Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 42
The Rotational and Vibrational Spectroscopy

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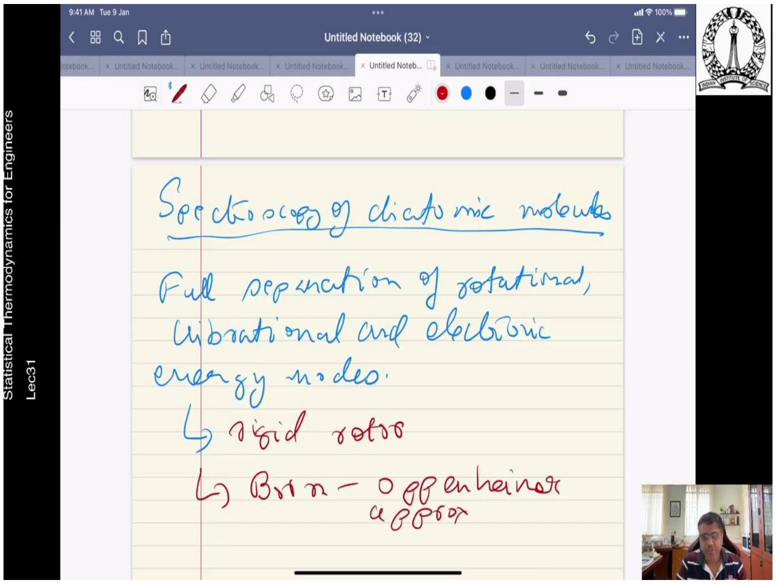
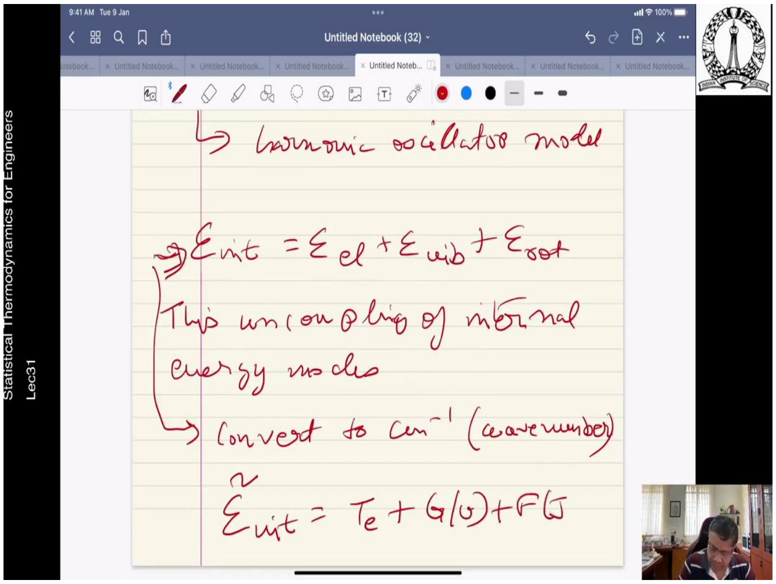


Spectroscopy of diatomic molecules

Full separation of rotational, vibrational and electronic energy modes.

↳ rigid rotor

↳ Born – Oppenheimer approx



↳ harmonic oscillator model

$$\Rightarrow \varepsilon_{int} = \varepsilon_{el} + \varepsilon_{vib} + \varepsilon_{rot}$$

This uncoupling of internal energy modes

↳ convert to cm^{-1} (wavenumber)

$$\tilde{\varepsilon}_{int} = T_e + G(v) + F(J)$$

So, welcome to lecture number 31 of the Statistical Thermodynamics for Engineers. So, in this particular course, in this particular lecture we are going to look at the spectroscopy of diatomic molecules. So, spectroscopy of diatomic molecules. So, we presented a quantum mechanical analysis of the energy modes for a diatomic molecule. A significant aspect of this analysis was the full separation of the rotational, vibrational and the electronic energy nodes.

So, we saw there was a full separation, separation of rotational, vibrational and electronic energy modes. This was successively implemented. What did we do? We implemented the rigid rotor, the rigid rotor model, then we did the Bron-Oppenheimer approximation, approximation and of course we had the harmonic, harmonic oscillator, harmonic oscillator model.

So, we therefore expressed that if this is the internal energy, remember the external energy was all translational. So, the internal energy is written as electronic plus energy due to vibration, energy due to rotation. The uncoupling, this uncoupling, uncoupling of internal energy modes is a rudimentary model, and it provides a simplest explanation for its various spectral features that we will see.

So, this is, now if we convert this equation now to the units wave number. So, convert to centimeter inverse, which is basically your wave number, so the internal energy is written as T e plus G v plus F J. So, these are the three different energies that we write it in terms of the wave number.

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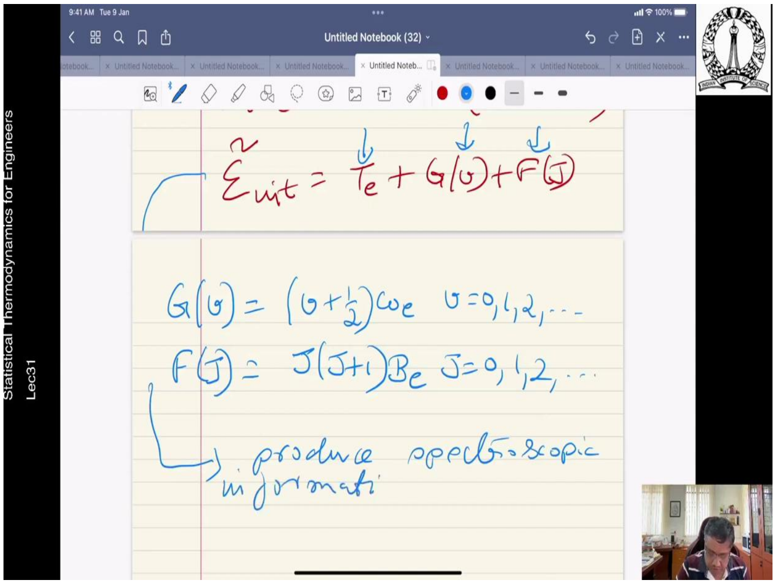

$$\tilde{\mathcal{E}}_{int} = T_e + G(v) + F(J)$$

$$G(v) = \left(v+\frac{1}{2}\right)\omega_e \quad v = 0, 1, 2, \ldots$$

$$F(J) = J(J+1)B_e \quad J = 0, 1, 2, \ldots$$

produce spectroscopic informati

So, this is a simplest model, simplistic model which provides simplistic explanation also for the various spectral features that we might have. Now, this G v, G v is given as v plus half into the w e, omega e equal to 0, 1, 2, da, da, da. And F J, this is a recap, this we already know, so this is given as J into J plus 1 B e. So, J is equal to 0, 1, 2 da, da, da.

