Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 47
Working with Spectroscopic Schemes, Notations and Term Symbols

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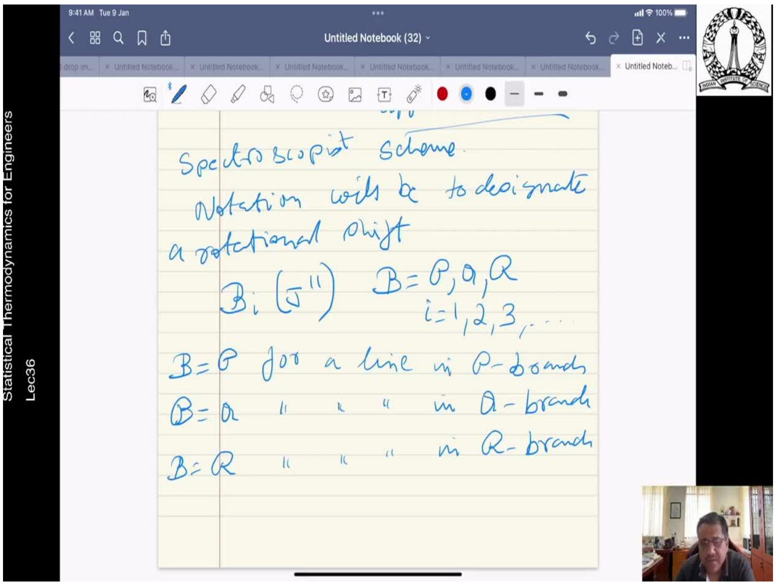

Spectroscopic scheme.

Notation will be to designate a rotational shift

$B_i (J'')$ $B = P, Q, R$

$i = 1, 2, 3, \ldots$

$B = P$ for a line in P-branch

$B = Q$ " " " in Q-branch

$B = R$ " " " in R-branch

Welcome to lecture number 36. So, the statistical thermodynamics course. So, as you can see that we have now done quite a bit of work now, like for the Ro-vibrational case, to identify individual ro-vibronic transitions occurring within a visible of the UV spectrum, the spectroscopy still developed a scheme similar to the ro-vibration of spectroscopy scheme or the ro-vibrational part of the spectrum ro-vibronic part of the spectrum.

So, the notation going to be the notation invoked patient will be something like this be to designate rotational shift is the time G W prime is equal to P Q R equal to 1 2 3 so on and so forth. So, B is equal to p for a line in p branch. B equal to Q for a line in the Q branch which we already saw and B is equal to R for a line in R branch.

The numerical subscript is less significant it is sometimes used to identify closely spaced transitions. Various spin split levels will be multiplate.

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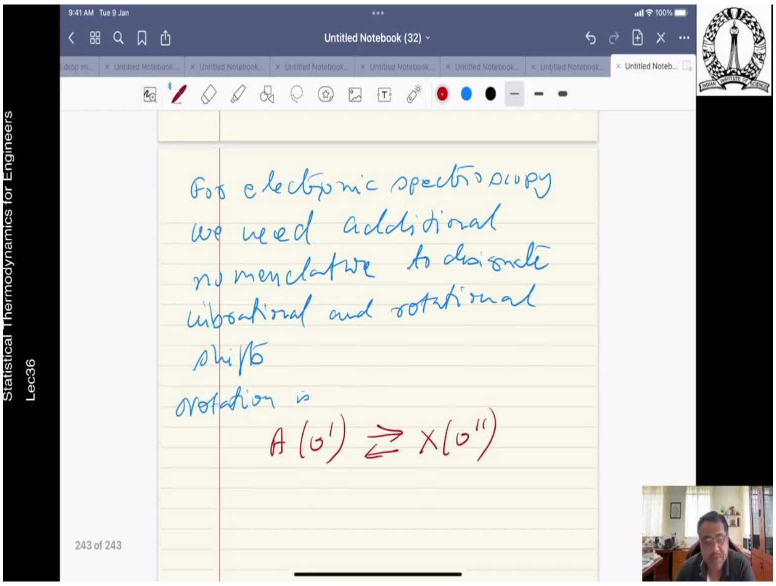
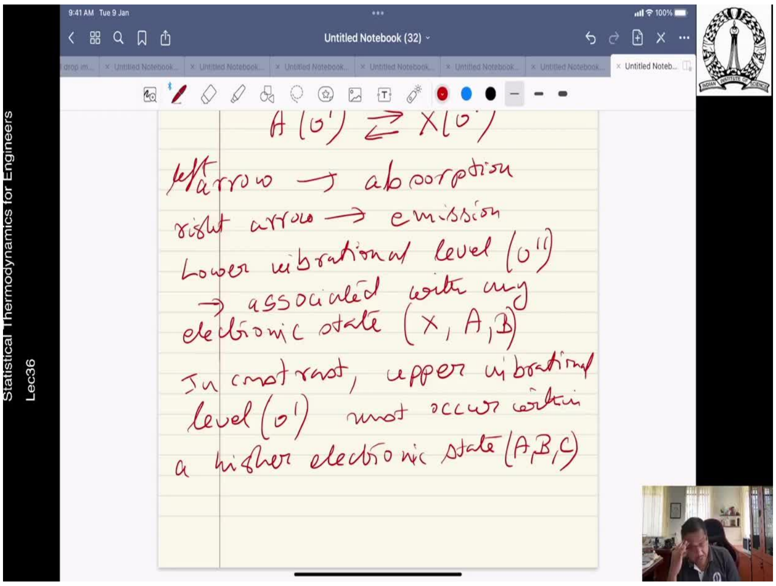


