Adamantane ($^1H/^{13}C$ Pulse Calibration/Shimming/Chemical Shift Reference)

I. Adamantane – ^{1}H pulse calibration

NOTE: Adamantane has a high-degree of symmetry resulting in a high degree of motion. Thus both ^{13}C and ^{1}H lines will be much narrower than observed in typical organic solids.

(1) Spin adamantane at 10 kHz and check tuning. Re-tune if necessary

(2) Using one-pulse experiment, acquire ^{1}H spectrum and set adamantane ^{1}H to be on-resonance.

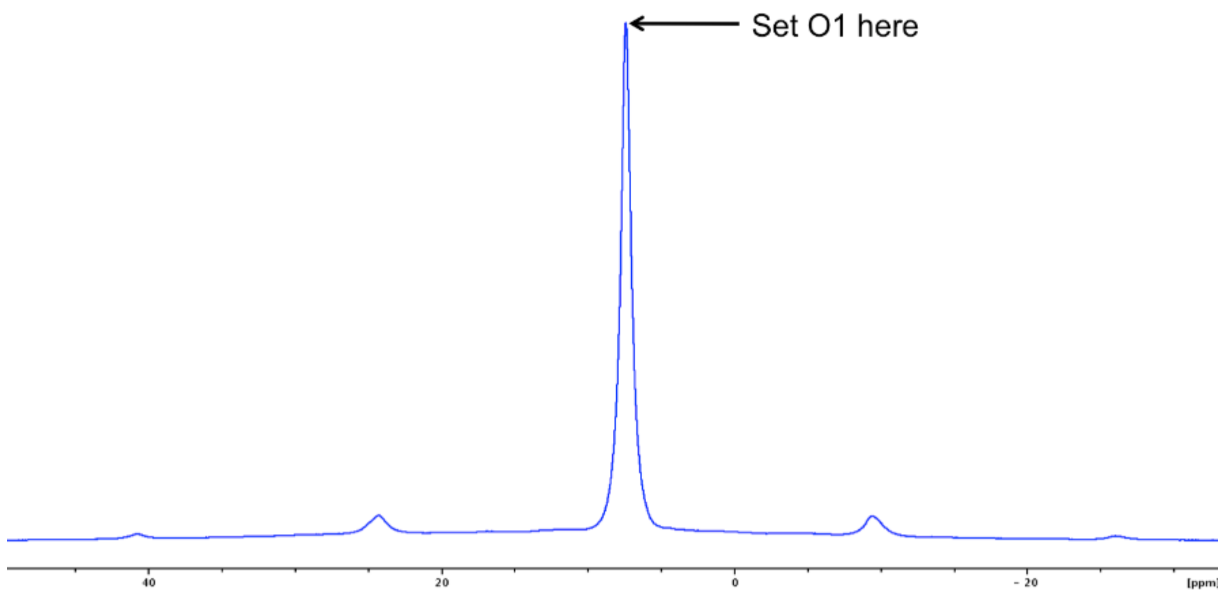


Figure 1: *^{1}H spectrum of adamantane.*

NOTE: For ^{1}H and ^{13}C pulse calibrations it is important to set recycle delay to at least 5 x T_1. Insufficiently long delays will shift the maxima of nutation curves (**Figure 2**).

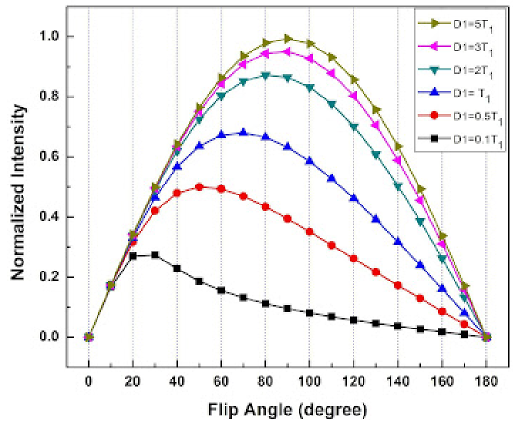


Figure 2: *Effect of recycle delays with respect to T_1 on nutation curve. From Glenn Facey NMR Blog: http://u-of-o-nmr-facility.blogspot.com/2009/06/90-degree-pulse-determinations.html*

(3) To calibrate pulse width – measure nutation curves as a function of ^{1}H pulse power with the major adamantane peak on-resonance (**Figure 3**).

