A Brief Introduction to NMR

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Overview

This booklet attempts to introduce NMR spectroscopy to students that have college-level physics and chemistry background, and have an interest in learning about this powerful yet complex tool, but only have a small amount of time to spare. It requires no prior NMR knowledge.

There are three major areas of NMR spectroscopy in terms of applications: solution NMR, solid-state NMR, and magnetic resonance imaging (MRI). Solution NMR is the best friend of chemists and biochemists, as it helps them to see molecules, much like the telescopes for astronomers. In fact, it is not only a useful tool, but also a charming story in which the daunting world of quantum mechanics manifest its simple beauty in front of our naked eyes. Solid-state NMR (ssNMR) is a characterization tool that is unique in both its capabilities and difficulties. It can probe many aspects of materials, including chemical structure, molecular dynamics (at a broad rate window of 10^0 – 10^{10} s^{-1}), and organization (crystalline vs. amorphous; domain structures; etc.). On the other hand, there are also severe challenges learning and using this technique. Proper setup of a ssNMR experiment often involves adjustment of dozens of experimental parameters, and interpretation of results is often not very intuitive, both of which require substantial background in the physics of materials and NMR. So my approach here is to tell a small subset of stories by introducing several essential concepts and several most commonly-used techniques, and hopefully crack the door of ssNMR open for you.

In this booklet, the first four chapters discuss fundamental principles relevant to all NMR experiments. Chapter 5 discusses a special solution NMR technique, diffusion NMR, which is essentially the MRI of molecules. Chapter 6 discusses several important ssNMR techniques.

1. Basic Working Principle of an NMR Experiment

Running an NMR experiment is similar to playing a music instrument. To play music on a piano, you need three components: the string – the material that generates the music; the tension on the string – a loose string won't do; and the strike (you strike the key, which drives the hammer, which strikes the string). An NMR experiment also requires three basic components, as the name NMR – Nuclear Magnetic Resonance - indicates: nuclei – the source of the signal; the big magnet – to set the nuclei on tension; and pulse – the strike that excites the nuclei so that we can hear their music. The pulse frequency must match the "tension" of the nuclei set by the magnetic field to be able to excite them, thus the name "resonance".

Larmor Equation

Just as the pitch of a piano string increases with increasing tension, the frequency of the NMR signal also increases with magnetic field. The relationship is called the Larmor Equation:

$$\omega_L = \gamma B$$

where ω_L is signal frequency of the nucleus, or Larmor frequency. γ is gyromagnetic ratio, a property of the nucleus. B is magnetic field strength.

There are many contributors to B. By far the biggest contributor is of course the field generated by the big superconducting magnet, which is termed B_0. The direction of the B_0 field is usually defined as z direction. Electrons surrounding the nuclei, when immersed in B_0, generate a tiny field that is opposite in direction to B_0. This is a shielding effect and is the mechanism of the vitally important concept of chemical shift. Each nucleus is also a small magnet and generates tiny field at its close neighbors. This is the mechanism of dipolar coupling and J-coupling. Finally, everything in a big magnetic field is magnetized and also contributes to B. This is why we need good quality NMR tubes, as bad ones generate inhomogeneous magnetic field and destroy the spectral resolution.

All nuclei of the same isotope have exactly the same γ, regardless of their chemical environments. Different isotopes have different γ. For example, γ (^{13}C) ~ ¼ of γ (^{1}H). According to the Larmor Equation, this would mean that in the same magnet, ^{13}C signal frequency would be about one quarter of ^{1}H signal frequency. Some isotopes have γ of zero – such as ^{12}C, thus are useless in NMR. To probe carbons, we have to reply on its rare isotope, ^{13}C, which has a natural abundance of only 1.1%.

In this booklet, most examples will be discussed using the two most important NMR nuclei: ^{1}H and ^{13}C. ^{1}H is so abundant in organic materials that it deserves a category of its own. The NMR properties of most other nuclei resemble those of ^{13}C.

Question 1

A ^{1}H NMR spectrum often contains many peaks, i.e., signals of many different frequencies. But, according to the Larmor Equation, if all the ^{1}H nuclei in your sample have exactly the same γ, and they are immersed in the same magnetic field, how can it give out signals of many different frequencies?

Question 2

We often hear an NMR spectrometer is referred to as such and such MHz. For example, a "600 MHz NMR" means that its ^{1}H frequency is 600MHz. What would be the ^{13}C signal frequency on this spectrometer?

Pulse program

Pulse programs are often used to describe NMR experiments. Figure 1 shows an example of a simple NMR experiment.

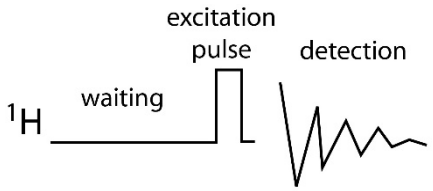

Figure 1. A simple pulse program

The baseline in the beginning of the pulse program indicates waiting time, during which nothing is done – but waiting is a necessary part of an NMR experiment, as the little nuclear magnets need time to "recover" after being worked. This will be discussed in Chapter 4. The peg stands for a radio frequency (RF) pulse at ^{1}H frequency. The pulse excites ^{1}H nuclei. After we stop the pulse, the excited ^{1}H nuclei would emit signal, represented by the decaying wave, which is captured by a detector in the spectrometer.

Note that the pulses will have to be at the Larmor Frequency (i.e. "resonance") to excite the target nuclei. For example, on a 600 MHz NMR spectrometer, a pulse at 600 MHz would excite ^{1}H nuclei, which give a signal also at ca. 600 MHz. A pulse at 150 MHz on the same spectrometer would excite ^{13}C nuclei. A typical "hard" pulse (means high power pulse, which is

what we use most often) has a bandwidth of tens of kHz and can excite all the nuclei within this broad window.

The NMR signal is often called FID, which stands for Free Induction Decay, a terminology passed on from the old days. Then we perform Fourier Transformation on the FID and obtain a spectrum, which is a function of frequency.

Fourier Transformation

The NMR signal is a wave, and to understand information contained in a wave, we need Fourier Transformation (FT). FT analyzes waves by decomposing them into various frequency components.

In FT, there is a particularly useful relationship which we will use again and again:

$$\Delta\nu = \frac{1}{\pi\Delta t}$$

Δt is the decay constant of the wave (time domain), and $\Delta\nu$ is the width of the peak after FT (frequency domain). This relationship means that a slow-decaying wave would correspond to a sharp peak in the frequency domain, while a quick decay would correspond to a broad peak.

This relationship is in fact the essence of the famous Uncertainty Principle in quantum mechanics. So neither quantum mechanics nor its Uncertainty Principle is that mysterious. Simply, when particles behave like waves, they follow the rules that govern waves.

One application of this relationship is a mathematical treatment of FID before FT: applying a weighting factor to the FID data points. For example, if we apply an exponentially decaying weighting factor, we make the weighted FID decay quicker, and the result is that the peaks on the spectrum become broader. Why would anybody want to intentionally make his/her peaks broader and lose resolution? Because it has an important benefit: the operation suppresses noise in the later part of the FID. This operation is called line broadening, which is especially useful when your sample peaks are already quite broad – so there is not much to lose – and noise are high – so there would be a lot to gain. When wisely used, line broadening could dramatically improve the signal-to-noise ratio (S/N) of your spectra.

2. Theoretical Descriptions of NMR

Rigorous treatment of NMR requires quantum mechanics, in which the nuclear magnetic moments are represented by vectors, and the forces (or interactions, or Hamiltonians in quantum mechanics terminology) by matrices. There is a lot of math and a great challenge to visualize such operations for beginning level users. Fortunately, there are two simpler approximations which are much more intuitive and suitable for circumstances encountered by most entry-level ssNMR experiments. They are energy level model and vector model.

Energy Level Model

In the quantum world, a spin-1/2 nucleus occupies two states: spin-up (parallel to B_0) and spin-down (antiparallel to B_0). In a magnetic field (B_0), the two states would occupy different energy levels. The amount of the split is determined by the Larmor Equation. The spin-up state (parallel to B_0) has slightly lower energy and thus is slightly more populous. The spin-down state (antiparallel to B_0) has slightly higher energy and thus is slightly less populous. How slightly? Around room temperature, on a typical commercial NMR spectrometer, the difference between the two populations is less than 0.01% of their sum.

According to the energy level model, upon absorbing a photon, the low-energy state would be excited to the high-energy state. During relaxation, the reverse would occur. This model is unsuitable to understand modern pulsed NMR experiments, but is a suitable approximation for understanding nuclear magnetic relaxation phenomena.

