thulium ethyl sulfate were simultaneously performed by Hüfner et al.[14]; in interpreting their data, Hüfner et al. did not take into acount the electronic shielding factors σ_2 and R, which led to discrepancy between the experimental and theoretical value of the relevant nuclear quadrupole moment.

The authors would like to thank Professor F. H. Spedding for making available the samples of thulium ethyl sulfate. It is a pleasure to acknowledge stimulating discussions with Professor R. Orbach, Dr. E. Y. Wong, and Dr. D. A. Shirley.

*Work supported by the U. S. Atomic Energy Commission.

†On leave from Iowa State University, Ames, Iowa.

[1]H. M. Foley, R. M. Sternheimer, and D. Tyko, Phys. Rev. 93, 734 (1954); R. M. Sternheimer and H. M. Foley, Phys. Rev. 102, 731 (1956); R. M. Sternheimer, Phys. Rev. 130, 1423 (1963).

[2]R. M. Sternheimer, Phys. Rev. 84, 244 (1951); 95, 736 (1954).

[3]R. G. Barnes, E. Kankeleit, R. L. Mössbauer, and J. M. Poindexter (to be published).

[4]R. Cohen, U. Hauser, and R. L. Mössbauer, in The Mössbauer Effect, edited by D. M. J. Compton and A. H. Schoen (John Wiley & Sons Inc., New York, 1962).

[5]E. Y. Wong and I. Richman, J. Chem. Phys. 34, 1182 (1961).

[6]B. R. Judd and I. Lindgren, Phys. Rev. 122, 1802 (1961).

[7]I. Lindgren, Nucl. Phys. 32, 151 (1962).

[8]M. C. Olesen and B. Elbek, Nucl. Phys. 15, 134 (1960).

[9]E. G. Wikner and G. Burns, Phys. Letters 2, 225 (1962).

[10]G. Burns, Phys. Rev. 128, 2121 (1962).

[11]C. J. Lenander and E. Y. Wong (to be published).

[12]D. T. Edmonds, Phys. Rev. Letters 10, 129 (1963).

[13]J. Blok and D. A. Shirley (private communication).

[14]S. Hüfner, M. Kalvius, P. Kienle, W. Wiedemann, and H. Eicher (to be published).

NUCLEAR MAGNETIC RESONANCE LINE NARROWING BY A ROTATING rf FIELD*

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In most crystalline solids the breadth of the nuclear magnetic resonance (nmr) absorption line arises mainly from the dipole interactions between the nuclear spins. This interaction is often of sufficient strength to mask the effect of other, more interesting, interactions which broaden the absorption line or shift its frequency. We wish to report here a type of nmr measurement which is not very sensitive to the presence of the dipole interactions and therefore may facilitate observation of relatively small chemical shifts, Knight shifts, and various types of imperfection-induced line broadening which cannot be seen in solids by conventional nmr techniques.

Our experimental method is in many respects equivalent to the observation of a free-induction decay in a rotating sample. In such rotation experiments it has been shown both experimentally and theoretically[1] that the free-induction decay time is increased by this rotation provided the rotational velocity Ω is large compared to the linewidth, i.e.,

$$\Omega \gg \langle \Delta\omega \rangle, \tag{1}$$

where $\langle \Delta\omega \rangle$ is the square root of the second moment of the absorption line of the stationary sample. This increased decay time corresponds, of course, to a narrowing of the absorption line. If the axis of sample rotation is inclined at an angle Φ with respect to the external field $\vec{H}_0$ so that

$$\cos^2\Phi = 1/3, \tag{2}$$

then the dephasing effect of the dipole interaction can be shown to vanish completely (in the limit $\Omega/\langle \Delta\omega \rangle \to \infty$), and the free-induction decay should persist for a time of the order of T_1, the spin-lattice relaxation time.