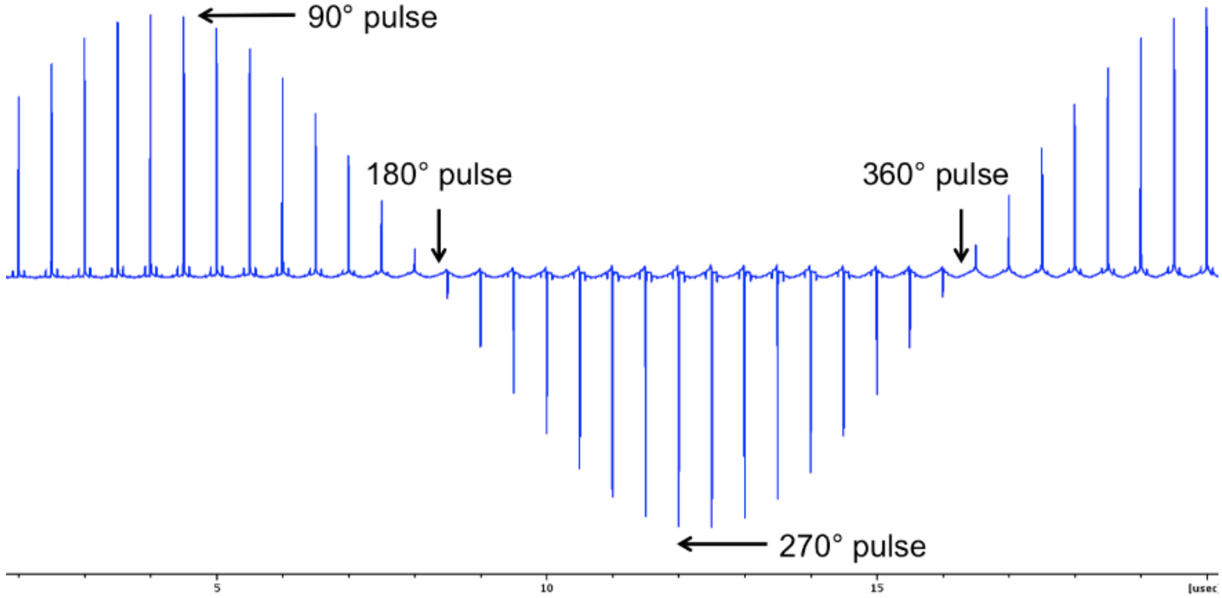


Figure 3: *Nutation curve for ^{1}H pulse length of adamantane.*

(4) Calculate the 90° pulse length from the signal null occurring at the 180° or 360° pulse lengths.

NOTE: For a typical solids experiment determine the power level for 2.5μs (100kHz) and 4 μs (62.5kHz) 90° pulses. The actual power that the probe can handle and amplifiers can provide will be specific to the current setup.

II. Adamantane – ^{13}C pulse calibration

NOTE: Adamantane has a high-degree of symmetry with a high degree of motion resulting in much smaller ^{13}C-^{1}H dipolar coupling than observed in typical organic solids. With moderately fast MAS rates (10 kHz), low power ^{1}H decoupling is sufficient to decouple the ^{1}H's. Typically this power is less than 0.1W, but will be dependent on the probe/amplifier setup.

(1) Spin adamantane at 10 kHz and use a single-pulse with ^{1}H decoupling experiment to acquire a ^{13}C spectrum of adamantane.

