Theory of chemical exchange in zero field NMR: Two-site flips

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In zero field NMR, the spectra are characterized purely by the quadrupolar or dipolar interactions, which are sensitive to molecular motion. An analytical theory is presented which describes the effect of two-site flips of a deuteron on its zero field NMR spectrum and demonstrates the potential of this novel technique in the investigation of molecular dynamics.

INTRODUCTION

With conventional NMR of polycrystalline solids, broad and often featureless spectra are frequently obtained and the effects of some molecular motions are not readily observed.¹ The resolution and sensitivity of nuclear quadrupole resonance (NQR) and broadline NMR is often so low that only the rigid and rapid motional regimes can be studied. In the intermediate region, where the exchange rate is comparable to the quadrupole interaction, the lines broaden appreciably and cannot be detected.² Zero field NMR represents an attractive approach to overcome these difficulties.³

In this paper, a theory is presented which deals with two-site motions of single deuterons, or pairs of dipolar coupled spin-1/2 nuclei. In previous work, Hennel et al. have developed analytical expressions for axially symmetric tensors.⁴ The work described here differs in that a spherical tensor basis set is used and there is no assumption of axial symmetry. Two-site exchange forms a good model for illustrating the effects of motion on zero field NMR spectra. It features in a number of chemical systems including: crystalline water; twofold flips of aromatic rings in liquid crystals, polymers, and proteins; chain motions in polymers and solids. There are several assumptions made in this calculation: (1) the motional model is a stationary Markov process; (2) the duration of the jump is negligible; (3) there are no couplings between the sites; and (4) only the spatial part of the Hamiltonian changes when a jump occurs. Assumption (3) may not always be satisfied in zero field NMR since dipolar coupling between deuterons is often observed.⁵ However, this interaction is small compared to the quadrupole couplings and can be further reduced by using partially deuterated samples. The effects of multisite exchange, as well as coupling between sites, will be examined in the following paper.9

TWO-SITE EXCHANGE IN ZERO FIELD

Typically in NMR, molecular dynamics are modeled by solving the stochastic Liouville equation. The multilinear spherical tensor operators in this equation are treated as the k th rank tensors irreducible under the rotation group. This choice of basis set proves to be very suitable for spin dynamic calculations.⁶ For the quadrupolar or dipolar Hamiltonian, there are nine such operators, but as the trace of these interactions is zero only eight of them are required. The motion we shall consider is a flip of the molecule by an arbitrary angle around some axis.

Zero field Hamiltonian

The diagonal zero field quadrupolar Hamiltonian is usually written

$$H_Q^{\text{PAS}} = A(3I_z^2 - I^2) + \eta A(I_x^2 - I_y^2), \qquad (1)$$

where PAS denotes the principal axis system, and can be described in a spherical tensor basis set T_{ka} as

$$H_Q^{\text{PAS}} = A \left[6^{-1/2} T_{20}^{\text{PAS}} + \eta \left(T_{22}^{\text{PAS}} + T_{2-2}^{\text{PAS}} \right) \right], \qquad (2)$$

where the quadrupole frequency $A = e^2 q Q / 4$ (for I = 1) and the asymmetry parameter $\eta = |(V_{XX} - V_{YY})| / V_{ZZ}$.

Zero field frames of reference

Typically, four coordinate systems are required to describe molecular motions in zero field. They are: (a) the principal axis system, PAS, (XYZ) representing the diagonal interaction; (b) the tilt frame, which characterizes the molecular motion axis $(X_T Y_T Z_T)$; (c) the molecular frame $(X_M Y_M Z_M)$ which is fixed on the molecule; (d) the laboratory frame, with the z axis along the applied magnetic field $(X_L Y_L Z_L)$. $R(\alpha'\beta'\gamma')$ is the rotation operator relating the tilt frame to the PAS; $R(\theta)$ is the transformation that rotates the tilt frame into a common molecular frame; $R(\alpha\beta\gamma)$ then transforms each molecular frame into the laboratory frame. These reference frames, coordinate systems, and rotation operators can be found in Table I. The R's are represented by the Wigner rotation matrices D. It is most convenient to analyze the effects of motion in the molecular frame where the zero field Hamiltonian is homogeneous, i.e., the same for all molecules. The results are then transformed into the laboratory frame by $R(\alpha\beta\gamma)$. As a consequence, only one diagonalization is required since the molecular frame is common to all the possible molecular orientations. The relationship between the PAS, tilt, and molecular frames is depicted pictorially in Fig. 1.

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TABLE I. Zero field frames of reference.

