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Strong-Radio-Frequency-Field Effects in Nuclear Magnetic Resonance and Electron Paramagnetic Resonance

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A change in the rotating-coordinate transformations that are used in making calculations of magnetic-resonance phenomena with large rf fields permits a definition for the quantization axis of the spin system which is continuous in both the driving rf field strength and the departure of the rf frequency from resonance. This modified procedure is used to compute the line narrowing, which is expected in spin-stirring experiments with inhomogeneously broadened systems, as a function of stirring rf field strength. The increase in transverse relaxation time in correlation-time-narrowed inhomogeneously broadened spin systems is calculated. The behavior of the magnetization in the rotating frame in adiabatic fast-passage experiments is predicted. The increase in transverse relaxation time in multiple-pulse experiments in homogeneously broadened systems is calculated. These predictions agree with observations or with exact calculations made with trace-sum methods. It is shown that previous experiments which were predictable and in accord with the usual procedure are also in accord with the modified procedure proposed here.

I. INTRODUCTION

The problem of coupled microscopic magnetic moments in the presence of a strong static magnetic field and a transverse rf field is at the center of the following discussion. There is certainly a wealth of understanding of empirical and analytical aspects of the effect of strong rf fields on the spin-spin interaction in paramagnetic materials.[1-15] However, the theoretical predictions of the behavior of the resonant spin system are difficult to understand physically. In an attempt to understand some recent experimental results of the measurement of spin decoupling in electron paramagnetic systems, the author developed a variant of the usual analytical procedure which allows one to predict some properties of the spin system in a heuristic and more physical fashion. These predictions are applicable to nuclear paramagnetic systems also, and they allow one to make interesting interpretations of some previously reported experimental observations on nuclear resonant systems.

This revised treatment of inhomogeneously

broadened spin systems is a simple modification of the conventional method of carrying out these calculations. The modification involves only a redefinition of the instantaneous doubly rotated axis of quantization, so that it is determined not only by the static and rf fields but also by an effective spin-spin interaction field that is a measure of the interaction of the observed spin with the surrounding, nonresonant magnetic moments. The spin decoupling observed in the free radical diphenyl picryl hydrazyl (DPPH) may be discussed in terms of the predictions of this procedure.[16]

It is conceptually more difficult to extend the use of the effective spin-spin-interaction field to a system of equivalent interacting spins. One can test the suggested modification of the usual procedure, however, by comparing the prediction of this effective-field treatment with the prediction of the exact calculation for the behavior of a spin system in a rotating-frame adiabatic-demagnetization experiment.[17] The double-resonance line-narrowing experiments with NaF, reported by Sarles and Cotts,[18] may also be compared with the predictions of this modified procedure, and it is found that their experimental results are predicted quantitatively. Finally, use can be made of the idea of a spin-spin effective field to discuss the pulsed-NMR experiments of Waugh and his collaborators, and of others, in which the nuclear-spin decoupling has been observed in homogeneously broadened systems.[19]

The predictions of this effective-field procedure can thus be checked experimentally for inhomogeneously broadened systems with and without correlation-time narrowing.

II. GENERAL THEORY

The essential problem encountered in making magnetic-resonance calculations in the presence of a nonvanishing rf field has been lucidly discussed by Wangsness, Bloch, Redfield, Abragam, and others.[1-15] In the presence of a radio-frequency field, of any magnitude, an explicitly time-dependent Schrödinger problem has to be solved in the laboratory frame of reference. The statistically averaged behavior of the system observables is therefore difficult to discuss. The explicit time dependence of the problem can be eliminated by transforming the variables into a frame of reference rotating about the static-field axis at the angular frequency of the perpendicular rf field. Since the Zeeman energy is assumed to be large compared with the spin-spin or spin–rf-field energies, only the secular part of the spin-spin interaction need be retained; thus the explicit time dependence disappears from the problem. This rotating frame is the singly rotating, or precessional, coordinate system. The statistical properties of the system are then conveniently studied by using a second rotation of coordinates about the axis perpendicular to the rf and Zeeman field, so that the new z axis of quantization is in the direction of the effective magnetic field that remains after the first transformation. This direction is determined by the applied static field and the applied rf field. The eigenenergies of the spin on this axis of quantization are the Zeeman energies of the spin moment in the presence of the effective field. The eigenmotion of the magnetic moment in the second frame is a precession about this axis. The second frame is called the doubly rotating frame, and the motion a nutation.

Explicitly, the transformations are described as follows. The Hamiltonian is the sum of Zeeman, spin-spin, spin-lattice, and spin–rf-field terms, the rf field being taken on the x axis:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{ss} + \mathcal{H}_{sl} + \mathcal{H}_{srfx} \,. \tag{1}$$

The transformation to the precessing frame is

$$R_{z\omega t} = \exp(-i\omega t \textstyle\sum_j S_{zj}) \,, \tag{2}$$

where S_j is the spin angular momentum at space position j.

The doubly rotating frame is obtained with the rotation about the y axis:

$$R_{y\theta} = \exp(-i\theta \textstyle\sum_j S_{yj}) \,, \tag{3}$$

where $\tan\theta = \gamma H_1/(\omega - \gamma H_0)$, with γ the spin magnetogyric factor, H_0 the static field, and H_1 the amplitude of the one circular component of the rf field rotating in the direction of the spin precession.

The conceptual difficulty of this last transformation is that the effective-field axis is always normal to the static-field axis for $\omega = \gamma H_0 = \omega_0$; hence, unless the rf field is very large compared with $\mathcal{H}'_{ss}$, the secular terms in the spin-spin term, the quantization axis is quite arbitrarily taken as the x axis, and the nutational eigenenergies are those of the spin in the rf field alone.

