Advanced NMR Techniques in Solution and Solid-State
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Module-55
Introduction to Solid State NMR
Lecture – 55

Welcome all of you. Till now, we were discussing about varieties of concepts, varieties of experiments both one dimensional and two dimensional as far as the solution NMR of spin half nuclei are concerned. And we discussed several things, complexity of the spectrum? How we can simplify the spectrum? How we can analyze the spectrum? What are the spins system nomenclature? What are the types of 2D experiments? What is the correlation experiment? What is the resolved experiment? both for homonuclear and heteronuclear spins, varieties of things we discussed. We also understood about the relaxation phenomena; NOE phenomena and some mathematical understanding by using Fourier transformation. What are is the Fourier transformation? What are the general some theorems of Fourier transformation? How they can be utilized in NMR spectroscopy? All those things we discussed. And we understood the product operators formalism, varieties of experiments have been designed in 1d and 2d NMR. How we can understand, what is happening? How the magnetization is evolving in different pulse sequences, or at different stages in a given pulse sequence, etc. we understood by product operators. This understanding helps us to design the pulse sequence so that you can get the information what you want in an orchestrated manner. So, all these things we discussed a lot in over several classes or till now. As I said all these things we were discussing only in the solution state, where in the beginning itself, we understood when we were discussing about the internal interaction parameters. The majority of the internal interactions like dipolar couplings, quardrupolar couplings, and all other anisotropic interactions get averaged out in the solution state. That is what I said, and they will not be present. So, we get a simple spectrum where only chemical shifts and couplings are present. So the analysis gives you only this. Of course, T1 another thing you can do to get some other dynamics information, etc. Basically, if you get 1D spectrum, a conventional simple one dimensional spectrum, we get scalar couplings and chemical shifts by the analysis of the spectrum.

OK. Lot of experiments have been designed to understand varieties of things in the complex spin systems. But today, we will understand something more, identical NMR spectrum you want to get in solids, how difficult it is? Or how easy it is? How we can get a good spectrum in solids? Why I am telling? It is entirely a different thing in solids, because interactions present in the solids are different compared to what the interactions you saw in the liquid state. So, accordingly we now start discussing something about solid state NMR in the next couple of classes. And of course, solid state NMR, again it is a huge topic, we can start discussing this for several hours, not one hour, maybe one semester we can talk

But since lack of time, I will give you some of the important principles and concepts and basic ideas of utilization of the solid state NMR.

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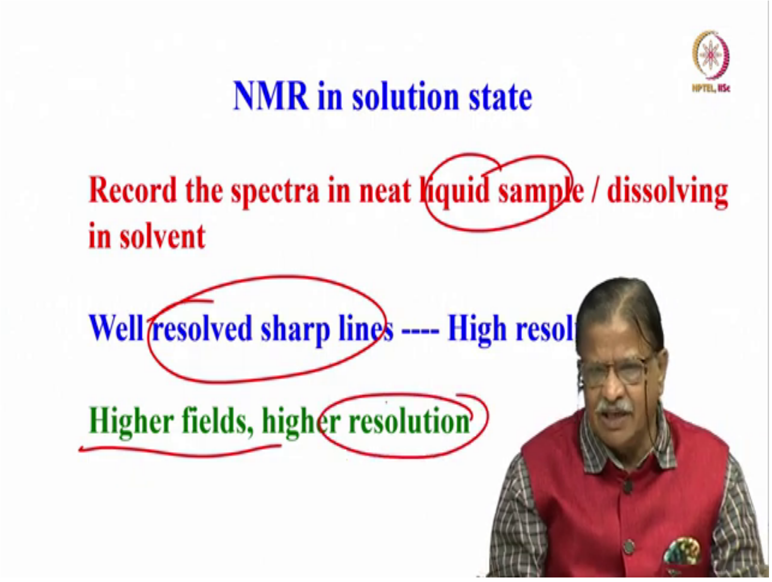

NMR in solution state

Record the spectra in neat liquid sample / dissolving in solvent

Well resolved sharp lines ---- High resol

Higher fields, higher resolution

Before that of course, you know just to recapitulate, you know what is NMR in the solution state; what you do? Record the spectra in neat liquid sample are dissolve in a deuterated solvent and get the spectrum. That in the previous course and in this course beginning also we understood. In the solution state, except in a viscous solvent or when there is aggregation of the molecules, most of the times we get well resolved sharp lines, sharp peaks you are going to get. And this is called a high resolution NMR. In a solution state, you always get high resolution NMR spectrum. And further you also understood, as you keep on increasing the magnetic field, external magnetic field, B0 field, higher the magnetic field you get higher resolution. That is what we discussed. So, this is for the solution state NMR.

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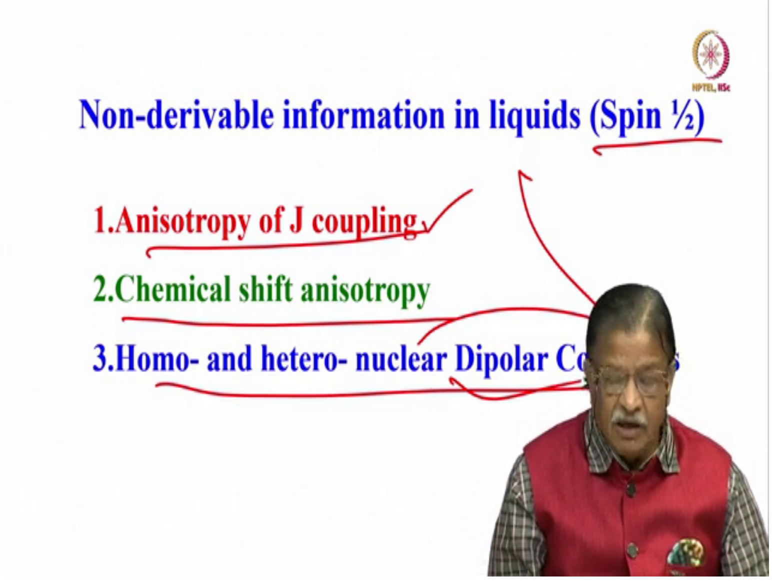

Non-derivable information in liquids (Spin ½)

1.Anisotropy of J coupling

2.Chemical shift anisotropy

3.Homo- and hetero- nuclear Dipolar Co s

Now, what did you derive from the solution state, especially I was focusing on spin half nuclei. We never touched upon more than spin half nuclei, except although we saw the couplings, etc. in the analysis the spectrum. But we did not understand the NMR spectrum of quardrupolar spins; that maybe some other time we can discuss. But in the spin half nuclei case, the analysis the spectrum gives me chemical shifts, that we have been discussing, the indirect spin spin couplings; and you can also get T1 and T2 and get the information about the molecular dynamics. Of course, the NOE and various other things you can detect. Then what it cannot get in solution state that is another important thing you should know, for the same spin half nuclei. You cannot get anisotropy of the J coupling. You cannot get chemical shift anisotropy. You cannot get homo- and hetero-nuclear dipolar couplings.

Remember, all these are NMR parameters, they have tensorial properties; they are tensors which are present. But in the solution state J coupling what you have been measuring so far is an average value. Only isotropic component you are seeing, anisotropy part gets averaged out. Similarly, chemical shift is actually average chemical shift you are going to get in the solution state. The chemical shift anisotropy part which is present gets averaged in the solution state. Similarly, dipolar coupling which is direction dependent, also averages out. So, as a consequence these are the information you do not derive. But you may ask me a question, so, what? What do I get out of them? All these have lot of information content, which helps us in understanding the molecular structure and conformation, we will come to that now.

