

# USEQIP NMR Laboratory 1

In this laboratory you will be introduced to a two-qubit molecule, determine its Hamiltonian, calculate the relaxation constant  $T_1$  and perform a spin echo experiment.

## 1 System

You will be working with a two-qubit molecule of  $^{13}\text{C}$  labelled chloroform as seen in Figure 1. The proton is a spin-1/2 nucleus. Most (99%) of the carbon found in nature is  $^{12}\text{C}$ , which has no nuclear spin. But you will be using samples which have been synthesized with 99%  $^{13}\text{C}$ , which has a spin-1/2 nucleus. Both natural isotopes of chlorine have spin-3/2, which have quadrupolar coupling to electric field gradients and have a very fast  $T_1$  relaxation rate. This causes them to ‘self-decouple’ and so we can essentially ignore them. The sample is a diluted solution in a deuterated acetone. The concentration of the sample is low enough such that interactions between the molecules is negligible. The deuterium nuclei in the solvent provide another NMR signal which the spectrometer is continually monitoring via the ‘lock’. This allows the spectrometer to monitor and compensate for the drift of the superconducting magnetic field from environmental changes or the slow dissipation of the superconducting current.

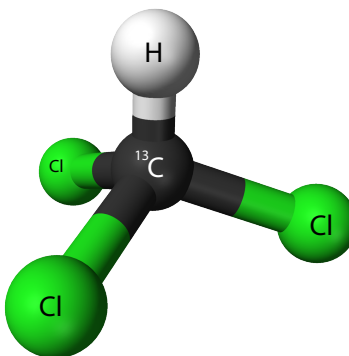


Figure 1: 3D molecular structure of  $^{13}\text{C}$  labeled chloroform. (Image modified from Wikipedia.)

## 2 Introductory Experiments

### 2.1 Sample Loading

You must begin by loading the sample into the spectrometer. The sample tubes are loaded into a plastic sample holder which will ensure the sample is in the middle of the r.f. coils and allows the sample to be spun to average out static field inhomogeneities. Where the tube sits in the holder is set by the depth meter. Double check with the TA that the tube is loaded correctly as otherwise you may damage the probe.

The sample is loaded from the top of the magnet and is supported by a column of air. To load the sample:

1. Press the sample 'LIFT ON/OFF' button on the BSMS panel to start the air flow.
2. Gently place the sample at the top of the bore and let it float on the air flow.
3. Press the 'LIFT ON/OFF' button again to stop the air flow and wait for the sample to drop into the magnet. You should hear a click when it settles in place.
4. Place the cap on top of the bore to keep dust out.

Once the sample is loaded start the lock by pushing the 'LOCK ON/OFF' button. The spectrometer will automatically find the lock signal and adjust some of the lock parameters which may take up to half a minute. The lock display window on the side of your screen shows the 'lock-level' which gives you some indication of the level of static field homogeneity. If you notice it decrease during the experiment you may need to reshim. Start automatic shimming to prevent this by pushing 'AUTOSHIM'.

Check that the probe is tuned to the correct frequency by typing 'wobb' in the Topspin command line. The dip in the resonance line should be centered on the red line that indicates the reference frequency.

### 2.2 Hamiltonian Determination

As you have learned in the lecture the doubly-rotating frame liquid-state Hamiltonian can be written down as:

$$\mathcal{H}_{nat} = \frac{\omega_H}{2} Z \otimes I + \frac{\omega_C}{2} I \otimes Z + \frac{\pi}{2} J_{HC} Z \otimes Z \quad (1)$$

$\omega_H$  and  $\omega_C$  are the proton and carbon chemical shifts with respect to the spectrometer proton and carbon transmitter frequencies. For example on the 400 the base frequency for proton is 400.13MHz. In this section you will try to measure  $J_{HC}$  and set  $\omega_H = \omega_C = 0$  to simplify the Hamiltonian.

