Chemistry II: Introduction to Molecular Spectroscopy
Prof. Mangala Sunder
Department of Chemistry and Biochemistry
Indian Institute of Technology, Madras

Lecture – 22
Introduction to Tensors

Welcome back to the lectures on chemistry and the lectures on molecular spectroscopy. This is the last week of this particular course and what I propose to do is to give you some topics for you to think about along with one more tutorial, but one of these topics will definitely be also part of it be part of the examination namely Raman spectroscopy.

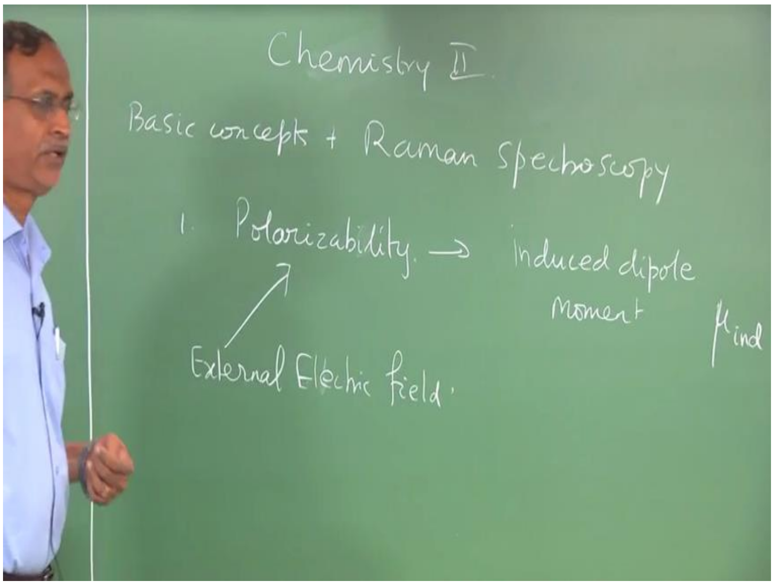
Raman spectroscopy is the important spectroscopy which was discovered by Professor Chandrashekara Venkata Raman; sir C V Raman. He won the Nobel Prize in 1930 for his discovery of the effect by what is called as the scattering effect. It is unique in the entire molecular spectroscopy. In that it studies the scattered light whereas, every other branch of spectroscopy that T have taught you so far studies either the absorbed light or it studies the emitted light and the scattered light is usually studied by passing the radiation through the sample, but looking at the lights scattered from the sample at 90 degrees to the sample tube. So, we will see a little bit of that, but in order to understand even the rudimentary aspects of Raman spectroscopy one needs to understand what is called the concept of polarizability.

Polarizability is not easy to describe even in elementary terms or without (Refer Time: 02:09) mathematical terms therefore, what I would do is that this segment of the lecture I will not talk about the Raman spectroscopy, but I will introduce you to the idea what are called the tensors. You already have being using tensors in an indirect fashion in the sense you have being using moment of inertia. You have been using it as three components for asymmetric top, two components of moment of inertia for symmetric top and one component for (Refer Time: 02:38) top, but those are what are called the principle moments if inertia and they are special quantities. Moment of inertia as it is what is called as a second rank tensor in mathematical sense.

In the same way polarizability of a molecule which is the extent to which the molecular electronic distribution gets distorted in the presence of an external electric field and on top of that external electric field it gets further distorted when the molecule itself is undergoing vibrational motion. So, there are two concepts which are involved; the distortion of the molecular electric field due to the external field and the distortion of the molecular electric field due to the internal motion in a sense you have seen part of this in a different concepts namely in the dipole moment where the charge centers simply separate and therefore, the dipole variation is what is studied in absorption and emission spectroscopy.

On the other hand in Raman spectroscopy it is the polarizability which results in what is known as an induced dipole moment, and the extent of the induced dipole moment is directly proportional in the linear approximation.

