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

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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 A_nX_m type molecules where $m, n \leq 3$, and their spin-decoupling behavior is presented in graphical form. Good correlations are observed with the experimental proton double-resonance spectra of acetaldehyde, diethyl succinate, and 1,1,2 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_m molecules, but for A_nX_m molecules where $n > 1$ 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,¹ 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 shown² to be due to a scalar coupling $\mathbf{I} \cdot \mathbf{S}$ of the spins of chemically shifted nuclei through the valency electrons.³ The effect of the coupling can be made to disappear if one group is subjected to a rf field H_2 such that $\gamma H_2 \gg 2\pi |J|$, 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.⁴ The application of this technique to the accurate measurement of chemical shifts of hidden resonance lines⁵ and to the determination of relative signs of spin-coupling constants^{6,7} led to the realization that in many circum-

stances intermediate strengths of the field H_2 may have to be employed such that $\gamma H_2 \sim 2\pi J$. Recently Freeman and Whiffen⁸ have shown that a calculation along the lines of that given by Bloom and Shoolery⁴ 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 γH_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 $\omega_I = \gamma_I H_0$ represent the total spin values and the Larmor frequency of the first group, and S and $\omega_S = \gamma_S H_0$ 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 ω_2 is applied along the X axis so that it causes transitions of the nuclei with spin S . A "weak" rf field of magnitude $2H_1$ and angular frequency ω_1 is also applied along the X axis so that it causes transitions of the nuclei

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¹ F. Bloch, Phys. Rev. **93**, 944 (1954); Phys. Today **7**, 30 (1954).

² N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952); N. F. Ramsey, Phys. Rev. **91**, 303 (1953).

³ Useful references for review are: (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959); (b) J. D. Roberts, *Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959); (c) J. D. Baldeschwieler and E. W. Randall, Chem. Revs. (to be published); (d) Varian Staff, N. M. R. and E. P. R. *Spectroscopy* (Pergamon Press, New York, 1960); (e) J. D. Roberts, *An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra* (W. A. Benjamin, Inc., New York, 1961).

⁴ A. L. Bloom and J. N. Shoolery, Phys. Rev. **97**, 1261 (1955).

⁵ J. A. Elvidge and L. M. Jackman, J. Chem. Soc. **1961**, 859.

⁶ J. P. Maher and D. F. Evans, Proc. Chem. Soc. **1961**, 208.

⁷ R. Freeman and D. H. Whiffen, Mol. Phys. **4**, 321 (1961).

⁸ R. Freeman and D. H. Whiffen, Proc. Phys. Soc. (London) **79**, 794 (1962).

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 shown⁹ 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 is¹⁰

$$H = H_0 \hat{k} + (H_1 \cos \omega_1 t + H_2 \cos \omega_2 t) \hat{i} - (H_1 \sin \omega_1 t + H_2 \sin \omega_2 t) \hat{j}. \quad (1)$$

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

$$\mathcal{H} = -[\omega_I I^z + \omega_S S^z - 2\pi \mathbf{J} \cdot \mathbf{S} + \gamma_I H_2 (I^x \cos \omega_2 t - I^y \sin \omega_2 t) + \gamma_S H_2 (S^x \cos \omega_2 t - S^y \sin \omega_2 t)]. \quad (2)$$

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

$$\mathcal{H}' = -[\gamma_I H_1 (I^x \cos \omega_1 t - I^y \sin \omega_1 t) + \gamma_S H_1 (S^x \cos \omega_1 t - S^y \sin \omega_1 t)]. \quad (3)$$

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

$$i\dot{\psi} = \mathcal{H}\psi. \quad (4)$$

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

$$\psi_T = T\psi \quad \text{and} \quad \psi = T^{-1}\psi_T. \quad (5)$$

In addition, if the Hamiltonian is transformed by the transformation

$$\mathcal{H}_T = T\mathcal{H}T^{-1} + i\dot{T}T^{-1}, \quad (6)$$

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

$$i\dot{\psi}_T = \mathcal{H}_T\psi_T.$$

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

$$T = \exp[-i\omega_2 t (I^z + S^z)]. \quad (7)$$

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

$$\mathcal{H}_T = -[(\omega_I - \omega_2)I^z + (\omega_S - \omega_2)S^z - 2\pi \mathbf{J} \cdot \mathbf{S} + \gamma_I H_2 I^x + \gamma_S H_2 S^x], \quad (8)$$

$$\mathcal{H}_T' = -\{\gamma_I H_1 [I^x \cos(\omega_1 - \omega_2)t - I^y \sin(\omega_1 - \omega_2)t] + \gamma_S H_1 [S^x \cos(\omega_1 - \omega_2)t - S^y \sin(\omega_1 - \omega_2)t]\}. \quad (9)$$

⁹ F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940); N. F. Ramsey, Phys. Rev. **100**, 1191 (1955).

¹⁰ This equation is identical to that given by J. D. Balde-schwiler, J. Chem. Phys. **34**, 718 (1961).

¹¹ I. I. Rabi, N. F. Ramsey, and J. Schwinger, Revs. Modern Phys. **26**, 167 (1954).

2.1 Weakly Coupled Systems, $|\omega_I - \omega_S| \gg 2\pi |J|$

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 $A_n X_m$ in the NMR literature.¹² For such a case only the diagonal matrix elements of the term $\mathbf{J} \cdot \mathbf{S}$ are kept in the Hamiltonian. One may assume that the frequency of the "weak" rf field ω_1 is near ω_I and that ω_2 is near ω_S . Under these conditions

$$|\omega_I - \omega_2| \gg \gamma_I H_2$$

and the term $\gamma_I H_2 I^x$ may be dropped from Eq. (8). A similar reasoning shows that the term involving $\gamma_S H_1$ may be dropped from Eq. (9). With these approximations, the Hamiltonians are given by

$$\mathcal{H}_T = -[(\omega_I - \omega_2)I^z + (\omega_S - \omega_2)S^z - 2\pi J I^z S^z + \gamma_S H_2 S^x], \quad (10)$$

$$\mathcal{H}_T' = -\{\gamma_I H_1 [I^x \cos(\omega_1 - \omega_2)t - I^y \sin(\omega_1 - \omega_2)t]\}. \quad (11)$$

Another transformation by the rotation operator

$$V = \exp[i\theta(m)S^y], \quad (12)$$

where

$$\theta(m) = \tan^{-1}[\gamma_S H_2 / (\omega_S - \omega_2 - 2\pi J m)], \quad (13)$$

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

$$\mathcal{H}_V = -[(\omega_I - \omega_2)I^z + A(m)S^z], \quad (14)$$

with

$$A(m) = [(\omega_S - \omega_2 - 2\pi J m)^2 + \gamma_S^2 H_2^2]^{\frac{1}{2}}. \quad (15)$$

Here m represents the eigenvalue of the operator I^z . The rotation operator V did not change the Hamiltonian \mathcal{H}_T' given by (11) since it commutes with it.

The well-known spin wave functions which diagonalize $(\mathbf{I})^2$, I^z and $(\mathbf{S})^2$, S^z with eigenvalues $I(I+1)$, m and $S(S+1)$, M , respectively, will diagonalize \mathcal{H}_V . The wave functions ψ_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

$$E_V(m, M) = -[(\omega_I - \omega_2)m + A(m)M]. \quad (16)$$

It will be shown below that the selection rules for transitions produced by ω_1 are those in which $\Delta m = \pm 1$ and $\Delta M = 0, \pm 1, \pm 2, \dots, \pm 2S$. The transition frequencies in the laboratory system are given by

$$\omega(m, M; m-1, M') = E_V(m-1, M') - E_V(m, M) + \omega_2 = \omega_I + A(m)M - A(m-1)M'. \quad (17)$$

Under the conditions of weak rf fields H_1 , the inten-

¹² Reference 3(a), p. 98.

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^x between wave functions of the laboratory system.¹³ Since the eigen wave functions $\psi_V(I, m, S, M)$ in the "V 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

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

The line intensities L are thus proportional to

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

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

TABLE I. Transition frequencies and intensities which may be observed with a weak rf field near the resonant frequencies of spin I while a second rf field is applied near the resonance frequencies of spin S . The initial and final states are denoted by (I, m, S, M) and $(I, m-1, S, M')$ where $S = \frac{1}{2}$.

$$A(m) \equiv [(\omega_S - \omega_2 - 2\pi Jm)^2 + \gamma_S^2 H_2^2]^{\frac{1}{2}}$$

and

$$\phi(m) = \tan^{-1}[\gamma_S H_2 / (\omega_S - \omega_2 - 2\pi J(m-1))] - \tan^{-1}[\gamma_S H_2 / (\omega_S - \omega_2 - 2\pi Jm)].$$

M	M'	$\omega_1 - \omega_I$	$L / [(I-m+1)(I+m)]$
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}[A(m) - A(m-1)]$	$\frac{1}{2}[1 + \cos\phi(m)]$
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}[A(m) - A(m-1)]$	$\frac{1}{2}[1 + \cos\phi(m)]$
$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}[A(m) + A(m-1)]$	$\frac{1}{2}[1 - \cos\phi(m)]$
$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}[A(m) + A(m-1)]$	$\frac{1}{2}[1 - \cos\phi(m)]$

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

$$|\langle U^\dagger(I, m) \exp(-i\omega_2 I^z) | I^x | \exp(i\omega_2 I^z) U(I, m') \rangle \times \langle U^\dagger(S, M) \exp\{-i[\theta(m') - \theta(m)]S^y\} U(S, M') \rangle|^2.$$

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

$$\langle U^\dagger(I, m) | I^x | U(I, m') \rangle.$$

This matrix element has nonvanishing terms¹⁴ only if $m' = m \pm 1$. The evaluation of the second term of the

TABLE II. Transition frequencies and intensities for spin I arbitrary and $S = 1$.

