Two-dimensional correlation spectroscopy in solids

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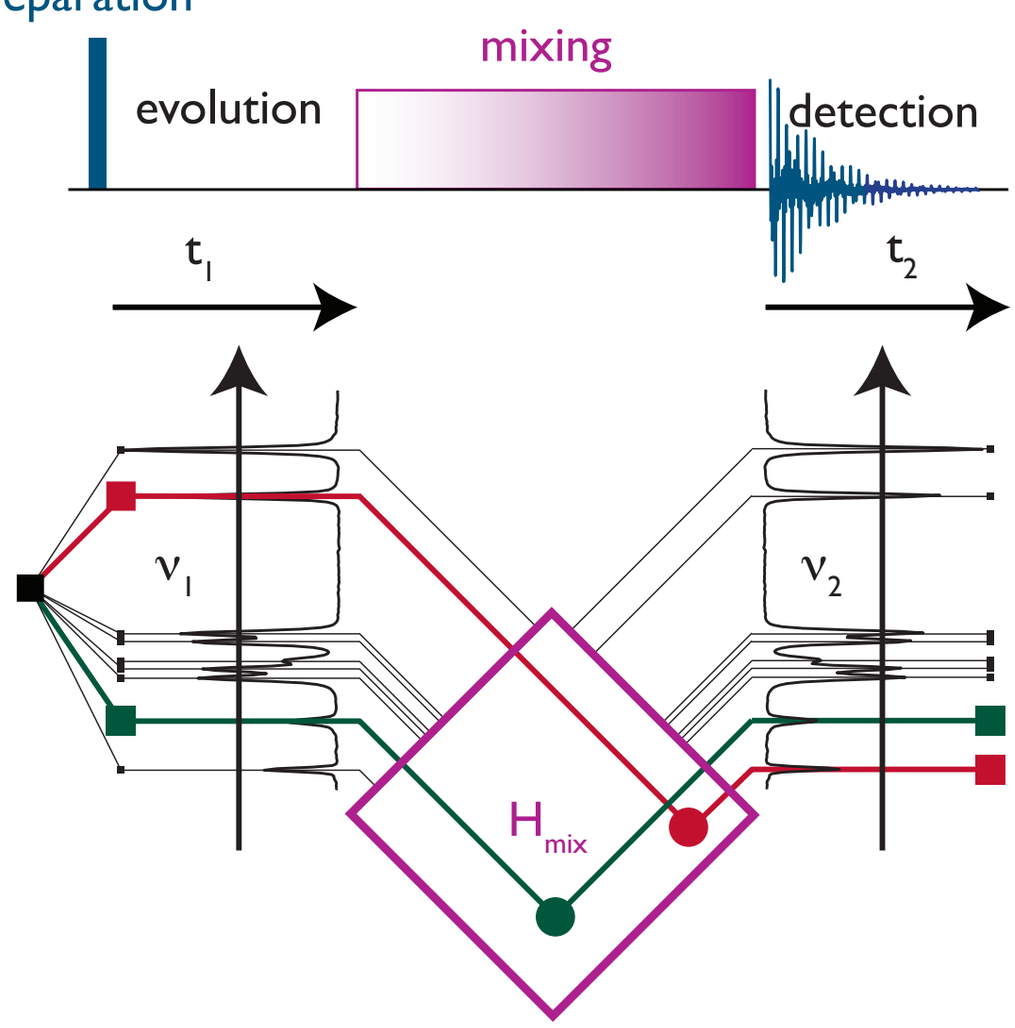
Two-dimensional correlation spectroscopy

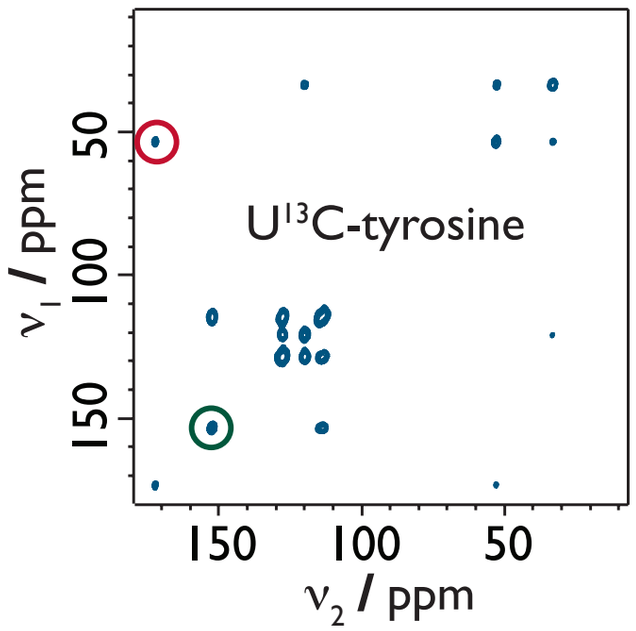
A two-dimensional correlation experiment consists of four time periods: Preparation, evolution, mixing and detection.

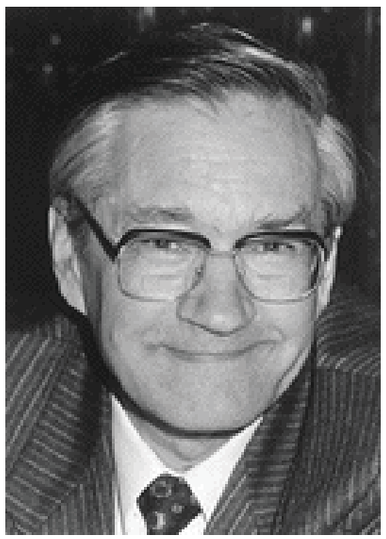
- Magnetization is transferred between the spins during the mixing period.
- The signal $S(t_1,t_2)$ is a function of both the evolution and the detection time.

A two-dimensional Fourier transform generates a two-dimensional spectrum $S(\nu_1,\nu_2)$.



two-dimensional Fourier transform





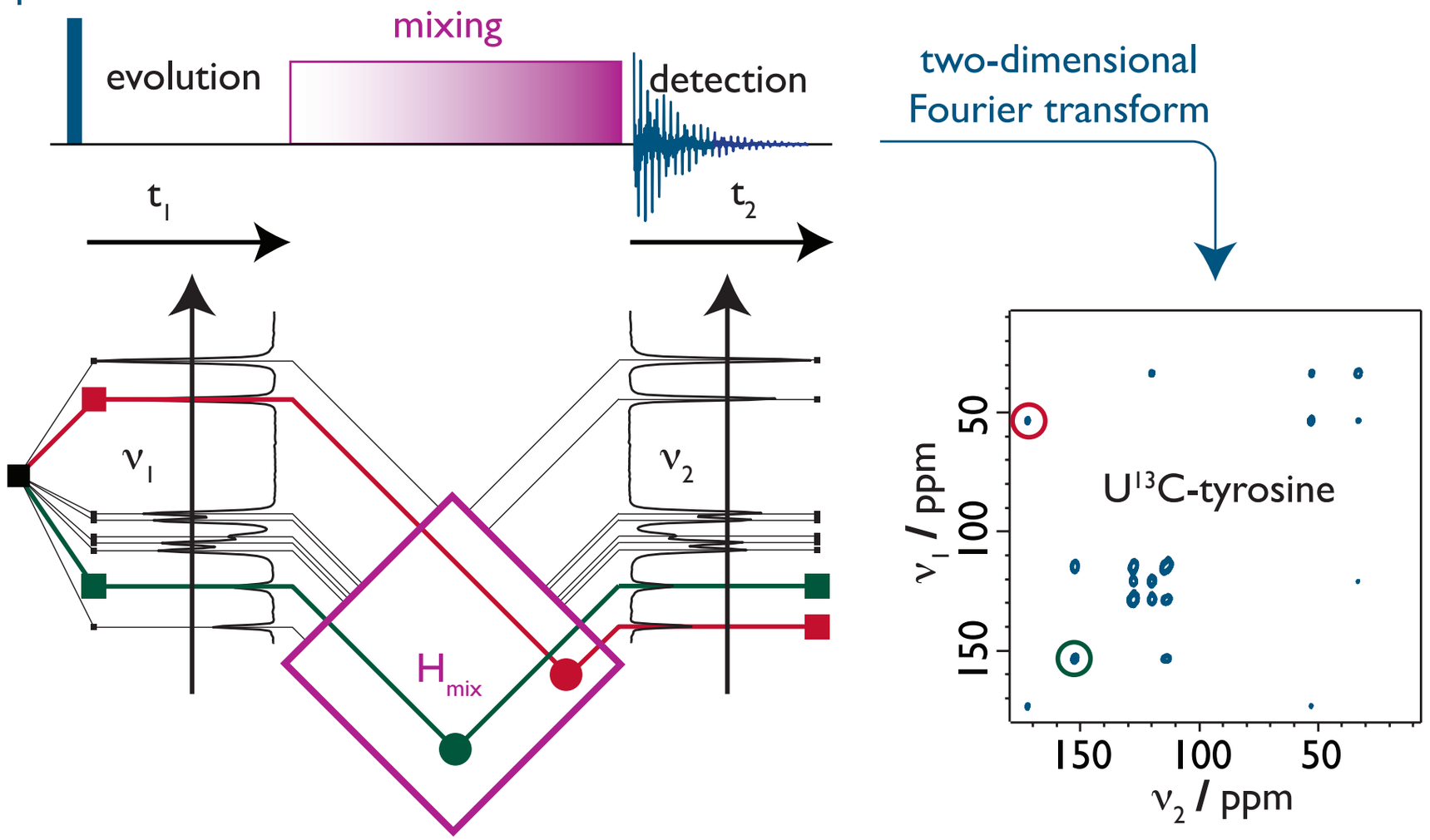
Richard Ernst

Cross and diagonal peaks

Two types of peaks can be observed in correlation spectra:

- Diagonal peaks for which $\nu_1 = \nu_2$. This indicates that the mixing process did not transfer magnetization between spins.
- Cross peaks for which $\nu_1 \neq \nu_2$. This indicates that magnetization has been transferred from a spin precessing at a frequency ν_1 in the first dimension to a spin precessing at ν_2 in the second.

The nature of the mixing process dictates the information content of the two-dimensional spectrum.



Types of correlation

Dipolar correlations

- Cross peaks link pairs of spins which are dipolar coupled to one another. These are close together in space, but not necessarily bonded.
- Because the magnitude of the dipolar interaction depends on the internuclear distance, these experiments can be used to measure atomic separations in molecules.
- The dipolar coupling is motionally averaged in solution, so cross relaxation is used. In a solid the magnetization transfer can be achieved coherently.

Scalar correlations

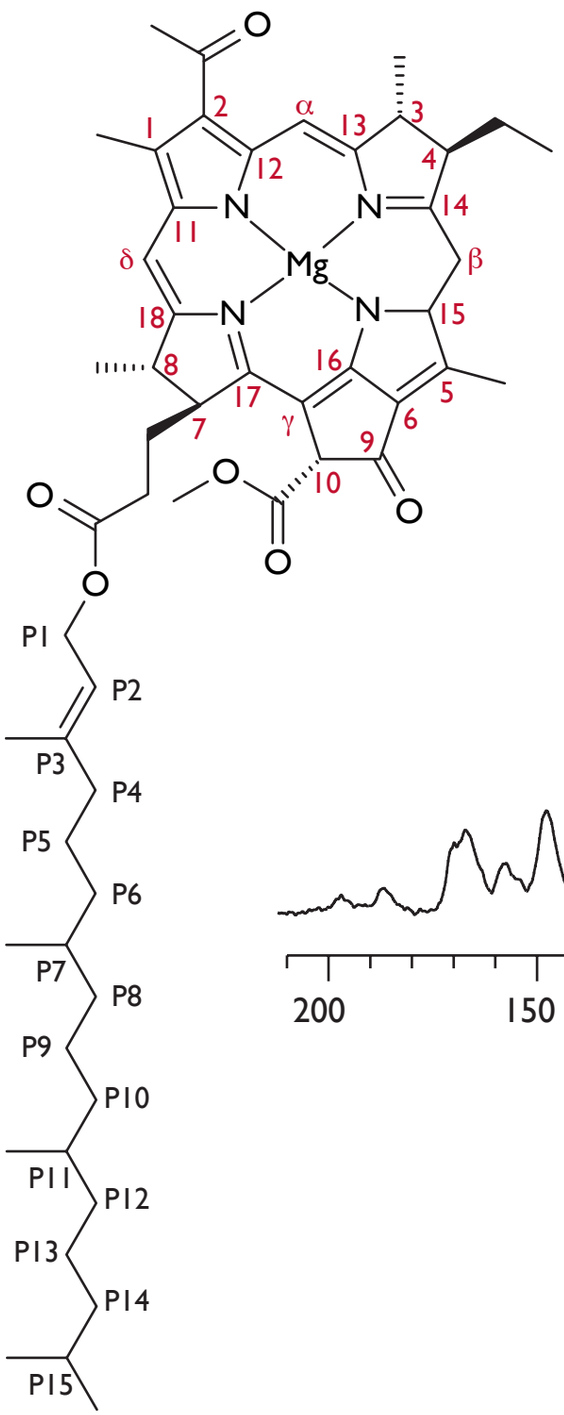
- Cross peaks link pairs of spins with a mutual J coupling. Because this interaction requires a chemical bond between the coupled spins, cross peaks link sites in the molecule which are bonded together.
- This is useful for assigning lines in a complicated spectrum to sites in the molecule and for establishing molecular structure.

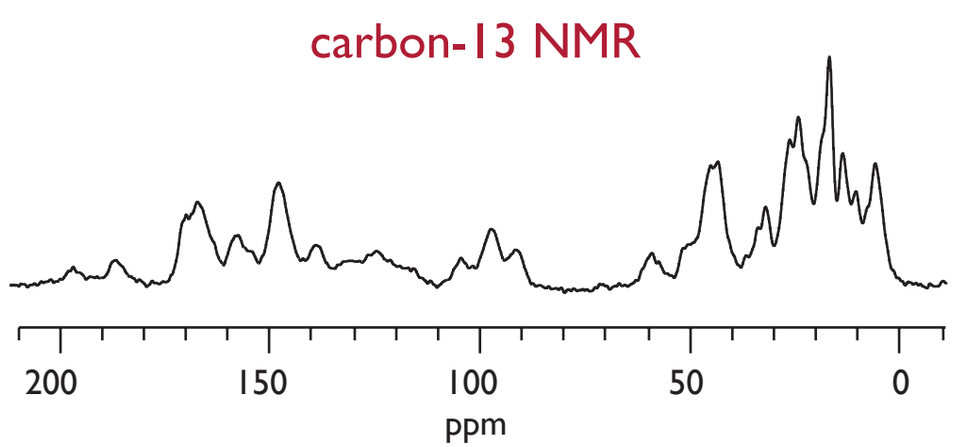
Philosophy

"Solution-like" approach:
Rapid MAS, Efficient Decoupling
$H = H_{iso}$
No orientational information; recoupling

"Classical solids" approach:
Slow (or no) MAS
H = ?
Retain orientational information

Carbon-13 assignment for bacteriochlorophyll a



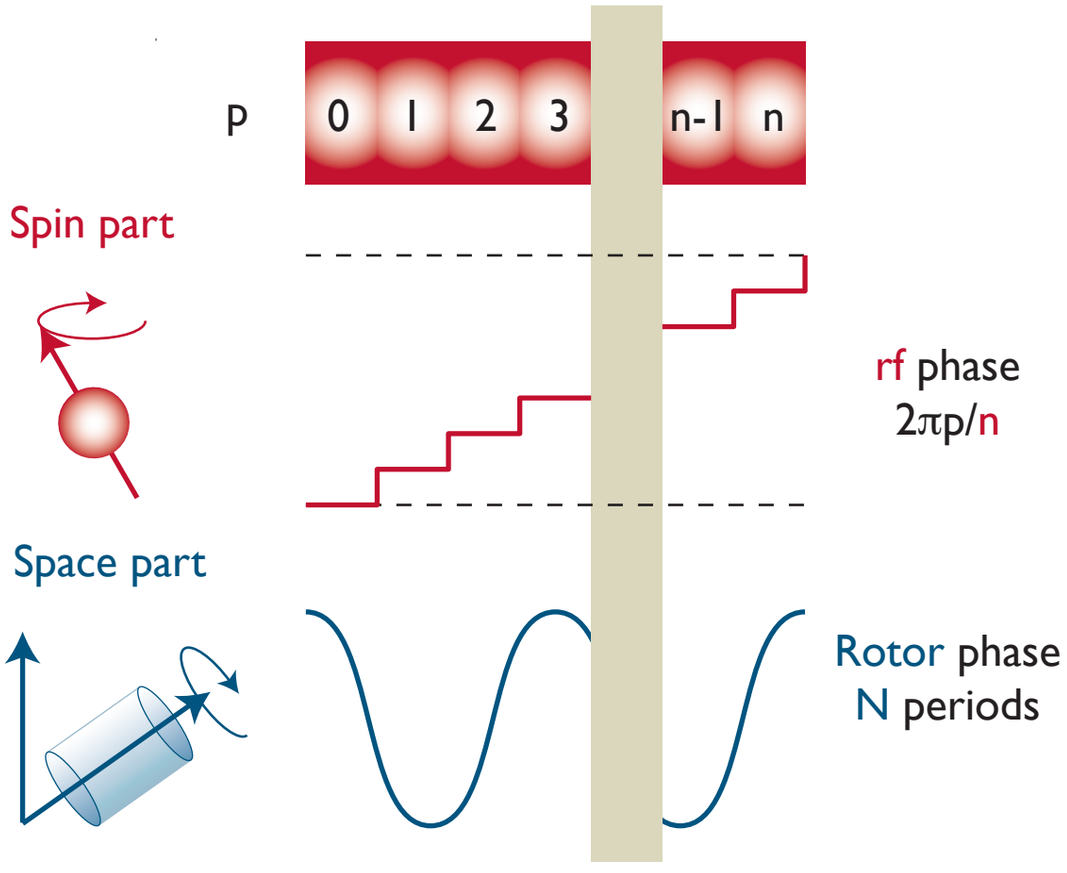


What is the assignment of the sites to the resonances?

