Statistical Thermodynamics for Engineers
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Lecture 41
Selection Rules

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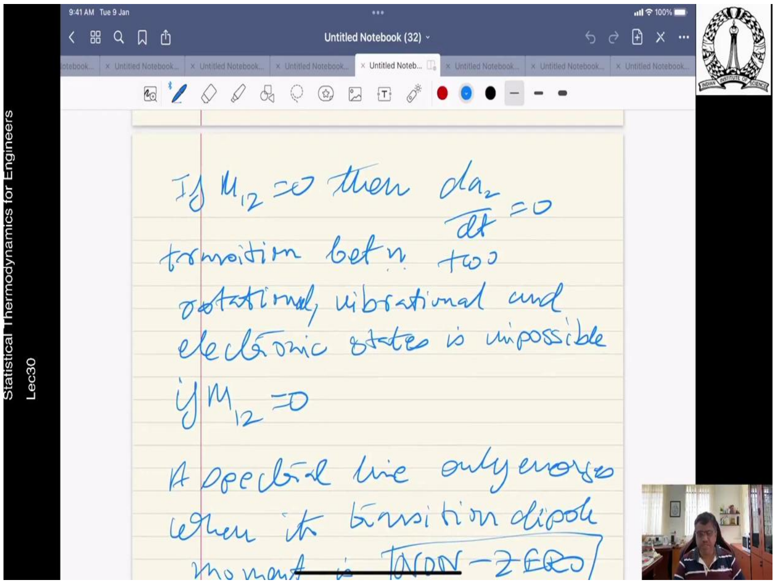
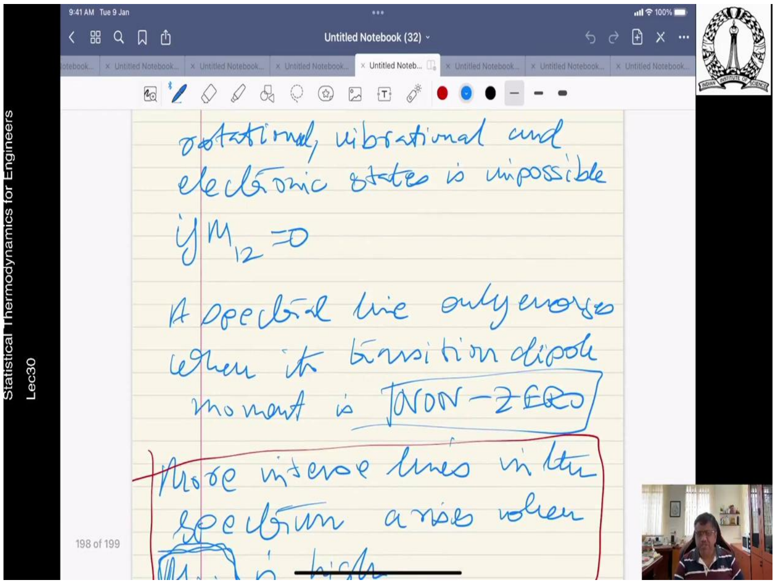


If $M_{12}=0$ then $\frac{da_2}{dt}=0$

transition betn two rotational, vibrational and electronic states is impossible if $M_{12}=0$

A spectral line only emerges when its transition dipole moment is $\boxed{\text{NON-ZERO}}$



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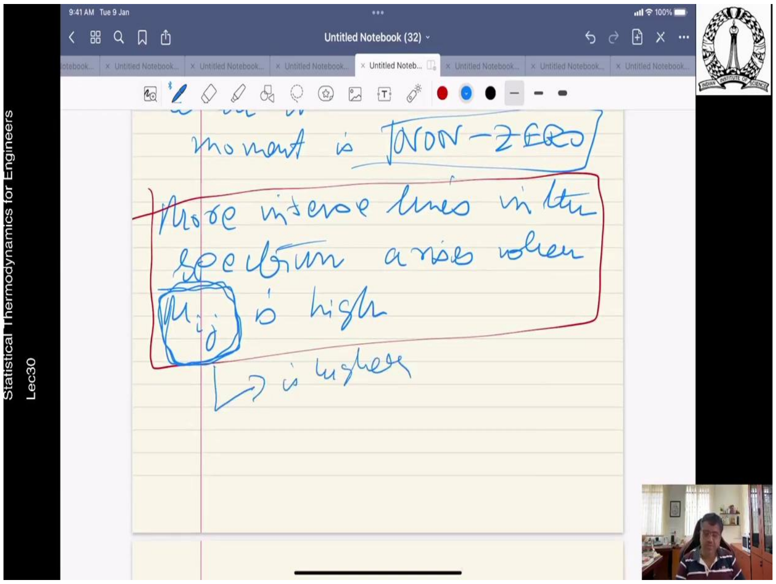
A spectral line only emerges when its transition dipole moment is $\boxed{\text{NON-ZERO}}$

More intense lines in the spectrum arises when M is high



moment is NON-ZERO

More intense lines in the spectrum arises when M_{ij} is high

↳ is higher

Welcome to lecture number 30 in this Statistical Thermodynamics course. So, we have already, in the previous lectures, covered what is called a transition dipole moment and we also saw that if M 1 2, which is a transition dipole moment is 0 the transition between two rotational, vibrational and electronic states is impossible. A spectral line only emerges when it is transition dipole moment is non-zero. And usually the more intense lines in the spectrum arises when M i j, which is the transition dipole moment is higher.