M	M'	$\omega_1 - \omega_I$	$L / [(I-m+1)(I+m)]$
1	1	$A(m) - A(m-1)$	$\frac{1}{4}[1 + \cos\phi(m)]^2$
0	0	0	$\cos^2\phi(m)$
-1	-1	$-[A(m) - A(m-1)]$	$\frac{1}{4}[1 + \cos\phi(m)]^2$
1	0	$A(m)$	$\frac{1}{2}\sin^2\phi(m)$
0	-1	$A(m-1)$	$\frac{1}{2}\sin^2\phi(m)$
0	1	$-A(m-1)$	$\frac{1}{2}\sin^2\phi(m)$
-1	0	$-A(m)$	$\frac{1}{2}\sin^2\phi(m)$
1	-1	$A(m) + A(m-1)$	$\frac{1}{4}[1 - \cos\phi(m)]^2$
-1	1	$-[A(m) + A(m-1)]$	$\frac{1}{4}[1 - \cos\phi(m)]^2$

product has also been given in the literature.¹⁵ Combining these two results yields an expression for the line intensities. The relative line intensity of a transition between a state specified by $\psi(I, m, S, M)$ and

TABLE III. Transition frequencies and intensities for spin I arbitrary and $S = \frac{3}{2}$.

M	M'	$\omega_1 - \omega_I$	$L / [(I-m+1)(I+m)]$
$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}[A(m) - A(m-1)]$	$\frac{1}{8}[1 + \cos\phi(m)]^3$
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}[A(m) - A(m-1)]$	$\frac{1}{8}[1 + \cos\phi(m)] [3\cos\phi(m) - 1]^2$
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}[A(m) - A(m-1)]$	$\frac{1}{8}[1 + \cos\phi(m)] [3\cos\phi(m) - 1]^2$
$-\frac{3}{2}$	$-\frac{3}{2}$	$-\frac{3}{2}[A(m) - A(m-1)]$	$\frac{1}{8}[1 + \cos\phi(m)]^3$
$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}A(m) - \frac{1}{2}A(m-1)$	$\frac{3}{8}\sin^2\phi(m) [1 + \cos\phi(m)]$
$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}A(m) + \frac{1}{2}A(m-1)$	$\frac{1}{8}[1 - \cos\phi(m)] [3\cos\phi(m) + 1]^2$
$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}A(m) + \frac{3}{2}A(m-1)$	$\frac{3}{8}\sin^2\phi(m) [1 + \cos\phi(m)]$
$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}A(m) - \frac{3}{2}A(m-1)$	$\frac{3}{8}\sin^2\phi(m) [1 + \cos\phi(m)]$
$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}A(m) - \frac{1}{2}A(m-1)$	$\frac{1}{8}[1 - \cos\phi(m)] [3\cos\phi(m) + 1]^2$
$-\frac{3}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}A(m) + \frac{1}{2}A(m-1)$	$\frac{3}{8}\sin^2\phi(m) [1 + \cos\phi(m)]$
$\frac{3}{2}$	$-\frac{1}{2}$	$\frac{3}{2}A(m) + \frac{1}{2}A(m-1)$	$\frac{3}{8}\sin^2\phi(m) [1 - \cos\phi(m)]$
$\frac{1}{2}$	$-\frac{3}{2}$	$\frac{1}{2}A(m) + \frac{3}{2}A(m-1)$	$\frac{3}{8}\sin^2\phi(m) [1 - \cos\phi(m)]$
$-\frac{1}{2}$	$\frac{3}{2}$	$-\frac{1}{2}A(m) - \frac{3}{2}A(m-1)$	$\frac{3}{8}\sin^2\phi(m) [1 - \cos\phi(m)]$
$-\frac{3}{2}$	$\frac{1}{2}$	$-\frac{3}{2}A(m) - \frac{1}{2}A(m-1)$	$\frac{3}{8}\sin^2\phi(m) [1 - \cos\phi(m)]$
$\frac{3}{2}$	$-\frac{3}{2}$	$\frac{3}{2}A(m) + \frac{3}{2}A(m-1)$	$\frac{1}{8}[1 - \cos\phi(m)]^3$
$-\frac{3}{2}$	$\frac{3}{2}$	$-\frac{3}{2}A(m) - \frac{3}{2}A(m-1)$	$\frac{1}{8}[1 - \cos\phi(m)]^3$

¹³ F. Bloch, Phys. Rev. **102**, 104 (1956), Eq. 5.10.

¹⁴ See, for example, E. Feenberg and G. E. Pake, *Notes on the Quantum Theory of Angular Momentum* (Addison-Wesley Publishing Company, Inc., Cambridge, Massachusetts, 1953), p. 25.

¹⁵ See, for example, M. E. Rose *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), pp. 52 and 228.

one specified by $\psi(I, m-1, S, M')$ will be denoted by $L(m, M; m-1, M')$ which is given by

$$L(m, M; m-1, M') = (I-m+1)(I+m)d^2(S, M, M', \phi), \quad (19)$$

where

$$\begin{aligned} \phi &= \phi(m) = \theta(m-1) - \theta(m) \\ &= \tan^{-1} \frac{\gamma_S H_2}{\omega_S - \omega_2 - 2\pi J(m-1)} - \tan^{-1} \frac{\gamma_S H_2}{\omega_S - \omega_2 - 2\pi Jm}, \end{aligned} \quad (20)$$

$$\begin{aligned} d(S, M, M', \phi) &= [(S+M)!(S-M)!(S+M')!(S-M')!]^{\frac{1}{2}} \\ &\times \sum_K \frac{(-1)^K (\cos \frac{1}{2}\phi)^{2S+M-M'-2K} (\sin \frac{1}{2}\phi)^{M'-M+2K}}{(S-M'-K)!(S+M-K)!(K+M'-M)!K!}. \end{aligned} \quad (21)$$

The sum is over the integral values of K for which the factorial arguments are greater than or equal to zero.¹⁶ In evaluating the quantities $d^2(S, M, M', \phi)$, the following relationships prove useful:

$$d(S, M', M, \phi) = (-1)^{M'-M} d(S, M, M', \phi), \quad (22)$$

$$d(S, M', M, \phi) = d(S, -M, -M', \phi), \quad (23)$$

$$\sum_M d^2(S, M', M, \phi) = \sum_{M'} d^2(S, M', M, \phi) = 1. \quad (24)$$

For the case of $S = \frac{1}{2}$, the squares of the matrix elements are given by

$$d^2(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \phi) = d^2(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \phi) = \sin^2(\frac{1}{2}\phi),$$

$$d^2(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \phi) = d^2(\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, \phi) = \cos^2(\frac{1}{2}\phi),$$

a result which is identical to that calculated by Bloom and Shoolery.⁴

In nuclear resonance problems, one often encounters nuclear spins or groups of magnetically equivalent nuclei which form states with total spin values of $\frac{1}{2}$, 1, and $\frac{3}{2}$. The solutions to cases containing two groups of nuclei can be obtained by considering the possible values of S separately, since the transition intensities depend in a rather complex way upon S , while the dependence upon I is rather simple. Of course, the transition frequencies depend only upon the initial and final values of M and m and are independent of S and I . The solutions of general interest corresponding to values of S equal to $\frac{1}{2}$, 1, and $\frac{3}{2}$ are given in Tables I, II, and III, respectively. The frequencies are determined by Eq. (17) and the line intensities from Eqs. (19) and (21).