Vector Model

As the spin-up and spin-down populations are different, there is a net magnetization, which can be represented by a vector. Motions of the vector follow classical electromagnetic laws and behave exactly the same as a bar magnet. Just as a changing current would twist a bar magnet nearby, a RF pulse would turn our vector in various directions. The following rules in the electromagnetic world would help you understand the Vector Model:

- A radio frequency pulse would generate an oscillating magnetic field on the horizontal plane, usually termed B_1.
- When a magnetization is parallel to the external magnetic field (either B_0 or B_1), it would stay still.
- When a magnetization is not parallel to the external magnetic field (either B_0 or B_1), it would precess around the field. This is the same phenomenon as a spinning top, which, when it is tilted, its spinning axis will slowly turn around the gravity direction. This is called precession.

The tiny difference between the spin-up and spin-down populations means that the net magnetization is tiny, which means that the NMR signal is tiny. A lot of samples (usually in the milligrams) are often needed to generate enough signal to win the battle against noise. Usually

many repetitions (each repetition is called a scan) are acquired. The signal strength would be proportional to the number of scans (NS), while the noise would be proportional to the square root of NS (why?). Therefore, the signal-to-noise ratio (S/N) is proportional to the square root of NS. This means that if you double your sample concentration, you can reduce the required experiment time by a factor of four.

The vector model is suitable for understanding the effect of pulses on a single spin (or a group of spins that do not interact with each other), but inadequate in describing the behaviors of coupled spins, which must be treated by quantum mechanics.

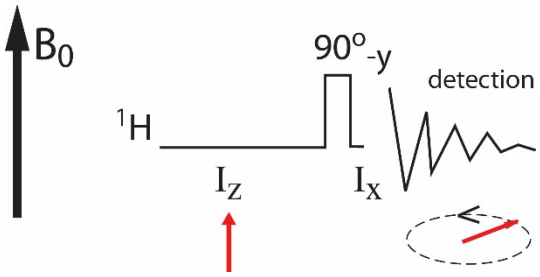

Figure 2. Evolution of the magnetization in a pulse program, according to the Vector Model

In the figure above, at the beginning, the magnetization points to z direction, which we can write as I_z. I_z is parallel to B_0, so according to the electromagnetic rules, it just sits still and does nothing. Next, the pulse creates an oscillating magnetic field, B_1. Since the frequency of the pulse satisfies the Larmor Equation, it creates an effect such that the oscillating magnet field generated by this pulse cancels out the effect of the big field B_0, so we can view our objects in a reference frame ("rotating frame") in which B_0 is non-existent and B_1 is a static magnetic field in the -y direction. The B_1 field forces the magnet to precess around it. We program the pulse to be long enough so that the magnetization is turned by 90 degrees, so that I_z become I_x. Now we stop the pulse, so the "rotating frame" ceases to exist, and the "lab frame" resumes in which B_0 is dominant. Since I_x is not parallel with B_0, again according to our rules, I_x would precess around B_0, which is along z direction. This precession on the horizontal plane generates a signal which we can collect.

So a NMR spectroscopist must properly design his/her pulses. There are four traits of a radio frequency pulse:

- Frequency (what criterion it must satisfy to excite magnetization?)
- Duration (default unit is μs). If you double your pulse length, you would double the angle that the magnetization is turned. A typical 90° pulse on a solution NMR spectrometer is around 10 μs.
- Amplitude. If you keep the pulse duration constant, but double the amplitude, you also double the angle that the magnetization is turned.

- Phase (in the figure above, the pulse has a phase -y, which turns I_z toward I_x direction. If you inverse the phase, you would turn the magnetization toward the opposite direction.)

Only horizontal component of the magnetization generates observable NMR signal. Thus we would predict that if you double a 90° pulse, you will flip the magnetization to -z direction, which has no horizontal component and thus generates no signal. If you triple a 90° pulse, you will generate a full-amplitude signal again, but all the peaks will show negative intensity. You can easily observe this effect on a spectrometer.

The default pulse program used in our proton NMR experiments uses a 30° pulse instead of a 90° one due to T_1 relaxation considerations (to be discussed in Chapter 4).

There is no way the energy level model would predict, when you irradiate your sample more, the signal goes from maximum to zero, then to negative maximum. Hence we see that simplifications do have their limitations.

3. Major Interactions in NMR

There are three major magnetic interactions in NMR that influence the NMR spectra: chemical shift, J-coupling, and dipolar coupling.

Chemical Shift

The shielding effect from electrons surrounding the target nuclei is chemical shift. It is called chemical shift because the amount of shielding (which is the shift in signal frequency) is determined by the chemical structure. For example, in solution ^{13}C NMR, aliphatic carbons usually appear at 10 – 45 ppm, ether carbons often at 60-70 ppm, aromatic carbons 115 – 145 ppm, and carbonyls 160 – 180 ppm.

In the solid state, chemical shift is not a number, but a tensor, which means that its value is dependent on the relative orientation of the molecule with regard to the magnetic field, B_0. For example, an aromatic ring that is perpendicular to B_0 would have a different chemical shift than one that is parallel. This property is called "chemical shift anisotropy" (CSA).

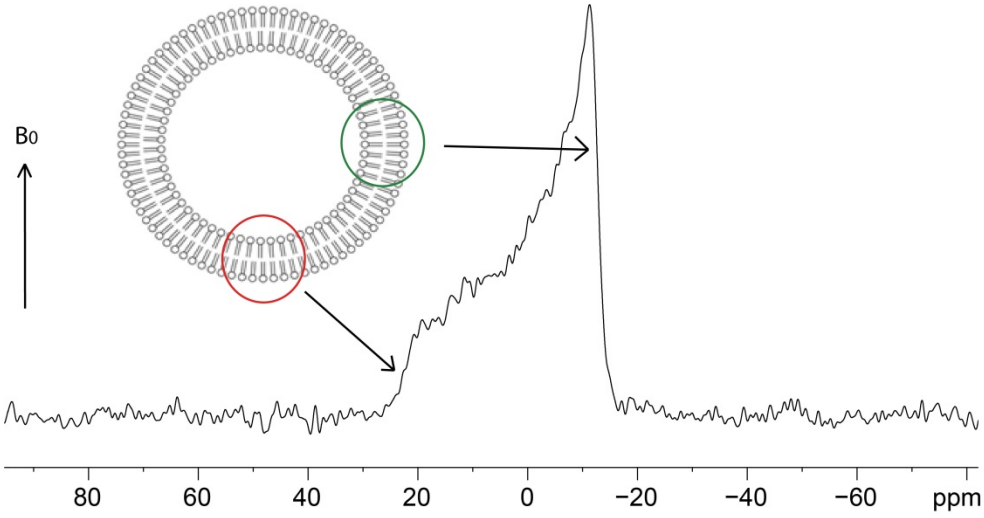

Figure 3. ^{31}P powder pattern of a phospholipid

Figure 3 shows a ^{31}P spectrum of a phospholipid. The lipid molecules that are parallel to B_0 gives a signal at ca. 22 ppm, while those perpendicular to B_0 show up at ca. -11 ppm. The former population is less populous than the latter, as the former is on the poles while the latter is on the equator. Thus the equatorial population generates a taller peak than the polar population. The molecules whose orientations are between these two extremes would appear somewhere between 22 and -11 ppm. Therefore, the pattern would be continuously distributed between 22 and -11 ppm. Such a shape is called a "powder pattern" (by "powder", we mean that there are all sorts of orientations in the sample).

As chemical shift originates from the shielding effect of electrons, and shielding effect is proportional to the external magnetic field, chemical shifts are usually expressed in unit of ppm. ppm is a relative unit – it is one millionth of the spectrometer frequency. On a 600MHz spectrometer, on ^{1}H spectra, 1 ppm = 600 Hz.

Question
On 13C spectra acquired on a 600 MHz NMR, what is the conversion factor between ppm and Hz?

Dipolar Coupling and J-Coupling

Dipolar coupling comes from the interaction between neighboring nuclei, e.g., between the two protons on a CH_2 group. This is exactly the same thing as the attractive or repulsive force when you bring two bar magnets close to each other, except that the magnets in question here are nuclei. Amazingly, the laws governing bar magnets and nuclear magnets are the same. Although the nuclear magnets are tiny, they can be quite close to each other – e.g. 1.5 – 3 Å apart, so the interaction can be quite strong. In NMR, the strengths of interactions are usually expressed in Hz – which can be easily converted to real energy units by multiplying with the Planck Constant. Note that the word "dipolar" refers to the nuclear magnetic dipole, not the electron dipole in polar molecules.