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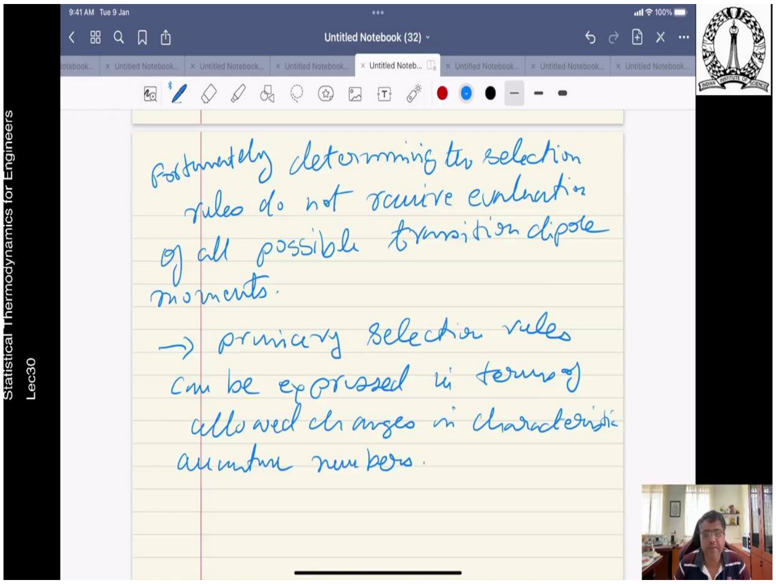
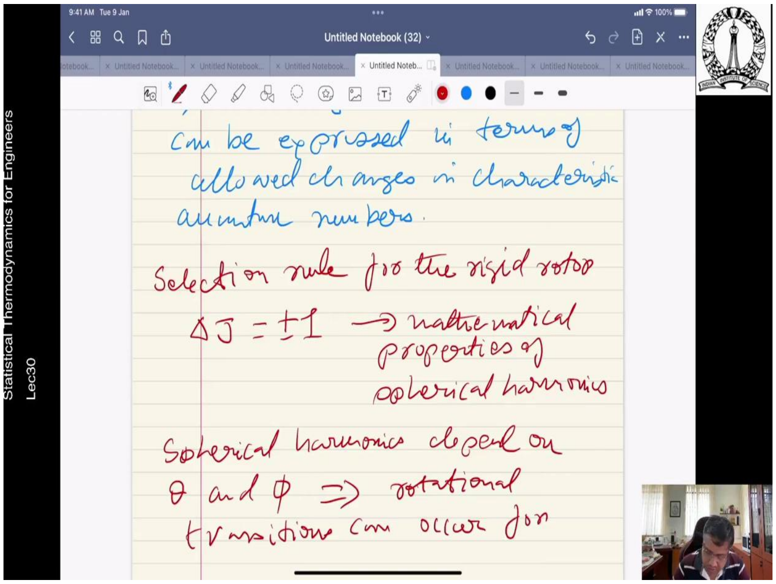


Fortunately determining the selection rules do not require evaluation of all possible transition dipole moments.

→ primary selection rules can be expressed in terms of allowed changes in characteristic quantum numbers.

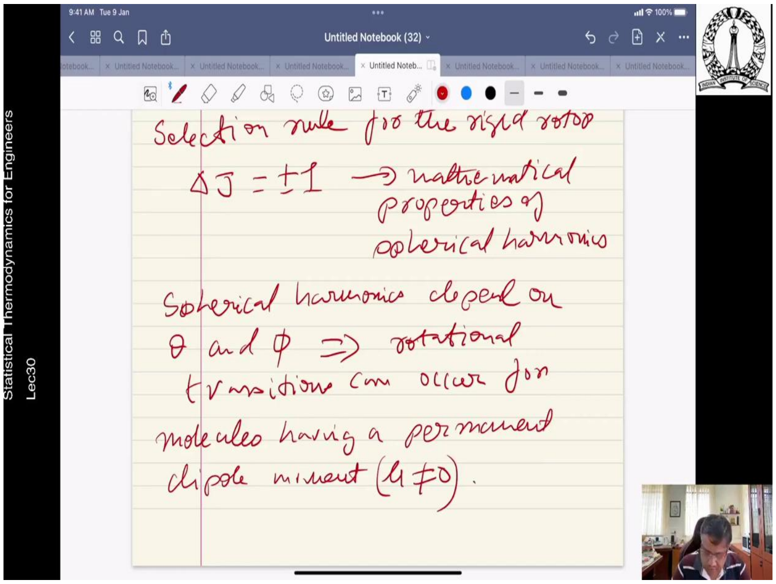


can be expressed in terms of allowed changes in characteristic quantum numbers.

Selection rule for the rigid rotor

$\Delta J = \pm 1 \rightarrow$ mathematical properties of spherical harmonics

Spherical harmonics depend on θ and $\phi \Rightarrow$ rotational transitions can occur for



Selection rule for the rigid rotor

$\Delta J = \pm 1 \rightarrow$ mathematical properties of spherical harmonics

Spherical harmonics depend on θ and $\phi \Rightarrow$ rotational transitions can occur for

molecules having a permanent dipole moment ($\mu \neq 0$).

So, this we already covered in the previous class in the previous lecture. So, this time we are going to look at some of the, when we look at all these things that you can see that it is actually a Runera's task to determine the transition dipole moment but however fortunately, determining the selection rules, determining the selection rules, the selection rules, the selection, basically, rules do not, do not actually require evaluation, evaluation of all possible transition dipole moments, transition dipole moments. So, this is good news, all transition dipole moments.

Indeed, if you look at the mathematical symmetry of a wave function, it is defined through its quantum numbers. So, that you can distinguish between the 0 and the non-zero values. This can be usually be done by each section. So, the primary selection rules can be expressed quite simply in terms of the allowed change in characteristics quantum numbers. So, therefore, the primary selection rules, selection rules can be expressed, can be expressed in terms of, in terms of allowed changes, changes in characteristic quantum numbers, characteristic quantum numbers.

So, we already have seen, for example, in the book Table 6.9 lists all the selection rules that can be derived. So, the selection rule, let us look at the selection rules, the selection rule for the rigid rotor for the rigid rotor delta J is plus minus 1. So, this is, this comes from the mathematical properties, mathematical properties of spherical harmonics.

Since the spherical harmonics depends, we know that the spherical harmonics depend on theta and phi. The rotational this implies that the rotational transitions, transitions, transitions can occur can occur for molecules, for molecules having a permanent dipole moment, permanent dipole moment, which in other words means, meaning is not equal to 0.

