

Planar 'coupled water pair' cluster in disordered solids: Theory of the ^1H NMR dipolar Hamiltonian

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Abstract. The proton NMR dipolar interaction Hamiltonian is set up for the model of planar 'coupled water pair' clusters in disordered solids. The Hamiltonian, when analytically solved, leads to interesting predictions of structured dipolar lineshapes when (a) the four protons are tightly coupled and (b) when the dipolar interaction is modulated by water molecules flipping between fixed directions. Detailed features of the line positions and intensities are worked out for both these models, and a suitable formulation is presented for simulating powder lineshapes in a variety of experimental situations.

Keywords. Proton NMR powder lineshapes; planar water pair; dipolar Hamiltonian.

1. Introduction

During the course of our ^1H NMR spectroscopic investigations of the location and dynamics of H_2O molecules in several hydrated powder and amorphous solids it has become necessary for us to develop theoretical models for a planar cluster of four interacting spin $I = \frac{1}{2}$ sites arising from 'coupled water pairs'. The NMR dipolar interaction Hamiltonian corresponding to this model, when solved fully, leads to interesting predictions of structured dipolar lineshapes when (a) the four protons remain tightly coupled, and (b) when the dipolar interaction is modulated by flipping water molecules. Apart from early preliminary studies of a static 'water pair' model by Itoh *et al* (1953) and of a roughly trapezoidal geometrical arrangement corresponding to nearest neighbour water pairs by Holcomb and Pedersen (1962) to explain ^1H NMR absorption in some hydrated single crystals, no detailed treatment of the NMR dipolar Hamiltonian which is adapted to studies of both static and dynamic aspects of the proton motion in such coupled water clusters is available in the literature. Interestingly, generalised NMR lineshape calculations are available to simulate the dynamics of four dipolar-coupled protons in tetrahedral (Lalowicz *et al* 1979), parallelogram and square (Nicol 1980) configurations.

In this paper, complete computations of the various allowed NMR transitions and spectral intensities for the planar coupled water pair model are reported, and detailed features of the line positions and intensities are worked out. A suitable formulation of our theory is also presented in a form which is most useful for simulating powder lineshapes in a variety of experimental situations. Some examples are mentioned.

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2. The dipolar Hamiltonian matrix

The NMR Hamiltonian for our four-proton system is

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_d \quad (1)$$

where \mathcal{H}_z and \mathcal{H}_d are, respectively, the Zeeman and dipolar Hamiltonians. If \mathbf{I}_1 , \mathbf{I}_2 , \mathbf{I}_3 and \mathbf{I}_4 are the individual spin vectors of the four protons, γ is their gyromagnetic ratio and \mathbf{B}_0 the applied magnetic field, then the Zeeman term is

$$\mathcal{H}_z = -\gamma\hbar B_0 \sum_{i=1}^4 I_{iz}. \quad (2)$$

It is well-known that the dipolar Hamiltonian, \mathcal{H}_d , is separable into a secular and a non-secular part (Slichter 1980), namely,

$$\mathcal{H}_d = \sum_{i<j} (\mathcal{H}_{dij}^0 + \mathcal{H}'_{dij}). \quad (3)$$

It turns out that, since we are interested only in transitions in which angular momentum components change by \hbar , only the secular part of the dipolar Hamiltonian, \mathcal{H}_{dij}^0 , which commutes with the Zeeman Hamiltonian, needs to be considered. Accordingly, our effective dipolar Hamiltonian assumes the truncated form

$$\begin{aligned} \mathcal{H}_d^0 &= \sum_{i<j} \mathcal{H}_{dij}^0 \\ &= \sum_{i<j} (\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{zi}I_{zj}) A_{ij}, \end{aligned} \quad (4)$$

where A_{ij} are the terms containing only the spatial coordinates of our problem. Explicitly,

$$\begin{aligned} A_{ij} &= (\gamma^2 \hbar^2 / 2r_{ij}^3) (3 \cos^2 \theta_{ij} - 1) \\ &= (\gamma^2 \hbar^2 / 2r_{ij}^3) P_2(\cos \theta_{ij}) \end{aligned} \quad (5)$$

where θ_{ij} is the angle between \mathbf{B}_0 and \mathbf{r}_{ij} , the vector connecting dipoles i and j .

