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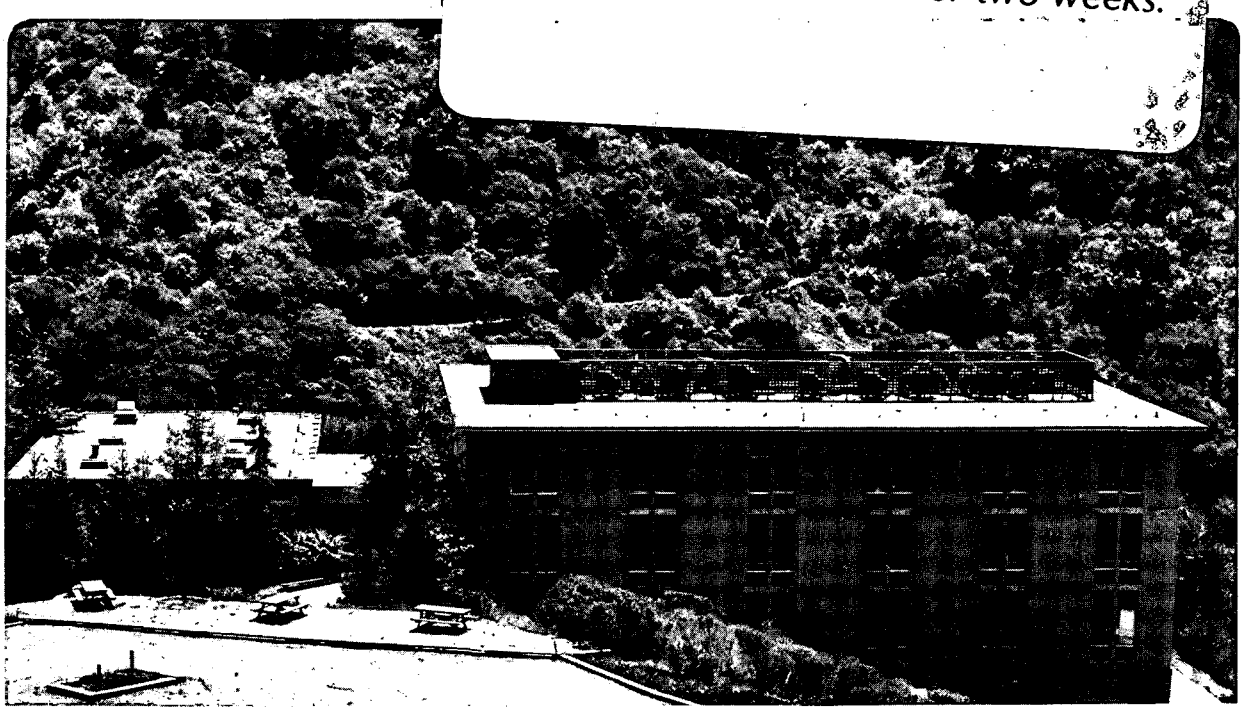

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THEORY OF CHEMICAL EXCHANGE IN ZERO FIELD NMR:

TWO-SITE FLIPS.

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FOOTNOTE TO TITLE PAGE.

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ABSTRACT.

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 can not 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 symmmetry. 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; two-fold 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 neglible;

(3) there are no couplings between the sites;

(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 multi-site 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 in NMR 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.

(a) Zero Field Hamiltonian.

The diagonal zero field quadrupolar Hamiltonian is usually written:

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

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

$$H_Q^{PAS} = A(6^{-1/2}T_{20}^{PAS} + \eta(T_{22}^{PAS} + T_{2-2}^{PAS})) \tag{2}$$

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

(b) 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 characterises the molecular motion axis ($X_TY_TZ_T$); (c) the molecular frame ($X_MY_MZ_M$) which is fixed on the molecule; (d) the laboratory frame, with the z-axis along the applied magnetic field ($X_LY_LZ_L$). $R(\alpha'\beta'\gamma')$ 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 diagonalisation 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.

(c) Spin-operators.

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

$$
\begin{aligned}
T_{10} &= 2^{-1/2} I_z \\
T_{1\pm1} &= \mp I_\pm/2 \\
T_{20} &= 2^{-1/2}(3I_z^2 - I^2) \\
T_{2\pm1} &= \mp(I_z I_\pm + I_\pm I_z)/2 \\
T_{2\pm2} &= I_\pm I_\pm/2 \\
T_{00} &= 0
\end{aligned}
\tag{3}
$$

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:

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

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 normalised components of the magnetisation in the molecular frame are defined as:

$$g_{kq}^{M}(t) = \langle T_{kq}^{M} | \rho(t) \rangle = \mathrm{Tr}\{T_{kq}^{M} \rho(t)\} \tag{5}$$

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 magnetisation, 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 Eqn. (4).

$$g_{10}^L(t) = g_{10}^M(t)\cos\beta - 2^{-1/2}(g_{11}^M(t) - g_{1-1}^M(t))\cos\alpha\sin\beta$$
$$+ i2^{-1/2}(g_{11}^M(t) + g_{1-1}^M(t))\sin\alpha\sin\beta \qquad (6)$$

(d) 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 Liouville equation, in the molecular frame, reads:

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

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. $\Omega_{k'q'kq}$ are defined as:

$$\Omega_{k'q'kq} = \sum_{\substack{q_1,q_3=-k' \\ q_2,q_4=-k}}^{k,k'} d^{(k')}_{q_1q_3}(\theta)d^{(k)}_{q_2q_4}(\theta)D^{(k')}_{q_3q'}(\alpha'\beta'\gamma')D^{(k)}_{q_4q}(\alpha'\beta'\gamma')$$

$$\times\langle T^{PAS}_{k'q_1}|H^{PAS}_Q|T^{PAS}_{kq_2}\rangle \tag{8}$$

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

$$\omega_{k'q_1kq_2} = \langle T^{PAS}_{k'q_1}|H^{PAS}_Q|T^{PAS}_{kq_2}\rangle \tag{9}$$

