Fundamentals of Spectroscopy

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Lecture 41
Polarizability and Polarizability Ellipsoid

Hello all welcome to that lecture on Raman spectroscopy. In the last couple of lectures we have discussed rotational Raman spectroscopy and the effect of nuclear spin effect of nuclear spin on the rotational Raman spectra. There is another kind of Raman spectroscopy which is the vibrational Raman spectroscopy. But before going into the vibrational Raman spectroscopy in today's lecture we will cover the concept of polarizability and polarizability ellipsoid.

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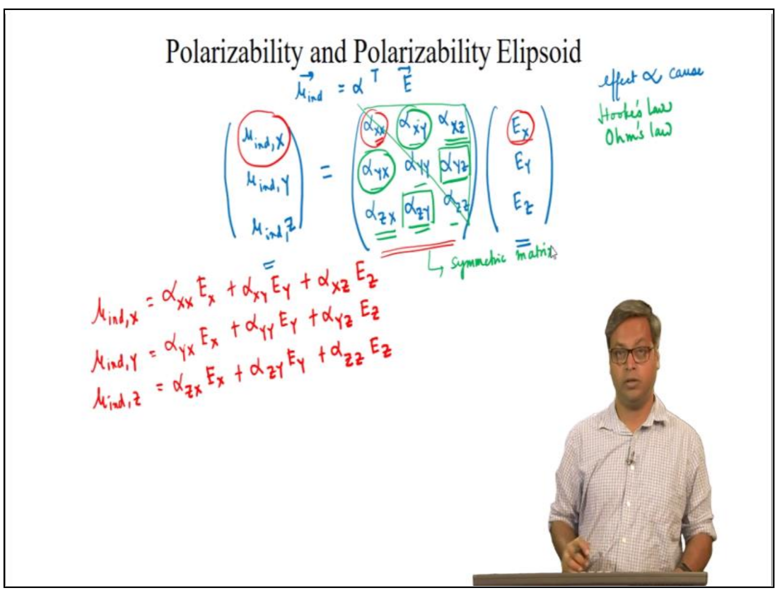

So in the first lecture on Raman spectroscopy we had stated that as long as the electric field of the electromagnetic radiation is not too strong the induced dipole moment which we can write as mu induced so this mean deuced dipole moment is directly proportional to the applied electric field which is given by E and so we can write mu induced equals alpha times E where alpha here is polarizability. The polarizability is a characteristic of the molecule that depends on the molecular structure and the nature of the bonds.

So in this equation the induced dipole moment is a vector also the electric field is a vector but the polarizability alpha is a tensor. So, we can see that the polarizability tensor changes the electric field to give rise to the induced dipole moment. So, what exactly is this picture let us say we draw electric fields in this direction. And let us say we have a molecule which is N O that is N double bond O and N O is in this direction which is kind of perpendicular to the electric field.

So we know that the bonding electron of N O is between N and O or we can say the electron density is concentrated between N and O. Now in the presence of this electric field the electron density will adjust itself to what extent the molecule can polarize itself that is at just itself in the external field E and undergo simple changes in his geometry that is given by the term alpha. If you now think about a different molecule let us say we have H C triple bond N.

So, this HCl molecule itself has a dipole moment and it has the vibrational modes like the symmetric stretch, the asymmetric stretch and the bending modes. If such a molecule which has some dipole moment and undergoing vibration is put in an external electric field. So, this electric field may induce an additional dipole moment. So, let us say it already had some dipole moment mu but the electric field will induce some additional dipole moment.

So the dipole moment will be mu plus mu induced. So, we can see the induced dipole moment is directly a property of the electric field the induced dipole moment may not be in the direction of the electric field and that is why we have the polarizability that is alpha as a tensor. Because induced dipole is a vector it has three components. So, let us first write the equation that is mu induced which is a vector equals alpha which is a tensor times electric field which is a vector.

So this induced dipole moment has 3 components that is we can write mu induced X mu induced why and new induced Z in the axis system that also defines the electric field. So, the electric field itself has three components E X, E Y and E Z. So, then alpha or the polarizability is given by a 3 by 3 matrix and the components of alpha or the indices of alpha are related to the direction of the component of the electric field on the right as well as the direction of the component of the induced dipole on the left side.