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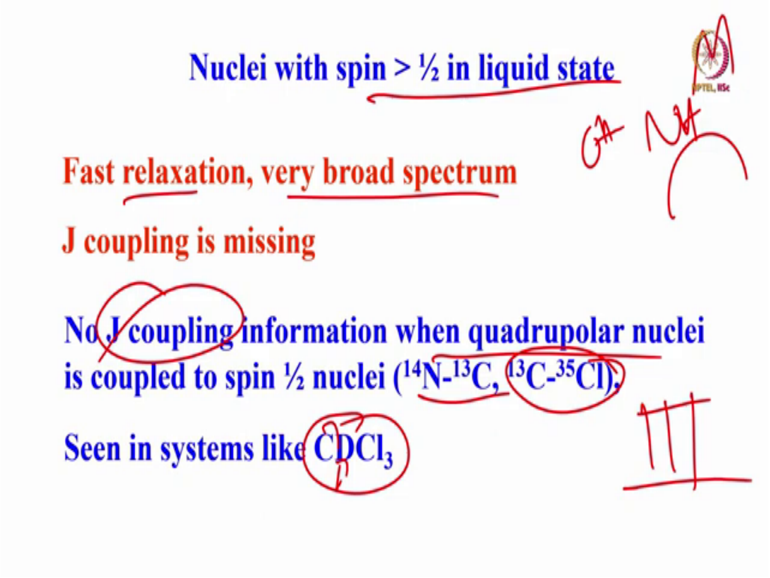

Nuclei with spin > ½ in liquid state

Fast relaxation, very broad spectrum

J coupling is missing

No J coupling information when quadrupolar nuclei is coupled to spin ½ nuclei (^{14}N-^{13}C, ^{13}C-^{35}Cl)

Seen in systems like $CDCl_3$

But nuclei with spin greater than half if I look in the solution state, what will happen? it is just for your information, generally because of the fast relaxation, you get very broad spectrum. And you do not get J coupling. For example an NH peak if you see, sometimes very rarely, you get doublet or otherwise you get a broad peak; OH peak you get a broad peak. So, no J coupling information will be generally seen when you see a spin half nucleus coupled to nuclei coupled to spin one nucleus, or anything greater than spin half.

For example, chlorine 35 and carbon 13, if they are coupled, J coupling even though it is there, you will not see. Chlorine has enormous quardrupolar moment, quardrupolar coupling is so large you will not see that. Similarly, carbon 13 and nitrogen 14; that coupling is very difficult to see. But on the other hand in CDCl3 we saw a triplet. Not triplet 3 line pattern of equal density, carbon 13 coupled to deuterium gives rise to 3 peaks. We saw that because this deuterium has a very small quardrupolar coupling. So, very rarely you will see that; but most of these things will not be seen. Quardrupolar coupling and everything. This type of thing you will see only in the solid state. Similarly, J coupling information because in the case of solids we are going to get a very very broad spectrum, very difficult to get the J coupling information. Of course it is not impossible, there are experiments to determine J coupling in solid state; but by and large is not easy, because the signal lines will be very broad.

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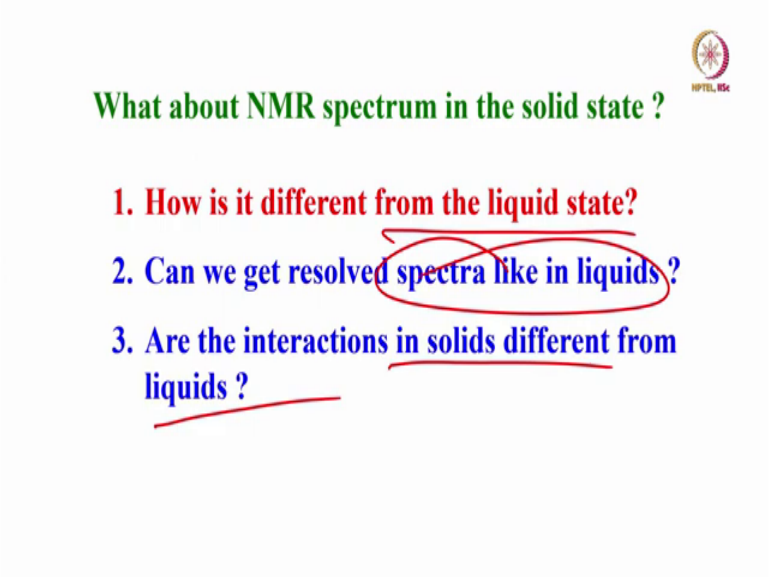

What about NMR spectrum in the solid state ?

1. How is it different from the liquid state?
2. Can we get resolved spectra like in liquids ?
3. Are the interactions in solids different from liquids ?

Now, with this we will discuss what about the NMR spectrum in the solid state? We will ask the question? how is it different from liquid state? One question, can we get a spectrum similar to that in the case of liquids, like a high resolution spectrum? Are interactions in solid different from that of the liquids? Of course, we all know solid is rigid structure there is no translational motion for the molecules, whereas in the liquids the thermal agitation will be going on; molecules are undergoing translational motion. So, interactions need be same.

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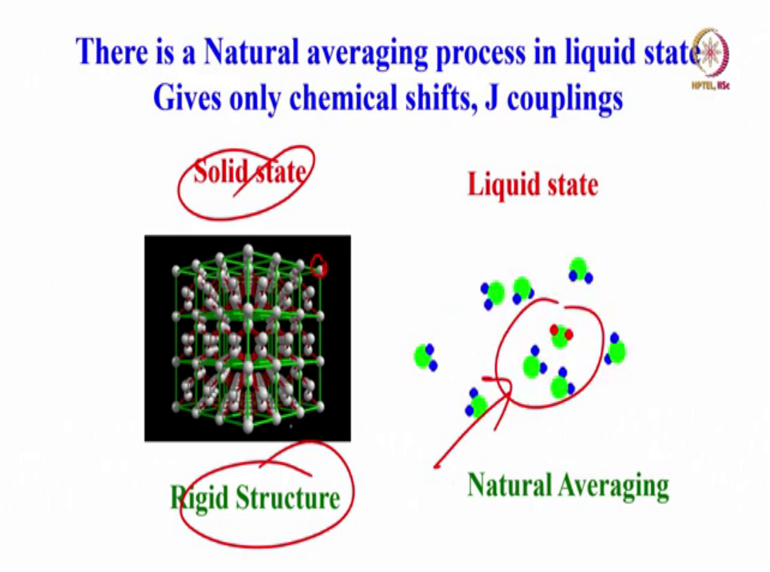

There is a Natural averaging process in liquid state
Gives only chemical shifts, J couplings

Solid state

Liquid state

Rigid Structure

Natural Averaging

So, this is simple example. Look at the solution state here. There is a natural averaging process going on, molecules are undergoing rapid tumbling motion. As a consequence, all these anisotropic interactions get averaged out, you will not see that. Whereas in the case of the solid state, there is a rigid structure, there is rigidity; there is no translational motion. Of course sitting in a place each molecule may undergo rotation that is possible.

Translational motion is not there but rotational motion maybe present, does not matter. But because of this thing, the natural averaging is present in the case of solutions but not present in the case of solids.

