Introduction to Molecular Thermodynamics
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Lecture – 22
Ideal Gases (Contd.)

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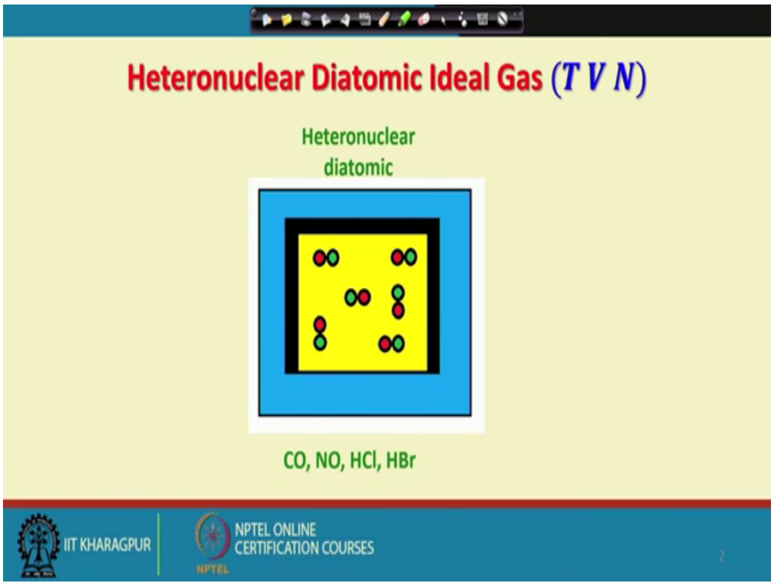

Heteronuclear Diatomic Ideal Gas (T V N)

Heteronuclear
diatomic

CO, NO, HCl, HBr

Welcome back. So, we are discussing here the statistical thermodynamics of a diatomic ideal gas, where we have already seen that how to think about the description of the microscopic state of a heteronuclear diatomic ideal gas that is maintained under the macroscopic condition of a given temperature volume and number of particles.

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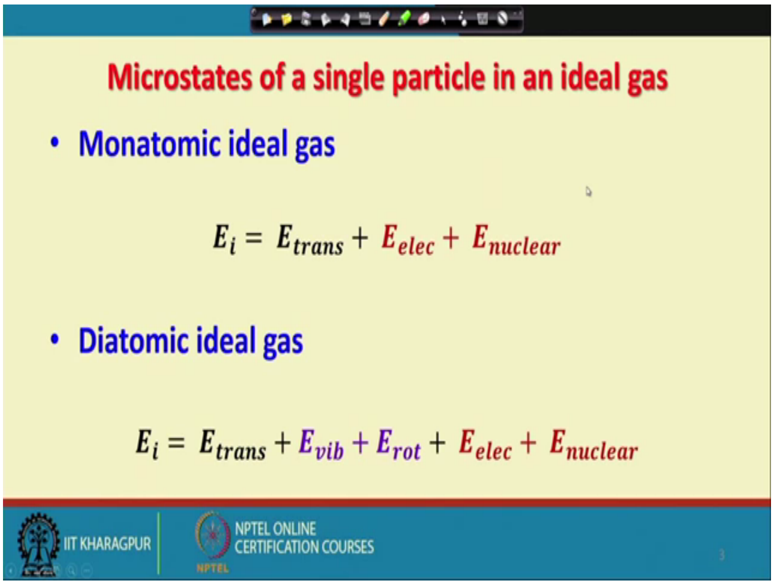

Microstates of a single particle in an ideal gas

- Monatomic ideal gas

$$E_i = E_{trans} + E_{elec} + E_{nuclear}$$

- Diatomic ideal gas

$$E_i = E_{trans} + E_{vib} + E_{rot} + E_{elec} + E_{nuclear}$$

And here we have highlighted the fact that we could do the statistical thermodynamics in case of the monatomic ideal gas because of the seperabilty of the total energy of a single atom of the system into the translational motion of the atom plus the underlying microscopic structure of the atom. And in the case of diatomic ideal gas, we have also shown that this separation is also possible into the translational motion of the overall molecule as well as the underlying microscopic structure of the molecule that we have at hand.

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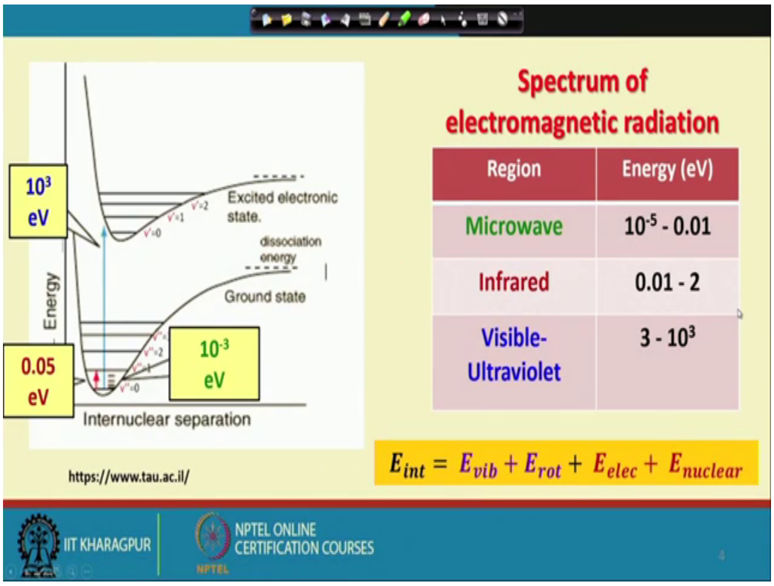

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Spectrum of electromagnetic radiation

Region	Energy (eV)
Microwave	10^{-5} - 0.01
Infrared	0.01 - 2
Visible-Ultraviolet	3 - 10^3

$$E_{int} = E_{vib} + E_{rot} + E_{elec} + E_{nuclear}$$

Specifically, we talked about how to separate out the effect of the internal structure of the molecule in terms of not only the nuclear energy levels and the electronic energy levels, but also taking into account the separation into the vibrational energy levels and rotational energy levels associated with each electronic energy level of the molecule. So, now we are quite ready to start calculating the single particle canonical partition function using these results.

