Advanced NMR Techniques in Solution and Solid State
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Module-58
WAHUHA and Cross Polarization
Lecture – 58

Welcome all of you. Now we have been discussing about solid state NMR in the last two or three classes. As you know in the last class, I discussed extensively about the magic angle spinning. I said initially if I consider the dipolar Hamiltonian there are three products; 1 over r IJ cube and space part and the spin part. I said since they are products, any of these terms, if becomes zero, the dipolar coupling becomes zero.

I just gave you the hand waving argument with the dipolar coupling. I showed that in the case of carbon 13-carbon 13 coupling if you consider two spins which are in carbon 13 state, it less probable, only one in 10,000. As a consequence, what happens is the dipolar coupling between two carbon 13 in the natural abundance, that is between dilute spins, is almost negligible or it is not there. That means, in other words, you can say the distance between these two spins are infinite that is one way. Secondly, we can consider the space part. In the space part we have 3 cos square theta – 1 / 2 term. I said put the sample at magic angle, start rotating at a high speed, that is, physically you are rotating the sample at a particular angle. If you rotate then I said several infinite internuclear vectors which are present in the sample, each of them making different angles with respect to the magnetic field, finally, they align. You can deem them to be aligned along the spinning axis, which makes 54.7 degree with respect to the magnetic field. This angle is called magic angle; and I also said it can be considered as a dynamic implementation of the cubic symmetry. Consider a cuboid and then find out what is the body diagonal of the cuboid, if we find out, it makes angle 54.7 degree with respect to any of the three axis. Analogous to that if you spin the sample at 54.7 degree we are dynamically implementing cubic symmetry, for the molecule. Artificially you are creating cubic symmetry. And this eliminates heteronuclear dipolar couplings, eliminates chemical shift anisotropy, and all the second rank interaction tensors. Homonuclear couplings, of course, I said it is not possible to eliminate using magic angle spinning.

And what should be the spinning speed? It depends upon the interaction strengths. The spinning speed should be larger than the interaction strength. That means it should be larger than heteronuclear dipolar couplings. It should be larger than chemical shift anisotropy. In powder samples these two parameters are not independent, and they are all present; both are present. So, if you look at the powder pattern, the profile of a powder pattern you are going to get; and then take this powder pattern; that gives you the idea of the interaction strength. And your spinning speed should be larger than that, then these things will be eliminated out.

We saw that when you eliminate the heteronuclear interactions and CSA, lines becomes sharper and signal to noise ratio becomes more. There is a sensitivity enhancement; and all the sidebands will overlap. As I said if you spin at a low speed; lower than the interaction strengths, the powder pattern breaks into sidebands. And the sidebands are separated by the spinning frequency. Measure any of the two sidebands, adjacent sidebands, that separation frequency corresponds to spinning frequency, because the precesional frequency of the nuclear spins get modulated by the spinning frequency, physically when you are spinning the samples. And then if you want to identify the isotropic chemical shift, isotropic peak, when you are having N number of spinning sidebands, do at two or three different spinning speeds; then the center band will always remain same, it will not move. Whereas the sidebands keep moving away. That way you can identify what is the Centre band; what is the isotropic chemical shift. So, all these things we discussed and took number of examples to see what happens. Today, we will go further and see how we can utilize magic angle spinning along with this dipolar decoupling also we can do. I was telling you about only magic angle spinning. Now what happens if I take magic angle spinning, I start spinning, simultaneously I also apply decoupling power; this is what we are going to discuss today.

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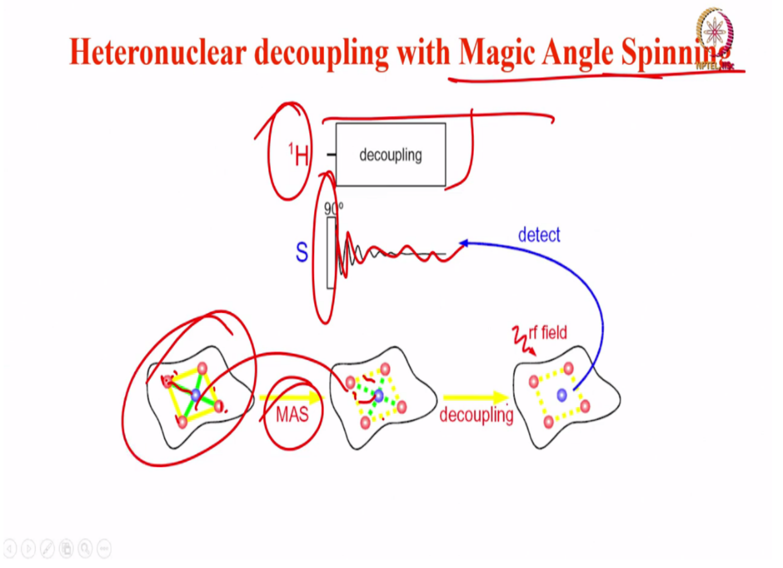

Heteronuclear decoupling with Magic Angle Spinning

The heteronuclear decoupling with magic angle spinning. This is the pulse sequence, it is very simple. It is the proton channel; in the carbon 13 nuclei channel apply 90 degree hard pulse excite all the carbon 13 spins, the signal starts decaying, start collecting the signal; continuously apply the C wdecoupling. What is going to happen here; look at this in the previous case you have homonuclear dipolar coupling, heteronuclear dipolar couplings everything is present. For example, these are all homonuclear spins; like protons. These couplings are also there. These are all heteronuclear couplings from blue to red; they are all present. But what is going to happen if we start spinning; magic angle spinning if we do spinning with whatever available spinning speed or high speed, then you see this will become weaker. You can see dotted lines here; from solid lines it has become dotted lines. That means you reduced the interaction strength a lot. In addition to that if you do the decoupling you break all the couplings between heteronuclei carbon and proton dipolar couplings. All these things you can remove. But you see the homonuclear dipolar couplings are not removed, it has only weakened little bit, you reduce the strength a bit, but you are unable to eliminate here; you can see here. You are not able to eliminate homonuclear dipolar couplings, we are only reducing a bit. Whereas heteronuclear dipolar couplings are completely removed. So, the combination of magic angle spinning with heteronuclear dipolar decoupling is much more advantageous.