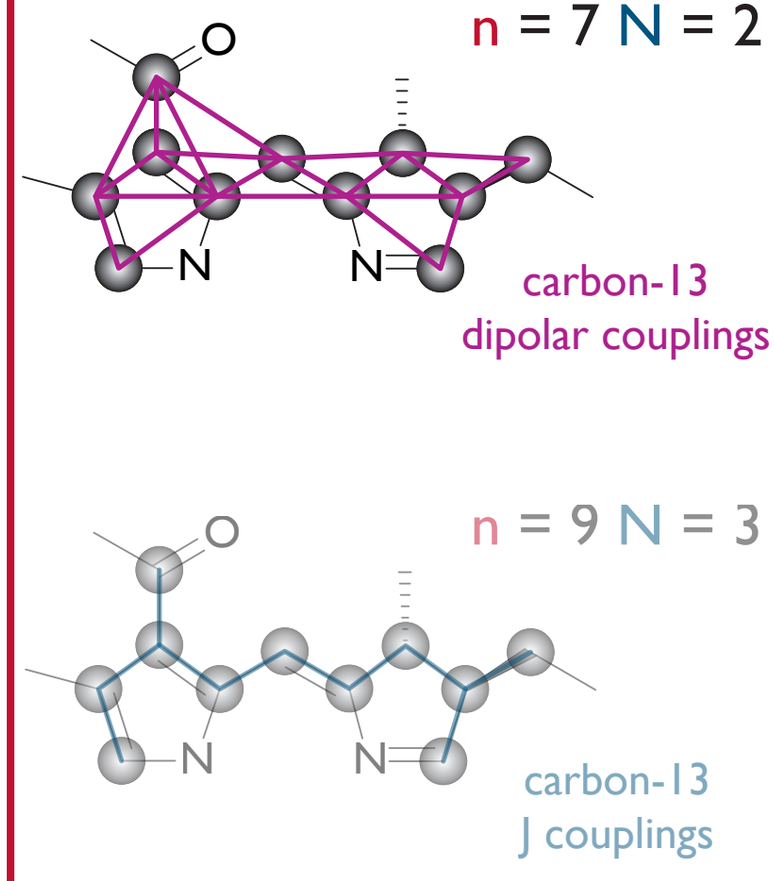
Dipolar recoupling

The double-quantum dipolar Hamiltonian is recoupled in the mixing period, causing magnetization transfer between dipolar-coupled spins.

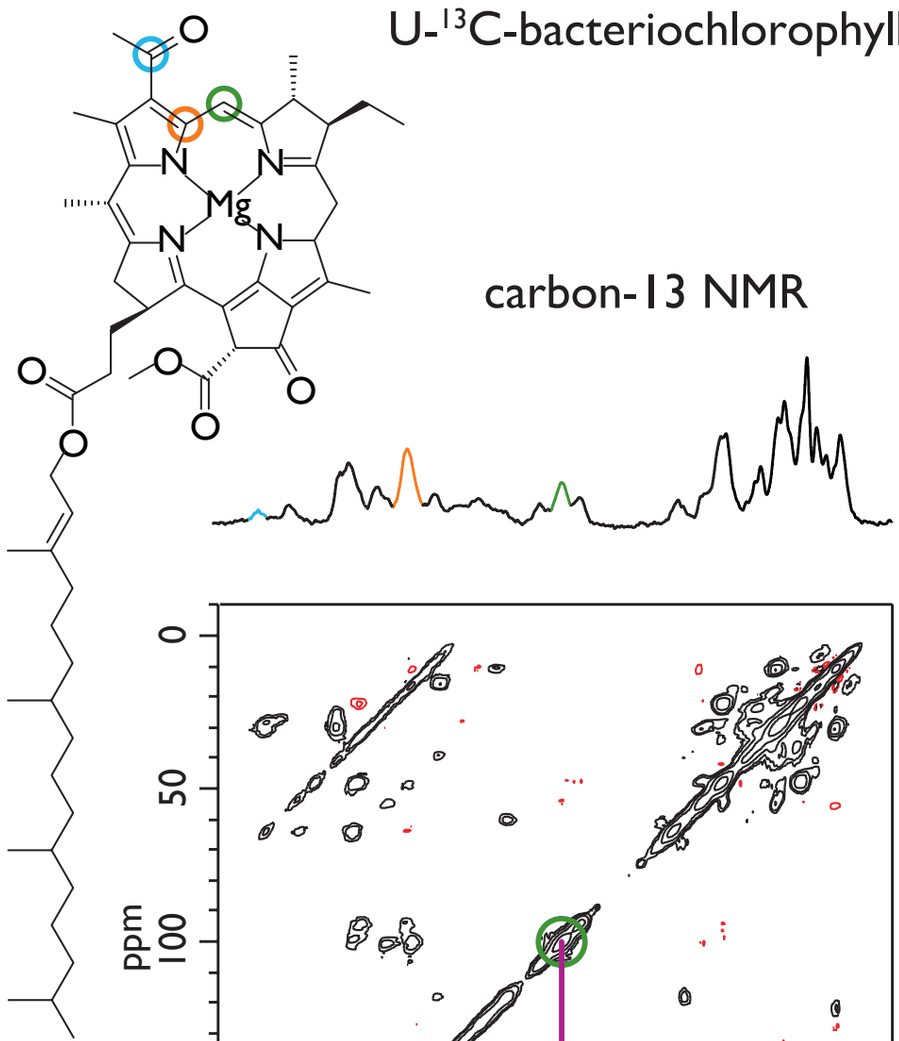
$$H_{mix} \propto \left(I_1^+ I_2^+ + I_1^- I_2^- \right)$$

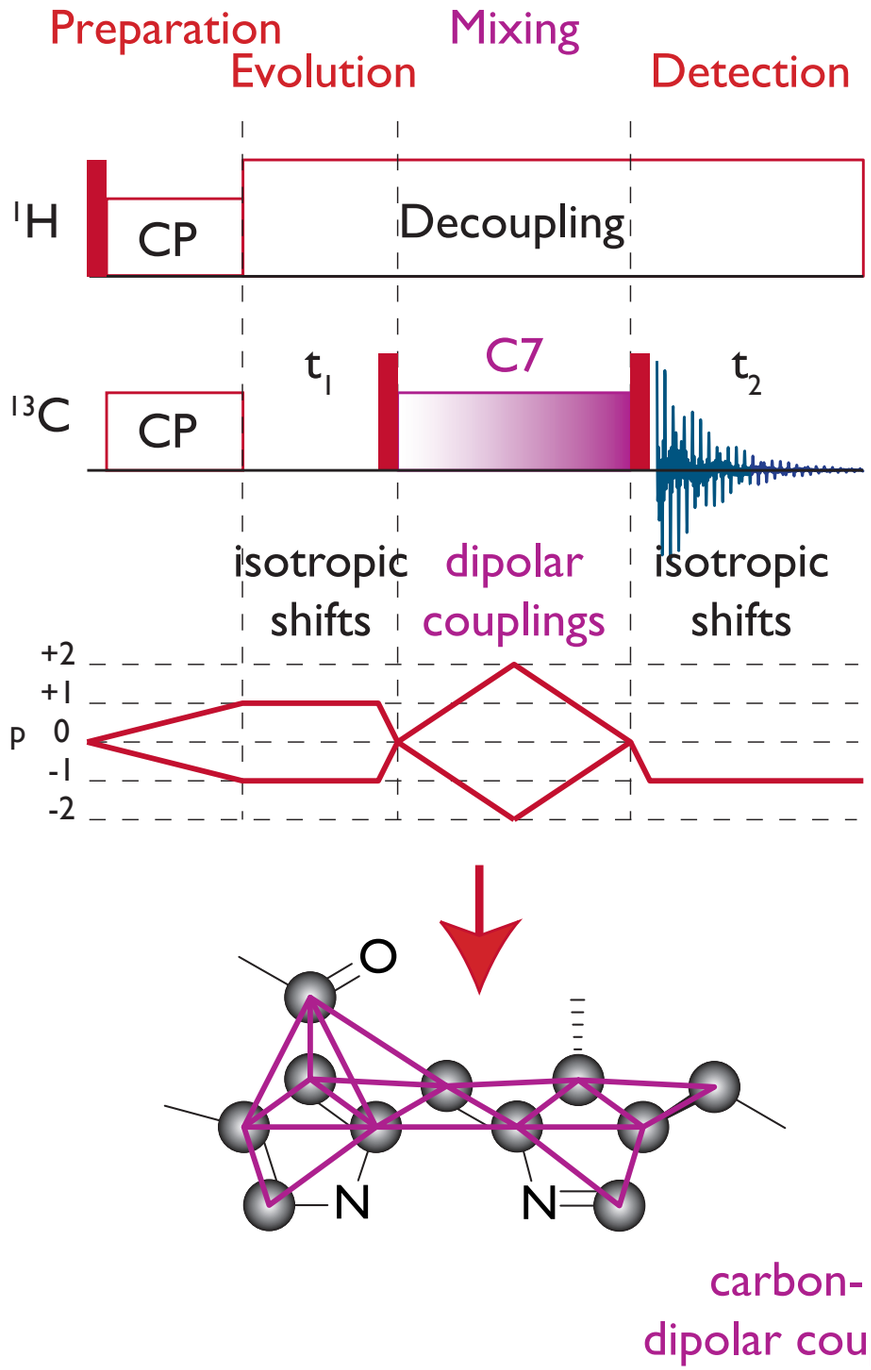


Average Hamiltonian



Dipolar correlation



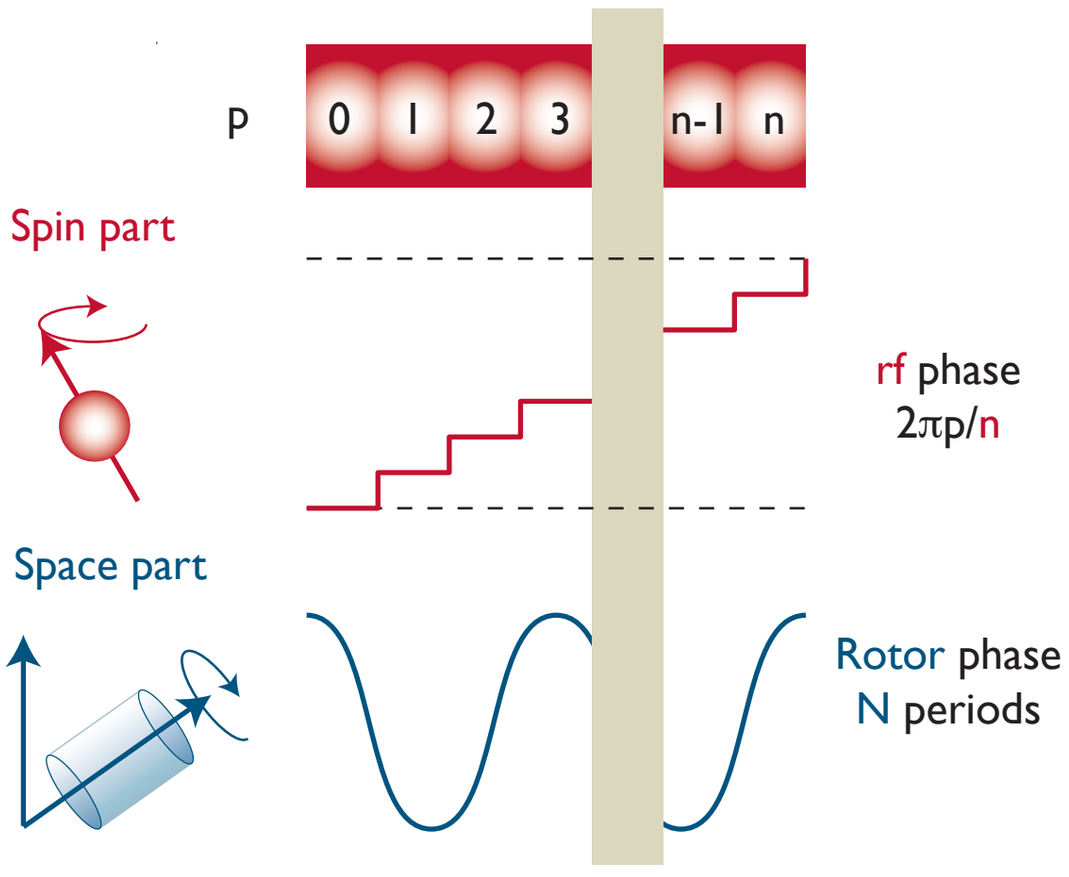


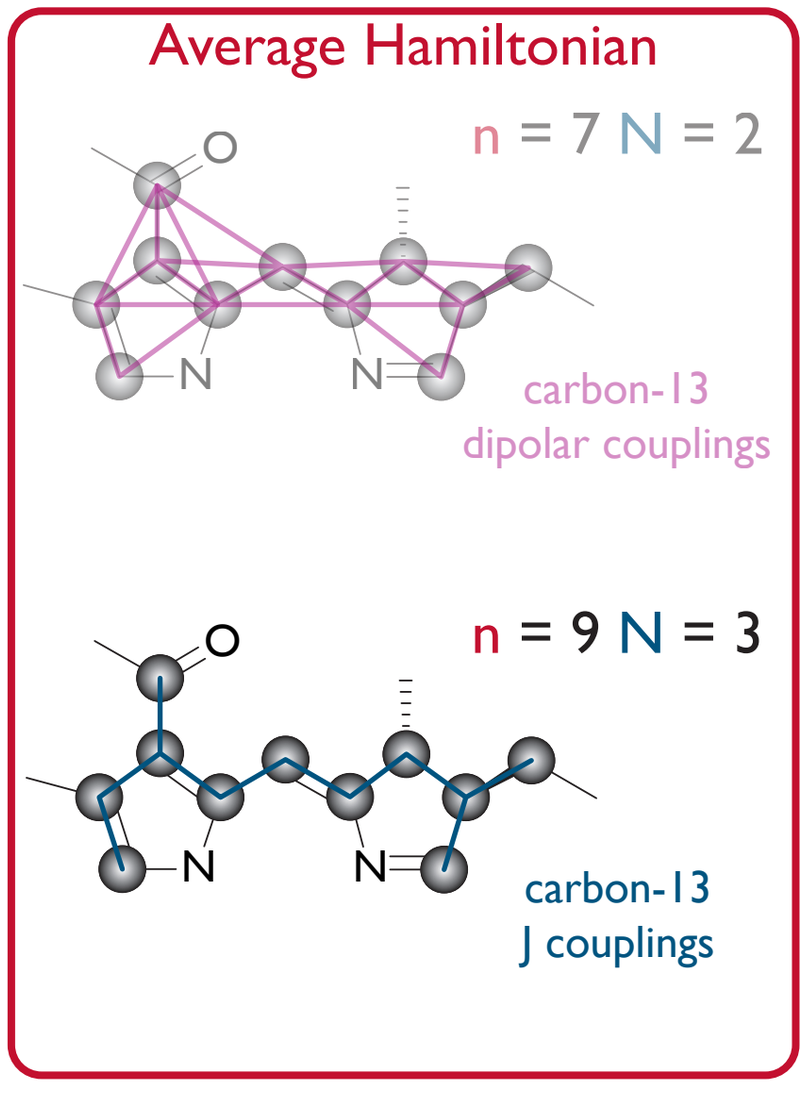
carbon-13
dipolar couplings

Pulse sequence symmetry

Changing the pulse sequence symmetry reintroduces the isotropic mixing scalar Hamiltonian during the mixing time, causing magnetization transfer between scalar-coupled spins.

