"Slow Beats" in F^{19} Nuclear Spin Echoes*

E. B. McNeil, C. P. Slichter, and H. S. Gutowsky
University of Illinois, Urbana, Illinois
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HAHN has reported[1] a modulation, or "slow beat," in the proton spin echo envelope of ethanol. Steady state observations[2] of the F^{19} nuclear magnetic resonance in BrF_5 and IF_5 revealed a complex line structure which has been associated[3] with an interaction among the F^{19} nuclei, via a coupling with the nuclear magnetic shielding fields.[4] We have found that the F^{19} spin echoes in these compounds exhibit slow beats.[5] Herein are presented the results and an analysis, which show that the slow beats originate from the interaction responsible for the steady state multiplets.

The F^{19} steady state resonance[2] in BrF_5 and IF_5 consists of two groups of lines, the centers of which are separated by a chemical shift $\delta\Omega$. The components in each group are separated equally by an amount $\delta\omega$. Typical echo envelopes for BrF_5 are shown in Figs. 1 and 2. Each echo[1] occurs at 2τ, where τ is the time between the two rf pulses. There are two slow beat "frequencies" in the envelope. The difference in τ between successive maxima of the rapid variation satisfies the equation $\Delta\tau=2\pi/\delta\Omega$. The slower variation satisfies the relation $\Delta\tau=2\pi/\delta\omega$. Steady state experiments show that $\delta\Omega$ is proportional to applied magnetic field[4] and that $\delta\omega$ is independent of field.[3] The echo envelopes were observed at two different applied fields, and the "frequencies" satisfied the above equations.

Figures 3(a) and 3(b) show individual echoes. It is seen that they are similar to echoes obtained from samples containing two noninteracting nuclei whose Larmor frequencies differ by a chemical shift,[1] except for an asymmetry in our echoes. Qualitatively, the echo shape is similar to that obtained by multiplying a symmetrical echo by a function having the general shape of the echo envelope. Thus echoes of maximum or minimum height are symmetrical.

Simple interference among magnetic moments precessing at the different frequencies known from steady state experiments does not explain the observed slow beat amplitudes. It has been pointed out elsewhere[3] in connection with steady state experiments that there are good grounds for assuming two nuclei of spin $\mathbf{I}_1$ and $\mathbf{I}_2$ are coupled by an interaction of the form $\mathbf{I}_1\cdot\mathbf{I}_2$. Hahn and Maxwell have predicted[6] the echo envelope for a system of two spins on the assumption that there is a chemical shift between their Larmor frequencies and such a dot product coupling between the spins. Subsequently we have made calculations using the following

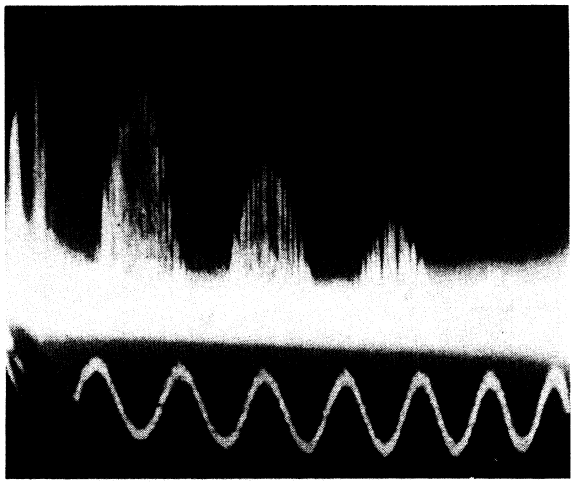

FIG. 1. The F^{19} echo envelope in BrF_5 at 30 Mc showing two modulation "frequencies." The envelope is obtained by multiple exposures; 60 cps timing below.

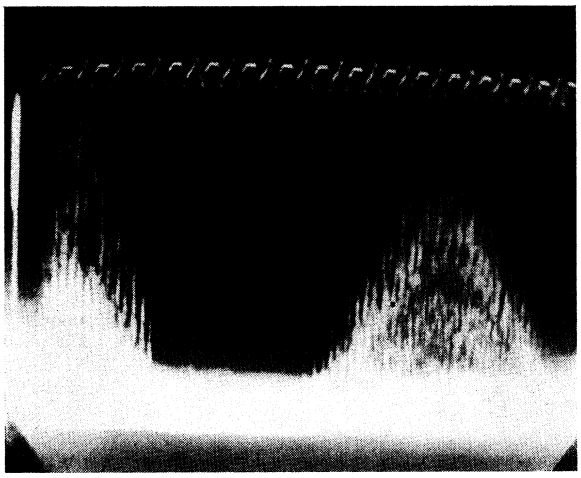

FIG. 2. First two groups of Fig. 1 on faster sweep to show the details better. Each of the sharp peaks is composed of several individual echoes.

