Selective determination of dipole-dipole interaction from high-resolution NMR powder spectra

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The influence of magnetic dipole-dipole interaction in isolated pairs of nuclei between sparse spins $S = 1/2$ and closely spaced spins $I = 1/2$ on high-resolution NMR powder spectra is calculated. This interaction is restored by simultaneous mechanical rotation of the sample and application of radiofrequency fields, thus allowing the use of the two-dimensional Fourier-transform method for a selective study of individual dipole-dipole interactions between the nuclei under high-resolution conditions. Under certain conditions, the effective Hamiltonian of the spin system contains only the term of dipole-dipole interaction between heteronuclear spins, which allows this interaction to be studied in pure form. In a limiting approximation and in the case of two rf fields h_{ef}, these conditions are either $|h_{ef}^{S} - h_{ef}^{I}| = \omega_r$ or $|h_{ef}^{S} - h_{ef}^{I}| = 2\omega_r$. For the case of a single rf field, acting only on the I spins, condition $h_{ef}^{I} = 2\omega_r$ must be satisfied. The NMR spectrum and the line shape can be used to determine the constants of dipole-dipole interaction.

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1. INTRODUCTION

The sharply increasing information content of NMR methods in the study of the structure of solids is connected with the development of high-resolution NMR, the basic idea of which is the selective averaging of the individual interactions between nuclear spins.

The selective suppression in the experiment of individual undesirable interactions can be accomplished by the method of coherent averaging. The structural properties of the sample are usually studied by the measurement of the components of the chemical-shift tensor. Here the dipole-dipole interaction between like[1–4] or unlike[5–7] spins is suppressed.

It was shown in Refs. 8 and 9 that more extensive information on the structure of a solid can be obtained by use of the method of two-dimensional Fourier NMR spectroscopy, which allows us to determine such parameters as the chemical-shift tensor and the dipole-dipole interaction between the magnetic moments of the nuclei.

In comparison with the chemical shift, the dipole-dipole interaction reflects more completely the space-structure features of the sample, since the connection between the structure of the crystal and the magnitude of the dipole-dipole splitting is simple, being $v_d \sim r_{ij}^{-3} P_2(\cos\theta_{ij})$. Along with explicit advantages, there are also great difficulties, as noted by Waugh.[10] The problem is that the NMR spectrum in the general case reflects the dipole-dipole interaction of very many spins, the theoretical account of which is practically impossible.

The possibility of the use of dipole-dipole interaction for obtaining information on the structure was first demonstrated by Pake for gypsum,[11] in which the nuclear magnetic moments are encountered in the form of pairs. The dipole-dipole interaction between like nuclei was investigated and the spectrum of the single crystal and the line shape of gypsum powder were obtained.

For the study of dipole-dipole interaction between heteronuclei the interaction under investigation is recast in this paper, along with the suppression of other interactions, in a very simple form that is convenient for interpretation. By the simultaneous use of fast mechanical rotation of the solid sample at the magic angle and of high frequency fields, we can selectively preserve or restore the effect of individual interactions on the evolution of the spin system even under the conditions of fast magnetic rotation of the sample,[12,13] i.e., under conditions of high resolution.

The mechanical rotation of the sample produces a harmonic dependence of the spatial coordinates on the time in the spin Hamiltonian. At fast rotation of the sample (high frequency ω_r), at the magic angle ($\theta_m = \arccos 1/\sqrt{3}$) with the direction of the constant magnetic field H_0, the anisotropic interactions are averaged.[14] The spectrum obtained in the corresponding experiment consists of narrow lines of the individual nuclei with different chemical shifts and does not contain information on the anisotropy of the interactions. On the other hand, the action of continuous rf fields[15,16] or rf pulses[2] on the sample gives rise to harmonic time dependences of the spin coordinates in the spin Hamiltonian. At a suitable choice of parameters of the mechanical rotation and of the high frequency fields, we can obtain the synchronous change in the spin and spatial coordinates and, by the same token, selectively remove the time dependence of certain terms of the Hamiltonian.[2] This allows us to apply the well-known methods of two-dimensional Fourier transformation[17,18] for a selective investigation of the individual internuclear interactions under high resolution conditions, in spite of the fact that the same interactions should be completely suppressed for recording of high-resolution NMR spectra.