$$H_{mix} = 2\pi J \mathbf{I}_2 . \mathbf{I}_2$$



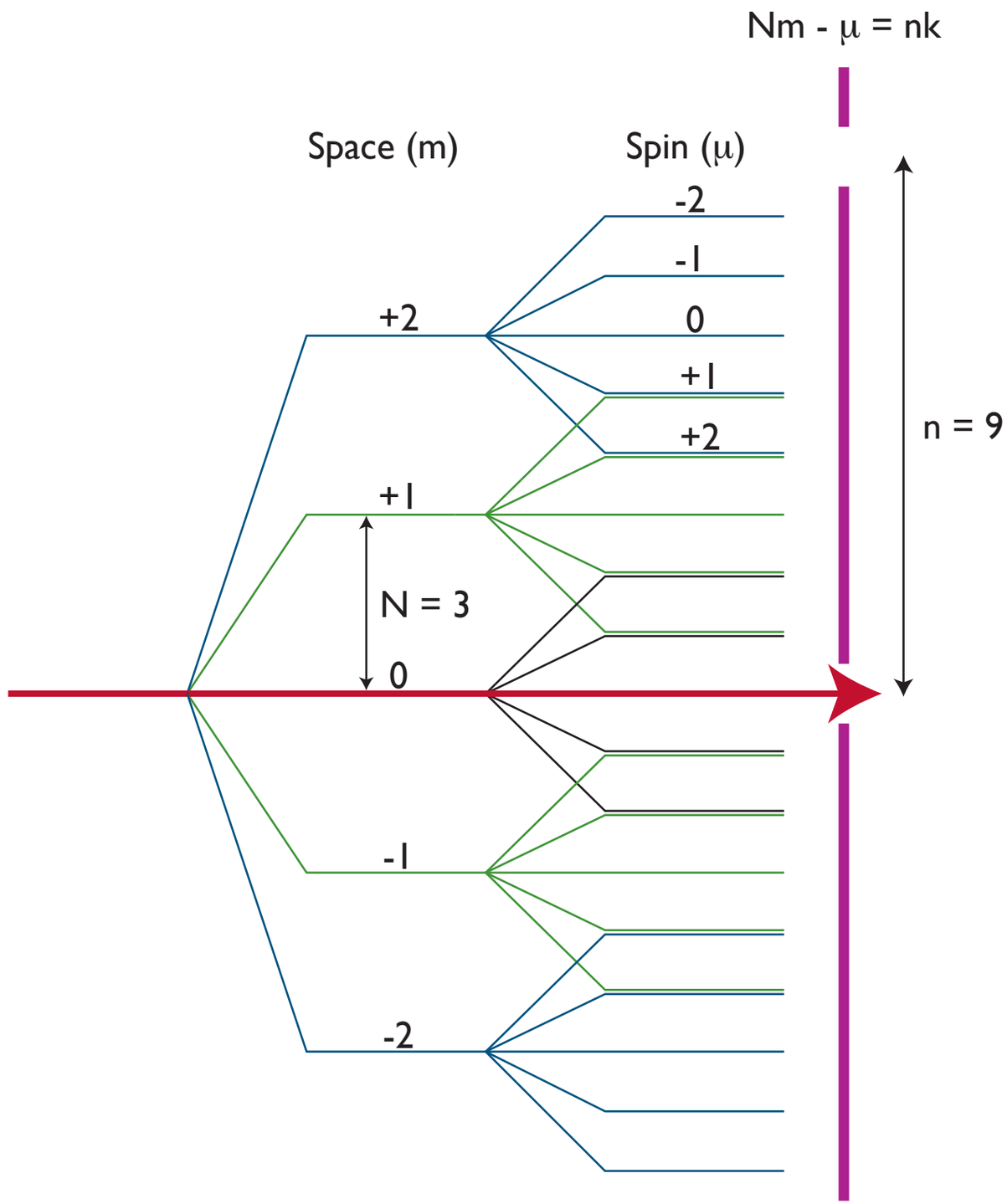


C9 sequence

The spin-space selection diagram illustrates which combinations of spin and space components are retained in the average Hamiltonian for the recoupling sequence.

The spin-space selection diagram shows that with n = 9 and N = 3 only space-spin $(m, \mu) = (0,0)$ components are retained in the average Hamiltonian.

$$\bar{H}^{(0)} = 2\pi J \mathbf{I}_2 . \mathbf{I}_2$$



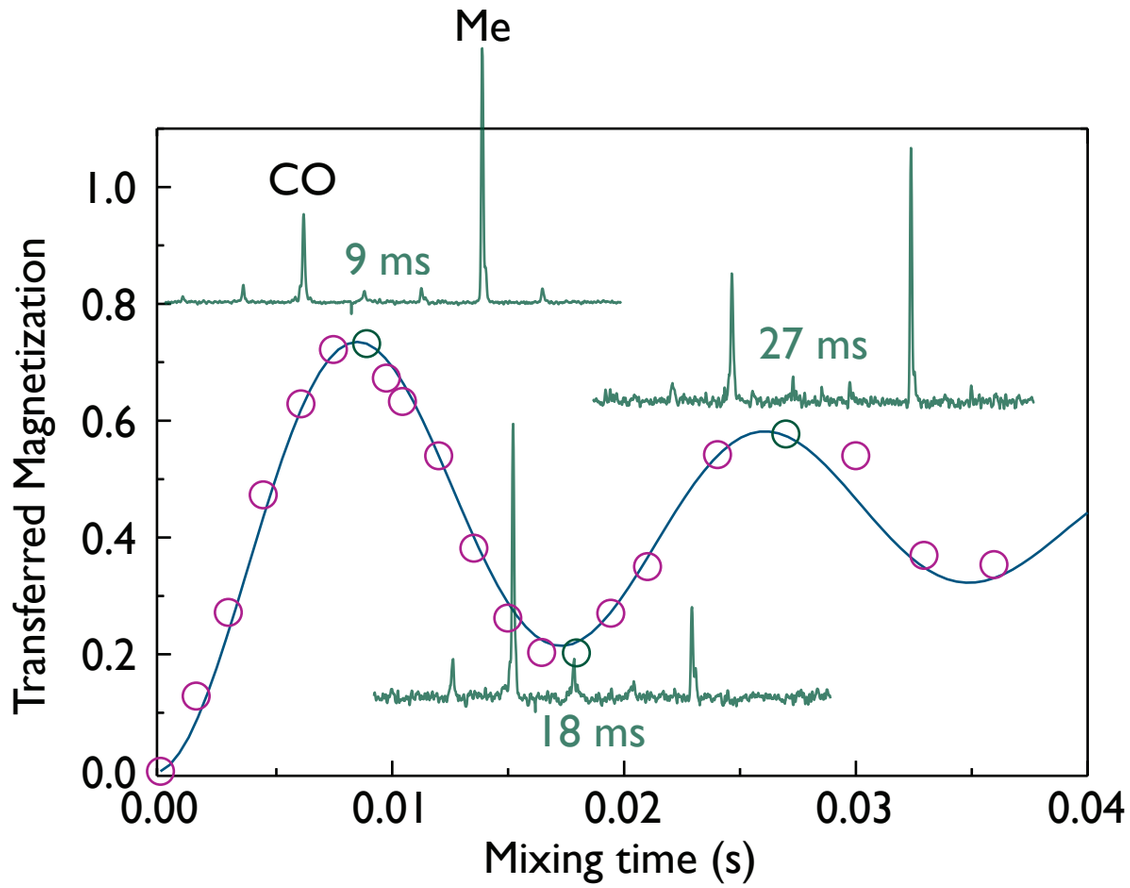
A. S. D. Heindrichs, H. Geen and J. J. Titman, *Chem. Phys. Lett.*, **335**, 89 (2001).

Isotropic mixing

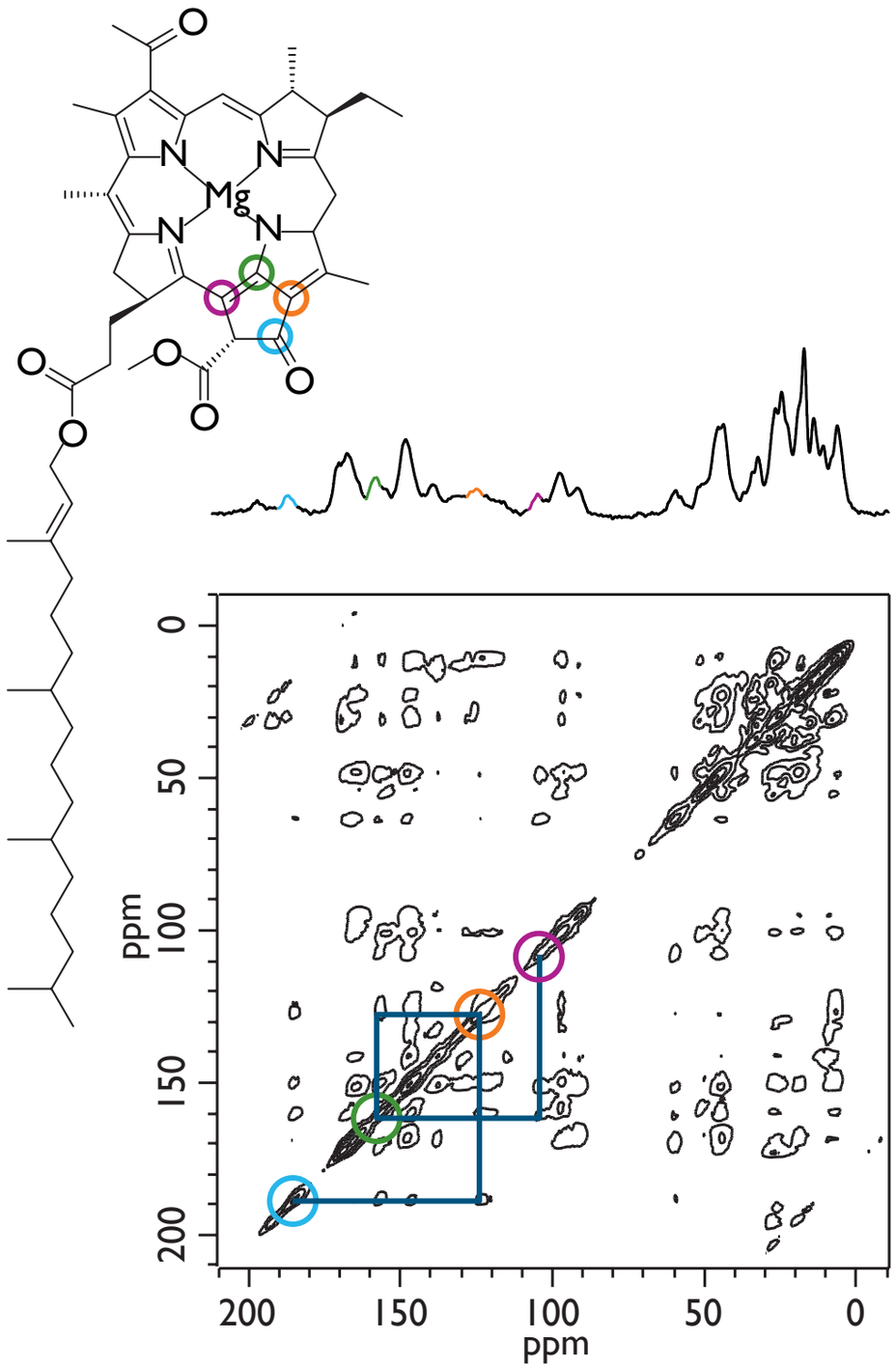
Isotropic mixing

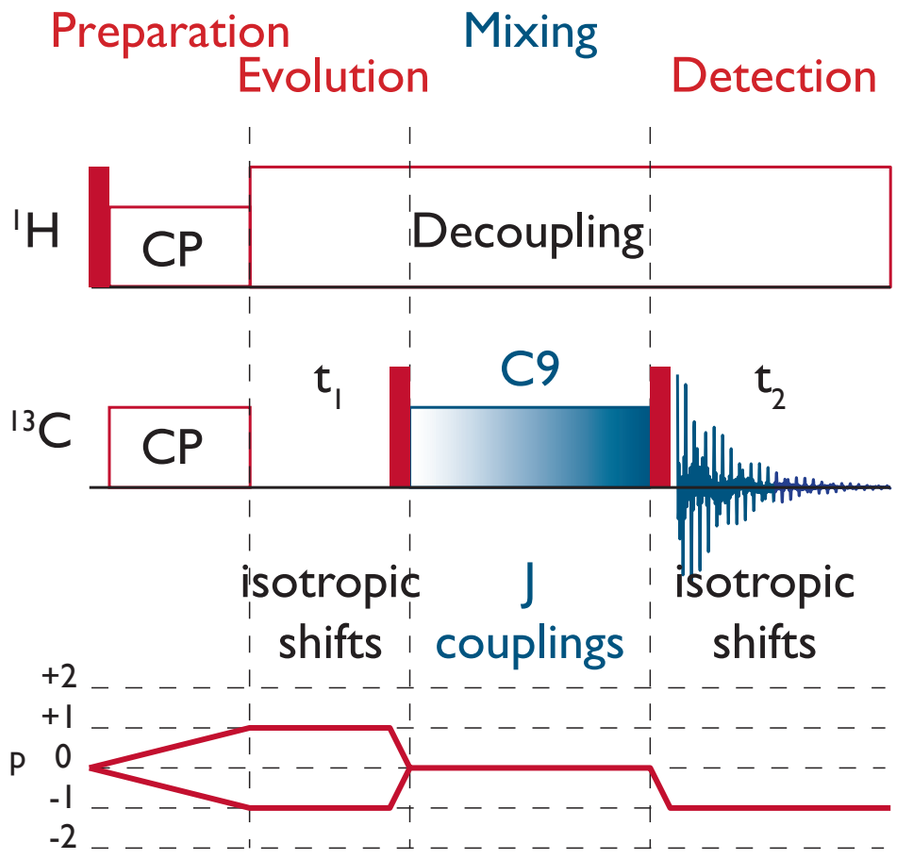
The isotropic mixing Hamiltonian transfers magnetization directly between in-phase states. This is the basis of the solution-state TOCSY experiment.