Reference frame	Coordinate axes	Tensor	Rotation operator	
Principal axis	X,Y,Z	TPAS	-in- 	
System			$R(\alpha'\beta'\gamma')$	
Tilt	X_T, Y_T, Z_T	T^{T}	D (A)	
Molecular	X_M, Y_M, Z_M	ТМ	$\mathbf{K}(\boldsymbol{\theta})$	
Laboratory	X_L, Y_L, Z_L	T^{L}	<i>R</i> (αβγ)	

Spin operators

The irreducible spherical tensor spin operators pertaining to this calculation are defined as

$$T_{10} = 2^{-1/2} I_z ,$$

$$T_{1\pm 1} = \mp I_{\pm} / 2 ,$$

$$T_{20} = 2^{-1/2} (3I_z^2 - I^2) ,$$

$$T_{2\pm 1} = \mp (I_z I_{\pm} + I_{\pm} I_z) / 2 ,$$

$$T_{2\pm 2} = I_{\pm} I_{\pm} / 2 ,$$

$$T_{00} = 0 .$$
(3)

Each of the above irreducible spherical tensors T_k of rank k, with the components T_{kq} , transforms according to the irreducible representation D_k of the rotation group. Therefore, upon transformation from the PAS to the tilt frame, the T_{kq}^{PAS} should be replaced by the components in the tilt frame according to

$$T_{kq}^{\text{PAS}} = R(\alpha'\beta'\gamma')T_{kq}^{T}R^{-1}(\alpha'\beta'\gamma')$$
$$= \sum_{q'=-k}^{+k} T_{kq'}^{T}D_{q'q}^{(k)}(\alpha'\beta'\gamma'), \qquad (4)$$

where the $D_{q'q}^{k}$ represents an element of the k th rank Wigner rotation matrix $D_{q'q}^{(k)}(\alpha'\beta'\gamma') = e^{-i\alpha'q'}d_{q'q}^{(k)}(\beta')e^{-i\gamma'q}$, where $d_{q'q}^{(k)}(\beta')$ are the reduced Wigner rotation matrices.

The normalized components of the magnetization in the molecular frame are defined as



FIG. 1. The zero field reference frames for a deuteron undergoing rotational flips about a twofold axis. This model is identical to that of Barnes (Ref. 7).

$$g_{kq}^{M}(t) \equiv \langle T_{kq}^{M} | \rho(t) \rangle = \operatorname{Tr} \{ T_{kq}^{M} \rho(t) \}, \qquad (5)$$

where $\rho(t)$ is the spin density operator. In a sudden version of the zero field experiment, the evolution period in zero field starts with the z component of the magnetization I_z^L . Hence, the correlation function of interest is $g_{10}^L(t)$, which can be transformed into the molecular frame according to a similar transformation as shown in Eq. (4),

$$g_{10}^{L}(t) = g_{10}^{M}(t)\cos\beta$$

- 2^{-1/2} [$g_{11}^{M}(t) - g_{1-1}^{M}(t)$] cos α sin β
+ $i2^{-1/2}$ [$g_{11}^{M}(t) + g_{1-1}^{M}(t)$] sin α sin β . (6)

Equations of motion in zero field NMR

In the two-site exchange problem, the nucleus jumps between θ and $-\theta$ about Y_T which is chosen to coincide with Y_M (see Fig. 1). The stochastic Liousville equation, in the molecular frame, reads

$$\frac{d}{dt}g_{k'q'}^{(1)}(t) = -i\sum_{k=1}^{+2}\sum_{q=-k}^{+k}\Omega_{k'q'kq}^{(1)}g_{kq}^{(1)} -\kappa g_{k'q'}^{(1)} +\kappa g_{k'q'}^{(2)},$$

$$\frac{d}{dt}g_{k'q'}^{(2)}(t) = -i\sum_{k=1}^{+2}\sum_{q=-k}^{+k}\Omega_{k'q'kq}^{(2)}g_{kq}^{(2)} -\kappa g_{k'q'}^{(2)} +\kappa g_{k'q'}^{(1)},$$
(7)

where the effects of motion appear in the last two terms. Ω is a 8×8 coupling frequency matrix; κ is the exchange rate of a particular site. $\Omega_{k'q'kq}$ is defined as

$$\Omega_{k'q'kq} = \sum_{\substack{q_1,q_3 = -k' \\ q_2,q_4 = -k}}^{k,k'} d_{q_1q_3}^{(k')}(\theta) d_{q_2q_4}^{(k)}(\theta) D_{q_3q'}^{(k')}(\alpha'\beta'\gamma') \\
\times D_{q_4q}^{(k)}(\alpha'\beta'\gamma') \langle T_{k'q_1}^{PAS} | H_Q^{PAS} | T_{kq_2}^{PAS} \rangle, \quad (8)$$

where $\Omega_{kqk'q'} = \Omega_{k'q'kq}$ and $d_{q'q}^{(k)}(\theta) = D_{q'q}^{(k)}(0,\theta,0)$. We define another frequency ω where

$$\omega_{k'q_1kq_2} = \langle T_{k'q_1}^{\text{PAS}} | H_Q^{\text{PAS}} | T_{kq_2}^{\text{PAS}} \rangle .$$
(9)