The four-spin problem in general yields $2^4 = 16$ states, and the most general representation of these states is the so-called |LSIM> basis (Bersohn and Gutowsky 1954; Lalowicz *et al* 1979) where $\mathbf{L} = \mathbf{I}_1 + \mathbf{I}_2$, $\mathbf{S} = \mathbf{I}_3 + \mathbf{I}_4$, $\mathbf{I} = \mathbf{L} + \mathbf{S}$, and \mathbf{M} , the z -component of \mathbf{I} projected along the direction of \mathbf{B}_0 , is such that $-I < M < +I$. In zero-order, our 16 states thus group into two singlets ($M = \pm 2$), two quartics ($M = \pm 1$) and a sextic ($M = 0$); the sextic will further factor out into two cubics if our states are labelled by I , the total angular momentum quantum number. Dipolar interactions between the spins, given by $\mathcal{H}_d^0 (\ll \mathcal{H}_z)$, constitute the perturbation which, to first order, further splits the above degeneracies. The representation of the dipolar Hamiltonian in our |LSIM> basis can then be divided into six submatrices with zero non-diagonal terms between them. The dipolar elements of our overall Hamiltonian matrix are then

$$\begin{aligned} a &= A_{12} + A_{34}, \\ b &= A_{13} + A_{14} + A_{23} + A_{24}, \end{aligned}$$

$$c = A_{13} + A_{14} - A_{23} - A_{24},$$

$$d = A_{13} - A_{14} + A_{23} - A_{24},$$

$$e = A_{13} - A_{14} - A_{23} + A_{24}. \quad (6)$$

3. The 'tightly coupled' model

For a general orientation of the magnetic field, the Hamiltonian matrix is only partially solvable analytically in the case of a fully ordered rigid structure (Itoh *et al* 1953), but we may obtain a complete analytical solution by imagining the component H_2O molecules to be simultaneously flipped in phase about their respective C_2 axes. We shall refer to this as a 'tightly-coupled model', which effectively leads to a disordered, but equivalent, average structure of 4 protons interacting in a plane. We emphasize that this 'disordered' cluster differs from the ordered, rigid cluster only by an inversion; the point has been made in the earlier literature that the discrete NMR spectrum for such cases will be the same (Bersohn and Gutowsky 1954; Holcomb and Pedersen 1962). For a pair of water molecules, our tightly-coupled model then leads to an average of \mathcal{H}_d^0 over the equivalent conformations shown in figure 1. It is readily seen

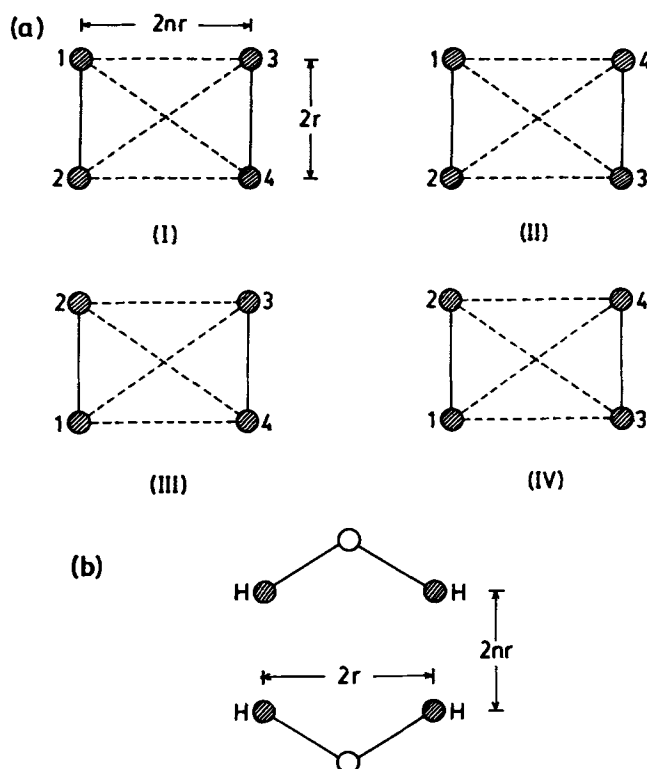


Figure 1. (a) Equivalent conformations of the proposed 'tightly-coupled' water pair model. The shaded circles represent the hydrogen sites with their respective numerical labels as depicted. (b) The two H_2O molecules oriented to define the inter and intra proton-proton distances.

which gives

$$E = (1/2)(k + 2l) \pm [(k + 2l)^2 + 8(k - l)^2]^{1/2}$$

$$= X \pm Y, \tag{8}$$

where the short-hand notations X and Y have an obvious meaning.

