Acquisition of High Resolution Solid-State NMR Spectra of Organic Solids

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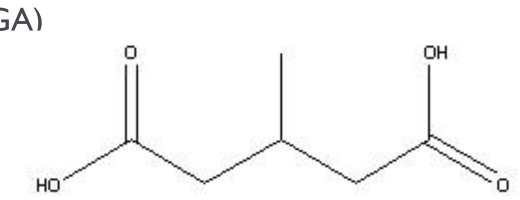
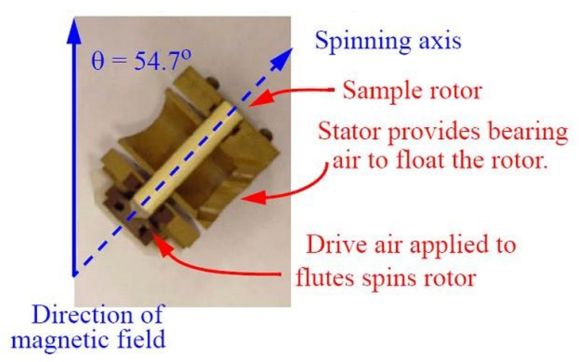
Introduction

- High Resolution-creating experimental conditions that produce narrow spectral lines
- Enhances signal
  - Increases signal-to-noise ratio since peak heights are increased when line widths are reduced
- To acquire data the spectrometer must first be optimized
  - Methylglutaric Acid (MGA)



Magic Angle Spinning

- Magic Angle: 54.73°
  - Related to Legendre's second associated polynomial
- Provides mechanical averaging of sample with respect to external field
- Dramatically improves spectrum



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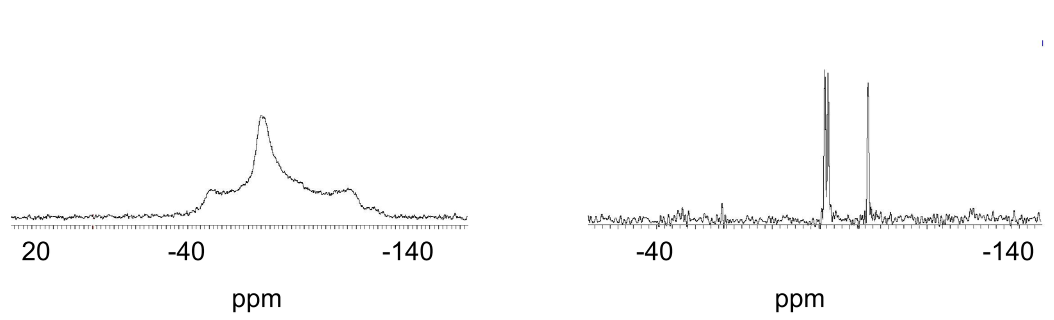
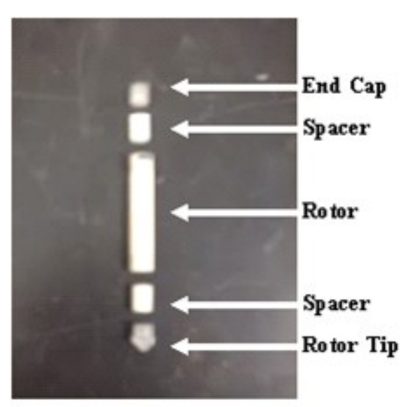


