$ potential energy

$E = \frac{1}{2}K(r - r_0)^2$

$\omega_0 = \sqrt{\frac{K}{\mu}}$

$\overline{\omega_0} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$

$E_v = (v + 1/2)\hbar\omega_0$ $\quad \varepsilon_v = (v + 1/2)\overline{\omega_0}$

$\bar{\nu}_v = \varepsilon_{v+1} - E_v = \overline{\omega_0}$

selection rule

$\Delta v = \pm 1$

So, here also minus case 1 is Harmonic Oscillator. So, their vibration will behave like harmonic oscillator and another is anharmonic oscillator. So, in case of a harmonic oscillator this energy of force is minus k r minus r0.

So, corresponding potential energy will be half k r minus r 0 square and there harmonic oscillator the standard solution from quantum mechanics.

So, this Ev equal to v plus half h cross omega 0, so here v is vibrational quantum number. So, in wave number so this is the omega 0 bar. So, spectral lines energy of the spectral lines it seems it is independent of v so; that means, all spectral lines whatever following this selection rule, so all will have the same energy.

So, practically we will see just only 1 spectral lines see if it is molecule behaves like harmonic oscillator, again it is practically it is it is different. So, we see it is vibration it is not like harmonic oscillation.

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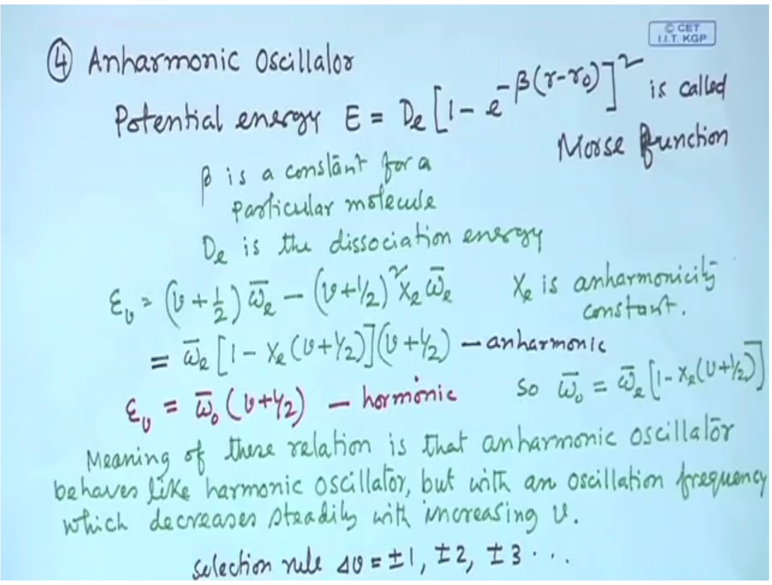

④ Anharmonic Oscillalor

Potential energy $E = D_e\left[1 - e^{-\beta(r-r_0)}\right]^2$ is called Morse function

β is a constant for a particular molecule

D_e is the dissociation energy

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

x_e is anharmonicity constant.

$$= \bar{\omega}_e\left[1 - x_e\left(v+\tfrac{1}{2}\right)\right]\left(v+\tfrac{1}{2}\right) \text{ — anharmonic}$$

$$\varepsilon_v = \bar{\omega}_0\left(v+\tfrac{1}{2}\right) \text{ — hormonic}$$

So $\bar{\omega}_0 = \bar{\omega}_e\left[1 - x_e\left(v+\tfrac{1}{2}\right)\right]$

Meaning of there relation is that anharmonic oscillator behaves like harmonic oscillator, but with an oscillation frequency which decreases steadily with increasing v.

selection rule $\Delta v = \pm 1, \pm 2, \pm 3 \ldots$

So, it is basically anharmonic oscillation means your (Refer Time: 10:34) stretching and this compression and this is not in same magnitude. So, it is they are in different magnitude. So, in this case this potential energy to fit the experimental data mores has given p m mores has given suitable potential energy for this anharmonic oscillator and that is E equal to De 1 minus e to the power minus beta r minus r 0 whole square.