2. EXPERIMENTAL CONDITIONS

In the present work, we study the effect of dipole-dipole interaction on high-resolution NMR spectra of a sparse spin

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$S = 1/2$ in the case of a powdered sample whose spin system contains a large number of spins $I = 1/2$ in addition to the spin S.

For the theoretical explanation of the proposed experiments, we consider, as was done in Ref. 12, one single crystal which rotates in a powder from the time $t = 0$ with a frequency ω_r in a strong external magnetic field H_0 directed along the z axis of the laboratory system of coordinates (LS). The axis of rotation in the yz plane of the LS forms an angle θ_m with the z axis.

We describe two variants of the experiment. In the first variant, at the time $t = 0$, two rf fields with frequencies ω_1 and ω_2, respectively, directed along the x axis of the LS are turned on. They influence correspondingly the I and S spins;

$$H(t)=i[2H^I \cos \omega_1 t+2H^S \cos \omega_2 t]. \tag{1}$$

In the second variant, one HF field that influences the spins I is turned on at the instant $t = 0$.

The change of the state of the spin system obeys Liouville's equation

$$\dot{\rho}=-iL(H)\rho, \tag{2}$$

where

$$L(H)\rho=[H, \rho]. \tag{3}$$

The Hamiltonian in Eq. (2) can be represented as a sum of terms describing the different interactions in the spin system

$$H=H_z{}^I+H_c{}^I+H_d{}^{II}+H_J{}^{II}+H_z{}^S+H_c{}^S+H_d{}^{IS}+H_J{}^{IS}+H_{rf}{}^I+H_{rf}{}^S. \tag{4}$$

In (4), we have used the standard notation (see, for example, Ref. 12).

3. ACCOUNT OF MECHANICAL ROTATION OF THE SAMPLE

For a rotating sample, it is useful to employ in the Hamiltonian spherical tensors[19,20] for the description of the interactions

$$H_\lambda=C_\lambda \sum_k \sum_{q=-k}^{k} (-1)^q A_{kq}{}^\lambda T^\lambda_{k-q}, \tag{5}$$

where λ denotes the type of interaction. The tensors A and T describe the spatial and spin parts of the interaction, respectively. The spherical tensors transform in the rotations in accord with the representation of the rotation group $D(\alpha, \beta, \gamma)$:

$$R(\alpha, \beta, \gamma) T_{kq} R^{-1}(\alpha, \beta, \gamma)=\sum_{p=-k}^{k} T_{kp} D_{pq}{}^k(\alpha, \beta, \gamma). \tag{6}$$

Here R is the rotation operator and α, β, γ are the Euler angles,

$$D_{pq}{}^k(\alpha, \beta, \gamma)=e^{-i\alpha p} d_{pq}{}^k(\beta) e^{-i\gamma q},$$

d^k_{pq} are reduced rotation matrices.[21]

The tensor A_{kq}, which characterizes the spatial part, transforms according to (6) from the system of coordinates, connected with the sample, to the LS, where the measurements are carried out:

$$A_{kq}{}^L=\sum_{p=-k}^{k} A_{kp} e^{i\pi/2(p-q)} e^{-ip\omega_r t} d_{pq}{}^k(\theta_m). \tag{7}$$

The quantities in the LS are labeled by the index L.

It can be seen from (7) that the time dependence of the Hamiltonian is described by the frequencies $p\omega_r$.

For our purposes, we write out in greater detail the dipole-dipole interaction and confine ourselves in it to spherical tensors up to second rank, i.e., $k = 2$. The term of the dipole-dipole interaction between the identical I-spins is then expressed by

$$H_d^{LII}=\sum_{i<j} \sum_{q=-2}^{2} (-1)^q A_{2q}^{Lij} T_{2-q}^{ij}, \tag{8}$$

where

$$T_{2-q}^{ij}=\sum_{M_1=-1}^{1} C(112; M_1, -q-M_1) I^i_{1M_1} I^j_{1,-q-M_1},$$

C are Clebsch-Gordan coefficients.

A similar expression is obtained for the dipole-dipole interaction between the spins I and S;

$$H_d^{LIS}=\sum_{n} \sum_{q=-2}^{2} (-1)^q A_{2q}^{nL} T_{2,-q}^{nIS},$$

$$T_{2-q}^{nIS}=\sum_{M_1=-1} C(112; M_1, -q-M_1) I_{1M_1} S_{1,-q-M_1}. \tag{9}$$

In Eqs. (8) and (9), the tensor A^L can be found from Eq. (7).

