Dipolar Couplings in Solids:

Measurement and Assignment Using Novel Techniques

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NMR Crystallography ...

The Goal:

Measure enough distances to determine structure in a single experiment.

Liquid State

PrP^{C}

Many methods including NOE yield distance constraints for determining structure

Solid State

PrP^{SC}

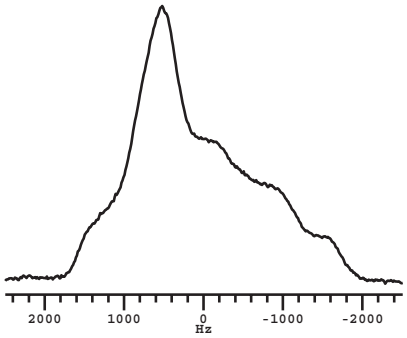
Solid

Few methods exist for the simlultaneous determination of multiple distances

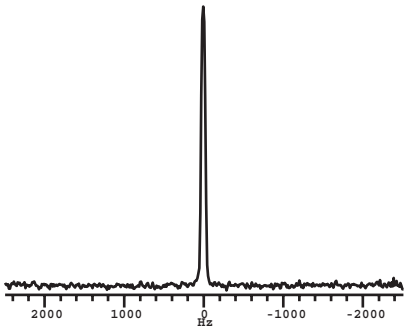
Riek et al., *Nature*, ***382,*** 180-182 (1996).

Recoupling Methods

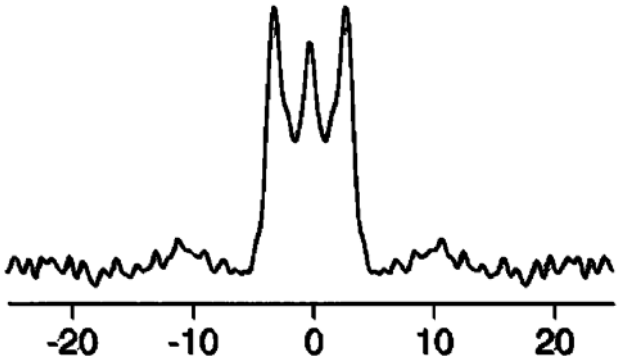
The static experiment contains everything including dipolar couplings



MAS improves resolution, however dipolar couplings are lost.



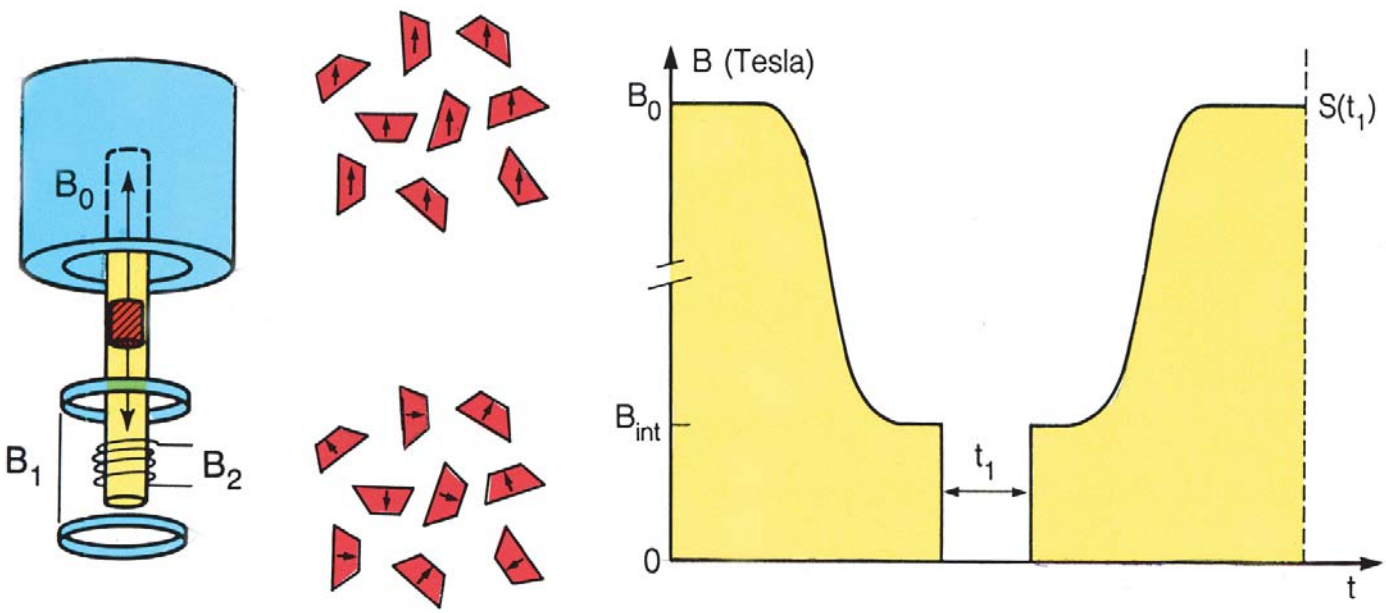
Recoupling techniques such as DRAMA, C7,REDOR, RN, etc. reintroduce dipolar couplings under MAS.

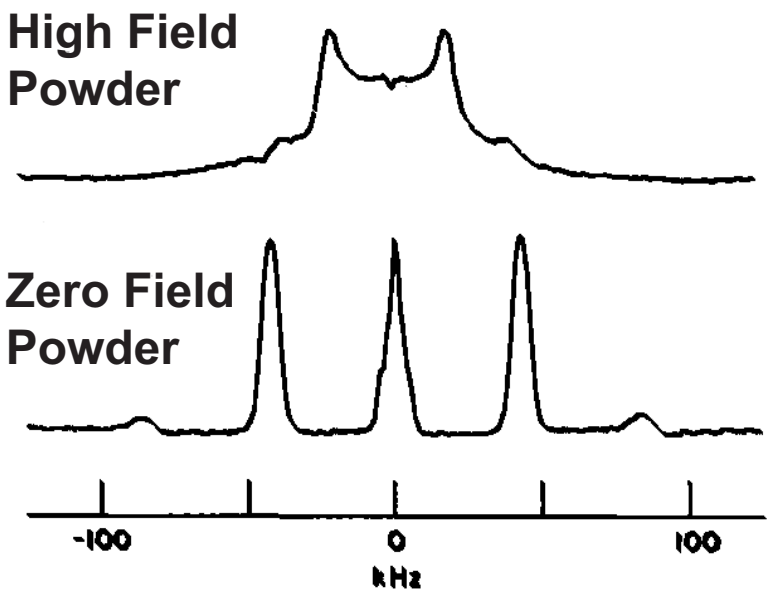


However, all of these methods for determining dipolar couplings have a theta dependence leading to anisotropic spectra.