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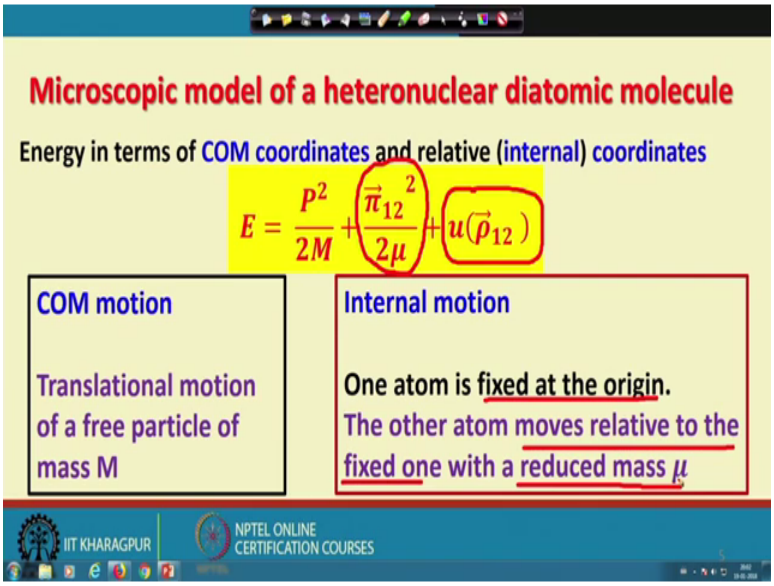

Microscopic model of a heteronuclear diatomic molecule

Energy in terms of COM coordinates and relative (internal) coordinates

$$E = \frac{P^2}{2M} + \boxed{\frac{\vec{\pi}_{12}^{\,2}}{2\mu}} + \boxed{u(\vec{\rho}_{12})}$$

COM motion

Translational motion of a free particle of mass M

Internal motion

One atom is fixed at the origin.
The other atom moves relative to the fixed one with a reduced mass μ

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So, that is exactly what we will do next, but before that let us go back and revise the model that we are discussing here at the microscopic level for the heteronuclear diatomic molecule in terms of the center of mass coordinates and the relative or internal coordinates. And as you see here, this is the expression that we have already obtained through a series of coordinate transformations. Now, here the highlighting portion is that the first term that you see here that corresponds to the center of mass motion in the three-dimensional volume without any interaction term appearing in the energy. And therefore, I can say that for every molecule in this gas the translational motion of the molecule can be modelled as the translational motion of a free particle or of mass M in the volume v clear.

Now, the other things that we can say from here are as follows. We can say that the internal motion which is characterized by these two terms. So, this is a kinetic energy term and the internal motion is associated with this potential energy term. What I am actually looking at that one atom is fixed at origin, and the other atom in this diatomic molecule is moving relative to the first a fixed one with a reduced mass of mu.

We have already discussed the feasibility, and how to obtain or how to separate out the total energy of the system in these two separate contributions. We have also seen that the internal structure of a molecule should be associated with the vibrational and the rotational fine a kind of energy states. But how do I go from this kind of an expression to the different and associate the internal motion with the vibrational and rotational motion. So, that is the question that we are going to ask next.

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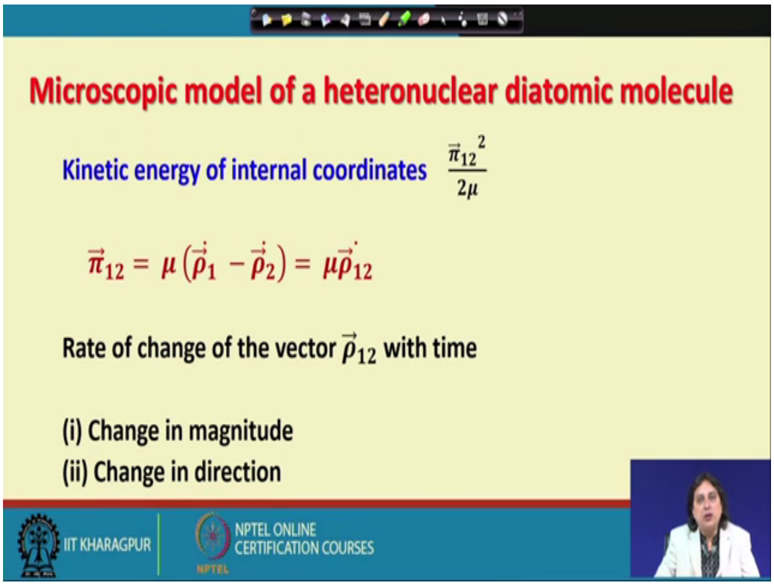

Microscopic model of a heteronuclear diatomic molecule

Kinetic energy of internal coordinates $\frac{\vec{\pi}_{12}^{\,2}}{2\mu}$

$$\vec{\pi}_{12} = \mu\left(\dot{\vec{\rho}}_1 - \dot{\vec{\rho}}_2\right) = \mu\dot{\vec{\rho}}_{12}$$

Rate of change of the vector $\vec{\rho}_{12}$ with time

(i) Change in magnitude

(ii) Change in direction

So, let us have a look at the kinetic energy of the internal coordinates. So, this term is given in terms of the reduced momentum pi 12. So, it is pi 12 square divided by 2 mu. Now, let me revisit the definition of pi 12, so that is the reduced mass mu multiplied by the rho 12 dot that is the rate of change of the vector rho 12 with time.

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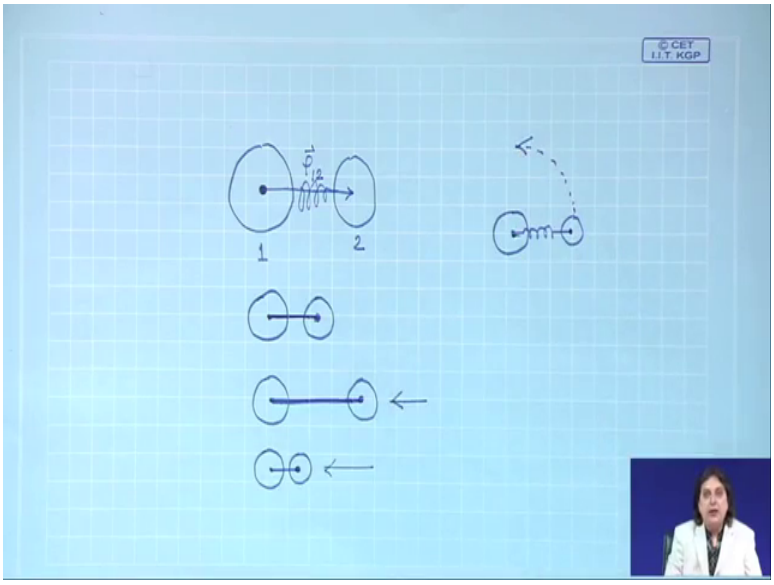

If I may remind you that when I had this is my molecule one and this is my molecule 2, if I sit on this molecule 1, then rho 1 2 is the vector separating the two nuclei if the origin is on the particle 1. So, now or vice versa you can use the definition that you want. Now, how can the vector rho 1 2 changes with time? A vector can change with time either by a change in magnitude or by a change in the direction. So, let us now examine what happens when in a diatomic molecule there lily relative separation vector rho 1 2 changes either in magnitude or in direction, and what kind of internal motion we are talking about.