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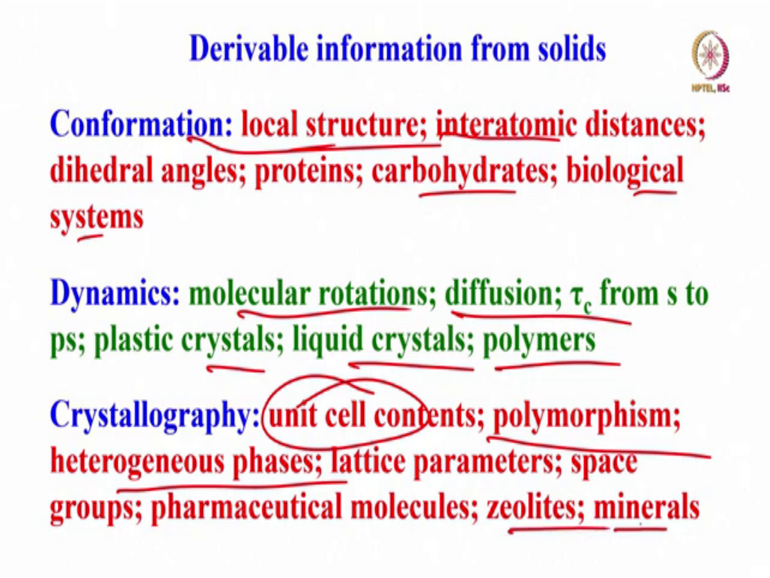

Derivable information from solids

Conformation: local structure; interatomic distances; dihedral angles; proteins; carbohydrates; biological systems

Dynamics: molecular rotations; diffusion; τ_c from s to ps; plastic crystals; liquid crystals; polymers

Crystallography: unit cell contents; polymorphism; heterogeneous phases; lattice parameters; space groups; pharmaceutical molecules; zeolites; minerals

So, what is the derivable information you get from solids? We knew what we can derive from liquids. Let us see what we can derive in solids. Of course, most of the solids you can get the conformational information, what you get like in liquids; interatomic distances, local structure, dihedral angle, if you have proteins, you can study proteins, carbohydrates and many biological systems, like you do in liquid state. Dynamics like molecular motions, not translational motion, rotational motion like diffusion if there is any; plastic crystals, liquid crystals, polymers, they can be studied; you can get a crystallographic unit information, how many molecules are there in unit cell? You can study polymorphism, please remember polymorphism cannot be studied in the solution state, you need to have the system in the solid state. Heterogeneous phases if they are present you can study in solid state; and many important materials, like zeolites, minerals and those things, some of them which are not soluble, insoluble material scould be there; you can study.

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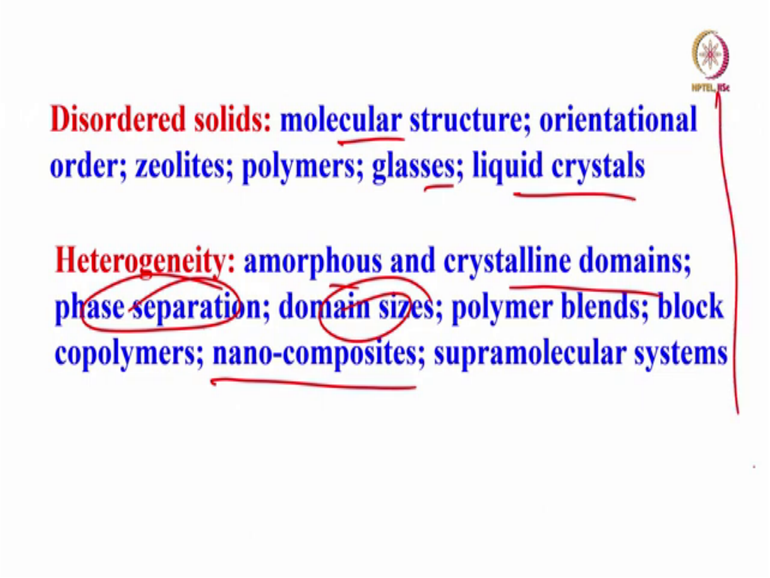

Disordered solids: molecular structure; orientational order; zeolites; polymers; glasses; liquid crystals

Heterogeneity: amorphous and crystalline domains; phase separation; domain sizes; polymer blends; block copolymers; nano-composites; supramolecular systems

You can study disordered solids like molecules, structure, orientational order, polymers, glasses, liquid crystals, can be studied. Heterogeneity can be studied like amorphous or crystalline domains, if it is present in the system, there is a phase separation in solid you can understand, like if you have a crystalline portion and amorphous portion, you can understand. Domain size you can understand, polymers, varieties of information you can get the solids. Similarly, what you get in liquid, in fact, more information you can get in the solid because you can get a solid state structure, solid state conformation which could be different from the solution state. So, a lot of information you can get in the NMR spectrum of the solids.

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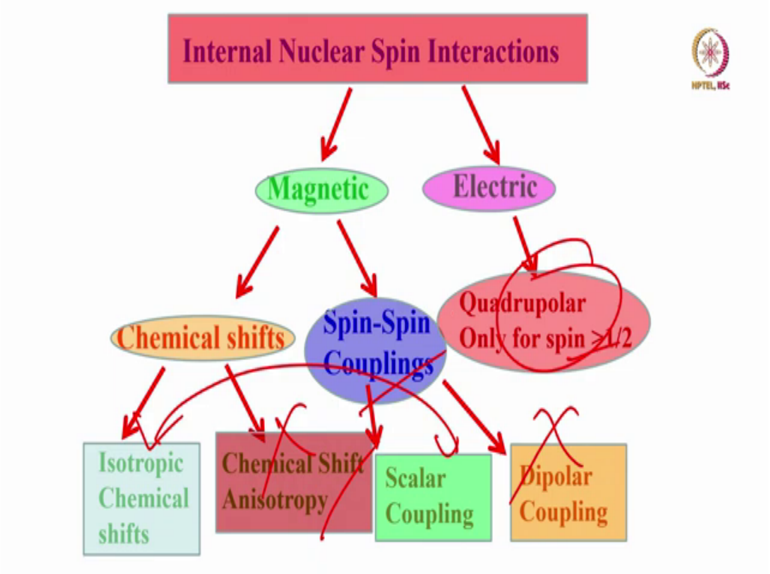

Internal Nuclear Spin Interactions

Magnetic

Electric

Chemical shifts

Spin-Spin Couplings

Quadrupolar Only for spin >1/2

Isotropic Chemical shifts

Chemical Shift Anisotropy

Scalar Coupling

Dipolar Coupling

Now, we need to discuss one thing; internal nuclear spin interactions. We have discussed this in the beginning in the very first class. Let us see what are the internal nuclear interactions, one is magnetic and the other is electric, we discussed. The magnetic interactions are chemical shifts, spin-spin couplings both are present, they are internal interactions, and the electric interaction is there that is a quardrupolar coupling for spin greater than half; this also we discussed.

And the chemical shift again I said it can be isotropic and isotropic chemical shift and chemical should anisotropy, both could be present. If you go to spin-spin coupling, it could be scalar coupling and dipolar coupling. What we understood in the case of solution was; this was missing and this was missing, I said these things are averaged out, you do not see it. We were always concentrating only on this and this. That is why all these things we discussed. The varieties of experiments we discussed. Of course, in the solid state this is also present. In the solution it was missing.