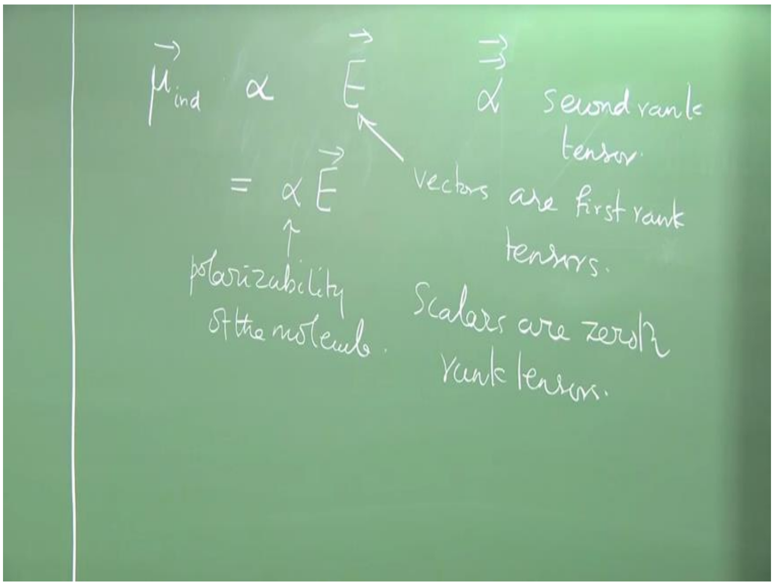
(Refer Slide Time: 04:05)



So, what we wanted to do is basic concepts plus Raman spectroscopy in this week's lecture. Some of these ideas are directly given as tutorial also applied as tutorial which means you should study them for the exam and the others are given to you as information.

So, the first thing we will study is what is called the polarizability and this leads to what is known as the induced dipole moment in the molecule; mu induced this is due to the presence of the external electric field.

(Refer Slide Time: 05:14)

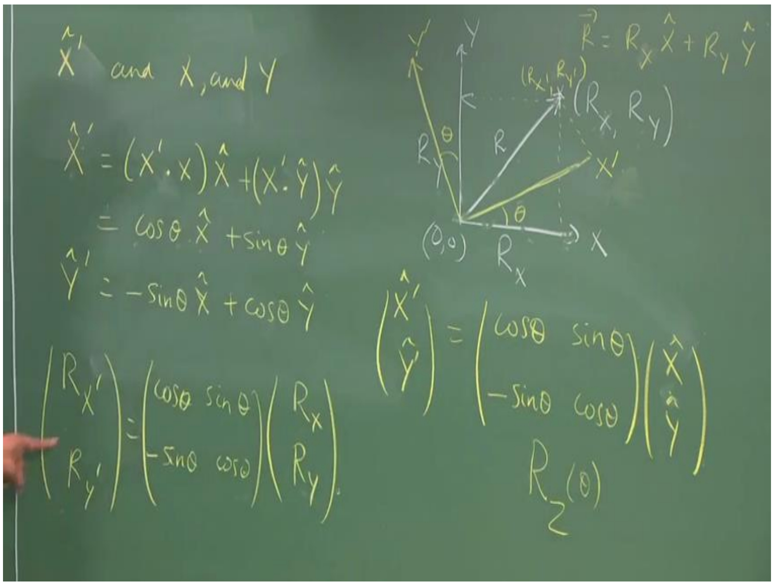


So, what is the relation? The simple relation is that the induced dipole moment which is a vector is proportional to the applied electric field which is also a vector, but the important thing to note is that the two vectors are proportional; that means, the proportionality constant can be a constant that is assuming that the induced dipole moment is in the same directions as the electric field. Therefore, the two vectors are sort of collinear; I mean they are in the same direction; if it is a constant the proportionality constant unfortunately this a proportionality constant, but in the next step I will right this as alpha E that alpha called the polarizability of the molecule.

Now, if the alpha is a scalar; quite obviously, the induced dipole moment and the electric field are in the same direction, but it does not have to be the induced dipole moment need not be in the direction of the applied field. Then what happens? Then how can two vectors be related to each other? That is when you need idea what is known as a second rank tensor. Alpha is actually a second rank tensor and the symbol for that is to write two arrows and in order to make you feel comfortable with that terminology I must tell you that vectors that we have here are first rank tensors and scalars are 0-th rank tensors. So, in this mathematical representations of the polarizability as well as the moment of inertia you will realize when you studying more and more that the polarizability and moment of inertia and later when we study the chemical shift in the nuclear magnetic resonance when a related time that I will give you a course on the chemical shift is also known as is also related to what is called the chemical shielding tensor which is also your second rank tensor.

Therefore things gets a little more complicated as we go higher up in the understanding of these concepts and we start exploring them, but you do not need to get very worried about what is a tensor how do I understand it. So, the rest of these 5 or 10 minutes, that I have I will explain to you what is meant by the tensor not what how do we get to a tensor and so on just to give you an introductory concept.

(Refer Slide Time: 08:40)



All of you know that in two dimensions you have two mutually perpendicular axis X and Y and any point in the coordinate plane that is in the two dimensional plane represents a vector which is pointing in this direction and if you write to the coefficients as R X and R Y; the X coordinate is the projection of the vector R which is from 0 this the 0 the origin the projection of R on to the X axis gives you the length R X and the projection of R on the Y axis gives you R Y. Those are the coordinate points that you have being plotting into dimensions.