The mechanical rotation experiments are quite difficult because of the very great angular velocities required to satisfy (1). With the line-narrowing technique described here this difficulty is absent, for it is a relatively small rf field which is "rotated" rather than the sample. In an analysis of our experiment there enters a frequency $\omega_1 \equiv \gamma H_1$, where γ is the gyromagnetic ratio of the resonant nuclei and $2H_1$ is the amplitude of an rf field applied in a direction perpendicular to $\vec{H}_0$. The frequency ω_1 plays exactly the same role as does Ω in the mechanical rotation experiments. For example, it is found that line narrowing is appreciable when

$$\omega_1 \gg \langle \Delta\omega \rangle, \tag{3}$$

and that, if (3) is satisfied, the dephasing effect of the dipole interaction vanishes completely at the angle θ such that

$$\cos^2\theta = 1/3, \tag{4}$$

where

$$\cos^2\theta = (\omega_0 - \omega)^2/[\omega_1^2 + (\omega_0 - \omega)^2], \tag{5}$$

and ω_0 is the Larmor frequency of the resonant spins, i.e., $\omega_0 \equiv \gamma H_0$.

The sequence of experimental operations in this field-rotation experiment is as follows: The spin system under study is permitted to come to thermal equilibrium in a large external dc field $H_0 \cong 2.5$ kG. Then an rf pulse is applied to the sample for a time τ. This rf pulse is of frequency ω and its effective rotating component is of amplitude H_1.

Quickly following abrupt turnoff of this rf pulse, a second, very short $(1/2)\pi$ pulse is applied to the system, and the subsequent free-induction decay signal is observed on an oscilloscope. This signal provides a measure of $M_z(\tau)$, the component of magnetization of the spin system that lies along $\vec{H}_0$ following turnoff of the first pulse. The time interval between turnoff of the first pulse and initiation of the second is much less than T_1 but much greater than T_2, the spin-spin relaxation time. The maximum length of the first pulse is also much less than T_1, so spin-lattice relaxation effects can be entirely neglected in the interpretation of the results.

A single run consists of a series of measurements of $M_z(\tau)$ for various τ but with a fixed H_1 and ω. To simplify comparison between experiment and theory, the measurements were made on the fluorine nuclei in single crystals of calcium fluoride. In this material all interactions other than the dipole interactions between fluorine nuclei are very small.

Figure 1 shows $M_z(\tau)/M_z(0)$ vs τ for a crystal oriented so that its [111] axis was parallel to $\vec{H}_0$. In this run the frequency of the first pulse was ω_0. The dashed line is drawn smoothly through the data points.

To interpret the results of this type of experiment, consider first the case where the nuclei interact only with the Zeeman field $\vec{H}_0$ and the rotating rf field of amplitude H_1. From elementary considerations[2] one expects the nuclear magnetization $\vec{M}(\tau)$ to precess without damping about an external field $\vec{H}_{er}$ with frequency γH_{er}, where

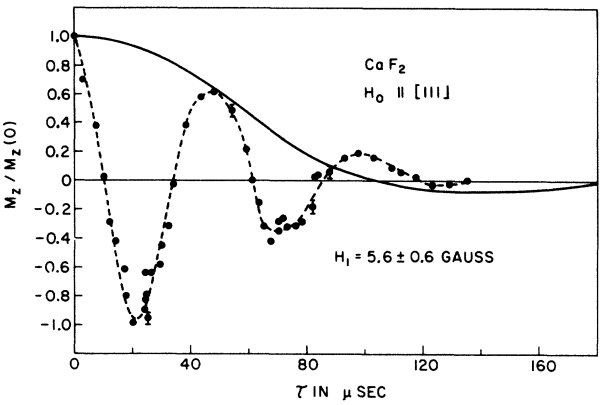

FIG. 1. Relative magnetization in CaF_2 versus duration of first long pulse with $\omega = \omega_0$. Dashed line is drawn by eye through the points. The solid line is a normal free-induction decay with the time scale expanded by a factor of 2. The quantity $M_z(0)$ is the equilibrium magnetization, often designated as M_0.

$$\vec{H}_{er} = \hat{k}(H_0 - \omega/\gamma) + \hat{i}'H_1. \tag{6}$$

The field $\vec{H}_{er}$ is static in a reference frame which rotates about $\vec{H}_0$ with frequency ω. The unit vector $\hat{i}'$ lies along the x axis in this rotating frame. In the absence of intranuclear interactions one therefore expects that at exact resonance, $M_z(\tau)/M_z(0) = \cos\omega_1\tau$. The oscillations of $M_z(\tau)$ are quite apparent in Fig. 1. The damping of the oscillations is produced, of course, by the dipole interactions, which cause the nuclei to get increasingly out of phase as time (τ) progresses.