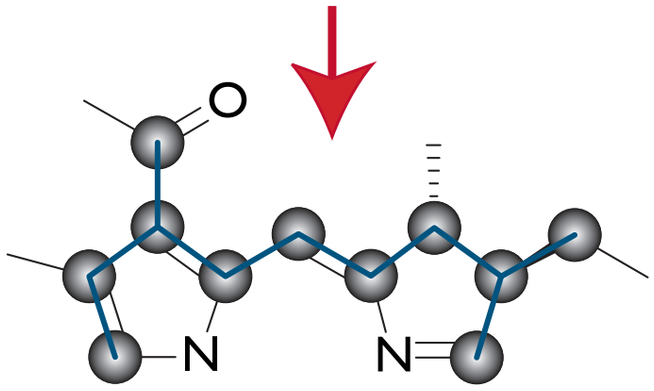
$$\hat{I}_{1x} \xrightarrow{\hat{H}_{iso}=2\pi J \mathbf{I}_1.\mathbf{I}_2} \hat{I}_{2x}$$



Scalar correlation





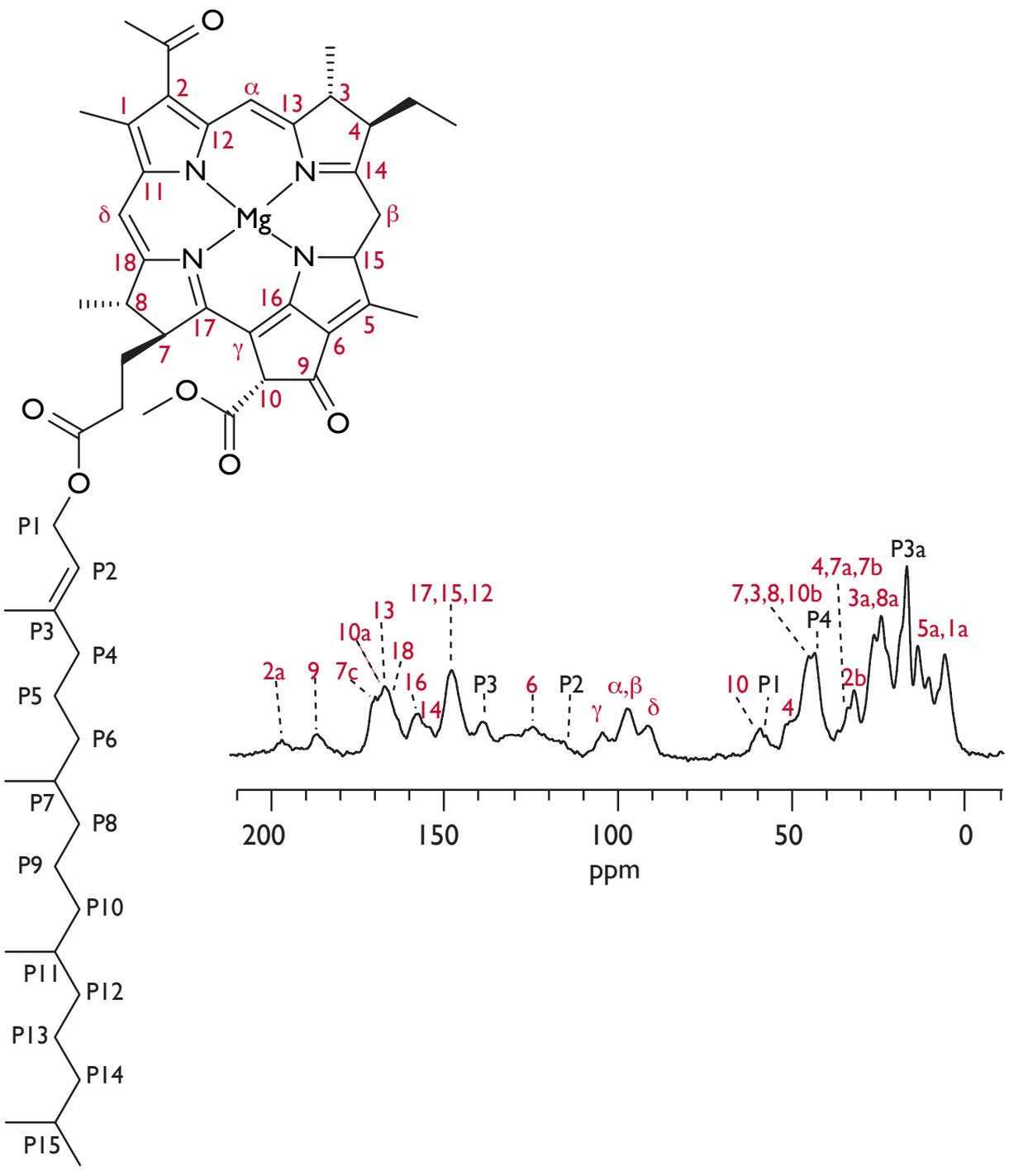


carbon-13
J couplings

A. S. D. Heindrichs, H. Geen and J. J. Titman, *Chem. Phys. Lett.*, **335**, 89 (2001).

Carbon-13 assignment

The combination of dipolar and scalar correlation information allows all the carbon-13 resonances to be assigned, with the exception of the mobile chain P5 - P15.



Mechanisms for dipolar transfer

Recoupled dipolar Hamiltonian

A pulse sequence during the mixing period recouples the double- or zero-quantum dipolar Hamiltonian. Both of these cause magnetization transfer between dipolar-coupled pairs of spins.

$$H_{ZQ} \propto 2I_{1z}I_{2z} - \frac{1}{2}\left(I_1^+I_2^- + I_1^-I_2^+\right)$$

$$H_{DQ} \propto \left(I_1^+I_2^+ + I_1^-I_2^-\right)$$

Proton driven spin diffusion

During the mixing period the decoupler is turned off so that magnetization is transferred between (carbon-13) spins via spin diffusion in the dipolar-coupled proton network.

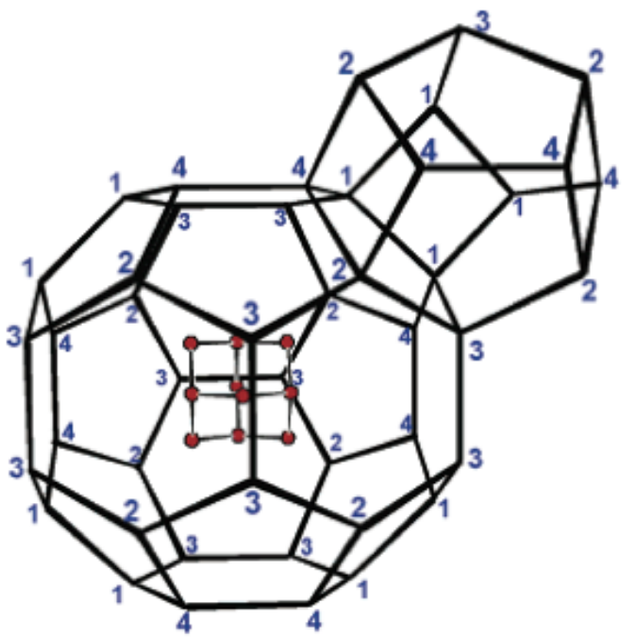
Cross polarization

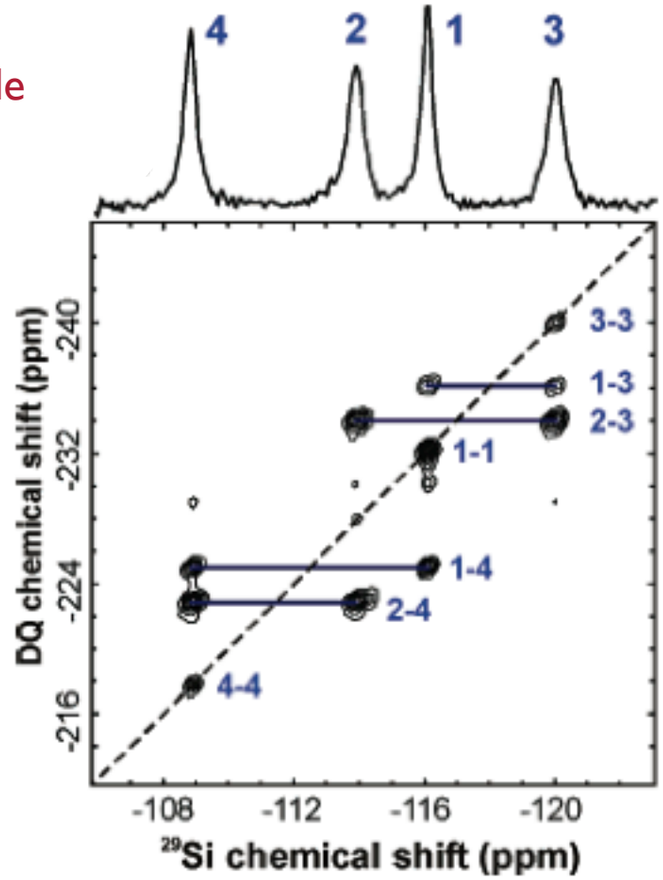
In a heteronuclear correlation experiment the mixing period consists of a cross polarization step to transfer magnetization between heteronuclei. To ensure that magnetization is transferred only to near neighbors special cross polarization sequences must be used which eliminate proton dipolar couplings and prevent spin diffusion.

Zeolite framework structure

- Zeolite framework structures are not easily solved by X-ray diffraction.
- The $SR26_4^{11}$ recoupling sequence used in this silicon-29 dipolar correlation experiment is a robust method for recoupling weak homonuclear dipolar interactions while decoupling weak heteronuclear ones.
- The resulting cross peak build up curves can be simulated in terms of a histogram of Si-Si distances which together with the lattice parameters and the space group from X-rays can be used to solve the zeolite framework structure.

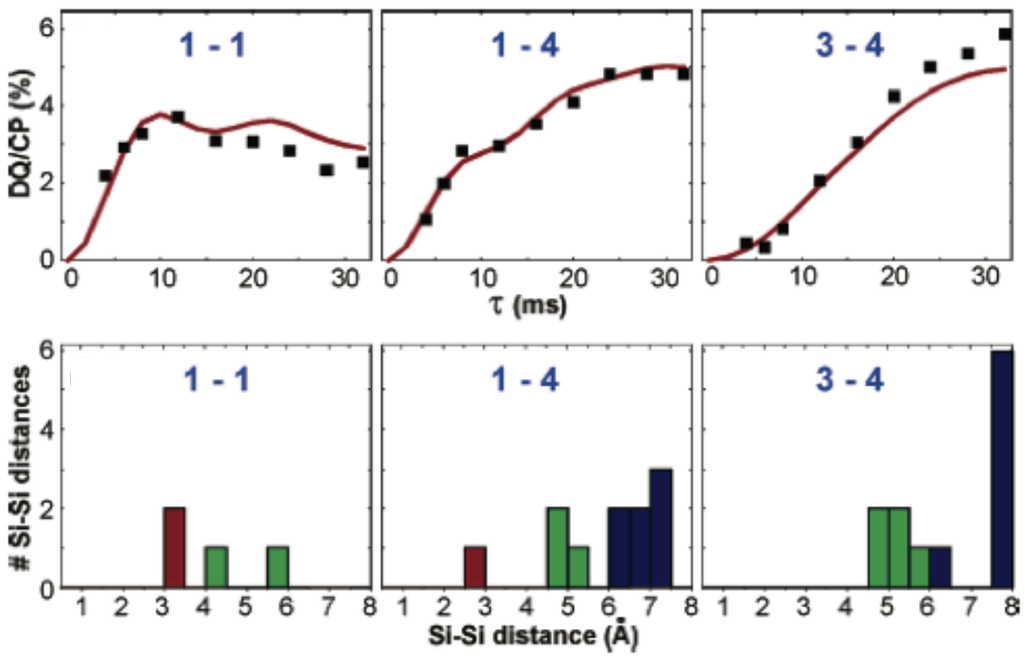
Clathrasil Sigma-2 hosting a 1-aminoadamantane template molecule





Natural abundance silicon-29 dipolar INADEQUATE spectrum

Cross peak build-up curves and the extracted Si-Si distance histogram



D. H. Brouwer, P. Eugen Kristiansen, C. A. Fyfe and M. H. Levitt, *J. Am. Chem. Soc.*, **127**, 542 (2005).

Problems with dipolar correlations

Dipolar Truncation

In a multi-spin system the spin dynamics is dominated by the largest dipolar couplings which are often between bonded spins and of little use in studies of conformation (although they are very useful for making assignments).

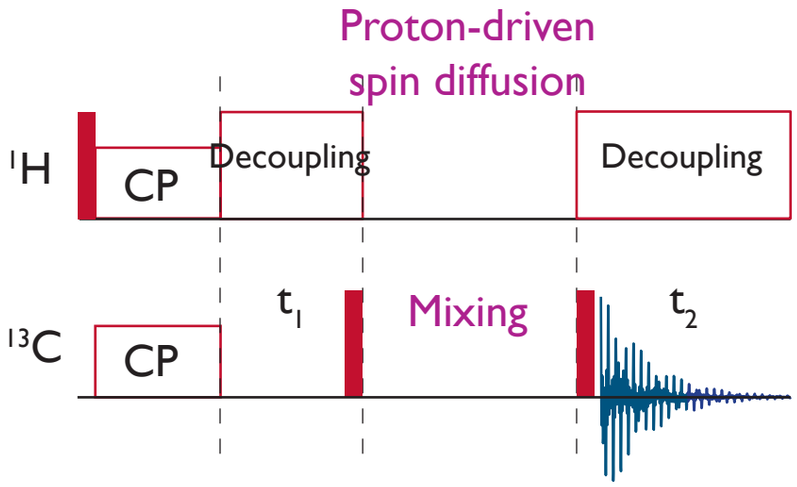
This makes the observation of long-range distance restraints difficult.

Dipolar truncation can be overcome by:

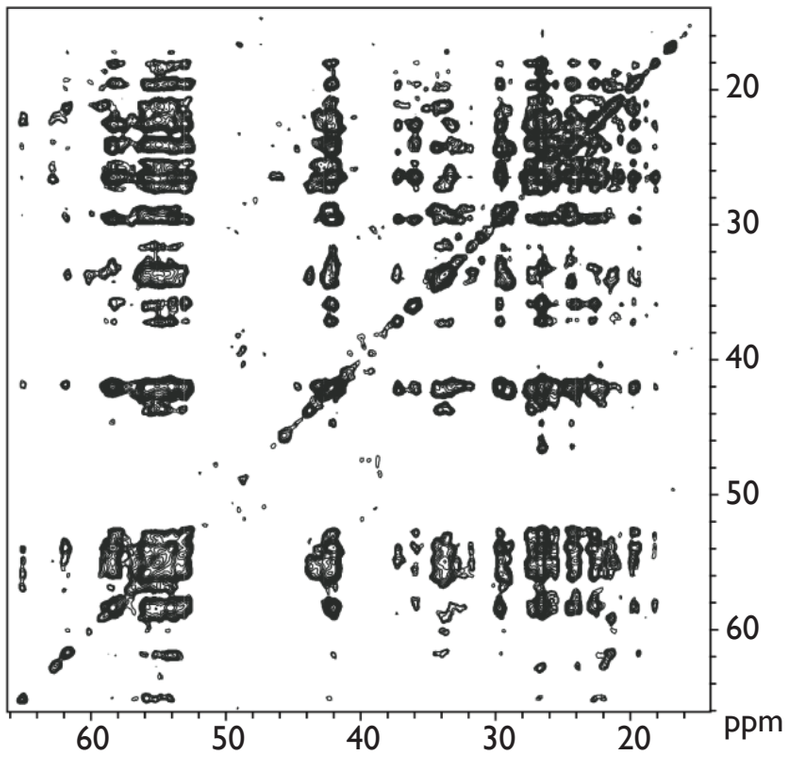
- uniform labeling and frequency-selective recoupling
- broadband recoupling and restricted labeling

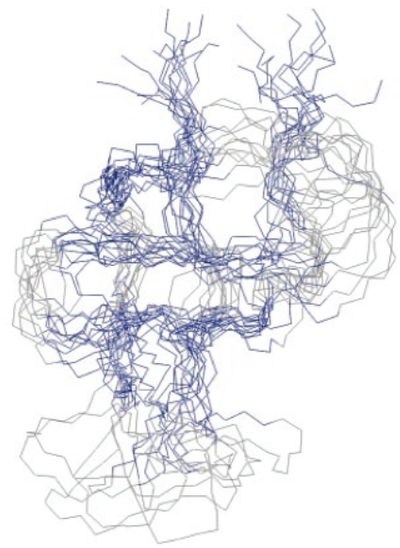
Structure of SH3 by PDSD

- This study used a micro-crystalline preparation of the α-spectrin Src-homology 3 (SH3) domain.
- Proton-driven ^{13}C-^{13}C spin diffusion spectra were obtained from biosynthetically site-directed labelled samples obtained from bacteria grown on [1,3-$^{13}C_2$]glycerol or [2-^{13}C]glycerol.
- This labeling strategy reduces dipolar truncation and hence allowed 286 inter-residue ^{13}C-^{13}C restraints to be extracted from the spectra.
- Distances were estimated by measuring the build-up of cross peak intensity as a function of mixing time and comparing this with conformation independent reference distances.



