Two Dimensional NMR and NMR Relaxation Studies
of Coal Structure

PROGRESS REPORT

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ABSTRACT

This report covers the progress made on the title project for the project period. Four major areas of inquiry are being pursued. Advanced solid state NMR methods are being developed to assay the distribution of the various important functional groups that determine the reactivity of coals. Special attention is being paid to methods that are compatible with the very high magic angle sample spinning rates needed for operation at the high magnetic field strengths available today. Polarization inversion methods utilizing the difference in heat capacities of small groups of spins are particularly promising. Methods combining proton-proton spin diffusion with ^{13}C CPMAS readout are being developed to determine the connectivity of functional groups in coals in a high sensitivity relay type of experiment. Additional work is aimed at delineating the role of methyl group rotation in the proton NMR relaxation behavior of coals.

Introduction

The combination of cross polarization and magic angle spinning (CPMAS) methods for acquiring C-13 spectra is one of the most important structural analysis techniques available to the fuels chemist. At the high field strengths available today both sensitivity and spectral dispersion are significantly increased making it possible to apply CPMAS methods in an ever wider range of studies. However, the requirement for ever greater MAS spin rates also causes problems with the cross polarization process. At very high MAS rates the CP process can become very inefficient and result in distorted spectral intensities. In our last report we presented a detailed theoretical and experimental study of cross polarization (CP) under high speed magic angle sample spinning (MAS) and suggested some solutions to this problem. We also noted that the application of Floquet theory could provide additional insight into the effects of rapid sample rotation on the CP process. In this report we outline our initial progress in using Floquet theory to understand cross polarization dynamics. As a first step we have considered the problem of decoupling protons from C-13 nuclei using Floquet theory.

Floquet theory is a method for handling time dependent quantum mechanical problems in which several harmonically varying perturbations can be handled simultaneously. The following preprint details how this theory can be applied to the decoupling problem and provides the background required to apply Floquet theory to cross polarization dynamics. The problem revisited is that of the second order dipolar shifts observed by VanderHart in the C-13 CPMAS spectra of simple organic molecules and polymers.

Field Dependent Isotropic Chemical Shifts in Solid State NMR:

A Floquet Treatment

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Abstract

The apparent field dependence of the isotropic shift of an I spin under conditions of S spin decoupling due to nonsecular portions of the heteronuclear dipolar interaction is re-investigated using the Floquet formalism. Second order dipolar shifts are derived that largely agree with the experimental observations made by VanderHart and his treatment of the problem using second order perturbation theory. The Floquet treatment presented here resolves difficulties noted before in using a secular approximation to handle what is inherently a time dependent problem. The additional terms in the dipolar hamiltonian which can be included in this approach are shown to give rise to both frequency shifts and line broadening. Under some circumstances these can be comparable to those previously identified as significant in $^{13}\text{C} - ^1\text{H}$ spin pairs. One of the more important line broadening terms arises from a second - order coupling of the rf field with the $I - S$ dipolar interaction producing a *pseudo - power* broadening.

Introduction

In 1986 VanderHart¹ reported on the observation of an apparent field dependence in the isotropic ^{13}C chemical shifts measured in high resolution solid state NMR spectra of organic solids using high power ^1H decoupling² and magic angle sample spinning (MASS).³ While the changes in shift with field were small, they were sufficiently large to be problematic in certain applications, hence casting doubt upon the suitability of some secondary chemical shift reference materials.⁴ One of the key observations made was that this field dependence appeared to be proportional to the magnitude of the $^{13}\text{C} - ^1\text{H}$ dipolar coupling despite the application of strong on resonance ^1H decoupling. The field dependence was largely absent in motionally averaged systems such as methyl groups and plastic crystals, and for quaternary carbons as well. Methine and methylene carbon centers displayed the largest field dependence with the shifts for methylenes being somewhat larger. Further measurements demonstrated that the isotropic shifts approached a limiting value with increasing applied field, B , and that the size of the shift was directly proportional to the square of the ratio of the $^{13}\text{C} - ^1\text{H}$ dipolar coupling to B .

These observations, especially the latter, suggested to VanderHart that the field dependence of the shifts was due to second order corrections to the NMR transition frequencies from nonsecular terms in the heteronuclear dipolar interaction. Such an analysis in the framework of perturbation theory does indeed correctly account for the dependence of the shift on the dipolar coupling, ω_D , and B . To obtain an exact expression for the field dependence of the isotropic shift, one would have to solve the Schrödinger equation for an $I - S$ spin pair including all secular and nonsecular terms in the dipolar interaction in addition to the time dependent rf field. Unfortunately, there is no interaction representation in which this hamiltonian can be rendered fully independent of time. The typical solution is then to choose an appropriate interaction representation and to neglect the remaining time dependent terms in the hamiltonian. A fundamental problem

with this approach is that seemingly similar interaction representations can produce very different results.

These difficulties were already alluded to in reference 1. In this paper we present an alternative theoretical analysis, promised at that time, using the Floquet formalism.⁵ The advantage of this method is that the results are independent of the basis set chosen; i.e. they do not depend upon a judicious choice of interaction representation. It is found that all of the nonsecular terms in the heteronuclear dipolar interaction can make important contributions to the observed second order shifts although the relative sizes of these terms depends upon the ratio of the dipolar coupling to sums and differences of Larmor frequencies. The analysis largely corroborates the conclusions of VanderHart with respect to the commonly encountered case of a ^{13}C coupled to a ^1H . In other cases different dipolar terms than previously considered dominate, suggesting that additional effects may be observable experimentally.

Theory

We begin by considering the decoupling of the I spin resonance of a dipolar coupled $I - S$ spin pair by application of an rf field, $\mathbf{B}_1$, close to the Larmor frequency of the S spin. The relevant laboratory frame hamiltonian in angular frequency units can be written in standard fashion as

$$\mathcal{H}_L = -\omega_I I_z - \omega_S S_z - 2\omega_d \cos \omega_s t (\gamma I_z + S_z) + \omega_d (A + B + C + D + E + F)$$

where the substitution $\gamma = \gamma_I/\gamma_S$ has been used. The dipolar "alphabet" terms A - F have their usual meaning and are given by

$$\begin{aligned}
A &= I_z S_z (1 - 3 \cos^2 \vartheta) & B &= \frac{1}{4} (I_+ S_- + I_- S_+) (3 \cos^2 \vartheta - 1) \\
C &= -\frac{3}{2} (I_+ S_z + I_z S_+) \sin \vartheta \cos \vartheta e^{-i\varphi} & D &= C^* \\
E &= -\frac{3}{4} I_+ S_+ \sin^2 \vartheta e^{-2i\varphi} & F &= E^*
\end{aligned}
\tag{1}$$

where the polar angles ϑ and φ provide the orientation of the $I \cdot S$ internuclear vector in this frame.⁶ The dipolar coupling constant has been defined here as $\omega_D = \gamma_I \gamma_S \hbar / r_{IS}^3$. In what follows it will be convenient to separate the angular factors from the spin operators. A useful set in this instance are the Ω_n , as defined below.

$$\begin{aligned}
\Omega_1 &= \omega_D (1 - 3 \cos^2 \vartheta) & \Omega_2 &= \frac{\omega_D}{4} (3 \cos^2 \vartheta - 1) \\
\Omega_3 &= -\frac{3\omega_D}{2} \sin \vartheta \cos \vartheta e^{-i\varphi} & \Omega_4 &= -\frac{3\omega_D}{4} \sin^2 \vartheta e^{-2i\varphi}
\end{aligned}$$