The ω's are presented in Table II where non-zero 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. $\alpha',\beta',\gamma'=0$, Eqn. (8) can be simplified to:

$$\begin{aligned}\Omega_{1q'2q} = \; & 3A(d^{(1)}_{1q'}(\theta)d^{(2)}_{1q}(\theta) - d^{(1)}_{-1q'}(\theta)d^{(2)}_{-1q}(\theta)) \\ & + A\eta(d^{(1)}_{1q'}(\theta)d^{(2)}_{-1q}(\theta) - d^{(1)}_{-1q'}(\theta)d^{(2)}_{1q}(\theta)) \\ & +2^{1/2}A\eta(d^{(1)}_{0q'}(\theta)d^{(2)}_{-2q}(\theta) - d^{(1)}_{0q'}(\theta)d^{(2)}_{2q}(\theta))\end{aligned} \tag{10}$$

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

$$
\begin{aligned}
g_{1+} &= g_{11} + g_{1-1} \\
g_{1-} &= g_{11} - g_{1-1} \\
g_{2+} &= g_{21} + g_{2-1} \\
g_{2-} &= g_{21} - g_{2-1} \\
g_{22+} &= g_{22} + g_{2-2} \\
g_{22-} &= g_{22} - g_{2-2}
\end{aligned}
\tag{11}
$$

then:

$$
\begin{aligned}
g_{10} &= 2^{1/2} g_{10} \\
g_{20} &= 2^{1/2} g_{20}
\end{aligned}
\tag{12}
$$

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

$$
\begin{bmatrix} g_{10} \\ g_{1-1} \\ g_{11} \\ g_{20} \\ g_{2-1} \\ g_{21} \\ g_{2-2} \\ g_{22} \end{bmatrix}
\xrightarrow[\longrightarrow]{\text{Eqn. (11)}}
\begin{bmatrix} g_{10} \\ g_{1+} \\ g_{1-} \\ g_{20} \\ g_{2+} \\ g_{2-} \\ g_{22+} \\ g_{22-} \end{bmatrix}
\xrightarrow[\longrightarrow]{\text{Eqn. (12)}}
\begin{bmatrix} 2^{1/2} g_{10} \\ g_{2+} \\ g_{22-} \\ g_{1-} \\ g_{1+} \\ 2^{1/2} g_{20} \\ g_{2-} \\ g_{22+} \end{bmatrix}
\longrightarrow
\begin{bmatrix} g_1 \\ g_2 \\ g_3 \\ g_4 \\ g_5 \\ g_6 \\ g_7 \\ g_8 \end{bmatrix}
\tag{13}
$$

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 (Eqns. A.2 and A.1 respectively).

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

$$\frac{d}{dt}\begin{bmatrix} g^{(1)}(t) \\ g^{(2)}(t) \end{bmatrix} = \left[-i\begin{bmatrix} \Omega^{(1)} & 0 \\ 0 & \Omega^{(2)} \end{bmatrix} - \kappa\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}\right]\begin{bmatrix} g^{(1)}(t) \\ g^{(2)}(t) \end{bmatrix} \tag{14}$$

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 Eqn. A.3). The frequencies of Eqn. (10) in these two subspaces are either even or odd functions of θ with respect to sites 1 and 2. This property can be utilised in another transformation involving the correlation functions of both sites. This transformation can be represented by the following:

$$\begin{aligned} g_{ns} &= g_n^{(1)} + g_n^{(2)} \\ g_{na} &= g_n^{(1)} - g_n^{(2)} \end{aligned} \tag{15}$$

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:

$$\begin{bmatrix} \dot{g}_{1s} \\ \dot{g}_{2a} \\ \dot{g}_{3s} \\ \dot{g}_{4a} \end{bmatrix} = \begin{bmatrix} 0 & ia_1 & ia_2 & 0 \\ ia_1 & -2\kappa & 0 & -ia_5 \\ ia_2 & 0 & 0 & -ia_1 \\ 0 & -ia_5 & -ia_1 & -2\kappa \end{bmatrix} \begin{bmatrix} g_{1s} \\ g_{2a} \\ g_{3s} \\ g_{4a} \end{bmatrix} = M_1 \begin{bmatrix} g_{1s} \\ g_{2a} \\ g_{3s} \\ g_{4a} \end{bmatrix} \tag{16a}$$

$$\begin{bmatrix} \dot{g}_{4s} \\ \dot{g}_{3a} \\ \dot{g}_{2s} \\ \dot{g}_{1a} \end{bmatrix} = \begin{bmatrix} 0 & -ia_1 & -ia_5 & 0 \\ -ia_1 & -2\kappa & 0 & ia_2 \\ -ia_5 & 0 & 0 & ia_1 \\ 0 & ia_2 & ia_1 & -2\kappa \end{bmatrix} \begin{bmatrix} g_{4s} \\ g_{3a} \\ g_{2s} \\ g_{1a} \end{bmatrix} = M_2 \begin{bmatrix} g_{4s} \\ g_{3a} \\ g_{2s} \\ g_{1a} \end{bmatrix} \tag{16b}$$

$$\begin{bmatrix} \dot{g}_{5s} \\ \dot{g}_{6a} \\ \dot{g}_{7s} \\ \dot{g}_{8a} \end{bmatrix} = \begin{bmatrix} 0 & 3^{1/2}ia_1 & ia_6 & -ia_1 \\ 3^{1/2}ia_1 & -2\kappa & 0 & 0 \\ ia_6 & 0 & 0 & 0 \\ -ia_1 & 0 & 0 & -2\kappa \end{bmatrix} \begin{bmatrix} g_{5s} \\ g_{6a} \\ g_{7s} \\ g_{8a} \end{bmatrix} = M_3 \begin{bmatrix} g_{5s} \\ g_{6a} \\ g_{7s} \\ g_{8a} \end{bmatrix} \tag{16c}$$

$$\begin{bmatrix} \dot{g}_{5a} \\ \dot{g}_{6s} \\ \dot{g}_{7a} \\ \dot{g}_{8s} \end{bmatrix} = \begin{bmatrix} -2\kappa & 3^{1/2}ia_1 & ia_6 & -ia_1 \\ 3^{1/2}ia_1 & 0 & 0 & 0 \\ ia_6 & 0 & -2\kappa & 0 \\ -ia_1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} g_{5a} \\ g_{6s} \\ g_{7a} \\ g_{8s} \end{bmatrix} = M_4 \begin{bmatrix} g_{5a} \\ g_{6s} \\ g_{7a} \\ g_{8s} \end{bmatrix} \tag{16d}$$