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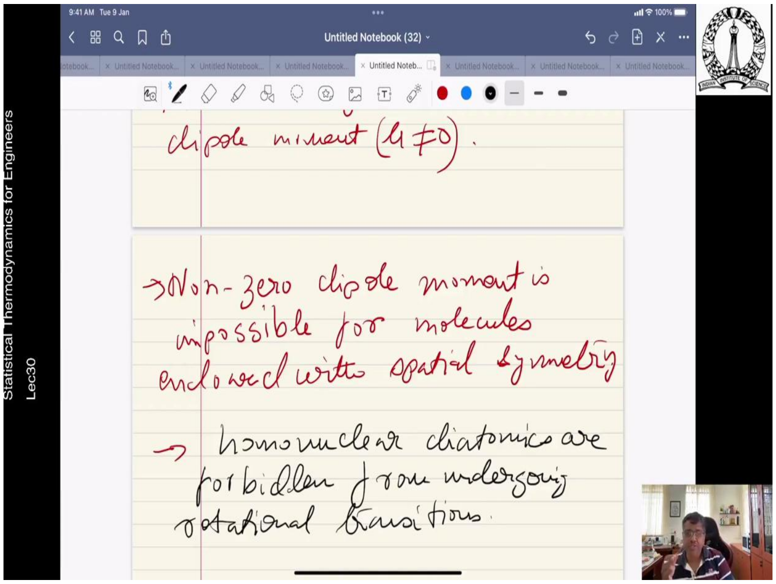
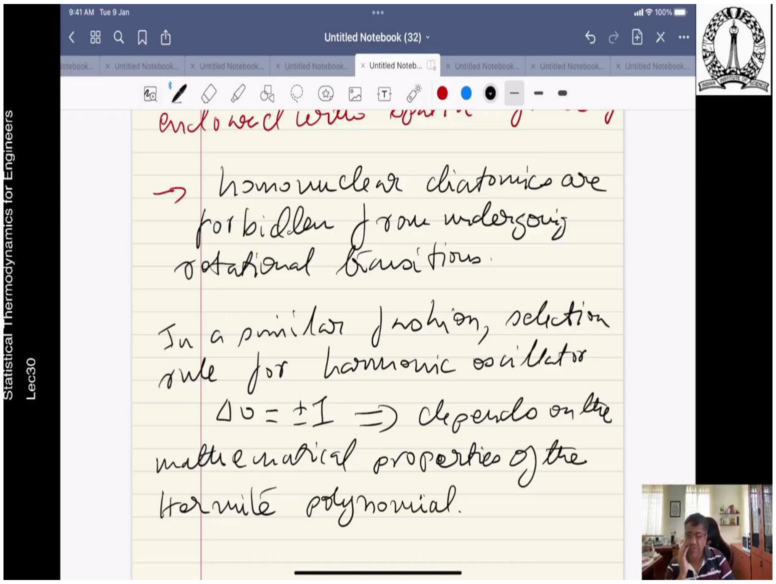


dipole moment ($\mu \neq 0$).

→ Non-zero dipole moment is impossible for molecules endowed with spatial symmetry

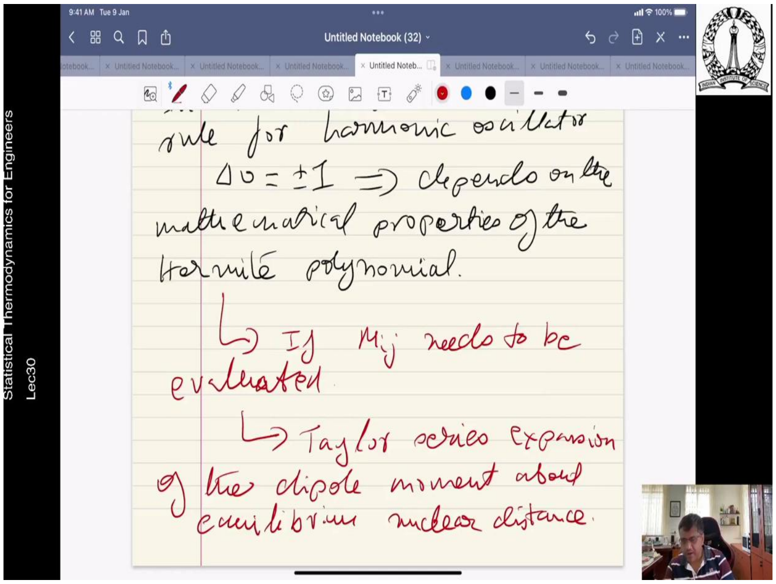
→ homonuclear diatomics are forbidden from undergoing rotational transitions.



endowed with

→ homonuclear diatomics are forbidden from undergoing rotational transitions.

In a similar fashion, selection rule for harmonic oscillator
$\Delta v = \pm 1 \Rightarrow$ depends on the mathematical properties of the Hermite polynomial.



rule for harmonic oscillator
$\Delta v = \pm 1 \Rightarrow$ depends on the mathematical properties of the Hermite polynomial.

↳ If M_{ij} needs to be evaluated

↳ Taylor series expansion of the dipole moment about equilibrium nuclear distance.

So, if you look at this now, the permanent dipole moments or the non-zero dipole moments are impossible for molecules endowed it is very spatial symmetry. So, non-zero dipole moment, because it will cancel out, dipole moment is impossible, impossible for molecules, molecules endowed, endowed with spatial symmetry. So, for this reason, precisely because of this reason, the homonuclear diatomics, homonuclear diatomics are forbidden, forbidden from undergoing rotational transitions, rotational transitions.

So, homonuclear diatomics are actually forbidden from undergoing rotational transitions, non-zero dipole moment is essential for rotational transitions but because of the spatial symmetry, the homonuclear diatomics do not, cannot undergo this kind of transitions. So, now in a similar fashion, in a similar fashion, fashion, selection rules for harmonic oscillator, for harmonic oscillator gives us plus minus 1. This depends on, depends on the mathematical properties, mathematical properties, properties of the Hermite polynomial. Interesting.