For electronic spectroscopy we need additional nomenclature to designate vibrational and rotational shifts

notation is

$$A(\upsilon') \rightleftarrows X(\upsilon'')$$



$$A(\upsilon') \rightleftarrows X(\upsilon'')$$

left arrow → absorption

right arrow → emission

Lower vibrational level (υ'')

→ associated with any electronic state (X, A, B)

In contrast, upper vibrational level (υ') must occur within a higher electronic state (A, B, C)

For the electronic spectroscopy however, we need additional electronics spectroscopy we need additional nomenclature to designate the vibrational and the electronic… this is only for the rotational part that we just did right now, vibrational and rotational shifts. So, the usual notation would be rotation is to do the notation part it is A X double v double prime (())(3:07) something like that.

So, where only one arrow can be used to the left for absorption or to the right for (())(3:16) left arrow designates absorption right arrow designates emission. So, the lower vibrational level can be associated, so the lower vibrational level which is the double prime it is associated and see if it okay with any electronic levels, with any electronic state which is given as X A B.

In contrast, if the upper vibrational level, this was for the lower, upper vibrational level is v prime (())(4:32) should have occurred must occur being higher electronic state A B C. So, as an example, a specific transition in the ultraviolet sector of hydroxyl radical for example, which is very important in the case combustion research would be identified like this.

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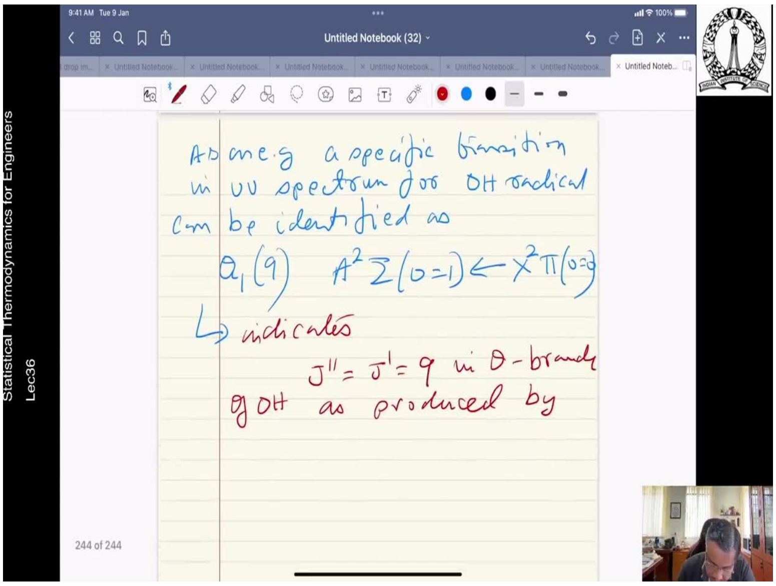
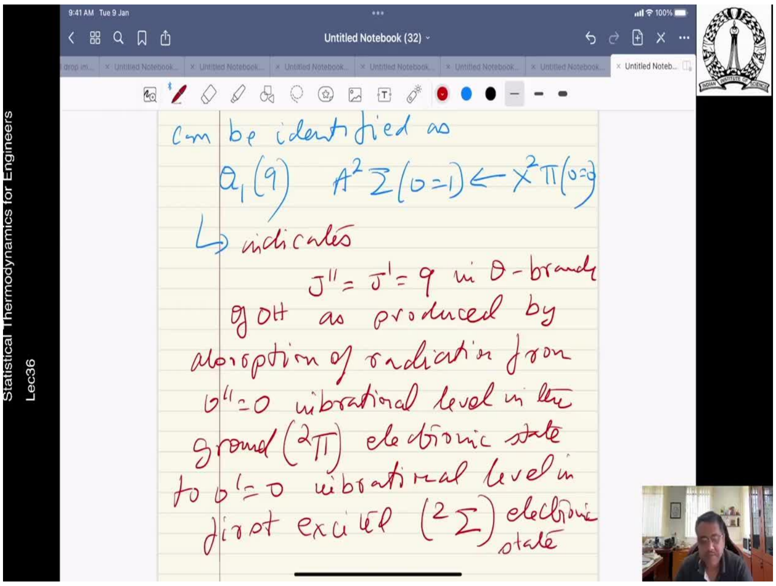


As one e.g a specific transition in UV spectrum for OH radical can be identified as

$Q_1(9)$ $A^2\Sigma(v=1) \leftarrow X^2\Pi(v=0)$

↳ indicates

$J'' = J' = 9$ in Q-branch of OH as produced by



can be identified as

$Q_1(9)$ $A^2\Sigma(v=1) \leftarrow X^2\Pi(v=0)$

↳ indicates

$J'' = J' = 9$ in Q-branch of OH as produced by absorption of radiation from $v''=0$ vibrational level in the ground $(^2\Pi)$ electronic state to $v'=0$ vibrational level in first excited $(^2\Sigma)$ electronic state

So let us go to the next page for hydroxyl radical what will happen. So, as an example specific transition in UV spectrum for OH radical can be identified as Q1 9 A2 equal to 1 X2 indicating, this indicates J double prime to J prime equal to 9 in 2 branch of OH as produced by the absorption of radiation.