Using these we can rewrite the laboratory frame hamiltonian as follows:

$$\begin{aligned}
\mathcal{H}_L &= -\omega_I I_z - \omega_S S_z - 2\omega_D \cos \vartheta (\gamma I_z + S_z) + \Omega_1 I_z S_z + \Omega_2 (I_+ S_- + I_- S_+) \\
&\quad + \Omega_3 (I_+ S_z + I_z S_+) + \Omega_4 (I_- S_z + I_z S_-) + \Omega_5 I_+ S_+ + \Omega_6 I_- S_-
\end{aligned}
\tag{2}$$

In the typical treatment of the heteronuclear decoupling problem, only the A term in the dipolar hamiltonian is retained as it is the only term that contributes to the lineshape in first order. A rotating frame transformation is also usually applied to render the interaction between the S spins and the rf field independent of time. Using these approximations and suppressing Bloch-Siegert type rf terms⁷, the following hamiltonian is obtained:

$$\mathcal{H}^{(0)} = -\omega_I S_x + \Omega_1 I_z S_z$$

This hamiltonian can be diagonalized using the transformation matrix, T written below in the direct product basis

$$T = \begin{array}{c} \langle \alpha\alpha | \\ \langle \alpha\beta | \\ \langle \beta\alpha | \\ \langle \beta\beta | \end{array} \begin{array}{c} |1\rangle \quad |2\rangle \quad |3\rangle \quad |4\rangle \\ \left[\begin{array}{cccc} \cos \xi & \sin \xi & 0 & 0 \\ -\sin \xi & \cos \xi & 0 & 0 \\ 0 & 0 & \cos \xi & -\sin \xi \\ 0 & 0 & \sin \xi & \cos \xi \end{array} \right] \end{array}$$

where $\tan 2\xi = 2\omega_{rf}/\Omega_I$. The resulting eigenvalues of $\mathcal{H}^{(0)}$ are

$$E_{|1\rangle} = -\frac{\omega_I}{2} + \frac{\Omega_I}{4} \cos 2\xi + \frac{\omega_Q}{2} \sin 2\xi$$

$$E_{|2\rangle} = -\frac{\omega_I}{2} - \frac{\Omega_I}{4} \cos 2\xi - \frac{\omega_Q}{2} \sin 2\xi$$

$$E_{|3\rangle} = +\frac{\omega_I}{2} - \frac{\Omega_I}{4} \cos 2\xi - \frac{\omega_Q}{2} \sin 2\xi$$

$$E_{|4\rangle} = +\frac{\omega_I}{2} + \frac{\Omega_I}{4} \cos 2\xi + \frac{\omega_Q}{2} \sin 2\xi$$

In the limit of good decoupling ($\omega_{rf} \gg \Omega_I$, giving $\xi = \pi/2$) the only allowed transitions are $|1\rangle \rightarrow |4\rangle$ and $|2\rangle \rightarrow |3\rangle$ which are found at the common transition frequency, ω_I .⁸ Even under less than optimal decoupling conditions, the average of the band formed by the overlap of all the allowed lines falls at the same frequency. This is the generally accepted understanding of the decoupled transition frequency - in the limit of good decoupling it is independent of the dipolar coupling between the two spins and falls at the chemical shift.

The Second Order Shift

The frequency resolution of MASS NMR spectroscopy is sufficiently good such that the small line shifts due to hamiltonian terms neglected in the foregoing treatment can be

detected. Keeping these terms and transforming to the rotating frame as before produces the following hamiltonian:

$$\begin{aligned} \mathcal{H}_R(t) = & -\omega_I I_z - \omega_S S_z + \Omega_1 I_+ S_- + \Omega_2 I_- S_+ + \Omega_3 I_+ S_+ + \Omega_4 I_- S_- + e^{i\omega_S t} (-\gamma \omega_S I_z + \Omega_2 I_- S_- + \Omega_3 I_+ S_- + \Omega_4 I_- S_-) \\ & + e^{-i\omega_S t} (-\gamma \omega_S I_z + \Omega_2 I_+ S_+ + \Omega_3 I_- S_+ + \Omega_4 I_+ S_+) - e^{2i\omega_S t} \left(\frac{\omega_S}{2} S_- \right) - e^{-2i\omega_S t} \left(\frac{\omega_S}{2} S_+ \right) \end{aligned} \quad 3$$

In addition to the terms previously included, the hamiltonian in 3 has an rf term oscillating at $2\omega_S$, which produces the well known Bloch - Siegert shift ⁷, and a series of dipolar terms oscillating at $\pm\omega_S$. $\mathcal{H}_R(t)$ will be considered in two separate pieces; a time independent portion $\mathcal{H}_R^{(0)}$ and a time dependent portion $\mathcal{H}(t)$. The matrix elements of these two parts of $\mathcal{H}_R(t)$ in the direct product basis $\langle m_I, m_S \rangle$ are tabulated for later use in Appendix I.

The standard treatment of the hamiltonian in 3 would be to use the "secular approximation" from time dependent perturbation theory. Since we have already transformed out the principal source of time dependence from the problem, one can justify discarding any remaining time-dependent terms as they should produce very small corrections to the transition frequencies. Such is the rationale, for instance, in dropping the rf terms leading to the Bloch-Siegert shift. In the same spirit one could reduce the problem at hand by considering only the time independent portion of $\mathcal{H}_R(t)$:

$$\mathcal{H}_R^{(0)} = -\omega_I I_z - \omega_S S_z + \Omega_1 I_+ S_- + \Omega_2 I_- S_+ + \Omega_3 I_+ S_+$$

In the interaction picture chosen here, two additional heteronuclear dipolar terms multiplied by Ω_3 and Ω_3^* then survive. These are the terms VanderHart¹ identified as being responsible for the ω_D transition frequency dependence. While they do not

contribute to the spin energy levels in first order, the second order corrections are of the form

$$E_n^{(2)} = \frac{|\Omega_n|^2}{4 \left(\omega_n + \frac{\Omega_1}{2} \cos 2\xi + \omega_n \sin 2\xi \right)}$$

as identified by VanderHart .

While this treatment reproduces in large measure the experimental observations, it is distressingly dependent on how the problem is formulated. One might, for example, equally well choose to treat the problem in the double rotating frame as is routinely used in analyses of $I-S$ cross polarization dynamics.⁹ In this frame the Ω_3 and Ω_3^* terms again become time dependent placing them once again on equal footing with the other terms in Equation 3 that are usually suppressed. The problem is that the manner in which the secular approximation is applied in this type of problem must be sharpened. One is simply not justified in discarding such terms solely on the basis of their time dependence. Rather, it is the fact that these terms only have off diagonal elements in the eigenbasis of the principal hamiltonian, and the rms value of these off diagonal terms is small. When viewed in this context it is readily seen that all of the nonsecular dipolar terms and the Bloch-Siegert terms must be treated on an equal footing. There is simply no justification in the present instance to include any one of these terms in favor of the others on the basis of their time dependence.

With this realization one could conclude that the problem is for all intents and purposes intractable. Fortunately the Floquet formalism provides an efficient means of solving such hamiltonians with several time dependencies.¹⁰

The Floquet Formalism

The time independent Floquet Hamiltonian, H_F , associated with a time dependent Hamiltonian, $\mathcal{H}(t)$, is simply derived from the rules outlined by Goelman, Zax and Vega⁵

$$\langle i, n | H_F | j, k \rangle = H_{i,j}^{(n-k)} + n\omega \delta_{k,n} \delta_{i,j} \quad 4$$

where the $H_{i,j}^{(n-k)}$ are the $(n - k)$ th time dependent Fourier coefficients coupling spin states $|i\rangle$ and $|j\rangle$. A basis set for H_F is constructed by taking the direct product of the bras and kets describing $\mathcal{H}(t)$ in whatever basis set is convenient and a Fourier mode index, n . The resulting basis set is referred to as an infinite collection of dressed spin states.¹¹ Formally, H_F is an infinite matrix since n can take on all values from $-\infty$ to $+\infty$. The diagonal elements of H_F are identical to those of $\mathcal{H}(t)$, except for an additional $n\omega$ term which essentially keeps track of the mode index of the Fourier expansion.

