Effects of Perturbing Radiofrequency Fields on Nuclear Spin Coupling

ARNOLD L. BLOOM AND JAMES N. SHOOLERY
Varian Associates, Palo Alto, California

(Received October 8, 1954; revised manuscript received November 24, 1954)

An analysis is made of double resonance experiments in which the $\mathbf{I}_1\cdot\mathbf{I}_2$ interaction observable in certain nuclear magnetic resonance spectra is perturbed by a strong radiofrequency field. The problem is treated by transforming to a rotating coordinate system in which all terms in the Hamiltonian are stationary except for the weak rf field used to investigate the spectrum. Transition energies and intensities are computed in the rotating frame and the spectrum transformed back to the laboratory frame by adding a constant factor to the energy. A double-resonance experiment involving the nuclei F^{19} and P^{31} is described and the experimental results compared with those computed from the theory.

I. INTRODUCTION

WHEN a molecule in a liquid contains several nuclei that have different Larmor frequencies in a given magnetic field, it is often found that the magnetic resonance line for a given nucleus is split into a multiplet whose separation is independent of the applied field.[1] The origin of this line splitting has been discussed by Ramsey,[2] and by Ramsey and Purcell,[3] who show that a coupling between nuclei transmitted via the surrounding electron cloud produces an $\mathbf{I}_1\cdot\mathbf{I}_2$ type of interaction. Recently, experiments have been performed in this laboratory and at Stanford University in which the spin-spin interaction has been disturbed by the application of a strong rf in the vicinity of resonance of one of the nuclei.[4–6] If the rf is strong enough, the spin-spin coupling can be completely destroyed, but for intermediate rf amplitudes the multiplet structure of the spectrum from the undisturbed nucleus often increases in complexity. The purpose of this paper is to discuss the more complex multiplet structure and its behavior as a function of the disturbing rf.

II. THEORY

We shall consider the simplest possible case, that of a system of two nuclei with different gyromagnetic ratios γ_1 and γ_2 respectively. A steady magnetic field H_0 is applied in the z direction which, in the absence of any spin-spin interaction, would provide Larmor angular frequencies γ_1H_0 and γ_2H_0 for the respective nuclei. The γ's are here defined to be observed gyromagnetic ratios and thus include the effects of any chemical shifts (i.e., induced local fields) that may be present. With the spin-spin interaction, the Hamiltonian for the system is

$$\mathcal{H}=-\hbar[\gamma_1(\mathbf{I}_1\cdot\mathbf{H})+\gamma_2(\mathbf{I}_2\cdot\mathbf{H})+J(\mathbf{I}_1\cdot\mathbf{I}_2)]. \quad (1)$$

We are concerned with the usual experimental conditions of nuclear magnetic resonance where H is predominantly in the z direction, the Larmor frequencies and their difference are of the order of megacycles/second, and $J/2\pi$ is a kilocycle/second or less. Under these conditions only the expectation values for spin in the z direction are effective in the spin-spin interaction, and the allowed transitions between energy levels of Eq. (1) occur at $\gamma_1H_0+m_2J$, $\gamma_2H_0+m_1J$, $(m=I, I-1, \cdots, -I)$; thus each of the original Larmor frequencies is split into a field-independent multiplet. We now propose to do the following experiment: A strong rf magnetic field H_2, rotating in the xy plane with angular frequency ω_2 in the vicinity of γ_2H_0 is impressed on nucleus 2; simultaneously the transitions in the vicinity of γ_1H_0 are investigated by producing resonance with a weak rf field H_1 whose angular frequency is ω_1. The field H_1 is to be weak enough so that it does not appreciably affect the line width of the observed transitions.

The problem is most easily solved by transforming to a coordinate system rotating with H_2. In the rotating frame of reference, terms in the Hamiltonian including H_2, H_0, and $\mathbf{I}_1\cdot\mathbf{I}_2$ are time-independent and the effect of H_1 can be considered as a perturbation inducing transitions between otherwise well-defined energy levels. Since the effect of H_2 and the spin-spin coupling term is at best only a small perturbation on the precession of the spin of nucleus 1, the resonance radiation will be predominantly polarized in the xy plane and spectrum frequencies calculated in the rotating frame can be transferred to the laboratory frame merely by adding to them the factor $\omega_2/2\pi$.

