Fundamentals of Spectroscopy

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Lecture-12
Rotational Spectroscopy: Correspondence between Linear Motion and Rotational Motion

Hello everyone, welcome to this lecture. In this lecture, we will start a new module where we will look into rotational spectroscopy in detail. So, as we have already discussed before we can have rotational spectroscopy in the microwave region of the electromagnetic spectrum.

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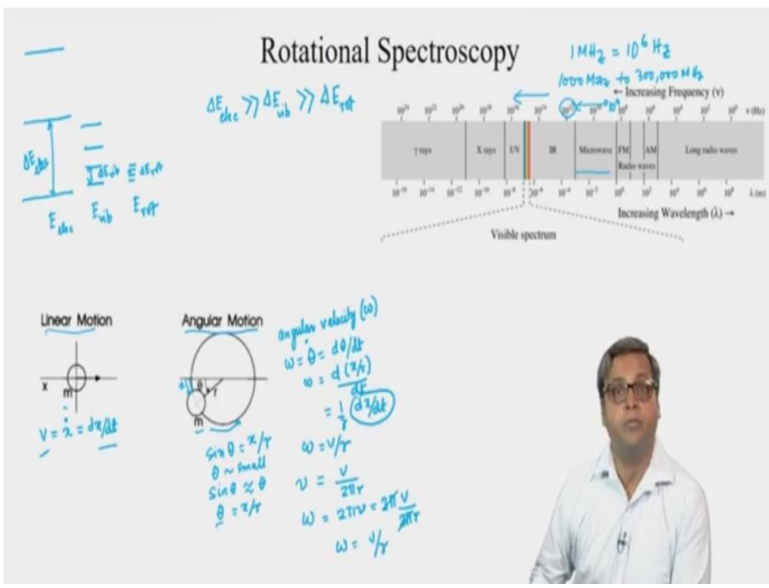

So, let us look into the electromagnetic spectrum again. So, this is the microwave region. So, the frequency range for the microwave electromagnetic region is from 1000 megahertz to 300,000 megahertz and we know that 1 megahertz equals 10 to the power 6 hertz. So, roughly speaking, so, the microwave region falls between 10 to the power 9 to 10 to the power 12 hertz and in this electromagnetic spectrum the frequency is increasing towards the left and as we have also discussed before for this different transitions like electronic rotational vibrational.

So, the delta E electronic is much better than delta E vibrational which is much greater than delta E rotation. So, if we draw the energy levels, let us say we have this electronic energy levels E electronic. So, this is my delta E electronic. So, for each electronic energy level, we have these different vibrational energy levels this is E vibrational. So, a transition here the energy difference is delta E vibrational, and for each vibrational level, there are different rotational levels.

So, this is delta E rotational, and we are plotting here the rotational levels. So, because today we are talking about rotation or rotational spectroscopy, let us consider a rotating rigid body the classical mechanics of rotational motion of a rigid body is relatively complicated. So, it is useful to note the extensive correspondence between a linear motion and the angular motion or the rotational motion of a point particle of mass m. So, let us consider this particle of mass m is rotating in a circle of radius r.

So, for us small displacement x from any point on the circle, we can assume this small segment is linear. That is, although this is linear it is part of this circumference of the circle. So, we can write sin theta equals x by r. So, because we have considered this displacement to be very small. So, the theta actually is also very small, and because it is small, we can write sin theta is approximately equal to theta. So, because sin theta is approximately equal to theta, we can write theta equals x / r. So, here r is a constant as the particle is rotating in a circle of constant radius.

However, x is a variable and so is theta, so thus we can think the distance in linear motion is analogous to the angle swept out by the particle in angular or rotational motion, and we also know any linear motion is associated with a linear velocity v, which is given by x dot that is dx dt. So, for angular motion, similarly, we have a velocity, which is known as angular velocity, which is denoted by omega and omega is given by as we see from the analogy from the linear motion, omega is given by theta dot that is d theta dt.