Field Cycling Experiments

Field cycling experiments utilize the fact that in zero field a dipolar coupling exists as 3 sharp lines:





Weitekamp, Bielecki, Zax, Zilm, and Pines, Phys. Rev. Lett. (1983) 1807-1810.

Zero Field at High Field

$$H_D^{ZF} = \omega_D \left(\vec{I^1} \cdot \vec{I^2} - 3\left(\vec{I^1} \cdot \hat{r}_{12} \right)\left(\vec{I^2} \cdot \hat{r}_{12} \right) \right)$$

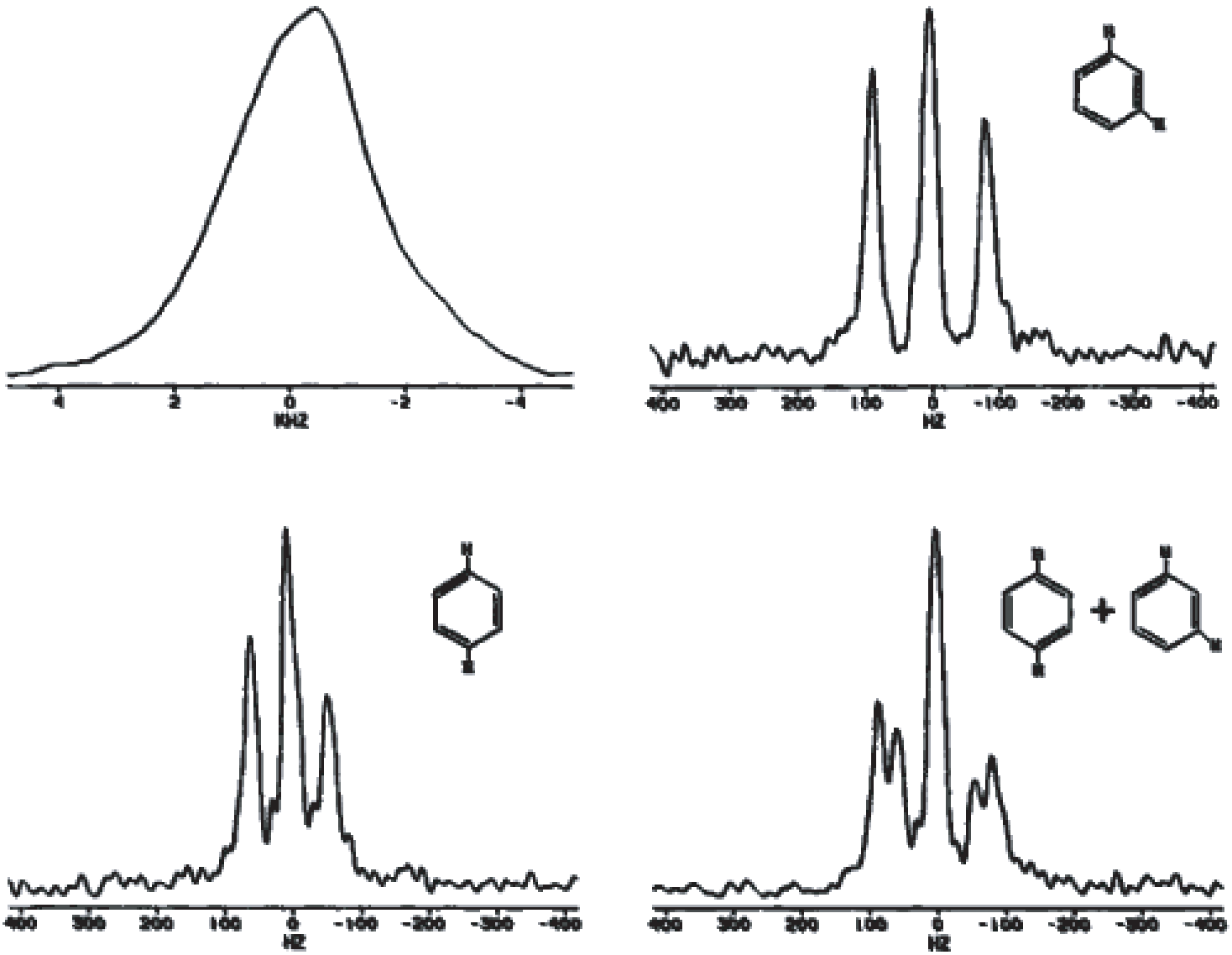
$$= \omega_D \sum_{m=-2}^{2} (-1)^m A_{2,m}^{12}(\theta_{12}, \phi_{12}) T_{2,-m}^{12}$$

$$H_D^{HF} = \omega_D A_{2,0}^{12} T_{2,0}^{12}$$

$$= \omega_D \sum_{l=0,2,4} C(2,2,l,0) F_{l,0}$$

$$\overline{H} \propto F_{0,0} = \sigma H_D^{ZF}$$

Tycko's ZFHF Results



R. Tycko, J. Chem. Phys. (1990) 5776-5793.

Inspiration

We want an isotropic spectrum similar to zero field.

$$H_D \propto \omega_D \left(3\cos^2\theta - 1\right)$$

So we have $\cos^2\theta$ ...

How can θ be eliminated to leave ω_D ?

Generating an Isotropic Signal

$$\rho(0) = I_z^1 + I_z^2$$

$$H = \omega_D h(\theta)(3I_x^1 I_x^2 - \overrightarrow{I^1}\overrightarrow{I^2})$$

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

for a time t not at the magic angle

$$\rho(t) = \cos(\frac{3}{2}\omega_D h(\theta)t)I_Z + i\sin(\frac{3}{2}\omega_D h(\theta)t)(T_{2,2} - T_{2,-2})$$

$$= \rho_0(t) + \rho_2(t)$$

$$\rho_o(\mathrm{t}) + \rho_2(t)$$

$$H^{EVO} = \omega_D(gA_{2,-2}T_{2,2} + gA_{2,2}T_{2,-2})$$

for a time τ

$$g(\theta) = \frac{3}{2} g \sin^2\theta$$

$$A_{22} = \frac{3}{4}\sin^2\theta \cdot e^{i2\phi}$$

$$\begin{aligned}\langle I_z(t,\tau)\rangle_1 &= Tr(\rho_o(t,\tau)I_z) \\ &= \cos(\omega_{\mathrm{D}} h(\theta)t) \\ &\quad \cdot\cos(\omega_{\mathrm{D}} g(\theta)\tau)\end{aligned}$$