2.2 Graphical Presentation

It is convenient when discussing spin-decoupling experiments to introduce a simple extension of the nomenclature of Pople *et al.*¹² and to use the letters at

the end of the alphabet to designate the group to be irradiated by the strong field H_2 , and those at the beginning for the group whose resonance is to be investigated by the weak field H_1 . For example, acetaldehyde would be referred to as an A_3X molecule if H_2 is set on the quadruplet, but as AX_3 when H_2 is set on the doublet resonance. In this nomenclature, ω_I becomes ω_A and ω_S becomes ω_X . Double irradiation of strongly coupled spin systems (for example AB-type molecules) will not be considered here. With the further restriction that all nuclei in a given group are magnetically equivalent—that is to say, the coupling between two groups can be described by a single constant J_{AX} —the calculations of Sec. 2.1 can be seen to be quite general, extending the AX calculation of Whiffen to all cases of interest. The treatment is not, of course, limited to spin $\frac{1}{2}$ nuclei or to nuclei of the same species, although high-resolution proton-resonance spectra appear to provide the richest field of investigation at the present time, and therefore the practical examples are all proton-proton decoupling experiments.

The results of the calculations of Sec. 2.1 have been represented graphically in a form which is similar to, but not identical with that used by Freeman and Whiffen.⁸ Dimensionless quantities Δ and Ω have been defined by

$$\Delta = (\omega_2 - \omega_X)/2\pi |J|, \quad \Omega = (\omega_1 - \omega_A)/2\pi |J|,$$

where $\omega_A = \omega_I = \gamma_A H_0$, $\omega_X = \omega_S = \gamma_X H_0$, 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 ω_1 , ω_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 Ω versus Δ , and their intensities L are conveniently expressed as a function of Δ (See Figs. 1, 2, and 3).

In a "frequency-sweep" experiment,⁸ ω_2 and H_0 are either held constant or locked together by some kind of nuclear resonance controller and ω_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 Δ . An experiment which is more common because of the simplicity of the instrumentation required, is the "field-sweep" method⁸ which consists in holding ω_1 and ω_2 constant and varying H_0 , corresponding to varying Ω and Δ simultaneously. On the figure this is a line with a slope γ_A/γ_X and an intercept on the Δ axis which may be called Δ' corresponding to the deviation from the resonance condition of ω_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

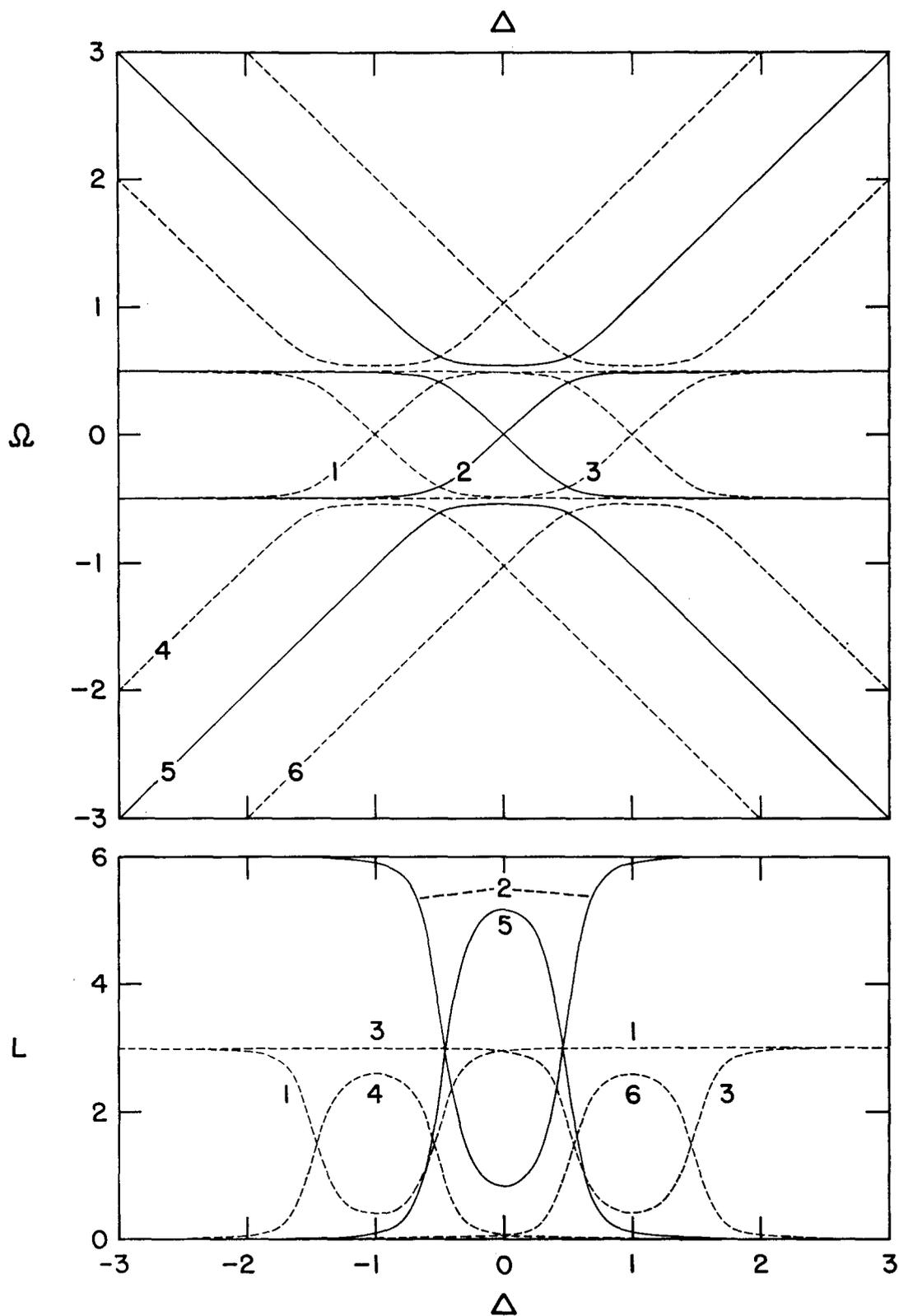


FIG. 1(a). The transition frequencies Ω and intensities L of the A resonance plotted against the offset parameter Δ for an AX system (full lines) and an A_3X system (full and broken lines) for $\gamma H_2/2\pi = 0.2J$.

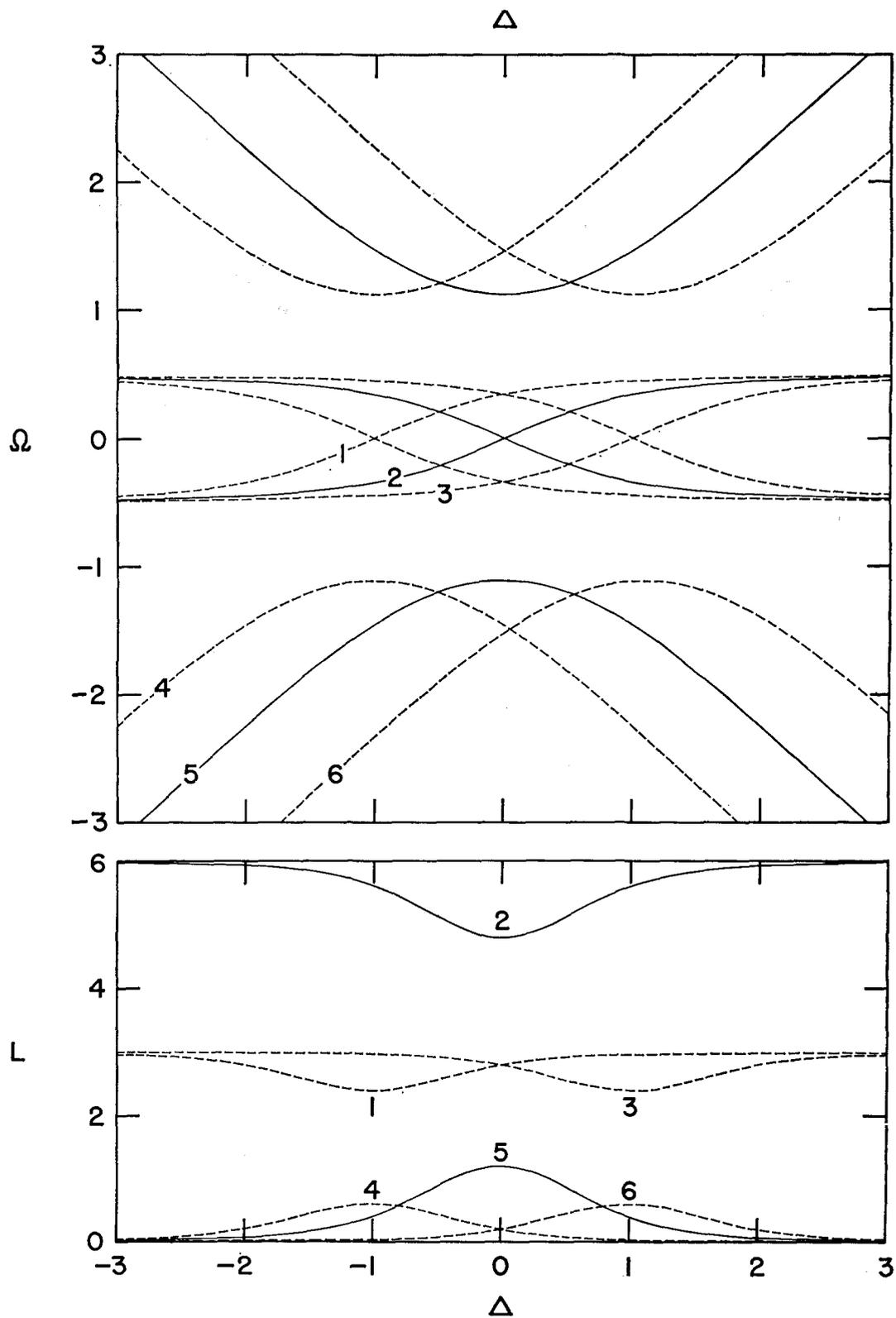


FIG. 1(b). The transition frequencies Ω and intensities L of the A resonance plotted against the offset parameter Δ for an AX system (full lines) and an A_3X system (full and broken lines) for $\gamma H_2/2\pi = J$.