So, this depends on the mathematical properties of the Hermite polynomials. For such polynomials, if you want to evaluate M i j, it requires, so if you want to, for these kind of polynomials, if M i j needs to be evaluated, needs to be evaluated, then what you do, is basically you expand a Taylor series. A Taylor series expansion of the dipole moment, Taylor series expansion of the dipole moment about the equilibrium nuclear separation.

So, this requires a Taylor series, Taylor series expansion, expansion, a Taylor series expansion of the dipole moment, of the dipole moment about equilibrium, equilibrium nuclear distance. Because remember, the harmonic oscillator was only true for very small magnitude of oscillations. It is very near, it is the most potential actually. The harmonic oscillator was only valid for a very small distance, inter-nuclear distance.

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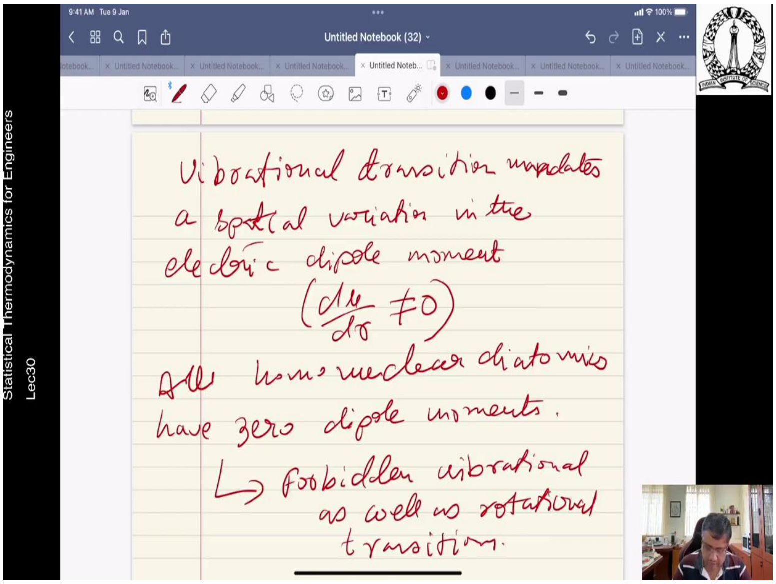
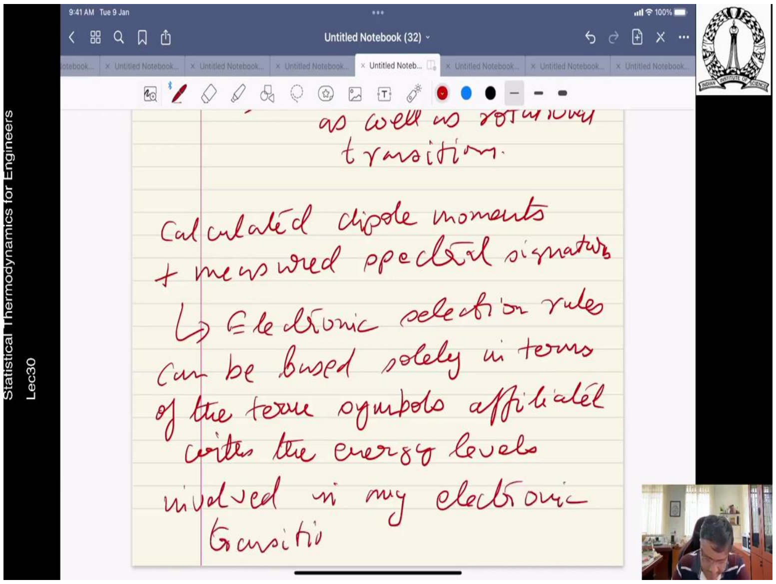


Vibrational transition mandates a spatial variation in the electric dipole moment

$$\left(\frac{d\mu}{dr} \neq 0\right)$$

All homonuclear diatomics have zero dipole moments.

↳ Forbidden vibrational as well as rotational transition.



as well as rotational
transition.

Calculated dipole moments
+ measured spectral signatures
↳ Electronic selection rules
can be based solely in terms
of the term symbols affiliated
with the energy levels
involved in any electronic
transitio

So, if you follow this procedure, we find, so vibrational transition, mandates a spatial variation, in the electric dipole moment, electric dipole moment, moment, which means d mu by d r cannot be equal to 0. So, this is what is required because all homonuclear diatomics have 0 dipole moments, so all homonuclear, nuclear diatomics, diatomics have 0 dipole moments, dipole moments, this translates to orbital, orbital, vibrational, vibrational as well as rotational transitions.

So, implying this calculated dipole moments and measures spectrum signatures, so what do spectroscopic, spectroscopies do is that they calculate it, calculate the dipole moments, moments plus the measured spectral signatures, signatures. We found the electronic selection rules, electronic selection rules, selection rules can be based solely, can be based solely in terms on the term symbols, in terms of the term symbol, symbols related with the energy levels, related with the energy levels, energy levels associated with the energy levels involved in any electronic transition.

