Homonuclear Dipolar Recoupling in Solid State NMR: Analysis with Average Hamiltonian Theory

(lecture notes for the first Winter School on Biomolecular Solid State NMR,

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Definition of homonuclear recoupling

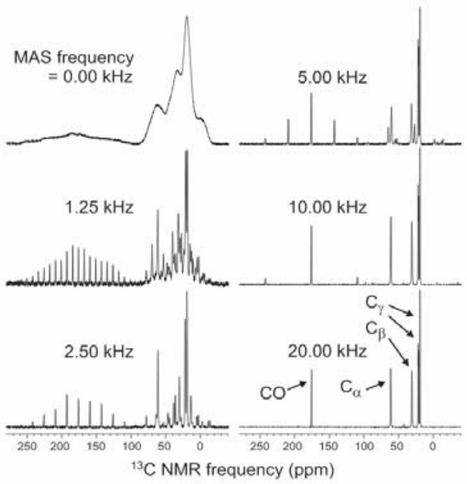
Pulse sequences that create non-zero effective (i.e., average) dipole-dipole couplings among like spins (e.g., ^{13}C-^{13}C couplings) during magic-angle spinning (MAS).

Motivations for homonuclear recoupling (partial list)

(1) to measure distances between like nuclei
(2) to produce crosspeaks between like nuclei in 2D or 3D MAS NMR spectra
(3) to permit double-quantum filtering, for selective observation of NMR signals arising from pairs or groups of dipole-coupled nuclei
(4) to permit spin polarization transfers, as required for various other structural techniques (e.g., "tensor correlation" techniques)

Why are pulse sequences necessary?

MAS is usually required for sufficient resolution and sensitivity in solid state NMR of unoriented systems. MAS produces narrow lines by averaging out anisotropy of chemical shifts and magnetic dipole-dipole couplings. Recoupling sequences are needed to restore these interactions.



^{13}C NMR spectra of uniformly ^{15}N,^{13}C-labeled L-valine powder, obtained in a 14.1 T magnetic field at the indicated MAS frequencies.

Outline

DISCLAIMERS:

1. THE PRESENTATION OF DIPOLAR RECOUPLING TECHNIQUES AND OTHER TOPICS IN THESE NOTES IS MOTIVATED SOLELY BY PEDAGOGICAL CONSIDERATIONS. MANY USEFUL TECHNIQUES AND BRILLIANT IDEAS ARE OMITTED, AND MANY IMPORTANT PAPERS ARE NOT CITED. THE GOAL OF THESE NOTES IS SOLELY TO SUMMARIZE THE THEORETICAL/MATHEMATICAL BACKGROUND REQUIRED FOR AN UNDERSTANDING OF DIPOLAR RECOUPLING AND RELATED TECHNIQUES IN SOLID STATE NMR.

2. THESE NOTES MAY CONTAIN MISTAKES. PLEASE LET ME KNOW IF YOU NOTICE ANYTHING THAT SEEMS TO BE INCORRECT.

I. Relevant quantum mechanical principles

If a spin system is in a single, well-defined state, that state is represented by a state vector $|\psi(t)>$. For example, a system of three spin-1/2 nuclei could be in the state $|\psi(0)>=|+-+>$ at time t = 0.

The evolution of $|\psi(t)>$ with time is determined by the Schrodinger equation:

$$i\frac{d}{dt}|\psi(t)>=H(t)|\psi(t)> \tag{I.1}$$

where H(t) is the Hamiltonian operator (in angular frequency units), which contains terms that represent each of the nuclear spin interactions. If H(t) is constant (i.e., H(t) = H), then Eq. (I.1) has the solution

$$|\psi(t)>=e^{-iHt}|\psi(0)> \tag{I.2}$$

If H(t) is not constant, the solution to Eq. (I.1) is

$$|\psi(t)>=U(t)|\psi(0)> \tag{I.3a}$$

$$U(t)=\vec{T}\exp\{-i\int_0^t dt'H(t')\} \tag{I.3b}$$

where $\vec{T}$ is the Dyson time-ordering operator. U(t) is the evolution operator. If the time interval from 0 to t is divided into N intervals with lengths τ_j during which the Hamiltonian is H_j, Eq. (I.3b) is short-hand for

$$U(t)=e^{-iH_N\tau_N}e^{-iH_{N-1}\tau_{N-1}}...e^{-iH_2\tau_2}e^{-iH_1\tau_1} \tag{I.3c}$$

which is simply an extension of Eq. (I.2). Also, Eqs. (I.1) and (I.3a) imply

$$i\frac{d}{dt}U(t)=H(t)U(t) \tag{I.4}$$

Signals in quantum mechanics are "expectation values" of Hermitean operators, evaluated according to

$$S_A(t)=<\psi(t)|A|\psi(t)> \tag{I.5}$$

$|\psi(t)>$ and $<\psi(t)|$ are called "ket" and "bra" vectors.

In actual calculations, Eq. (I.5) would be evaluated by choosing a complete basis of states for the system, {|n>}, that satisfies $< n \mid n' >= \delta_{n,n'}$. $\mid \psi(t) >$ would be represented as a column vector with elements $< n \mid \psi(t) >$. $< \psi(t) \mid$ would be represented by a row vector with elements $< n \mid \psi(t) >^*$. A would be a matrix with elements $< n \mid A \mid m >$ in the nth row and mth column.

In NMR, we don't usually have spin systems in single, well-defined states. Therefore, we use <u>density operators</u> instead of state vectors. The density operator is defined as

$$\rho(t) = \overline{\mid \psi(t) >< \psi(t) \mid} \qquad \text{(I.6)}$$

where the bar represents a weighted average over the spin states that are present in the sample. It can be shown that Eq. (I.1) implies that ρ(t) satisfies the equation

$$i \frac{d}{dt} \rho(t) = [H(t), \rho(t)] \qquad \text{(I.7)}$$

where [A,B] ≡ AB - BA means the <u>commutator</u> of operator A and operator B. Eq. (I.7) implies

$$\rho(t) = U(t)\rho(0)U(t)^{-1} \qquad \text{(I.8)}$$

We usually assume that the initial condition $\rho(0)$ before applying our pulse sequence is proportional to the sum of the z components of spin angular momentum for the relevant nuclei, i.e., $\rho(0) \propto I_z = \sum_k I_{zk}$. This is appropriate at normal temperatures when the spins are at thermal equilibrium in a strong magnetic field along z.

Signals are

$$S_A(t) = \mathrm{Tr}\{A\rho(t)\} \qquad \text{(I.9)}$$

where Tr{B} is the <u>trace</u> of operator B, defined as $\mathrm{Tr}\{B\} = \sum_n < n \mid B \mid n >$ if {|n>} is a basis of states as discussed above. Conventional NMR signals are proportional to the transverse components of spin angular momentum. In the rotating frame (see Exercises), the NMR signals have real and imaginary parts, proportional to $I_x = \sum_k I_{xk}$ and $I_y = \sum_k I_{yk}$. These are usually combined into one complex signal S(t), which is then

$$\begin{aligned} S(t) &= S_{real}(t) + iS_{imag}(t) \\ &\propto \mathrm{Tr}\{I_x\rho(t)\} + i\mathrm{Tr}(I_y\rho(t)\} \\ &= \mathrm{Tr}\{I_+\rho(t)\} \\ &= \mathrm{Tr}\{I_+U(t)I_zU(t)^{-1}\} \end{aligned} \qquad \text{(I.10)}$$

where $I_\pm = I_x \pm iI_y$ and U(t) is the evolution operator for the nuclear spin system, resulting from a combination of interactions with rf pulses and internal spin interactions.

II. Useful mathematical identities and tricks

If A, B, and C are normal quantum mechanical operators, then

$$\mathrm{Tr}\{ABC\} = \mathrm{Tr}\{CAB\} \qquad \text{(II.1)}$$

If the operator A has an inverse A^{-1}, such that $AA^{-1} = 1$, then

$$\mathrm{Tr}\{B\} = \mathrm{Tr}\{ABA^{-1}\} \qquad \text{(II.2)}$$

$$Ae^{B}A^{-1} = e^{ABA^{-1}} \qquad \text{(II.3)}$$

If I_x, I_y, and I_z are the operators for the x, y, and z components of spin angular momentum, then rotations of spin angular momentum (for example, by rf pulses) are expressed mathematically by equations such as

$$e^{-iI_x\theta}I_y e^{iI_x\theta} = I_y\cos\theta + I_z\sin\theta \qquad \text{(II.4a)}$$

$$e^{-iI_x\theta}I_z e^{iI_x\theta} = I_z\cos\theta - I_y\sin\theta \qquad \text{(II.4b)}$$

The same equations hold if the following substitutions are made: $\{I_x \to I_y,\ I_y \to I_z$, and $I_z \to I_x\}$ or $\{ I_x \to I_z,\ I_y \to I_x$, and $I_z \to I_y\}$. These are cyclic permutations of x, y, and z.

It is often useful to represent spin angular momenta by raising and lowering operators, which have the properties

$$I_\pm \equiv I_x \pm iI_y \qquad \text{(II.5a)}$$

$$e^{-iI_z\theta}I_\pm e^{iI_z\theta} = e^{\mp i\theta}I_\pm \qquad \text{(II.5b)}$$

When two operators A and B satisfy AB = BA, these operators are said to commute with one another. In general, quantum mechanical operators do not commute with one another. In other words, $[A,B] \equiv AB - BA \neq 0$. This means they can not be permuted without changing the result. However, if B has an inverse B^{-1}, then permutations can be accomplished (i.e., the order or grouping of A and B can be rearranged) by using the following trick:

$$AB = BA' \qquad \text{(II.6a)}$$

$$A' = B^{-1}AB \qquad \text{(II.6b)}$$

Therefore, if you have a set of N operators $\{A_j\}$ and a set of N invertible operators $\{B_j\}$, by applying Eqs. (II.6a,b) repeatedly, you can show that

$$A_N B_N A_{N-1} B_{N-1} A_{N-2} B_{N-2} \ldots A_2 B_2 A_1 B_1 = B_N B_{N-1} B_{N-2} \ldots B_2 B_1 A_N' A_{N-1}' A_{N-2}' \ldots A_2' A_1' \tag{II.7a}$$

$$A_k' = B_1^{-1} B_2^{-1} \ldots B_{k-2}^{-1} B_{k-1}^{-1} B_k^{-1} A_k B_k B_{k-1} B_{k-2} \ldots B_2 B_1 \tag{II.7b}$$

Eqs. (II.7a,b) are one of the keys to understanding Average Hamiltonian Theory and recoupling sequences, as shown below. These equations show that all of the operators $\{B_j\}$ can be pulled to one side, leaving the operators $\{A_j\}$ on the other side, but in the altered form $\{A_j'\}$.

As mentioned above, actual calculations or numerical simulations are usually performed by choosing a complete basis of states for the system, $\{|n\rangle\}$, that satisfies $\langle n | n' \rangle = \delta_{n,n'}$ and representing the density operator, Hamiltonian, and other operators as N X N matrices (where N is now the number of states in the basis set). For an operator A, the number in the n^{th} row and m^{th} column would be $\langle n | A | m \rangle$. In general, $\langle n | A | m \rangle$ is a complex number. The adjoint of A is another operator $A^\dagger$ with matrix elements $\langle n | A^\dagger | m \rangle = \langle m | A | n \rangle^*$.

A <u>Hermitean</u> operator is one for which $A = A^\dagger$, or $\langle n | A | m \rangle = \langle m | A | n \rangle^*$. In quantum mechanics, H, ρ, and all operators that represent observable quantities are Hermitean.

A <u>unitary</u> operator is one for which $A^{-1} = A^\dagger$, which implies that $\sum_{m=1}^{N} \langle n | A | m \rangle \langle m | A | n' \rangle^* = \delta_{n,n'}$. Quantum mechanical evolution operators U(t) are unitary. In general, if A is Hermitean, then e^{iA} and e^{-iA} are unitary. Angular momentum operators I_x, I_y, and I_z (but not I_+ and I_-) are Hermitean, so rotation operators (e.g., $e^{-iI_x\theta}$) are unitary.

For non-commuting operators,

$$(ABC)^\dagger = C^\dagger B^\dagger A^\dagger \tag{II.8a}$$

$$(ABC)^{-1} = C^{-1} B^{-1} A^{-1} \tag{II.8b}$$

According to Eqs. (II.8), we must reverse the order of noncommuting operators when we take the adjoint or inverse of a product of these operators.

In general, if $[A,B] \neq 0$, then $e^A e^B \neq e^{A+B} \neq e^B e^A$ (or $e^{iA} e^{iB} \neq e^{i(A+B)} \neq e^{iB} e^{iA}$ if we are concerned with making unitary operators from Hermitean operators A and B). However, if <u>both</u> A and B are very small, then the following approximations can be made (see Exercises):

$$e^A e^B \approx e^{A+B} \approx e^B e^A \tag{II.9}$$

On the other hand, if [A,B] = 0, Eqs. (II.9) are exactly true even if A and/or B are not small.

III. Nuclear spin interactions under MAS

NMR experiments are performed in the rotating frame (see Exercises). For present purposes, we assume that the nuclear spin Hamiltonian in the rotating frame contains only four terms, representing homonuclear dipole-dipole couplings, chemical shift anisotropy, isotropic chemical shifts, and interactions with rf pulses:

$$H(t) = H_D(t) + H_{CSA}(t) + H_{ICS} + H_{RF}(t) \tag{III.1}$$

A. Magnetic dipole-dipole coupling under MAS

For a pair of spins I_1 and I_2, the dipole-dipole coupling under MAS can be expressed as:

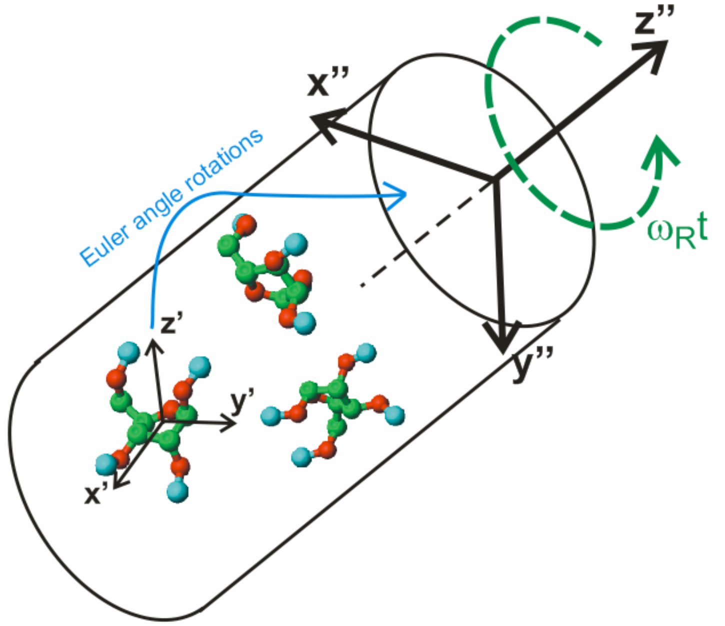
$$\begin{aligned} H_D(t) = [&A(\alpha,\beta)\cos(\omega_R t + \gamma) + B(\alpha,\beta)\sin(\omega_R t + \gamma) + C(\alpha,\beta)\cos(2\omega_R t + 2\gamma) \\ &+ D(\alpha,\beta)\sin(2\omega_R t + 2\gamma)] \times (3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2) \end{aligned} \tag{III.2}$$

This is the "truncated" dipole-dipole coupling, *i.e.*, the part for which $[\omega_0 I_z, H_D(t)] = 0$, where ω_0 is the NMR frequency (in rad/s) and $\omega_0 I_z$ is the Zeeman interaction with the large external static field along z (which vanishes in the rotating frame). The full dipole-dipole coupling includes other terms (see the Appendix), which normally don't affect high-field NMR spectra directly because they do not commute with the very strong Zeeman interaction, but do contribute to spin relaxation. Eq. (III.2) is one useful way to express $H_D(t)$, but there are others (see Section VI, for example).

