Advanced NMR Techniques in Solution and Solid State
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Module-56
CSA and Dipolar Couplings
Lecture – 56

Welcome all of you. In the last class we started discussing about the solid state NMR. I introduced the new terms which gets reflected in the NMR spectrum of solids called dipolar couplings and chemical shift anisotropy. These two terms I said they get averaged out in the solution state, because of rapid tumbling motion of the molecules and they will not be seen. In the isotropic spectrum we get only chemical shifts and J couplings. Whereas, in the case of the solids due to its rigidity, and there is no translational motion, there could be some rotational motion, most of the time, we are going to see all these interaction parameters, like CSA, that is chemical shift anisotropy and dipolar couplings. And they are all direction dependent. They depend upon term called 3 cos square theta – 1 over 2. Thus, they depend upon how they are oriented with respect to the external magnetic field.

For example, 3 cos square theta – 1 ver 2 if you take, depending upon theta = 0 or 90 the dipolar coupling strength can be 2 or minus half. It can change its sign, and strength can change. In a given solid sample, microcrystalline or amorphous sample, let us say in a powder sample, there could be infinite number of microcrystals present. Various possible orientations are present. As a consequence, each crystalline orientation gives rise to a spectrum. Finally all of them are unresolved and give rise to what is called as broad powder pattern. And I showed the example for a dipolar coupled case when there are dipolar couplings how we get a broad hump by taking one of these internuclear vectors, and when we change its orientation how tthe splitting changes. We saw that finally the overlap of all those things give rise to what is called by a powder pattern, this is what we discussed a lot.

Of course, we also came to know and we understood the study in the solids has lot of advantages. We get more information which we will miss in the solution state, like CSA and dipolar couplings. They give rise to more additional information about the molecules. This is useful to understand in the case of solids because some samples which are not soluble or some polymorphism etc. which you cannot study in liquids, we have to study invariably in the solids.

So solid sate in NMR is very useful. So, we discussed about the dipolar couplings a lot. Today we will start with chemical anisotropy. This is chemical shift anisotropy.

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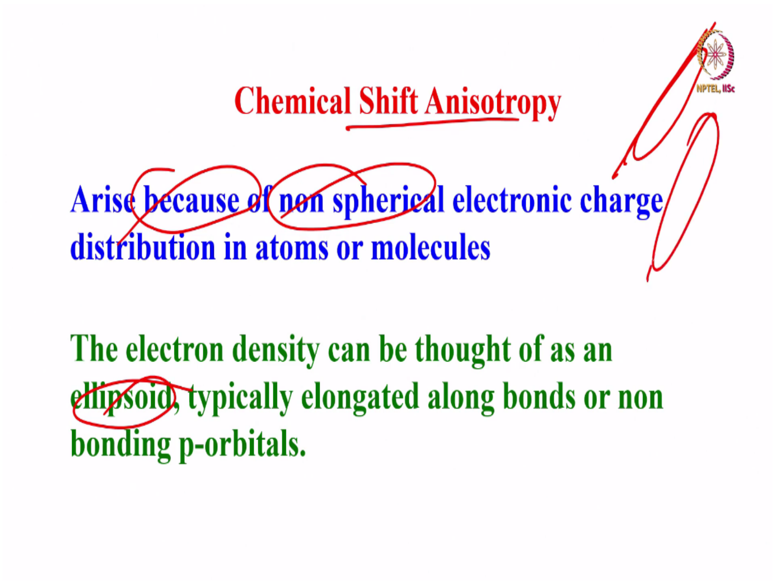

Chemical Shift Anisotropy

Arise because of non spherical electronic charge distribution in atoms or molecules

The electron density can be thought of as an ellipsoid, typically elongated along bonds or non bonding p-orbitals.

Why do, this chemical shift anisotropy comes? It comes because of non-spherical electronic charge distribution in atoms or molecules. If the charge distribution is not spherical, then you can think of electronic density as an ellipsoid; more like an ellipsoid like this, elongated along the bonds usually or non bonding p-orbitals. So electron density can be treated like an ellipsoid like this.

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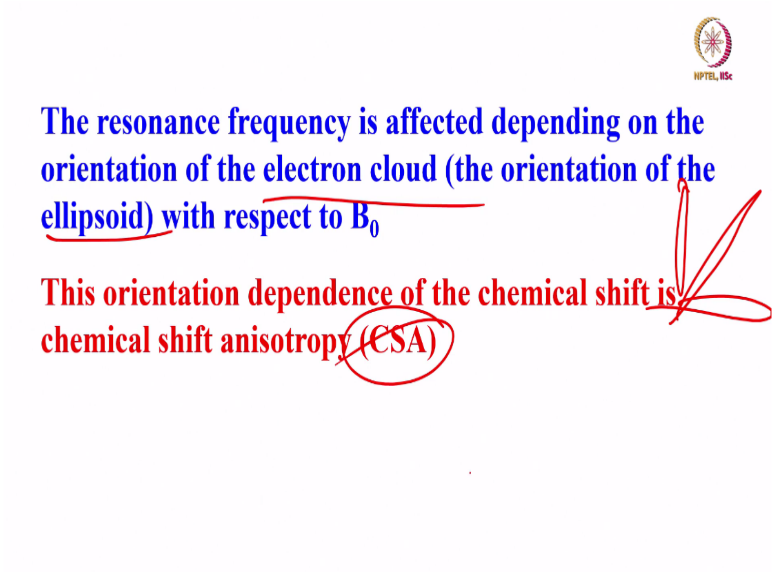

The resonance frequency is affected depending on the orientation of the electron cloud (the orientation of the ellipsoid) with respect to B_0

This orientation dependence of the chemical shift is chemical shift anisotropy (CSA)

Now the resonance frequency gets affected depending upon the orientation of this electron cloud or the orientation of ellipsoid. If the ellipsoid is in this direction, there is one value. If it is in this direction, it is another value. Similar to dipolar couplings the direction of the orientation of the ellipsoid gives rise to different chemical shifts, depending how they are oriented with respect to magnetic field there are different values

The orientation dependence of chemical shift is what is called CSA. See this orientational dependence of chemical shift is what is averaged out in the solution state, but this is present fully in the case of solids, and its orientation dependence is CSA.

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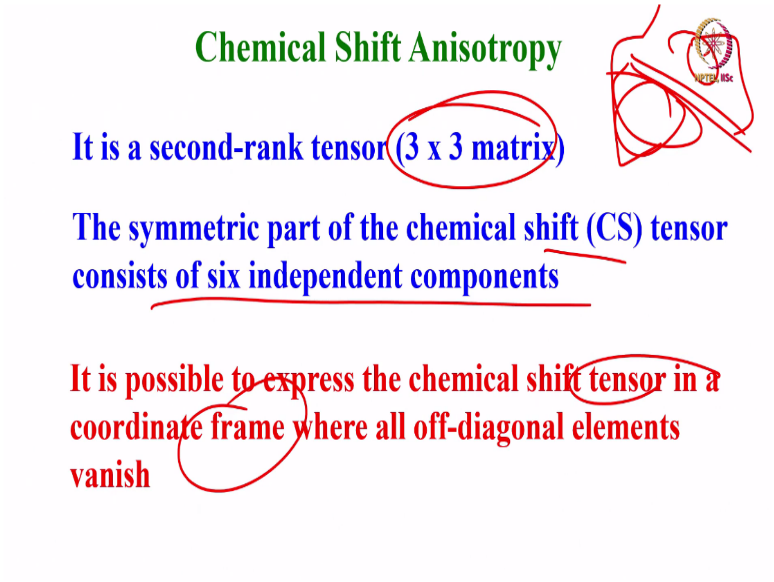

