

INSTRUCTOR'S MANUAL – NMR SPECTROSCOPY

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General Instructions about this Module:

The problem sets on NMR spectroscopy are meant to be used as in-class, collaborative learning exercises. Groups of 3-4 students work together in discussing and working through the problems. When using the problem sets in this manner, the instructor must actively facilitate and guide students through the material. This manual will guide instructors through each of the problem sets, identifying possible student responses to the questions and the response and activities of the instructor during the progression of the problem.

There is no perfect way to assemble groups for such collaborative learning activities. I gather information on the first day of class (year in college, major, prior chemistry courses) and then use this to set groups of 3-4 students that start on the second day of class. I try to make the groups as heterogeneous as possible and they work together for the entire semester. Another strategy is to assign groups for a shorter period of time that might encompass completion of a specific topic or unit, and to then create new groups for the next unit. One other possibility is to have different groups every day of class. Since it is important for groups to work well together, having new groups every day may be less successful than allowing groups to work together for more extended periods of time. I would recommend that the instructor assign groups rather than allowing the students to pick their own. This avoids the potential problem of friends who want to be in the same group but who then do not work well together or stay focused on the assigned task. It also avoids the problem of the student who is left without a group at the end of the selection process, something that can be especially problematic if it is a member of a minority group. When using collaborative groups, it is also important for the instructor to monitor the functioning of the groups and to step in to address either dysfunctional groups or the recalcitrant individual within a group. Peer-evaluation processes are often used by instructors who employ group activities as a way of assessing how well groups are working.

I also expect the groups to meet outside of class for any homework assignments, something that is aided because I am at a residential college. An alternative to this is to schedule a room on the evening before a homework assignment is due and encourage them to come to this place and work in any arrangement they wish on the homework. I have run such sessions for several years now and attend them as a facilitator (one result is that it has cut down considerably the individual traffic to my office seeking help on the homework problems) and it has been an excellent way to promote collaboration among the students.

The instructor has an especially important role to fulfill during such group activities. I have observed that the more engaged that I am in the process in helping to guide the students through the material, the more effective the learning that occurs. In most instances, it seems that the students are initially stumped by the question, that they begin to explore things that they do know that might apply to answering the question, and that help from the instructor either by letting them know that they are on the right track or by suggesting another direction in which to take their thinking is necessary. As they begin a question, I roam around the room listening in on conversations and looking over their shoulders at what might be written in their notebook. If I hear something interesting, I indicate that to the group. If I see that someone has written something interesting and relevant in their notebook, I tell other group members that they ought to talk with this individual about what they have written, and that the individual should explain to the other group members why they wrote that down. If I hear a group going entirely in the wrong direction, I probe them on why they are heading in that way and then offer

suggestions about things to consider that will set them off in the right direction. When all groups have realized an important point, I call time out and summarize the concept at the board. Then I send them back to continue with the next part of the problem. Most of the problems are handled in such an iterative manner where the students work through some important part of the problem, I summarize it at the board when they have developed the concept, and then they return to the next part of the problem. Occasionally a group will just not see something, whereas every other group has gotten the point, and it may require a direct intervention from the instructor with that group to explain the concept. Similarly, there are times when I call their attention to the board to summarize a point when one of the groups still has not gotten the concept but waiting would slow down the remainder of the class to an unacceptable level.

When using these materials, I want the students to discuss and discover the concepts inherent in the problems, so they do not have the text when working on the problems. After they have completed a particular problem, I then make available to them a copy of that portion of the text. The text thoroughly goes through the thought process for solving each problem and I encourage the students to read it over that evening to reinforce the concepts developed in class that day. I also give homework problems designed to reinforce the concepts developed in class.

Specific Instructions about the In-class NMR Problems:

I have developed in-class question sets for a number of modules on the ASDL site. With these other modules, it is typically the case that the sets of questions can be given to the students with minimal pre-lecturing from the instructor before they begin working on them. Also, in these other modules, later questions in the set may not give away the answer to earlier questions. Because of this, I give out hard copies of the entire question set to the students and they begin with the first question and we eventually work our way through the entire set.

