Chemistry II: Introduction to Molecular Spectroscopy

Prof. Mangala Sunder
Department of Chemistry and Biochemistry
Indian Institute of Technology, Madras

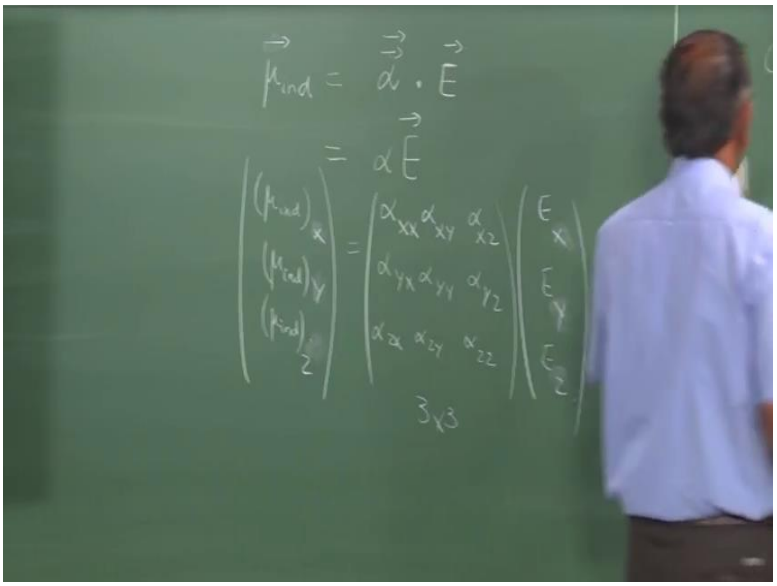
Lecture – 23
Polarizability Tensors

Welcome back to the lectures in chemistry and the introduction to molecular spectroscopy. I just finished in the last lecture, with a very simple and a quick definition of what is known as a tensor and I think it is important for you to understand even in a rudimentary form, the idea of a tensor because the molecular spectroscopy, a spectroscopy quantities is that you deal with some of them, have components from the higher rank tensors and some of them are vectors. The dipole moment is a vector, for example, the Polarizability is a second rank tensor. As I told you earlier, the high per Polarizability, which is often measure for non-linear spectroscopic systems, is a third rank tensor and then there are higher rank tonsorial properties, which are often study.

In the introductory course, we do not know to go as far as the, but in even the study of an elementary account of Raman spectroscopy, it is important for us to have an appreciation of the idea of tensor. Now if you remember, we will start with the Polarizability tensor first.

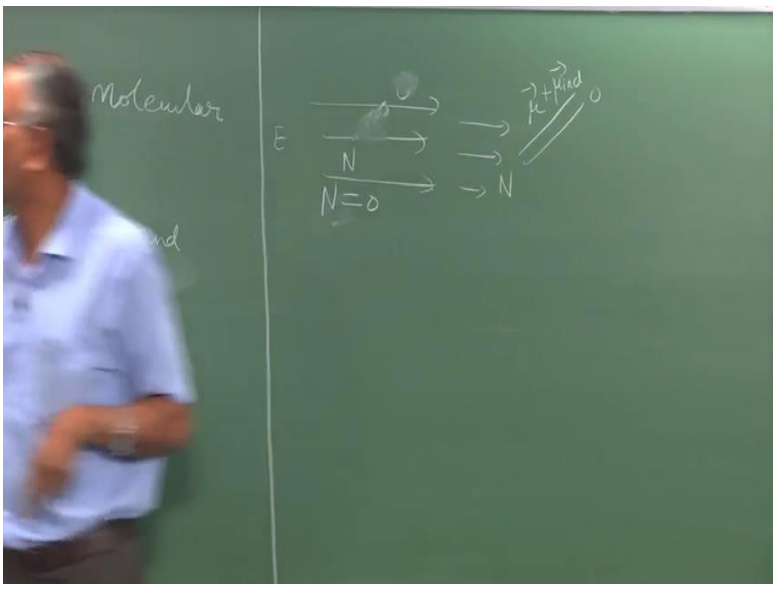
In this lecture and if there is enough time, I will also introduce you to the idea of moment of inertia, being the second rank tensor and what the components are.