So, this called mores function, where beta is a constant for a particular molecule and D is the dissociation energy means it is due to vibration it will this molecule will dissociate to the atom ok. So, this bond will breaks basically and due to this anharmonic oscillation, so this energy terms again it is corrected by this term. So, v plus half omega E bar. So, here for this omega e is different from the omega 0 bar in case of harmonic oscillator whatever we have seen, so it will it is different ok.

So, v plus half omega E bar minus v plus half square x omega bar x is called anharmonic constant anharmonicity constant and yeah. So, if we just rearrange this expression so this one can write omega e bar 1 minus xe v plus half. So, this whole bracket v plus half so this anharmonic case and harmonic case we have seen this energy expression omega 0 bar v plus half these the harmonic case.

So, if you compare these two as if this omega 0 bar equal to omega e bar 1 minus xe v plus half ok. So, one can consider that that an anharmonic oscillator as if we can consider that it will behave like a harmonic oscillator but with different frequency, but with different frequency and that frequency depends on the on the wave number and that frequency will decrease with steadily increasing of this of this vibrational quantum number ok.

So, and in case of anharmonic oscillator so this selection rule is different it is not del v equal to plus minus 1. So, other plus minus 2 plus minus 3 etc these are also allowed ok. So, this so now there are some molecules.

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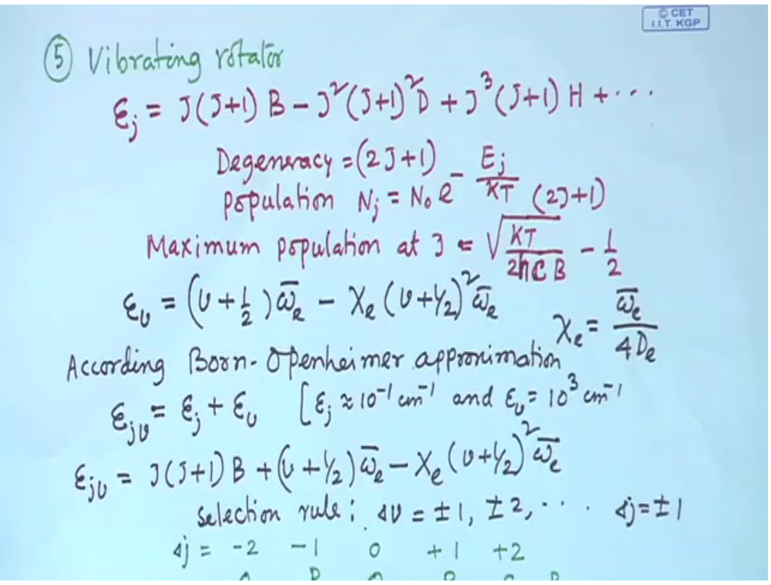

⑤ Vibrating rotator

$$\varepsilon_j = J(J+1)B - J^2(J+1)^2 D + J^3(J+1)H + \cdots$$

Degeneracy $= (2J+1)$

population $N_j = N_0 e^{-\frac{E_j}{KT}}(2J+1)$

Maximum population at $J = \sqrt{\frac{KT}{2hcB}} - \frac{1}{2}$

$$\varepsilon_v = \left(v+\frac{1}{2}\right)\bar{\omega}_e - X_e\left(v+\tfrac{1}{2}\right)^2\bar{\omega}_e \qquad X_e = \frac{\bar{\omega}_e}{4D_e}$$

According Born-Openheimer approximation

$$\varepsilon_{jv} = \varepsilon_j + \varepsilon_v \quad [\varepsilon_j \approx 10^{-1}\,cm^{-1} \text{ and } \varepsilon_v = 10^3\,cm^{-1}$$

$$\varepsilon_{jv} = J(J+1)B + \left(v+\tfrac{1}{2}\right)\bar{\omega}_e - X_e\left(v+\tfrac{1}{2}\right)^2\bar{\omega}_e$$