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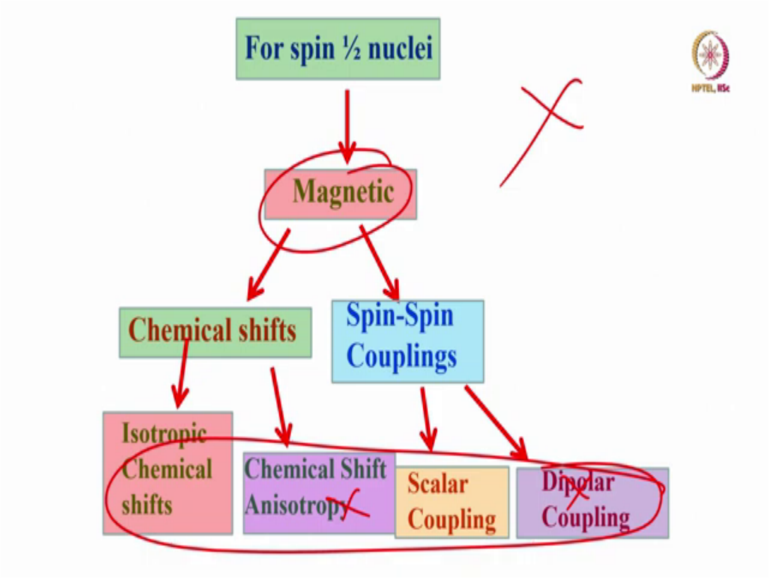
For spin ½ nuclei

Magnetic

Chemical shifts

Spin-Spin Couplings

Isotropic Chemical shifts

Chemical Shift Anisotropy

Scalar Coupling

Dipolar Coupling

Now, if you go to spin half nuclei that we have been discussing, this course is more focused on spin half nuclei. Now, if you go to magnetic interactions, so, electrical interaction is out, we do not discuss about quardrupolar coupling. Then all the four interactions are present, all are needed, and are present. We need to understand everything we need to discuss all those things. So, these are the things which are present makes this solid state NMR different from the liquid state.

So, these two parameters are absent in the solution state but they are present in the solid state. These make the NMR spectrum of solid different from that of the liquids.

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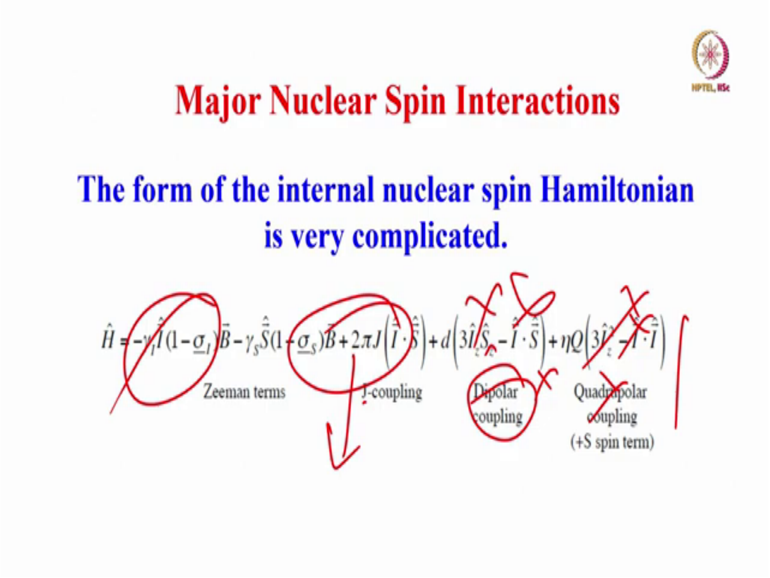

Major Nuclear Spin Interactions

The form of the internal nuclear spin Hamiltonian is very complicated.

$$\hat{H} = -\gamma_I \hat{\vec{I}}(1-\underline{\sigma}_I)\vec{B} - \gamma_S \hat{\vec{S}}(1-\underline{\sigma}_S)\vec{B} + 2\pi J\left(\hat{\vec{I}}\cdot\hat{\vec{S}}\right) + d\left(3\hat{I}_z\hat{S}_z - \hat{\vec{I}}\cdot\hat{\vec{S}}\right) + \eta Q\left(3\hat{I}_z^2 - \hat{\vec{I}}\cdot\hat{\vec{I}}\right)$$

Zeeman terms

J-coupling

Dipolar coupling

Quadrupolar coupling (+S spin term)

Now, if you go to the nuclear spin interactions, as I said nuclear spin does not know whether it is in the solid state or in solution state, except the interactions are different. See for example, Zeeman interaction is present which is there in the solution state. J coupling is present that is also presented the solution state. Dipolar coupling and quardrupolar coupling terms are also there, this is for spin greater than half, but they are averaged out in the solution state.

And of course, this you can further break into anisotropic part and isotropic part, etc. This can be broken into homonuclear part and heteronuclear part, etc. Basically the internal spin Hamiltonian is still complicated; it is there. But only thing is certain terms we remove it, we do not consider it in the solution state because they are not present. But now, we have to consider all these parameters; all these terms when you are interested in solid state NMR. NMR of your molecule in the solid state.

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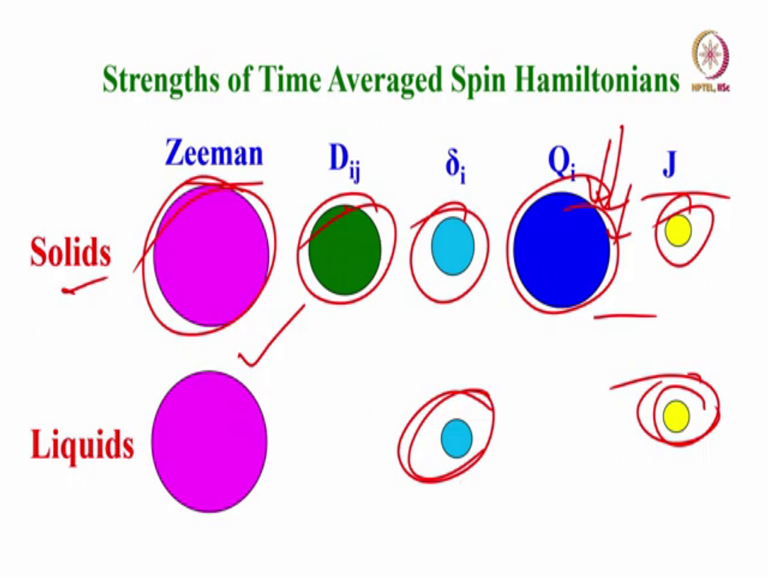

Now, you may ask me what is the strength of such interactions? Whether the interactions strengths are different from solution state and the solid state. Of course I am not taking into account RF interaction that also one can consider. But I am considering only external interactions as Zeeman and the rest are all internal interactions. Like dipolar coupling, quardrupolar coupling; chemical shift and J coupling.

Now, solids if you consider the more Zeeman interaction is the largest strength very large then comes dipolar coupling; then comes chemical shift; and if you go to spin greater than half quardrupolar coupling; this is quite large shift, very much larger than dipolar coupling. Sometimes comparable to Zeeman or even more than Zeeman. If this is smaller than Zeeman interaction, it is called quardrupolar perturbed Zeeman. If this is very much larger than Zeeman, then it is called Zeeman perturbed quadrupolar. See the way we have to deal with depending upon its strength. And of course, J coupling is much smaller as always; and all these things are present in solids. Several types of interactions are there. If you go to the liquids interestingly, we have only Zeeman interaction, chemical shift interaction; chemical shift which is present and what is called J coupling. These were not present. See the interaction strengths are much smaller, that is why the NMR spectrum of the solution state are simpler. Now, when you bring in this and this, spectrum gets more complex.