The MAS frequency is $\omega_R = 2\pi / \tau_R$. The angles α,β,γ are "Euler angles" that relate the orientation of a particular molecule within the MAS rotor to an axis system that is fixed with respect to the rotor:

$$R_{z''}(\alpha) R_{y''}(\beta) R_{z''}(\gamma) \begin{pmatrix} \mathbf{x}' \\ \mathbf{y}' \\ \mathbf{z}' \end{pmatrix} = \begin{pmatrix} \mathbf{x}'' \\ \mathbf{y}'' \\ \mathbf{z}'' \end{pmatrix} \tag{III.3}$$

In Eq. (III.3), {**x'**,**y'**,**z'**} are the molecule-fixed axes and {**x''**,**y''**,**z''**} are the rotor-fixed axes. $R_{z''}(\phi)$ and $R_{y''}(\phi)$ are rotations of the axes about **z''** and **y''** by angle ϕ. These axis systems are depicted below:



Schematic depiction of an MAS rotor, showing rotor-fixed axes {**x**'',**y**'',**z**''} and randomly oriented molecules with molecule-fixed axes {**x**',**y**',**z**'}. The two axis systems are related by rotations by Euler angles, as in Eq. (III.3), which are different for different molecules. The MAS rotor rotates about its **z**'' axis.

The coefficients A(α,β), B(α,β), C(α,β), and D(α,β) in Eq. (III.2) are proportional to γ_I^2/R^3, where γ_I is the gyromagnetic ratio and R is the internuclear distance. We shall not worry about the detailed functional form of these coefficients in the analyses of recoupling sequences presented below. See the Appendix for a complete derivation of Eq. (III.2), including general expressions for these coefficients. The maximum value of the total coefficient of $(3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2)$ is $\gamma_I{}^2\hbar / R^3$. For ^{13}C spin pairs, this is 2π×7.59 kHz when R = 1.00 Å.

Note that the dependence on the Euler angle γ always appears as $\omega_R t + \gamma$. This is because molecules with different values of γ (but the same α and β) differ in their orientations by a rotation about **z**", which is the MAS rotation axis. So, as the sample spins, molecules with different values of γ are rotated into one another, thus having the same coefficient of $(3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2)$ at different values of t.

Note that the time average of $H_D(t)$ is zero under MAS. Note also that $H_D(t)$ contains terms that oscillate at ω_R and terms that oscillate at $2\omega_R$.

Finally, note that $H_D(t)$ is a “zero-quantum operator”. This means that $H_D(t)$ has non-zero matrix elements only between states that have the same total z component of angular momentum. For a system of two spin-1/2 nuclei, the only non-zero matrix elements are

$$< ++ | (3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2) | ++ > = < -- | (3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2) | -- > = 1/2 \qquad \text{(III.4a)}$$

$$<+-|(3I_{z1}I_{z2}-\mathbf{I}_1\cdot\mathbf{I}_2)|-+>=<-+|(3I_{z1}I_{z2}-\mathbf{I}_1\cdot\mathbf{I}_2)|+->=-1/2 \quad \text{(III.4b)}$$

The dipole-dipole coupling for a static sample is obtained by setting ω_R to zero in Eq. (III.2). Recoupled dipole-dipole interactions generally have different orientation dependences than static couplings (i.e., different dependences on α,β,γ), and can be zero-quantum, one-quantum, or two-quantum operators (or a mixture of these).

B. Chemical shift anisotropy and isotropic chemical shift

For one spin I,

$$\begin{aligned} H_{CSA}(t) = {} & [A'(\alpha,\beta)\cos(\omega_R t+\gamma)+B'(\alpha,\beta)\sin(\omega_R t+\gamma) \\ & +C'(\alpha,\beta)\cos(2\omega_R t+2\gamma)+D'(\alpha,\beta)\sin(2\omega_R t+2\gamma)]I_z \end{aligned} \quad \text{(III.5a)}$$

$$H_{ICS}=\omega_I I_z \quad \text{(III.5b)}$$

The isotropic chemical shift ω_I is defined here to be the time-independent part of the difference between the actual NMR frequency of spin I and the rf carrier frequency ω_{rf}. Under MAS, the chemical shift anisotropy (CSA) has the same type of time-dependence as the dipole-dipole coupling (i.e., terms that oscillate at ω_R and $2\omega_R$), but the operator part is simply I_z. An important difference is that

$$e^{-iI_x\pi}H_D(t)e^{iI_x\pi}=H_D(t) \quad \text{(III.6a)}$$

but

$$e^{-iI_x\pi}H_{CSA}(t)e^{iI_x\pi}=-H_{CSA}(t) \quad \text{(III.6b)}$$

This allows chemical shifts and dipole-dipole couplings to be affected differently by pulse sequences, especially recoupling sequences.

C. Radio-frequency pulses

$$H_{RF}(t)=\omega_1(t)[I_x\cos\phi(t)+I_y\sin\phi(t)] \quad \text{(III.7)}$$

The rf amplitude is $\omega_1(t)$. The rf phase is $\phi(t)$.

When a pulse sequence contains short pulses with amplitudes that greatly exceed the strengths of dipole-dipole and chemical shift interactions and the MAS frequency, the pulses can be treated as instantaneous rotations of spin angular momenta. This is the delta-function pulse limit. In this limit, the rotation (i.e., the evolution operator) produced by a pulse of length t_p is the operator

$$\begin{aligned} R(\theta,\phi) &= e^{-i(I_x \cos\phi + I_y \sin\phi)\theta} \\ &= R_z(\phi) e^{-iI_x\theta} R_z(-\phi) \\ &= R_z(\phi) R_x(\theta) R_z(-\phi) \end{aligned} \tag{III.7}$$

where $\theta = \omega_1 t_p$ is the pulse flip angle.

In general, the net rotation produced by a pulse sequence alone (i.e., ignoring $H_D(t)$, $H_{CSA}(t)$, and H_{ICS}) is

$$U_{RF}(t) = \vec{T}\exp\{-i\int_0^t dt'\,\omega_1(t')[I_x \cos\phi(t') + I_y \sin\phi(t')]\} \tag{III.8}$$

If all pulses in a pulse sequence are phase-shifted by $\Delta\phi$, then the net rotation becomes

$$\begin{aligned} U_{RF}(t;\Delta\phi) &= \vec{T}\exp\{-i\int_0^t dt'\,\omega_1(t')[I_x \cos(\phi(t') + \Delta\phi) + I_y \sin(\phi(t') + \Delta\phi)]\} \\ &= \vec{T}\exp\{-i[e^{-iI_z\Delta\phi}\int_0^t dt'\,\omega_1(t')[I_x \cos\phi(t') + I_y \sin\phi(t')]e^{iI_z\Delta\phi}]\} \\ &= e^{-iI_z\Delta\phi}\vec{T}\exp\{-i\int_0^t dt'\,\omega_1(t')[I_x \cos\phi(t') + I_y \sin\phi(t')]\}\, e^{iI_z\Delta\phi} \\ &= e^{-iI_z\Delta\phi}U_{RF}(t;0)e^{iI_z\Delta\phi} \end{aligned} \tag{III.9}$$

Similarly, if we include all four Hamiltonian terms, the evolution operator for the pulse sequence is

$$U(t) = \vec{T}\exp\{-i\int_0^t dt'[\omega_1(t')[I_x \cos\phi(t') + I_y \sin\phi(t')] + H_D(t') + H_{CSA}(t') + H_{ICS}]\} \tag{III.10}$$

and a phase shift changes the evolution operator to

$$\begin{aligned} U(t;\Delta\phi) &= \vec{T}\exp\{-i\int_0^t dt'[\omega_1(t')[I_x \cos(\phi(t') + \Delta\phi) + I_y \sin(\phi(t') + \Delta\phi)] + H_D(t') + H_{CSA}(t') + H_{ICS}]\} \\ &= \vec{T}\exp\{-i[e^{-iI_z\Delta\phi}\int_0^t dt'[\omega_1(t')[I_x \cos\phi(t') + I_y \sin\phi(t')] + H_D(t') + H_{CSA}(t') + H_{ICS}]e^{iI_z\Delta\phi}]\} \\ &= e^{-iI_z\Delta\phi}U(t;0)e^{iI_z\Delta\phi} \end{aligned} \tag{III.11}$$

Eq. (III.11) is valid because $H_D(t)$, $H_{CSA}(t)$, and H_{ICS} all commute with I_z. If this were not true (i.e., if we were not in the high-field limit), the effect of an overall rf phase shift could be more complicated.

Another useful operation is an rf phase reversal, meaning $\phi(t) \rightarrow -\phi(t)$. The effect of a phase reversal is to change the evolution operator to

$$\begin{aligned}
U'(t) &= \vec{T}\exp\{-i\int_0^t dt'[\omega_1(t')[I_x\cos(-\phi(t')) + I_y\sin(-\phi(t'))] + H_D(t') + H_{CSA}(t') + H_{ICS}]\\
&= \vec{T}\exp\{-i\int_0^t dt'[\omega_1(t')[I_x\cos\phi(t') - I_y\sin\phi(t')] + H_D(t') + H_{CSA}(t') + H_{ICS}]\\
&= \vec{T}\exp\{-i\int_0^t dt' e^{-i\pi I_x}[\omega_1(t')[I_x\cos\phi(t') + I_y\sin\phi(t')]e^{i\pi I_x} + H_D(t') + H_{CSA}(t') + H_{ICS}]\\
&= \vec{T}\exp\{-i\int_0^t dt' e^{-i\pi I_x}[[\omega_1(t')[I_x\cos\phi(t') + I_y\sin\phi(t')] + H_D(t') - H_{CSA}(t') - H_{ICS}]]e^{i\pi I_x}\\
&= e^{-i\pi I_x}U''(t)e^{i\pi I_x}
\end{aligned}$$

(III.12)

Thus, a phase reversal is equivalent to changing the sign of chemical shifts and rotating the resulting evolution operator U''(t) by 180° around x.

IV. Average Hamiltonian Theory in simple terms

AHT [Haeberlen and Waugh, Phys. Rev. **175**, 453 (1968)] is a mathematical formalism that allows us to analyze how pulse sequences affect internal spin interactions[1,2]. AHT is particularly useful in the derivation and analysis of pulse sequences that consist of a block of rf irradiation that is repeated many times. This is precisely the situation that arises in dipolar recoupling experiments. If the rf block has length τ_c (called the cycle time), then AHT is applicable when the following conditions are met:

$$H_{RF}(\tau_c + t) = H_{RF}(t) \tag{IV.1a}$$
$$H_D(\tau_c + t) = H_D(t) \tag{IV.1b}$$
$$H_{CSA}(\tau_c + t) = H_{CSA}(t) \tag{IV.1c}$$

$$U_{RF}(\tau_c) = 1 \tag{IV.2}$$

$$\| H_D \| \tau_c << 1, \quad \| H_{CSA} \| \tau_c << 1, \quad \| H_{ICS} \| \tau_c << 1 \tag{IV.3}$$

Eqs. (IV.1) says that the rf pulse sequence is periodic and the internal spin interactions are also periodic. In recoupling sequences, this means τ_c should be a multiple of τ_R. Eq. (IV.2) says that the net rotation produced by the rf block is zero (or sometimes a multiple of 2π). The rf block is then called a "cycle". Eq. (IV.3) says that τ_c is short enough that the dipole-dipole and chemical shift interactions can not produce a large change in the state of the spin system in one cycle. This allows a "perturbation theory" approach such as AHT to be employed, based on Eq. (II.9).

AHT depends on changing the picture in which we view the evolution of the spin system from the usual rotating frame (in which H_{RF}, H_D, H_{CSA}, and H_{ICS} together determine the spin evolution) to a new frame of reference in which the rf pulses no longer appear directly. Instead, the rf pulses cause additional time dependences in H_D, H_{CSA}, and H_{ICS}. This new frame of reference is called the interaction representation with respect to H_{RF}.

Mathematically, the interaction representation works as follows: If U(t) is the evolution operator for the entire rotating frame Hamiltonian, we define a new evolution operator $\tilde{U}(t)$ that satisfies $U(t) = U_{RF}(t)\tilde{U}(t)$. Then we ask, "What is the new Hamiltonian that corresponds to $\tilde{U}(t)$?" This is easily calculated, using the general relations $i\frac{d}{dt}U(t) = H(t)U(t)$ [see Eq. (I.4)] and $i\frac{d}{dt}[U(t)^{-1}] = -U(t)^{-1}H(t)$ [see Eqs (II.8) and recall that U(t) is unitary and H(t) is Hermitean; also, the adjoint of the number i is –i].

$$\begin{aligned} i\frac{d}{dt}\tilde{U}(t) &= i\frac{d}{dt}[U_{RF}(t)^{-1}U(t)] \\ &= \left(i\frac{d}{dt}[U_{RF}(t)^{-1}]\right)U(t) + U_{RF}(t)^{-1}\left(i\frac{d}{dt}U(t)\right) \\ &= -U_{RF}(t)^{-1}H_{RF}(t)U(t) + U_{RF}(t)^{-1}[H_{RF}(t) + H_D(t) + H_{CSA}(t) + H_{ICS}]U(t) \\ &= U_{RF}(t)^{-1}[H_D(t) + H_{CSA}(t) + H_{ICS}]U_{RF}(t)\tilde{U}(t) \end{aligned} \tag{IV.4}$$

Therefore,

$$\tilde{H}(t) = \tilde{H}_D(t) + \tilde{H}_{CSA}(t) + \tilde{H}_{ICS} \tag{IV.5}$$

with

$$\tilde{H}_D(t) = U_{RF}(t)^{-1}H_D(t)U_{RF}(t) \tag{IV.6a}$$
$$\tilde{H}_{CSA}(t) = U_{RF}(t)^{-1}H_{CSA}(t)U_{RF}(t) \tag{IV.6b}$$
$$\tilde{H}_{ICS} = U_{RF}(t)^{-1}H_{ICS}U_{RF}(t) \tag{IV.6c}$$

So the dipole-dipole and chemical shift Hamiltonian terms in the interaction representation are the same as in the usual rotating frame, but with their spin operator parts rotated by $U_{RF}(t)^{-1}$. (Note that this rotation is the inverse of $U_{RF}(t)$, so the order of the pulses in a pulse sequence is reversed and the sign of the flip angles is changed. This is very important in AHT calculations.)

$U_{RF}(t)^{-1}$ acts on the spin operator parts of $H_D(t)$, $H_{CSA}(t)$, and $H_{ICS}(t)$, making these spin operator parts time-independent. In recoupling techniques, the time-dependence of the spin operator parts induced by the rf pulses interferes with the spatial time dependence from MAS, in general preventing $\tilde{H}_D(t)$ and/or $\tilde{H}_{CSA}(t)$ from averaging to zero.