On this basis that how these terms that we see over here like this, this and this can produce spectroscopic information. So, that is the main goal that how each of these terms, so electronic energy, rotational and vibrational can produce spectroscopically relevant information. How these can produce spectroscopic information. So, we first isolate the various regimes of the electromagnetic spectrum, and these regimes are written in terms of both wavelength or wave number whatever it is, and but there are certain indicative borders that you will see, but let us let us write down the regions.

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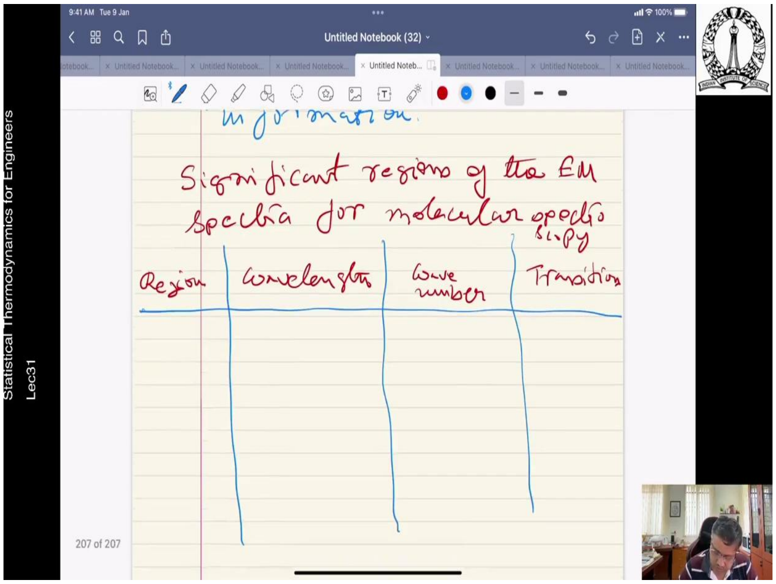
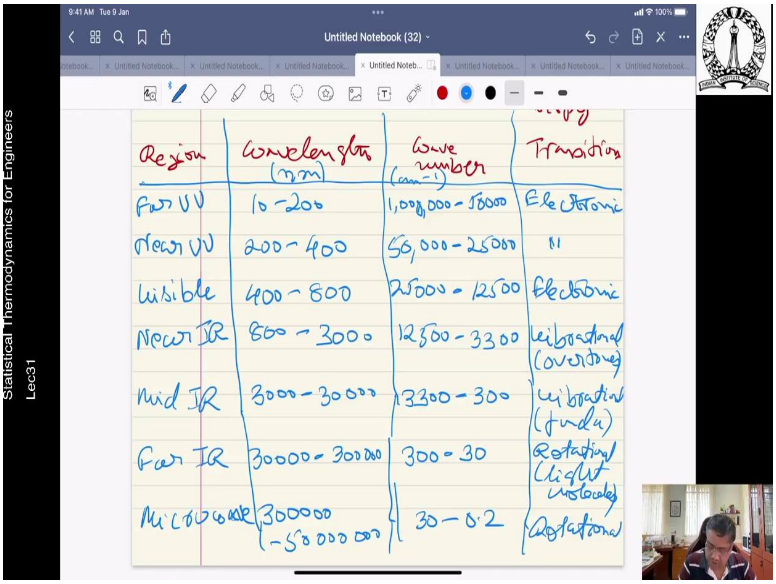


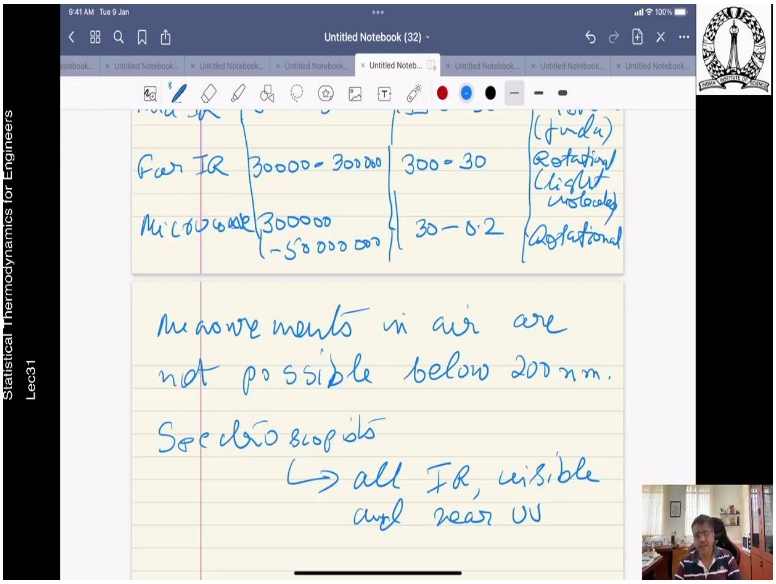
information.

Significant regions of the EM spectra for molecular spectroscopy

Region	Wavelength	Wave number	Transition



Region	Wavelength (nm)	Wave number (cm⁻¹)	Transition
Far UV	10 - 200	1,000,000 - 50000	Electronic
Near UV	200 - 400	50,000 - 25000	″
Visible	400 - 800	25000 - 12500	Electronic
Near IR	800 - 3000	12500 - 3300	Vibrational (overtones)
Mid IR	3000 - 30000	3300 - 300	Vibrational (funda)
Far IR	30000 - 300000	300 - 30	Rotational (light molecules)
Microwave	300000 - 50000000	30 - 0.2	Rotational



Far IR	30000 - 300000	300 - 30	Rotational (light molecules)
Microwave	300000 - 50000000	30 - 0.2	Rotational

Measurements in air are not possible below 200 nm.

Spectroscopists → all IR, visible and near UV

So, the, this we call it as significant regions of the electromagnetic spectrum for molecular spectroscopy. So, first is the region, then there is the wavelength, wavelength, then there is a wave number, then there are the transitions. So, this is Far UV, in the nanometer, this is nanometer, it is in centimeter inverse. So, 10 to 200 is Far UV, in the, and the transition is usually electronic. It is approximate, once again. This is written as one six zeroes(())(06:17). Then there is near UV. This is 200 to 400. This is starting to combustion experimentation routinely. Spectroscopy. This is also electronic, I am just putting equals sign here.

Then of course comes visible. Visible is 400 to 800. So, this is 25,000 to 12,500. This is also electronic. Then of course there is Near IR or infrared, which is between 800 to 3,000. It is once again in nanometer, 12,500 to 3,300, this is vibrational, but it is overtones. So, we will come to that, what overtones. Then of course, there is the Mid IR, Mid IR which is 3,000 to 30,000 in terms of the wave number, this is about up to 300. This is once again vibrational, but this is fundamental.