Now, if instead of this X Y axis suppose we use a slightly rotated axis by an angle theta that is X Y axis; the axis system is rotated by an angle theta, which means this new Y prime and the X prime or about or an angle theta from the old X and Y. Now what is the relation between X prime, X Y prime, X and Y and Y prime X and Y? What is the relation between X prime and X and Y? These are unique vectors; you can write X as a unique vector and R X is the number that multiplies the unit vector to give the component in the X direction and then to that you add the vector that is along the Y axis by multiplying the unit vector along the Y axis with the magnitude R Y and you add that the triangle the parallelogram law tells you or the triangle whatever it is Pythagoras theorem you know all these things they tell you essentially what is the vector R is.

So, if you write the vector R in this notation; it is R X times X unit vector plus R Y Y unit vector. Now X prime is now the unit vector in this direction and obviously it has components in both the directions of X and Y therefore, X prime has components in both this directions therefore, the best way to write X prime is to write the scalar product of X prime on to the X axis times the unit vector X plus the scalar product of X prime on to the Y axis times the unit vector Y. Exactly the same way you would write the R quantity this way.

So, in a coordinate rotation this is nothing, but cos theta times X plus sine theta times Y. The scalar product between these two vectors X and X prime unit vectors is of course, a magnitude of X times the magnitude of X prime times are cos theta the angle between the two were given that since the magnitudes are all 1; you have cos theta times X and sine theta times Y and likewise you write Y prime as minus sine theta times X plus cos theta times Y.

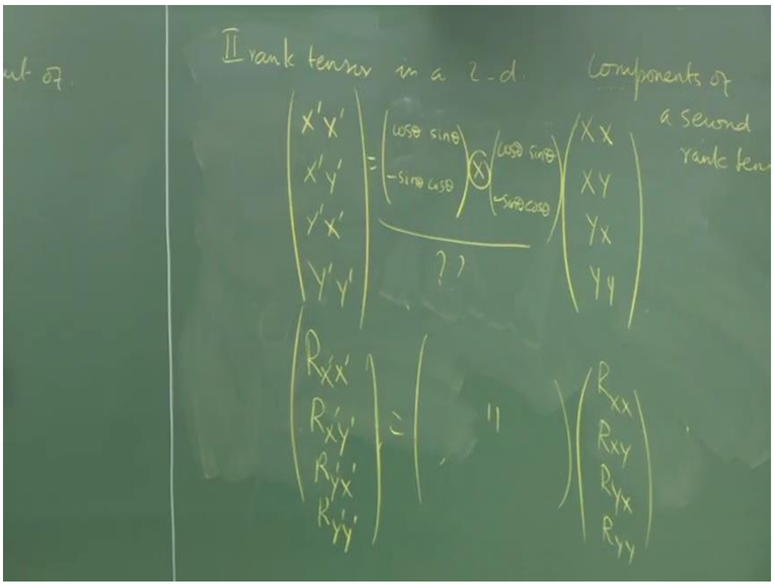
Now, this is the property of the rotated coordinate system and it is relation to the unrotated coordinate system. That is under coordinate rotations the quantity X prime and Y prime the two unit vectors are connected to the two unrotated coordinate system by this matrix relation minus sine theta cos theta times X Y all are unit vectors. T his is called the rotation matrix actually about the Z axis which does not exist in this plane, but you know it is an axis about which is perpendicular to that because the rotation is happening in plane and the rotation basically tells you that the rotation axis is perpendicular to the plane of rotation therefore, normally we write this as R Z theta, but the Z coordinate does not exist in two dimensional plane its basically perpendicular to that plane.

Therefore what is a vector? Any pair of quantities X and Y; now will have a new component R X prime and R Y prime because the axis system is now the X prime and Y prime. The relation between R X prime R Y prime and R X and R Y; if this relation is the same relation that you have there cos theta sine theta minus sine theta cos theta; then the two quantities R X and R Y are said to be components of the vector; this is the definition of vector not something that you call as a quantity with the direction and the quantity with the magnitude that is how you will get introduced to the elementary idea, but a proper mathematical definition of a vector is vectors are the number of components of the given quantity whose transformation property from one coordinate system to another coordinate system is identical this is the transformation matrix that takes R X, R Y to R X prime R Y prime.

This transformation property is identical to the transformation property of the coordinate system themselves the unrotated coordinate system to the rotated coordinate system whatever matrix that transforms the coordinate system if it also gives you the new vector quantities from the old vector quantities of any pair of numbers then those pair of numbers form the vector; this is the definition.