$$\begin{aligned}\langle I_z(t,\tau)\rangle_2 &= Tr(\rho_2(t,\tau)I_z) \\ &= -\cos(2\phi) \\ &\quad \cdot\sin(\omega_{\mathrm{D}} h(\theta)t) \\ &\quad \cdot\sin(\omega_{\mathrm{D}} g(\theta)\tau)\end{aligned}$$

$$H_{\pm 1}^{DET} = \omega_D f (A_{2,\pm 1} T_{2,2} - A_{2,\mp 1} T_{2,-2})$$

for a constant time τ_{DET}

$$S_1 = \langle I_z(t,\tau) \rangle_1 = -\cos(\omega_D h(\theta) t) \cdot \cos(\omega_D g(\theta)\tau) \cdot \sin^2(\omega_D f(\theta)\tau_{DET})$$

$$S_2 = \langle I_z(t,\tau) \rangle_2 = \cos^2(2\phi) \cdot \sin(\omega_D h(\theta) t) \cdot \sin(\omega_D g(\theta)\tau) \cdot \sin^2(\omega_D f(\theta)\tau_{DET})$$

using:

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

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

$$\propto \cos\left[h\omega_D t(3\cos^2(\theta) - 1) \pm g\omega_D \tau \sin^2(\theta) \right]$$ Final Signal