Because of Eq. (IV.2), $U(\tau_c) = \tilde{U}(\tau_c)$. Because of Eq. (IV.1), $U(N\tau_c) = \tilde{U}(\tau_c)^N$. Because of Eq. (IV.3), we can approximate $\tilde{U}(\tau_c)$ by

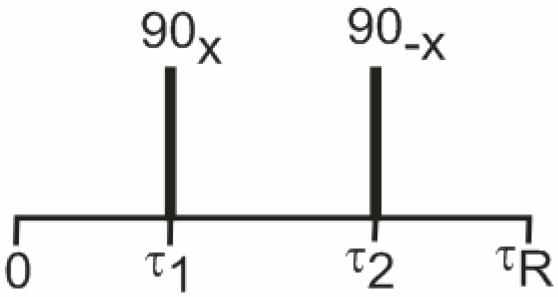
$$\begin{aligned}\tilde{U}(\tau_c) &\approx \exp\{-i\int_0^{\tau_c} dt\tilde{H}(t)\} \\ &= e^{-i\tilde{H}_{ave}\tau_c}\end{aligned} \tag{IV.7}$$

with $\tilde{H}_{ave} = \frac{1}{\tau_c}\int_0^{\tau_c} dt\tilde{H}(t)$. Therefore, as long as we care only about the state of the spin system at multiples of τ_c (and not in the middle of the rf blocks), then it is sufficient to calculate the average Hamiltonian in the interaction representation. To a good approximation, the NMR signals will be determined by $\tilde{H}_{ave}$ alone.

V. Homonuclear dipolar recoupling mechanisms

A. Delta-function pulse sequences

Consider the following simple pulse sequence, called DRAMA [see R. Tycko and G. Dabbagh, Chem. Phys. Lett. **173**, 461 (1990)][3]:



How do we use AHT to calculate what this does to homonuclear dipole-dipole couplings and chemical shifts?

Because the sequence consists of delta-function pulses, $U_{RF}(t)$ is piecewise-constant:

$$U_{RF}(t) = \begin{cases} 1, 0 < t < \tau_1 \\ e^{-iI_x\pi/2}, \tau_1 < t < \tau_2 \\ 1, \tau_2 < t < \tau_R \end{cases} \tag{V.1}$$

Abbreviating $A\cos(\omega_R t + \gamma) + B\sin(\omega_R t + \gamma) + C\cos(2\omega_R t + 2\gamma) + D\sin(2\omega_R t + 2\gamma)$ from Eq. (III.2) by (A,B,C,D), the interaction representation Hamiltonians are

$$\tilde{H}_D(t) = \begin{cases} (A,B,C,D)\times(3I_{z1}I_{z2} - \mathbf{I}_1\cdot\mathbf{I}_2),\ 0 < t < \tau_1 \\ (A,B,C,D)\times(3I_{y1}I_{y2} - \mathbf{I}_1\cdot\mathbf{I}_2), \tau_1 < t < \tau_2 \\ (A,B,C,D)\times(3I_{z1}I_{z2} - \mathbf{I}_1\cdot\mathbf{I}_2),\ \tau_2 < t < \tau_R \end{cases} \tag{V.2}$$

$$\tilde{H}_{CSA}(t) = \begin{cases} (A',B',C',D')\times I_z,\ 0 < t < \tau_1 \\ (A',B',C',D')\times I_y, \tau_1 < t < \tau_2 \\ (A',B',C',D')\times I_z,\ \tau_2 < t < \tau_R \end{cases} \tag{V.3a}$$

$$\tilde{H}_{ICS}(t) = \begin{cases} \omega_I I_z,\ 0 < t < \tau_1 \\ \omega_I I_y, \tau_1 < t < \tau_2 \\ \omega_I I_z,\ \tau_2 < t < \tau_R \end{cases} \tag{V.3b}$$

The average Hamiltonians are

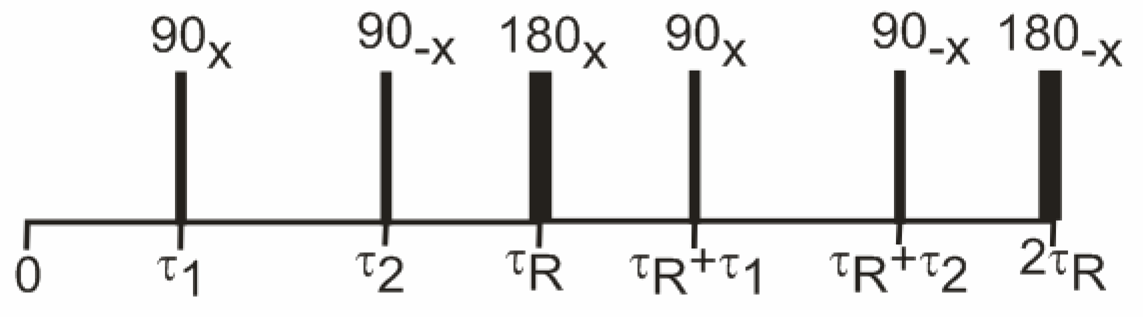
$$\begin{aligned} \tilde{H}_{D,ave} = 3(I_{y1}I_{y2} - I_{z1}I_{z2})\{&\frac{A}{2\pi}[\sin(\omega_R\tau_2+\gamma)-\sin(\omega_R\tau_1+\gamma)] - \frac{B}{2\pi}[\cos(\omega_R\tau_2+\gamma)-\cos(\omega_R\tau_1+\gamma)] \\ &+\frac{C}{4\pi}[\sin(2\omega_R\tau_2+2\gamma)-\sin(2\omega_R\tau_1+2\gamma)] - \frac{D}{4\pi}[\cos(2\omega_R\tau_2+2\gamma)-\cos(2\omega_R\tau_1+2\gamma)]\} \end{aligned} \tag{V.4}$$

$$\begin{aligned} \tilde{H}_{CSA,ave} = (I_y - I_z)\{&\frac{A'}{2\pi}[\sin(\omega_R\tau_2+\gamma)-\sin(\omega_R\tau_1+\gamma)] - \frac{B'}{2\pi}[\cos(\omega_R\tau_2+\gamma)-\cos(\omega_R\tau_1+\gamma)] \\ &+\frac{C'}{4\pi}[\sin(2\omega_R\tau_2+2\gamma)-\sin(2\omega_R\tau_1+2\gamma)] - \frac{D'}{4\pi}[\cos(2\omega_R\tau_2+2\gamma)-\cos(2\omega_R\tau_1+2\gamma)]\} \end{aligned} \tag{V.5a}$$

$$\tilde{H}_{ICS,ave} = \omega_I[(I_y - I_z)\frac{\tau_2-\tau_1}{\tau_R} + I_z] \tag{V.5b}$$

So both the dipole-dipole coupling and the CSA are recoupled, and the isotropic chemical shift is altered. Note that only the $3I_{z1}I_{z2}$ part of $H_D(t)$ contributes to the recoupled dipole-dipole Hamiltonian. This is a general rule, because the $\mathbf{I}_1\cdot\mathbf{I}_2$ part is not affected by the rf pulses.

Now consider a longer DRAMA pulse sequence with additional 180° pulses:



For this sequence

$$U_{RF}(t)=\begin{cases} 1, 0<t<\tau_1 \\ e^{-iI_x\pi/2}, \tau_1<t<\tau_2 \\ 1, \tau_2<t<\tau_R \\ e^{-iI_x\pi}, \tau_R<t<\tau_R+\tau_1 \\ e^{-iI_x 3\pi/2}, \tau_R+\tau_1<t<\tau_R+\tau_2 \\ e^{-iI_x\pi}, \tau_R+\tau_2<t<2\tau_R \end{cases} \tag{V.6}$$

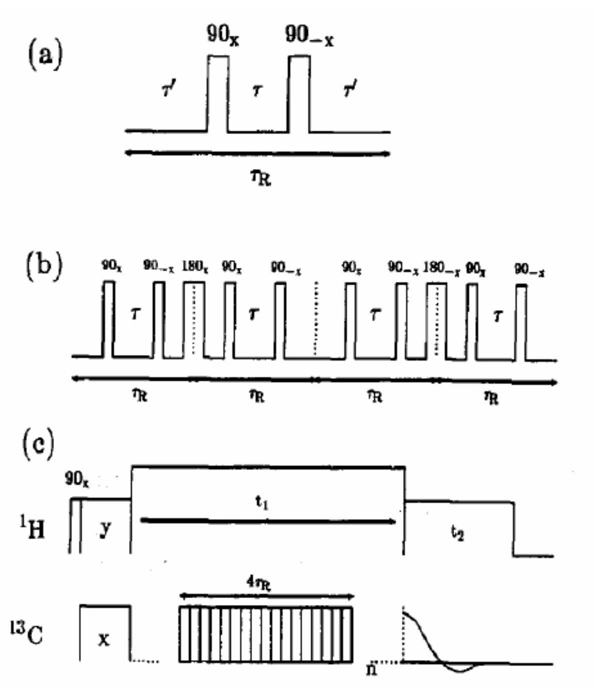
$$\tilde{H}_D(t)=\begin{cases} (A,B,C,D)\times(3I_{z1}I_{z2}-\mathbf{I}_1\cdot\mathbf{I}_2), 0<t<\tau_1 \\ (A,B,C,D)\times(3I_{y1}I_{y2}-\mathbf{I}_1\cdot\mathbf{I}_2), \tau_1<t<\tau_2 \\ (A,B,C,D)\times(3I_{z1}I_{z2}-\mathbf{I}_1\cdot\mathbf{I}_2), \tau_2<t<\tau_R \\ (A,B,C,D)\times(3I_{z1}I_{z2}-\mathbf{I}_1\cdot\mathbf{I}_2), \tau_R<t<\tau_R+\tau_1 \\ (A,B,C,D)\times(3I_{y1}I_{y2}-\mathbf{I}_1\cdot\mathbf{I}_2), \tau_R+\tau_1<t<\tau_R+\tau_2 \\ (A,B,C,D)\times(3I_{z1}I_{z2}-\mathbf{I}_1\cdot\mathbf{I}_2), \tau_R+\tau_2<t<2\tau_R \end{cases} \tag{V.7}$$

$$\tilde{H}_{CSA}(t)=\begin{cases} (A',B',C',D')\times I_z, 0<t<\tau_1 \\ (A',B',C',D')\times I_y, \tau_1<t<\tau_2 \\ (A',B',C',D')\times I_z, \tau_2<t<\tau_R \\ -(A',B',C',D')\times I_z, \tau_R<t<\tau_R+\tau_1 \\ -(A',B',C',D')\times I_y, \tau_R+\tau_1<t<\tau_R+\tau_2 \\ -(A',B',C',D')\times I_z, \tau_R+\tau_2<t<2\tau_R \end{cases} \tag{V.8a}$$

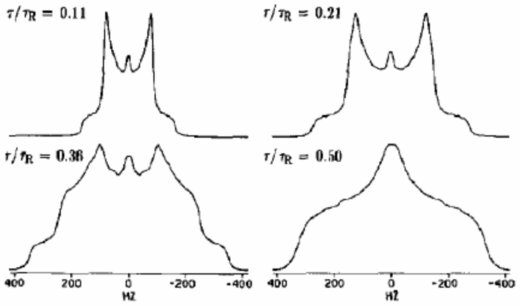
$$\tilde{H}_{ICS}(t)=\begin{cases} \omega_I I_z, 0<t<\tau_1 \\ \omega_I I_y, \tau_1<t<\tau_2 \\ \omega_I I_z, \tau_2<t<\tau_R \\ -\omega_I I_z, \tau_R<t<\tau_R+\tau_1 \\ -\omega_I I_y, \tau_R+\tau_1<t<\tau_R+\tau_2 \\ -\omega_I I_z, \tau_R+\tau_2<t<2\tau_R \end{cases} \tag{V.8b}$$

Now, $\tilde{H}_{D,ave}$ is the same as before (because $\tilde{H}_D(t)$ is not affected by the additional 180° pulses), but $\tilde{H}_{CSA,ave} = \tilde{H}_{ICS,ave} = 0$ (because the 180° pulses change the signs of $\tilde{H}_{CSA}(t)$ and $\tilde{H}_{ICS}(t)$ in the second rotor period). Dipole-dipole couplings are now selectively recoupled.

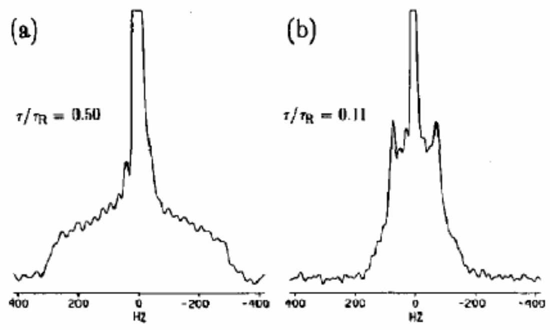
Through the dependence on α, β , and γ, $\tilde{H}_{D,ave}$ depends on molecular orientation in the MAS rotor. Dipolar lineshapes are then powder patterns. The lineshape depends on $\tau_2 - \tau_1$, because the A, B, C, and D terms have different relative magnitudes for different values of $\tau_2 - \tau_1$. In the limit that $(\tau_2 - \tau_1)/\tau_R << 1$, the lineshape resembles the Pake doublet pattern of a static sample for a two-spin system (see Exercises). Note that the operator part of $\tilde{H}_{D,ave}$ under DRAMA is different from the operator part of $H_D(t)$. Under the DRAMA sequences depicted above, $\tilde{H}_{D,ave}$ contains both zero-quantum and double-quantum terms.



Pulse sequences used in DRAMA experiments [Chem. Phys. Lett. **173**, 461 (1990)]



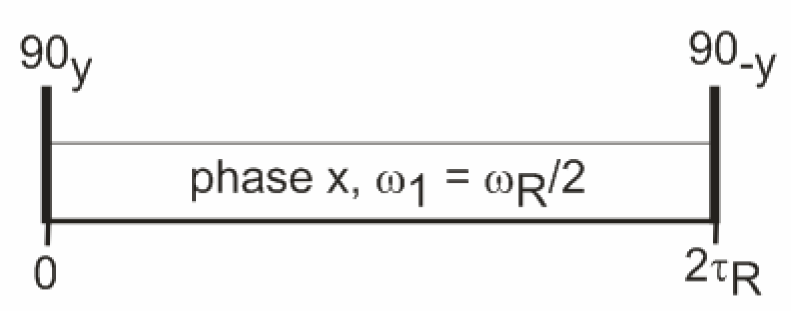
Simulated dipolar powder patterns for two-spin ^{13}C system with maximum splitting = 1.5 kHz (R = 2.48 Å)



Experimental dipolar powder patterns (Fourier transform with respect to t_1) for $(^{13}CH_3)_2C(OH)SO_3Na$ powder, for which R = 2.51 Å.