(Refer Slide Time: 01:45)



First let us write the relation that we left in between, namely the induced dipole moment mu which is vector in terms of a second rank tensor alpha, which changes the electric field to give you the induced dipole movement what exactly is this picture? Suppose you have electric fields in this direction and you have a molecule for example, say N O.

(Refer Slide Time: 02:13)



Let us consider N O to be in this direction, suppose the field is, in this direction is moving in this right field, is pointing in this direction and N O molecule is sitting in a perpendicular direction, you know that the bonding electron of the N O is between the 2

nitrogen and oxygen. The electron density is concentrated there and the electron density will try to adjust itself with the positive side of the electric field and the negative side of the electric field in such a way that the molecule will have a slight orientation and there may be a slight deformation of the electron density, if the fields are very large.

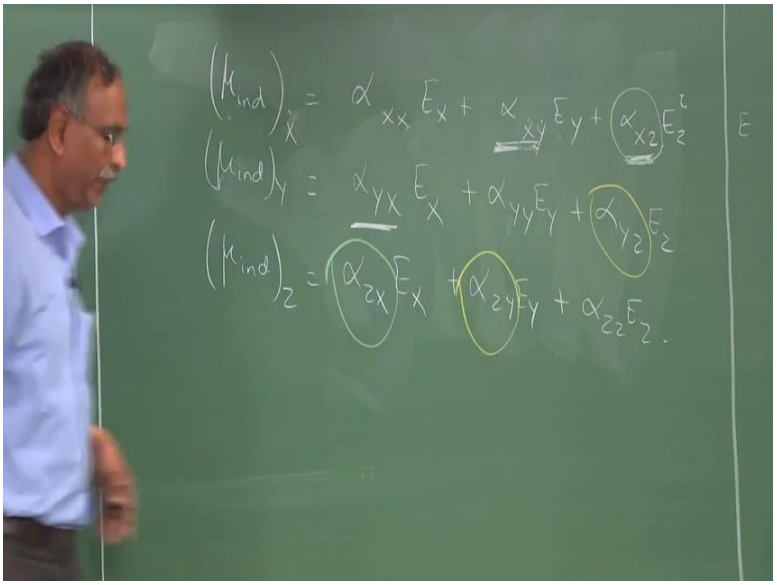
To what extent the molecule is able to polarize itself to adjust itself to the external field and undergo simple changes in its geometry, that number is given by the number is by this quantity in a certain form. If the molecule is like say H C M, it has the bending vibrational modes, it has stretching vibrational modes, it has a, what is also known as the I mean a symmetrical in the sense, both the hydrogen and nitrogen atom going 1 way and then the hydrogen and nitrogen atom going in the opposite direction and so on, that is a normal motion.

Now if you put such a molecule, which is undergoing vibration in an electric field, the electric field may induce an additional dipole movement and that induce to dipole movement is directly a function of the property of the electric field and remember, I put a double arrow on top of it instead of writing it simply as alpha E, because it is possible that induced dipole movement of say N O in the field in the presence of the field, see N O itself is undergoing some vibrations. If I have to write N double bond O there is a mu and now if this molecule is in the electric field E, there may be additional induced dipole movement and that may not be in the direction of the electric field and therefore, you have this quantity called that the second rank tensor.

Exactly how do we write this is a vector? Therefore, you have 3 components mu induced X, then mu induced Y and mu induced Z in the axis system which defines also the electric field. If the electric field is in the Z direction then you know in a plane perpendicular to the Z direction is where the X and Y axis are and with respect to that axis system, the mu induced is a vector. Therefore, it has 3 coordinates and if you put this together and the electric field itself has 3 components E X E Y and E Z in an arbitrary direction and suppose we will put this as 3 components then alpha is given by a 3 by 3 matrix and the components of alpha, the sub the indexes the indices that you see here is not 1 1 1 2 1 3, but they are related to the direction on this side as well as the direction of the component on this side, which is the effect. This is the cause, this is the effect and the alpha connects the cause to the effect and therefore, the directions of the cause and the effect are written as X X you write all of these as capitals X Y Z.