J-coupling is another interaction between neighboring nuclei. As a nucleus is a magnet (let's say it is nucleus A), it would generate a magnetic field, which would twist the electrons surrounding it (electrons A). The twist would propagate through chemical bonds, and twist the electrons in the neighboring atom B. Such a twisting would generate a magnetic field that can be felt by the nucleus that these electrons surround, nucleus B. So the sequence of the relay is nucleus A → electrons A → electrons B → nucleus B. This interaction between nucleus A and nucleus B is J-coupling.

Dipolar coupling, which ssNMR people deal with daily, and J-coupling, which solution NMR users are very familiar with, are both interactions between neighboring nuclei. Their differences are: (1) Dipolar coupling is through space (direct interaction), while J-coupling is through bond (indirect interaction). Dipolar coupling is proportional to the inverse cubic power of the internuclear distance, while J-coupling goes down quickly as the number of bonds between the pair of interacting nuclei increases. (2) dipolar couplings are much stronger, often in the tens of kHz, while J-couplings in solution NMR are usually 1-200 Hz. (3) Like CSA, dipolar couplings are

also tensors, which means that its strength is also orientation dependent. On the other hand, J-couplings in liquids are scalars.

Dipolar coupling, though very strong, is often invisible in liquid, as it is "averaged out" by the very fast molecular motion. So is CSA. In solids, dipolar couplings and CSA are both present, which make the NMR spectra extremely messy. Special techniques must be used to tackle these challenges.

There are dipolar couplings both between the same kinds of nuclei (termed *homonuclear dipolar coupling*; e.g. ^{1}H-^{1}H) and between different kinds of nuclei (termed *heteronuclear dipolar coupling*; e.g. ^{1}H-^{13}C).

J-couplings in Solution NMR

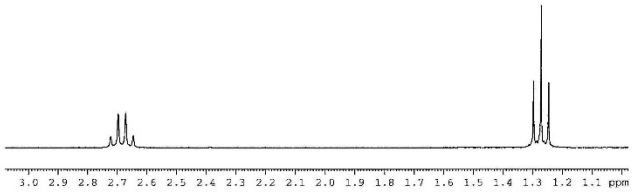

Figure 4. A section of a ^{1}H spectrum of ethylbenzene

Figure 4 shows a solution ^{1}H NMR spectrum of ethylbenzene (only the ethyl branch section of the spectrum is shown). The beautiful splitting – the 1:2:1 triplet at 1.27 ppm and the 1:3:3:1 quartet at 2.68 ppm – are the result of J-coupling. Such splittings can be simply explained using Larmor Equation. Nucleus A generates a field that is felt by nucleus B, and since nucleus A is split into two populations, A-up and A-down, the fraction of nucleus B that is next to the A-up nuclei would feel slightly different magnetic field than the fraction that is next to the A-down nuclei. The result is that nucleus B would give two peaks. Since the A-up and A-down populations are roughly equal, the two peaks given by nucleus B have an area ratio of ca. 1:1.

If the nucleus B has two equivalent A neighbors, let's say A1 and A2, the B population would be split into three fractions: those next to A1-up/A2-up; those next to A1-up/A2-down and A1-down/A2-up; and those next to A1-down-A1-down. So nucleus A would give three peaks with area ratio 1:2:1, which is the situation for the 1.27 ppm peak in the above spectrum.

We can also look at this interpretation in the reverse way: the splittings on the ^{1}H NMR spectra confirm the prediction of quantum mechanics that the distribution of energy state in the atomic world is not continuous but discrete. Have you ever asked yourself: is the atomic world really quantum, like what the professors say, though unlike anything we see in our everyday life? Now you have an eyewitness: the NMR spectra. You can see quantum mechanics with your naked eye on a NMR spectrum!

So far we have discussed only the simplest kind of nuclei – those having spins of ½. Many nuclei have spins of higher than ½, which brings about some additional complexity. These nuclei are called quadrupolar nuclei, as they possess an electric quadrupole that the spin ½ nuclei do not. The most important quadrupolar nucleus is ^{2}H. ^{2}H has a spin of 1, which means that in a magnetic field, it would split into three populations: +1, 0, and -1, with a population ratio of approximately 1:1:1 (why do I say approximately, not exactly?).

> Question
>
> On ^{13}C spectra using $CDCl_3$ as solvent, you would notice that the solvent peak is a triplet, but the area ratio between the triplet is different from a ^{1}H triplet (1:2:1). Why? If you have never seen such spectra before, can you predict the area ratio of this triplet? Hint: the signal is from the carbon that directly bonds to a ^{2}H. You can ignore the effect of the chlorines to your ^{1}H and ^{13}C NMR spectra.

As dipolar coupling and J-coupling strengths are independent of the external field strength, they are always expressed in unit of Hz or kHz rather than ppm. To put it in another way, chemical shift is the shielding effect of the electrons, which is an induced magnet, so the suitable unit is ppm, a relative unit. On the other hand, dipolar couplings and J-couplings are the effect of neighboring nuclei, which are permanent magnets (independent of the value of B_0), so the suitable unit is Hz, an absolute unit.

The strength of J-coupling can be directly read off a solution NMR spectrum – it is simply the distance between two adjacent multiplet peaks. You do need to convert the distance from ppm to Hz. The strength of dipolar coupling can also be read off a ssNMR spectrum – though this will be a much messier problem, which we will discuss in the next section.

Dipolar Couplings in ssNMR

Just as J-couplings would produce multi-peak splittings in solution NMR spectra, so would dipolar coupling in ssNMR spectra. However, the splittings won't look as neat as on those solution NMR spectra due to two complexities. First, it is orientation dependent, so each interacting pair of nuclei would produce its own "powder pattern". Second, organic solids are so crowded of protons, so there are many, many pairs of ^{1}H-^{1}H dipolar couplings (let's use ^{1}H-^{1}H dipolar coupling as an example here), including both intramolecular and intermolecular couplings. The summary effect is that the signal would just be a continuous and broad hump. The width of the hump represents the amplitude of the strongest dipolar coupling in your sample, which is between the closest proton pairs.

The dipolar couplings would make the NMR signals very broad. As a result of ^{1}H-^{1}H coupling, solid-state ^{1}H spectra of rigid polymer is often 30-70 kHz wide. The ^{1}H-^{13}C coupling would result in ^{13}C spectra that are > 10 kHz wide.

Since solid-state ^{1}H spectra are so broad that all of the chemical structure specificities are masked, we do not need FT anymore, but could directly analyze the time domain signal (FID) instead. This in fact has many advantages as the time domain decays can often be nicely fitted by well-known decaying functions such as exponential or Gaussian.

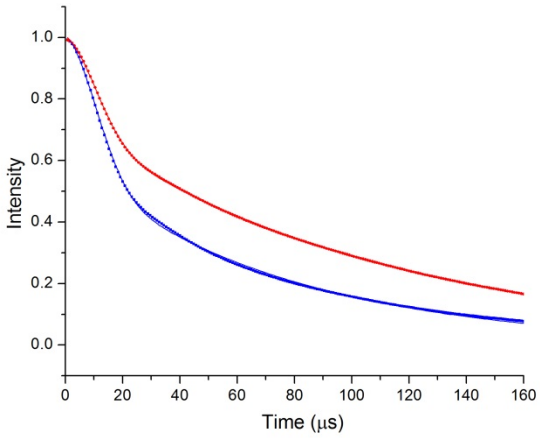

Figure 5. ^{1}H time-domain signal (FID) and their fits for a poly(urethane urea) sample

The figure above shows time-domain ^{1}H FID of a poly(urethane urea) (PUU) sample at two temperatures. The FID (symbols) was fitted with a two-component model (lines), a fast-decaying Gaussian and a slow-decaying exponential. Later we will discuss the physical significance of these components. Remember that PUU is a very complex polymer – it is a product of three ingredients (diisocyanate, diol, and diamine) polymerized in a two-step process, and has rather complex morphology, so it is quite amazing that its ^{1}H NMR signal can be fitted with two simple components, with only three adjustable parameters.

^{1}H-^{1}H dipolar coupling results in a phenomenon that plays many roles in ssNMR – spin diffusion. Protons that are coupled through dipolar interaction can exchange magnetization. As a result, ^{1}H magnetization can diffuse throughout the sample whenever there is a magnetization gradient. This is similar to the diffusion of heat in water wherever there is a temperature gradient. Such a gradient can be created by many methods and can yield interesting insights to materials.

