Advanced NMR Techniques in Solution and Solid State

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Module-60
CP at High Speeds Side Band Suppression TOSS
Lecture – 60

Welcome all of you; probably this is the last class of this course. I do not know may be still lot more things to cover. Possibly I may come back with short one or two classes maybe after sometime, but as far as I am concerned for the solid state NMR there is lot more to discuss. I have not even brought in two dimensional NMR in solids. There are many things which we can discuss. If I start that it will take another 10 hours to discuss.

There is no time, because this is a course restricted only to 30 hours. I cannot go in depth and discuss everything. So, solid state NMR we will finish and this could be the last class. Just to give you the information about some one or two things, I will come back later, maybe one or two extra classes. So as in the last class we discussed about solid state NMR especially last couple of classes we have been discussing. We discussed a lot about magic angle spinning, WAHUHA techniques, averaging in the spin space, physical space averaging, varieties of things. In the last class we discussed extensively about the CP mechanism, cross polarization where you can transfer the magnetization from abundant spins to rare spins. This mechanism involves heteronuclear dipolar interaction, dipolar coupling is essential. And we consider understanding by using thermodynamics approach. You can consider protons and carbons as thermal baths and by the spin temperature concept we understood carbon 13 in the rotating frame is extremely hot, whereas proton is very, very cold, extremely cold. At lattice temperature we have got protons is at 300 K; in the rotating frame in the doubly rotating frame it is at 0.5 k, so very, very small. And because it is so cold carbon 13 because of lack of magnetization assuming there will be in a in the saturated state; they are very hot. Now somehow if I bring them into contact which is not possible in the lattice temperature, at the room temperature because if we increase the magnetic field for one spin, it linearly changes in other also. Whereas in the rotating frame there is a possibility I can tune the RF power of one of them, so that the energy levels between these two become equal. This condition is called Hartmann Hahn condition, which is nothing but the gamma of proton into B1 of proton = gamma of carbon 13 into B1 of carbon 13. It is carbon 13 or it could be any dilute spin. If you match this condition called Hartmann and Hahn condition, then the spins lose their identity; both the energy levels of proton and carbon are identical. In which case spins can simply transfer this magnetization because of the thermodynamically we understood protons are at very low temperature and carbon 13 is very hot.

There is a transfer of magnetization between proton to carbon 13. So, there is enormous gain in the signal intensity. And of course we discussed a lot about T1 rho and everything; how initially the signal builds up and then if you wait for a long time it starts decaying because of T1 rho. So, we have to optimize the mixing time accordingly. And in the last class we also saw the enhanced intensity for one of the silicon spectrum.

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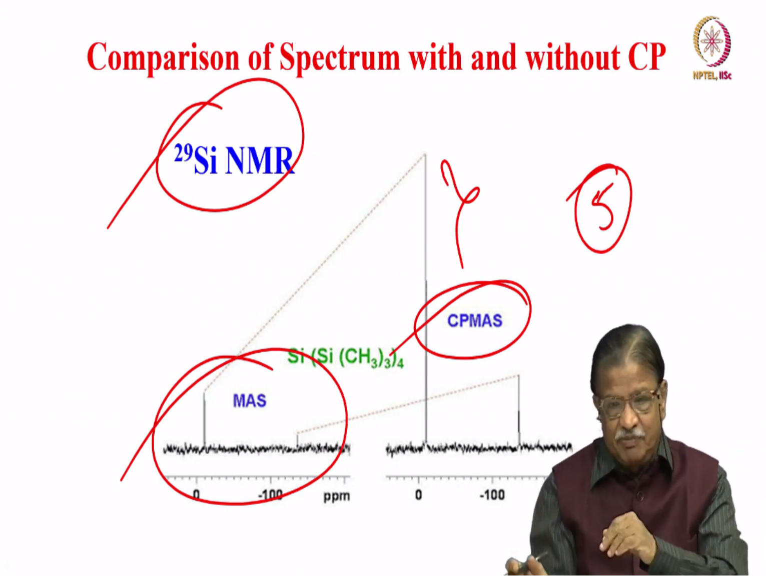

Comparison of Spectrum with and without CP

So, we will start with that today and see how we are going to see this. This is silicon NMR which is showed in the last class. You see this is only with magic angle spinning, no cross polarization. With cross polarization and magic angle spinning you see nearly 5 times enhancement in the signal intensity. This is the biggest advantage of cross polarization. So, for any dilute spins, if they contain proton or any other abundant spins like fluorine you can do the polarization transfer from one spin to other spin; or especially from abundant spin to dilute spin.

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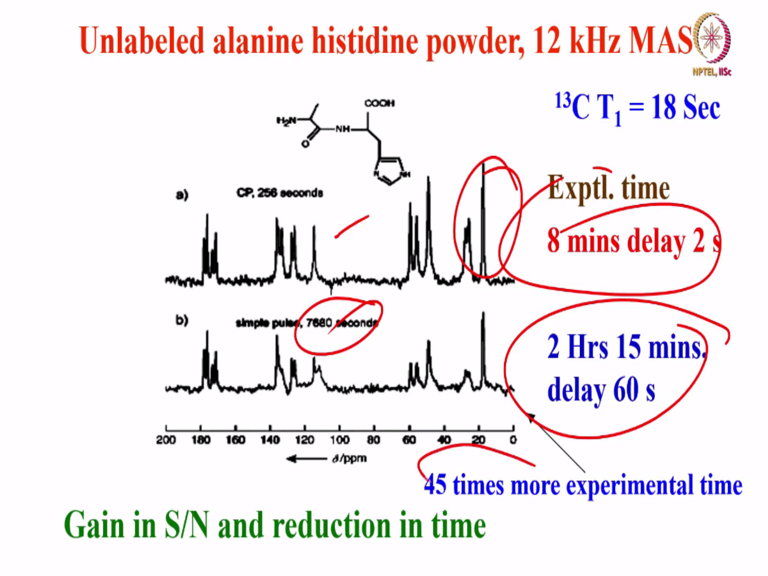

Unlabeled alanine histidine powder, 12 kHz MAS

$^{13}C\ T_1$ = 18 Sec

Exptl. time

8 mins delay 2 s

2 Hrs 15 mins, delay 60 s

45 times more experimental time

Gain in S/N and reduction in time

Now just for comparison I also showed this. It is the histidine spectrum alaninehistidine powder. And we saw that there is an enormous gain in the signal intensity by doing the cross polarization here. Here it took lot of time, 2 hours and 15 minutes. But with CP we took only 8 minutes. So, there is a gain in the signal to noise ratio and 45 times experimental time more; here. It reduced here.

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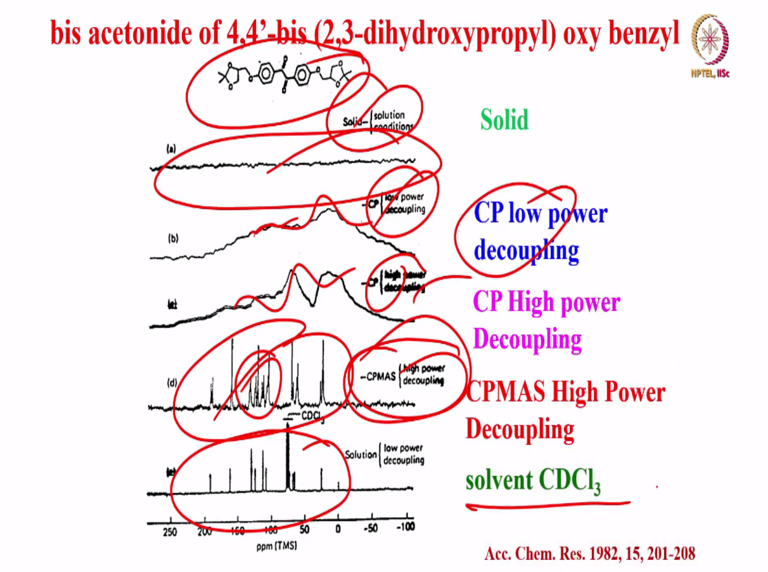

bis acetonide of 4,4'-bis (2,3-dihydroxypropyl) oxy benzyl

Solid

CP low power decoupling

CP High power Decoupling

CPMAS High Power Decoupling

solvent $CDCl_3$

Acc. Chem. Res. 1982, 15, 201-208

So, this is what I wanted to show you how the signal intensity and the resolution can be compared for different experiments you do. Consider a sample like this which is in a solid form; you know it is a powder, whatever it is. Take the carbon 13 spectrum under solution condition; that is why you do not do anything, simply put the sample in a spectrometer and collect the signal, and you do not see anything here.