The ω 's are presented in Table II where nonzero frequencies occur only for k' = 1 and k = 2 or k' = 2 and k = 1. Restricting ourselves to the case where X,Y,Z coincides with X_T, Y_T, Z_T , i.e., $\alpha', \beta', \gamma' = 0$, Eq. (8) can be simplified to

$$\Omega_{1q'2q'} = 3A \left[d_{1q'}^{(1)}(\theta) d_{1q}^{(2)}(\theta) - d_{-1q'}^{(1)}(\theta) d_{-1q}^{(2)}(\theta) \right] + A\eta \left[d_{1q'}^{(1)}(\theta) d_{-1q}^{(2)}(\theta) - d_{-1q'}^{(1)}(\theta) d_{1q}^{(2)}(\theta) \right] + 2^{1/2}A\eta \left[d_{0q'}^{(1)}(\theta) d_{-2q}^{(2)}(\theta) - d_{0q'}^{(1)}(\theta) d_{2q}^{(2)}(\theta) \right].$$
(10)

TABLE II. Reduced zero field coupling frequencies $\omega_{k'q_1kq_2}$.

Frequencies/ $[v]$ 3A	Αη	$2^{1/2}A\eta$	
<i>ω</i> ₁₁₂₁	ω_{112-1}	ω _{102 - 2}	
ω_{2111}	ω_{2-111}	ω_{2-210}	
$-\omega_{1-12-1}$	$-\omega_{1-121}$	$-\omega_{1022}$	
$-\omega_{2-11-1}$	$-\omega_{211-1}$	$-\omega_{2210}$	

TABLE III. Zero field coupling frequencies $\Omega_{k'q'kq}$.

k'	q'	k	q	Frequency	Matrix notation
1	0	2	0	0	0
1	1	2	- 2	0	0
1	- 1	2	2	0	0
1	0	2	± 1	$2^{-1/2}A(\eta-3)\sin\theta\cos\theta$	$-2^{-1/2}a_1$
1	0	2	2	$-2^{-1/2}A[(3+\eta)\sin^2\theta-2\eta\cos^2\theta]$	$-2^{-1/2}a_2$
1	0	2	- 2	$2^{-1/2} A[(3+\eta)\sin^2\theta - 2\eta\cos^2\theta]$	$2^{-1/2}a_2$
1	1	2	2	$A(3-\eta)\sin\theta\cos\theta$	<i>a</i> ₁
1	- 1	2	- 2	$A(3-\eta)\sin\theta\cos\theta$	<i>a</i> ₁
1	1	2	1	$(3A/2)(3\cos^2\theta - 1 + \eta\sin^2\theta)$	$-a_3$
1	- 1	2	- 1	$-(3A/2)(3\cos^2\theta-1+\eta\sin^2\theta)$	<i>a</i> ₃
1	1	2	1	$(A/2)(3\sin^2\theta + \eta(2-\sin^2\theta))$	a4
1	- 1	2	1	$-(A/2)(3\sin^2\theta + \eta(2-\sin^2\theta))$	$-a_{4}$
1	± 1	2	0	$-(3/2)^{1/2}A(3-\eta)\sin\theta\cos\theta$	$-(3/2)^{1/2}a_1$

These frequencies are presented in Table III. Ω can be transformed into a block-diagonal form by the following transformations:

$$g_{1+} \equiv g_{11} + g_{1-1},$$

$$g_{1-} \equiv g_{11} - g_{1-1},$$

$$g_{2+} \equiv g_{21} + g_{2-1},$$

$$g_{2-} \equiv g_{21} - g_{2-1},$$

$$g_{22+} \equiv g_{22} + g_{2-2},$$

$$g_{22-} \equiv g_{22} - g_{2-2};$$
(11)

then:

$$g_{10} \equiv 2^{1/2} g_{10} ,$$

$$g_{20} \equiv 2^{1/2} g_{20} .$$
(12)