Question

^{13}C-^{13}C dipolar coupling is usually not a major concern, and ^{13}C spin diffusion is rarely observed. Why? (hint: consider the natural abundance of ^{13}C)

4. Molecular Motions and Nuclear Magnetic Relaxations

One of the most unique capabilities of NMR is its sensitivity to molecular motions in a broad rate window (10^0 – 10^{10} s^{-1}). Many NMR spectral features and relaxation behaviors reveal such information.

Molecular Dynamical Processes

Many dynamical processes exist in organic materials. For example, in a liquid, molecules tumble very fast, with a rate of often > 10^{12} s^{-1} for small molecules. Note that such motion is in random direction and at random speed, thus the rate here is an "average". Sometimes we also describe a random motion in terms of its correlation time (τ_c), which is simply the inverse of average rate.

Different from other techniques such as scattering, which takes instantaneous "snapshots" of the sample, NMR is a technique that detects time-averaged effects. This has many interesting implications. For example, a molecule might assume many different orientations with regard to the external magnetic field, B_0. A sample that contains many of these molecules would thus generate a powder pattern (see Figure 3 for an example). However, if this sample is a liquid, then each molecule would tumble so fast that all the orientation dependences are averaged out to zero. Consequently, we would see needle-sharp peaks (width often < 1 Hz; see Figure 4 for an example) instead of a very broad powder pattern.

If the motion of your molecules is not as fast as that in a true liquid, then the situation gets complex. Generally, you can tell a lot by comparing the motional rate Ω and the rigid-limit signal width (i.e., the signal width when the molecules are not moving at all) $\Delta\nu$. If $\Omega >> \Delta\nu$, then the spectrum will be liquid-like. If $\Omega << \Delta\nu$, the spectrum will be at its rigid limit. In between, the signal will be partially narrowed by dynamics.

There are many kinds of dynamic processes in solids. Polymers above T_g would have backbone rotations of 10^1 to 10^9 s^{-1}, faster at higher temperature. Phospholipid molecules in liquid crystalline state would have fast rotational motions around the bilayer normal direction. Methyl groups could rotate, and aromatic rings and carbonyl planes could flip.

Molecular motions could be translational and/or rotational. Translational motions can be detected by diffusion NMR techniques, which use pulsed-field-gradients (PFG) to locate the spatial location of molecules (see Chapter 5). Most other NMR techniques are only sensitive to rotational motions – the rotation would interfere with the orientation dependence of the major magnetic interactions such as CSA and dipolar coupling, and produce various detectable effects.

One of the most important effects of molecular motion is that it attenuates dipolar coupling. The extreme case would be liquids in which the molecules tumble so much faster than the dipolar coupling that the dipolar coupling strength becomes zero, and we see needle-sharp

peaks on ^{1}H spectra. In solids, for the molecular segments that do have mobility but not as fast as in true liquids, there will be some narrowing of the ^{1}H spectra. How much the ^{1}H spectra are narrowed by molecular motion is again determined by the "fight" between the motional rate (Ω) and the rigid-limit signal width $\Delta\nu$ (usually 30-60 kHz). If $\Omega << \Delta\nu$, the spectrum will be at its rigid (broadest) limit. If $\Omega \sim \Delta\nu$, the spectrum will begin to narrow. If $\Omega >> \Delta\nu$, then the spectrum will begin to look like that of solution NMR.

Another aspect of the molecular motion is how isotropic the motion is. The tumbling of molecules in liquid is completely isotropic, thus generates sharp peaks. On the other hand, the rotation of lipid molecules in bilayers is uniaxial, so its ^{31}P spectrum would still be a powder pattern (see Figure 3).

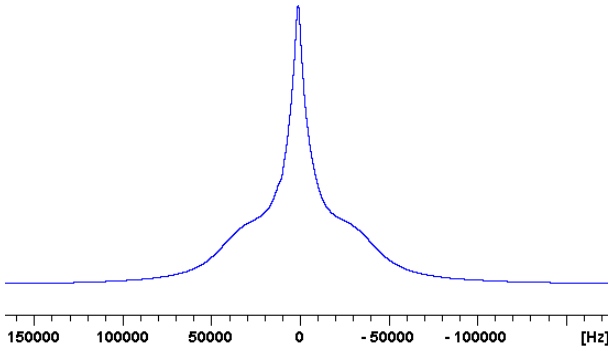

Figure 6. ^{1}H Spectrum of a solid HDPE.

Figure 6 shows a ^{1}H spectrum of solid high density polyethylene (HDPE). First, see how broad the peak is – ca. 100 kHz. Next, see that there are two components on top of each other. The broad component on the bottom, sort of a smoothed trapezoid-shape, is the crystalline phase, in which there is no appreciable segmental mobility, resulting in a very broad peak (FWHM = ca. 80 kHz). The narrow component on the top is the amorphous phase, which has fast segmental mobility, resulting in a narrower pattern (FWHM = ca. 20 kHz).

Molecular dynamics could be a unique tool to probe the heterogeneity of materials. If we know that peak A has high mobility while peak B has the signature of a completely rigid segment, then we know that molecules A and B must not belong to the same domain. Molecules in the same domain usually have similar backbone mobilities.

Question

In the PUU ^{1}H FID figure (Figure 5), (1) is the fast-decaying Gaussian component from a rigid or a mobile phase? (2) the two curves are signals from the same sample at two different temperatures. Can you tell which signal was run at higher temperature and which one at lower temperature?

T_1 and T_2 Relaxations

Relaxations are the processes when a system recovers from a high-energy state, or excited state, to a low-energy state, or equilibrium state. Relaxations processes are found in all the length scales – macroscopic (e.g. that of a stretched rubber band), molecular, atomic, and nuclear levels. The relaxation processes that are relevant to NMR of course occur at the nuclear level, but they tell a lot about what is going on at larger levels.

We can use the simple pulse program shown in Figure 2 to discuss the magnetic relaxation processes. In the beginning, the system is in the lowest-energy state (equilibrium), in which I_z is at full magnitude and I_x and I_y are both zero. When pulsed, the magnetization is excited, i.e., it moves away from equilibrium. When the pulse ceases, the system would want to go back to equilibrium, which involves two processes: (1) T_1 relaxation, which is the recovery process of the z component back to maximum; and (2) T_2 relaxation, which is the recovery process of the x and y components back to zero.

It is to be noted that T_1 and T_2 are related – both are driven by molecular dynamics – but are independent processes. T_1 is usually longer than T_2.

We usually run many repetitions of the pulsing – detection – recovery cycle (each cycle is called a scan), and ideally begin each scan with the magnetization at equilibrium (with I_z at maximum and I_x and I_y at zero). If the T_1 relaxation is not complete at the end of each scan, we will have diminished signal intensity at the next scan. We could use this fact to design an experiment that measures T_1: we use the pulse program depicted in Figure 2, systematically increment recovery time t_{RD} (RD stands for recycle delay), and record signal intensity I at each increment, then we could fit the data with this equation and find out T_1. It is an exponentially saturating process:

$$I = I_0(1 - e^{-\frac{t_{RD}}{T_1}})$$

This is called the saturation recovery experiment.

Alternatively, T_1 is often measured by the Inversion Recovery technique, the pulse program of which is shown in Figure 7. The solid, wide pulse is a 180° pulse, which inverses the magnetization to the –z direction. Following a variable delay period, a 90° pulse (the narrow pulse) is applied and the signal is detected. The signal strength as a function of the variable delay (vd) would follow the equation

$$I = I_0(1 - 2e^{-\frac{t_{vd}}{T_1}})$$

At increasing variable delay, the signal would go from negative full amplitude, passing zero, and eventually recover to positive full amplitude.

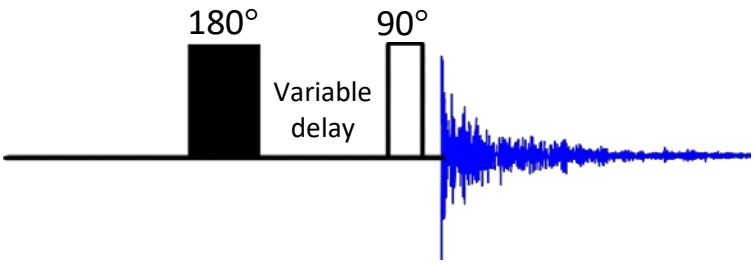

Figure 7. Inversion Recovery experiment.

