

Determination of Dipolar Couplings in Strongly Oriented Liquid Crystals and in Solids

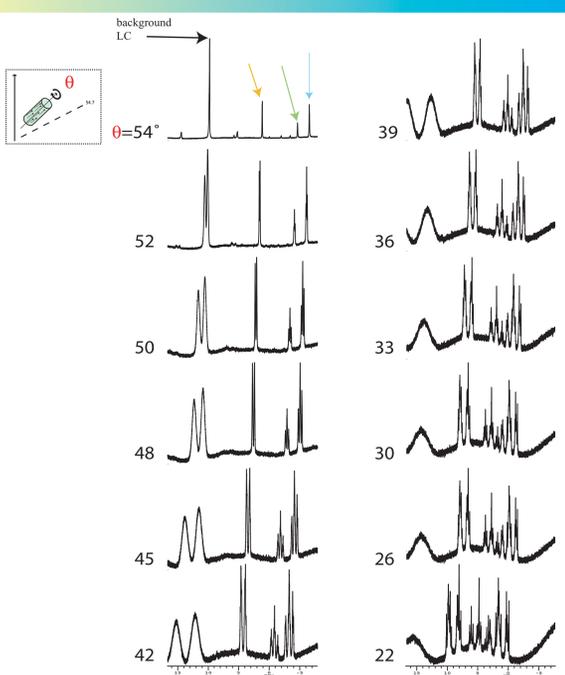
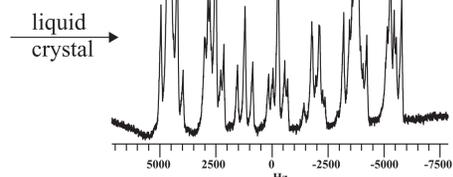
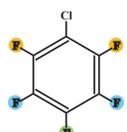
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Summary: Utilizing the $1/r^3$ dependence of dipolar coupling for structure determination remains a challenging goal of NMR spectroscopy. We present here two methods which are applicable for the determination of dipolar couplings in liquid crystals and solids.

Measuring Dipolar Couplings in Oriented Liquid Crystals

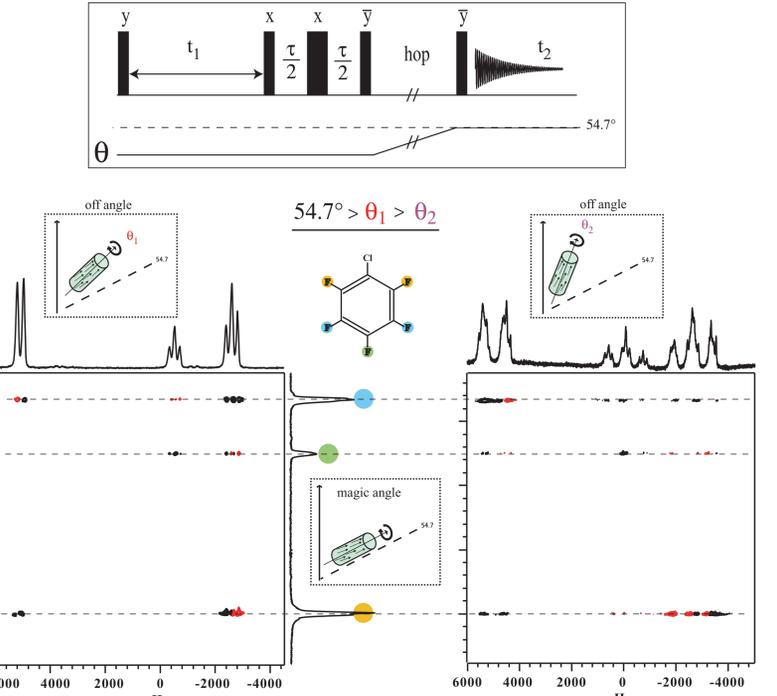
Second Order Dipolar Couplings in Oriented Liquid Crystals