The basis vector set would change according to the above transformations as

$$\begin{bmatrix} g_{10} \\ g_{1-1} \\ g_{11} \\ g_{20} \\ g_{2-1} \\ g_{21} \\ g_{2-2} \\ g_{22} \end{bmatrix} \xrightarrow{g_{22}} \begin{bmatrix} g_{10} \\ g_{1+} \\ g_{1-} \\ g_{20} \\ (11) \\ g_{20} \\ (11) \\ g_{20} \\ g_{2+} \\ g_{20} \\ (12) \\ g_{2+} \\ g_{1-} \\ g_{2-} \\ g_{2-} \\ g_{2-} \\ g_{2-} \\ g_{2-} \\ g_{22+} \\ g_{22-} \\ g_{22+} \\ g_{22-} \\ g_{22+} \\ g_{22-} \\ g_{22+} \\ g_{22+} \\ g_{22-} \\ g_{22+} \\ g_{22+} \\ g_{22+} \\ g_{22+} \\ g_{22+} \\ g_{22+} \\ g_{2-} \\ g_{22+} \\ g_{22-} \\ g_{22+} \\ g_{$$

where the last transformation represents only the renaming of the correlation functions. The block-diagonal matrix and the initial frequency matrix can be found in the Appendix [Eqs. (A2) and (A1), respectively].

The stochastic Liouville equation, for two-site exchange, can then be written in a compact form:

$$\frac{d}{dt} \begin{bmatrix} \mathbf{g}^{(1)}(t) \\ \mathbf{g}^{(2)}(t) \end{bmatrix} = \begin{bmatrix} -i \begin{bmatrix} \mathbf{\Omega}^{(1)} & 0 \\ 0 & \mathbf{\Omega}^{(2)} \end{bmatrix} - \kappa \begin{bmatrix} \mathbf{1} & -\mathbf{1} \\ -\mathbf{1} & \mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{g}^{(1)}(t) \\ \mathbf{g}^{(2)}(t) \end{bmatrix}.$$
(14)

The $\Omega^{(1)}$, $\Omega^{(2)}$ are the 8×8 frequency matrices of a particular site, 1 is the 8×8 unit matrix, κ is the jump rate. The dimension of the matrix is now raised to 16. It can be decoupled into two subspaces of dimension 8, where the components of the vector **g** are $(g_1^{(1)}, g_2^{(1)}, g_3^{(1)}, g_4^{(1)}, g_1^{(2)}, g_2^{(2)}, g_3^{(2)}, g_4^{(2)})$ for the first subspace and $(g_5^{(1)}, g_6^{(1)}, g_7^{(1)}, g_8^{(1)}, g_5^{(2)}, g_6^{(2)}, g_7^{(2)}, g_8^{(2)})$ for the second. These two matrices can be found in the Appendix [see Eq. (A3)]. The frequencies of Eq. (10) in these two subspaces are either even or odd functions of θ with respect to sites 1 and 2. This property can be utilized in another transformation involving the correlation functions of both sites. This transformation can be represented by the following:

$$g_{ns} \equiv g_n^{(1)} + g_n^{(2)},$$

$$g_{na} \equiv g_n^{(1)} - g_n^{(2)},$$
(15)

where n = 1, 2, 3, ..., 8. Thus four subspaces of dimension 4 are obtained. The relevant equations of motion in each of the subspaces are

$$\begin{bmatrix} \dot{g}_{s_{1s}} \\ \dot{g}_{2a} \\ \dot{g}_{3s} \\ \dot{g}_{4a} \end{bmatrix} = \begin{bmatrix} 0 & ia_{1} & ia_{2} & 0 \\ ia_{1} & -2\kappa & 0 & -ia_{5} \\ ia_{2} & 0 & 0 & -ia_{1} \\ 0 & -ia_{5} & -ia_{1} & -2\kappa \end{bmatrix} \begin{bmatrix} g_{1s} \\ g_{2a} \\ g_{3s} \\ g_{4a} \end{bmatrix} = \mathbf{M}_{1} \begin{bmatrix} g_{1s} \\ g_{2a} \\ g_{3s} \\ g_{4a} \end{bmatrix},$$
(16a)
$$\begin{bmatrix} \dot{g}_{4s} \\ g_{3a} \\ g_{4a} \end{bmatrix} = \begin{bmatrix} 0 & -ia_{1} & -ia_{5} & 0 \\ -ia_{1} & -2\kappa & 0 & ia_{2} \\ -ia_{5} & 0 & 0 & ia_{1} \\ 0 & ia_{2} & ia_{1} & -2\kappa \end{bmatrix} \begin{bmatrix} g_{4s} \\ g_{3a} \\ g_{2s} \\ g_{1a} \end{bmatrix} = \mathbf{M}_{2} \begin{bmatrix} g_{4s} \\ g_{3a} \\ g_{2s} \\ g_{1a} \end{bmatrix},$$
(16b)