Broad hump, if you enhance intensity vertically you may see a broad hump. Whereas, let us say we do the decoupling with low power, you see some profile started coming up. With high power decoupling something more happened, more resolution is there. Now simultaneously with high power decoupling, do magic angle spinning and also cross polarization simultaneously. All the three you can do. You can do cross polarization, magic angle spinning and high power decoupling. Look at it how sharp lines we are going to get. And this is the spectrum in solution state. Of course there is no comparison in the resolution between this and this. And also you see sometimes you get more peaks than here. This is for varieties of reasons there could be spinning sidebands or it could be different polymorphism, different structure in solid state compared to solution state, varieties of reasons.

But nevertheless, you can get sharp peaks with all the techniques combined together. This is what it is. This is for the solid, low power decoupling, high power decoupling, Cross polarization with magic angle, and the same sample dissolved in the solvent CDCl3.

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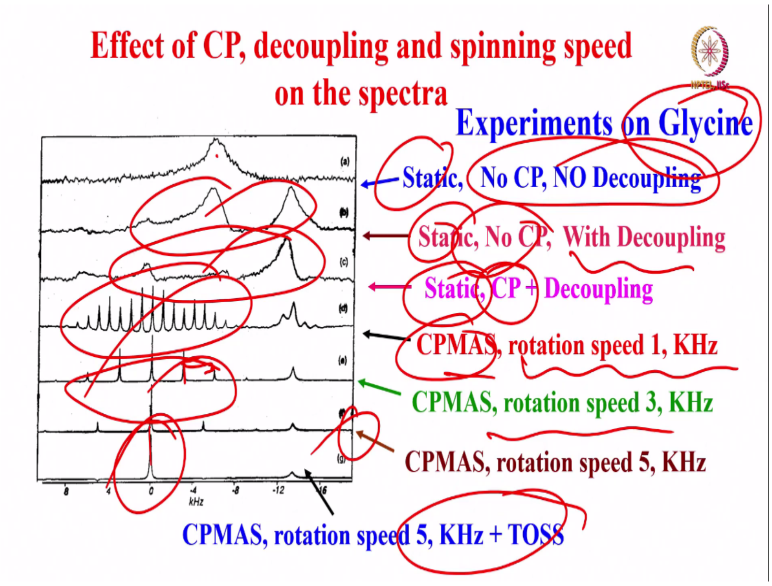
Effect of CP, decoupling and spinning speed on the spectra

Experiments on Glycine

Static, No CP, NO Decoupling

Static, No CP, With Decoupling

Static, CP + Decoupling

CPMAS, rotation speed 1, KHz

CPMAS, rotation speed 3, KHz

CPMAS, rotation speed 5, KHz

CPMAS, rotation speed 5, KHz + TOSS

So, look at this. Another spectra like this. These are the experiments on glycine molecule. This is the spectrum, look at this one this is static, no cross polarization and no decoupling at all. Here this is again a static sample no cross polarization, but there is a decoupling. So, because of decoupling you can see there is a resolution already, we have already broken some of the heteronuclear dipolar couplings. This is static, cross polarization with decoupling then what is happening is you already enhancement in the signal intensity. Now this is a situation cross polarization along with magic angle spinning, and also decoupling. And look at it, there is a rotation speed is only 1 kilohertz. So, we get lots of sidebands and then keep on increasing the spinning speed, 3 kilohertz sideband gets reduced, as I told you I have been telling you again and again, the separation between two spinning sidebands correspond to the spinning frequency. Again this is at 5 kilohertz and this is a typical experiment, what is called a TOSS experiment. TOSS means total suppression of the spinning sidebands. I will tell you if there is a time today, how we can remove this spinning sidebands, so that you can get only isotropic chemical shift peaks in the solid state. So, this is effect of CP, decoupling and high speed spinning of the sample; varieties of experiments you can do and finally this is what you are interested to see.

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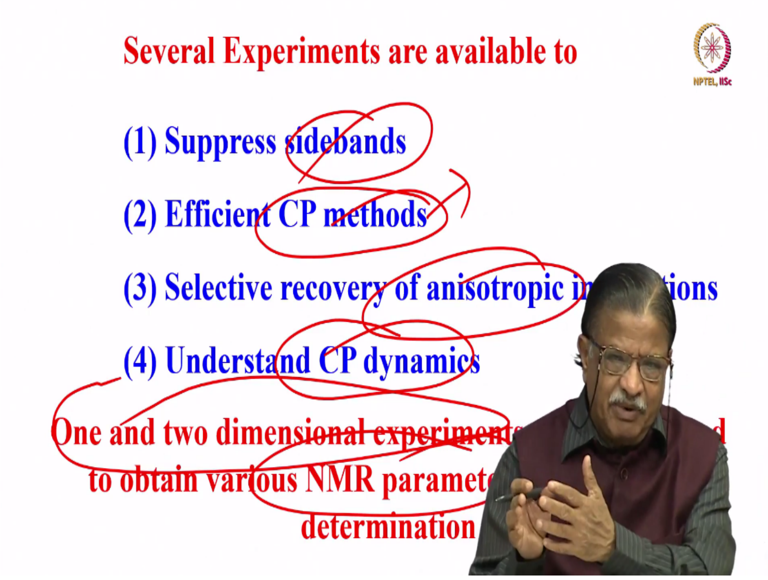

Several Experiments are available to

(1) Suppress sidebands

(2) Efficient CP methods

(3) Selective recovery of anisotropic i ions

(4) Understand CP dynamics

One and two dimensional experiments d

to obtain various NMR paramet

determination

So, now we have several sidebands I told you. Several spinning sidebands you can see if we are spinning at a slow speed; for example look at this one in this example, here you can see lot of sidebands. And these sidebands could be messy, so how do you eliminate it? There are several ways, several experiments you can do to suppress the spinning sidebands. You can do efficient cross polarization method. We understood the cross polarization by thermodynamic approach, how using spin temperature concept. But there are several ways to enhance the signal intensity because it is not easy. It depends upon several parameters, depends upon homonuclear dipolar coupling, spinning speed, heteronuclear dipolar couplings, varieties of parameters. So, how do you make the efficient cross polarization, what are the methods for it that we can understand that is applicable to all spinning speeds. And selectively I can recover anisotropic interactions while doing all these experiments together cross polarization, magic angle spinning and decoupling, that also we can do.

Simultaneously we can extract; get back anisotropic interactions that is also possible. If there are ways you can understand this spin dynamics, how CP dynamics, how the cross polarization dynamics takes place what is happening, how the polarization transfer takes place; all those things can be understood. Now based on these things, number of one and two dimensional experiments have been designed in the solid state also.

In the solid state NMR also varieties of NMR experiments have been designed and now we can obtain various NMR parameters, like, selectively I can get chemical shift anisotropy, selectively I can get heteronuclear dipolar coupling, selectively I can get information about homonuclear dipolar couplings or I can remove heteronuclear dipolar coupling, CSA and I can get only sharp peaks in carbon 13 and get chemical shifts. All these things are possible.

Varieties of experiments can be designed. There are number of 2D and 3D experiments are there in solid state to derive the spectral information like we have umpteen number of pulse sequences, umpteen number of two dimensional experiments in solution state, 2D or 3D, 4D. Similarly we have 2D, 3D experiments number of possible experiments are there, we can derive information in solid state also.

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Suppression of Spinning Side Bands

1.VSMAS, Variable spinning Magic Angle Spinning

2.ROTOR Synchronization

3.TOSS : Total Sideband Suppression

Now with available time we will not discuss many things possibly. I will try to discuss today something about suppression of the spinning sidebands. It is normally you come across. See in all laboratories you may not have the spectrometer facility to spin at 70 kilohertz to 80 kilohertz like that. Generally we may have spectrometers to spin at 5 kilohertz, 10 kilohertz of that order.