A. Inhomogeneous Systems: Broadening by Inequivalent Spins

An observation that we would like to make is that one can derive some of the results of calculations for this system in a heuristic manner. Consider a simple system, that of a set of spins interacting primarily with another set of nonidentical spins. Such a system, for example, would be the Na nuclei interacting with the F nuclei in NaF, or the free-radical electron spin in dilute DPPH interacting with the two neighboring nitrogen nuclei. In the presence of a strong static magnetic field, these two spin systems form nearly commuting systems, quantized on the z axis, with the Zeeman levels of

one set of spins being nondegenerate with those of the second-spin species. The effect of one spin system on the second spin system can be described by an effective magnetic field H_{Li} on the static-field axis interacting with the second spin S_{zi} to add to the Zeeman energy of this second spin. To do this analytically, the unit matrix and the sum of the operators $\gamma H_{Li} S_{zi}$ are considered to be elements of a set of orthogonal operators which form a complete set of orthogonal vectors in matrix space, and into which $\mathcal{H}'_{ss}$ is expanded.[20] The projection of $\mathcal{H}'_{ss}$ on the unit matrix is zero since it has zero trace. The projection of $\mathcal{H}'_{ss}$ on S_{zi} is also zero, but H_{Li} breaks the orthogonality since it is some function of the other spin states. Thus H_{Li} has zero trace because S_{zi} has zero trace. The tedious calculation of the projection of $\mathcal{H}'_{ss}$ on $H_{Li}S_{zi}$ can be avoided if the expansion is terminated with this term. Then one need only determine the normalization of the expansion, and in order that the expansion be normalized the square of the ensemble-averaged local field must be taken to be

$$\langle H_L^2 \rangle = \mathrm{Tr}\,\mathcal{H}'^2_{ss}/\mathrm{Tr}(\gamma^2 S_z^2) \,. \tag{4}$$

Truncation of the orthogonal operator set to its first two elements is not as naive as it may appear at first sight. The expansion preserves the two invariants of the problem, the traces of the first two powers of $\mathcal{H}'_{ss}$. If one asks questions about macroscopic variables which are simple enough to require only these two invariants in their solution, then the prediction will be exact. Undoubtedly there are other observables which depend upon higher-order invariants and for which this truncated expansion is not valid. In the calculations which follow, the observables for which predictions are made are too simple to be of this type.

Furthermore, one can estimate the projection of $\mathcal{H}'_{ss}$ on $H_{Li}S_{zi}$ to be the absolute value of H_{Li}. This exhausts the normalization given by Eq. (4), and so the remaining operators in the set may be assumed to have negligible weight.

In summary, the ensemble average of the local field $\langle H_L \rangle$ will be taken to be zero, and the ensemble average of the local field squared will be as given by Eq. (4).

In the precessing frame the effective field is

$$\vec{H}_e = \hat{i} H_1 + \hat{k}(\omega/\gamma_i - H_0 - H_{Li}) \,. \tag{5}$$

Expressed in the second rotating frame, this field is

$$\vec{H}_e = \hat{i}\,'[H_1 \cos\theta - (\omega/\gamma_i - H_0 - H_{Li}) \sin\theta] + \hat{k}\,'[H_1 \sin\theta + (\omega/\gamma_i - H_0 - H_{Li}) \cos\theta] \,. \tag{6}$$

With θ chosen so that the $\hat{i}'$ component vanishes, then[21]

$$\cos^2\bar{\theta} = [1 + \omega_1^2/(\Delta_i^2 + \gamma_i^2 \langle H_{Li}^2 \rangle)]^{-1} \,, \tag{7}$$

with $\gamma_i H_1 = \omega_1$, and $\Delta_i = \omega - \gamma_i H_0$. The eigenvalues of the Hamiltonian in the second rotating frame are

$$\lambda = \pm (\omega_1^2 + \Delta_i^2 + \gamma_i^2 \langle H_{Li}^2 \rangle)^{1/2} \,. \tag{8}$$

To determine the effect of this rf-field-induced change of quantization axis on the mean-square-frequency linewidth and the transverse relaxation time, one proceeds as follows. The usual source of inhomogeneous broadening in NMR systems is the dipolar interaction between unlike magnetic moments. In the presence of a strong static magnetic field, these two spin systems form almost commuting systems, and the secular part of their dipolar interaction is

$$(\mathcal{H}'_{ss})_{AB} = \sum_{ij} \gamma_A \gamma_B I_{zAi} S_{zBj} \,. \tag{9}$$

There will also be homogeneous-broadening terms that arise from the secular part of the like spin dipolar interaction within each spin system which must be added to the Hamiltonian. The model of the preceding calculation may be approximated by taking $\gamma_B \ll \gamma_A$ so that for spin system B the inhomogeneous term dominates in the broadening. Adjust the stirring-rf-field frequency to be near resonance with system B. Then in terms of operators for system B taken on the quantization axis defined by $\bar{\theta}$, and operators for system A on the axis defined by the static field, the inhomogeneous-broadening term is written

$$(\mathcal{H}'_{ss})_{AB} = \sum_{ij} \gamma_A \gamma_B I_{zAi} (S_{z''Bj} \cos\bar{\theta} + S_{x''Bj} \sin\bar{\theta}) \,. \tag{10}$$

The first term in $\mathcal{H}'_{ss}$ is time independent and yields a variation of the contribution to the second moment for both systems which behaves as $\cos^2\bar{\theta}$. This term we call the central-line broadening. For $\bar{\theta} = 0$ ($\omega_1 = 0$), this term yields a contribution to the linewidth of each which is $\langle \Delta\omega_{AB}^2 \rangle$. The $\bar{\theta}$-dependent contribution from this term will thus be $\langle \Delta\omega^2 \rangle_{AB} \cos^2\bar{\theta}$.

The second term has a time dependence of $e^{\pm i\lambda t}$, and it gives rise to a time-dependent frequency modulation of the resonance of system A. This has the effect of putting weak satellite sidebands on the NMR resonance at frequencies $\pm N\lambda$, $N = 1, 2, \ldots$, removed from the main NMR resonance of system A. We ignore this term for the moment, and our analysis predicts that the second moment for the central-system A NMR signal will vary as

$$\langle \Delta\omega^2 \rangle_A = \langle \Delta\omega^2 \rangle_{AB} \cos^2\bar{\theta} + \langle \Delta\omega^2 \rangle_{AA} \,. \tag{11}$$

