useful for the particularly difficult class of atoms with small hfs and short lifetime. A limitation of the technique is that an inversion of the hfs levels may be necessary to avoid a first-order repulsion of levels with the same magnetic quantum number.

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[2] This identification is based on preliminary optical spectroscopy results kindly supplied to us by S. Gerstenkorn: $A = 3 \pm 1$ mK and $B = 19 \pm 3$ mK. Our experiments cannot rule out the possibility of an inversion of the $F = \frac{7}{2}$ and $F = \frac{3}{2}$ levels. In that case, our work implies $A = 59.7$ Mc/sec and $B = 983$ Mc/sec. Such an inversion has been reported by J. S. Ross and K. Murakawa [J. Phys. Soc. Japan 19, 249 (1964)], who found $A = 1.3$ mK and $B = 23.2$ mK. Our alternative value for B given below is in much better agreement with Gerstenkorn's value and we have therefore taken the level order to be as in Fig. 2.

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APPROACH TO HIGH-RESOLUTION nmr IN SOLIDS*

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Consider a spin system having an internal static Hamiltonian $\mathcal{H}$, initially prepared in the state $|0\rangle$ and then subjected to a train of brief, intense, magnetic field pulses whose effects can be represented by the rotations

$$P_k = \exp(-i\theta_k \vec{n}_k \cdot \vec{I}), \tag{1}$$

where $\vec{n}_k$ is a unit vector in the direction of the pulse field in the rotating frame. The state of the system following the nth pulse at time

$$T = \sum_{k=1}^{n} \tau_k$$

is

$$|T\rangle = \left\{ \prod_{k=1}^{n} [P_k \exp(-i\mathcal{H}\tau_k)] \right\} |0\rangle. \tag{2}$$

As usual, it is to be understood that the operators in a product act successively in order of increasing index. Equation (2) can be rewritten as

$$|T\rangle = \left\{ \prod_{k=1}^{n} \exp(-i\tau_k \mathcal{H}_{nk}) \right\} \left\{ \prod_{m=1}^{n} P_m \right\} |0\rangle, \tag{3}$$

where

$$\mathcal{H}_{nk} = \left\{ \prod_{l=k}^{n} P_l \right\} \mathcal{H} \left\{ \prod_{l=k}^{n} P_l \right\}^{-1}. \tag{4}$$

Imagine that the n pulses are so chosen that

$$\prod_{m=1}^{n} P_m = 1.$$

A sequence having this property will be called a <u>cycle</u>. The pulse trains used by Carr and Purcell,[1] Ostroff and Waugh,[2] and Waugh and Huber[3] are cyclic for $n = 2$, 4, and 2, respectively. After N cycles (time $t = NT$) the state of the system is

$$|t\rangle = \left\{ \prod_{k=1}^{n} \exp(-i\tau_k \mathcal{H}_{nk}) \right\}^N |0\rangle. \tag{5}$$

It can be shown[4] that if $T \ll T_2$, where T_2 is a natural time of the system associated with $\mathcal{H}$, and often under less restrictive conditions, $|t\rangle$ becomes describable in terms of an <u>average Hamiltonian</u> $\bar{\mathcal{H}}$:

$$|t\rangle \approx \exp(-i\bar{\mathcal{H}}t)|0\rangle, \tag{6}$$

$$\bar{\mathcal{H}} = \frac{1}{T} \sum_{k=1}^{n} \mathcal{H}_{nk} \tau_k. \tag{7}$$

This result is in some ways reminiscent of the phenomenon of motional averaging,[5] but here it is the spin operators rather than the lattice operator which are time dependent, and the "fluctuations" of $\mathcal{H}$ are periodic rather than random. More importantly, the average Hamiltonian obtained is under the control of the experimenter through choice of the pulses P_k and weighting factors τ_k/T.

An interesting case arises when $\mathcal{H}$ consists of static, homonuclear, dipolar interactions

$\mathcal{H}_d$ and chemical shifts or Knight shifts $\mathcal{H}_\delta$:

$$\mathcal{H}_d = \sum_i < \sum_j d_{ij} (\vec{I}_i \cdot \vec{I}_j - 3 I_{zi} I_{zj}), \tag{8}$$

$$\mathcal{H}_\delta = \sum_i \delta_i I_{zi}. \tag{9}$$

Many cycles can be found for which $\overline{\mathcal{H}}_d = 0$, $\overline{\mathcal{H}}_\delta \neq 0$. One such is a cycle ($\tau$, P_x, 2τ, P_{-x}, τ, P_y, 2τ, P_{-y}), where all pulses are 90° rf pulses and the subscripts indicate their directions in the rotating frame (carrier phases in the laboratory). One easily finds from the definition of $\overline{\mathcal{H}}$ that $\overline{\mathcal{H}}_d = 0$, $\overline{\mathcal{H}}_\delta = 3^{-1/2} \sum \delta_i I_{zi}'$, where the z' axis lies along the (111) direction in the rotating frame.