To include the effect of the dipole interactions in a calculation of $M_z(\tau)$, a simple extension of the method of Lowe and Norberg[3] can be used. One first transforms the Hamiltonian of the spin system (including the term due to the rf field) to the rotating reference frame and discards nonsecular terms.[4] Then, with a simple relabeling of the coordinate axes,[4] it becomes obvious that the problem of calculating the envelope of the damped oscillations is almost identical to that of calculating a free-induction decay envelope with the field H_1 (which is static in the rotating frame) playing the role of H_0 in the usual free-induction decay experiment. The discarding of the nonsecular terms in the dipole interaction is permissible only if (3) is satisfied. A complete calculation shows that the envelope of the damped oscillations observed in this type of experiment is exactly the same as that of the

ordinary free-induction decay envelope except that the time scale is stretched by a factor

$$\lambda = 2/|(3\cos^2\theta - 1)|, \qquad (7)$$

where $\cos^2\theta$ is defined in Eq. (5). (We assume that only one magnetically active nuclear species is present in the sample and treat the lattice as perfectly rigid.)

The measurements in Fig. 1 confirm the results outlined above for the case $\omega = \omega_0$. From Eqs. (5) and (7), it is found that at exact resonance $\lambda = 2$. The solid line in Fig. 1 shows a photographed free-induction decay in CaF_2 (again with $H_0 \parallel [111]$) with the time scale stretched by a factor of two. This solid line falls very closely on the measured decay envelope for $\tau \lesssim 80$ μsec. The discrepancy between theory and experiment for longer τ may be due to an unjustified neglect of nonsecular terms in the transformed spin Hamiltonian (the experiment was performed at the largest rf field available, for which $\omega_1/\langle\Delta\omega\rangle \cong 4$). It is not too difficult to take approximately into account the effect of these nonsecular terms. Such calculations have been performed, but the requisite numerical work is incomplete.

Instead of measuring $M_z(\tau)$, as was done here, it is also possible to measure $M_x(\tau)$ by observation of the free-induction decay immediately following the first pulse. Experiments of this type, performed by Barnaal and Lowe,[5] also demonstrate, with considerable accuracy, that the absorption line in CaF_2 is narrowed by a factor of 2 when $\omega = \omega_0$.

Our most interesting measurements, which are shown in Fig. 2, were made under conditions such that Eq. (4) was almost satisfied. The sample was a single crystal of uranium-doped calcium fluoride (0.1% U^{+++} by weight). Also shown as a solid line in Fig. 2 is the envelope of an ordinary fluorine free-induction decay in the uranium-doped sample. All measurements were made at the same crystal orientation. A comparison of the solid and dashed curves shows an effective narrowing of the flourine absorption line by a factor of 5.

It is to be noted in Fig. 2 that the quasi-equilibrium value of $M_z(\tau)/M_z(0)$ ($\lambda T_2 \ll \tau \ll T_1$) is not zero but rather is approximately 0.2. This result is in accord with Redfield's hypothesis[4] that a spin system after a sufficiently long time reaches a state of thermal equilibrium in the rotating reference frame with its quasi-equilibrium magnetization $M_z(\infty)$ lying along $\vec{H}_{er}$.