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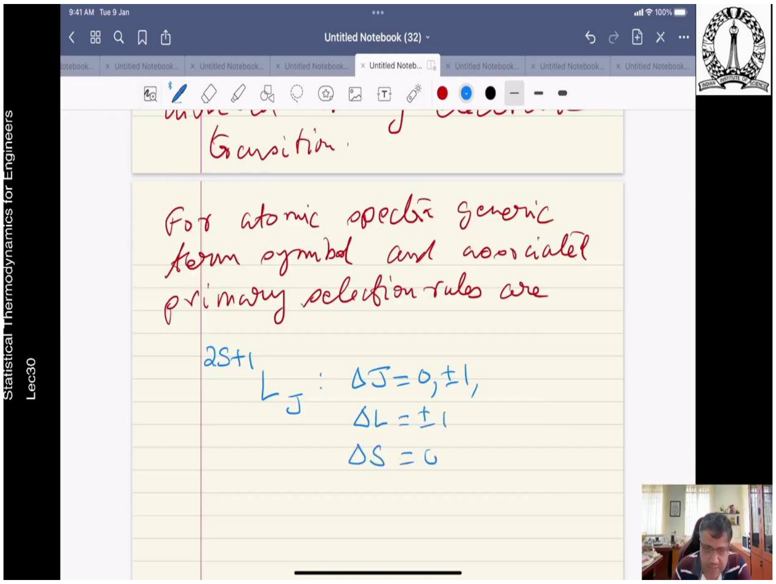
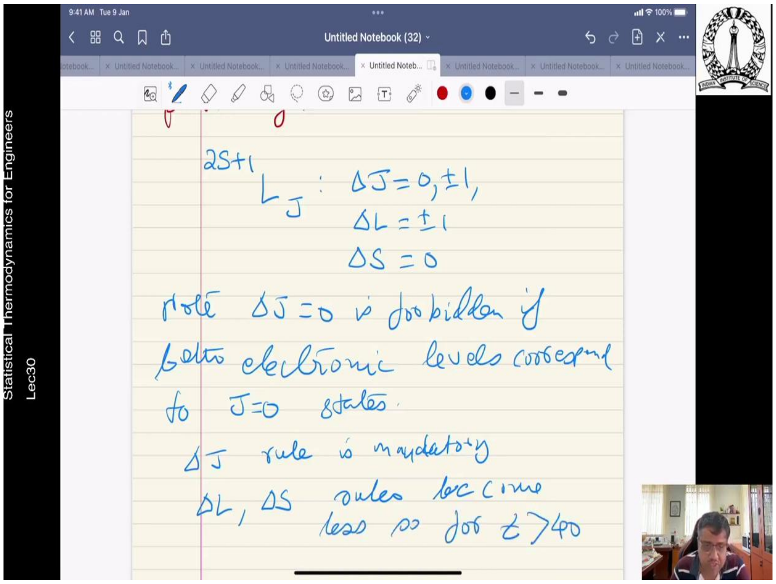


transition.

For atomic spectra generic term symbol and associated primary selection rules are

$^{2S+1}L_J$: $\Delta J = 0, \pm 1,$
$\Delta L = \pm 1$
$\Delta S = 0$

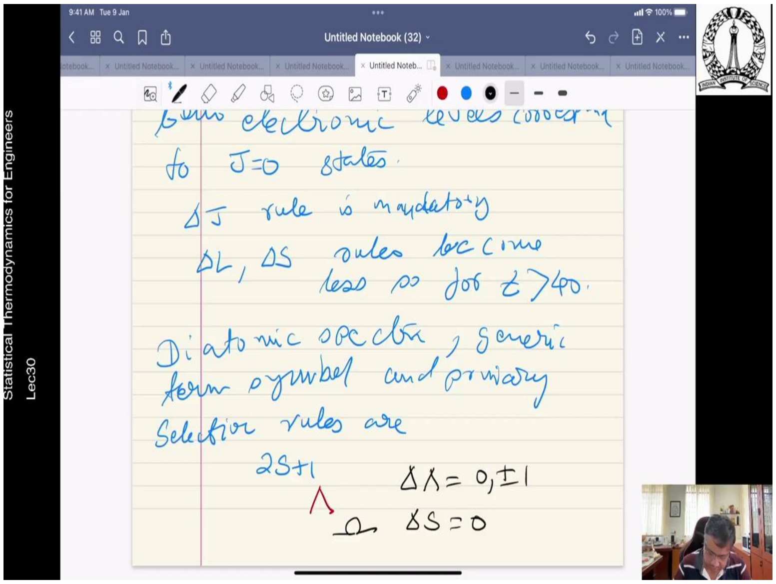


$^{2S+1}L_J$: $\Delta J = 0, \pm 1,$
$\Delta L = \pm 1$
$\Delta S = 0$

note $\Delta J = 0$ is forbidden if both electronic levels correspond to $J=0$ states.

ΔJ rule is mandatory

ΔL, ΔS rules become less so for $Z > 40$



both electronic levels correspond to $J=0$ states.

ΔJ rule is mandatory

ΔL, ΔS rules become less so for $Z > 40$.

Diatomic spectra, generic term symbol and primary selection rules are

$${}^{2S+1}\Lambda_{\Omega} \qquad \Delta\Lambda = 0, \pm 1 \qquad \Delta S = 0$$

So, for the, so let us look at it. For atomic spectra, for atomic spectra, the generic term symbol, term symbol and associated primary selection rules, selection rules are 2S plus 1 L J delta J 0 plus minus 1 delta L plus minus 1 delta S is equal to 0. But note delta J equal to 0 is forbidden if both electronic levels, electronic levels correspond to J equal to 0 states.

Moreover, delta J rule is mandatory, is mandatory. Delta L and delta S rules, rules become less, less so for z greater than 40. Now, let us look at the diatomic spectra, diatomic spectrum. So, here the generic term symbol term symbol and primary selection rules are, primary selections are 2S plus 1 0 plus minus 1, delta S is equal to 0.