Figure 1(a) shows the phase-detected ^{19}F Bloch decay of a sample consisting of a small single crystal of CaF_2 and some liquid $C_6H_5CF_3$. The fast decay of the solid signal is followed by a much longer decay of the liquid signal, and the latter shows a sinusoidal modulation because the magnet was set slightly off resonance. To obtain Fig. 1(b), the abovementioned pulse sequence was employed on the same sample with $\tau = 6$ μsec. The magnetization was detected at a given point in each cycle with a sample-and-hold circuit. A compound modulation is obtained because there is a difference in chemical shift between the CaF_2 and $C_6H_5CF_3$ spins, and the dipolar interactions in the solid have been effectively removed.

According to a well-known theorem,[6,7] the Bloch decay is a Fourier transform of the unsaturated slow-passage spectrum. According to (6), the Fourier transform of Fig. 1(b) is the slow-passage spectrum which would be obtained from a system in which dipolar broadening had been removed and all chemical shifts had been reduced by $\sqrt{3}$. This scale factor has been accurately verified by means of extensive measurements on liquid samples, in which the beat frequency in the multiple-pulse experiment is compared with that for the Bloch decay, for varying offsets from resonance.

Figures 1(c) and 1(d) show the computed Fourier transforms of the decays in Figs. 1(a) and 1(b). As expected, the dipolar broadening of the solid has been suppressed without loss of the chemical shift. The residual linewidths are largely governed by instrumental effects, including warping of the Zeeman field by bulk diamagnetic effects associated with the highly nonideal sample geometry employed. In other experiments with slightly better geometry, we have obtained linewidths more than three times smaller.

The separation of the peaks in Fig. 1(d) corresponds, after applying the $\sqrt{3}$ scale factor,

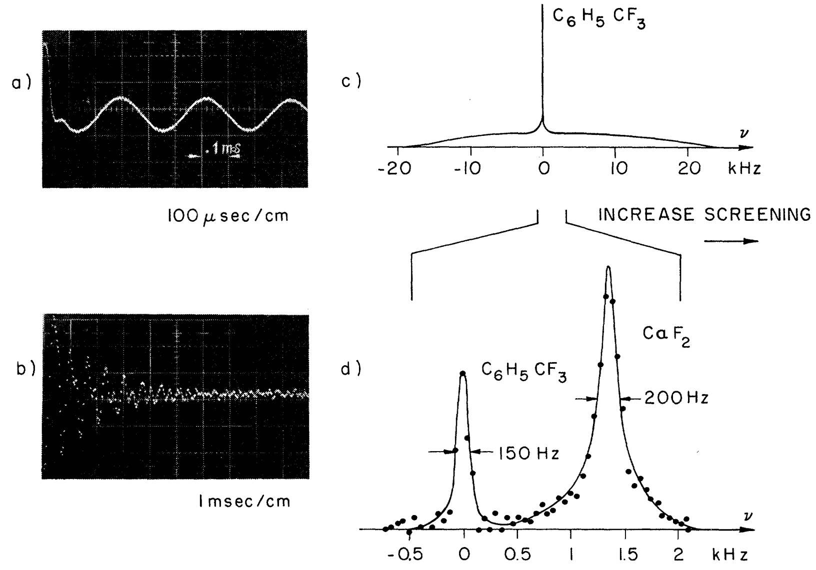

FIG. 1. (a) ^{19}F Bloch decay in a sample consisting of a CaF_2 crystal wet with liquid $C_6H_5CF_3$. The CaF_2 signal disappears quickly and is followed by an off-resonance beat from the liquid. (b) Sampled precession signal from the same sample during a multiple pulse experiment with $\tau = 6$ μsec. Both components of the signal are visible for a relatively long time. (c) Computed Fourier transform of the signal in (a). The sharp resonance of the liquid goes many times off scale. (d) Computed Fourier transform of the signal in (b), showing narrowing of the CaF_2 resonance and chemical shift.

to a shift of the CaF_2 resonance from $C_6H_5CF_3$ by 43 ppm in the direction of increased diamagnetic screening. This is of the same order of magnitude as the shift of 53 ppm reported for aqueous F^- vs $C_6H_5CF_3$,[8,9] but the difference is significant.