Now for the corresponding eigenfunctions $|\pm\rangle$, the coefficients are evaluated by substituting $E = X \pm Y$. We get, after normalization,

$$|\pm\rangle = \frac{1}{[1 + R_{\pm}^2]^{1/2}} |1100\rangle + \frac{R_{\pm}}{[1 + R_{\pm}^2]^{1/2}} |1120\rangle, \tag{9}$$

where

$$R_{\pm} = -\frac{X \pm Y}{(\sqrt{2})(k - l)}. \tag{10}$$

The dipolar interaction energy level diagram for the four spin $\frac{1}{2}$ system is shown in figure 2. Applying the selection rule $\Delta M = \pm 1, \Delta L = 0, \Delta S = 0, \Delta I = 0$, the various

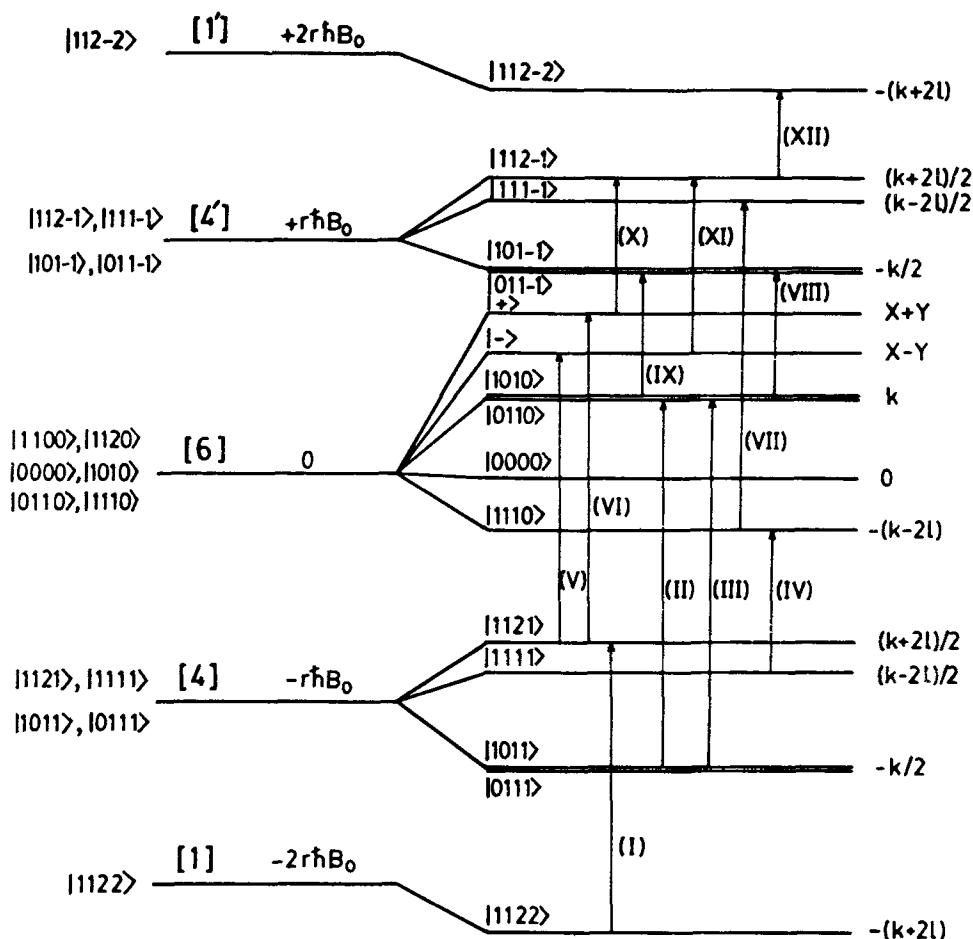


Figure 2. Energy levels of the dipolar interaction Hamiltonian for the 'four spin $\frac{1}{2}$ ' system, showing the allowed transitions between the derived eigenstates.

transition probabilities $|\langle \psi_i | I_x | \psi_f \rangle|^2$ are calculated. For the allowed transitions, the computed theoretical line intensities and line positions are shown in table 1. The theoretical NMR stick spectrum of the four-spin $\frac{1}{2}$ system corresponding to our tightly-coupled model, drawn from the calculated values of table 1, is shown in figure 3.