The dynamics of magnetic resonance problems in a rotating coordinate system has been discussed by Rabi, Ramsey, and Schwinger,[7] and by others. For a nucleus with gyromagnetic ratio γ_i, the H_0 field in the z direction must be replaced by the "effective" z component $(H_0-\omega/\gamma_i)$. Thus, the Hamiltonian for our problem, including only stationary terms, can be described in the

[1] Gutowsky, McCall, and Slichter, J. Chem. Phys. **21**, 279 (1953). References to earlier experimental work are given here.
[2] N. F. Ramsey, Phys. Rev. **91**, 303 (1953).
[3] N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952).
[4] F. Bloch, Phys. Rev. **93**, 944 (1954).
[5] V. Royden, Phys. Rev. **96**, 543 (1954).
[6] For other experiments involving double resonance see J. Brossel and F. Bitter, Phys. Rev. **86**, 308 (1952); T. R. Carver and C. P. Slichter, Phys. Rev. **92**, 212 (1953).
[7] Rabi, Ramsey, and Schwinger, Revs. Modern Phys. **26**, 167 (1954).

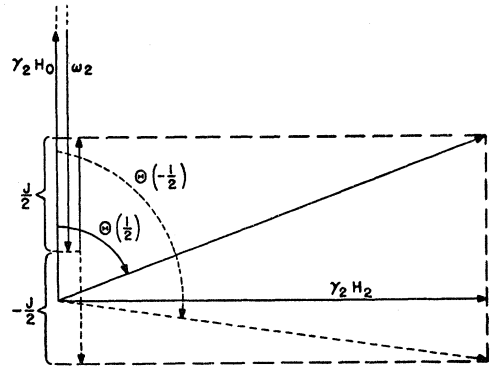

FIG. 1. Vector diagram of forces acting on I_2 in the rotating coordinate system, showing the effect of different orientations of I_1. The special case shown is $I_1=I_2=\frac{1}{2}$.

rotating frame as

$$\mathcal{H}'=-\hbar[\mathbf{I}_1\cdot\mathbf{k}(\gamma_1H_0-\omega_2)+\mathbf{I}_2\cdot\mathbf{k}(\gamma_2H_0-\omega_2)+\mathbf{I}_1\cdot\mathbf{i}(\gamma_1H_2)+\mathbf{I}_2\cdot\mathbf{i}(\gamma_2H_2)+J\mathbf{I}_1\cdot\mathbf{I}_2]. \quad (2)$$

For simplicity, and because it is obviously valid in the experimental case considered here, we shall assume the first term large compared to the others involving $\mathbf{I}_1$. This is equivalent to saying that the nucleus 1 spin is quantized only in the z direction. Spin 2, on the other hand, is quantized in the direction of its effective field, at an angle Θ from the z axis. To determine Θ we consider $J\mathbf{I}_1\cdot\mathbf{I}_2$ in terms of an equivalent magnetic field acting at the site of the nucleus. Refer to Fig. 1. We have

$$a(m_1)=[(\gamma_2H_0+Jm_1-\omega_2)^2+\gamma_2^2H_2^2]^{\frac{1}{2}}, \quad (3)$$

$$\cos\Theta(m_1)=(\gamma_2H_0+Jm_1-\omega_2)/a(m_1), \quad (4)$$

$$\sin\Theta(m_1)=\gamma_2H_2/a(m_1); \quad (5)$$

then the energy levels in the rotating frame are

$$W(m_1,m_2)=\hbar[m_1(\gamma_1H_0-\omega_2)+m_2(\gamma_2H_0-\omega_2+m_1J)\times\cos\Theta(m_1)+m_2\gamma_2H_2\sin\Theta(m_1)], \quad (6)$$

where m_1 is the z component of spin of nucleus 1 and m_2 is now the nucleus 2 spin component in the direction of the effective field.