Many of the questions in the NMR module are quite different. They often require a brief presentation by the instructor that sets the stage for the ensuing question. Also, in a number of cases the later questions in a particular set give away the answer to an earlier question.

I would recommend that an instructor using the in-class question sets with this NMR module put the questions into a Powerpoint presentation. Then when the topic is developed to the point that a question is now relevant for the students to consider, it can be projected for the groups to work on.

Specific answers to the questions below are given in the text that accompanies this module. Usually, students going through this module in an analytical chemistry course have some knowledge of NMR spectroscopy through an organic chemistry course.

In-class Questions – Set 1 – Basic Concepts

I usually start by pointing out what each of the terms in “nuclear magnetic resonance spectroscopy” implies about this instrumental analysis method. Then they are asked the following question.

What makes up the nucleus of a hydrogen atom?

Groups always are able to remember that there is a single proton in the nucleus. I then remind them of what they have already learned about electron configurations and point out that there are nuclear configurations for the protons and neutrons, and that these particles also have quantum numbers analogous to the electron quantum numbers. They are then asked the following two questions.

What are the allowable spin quantum numbers for an electron?

What do you think are the allowable spin quantum numbers for a proton?

They usually have no problem answering these two questions. After describing what is meant by I , the total spin quantum number, they are asked the following.

What is the magnitude of I , the total nuclear spin, for a hydrogen nucleus?

Groups typically have no problem answering this.

What do you think is produced by the spinning, charged proton that is the hydrogen nucleus?

Students' ability to answer this may depend on whether they have recently taken a physics course where magnetism has been discussed. Others can often guess at an answer given that we're talking about nuclear *magnetic* resonance spectroscopy.

I then identify for them that we will use of B_p to express the magnetic field of the hydrogen nucleus. I also point out that magnetic fields have a direction and that we use the right-hand rule to determine the orientation of the magnetic field produced by a spinning proton. I then indicate that a sample is placed into an applied magnetic field when recording an NMR spectrum. They are then asked the following question.

What happens when two magnetic fields (B_p and B_{APPL}) are in contact with each other?

Students realize that these will interact with each other. I give them the formula to determine how many orientations the proton's magnetic field will have relative to the applied magnetic field and we determine that there are two possible orientations.

What do you think are the two allowable orientations of B_p relative to B_{APPL} ?

Students intuitively propose the “with” and “against” orientations. I then draw a picture similar to that shown in Figure 2 in the text.

Do you think the two allowable orientations have the same or different energy?

Students intuitively think they have different energy, in part because they realize it must be necessary if we are to actually be able to perform NMR spectroscopy.

Which of the two do you think is lower in energy?

Again, students intuitively propose that the “with” state is lower in energy. After this, I draw a picture similar to that shown in Figure 3 in the text. We also look at the nature of the “spin flip” that will occur for an individual proton as it is excited. Finally, we consider how there is a specific frequency that will lead to the excitation.

In-class Questions – Set 2 – Energy Transition and Population

What frequency of electromagnetic radiation is needed to excite a nuclear spin flip?

Students will not know the answer to this unless (1) they remember it from coverage of NMR spectroscopy in a prior organic course or (2) they know something about the NMR spectrometer in the department and can reason out that the MHz designation is a frequency that occurs in the RF part of the spectrum (prompting them with the department's spectrometer is a way to get them to consider this).

Where is radiofrequency (RF) radiation on the energy scale of the electromagnetic spectrum?

Groups usually know that RF radiation is at the low energy end of the spectrum, especially if this unit is being done in a course where other spectroscopic methods have been developed.

I then set up the next question by asking the students to think about a valence electron π - π^* transition that occurs in the UV part of the spectrum compared to a nuclear spin-flip in the RF region. That allows us to draw an energy level diagram like that shown in Figure 4 in the text, although without showing the populations of the levels. I further point out the idea that there is thermal energy and ask them the following question.