4. The 'weakly-coupled model' of rapidly reorienting nuclear pairs

We now wish to derive average values of the A_{ij} when the two proton-pairs behave not as a tightly-coupled group but as relatively isolated pairs which interact while rapidly reorienting between two fixed directions. Andrew and Brookeman (1970) have considered such a model, and we may determine the A_{ij} of our dipolar Hamiltonian by taking over some of their results. Evidently,

$$\langle A_{ij} \rangle = \sum_{c=1}^{IV} A_{ij}(c),$$

where c is one of the nuclear pair conformations (I to IV) given in figure 1.

The physical situation of the orientation of nuclear pairs may be considered with the help of a stereogram (figure 4). The stereogram shows only a pair of nuclei for

Table 1. Allowed transitions, with corresponding energies, intensities and line positions, for the tightly-coupled water pair model.

Allowed transitions ^a	$\Delta E^b = E_f - E_i$	Intensity $I_{(\psi_f - \psi_i)}$	Normalized intensity	Relative intensity	Line position ^b
$ 1011\rangle \rightarrow 1010\rangle$ $ 0111\rangle \rightarrow 0110\rangle$	$(3/2)k$	1/2	1/8	2	$(3/2)k[2]^*$
$ 1010\rangle \rightarrow 101-1\rangle$ $ 0110\rangle \rightarrow 011-1\rangle$	$(-3/2)k$	1/2	1/8	2	$(-3/2)k[2]$
$ 1122\rangle \rightarrow 1121\rangle$	$(3/2)(k+2l)$	1	1/8	2	$(3/2)(k+2l)[1]$
$ 112-1\rangle \rightarrow 112-2\rangle$	$(-3/2)(k+2l)$	1	1/8	2	$(-3/2)(k+2l)[1]$
$ 1110\rangle \rightarrow 111-1\rangle$	$(3/2)(k-2l)$	1/2	1/16	1	$(3/2)(k-2l)[1]$
$ 1111\rangle \rightarrow 1110\rangle$	$(-3/2)(k-2l)$	1/2	1/16	1	$(-3/2)(k-2l)[1]$
$ 1112\rangle \rightarrow +\rangle$ $ -\rangle \rightarrow 112-1\rangle$	$(1/2)[(k+2l)^2 + 8(k-l)^2]^{\frac{1}{2}}$	3/2	3/16	3	$(1/2)[(k+2l)^2 + 8(k-l)^2]^{\frac{1}{2}}[2]$
$ +\rangle \rightarrow 112-1\rangle$ $ 1121\rangle \rightarrow -\rangle$	$(-1/2)[(k+2l)^2 + 8(k-l)^2]^{\frac{1}{2}}$	3/2	3/16	3	$(-1/2)[(k+2l)^2 + 8(k-l)^2]^{\frac{1}{2}}[2]$

* The numerics inside the square brackets in the last column indicate the possible number of lines for the corresponding energies

$$|\pm\rangle = 1/[1 + R_{\pm}^2]^{\frac{1}{2}}|1100\rangle + R_{\pm}/[1 + R_{\pm}^2]^{\frac{1}{2}}|1120\rangle$$

and

$$R_{\pm} = -\frac{X \pm Y}{(\sqrt{2})(k-l)},$$

$$X \pm Y = (\frac{1}{2})(k+2l) \pm (\frac{1}{2})[(K+2l)^2 + 8(k-l)^2]^{\frac{1}{2}}.$$