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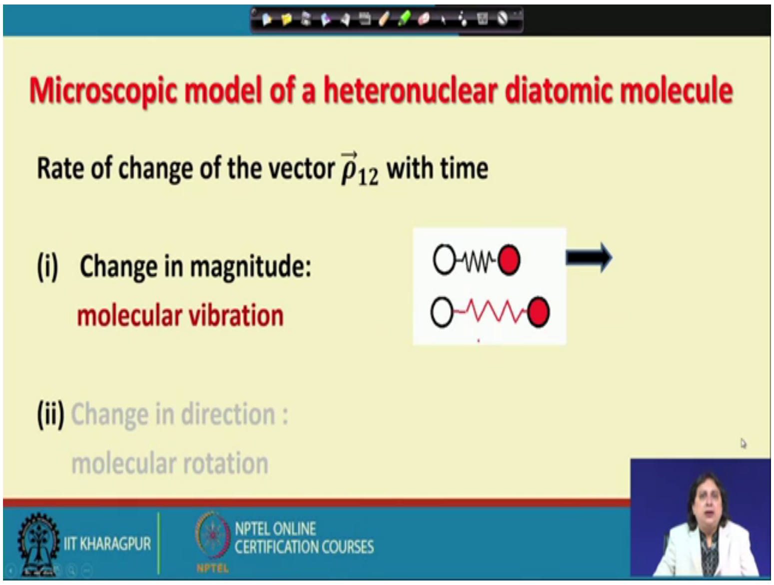

Microscopic model of a heteronuclear diatomic molecule

Rate of change of the vector $\vec{\rho}_{12}$ with time

(i) Change in magnitude: molecular vibration

(ii) Change in direction : molecular rotation

So, let us first focus on the change in magnitude. So, when you are having a change in magnitude, so basically what you are saying is if this is the equilibrium bond length of the two atoms, then when this vector changes in magnitude, you are going to have one kind of situation where the vector is now longer than the equilibrium bond length. Or it may so happen that the vector is now smaller than the equilibrium bond length. As a result, I can say that it is essentially like if a spring is connecting the two particles, there is a bond which is vibrating about its mean position of the equilibrium bond length, this is when the bond is stretched, and this is when the bond is compressed.

So, this is exactly what we have shown here. And therefore, I understand that the rate of change of the vector rho 1 2 with time can happen, when the bond is executing a vibrational motion, so that the two atoms they are as if they are connected by a spring. And this spring is either expanding or it is contracting giving rise to some kind of a vibrational motion.

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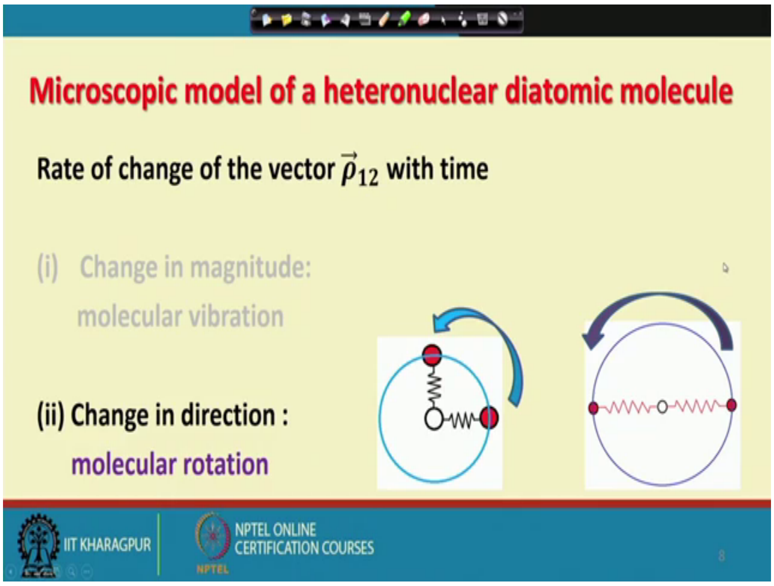

Microscopic model of a heteronuclear diatomic molecule

Rate of change of the vector $\vec{\rho}_{12}$ with time

(i) Change in magnitude: molecular vibration

(ii) Change in direction : molecular rotation

Now, let us next consider apart after this representation of molecular vibration, let us then consider the change in direction of this separation vector rho 1 2. So, this is the one obviously, that we are going to associate with the molecular rotation. So, this is one of the situations. You started with the two atoms, which are connected by a spring. Now, this spring is in some stretched condition and then between the time, it goes from here to a stretch it another stretch it condition, what can happen is this molecule can move about this position around this axis, and that is what will give rise to a rotation.

So, as you see here, this is exactly what we have represented saying that for a given length of the spring which means that for a given distance between the two atoms, when it is fixed in this length, the molecule can rotate. Once again, if the molecule if the bond is now stretched further, the molecule can again rotate like this. So, what you see is the importance here is that the time scales because of the difference in the energy scales. The time skills that are required to stretch is much, much longer than the time scale that the molecule requires to execute this rotational motion.

So, basically what will happen is that two atoms will stretch, the bond will stretch, and go like this or go like this. So, the time they require to do this is let us say some time t, but while they are here before they can start compressing or expanding further, the molecule can rotate. And this is because of the separation in the energy scales that you see in that we have already seen.

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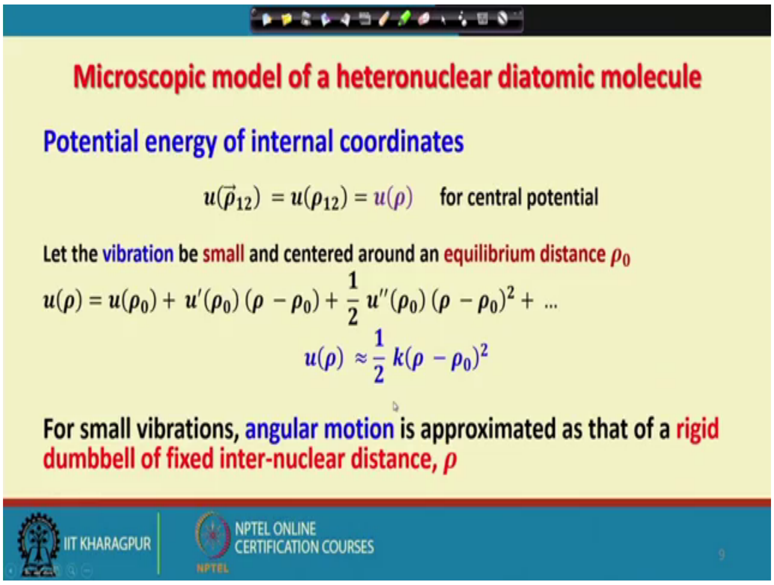

Microscopic model of a heteronuclear diatomic molecule

Potential energy of internal coordinates

$u(\vec{\rho}_{12}) = u(\rho_{12}) = u(\rho)$ for central potential

Let the vibration be small and centered around an equilibrium distance ρ_0

$$u(\rho) = u(\rho_0) + u'(\rho_0)\,(\rho - \rho_0) + \frac{1}{2}\,u''(\rho_0)\,(\rho - \rho_0)^2 + \dots$$

$$u(\rho) \approx \frac{1}{2}\,k(\rho - \rho_0)^2$$

For small vibrations, angular motion is approximated as that of a rigid dumbbell of fixed inter-nuclear distance, ρ

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And therefore, under such condition the microscopic model of a heteronuclear diatomic molecule requires us to examine the potential energy of the internal coordinates as well. Now, the potential energy usually depends only on the magnitude of the vector for central potentials. So, let me assume that the vibration is very small for this chemical bond, and it takes place around an equilibrium distance of rho naught. Now, if that is so then I can write down using Taylor expansion rho u as rho of rho is equal to u of rho naught plus u prime evaluated at rho naught into rho minus rho naught plus half u double prime evaluated at rho naught into rho minus rho naught whole square and so on and so forth.