Restricting ourselves for the time being to $I_1=I_2=\frac{1}{2}$, let us call the $W(m_1=+\frac{1}{2})$ initial states and the $W(m_1=-\frac{1}{2})$ final ones. Of the four possible transitions only two are allowed by selection rules in the unperturbed case where $H_2=0$. In our experiment, however, all four transitions may be observable because Θ changes during the transition, as indicated in Fig. 1; thus the final states of m_2 may not be orthogonal to the initial ones. The relative transition probability for a single nucleus is given by the square of the matrix element connecting initial and final states of nucleus 2, and for $I_2=\frac{1}{2}$ it is

$$P=\cos^2(\xi/2), \quad (7)$$

where ξ is the angle between initial and final states. However, the observed line intensity depends not only on P but also on the population distribution among the various energy levels, and the presence of H_2 changes the distribution from the usual Boltzmann distribution among the energy levels. The type of spin-spin interaction considered here generally does not enter into the thermal relaxation process to any significant extent, and the population distribution can then be calculated as if the two species of nuclei were completely separate and noninteracting. Thus, the total spin population for each value of m_1 is governed by the Boltzmann distribution, but at each value of m_1 the population difference between adjacent levels of m_2 is proportional, not to the Boltzmann distribution value M_0, but to M_z, where M_z is the "slow passage" population difference[8] and is a function of H_2 and Θ. An example of a calculation making use of this change in distribution is given at the end of Sec. IV.

Recently, Overhauser[9] has shown that the hyperfine coupling between electronic and nuclear spins in metals provides a means for greatly enhancing the net nuclear polarization in double resonance experiments, and Bloch[4] and Korringa[10] have predicted a similar effect in nonconducting paramagnetic substances. In order that the "Overhauser effect" take place it is necessary that the primary means of thermal relaxation available to the nucleus (here equivalent to our nucleus 1) be through the spin-spin coupling. However, in the experimental case considered here the thermal relaxation process for each species of nucleus is almost entirely through direct interaction with the lattice, as the J-coupling plays an insignificant role; thus it follows that an enhancement of polarization analogous to that predicted by Overhauser will *not* take place.

In the general case, including spins greater than $\frac{1}{2}$, the spin-spin multiplet in the absence of H_2 contains $(2I_2+1)$ lines. When H_2 is applied, the selection rule ($\Delta m_2=0$ in the laboratory frame) no longer holds strictly, as explained above, and in addition transitions starting from different m_1 levels may no longer be superimposed, since Eq. (6) is not a linear function of m_1. Thus there may be as many as $(2I_1)(2I_2+1)^2$ lines in the multiplet when H_2 is present. In addition, it appears possible that the selection rule ($\Delta m_1=\pm1$) is partially broken down by the effect of H_2, making possible the observation of multiple-quantum transitions.

III. CALCULATIONS

We present some calculated results for the simple case of two nuclei each of spin $\frac{1}{2}$, showing how the multiplet varies as a function of experimental conditions. For simplicity we define the four possible transitions by subscripts a, b, c, d, and the energies of transition in the laboratory frame as follows:

$$\Delta W_a=W(\tfrac{1}{2},\tfrac{1}{2})-W(-\tfrac{1}{2},\tfrac{1}{2})+\hbar\omega_2, \quad (8a)$$

[8] F. Bloch, Phys. Rev. **70**, 460 (1946).
[9] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).
[10] J. Korringa, Phys. Rev. **94**, 1388 (1954).

$$\Delta W_b = W(\tfrac{1}{2}, -\tfrac{1}{2}) - W(-\tfrac{1}{2}, -\tfrac{1}{2}) + \hbar\omega_2, \quad (8b)$$

$$\Delta W_c = W(\tfrac{1}{2}, \tfrac{1}{2}) - W(-\tfrac{1}{2}, -\tfrac{1}{2}) + \hbar\omega_2, \quad (8c)$$

$$\Delta W_d = W(\tfrac{1}{2}, -\tfrac{1}{2}) - W(-\tfrac{1}{2}, \tfrac{1}{2}) + \hbar\omega_2. \quad (8d)$$

Case 1. $\omega_2 = \gamma_2 H_0$ (center of nucleus 2 doublet). ω_1 and amplitude of H_2 variable.

