Influence of a Second Radiofrequency Field on High-Resolution Nuclear Magnetic Resonance Spectra

Article in The Journal of Chemical Physics · July 1962
DOI: 10.1063/1.1732980

2 authors, including:

Ray Freeman
University of Cambridge
301 PUBLICATIONS 23,187 CITATIONS

All content following this page was uploaded by Ray Freeman on 20 March 2014.
The user has requested enhancement of the downloaded file.
Influence of a Second Radiofrequency Field on High-Resolution Nuclear Magnetic Resonance Spectra

W. A. Anderson and R. Freeman

Varian Associates, Instrument Division, Palo Alto, California

(Received March 8, 1962)

A theoretical treatment of nuclear-magnetic double-irradiation experiments is given which is applicable to two groups of nuclei of arbitrary spin, either of different nuclear species or in a situation where the chemical shift is large in comparison with the spin-coupling constant. A convention is introduced whereby the group which experiences the "strong" rf field \( H_2 \) is given the symbol X, while the group to be investigated is represented by A. Particular attention is given to groups of spin \( \frac{1}{2} \) nuclei in \( AX_n \) type molecules where \( n, n \leq 3 \), and their spin-decoupling behavior is presented in graphical form. Good correlations are observed with the experimental proton double-resonance spectra of acetone, diethyl succinate, and 1,2,3 trichloroethane. When a single \( X \) transition is irradiated with a very weak \( H_2 \) a splitting of the \( A \) spin-multiplet lines into submultiplets is observed; at the same time an Overhauser-type redistribution of intensities may occur in certain molecules. Intermediate strengths of \( H_2 \) centered on the \( X \) multiplet coalesce the \( A \) spectrum to what is essentially a single line for \( AX_n \) molecules, but for \( AX_2 \) molecules where \( n \geq 1 \) there is a "residual splitting" which, although it decreases as \( H_2 \) is made stronger, may never disappear completely. At high powers it is necessary to displace \( H_2 \) slightly off resonance for group \( X \) towards the A resonance in order to obtain optimum decoupling, a correction which can be important in the accurate measurement of proton chemical shifts by spin-decoupling techniques.

1. INTRODUCTION

It is becoming increasingly apparent that the technique of double irradiation, originally proposed by Bloch, can be profitably applied to a variety of problems that arise in the study of high-resolution nuclear magnetic resonance spectra. The multiplet structure that is observed on many nuclear resonance signals of liquid samples has been shown to be due to a scalar coupling \( J \) of the spins of chemically shifted nuclei through the valency electrons. The effect of the coupling can be made to disappear if one group is subjected to a rf field \( H_2 \) such that \( \gamma H_2 > 2\pi J \), and when the resonance of the other group is investigated by means of a weak radiofrequency field \( H_1 \) in the simple case where there are no other couplings present, it is found to have coalesced to a single sharp line. The application of this technique to the accurate measurement of chemical shifts of hidden resonance lines and to the determination of relative signs of spin-coupling constants led to the realization that in many circumstances intermediate strengths of the field \( H_2 \) may have to be employed such that \( \gamma H_2 \sim 2\pi J \). Recently Freeman and Whiffen have shown that a calculation along the lines of that given by Bloom and Shoolery for two dissimilar spin \( \frac{1}{2} \) nuclei can be used to predict the patterns obtained in double irradiation of AX type proton systems with a high degree of accuracy for values of \( \gamma H_2 \) comparable with \( 2\pi J_{AX} \). A convenient graphical representation of the results was proposed. The present work extends these calculations to cover all the cases of interest for the proton resonance spectra of organic molecules with the restriction that the groups concerned contain only magnetically equivalent protons, and where the mutual coupling is weak in comparison with the chemical shift. A modification of the graphical presentation allows the same scheme to be used both for nuclei of the same species and for nuclei of different species.

2. THEORY OF DOUBLE RESONANCE

Consider the case of two groups of nuclei placed in a large static magnetic field \( H_0 \) in the \( Z \) direction. Let \( I \) and \( \omega_I = \gamma_1 H_0 \) represent the total spin values and the Larmor frequency of the first group, and \( S \) and \( \omega_S = \gamma_2 H_0 \) represent the total spin values and Larmor frequency of the second group. Let \( J \) represent the magnitude of the spin-spin coupling measured in units of cps. In the experiments described here, the "strong" rf field with magnitude \( 2H_2 \) and angular frequency \( \omega_2 \) is applied along the \( X \) axis so that it causes transitions of the nuclei with spin \( \frac{1}{2} \). A "weak" rf field of magnitude \( 2H_2 \) and angular frequency \( \omega_2 \) is also applied along the \( X \) axis so that it causes transitions of the nuclei...
with spin $I$. This weak field is used to observe the resonant frequencies of the system, and it will be assumed that it is sufficiently small so that it does not appreciably perturb the system.

The oscillating fields $2H_1$ and $2H_2$ may be visualized as two counterrotating fields, each with a magnitude of half the peak value. It can be shown\(^8\) that only the component which rotates in the same sense as the nuclear precession is effective in appreciably perturbing the system. Thus, the effective magnetic field seen by the nuclei is\(^9\)

$$H = H_0 + (H_1 \cos \omega_1 t + H_2 \cos \omega_2 t) \cos \theta.$$  

(1)

The Hamiltonian, measured in units of angular frequency, representing the interaction of the molecular system with the "strong" external fields is given by

$$\mathcal{H} = -[\omega_1 I_x + \omega_2 S_z - 2\pi JI \cdot S + \gamma_1 H_1 (I \cos \omega_1 t - I \sin \omega_1 t)] + \gamma_2 H_2 (S_x \cos \omega_2 t - S_y \sin \omega_2 t).$$  

(2)

The "weak" rf field will be considered as a small perturbation and is represented by the Hamiltonian $\mathcal{H}'$.

$$\mathcal{H}' = -[\gamma_1 H_1 (I \cos \omega_1 t - I \sin \omega_1 t)] + \gamma_2 H_2 (S_x \cos \omega_2 t - S_y \sin \omega_2 t).$$  

(3)

When the Hamiltonian is expressed in units of angular frequency, the Schrödinger equation has the form

$$i\frac{\partial \psi}{\partial T} = \mathcal{H}' \psi.$$  

(4)

One may transform the coordinates of the wave functions $\psi$ to a new set by the operator $T$ such that

$$\psi_T = T \psi$$  

(5)

and $\psi = T^{-1} \psi_T$. In addition, if the Hamiltonian is transformed by the transformation

$$\mathcal{H}_T = T \mathcal{H} T^{-1} + i T \frac{\partial}{\partial T} T^{-1},$$  