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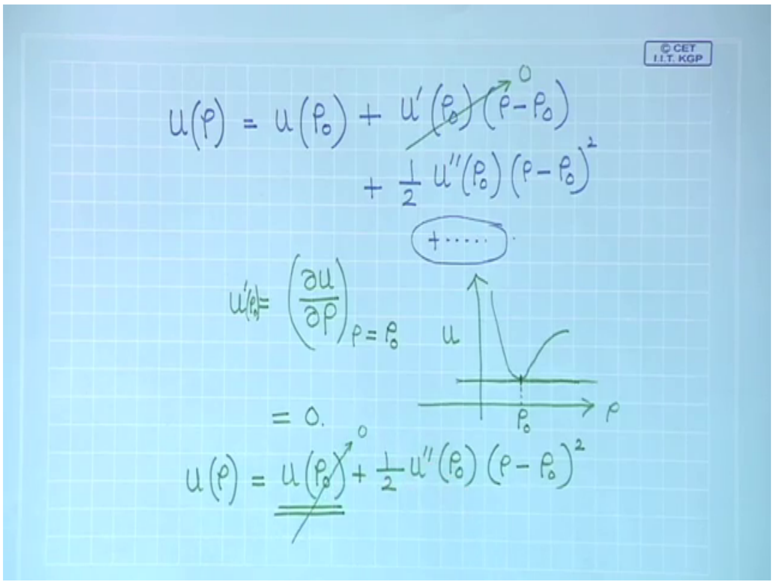

$$u(\rho) = u(\rho_0) + \cancelto{0}{u'(\rho_0)(\rho-\rho_0)} + \frac{1}{2}u''(\rho_0)(\rho-\rho_0)^2 \boxed{+\cdots}$$

$$u'(\rho_0) = \left(\frac{\partial u}{\partial \rho}\right)_{\rho=\rho_0} = 0.$$

$$u(\rho) = \underline{\underline{\cancelto{0}{u(\rho_0)}}} + \frac{1}{2}u''(\rho_0)(\rho-\rho_0)^2$$

I can very easily neglect this higher order terms in rho minus rho naught if the displacement from the equilibrium bond length is small. I can also have some more simplification, because here what is u prime, u prime is equal to del u del rho evaluated at rho equal to rho naught that is equilibrium bond length. If you will remember then we have already shown that as a function of rho, if I show u rho that shows a minimum for rho naught. And therefore, when evaluated at rho naught, this term must be equal to 0, and therefore, this goes to 0. And then I have u rho simplifying to u of rho naught plus half of u double prime that is the second derivative of u with respect to rho evaluated at rho equal to rho naught that is the equilibrium bond length into rho minus rho naught whole square.

Now, let us say that I assume that this is the zero of the energy scale for this kind of vibrational motion. So, I put this equal to 0. So, essentially the potential energy term that we saw in our total energy is a harmonic energy term that is given by that is proportional to rho minus rho naught whole square. So, what do I learn from here, what I learn is first this kind of expansion is valid if rho minus rho naught is small. And when will rho minus rho naught be small, of course if you have a stable chemical bond. You can see that it is being held by a very high force constant k. Therefore, any amount of stretching or change in the bond length from the equilibrium bond length will require a very high energy, and therefore you would say that this is going to be less possible if a certain amount of energy is available to the system. And therefore, I can very easily say that the kind of motion that is being executed by the diatomic molecule, when I fix the atom one here and the other one is moving about with respect to it in a vibrational mode then it must be something like the simple harmonic vibration.

So, this simple harmonic vibration is related to the change in magnitude of the separation vector rho 1 2 keeping this atom fixed, and another mass of another body of mass mu moving about with respect to it. Then where does the rotation come into the picture of course, then I would say that if I have small vibrations, for each vibrational state I will have the angular motion. And this angular motion can then be approximated as that of a rigid dumbbell of fixed inter-nuclear distance. So, once again simply because there is a difference in time scale in which the vibrational motions occur, and the time scale which is associated with the rotational motion this appears to be a reasonable approximation.

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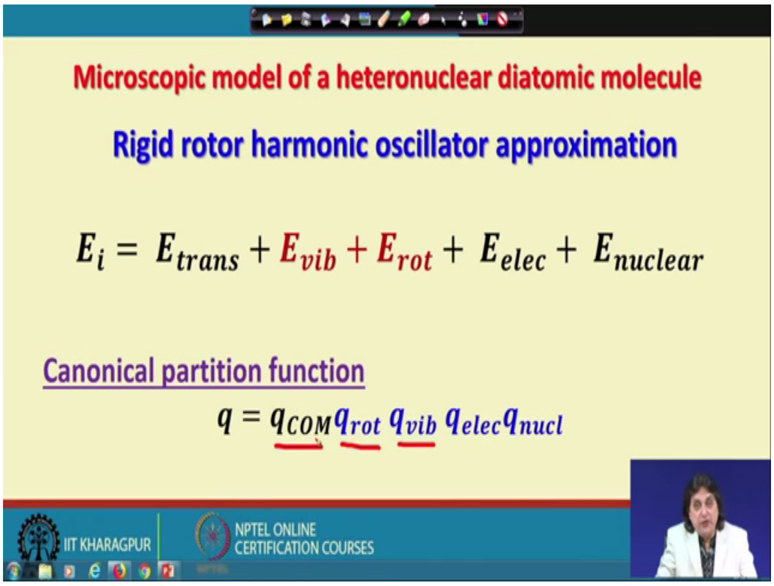

Microscopic model of a heteronuclear diatomic molecule

Rigid rotor harmonic oscillator approximation

$$E_i = E_{trans} + E_{vib} + E_{rot} + E_{elec} + E_{nuclear}$$

Canonical partition function

$$q = \underline{q_{COM}}\,\underline{q_{rot}}\,\underline{q_{vib}}\,q_{elec}\,q_{nucl}$$

So, where do we go from here? We go from here to establish the fact that now I have a rigid rotor harmonic oscillator approximation for the contribution of vibrational and rotational energies to the overall energy of a single molecule in the diatomic case. Now, if that is so, we have now established how we are going to model the E vibration and E rotation. E vibration will be essentially modelled in terms of a harmonic oscillation; and E rotation is going to be modelled in terms of a rigid rotor. So, accordingly we can write down the canonical partition function as a product of all these different contributions for the single particle. E trans is giving us the giving rise to the term q of the center of mass. The E vibration term giving rise to the canonical partition function due to the vibration E rot gives the rotational partition function contribution. Similarly, we have seen how to get the q electronic and the q nuclear part.

Therefore, the only thing that I find here as new is how to model these two parts. I am going to model this part as the motion of a single particle, how to calculate the single particle canonical partition function when our free particle is moving about in a three-dimensional box, so that is the small q that we have already derived in the last class.