The subscripts indicate the Van Vleck second moment arising from the dipolar interaction between the two systems and from the dipolar interaction within system A. Also we have

$$\cos^2\bar{\theta} = [1 + (\gamma_B H_1)^2/(\langle\Delta\omega^2\rangle_{AB} + \Delta_B^2)]^{-1} \quad (12)$$

in the absence of scalar exchange spin coupling, since from Eq. (4) one computes $\langle\gamma_B^2 H_L^2\rangle_B = \langle\Delta\omega^2\rangle_{AB} + \frac{1}{3}\langle\Delta\omega^2\rangle_{BB} \simeq \langle\Delta\omega^2\rangle_{AB}$. For $\gamma_B H_1 \ll \langle\Delta\omega^2\rangle_A^{1/2}$ this prediction will seem to be poor, but this is not the case. For these field strengths, the system-B nutational frequency is less than the system-A linewidth, and the satellite contribution to the second moment of system A cannot be separated from that of the central line in the experimental data. The sum of the mean-square frequency deviations of a pair of satellite lines is evidently $2N^2\lambda^2$. The intensity of the satellite lines of harmonic order N with respect to the central line is given by frequency-modulation theory[22] as the square of the Bessel function of order N with an argument which is the frequency deviation divided by the modulation frequency. This argument is small in the present case, and so only the first-order term $N = 1$ need be considered. In this case, the relative intensity of each satellite line is $\langle\Delta\omega^2\rangle_{AB}(\sin^2\bar{\theta})/2\lambda^2$. The intensity-weighted mean-square-frequency contribution of the first two satellite lines is

$$(2\lambda^2)\,[\langle\Delta\omega^2\rangle_{AB}(\sin^2\bar{\theta})/2\lambda^2] = \langle\Delta\omega^2\rangle_{AB}\sin^2\bar{\theta}. \quad (13)$$

Since the central-line contribution is $\langle\Delta\omega^2\rangle_{AB}\cos^2\bar{\theta}$, the total mean-square frequency is constant. Hence, for weak rf fields, the frequency moment of the central line will appear to remain constant because of the overlap of the small but finite satellite contribution. For larger rf fields, the satellite frequency is sufficient to put the satellite lines in the wings of the central line, and they become weak enough so that their contribution is lost in the noise in the experimental data. The effect has been discussed in detail by Bloch.[23]

A previous calculation[10] has shown that the inverse of the effective transverse relaxation time T_{2e}^{-1} varies as the square of the vector projection from one axis of quantization to the other. Hence it varies as $\cos^2\bar{\theta}$.

Now since both the second moment and T_{2e}^{-1} vary as $\cos^2\bar{\theta}$, the line shape must change as the rf amplitude increases. The ratio of the half-amplitude half-width T_{2e}^{-1} to the rms frequency width varies as $(\cos^2\bar{\theta})^{1/2}$. This ratio thus becomes small as the rf field increases, and the resonance curve is expected to become more peaked, or of a Lorentz form, as the rf-field strength increases.

In more detail, not only the contribution of the secular terms of $\mathcal{H}_{ss}$ to the spin relaxation but also the contribution of the nonsecular terms must be included. The latter terms account for line broadening by processes involving a change of energy of the spin system by one quantum of Zeeman energy. These terms bring the whole system of spin and environment into thermal equilibrium, and are called the longitudinal, or spin-lattice, relaxation terms. In the terminology proposed here, the effective spin-spin relaxation time is written

$$\frac{1}{T_{2e}} = \frac{1}{T_{20}}\cos^2\bar{\theta} + \frac{1}{2T_1}, \quad (14)$$

with

$$\cos^2\bar{\theta} = [1 + \omega_1^2/(\Delta^2 + \gamma^2\langle H_L^2\rangle)]^{-1}.$$

Now in the usual method of calculation [Ref. 10, Eq. (2.15)], T_{2e} is found for the case in which $\tau^{-2} \gg \gamma^2\langle H_D^2\rangle$ (the mean-square dipolar linewidth) to be

$$\frac{1}{T_{2e}} = \frac{1}{T_{20}}\left(1 + \frac{\omega_1^2}{(\Delta^2 + \tau^{-2})}\right)^{-1} + \frac{1}{2T_1}. \quad (15)$$

To say that a spin system has a short correlation time implies that the spin coupling includes a strong scalar exchange term. Hence the expression for the local field squared used in Eq. (12) will be augmented by the term ω_E^2. This factor is much larger than the dipolar contributions, and it is equal to τ^{-2}; Eqs. (14) and (15) are thus equivalent.

For the opposite extreme $\tau^{-2} \ll \gamma^2\langle H_D^2\rangle$ and for $\omega_1^2 > \gamma\langle H_D^2\rangle^{1/2}\tau^{-1}$, Tomita's result is approximated at resonance, $\Delta = 0$, by

$$T_{2e} = \tau(\omega_1^2/\gamma^2\langle H_D^2\rangle), \quad (16)$$

while Eq. (14) reduces to

$$T_{2e} = T_{20}(1 + \omega_1^2/\gamma^2\langle H_L^2\rangle). \quad (17)$$

In this extreme these two results differ by a factor of $\sim T_{20}/\tau$. Thus experimental measurements of the variation of T_2 with applied rf field in paramagnetic crystals for which this factor should be large would be decisive in determining the valid expression.

Measurements of the variation of T_2 in strong rf fields have been made on the paramagnetic free radical DPPH.[16,24] The correlation time can be varied in this substance by dilution in polystyrene. The measurements on samples with strong correlation-time narrowing are limited by the rf-field strength, but it does appear that they do behave as predicted by Eqs. (14) and (15). The samples showing little correlation time narrowing yield results which cannot be said to disagree either with Eq. (16) or Eq. (17) since the correlation time is unknown. Furthermore, though the samples are homogeneous, the paramagnetic sites may be distributed randomly rather than uniformly. Hence, the relationship between the observed linewidth and the effective local field or effective correlation time is unknown.

B. Homogeneous Systems: Broadening by Equivalent Spins

The application of this procedure to systems in which $\mathcal{H}_{ss}$ is a dipolar interaction between identi-

cal spins is more difficult to justify. The dipolar contribution now transforms like a rank-two tensor, while the Zeeman terms transform as vectors. A simple rotation of axes to the second rotating frame cannot be used to obtain a quantization axis for which the effective Hamiltonian is diagonal. Furthermore, one spin cannot be looked at alone; all spins must be looked at, and this degeneracy of eigenstates is awkward to handle. In this sense, the Schrödinger equation for the system is not solvable. We are reduced to talking about quantities that are defined by trace sums such as the frequency moments of the absorption line. The eigenenergies on this second axis take a simple form only in extremes of the rf field. In more detail, the wave functions for the coupled identical spins must be symmetrized products of single-spin wave functions in order to have the two spins indistinguishable. The simplest extreme of this problem is two spins of spin $\frac{1}{2}$ with wave functions

$$\psi_1=(++)\,,\quad \psi_2=(--)\,,\quad \psi_{3,4}=(\sqrt{\tfrac{1}{2}})[(+-)\pm(-+)]\,. \tag{18}$$

The spin-spin and rf Zeeman terms couple the three symmetric states. The eigenenergies are thus determined by a cubic equation and are those of a linear combination of the symmetric states, plus that of the asymmetric state. The choice of a particular direction of quantization does not diagonalize the Hamiltonian, as in the case we discussed above—that of inhomogeneous broadening.