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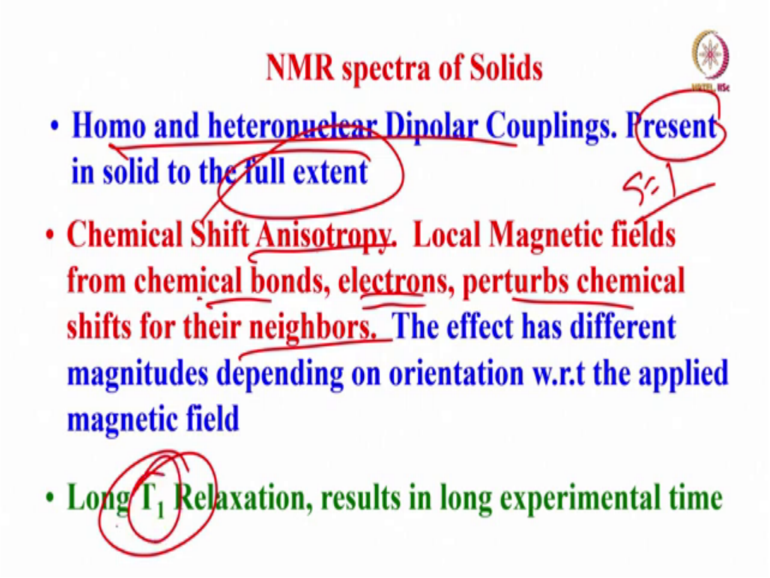

NMR spectra of Solids

- Homo and heteronuclear Dipolar Couplings. Present in solid to the full extent
- Chemical Shift Anisotropy. Local Magnetic fields from chemical bonds, electrons, perturbs chemical shifts for their neighbors. The effect has different magnitudes depending on orientation w.r.t the applied magnetic field
- Long T_1 Relaxation, results in long experimental time

So, now, if we go to NMR spectrum of the solids, why it is complex? what makes the NMR spectrum different from that of a solution state? As I said, homo and heteronuclear dipolar couplings, are present in the solid to the full extent. Remember my statement, it is present to the full extent; the order parameter in solid is 1, S is equal to 1. And you can have a partially ordered system, ordered parameter in the solution state is 0. For molecules there is no preferential ordering, no ordering at all. Solutions are undergoing thermal agitation, random motion is there; so, order parameter is 0. Whereas, in the case of a solid because of the rigid structure order parameters is 1, you can think of a situation in between liquids and solids by doping the molecule in a semi ordered state, like liquid crystalline phase. Then the order parameter is between 0 and 1. In which case the dipolar couplings, quardrupolar couplings everything gets reduced. They are present in the reduced form. whereas, in the case of solids, they are present in full form, full extent; that is why I said full extent. please understand. Chemical shift anisotropy. The local magnetic field at the site of each nucleus comes because of chemical bonds, electrons, etc and they perturb the chemical shift of the neighbours.

So, the neighbour chemical shifts are perturbed because of chemical bonds and electrons. The effect is different depending upon the orientation with respect to applied field. What is this? So, far we never discussed about the orientation of the chemical shift; In the isotropic case we are not discussing that, because were having only average orientation. But chemical shift anisotropy is also direction dependent.

As you go ahead further, I will tell you, we can treat chemical shift anisotropy like an ellipsoid. The charge distribution and depending upon its orientation, of the ellipsoid we can have different chemical shifts in different directions depending upon how it is oriented in the external magnetic field. So, we will discuss those things. And another major problem we come across in the case of solids is very long T1 relaxation.

Unless in the solution state where the motion average creates a local field at the site of the given nucleus, so that the nuclear spins undergo relaxation fast by giving its energy. There is a local field created at the Larmor frequency. So, the spins undergo relaxation, whereas in the case of solids T1 is quite long. It takes several hours, minutes, days, there are some systems where which spin lattice relaxation T1 can be of the order of days. You will send a pulse today collect the signal, you have to wait for a couple of days or weeks to send another pulse to collect the signal. So that is because of a long relaxation; all these are problems in solids. But of course we can overcome them.

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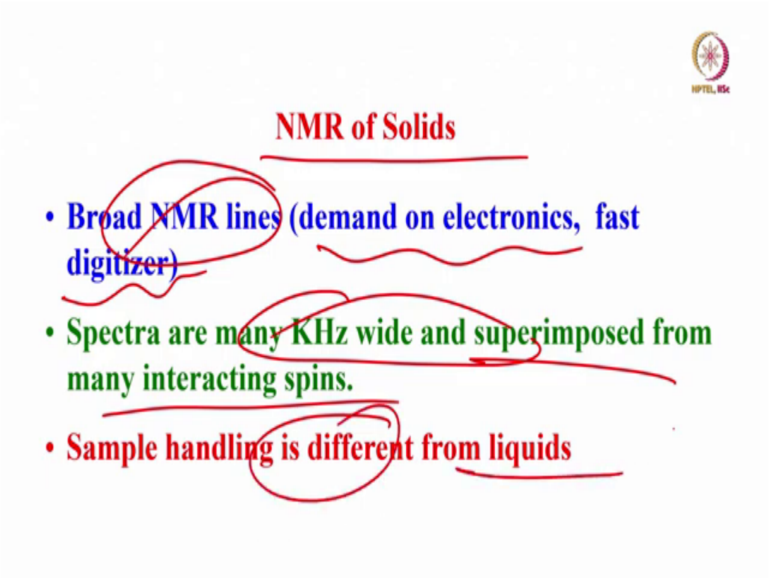

NMR of Solids

- Broad NMR lines (demand on electronics, fast digitizer)
- Spectra are many KHz wide and superimposed from many interacting spins.
- Sample handling is different from liquids

NMR of solids: Basically with this I can tell you which is what we discussed gives rise to broad NMR lines, generally. There is a demand on electronics for fast digitization. Of course, nowadays what happens if you go for high resolution, it is still okay, you get a free induction decay which decays exponentially similar to like that of a liquid during high resolution. But if you get a wideline spectrum, the signal decays so, fast. There is a heavy demand on electronics, you need fast analog to digital converter. And the spectral is many kilohertz wide, especially in the wide line case and superimposed from many interacting spins. Even if you are doing the magic angle spinning and various experiments, I show you as we go ahead for getting high resolution spectra can be broader. And the sample handling is different from that of the liquid state; it is not easy.

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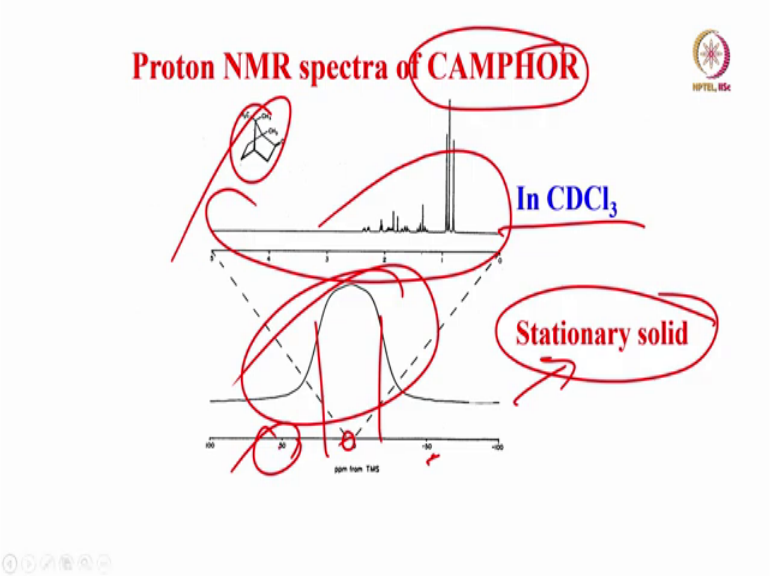

Proton NMR spectra of CAMPHOR

In $CDCl_3$

Stationary solid

So, just to compare, let us look at a spectrum of a camphor molecule. You know the camphor which is used in most of the temples and others. This is the camphor structure. This is the spectrum in CDCl3, dissolve the molecule in the solvent chloroform. This is in the stationary solid. Remember, I am using the word stationary solid. Why I am using that word stationary. We can make the solid sample to undergo spinning and we get sharp lines. It means nothing is being done. Simply take the sample, put it in a magnetic field and record the spectrum. You are going to get a broad hump like this. Imagine this is in ppm, 50 ppm. if you see 50 to 100 ppm. Let us say, if you go to 500 megahertz, 1pp ppm means 50 kilohertz. See the line with itself is about 30 to 40 kilohertz. Whereas, the entire spectral width in the solution state is within this range; 0 to 5 PPM.