Chemical Shift Anisotropy

It is a second-rank tensor (3 x 3 matrix)

The symmetric part of the chemical shift (CS) tensor consists of six independent components

It is possible to express the chemical shift tensor in a coordinate frame where all off-diagonal elements vanish

So, now discussing more about the CSA, you should know that it is a 3 by 3 tensor. It is a second rank tensor. All NMR interaction parameters are tensors. They are all tensorial interactions. And this has a symmetric part and anti symmetric part. The symmetric part of the chemical shift consists of 6 independent components. It is a symmetric tensor means one we have 6 components here, 3 diagonal and 3 off diagonal terms. This is anyway symmetric does not matter. So, we are going to have only 6 independent components of the chemical shift tensor. Now it is possible to express this chemical shift tensor in a particular coordinate frame, such that all these off diagonal limits can be removed, they become diagonal. You have understood about the diagonalization of the matrices. Exactly similar to that we can express in a particular coordinate frame, where we can get only diagonal terms. The off diagonal terms are not there, they will vanish. So in which case we can represent CSA like this.

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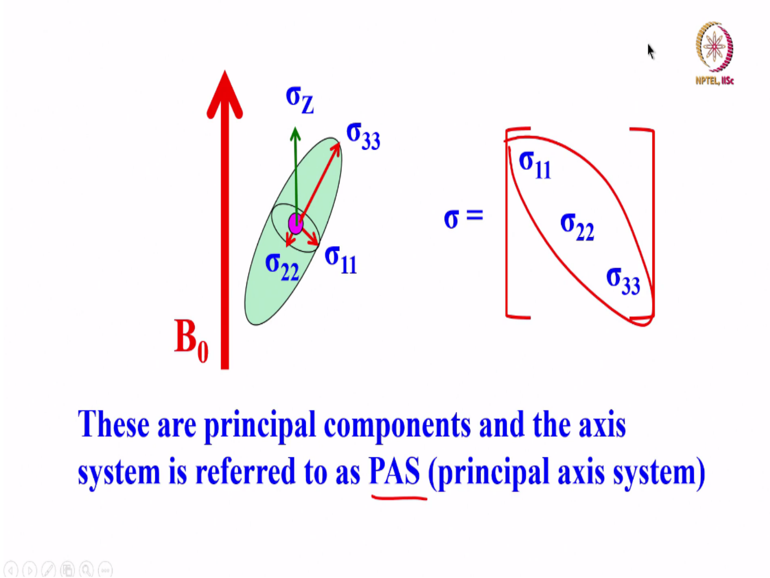

$$\sigma = \begin{bmatrix} \sigma_{11} & & \\ & \sigma_{22} & \\ & & \sigma_{33} \end{bmatrix}$$

These are principal components and the axis system is referred to as PAS (principal axis system)

This is a beautiful drawing you can see; this is ellipsoid; which is CSA ellipsoid. It has 3 possible orientations. This is the sigma z, the orientation in the direction of the magnetic field in the laboratory frame. In the molecular frame I can consider 3 orientations; sigma 11, sigma 22 in this direction perpendicular to that, and sigma 33 in this direction. And 3 possible orientations I call them as sigma 11, sigma 22 and sigma 33.

These are the three terms in three different directions of CSA; and now when I diagonalize the matrix all these off diagonal elements are removed, and we are going to get only three terms called sigma 11, sigma 22 and sigma 33. These are the three terms which we are going to get when we diagnolize. And these are called principal components, and it is called principal axis system.

This is the three chemical shifts when expressed like this in the diagonal form, it is a principal axis system and these are called principal components.

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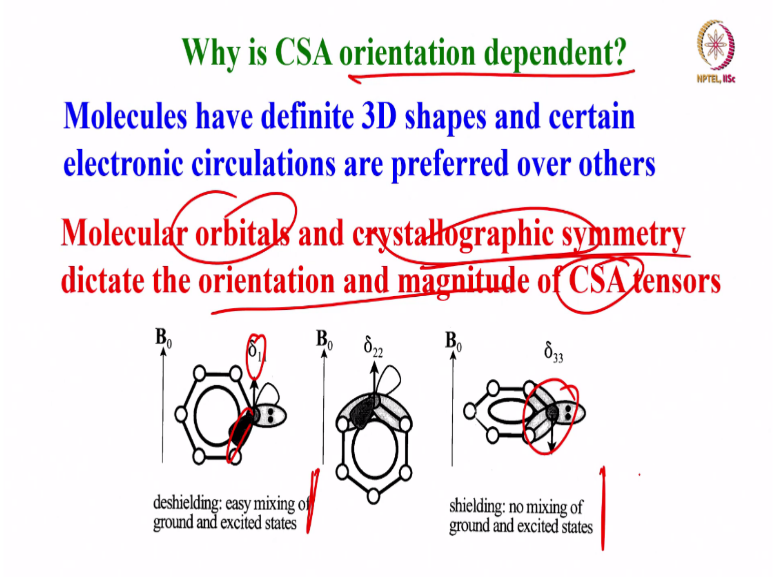

Why is CSA orientation dependent?

Molecules have definite 3D shapes and certain electronic circulations are preferred over others

Molecular orbitals and crystallographic symmetry dictate the orientation and magnitude of CSA tensors

deshielding: easy mixing of ground and excited states

shielding: no mixing of ground and excited states

Now you may ask me a question, this is much more discussion. Of course more of you may be knowing, in chemistry. Why CSA is orientation dependent? The molecules have definite three-dimensional shapes and when we see this, certain electronic configurations are preferred over others. if you look at the molecular structure, the molecular orbitals and crystallographic symmetry decide about the orientation of the magnitude of CSA.

In the CSA which one is larger? sigma 11, sigma 22 is larger or sigma 33 is larger? How it is orienting in a different direction. This is dictated by molecular orbitals in crystallographic symmetry of the molecules. Take for example in a benzene ring like this. If you have this direction sigma 11 this is one, here the deshielding takes place, easy mixing of ground and excited states takes place in this orientation. Similarly in this orientation if we consider, we make it horizontal like this, then what will happen in this case there is no mixing of ground and excited states. This is what happens.