Discouraging as it may seem, however, we can still try an effective field phenomenologically and test its predictions on some problem that can be solved in terms of trace sums.

Stated in these terms, the idea is made to seem overly naive. On the contrary, the basic motivation here is to find some nontrivial way to interpolate between the simple eigenstates of the system in the two extremes for which the system is simple to understand. For $H_1 \to 0$, the quantization axis is definitely the static-field axis and the eigenenergies are those of the spin system projected on that axis and measured by $\langle H_L^2\rangle$. These are perturbed slightly in the limit $H_1 \to 0$. This situation, in any case, is the one that we supposedly understand. For $H_1 \gg \langle H_L^2\rangle^{1/2}$, the eigenaxis is the axis defined by H_1 and Δ, and the eigenenergies are the Zeeman energies of the spin in the effective field, perturbed slightly by $\langle H_L^2\rangle$. Introducing the random effective field simply allows us to bridge the gap between two regions of known behavior for the spin system in a reasonable simple manner.

To try out this approach, assume, as above, a local field, H_{Li} at spin i. The ensemble average of H_{Li} is zero, and its mean-square ensemble average is given by Eq. (4). Define the angle of the quantization axis as before in terms of H_1, H_0, and this local field.

We can check this model by comparing its prediction with that of a trace-sum calculation for the behavior of the spin-system magnetic moment with adiabatic fast passage in the rotating frame.[11] The thermodynamic trace-sum calculation predicts that the component of the magnetic moment on the rotating-frame field axis defined by the direction of the conventional effective-field vector, $\hat{i}H_1 + \hat{k}\Delta/\gamma = \vec{H}$, should be related to the initial magnetization by

$$M(\vec{H}) = M_i\left[\,|\vec{H}|/(H^2+\langle H_L^2\rangle)^{1/2}\right]\,. \tag{19}$$

The local-field model would have the magnetization adiabatically follow the field axis:

$$\vec{H}_e = \hat{i}H_1 + \hat{k}(\Delta/\gamma - H_L)\,.$$

The magnetization would have a projection on the axis $\vec{H}$ which is $M_i\cos\phi$ where ϕ is the angle between $\vec{H}$ and $\vec{H}_e$. Since $\cos\phi = \vec{H}\cdot\vec{H}_e/|\vec{H}|\,|\vec{H}_e|$, it is readily seen that the local-field model predicts

$$\cos\phi = |\vec{H}|/(H^2+\langle H_L^2\rangle)^{1/2}\,, \tag{20}$$

in agreement with the trace-sum calculation.

One can thus think of the loss in magnetic moment that occurs in rotating-frame fast-passage experiments as being due to the essential indeterminacy of the magnetization axis once it is rotated away from the large-static-field direction. The magnetization axis is determined at resonance only by the x-axis rf field, and hence the loss in coherent magnetization observable on the x axis must be large when the rf field is small compared with the field $\langle H_L^2\rangle^{1/2}$, and vice versa. The formula says this by stating that the reduction in the rotating-frame magnetization is the factor given by the ratio of the mean effective field to the rms effective field.

With this empirical "proof" for the validity of the concept of a local field in the case of homogeneous broadening, we proceed to examine the spin-spin problem in more detail. For the discussion, it will suffice to consider a pair of equivalent spins dipolar coupled in a strong Zeeman field. We are trying to understand some properties of this system, and though two spins do not have all of the properties of N coupled spins, they do have most of them. The N-spin system can be approximated by an ensemble average over two-spin systems. We have said that if the spins are equivalent, then the representation must be as given before in Eq. (18). This representation forms a singlet spin state with odd parity and a triplet spin state with even parity. These two systems can be coupled only by an operator that is odd with exchange of electrons. Since no such operator exists, we need to consider the triplet-state properties only. It is

easy to show that the singlet-state spin-spin energy is always zero, so it does not even contribute to the trace sum of the spin-spin operator. Since $\mathcal{H}'_{ss}$ is a rank-two tensor operator, its trace sum is zero.

Explicitly, on the static-field axis, the truncated spin-spin Hamiltonian with only dipolar or pseudo-dipolar exchange terms (scalar exchange assumed to be negligible) is written

$$\mathcal{H}'_{ss} = 4\alpha[S_z^1 S_z^2 - \tfrac{1}{4}(S_+^1 S_-^2 + S_-^1 S_+^2)]\hbar\,, \tag{21}$$

where

$$S_\pm = S_x \pm iS_y\,, \quad \alpha = \gamma^2\hbar\sum_{ij} R_{ij}^{-3}(3\cos^2\theta_{ij} - 1)\,.$$

In a frame rotated an angle θ from the z axis about the y axis, this term takes the form

$$\begin{aligned}\mathcal{H}'_{ss}/\hbar = {} & 2\alpha[S_z^1 S_z^2 - \tfrac{1}{4}(S_+^1 S_-^2 + S_-^1 S_+^2)](3\cos^2\theta - 1) \\ & + 12\alpha[S_z^1(S_+^2 + S_-^2) + (S_+^1 + S_-^1)S_z^2]\sin\theta\cos\theta \\ & + 12\alpha(S_+^1 S_+^2 + S_-^1 S_-^2)\sin^2\theta\,. \end{aligned} \tag{22}$$

Another great simplification of the triplet system is possible at this point by choosing as representations the combinations $\sqrt{\frac{1}{2}}[(++) \pm (--)]$, since in this case the last component of the transformed $\mathcal{H}'_{ss}$ can be made diagonal.