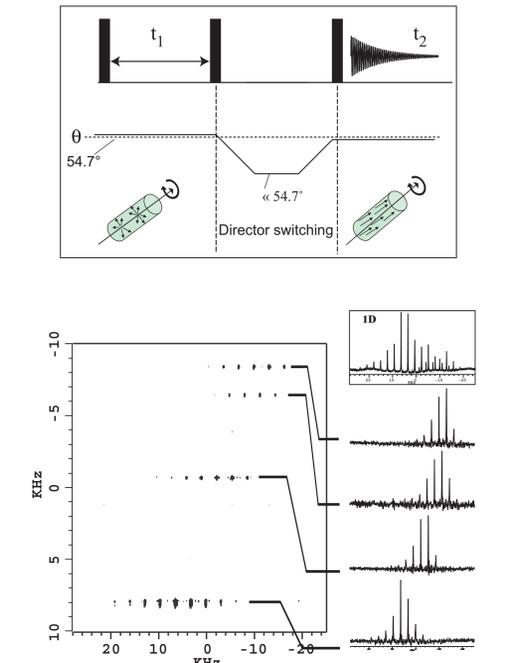
The simple molecule perfluorochlorobenzene produces a second order ^{19}F spectrum when dissolved in the liquid crystal (LC) I52. However, this spectrum can be simplified to yield readily assignable dipolar couplings by rotating the sample at an angle θ with respect to the magnetic field (1). By spinning the sample, the director of the liquid crystal reorients to align parallel to the spinning axis; thus the uniaxial motion of the liquid crystals averages the interactions. The dipolar couplings that create the second order spectrum are then scaled by $(3\cos^2\theta - 1)/2$, As shown to the right.

Switched angle spinning 2D correlations

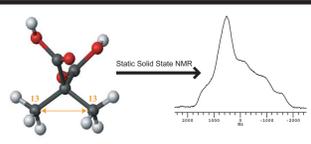
As shown above, rotating the sample at the magic angle can reduce a complicated second order spectrum to a simple first order spectrum and even completely average the dipolar couplings to yield an isotropic spectrum. Using this principle, the evolution of the oriented liquid crystal sample above was correlated in a 2D experiment (shown below to the left) creating the first order dipole coupled spectrum in one dimension and the isotropic spectrum in the second dimension. The crosspeaks readily provide assignment of the isotropic shifts of the coupling pairs. In addition, a second 2D correlation was performed such that the couplings were approaching second order in the first dimension. The crosspeaks now reveal couplings off all spins to each other; thus the onset of a second order type spectrum.



The director alignment can also be changed during the course of a 2D experiment to provide a different type of correlation. In the experiment shown below, the director orientation becomes time dependent (the directors are aligned perpendicular to the spinning axis) by spinning at an angle larger than the magic angle. The spinning sidebands obtained in this dimension are then correlated with the isotropic spectrum obtained with the directors aligned at the magic angle. In this way, we hope to simplify the task of determining anisotropic interactions such as the CSA in oriented systems.



Creating Isotropic Dipolar Couplings in Solids



Characteristic solid state NMR spectra include broad lines such as the one shown to the left for dimethyl malonic acid. The broad nature of the lines are the result of the spatial (θ, ϕ) dependence of the dipolar coupling and chemical shift anisotropy. Ideally, an experiment would observe the interatomic distance dependent dipolar coupling without the θ, ϕ dependence, leaving just a scalar value. Previous experiments did this by shuttling or creating the zero-field Hamiltonian using RF pulses (2,3). Here we demonstrate an alternate method to create an isotropic dipolar spectrum using a series of recoupling sequences based on C7 (4).

Use $\sin^2\theta + \cos^2\theta = 1$ to remove the θ dependence of the dipolar coupling

Starting with z-magnetization on an isolated homonuclear dipolar coupled spin 1/2 pair

$$\rho(0) = I_x^2 + I_z^2$$

$$H = \omega_p h(\theta) (3I_x^2 I_z^2 - I^2 I^2)$$

$$h(\theta) = h \frac{3\cos^2\theta - 1}{2}$$

for a time t not at the magic angle

$$\rho(t) = \cos\left(\frac{3}{2}\omega_p h(\theta)t\right) I_z^2 + i \sin\left(\frac{3}{2}\omega_p h(\theta)t\right) (I_{2,2} - I_{2,-2})$$

for a time τ

$$H^{DET} = \omega_p f (A_{2,2} T_{2,2} - A_{2,-2} T_{2,-2})$$

for a constant time τ_{DET}

$$S_1 = \langle I_x(t, \tau) \rangle = -\cos(\omega_p h(\theta)\tau) - \cos(\omega_p g(\theta)\tau) - \sin^2(\omega_p f(\theta)\tau_{DET})$$

$$S_2 = \langle I_x(t, \tau) \rangle = \cos^2(2\phi) - \sin(\omega_p h(\theta)\tau) - \sin(\omega_p g(\theta)\tau) - \sin^2(\omega_p f(\theta)\tau_{DET})$$