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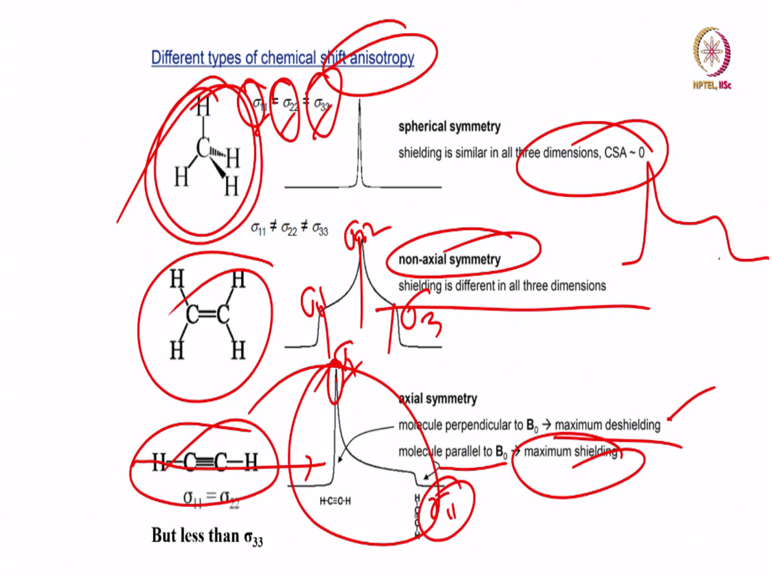

Different types of chemical shift anisotropy

$\sigma_{11} = \sigma_{22} = \sigma_{33}$

spherical symmetry

shielding is similar in all three dimensions, CSA ~ 0

$\sigma_{11} \neq \sigma_{22} \neq \sigma_{33}$

non-axial symmetry

shielding is different in all three dimensions

axial symmetry

molecule perpendicular to B_0 → maximum deshielding

molecule parallel to B_0 → maximum shielding

$\sigma_{11} = \sigma_{22}$

But less than σ_{33}

So different types of chemical shift anisotropy are present. For example consider a molecule like CH4. Here sigma = 11 = sigma 22 = sigma 33. All the three principal components are same, identical, they are equal. You know why? because the molecule has spherical symmetry. Shielding is same in all the three dimensions; in which case chemical shift anisotropy is 0. So, what I am trying to say is the chemical shielding anisotropy is also dictated by the symmetry of the molecules.

In case of CH4 there is spherical symmetry. As a consequence sigma 11 = sigma 22 = sigma 33. And that shows there is no CSA at all. Put your molecule like this, ethylene, it has a non-axial symmetry; the axial symmetry is different, non axial symmetry is different. Of course you know when you understand matrices and everything you know what is the axial symmetry AT = - of A. All those things you would have understood; I do not want to go into the details.

Remember in the symmetry you can have axial symmetry and non axial symmetry. If there is no axial symmetry, then the shielding in all the three possible directions are different. We have sigma 11, sigma 22 and sigma 33 all are present. The kinks here correspond to 3 principal components of the chemical shielding tensor. So, that is a molecule which has a non axial symmetry, all the three components of chemical shift anisotropy tensors are present.

Consider molecule like this, Acetylene, it has axial symmetry along this axis. When there is axial symmetry then what is going to happen? it has only two possible orientations. The maximum shielding in the direction perpendicular, this direction. This is parallel to it. Why this intensity is larger? in a perpendicular direction there are n possible orientations of the internuclear vectors. As a consequence, it has larger intensity. So, this is maximum deshielding here, in the perpendicular direction. Here maximum shielding is there, in this parallel direction. For a molecule having the axially symmetric tensor, this is the pattern for CSA; remember this is the pattern for CSA.

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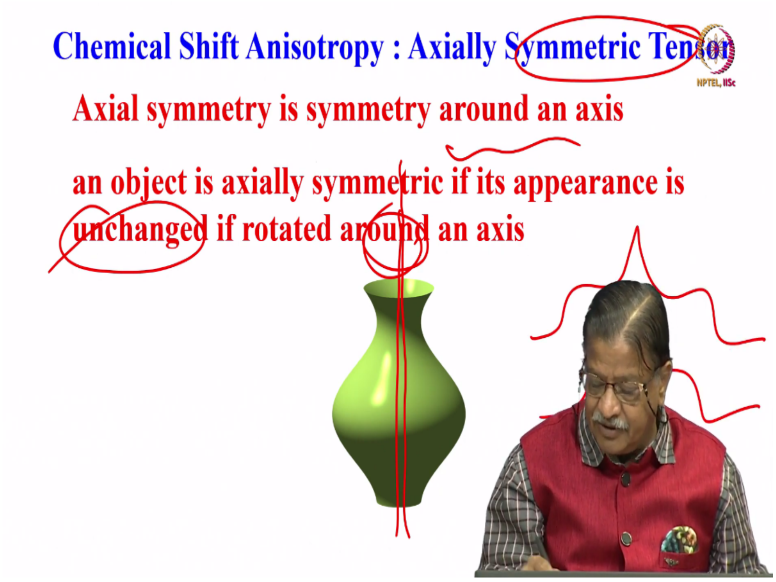

Chemical Shift Anisotropy : Axially Symmetric Tensor

Axial symmetry is symmetry around an axis

an object is axially symmetric if its appearance is unchanged if rotated around an axis

So, just to brief you about the axially symmetric tensor which I do not need to explain in detail. The axial symmetry defines about the symmetry around an axis. When an object is axially symmetric, you would have studied in your matrices. Object is axially symmetric if its appearance remain unchanged when rotated about an axis. For example, on this axis I am going to rotate, the appearance of this object will remain unchanged; that means this molecule has an axial symmetry along this axis. You understood? Similarly, depending upon the molecular structure you can find out the molecule whether it has axial symmetry or not. So, based on the axial symmetry and axial asymmetry we have two different types of powder patterns for chemical shift anisotropy. This is for asymmetric tensor, this is for axially symmetric tensor.

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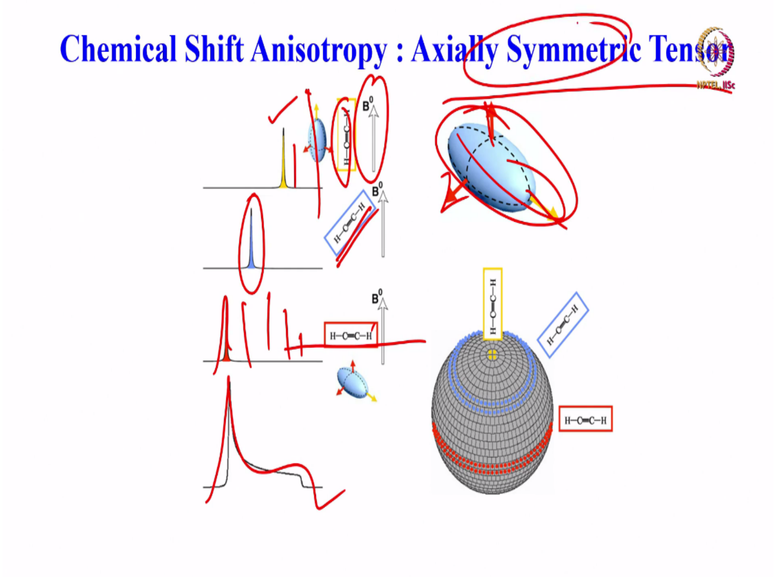

Chemical Shift Anisotropy : Axially Symmetric Tensor

So, now chemical shift anisotropy for axial symmetric tensor if we consider an have example of ellipsoid like this, there are three possible orientations like this. If acetylene is taken with the long axis of the ellipsoid in the direction of magnetic field like this, then this is the chemical shift. If the long axis of the molecule make an angle with respect to magnetic field like this, then this is the chemical shift. If the long axis of the ellipsoid makes an angle of 90 degree, that is, perpendicular to the magnetic field its chemical shift is here. But in reality in the case of solids all possible orientations are present. As a consequence, we have chemical shifts here, here all are present. So, in reality all of them will overlap and you get a pattern like this. This is called a powder pattern for axially symmetric tensor.