So, it is the Q branch OH T double prime equals the J prime as produced by absorption of radiation from double prime equal to 0 vibrational level in the ground is electronic state in either prime equal to 0 vibrational level in first excited which is 2 sigma electronics.

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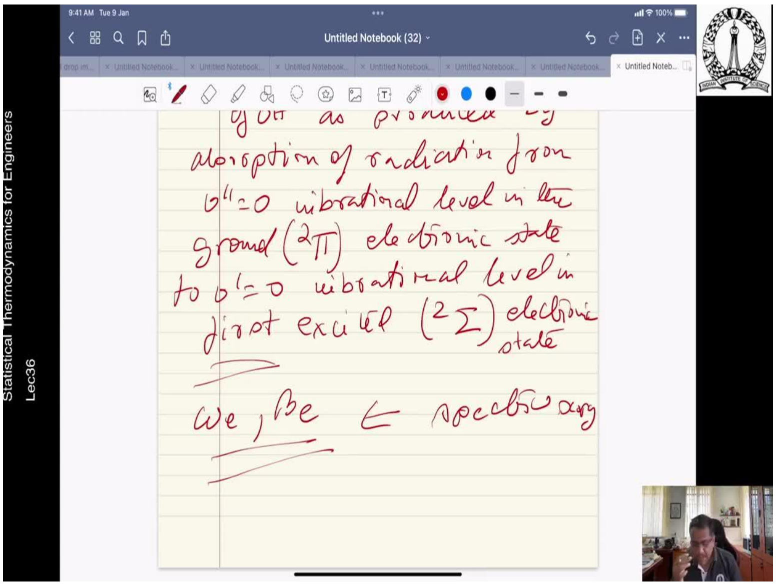
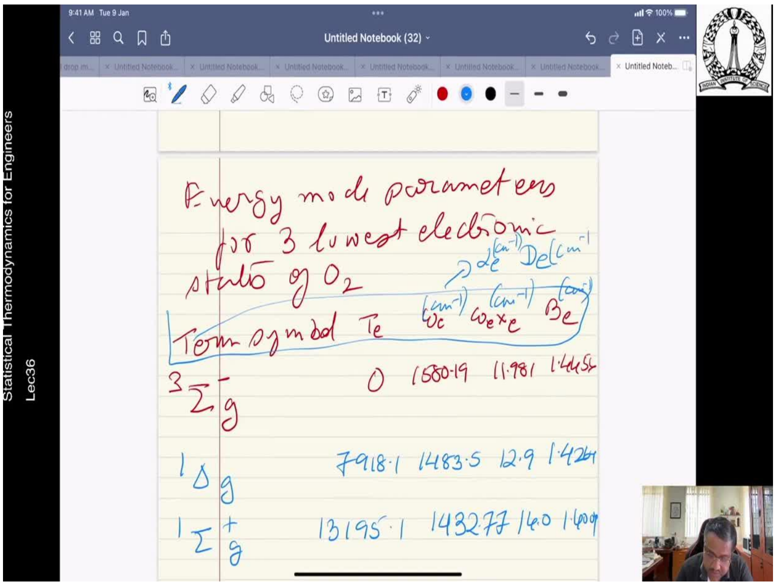


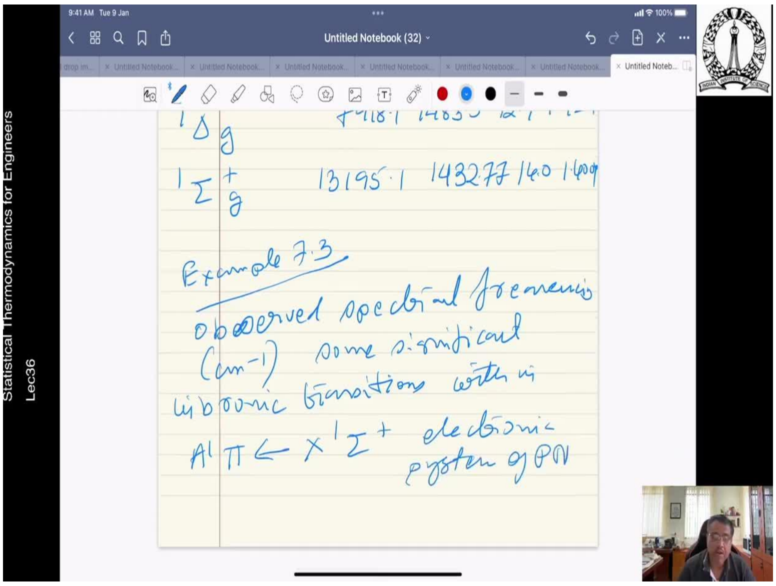
of OH as produced by absorption of radiation from $v''=0$ vibrational level in the ground ($^2\Pi$) electronic state to $v'=0$ vibrational level in first excited ($^2\Sigma$) electronic state