$${}^b k = (\frac{1}{2})[a_{12} + a_{34}],$$

$$l = (\frac{1}{2})[a_{13} + a_{14} + a_{23} + a_{24}].$$

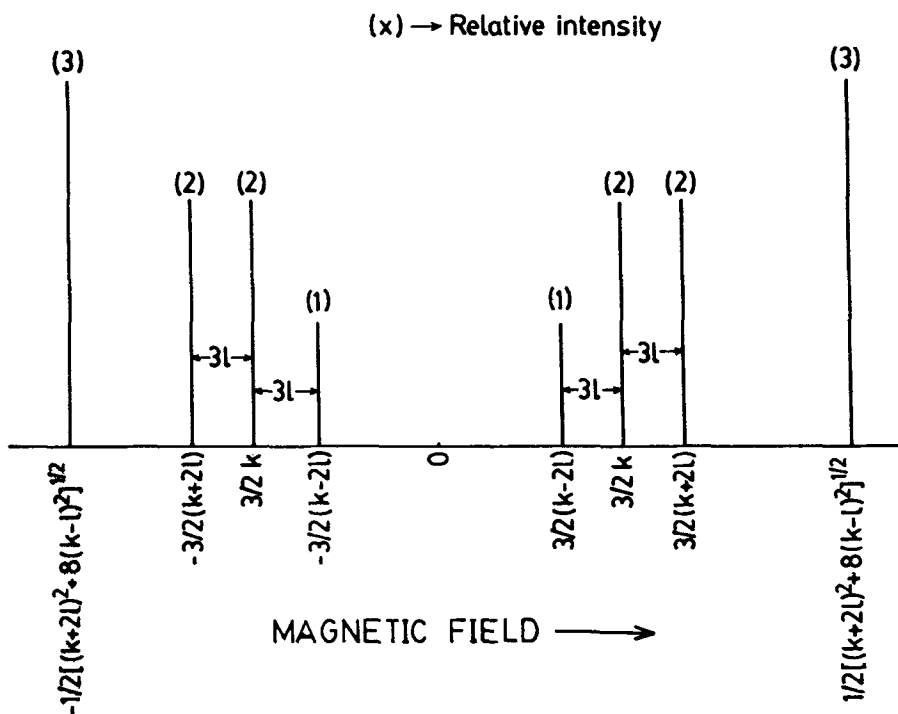


Figure 3. Theoretical proton NMR dipolar coupling pattern for the planar 'tightly-coupled' model, using the results of table 1.

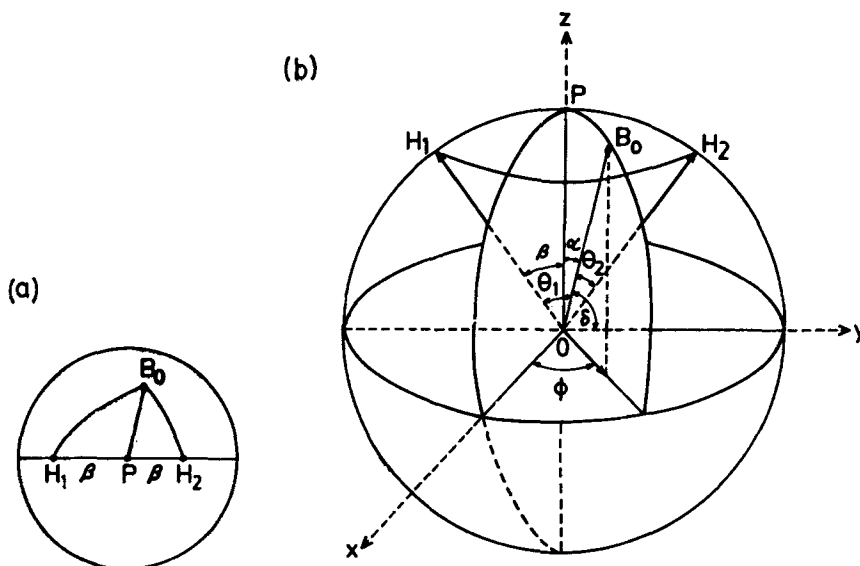


Figure 4. The orientation of a nuclear pair (H_1, H_2) shown in (a) stereographic projection, (b) the corresponding spherical polar coordinate system.

simplicity, but can be modified for any number of pairs. The definitions of the angles appearing in the stereographic projections shown in figure 4a, which has been used in a previous study (Andrew and Brookeman 1970), become clearer if we consider the spherical polar system drawn in figure 4b. Two nuclear vectors OH_1 and OH_2 of one water molecule make equal angles β with the Z -axis (figure 4b) which forms the pole of the stereogram; these vectors make angles θ_1 and θ_2 , respectively, with the direction of the applied magnetic field, \mathbf{B}_0 . α is the angle between the Z -axis and the field direction and ϕ is the azimuthal angle. \mathbf{B}_0 makes an angle δ with the Y -axis.