In this case $\Theta(-\frac{1}{2}) = -\Theta(\frac{1}{2})$. The transition angular frequencies become

$$\begin{aligned} \Delta W_a/\hbar &= \Delta W_b/\hbar = \gamma_1 H_0, \\ \Delta W_c/\hbar &= \gamma_1 H_0 + \tfrac{1}{2}J', \\ \Delta W_d/\hbar &= \gamma_1 H_0 - \tfrac{1}{2}J', \end{aligned} \quad (9)$$

where

$$J' = (J^2 + 4\gamma_2^2 H_2^2)^{\frac{1}{2}}. \quad (10)$$

The relative transition probabilities are

$$\begin{aligned} P_a &= P_b = 4\gamma_2^2 H_2^2/(J')^2, \\ P_c &= P_d = J^2/(J')^2. \end{aligned} \quad (11)$$

When $H_2 = 0$, $J' = J$ and transitions c and d form the doublet.[11] As the rf level H_2 is increased, the original doublet lines are spread apart and weakened; simultaneously a new line appears at the center frequency $\gamma_1 H_0$ and grows at the expense of the doublet. When $\gamma_2 H_2 \gg J$ there is only the single line due to transitions a and b, twice as intense as each of the original doublet lines. This result for strong H_2 agrees with the one obtained by using the concept of an "averaging out" of the spin-spin interaction due to rapid transitions in the laboratory frame.

Case 2. $\omega_2 = \gamma_2 H_0$, ω_1 fixed at $\gamma_1 H_0$, a sweep field ΔH is used to investigate the spectrum.

This case is generally more amenable to study in the laboratory than Case 1. By substituting $(H_0 + \Delta H)$ for H_0 in Eq. (6) and solving for transitions at $\Delta W = \hbar\omega_1$ in Eq. (8), we obtain lines at

$$\Delta H = 0, \quad (12a)$$

$$(\Delta H)^2 = \frac{J^2(\gamma_1^2 - \gamma_2^2) + 4\gamma_1^2\gamma_2^2 H_2^2}{4\gamma_1^2(\gamma_1^2 - \gamma_2^2)}. \quad (12b)$$

The intensity of the line at $\Delta H = 0$ is given by P_a in Eq. (11); for the other lines it must be determined with the aid of Eq. (7). If $\gamma_1 > \gamma_2$, the results are similar to those of Case 1. If $\gamma_1 < \gamma_2$, the line structure collapses with increasing H_2, giving only a single line for $4\gamma_2 H_2 \geq J$.

Case 3. $\gamma_2 H_2 \gg \frac{1}{2}J$, ω_1 and ω_2 variable.

By $\gamma_2 H_2 \gg \frac{1}{2}J$, we imply that to good approximation $\Theta(\frac{1}{2}) = \Theta(-\frac{1}{2}) = \Theta_0$, where Θ_0 is the effective field angle on nucleus 2 in the absence of any spin-spin interaction. In this case there are no more than two lines, located at

$$\Delta W/\hbar = \gamma_1 H_0 \pm \tfrac{1}{2}J\cos\Theta_0. \quad (13)$$

[11] Note that in the limit $H_2 = 0$ the effective field reverses direction during a transition, for $\omega_2 = \gamma_2 H_0$. Thus it requires a double transition (m_1 and m_2 both changing) in the rotating frame to agree with the selection rule ($\Delta m_2 = 0$) in the laboratory frame.

IV. EXPERIMENTAL RESULTS

To check the theory, an experiment was performed on the spin-spin interaction between F^{19} and P^{31}, with the former taken to be nucleus 1. Both nuclei have spin $\frac{1}{2}$ and their gyromagnetic ratios differ by more than a factor of two, thus the approximations used in the theory are valid to a high order of accuracy. The molecule studied was Na_2PO_3F in aqueous solution; since the Na atoms are ionically bonded or ionized in solution, they do not contribute to the spin interaction. The field-independent splitting of the fluorine resonance in this molecule has been reported previously by Gutowsky, McCall, and Slichter.[1]

The apparatus used was a Varian Associates V-4300 High Resolution Spectrometer and V-4012 Electromagnet operating at about 7500 gauss. The transmitter coil input circuit was modified so it was resonant at both the fluorine Larmor frequency of 30.00 Mc/sec and the phosphorous frequency of 12.91 Mc/sec. An auxiliary oscillator and power amplifier provided rf power for the H_2 field at the latter frequency. Both oscillators were crystal controlled; the one providing H_2 was tuneable over a range of several hundred cycles. The receiver coil and amplifiers were tuned only to the 30-Mc/sec fluorine signal. The V-4300 Spectrometer utilizes a slow linear magnetic field sweep and the signal intensity is displayed directly on the oscilloscope or recording meter.

