

CHAPTER 5

DIPOLAR COHERENCE TRANSFER IN THE PRESENCE OF CHEMICAL SHIFT FOR UNORIENTED AND ORIENTED HOMONUCLEAR TWO SPIN- $\frac{1}{2}$ SOLID STATE SYSTEMS

Introduction

In this chapter, coherence transfer is examined for the full coupling NMR Hamiltonian, with the addition of chemical shift. The effects of the full coupling Hamiltonian are examined for both oriented and unoriented samples using computer simulation of the full analytical coherence transfer functions. As we have seen in previous chapters, modeling of dipolar coherence transfer (DCT) for various experiments and conditions can yield information not easily gained from the end products of numerical modeling methods. However, the analysis of dipolar coherence transfer, while not strictly trivial, can seem much more simple when regarding the challenge of simultaneously modeling all the important interactions present in solid-state NMR. Many numerical-calculation NMR software packages do very well at modeling pulse sequences and NMR experiments. Modeling experimental pulse sequences numerically is an attractive alternative to time-consuming calculations for the analytical expressions of the Hamiltonian interactions; perhaps so attractive that a complete analysis of the behavior of two nuclei under dipolar and scalar coupling with a chemical shift addition has not yet been analyzed extensively in the literature. Equations for all these interactions are readily

available [41, 60, 61, 65-68] , but a full analysis was left for calculations in the context of developing specific experiments.

Solving the analytical expressions for CS , scalar, and dipolar CT relies on two calculational steps for oriented samples, with an additional third for unoriented (powder) samples:

Step 1. Calculate analytical expressions for the total interaction Hamiltonian, for the chemical shift with the scalar and dipolar coupling.

Step 2. Rotationally transform each interaction tensor from its individual frame of reference into a common (laboratory) observation frame. Calculate the frequencies of these interactions in this new common frame for their particular values and angular dependencies, then evaluate these frequencies in the coherence transfer functions.

Step 3. (Unoriented samples) Sum the coherence transfer functions over a number of crystallite orientations in their arguments to simulate a “powder pattern.”

We find that the steps outlined above can yield complex results. For instance, the rotational transformation in step 2 can yield some impressively complicated (some might say Byzantine) trigonometric expressions. In the interests of space, a simplified example calculation using the chemical shift principal values in the PAS to laboratory transformation is shown in Figure 5-1 for spin I. The angles (α, β, γ) reflect the rotational variables for a the final Wigner rotation from the rotor to the laboratory frame (the other variables are listed in the caption). Note that Fig. 5-1 is just a deliberate example to show the typical complexity when facing a problem such as this; the real transform, with all numerical variables, results in simple frequency components. It is easy to see why numerical simulations would be widely employed over the analytical....even this simplified equation took a computer several minutes of processing time.

$$\begin{aligned}
& \left\{ \frac{1}{2} (-1 + 3 \text{Cos}[\theta]) \right. \\
& \quad \left. ((33.379 + 0. \text{i}) (-1 + 3 \text{Cos}[\beta]) - (83.7893 + 0. \text{i}) \text{Cos}[\beta] \text{Sin}[\beta] + (4.32567 + 0. \text{i}) \text{Sin}[\beta]^2) - \right. \\
& \quad \sqrt{\frac{3}{2}} e^{-\text{i}\varphi} \text{Cos}[\theta] ((17.1034 - 8.80442 \text{i}) e^{-\text{i}\gamma} (1 + \text{Cos}[\beta]) (-1 + 2 \text{Cos}[\beta]) - \\
& \quad (17.1034 + 8.80442 \text{i}) e^{-\text{i}\gamma} (1 - \text{Cos}[\beta]) (1 + 2 \text{Cos}[\beta]) - \\
& \quad (1.76595 + 2.10476 \text{i}) e^{-\text{i}\gamma} (-1 + \text{Cos}[\beta]) \text{Sin}[\beta] + (81.7615 + 0. \text{i}) e^{-\text{i}\gamma} \text{Cos}[\beta] \text{Sin}[\beta] - \\
& \quad (1.76595 - 2.10476 \text{i}) e^{-\text{i}\gamma} (1 + \text{Cos}[\beta]) \text{Sin}[\beta]) \text{Sin}[\theta] + \\
& \quad \sqrt{\frac{3}{2}} e^{\text{i}\varphi} \text{Cos}[\theta] ((-17.1034 - 8.80442 \text{i}) e^{\text{i}\gamma} (1 + \text{Cos}[\beta]) (-1 + 2 \text{Cos}[\beta]) + \\
& \quad (17.1034 - 8.80442 \text{i}) e^{\text{i}\gamma} (1 - \text{Cos}[\beta]) (1 + 2 \text{Cos}[\beta]) + \\
& \quad (1.76595 - 2.10476 \text{i}) e^{\text{i}\gamma} (-1 + \text{Cos}[\beta]) \text{Sin}[\beta] - (81.7615 + 0. \text{i}) e^{\text{i}\gamma} \text{Cos}[\beta] \text{Sin}[\beta] + \\
& \quad (1.76595 + 2.10476 \text{i}) e^{\text{i}\gamma} (1 + \text{Cos}[\beta]) \text{Sin}[\beta]) \text{Sin}[\theta] + \frac{1}{2} \sqrt{\frac{3}{2}} e^{-2\text{i}\varphi} \\
& \quad \left((3.53189 + 4.20952 \text{i}) e^{-2\text{i}\gamma} \text{Sin}\left[\frac{\beta}{2}\right]^4 + (3.53189 - 4.20952 \text{i}) e^{-2\text{i}\gamma} \text{Cos}\left[\frac{\beta}{2}\right]^4 \text{Sin}\left[\frac{\beta}{2}\right]^4 + \right. \\
& \quad (17.1034 + 8.80442 \text{i}) e^{-2\text{i}\gamma} (-1 + \text{Cos}[\beta]) \text{Sin}[\beta] + \\
& \quad \left. (17.1034 - 8.80442 \text{i}) e^{-2\text{i}\gamma} (1 + \text{Cos}[\beta]) \text{Sin}[\beta] + (40.8807 + 0. \text{i}) e^{-2\text{i}\gamma} \text{Sin}[\beta]^2 \right) \text{Sin}[\theta]^2 + \\
& \quad \frac{1}{2} \sqrt{\frac{3}{2}} e^{2\text{i}\varphi} \left((3.53189 - 4.20952 \text{i}) e^{2\text{i}\gamma} \text{Sin}\left[\frac{\beta}{2}\right]^4 + (3.53189 + 4.20952 \text{i}) e^{2\text{i}\gamma} \right. \\
& \quad \left. \text{Cos}\left[\frac{\beta}{2}\right]^4 \text{Sin}\left[\frac{\beta}{2}\right]^4 + (17.1034 - 8.80442 \text{i}) e^{2\text{i}\gamma} (-1 + \text{Cos}[\beta]) \text{Sin}[\beta] + \right. \\
& \quad \left. (17.1034 + 8.80442 \text{i}) e^{2\text{i}\gamma} (1 + \text{Cos}[\beta]) \text{Sin}[\beta] + (40.8807 + 0. \text{i}) e^{2\text{i}\gamma} \text{Sin}[\beta]^2 \right) \text{Sin}[\theta]^2 \Big\}
\end{aligned}$$

Figure 5-1: Example results for the chemical shift frequency A_0^{LAB} for spin I in the laboratory frame after transformation from the principal axis system. The angles relating the CS PAS to the molecular frame were assigned the values $\alpha_1 = 5^\circ$, $\beta_1 = 20^\circ$, $\gamma_1 = 25^\circ$ with the values of the chemical shift for spin I being $\sigma_{11}^I = 46.8 \text{ ppm}$, $\sigma_{22}^I = 3.8 \text{ ppm}$, and $\sigma_{33}^I = 73.2 \text{ ppm}$, with $\sigma_1 = 1/3 (\sigma_{11}^I + \sigma_{22}^I + \sigma_{33}^I)$.