As before, the truncated dipolar Hamiltonian for one nuclear pair is

$$\mathcal{H}_d^0 = 1/2(\gamma^2 \hbar^2 r^{-3})(\mathbf{I}_1 \cdot \mathbf{I}_2 - 3I_{z1}I_{z2})(3 \cos^2 \theta - 1). \quad (11)$$

If r moves rapidly between the two directions OH_1 and OH_2 spending equal times in each orientation, then we have to replace the \mathcal{H}_d^0 by its average value, $\overline{\mathcal{H}_d^0}$, over the two orientations (Gutowsky and Pake 1950; Abragam 1961). As θ is the parameter undergoing temporal modulation, the spectrum of such oriented nuclear pairs would contain two lines of equal intensity, as is well-known (Pake 1948; Gutowsky and Pake 1950),

$$h = \pm h_0(3 \cos^2 \theta - 1), \quad \text{where } h = \mathbf{B} - \mathbf{B}_0. \quad (12)$$

Taking the average over two orientations and using simple spherical trigonometric relationships (figure 4b), we may write the above equation as

$$\begin{aligned} h &= \pm \frac{1}{2} h_0 [(3 \cos^2 \theta_1 - 1) + (3 \cos^2 \theta_2 - 1)] \\ &= \pm h_0 (3 \cos^2 \alpha \cos^2 \beta + 3 \sin^2 \alpha \sin^2 \beta \cos^2 \phi - 1). \end{aligned} \quad (13)$$

(13) provides the starting point for our four-spin system composed of two H_2O molecules oriented face-to-face and executing 180° flips. Since the inter-nuclear vectors $\mathbf{r}_{12}, \mathbf{r}_{34}$ are oriented through 0° or 180° , A_{12} and A_{34} of our model would become (see figure 1),

$$A_{12} = A_{34} = A' = \gamma \hbar / 8r^3 (3 \sin^2 \alpha \cos^2 \phi - 1). \quad (14)$$

For evaluating A_{13}, A_{24}, A_{14} and A_{23} , we take the average value of all contributions for different reorientations, namely,

$$A_{13} = A_{24} = A_{14} = A_{23} = A'', \quad (15)$$

where

$$\begin{aligned} A'' &= \frac{1}{4} \left\{ \begin{array}{c} \circ \\ | \\ \bullet \end{array} \right\} + \begin{array}{c} \bullet \\ | \\ \circ \end{array} + \begin{array}{c} \circ \\ / \\ \bullet \end{array} + \begin{array}{c} \bullet \\ / \\ \circ \end{array} \left. \right\} \\ &= \frac{1}{2} \left(\begin{array}{c} \circ \\ | \\ \bullet \end{array} \right) + \frac{1}{2} \left[\frac{1}{2} \left(\begin{array}{c} \circ \\ / \\ \bullet \end{array} + \begin{array}{c} \bullet \\ / \\ \circ \end{array} \right) \right], \end{aligned} \quad (16)$$

(refer to figure 1) $\circ - \bullet$ - denotes water-proton pair.

From our model, figure 1b,

$$A'' \left(\begin{array}{c} \circ \\ | \\ \bullet \end{array} \right) = (\gamma\hbar/8n^3r^3)(3\cos^2\alpha - 1),$$

$$A'' \left[\left(\frac{1}{2} \right) \left(\begin{array}{c} \circ \\ | \\ \bullet \end{array} + \begin{array}{c} \circ \\ | \\ \bullet \end{array} \right) \right] = \gamma\hbar/[2r\sqrt{(1+n^2)}]^3 +$$

$$+ \left[\frac{3n^2}{(1+n^2)}\cos^2\alpha + \frac{3}{(1+n^2)}\sin^2\alpha\cos^2\phi - 1 \right],$$

and

$$\beta = \sin^{-1} \left[\frac{1}{\sqrt{(1+n^2)}} \right]. \quad (17)$$

Combining (16) and (17), we obtain

$$A'' = (\gamma\hbar/16n^3r^3)(3\cos^2\alpha - 1) + [\gamma\hbar/16(1+n^2)^{3/2}r^3] \times$$

$$\times \left[\frac{3n^2}{(1+n^2)}\cos^2\alpha + \frac{3}{(1+n^2)}\sin^2\alpha\cos^2\phi - 1 \right]. \quad (18)$$