The terms in $\mathcal{H}(t)$ whose time dependence is of the form $e^{im\omega t}$ couple dressed spin states whose mode numbers differ by m . The Floquet Hamiltonian, H_F , associated with $\mathcal{H}_R(t)$ (Equation 3) is shown below in matrix form.

	$ \alpha\alpha, k\rangle$	$ \alpha\beta, k\rangle$	$ \beta\alpha, k\rangle$	$ \beta\beta, k\rangle$
$\langle\alpha\alpha, n $	$\left(-\frac{\omega_1}{2} + \frac{\Omega_1}{4} + n\omega_s\right)\delta_0$	$-\frac{\omega_\pi}{2}(\delta_{-2} + \delta_0) + \frac{\Omega_3}{2}\delta_{-1}$	$-\frac{\omega_\pi\gamma}{2}(\delta_{-1} + \delta_{-1}) - \frac{\Omega_3}{2}\delta_0$	$\Omega_4\delta_{-1}$
$\langle\alpha\beta, n $	$-\frac{\omega_\pi}{2}(\delta_{-2} + \delta_0) + \frac{\Omega_3}{2}\delta_{-1}$	$\left(-\frac{\omega_1}{2} - \frac{\Omega_1}{4} + n\omega_s\right)\delta_0$	$\Omega_2\delta_{-1}$	$-\frac{\omega_\pi\gamma}{2}(\delta_{-1} + \delta_{-1}) - \frac{\Omega_3}{2}\delta_0$
$\langle\beta\alpha, n $	$-\frac{\omega_\pi\gamma}{2}(\delta_{-1} + \delta_{-1}) - \frac{\Omega_3}{2}\delta_0$	$\Omega_2\delta_{-1}$	$\left(+\frac{\omega_1}{2} - \frac{\Omega_1}{4} + n\omega_s\right)\delta_0$	$-\frac{\omega_\pi}{2}(\delta_{-2} + \delta_0) - \frac{\Omega_3}{2}\delta_{-1}$
$\langle\beta\beta, n $	$\Omega_4\delta_{-1}$	$-\frac{\omega_\pi\gamma}{2}(\delta_{-1} + \delta_{-1}) - \frac{\Omega_3}{2}\delta_0$	$-\frac{\omega_\pi}{2}(\delta_{-2} + \delta_0) - \frac{\Omega_3}{2}\delta_{-1}$	$\left(+\frac{\omega_1}{2} + \frac{\Omega_1}{4} + n\omega_s\right)\delta_0$

The $\delta_{n,k}$ functions indicate the presence of an element coupling dressed spin states in a given sub-block that differ in mode numbers by $n - k$. The δ_0 components of H_F are just the secular elements of $\mathcal{H}_R(t)$ in the basis set we have chosen. Clearly then all of the non-secular time dependent terms of $\mathcal{H}_R(t)$ are relegated to off diagonal positions in a given subblock of H_F .

Our goal is to calculate the eigenvalues of H_F , and thus the NMR transition frequencies. This may appear to be a daunting prospect as H_F is infinite, however, this can largely be accomplished by considering what is required to diagonalize any sub-manifold of H_F . The remaining off diagonal elements will be found to be small and can be treated using perturbation theory. In analogy with the previous treatment of the decoupling problem, we expect the infinite transformation matrix T_F shown below to approximately diagonalize H_F .

$$\tau_F = \begin{matrix} & |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \\ \begin{matrix} \langle\alpha\alpha,k| \\ \langle\alpha\beta,k| \\ \langle\beta\alpha,k| \\ \langle\beta\beta,k| \end{matrix} & \begin{bmatrix} \cos \xi\delta_0 & \sin \xi\delta_0 & 0 & 0 \\ -\sin \xi\delta_0 & \cos \xi\delta_0 & 0 & 0 \\ 0 & 0 & \cos \xi\delta_0 & -\sin \xi\delta_0 \\ 0 & 0 & \sin \xi\delta_0 & \cos \xi\delta_0 \end{bmatrix} \end{matrix}$$

The prediagonalized matrix, H_F^λ ,

$$H_F^\lambda = \tau_F^{-1} \cdot H_F \cdot \tau_F$$

in terms of its individual matrix elements can be written in the usual fashion¹²

$$\langle j,n | H_F^\lambda | k,m \rangle = \sum_{\ell,\ell'} \langle j,n | \tau_F^{-1} | \ell,n \rangle \langle \ell,n | H_F | \ell',m \rangle \langle \ell',m | \tau_F | k,m \rangle$$

where the first index refers to states of the I - S spin system and n and m are the Fourier mode indices. For $\tan 2\xi = 2\omega_I/\Omega_I$ all of the interactions between nearly degenerate basis state vectors are moved to the infinite diagonal of H_F , leaving only off diagonal terms between dressed spin states having energy differences on the order of ω_S and ω_I . It is important to note that all of the terms originally in the time dependent Hamiltonian, $\mathcal{H}_R(t)$, still appear. The zeroth order energies of H_F^λ are just the eigenvalues previously obtained for $\mathcal{H}_R^{(0)}$ upon omission of the Ω_3 and Ω_3^* terms, plus an additional term, $\ell\omega_S$, which is a direct consequence of the Floquet expansion of $\mathcal{H}_R(t)$ (Equation 4).

The completely transformed matrix, H_F^λ , under strong decoupling conditions is presented in Appendix II. The relative size of the off diagonal elements in H_F^λ are uniformly small in comparison to the difference in the corresponding diagonal elements. As a result, the effect of these cross terms can be calculated using the standard methods of

non - degenerate perturbation theory. First order perturbation corrections have been accounted for above. The second order shifts can be calculated using

$$E_{|q,m\rangle}^{(2)} = \sum_{p \neq q} \sum_{\ell} \frac{K_{p,\ell} |\mathcal{H}|q,m\rangle|^2}{E_{|q,m\rangle} - E_{|p,\ell\rangle}}$$

where $|p,\ell\rangle$ and $|q,m\rangle$ are dressed spin states. Notice that the Floquet treatment of $\mathcal{H}_R(t)$ has eliminated the arbitrary distinction initially made between secular and non - secular terms. However, these terms can still be identified because the secular terms correspond to matrix elements which couple Floquet states differing only in the spin portion of the basis vector and the nonsecular terms couple states of different mode number. Clearly, the secular and nonsecular portions of $\mathcal{H}_R(t)$ result in a coupling between dressed spin states of widely different energies.