(6)

the Schrödinger equation will remain invariant, i.e.,

$$i\frac{\partial \psi_T}{\partial T} = \mathcal{H}_T \psi_T.$$  

Although the initial Hamiltonian is time dependent, it is possible to transform it to a rotating coordinate system where it is time independent.\(^11\) The required transformation has the form

$$T = \exp[-i \omega_1 (I_x + S_x)].$$  

(7)

The transformed Hamiltonian $\mathcal{H}_T$ is given by

$$\mathcal{H}_T = -[\omega_1 I_x + \omega_2 S_z - 2\pi JI \cdot S + \gamma_1 H_1 (I \cos \omega_1 t + I \sin \omega_1 t)] + \gamma_2 H_2 (S_x \cos \omega_2 t - S_y \sin \omega_2 t).$$  

(8)

$$\mathcal{H}_T' = -[\gamma_1 H_1 (I \cos \omega_1 t - I \sin \omega_1 t)] + \gamma_2 H_2 (S_x \cos \omega_2 t - S_y \sin \omega_2 t).$$  

(9)

2.1 Weakly Coupled Systems, $| \omega_1 - \omega_2 | \gg 2\pi | J |

A simplification may be made when the two groups of nuclei have different gyromagnetic ratios, or when the chemical shift of the two groups is large compared to their spin–spin coupling. Such a system is often denoted by $A_XB_m$ in the NMR literature.\(^12\) For such a case only the diagonal matrix elements of the term $JI \cdot S$ are kept in the Hamiltonian. One may assume that the frequency of the "weak" rf field $\omega_1$ is near $\omega_1$ and that $\omega_2$ is near $\omega_2$. Under these conditions

$$| \omega_1 - \omega_2 | \gg \gamma_1 H_1$$  

and the term $\gamma_2 H_2 I_x$ may be dropped from Eq. (8). A similar reasoning shows that the term involving $\gamma_1 H_1$ may be dropped from Eq. (9). With these approximations, the Hamiltonians are given by

$$\mathcal{H}_T = -[\omega_1 I_x + (\omega_2 - \omega_1) S_z - 2\pi JI \cdot S + \gamma_2 H_2 S_z],$$  

(10)

$$\mathcal{H}_T' = -[\gamma_1 H_1 (I \cos \omega_1 t - I \sin \omega_1 t)] + \gamma_2 H_2 S_z. $$  

(11)

Another transformation by the rotation operator

$$V = \exp[i \theta (m) S_z],$$  

(12)

where

$$\theta (m) = \tan^{-1}[\frac{\gamma_2 H_2}{(\omega_2 - \omega_1 - 2\pi J m)}]$$  

transforms the Hamiltonian (10) into diagonal form. The transformed Hamiltonian has the form

$$\mathcal{H}_V = -[\omega_1 I_x + A (m) S_z],$$  

(13)

with

$$A(m) = [\omega_2 - \omega_1 - 2\pi J m] + \gamma_2 H_2.$$  

(14)

Here $m$ represents the eigenvalue of the operator $I_z$. The rotation operator $V$ did not change the Hamiltonian $\mathcal{H}_V$ given by (11) since it commutes with it. The well-known spin wave functions which diagonalize $I_x^2$, $I^2$, and $S^2$ with eigenvalues $I(I+1)$, $m$, and $S(S+1)$, respectively, will diagonalize $\mathcal{H}_V$. The wave functions $\psi_V$ will be product wave functions which may be denoted by

$$\psi_V (I, m, S, M) = U(I, m) U(S, M).$$  

The eigenvalues of $\mathcal{H}_V$ are independent of $I$ and $S$ and are given by

$$E_V (m, M) = -[\omega_1 - \omega_2 - A(m)] M.$$  

(15)

It will be shown below that the selection rules for transitions produced by $\omega_1$ are those in which $\Delta m = \pm 1$ and $\Delta M = 0, \pm 1, \pm 2, \cdots \pm 2S$. The transition frequencies in the laboratory system are given by

$$\omega(m, M; m-1, M') = E_V (m-1, M') - E_V (m, M) + \omega_2$$  

$$= \omega_1 + A(m) M - A(m-1) M'. $$  

(17)

Under the conditions of weak rf fields $H_0$, the inten-
sity of these transitions can be shown from first-order time-dependent perturbation theory to be proportional to the square of the matrix element of $I^z$ between wave functions of the laboratory system. Since the eigen wave functions $\psi_r(I, m, S, M)$ in the $I^z$ system are known, the wave functions of the laboratory frame $\psi(I, m, S, M)$ may be calculated since they are related through the transformations

$$\psi(I, m, S, M) = T^{-1} V^{-1}(m) \psi_r(I, m, S, M).$$  \hspace{1cm} (18)

The line intensities $L$ are thus proportional to

$$| \langle \psi^+(I, m, S, M) | I^z | \psi(I, m', S, M') \rangle |^2.$$

This expression may be solved to yield the line intensities by substituting into this matrix element the wave functions of Eq. (18) and the transformations of Eqs. (7) and (12). Use is made of the fact that the wave functions are product wave functions, and that operators involving only $I$ commute with operators involving only $S$. The matrix element then takes the product form

$$| \left\langle U^+(I, m) \exp(-i\omega_2 I^z) | I^z | \exp(i\omega_2 I^z) U(I, m') \right\rangle |^2 \times | \left\langle U^+(S, M) \exp(-i\theta(m') - \theta(m)) S | U(S, M') \right\rangle |^2.$$

The first term of this product restores the time dependence to the resonance signal. Since the quantity of interest is the relative magnitude of the observed signals we may replace this product by just the simple matrix element

$$\left\langle U^+(I, m) | I^z | U(I, m') \right\rangle.$$

This matrix element has nonvanishing terms only if $m' = m \pm 1$. The evaluation of the second term of the

---

13 F. Bloch, Phys. Rev. 102, 104 (1956), Eq. 5.10.
one specified by \( \psi(I, m-1, S, M') \) will be denoted by \( L(m, M; m-1, M') \) which is given by
\[
L(m, M; m-1, M') = (I-m+1) (I+m) d^2(S, M, M', \phi),
\]
where
\[
\phi = \phi(m) = \theta(m-1) - \theta(m)
\]
and
\[
\phi = \phi(m) = \theta(m-1) - \theta(m)
\]
represent the difference in the argument of two terms. The sum is over the integral values of \( K \) for which the factorial arguments are greater than or equal to zero.

\[
L(m, M; m-1, M') = (I-m+1) (I+m) d^2(S, M, M', \phi),
\]
where
\[
\phi = \phi(m) = \theta(m-1) - \theta(m)
\]
and
\[
\phi = \phi(m) = \theta(m-1) - \theta(m)
\]
are the arguments of two terms. The sum is over the integral values of \( K \) for which the factorial arguments are greater than or equal to zero.