$$\begin{bmatrix} \dot{g}_{5s} \\ \dot{g}_{6a} \\ \dot{g}_{7s} \\ \dot{g}_{8a} \end{bmatrix} = \begin{bmatrix} 0 & 3^{1/2}ia_1 & ia_6 & -ia_1 \\ 3^{1/2}ia_1 & -2\kappa & 0 & 0 \\ ia_6 & 0 & 0 & 0 \\ -ia_1 & 0 & 0 & -2\kappa \end{bmatrix} \begin{bmatrix} g_{5s} \\ g_{6a} \\ g_{7s} \\ g_{8a} \end{bmatrix} = \mathbf{M}_3 \begin{bmatrix} g_{5s} \\ g_{6a} \\ g_{7s} \\ g_{8a} \end{bmatrix},$$
(16c)
$$\begin{bmatrix} \dot{g}_{5a} \\ \dot{g}_{5a} \\ \dot{g}_{5a} \\ \dot{g}_{5a} \\ \dot{g}_{5a} \end{bmatrix} = \begin{bmatrix} -2\kappa & 3^{1/2}ia_1 & ia_6 & -ia_1 \\ 3^{1/2}ia_1 & 0 & 0 & 0 \\ ia_6 & 0 & -2\kappa & 0 \\ -ia_1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} g_{5a} \\ g_{6s} \\ g_{7a} \\ g_{8s} \end{bmatrix} = \mathbf{M}_4 \begin{bmatrix} g_{5a} \\ g_{6s} \\ g_{7a} \\ g_{8s} \end{bmatrix},$$
(16d)

where $a_5 = a_4 - a_3$ and $a_6 = a_4 + a_3$.

At this stage it becomes convenient to focus attention on the initial condition vectors $\mathbf{g}(t=0)$ in the molecular frame. As was stated earlier, in the sudden version of the zero field experiment, one starts with the magnetization along the laboratory z axis, i.e., $\langle I_z^L(t=0) \rangle = 1 = 2^{1/2} g_{10}^L(t=0)$. Since $g_{10}^L(t=0) \equiv \langle T_{10}^L(t=0) \rangle$, the transformed correlation functions from the laboratory frame in the molecular frame are

 $\langle T_{10}^{M}(t=0) \rangle = \cos\beta \langle T_{10}^{L}(t=0) \rangle ,$ $\langle T_{11}^{M}(t=0) \rangle = (-e^{i\alpha}2^{-1/2})\sin\beta \langle T_{10}^{L}(t=0) \rangle ,$ (17) $\langle T_{1-1}^{M}(t=0) \rangle = (e^{-i\alpha}2^{-1/2})\sin\beta \langle T_{10}^{L}(t=0) \rangle .$

Thus, the nonzero initial conditions in the molecular frame, which appear in Eq. (16), are



FIG. 2. Simulated spectra for $2\theta = 20^\circ$. Only the positive half of the spectra are shown. κ/A is the ratio of the exchange rate and the quadrupolar frequency. It is shown to vary from the rigid regime (bottom) to the rapid motional limit (top). The ratio of the residual line broadening $(1/T_2)$ to the quadrupolar frequency is $\alpha/A = 0.02$. Note the lines are sharp at the extreme limits but are broad in the intermediate regime ($\kappa/A \approx 1$).

$$g_{1s}(t=0) = 2^{1/2} g_{10}^{M}(t=0) = \cos \beta,$$

$$g_{4s}(t=0) = g_{11}^{M}(t=0) + g_{1-1}^{M}(t=0) = -\cos \alpha \sin \beta,$$

(18)

$$g_{5s}(t=0) = g_{11}^{M}(t=0) - g_{1-1}^{M}(t=0)$$

$$= -i \sin \alpha \sin \beta$$
.

Zero field NMR spectrum

NMR spectra are usually presented in the frequency domain. This transformation is performed conveniently by the Laplace transformation

$$\mathbf{g}(i\omega) = (i\omega 1 - \mathbf{M})^{-1}\mathbf{g}(t=0), \qquad (19)$$

where 1 is a 4×4 unit matrix. By substituting Eq. (18) into Eq. (6) and then into Eq. (19), the following expression is obtained for the frequency domain:



FIG. 3. Simulated spectra for $2\theta = 70^{\circ}$. The spectral parameters are as for Fig. 2. For this jump angle, an asymmetry parameter close to unity is obtained in the extreme line narrowing limit.

$$2^{1/2}g_{10}^{L}(i\omega) = \cos\beta g_{1s}(i\omega) - \cos\alpha \sin\beta g_{4s}(i\omega) + i \sin\alpha \sin\beta g_{5s}(i\omega) .$$
(20)

The correlation functions $g_{1s}(i\omega), g_{4s}(i\omega), g_{5s}(i\omega)$ are

$$g_{1s}(i\omega) = \frac{N_1}{\Delta_1} g_{1s}(t=0) = \frac{N_1}{\Delta_1} \cos\beta,$$