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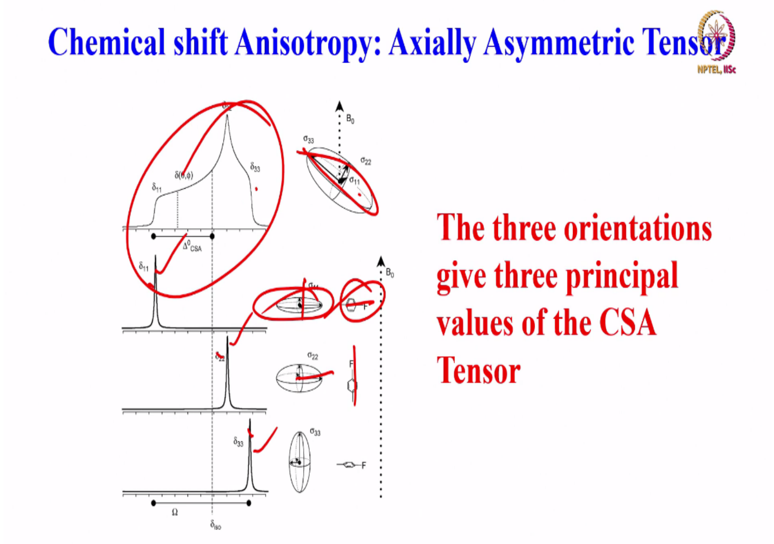

Chemical shift Anisotropy: Axially Asymmetric Tensor

The three orientations give three principal values of the CSA Tensor

Now for axially asymmetric tensor how does the powder pattern come? Look at this another simple molecule like this. Symmetry is not there, it has axially asymmetric tensor, then depending upon the orientation of sigma 11, sigma 22 and sigma 33, if this is the molecule let us say, sigma 11 when it is oriented is like this; sigma 22 is oriented like this; sigma 33 is orient like this, then have look the molecule. Once it is oriented like this, once it is oriented, then different chemical shifts are there. Once chemical shift is here, here and here. Depending upon the direction of orientation of the ellipsoid with respect to the external magnetic field. As I said in the previous case, here also all possible orientations are present, they are all overlapped and gives rise to a powder pattern like this. This is the powder pattern for an axially asymmetric tensor.

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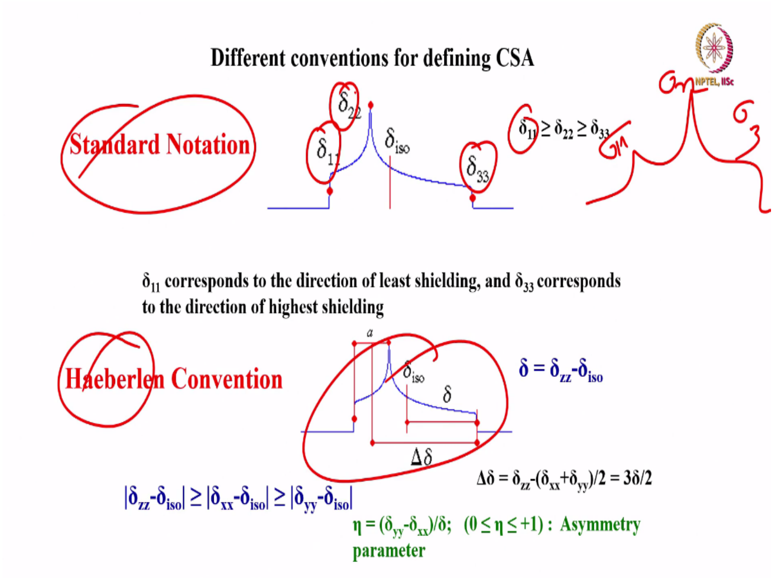

Different conventions for defining CSA

Standard Notation

$\delta_{11} \geq \delta_{22} \geq \delta_{33}$

δ_{11} corresponds to the direction of least shielding, and δ_{33} corresponds to the direction of highest shielding

Haeberlen Convention

$\delta = \delta_{zz} - \delta_{iso}$

$\Delta\delta = \delta_{zz} - (\delta_{xx} + \delta_{yy})/2 = 3\delta/2$

$|\delta_{zz} - \delta_{iso}| \geq |\delta_{xx} - \delta_{iso}| \geq |\delta_{yy} - \delta_{iso}|$

$\eta = (\delta_{yy} - \delta_{xx})/\delta$; $(0 \leq \eta \leq +1)$: Asymmetry parameter

So, different conventions are there for defininf the CSA, but you do not need to worry about it as we are not going to discuss. Just to tell you generally this is delta 11, this is delta 22, this is delta 33, or sigma 11, sigma 22, sigma 33. And when delta 11 is larger, then 22 larger than 33, this is the standard convention, when you get a auxiliary asymmetric powder pattern like this. This is called sigma 11, sigma 22, sigma 33 here. And this is one convention. This is another convention called Haeberlen convention. Here this is defined in a different way. Just to tell when you get an axially asymmetric pattern, we will have three different things like this each of them pertains to sigma 11, sigma 22 and sigma 33 orientations. So, we do not need to discuss there are lot more to discuss about it I just wanted to tell you

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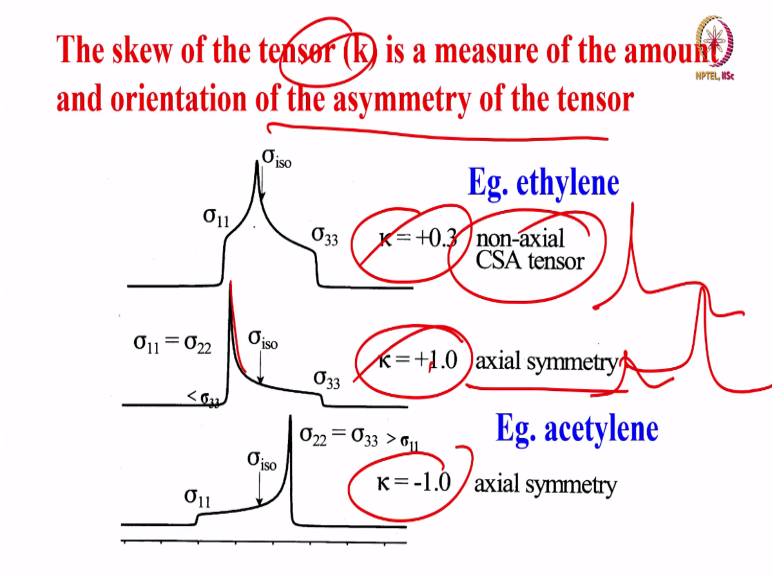

The skew of the tensor (k) is a measure of the amount and orientation of the asymmetry of the tensor

I want to introduce one new term called skew of the tensor. It is a measure of amount orientation of the asymmetry of the tensor. If the tensor is asymmetry, how much is the measure of amount of the asymmetry and orientation is given by skew of the tensor. For example if it is a non axially asymmetric tensor; you can find out the value of k; some expressions are there. You can easily find out, if it is axially asymmetric what is the asymmetric parameter. For example, axially symmetric tensor if it is like this, let us say. this is asymmetric parameters plus 1, It is given as k, the asymmetric parameter. If instead of plus 1 it becomes minus 1, what is the difference? you see this thing became like this; completely gets reversed. The skew of the tensor defines its orientation. So, here skew became negative the orientation, changed that is all. This is the way you have to define skew of the tensor; skew for non axially symmetric tensor.