The solutions of general interest corresponding to varying \( J \) and \( I \), respectively. The frequencies are determined by Eq. (17) and the line intensities from Eqs. (19) and (21).

\[
\Delta = (\omega_2 - \omega_X)/2\pi | J | , \quad \Omega = (\omega_2 - \omega_A)/2\pi | J | ,
\]
where \( \omega_A = \gamma_A H_0 \), \( \omega_X = \gamma_X H_0 \), and \( H_0 \) is the static or slowly varying main magnetic field, and \( J = J_{AX} \) is the spin–spin coupling between the two groups of nuclei.

The experimental variables are \( \omega_1, \omega_2, \) and \( H_0 \), and it is usual to keep any two of these constant and vary the third. The frequencies of the observed \( A \) transitions can then be represented on a graph of \( \Omega \) versus \( \Delta \), and their intensities \( L \) are conveniently expressed as a function of \( \Delta \) (See Figs. 1, 2, and 3).

In a “frequency-sweep” experiment, \( \omega_2 \) and \( H_0 \) are either held constant or locked together by some kind of nuclear resonance controller and \( \omega_1 \) is swept through the A resonance. This results in a spectrum which may be predicted by drawing a vertical line on the diagram at the requisite value of \( \Delta \). An experiment which is more common because of the simplicity of the instrumentation required, is the “field-sweep” method which consists in holding \( \omega_2 \) and \( \omega_2 \) constant and varying \( H_0 \), corresponding to varying \( \Omega \) and \( \Delta \) simultaneously. On the figure this is a line with a slope \( \gamma_A/\gamma_X \) and an intercept on the \( \Delta \) axis which may be called \( \Delta' \) corresponding to the deviation from the resonance condition of \( \omega_2 \) when \( \omega_1 = \omega_A \). For proton–proton decoupling the slope of the line is extremely close to 45°, and
\[
\Delta' = [2\pi \delta_{AX} - (\omega_1 - \omega_2)]/2\pi | J | ,
\]
that is, the discrepancy between the chemical shift and the frequency difference between the two oscillators. A third possible experiment consists in holding
FIG. 1(a). The transition frequencies $\Omega$ and intensities $L$ of the A resonance plotted against the offset parameter $\Delta$ for an AX system (full lines) and an A$_2$X system (full and broken lines) for $\gamma H_d/2\pi = 0.2J$. 

NUCLEAR MAGNETIC RESONANCE SPECTRA

89
Fig. 1(b). The transition frequencies $\Omega$ and intensities $I$ of the A resonance plotted against the offset parameter $\Delta$ for an AX system (full lines) and an A$_2$X system (full and broken lines) for $\gamma J/2\pi = J$. 
Fig. 2(a). The transition frequencies $\Omega$ and intensities $L$ of the A resonance of an AX$_2$ system plotted against the offset parameter $\Delta$ for $\gamma H/2\pi = 0.2J$. 
Fig. 2(b). The transition frequencies $\Omega$ and intensities $L$ of the $\Delta$ resonance of an $\Delta X_2$ system plotted against the offset parameter $\Delta$ for $\gamma H_d/2\pi = J$. 
FIG. 3(a). The transition frequencies $\Omega$ and intensities $I$ of the A resonance of an $AX_2$ system plotted against the offset parameter $\Delta$ for $\gamma H_2/2\pi = 0.2J$. 
Fig. 3(b). The transition frequencies $\Omega$ and intensities $L$ of the $A$ resonance in an $AX_3$ system plotted against the offset parameter $\Delta$ for $\gamma H_0/2\pi = J$. 
\( \omega_1 \) and \( H_0 \) constant (or controlled in such a way that they remain in constant proportion) and sweeping the frequency \( \Omega \). On the diagrams, this means operation at constant \( \Omega \), and the results of such experiments may be predicted by drawing a horizontal line at a height determined by \( \Omega \).

The advantage of this presentation over that used by Freeman and Whiffen is that it applies generally, to nuclei of unlike species as well as to like nuclei. It also illustrates the results to be expected in a decoupling experiment where the strong field \( H_2 \) is swept through one resonance while the investigating field \( H_1 \) is held steady at one point in the spectrum of another group, a method to some extent paralleling the "Endor" technique.

Since carbon atoms can form no more than four bonds, the magnetic resonance spectra of any two groups of protons in an organic molecule can usually be represented by one of the nine designations

\[
\begin{align*}
AX & \quad AX_2 & \quad AX_3 \\
A_2X & \quad A_2X_2 & \quad A_2X_3 \\
A_3X & \quad A_3X_2 & \quad A_3X_3
\end{align*}
\]

Fortunately it is not necessary to consider each case separately. For example, the \( A_2X \) molecule contains three magnetically equivalent spin \( \frac{1}{2} \) nuclei which form a state with \( I=\frac{1}{2} \) which has a statistical weight of 2, and a state with \( I=\frac{3}{2} \) which has a statistical weight of 1. The first state corresponds exactly to an AX system (the full curves of Fig. 1, calculated from Table I) and the second gives rise to the same pattern plus identical patterns displaced by one unit of \( \Delta \) to the left and right (the dotted curves of Fig. 1). This is because replacement of \( m \) by \( m\pm 1 \) in Eqs. (15) and (17) merely reproduces the same set of frequencies except that the \( \Omega \) axis is shifted by one unit of \( \Delta \). Except for a proportionality factor which reflects the statistical weights of the states and the relative transition probabilities, the curves for the intensities will be translated in the same way. For \( A_3X \) molecules the intensity ratio is 1:2:1 as indicated in Fig. 1.

The expected pattern for any case of the form \( A_nX \) can thus be obtained from a superposition of \( n \) of the solid curves of Fig. 1, shifted from each other by one unit of \( \Delta \). The relative intensities are simply given by the binomial coefficients

\[
\binom{n}{p}
\]

where \( p \) is the number of identical curves to either side of the one being considered. This is a general result. \( A_2X_3 \) cases can be deduced simply from a knowledge of the curves for the \( AX_3 \) and \( AX_2 \) cases. In practice for the “field-sweep” or “frequency-sweep” experiments it is not even necessary to construct these composite curves by superposition. It is sufficient to consider \( n \) intersections with the simple curves (\( AX, AX_2 \), or \( AX_3 \)) separated from each other by one unit on the \( \Delta \) axis, and to combine them with relative intensities which go as the binomial coefficients.

Consider next the \( AX_2 \) case. Here two nuclei of spin \( \frac{1}{2} \) form states with \( S=1 \) and \( S=0 \), having equal statistical weights. Transitions in the \( A \) group with \( S=0 \) yield only a single line with one unit of intensity which is not perturbed by \( H_2 \). The transitions in the \( A \) group with \( S=1 \) are found in Table II. Combining these two cases yields the curves shown in Fig. 2. This figure suffices for all \( A_nX_2 \) molecules.