So, because theta is x / r we can right omega equals d of x / r dt and as I already mentioned, the particle of mass m is rotating in a circle of constant radius. So r is a constant. So you can write 1 / r dx dt and this dx dt is the velocity, as a linear velocity. So we can write omega equals v / r. So we can think this angular velocity as the number of radians of angle swept out in any time by a rotating system. So we can also calculate that for a particle moving with a linear velocity v, the frequency nu or how many revolutions of circumference 2 pi r.

That is the circumference of the circle with radius r is completed per unit time. So, nu is v / 2 pi r, and as for every revolution, it sweeps out an angle of 2 pi. or in other words, we know that omega equals 2 pi nu. So, we can write omega equals 2 pi and nu is v / 2 pi r. So, we can again show that omega equals v / r.

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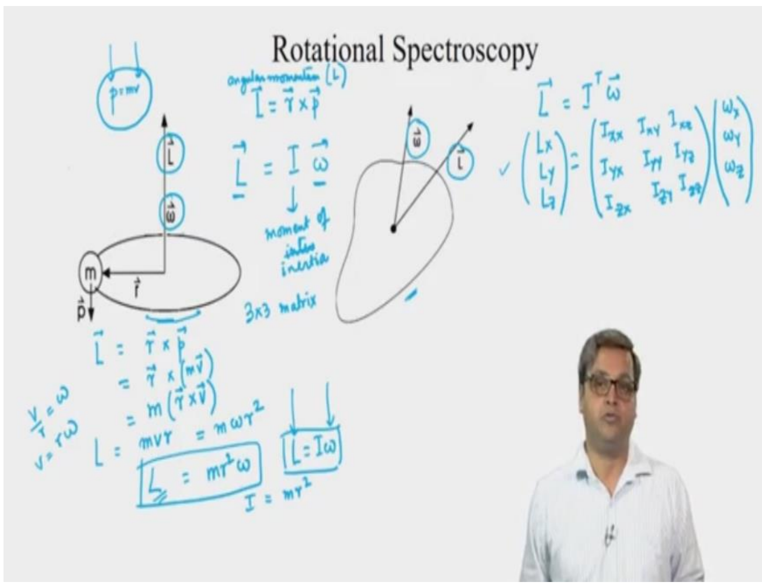

So, as a linearly moving body has linear momentum given by p equals mv. Our rotating body has also momentum known as the angular momentum which is denoted by L. So, we can see, L is given by r cross p. So if r and p are in the same direction, then the cross border becomes 0. So L become 0 otherwise L exists. So for a single particle I shown here in this figure, we can see, the omega and L are vectors that point out of the plane of rotation.

However, we should remember that if an extended object is rotating this omega and L need not point in the same direction and so, in general L is related to omega with the relation L equals I omega. So, here we see this angular momentum L and the angular velocity omega are vectors. So, if they are in the same direction, as we see in this figure where single particle of mass m is rotating, then I is a scalar quantity, but in general, they are not in the same direction as mentioned, for this extended object, for example, a molecule.

So, I is defined as a tensor and I is known as the moment of inertia so, this tensor is represented by a matrix. So, if you consider a 3 dimensional space, it is a 3 / 3 matrix. In other words, in a 3 / 3 matrix, we have 9 components. So we can write L equals I, which is a tensor omega is a vector in 3 dimensional space we can write L as Lx Ly Lz equals I is a 3 by 3 matrix that is Ixx, Ixy, Ixz, Iyx, Iyy, Iyz, Izx, Izy, Izz and then the angular velocity which is also vector we can write omega x omega y omega z.

So, in a 3 dimensional space we can represent L = I omega this way. So, now let us go back to a single particle rotating in a circle. So, L = r cross p. So, p we know is p is given by p = mv so, we can write that is r cross mv, we can write this as m r cross v and because r and v are perpendicular. So we can write L equals mvr, and as we know v / r = omega or v = r omega we can write L = m omega r square.

So, if we compare this expression that is L = mr square omega with the other expression that is L = I omega. So, we can see the analogy that I = m r square and also, L is the angular momentum and p is the linear momentum. So we see that p = mv. So linear momentum and is a linear velocity. So, we have angular momentum L, we have angular velocity omega. So, comparing this p = mv with L = I omega, grossly we can think what a mass is for linear motion, moment of inertia is for rotational motion.