B. Continuous rf irradiation

Consider the following pulse sequence, called 2Q-HORROR [see N.C. Nielsen, H. Bildsoe, H.J. Jakobsen, and M.H. Levitt, J. Chem. Phys. **101**, 1805 (1994)]^4:



In other words, the cycle here is a 90_y-360_x-90_{-y} sequence, with delta-function 90° pulses and a very long, weak 360° pulse. For this sequence,

$$\begin{aligned} U_{RF}(t) &= e^{-iI_x\omega_1 t}e^{-iI_y\pi/2} \\ &= e^{-iI_x\omega_R t/2}e^{-iI_y\pi/2} \end{aligned} \qquad \text{(V.9)}$$

for $0 < t < 2\tau_R$. The interaction representation Hamiltonians are then

$$\begin{aligned} \tilde{H}_D(t) &= (A,B,C,D)\times[3(-I_{x1}\cos\frac{\omega_R t}{2} + I_{y1}\sin\frac{\omega_R t}{2})(-I_{x2}\cos\frac{\omega_R t}{2} + I_{y2}\sin\frac{\omega_R t}{2}) - \mathbf{I}_1\cdot\mathbf{I}_2] \\ &= (A,B,C,D)\times[3(I_{x1}I_{x2}\cos^2\frac{\omega_R t}{2} + I_{y1}I_{y2}\sin^2\frac{\omega_R t}{2} - (I_{y1}I_{x2} + I_{x1}I_{y2})\sin\frac{\omega_R t}{2}\cos\frac{\omega_R t}{2} - \mathbf{I}_1\cdot\mathbf{I}_2] \\ &= (A,B,C,D)\times[\frac{3}{2}((I_{x1}I_{x2} - I_{y1}I_{y2})\cos\omega_R t + (I_{x1}I_{x2} + I_{y1}I_{y2}) - (I_{y1}I_{x2} + I_{x1}I_{y2})\sin\omega_R t) - \mathbf{I}_1\cdot\mathbf{I}_2] \\ &= (A,B,C,D)\times[\frac{3}{4}((I_{+1}I_{+2} + I_{-1}I_{-2})\cos\omega_R t + i(I_{+1}I_{+2} - I_{-1}I_{-2})\sin\omega_R t + (I_{+1}I_{-2} + I_{-1}I_{+2})) - \mathbf{I}_1\cdot\mathbf{I}_2] \end{aligned}$$

(V.10)

$$\tilde{H}_{CSA}(t) = (A',B',C',D')\times(-I_x\cos\frac{\omega_R t}{2} + I_y\sin\frac{\omega_R t}{2}) \qquad \text{(V.11a)}$$

$$\tilde{H}_{ICS}(t) = \omega_I(-I_x\cos\frac{\omega_R t}{2} + I_y\sin\frac{\omega_R t}{2}) \qquad \text{(V.11b)}$$

Eq. (V.10) makes use of the identities $\cos^2\theta = (1+\cos 2\theta)/2$ and $\sin^2\theta = (1-\cos 2\theta)/2$, as well as $I_\pm = I_x + iI_y$. Although $\tilde{H}_D(t)$ contains both double-quantum and zero-quantum operator terms, only the double-quantum terms oscillate in time. Therefore, only the double-quantum terms are recoupled. Using the relations $\int_0^{2\tau_R} dt\cos\frac{k\omega_R t}{2}\cos\frac{n\omega_R t}{2} = \tau_R\delta_{k,n}$,

$\int_0^{2\tau_R} dt \sin\frac{k\omega_R t}{2}\sin\frac{n\omega_R t}{2} = \tau_R\delta_{k,n}$, and $\int_0^{2\tau_R} dt \sin\frac{k\omega_R t}{2}\cos\frac{n\omega_R t}{2} = 0$ for integers k and n, it is straightforward to show that $\tilde{H}_{CSA,ave} = \tilde{H}_{ICS,ave} = 0$ and that

$$\tilde{H}_{D,ave} = \frac{3}{8}[(I_{+1}I_{+2} + I_{-1}I_{-2})(A\cos\gamma + B\sin\gamma) + i(I_{+1}I_{+2} - I_{-1}I_{-2})(-A\sin\gamma + B\cos\gamma)] \qquad \text{(V.12)}$$

Thus, the 2Q-HORROR sequence creates a pure double-quantum recoupled Hamiltonian (assuming that the AHT approximation is valid and that the pulses are perfect). The average Hamiltonian contains two double-quantum terms, whose magnitudes depend on the Euler angles α,β,γ. Interestingly, the overall magnitude of $\tilde{H}_{D,ave}$ is independent of the γ angle (see Exercises). Recoupling sequences with this property are called "γ-encoded". This property causes the dipolar powder pattern lineshape under 2Q-HORROR and other γ-encoded sequences to have two sharp horns (see below), which means that the signal decay under $\tilde{H}_{D,ave}$ is strongly oscillatory. This is good for quantitative measurements of internuclear distances, and also for double-quantum filtering efficiencies.

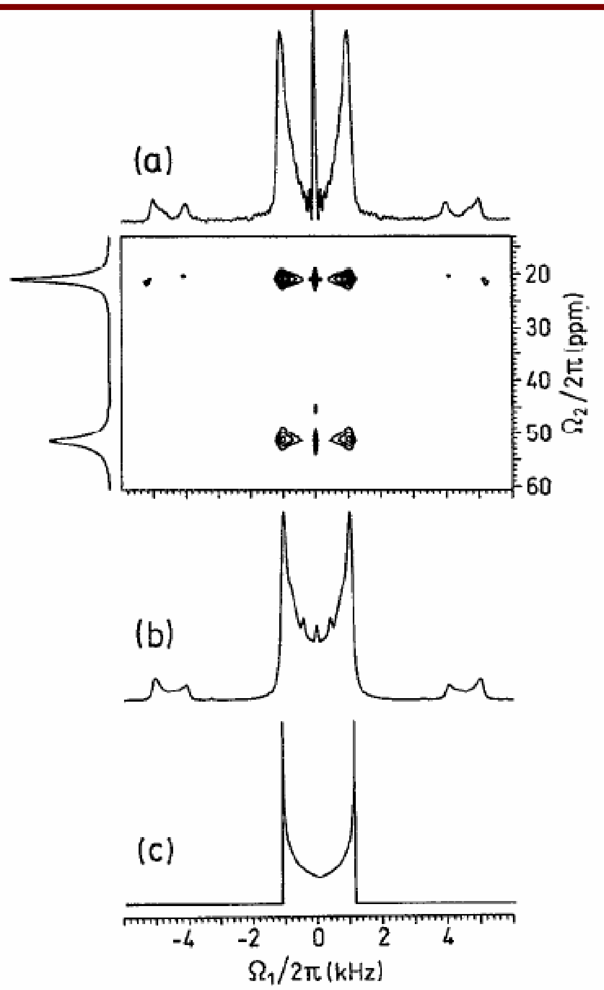
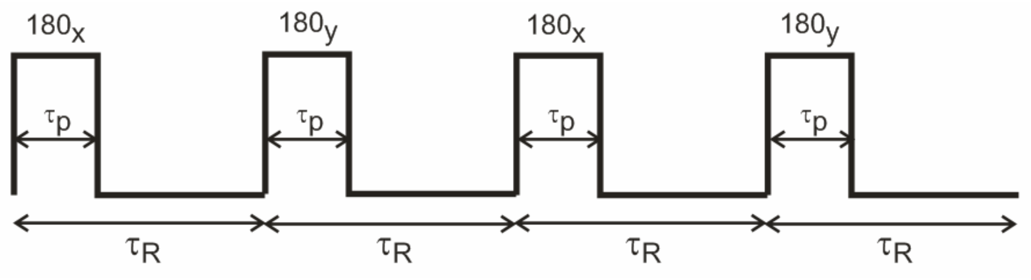


FIG. 5. Experimental and simulated ^{13}C 2Q-HORROR nutation spectra of $^{13}C_2$-2,3-*L*-alanine corresponding to the pulse sequence in Fig. 2(c). (a) Experimental 2D contour plot with a Ω_1 slice through the CH resonance (horizontal) and a projection onto the Ω_2 axis (vertical). The experimental spectrum were obtained using the conditions in Ref. 20 with $\omega_r/2\pi=9178$ Hz, $\omega_1/2\pi=4370$ Hz, and 96 t_1 increments (40 transients each) separated by 80 μs. (b) Exact numerical simulations employing the parameters in Ref. 21. (c) Simulation using the analytical expressions in Eqs. (18) and (19). Linewidths of 50 and 125 Hz (Lorentzian, FWHM) were used for the Ω_1 slice (additional linebroadening) and the simulation in (b), respectively.

Simulated and experimental 2Q-HORROR data for a ^{13}C-^{13}C pair with R ≈ 1.54 Å [from Nielsen et al, J. Chem. Phys. **101**, 1805 (1994)].

C. Finite-pulse recoupling sequences

Consider the following sequence, called “finite-pulse Radio-Frequency-Driven Recoupling” or fpRFDR [see Y. Ishii, J. Chem. Phys. **114**, 8473 (2001) and A.E. Bennett, C.M. Rienstra, J.M. Griffiths, W.G. Zhen, P.T. Lansbury, and R.G. Griffin, J. Chem. Phys. **108**, 9463 (1998)][5,6]:



The cycle time is $4\tau_R$, there is one 180° pulse in each rotor period, and the pulse length is a significant fraction of the rotor period. The rf amplitude during each pulse is $\omega_1 = \frac{\pi}{\tau_p}$. For this pulse sequence,

$$U_{RF}(t) = \begin{cases} e^{-i\pi I_x t/\tau_p}, 0 < t < \tau_p \\ e^{-i\pi I_x}, \tau_p < t < \tau_R \\ e^{-i\pi I_y (t-\tau_R)/\tau_p} e^{-i\pi I_x}, \tau_R < t < \tau_R + \tau_p \\ e^{-i\pi I_y} e^{-i\pi I_x}, \tau_R + \tau_p < t < 2\tau_R \\ e^{-i\pi I_x (t-2\tau_R)/\tau_p} e^{-i\pi I_y} e^{-i\pi I_x}, 2\tau_R < t < 2\tau_R + \tau_p \\ e^{-i\pi I_x} e^{-i\pi I_y} e^{-i\pi I_x}, 2\tau_R + \tau_p < t < 3\tau_R \\ e^{-i\pi I_y (t-3\tau_R)/\tau_p} e^{-i\pi I_x} e^{-i\pi I_y} e^{-i\pi I_x}, 3\tau_R < t < 3\tau_R + \tau_p \\ e^{-i\pi I_y} e^{-i\pi I_x} e^{-i\pi I_y} e^{-i\pi I_x}, 3\tau_R + \tau_p < t < 4\tau_R \end{cases} \qquad \text{(V.13)}$$

Using the identity $e^{-i\pi I_y} e^{-i\pi I_x} = e^{i\pi I_z}$ (see Exercises), Eq. (V.13) can be simplified:

$$U_{RF}(t)=\begin{cases} e^{-i\pi I_x t/\tau_p}, 0<t<\tau_p \\ e^{-i\pi I_x}, \tau_p<t<\tau_R \\ e^{-i\pi I_y (t-\tau_R)/\tau_p} e^{-i\pi I_x}, \tau_R<t<\tau_R+\tau_p \\ e^{i\pi I_z}, \tau_R+\tau_p<t<2\tau_R \\ e^{-i\pi I_x (t-2\tau_R)/\tau_p} e^{i\pi I_z}, 2\tau_R<t<2\tau_R+\tau_p \\ e^{-i\pi I_x} e^{i\pi I_z}, 2\tau_R+\tau_p<t<3\tau_R \\ e^{-i\pi I_y (t-2\tau_R)/\tau_p} e^{-i\pi I_x} e^{i\pi I_z}, 3\tau_R<t<3\tau_R+\tau_p \\ 1, 3\tau_R+\tau_p<t<4\tau_R \end{cases} \qquad \text{(V.14)}$$

Ignoring the $\mathbf{I}_1\cdot\mathbf{I}_2$ term (which is not recoupled, as explained above), the interaction-representation dipole-dipole Hamiltonian is then

$$\tilde{H}_D(t)=\begin{cases} (A,B,C,D)\times[3(I_{z1}\cos\frac{\pi t}{\tau_p}+I_{y1}\sin\frac{\pi t}{\tau_p})(I_{z2}\cos\frac{\pi t}{\tau_p}+I_{y2}\sin\frac{\pi t}{\tau_p})], 0<t<\tau_p \\ (A,B,C,D)\times(3I_{z1}I_{z2}), \tau_p<t<\tau_R \\ (A,B,C,D)\times[3(I_{z1}\cos\frac{\pi(t-\tau_R)}{\tau_p}+I_{x1}\sin\frac{\pi(t-\tau_R)}{\tau_p})(I_{z2}\cos\frac{\pi(t-\tau_R)}{\tau_p}+I_{x2}\sin\frac{\pi(t-\tau_R)}{\tau_p})], \tau_R<t<\tau_R+\tau_p \\ (A,B,C,D)\times(3I_{z1}I_{z2}), \tau_R+\tau_p<t<2\tau_R \\ (A,B,C,D)\times[3(I_{z1}\cos\frac{\pi(t-2\tau_R)}{\tau_p}-I_{y1}\sin\frac{\pi(t-2\tau_R)}{\tau_p})(I_{z2}\cos\frac{\pi(t-2\tau_R)}{\tau_p}-I_{y2}\sin\frac{\pi(t-2\tau_R)}{\tau_p})], 2\tau_R<t<2\tau_R+\tau_p \\ (A,B,C,D)\times(3I_{z1}I_{z2}), 2\tau_R+\tau_p<t<3\tau_R \\ (A,B,C,D)\times[3(I_{z1}\cos\frac{\pi(t-3\tau_R)}{\tau_p}-I_{x1}\sin\frac{\pi(t-3\tau_R)}{\tau_p})(I_{z2}\cos\frac{\pi(t-3\tau_R)}{\tau_p}-I_{x2}\sin\frac{\pi(t-3\tau_R)}{\tau_p})], 3\tau_R<t<3\tau_R+\tau_p \\ (A,B,C,D)\times(3I_{z1}I_{z2}), 3\tau_R+\tau_p<t<4\tau_R \end{cases}$$

$$\text{(V.15a)}$$

This can be rewritten as

$$\tilde{H}_D(t)=\begin{cases} (A,B,C,D)\times[3(I_{z1}I_{z2}\cos^2\frac{\pi t}{\tau_p}+I_{y1}I_{y2}\sin^2\frac{\pi t}{\tau_p}+(I_{z1}I_{y2}+I_{y1}I_{z2})\sin\frac{\pi t}{\tau_p}\cos\frac{\pi t}{\tau_p})], 0<t<\tau_p \\ (A,B,C,D)\times(3I_{z1}I_{z2}), \tau_p<t<\tau_R \\ (A,B,C,D)\times[3(I_{z1}I_{z2}\cos^2\frac{\pi(t-\tau_R)}{\tau_p}+I_{x1}I_{x2}\sin^2\frac{\pi(t-\tau_R)}{\tau_p}+(I_{z1}I_{x2}+I_{x1}I_{z2})\sin\frac{\pi(t-\tau_R)}{\tau_p}\cos\frac{\pi(t-\tau_R)}{\tau_p})], \tau_R<t<\tau_R+\tau_p \\ (A,B,C,D)\times(3I_{z1}I_{z2}), \tau_R+\tau_p<t<2\tau_R \\ (A,B,C,D)\times[3(I_{z1}I_{z2}\cos^2\frac{\pi(t-2\tau_R)}{\tau_p}+I_{y1}I_{y2}\sin^2\frac{\pi(t-2\tau_R)}{\tau_p}-(I_{z1}I_{y2}+I_{y1}I_{z2})\sin\frac{\pi(t-2\tau_R)}{\tau_p}\cos\frac{\pi(t-2\tau_R)}{\tau_p})], 2\tau_R<t<2\tau_R+\tau_p \\ (A,B,C,D)\times(3I_{z1}I_{z2}), 2\tau_R+\tau_p<t<3\tau_R \\ (A,B,C,D)\times[3(I_{z1}I_{z2}\cos^2\frac{\pi(t-3\tau_R)}{\tau_p}+I_{x1}I_{x2}\sin^2\frac{\pi(t-3\tau_R)}{\tau_p}-(I_{z1}I_{x2}+I_{x1}I_{z2})\sin\frac{\pi(t-3\tau_R)}{\tau_p}\cos\frac{\pi(t-3\tau_R)}{\tau_p})], 3\tau_R<t<3\tau_R+\tau_p \\ (A,B,C,D)\times(3I_{z1}I_{z2}), 3\tau_R+\tau_p<t<4\tau_R \end{cases}$$