The full analytical equation for the equation simplified in Fig. 5-1, with all variables expressed symbolically, would take up three 8" x 11" sheets of paper. This minute analysis is not exactly interesting and is time consuming; it yields the right answers but no new information in itself. However, studying the results of transformations like those in Figure 5-1 can have limited use. For instance, one can analyze the frequency dependence on one or more angles. This analysis is necessary for in-depth study of the coherence transfer with the full coupling Hamiltonian, and will be important for the

further development of experimental pulse sequences. It will also helpfully act as a solid roadmap for further work in this direction. In fact, Glaser and Luy have recently published the coherence transfer functions for three dipolar coupled spins [39] as well as the superposition of the scalar couplings on the dipolar coherence transfer [125]. These important papers, coupled with further study of the effects of chemical shift, will help in the development of experiments to manipulate the Hamiltonians for three or more spins.

Theory for an Oriented Strongly Coupled System

In this chapter, we set out to express the full analytical result for the free evolution under the full interaction Hamiltonian for a two-spin 1/2 homonuclear system in uniaxially oriented (or single crystal) samples. We assume that the dipolar coupling as well as the scalar coupling between the two nuclei is nonzero. Further, relaxation effects are ignored in the present theoretical study, as we are interested in the dephasing of the coherence among particular elements of the density matrix describing the system.

The total internal free-evolution Hamiltonian for a two-spin 1/2 homonuclear system in the presence of a static external magnetic field consists of chemical shift, scalar coupling, and dipolar coupling terms:

$$H_T = H_D + H_{CS} + H_J \quad (5-1)$$

This Hamiltonian is equivalent to the creation of a zero-field or rotating-frame Hamiltonian in a solid-state NMR experiment with a non-zero anisotropic chemical shift offset between two ^{13}C nuclei.

In this work, coherence transfer modes are analyzed under the total coupling Hamiltonian, H_T . H_{CS} can be selectively refocused with π pulses during SSNMR experiments, but many experiments [7, 20, 57, 91, 93, 96, 114, 127-129] study both chemical shift and dipolar coupling simultaneously. Chemical shifts can rival H_J and experimentally recovered H_D to maintain a significant contribution to the coherence

transfer in solids. Additionally, the relative orientation of the chemical shift anisotropies to the dipolar frame can make a difference in the behavior of the system. The superposition of the scalar and dipolar coupling on the chemical shift frequencies are therefore included in our calculation of the total Hamiltonian.

To begin, the total Hamiltonian, H , for any single interaction can be expressed in terms of spherical tensors:

$$H = \sum_{k=0}^2 \sum_{q=-k}^{+k} (-1)^q A_{kq}(t) T_{k-q}(t') \quad (5-2)$$

with the spin parameters represented by T_{k-q} and the spatially-dependent parameters in the spatial tensor A_{kq} . We are specifically interested in the behavior of the system under free evolution (no RF); i.e. with the average Hamiltonian, and in the laboratory frame of reference.

The antisymmetric part of the spin interaction A_{10} will be neglected because it does not contribute to the spectrum in first order. In this case, Eq. 5-2 reduces to the two-term secular expression of the Hamiltonian in spherical coordinates for the chemical shift in its principal axis system:

$$H_{CS} = A_{00}T_{00} + A_{20}(t)T_{20} \quad (5-3a)$$

which can be cast in the more usual Cartesian basis in the CS principal axis system as:

$$H_{CS} = \mathbf{s}_i \mathbf{w}_0 \mathbf{I}_z + \frac{1}{2}(3\cos^2 \mathbf{q} - 1)(\mathbf{s}_{33} - \mathbf{s}_i) \mathbf{w}_0 \mathbf{I}_z \quad (5-3b)$$

The unitary transformation of a spherical tensor is a rotation, and such a rotation can be achieved by the use of the Wigner rotation formalism. For brevity, we shall just show the familiar transformation equation from A''_{2p} to A'_{20} without addressing the details, which are present in references such as Mehring [60]:

$$A'_{20} = \sum_{q,p=-2}^{+2} A''_{2p} e^{-ipa} d_{pq}^{(2)}(\mathbf{b}) e^{-iqg} e^{-iqj} d_{q0}^{(2)}(\mathbf{q}) \quad (5-4)$$

A total transformation from the dipolar PAS to the experimental frame can be obtained with this equation. Since we wish to include the dipolar coupling with the chemical shift, this equation alone is not sufficient to put both of these interactions in the same frame. First, the chemical shift principal axis frame must be rotated into the molecular (dipolar) frame, and only then can both interactions be simultaneously rotated into the laboratory frame so that the correct calculations can be made.

The secular part of the dipolar coupling Hamiltonian can be expressed in the form of Eq. 5-5:

$$H_D = \sum_{q=-2}^{+2} (-1)^q D_{2q} T_{2-q} \quad (5-5)$$

where the second-rank tensors D_{2q}^2 and T_{2q}^2 define the spatial and spin parts of the dipolar coupling Hamiltonian (see for example [60]). The secular dipolar coupling Hamiltonian can be written as

$$H_D = \frac{\hbar \gamma_I \gamma_S}{4 \pi r_{IS}^3} [1 - 3 \cos^2 \theta] (3I_z S_z - I \cdot S) \quad (5-6)$$

where θ is the angle between the magnetic field and the vector connecting the two spins, r_{IS} is the distance between I and S nuclei, and γ_i is the gyromagnetic ratio of nucleus i .

Since the structure of the direct and indirect coupling Hamiltonians for a homonuclear spin system is similar, the total *coupling* Hamiltonian is given as

$$H_{JD} = (2D_{IS} + J)I_z S_z - (D_{IS} + J)\{I_x S_x + I_y S_y\} \quad (5-7)$$

where J is the scalar-coupling constant and D_{IS} is the dipolar coupling frequency is once again defined as

$$D_{IS} = \frac{\hbar \gamma_I \gamma_S}{4 \pi r_{IS}^3} [1 - 3 \cos^2 \theta] \quad (5-8)$$

In order to evaluate the coherence transfer modes due to the evolution under the coupling Hamiltonian, we assume a uniaxially oriented system with $\theta = 0^\circ$. Any change in the value of θ will only change the magnitude of the D_S constant. Equation 5-8 is therefore the spatial form of the dipolar Hamiltonian in the molecular frame.

The Full Free-Precession Hamiltonian for a strongly coupled oriented sample

The full free-precession Hamiltonian for a strongly coupled, oriented homonuclear two-spin system in the solid state is a combination of H_{CS} (Eq. 5-3b) and H_{JD} (Eq. 5-7) in the principal axis system of the dipolar interaction:

$$\hat{H} = -\Omega_I I_z - \Omega_S S_z + 3DI_z S_z + (2pJ - D)\mathbf{I} \cdot \mathbf{S} \quad (5-9)$$

which can be rewritten for the laboratory reference frame as:

$$\hat{H}_t = -\Sigma_0^{LAB} (I_z + S_z) - \frac{1}{2}\Delta_0^{LAB} (I_z - S_z) + (2D_0^{LAB} + 2pJ)I_z S_z + (2pJ - D_0^{LAB})(I_x S_x + I_y S_y) \quad (5-10)$$

where D_0^{LAB} is the dipolar constant expressed in laboratory frame in Hz, and J is the scalar coupling constant in Hz.

The term Σ_0^{LAB} is the average frequency of the chemical shifts in the laboratory frame:

$$\Sigma_0^{LAB} = \frac{1}{2}(\mathbf{w}_0^{I,L} + \mathbf{w}_0^{I,S}) \quad (5-11)$$

and Δ_0^{LAB} is the frequency difference in the laboratory frame:

$$\Delta_0^{LAB} = (\mathbf{w}_0^{I,L} - \mathbf{w}_0^{S,L}) \quad (5-12)$$

However, since the chemical shift tensor and the dipolar tensor are not assumed to be colinear, and the chemical shift tensor is not assumed to be axially symmetric, both these frequencies originate in non-congruent principal axis systems. We must therefore express the CS frequencies Ω_I and Ω_S in terms of the dipolar principal axis system. This requires

that the chemical shift interaction will be colinear with the dipolar interaction and the combined frequencies can be transformed identically into the laboratory frame. In Chapter 2, we have derived the transformation from the dipolar principal axis system to the laboratory frame. The expression of transformation from the chemical shift principal axis system to the dipolar principal axis system uses Wigner rotation matrices, \mathfrak{R} . An additional transformation from those presented in Chapter 2, that of a rotation from the chemical shift principal axis system into the dipolar principal axis system, is also necessary.

