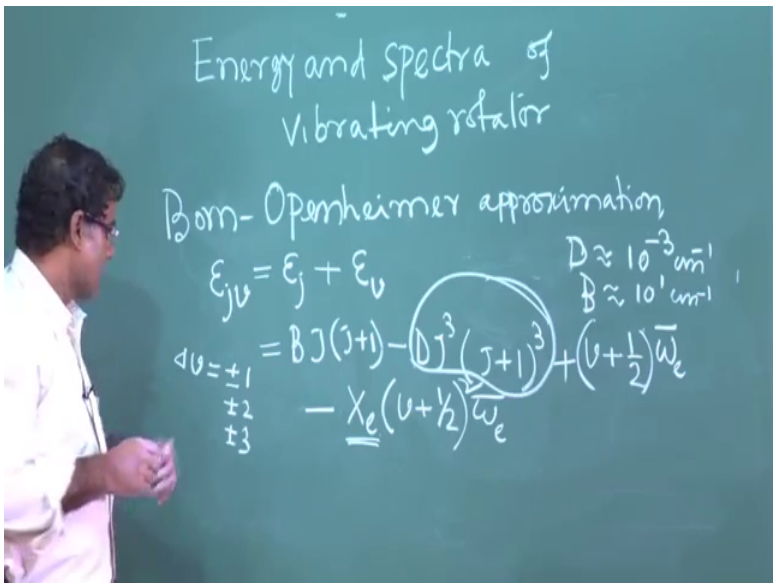
Atomic and Molecular Physics
Prof. Amal Kumar Das
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture - 50
Vibration of a molecule (Contd.)

(Refer Slide Time: 00:21)



So, I was discussing the energy and spectra of vibrating rotator. So we have seen that for Born-Openheimer approximation I think this is Openheimer. So, according to Born-Openheimer approximation, this total energy for rotation and vibration that means, vibrating rotator so that will be just summation of the individual energy of a rotator plus individual energy of a of a vibrator ok. Because this energy is del e J or del e v.

So, this energy in the order of 10 to the power minus 1 centimetre inverse and it is in the 10 to the power 3 centimetre inverse so their separation is quite high. So, there will not be any interaction energy term for rotation of the molecule and the vibration of the molecule.

So, just this total energy will be simply the summation of the individual energy. And that we have written that this is B J J plus 1 minus D J I think that is J cube J plus 1 cube. I think this I will erase it so that was the rotational energy and plus the vibration energy I can write V plus half omega e bar omega e bar minus I think minus X e V plus half omega e half square omega e bar ok, so that was the energy.

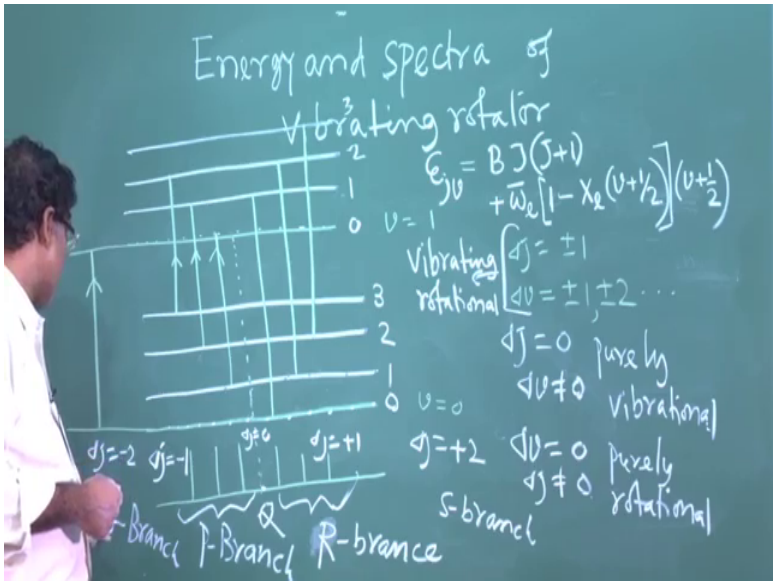
So, here I have I have I have drawn they were drawn the energy levels and shown the transition. So, here basically when I was drawing, so here simply this term neglected in this case, because this D value is very very D value and B value D is in the order of I think it is it is order of 10 to the power minus 3 centimetre inverse, this d value the order of 10 to the minus 3 inverse.