The \( AX_3 \) molecule contains three identical nuclei of spin \( \frac{1}{2} \) and forms a state with \( S=\frac{3}{2} \) having a statistical weight of 1, and a state with \( S=\frac{1}{2} \) with a statistical weight of 2. Combining the results of Tables II and Table I with these statistical weights, yields the curves given in Fig. 3, which may be extended to \( A_nX_3 \) molecules in the way described above. In these cases, there will be a coincidence of inner pairs of lines in which \( M \) and \( M' \) differ by one unit.

### 2.3 Special Case of a Small Perturbing Field \( H_2 \)

If the frequency \( \omega_2 \) is adjusted to one of the transition frequencies of spin \( S \) (i.e., a line in the spectrum of \( X \)), a change of the pattern of the \( A \) spectrum may be detectable even with \( \gamma_2 H_2 < 2\pi | J \) provided that \( \gamma_2 H_2 \) is larger than the linewidths observed in the \( A \) spectrum. If \( \omega_2 \) satisfies the condition

\[
\omega_2 = \omega_1 + 2\pi m' \cdot m = 0,
\]

then with the approximation \( \gamma_2 H_2 << 2\pi | J | \), Eq. (17) takes the form

\[
\omega(m', M'; m'-1, M) \approx \omega_1 - 2\pi J M + \gamma_2 H_2 M',
\]

\[
\omega(m'+1, M; m, M) \approx \omega_1 + 2\pi J M - \gamma_2 H_2 M',
\]

\[
\omega(m''; M; m''-1, M) = \omega_1 + 2\pi J M,
\]

where \( m'', m'-1 \neq m' \). In the same approximation the transition frequencies \( \omega(m'', M; m''-1, M') \) with \( M' \neq M \) have negligible intensities, and therefore will not be considered. Eqs. (25) and (26) show that each of the \( 2S+1 \) lines of the original multiplet is split into a submultiplet having \( 2S+1 \) lines. Eq. (27) shows that if \( I > 1 \), an additional line appears in the center of each submultiplet which will coincide with an existing line if \( S \) is an integer. The relative intensities of these lines may be readily calculated with the aid of Eq. (19). The relationship (24) shows that the sum of the line intensities of a submultiplet is just equal to the corresponding line intensity of the unperturbed multiplet line from which it came.

For the case under consideration, Eq. (20) yields

\[
\phi(m) = \begin{cases} 
\pm \frac{1}{2} \pi & \text{if } m = m' \text{ or } m' + 1 \\
0 & \text{for all other } m 
\end{cases}
\]
The relative intensities of each line of a submultiplet (excluding the line given by Eq. (27) which is absent if \( I = \frac{1}{2} \)) is proportional to \( d^2(S, M, M', \frac{1}{2} \pi) \). The relative intensities of the lines of the first and last submultiplets \( (M = \pm \frac{1}{2}) \) are just proportional to the binomial coefficients since

\[
d^2(S, s, M', \frac{1}{2} \pi) = \frac{(\frac{1}{2})^{2S} (2S)!}{(S + M')! (S - M')!}
\]

Further, it may be shown that if the \( X \) group is composed of \( N \) magnetically equivalent nuclei of spin \( \frac{1}{2} \), the relative intensities of the lines of any submultiplet group will be proportional to the binomial coefficient

\[
\left( \frac{2S}{S + M'} \right)
\]

where \( S = \frac{1}{2} N \).

Equations (25) through (27) predict that a transition line of group \( A \) is split into a submultiplet when it has an energy level in common with a transition produced by \( \omega_s \). This is a general result; a resonance will be split into a submultiplet if it has an energy level in common with a second resonance which is simultaneously being excited with a sufficiently large rf field.

The technique of applying a quite weak perturbing field to a single line of a high-resolution spectrum may have practical applications in attacking analysis problems for strongly coupled systems. It appears that a relatively complicated energy-level diagram could be traced out using this type of marking technique. The technique may also be used to determine the relative signs of spin-coupling constants in a manner analogous to that used by Freeman and Whiffen.

### 2.4 Special Case of a Strong Perturbing Field \( H_2 \)

It may be noted from the curves for the \( AX_m \) cases that the \( A \) multiplet coalesces to a single line for \( \Delta = 0 \), except for satellite lines that are very weak when \( H_2 \) is strong. For \( AX_m \) molecules where \( n > 1 \), although the \( A \) multiplet is considerably modified by the influence of \( H_2 \), this feature is always absent, and for \( \Delta = 0 \) there is what may be called a "residual splitting" even at strong \( H_2 \).

The following simple expressions are obtained for the transition frequencies and line intensities using the approximation of \( \gamma_2 H_2 \gg 2\pi | J | I \):

\[
\omega(m, M; m-1, M) \propto \omega_I \\
-(2\pi J/\gamma_2 H_2) [\omega_I - \omega_S - 2\pi J (m-\frac{1}{2})] M,
\]

\[
L(m, M; m-1, M) \propto [(I-m+1)(I+m)] d^2(S, M, M, 0) = (I-m+1)(I+m).
\]

These equations show that in this limit the intensities of these lines depend only on the statistical weight factors and approach the intensities found with \( H_2 = 0 \). However, the spacings between some of the lines vanish and others are greatly reduced. In an experiment in which the frequency \( \omega_s \) is swept while the frequency \( \omega_I = \omega_0 \), the splitting is reduced by the factor

\[
2\pi J (m-\frac{1}{2})/\gamma_2 H_2.
\]

The splitting will be reduced by nearly this same factor in a magnetic-field-sweep experiment if the additional inequality \( \gamma_2 H_2 \gg 2\pi | J | I \) is satisfied.

These equations predict that the spectrum coalesces to a single line if \( I = \frac{1}{2} \). This is indeed seen to be true from Figs. 2 and 3 even when the inequality

\[
\gamma_2 H_2 \gg 2\pi | J | I
\]

is not satisfied, but at low values of \( H_2 \) the satellite lines have appreciable intensity and are in the same region as the normal transitions. If \( I > \frac{1}{2} \), these equations predict the residual splittings which clearly persist even with very large values of \( H_2 \).

### 2.5 Effects of Finite Chemical Shift

Some of the additional complexities which arise because the resonant frequencies of the two groups of nuclei are separated by a finite frequency-interval will now be considered. They arise from the fact that neither the spin-coupling constant \( 2\pi | J | I \), nor the effective radiofrequency field \( \gamma H_2 \) are negligibly small compared with the difference frequency \( | \omega_I - \omega_S | \).

Since the second- and third-order corrections to the transition frequencies by the perturbation parameter \( 2\pi J/(\omega_I - \omega_S) \) have been considered elsewhere only the additional perturbation proportional to

\[
\gamma H_2/(\omega_I - \omega_S)
\]

will be considered here.