Then you have Far IR which is 30,000 all the way up to 300,000. 300-30. This is rotational light molecules. And then there is a Microwave. So, the microwave is 300,000 all the way up to 5 0 0, see if I put all the zeros correctly. 30 to 0.2. And this is rotational. So, this are, this is the main regions. Of course, the demarcation is a little tentative in nature.

So, spectroscopies, typically report all infrared, visible, near, ultraviolet wavelengths in air, vacuum wavelengths are used for Far UV because measurements in air are not possible below 200 nanometer. So, measurements in air are not possible below 200 nanometer. So, you report, so the spectroscopist, if you are a spectroscopist, so they report all values in all IR visible and Near UV, Near ultraviolet. Combustion work usually uses for example which type of measurements we use in air for ultraviolet. So, these are the different types of the spectrum and these are the kind of fundamental demarcations that we have.

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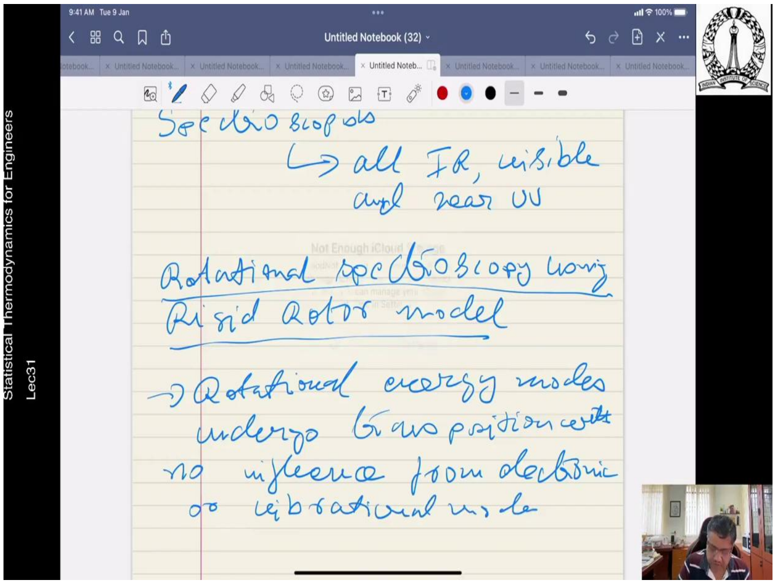
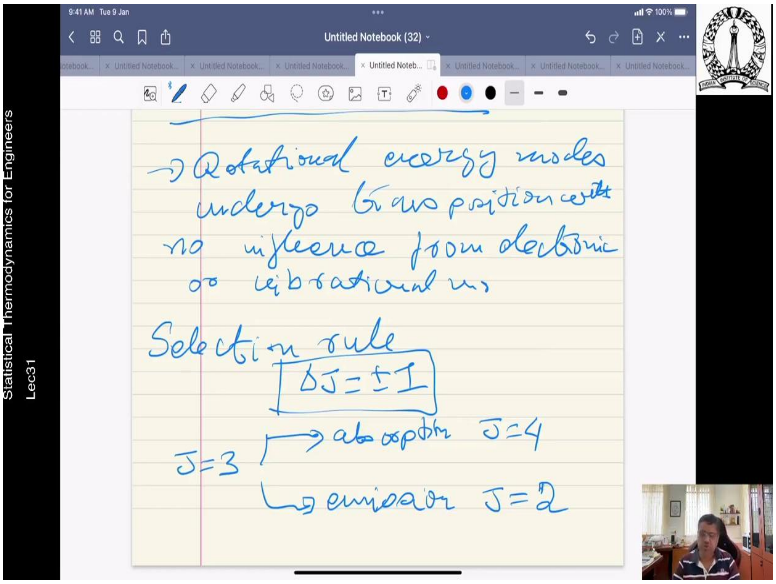


Spectroscopists
↳ all IR, visible
and near UV

Rotational spectroscopy using
Rigid Rotor model

→ Rotational energy modes
undergo transposition with
no influence from electronic
or vibrational mode



→ Rotational energy modes undergo trans position with no influence from electronic or vibrational m

Selection rule

$\boxed{\Delta J = \pm 1}$

$J=3$ → absorption $J=4$

↳ emission $J=2$

So, in a nutshell let us first start looking at the rotational spectroscopy, rotational spectroscopy, spectroscopy using rigid rotor model. So, we begin by considering that the rotational energy modes under those transposition with no influence from vibrational or electron chemistry. So, the fundamental assumption is the rotational energy modes, energy modes undergo trans position with no influence, no influence from electronic or vibrational modes. Sounds fair and square, I guess.

So, the selection rule, selection rule, rule we know is delta J is equal to plus minus 1. This is the selection rule. So, if say J is equal to 3, so absorption or emission, if it is absorption it will go to J equal to 4, or if it is emission, it go to J equal to 2. So, these are the only two modes that are possible because J final minus J initial is plus 1 or minus 1. So, these are the two things that are possible, J equal to 2 or J equal to 4.

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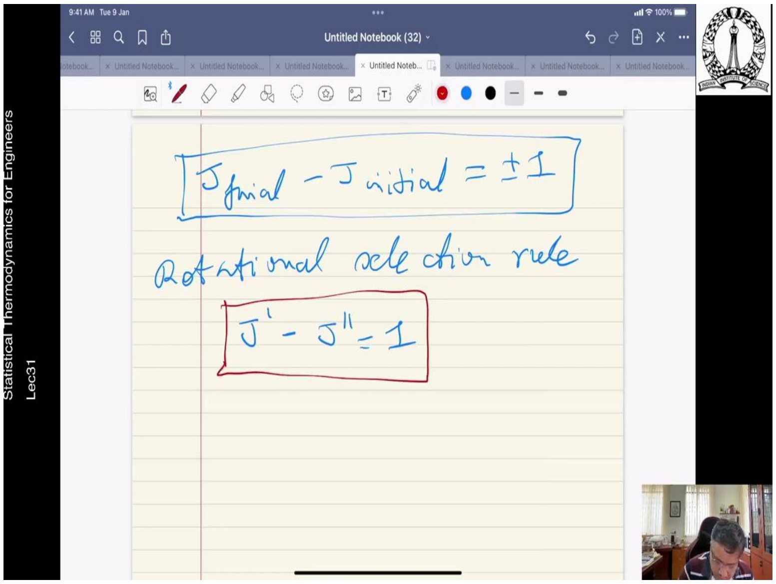
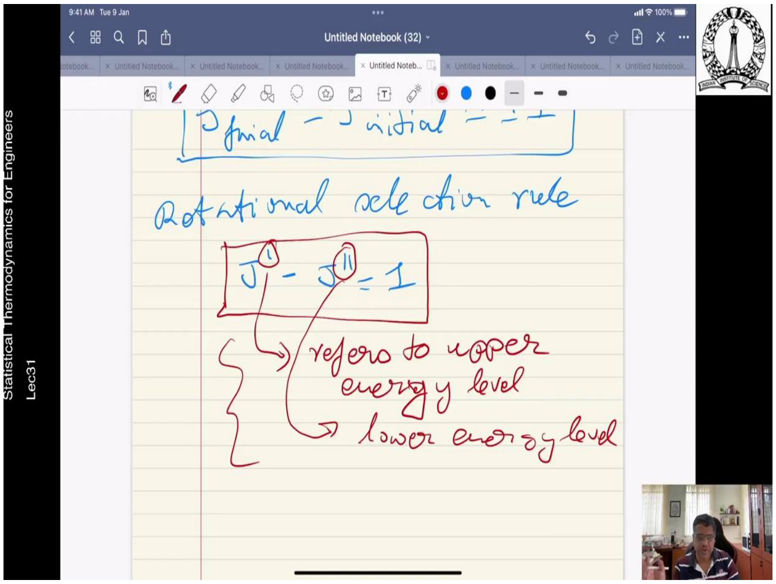