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, $g(t=0)$ in the molecular frame. As was stated earlier, in the sudden version of the zero field experiment, one starts with the magnetisation along the laboratory z-axis, i.e. $\langle I_z^L(t=0)\rangle = 1 =$

$2^{1/2}g^L_{10}(t=0)$. Since $g^L_{10}(t=0) = \langle T^L_{10}(t=0)\rangle$, the transformed correlation functions from the laboratory frame in the molecular frame are:

$$\begin{aligned}
\langle T^M_{10}(t=0)\rangle &= \cos\beta\langle T^L_{10}(t=0)\rangle \\
\langle T^M_{11}(t=0)\rangle &= (-e^{i\alpha}2^{-1/2})\sin\beta\langle T^L_{10}(t=0)\rangle \\
\langle T^M_{1-1}(t=0)\rangle &= (e^{-i\alpha}2^{-1/2})\sin\beta\langle T^L_{10}(t=0)\rangle
\end{aligned} \tag{17}$$

Thus, the non-zero initial conditions in the molecular frame, which appear in Eqn. (16), are:

$$\begin{aligned}
g_{1s}(t=0) &= 2^{1/2}g^M_{10}(t=0) &&= \cos\beta \\
g_{4s}(t=0) &= g^M_{11}(t=0) + g^M_{1-1}(t=0) &&= -\cos\alpha\sin\beta \\
g_{5s}(t=0) &= g^M_{11}(t=0) - g^M_{1-1}(t=0) &&= -i\sin\alpha\sin\beta
\end{aligned} \tag{18}$$

<u>(e) Zero Field NMR Spectrum.</u>

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

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

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

domain:

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

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

$$\begin{aligned} g_{1s}(i\omega) &= \frac{N_1}{\Delta_1} g_{1s}(t=0) = \frac{N_1}{\Delta_1}\cos\beta \\ g_{4s}(i\omega) &= \frac{N_2}{\Delta_2} g_{4s}(t=0) = -\frac{N_2}{\Delta_2}\cos\alpha\sin\beta \\ g_{5s}(i\omega) &= \frac{N_3}{\Delta_3} g_{5s}(t=0) = -i\frac{N_3}{\Delta_3}\sin\alpha\sin\beta \end{aligned} \qquad (21)$$

where the Δ_i's are the determinants of the respective M_i 4×4 matrices of Eqn. (16), the N_i's are the respective cofactors corresponding to the non-zero initial condition vector components: $g_{1s}(t=0)$; $g_{4s}(t=0)$; $g_{5s}(t=0)$. Substitution of Eqn. (21) into Eqn. (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 Eqn. (22). For a polycrystalline or powdered sample, an average is taken over α and β, and the spectrum is then given by:

$$I(\omega) = \mathrm{Re}\left|<2^{1/2} g_{10}^{L}(i\omega)>\right| = \mathrm{Re}\left|\frac{1}{3}\left[\frac{N_1}{\Delta_1} + \frac{N_2}{\Delta_2} + \frac{N_3}{\Delta_3}\right]\right| \tag{23}$$

Natural linewidths can be taken into account by adding a real term, $\alpha = 1/T_2$, onto the leading diagonal elements of Eqn. (16). Such a natural linewidth arises from EFG inhomogeneities caused by lattice defects, an inhomogenous 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.

(f) 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 porphyrins,[8] the 180° flip of crystalline bound water[7] and of aromatic rings in polymers and proteins.

Eqn. (14) can also be solved numerically. The spectrum using this method, which is also applicable to larger site problems and will be the subject of a future publication,[9] is given by:[10,11]

$$I(\omega) = \mathrm{Re}\left| \sum_j \frac{(g.S^{-1})_j (S.1)_j}{i\omega - \lambda_j} \right| \tag{24}$$

where S and S^{-1} are the eigen- and inverse eigen-vector matrices respectively of the diagonalised frequency-exchange matrix of Eqn. (14), λ are the eigen-values 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 two-fold 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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APPENDIX.

(i) Frequency Matrices and Basis Transformations.

The frequency matrix of Eqn. (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:

$$\Omega = \begin{bmatrix} 0 & 0 & 0 & 0 & \frac{-a_1}{2^{1/2}} & \frac{-a_1}{2^{1/2}} & \frac{a_2}{2^{1/2}} & \frac{-a_2}{2^{1/2}} \\ 0 & 0 & 0 & -\left(\frac{3}{2}\right)^{1/2}a_1 & a_3 & -a_4 & a_1 & 0 \\ 0 & 0 & 0 & -\left(\frac{3}{2}\right)^{1/2}a_1 & a_4 & -a_3 & 0 & a_1 \\ 0 & -\left(\frac{3}{2}\right)^{1/2}a_1 & -\left(\frac{3}{2}\right)^{1/2}a_1 & 0 & 0 & 0 & 0 & 0 \\ \frac{-a_1}{2^{1/2}} & a_3 & a_4 & 0 & 0 & 0 & 0 & 0 \\ \frac{-a_1}{2^{1/2}} & -a_4 & -a_3 & 0 & 0 & 0 & 0 & 0 \\ \frac{a_2}{2^{1/2}} & a_1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{-a_2}{2^{1/2}} & 0 & a_1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad (A.1)$$

After the transformations depicted in Eqn. (11), Eqn. (12) and Eqn. (13), the block diagonal frequency matrix is:

$$\Omega = \begin{bmatrix} 0 & -a_1 & -a_2 & 0 & 0 & 0 & 0 & 0 \\ -a_1 & 0 & 0 & a_5 & 0 & 0 & 0 & 0 \\ -a_2 & 0 & 0 & a_1 & 0 & 0 & 0 & 0 \\ 0 & a_5 & a_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -3^{\frac{1}{2}}a_1 & -a_6 & a_1 \\ 0 & 0 & 0 & 0 & -3^{\frac{1}{2}}a_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -a_6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & a_1 & 0 & 0 & 0 \end{bmatrix} \qquad (A.2)$$

(ii) Frequency-Exchange Matrix.