So, this is the difference; the spectrum in the case of the solids is very very broad because of the rigid structure. Whereas, in the case of the solution state, you will get only very narrow lines within a narrow range. So, there is a 40 fold scale difference between these two.

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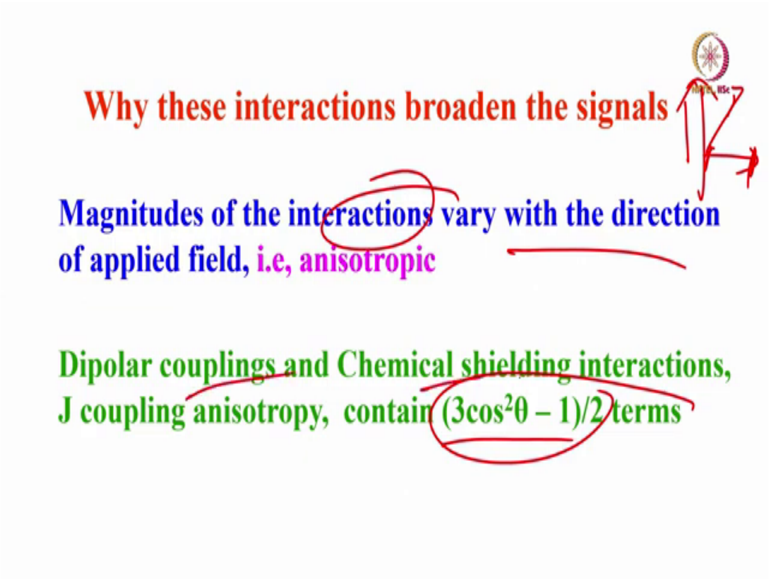

Why these interactions broaden the signals

Magnitudes of the interactions vary with the direction of applied field, i.e, anisotropic

Dipolar couplings and Chemical shielding interactions, J coupling anisotropy, contain $(3\cos^2\theta - 1)/2$ terms

Next, you may ask me a question fine is different, why do these interactions broaden the signals. If the dipolar coupling is there, the chemical shift anisotropy is there, why the NMR signals have to be broad? You can understand like this, magnitudes of these interactions vary with the direction of the applied field; that is because they are anisotropic. If there is a direction of the magnetic field, if I have an internuclear vector oriented like this, it has one value. If it is oriented like this, it is one value, if it is oriented in this direction, it is one value. So, magnitudes of interactions, all these anisotropic interactions, vary with the direction of the applied field. And for example, the dipolar coupling and chemical shift terms, contain a term called 3 cos square theta – 1 by 2. It is a term, when we go ahead I will tell you, this term is there for are J anisotropy also. Not only this dipolar coupling and the chemical shift anisotropy even J anisotropy also has 3 cos square theta – 1 by 2 term.

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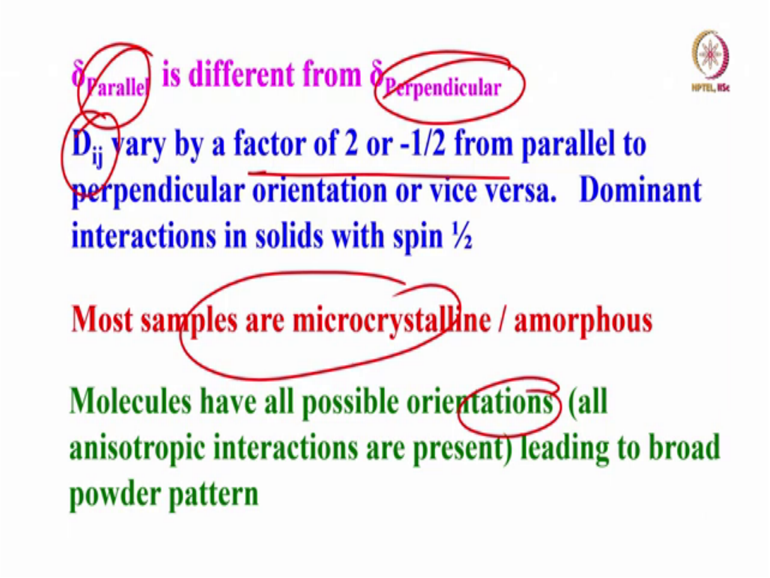

$\delta_{Parallel}$ is different from $\delta_{Perpendicular}$

D_{ij} vary by a factor of 2 or -1/2 from parallel to perpendicular orientation or vice versa. Dominant interactions in solids with spin ½

Most samples are microcrystalline / amorphous

Molecules have all possible orientations (all anisotropic interactions are present) leading to broad powder pattern

All these things make it very complex. Let us understand, let us look at the chemical shift. The chemicals shift, let us say, if I measure in the parallel orientation is different from the perpendicular orientation. I may have a molecule, let us say it has anisotropy. If I put the molecule in the direction of the magnetic field like this, I can get one value. If I put it in the direction perpendicular to the magnetic field, I get another value. Secondly dipolar coupling vary by a factor of two or minus half, depending upon the internuclear whether it is in the direction of the field or in the direction perpendicular to the magnetic field, and it is the dominant interaction. And in between, for different angles, what happens? accordingly they get scaled. So, the most of the samples, what we study in solids, there are micro crystalline and amorphous in nature. The molecules have all possible orientations, all anisotropic interactions are present. In these isotropic interactions varieties of directions you can think of; all possible orientations of the internuclear vectors are present. They all give rise to spectrum individually; they lead to overlap and result in what is called a broad powder pattern.

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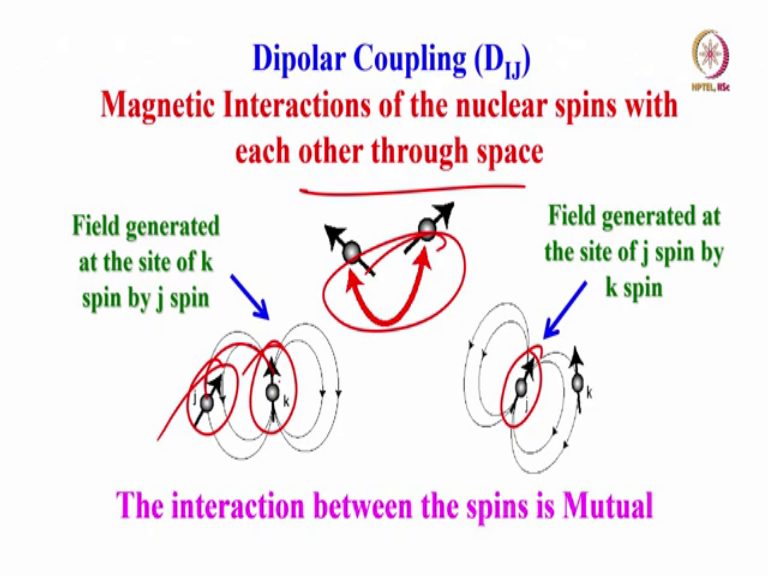

Dipolar Coupling (D_{IJ})

Magnetic Interactions of the nuclear spins with each other through space

Field generated at the site of k spin by j spin

Field generated at the site of j spin by k spin

The interaction between the spins is Mutual

Now, let us go look at the dipolar coupling. Dipolar coupling is a magnetic interaction of the two nuclear spins through space. Let us say I have two nuclear spins like this. And there is a interaction between these two. Remember we discussed about the interaction of the two nuclear spins through covalent bond, that is the J coupling interaction. But through space interaction is the dipolar coupling interaction.