A time dependence in the spatial component of the total Hamiltonian will appear during MAS as a function of the rotor frequency ω_r . We assume a time independent Hamiltonian free of the specific MAS time dependence. We use the secular approximation when choosing terms from Eq. 5-2 for the total Hamiltonian, that is, we discard terms of the Hamiltonian with $q \neq 0$. This is possible because of stroboscopic sampling. In MAS, the “first averaging” is taken by sampling at integer multiples of the Larmor frequency, $n2\pi/\omega_0$, which neglects nonsecular terms. This is valid when $\omega_r \uparrow \omega_0$. For ^{13}C in a 600MHz magnet, $\nu^{\text{C}}_0 = 150.96\text{MHz}$, therefore at a MAS spinning speed of 8kHz, $\nu_r/\nu_0 = 5.3 \times 10^{-5}$, which leaves the secular approximation valid under MAS with proper stroboscopic sampling.

The principal axis system of the chemical shift tensor is the frame in which the symmetric part of its A_{2q} is diagonal. For the interaction between two homonuclear spins, the expression for the chemical shift tensor in the principal axis system (PAS) follows Eq. 5-4 with A_{kq} components for the chemical shift:

$$A''_{00} = \sqrt{\frac{1}{3}} \text{Tr}\{\mathbf{g} \tilde{\mathbf{s}}\} \quad (5-13a)$$

$$A_{20}'' = \sqrt{\frac{3}{2}} \mathbf{g}(\mathbf{s}_{33} - \mathbf{s}_i) \quad (5-13b)$$

$$A_{2\pm 2}'' = \frac{1}{2} \mathbf{g}(\mathbf{s}_{11} - \mathbf{s}_{22}) \quad (5-13c)$$

with the isotropic chemical shift is defined as $\sigma_i = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ and γ is the gyromagnetic ratio. The double hash notation in A_{kq}'' indicates that this is the form of the spatial term in the chemical shift PAS. All other A_{kq} are non-diagonal and therefore zero in the PAS.

The observed (laboratory frame) spectral frequency of the chemical shift interaction is, to first order, determined by the spherical tensor component A_{20}' , which results from the transformation of the principal axis system, through the goniometer frame, to the laboratory frame whose z-axis is defined by $\mathbf{B}_0 = B_{zz}$.

The unitary transformation (rotation) of a spherical tensor is expressed as [60]:

$$A_{kq}' = R(\mathbf{abg}) A_{kq} R^{-1}(\mathbf{abg}) \equiv \sum_{p=-k}^{+k} A_{kp}'' \mathfrak{R}_{pq}^{(k)}(\mathbf{abg}) \quad (5-14)$$

where A_{kq}' is the spherical tensor expressed in a new frame (x, y', z') obtained by this transformation operator $\hat{A}(\alpha\beta\gamma)$ from the original frame (x,y,z) in which A_{kp} is defined. With Equation 5-14 we wish to rotate the chemical shift principal axis system to the molecular (dipolar PAS) frame. Therefore, we must perform three successive rotations, (that is, three applications of Eq. 5-14) from the chemical shift PAS to the laboratory frame for both spins I and S independently.

The usual order of operation for the transformation of the *molecular (dipolar PAS) frame* to the *laboratory (interaction) frame* is:

$$\text{Dipolar PAS} \xrightarrow{\mathfrak{R}(\Omega_{MG})} \text{Goniometer Frame} \xrightarrow{\mathfrak{R}(\Omega_{GL})} \text{Laboratory (interaction) frame}$$

while for the case of the chemical shift, the order of operations for transformation into the laboratory frame must contain one additional rotation:

$$\text{CS PAS} \xrightarrow{\mathfrak{R}(\Omega_{\text{PM}})} \text{Dipolar PAS} \xrightarrow{\mathfrak{R}(\Omega_{\text{MG}})} \text{Goniometer Frame} \xrightarrow{\mathfrak{R}(\Omega_{\text{GL}})} \text{Laboratory (interaction) frame.}$$

where $\Omega_{\text{PM}} = (\alpha_X \beta_X \gamma_X)$ are the rotation angles from the PAS of spin X (I or S) to the molecular frame, $\Omega_{\text{MG}} = (0, \beta, \gamma)$ are the angles from the molecular frame to the goniometer frame, and $\Omega_{\text{GL}} = (\varphi, \theta, 0) = (\omega_r t, \theta, 0)$ are the angles from the goniometer frame to the laboratory frame, which also is the same as the angles from the rotor frame (in MAS) to the laboratory frame.

Utilizing the equation 5-14, the three successive rotations can be combined into one expression for the total rotation from the principal axis system to the laboratory frame:

$$A_0^{X,L} = \sum_{m=-2}^2 \sum_{q=-2}^2 [A_0^{CS,P} \mathfrak{R}_{0q}^2(\Omega_{PM}^{CS}) + A_2^{CS,P} \{ \mathfrak{R}_{2q}^2(\Omega_{PM}^{CS}) + \mathfrak{R}_{-2q}^2(\Omega_{pm}^{CS}) \}] \mathfrak{R}_{qm}^2(\Omega_{MG}) \mathfrak{R}_{m0}^2(\Omega_{GL}) \quad (5-15)$$

in which we have already expanded the frequency term (A_n) in the principal axis system of the chemical shift (CS, P) inside the square brackets.

Each interaction can be rotated from its own principal axis system to the laboratory frame. Drawing on an earlier example, the transformation of the dipolar coupling spatial coefficient in Eq. 5-8 to the laboratory frame using the rotation in Eq. 5-15 results in Eq. 5-16, the expression for the dipolar coefficient in the laboratory frame (also seen in Chapter 2):

$$\begin{aligned} D^{LAB} = & d_{IS} \left(\frac{3}{4} \sin^2 \mathbf{q}_m \sin^2 \mathbf{q} \cos(2\mathbf{w}_r t + 2\mathbf{j}) \right. \\ & \left. - \frac{3}{4} \sin 2\mathbf{q}_m \sin 2\mathbf{q} \cos(\mathbf{w}_r t + \mathbf{j}) \right) \quad (5-16) \\ & + \frac{1}{4} (3 \cos^2 \mathbf{q}_m - 1)(3 \cos^2 \mathbf{q} - 1) \end{aligned}$$

After transformation of the chemical shift tensor frame to the dipolar (molecular) frame and then to the laboratory frame, the resulting frequency of spin (I or S) in the laboratory frame is expressed as $\omega_0^{X,L}$, as a sum of terms involving the Euler angles α_{PM}^X , β_{PM}^X , γ_{PM}^X for spin X (I or S) which transform the CS PAS to the molecular frame; the angles β and γ , which relate the Euler angle rotations from the molecular frame (dipolar PAS) to the goniometer frame, and the angles θ and ϕ which relate the rotation from the rotor frame/goniometer frame to the laboratory frame.

Transformation of the Spin Part of H_T

Because the sum of the non-secular terms $(I_x S_x + I_y S_y)$ does not commute with the difference operator $(I_z - S_z)$, we may not decompose H_t into independent rotations for each of the operator terms as could be done for H_D in Chapters 3 and 4. We must first find a frame in which the Hamiltonian for these two interactions is diagonal so that we might apply consecutive rotations. We can then transform the operators into that reference frame. It so happens that when two operators share the same (diagonal) Hamiltonian, they commute. We will therefore use the properties of commutation to bring us into the common frame necessary for calculation.

In order to transform the Hamiltonian into a tilted reference frame in which the Hamiltonian is diagonal for both the terms $(I_z - S_z)$ and $(I_x S_x + I_y S_y)$, one must choose an appropriate axis perpendicular to the two non-commuting operators by which to rotate. To cause a rotation in a plane (\hat{A}, G) , where \hat{A} and G are two cyclically commuting product operators, an axis C is needed, $C = i[\hat{A}, G]$, where C is another product operator. The problem is solved by transforming H_t into a tilted reference frame, a plane created between the two axes of $(I_z - S_z)$ and $(I_x S_x + I_y S_y)$, where the Hamiltonian is diagonal. This orthogonal operator, $(I_x S_y - I_y S_x)$, cyclically commutes with $(I_z - S_z)$ and $(I_x S_x + I_y S_y)$ and will rotate the Hamiltonian to a tilted reference frame.