Selection rule; $\Delta v = \pm 1, \pm 2, \cdots \quad \Delta j = \pm 1$

$\Delta j = -2 \quad -1 \quad 0 \quad +1 \quad +2$

So far, whatever we have discussed a pure rotation of a molecule or pure vibration of a molecule, but in reality there are some molecules where we see this during vibration of the molecule it rotates also ok, so it is called vibrating rotator. So, in case of vibrating rotator means simultaneous vibration and rotation due to this what will happen so this called vibrating rotator and corresponding energy here we have written this for you know this for rotation. So, these the energy expression so higher terms we have neglected and in this case degeneracy is 2 J plus 1.

So, population is like this by Boltzmann factor one can write population and these degeneracy and we have seen also this maximum population will be at J equal to this ok, it depends on temperature and so this is the for rotation and for vibration this energy expression is this.

Now, for vibrating rotator, so this both energy will be their rotation as well as vibration as well as there should be another term that is a interference term coupling term between these rotational vibration. But fortunately this we can neglect this coupling term because, according to born openheimer approximation since their energy order of energy of this rotational vibration is different by a factor of 10 to the power 4 ok.

So, this energy generally energy of this rotational rotational and spectral lines or energy levels it is 10 to the power minus 1 centimetre inverse. So, it has vibrational case it is 10 to the power 3 centimetre inverse.

So, huge energy difference between these two system rotational and vibration, so this according to born openheimer approximation. So, they will not interfere so one can take the total energy of this vibrating rotator as a sum of this individual energy ok. So, Ejv equal to EJ plus Ev. So, Ej term one can write and here we have neglected this higher term whereas, in case of vibration we have taken this both term.

So, here reason is that this D value is really very very small compared to the compared to the B value and of course, this anharmonicity constant also small, but this we have kept because otherwise we cannot take the selection rule del v equal to plus minus 1 plus minus 2 etc and that is what it demands this experimental result demands that it is this anharmonicity this term has importance.

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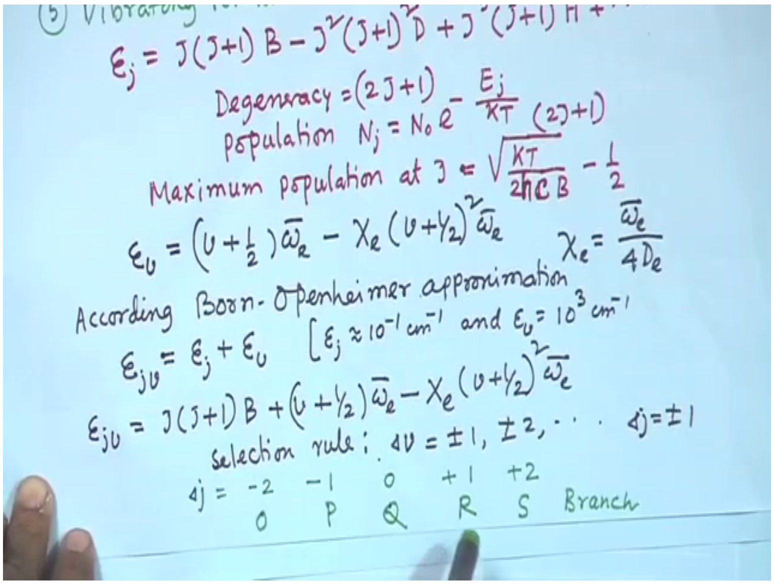