And whereas, B value is B value is around 10 to the power 1 centimetre inverse since 10 centimetre inverse ok. So, compared to B value compared to this term this term one can neglect. And of course, this anharmonicity constant also is very small value, but this we will not neglect, we do not neglect because then we will lose this selection rule del v equal to plus minus 1 plus minus 2 plus minus 3. So, this selection rule was valid because of anharmonicity ok.

If an unknown city we neglect this anharmonicity, then one cannot only one has to use selection rule del e equal to plus minus 1, so that is why this will not although this X e anharmonicity constant term is small, but still will keep this term because then only one can use this these selection rules.

So, this energy is for vibrating rotator so this energy expression, one can one can write this, this is the energy expression ok. And for this now here one thing I would like to tell you that, yes, so I think if I consider this energy level and so I think this I can write here, and later on it may be useful for me.

(Refer Slide Time: 06:56)



Del so this energy J V equal to bj J plus 1 minus sorry here I have I should not need that one, so that was omega e bar plus omega e bar I think it was 1 minus X e v plus half ok, then this and then v plus half. So, this is the energy expression. And if I draw this here, now I do not need this one, so this I am repeating this discussion because this very important. And real system most of the molecules basically it it shows this behaviour ok, it is vibrating rotator it is so that that model is applicable appropriate for most of the molecules.

So, pure vibration pure rotation some of the molecules, but most of the molecule shows this vibrating rotator. And if I draw the energy levels, so I was I have. So, this for vibration this is the energy level for vibration these the energy levels. So, this the say v equal to 0, and then this is the energy level for vibration energy level v equal to 1. Similarly, v equal 2, v equal to 3, one can draw.

Now, this energy separation is as I told this is a 10 to the power in the range of 10 to the power 3 centimetre inverse. Whereas, here now for v equal to 0, v equal to 0, whatever the value that is this value. Now, if I put different value of J different value of J, starting from J equal to 0, 1, 2, 3, J equal to 0, 1, 2, 3, so J equal to 0, it will not contribute, so the same value. So, it is J equal to 0 also it is the same line. So, that is the J equal to 0, and then J equal to 1.

So, it is you will get J equal to 1 ok, then J equal to 2, J equal to 3 ok. So, it is not in scale just I have I have drawn because separation will not be there fine, stay very close to it. Similarly, for v equal to 1, I will get a set of so this for J equal to 1 J equal to 0 now I will get 1, 2 then 3 ok, this is J value.

Now, transition is this, so this transition is not allowed basically J equal to 0 to J equal to 0, because del J equal to 0 selection rule, del J equal to plus minus 1 del J equal to 0 is not allowed. Similarly, del v equal to plus minus 1 plus minus 2 etcetera ok. So, this so this transition J equal to 0 to J equal to 0 is not allowed in case of vibrating rotator because both selection rule has to be satisfied.

So, this line spectral lines will be horizontal spectral lines will be missing ok, but instead of if it is if it is only vibration, if it is only vibration ok, so I will get the spectral lines, I will get the spectral lines, I will get the spectral lines, I will get the spectral lines ok, because this del v equal to 1, del v equal to 1 ok, so I will get the spectral lines.

So, if it is pure, if it is pure vibrational vibration of the molecule, so so that is why we tell so and whereas here you are seeing this transition in case of vibrating rotator this transition is not allowed, so that spectral line should be missing ok. So, only we will get when we will get only when it is purely vibrational ok. When it is vibrational rotating spectra, in that case it will be missing, but corresponding will get in place of it, we will get a bunch of lines.

So, from where these bunch of lines are coming so that was I was trying to explain. So, this transition is allowed 0 to for del J equal to minus 1, so starting from 1 to 0 ok, 1 to 0. So, here J equal to 1, here J equal to 0. So, del J equal to minus 1. For del J equal to minus 1 that is allowed, so del J equal to minus 1 these then these transition then this transition will be allowed ok.

So, I will get these spectral lines, I will get these spectral lines right. Similarly, for del J equal to plus 1, so it started from 0. So, this J equal to 0 to J equal to plus 1 ok, so this transition will be allowed. So, these transition is not allowed, J equal to 0 to J equal to 1, this transition is not allowed because then del v will be 0 ok, then del v equal to 0 ok.