$$\text{(V.15b)}$$

Note that the signs of $I_{z1}I_{x2}+I_{x1}I_{z2}$ and $I_{z1}I_{y2}+I_{y1}I_{z2}$ are reversed in the third and fourth rotor periods, relative to the first and second rotor periods. This is a consequence of the choice of phases in the fpRFDR sequence [called XY-4 phases[7]], and it causes these single-quantum terms to cancel out in the average Hamiltonian. Evaluating the integrals in the average Hamiltonian, we find (omitting many intermediate steps)

$$
\begin{aligned}
\tilde{H}_{D,ave} &= \frac{1}{4\tau_R}\{4\int_{\tau_p}^{\tau_R} dt\ \tilde{H}_D(t) + \int_0^{\tau_p} dt\ \tilde{H}_D(t) + \int_{\tau_R}^{\tau_R+\tau_p} dt\ \tilde{H}_D(t) + \int_{2\tau_R}^{2\tau_R+\tau_p} dt\ \tilde{H}_D(t) + \int_{3\tau_R}^{3\tau_R+\tau_p} dt\ \tilde{H}_D(t)\} \\
&= \frac{1}{4\tau_R}\{4\int_{\tau_p}^{\tau_R} dt\ (A,B,C,D)\times(3I_{z1}I_{z2}) + 4\int_0^{\tau_p} dt\ (A,B,C,D)\times(3I_{z1}I_{z2}\cos^2\frac{\pi t}{\tau_p}) \\
&\quad + 2\int_0^{\tau_p} dt\ (A,B,C,D)\times(3I_{x1}I_{x2} + 3I_{y1}I_{y2})\sin^2\frac{\pi t}{\tau_p}\} \\
&= \{\frac{3(\omega_R{}^2 + 4\omega_1{}^2)}{8\pi(\omega_R{}^2 - 4\omega_1{}^2)}[\sin(\omega_R\tau_p + \gamma) - \sin\gamma]A - \frac{3(\omega_R{}^2 + 4\omega_1{}^2)}{8\pi(\omega_R{}^2 - 4\omega_1{}^2)}[\cos(\omega_R\tau_p + \gamma) - \cos\gamma]B \\
&\quad + \frac{3(\omega_R{}^2 + \omega_1{}^2)}{8\pi(\omega_R{}^2 - \omega_1{}^2)}[\sin(2\omega_R\tau_p + 2\gamma) - \sin 2\gamma]C - \frac{3(\omega_R{}^2 + \omega_1{}^2)}{8\pi(\omega_R{}^2 - \omega_1{}^2)}[\cos(2\omega_R\tau_p + 2\gamma) - \cos 2\gamma]D\} \\
&\quad \times[I_{z1}I_{z2} - \frac{1}{2}(I_{x1}I_{x2} + I_{y1}I_{y2})] \\
&= \{\frac{3(\omega_R{}^2 + 4\omega_1{}^2)}{16\pi(\omega_R{}^2 - 4\omega_1{}^2)}[\sin(\omega_R\tau_p + \gamma) - \sin\gamma]A - \frac{3(\omega_R{}^2 + 4\omega_1{}^2)}{16\pi(\omega_R{}^2 - 4\omega_1{}^2)}[\cos(\omega_R\tau_p + \gamma) - \cos\gamma]B \\
&\quad + \frac{3(\omega_R{}^2 + \omega_1{}^2)}{16\pi(\omega_R{}^2 - \omega_1{}^2)}[\sin(2\omega_R\tau_p + 2\gamma) - \sin 2\gamma]C - \frac{3(\omega_R{}^2 + \omega_1{}^2)}{16\pi(\omega_R{}^2 - \omega_1{}^2)}[\cos(2\omega_R\tau_p + 2\gamma) - \cos 2\gamma]D\} \\
&\quad \times[3I_{z1}I_{z2} - \mathbf{I}_1\cdot\mathbf{I}_2]
\end{aligned}
\tag{V.16}
$$

Miraculously (or as a consequence of symmetry, as described below), the average dipole-dipole Hamiltonian under the fpRFDR sequence is a zero-quantum operator with the same operator form as the dipole-dipole coupling in a non-spinning sample. This has useful consequences in certain applications, for example by allowing ideas that were originally developed for NMR of static solids to be applied in MAS experiments[8,9].

Under fpRFDR, it is also true that $\tilde{H}_{CSA,ave} = \tilde{H}_{ICS,ave} = 0$ (see Exercises).

ω_1 in Eq. (V.16) is the rf amplitude during the 180° pulses. Note that $\tilde{H}_{D,ave}$ vanishes as $\omega_1 \rightarrow \infty$ and $\tau_p \rightarrow 0$ (i.e., in the delta-function pulse limit). As shown below, a different recoupling mechanism, leading to a different average dipole-dipole Hamiltonian, comes into play when the coupled spins have large chemical shift differences. This chemical-shift-driven recoupling mechanism <u>does not</u> disappear in the delta-function pulse limit.

D. Chemical-shift-driven recoupling

1. Rotational resonance

Now consider the case where two dipole-coupled spins have a large difference in their isotropic chemical shifts. Ignore chemical shift anisotropy for now. The nuclear spin Hamiltonian under MAS is then

$$\begin{aligned} H(t) &= \omega_{I1} I_{z1} + \omega_{I2} I_{z2} + H_D(t) \\ &= \tfrac{1}{2}(\omega_{I1} + \omega_{I2})(I_{z1} + I_{z2}) + \tfrac{1}{2}(\omega_{I1} - \omega_{I2})(I_{z1} - I_{z2}) + H_D(t) \\ &= \tfrac{1}{2}\Sigma(I_{z1} + I_{z2}) + \tfrac{1}{2}\Delta(I_{z1} - I_{z2}) + H_D(t) \end{aligned} \qquad \text{(V.17)}$$

where Σ and Δ are the sum and difference of the two chemical shifts (actually, resonance offsets). Now go into an interaction representation with respect to the chemical shift terms. If U(t) is the evolution operator for H(t), this interaction representation is defined by

$$U(t) = U_{ICS}(t)\tilde{U}(t) \qquad \text{(V.18a)}$$

$$\begin{aligned} U_{ICS}(t) &= \exp\{-i[\tfrac{1}{2}\Sigma(I_{z1} + I_{z2}) + \tfrac{1}{2}\Delta(I_{z1} - I_{z2})]t\} \\ &= \exp[-\tfrac{i}{2}\Sigma(I_{z1} + I_{z2})t]\exp[-\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t] \end{aligned} \qquad \text{(V.18b)}$$

$$\tilde{U}(t) = \vec{T}\exp\{-i\int_0^t dt'\tilde{H}_D(t')\} \qquad \text{(V.18c)}$$

$$\begin{aligned} \tilde{H}_D(t) &= U_{ICS}(t)^{-1} H_D(t) U_{ICS}(t) \\ &= \exp[\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t] H_D(t) \exp[-\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t] \\ &= (A,B,C,D) \times \exp[\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t](3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2)\exp[-\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t] \\ &= (A,B,C,D) \times \exp[\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t][2I_{z1}I_{z2} - \tfrac{1}{2}(I_{+1}I_{-2} + I_{-1}I_{+2})]\exp[-\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t] \\ &= (A,B,C,D) \times (2I_{z1}I_{z2}) \\ &\quad - \tfrac{1}{2}(A,B,C,D) \times \exp[\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t](I_{+1}I_{-2} + I_{-1}I_{+2})]\exp[-\tfrac{i}{2}\Delta(I_{z1} - I_{z2})t] \end{aligned}$$

(V.19)

Eq. (V.19) uses the facts that $[(I_{z1}+I_{z2}),H_D(t)] = 0$, so the Σ part of the chemical shift does not affect $\tilde{H}_D(t)$, and that $[(I_{z1}-I_{z2}),I_{z1}I_{z2}] = 0$, so the $I_{z1}I_{z2}$ part of $H_D(t)$ is not affected by the chemical shifts. Also, Eq. (V.19) uses the identity $\mathbf{I}_1 \cdot \mathbf{I}_2 = I_{z1}I_{z2} + \tfrac{1}{2}(I_{+1}I_{-2} + I_{-1}I_{+2})$. Now, using the identity $e^{iI_z\phi}I_{\pm}e^{-iI_z\phi} = e^{\pm i\phi}I_{\pm}$, Eq. (V.19) becomes

$$\begin{aligned} \tilde{H}_D(t) &= (A,B,C,D) \times (2I_{z1}I_{z2}) - \tfrac{1}{2}(A,B,C,D) \times (e^{i\Delta t}I_{+1}I_{-2} + e^{-i\Delta t}I_{-1}I_{+2}) \\ &= (A,B,C,D) \times (2I_{z1}I_{z2}) - \tfrac{1}{2}(A,B,C,D) \times [(\cos\Delta t + i\sin\Delta t)I_{+1}I_{-2} + (\cos\Delta t - i\sin\Delta t)I_{-1}I_{+2}] \end{aligned}$$

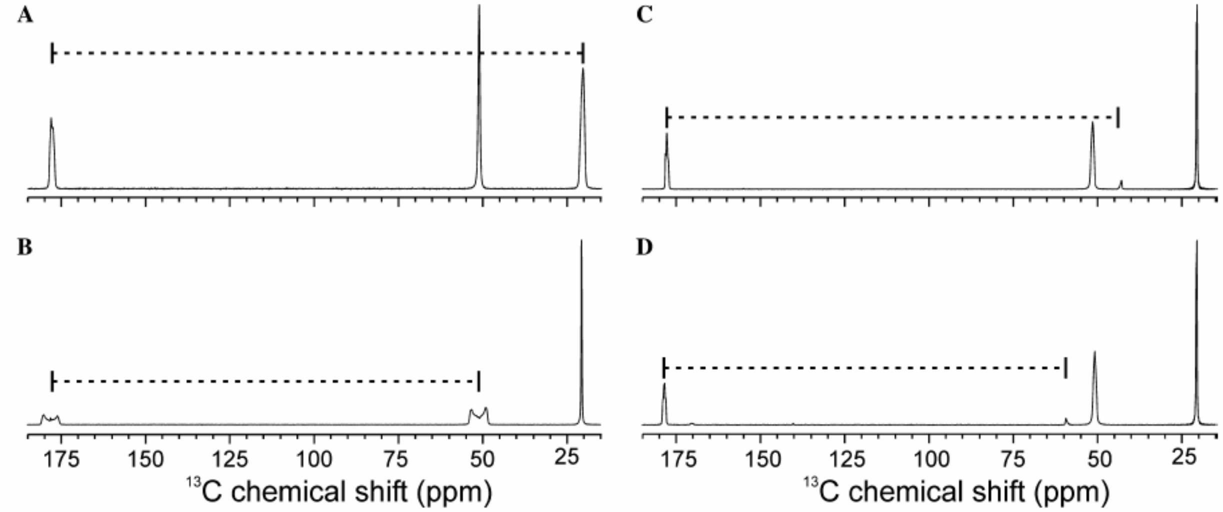
(V.20)

Eq. (V.20) shows that the $I_{z1}I_{z2}$ part of the dipole-dipole coupling is not recoupled by the chemical shift difference, but the “flip-flop” part can be recoupled if $|\Delta| = \omega_R$ or $|\Delta| = 2\omega_R$. These are the “n = 1” and “n = 2” rotational resonance conditions[10-14]. At the rotational resonance conditions, $\tilde{H}_D(t)$ is periodic with period τ_R and AHT can be applied. The average dipole-dipole Hamiltonian at rotational resonance is

$$\tilde{H}_{D,ave} = -\frac{1}{4}[(A+iB)e^{-i\gamma}\delta_{1,n} + (C+iD)e^{-2i\gamma}\delta_{2,n}]I_{+1}I_{-2} - \frac{1}{4}[(A-iB)e^{i\gamma}\delta_{1,n} + (C-iD)e^{2i\gamma}\delta_{2,n}]I_{-1}I_{+2} \qquad (V.21)$$

for n = 1 or n = 2. Note that this is a zero-quantum operator, but it is not the same as the zero-quantum operator created by the fpRFDR sequence.

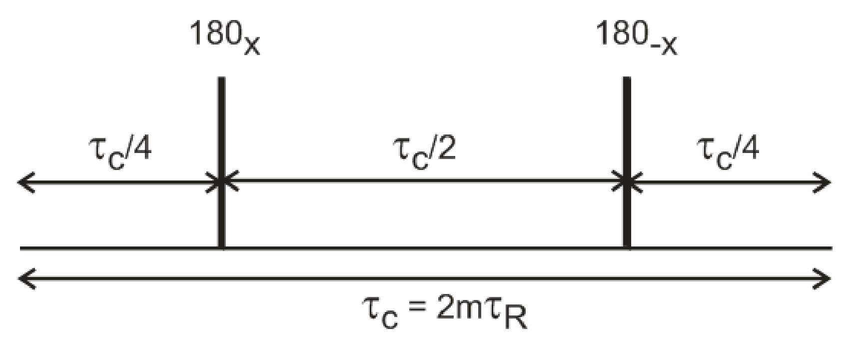
In a system with many ^{13}C-labeled sites, rotational resonance allows pairs of spins with particular chemical shift differences to be recoupled selectively[15,16], as shown below. However, unless the MAS frequency is varied during the pulse sequence, the couplings can not be switched on and off. Therefore, other approaches to frequency-selective homonuclear dipolar recoupling that employ rf pulses and do not depend on being exactly on rotational resonance have been developed by several groups[17-22].



^{13}C NMR spectra of U-^{15}N,^{13}C-alanine powder, recorded at 100.8 MHz, with MAS frequencies indicated by dashed lines. At the rotational resonance conditions, the recoupled lines become dipolar powder patterns, while other lines remain sharp. Close to rotational resonance conditions (C and D), the main NMR lines of strongly coupled pairs exhibit apparent shifts on the order of 0.5 ppm, which can complicate accurate measurements of chemical shifts in uniformly labeled samples.