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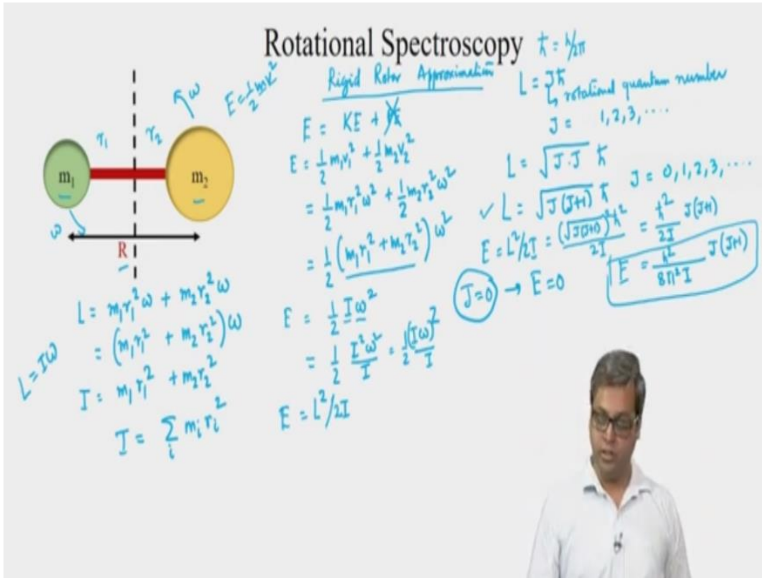

So, now moving back to polyatomic molecules, so, diatomic molecules are the easiest examples of polyatomic molecules. So, let us start with diatomic molecules and also although the diatomic molecules undergo simultaneous rotation and vibration, let us just consider the rotational effects for now. So, this is known as the rigid rotor approximation so, we will first consider diatomic rigid rotors which means the bond length is not changing just the molecule is rotating.

So, for a diatomic molecule with masses m 1 and m 2 and bond length R and such that m 1 is r 1 distance away from the center of mass and m 2 is r 2 distance away from the center of mass. So, if this molecule is rotating, and because both the atoms are rotating with constant angular velocity omega, so we can write L = m 1 r 1 square omega + m 2 r 2 square omega that is m 1 r 1 square + m 2 r 2 square omega. So, if we compare this expression with L = I omega, so we can get or we can see that I = m 1 r 1 square + m 2 r 2 square.

So, when we were talking about a single rotating particle, we saw I is m r square, where mass where m was the mass of the particle. And when we have a diatomic molecule with mass is m 1 and m 2 then I is m 1 r 1 square + m 2 r 2 square. So, in general, the expression of I for a polyatomic molecule is I = summation i m i r i square, where r i is the distance of the highest particle of mass m i from the center of mass of the system. So after we have considered the angular momentum L let us now consider the energy of a rotating diatomic rigid rotor.

So a rotating molecule has no potential energy. So normally energy is given by the sum of kinetic energy plus potential energy. In this particular case, the potential energy is 0. So, the energy or the total energy counts only from the kinetic energy, so thus we can write E = 1 / 2 m 1 v 1 square + 1 / 2 m 2 v 2 square and putting the value of v we can half m 1 r 1 square omega square + 1 / 2 m 2 r 2 square omega square.

So, that is 1 / 2 m 1 r 1 square + m 2 r 2 square omega square and as we know, this m 1 r 1 square + m 2 r 2 square is nothing, but the moment of inertia I so the energy becomes half I omega square. So, now, let us look into this expression and the analogy from the linear motion, for linear motion the kinetic energy is given by equals half mv square. So, as we saw, the analogous part of mass in linear motion is moment of inertia in the rotational motion and here we have linear velocity here we have angular velocity.

So, half mv square in linear motion, it is half I omega square in angular motion. So, we can write this half I omega square as half I square omega square / I that is half I omega whole square / I. So, we know I omega is the angular momentum L. So this energy expression becomes L square / 2I, again we know in linear motion, the linear momentum p. So energy or the kinetic energy is related to p / p square / 2 m. so here the kinetic energy in the rotational motion is related to the angular momentum by L square / 2I.