In Eq. (8), it is no longer possible to neglect \( \gamma H_2 \) compared to \( \omega_I - \omega_S \), and a transformation \( V \) will be applied to bring the wave function of the \( I \) spin into diagonal form. The required transformation is

\[
V = \exp(i\theta \Lambda F),
\]

with

\[
\tan \theta = \gamma H_2/(\omega_I - \omega_S).
\]

---

20 F. Bloch (to be published).
21 W. A. Anderson, Phys. Rev. 102, 151 (1956).
The transformed Hamiltonian is
\[ \mathcal{H}_v' = -\left[ A I^z + \left( \omega_S - \omega_0 - 2\pi J \cos \theta_A I^z \right) S^z \right. \]
\[ \left. + \left( \gamma H_2 - 2\pi J \sin \theta_A I^z \right) S^z \right. \]
\[ \left. - 2\pi J (I^z S^z \cos \theta_A - I^z S^z \sin \theta_A + I^z S^z) \right] \enspace , \tag{32} \]
with
\[ A = \left[ \left( \omega_t - \omega_0 \right)^2 + \left( \gamma H_2 \right)^2 \right]^{\frac{1}{2}} \enspace . \tag{33} \]
The last three terms of Eq. (32) will be neglected since they represent a second-order perturbation due to the spin coupling.

A final transformation will now be applied to diagonalize the S spin wave function. This is given by
\[ W = \exp[i\theta_X(m_A) S^z] \enspace , \tag{34} \]
with
\[ \tan \theta_X(m_A) = \frac{\gamma H_2 - 2\pi J m_A \cos \theta_A}{\omega_S - \omega_0 - 2\pi J m_A \cos \theta_A} \enspace . \tag{35} \]
The transformed Hamiltonian is simply
\[ \mathcal{H}_v'' = -\left[ A I^z + X(m_A) S^z \right] \enspace , \tag{36} \]
where
\[ X(m_A) = \left[ \left( \omega_S - \omega_0 - 2\pi J m_A \cos \theta_A \right)^2 \right. \]
\[ \left. + \left( \gamma H_2 - 2\pi J m_A \sin \theta_A \right)^2 \right]^{\frac{1}{2}} \enspace . \tag{37} \]

Equations (33) and (37) may be approximated by making use of the inequalities
\[ (\omega_t - \omega_0)^2 > \left( \gamma H_2 \right)^2 > (\omega_t - \omega_0)^2 + (2\pi J)^2 m_A^2 \enspace , \]
to yield
\[ A \approx \omega_t - \omega_0 + \left( \gamma H_2 \right)^2 / (\omega_t - \omega_0) \enspace . \]
\[ X(m_A) \approx \gamma H_2 - 2\pi J m_A \sin \theta_A + \left( \omega_S - \omega_0 - 2\pi J m_A \cos \theta_A \right)^2 / (\gamma H_2) \]
\[ + \left( \frac{1}{2} \right) \left( 2\pi J m_A \sin \theta_A \right)^2 / (\gamma H_2) \]
\[ - \left( \omega_S - \omega_0 - 2\pi J m_A \cos \theta_A \right) / (\gamma H_2) \enspace . \]

Substitution of these values into Eq. (39) yields
\[ \omega(m_A, m_X; m_A - 1, m_X) = \omega + \left( \frac{1}{2} \right) (\gamma H_2)^2 / (\omega_t - \omega_0) \]
\[ \times \left[ \left( 2\pi J \cos \theta_A \right) / (\gamma H_2) \right] \omega_S - \omega_0 \]
\[ - 2\pi J \cos \theta_A (m_A - \frac{1}{2}) + \gamma H_2 \tan \theta_A m_X \enspace . \tag{40} \]

Study of Eq. (40) leads to a number of interesting conclusions. This equation yields the transition frequencies which are observed when
\[ \omega_1 = \omega(m_A, m_X; m_A - 1, m_X) \enspace . \]

The first term on the right-hand side of Eq. (40) represents the resonance frequency of group A in the absence of any couplings to other groups and in the limit of \( H_2 \to 0 \). The second term represents a shift of the observed resonance-frequency by the presence of the strong radiofrequency field \( H_2 \). The remaining terms represent the residual spin coupling, and except for the last, correspond to those found in Eq. (28), and they vanish if \( \omega_t = \omega_0 \) and \( J = \frac{1}{2} \). The last term in the bracket represents a splitting that increases with increasing \( H_2 \). This effect has been pointed out by Bloch for the special case of two coupled spin \( \frac{1}{2} \) nuclei. In the limit of extremely large values of \( H_2 \), i.e., \( \gamma H_2 \gg | \omega_t - \omega_0 | \) this term yields back the original coupling \( 2\pi J \), since now both spins are quantized along the same axis in the rotating coordinate frame.

If \( \omega_t \) is chosen so as to satisfy the equation
\[ \omega_t - \omega_S = \gamma H_2 \tan \theta_A = \frac{(\gamma H_2)^2}{(\omega_t - \omega_0)} \tag{41} \]
then the first and third terms in the bracket of Eq. (40) cancel and the spectrum will be completely collapsed if \( J = \frac{1}{2} \); if \( J > \frac{1}{2} \) all lines with the initial state \( m_A = \frac{1}{2} \) will coincide. Thus, the most complete collapse is not obtained with \( \omega_t = \omega_0 \), but with the value of \( \omega_t \) displaced slightly towards the other group. This correction is of particular importance if one is to determine accurate chemical shift values by double-resonance techniques. If one employs the "field-sweep" method keeping the difference frequency \( \omega_t - \omega_0 \) constant while sweeping \( H_2 \), one finds that the most collapsed spectrum is ob-

\textsuperscript{22} W. A. Anderson, reference 3 (d), p. 164.

\textsuperscript{23} Reference 13, Eq. 7.121.
3. EXPERIMENTAL

Spectra were obtained at room temperature using a Varian HR-60 high-resolution spectrometer. Double irradiation by the field-sweep method was accomplished by using the spectrometer rf field as $H_2$ and a field-modulation sideband as $H_0$. A synchronous detector driven by the modulation frequency was used to separate the signals from the resonances excited at the centerband frequency. This system was similar to those described by Pound, Kaiser, and Freeman. The rf field $H_2$ was calibrated by the method described by Anderson.