2. *Radio-Frequency-Driven Recoupling*

Consider the Hamiltonian in Eq. (V.17), but with an additional $H_{RF}(t)$ term that corresponds to the following pulse sequence, with m being an arbitrary positive integer:



This sequence, called SEDRA[23] or more commonly RFDR[6,24], can be analyzed by first transforming the Hamiltonian into an interaction representation with respect to $H_{RF}(t)$, and then into an interaction representation with respect to the chemical shifts. Following the same principles as used above for other recoupling sequences, the Hamiltonian in the interaction representation with respect to $H_{RF}(t)$ is

$$\tilde{H}(t) = \begin{cases} \frac{1}{2}\Sigma(I_{z1}+I_{z2}) + \frac{1}{2}\Delta(I_{z1}-I_{z2}) + H_D(t),\ 0 < t < \tau_c/4 \\ -\frac{1}{2}\Sigma(I_{z1}+I_{z2}) - \frac{1}{2}\Delta(I_{z1}-I_{z2}) + H_D(t),\ \tau_c/4 < t < 3\tau_c/4 \\ \frac{1}{2}\Sigma(I_{z1}+I_{z2}) + \frac{1}{2}\Delta(I_{z1}-I_{z2}) + H_D(t),\ 3\tau_c/4 < t < \tau_c \end{cases} \qquad \text{(V.21)}$$

$H_D(t)$ is not affected directly by the delta-function 180° pulses, but the chemical shifts change sign between the two 180° pulses. Therefore, the isotropic chemical shifts now appear to be time-dependent. In the second interaction representation, the dipole-dipole coupling becomes

$$\tilde{\tilde{H}}_D(t) = \begin{cases} \exp[\frac{i}{2}\Delta(I_{z1}-I_{z2})t]H_D(t)\exp[-\frac{i}{2}\Delta(I_{z1}-I_{z2})t],\ 0 < t < \tau_c/4 \\ \exp[\frac{i}{2}\Delta(I_{z1}-I_{z2})(\frac{\tau_c}{2}-t)]H_D(t)\exp[-\frac{i}{2}\Delta(I_{z1}-I_{z2})(\frac{\tau_c}{2}-t)],\ \tau_c/4 < t < 3\tau_c/4 \\ \exp[\frac{i}{2}\Delta(I_{z1}-I_{z2})(t-\tau_c)]H_D(t)\exp[-\frac{i}{2}\Delta(I_{z1}-I_{z2})(t-\tau_c)],\ 3\tau_c/4 < t < \tau_c \end{cases} \qquad \text{(V.22)}$$

Ignoring the $I_{z1}I_{z2}$ part of $H_D(t)$, which as shown above is not recoupled, Eq. (V.22) can be written as

$$\tilde{\tilde{H}}_D(t) = \begin{cases} -\frac{1}{2}(A,B,C,D)\times[e^{i\Delta t}I_{+1}I_{-2} + e^{-i\Delta t}I_{-1}I_{+2}],\ 0 < t < \tau_c/4 \\ -\frac{1}{2}(A,B,C,D)\times[e^{i\Delta(\tau_c/2-t)}I_{+1}I_{-2} + e^{-i\Delta(\tau_c/2-t)}I_{-1}I_{+2}],\ \tau_c/4 < t < 3\tau_c/4 \\ -\frac{1}{2}(A,B,C,D)\times[e^{i\Delta(t-\tau_c)}I_{+1}I_{-2} + e^{-i\Delta(t-\tau_c)}I_{-1}I_{+2}],\ 3\tau_c/4 < t < \tau_c \end{cases} \qquad \text{(V.23)}$$

The average Hamiltonian is then

$$\overset{\approx}{H}_{D,ave} = [(-1)^m \frac{\Delta \sin(m\Delta\tau_R / 2)}{m\tau_R\,(\omega_R{}^2 - \Delta^2)}(A\cos\gamma + B\sin\gamma) + \frac{\Delta \sin(m\Delta\tau_R / 2)}{m\tau_R\,(4\omega_R{}^2 - \Delta^2)}(C\cos 2\gamma + D\sin 2\gamma)](I_{+1}I_{-2} + I_{-1}I_{+2}) \tag{V.24}$$

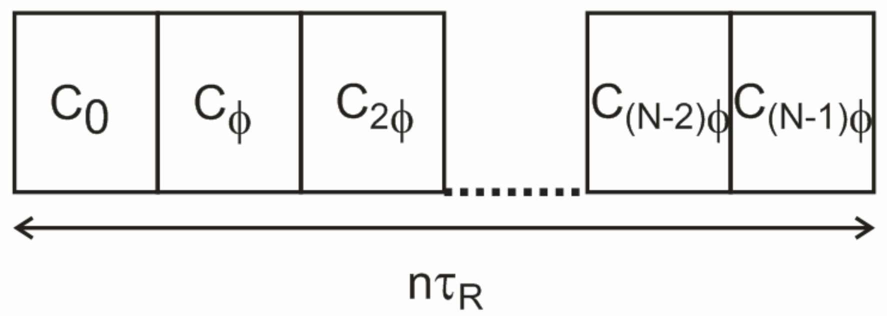
Note that the average dipole-dipole Hamiltonian, evaluated in the double interaction representation described above, is non-zero for nearly all values of the chemical shift difference Δ. This is because the 180° pulses, spaced $m\tau_R$ apart, force the flip-flop term in $\overset{\approx}{H}_D(t)$ to be periodic with period $2m\tau_R$. For nearly all values of Δ, $\overset{\approx}{H}_D(t)$ has non-zero Fourier components at ω_R and/or $2\omega_R$. However, $\overset{\approx}{H}_{D,ave} \to 0$ as $\Delta \to 0$. Thus, the recoupling mechanism for RFDR in the delta-function pulse limit (i.e., when the 180° pulses are very short compared with τ_R) is qualitatively different from the recoupling mechanism in the finite-pulse limit (i.e., when the 180° pulses occupy a significant fraction of the rotor period).

In actual experiments, the phases of the 180° pulses are usually chosen to follow an XY-4 or high XY-n phase pattern[7], because XY-n phase patterns compensate for rf inhomogeneity, resonance offsets, and other imperfections in the 180° pulses. This makes the RFDR technique (and the fpRFDR version) quite robust and useful in many experimental situations.

VI. Symmetry principles for recoupling sequences

A. Levitt's "C" sequences

Malcolm Levitt and his colleagues have developed an approach to the development of recoupling sequences that relies on general symmetry properties of pulse sequences, which lead to "selection rules" that reveal which types of interactions can be recoupled by a sequence with a given symmetry. Sequences belonging to two distinct symmetry classes have been described. The first class includes "C" sequences, comprised of rf blocks (called C elements) that produce no net rotation of spin angular momenta[25,26]. The general form for a C sequence is:



In other words, the C sequence contains N repetitions of the C element, with overall rf phase shifts that increase in units of ϕ, and with a total cycle time of n rotor periods. The phase increment satisfies $\phi = 2\pi\nu / N$. N, n, and ν are positive integers. The symmetry is represented by the symbol CN_n^ν.

To analyze the effect of a CN_n^ν sequence with AHT, one considers a general nuclear spin Hamiltonian under MAS that is a sum of terms of the form $H_{m\lambda 0}(t) = A_m e^{im\omega_R t} T_{\lambda 0}$ in the rotating frame [*i.e.*, before transforming to an interaction representation with respect to $H_{RF}(t)$]. A_m is a function of the Euler angles α,β,γ discussed above. m is -2, -1, 1, or 2, and λ is another positive integer.

$T_{\lambda 0}$ is the "element of an irreducible tensor operator of rank λ" that commutes with the total spin angular momentum I_z. Without going into the details of irreducible tensor operators, this means $T_{\lambda 0}$ is an operator that is a member of a set of 2λ+1 operators $\{T_{\lambda\mu}\}$, with μ being an integer that satisfies $-\lambda \le \mu \le \lambda$. For dipole-dipole couplings, λ = 2 and the relevant set of operators is

$$
\begin{aligned}
T_{2\pm2} &= \frac{1}{2} I_{\pm1} I_{\pm2} \\
T_{2\pm1} &= \mp\frac{1}{2}(I_{z1}I_{\pm2} + I_{\pm1}I_{z2}) \qquad \text{(VI.1)} \\
T_{20} &= \frac{1}{\sqrt{6}}(3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2)
\end{aligned}
$$

Thus, $T_{2\mu}$ is a μ-quantum operator. For isotropic and anisotropic chemical shifts, the relevant operators have λ = 1.

Important properties of irreducible tensor operators include:

$$e^{iI_z\theta} T_{\lambda\mu} e^{-iI_z\theta} = e^{i\mu\theta} T_{\lambda\mu} \qquad \text{(VI.2a)}$$

$$e^{-iI_x\pi} T_{\lambda\mu} e^{iI_z\pi} = (-1)^{\lambda} T_{\lambda-\mu} \qquad \text{(VI.2b)}$$

$$T_{\lambda\mu}{}^{\dagger} = (-1)^{\mu} T_{\lambda-\mu} \qquad \text{(VI.2c)}$$

Elements of the set of operators $\{T_{\lambda\mu}\}$ are transformed into one another by rotations of spin angular momentum (i.e., by rf pulses in NMR experiments). Therefore, in the interaction representation with respect to the first C element, the nuclear spin Hamiltonian is a sum of terms of the form $\tilde{H}_{m\lambda\mu}(t) = \tilde{A}_{m\lambda\mu}(t) e^{im\omega_R t} T_{\lambda\mu}$ in the interval $0 < t < n\tau_R/N$. There are 4×(2λ+1) such terms. The interaction representation Hamiltonian for the k^th C element must then be a sum of terms of the form

$$\tilde{H}_{m\lambda\mu}(t) = \tilde{A}_{m\lambda\mu}(t) e^{im\omega_R t}(e^{-iI_z(k-1)\phi} T_{\lambda\mu} e^{iI_z(k-1)\phi}) \qquad \text{(VI.3)}$$

in the interval $(k-1)n\tau_R/N < t < kn\tau_R/N$, taking into account the effect of the overall rf phase shift as in Eqs. (III.8-III.11). The average Hamiltonian for the k^th C element will then be a sum of terms of the form

$$\begin{aligned}\tilde{H}_{m\lambda\mu,ave}(k) &= \frac{N}{n\tau_R}\int_{(k-1)n\tau_R\,/\,N}^{kn\tau_r\,/\,N} dt\,\tilde{H}_{m\lambda\mu}(t)\\ &= T_{\lambda\mu}\,\frac{N}{n\tau_R}\,e^{-i\mu(k-1)\phi}e^{im\omega_R\,(k-1)n\tau_R\,/\,N}\int_0^{n\tau_r\,/\,N} dt\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R\,t}\end{aligned} \tag{VI.4}$$

Eq. (VI.4) makes use of Eq. (VI.2a) and the fact that $\tilde{A}_{m\lambda\mu}(t)$ is periodic, with period equal to $n\tau_R/N$ (the length of one C element). The total average Hamiltonian, for the entire cycle time $n\tau_R$, is obtained by summing over contributions from all C elements. The total average Hamiltonian will then contain $4\times(2\lambda+1)$ terms of the form

$$\begin{aligned}\tilde{H}_{m\lambda\mu,ave} &= T_{\lambda\mu}\,\frac{N}{n\tau_R}\sum_{k=1}^{N}\{e^{-i\mu(k-1)\phi}e^{im\omega_R\,(k-1)n\tau_R\,/\,N}\int_0^{n\tau_r\,/\,N} dt\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R\,t}\}\\ &= T_{\lambda\mu}\,\frac{N}{n\tau_R}\int_0^{n\tau_r\,/\,N} dt\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R\,t}\sum_{k=1}^{N} e^{-i\mu(k-1)\phi}e^{im\omega_R\,(k-1)n\tau_R\,/\,N}\\ &= T_{\lambda\mu}\,\frac{N}{n\tau_R}\int_0^{n\tau_r\,/\,N} dt\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R\,t}\sum_{k=1}^{N} e^{-i2\pi(k-1)(\mu\nu-mn)/N}\end{aligned} \tag{VI.5}$$

For such a term to be non-zero, the sum over k must be non-zero. But it turns out that the following relation is always true, for any positive integer N:

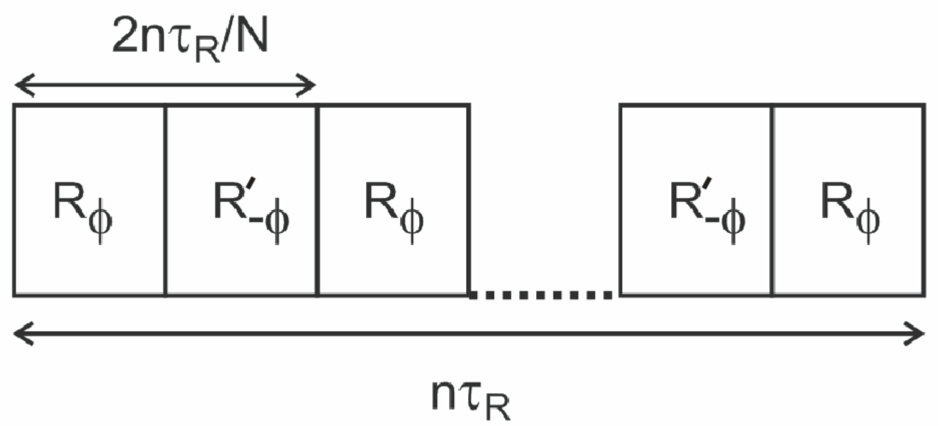
$$\sum_{k=1}^{N} e^{-i2\pi(k-1)q/N} = \begin{cases} N, & q = NZ \\ 0, & q \neq NZ \end{cases} \tag{VI.6}$$

where Z is some other integer. So the quantity $\mu\nu$ - mn must be zero or another integer multiple of N for the average Hamiltonian under a C sequence to contain non-zero μ-quantum terms that arise from MAS-induced oscillations at frequency $m\omega_R$. This is the selection rule for CN_n^ν sequences.

The C7 and POST-C7 recoupling sequences[27,28] are good examples. For these sequences, N = 7, n = 2, and $\nu = 1$, which imply the selection rule that μ-2m = 0, 7, 14, etc. Thus, terms with $\mu = 2$ and m = 1 or $\mu = -2$ and m = -1are recoupled (corresponding to double-quantum dipolar recoupling). Terms with $\mu = 0$ and 1 are not recoupled, corresponding to the absence of CSA recoupling and the absence of both zero-quantum and one-quantum dipolar recoupling. (Recall that m has only the values ±1 and ±2, but not 0, under MAS.) C7 and POST-C7 differ in the choice of the C element itself, which is better compensated for resonance offsets in the POST-C7 case.

B. Levitt's "R" sequences

The second symmetry class considered by Levitt and coworkers includes the "R" sequences[29,30], which have the general form



The sequence consists of N repetitions of an "R element" in a cycle time $n\tau_R$. N is an even integer. The rf pulses in the R element produce a net rotation by 180° around x. The R_ϕ version alternates with the $R'_{-\phi}$ version. For the R_ϕ version, all rf pulses in the R element are phase-shifted by $\phi = \pi\nu / N$. For the $R'_{-\phi}$ version, all rf pulses in the R element are first reversed in sign, then phase-shifted by $-\phi$. The symmetry is represented by the symbol RN_n^ν.

Analysis of R sequences is similar to analysis of C sequences, but the fact that one R element produces a net 180° rotation means that $T_{\lambda\mu}$ and $T_{\lambda-\mu}$ terms must be treated together [see Eq. (VI.2b)]. For the Hamiltonian to be Hermitean, these must occur in the interaction representation as terms of the form $\tilde{H}_{m\lambda\mu}(t) = \tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t) * e^{-im\omega_R t}T_{\lambda-\mu}$ [so that $\tilde{H}_{m\lambda\mu}(t) = \tilde{H}_{m\lambda\mu}(t)^\dagger$; see Eq. (VI.2c)].