With quantization on this rotated z axis, in the symmetrized spin representations described above, the effective Hamiltonian becomes

$$(\mathcal{H}) = \begin{pmatrix} \alpha & \Delta c + \omega_1 s & -\Delta s + \omega_1 c & 0 \\ \Delta c + \omega_1 s & (3c^2 - 2)\alpha & 3sc\,\alpha & 0 \\ -\Delta s + \omega_1 c & 3sc\,\alpha & -(3c^2 - 1)\alpha & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{23}$$

$$\psi_1 = \sqrt{\tfrac{1}{2}}\,[(++) + (--)]\,, \quad \psi_2 = \sqrt{\tfrac{1}{2}}\,[(++) - (--)]\,, \tag{24}$$

$$\psi_3 = \sqrt{\tfrac{1}{2}}[(+-) + (-+)]\,, \quad \psi_4 = \sqrt{\tfrac{1}{2}}[(+-) - (-+)]\,.$$

The only awkward part that the spin energy introduces is the one off-diagonal term $3sc$ from the $S_z^1(S_+^2 + S_-^2) + (S_+^1 + S_-^1)S_z^2$ term. The eigenenergies of this Hamiltonian are simple in four cases: when $\Delta = 0$, $H_1 = 0$ (a case of no present interest); when $\Delta = 0$ (on resonance) and $\omega_1 \neq 0$; for Δ, $\omega_1 \gg \alpha$ (that is, for quantization on the direction determined by Δ and ω_1); and for $\Delta^2 = \frac{1}{2}\omega_1^2 + \alpha^2$. In each of these cases the determination of the eigenenergies reduces to the solution of a quadratic secular determinant.

For large Δ and/or ω_1, the spin-spin-term coupling between states 2 and 3 can be treated as a perturbation, and the eigenenergies are found to be

$$\begin{aligned} & \lambda_{1,2} = \tfrac{1}{2}\alpha(3c^2 - 1) \pm [\Delta^2 + \omega_1^2 + (\tfrac{9}{4}\alpha^2)s^2(3c^2 + 1)]^{1/2}\,, \\ & \lambda_3 = -\alpha(3c^2 - 1)\,, \quad \lambda_4 = 0\,, \\ & c^2 = \Delta^2/(\Delta^2 + \omega_1^2)\,, \quad s^2 = \omega_1^2/(\Delta^2 + \omega_1^2)\,. \end{aligned} \tag{25}$$

This expression is exact for $\Delta^2 = 0$ or for $\omega_1^2 = 0$. By hypothesis, if these eigenenergies are averaged over many spin pairs, the terms linear in α vanish and there remain

$$\begin{aligned} & \lambda_{1,2} = \pm[\Delta^2 + \omega_1^2 + (\tfrac{9}{4}\alpha^2)s^2(3c + 1)]^{1/2}\,, \\ & \lambda_{3,4} = 0\,. \end{aligned} \tag{26}$$

The triplet states behave in the limit of high rf fields or on resonance as a simple $S = 1$ Zeeman system; the mean-square effective field is thus defined to be

$$\gamma^2\langle H_L^2\rangle = \tfrac{9}{4}\alpha^2\sin^2\theta(3\cos^2\theta + 1)\,;$$

the trace-sum definition yields $\frac{12}{4}\alpha^2$, and it includes no dependence on the degree of resonance. The agreement is exact at the magic angle, $\sin^2\theta = \frac{2}{3}$. The resonance factor varies from 1 to $\frac{4}{3}$ to 1 as Δ^2 varies from 0 to $2\omega_1^2$. The agreement with the trace sum is probably satisfactory for the present purpose of investigating why an effective field might make sense in the case of a homogeneously broadened system.

The diagonalization here is a rotation in function space. For example, for the solution with $\Delta = 0$, the eigenrepresentations are the basic set rotated by an angle

$$\begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_3 \end{pmatrix}, \tag{27}$$

where

$$\tan 2\phi = 2(1\,|\mathcal{H}'_{ss}|\,3)/[(3\,|\mathcal{H}'_{ss}|\,3) - (1\,|\mathcal{H}'_{ss}|\,1)] = H_1/H_L\,.$$

The diagonal contributions of the spin-spin terms are

$$\begin{aligned} & (A\,|\mathcal{H}'_{ss}\,|A) = (3\cos^2\phi - 2)\,\alpha\,, \\ & (B\,|\mathcal{H}'_{ss}|B) = -(3\cos^2\phi - 1)\,\alpha\,. \end{aligned} \tag{28}$$

The finite trace makes the asymmetry here. Eliminating the trace from these terms (for the same reason that we argued to do so in the eigenvalues), these contributions vary as $\pm\alpha(3\cos^2\phi - \frac{3}{2}) = \pm\frac{3}{2}\cos 2\phi$. Now in real space we have argued that $\tan\bar{\theta} = H_1/\langle H_L^2\rangle^{1/2} = \tan 2\phi$. Hence in terms of $\bar{\theta}$ these spin contributions transform as $\pm\frac{3}{2}\alpha\cos\bar{\theta}$, as would be necessary if the effective-field picture is to make sense.

A more precise or formal analysis of this system can be carried out, but the results are approximately the same. We find that the secular equation for spin-spin Hamiltonian is

$$\lambda^3 - (3\alpha^2 + \omega_1^2 + \Delta^2)\lambda + \alpha(\omega_1^2 - 2\Delta^2 + 2\alpha^2) = 0\,. \tag{29}$$

This can be simply solved for $\Delta^2 = \frac{1}{2}\omega_1^2 + \alpha^2$, with roots $\lambda = 0, \pm(3\alpha^2 + \omega_1^2 + \Delta^2)^{1/2}$, as we have remarked before.

In the following discussion, it will not be necessary to compute the roots precisely, and second-

order perturbation will be used for $\omega_1 < 3\alpha$, or the solution in Eq. (25) will be used for $\omega_1 > 3\alpha$.

The diagonalizing transformation is in function space. The actual transformation can be readily determined once the eigenvalues are known. The zeros in the secular determinant make the elements of the transformation matrix simple in form and similar to the ones that we have already determined; that is, the diagonal elements of $\mathcal{H}'_{ss}$ project as $\cos\bar{\theta}$ times the effective local field, as vectors and not as rank-two tensors. The diagonalizing matrix D_{ij} is conveniently written in the form

$$\begin{aligned} D_{i1} &= \cos\phi_i \sin\zeta_i \,, \\ D_{i2} &= \sin\phi_i \sin\zeta_i \,, \\ D_{i3} &= \cos\zeta_i \,, \end{aligned} \tag{30}$$

with $\psi_1 = (+\,+)$, $\psi_2 = (-\,-)$, $\psi_3 = \sqrt{\frac{1}{2}}[(+\,-) + (-\,+)]$. The angles ϕ_i and ζ_i are determined for each root λ_i by the equations

$$\tan\phi_i = (\alpha + \Delta - \lambda_i)/(\alpha - \Delta - \lambda_i) \,, \tag{31}$$

$$(\cos\phi_i + \sin\phi_i)\tan\zeta_i = \sqrt{2}\,(2\alpha + \lambda_1)/\omega_1 \,. \tag{32}$$