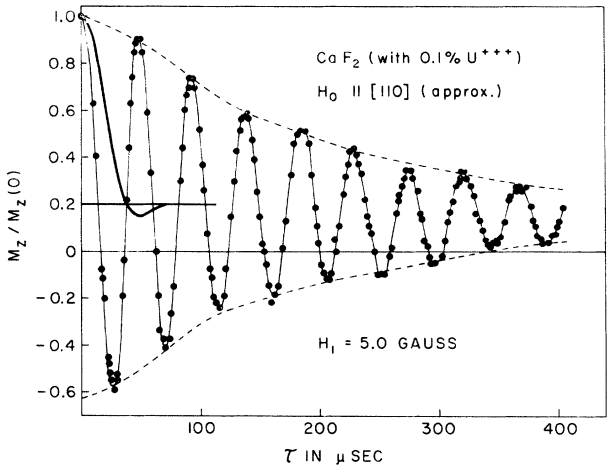

FIG. 2. Relative magnetization in CaF_2 versus duration of first pulse with $\omega - \omega_0 = 2\pi \times 13.83$ kc/sec. Heavy line is normal free-induction decay; the light line is drawn by eye through the data points. The dashed line is the envelope of the damped oscillations resulting from this experiment.

It was not possible to calculate $M_z(\infty)/M_z(0)$ because the orientation of the uranium-doped crystal was unknown.[6]

In conclusion we wish to note that line narrowing in solids can also be produced by rotary saturation.[4,7] The line shape observed in a rotary saturation experiment should, in the limit of large H_1, be the Fourier transform of the envelope of the damped oscillations measured by the technique described here.

The authors are grateful to H. Kessemeier for stimulating and informative discussions. The Harshaw Chemical Company kindly furnished the crystals used in these experiments.

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*This work was supported by grants from the National Science Foundation and the U. S. Army Research Office, Durham, North Carolina.

[1]See, for example, E. R. Andrew, A. Bradbury, and R. G. Eades, Nature 182, 1659 (1958); E. Andrew and R. Newing, Proc. Phys. Soc. (London) 72, 959 (1958); I. Lowe, Phys. Rev. Letters 2, 285 (1959); Joseph Dreitlein and Horst Kessemeier, Phys. Rev. 123, 825 (1961); Horst Kessemeier, Abstracts from 4th OCEANS, Mellon Institute, Pittsburgh, Pennsylvania, 1963 (unpublished).

[2]Charles P. Slichter, Principles of Magnetic Resonance (Harper and Row, New York, 1963), Chap. 2, Sec. 2.4.

[3]I. J. Lowe and R. E. Norberg, Phys. Rev. 107, 46 (1957).

[4]A. G. Redfield, Phys. Rev. 98, 1787 (1955).
[5]D. Barnaal and I. J. Lowe, Abstracts from 4th OCEANS, Mellon Institute, Pittsburgh, Pennsylvania, 1963 (unpublished); following Letter [Phys. Rev. Letters 11, 258 (1963)].
[6]The calculation of $M_z(\infty)/M_z(0)$ requires a knowledge of the orientation-dependent quantity, H_l, the local field in the crystal. For details see C. P. Slichter and W. C. Holton, Phys. Rev. 122, 1701 (1961); Walter I. Goldburg, Phys. Rev. 128, 1554 (1962).
[7]S. Clough, K. W. Gray, and I. R. McDonald (to be published).

EFFECTS OF ROTATING MAGNETIC FIELDS ON FREE-INDUCTION DECAY SHAPES*

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(Received 5 August 1963)

The lengthening of a nuclear magnetic resonance free-induction decay by applying a rotating magnetic field to a spin system has been observed.

In order to find out how such an effect might occur, let us analyze the behavior of a set of N particles with spin s and magnetogyric ratio γ, placed in a magnetic field $H_1(\cos\omega t\hat{i}+\sin\omega t\hat{j})+H_0\hat{k}$. The spin system, when referred to a frame of reference rotating about the z axis with angular speed ω, has the following magnetic Hamiltonian[1]:

$$\mathcal{H}_1=-\gamma\hbar\sum_{j=1}^{N}[H_1 s_{jy}+(H_0+\omega/\gamma)s_{jz}+\tfrac{1}{2}\sum_{j\neq k}(A_{jk}\vec{s}_j\cdot\vec{s}_k+B_{jk}s_{jz}s_{kz})]. \quad (1)$$