$$\boxed{J_{final} - J_{initial} = \pm 1}$$

Rotational selection rule

$$\boxed{J' - J'' = 1}$$



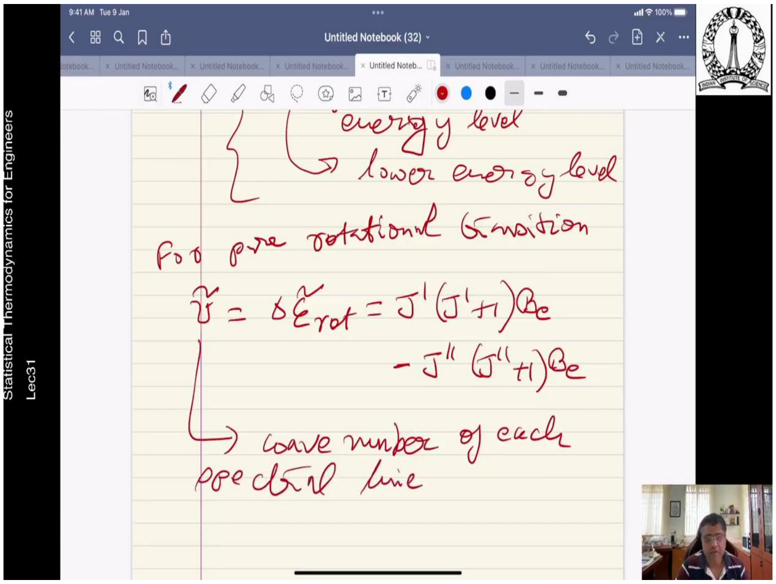
$$J_{final} - J_{initial} = \pm 1$$

Rotational selection rule

$$\boxed{J' - J'' = 1}$$

J' → refers to upper energy level

J'' → lower energy level



energy level

lower energy level

For pure rotational transition

$$\tilde{\nu} = \Delta \tilde{E}_{rot} = J'(J'+1)B_e - J''(J''+1)B_e$$

wave number of each spectral line

So, in other words J final minus J initial is equal to plus minus 1. That is the, that is the, that is the rule. So, so the, the potential complexity is kind of reduced. So, a convenient method of writing the rotational selection rule, rotational selection rule, selection rule can be written as J prime minus J double prime is equal to 1. The single prime, this, refers to upper energy level.

And this double prime actually refers to the lower energy level, energy level or any transition, any transition whether absorption or emission, absorption or emission. So, applying this nomenclature for each spectral line for pure rotational transition, for pure rotational transition, for pure rotational, transition, transition, e rotation change. J prime plus J prime plus 1 into B e minus J double prime J double prime plus 1. Wave number of each spectral line, wave number of each spectral line.

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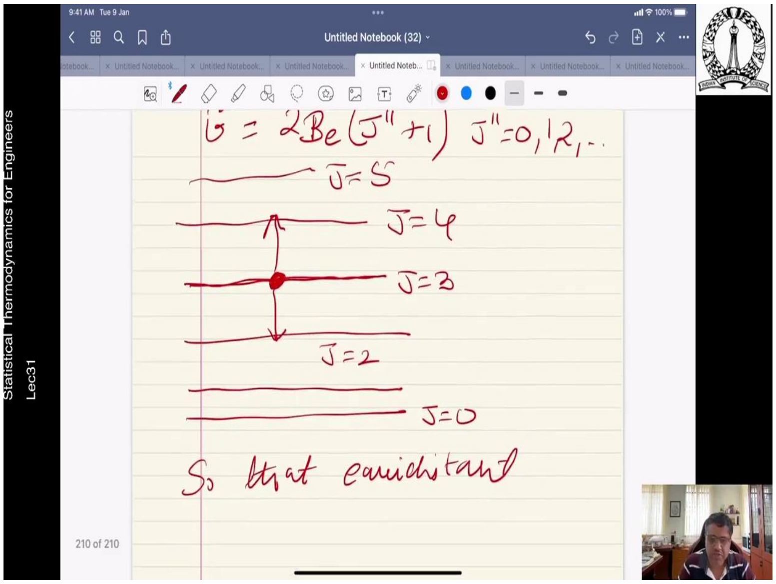
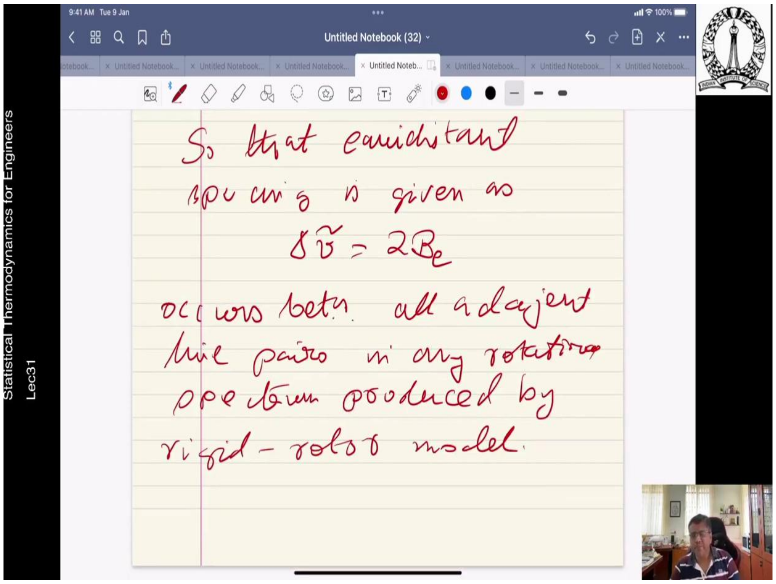