adjust t and τ to add

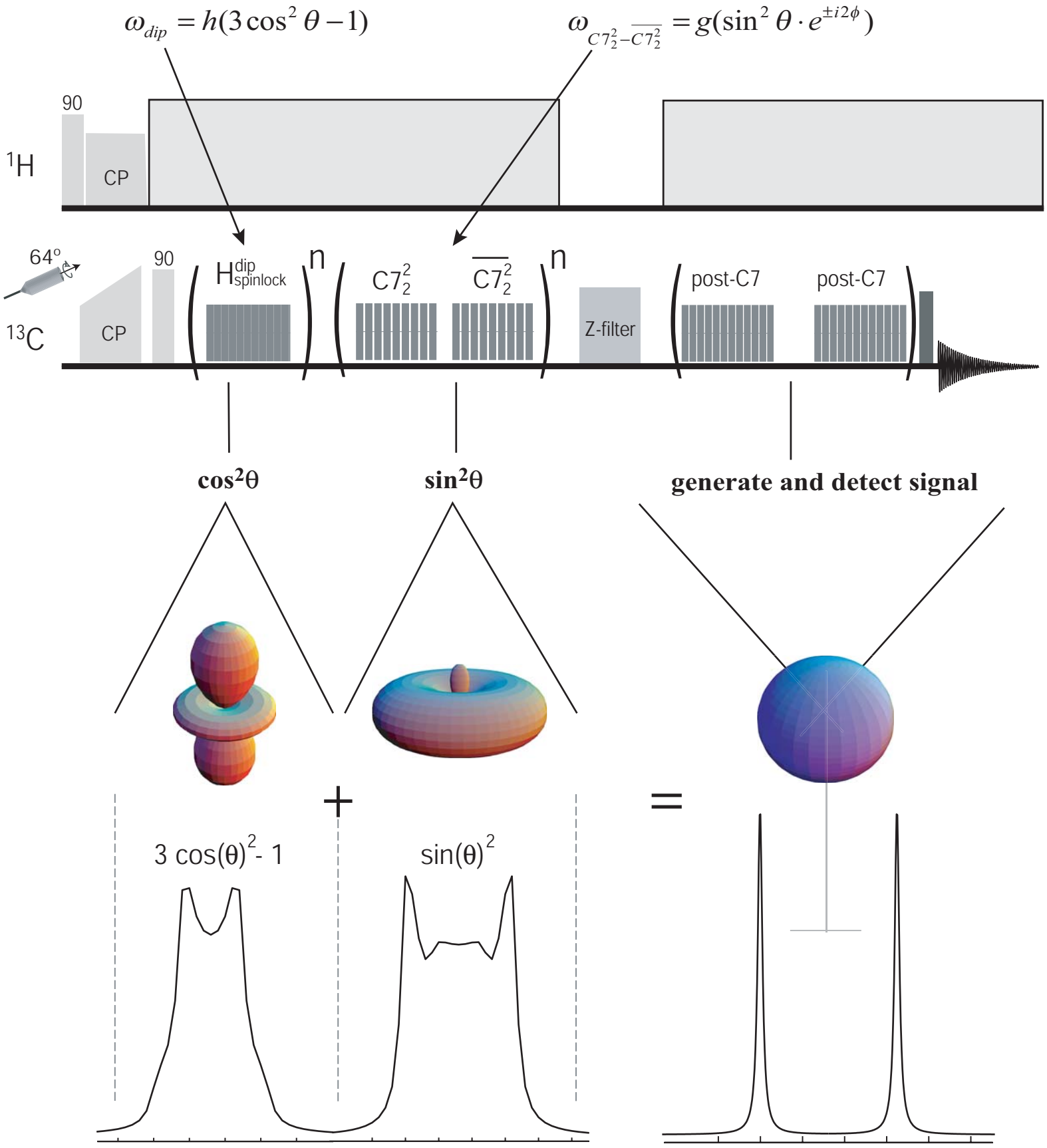
$$\propto \cos(\sigma \omega_D t_1)$$

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

$\sigma_{max} = 0.30$

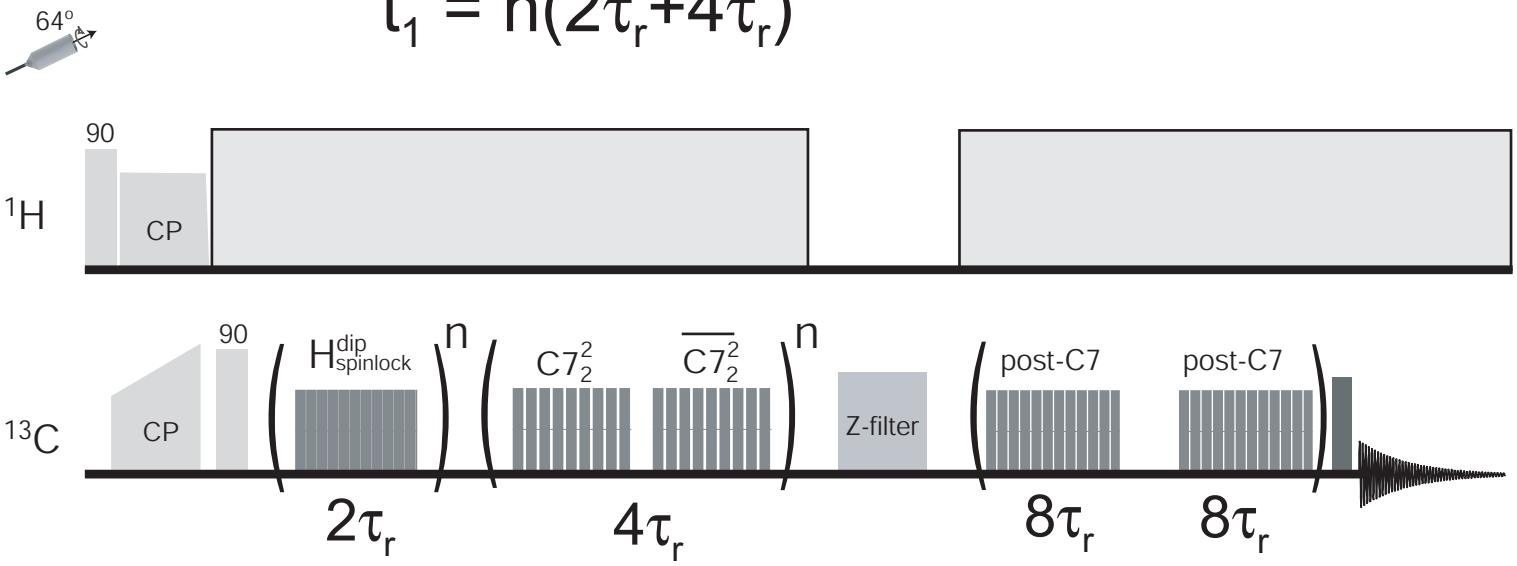
Homonuclear Isotropic Evolution

HOMIE Pulse Sequence



HOMIE Sequence Details

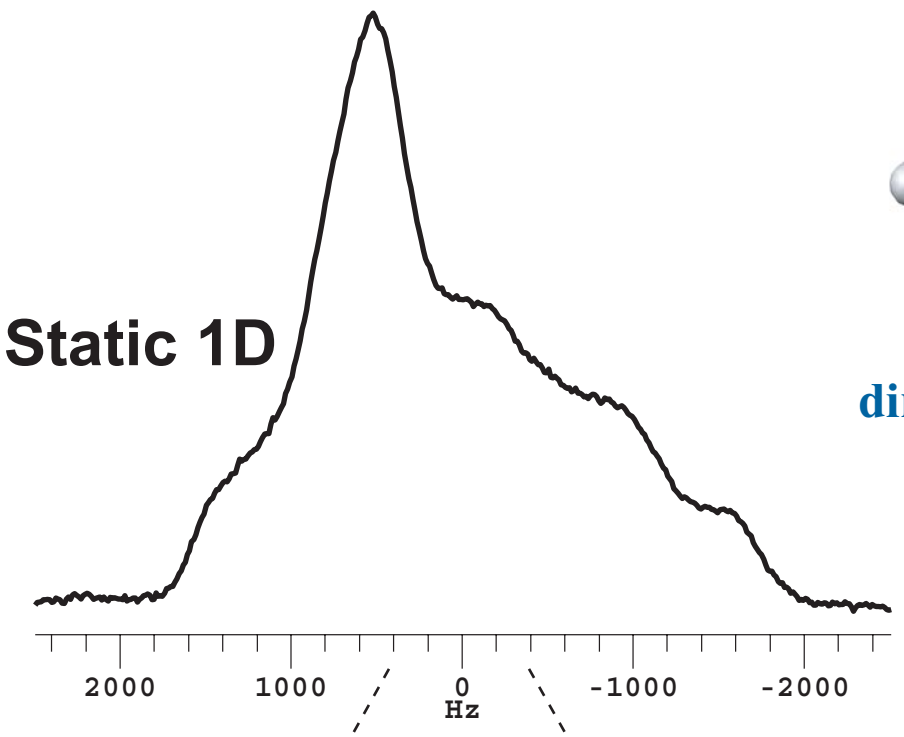
$$t_1 = n(2\tau_r + 4\tau_r)$$

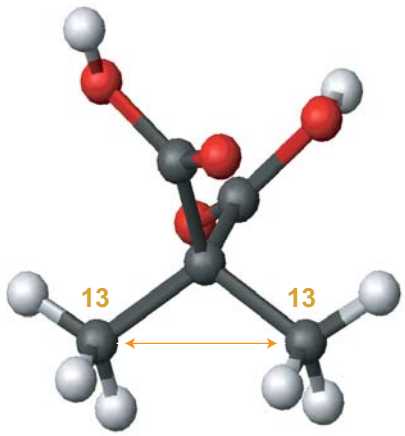


	experiment	Hdip phase	DET phase	post-C7	receive phase
S_1	X_1	0	0		-1
	X_2	0	90		1
	Y_1	90	0		-1
	Y_2	90	90		1
S_2	2x X_3	0	0	reverse order	1
	2x X_4	0	90	reverse order	-1
	2x Y_3	90	0	reverse order	-1
	2x Y_4	90	90	reverse order	1