Then alpha X X times, E X meaning that this is the component, which tells you that the X component of the induced dipole movement with respect to the X component of the electric field and likewise alpha X Y alpha X Z and alpha Y X alpha Y Y alpha Y Z alpha Z X alpha Z Y alpha Z Z, what is this mean? This essentially means that the induced X component dipole movement mu induced.

(Refer Slide Time: 07:20)



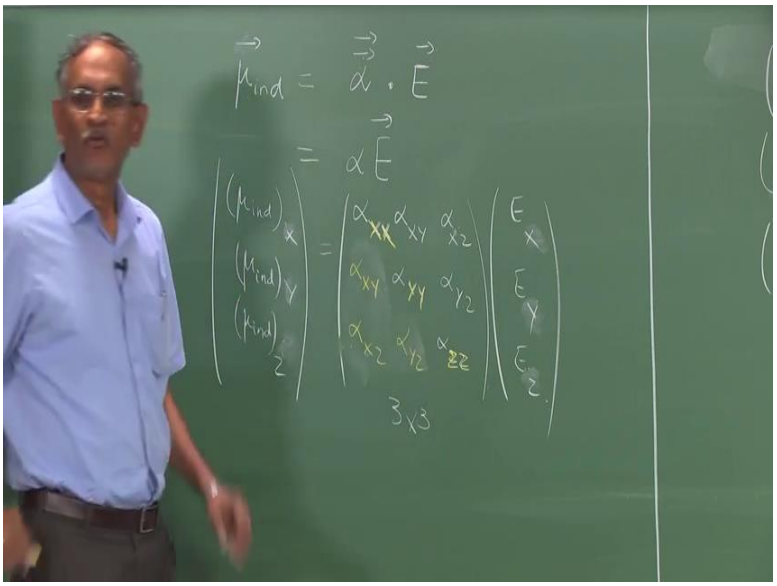
X is given by the effect of the E X alpha X X the E Y alpha Y Y and the E Z alpha, sorry alpha X Y and alpha X Z this relation that the induced dipole movement is actually a function of all the 3 components of the applied electric field and the respective co efficient connect them to give you the total value. This is the tonsorial relation. What about mu induce to Y? This is capital X, this is capital Y, it is all for Y X E X plus alpha Y Y E Y plus alpha Y Z E Z and likewise mu induced Z is alpha Z X E X plus alpha Z Y E Y plus alpha Z Z E Z. Therefore, you have got these 9 components. X X X Y all the way down to Z Z, these 9 components in the definition of the tenser that I gave you in the last lecture.

These 9 components behave under coordinate rotation the same way, the unit diodes, the X X X Y X Z, there are 9 unit diodes, these are these 9 diodes, how do they transform under the coordinate rotation? In the same way these quantities transform in the four ways they become the quantities of a second rank the component of a second rank tensor.

Now, 1 interesting thing is the fundamental property of the microscopy system appears to tell us now the X Y and Y X see the connection between them. They are equal first of all, that is a result that comes from the microscope consideration, and first of all you see the X Y is a component due to the Y component of the electric field inducing a change in the X. There is a mu induce to dipole moment, but in X component that connects X Y, connects E Y to mu induce to X Y, X connects the X component of the electric field lead into your Y component of the mu induced. They are switched around, there are beautiful principals known as there is a positive relation in basic physics. I do not want to say much about them.