FIG. 4. Simulated spectra for $2\theta = 90^\circ$: (a) $\eta = 0$, these spectra are identical to that of Hennel *et al.* (Ref. 4) (b) $\eta = 0.2$. All the other spectral parameters are as for Fig. 2.

$$g_{4s}(i\omega) = \frac{N_2}{\Delta_2} g_{4s}(t=0) = -\frac{N_2}{\Delta_2} \cos \alpha \sin \beta, \quad (21)$$
$$g_{5s}(i\omega) = \frac{N_3}{\Delta_3} g_{5s}(t=0) = -i \frac{N_3}{\Delta_3} \sin \alpha \sin \beta,$$

where the Δ_i 's are the determinants of the respective M_i 4×4 matrices of Eq. (16), the N_i 's are the respective cofactors corresponding to the nonzero initial condition vector components: $g_{1s}(t=0)$; $g_{4s}(t=0)$; $g_{5s}(t=0)$. Substitution of Eq. (21) into Eq. (20) gives the following:

$$2^{1/2}g_{10}^{L}(i\omega) = \cos^{2}\beta \, \frac{N_{1}}{\Delta_{1}} + \cos^{2}\alpha \, \sin^{2}\beta \, \frac{N_{2}}{\Delta_{2}}$$
$$+ \sin^{2}\alpha \, \sin^{2}\beta \, \frac{N_{3}}{\Delta_{3}}. \qquad (22)$$

The spectrum is obtained by taking the real part of Eq. (22). For a polycrystalline or powdered sample, an average is taken over α and β , and the spectrum is then given by

$$I(\omega) = \operatorname{Re}\left|\left\langle 2^{1/2}g_{10}^{L}(i\omega)\right\rangle\right| = \operatorname{Re}\left|\frac{1}{3}\left[\frac{N_{1}}{\Delta_{1}} + \frac{N_{2}}{\Delta_{2}} + \frac{N_{3}}{\Delta_{3}}\right]\right|.$$
(23)

Natural linewidths can be taken into account by adding a real term $\alpha = 1/T_2$ onto the leading diagonal elements of Eq. (16). Such a natural linewidth arises from EFG inhomogeneities caused by lattice defects, an inhomogeneous zero field, or spin lattice relaxation. The expressions of the N's and Δ 's, for the sudden zero field experiment, are given in the Appendix with this broadening parameter included.



FIG. 5. Simulated spectra for $2\theta = 109.4^\circ$; $\eta = 0.1$. The other parameters are as for the previous simulations. The spectra here are those predicted for a water molecule undergoing a twofold rotation about its C_2 axis in crystal-line hydrates (Ref. 2).

Simulations of zero field NMR spectra

Spectral simulations for various θ 's are presented in Figs. 2–5. In the extreme limits, the results agree with those as observed by conventional NQR experiments.⁷ However, in the intermediate region, when the exchange rate is comparable to the interaction frequency, the linewidths are very large. Typically, NQR spectroscopy has not detected signals in this regime.² The simulations shown in Figs. 2–5 are for jump angles of $2\theta = 20^{\circ}$, 70°, 90°, 109.4°, respectively. Examples of some of these jumps are relevant to amide deuterons in prophyrins,⁸ the 180° flip of crystalline bound water⁷ and of aromatic rings in polymers and proteins.

Equation (14) can also be solved numerically. The spectrum using this method, which is also applicable to large site problems and will be the subject of a future publication,⁹ is given by ^{10,11}

$$I(\omega) = \operatorname{Re}\left|\sum_{j} \frac{(\mathbf{g} \cdot \mathbf{S}^{-1})_{j} (\mathbf{S} \cdot \mathbf{1})_{j}}{i\omega - \lambda_{j}}\right|, \qquad (24)$$

where S and S^{-1} are the eigen- and inverse eigenvector matrices, respectively, of the diagonalized frequency-exchange matrix of Eq. (14), λ are the eigenvalues of the frequency-exchange matrix, and 1 is the unit vector.

SUMMARY

We have presented an analytical theory which predicts the zero field NMR spectra of a deuteron undergoing twofold flips for a variety of exchange rates. Of considerable interest is the intermediate regime where, in some cases, the lines are shown to be extremely broad. The width, shape, and position of these lines should provide accurate information concerning the exchange rate and jump angle of a particular deuteron. This demonstrates the great potential of zero field NMR for studying slow molecular dynamics in amorphous or polycrystalline materials, biopolymers, and liquid crystals.