$\tilde{\nu} = 2B_e(J''+1)$ $J''=0,1,2,\dots$

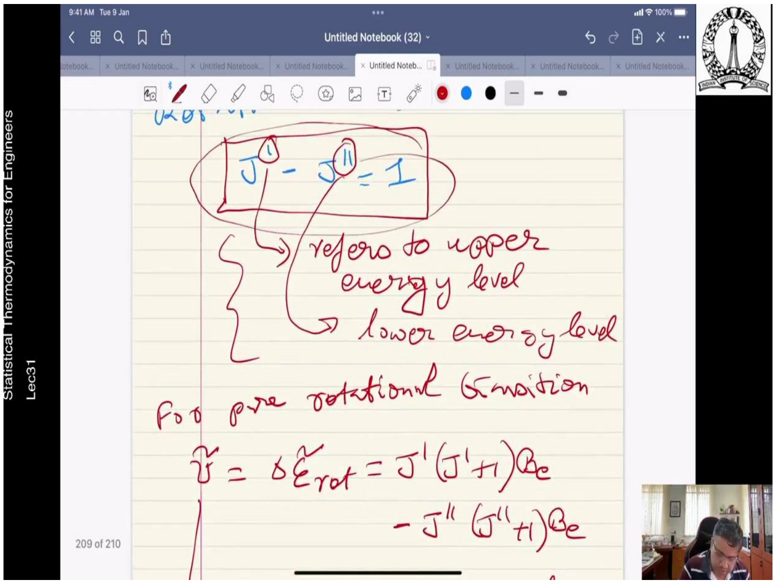
So that equidistant



So that equidistant spacing is given as

$\delta\tilde{\nu} = 2B_e$

occurs betn all adjacent line pairs in any rotation spectrum produced by rigid-rotor model.



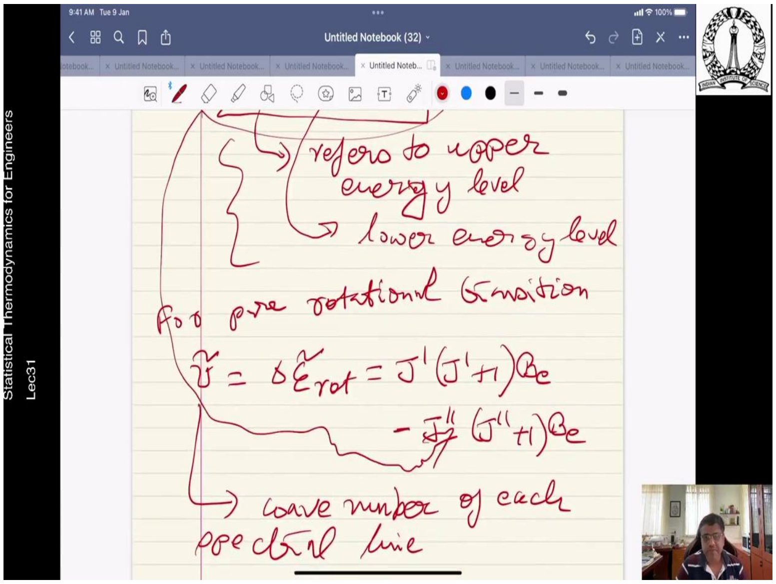
$$\boxed{J' - J'' = 1}$$

J' → refers to upper energy level

J'' → lower energy level

For pure rotational transition

$$\tilde{\nu} = \Delta \varepsilon_{rot} = J'(J'+1)B_e - J''(J''+1)B_e$$



J' → refers to upper energy level

J'' → lower energy level

For pure rotational transition

$$\tilde{\nu} = \Delta \varepsilon_{rot} = J'(J'+1)B_e - J''(J''+1)B_e$$

→ wave number of each spectral line

So, this becomes 2 B e into J double prime plus 1. J double prime is equal to 0, 1, 2, et cetera. What we have done? We have substituted this expression, this expression over here. So, that gives rise to this. So, if you look at this, so, for example, energy level diagram, this is say, J equal to 3, say J equal to 2, J equal to 4, and this is the, we are sitting there. So, it is so that way and of course there will be higher energy levels available but it is not accessible.

And then there is ground part, J equal to 0, or 0 level energy. So, that. So, this is what it is. So, that equidistant spacing, so that an equidistant spacing is given by, so that equidistant, so that equidistant spacing, if we look at equidistant spacing is given as 2 B e. So, occurs, this occurs between all adjacent line pairs in any rotational spectrum, any rotational spectrum produced by the rigid-rotor model.

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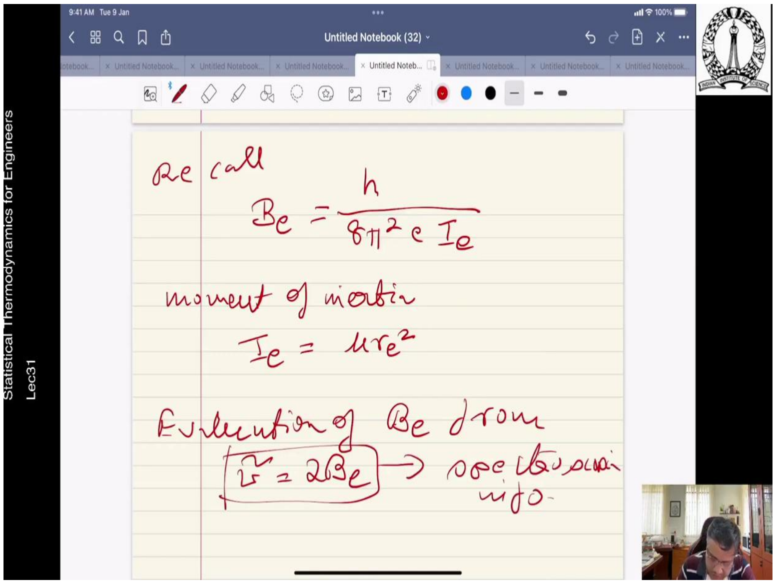