ω_e, B_e ← spectroscopy



Energy mode parameters for 3 lowest electronic states of O_2

Term symbol	T_e	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	D_e (cm^{-1})
$^3\Sigma_g^-$	0	1580.19	11.981	1.4456		
$^1\Delta_g$	7918.1	1483.5	12.9	1.4264		
$^1\Sigma_g^+$	13195.1	1432.77	14.0	1.400		

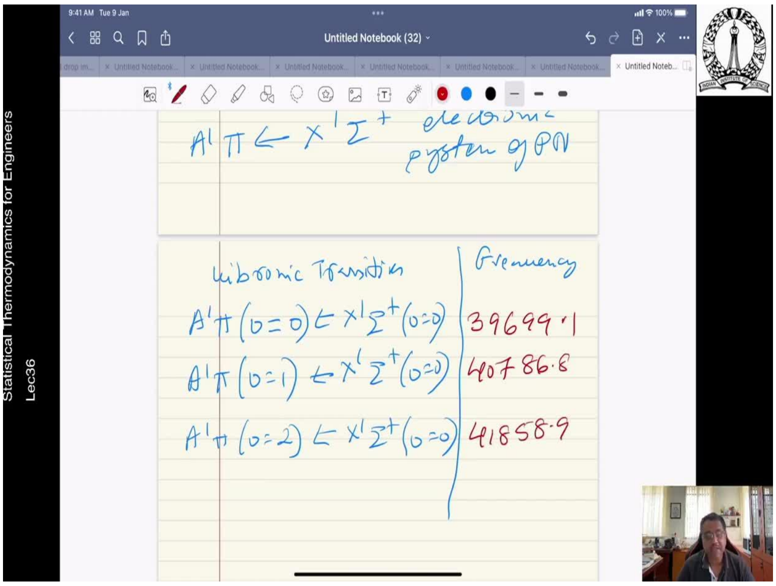


$^1\Delta_g$

$^1\Sigma_g^+$ 13195.1 1432.77 14.0 1.4009

Example 7.3

observed spectral frequencies (cm-1) some significant vibronic transitions with in $A^1\Pi \leftarrow X^1\Sigma^+$ electronic system of PN



$A^1\Pi \leftarrow X^1\Sigma^+$ electronic system of PN

Vibronic Transition	Frequency
$A^1\Pi(\upsilon=0) \leftarrow X^1\Sigma^+(\upsilon=0)$	39699.1
$A^1\Pi(\upsilon=1) \leftarrow X^1\Sigma^+(\upsilon=0)$	40786.8
$A^1\Pi(\upsilon=2) \leftarrow X^1\Sigma^+(\upsilon=0)$	41858.9

So, we have established in this particular chapter, practical link between quantum mechanics and statistical thermodynamics in spectroscopy. So, basically as you if you recall that thermodynamics properties of atoms and molecules to be evaluated for their given energy levels and degeneracies(())(8:00) that is why we needed the quantum mechanics.

These microscopic parameters can be predicted and understood definitely using quantum mechanics. So, but however, quantum mechanics models are pretty complicated and so, we need to resort to spectroscopic measurements for determination of various energy what parameters such as omega e for example, rotational concept B and all these things.

So, in order to determine all these things, we needed spectroscopy. To fill in that in those gaps. So, through spectroscopy, we can determine the energies and the degeneracies of electronic states. And this allows us to now use these parameters in the statistical thermodynamics renown and to calculate the various thermodynamic properties for example.

So, before we go further, let us take one example of molecular oxygen, this we call the energy mode parameters for 3 lowest electronic states. States of oxygen O2 so, this is essential because this is how these things are tabulated. So, just to show at how things are tabulated, so, that we can find out all these degeneracies other things so, that there is Te then there is omega E under this omega Xe.

Remember this comes from a complex model that Be and the you can find alpha e, I will not write all the terms but I mean definitely you can write both. For example, 0 this is 1580.19 in this 11.981 then B is equal to 1.446 then of course, you have 1 delta g which is 7918.1 1483.5 is 12.9 is 1.4264. So, similarly, you could write it for alpha e and g also and 1 sigma g 13195.1 1432.77 is 14.0 this is 1.4004 and so on and so forth.

So, these are the different term symbols you can write it also for alpha e and you can also write it for De. These are all in centimeter inverse. They are all in centimeter inverse. It is in the wave number space equal to(())(11:14) centimeter inverse. So, you can write it like that. So, this is how you actually calculate the different things.

So, if we can give you an example say for example, we observed so, this is also example, the book may 7.3 book see the observed frequency and you will have tutorials on this because frequencies are said to be centimeter inverse(())(11:57) are corresponding to (())(12:02) to some significant vibronic with in A 1 pi X 1(())(12:21) electronic system of here. So, let us look at disabled so, the vibronic it is given like this vibronic transition so A1 pi x1 sigma plus 0 equal to 0 then of course A1 pi equal to 2 X1 sigma plus 0 equal 0. This is 39699.1 40786.8 41858.9.