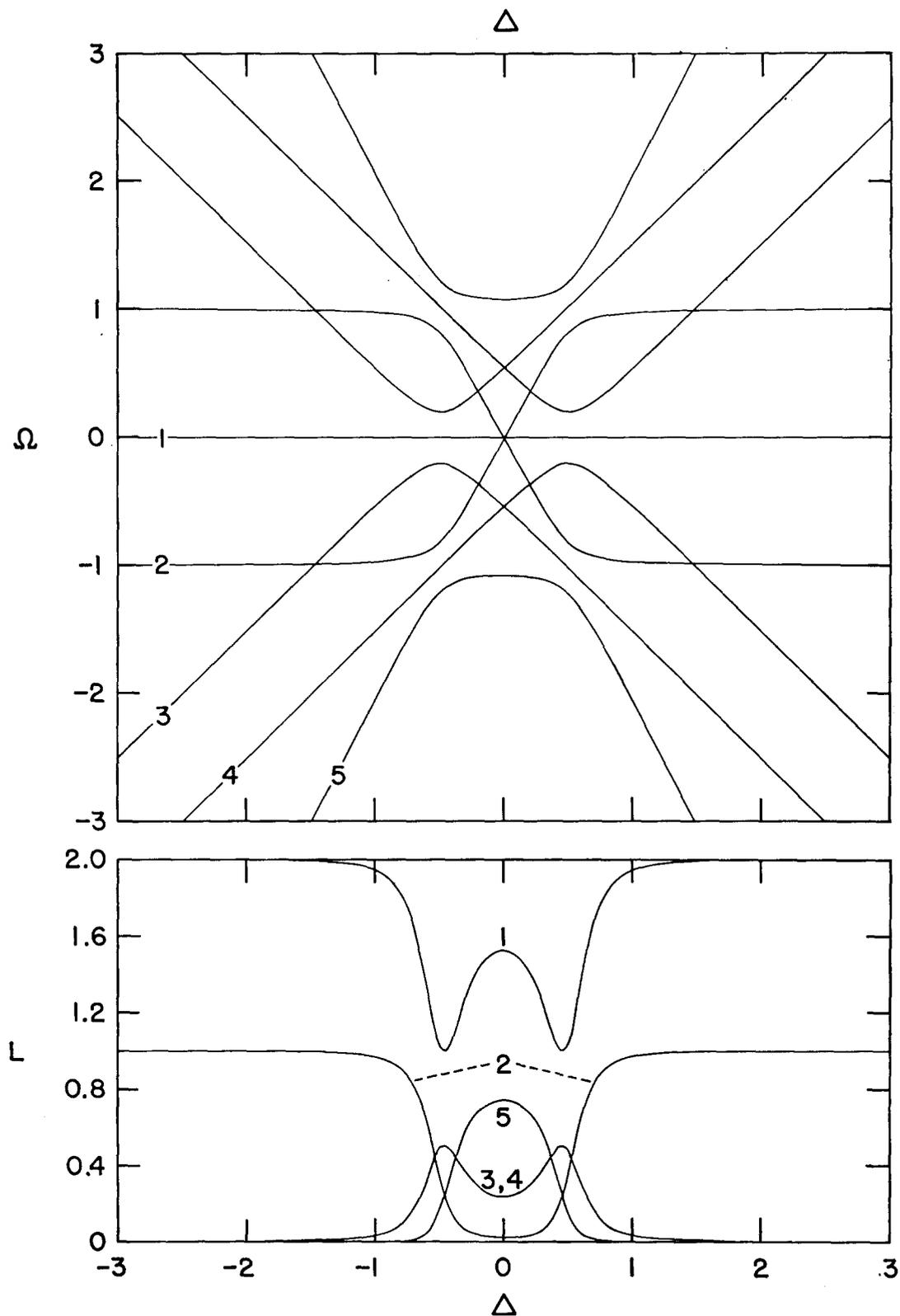


FIG. 2(a). The transition frequencies Ω and intensities L of the A resonance of an AX_2 system plotted against the offset parameter Δ for $\gamma H_2/2\pi = 0.2J$.

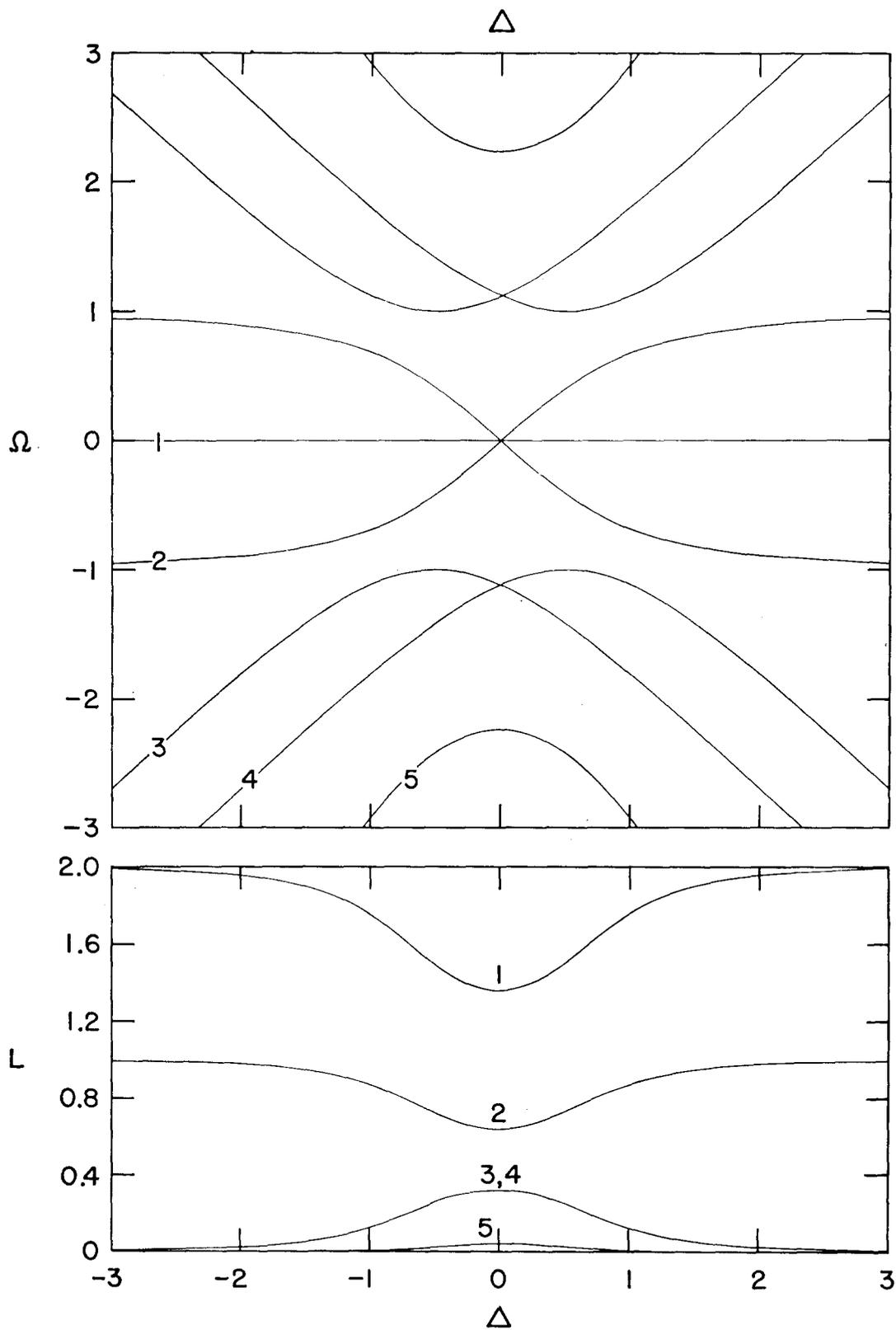


FIG. 2(b). The transition frequencies Ω and intensities L of the A resonance of an AX_2 system plotted against the offset parameter Δ for $\gamma H_2/2\pi = J$.