Hamiltonian

$$H=\hbar\Omega I_{1z}+\hbar(\Omega+\delta\Omega)I_{2z}+\hbar\delta\omega I_{1z}I_{2z},$$

where Ω is the Larmor frequency of nucleus number one, and I_{1z} and I_{2z} are the components of spin of the two nuclei along the static applied field. Since in practice $\delta\Omega\gg\delta\omega$, this Hamiltonian is a close approximation to that obtained with dot product coupling, and may be considered as the Hamiltonian for a first-order per-

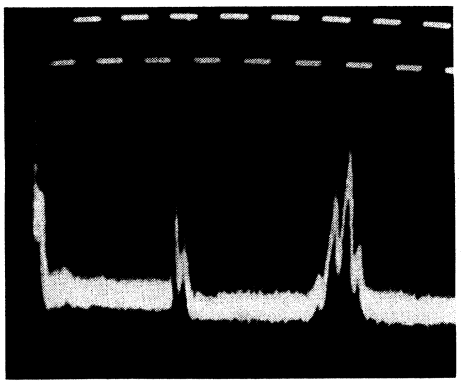

FIG. 3(a). Individual echo occurring slightly left of a maximum in the faster variation in Figs. 1 and 2. The distortion tends to follow the envelope shape.

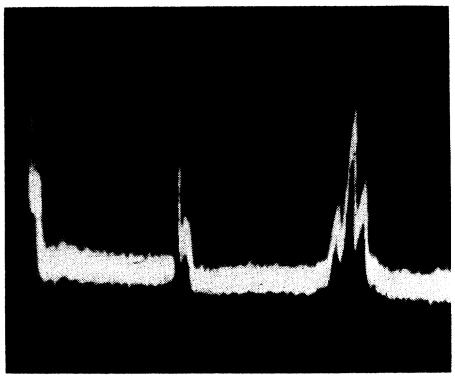

FIG. 3(b). Individual echo occurring slightly right of same maximum.

turbation calculation. We have carried through such calculations for $\omega_1 t_w = \pi/2$ in Hahn's notation[1] (spins turned through $\pi/2$ by the radiofrequency pulses) and $\omega_1 \gg \delta\Omega$, $\delta\omega$. We find the echo envelope is proportional to

$$|1+\cos\delta\omega\tau+(1-\cos\delta\omega\tau)\cos\delta\Omega\tau|.$$

This agrees with the results of Hahn and Maxwell.[6]

In addition, our calculation explains the echo asymmetries in the following manner. We consider separately the two spin groups 1 and 2 whose Larmor frequencies are chemically shifted relative to one another. At time $t=2\tau$ there is a resultant magnetization of group 1 and of group 2. The echo amplitude and asymmetry result from the following: (a) The length of the magnetization vectors is a function of τ. (b) The relative spatial orientation of the vectors at $t=2\tau$ depends on τ. Feature (b) accounts for the asymmetry, since if the vectors are not in phase at $t=2\tau$, their different precession frequencies cause a more perfect alignment at times either before or after $t=2\tau$. For example, the vectors might reach alignment on the leading edge of the echo, but not on the trailing edge with the result that the leading edge would be stronger than the trailing edge. The analysis shows that when $\delta\Omega\tau = n\pi$, where n is an integer, the vectors are in phase at $t=2\tau$, and the echo is symmetrical. This result is in agreement with the experimental facts mentioned earlier since these values of τ are the ones for which the envelope has a maximum or a minimum.

* Supported by the ONR.

[1] E. L. Hahn, Phys. Rev. **80**, 58 (1950).
[2] H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. (to be published.)
[3] Gutowsky, McCall, and Slichter, Phys. Rev. **84**, 589 (1951).
[4] W. C. Dickinson, Phys. Rev. **81**, 717 (1951); W. G. Proctor and F. C. Yu, Phys. Rev. **81**, 20 (1951).
[5] In a letter to HSG, E. L. Hahn stated he had found proton slow beats only in compounds having a fine structure in chemically shifted lines.
[6] E. L. Hahn and D. E. Maxwell, Phys. Rev. **84**, 1246 (1951). We are indebted to Dr. Hahn for sending us a copy of their letter in advance of publication.