The second order perturbation corrections to the eigenvalues of H_F^λ are independent of mode number because both the energy differences and the off diagonal terms depend upon the Fourier mode through the difference $\ell - m$ and the spin eigenstate value. The second order eigenvalue corrections in the standard limit that $\omega_I \gg \Omega_I$ and ω_{rf} are shown below.

$$\begin{aligned} E_{|1,\ell\rangle}^{(2)} = -E_{|1,\ell\rangle}^{(2)} = & -\frac{\cos 2\xi}{8\omega_1} (\omega_s^2 + 2|\Omega_s|^2) - \frac{|\Omega_s|^2}{4\omega_1} \\ & - \frac{1}{4(\omega_1 + \omega_s)} [4\cos^2 \xi |\Omega_s|^2 + \gamma^2 \omega_s^2 + \gamma \omega_s \sin 2\xi (\Omega_s + \Omega_s^*)] \\ & - \frac{1}{4(\omega_1 - \omega_s)} [4\sin^2 \xi |\Omega_s|^2 + \gamma^2 \omega_s^2 + 2\gamma \omega_s \sin 2\xi \Omega_s] \end{aligned}$$

$$\begin{aligned}
E_{|2,\ell\rangle}^{(2)} = -E_{|3,\ell\rangle}^{(2)} = & \frac{\cos 2\xi}{8\omega_1} (\omega_a^2 + 2|\Omega_a|^2) - \frac{|\Omega_a|^2}{4\omega_1} \\
& - \frac{1}{4(\omega_1 + \omega_a)} [4\sin^2 \xi |\Omega_a|^2 + \gamma^2 \omega_a^2 - \gamma \omega_a \sin 2\xi (\Omega_a + \Omega_a^*)] \\
& - \frac{1}{4(\omega_1 - \omega_a)} [4\cos^2 \xi |\Omega_a|^2 + \gamma^2 \omega_a^2 - 2\gamma \omega_a \sin 2\xi \Omega_a]
\end{aligned}$$

Selection rules that determine the observed NMR spectrum are, as usual, governed by the matrix elements of I_X . Using the transformation matrix, T_F , this operator in the Floquet basis is

$$I_X = \begin{matrix} & \begin{matrix} |1,m\rangle & |2,m\rangle & |3,m\rangle & |4,m\rangle \end{matrix} \\ \begin{matrix} \langle 1,\ell| \\ \langle 2,\ell| \\ \langle 3,\ell| \\ \langle 4,\ell| \end{matrix} & \begin{bmatrix} 0 & 0 & \cos 2\xi \delta_0 & -\sin 2\xi \delta_0 \\ 0 & 0 & \sin 2\xi \delta_0 & \cos 2\xi \delta_0 \\ \cos 2\xi \delta_0 & \sin 2\xi \delta_0 & 0 & 0 \\ -\sin 2\xi \delta_0 & \cos 2\xi \delta_0 & 0 & 0 \end{bmatrix} \end{matrix}$$

The states coupled by nonzero elements of I_X correspond to allowed transitions.¹³ Under conditions of good decoupling, $\omega_{rf} \gg \Omega_1$, therefore, $\cos 2\xi \approx 0$ and $\sin 2\xi \approx 1$. The only allowed transitions are $|1,\ell\rangle \rightarrow |4,\ell\rangle$ at frequency $\Delta\omega_{41}$ and $|2,\ell\rangle \rightarrow |3,\ell\rangle$ at a frequency $\Delta\omega_{32}$. Additional transitions between $\Delta\ell \neq 0$ Floquet states are also present and are displaced about the $\ell = 0$ transition by $\pm \ell \omega_S$. Selection rules for these satellite transitions can be determined by transforming I_X in the pre-diagonalized Floquet basis set into the approximate eigenbasis using the first order eigenfunctions as derived from perturbation theory. The intensity of these satellite transitions is vanishingly small in the high field limit, and therefore are not relevant to the present problem.

The corrected transition frequencies are calculated as:

$$\Delta\omega_{+} = \omega_1 + \frac{|\Omega_2|^2}{2\omega_1} + \frac{1}{2(\omega_1 + \omega_s)} [2|\Omega_4|^2 + \gamma^2\omega_s^2 + \gamma\omega_s(\Omega_4 + \Omega_4^*)] \\ + \frac{1}{2(\omega_1 - \omega_s)} [2|\Omega_2|^2 + \gamma^2\omega_s^2 + 2\gamma\omega_s\Omega_2] \quad 5$$

$$\Delta\omega_{-} = \omega_1 + \frac{|\Omega_2|^2}{2\omega_1} + \frac{1}{2(\omega_1 + \omega_s)} [2|\Omega_4|^2 + \gamma^2\omega_s^2 - \gamma\omega_s(\Omega_4 + \Omega_4^*)] \\ + \frac{1}{2(\omega_1 - \omega_s)} [2|\Omega_2|^2 + \gamma^2\omega_s^2 - 2\gamma\omega_s\Omega_2] \quad 6$$

Under actual experimental conditions one would not generally resolve each transition separately. In most cases, all that will be observed is an average transition frequency

$$\Delta\omega_{\text{av}} = \omega_1 + \frac{|\Omega_2|^2}{2\omega_1} + \frac{1}{2(\omega_1 + \omega_s)} [2|\Omega_4|^2 + \gamma^2\omega_s^2] + \frac{1}{2(\omega_1 - \omega_s)} [2|\Omega_2|^2 + \gamma^2\omega_s^2] \quad 7$$

with excess width

$$\Delta\omega_{\pm} = \frac{\gamma\omega_s(\Omega_4 + \Omega_4^*)}{\omega_1 + \omega_s} + \frac{2\gamma\omega_s\Omega_2}{\omega_1 - \omega_s} \quad 8$$

Some comments on these formulae are appropriate. The single transition frequency appears shifted from the *chemical shift* frequency, ω_I , by a series of terms which depend upon both the square of the rf field strength and the square of the dipole - dipole coupling divided by ω_I , $\omega_I + \omega_S$ or $\omega_I - \omega_S$. The Ω_n independent terms produce the well known off resonance Bloch - Siegert shift which moves the resonances for all I - spin sites equally.⁷ Terms containing the Ω_n comprise the dipolar coupling dependent second order shift identified by VanderHart.¹ These terms include contributions from not only the $|\Omega_3|^2$ terms, as previously identified, but also from all the other off diagonal portions of the

dipolar coupling hamiltonian. The dominating terms depend upon the relationship between the energy denominators ω_I , $\omega_I + \omega_S$ and $\omega_I - \omega_S$ and the orientation of r_{IS} with respect to B . The dipolar coupling terms transform in space as second rank tensors, indicating that the additional shift transforms as a sum of zeroth (isotropic), second and fourth rank tensors.

The linewidth depends not only on the size of dipole - dipole couplings, but, suprisingly on the strength of the decoupling field, ω_{rf} . It is possible that this later effect may be observed in, for example, $^1H - ^{19}F$ dipole - dipole couplings in powdered samples as we shall demonstrate later. Because this additional *pseudo - power* broadening depends on the product of an isotropic (rf field) and a second rank tensorial interaction, the product will transform as an ordinary second rank tensor. It is also pleasing to note that Equations 5, 6 and 7 are also obtained under strong decoupling conditions when diagonalization of the $\delta\sigma$ components of H_F is extended to include the small Ω_3 terms, demonstrating that such a Floquet treatment gives a basis set independent result.

Despite having chosen a particular rotating frame representation to simplify some of the calculations, each of the off diagonal terms in the dipolar Hamiltonian has been treated equivalently, and each makes some contribution to the second order dipolar shift. The dominating term depends somewhat on ω_I and ω_S as well as the specific orientation of a given r_{IS} . These frequency dependences are best illustrated by considering the powder averaged lineshapes corresponding to Equations 5 and 6. Such lineshapes could be observed, for example, in a static sample having no chemical shift anisotropy (CSA).