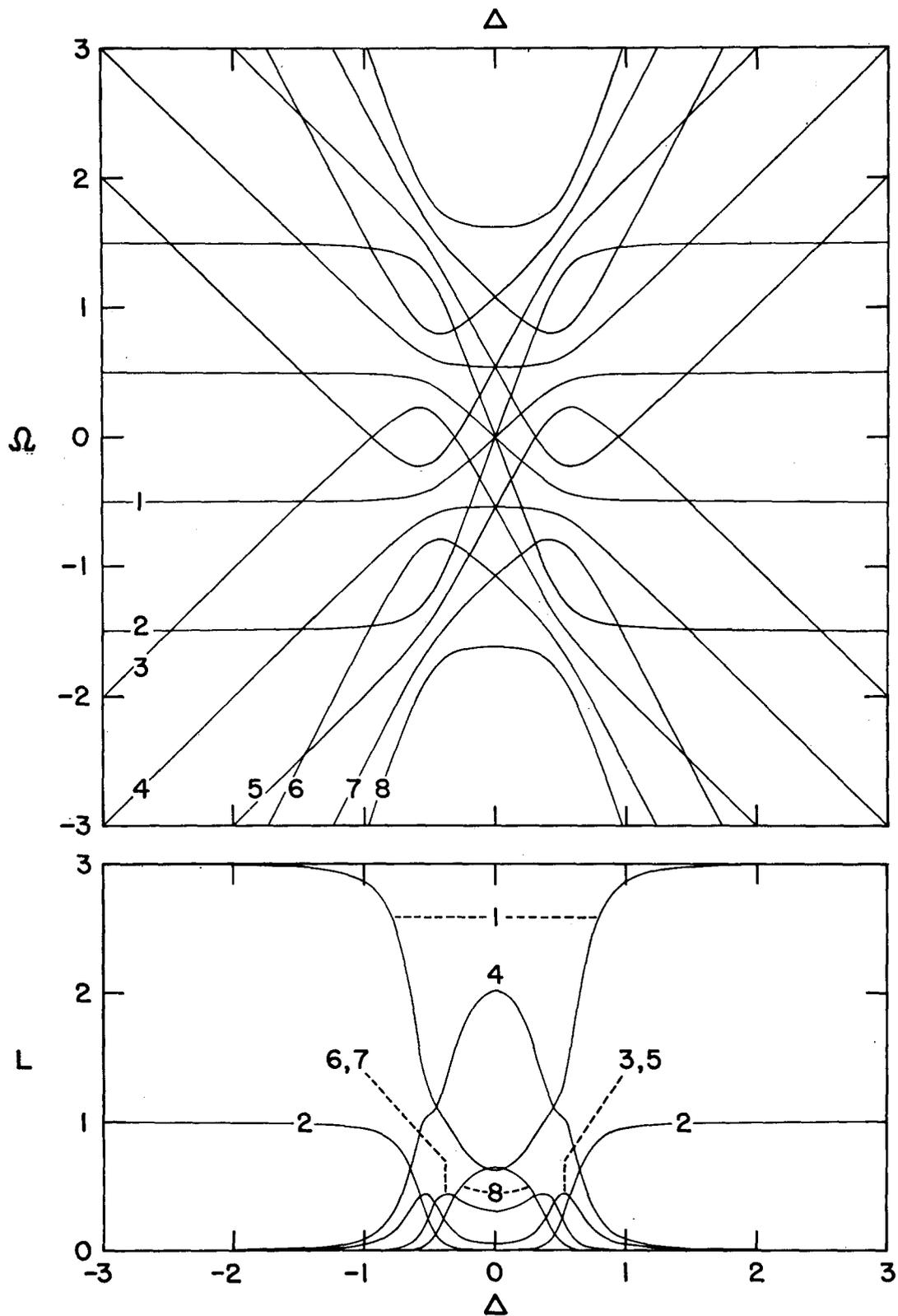


FIG. 3(a). The transition frequencies Ω and intensities L of the A resonance of an AX_3 system plotted against the offset parameter Δ for $\gamma H_2/2\pi = 0.2J$.

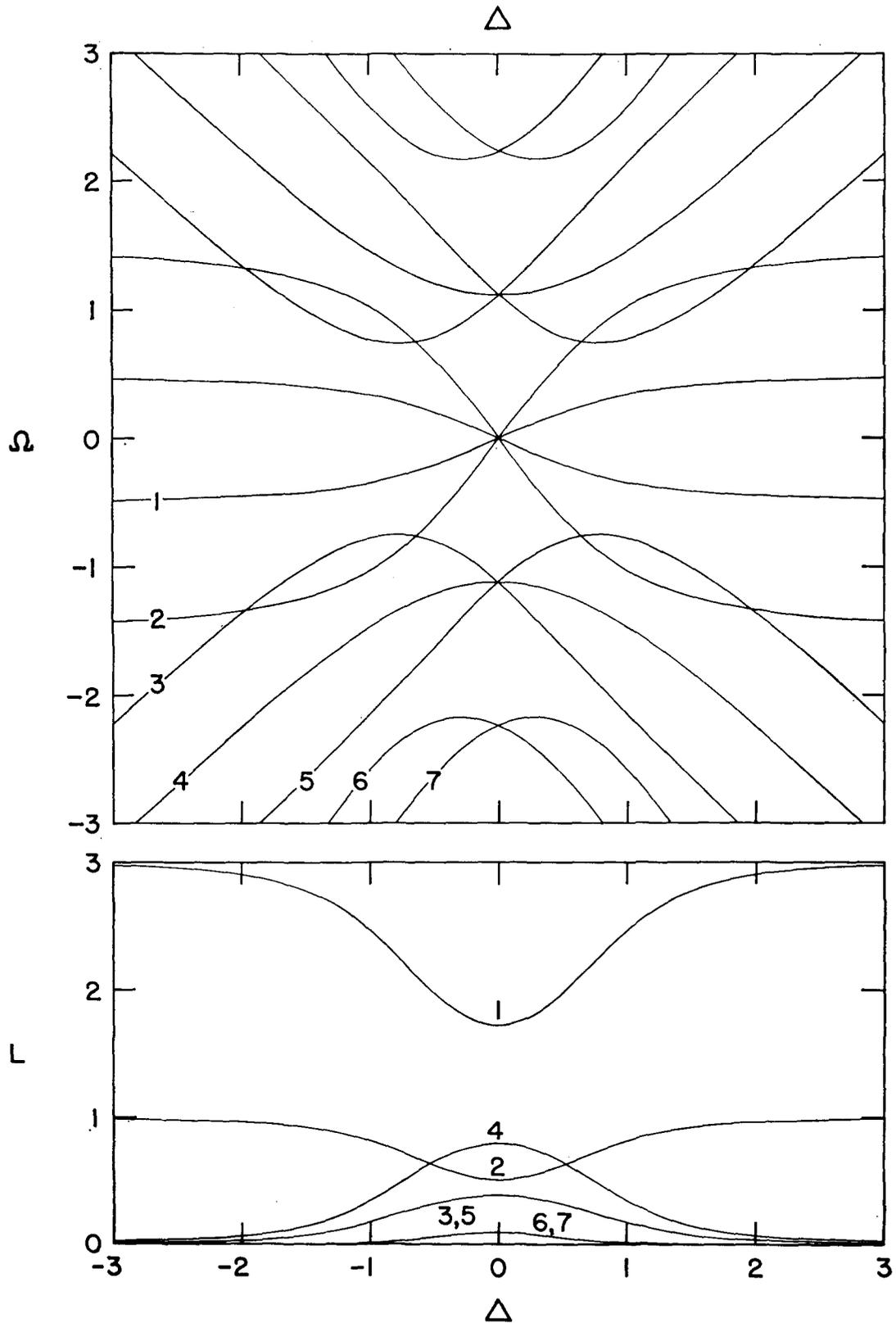


FIG. 3(b). The transition frequencies Ω and intensities L of the A resonance in an AX_3 system plotted against the offset parameter Δ for $\gamma H_2/2\pi = J$.

ω_1 and H_0 constant (or controlled in such a way that they remain in constant proportion) and sweeping the frequency ω_2 . On the diagrams this means operation at constant Ω , and the results of such experiments may be predicted by drawing a horizontal line at a height determined by Ω .