Chemical Shift and Field Independent Frequency Modulation of the Spin Echo Envelope*

E. L. Hahn† and D. E. Maxwell
Stanford University, Stanford, California
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FURTHER investigation of the echo envelope modulation effect[1] has been carried out and related to measurements made by slow passage nuclear resonance methods.[2,3] According to the echo method, two short, intent pulses of radiofrequency power are applied to the spin ensemble at the nuclear resonance condition, and are separated by time interval τ. The echo appears with a given maximum amplitude at time 2τ. At the onset of the first radiofrequency pulse the spin system is at thermal equilibrium. For each setting of τ the maximum of the echo signal is measured and plotted as a function of increasing τ. If the spin ensemble consists of magnetic moments located in equivalent chemical environments [i.e., protons in H_2O or $(CH_3)_2O$], a monotonic decay in the echo envelope is obtained.

The envelope modulation effect is observed in molecules in which nuclear magnetic dipoles have neighboring nuclear dipoles in nonequivalent chemical environments. Examples are dichloroacetaldehyde ($CHCl_2CHO$), 1-fluoro-1,2,2 trichloro-ethane ($CFClH-CCl_2H$), and ethyl alcohol (C_2H_5OH), where H and F^{19} are the resonant nuclei concerned. In general these molecules may fall into either of two classes which contain resonant nuclear moments in the following arrangements: A resonant nucleus (or chemically equivalent nuclei) may have one or more neighboring dipole nuclei which are (1) identical with the resonant one, but chemically nonequivalent, or (2) not identical.

In molecules such as $CHCl_2CHO$, C_2H_5OH,[1] and $CCl_3(CHCl)_3$-CCl_3, two distinct modulation frequencies appear on the echo envelope: (1) One frequency corresponds to the difference in chemical shift,[4,5] δ, between two nonequivalent spin groups, which is measured by the slow passage method as a frequency difference between peaks of resonance signals.[2,3] (2) A second frequency, J, appears which is generally smaller than the frequency due to the chemical shift. This frequency is observed to be independent of the dc magnetic field H_0. In cases where it can be resolved[6] by the slow passage method[3,7] it is measured by the splitting of resonance lines belonging to equivalent spin groups.

If either of these frequencies is zero the modulation is absent. Many molecules exist (i.e., CH_3COOH) which have a chemical shift between nonequivalent nuclei as measured by the slow passage method. This shift, however, does not always appear on the echo envelope, but will only appear in those molecules in which these nuclei are sufficiently close neighbors. For these molecules the frequency J becomes finite, which in turn makes possible the appearance of the chemical shift on the echo envelope. For the special case involving two nonequivalent nuclei in CCl_2HCHO[8,9] these properties and the shape of the echo envelope can be predicted if the empirical Hamiltonian operator

$$\mathcal{H} = -\hbar[\gamma\sigma_{1z}(H_0+h_1)+\gamma\sigma_{2z}(H_0+h_2) + J(\sigma_{1x}\sigma_{2x}+\sigma_{1y}\sigma_{2y}+\sigma_{1z}\sigma_{2z})] \quad (1)$$

is chosen to describe the system. h_1 and h_2 are the absolute chemical shifts in gauss of the nuclei 1 and 2, respectively, and $\gamma(h_1-h_2)=\delta$. γ is the gyromagnetic ratio and $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$ are Pauli spin operators. The eigenvalues and the splitting which results in the stationary state are shown by the Zeeman level diagram in Fig. 1. The top and bottom levels are pure triplet states and each of the two closely spaced levels is a linear combination of singlet and triplet states. For $\delta\to 0$ the mixed state with the energy eigenvalue $J+(4J^2+\delta^2/4)^{\frac{1}{2}}$ now becomes a pure singlet state. The J splitting therefore disappears because transitions to and from the pure singlet state are forbidden. This supports the fact in the case of two equivalent nuclei that no J splitting is observed.[2,3,10]

The time-dependent population coefficients of each state have been evaluated under the initial conditions imposed by the application of two radiofrequency pulses. Each pulse at H_1 gauss maximum amplitude lasts for t_w seconds, where $t_w \ll \tau$ and $1/t_w$, $\gamma H_1 (=\omega_1) \gg \gamma\Delta H$, δ, J. ΔH is the magnitude of the external field inhomogeneity over the sample. For the case $\delta \gg J$ the expression for the observed echo amplitude (excluding damping due to relaxation) is given by

$$V = M_0|\sin^2(\omega_1 t_w/2)\sin(\omega_1 t_w)\cos(4J\tau)\sin^2(\delta\tau/2) - \cos(\omega_1 t_w)\cos^2(\delta\tau/2)+\tfrac{1}{2}\sin^3\omega_1 t_w\cos^2(\delta\tau/2)|, \quad (2)$$

where M_0 is the macroscopic magnetic moment. For $\omega_1 t_w = \pi/2$ the observed plot of the envelope due to protons in CCl_2HCHO is given in Fig. 2. The plot agrees with (2) within experimental error when normalized to unity in order to correct for damping due to T_2 (total relaxation time) and molecular diffusion.[1] A generalized form of the Hamiltonian operator (1) containing terms with more than two spin operators is now being used to calculate the shape of the echo envelope. The results thus obtained will be