Thus, expressions are obtained also for the other terms of the Hamiltonian in the LS. These terms contain, in addition to the time independent terms, other terms that depend harmonically on the time, with frequencies ω_r and $2\omega_r$.

4. SPECTRUM AND LINE SHAPE IN THE CASE OF TWO RF FIELDS

In accord with the conditions noted above for the first variant of the experiment, we assume that, along with the rapid mechanical rotation of the sample, the observed spin system is acted upon by two rf fields (1), which are turned on at the time instant $t = 0$, and which are applied to the spins I and S, respectively. We consider the Hamiltonian terms that are essential from the viewpoint of the evolution of the state of the spin system. For this, we carry out a rotation transformation of the operators in Eq. (2):

$$\begin{gathered} Q_V=V^{-1}T^{+1}R^{-1}QR^{+1}T^{-1}V^{+1}, \\ R^{\pm 1}=\exp\left(\pm i\omega_1 t \sum_n I_z{}^n \pm i\omega_2 t S_z\right), \\ T^{\pm 1}=\exp\left(\pm i\theta^I \sum_n I_y{}^n \pm i\theta^S S_y\right), \\ V^{\pm 1}=\exp\left(\pm i h_{ef}{}^I t \sum_n I_z{}^n \pm i h_{ef}{}^S t S_z\right). \end{gathered} \tag{10}$$

The departures of the rf fields $\Delta^{I,S} = \omega^{I,S} - \omega_{1,2}$ from the Larmor frequencies $\omega^{I,S}$ and the amplitudes of the rf fields determine the effective magnetic field in the rotating system of coordinates for both spins:

$$h_{ef}^{I,S}=[(\Delta^{I,S})^2+(\gamma^{I,S}H^{I,S})^2]^{1/2}, \quad \cos\theta^{I,S}=\Delta^{I,S}/h_{ef}^{I,S}.$$

After the transformation (10), the Liouville equation (2) takes the form

$$\dot{\rho}_v=-i(\tilde{H})\rho_v, \tag{11}$$

$$\tilde{H}=H_{cv}{}^I+H_{dv}^{II}+H_{Jv}^{II}+H_{cv}{}^S+H_{dv}^{IS}+H_{Jv}^{IS}+H_{rf,v}^{I}+H_{rf,v}^{S}.$$

The transformations shown above affect exclusively the Hamiltonian spin part determined by the spherical tensors T, which makes it possible to use (6) in the transformation (10).

The equation for the dipole-dipole interaction of the spin S with n neighboring spins I is the following:

$$\begin{aligned} H_{dv}^{IS} = & \sum_{n} \sum_{q=-2}^{2} \sum_{p=-2}^{2} A_{2p}(\varphi_n, \theta_n)\, e^{i\pi/2(p-q)}\, e^{-ip\omega_r t}\, d_{pq}^2(\theta_m) \\ & \times \sum_{M_1=-1}^{1} C(112; M_1, -q-M_1)\, e^{-iM_1\omega_1 t} \sum_{M_1'=-1}^{1} (-1)^{M'} d_{M'M_1}^1(\theta^I) \\ & \times I_{1M'}^n e^{-iM' h_{ef}^I t}\, e^{+i(q+M_1)\omega_2 t} \sum_{N'=-1}^{1} (-1)^{N'} d_{N',\,-q-M_1}^1(\theta^S)\, S_{1N'} e^{-iN' h_{ef}^S t}. \end{aligned} \tag{12}$$

Here φ_n and θ_n are the spherical coordinates of the spin I; the spin S is located at the origin of the coordinates.