While T_1 governs signal intensity, T_2 governs signal resolution (or peak width). As the signal strength is proportional to the magnitude of horizontal magnetization at each moment of the detection, if the horizontal magnetization shrinks fast, the signal would decay fast. Then, according to the relationship that we mentioned in the Fourier Transformation section, fast decaying signal corresponds to a short T_2 and broad peaks.

The relationship between the signal intensity and acquisition time t_{AQ} is as follows:

$$I = I_0 e^{-\frac{t_{AQ}}{T_2}}$$

Practically, the decay of the FID is affected not only by T_2 relaxation, but also by some other factors such as imperfect shimming. Therefore, T_2 is often measured by a technique called CPMG, which is named after its inventors, Carr, Purcell, Meiboom, and Gill. This technique removes the effects of other contributions and gives an accurate measurement of T_2 relaxation.

Relationship between Molecular Motion and T_1, T_2

Nuclear magnetic relaxations are different from most other relaxation processes in that they cannot occur spontaneously, but rather must rely on “kicks” from the outside to force the process. The reason for the reluctance of the nuclear magnetic relaxations is that the energy

level splittings in NMR are so tiny that there is not much incentive to come back to the lower level.

The most important "kicks" in ssNMR are the molecular dynamical processes, which generates a random force that make the relaxations happen. This is like the apples on a tree, though in an "excited" state as compared to the "equilibrium" state when they lie on the ground, the "relaxation" process does not easily happen, and you must vigorously kick and shake the tree to help the falling. Complete rigid molecules could have magnetic relaxation times of > several thousand seconds.

A random molecular dynamical process has many frequency components, which can be described mathematically as spectral density functions. Out of these many frequency components, only the component that equals to the Larmor frequency would be useful in driving T_1 relaxation. So the dynamical process that is most effective in driving T_1 relaxation would be one that has the largest spectral density at ω_L. This happens when the average rate of the process equals to ω_L.

This means that the dynamics that is much faster than or much slower than ω_L will both result in long T_1. So if we construct a chart of T_1 as a function of the rate (or correlation time) of the dynamics, we will see that the curve has a minimum.

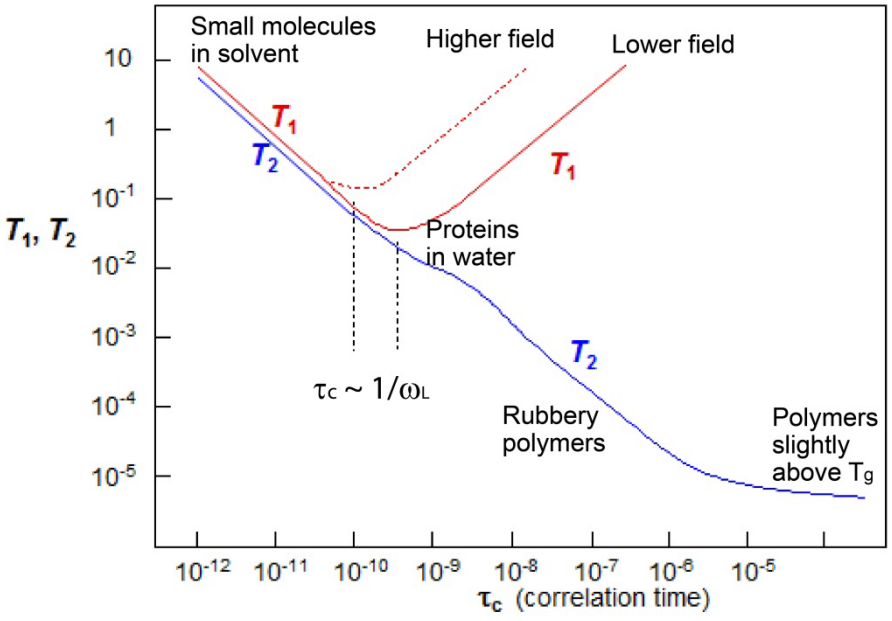

Figure 8. Relationship of T_1 and T_2 with molecular motion

This figure shows the dependence of T_1 and T_2 on dynamics. The regime to the left of the minimum is the fast motion regime, in which the molecular motional rate is faster than ω_L, the Larmor frequency, and T_1 increases with increasing temperature (move toward left). The

regime on the right of the minimum is the slow motion regime, in which the molecular motional rate is slower than ω_L and T_1 decreases with increasing temperature. T_1 is the shortest when the motional rate approaches ω_L (so the location of the T_1 minimum is different for different magnetic fields, as shown on the figure).

Though in liquids everything just seems to tumble extremely quickly, there are many shades of dynamics in liquids. For example, proteins, which usually assume a folded configuration, tumble in water as a whole. On the other hand, synthetic polymers in solutions are usually random coils and each segment can rotate relatively independently. So the T_1 of proteins are usually quite short, while the T_1 of synthetic polymers are not too different from small molecules. End groups of polymers have longer T_1 than the middle units (why?)

As seen in Figure 8, in liquids (fast motion regime), T_1 and T_2 have similar values and follow similar trends. In solids (slow motion regime), T_2 becomes a tricky concept. Often times the signal decays very fast not because of a true relaxation process, but rather because of dephasing due to very strong dipolar couplings. In this case, the T_2 that is calculated from the signal decaying rate is an apparent T_2, not a true T_2. T_1 and apparent T_2 depend on dynamics in very different ways. The T_2 shown in Figure 8 is true T_2 for fast motion regime and apparent T_2 for slow motion regime, respectively.

Note: don't confuse T_1 and T_2 relaxations with molecular relaxation processes. T_1 and T_2 relaxations are the relaxations of nuclear magnetization, not of the molecules themselves.

Quantitative NMR

NMR is fundamentally a quantitative technique, which means that, when experiments are done right, its peak areas are proportional to the number of the nuclei contributing to the peaks. This makes NMR a very useful method to quantify various chemical species and to calibrate other non-quantitative experiments. But to produce quantitative NMR results, you need to conduct your experiments right and process your data right.

The most important concept to understand in this respect is T_1 relaxation. If your experiment condition is such that T_1 relaxation is complete for all the structures in your sample, you will produce quantitative result. This is often relatively straightforward for ^1H spectra, whose T_1 relaxation is relative fast. For ^{13}C and ^{29}Si, T_1 can be quite long, in which we can add a small amount of chemicals containing unpaired electrons which can substantially speed up the T_1 relaxation and produce quantitative results. Popular choices for such chemicals are $Cr(acac)_3$ for organic solvents and $GdCl_3$ for water.

If you use decoupled pulse sequences for quantification, there is one more thing to worry about: the relaxation properties of the decoupling nucleus (usually ^1H). The usual solution is to use the

Inversed Gated sequence and have recycle delay long enough such that both the observe nucleus and the decoupling nucleus are fully relaxed.

When you conduct experiments on a solution NMR spectrometer with samples that have large aggregates (e.g. > 50 nm), these aggregates might not contribute NMR signal at all. Their signals would be so broad that they are in the baseline. If you suspect that some of your solutes might not be generating NMR signal, you could consider adding some internal standard in the sample, then compare the signal area of your solutes again that of the internal standard.

Practically, you will also need to do proper phase correction and baseline correction during processing. Broad NMR peaks could confuse the automatic phase and baseline correction algorithms, so you might need to perform manual corrections to achieve the best result.

5. Diffusion of Molecules and Aggregates in Liquids by NMR

Besides T_1 and T_2 relaxations, another interesting NMR technique to probe the physical behaviors of your molecules or aggregates is diffusion NMR. It is capable of detecting the diffusion coefficients of objects from single molecules to aggregates of ca. 50 nm in diameter. The technique is quantitative and works well for mixtures. Every molecule or aggregate in a system can be probed as long as it has a distinct peak on a NMR spectrum. Dynamic exchange processes between single-molecular state and aggregate state can also be probed. The diffusion NMR technique utilizes two tricks, magnetic field gradients and echoes.

Magnetic Field Gradient

One of the preparatory steps of a solution NMR experiments is shimming. The purpose of the shimming is to make the magnetic field across your sample volume homogeneous, or, in other words, to minimize the field gradients. According to the Larmor Equation, if different parts of your sample experience different magnetic field strength, the same structure will generate a broadened and often ugly-shaped peak.

On the other hand, the creative utilization of magnetic field gradient has revolutionized NMR in a number of fronts. Modern solution NMR probes can generate field gradient that can be quickly turned on and off, which are called pulsed gradients, or gradient pulses. The direction of the gradient is usually along the z direction, which means that when the gradient is applied, the magnetic field strength that your sample feels is a linear function of z, the tube length direction. Gradient pulses are crucial for Magnetic Resonance Imaging (MRI), automatic gradient shimming ("topshim" on Bruker spectrometers), most multidimensional NMR experiments, and diffusion NMR experiments.