It will prove helpful to re-express the results derived above in a form which better emphasizes rotational properties i.e. by rewriting the terms which depend upon angular factors in terms of the Wigner rotation matrices by using vector coupling coefficients.

$$\begin{aligned}
\Omega_2 &= \frac{\omega_D}{4} (3 \cos^2 \vartheta - 1) &= \frac{\omega_D}{2} d_{00}^{(2)}(\vartheta) \\
\Omega_4 + \Omega_4^* &= -\frac{3\omega_D}{4} \sin^2 \vartheta (e^{-2i\varphi} + e^{2i\varphi}) &= -\sqrt{6} \omega_D d_{02}^{(2)}(\vartheta) \cos 2\varphi \\
|\Omega_2|^2 &= \frac{\omega_D^2}{16} (3 \cos^2 \vartheta - 1)^2 &= \frac{\omega_D^2}{140} (18 d_{00}^{(4)}(\vartheta) + 10 d_{00}^{(2)}(\vartheta) + 7) \\
|\Omega_3|^2 &= \frac{9\omega_D^2}{4} \sin^2 \vartheta \cos^2 \vartheta &= \frac{3\omega_D^2}{70} (-12 d_{00}^{(4)}(\vartheta) + 5 d_{00}^{(2)}(\vartheta) + 7) \\
|\Omega_4|^2 &= \frac{9\omega_D^2}{16} \sin^4 \vartheta &= \frac{3\omega_D^2}{70} (3 d_{00}^{(4)}(\vartheta) - 10 d_{00}^{(2)}(\vartheta) + 7)
\end{aligned} \tag{9}$$

The reduced rotation matrices used above have their usual meaning i.e. $d_{00}^{(2)}(\vartheta) = (3 \cos^2 \vartheta - 1)/2$, $d_{02}^{(2)}(\vartheta) = (3/8)^{1/2} \sin^2 \vartheta \cos 2\varphi$ and $d_{00}^{(4)}(\vartheta) = (3 - 30 \cos^2 \vartheta + 35 \cos^4 \vartheta)/8$. In this form we emphasize that there are isotropic, second and fourth rank tensors contributing to the angular dependence of each of the terms of the second order dipolar shift. In powder samples the isotropic component corresponds to a shift in the center of gravity of the resonance line, while the second and fourth rank tensorial components contribute to orientational broadening. The additional *pseudo-power* broadening mentioned above is purely second rank and depends upon a linear combination of terms which transform in space as $T_0^{(2)}$ from the $\Omega_2 \omega_{rf}$ terms and as $T_{\pm 2}^{(2)}$ from the $(\Omega_4 + \Omega_4^*) \omega_{rf}$ terms.

Equations 5 and 6 are rewritten below in terms of the reduced matrix elements in order to more fully illustrate the result of different choices of ω_I , ω_S and ω_{rf} on the static lineshape.

$$\begin{aligned}
\Delta \omega_{32}^{41} &= \frac{\omega_D^2}{10} \left(\frac{3}{2\omega_I} + \frac{3}{(\omega_I + \omega_S)} + \frac{1}{2(\omega_I - \omega_S)} \right) \mp \frac{\sqrt{6} \gamma \omega_{rf} \omega_D}{2(\omega_I + \omega_S)} d_{02}^{(2)}(\vartheta) \cos 2\varphi \\
&+ \left(\frac{\omega_D^2}{7\omega_I} + \frac{3\omega_D^2}{7(\omega_I + \omega_S)} + \frac{\omega_D^2}{14(\omega_I - \omega_S)} \pm \frac{\gamma \omega_{rf} \omega_D}{2(\omega_I - \omega_S)} \right) d_{00}^{(2)}(\vartheta) \\
&+ \frac{9\omega_D^2}{35} \left(-\frac{1}{\omega_I} + \frac{1}{2(\omega_I + \omega_S)} + \frac{1}{2(\omega_I - \omega_S)} \right) d_{00}^{(4)}(\vartheta)
\end{aligned}$$

The lineshapes resulting from these formulae were obtained using a computer program to step over the polar angles present in the above equations in a standard fashion. Figure 1 shows the patterns for methine $^{13}\text{C} - ^1\text{H}$ pairs having $\omega_D = 146$ kHz (which is appropriate for a spin separation of 1.09 Å) and ν_{rf} set to (a) 40 kHz and (b) 100 kHz. *Pseudo - power* broadening is clearly illustrated by comparing the widths of the transitions at different decoupling field amplitudes i.e. the full width (FW) of the lineshape increases from 17 to 22 Hz upon increasing ν_{rf} from 40 kHz to 100 kHz. Figure 2 shows the expected dipolar spectra for the standard $^{19}\text{F} - ^1\text{H}$ spin pair found in KHF_2 with $\omega_D = 73$ kHz resulting from a spin separation of 1.15 Å and using the same decoupling field strengths as mentioned above. These lineshapes also confirm the presence of the *pseudo - power* broadening mechanism.

The existence of this broadening component of the second rank shift would probably best be observed in a nematic phase liquid crystalline environment. For small molecules dissolved in a nematic phase, linewidths are naturally small because the average orientation of all molecules is identical. Dipolar couplings are only partially averaged within a given molecule. One could also test for this shift in single crystals since there is no Chemical Shift Anisotropy (CSA) present. Thus, it may prove possible to observe the differential broadening predicted by Equation 8 above as a power dependent resonance shift in these cases. Equations 7 and 8 indicate that the lineshift depends upon terms of the form $|\Omega_n|^2 \omega_{rf}$ while the *pseudo - power* broadening depends upon $\Omega_n \omega_{rf}$. Each depends explicitly on orientation and therefore these additional terms will be (at least) partially averaged under MASS.

The consequences of MASS on the centerband lineshape can be quite simply described using the reduced rotation matrices and some simple geometry. The angles θ and ϕ describing the relative orientation of the internuclear vector, r_{IS} , in the laboratory frame of reference are made time dependent by mechanically rotating the sample about

some axis. We define ζ as the angle that the sample is being rotated about with respect to $\mathbf{B}$, $\omega_r t + \alpha_0$ as the (time dependent) angle swept out during rotation and η as the angle between the rotation axis and the internuclear vector, r_{IS} . It can be shown using direction cosines that

$$\cos(\vartheta(t)) = \cos \zeta \cos \zeta_{I-S} - \sin \zeta \sin \zeta_{I-S} \cos(\omega_r t + \alpha_0)$$

and

$$\sin(\vartheta(t)) = \sin \zeta \cos \zeta_{I-S} - \cos \zeta \sin \zeta_{I-S} \cos(\omega_r t + \alpha_0)$$

with similar expressions for $\sin\phi(t)$ and $\cos\phi(t)$. The magic angle centerband or isotropic band corresponds to the time averaged transition frequency and requires that we analyze for the time independent portion of the trigonometric functions $d_{00}^{(4)}(\vartheta(t))$, $d_{00}^{(2)}(\vartheta(t))$ and $d_{02}^{(2)}(\vartheta(t))\cos(2\phi(t))$. Straightforward algebraic manipulation yields

$$\langle d_{00}^{(2)}(\vartheta(t)) \rangle_t = d_{00}^{(2)}(\zeta) d_{00}^{(2)}(\zeta_{I-S})$$

$$\langle d_{00}^{(4)}(\vartheta(t)) \rangle_t = d_{00}^{(4)}(\zeta) d_{00}^{(4)}(\zeta_{I-S})$$

$$\langle d_{02}^{(2)}(\vartheta(t)) \cos 2\phi(t) \rangle_t = d_{02}^{(2)}(\zeta) d_{00}^{(2)}(\zeta_{I-S})$$

All interactions proportional $d_{00}^{(2)}(\vartheta(t))$, including CSA, are averaged to zero when we choose $3\cos^2\zeta - 1 = 0$. Other interactions are partially averaged in the amount of $-7/18$ for those terms proportional to $d_{00}^{(4)}(\vartheta(t))$ and $6^{-1/2}$ for those containing a $d_{02}^{(2)}(\vartheta(t))\cos(2\phi(t))$ dependence. The transition frequencies for the MASS centerband ($\zeta = 54.74^\circ$) associated with a particular set of orientations described by η are shown below.