Is the thermal energy at room temperature large or small compared to the energy of a π - π^* transition and to the energy of a nuclear spin flip? What are the consequences of your answers to these questions?

Students can rationalize that thermal energy is insufficient to excite valence electrons but have a hunch that it is sufficient to excite nuclear spin flips given that they are being asked this question. When it comes to the consequences, they may be tempted to think that all the nuclei are excited. That leads to a discussion about how we can use the Boltzmann distribution to calculate the populations of the two levels. I then provide the example populations shown in Figure 4 in the text and ask them the following question.

If thermal energy has sufficient energy to excite nuclear spin flips, why are there still more in the ground than excited state?

They can reason out that because the ground state is lower in energy, chemical systems will have a preference for that state. But I make a point of emphasizing how the two populations are almost equal and that will have important consequences for us later with the sensitivity of NMR spectroscopy and with coupling.

Can you think of two processes by which a specific excited state nucleus can get rid of its excess energy?

Students' ability to answer this may depend on when this unit is done in a course. If it is later in a course on spectroscopy, they are more likely to come up with the loss of energy to the surroundings as heat and spin-lattice relaxation. If they have had a prior unit on fluorescence or atomic emission they are likely to come up with the idea of spin-spin relaxation. There is also a good chance that some groups may need to be prompted on both of these processes by asking how other systems lose excess energy or by pointing out how excited state nuclei have exactly the same amount of extra energy as is needed to excite ground state nuclei.

Do excited state nuclei have short or long relaxation times?

Students can usually rationalize that the relaxation times are long because of the small energy gap and the small difference in population. That allows us to examine the change in population that occurs

when a high power RF is applied as shown in Figure 5 in the text. They are then given the following question.

When the populations of the two levels are equal, can we continue to excite ground state nuclei up to the excited state such that the population of the excited state becomes larger than the population of the ground state, creating what is known as a population inversion?

Students' ability to answer this will depend on whether they are in a course where lasers were previously discussed. If not, they likely will have no idea that it is impossible to have a population inversion in a 2-level system. If so, they may need to be reminded about what they learned previously when discussing how a laser worked.

I then either remind them or discuss the idea of absorption versus stimulated emission and use a diagram like that in Figure 6 in the text to show what will happen. This allows us to understand what is meant by a saturated transition.

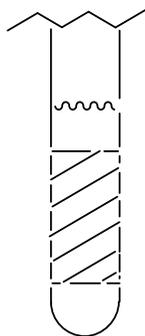
I then explain that the observation that the populations of the two levels are almost equal is the reason NMR spectroscopy has low sensitivity. After that, I point out how the difference in energy between the ground and excited states depends on the magnitude of the applied magnetic field and show them Figure 7 in the text. Then they are given the following question.

What happens to the population distribution as the energy gap between the ground and excited state is increased?

Based on our prior discussion of the population differences between the two levels in a π - π^* transition and nuclear spin transition they expect that the population difference will be larger the greater the energy gap. I then go over other things that can be done to improve the sensitivity of NMR spectroscopy: (1) use of microtubes, (2) use of a cryoprobe and (3) recording multiple spectra and adding them together.

I then present some additional equations for the energy gap between the ground and excited state that bring in the magnetogyric ratio and magnetic moment of the hydrogen nucleus (Equations 2-5 in the text), which raises the important distinction that the energy gap ultimately depends on the magnetic field experienced by the nucleus, which is different than the applied magnetic field. I describe how the magnetic field experienced by a nucleus is the sum of all the magnetic fields that exert a force on a particular nucleus.

Consider a sample in an NMR tube. The crosshatched region in the tube is the area over which signal is recorded. Why is it important that B_{APPL} be homogeneous over this entire region?



It may be necessary to prompt groups to look back at the equations and track how the applied magnetic field influences the experienced magnetic field, which influences the energy gap and then the frequency of excitation. When they realize that different molecules may have different frequencies of excitation, then you can ask them what this would do to the resulting resonance in the NMR spectrum.