Recall

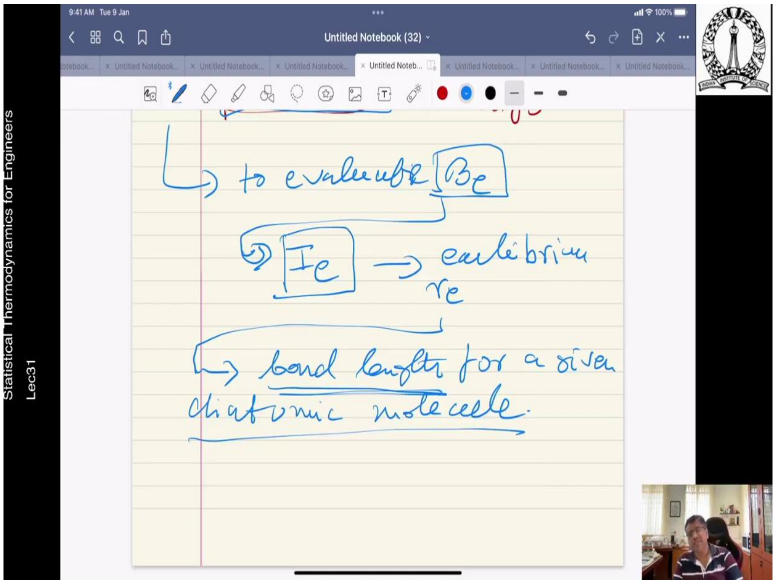
$$B_e = \frac{h}{8\pi^2 c I_e}$$

moment of inertia

$$I_e = \mu r_e^2$$

Evaluation of B_e from

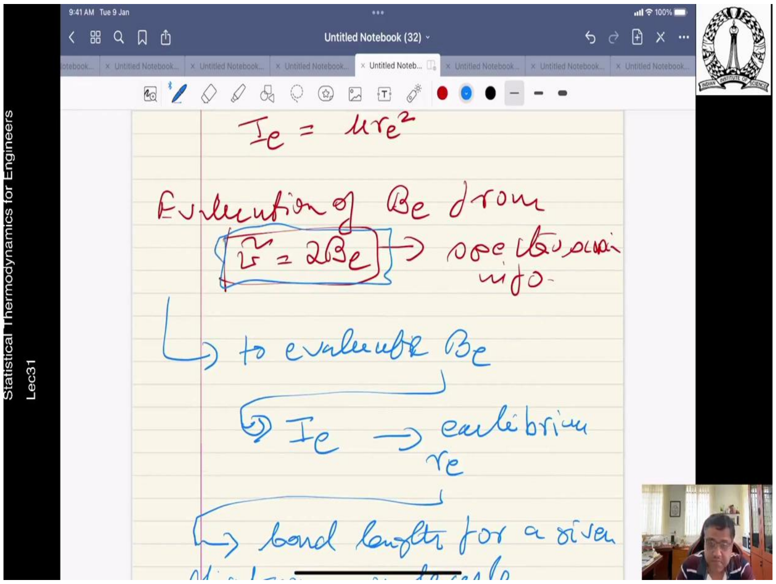
$\boxed{\tilde{\nu} = 2B_e} \rightarrow$ spectroscopic info.



↳ to evaluate $\boxed{B_e}$

↳ $\boxed{I_e} \rightarrow$ equilibrium r_e

↳ bond length for a given diatomic molecule.



$I_e = \mu r_e^2$

Evaluation of B_e from

$\boxed{\tilde{\nu} = 2B_e} \rightarrow$ spectroscopic info.

↳ to evaluate B_e

↳ $I_e \rightarrow$ equilibrium r_e

↳ bond length for a given

This is an approximation, but this is simple but powerful prediction. So, also recall, also recall that B e is equal to h divided by 8 pi square c into I e, by the moment of inertia, moment of inertia I e is given as mu r e square. So, if you try to evaluate the value, evaluation of B e by using this, to a specific rotational spectrum, results in an experimental value for the moment of inertia.

So, thus providing that equilibrium internuclear separation and bond length for any given diatomic molecule. So, evaluation of B e from this, this comes from the spectrum. This is this is spectroscopic information, spectroscopic information. So, this enables us to evaluate, this enables us to evaluate, evaluate B e. And from B e, we can evaluate I e.

And from I e, we can find out the equilibrium internuclear distance, you can find out the equilibrium r e, which further gives rise to the bond length, bond length for given diatomic molecule. So, just by measuring the spectrum or the wave number of the spectrum we can get an idea of what is going to be B e.

And since B e incorporates I e, which is only variable here, and I e incorporates the moment of inertia which is essentially involves the internuclear equilibrium separation length, this gives an idea of the bond length for any given diatomic molecule. So, but this is an approximate issue because we still use the rigid rotor model which we know that is not exactly correct.

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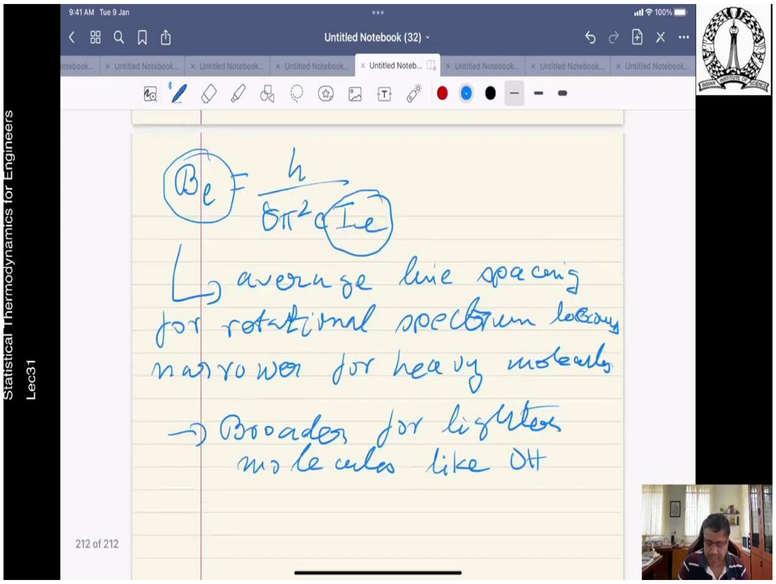
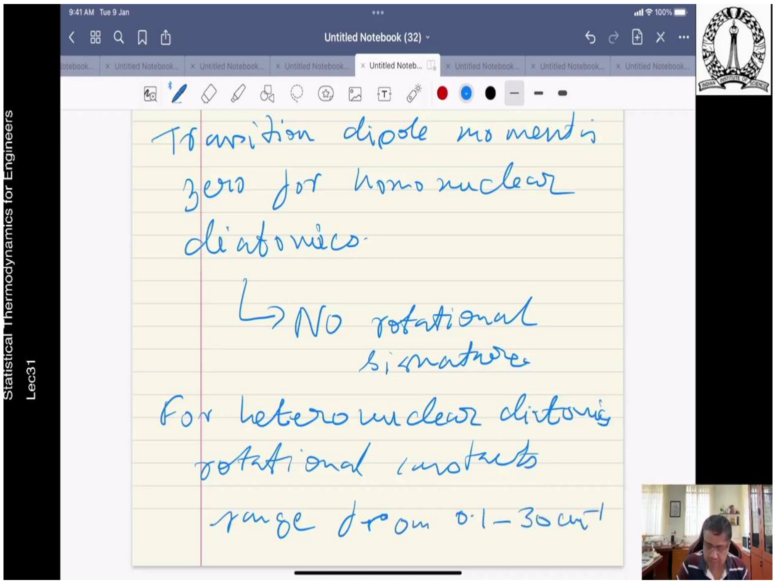


$$\boxed{B_e} = \frac{h}{8\pi^2 c \boxed{I_e}}$$

↳ average line spacing for rotational spectrum becoming narrower for heavy molecules

→ Broader for lighter molecules like OH



Transition dipole moment is zero for homonuclear diatomics.

