

Two Dimensional Dipolar-Isotropic Shift Correlations in Oriented Systems Using Dynamic Angle Spinning

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ABSTRACT:

Utilizing a dynamic angle spinning (DAS) probe we have investigated the ability to correlate dipolar couplings with isotropic chemical shifts in oriented systems. We have employed the efficient decoupling capabilities of magic angle spinning (MAS) to provide an isotropic chemical shift detection dimension following a dipolar coupling evolution dimension at an angle different than the magic angle. In the weak coupling limit, this technique provides a method to obtain dipolar coupling information while maintaining correlations of the isotropic chemical shift.

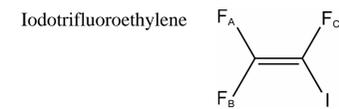
We have demonstrated correlations of evolutions at two spinning axes in the molecule iodotrifluoroethylene ($CF_2=CFI$) dissolved in the liquid crystal 4-octylphenyl 2-chloro-4-(4-heptylbenzoyloxy) benzoate. The resulting spectrum is first order and shows chemical shifts, dipolar couplings and J couplings in the indirect dimension and chemical shifts + J couplings in the direct dimension.

INTRODUCTION:

The study of oriented liquid crystals and ordered phases has received much attention in recent years[1,2,3] and has provided insight into their orienting properties as well as their structure. In addition to studying the ordering phase itself, many have studied molecules dissolved in the oriented phase[4,5]. Solutes dissolved in the liquid crystal solvent also show a degree of orientation due to the alignment properties of the liquid crystal.

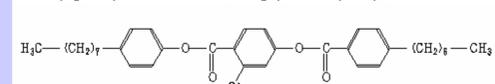
However, the complexity of single quantum spectra in homonuclear spin systems in oriented liquid crystals becomes a problem beyond approximately 10 spins due to the large number of one-quantum transitions that exist. For example, the maximum number of single quantum transitions that can occur in a 4 spin system is 56, a somewhat tractable number. However, in a system with 10 spins a rather difficult to interpret 167,960 transitions exist. Thus efforts have been made to attempt to simplify these complex spectra.

In this work we are presenting our efforts towards simplifying dipolar coupled spectra by adding an isotropic chemical shift dimension. The isotropic chemical shift dimension is obtained by exploiting the alignment properties of a spinning liquid crystal solvent which has an alignment axis related to the spinning axis. Upon changing the sample spinning axis, we have the ability to scale dipolar interactions according to $3\cos^2\theta - 1$ where θ is the angle the spinning axis forms with the magnetic field. Thus, at the magic angle we have no dipolar couplings and an effectively decoupled evolution; this far exceeds the decoupling ability of any existing homonuclear multiple-pulse decoupling method.

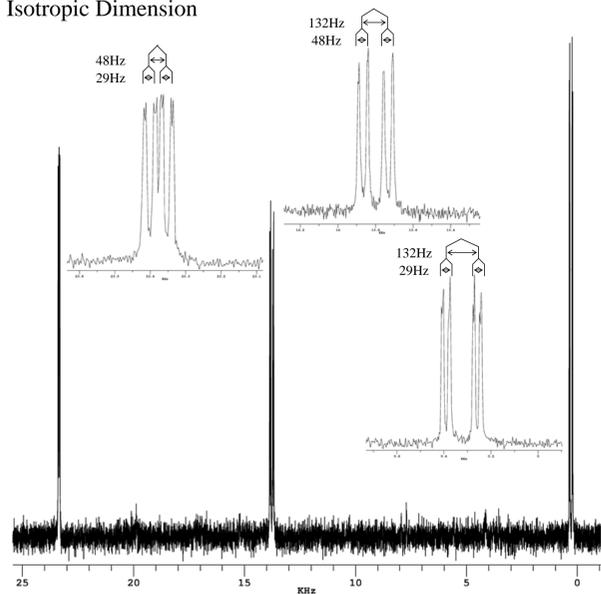


Dissolved in the liquid crystal solvent:

4-octylphenyl 2-chloro-4-(4-heptylbenzoyloxy) benzoate

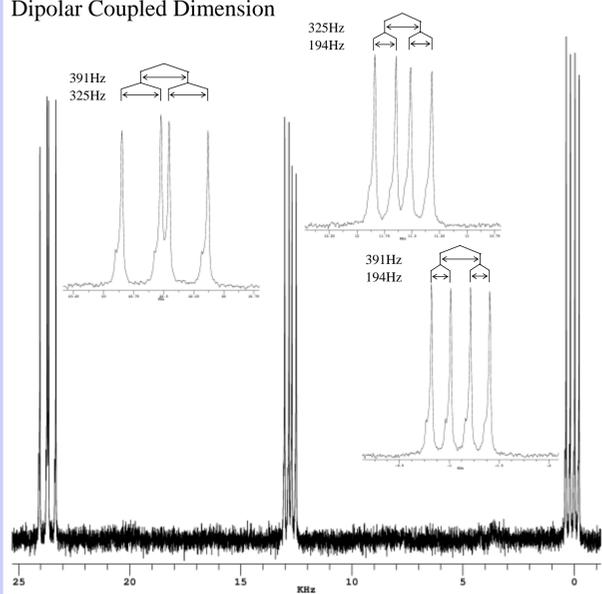


Isotropic Dimension



^{19}F 1D spectrum of iodotrifluoroethylene 20%/wt in the nematic liquid crystal 4-octylphenyl 2-chloro-4-(4-heptylbenzoyloxy) benzoate. $\theta \approx 54^\circ$ spinning at 3.5kHz.

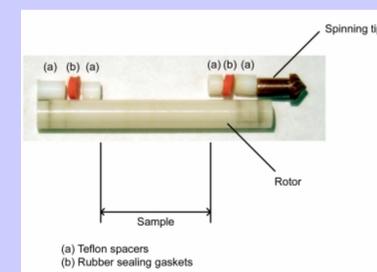
Dipolar Coupled Dimension



^{19}F 1D spectrum of iodotrifluoroethylene 20%/wt in the nematic liquid crystal 4-octylphenyl 2-chloro-4-(4-heptylbenzoyloxy) benzoate. $\theta \approx 30^\circ$ spinning at 3.5kHz.

SAMPLE:

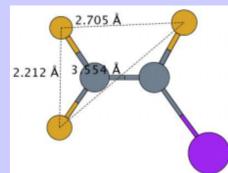
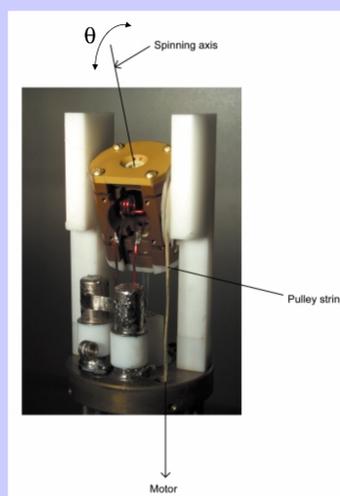
Iodotrifluoroethylene was dissolved in 4-octylphenyl 2-chloro-4-(4-heptylbenzoyloxy) benzoate to 20%/wt. The nematic liquid crystalline phase was then sealed in the MAS rotor with sealing gaskets and spacers as shown below. The use of the sealing gaskets prevents sample leakage while allowing stable spinning, in contrast to problems associated with flame sealed rotor inserts. Spinning speeds achievable in this design were equal to those with powdered solids (~10KHz), with no loss in sample mass.



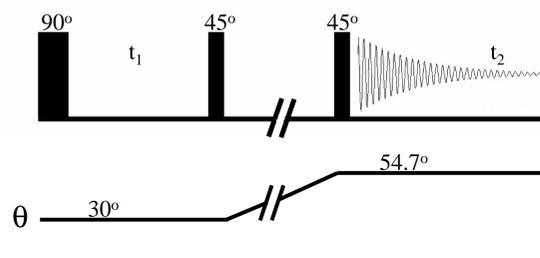
PROBE:

One of the most difficult components of performing DAS experiments is the stability of both the hopping position and the RF circuit over the course of a two-dimensional experiment with $\gg 10,000$ hops.