carbon-13 PDSD spectrum



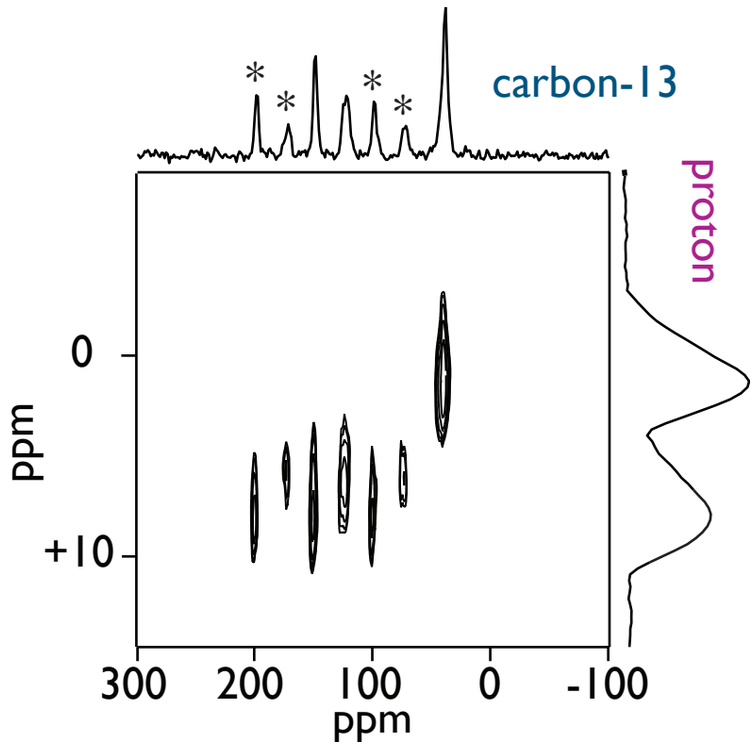


structure by
solid-state NMR

F. Castellani, B van Rossum, A. Diehl, M. Schubert, K. Rehbein and H. Oschkinat, *Nature*, **420**, 98 (2002).

Heteronuclear correlation experiments

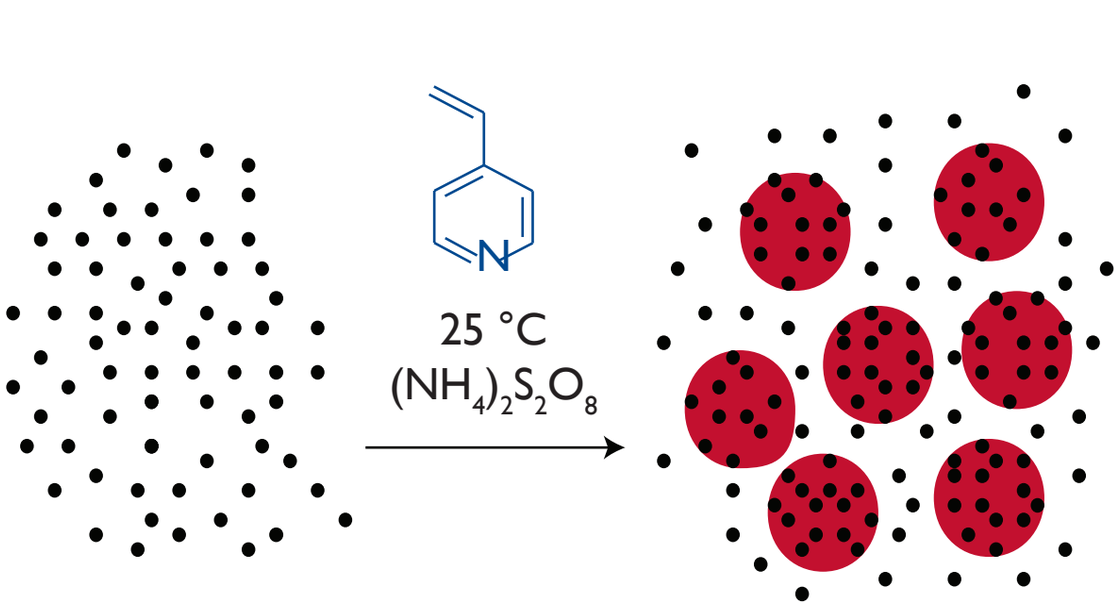
- The high-resolution spectra which are observed in ν_1 and ν_2 correspond to different nuclei.
- The mixing period involves heteronuclear magnetization transfer.



Nature of the interface in PVP-silica nanocomposites

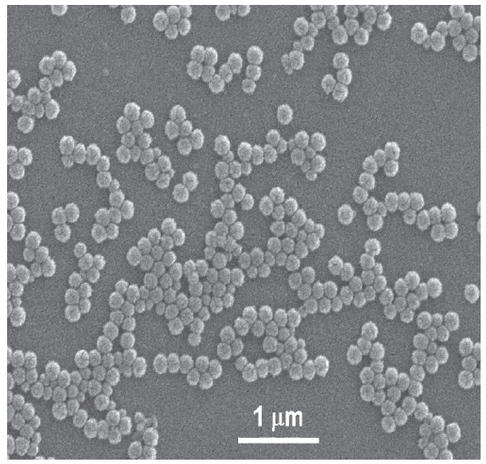
- Vinyl pyridine is polymerized in the presence of an aqueous silica sol to produce nanocomposite particles 200 nm in diameter.
- Inorganic phase adds mechanical strength, fire retardancy etc. to the polymer.

What is the nature of the interaction between the inorganic and organic phases?

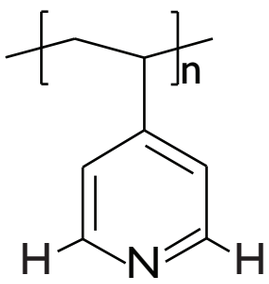


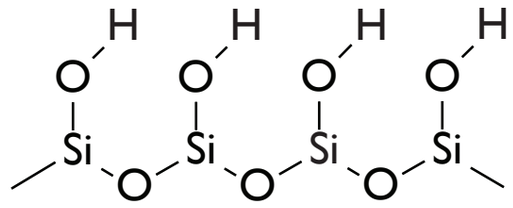
Ultrafine silica sol

Vinyl polymer/silica
colloidal nanocomposite particles



poly(vinylpyridine)

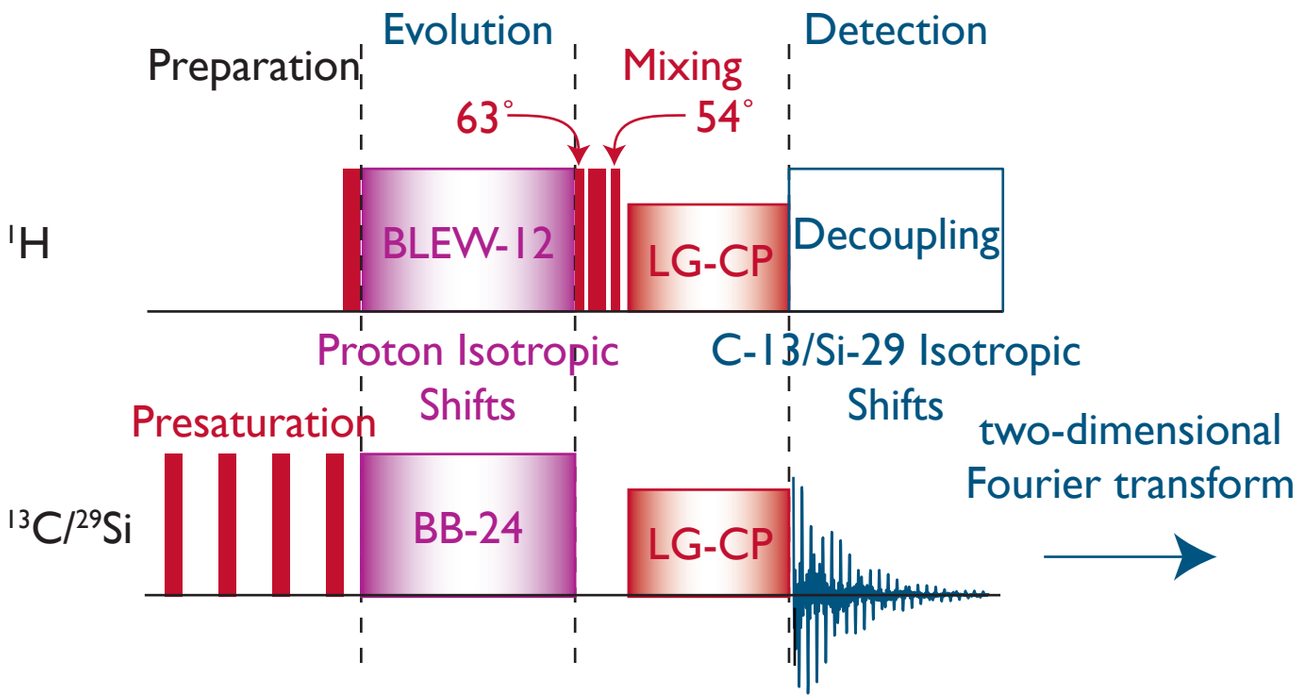




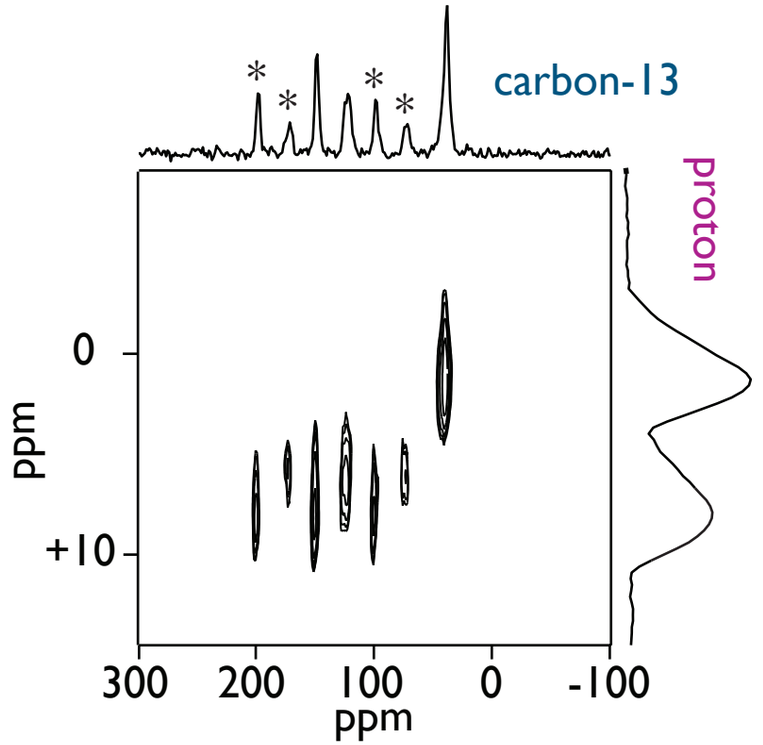
silica

BLEW-LGCP heteronuclear correlation

- The preparation period involves presaturation to ensure that no carbon-13/silicon-29 magnetization is present at the start of the experiment
- In the evolution period the experiment measures the high-resolution proton spectrum obtained using CRAMPS (in this case the BLEW-12 windowless decoupling sequence). Note the use of the BB-24 sequence on carbon-13/silicon-29 to decouple these spins from the protons.
- During the mixing period a selective cross polarization scheme (in this case Lee-Goldberg CP) is used to transfer the proton magnetization to near neighbor carbon-13/silicon-29 spins.
- In the detection period the experiment measures the high-resolution carbon-13/silicon-29 spectrum using decoupling.



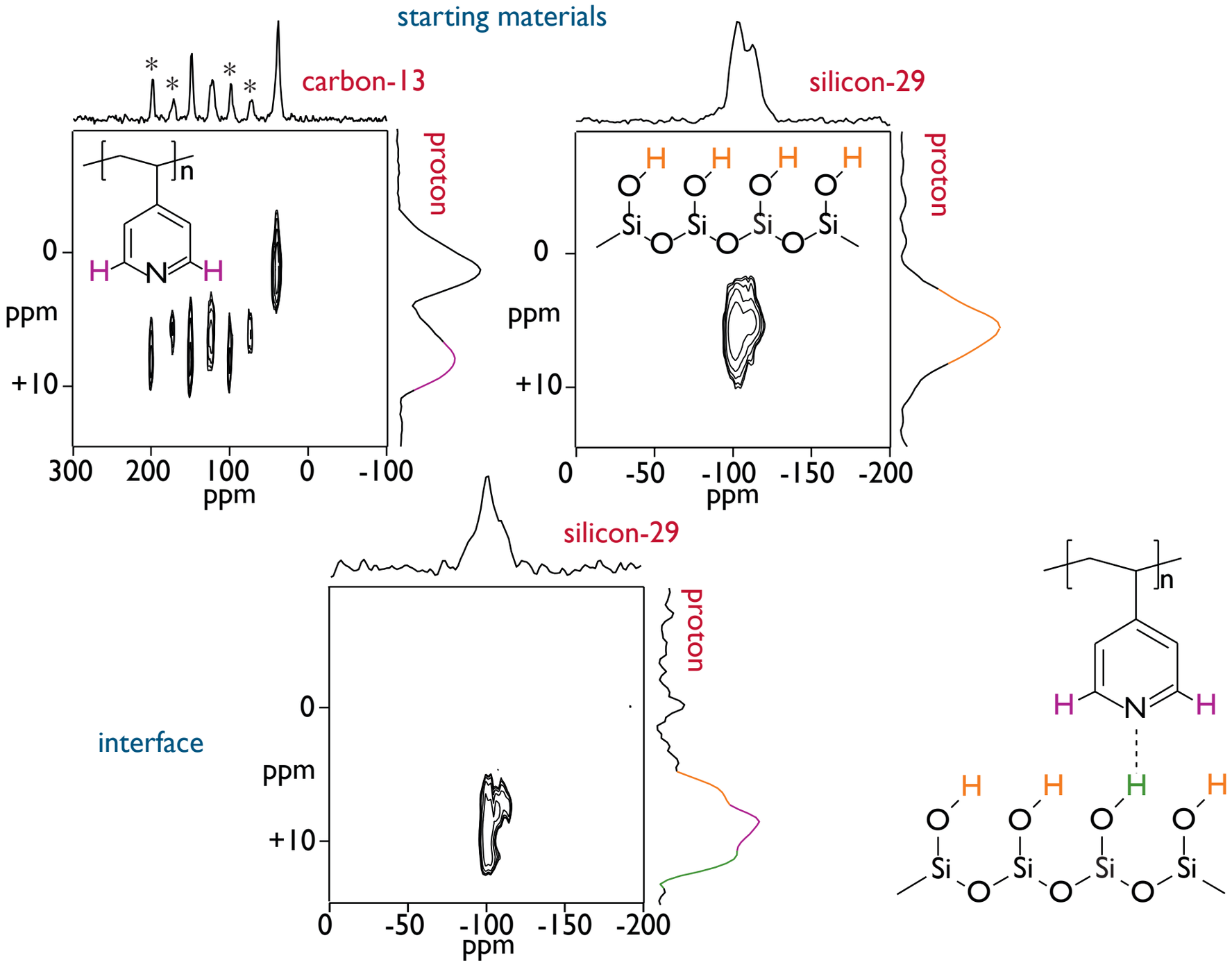
two-dimensional Fourier transform



G. K. Agarwal, J. J. Titman, M. J. Percy and S. P. Armes, *J. Phys. Chem. B.*, **107**, 12497 (2003).

Nature of the interface in PVP-silica nanocomposites

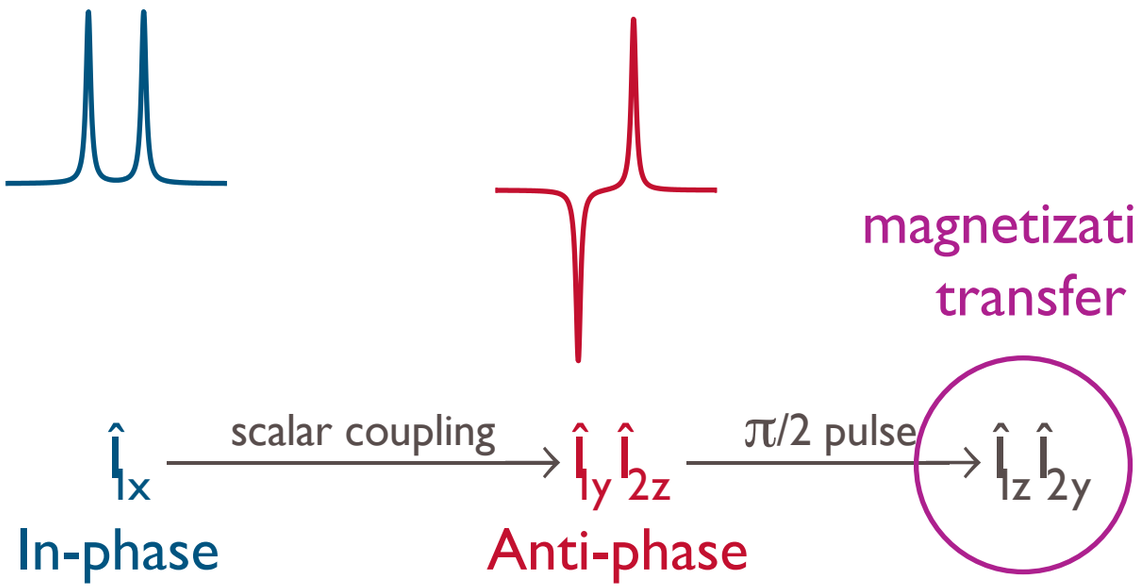
- Heteronuclear correlation spectra of the starting materials allow the protons to be assigned.
- The observation of a new proton resonance in the interface at 11 ppm suggests a hydrogen bond.



Mechanisms for scalar transfer

Anti-phase magnetization

Solution-state scalar correlation experiments like COSY and INADEQUATE rely on the generation of magnetization which is anti-phase with respect to the active J coupling.