Still you may get lots of spinning sidebands in some exotic nuclei. For example, if you look for the silicon or aluminum or carbon you know varieties of nuclei you may get lot of spinning sidebands. B ut we do not want to get spinning sidebands. We want to remove the spinning sideband get only isotropic chemical shifts. Remember I told you also last time, if we do experiments at two or three spinning speeds, what will happen to the centre band, centre frequency corresponding to isotropic chemical shift? that will not change the spinning frequency. it remains same. Whereas, the sidebands start moving away; that is what happens. So, we can efficiently suppress the sideband. You do not have to do two or three such experiments; then we can get only peaks pertaining to isotropic chemical shift in the solid state.

There are several experiments like this I will discuss only two or three of them, for example, one is called the VSMAS, means variable spinning, magic angle spinning. You can vary the spinning speed while you are doing the magic angle spinning. It means I have put the rotor here at magic angle and start rotating. Simultaneously when I am acquiring, each time when I acquire the signal, every time, every accumulation, I can keep on changing the speed. It is little difficult task, a challenging task, but it can still be done.

I can vary the spinning speed while doing magic angle spinning. Each time we will acquiring the signal. This is called variable spinning magic angle spinning. And also we have rotor synchronization. I can synchronize rotor in such a way spinning sidebands can be eliminated. Rotor keeps on rotating and I see that for exactly at one rotation I collect the signal; then in between it can have the powder pattern, for half rotation it will come like this, in the next half rotation it will get averaged out. So in one full rotation if I go and acquire the signal, wait for it to go one more rotation, acquire the signal, I can synchronize the acquisition with respect to rotor speed. While spinning the sample at the rotation speed, I can synchronize the data acquisition, which is called rotor synchronization. That can also remove spinning sidebands. Also I am using a pulse sequence experiment by 4 pulse or 5 pulse experiment this is called the total sidebands separation. We can adapt this and do this experiment we can remove the sidebands completely. So, these are all the things which can be adopted.

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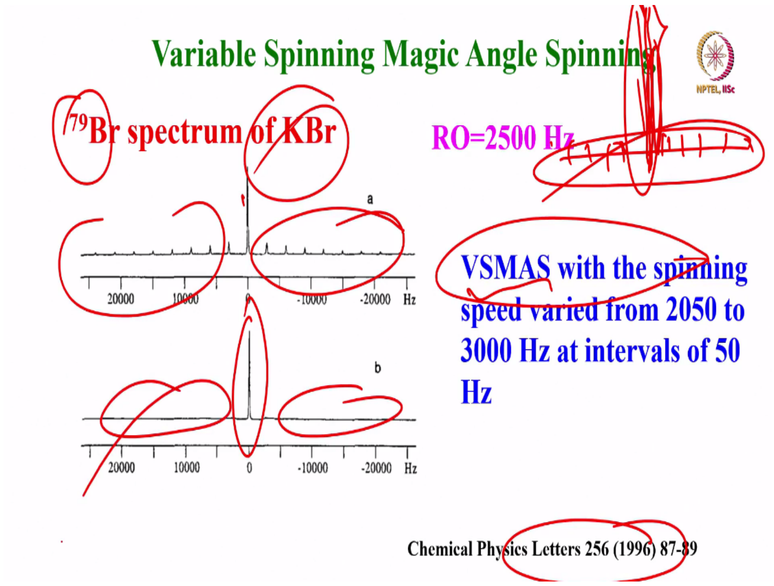

Variable Spinning Magic Angle Spinning

NPTEL, IISc

^{79}Br spectrum of KBr

RO=2500 Hz

VSMAS with the spinning speed varied from 2050 to 3000 Hz at intervals of 50 Hz

Chemical Physics Letters 256 (1996) 87-89

So, look at this one; variable spinning magic angle spinning. It is one simple experiment. This is taken from the paper Chemical Physics Letter 1996. This is a bromine 79 NMR spectrum of potassium bromide. Look at this one. As I told you when we use potassium bromide, look for bromine 79 NMR, and we tune the magic angle until we get maximum number of spinning sidebands. That is what we have to do to adjust the magic angle very precisely. So, now you have lot of sidebands here. In the case of bromine you know this is the centre peak, it is the only one peak I know. But in some other cases what you will do? In some other nuclei like carbon 13 with several carbons present; each may have a different CSA, and each may have a different powder pattern and then different spinning sidebands.

In which case what you will do? they will all overlap. So, what to do is better to remove spinning sidebands. What we will do is we acquire signal. At every time we acquire we vary the spinning speed, for example, once I acquire the signal and this is spinning speed, I get spinning sideband. Second time what will happen the centre band? it remains same, this gets added up. Whereas next time I get the sideband at different place, because the spinning speed is different. Again I acquire once more, because I change the speed centre band again added up this will move away. So, like this every time I keep changing the spinning speed, keep acquiring the signal then centre band keep on adding up, and sidebands keep on moving away. So, if you acquire for a long duration, because of signal averaging this will grow and all the sidebands get suppressed. very nice idea, fantastic idea.

This is called variable spinning, magic angle spinning. If you do that look at it we can get only centre band chemical shift at the isotropic frequency, all these things are removed; no side bands, they are completely removed.

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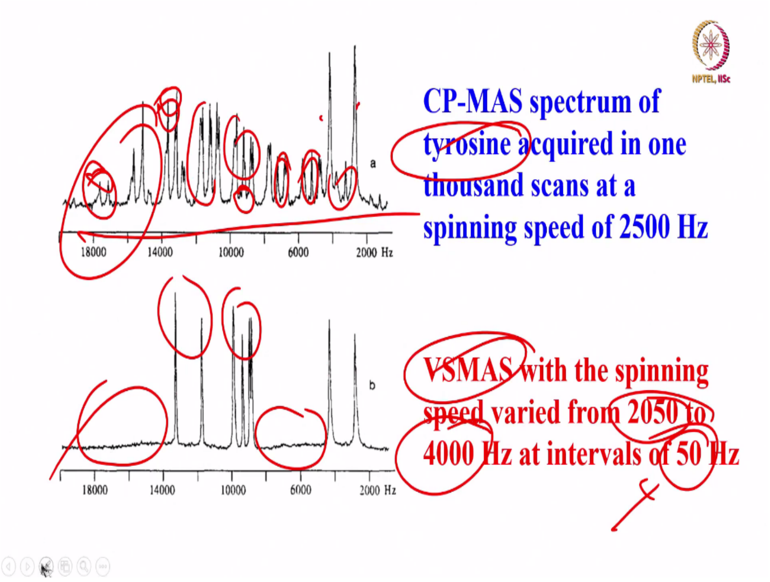

CP-MAS spectrum of tyrosine acquired in one thousand scans at a spinning speed of 2500 Hz

VSMAS with the spinning speed varied from 2050 to 4000 Hz at intervals of 50 Hz

And this is like a complicated spin system; see for example amino acid tyrosine. CPMAS spectrum of it. Look at it there are so many sidebands here. How do you identify the sidebands now? How do you know which are your peaks. For example, this could be sidebands; if you look at it this maybe exactly equal to this, and similarly you can see another sideband at equidistance here. But they all overlap, sidebands and centre bands everything are overlapped here. How do identify? okay we can do another spinning speed. It may so happen when we do another speed, it may overlap with the isotopic peak, somewhere here or there. So, we may have to do at two, three speeds or four speeds to identify completely all the sidebands and distinguish them from the isotropic peaks.

On the other hand, do this VSMAS. In one experiment while acquiring the data the spinning speed is varied from 2,000 to 4,000 hertz. Every time when you acquire, the speed is changed by 50 hertz. Fantastic; look at it, these are all the sidebands; they are all removed here, here also sidebands are removed. Only centre bands here, these are the two peaks of the centre bands. And these are the peaks; they are all retained, these two are retained.

All other peaks practically are spinning sidebands, and over the period when you acquire this thing as a function of various spinning speeds, then you are removing these things and you are retaining only isotropic peaks. This is what is happening and you see you get only isotropic peaks here.