The dipole-dipole interaction between the spins I is expressed in the following way after the transformation (10):

$$\begin{aligned} H_{dv}^{II} = & \sum_{i<j} \sum_{q=-2}^{2} \sum_{p=-2}^{2} A_{2p}(\theta_{ij}, \varphi_{ij})\, e^{i\pi/2(p-q)}\, e^{-ip\omega_r t}\, d_{pq}^2(\theta_m) \\ & \times \sum_{M_1=-1}^{1} C(112; M_1, -q-M_1)\, e^{iq\omega_1 t} \\ & \times \sum_{L=-1}^{1} (-1)^L d_{LM_1}^1(\theta^I)\, I_{1L}^i e^{-iLh_{ef}^I t} \\ & \times \sum_{L'=-1}^{1} (-1)^{L'} d_{L',\,-q-M_1}^1(\theta^I)\, I_{1L'}^j e^{-iL'h_{ef}^I t}. \end{aligned} \tag{13}$$

For further exposition, we assume that all the frequencies are sufficiently large in comparison with the frequencies of the local fields, i.e.,

$$|\omega_1|,\ |\omega_2| \gg \omega_r, \quad |h_{ef}{}^I|,\ |h_{ef}{}^S| \gg |h_L|, \tag{14}$$

where h_L is the local field in the solid.

This assumption allows us to use the secular part ($q = 0$) in the terms of the Hamiltonian, and to consider only those variants of the experiment in which the time-independent part H_{ef} of the Hamiltonian $\tilde{H}$ is significant in Eq. (11). Then the solution of the Liouville equation is

$$\rho_v(t) = e^{-itL(H_{ef})}\rho_{0v}. \tag{15}$$

The operator ρ_{0v} describes the spin-system state at the instant $t = 0$.

The terms of $\tilde{H}$ can contain two types of time-independent components. The first group contains terms that are constant in time, independent of the specific values $\omega_r, h_{ef}^I, h_{ef}^S$. The second group consists of terms which are constant and enter into H_{ef} only at certain relations among $\omega_r, h_{ef}^I, h_{ef}^S$. In the case of exact tuning of the rf fields, when $\Delta^I = \Delta^S = 0$, and at inclination of the axis of rotation to the z axis of the LS at the magic angle θ_m, $\tilde{H}$ does not contain constant terms of the first type, except the spin-spin coupling H_{Jv}^{II} between the I spins. At a suitable choice of $\omega_r, h_{ef}^I, h_{ef}^S$, we can selectively include in H_v the constant terms of the individual interactions of the nuclear spins.

For our purposes, we can determine from (12) and (13) a set of $\omega_r, h_{ef}^I, h_{ef}^S$ such that only the term H_{dv}^{IS} or H_{dv}^{II} is time independent.

Actually, in the case

$$M' h_{ef}{}^I + N' h_{ef}{}^S + p\omega_r = 0 \tag{16}$$

the constant terms of second type contain only H_{dv}^{IS}, while in the case

$$(L+L')h_{ef}{}^I + p\omega_r = 0 \tag{17}$$

only the interaction H_{dv}^{II}.

The coefficients M', N', L, L' take on the values -1, 0, 1, and p changes from -2 to 2.

We further determine next the spectrum of frequencies of the NMR signal of the spin S in the single crystal in the case of a time-independent Hamiltonian, which contains only terms corresponding to H_{dv}^{IS}. This is realized if we consider that the conditions (14) and (16) are satisfied and the term H_{Jv}^{II} is small. In accord with (16), we consider two possible relations among h_{ef}^I, h_{ef}^S, and ω_r.

If $|h_{ef}^S - h_{ef}^I| = \omega_r$, we have for H_{ef}

$$H_{ef} = H_{dv}^{IS} = i\sum_n 2\omega_{Dn}\,(e^{i\varphi_n} I_{11}{}^n S_{1-1} - e^{-i\varphi_n} I_{1-1}^n S_{11}), \tag{18}$$

while under the condition $|h_{ef}^S - h_{ef}^I| = 2\omega_r$,

$$H_{ef} = H_{dv}^{IS} = \sum_n (-2\omega_{Dn}')\,(e^{-i2\varphi_n} I_{1-1}^n S_{11} + e^{i2\varphi_n} I_{11}{}^n S_{1-1}). \tag{19}$$

Here

$$\begin{gathered} \omega_{Dn} = \frac{3}{16} C_n \sin 2\theta_m \sin 2\theta_n \equiv K \sin 2\theta_n, \\ C_n = \gamma_I\gamma_S\hbar/r_n{}^3, \quad \omega_{Dn}' = \frac{3}{16} C_n \sin^2\theta_m \sin^2\theta_n \equiv L \sin^2\theta_n. \end{gathered} \tag{20}$$