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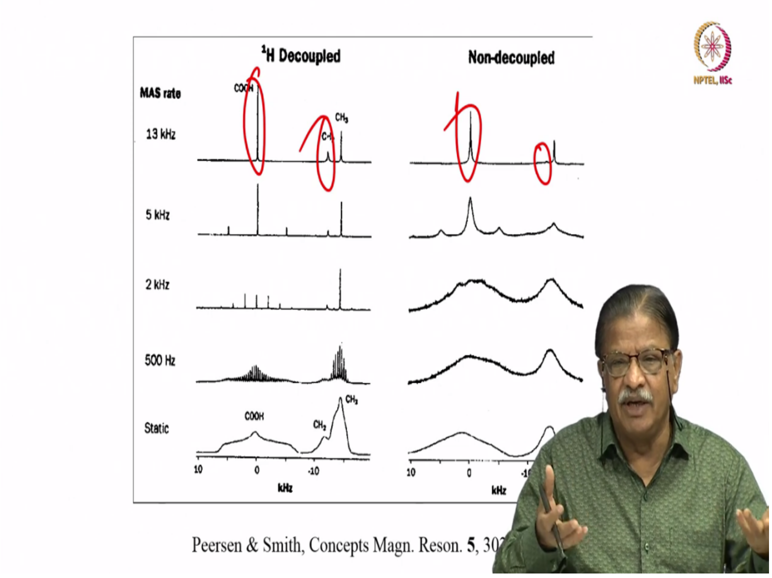

Peersen & Smith, Concepts Magn. Reson. 5, 30

Now look at the spectrum this is from the concept of the magnet resonance. You can see this is the proton spectrum of one of the molecules, CH3, CH2, COOH all the three are, must be alanine. Look at it this, it is the powder pattern; COOH, CH2 and CH3 are there; static case. No decoupling here. First we will start with this. No decoupling here in which case you can see that there is no decoupling you get a very, very broad powder pattern like this, in the static case.

Now spin at 500 hertz, half kilohertz; this is what it is. Go to 2 kilohertz this is what it is; small things started coming; no improvement; go to 5 kilohertz; you see sidebands, lines are very broad still. This is CH3 and CH2, this is COOH. Look at this one at 13 kilohertz you are getting one peak here. Of course this peak is still not visible and only one peak here, you have removed the sidebands. Of course, you are not doing any decoupling here, still okay. This is simple; only magic angle spinning at different speeds.

Now we will do another experiment along with the magic angle spinning. Do the simultaneously decoupling also at the same speed. This is what happens now, static case with the decoupling is like this; look at this pattern and this pattern, there is enormous change here. Already you started seeing the powder pattern, axial asymmetric powder pattern here. Now starts spinning look at this one and this one, because of the decoupling sidebands started seeing. Look at here much better compared to this, here to here. And come to this last one 13 kilohertz, look at this one not only you have removed the sidebands and compared to the line width between this and this, there is a enormous reduction in the line width. Look at this, look at this, look at this; the decoupling has drastically reduced the line width. This is much better look at this, this is much better now, which was not even visible.

So, magic angle spinning alone is not sufficient; you need some sort of a decoupling also. With both of them, a blend of magic angle spinning with heteronuclear decoupling is beneficial. You get sharper peaks because both of them will aid in removing heteronuclear dipolar couplings like this.

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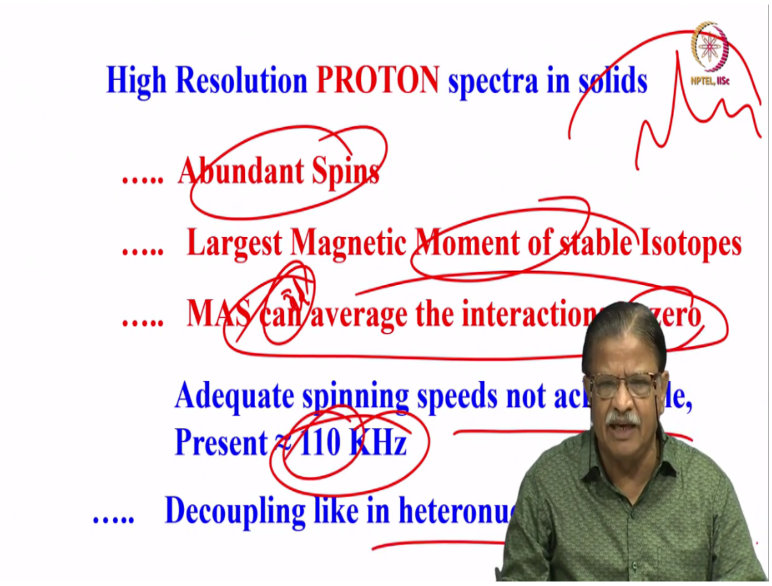

High Resolution PROTON spectra in solids

….. Abundant Spins

….. Largest Magnetic Moment of stable Isotopes

….. MAS can average the interaction zero

Adequate spinning speeds not ac le,
Present ≈ 110 KHz

….. Decoupling like in heteronu

With this we are talking about heteronuclear dipolar coupling alone. But I said homonuclear dipolar coupling cannot be eliminated by magic angle spinning you may have reduced little bit; you can reduce some size, but it cannot be eliminated completely; you can only weaken a bit. But can we get high resolution proton spectrum in solids. You can get it, you can never imagine that you get the lines as sharp as that you get in the case of liquid state. But still instead of getting broad hump like this, a mountain, we can try to get some peaks like this, it is possible. How you do that? Most important thing in the case of protons, the abundance spins, the dipolar coupling between two protons is very, very large; and these dipolar couplings among the homonuclear spins is a homogenous interaction, which cannot be eliminated by magic angle spinning alone.

That is why I said it is not possible; other interactions like heteronuclear dipolar couplings are heterogeneous interactions that can be removed. So, proton dipolar couplings is the homogenous interaction and as a consequence, you cannot eliminate just by spinning. You need enormous amount of spinning speed; several orders of magnitude larger. So, this is the abundant spin largest the magnetic moment, MAS cannot average the interaction to 0, but not can average but not completely. The MAS cannot average this interaction to 0. And adequate spinning speed are not achievable. Right now 110 kilohertz is available at present; even little larger also now; even then it is not sufficient. And you cannot do homonuclear broad band decoupling, because you have to do the decoupling when you are acquiring the signal or collecting the signal, at the same time doing the decoupling is not possible, you are disturbing the spins so it is not possible.

So, homonuclear decoupling while acquiring the signal is not possible like heteronuclear decoupling; so these are the difficulties. You remember in short, homonuclear dipolar couplings are homogenous interactions. Magic angle spinning alone cannot average out the interactions you need adequate spinning speed much, much more, several orders of magnitude larger. And current available spinning speed 110 kilowatt, it cannot do that and homonuclear decoupling like heteronuclear decoupling is not possible.