Diffusion NMR Experiments

Diffusion NMR experiments use a pulse technique called echo. An echo is one or a number of radio frequency pulses that first spreads out the NMR signal coherence, then reverses the direction of its evolution and causes the coherence to bounce back. The bounced coherence will refocus and create an echo when the refocusing is complete. This is much like how a voice echo works.

If the coherence evolves in the same way during the advancing and refocusing periods, then the path going out and coming back are the same, and we obtain a perfect echo. If different, the echo strength will be attenuated.

Here the pulsed gradients come into play. In Figure 9, the ^1H channel is applied a pulse sequence with three periods: advancing, diffusion, and refocusing. If the object molecule is

large and its diffusion slow, then the evolution of its signal during advancing and the reversed evolution during refocusing will be the same, and a perfect echo will result.

On the other hand, if the object molecule diffuses fast, the situation will be different. Due to the existence of the long diffusion period (usually 20-500 ms, which is much longer than both the advancing and refocusing periods, which are both 1-3 ms), the molecule will be in different places during advancing and refocusing. If no gradient is applied during these periods, the evolution of the signal during advancing and the reversed evolution during refocusing will still be the same, since the magnetic field is homogeneous. This would result in a perfect echo. However, if gradients are applied during both periods, the evolution during them will be different because the magnetic field strengths experienced by the signal will be different. This would result in an attenuated echo. The decay of the echo strength as a function of the gradient strength can be fitted by mathematical models and diffusion coefficients of the object molecules or aggregates can be calculated.

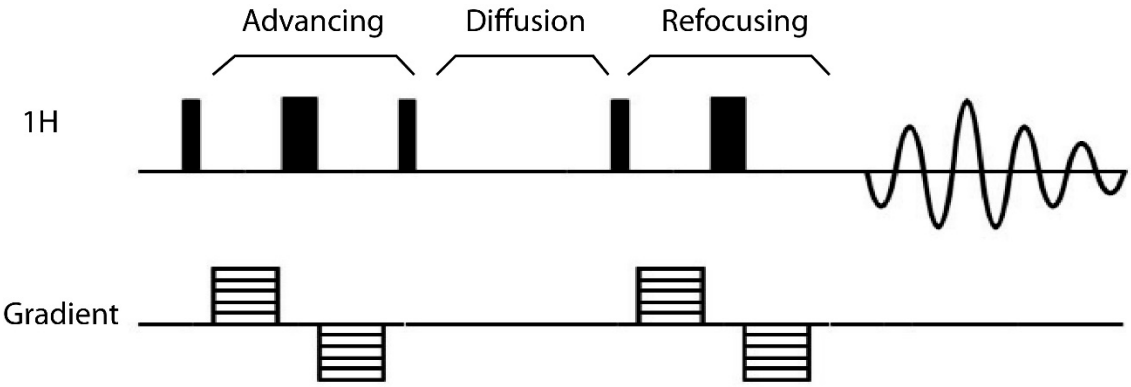

Figure 9. A version of the Pulsed-Field-Gradient NMR pulse sequence.

Diffusion NMR techniques are also often called pulsed-field-gradient (PFG) NMR techniques. Many variations of the techniques have been developed. The one shown in Figure 8 being one of the versions that use stimulated echo and a pair of bipolar gradient pulses.

Figure 9 shows echo intensities of a monodisperse polystyrene (PS) as a function of squared gradient strength. The dots are experimental data points and the line is a Gaussian decay fit. The quality of the fit indicates that the PS molecules follow an ideal Gaussian diffusion behavior.

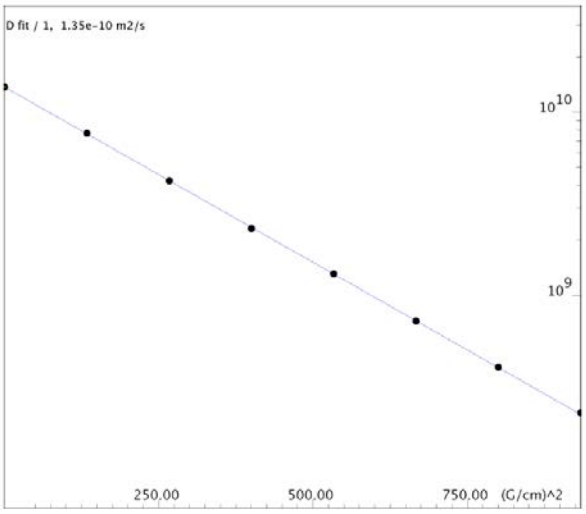

Figure 10. Echo intensity of a PS sample as a function of squared gradient strength.

Note that T1/T2 and diffusion reflect quite different aspects of a molecule's physical behavior. First, T1 and T2 are driven by motion of chemical bonds, which is usually less than 1 nm in length scale, while diffusion is the motion of the entire molecule, whose length scale can be quite large for random-coil polymers. Second, the motion that drives T1 and T2 relaxations is the rotation of chemical bonds with respect to the magnetic field, while diffusion is a translational motion. A high-molecular-weight PS molecule would exhibit the T1 and T2 characteristics of a small molecule, as each bond of the molecule would rotate quite freely. On the other hand, this molecule would diffuse much slower than a small molecule.

Practically, T2 relaxation occurs during advancing and refocusing periods, and T1 relaxation occurs during diffusion period, both of which could affect experimental results. To minimize these effects, the lengths of all three periods are fixed in most diffusion NMR experiments. A number of 1D data (each is called a slice) are collected, in which the only variable is the gradient strength, which is incremented. This ensures that the effects due to T1 and T2 relaxations are held constant for all the data points.

Once diffusion coefficients are determined, particle size can be conveniently calculated from the Stokes-Einstein Equation.

6. Several Important ssNMR Techniques

Magic-Angle Spinning (MAS)

To remove the orientation dependence of chemical shifts (CSA), we often use a technique called magic-angle spinning (MAS). During NMR experiments, the sample is spinning at a high speed (often > 3 kHz) along an axis that forms a ca. 57° angle (the angle θ satisfies $3\cos^2\theta - 1 = 0$) with the external magnetic field. This angle is called the Magic Angle. When the sample spins at this angle, the CSA will average to zero and the spectrum would show sharp peaks rather than powder patterns.

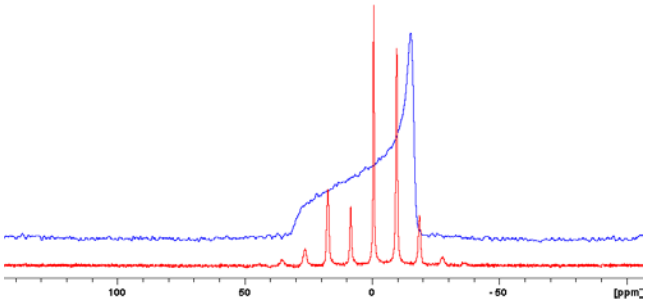

Figure 11. 31P Spectra of a phospholipid

In Figure 11, the top spectrum is a ^{31}P spectrum of a phospholipid (DOPC). It was acquired with ^{1}H decoupling during detection, which removes ^{31}P-^{1}H dipolar coupling. The only major magnetic interaction that is left on the spectrum is ^{31}P CSA, which generates a "powder pattern".

The bottom spectrum is the same sample run with the same pulse sequence (90° excitation, decoupling etc), but with the sample spinning at Magic Angle. At the magic angle, one important magnetic interaction tensor, the CSA, is averaged to 0. But there is still a residual effect – the spinning sidebands.

The spinning generates a regularly spaced multi-peak pattern. The distance between adjacent peaks, expressed in Hz, is the spinning speed. So the sidebands are easily recognized. If you spin the sample at a different speed, the center band (in the case above, the tallest peak at ca. 0 ppm) will not move, while the sidebands will, so they can be easily distinguished. Note that the distribution of sideband intensities somewhat resembles the powder pattern – in the case above, the side bands on the right are taller than those on the left, just like the powder pattern. Sideband intensities outside the limits of the powder pattern (in the case above, in the regions > 30 ppm and < -20 ppm) are very small. So you can imagine that as you spin your sample faster and faster, more and more of the sidebands will move out of the limits of the powder pattern and thus will become smaller and smaller.