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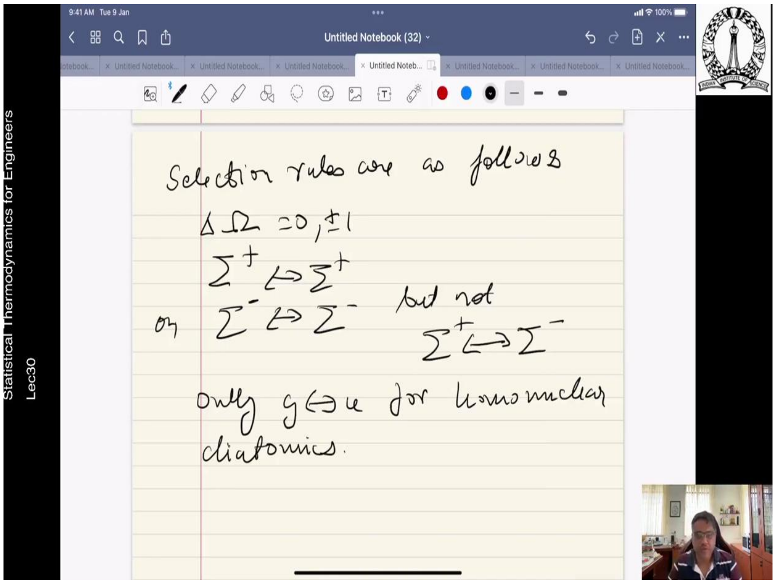


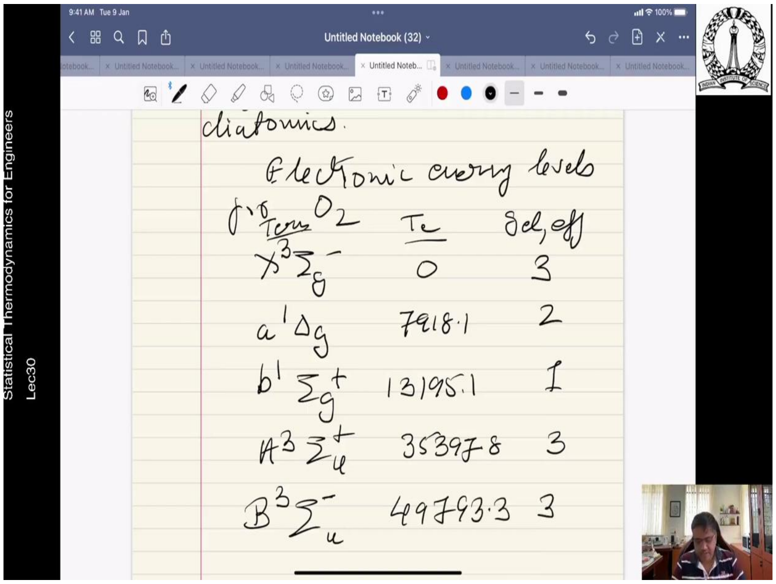
Selection rules are as follows

$\Delta\Omega = 0, \pm 1$

$\Sigma^+ \leftrightarrow \Sigma^+$

or $\Sigma^- \leftrightarrow \Sigma^-$ but not $\Sigma^+ \leftrightarrow \Sigma^-$

Only $g \leftrightarrow u$ for homonuclear diatomics.

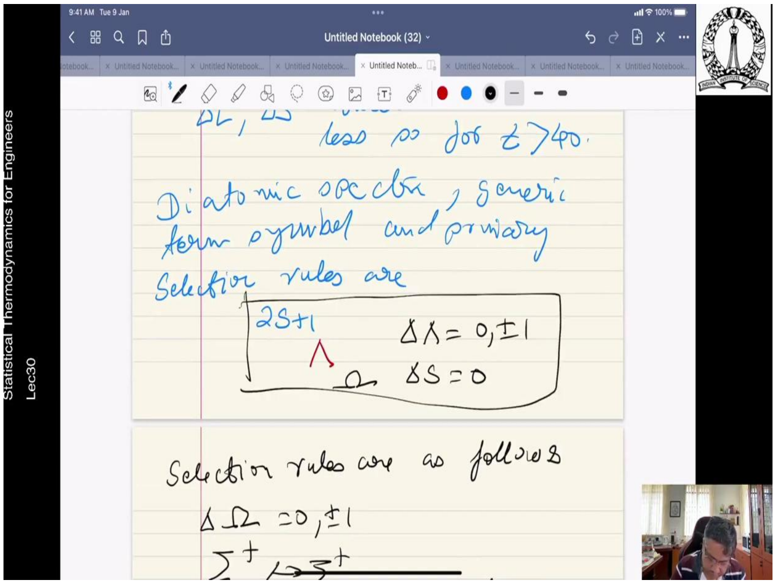


diatomics.

Electronic energy levels

for O_2

Term	T_e	$g_{el,eff}$
$X^3\Sigma_g^-$	0	3
$a^1\Delta_g$	7918.1	2
$b^1\Sigma_g^+$	13195.1	1
$A^3\Sigma_u^+$	35397.8	3
$B^3\Sigma_u^-$	49793.3	3



ΔL, ΔS

less so for $Z > 40$.

Diatomic spectra, generic term symbol and primary Selection rules are

$$\boxed{{}^{2S+1}\Lambda_{\Omega} \qquad \Delta\Lambda = 0, \pm 1 \qquad \Delta S = 0}$$

Selection rules are as follows

$\Delta\Omega = 0, \pm 1$

$\Sigma^+ \leftrightarrow \Sigma^+$

Selection rules when needed are as follows, selection rules are as follows. 0 plus or but not, homonuclear diatomics. So, if you look at this particular equation now, so let us call this 1. And we note that now let us perhaps do table 6, if you look at table 6.8 very quickly, let us go to table 6.8, 6.7, this is, let us go to table 6.8.

So, if you recall that electronic energy levels, levels are O2, say for example, where the term symbol was X3 g minus T e, this is T e, this is the term, is 0 and then you have g electronic, this is the degeneracy, effective degeneracy was 3. Then you had a1, g so 7918 or so, 2. So, I am going to write b1, this is just a recap so that will give you an idea, 13195.1. And then there is A3 mu plus 35397.8, 3. Then there is B3 minus mu, which is 49793.3. And this is 3.

So, this was the oxygen, the oxygen, electronic energy levels of oxygen which we already know. Now, this was already done. And then if you look at the figure which is for oxygen, if you recall this figure once again, it is basically Figure 6.10 from the text where basically the same energy levels are represented in a pictorial fashion, if you recall. So, if you take both of those two things into consideration, this table and the corresponding figure which is drawn in the form of a potential well, you will find that most transitions from the ground to the upper electronic states of oxygen are forbidden.