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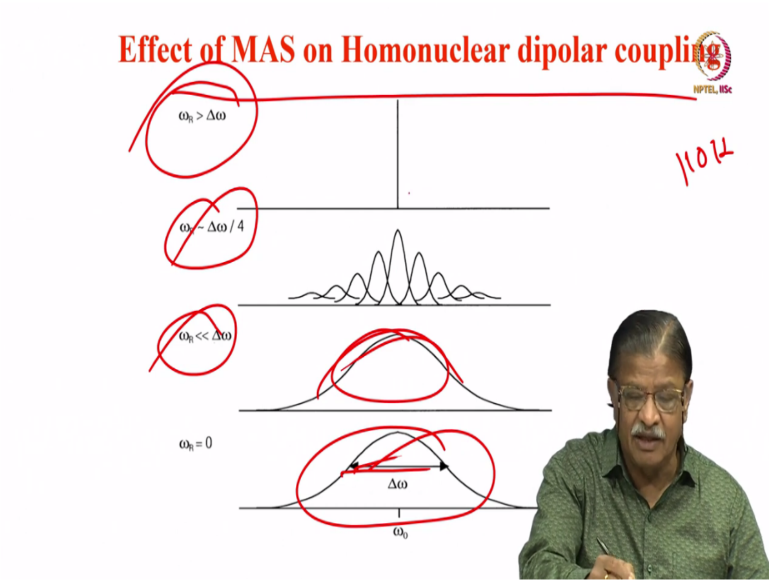

Effect of MAS on Homonuclear dipolar coupling

So, that is why if you look at the powder pattern for magic angle spinning and homonuclear dipolar coupling. This is a powder pattern and you start spinning at a rate smaller than the width of the powder pattern, absolutely no change, you do not see anything. Start spinning at a rate slightly larger than this. Now you see it breaks into sidebands; we have to go to omegaR several orders of magnitude larger, it is about 50 kilohertz or 100 kilohertz, or even more. See several kilohertz width is there in which case with the available spinning is 110 kilohertz; you can partially reduce something; and you cannot get sharp peaks like this, you may start getting peak like this.

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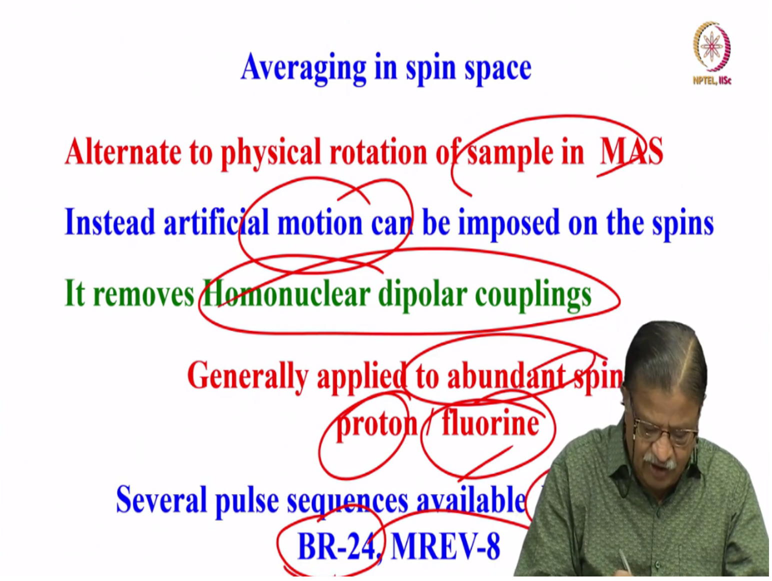

Averaging in spin space

Alternate to physical rotation of sample in MAS

Instead artificial motion can be imposed on the spins

It removes Homonuclear dipolar couplings

Generally applied to abundant spin

proton / fluorine

Several pulse sequences available

BR-24, MREV-8

In such cases what we do? can we average out the dipolar coupling in some other way especially homonuclear dipolar couplings. Please remember in the dipolar Hamiltonian equation which I gave you, we dealt with rIJ part, we dealt with space part magic angle spinning, but what about the spin part? remember there was a spin part. Can I make these nuclear spins undergo rotation, similar to magic angle spinning, by doing some trick.

So, instead of physical rotation of the sample can I impose artificially motion on these spins? I can do that. Then it removes homonuclear dipolar couplings. We can do that and this is generally applied to abundant spins. Which are the abundant spins? which has largest magnetic moments. One is proton and next is fluorine, and all other like nuclei like phosphorous which in spite of the fact that their abundance is high, but still you can eliminate it in some way by magic angle spinning and decoupling, etcetera.

But these are the two nuclei with abundant spins you cannot remove homonuclear dipolar couplings so easily. But averaging of the spins where we can try to do that, and then see by imposing artificial motion of the spins and creates analogous to the physical rotation like magic angle spinning, we can eliminate homonuclear dipolar couplings. At least we can significantly reduce its strength, and there are several such sequences. Pulse sequences are called WAHUHA, means Waugh-Huber-Haeberlen; BR24 and MREV; these are all names of the scientists who have given this type of pulse sequences.

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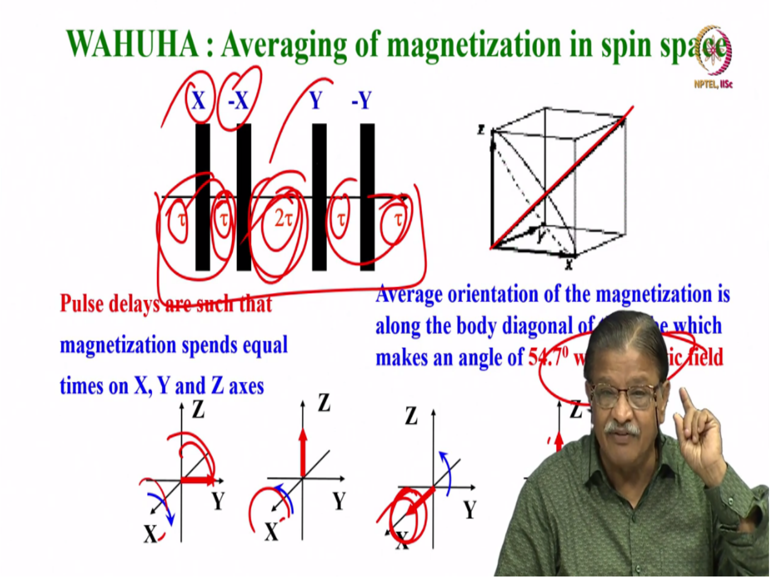
WAHUHA : Averaging of magnetization in spin space

Pulse delays are such that magnetization spends equal times on X, Y and Z axes

Average orientation of the magnetization is along the body diagonal of … e which makes an angle of 54.7^0 w … ic field

Let us see how WAHUHA works for averaging of homonuclear dipolar coupling in spin space. How we can do? We will understand WAHUHA, there is a lot of theory, lot of discussion we have to do and deeper understanding is required. But it is just a hand waving argument I am going to give you. This is enough for this course to understand now. It is a 4 pulse sequence. Look at it these are all 90 degree pulses, which are applied on axis – x axis + x, y – y. You remember, we discussed the pulse phase and receiver phases, we said in which direction you can apply pulse and how it undergoes rotation everything we have discussed long back. So, this is sequence we are considering, basically a 4 pulse sequence called WAHUHA.