In three dimension you have to add the Z axis to it and then what is meant by a rotation in three dimension is slightly more complicated than your rotation in two dimension because your rotation in two dimension involves only one angle; your rotation in three dimension involves three angles and these are called Euler angles. Therefore, let us get to the point even with this two dimensional representation what is meant by a second rank tensor in a two dimensional system.

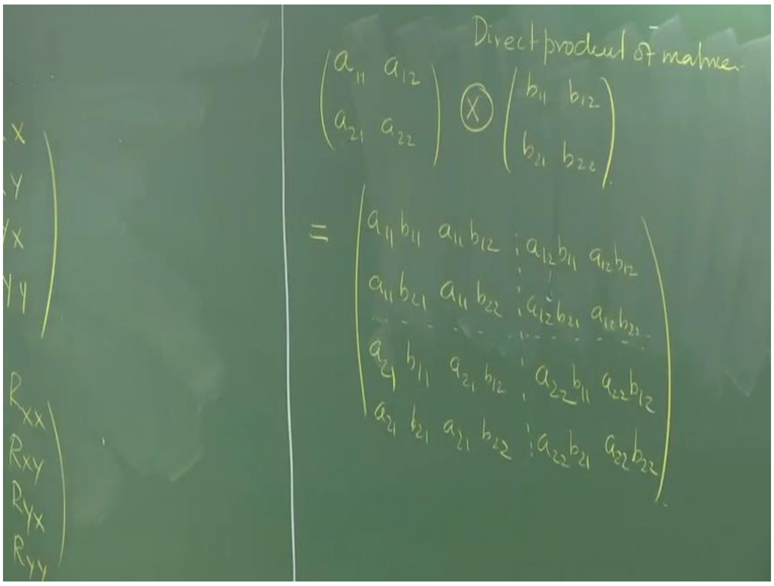
(Refer Slide Time: 16:15)



In a two coordinate system X and Y; the second rank tensor is essentially four components and in the case of coordinates the components are written as XX, XY, YX, YY; they are the products the regular multiples and these four components under coordinate rotation by the same value of theta these four components become the four coordinates becomes X prime X prime, X prime Y prime, Y prime X prime, Y prime Y prime and there is a rotation matrix and these are called the unit tensors of the second rank in the two dimensional system and therefore, any quantity which has four components whose properties under coordinate rotation follow from the four components in the unrotated directions to the four components in the new rotated direction and connected by the same rotation matrix as the rotation matrix that connects the coordinate systems those four quantities are called components of a second rank tensor.

These four; the same rotation matrix ditto and they are connected to the unrotated components X Y, YX and Y Y. These are called the second rank tensor and what is this rotation matrix and this rotation matrix I mean what is it compared to the rotation matrix 2 by 2 that we talked about? There is something called the direct product of let me go to the side something called the direct product of these rotation matrices.

(Refer Slide Time: 18:46)



I will be done in another 3 minutes so that you should get a picture that if you take a matrix a11, a12, a21, a22; the direct product of the matrix with for example itself let us write another one b11, b12, b21, b22 is equal to a11 multiplying all the four as four elements b11, a11 b12, a11 b21, a11 b22 let us sort of put a (Refer Time: 19:25) partition so that we know what we are writing and this set of the four elements are obtained by multiplying a12 with all the four elements here therefore, you get a12 b11, a12 b12, a12 b21, and a12 b22 and the lower two elements are a21 the second row multiplying all the four elements a21 b11, a21 b12, a21 b21, a21 b22 and the last set is the second row second column a22 b11, a22 b21, a22 b12 and a22 b22. This is called the direct product; this symbol represents direct product of two matrices.

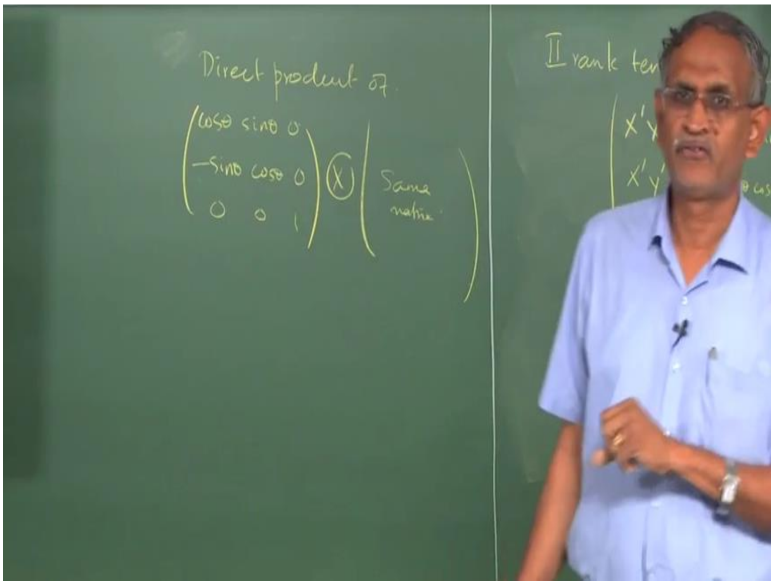
Now what you have to do in order get this rotation matrix is to do the direct product of the two rotation matrixes that you had; mainly the one rotation matrix cos theta sine theta that you had, so you would write this as cos theta sine theta minus sine theta cos theta direct product of cos theta sine theta minus sine theta cos theta ok.