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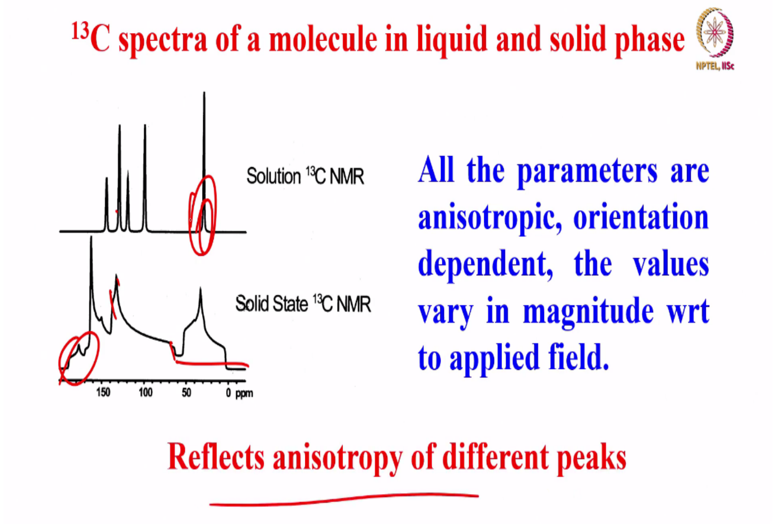

^{13}C spectra of a molecule in liquid and solid phase

All the parameters are anisotropic, orientation dependent, the values vary in magnitude wrt to applied field.

Reflects anisotropy of different peaks

Now let us look at the 13C spectra of molecule in the liquid and solid phase. How does it look? We do not do much about proton for the routine analysis, except there are many, many stalwarts in NMR who are doing enormous research to get the sharp lines in NMR, to reduce the internuclear interaction strengths, reduce the linewidths and large sharp lines. But most of the application is concentrated only on carbon 13 and other x nuclei instead of proton and fluorine.

Let us take the example of carbon 13 NMR spectra of a molecule in a liquid and solid phase. Some molecule I do not know about the molecule. Let us say I take the carbon 13 spectrum of that in a solution state. I dissolve the sample in a solvent and record the carbon 13 NMR spectrum. You see all these lines are sharp. The same molecule in a solid state, the static solid without doing anything. Put the sample in a powder form in the NMR tube or whatever it is; put it in a magnetic field and record the spectrum of carbon 13 NMR spectrum. This is what you are going to get. This single sharp line appears like this. What do you understand from this? See all the parameters are orientation dependent; and the value vary with the orientation, I said. So they are all anisotropic. Now the anisotropy is getting reflected.

This one, this particular peak, and in a given molecule there are different carbons; each carbon can have a different asymmetry. One can be axially symmetric and other can be axially asymmetric. So, this particular carbon, it means from the NMR spectrum itself, looking at it I can tell you, it is axially asymmetric. You can look at it, this is what we understood about axially isometric pattern.

This carbon is axially asymmetric. Look at this carbon it has a orientation like this; it is axially symmetric. Similarly, it has two kinks here if you can look at it carefully there are two kinks here and here, that means this has two carbons here which have overlapped; both are axially symmetric and other one again axially asymmetry here. Like that you can even get the information about the axial symmetry and axial asymmetry just by looking at the spectrum of the molecule.

At this carbon site I can say there is no axial symmetry. Like that you can discuss all these get reflected in the spectrum. Anisotropy gets reflect in the NMR spectrum especially in a non spinning sample.

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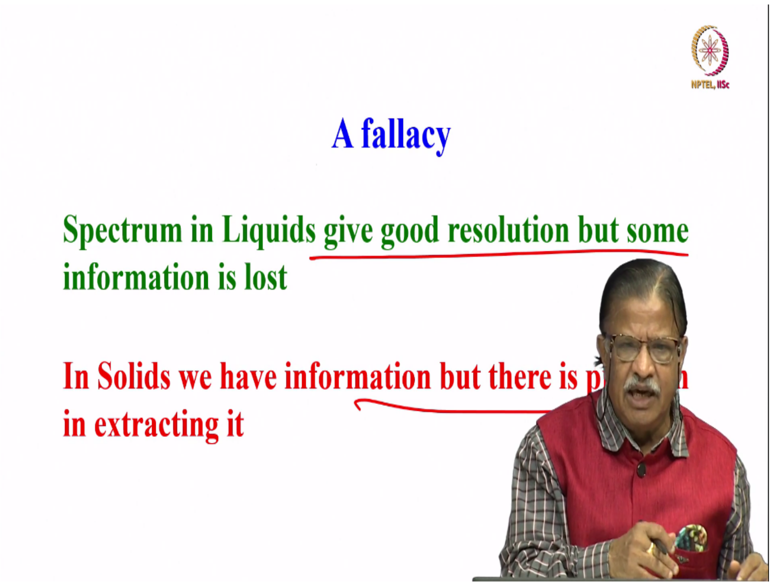

A fallacy

Spectrum in Liquids give good resolution but some information is lost

In Solids we have information but there is p n in extracting it

Now with this we can thus come to a fallacy. After understanding some basic concepts about parameters which are responsible to make the NMR spectrum of a solid very broad; there is a fallacy. Spectrum in liquid give good resolution. We saw very sharp lines, easy to analyze, but information is lost. Most important CSA, because in the previous example I showed you this will tell me about the anisotropy and I can tell you what is the charge distribution at the site of this carbon. So, all this information are present in solids, so that information is going to be lost in solution. But in the solids you have all this information, but there is a problem in extracting it. In the previous spectrum I showed you there are only 4 or 5 carbons. In reality there are many carbons, lots of anisotropy are present; each carbon has a different type of anisotropy and they all overlap giving rise to broad peak, very difficult to extract information.

So it is a fallacy. The spectrum in liquids gives good resolution, but information is lost. In solid information is present, but difficult to extract; so we have to overcome some of these problems.

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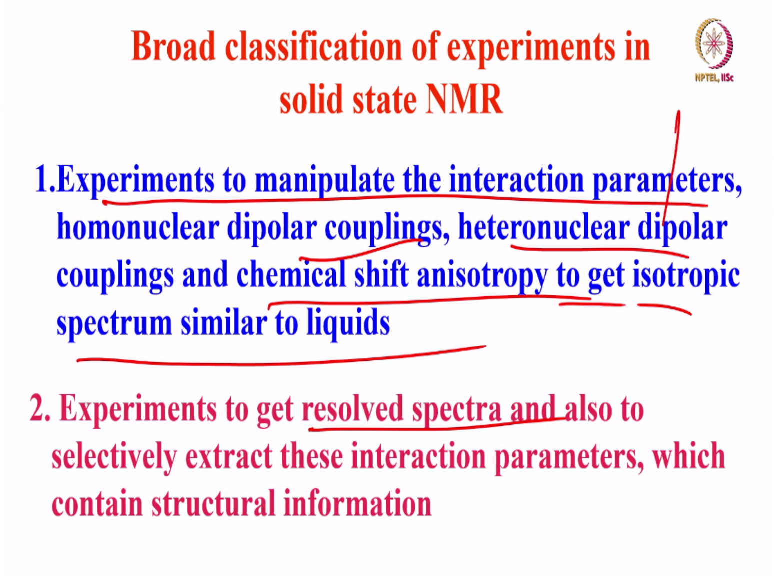

Broad classification of experiments in solid state NMR

1.Experiments to manipulate the interaction parameters, homonuclear dipolar couplings, heteronuclear dipolar couplings and chemical shift anisotropy to get isotropic spectrum similar to liquids

2. Experiments to get resolved spectra and also to selectively extract these interaction parameters, which contain structural information

So as a consequence, the NMR experiments in solids can be broadly classified into two categories. I mean this is my way of understanding it need not be seen in the books. One is experiments to manipulate the interaction parameters, homonuclear dipolar couplings, heteronuclear dipolar couplings, CSA etcetera. I can manipulate the interaction parameters such that all of them are removed and get the spectrum similar to that of liquids.