⑤ Vibrating

$\varepsilon_j = J(J+1)B - J^2(J+1)^2 D + J(J+1)H + \cdots$

Degeneracy $= (2J+1)$

population $N_j = N_0 e^{-\frac{E_j}{KT}} (2J+1)$

Maximum population at $J = \sqrt{\frac{KT}{2hcB}} - \frac{1}{2}$

$\varepsilon_v = (v+\frac{1}{2})\bar{\omega}_e - x_e(v+\frac{1}{2})^2\bar{\omega}_e$ $\qquad x_e = \frac{\bar{\omega}_e}{4D_e}$

According Born-Openheimer approximation

$\varepsilon_{Jv} = \varepsilon_j + \varepsilon_v$ $\quad [\varepsilon_j \approx 10^{-1}\ cm^{-1}$ and $\varepsilon_v = 10^3\ cm^{-1}$

$\varepsilon_{Jv} = J(J+1)B + (v+\frac{1}{2})\bar{\omega}_e - x_e(v+\frac{1}{2})^2\bar{\omega}_e$

selection rule: $\Delta v = \pm 1, \pm 2, \cdots$ $\quad \Delta J = \pm 1$

$\Delta J = -2 \quad -1 \quad 0 \quad +1 \quad +2$

O P Q R S Branch

So, so considering the selection rule del v equal to plus minus 1 plus minus 2 and del J equal to plus minus 1, one can show the transition ok. So, this vibrational transition between the vibrational level and then this in each transition this rotational transition also is accompanied and if you for a particular vibrational transition say del that v has to be double dash so and their rotational transition from J dash to J double dash. So, if del J equal to say minus 2 minus 1 0 plus 1 plus 2, although here we have written del J equal to plus 1 and minus 1.

So, del J equal to 0 is not allowed, but anyway this whatever spectral lines we see this we see as a branch ok. So, for del following the del J equal to plus 1, whatever the branch of spectral lines we will see this called r branch and following the del J equal to minus 1 whatever the branch of lines we will see that is called b branch and if possible if it happens that del J equal to 0, if in some cases if it for basically not diatomic molecule for other complicated molecule. If this transition other transitions occurs other than this del J equal to plus minus 1, so this series name is given like this.

So, this del J equal to 0, so that lines is called Q line. So, Q branch and similarly s branch and o branch ok, so these are the summary of our earlier study about the vibration and rotation and now let us continue the discussion of electronic spectroscopy of molecules. So, so what we have seen that already we have discussed that this energy levels of spectral of rotational lines, that is basically is 10 to the power minus 1 centimetre in case of vibration into the 3 centimetres inverse and in case of electronic transition or so this energy is 10 to the power 5 centimetre inverse.

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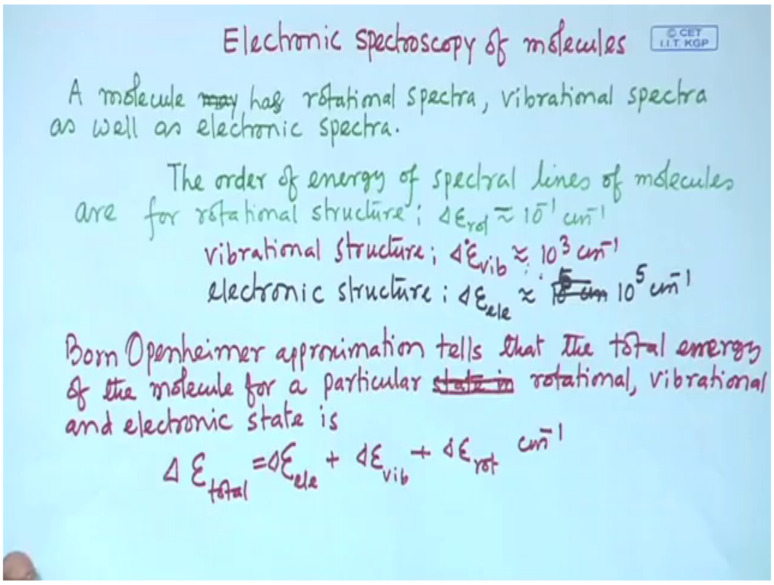

Electronic spectroscopy of molecules

A molecule ~~may~~ has rotational spectra, vibrational spectra as well as electronic spectra.