"Frequency-sweep" spectra were obtained by introducing a control loop to maintain $\omega_2$ and $H_0$ in a constant proportion, while $\omega_2$ was swept through the A resonance. The system was similar to those used by Anderson and Primas. A dispersion-mode signal from a small quantity of tetramethylsilane (the internal reference compound) was fed as an error signal to the galvanometer of the flux stabilizer of the Varian spectrometer. Three separate magnetic-field modulations were used, all at sufficiently high frequency to ensure that there could be no magnetic-resonance responses excited by the centerband frequency ($\omega_2$) or the three unused sidebands, and all at low modulation index so as not to interfere with one another. A sideband at $\omega_2$ excited the tetramethylsilane signal and this was separated from other signals appearing at the output of the Varian spectrometer by means of a synchronous detector driven by a reference signal at the modulation frequency $\omega_2 - \omega_1$ and phased so as to produce the dispersion mode signal. The galvanometer of the flux stabilizer integrates this signal and holds the magnetic field $H_0$ to the resonance condition within about $\pm 0.01$ mG. This was estimated by adjusting a second modulation frequency to the side of a sharp resonance and noting the excursions caused by the small residual magnetic-field fluctuations. It was quite feasible to leave this system "locked" indefinitely without further attention if gross degradation of the magnetic-field homogeneity was avoided. A field-modulation sideband at $\omega_1$ was then used to investigate the A-group resonance, these signals being separated in a second synchronous detector supplied with a reference signal at $\omega_1 - \omega_1$ and phased so as to give the absorption mode. The modulation (and reference) frequency was then swept through the A spectrum by driving the tuning control of the audiofrequency oscillator by means of an electric motor and a reduction gear. A Hewlett-Packard 300 CD oscillator was used and although this had a nonlinear frequency scale, the sweep range was so small that no sign of this could be detected in the

$$\omega_1 - \omega_2 = \omega_2 - \omega_3 - \frac{(\gamma H_2)^2}{2(\omega_1 - \omega_3)}. \quad (42)$$

Both of the shifts described above may be given a simple geometric interpretation. The first shift corresponds to the fact that the effective field in the coordinate system rotating at $\omega_2$ as seen by the nuclei of group $A$ is the vector sum of the field $\omega_2 - \omega_2$ along the $Z$ axis and $\gamma H_2$ along the $X$ axis, yielding the vector $A$ as indicated in Fig. 4. Here all fields have been expressed in units of angular frequency. The difference in the length of $A$ and $|\omega_2 - \omega_2|$ corresponds to the correction.

To achieve the maximum decoupling the spins of group $A$ and group $X$ must be quantized substantially at right angles to each other, so that the scalar product $I \cdot S$ becomes small. The effective field in the rotating system as seen by the $X$ spins is indicated by the vector $X$ of Fig. 4, corresponding to the vector sum of $\gamma H_2$ along the $X$ axis and $\omega_2 - \omega_2$ along the $Z$ axis. The effect of the spin coupling upon $X$ has not been included here as it was in Eq. (37) since with $\gamma H_2 \gg 2\pi |J|$ its effect will be considered separately by treating $2\pi J I \cdot S$ as a perturbation. With this approximation, the spin operator $J$ will be quantized along the vector $A$ and the spin operator $S$ will be quantized along the vector $X$. By making the vectors $A$ and $X$ perpendicular to each other, the quantity $2\pi J I \cdot S$ will have no diagonal matrix elements, and thus the effect of the spin coupling appears as a second-order effect. The condition which yields these two vectors perpendicular is just that given by Eq. (41) and it may be achieved provided that $\gamma H_2 < \frac{1}{2} |\omega_2 - \omega_2|$. When $\omega_2$ is chosen to satisfy Eq. (41), the residual splittings $(R \text{ rad/sec})$ observed in spectra of molecules where $I > \frac{1}{2}$ are given by the expression

$$R = \left[ (\omega_2 - \omega_3)^2 + \gamma^2 H_2^2 + 4\pi^2 J^2 m_A^2 \right]^{1/2}$$

$$- \left[ (\omega_2 - \omega_2)^2 + \gamma^2 H_2^2 + 4\pi^2 J^2 (m_A - 1)^2 \right]^{1/2}, \quad (43)$$

which, when $\gamma H_2 \gg 2\pi |J|$, reduces (to a good approximation) to the expression derived in Sec. 2.4 for the residual splitting

$$R = (2\pi J)^2 (m - \frac{1}{2}) / \gamma_0 H_2. \quad (44)$$

---

27. W. A. Anderson (unpublished work).
spectra. A third field-modulation sideband provided the perturbing radiofrequency field at \( \omega \) and was adjusted in modulation index to have the required field strength \( H_2 \). It was set at the required position in the X spectrum by comparing \( \omega - \omega_0 \) with the chemical shift of X referred to tetramethylsilane. The exact position of the X-resonance lines could be determined with low \( H_2 \) by adjusting \( \omega \) while observing the audio-frequency signal it induced on the spectrometer oscilloscope. Under certain circumstances it was found convenient to use the centerband as \( H_2 \), in order that \( H_2 \) be precisely calibrated. This introduces the problem of phasing the two synchronous detectors (or at least the one used to investigate the A resonance) to reject the centerband response, the condition for complete rejection being zero phase shift between the audiofrequency modulation and the reference.

4. RESULTS

The aim of this section is to demonstrate that the calculations of Sec. 2 do in fact predict the behavior of high-resolution nuclear magnetic resonance spectra when a second rf field is present. For this purpose, it is convenient to consider separately three ranges of strength of this field, where \( \gamma H_2 / 2\pi \) is very much less than, comparable with, and very much greater than \( 21\pi |J_{AX}| \).

4.1 Weak Perturbing Field

As might be expected intuitively, the second radiofrequency field does not produce observable effects in the spectrum under these conditions unless \( \omega \) is very close to the frequency of one of the X transitions. This can be seen clearly from Figs. 1(a), 2(a), and 3(a) which have been calculated for \( \gamma H_2 / 2\pi = 0.2J_{AX} \). This is an example of a situation where the “frequency-sweep” method produces spectra that are quite clear to interpret, but where the “field-sweep” technique gives complicated results. In the latter method, one of the A lines will be split whenever \( \omega \) is set close to the frequency separation of an A and an X line, except that for certain pairs of lines this effect will be completely obscured because of the spurious line broadening that can occur in field-sweep spectra, a phenomenon which is particularly marked at low values of \( H_2 \).

Consequently, the investigations of this section were made by the “frequency-sweep” method with the instrumentation as described above. The sample was acetaldehyde \((\delta = 455.5 \pm 0.2 \text{ cps}, J = 2.8 \pm 0.2 \text{ cps})\) and \( \omega \) was first set on one of the strong lines of the CHO quadruplet. As discussed in Sec. 2.3 and illustrated in Fig. 1(a), this is a case where the A resonance should split into submultiplets which contain three lines each but do not show a binomial distribution of intensities. Figure 1(a) also indicates that for \( \Delta = \pm 0.5 \) each line of the methyl group doublet should split into triplets whose relative intensities should be very sensitive to the setting of \( \omega \). Figure 5 illustrates the spectra obtained \((a)\) with \( H_2 = 0 \), \((b)\) with \( \gamma H_2 / 2\pi \) approximately \( 0.2J_{AX} \), and \( \Delta \) very near to 0.5. The intensities of each line of the submultiplets are seen to be very roughly equal, in reasonable agreement with the theory \([\text{Fig. 1(a)}]\).

