# CHEM / BCMB 4190/6190/8189

# Introductory NMR

Lecture 6

Jan 28

Lab Concepts:

Shims:

- small magnetic fields used to cancel out errors in the static field.
- shim coils are wrapped around a cylindrical former which is inserted into the magnet.
- the NMR probe is then mounted inside the shim assembly so that the sensitive volume is at the center of the Z-gradient coil.
- z-coils are aligned along vertical axis of the magnet.
- spinning can average out many defects of the magnetic field in the x-y plane but does not affect the vertical gradients.
- Z-gradients affect lineshape and linewidth.
- some of the gradients are interacting (ie $Z/Z^2$)

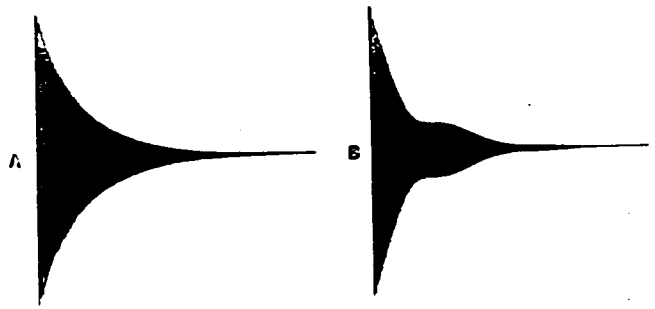
Deuterium Lock:

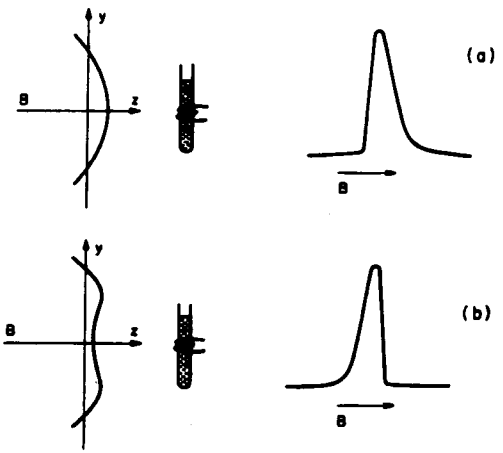
- the means by which long term stability of the magnetic field is maintained.
- the basic idea is to observe an NMR line and compare its frequency with a constant reference, then make adjustments to the magnetic field to maintain that frequency.
- use the deuterium line of the solvent for this purpose.
- the lock channel is an extra deuterium spectrometer operating in parallel with whatever other nucleus you happen to be observing.
- lock power and lock gain are independent.
- with lock power you must avoid saturation and then adjust lock gain.

Adjusting the shims:

- use the lock system to optimize.
- Z, $Z^3$ and $Z^5$ cause symmetrical broadening and $Z^2$ and $Z^4$ cause unsymmetrical broadening.
- horizontal shims affect side bands and must be adjusted without spinning.

Double Resonance Experiments:




"Domed" (a) and "dished" (b) magnetic fields and the signal shapes which they yield.