It is a 90 degree pulse sequence and we apply 4 pulses one, on + X axes other – X, + Y – Y. Interesting point you have to note is there is a time delay here tau, time delay tau, time delay 2 tau, tau and tau. What is happening between these two tau delays? We have to adjust the delay such that we make sure the magnetization spend equal time on X, Y and Z axes by applying this. How it happens? let us look at it. First let us assume the magnetization is along Z axis. You bring the magnetization by applying 90 degree pulse along Y axis, consider along Y axes you have brought it. Allow the magnetization to stay in this axis for the time period tau; then apply minus 90 degree X pulse, then you are taking it back to Z axis. Now the rotation is like this; in the opposite rotation, the magnetization goes back to Z axes again. Now allow the magnetization to stay in this Z axis for two tau period.

Now apply Y pulse then the magnetization comes along X axis. Allow the magnetization to spend for tau period here. Apply – 90 pulse, take it to Z axis. You see every time when you keep doing; you take the whole sequence like this. Now magnetization is spending equal time 2 tau, 2 tau, 2 tau on all the three X, Y and Z axes. It spends two times time 2 tau along Z axes; 2 tau along X axes and 2 tau along Y axes; all the three are there. And identical time it spends. Now what we do is you apply this rapidly. Rapidly keep applying; the spins, bring it here you take it back, bring it here take it back, like this keep on applying so rapidly. Then what happens the magnetization? It spends equal amount of time on all the three axes X, Y and Z axis. Rapidly apply these pulses; it is as good as telling the magnetization spends equal amount of time. The spins spends equal amount of time on all the three X, Y and Z axis. It is like you can again think of a cuboid. It is again the average orientation of magnetization is along the body diagonal of the cuboid, which makes an angle of 54.7 degree with respect to the magnetic field. This is one way. So what did you do? You eliminated the one set of interaction by making the spins to undergo rotations rapidly where spins spend equal amount of time along X axis, Y axis and Z axes. You create a sort of a dynamic implementation of the cubic symmetry here again.

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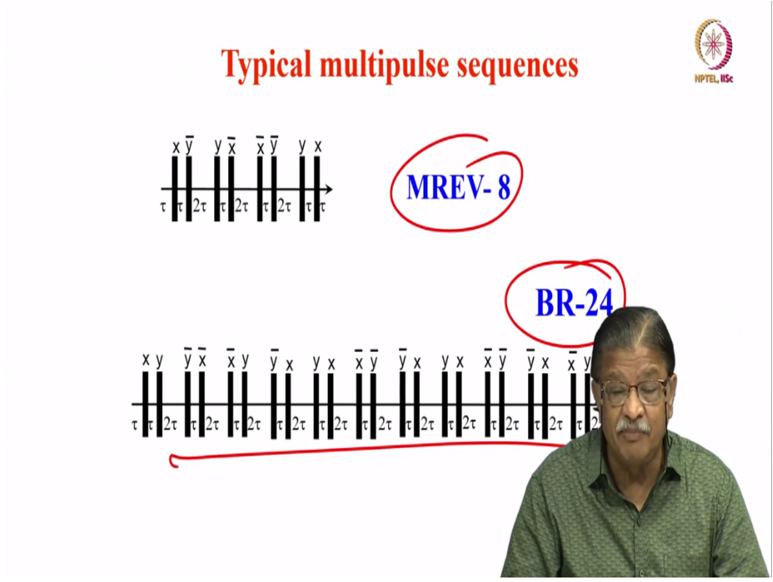

Typical multipulse sequences

MREV- 8

BR-24

So, there are varieties of pulse sequences like MREV, BR24, these are 24 sequences. Remember all these things have to be applied in a short time; the pulses have to be very, very sharp and the delays have to be very precise, so that the nuclear spins should spend equal amount of time on all the three axes X, Y and Z axes.

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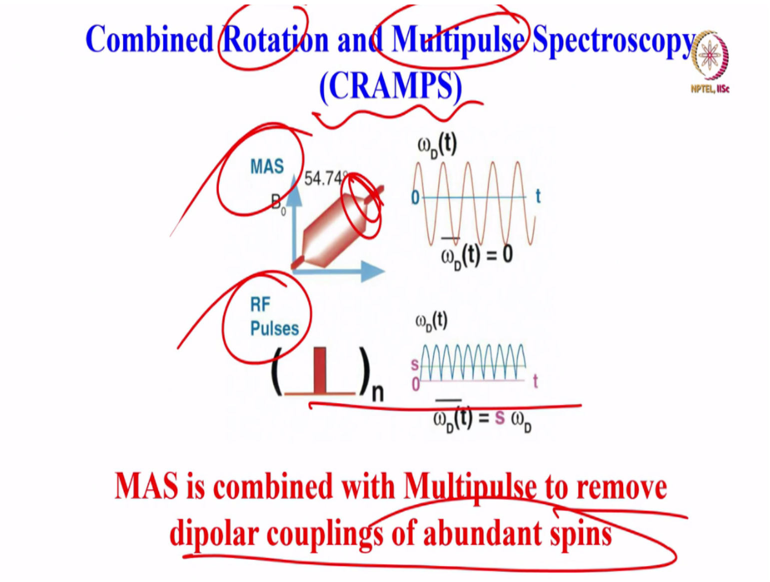
Combined Rotation and Multipulse Spectroscopy (CRAMPS)

MAS is combined with Multipulse to remove dipolar couplings of abundant spins

Now you may ask me a question? okay I can physically rotate the sample, I can apply radiofrequency pulses; that means I can do the averaging in physical space; I can also do the averaging in the spin space. Both I can do independently. Now can I not couple that? while rotating the sample physically can I not apply pulses? of course it is possible. So, I can do both rotation physically and also apply multi pulses; then it is double advantage for me. We can do that, such type of experiment. It is called CRAMPS; means combined rotation and multipulse spectroscopy. Here we are not only rotating the sample physically, we are also applying radiofrequency pulses. Then as a consequence we can remove the dipolar couplings of abundant spins also. That is the advantage of CRAMPS.