Isotropic mixing

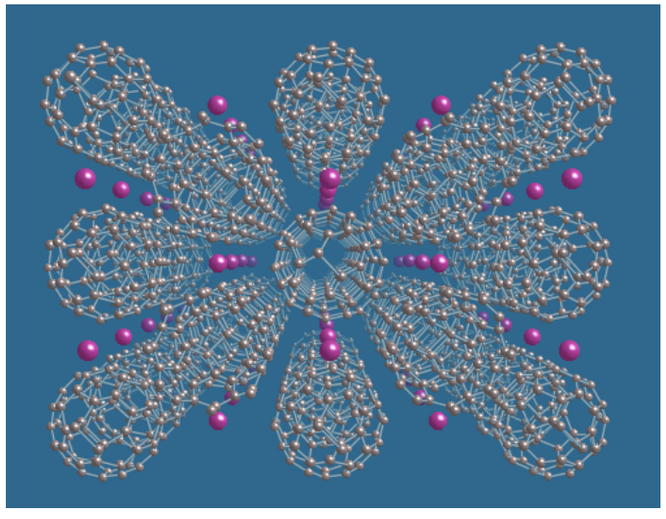
The isotropic mixing Hamiltonian transfers magnetization directly between in-phase states. This is the basis of the solution-state TOCSY experiment.

$$\hat{I}_{1x} \xrightarrow{\hat{H}_{iso}=2\pi J\mathbf{I}_1.\mathbf{I}_2} \hat{I}_{2x}$$

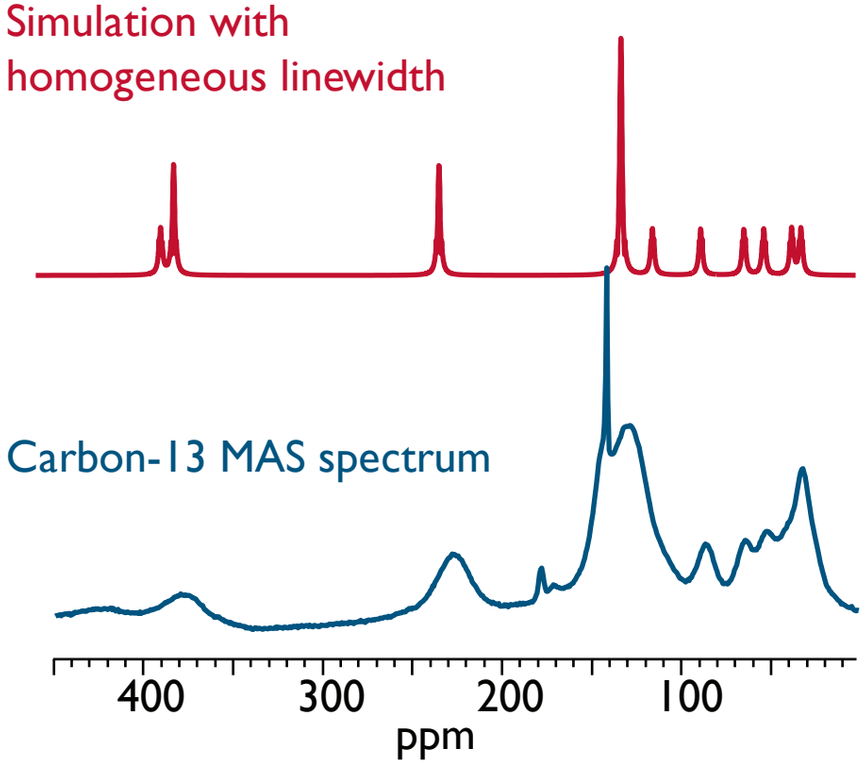
Linewidths in MAS spectra

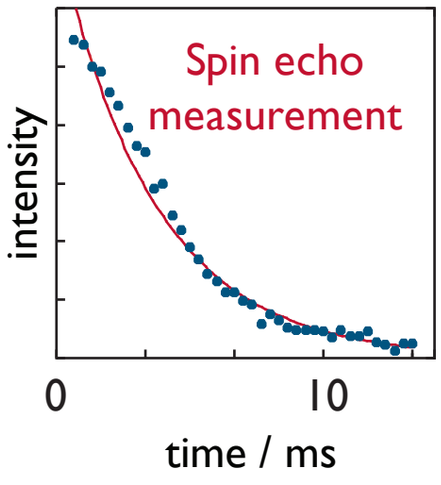
In solids even for dilute spin-1/2 nuclei with MAS and decoupling the NMR linewidth is significantly broader than in solution due to:

- Homogeneous contributions. These arise from incomplete decoupling or molecular motion.
- Inhomogeneous contributions. These arise from an inhomogeneous B_0 field or shift distributions due to sample heterogeneity. They can be refocused by a spin echo.



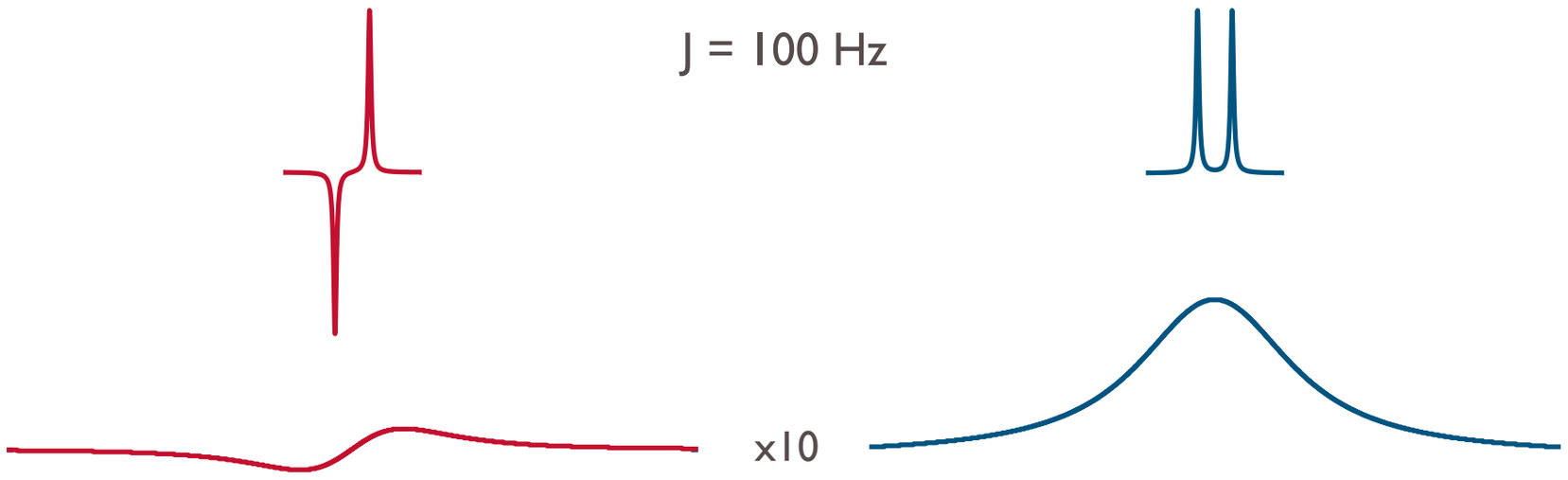
polymeric CsC_{60}



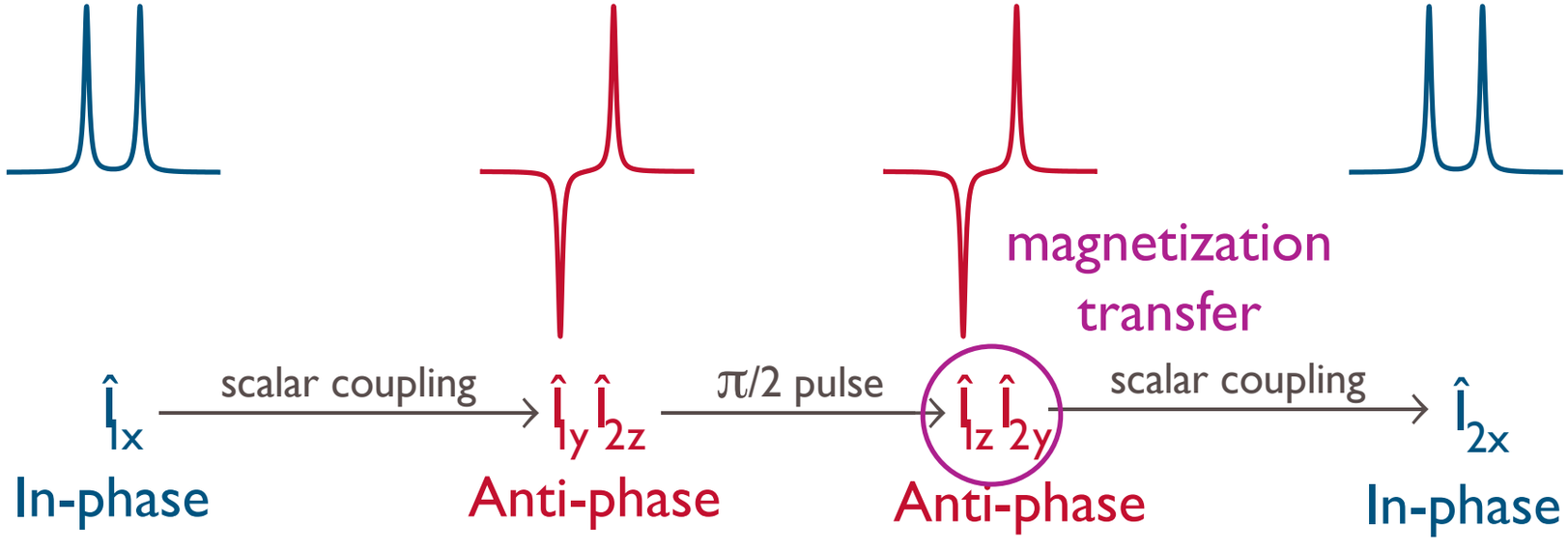


Effect on cross peak sensitivity

When J is within the linewidth the multiplet components cancel and experiments based on anti-phase magnetization transfer have very low sensitivity.



Solid-state scalar correlation experiments are usually "refocused" so that the cross peaks are in-phase, resulting in a significant improvement in sensitivity since the multiplet components reinforce.



SAR-COSY

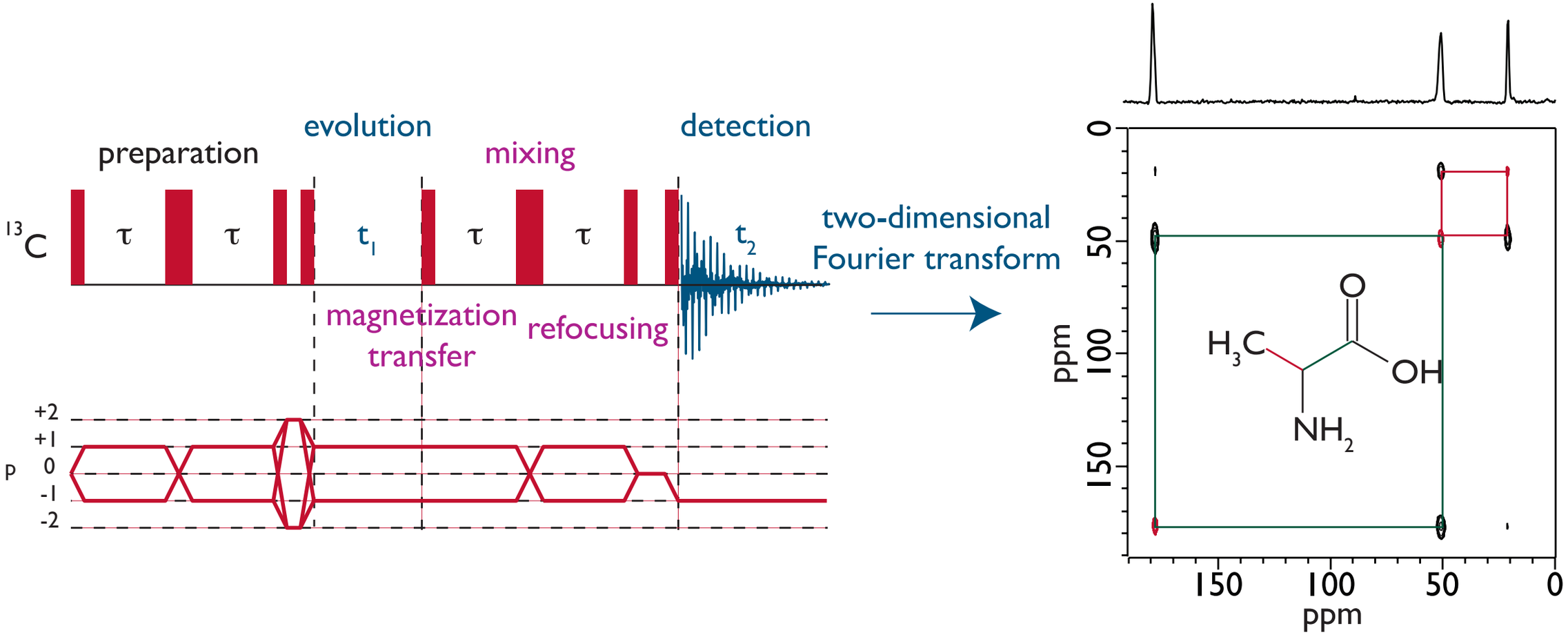
Sensitive, Absorptive, Refocused-COSY

Magnetization transfer occurs via anti-phase magnetization which is refocussed during the mixing period, so that the cross peaks are in-phase and absorptive in both dimensions. This maximizes sensitivity when J is within the linewidth.

The diagonal peaks are anti-phase and dispersive in ν_1 which means they have low intensity and their intensities vary with the preparation time according to:

$$\sin(2\pi J\tau)\cos(2\pi J\tau)$$

which is zero when $\tau = 1/(4J)$.



D. Lee and J. J. Titman, unpublished.

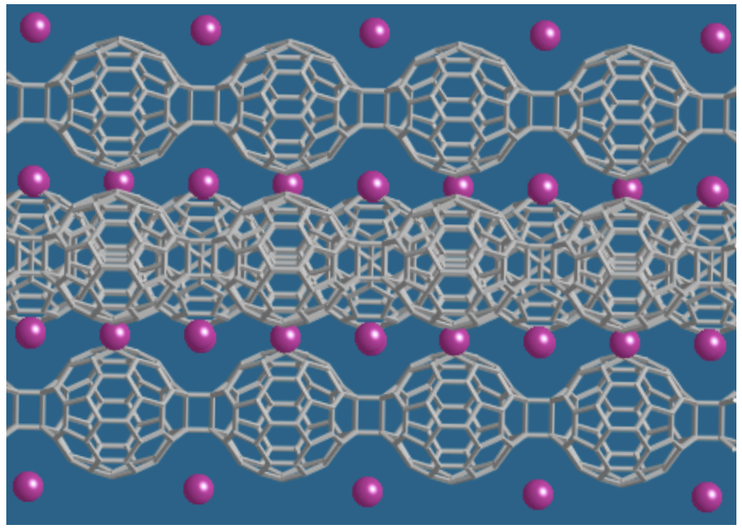
Alkali fullerides

CsC_{60}, RbC_{60}

These materials show interesting phase transitions:

- the high temperature phase is fcc with alkali metals in octahedral interstices
- the low temperature phase is formed from a reversible solid-state transformation which involves a shortening of the *a* lattice dimension

The inter-fullerene distance along *a* is only 9.138 Å which suggests the formation of polymeric C_{60} chains by a 2+2 cyclo-addition reaction.