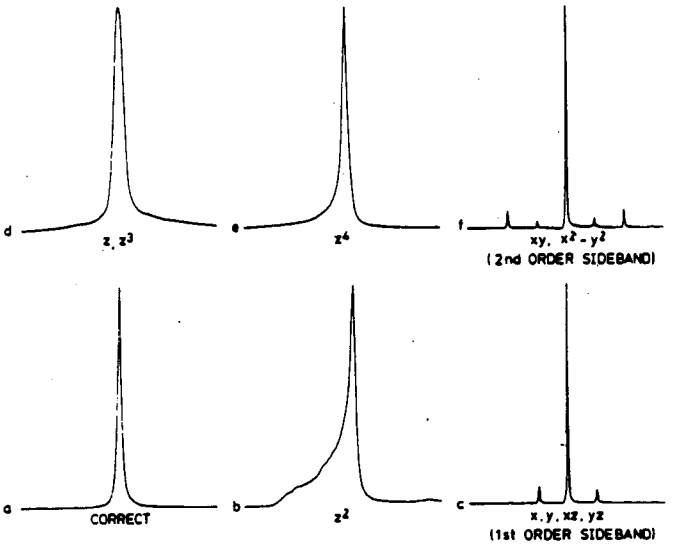


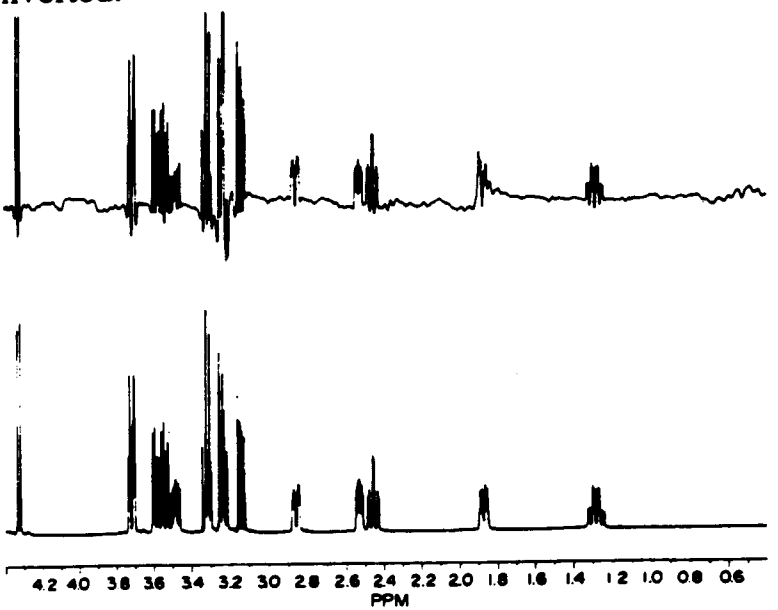

**Table 3.2** Principal shim interactions. When each gradient in the first column is changed, those in the second column will be most strongly affected. If large changes are made then gradients in the third column are also likely to need readjustment.

| *Adjusted gradient* | *Principal interactions* | *Other interactions* |
|---|---|---|
| $Z$ | - | - |
| $Z^2$ | $Z$ | - |
| $Z^3$ | $Z$ | $Z^2$ |
| $Z^4$ | $Z^2$ | $Z$, $Z^3$ |
| $Z^5$ | $Z$, $Z^3$ | $Z^2$, $Z^4$ |
| $X$ | $Y$ | $Z$ |
| $Y$ | $X$ | $Z$ |
| $XZ$ | $X$ | $Z$ |
| $YZ$ | $Y$ | $Z$ |
| $XY$ | $X$, $Y$ | - |
| $X^2$-$Y^2$ | $XY$ | $X$, $Y$ |
| $XZ^2$ | $XZ$ | $X$, $Z$ |
| $YZ^2$ | $YZ$ | $Y$, $Z$ |
| $ZXY$ | $XY$ | $X$, $Y$, $Z$ |
| $Z(X^2$-$Y^2)$ | $X^2$-$Y^2$ | $X$, $Y$, $Z$ |
| $X^3$ | $X$ | - |
| $Y^3$ | $Y$ | - |

**Solvent** - Your solvent must be **deuterated** or contain deuterated solvent (commonly $D_2O$, $CDCL_3$, Acetone-$d_6$, DMSO-$d_6$, MeOH-$d_6$).

1) LOCK on deterium signal. In order to compensate for magnetic field draft and changing field frequencies, there is a "mini-spectrometer" running constantly in the background. The lock circuit detects the resonance frequency of deuterium and uses it as an internal standard. Any change in $B_0$ causes the lock circuit to produce a compensating field which then stabilizes $B_0$.

2) Reduce the signal from the solvent. The detected NMR signal (sample voltage) will be converted as a binary number proportional to the signal by the analogue-to-digital-converter (ADC). There is a limit to the ratio of largest to smallest signals output by an ADC. This is called **dynamic range** of ADC. For a 12-bit ADC, the dynamic range is 2000:1 ( $2^{11}$ -1 : 1). If the solvent signal is too high, the signals from your sample cannot be converted.



# NMR Solvent Data Chart

† The $^1H$ spectra of the residual protons and $^{13}C$ spectra were obtained on a Varian Gemini 200 spectrometer at 295° K The sample for the proton and $^{13}C$ spectra contain a maximum of 0.05% and 1.0% TMS (v/v) respectively. Since deuterium has a spin of 1, triplets arising from coupling to deuterium have the intensity ratio of 1:1:1. 'm' denotes a broad peak with some fine structures. It should be noted that the chemical shifts, in particular, can be dependent on solute, concentration and temperature.

— Approximate values only, may vary with pH, concentration and temperature.