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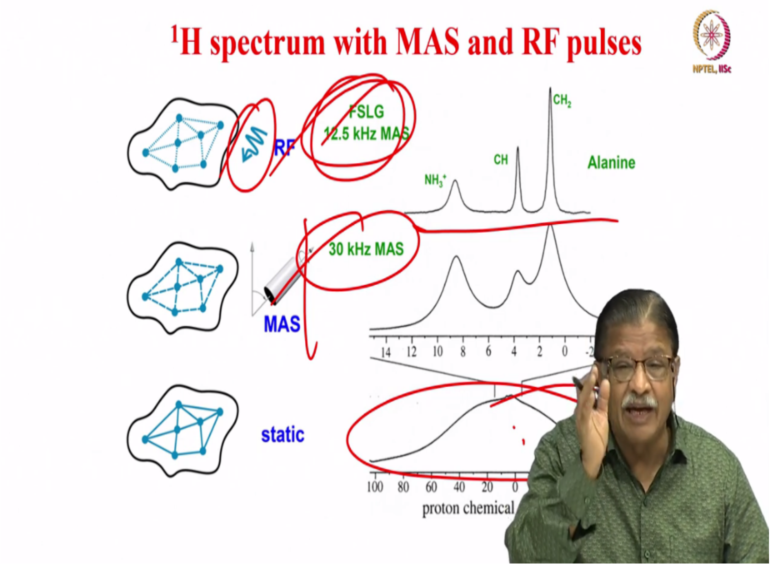
^{1}H spectrum with MAS and RF pulses

So, this is just to show you the advantage of magic angle spinning along with multi pulse etcetera. It is a static case, for example. It is a magic angle spinning at 30 kilohertz this is some decoupling, do not worry along with radiofrequency pulse being applied. These are called off resonance decoupling called Lee-Goldberg; do not worry this is where you are going to get. Nowadays we can do the decoupling, homonuclear decoupling in addition. The broad hump in static case, now became to like this, by magic angle spinning. In addition to this if you also have FSLG, we can give sharp peaks like this. So, now all these are independent. This is static, this is magic angle spinning, this is only RF pulses applied, but this is not WAHUHA, but a different sequence called FSLG. There are number of such sequences; Lee-Goldberg sequences are there. I am just giving one spectrum and I am not touching upon those things in this class, there is no time for that. But remember this is off resonance decoupling called Lee-Goldberg decoupling; which can be utilized to remove homonuclear dipolar coupling. Lee-Goldberg can be used to remove homonuclear dipolar coupling.

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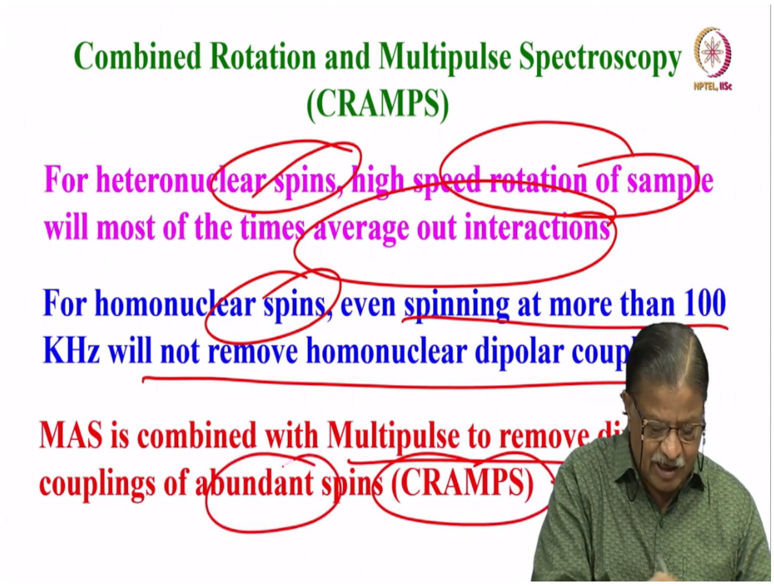

Combined Rotation and Multipulse Spectroscopy (CRAMPS)

For heteronuclear spins, high speed rotation of sample will most of the times average out interactions

For homonuclear spins, even spinning at more than 100 KHz will not remove homonuclear dipolar coup

MAS is combined with Multipulse to remove di
couplings of abundant spins (CRAMPS)

Now combined rotation and MAS if you do, heteronuclear dipolar couplings, high speed rotation of the samples most of the times, averaged out the interactions. For homonuclear spins even spinning at more than 100 kilohertz will not remove homonuclear dipolar couplings. So, MAS is combined with multipulse to remove dipolar couplings of abundance spins.

So, for the case of abundant spins lot more technique is required. You have to apply magic angle spinning, plus multipulses you have to apply. Both averaging in the physical space and spin space you have to do, so that dipolar coupling among abundant spins can be removed. This is important.

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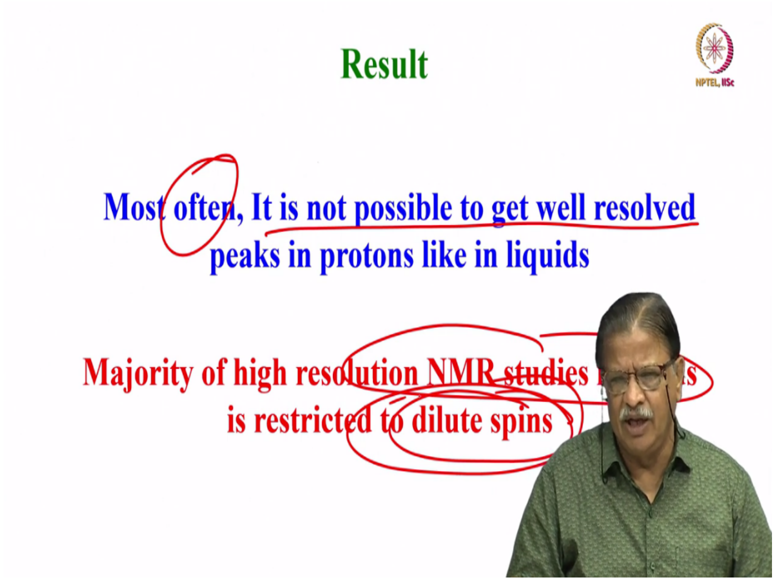

Result

Most often, It is not possible to get well resolved peaks in protons like in liquids

Majority of high resolution NMR studies is restricted to dilute spins

What does it mean? Most of the times, although we say we can get high resolution in protons. As I said it is no way near the comparison with solution state NMR spectrum. Even now the line width is of the order of 40 to 50 hertz, in spite of all technological developments. Lot of stalwarts have devised number of experiments to reduce the line width; varieties of decoupling sequences they have introduced.

Even then line width are no way near that you can get from liquid state. So, it is most often it is not possible to get the well resolved peaks like in liquids and majority of the high resolution NMR that way is restricted to dilute spins, not protons. That is why we did not discuss much about protons. Protons are not going to be studied, although now there are lots of people who are working; several groups are working in this direction. They are doing research on how to reduce the line width and get sharper and sharper peaks. That is a different purpose. For the routine analysis this type of thing is of course is becoming popular But I cannot say I have got a spectrum similar to what we get in the liquid state. So, most of the time especially conventionally the routine users restrict the applications for study of dilute spins.