I then go over why samples are spun when recording a spectrum. I also talk about the use of the deuterium signal in deuterated solvents as a means of tuning the spectrometer and locking on to a signal to account for any drift that may occur as spectra are recorded.

In-class Questions – Set 3 – Electron Shielding

Students are then asked the following question.

What “things” in a molecule generate magnetic fields that will influence B_0 for a particular hydrogen nucleus?

Most students have had some introduction to NMR from a prior course and have some recollection of shielding and coupling so know that electrons and other nuclei have an effect. Also, there's a realization from prior parts of this module that hydrogen nuclei produce a magnetic field that should influence neighbors.

I then describe how electron shielding occurs in a molecule using a drawing similar to Figure 9 and give them the following question.

Does electron density affect the magnitude of B_e ? If so, what is the relationship?

Many students already know this from their prior experience with NMR from organic chemistry, but even if they have not taken this course, it makes intuitive sense that more electron density will lead to larger shielding.

Does a more highly shielded nucleus absorb higher frequency (higher energy) or lower frequency (lower energy) radiation?

Groups can rationalize out the relationship between shielding and relationship to excitation frequency using equations previously developed in the unit. That allows me to draw Figure 10 in the text for them.

I then point out how NMR spectrometers are designated by the frequency at which hydrogen nuclei are excited and not the applied magnetic field strength. I also describe why it is essential to use a zero reference in NMR spectroscopy, that the ppm scale has been devised as a way to report the location of resonances in the spectrum, and give them the equation for determining the ppm of a resonance. Then I give them the following question.

Suppose the resonant frequency of the TMS singlet on a 400 MHz NMR spectrometer is exactly 400 MHz. What is the chemical shift in ppm for a signal that has a resonant frequency of 400,000,400 Hz?

Groups are able to plug the values into Equation 10 and determine that the answer is 1 ppm. I then draw a spectrum from 1 to 10 ppm and indicate which end of the spectrum corresponds to higher energy and higher frequency. I also indicate which end is deshielded and the distinction between the upfield and downfield part of the spectrum. I then ask them the following question.

What is different as B_{APPL} is varied?

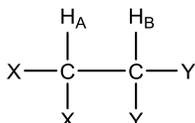
It is helpful to prompt the students to consider a peak at 1 ppm on a 100 or 600 MHz instrument. When they think about the values in the equation, they realize that the Hz/ppm varies with field strength.

At this point, I like to describe some examples of unusual shielding effects produced by aryl rings and double bonds as shown in Figure 12 in the text.

In-class Questions – Set 4– Nuclear Coupling

I begin this part of the unit by presenting the students with the following question.

Consider the two hydrogen atoms H_A and H_B in the compound shown below. The X and Y groups are not hydrogen atoms and produce no magnetic fields. In particular, let's focus on the effect that H_B has on H_A . We can think of H_A "looking over" at H_B and ask ourselves about the magnetic field produced by H_B .



What do you know from earlier in this unit about the magnetic field produced by H_B ?

The students remember that the two possibilities are "with" and "against". I also ask them about the distribution of the two states and they remember that it is essentially 50:50.

Is the flip of H_B 's spin between the "with" and "against" states rapid or slow?

Most groups are able to reason this out by thinking about the relaxation time, but it may be necessary to prompt some groups to consider this. Once we've answered the question, I describe the difference between a case where the flipping is fast (time average of the magnetic field is zero), and the flipping is slow (either "with" or "against" the applied field).

This allows us to draw something similar to Figure 13 on the text. I also like to point out more specifically how the magnetic field of H_B is actually transmitted to H_A through the intervening electrons as shown in Figure 14 in the text and is not a through-space effect.

What does the resonance for H_A look like in the NMR spectrum?

Many students may already know that it should look like a doublet based on prior experience with NMR through an organic course, but now they often understand at a deeper level why the two peaks are observed and why they have the same area.