Since the two terms in $(I_x S_y - I_y S_x)$ already commute, the rotation operator for conversion to the tilted frame is easily defined as a sequential operation (5-17a) and the rotation back to the laboratory frame is merely the reverse operation (5-17b):

$$\mathfrak{R}_T = \exp(i\theta I_x S_y) \exp(-i\theta I_y S_x). \quad (5-17a)$$

$$\mathfrak{R}_T^\dagger = \exp(i\theta I_y S_x) \exp(-i\theta I_x S_y). \quad (5-17b)$$

The rotation from the lab frame of reference to the tilted frame can be accomplished with the rotation $T = \mathfrak{R}_T L \mathfrak{R}_T^\dagger$ and back again into the laboratory frame with the rotation $L = \mathfrak{R}_T^\dagger T \mathfrak{R}_T$.

Now that we have the mechanism to transfer the laboratory-frame operators into a tilted frame, we must also transform our Hamiltonian into the tilted frame as well. Using the rotation operator \mathfrak{R}_T , H_T is rotated into the common frame, resulting in H_T' :

$$H_T' = -\Omega_I' I_z - \Omega_S' + A I_z S_z \quad (5-18)$$

with transformed frequencies:

$$\Omega_I' = \Sigma + \frac{1}{2}R \quad (5-19a)$$

$$\Omega_S' = \Sigma - \frac{1}{2}R \quad (5-19b)$$

$$A = J + 2D \quad (5-19c)$$

$$\Sigma = 1/2(\omega_I^{\text{LAB}} + \omega_S^{\text{LAB}}) \quad (5-19d)$$

$$\Delta = \omega_I^{\text{LAB}} - \omega_S^{\text{LAB}} \quad (5-19e)$$

$$B = (J - D). \quad (5-19f)$$

The rotation frame relations

$$\sin ? = \frac{B}{R} \quad (5-20a)$$

$$\cos ? = \frac{?}{R} \quad (5-20b)$$

$$R = \sqrt{\Delta^2 + B^2} \quad (5-20c)$$

describe the relation of the frequencies within the original laboratory frame to that of the new tilted frame. The combined coupling constant $B = (J - D)$, and the chemical shift

difference Δ are the frequencies modulating the original frame's operators; and the magnitude of the rotated reference frame operator is defined as R in Eq. 5-20c.

In summary, the order of operation on transforming the spin part of the dipolar Hamiltonian is:

1. Rotate all operators in the laboratory frame to the new, rotated frame with Eq. 5-17a.
2. Operate on operators thus transformed with the Hamiltonian of Eq. 5-18.
3. Return the resultant operators back to the laboratory frame with Eq. 5-17b.

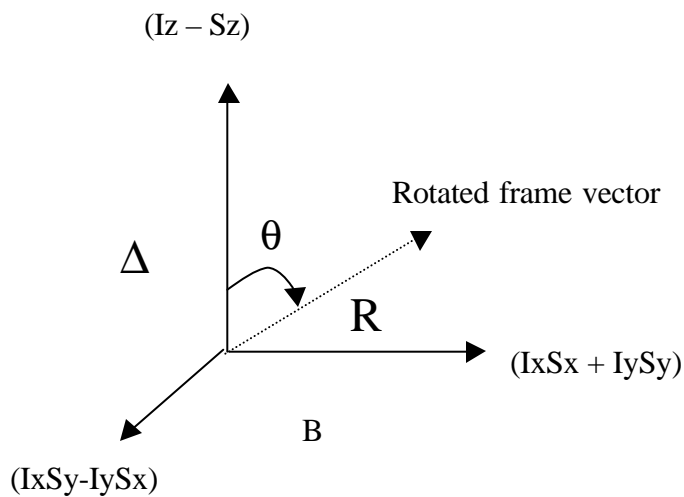


Figure 5-2. The coordinate system for the rotation to the "tilted frame" that uses the operator $(I_x S_y - I_y S_x)$, which commutes with both $\Delta(I_z - S_z)$ and $B(I_x S_x + I_y S_y)$. The transformation is achieved by a rotation angle θ around $(I_x S_y - I_y S_x)$. See Eq. 5-20 and following for definitions of the constants.

Methods

Using the methods outlined in the introduction, the resulting operators and their modulating frequencies can be used to calculate the behavior of a strongly coupled unoriented system. However, in the strongly coupled oriented system, D_{IS} is dependent only on r_{IS} assuming θ is equal over all crystallites. In an unoriented system, D_{IS} gains an angular dependence through the distribution of θ_{IS} . Therefore, the characteristic DCT spectrum of an unoriented system is comprised of the superposition of many frequencies resulting from the summation over the spatial distribution of D_{IS} . We expect the time- and frequency-domain components of a sample to reflect the random characteristic of the spatial anisotropy and produce a spectrum indicative of an unoriented sample; a Pake doublet (powder pattern) in the case of the frequency-domain, and therefore some kind of weighted approximate Fourier sum in the case of the time-domain signal (see Fig. 4-2).

Solutions for the unoriented sample $F_D(t)$ are calculated numerically over all space in the analytical functions $F'(\theta, t)$. For each initial state $\sigma(0)$, resulting coherences evolve, each modulated by frequencies particular to the Hamiltonian. Numerical simulations of the coherence transfer functions were performed using 250,000 crystallite orientations with assorted FORTRAN programs performing a Riemann sum over the analytical coherence transfer functions $F'(\theta, t)$, with the angular dependent functions inside the coherence transfer functions generated by the Wigner transformation in the program IS.F (see Appendix A). When providing the same results, a smaller number of crystallites (90,000) are used to speed up computational time.

Results and Discussion

Figure 5-1 gave a glimpse into the complexity of the analytical expressions of the rotation operations. Even with several parameters expressed numerically, the spatial Hamiltonian transformation produces a non-trivial collection of terms, much simplified in

Figure 5-1. Such a large collection of terms cannot be easily transferred to a computer program, let alone efficiently powder averaged over the values of the Euler angles α, β, γ . A solution is to instead allow the computer program to calculate the frame transformations from an initial set of PAS values and simultaneously calculate the powder averaging incrementally over the Euler angles. The program in Appendix A, IS.F, calculates the PAS \rightarrow LAB frame transformation for each orientation of the Euler angles and then sums the frequencies over all space to gain the powder-averaged spectrum of the full Hamiltonian. The program IS.F uses Wigner matrices to transform the principal values of the chemical shift and dipolar interactions to a common laboratory frame. To simulate unoriented sample (powder) patterns, a Riemann sum is executed over the final Wigner transformation to give the averaging of all crystallites over all space.

Effects of chemical shift coherence transfer in unoriented samples: calculations from the tilted frame.

Using the transformations and rotations in Eqs.5-16 to 5-19, the coefficients after evolution with the frame-transformed Hamiltonian for the case of $\sigma(0)=I_x$ are given in Eq. 5-21 and $\sigma(0)=I_z$ in Eq. 5-22.

In the coefficients of the I_x operator resulting from evolution of $\sigma(0)=I_x$ under the pure dipolar Hamiltonian (see Table 4-1), we have previously seen that the frequency distribution for an oriented sample with only the coupling Hamiltonian results in a "beat" phenomenon where two frequencies, $3/2 D$ and $1/2 D$, create a unique coherence transfer pattern evidenced in Figure 4-1(a) for Equation A in the case of transverse self-magnetization. However, by including the chemical shift and using the tilted frame transformation, the resultant coefficient equations for I_x and S_x coherences, are