For $n = 1$ (i.e., water molecules flipping in a square configuration),

$$A'' = (\gamma\hbar/16r^3) \left\{ \frac{3}{4\sqrt{2}}(4\sqrt{2} + 1)\cos^2\alpha + \frac{3}{4\sqrt{2}}\sin^2\alpha\cos^2\phi - \frac{2\sqrt{2} + 1}{2\sqrt{2}} \right\}. \quad (19)$$

In a simpler form, (18) may be rewritten as

$$A'' = (\gamma\hbar/16r^3)(k_1\cos^2\alpha + k_2\sin^2\alpha\cos^2\phi + k_3),$$

where

$$k_1 = (3/2)\{1/n^3 + [n^2/(1+n^2)^{5/2}]\},$$

$$k_2 = (3/2)[1/(1+n^2)^{5/2}],$$

and

$$k_3 = -(1/2)[1/n^3 + 1/(1+n^2)^{3/2}], \quad (20)$$

where n is the ratio of r_{13}/r_{12} (figure 1b) and r is half the H-H distance in a water molecule.

We notice that, in this weakly-coupled model, the k and l elements of the matrix of (7) are given by

$$k = A(3\sin^2\alpha\cos^2\phi - 1),$$

$$l = A(k_1\cos^2\alpha + k_2\sin^2\alpha\cos^2\phi + k_3), \quad (21)$$

where $A = (\gamma\hbar/8r^3)$ and k_1 , k_2 and k_3 are defined in (20). The proton NMR dipolar spectrum is again computed by using the above k, l values in the matrix (7), and the general proton NMR dipolar coupling pattern is as shown in figure 5. The spectrum consists of ten lines of which the $\pm (3/2)k$ lines are each doubly degenerate (this is to

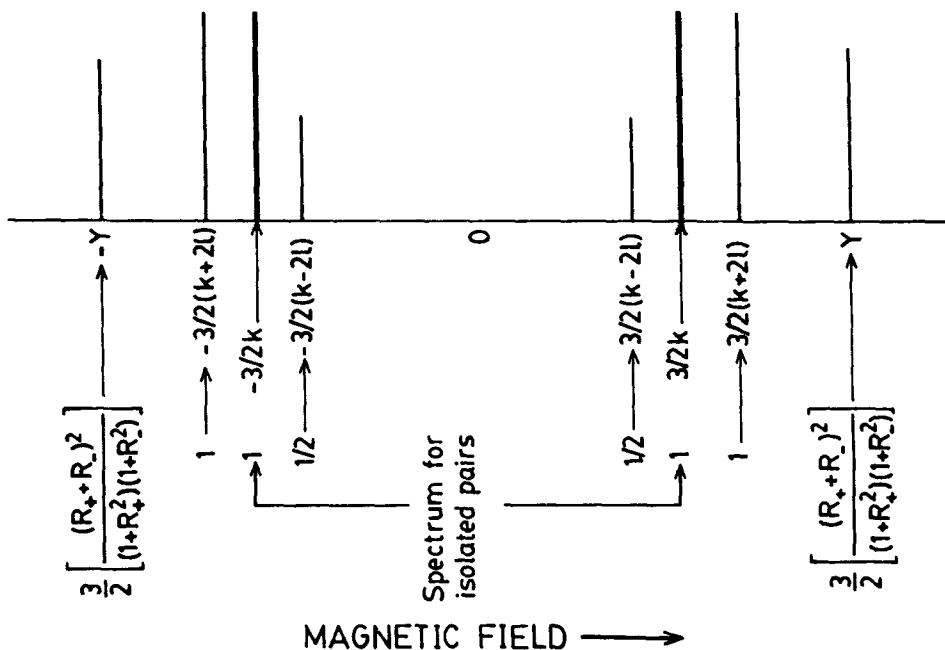


Figure 5. Theoretical proton NMR dipolar coupling pattern for the 'weakly-coupled' model.

be contrasted with figure 3). An instructive check on our calculations is to make $r_{13} = r_{24} \gg r_{12}, r_{34}$ (figure 1a) when the spectrum should just collapse to two lines separated by the rigid lattice proton-proton interaction (Pake 1948). Since $l \cong 0$ for this model, then $Y = (3/2)k$, $X = (1/2)k$, and we see that, indeed, all the lines collapse to $\pm 3/2$, intensities of the two lines being equal.