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

$$\begin{bmatrix} -\kappa & ia_1^{(1)} & ia_2^{(1)} & 0 & \kappa & 0 & 0 & 0 \\ ia_1^{(1)} & -\kappa & 0 & -ia_5^{(1)} & 0 & \kappa & 0 & 0 \\ ia_2^{(1)} & 0 & -\kappa & -ia_1^{(1)} & 0 & 0 & \kappa & 0 \\ 0 & -ia_5^{(1)} & -ia_1^{(1)} & -\kappa & 0 & 0 & 0 & \kappa \\ \kappa & 0 & 0 & 0 & -\kappa & ia_1^{(2)} & ia_2^{(2)} & 0 \\ 0 & \kappa & 0 & 0 & ia_1^{(2)} & -\kappa & 0 & -ia_5^{(2)} \\ 0 & 0 & \kappa & 0 & ia_2^{(2)} & 0 & -\kappa & -ia_1^{(2)} \\ 0 & 0 & 0 & \kappa & 0 & -ia_5^{(2)} & -ia_1^{(2)} & -\kappa \end{bmatrix} \qquad \text{(A.3a)}$$

$$\begin{bmatrix} -\kappa & 3^{1/2}ia_1^{(1)} & ia_6^{(1)} & -ia_1^{(1)} & \kappa & 0 & 0 & 0 \\ 3^{1/2}ia_1^{(1)} & -\kappa & 0 & 0 & 0 & \kappa & 0 & 0 \\ ia_6^{(1)} & 0 & -\kappa & 0 & 0 & 0 & \kappa & 0 \\ -ia_1^{(1)} & 0 & 0 & -\kappa & 0 & 0 & 0 & \kappa \\ \kappa & 0 & 0 & 0 & -\kappa & 3^{1/2}ia_1^{(2)} & ia_6^{(2)} & -ia_1^{(2)} \\ 0 & \kappa & 0 & 0 & 3^{1/2}ia_1^{(2)} & -\kappa & 0 & 0 \\ 0 & 0 & \kappa & 0 & ia_6^{(2)} & 0 & -\kappa & 0 \\ 0 & 0 & 0 & \kappa & -ia_1^{(2)} & 0 & 0 & -\kappa \end{bmatrix} \qquad \text{(A.3b)}$$

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 Eqn. (A.3a); $(g_5^{(1)}, g_6^{(1)}, g_7^{(1)}, g_8^{(1)}, g_5^{(2)}, g_6^{(2)}, g_7^{(2)}, g_8^{(2)})$ for Eqn. (A.3b). The transformation described

in Eqn. (15) then produces the four subspaces of Eqn. (16).

(iii) Spectral Simulation of the Sudden Zero Field NMR Experiment.

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

$$N_1 = -\omega^2(4\kappa+3\alpha) + \alpha(4\kappa^2+a_1^2+a_5^2+4\alpha\kappa+\alpha^2) + 2a_1^2\kappa$$
$$-i\omega^3 + i\omega(4\kappa^2+a_1^2+a_5^2+8\alpha\kappa+3\alpha^2)$$

$$\Delta_1 = \omega^4 - \omega^2(2a_1^2+a_2^2+a_5^2+4\kappa^2-6\alpha^2-12\alpha\kappa) + \alpha(4\kappa(a_1^2+a_2^2+\alpha^2)+$$
$$\alpha(2a_1^2+a_2^2+a_5^2+4\kappa^2+\alpha^2)) + a_1^4 - 2a_1^2a_2a_5 + a_2^2a_5^2 + 4\kappa^2a_2^2$$
$$-4i\omega^3(\kappa+\alpha) + 2i\omega(2\alpha^3+\alpha(2a_1^2+a_2^2+a_5^2+4\kappa^2)+2\kappa(3\alpha^2+a_1^2+a_2^2))$$

$$N_2 = -\omega^2(4\kappa+3\alpha) + \alpha(4\kappa^2+a_1^2+a_2^2+4\alpha\kappa+\alpha^2) + 2a_1^2\kappa$$
$$-i\omega^3 + i\omega(4\kappa^2+a_1^2+a_2^2+8\alpha\kappa+3\alpha^2)$$

$$\Delta_2 = \omega^4 - \omega^2(2a_1^2+a_2^2+a_5^2+4\kappa^2-6\alpha^2-12\alpha\kappa) + \alpha(4\kappa(a_1^2+a_5^2+\alpha^2)+$$
$$\alpha(2a_1^2+a_2^2+a_5^2+4\kappa^2+\alpha^2)) + a_1^4 - 2a_1^2a_2a_5 + a_2^2a_5^2 + 4\kappa^2a_5^2$$
$$-4i\omega(\kappa+\alpha) + 2i\omega(2\alpha^3+\alpha(2a_1^2+a_2^2+a_5^2+4\kappa^2)+2\kappa(3\alpha^2+a_1^2+a_5^2))$$

$$N_3 = -\omega^2(4\kappa+3\alpha) + \alpha(4\kappa^2+4\alpha\kappa+\alpha^2)$$
$$-i\omega^3 + i\omega(4\kappa^2+8\alpha\kappa+3\alpha^2)$$

$$\Delta_3 = \omega^4 - \omega^2(4a_1^2+a_6^2+4\kappa^2-6\alpha^2-12\alpha\kappa) + \alpha(4\kappa(2a_1^2+a_6^2+\alpha^2)+$$
$$\alpha(4a_1^2+a_6^2+4\kappa^2+\alpha^2)) + 4a_6^2\kappa^2$$
$$-4i\omega^3(\kappa+\alpha) + 2i\omega(2\alpha^3+a(4a_1^2+a_6^2+4\kappa^2+2\kappa(3\alpha^2+2a_1^2+a_6^2))$$

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TABLES.

Table I. Zero Field Frames of Reference.

Reference Frame	Coordinate axes	Tensor	Rotation Operator
Principal axis System	X,Y,Z	T^{PAS}	
			$R(\alpha'\beta'\gamma')$
Tilt	X_T, Y_T, Z_T	T^T	
			$R(\theta)$
Molecular	X_M, Y_M, Z_M	T^M	
			$R(\alpha\beta\gamma)$
Laboratory	X_L, Y_L, Z_L	T^L	

Table II. Reduced Zero Field Coupling Frequencies, $\omega_{k'q_1kq_2}$

Frequencies/ [ν] 3A	$A\eta$	$2^{1/2}A\eta$
ω_{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	$A(3-\eta)\sin\theta\cos\theta$	a_1
1	-1	2	-2	$A(3-\eta)\sin\theta\cos\theta$	a_1
1	1	2	1	$(3A/2)(3\cos^2\theta-1+\eta\sin^2\theta)$	$-a_3$
1	-1	2	-1	$-(3A/2)(3\cos^2\theta-1+\eta\sin^2\theta)$	a_3
1	1	2	-1	$(A/2)(3\sin^2\theta+\eta(2-\sin^2\theta)$	a_4
1	-1	2	1	$-(A/2)(3\sin^2\theta+\eta(2-\sin^2\theta)$	$-a_4$
1	±1	2	0	$-(3/2)^{1/2}A(3-\eta)\sin\theta\cos\theta$	$-(3/2)^{1/2}a_1$

FIGURE CAPTIONS.