$$\mathbf{s}_x(t) = \begin{pmatrix} I_z S_y \frac{B}{R} \cos\left[\frac{At}{2}\right] \cos[tS] \sin\left[\frac{Bt}{2}\right] + \frac{B}{R} S_x \cos[t\Sigma] \sin\left[\frac{At}{2}\right] \sin\left[\frac{Bt}{2}\right] \\ + \frac{B}{R} I_z S_x \cos\left[\frac{At}{2}\right] \sin[tS] \sin\left[\frac{Bt}{2}\right] - \frac{B}{R} S_y \sin\left[\frac{At}{2}\right] \sin[tS] \sin\left[\frac{Bt}{2}\right] \\ + I_y \left(\frac{?}{R} \cos\left[\frac{At}{2}\right] \cos[tS] \sin\left[\frac{Bt}{2}\right] - \cos\left[\frac{At}{2}\right] \sin[tS] \cos\left[\frac{Bt}{2}\right] \right) \\ + I_x S_z \left(\frac{?}{R} \sin\left[\frac{At}{2}\right] \cos[tS] \sin\left[\frac{Bt}{2}\right] - \sin\left[\frac{At}{2}\right] \sin[tS] \cos\left[\frac{Bt}{2}\right] \right) \\ + I_x \left(\cos\left[\frac{At}{2}\right] \cos[tS] \cos\left[\frac{Bt}{2}\right] + \frac{?}{R} \cos\left[\frac{At}{2}\right] \sin[tS] \sin\left[\frac{Bt}{2}\right] \right) \\ - I_y S_z \left(\sin\left[\frac{At}{2}\right] \cos[tS] \cos\left[\frac{Bt}{2}\right] + \frac{?}{R} \sin\left[\frac{At}{2}\right] \sin[tS] \sin\left[\frac{Bt}{2}\right] \right) \end{pmatrix} \quad (5-21)$$

$$\mathbf{s}(t) = \frac{(-B\Delta + B\Delta \cos[Bt])}{2R} (I_x S_x + I_y S_y) - \left(\frac{B \sin[Bt]}{2R} \right) (I_y S_x - I_x S_y) \\ + \frac{R^2 + \Delta^2 + B^2 \cos[Bt]}{2R^2} I_z + \frac{R^2 - \Delta^2 - B^2 \cos[Bt]}{2R^2} S_z \quad (5-22)$$

$$I_x \xrightarrow{H_T} I_x \left(\cos\left[\frac{Bt}{2}\right] \cos[\Sigma t] \cos\left[\frac{At}{2}\right] + \frac{\Delta}{R} \sin\left[\frac{Bt}{2}\right] \sin[\Sigma t] \cos\left[\frac{At}{2}\right] \right) + o.t. \quad (5-23a)$$

$$I_x \xrightarrow{H_T} S_x \sin\left[\frac{At}{2}\right] \sin\left[\frac{Bt}{2}\right] \cos[\Sigma t] + o.t. \quad (5-23b)$$

Equation 5-23a and 5-23b reduce correctly for the dipolar Hamiltonian alone, $H_T = H_D$, when $J = \Sigma = \Delta = 0$, and in that case the remaining coefficient for I_x is $\cos(0.5At)\cos(0.5Bt)$, while that for S_x is $\sin(0.5At)\sin(0.5Bt)$. These reductions are exactly what is calculated for evolution under H_D (Table 4.1) for functions A and B in Table 4-1.

Likewise, if one sets $J = D = 0$, so that $H_T = H_{CS}$, the coefficient of I_x reduces to $\cos(\Sigma t)$ and that of S_x to $\cos(\Sigma t)$ as expected, as both are transverse operators evolving under a chemical shift term.

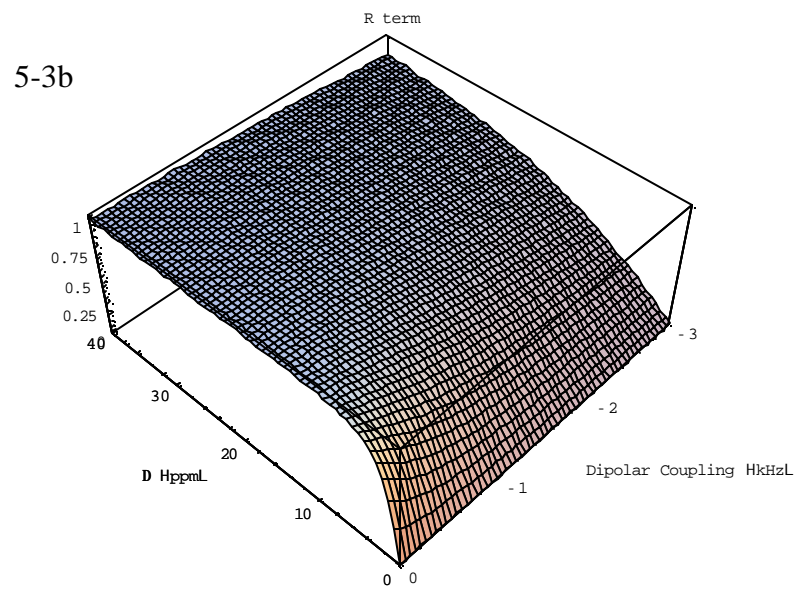
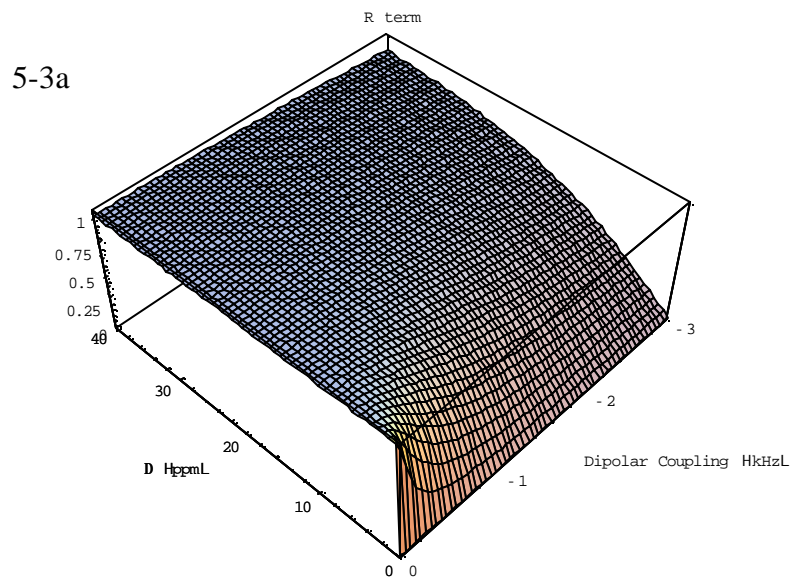


Figure 5-3. A graph of the value of $\frac{\Delta}{R}$ where $R = \sqrt{\Delta^2 + B^2}$, as a function of dipolar coupling and Δ , where $(B = 2\pi J - D)$. (a) $J = 0$ Hz. Note the fast shoulder at $D = \Delta = 0$. (b) $J = 53$ Hz. Since J is of opposite sign to D , term $\frac{\Delta}{R}$ reaches the value of “1” for larger values of Δ .