You see in the case of solids if you remove everything all these anisotropy parameters it is similar to liquid. That does not mean you can dissolve it in the solvent and do it; retaining in its solid form. If I somehow design the experiments to manipulate these parameters and remove them, then I get a spectrum; isotropic spectrum similar to liquids. So, experiments to get the resolved spectrum is one thing, like this, removing all the parameters.

Further, I can reintroduce these parameters, you understand the interesting phenomenon. Lines are broad I remove it, and get the resolved spectrum, but then selectively I can bring back these parameters so that can get it reflected in the spectrum and I get the information. So, spectrum is still retain the high resolution character, plus information from one of the parameters which I am interested can be obtained.

So, like this we can have this broad classification of NMR experiments; and number of techniques are available. I mean number of one and two NMR experiments have been designed to understand and get the sharp lines, that is high resolution spectrum in the solids.

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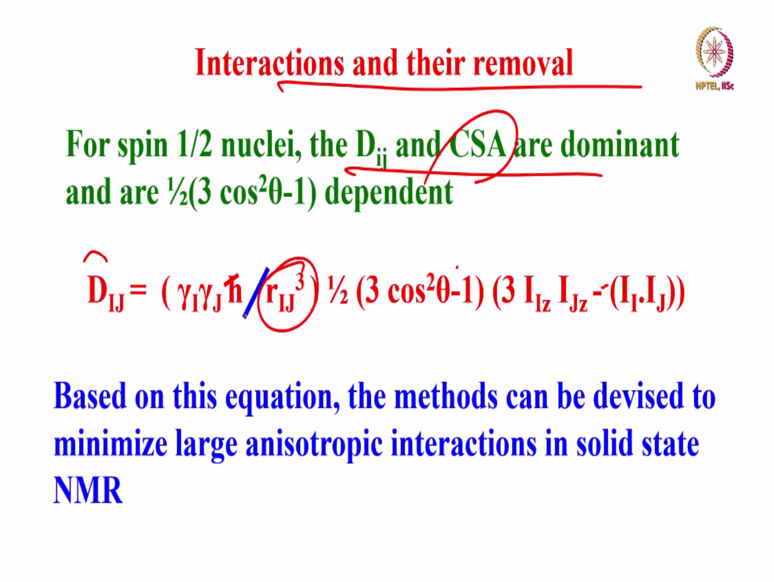

Interactions and their removal

For spin 1/2 nuclei, the D_{ij} and CSA are dominant and are ½(3 cos²θ-1) dependent

$$\hat{D}_{IJ} = (\gamma_I\gamma_J\hbar/r_{IJ}^3)\ \tfrac{1}{2}(3\cos^2\theta-1)\ (3 I_{Iz} I_{Jz} - (I_I.I_J))$$

Based on this equation, the methods can be devised to minimize large anisotropic interactions in solid state NMR

Now to get the sharp lines in the spectrum of solids what I have to do? I have to retain the solid in its form plus remove the parameter, that is anisotropic interaction parameters like CSA, dipolar coupling etcetera. How do you do that? First, all of you should understand for spin half nuclei dipolar coupling and CSA have term 3 cos square theta – 1 divided by 2. So, let us look at this equation. This is the equation for dipolar coupling.

We will come to that CSA later. The equation for dipolar coupling is given by this. Dij is a dipolar coupling between any two nuclei i and J. It is given by gamma I gamma J into h cross over r IJ cube into half of 3 cos square theta – 1 divided by 2; and 3 I1Z into IJZ – I1 dot IJ. So there are three parameters here; 3 multiplications. Now 3 terms are multiplied by one another. Look at this one here. Look at this on,e this is one term, another term and all the three terms are multiplied. What does it mean? If I have to remove dipolar couplings what should I do? Make one of the term 0; they are all multiplied automatically dipolar coupling becomes 0. That is one way to remove, right. So like that based on this equation we can devise the methods to minimize large anisotropic interaction in the solid state, because same parameter 3 cross square theta 1 – 1 divided 2 dependency is there for CSA also.

Whatever happens for the dipolar coupling; of course except this and this; it happens for CSA also, especially this dependence curve. If I can reduce dipolar coupling and remove dipolar coupling based on this by manipulating this term by some method; same thing I can do for CSA also; that is what it means. Now go back to this equation, I can introduce the term called one important term called dilution in solids. So, you look at this one, here rIJ cube rIJ cube is in the denominator; that is what I wanted to say.

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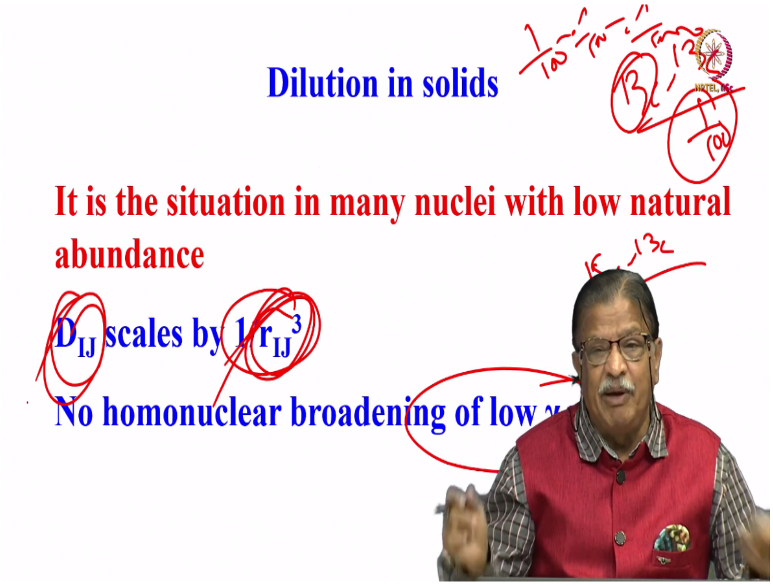

Dilution in solids

It is the situation in many nuclei with low natural abundance

D_{IJ} scales by $1/r_{IJ}^3$

No homonuclear broadening of low γ

It is a situation when you look up for low gamma nuclei like dipolar coupling between, carbon 13 and carbon 13. If I want to see two carbon 13; which are close in space what is the probability? Probability of seeing any two carbon-13 next to each other is 1 in 10,000. See with 1% abundance carbon in his carbon 13 state is for any one of the carbon is 1 over 100. If there are two carbons together if I have to see both the carbons in the carbon 13, state it is 1 over 100 into 1 over 100. It is going to be 1 over 10,000.