Figure 1.

The zero field reference frames for a deuteron undergoing rotational flips about a two-fold axis. This model is identical to that of Barnes.[7]

Figure 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 linebroadening ($1/T_2$) 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 ($\kappa/A\approx1$).

Figure 3.

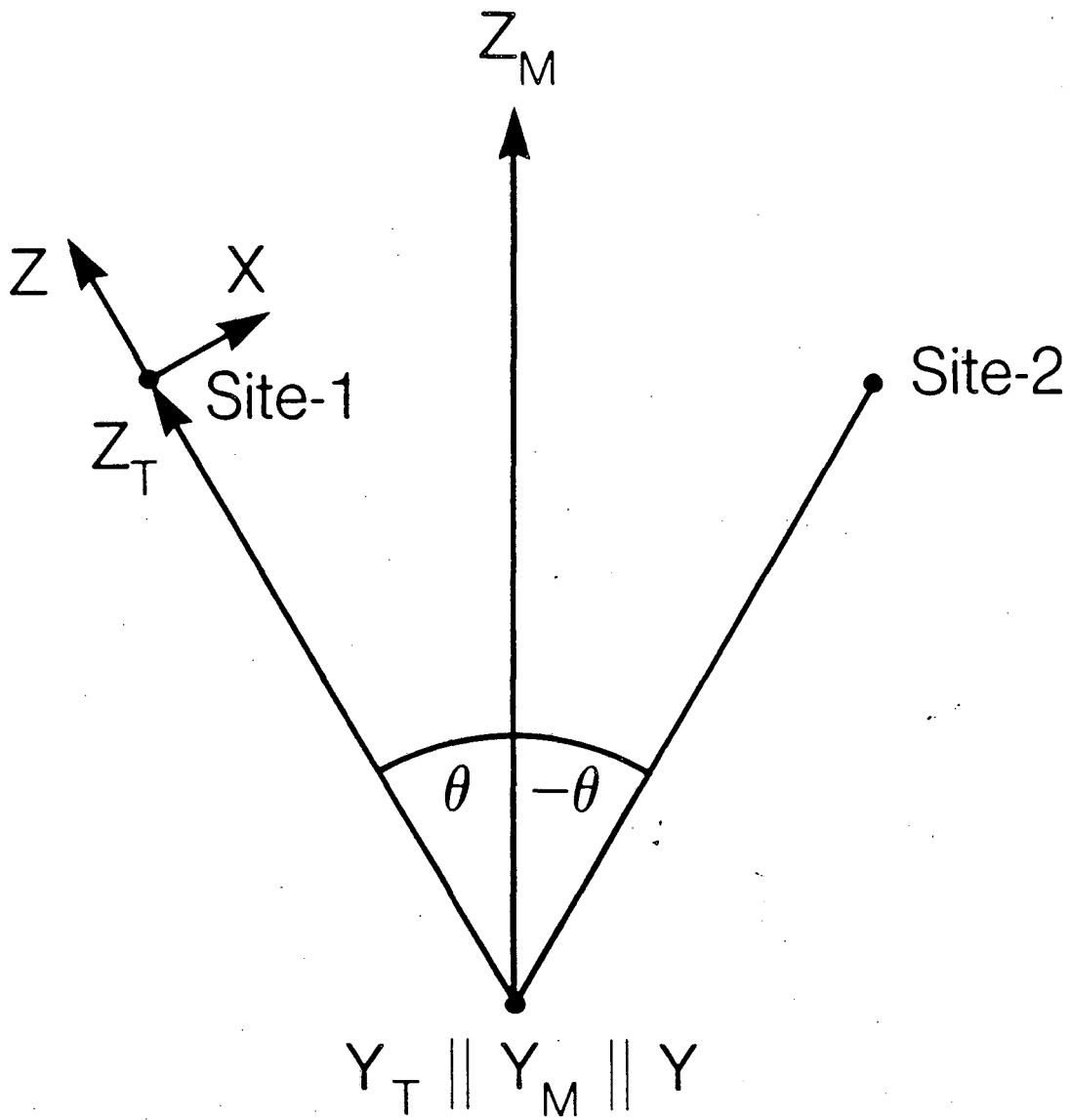
Simulated spectra for $2\theta=70^{\circ}$. The spectral parameters are as for Fig. 2. For this jump angle, an asymmetry parameter close to unity is obtained in the extreme line narrowing limit.

Figure 4.