Rotor Preparation

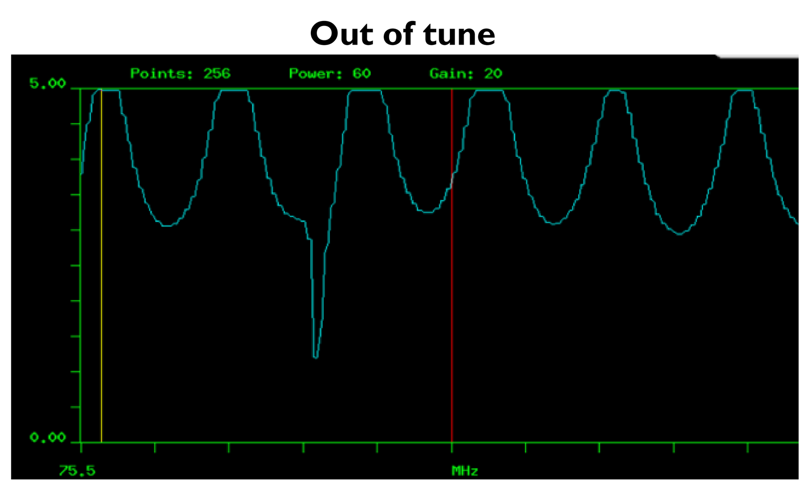
- Key aspect of proper MAS
- Rotor holds sample and must be able to withstand high spinning rate
  - Ceramic zirconia
  - Rotor explosions



High Powered Decoupling

- Direct dipolar coupling
  - Broadening due to local magnetic field of neighboring nuclei
  - Averages out in liquids due to motion
- Proton-Carbon dipolar coupling is strong
  - Directly bonded protons can produce couplings as large as 40KHz
  - To remove, MAS rate must exceed dipolar coupling
- Irradiate the sample at the proton's resonance frequency while acquiring ^{13}C signal
  - NMR coil needs ~300 watts to achieve 100KHz RF

Graphical Tuning



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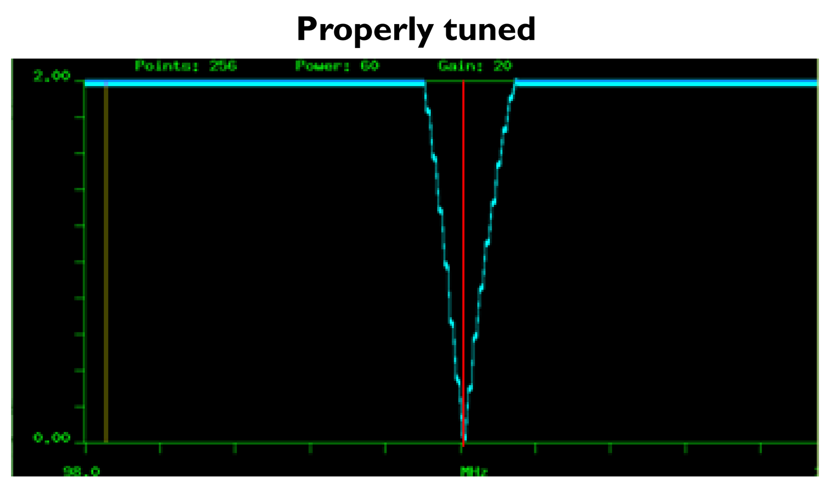
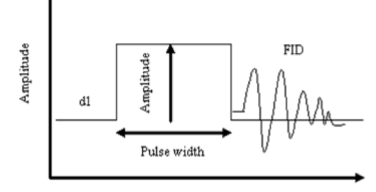


Pulse Sequences

- Describes what the spectrometer "does" during an experiment
  - Explains the RF pulses by indicating amplitude, phase, and duration
  - Shows delays
  - Shows acquisition (receiver)
- Single Pulse Excitation (SPE) pulse sequence
  - Most basic pulse sequence