This is a case of "frequency fight" that can be seen everywhere in NMR: we are using MAS to fight with CSA, and both of them are frequencies. When the former frequency is much larger, we have a single peak with minimal sideband intensities. When the latter frequency is much larger, we will have so many sidebands and their envelope will look like the powder pattern. The effect of molecular motion on ^{1}H ssNMR spectra that we discussed previously is another case of "frequency fight".

High-Power Decoupling

Unlike in solution-state NMR in which ^{1}H spectra are the most popular technique, solid-state ^{1}H spectra usually do not have much chemical resolution. Therefore, ^{13}C and other nuclei (e.g. ^{29}Si, ^{31}P, etc.) are especially useful. Let's use ^{13}C as an example (other nuclei follow the same principles). On ^{13}C spectra, with the removal of CSA by MAS, the dominant interaction would be the strong ^{1}H-^{13}C dipolar coupling. There is a relatively simple way to remove it, by applying a high-power continuous pulse on ^{1}H frequency during detection on ^{13}C. As the frequencies of ^{1}H and ^{13}C are very different, applying a decoupling pulse at ^{1}H frequency does not interfere with collection of ^{13}C frequency signal.

Decoupling is also widely used in solution NMR, and both its purpose (to remove spectral messiness due to ^{1}H-^{13}C couplings) and its working principle (by applying a continuous pulse at ^{1}H frequency while detecting ^{13}C) are the same as the decoupling in ssNMR. The differences are: the former aims to remove J-coupling, while the latter dipolar coupling, and the former uses low power pulses while the former high power pulses.

Cross Polarization

As ^{13}C has a natural abundance of only 1.1%, ^{13}C signal strength is often challenging. Cross polarization (CP) was invented for signal intensity improvement during ^{13}C detection. The CP/MAS (usually done with high power decoupling during detection) technique is the best-known ssNMR technique. The observed nucleus is often ^{13}C but people also frequently detect ^{29}Si, ^{31}P, etc. During the detection, decoupling is applied at ^{1}H frequency, which removes ^{1}H-X dipolar coupling (in NMR convention, X stands for any nuclei except ^{1}H).

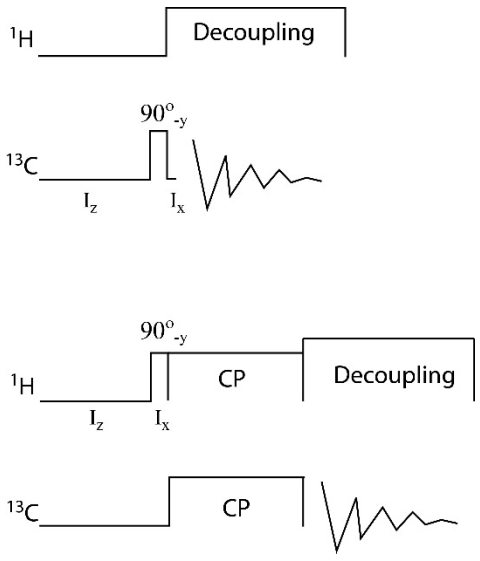

Figure 12. DP (top) and CP (bottom) pulse programs.

In the figure above, two pulse sequences are shown. The top diagram shows a Direct Polarization (DP) technique, in which ^{13}C magnetization is directly excited by a 90° pulse on ^{13}C frequency. The bottom diagram is CP, in which a 90° pulse on ^{1}H frequency is first applied, which excites ^{1}H magnetization. Then the experiment goes into a period during which two long pulse (often 0.5 – 5 ms) are applied at the same time, one on ^{1}H and the other on ^{13}C. During this period, ^{1}H and ^{13}C exchange magnetization, and ^{13}C are "cross polarized" by ^{1}H.

In CP, although it seems like a "detour" to first excite ^{1}H, then transfer to ^{13}C (or other nuclei), such a detour has many advantages. First, the magnetization strength, or in other words, the signal strength, of a nucleus is proportional to its gyromagnetic ratio, γ. Since γ of ^{1}H is ca. 4 times that of ^{13}C, by doing CP, you gain 4x signal strength. Second, DP relies on the T_1 relaxation of ^{13}C to get full intensity, while CP relies on the T_1 of ^{1}H. This would make a big difference in many situations. Spin diffusion plays a big role in ^{1}H relaxation: the protons that relax quickly would transfer their recovered magnetization to the protons that relax slowly. If the sizes of the slow-relaxing and the fast-relaxing domains are small enough (e.g. < 20 nm), all the protons will have the same apparent T_1. This is the case for many semicrystalline polymers and block copolymers.

On the other hand, there is essentially no ^{13}C spin diffusion, so each ^{13}C on a molecule will relax at its own intrinsic pace. For example, the ^{13}C T_1 for crystalline and amorphous polyethylene (PE) segments are > 500 s and ca. 0.4 s, respectively. On the other hand, both crystalline and amorphous PE have the same ^{1}H T_1.

If you monitor the ^{13}C signal intensity as a function of CP time (also often called contact time), you will find that the signal first increases, then decreases with increasing CP time. The transfer

of signal from ^{1}H to ^{13}C needs time, which results in the rise of ^{13}C signal at the beginning of CP. The time constant of the rise is dependent on the strength of dipolar coupling between ^{1}H and ^{13}C. If a structure has weak dipolar coupling, which could be either due to longer distance between ^{1}H and ^{13}C (such is the case for unprotonated carbon sites) or high mobility, then CP would be less effective and the time constant of the rise would be long. In fact, CP does not work for true liquids at all.

The eventual decrease of ^{13}C signal at increasing CP time is due to a relaxation process called $T_{1\rho}$ relaxation. $T_{1\rho}$ relaxation occurs on the horizontal plane, under the influence of B_1 generated by the ^{1}H irradiation pulse during CP, which has a field strength of typically 50 – 100 kHz. Therefore, $T_{1\rho}$ is sensitive to segmental motions at a rate window near 10^5 s^{-1}. Measuring $T_{1\rho}$ would give us knowledge about certain motional processes that are too slow for T_1.

Due to these complex processes during CP, CP is not a quantitative technique. On the other hand, DP, if all the carbons are fully relaxed, is a quantitative technique.

Spin Diffusion

In a heterogeneous material, different domains often have different magnetic relaxation characteristics. This could be used to generate a magnetization gradient, which would allow spin diffusion to occur across the different domains. By monitoring this process, we could probe the spatial organization of the material. For example, the crystalline and amorphous domains in PE have different T_2, as shown in Figure 6. So a pulse sequence could be created to generate a magnetization gradient based on the T_2 difference.

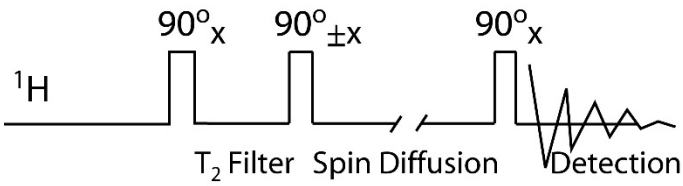

Figure 13. Goldman-Shen spin diffusion pulse program.

In Figure 13, a free-evolution period is given after the first 90° pulse, during with T_2 relaxation would occur. As the T_2 of crystalline PE is much shorter than that of amorphous PE, we could choose a suitable time at which the former signal will cease while the latter signal is still plenty. At this point, we could give it another 90° pulse, to flip the surviving amorphous signal back to the z direction. During the time period that follows, this amorphous magnetization would diffuse into the crystalline domain. Finally, we use a third 90° pulse to detect how much signal goes in the crystalline domain and how much is left in the amorphous domain. This technique is

called the Goldman-Shen experiment. An example of this experiment is discussed in the next section.

This experiment could be done either with ^{1}H detection, as shown in Figure 10, or we could add a CP block after the third 90° pulse and detect ^{13}C instead. Generally, you can design NMR pulse sequences simply by assembling various modules together.