If we record only the signal of spin S, we can limit ourselves in Eq. (15) to that part of the density matrix ρ_0^S which characterizes only the S spins. Let the spin system at the instant of turning on the radiofrequency fields be characterized by the initial density

$$\rho_0{}^S = DS_z + ES_x + FS_y. \tag{21}$$

Then, after the transformations R, T and V, in the case of exact tuning of the rf fields, this part of the density matrix is transformed into

$$\rho_{0v}{}^S = ES_z - DS_x + FS_y. \tag{22}$$

From (15), we obtain the matrix elements of the density operator on the basis of the eigenfunctions of H_{ef}:

$$(\rho_v{}^S(t))_{mn}=e^{-it\varepsilon_{mn}}(\rho_{0v}{}^S)_{mn}, \qquad (23)$$

where $\varepsilon_{mn}=(H_{ef})_{mm}-(H_{ef})_{nn}$.

In accord with (22), the signal $S(t)$ induced in the detection coil and oriented along the y axis of the LS, is

$$S(t)\sim\frac{d}{dt}\,\mathrm{Sp}\,(S_y\rho^S(t)). \qquad (24)$$

In the case of only one nearest spin I ($n=1$, $\omega_{D1}\equiv\omega_D$), taking into account the transformation (10), the exact tuning of the rf fields, and the expressions (22), (23) and (24) for the density matrices, we obtain the following for the signal from the spin S under the condition $|h_{ef}^S-h_{ef}^I|=\omega_r$:

$$S(t)\sim\frac{d}{dt}[F\cos\omega^S t\cos h_{ef}{}^S t\cos\omega_D t$$
$$+D\cos\omega^S t\sin h_{ef}{}^S t\cos\omega_D t-E\sin\omega^S t], \qquad (25)$$

while under the condition $|h_{ef}^S-h_{ef}^I|=2\omega_r$

$$S(t)\sim\frac{d}{dt}[F\cos\omega^S t\cos h_{ef}{}^S t\cos\omega_D{}' t$$
$$+D\cos\omega^S t\sin h_{ef}{}^S t\cos\omega_D{}' t-E\sin\omega^S t]. \qquad (26)$$

Fourier transformation allows us to obtain from (25) and (26) the expression for the frequency spectrum of the observed signal.

As follows from Eqs. (25) and (26), the spectrum of the spin S depends on the initial polarization of the spin S, on the parameters of dipole interaction, and on the orient of the single crystal relative to the external magnetic field.

The dependence of the shape of the spectrum on the initial polarization under the condition $|h_{ef}^S-h_{ef}^I|=\omega_r$ is

a) at D, E, $F\neq 0$, the spectrum contains 5 lines at the frequencies

$$\omega_{\mathrm{I,II}}=\omega^S+h_{ef}{}^S\pm\omega_D,\quad \omega_{\mathrm{III,IV}}=\omega^S-h_{ef}{}^S\pm\omega_D,\quad \omega_{\mathrm{V}}=\omega^S;$$

b) at $F\neq 0$, $D\neq 0$ but $E=0$ (magnetization in the zy plane), the spectrum consists of 4 lines at the frequencies $\omega_{\mathrm{I}}, \omega_{\mathrm{II}}, \omega_{\mathrm{III}}, \omega_{\mathrm{IV}}$;

c) at $E\neq 0$ but $F=D=0$ (the magnetization directed along the x axis) we have in the spectrum a single line at the frequency ω^S.

Under the condition $|h_{ef}^S-h_{ef}^I|=2\omega_r$, the signal is expressed by Eq. (26) and the spectrum is the same, only ω_D is replaced by ω_D'.

The NMR spectrum of a powdered sample is a superposition of lines from all its constituent single crystals.