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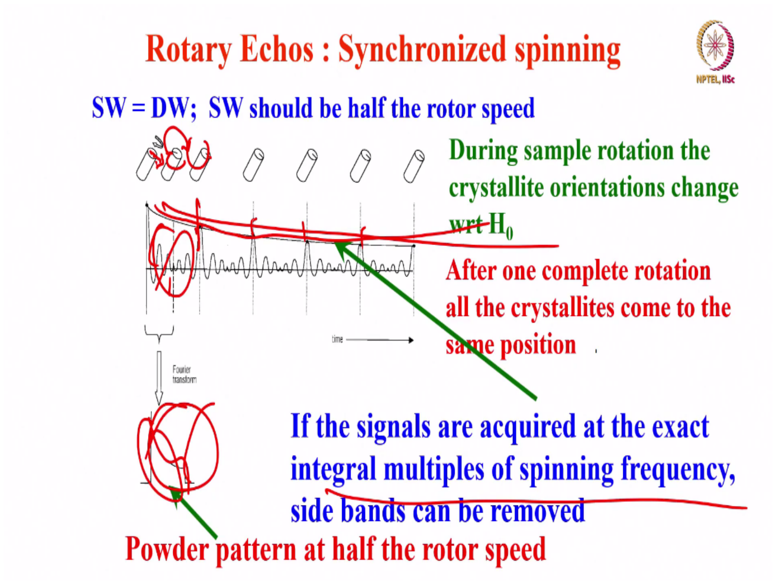

Rotary Echos : Synchronized spinning

SW = DW; SW should be half the rotor speed

During sample rotation the crystallite orientations change wrt H_0

After one complete rotation all the crystallites come to the same position

If the signals are acquired at the exact integral multiples of spinning frequency, side bands can be removed

Powder pattern at half the rotor speed

Second method is called the rotary echo. This is what I said rotor synchronization. While spinning is going on I can synchronize with the spinning I can acquire the signal. Every time, when it goes for one rotation collect the signal, like that. So for example how it happens is like this. We know we discuss about the rotary echo rotary. Rotary echo comes exactly at the spinning speeds. When the rotor starts, let us say, this is a marker here, this side.

When it rotates comes exactly at the same place where it started, we are going to see a echo pattern here. This is called the rotary echo. And now it keeps going like this. As we keep on acquiring the FID and it decays also with time. But in between what happens if you consider half the rotor time, let us say this is the time at which the marker is there, the rotor is in this position. Now you keep rotating, for half the rotor time this marker has gone to opposite side. Now continue further, comeback. For half for another speed of rotation now marker come back to the same place, fantastic. Now just for one rotation it started from here and came back to the same place. In between it goes with the powder pattern or half the rotor period and then again goes back and averages out. This is the powder pattern within one rotor period. So, what I will do is I do not acquire the signal in between. I will acquire the signal at the intervals exactly for one rotation period. I synchronize my acquisition at the rotor speed, then what will happen? I collect the signal like this, like a rotary echo; that is what it is. So, during the sample rotation the crystal orientation keeps on changing with respect to magnetic field.

But remember as I said after one complete rotation they come back to thesame orientation, same position where we started with. So that is what we do. We acquire the signal exactly at the integral multiple of this spinning frequency, then you remove the sidebands; you get only isotropic chemical shifts. So, powder pattern which will come at half the rotor period, for remaining half it will disappear, it will get nullified and you get only isotropic chemical shift. If you acquire signal exactly at the integral multiples of the rotor speed.

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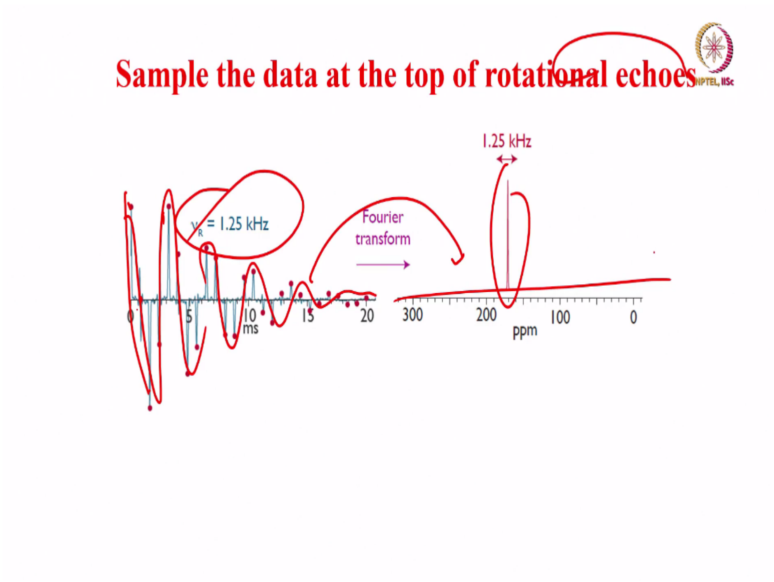

Sample the data at the top of rotational echoes

This is an example to show. A simple experiment. Look at it, this is for some sample, do not worry. This is spinning at 1.25 kilohertz. You see these are all called rotary echoes. So, now keep on acquiring the FID like this, exactly on the top you have a decaying signal. Do the Fourier transformation of it while collecting the signal exactly at the top of it you get a sharp peak; where are the sidebands? They disappear because you synchronize your acquisition with the spinning speed. If you acquire the data at the top of the rotational echoes you will remove the spinning sidebands you are going to get only isotropic chemical shift. This is a simple experiment called rotor synchronization.

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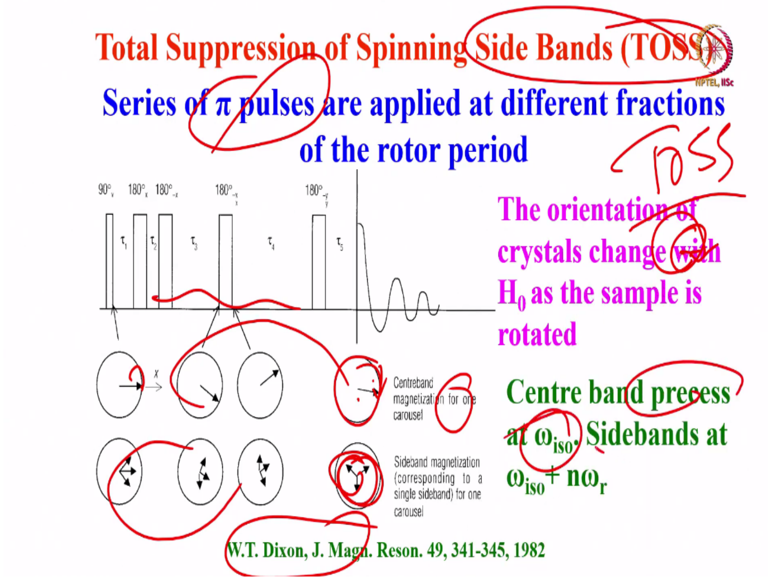

Total Suppression of Spinning Side Bands (TOSS)

Series of π pulses are applied at different fractions of the rotor period

TOSS

The orientation of crystals change with H_0 as the sample is rotated

Centre band precess at ω_{iso}. Sidebands at $\omega_{iso} + n\omega_r$

W.T. Dixon, J. Magn. Reson. 49, 341-345, 1982

We will go to another method. This another method is called total suppression of the spinning sidebands, called TOSS experiment. TOSS means total suppression of the spinning sidebands. This is an experiment which we do by playing with the spin dynamics. What we do? this is from a famous paper the Dixon paper in 1982 he has published in JMR. We will apply series of pulses sometimes, 4 pulse sequence, Dixon 5 pulse sequences are there, at different fractions of the rotor period. There is one rotor period. I showed you, it started like this go back and come back to the same place, it is one rotor period. During this one rotor period at different fractions of the rotor period, we apply RF pulses and it is manipulated in such a way what happens? the orientation of the crystal changes with the magnetic field, as the sample is rotated. But what happens when you acquire the signal at different RF pulse you apply? for one rotation the magnetization is here, goes back, goes back, like this and comes back to the same place.

It is tuned in such a way the centre band comes back; start from this place they come back to the same place, where you started after one rotation. Whereas the sidebands will keep on dispersing; they will not come back to the same place, the complete dispersion takes place, like what you saw in the XY plane. So, there is a dispersion of the signal, the sideband magnetization and you are not going to collect that at all. You are collecting only centre band signal by applying series of RF pulses. The centre band is made to come back to the same place, the centre band magnetization after one rotation, it will come to the starting point where it started. Whereas sidebands completely get nullified because of dispersion like this. And centre band precesses at the isotropic frequency, and the sidebands precesses at n omega r frequency.