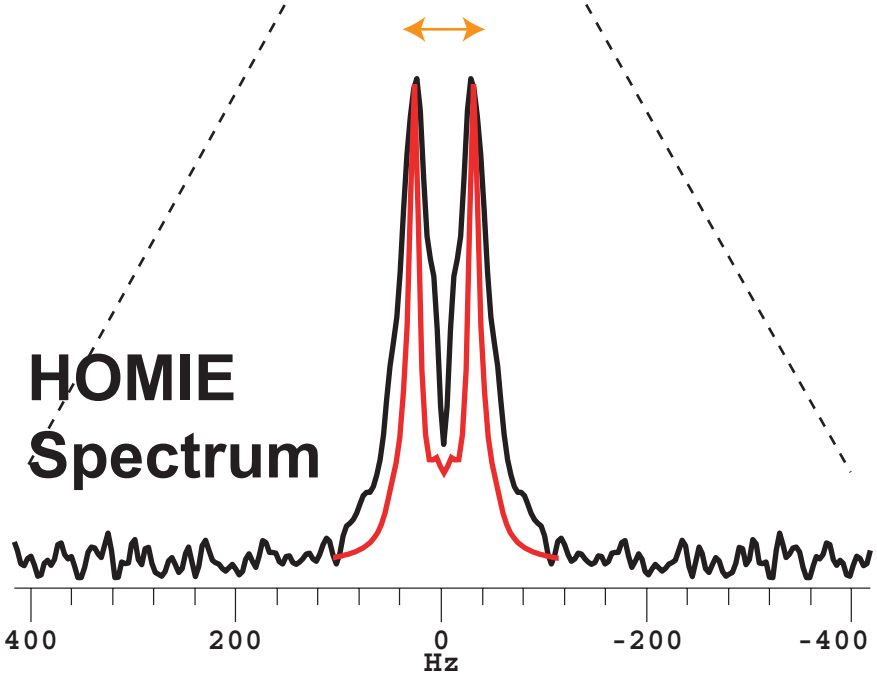
remaining signal $\cong 23\%$

Homonuclear Results





dimethyl-malonic acid

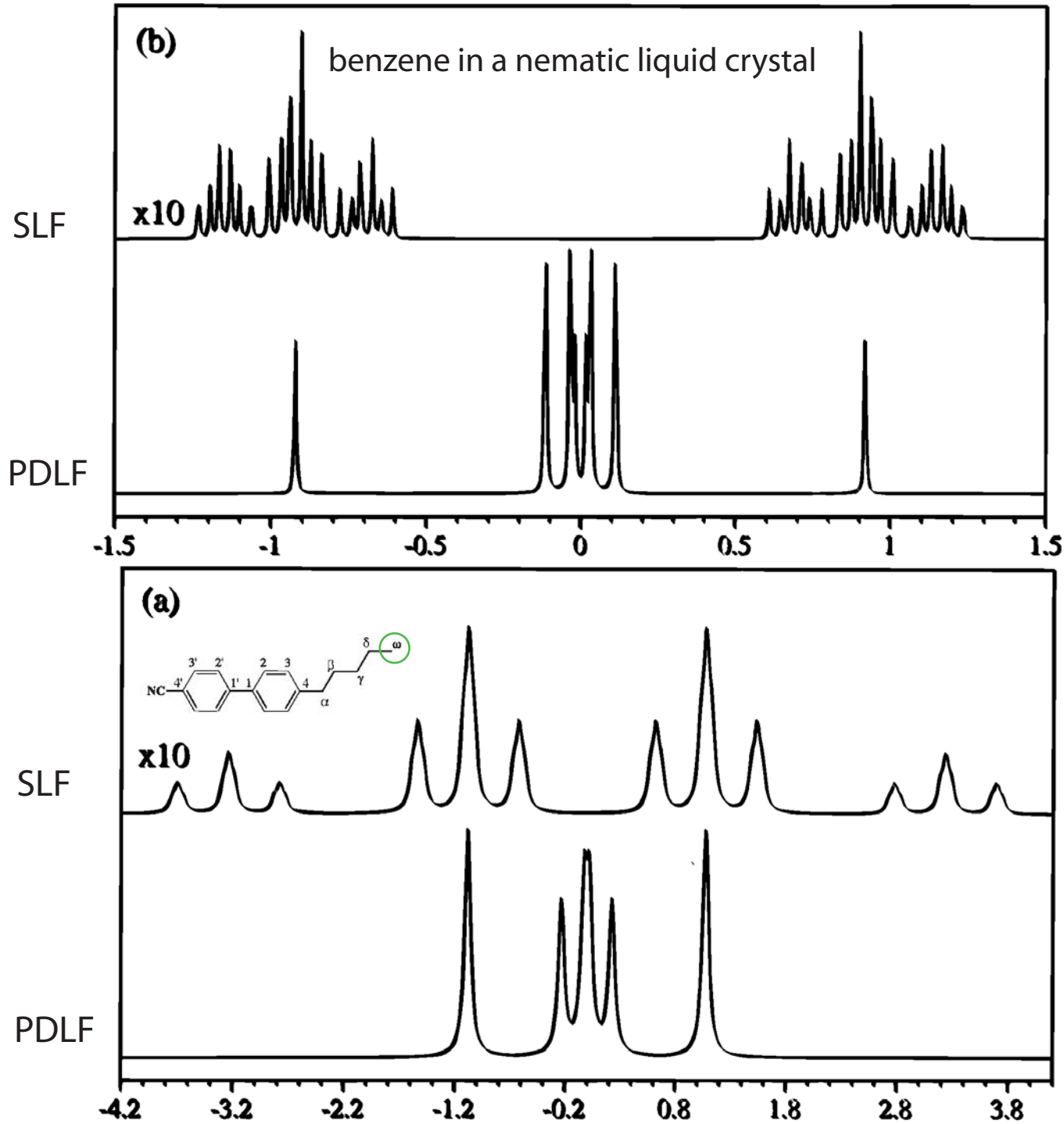


Experimental

Simulation

σ=0.056

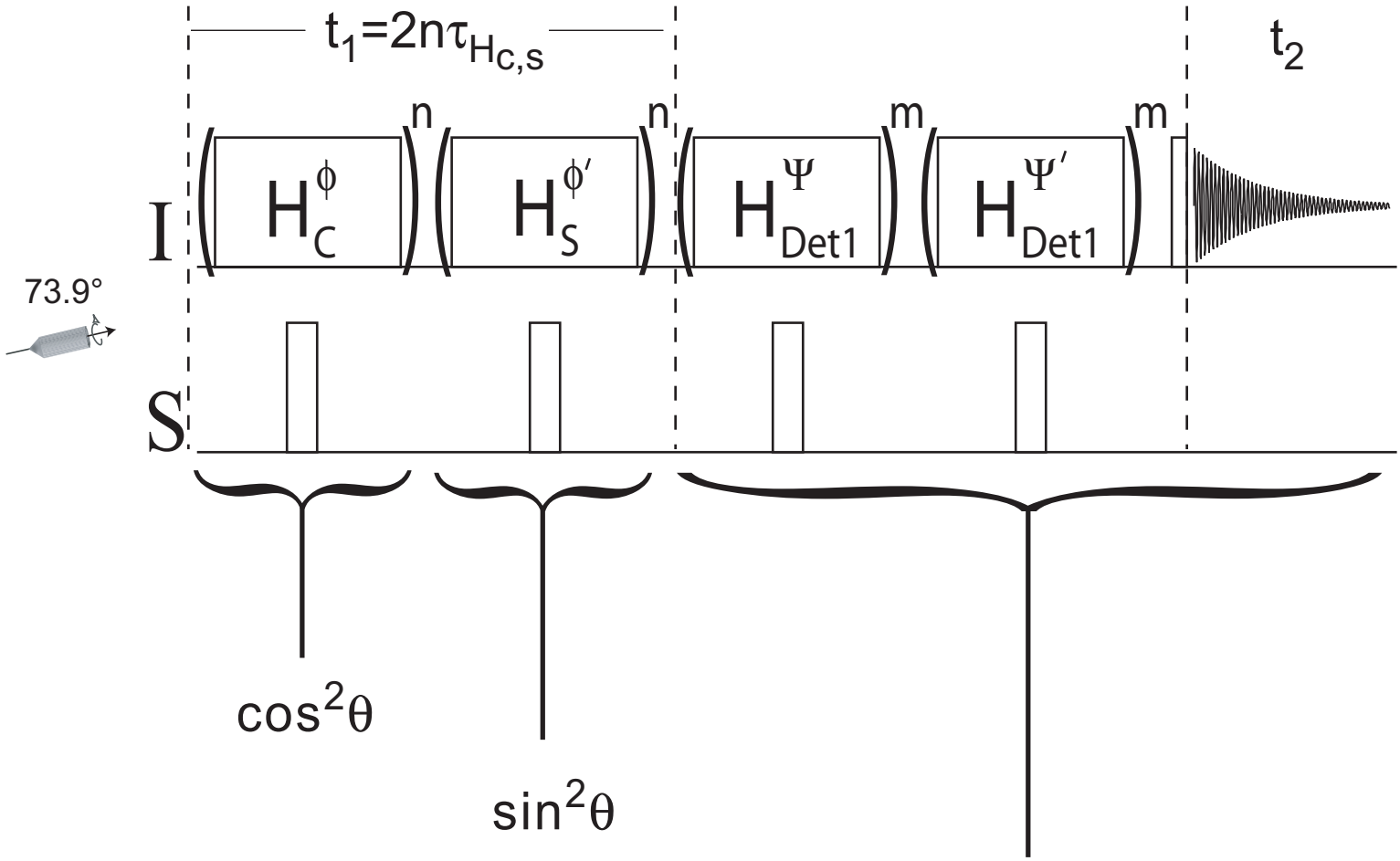
Local Field Spectroscopy



Caldarelli, Hong, Emsley and Pines, JPC 100, 18699.

Linear with the couplings

Heteronuclear Isotropic Sequence

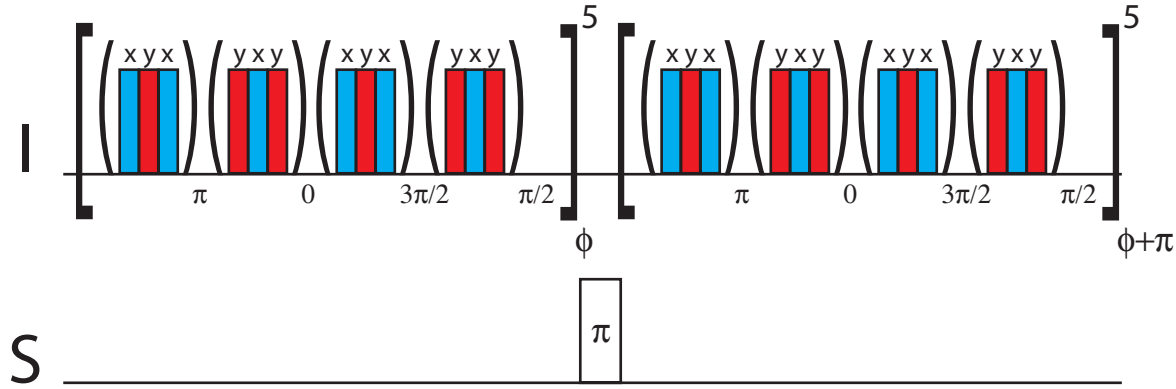