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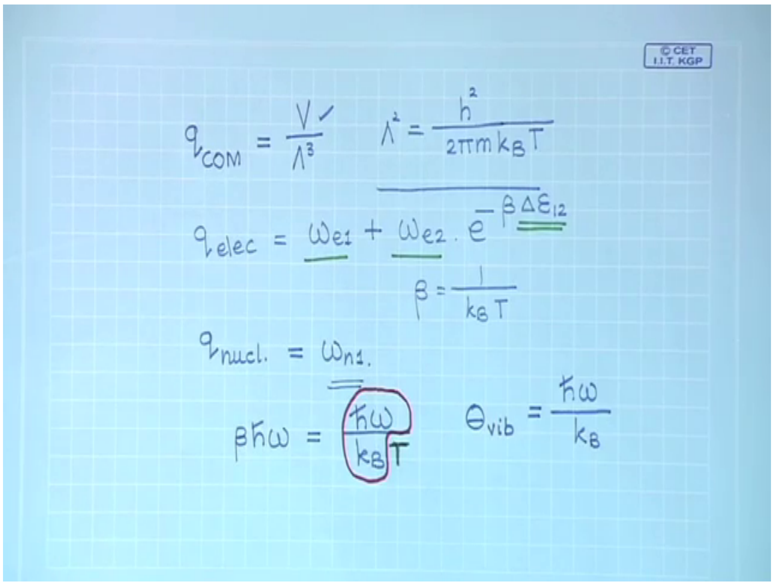

$$q_{COM} = \frac{V}{\Lambda^3} \checkmark \qquad \Lambda^2 = \frac{h^2}{2\pi m k_B T}$$

$$q_{elec} = \underline{\omega_{e1}} + \underline{\omega_{e2}} \cdot e^{-\beta \underline{\underline{\Delta\varepsilon_{12}}}}$$

$$\beta = \frac{1}{k_B T}$$

$$q_{nucl.} = \underline{\underline{\omega_{n1}}}.$$

$$\beta\hbar\omega = \frac{\hbar\omega}{k_B T} \qquad \Theta_{vib} = \frac{\hbar\omega}{k_B}$$

And we know that this small q center of mass is going to be nothing but V by lambda cubed where lambda squared is related to h square divided by 2 pi m k B T, and therefore, this is a function of temperature, and this is known as the thermal de Broglie wavelength. And this is the volume in which this particle is moving about. We have also seen how to get q electronic and q electronic is generally written as w e 1 that is the degeneracy of the ground electronic state then w e 2 into E to the power of minus beta delta E 1 2, where beta is equal to 1 by k B T. We have already done this.

And therefore, if from experiments or from some calculations, we can know what delta epsilon 1 2 are and we have information what these degeneracy's are, I can find out q electronic. Similarly, I have also shown you how to get the q nuclear as omega n 1 because the other terms are unimportant at finite temperature. And this is a constant term you can have some idea about this constant term, but this will eventually not appear in the final thermodynamic expressions. So, therefore, in the diatomic molecule case, the important thing that we are going to show you here is how to calculate q rot and how to calculate q vib.

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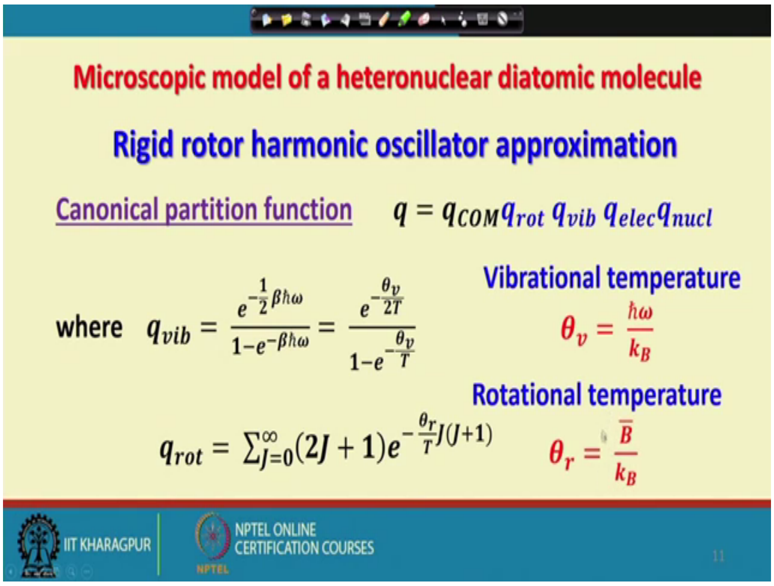

Microscopic model of a heteronuclear diatomic molecule

Rigid rotor harmonic oscillator approximation

Canonical partition function $q = q_{COM} q_{rot}\, q_{vib}\, q_{elec} q_{nucl}$

where $q_{vib} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{e^{-\frac{\theta_v}{2T}}}{1-e^{-\frac{\theta_v}{T}}}$

Vibrational temperature

$\theta_v = \frac{\hbar\omega}{k_B}$

Rotational temperature

$q_{rot} = \sum_{J=0}^{\infty}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)}$

$\theta_r = \frac{\bar{B}}{k_B}$

So, let us have a look as to how to what would be the analytical expressions of these two parts, if I assume that the vibrational motion of this chemical bond is going to be approximated by a simple harmonic oscillator with an intrinsic angular frequency omega. And therefore, I can very easily say that q vib is given by an expression like this clear. Now, as you see here I have the information regarding the microscopic properties of the system in this angular frequency omega and therefore, it is found easier if you introduce one particular constant. So, I have this term beta h cross omega.

And if I write it down I explicitly by in terms of beta, so I have h cross omega by T. So, what is a constant for a given substance given chemical type of chemical bond, this is a constant for a given type of chemical bond, and the temperature is decided by the experimental condition that you are controlling at the macroscopic level. So, the characteristic property of the system is now reflected in terms of this quantity which I call theta vib, and I define it as h cross omega divided by k B.

So, what is theta vib, theta vib must be having the dimensions of temperature. And if I put it back then the expression for q vib in terms of theta v now turns out to be this. Therefore, if from your experiments, you know what theta v is then you can calculate q vib. Similarly, we can have within the approximation of a rigid rotors harmonic oscillator, q rot is this. And here also what we have done is we have introduced a characteristic constant theta r or theta rot. And by definition this is also having the dimension of temperature and this is given by B bar by k B, where this is the rotational constant as appropriate for the underlying energy levels which are for the Jth energy level, the degeneracy is 2 J plus 1. And I know that then this contribution that will come here is theta r and here I should have also J into J plus 1. So, I am sorry this needs a correction.

[FL].

Student: (Refer Time: 20:57).

[FL]

So, once we have established the seperabilty of the canonical partition function for the single particle into these different contributions, then we can go ahead and calculate the canonical partition function under the rigid rotor simple harmonic oscillator approximation. Now, what we have shown here are the expressions for this small q vib and small q rot. Under the condition of a simple harmonic oscillator, approximation q is given by this.