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

AX	AX ₂	AX ₃
A ₂ X	A ₂ X ₂	A ₂ X ₃
A ₃ X	A ₃ X ₂	A ₃ X ₃

Fortunately it is not necessary to consider each case separately. For example, the A₃X 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 Δ 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 Ω axis is shifted by one unit of Δ . 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 A₃X 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 Δ . 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_nX₂ and A_nX₃ cases can be deduced simply from a knowledge of the curves for the AX₂ and AX₃ 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, AX₂, or AX₃) separated from each other by one unit on the Δ axis, and to combine them with relative intensities which go as the binomial coefficients.

Consider next the AX₂ 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_nX₂ molecules.

The AX₃ 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 Table III and Table I with these statistical weights, yields the curves given in Fig. 3, which may be extended to A_nX₃ 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 ω_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 $\gamma_S H_2 \ll 2\pi |J|$ provided that $\gamma_S H_2$ is larger than the linewidths observed in the A spectrum. If ω_2 satisfies the condition

$$\omega_S - \omega_2 + 2\pi Jm' = 0,$$

then with the approximation $\gamma_S H_2 \ll 2\pi |J|$, Eq. (17) takes the form

$$\omega(m', M'; m'-1, M) \cong \omega_I - 2\pi JM + \gamma_S H_2 M', \quad (25)$$

$$\omega(m'+1, M; m', M') \cong \omega_I + 2\pi JM - \gamma_S H_2 M', \quad (26)$$

$$\omega(m'', M; m''-1, M) = \omega_I + 2\pi JM, \quad (27)$$

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 $I > \frac{1}{2}$, 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 ($M = \pm S$) are just proportional to the binomial coefficients since

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

$$= (\frac{1}{2})^{2S} \binom{2S}{S+M'}$$

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

$$\binom{2S}{S+M'}$$

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 ω_2 . 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.¹⁶⁻²⁰

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.⁷

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 A_nX_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

¹⁶ A. Javan, Phys. Rev. **107**, 1579 (1957).

¹⁷ A. M. Clogston, J. Phys. and Chem. Solids **4**, 271 (1958).

¹⁸ J. H. Burgess, J. phys. radium **19**, 845 (1958).

¹⁹ S. Yatsiv, Phys. Rev. **113**, 1538 (1959).

²⁰ F. Bloch (to be published).

the transition frequencies and line intensities using the approximation of $\gamma_S H_2 \gg 2\pi |J| I$:

$$\omega(m, M; m-1, M) \cong \omega_I$$

$$- (2\pi J / \gamma_S H_2) [\omega_S - \omega_2 - 2\pi J (m - \frac{1}{2})] M, \quad (28)$$

$$L(m, M; m-1, M)$$

$$\cong [(I-m+1)(I+m)] d^2(S, M, M, 0)$$

$$= (I-m+1)(I+m). \quad (29)$$

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 ω_1 is swept while the frequency $\omega_2 = \omega_S$, the splitting is reduced by the factor

$$2\pi J (m - \frac{1}{2}) / \gamma_S H_2.$$

The splitting will be reduced by nearly this same factor in a magnetic-field-sweep experiment if the additional inequality $\gamma_I H_2 \gg 2\pi |J| S$ 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

$$\gamma_S H_2 \gg 2\pi |J| I$$

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 $2\pi |J|$, nor the effective radiofrequency field γH_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 elsewhere²¹ 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 γH_2 compared to $\omega_I - \omega_2$, and a transformation V will be applied to bring the wave function of the I spin into diagonal form. The required transformation is

$$V = \exp(i\theta_A I^y), \quad (30)$$

with

$$\tan\theta_A = \gamma H_2 / (\omega_I - \omega_2). \quad (31)$$

²¹ W. A. Anderson, Phys. Rev. **102**, 151 (1956).

The transformed Hamiltonian is

$$\mathcal{H}_V = -[AI^z + (\omega_S - \omega_2 - 2\pi J \cos\theta_A I^z) S^z + (\gamma H_2 - 2\pi J \sin\theta_A I^z) S^x - 2\pi J (I^x S^x \cos\theta_A - I^x S^z \sin\theta_A + I^y S^y)], \quad (32)$$

with

$$A = [(\omega_I - \omega_2)^2 + (\gamma H_2)^2]^{\frac{1}{2}}. \quad (33)$$

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

$$W = \exp[i\theta_X(m_A) S^y], \quad (34)$$

with

$$\tan\theta_X(m_A) = \frac{\gamma H_2 - 2\pi J m_A \sin\theta_A}{\omega_S - \omega_2 - 2\pi J m_A \cos\theta_A}. \quad (35)$$

The transformed Hamiltonian is simply

$$\mathcal{H}_W = -[AI^z + X(m_A) S^z], \quad (36)$$

where

$$X(m_A) = [(\omega_S - \omega_2 - 2\pi J m_A \cos\theta_A)^2 + (\gamma H_2 - 2\pi J m_A \sin\theta_A)^2]^{\frac{1}{2}}. \quad (37)$$

As in Eq. (16) the energy eigenvalues in this transformed system are independent of I and S and are given by

$$E_W(m_A, m_X) = -[A m_A + X(m_A) m_X]. \quad (38)$$

A weak rf field H_1 with a frequency ω_1 will induce transitions between these levels. The frequency ω_2 will be near the resonance frequency ω_S , and ω_1 will be near the frequency ω_I . The transitions of particular interest are those with $\Delta m_A = \pm 1$ and $\Delta m_X = 0$ corresponding to the strong lines of the spectrum when $\gamma H_2 \geq 2\pi |J|$.

Let the laboratory frame transition frequencies between states with m_A, m_X and $m_A - 1, m_X$ be denoted by $\omega(m_A, m_X; m_A - 1, m_X)$. Then

$$\omega(m_A, m_X; m_A - 1, m_X) = \omega_2 + A + [X(m_A) - X(m_A - 1)] m_X. \quad (39)$$

The first term on the right-hand side represents the transformation to the rotating coordinate frame. The second term gives the effective transition frequencies of the I spin group neglecting the spin-spin coupling. The exact values of these frequencies depend upon the strength of the radiofrequency field, a fact that has been used to measure the radiofrequency field strength at the sample.^{21,22} The last two terms predict the effect of the coupling in the presence of the strong radiofrequency field H_2 . The magnitude of the coefficient of m_X determines the residual splitting of the spectrum.

Equations (33) and (37) may be approximated by making use of the inequalities

$$(\omega_I - \omega_2)^2 \gg (\gamma H_2)^2 \gg (\omega_S - \omega_2)^2 + (2\pi J)^2 m_A^2,$$

to yield

$$A \cong \omega_I - \omega_2 + \frac{1}{2} (\gamma H_2)^2 / (\omega_I - \omega_2).$$

$$X(m_A) \cong \gamma H_2 - 2\pi J m_A \sin\theta_A + \frac{1}{2} (\omega_S - \omega_2)^2 / (\gamma H_2)$$

$$+ (\frac{1}{2}) (2\pi J m_A \cos\theta_A)^2 / (\gamma H_2)$$

$$- (\omega_S - \omega_2) (2\pi J m_A \cos\theta_A) / (\gamma H_2).$$

Substitution of these values into Eq. (39) yields

$$\omega(m_A, m_X; m_A - 1, m_X) = \omega_I + (\frac{1}{2}) (\gamma H_2)^2 / (\omega_I - \omega_2)$$

$$\times [(2\pi J \cos\theta_A) / \gamma H_2] [\omega_S - \omega_2 - 2\pi J \cos\theta_A (m_A - \frac{1}{2}) + \gamma H_2 \tan\theta_A] m_X. \quad (40)$$

Study of Eq. (40) leads to a number of interesting conclusions. This equation yields the transition frequencies which are observed when

$$\omega_1 = \omega(m_A, m_X; m_A - 1, m_X).$$

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 $H_2 \rightarrow 0$. 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 $\omega_2 = \omega_S$ and $I = \frac{1}{2}$. 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.²³ In the limit of extremely large values of H_2 , i.e., $\gamma H_2 \gg |\omega_I - \omega_S|$ 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 ω_2 is chosen so as to satisfy the equation

$$\omega_2 - \omega_S = \gamma H_2 \tan\theta_A = \frac{(\gamma H_2)^2}{\omega_I - \omega_2} \approx \frac{(\gamma H_2)^2}{\omega_I - \omega_S}, \quad (41)$$

then the first and third terms in the bracket of Eq. (40) cancel and the spectrum will be completely collapsed if $I = \frac{1}{2}$; if $I > \frac{1}{2}$ all lines with the initial state $m_A = \frac{1}{2}$ will coincide. Thus, the most complete collapse is *not* obtained with $\omega_2 = \omega_S$, but with the value of ω_2 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 $(\omega_1 - \omega_2)$ constant while sweeping H_0 , one finds that the most collapsed spectrum is ob-

²² W. A. Anderson, reference 3(d), p. 164.

²³ Reference 13, Eq. 7.121.