Considering only one m,λ combination initially, the evolution operator for the R element, starting at t = 0, is

$$U_R = \vec{T}\exp\{-i\int_0^{n\tau_R/N} dt\,[H_{RF}(t) + (A_m e^{im\omega_R t} + A_m{}^* e^{-im\omega_R t})T_{\lambda 0}]\} \tag{VI.7a}$$

Then, in the AHT approximation and considering only one m,λ,μ combination,

$$U_R \approx e^{-iI_x\pi}\exp[-i\int_0^{n\tau_R/N} dt\,(\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda-\mu})] \tag{VI.7b}$$

In going from Eq. (VI.7a) to Eq. (VI.7b), the fact that $H_{RF}(t)$ produces a net rotation by 180° around x has been used. In the interaction representation with respect to $H_{RF}(t)$, $T_{\lambda 0}$ becomes a sum of terms of the form $c_{\lambda\mu}(t)T_{\lambda\mu} + (-1)^\mu c_{\lambda\mu}(t)^* T_{\lambda-\mu}$. In Eq. (VI.7b), $\tilde{A}_{m\lambda\mu}(t) \equiv A_m c_{\lambda\mu}(t)$.

Terms proportional to $e^{-im\omega_R t}T_{\lambda\mu}$ and $e^{im\omega_R t}T_{\lambda-\mu}$ are not shown explicitly, but of course are also present.

The corresponding equations for the phase-reversed element R', starting at t = 0, are [see Eq. (III.12)]

$$U_{R'} = \vec{T}\exp\{-i\int_0^{n\tau_R/N} dt\,[e^{-iI_x\pi}H_{RF}(t)e^{iI_x\pi} + (A_m e^{im\omega_R t} + A_m{}^* e^{-im\omega_R t})T_{\lambda 0}]\} \tag{VI.8a}$$

$$\begin{aligned} U_{R'} &\approx e^{-iI_x\pi}\{e^{-iI_x\pi}\exp[-i(-1)^\lambda \int_0^{n\tau_R/N} dt\,(\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda-\mu})]\}e^{iI_x\pi} \\ &= e^{-iI_x\pi}\exp[-i\int_0^{n\tau_R/N} dt\,(\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda-\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda\mu})] \end{aligned} \tag{VI.8b}$$

Eqs. (VI.7) and (VI.8) show that U_R and $U_{R'}$ differ by exchange of $T_{\lambda\mu}$ and $T_{\lambda-\mu}$ in the interaction representation.

Including rotations about z to account for the phase shifts, the evolution operator for the first $R_\phi R'_{-\phi}$ pair is

$$\begin{aligned} U_0 &= e^{iI_z\phi}e^{-iI_x\pi}\exp\{-i\int_{n\tau_R/N}^{2n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda-\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda\mu}]\}e^{-iI_z\phi} \\ &\times e^{-iI_z\phi}e^{-iI_x\pi}\exp\{-i\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda-\mu}]\}e^{iI_z\phi} \\ &= e^{iI_z\phi}e^{-iI_x\pi}\exp\{-i\int_{n\tau_R/N}^{2n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda-\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda\mu}]\} \\ &\times e^{-iI_x\pi}e^{2iI_z\phi}\exp\{-i\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda-\mu}]\}e^{iI_z\phi} \\ &= e^{iI_z\phi}e^{-iI_x\pi}\exp\{-i\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{i2\pi mn/N}e^{im\omega_R t}T_{\lambda-\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-i2\pi mn/N}e^{-im\omega_R t}T_{\lambda\mu}]\} \\ &\times e^{-iI_x\pi}e^{2iI_z\phi}\exp\{-i\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda-\mu}]\}e^{iI_z\phi} \\ &= e^{iI_z\phi}\exp\{-i\int_0^{n\tau_R/N} dt(-1)^\lambda[\tilde{A}_{m\lambda\mu}(t)e^{i2\pi mn/N}e^{im\omega_R t}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-i2\pi mn/N}e^{-im\omega_R t}T_{\lambda-\mu}]\} \\ &\times e^{2iI_z\phi}\exp\{-i\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}T_{\lambda-\mu}]\}e^{iI_z\phi} \\ &= e^{4iI_z\phi}\exp\{-i\int_0^{n\tau_R/N} dt(-1)^\lambda[\tilde{A}_{m\lambda\mu}(t)e^{i2\pi mn/N}e^{im\omega_R t}e^{-3i\mu\phi}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-i2\pi mn/N}e^{-im\omega_R t}e^{3i\mu\phi}T_{\lambda-\mu}]\} \\ &\times \exp\{-i\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}e^{-i\mu\phi}T_{\lambda\mu} + (-1)^\mu \tilde{A}_{m\lambda\mu}(t)^* e^{-im\omega_R t}e^{i\mu\phi}T_{\lambda-\mu}]\} \end{aligned} \tag{VI.9}$$

The total evolution operator is

$$U_{total} = e^{i2NI_z\phi}\prod_{k=0}^{(N/2)-1}\tilde{U}_{R'}(k)\tilde{U}_R(k) \tag{VI.10}$$

with $\tilde{U}_R(k)$ and $\tilde{U}_{R'}(k)$ defined by

$$\begin{aligned}\tilde{U}_R(k) = \exp\{-i\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{i4\pi mnk/N}e^{im\omega_R t}e^{-i(4k+1)\mu\phi}T_{\lambda\mu} \\ +(-1)^\mu\tilde{A}_{m\lambda\mu}(t)^* e^{-i4\pi mnk/N}e^{-im\omega_R t}e^{i(4k+1)\mu\phi}T_{\lambda-\mu}]\}\end{aligned} \qquad \text{(VI. 11a)}$$

$$\begin{aligned}\tilde{U}_{R'}(k) = \exp\{-i\int_0^{n\tau_R/N} dt(-1)^\lambda[\tilde{A}_{m\lambda\mu}(t)e^{i2\pi mn(2k+1)/N}e^{im\omega_R t}e^{-i(4k+3)\mu\phi}T_{\lambda\mu} \\ +(-1)^\mu\tilde{A}_{m\lambda\mu}(t)^* e^{-i2\pi mn(2k+1)/N}e^{-im\omega_R t}e^{i(4k+3)\mu\phi}T_{\lambda-\mu}]\}\end{aligned} \qquad \text{(VI.11b)}$$

Note that $2N\phi$ in Eq. (VI.10) is a multiple of 2π, so the operator $e^{i2NI_z\phi}$ has no effect. The average Hamiltonian for the entire R sequence is obtained by summing the exponents in $U_R(k)$ and $U_{R'}(k)$ over all values of k and dividing by $n\tau_R$. Therefore, the coefficient of $T_{\lambda\mu}$ in the average Hamiltonian arising from MAS-induced oscillations at $m\omega_R$ is proportional to

$$\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}]e^{-i\pi\mu\nu/N}\left\{\sum_{k=0}^{(N/2)-1}\exp[i4\pi(mn-\mu\nu)k/N]+(-1)^\lambda\sum_{k=0}^{(N/2)-1}\exp[i4\pi(mn-\mu\nu)(k+1/2)/N]\right\}$$

$$=\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}]e^{-i\pi\mu\nu/N}\left\{\sum_{\substack{k=0\\(\text{even})}}^{N-2}\exp[i2\pi(mn-\mu\nu)k/N]+(-1)^\lambda\sum_{\substack{k=1\\(\text{odd})}}^{N-1}\exp[i2\pi(mn-\mu\nu)k/N]\right\}$$

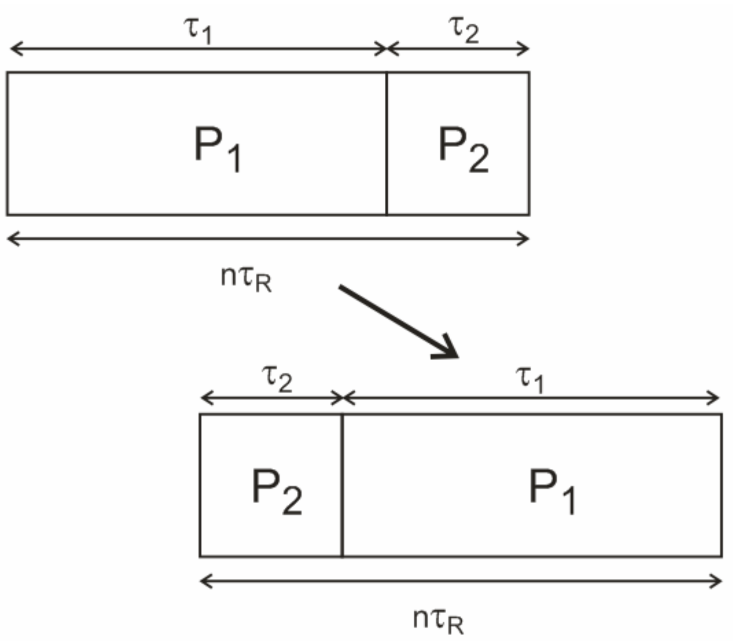
$$=\int_0^{n\tau_R/N} dt[\tilde{A}_{m\lambda\mu}(t)e^{im\omega_R t}]e^{-i\pi\mu\nu/N}\left\{\sum_{\substack{k=0\\(\text{odd and even})}}^{N-1}(-1)^{k\lambda}\exp[i2\pi(mn-\mu\nu)k/N]\right\} \qquad \text{(VI.12)}$$

Eq. (VI.12) shows that if λ is even, the coefficient of $T_{\lambda\mu}$ is zero (i.e., no recoupling) unless $mn - \mu\nu$ is an even multiple of N/2. If λ is odd, the coefficient of $T_{\lambda\mu}$ is zero unless $mn - \mu\nu$ is an odd multiple of N/2. These are the selection rules for RN_n^ν sequences.

Many examples of RN_n^ν recoupling sequences have been reported. The fpRFDR sequence described above is a very simple example, for which n = 4, N = 4, and $\nu = 1$. The symmetry selection rules indicate that dipole-dipole couplings ($\lambda = 2$) can be recoupled in a zero-quantum ($\mu = 0$) form, with $|m| = 1$ or $|m| = 2$. Chemical shifts ($\lambda = 1$; $|\mu| = 0$ or 1) can not be recoupled. This is in agreement with the detailed calculations described above.

C. Cyclic time displacement symmetry and constant-time recoupling

Another useful symmetry property of recoupling sequences involves their behavior when all pulses are cyclically displaced in time within the cycle time $\tau_c = n\tau_R$. In the picture below, a block of pulses (or delays) of length τ_1, called P_1, is displaced by τ_2, causing the remaining block P_2 to move from the end to the beginning of the cycle:



What is the effect of this cyclic displacement on a recoupled Hamiltonian? If the rotations produced by rf pulse blocks P_1 and P_2 are $U_1(t)$ and $U_2(t)$, with time t measured from the beginning of each block, then the total rotation before the cyclic displacement is $U_{RF}(t)$:

$$U_{RF}(t) = \begin{cases} U_1(t), 0 < t < \tau_1 \\ U_2(t - \tau_1)U_1(\tau_1), \tau_1 < t < n\tau_R \end{cases} \tag{VI.13}$$

The total rotation after the cyclic displacement is $U_{CD}(t)$:

$$U_{CD}(t) = \begin{cases} U_2(t), 0 < t < \tau_2 \\ U_1(t - \tau_2)U_2(\tau_2), \tau_2 < t < n\tau_R \end{cases} \tag{VI.14}$$

In the interaction representation with respect to the original pulse sequence, a Hamiltonian term of the form $H_{\lambda m}(t) = A_{\lambda m} e^{im\omega_R t} T_{\lambda 0}$ under MAS becomes (recalling that $\tau_1 + \tau_2 = n\tau_R$)

$$\begin{aligned} \tilde{H}_{\lambda m}(t) &= \begin{cases} A_{\lambda m} e^{im\omega_R t} U_1(t)^{-1} T_{\lambda 0} U_1(t), 0 < t < \tau_1 \\ A_{\lambda m} e^{im\omega_R t} U_1(\tau_1)^{-1} U_2(t - \tau_1)^{-1} T_{\lambda 0} U_2(t - \tau_1) U_1(\tau_1), \tau_1 < t < n\tau_R \end{cases} \\ &= \begin{cases} A_{\lambda m} e^{im\omega_R t} U_1(t)^{-1} T_{\lambda 0} U_1(t), 0 < t < \tau_1 \\ A_{\lambda m} e^{-im\omega_R \tau_1} e^{im\omega_R t'} U_1(\tau_1)^{-1} U_2(t')^{-1} T_{\lambda 0} U_2(t') U_1(\tau_1), 0 < t' < \tau_2 \end{cases} \end{aligned} \tag{VI.15}$$

with $t' = t + \tau_1$. In the interaction representation with respect to the cyclically displaced pulse sequence, the same Hamiltonian term becomes

$$\hat{H}_{\lambda m}(t) = \begin{cases} A_{\lambda m} e^{im\omega_R t} U_2(t)^{-1} T_{\lambda 0} U_2(t), 0 < t < \tau_2 \\ A_{\lambda m} e^{im\omega_R t} U_2(\tau_2)^{-1} U_1(t-\tau_2)^{-1} T_{\lambda 0} U_1(t-\tau_2) U_2(\tau_2), \tau_2 < t < n\tau_R \end{cases}$$
$$= \begin{cases} A_{\lambda m} e^{im\omega_R t} U_2(t)^{-1} T_{\lambda 0} U_2(t), 0 < t < \tau_2 \\ A_{\lambda m} e^{-im\omega_R \tau_2} e^{im\omega_R t''} U_2(\tau_2)^{-1} U_1(t'')^{-1} T_{\lambda 0} U_1(t'') U_2(\tau_2), 0 < t'' < \tau_1 \end{cases} \quad \text{(VI.16)}$$

with t’’ = t + τ_2. In both cases, the average Hamiltonian is the integral of the interaction representation Hamiltonian over time from 0 to $n\tau_R$, divided by $n\tau_R$. According to Eqs. (VI.15) and (VI.16), the integral in both cases is the sum of two integrals, over time intervals of length τ_1 and τ_2. Recalling that $e^{im\omega_R \tau_1} e^{im\omega_R \tau_2} = 1$ and $U_2(\tau_2) U_1(\tau_1) = 1$, it can be shown that the integrands for the cyclically displaced pulse sequence are equal to the integrands for the original pulse sequence after rotation by $U_2(\tau_2)^{-1} = U_1(\tau_1)$ and multiplication by $e^{im\omega_R \tau_2}$. Thus,

$$\hat{H}_{\lambda m,ave} = e^{im\omega_R \tau_2} U_2(\tau_2)^{-1} \tilde{H}_{\lambda m,ave} U_2(\tau_2) \quad \text{(VI.17)}$$

Eq. (VI.17) summarizes the effect of a cyclic time displacement on the average Hamiltonian for an arbitrary recoupling sequence.