So, now, let us move on to quantum mechanics. Although a complete quantum mechanical description can we obtained by solving the Schrödinger equation for a rotating linear system. At first it is more informative to see what is obtained by applying bortz condition that the angular momentum is quantized. We know the angular momentum is quantize in the units of h cross that is h / 2 pi. So, the quantized angular momentum condition requires L that is angular momentum is J h cross, where J is the rotational quantum number and J can take values like 1 2 3.

So, we can write L equals J h cross as L equals root over J times J times h cross but the correct quantum mechanical treatment however, gives if J is an integral quantum number, the angular momentum L is given by not as square root of J square h cross, but root over J into J + 1 h cross. So, we can see that energy which is given by L square / 2I we can write as root over J times J + 1 square h cross square / 2I, that is h cross square / 2I J x J + 1 and because h cross is h / 2pi, so we can write this as h square / 8 pi square I J times J + 1

So, we can obtain the same expression of energy that is equals 8 square / 8 pi square I times J times J + 1 by solving the Schrodinger equation. So, because J is the rotational quantum number we see that as the value of J increases, the energy increases. So, if we go from 0 to 1 to 2 to J equals 3, the energy of this rotating particle or the rotating a molecule will increase. So, when J = 0, then the energy expression becomes 0 or as if the molecule is not rotating.

So, now, if we look into the angular momentum expression, we see the angular momentum increases with increasing J. So what does it mean? Angular momentum is given by I omega and I is nothing but related to the masses of the atoms and the distance or the radius r which is constant for rotational motion. So, that will not change. So, if I change J, what will change is the angular velocity. So, what we might think is as we have increased in J or increased the value of J, the molecule will start rotating in a like a larger velocity, larger angular velocity. So, before we end this lecture.

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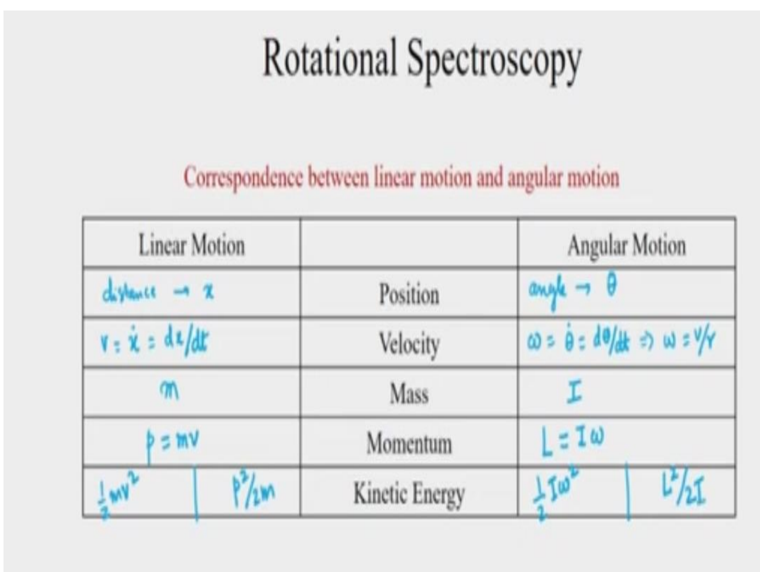

Let us look back to the correspondence between the linear motion and the angular motion. So, if you want to define position in linear motion, it is defined in terms of distance, that is x. In angular motion, it is defined in terms of angle that is given by theta. In linear motion, there is a linear velocity which is given by v that is x star that is dx dt in angular motion, there is an angular velocity omega that is given by theta star that is d theta dt, and we saw that omega = v r. The mass for a linear motion is the mass m.

The analogous thing in the angular motion is the moment of inertia. So, the momentum or the linear momentum for linear motion is p = mv. With this correspondence we can say the angular momentum L equals what is equivalent to mass that is I and what is equivalent to linear velocity is linear motion and angular of motion we have angular velocity So, equals how you make similarly for kinetic energy, expression is half mv square, or p square / 2m and an angular motion, we have write half I angular velocity square, or angular momentum square / 2I.