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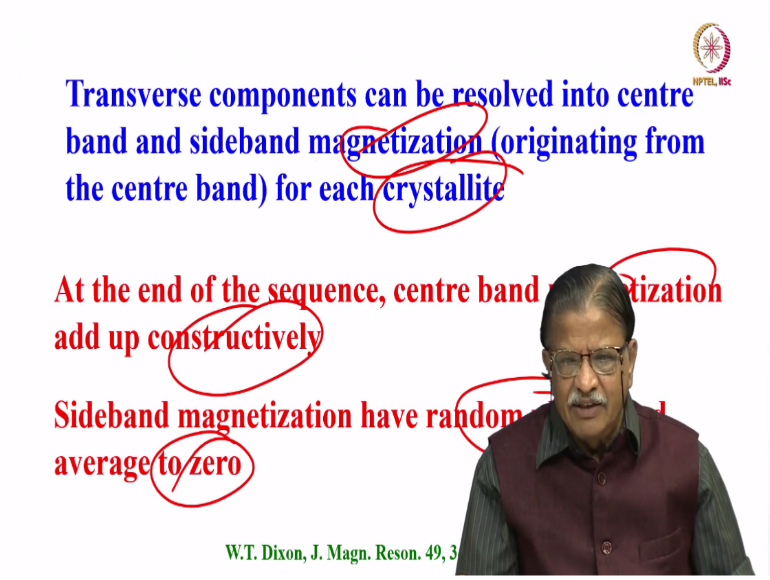

Transverse components can be resolved into centre band and sideband magnetization (originating from the centre band) for each crystallite

At the end of the sequence, centre band tization add up constructively

Sideband magnetization have random d average to zero

W.T. Dixon, J. Magn. Reson. 49, 3

Now this transverse component can be resolved into centre band and sideband magnetization for each crystallite. At the end of the sequence it so happen centre band magnetization adds up constructively, side band magnetization have random phases, they will add destructively. They average out to 0. That is what happens, the centre band magnetization adds up constructively after at the end of the Dixon sequence. Whereas, the sideband magnetization gets nullified, they average out to 0.

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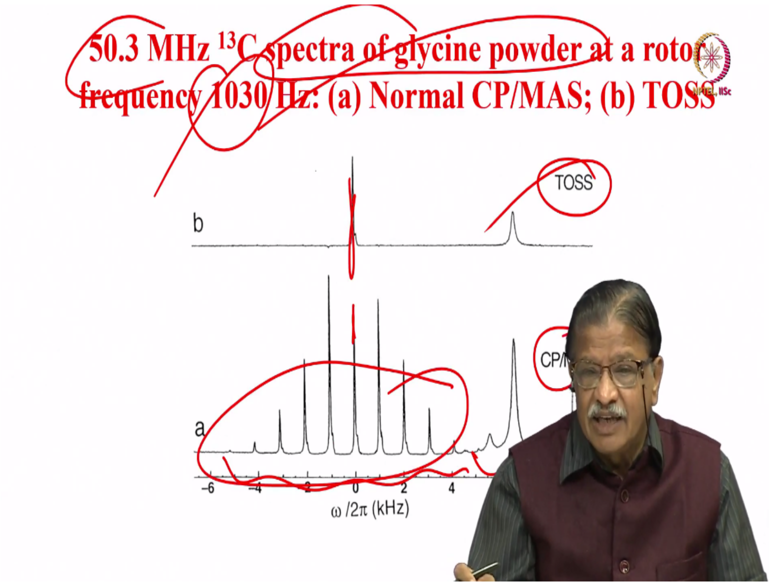

50.3 MHz ^{13}C spectra of glycine powder at a rotor frequency 1030 Hz: (a) Normal CP/MAS; (b) TOSS

This is simple experiment to show 50.3 megahertz carbon 13 spectrum of glycine powder at this rotor spinning frequency of 1 kilohertz approximately. And this is a normal CP mass spectrum of glycine. Look at it this is for the CO carbon, this is CH3 carbon. Look at this one, how many sidebands are here, lot of sidebands are there. Now, if you do only one experiment and if I do not know where the isotropic chemical shift comes, how do you say which is the side band and which is isotropic chemical shift, you cannot say so easily. So, what we do is, we do the TOSS experiment, total suppression of the spinning sidebands by using this Dixon method. Then all the sideband disappear; only centre band will be retained sidebands add destructively, centre band keeps on adding up constructively, that is retained.

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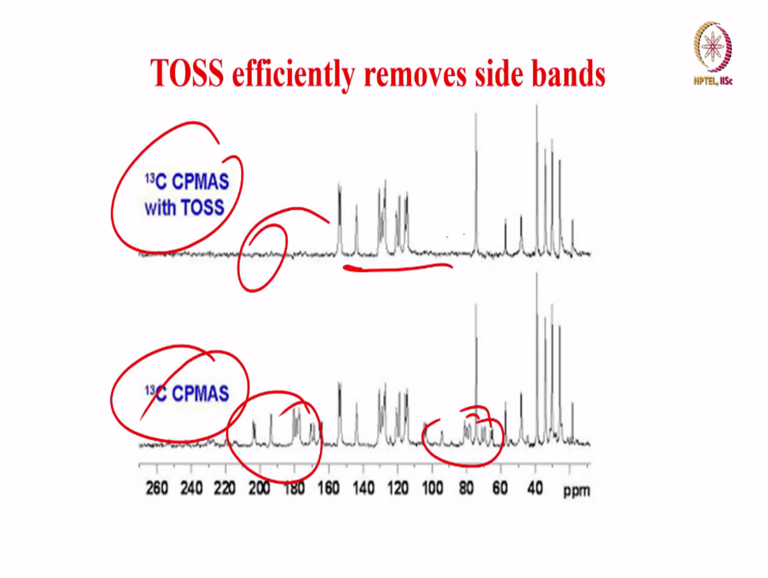

TOSS efficiently removes side bands

This is the TOSS comparison of glycine powder. It can efficiently remove sidebands in a very complex spectrum like this. Look at this complex molecule carbon 13 CPMA. This is with TOSS, and this is without TOSS. See without TOSS so many sidebands are there. Here now with TOSS all the sidebands are removed; no sidebands. This is an advantage.

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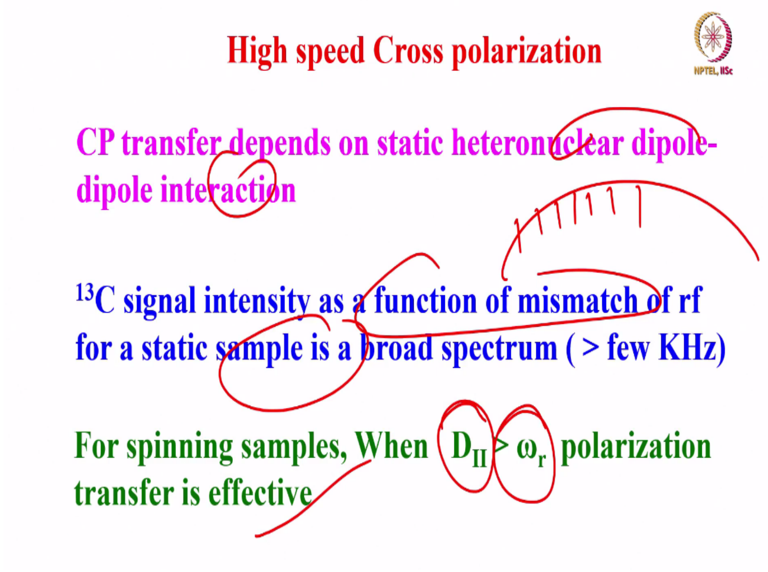

High speed Cross polarization

CP transfer depends on static heteronuclear dipole-dipole interaction

^{13}C signal intensity as a function of mismatch of rf for a static sample is a broad spectrum (> few KHz)

For spinning samples, When $D_{II} > \omega_r$ polarization transfer is effective

So, now quickly I will introduce few terms, there is no time to go into the details. Let us see for another 5 minus, 10 minutes I will give you some ideas about high speed cross polarization. This cross polarization transfer depends upon static heteronuclear dipolar interaction. The 13C signal intensity, as a function of RF mismatch we can plot it. For a static sample it is broad powder sample, no problem.

You can keep on varying the RF power; and see where you can get the CP matching, cross polarization Hartmann Hahn matching; where we are going to see. For spinning samples when homonuclear interaction is sufficiently larger than omega r, the polarization transfer is effective; that is what I said, it depends upon the interaction strengths also.