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

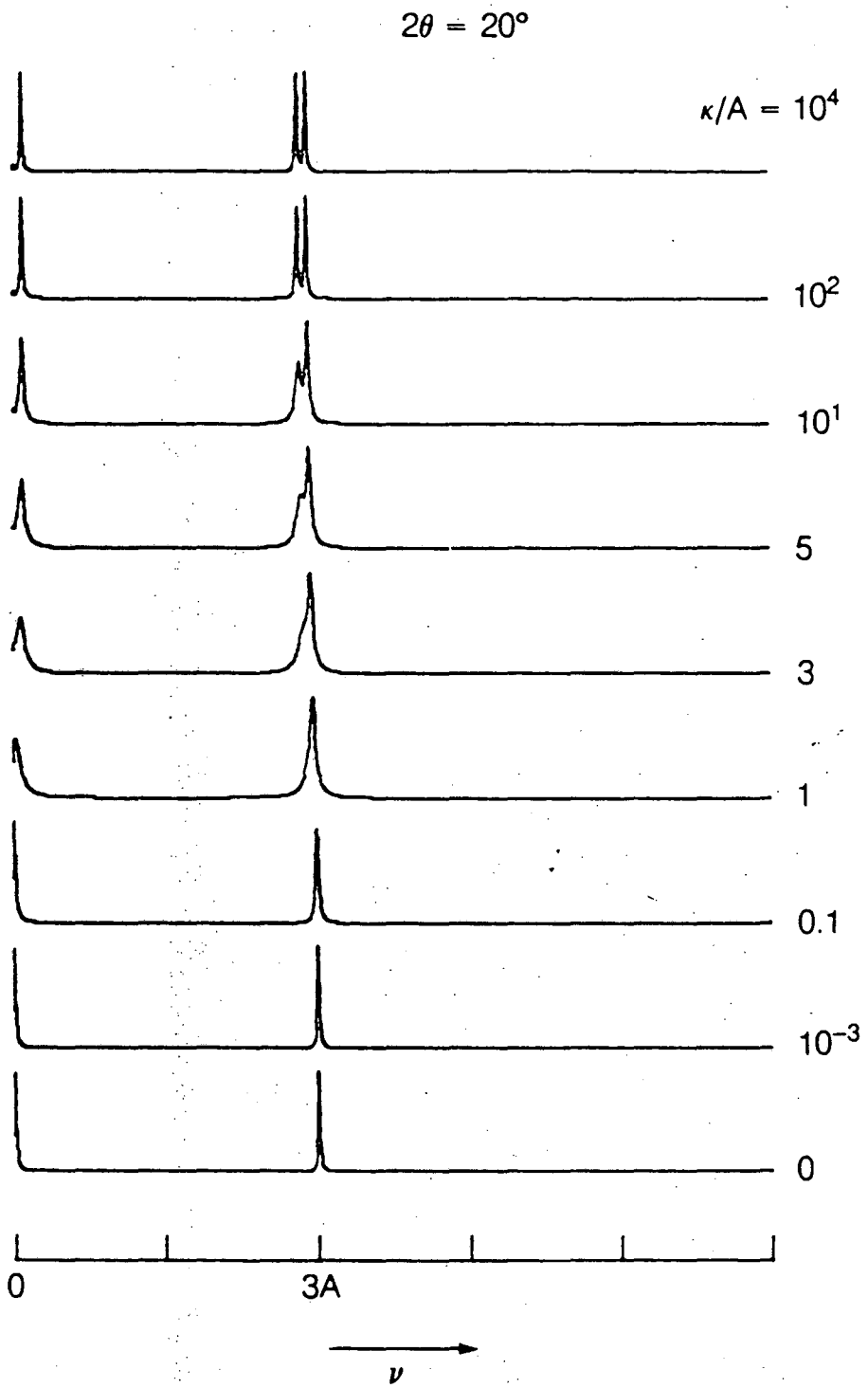
Figure 5.

Simulated spectra for 2θ=109.4°; η=0.1. The other parameters are as for the previous simulations. The spectra here are those predicted for a water molecule undergoing a two-fold rotation about its C_2 axis in crystalline hydrates.[2]



XBL 863-9780

Fig. 1.



XBL 8511-12513

Fig. 2.