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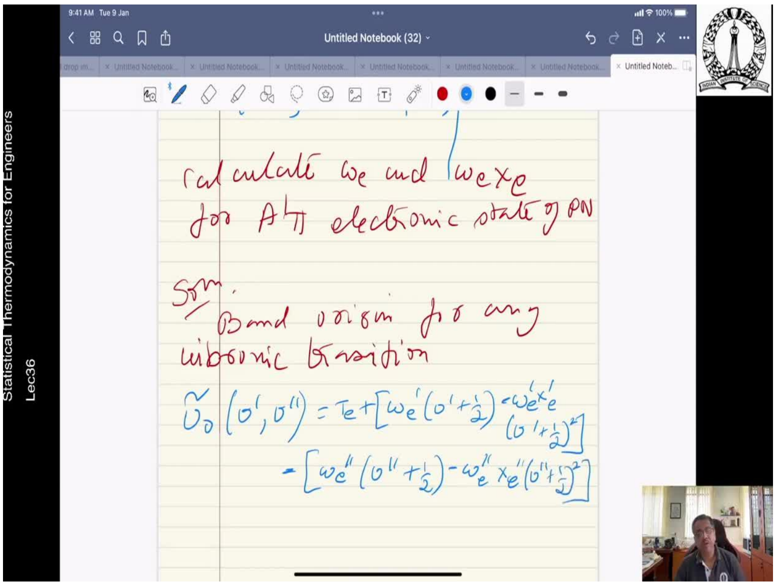

calculate ω_e and $\omega_e x_e$ for $A^1\Pi$ electronic state of PN

Soln.

Band origin for any vibronic transition

$$\tilde{\upsilon}_0(\upsilon', \upsilon'') = T_e + \left[\omega_e'\left(\upsilon'+\tfrac{1}{2}\right) - \omega_e' x_e' \left(\upsilon'+\tfrac{1}{2}\right)^2\right] - \left[\omega_e''\left(\upsilon''+\tfrac{1}{2}\right) - \omega_e'' x_e''\left(\upsilon''+\tfrac{1}{2}\right)^2\right]$$

So, using this data calculate the question is calculate omega e and omega exe for A1 pi electronic state of PN. That is a requirement so, the band origins, so, in order to solve the solution part like this, so the band origin for any vibronic transition, it is given as… Just follow the steps these are all we already have done.

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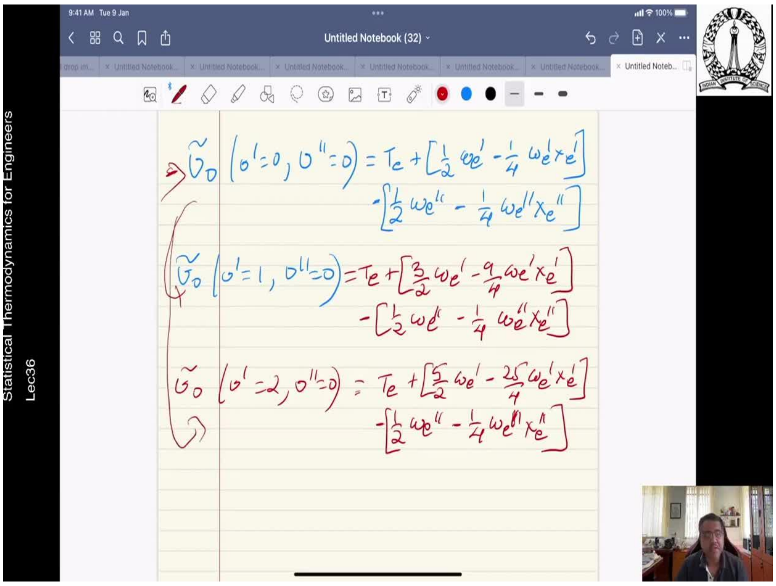
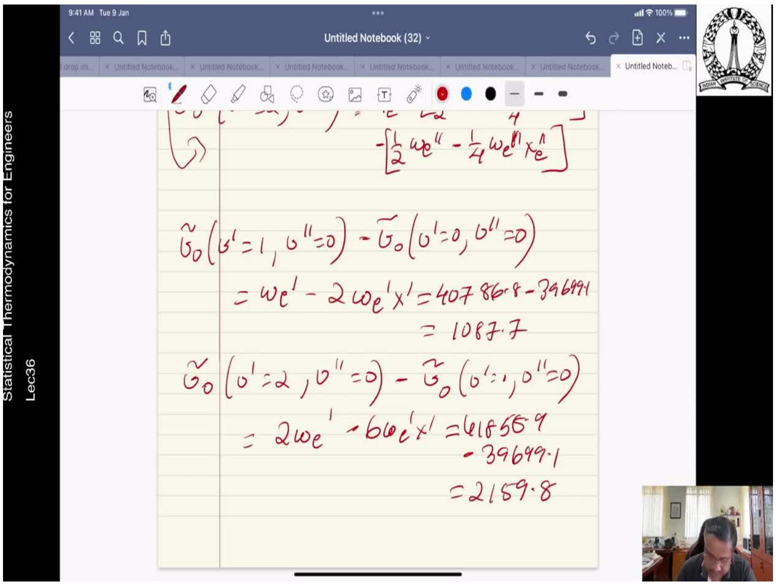


$$\tilde{\upsilon}_0(\upsilon'=0, \upsilon''=0) = T_e + \left[\tfrac{1}{2}\omega_e' - \tfrac{1}{4}\omega_e' x_e'\right] - \left[\tfrac{1}{2}\omega_e'' - \tfrac{1}{4}\omega_e'' x_e''\right]$$