An interesting complication arose when the reverse experiment was attempted. When \( \omega \) was set on the low-field line of the methyl group doublet and the strength of \( H_2 \) gradually increased, a perturbation of the relative intensities of the quadruplet was observed.
Figure 6 shows the spectra obtained when the frequency was swept in the sense which corresponds to the convention for field-sweep spectra—low to high applied field going from left to right. Figure 6(a) shows the unperturbed quadruplet while (b), (c), and (d) are at increasing strengths of $H_2$. Figure 6 shows the spectra obtained when the frequency was irradiated, the spectra obtained were essentially mirror images of those shown in the figure.

This change in relative intensities arises because $H_2$ causes a rearrangement of the energy-level populations in principle indicate which relaxation mechanism is dominant, as in the double-irradiation experiments of Pound on sodium nitrate. Some very simple experiments which consisted in saturating the whole of the methyl-group resonance and then quickly displaying the aldehyde-proton resonance, produced no detectable increase or decrease in the total intensity of the latter. Similarly, it appears from Fig. 6 that the total quadruplet intensity remains constant as $H_2$ is increased from zero. This suggests that the two groups are relaxed independently and not through their mutual coupling $J_1S$ or by dipole–dipole interaction within the molecule. In the sample used, the measured spin-lattice relaxation times were $30 \pm 2$ sec (aldehyde proton) and $17 \pm 2$ sec (methyl-group protons). Assuming independent relaxation with relative efficiencies $1:2$ it is possible to calculate the new energy-level populations when the low-field line of the methyl doublet is saturated, by making use of the electrical-circuit analogy proposed by Bloch. The predicted relative intensities are then $-0.2$, $+2.1$, $+3.9$, $+2.2$ which are to be compared with the approximate experimental values $-0.15$, $+2.0$, $+3.9$, $+1.8$ obtained by integrating the areas under the submultiplets of Fig. 6(d) and comparing with Fig. 6(a), making use of the rule that the total intensity of a submultiplet is equal to the intensity of the single multiplet line from which it came, a consequence of Eq. (24).

This is a manifestation of proton magnetic resonance of the general Overhauser effect of which only isolated examples appear to have been reported in the literature for nuclear-magnetic double-resonance at high resolution. However, since a detailed quantitative study might reasonably be regarded as beyond the scope of the present communication, and because such a study would require more careful attention to the effects of the molecular environment, sample purity, dissolved oxygen, etc., it is planned to reinvestigate this interesting system and present the results at a later date.

Figure 6(d) shows that in fact the expected splitting of the lines of the quadruplet into submultiplets that are also $1:3:3:1$ quadruplets does occur, as predicted in Sec. 2.3 and illustrated in Fig. 3(a).

### 4.2 Perturbing Field of Intermediate Strength

One interesting aspect of the curves in Figs. 1, 2, and 3 is the presence of the satellite responses which correspond to A transitions that occur simultaneously with an X transition. These latter may change the spin quantum number by one, two, or more units giving rise to what may be termed first-, second- and nth-order satellites. The presence of these is well illustrated at exact resonance ($\Delta = 0$) in a “frequency-sweep” investigation of the acetaldehyde CHO resonance with $\gamma H_2 = 2 \pi J_{XY}$ (Fig. 7). The calculated spectrum obtained from Fig. 3(b) fits very well, and as predicted the “third-order” satellites are too weak to be observed.

The “field-sweep” method has been used in the rest of this section, partly on grounds of instrumental simplicity, and partly because most current applications of double irradiation seem to employ this method, so it is important to recognize the type of spectra which may be obtained. Figure 8 illustrates the spectra observed for the CHO resonance of acetaldehyde when $\omega_0$ is near the methyl-group doublet and $\gamma H_2/2\pi = 2J_{AX}$. Predicted spectra were obtained from a figure similar to Fig. 3(b) by drawing lines across at $45^\circ$. As discussed by Freeman and Whiffen certain lines tend to broaden in a field-sweep experiment because lines drawn across the figure at $45^\circ$ sometimes intersect the curve at a very acute angle, and the curves have a

---


Reference 13, p. 112.
natural linewidth of their own. In addition these lines may have greater relative height because the sweep rate is nearer the ideal slow-passage condition. Where such excessive broadening would be expected it has been indicated (schematically not quantitatively) by a triangular line in the theoretical spectrum.

The calculations for the $AX_2$ case were compared with the experimental results obtained with diethyl succinate. The ethyl group resonance of this compound forms an $AX_2$ system where the chemical shift ($171.3\pm0.2$ cps) is sufficiently large compared with the coupling constant ($7.5\pm0.2$ cps) that second-order spin coupling is not apparent in the spectrum. Fieldsweep spectra with $\gamma H_2$ set equal to $2\pi J_{AX}$ are compared in Fig. 9 with theoretical spectra obtained by drawing lines across Fig. 2(b) at $45^\circ$ slope at $(\Delta'-1)$, $(\Delta'-1)$, and by combining these partial spectra in the relative intensities 1:2:1. An equivalent result is obtained by constructing composite curves specifically for the $A_2X$ case in the way illustrated for $A_2X$ in Fig. 1.

It is interesting to note that in systems of this type the only easily recognizable feature of the spectrum that is peculiar to the exact resonance condition $\Delta'=0$ is the symmetry about the center, and in practice this is quite often obscured. The height of the central strong line is no indication at all of how near $\omega_2$ is to $\omega_X$. Recognition of the condition $\Delta'=0$ from observed spectra is an essential part both of chemical shift measurement by double irradiation and the determination of relative signs of spin-coupling constants. It is therefore perhaps worth re-emphasizing here that although double irradiation of $AX_m$ type spectra with $H_2$ of intermediate strength does give an easily recognizable pattern for $\Delta'=0$ (essentially a single line in a field-sweep experiment), for $A_2X_m$ spectra there is a residual splitting which makes recognition of the exact resonance condition considerably more difficult.

### 4.3 Strong Perturbing Fields

1,1,2 trichloroethane proved to be a very convenient sample for the investigations of this section. In the neat liquid, the chemical shift ($110.2\pm0.2$ cps) is sufficiently small to permit illustration of the correction discussed in Sec. 2.5, Eq. (42), while the coupling constant is reasonably large ($6.0\pm0.2$ cps) without second-order spin–spin splittings being apparent in the spectrum. It provides an example of the $AX_2$ and $A_2X$ cases.