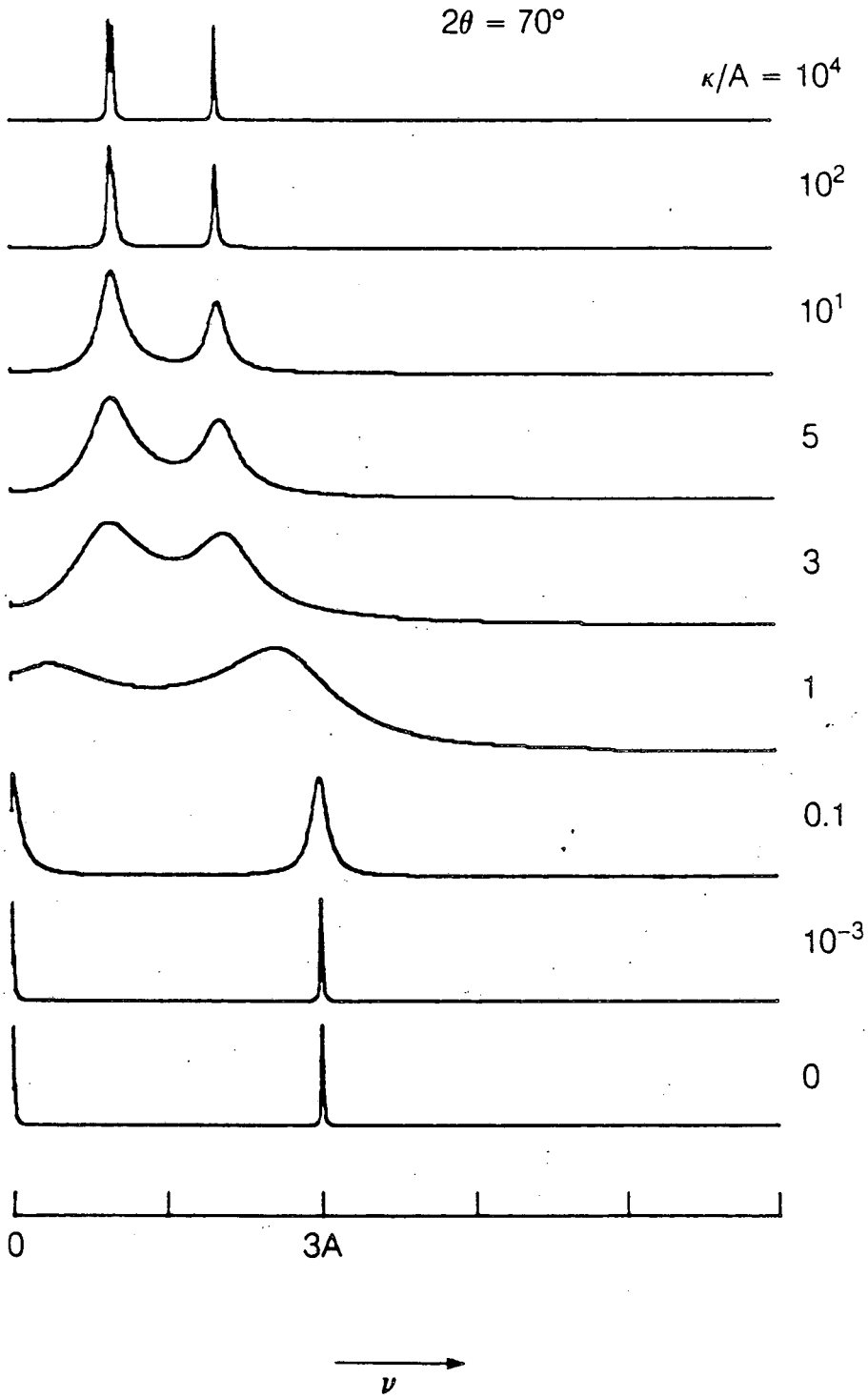
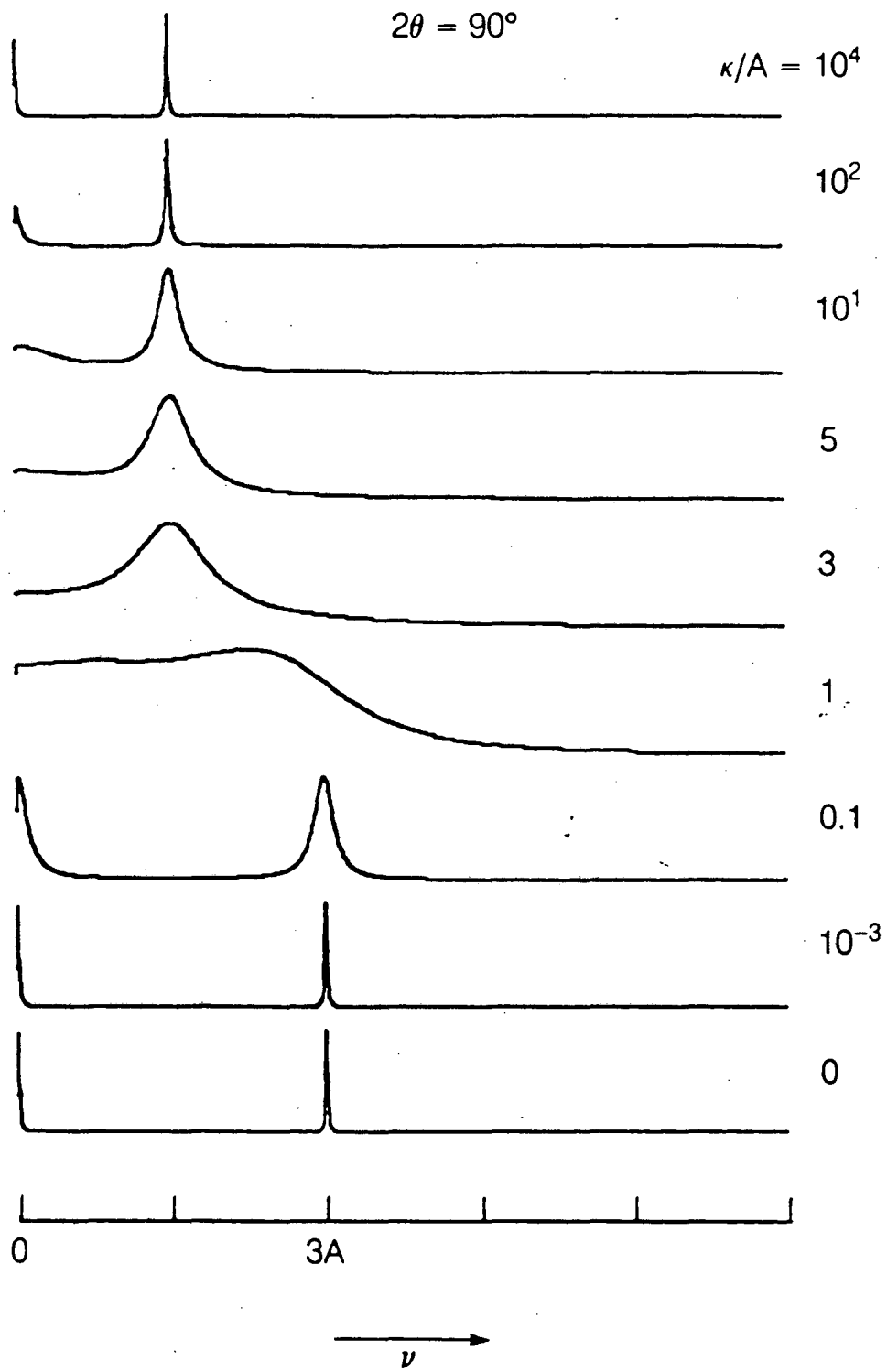


Fig. 3.

XBL 8511-12514



XBI 8511-12517

Fig. 4(a).