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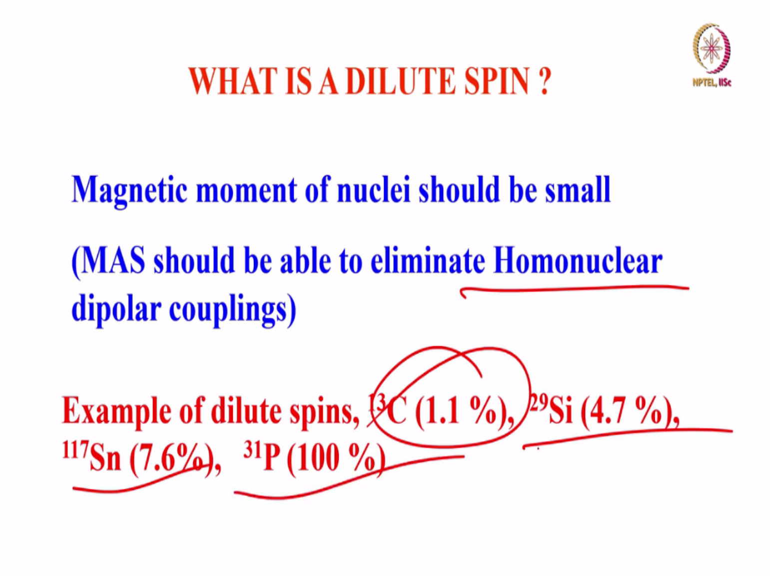

WHAT IS A DILUTE SPIN ?

Magnetic moment of nuclei should be small

(MAS should be able to eliminate Homonuclear dipolar couplings)

Example of dilute spins, ^{13}C (1.1 %), ^{29}Si (4.7 %), ^{117}Sn (7.6%), ^{31}P (100 %)

Next the question is what is the dilute spin? Of course you know, that magnetic moment of the nuclei should be very small. MAS should be able to eliminate the homonuclear dipolar couplings. For example, if you consider the homonuclar dipolar couplings of dilute spins, I am talking not I am not talking about the abundant spins. The homonuclear dipolar couplings is still the correct statement. It is the homonuclear dipolar couplings of dilute spins not abundant spins. So, this is important, for example, carbon 13 carbon 13 dipolar coupling magic angle spinning can remove it. Silicon, silicon coupling it will remove. Similarly, nitrogen, tin, phosphorus; all these homonuclear couplings can be removed by magic angle spinning.

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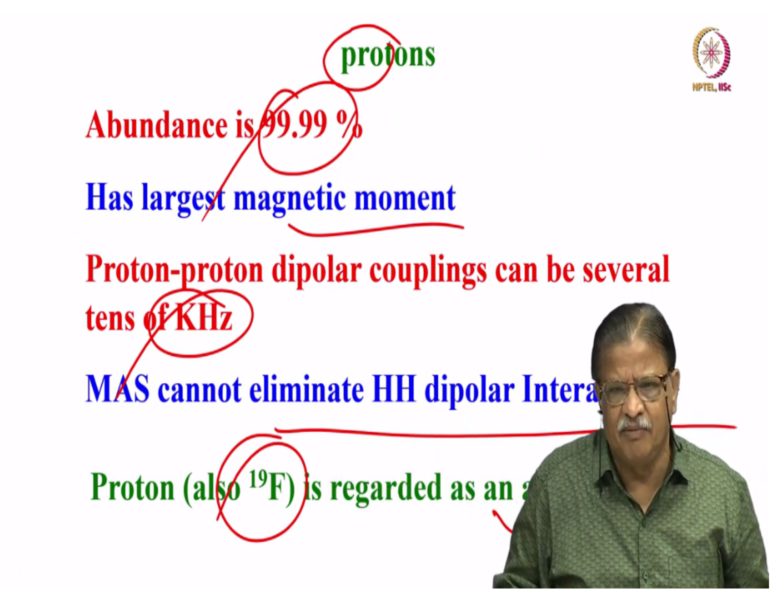

protons

Abundance is 99.99 %

Has largest magnetic moment

Proton-proton dipolar couplings can be several tens of KHz

MAS cannot eliminate HH dipolar Intera

Proton (also ^{19}F) is regarded as an a

In the case of protons as I told you abundance are 99.99% ; has a largest magnetic moment and proton-proton dipolar couplings can be order of several tens of kilohertz magic angle spinning cannot eliminate homonuclear proton-proton dipolar couplings. So, as a consequence, proton and fluorine which is another abundant spin, are considered as abundant spins. Apart from proton and fluorine, all other spins can be considered as dilute spins.

Please remember when you are concentrating on the solid state NMR studies; except proton and fluorine which are abundant spins; you can consider them as abundant spins; all other spins other than this in the periodic table can be considered as the dilute spins.

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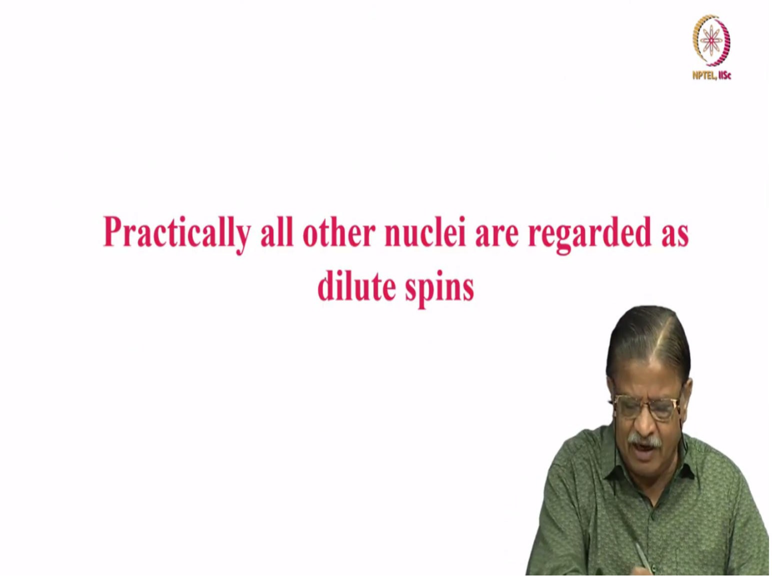

Practically all other nuclei are regarded as dilute spins

So, practically all other nuclei are dilute spins.

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For Organic systems

^{1}H is the abundant spin

^{13}C is the dilute spin

Now let us come to a different topic. We will come to that slowly. I want to study organic molecule; what does it contain? Majority of the time you have a proton which is an abundant spin; you have carbon 13 present in that which is a dilute spin. So, now I will detect the carbon 13 in most of our organic systems, which you are interested. Then what can I do? very simple only the magic angle spinning, because I can come across only heteronuclear dipolar couplings, Homonuclear anyway we cannot remove, so we do not worry. We are not looking at proton also. When I am looking at carbon 13 the proton-proton dipolar couplings has a different effect; we do not worry about it, we ignore it. So, we have to break the coupling between proton and carbon; can you do that? Yes we can do the magic angle spinning and also heteronuclear decoupling we can do that.