So, DIJ scales by rIJ cube. Inverse of rij cube. So. larger the rIJ then DIJ becomes small. Now if I consider homonuclear two coupled spins of low gamma nuclei like nitrogen 15 or carbon 13; because the abundance is so small what is the probability of seeing them together? It is 0, close to 0, I would not say 0; very, very small; extremely small. For example carbon 13 carbon 13 state is 1 in 10,000; Two nitrogens in nitrogen 15 state, nitrogen abundance is 0.37 so much, much smaller. That means, in other words I can say they are not close in space; because that possibility is not there; very low. So, I can say this rIJ is infinity, between two carbons to be seen in carbon 13 state. So the spetial proximity I will call it infinite. So DIJ scales or rIJ cube, means for low abundance spins I can say r IJ is infinity. As a consequence, dipolar couplings, goes to 0. I do not want to do anything nature is helping me.

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$^{13}C/^{13}C$
Dipolar

If there is heteronuclear dipolar coupling

Removed by high power decoupling

Number of decoupling schemes are available

Because two carbon 13, probability of seeing them together in carbon 13 state, is so low, the probability is only in 10,000 we can consider them to be at infinite distance, separated by infinite distance, so that can automatically help us. So, that is the reason why carbon 13 carbon 13 natural dependence dipolar coupling are rarely seen; very rarely it is seen. Now another thing can happen carbon 13 proton can have a dipolar interaction, that is possible.

Carbon 13, carbon 13 is ruled out, I agree, probability is low. Carbon 13 proton dipolar coupling can be present, but it is a heteronuclear dipolar coupling. Heteronuclear in fact, its strength is small compared to homonuclear dipolar coupling strength. Then I can remove this by high power decoupling, that is possible. And how do you remove it? There are varieties of decoupling schemes are available; I can use them and start removing the dipolar interactions, the heteronuclear dipolar interactions; it is possible.

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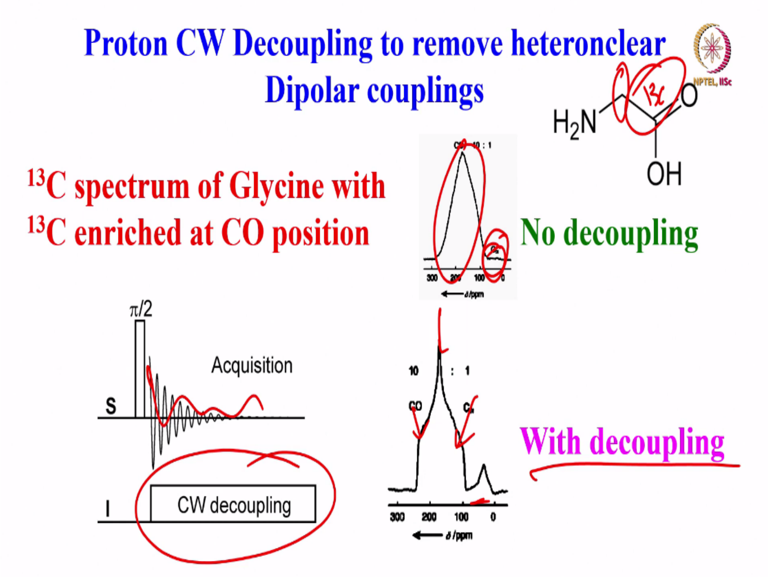

Proton CW Decoupling to remove heteronclear Dipolar couplings

^{13}C spectrum of Glycine with ^{13}C enriched at CO position

No decoupling

With decoupling

So, proton continuous wave decoupling is normally adapted if you want to remove heteronuclear dipolar couplings. What I will do is, I look for the carbon 13 or nitrogen 15; any less abundant spins, decouple proton and look at the spectrum. That is what we do. That is called a continuous wave decoupling. Continuously I am applying the radio frequency power to remove the interaction strengths. Take for example a glycine molecule. The 13 spectrum of glycine where 13C is in the CO position. This CO carbon is 13C labeled. If you look at the spectrum of CO, with no decoupling is done, simply record the spectrum with no decoupling, just static sample. Look at the carbon 13; signal to noise ratio is like this. It is very broad. And what we do is we can do decoupling. This is what here without decoupling here no decoupling is done. But now what we are going to do is we are going to do the decoupling and at the same time we acquire the signal, at the same time we do the decoupling. This is signal acquisition, continuously I am breaking the coupling between carbon and proton by applying decoupling power; this is what it is. Now if I do the decoupling, with decoupling there is very interesting observation, which I wanted to show you. This is the carbon 13 spectrum of glycine. We saw a big peak for carbonyl carbon. There is another carbon CH2, where is that peak, OK, look, it is here; invisible without any decoupling. And on the other hand when we do the decoupling ; you will just put it in a static state we already see the powder pattern; three kinks are seen. So, look at the signal to noise ratio and look the powder pattern of this CO carbon, it is very clearly seen.

Interestingly C alpha which is not even visible started visible here. So, decoupling helps. If you remove the heteronuclear dipolar coupling, we get better spectrum. So, most of the time while detecting carbon 13 we do decoupling. So if there is heteronuclear dipolar coupling we remove by what is called heteronuclear dipolar decoupling.

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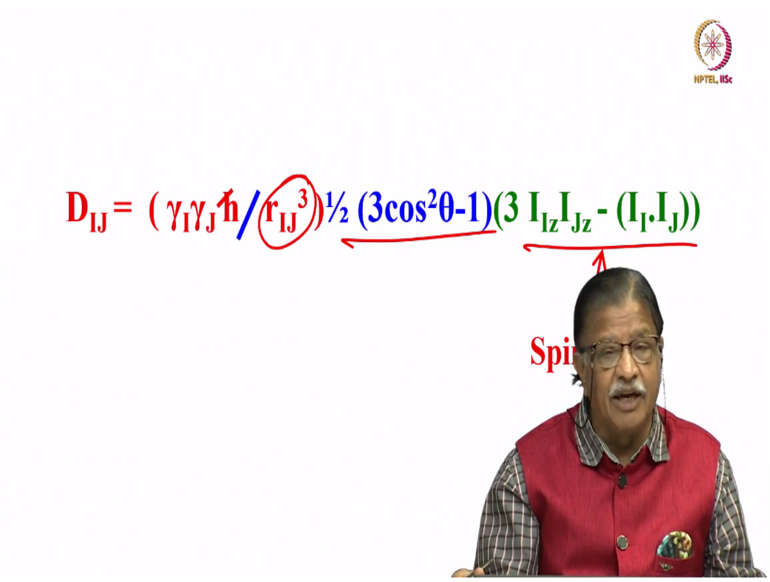

$$D_{IJ} = \left(\gamma_I \gamma_J \hbar / \underline{r_{IJ}^{3}}\right) \tfrac{1}{2}\,\underline{(3\cos^2\theta - 1)}\,\underline{(3\, I_{Iz} I_{Jz} - (I_I . I_J))}$$

Spi

With this we will go back to this DIJ; dipolar coupling expression. We understood this; it is called dilution in solids, infinite distance we can think of between two naturally abundant carbon 13, and nitrogen 15. So, this one factor which can make dipolar coupling between two dilute spins homonuclear spins 0. What about these two terms? There are two other terms? can I not make them 0? is it possible for me to make this term 0. Is it possible for me to make this term 0. This is called space part and this is called spin part. Now, I can remove the dipolar coupling by doing something in the space part or I can do something to the nuclear spins in the spin space. Both I can do individually or both simultaneously I can do both. All is possible.