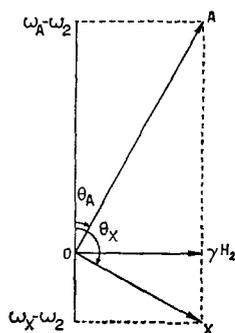


FIG. 4. The effective fields experienced by the A and X nuclei in a frame rotating at ω_2 . For optimum decoupling of the A and X spins, $\theta_X - \theta_A = \frac{1}{2}\pi$.

tained when

$$\omega_1 - \omega_2 \approx \omega_I - \omega_S - (\gamma H_2)^2 / 2(\omega_I - \omega_S). \quad (42)$$

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 ω_2 as seen by the nuclei of group A is the vector sum of the field $\omega_A - \omega_2$ along the Z axis and γH_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 $|\omega_A - \omega_2|$ corresponds to the correction.²¹

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 $\mathbf{I} \cdot \mathbf{S}$ 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 γH_2 along the X axis and $\omega_X - \omega_2$ 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 $2\pi \mathbf{J} \cdot \mathbf{S}$ as a perturbation. With this approximation, the spin operator I 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 $2\pi \mathbf{J} \cdot \mathbf{S}$ 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 $\gamma H_2 < \frac{1}{2} |\omega_A - \omega_X|$.

When ω_2 is chosen to satisfy Eq. (41), the residual splittings (R rad/sec) observed in spectra of molecules where $I > \frac{1}{2}$ are given by the expression

$$R = [(\omega_S - \omega_2)^2 + \gamma^2 H_2^2 + 4\pi^2 J^2 m_A^2]^{\frac{1}{2}} - [(\omega_S - \omega_2)^2 + \gamma^2 H_2^2 + 4\pi^2 J^2 (m_A - 1)^2]^{\frac{1}{2}}, \quad (43)$$

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

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

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_1 . 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,²⁴ Kaiser,²⁵ and Freeman.²⁶ The rf field H_2 was calibrated by the method described by Anderson.^{21,22}

"Frequency-sweep" spectra were obtained by introducing a control loop to maintain ω_2 and H_0 in a constant proportion, while ω_1 was swept through the A resonance. The system was similar to those used by Anderson²⁷ and Primas.²⁸ 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 (ω_0) or the three unused sidebands, and all at low modulation index so as not to interfere with one another. A sideband at ω_3 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 $\omega_3 - \omega_0$ 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 ± 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 ω_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 $\omega_1 - \omega_0$ 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

²⁴ R. V. Pound, Rev. Sci. Instr. **28**, 966 (1957); R. Freeman and R. V. Pound, Rev. Sci. Instr. **31**, 103 (1960).

²⁵ R. Kaiser, Rev. Sci. Instr. **31**, 963 (1960).

²⁶ R. Freeman, Mol. Phys. **3**, 435 (1960).

²⁷ W. A. Anderson (unpublished work).

²⁸ H. Primas, Fifth European Congress on Molecular Spectroscopy, Amsterdam (1961).

spectra. A third field-modulation sideband provided the perturbing radiofrequency field at ω_2 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 $\omega_3 - \omega_2$ 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 ω_2 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 γH_2 is very much less than, comparable with, and very much greater than $2\pi |J_{AX}|$.

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 ω_2 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

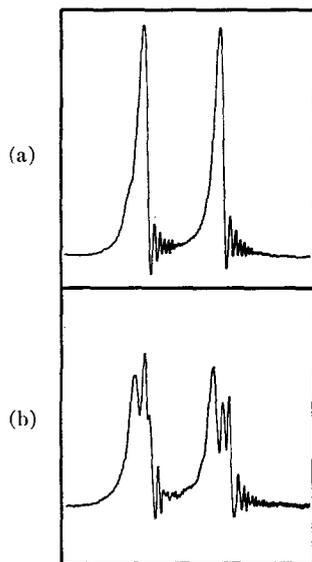


FIG. 5. The methyl-group doublet of acetaldehyde recorded by the frequency-sweep method: (a) unperturbed and (b) with H_2 irradiating one of the strong lines of the CHO quadruplet, with $\gamma H_2/2\pi \approx 0.2J$.

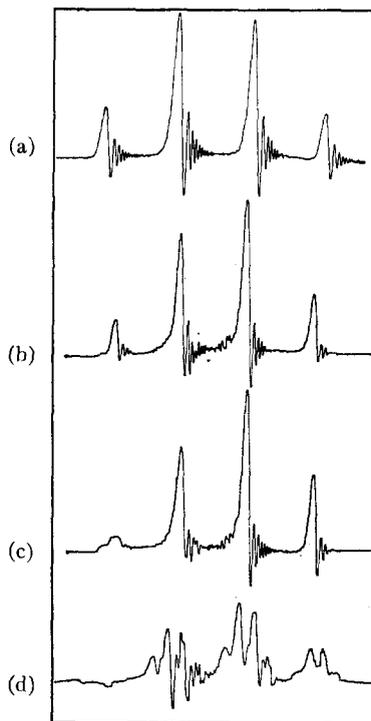


FIG. 6. The aldehyde proton resonance of acetaldehyde recorded by the frequency-sweep method: (a) unperturbed and (b), (c), and (d) with increasing strengths of H_2 irradiating the low-field line of the methyl-group doublet. In (d) $\gamma H_2/2\pi \approx \frac{1}{4}J$.

to interpret, but where the "field-sweep" technique gives complicated results. In the latter method, one of the A lines will be split whenever $(\omega_1 - \omega_2)$ 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,⁸ 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 ($\delta = 455.5 \pm 0.2$ cps, $J = 2.8 \pm 0.2$ cps) and ω_2 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 ω_2 . Figure 5 illustrates the spectra obtained (a) with $H_2 = 0$, (b) with $\gamma H_2/2\pi$ approximately $0.2J_{AX}$, and Δ 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 [Fig. 1(a)].

An interesting complication arose when the reverse experiment was attempted. When ω_2 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.

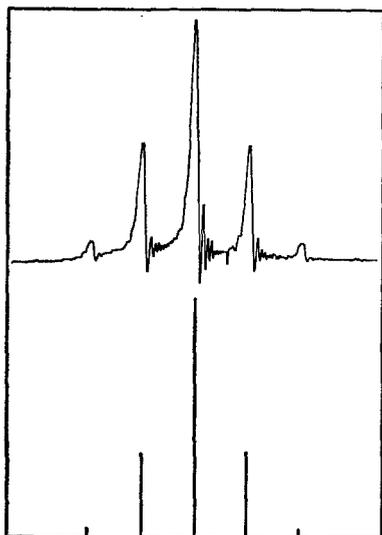


FIG. 7. The aldehyde-proton resonance of acetaldehyde recorded by the frequency-sweep method with $\Delta=0$, $\gamma H_2/2\pi=J$, showing first- and second-order satellite lines. The theoretical spectrum was obtained from Fig. 3(b).

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 up to $\gamma H_2/2\pi \approx \frac{1}{4}J$ for the last trace. When the high-field line of the methyl group was irradiated, the spectra obtained were essentially the 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 so that they are no longer described by the Boltzmann distribution law. The quantitative aspects of the changes, which are unfortunately somewhat obscured here because of the formation of submultiplets, should in principle indicate which relaxation mechanism is dominant, as in the double-irradiation experiments of Pound on sodium nitrate.²⁹ 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 $J\mathbf{I}\cdot\mathbf{S}$ or by dipole-dipole interaction within the molecule. In the sample used, the measured spin-lattice relaxation times were 30 ± 2 sec (aldehyde proton) and 17 ± 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.³⁰ The predicted relative intensities are then -0.2 , $+2.1$, $+3.9$, $+2.2$ which are to be

²⁹ R. V. Pound, Phys. Rev. **79**, 685 (1950).

³⁰ Reference 13, p. 112.

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 in proton magnetic resonance of the general Overhauser effect^{1,30,31,32} of which only isolated examples appear to have been reported in the literature for nuclear-magnetic double-resonance at high resolution.^{33,34} 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 n th-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 $\gamma H_2 = 2\pi J_{VX}$ (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 ω_2 is near the methyl-group doublet and $\gamma H_2/2\pi = 2J_{AX}$. Predicted spectra were obtained from a figure similar to Figure 3(b) by drawing lines across at 45° . As discussed by Freeman and Whiffen⁸ certain lines tend to broaden in a field-sweep experiment because lines drawn across the figure at 45° sometimes intersect the curve at a very acute angle, and the curves have a

³¹ A. W. Overhauser, Phys. Rev. **91**, 476 (1953); **92**, 411 (1953); **94**, 768 (1954).

³² A. Abragam, Phys. Rev. **98**, 1729 (1955).

³³ I. Solomon, Phys. Rev. **99**, 559 (1955); I. Solomon and N. Bloembergen, J. Chem. Phys. **25**, 261 (1956).

³⁴ J. Wertz, P. L. Jain, and R. L. Batdorf, Phys. Rev. **102**, 920 (1956).