With account of the dipole-dipole interactions only between nearest neighbors in I-S pairs, the line shape in the spectrum of the powder under the condition $|h_{ef}^S-h_{ef}^I|=\omega_r$ was obtained by us in Ref. 23:

$$I(\omega)=\frac{\{1-[1-(\omega/K)^2]^{1/2}\}^{1/2}+\{1+[1-(\omega/K)^2]^{1/2}\}^{1/2}}{2\sqrt{2}K[1-(\omega/K)^2]^{1/2}}. \qquad (27)$$

Under the condition $|h_{ef}^S-h_{ef}^I|=2\omega_r$, we obtain the line shape in the form

$$I(\omega)=\frac{1}{2L(1-\omega/L)^{1/2}}, \qquad (28)$$

where, according to (20),

$$K=\frac{3}{16}\frac{\gamma_I\gamma_S\hbar}{r_n{}^3}\sin 2\theta_m,\qquad L=\frac{3}{16}\frac{\gamma_I\gamma_S\hbar}{r_n{}^3}\sin^2\theta_m. \qquad (29)$$

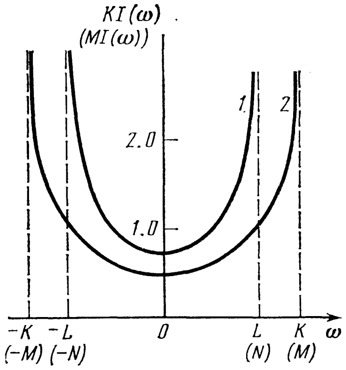

FIG. 1.

The line shapes obtained from (27) for the condition $|h_{ef}^S-h_{ef}^I|=\omega_r$ and from (28) for $|h_{ef}^S-h_{ef}^I|=2\omega_r$, are shown in the figure.

In the spectrum of the powder, besides the case when the initial magnetization is directed along the x axis, a pair of lines appears symmetric about the frequency ω^S appears. The centers of the lines are located at the frequencies $\omega_S+h_{ef}^S$ and $\omega_S-h_{ef}^S$. In the figure, ω denotes the departure from the center of the line.

We can determine with good accuracy the constants K and L characterizing the dipole-dipole interactions between the spins I and S from the line shapes.

5. SPECTRUM AND LINE SHAPE IN THE CASE OF A SINGLE RF FIELD

Along with the mechanical rotation of the sample, one strong radiofrequency field with frequency ω_1 is turned on at the time $t=0$ and acts on the spins I and is directed along the x axis of the LS:

$$\mathrm{H}(t)=\mathrm{i}2H^I\cos\omega_1 t.$$

In this case, we can use the formulas obtained in Sec. 4 with account of the fact that the amplitude H_S and the frequency ω_2 of the radiofrequency field are equal to zero.

We then obtain from Eq. (12) for the secular part of the dipole-dipole interaction between the spins I and S:

$$H_{dv}^{IS}=\sqrt{\frac{2}{3}}\sum_n\sum_{p=-2}^{2}A_{2p}(\varphi_n\theta_n)\,e^{i\pi/2p}e^{-ip\omega_r t}d_{p0}^2(\theta_m)$$
$$\times\sum_{M'=-1}^{1}(-1)^{M'}d_{M'0}^1(\theta^I)\,e^{-iM'h_{ef}^I t}I_{1M'}^n S_{10}. \qquad (30)$$

Here we have not taken into account the time-dependent oscillating terms with the high frequencies ω^I and ω^S.

The term of the dipole-dipole interaction between the spins I and H_{dv}^{II}, was obtained previously (13). According to the assumption (14) for ω_1, we must consider only those variants of the experiment in which the time-independent part H_{ef} of the Hamiltonian in the Liouville equation (15) is important:

$$H_{ef}=H_c{}^S+H_{dv}{}^{IS}+H_{dv}{}^{II}+H_{cv}{}^{I}. \tag{31}$$

In contrast with the case of two rf fields, the terms of the chemical shift, H^S_c and H^I_{cv}, remain here. We assume H^I_{cv} to be small in the first approximation when determining the signal of the spin S. The quantity H^S_c contains oscillating terms which depend on the time, with the frequencies ω_r and $2\omega_r$. According to assumption (14), the frequency ω_r is large and these terms need not be taken into account. Then $H^S_c = 1/3\ \mathrm{Sp}\{\sigma^S\}\omega^S S_{10}$.