Generate and detect

$\sin^2\theta + \cos^2\theta = 1$

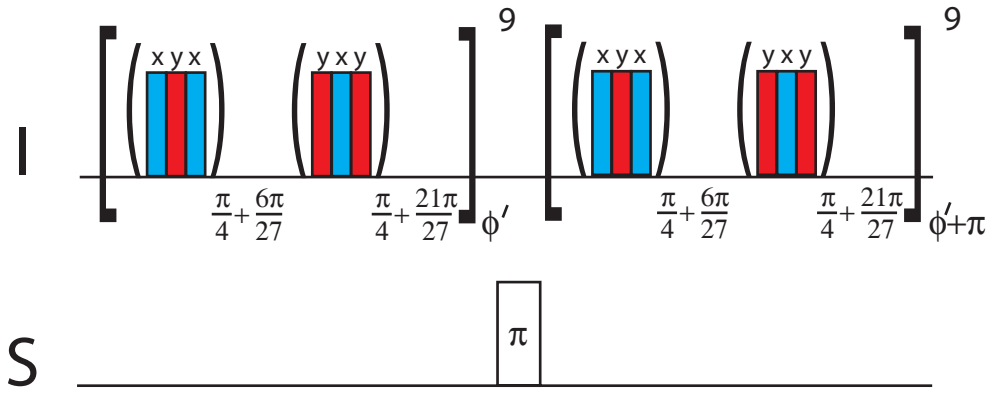
All while eliminating homonuclear dipolar couplings

$H_C^{\phi} =$



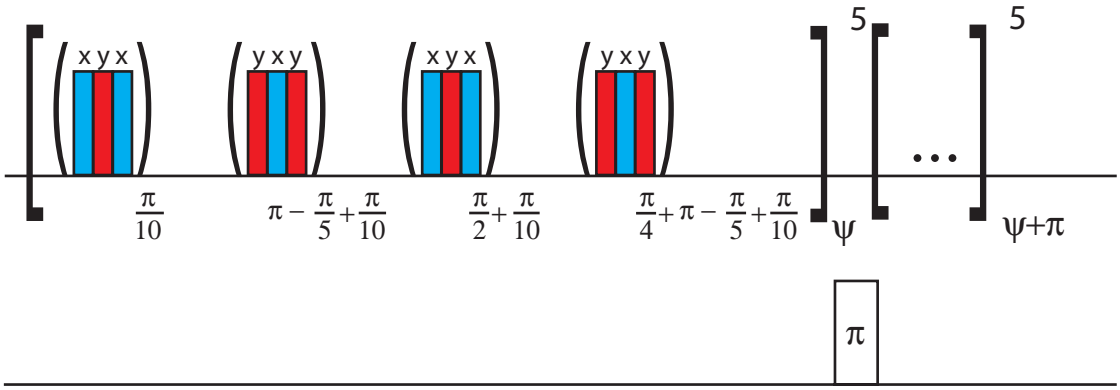
$$\overline{H}_C \propto \left(3\cos^2\theta_R - 1\right)\left(3\cos^2\theta - 1\right) I_X S_Z$$

$H_S^{\phi'} =$



$$\overline{H}_S \propto \sin^2\theta_R \sin^2\theta \left(e^{i2\phi} I_+ + e^{-i2\phi} I_-\right) S_Z$$