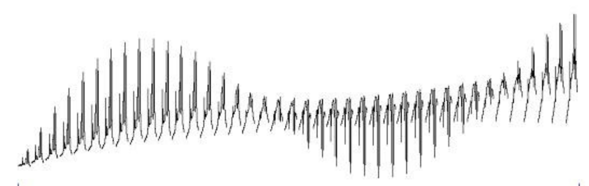


SPE Variables

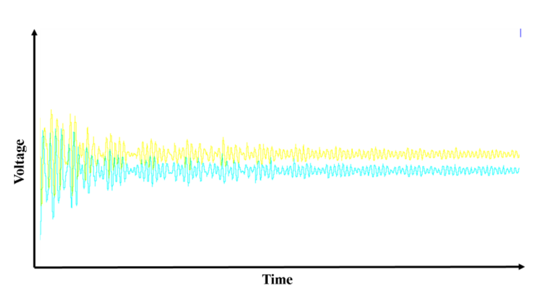
- d1-delay that allows nuclei to reach equilibrium in magnetic field
- Amplitude - strength of pulse
- Pulse width-duration of excitation
  - 90° pulse width
    - pulse that tips magnetization from the z axis into the xy plane
- Free induction decay (FID)-oscillating voltage induced in coil from the sample. NMR signal that is digitized by the receiver.

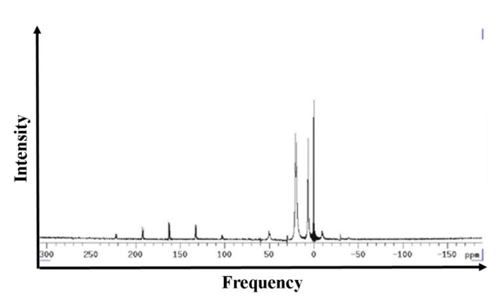
Pulse Width

- ^1H is easiest to observe
  - Broad signal may cause baseline distortion
- Peak intensity should form sine wave for both the ^1H and ^{13}C arrays
  - Easier to observe 180° than 90°
    - 180° occurs at first null
    - Half of this value ~ 90° pulse width



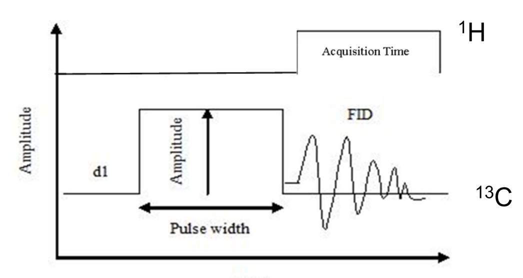
Fourier Transform





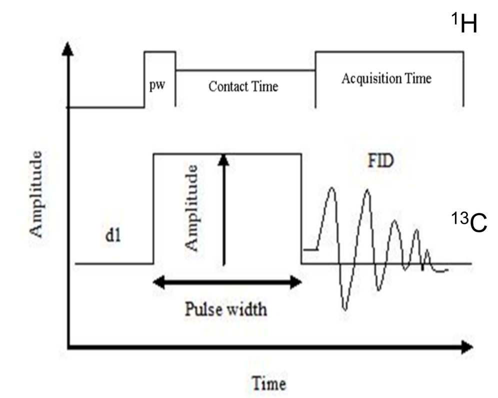
Dual Channel SPE

- Allows for decoupling while acquiring
- Double resonant experiment
- Coil is tuned to two frequencies simultaneously
  - ^1H~400MHz
  - ^{13}C~100MHz



Cross Polarization

- Allows for transfer of magnetization
  - Proton to Carbon
  - Occurs during contact time
- Increases signal by a factor of 2
- Allows for increased rate of pulsation
  - T_1 of ^{13}C is often at least 10 times that of ^1H