These are dipolar couplings, what will happen is if they are coming close in space; because of this close spacial proximity, let us say I have a spin j. The spin j can create a local field at the site of spin k. Similarly, spin k can create the local field at the state spin j, why? Because I have been telling you all interactions in NMR are mutual. As a consequence, the spins j and k will produce local fields between themselves.

This is an interaction through space, called dipolar coupling, dipolar interaction. This can couple to each other, it gives rise to this splitting of transitions and it can give rise to complex multiplicity pattern in the spectrum.

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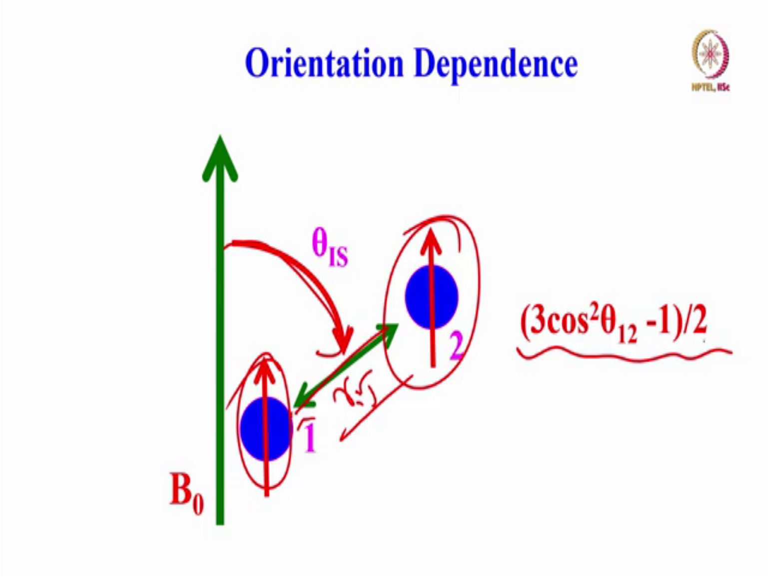

Orientation Dependence

So, they are orientational dependence that can be seen from this figure. Let us say I have nuclear spin 1, I have a nuclear spin 2, let us say separated by internuclear vector here, rij, I will call it, it has some value. And this is the orientation angle theta with respect to the magnetic field. Then the dipolar coupling scaling is given by 3 cos square theta– 1 by 2. It has a direction dependence.

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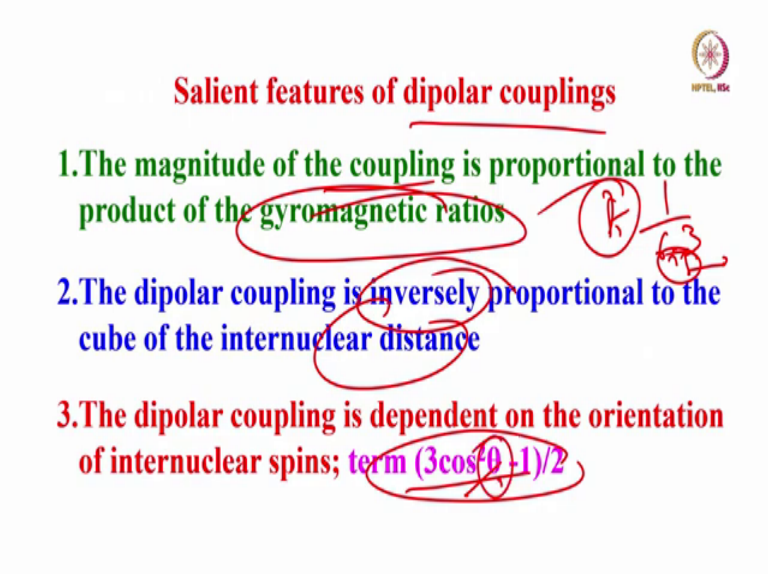

Salient features of dipolar couplings

1.The magnitude of the coupling is proportional to the product of the gyromagnetic ratios

2.The dipolar coupling is inversely proportional to the cube of the internuclear distance

3.The dipolar coupling is dependent on the orientation of internuclear spins; term $(3\cos^2\theta - 1)/2$

The salient features of dipolar couplings: of course, each of these things we could discuss derive, understand a lot of things. But in a short span of next another one or two hours, we have or maybe 3 hours maximum to discuss entire solid state NMR, I will only give you the conceptual understanding without going into the complete details. So, please remember these are important salient features of dipolar couplings.

The dipolar coupling as I told you in the earlier of the couple of slides before, the strength of this quite large compared to J coupling. We saw some spheres you know, the coloured spheres, the magnitude of this coupling depends upon one important thing is gyromagnetic ratios, gamma. The gamma of the nuclei. And it is inversely proportional to the cube of the internuclear distance.It depends upon one over rij cube. Rij is the distance between two internuclear spins, it is an internuclear vector, between spins i and j. It is the inverse of rij cube. So, as r keeps changing, when r increases slightly, Dii comes down a lot. As the distance becomes closer and closer, when there is a close proximity, the dipolar coupling becomes larger and larger. So, this depends upon distance and it complicates the NMR spectrum.

And it is a orientation dependent just now we discussed in the previous slide, it depends upon the term 3 cos square theta – 1 by 2. And it gets scaled because of the orientation of the internal vector making an angle theta with respect to the magnetic field direction.

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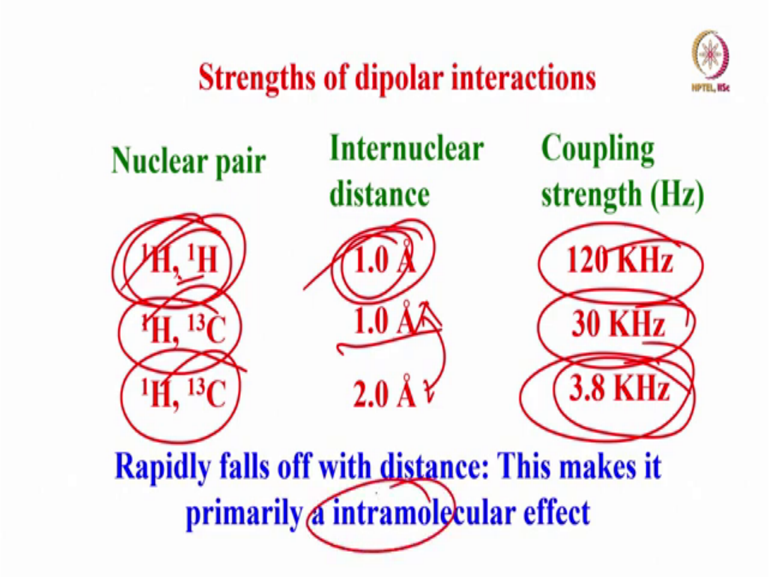

Strengths of dipolar interactions

Nuclear pair	Internuclear distance	Coupling strength (Hz)
$^{1}H, ^{1}H$	1.0 Å	120 KHz
$^{1}H, ^{13}C$	1.0 Å	30 KHz
$^{1}H, ^{13}C$	2.0 Å	3.8 KHz

Rapidly falls off with distance: This makes it primarily a intramolecular effect

Just to give you a bit idea about the strength of dipolar interactions. Consider, let us say, two nucleus proton and proton. Internuclear distance is 1 Angstrom. Of course, it may be more, I am just taking a hypothetical case I am considering. Yhe internuclear distance is only 1 Amgstrom. The coupling strength, the dipolar coupling strength is 120 kilohertz. Remember J coupling we discussed, it is only few hertz. In heteronuclear case few 100 Hertz but here, remember the dipolar coupling among the homonuclear spins, is kilohertz. Just the proton dipolar coupling if you consider separated by 1 Amgstrom, it is 120 kilohertz. If you take proton and carbon; here carbon has a gamma 4 times less than that of protons. Assuming the same distance it comes down by 4 times. because gamma of carbon is 4 times less than that of the proton. It is thus 30 kilohertz. Let us consider the same proton and carbon. Let me double the internuclear distance; the coupling strength came to 3.8 kilohertz. Imagine, how strongly it depends upon the inter nuclear distance. How strongly it depends upon the gyromagnetic ratios between the interacting spins. And remember as the distance becomes larger and larger, as you go far away, the dipolar coupling drastically falls down, it depends upon the distance. So that is why very rarely you come across intermolecular dipolar interaction. Of course, it can be present in rigid solid. Basically it can be intramolecular effect.