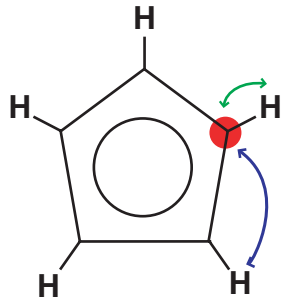
$H_{Det1}^{\psi} =$

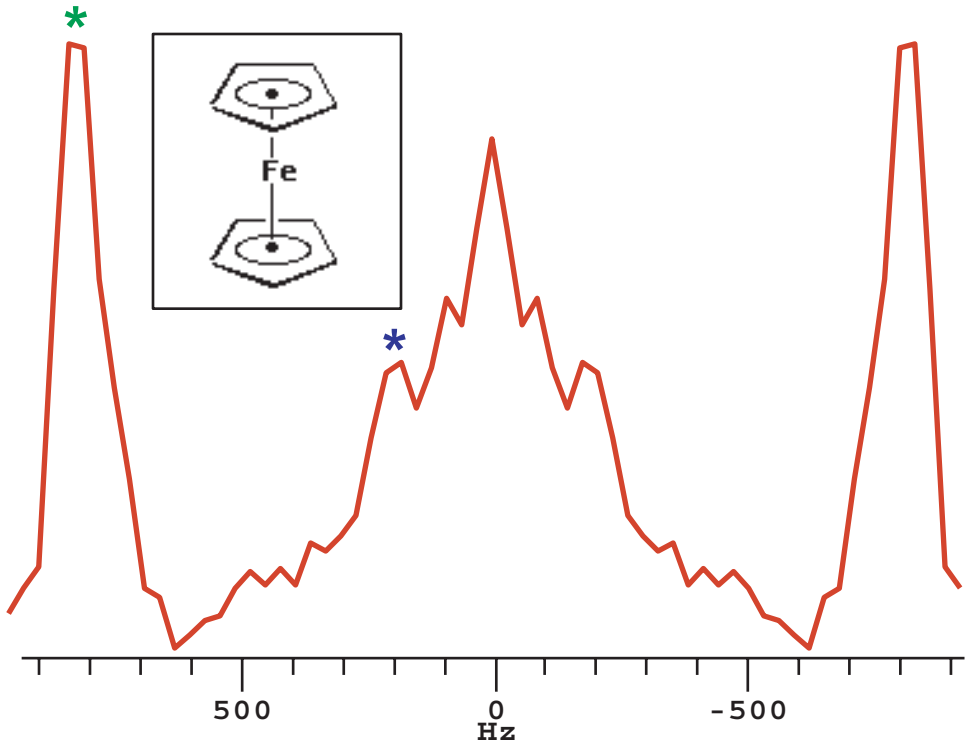


$$\overline{H}_{Det} \propto \sin 2\theta_R \sin 2\theta \left(e^{i\phi} I_+ - e^{-i\phi} I_-\right) S_Z$$