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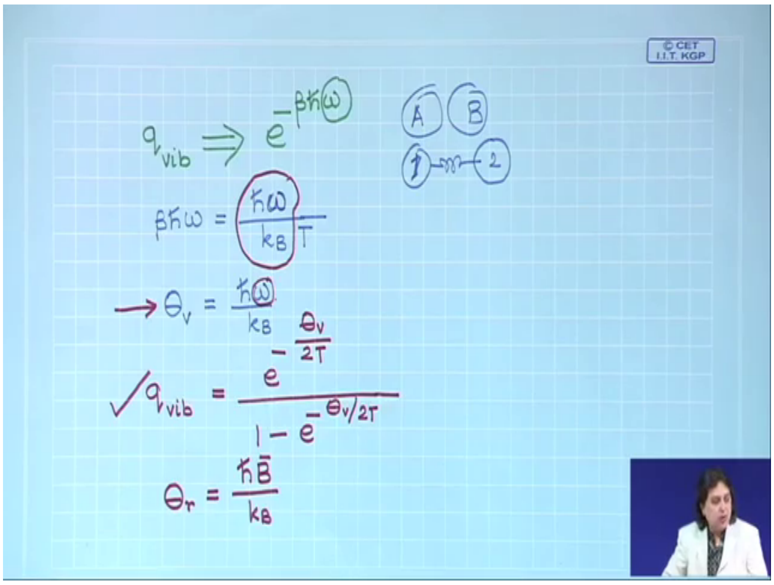

$$q_{vib} \Rightarrow e^{-\beta \hbar \omega}$$

$$\beta \hbar \omega = \frac{\hbar \omega}{k_B T}$$

$$\rightarrow \Theta_v = \frac{\hbar \omega}{k_B}$$

$$\checkmark\, q_{vib} = \frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\Theta_v/2T}}$$

$$\Theta_r = \frac{\hbar \bar{B}}{k_B}$$

Now, if I have a closer look at what are the contributions here so q vib is equal to it depends on this quantity E to the power of minus beta h cross omega. So, what is omega, omega is the intrinsic angular frequency of vibration of the bond between my molecule A B or between my molecule one and my molecule two. Now, therefore this is a characteristic property of the system that I am considering.

So, now, let us have a look and write it out in a little different way. So, I am writing out beta h cross omega as h cross omega by k B T. And I understand that this part this h cross omega by k B, this is going to be a constant for a given system, because h cross is a universal constant, k B is a universal constant, and the system dependent property omega is here. So, let me define here as theta v this quantity h cross omega by k B. So, theta v is a characteristic property of the type of chemical bond that I am considering. And here I understand that theta v must be having a dimension of temperature.

If that is so then I can go back and write down q vib as into the power of minus theta v by 2 T divided by 1 minus e to the power of minus theta v by 2 T. Now, if I know which harmonic frequency I am going to assign to my bond, then I can calculate theta v and accordingly I can compute what q vib is going to be at a given temperature T. Similarly, in the case of the rotational partition function, you see that here and summing over all the rotational energy levels and each of the rotational energy levels they have 2 J plus 1 degeneracy that is the source of this term here. And this is what I have where I have used the notation that theta r is equal to h cross then B by k T k B.

Now, once again the B bar that is the rotational constant that contains information regarding specific to the molecule that I consider. So, this is also a characteristic property of the molecule. And I can perform experiments in rotational spectroscopy to find out B bar, and hence I should be able to find out theta r. And therefore, what I have achieved over here is as follows. We have achieved the computation of the small q vibration and small q rotation in terms of these characteristic properties vibrational temperature and rotational temperature of the kind of bond that we are talking about at a given temperature T.

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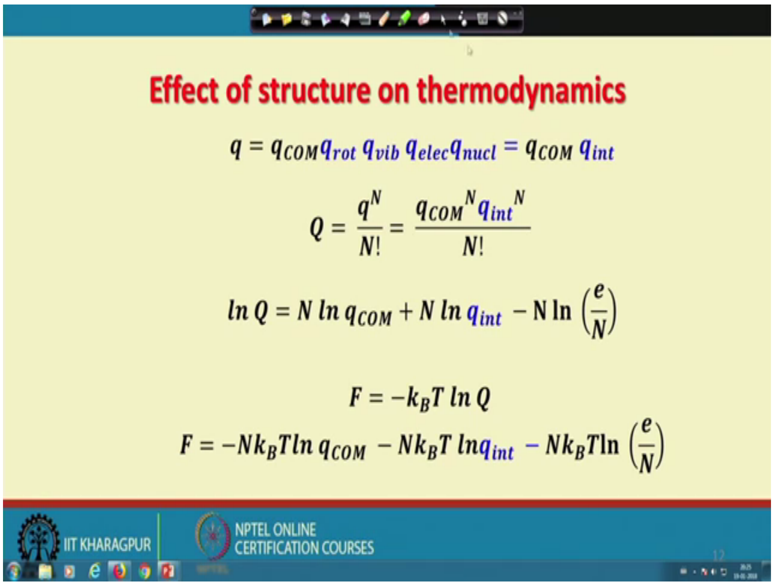

Effect of structure on thermodynamics

$$q = q_{COM} q_{rot}\, q_{vib}\, q_{elec} q_{nucl} = q_{COM}\, q_{int}$$

$$Q = \frac{q^N}{N!} = \frac{{q_{COM}}^N {q_{int}}^N}{N!}$$

$$ln\, Q = N\, ln\, q_{COM} + N\, ln\, q_{int}\; - \text{N ln} \left(\frac{e}{N}\right)$$

$$F = -k_B T\, ln\, Q$$

$$F = -Nk_B T ln\, q_{COM}\; - Nk_B T\; ln q_{int}\; - Nk_B T \text{ln} \left(\frac{e}{N}\right)$$

Now at this stage what we have to talk about is we are trying to understand the effect of the underlying structure of the molecule on thermodynamics. So, let us see and try to understand what I mean by the effect of internal structure of the molecule on the thermodynamic property of the system. So, first we have already seen that small q can be separated into a contribution from the center of mass and the internal structure. And therefore, the capital Q for the N particle system, where all the particles are non-interacting and indistinguishable, I can write it like this. And accordingly the ln q term now has contributions from the center of mass term it has some contribution which is dependent only on N and there is another contribution which adds up from the internal structure of the molecule.

So, what is the consequence of this the consequence of this is since I have f is equal to minus k B T ln Q, then if will have an expression like this. So, as you see in f I have one term that is a direct contribution of the center of mass exist a separable separation of the partition function into a center of mass contribution this is where it comes from the dependence on N. And here what I have is the effect of the internal structure is present in this term.

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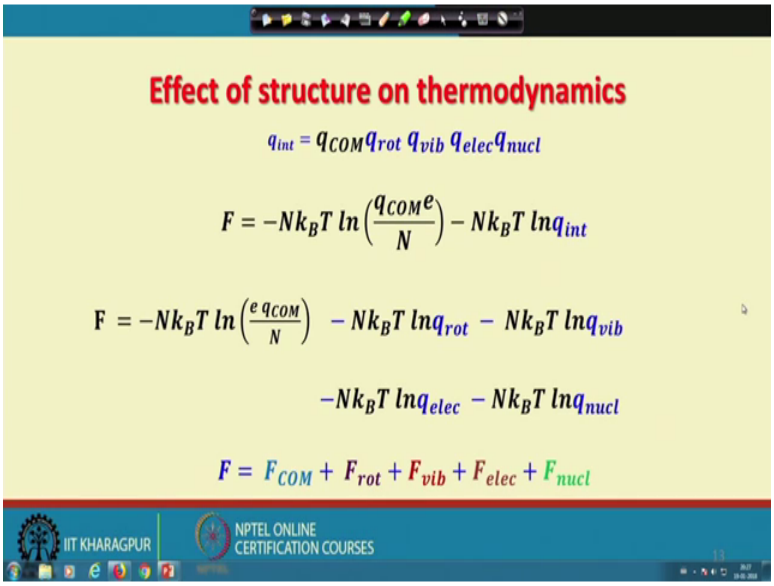