Before the splitting could be studied as a function of H_2, the interaction factor J had to be determined. An audiofrequency sine wave modulation of the magnetic field was superimposed on the sawtooth sweep with the result that satellites were produced on each side of each doublet line. The satellites occur because a field modulation is in every way equivalent to a frequency modulation of the rf, insofar as the equations of motion of the nuclear ensemble are concerned.[8] The satellites thus have positions and intensities determined by the "sidebands" of the equivalent frequency modulation. The splitting $J/2\pi$ was thus determined as twice the value of the audiofrequency which superimposed the first satellites from each line in the center of the doublet. This measurement gave $J/2\pi = 860 \pm 4$ cps, which when converted to equivalent magnetic field difference gives a splitting of 0.214 gauss. The value obtained by Gutowsky *et al.*[1] by measurement of the field difference was 0.195 gauss. We have not explored the reasons for the discrepancy between our results and those of Gutowsky, but it should be pointed out that the accuracy of our method depends only on the calibration of the audio-oscillator and on the linewidth. In our measurements the audiofrequency was counted directly on a Hewlett-Packard 524-A frequency counter, and with sufficiently slow sweep the two satellites were clearly resolved if the frequency was varied by 5 cps on either side of its center value.

When the perturbing rf field was turned on at maxi-

mum amplitude, the doublet separation was found to be a function of ω_2, as expected. This is illustrated in Fig. 2. The angular frequency ω_2 was taken to be in the center of the phosphorous doublet when the two lines coalesced into one, and the deviations $\Delta\nu$ in Fig. 2 were measured from this value. The frequencies were determined by counting the crystal fundamental frequency with the 524-A counter. Owing to the existence of chemical shifts which are not known to sufficient accuracy, one cannot set ω_2 for $\Delta\nu=0$ in advance of actually seeing the spectrum.

Figure 3 shows the relative separation as a function of ω_2, compared with the theoretical separation calculated with the aid of Eq. (13). In this calculation $\gamma_2 H_2$ was taken to be 5000. However, it should be pointed out that H_2 was not strong enough to justify entirely the approximation $\Theta=\Theta_0$; this is evident in Fig. 2 from the fact that all four lines are visible instead of only the center two. A more exact calculation shows that the asymmetry of the intensities in some of the traces is a real effect and the direction of asymmetry can be reversed by changing the sign of $\Delta\nu$; this has been verified experimentally.

With $\Delta\nu$ set at zero, the amplitude of H_2 was varied and typical results were as shown in Fig. 4. At each setting of the H_2 attenuator, the alternating field $2H_2\cos(\omega_2 t)$ was investigated by means of a small search coil placed in the probe and connected to an electronic voltmeter. The search coil measurements were subject to large systematic errors owing to uncertainties in the effective area of the coil, and in addition were not very reproducible because it was difficult to place the coil in exactly the same spot each time, but the results indicate the order of magnitude of the field. Measurements were taken on the spectrometer traces of the relative separation of the outside lines (with the separation at $H_2=0$ taken as unity), and of the ratio of the center line peak amplitude to the average amplitude of the outside lines.