Examples

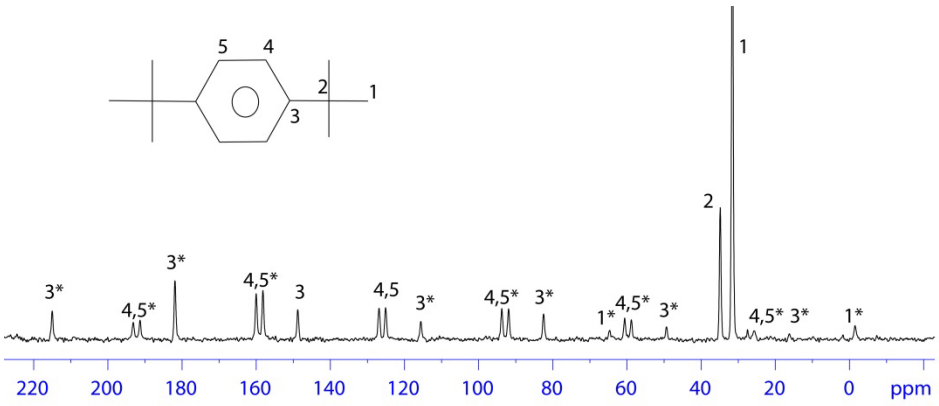

Figure 14. CP/MAS spectrum of PDTBB. The molecular structure of PDTBB is shown in the inset.

Above is a ^{13}C CP/MAS spectrum of 1,4-di-tert-butylbenzene (PDTBB) at spinning speed of 5 kHz. The spectrum was collected on a 600MHz spectrometer. There are a lot of peaks, but many of them are spinning sidebands, which are labeled with asterisks. It is striking how much stronger sidebands aromatic carbons generate than do aliphatic ones. This is because aliphatic carbons are sp^3 hybridized and have a relatively symmetric electron environment and thus small CSA, while aromatic carbons have a planar electron environment and thus much bigger CSA. At the same spinning speed, larger CSA generate larger sidebands. Note that some of the sidebands can be taller than centerbands.

Though the MAS NMR peaks are still much broader (often > 0.2 ppm) than what you would get in solution NMR (usually < 0.01 ppm), it is much better than many powder patterns overlapping with each other. The powder pattern of each chemical structure is often tens of ppm wide.

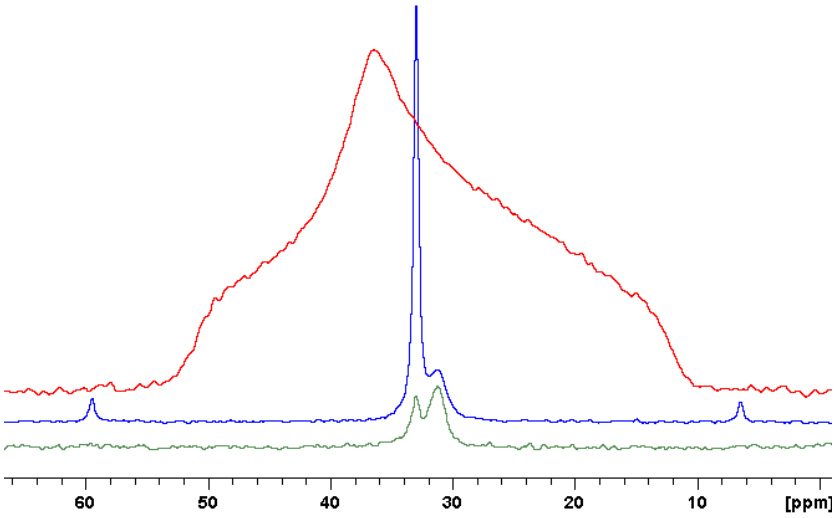

Figure 15. Several ssNMR spectra of a HDPE

The figure above shows several spectra of high-density polyethylene (HDPE; $(CH_2)_n$): (top) non-spinning CP spectrum; (middle) CP/MAS; and (bottom) DP/MAS (RD = 10 s). We can see that MAS results in dramatic improvement of spectral resolution, allowing us to see two peaks. Two very small spinning sidebands can be seen in the middle spectrum.

Though PE is nothing but infinitely repeating CH_2 (disregard end groups, which is usually one in many thousands), both CP/MAS and DP/MAS spectra have two peaks. The sharp peak on the left is crystalline (cr) peak, and the broader one on the right is amorphous (nc, stands for noncrystalline) peak. Their peaks appear in different positions because the segments in both phases have different conformations. The cr segments are all *trans*, while the nc segments are in a fast ($> 10^9$ s^{-1}) dynamic exchange between *trans* and *gauche*.

Question
The crystallinity of this sample is ca. 60%, but in the middle spectrum, the nc peak clearly occupies less than 40% of the total area. Why?

The top spectra were acquired with CP, greatly emphasizing crystalline signal, thus the powder pattern reflects the CSA of the crystalline PE segments. We can easily read off the three principal values of the CSA, at 12 (right shoulder), 36 (tip), and 51 ppm (left shoulder).

The nc PE segments have high mobility, so it has short ^{13}C T_1 (ca. 0.4 s). Crystalline PE has very long T_1: for HDPE, it is usually > 500 s. What would happen to the intensity of a peak on a DP spectrum when the recycle delay (RD) is much shorter than its T_1?

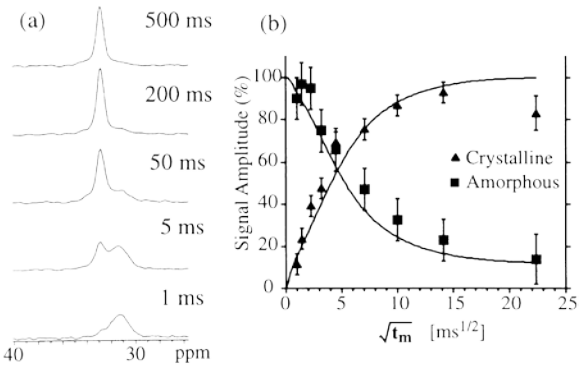

Figure 16. Spin diffusion in UHMWPE fibers (Hu and Schmidt-Rohr, Polymer, 41, 2979).

Figure 16 shows the spin diffusion result of an ultra-high molecular weight polyethylene (UHMWPE) fiber, which is a high-crystallinity PE. The experiments were detected on ^{13}C, by adding a CP "module" after the third 90° pulse of the original Goldman-Shen sequence (Figure 10). The T_2 filter time was 29.3 μs for all the experiments. At very short spin diffusion time (1 ms), only nc signal is observed, then cr signal grows at increasing diffusion time. The increase of cr signal and the decrease of nc signal during the beginning stage of spin diffusion is linear with square root of diffusion time – this proves that it is indeed a diffusion process. At later stage, the magnetization levels off and an equilibrium is eventually reached.

Instructions on ssNMR Experiments

Safety

- Magnet safety
- Rotors are spinning at very fast speed – no liquid in rotors; mass distribution must balance; rotor explosion hazard
- Avoid excessive pulsing power (too long or too strong) in your experiments. It could damage the amplifier and/or the probe. Do not change experimental parameters that you do not understand
- Two dangers during wobb (tune and match): you could lose the dip; you could get the knobs stuck and result in a factory repair, which would cost > $1000 and delay work for > 1 month.

Sample preparation

- 4mm rotors can be bought at the Bruker online store.
- Caps are made of soft plastics and can be easily damaged. Never use finger nails, pliers, or other steel tools to open caps. Rotor with damaged cap will not spin. Best tool to open the cap is liquid nitrogen.
- Prepare sample where there is a mat on the floor so that the rotors do not develop microcracks when they fall to the floor. Microcracks might cause rotor explosion when spinning at high speed, and damage both the rotor and the probe. The repair would be expensive (>$2k) and with extensive instrument down time (> 1 month).
- Weigh empty rotor and filled rotor, and determine sample weight. For quantitative experiments using external standard, the sample and the standard should be packed to a same volume (usually, beginning 4mm from rotor bottom and stopping 4mm from the rotor top). Fill the rest of the volume with Teflon tape.

Sample insert and spinning

- You must eject the sample first.
- When you run up the spinning speed, if you hear the rubbing noise stop the spin immediately
- When the target speed is reached, if you see the spinning speed fluctuate wildly (> ± 50 Hz), stop the spin immediately.

Experiment

- Beginning users: create a new file out of a most recent data file that contains all the needed parameters. You need to understand T1 relaxation, CP, and DP.

- Intermediate users: you need to know how to calibrate magic angle, shimming, chemical shifts, 90° pulse length for 1H and X, Hartmann-Hahn match, etc.
- Carefully check experimental parameters before proceeding. High power pulses (usually p6 + p15 + aq) should not be longer than 50ms.
- During wobb, if you do not see a dip, do not proceed to make many turns on the tune or match knob. Excessively turning the knobs could result in expensive repair and long instrument down time.

Wrap up

- When done, stop spinning. Do not keep the sample spinning when you are not running experiments – the fast spinning wears down the probe.
- Press Eject. Cap your left hand around the catch pan while turn the little door open with your right hand. This will prevent the sample from falling to the floor.
- Close Topspin.
- Promptly log off your account.

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