The diagonalized Hamiltonian has elements

$$\begin{aligned} \mathcal{H}_{ii} = {} & \alpha(1 - 3\cos^2\zeta_i) + \sqrt{2}\,\omega_1 \sin\zeta_i \cos\zeta_i(\cos\phi_i + \sin\phi_i) \\ & + \Delta(\cos^2\phi_i - \sin^2\phi_i)\sin^2\zeta_i \,. \end{aligned} \tag{33}$$

Now, for example, for $\Delta > \omega_1^2/12\alpha$, $\omega_1 < 3\alpha$, we find

$$\begin{aligned} &\cos\zeta_{1,2} \cong \omega_1/\sqrt{2}\,(3\alpha \pm \Delta) \,, \\ &\sin\zeta_{1,2} \cong \pm(1 - \tfrac{1}{2}\cos^2\zeta_{1,2}) \,, \\ &\sin\zeta_3 \cong 3\alpha\omega_1/[(3\alpha)^2 + \Delta^2] \,, \\ &\phi_1 \cong 0 \,, \quad \phi_2 \cong -\tfrac{1}{2}\pi \,, \quad \phi_3 \cong \tfrac{1}{4}\pi \,. \end{aligned} \tag{34}$$

Hence the spin-spin contribution to the eigenenergy varies as

$$\begin{aligned} (\mathcal{H}'_{ss})_{11} &= (\mathcal{H}'_{ss})_{22} = \alpha[1 - 3\omega_1^2/2(3\alpha \pm \Delta)^2] \rightarrow \alpha[1 - 3\omega_1^2/2(9\alpha^2 + \Delta^2)] \,, \\ (\mathcal{H}'_{ss})_{33} &= \alpha\{1 - 3 + 3\omega_1^2/[3\alpha + (\Delta^2/3\alpha)]^2\} \rightarrow -2\alpha[1 - 3\omega_1^2/2(9\alpha^2 + 2\Delta^2)] \,. \end{aligned} \tag{35}$$

In the expressions on the right-hand side the ensemble average has been made. These all transform nearly identically. We observe that the transformation of $\mathcal{H}'_{ss}$ is the same as a real-space vector transformation $\alpha\cos\bar{\theta}$, where $\cos\bar{\theta} = 1 - \frac{1}{2}\tan^2\bar{\theta}$, $\theta \ll 1$, and $\sin\bar{\theta} \cong \omega_1/(3\alpha^2 + \frac{1}{3}\Delta^2)^{1/2}$; that is, $3\alpha^2$ is the effective local field squared.

The appearance of the spin-spin transformation is the same as that of the diagonal part of a rank-two tensor, but its properties are different. As ω_1 varies from zero to $\gg 3\alpha$, ζ_1 varies from $\frac{1}{2}\pi$ to $\frac{1}{4}\pi$, ζ_2 varies from $-\frac{1}{2}\pi$ to $-\frac{1}{4}\pi$, and ζ_3 varies from 0 to $-\frac{1}{4}\pi$.

The mean-square line frequency and the mean-square local field are simple to determine from the Hamiltonian in the form of Eq. (23). The mean-square frequency may be determined by using the expression

$$\langle\Delta\omega^2\rangle = [\mathrm{Tr}(\mathcal{H}, S_x)^2/\mathrm{Tr}(S_x)^2] - \omega_0^2 \,.$$

If we evaluate the trace sums for the Hamiltonian transformed to a frame rotating with an angular frequency $\omega = \omega_0$, it is obvious that we obtain $\langle\omega^2\rangle$. For $H_1 \rightarrow 0$ and $\Delta \rightarrow 0$, S_x has matrix elements between levels 1 and 3 and 2 and 3, and they are equal to $\sqrt{\frac{1}{2}}$; hence

$$\mathrm{Tr}[\mathcal{H}, S_x]^2 = [(\lambda_1 - \lambda_3)S_{x13} + (\lambda_2 - \lambda_3)S_{x23}]^2 = 9\alpha^2 \,,$$

$$\mathrm{Tr}S_x^2 = [(\sqrt{\tfrac{1}{2}})^2 + (\sqrt{\tfrac{1}{2}})^2] = 1 \,,$$

and so $\langle\Delta\omega^2\rangle = 9\alpha^2$.

The mean-square local field is defined as

$$\langle H_L^2\rangle = \mathrm{Tr}[\mathcal{H}'_{ss}]^2/\mathrm{Tr}\gamma^2 S_z^2 \,;$$

by inspection we have

$$\mathrm{Tr}[\mathcal{H}'_{ss}]^2 = 6\alpha^2 \,, \quad \mathrm{Tr}[S_{z1}^1 + S_{z2}^2]^2 = 2 \,.$$

Hence the mean local field squared is $3\alpha^2/\gamma^2$.

In the presence of a nonvanishing rf field, S_x will have matrix elements given by

$$\begin{aligned} (S_x)_{ij} = \sqrt{\tfrac{1}{2}}[&(\cos\phi_i + \sin\phi_i)\sin\zeta_i \cos\zeta_j \\ &+ (\cos\phi_j + \sin\phi_j)\cos\zeta_i \sin\zeta_j] \,. \end{aligned} \tag{36}$$

Since S_x commutes with the rf-field Zeeman term and $\mathrm{Tr}S_x^2 = \mathrm{Tr}DS_x^2D^{-1}$, it is evident that the rf field will not change $\langle\Delta\omega^2\rangle$ when computed in this manner. Although the transition-inducing moment S_{xij} varies with rf field, the rf-field contribution to the nutational eigenenergies keeps $\langle\Delta\omega^2\rangle$ constant. On the other hand, if we ignore the variation in nutational energy with ω_1, and compute the mean-square moment arising from the contribution of $\mathcal{H}'_{ss}$ to the nutational energy, there will be a change in $\langle\Delta\omega^2\rangle$ with rf-field strength. Call this component of $\langle\Delta\omega^2\rangle$ the dipolar component $\langle\Delta\omega_D^2\rangle$, and the rf-field component $\langle\Delta\omega_{rf}^2\rangle$, then $9\alpha^2 = \langle\omega_D^2\rangle + \langle\Delta\omega_{rf}^2\rangle$. The rf component will arise from the splitting of the dipolar line produced by the nutational energy contributed by the rf field.