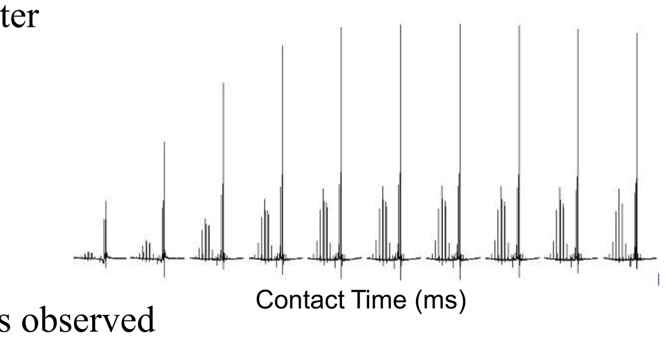


Sample Dependent Parameters

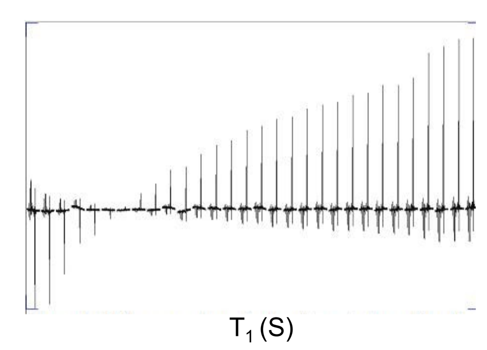
- Pulse delay (d1)-determined by calculating T_1
- T_1 is the decay constant for the z component of the nuclear spin magnetization
- Optimal pulse delay is 1.26 times the T_1 value
- Contact time-period in which magnetization is transferred from ^1H to ^{13}C

Parameter Arrays

- Experiment repeated with only one parameter changed
- Spectra plotted horizontally
- Intensity changes observed

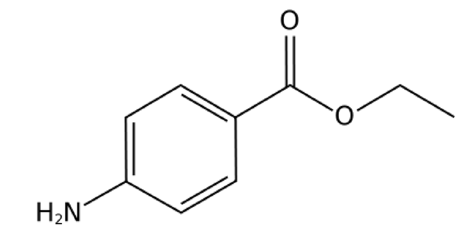


Parameter Arrays

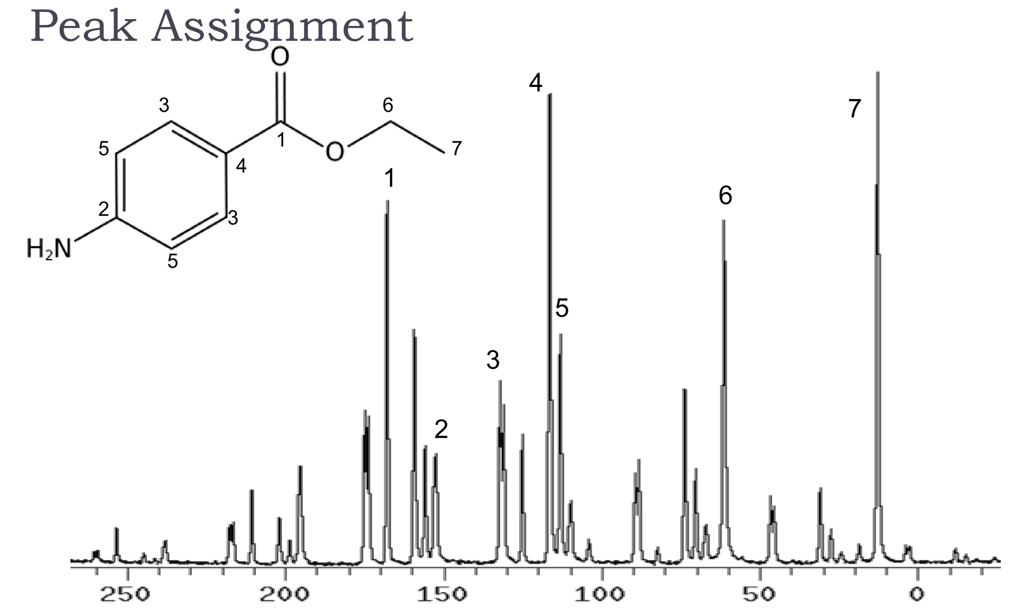


Acquire Data

- Spectrometer is now ready to acquire high resolution solid-state NMR spectra of organic solids



Peak Assignment



Conclusion

- Solid-State NMR is becoming mainstream
  - Industry
  - Undergraduate level
- Research interests
- Documentation

Acknowledgements

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