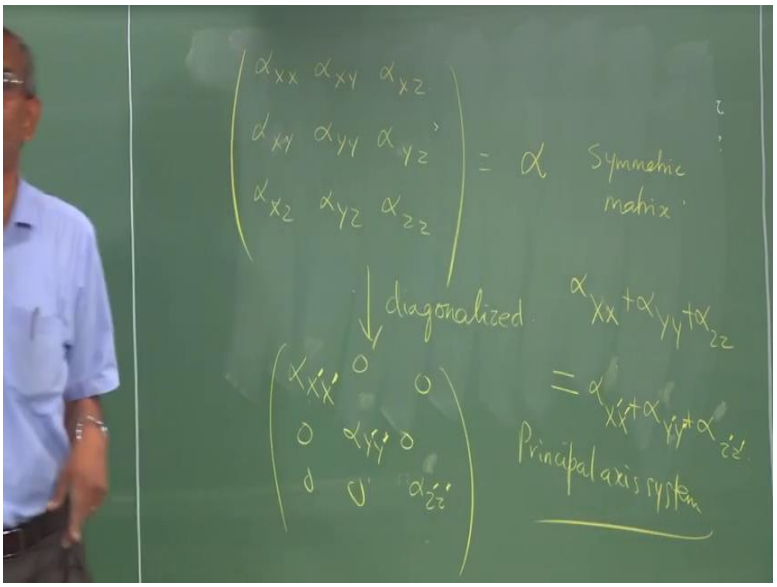
But in this case the property is that such quantities, which are connected with the reversal of directions of the electric field and the outcome, they are both equal by geometrical as well as the physical consideration. In the same way alpha X Z and let me write that alpha X Z and alpha D X are identical. Alpha Y X and alpha Z Y are identical. Therefore, what we have here is not 9 independent components, but only 6 independent components because all this of diagonal components, this is the diagonal, these are the 3 of diagonal components, this is the same as alpha X Y, this is the same of alpha X Z, diagonally opposite, diagonally opposite it is alpha Y Z.

(Refer Slide Time: 11:15)



What you have is essentially X X, X Y Y, Z Z, X Y, X Z, Y Z. 6 independent components for the Polarizability tensor that is one more. Let me start, this is with respect to the coordinate system X Y Z.

(Refer Slide Time: 11:56)



But all the matrix that we have here, the alpha X X, alpha X Y, alpha X Z, alpha X Y, alpha Y Y, alpha Y Z, alpha X Z, alpha Y Z, alpha Z , this matrix is called the second rank tensor matrix of alpha and it is a symmetric matrix. Symmetric matrices have the property that they can be diagonalized to give only what are known as diagonal elements; that means, this can be diagonalized to give the final form of sum alpha X X, prime alpha prime alpha Y Y prime, This is not the same as that, but it comes after that diagonalizing this matrix, we get alpha Z Z prime with 0s every were, else this property of transformation defines 3 angles or 3 real coordinates.

And therefore, of this 6 quantity that you have 6 independent quantities that you have, you reduce into only 3 independent quantities by removing the 3 quantities constrains as coordinates as rotation axis or rotation angles. Therefore, what is left over is 3, but there is 1 more property such a diagonalization, also ensures that the trace of the matrices alpha X X plus alpha Y Y plus alpha Z Z is always equal to alpha prime X X plus alpha prime Y Y plus alpha prime Z Z, that case of the matrices, the trace is some of the diagonal elements of the matrices, the some of the diagonal elements of the matrices. The trace of the matrices is invariant to the process of diagonalization. In this case, this is

a similarity transformation and this being a real matrices and symmetric matrices. This similarity transformation is also known as an orthogonal transformation.

Therefore what happen is that, not only do we have 6 quantities combined to what is called 3 quantities with respective some new axis system. Better would be to write this as X prime X prime Y prime Y prime Z prime Z prime to indicate that we have a new axis system. This is some fixed axis system and in the new axis system, we have only 3 quantities and therefore, accordingly this will also be X prime X prime Y prime Y prime and Z prime Z prime. This axis system is called the principal axis system therefore, our idea in doing experiment is to find that particular axis system known as the principal axis system in which we have only 3 miserable quantities X X Y Y Z Z, but they are connected by the fact that this is a constant because if you do not choose the principal axis system, but some other axis system, you still have the relation that the sum of the 3 is the same as the sum of the 3 in that axis system.

There is constrain that, there is a constant. The constant is the sum of the 3 therefore; we have 3 independent quantities, but with 1 constrain, 3 variables, 3 quantities. With 1 constrain therefore, finally, we have only 2 independent quantities. These are called the Polarizability parallel and Polarizability perpendicular that we will talk about in Raman spectroscopy in the next lecture. Therefore, what you see here is the property of what is known as a Polarizability as here tensor and later the tensor being transformed to something called a principal system and then removing the constancy of the sum of the 3 components, we see that there were 2 independent Polarizability components are, we can measure and Raman spectroscopy gives beautiful results about the experimental from the experiment. It gives you beautiful information about the molecular Polarizability will continue now with the Raman spectroscopy in the next lecture.

Thank you.