$$\tilde{\upsilon}_0(\upsilon'=1, \upsilon''=0) = T_e + \left[\tfrac{3}{2}\omega_e' - \tfrac{9}{4}\omega_e' x_e'\right] - \left[\tfrac{1}{2}\omega_e'' - \tfrac{1}{4}\omega_e'' x_e''\right]$$

$$\tilde{\upsilon}_0(\upsilon'=2, \upsilon''=0) = T_e + \left[\tfrac{5}{2}\omega_e' - \tfrac{25}{4}\omega_e' x_e'\right] - \left[\tfrac{1}{2}\omega_e'' - \tfrac{1}{4}\omega_e'' x_e''\right]$$



$$-\left[\frac{1}{2}\omega_e'' - \frac{1}{4}\omega_e''x_e''\right]$$

$$\tilde{G}_0(v'=1, v''=0) - \tilde{G}_0(v'=0, v''=0)$$

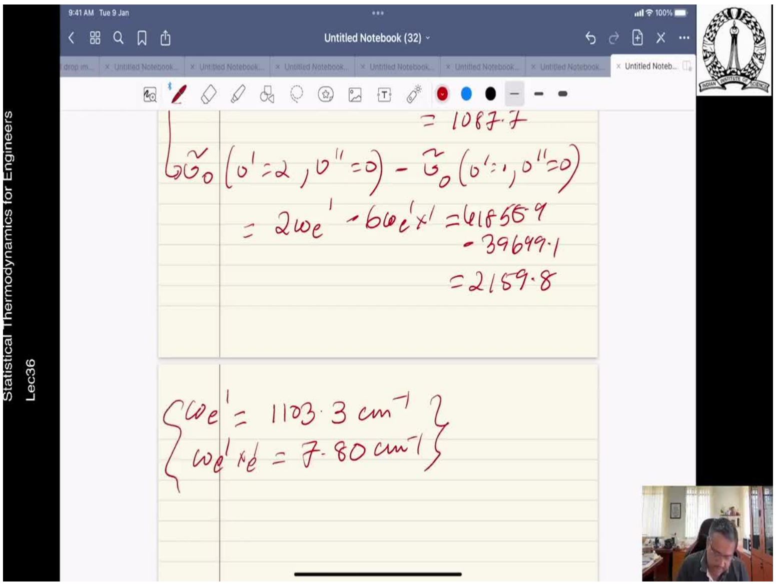
$$= \omega_e' - 2\omega_e'x' = 40786.8 - 39699.1$$

$$= 1087.7$$

$$\tilde{G}_0(v'=2, v''=0) - \tilde{G}_0(v'=1, v''=0)$$

$$= 2\omega_e' - 6\omega_e'x' = 41855.9 - 39699.1$$

$$= 2159.8$$



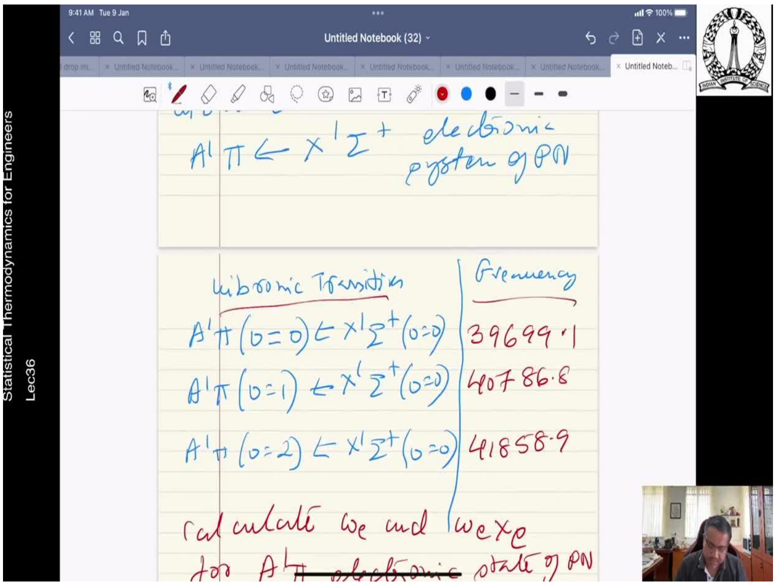
$$= 1087.7$$

$$\tilde{G}_0(v'=2, v''=0) - \tilde{G}_0(v'=1, v''=0)$$

$$= 2\omega_e' - 6\omega_e'x' = 41855.9 - 39699.1$$

$$= 2159.8$$

$$\left\{\begin{array}{l} \omega_e' = 1103.3\ \text{cm}^{-1} \\ \omega_e'x_e' = 7.80\ \text{cm}^{-1} \end{array}\right\}$$



$A^1\Pi \leftarrow X^1\Sigma^+$ electronic system of PN

Vibronic Transition	Frequency
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Calculate ω_e and $\omega_e x_e$ for $A^1\Pi$ electronic state of PN

For this specific transitions indicated by the above table so, we will take the specific transitions h, trying to both zero equal to zero for this particular transition Te and one fourth prime x prime minus double prime minus one fourth double prime it is x then of course, you have V naught prime equal to 1 double prime is equal to 0 is equal to Te 3 by 2 omega times 9 and 4 X e prime and(())(16:20) double prime.