$$\begin{aligned}
\Delta\omega_{32}^{41} = & \frac{\omega_D^2}{10} \left(\frac{3}{2\omega_I} + \frac{3}{(\omega_I + \omega_S)} + \frac{1}{2(\omega_I - \omega_S)} \right) \\
& + \frac{\omega_D^2}{10} \left(\frac{1}{\omega_I} - \frac{1}{2(\omega_I + \omega_S)} - \frac{1}{2(\omega_I - \omega_S)} \right) d_{00}^{(4)}(\zeta_{I-S}) \\
& \mp \frac{\sqrt{6}\gamma\omega_H\omega_D}{3(\omega_I + \omega_S)} d_{00}^{(2)}(\zeta_{I-S})
\end{aligned} \tag{10}$$

Equation 10 predicts that, for powder samples, the MASS centerband will be a super-position of powder patterns resulting from the two separate transitions. Powder patterns are observed under conditions of MASS only in more unusual circumstances, for example in the homonuclear dipole - dipole coupled systems where the frequency separation between coupled spins matches the spinning rate,¹⁴ and, more routinely, in quadrupolar systems where second order quadrupolar broadening dominates the observed spectrum.¹⁵ These second order quadrupolar powder patterns are similar to those encountered here as they also depend upon both $d_{00}^{(2)}(\eta)$ and $d_{00}^{(4)}(\eta)$. In these situations, the first order second rank interactions are averaged under MASS leaving a magic angle spun powder pattern which depends only on $d_{00}^{(4)}(\eta)$. These second order effects can be averaged away completely by spinning about a second axis magic for $d_{00}^{(4)}(\eta)$. Our powder patterns are an unusual type, they are predicted to depend upon three different geometric functions, $d_{00}^{(2)}(\eta)$, $d_{00}^{(4)}(\eta)$ and $d_{02}^{(2)}(\eta)$. Complete removal of all second order broadening requires, therefore, simultaneous spinning about three separate axes magic for each of these functions.

MASS centerbands for the methine $^{13}\text{C} - ^1\text{H}$ and the $^{19}\text{F} - ^1\text{H}$ spin pairs with the same dipolar coupling constants mentioned above are shown in Figures 3 and 4. These Figures illustrate two important features of Equations 5 and 6 under conditions of MASS. Firstly, the *pseudo - power* broadening survives sample rotation. For example, in the $^{19}\text{F} - ^1\text{H}$ case under normal MASS conditions ($\zeta = 54.74^\circ$) the FW of the centerband increases from 140 to 176 Hz upon increasing the decoupling field from 40 to 100 KHz. A similar, less noticeable trend is also observed in the $^{13}\text{C} - ^1\text{H}$ spin system. Secondly, the observed

lineshape is rotor axis sensitive, in that different portions of Equations 5 and 6 are averaged to zero depending on the choice of ζ . Equation 10 indicates that rotation about an angle magic for $d_{00}^{(2)}(\zeta)$ (54.74°) provides a mixture of $d_{00}^{(4)}(\eta)$ and $d_{00}^{(2)}(\eta)$ angular dependence. The chief reduced matrix element contributor to the total lineshape depends explicitly on the choice of ω_I , ω_S , ω_D and ω_{rf} as seen in Figures 1 - 4. MASS centerbands for these spin pairs corresponding to sample rotation about angles magic for $d_{00}^{(4)}(\zeta)$ (30.56° and 70.12°) are also included. Usually, single angle rotation about 54.74° provides the narrowest possible NMR line as it eliminates first order second rank interactions. However, in the $^{13}\text{C} - ^1\text{H}$ case, rotation about 30.56° or 70.12° produces a narrower line. This narrowing results from a combination of the frequency coefficients in Equations 5 and 6 and the $d_{02}^{(2)}(\zeta)d_{00}^{(2)}(\eta)$ term. These second order effects are usually not a nuisance in conventional ^1H decoupling experiments, as the predicted broadening is on the order of spectrometer resolution (0.1 ppm). However, such effects become important when considering decoupling experiments on other nuclei as Figure 4 indicates.

The presence of powder patterns under conditions of MASS also make it difficult to probe the isotropic shift of the magnetic resonance signal. The isotropic or average shift of the I spin (in angular units of Hz) while correcting for Bloch- Siegert effects is obtained by averaging the angular dependences in Equation 7 over a solid angle of 4π ¹⁶.

$$\Delta\nu_{\text{iso}} = \frac{\omega_D^2}{2\pi} \left\{ \frac{3}{20\omega_I} + \frac{3}{10(\omega_I + \omega_S)} + \frac{1}{20(\omega_I - \omega_S)} \right\} \quad 11$$

In the case of methine $^{13}\text{C} - ^1\text{H}$ pairs Equation 11 predicts a shift of $\Delta\nu_{\text{ISO}} = 0.46$ ppm at 15 MHz for ^{13}C and 0.04 ppm at 50 MHz. This corresponds to a difference of 0.42 ppm between the low field and high field measurements which is somewhat larger than the values provided by VanderHart.¹ This can be accounted for by considering that $^{13}\text{C} - ^1\text{H}$ couplings are always averaged to some extent. Whereas a typical $^{13}\text{C} - ^1\text{H}$ dipolar

coupling is calculated as 23 kHz assuming a $^{13}\text{C} - ^1\text{H}$ bond length of 1.09 Å, in fact one usually measures something 20 % less.¹⁷ Employing a motionally averaged $^{13}\text{C} - ^1\text{H}$ dipolar coupling of 18.4 kHz results in a calculated second order dipolar shift of 0.26, which is in much better agreement with the experimental observations. The agreement between measured and calculated second order shifts using the previous theory which included only the Ω_3 terms can be seen as somewhat fortuitous. This was in fact realized by VanderHart who pointed out that the nominal dipolar coupling needed to account for the observed field dependent shifts was in fact too large when the usual degree of motional averaging was admitted to.

The most serious consequences of ignoring the terms other than Ω_3 and Ω_3^* occurs in the case of an $^{19}\text{F} - ^1\text{H}$ spin pair with the ^1H being decoupled. The field dependent ($B = 1.4 \text{ T}$ and 4.7 T) isotropic shift upon ignoring all terms except for those proportional to Ω_3 and Ω_3^* is 0.23 ppm. The equations above that reflect all effects of the dipolar interaction, however, predict a different shift of -0.76 ppm. Additionally, in the case of the $^{19}\text{F} - ^1\text{H}$ spin pair, the *pseudo - power* broadening should be present. These results suggest that the conventional secular approximation is nearly correct for the specific case of a $^{13}\text{C} - ^1\text{H}$ spin system. However, such an approximation becomes increasingly worse upon considering spin systems having Larmor frequencies of similar size and a large dipolar coupling.

This theory additionally predicts the presence of a *pseudo - power* broadening of the resonance line resulting from a coupling of the applied decoupling field and the dipolar interaction of two spins. This second rank broadening suprisingly survives mechanical averaging by sample rotation, suggesting that rf inhomogeneity will be a problem in observing these effects. An inhomogeneous distribution in rf throughout a sample will provide a corresponding spread in *pseudo power* broadening. Insight into the effects of rf inhomogeneity on the MASS centerbands for $\zeta = 54.74^\circ$ can be obtained from Figure 5. Figure 5 shows the MASS centerband with (solid line) and without inhomogeneous rf field

for the same $^{13}\text{C} - ^1\text{H}$ and $^{19}\text{F} - ^1\text{H}$ pairs used above. This figure clearly illustrates that rf inhomogeneity significantly alters MASS centerbands, especially in the $^{19}\text{F} - ^1\text{H}$ case, which is unfortunate as the second order effects predicted by this theory are most easily realized in this system.