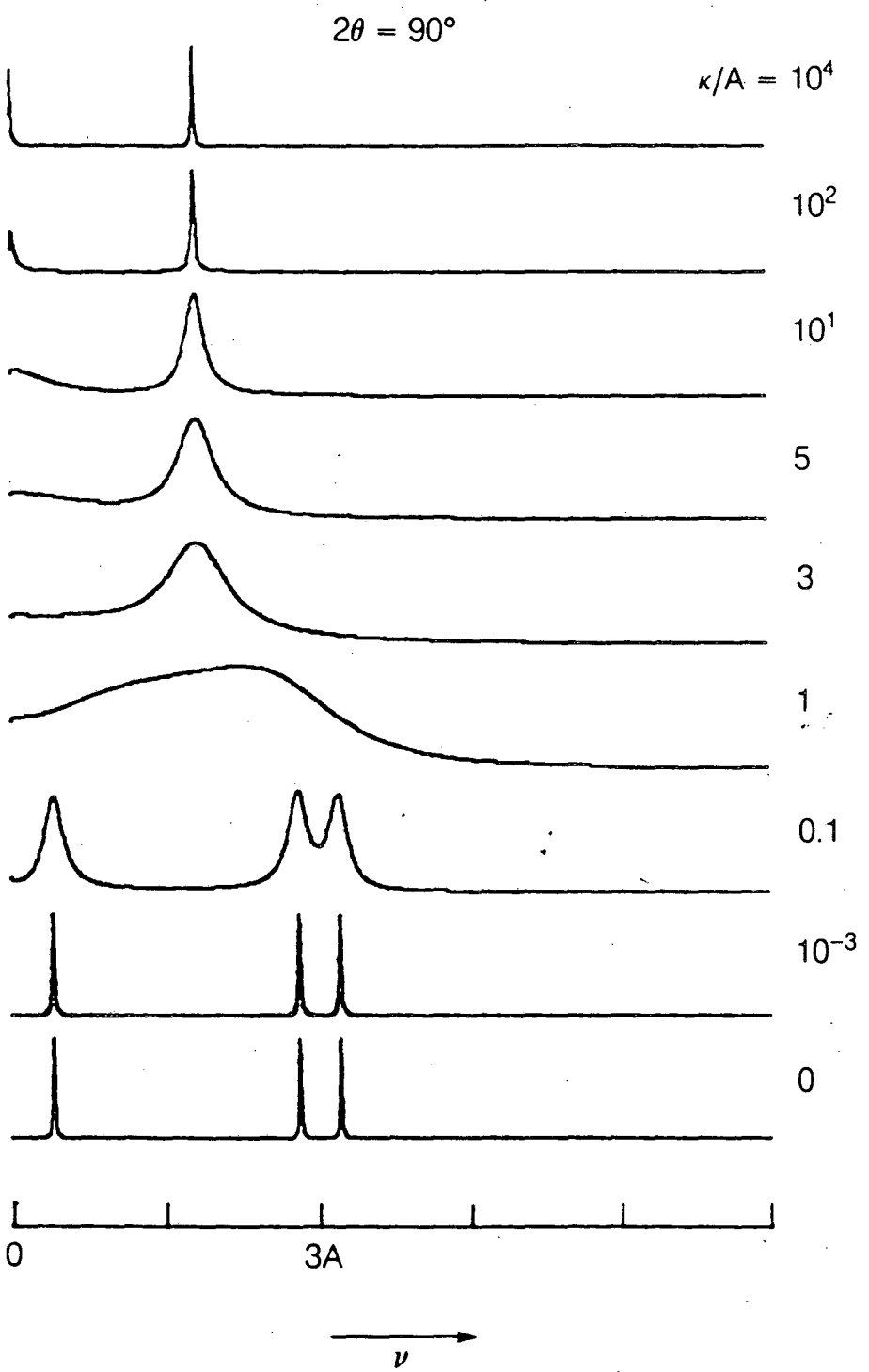
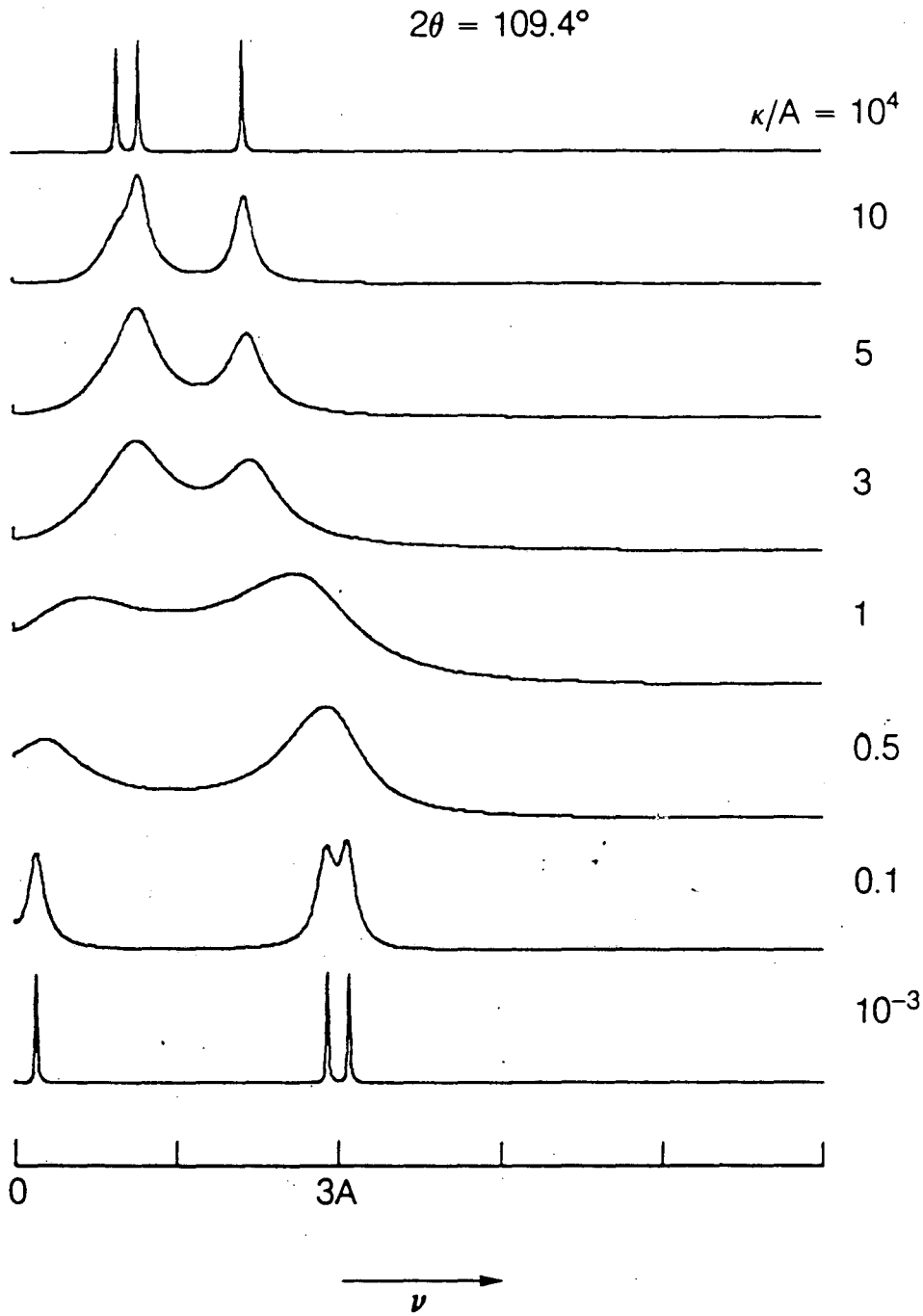


Fig. 4(b).

XBL 8511-12515



XBL 866-2227

Fig. 5.

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