The order of energy of spectral lines of molecules are for rotational structure; $\Delta\varepsilon_{rot} \approx 10^{-1}\ cm^{-1}$

vibrational structure; $\Delta\varepsilon_{vib} \approx 10^{3}\ cm^{-1}$

electronic structure : $\Delta\varepsilon_{ele} \approx$ ~~10 cm~~ $10^{5}\ cm^{-1}$

Born Openheimer approximation tells that the total energy of the molecule for a particular ~~state in~~ rotational, vibrational and electronic state is

$$\Delta\varepsilon_{total} = \Delta\varepsilon_{ele} + \Delta\varepsilon_{vib} + \Delta\varepsilon_{rot}\ cm^{-1}$$

So, so here again you can see these three rotational vibrational electronic transitions this or their energy levels; so, their magnitude or different in order of in few orders ok. So, experts born openheimer approximation again for this electronic transition total energy del E total you can write energy change due to electronic transition plus vibration plus rotation.

So, total energy due in electronic transition or the spectral energy of the spectral lines in electronic transition, that will be daily total equal to sum of the change of the energy due to the electronic vibrational as well as rotational ok.

So, this we have written as for the born openheimer approximation. So, so, here we have to we have to we have to make clear that this that will get spectral lines due to the electronic conditions and in these spectral lines it is not a single line and that line basically it is composed of many lines. So, it is it is divided into two part one is called core structures of this electronic spectral lines.

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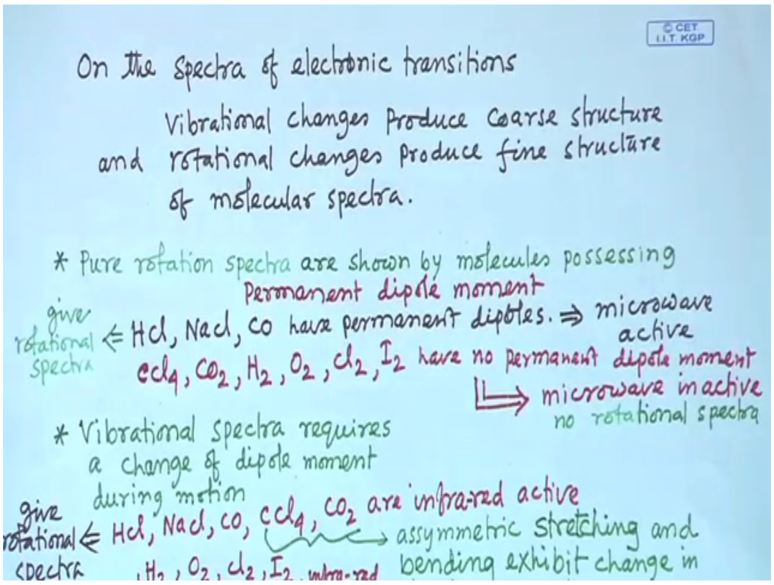

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On the spectra of electronic transitions

Vibrational changes produce coarse structure and rotational changes produce fine structure of molecular spectra.

* Pure rotation spectra are shown by molecules possessing permanent dipole moment

give rotational spectra ⇐ Hcl, Nacl, co have permanent dipoles. ⇒ microwave active

ccl_4, CO_2, H_2, O_2, cl_2, I_2 have no permanent dipole moment ⟹ microwave inactive no rotational spectra

* Vibrational spectra requires a change of dipole moment during motion

give rotational spectra ⇐ Hcl, Nacl, co, ccl_4, co_2 are infra-red active

ccl_4, co_2 → assymmetric stretching and bending exhibit change in

, H_2, O_2, cl_2, I_2 infra-red

So, that is due to the vibrational changes and this again this core structure again it is a each spectral lines, of course structure again it has fine structure and this fine structure is due to the rotation of the molecules ok.