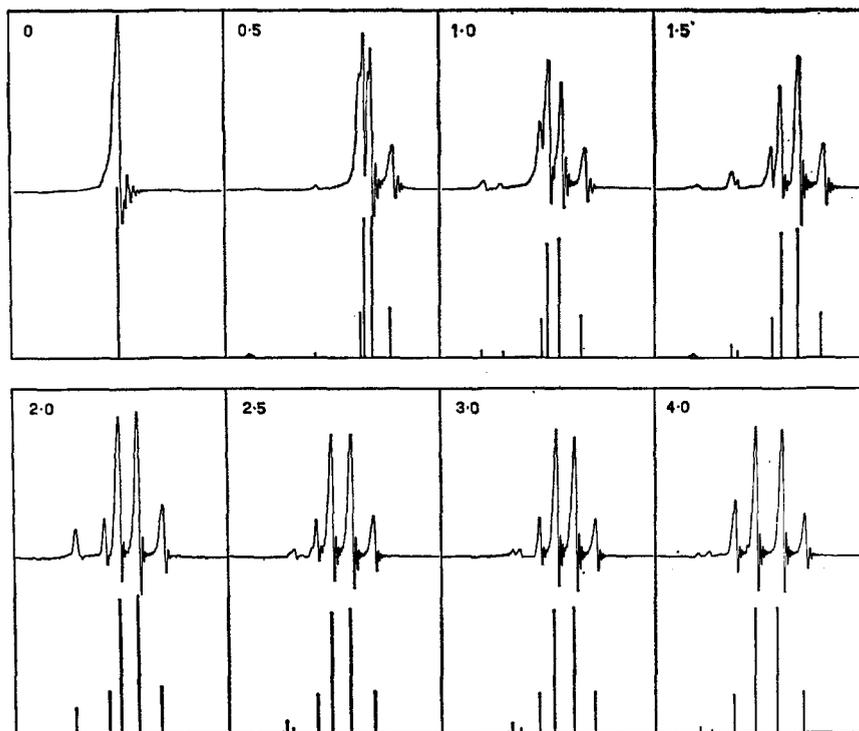


FIG. 8. The aldehyde-proton resonance of acetaldehyde recorded by the field-sweep method while the methyl group is irradiated with $\gamma H_2/2\pi = 2J$, at several values of the offset parameter Δ' . The coincidence of three satellite lines for $\Delta' = 2.0$ should be noted.

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 A_3X_2 system where the chemical shift (171.3 ± 0.2 cps) is sufficiently large compared with the coupling constant (7.5 ± 0.2 cps) that second-order spin coupling is not apparent in the spectrum. Field-sweep spectra with γH_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° slope at $(\Delta' - 1)$, Δ' and $(\Delta' + 1)$, 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_3X_2 case in the way illustrated for A_3X 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 ω_2 is to ω_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_nX_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 ± 0.2 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 ± 0.2 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_2Cl protons were irradiated while the $CHCl_2$ 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 $(\omega_A - \omega_X)/2\pi$ 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

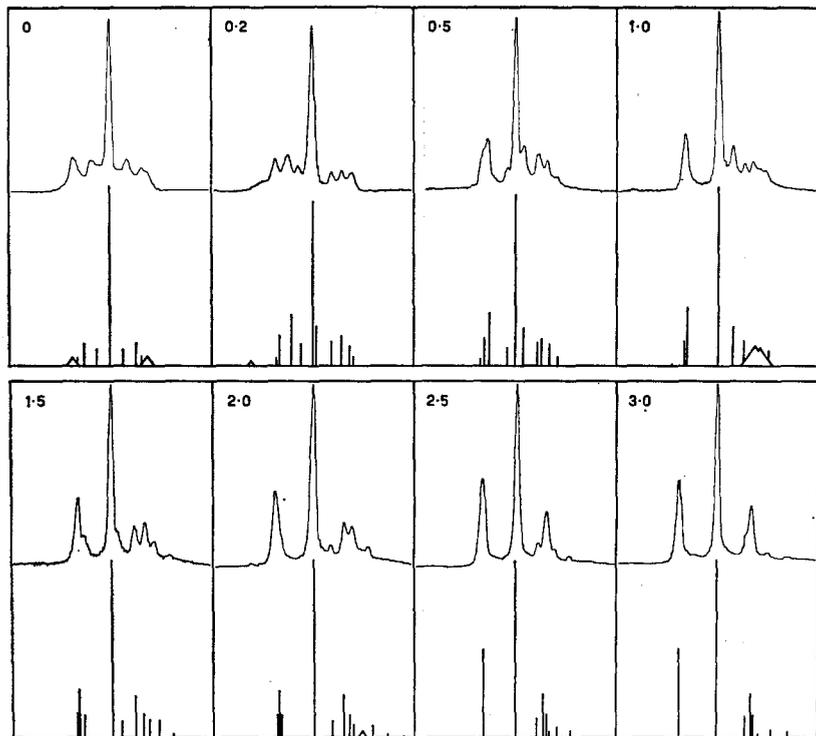


FIG. 9. The methyl-group resonance of diethyl succinate recorded by the field-sweep method while the coupled methylene group is irradiated with $\gamma H_2/2\pi = J$, at several values of the offset parameter Δ' . Theoretical spectra were obtained from Fig. 2(b) by the method described in the text for A_3X_2 molecules. Lines expected to be abnormally broad have been represented schematically by a triangle.

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 $\gamma H_2 \approx 2\pi J$ 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 $(\omega_I - \omega_S)/2\pi = 110.2$ 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.²¹ 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.

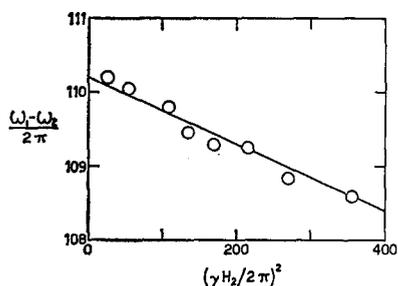


FIG. 10. The experimentally determined settings of $\omega_1 - \omega_2$ for optimum decoupling of the CHCl_2 proton in 1,1,2 trichloroethane by irradiation of the CH_2Cl protons at several values of H_2 . The full line represents Eq. (42) for a chemical shift of 110.2 cps.

³⁵ R. Freeman, *Mol. Phys.* 4, 385 (1961).

The sample was next investigated as an A_2X case with H_2 applied to the CHCl_2 proton and the CH_2Cl resonance displayed by the field-sweep technique. The residual splitting of the resonance was then determined by comparison with the splitting (J) observed when ω_2 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).

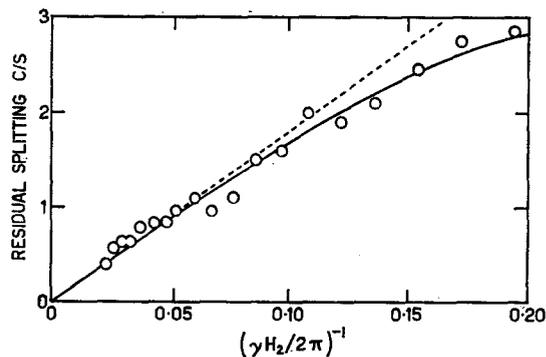


FIG. 11. The residual splittings observed in the resonance of the CH_2Cl protons of 1,1,2 trichloroethane when the CHCl_2 proton is irradiated at several different values of H_2 . The full curve represents Eq. (43), while the broken curve represents Eq. (44), which is only valid for $\gamma H_2 \gg 2\pi |J|$.

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 ω_2 , 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 paper⁸ has compared observed and predicted spectra for AX proton systems under double-

irradiation conditions. The extension of these calculations to AX₂ and AX₃ systems is here given experimental confirmation for irradiating field strengths γH_2 comparable with $2\pi J$. A simple method of deriving the spectra predicted for A_nX₂ and A_nX₃ molecules has been described and applied to the calculation of the patterns observed in the double irradiation of diethyl succinate.

It has long been realized²¹ 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 $(\gamma H_2)^2/2(\omega_A - \omega_X)$ in rad/sec. It is therefore natural to apply this correction when calculating the optimum setting of $(\omega_1 - \omega_2)$ 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

$$\omega_1 - \omega_2 \approx \omega_A - \omega_X - (\gamma H_2)^2/2(\omega_A - \omega_X).$$

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_m. But for A_nX_m systems where $n > 1$ a residual splitting of the resonance line persists as H_2 is increased. For $\gamma H_2 \gg 2\pi |J|$ this splitting is given by the simple formula

$$R = (2\pi J)^2(m_A - \frac{1}{2})/\gamma H_2 \text{ rad/sec.}$$

For fields strong enough to satisfy the condition $\gamma H_2 > \frac{1}{2} |\omega_A - \omega_X|$ this splitting actually begins to increase with increase of H_2 , reaching $2\pi J$ 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

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