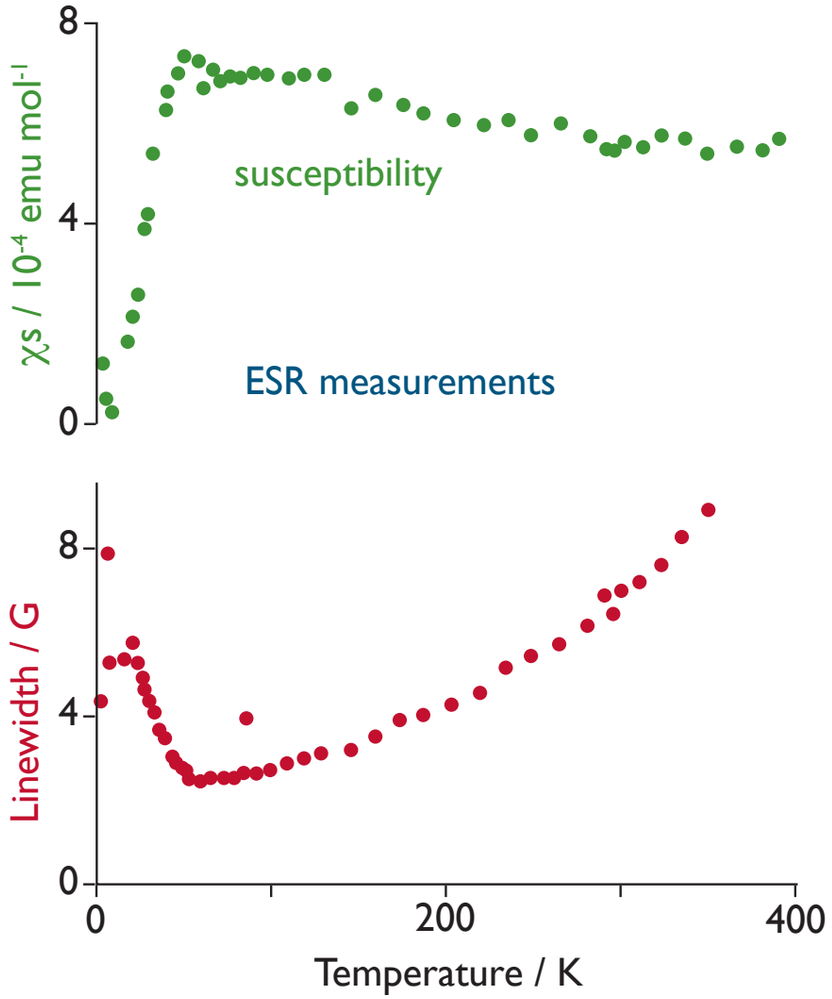
Models for the electronic structure of CsC_{60}

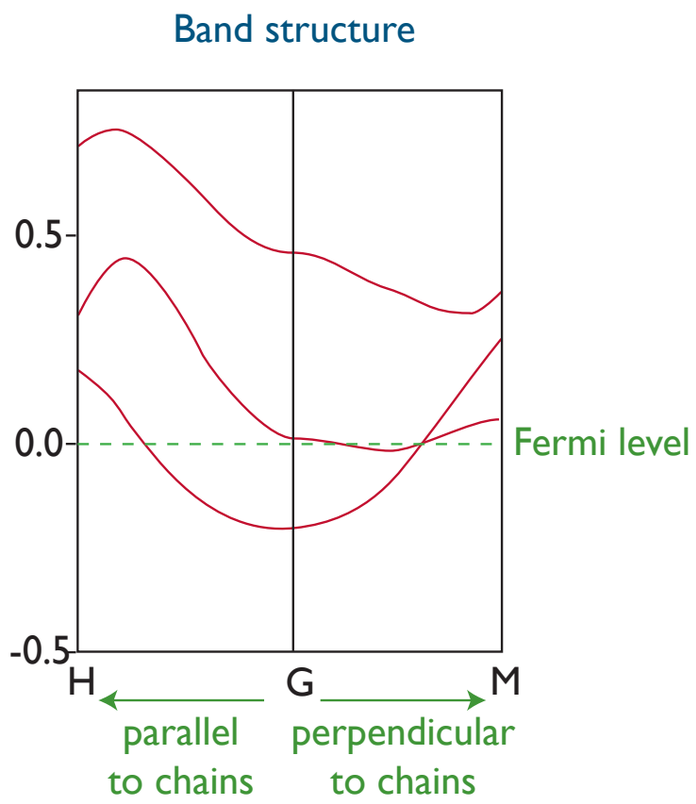
Quasi-1D metal

- Overlap of MOs along *a* results in a half-filled conduction band
- Electronic spin susceptibility depends only weakly on temperature

3D Semi-metal

- The dispersion perpendicular and parallel to the polymer chains is similar, resulting in a three-dimensional Fermi surface.



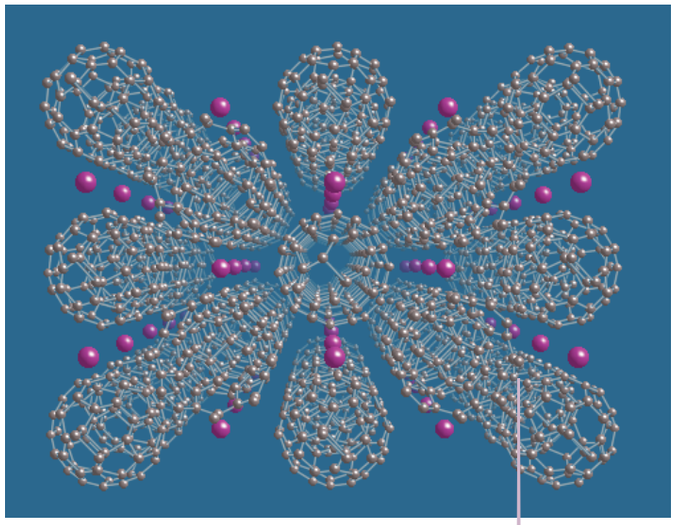


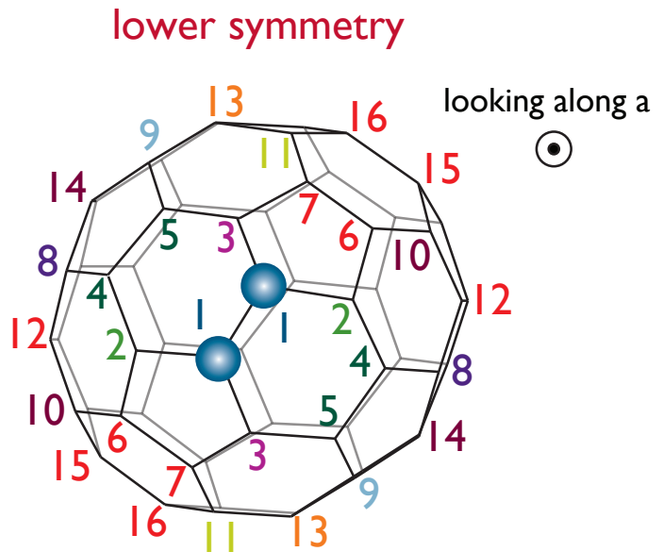
O. Chauvet, G. Oszlànyi, L Forró, P. W. Stephens, M. Tegze, G. Faigel and A. Jánossy, *Phys. Rev. Lett.*, **72**, 2721 (1994);
S. C. Erwin, G.V. Krishna and E. J. Mele, *Phys. Rev. B*, **51**, 7345 (1995).

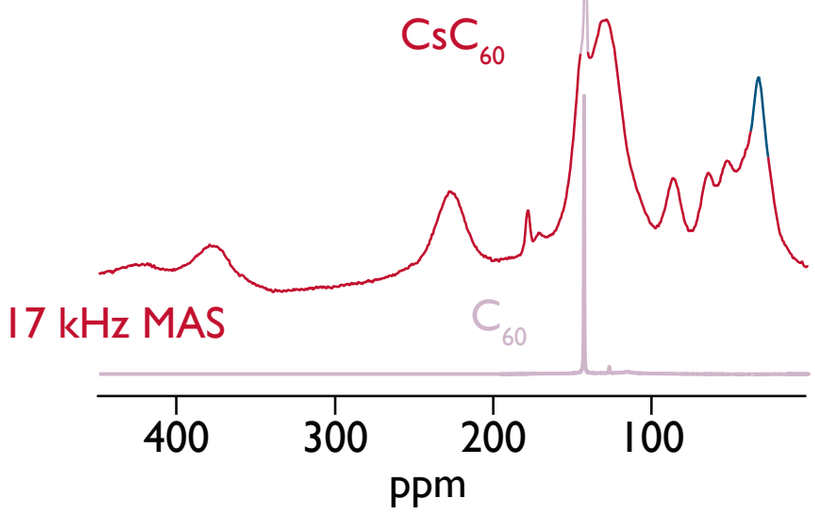
Carbon-13 MAS NMR of CsC_{60}

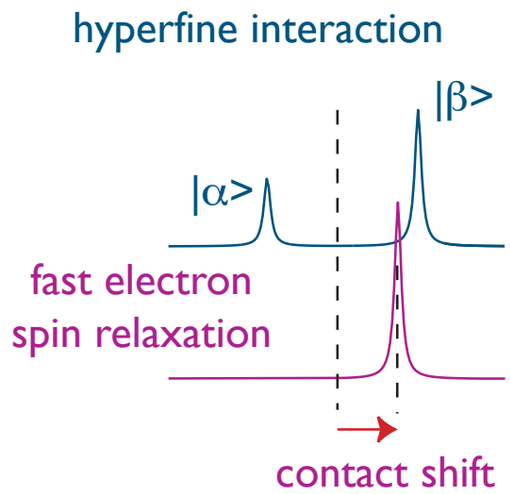
The polymerization reaction lowers the symmetry, resulting in 16 inequivalent carbon sites.

The hyperfine interaction with the unpaired electron donated from the caesium atom results in contact shifts.









50% U-^{13}C CsC_{60}

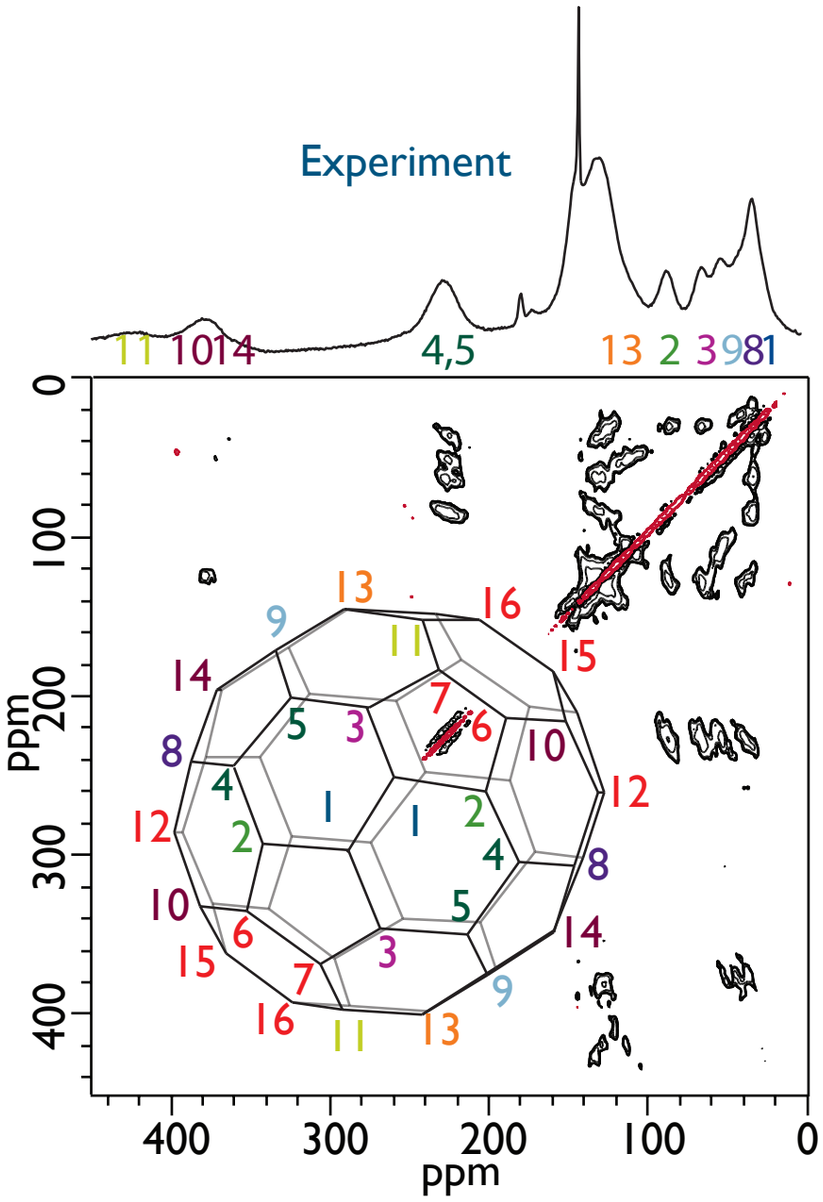
Carbon-13 enriched amorphous carbon packed into graphite tubes; 60 A 25 V dc arc between enriched rods under 3 psi He; Enriched C_{60} and Cs mixed and heated for 1 week at 350 °C

Comparison with DFT calculations

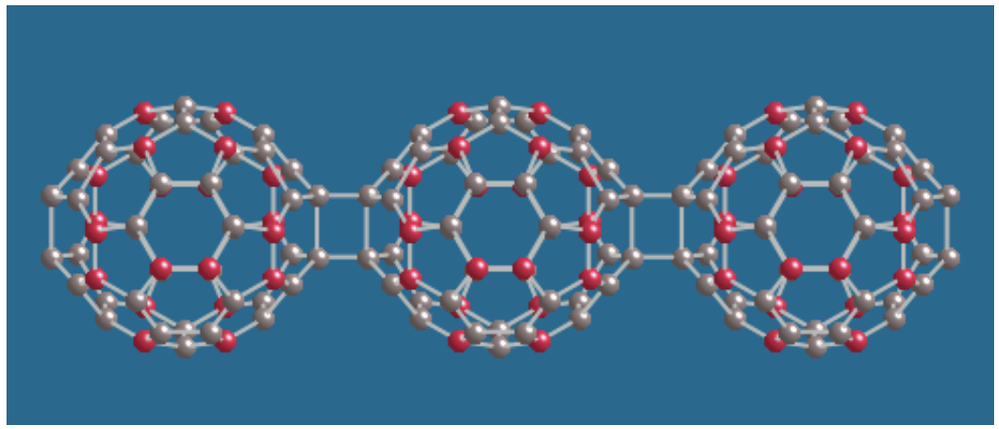
Starting from the aliphatic inter-fullerene linkage (1) all the experimental carbon-13 lines can be assigned.

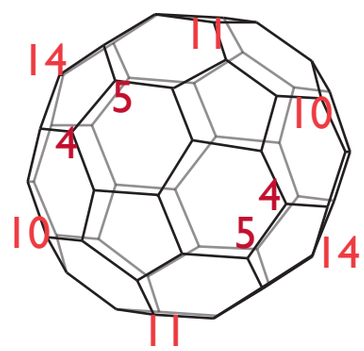
DFT calculations on a C_{60} trimer based on the 3D semi-metal band structure show two groups of carbon sites with large hyperfine couplings.

These are the lines which show the largest experimental contact shifts, so the 3D semi-metal is the correct model.