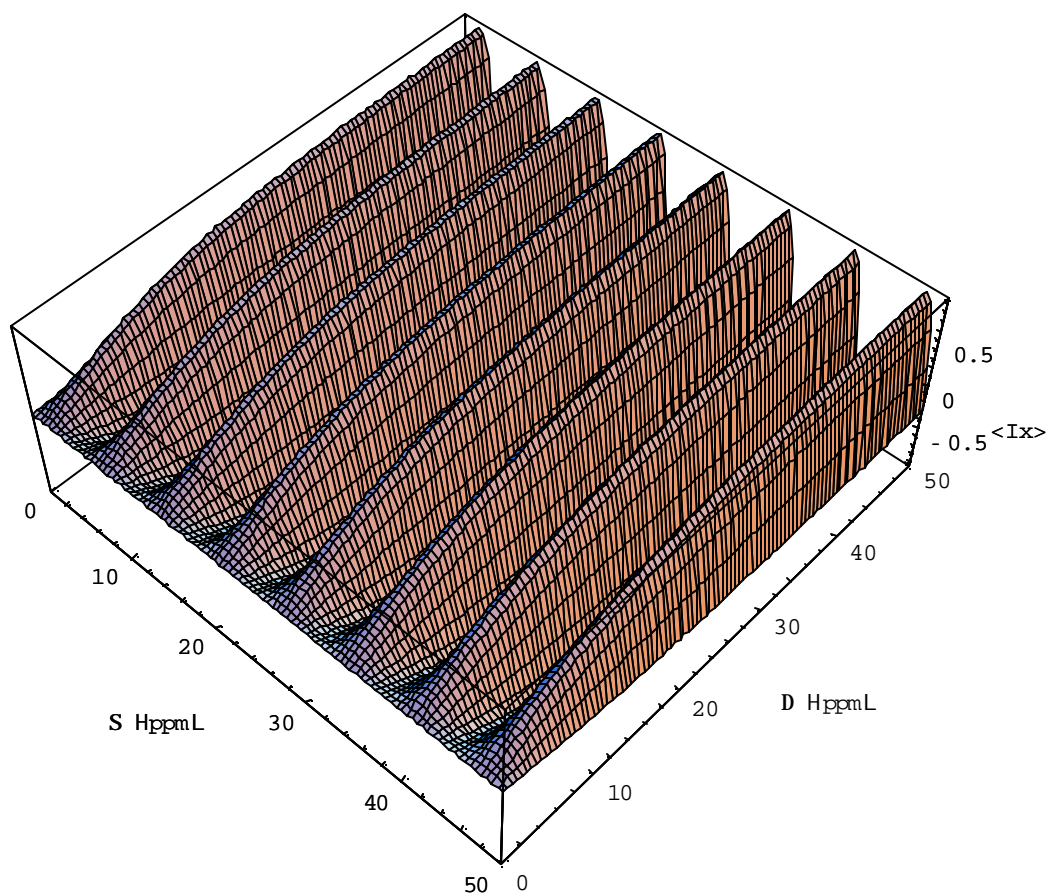


Figure 5-4: Graph of the “odd term” in I_x for an oriented sample, Eq. , as a function of the chemical shift average frequency in the lab frame (Σ) and chemical shift difference in the lab frame (Δ) where $t = 1\text{ms}$, and the internuclear distance $r = 1.53\text{\AA}$. The scalar coupling $J = 0$

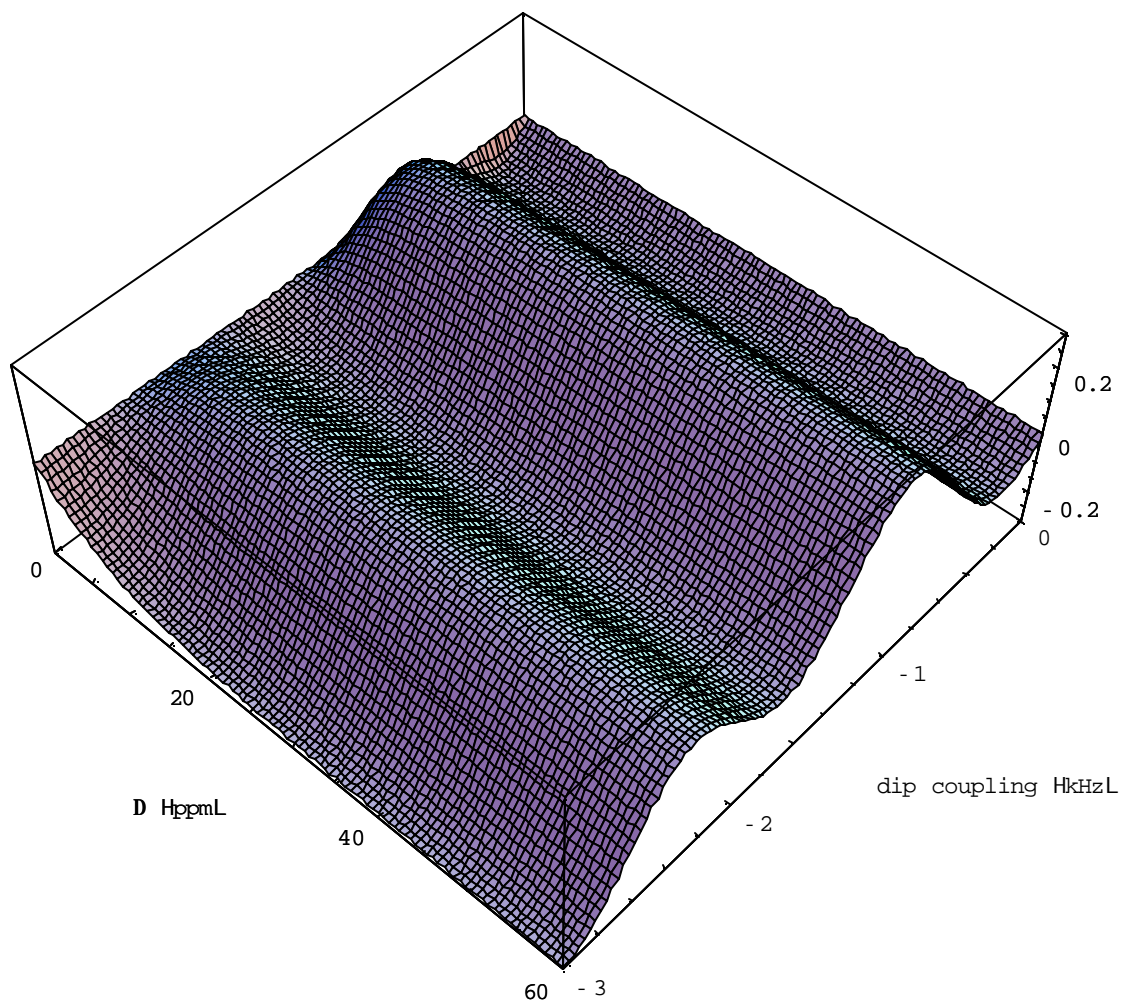


Figure 5-5: Graph of the “odd term” in I_x for an oriented sample, as a function of the dipolar coupling frequency in the lab frame in kHz, and the chemical shift difference in the lab frame (Δ) where $t=3\text{ms}$, and the CS average frequency in the lab frame is $\Sigma=50\text{ ppm}$. The scalar coupling $J=0$

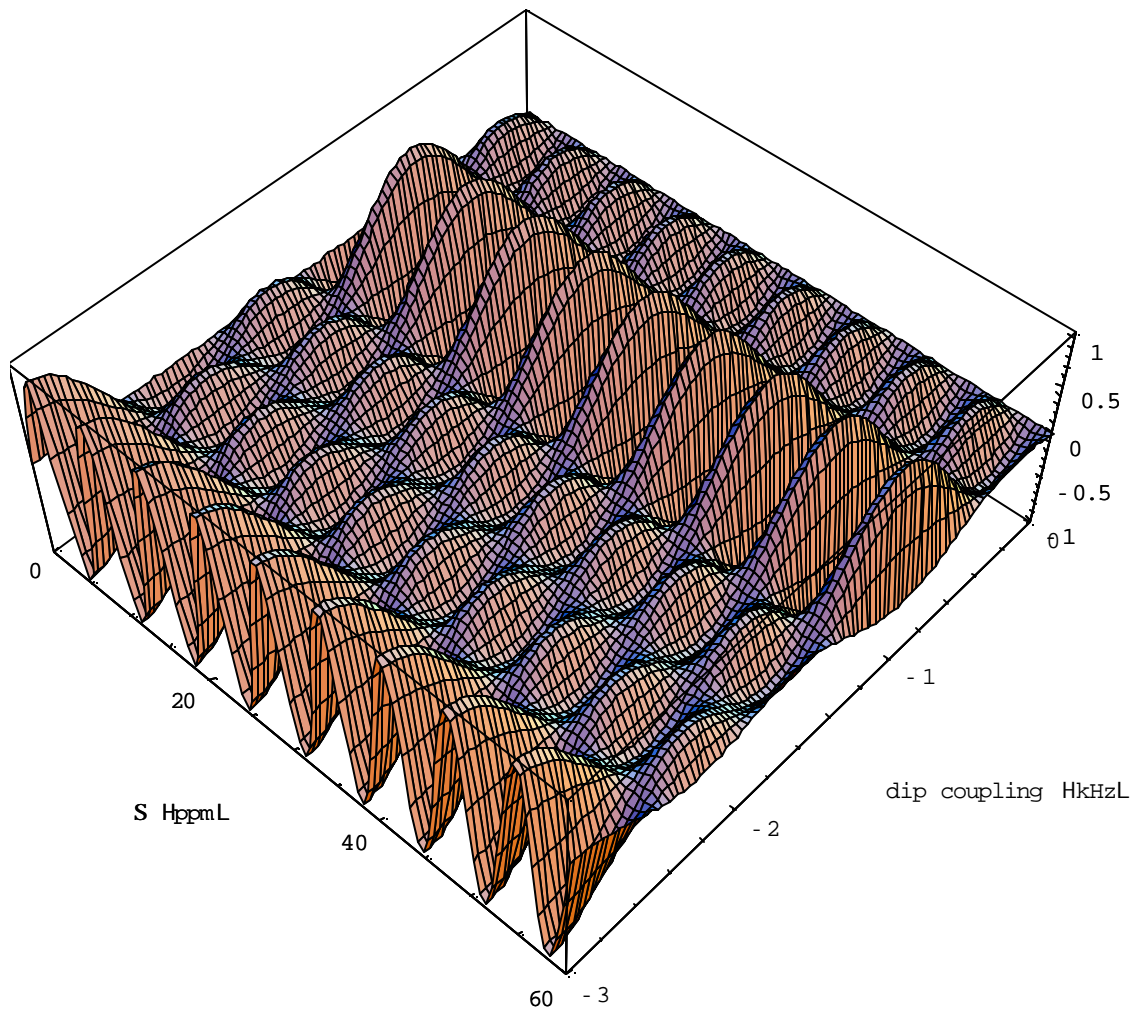


Figure 5-6: Graph of the “odd term” in I_x for an oriented sample, as a function of the dipolar coupling frequency in the lab frame in kHz, and the chemical shift average in the lab frame (Σ) where $t=3\text{ms}$, and the CS difference frequency in the lab frame is $\Delta=50\text{ ppm}$. The scalar coupling $J=0$.