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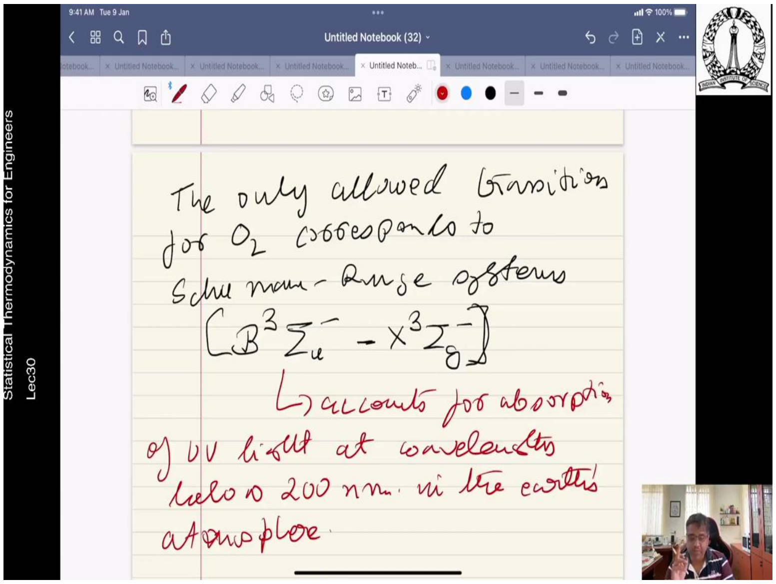
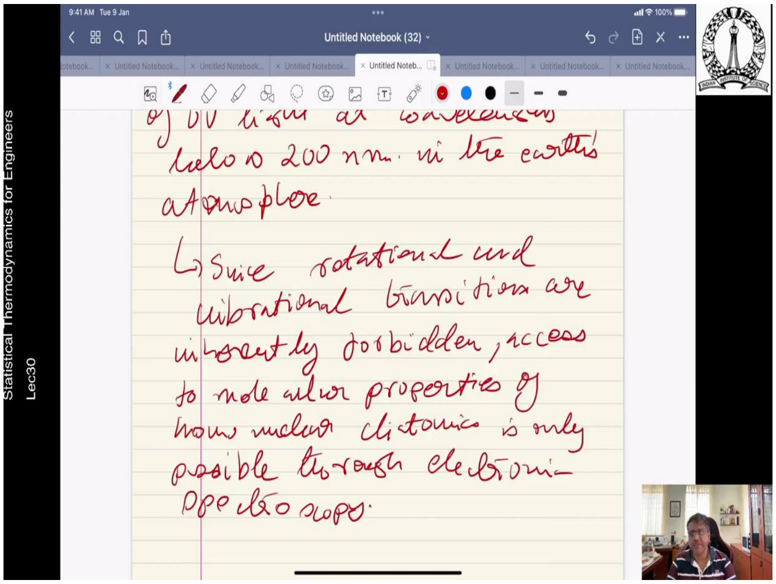


The only allowed transitions for O_2 corresponds to Schumann-Runge systems

$$[B^3\Sigma_u^- - X^3\Sigma_g^-]$$

↳ accounts for absorption of UV light at wavelengths below 200 nm. in the earth's atmosphere.



below 200 nm. in the earth's atmosphere.

↳ Since rotational and vibrational transitions are inherently forbidden, access to molecular properties of homonuclear diatomics is only possible through electronic spectroscopy.

The only about transitions, the only allowed transitions, transitions for oxygen, for oxygen corresponds to a Schumann-Runge systems, which would mean B3 minus mu to X3 minus, which accounts for, this basically, what does it do? It accounts for, accounts for absorption of UV light at wavelengths, at wavelengths below 200 nanometer in the earth's atmosphere. So, given this electronic transition for oxygen, we realize that the permanent dipole moment is unnecessary for homonuclear diatomics.

The general conclusion is significant. First, as it may be expected that the shifts between electronic orbitals, the transition dipole moment depends preferentially on the portion of the dipole moment established by the electrons and not so by the two nuclei. Second, because the rotational and vibrational transitions are inherently forbidden, access to molecular properties is only possible through electronic spectroscopy.

So, since a homonuclear, since rotational, rotational and vibrational transitions, vibrational transitions are inherently forbidden access to molecular properties of homonuclear diatomic is only possible through electronics spectroscopy. So, through the electronic spectroscopy is the only way in which you can access those levels.