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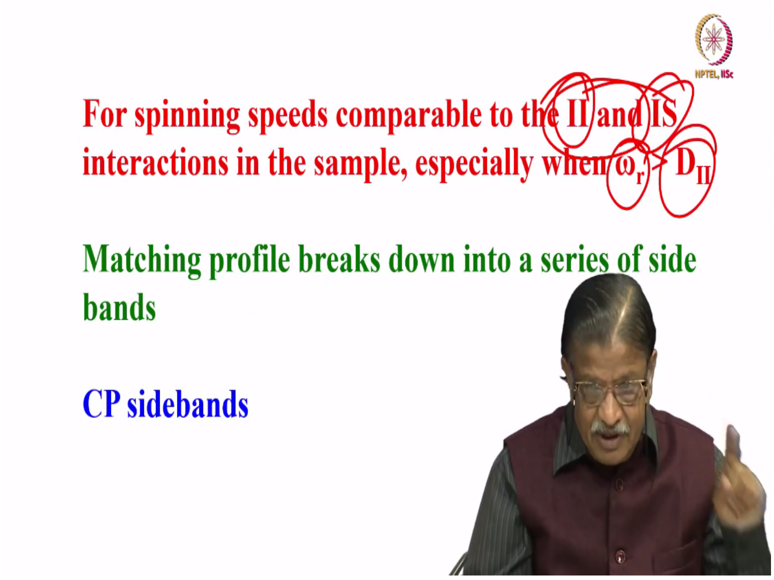

For spinning speeds comparable to the II and IS interactions in the sample, especially when $\omega_r > D_{II}$

Matching profile breaks down into a series of side bands

CP sidebands

And on the other hand for spinning speed comparable to proton-proton homonuclear or heteronuclear dipolar coupling. Especially in the sample when omega r is larger than the homonuclear interactions, the matching of the profile breaks into sidebands. Remember this is different from spinning sidebands. These are called CP sidebands.

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How to achieve Hartman-Hahn Condition

$$\gamma_H B1_H = \gamma_{13C} B1_{13C}$$

Keep the power on the ^{1}H channel constant while varying the power level on the ^{13}C until the maximum signal is obtained

To make you understand I will tell you once we go ahead further. We achieved the Hartmann Hahn condition by this. What you can do is keep the power on one of the channels, say proton or carbon 13; and keep on varying the power strength of the other one, until you get the maximum signal and starting plotting intensity as a function of rf power.

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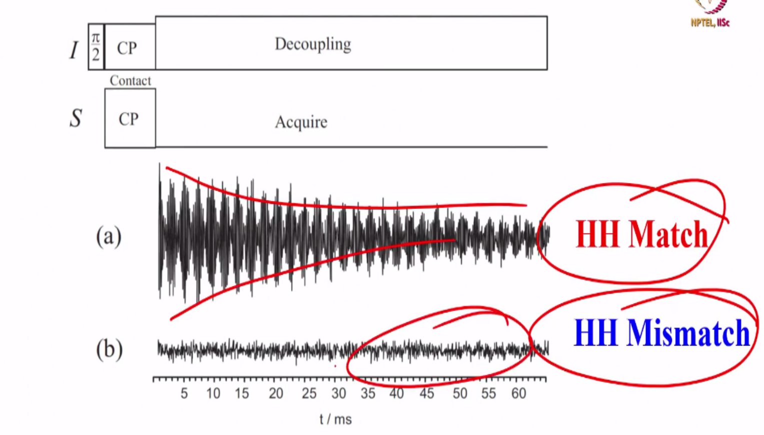

This is the way you adjust the Hartmann Hahn. This is a Hartmann Hahn mismatch condition, the Hartmann Hahn match condition, look beautiful FID you are seeing, when your Hartmann is mismatched, there is no signal at all. This is a normal conventional decouple CP sequence which I said.

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Carryout Two Experiments

For a sample static, keep the ^{13}C rf power constant and keep varying the ^{1}H rf power, at regular intervals

Each time, measure the intensity of the peak

Repeat the same experiment for a Spinning Sample

Plot the graph of intensity of the peak as a function of ^{1}H rf power

And now we can carry out two experiments. Keep a static sample, that means no spinning; put a sample in magnetic field. Keep RF power of one of them, like carbon or proton constant. And let us say I keep carbon RF power constant. Keep on varying the RF power of the proton at regular intervals. I am not spinning the sample yet. Each time measure the intensity of the peak, one of the peaks we take as a standard, keep on measuring the intensity. Now repeat the experiment with the spinning speed. Plot the graph of the intensity of the peak as a function of the RF power; you do this experiment.

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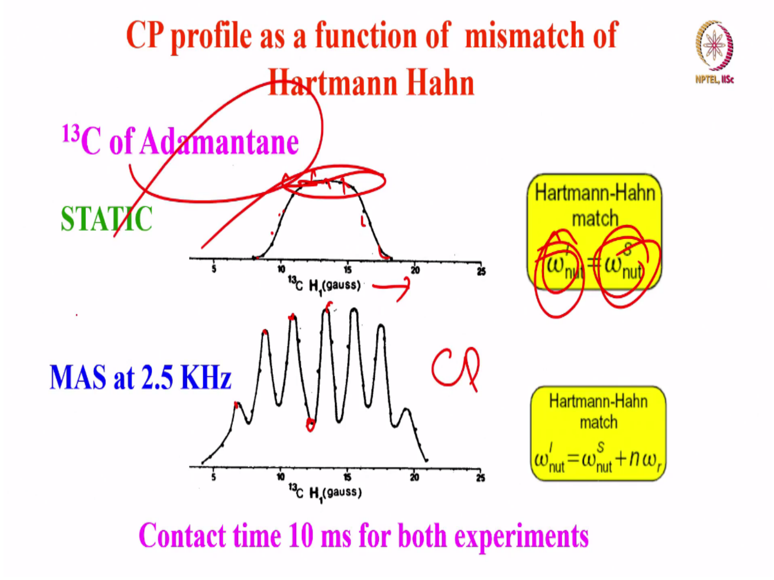

CP profile as a function of mismatch of Hartmann Hahn

^{13}C of Adamantane

STATIC

MAS at 2.5 KHz

Hartmann-Hahn match $\omega_{nut}^{I} = \omega_{nut}^{S}$

Hartmann-Hahn match $\omega_{nut}^{I} = \omega_{nut}^{S} + n\,\omega_{r}$

Contact time 10 ms for both experiments

Now we see for the static sample, you have collected the data different RF powers, for the carbon 13 RF power. Now what is going to happen is Hartmann Hahn match, when the RF power of the omega I channel the proton; and then for the S channel are equal, Hartmann

Hahn matching is there. In the static sample, you see we can get the matching at any of these places.

So, what is happening is now Hartmann Hahn matching is there between this and this. And you keep on measuring, the intensity. It is a broad profile anywhere you put the CP condition you get the signal, very beautiful. Now at the same time you will spin the sample see when you are here, you get the signal when you are here you get the maximum signal. When you are here you do not get the maximum signal, it is 0 or less signal, less intensity. So, again you plot the intensities as a function of rf. You see it looks like a sideband, but they are not spinning sidebands. These are called CP sidebands; and now that means in a situation like this, for example, adamantane which is a plastic crystal natural averaging has removed the dipolar interactions.

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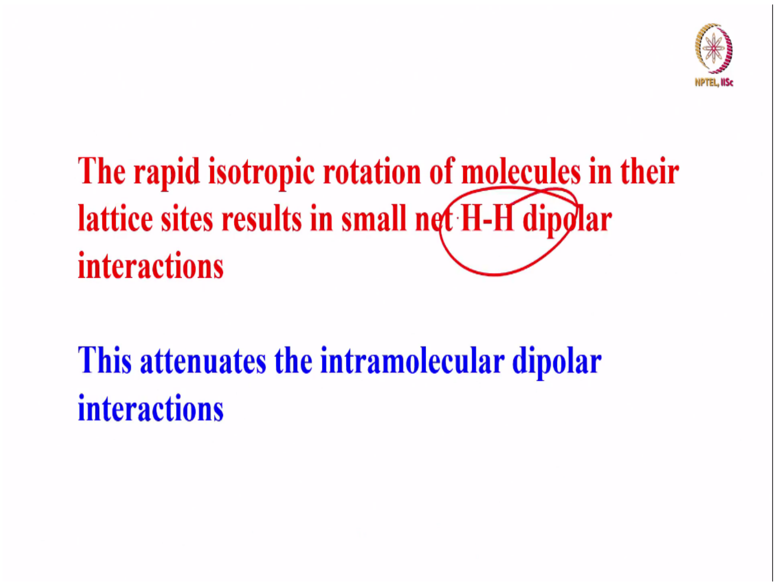

NPTEL, IISc

The rapid isotropic rotation of molecules in their lattice sites results in small net H-H dipolar interactions

This attenuates the intramolecular dipolar interactions

So, rapid isotropic motion is there, the H-H dipolar couplings are small. This is attenuating the intramolecular dipolar interactions.