There appears to be no limit in principle to the extent to which static dipolar broadening can be reduced by this and related methods. In practice, our measurements to date seem to be limited by (a) inhomogeneity of H_0, (b) inhomogeneity of the rf field H_1, (c) the extent to which T/T_2 can be practically reduced, and (d) finite pulse width (1 μsec in these experiments). These limitations can certainly be largely removed. (c) and (d) can be simultaneously removed to first order, for example, by using an 8-pulse cycle in which the first half is as described and the second half employs a reversal of all rf phases.

The present experiment has an interesting analogy to the method of Lee and Goldburg.[10] The average Hamiltonian is in fact the same as the Lee-Goldburg effective Hamiltonian for the appropriate limit $H_1/H_{\text{loc}} \to \infty$. It is, however, not clear that the limiting behavior is approached in the same way in the two experiments when $H_1/H_{\text{loc}} \neq \infty$, $T/T_2 \neq 0$.

The analogy does suggest a pulse experiment in which a train of identical current pulses, each producing a field containing an rf component of amplitude $2H_1$ and a video "pedestal" of amplitude H_v, are applied to a coil whose axis is inclined to H_0 at an angle α. If H_1, H_v, and α are adjusted so that

$$(H_1/H_v)\tan\alpha = \sqrt{2}, \qquad (10)$$

a pulsed analog of the Lee-Goldburg situation is realized. In addition to the useful feature that the magnetization can be "continuously" observed, note that the first-order effects of inhomogeneity of the coil field are removed because of the fact that both H_1 and H_v arise from the same current distribution. Therefore, the "magic angle" condition (10) is maintained throughout the sample.

The theory outlined in the first part of this Letter can be generalized to allow for finite pulse widths, and indeed, for arbitrarily time-dependent applied fields, by use of a generalized interaction representation appropriate to continuously time-varying noncommuting operators. We will report on this subject elsewhere.

The experiments reported here were performed with a single-coil pulse spectrometer operating at 54.0 MHz and producing a peak rotating field of 60 Oe.

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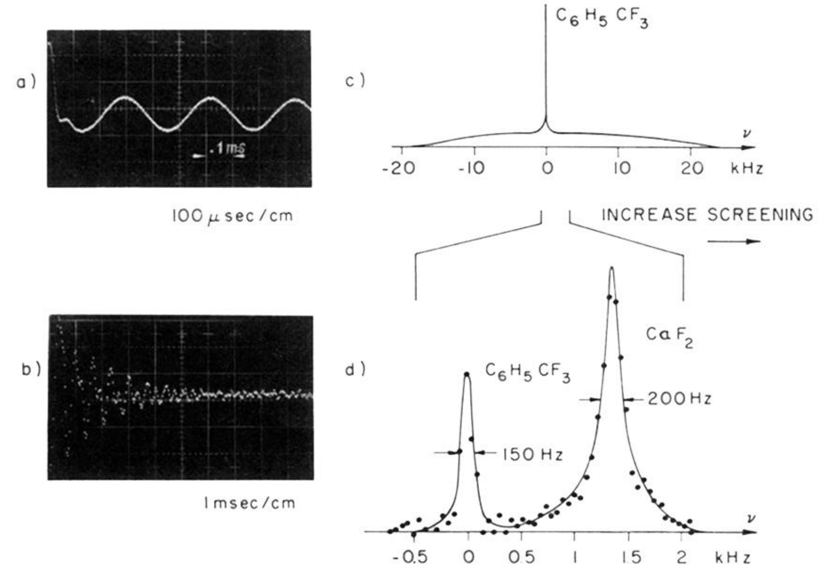

FIG. 1. (a) ^{19}F Bloch decay in a sample consisting of a CaF_2 crystal wet with liquid $C_6H_5CF_3$. The CaF_2 signal disappears quickly and is followed by an off-resonance beat from the liquid. (b) Sampled precession signal from the same sample during a multiple pulse experiment with $\tau = 6\ \mu$sec. Both components of the signal are visible for a relatively long time. (c) Computed Fourier transform of the signal in (a). The sharp resonance of the liquid goes many times off scale. (d) Computed Fourier transform of the signal in (b), showing narrowing of the CaF_2 resonance and chemical shift.