↳ No rotational signature

For heteronuclear diatomics rotational constants range from 0.1 – 30 cm^{-1}

So, equation, this particular thing verifies that if you look at B e, that average line spacing, so B e is equal to h 8 pi Square c I e, this gives out important information that average line spacing, average line spacing for rotational spectrum, for rotational spectrum, spectrum becomes, becomes narrower, narrower for heavy molecules or heavier molecules.

This is given. I e becomes large because mu becomes large. As I e becomes large, B e becomes small, so delta v becomes smaller. So, the line spacing becomes narrower. As the line spacing becomes narrower for heavier molecules, the lines are more congested. So, and it is broader, broader for lighter molecules, like OH, for example, which is a lighter molecule.

So, but for however the trans, as we saw the transition dipole moment, transition dipole moment is zero for homonuclear diatomics, for homonuclear diatomic, it is 0. So, the obvious result is no rotational signature, no rotational signature for homonuclear diatomics. For heteronuclear diatomics, for heteronuclear diatomics, diatomics, the rotational constants, the rotational constants, constants range from 0.1 to 30-centimeter inverse.

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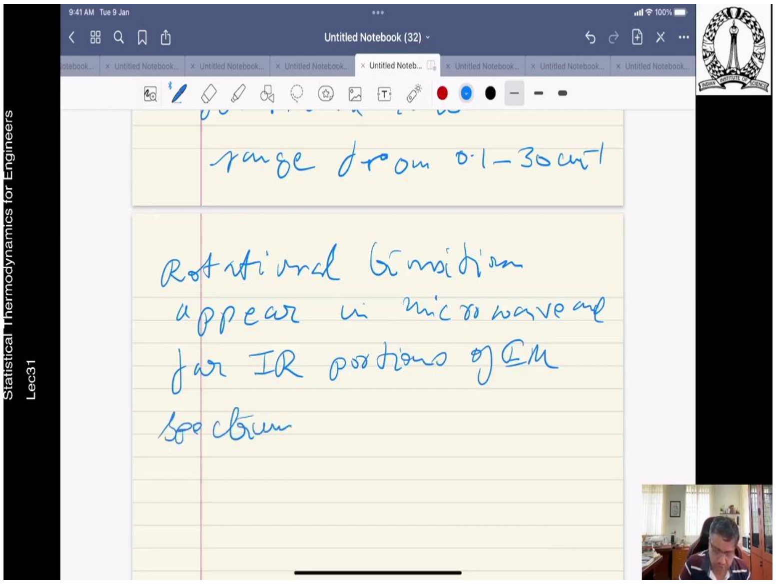
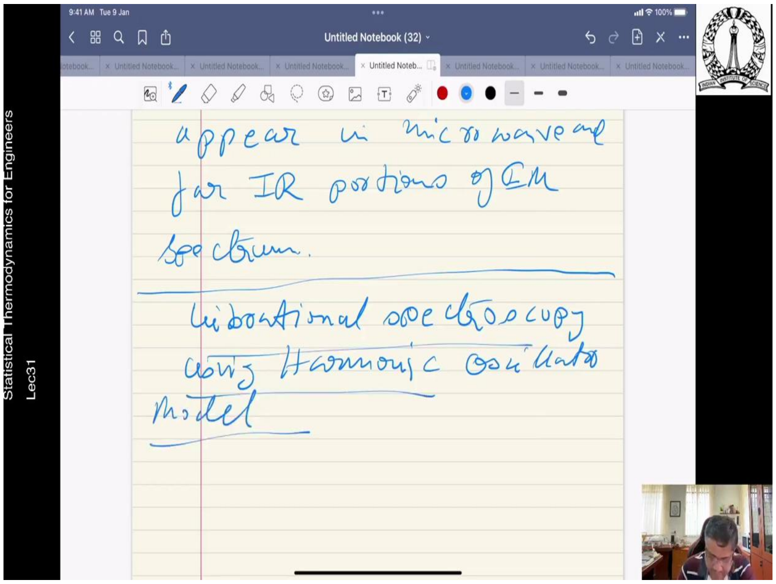


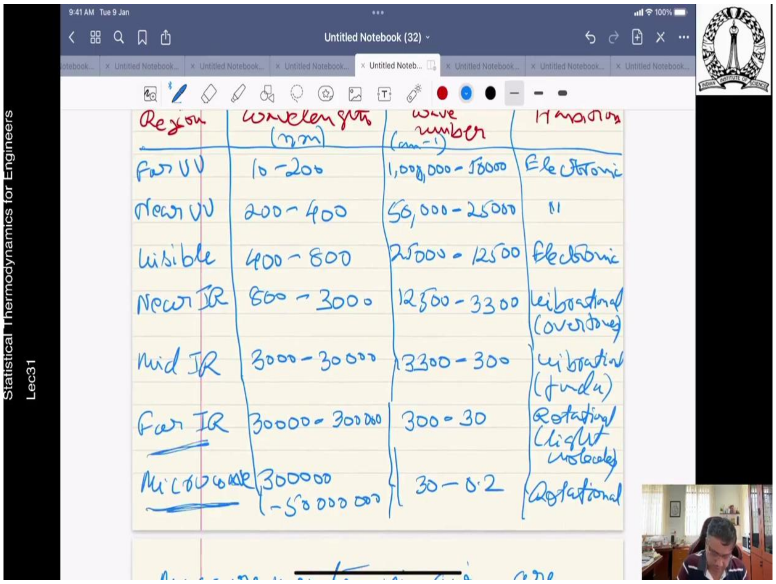
range from 0.1 – 30 cm^{-1}

Rotational transition appear in microwave and far IR portions of EM spectrum



appear in microwave and far IR portions of EM spectrum.

Vibrational spectroscopy using Harmonic Oscillator Model



Region	wavelength (nm)	wave number (cm⁻¹)	transition
Far UV	10 - 200	1,000,000 - 50000	Electronic
Near UV	200 - 400	50,000 - 25000	"
Visible	400 - 800	25000 - 12500	Electronic
Near IR	800 - 3000	12500 - 3300	vibrational (overtones)
Mid IR	3000 - 30000	3300 - 300	vibrational (funda)
Far IR	30000 - 300000	300 - 30	Rotational (light molecules)
Microwave	300000 - 50000000	30 - 0.2	Rotational

So, these rotational transitions, they appear, this rotational transition appear in microwave and in IR portions of EM spectrum. This, see we already saw in the table. So, if you have forgotten just the table, just look at this particular table that we just did. Microwave, IR, nature of the spectrum. So, it is rather good. So, that, so the rotational transitions we now have a very good idea. Now, next comes of course the Vibrational Spectroscopy, vibrational spectroscopy using harmonic oscillator model.