using: $\cos a \cos b \mp \sin a \sin b = \cos(a \pm b)$

$$S_1 \pm 2S_2 \propto \cos(\omega_p [h(\theta)\tau \pm g(\theta)\tau])$$

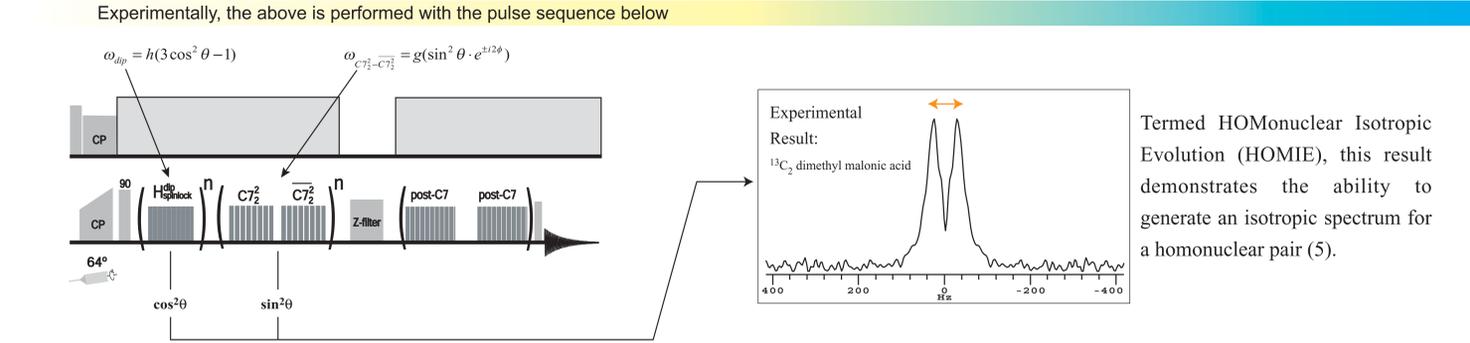
$$\propto \cos [h\omega_p t (3\cos^2(\theta) - 1) \pm g\omega_p \tau \sin^2(\theta)]$$

adjust t and τ to add

$$\propto \cos(\sigma\omega_p t)$$

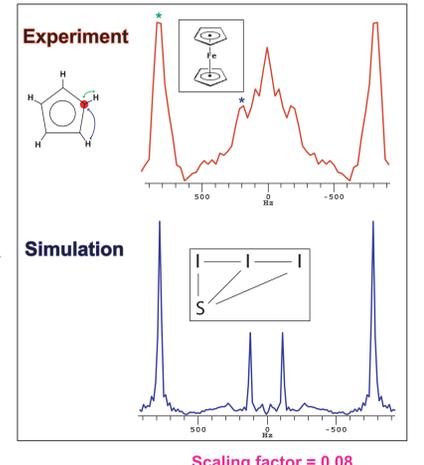
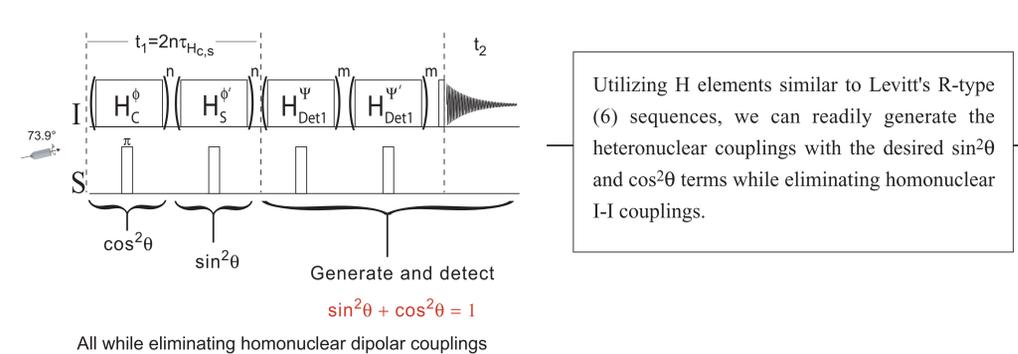
Scaling Factor $\sigma = \frac{3ht}{2(t+\tau)}$

$\sigma_{max} = 0.30$



Heteronuclear Isotropic Evolution (HETIE) Experiments

The real potential for the isotropic evolution experiment utilizes the fact that the principle can be applied to an $I_N S$ spin system. Particularly, a proton-detected-local-field version of the HETIE experiment could provide valuable structural information obtainable for real solid state samples.



Conclusion

Future Work:

The correlations demonstrated in liquid crystals are a simple test case and we hope to apply these methods on more complex samples where useful structural information may be obtained.

The isotropic dipolar coupling experiment in solids is demonstrative of the principle of combining evolutions to create isotropic spectra. We are working towards improving the performance of the heteronuclear proton detected local field experiment to enable its use in structure determination.

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