Low-E Inverse Detection MAS Probe and Gradient Spectroscopy in Solid State NMR.

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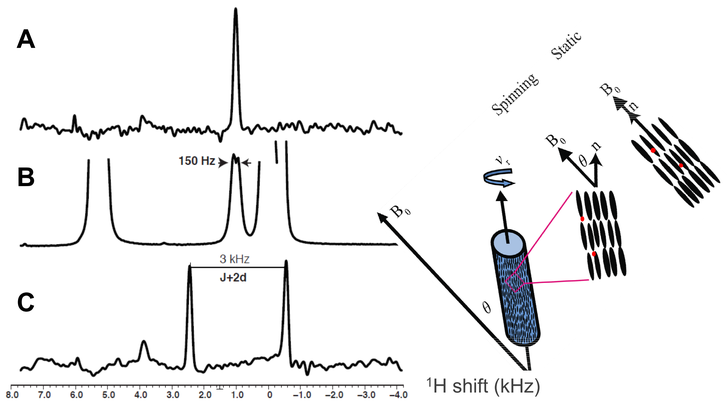
Introduction

^{1}H detected solid-state NMR experiments have been rapidly evolving in past decade enabling sensitivity enhanced experiments to be applied in solid samples. On the other hand pulse field gradients (PFGs) are routinely used in solution NMR facilitating rapid acquisition of multi-dimensional experiments with efficient coherence selection pathways, diffusion studies and in magnetic resonance imaging as well. By combining the above two techniques it is possible to broaden solid state NMR applications beyond its current capabilities. Hence, there has been an increasing focus at Doty Scientific on design and development of high-resolution probes for moderate and fast magic angle spinning with the inclusion of gradient coils. Here the design, construction and performance of at least two different solid state probes equipped with gradient coils: (1) **Magic angle spinning-magic angle gradient (MAS-MAG) probe optimized for inverse 1H detection**; (2) Static triple resonance probe for solid state NMR of mechanically and magnetically oriented samples. Further, these probes have sufficient tuning flexibility to work efficiently with high loss biological samples and less sample heating. Additionally, gradient coils producing fields up to **500 G/cm** and fast recovery time enables acquisition of high-resolution ^{1}H spectra for combined rotation and multiple pulses (CRAMPS) experiments under moderate MAS. Experimental results obtained from a stationary probe operating at 900 MHz ^{1}H frequency and new methodologies for gradient enhanced spectroscopy are demonstrated.

^{1}H detected magic angle setting

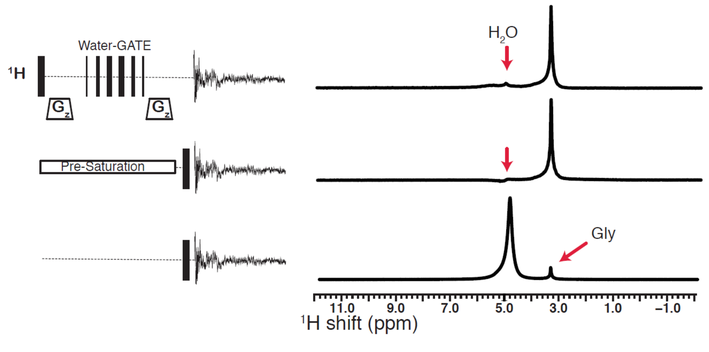
High accuracy magic angle setting with proton detection is obtained using a sample with carbon labeled chloroform dissolved in partially oriented liquid crystalline (LC) matrix. The director(n) of the LC matrix align along the magnetic field when stationary, but aligns along the axis of rotation under rotor spinning. Here, scaled dipolar couplings are measured to monitor rotor angles.



300 MHz ^{1}H signal of chloroform in nematic 5CB. A) ^{13}C decoupled 10 ms spin echo signal obtained under MAS. B) 1ms echo signal under MAS and no ^{13}C decoupling applied. C) ^{13}C coupled 1 ms echo signal under stationary conditions. 3 kHz splitting in C accounts for sum of J_{CH}-coupling and twice d_{CH}-coupling.