From the relative line splitting, we calculated H_2 with the aid of Eq. (12b) and compared it with the search coil measurements. Assuming the calculated H_2 to be correct, we calculated the relative intensity of the center line [Eq. (11)] and the outside lines, obtained by first calculating $\Theta(\frac{1}{2})$ and $\Theta(-\frac{1}{2})$. To these intensities a correction had to be made for changes in the population distribution. From the argument given in Sec. II it is easy to show that, for the line at $\Delta H>0$ the ratio of the true to the uncorrected line intensity is given by

$$1-(\gamma_2/2\gamma_1 M_0)[M_z(m_1=\tfrac{1}{2})-M_z(m_1=-\tfrac{1}{2})], \quad (14)$$

with an analogous expression for the other outside line (the center line requires no correction). An exact expression for M_z requires a knowledge of T_1 and T_2, which we did not have; however, under the circumstance that $\gamma_2^2 H_2^2 T_1 T_2 \gg 1$ we could use, to excellent approximation,

$$M_z=M_0\cos^2\Theta. \quad (15)$$

The correction was relatively small, amounting at most to about 15 percent.

The results of the measurements and calculations are summarized in Table I. The line intensities are summarized as the ratios of the center to the average outside line amplitudes; uncertainties are based on the

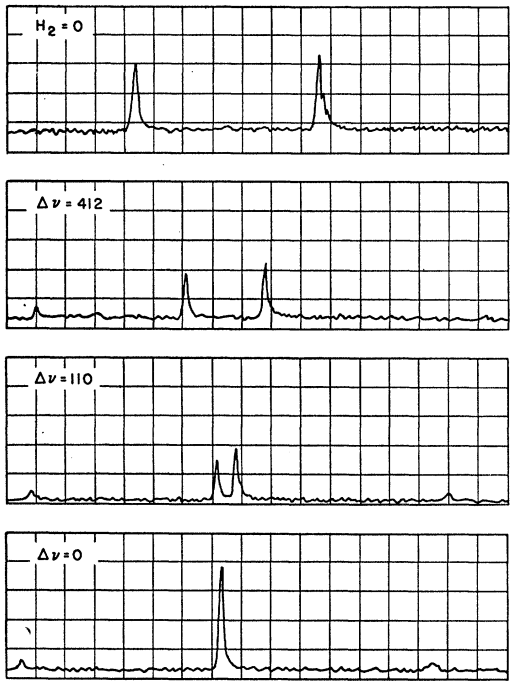

FIG. 2. Effect on the fluorine spectrum of varying the phosphorous rf frequency, with H_2 fixed at 0.464 gauss. The top trace shows the unperturbed spectrum ($H_2=0$) for comparison. We define $\Delta\nu=(\gamma_2 H_0-\omega_2)/2\pi$.

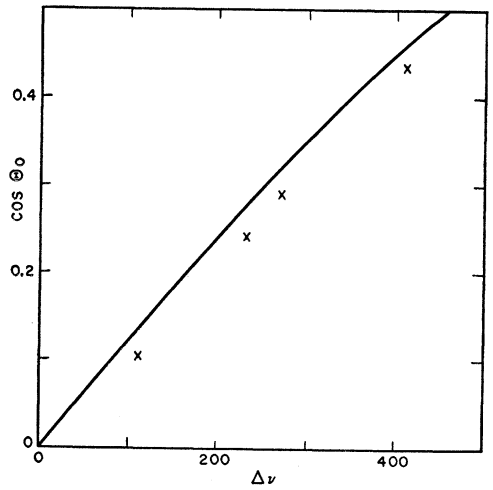

FIG. 3. Measured and calculated splitting as a function of the perturbing field frequency deviation, $\Delta\nu$, from the "center" frequency. In the calculation, we assume $\gamma_2 H_2=5000$.

TABLE I. Relative line splitting and intensity as a function of the perturbing field amplitude.

Relative splitting measured	H_2 (gauss) from search coil	H_2 (gauss) from splitting	Intensity ratio, measured	Intensity ratio from splitting
1.00	0	0	0	0
1.15	0.13	0.128	0.40±0.03	0.60
1.26	0.18	0.172	0.85±0.05	1.21
1.43	0.26	0.231	1.76±0.08	2.37
1.72	0.34	0.315	4.45±0.33	4.83
1.90	0.39	0.364	6.30±0.63	6.38
2.02	0.42	0.395	8.5 ±1.1	7.69
2.09	0.49	0.414	10.9 ±1.7	8.50
2.24	0.48	0.451	14.8 ±3.0	10.2
2.29	0.49	0.464	12.0 ±1.2	10.7
2.30	0.51	0.466	18.5 ±4.6	10.9

estimated rms noise level. In all calculations we used $\gamma_1=2.52\times10^4$, $\gamma_2=1.083\times10^4$, and $J=5400$.