■ Melting and boiling points are those of the corresponding unlabeled compound (except for $D_2O$). These temperature limits can be used as a guide to determine the useful liquid range of the solvents.

| SOLVENT | $^1H$ Chemical Shift (ppm from TMS) (multiplicity) | J$_{HD}$ (Hz) | Carbon-13 Chemical Shift (ppm from TMS) (multiplicity) | J$_{CD}$ (Hz) | $^1H$ Chemical Shift of HOD — (ppm from TMS) | Density at 20°C | Melting Point (°C) ■ | Boiling Point (°C) ■ | Dielectric Constant |
|---|---|---|---|---|---|---|---|---|---|
| Acetic Acid-$d_4$ | 11.65 (1)<br>2.04 (5) | 2.2 | 178.99 (1)<br>20.0 (7) | 20 | 11.5 | 1.12 | 17 | 118 | 6.1 |
| Acetone-$d_6$ | 2.05 (5) | 2.2 | 206.68 (13)<br>29.92 (7) | 0.9<br>19.4 | 2.8 | 0.87 | -94 | 57 | 20.7 |
| Acetonitrile-$d_3$ | 1.94 (5) | 2.5 | 118.69 (1)<br>1.39 (7) | 21 | 2.1 | 0.84 | -45 | 82 | 37.5 |
| Benzene-$d_6$ | 7.16 (1) | | 128.39 (3) | 24.3 | 0.4 | 0.95 | 5 | 80 | 2.3 |
| Chloroform-d | 7.27 (1) | | 77.23 (3) | 32.0 | 1.5 | 1.50 | -64 | 62 | 4.8 |
| Cyclohexane-$d_{12}$ | 1.38 (1) | | 26.43 (5) | 19 | | 0.89 | 6 | 81 | 2.0 |
| Deuterium Oxide | 4.80 (DSS)<br>4.81 (TSP) | | | | 4.8 | 1.11 | 3.8 | 101.4 | 78.5 |
| N,N-Dimethyl-formamide-$d_7$ | 8.03 (1)<br>2.92 (5)<br>2.75 (5) | 1.9<br>1.9 | 163.15 (3)<br>34.89 (7)<br>29.76 (7) | 29.4<br>21.0<br>21.1 | 3.5 | 1.04 | -61 | 153 | 36.7 |
| Dimethyl Sulfoxide-$d_6$ | 2.50 (5) | 1.9 | 39.51 (7) | 21.0 | 3.3 | 1.18 | 18 | 189 | 46.7 |
| p-Dioxane-$d_8$ | 3.53 (m) | | 66.66 (5) | 21.9 | 2.4 | 1.13 | 12 | 101 | 2.2 |
| Ethanol-$d_6$ | 5.29 (1)<br>3.56 (1)<br>1.11 (m) | | <br>56.96 (5)<br>17.31 (7) | <br>22<br>19 | 5.3 | 0.91 | <-130 | 79 | 24.5 |
| Methanol-$d_4$ | 4.87 (1)<br>3.31 (5) | 1.7 | <br>49.15 (7) | <br>21.4 | 4.9 | 0.89 | -98 | 65 | 32.7 |
| Methylene Chloride-$d_2$ | 5.32 (3) | 1.1 | 54.00 (5) | 27.2 | 1.5 | 1.35 | -95 | 40 | |
| Pyridine-$d_5$ | 8.74 (1)<br>7.58 (1)<br>7.22 (1) | | 150.35 (3)<br>135.91 (3)<br>123.87 (5) | 27.5<br>24.5<br>25 | 5 | 1.05 | -42 | 116 | 12.4 |
| Tetrahydrofuran-$d_8$ | 3.58 (1)<br>1.73 (1) | | 67.57 (5)<br>25.37 (1) | 22.2<br>20.2 | 2.4-2.5 | 0.99 | -109 | 66 | 7.6 |
| Toluene-$d_8$ | <br>7.09 (m)<br>7.00 (1)<br>6.98 (m)<br>2.09 (5) | <br><br><br><br>2.3 | 137.86 (1)<br>129.24 (3)<br>128.33 (3)<br>125.49 (3)<br>20.4 (7) | <br>23<br>24<br>24<br>19 | 0.4 | 0.94 | -95 | 111 | 2.4 |
| Trifluoroacetic Acid-d | 11.50 (1) | | 164.2 (4)<br>116.6 (4) | | 11.5 | 1.50 | -15 | 72 | |
| Trifluoroethanol-$d_3$ | 5.02 (1)<br>3.88 (4x3) | 2(9) | 126.3 (4)<br>61.5 (4x5) | 22 | 5 | 1.45 | -44 | 75 | |