1. You can move between experiments by typing 're 1' e.g. to move to experiment number 1. Move to experiment number 1 and type 'cpg 10' to copy it to number 10. You can change the title of the experiment with the 'setti' command. The changed title will not be updated until you change experiment numbers. The basic parameters of the spectrometer have been setup but you will need to adjust the pulse program for what sequence you want to run. The first pulse program is called zg\_USEQIP\_H. Set it by typing 'pulprog' and then entering 'zg\_USEQIP\_H'. To edit the pulse program, locate it in the folder

*/opt/topspin/exp/stan/nmr/lists/pp*

and open it using "Texteditor". The basic pulse program for a proton readout pulse is shown below (numbers and variable names may vary. DO NOT change the pulse length):

```
#include <Avance.incl>
```

```
define pulse H90
```

```
"H90 = 15u"
```

```
define pulse C90
```

```
"C90 = 20u"
```

```
1 ze
```

```
2 30m
```

```
d1
```

```
10u reset:f1 reset:f2
```

```
;Proton readout pulse
```

```
( H90 ph1 ):f1
```

```
go=2 ph31
```

```
30m mc #0 to 2 F0(zd)
```

```
exit
```

```
ph0 = (4) 0
```

```
ph1 = (4) 1
```

```
ph2 = (4) 2
```

```
ph3 = (4) 3
```

```
ph31=0
```

Some basic pulse program commands are explained here:

- '#include<Avance.incl>' loads a header file with definitions for spectrometer macros.
- We can define the length of pulses using the define pulse syntax. So we define our proton 90 degree rotation pulse length to be variable H90 and to equal  $15\mu\text{s}$  and similarly we define a variable for the carbon 90 degree pulse length to be  $20\mu\text{s}$ . In the pulse program language u stands for  $\mu$  and you can also use m for milli and n for nano.

- Lines can be numbered as in *1 ze*. *ze* stands for zero everything and clears the memory in the acquisition board. Labels can also be variables followed by a comma.
  - Delays can be specified as a time as in *2 30m*.
  - Delays can also be specified by through the delay variable d0-d31 which are set in the Topspin command line. By convention d1 is used for the recycle delay: the delay between experiments to let the spins rethermalize.
  - *10u reset:f1 reset:f2* The reset commands happen during the  $10\mu\text{s}$  delay and reset the clocks of the logical channels so that they are synchronized.
  - *;Proton readout pulse* Comments are marked by a semicolon.
  - *( H90 ph1 ):f1* Pulses are sent by specifying the pulse length, the pulse phase and the logical channel to the send the pulse on. In this experiment we will use channel :f1 for proton pulses; f2 for carbon pulses. :f1 is also by definition the channel for observation observation. The pulse phases are defined at the end of the pulse program (see below for how to set them).
  - *go=2 ph31* is a macro that starts acquisition and loops back to line 2. It sets the acquisition phase to ph31. The number of times it loops back is set by the number of scans variable ns.
  - *30m mc #0 to 2 F0(zd)* writes the data in the receiver memory to the computer hard disk.
  - *exit* finishes the pulse program.
  - There are 31 possible phase programs ph0-ph31. They are defined at the end of the file. The number in brackets the resolution the circle is broken up into. The maximum phase resolution is 16 bits. The second number defines the portion of the circle. By convention we will consider 0 to be the positive  $x$  axis (therefore  $\text{ph}(4) = 1$  would be the positive  $y$  axis).
2. Type 'edasp' in the command line and make sure the spectrometer is properly wired.
  3. Before you run any experiment you should always check whether the pulse sequence compiles and make sure the pulse sequence is what you expected by clicking the PulseProg tab and then the graphical display button.
  4. The power of each pulse has been set ahead of time. Please do not change them.
  5. Run the pulse sequence by typing 'zg', which stands for 'zero-go'.
  6. Type 'a' to watch the FID recorded in real-time.
  7. The FID is difficult to interpret so we transform to the frequency domain by taking the fourier transform by typing 'ft'. The FID is the quadrature detected magnetization in the  $x$ - $y$  plane. The  $x$ -axis must be defined by appropriately choosing the phase of the spectrum. By convention we choose to have signals along the  $x$ -axis to be absorption lorentzians. Since the pulse sequence performed a rotation about the  $y$ -axis, the signal will be along the  $+x$ -axis and should be a positive absorption peak. Click on the Interactive Phase Correction button and then click and hold the ph0 button while moving the mouse up and down to phase

the spectrum with zeroth order phase correction. Return and save the phase correction. Alternately, you can type *apk* into the command line and this will automatically phase the spectrum to a positive lorentzian.

This will calibrate the phase of the Fourier transform. In order to be consistent from one experiment to the next, we need to always apply the same phase correction. To apply the phase correction in future we can fourier transform with phase correction by using the ‘fp’ command.