V. DISCUSSION

A comparison of the experimental and calculated results in Fig. 3 and Table I seems to indicate that the concept of a Hamiltonian which is made stationary by transforming to a rotating coordinate system provides an adequate working model for prediction of the spectrum in magnetic double-resonance experiments. Since the lattice motions have about the same appearance in the rotating frame as in the laboratory frame, one would also predict that there should be no gross changes in linewidth due to the presence of the perturbing rf; this is also borne out by the experiment. Although it is probable that there are small changes in natural linewidth owing to changes in the matrix elements which affect the relaxation probability,[12] such changes would not be observable in our experiments because other work has shown that the observed linewidth is due almost entirely to instrumental effects, i.e., H_0 field inhomogeneity and rate of sweep.

The intensity measurements were based entirely on peak height, rather than on area, because it is much more difficult to measure the area accurately. It is therefore evident that any instrumental effects which preferentially broaden either the center or the outside lines will introduce systematic discrepancies between the observed and the calculated intensity ratios. Thus, if H_2 were not set exactly in the center of the phosphorous doublet, then the center line would in reality be a closely spaced doublet and an amplitude measurement would not give the full intensity. Such an effect, which is most important when H_2 is small, is noticeable in the traces of Fig. 4 and almost certainly accounts for the systematic discrepancies in Table I for values of H_2 less than 0.3 gauss. There is apparently a systematic discrepancy at large values of H_2 whose origin is not completely understood; however, it can be shown that an inhomogeneity in the H_2 field of the order of one percent would broaden the outside lines enough to account for the observed discrepancy. From the known geometry of the probe, one would expect inhomogeneities of this order of magnitude to be present.

[12] J. P. Lloyd and G. E. Pake, Phys. Rev. **94**, 579 (1954).

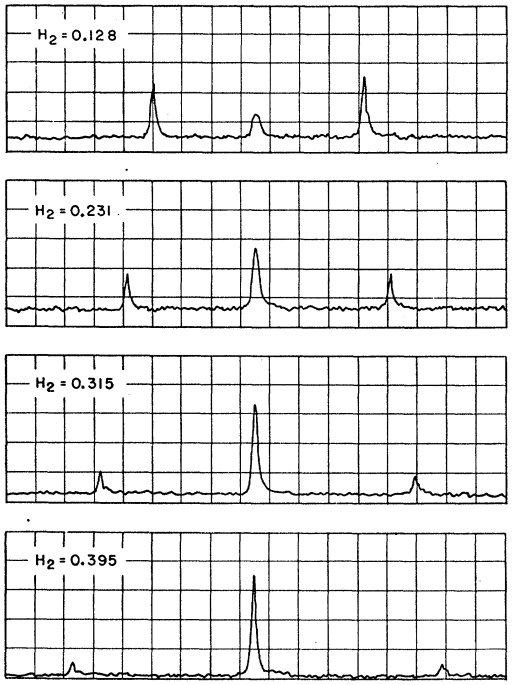

FIG. 4. Effect on the fluorine spectrum of varying the phosphorous rf amplitude H_2, with $\omega_2=\gamma_2 H_0$. The top and bottom traces of Fig. 2 are also part of this series.

The data of this experiment, and other data taken in H_2 fields as high as 0.7 gauss, show that in the limit of very large H_2 the intensity of the center line becomes exactly twice the height of the original doublet lines, within experimental error. Had an enhancement of the type predicted by Overhauser[9] been present, the center line intensity would have been increased still further by a factor $(1+|\gamma_2/\gamma_1|)$ or about 1.4. The absence of even a partial enhancement agrees with the statements made in Sec. II regarding the absence of the Overhauser effect in connection with the indirect nuclear spin-spin coupling.

We wish to thank Dr. M. E. Packard for advice and encouragement, and Virginia Royden for assistance in performing the experiment. The Na_2PO_3F was kindly lent by Ozark-Mahoning Company, Tulsa, Oklahoma. We are indebted to Professor F. Bloch for several stimulating discussions on this subject.