Therefore if you took the direct product of this you will get a four by four matrix of which the first two this square is cos theta multiplying all these four elements and next is the sine theta applying all the four minus sine theta multiplying. So, that is known as the direct product of rotation matrixes and this direct product defines the components of a second rank tensor.

Under coordinate rotation; the unit tensors the coordinate system defining these unit tensors they will undergo transformation to give you this and therefore, any pair of four quantities that you have vectorial in one dimension the two quantities can be vector; therefore, any pair of four quantities which follow the same multiplication property for coordinate transfer is known as a second rank tensor.

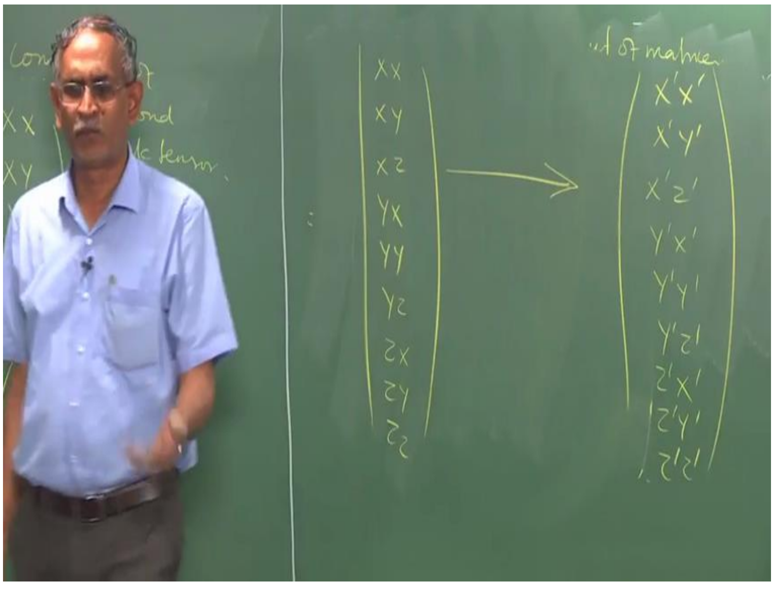
The same idea when it is extended to three dimensions with the help of a 3 by 3 rotation matrix because you have X Y Z it is known as a second rank tensor in three dimensions.

(Refer Slide Time: 22:42)



So, what I would suggest you is to try out as the as an example what is a direct product of this one what is the result; do this multiplication and I will give you one more which is cos theta sine theta 0 minus sine theta cos theta 0001 with itself the same matrix. Put the same matrix here. So, with a simple practical exercise of this kind will give you some confidence in the elementary mathematics associated with what are known as tensors and therefore, now you see is in three dimensions that instead of four quantities that we talked about in two dimensions for the second rank it will be three by three multiply multiplying 3 by 3.

(Refer Slide Time: 23:50)



And therefore, you will have nine quantities namely XX, XY, XZ, YX, YY, YZ, ZX, ZY, ZZ. How do they transfer form during coordinator rotation to the nine quantities X prime X prime, X prime Y prime, X prime Z prime, Y prime X prime, Y prime Y prime, Y prime Z prime and Z prime X prime, Z prime Y prime, Z prime Z prime.

And correspondingly like moment of inertia, the polarizability, mechanical the shielding tensor all have nine components, but they have additional special properties called they are all symmetric and therefore, what happens is certain components are equal and finally, you realize that the concept of tensor is ultimately to find the correct direction in which we have the minimum set of experimentally measurable quantities and those are called principle movements of inertia principle values for polarizability and principle value for chemical shielding tensor.

We will use some of these ideas in the next lecture in determining what is known as the Raman Effect therefore, this is a preliminary lecture this is not part of the examination for this course, but this is something important for you to understand if you want to know more about spectroscopy in the future.

Thank you very much.