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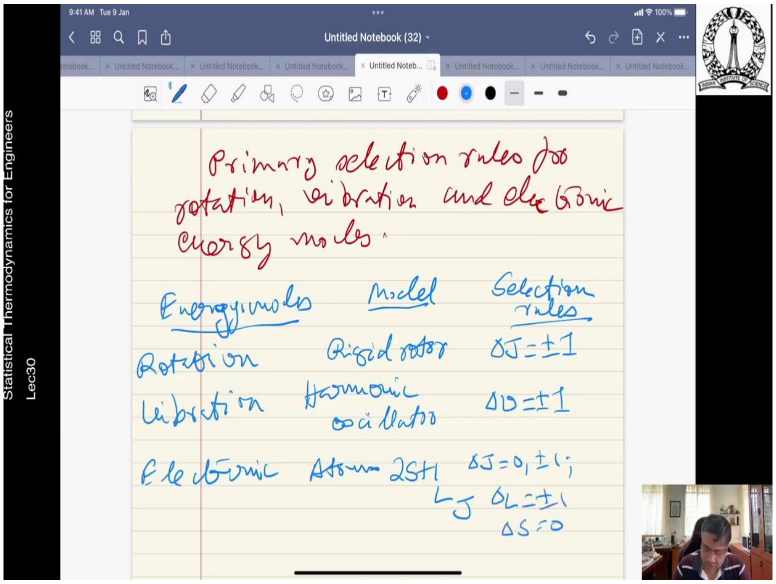
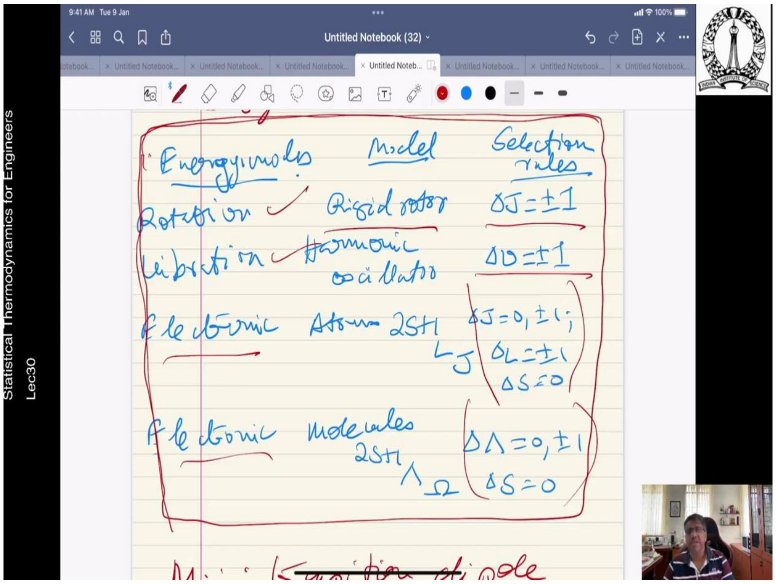
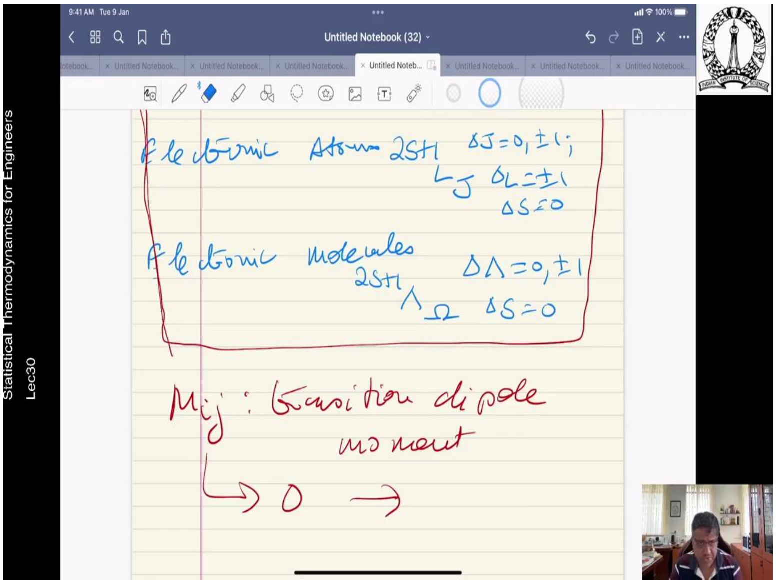


Primary selection rules for rotation, vibration and electronic energy modes.

Energy modes	Model	Selection rules
Rotation	Rigid rotor	$\Delta J = \pm 1$
Vibration	Harmonic oscillator	$\Delta v = \pm 1$
Electronic	Atoms $^{2S+1}L_J$	$\Delta J = 0, \pm 1$; $\Delta L = \pm 1$ $\Delta S = 0$



Energy modes	Model	Selection rules
Rotation	Rigid rotor	$\Delta J = \pm 1$
Vibration	Harmonic oscillator	$\Delta v = \pm 1$
Electronic	Atoms $^{2S+1}L_J$	$\Delta J = 0, \pm 1$; $\Delta L = \pm 1$ $\Delta S = 0$
Electronic	Molecules $^{2S+1}\Lambda_\Omega$	$\Delta \Lambda = 0, \pm 1$ $\Delta S = 0$



Electronic Atom $^{2S+1}L_J$ $\Delta J = 0, \pm 1$; $\Delta L = \pm 1$ $\Delta S = 0$

Electronic molecules $^{2S+1}\Lambda_\Omega$ $\Delta\Lambda = 0, \pm 1$ $\Delta S = 0$

M_{ij} : transition dipole moment

$\hookrightarrow 0 \rightarrow$

So, let us now let us also write the selection rules in a more compact form so that you have an idea, so a way to look up. So, this is primary, primary selection rules for rotational, vibrational and electronic energy molecules. So, if we look at the table now, this is the energy nodes, this is the model that corresponding leads the selection rules. So, there is first is rotation. So, the model is a rigid rotor, and the selection rule is delta J is equal to plus minus 1.

Then of course, the second is vibration, this is for the harmonic oscillator. So, the most potential is the more apt description but it is valid for low amplitude oscillation. So, this is plus minus 1. Then of course electronic atoms is 2S, for atoms, it is 2S plus 1 J. So, here, the selection rule is delta J equal to 0 plus minus 1. Out of that, we know what is forbidden. And delta L is equal to plus minus 1, delta S is equal to 0.

Then of course, electronic, and this is the last one, this is for molecules. 2S plus 1, this equal plus minus 1, delta S is equal to 0. So, these are the different modes, and evaluation and we remember that M i j for the transition dipole moment. If this is equal to 0, then you see those transitions are not possible in the first place.

So, now we have got a very good idea about what are the different energy levels, what is a transition type of moment, how the transition dipole moment can be evaluated from a perturbed portion of the time dependent Schrodinger's wave equation and what are the corresponding rotational and electronic transitions that are possible for homonuclear diatomics, which is only electronic spectroscopy or electronic transitions that you can access, not any other transitions.

And the selection rules are given in this particular table that I just did. For rotation. It is rigid rotor you have this vibration harmonic oscillator, and for the electronic, you have this, depending on whether it is an atom or atomic molecule. These are the kind of rules that we prescribe. So, in the next class what we are going to do, we are going to go into the spectroscopy of diatomic molecules and we are going to present a quantum mechanical analysis of the internal energy modes and see that how these energy modes can be used to find out what are the different spectroscopic possibilities. So, till then, we go for the next lecture, this lecture is concluded herewith.