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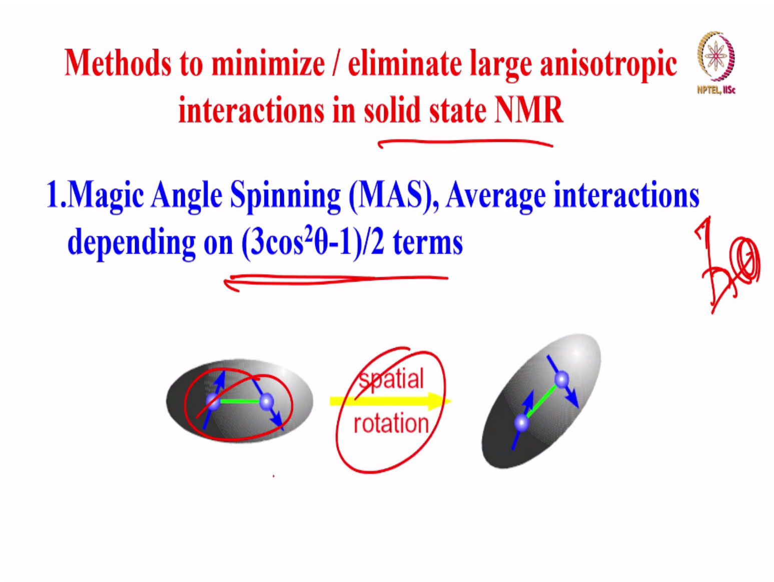

Methods to minimize / eliminate large anisotropic interactions in solid state NMR

1.Magic Angle Spinning (MAS), Average interactions depending on $(3\cos^2\theta-1)/2$ terms

So, then we can device the methods to eliminate or minimize the large anisotropic interactions in the solid state. We can do with this understanding; especially the dominant interaction, the dipolar coupling I said for spin half nuclei. So, how do you remove this things interactions? I can deal the space part or I can deal with the spin part; either of them. Now in the case of space part what we are going to do is we put the sample, let us say the internculear vector, at an angle in the magnetic field called magic angle spinning. We put it at angle called the magic angle and start spinning the sample rapidly. What will happen there? I will come to that later. I can do this put the sample at an angle called magic angle and rapidly rotate this sample, then average interaction that depends upon 3 cos square theta – 1 divided by 2, this term can be eliminated.

The dipolar couplings depend upon this; especially heteronuclear dipolar coupling depends upon this term that can be immediately removed by putting a sample at an angle and rapidly rotating at high speed. This we can do spatial rotation; physically we can rotate the sample, that is why it is called physical space averaging. I can manipulate in the physical space.

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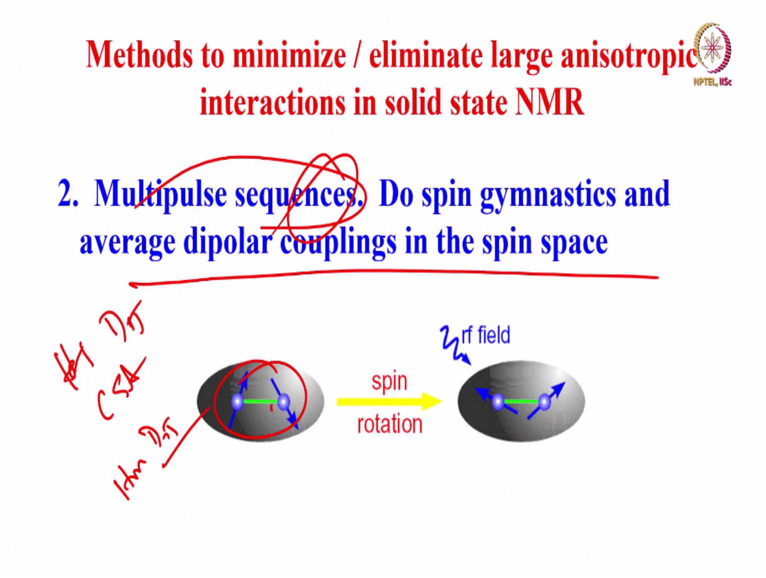

Methods to minimize / eliminate large anisotropic interactions in solid state NMR

2. Multipulse sequences. Do spin gymnastics and average dipolar couplings in the spin space

Alternately I can use multiple pulse sequences, I can do some spin gymnastics. The same thing what I said, I can make the sample rotate at magic angle to remove. Instead of rotating the sample I can rotate the spins. I can do some spin gymnastics make the spins to undergo rotations like this. How I tell you as we go ahead, how we can do that; and I can do the spin gymnastics that can also eliminate dipolar coupling in the spin space.

Again everything, all interactions cannot be eliminated. Using these things we can eliminate homonuclear or reduce or minimize the homonuclear interactions like homonuclear dipolar couplings. Whereas by magic angle spinning we can remove or minimize heteronuclear dipolar couplings or CSA; we can do that. So, depending upon whether you use physical rotation or spin rotation, if we are using physical rotation, we can remove heteronuclear dipolar coupling and CSA. If we are using multiple pulse sequence, we can remove homonuclear dipolar coupling or reduce quite a bit, reduce significantly. So, these two things we can adapt. Next I will discuss about magic angle spinning. What is a magic angle spinning, how it is done, how it will remove anisotropic interactions of the second rank tensors; everything we will discuss in the next class. But today continuing with the solid state NMR we discussed about chemical shift anisotropy. Patterns of the chemical shift anisotropy, how we get the powder pattern for CSA, if this tensor is axially symmetric, how do you see that if this tensor is axially asymmetric. And we discuss about the skew factor which also determines the appearance of the powder pattern. And of course we know how the chemical shift anisotropy comes into the picture, it is because of the charge distribution is non spherical at the site of the nucleus.

We can think of an ellipsoid and a direction of orientation of this ellipsoid in different directions give rise to different chemical shifts; and it is tensor which has 6 elements; it is a symmetric tensor. So, basically we can diagonalize it and get only three principal components sigma 11, sigma 22 and sigma 33. And for asymmetric axially asymmetric tensor all the three sigma 11, sigma 22, sigma 33 are different.

For axially symmetric tensor, two of them are equal and one of them are different that is the important thing you should understand. For axially asymmetric tensor all the components sigma 11, sigma 22, sigma 33 are different. For axially symmetric tensor two of them are equal and one of them is different from the two; that is what we understood. And I said we can manipulate the dipolar couplings in spin space or in physical space to eliminate some of the interaction tensors.

Physical rotation, with this we can manipulate and remove heteronuclear dipolar couplings and also CSA. Heteronuclear dipolar coupling can also be removed by decoupling; heteronuclear decoupling with a continuous wave RF pulse with high power pulse. And of course these all can be combined together, need not be individual; they can all go together. All this experiments can be done together. So, this is what we discussed a lot, about these things.

We took some examples for decoupling, how you see the anisotropy of the different peaks if it is a non spinning sample; the stationary solid if we take, look at the carbon 13 spectrum, the anisotropy gets reflected in the carbon 13 spectrum. And we could see whether at the site of the particular carbon there is a axially symmetry or not; you can understand. So, lot of things we discussed about CSA and methods of elimination and everything.

We go into the individuals methods like magic angle spinning and all other things in the next class. So, we will continue further. I am going to stop here. In the next class we will start with magic angle spinning. Thank you.