Effect of structure on thermodynamics

$$q_{int} = q_{COM} q_{rot}\, q_{vib}\, q_{elec} q_{nucl}$$

$$F = -Nk_BT\, ln\left(\frac{q_{COM}e}{N}\right) - Nk_BT\, lnq_{int}$$

$$F = -Nk_BT\, ln\left(\frac{e\, q_{COM}}{N}\right) - Nk_BT\, lnq_{rot} - Nk_BT\, lnq_{vib}$$

$$-Nk_BT\, lnq_{elec} - Nk_BT\, lnq_{nucl}$$

$$F = F_{COM} + F_{rot} + F_{vib} + F_{elec} + F_{nucl}$$

And the consequence is that I would say that in this case, I can very easily write out the different terms possible and so I can very easily identify that now my F the overall free energy Helmholtz free energy of the system has one contribution that is entirely due to the center of mass which is this. There is one contribution which is entirely related to the q rot which is F rot. And another contribution coming from the q vib which adds this correction F vib here. And similarly there are corrections to F in terms of electronic and nuclear.

In the last class, when we calculated F for the monatomic case, we did not have these two terms. They are also the Helmholtz free energy separated into these three different terms. And here in the diatomic case, we have in addition and an additional two additional terms coming because of a contribution of rotation and vibration to the overall thermodynamic property of the system. So, this is what we mean by the effect of structure on thermodynamics.

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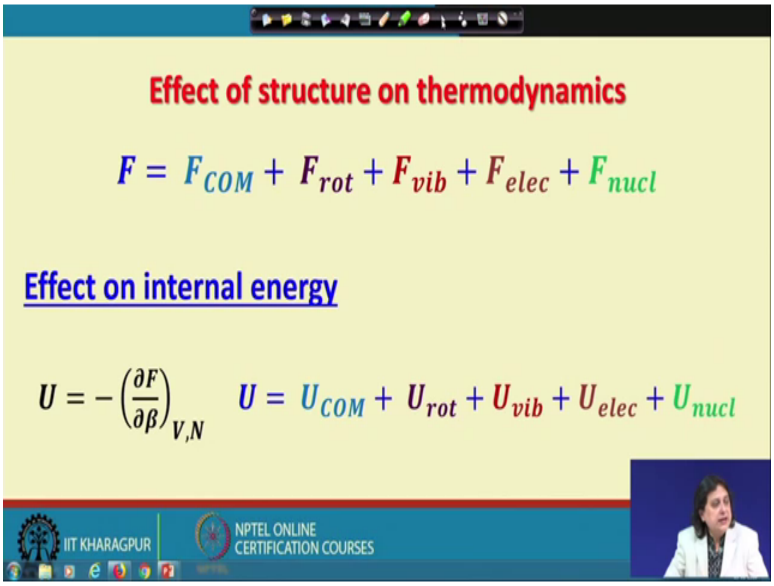

Effect of structure on thermodynamics

$$F = F_{COM} + F_{rot} + F_{vib} + F_{elec} + F_{nucl}$$

Effect on internal energy

$$U = -\left(\frac{\partial F}{\partial \beta}\right)_{V,N} \qquad U = U_{COM} + U_{rot} + U_{vib} + U_{elec} + U_{nucl}$$

Now, let us go and have a look at the further consequence of this. Now, if I can separate out the free energy into different contributions like this, what would be the effect of structure on internal energy, do I expect any structure? Well, U is a derivative of F with respect to beta, therefore, in general I expect that if F is separable into such different contributions, U should also be separable into all these contributions. Therefore, can I identify the terms that are telling me about the effect of the internal structure of the diatomic molecule, yes, these are the two terms, which will tell me about the internal structure present in the molecule. Going further, we can say that this will have impact in our measurements as well.

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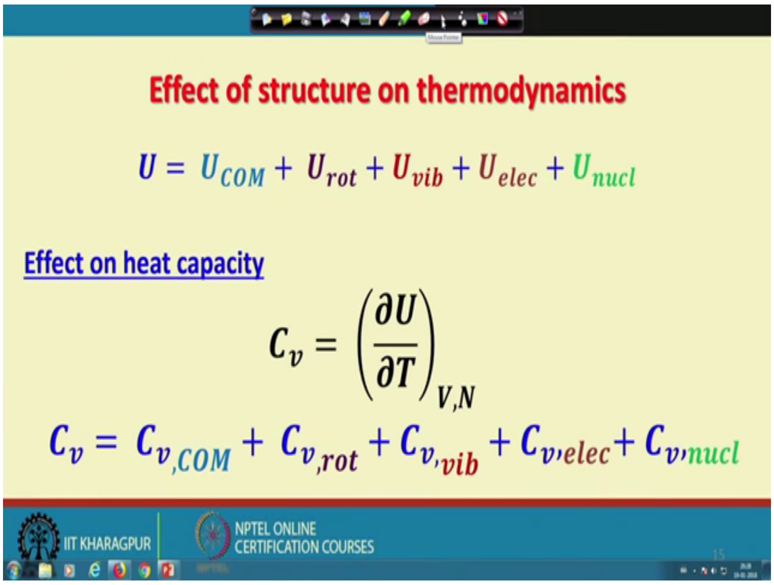

Effect of structure on thermodynamics

$$U = U_{COM} + U_{rot} + U_{vib} + U_{elec} + U_{nucl}$$

Effect on heat capacity

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

$$C_v = C_{v,COM} + C_{v,rot} + C_{v,vib} + C_{v,elec} + C_{v,nucl}$$

When I measure then I am basically measuring properties like heat capacity. By definition heat capacity is derivative of U; and U is separable into all these terms for the non interacting particles. And therefore, while measure I should be able to separate out contributions that arise from the center of mass, the rotational motion, the vibrational motion of the bond about its equilibrium bond length and also contributions coming from electronic and the nuclear degrees of freedom. So, is it possible to actually separate out these? The answer is yes, it is possible.