So, we have seen that this pure rotation spectra because, a molecule and we are seeing this for a particular molecule it may have rotation it may have vibration and it may have this it may have this electronic transition ok. So, all molecules have rotation have vibration and have the electronic transition ok. But spectra whatever you see in spectroscopy that spectra we see that some molecules show only rotational spectra, no vibration, no electronic spectra; some molecules show vibrational spectra accompanied with the rotational spectra or pure vibration spectra.

Some molecules show the electronic spectra, but in case of electronic spectra all the time this rotational and vibrational spectra are accompanied ok, means this in case of electronic transition molecule molecules this. This vibrational vibration of the molecule is active means infrared active yes and rotational rotational spectra is the microwave active ok, although this same molecule it is not active only for rotational or only for vibration ok.

If there is no electronic transition, so here for pure rotation spectra are shown by the molecules which are possessing the permanent dipole, if the molecules have permanent dipole moment only they will show the pure rotational spectra ok. If molecules do not have permanent dipole moment they will not show rotational spectra pure rotational spectra ok. Now, example said that we have seen that HCl sodium chloride carbon monoxide have permanent dipole.

So, they are microwave active they are microwave active and it will give rotational spectra fine now in case of yeah. So, these other molecules like CC l4 CO 2 carbon dioxide hydrogen molecule oxygen molecule chlorine molecule iron molecule do not have the permanent dipole moment, they are microwave inactive and they will not show any rotational spectra.

Now, in case of vibrational spectra, so in case of to show to see the vibrational spectra actually there should be dipole change of dipole moment during motion during vibration ok; there may not be permanent dipole moment, but due to the vibration there will be change of dipole moment. So, in that case that molecule will not show rotational spectra, but it will show the vibrational spectra. So, here we have given example like here HCl sodium chloride carbon monoxide.

So, as usual they have rotational spectra as well as they will have the vibrational spectra because, of the change of the dipole moment due to the motion already it has permanent dipole moment. But during the motion there will be change of dipole moment fluctuation of a dipole moment due to the vibration, so it will show the vibrational spectra ok.

So, I think here I have to I have to write not vibrational rotational not rotational it should be vibrational it should be vibrational ok. So, but other than that CCL 4 CO 2 carbon dioxide are infrared active. So, these CCL 4 see CO 2 they do not have permanent dipole moment.

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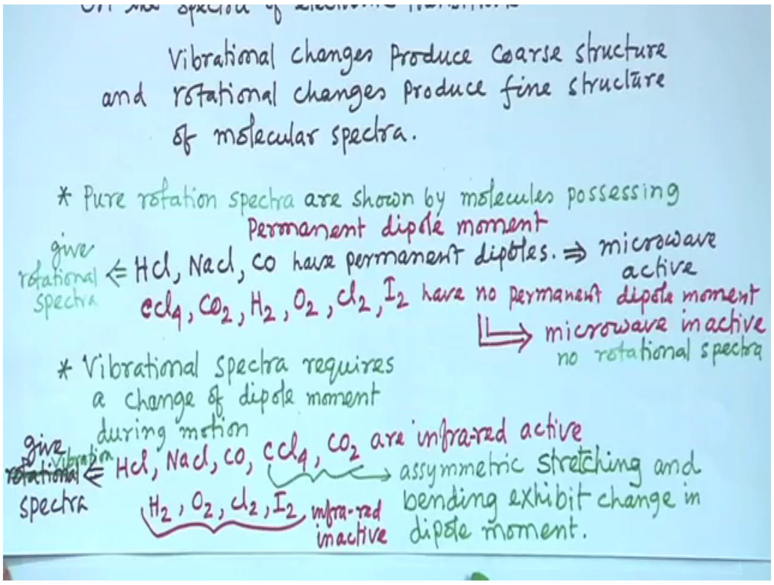

Vibrational changes produce coarse structure and rotational changes produce fine structure of molecular spectra.