Only the time-independent terms of the interaction between the spins, as viewed from the rotating reference frame, are listed, since for large H_0 these are the only magnetic terms that determine the free-induction decay shape.[1]

In this rotating coordinate system (rotating coordinate system No. 1), there is a magnetic field

$$\vec{H}_{\rm eff}=H_1\hat{y}+(H_0+\omega/\gamma)\hat{z} \quad (2)$$

that makes an angle $\theta=\arctan H_1/(H_0+\omega/\gamma)$ with the z axis. By making a transformation to a coordinate system rotating about $\vec{H}_{\rm eff}$ with angular speed $\omega_{\rm eff}=-\gamma H_{\rm eff}$ (rotating coordinate system No. 2), one obtains a new magnetic Hamiltonian whose time-independent terms are

$$\mathcal{H}_2=\tfrac{1}{2}(3\cos^2\theta-1)[\tfrac{1}{2}\sum_{j\neq k}B_{jk}(s_{jz}'s_{kz}'-\tfrac{1}{3}\vec{s}_j'\cdot\vec{s}_k')]+\tfrac{1}{2}\sum_{j\neq k}(A_{jk}+\tfrac{1}{3}B_{jk})\vec{s}_j'\cdot\vec{s}_k'. \quad (3)$$

If there are only magnetic dipole interactions between the spins, $A_{jk}=-\frac{1}{3}B_{jk}$, making the second summation of (3) vanish. The omission of the time-dependent terms in $\mathcal{H}_2$ is a reasonable approximation only if $|\omega_{\rm eff}|$ is much greater than the regular nmr absorption linewidth.

For the case of $H_1=0$, the rate of decay of the component of magnetization perpendicular to $H_0\hat{z}$ is determined by $\mathcal{H}_1$ and is just the normal free-induction decay in rotating reference frame No. 1.[2] Using the same arguments as in reference 2, we conclude that as long as spin-lattice relaxation effects may be ignored, the rate of decay of any component of magnetization perpendicular to $\vec{H}_{\rm eff}$ is determined by $\mathcal{H}_2$ for $|\omega_{\rm eff}|$ large enough. For pure dipolar interactions between the spins, $\mathcal{H}_2$ has the same form as $\mathcal{H}_1$ except for a multiplying factor of $\frac{1}{2}(3\cos^2\theta-1)$. Thus a free-induction decay (f.i.d.) about $\vec{H}_{\rm eff}$ should have the shape of a normal f.i.d. about $H_0\hat{z}$, with the time axis stretched by a factor of $2/|3\cos^2\theta-1|$. For $\theta=90°$, one need only replace t in the free-induction decay formula[2] by $\frac{1}{2}\tau$, while for $\theta=\arccos 1/\sqrt{3}\approx 54.7°$, the magnetization perpendicular to $\vec{H}_{\rm eff}$ will not decay at all (within the limits that one can ignore the time-dependent terms not listed in $\mathcal{H}_2$).

We have been able to include the time-dependent terms, omitted in the above discussion of $\mathcal{H}_2$, in the computation of the rate of decay of magnetization perpendicular to $\vec{H}_{\rm eff}$ for the special case that $s=\frac{1}{2}$, that $\theta=90°$, and that each spin interacts with only one other spin (such as approximately occurs in gypsum). We find that $M_x(t)$, the x component of magnetization in the first rotating coordinate system, is given by the formula

$$M_x(t)=M(0)(\omega_1/\Omega)\sin\tau\Omega\cos(B_{12}/2\hbar)(t+\tfrac{1}{2}\tau), \quad (4)$$

where $\Omega=[(B_{12}/4\hbar)^2+\omega_1^2]^{1/2}$, $\omega_1=\gamma H_1$, $M(0)$ is the equilibrium magnetization just before the rotating magnetic field H_1 is turned on, τ is the length of time H_1 is on, and t is the length of time between