Given the steady increase in field strengths that are being routinely employed in CP - MAS experiments, it is natural to ask how high a field is necessary to render the effects discussed here insignificant. In the case of $^{13}\text{C} - ^1\text{H}$ it can be seen from MASS centerband calculations that above a field strength of 4.7 T the excess linewidth resulting from *pseudo - power* broadening becomes insignificant in comparison to 0.1 ppm. This is about the resolution one can expect in CP - MAS experiments given other linebroadening factors such as magnetic susceptibility effects, off resonance ^1H decoupling contributions or simple site to site variations in chemical shifts due to lattice disorder.¹⁸ For ^{19}F these effects persist longer, but by the time a field of 7.04 T is reached they also will become less important than other limitations on resolution.

Conclusions

We have provided a more complete description of the problem of second order dipolar shifts in high resolution solid state NMR spectroscopy. The suggestion that the dominant features of the shift were associated with the Ω_3 elements of the dipolar hamiltonian is largely correct for the specific case of ^{13}C NMR with high power decoupling. These specific terms dominate because the denominators associated with the different terms in the effective Hamiltonian are large except for the term containing $|\Omega_3|^2$. However, this is not generally the case. In $^{19}\text{F} - ^1\text{H}$ systems where the denominators are the smallest should have drastically different, and experimentally observable field dependent isotropic resonance shifts and static (FW $\approx$ 800 Hz. at $B = 1.4$ T) and spinning lineshapes (FW $\approx$ 80 Hz at $B = 1.4$ T). These second order shifts will survive

in both decoupled and coupled systems. The shifts (-0.35 ppm for ^{19}F - ^1H and 0.42 ppm for ^{13}C - ^1H) are large enough to be important in the analysis of liquid crystal data.

The theoretical results summarized in Equations 5 and 6 suggest the possibility of some interesting experiments. One could envision, for example, an NMR probe capable of rotating samples simultaneously about three separate angles or a 3 - D Dynamic Angle Spinning experiment. Such experiments could be used to investigate mechanical narrowing effects on the lineshapes of ^{19}F - ^1H dipolar coupled systems. This paper demonstrates that the Floquet formalism provides a more general description of the problem of field dependent isotropic shifts which was unavailable using other common theoretical tools to deal with this inherently time dependent problem.

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Appendix I

The time dependent Hamiltonian matrix, $\mathcal{H}_R(t)$ is shown below where

$$\mathcal{H}_R(t) = \mathcal{H}_R^{(0)} + \mathcal{H}(t)$$

$$\mathcal{H}_R^{(0)} = \begin{array}{c} \langle \alpha\alpha | \\ \langle \alpha\beta | \\ \langle \beta\alpha | \\ \langle \beta\beta | \end{array} \begin{array}{c} | \alpha\alpha \rangle \\ | \alpha\beta \rangle \\ | \beta\alpha \rangle \\ | \beta\beta \rangle \end{array} \begin{bmatrix} -\frac{\omega_1}{2} + \frac{\Omega_1}{4} & -\frac{\omega_\pi}{2} & \frac{\Omega_2}{2} & 0 \\ -\frac{\omega_\pi}{2} & -\frac{\omega_1}{2} - \frac{\Omega_1}{4} & 0 & -\frac{\Omega_2}{2} \\ \frac{\Omega_2}{2} & 0 & \frac{\omega_1}{2} - \frac{\Omega_1}{4} & -\frac{\omega_\pi}{2} \\ 0 & -\frac{\Omega_2}{2} & -\frac{\omega_\pi}{2} & \frac{\omega_1}{2} + \frac{\Omega_1}{4} \end{bmatrix}$$

$$\mathcal{H}(t) = \begin{array}{c} \langle \alpha\alpha | \\ \langle \alpha\beta | \\ \langle \beta\alpha | \\ \langle \beta\beta | \end{array} \begin{array}{c} | \alpha\alpha \rangle \\ | \alpha\beta \rangle \\ | \beta\alpha \rangle \\ | \beta\beta \rangle \end{array} \begin{bmatrix} 0 & -\frac{\omega_\pi}{2} e^{-2i\omega_1 t} & -\frac{\omega_\pi \gamma}{2} \left(e^{i\omega_1 t} + e^{-i\omega_1 t} \right) & \Omega_2 e^{-i\omega_1 t} \\ -\frac{\omega_\pi}{2} e^{2i\omega_1 t} & 0 & \Omega_2 e^{i\omega_1 t} & -\frac{\omega_\pi \gamma}{2} \left(e^{i\omega_1 t} + e^{-i\omega_1 t} \right) \\ -\frac{\omega_\pi \gamma}{2} \left(e^{i\omega_1 t} + e^{-i\omega_1 t} \right) & \Omega_2 e^{-i\omega_1 t} & 0 & -\frac{\omega_\pi}{2} e^{-2i\omega_1 t} \\ \Omega_2 e^{i\omega_1 t} & -\frac{\omega_\pi \gamma}{2} \left(e^{i\omega_1 t} + e^{-i\omega_1 t} \right) & -\frac{\omega_\pi}{2} e^{2i\omega_1 t} & 0 \end{bmatrix}$$

Appendix II

The Floquet Hamiltonian in the pre - diagonalized basis is shown below in matrix form

$$H_F^1 = \begin{matrix} \langle 1, \ell | \\ \langle 2, \ell | \\ \langle 3, \ell | \\ \langle 4, \ell | \end{matrix} \begin{bmatrix} |1, m\rangle & |2, m\rangle & |3, m\rangle & |4, m\rangle \\ \hline & A & & B \\ \hline & & C & \\ \hline & & & D \end{bmatrix}$$

where the A, B, C and D sub - blocks are presented below.

$$A = \begin{matrix} \langle 1, \ell | & \begin{bmatrix} |1, m\rangle & |2, m\rangle \\ \hline \left(-\frac{\omega_1}{2} + \frac{\Omega_1}{4} \cos 2\xi \right. & \frac{\omega_{\pi}}{2} (\sin^2 \xi \delta_{+2} - \cos^2 \xi \delta_{-2}) \\ \left. + \frac{\omega_{\pi}}{2} \sin 2\xi + \ell \omega_s \right) \delta_0 & -\frac{1}{2} (\Omega_3 \sin^2 \xi \delta_{+1} - \Omega_3 \cos^2 \xi \delta_{-1}) \\ + \frac{\omega_{\pi} \sin 2\xi}{2} (\delta_{+2} + \delta_{-2}) & \\ - \frac{\sin 2\xi}{4} (\Omega_3^* \delta_{+1} + \Omega_3 \delta_{-1}) & \end{bmatrix} \\ \langle 2, \ell | & \begin{bmatrix} \left(-\frac{\omega_1}{2} - \frac{\Omega_1}{4} \cos 2\xi \right. & -\frac{\omega_{\pi}}{2} \sin 2\xi + \ell \omega_s \delta_0 \\ \frac{\omega_{\pi}}{2} (\sin^2 \xi \delta_{-2} - \cos^2 \xi \delta_{+2}) & -\frac{\omega_{\pi} \sin 2\xi}{2} (\delta_{+2} + \delta_{-2}) \\ -\frac{1}{2} (\Omega_3 \sin^2 \xi \delta_{-1} - \Omega_3^* \cos^2 \xi \delta_{+1}) & + \frac{\sin 2\xi}{4} (\Omega_3^* \delta_{+1} + \Omega_3 \delta_{-1}) \end{bmatrix} \end{matrix}$$