Which peak in the doublet corresponds to H_B "with" and which corresponds to H_B "against"?

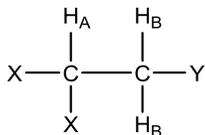
Students may need to go back to look up and remind themselves which end of the spectrum corresponds to the high and low energy gap and frequency, but groups are able to answer this question. I then describe the concept of a coupling constant.

Can you think of a way to decouple a hydrogen atom like H_B ?

This is often a difficult question for students. A good prompt is to remind them that if H_B were to rapidly undergo transitions between the ground (with) and excited (against) states, the magnetic field experienced by H_A would average out to zero. I then ask them if they can remember a previous discussion in the unit where this happened. Usually this is enough for some students to remember back to the idea of a saturated transition. This allows us to discuss how applying a high power RF at the frequency needed to excite H_B would lead to a decoupling.

What would the H_B resonance look like?

Groups have no problem realizing that this will be a doublet.

What would the resonance for H_A look like in the compound shown below where there are two H_B protons? Provide a rationale for your answer.

Before allowing students to answer this question, it is useful to remind them that there is rapid rotation about the C-C bond such that the two H_B protons are chemically equivalent. They may already know from prior knowledge that it should be a triplet, and with the realization about being chemically equivalent, they can usually rationalize why a triplet is observed.

I also like to point out how the coupling constant of a triplet is calculated. I show them how this peak can also be thought of as a doublet of doublets similar to that shown in Figure 17 in the text to convince them how one measures the coupling constant of a triplet.

Which peak of the triplet corresponds to the WW and which to the AA situation?

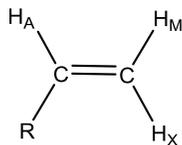
Given the previous discussion of which peak was which in a doublet, groups quickly figure this out.

I then introduce the use of Pascal's triangle (Figure 18 in the text) to show the number and intensity of peaks in the multiplets for coupled hydrogen atoms.

What factors do you think influence the magnitude of the coupling constant?

Groups are usually able to come up with distance as a factor. The idea that there is an angle term is something they don't usually think of, especially since in prior experiences with NMR, they have usually examined systems with rapidly rotating bonds. They can be presented with a rigid bicyclic system as a way of thinking of something else that might be important in determining coupling constants or it may be appropriate to just tell them that there is an angular dependence to the coupling constant.

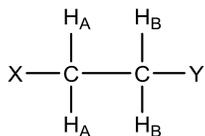
I then show them how the Newman projection can be used to define a dihedral angle, show them the two angular Karplus relationships for vicinal and geminal coupling, and ask them the following question.

Predict the coupling constants that would occur between H_A, H_M and H_X and the mono-substituted alkene shown below and draw the shape of each resonance.

Using the two Karplus relationships, students are able to draw the resulting resonances. This is an excellent exercise to have different groups do at the board by drawing up the different resonances.

I then present them with the following example as a way of demonstrating why it is beneficial to have a higher field spectrometer.

Consider the following compound in which $J_{AB} = 10$ Hz, $\delta_{HA} = 1.3$ ppm and $\delta_{HB} = 1.2$ ppm. Draw the resulting spectrum if the spectrum is recorded on a 100 MHz and 400 MHz spectrometer.



This is another problem that it may be good to have students work on at the board. I show them the two sets of X-axes with the chemical shift values identical for the two spectrometers, then encourage them to consider the Hertz in a ppm and draw the resonances. With this guidance, the groups are able to appreciate that the higher field instrument leads to better resolution of the two resonances.

I then describe how the situation is actually more complex than what is observed in their drawings and that coupled resonances with close chemical shifts exhibit a more complex behavior that complicates spectral interpretation. Figure 24 in the text is an example I show them to indicate how first-order rules of coupling break down when coupled resonances have close chemical shifts.