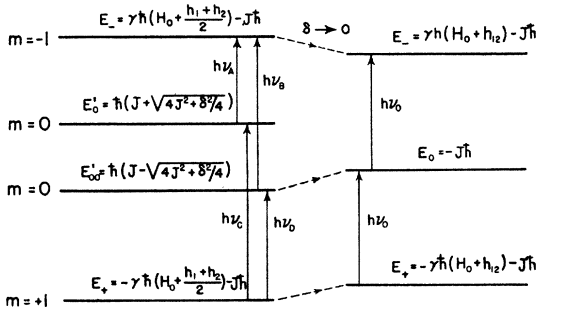
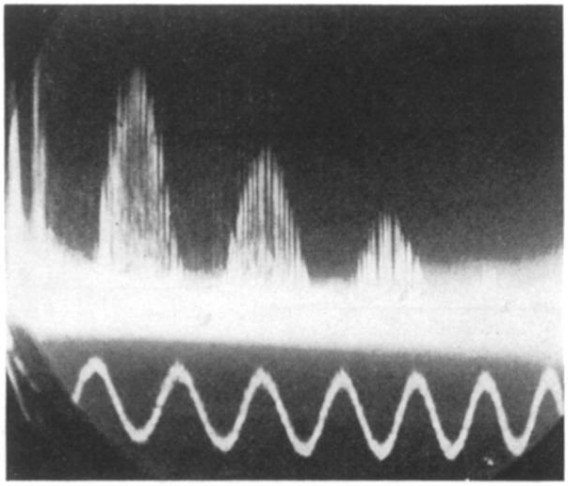


FIG. 1. Zeeman energy level diagram for a nonequivalent two spin system (for each spin, $I=\frac{1}{2}$). For $\delta\to 0$ the magnitude of $h_{12}=h_1=h_2$ chosen is arbitrary. For $\delta\sim J$ the intensities of the transitions indicated are determined by the particular transition probabilities between the given states as well as by their statistical weights. For δ finite, two pairs of resonance lines results where $h(\nu_C-\nu_B)=h(\nu_D-\nu_A)=4J\hbar$ is the separation between lines in each pair, and $h(\nu_B-\nu_A)=h(\nu_C-\nu_D)=2\hbar(4J^2+\delta^2/4)^{\frac{1}{2}}$.



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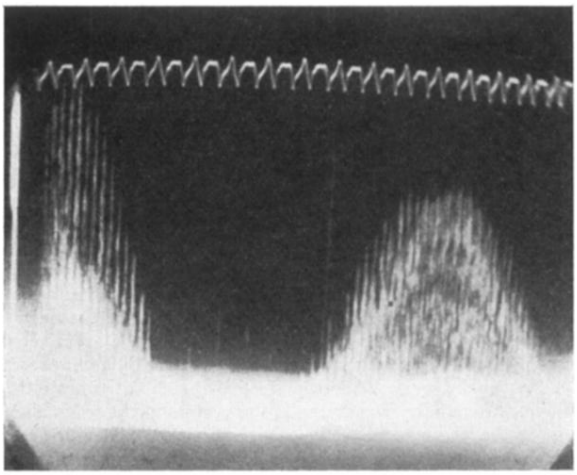

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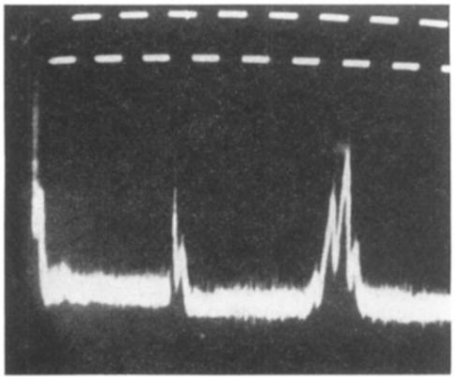

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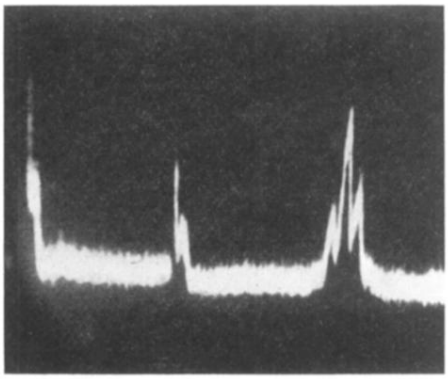

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