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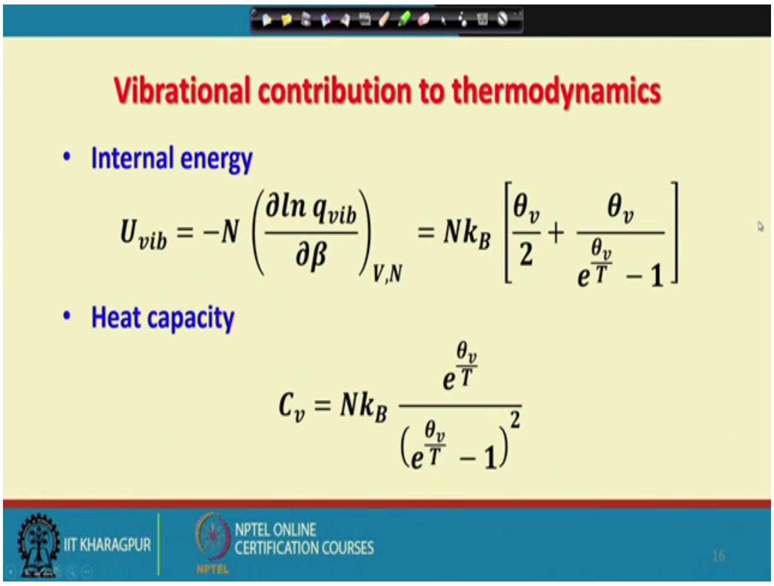

Vibrational contribution to thermodynamics

- Internal energy

$$U_{vib} = -N\left(\frac{\partial \ln q_{vib}}{\partial \beta}\right)_{V,N} = Nk_B\left[\frac{\theta_v}{2} + \frac{\theta_v}{e^{\frac{\theta_v}{T}} - 1}\right]$$

- Heat capacity

$$C_v = Nk_B \frac{e^{\frac{\theta_v}{T}}}{\left(e^{\frac{\theta_v}{T}} - 1\right)^2}$$

Because if you look at the for this diatomic case, what is the vibrational contribution to the internal energy that is nothing but you know ln q vib you take a del del beta of this quantity at constant volume and number of particles. You see that what I have is one term which is theta v by 2 plus some term which is coming here. And the heat capacity then takes up the following form. So, these terms were not there when I talked about the monatomic case, you can go back and check that very easily.

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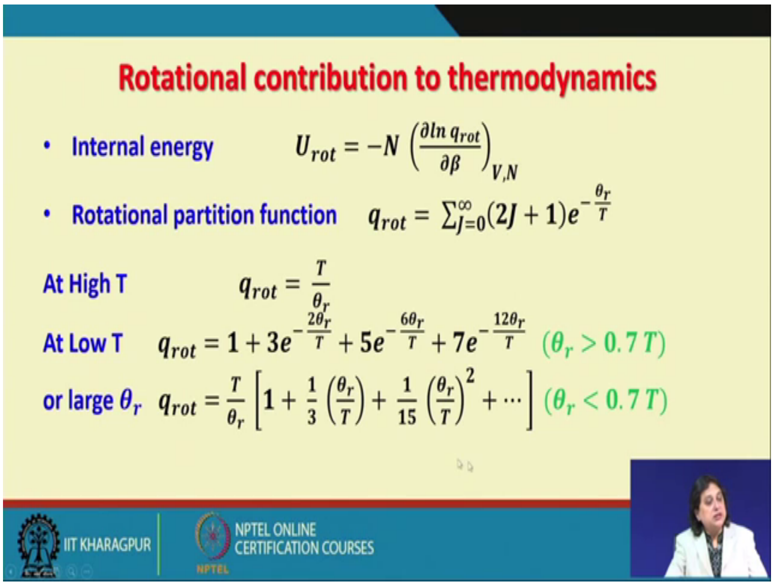

Rotational contribution to thermodynamics

- Internal energy $U_{rot} = -N\left(\frac{\partial \ln q_{rot}}{\partial \beta}\right)_{V,N}$
- Rotational partition function $q_{rot} = \sum_{J=0}^{\infty}(2J+1)e^{-\frac{\theta_r}{T}}$

At High T $q_{rot} = \frac{T}{\theta_r}$

At Low T $q_{rot} = 1 + 3e^{-\frac{2\theta_r}{T}} + 5e^{-\frac{6\theta_r}{T}} + 7e^{-\frac{12\theta_r}{T}}$ $(\theta_r > 0.7\,T)$

or large θ_r $q_{rot} = \frac{T}{\theta_r}\left[1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \cdots\right]$ $(\theta_r < 0.7\,T)$

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Then what happens is you can also find out the rotational contribution. Here actually before you go and try out the derivative of the rotational partition function, actually this infinite series sum can be simplified at different ranges, which are pretty well known. And as you can see that instead of evaluating an infinite summation at very high temperature, we can either have q rot given by t by theta r or by a finite summation or if the theta r values are large then some other summations are possible.

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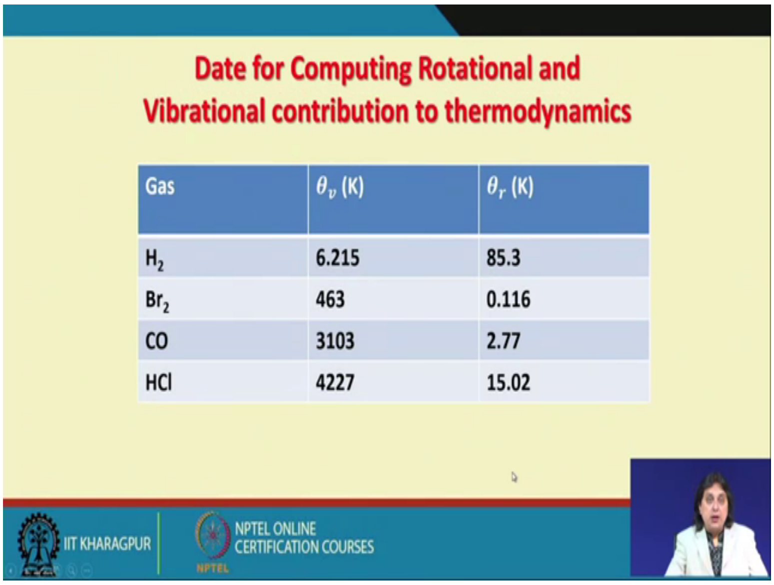

Date for Computing Rotational and Vibrational contribution to thermodynamics

Gas	θ_v (K)	θ_r (K)
H_2	6.215	85.3
Br_2	463	0.116
CO	3103	2.77
HCl	4227	15.02

And so if you know the theta v and theta r values from literature which has been tabulated by carrying out different kind of experiments. Then one can go ahead and find out what is going to be the vibrational contribution to the overall heat capacity of the ideal diatomic gas or one can even assess what is going to be the rotational contribution to the specific heat. Or in other words, when you sub, when you are looking at measuring specific heat, what you are doing is you are supplying changing the temperature of the system under either constant volume or constant pressure condition. In this case, at constant volume, you are essentially looking at what is the amount of energy that for this particular system is required to excite some population amongst its rotational energy states.

What fraction of energy will be used up in changing the population of the rotational energy states, what fraction will be used to change the population of the vibrational states. And if at all the amount of energy that you give is sufficient to cause a change in population as you go from the ground electronic state to the excited first or the second excited electronic state. So, when you do a measurement, you do not have any idea as to which part of the total supplied energy is being partitioned into the different underlying microscopic degrees of freedom available to the system.

So, by using statistical thermodynamics we can precisely do that, but the point to note down here is we have been able to do it only for the ideal gases. But even then it is a jointly forward, we started from the Hamiltonian of the system, we looked at a wide variety of data from experiments, we understood how to separate out the contributions of the underlying quantized degrees of freedom into separate contribution, and calculate the thermodynamics of the ideal gas in this case. In next lectures, we will have a closer look at the different quantities, their relative magnitudes, and whether the structure is going to be important in controlling the overall thermodynamic property of the system.

Thank you.