So, here although del J equal to plus 1, 0 to 1 rotationally it is allowed, but for vibration is not allowing, because del v in this case v equal to 0 to v equal to 0 this transition del v equal to 0 that is not allowed ok. So, in this case this transition is not allowed, but this transition is allowed from J equal to 0 to other vibrational level, J equal to 1 del J is plus 1. Similarly, in this case del J J equal to 1 to J equal to 2, J equal to 2 to J equal to 3 del J plus 1. So, these lines spectral lines spectral lines we will see.

And this separation you see this separation this (Refer Time: 15:56), so here this all all the energy whatever separation we are getting that is the separation of the is the separation is equal to the separation of of of rotational energy levels you know. So, rotational energy levels, so they are very closely spaced ok. This original energy, so this original energy is this it is a 10 to the power 3 centimetre inverse in that order.

Now, so this one is slightly lower than these 10 to the power 3 centimetre inverse. And these are slightly more lower side lower side, slightly higher side. So, I this these spectral lines these spectral lines is basically as if you are getting these spectral lines, you are getting now very closely spaced. This is missing basically. This is missing very closely spaced many spectral lines. So, instead of one you are getting many.

So, you are getting basically this we are telling instead of lines, you will get it you will get a band ok. So, here I have I told you that when I will get only one line, and when I will get this band. So, only one line will get only one line will get when it is purely it is purely vibrational ok. In case of vibrating rotator, this transition is not allowed, then it will be J equal to 0 to J equal to 0, so del J equal to 0. When del J equal to 0 this, then if it is allowed then it will be purely vibrational energy vibrational energy ok, so that is why we tell when del J equal to 0, del v is not equal to 0, it is purely it is purely vibrational, it is purely vibrational ok.

Similarly, as it also told that this J equal to 0 to J equal to 1, it is allowed, it is allowed, but del v equal to 0 that is not allowed ok. So, when we will see this kind of transition del v equal to 0, but del J is not equal to 0 ok; when del v equal to 0 if it is allowed, but del J is not equal to 0 ok. Del J equal to plus plus minus 1 del v equal to 0 so that means, this transition, this transition is allowed. So, it will be purely rotational ok. So, when this condition will satisfied, then it will be purely rotational ok, purely rotational. When this condition will satisfy it simultaneously, then it will be vibrating rotation vibrating rotational ok.

So, now this as I told this branch basically, we will see the branch. So, higher side and lower side ok, so this is called this is this is P-branch, P-branch this called P-branch ok. And this higher will be number side this is called R-branch R-branch ok. And middle it is not there, but if anything is there then it is called Q-branch, Q, Q-line ok.

So, this for this for this for del J equal to minus 1 this side, and this del J equal to plus 1 ok. So, so basically for different J value, because del J equal to minus 1 del J equal to plus 1 this is valid yeah. So, if there is a violation of this violation for any case, if it is violation of this del J equal to 0, they say this Q del J equal to 0 is Q ok. And if del J equal to minus 2, so then it is extended ok. So, then it is called O-branch If del J equal to plus 2, then it is called S-branch these are the.

So, in our case it is this for vibrating rotation it is this the this is the situation in vibrating rotation this is the situation ok, you will get basically P-branch and Q-branch sorry R-branch and yeah there will be no branch for Q, but it is in (Refer Time: 22:26) nomenclature for del J equal to 1 so Q-branch, then minus 1 P-branch, minus 2 O-

branch, plus 1 P-branch minus plus 2 is S-branch. So, these are the this is the nomenclature ok.

So, so I think yeah. So, so whether it is purely rotational whether it is purely vibrational or it is vibrating rotational, so one can seeing the spectral lines, studying the studying the microwave spectra, studying the microwave spectra and infrared spectra so one can tell which kind of molecule it is ok. Whether these molecules have only rotational or only vibrational or it have it has both of rotational and vibrational ok.

So, seeing the nature of the spectra, one can conclude one can conclude about the about the molecules and yeah defined information about the molecules from the from studying the microwave spectroscopy or and the infrared spectroscopy one can one can get lot of information about the molecules ok.

So, this I think in simpler way that is, this molecular physics so far whatever I thought this in simpler way simple cases I chosen I have chosen and these are basic study basic things, but there are some complicated for as I told this we are considering only di diatomic linear molecule, but for other molecule polyatomic and non-linear molecule, it is slightly complicated and that that is what it is I think it is not necessary for undergraduate student.

Whatever I am teaching you that is the basic and requirement for the undergraduate student; other things I think one has to study in higher class. So, I will stop here today. In next class probably I will start these electronic spectra of molecules ok.

So, thank you for your kind attention.