To obtain H_{ef} from Eq. (31), we use (30) for H^{IS}_{dv} and (13) for H^{II}_{dv}. Summation over all possible terms in H^{II}_{dv} (6 different combinations of coefficients), satisfying the condition (17) for the coefficients upon satisfaction of $h^I_{ef} = \omega_r$, and at exact tuning of the rf field, leads to the expression

$$H_{ef}=-a\omega^S S_{10}+i\sqrt{2}\sum_n\Delta\omega_n'(e^{i\varphi_n}I_{1-1}^{1}+e^{-i\varphi_n}I_{11}{}^{n})S_{10}$$

$$+\sum_{n<l}\Delta\omega_{nl}'(e^{2i\varphi_{nl}}I_{1-1}^{n}I_{1-1}^{l}+e^{-2i\varphi_{nl}}I_{11}{}^{n}I_{11}{}^{l}), \tag{32}$$

where $a = 1 - 1/3\ \mathrm{Sp}\{\sigma^S\}$,

$$\Delta\omega_n'=\frac{C_n}{2\sqrt{2}}\sin 2\theta_n\equiv M\sin 2\theta_n,\quad C_n=\frac{\gamma_I\gamma_S\hbar}{r_n{}^3}, \tag{33}$$

$$\Delta\omega_{nl}'=\frac{3}{8}C_{nl}\sin^2\theta_{nl},\qquad C_{nl}=\frac{\gamma_I{}^2\hbar}{r_n{}^3}. \tag{34}$$

At $h^I_{ef} = 2\omega_r$ and after summation of all terms (4 different combinations) satisfying the condition for the coefficients (17), we obtain the following for H^{II}_{dv}

$$H^{II}_{vd}=\frac{9}{16\sqrt{2}}\sum_{n<l}\frac{\gamma_I{}^2\hbar}{r_n{}^3}\sin^2\theta_{nl}\sin^2\theta_m\sin 2\theta^I$$

$$\times\{e^{-2i\varphi_{nl}}(I_{10}{}^nI_{11}{}^l+I_{11}{}^nI_{10}{}^l)-e^{2i\varphi_{nl}}(I_{10}{}^nI_{1-1}^{l}+I_{1-1}^{n}I_{10}{}^l)\}. \tag{35}$$

In the case of exact tuning of the rf field, $\cos\theta^I = 0$ and the term $H^{II}_{dv} = 0$. This makes it possible to investigate the dipole-dipole interaction between the spins I and S in pure form.

The effective Hamiltonian under such conditions is obtained in the form

$$H_{ef}=-a\omega^S S_{10}+\sqrt{2}\sum_n\Delta\omega_n(e^{-i2\varphi_n}I_{11}{}^n-e^{i2\varphi_n}I_{1-1}^{n})S_{10}, \tag{36}$$

$$\Delta\omega_n=(C_n/4)\sin^2\theta_n\equiv N\sin^2\theta_n. \tag{37}$$

The effective Hamiltonian (32) and (36) can easily be diagonalized. As a preliminary, we diagonalize R', which is equivalent to changing to the rotating system of coordinates:

$$R'^{\mp1}=\exp(\pm ita\omega^S)S_z. \tag{38}$$

As earlier, we obtain from (15) the matrix elements of the density operator on the basis of the eigenfunctions of the effective Hamiltonian H_{ef}; these elements are expressed here by Eqs. (32) and (36).

Taking (24) into account, the expression for the signal from the spin S for an isolated I-S pair (the deviation of the frequency is $\Delta\omega_n = \Delta\omega_1$) has the form

$$S(t)\approx\frac{d}{dt}\{2\cos(\Delta\omega_1 t)[F\cos(a\omega^S t)+E\sin(a\omega^S t)]\}. \tag{39}$$

Under the condition $h^I_{ef} = 2\omega_r$ $\Delta\omega_1$ is given by Eq. (37), while under the condition $h^I_{ef} = \omega_r$ it is given by Eq. (33).

The frequency spectrum of the observed spins is obtained from (39) by a Fourier transformation. If the initial magnetization is located in the xy plane, the spectrum of the single crystal contains two terms at the frequencies $\omega = a\omega^S \pm \Delta\omega_1$. A single line appears in the spectrum of the powder, with center at the frequency $a\omega^S$. The line shape is expressed also by Eqs. (27) and (28) which were obtained for the case of two rf fields, the only difference being that the constant K in Eq. (27) is replaced at $h^I_{ef} = \omega_r$ by M according to Eq. (33), while in Eq. (28), the constant L is replaced by N according to Eq. (37). If we take into account the substitution of the constants, the line shapes shown in the figure can be used to determine the constants M and N of the dipole-dipole interaction between the spins I and S.

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