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(A1)

(A2)

APPENDIX

Frequency matrices and basis transformations

The frequency matrix of Eq. (10), in the basis set $(g_{10}, g_{1-1}, g_{11}, g_{20}, g_{2-1}, g_{21}, g_{2-2}, g_{22})$ is

[0	0	0	0	$\frac{-a_1}{2^{1/2}}$	$\frac{-a_1}{2^{1/2}}$	$\frac{-a_2}{2^{1/2}}$	$\frac{-a_2}{2^{1/2}}$	
$\Omega =$	0	0	0	$-\left(\frac{3}{2}\right)^{1/2}a_1$	<i>a</i> ₃	$-a_4$	<i>a</i> ₁	0	
	0	0	0	$-\left(\frac{3}{2}\right)^{1/2}a_1$	<i>a</i> ₄	$-a_{3}$	0	<i>a</i> ₁	
	0	$-\left(\frac{3}{2}\right)^{1/2}a_1$	$-\left(\frac{3}{2}\right)^{1/2}a_1$	0	0	0	0	0	
	$\frac{-a_1}{2^{1/2}}$	<i>a</i> ₃	<i>a</i> ₄	0	0	0	0	0	
	$\frac{-a_1}{2^{1/2}}$	$-a_4$	$-a_{3}$	0	0	0	0	0	
	$\frac{-a_2}{2^{1/2}}$	<i>a</i> ₁	0	0	0	0	0	0	
	$\frac{-a_2}{2^{1/2}}$	0	<i>a</i> ₁	0	0	0	0	0	

After the transformations depicted in Eqs. (11)-(13), the block diagonal frequency matrix is

Frequency-exchange matrix

The frequency-exchange matrix of Eq. (14) can, by inspection, be reduced to two subspaces of dimension 8. These two matrices are

$$\begin{bmatrix} -\kappa & ia_{1}^{(1)} & ia_{2}^{(1)} & 0 & \kappa & 0 & 0 & 0 \\ ia_{1}^{(1)} & -\kappa & 0 & -ia_{3}^{(1)} & 0 & \kappa & 0 & 0 \\ ia_{2}^{(1)} & 0 & -\kappa & -ia_{1}^{(1)} & 0 & 0 & \kappa & 0 \\ 0 & -ia_{3}^{(1)} & -ia_{1}^{(1)} & -\kappa & 0 & 0 & 0 & \kappa \\ \kappa & 0 & 0 & 0 & -\kappa & ia_{1}^{(2)} & ia_{2}^{(2)} & 0 \\ 0 & \kappa & 0 & 0 & ia_{1}^{(2)} & -\kappa & 0 & -ia_{3}^{(2)} \\ 0 & 0 & \kappa & 0 & ia_{2}^{(2)} & 0 & -\kappa & -ia_{1}^{(2)} \\ 0 & 0 & 0 & \kappa & 0 & -ia_{5}^{(2)} & -ia_{1}^{(2)} & -\kappa \end{bmatrix},$$

$$\begin{bmatrix} -\kappa & 3^{1/2}ia_{1}^{(1)} & ia_{6}^{(1)} & -ia_{1}^{(1)} & \kappa & 0 & 0 & 0 \\ 3^{1/2}ia_{1}^{(1)} & -\kappa & 0 & 0 & 0 & \kappa & 0 \\ -ia_{1}^{(1)} & 0 & 0 & -\kappa & 0 & 0 & 0 & \kappa \\ \kappa & 0 & 0 & 0 & -\kappa & 3^{1/2}ia_{1}^{(2)} & ia_{6}^{(2)} & -ia_{1}^{(2)} \\ 0 & \kappa & 0 & 0 & 3^{1/2}ia_{1}^{(2)} & -\kappa & 0 & 0 \\ 0 & 0 & \kappa & 0 & ia_{6}^{(2)} & 0 & -\kappa & 0 \\ 0 & 0 & \kappa & 0 & ia_{6}^{(2)} & 0 & -\kappa & 0 \\ 0 & 0 & \kappa & 0 & ia_{6}^{(2)} & 0 & -\kappa & 0 \\ 0 & 0 & \kappa & 0 & ia_{6}^{(2)} & 0 & -\kappa & 0 \\ 0 & 0 & 0 & \kappa & -ia_{1}^{(2)} & 0 & 0 & -\kappa \end{bmatrix},$$
(A3a)

where the components of the vector **g** are $(g_1^{(1)}, g_2^{(1)}, g_3^{(1)}, g_4^{(1)}, g_1^{(2)}, g_2^{(2)}, g_3^{(2)}, g_4^{(2)})$ for Eq. (A3a); $(g_5^{(1)}, g_6^{(1)}, g_7^{(1)}, g_8^{(1)}, g_5^{(2)}, g_6^{(2)}, g_7^{(2)}, g_8^{(2)})$ for Eq. (A3b). The transformation described in Eq. (15) then produces the four subspaces of Eq. (16).