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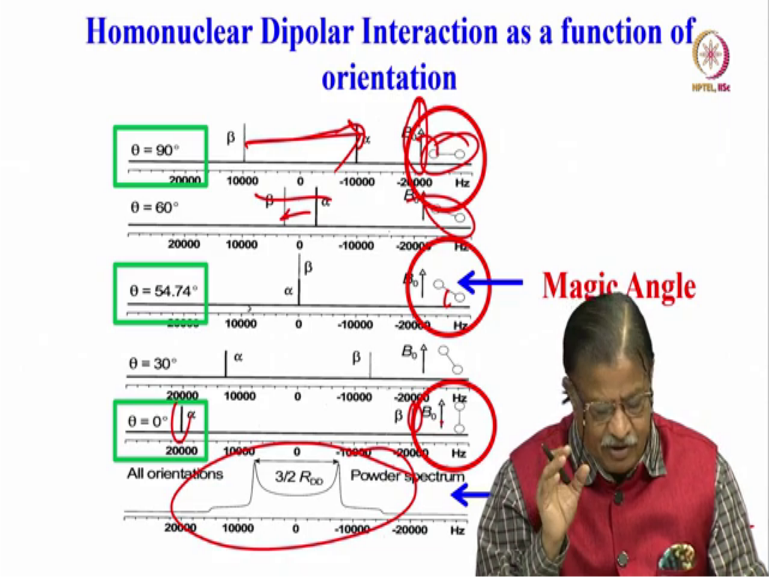

Homonuclear Dipolar Interaction as a function of orientation

Let us look at homonuclear dipolar interaction as a function of the orientation. Let us say, I have internuclear vector here; oriented with the magnetic field B naught. Now, this spin has got two orientations alpha and beta. So, it gives us a doublet like this. Now, this angle when it is exactly perpendicular to magnetic field; the internuclear vector is making 90 degrees with respect to the magnetic field.

Now, change the orientation of internuclear vector here, the separation came down, you see. beta alpha, the separation was this large, became this small. Go to a situation here at a particular angle. This both alpha and beta orientation collapses. There is no separation at all. And there is no separation, no splitting at all, no dipolar coupling. Keep on changing the orientation further. Now, this became again larger.

Another interesting thing what happens is, this alpha is moving towards left beta is moving towards the right. Now, there is a switchover of alpha and beta. That is why I said the dipolar coupling changes from + 2 to – half, depending upon the orientation. Now, the sign is changed. So, far it has been perpendicular to the magnetic field direction, it was – half now, it becomes + 2 times; that is what it is.

So, like this keep on changing and come to a situation, when it becames exactly parallel the alpha and beta are very well separated here, you can see. Look at this one; this is parallel to this, this is alpha and this is beta; that is very well separated here. Almost doubled this one. That is why I said it changes two times. So, in principle what happens is all possible orientations are present, infinite orientations are there.

I am showing you only a couple of them and each of them gives different type of splitting. Splitting patterns are different, strengths are different, separations are different. As a consequence, in a real sample, every orientation is present, all possible orientations are present. Each and every orientation you should consider. Finally, they all overlap and gives rise to a spectrum like this. This is called the powder spectrum.

Powder spectrum comes because of orientation of all the internuclear vectors, in all possible orientations. This is the powder spectrum. What is a powder spectrum? it comes because of all possible orientations of internuclear vectors in a molecule with respect to the magnetic field.

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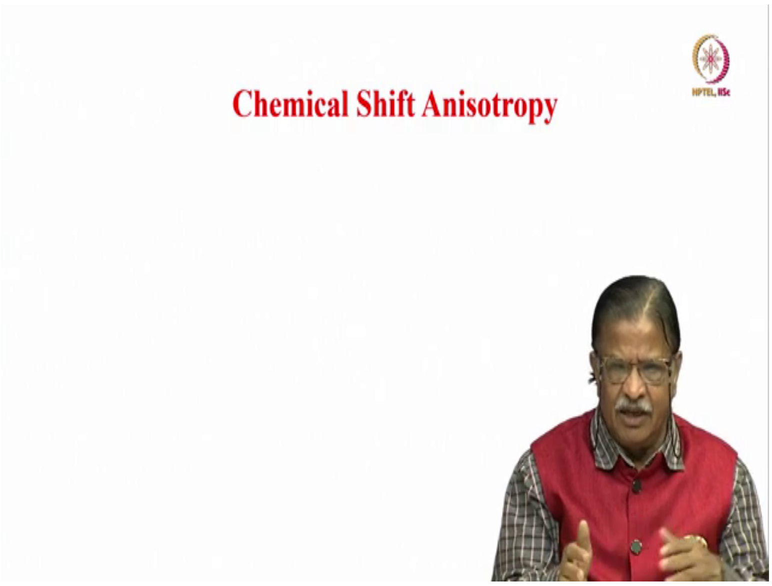

Chemical Shift Anisotropy

So now, we understood what is the dipolar coupling, we can discuss much more, there is a dipolar alphabet expansion, a big theory one can give and find out different terms, A B C D E F; and what A does, B does, C does, everything we can discuss; But there is no time for it. This is the basic idea, about dipolar coupling of what I have given you. Please remember that.

Next is CSA we can discuss CSA and then we will understand what CSA will contribute and everything. Since the time is getting over what I will do is I will stop here; come back and continue CSA and other interactions. And how we get NMR spectrum all those things later.

So, today, we started introducing a new topic, new subject called solid state NMR of spin half nuclei. We understood it has different interactions present which are different from that of the liquids. Some are different, like dipolar coupling. Chemicals shift anisotropy and J anisotropy are present. The chemical shift anisotropy J anisotropy, dipolar coupling, they all get averaged in the solution state. We are dealing with only spin half nuclei.

So, we do not bother about quardrupolar coupling. So, all the anisotropic parameters are averaged out in the solution. Whereas in the case of solids, they are fully present. And that gives us a lot of complications; gives us a very broad spectrum, because they are orientation dependent; example of a dipolar coupling we saw. Depending upon the orientation the alpha and beta spin states of a particular spin, the doublet separation keeps on changing. And after a certain angle they switches over, sign changes and then coupling strength starts increasing. Similarly, CSA also depending upon the orientation, it will have a different value. All these things are present. There are infinite micro crystalline orientations are present in the powder. In the powdered solid all the possible orientations are present. As a consequence, the spectrum has varieties of such doublet separations which are present. They all overlap and give us what is called as a powder pattern; that is a powder pattern. We discussed for dipolar coupling. Then you may ask me what happen to the chemical shift anisotropy. For discussion I took dipolar coupling; not that CSA is not present. it is also present will discuss later.

So, we will come to chemical shift anisotropy and all those things in the next class. So, I stop here we will meet again in the next class. Thank you