$$\begin{array}{c}
\langle 1, \ell | \\
\langle 2, \ell |
\end{array}
B =
\begin{array}{cc}
|3, m\rangle & |4, m\rangle \\
\frac{\Omega_3}{2} \delta_0 - \frac{1}{2} (\Omega_2 \sin 2\xi \\
+ \omega_{\pi} \gamma \cos 2\xi) \delta_{+1} & \left(\Omega_4 \cos^2 \xi + \frac{\omega_{\pi} \gamma}{2} \sin 2\xi \right) \delta_{-1} \\
+ \frac{1}{2} (\Omega_4 \sin 2\xi \\
- \omega_{\pi} \gamma \cos 2\xi) \delta_{-1} & + \left(\Omega_2 \sin^2 \xi + \frac{\omega_{\pi} \gamma}{2} \sin 2\xi \right) \delta_{+1} \\
\left(\Omega_4 \sin^2 \xi - \frac{\omega_{\pi} \gamma}{2} \sin 2\xi \right) \delta_{-1} & - \frac{\Omega_3}{2} \delta_0 - \frac{1}{2} (\Omega_2 \sin 2\xi \\
+ \omega_{\pi} \gamma \cos 2\xi) \delta_{+1} & + \frac{1}{2} (\Omega_4 \sin 2\xi \\
+ \left(\Omega_2 \cos^2 \xi - \frac{\omega_{\pi} \gamma}{2} \sin 2\xi \right) \delta_{+1} & - \omega_{\pi} \gamma \cos 2\xi) \delta_{-1}
\end{array}$$

$$\begin{array}{c}
\langle 3, \ell | \\
\langle 4, \ell |
\end{array}
C =
\begin{array}{cc}
|1, m\rangle & |2, m\rangle \\
\frac{\Omega_3}{2} \delta_0 - \frac{1}{2} (\Omega_2 \sin 2\xi \\
+ \omega_{\pi} \gamma \cos 2\xi) \delta_{-1} & \left(\Omega_4 \sin^2 \xi - \frac{\omega_{\pi} \gamma}{2} \sin 2\xi \right) \delta_{+1} \\
+ \frac{1}{2} (\Omega_4 \sin 2\xi \\
- \omega_{\pi} \gamma \cos 2\xi) \delta_{+1} & + \left(\Omega_2 \cos^2 \xi - \frac{\omega_{\pi} \gamma}{2} \sin 2\xi \right) \delta_{-1} \\
\left(\Omega_4 \cos^2 \xi + \frac{\omega_{\pi} \gamma}{2} \sin 2\xi \right) \delta_{+1} & - \frac{\Omega_3}{2} \delta_0 - \frac{1}{2} (\Omega_2 \sin 2\xi \\
+ \omega_{\pi} \gamma \cos 2\xi) \delta_{-1} & + \frac{1}{2} (\Omega_4 \sin 2\xi \\
+ \left(\Omega_2 \sin^2 \xi + \frac{\omega_{\pi} \gamma}{2} \sin 2\xi \right) \delta_{-1} & - \omega_{\pi} \gamma \cos 2\xi) \delta_{+1}
\end{array}$$

$$\begin{array}{c}
\begin{array}{cc}
|3, m\rangle & |4, m\rangle \\
\hline
\langle 3, \ell | & \begin{array}{l}
\left(\frac{\omega_1}{2} - \frac{\Omega_1}{4} \cos 2\xi \right. \\
\left. - \frac{\omega_\pi}{2} \sin 2\xi + \ell \omega_s \right) \delta_0 \\
+ \frac{\omega_\pi \sin 2\xi}{4} (\delta_{+2} + \delta_{-2}) \\
- \frac{\sin 2\xi}{4} (\Omega_3^* \delta_{+1} + \Omega_3 \delta_{-1})
\end{array} \\
D = & \begin{array}{l}
\frac{\omega_\pi}{2} (\sin^2 \xi \delta_{+2} - \cos^2 \xi \delta_{-2}) \\
+ \frac{1}{2} (\Omega_3^* \sin^2 \xi \delta_{+1} - \Omega_3 \cos^2 \xi \delta_{-1})
\end{array} \\
\langle 4, \ell | & \begin{array}{l}
\left(\frac{\omega_1}{2} + \frac{\Omega_1}{4} \cos 2\xi \right. \\
\left. + \frac{\omega_\pi}{2} \sin 2\xi + \ell \omega_s \right) \delta_0 \\
+ \frac{\omega_\pi \sin 2\xi}{2} (\delta_{+2} + \delta_{-2}) \\
+ \frac{\sin 2\xi}{4} (\Omega_3^* \delta_{+1} + \Omega_3 \delta_{-1})
\end{array}
\end{array}
\end{array}$$

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Figure Captions

Figure 1. Expected dipolar spectra assuming no CSA at $B = 1.4$ T. for methine $^{13}\text{C} - ^1\text{H}$ pairs separated by 1.09 Å. The FW of the lineshapes increase from (a) 17 Hz. at $\nu_{\text{rf}} = 40$ kHz. to (b) 22 Hz. at $\nu_{\text{rf}} = 100$ kHz.

Figure 2. Simulated dipolar lineshapes again assuming no CSA at $B = 1.4$ T. for the $^{19}\text{F} - ^1\text{H}$ spin pair found in KHF_2 . The FW of the lineshape increases from (a) 889 Hz. at $\nu_{\text{rf}} = 40$ kHz. to (b) 1935 Hz. at $\nu_{\text{rf}} = 100$ kHz.

Figure 3. MASS centerband simulations at $B = 1.4$ T. for methine $^{13}\text{C} - ^1\text{H}$ pairs having $\zeta = 30.56^\circ, 54.74^\circ, 70.12^\circ$ and 90° and $\nu_{\text{rf}} = 40$ and 100 kHz. The lineshapes indicate that the pseudo - power broadening survives sample rotation. Suprisingly, the centerbands corresponding to sample rotation at $\zeta = 30.56^\circ$ and 70.12° are narrower than those obtained under normal ($\zeta = 54.74^\circ$) MASS conditions.

Figure 4. MASS centerband lineshapes at $B = 1.4$ T. and with no CSA for the $^{19}\text{F} - ^1\text{H}$ spin pair found in KHF_2 having $\zeta = 30.56^\circ, 54.74^\circ, 70.12^\circ$ and 90° and $\nu_{\text{rf}} = 40$ and 100 kHz. Again, the pseudo - power broadening is readily evident. The lineshape corresponding to $\zeta = 54.74^\circ$ is the narrowest resonance in contrast to that of the $^{13}\text{C} - ^1\text{H}$ spin pair shown in Figure 3.

Figure 5. Conventional MASS centerbands showing the effects of rf inhomogeneity on the expected lineshapes for the (a) methine $^{13}\text{C} - ^1\text{H}$ spin pair and the (b) $^{19}\text{F} - ^1\text{H}$ spin pair in KHF_2 at $B = 1.4$ T. and $\nu_{\text{rf}} = 60$ kHz. The z - component of the magnetic field as a function of position inside a solenoid coil having a diameter of 5 mm and a length of 7.5 mm was used to estimate the decoupling field strength across a sample filling the entire coil volume.

(a) $\nu_{rf} = 40$ kHz.

(b) $\nu_{rf} = 100$ kHz.

Figure 1

(a) $\nu_{rf} = 40$ kHz.

(b) $\nu_{rf} = 100$ kHz.

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 5

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