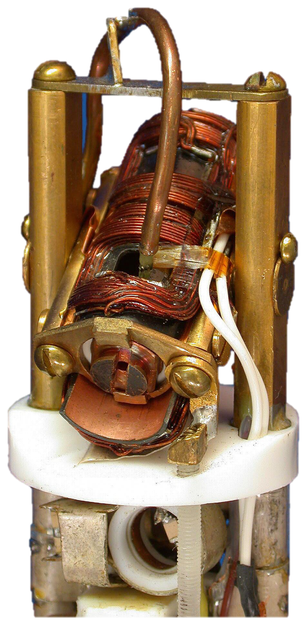
Water Suppression using RF and PFGs

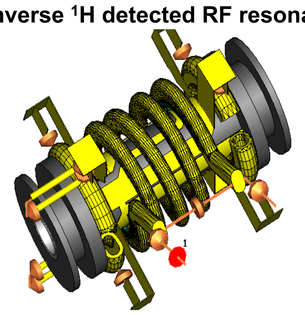
Efficient solvent suppression is achieved by applying long low power RF and gradient pulses. Spectra are shown for glycine dissolved in deuterated water. Residual water signal is noted at 5 ppm and glycine peak near 3 ppm.



DOTY Low-E MAG-MAS Probe

Low-E Inverse ^{1}H detected RF resonator

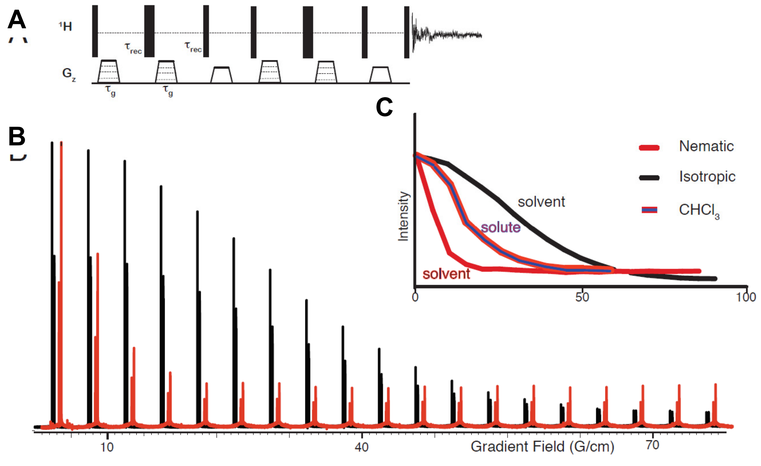




- Low-E RF resonator optimal for inverse ^{1}H detection and solenoid coil for low-γ nuclei.
- HR-MAS for high viscous solution, solids, and biological macromolecules.
- CRAMPs experiments.
- Gradient spectroscopy and imaging
- >10 fold reduction in RF heating.
- Spectral resolution of 0.015 ppm.

Stimulated Echo PFG- diffusion NMR under MAS

Liquid crystals are viscous semi solids. They are often used in commercial products, chemical synthesis and as orienting media for NMR study of small molecules. A combination of MAS and PFG techniques are applied to study self diffusion of liquid crystals and the solutes in nematic and in isotropic phases. The technique enables measurement of varying diffusion coefficients in solids with respect to molecular sizes, viscousity, and temperature, suggesting a wider application in polymer chemistry and biological sciences.



A) Stimulated echo pulse sequence for PFG-diffusion NMR study of a nematic liquid crystal 5CB under MAS. B) Array of ^{1}H spectra recorded under 7 kHz MAS with varying gradient strength. Black and red colors indicate isotropic and nematic phase of 5CB. C) Graphical demonstration of signal decay for solvent (5CB) and the solute ($CHCl_3$).