A series of experiments was performed where the CH$_2$Cl protons were irradiated while the CHCl$_3$ proton was investigated by the field-sweep method (the $AX_2$ case). Decoupled spectra were recorded with $(\omega_1-\omega_2)/2\pi$ set at intervals of 0.1 cps over a range near $(\omega_2-\omega_X)/2\pi$ to discover the setting which gave optimum decoupling. For this purpose, the only criterion which seems to be both sensitive and practicable is the height of the coalesced line. Although the total intensity of the observed lines does not go through a maximum for optimum decoupling, the coincidence of all the strong lines causes the peak height to be a maximum for this condition, so that if a sufficiently large number of measurements are made, the optimum
setting of \((\omega_1 - \omega_2)/2\pi\) can be determined within a few tenths of a cycle per second. 35

These experiments were then repeated at several different values of \(H_2\), starting at \(\gamma H_2 = 2\pi J\) and increasing until the optimum setting could no longer be determined accurately. Figure 10 shows \((\omega_1 - \omega_2)/2\pi\) determined in this way plotted against \((\gamma H_2/2\pi)^2\). The experimental points show a good fit to the line which represents Eq. (42) with \((\omega_1 - \omega_2)/2\pi = 110.2\) cps. Certainly there is clear support for the sense of the correction calculated in Sec. 2.5; it is in the opposite direction to the correction which has to be applied to the position of modulation-sideband responses. 31 In the measurement of chemical shifts by spin-decoupling experiments, and in the determination of relative signs of spin-coupling constants this effect could be quite significant at high values of the perturbing field or at low values of the chemical shift.

The sample was next investigated as an \(A_2X\) case with \(H_2\) applied to the CHCl\(_2\) proton and the CH\(_2\)Cl resonance displayed by the field-sweep technique. The residual splitting of the resonance was then determined by comparison with the splitting \((J)\) observed when \(\omega_1\) was set far off resonance with a low value of \(H_2\). These measurements were repeated at increasing values of \(H_2\) until the residual splitting was too small to be observed, with settings of \((\omega_1 - \omega_2)/2\pi\) appropriate to the power levels \((\gamma H_2/2\pi)\). The results are plotted in Fig. 11 against \((\gamma H_2/2\pi)^{-1}\) to illustrate that Eq. (44) applies at high powers. The full curve represents the exact expression of Eq. (43).

---

5. CONCLUSIONS

The decoupling effect of a second rf field \( H_2 \) on nuclear magnetic resonance spectra can be predicted theoretically by transforming the spin Hamiltonian into a frame of reference rotating at \( \omega_0 \), the frequency of \( H_2 \). This removes the time dependence, and the Hamiltonian matrix may then be diagonalized by further simple transformations. The calculation of transition frequencies and intensities in the laboratory frame is then straightforward, and these are given in tabular form. Applied to groups of magnetically equivalent nuclei, these allow the spin-decoupling behavior of most of the interesting proton systems to be calculated, provided that the chemical shift is large in comparison with the coupling constant. A graphical method of presentation illustrates the three principle practical methods of investigating decoupled spectra, and has the advantage of being applicable to double irradiation of molecules containing nuclei of different species.

Irradiation with fields weak with respect to the coupling constant at frequencies very near to a transition frequency, has been shown to give rise to splitting of the individual lines of multiplets into submultiplets. It is suggested that this technique may be useful as a preliminary attack on the analysis of a complex strongly coupled spin system by identifying those transitions that have an energy level in common with the transition produced by \( H_2 \). The method has the practical virtue that the perturbation of other lines in the spectrum could be kept small. The technique may also prove to be a useful refinement of the double-irradiation method of determining relative signs of spin-coupling constants in molecules where not all chemical shifts are large compared with the respective couplings.

In acetaldehyde irradiation of one of the lines of the methyl group has been shown to modify the relative intensities of the lines of the aldehyde quadruplet, a nuclear Overhauser effect. The final integrated intensities are consistent with independent spin-lattice relaxation of the two proton groups, as suggested by the fact that no Overhauser effect is observed when the whole of the methyl group is saturated. It is interesting to note that some type of precise field-frequency control is necessary to make possible experiments of the first type where a single line of a multiplet resonance is saturated. Such instrumentation is now becoming more and more common and one might therefore expect similar effects to be brought to light in other molecules in the near future.

A previous paper has compared observed and predicted spectra for AX proton systems under double-irradiation conditions. The extension of these calculations to AX\(^2\) and AX\(_2\) systems is here given experimental confirmation for irradiating field strengths \( \gamma H_2 \) comparable with \( 2\pi J \). A simple method of deriving the spectra predicted for AX\(_2\) and AX\(_3\) molecules has been described and applied to the calculation of the patterns observed in the double irradiation of diethyl succinate.

It has long been realized that the presence of a strong radiofrequency field produces a small shift in the observed resonance frequency of a nearby line. It is for this reason that in field-sweep experiments modulation-sideband responses are observed to be separated from the centerband signal by slightly less than the modulation frequency. The correction amounts to \( \left( \gamma H_2 \right)^2/2(\omega_2-\omega_1) \) in rad/sec. It is therefore natural to apply this correction when calculating the optimum setting of \( (\omega_2-\omega_1) \) in spin-decoupling experiments if a strong perturbing field is used or if the chemical shift is small. However, for this situation it may be shown that a further correction is necessary and this turns out to be twice as large and in the opposite sense, so that the total correction is now

\[
\omega_1-\omega_2=\omega_2-\omega_1-(\gamma H_2)^2/2(\omega_2-\omega_1).
\]

The effect must be allowed for when accurate measurements of proton chemical shifts are to be obtained by spin-decoupling techniques.

Strong fields applied at exact resonance cause spin multiplets to coalesce to a single line for molecules of the type AX\(_n\). But for AX\(_n\) systems where \( n>1 \) a residual splitting of the resonance line persists as \( H_2 \) is increased. For \( \gamma H_2>>2\pi |J| \) this splitting is given by the simple formula

\[
R=(2\pi |J|)^2(m_\Delta-\frac{1}{2})/\gamma H_2 \text{ rad/sec}.
\]

For fields strong enough to satisfy the condition \( \gamma H_2>>\frac{1}{2} |\omega_2-\omega_1| \) this splitting actually begins to increase with increase of \( H_2 \), reaching \( 2\pi J \text{ rad/sec} \) in the limit. These are somewhat surprising results if one relies on one of the very simple pictures of spin-decoupling which suggests that the strong field merely causes such rapid transitions of the X-group resonance that the A-group multiplet is "washed out."

ACKNOWLEDGMENTS

The authors would like to thank Professor Bloch for allowing them to make use of his calculations on the nuclear Overhauser effect prior to publication, and B. Mecklenburg for the numerical calculations involved in preparing Figs. 1, 2, and 3.