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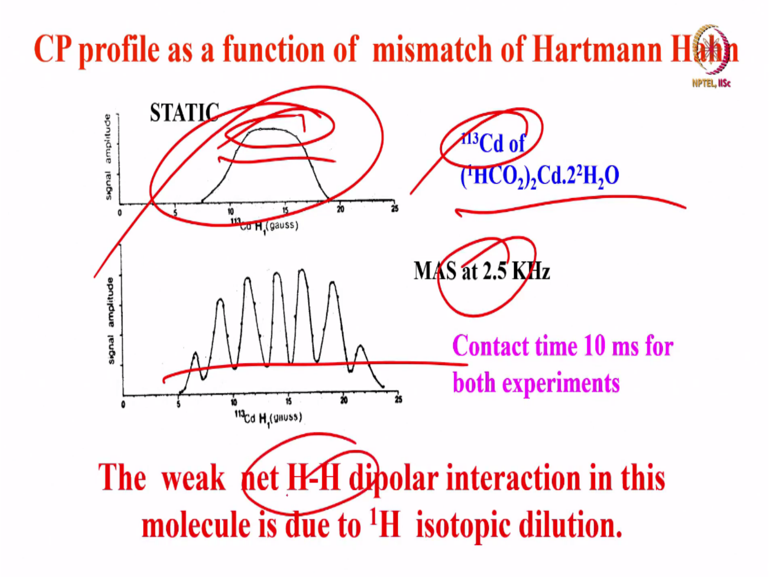

CP profile as a function of mismatch of Hartmann Hahn

STATIC

^{113}Cd of $(^1HCO_2)_2Cd.2^2H_2O$

MAS at 2.5 KHz

Contact time 10 ms for both experiments

The weak net H-H dipolar interaction in this molecule is due to ^{1}H isotopic dilution.

So, now CP profile for this is very bad, and if you start doing the experiment there is a Hartmann Hahn mismatch. So, look at another example of the cadmium 113 spectrum of this molecule. Again in the static case is a broad hump you are going to get, the matching profile is over a wide range. Whereas here matching profile breaks into sidebands. It is spinning at 2.5 kilohertz. Now this is again because of weak dipolar interaction in this molecule due to isotropic dilution.

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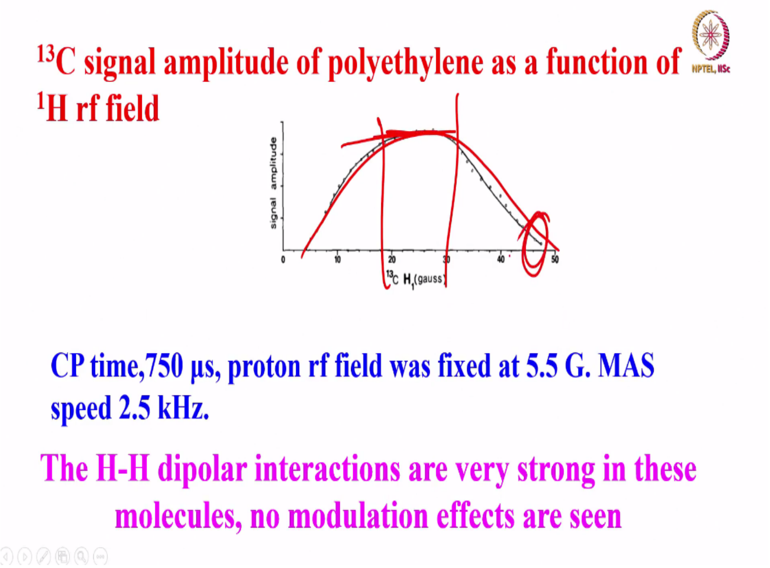

^{13}C signal amplitude of polyethylene as a function of ^{1}H rf field

CP time,750 µs, proton rf field was fixed at 5.5 G. MAS speed 2.5 kHz.

The H-H dipolar interactions are very strong in these molecules, no modulation effects are seen

On the other hand look at the carbon 13 signal amplitude of the polyethyelene, another molecule. Again this is a static sample; look at it, the intensity keeps on varying. At this place if you are sitting you are sure to get the maximum signal intensity. If you are sitting here, of then very low intensity. You understand how you can set the CP condition, keep on varying the RF power of one of them, in the static case. Keep on measuring the intensity and draw a plot. Identical condition we will do with the magic angle spinning. You will see, you will have a different profile this breaks into spinning sidebands. We will not worry about it.

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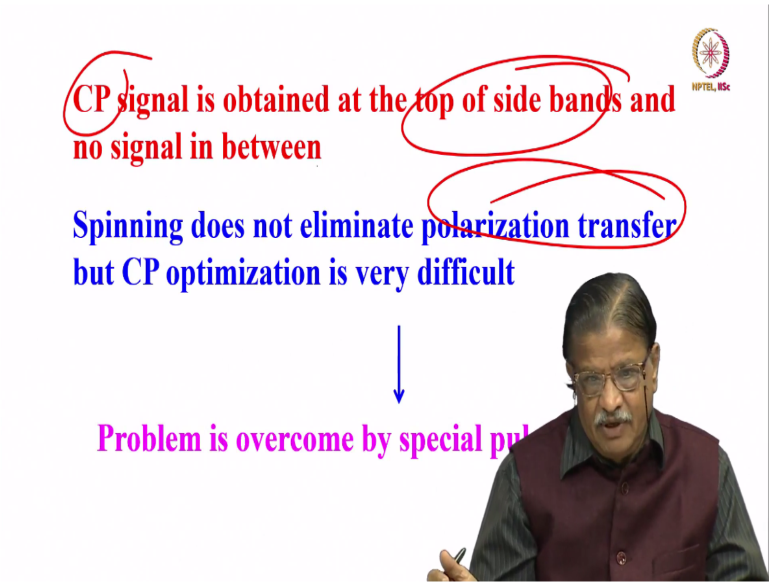

CP signal is obtained at the top of side bands and no signal in between

Spinning does not eliminate polarization transfer but CP optimization is very difficult

↓

Problem is overcome by special pu

Now CP obtained at the top of the sidebands, you get a signal and in between you would not get the signal at all. So, spinning does not eliminate the polarization transfer. Remember spinning is not eliminating the polarization transfer, but CP optimization is difficult, in regular interval multiples of that CP sidebands. At the top of the CP sidebands you get the signal, anywhere in between the intensity is lower. So, this is the problem you have to overcome by special pulse sequences.

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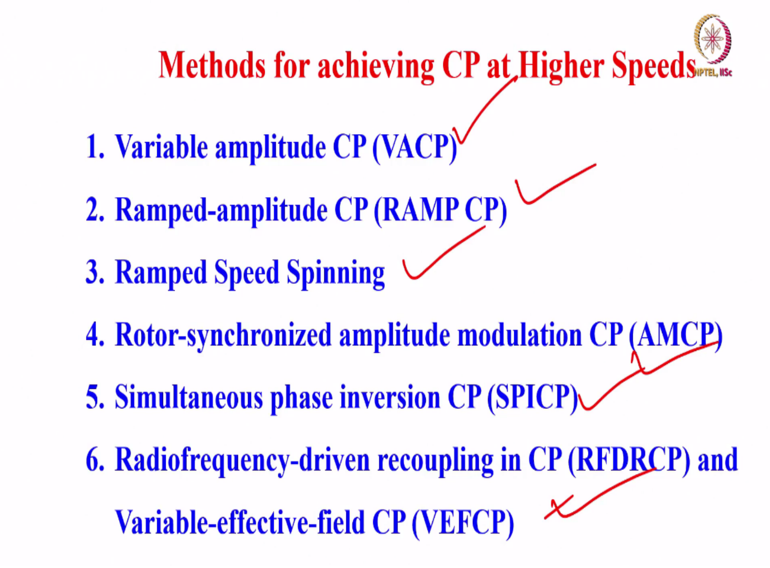

Methods for achieving CP at Higher Speeds

1. Variable amplitude CP (VACP)
2. Ramped-amplitude CP (RAMP CP)
3. Ramped Speed Spinning
4. Rotor-synchronized amplitude modulation CP (AMCP)
5. Simultaneous phase inversion CP (SPICP)
6. Radiofrequency-driven recoupling in CP (RFDRCP) and Variable-effective-field CP (VEFCP)

And there are number of methods available for this. For example variable amplitude cross polarization, ramped amplitude CP, ramped speed spinning, rotors synchronized amplitude modulation, simultaneous phase inversion, RF driven CP and variable effective field CP. Lot of things are there; several experiments are designed to overcome this, and especially when you have a dipolar coupling. This can happen in some systems when the homonuclear dipolar couplings are very small because of the natural averaging. Then you are going to get CP sidebands. CP adjustment is very, very difficult in such cases. Then you would adopt any one of these methods you are going to get fantastic comparison of the intensity.