So let us write the components now so we have alpha XX alpha XY alpha XZ and then we have alpha YX alpha YY and alpha YZ and we have alpha ZX alpha ZY and alpha ZZ does the electric field is the cause and the induced dipole is the effect. So, this is a general rule stating that effect is directly proportional to the cause and we can see similar examples in cases of Hooke's law or in case of Ohm's law. So, coming back to polarizability connects the cause to the effect and we can write the components of alpha.

So therefore we have here the components of alpha and therefore the directions of the cause and the effect are written as subscripts. Let us say we have XX here thus Alpha XX times E X gives mu induced in the X direction this means the Alpha XX tells us the X component of the induced dipole moment with respect to the X component of the electric field. This essentially means that the X component of the induced dipole moment is given by so we can write mu induced X equals alpha XX EX + alpha XY E Y + alpha XZ EZ.

Similarly for mu induced Y and musi we can write mu induced y equals alpha YX times EX + alpha YY X EY + alpha YZ times easy and mu induced Z we can write alpha ZX times EX + alpha ZY X EY + alpha ZZ times EZ. So, we can see we have 9 components 1, 2 3 4 5 6 7 8 and 9 and out of these 9 components the Alpha XY and alpha YX are equal. So, this alpha XY is arising from the Y component of the electric field inducing a change in the X component of the induced dipole moment.

On the other hand alpha YX term arises from the X component of the electric field inducing a change in the Y component of the mu induced the properties connected by the reversals of the direction of the electric field and the induced dipole moment are equal. So, similarly we can see that this XZ term and alpha ZX term they are equal and this alpha ZY term is equal to alpha YZ. So, in other words if you think this has the diagonal then elements diagonally opposite are equal.

So XY is equals to YZ then ZX equals to XZ and ZY is equal to YZ so we do not have 9 independent components anymore but all we have are this 6 independent candidates or the components. So, this is with respect to the XYZ coordinate system the Alpha matrix here this is a symmetric matrix so the symmetric matrices can be diagonalized.

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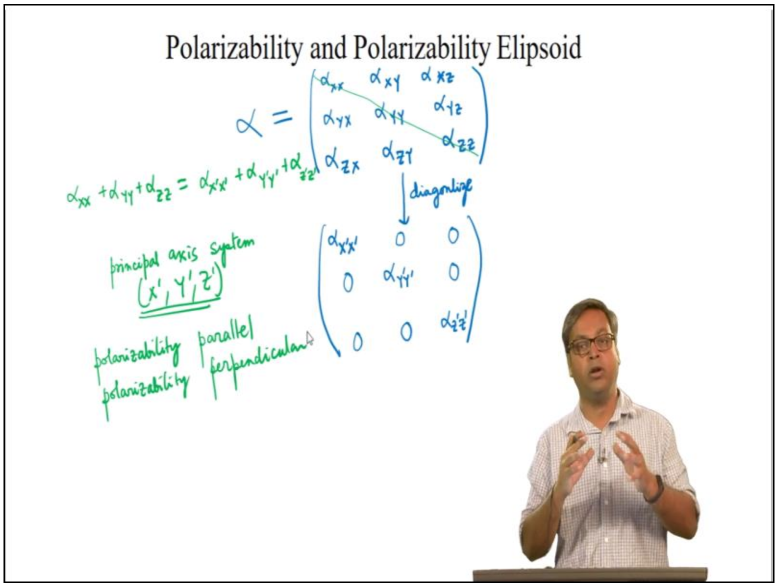

So, what do we mean by that so let us write the matrix of Alpha again. So we have alpha XX alpha XY alpha XZ then alpha YX alpha YY and alpha YZ alpha ZX alpha ZY and alpha ZZ. So, alpha we can write in this 3 by 3 matrix and as I had mentioned this is a symmetric matrix and can be diagonalized that means if we diagonalize this matrix we will get another matrix where we will have only the diagonal terms.