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give rotational spectra ⇐ HCl, NaCl, CO have permanent dipoles. ⇒ microwave active

CCl_4, CO_2, H_2, O_2, Cl_2, I_2 have no permanent dipole moment ⟹ microwave inactive no rotational spectra

* Vibrational spectra requires a change of dipole moment during motion

give ~~rotational~~ vibration spectra ⇐ HCl, NaCl, CO, CCl_4, CO_2 are infra-red active → assymmetric stretching and bending exhibit change in dipole moment.

H_2, O_2, Cl_2, I_2 infra-red inactive

But due to asymmetric stretching and bending exhibit change in the dipole moment exhibit change in the dipole moment. So, this will be infrared active and we will get the vibrational spectra. Whereas, H 2 O, 2 Cl 2, I 2 id molecule. So, they are infrared inactive means they will not show any vibrational spectra ok.

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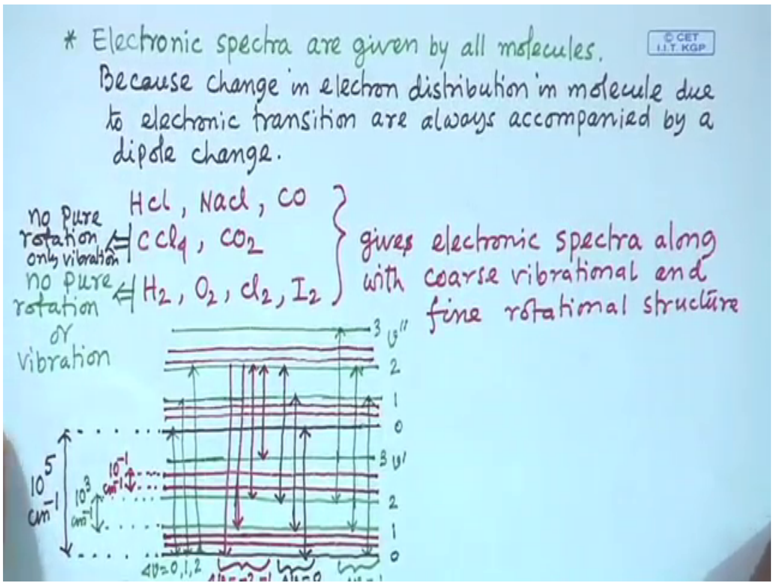

* Electronic spectra are given by all molecules. Because change in electron distribution in molecule due to electronic transition are always accompanied by a dipole change.

HCl, NaCl, CO
no pure rotation only vibration ⇐ CCl_4, CO_2
no pure rotation or vibration ⇐ H_2, O_2, Cl_2, I_2

} gives electronic spectra along with coarse vibrational and fine rotational structure

So, next if we take these electronic spectra given by which molecules, so electronic spectra that is because electronic spectra is are given by all molecules. So, whatever sodium chloride hydrogen chloride HCl carbon monoxide CCl4 carbon dioxide H 2 O, 2

Cl 2, I 2 iodine molecules ok, all these molecules will give will give this electronic spectra, as well as it will give vibrational spectra and rotation spectra.

Although they although they do not show the some of them do not show the pure rotational spectra or pure vibrational spectra, but here all will show the rotational and vibrational spectra and that is because of the electronic transition and when there will be electronic transition. So, it is it is automatically automatically it is distribution of the charge will change and there will be the change fluctuation of the charge and that is equivalent to that if any fluctuation of the charge.

So, it will be active for it will be active this microwave active and infrared active and it will show this rotational and vibrational spectra associated with the electronic transition if there is the electronic transitions. So, they may not show the rotational vibration but if any electronic transitions is there. So, this vibrational and rotational also it will be it will be active and it will it will give these spectral lines for rotation and vibration ok.

So, I will stop here and then I will continue next class.

Thank you.