(2) Set the ^{1}H decoupling frequency to that determined previously for the ^{1}H spectrum. The ^{1}H decoupling power will be low (~0.1W) which will allow for long acquisition times (200 to 300ms).

(3) Set the carrier to be between the two ^{13}C resonances (**Figure 4**)

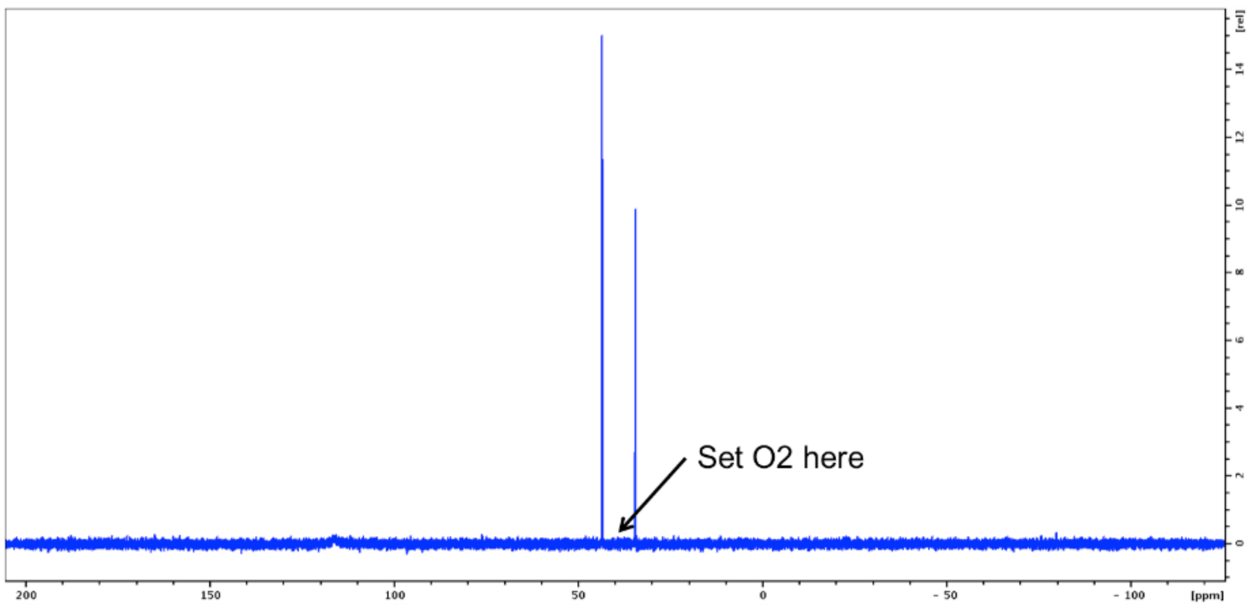


Figure 4: *^{13}C spectrum of adamantane, with proper shimming (FWHM ~ 4.5 Hz), collected using ultra low power ^{1}H decoupling.*

(4) To calibrate pulse width, measure ^{13}C nutation curve **(Figure 5)** – peak height as a function of ^{13}C pulse power. Determine power levels for 90° pulse lengths of 5μs (50kHz), and 4 μs (62.5kHz) (depending on power handling of the probe).

NOTE: For ^{1}H and ^{13}C pulse calibrations it is important to set recycle delay to at least 5 x T_1. Insufficiently long delays will shift the maxima of nutation curves (**Figure 2**).