Explicitly, we find the random line broadening contributed by the dipolar coupling to be

$$\langle\Delta\omega_D^2\rangle = 9\alpha^2\left(\sum_{\substack{i=1,2\\ j=3}} \frac{3\alpha}{\omega_1}(\cos^2\zeta_j - \cos^2\zeta_i)\cos\zeta_i \cos\zeta_j\right)^2 \,. \tag{37}$$

For $\omega_1^2 < 3\alpha^2$, $\Delta > \omega_1^2/12\alpha$, we find

$$\langle \Delta\omega_D^2 \rangle \cong 9\alpha^2 \cos^4\bar{\theta} \,, \tag{38}$$

and for $\omega_1^2 \gg 3\alpha^2$, the same procedure yields

$$\langle \Delta\omega_D^2 \rangle \cong 9\alpha^2 (\tfrac{3}{4})^2 \cos^4\bar{\theta} . \tag{39}$$

It thus seems that the dipolar contribution to the mean-square linewidth should vary as $\cos^4\bar{\theta}$, and that the splitting by the rf field should vary as $9\alpha^2(1-\cos^4\bar{\theta})$, $\bar{\theta} \to 0$, or $9\alpha^2(1-\frac{9}{16}\cos^4\bar{\theta})$, $\bar{\theta} \to \frac{1}{2}\pi$. The usual considerations lead one to expect the rf-field dependence of T_{2e}^{-1} to be the square of the transformation of $\mathcal{H}_{ss}'$ or $\cos^2\bar{\theta}$. For the case considered here, that of the solid lattice in which the dipolar field correlation time τ is long compared with $(\gamma^4 \langle H_L^2 \rangle^{1/2})^{-1}$, Tomita obtained a result which may be approximated at resonance and for $\omega_1^2 > \gamma \langle H_L^2 \rangle^{1/2} \tau^{-1}$ as

$$1/T_{2e} \simeq \tfrac{3}{7} \gamma^2 \langle H_L^2 \rangle / \omega_1^2 \tau \,. \tag{40}$$

The present result is

$$1/T_{2e} = (1/T_{20}) \cos^2\bar{\theta} \,, \tag{41}$$

which reduces on resonance to

$$1/T_{2e} = (1/T_{20}) [\gamma^2 \langle H_L^2 \rangle / (\omega_1^2 + \gamma^2 \langle H_L^2 \rangle)] \,. \tag{42}$$

These expressions differ by the large factor τ/T_{20}.[25]

If we look to experiments for guidance, there seem to be no useful data on the behavior of the spin-spin relaxation time in homogeneous-broadened systems. Experiments on systems with both homogeneous and inhomogeneous broadening are of little use. For example, if, according to our predictions, the homogeneous contribution to T_{2e}^{-1} varies as $\cos^2\bar{\theta}$, it will always be masked by the inhomogeneous contribution which also varies as $\cos^2\bar{\theta}$.

The spin-stirring experiments of Sarles and Cotts[18] using NaF can be discussed in terms of the calculations presented above. If Na NMR resonance is observed with a weak rf field, and the F nuclei are subjected to a strong rf field near the F NMR resonance, then one expects the Na inhomogeneous broadening to be reduced according to the expression

$$\langle \Delta\omega^2 \rangle_{Na} = \langle \Delta\omega^2 \rangle_{Na\text{-}Na} + \langle \Delta\omega^2 \rangle_{Na\text{-}F} \cos^2\bar{\theta}_F \,, \tag{43}$$

with

$$\cos^2\bar{\theta}_F = \left(1 + \frac{\omega_1^2}{\frac{1}{3}\Delta_F^2 + \gamma_F^2 \langle H_L^2 \rangle_F}\right)^{-1} .$$

The factors $\langle \Delta\omega^2 \rangle_{Na\text{-}Na}$ and $\langle \Delta\omega^2 \rangle_{Na\text{-}F}$ are the contributions to the Van Vleck second moments of Na from the homogeneous Na broadening and the inhomogeneous Na-F interaction. The quantization angle $\bar{\theta}_F$ of the fluorine nuclei is determined primarily by the local field arising from the F-F homogeneous broadening. Explicitly, using Eq. (4), one finds

$$\gamma_F^2 \langle H_L^2 \rangle_F = \tfrac{1}{3} \langle \Delta\omega^2 \rangle_{F\text{-}F} + \langle \Delta\omega^2 \rangle_{Na\text{-}F}$$

$$= (2\pi)^2 \ 40.8 \ \text{kHz}^2 \,.$$

Using these values, the predicted variation of the Na second moment of the central resonance is found to be that shown by the solid line in Fig. 1. This figure also presents the experimental data of Sarles and Cotts. As we have noted previously, the experimental data do not separate the contribution of the central-line moment from the

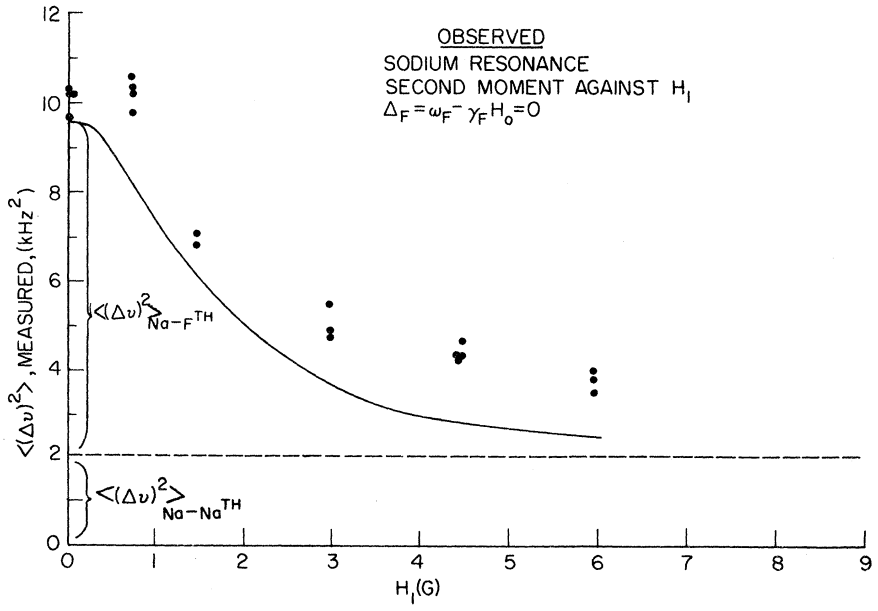

FIG. 1. Measured second moment of the Na resonance vs the amplitude of the rf-field stirring fluorines with prediction calculated from Eq. (43). [Experimental data from Sarles and Cotts (Ref. 18). Note that their $(\Delta\nu)^2$ corresponds to $(\Delta\omega)^2/(2\pi)^2$ in the notation of this paper.]

satellite-line moment for $H_1 \leq 1$ G. At higher rf-field strength the data lie consistently above the predicted curve, as if the Na resonance homogeneous broadening were greater than that computed from the Na-Na interaction alone. The addition of 1 kHz^2 to the Na homogeneous broadening brings the experimental data and the theoretical prediction into very good agreement.