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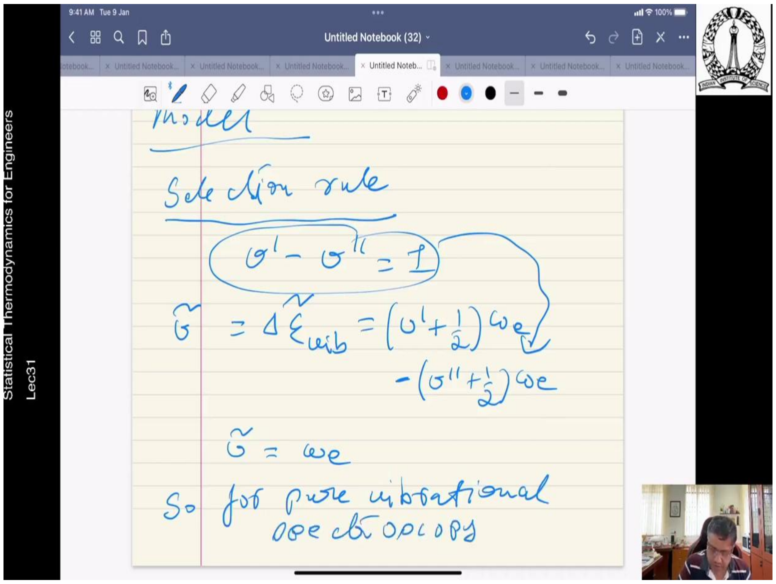


model

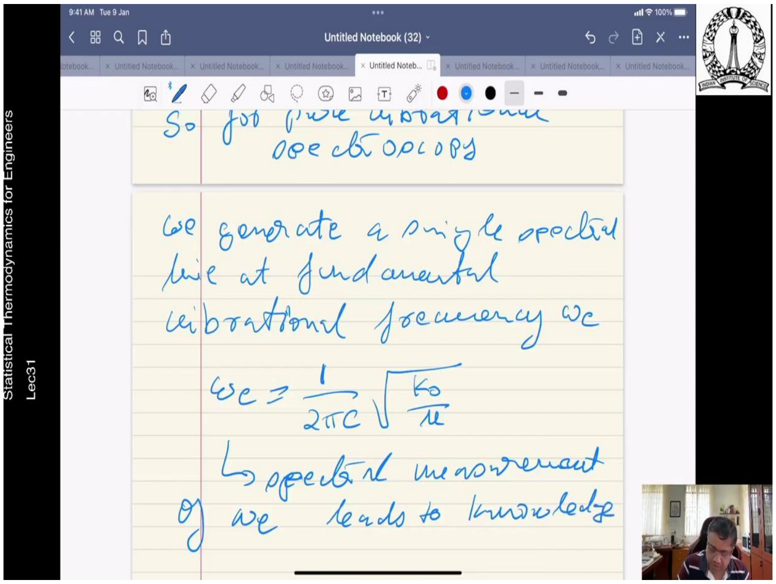
Selection rule

$$\boxed{v' - v'' = 1}$$

$$\tilde{\nu} = \Delta\tilde{\varepsilon}_{vib} = \left(v' + \frac{1}{2}\right)\omega_e - \left(v'' + \frac{1}{2}\right)\omega_e$$

$$\tilde{\nu} = \omega_e$$

So for pure vibrational spectroscopy

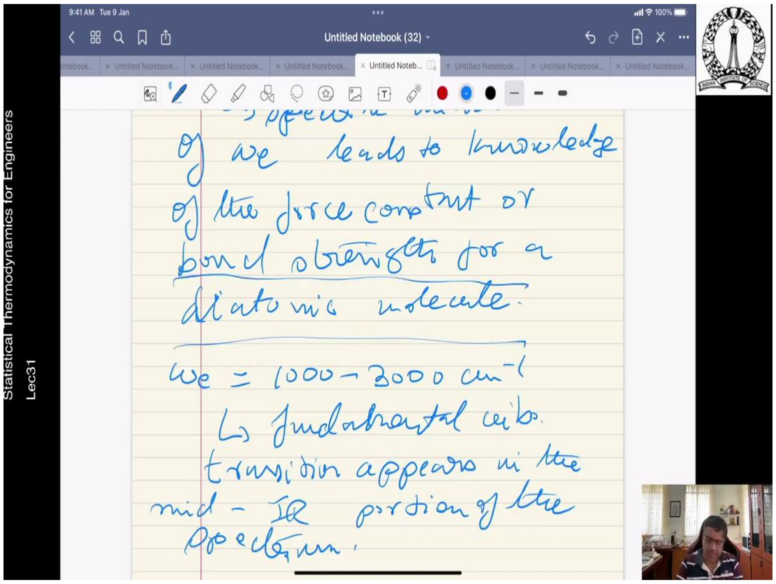


So for pure vibrational spectroscopy

We generate a single spectral line at fundamental vibrational frequency ω_e

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_0}{\mu}}$$

↳ spectral measurement of ω_e leads to knowledge



of ω_e leads to knowledge of the force constant or bond strength for a diatomic molecule.

$\omega_e = 1000-3000\ \text{cm}^{-1}$

↳ fundamental vib. transition appears in the mid-IR portion of the spectrum.

So harmonic oscillator model, the selection rule, selection rule, rule is similar to the rotational, selection rule is v prime minus v double prime is equal to 1. Once again, v prime corresponds to a higher vibrational energy level, v double prime corresponds to a lower vibration energy level. So, therefore, similarly, we write wave number, tilde given as v prime plus half omega e minus e double prime plus half omega e.

So, if you now substitute this into this you get v prime is equal to omega e. So, for pure vibrational spectroscopy, we generate only a single spectral line at the fundamental frequency. So, for pure vibrational spectroscopy, spectroscopy, we generate, generate a single, single spectral line at fundamental, fundamental vibrational frequency omega e.

So, we generate only a single spectral line. And if we recall what was omega e? Omega e was 1 by 2 pi c K naught by mu, K naught by mu. Hence, the spectral measurements of this fundamental vibrational wavelength leads to knowledge of the force constant or the bond strength of a particular diatomic molecule.

So, the spectral measurement, measurement of omega e, omega e of the fundamental vibrational wavelength leads to, leads to knowledge, knowledge of the force constant, force constant or bond strength, or bond strength for a diatomic molecule, molecule, for the diatomic molecule. So, typically, omega e is equal to 1,000 to 3,000 in terms of the wave number.

So, the fundamental vibration or transitions appear in the fundamental vibrational transition, vibrational transition, transition, it appears years in the Mid, in the Mid IR portion, portion of the spectrum. So, we will see a little bit more on this that why vibration also means rotation and stuff like that, but the fundamental vibrational wavelength leads to the knowledge of the force constant or the bond strength of a diatomic molecule. So, in the next class, we will see that how this vibration and rotation, they actually kind of coexist and that will be the subject of the next lecture. Thank you.