In-class Questions – Set 5 – Exchange Effects

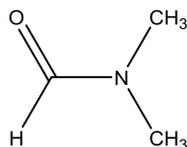
Considering the spectrum of a compound such as methanol (CH₃OH). Using the rules for coupling we have established, predict the number of resonances and identify their multiplet structure.

Groups are usually able to determine this, although they may ask a question about whether having oxygen as one of the atoms makes a difference. If they ask that, I indicate that they should only count the number of bonds between the hydrogen atoms.

However, in other situations the spectrum of methanol appears as two singlets, one of area three and the other of area one. Propose a reason why singlets are observed instead of coupled multiplets.

Some groups may need a prompt about the ability of methanol to form hydrogen bonds. It can be useful to ask them to draw pictures of two hydrogen bonded methanol molecules and include the lone pairs as a way of getting them to realize that the hydrogen atoms can exchange between different methanol molecules.

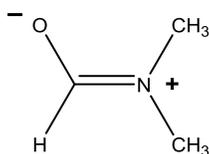
Another time-dependent aspect to consider about NMR spectra can be illustrated by considering the ¹H NMR spectrum of *N,N*-dimethylacetamide (DMA) shown below.



What does the NMR spectrum of DMA look like?

They are able to determine that rapid rotation causes the two methyl groups to be equivalent and there is a singlet of area 6 for the methyl groups and a singlet of area 1 for the aldehyde hydrogen.

DMA has the following contributing resonance form. What would the NMR spectrum of DMA look like in this resonance form?



Groups are able to determine that in this form the methyl groups are inequivalent and two singlets would be observed of area 3 for these two different methyl groups.

In-class Questions – Set 6 – Classical Description

The questions in this set must be prefaced by a short lecture that describes the actual motion of a proton in an applied magnetic field. The idea that the proton has both a spin and a precessional motion needs to be developed. The idea that there is an ensemble of protons so that the X and Y components of magnetization cancel out is important to get across. It will be necessary to draw a picture like that shown in Figure 26 in the text to illustrate this situation.

The aspect of the precessional velocity and precessional frequency needs to be developed. Also the result that the precessional frequency from the classical description equals the excitation frequency obtained through a quantum mechanical description is important to point out. Finally, it is useful to mention the idea of a rotating frame that allows the observer to only consider the net magnetization vectors. After indicating that a coil of wire is on the X-axis, students are asked the following question.

What happens when an electrical current is run through a wire coil?

Most groups have one or more students who know the answer to this because of a prior physics course they have taken. Others are often able to guess that this is the answer.

Then using an example of a sample with only one signal, I provide them information about how the field on the X-axis will exert a torque on the precessing nucleus if the applied frequency matches the precessional frequency – Figure 27 in the text. I also point out that the length of time over with the field on the X-axis is applied influences how far the magnetization vector of the nucleus tips off the Z-axis – Figure 28 a and b in the text. They are then given the following question.

What happens to the nucleus after B_1 is turned off?

Groups are often able to figure this out, but some may need to be prompted to remember that the only field now is B_{APPL} to realize that after B_1 is turned off, the nucleus will precess about B_{APPL} . They also usually propose that it does not immediately assume the starting point shown in Figure 28a but instead more slowly relaxes back and thereby undergoes the spiraling motion shown in Figure 28 c in the text.

At this point I also like to point out the distinction between spin-lattice relaxation and spin-spin relaxation and the effect that each has on the phase of the nuclei that have been tipped.

Suppose a wire coil is placed on the Y-axis. What happens in the wire coil as the magnetic field of the tipped nucleus is imparted on it?

Since we have looked at the reverse situation (a current of electricity through a wire produces a magnetic field), most groups are able to propose that a magnetic field imparted on a wire coil will produce a current of electricity. Some may need to be prompted to think of the prior situation we examined as a hint to figure out what will occur here.

Draw the current profile that would result in the wire coil on the X-axis as the tipped nucleus relaxes back to its ground state.