The variation of the Na second moment as the frequency of the strong rf is removed from resonance $\Delta_F \neq 0$, determined experimentally by Sarles and Cotts, fits Eq. (43) equally well; that is, if 1 kHz^2 is added to the homogeneous-broadening term, the prediction of Eq. (43) is in agreement with the experimental data.

There is also one indirect experimental observation with which the prediction for the variation of the mean-square linewidth $\langle \Delta\omega^2 \rangle$ and T_{2e} with ω_1 and Δ may be compared. Waugh and his collaborators have demonstrated that the effective T_2 decay in spin-echo experiments in homogeneously broadened systems can be lengthened by an order of magnitude by using a series of 90° pulses spaced at time intervals less than T_{20}.

The proper pulse analysis of this experiment can be avoided by examining the Fourier decomposition of the pulsed rf field. For a pulse interval between *equivalent* pulses τ, less than T_{20}, and with the carrier frequency at NMR resonance, the pulse sidebands will be outside NMR resonance and may be ignored. The experiment is thus essentially a cw experiment, with pulse operation allowing the observation of the decay of the nuclear magnetization.

For this case, our arguments, using the effective field, would predict that the second moment of the NMR line should vary with rf field proportional to $\cos^4\bar{\theta}$.

The induction decay in a short interval after the first pulse may be written in terms of the second moment as [11,13]

$$F(t) \propto 1 - \tfrac{1}{2}\langle \Delta\omega^2 \rangle_e t^2 , \tag{44}$$

where, for $\omega_1^2 > 3\alpha^2$,

$$\langle \Delta\omega^2 \rangle_e \cong \langle \Delta\omega^2 \rangle_0 \tfrac{9}{16} \cos^4\bar{\theta} ,$$

$$\cos^2\bar{\theta} = [1 + \omega_1^2/(\gamma^2\langle H_L^2 \rangle + \tfrac{1}{3}\Delta^2)]^{-1} .$$

After N pulses spaced at intervals of τ in time, we expect

$$F(N\tau) \propto (1 - \tfrac{1}{2}\langle \Delta\omega^2 \rangle_e \tau^2)^N \sim \exp(-\tfrac{1}{2}\langle \Delta\omega^2 \rangle_e N\tau^2) .$$

If we write the mean-square field in terms of the peak x-axis field, one circular component will have a mean-square amplitude

$$\langle H_1^2 \rangle = \tfrac{1}{4}(\tau'/\tau)^2 \hat{H}_{rf}^2 , \tag{45}$$

with τ' the pulse length and τ the pulse interval. For large $\langle H_1^2 \rangle$,

$$\cos^2\bar{\theta} \approx \langle H_L^2 \rangle / \langle H_1^2 \rangle . \tag{46}$$

Taking $N\tau = t$, introducing these factors and the fact that the pulse is a 90° pulse, we find

$$F(t) \propto \exp\left[-\delta^6 \frac{8}{\pi^4} \left(\frac{\tau}{T_{20}}\right)^5 \left(\frac{\tau}{T_{20}}\right) \right] . \tag{47}$$

with $\gamma^2\langle H_L^2 \rangle = \delta^2/3T_{20}^2 = \tfrac{1}{3}\langle \Delta\omega^2 \rangle$. For a Gaussian line $\delta^2 = (\ln 4)^{-1} = 0.72$. First we note that the observed decay varies as τ^5. This experimental observation can be taken to indicate that the second moment does indeed vary as $\cos^4\bar{\theta}$, in agreement with our predictions for the strong rf-field dependence of the mean-square-frequency moment.

For one experimental result with enough data to compare the quantitative prediction, that of Co $(NH_3)_6(BF_4)_3$, we note that $T_{20} = 45$ μsec, $\tau = 10$ μsec, the induction signal decays exponentially to e^{-1} when $t \approx 4$ msec. Equation (47) predicts the decay to be down to e^{-1} in 2800 msec for a Gaussian, in poor numerical agreement with the experiment.

On the other hand, the effective transverse relaxation time would be predicted by the arguments we present here to be

$$T_{2e} = T_{20} \cos^2\bar{\theta} = T_{20}\left(\frac{3\pi^2 T_{20}^2}{4^2\tau^2\delta^2}\right) = 2.3 \text{ msec.} \tag{48}$$

This is in good agreement with the observed decay time. Possibly the numerical factors in our calculation of the induction-signal decay are in error, or the calculation itself is at fault. The induction-decay rate in our calculation will always differ from the effective transverse relaxation time by a factor

$$T_{2e}/T_{decay} = 9\delta^2\tau \cos^2\bar{\theta}/32T_{20} = (\delta^4/2\pi^2)(\tau/T_{20})^3$$

$$\approx (\tau/2T_{20})^3 . \tag{49}$$

At this point, it can be said that we have quantitative agreement only about the variation of the second moment with $\cos^4\bar{\theta}$. NMR multiple-pulse experiments, or induction-decay measurements, would seem to be the ideal experimental method for the study of strong-field effects at exact resonance.

No truly homogeneously broadened EPR system has been observed in second-harmonic experiments, [16] so there is no guidance to be had from those experiments.

There are other observations that do not disagree with the predictions of the procedure suggested here for analyzing the behavior of T_{2e} with intermediate rf-field strength. [9,11,26] Unfortunately, all of the observations are on systems with some inhomogeneous broadening, and so it must be said that it is not altogether certain whether the effect of strong rf fields on homogeneously broadened systems may be completely understood through the use of the heuristic approach which

has been described in this paper.

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