V prime(())(16:38) equal to 2 double prime equal to 0 which is equal to Te double price 25 by 4… double prime Xe. So, if we subtract the first of the situation which is this one from each of the remaining 2 equation so, you subtract this from this and this. So, we get minus 0 is equal to omega e prime minus 2 omega prime X 1 that is equal to 40786.8 minus 39699.1 which gives you 87.7.

And then you do the same to as v double prime equals zero minus again V naught 0 e prime equal to 0 double prime equal 0 subtract this, this will give you 2 omega e minus 6x prime which will give you 41858.9 minus 39699.1 which is equal to 2159.8. Now, if you solve these 2 equations now, simultaneously they will take in a solution of these 2 equations will give you omega e prime is equal to 1103.3 centimeter inverse prime xi 7.80.

So, this is the standard solution that we did by subtracting the method of subtraction equation. So, this will enable us to calculate as you can see, given the spectroscopic tables of spectroscopic transmissions, if somebody has measured this for you, you can find out this varieties of spectro parameters.

So, as you can see that, that we saw that we have covered a lot of materials in this particular part of this chapter and we know what are the different transitions. What are the different ro-hydronic transitions and stuff like that. So, let us right now put the energy and the degeneracy or the energy modes of an atom or diatomic molecule.

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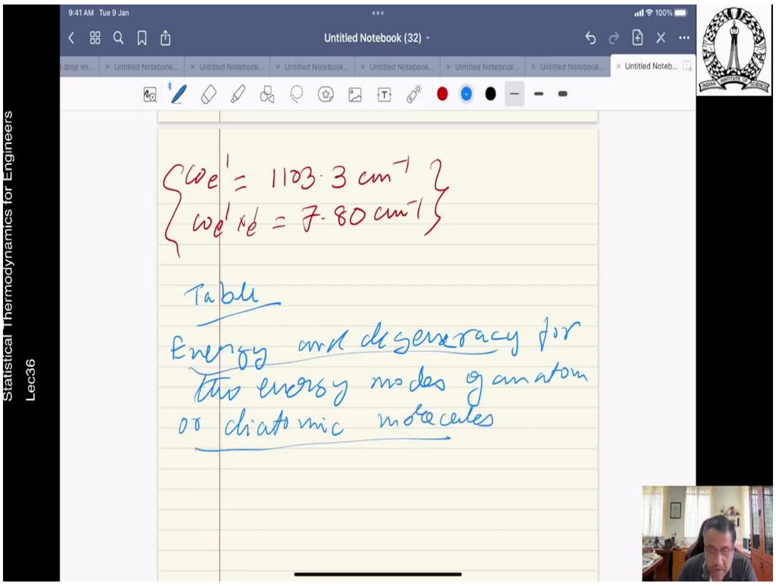
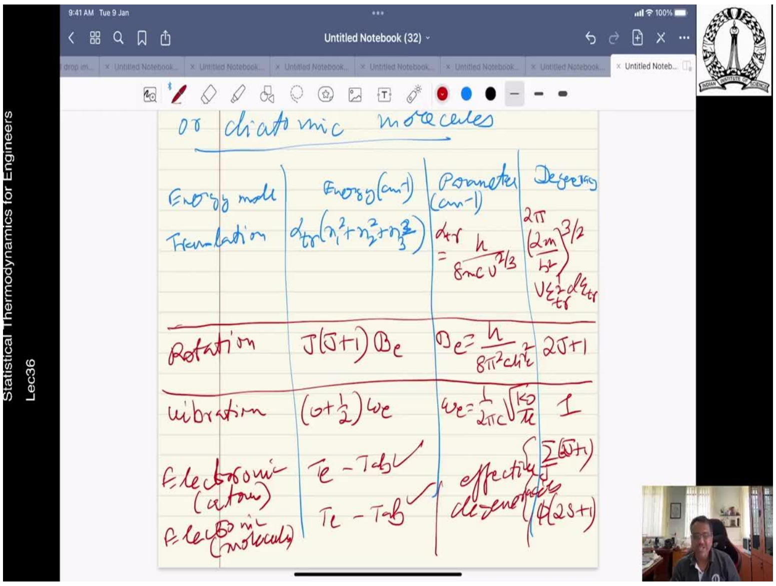


$$\left\{ \begin{aligned} \omega_e' &= 1103.3\ \text{cm}^{-1} \\ \omega_e' x_e' &= 7.80\ \text{cm}^{-1} \end{aligned} \right\}$$