Why is this useful? As an example, consider a general recoupling sequence that ends in two periods of length $\tau_R/3$. During these final two periods, either no pulses are applied or the applied pulses produce a net rotation of 2π. For such a sequence, two successive cyclic displacements by $\tau_R/3$ multiply the average Hamiltonian by $e^{i2m\pi/3}$ and $e^{i4m\pi/3}$. For m = ±1 and m = ±2, the total average Hamiltonian for the pulse sequence obtained by concatenating the original sequence with the two displaced versions will be zero, because $1 + e^{i2m\pi/3} + e^{i4m\pi/3} = 0$. This provides a simple means of creating a “constant-time” dipolar recoupling technique[31], as shown below using cyclically displaced versions of the fpRFDR sequence:

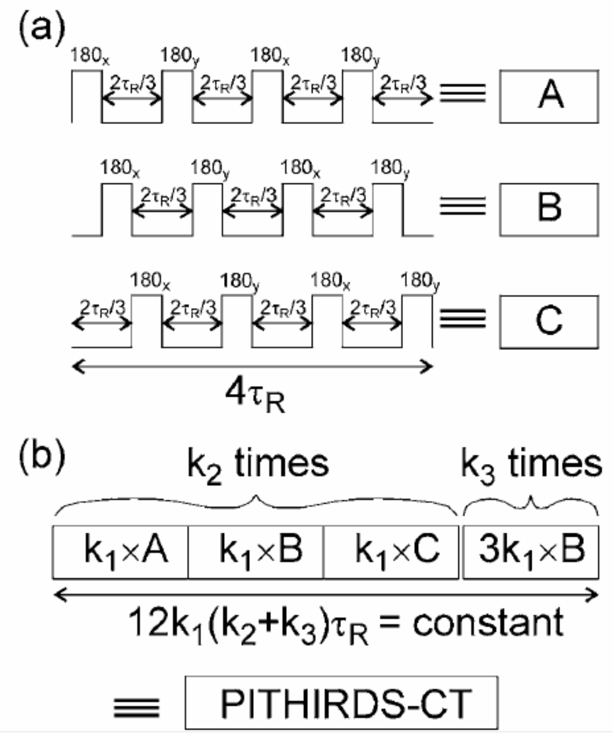
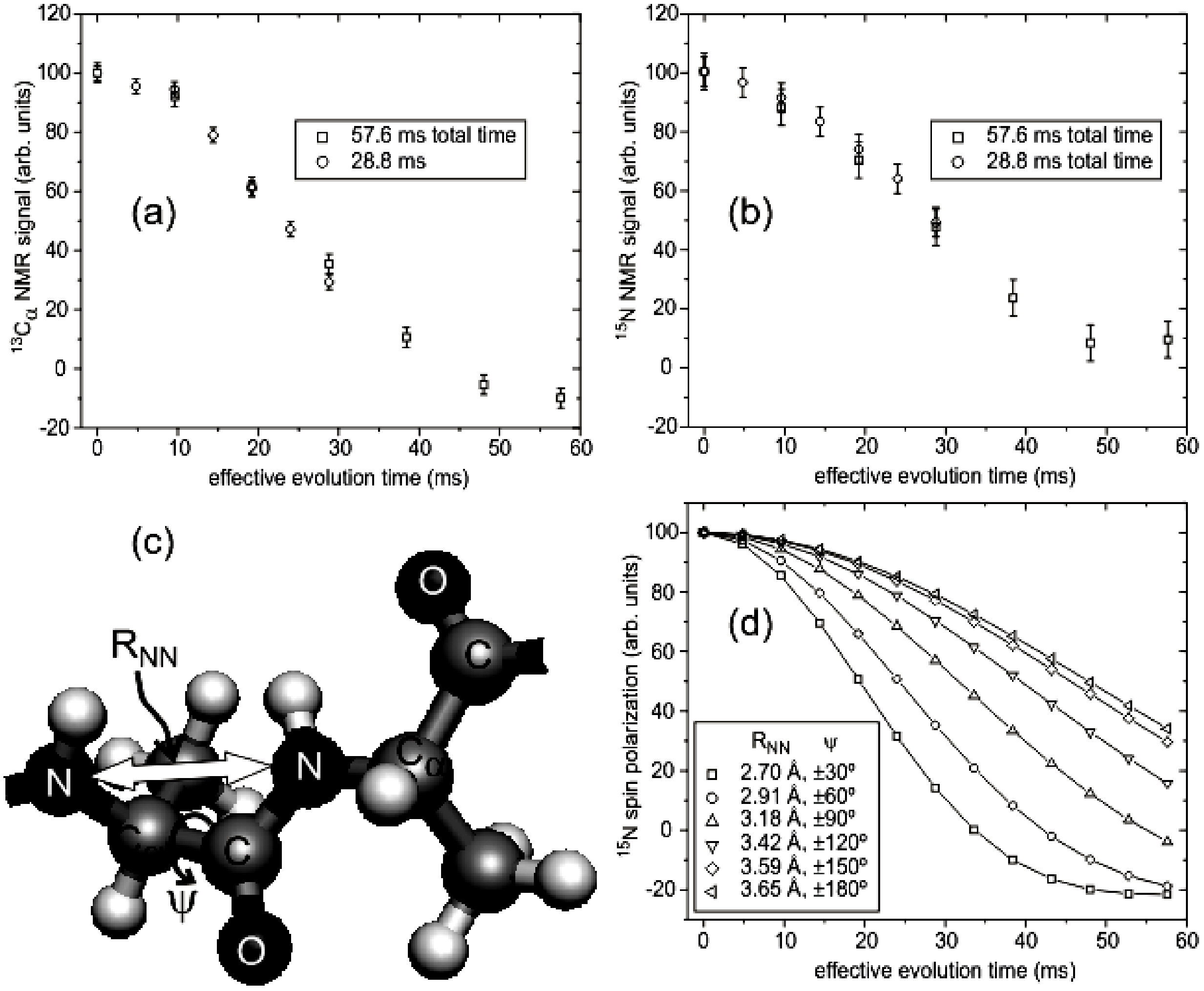


FIG. 1. (a) Three pulse sequence blocks used in symmetry-based constant-time homonuclear dipolar recoupling experiments, consisting of the fpRFDR dipolar recoupling sequence (Ref. 12) with π pulse lengths equal to $\tau_R/3$ and displacements in time of 0, $\tau_R/3$, and $2\tau_R/3$ relative to the MAS rotation period τ_R. Phases of π pulses shown here follow the *XY*-4 pattern, but *XY*-16 patterns (Ref. 14) are used in experiments when longer pulse trains occur. (b) PITHIRDS-CT pulse sequence for constant-time dipolar recoupling. Because the average homonuclear dipole-dipole coupling Hamiltonians of blocks A, B, and C sum to zero, the effective dipolar evolution period is $\tau_D' = 12k_1k_3\tau_R$, which is the length of the final period of B blocks.

Construction of a constant-time dipolar recoupling sequence from the fpRFDR sequence. During the "k_2" period, dipolar recoupling by the A, B, and C blocks cancels due to Eq. (VI.17). Only the "k_3" period has a net recoupling effect. Thus, by decrementing k_2 and incrementing k_3 while keeping $k_2 + k_3$ constant, the effective recoupling period τ_D' can be increased from 0 to $12k_1(k_2 + k_3)\tau_R$. For all values of τ_D', the total fpRFDR period is $12k_1(k_2 + k_3)\tau_R$ and the total number of pulses is constant. Thus, signal decay due to spin relaxation, incomplete proton decoupling, and pulse imperfections is minimized. The dependence of NMR signals on τ_D' is due primarily to dipole-dipole couplings rather than these extraneous effects, allowing the recoupling data to be analyzed in a quantitative manner. [from J. Chem. Phys. **126**, 064506 (2007)]



Measurements of backbone ^{15}N-^{15}N distances (which constrain the ψ torsion angle) in a model helical peptide in lyophilized form using the PITHIRDS-CT recoupling technique. Both ^{15}N-detected data (b) and $^{13}C_\alpha$-detected data (a) are shown, along with numerical simulations (d). [from J. Chem. Phys. **126**, 064506 (2007)]

Appendix: Derivation of time-dependent dipole-dipole coupling under MAS

In angular frequency units and in a molecule-fixed frame (*i.e.*, in an axis system that has any specific orientation relative to the molecular structure or crystallite unit cell), the full dipole-dipole coupling can be written as

$$H_D = \frac{3\gamma_I{}^2\hbar}{R^3}\sum_{m=-2}^{2}(-1)^m Y_{2m}T_{2-m} \tag{A.1}$$

with

$$\begin{aligned}
T_{2\pm2} &= \tfrac{1}{2} I_{\pm1}I_{\pm2} \\
T_{2\pm1} &= \mp\tfrac{1}{2}(I_{z1}I_{\pm2} + I_{\pm1}I_{z2}) \qquad \text{(A.2)} \\
T_{20} &= \tfrac{1}{\sqrt{6}}(3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2)
\end{aligned}$$

$$\begin{aligned}
Y_{2\pm2} &= \tfrac{1}{2}\sin^2\theta e^{\pm2i\phi} \\
Y_{2\pm1} &= \mp\sin\theta\cos\theta e^{\pm i\phi} \qquad \text{(A.3)} \\
Y_{20} &= \tfrac{1}{\sqrt{6}}(3\cos^2\theta - 1)
\end{aligned}$$

In Eq. (A.3), θ and ϕ are angles that specify the direction of the internuclear vector in the molecule-fixed frame. It is important to realize that the Y_{2m} functions are simply (complex) numbers for a given pair of coupled nuclei. These numbers do not change when the transformations described below are carried out. It is the T_{2m} operators that change under these transformations.

Suppose the molecule-fixed frame (with axes x',y',z' as in Section III.A) is related to a MAS-rotor-fixed frame (with axes x",y",z") by Euler angles $\alpha\beta\gamma$. The spinning axis is taken to be z". x" and y" are perpendicular to the spinning axis. In other words, the x',y',z' axes are transformed to the x",y",z" axes by three consecutive rotations: first, a rotation about z' by α; second, a rotation about the intermediate y axis by β; third, a rotation about the z" axis by γ. Then the irreducible tensor operator components are transformed according to

$$\begin{aligned}
T_{2m} &\rightarrow \sum_{m'=-2}^{2} D_{m'm}{}^{(2)}(\alpha,\beta,\gamma)T_{2m'} \qquad \text{(A.4)} \\
D_{m'm}{}^{(2)}(\alpha,\beta,\gamma) &= e^{im\gamma}d_{m'm}{}^{(2)}(\beta)e^{im\alpha}
\end{aligned}$$

with

$$
\begin{aligned}
&d_{00}{}^{(2)}(\beta) = 3\cos^2\beta - 1 \\
&d_{0\pm1}{}^{(2)}(\beta) = -d_{0\pm1}{}^{(2)}(\beta) = \mp\frac{\sqrt{6}}{2}\sin\beta\cos\beta \\
&d_{0\pm2}{}^{(2)}(\beta) = d_{\pm20}{}^{(2)}(\beta) = \frac{\sqrt{6}}{4}\sin^2\beta \\
&d_{1\pm1}{}^{(2)}(\beta) = \tfrac{1}{2}(1\pm\cos\beta)(2\cos\beta\mp1) \\
&d_{-1\pm1}{}^{(2)}(\beta) = \tfrac{1}{2}(1\mp\cos\beta)(2\cos\beta\pm1) \\
&d_{1\pm2}{}^{(2)}(\beta) = \pm\tfrac{1}{2}\sin\beta(1\pm\cos\beta) \\
&d_{-1\pm2}{}^{(2)}(\beta) = \pm\tfrac{1}{2}\sin\beta(1\mp\cos\beta) \\
&d_{2\pm1}{}^{(2)}(\beta) = -\tfrac{1}{2}\sin\beta(1\pm\cos\beta) \\
&d_{-2\pm1}{}^{(2)}(\beta) = \tfrac{1}{2}\sin\beta(1\mp\cos\beta) \\
&d_{2\pm2}{}^{(2)}(\beta) = \tfrac{1}{4}(1\pm\cos\beta)^2 \\
&d_{-2\pm2}{}^{(2)}(\beta) = \tfrac{1}{4}(1\mp\cos\beta)^2 \qquad\qquad (A.5)
\end{aligned}
$$

$\{ D_{m'm}{}^{(2)}(\alpha,\beta,\gamma) \}$ are Wigner rotation matrix elements. $\{ d_{m'm}{}^{(2)}(\beta) \}$ are reduced rotation matrix elements. The following article is a useful review of rotations, Euler angles, irreducible tensors, spherical harmonics, and Wigner rotation matrices: A.A. Wolf, "Rotation Operators", Am. J. Phys. **37**, 531-536 (1969).

In Eq. (A.1), the T_{2m} operators are functions of spin angular momentum components in the molecule-fixed frame. When written in terms of spin angular momentum components in the rotor-fixed frame, H_D becomes

$$H_D = \frac{3\gamma_I{}^2\hbar}{R^3}\sum_{m,m'=-2}^{2}(-1)^m Y_{2m}e^{im'\gamma}d_{m'-m}{}^{(2)}(\beta)e^{-im\alpha}T_{2m'} \qquad (A.6)$$

In Eq. (A.6), the $T_{2m'}$ operators are functions of spin angular momentum components in the rotor-fixed frame. Next, the rotor fixed frame is transformed to the laboratory-fixed frame (with axes x,y,z) by a time-dependent rotation about z" by $\omega_R t$ that makes y" perpendicular to z and coincident with y (because z" is the spinning axis and because we define t = 0 to be a time when y" and y coincide), followed by a rotation about y by the magic angle θ_M that brings z" to z. Under these rotations,

$$T_{2m'} \rightarrow \sum_{m''=-2}^{2} D_{m''m'}{}^{(2)}(0,\theta_M,\omega_R t)T_{2m''} \qquad (A.7)$$

$$\begin{aligned} H_D &= \frac{3\gamma_I{}^2\hbar}{R^3} \sum_{m,m',m''=-2}^{2} (-1)^m Y_{2m} e^{im'\gamma} d_{m'-m}{}^{(2)}(\beta) e^{-im\alpha} d_{m''m'}{}^{(2)}(\theta_M) e^{im'\omega_R t} T_{2m''} \\ &= \frac{3\gamma_I{}^2\hbar}{R^3} \sum_{m,m',m''=-2}^{2} (-1)^m Y_{2m} d_{m'-m}{}^{(2)}(\beta) e^{-im\alpha} d_{m''m'}{}^{(2)}(\theta_M) e^{im'(\omega_R t+\gamma)} T_{2m''} \end{aligned} \tag{A.8}$$

H_D in Eq. (A.8) is the full dipole-dipole coupling as it appears in the laboratory frame under MAS, written in terms of the angles θ and ϕ that specify the direction of the internuclear vector relative to the molecule-fixed axes and the angles α, β, and γ that specify the orientation of the molecule in the rotor. The $T_{2m''}$ operators in Eq. (A.8) are functions of spin angular momentum components in the laboratory frame.

In high field, terms in Eq. (A.8) with $m'' \neq 0$ are truncated by the much larger Zeeman interaction with the external magnetic field. In other words, only the $m'' = 0$ term affects the frequencies and intensities of NMR signals or affects coherent spin dynamics in high field. Furthermore, at the magic angle, the $m' = 0$ term vanishes because $d_{00}{}^{(2)}(\theta_M) = 0$. This what makes the magic angle so magical. Then the remaining terms oscillate at ω_R and $2\omega_R$, and average to zero unless recoupling techniques are employed.

$$H_D \to \frac{3\gamma_I{}^2\hbar}{R^3} \sum_{\substack{m,m'=-2 \\ m'\neq 0}}^{2} (-1)^m Y_{2m} d_{m'-m}{}^{(2)}(\beta) e^{-im\alpha} d_{0m'}{}^{(2)}(\theta_M) e^{im'(\omega_R t+\gamma)} T_{20} \tag{A.9}$$

Explicit expressions for the A, B, C, and D coefficients in Eq. (III.2) and the A_m coefficients used in Section VI can be derived from Eq. (A.9).

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