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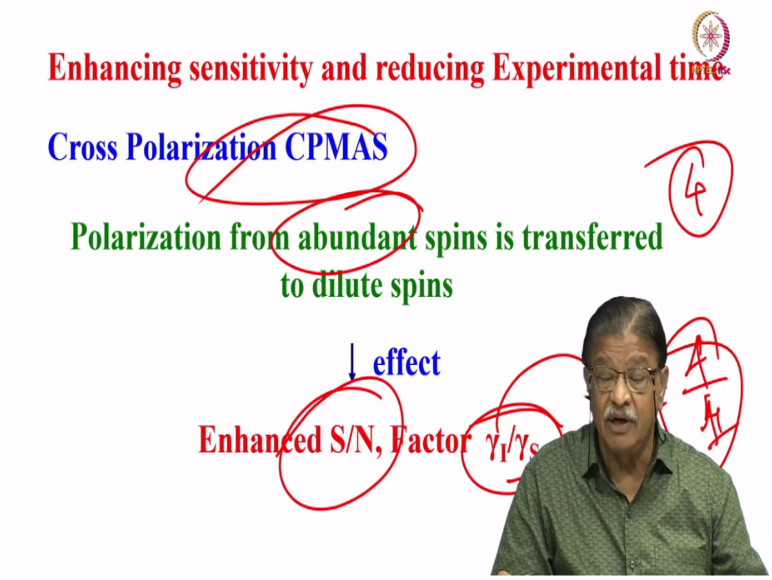

Enhancing sensitivity and reducing Experimental time

Cross Polarization CPMAS

Polarization from abundant spins is transferred to dilute spins

↓ effect

Enhanced S/N, Factor γ_I/γ_S

4

So, when we do that we get carbon 13 spectrum. Simply take the molecule of your interest put it an angle magic angle with respect to the sample magnetic field, and then start rotating detect carbon 13. While detecting carbon 13, decouple protons simultaneously do the magic angle spinning. Then you get sharp peaks for carbon 13; that is fine, but we also know what is the carbon 13 sensitivity. Carbon 13 is less sensitive compared to proton we know that 64 times it is less sensitive; all those things we discussed earlier. But then is there any way I can enhance the sensitivity of the carbons? because when I detect carbon I am spending lot of time because of low sensitivity. How can I enhance the sensitivity? there is a procedure called cross polarization. I can do cross polarization along with magic angle spinning; that is what it is.

What is a cross polarization? that is something interesting. It means I take the polarization of the abundant spins and transfer it to dilute spins. How do I do that? It is not I can pull it from here and give it here, it is not that simple. But there is a method we can do that, we can adapt.

There is a possibility we can take the polarization from abundant spins, because if you take proton and carbon 13 proton gamma is 4 times larger. Separation of the energy stated is 4 times larger than carbon 13. I mean the separation is larger, population difference is larger all those things we have understood. Now I can take this large polarization of the protons and give it to carbon, which has small polarization. Then in turn this will become sensitive, because intensity will go up. I can enhance the sensitivity. This is called cross polarization.

So in effect what we are going to get is the enhanced sensitivity. The question is how much is the enhancement of the sensitivity, I cannot get in 1,000. But it grows in the ratio of gyromagnetic ratio; gyromagnetic ratio of abundant spin divided by dilute spin. Abundant spin is proton, dilute spin is carbon 13; this is 1 is to 4. Of course, gamma is 4 times larger so that means 4 times enhancement you get in the intensity, if you do the cross polarization between proton and carbon.

Take the proton magnetization give it to carbon, you can enhance the sensitivity by 4 times. Remember enhancing the sensitivity by 4 times we will reduce the experimental time by 16 times; 4 square; so that is an advantage. Lot of things you can do; you can reduce experimental time by enhancing the sensitivity. Then how do we do this polarization transfer?

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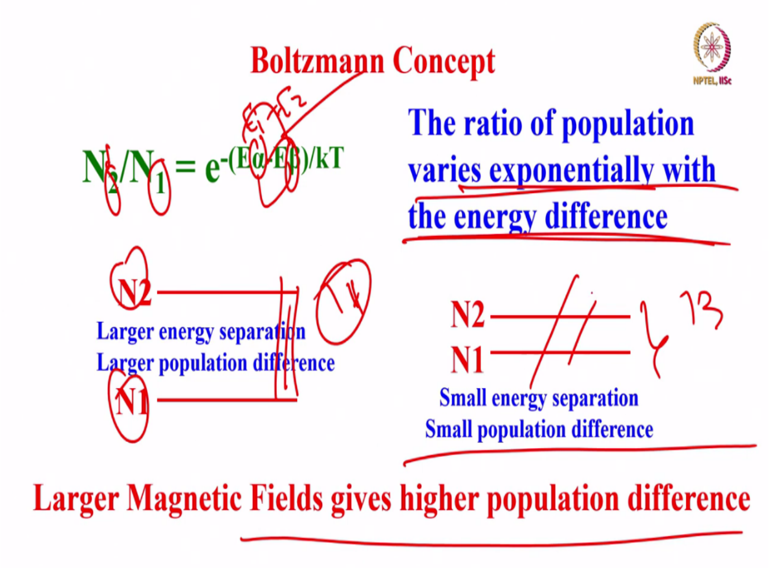

Boltzmann Concept

$N_2/N_1 = e^{-(E\alpha - E\beta)/kT}$

The ratio of population varies exponentially with the energy difference

Larger energy separation
Larger population difference

Small energy separation
Small population difference

Larger Magnetic Fields gives higher population difference

This is an interesting concept which I understand. So, this is where we need to understand bit of Boltzmann concept. I will introduce the Boltzmann concept today. And how we do the polarization transfer everything we can discuss in the next class. But today I will tell you what is a Boltzmann constant which of course is nothing new for all of you. We have discussed this long ago in the previous course and in this course also; in the very first class or second class we discussed this thing.

The Boltzmann population ratio between two energy states N2 and N1 is given by this equation exponential of negative E alpha – E beta divided by kT. This is the ratio of the population, that means it says it varies exponentially with the energy difference. The energy difference between alpha and beta states or in other words N2 and N1, I should have written. N2 and N]1 if I consider this should go exponentially, the energy difference.

So, this if I write beta alpha I should have written like this, because I have taken N2, N1 this should be, not alpha beta N2 N 1. Please note the change it should be N2 / N1. So, this is beta is N2 this is N1 this is E1 – E2; this should be E1 not E alpha / E beta it is E1 – E2. The ratio of the population varies exponentially with the energy difference. If I have N2 here and N1, here larger separation; you have larger population difference.