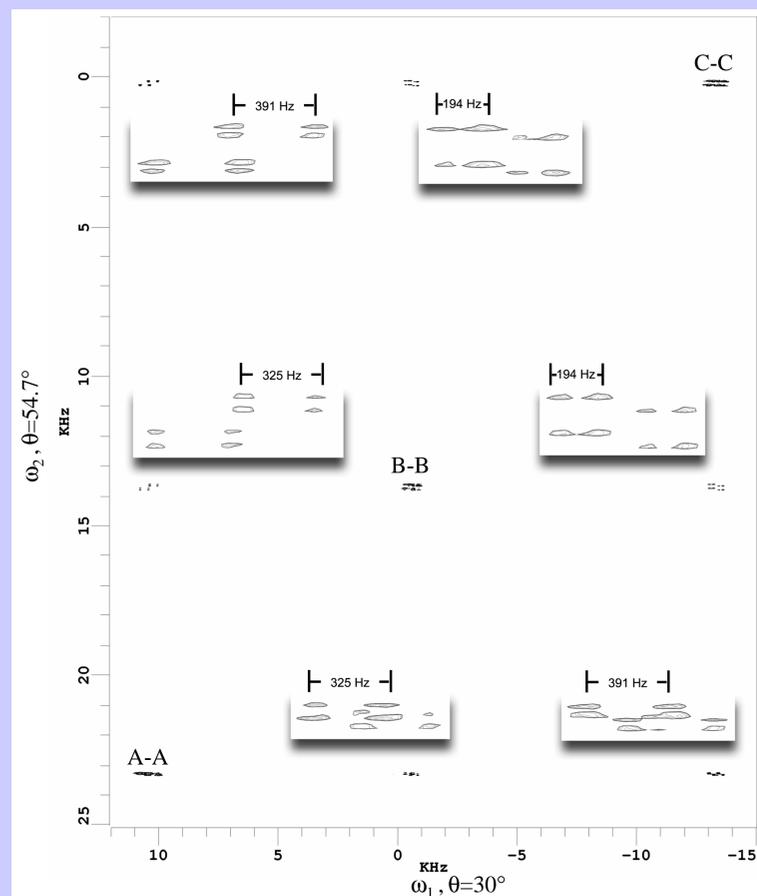
We have designed a DAS probe composed of a modified Chemagnetics 4mm pencil rotor HX probe with motion controlled by a stepping motor. We have optimized RF stability by utilizing a fixed split-solenoid detection coil such that the motion of the spinning axis has little effect on the tuning and RF pulse amplitudes while maintaining pulse amplitudes of ~70kHz. The position of the spinning axis is controlled with an accuracy of $<0.3^\circ$ with an internal motor feedback circuit. In this design, we can achieve axis switching times of ~20ms.



DAS-COSY45 Pulse Sequence



(Hz)	$F_A - F_B$	$F_A - F_C$	$F_B - F_C$
Isotropic J_{FF}	-64	51	128
$J_{FF} + \langle D_{30} \rangle$	325	391	194



^{19}F DAS-COSY45 spectrum of iodotrifluoroethylene 20%/wt in the nematic liquid crystal 4-octylphenyl 2-chloro-4-(4-heptylbenzoyloxy) benzoate. $\theta = 30^\circ$, 54.7° spinning at 2kHz.

CONCLUSIONS:

We have demonstrated the ability to correlate dipolar couplings with isotropic chemical shifts in a small molecule dissolved in a liquid crystal solvent. The analysis of the 2D correlation spectrum reveals structural information about the solute. Although this simple demonstration provides little structure determination in this small molecule, it is a first step in applying this technique to larger more interesting systems.

Currently we are investigating the possibilities of studying molecules with strong couplings. In the strong coupling regime, the decoupling ability of the MAS dimension shows much promise where it can provide liquid-like spectra.

ACKNOWLEDGEMENTS:

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