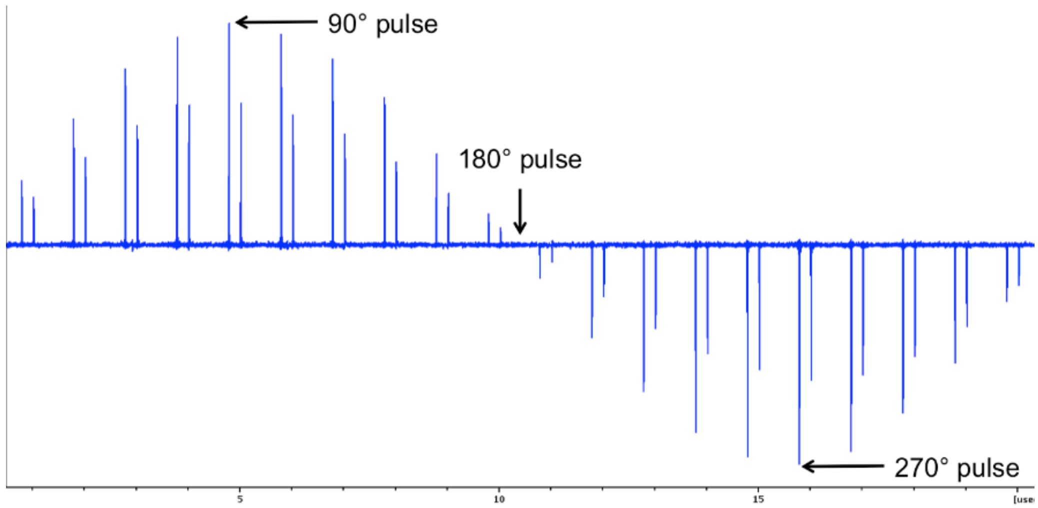


Figure 5: *Nutation curve for ^{13}C pulse length on adamantane, collected with ^{13}C one-pulse with ^{1}H decoupling pulse program.*

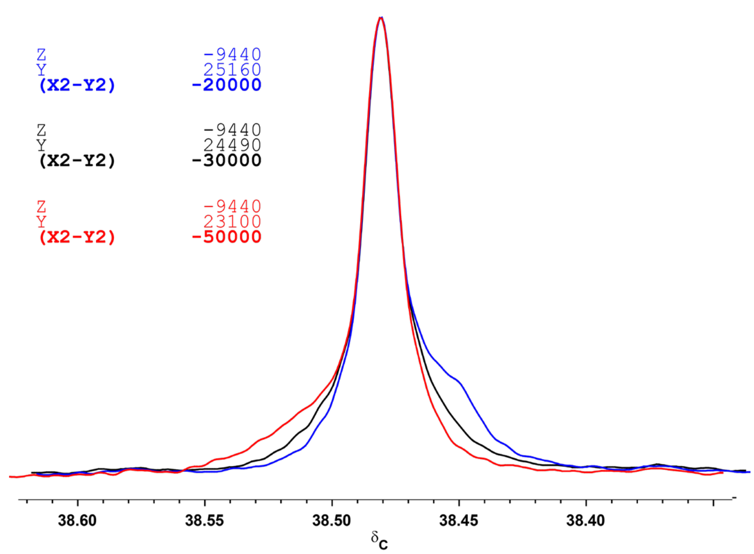
(5) Adamantane – Shimming

a. At the magic-angle, shims will behave differently than solution samples see (A. Sodickson, D.G. Cory, Shimming a High-Resolution MAS Probe, J. Magn. Reson. (1997) 128: 87-91 https://doi.org/10.1006/jmre.1997.1218)

b. Align the probe with the spinning module rotor axis along either the X or Y – axis of the RT shims.

NOTE: If the rotor-axis is aligned along the Y-axis, applying current to the X shim will minimally affect the ^{13}C line width.

c. One should be able to obtain a FWHM below 10 Hz for the ^{13}C adamantane resonances. Typically, Z and Y shims (or X depending on direction that probe is oriented) can reduce the ^{13}C line width. Large values of X2-Y2 will typically reduce the asymmetric foot at the base of the ^{13}C resonance.



(6) Adamantane can be used as an external chemical shift standard by setting the downfield (left-most) ^{13}C resonance to 38.48ppm. (see Morcombe CR, Zilm KW. Chemical shift referencing in MAS solid state NMR. J Magn Reson. 2003 162:479-86. https://doi.org/10.1016/s1090-7807(03)00082-x)