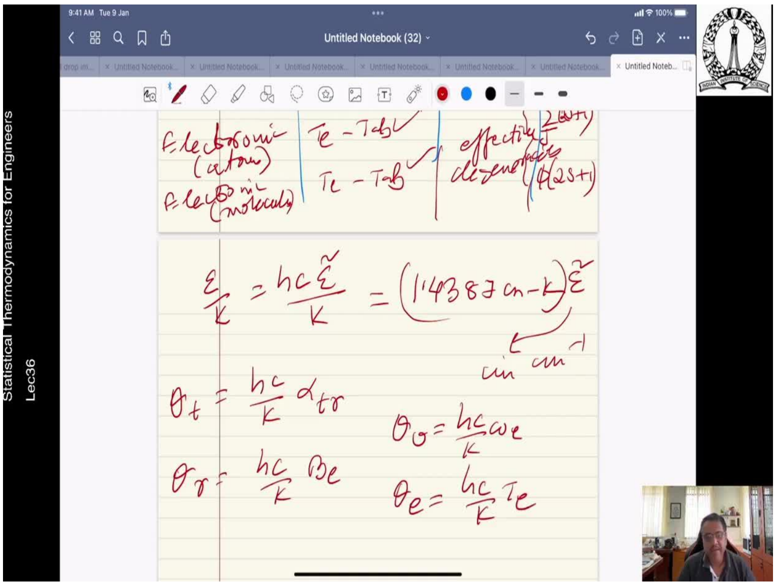
Table

Energy and degeneracy for the energy modes of an atom or diatomic molecules



or diatomic molecules

Energy mode	Energy (cm-1)	Parameter (cm-1)	Degeneracy
Translation	$\alpha_{tr}(n_1^2+n_2^2+n_3^2)$	$\alpha_{tr} = \frac{h}{8mcV^{2/3}}$	$2\pi\left(\frac{2m}{h^2}\right)^{3/2} V\varepsilon_{tr}^{1/2}\,d\varepsilon_{tr}$
Rotation	$J(J+1)B_e$	$B_e = \frac{h}{8\pi^2 c I_e}$	$2J+1$
vibration	$(v+\frac{1}{2})\omega_e$	$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_0}{\mu}}$	1
Electronic (atom)	T_e – Tab ✓	effective degeneracies	$\sum_J (2J+1)$
Electronic (molecules)	T_e – Tab ✓		$\Phi(2S+1)$



$$\frac{\varepsilon}{k} = \frac{hc\tilde{\varepsilon}}{k} = (1.4387\ \text{cm-K})\tilde{\varepsilon}$$

cm cm^{-1}

$$\theta_t = \frac{hc}{k}\alpha_{tr} \qquad \theta_v = \frac{hc}{k}\omega_e$$

$$\theta_r = \frac{hc}{k}B_e \qquad \theta_e = \frac{hc}{k}T_e$$

So, let us look at this table. We can name this table as energy and degeneracy in a receipt for the energy notes or the energy most have an atom or diatomic molecules. So, let us do this, the first one is energy note then it is the energy all that include parameter was inserted into reverse and then of course, the degeneracy. The first one is the translation session. So, that is given as you recall one square plus n2 square plus n3 square.

Then you have some markers so, it is easier for us to write and alpha TR was equal to if you recall each divided by 8 mc 2 the power 2 third and the degeneracy was quite a bit 2 pi 2m. This almost appears continuous, that is why it is spectroscopy this is not a very good thing in translation on… So, that was the degeneracy for the translation.

Then comes rotation, the mode is rotation is J 2 J plus 1 Be, the parameter Be is H divided by 8pi square c mu r e square and the degeneracy was 2 J plus 1. Then of course, comes vibration, vibration a vibration is half it was half omega e and then omega e is given as 1 upon 2 pi c root over k naught by mu and the degeneracy was 1. Then you have electronic or atoms. So, this is tabulated and degeneracy is J 2 J plus 1(())(23:18) and for molecules, the molecules again this is tedious tabulated related this is parameter phi 2s plus 1.

So, we have the translational energy and we also have the other energy mode is affected by the macroscopic properties unlike translational. The internal energy moves the degeneracy is like a probability distribution function for translational mode for the internal modes. We recall the rotational concept of a rigid rotor and vibrational frequency omega for the harmonic oscillator.

Similarly, spectroscopic measurements provide tabulations for the electronic energies of atoms and molecules that you see over here, atoms molecules or atoms that require degeneracies evaluated by solving over a multiple multi plate across for the different G values or molecules typically sum(())(24:34) over a multiplet caused by spin-splitting and doubling.

In other words, both atoms and molecules the relative expressions are the effective degeneracy(()) (24:44) so these are as we know the effective degeneracy. Correct. So now, in calculating the thermodynamic properties, it may be prudent to cast all this energies in terms of the temperature. So, for example, if you can easily convert it to temperature by your k which is hc k is about 1.487 integrated energy.

(())(25:29)where h is Planck’s, k is Boltzmann’s constant and this is the energy he said to reverse. So, this gives you energy in terms of kelvin, in terms of temperature that is useful in calculating the thermodynamic properties. So, we can define different types of temperatures, for example, translational temperature is h c by k into alpha tr, the rotational temperature is given as hc by k into Be.

The vibrational temperature is given as hc by k into omega e, the electronic temperature is given by Te. So, the translational temperature usually would not be in the range of 10 to the power minus 16 Kelvin. So, even though as the translational temperatures rotate or more massive molecules are the temperature for the rotation is about 10 kelvin and vibration is about 10 to the power of 3 kelvin and electronic 10 to the power of 5 kelvin.

So therefore, we find that both translational and rotational modes are fully operating below the room temperature. Vibrational and electronic modes becomes operative when the temperature is considerably above 300 Kelvin, which is the room temperature level. In the next class we are going to look at some of these pieces in a little bit details. So, then we will try to see how this translational and what is the… how these temperatures now can be used for calculating the thermodynamic properties. Thank you.