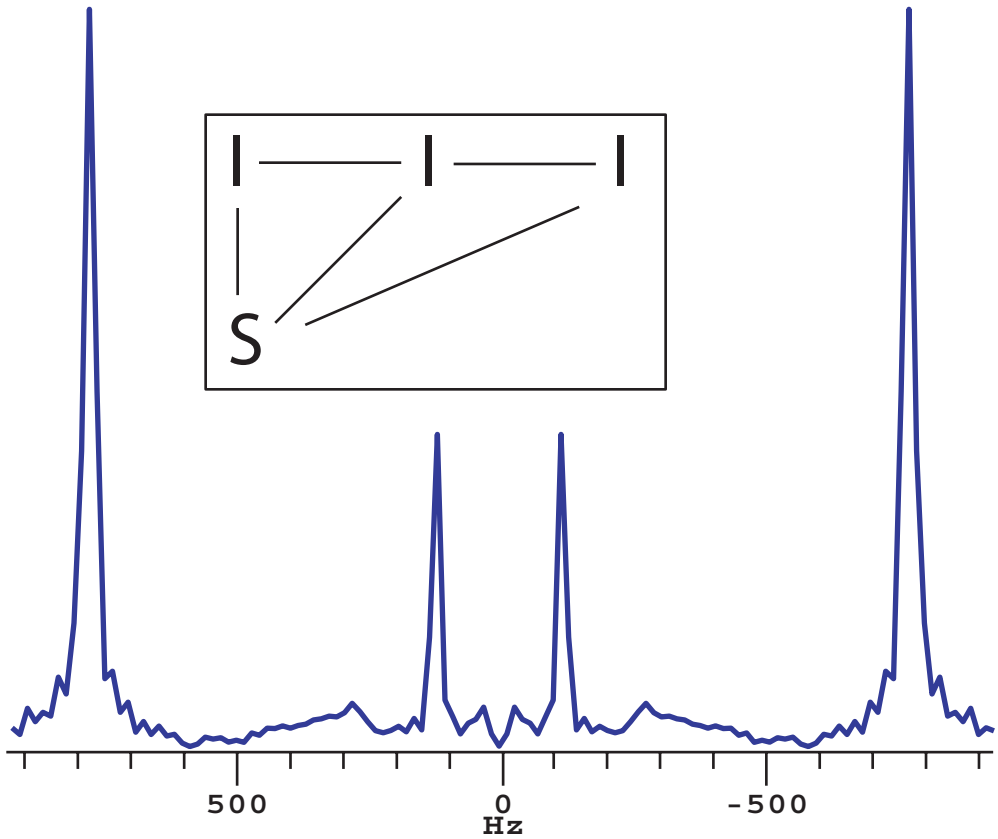
Heteronuclear Results

Experiment





Simulation

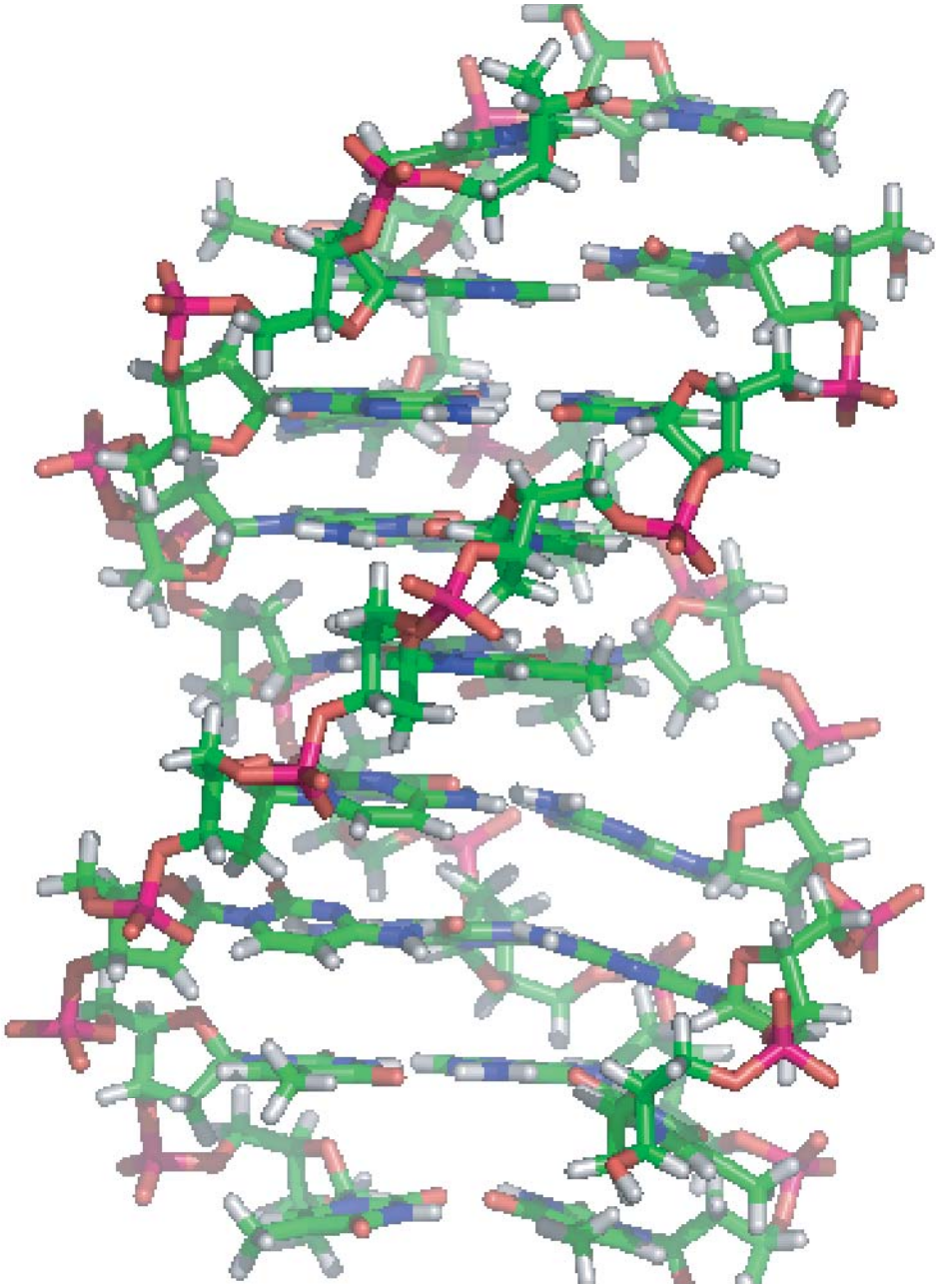


Scaling factor = 0.08

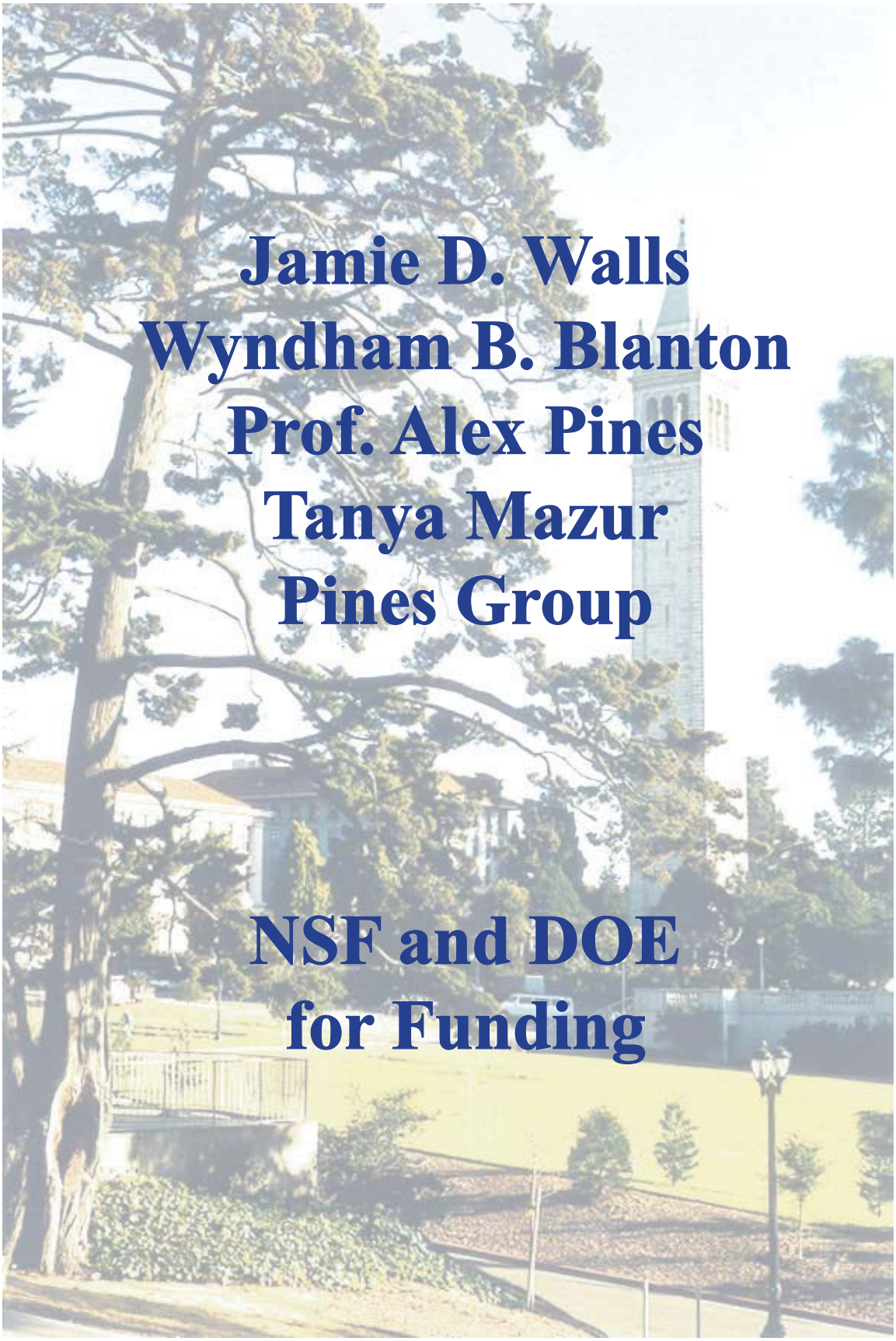
Future Possibilities

Using selectively introduced labels or even naturally occuring ones, we can approach NMR crystallography.

Additionally, angles can also be determined!



Acknowledgements



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