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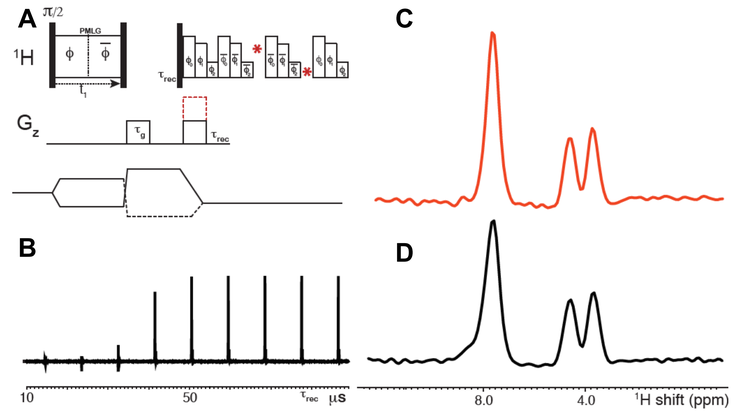
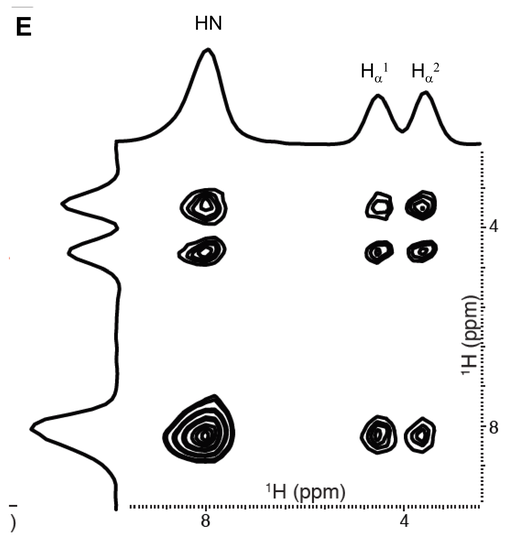
Coherence selection using gradients in MAS-NMR

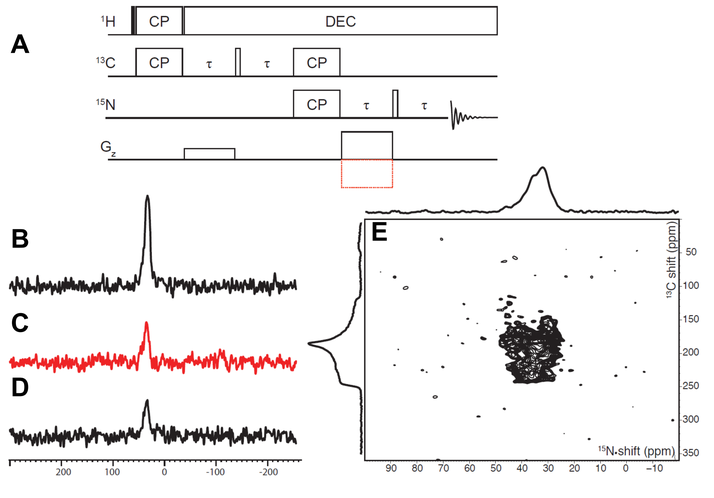
Solution NMR experiments used for coherence selected pathways using PFGs are modified to accommodate solid samples under MAS. Amplitude and phase modulated Lee-Goldburg RF pulses are applied for homonuclear dipolar decoupling during windowed acquisition to compensate for phase transients and to improve spectral resolution.





A) Radio frequency pulse sequence used for ^{1}H detection and homo-nuclear chemical shift correlation. B) Gradient recovery time of the probe for a 2 ms gradient pulse (100 G/cm) applied. Note that the probe recovers within 50 micro sec. C and D) Gradient assisted double and single quantum filtered spectra of Glycine powder recorded under 7.5 kHz MAS on a 300 MHz spectrometer. E) Two-dimensional ^{1}H- ^{1}H chemical shift correlation spectrum of Glycine. Direct detected 1D spectra are shown on top and left.

Gradient selected echo/anti-echo phase cycling in triple-resonance experiments at 900 MHz ^{1}H NMR.



Triple resonance pulse sequence (A) used for ^{13}C edited ^{15}N detection (B) and ^{13}C-^{15}N correlation (E) under gradient selected echo/anti-echo phase cycling. C) Echo and D) anti-echo (red). Sample: ^{13}C, ^{15}N labeled Valine powder.