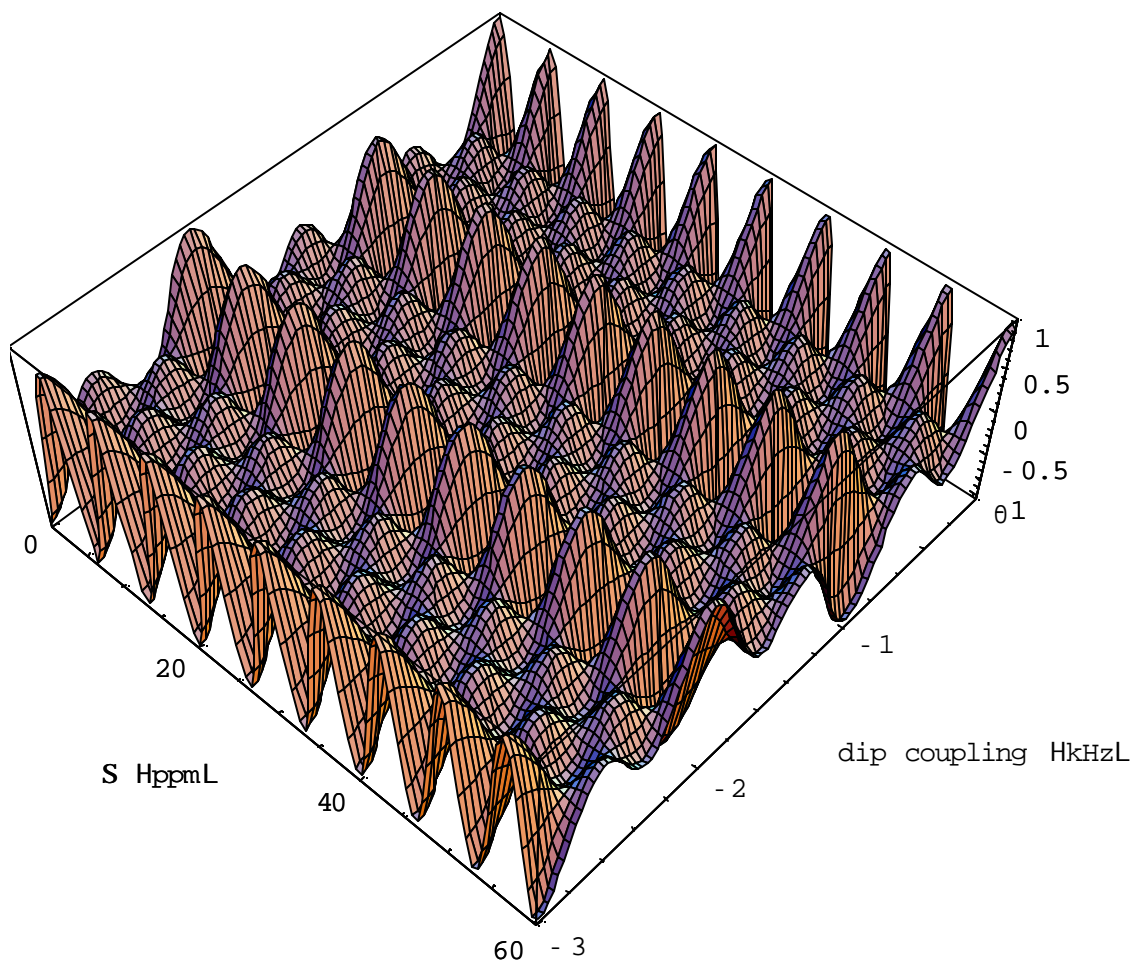


Figure 5-7: Graph of the “even term” for I_x for an oriented sample, as a function of the dipolar coupling frequency in the lab frame in kHz, and the chemical shift average in the lab frame (Σ) where $t=3\text{ms}$. The scalar coupling $J=0$.

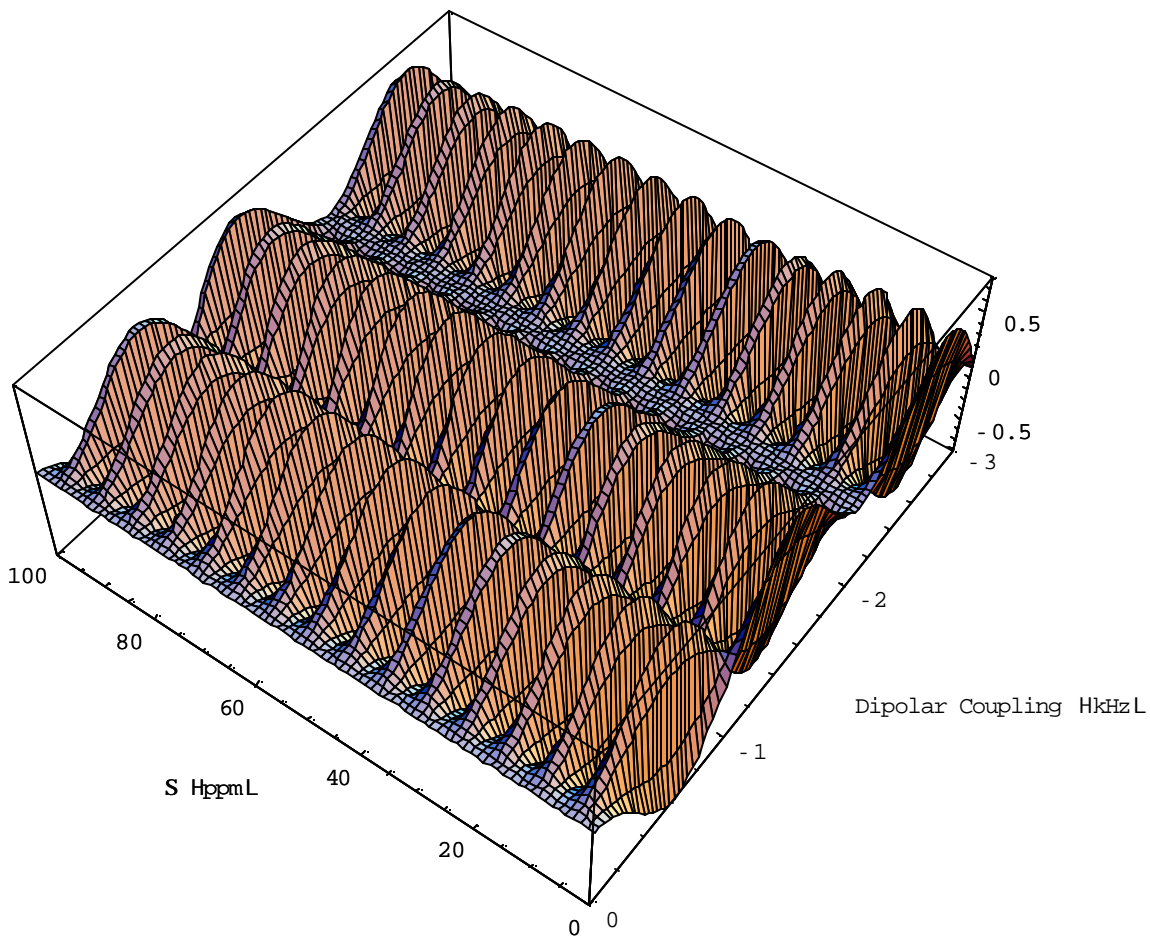


Figure 5-8: Graph of the CT function for S_x when $\sigma(0)=I_x$ for an oriented sample, as a function of the dipolar coupling frequency in the lab frame in kHz, and the chemical shift average in the lab frame (Σ) where $t=1\text{ms}$, and the CS difference frequency in the lab frame is $\Delta=0$ ppm. The scalar coupling $J=0$. See Eq. 5-21.