5. Powder lineshapes and formulation for the computer

Relating the experimental spectra of powdered polycrystalline specimens to (1) requires that our NMR spin-Hamiltonian be diagonalized to yield spectral lineshape profiles generated when the various line positions, $F(\bar{B}_M)$, made up of suitable angular averages of the k and l values (see figures 3 and 5), are computed in $(\cos \alpha, \phi)$ space and suitably weighted by the appropriate transition intensities. A fast and efficient procedure is to solve for the densities of these resonance fields at a random distribution of points in a grid of $(\cos \alpha, \phi)$ space using a Monte Carlo algorithm (Raghunathan and Sur 1984; Raghunathan and Sivasubramanian 1986; Raghunathan 1987; Raghunathan and Das 1989). The ensemble of lines thus generated is convoluted with a suitable shape function, $s(\bar{B}_M - B_0)$ representing the unresolvable, small extra dipolar interaction of a certain 4-spin cluster with its neighbours. The final, convoluted lineshape function in compact form is then

$$S(\bar{B}) = \left[\int_0^{2\pi} \int_0^\pi F(\bar{B}_M) d(\cos \alpha, \phi) \right] s(\bar{B}_M - B_0). \quad (22)$$

Calculations of several typical NMR lineshape simulations based on our line position and transition intensity computations [(8) to (10)] followed by the convolution procedure, (22), have been carried out in our laboratory for both the 'tightly-coupled' and 'weakly-coupled' models by making various choices of the parameters r and n . Figure 6 demonstrates, for example, two typical polycrystalline lineshapes expected for the two models. Good agreement between our theory and experiment is found from the proton NMR of several crystalline hydrates. For example, ^1H NMR lineshapes recorded for the polycrystalline hydrate of K_2HgCl_4 at liquid helium temperature contain well-resolved dipolar couplings which are analysable by our 'tightly-coupled' 4-spin model, whereas at temperatures above 77 K the lineshapes of this hydrate change over to the pattern predicted by figure 5, indicating a change in the crystal dimensions as well as in the motional dynamics of H_2O molecules. Further detailed lineshapes and proton T_1 measurements on this hydrate as well as on the analogous hydrate of K_2SnCl_4 are in progress and will be reported in a subsequent communication.

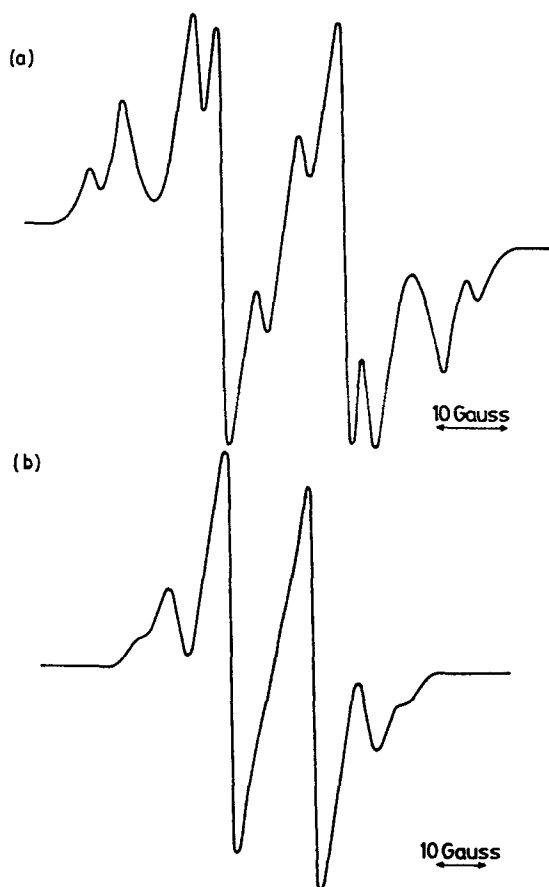


Figure 6. Polycrystalline proton NMR lineshapes computed for (a) the 'tightly-coupled' model, and (b) the 'weakly-coupled' model. In both cases, the intramolecular proton-proton distance ($2r$) = 1.607 \AA , the intermolecular distance ($2nr$) = 1.70 \AA , and the Gaussian broadening parameter = 3.0 gauss.

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