Calculations





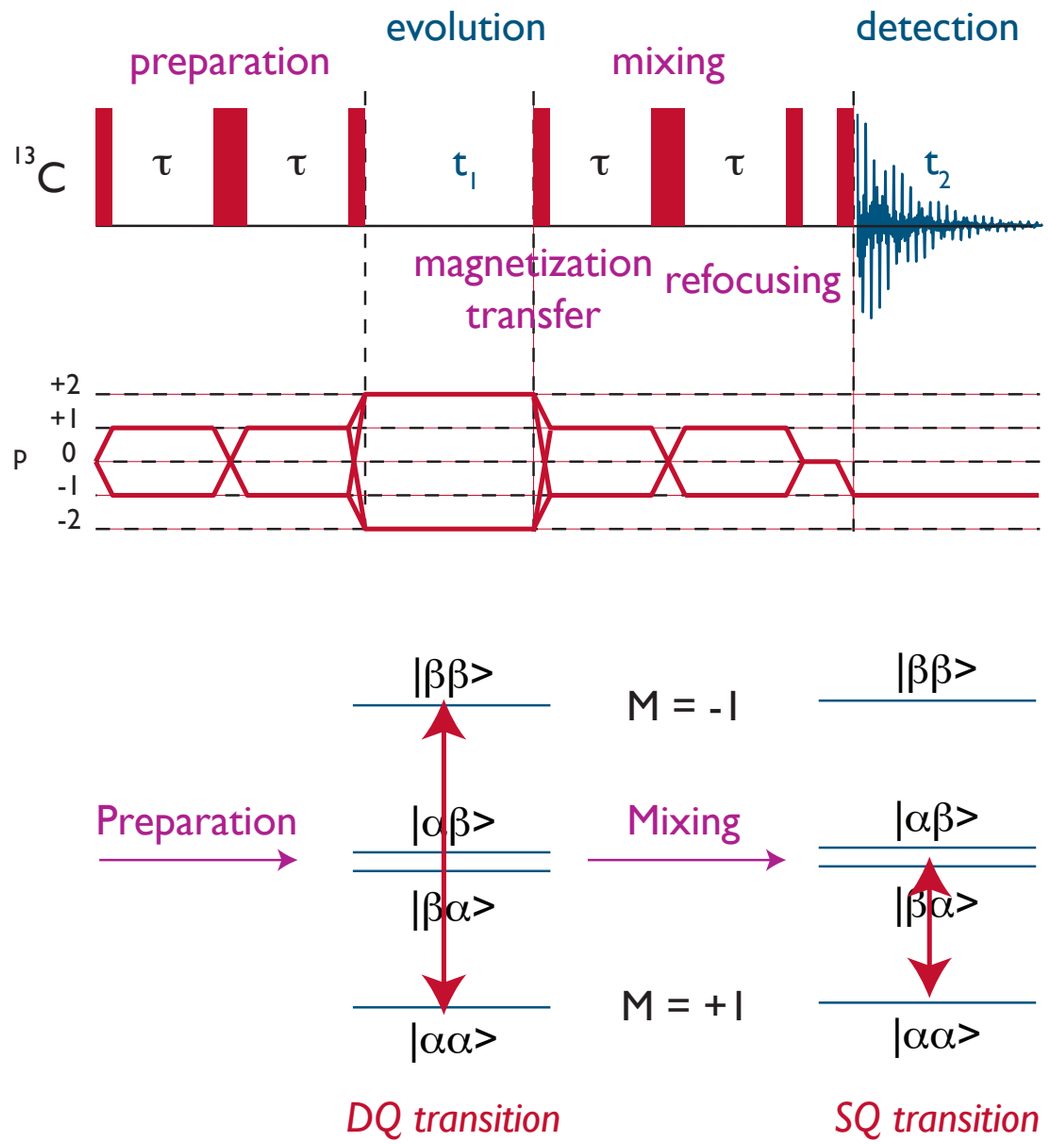
hyperfine coupling / MHz

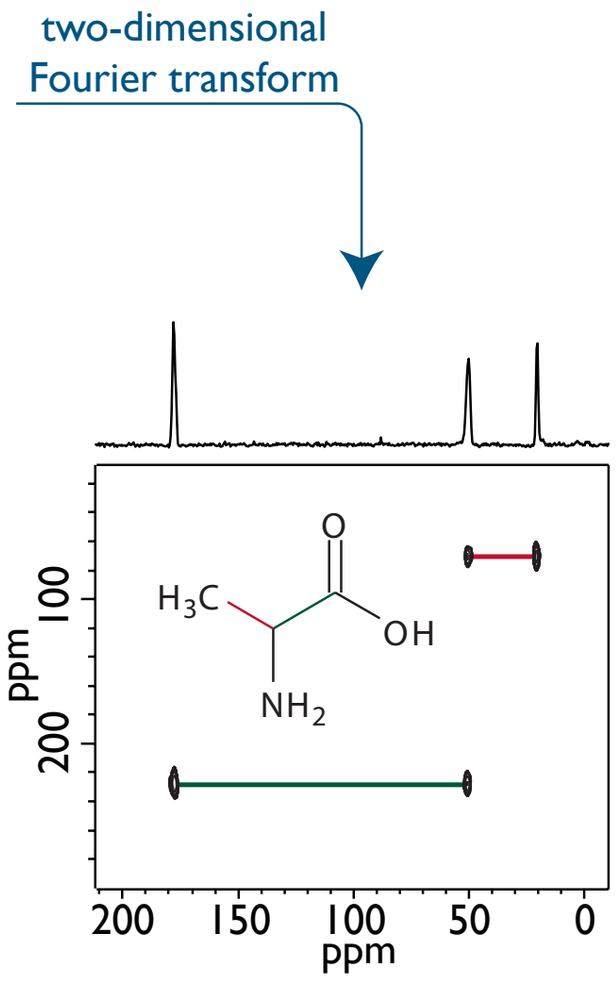
	(4,5)	2.2
	(14,10,11)	6.8

T. M. de Swiet, J. L. Yarger, T. Wagberg, J. Hone, B. J. Gross, M. Tomaselli, J. J. Titman, A. Zettl and M. Mehring, *Phys. Rev. Lett.*, **84**, 717 (2000).

Refocused INADEQUATE

- During the preparation period unobservable double-quantum coherences are excited.
- These evolve at the sum of the chemical shifts of the spins involved in the evolution period.
- They are reconverted to observable anti-phase magnetization which is refocussed during the mixing period, so that the peaks are in-phase and absorptive.

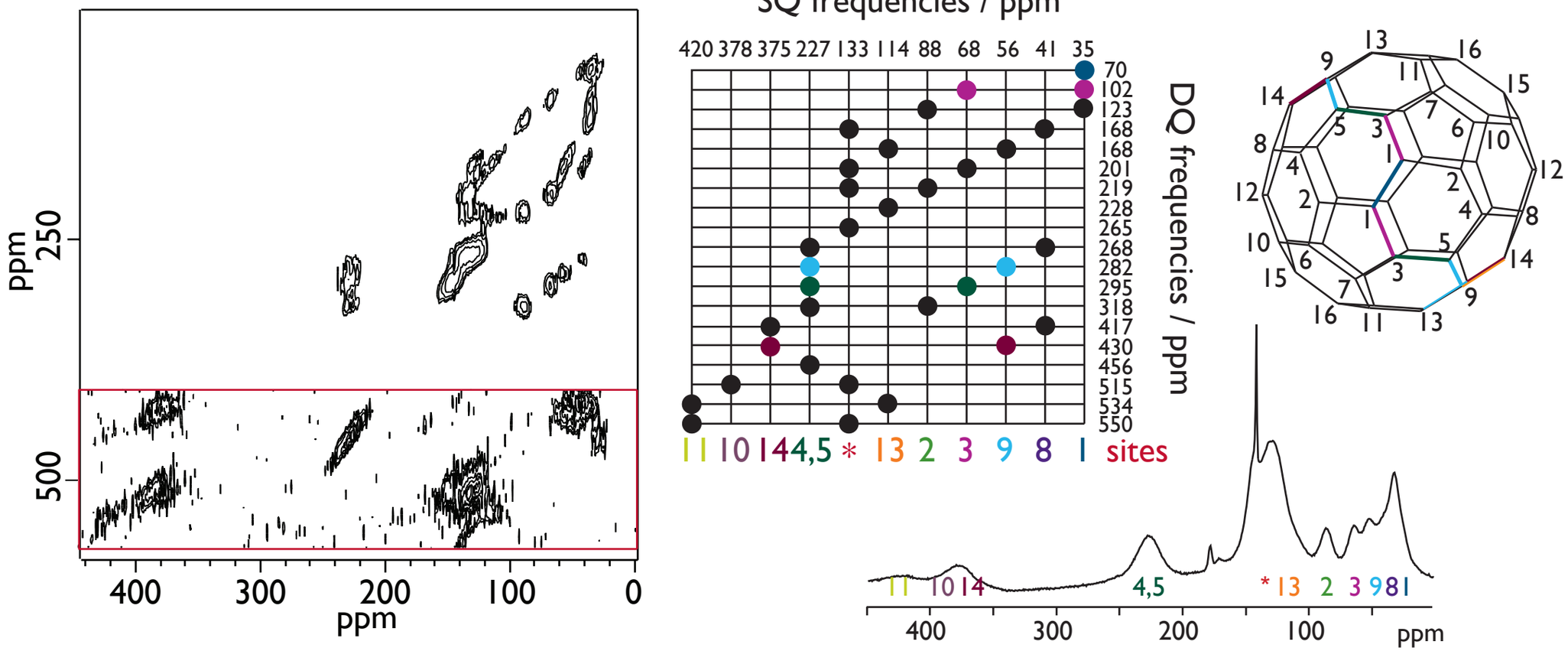




A. Lesage, C. Auger, S. Caldarelli, and L. Emsley, *J. Am. Chem. Soc.*, **119**, 7867 (1997).

Comparison of methods

SAR-COSY and refocussed INADEQUATE result in similar sensitivity and contain similar information.

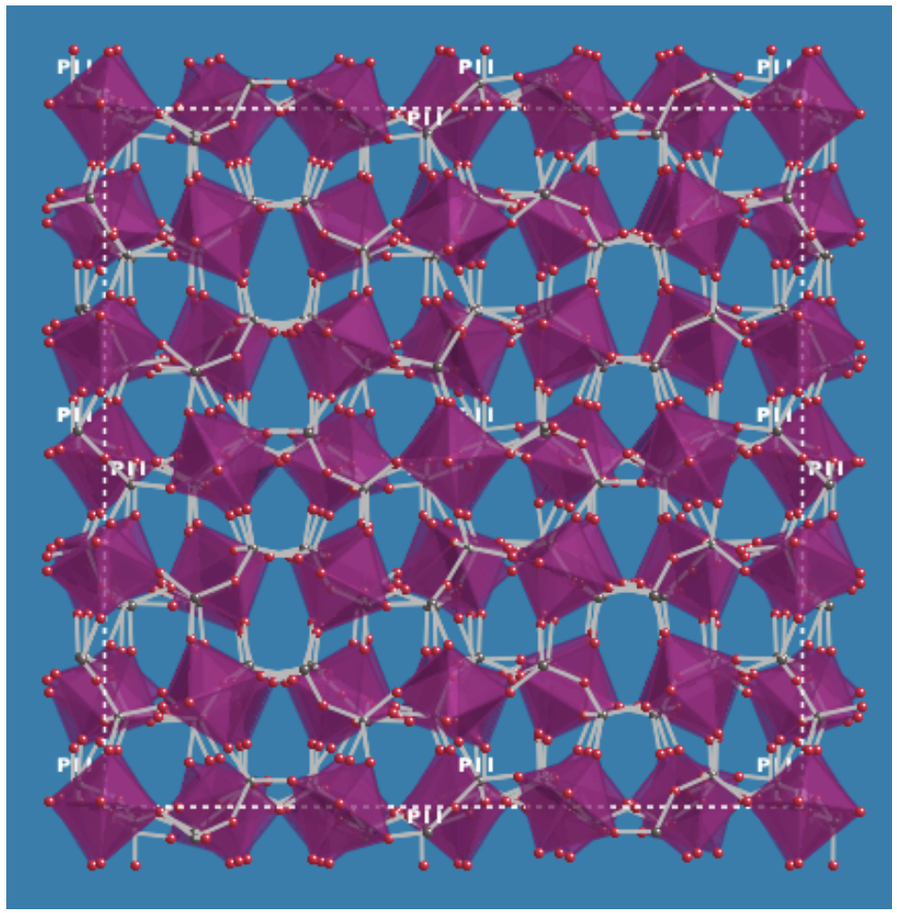


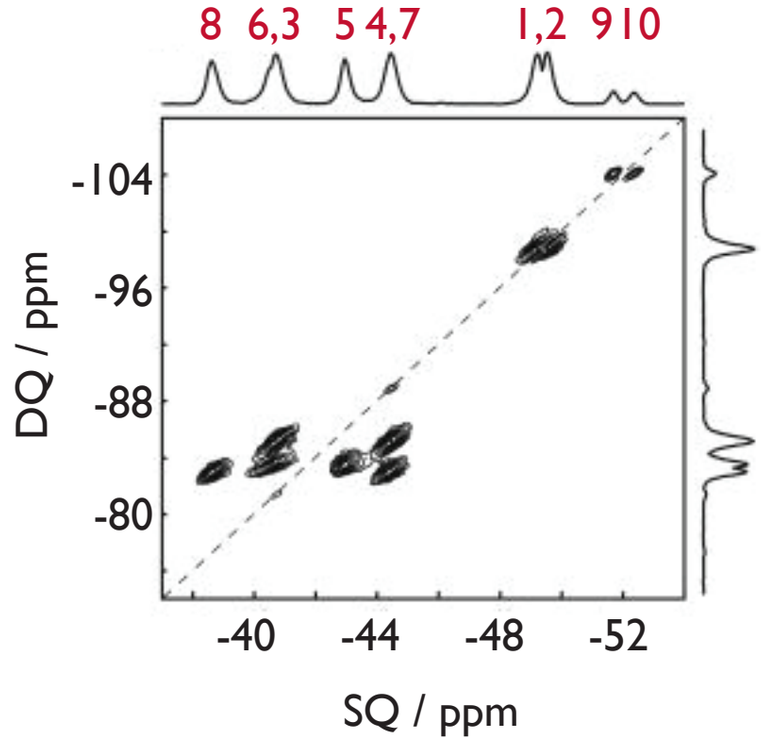
G. Grasso, T de Swiet and J. J. Titman, *J. Phys. Chem. B,* **106**, 8676, (2002).

Structures of pyrophosphates

TiP_2O_7

- This material has a cubic crystal structure with space group PA3-, *a* = 23.534 Å, Z=108
- Scalar correlation experiments can distinguish 5 pairs of inequivalent ^{31}P resonances bonded via a bridging oxygen atom and one equivalent pair.
- This experiment can be used to distinguish between dynamic and static disorder in the P-O-P bond angle.

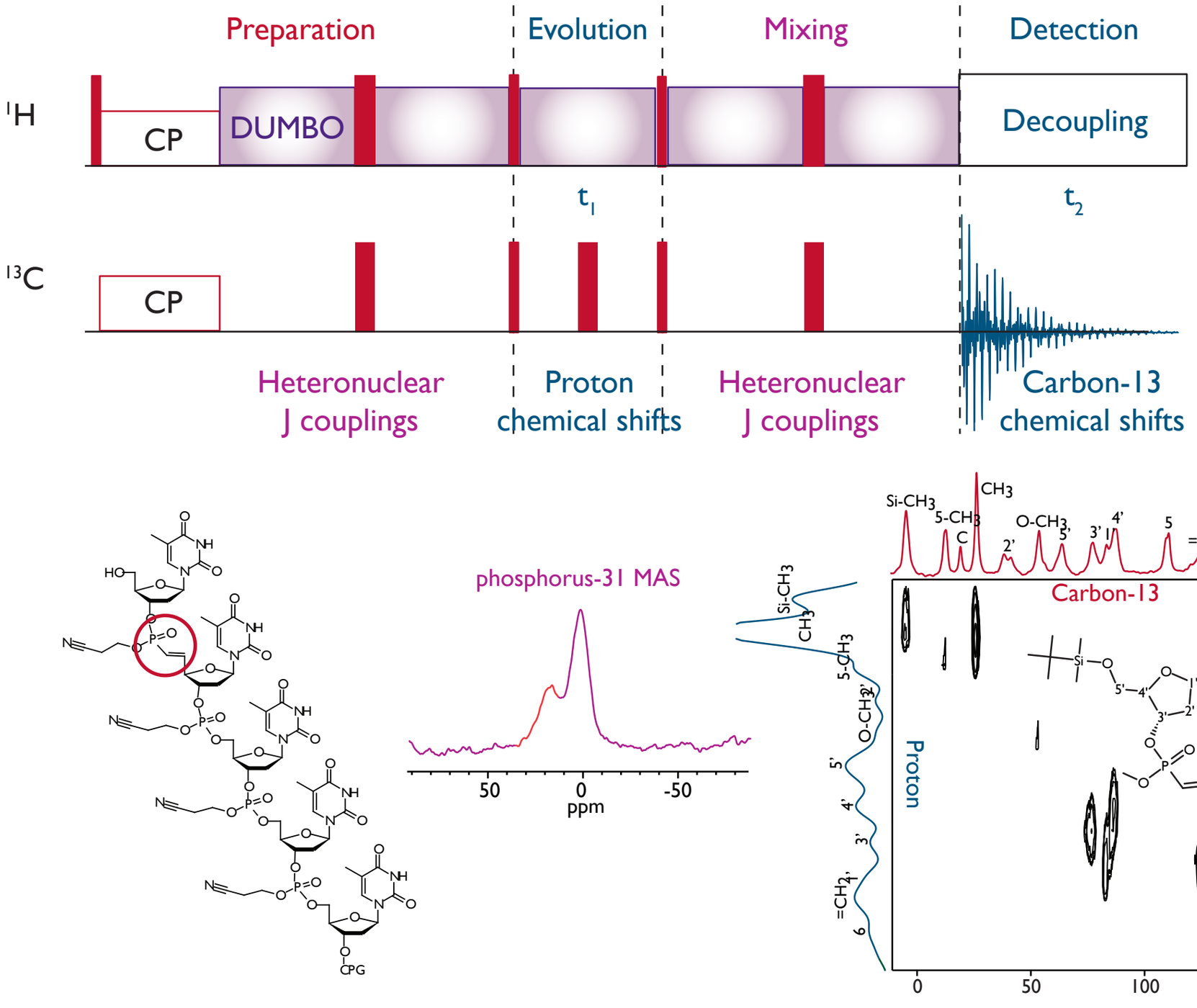




F. Fayon, D. Massiot, M. H. Levitt, J. J. Titman, D. H. Gregory, L. Duma, L. Emsley, S. P. Brown, *J. Chem. Phys.* **122**, 194313 (2005).

HMQC-J-MAS

With rapid MAS and efficient decoupling, many solid-state analogues of two-dimensional solution-state NMR experiments can be designed.



A. Lesage, D. Sakellariou, S. Steuernagel and L. Emsley, *J. Am. Chem. Soc.*, **120**, 13194 (1998).

Summary

Two-dimensional **scalar and dipolar correlation** experiments show a high resolution spectrum in each dimension with cross peaks which map the correlations due to the mixing Hamiltonian.

Scalar correlations can be used for structural studies and for assignments, while dipolar correlations provide information about conformation.

Increasingly, solid-state NMR correlation experiments resemble their solution-state counterparts and make use of efficient decoupling, rapid MAS and anti-phase magnetization transfer under scalar couplings.