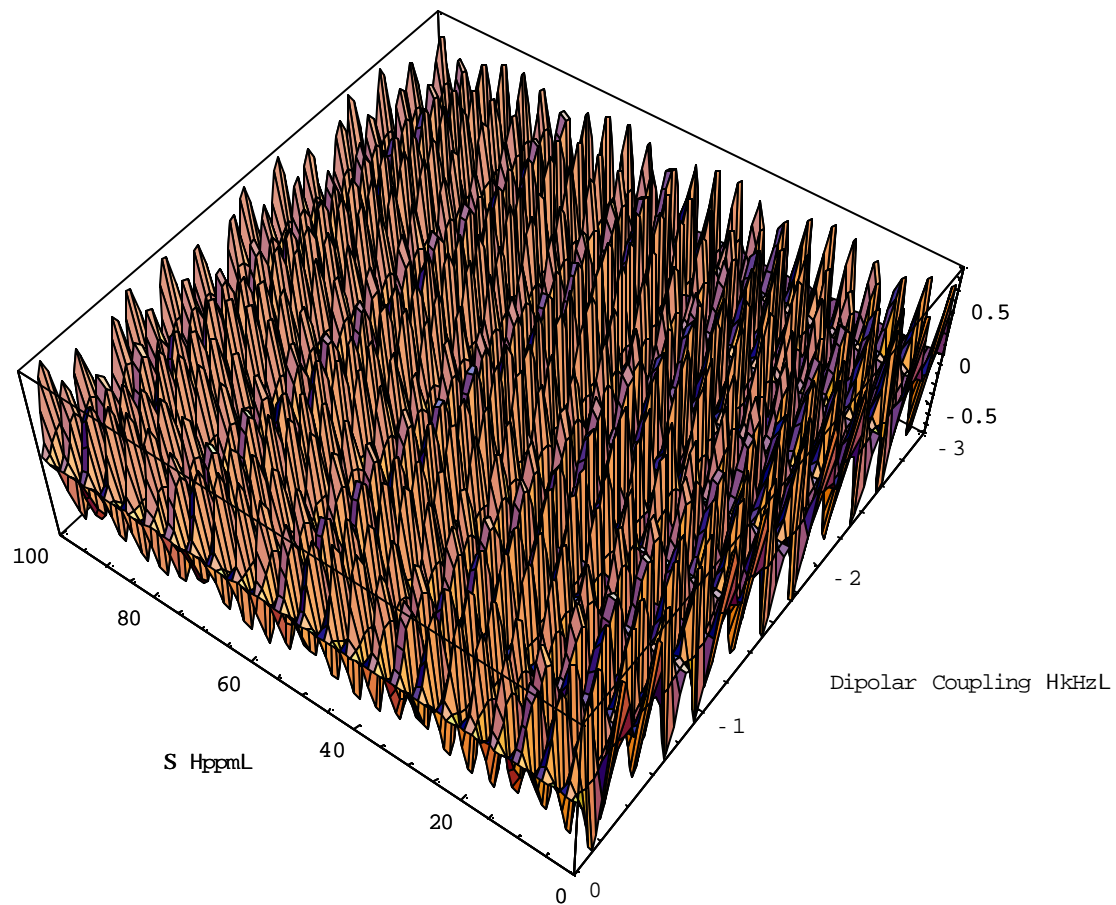


Figure 5-9: Graph of the CT function for S_x when $\sigma(0)=I_x$ for an oriented sample,, as a function of the dipolar coupling frequency in the lab frame in kHz, and the chemical shift average in the lab frame (Σ) where $t=5\text{ms}$, and the CS difference frequency in the lab frame is $\Delta=0$ ppm. The scalar coupling $J=0$. See Eq. 5-21.

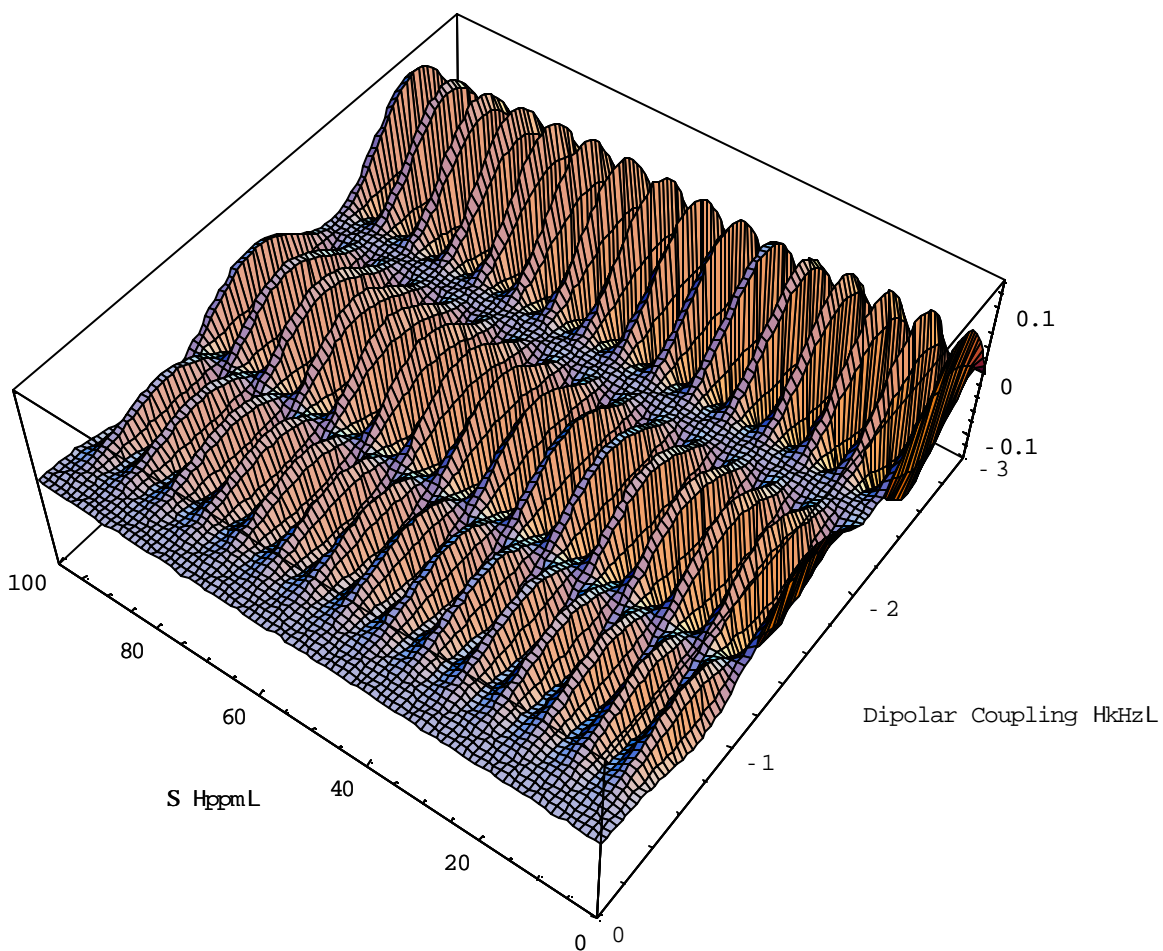


Figure 5-10: Graph of the CT function for S_x when $\sigma(0)=I_x$ for an oriented sample,, as a function of the dipolar coupling frequency in the lab frame in kHz, and the chemical shift average in the lab frame (Σ) where $t=5\text{ms}$, and the CS difference frequency in the lab frame is $\Delta=50\text{ ppm}$. The scalar coupling $J=0$. See Eq. 5-21.