Spectral simulation of the sudden zero field NMR experiment

The expressions of N_i and Δ_i of Eq. (23), including the effect of a natural linewidth ($\alpha = 1/T_2$), are

$$\begin{split} N_{1} &= -\omega^{2}(4\kappa + 3\alpha) + \alpha(4\kappa^{2} + a_{1}^{2} + a_{5}^{2} + 4\alpha\kappa + \alpha^{2}) + 2a_{1}^{2}\kappa \\ &- i\omega^{3} + i\omega(4\kappa^{2} + a_{1}^{2} + a_{5}^{2} + 8\alpha\kappa + 3\alpha^{2}) , \\ \Delta_{1} &= \omega^{4} - \omega^{2}(2a_{1}^{2} + a_{2}^{2} + a_{5}^{2} + 4\kappa^{2} - 6\alpha^{2} - 12\alpha\kappa) + \alpha \left[4\kappa(a_{1}^{2} + a_{2}^{2} + \alpha^{2}) \\ &+ \alpha(2a_{1}^{2} + a_{2}^{2} + a_{5}^{2} + 4\kappa^{2} + \alpha^{2})\right] + a_{1}^{4} - 2a_{1}^{2}a_{2}a_{5} + a_{2}^{2}a_{5}^{2} + 4\kappa^{2}a_{2}^{2} \\ &- 4i\omega^{3}(\kappa + \alpha) + 2i\omega \left[2\alpha^{3} + \alpha(2a_{1}^{2} + a_{2}^{2} + a_{5}^{2} + 4\kappa^{2}) + 2\kappa(3\alpha^{2} + a_{1}^{2} + a_{2}^{2})\right] , \\ N_{2} &= -\omega^{2}(4\kappa + 3\alpha) + \alpha(4\kappa^{2} + a_{1}^{2} + a_{2}^{2} + 4\alpha\kappa + \alpha^{2}) + 2a_{1}^{2}\kappa \\ &- i\omega^{3} + i\omega(4\kappa^{2} + a_{1}^{2} + a_{2}^{2} + 8\alpha\kappa + 3\alpha^{2}) , \\ \Delta_{2} &= \omega^{4} - \omega^{2}(2a_{1}^{2} + a_{2}^{2} + a_{5}^{2} + 4\kappa^{2} - 6\alpha^{2} - 12\alpha\kappa) + \alpha \left[4\kappa(a_{1}^{2} + a_{5}^{2} + \alpha^{2}) \\ &+ \alpha(2a_{1}^{2} + a_{2}^{2} + a_{5}^{2} + 4\kappa^{2} - 6\alpha^{2} - 12\alpha\kappa) + \alpha \left[4\kappa(a_{1}^{2} + a_{5}^{2} + \alpha^{2}) \\ &+ \alpha(2a_{1}^{2} + a_{2}^{2} + a_{5}^{2} + 4\kappa^{2} + \alpha^{2})\right] + a_{1}^{4} - 2a_{1}^{2}a_{2}a_{5} + a_{2}^{2}a_{5}^{2} + 4\kappa^{2}a_{5}^{2} \\ &- 4i\omega(\kappa + \alpha) + 2i\omega \left[2\alpha^{3} + \alpha(2a_{1}^{2} + a_{2}^{2} + a_{5}^{2} + 4\kappa^{2}) + 2\kappa(3\alpha^{2} + a_{1}^{2} + a_{5}^{2})\right] , \\ \Lambda_{3} &= \omega^{4} - \omega^{2}(4a_{1}^{2} + a_{6}^{2} + 4\kappa^{2} - 6\alpha^{2} - 12\alpha\kappa) + \alpha \left[4\kappa(2a_{1}^{2} + a_{6}^{2} + \alpha^{2}) \\ &+ \alpha(4a_{1}^{2} + a_{6}^{2} + 4\kappa^{2} - 6\alpha^{2} - 12\alpha\kappa) + \alpha \left[4\kappa(2a_{1}^{2} + a_{6}^{2} + a_{1}^{2} + a_{5}^{2})\right] , \\ \Lambda_{3} &= \omega^{4} - \omega^{2}(4a_{1}^{2} + a_{6}^{2} + 4\kappa^{2} - 6\alpha^{2} - 12\alpha\kappa) + \alpha \left[4\kappa(2a_{1}^{2} + a_{6}^{2} + \alpha^{2}) \\ &+ \alpha(4a_{1}^{2} + a_{6}^{2} + 4\kappa^{2} + \alpha^{2})\right] + 4a_{6}^{2}\kappa^{2} \\ &- 4i\omega^{3}(\kappa + \alpha) + 2i\omega \left[2\alpha^{3} + \alpha(4a_{1}^{2} + a_{6}^{2} + 4\kappa^{2}) + 2\kappa(3\alpha^{2} + 2a_{1}^{2} + a_{6}^{2})\right] . \end{split}$$

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