Most groups have a hunch that as the nucleus goes from a +Y to -Y direction, that the current may flow in the opposite direction through the coil such that an oscillating current is observed. Once assured that this is what occurs, they are able to draw something approximating a free induction decay.

I then give a brief lecture about time versus frequency domain spectra and the use of a Fourier transform as a way to convert between the two and show them Figure 29 in the text. I also spend a little time pointing out that an FID cannot actually be measuring the true precession of the nucleus as that is happening too quickly to digitize. Instead, I point out without going into all the details how there is an electronic way to measure the difference of each precessing nucleus from the central frequency of an applied pulse. So if the applied pulse is centered at 400 MHz, what actually is reflected in the FID are the differences in frequency between each precessing nucleus and the center frequency. These differences are in the Hertz range and are easily measured using digital electronics.

Draw the FID that would result if the nucleus had a much shorter relaxation time.

Groups are able to draw something similar to the FID shown in Figure 30 in the text.

Do you see a problem with performing a FT on an FID with a very short relaxation time? If so, what would happen in the resulting frequency domain spectrum?

Groups are usually able to realize that if the FID is too short, it will become a challenge to accurately determine the frequency components that make it up. When asked what that means for the resulting spectrum, they usually are able to suggest that it must lead to peak broadening.

I then give a brief lecture about how a broadband pulse of RF is applied that excites all the nuclei in a sample at once. We look at how this will produce a composite wave in the time domain, but that the Fourier transform is able to sort out all the contributing frequency components and their amplitude. We look at Figure 31 in the text as an example of the FID and resulting frequency domain spectrum of a sample consisting of two singlets.

Where is the amplitude of peaks determined in the FID?

It may be necessary to remind some groups to consider that different nuclei can have different relaxation times. As they think about this, they realize that the first point of the FID is the only point that has accurate data on the relative intensity for the different signals.

I then describe the typical pulse sequence used for obtaining NMR spectra that is shown in Figure 32 in the text.

Why is a delay time incorporated into the sequence?

Groups realize immediately that this must be done to help insure relaxation of the nuclei back to the ground state. I then point out that it is often more common to use 30° pulses instead of 90° pulses and ask them the following question.

Why are the advantages and disadvantages of using 30° pulses instead of 90° pulses?

It may be helpful to ask students to draw out the two net magnetization vectors as shown in Figure 33 and to then consider the component of magnetization that is actually measured on the X-axis in the instrument.

What is the advantage of recording several FIDs and adding them together?

Groups quickly realize that adding several FIDs together will improve the signal-to-noise ratio.

I then set up the situation of nuclei with long relaxation times and provide them the following situation to consider.

Suppose the following pulse sequence is used to obtain the spectrum of a ^{13}C nucleus with a spin-lattice relaxation time of 100 seconds (90° pulse, 1 second collection of the FID, 1 second delay).

Note, carbon atoms with no directly bonded hydrogen atoms can have relaxation times as long as 100 seconds. This pulse sequence is repeated four times.

- **Draw the position of the ^{13}C magnetization vector after each of the four pulses.**
- **Draw the corresponding FID that would be obtained after each pulse.**
- **Draw the composite FID obtained by adding the four individual FIDs together.**
- **What do you observe for this carbon in the resulting frequency domain spectrum?**

This is another exercise that may be good for groups to work on at the board, or to have one group present their results at the board. It may first be helpful to ask them to consider whether, for all practical purposes, any of the nuclei really relax in the two seconds between pulses. I usually find that the groups are able to draw the four vectors shown in the top of Figure 34 in the text – although they may at first be hesitant to draw the one going in the negative Z direction and want reassurance that it is correct. From there, they are able to draw the resulting FIDs and realize that the two with actual signal are out of phase with each other and therefore cancel each other out and that no peak will be observed in the resulting frequency domain spectrum.

Finally, I use this as an entry point to talk a bit about magnetic resonance imaging, which is based on the fact that the hydrogen atoms of water have different relaxation times in different tissues in the presence of a paramagnetic substance like oxygen gas or gadolinium(III).