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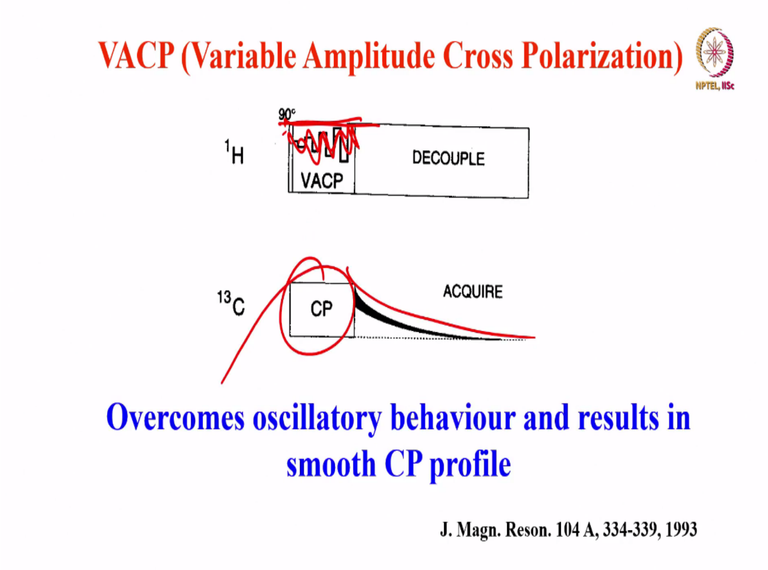

VACP (Variable Amplitude Cross Polarization)

Overcomes oscillatory behaviour and results in smooth CP profile

J. Magn. Reson. 104 A, 334-339, 1993

I will show you one example. Here the same CP condition. Instead of RF power being uniform; keep on varying the amplitude of the RF power or CP power here. In the case of protons, I do not make it uniform. I keep on varying the amplitude over the entire mixing cycle. For carbon 13, I do not do anything. Conventionally you do this, and then start acquiring the signal. It overcomes the oscillatory behaviour and the CP side band profile will be removed.

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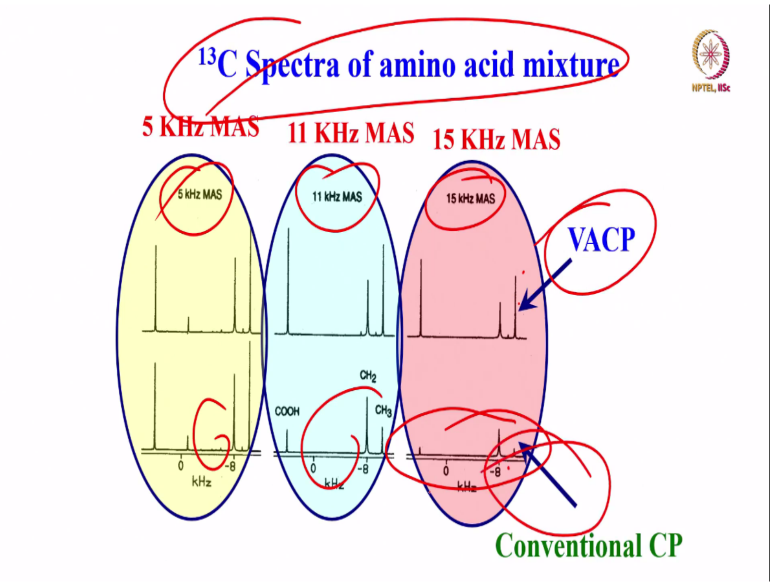

^{13}C Spectra of amino acid mixture

5 KHz MAS 11 KHz MAS 15 KHz MAS

VACP

Conventional CP

Look at this one. This is what happens if I take the 13 spectrum of different amino acid mixture. Here this is at 15 kilohertz, 11 kilohertz and 5 kilohertz spinning. And here you see the intensity, it is very difficult to match the intensity. Ok, 5 kilohertz is little better. But look at this one,15 kilohertz here, it is very bad now. This is the speed, the intensity of the peaks here. This is because here in these experiments VACP has been done.

Here this is with VACP; variable amplitude cross polarization. Here is a conventional CP. What it does is, it can overcome the oscillatory behaviour. And we can start discussing about various other pulse sequences, the other experimental techniques which are adopted for this thing. So, I do not think there is time to discuss all those things and also I tell you all these experiments I was discussing only for the one dimensional experiment where we get sharp lines. We understood CP mechanism. What happens at a high speed spinning and low speed spinning and why CP adjustment is difficult for high speed spinning; because CP profile breaks into CP sidebands. We discussed these things and then we have overcome these by varieties of pulse sequences designed, like VACP variable amplitude cross polarization, variable phase. All these experiments have been designed so that CP efficiency, the transfer of magnetization is efficient.

So, we do not have time to discuss everything, but then the 2D experiments have been designed in such a way all these techniques you can incorporate in the T1 dimension and also the T2 dimension. And with the 2D experiment you can get the results what you want; that means you can also extract particular information of your choice. You can remove the interactions and correlate like our chemical shift correlation COSY and TOCSY, in the homonuclear protons in the solution state. Here also you can do carbon 13, carbon 13 correlation, but that is an experiment called RFDR. Similarly, I can design an experiment to get only proton proton dipolar coupling, homonuclear coupling, I can get only heteronuclear couplings, I can get only chemical shift anisotropy like that. I can remove the sidebands, and I can get only isotopic in one direction and other dimension I can incorporate TOSS. In other dimension I can incorporate deTOSs. I can do all these things. The varieties of combination of pulse sequences are there. As I said there is not much time; since this is the last class. I have not discussed, but I wanted to give you an idea. pProbably in the next course when there is an opportunity I will come back and discuss lot of solid state NMR experiments for the benefit of those who want to specialize in NMR. So, right now I am going to stop here. The broad classification of solid state NMR experiments I discussed. And I give you idea what is magic angle spinning, I gave you idea about what is spin space averaging, what is the cross polarization, how the cross polarization works, and what happens at the lower spinning speed, what happens at the higher spinning speed; and all those things we discussed. All of them are very, very important very, very useful. So, you understand these things; these are all important techniques.

So, possibly I do not know if I time is available, quickly I will come and give one or two simple 2D experiments in the case of solids. in fact, mind you, I have not even discussed DOSY, I have not discuss the pure shift experiments. You see the time is too short to discuss everything. I tried my level best to cover maximum. If I keep on going at the rapid speed, then may not be able to follow everything.

So, with the available time it is impossible to cover everything, but if there is a time I will come back and talk something about pure shift and if possibly in one class, one or 2D experiments of solids I will discuss. Let me see, I will think over it and come back. But as far as I am concerned today our course is coming to an end. Please go back, as I said NMR is a big ocean whatever I have been discussing is only tip of an iceberg. Lot more things are there to discuss. Each and every topic we discussed, one can discuss for hours. Lot of developments are there, several stalwarts in NMR have designed experiments. Every time they have improved upon the methodologies. We can understand all those things. So, it is a big ocean. So with this, I have given ideas, some general principles, concepts and type of experiments one can do, type of information you can derive. So you have got a basic knowledge, the basic idea.

Further improvement about your knowledge you can do by going into the literature and understand other recent developments. Thank you, I am going to stop here. Thank you.