So we can write alpha X prime X prime because now the coordinate system has changed we can write alpha Y prime Y Prime and alpha Z prime Z prime. So, this are the diagonal elements but all the off diagonal elements would be 0. So, we can diagonalize the symmetric matrix into this diagonal matrix. However one property remains is that the trace of the matrix for a symmetric matrix is invariant to the process of diagonalization. So, we can write Alpha XX + alpha YY + alpha ZZ so this is the trace that is the sum of the diagonal elements that should be equal to Alpha X prime X prime + alpha Y prime Y prime + alpha Z prime Z prime.

So we have a new axis system that is X prime Y prime and Z Prime the axis system after diagonalization is called the principal axis system. So, this X prime Y prime Z prime this is the principal axis system because the traces are equal we have 2 independent quantities are not 3 which are known as polarizability parallel and polarizability perpendicular. So, in a nutshell the property of the sample which determines the degree of scattering when subjected to the incident radiation is the polarizability alpha.

The polarizability is a measure of the degree to which the electrons in the molecule can be displaced relative to the nuclei. In general the polarizability of a molecule is an anisotropic property which means that at equal distances from the center of the molecule alpha may have different magnitudes when measured in different directions.

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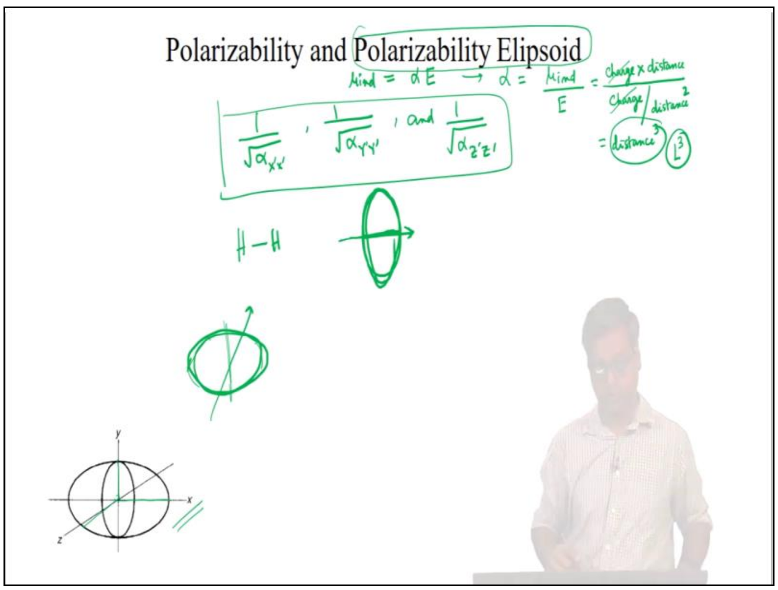

So, now let us look into the dimension of alpha so as we know mu induced equals alpha times electric field. So, we can write from here alpha equals mu induced divided by electric field. So, a dipole moment we know is charge times distance and the electric field is charge divided by distance squared. So, this charge, charge will cancel if we do the dimension analysis and what we get is distance cubed. So, alpha has the dimension of distance cubed or we can say L cubed or length cubed that is that of the volume.

So after diagonalization we saw that there are 3 components of the polarizability tensor now if we draw an ellipsoid with one by root over alpha X prime X prime one by root over alpha Y prime Y prime and one by root over alpha Z prime Z prime. So, if we draw an ellipsoid with this 1 by root over alpha X prime x prime etc as the major axis we get a polarizability ellipsoid. So, what we get is a polarizability ellipsoid.

In general this has elliptical cross section let us say in the XY and the YZ plane as shown in this figure. And the lengths of the axis in the X Y and Z direction are unequal. So, for hydrogen molecule the convenient 3 axis are one along the bond and the other 2 perpendicular to the bond. So, the bond as we know in hydrogen consists of 2 electrons the polarizability is greater along the bond axis and less along any axis perpendicular to the bond.

So if we want to draw the polarizability ellipsoid for hydrogen let us say we have height and we are drying the polarizability along the bond, so let us say this is the bond so the polarizability will look like this. So, it will be fatter at the bond and kind of it will be narrower at the top that is why it looks like an ellipsoid. On the other hand the polarizability ellipsoid when the electric field so this was the direction of the electric field.

So the polarizability ellipsoid when the electric field is across the bond axis let us say the electric field is now in this direction then the polarizability ellipsiod will look more like this again it will be fatter in the middle and narrower at the two ends.