If you go here the N2 / N1 we have a smaller separation, I have a smaller population difference. This is for the carbon 13, this is for the proton; that is what we get. This is a Boltzmann population if you consider the ratio for proton it is larger than carbon 13. So, larger magnetic field also gives larger population difference; that is another thing that also we know. This energy separation we can keep on enhancing by going to higher and higher magnetic fields. The same way the same ratio this also gets enhanced.

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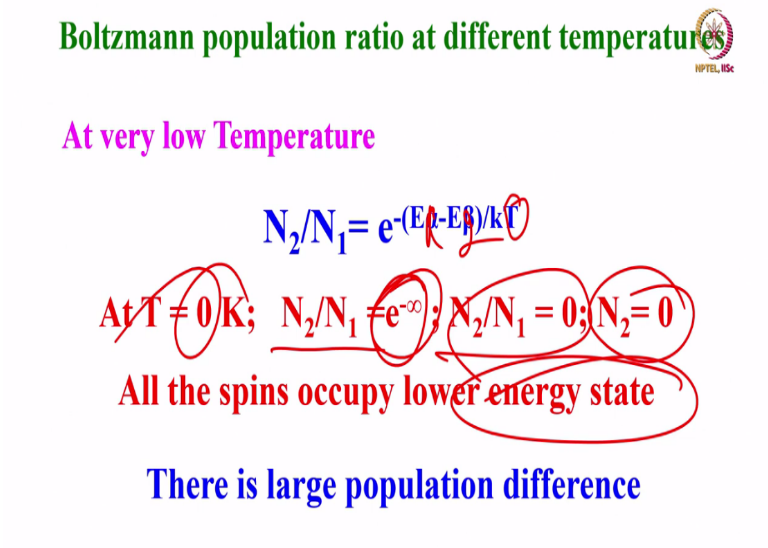

Boltzmann population ratio at different temperatures

At very low Temperature

$$N_2/N_1 = e^{-(E\overset{1}{\alpha}-E\overset{2}{\beta})/kT}$$

At T = 0 K; $N_2/N_1 = e^{-\infty}$; $N_2/N_1 = 0$; $N_2 = 0$

All the spins occupy lower energy state

There is large population difference

So, now we will understand what is the Boltzmann population ratio at different temperatures. We go to very low temperature; think of 0 very low, it is 0 degrees, although practically it is not possible to achieve absolute 0, but you can go very close, say, 0.0001 degree consider it is 0 degree we get it. At when N2 / N1 if you consider then at T = 0, N2 = N1; I am sorry N2 / N1 = e to the power of N2 / N1; at T = 0 this will become, with 0 in the denominator then it is becoming e to the power of – infinity. So my N2 / N1 = 0 now that means N2 is 0. N2 is 0 means what? It means all the spins are in the lower energy level. When all the spins are in the lower energy level there are no spins in the higher energy level; the population difference is enormous. There is a large population difference at low temperature. As you go to lower and lower in temperature there is enhancement in the population difference.

Now at very high temperature, another case. I go to very high temperature,e the same equation if you consider at T = infinity now N 2 / N 2 is e to the power of – 0. That means N2 / N1 = 1. It means N1 = N;2 this is a situation called saturation, no signal will be seen. Please understand this is a situation called saturation, and the population between two energy states are equal. And no signal will be seen.

So, with this concept we will come back and understand what is cross polarization in the next class. Here in this class I wanted to tell you something about Boltzmann population difference, Boltzmann population ratio, and how it changes with the temperature. That is what you should get the concept; and in the next class we will go deeper and understand cross polarization.

So, in this class we discussed a lot about magic angle spinning and how to eliminate the homonuclear dipolar coupling by averaging in the spin space, various pulse sequences are available. I took the example of 4 pulse sequence WAHUHA. I said it is analogous to dynamic implementation in the cubic symmetry in the spin space, where the nuclear spins are allowed to spend equal time along X axis, Y axis and Z axis, all the 3 axes.

And rapidly if we keep on changing the state of the nuclear spins from X, Y and Z axes; keep on changing rapidly allowing the spins to spend equal time on all the three axis; then it is as good as telling you are doing averaging in the spin space. It is analogous with the physical rotation. But this eliminates dipolar couplings; homonuclear dipolar couplings; whereas heteronuclear dipolar coupling is eliminated by physical rotation at magic angle.

And dipolar decoupling can also be done; it can remove heteronculear decoupling. So, combined rotation of magic angle spinning and RF pulses can also be applied called CRAMPS, so that we can get the better resolution of the proton spectrum. I said protons are highly abundant spins; dipolar couplings are quite large. The magic angle spinning alone will not remove it even with the combined utility of multiple sequences; varieties of sequences which have been developed. Line width have not come down enormously; it will be still around 40 or 45 hertz for each peak. So, essentially it means it is we are no way near the high resolution spectrum that we get in solution state. And most of the time the concentration is only high, I said dilute spins, are the ones whose homonuclear dipolar couplings can be removed magic angle spinning, eg carbon 13 carbon 13 dipolar coupling, Carbon 13 and nitrogen, like that all those things can be removed, nitrogen-nitrogen dipolar coupling can also be removed. They are all dilute spins. And for all practical purpose other than fluorine and proton most of the nuclei can be considered as dilute spins. And abundant spins are only proton and fluorine. And we can detect the carbon 13 by simultaneously rotating the samples at the same time doing the dipolar decoupling. Direct detection, of course, the carbon is less sensitive because gamma is 4 times less than that of proton; but can we not enhance the sensitivity of this. Of course, there is a way we can enhance the sensitivity of it by doing polarization transfer from proton to carbon. This enhancement ratio is proportional to the ratio of the gyromagnetic ratios between these two spins.

For proton and carbon it is 4 times; for proton nitrogen it is 10 times. How it happens we will understand later. And before that I introduced the concept of Boltzmann population difference. We have understood larger population difference for the larger energy separation and smaller population difference for small energy separation; and it also depends upon the magnetic field strength. And what I said is, somehow if I can take the magnetization from the abundant spins with larger population difference, give it to carbon 13; then we can enhance the sensitivity. For this, we understood the Boltzmann concept of what happens to population difference that at very low temperature and very high temperatures. So, with this I will stop here we will come back in the next class; continue the cross polarization and that is another interesting topic in solid state.

We will try to understand and see one or two simple spectra with CPMAS. And of course we can do all sorts of 1D experiments and 2D experiments. There are umpteen number of two dimensional experiments, similar to liquid state, different types of experiments are there in solids. We can do that, but I do not know only I am left with two more classes.

I will not be able to cover solid state two dimensional techniques, but I will at least show one or two simple examples, but we will discuss cross polarization in the next class. So, I will stop here. Thank you very much; we will see you in the next class.