8. The proton spectrum shows two peaks from the coupling to the carbon. To eliminate the chemical shift term in the rotating-frame Hamiltonian we want to center the two peaks in the spectrum. If they are not centered you may need to adjust the variables ‘o1’, ‘o2’ and ‘sr’. o1 and o2 are transmitter frequencies for the channels f1 and f2. sr is the spectrometer reference which sets the center of the displayed frequency axis. You want to set *sr* to *o1* for consistent results. Type ‘o1’ to find the value and ‘sr’ to change the reference.

You can also set the ‘o1’ and ‘o2’ frequency by clicking of the “Set RF from Cursor” button and then selecting the desired frequency on the spectrum.

9. To zoom in or to measure the distance between two points, you can “click and drag” on the spectrum. Use this to measure the J coupling term in the Hamiltonian and the approximate width of the peaks to estimate the  $T_2^*$ .
10. We will now look at the Carbon signal. Go to experiment number 3 and confirm that the electronics is properly wired (since we are now observing Carbon, f1 needs to be set to carbon. Therefore, we can pulse on Carbon using f1 and pulse on Hydrogen with f2. Make sure the transmitter is set to the correct frequency o1 and o2. Copy the carbon template experiment 3 to experiment 11. The pulse program for carbon is zg\_USEQIP\_C. Run the pulse sequence and observe the carbon spectrum. Adjust *o1*, *o2* and *sr* if necessary. Confirm the J coupling that you measured in the proton spectrum and estimate the carbon  $T_2^*$ .

### 3 $T_1$ Measurement

To ensure repeatable measurements it is important to let the spins return to their thermal equilibrium state between every experiment.  $T_1$  is the time constant on which this happens. In this section you will measure the proton  $T_1$ ’s using an inversion recovery experiment.

1. Copy the modified proton template to experiment 12. This will be your reference spectrum. Give the experiment an appropriate title.
2. Modify the pulse program zg\_USEQIP\_H to do two 90 degree pulses; a delay specified by d2 and then a 90 degree readout pulse. Save this new pulse program as zg\_USEQIP\_T1 and then change the pulse program being used in the experiment by typing *pulprog zg\_USEQIP\_T1* into the command line.

3. Set d2 to zero by typing *d2 0* into the command line. Run the pulse program. Integrate this reference spectrum:
  - (a) Click on the 'Integrals' tab and make sure there are no saved integrals (if there are, right-click and delete)
  - (b) Back to the spectrum, click on the 'Interactive Integral' button and select an integration region by click and drag on the spectrum. Then click 'Return and Save Regions'.
  - (c) Go back to the 'Integrals' tab, right-click on the integral value and "Define as reference".
4. In datasets 13-20 repeat the experiment and vary d2 at 100m, 500m, 1s, 2s, 5s, 10s, 20s, 60s. Integrate these and compare to the reference:
  - (a) Move to the dataset you want to integrate. Make sure no integrals are saved in the 'Integrals' tab. Enter integrate mode and again mark out the area you want to integrate.
  - (b) Go to the 'Integrals' tab, right-click on the integral and 'Calibrate by reference'. This will give you the relative integral with respect to the reference spectrum. Be sure to record this value.
5. Using matlab's cftool (or your favourite fitting software) fit the data to the following equation to estimate  $T_1$ .

$$S(t) = 1 - 2A \exp\left(\frac{-t}{T_1}\right) \quad (2)$$

Where does this equation come from? How does this describe the physical relaxation? A is not in the theoretical equation of the signal but is a fitting parameter to account for pulse imperfections.

6. How long do you need to wait between experiment (in other words what should the recycle delay d1 be set to) so that there is less than 1% fluctuation between experiments.

## 4 Spin Echo

One can use a spin echo to refocus spins and to measure  $T_2$ . Here you will design your own spin echo pulse sequence and see if you can find  $T_2$  of your chloroform sample.

1. Move to a new experiment.
2. Consider how to create a spin echo and modify the pulse sequence accordingly. You will have to decide the length of the pulse(s) and where to place delay times.
3. Measure the amplitude of the spin echo.
4. Repeat the experiment varying the length of the relevant time.
5. The amplitude of the spin echo should vary as  $\exp(-t/T_2)$ . Fit the data in MATLAB to find  $T_2$ .